Synthesis of Functionalized Trisubstituted Cyclohexenes and Polycyclic Cores from a Dihapto-Coordinated Tungsten-Phenyl Sulfone Complex

Paolo Siano

Germignaga, Varese, Italy

M.S. Chemistry

University of North Carolina at Charlotte, **2020**

B.S. Chemistry

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Committee Members:

W. Dean Harman (Advisor)

Jetze J. Tepe (Chair)

Michael K. Hilinski

Charles Machan

Huiwang Ai

Dissertation Abstract

Chapter 1 introduces the concept of chemical space and addresses current challenges in identifying lead compounds. Furthermore, Chapter 1 argues for the adoption of new synthetic approaches aimed at enhancing molecular three-dimensionality, proposing the use of alkene reactivity in aromatic molecules as a viable solution. To this end, dearomatization is proposed as a means to convert planar aromatic compounds into complex three-dimensional small molecules. The Chapter otulines the different synthetic approaches to dearomatization, such as enzymatic, photochemical/thermal, and transition metal-mediated. Lastly, emphasis is given on transition-metal mediated dearomatization reactions, specifically those promoted via dihapto-coordination of electron-deficient aromatic substrates to transition metals.

Chapter 2 looks at different ways to synthesize y-lactams and hydroindolone cores, which can be found in drugs and Lycorine-type natural products. Moreover, it introduces how the technology developed throughout my PhD using electron deficient arenes allows for the synthesis of novel hydroindolone cores (**Chapter 4**) and novel multicyclic molecules (**Chapter 5**).

In **Chapter 3** A novel process is described for the synthesis of di- and trisubstituted cyclohexenes from an arene. These compounds are prepared from three independent nucleophilic addition reactions to a phenyl sulfone ($PhSO_2R$; R = Me, Ph, and NC_4H_8) dihapto-coordinated to the tungsten complex {$WTp(NO)(PMe_3)$}(Tp = trispyrazolylborate). The resulting arenium species readily reacts with the first nucleophile to form a dihapto-coordinated sulfonylated diene complex. This complex can again be protonated, and the subsequent nucleophilic addition forms a trisubstituted cyclohexene species bearing a sulfonyl group at an allylic position. Loss of the sulfinate anion forms a π-allyl species, to which a third nucleophile can be added. The trisubstituted cyclohexene can then be oxidatively decomplexed, either before or after substitution of the sulfonyl group. Of the 12 novel functionalized cyclohexenes prepared as examples of this methodology, nine compounds meet five independent criteria for evaluating drug likeliness.

In **Chapter 4** a synthetic strategy for functionalized *cis-hydro*-2-oxindoles is described. This involves the initial coordination of phenyl sulfones to the tungsten fragment

WTp(NO)(PMe_3), followed by a tandem protonation and addition of an ester nucleophile. The resulting species is then protonated and a primary amine is introduced. *Dihydro*-2-oxindoles are formed through the construction of γ-lactam followed by elimination of sulfinic acid to form the η^2-diene complex. Finally, *cis-hydro*-2-oxindoles are obtained via oxidative decomplexation of the tungsten complex. The methodology described offers a modular approach for accessing functionalized *cis-hydro*-2-oxindole derivatives. The reported approach provides a robust alternative to existing methodologies for the construction of these biologically relevant skeletons.

Chapter 5, the field of dearomatization seeks to leverage the synthetic potential of aromatic molecules through approaches ranging from photoactivation, high pressures, enzymatic protocols, to activation through transition metals. The aim of this study is to develop heteropolycyclic molecules that resemble cores of natural products from a phenylsulfone. In this approach the aromatic ring is dihapto-coordinated to a π-basic tungsten complex, and through a series of additions to the ring carbons, a wide array of chemically diverse polycyclic systems is prepared. These compounds resemble the size, shape and polarity of known biologically active compounds, yet these polycyclic cores are completely unique, having virtually no reported counterparts.

Copyright Information

Chapter 3 is a modified version of a previously published work.

Spenser R. Simpson, **Paolo Siano**, Daniel J. Siela, Louis A. Diment, Brian C. Song, Karl S. Westendorff, Megan N. Ericson, Kevin D. Welch, Diane A. Dickie, and W. Dean Harman Phenyl Sulfones: A Route to a Diverse Family of Trisubstituted Cyclohexenes from Three Independent Nucleophilic Additions *Journal of the American Chemical Society* **2022** 144 (21), 9489-9499 DOI: 10.1021/jacs.2c03529

Chapter 4 is a version of a manuscript under internal revision for publication.

Paolo Siano[‡], Louis A. Diment[‡], Daniel J. Siela, Brian Song, Matt McGraw, Diane A. Dickie, and W. Dean Harman *. *Journal of American Chemical Society*

Chapter 5 is a version of a manuscript under internal revision for publication.

Paolo Siano, Louis A. Diment, Daniel J. Siela, Matt McGraw, Megan Ericson, Diane A. Dickie, and W. Dean Harman*. *Nature*

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I would like to thank my family and friends for their support and love.

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"Fatti non foste a viver come bruti, ma per seguir virtute e canoscenza" verso 119 del Canto XXVI dell'*Inferno, Divina Commedia, Dante Alighieri*

List of Abbreviations

Å	Angstrom
aq	Aqueous
CAN	Cerin ammonium nitrate
c.d.r.	Coordination diastereomer ratio
COSY	Correlation Spectroscopy
CV	Cyclic Voltammetry
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicyanoquinone
DCM	Dichloromethane
DFT	Density functional theory
DiPAT	Diisopropylammonium triflate
DMAP	4-Dimehtylaminopyridine
DME 1	1,2-Dimethoxyethane
DMF	*N,N*-Dimethylformamide
DMM	Dimethyl malonate
DMSO	Dimethyl sulfoxide
DPhAT	Diphenylammonium triflate
EA	Elemental Analysis
EDG	Electron donating group
e.e.	Enantiomeric excess
Et_3N	Triethylamine
Et_2O	Diethyl ether
EtOAc	Ethyl Acetate
EVK	Ethyl vinyl Ketone
EWG	Electron withdrawing group
HMBC	Heteronuclear Multiple Bond Coherence Spectroscopy
HRMS	High-Resolution Mass Spectroscopy
HSQC	Heteronuclear Sing Quantum Correlation Spectroscopy
Hz	Hertz
IR	Infrared
LiDMM	Lithium dimethyl malonate
LUMO	Lowest unoccupied molecular orbital
mCPBA	m-Chloroperbenzoic acid
MeCN	Acetonitrile
MeIm	N-Methylimidazole

MTDA/MMTP	1-methoxy-2-methyl-1-trimethylsiloxypropene
MVK	Methyl vinyl ketone
NHE	Normal Hydrogen Electrode
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
NOESY	Nuclear Overhauser Effect Spectroscopy
NOPF6	Nitrosonium hexafluorophosphate
ORTEP	Oak Ridge Thermal Ellipsoid Program
OTf	Trifluoromethanesulfonate or triflate
PMe3	Trimethylphosphine
Ppm	Parts Per Million
Pz	pyrazole ring
SAR	Structure-activity relationship
SOMO	Single Occupied Molecular Orbital
TBAB	Tetrabutylammonium borohydride
TBAH	Tetrabutylammonium hexafluorophosphate
TFT	α,α,α-Trifluorotoluene
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
Tp	Hydridotris(pyrazolyl)borate

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Chapter 1 : Introduction to Dearomatization

1.1 Introduction

Over the past decades, high throughput bioassays and small molecule libraries have increased the efficiency of identifying promising pharmaceutical leads. Consequently, synthetic and medicinal chemists have sought to explore stereo-controlled synthesis of novel molecular scaffolds. With the ability of high-throughput screening to test a myriad of compounds swiftly the number of pharmaceutical leads has increased substantially. However, the success rate in phase III clinical trial has decreased in the past decade from 59% between 1991-1995[1-3] to approximately 5%. These types of bioassays have traditionally focused on maximizing the number of compounds tested rather than diversifying their topological qualities.[4-6] Consequently, scientists have relied on utilizing traditional synthetic methods which produce molecules that are relatively easy to access. For this reason, so called "flat" compounds[7] made from aromatic rings coupled together predominate medchem libraries. Although these overused methodologies are able to functionalize arenes, aromaticity is often conserved, causing a lack of stereocenters and predominance of sp^2 carbon rich molecules.[7,8] This focus on synthesizing small flat molecules contrasts the targeting of natural products. Natural products (NPs) and their derivatives continue to play a vital role in the discovery of new medicines, especially for cancer and infectious deseases.[1] These have well-defined three-dimensional architectures, rich in carbon stereocenters, that are optimized for specific interactions with proteins. Since more complex molecules are better able to selectively fill space in receptor binding sites, molecular complexity is strongly correlated with clinical success.[2] The reliance on low-diversity combinatorial methods has led to a decrease in structural complexity (e.g., fraction of sp^3 carbons) in drug discovery libraries.[3,4] This realization has brought a renewed focus on natural product-like motifs.[5] Pseudo-natural products (PNPs), defined as natural product-like fragments not accessible through biosynthesis,[6] are increasingly being recognized as valuable compounds in drug discovery. Specifically, Lovering et al. have demonstrated that the success of drug development in clinical trials is directly correlated to the presence of chiral centers and the fraction of sp^3 hybridized carbons, suggesting that the increased complexity in a molecule is related to its specificity in receptor-ligand interactions.[9] Moreover, Brown and Boström[8] have shown that the established synthetic methodologies used in coupling reactions have caused an overemphasis of similar molecular shapes and properties to the exclusion of others. Consequently, the diversity of a chemical library is directly proportional to the diversity of the methodologies used. Therefore, it is desirable to generate new classes of compounds with both structural diversity and complexity in a manner that is accessible to medicinal

chemists. However, overutilization of previously mentioned existing synthetic coupling methodologies has led to an abundance of flat compounds with similar physical and chemical properties, limiting the efficacy of screening molecular libraries.

Targeting compounds with structural features similar to natural products has been the goal of diversity-oriented synthesis, generating molecular libraries teeming with complex three-dimensional molecules.[7,10] Such molecules allow the exploration of uncharted chemical space, increasing diversity of molecular libraries while generating compounds with different physical and chemical properties for structure-activity relationship (SAR) studies.[11-13] Within the context of drug development, aromatic molecules could serve as attractive precursors to bioactive small molecules (**Figure 1.1**) . The multiple alkene bonds within an aromatic framework afford opportunities for chemical elaboration toward the synthesis of alicyclic systems. However, their stability renders these compounds unstable towards additions reaction under most conditions, while favoring electrophilic substitutions under harsh conditions.

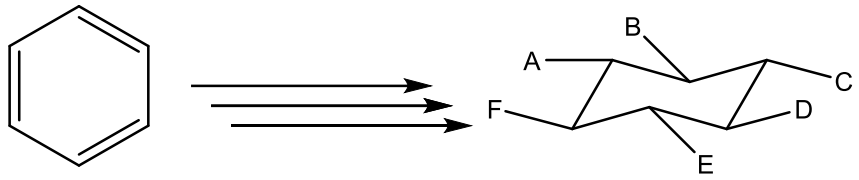


Figure 1.1 Aromatic molecules could serve as attractive precursors to bioactive small molecules. The multiple alkene bonds within an aromatic framework afford opportunities for chemical elaboration toward the synthesis of alicyclic systems.

1.2 Aromaticity

As opposed to other unsaturated molecules, such as olefins or alkynes, arenes do not readily undergo chemical transformations, due to their inherent stability. However, they are 1) commonly found in nature as structural motifs of natural products, 2) synthesized by the human body, and 3) can even be found in the interstellar medium.[14,15] Their ubiquitous presence in nature makes these molecules desirable precursors toward the synthesis of more complex leads. Nonetheless, functionalizing such molecules requires harsh reaction conditions which are not compatible with most coveted functional groups. Furthermore, because such reactions are substitution reactions the final compound is still "flat". Nonetheless, synthetic chemists have worked with arenes as starting material toward the synthesis of medicines, natural products, and petrochemical additives.[16-20]

Despite these functionalization challenges, aromatics are still considered a potential platform onto which develop pharmaceutical drugs. Many aromatics contain heteroatoms or functionalities associated with an increase in efficacy of the active pharmaceutical ingredients (API) of a drug.[19]

1.3 Defining Aromaticity

Aromatics stability is caused by an array of delocalized π electrons (**Figure 1.2**). π bonds in conjugation form very stable structures such as benzene, which is about 36 kcal/mol more stable than 1,3-cyclohexadiene. The fully conjugated π system, in agreement with to Huckel's rule of 4n+2 electrons, allows these molecules to have diagnostic resonance shift in ^{1}H and ^{13}C nuclear magnetic resonance (NMR) due to ring anisotropy.[19,21]

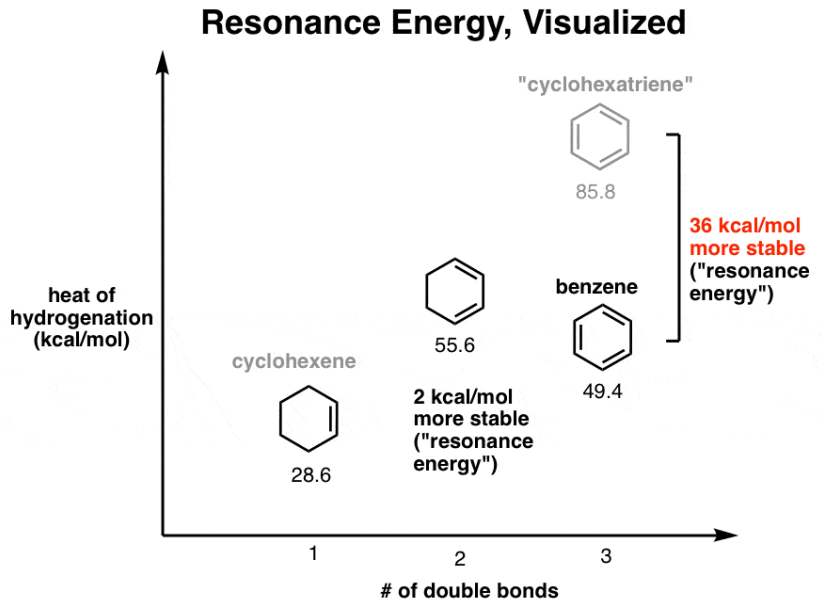


Figure 1.2 Comparison of the resonance energy stabilization. π bonds in conjugation form very stable structures such as benzene, which is about 36 kcal/mol more stable than 1,3-cyclohexadiene (Figure adopted from *Chem. Soc. Rev.*, 2018,47, 7996-8017).[21]

For a molecule to be considered aromatic it must follow certain rules: 1) there must be 4n+2π electrons, 2) the molecule must be a planar ring and 3) it has to exhibit alternating π-bonds. All of these contribute to aromaticity along with π-bond symmetries[22-24] Aromatics have the potential to be functionalized into more topologically diverse complexes that would add diversity to small-molecule libraries. However, the inherent stability of these aromatic molecules will need to be overcome to access addition

reactions versus the more typical substitution reactions. Dearomatization processes have exponentially increased in the past two decades for their ability to disrupt aromaticity and functionalize arenes, while giving access to alicyclic compounds (**Figure 1.3**).

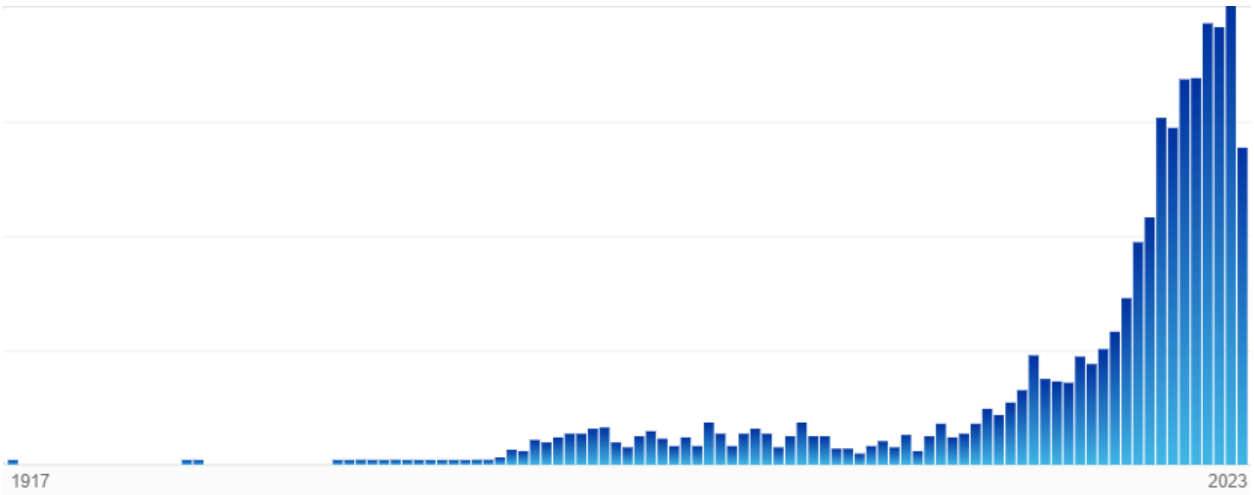
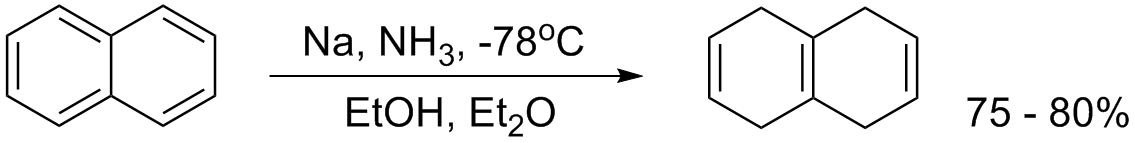


Figure 1.3 Dearomatization processes have been exponentially risen in interest in the past two decades for their ability to disrupt aromaticity and functionalize arenes, while giving. access to alicyclic compounds (Image produced from Scifinder).

1.4 Classical Dearomatization Methods

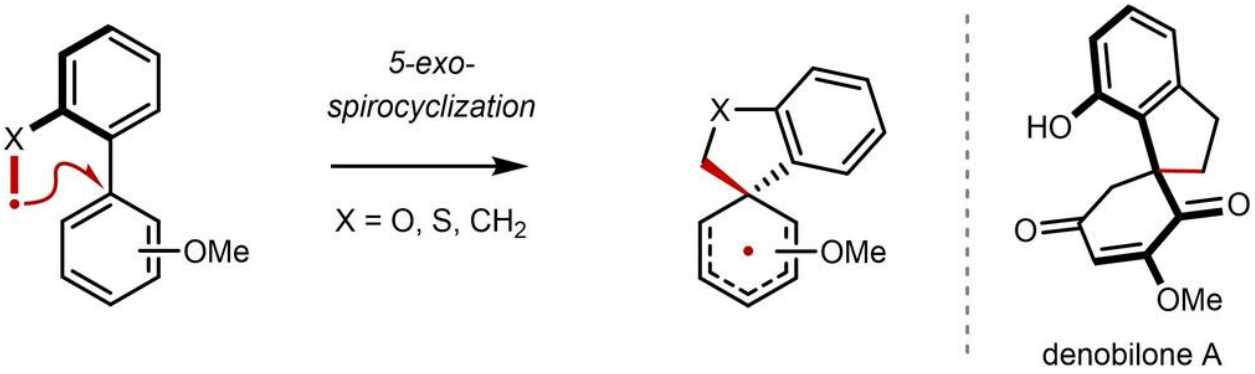
Radical mechanisms are an effective way to disrupt the aromaticity of an arene. The Birch reduction is the most common example of such reactions in which an aromatic molecule gives access to 1,4-cyclohexadienes.[25] This methodology requires harsh conditions, limiting the types of accessible functional groups, in the use of Na or Li metal in liquid ammonia (NH_3) and a protic solvent, giving rise to alicylic compounds (**Scheme 1.1**). This tool has proven to be effective in the synthesis of many natural products.[25]



Scheme 1.1 The Birch reduction is the most common example of reactions in which an aromatic molecule gives access to 1,4-cyclohexadienes.

Furthermore, radical dearomatization methods have been employed toward the synthesis of quaternary spyro compounds.[26] Radical cyclization reactions can facilitate the synthesis of complex polycyclic systems that find applications in medicinal chemistry and natural product synthesis.[27,28] The authors describe the synthesis of spirocyclic cyclohexadienones from biaryls under mild reaction conditions. Moreover, the polarity mismatch from the

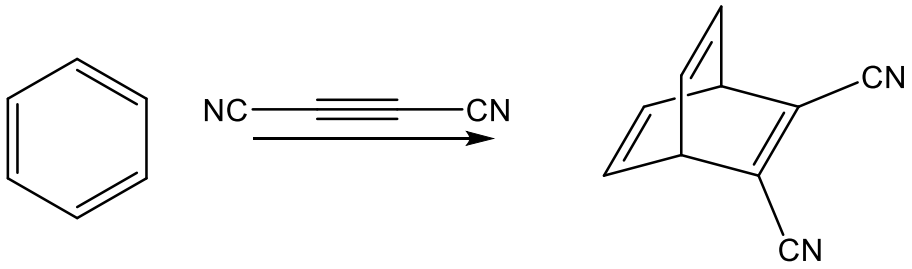
addition of a nucleophilic radical to an electron rich arene allows the regioselective synthesis of 2,4- or 2,5-cyclohexadienones with broad functional group tolerance. By transforming biaryls into spirocycles, underexplored three-dimensional chemical space can be accessed, providing an efficient means of generating quaternary spirocenters (**Scheme 1.2**).[28]



Scheme 1.2 Radical dearomatization methods have been employed toward the synthesis of quaternary spyro compounds. Radical cyclization reactions can facilitate the synthesis of complex polycyclic systems that find applications in medicinal chemistry and natural product synthesis (Scheme adopted from *Angew. Chem. Int. Ed.* 2023, 62, e202215422).

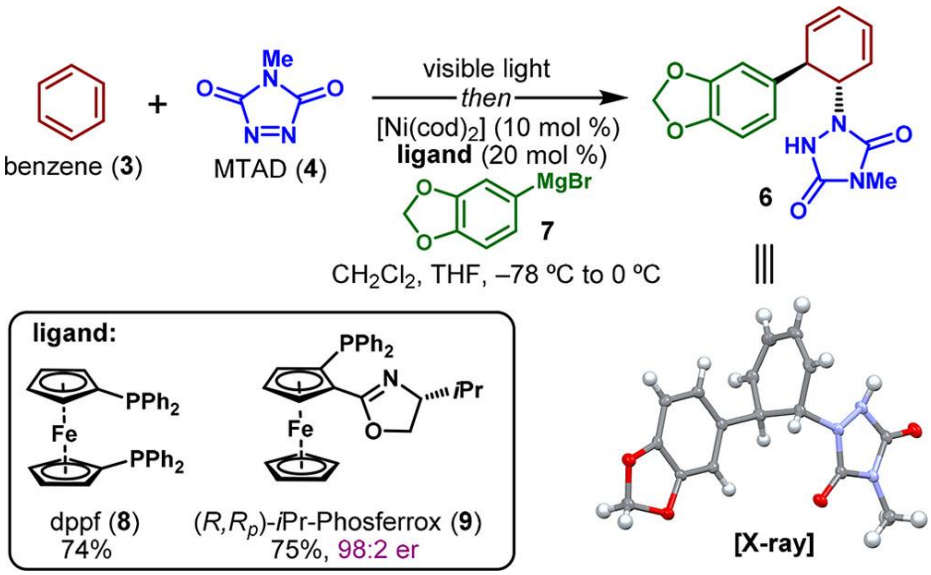
1.5 Photochemical Dearomatization Reactions

The inherent stability of aromatic rings renders thermal [4+2] cycloaddition difficult to carry out. However, under high temperature and activated dienophiles such as dicyanoacetylene, it is possible to perform thermal cycloaddition reactions to an aromatic molecule **(Scheme 1.3**).[29]



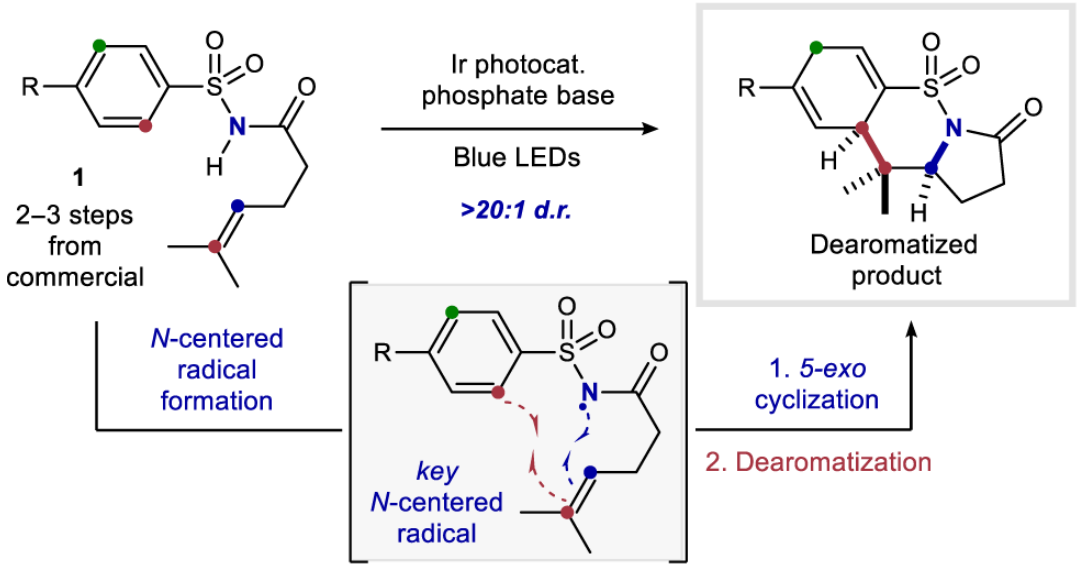
Scheme 1.3 Under high temperature and activated dienophiles such as dicyanoacetylene, thermal cycloaddition reactions to an aromatic molecule can be performed.

Nonetheless, thermal cycloaddition dearomatization reactions work sluggishly for aromatic compounds. More success has been found in photochemical activation with alkenes, as shown by Sarlah's synthetic pathway toward the synthesis of (+)-pancratistatins (**Scheme 1.4**).[30]



Scheme 1.4 Photochemical activation with alkenes toward the synthesis of (+)-pancratistatins (Scheme adopted from *J. Am. Chem. Soc.* 2017, 139, 44, 15656–15659).

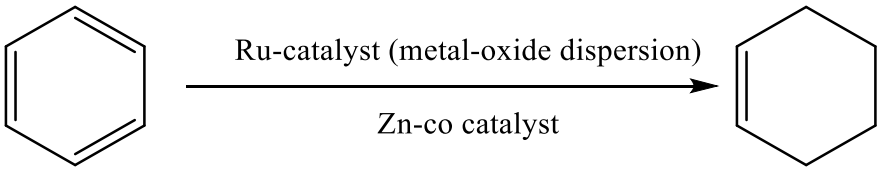
Another report showing photocatalytic cycloaddition dearomatization reactions initiates a carboamination/dearomatization cascade that proceeds through transient sulfonamidyl radical intermediates; these were formed from native sulfonamide N–H bonds, leading to 1,4-cyclohexadiene-fused sultams which generated richly substituted, three-dimensional compounds. These reactions occured at room temperature under visible light irradiation and are catalyzed by the combination of an iridium(III) photocatalyst and a dialkyl phosphate base (**Scheme 1.5**).[31]



Scheme 1.5 Carboamination/dearomatization cascade that proceeds through transient sulfonamidyl radical intermediates formed from native sulfonamide N–H bonds leading to 1,4-cyclohexadiene-fused sultams (Scheme adopted from *Nat. Commun* 11, 2528 (2020)).

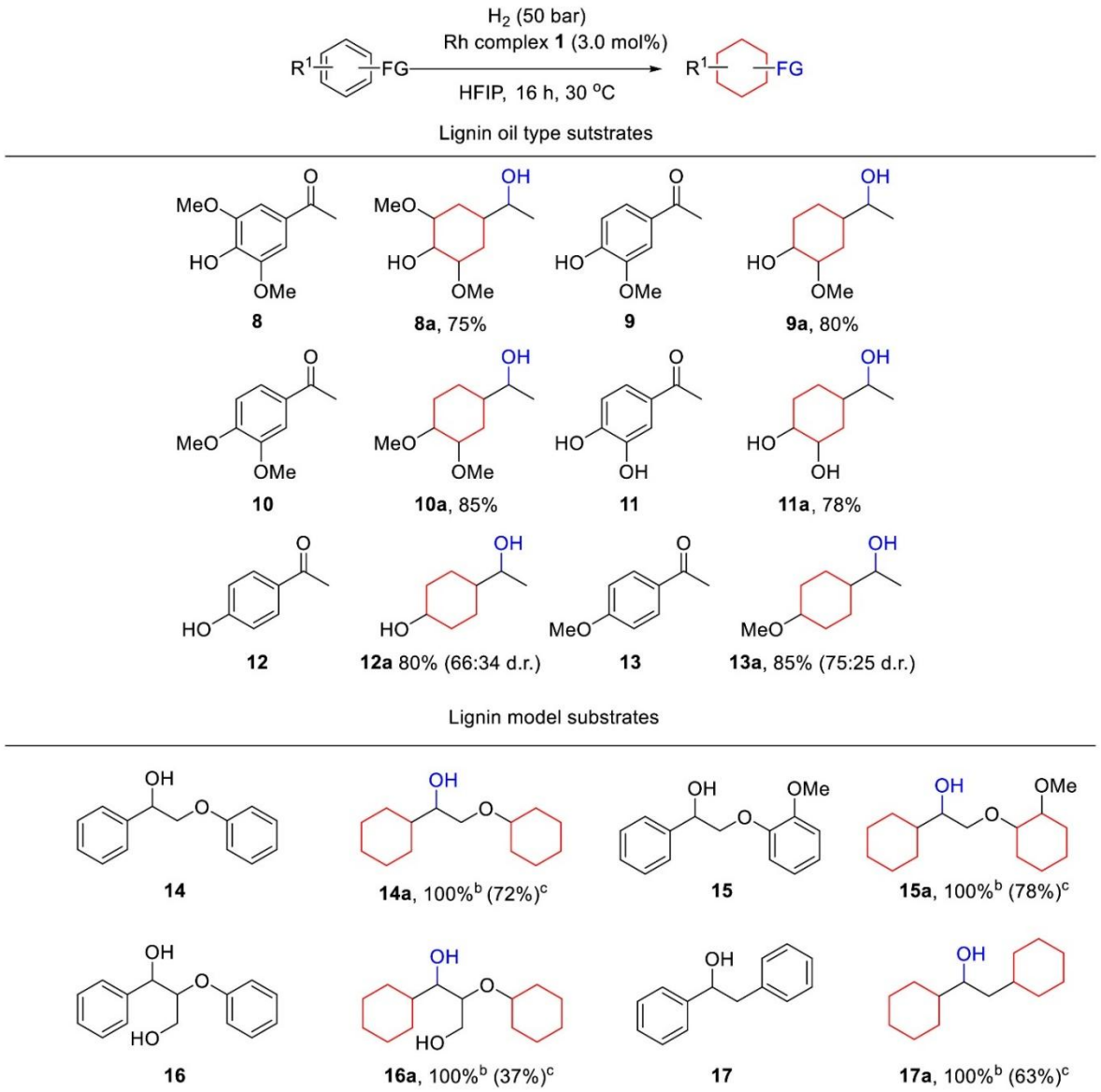
1.6 The Asahi Process

The successful synthesis of cyclohexanol and cyclohexenes from benzene has historically been challenging. In 1997, Asahi Chemical Industry Co. developed a technology toward highly selective partial hydrogenation of benzene to cyclohexene and commercialized a new process for producing cyclohexanol from benzene through cyclohexene. The catalyst was obtained by reducing a ruthenium complex containing a zinc compound, which acted as a co-catalyst. One of the remarkable features of the reaction was the setup. This is comprised of four phases: vapor (hydrogen), oil, aqueous and solid (ruthenium catalyst). The catalyst was used in the aqueous phase, and the reactants (benzene and hydrogen) were dissolved in the aqueous phase, where the reaction proceeded. Therefore the products and reactants transfer between the four phases through dissolution, diffusion and extraction, rendering quick transfer was a very important factor in enhancing reaction selectivity (**Scheme 1.6**).[32]



Scheme 1.6 In 1997, Asahi Chemical Industry Co. developed a technology toward highly selective partial hydrogenation of benzene to cyclohexene and commercialized a new process for producing cyclohexanol from benzene through cyclohexene.

The Asahi process can be used for the catalytic hydrogenation of aromatic rings. This methodology represents an essential industrial chemical process for the synthesis of commodity chemicals and intermediates in pharmaceuticals, polymers, and fine chemicals. The authors report the hydrogenation of lignin-derived acetophenones, benzoic acids as well as other functionalized aromatics to the corresponding alicyclic products by reducing the aryl groups (**Scheme 1.7**).[33]

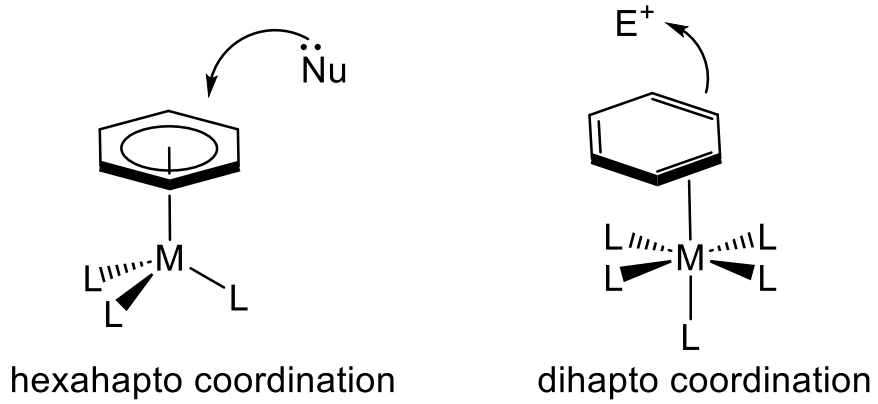


Scheme 1.7 Hydrogenation of lignin-derived acetophenones, benzoic acids as well as other functionalized aromatics to the corresponding alicyclic products by reducing the aryl groups (Scheme adopted from *Journal of Organometallic Chemistry* 997 (2023)).

The Harman Lab has worked on developing transition-metal mediated dearomatization of functionalized aromatics for the direct synthesis of highly functionalized and saturated small-molecule libraries. The Harman Lab previously reported the successful manipulations of dearomatized functionalized electron-rich arenes such as anisoles, phenols, anilines and other aromatic examples, through dihapto coordination to the π-basic metal fragment WTp(tris-pyrazolylborate)(NO)(PMe_3).[32,34-40]

1.7 Transition Metal-Mediated Dearomatization

Transition metal complexes are distinguished in their dearomatization ability by the mode an aromatic compound coordinates to said metal center.[41] Typically, this binding mode can occur in either a hexahapto fashion, where the compound's aromaticity is broken as it coordinates with six adjacent carbon atoms (η^6) to a π-acidic metal,[42] or in a dihapto fashion, where the compound binds through to adjacent carbon atoms (η^2) to a π-basic metal (**Scheme 1.8**).[35,43]



Scheme 1.8 Different modes of metal coordination. Hexahapto fashion, where the compound's aromaticity is broken as it coordinates with six adjacent carbon atoms (η^6) to a π-acidic metal, or in a dihapto fashion, where the compound binds through to adjacent carbon atoms (η^2) to a π-basic metal.

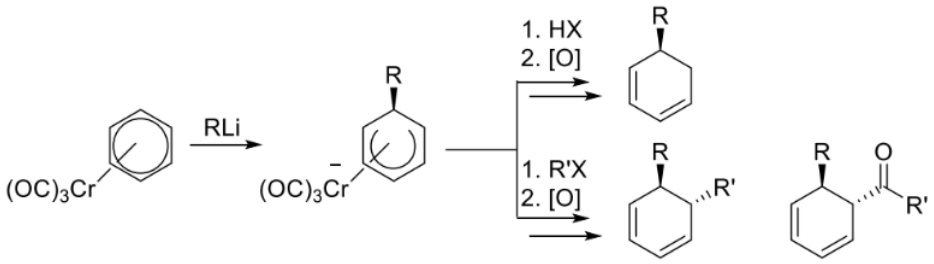
In the former case, when the arene coordinates in a hexahapto fashion, the incoming aromatic donates electron density from its π system to an electron deficient metal center, rendering the complex susceptible to nucleophilic additions.[42] In contrast, in the latter case dihapto coordination occurs in the presence of a π-basic metal, which contributes electron density from a d_π orbital to the lowest unoccupied molecular orbital (LUMO) of a coordinated π bond of an olefin. This specific type of electron donation, called π-backbonding, results in the formation of a metallocylopropane, as the carbon atoms of the coordinated alkene structurally resemble C_{sp3} centers upon coordination to the metal center. Consequently, the uncoordinated part of the aromatic molecule takes on a structural and electronic resemblance to a diene, allowing for electrophilic additions.[35]

1.71 Effects of Electron-Deficient Metal Complexes on Aromatic Reactivity

The first category of dearomatization agents involves widespread electron-deficient metal complexes that are frequently bound to potent π-acceptor ligands such as carbonyl or nitrosyl ligands, which exist in cationic forms. When potent acceptor ligands

are bound to metal centers, it significantly reduces their electron density and spurs their η^6-coordination to electron rich aromatic compounds. Such mode of interaction results in a transfer of electron density from the π-cloud of the incoming aromatic ligand to the electron-deficient metal center, thus stabilizing the complex.[41] Consequently, hexahapto coordination leads to increased susceptibility of the coordinated aromatic compound to nucleophilic additions. Examples of such complexes include $Cr(CO)_3$, $Mo(CO)_3$, $[Mo(CO)_3]^+$, $[Mo(CO)_2(NO)]^{2+}$, and $[FeCp]^+$. These can undergo nucleophilic additions with various nucleophiles, which result in substituted arenes, as the product's isolation restores aromaticity.[41,42,44,45]

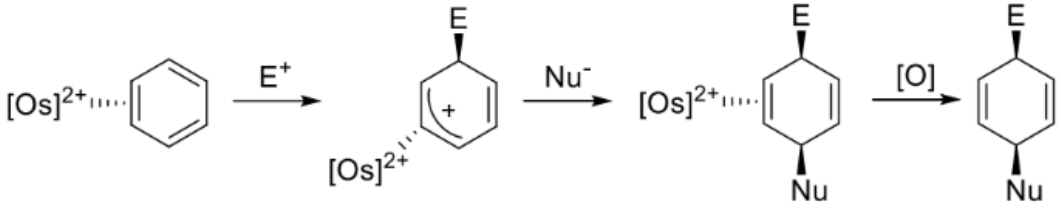
In the case of $Cr(CO)_3$, strong nucleophiles can also be employed toward the synthesis of alicyclic compounds. Dearomatization can be achieved by employing a strong nucleophile, such as an organolithium or Grignard reagent, followed by an electrophile (**Scheme 1.9**).[46,47] In the route shown, the nucleophile **R** adds anti to the metal center, generating a new stereocenter and an anionic chromium-supported cyclohexadienyl species. Acid addition follows this step to produce a 1,3-cyclohexadiene product (**Scheme 1.9**, top compound). However, different addition patterns are observed when carbon nucleophiles are utilized.[41,42] Indeed, when a subsequent nucleophile **R'** is used, the addition occurs syn to the metal as a consequence of the initial attack of the electrophile to the metal center, delivering it endo to the cyclohexadienyl ligand.[48] Moreover, during this process the electrophile can insert into the carbonyl group, leading to the *trans* addition of a ketone across one of the double bonds (**Scheme 1.9**, bottom compounds).



Scheme 1.9 In the route shown, the nucleophile adds anti to the metal center, forming an anionic chromium-supported cyclohexadienyl species. Acid addition follows this step, affording a newly formed stereocenter to the depicted anionic species to produce a 1,3-cyclohexadiene product.

1.72 Effects of Electron-Rich Metal Complexes on Aromatic Reactivity

Metal fragments, with π-basic d^6 18e- configurations, represent the second category of dearomatization agents for involving transition metals.[35,42,43] In this process, the electron-rich metal fragment can induce dearomatization through backbond donation upon coordination with the arene, in contrast to the η^6-coordination system where dearomatization necessitates a nucleophilic addition. Dearomatization of aromatics bound to a basic metal fragment can be inferred in the supporting information for the crystal structure data of η^{2-}coordinated benzene. In benzene, a C-C bond length is approximately 1.40 Å. However, in bound benzene the two contiguous atoms interacting with the metal fragment show an elongated bond length of 1.46 Å, indicating the formation of a metallocyclopropane.[49] Furthermore, the uncoordinated olefin portions now exhibit contracted bond lengths, more closely resembling double bonds not present in the uncoordinated benzene ring. This chemical transformation allows for stereo and regioselective electrophilic additions to the arene ligand, which can be followed by various nucleophiles. Originally, η^2 coordination chemistry was observed with a pentaammineosmium(II) system.[50] Reducing $(NH_3)_5Os(OTf)_3$ in the presence of benzene rendered the resulting osmium(II) species electron-rich enough to engage in η^2-coordination with the aromatic. The pentaammineosmium(II) metal fragment showed great reaction versality once benzene was coordinated to the Os(II) fragment.[51-55] It could undergo electrophilic additions with a wide range of carbon electrophiles, including Michael acceptors and acetals. In this context, nucleophilic additions to the newly formed allyl species could occur using mild reagent, such as masked enolates, resulting in the formation of 1,4-cyclohexadiene species (**Scheme 1.10**).[56]



Scheme 1.10 Nucleophilic additions to the newly formed allyl species could occur using a mild reagent such as masked enolates or a stronger one, like alkyl lithium compounds. This results in the formation of 1,4-cyclohexadiene species.

In this scenario, both the electrophile and nucleophile are added to the aromatic compound's face that is opposite to the metal. Furthermore, detailed studies showed that the Os(II) fragment could coordinate with aniline, anisole, phenol, naphthalene, and pyrroles, significantly expanding the scope of aromatic functionalization.[51-54,57]

However, finding an alternative that would overcome the major drawbacks associated with the osmium metal fragment would be beneficial in the quest toward the synthesis of functionalized cyclohexenes. These issues include: 1) Osmium's substantial cost, 2) its elevated toxicity, 3) the achiral nature of the dearomatization agent, which would curtail the formation of enantioenriched targets and 4) the inherent acidity of the ammine ligands, inhibiting additions of strong reagents such as alkyl lithiums.

To effectively coordinate in a dihapto fashion to a metal fragment, a reduction potential of 0.00 V (NHE) needs to be taken into consideration. Such potential is involved in the d^5/d^6 reduction potential of transition metals.[58,59] Numerous studies eventually pointed to the development of the π-basic ReTp[(MeIM)(CO)] fragment, which acts both as a stronger π-base compared to the Os(II) system and introduces chirality into the system.[49,60] Moreover, in order to tune the reduction potential and chirality of the metal fragment the trispyrazolylborate (Tp) ligand, pioneered by Trofimenko, was introduced in the complex.[61] The added advantage in the utilization of said tridentate scorpionate ligand was in its enhancement of the octahedral geometry of the metal complex, limiting the formation of a seven-coordinate system potentially resulted from oxidative addition (**Figure 1.4**).

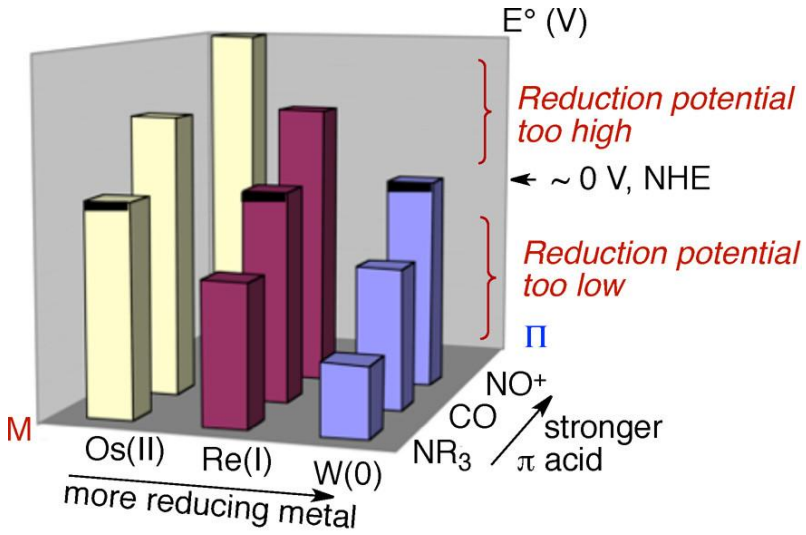
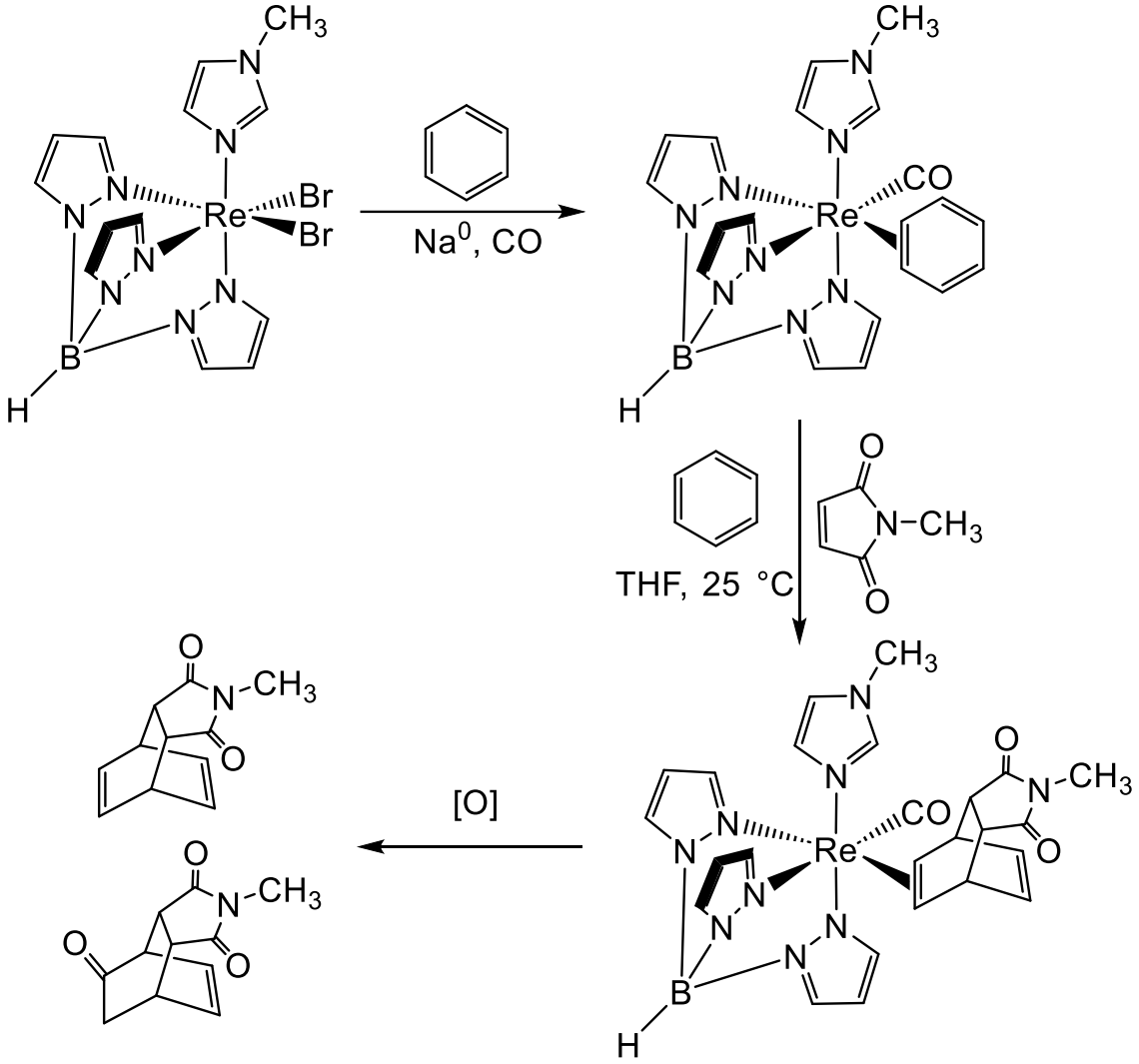


Figure 1.4 Effectively coordinate in a dihapto fashion to a metal fragment, a reduction potential of 0.00 V (NHE) needs to be taken into consideration. Such potential involved the d^5/d^6 reduction potential of transition metals (Figure adopted from *Chem. Rev.* 2017, 117, 22, 13721–13755).[35]

A similarity in reduction potentials of metal fragment does not imply similar reactivity. Nevertheless, the Re(I) fragment, like the Os(II) fragment, can coordinate to a similar range of aromatics and pyridine derivatives.[35,56] Furthermore, this metal fragment

enabled the formation of novel compounds through easy-to-access Diels-Alder reactions. For examples, dearomatization of benzene using the Re(I) fragment enables a Diels-Alder reaction with NMM, resulting in a bicyclo[2.2.2]octene core (**Scheme 1.11**).[49,62]



Scheme 1.11 Dearomatization of benzene using the Re(I) fragment enables a Diels-Alder reaction with NMM, resulting in a bicyclo[2.2.2]octene core.

The Re(I) dearomatization agent also allows for tandem electrophilic/nucleophilic additions, akin to the Os(II) system, yielding *cis*-disubstituted 1,4-cyclohexadiene products. Gratifyingly, the yields for the organic transformations enabled by the Re(I) system were significantly higher in comparison to the Os(II) system.[63]

Challenges in the preparation and scalability of the Re metal fragment spurred the studies into the development of dearomatization agents based on other electron rich transition metals, represented as shown in **Figure 1.5**.

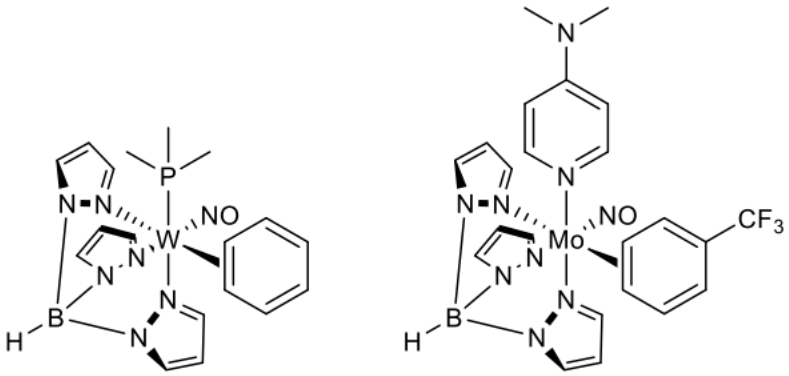


Figure 1.5 Novel dearomatization agents with electron rich transition metal from Group 6.

The development of a novel platform followed a similar electrochemical rationale, as the 1st dearomatization revolution that took place in the establishment of a Re-based metal fragment from an Os-based agent. Mo(0) dearomatization agents were proposed and employed using a potent π-acceptor nitrosyl ligand instead of a carbonyl, to tame aromatic coordination.[42] These fragments proved useful in scalability and synthesis of pharmaceutically relevant molecules and metal oxidation, liberating novel organic compounds, could be easily performed in air (**Figure 1.6**). However, the fragment's air sensitivity soon proved to be a disadvantage toward purification processes and set ups outside a glovebox.

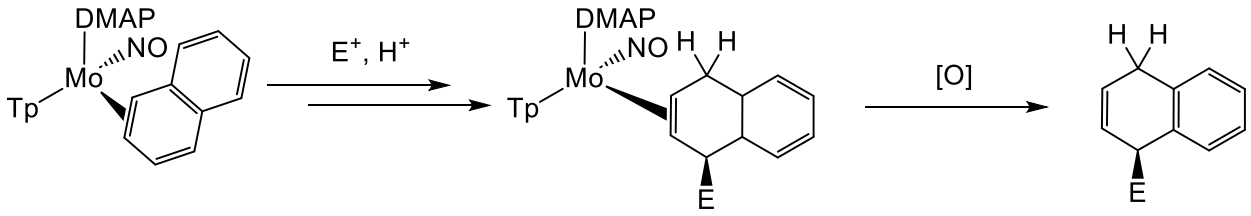
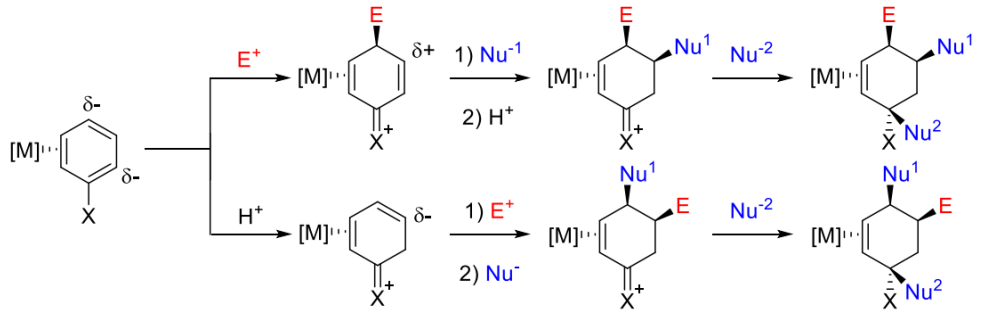


Figure 1.6 These fragments proved extremely useful in scalability and synthesis of pharmaceutically relevant molecules. Furthermore, metal oxidation liberating novel organic compounds could be run in air.

The 3rd dearomatization revolution employed a W(0) fragment. This would stand out as the most π-basic among the four dearomatization agents developed in the Harman lab. It has also proven to be the most versatile in binding the greatest number of electron rich and electron deficient arenes, heterocycles, and polycyclic aromatic hydrocarbons (**Scheme 1.12**).[64,65] In contrast, the Mo(0) fragment serves as a notably weaker π-base in comparison to the W(0) fragment, leading to limitations in the range of aromatics that can bind to it.[66]



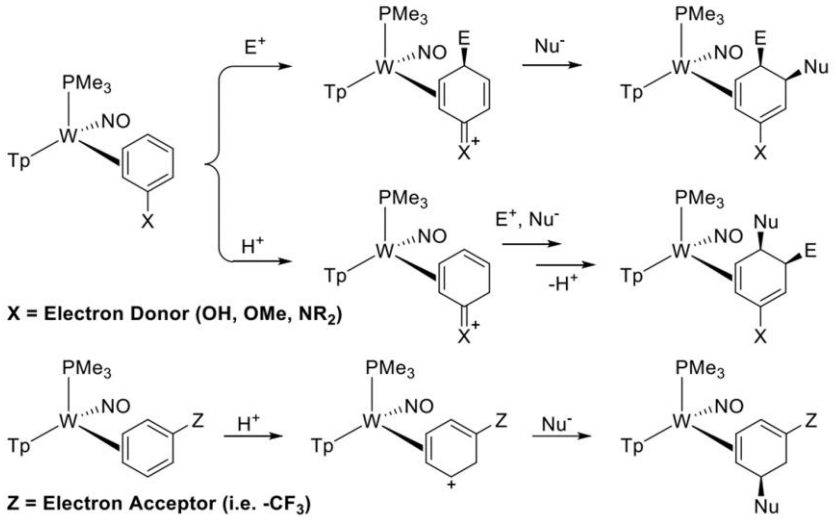
Scheme 1.12 Electron-rich and electron-deficient transition metal dearomatization.

1.73 Electron-Deficient Arenes Coordinated to Electron-Rich Metal

The Harman Lab has been actively involved in developing transition-metal-mediated dearomatization processes for the direct synthesis of highly functionalized and saturated small-molecule libraries using cheap and abundant aromatics. The Lab has previously reported successful manipulations of dearomatized functionalized arenes, such as anisoles, phenols, anilines, and other aromatic compounds, through dihapto coordination to the π-basic metal fragment WTp(trispyrazolylborate)(NO)(PMe_3).[34,36-40,67]

Numerous examples can be found regarding the exploration of the reactivity of functionalized benzene systems and electron-rich aromatics.[43,54,55,57,68-71] However, the potential of W(0) and Mo(0) systems to stimulate reactivity in electron-deficient arenes remained relatively uncharted.

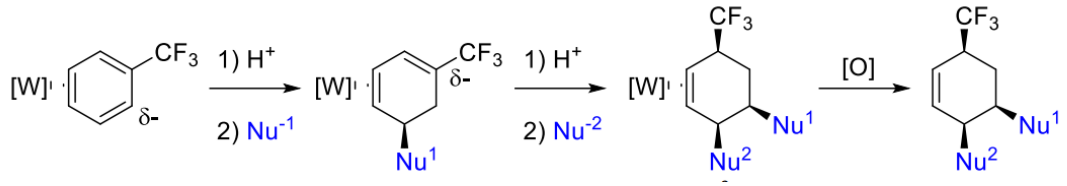
Until recently, it was thought that although arenes with electron-withdrawing groups (EWGs) are better π-acids, they would be inferior as η^2-aromatic substrates for organic reactions since this type of substituent and the electron-donating metal are at cross-purposes (**Scheme 1.13**).



Scheme 1.13 Comparison between the chemical reactivity of electron-rich and electron deficient aromatics coordinated to a W metal fragment.

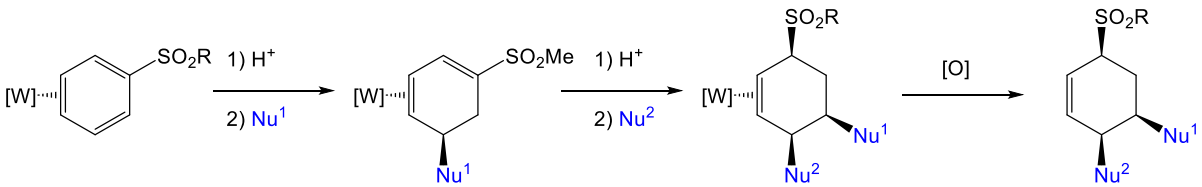
Prior to the introduction of the W(0) and Mo(0) systems of trifluorotoluene complexes,[72,73] the only examples of thermally stable η^2-benzene complexes featuring electron-withdrawing groups were found in pentaammineosmium(II) complexes with trifluorotoluene, benzophenone, and pivalophenone.[74] However, no further chemistry was explored.

In our previous research, Dr. Wilson explored electron-deficient derivatives, including coordinated trifluorotoluene (TFT), and observed intriguing addition patterns resulting from variations in electron density distribution within the arene ring, akin to directing groups in organic chemistry (**Scheme 1.14**).[75] Electron-withdrawing groups were found to polarize the arene in such a way that protonation occurred ortho to the CF_3 group, with nucleophilic additions taking place adjacent to the sp^3 carbon. This led to the formation of η^2-diene complexes that were electronically complementary to those derived from electron-rich arenes, offering the potential for further elaboration into novel, trisubstituted cyclohexenes.[75]



Scheme 1.14 Reactivity of electron-deficient trifluorotoluene upon η^2-coordination to a π-basic metal fragment.

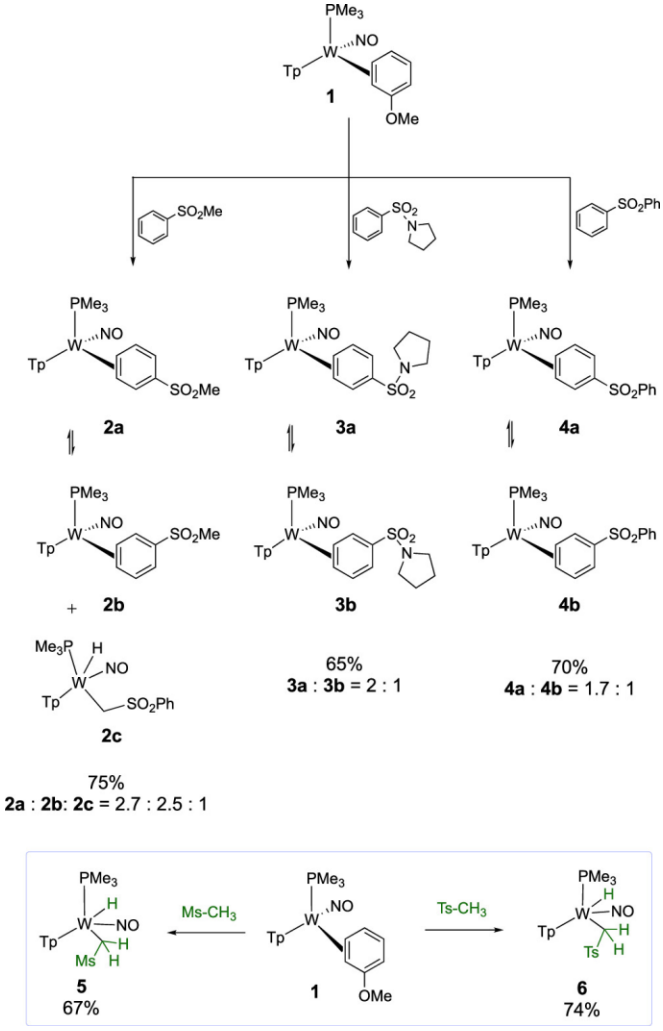
Furthermore, Dr. Simpson has also initiated investigations into other electron-deficient arenes, particularly those relevant to pharmaceutical design, such as sulfones.[76] Sulfones are attractive functional groups for use in dearomatization processes, as sulfur is the third most common heteroatom in marketed pharmaceuticals, following nitrogen and oxygen.[77,78] Sulfones and sulfonamides are prevalent in various pharmaceuticals, including antibiotics, cancer therapeutics, COX-2 inhibitors, diuretics, and ulcer preventatives (**Scheme 1.15**).[77,79]



Scheme 1.15 Reactivity of electron-deficient sulfone aromatics upon η^2-coordination to a π-basic metal fragment.

1.8 Phenyl Sulfones Coordination to the W fragment

Among the several attempts to bind phenyl sulfones to the W(0) metal fragment only three proved successful in the full exchange from the original anisole complex (**Scheme 1.16**, compound **1**). The conversion with $PhSO_2Me$, $PhSO_2NH(CH_2)_2$), and Ph_2SO_2 all resulted in a mixture of coordination diastereomers, with ratios of 1.1:1, 2:1 and 1.7:1., respectively. Although products generated from $PhSO_2NH(CH_2)_2$ and Ph_2SO_2 showed lower yields, this initial disadvantage could be overcome by increasing the solution concentration and the amount of phenyl sulfone used. Furthermore, the reaction mixture resulting from the $PhSO_2Me$ exchange contained three species in a ratio of 2.7: 2.5: 1, where the third species was assumed to be the sulfonylmethyl hydride **2C**. The formation of **2C** was further supported by reacting the anisole coordinated complex (**1**) with dimethyl sulfone and 4-(methylsulfonyl)toluene, which yielded tungsten hydrides only, exhibiting similar spectroscopic features as **2C** for the hydride and methylene set (**Scheme 1.16**). Previously, the $WTp(NO)(PMe_3)$ system has been observed to insert into N-H,[40] O-H,[80] C-H,[81] and C-F bonds,[82] but to our knowledge, this is the first example involving an sp^3 carbon with this tungsten fragment. It should be noted, however, that seminal work by the Legzdins group includes many such examples for the {WCp*(NO)} system.[83,84]



Scheme 1.16 Among the several attempts to bind phenyl sulfones to the W metal fragment only three proved successful in the full exchange from the original anisole complex. The conversion with $PhSO_2Me$, $PhSO_2NH(CH_2)_2$), and Ph_2SO_2 (Figure adopted from *J. Am. Chem. Soc.* 2022, 144, 21, 9489–9499).[76]

Despite the formation of tungsten hydrides, complexes **2a** and **2b** proved more suitable for reaction purposes as **3a**, **3b** and **4a**, **4b** reacted sluggishly to addition reactions, providing low yields and low purities. In investigated projects throughout this thesis, aromatics containing electron-withdrawing functional groups such as sulfones have been explored. The challenge lies in the fact that many electron-deficient functional groups feature double or triple bonds that can compete with the arene for coordination to the metal. However, calculations have shown that the S-O bonds in sulfones behave more like single bonds due to S-O bond polarization, preventing multiple bonds from coordinating to the metal. This induces similar reactivity patterns as observed with the TFT system, which will be discussed in **Chapter 3**.

An additional advantage of the sulfone-coordinated complex is the potential for chemical removal of the sulfone group,[78] allowing for a third addition reaction. This feature is believed to provide a pathway for additional functionalization in synthesized molecules, significantly expanding the diversity of trisubstituted cyclohexene products beyond the expected sulfone and sulfonamide derivatives. Chemical reactivity of compounds generated from sulfone removal will be explored in detail throughout the rest of this work.

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Chapter 2 : Hydroindolone Cores

2.1 Introduction

Hydroindolone cores are commonly found in Lycorine-type molecules. These represent biologically relevant alkaloids, whose anticancer and antiviral properties have been extensively discussed and studied for medication development.[1-4] Hydroindolone derivatives have attracted much attention among medicinal chemists due to their biological properties: *Tazettine* exhibits activity against certain tumor cell lines,[5] *(+)-Pretazettine* and *6a-epiPretazettine* show antiviral and anticancer activity among their many properties,[6] while (-)-*Haemanthidine* is known as a novel anticancer agent due to its ability to overcome cancer cell resistance to apoptosis (**Figure 2.1**).[7]

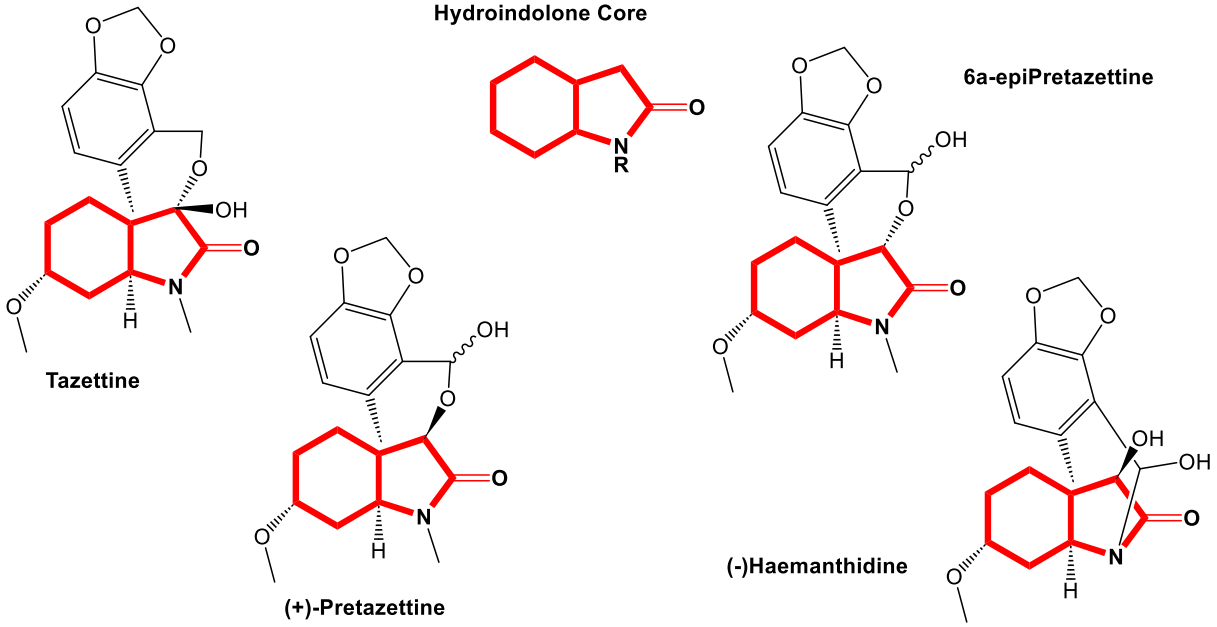


Figure 2.1 Examples of biologically active compounds which embody a hydroindolone core.

This class of compounds displays small molecules with high structural complexity and potent biological activity. A recent report of an isolated Lycorine-type alkaloid shows the inherent structural complexity for these cores and the evident difficulty toward their synthesis. Amarbellisine was extracted from the bulbs of Egyptian *Amaryllis belladonna L* (**Figure 2.2**).[8]

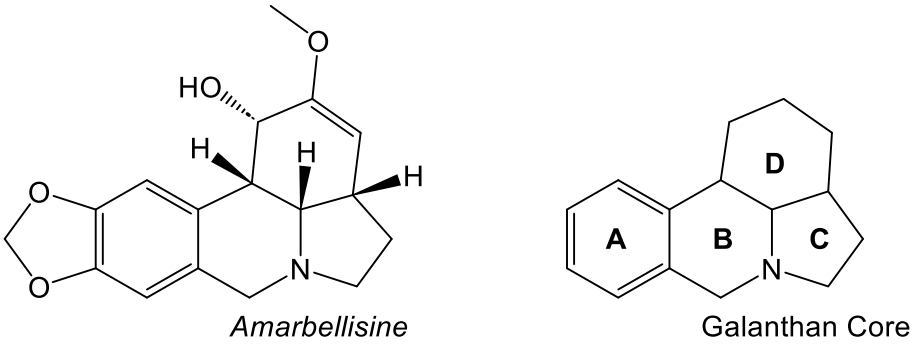


Figure 2.2 Amarbellisine was extracted from the bulbs of Egyptian Amaryllis belladonna L. A Lycorine derivative which displays the characteristic Galanthan core found in this class of molecules.

2.2 Synthesis of γ-lactams

Galanthan cores are predominantly featured within biologically active natural products. However, said cores are not an easy feat to synthesize. Common strategies toward the synthesis of these skeletons involve γ-lactams generation first. Furthermore, γ-lactams themselves represent the main framework of a wide array of natural products.[9] These molecules are found within a set of small nitrogen-containing heterocycles, which are ubiquitous in naturally occurring bioactive compounds, and non-natural compounds covering a broad spectrum of biological activities. Consequently, γ-lactams have been of primary interest in medicinal chemistry. Throughout the years, several strategic pathways have been developed toward the synthesis of this structural moiety.[10-13] γ-lactams have been intensely investigated, especially after the first analogues of penicillin as antibiotic were reported independently by Baldwin *et al*. and researchers from Eli Lilly.[14-15] Moreover, γ-lactams analogues of penicillin were regarded to displace a higher biological activity compared to penems. Baldwin stated that the augmented biological relevance was due to delocalization of the lactam nitrogen lone pair into the olefin π system (**Figure 2.3**).[16]

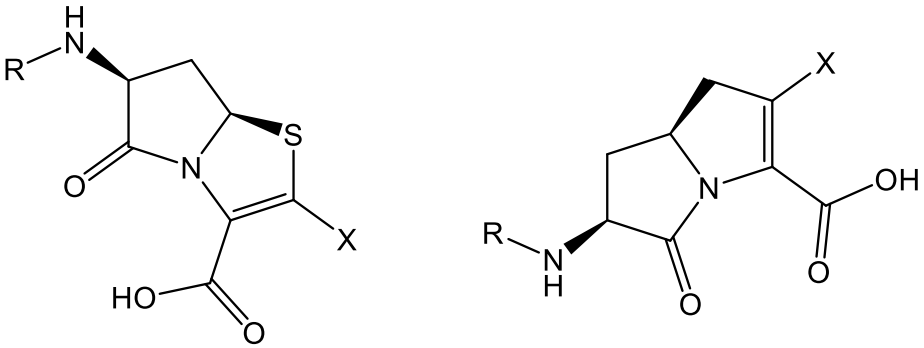


Figure 2.3 γ-lactams derivatives of common β-lactams antibiotics.

Consequently, many medicinal chemists have been inspired to pursue the synthesis of these novel moieties. In fact, a very large number of pharmaceutically active γ-lactams have been reported, including antibiotics, anti-inflammatory, cytotoxic and antitumor compounds.[16] The most common way to synthesis γ-lactams is from the cyclization and annulation reactions of a carboxylic group and an amine precursor (**Figure 2.4**);[17] N-C bond coupling has also been investigated, although to a smaller extent.[16]

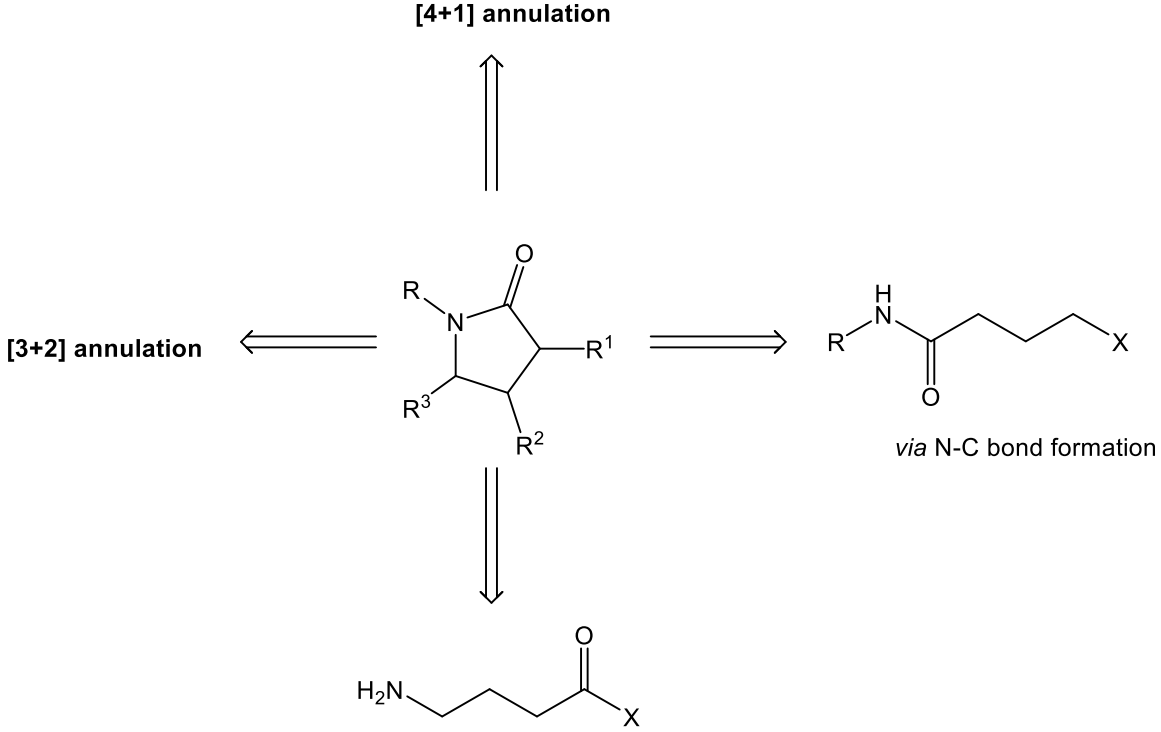
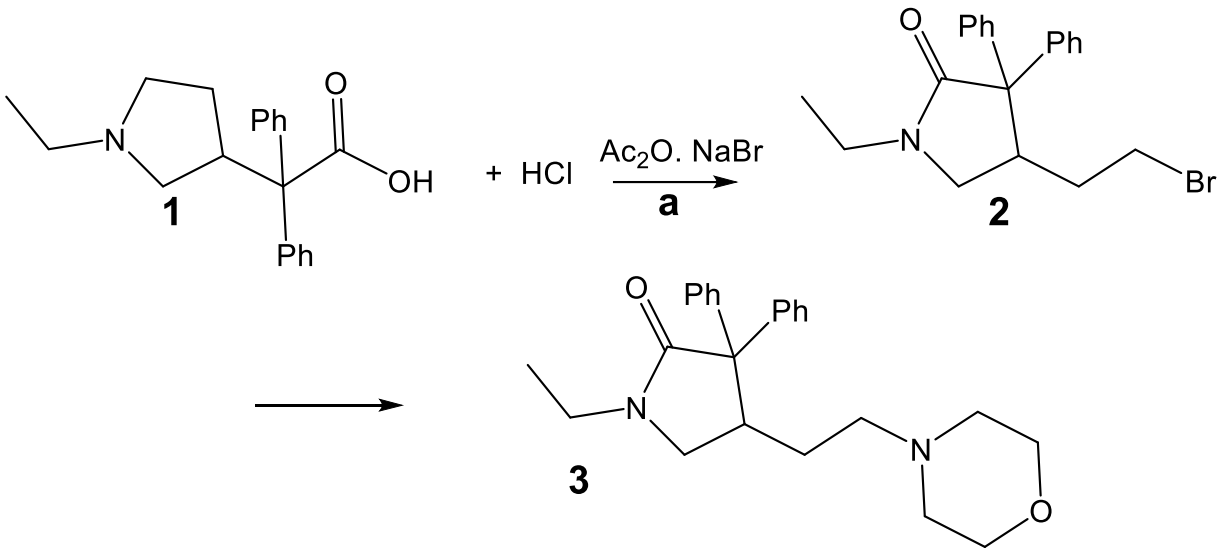


Figure 2.4 shows the most common methodologies toward the synthesis of γ-lactams.

2.2.1 Cyclization

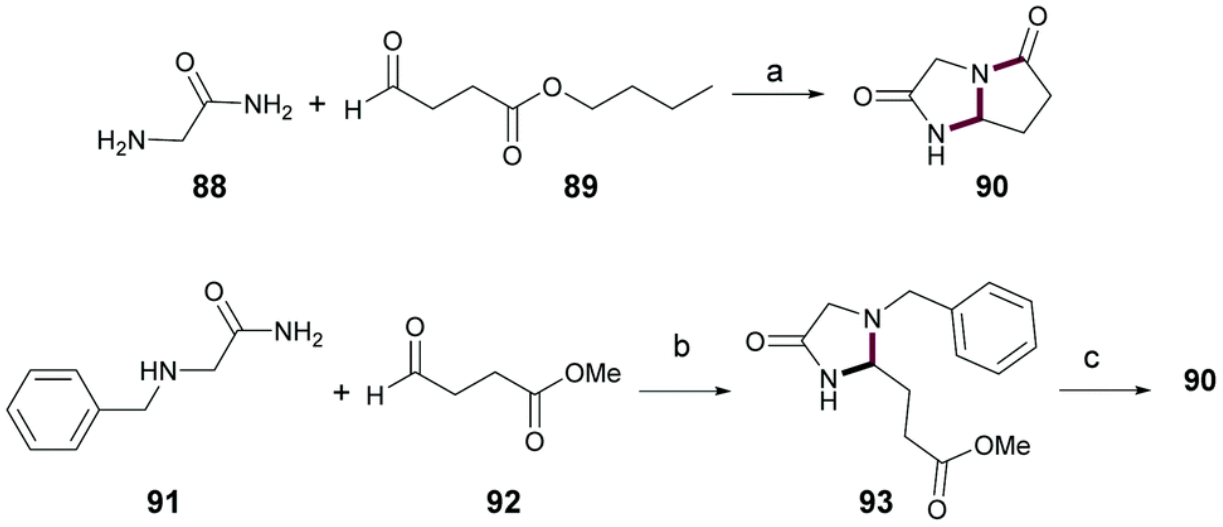
A common way to synthesize γ-lactams is through cyclization reactions of amines with carboxylic acids, esters or acyl chlorides, to make amide bonds. One of the first reported attempts using this approach was described by Jenkins *et al.* in 1964.[19] Herein, the synthesis of doxapram (**Scheme 2.1**, compound **3**) was carried out from a pyrrolidine derivative (**1**). This was converted in situ into an acyl bromide with subsequent intramolecular addition of a tertiary amine to produce compound **2** (**Step a**), after cleavage of the 1-5 bond. Finally, doxapram was recovered after substitution of bromide by morpholine (**Step b**). The ease of this synthesis underlines the ability to access biologically active compounds that bear γ-lactams moieties. Furthermore, compound **3** is a respiratory stimulant which increases the rate and depth of breathing by activating chemoreceptors found within the carotids (the activation encourages deeper breathing).[19]



Scheme 2.1 The synthetic pathway for doxapram, a common respiratory stimulant.

2.2.2 [4+1] Annulation

Another common method toward the synthesis of γ-lactams is through [4+1] annulation reactions. Dorigotti et al. reported what is believed to be the first synthetic example toward the annulation of a biologically active γ-lactams.[20] In this investigation 1-azabicyclo[3.3.0]octan-3,8-dione (**Scheme 2.2**, compound **90**) was synthesized under basic water reflux using an aldehyde **89** and glycinamide. This reaction proved more efficient if carried out using benzyl protected α-aminoamide **91** and aldehyde **92**. Indeed, after deprotection, the obtained aminal **93** cyclizes to provide the bicyclic lactam **90** in 80% overall yield.



Scheme 2.2 The synthetic pathway for 1-azabicyclo[3.3.0]octan-3,8-diones, a structural analog to oxiracetam (Scheme adopted from *J. Med. Chem.* 1993, 36, 26, 4214–4220).

Compound **90** is Dimiracetam, a patented nootropic drug of the racetam family, which is class of drugs containing a pyrrolidone core. Moreover, compound **90** is a structural analog to the most famous racetam drug, oxiracetam (**Figure 2.5**), which is reported to be a potent cognition enhancer.[21,22]

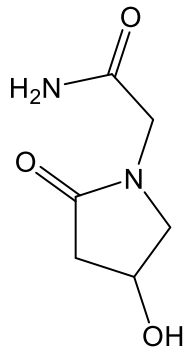
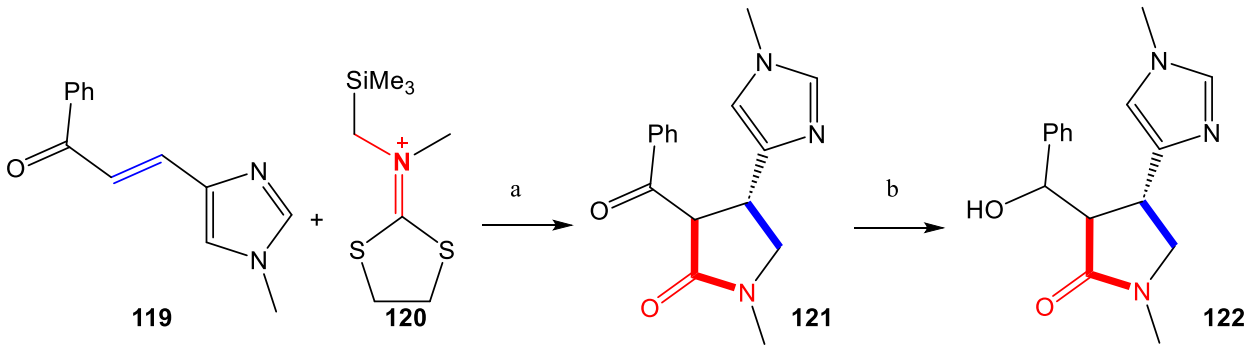


Figure 2.5 The molecular structure for oxiracetam, a potent cognition enhancer.

2.2.3 [3 + 2] annulation

[3+2] annulation reactions also proved effective in the strategic synthesis of γ-lactam.[23] **122** was synthesized through a 1,3-dipolar cycloaddition between an enone **119** and an iminium ylide **120** bearing a dithiolane group (**Scheme 2.3**). A final deprotection reaction allowed for the γ-lactam functionality.



Scheme 2.3 [3+2] Annulation reactions toward the strategic synthesis of 122. a) CsF; b) $NaBH_4$ and H_2O.

The key benefit to this novel methodology is its ease of reaction, its high regio- and stereo-selective method to access this five-membered ring. Moreover this methodology was applied toward the synthesis of a natural analgesic, cynometrine (**Figure 2.6**).[24]

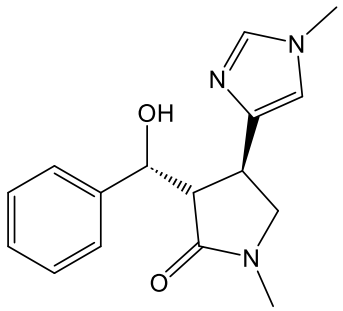
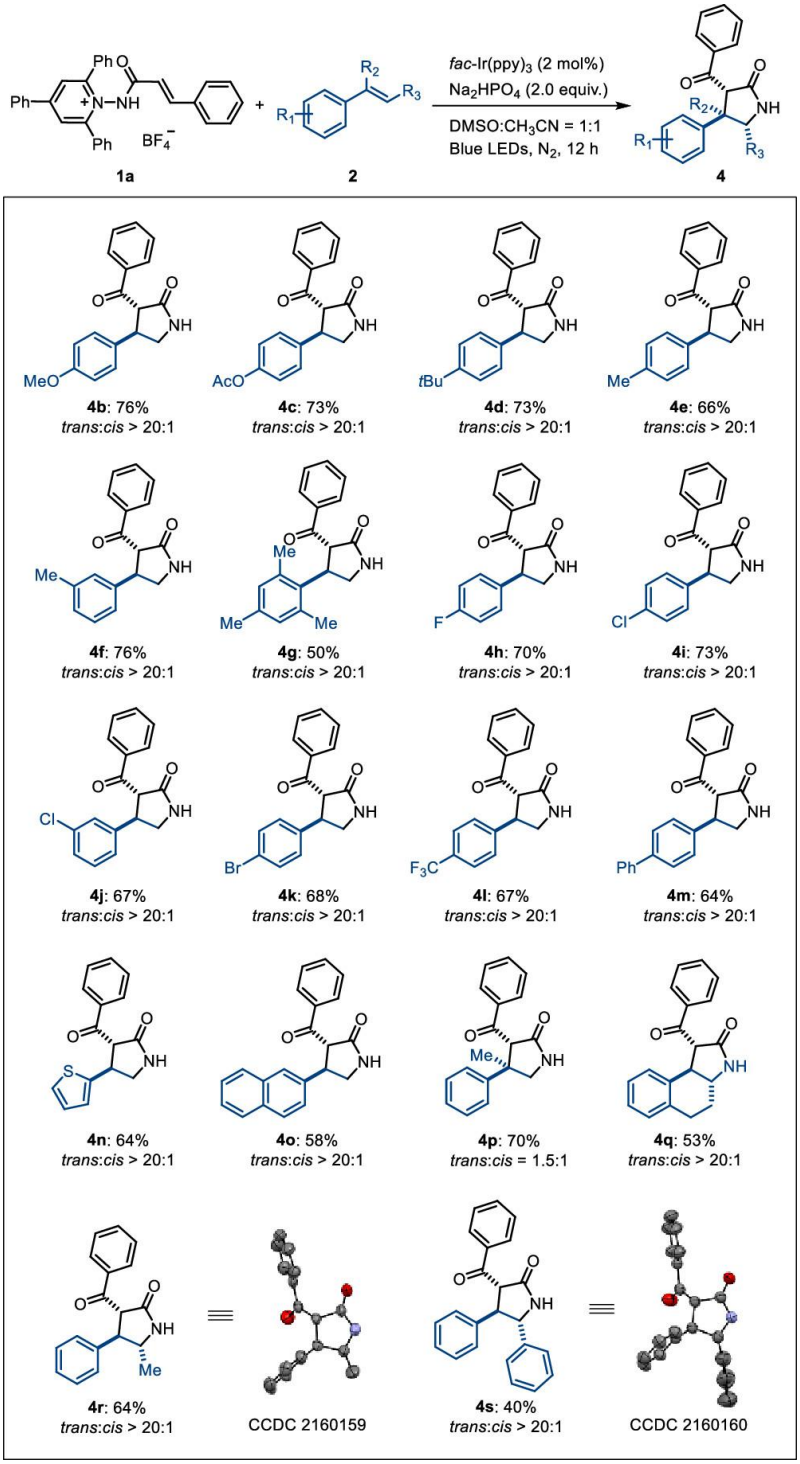


Figure 2.6 The molecular structure for cynometrine.

Additionally, in a recent study carried out by Xia et al., [3 + 2] deaminative annulation method for the synthesis of γ-lactam compounds was investigated via the photoredox catalysis of *N*-aminopyridinium salts and alkenes. This synthetic method afforded a broad substrate scope and excellent control of the diastereoselectivity for most of the γ-lactam products, significantly improving the diversity for γ-lactam synthesis (**Scheme 2.4**).[24]



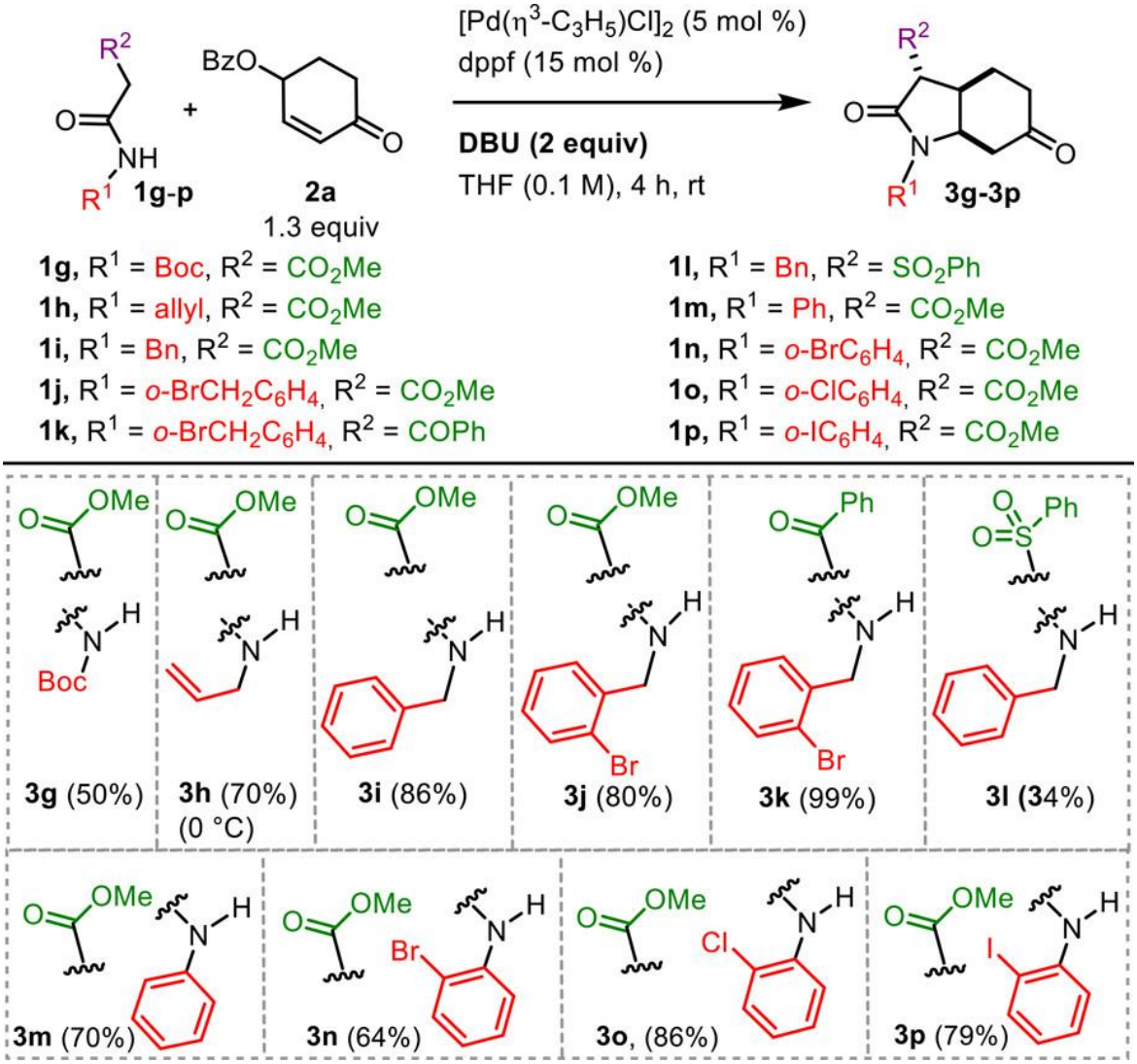
Scheme 2.4 [3 + 2] deaminative annulation method for the synthesis of γ-lactam compounds via the photoredox catalysis of N-aminopyridinium salts and alkenes (Scheme adopted from *Org. Lett.* 2022, 24, 24, 4365–4370).

2.3 Synthesis of Hydroindolone cores

γ-lactams are found in natural products and pharmaceuticals, with several therapeutic benefits, as described above.[23,24] However, in order to access hydroindolone cores, *bicyclic* γ-lactams are an important precursor.[25] Hydroindolone cores represent an understudied moiety, which is found to be a precursor toward the synthesis of Lycorine-type derivatives.[26,27] The general approached to form these moieties involve Metal-Promoted synthesis,[28,29] Radical-Mediated[30] and Transition-Metal mediated pathways.[31]

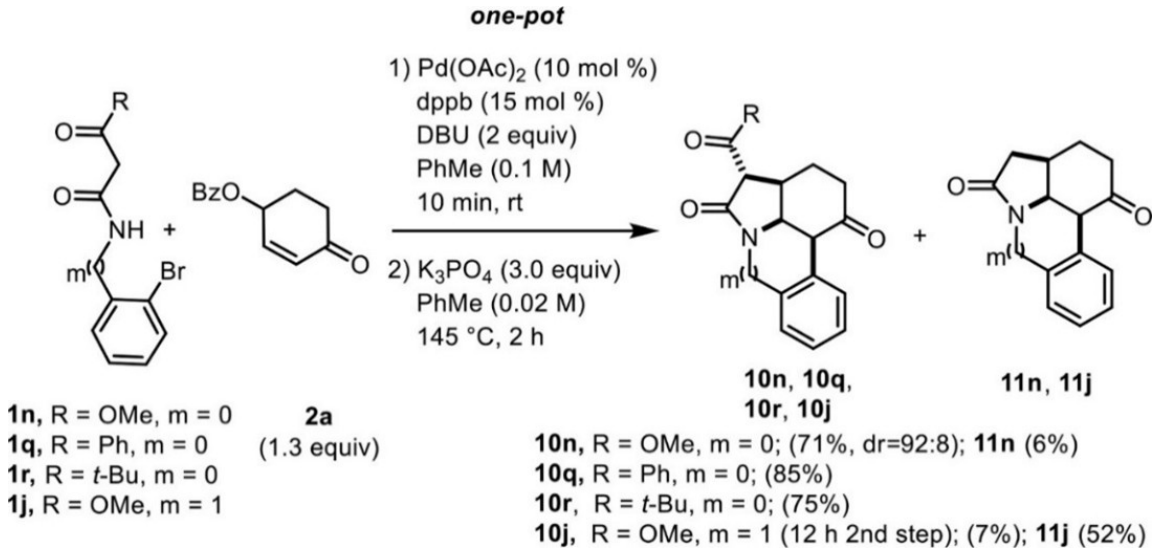
2.3.1 Metal-Promoted Synthesis

Metal-catalyzed formation of bicyclic lactams has proved to be an effective way to synthesize this coveted class of compounds. Recently Poli et al. have described the efficient synthesis of complex bicyclic lactams through a Pd-catalyzed cascade reaction between resonance-stabilized acetamides and various cyclic α,β-unsaturated-γ-oxycarbonyls. The conditions optimized in the study allow for [3 + 2]-C–C/N–C bond-forming annulation, as previously reported.[32] The approach described was carried out through an intermolecular C–C bond formation at the electrophilic γ position, preceding intramolecular N–C bond formation at the electrophilic β position (**Scheme 2.5**).



Scheme 2.5 Synthesis of bicyclic γ-lactams through a [3 + 2]-C–C/N–C bond-forming annulation (Scheme adopted from *J. Org. Chem.* 2018, 83, 7, 3879–3888).

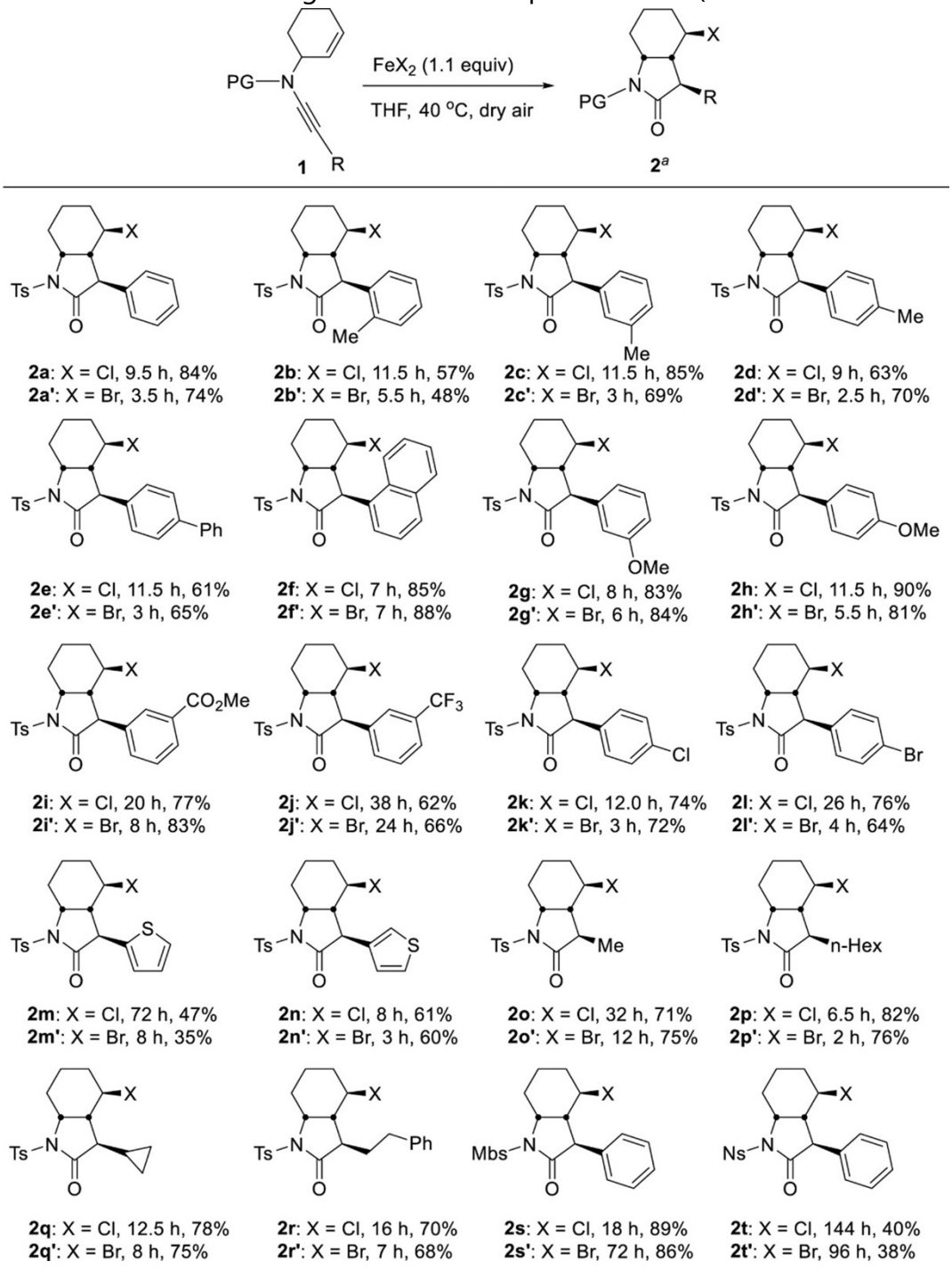
Moreover, *o*-haloaryl moieties located at the nitrogen substituent were seen to spur further reactivity. As shown, these fragments underwent further steps toward intramolecular keto α-arylation at the end of the cascade process. This was in line with the synthesis of sought after compounds such as Lycorine-type alkaloids,[9] daphniphyllum alkaloids,[33] and aeruginosins (**Scheme 2.6**).[34]



Scheme 2.6 Intramolecular keto α-arylation at the end of the cascade process for the synthesis of lycorine-type alkaloids (*J. Org. Chem.* 2018, 83, 7, 3879–3888).

Another study showing effective synthesis of bicyclic γ-lactams was carried out by Hong et al. The researchers have investigated the synthesis of halogenated bicyclic γ-lactams using an iron (II) halide to spur cyclization of enynamides. In the report, a wide selection of six and five-membered enynamides were converted into lactams using a Lewis Acid at room temperature and under nitrogen atmosphere. This simple methodology allowed the development of [4.3.0] and [3.3.0] γ-lactams from ethered enynes with four stereocenters

in a single step (**Scheme 2.7**).[35]

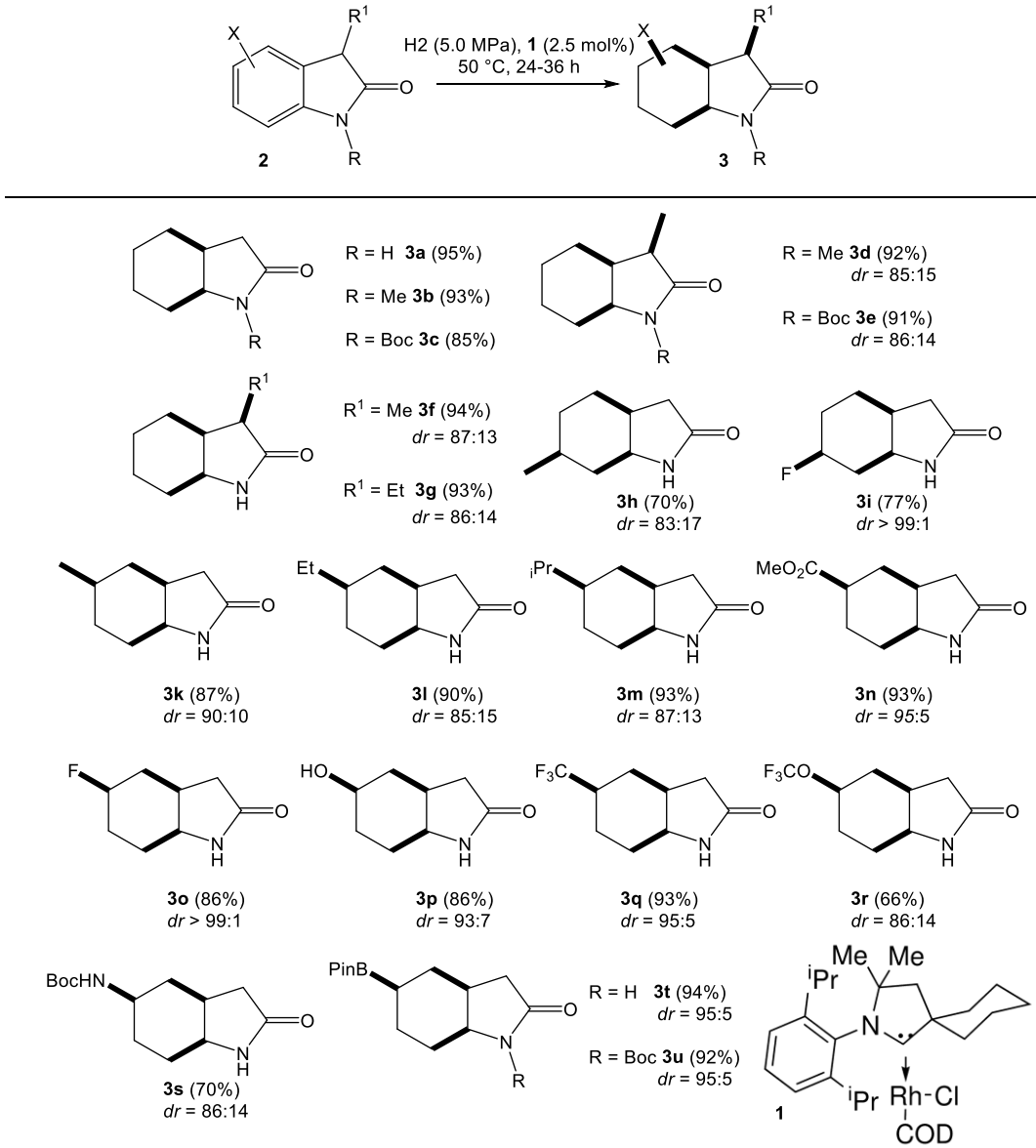


Scheme 2.7 Synthesis of a wide variety of [4.3.0] and [3.3.0] γ-lactams from tethered enynes with four stereocenters in a single step (Scheme adopted from *Org. Lett.* 2016, 18, 10, 2407–2410).

Rhodium-catalyzed hydrogenation of 2-oxindoles and 3-4 hydroquinolones was used to obtain such coveted moieties.[28] Limited studies have shown the efficacy of catalyzed hydrogenation of indolones, particularly focusing on platinum[36,37] or palladium.[38] Herein,

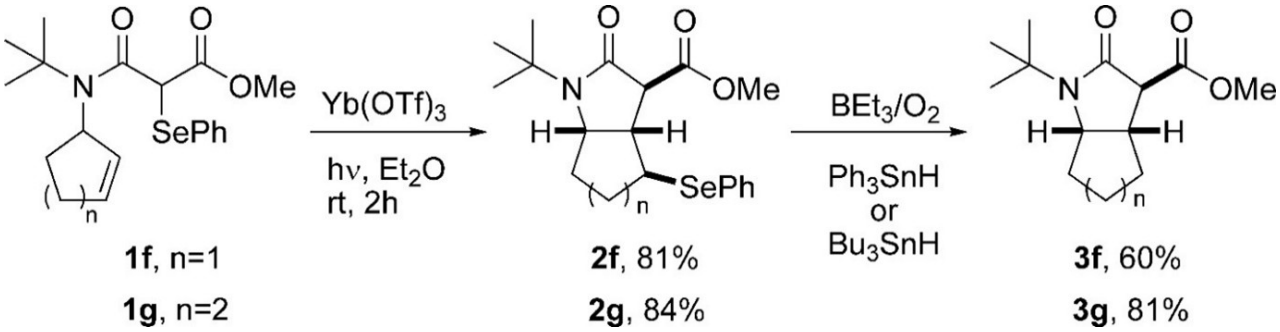
Bach et al. have reported the synthesis of 21 novel hexahydroindolin-2(3H)-ones with high stereoselevtivity and enantioenrichment. The hydrogenation of substrate **2** was carried out using a Rhodium complex ^{Cy}(CAAC)Rh(cod)Cl under reduced pressure in the presence of H_2. Although the scope seems broad, the study shows limited N functionalization, predominantly a Boc group, Me or H, and little functionalization at the α carbon to the carbonyl (**Table 2.1**).[28,39]

Table 2.1 Rhodium-catalyzed hydrogenation of 2-oxindoles and 3-4 hydroquinolones was used to obtain novel hexahydroindolin-2(3H)-ones with high stereoselectivity and enantioenrichment.



2.3.2 Radical-Mediated Pathways

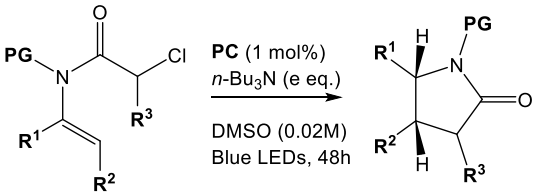
Radical-mediated cyclization reactions are a common strategy used to build up cyclic compounds. Specifically, atom or group transfer reactions involving halogens (I, Br or Cl) are particularly effective toward the construction of ring skeletons.[40] Yang et al. have reported a novel methodology, which affords bicyclic nitrogen heterocycles that are regiospecific and highly stereoselective. This study involved the group transfer cyclization of a phenylseleno amide ester promoted by a Lewis Acid ($Yb(OTf)_3$), under UV-light (**Scheme 2.8**).[41]

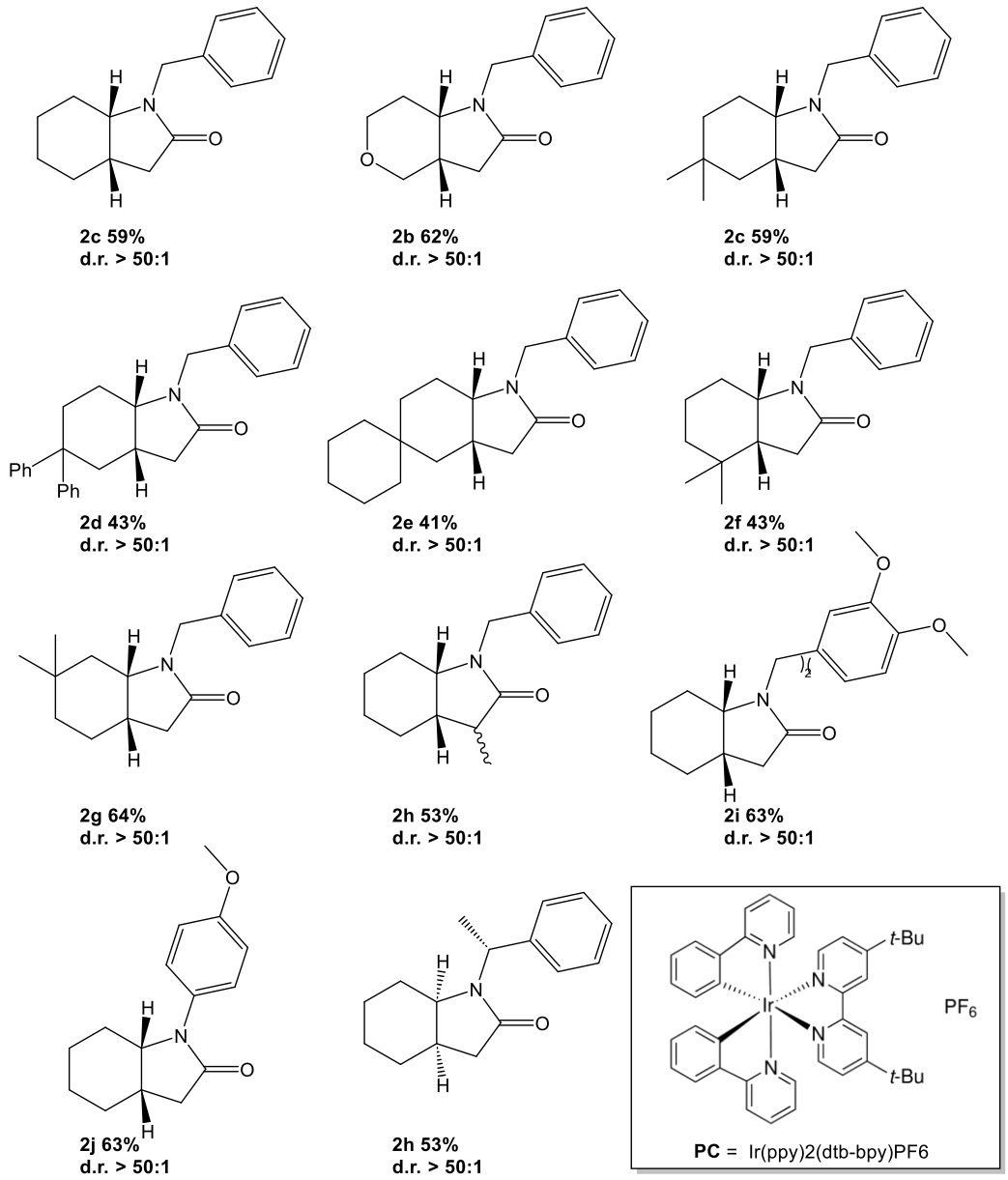


Scheme 2.8 Group transfer cyclization of a phenylseleno amide ester promoted by a Lewis Acid ($Yb(OTf)_3$), under UV light (Scheme adopted from *J. Org. Chem.* 2010, 75, 10, 3232–3239).

Rueping et al.[30] has developed a synthetic approach to bicyclic γ-lactams, developing protocols involving the formation of free radicals by single-electrons transfer (SET) processes. Organochlorides derivatives were used in this study due to their low cost and safety compared to more toxic reagents commonly used in the synthesis of γ-lactams, such as Bu_3SnH.[42-44] The researchers reported the development of a mild and tin-free method for the preparation of synthetically valuable γ-lactams in good yields and high diastereomeric ratios, using a Photo Catalyst (**PC**). The table below highlights the scope of this novel reactivity pattern. Although novel bicyclic γ-lactams are formed using a milder and less toxic reaction conditions, functionalization on the nitrogen is limited to electron rich arenes, while no functionalization on the α carbon to the carbonyl is present. Furthermore, the 6-membered ring adjacent to the γ-lactams shows little functionalization (**Table 2.2**). [30]

Table 2.2 Novel synthetic approach to bicyclic γ-lactams involving the formation of free radicals by single-electrons transfer (SET) processes.

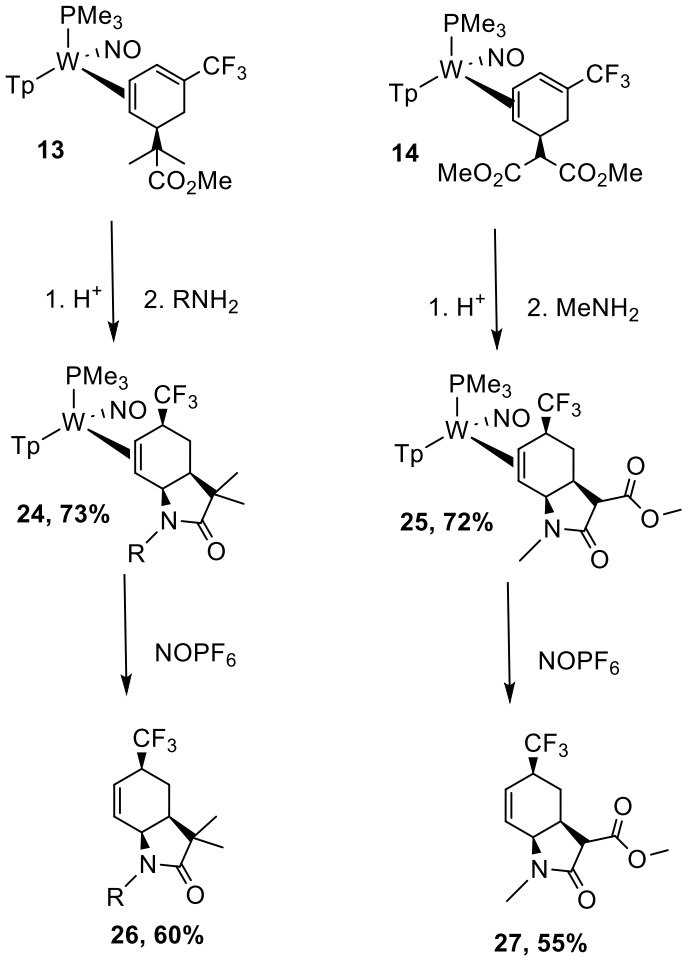




2.3.3 Transition metal-mediated Synthesis of Hydroindolone cores

Lastly, dearomatization techniques have proved throughout the years to be an excellent way to transform cheap and abundant aromatics into saturated moieties. The Harman lab

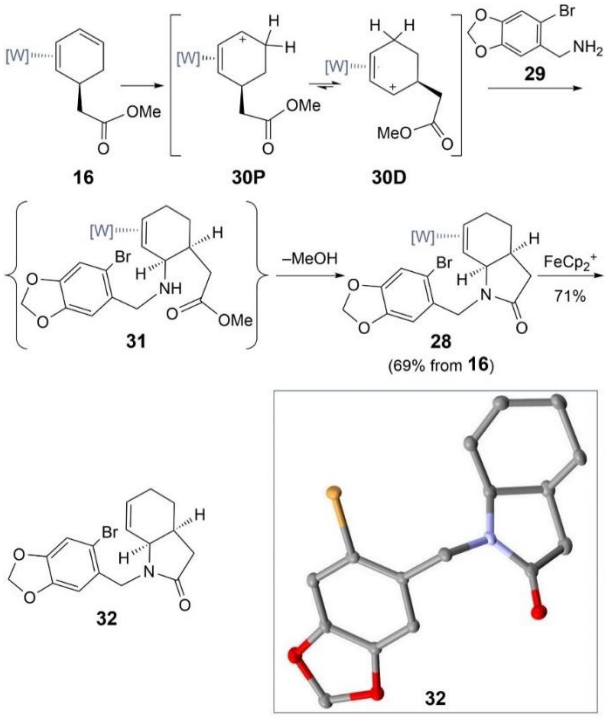
has focused on η^2 dearomatization methodologies toward numerous arenes, bearing different functional groups (as explained in **Chapter 1**). In the realm of pseudo-natural-product synthesis (PNP), a WTp(NO)(PMe_3)($PhCF_3$) system was used to synthesize substituted hydroindolone cores. Wilson et al. have shown that complexes bearing an ester group (**Scheme 2.9**, compounds **13**, **14**) were transformed to γ-lactams after addition of excess primary amine (**24**, **25**). Finally, the novel hydroindolone cores were liberated from the metal using an oxidant, such as $NOPF_6$ (**Scheme 2.9**, compounds **26**, **27**). [45]



Scheme 2.9 Synthesis of functionalized bicyclic γ-lactams from WTp(NO)(PMe_3)($PhCF_3$).

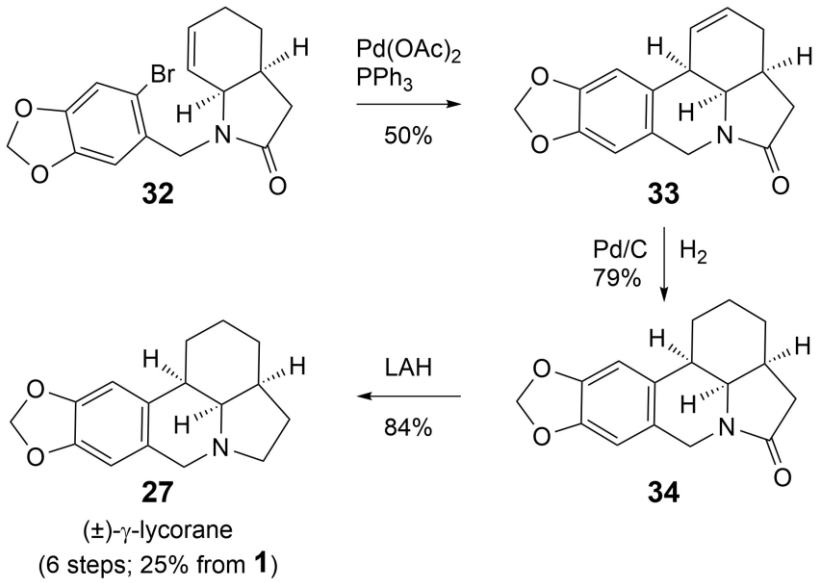
This study was useful toward our understanding in the synthesis of γ-lactams using our dearomatization technology. Moreover, these hydroindolone cores are easily accessible by our methodology and would enable us to tackle PNP synthesis of novel compounds (**Chapters 4**, **5**). Indeed, Wilson et al. successfully reported the synthesis of γ-Lycorane from WTp(NO)(PMe_3)(C_6H_6). As shown, subjecting coordinated benzene to the same type

of reaction pattern described in the WTp(NO)(PMe_3)($PhCF_3$) example above, a Lycorine-type precursor can be synthesized in modest yields (**Scheme 2.10**, compound **32**).[31]



Scheme 2.10 Synthesis of 32, a precursor to γ-Lycorane synthesized from WTp(NO)(PMe_3)(C_6H_6) (Scheme adopted from *Helv. Chim. Acta* 2021, *104*, e2100103).

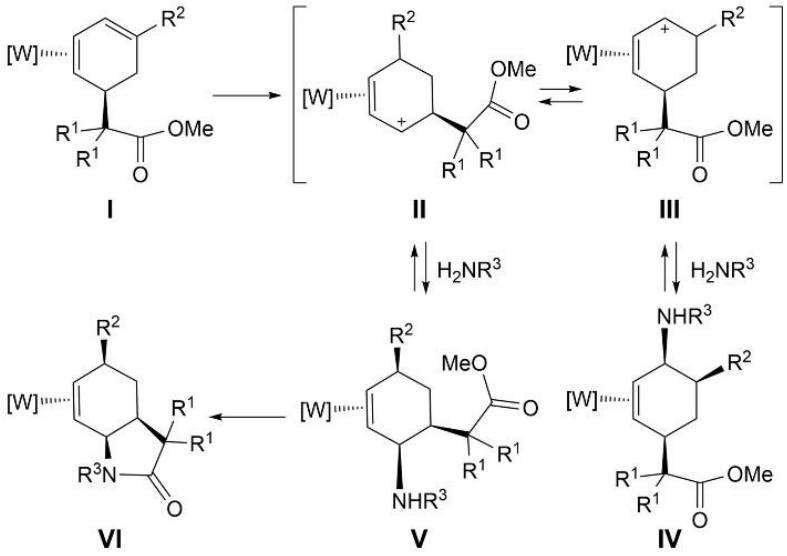
Further manipulation of **32** affords γ-Lycorane (**Scheme 2.11**, compound **27**).[33] The methodology and reactivity pattern described in this study will be the bedrock for the chemistry highlighted in **Chapters 4** and **5**, as it lays the foundation for the synthesis of more complex γ-lactams.



Scheme 2.11 Synthesis of γ-Lycorane from 27 (Scheme adopted from *Helv. Chim. Acta* 2021, *104*, e2100103)..

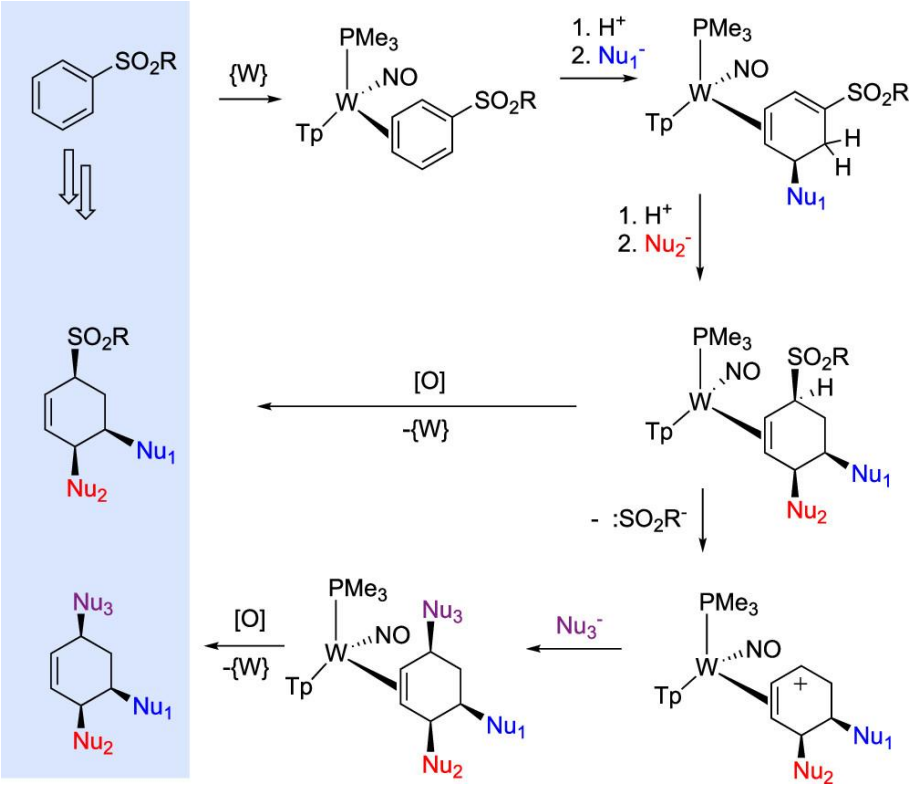
2.4 Novel Synthetic Approach from WTp(NO)(PMe$_3$)(PhSO$_2$Me)

Consequently, the Harman Lab has developed a general synthetic pathway toward the synthesis of cis-fused hydroindolone skeletons (**Scheme 2.12**) and has implemented its strategy for the successful generation of γ-Lycorane.[31,46] Specifically, a WTp(NO)(PMe$_3$)η^2-bound diene bearing an ester moiety (**I**) can be protonated (**II, III**) and further subjected to nucleophilic addition by a primary amine. This amination step can occur proximal (**IV**) or distal (**V**) (favored) to the PMe$_3$ ligand. Moreover, if left stirring at room temperature while the primary amine is at a distal position, the compound eventually undergoes lactamization, generating a *cis*-fused bicyclic-γ-lactam (**VI**).



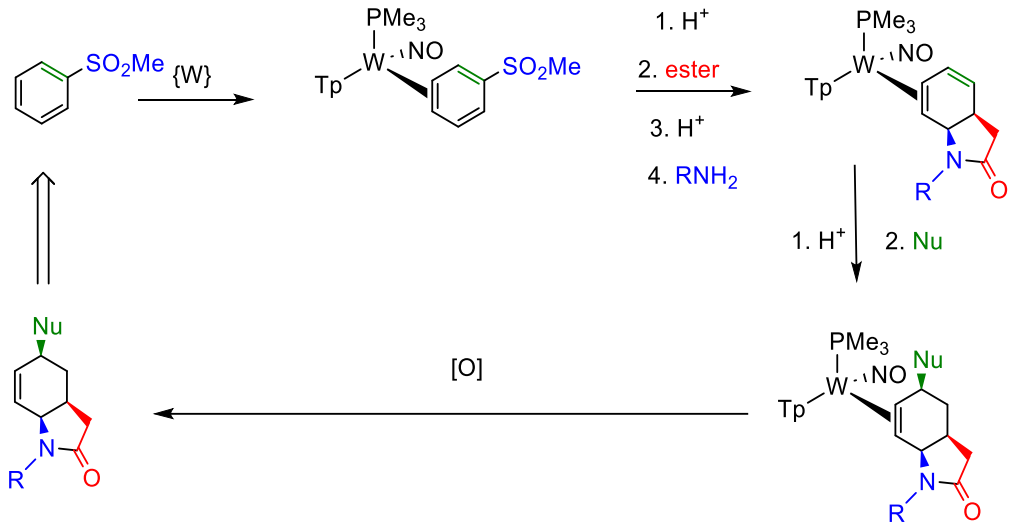
Scheme 2.12 Stereoselective preparation of cis-fused bicyclic-γ-lactams (Scheme adopted from *Helv. Chim. Acta* 2021, *104*, e2100103)..

The chemical feasibility of lactamization has increased our interest in pursuing such coveted chemical frameworks. The Harman Lab has investigated transition-metal mediated dearomatization of arenes for the direct synthesis of highly functionalized and saturated small molecules.[47] Previously, the successful manipulations of dearomatized electron-rich arenes such as anisoles, phenols, anilines and the like, were reported through dihaptocoordination to the π-basic metal fragment WTp(NO)(PMe_3).[48-54] Recently, in an effort to expand the Harman Lab's molecular library, electron-deficient arenes have been explored.[45,55] Among these, the WTp(NO)(PMe_3)($PhSO_2Me$) complex proved to be noteworthy. This is because the sulfone moiety showed a propensity to act as a leaving group when in an allyl position to the metal, while being chemically removed under mild acidic condition.[56-59] This chemical reactivity pattern has spurred the development of novel *trisubstituted* cyclohexenes, offering a greater level of architectural complexity. (**Scheme 2.13**).[56]



Scheme 2.13 development of novel trisubstituted cyclohexenes (Scheme adopted from *J. Am. Chem. Soc.* 2022, 144, 21, 9489–9499).

Consequently, trisubstituted hydroindolone cores can be synthesized following a similar approach, with a wide variety of primary amines and nucleophiles. **Chapter 4** will investigate the formation of novel *cis*-fused bicyclic-γ-lactams (**Scheme 2.14**) and the subsequent nucleophiles that can be added. The Harman Lab's goal is to generate novel functionalized hydroindolone cores that mimic the skeletons embodied in natural-like products.



Scheme 2.14 Synthetic pathway of novel cis-fused bicyclic-γ-lactams.

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Chapter 3 : Phenyl Sulfones: A Route to a Diverse Family of Trisubstituted Cyclohexenes from Independent Nucleophilic Additions

Spenser R. Simpson, **Paolo Siano**, Daniel J. Siela, Louis A. Diment, Brian C. Song, Karl S. Westendorff, Megan N. Ericson, Kevin D. Welch, Diane A. Dickie, and W. Dean Harman

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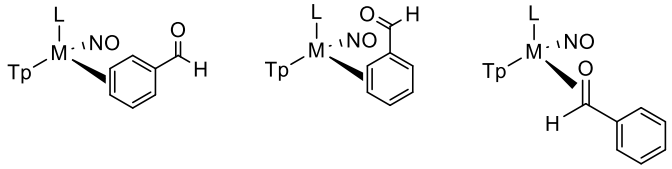
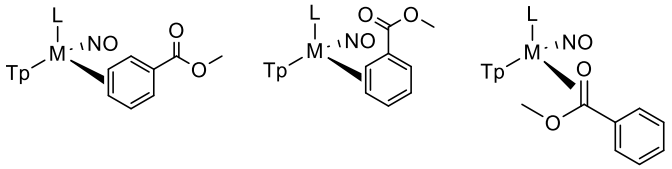
3.1 Introduction

For three decades the Harman group has focused on binding arenes bearing π-donor groups to a dearomatization agent.[1-10] Since electron-withdrawing functional groups (e.g., benzoates, benzonitrile, phenones) have π-bonds that can compete with the aromatic ring for metal coordination (**Table 3.1**),[11,12] it was not until recently that electron-deficient η^2-benzene complexes were explored.[13,14]

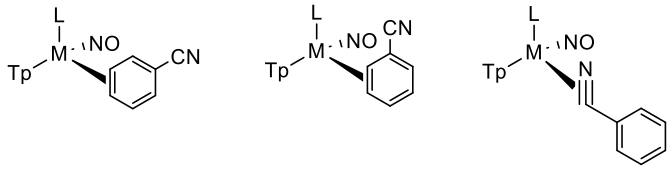
Table 3.1 DFT of Bond Dissociation Enthalpies for Electron-Deficient Benzenes at 298 K under Vacuum.[15]



BDE (kcal/mol)	M = Mo, L = DMAP	32.4	33.6	52.0
	M = W, L = PMe_3	38.9	37.4	61.0



BDE (kcal/mol)	M = Mo, L = DMAP	32.0	34.2	35.3
	M = W, L = PMe_3	38.2	38.1	46.8



BDE (kcal/mol)	M = Mo, L = DMAP	32.8	35.3	43.9
	M = W, L = PMe_3	38.5	41.2	54.9

However, in MoTp(NO)(DMAP)($PhCF_3$) and WTp(NO)(PMe_3)($PhCF_3$) complexes the metal binds exclusively to the benzene ring, due to a lack of double bonds in the -CF_3 moiety.[13,14] Consequently, our group has investigated the scope and binding selectivity of complexes prepared from several electron-deficient arenes.[15] This study revealed that while halobenzenes underwent oxidative addition, sulfones were well-tolerated by the fragment. The latter is an attractive functional group to study in the dearomatization of benzene as sulfur is the third most common heteroatom in marketed pharmaceuticals behind nitrogen and oxygen.[16-18] Moreover, sulfones and sulfonamides are prevalent in a variety of antibiotics, cancer therapeutics, COX-2 inhibitors, diuretics, and ulcer preventitives.[18,19]

It was postulated that the reactivity of WTp(NO)(PMe_3)($PhSO_2R$) (R= -Me, -$NH(CH_2)_2$), and -Ph) would show a similar pattern to that of WTp(NO)(PMe_3)($PhCF_3$), because of similar electronic environment (**Figure 3.1**).

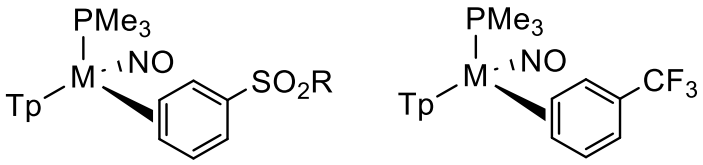
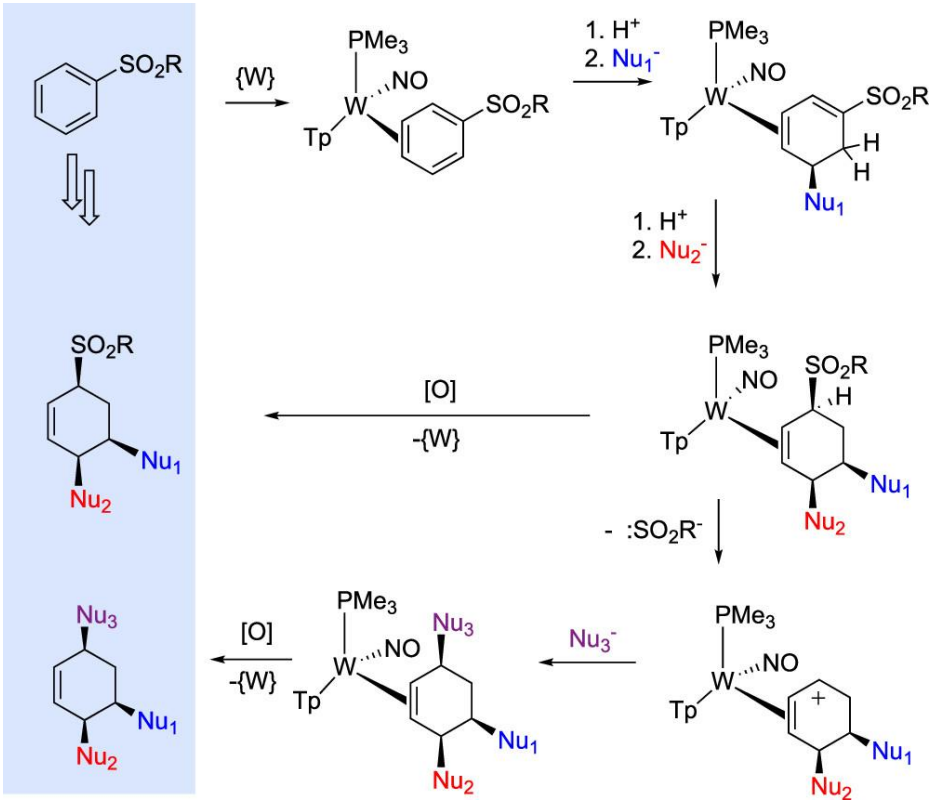


Figure 3.1 Similarity in electronic environment between WTp(NO)(PMe_3)($PhSO_2R$) and WTp(NO)(PMe_3)($PhCF_3$)

As mentioned in **Chapter 1**, unlike the CF_3 group, sulfinates ($:SO_2R^-$) have been observed to behave as leaving groups for nucleophilic substitution and elimination reactions.[13,20-27] The replacement of the sulfonyl group by other substituents could significantly expand the diversity of the anticipated trisubstituted cyclohexene products beyond sulfone and sulfonamide derivatives as proposed in **Scheme 3.1**.

Scheme 3.1 Proposed syntheses of highly functionalized cyclohexenes from sulfones or sulfonamides.



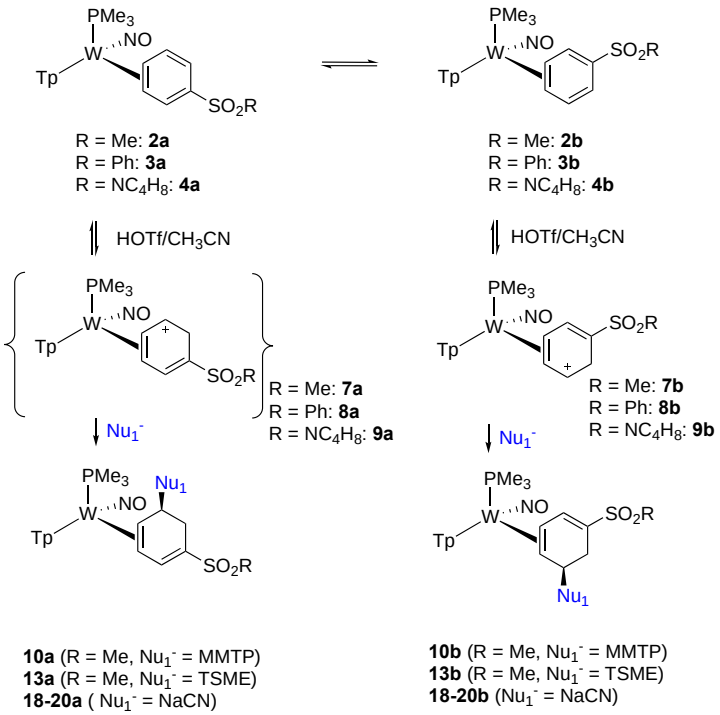
3.2 Results

3.2 1st Additions to WTp(NO)(PMe$_3$)(PhSO$_2$R)

Ligand exchange with PhSO$_2$R was described in **Chapter 1**, where it was shown that the coordination of methyl phenyl sulfone, diphenyl sulfone, and phenylsulfonyl pyrrolidine by the π-base WTp(NO)(PMe$_3$) increases the electron density of the phenyl ring. This enables the selective protonation of the carbon *ortho* to the sulfone group. Once the desired phenyl sulfone is bound to the metal, 1st addition reactions can be pursued. While subsequential protonation/addition reactions to the WTp(NO)(PMe$_3$)(PhCF$_3$) complex demonstrated high diastereoselectivity of the isomeric mixture at -30 °C,[13] when complexes **2, 3** and **4** were protonated with triflic acid (HOTf/CH$_3$CN) and then treated with NaCN at -30 °C, two products were formed in roughly a 1:2 ratio (**Table 3.2**, compounds **18a/18b**, **20a/20b**) and 1:1 for **19a/19b**. Repeating this reaction at room temperature degraded the complex. However, when the reaction was run at 0 °C, a single dominant product (**b**, dr > 20:1) was formed for all three different phenyl sulfones. Product **b** is referred as the "distal" product, as nucleophilic addition occurs away from the PMe$_3$, while a "proximal" product would be similar to those of type **a** with nucleophilic addition occuring near the PMe$_3$.

Similar diastereoselectivity was observed for other nucleophiles such as (1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane (MMTP) and TSME.

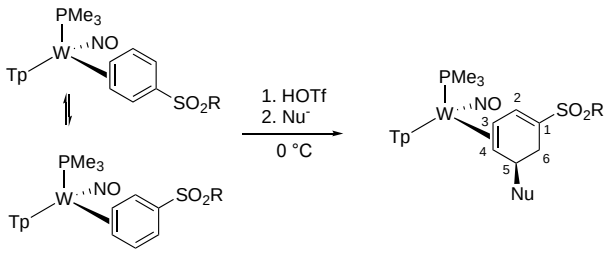
Table 3.2 Protonation of dihapto-coordinated phenyl sulfone ligands followed by nucleophilic addition.



Nu_1	R	Temperature (°C)	Ratio (b:a)
MMTP	Me (**10**)	-30 0	1.7:1 >20:1
TSME	Me (**13**)	-30 0	2:1 > 20:1
NaCN	Me (**18**)	-30 0	2:1 >20:1
NaCN	Ph (**19**)	-30 0	1:1 >20:1
NaCN	NC_4H_8 (**20**)	-30 0	2:1 >20:1

The high diastereoselectivity (dr >20:1) observed for these diene complexes at 0°C (**Table 3.3, 10-23**) is the result of the reversible isomerization for the η^2-arene coordination diastereomers (**Table 3.2**, **a** and **b**) coupled with a greater thermodynamic driving force to form the distal arenium isomer, analogous to that reported for trifluorotoluene.[13]

Table 3.3 Range of nucleophiles for 1st addition reactions.



Reagent (Nu^-)	R	Product	Yield
OTMS, OMe (MMTP)	Me (**10**) Ph (**11**) NC_4H_8 (**12**)	[W], SO_2R, CO_2Me	54% 67% 53%
OTBS, OMe (TSME)	Me (**13**) NC_4H_8 (**14**)	[W], SO_2R, CO_2Me	54% 53%
O, OLi, MeO, OMe	Me (**15**) Ph (**16**) NC_4H_8 (**17**)	[W], SO_2R, MeO_2C, CO_2Me	65% 61% 62%
NaCN	Me (**18**) Ph (**19**) NC_4H_8 (**20**)	[W], SO_2R, CN	56% 31% 50%
tBu_4NBH_4	Me (**21**) Ph (**22**)	[W], SO_2R, H	62% 68%
H, N, N	Me (**23**)	[W], SO_2R, N, N	43%

[W] = $WTp(NO)(PMe_3)$

2D NMR was used to characterize the complexes in **Table 3.3**. NOE correlations between the protons of the pyrazole ring trans to the PMe_3 ligand (Tp3A) and the methine proton of C5 support the conclusion that the nucleophile added adjacent to the site of arene protonation and exo to metal fragment (**Figure 3.2**).

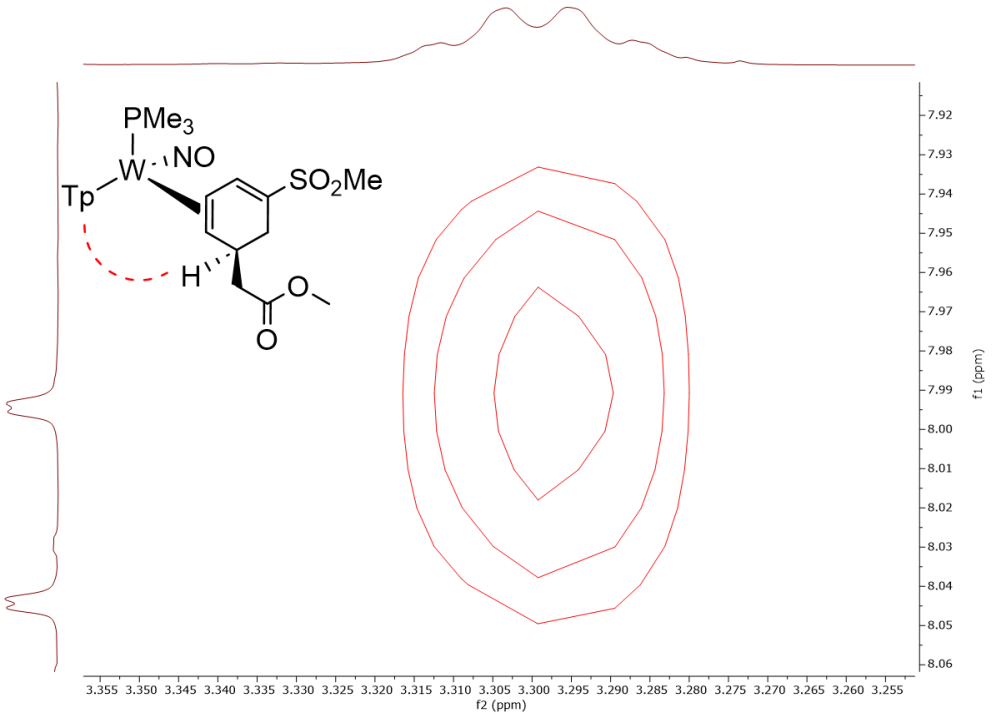


Figure 3.2 NOE interaction between Tp3A and C5 for 13.

TMSE, lithium dimethyl malonate (LiDMM), tetrabutylammonium borohydride (TBAB), and imidazole were added in a similar fashion, adding regio- and stereoselectively to the η^2-arenium intermediates **7b**, **8b**, **9b** (**Table 3.3**).

Single-crystal X-ray diffraction studies provided molecular structures of the diene complexes **10**, **11, 13, 14, 16, 17, 18, 19, 22** all of which are consistent with the assigned stereochemistries (**Figure 3.3**).[15]

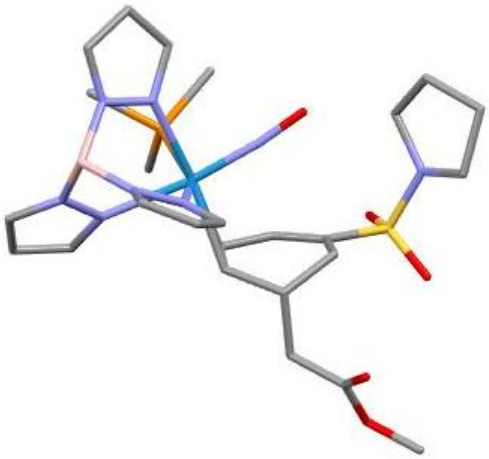


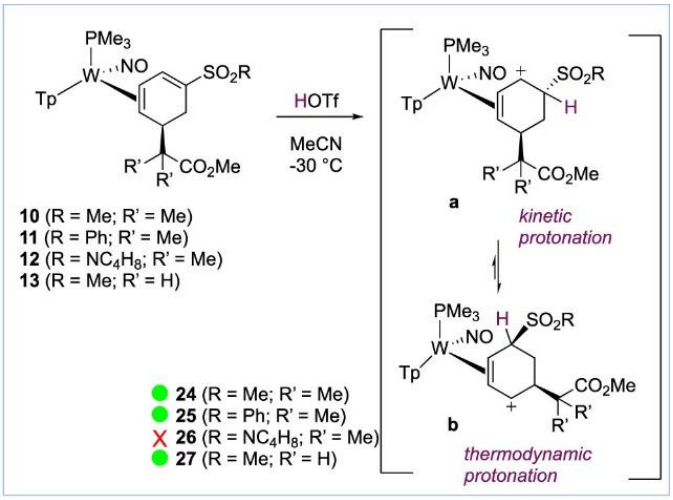
Figure 3.3 X-ray single-crystal of 14.

3.3 Synthesis of Trisubstituted Cyclohexenes

3.3.1 Formation of Allyl Complexes

The uncoordinated sp^2 carbons within the diene complexes are in conjugation with the tungsten dπ orbital and are expected to have a basic carbon at C1.[13,28] Protonation of dienes **10**, **11**, and **13** at -30 °C yields isolable η^2-allyl complexes **24**, **25**, and **27**, while protonation of **12** results in decomposition at various temperatures and acid strengths. Herein, only two of the three allyl carbons are strongly coordinated to the metal, typical for complexes of the form $[WTp(NO)(PMe_3)(\pi\text{-allyl})]^+$.[29] DFT calculations indicate that the carbenium distal (**b**) to the PMe_3 is favored by ~3 kcal/mole over the proximal allyl conformer (**a**),[29] possible to avoid placing the carbocation-like allyl carbon next to the electron-withdrawing SO_2R group (**Scheme 3.2**).

Scheme 3.2 Protonation of complexes 10, 11, 13, followed by a conformational change and epimerization of the resulting η^2-allyl complex.



NOE correlations between the methine bound to the sulfone and the PMe_3, support the notion that the sulfone group is oriented trans to tungsten, consistent with $WTp(NO)(PMe_3)(PhCF_3)$-derived analogs (**Figure 3.4**).[13] Based on previous deuterium studies with bound cyclohexadiene, we posited the initial protonation of the η^2-diene complex occurs *syn* to the metal,[30,31] causing a steric interaction between the sulfone and the PMe_3 and NO ligands. Subsequent epimerization of this stereocenter would provide the observed stereochemistry in which the sulfone group is *anti* to the metal.

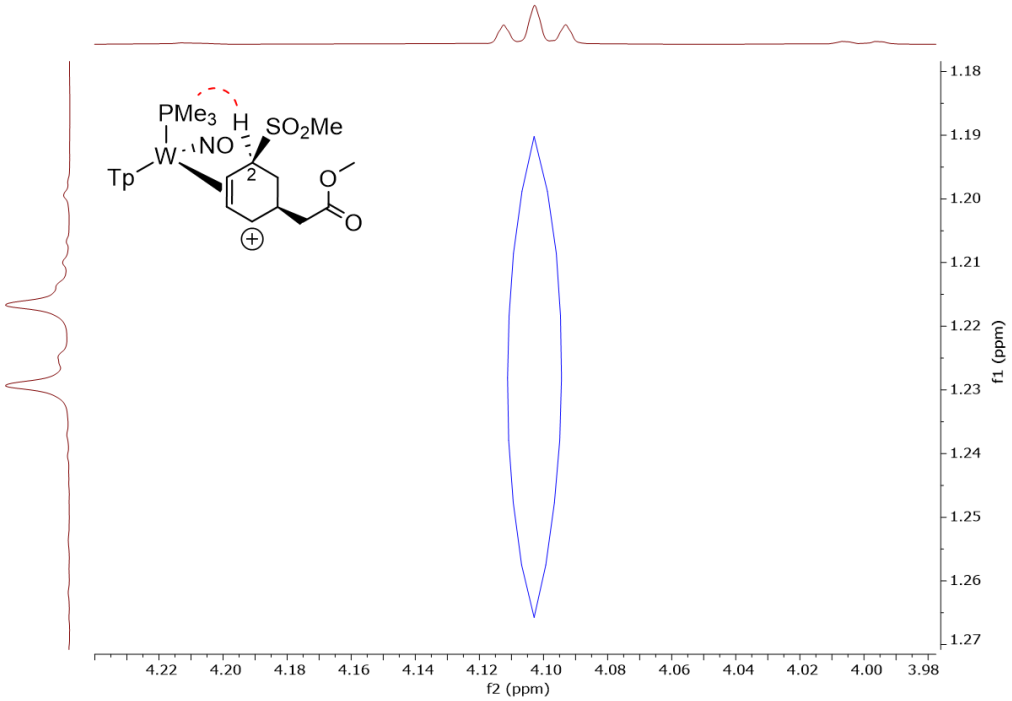
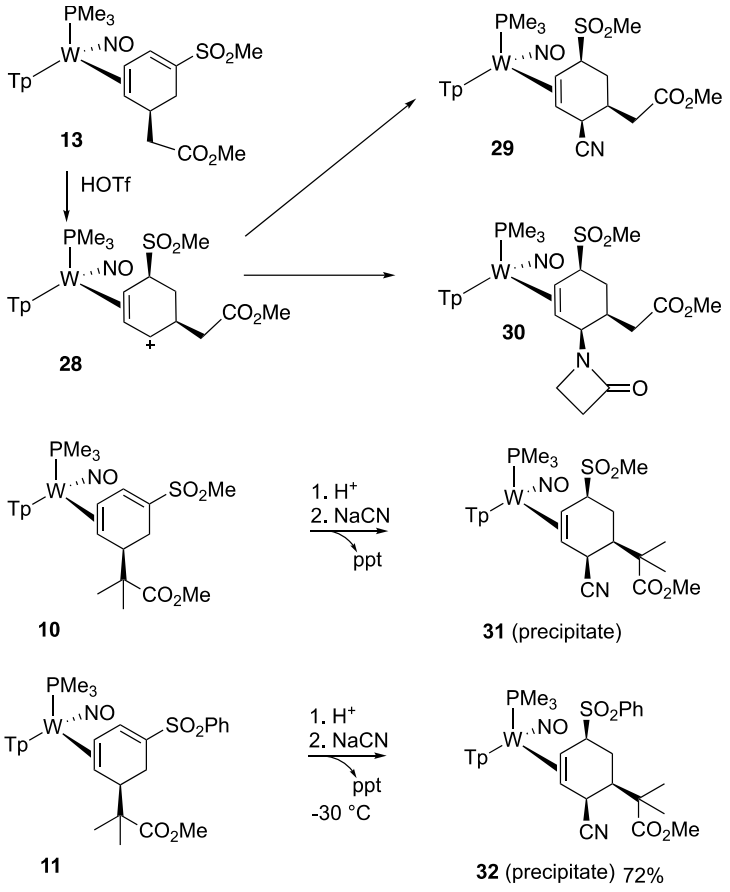


Figure 3.4 NOE interaction between PMe_3 and C2 for 27.

3.3.2 2nd addition reactions

Protonation of **10** at -30 °C, followed by addition of NaCN, generated a white precipitate. 2D NMR analysis of the solid confirmed the desired trisubstituted η^2-cyclohexene complex **31** (65%; **Scheme 3.3**). Repeating this reaction at -60 °C increased the yield of **31** to 82%. NOE and COSY data indicate that the CN^- adds *anti* to the metal. Analogous reactions converted sulfonylated diene complexes **11** and **13** into trisubstituted cyclohexene complexes (**Scheme 3.3**, compounds **29**, **32**). Similarly, replacing NaCN with a solution of azetidinone deprotonated with NaO^tBu added to **28,** would give trisubstituted cyclohexene **30**.

Scheme 3.3 Conversion of sulfonyldiene complexes to sulfonyl-substituted cyclohexene complexes (29-32) via allyl intermediates (e.g., 28).



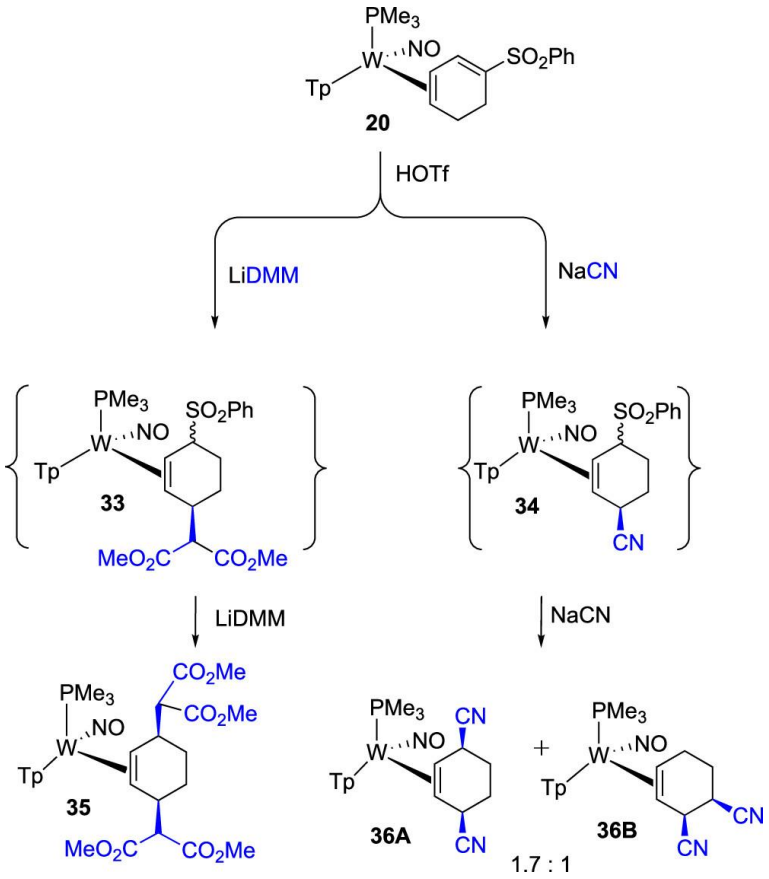
3.4 3rd additions

3.4.1 Reactivity after loss of sulfone in the presence of salts

Sulfones are robust functional groups, with elimination occurring only at high temperatures (ca. 500 °C) through an intramolecular process (E_i).[21] However, previous reports describe the elimination of sulfinic acid to occur on *silica* for a tosylated glucopyranoside in which the tosylated carbon was attached to an oxygen.[23] Moreover, Ley et al. demonstrated that sulfonated cyclic ethers or cyclic amides undergo substitution or elimination with a suitable nucleophile in the presence of a *Lewis acid* such as $MgBr_2$.[25,26] Also, Pd(0) has been used to catalyze the substitution of allylic sulfones,[32] where one can consider the metal as stabilizing both allyl and sulfonate fragments. Consequently, we can expect elimination of the sulfone group to occur either in the presence of silica or a *Lewis Acid*, when the group is found in an allylic position relative to the metal fragment. In fact, the tungsten-bound alkene moiety serves as the π-donor, facilitating loss of a sufinate anion in tandem with a Lewis acid.

The general reactivity pattern highlighted in **Scheme 3.3** can be explained using DFT calculations. However, steric interactions and nucleophilicity between the incoming nucleophiles and ring substituents also determine regiochemistry of subsequent additions. Indeed, subjecting complex **20** to acid followed by NaCN generated two complexes (**36A** and **36B**), which resulted from double addition of the cyanide ion, *with concomitant loss of the sulfone group*, presumably, via the intermediate sulfonylcyclohexene **34**. Subsequent loss of the sulfinate anion generates an allyl complex that can react with CN^- with either the distal (**36B**) or proximal (**36A**) conformer of the allyl complex to generate the 3,4-dicyano (**36B**) or 3,6-dicyanocyclohexene species (**36A**), respectively (**Scheme 3.4**). Similarly, the 3,6-disubstituted bis-malonate **35** was generated via the allyl sulfone complex **33**. However, only the 3,6-substitution pattern is observed, presumably due to the steric bulkiness of the incoming LiDMM ligand, which would inhibit a similar pattern to **36B**.

Scheme 3.4 Second protonation/nucleophilic addition of cyanide to the arene ring.

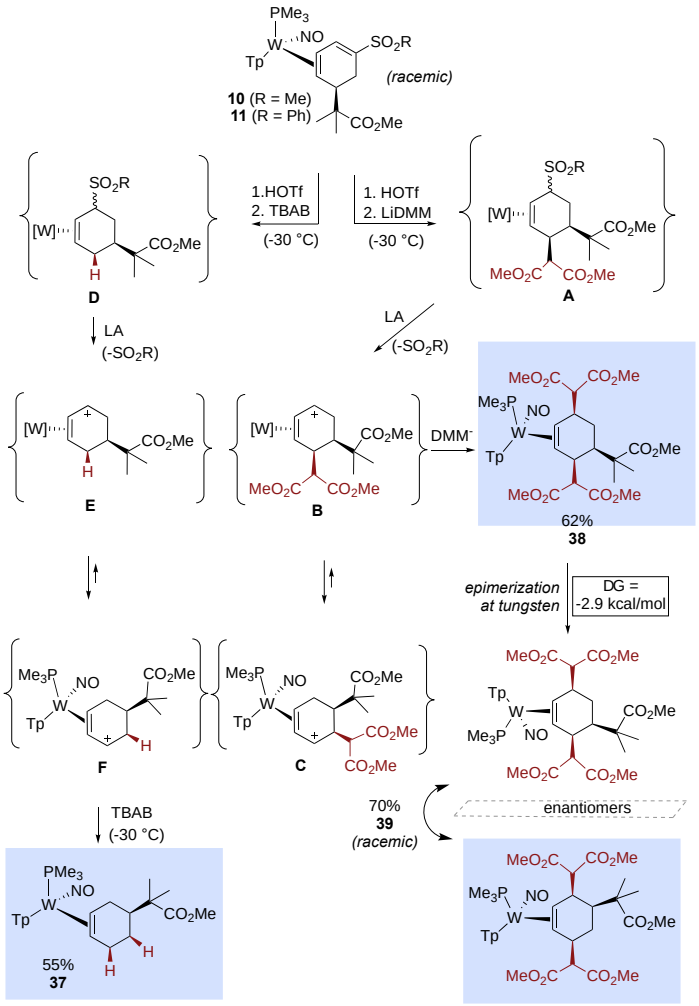


Similarly, protonation of either diene complex **10** or **11** followed by addition of TBAB resulted in the monosubstituted cyclohexene complex **37**. The presence of a Lewis Acid

such as Li^+ or Na^+ induced loss of sulfone allowing for a second hydride to add (**Scheme 3.5**). This has also been observed at low equivalence of TBAB relative to **10** or **11**. After loss of the sulfinate ion, species **E** is considered to be less stable than **F**,[29] encouraging hydride addition to the distal position relative to the PMe_3 ligand (**Scheme 3.4**, compound **37**).

In contrast, compound **38** was produced when **10** or **11** were treated with acid followed by excess LiDMM. In this scenario, LiDMM adds readily, and allyl **B** is formed after loss of sulfinate. Presumably due to the steric hindrance that an addition on **C** would pose, another LiDMM adds readily to **B**, generating species **38**, in less than 10 minutes. Repeating this reaction with only one equivalent of LiDMM generates half an equivalent of product and the parent allyl **B**. Finally, if the reaction is allowed to stir in a solution overnight, the product undergoes an isomerization to form **39**, where epimerization of the tungsten stereocenter occurs to minimize steric interactions for this unusually congested species. Indeed, DFT calculations show that **39** is thermodynamically favored over its isomer **38** (**Scheme 3.5**) by 2.9 kcal/mol. Of note, if **38** is isolated and dried no epimerization is observed.

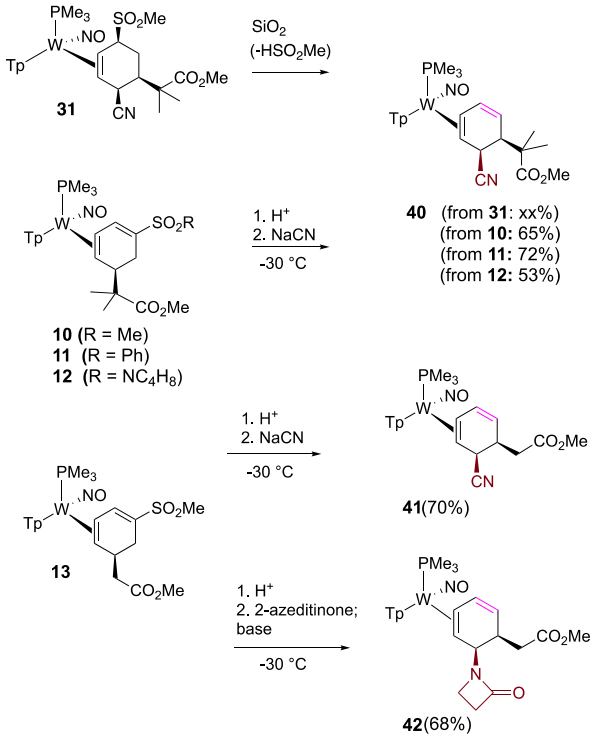
Scheme 3.5 Double nucleophilic additions to η2-1-sulfonyl-1,3-diene complexes.



3.4.2 Formation of novel η²-diene after loss of sulfone group

Given the tendency of allyl sulfones to undergo elimination we sought to prepare desulfonylated diene complexes to serve as synthons of the allyl sulfone complexes. Furthermore, while cleaning up trisubstituted cyclohexene complexes **31** (**Scheme 3.6**), η²-1,3-cyclohexadiene complex **40** was observed as a biproduct in the filtrate. Similarly, complex **41**, whose structure is confirmed by XRD data (**Figure 3.5**), was generated in the formation of **29** from **13**. Moreover, this diene complex **41** could be made exclusively if the reaction solution was worked-up through a silica column.

Scheme 3.6 Formation of disubstituted η²-diene complexes from sulfonylated cyclohexene or sulfonylated cyclohexadiene complexes.



Curiously, treatment of the sulfonylated cyclohexene **31** with acid (HOTf/MeOH, HOTf/CH_3CN, HOTf/acetone, diphenyl ammonium triflate (DPhAT) or base (triethylamine) alone failed to eliminate the sulfone or cause any other reaction. Consequently, diene complexes were formed simply by working up **31** in a solution with silica (**Scheme 3.6**, compounds **40**, **42**).

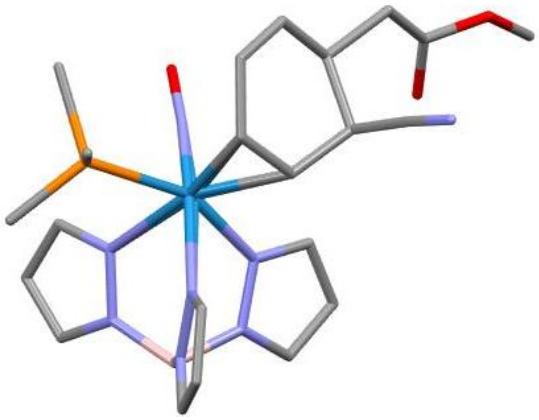


Figure 3.5 XRD structure for compound 41.

2D NMR was used to fully characterize compounds in **Scheme 3.6**. Characteristic peaks include NOE interaction between the PMe_3 and H6 and loss of the -CH_3 associated with the sulfone at 2.90 ppm. However, peaks H6 and H5 are considered diagnostic signals as they show up in very distinct shift in ^{1}H NMR underlining the formation of a diene, as will be shown later.

3.4.3 3rd addition reactions after formation of η²-diene

Diene complexes **40** and **42** could then be protonated and treated with a third independent nucleophile to generate trisubstituted cyclohexene complexes **46** and **47**. Alternatively, the sulfone group in **31** could undergo substitution with other nucleophiles, presumably through an allyl intermediate. This occurs with nucleophiles, which are accompanied by potential Lewis Acid such as LiDMM, TBAB, or NaCN generating cyclohexenes **43**, **44**, and **45** (**Figure 3.6**, XRD) respectively (**Scheme 3.7**).

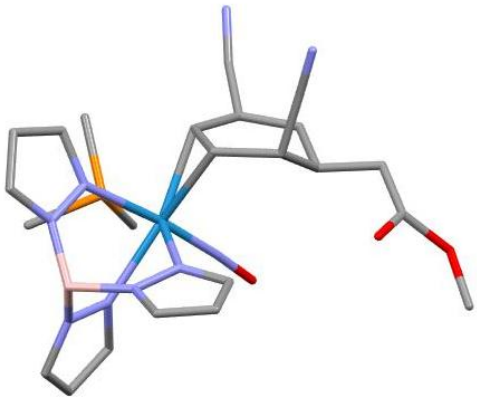
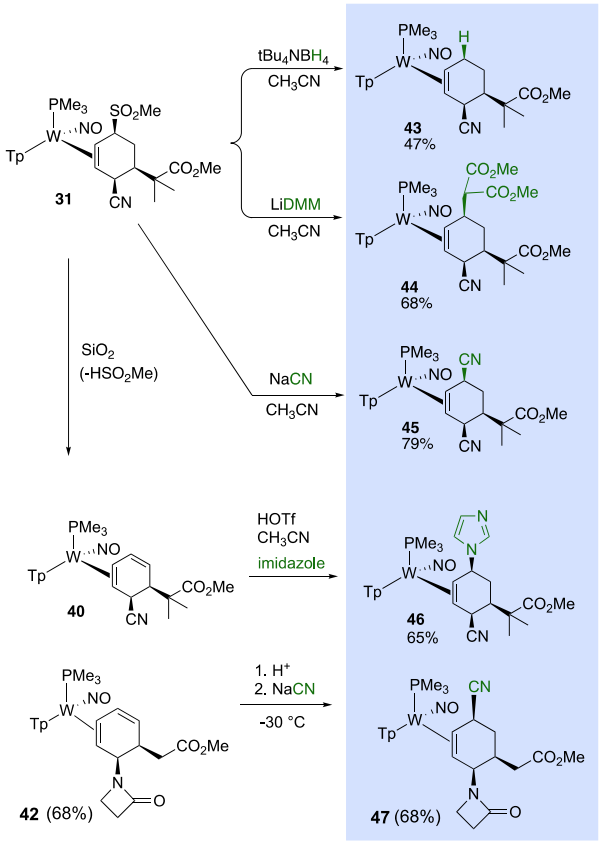


Figure 3.6 XRD structure for compound 45.

Substitution of sulfone was observed to be selective to anionic nucleophiles and did not proceed with neutral nucleophiles such as methylamine, dimethylamine, or MMTP, for which elimination followed by tandem protonation/addition was required. Furthermore, the sulfone group showed propensity toward substitution without the need for addition of acid.

Scheme 3.7 Addition of the third nucleophile either via replacement of the sulfone or from addition to the η^2-diene.



Characteristic peaks for compounds **43**-**47** include NOE interaction between Tp3A and H3, as well as H6 and the PMe_3 ligand, indicating the successful protonation/addition sequence. **Figure 3.7** shows the spectroscopic differences between the diene complex **42** shown in **Scheme 3.6** and the trisubstituted cyclohexene **47** derived from such diene. In the bottom spectrum, a singlet at 4.8 ppm for H3 can be observed, as well as loss of the multiplet H6 observed at 6.58 ppm for the diene complex **42**. Compound **47** partially oxidized in air during the 2D experiment, generating a liberated cyclohexene in a 1.0:0.4 ratio.

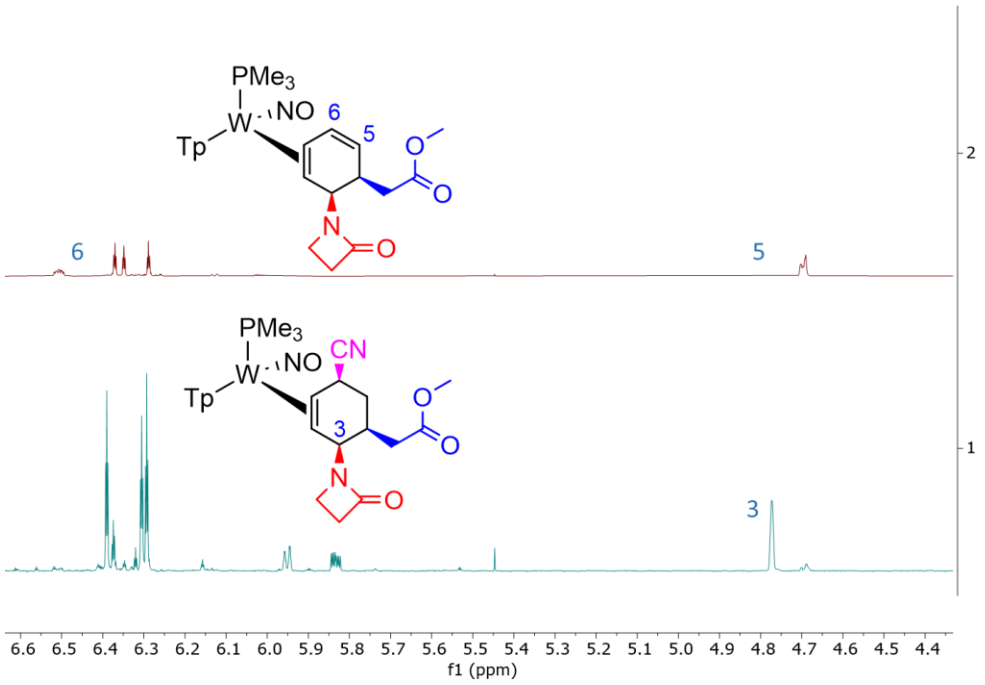
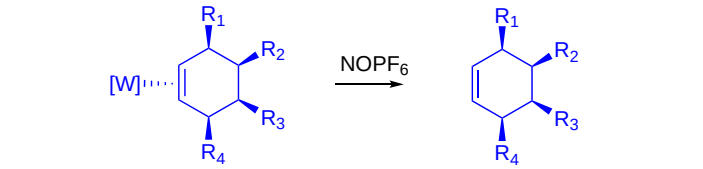


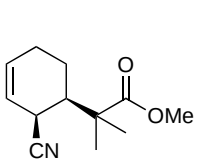
Figure 3.7 Spectroscopic comparison between 42 (top) and 47.

3.5 Liberation of Organics

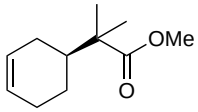
Previous studies have shown that cyclohexenes can be liberated from the metal fragment using a variety of different oxidants, including Ag^+, $[FeCp_2]^+$, DDQ, $NOPF_6$, CAN, and even O_2. Twelve examples are provided in **Table 3.4**. Cyclohexenes **48**, **49**, **50**, **51**, **52**, **53**, **54**, **55**, **56**, **57**, **58** and **59** were liberated from the metal through oxidation with $NOPF_6$ in yields ranging from 54 to 76 %.

Table 3.4 Decomplexation of functionalized cyclohexenes.

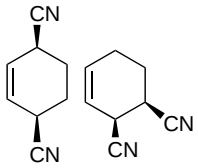




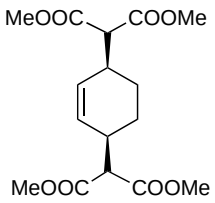
48 (63%)



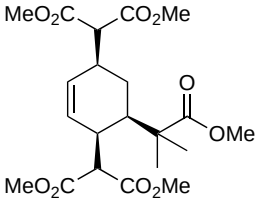
49 (63%)



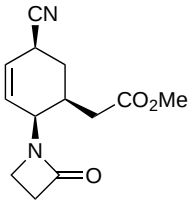
50A + **50B** (62%)



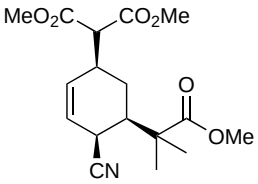
51 (68%)



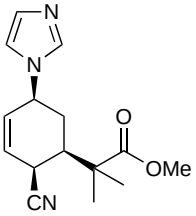
52 (59%)



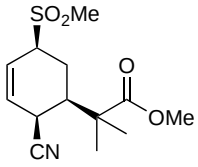
53 (63%)



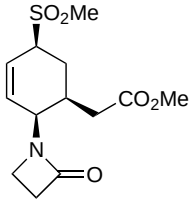
54 (58%)



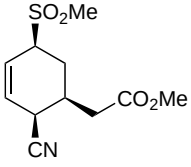
55 (54%)



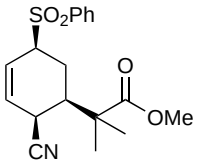
56 (64%)



57 (63%)



58 (54%)



59 (76%)

Key spectroscopic features for all organics shown in **Table 3.4** include two multiplets between 5.8 ppm and 6.2 ppm according to what functional groups are present in the cyclohexene ring (**Figure 3.8**).

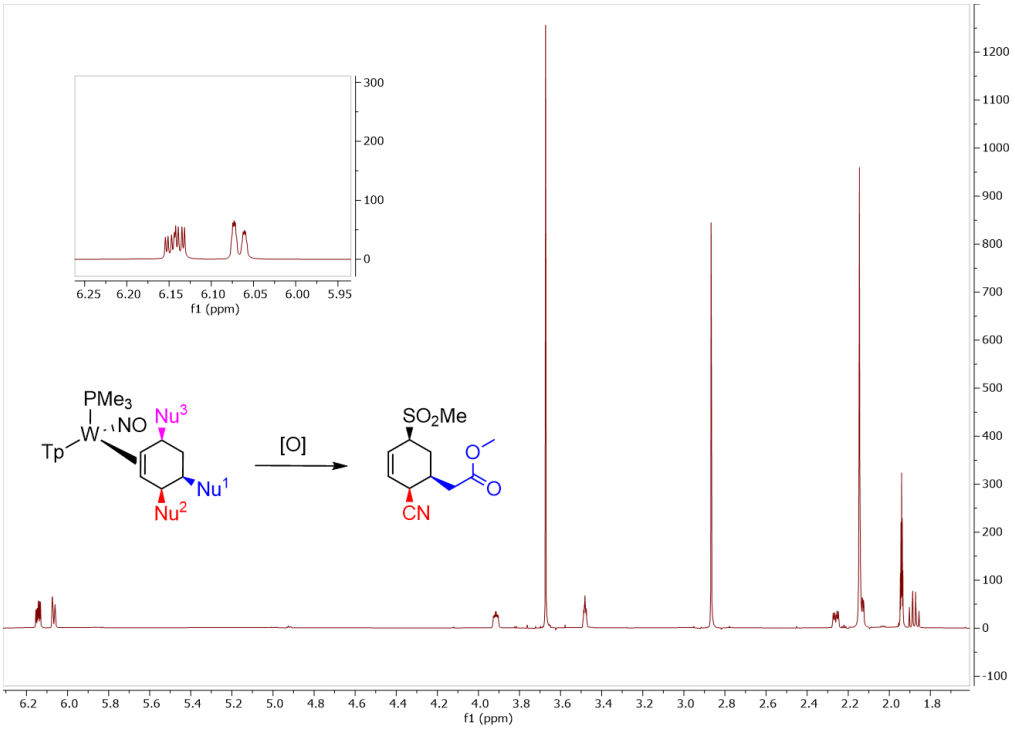


Figure 3.8 ^{1}H NMR of 58.

3.6 Conclusion

In this study, the synthesis of trisubstituted cyclohexenes from a dihapto-coordinate aromatic was explored. The only prior example from the Harman group in which a metal mediates three additions to an aromatic ring was a single example with an osmium anisole derivative,[33] in which an electrophile was followed by nucleophilic addition and subsequent reduction/substitution of the methoxy group.[34] In contrast, WTp(NO)(PMe_3)($PhSO_2R$) (R= -Me, -$NH(CH_2)_2$), and -Ph) is π-basic enough to promote protonation of the arene despite the presence of electron-withdrawing group. The resulting η^2-arenium complexes undergo nucleophilic addition with a range of nucleophiles to yield conjugated η^2-diene species. These undergo a second protonation and nucleophilic addition, leading to trisubstituted cyclohexenes. The sulfone can then be substituted for a third independent nucleophile. This reaction sequence produces a predictable regio- and stereochemical pattern for the cyclohexene ligand, which is liberated from the metal through oxidative decomplexation. Through this methodology, *cis, cis*- 3,4,6 trisubstituted cyclohexenes can be generated, and through the use of hydride, *cis*-3,4-, and *cis*-3,6-cyclohexene patterns are also achieved. Of the twelve novel substituted cyclohexenes prepared as examples of this methodology, nine (**48**, **51**, **53** - **59**) meet the criteria of Lipinski's rule of five[35] for evaluating drug likeliness, as well as the

criteria of Ghose,[36] Veber,[37] Egan,[38] and Muegge.[39] This indicates that these nine compounds have a high probability of showing desirable biological availability.

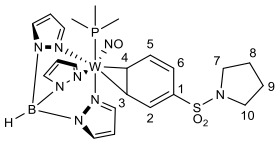
Experimental

(the compounds in this section have been synthesized by the author of this Thesis)

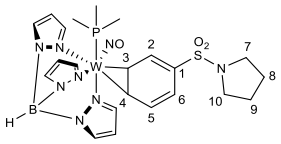
General Methods. NMR spectra were obtained on 500, 600, or 800 MHz spectrometers. Chemical shifts are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H signals of the deuterated solvents as internal standards. Chemical Shifts are reported in ppm and coupling constants (*J*) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a solid on a spectrometer with an ATR crystal accessory, and peaks are reported in cm^{-1}. Electrochemical experiments were performed under a nitrogen atmosphere. Most cyclic voltammetric data were recorded at ambient temperature at 100 mV/s, unless otherwise noted, with a standard three-electrode cell from +1.8 to −1.8 V with a platinum working electrode, acetonitrile or N,N-dimethylacetamide (DMA) solvent, and tetrabutylammonium (TBAH) electrolyte (~1.0 M). All potentials are reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V, −1.75 V) or ferrocene ($E_{1/2}$ = 0.55 V) as an internal standard. The peak separation of all reversible couples was less than 100 mV. All synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere unless otherwise noted. All solvents were purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes and were purged with nitrogen under an inert atmosphere. When possible, pyrazole protons of the tris(pyrazolyl)borate (Tp) ligand were uniquely assigned (e.g., "Tp3B") using two-dimensional NMR data (see Figure S1). If unambiguous assignments were not possible, Tp protons were labeled as "Tp3/5 or Tp4". All J values for Tp protons are 2(±0.4) Hz. BH peaks (around 4−5 ppm) in the 1 H NMR spectra are not assigned due to their quadrupole broadening; However, confirmation of the BH group is provided by IR data (ca 2500 cm^{-1}). Compounds 1,[40] 2,[15] 4,[15] 10,[15] 35,[28] 36A[28], 36B[28] and 51[28] have been previously reported. Ground-state structures were optimized at the M06 level of theory using the 6-31G**[LANL2DZ for W] basis set in Gaussian 16. Previous literature demonstrates that this functional and basis set choice accurately corroborates experimental results. Vibrational frequency analysis verified that optimized structures were minima, and rigid-rotor-harmonic-oscillator thermochemical chemical corrections were applied at 298 K and 1 atm utilizing Gaussian's default implementation. When solvent corrections were applied to estimate DG_{solv}, optimization and frequency calculations were performed using the SMD continuum solvent model with the appropriate solvent's parameters from Gaussian.

The experimental procedures reflect the compounds synthesized directly from the author of the Thesis. For more information regarding the remaining compounds refer to *J. Am. Chem. Soc.* 2022, 144, 21, 9489–9499.

Characterization of Compounds.

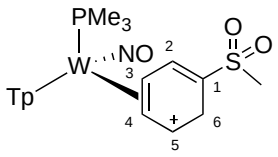


A

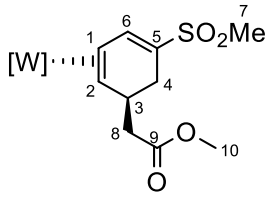


B

Compound 3.3. A 4-dram vial was charged with **1** (1.00 g, 1.64 mmol), phenylsulfonyl pyrrolidine (1.04 g, 4.92 mmol), a stir pea, and 3 mL of DME. The yellow heterogenous mixture was stirred at room temperature for 120 h. The reaction remained heterogeneous throughout the course of the reaction. The mixture underwent an observable color change of a dull gold to a light orange. The orange product was collected on a 30 mL fine porosity fritted disc, washed with ether (5 x 20 ml), and desiccated overnight, yielding **3A** and **3B** (0.760 g, 1.06 mmol, 65% yield). CV (DMA): $E_{p,a}$= + 0.10 V (NHE). IR: *ν*(SO) 1405 cm^{-1}, *ν*(NO) 1563 cm^{-1}, *ν*(BH) 2504 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.16 (1H, d, Tp3/5**B**), 8.15 (1H, d, Tp3/5**A**), 7.94 (1H, d, Tp3/5**A**), 7.93 (1H, d, Tp3/5**B**), 7.91 (3H, 2Tp3/5**A**, Tp3/5**B**), 7.89 (1H, d, Tp3/5**B**), 7.82 (2H, Tp3/5**A**, Tp3/5**B**), 7.80 (1H, d J = 6.6, H2**A**), 7.64 (1H, d J = 6.1, H2**B**), 7.30 (2H, Tp3/5**A**, Tp3/5**B**), 7.08 (1H, dd J = 9.6, 5.9, H5**B**), 6.93 (1H, dd J = 9.4, 5.1, H5**A**), 6.36 (3H, m, 2Tp4**A**, Tp4**B**), 6.33 (1H, t, Tp4**B**), 6.29 (2H, t, Tp4**A**, Tp4**B**), 6.28 (1H, t, Tp4**B**), 5.95 (1H, dd J = 9.4, 1.8, H6**A**), 5.88 (1H, dd J = 9.3, 1.7, H6**B**), 3.87 (1H, m, H4**A**), 3.79 (1H, m, H3**B**), 3.22 (8H, m, H10**A**, H10**B**, H7**A**, H7**B**), 2.16 (2H, m, H3**A**, H4**B**), 1.75 (4H, m, H9**B**, H8**B**), 1.72 (4H, m, H9**A**, H8**A**), 1.25 (9H, d J = 8.4, PMe_3**B**), 1.23 (9H, d J = 8.5, PMe_3**A**). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 145.3 (1C, Tp3**A**), 145.2 (1C, Tp3**B**), 145.1 (1C, C2**A**), 142.8 (1C, Tp3**A**), 142.3 (1C, Tp3**B**), 142.0 (2C, Tp3**A**, Tp3**B**), 142.2 (1C, C2**B**), 138.2 (2C, Tp5**A**, Tp5**B**), 137.5 (1C, Tp5**A**), 137.4 (1C, Tp5**B**), 137.1 (1C, Tp5**A**), 137.0 (1C, Tp5**B**), 136.6 (1C, C5**B**), 134.8 (1C, C5**A**), 126.0 (1C, C1**B**), 123.4 (1C, C1**A**), 113.7 (1C, C6**A**), 112.1 (1C, C6**B**), 107.6 (1C, Tp4**A**), 107.6 (1C, Tp4**B**), 107.3 (1C, Tp4**A**), 107.3 (1C, Tp4**B**), 107.1 (1C, Tp4**A**), 106.9 (1C, Tp4**B**), 65.1 (1C, d J = 8.6, C4**A**), 63.2 (1C, C4**B**), 62.5 (1C, d J = 8.2, C3**B**), 61.0 (1C, C3**A**), 48.6 (1C, C10/7**A**), 48.6 (1C, C10/7**B**), 25.7 (2C, C9**B**, C8**B**), 25.6 (2C, C9**A**, C8**A**), 13.6 (3C, d J = 28.6, PMe_3**B**), 13.0 (3C, d J = 28.8, PMe_3**A**). Anal. Calcd for $C_{22}H_{32}BN_8O_3PSW \cdot 1/2\ H_2O$ (present in ^{1}H NMR): C, 36.54; H, 4.60; N, 15.49. Found: C, 36.33; H, 4.53; N, 15.90.

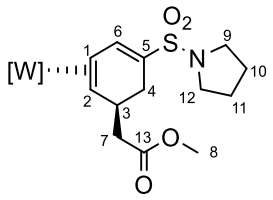


Compound 3.7. This species is thermally unstable and cannot be isolated. in situ ^{1}H-NMR data (d_3-MeCN, δ, 25 °C): 8.34 (1H, d, Tp3/5), 8.05 (1H, d, Tp3/5), 8.04 (1H, d, Tp3/5), 8.00 (1H, d, Tp3/5), 7.82 (1H, d, Tp3/6), 7.29 (1H, m, H5), 7.11 (1H, m, H2), 6.58 (1H, t, Tp4), 6.51 (1H, t, Tp4), 6.34 (1H, t, Tp4), 5.12 (1H, t J = 7.3, H3), 4.34 (1H, m, H4), 4.30 (1H, dm J = 25.7, H6a), 4.10 (1H, dm J = 25.5, H6b), 3.05 (3H, s, SO_2Me), 1.24 (9H, d J = 9.9, PMe_3).



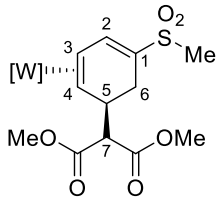
Compound 3.13. Compound **2** (500 mg, 0.758 mmol) was added to a test a tube along with minimal MeCN, and an orange heterogeneous solution formed. The solution was cooled at 0 °C for 15 min. Then, a 1 M HOTf/MeCN mixture (1.44 mL, 1.44 mmol, 0 °C) was added dropwise to the reaction. Once the acid was added, the solution turned to a dark homogeneous mixture. After 10 min, a yellow powder precipitated. The temperature was dropped to -30 °C and 1-(*tert*-Butyldimethylsilyloxy)-1-methoxyethene (713 mg, 0.827 mL, 3.79 mmol, −30 °C) was added dropwise to the reaction mixture. The solution stirred for 16h. The test tube was removed from the box and evaporated to dryness to form a dark oil, which was washed three times (H_2O/DCM), and dried with Na_2SO_4. A 60 mL medium-porosity frit was filled two-thirds with silica, and the previous mixture was placed on top. Hexanes (250 mL) was eluted through the column, followed by diethyl ether (100 mL) and by ethyl acetate (250 mL). The ethyl acetate portion eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 20 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight to yield **13** (325 mg, 0.443 mmol, 58.4%). CV (DMA): $E_{p,a}$= + 0.80 V (NHE). IR: *ν*(NO) 1558 cm^{-1}, *ν*(CO) 1732 cm^{-1}, *ν*(BH) 2503 cm^{-1}, *ν*(SO) 1407 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.04 (1H, d, TpB3), 7.99 (1H, d, TpA3), 7.87 (1H, d, TpC5), 7.87 (1H, d, TpB5), 7.78 (1H, d, TpA5), 7.66 (1H, dd, H6) 7.42 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.33 (1H, t, TpA4), 6.29 (1H, t, TpC4), 3.52 (3H, s, H10), 3.29 (1H, q, H3), 2.91 (1H, m, H1), 2.90 (3H, s, H7), 2.83 (1H, ddd J= 15.41 Hz, H4), 2.57 (1H, ddd J= 22.83, 15.99, 7.41 Hz, H8), 2.39 (1H, ddd, H8),

2.28 (1H, d, H4), 1.20 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 174.6 (1C, C9), 145.5 (1C, C6), 144.4 (1C, TpB3), 142.8 (1C, TpA3), 142.0 (1C, C5) 138.2 (1C, TpC3), 137.6 (2C, TpC5), 137.3 (1C, TpA5), 107.7 (1C, TpB4), 107.4 (1C, TpC4), 107.0 (1C, TpA4), 62.1 (1C, C2) 51.7 (1C, C10), 47.7 (1C, C7), 44.9 (2C, d J= 17.6 Hz, C8), 44.8 (1C, C1), 34.4 (1C, C3), 27.7 (2C, d J= 10.0 Hz C4), 13.7 (3C, d J= 29.9 Hz, PMe_3).

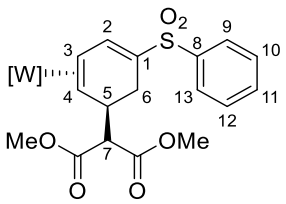


Compound 3.14. Compound **3** (500 mg, 0.758 mmol) was added to a test a tube along with MeCN, and an orange heterogeneous solution formed. The solution was cooled at 0 °C for 15 min, unti. Then, a 1 M HOTf/MeCN mixture (1.44 mL, 1.44 mmol, 0 °C) was added to the reaction using a syringe. Once the acid was added, the solution turned to a dark homogeneous mixture. After 10 min, the solution formed a yellow powder. The temperature was dropped to -30 °C and 1-(*tert*-Butyldimethylsilyloxy)-1-methoxyethene (713 mg, 0.827 mL, 3.79 mmol, −30 °C) was added dropwise to the reaction mixture. The solution stirred for 16h. The test tube was removed from the box and evaporated to dryness to form a dark oil, which was washed three times with an extraction (H_2O/DCM). A 60 mL medium-porosity frit was filled two-thirds with silica, and the previous silica mixture was placed on top. Hexanes (250 mL) was eluted through the column, followed by diethyl ether (100 mL) and by ethyl acetate (250 mL). The ethyl acetate eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 20 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight to yield **14** (371.3 mg, 0.471 mmol, 67.3%). CV (DMA): $E_{p,a}$= + 0.79 V (NHE). IR: *ν*(NO) 1554 cm^{-1}, *ν*(CO) 1724 cm^{-1}, *ν*(BH) 2502 cm^{-1}, *ν*(SO) 1405 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.16 (1H, d, TpB3), 8.03 (1H, d, TpA3), 7.99 (1H, d, TpA5), 7.97 (1H, d, TpB5), 7.84 (1H, d, TpC5), 7.65 (1H, dd, TpC3) 7.57 (1H, dd, H6), 6.42 (1H, t, TpB4), 6.35 (2H, m, TpA4/C4), 3.51 (3H, s, H8), 3.28 (1H, q, H9), 3.20 (1H, m, H12), 3.29 (1H, m H3), 2.99 (1H, m, H1), 2.81, 2.38 (2H, m, H4), 2.60, 2.35 (2H, dd, H7), 1.79 (2H, m, H10,11), 1.20 (1H, d, H2), 1.30 (9H, d, PMe_3). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 174.1 (1C, C13), 144.0 (1C, C6), 144.3 (1C, TpB3), 142.7 (1C, TpA3), 141.4 (1C, C3) 138.1 (1C, TpB5), 137.5 (2C, TpA5), 136.9 (1C, TpC5), 107.4 (1C, TpB4), 107.2 (1C, TpC4), 106.8 (1C, TpA4), 61.7 (1C, C2) 51.1 (1C, C8),

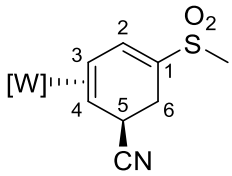
48.21 (1C, C9,12), 47.6 (2C, C1/C5), 44.3 (1C, C7), 34.4 (1C, C3), 28.4 (1C, C4), 25.9 (2C, C10/C11) 13.7 (3C, d J= 29.9 Hz, PMe_3).



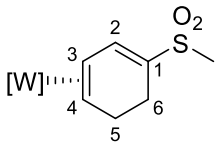
Compound 3.15. Compound **2** (0.100 g, 0.152 mmol) and MeCN were combined in a test tube to form an orange heterogeneous solution. Lithium dimethyl malonate (0.125 g, 0.910 mmol) and MeCN were combined in a second test tube to form a clear solution. Both solutions were cooled to 0 °C for 15 min. 1M HOTf/MeCN (0.30 mL, 0.303 mmol, -30 °C) was added to the reaction via syringe. Upon addition, the reaction became a dark red, homogeneous mixture. After 5 minutes, the cold bath was reduced to -30 °C. The protonated solution was added slowly to the lithium dimethyl malonate solution. The first test tube was rinsed with 0.5 mL of MeCN, which was added to the reaction. The reaction was stirred for 18 h. The test tube was removed from the glove box and evaporated to dryness. The resulting oil was purified by flash chromatography on a 12 g silica column (Combiflash) using a gradient elution of 0-100% ethyl acetate in hexanes. The fractions of 100% ethyl acetate containing the product were evaporated to dryness, picked up in minimal DCM, and precipitated into 10 mL of pentane yielding a light brown solid. The light brown precipitant was collected on a 15 mL fine porosity fitted disc, washed with hexanes (3 x 10 ml), and desiccated overnight to yield **15** (0.078 g, 0.099 mmol, 65%). CV (DMA): $E_{p,a}$= + 0.81 V (NHE). IR: *ν*(SO) 1406 cm^{-1}, *ν*(NO) 1556 cm^{-1}, *ν*(CO) 1726 cm^{-1}, *ν*(BH) 2489 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.05 (1H, d, TpB3), 7.98 (1H, d, TpA3), 7.88 (2H, d, TpB5, TpC5), 7.80 (1H, d, TpA5), 7.67 (1H, dd J = 5.7, 2.6, H2), 7.40 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.35 (1H, t, TpA4), 6.30 (1H, t, TpC4), 3.68 (3H, s, CO_2Me), 3.52 (2H, m, H5, H7). 3.44 (3H, s, CO_2Me), 2.91 (1H, m, H3), 2.90 (3H, s, SO_2Me), 2.86 (1H, ddm J = 17.1, 6.1, H6B), 2.27 (1H, d J = 16.8, H6A), 1.22 (9H, d J = 8.8, PMe_3), 1.11 (1H, d J = 9.2, H4). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 170.7 (1C, C=O), 170.3 (1C, C=O), 145.6 (1C, d J = 3.0, C2), 144.5 (1C, TpB3), 142.9 (1C, TpA3), 141.9 (1C, TpC3), 138.3 (1C, Tp5), 137.7 (1C, Tp5), 137.3 (1C, TpA5), 126.4 (1C, C1), 107.7 (1C, Tp4), 107.5 (1C, Tp4), 107.0 (1C, Tp4), 60.9 (1C, C7), 59.0 (1C, C4), 52.9 (1C, OMe), 52.6 (1C, OMe), 48.0 (1C, d J = 8.9, C3), 45.1 (1C, SO_2Me), 38.3 (1C, C5), 26.3 (1C, C6), 13.6 (3C, J = 30.2, PMe_3). Anal. Calcd for $C_{24}H_{35}BN_7O_7PSW \cdot H_2O$ (present in ^{1}H NMR): C, 35.62; H, 4.61; N, 12.12. Found: C, 35.37; H, 4.55; N, 12.46.



Compound 3.16. Compound **4** (0.100 g, 0.138 mmol) and MeCN were combined in a test tube to form an orange heterogeneous solution. Lithium dimethyl malonate (0.114 g, 0.832 mmol) and MeCN were combined in a second test tube to form a clear solution. Both solutions were cooled to 0 °C for 15 min. 1M HOTf/MeCN (0.277 mL, 0.277 mmol, -30 °C) was added to the reaction. Upon addition, the reaction became a dark red, homogeneous mixture. After 15 minutes, the cold bath was reduced to -30 °C. The protonated solution was added slowly to the lithium dimethyl malonate solution. The first test tube was rinsed with 0.5 mL of MeCN, which was added to the reaction. The reaction was stirred for 18 h. The test tube was removed from the box and evaporated to dryness. The resulting oil was purified by Combiflash flash chromatography on a 12 g silica column using a gradient elution of 0-100% ethyl acetate in hexanes. The fractions of 100% ethyl acetate contains the product were evaporated to dryness, picked up in minimal DCM, and precipitated into 10 mL of pentane yielding an off white solid. The off-white precipitant was collected on a 15 mL fine porosity fitted disc, washed with hexanes (3 x 10 ml), and desiccated overnight to yield **16** (0.072 g, 0.084 mmol, 61%). CV (DMA): $E_{p,a}$= + 0.82 V (NHE). IR: *ν*(SO) 1406 cm^{-1}, *ν*(NO) 1555 cm^{-1}, *ν*(CO) 1728 cm^{-1}, *ν*(BH) 2525 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.01 (1H, d, TpB3), 7.92 (1H, d, TpA3), 7.91 (1H, m, H2), 7.87 (1H, d, TpB5), 7.86 (1H, d, TpC5), 7.83 (2H, m, H9, H13), 7.76 (1H, d, TpA5), 7.58 (1H, m, H11), 7.52 (2H, m, H10, H12), 7.40 (1H, d, TpC3), 6.37 (1H, t, TpC4), 6.30 (1H, t, TpA4), 6.28 (1H, t, TpB4), 3.46 (3H, s, OMe), 3.40 (1H, m, H5), 3.35 (3H, s, OMe), 3.07 (1H, d J = 10.4, H7), 2.90 (1H, m, H3), 2.77 (1H, , J = 17.3, 6.5, H6b), 2.07 (1H, d J = 16.9, H6a), 1.24 (9H, d J = 8.7, PMe_3), 0.90 (1H, d J = 9.1, H4). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 170.3 (1C, C=O), 170.2 (1C, C=O), 147.1 (1C, d J = 2.7, C2), 144.5 (1C, TpB3), 143.2 (1C, C8), 142.8 (1C, TpA3), 141.7 (1C, TpC3), 138.3 (1C, Tp5), 137.7 (1C, Tp5), 137.2 (1C, TpA5), 133.3 (1C, C11), 129.9 (2C, C10, C12), 128.3 (2C, C9, C13), 126.5 (1C, C1), 107.7 (1C, Tp4), 107.4 (1C, Tp4), 107.0 (1C, TpB4), 59.9 (1C, C7), 58.4 (1C, C4), 52.9 (1C, OMe), 52.4 (1C, OMe), 48.4 (1C, d J = 8.6, C3), 37.9 (1C, C5), 26.3 (1C, C6), 13.4 (3C, d J = 28.8, PMe_3). Anal. Calcd for $C_{29}H_{37}BN_7O_7PSW$· 1/3DCM (present in ^{1}H NMR): C, 39.96; H, 4.31; N, 11.12. Found: C, 39.66; H, 4.33; N, 10.99.

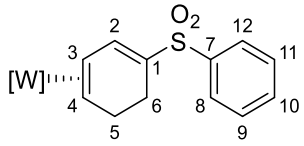


Compound 3.18. Compound **2** (0.100 g, 0.152 mmol) and MeCN were combined in a test tube to form an orange heterogeneous solution. NaCN (0.037 g, 0.760 mmol) and MeOH were combined in a second test tube to form a clear solution. Both solutions were cooled to 0 °C for 15 min. 1M HOTf/MeCN (0.230 mL, 0.230 mmol, -30 °C) was added to the reaction via syringe. Upon addition, the reaction became a dark red, homogeneous mixture. After 5 minutes, the protonated solution was added slowly to the NaCN solution. The first test tube was rinsed with 0.5 mL of MeCN, which was added to the reaction. The reaction was stirred for 15 h. The test tube was removed from the box and evaporated to dryness. The resulting oil was purified by flash chromatography (Combiflash) on a 12 g silica column using a gradient elution of 0-100% ethyl acetate in hexanes. The fractions of 100% ethyl acetate containing the product were evaporated to dryness, picked up in minimal DCM, and precipitated into 10 mL of pentane yielding white solid. The white precipitant was collected on a 15 mL fine porosity fitted disc, washed with hexanes (3 x 10 ml), and desiccated overnight to yield **18** (0.059 g, 0.085 mmol, 56%). CV (DMA): $E_{p,a}$= + 0.97 V (NHE). IR: *ν*(SO) 1405 cm^{-1}, *ν*(NO) 1571 cm^{-1}, *ν*(CN) 2225 cm^{-1}, *ν*(BH) 2502 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.05 (1H, d, TpB3), 7.89 (2H, d, TpA5, TpB5), 7.81 (1H, d, TpA3), 7.80 (1H, d, TpC5), 7.79 (1H, dd J = 5.7, 2.5, H2), 7.49 (1H, d, TpC3), 6.39 (1H, t, TpB4), 6.33 (2H, t, TpA4, TpC4), 3.91 (1H, m, H5), 3.03 (1H, m, H3), 2.94 (3H, s, SO_2Me), 2.87 (1H, ddm J = 16.8, 6.7, H6a), 2.67 (1H, d J = 16.8, H6b), 1.53 (1H, d J = 9.1, H4), 1.25 (9H, d J = 9.0, PMe_3). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 146.0 (1C, C2), 144.6 (1C, TpB3), 142.7 (1C, TpA3), 142.2 (TpC3), 138.4 (1C, Tp5), 138.0 (1C, Tp5), 137.5 (1C, TpC5), 127.5 (1C, CN), 125.9 (1C, C1), 107.8 (1C, Tp4), 107.6 (1C, Tp4), 107.4 (1C, Tp4), 57.67 (1C, d J = 2.5, C4), 47.0 (1C, d J = 9.3, C3), 45.1 (1C, SO_2Me), 30.0 (1C, C5), 26.9 (1C, C6), 13.6 (3C, d J = 30.1, PMe_3). Anal. Calcd for $C_{20}H_{28}BN_8O_3PSW \cdot 1/3DCM$ (present in ^{1}H NMR): C, 34.18; H, 4.04; N, 15.68. Found: C, 34.22; H, 4.19; N, 15.75.



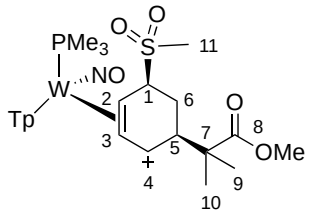
Compound 3.21. Compound **2** (0.100 g, 0.152 mmol) and MeCN were combined in a test tube to form an orange heterogeneous solution. Tetrabutylammonium borohydride

(0.117 g, 0.455 mmol) and MeCN were combined in a second test tube to form a clear solution. Both solutions were cooled to 0 °C for 15 min. 1M HOTf/MeCN (0.167 mL, 0.167 mmol, -30 °C) was added to the reaction. Upon addition, the reaction became a dark red, homogeneous mixture. After 5 minutes, the protonated solution was added slowly to the tetrabutylammonium borohydride solution. The first test tube was rinsed with 0.5 mL of MeCN, which was added to the reaction. Reaction may turn blue. The reaction was stirred for 18 h. The reaction was warmed to room temperature and removed from the glovebox. H_2O (13 mL) was added slowly to the stirring solution to induce precipitation of a white solid. The white solid was collected on a 15 mL fine porosity fritted disc, wash with ether (2 x 10 mL) and hexanes (3 x 10 mL), then desiccated overnight to yield **21** (0.062 g, 0.094 mmol, 62%). CV (DMA): $E_{p,a}$= + 0.72 V (NHE). IR: ν(SO) 1401 cm^{-1}, ν(NO) 1551 cm^{-1}, ν(BH) 2485 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.04 (1H, d, TpB3), 7.97 (1H, d, TpA3), 7.87 (1H, d, TpB5), 7.86 (1H, d, TpC5), 7.78 (1H, d, TpA5), 7.67 (1H, dd J = 5.8, 2.4, H2), 7.45 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.31 (1H, t, TpA4), 6.29 (1H, t, TpC4), 3.45 (1H, m, H5a), 2.94 (1H, m, H3), 2.90 (3H, s, SO_2Me), 2.82 (1H, ddm J = 14.2, 7.1, H5b), 2.56 (1H, m, H6b), 2.34 (1H, dd J = 15.9, 6.3, H6a), 1.36 (1H, m, H4), 1.25 (9H, d J = 8.6, PMe_3). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 145.7 (1C, d J = 2.7, C2), 144.4 (1C, TpB3), 142.7 (1C, TpA3), 142.0 (1C, TpC3), 138.1 (1C, TpC5), 137.5 (1C, TpB5), 137.1 (1C, TpA5), 129.1 (1C, C1), 107.6 (1C, TpB4), 107.3 (1C, TpC4), 107.0 (1C, TpA4), 57.1 (1C, C4), 48.9 (1C, d J = 8.5, C3), 45.1 (1C, SO_2Me), 27.0 (1C, C5), 23.0 (1C, C6), 13.8 (3C, d J = 28.7, PMe_3). Anal. Calcd for $C_{19}H_{29}BN_7O_3PSW$: C, 34.53; H, 4.42; N, 14.83. Found: C, 34.35; H, 4.27; N, 14.49.

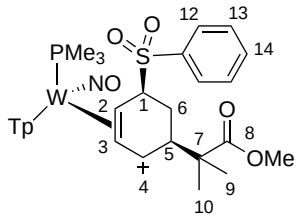


Compound 3.22. Compound **4** (0.100 g, 0.138 mmol) and MeCN were combined in a test tube to form an orange heterogeneous solution. Sodium borohydride (0.013 g, 0.344 mmol) and MeCN were combined in a second test tube to form a clear solution. Both solutions were cooled to 0 °C for 15 min. 1M HOTf/MeCN (0.150 mL, 0.150 mmol, -30 °C) was added to the reaction. Upon addition, the reaction became a dark red, homogeneous mixture. After 5 minutes, the protonated solution was added slowly to the sodium borohydride solution. The first test tube was rinsed with 0.5 mL of MeCN, which was added to the reaction. Reaction may turn blue. The reaction was stirred for 16 h. The reaction was warmed to room temperature and removed from the glovebox. H_2O (13 mL) was added slowly to the stirring solution to induce precipitation of a white solid. The white

solid was collected on a 15 mL fine porosity fritted disc, wash with ether (2 x 10 mL) and hexanes (3 x 10 mL), then desiccated overnight to yield **22** (0.068 g, 0.094 mmol, 68%). CV (DMA): $E_{p,a}$= + 0.72 V (NHE). IR: ν(SO) 1405 cm^{-1}, ν(NO) 1557 cm^{-1}, ν(BH) 2474 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 7.98 (1H, d, TpB3), 7.93 (1H, dd J = 6.0, 2.5, H2), 7.91 (1H, d, TpA3), 7.87 (2H, m, H12, H8), 7.84 (2H, d, TpB5, TpC5), 7.75 (1H, d, TpA5), 7.55 (1H, m, H10), 7.49 (2H, m, H11, H9), 7.46 (1H, d, TpC3), 6.35 (1H, t, TpB4), 6.28 (1H, t, TpC4), 6.26 (1H, t, TpA4), 3.25 (1H, m, H5a), 2.91 (1H, m, H3), 2.75 (1H, m, H5b), 2.41 (1H, m, H6b), 2.14 (1H, dd J = 16.2, 5.8, H6a), 1.32 (1H, d J = 10.0, H4), 1.26 (9H, d J = 8.6, PMe_3). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 147.7 (1C, d J = 2.7, C2), 144.3 (1C, TpB3), 143.9 (1C, C7), 142.6 (1C, TpA3), 142.0 (1C, TpC3), 138.1 (1C, Tp5), 137.5 (1C, Tp5), 137.1 (1C, Tp5), 133.1 (1C, C10), 129.7 (2C, C11, C9), 129.0 (1C, C1), 128.3 (2C, C12, C8), 107.4 (1C, TpB4), 107.3 (1C, TpC4), 106.9 (1C, TpA4), 57.3 (1C, C4), 49.5 (1C, d J = 8.6, C3), 27.3 (1C, C5), 22.9 (1C, C6), 14.1 (3C, d J = 29.4, PMe_3). Anal. Calcd for $C_{24}H_{31}BN_7O_3PSW \cdot 1/4\ NaOTf$: C, 38.01; H, 4.08; N, 12.80. Found: C, 38.18; H, 4.26; N, 13.10.

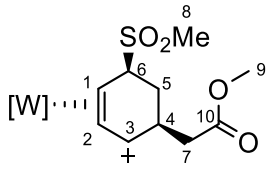


Compound 3.24. Complex is unstable in solution. Partial characterization ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.35 (1H, d, Tp3/5), 8.04 (1H, d, Tp3/5), 8.02 (1H, d, Tp3/5), 7.99 (1H, d, Tp3/5), 7.95 (1H, d, Tp3/5), 7.84 (1H, d, Tp3/5), 6.55 (1H, t, Tp4), 6.52 (1H, t, Tp4), 6.36 (1H, t, Tp4), 6.08 (1H, d J = 8.1, H4), 5.52 (1H, tm J = 7.8, H3), 4.61 (1H, ddm J = 15.5, 6.9, H2), 4.13 (1H, t J = 8.9, H1), 3.94 (1H, t J = 8.4, H5), 3.74 (3H, s, OMe), 3.01 (3H, s, SO_2Me), 1.35 (1H, s, H10/9), 1.33 (3H, s, H10/9), 1.22 (9H, d J = 9.3, PMe_3).

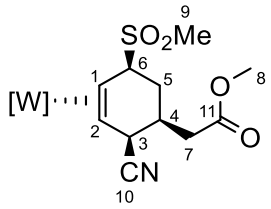


Compound 3.25. Complex is unstable in solution. Partial Characterization ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.34 (1H, d, Tp3/5), 8.05 (1H, d, Tp3/5), 8.00 (1H, d, Tp3/5), 7.99 (2H, m, H16, H12), 7.97 (1H, d, Tp3/5), 7.96 (1H, d, Tp3/5), 7.83 (1H, d, Tp3/5), 7.82 (1H, m, H14), 7.72 (2H, m, H15, H13), 6.58 (1H, t, Tp4), 6.52 (1H, t, Tp4), 6.34 (1H, t, Tp4), 6.00 (1H, d J =

8.2, H4), 5.50 (1H, tm J = 7.8, H3), 4.77 (1H, dd J = 15.7, 6.7, H2), 4.18 (1H, t J = 8.2, H1), 3.78 (1H, t J = 8.61, H5), 3.63 (3H, s, OMe), 3.01 (3H, s, SO_2Me), 1.26 (9H, d J = 9.8, PMe_3), 1.20 (3H, s, H10/9), 1.16 (3H, s, H10/9).

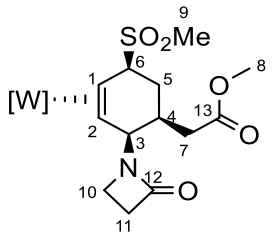


Compound 3.28. Compound **13** (150 mg, 0.758 mmol) was added to a test a tube along with minimal MeCN, and a pale-yellow heterogeneous solution formed. The solution was cooled at -30 °C for 15 min. Then, a 1 M HOTf/MeCN mixture (1.44 mL, 1.44 mmol, −30 °C) was added to the reaction dropwise and stirred overnight. The solution was then extracted with DCM and water three times with water. The organic layer was dried with anhydrous Na_2SO_4 and the resulting filtrate was evaporated to dryness. The resulting substance was dissolved in DCM and precipitated in pentane to yield **28** (113 mg, 0.153 mmol, 75.3%). ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.38 (1H, d, TpB3), 8.30 (1H, d, TpA3), 8.03 (1H, d, TpB5), 8.00 (1H, d, TpC3), 7.97 (1H, d, TpC5), 7.83 (1H, d, TpA5), 6.53 (2H, m, TpB4/C4), 6.35 (1H, t, TpA4), 3.61 (1H, d, H3), 5.45 (1H, t, H2), 4.54 (1H, m, H1), 4.10 (1H, t, H6), 3.94 (4H, m, H4), 3.72 (3H, s, H10), 3.08 (3H, s, H8), 2.83, 2.73 (2H, m, H7), 2.23, 1.50 (2H, m, H5). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 173.3 (1C, C10), 149.1 (1C, TpA3), 146.2 (1C, TpB3), 140.1 (1C, TpB5), 139.8 (2C, TpC5/C3), 134.4 (1C, TpA5), 109.8 (1C, TpB4), 109.0 (1C, TpC4), 108.4 (1C, TpA4), 134.6 (1C, C3), 62.7 (1C, C6), 61.4 (1C, C1), 55.3 (1C, C2), 52.7 (1C, C9), 42.7 (1C, C7), 38.5 (1C, C8), 32.3 (1C, C4), 26.8 (1C, C5), 27.7 (2C, d J= 10.0 Hz C4), 13.7 (3C, d J= 29.9 Hz, PMe_3).

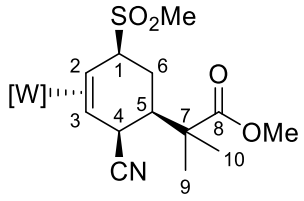


Compound 3.29. Compound **28** (150 mg, 0.204 mmol) was added to a test tube containing a solution of NaCN in MeOH. This stirred at -30 °C for 20 min. An extraction with DCM/H_2O was performed and the organic layer washed three times. This was dried over Na_2SO_4 and evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated

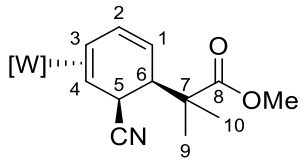
overnight to yield **29** (116 mg, 0.153 mmol, 75%). CV (DMA): $E_{p,a}$= + 0.69 V (NHE). IR: *ν*(NO) 1553 cm^{-1}, *ν*(CO) 1727 cm^{-1}, *ν*(BH) 2502 cm^{-1}, *ν*(SO) 1405 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.04 (1H, d, TpB3), 7.93 (1H, d, TpA3), 7.88 (1H, d, TpB5), 7.87 (1H, d, TpC5), 7.79 (1H, d, TpA5), 7.37 (1H, d, Tp3C), 6.37 (1H, t, TpB4), 6.31 (1H, t, TpC4), 6.29 (1H, t, TpA4), 4.43 (1H, t, H6), 3.70 (4H, m, H8/3), 3.72 (3H, s, H10), 3.02 (3H, s, H9), 2.97 (1H, m, H1), 2.80 (1H, t, H4), 2.56 (2H, m, H7), 1.98, 1.70 (2H, m, H5) 1.17 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 173.3 (1C, C10), 145.1 (1C, TpB3), 144.3 (1C, TpA3), 142.4 (1C, TpC3), 138.1 (3C, TpA5/B5/C5), 127.0 (1C, C10), 107.6 (1C, TpB4), 107.3 (2C, TpA4/C4), 63.5 (1C, C6), 55.9 (1C, C2), 52.4 (1C, C8), 39.7 (1C, C7), 37.0 (1C, C9), 36.7 (1C, C1), 34.9 (1C, C3), 29.2 (2C, C5/4),13.7 (3C, d J= 29.9 Hz, PMe_3).



Compound 3.30. Compound **28** (150 mg, 0.204 mmol) was added to a premade solution of 2-azetidinone (50 mg) in NaO^{t}Bu (2M/THF) (0.51 mL, 1.02 mmol). The reaction stirred at −60 °C for 1 h. An extraction with DCM/H_2O was performed and the organic layer washed three times. This was dried over $MgSO_4$ and evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **30** (126 mg, 0.157 mmol, 77%). CV (DMA): $E_{p,a}$= + 0.70 V (NHE). IR: *ν*(NO) 1554 cm^{-1}, *ν*(CO) 1736 cm^{-1}, *ν*(CO) 1797 cm^{-1}, *ν*(BH) 2502 cm^{-1}, *ν*(SO) 1406 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.22 (1H, d, TpA5), 8.04 (1H, d, TpB3), 7.87 (1H, d, TpB5), 7.86 (1H, d, TpC5), 7.73 (1H, d, TpA5), 7.33 (1H, d, Tp3C), 6.37 (1H, t, TpB4), 6.3 (1H, m, TpC4/A4), 4.69 (1H, s, H3), 4.51 (1H, t, H6), 3.66 (3H, s, H8), 3.61, 3.51 (2H, m, H10), 3.17 (1H, m, H1), 2.92 (3H, s, H9), 2.79, 2.64 (2H, m, H11), 2.72 (1H, m, H4), 2.50, 2.32 (2H, m, H7) 1.75,1.65 (2H, m, H5) 0.89 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 173.0 (1C, C13),167.8 (1C, C12) 144.9 (1C, TpA5/B3), 142.4 (1C, TpC3), 138.6 (1C, TpA3), 138.2 (2C, TpB5/C5), 107.6 (1C, TpB4), 107.5 (2C, TpA4/C4), 63.8 (1C, C6), 56.0 (1C, C2), 52.5 (1C, C3), 52.4 (1C, C8), 40.8 (1C, C10), 40.7 (1C, C1), 38.5 (2C, C7,9), 37.0 (1C, C11), 32.6 (1C, C4), 28.8 (1C, C5) 13.7 (3C, d J= 29.9 Hz, PMe_3).

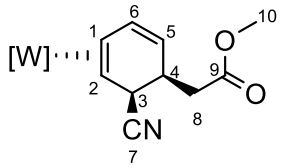


Compound 3.31. Compound **10** (0.700 g, 0.919 mmol) and MeCN were combined in a test tube. NaCN (0.135 g, 2.757 mmol), MeOH, and a stir pea were combined in a second test tube. Both solutions were cooled to -30 °C for 15 min. 1M HOTf/MeCN (1.10 mL, 1.10 mmol, -30 °C) was added to the solution of **10** and MeCN via syringe. The reaction turned a dark brown upon addition of the acid. After 15 min, the reaction was added to the solution of NaCN and MeOH. 2 mL of MeCN were used to rinse the first test tube and added to the reaction solution. The reaction was stirred for 24 h. A white precipitant formed in the solution overnight. The white solid was collected on a 30 mL fine porosity fritted disc and washed with ether (3 x 15 mL) and desiccated overnight yielding **31** (0.470 g, 0.596 mmol, 65%). CV (DMA): $E_{p,a}$= + 0.69 V (NHE). IR: *ν*(SO) 1405 cm^{-1}, *ν*(NO) 1542 cm^{-1}, *ν*(CO) 1719 cm^{-1}, *ν*(CN) 2215 cm^{-1}, *ν*(BH) 2517 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.05 (1H, d, TpB3), 7.87 (1H, d, TpC5), 7.86 (1H, d, TpB5), 7.78 (1H, d, TpA5), 7.66 (1H, d, TpA3), 7.36 (1H, d, TpC3), 6.36 (1H, t, TpB4), 6.31 (2H, m, TpA4, TpC4), 4.45 (1H, m, H1), 3.71 (3H, s, OMe), 3.39 (1H, bs, H4), 3.06 (3H, s, SO_2Me), 2.93 (1H, m, H2), 2.62 (1H, dt J = 13.2, 3.0, H5), 2.07 (1H, m, H6b), 1.87 (1H, m, H6a), 1.35 (3H, s, H10/9), 1.34 (3H, s, H10/9), 1.22 (9H, d J = 8.9, PMe_3), 1.20 (1H, d J = 11.3, H3). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 178.1 (1C, C=O), 145.2 (1C, TpB3), 143.9 (1C, TpA3), 142.4 (1H, TpC3), 138.2 (1H, Tp5), 138.0 (1C, Tp5), 137.9 (1C, Tp5), 127.0 (1C, CN), 107.6 (1C, TpB4), 107.4 (1C, Tp4), 107.3 (1C, Tp4), 64.5 (1C, C1), 59.1 (1C, C3), 52.3 (1C, OMe), 46.1 (1C, C7), 39.7 (1C, C5), 37.8 (1C, d J = 11.7, C2), 37.0 (1C, SO_2Me), 32.1 (1C, C4), 25.8 (1C, C10/9), 25.4 (1C, C6), 21.1 (1C, C10/9), 13.5 (3C, d J = 29.0, PMe_3). Anal. Calcd for $C_{25}H_{38}BN_8O_5PSW \cdot 1/4$ NaOTf: C, 36.48; H, 4.61; N, 13.48. Found: C, 36.83; H, 4.78; N, 13.69.



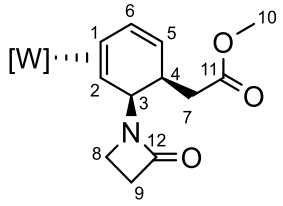
Compound 3.40. Compound **10** (0.400 g, 0.507 mmol) and 15 mL of THF were combined in a 4-dram vial with a stir pea. The heterogenous cloudy mixture was stirred for an hour. A 150 mL medium porosity fritted disc was filled ¾ full of silica and set in ether. The heterogenous reaction was loaded onto the silica column and eluted with 250 mL of ethyl

acetate. No bands visible to the eye were observed to have eluted. All eluant was combined and evaporated to dryness. The resulting oil was picked up in minimal DCM and precipitated into 20 mL of stirring pentane to yield a white solid. The white precipitant was collected on a 15 mL fine porosity fritted disc, was with hexanes (3 x 10 mL), and desiccated overnight to yield **40** (0.214 g, 0.302 mmol, 60%). CV (DMA): $E_{p,a}$= + 0.73 V (NHE). IR: *ν*(NO) 1575 cm^{-1}, *ν*(CO) 1718 cm^{-1}, *ν*(CN) 2359 cm^{-1}, *ν*(BH) 2503 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.03 (1H, d, TpB5), 7.87 (1H, d, TpB3), 7.85 (1H, d, TpC3), 7.79 (2H, TpA5, TpA3), 7.43 (1H, d, TpC5), 6.66 (1H, m, H2), 6.37 (1H, t, TpB4), 6.34 (1H, t, TpA4), 6.29 (1H, t, TpC4), 5.02 (1H, d J = 10.4, H1), 3.74 (3H, s, OMe), 3.34 (1H, m, H5), 3.16 (1H, m, H6), 3.01 (1H, m, H3), 1.37 (3H, s, H10/9), 1.32 (3H, s, H10/9), 1.24 (9H, d J = 8.7, PMe_3), 1.21 (1H, d J = 9.6, H4). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 178.5 (1C, C8), 144.4 (1C, TpB5), 142.4 (1C, TpA5), 141.8 (1C, TpC5), 138.0 (1C, TpC3), 137.6 (1C, TpB3), 137.1 (1C, TpA3), 133.9 (1C, C2), 127.4 (1C, CN), 116.8 (1C, C1), 107.5 (1C, Tp4), 107.4 (1C, Tp4), 107.3 (1C, Tp4), 59.2 (1C, C4), 52.4 (1C, OMe), 48.6 (1C, d J = 10.9, C3), 45.4 (1C, C7), 43.5 (1C, C6), 31.7 (1C, C5), 27.2 (1C, C10/9), 20.7 (1C, C10/9), 13.7 (3C, d J = 28.9, PMe_3). Anal. Calcd for $C_{24}H_{34}BN_8O_3PW$: C, 40.70; H, 4.84; N, 15.82. Found: C, 40.85; H, 4.76; N, 15.55.

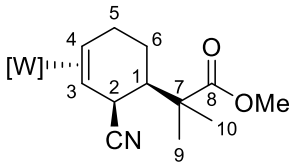


Compound 3.41. Compound **13** (150 mg, 0.204 mmol) was added to a test tube with minimal MeCN and stirred at -30 °C for 20 min. Then, a 1 M HOTf/MeCN mixture (0.409 mL, 0.409 mmol, −30 °C) was added to the reaction using a syringe, and the solution stirred at −30 °C. Once the acid was added, the solution turned to a dark homogeneous mixture. After 30 min, the formed allyl was added to a pre-made solution of NaCN (1.02 mL, 2.04 mmol) in minimal MeOH and the solution became a red homogeneous mixture. The reaction stirred at −30 °C for 16h. An extraction with DCM/H_2O was performed and the organic layer washed three times. This was dried over Na_2SO_4 and evaporated *in vacuo*. The resulting yellow film was dissolved in minimal DCM and pipetted in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **41** (98 mg, 144 mmol, 70.5%). CV (DMA): $E_{p,a}$= + 0.78 V (NHE). IR: *ν*(NO) 1551 cm^{-1}, *ν*(CO) 1668 cm^{-1}, *ν*(CN) 2211 cm^{-1} *ν*(BH) 2502 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.13 (1H, d, TpA3), 8.06 (1H, d, TpB3), 7.88 (1H, d, TpB5), 7.87 (1H, d, TpC5), 7.80 (1H, d, TpA5), 7.47 (1H, d, TpC3),

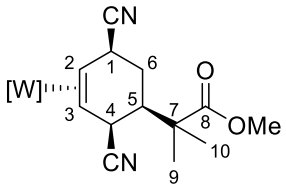
6.62 (1H, m, H6), 6.39 (1H, t, TpB4), 6.30 (1H, t, TpC4), 6.27 (1H, t, TpA4), 4.71 (1H, d, H5), 3.72 (1H, q, H3), 3.71 (3H, s, H10), 3.19 (1H, m, H4), 2.97 (1H, m, H1), 2.61 (1H, d, H8), 2.59 (1H, d, H8), 1.27 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 175.2 (1C, C9), 144.6 (1C, TpA5), 143.5 (1C, TpA3), 142.3 (1C, TpB3) 138.3 (1C, TpC3), 137.9 (1C, TpC5), 137.9 (1C, TpB5), 137.7 (1C, C10), 133.8 (1C, C6), 119.2 (1C, C5), 107.8 (1C, TpA4), 107.3 (1C, Tp4C) 106.8 (1C, Tp4B), 56.5 (1C, C2), 52.3 (1C, C10), 48.2 (1C, C1), 38.4 (1C, C8), 34.9 (1C, C3), 32.5 (1C, C4), 13.20 (3C, d J= 29.1 Hz, PMe3).



Compound 3.42. Compound **13** (150 mg, 0.204 mmol) was added to a test tube with minimal MeCN and stirred at -60 °C for 20 min. Then, a 1 M HOTf/MeCN mixture (0.409 mL, 0.409 mmol, −60 °C) was added to the reaction dropwise, and the solution stirred at −60 °C . Once the acid was added, the solution turned to a dark homogeneous mixture. After 30 min, the formed allyl was added to a pre-made solution of 2-azetidinone (50 mg, 0.708 mmol) in NaO^{t}Bu (2M/THF) (0.51 mL, 1.02 mmol). The reaction stirred at −60 °C for 16h. An extraction with DCM/H_2O was performed and the organic layer washed three times. This was dried over Na_2SO_4 and evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **42** (100 mg, 138 mmol, 67.6%). CV (DMA): $E_{p,a}$= + 0.79 V (NHE). IR: *ν*(NO) 1551 cm^{-1}, *ν*(CO) 1730 cm^{-1}, *ν*(CO) 1785 cm^{-1} *ν*(BH) 2502 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.13 (1H, d, TpA3), 8.03 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.78 (1H, d, TpA5), 7.43 (1H, d, TpC3), 6.50 (1H, dd, H6), 6.37 (1H, t, TpB4), 6.35 (1H, t, TpA4), 6.29 (1H, t, TpC4), 4.70 (2H, d, H3/5), 3.66 (3H, s, H10), 3.57 (1H, m, H9), 3.27 (1H, m, H4), 3.17 (1H, m, H9), 3.09 (1H, m, H1), 2.76 (1H, m, H8), 2.66 (1H, m, H8), 2.42 (2H, m, H7), 0.91 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 174.3 (1C, C12), 168.0 (1C, C11), 144.5 (1C, TpB3), 143.1 (1C, TpA3),141.7 (1C, TpC3), 137.9 (1C, Tp5B), 137.5 (1C, TpC5), 137.1 (1C, Tp5A), 133.5 (1C, C6), 120.7 (1C, C5),107.5 (1C, TpB4), 107.2 (1C, TpA4), 107.1 (1C, TpC4), 56.0 (1C, C2), 52.4 (1C, C3), 51.9 (1C, C10), 50.5 (1C, C1), 39.4 (1C, C9), 37.3 (1C, C7), 36.4 (1C, C8), 33.5 (1C, C4),13.7 (3C, d J= 29.9 Hz, PMe_3).

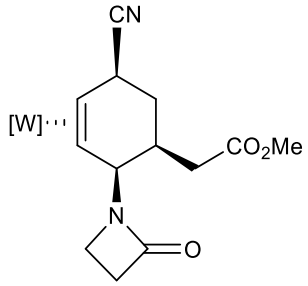


Compound 3.43. Compound **40** (0.200 g, 0.254 mmol), $NaCNBH_3$ (0.064 g, 1.02 mmol), MeCN, and a stir pea were added to a 4 dram to form a cloudy, yellow tinted solution. The reaction was allowed to stir overnight. A 60 mL course porosity fritted disc was then filled ¾ full of silica and set in ether. The reaction was evaporated to dryness, picked up in minimal DCM, and loaded onto the column. 200 mL of ethyl acetate was used to pull the product off the column. There is no colored band observed. The ethyl acetate was evaporated to dryness. The resulting oil was dissolved in minimal DCM and added dropwise to 20 mL of stirring pentane to yield a white solid. The resulting solid was collected on a 15 mL fine porosity fritted disc, washed with hexanes (2 x 10 mL), and desiccated overnight to yield **43**. (0.135 g, 0.190 mmol, 75%). CV (DMA): $E_{p,a}$= + 0.55 V (NHE). IR: *ν*(NO) 1561 cm^{-1}, *ν*(CO) 1718 cm^{-1}, *ν*(CN) 2219 cm^{-1}, *ν*(BH) 2505 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.02 (1H, d, TpB5), 7.85 (1H, d, TpB3), 7.82 (1H, d, TpC5), 7.81 (1H, d, TpA5), 7.78 (1H, d, TpA3), 7.33 (1H, d, TpC3), 6.36 (1H, t, TpB4), 6.35 (1H, t, TpA4), 6.26 (1H, t, TpC4), 3.71 (3H, s, OMe), 3.54 (1H, bs, H2), 3.01 (1H, m, H5), 2.82 (2H, m, H5, H4), 2.38 (1H, ddd J = 112.1, 3.7, 2.0 Hz, H1), 1.62 (1H, dm J = 13.3 Hz, H6), 1.53 (1H, m, H6), 1.29 (3H, s, H10/9), 1.28 (3H, s, H10/9), 1.20 (9H, d J = 8.1 Hz, PMe3), 1.04 (1H, d J =11.0 Hz, H3). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 178.6 (1C, C8), 144.4 (1C, TpB3), 143.5 (1C, TpA3), 141.5 (1C, TpC3), 137.8 (1C, Tp5), 137.5 (2C, Tp5), 127.8 (1C, CN), 107.5 (1C, Tp4), 107.4 (2C, Tp4), 59.1 (1C, C3), 52.3 (1C, OMe), 46.3 (1C, d J = 12.5 Hz, C4), 46.1 (1C, C7), 42.3 (1C, C1), 33.5 (1C, C2), 29.5 (1C, d J = 4.1 Hz, C5), 26.4 (1C, C10/9), 24.5 (1C, C6), 21.0 (1C, C10/9), 13.9 (3C, d J = 29.0 Hz, PMe_3). Anal. Calcd for $C_{24}H_{36}BN_8O_3PW \cdot DCM$: C, 37.76; H, 4.82; N, 14.09. Found: C, 37.51; H, 4.85; N, 14.37.



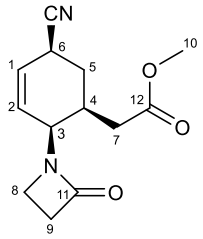
Compound 3.45. Compound **40** (0.100 g, 0.127 mmol), NaCN (0.032 g, 0.634 mmol), MeCN, and a stir pea were added to a 4 dram to form a cloudy, yellow tinted solution. The reaction was allowed to stir overnight. A white precipitant crashed out of solution overnight. The resulting solid was collected on a 15 mL fine porosity fritted disc, washed

with hexanes (2 x 10 mL), and desiccated overnight to yield **45** (0.074 g, 0.100 mmol, 79%). CV (MeCN): $E_{p,a}$= + 0.95 V (NHE). IR: *ν*(NO) 1540 cm^{-1}, *ν*(CO) 1714 cm^{-1}, *ν*(CN) 2226 cm^{-} *ν*(BH) 2527 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 8.04 (1H, d, TpB3), 7.87 (1H, d, TpB5), 7.86 (1H, d, TpC5), 7.81 (1H, d, TpA5), 7.71 (1H, d, TpA3), 7.36 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.34 (1H, t, TpA4), 6.30 (1H, t, TpC4), 3.96 (1H, m, H1), 3.72 (3H, s, OMe), 3.53 (1H, bs, H4), 2.79 (1H, m, H2), 2.36 (1H, dm J = 12.4, H5), 2.09 (1H, m, H6a), 1.80 (1H, q J = 12.6, H6b), 1.32 (3H, s, H10/9), 1.30 (3H, s, H10/9), 1.25 (9H, d J = 8.3, PMe_3), 1.05 (1H, d J = 11.3, H3). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 178.0 (1C, C=O), 144.7 (1C, TpB3), 143.7 (1C, TpA3), 141.8 (1C, TpC3), 138.1 (1C, Tp5), 138.0 (1C, Tp5), 137.9 (1C, Tp5), 126.8 (2C, CN), 107.8 (1C, TpC4), 107.6 (2C, TpA4, TpB4), 57.5 (1C, C3), 52.6 (1C, OMe), 45.9 (1C, C7), 43.8 (1C, d J = 12.9, C2), 41.0 (1C, C5), 32.5 (1C. C4), 30.7 (1C, C1), 28.9 (1C, C6), 26.2 (1C, C10/9), 21.0 (1C, C10/9), 14.17 (3C, d J = 28.9, PMe_3).



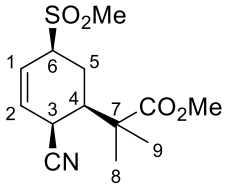
Compound 3.47. Compound **42** (120 mg, 0.184 mmol) was added to a test tube with MeCN and cooled to −30 °C for 15 min. Then, a 1 M HOTf/MeCN mixture (0.22 mL, 0.22 mmol, −30 °C) was added to the reaction using a syringe, and the solution stirred at −30 °C. NaCN (27 mg, 0.552 mmol) and minimal MeOH were mixed to a separate vial. To the NaCN/MeOH solution, the allyl solution was then added to the test tube. The solution became an orange homogeneous mixture. The solution stirred at -30°C for 16h. The test tube was removed from the box and added to a silica plug of a 30 mL medium-porosity frit filled two-thirds with silica. A yellow band was eluted with ether (150 ml). The band was evaporated to dryness, and a brown oil formed. This was picked up in DCM and dissolved in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated to yield compound **47** (83 mg, 0.104 mmol, 63.3%). CV (DMA): $E_{p,a}$= +0.52 V (NHE). IR: *ν*(NO) 1550 cm^{-1}, *ν*(CO) 1720 cm^{-1}, *ν*(CN) 2209 cm^{-1}, *ν*(CO) 1783 cm^{-1}, *ν*(BH) 2500 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.15 (1H, d, TpA5), 8.05 (1H, d, TpB3), 7.87 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.77 (1H, d, TpA3), 7.37 (1H, d, TpC3), 6.39 (1H, t, TpB4), 6.30 (1H, t, TpA4), 6.29 (1H, t, TpC4), 4.77 (1H, d, H3), 3.93 (1H, m, H6), 3.66 (3H, s, H10), 3.61, 3.41 (2H, m, H9), 2.93

(1H, m, H1), 2.83, 2.65 (2H, m, H8), 2.52 (1H, m, H4), 2.47 (1H, d, H7), 2.97 (1H, m, H1), 1.76, 1.65 (2H, dd, H5), 0.81 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 175.2 (1C, C12), 168.9 (1C, C13), 144.6 (1C, TpB3), 144.5 (1C, TpA5), 141.8 (1C, TpC3), 138.0 (1C, TpB5) 137.7 (1C, TpA3), 137.5 (1C, TpC5), 137.7 (1C, C10), 127.4 (1C, C6), 107.8 (1C, TpB4), 107.5 (1C, TpA4) 107.2 (1C, TpC4), 52.1 (1C, C1), 52.0 (1C, C3), 52.0 (1C, C10), 48.0 (1C, C2), 40.2 (1C, C9), 36.9 (1C, C7), 34.5 (1C, C8), 31.7 (1C, C4), 31.6 (1C, C5), 28.3 (1C, C6), 13.18 (3C, d J= 29.1 Hz, PMe3).

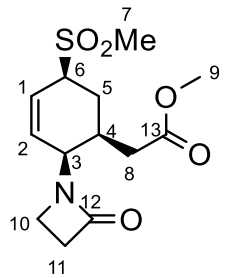


Compound 3.53. Compound **47** (120 mg, 0.184 mmol) was added to a test tube with MeCN and cooled to −30 °C for 15 min. Then, a 1 M HOTf/MeCN mixture (0.22 mL, 0.22 mmol, −30 °C) was added to the reaction using a syringe, and the solution stirred at −30 °C. NaCN (27 mg, 0.552 mmol) and minimal MeOH were mixed to a separate vial. To the NaCN/MeOH solution, the allyl solution was then added to the test tube. The solution became an orange homogeneous mixture. The solution stirred at -30°C for 16h. The test tube was removed from the box and added to a silica plug of a 30 mL medium-porosity frit filled two-thirds with silica. A yellow band was eluted with ether (150 ml). The band was evaporated to dryness, and a brown oil formed. This was picked up in DCM and dissolved in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated to yield compound **53** (83 mg, 0.104 mmol, 63.3%). CV (DMA): $E_{p,a}$= +0.52 V (NHE). IR: *ν*(NO) 1550 cm^{-1}, *ν*(CO) 1720 cm^{-1}, *ν*(CN) 2209 cm^{-1}, *ν*(CO) 1783 cm^{-1}, *ν*(BH) 2500 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 8.15 (1H, d, TpA5), 8.05 (1H, d, TpB3), 7.87 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.77 (1H, d, TpA3), 7.37 (1H, d, TpC3), 6.39 (1H, t, TpB4), 6.30 (1H, t, TpA4), 6.29 (1H, t, TpC4), 4.77 (1H, d, H3), 3.93 (1H, m, H6), 3.66 (3H, s, H10), 3.61, 3.41 (2H, m, H9), 2.93 (1H, m, H1), 2.83, 2.65 (2H, m, H8), 2.52 (1H, m, H4), 2.47 (1H, d, H7), 2.97 (1H, m, H1), 1.76, 1.65 (2H, dd, H5), 0.81 (1H, d, H2). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 175.2 (1C, C12), 168.9 (1C, C13), 144.6 (1C, TpB3), 144.5 (1C, TpA5), 141.8 (1C, TpC3), 138.0 (1C, TpB5) 137.7 (1C, TpA3), 137.5 (1C, TpC5), 137.7 (1C, C10), 127.4 (1C, C6), 107.8 (1C, TpB4), 107.5 (1C, TpA4) 107.2 (1C, TpC4), 52.1 (1C, C1), 52.0 (1C, C3), 52.0 (1C, C10), 48.0 (1C, C2), 40.2 (1C,

C9), 36.9 (1C, C7), 34.5 (1C, C8), 31.7 (1C, C4), 31.6 (1C, C5), 28.3 (1C, C6), 13.18 (3C, d J= 29.1 Hz, PMe3).

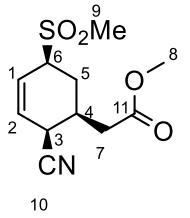


Compound 3.56. Outside of the glovebox, **31** (0.100 g, 0.126 mmol) and acetone were combined in a 4-dram vial. A stir pea and $NOPF_6$ (0.035 g, 0.202 mmol) were added to a separate 4-dram vial. The solution of **31** in acetone was then added to the vial with the stir pea and $NOPF_6$ while stirring. The initial solution was black and became a golden yellow as it stirred overnight. The golden solution was evaporated to dryness, picked up in minimal DCM, and added to 20 mL of stirring pentane. A green precipitant formed and was collected on a 15 mL medium porosity fritted disc and washed with hexanes (2 x 10 mL). The resulting filtrate was evaporated to dryness. The resulting oil was washed with 25 mL of hexanes followed by 25 mL of ether. The remaining oil was dissolved in ethyl acetate and ran through 30 mL of silica. The silica was washed with 60 mL of ethyl acetate. The filtrate was evaporated to dryness yielding **56** (0.023 g, 0.081 mmol, 64%). ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 6.14 (1H, ddd J = 9.9, 5.9, 2.48 Hz, H2), 6.07 (1H, dm J = 9.9 Hz, H1), 3.91 (1H, m, H6), 3.67 (3H, s, OMe), 3.48 (1H, m , H1), 2.87 (3H, s, SO_2Me), 2.26 (1H, dm J = 13.1, H5), 2.13 (1H, dd J = 4.3, 2.0 Hz, H4), 1.88 (1H, m, H5), 1.32 (6H, s, H9, H8). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 177.2 (1C, C=O), 130.0 (1C, C2), 124.2 (1C, C1), 119.4 (1C, CN), 62.9 (1C, C6), 52.7 (1C, OMe), 45.4 (1C, C7), 42.6 (1C, C4), 37.9 (1C, SO_2Me), 28.6 (1C, C3), 23.2 (1C, C5), 23.0 (1C, C9/8), 22.9 (1C, C9/8). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for 308.0927; found 308.0927.



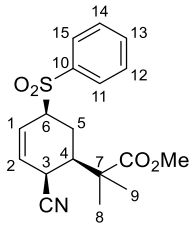
Compound 3.57. Outside of the glovebox, compound **30** (0.100 g, 0.140 mmol) and acetone were combined in a 4-dram vial. A stir pea and $NOPF_6$ (0.040 g, 0.228 mmol) were added to a separate 4-dram vial. The solution in acetone was then added to the vial with

the stir pea and $NOPF_6$ while stirring A 60 mL medium-porosity frit was filled two-thirds with silica, and the previous mixture was placed on top. Hexanes (250 mL) was eluted through the column, followed by diethyl ether (100 mL) and by ethyl acetate (250 mL). The ethyl acetate portion eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 20 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight. The solution was run through HPLC (100% ACN, C18 column) and the resulting compound desiccated overnight to yield **57** (23.6 mg, 0.078 mmol, 63%). IR: *ν*(CO) 1742 cm^{-1}, *ν*(CO) 1792 cm^{-1}, *ν*(SO) 1406 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 6.61 (1H, t, H2), 6.21 (1H, m, H1), 4.28 (1H, s, H3), 3.72 (3H, s, H9), 3.71 (1H, d, H6), 3.33-3.29 (2H, m, H10), 2.98-2.92 (2H, m, H11), 2.89 (3H, s, H7), 2.61, 2.36 (2H, dd, H8), 2.33 (1H, m, H4), 2.22, 1.84 (2H, m, H5). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 173.0 (1C, C13), 170.1 (1C, C12), 128.5 (1C, C2), 127.0 (1C, C1), 61.4 (1C, C6), 52.0 (1C, C9), 48.7 (1C, C3), 40.2 (1C, C10), 37.6 (1C, C7), 37.2 (1C, C8), 36.2 (1C, C11), 33.8 (1C, C4), 25.8 (1C, C5). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for 302.1062; found 302.1058.



Compound 3.58. Outside of the glovebox, compound **29** (0.100 g, 0.140 mmol) and acetone were combined in a 4-dram vial. A stir pea and $NOPF_6$ (0.040 g, 0.228 mmol) were added to a separate 4-dram vial. The solution in acetone was then added to the vial with the stir pea and $NOPF_6$ while stirring. A 60 mL medium-porosity frit was filled two-thirds with silica, and the previous mixture was placed on top. Hexanes (250 mL) was eluted through the column, followed by diethyl ether (100 mL) and by ethyl acetate (250 mL). The ethyl acetate portion eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 20 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight. The solution was run through HPLC (100% ACN, C18 column) and the resulting compound desiccated overnight to yield **58** (18 mg, 0.071 mmol, 54%). IR: *ν*(CO) 1743 cm^{-1}, *ν*(CN) 2205 cm^{-1}, *ν*(SO) 1407 cm^{-1}. ^{1}H-NMR (d_3-MeCN, δ, 25 ^{0}C): 6.14 (1H, t, H1), 6.10 (1H, m, H2), 3.91 (1H, d, H6), 3.67 (3H, s, H8), 3.61 (1H, m, H3), 2.84 (3H, 2, H9), 2.82 (1H, m, H4), 2.61-2.54 (2H, dd, H7), 1.70 (1H,

m, H5). ^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 172.3 (1C, C11), 128.8 (1C, C2), 124.9 (1C, C1), 118.6 (1C, C10), 61.8 (1C, C6), 52.7 (1C, C8), 38.5 (1C, C7), 37.8 (1C, C9), 32.0 (1C, C4), 31.4 (1C, C3), 26.5 (1C, C5). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for 258.0834; found 258.0735.



Compound 3.59. Outside of the glovebox, **32** (0.105 g, 0.123 mmol) and acetone were combined in a 4-dram vial. A stir pea and $NOPF_6$ (0.051 g, 0.291 mmol) were added to a separate 4-dram vial. The solution of **32** in acetone was then added to the vial with the stir pea and $NOPF_6$ while stirring. The initial solution was black and became a golden yellow as it stirred overnight. The golden solution was evaporated to dryness, picked up in minimal DCM, and added to 20 mL of stirring pentane. A green precipitant formed and was collected on a 15 mL medium porosity fritted disc and washed with hexanes (2 x 10 mL). The resulting filtrate was evaporated to dryness. The resulting oil was washed with 25 mL of hexanes followed by 25 mL of ether. The remaining oil was dissolved in ethyl acetate and ran through 30 mL of silica. The silica was washed with 60 mL of ethyl acetate. The filtrate was evaporated to dryness yielding **59** (0.033 g, 0.094 mmol, 76%). ^{1}H-NMR (d_3-MeCN, δ, 25 °C): 7.88 (2H, dm J = 8.6, H15, H11), 7.75 (1H, tm J = 7.6, H13), 7.64 (2H, tm J = 7.8, H14, aH12), 6.02 (2H, m, H2, H1), 4.09 (1H, m, H6), 3.61 (3H, s, OMe), 3.37 (1H, m, H3), 2.12 (1H, m, H5a), 2.03 (1H, ddd J = 12.9, 4.3, 2.0, H4), 1.70 (1H, m, H5b), 1.23 (6H, s, H9, H8). ^{13}C-NMR (d_3-MeCN, δ, 25 °C): 177.1 (1C, C=O), 137.2 (1C, C10), 135.3 (1C, C13), 130.3 (2C, C14, C12), 130.1 (2C, C15, C11), 129.9 (1C, C2), 124.4 (1C, C1), 118.9 (1C, CN), 64.1 (1C, C6), 52.6 (1C, OMe), 45.3 (1C, C7), 42.5 (1C, C4), 28.5 (1C, C3), 23.3 (1C, C5), 23.0 (1C, C9/8). 22.8 (1C, C9/8). HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for 370.1083; found 370.1083.

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Chapter 4 : A Synthetic Strategy for the Synthesis of Functionalized cis-hydro-2-oxindoles through Dearomatization of Dihapto-Coordinated Phenyl Sulfone

4.1 Introduction

Cis-hexahydro-2-oxindole skeletons are commonly found in drugs and Lycorine-type natural products.[1] This includes biologically relevant alkaloids, such as *Tazettine*[2] *(+)-Pretazettine* and *6a-epiPretazettine*[3] and (-)-*Haemanthidine*[4]. Common methods for the synthesis of these moieties include metal-catalyzed annulation reactions,[5-7] in which amides and cyclic enones are initially coupled through a stereoselective intermolecular Tsuji–Trost allylation and then the resulting product is cyclized through a Pt coupling ring closure (**Figure 4.1, Panel A**, **eq. 1**), or by visible-light mediated cyclization of α-chloroenamides[8,9] (**Panel A**, **eq. 2**). Alternatively, metal-catalyzed hydrogenation of 2-oxindoles can produce *hydro*-2-oxindole cores in high diastereoselectivity with hydrogen atoms in an all-*cis* arrangement.[10-12] This approach shows high tolerance toward functional groups and compatibility with existing stereogenic centers. Nevertheless, this methodology requires different aromatic precursors for every different hydro-2-oxindoles derivative (**Panel B**, **eq. 3**).

We considered a complementary approach in which the *cis-dihydro*-2-oxindole core could be prepared from an arene bound to the WTp(NO)(PMe_3) (**Panel C**, **eq. 4**). Herein, we show the synthesis of functionalized *cis-hydro*-2-oxindoles using this tungsten arenophile exploiting three key features: **1**) initial tandem protonation/addition of an ester followed by tandem protonation/addition of a primary amine generates coordinated 3a,8a-dihydrooxindoles[13] (**II**). **2**) this species can undergo elimination to an η^2-coordinated diene complex (**III**), through the loss of phenylsulfinate at an allylic position of an η^2-alkene complex of WTp(NO)(PMe_3).[14] **3**) these resulting dihapto-coordinated cyclohexadienes can be chemically elaborated into trisubstituted cyclohexenes through a tandem protonation/addition sequence (**IV**). Oxidative decomplexation allows for the formation of substituted *cis-hydro*-2-oxindole (**V**). The synthetic pathway described offers selective addition of nucleophiles at different steps of the synthesis, a modular approach toward the formation of the *cis-hydro*-2-oxindole moiety and generates a final compound with a site of unsaturation available for further functionalization.

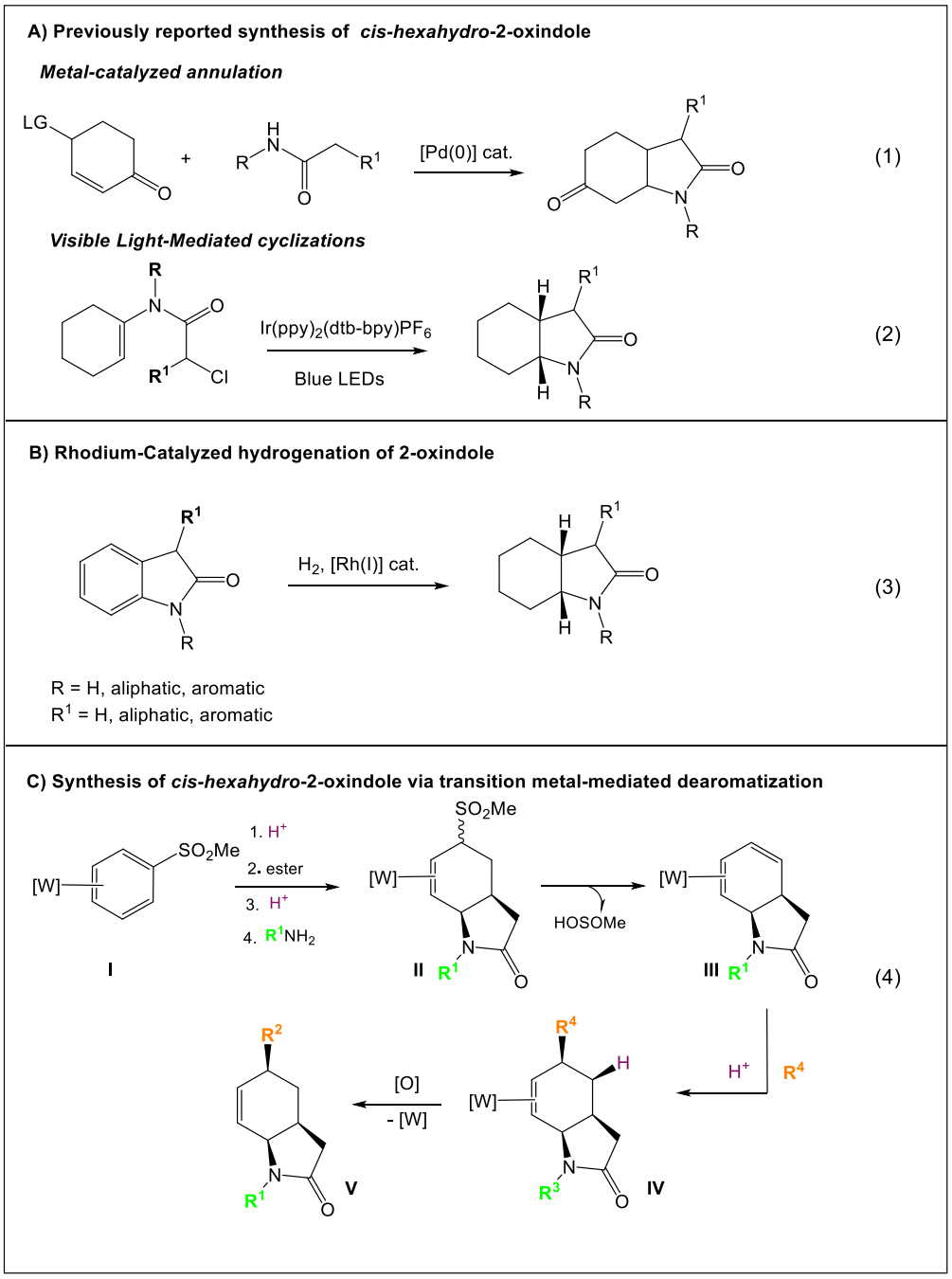


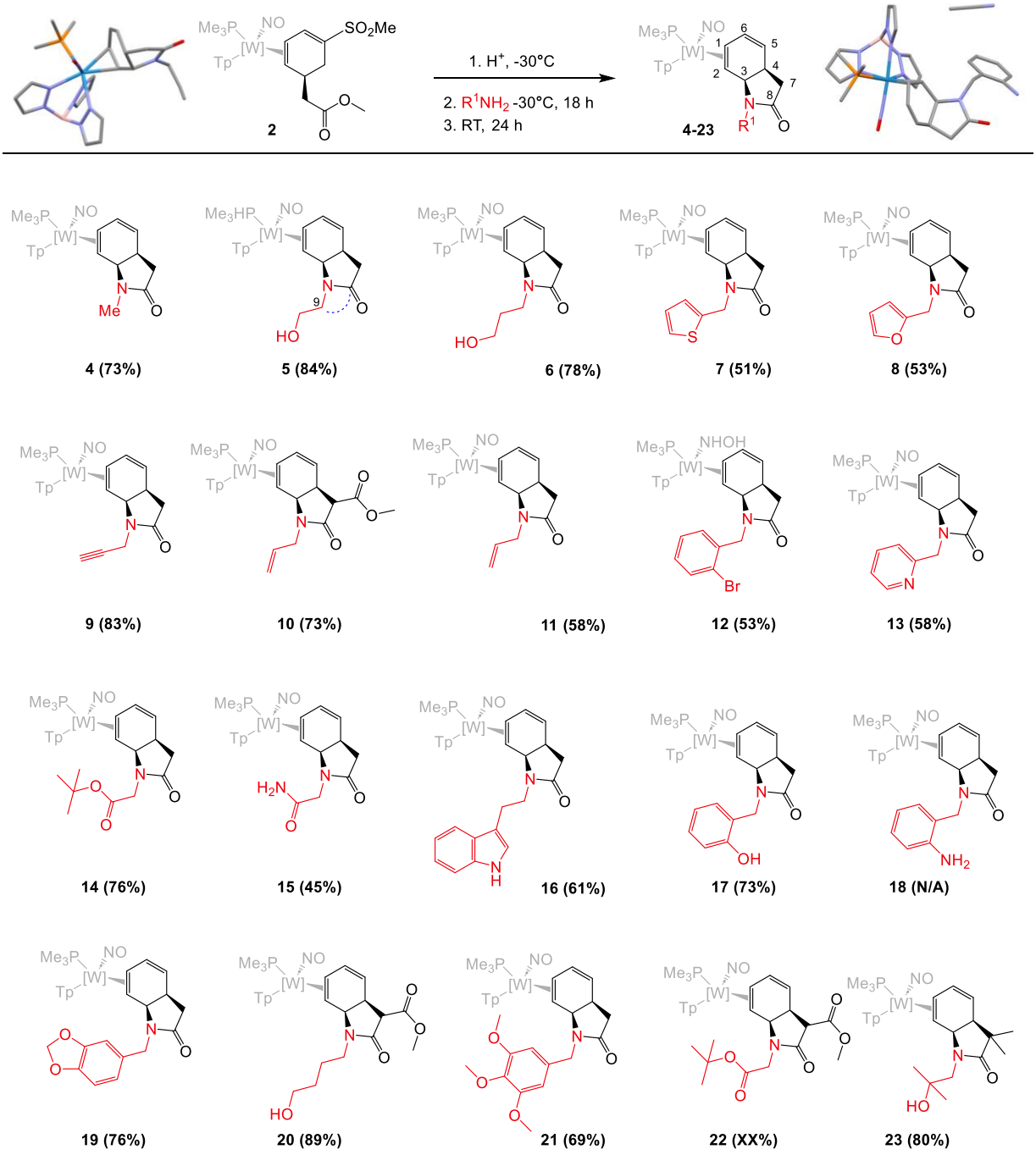
Figure 4.1 A) shows common methods for the synthesis of *cis-hexahydro*-2-oxindole skeletons **B**) shows metal-catalyzed hydrogenation of 2-oxindoles achieves *hydro*-2-oxindoles cores in high diastereoselectivity; **C)** highlights our chemical approach toward the synthesis of these relevant skeletons.

4.2 Results and Discussion

4.2.1 Addition of Primary Amines

Synthesis of cis-fused bicyclic γ-lactams was carried out in a previous report using TpW(PMe3)NO($C_6H_5CF_3$).[15] However, the published compounds lacked diverse *N*-functionalization, functionalization on the *α*-carbon, as well as further manipulation of C6. The TpW(PMe_3)NO($PhSO_2Me$) platform would expand ring functionalization on C6 due to the chemical lability of the -SO_2Me group.[14] Specifically, in this report we show that protonation of **2**, followed by excess amine and subsequent room temperature stirring, generates indolone cores, displaying cis stereochemistry only. **Figure 4.2** highlights the breadth of primary amines that were added, which can range from structurally simple ($MeNH_2$, **4**), to complex ones (tryptamine, **16**), with yields ranging from 45%-84%. These cores proved easy to access if excess of a primary amine is present. Generally, the reaction mixture containing **2** in the presence of an acid (HOTf, 1 M) is run at -30 ºC for 18h. After that time has elapsed, the mixture is left stirring at room temperature for 18h before being worked up. 2D NMR data was used to confirm the structure of compounds **4**-**23** (**Figure 4.2**) and SC-XRD data for **5, 6, 7, 8, 11, 14, 15, 17, 18** and **21** was obtained (**SI**). Key spectroscopic features include NOE interactions between H6 and the PMe_3, NOE interaction between H3 and Tp3A, and a diagnostic set of peaks at 6.5 ppm as a multiplet (H6) and a doublet at 4.5 ppm (H5), characteristic for dienes previously reported (**SI**).[14] Furthermore, all of these compounds show an intra-heteroatom HMBC interaction between H9 and C8 (**Figure 4.2**, compound **5**).

Figure 4.2 Synthesis of bicyclic γ-lactams dienes from addition of excess amine to an ester moiety. The figure shows the wide scope of derivatives that can be synthesized from *N*-functionalization.

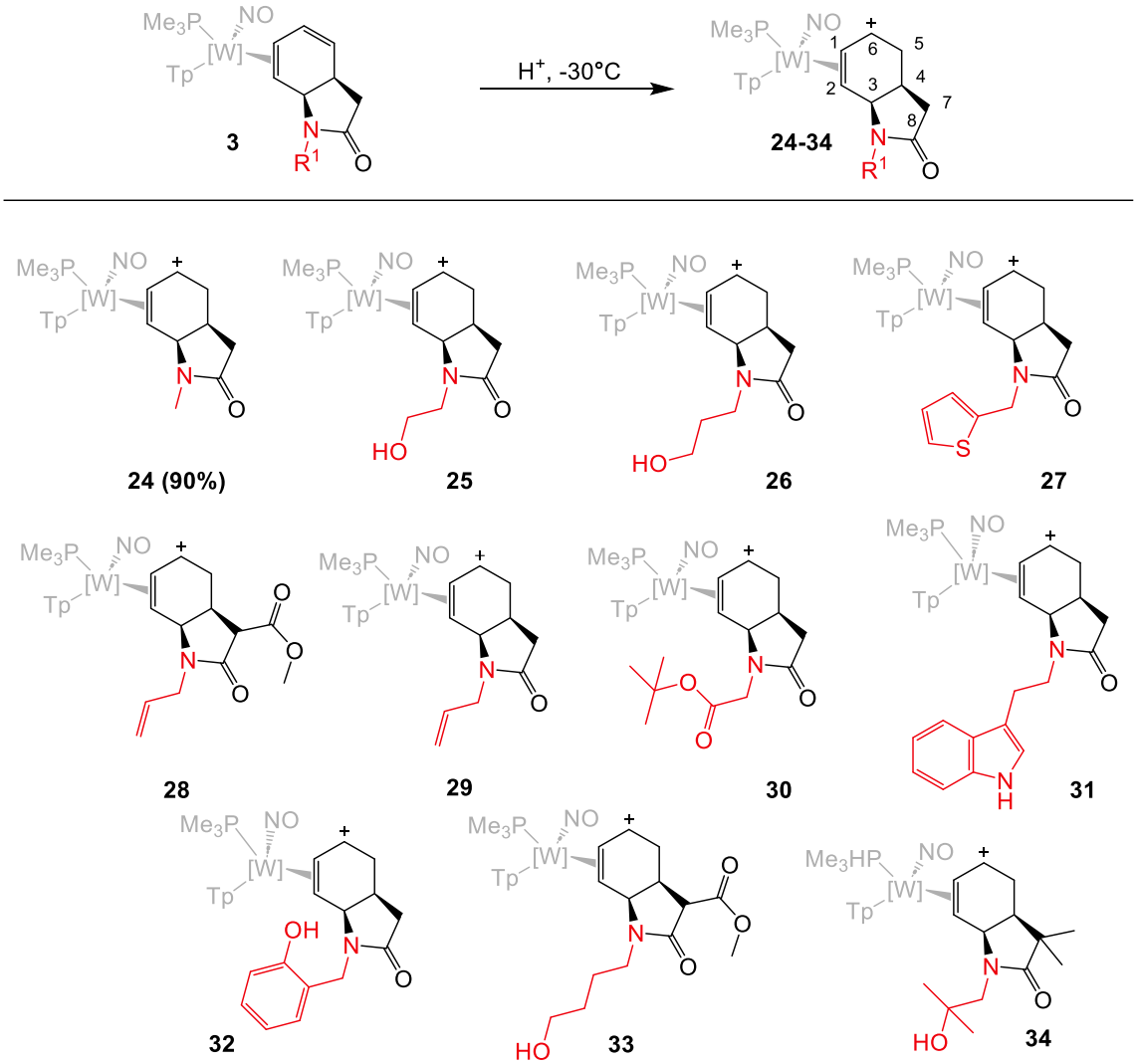


4.2.2 Formation of Allyl Lactams

Compounds in **Figure 4.2** were observed to be stable as solids under nitrogen atmosphere as well as at temperatures up to 200 °C, with no observable decomposition.

However, after air exposure the TpW(PMe_3)NO fragment was found to move to the other double bond producing a mixture of two constitutional isomers (1:1), especially for examples containing small substituents on the *N*-lactam (**Figure 4.2**, compounds **4**, **5**, and **6**). This posed difficulties for regioselective functionalization reactions. To overcome this hurdle, we treated the compounds **4**, **5**, **6**, **7**, **10**, **11**, **14**, **16**, **17. 20** and **23** with acid (HOTf, 1 M) in acetonitrile. After induced precipitation in ether, we were able to isolate compounds such as **24** (**Figure 4.3**). These compounds were observed to be stable as solids for up to 3 months under nitrogen atmosphere and at room temperature. Under air or mild heating (50 ºC) they were spectroscopically observed to decompose to an unknown mixture of compounds within one hour. 2D NMR data was used to confirm the structure of **24**. Key spectroscopic features include an NOE interaction between H6 and the PMe_3. The significant downfield shift for protons H1, H2, H3 and H6, relative to compounds in **Figure 4.2,** highlighting the formation of an electron deficient species was noteworthy.

Figure 4.3 Synthesis of 24 by treatment of dienes 3 with excess acid (HOTf, 1 M) in acetonitrile.



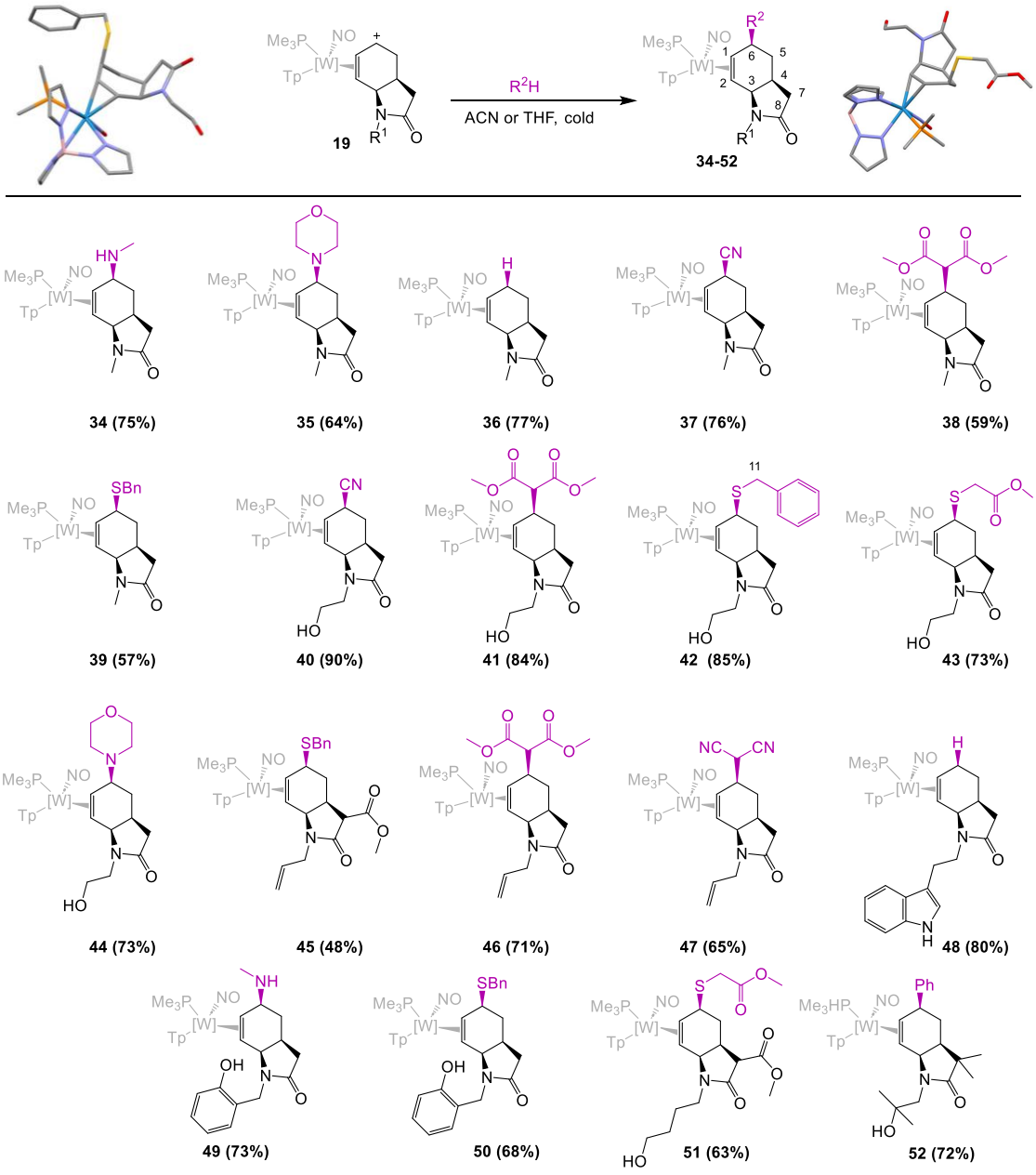
4.2.3 Synthesis of Trisubstituted Hydroindolones

To further expand the diversity of these hydroindolone cores, the authors sought nucleophiles present in drug-like molecules. These include carbon, sulfur and amine nucleophiles (**Figure 4.4**). As shown, addition of nucleophiles proved to be regio- and stereoselective from species **24**. All the proposed nucleophiles were added to a reaction mixture containing **24** in acetonitrile or THF at cold temperatures (-30 ºC to -60 ºC). Moreover, amine additions such as methylamine and morpholine needed subsequent base quench (e.g., trace K(^{t}B$_u$O)), to curtail the amine moiety to act as a leaving group and

generate back the original diene **3**. Sulfur nucleophiles needed to be deprotonated with a base to increase their nucleophilicity (generally K(^{t}B$_u$O)).

Compounds bearing carbon nucleophiles or hydrides were cleaned through a simple water extraction (H_2O:DCM). Initially, the workups for nucleophilic additions with amines proved challenging. In the presence of water, the amine or alcohol moiety can be protonated and generate **3**. Hence, dry workup conditions (such as using THF as the solution solvent) were employed followed by evaporation of the solvent and induced precipitation in a cold solution of THF and pentane. Apart from those run at -60 ºC, the aforementioned reactions are run for 10 minutes. The reactions were shown to be general with a variety of commercially available nucleophiles. A Full 2D NMR analysis confirmed the structures of all the compounds shown (**Figure 4.4**) along with SC-XRD data for **38**, **39**, **40**, **42**, **43**, **45**, **46**, **47**, and **50**. These compounds were observed to be stable as dry solids, with yields ranging from 48%-90%. Key spectroscopic features included the absence of the downfield peaks associated with **24**, strong NOE interactions between H6 (now a triplet at 3.70 ppm) and the PMe_3 ligand, as well as an HMBC interaction between H11 and H6 (**Figure 4.4**, compound **42**).

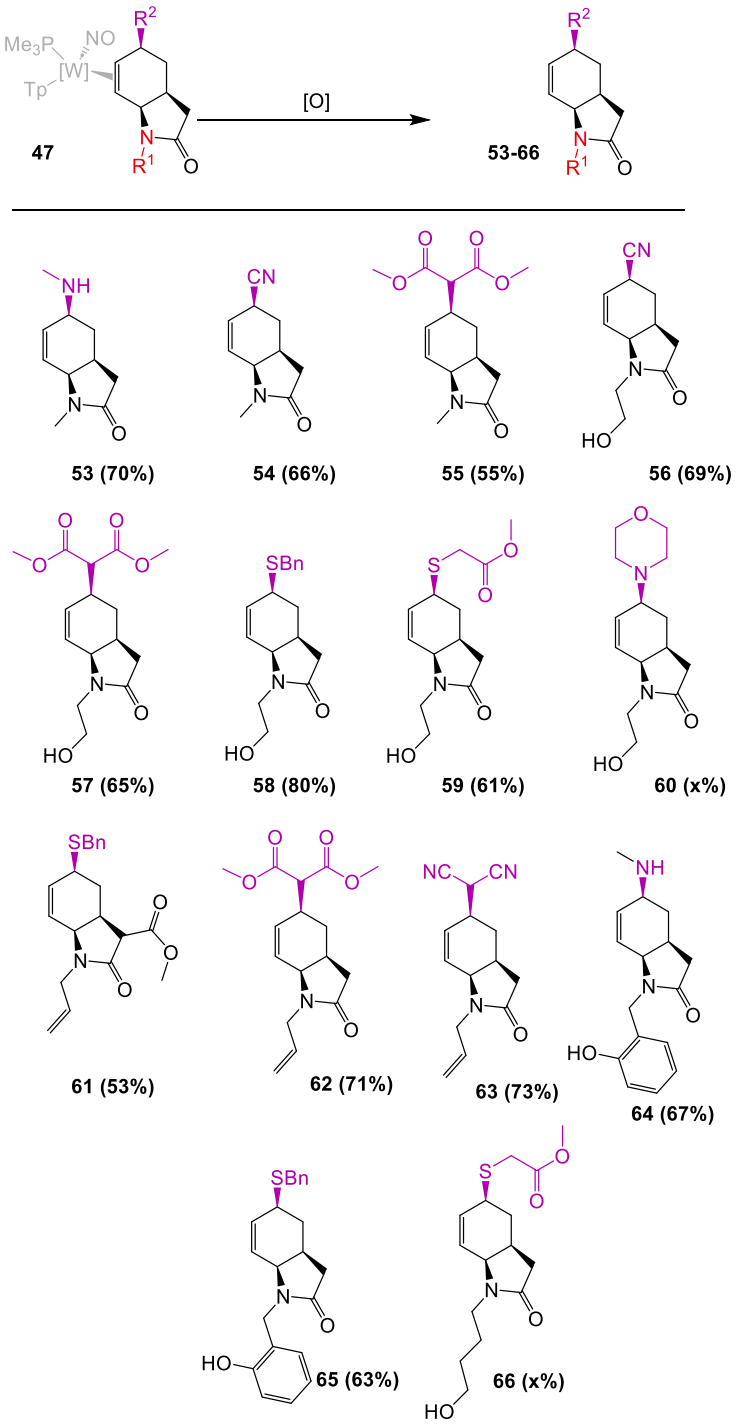
Figure 4.4 Selective addition of nucleophile to allyl lactam species. All the nucleophiles were added neat to a reaction mixture containing 19 in acetonitrile or THF at cold temperatures (-30 °C to -60 °C).



4.3 Liberation of the Hydroindolone Cores from the Dearomatization Agent

To liberate the synthesized hydroindolones from the metal fragment, different approaches were employed. In most cases, an oxidant such as $NOPF_6$ proved effective in liberating organic products. When the complex contained sulfur nucleophiles, DDQ was shown to effectively generate **54**, **55**, **57**, and **61** (**Figure 4.5**).

Figure 4.5 The liberation of organic hydroindolones using various oxidants.

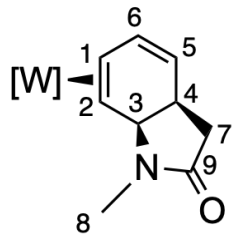


4.4 Conclusion

In conclusion, our study presents an efficient, modular approach for the synthesis of cis-hexahydro-2-oxindole derivatives, addressing challenges associated with regio- and stereoselectivity in previous methodologies. By employing the tungsten-based platform WTp(NO)(PMe3), we have successfully demonstrated the formation of functionalized cis-hydro-2-oxindole cores through a stepwise sequence of tandem additions, cyclization, and selective nucleophilic substitutions. This approach provides high functional group tolerance and allows for extensive derivatization, enabling the synthesis of diverse hydroindolone cores with applications in drug-like molecule development. Furthermore, the final oxidative decomplexation yields stable, structurally complex products, underscoring the synthetic utility and adaptability of this pathway. Our findings expand the toolkit available for constructing complex bioactive frameworks, offering potential applications in medicinal chemistry and natural product synthesis.

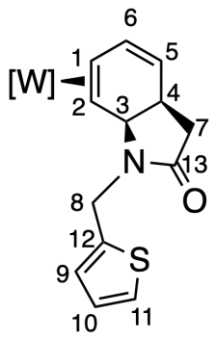
Experimental

NMR spectra were obtained on 500, 600, or 800 MHz spectrometers. Chemical shifts are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H signals of the deuterated solvents as internal standards. S46 Chemical Shifts are reported in ppm and coupling constants (J) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a solid on a spectrometer with an ATR crystal accessory, and peaks are reported in cm^{-1}. Electrochemical experiments were performed under a nitrogen atmosphere. Most cyclic voltammetric data were recorded at ambient temperature at 100 mV/s, unless otherwise noted, with a standard three-electrode cell from +1.8 to −1.8 V with a platinum working electrode, acetonitrile or N,N-dimethylacetamide (DMA) solvent, and tetrabutylammonium (TBAH) electrolyte (∼1.0 M). All potentials are reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2}$= −0.78 V, −1.75 V) or ferrocene ($E_{1/2}$= 0.55 V) as an internal standard. The peak separation of all reversible couples was less than 100 mV. All synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere unless otherwise noted. All solvents were purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes and were purged with nitrogen under an inert atmosphere. When possible, pyrazole protons of the tris(pyrazolyl)borate (Tp) ligand were uniquely assigned (e.g., "Tp3B") using two-dimensional NMR data (see Figure S1). If unambiguous assignments were not possible, Tp protons were labeled as "Tp3/5 or Tp4". All J values for Tp protons are 2(±0.4) Hz. BH peaks (around 4−5 ppm) in the ^{1}H NMR spectra are not assigned due to their quadrupole broadening; However, confirmation of the BH group is provided by IR data (ca 2500 cm^{-1}). Compound 2 has been previously reported. Full characterization of compounds is provided in the SI. Ground-state structures were optimized at the M06 level of theory using the 6-31G**[LANL2DZ for W] basis set in Gaussian 16. Previous literature demonstrates that this functional and basis set choice accurately corroborates experimental results. Vibrational frequency analysis verified that optimized structures were minima, and rigid-rotorharmonic-oscillator thermochemical chemical corrections were applied at 298 K and 1 atm utilizing Gaussian's default implementation. When solvent corrections were applied to estimate DGsolv, optimization and frequency calculations were performed using the SMD continuum solvent model with the appropriate solvent's parameters from Gaussian.



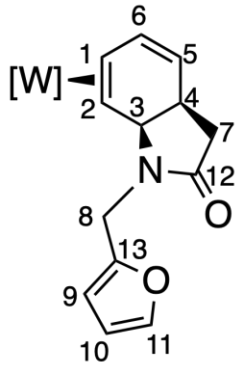
Compound 4.4:

Compound **2** (150 mg, 0.204 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.409 mL, 0.409 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 10 min. In a separate test tube, methylamine (1.02 mL, 2.04 mmol) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at cold temperatures for 24 h and subsequently at room temperature for 19 h. It was then washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous $MgSO_4$. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 30 mL of stirring hexane. An tan/white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **5** (100 mg, 0.153 mmol, 75.1%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25 C):** 8.06 (2H, d, TpB3/C5), 7.86 (2H, d, TpB5/A3), 7.77 (1H, d, TpA5), 7.50 (1H, d, TpC3), 6.43 (1H, m, H6) 6.37 (1H, t, TA4), 6.30 (1H, t, TpB4) 6.27 (1H, t, TpC4), 4.55 (1H, d, H3), 4.54 (1H, d, H5), 3.21 (1H, m, H4), 2.81 (1H, m, H1), 2.61 (3H, s, H8), 2.59 (1H, ddd J= 16.18 Hz, H7), 1.89 (1H, ddd, H7), 1.33 (1H, d, H2), 1.19 (d, *J* = 8.5 Hz, 9H, PMe_3). **^{13}C-NMR (201 MHz, CD_3CN, δ, 25 ^{0}C):** 175.4 (1C, C9), 145.5 (1C, TpB3), 144.6 (1C, TpC5), 137.9 (2C, TpCA/B5), 137.4 (1C, TpA5), 132.0 (1C, C6), 107.6 (1C, TpA4), 107.3 (1C, Tp4C) 106.8 (1C, Tp4B), 106.89 (1C, Tp4A), 64.3 (1C, C3), 58.9 (1C, C2), 49.2 (1C, C1), 48.3 (1C, C5), 40.3 (1C, C7) 32.9 (1C, C4), 27.8 (1C, C8), 13.6 (3C, d J= 29.30 Hz, PMe3). **CV (DMA):** $E_{p,a}$= 0.84 V (NHE).



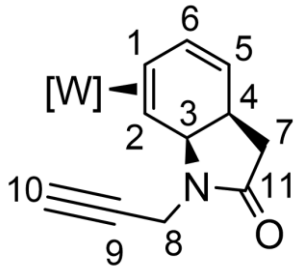
Compound 4.7:

Compound **2** (100mg, 0.136 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.341 mL, 0.341 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-Thiophenemethylamine (0.140 mL, 1.360 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **8** (51 mg, 0.069 mmol, 52%). **^{1}H NMR (800 MHz, $(CD_3)_2CO$) δ** 8.13 (s, 1H, TpB3), 7.97 (d, *J* = 2.3 Hz, 1H, TpC5), 7.94 (m, 1H, TpB5), 7.88 (s, 1H, TpA3), 7.79 (m, 1H, TpA5), 7.60 (d, *J* = 2.1 Hz, 1H, TpC3), 7.16 (dt, *J* = 5.1, 1.1 Hz, 1H, H11), 6.75 (ddd, *J* = 5.1, 3.4, 1.0 Hz, 1H, H10), 6.52 (dt, *J* = 3.4, 1.0 Hz, 1H, H9), 6.41 (d, *J* = 7.8 Hz, 1H, H6), 6.40 (tt, *J* = 2.2, 1.0 Hz, 1H, TpB4), 6.36 (td, *J* = 2.2, 0.9 Hz, 1H, TpC4), 6.15 (dt, *J* = 2.3, 1.1 Hz, 1H, TpA4), 4.81 (d, *J* = 15.3 Hz, 1H, H8A), 4.68 (d, *J* = 6.3 Hz, 1H, H3), 4.53 (d, *J* = 9.9 Hz, 1H, H5), 4.38 (d, *J* = 15.4 Hz, 1H, H8B), 3.31 (t, *J* = 8.2 Hz, 1H, H4), 2.78 (m, 1H, H1), 2.57 (dd, *J* = 16.0, 8.2 Hz, 1H, H7A), 1.94 (d, *J* = 16.1 Hz, 1H, H7B), 1.52 (d, *J* = 9.6 Hz, 1H, H2), 1.25 (d, *J* = 8.6 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz, $(CD_3)_2CO$) δ** 174.8 (1C, C13), 144.5 (1C, TpB3), 143.5 (1C, TpB5), 142.0 (1C, TpC3), 137.8 (1C, TpC5), 137.1 (1C, TpA5), 136.7 (1C, TpA3), 131.9 (d, *J* = 3.7 Hz, 1C, C6), 127.2 (1C, C10), 126.3 (1C, C9), 125.1 (1C, C11), 120.3 (1C, C5), 107.2 (1C, TpB4), 107.0 (1C, TpC4), 106.4 (1C, TpA4), 62.2 (1C, C3), 48.1 (1C, C2), 40.2 (1C, C7), 38.4 (1C, C8), 32.8 (1C, C4), 13.7 (d, *J* = 28.3 Hz, 1C, PMe_3)



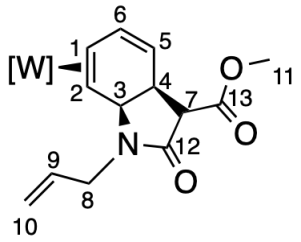
Compound 4.8:

Compound **2** (100mg, 0.136 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.341 mL, 0.341 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, Furfurylamine (0.120 mL, 1.364 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **9** (53%). **^{1}H NMR (800 MHz, CD_2Cl_2) δ** 8.05 (d, *J* = 2.0 Hz, 1H, TpB3), 7.86 (d, *J* = 2.0 Hz, 1H, TpA5), 7.78 (d, *J* = 2.3 Hz, 1H, TpC5), 7.76 (d, *J* = 2.4 Hz, 1H, TpB5), 7.66 (d, *J* = 2.4 Hz, 1H, TpA3), 7.35 (d, *J* = 2.2 Hz, 1H, TpC3), 7.15 (m, 1H, H11), 6.44 (ddd, *J* = 9.9, 5.1, 2.5 Hz, 1H, H6), 6.34 (m, 1H, TpB4), 6.27 (t, *J* = 2.1 Hz, 1H, TpC4), 6.17 (t, *J* = 2.3 Hz, 1H, TpA4), 6.15 (t, *J* = 2.6 Hz, 1H, H10), 5.83 (d, *J* = 3.2 Hz, 1H, H9), 4.64 (m, 3H, H3/H5/H8A), 4.21 (d, *J* = 15.7 Hz, 1H, H8B), 3.26 (t, *J* = 7.6 Hz, 1H, H4), 2.67 (m, 2H, H1/H7A), 2.05 (d, *J* = 16.3 Hz, 1H, H7B), 1.20 (d, *J* = 8.4 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz, CD_2Cl_2) δ** 175.4 (1C, C13), 152.3 (1C, C12), 143.8 (1C, TpB3), 143.0 (1C, TpA5), 141.7 (1C, C11), 140.9 (1C, TpC3), 137.1 (1C, TpC5, 136.4 (1C, TpA3), 136.1 (1C, TpB5), 131.2 (d, *J* = 3.8 Hz, 1C, C6), 120.1 (1C, C5), 110.4 (1C, C10), 107.3 (1C, C9), 106.8 (1C, TpB4), 106.4 (1C, TpC4), 105.9 (1C, TpA4), 62.6 (1C, C3), 49.2 (d, *J* = 9.3 Hz, 1C, C1), 47.6 (d, *J* = 15.2 Hz, 1C, C2), 40.1 (1C, C7), 36.8 (1C, C8), 32.3 (1C, C4), 13.8 (d, *J* = 28.2 Hz, 1C, PMe_3).



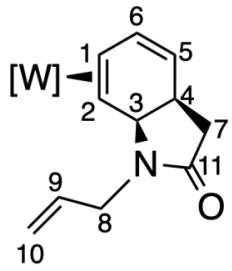
Compound 4.9:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.272 mL, 0.272 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 10 min. In a separate test tube, propargylamine (0.088 mL, 1.36 mmol) with ACN (2 mL) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 12 h then stirred at room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. An white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **10** (76 mg, 0.11 mmol, 82%).**^{1}H-NMR (800 MHz $(CD_3)_2CO$), δ, 25°C):** 8.22 (1H, d, TpA3), 8.17 (1H, d, TpB3), 7.96 (2H, t, TpB5/C5), 7.81 (1H, d, TpA5), 7.66 (1H, d, TpC3), 6.43 (2H, m, H6/TpB4), 6.34 (1H, t, TC4), 6.28 (1H, t, TpA4), 4.87 (1H, d, H3), 4.51 (1H, dd, H5), 4.40 (1H, m, H8), 3.72 (1H, dd, H8), 3.38 (1H, t, H4), 2.85 (1H, m, H1), 2.62 (1H, t, H7), 2.33 (1H, t, H10), 1.93 (1H, d, H7), 1.57 (1H, d, H2), 1.26 (9H, d, PMe_3).**^{13}C-NMR (201 MHz $(CD_3)_2CO$), δ, 25°C):** 174.7 (1C, C11). 144.5 (1C, TpA3) 143.9 (1C, TpB3), 142.0 (1C, TpC5), 137.8 (1C, TpB5), 137.0 (1C, TpA5), 136.8 (1C, TpC3), 132.1 (1C, C6), 120.1 (1C, C5), 107.3 (1C, TpB4), 107.0 (1C, TpC4), 106.3 (1C, TpA4), 80.2 (1C, C9), 72.4 (1C, C10), 62.7 (1C, C3), 49.7 (1C, d, C1), 46.8 (1C, C2), 40.3 (1C, s, C7), 32.7 (1C, s, C4), 29.1 (1C, C8), 13.5 (3C, d, PMe_3).



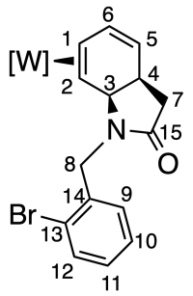
Compound 4.10:

Compound **4** (177 mg, 0.223 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.447 mL, 0.447 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 20 min. In a separate test tube, allylamine (0.167 mL, 2.023 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 12 h then stirred at room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. An white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **11** (107 mg, 73%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25°C):** 8.05 (1H, d, Tp3B), 7.93 (1H, d, Tp3A), 7.86 (2H, d, Tp5C/Tp5B), 7.77 (1H, d, Tp5A), 7.47 (1H, d, Tp3C), 6.48 (1H, m, H6), 6.38 (1H, t, Tp4B), 6.30 (1H, t, Tp4C), 6.29 (1H, t, Tp4A), 5.57 (1H, m, H9), 5.01 (1H, d, H3), 4.96 (1H, q, H10), 4.89 (1H, q, H10), 4.53 (1H, dd, H5), 3.97 (1H, dd, H8), 3.73 (3H, s, H11), 3.72 (1H, dd, H8), 3.69 (1H, d, H4), 3.02 (1H, s, H7), 2.81 (1H, m, H1), 1.24 (1H, d, H2), 1.19 (9H, d, PMe3) . **^{13}C-NMR (201 MHz, CD_3CN, δ, 25 o C):** 172.1 (1C, C13). 170.5 (1C, C12), 144.6 (1C, TpB3) 143.2 (1C, TpA3), 142.1 (1C, TpC3), 138.1 (1C, TpC5), 137.4 (2C, TpA5/TpB5), 134.4 (1C, C9), 133.1 (1C, d, C6), 120.4 (1C, C5), 116.1 (1C, C10), 107.6 (1C, TpB4), 107.3 (1C, TpC4), 106.9 (1C, TpA4), 61.8 (1C, C3), 57.9 (1C, C7), 52.9 (1C, C11), 49.0 (1C, C1), 47.6 (1C, C2), 42.5 (1C, C8), 38.2 (1C, C4), 13.7 (3C, PMe_3).



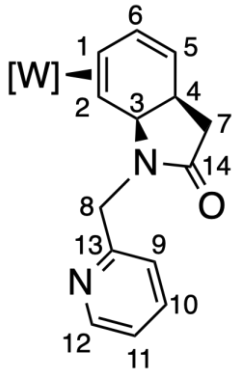
Compound 4.11:

Compound **2** (150 mg, 0.2045 mmo) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.409 mL, 0.409 mmol solution was added to the test tube and the solution was allowed to stir at -30 °C for 20 min. In a separate test tube, allylamine (0.153mL, 2.045 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C 12 h then stirred at room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. An white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **12** (59.6%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25°C):** 8.06 (1H, d, Tp3B), 8.04 (1H, d, Tp3A), 7.86 (2H, d, Tp5C, Tp5B), 7.76 (1H, d, Tp5A), 7.48 (1H, d, Tp3C), 6.45 (1H, m, H6), 6.38 (1H, t, Tp4B), 6.30 (1H, t, Tp4C), 6.25 (1H, t, Tp4A), 5.60 (1H, m, H9), 4.88 (2H, td, H10), 4.74 (1H, d, H3), 4.54 (1H, dd, H5), 3.92 (1H, dt, H8), 3.69 (1H, dd, H8), 3.24 (1H, t, H4), 2.77 (1H, ddd, H1), 2.66 (1H, dd, H7), 1.92 (1H, m, H7), 1.28 (1H, d, H2), 1.18 (9H, d, PMe_3). **^{13}C-NMR (201 MHz, CD_3CN, δ, 25 o C):** 175.4 (1C, s, C11). 144.6 (1C, d, Tp3B) 143.8 (1C, s, Tp3A), 142.1 (1C, s, Tp3C), 138.1/137.4 (1C, s, Tp5B/Tp5C), 137.2 (1C, s, Tp5A), 135.3 (1C, s, C9), 132.3 (1C, d, C6), 120.4 (1C, s, C5), 115.9 (1C, s, C10), 107.6 (1C, s, Tp4B), 107.2 (1C, s, Tp4C), 106.7 (1C, s, Tp4A), 62.7 (1C, s, C3), 49.7 (1C, d, C1), 48.2 (1C, s, C2), 42.4 (1C, s, C8), 40.2 (1C, s, C7), 33.2 (1C, s, C4), 13.7 (3C, d, PMe_3).



Compound 4.12:

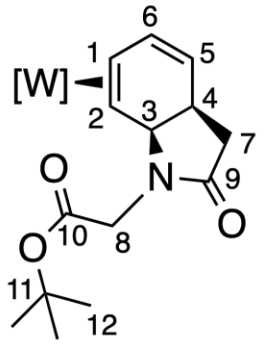
Compound **2** (50mg, 0.068 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.136 mL, 0.136 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-bromobenzylamine (0.088 mL, 0.682 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **13** (29 mg, 0.036 mmol, 53%). **^{1}H NMR (800 MHz, CD_3CN) δ** 8.00 (d, *J* = 2.0 Hz, 1H, TpB3), 7.82 (d, *J* = 2.4 Hz, 1H, TpB5), 7.81 (d, *J* = 2.3 Hz, 1H, TpC5), 7.71 (d, *J* = 2.0 Hz, 1H, TpA3), 7.67 (d, *J* = 2.4 Hz, 1H, TpA5), 7.27 (dd, *J* = 8.0, 1.1 Hz, 1H, H12), 7.23 (m, 3H, TpC3/H10/H9), 7.04 (ddd, *J* = 8.1, 6.7, 2.4 Hz, 1H, H11), 6.42 (ddd, *J* = 10.0, 4.9, 2.3 Hz, 1H, H6), 6.34 (t, *J* = 2.2 Hz, 1H, TpB4), 6.24 (t, *J* = 2.2 Hz, 1H, TpC4), 6.05 (t, *J* = 2.2 Hz, 1H, TpA4), 4.80 (dd, *J* = 9.9, 2.2 Hz, 1H, H5), 4.68 (d, *J* = 6.0 Hz, 1H, H3), 4.48 (d, *J* = 15.9 Hz, 1H, H8A), 4.42 (d, *J* = 15.9 Hz, 1H, H8B), 2.85 (m, 1H, H4), 2.58 (dddd, *J* = 12.5, 9.5, 4.8, 1.2 Hz, 1H, H1), 1.23 (d, *J* = 9.2 Hz, 1H, H2), 1.16 (d, *J* = 8.6 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz, CD_3CN) δ** 180.63 (1C, C15), 133.36 (1C, C12), 132.25 (d, *J* = 3.6 Hz, 1C, C6), 130.26 (1C, C11), 129.38 (1C, C10), 128.35 (1C, C9), 115.45 (1C, C5), 107.50 (1C, TpB4), 107.09 (1C, TpC4), 106.84 (1C, TpA4), 59.56 (1C, C3), 49.84 (d, *J* = 9.9 Hz, 1C, C1), 47.51 (1C, C2), 44.18 (1C, C8), 43.88 (1C, C4), 13.66 (d, *J* = 28.8 Hz, 1C, PMe_3).



Compound 4.13:

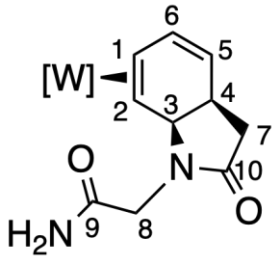
Compound **2** (100mg, 0.136 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-picolylamine (0.141 mL, 1.370 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **14** (72 mg, 0.099 mmol, 73%). **^{1}H NMR (800 MHz (CD_3)$_2$CO), δ, 25°C)** 8.27 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H, H12), 8.12 (d, *J* = 2.0 Hz, 1H, TpB3), 7.97 (d, *J* = 2.0 Hz, 1H, TpA3), 7.92 (d, *J* = 2.4 Hz, 1H, TpB5), 7.90 (d, *J* = 2.3 Hz, 1H, TpC5), 7.73 (d, *J* = 2.4 Hz, 1H, TpA5), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H, H10), 7.30 (dt, *J* = 7.8, 1.0 Hz, 1H, H9), 7.26 (d, *J* = 2.1 Hz, 1H, TpC3), 7.13 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H, H11), 6.41 (ddd, *J* = 9.7, 5.1, 2.6 Hz, 1H, H6), 6.38 (t, *J* = 2.2 Hz, 1H, TpB4), 6.28 (t, *J* = 2.2 Hz, 1H, TpC4), 6.15 (t, *J* = 2.2 Hz, 1H, TpA4), 4.89 (d, *J* = 6.3 Hz, 1H, H3), 4.63 (d, *J* = 16.1 Hz, 1H, H8A), 4.60 (dd, *J* = 9.7, 2.0 Hz, 1H, H5), 4.40 (d, *J* = 16.1 Hz, 1H, H8B), 3.37 (t, *J* = 7.5 Hz, 1H, H4), 2.73 (dd, *J* = 15.9, 8.2 Hz, 1H, H7A), 2.40 (dddd, *J* = 12.1, 9.5, 5.1, 1.1 Hz, 1H, H1), 2.02 (d, *J* = 16.0 Hz, 1H, H7B), 1.29 (m, 1H, H2), 1.19 (d, *J* = 8.6 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz (CD_3)$_2$CO), δ, 25°C)** 175.4 (1C, C14), 160.1 (1C, C13), 149.4 (1C, C12), 144.5 (1C, TpB3), 143.3 (1C, TpA3), 141.7 (1C, TpC3), 137.8 (1C, TpC5), 137.0 (2C, TpA5/TpB5), 136.7 (d, *J* = 5.4 Hz, 1C, C10), 132.2 (d, *J* = 3.6 Hz, 1C, C6), 122.6 (1C, C9), 122.2 (1C, C11), 120.5 (1C, C5), 107.3 (1C, TpB4), 106.8 (1C, TpC4), 106.4 (1C, TpA4), 63.8 (1C, C3), 50.0 (d, *J* = 10.0 Hz,

1C, C1), 48.6 (1C, C2), 46.5 (1C, C8), 40.3 (1C, C7), 33.2 (1C, C4), 13.6 (d, *J* = 28.2 Hz, 1C, PMe_3).



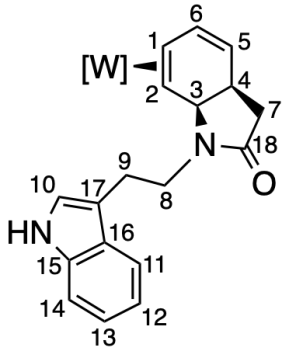
Compound 4.14:

Compound **2** (50 mg, 0.068 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.136 mL, 0.136 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 10 min. In a separate test tube, amino-Acetic acid tert-butyl ester (0.089 mg, 0.682 mmol) with ACN (2 mL) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 12 h then stirred at room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The green solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. A pale green solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **15** (39.2 mg, 0.052 mmol, 76.4-81.0%). **^{1}H-NMR (800 MHz (CD_3)$_2$CO, δ, 25°C):** 8.14 (1H, d, TpB3), 8.06 (1H, d, TpA3), 7.96 (2H, t, TpB5/C5), 7.79 (1H, d, TpA5), 7.64 (1H, d, TpC3), 6.41 (2H, m, H6/TpB4), 6.36 (1H, t, TC4), 6.26 (1H, t, TpA4), 4.87 (1H, d, H3), 4.50 (1H, dd, H5), 4.35 (1H, d, H8), 4.25 (1H, d, H8), 3.37 (1H, t, H4), 2.83 (1H, m, H1), 2.64 (1H, m, H7), 1.94 (1H, d, H7), 1.26 (1H, d, H2), 1.25 (9H, d, PMe_3) 1.12 (9H, s, H12).**^{13}C-NMR (201 MHz (CD_3)$_2$CO, δ, 25°C):** 175.1 (1C, C9), 169.0 (1C, C10), 144.6 (1C, TpB3) 143.6 (1C, TpA3), 141.9 (1C, TpB5), 137.8 (1C, TpC5), 137.1 (1C, TpA5), 136.7 (1C, TpC3), 132.3 (1C, C6), 120.4 (1C, C5), 107.3 (1C, TpB4), 107.0 (1C, TpC4), 106.6 (1C, TpA4), 81.1 (1C, C11), 62.7 (1C, C3), 49.0 (1C, d, C1), 48.6 (1C, C2), 42.7 (1C, C8), 40.2 (1C, s, C7), 33.5 (1C, s, C4), 28.3 (1C, C12), 13.8 (3C, d, PMe_3).



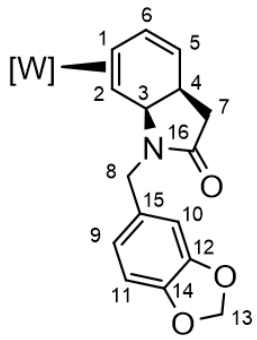
Compound 4.15:

Compound **2** (50mg, 0.068 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.136 mL, 0.136 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-Aminoacetamide (52 mg, 0.690 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **16** (18 mg, 0.026 mmol, 67%). **^{1}H NMR (800 MHz, $CD_3)_2CO$, δ, 25°C)** 8.15 (s, 1H, TpB3), 8.13 (s, 1H, TpA3), 7.95 (dd, *J* = 5.6, 2.8 Hz, 2H, TpB5/C4), 7.80 (d, *J* = 2.8 Hz, 1H, TpA5), 7.59 (s, 1H, TpC3), 6.53 (d, *J* = 18.5 Hz, 1H, H6), 6.42 (d, *J* = 2.2 Hz, 1H, TpB4), 6.34 (d, *J* = 2.6 Hz, 1H, TpC4), 6.26 (d, *J* = 2.7 Hz, 1H, TpA4), 4.88 (s, 1H, H3), 4.61 (d, *J* = 9.9 Hz, 1H, H5), 3.88 (dd, *J* = 16.9, 2.6 Hz, 1H, H8A), 3.61 (m, 1H, H8B), 3.38 (s, 1H, H4), 2.78 (m, 1H, H1), 2.71 (m, 1H, H7A), 1.97 (dd, *J* = 16.2, 2.5 Hz, 1H, H7B), 1.36 (m, 1H, H2), 1.26 (d, *J* = 6.7 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz, $CD_3)_2CO$, δ, 25°C)** 176.0 (1C, C10), 144.5 (1C, TpB3), 143.6 (1C, TpA3), 141.9 (TpC3), 137.03 & 136.25 (2C, TpC3/TpC5), 136.02 (1C, TpA5), 131.46 (d, *J* = 3.6 Hz, 1C, H6), 119.84 (1C, H5), 106.46 (1C, TpC4), 106.20 (1C, TpB4), 105.68 (1C, TpA4), 63.32 (1C, C3), 49.00 (d, *J* = 10.1 Hz, 1C, C1), 47.22 (1C, C2), 43.75 (d, *J* = 5.6 Hz, 1C, C8), 39.01 (1C, C7), 32.69 (1C, C4), 12.71 (d, *J* = 28.3 Hz, 1C, PMe_3).



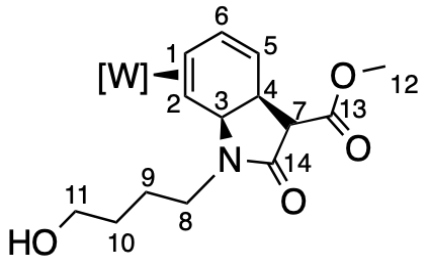
Compound 4.16:

Compound **2** (100mg, 0.136 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.272 mL, 0.272 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, Tryptamine (220 mg, 1.38 mmol) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:NaOH/DCM; 30 mL/30mL) and dried with anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **17** (210 mg, 0.268 mmol, 76%). **^{1}H NMR (800 MHz, $CD_3)_2CO$, δ, 25°C)** 10.0 (s, 1H, NH), 8.19 (d, *J* = 2.1 Hz, 1H, TpA3), 8.17 (d, *J* = 2.0 Hz, 1H, TpB3), 8.02 (d, *J* = 2.3 Hz, 1H, TpC5), 7.97 (d, *J* = 2.2 Hz, 1H, TpB5), 7.84 (d, *J* = 2.4 Hz, 1H, TpA5), 7.58 (d, *J* = 2.1 Hz, 1H, TpC3), 7.40 (dt, *J* = 8.1, 0.9 Hz, 1H, H10), 6.43 (ddd, *J* = 9.6, 5.0, 2.5 Hz, 1H, H6), 6.41 (t, *J* = 2.2 Hz, 1H, TpB4), 6.37 (t, *J* = 2.2 Hz, 1H, TpC4), 6.31 (t, *J* = 2.2 Hz, 1H, TpA4), 4.87 (d, *J* = 6.2 Hz, 1H, H3), 4.57 (dd, *J* = 9.7, 2.0 Hz, 1H, H5), 3.57 (m, 1H, H8A), 3.37 (m, 2H, H4/H8B), 2.81 (m, 3H, H1/H9A/H9B), 2.62 (dd, *J* = 15.7, 8.2 Hz, 1H, H7A), 1.93 (d, *J* = 15.6 Hz, 1H, H7B), 1.59 (d, *J* = 9.6 Hz, 1H, H2), 1.27 (d, *J* = 8.5 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz, $CD_3)_2CO$, δ, 25°C)** 174.7 (1C, C18), 144.6 (1C, TpA3), 143.4 (1C, TpB3), 142.0 (1C, TpC3), 137.8 (1C, TpC5), 137.1 (1C, TpA5), 137.0 (1C, TpB5), 131.9 (d, *J* = 3.5 Hz, 1C, C6), 120.5 (1C, C5), 119.6 (1C, C10), 107.3 (1C, TpB4), 107.2 (1C, TpC4), 106.6 (1C, TpA4), 62.6 (1C, C3), 49.4 (d, *J* = 10.0 Hz, 1C, C1), 48.2 (1C, C2), 41.4 (1C, C8), 40.4 (1C, C7), 33.0 (1C, C4), 24.6 (1C, C9), 13.7 (d, *J* = 28.2 Hz, 1C, PMe_3).



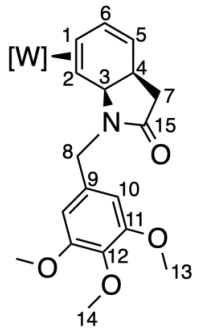
Compound 4.19:

Compound **2** (50 mg, 0.068 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.136 mL, 0.136 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 60 min. In a separate test tube, benzo[d][1,3]dioxol-5-ylmethanamine (0.085 mL, 0.68 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 12 h, then at room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. A deep red oil was collected in a vial and washed pentane (2 × 10 mL) desiccated overnight to yield **20** (36.4 mg, 0.047 mmol, 76.0%). **^{1}H-NMR (800 MHz, CD_2CCl_2) δ):** 8.03 (1H, d, TpB3), 7.77 (1H, d, TpB5), 7.75 (1H, d, TpC5), 7.73 (1H, d, TpA3), 7.63 (1H, d, TpA5), 7.25 (1H, d, TpC3), 6.51 (2H, m, H9/H11), 6.40 (1H, m, H6), 6.38 (1H, t, TpB4), 6.32 (1H, t, TpC4), 6.26 (1H, t, TpA4), 6.10 (1H, m, H10), 5.89 (1H, m, H13), 4.64 (1H, m H5), 4.59 (1H, dd, H3), 4.46 (1H, d, H8), 4.19 (1H, d, H8), 3.24 (1H, m, H4), 2.67 (1H, m, H7), 2.53 (1H, m, H1), 2.09 (1H, m, H7), 1.35 (1H, m, H2), 1.18 (9H, d, PMe3). **^{13}C-NMR (201 MHz, CD_2CCl_2) δ):** 176.0 (1C, C16), 143.8 (1C, C15), 142.6 (1C, TpB3), 142.7 (1C, TpC5), 140.7 (1C, TpC3), 137.0 (1C, TpB5), 136.1 (1C, TpA5), 136.0 (1C, TpA3), 131.0 (1C, C6), 120.0 (1C, C5), 108 (4C, C14/12/11/9), 106.7 (1C, TpB4), 106.3 (1C, TpC4), 105.8 (1C, TpA4), 100.9 (2C, C13/10), 62.4 (1C, C3), 49.1 (1C, C1), 47.8 (1C, C2), 43.9 (1C, C8), 40.4 (1C, C7), 32.3 (1C, C4), 13.8 (3C, d J= 28.6 Hz, PMe_3). **CV (DMA):** $E_{p,a}$= 1.2 V (NHE).



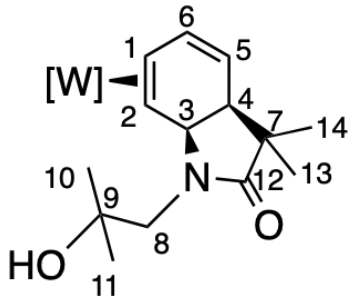
Compound 4.20:

Compound **4** (117 mg, 0.148 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.296 mL, 0.296 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 4-aminobutanol (0.136 mL, 1.480 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and room temperature for 24 h. The reaction was washed three times (H_2O:NaOH/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **21** (102 mg, 0.133 mmol, 89%). **^{1}H NMR (800 MHz, CD_3CN):** δ 8.06 (d, *J* = 2.1 Hz, 1H, TpB3), 7.98 (d, *J* = 2.2 Hz, 1H, TpA5), 7.87 (m, 2H, TpB5/TpC5), 7.80 (d, *J* = 2.4 Hz, 1H, TpA3), 7.50 (d, *J* = 2.2 Hz, 1H, TpC3), 6.49 (ddd, *J* = 9.3, 4.9, 2.4 Hz, 1H, H6), 6.38 (t, *J* = 2.2 Hz, 1H, TpB4), 6.32 (dt, *J* = 3.1, 2.2 Hz, 2H, TpA4/TpC4), 4.97 (d, *J* = 6.2 Hz, 1H, H3), 4.52 (dd, *J* = 9.6, 2.2 Hz, 1H, H5), 3.72 (s, 3H, H12), 3.36 (m, 4H, H4/H8A/H11A/H11B), 3.12 (dd, *J* = 12.0, 7.8 Hz, 1H, H8B), 2.99 (s, 1H, H7), 2.83 (m, 1H, H1), 1.31 (m, 5H, H2/H9A/H9B/H10A/H10B), 1.19 (d, *J* = 8.7 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN):** δ 172.1 (1C, C14), 170.5 (1C, C13), 144.7 (1C, TpB3), 143.1 (1C, TpA3), 142.2 (1C, TpC3), 138.1 (1C, TpC5), 137.5 (2C, TpA5/TpB5), 133.0 (1C, C6), 118.3 (1C, C5), 107.6 (1C, TpB4), 107.3 (1C, TpC4), 107.0 (1C, TpA4), 62.2 (1C, C11), 61.5 (1C, C3), 58.1 (1C, C7), 52.9 (1C, C12), 49.1 (1C, C1), 47.6 (1C, C2), 40.0 (1C, C8), 37.9 (1C, C4), 30.3 (1C, C9), 25.1 (1C, C10), 13.8 (3C, PMe3).



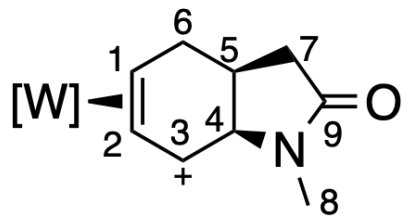
Compound 4.21:

Compound **2** (105 mg, 0.143 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.286 mL, 0286 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 3,4,5-trimethoxybenzylamine (282 mg, 1.430 mmol) with ACN (2 mL) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 h and room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **22** (81 mg, 0.099 mmol, 69%). **^{1}H NMR (800 MHz, CD_3CN):** δ 8.02 (d, *J* = 2.1 Hz, 1H, TpB3), 7.83 (d, *J* = 2.5 Hz, 1H, TpB5), 7.82 (d, *J* = 2.4 Hz, 1H, TpC5), 7.77 (d, *J* = 2.1 Hz, 1H, TpA3), 7.68 (d, *J* = 2.4 Hz, 1H, TpA5), 7.29 (d, *J* = 2.4 Hz, 1H, TpC3), 6.43 (ddd, *J* = 9.9, 5.2, 2.6 Hz, 1H, H6), 6.35 (t, *J* = 2.2 Hz, 1H, TpB4), 6.27 (t, *J* = 2.2 Hz, 1H, TpC4), 6.22 (s, 2H, H10), 6.05 (t, *J* = 2.2 Hz, 1H, TpA4), 4.57 (m, 2H, H3/H5), 4.47 (d, *J* = 15.1 Hz, 1H, H8A), 4.20 (d, *J* = 15.1 Hz, 1H, H8B), 3.63 (s, 3H, H13), 3.52 (s, 6H, H14), 3.19 (t, *J* = 7.3 Hz, 1H, H4), 2.71 (dd, *J* = 16.0, 8.1 Hz, 1H, H7A), 2.59 (ddd, *J* = 13.9, 9.7, 5.1 Hz, 1H, H1), 1.97 (d, *J* = 16.1 Hz, 1H, H7B), 1.27 (d, *J* = 9.7 Hz, 1H, H2), 1.15 (d, *J* = 8.7 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN):** δ 175.7 (1C, C15), 154.01 (2C, C11), 144.6 (1C, TpB3), 143.4 (1C, TpA3), 141.8 (1C, TpC3), 137.9 (1C, C12), 137.4 (1C, TpB5), 137.3 (1C, TpC5), 137.0 (1C, TpA5), 135.5 (1C, C9), 132.3 (1C, C6), 120.4 (1C, C5), 107.5 (1C, TpB4), 107.1 (1C, TpC4), 106.6 (1C, TpA4), 105.3 (2C, C10), 62.9 (1C, C3), 60.8 (1C, C13), 56.3 (2C, C14), 49.6 (1C, C1), 48.4 (1C, C2), 44.3 (1C, C8), 40.3 (1C, C7), 33.1 (1C, C4), 13.7 (3C, PMe3).



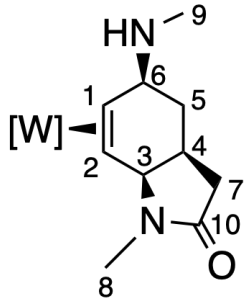
Compound 4.23:

Compound **3** (100mg, 0.131 mmol) was placed in a test tube with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.263 mL, 0.263 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 4-amino-2-methylbutan-2-ol (0.142 mL, 1.31 mmol) with ACN (2 mL) was cooled at -30 °C for 30 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and at room temperature for 24 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **23** (78 mg, 0.106 mmol, 80.4%). **^{1}H NMR (800 MHz, CD_3CN) δ** 8.06 (1H, d, TpB3), 7.98 (1H, TpA5), 7.86 (1H, d, Tp3A), 7.86 (d, 1H, TpC5), 7.76 (1H, d, TpB5), 7.48 (1H, d, TpC3), 6.43 (1H, m, H6), 6.37 (t, 1H, TpB4), 6.31 (t, 1H, TpC4), 6.26 (t, 1H, TpA4), 4.83 (1H, d, H3), 4.74 (1H, dd, H5), 3.16 (2H, s, H8), 2.90 (1H, m, H4), 2.82 (1H, m, H1), 1.40 (1H, d, H2), 1.27 (3H, s, H10), 1.18 (9H, d, PMe_3), 1.12 (3H, s, H11), 1.02 (3H, s, H13), 0.94 (3H, s, H14). **^{13}C NMR (201 MHz, CD_3CN) δ** 183.2 (1C, C12), 144.6 (1C, TpB3), 143.6 (1C, TpA5), 142.1 (1C, TpA3), 138.0 (1C, TpC5), 137.4 (1C, TpB5), 137.3 (1C, TpC3), 132.3 (1C, C6), 115.2 (1C, C5), 107.6 (1C, TpB4), 107.3 (1C, TpC4) , 106.9 (1C, TpA4), 72.6 (1C, C9), 61.9 (1C, C3), 52.7 (1C, C8), 50.2 (1C, C1), 47.3 (1C, C2), 44.8 (1C, C7), 44.7 (1C, C4), 28.7 (1C, C14), 28.3 (1C, C13), 25.3 (1C, C10), 20.8 (1C, C11), 13.6 (d, J = 28.5 Hz, 1C, PMe_3).



Compound 4.24:

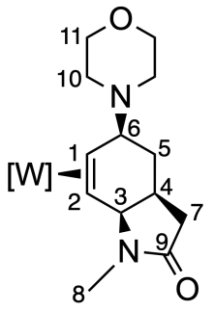
Compound **5** (50 mg, 0.077 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.15 mL, 0.415 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 15 min. The reaction mixture was pipetted in 30 mL of stirring diethyl ether. A tan solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield **24** (45 mg, 0.069 mmol, 90.0%).**^{1}H-NMR (800 MHz, CD$_3$CN C):** 8.57 (1H, d, TpB3), 8.39 (1H, d, TpB5), 8.27 (1H, d, TpB3), 8.21 (1H, d, TpA3), 8.20 (1H, d, TpB5), 8.03 (1H, d, TpA5), 6.65 (1H, t, TpB4), 6.63 (1H, t, TpA4) 6.49 (1H, t, TpC4), 5.73 (1H, t, H2), 5.48 (1H, d, H3), 5.33 (1H, m, H1), 5.05 (1H, d, H4), 3.33 (1H, m, H6), 3.07 (1H, s, H8), 3.02 (1H, d, H6), 2.63 (1H, t, H5), 2.36 (1H, m, H7), 2.23 (1H, d, H7), 1.36 (3C, d J= 29.30 Hz, PMe3). **^{13}C-NMR (201 MHz, CD$_3$CN C δ, 25 ^{0}C):** 172.7 (1C, C9), 147.8 (1C, TpC5), 147.7 (1C, TpA3),145.8 (1C, TpB3), 144.1 (1C, TpC3), 139.8 (1C, TpC5), 139.6 (1C, TpA5), 109.5 (1C, TpB4), 109.2 (1C, TpB4), 108.4 (1C, TpA4) 108.5 (1C, C2), 105.2 (1C, C3), 78.5 (1C, C1), 61.0 (1C, C4), 36.5 (1C, C7), 27.9 (1C, C5), 27.6 (1C, C8), 27.5 (1C, C5), 13.0 (3C, d J= 29.30 Hz, PMe3).



Compound 4.34:

Compound **24** (100 mg, 0.153 mmol) was placed in a test tube, with THF (2 mL), and chilled to -60 °C. In a separate test tube, methylamine in THF (0.766 mL, 2 M) was cooled at -60 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred cold for 10 min and then quenched with a solution of

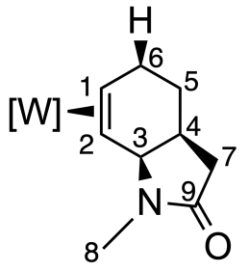
sodium tert-butoxide (0.265 mL, 0.459 mmol, 20%). The solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal THF and pipetted in 15 mL of cold stirring pentane. A tan solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **32** (78 mg, 0.110 mmol, 75%). **^{1}H-NMR (800 MHz, CD$_3$CN C δ, 25 ^{0}C):** 8.27 (TpA3), 8.14 (1H, d, TpB3), 7.94 (1H, d, TpB5), 7.93 (1H, d, TpC5), 7.84 (1H, d, TpA5), 7.59 (1H, d, TpC3), 6.41 (1H, t, TpB4), 6.34 (1H, t, Tpc4), 6.29 (1H, t, TpA4), 4.80 (1H, d, H3), 3.52 (1H, m, H6), 2.57 (1H, m, H4), 2.49 (1H, dd, H7), 2.46 (1H, s, H8), 2.48 (1H, m, H1), 2.45 (1H, s, H9), 2.28 (1H, d, H7), 1.96 (1H, m, H5), 1.39 (1H, d, H2), 1.27 (1H, m, H5), 1.27 (9H, s, PMe3), 1.16 (2H, m, H5/H2). **^{13}C-NMR (201 MHz, CD$_3$CN C δ, 25 ^{0}C):** 174.4 (1C, C10), 144.4 (1C, TpA3), 142.9 (1C, TpB3), 141.8 (1C, TpB5), 137.7 (1C, TpA5), 137.3 (1C, TpC5), 136.9 (1C, TpC3), 107.1 (1C, TpB4), 106.7 (1C, TpC4) 106.1 (1C, TpA4), 62.9 (1C, C3), 58.9 (1C, C6), 56.9 (1C, C1), 54.3 (1C, C4), 47.7 (1C, C2), 39.3 (1C, C7), 33.0 (1C, C9), 31.6 (1C, C5), 26.1 (1C, C8), 13.8 (3C, d J= 29.3 Hz, PMe3).



Compound 4.35:

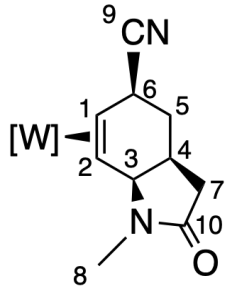
Compound **24** (100 mg, 0.153 mmol) was placed in a test tube, with THF (2 mL), and chilled to -60 °C. In a separate test tube, morpholine (0.132 mL, 1.53 mmol) with THF (2 mL) was cooled at -60 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred cold for 10 min and then quenched with a solution of sodium tert-butoxide (0.265 mL, 0.459 mmol, 20%). The solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal THF and pipetted in 15 mL of cold stirring pentane. A tan solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **33** (73 mg, 0.099, 64%). **^{1}H-NMR (800 MHz, CD$_3$CN C δ, 25 ^{0}C):** 8.18 (TpA3), 8.04 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.79 (1H, d, TpA5), 7.46 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.29 (1H, t, Tpc4), 6.24 (1H, t, TpA4), 4.71 (1H, d, H3), 3.73 (1H, m, H6), 3.68 (2H, m, H10), 2.98 (1H, m, H9), 2.64 (1H, m, H1), 2.58 (1H, dd, H7), 2.49 (1H, m, H9), 2.46

(1H, s, H8), 2.39 (1H, m, H4), 1.90 (1H, m, H7), 1.44 (1H, m, H5), 1.24 (9H, s, PMe3), 1.16 (2H, m, H5/H2). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 175.8 (1C, C11), 144.6 (1C, TpA3), 143.2 (1C, TpB3), 142.4 (1C, TpB5), 138.1 (1C, TpC5), 137.9 (1C, TpA5), 137.4 (1C, TpC3), 106.6 (1C, TpB4), 106.0 (1C, TpC4) 105.5 (1C, TpA4), 66.9 (2C, C10), 63.8 (1C, C6), 62.8 (1C, C3), 53.4 (1C, C1), 48.6 (1C, C9), 47.8 (1C, C2), 39.4 (1C, C7), 30.5 (1C, C4), 26.5 (1C, C8), 25.5 (1C, C5), 13.4 (3C, d J= 30.23 Hz, PMe3).



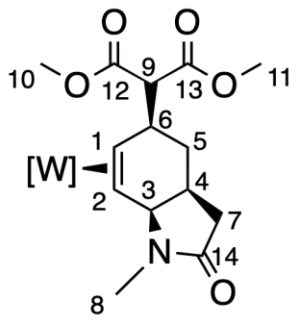
Compound 4.36:

Compound **24** (60 mg, 0.092 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. In a separate test tube, tetrabutylammonium borohydride (0.71 mg, 0.276 mmol) with ACN (2 mL) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise and stirred for 15 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Mg_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **34** (46.3 mg, 0.071 mmol, 77.2%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.29 (1H, d, TpA3), 8.06 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.84 (1H, d, TpA5), 7.81 (1H, d, TpC5), 7.45 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.29 (1H, t, TpA4), 6.27 (1H, t, TpC4), 4.82 (1H, d, H3), 3.08 (1H, m, H6), 2.72 (1H, m, H1), 2.50 (1H, m, H6), 2.48 (3H, s, H8), 2.40 (1H, m, H4) 2.38 (1H, dd, J= 15.47 Hz, H7), 2.09 (1H, H7), 1.66 (1H, ddd J= 12.68 Hz, H5), 1.35 (1H, ddd, H5), 1.15 (1H, d, H2). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 175.4 (1C, C9), 144.3 (1C, TpA5), 142.9 (1C, TpA3), 142.1 (1C, TpB3) 137.9 (1C, TpC3), 137.7 (1C, TpC5), 137.3 (1C, TpB5), 107.6 (1C, TpA4), 107.1 (1C, Tp4C) 106.5 (1C, Tp4B), 63.8 (1C, C3), 52.4 (1C, C1), 49.5 (1C, C2), 38.3 (1C, C7), 32.8 (1C, C4), 28.0 (1C, C8), 27.6 (1C, J= 4.48, C6), 27.5 (1C, J= 8.89 J, C5), 13.7 (3C, d J= 29.11 Hz, PMe3).



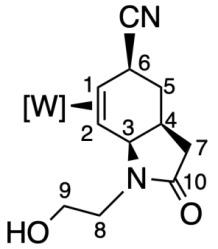
Compound 4.37:

Compound **24** (60 mg, 0.092 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. In a separate test tube, NaCN (13.5 mg, 0.276 mmol) with MeOH (2 mL) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise and stirred for 20 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Mg_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **35** (47.4 mg, 0.070 mmol, 75.6%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.13 (1H, d, TpA3), 8.06 (1H, d, TpB3), 7.87 (1H, d, TpB5), 7.87 (1H, d, TpC5), 7.81 (1H, d, TpA5), 7.47 (1H, d, TpC3), 6.39 (1H, t, TpB4), 6.30 (1H, t, TpC4), 6.27 (1H, t, TpA4), 4.73 (1H, d, H3), 3.68 (1H, q, H6), 2.72 (1H, m, H1), 2.57 (1H, d, H7), 2.52 (1H, m, H4), 2.48 (3H, s, H8), 2.03 (1H, m, H7), 2.03 (1H, ddd J= 13.59 Hz, H5), 1.58 (1H, ddd, H5), 1.15 (1H, d, H2). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 175.2 (1C, C10), 144.8 (1C, TpA5), 143.5 (1C, TpA3), 142.3 (1C, TpB3) 138.3 (1C, TpC3), 137.9 (1C, TpC5), 137.9 (1C, TpB5), 137.7 (1C, C9), 107.8 (1C, TpA4), 107.3 (1C, Tp4C) 106.8 (1C, Tp4B), 62.6 (1C, C3), 49.6 (1C, C1), 47.4 (1C, C2), 39.3 (1C, C7), 31.30 (1C, C4), 30.91 (1C, C6), 30.18 (1C, C7), 29.63 (1C, J= 3.72, C5), 27.5 (1C, C8), 13.20 (3C, d J= 29.08 Hz, PMe3).



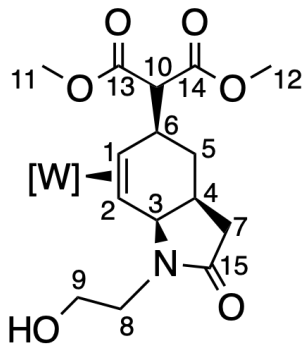
Compound 4.38:

Compound **24** (110 mg, 0.168 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Lithium dimethyl malonate (70 mg, 0.504 mmol) with ACN (2 mL) was cooled in a separate test tube, at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **36** (97 mg, 0.12 mmol, 74%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.12 (1H, d, TpB3), 7.98 (1H, d, TpA3), 7.87 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.76 (1H, d, TpA5), 7.28 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.31 (1H, t, TpC4), 6.25 (1H, t, TpA4), 4.48 (1H, dd, H3), 3.75 (1H, s, H10), 3.69 (4H, m, H11/9), 3.22 (1H, m, H6), 2.64 (1H, m, H7), 2.61 (3H, s, H8), 2.62 (1H, m, H4), 2.24 (1H, m, H5), 2.15 (1H, m, H1) 1.86 (1H, d, H7), 1.33 (1H, dt, H2), 1.19 (9H, PMe3), 1.07 (1H, d, H5). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 175.6 (1C, C14), 171.0 (1C, C12), 170.7 (1C, C13), 144.7 (1C, TpB3), 144.2 (1C, TpA3), 142.0 (1C, TpC3) 138.4 (1C, TpB5), 137.5 (2C, TpA5/C5), 107.5 (1C, TpB4), 107.4 (1C, TpC4) 107.0 (1C, TpA4), 63.7 (1C, C3), 63.2 (1C, C9), 53.8 (1C, C1), 52.9 (2C, C10/11), 47.5 (1C, C2), 43.5 (1C, C7), 39.4 (1C, C6), 31.4 (1C, C5), 27.3 (1C, C8), 27.2 (1C, C4), 13.5 (3C, d J= 29.11 Hz, PMe3).



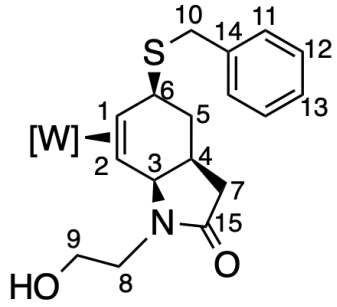
Compound 4.40:

Compound **25** (120 mg, 0.176 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. NaCN (26 mg, 0.527 mmol) with MeOH (2 mL) was cooled in a separate test tube, at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **38** (102.0 mg, 0.144 mmol, 81.9%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.07 (1H, d, TpB3), 8.05 (1H, d, TpA3), 7.88 (2H, d, TpC5/B5), 7.81 (1H, d, TpA5), 7.47 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.31 (1H, t, TpC4), 6.28 (1H, t, TpA4), 4.78 (1H, d, H3), 3.68 (1H, m, H9), 3.28 (1H, m, H8), 3.24 (1H, m, H9), 3.16 (1H, m, H6), 2.99 (1H, m, H8), 2.73 (1H, m, H4), 2.59 (1H, dd, H7), 2.53 (2H, m, H5/H1), 1.99 (1H, m, H7), 1.59 (1H, m, H5), 1.18 (1H, dd, H2), 1.10 (9H, d, PMe3), 1.08 (1H, d, H5). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 176.4 (1C, C15), 144.6 (1C, TpB3), 143.68 (1C, TpA3), 142.3 (1C, TpC3) 138.0 (1C, TpC5), 137.7 (1C, TpB5), 129.9 (1C, TpC5), 129.2 (1C, CN), 106.9 (3C, TpA4/B4/C4), 66.3 (1C, C3), 61.7 (1C, C9), 49.0 (1C, C1), 47.7 (1C, C2), 43.7 (1C, C8), 31.3 (1C, C7), 31.1 (1C, C6), 29.5 (1C, C5), 15.6 (1C, C4), 13.8 (3C, d J= 27.19 Hz, PMe3).



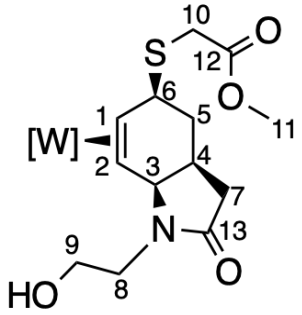
Compound 4.41:

Compound **25** (120 mg, 0.176 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Lithium dimethyl malonate (73 mg, 0.527 mmol) with ACN (2 mL) was cooled in a separate test tube, at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **39** (120.0 mg, 0.176 mmol, 84.0%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.12 (1H, d, TpB3), 7.99 (1H, d, TpA3), 7.87 (1H, d, TpC5), 7.83 (1H, d, TpB5), 7.77 (1H, d, TpA5), 7.29 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.31 (1H, t, TpC4), 6.26 (1H, t, TpA4), 4.70 (1H, d, H3), 3.71 (4H, m, H9/H10/12), 3.70 (3H, s, H11), 3.45 (1H, m, H8), 3.38 (1H, m, H9), 3.22 (1H, m, H6), 3.12 (1H, m, H8), 2.74 (1H, dd, H7), 2.66 (1H, m, H4), 2.19 (2H, m, H5/H1), 2.12 (1H, m, H7), 1.34 (1H, dd, H2), 1.18 (9H, d, PMe3), 1.08 (1H, d, H5). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 176.8 (1C, C15), 170.9 (1C, C13), 170.7 (1C, C14), 144.6 (1C, TpB3), 144.0 (1C, TpA3), 142.3 (1C, TpC3) 138.3 (1C, TpC5), 137.4 (2C, TpB5/C5), 107.5 (1C, TpB4), 107.4 (1C, TpC4) 106.9 (1C, TpA4), 63.1 (1C, C10), 62.3 (1C, C3), 60.5 (1C, C9), 53.9 (1C, C1), 52.8 (2C, C11/12), 47.5 (1C, C2), 43.5 (1C, C8), 43.2 (1C, C7), 39.3 (1C, C6), 31.2 (1C, C5), 27.3 (1C, C4), 13.5 (3C, d J= 27.19 Hz, PMe3).



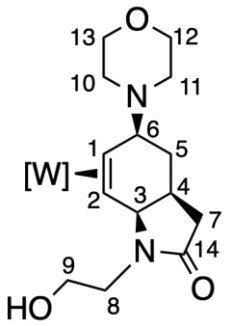
Compound 4.42:

Compound **25** (40 mg, 0.059 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Phenylmethanethiol (0.021 mL, 0.180 mmol) was cooled in a separate test tube, at -30 °C for 10 min with potassium tert-butoxide (0.071 mL, 0.120 mmol). After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **40** (32.0 mg, 0.059, 68.0%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.06 (1H, d, TpA3), 8.00 (1H, d, TpB3), 7.78 (2H, t, TpC5/A5), 7.78 (1H, d, TpB5), 7.40-7.22 (5H, m, Ph), 7.32 (1H, d, TpC3), 6.34 (1H, t, TpB4), 6.28 (1H, t, TpC4), 6.25 (1H, t, TpA4), 4.75 (1H, dd, H3), 3.87 (1H, s, H11), 3.71 (1H, t, H6), 3.39 (2H, m, H8), 3.20 (1H, m, H9), 3.01 (1H, m, H9), 2.64 (1H, m, H4), 2.59 (2H, m, H7), 2.41 (1H, dt, H1), 2.28 (1H, m, H5) 1.73 (1H, dt, H5), 1.14 (1H, dt, H2), 0.91 (9H, PMe3). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 176.9 (1C, C10), 144.3 (1C, TpA3), 143.8 (1C, TpB3), 142.2 (1C, TpC5) 138.1 (1C, TpA5), 137.3 (2C, TpB5/C3), 129-126 (6C, Ph), 106.7 (1C, TpB4), 106.2 (1C, TpC4) 105.9 (1C, TpA4), 61.1 (1C, C3), 60.5 (1C, C8), 53.3 (1C, C1), 48.2 (1C, C2), 43.2 (1C, C9), 42.8 (1C, C6), 40.0 (1C, C7), 35.8 (1C, C11), 30.1 (1C, C5), 28.6 (1C, C4), 12.8 (3C, d J= 28.07 Hz, PMe3).



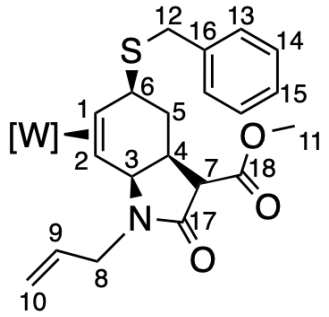
Compound 4.43:

Compound **25** (85 mg, 0.124 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Methyl 2-mercaptoacetate (0.034 mL, 0.373 mmol) was cooled in a separate test tube, at -30 °C for 10 min with potassium tert-butoxide (0.143 mL, 0.249 mmol). After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting white film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **41** (72.0 mg, 0.124, 73.0%). **^{1}H-NMR (800 MHz, CD_3CN C δ, 25 ^{0}C):** 8.06 (1H, d, TpB3), 8.04 (1H, d, TpA3), 7.86 (2H, t, TpC5/B5), 7.79 (1H, d, TpA5), 7.48 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.29 (1H, t, TpC4), 6.27 (1H, t, TpA4), 4.76 (1H, m, H3), 4.10 (1H, m, H6), 3.70 (3H, s, H11), 3.46 (1H, d, H10), 3.37 (3H, m, H10/9), 3.27 (1H, m, H8), 2.99 (1H, m, H8), 2.64 (1H, m, H4), 2.60 (1H, m, H7), 2.56 (1H, m, H1), 2.39 (1H, d, H7), 2.29 (1H, m, H5), 1.63 (1H, d, H5), 1.18 (1H, d, H2), 1.17 (9H, d, PMe3). **^{13}C-NMR (201 MHz, CD_3CN C δ, 25 ^{0}C):** 176.7 (1C, C13), 172.5 (1C, C12), 144.4 (1C, TpB3), 143.8 (1C, TpA3), 142.3 (1C, TpC3), 138.2 (1C, TpB5) 137.8 (1C, TpC5), 137.4 (1C, TpA5), 107.6 (1C, TpB4), 107.3 (1C, TpC4) 106.9 (1C, TpA4), 62.0 (1C, C3), 61.2 (1C, C9), 53.8 (1C, C1), 52.9 (1C, C11), 48.9 (1C, C2), 46.4 (1C, C6), 44.1 (1C, C8), 41.1 (1C, C7), 34.3 (1C, C10), 31.5 (1C, C5), 29.4 (1C, C4), 13.8 (3C, d J= 29.45 Hz, PMe3).



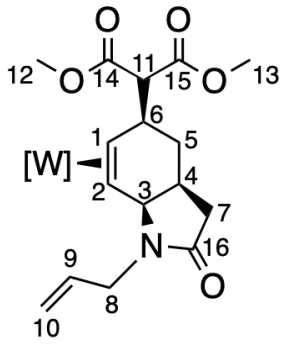
Compound 4.44:

Compound **25** (100 mg, 0.146 mmol) was placed in a test tube, with THF (2 mL), and chilled to -60 °C. In a separate test tube, morpholine (0.126 mL, 1.46 mmol) with THF (2 mL) was cooled at -60 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred cold for 10 min and then quenched with a solution of sodium tert-butoxide (0.253 mL, 0.439 mmol, 20%). The solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal THF and pipetted in 15 mL of cold stirring pentane. A tan solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **42** (97 mg, 0.13 mmol, 86%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25 C):** 8.09 (TpA3), 8.03 (1H, d, TpB3), 7.85 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.79 (1H, d, TpA5), 7.46 (1H, d, TpC3), 6.36 (1H, t, TpB4), 6.30 (1H, t, Tpc4), 6.25 (1H, t, TpA4), 4.75 (1H, d, H3), 3.76 (1H, m, H6), 3.69 (2H, m, H12), 3.56 (1H, m, H9), 3.26 (1H, m, H9), 3.21 (2H, m, H8), 3.08 (1H, m, H10), 2.98 (1H, m, H1), 2.61 (1H, dd, H7), 2.51 (1H, m, H4), 2.46 (2H, m, H11), 1.92 (1H, m, H7), 1.41 (1H, m, H2), 1.24 (2H, m, H5), 1.24 (9H, s, PMe3), 1.09 (2H, m, H5/H2). **^{13}C-NMR (201 MHz, CD_3CN, δ, 25 C):** 177.2 (1C, C14), 144.6 (1C, TpB3), 143.4 (1C, TpA3), 142.4 (1C, TpB5), 137.9 (2C, TpC5/A5), 137.4 (1C, TpA5), 107.6 (1C, TpC3), 107.1 (1C, TpB4), 106.7 (1C, TpC4), 68.1 (2C, C12/C13), 64.4 (1C, C6), 62.7 (1C, C3), 61.2 (1C, C9), 53.7 (1C, C1), 49.0 (1C, C2), 48.9 (1C, C10/C11), 43.8 (1C, C8), 40.4 (1C, C7), 32.1 (1C, C4), 31.4 (1C, C5), 14.4 (3C, d J= 30.23 Hz, PMe3).



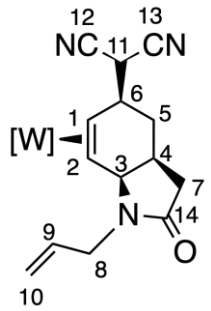
Compound 4.45:

Compound **26** (100 mg, 0.136 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Phenylmethanethiol (0.048 mL, 0.407 mmol) was cooled in a separate test tube, at -30 °C for 10 min in potassium tert-butoxide (0.164 mL, 0.271 mmol). After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **43** (92 mg, 0.11 mmol, 79%). **^{1}H NMR (800 MHz, CD_3CN) δ** 7.97 (t, *J* = 2.7 Hz, 2H, TpA3/TpB3), 7.83 (t, *J* = 2.2 Hz, 2H, TpB5/TpC5), 7.79 (d, *J* = 2.4 Hz, 1H, TpA5), 7.38 (dt, *J* = 8.0, 1.7 Hz, 2H, H13), 7.35 (dd, *J* = 8.6, 6.9 Hz, 2H, H14), 7.32 (d, *J* = 2.3 Hz, 1H, TpC3), 7.24 (tt, *J* = 7.2, 1.4 Hz, 1H, H15), 6.34 (t, *J* = 2.2 Hz, 1H, TpB4), 6.27 (t, *J* = 2.2 Hz, 1H, TpA4), 6.24 (t, *J* = 2.2 Hz, 1H, TpC4), 5.57 (ddt, *J* = 17.3, 9.8, 4.8 Hz, 1H, H9), 4.93 (d, *J* = 7.7 Hz, 1H, H3), 4.88 (dq, *J* = 10.3, 1.7 Hz, 1H, H10A), 4.81 (dq, *J* = 17.3, 1.8 Hz, 1H, H10B), 4.40 (d, *J* = 7.2 Hz, 1H, H7), 3.91 (ddt, *J* = 17.2, 4.9, 2.3 Hz, 1H, H8A), 3.86 (s, 2H, H12), 3.77 (d, *J* = 1.2 Hz, 1H, H11), 3.76 (m, 1H, H6), 3.26 (dd, *J* = 16.6, 5.4 Hz, 1H, H8B), 2.91 (qd, *J* = 7.2, 3.3 Hz, 1H, H4), 2.34 (m, 2H, H1/H5A), 1.06 (dt, *J* = 11.3, 1.7 Hz, 1H, H2), 0.88 (dd, *J* = 8.3, 1.3 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN) δ** 172.7 (1C, C17), 170.4 (1C, C18), 144.2 (1C, TpB3), 143.3 (1C, TpA3), 142.1 (1C, TpC3), 138.1 (1C, TpC5), 137.8 (1C, TpA5), 137.4 (1C, TpB5), 134.2 (1C, C9), 130.1 (1C, C13), 129.5 (1C, C14), 127.8 (1C, C15), 115.8 (1C, C10), 107.6 (1C, TpB4), 107.2 (1C, TpA4), 106.8 (1C, TpC4), 59.5 (1C, C3), 56.0 (1C, C7), 53.8 (1C, C1), 52.9 (1C, C11), 49.3 (1C, C2), 43.3 (1C, C6), 43.1 (1C, C8), 36.8 (1C, C12), 35.0 (1C, C4), 26.6 (1C, C5), 13.7 (3C, PMe3).



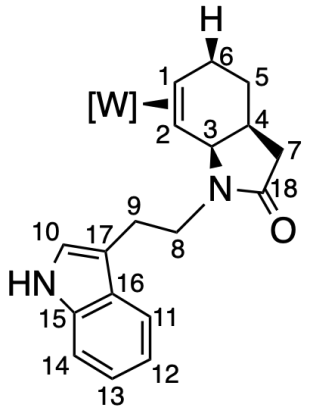
Compound 4.46:

Compound **27** (125 mg, 0.184 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Lithium dimethyl malonate (76.2 mg, 0.552 mmol) with ACN (2 mL) was cooled in a separate test tube, at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **44** (110 mg, 0.130 mmol, 71%). **^{1}H NMR (800 MHz, CD_3CN) δ** 8.14 (d, *J* = 2.0 Hz, 1H, TpB3), 7.98 (d, *J* = 2.1 Hz, 1H, TpA3), 7.88 (d, *J* = 2.3 Hz, 2H, TpB5/TpC5), 7.77 (d, *J* = 2.4 Hz, 1H, TpA5), 7.32 (d, *J* = 2.2 Hz, 1H, TpC3), 6.40 (t, *J* = 2.2 Hz, 1H, TpB4), 6.34 (t, *J* = 2.2 Hz, 1H, TpC4), 6.25 (t, *J* = 2.2 Hz, 1H, TpA4), 5.59 (dddd, *J* = 17.0, 10.7, 6.5, 4.6 Hz, 1H, H9), 4.84 (dq, *J* = 10.3, 1.5 Hz, 1H, H10A), 4.80 (dq, *J* = 17.3, 1.7 Hz, 1H, H10B), 4.73 (dt, *J* = 7.2, 1.9 Hz, 1H, H3), 4.21 (m, 1H, H8A), 3.78 (s, 3H, H12), 3.73 (s, 3H, H13), 3.61 (m, 1H, H8B), 3.26 (m, 1H, H6), 2.74 (dd, *J* = 16.9, 9.8 Hz, 1H, H7A), 2.67 (m, 1H, H4), 2.23 (m, 2H, H5A/H1), 1.70 (m, 1H, H7B), 1.33 (ddt, *J* = 10.3, 8.8, 1.6 Hz, 1H, H2), 1.23 (d, *J* = 8.5 Hz, 9H, PMe3), 1.11 (m, 1H, H5B). **^{13}C NMR (201 MHz, CD_3CN) δ** 175.5 (1C, C16), 171.0 (1C, C12), 170.7 (1C, C13), 144.6 (1C, TpB3), 144.2 (1C, TpA3), 142.1 (1C, TpC3), 138.3 (1C, TpA5), 137.4 (1C, TpB5), 137.3 (1C, TpC5), 134.4 (1C, C9), 116.6 (1C, C10), 107.5 (1C, TpB4), 107.3 (1C, TpC4), 106.7 (1C, TpA4), 61.2 (1C, C3), 53.7 (1C, C1), 53.0 (1C, C12), 52.9 (1C, C13), 47.2 (1C, C2), 43.2 (1C, C7), 42.6 (1C, C8), 39.3 (1C, C6), 31.2 (1C, C5), 27.3 (1C, C4), 13.8 (3C, PMe3).



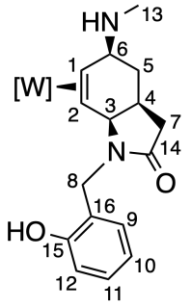
Compound 4.47:

Compound **27** (120 mg, 0.177 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Lithium Malononitrile (55.2 mg, 0.530 mmol) with ACN (2 mL) was cooled in a separate test tube, at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **45** (93 mg, 0.130 mmol, 71%). **^{1}H NMR (800 MHz, CD_3CN) δ** 8.12 (s, 1H, TpB3), 7.92 (s, 1H, TpA3), 7.89 (s, 1H, TpC5), 7.88 (s, 1H, TpB5), 7.77 (s, 1H, TpA5), 7.43 (s, 1H, TpC3), 6.39 (t, *J* = 1.9 Hz, 1H, TpB4), 6.34 (t, *J* = 2.2 Hz, 1H, TpC4), 6.25 (d, *J* = 2.1 Hz, 1H, TpA4), 5.58 (m, 1H, H9), 4.87 (m, 1H, H10A), 4.78 (m, 1H, H10B), 4.62 (d, *J* = 6.5 Hz, 1H, H3), 4.23 (dd, *J* = 10.0, 2.0 Hz, 1H, H11), 4.03 (dd, *J* = 15.5, 4.9 Hz, 1H, H8A), 3.60 (dd, *J* = 15.8, 6.7 Hz, 1H, H8B), 3.23 (s, 1H, H6), 2.76 (m, 1H, H7A), 2.71 (d, *J* = 8.4 Hz, 1H, H4), 2.50 (t, *J* = 11.2 Hz, 1H, H1), 2.43 (dt, *J* = 16.6, 8.2 Hz, 1H, H5A), 2.04 (d, *J* = 16.8 Hz, 1H, H7B), 1.48 (d, *J* = 15.7 Hz, 1H, H5B), 1.27 (d, *J* = 10.8 Hz, 1H, H2), 1.18 (dt, *J* = 8.4, 1.6 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN) δ** 175.7 (1C, C14), 144.5 (1C, TpB3), 144.4 (1C, TpC5), 142.0 (1C, TpC3), 138.4 (1C, TpA3), 137.6 (1C, TpB5), 137.5 (1C, TpA5), 134.1 (1C, C9), 117.4 (1C, C10), 115.7 (1C, C12), 115.1 (1C, C13), 107.7 (1C, TpB4), 107.5 (1C, TpC4), 106.9 (1C, TpA4), 61.5 (1C, C3), 51.5 (1C, C1), 47.0 (1C, C2), 43.0 (1C, C8), 42.9 (1C, C7), 41.2 (1C, C6), 35.9 (1C, C11), 30.5 (1C, C5), 27.4 (1C, C4), 13.3 (3C, PMe3).



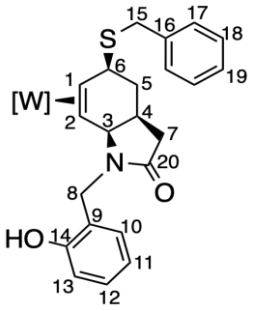
Compound 4.48:

Compound **28** (150 mg, 0.192 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. In a separate test tube, sodium borohydride (12 mg, 0.192 mmol) with ACN (2 mL) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise and stirred for 15 min. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried over anhydrous Mg_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield **46** (120 mg, 0.150 mmol, 80%). **^{1}H NMR (800 MHz, CD_3CN) δ** 8.21 (d, *J* = 2.1 Hz, 1H, TpA3), 8.05 (d, *J* = 2.0 Hz, 1H, TpB3), 7.92 (d, *J* = 2.3 Hz, 1H, TpC5), 7.86 (dt, *J* = 2.4, 0.7 Hz, 1H, TpB5), 7.75 (dd, *J* = 1.9, 1.2 Hz, 1H, TpA5), 7.45 (d, *J* = 2.2 Hz, 1H, TpC3), 7.28 (dt, *J* = 8.1, 0.9 Hz, 1H, H14), 7.00 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, H13), 6.85 (m, 1H, H10), 6.71 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H, H12), 6.57 (m, 1H, H11), 6.38 (t, *J* = 2.2 Hz, 1H, TpB4), 6.26 (t, *J* = 2.2 Hz, 1H, TpC4), 6.17 (t, *J* = 2.2 Hz, 1H, TpA4), 4.91 (dd, *J* = 5.6, 2.1 Hz, 1H, H3), 3.37 (ddd, *J* = 13.5, 10.9, 6.2 Hz, 1H, H9A), 3.01 (m, 1H, H9B), 2.96 (m, 1H, H6A), 2.79 (m, 1H, H1), 2.58 (m, 3H, H8A/H8B/H6), 2.52 (dd, *J* = 16.0, 7.7 Hz, 1H, H7A), 2.44 (ddt, *J* = 12.3, 10.1, 4.7 Hz, 1H, H4), 2.03 (m, 1H, H7B), 1.55 (m, 1H, H5A), 1.32 (m, 3H, H5B/H2), 1.15 (d, *J* = 8.4 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN) δ** 175.5 (1C, C18), 144.4 (1C, TpB3), 143.3 (1C, TpA3), 142.0 (1C, TpC3), 138.0 (1C, TpC5), 137.9 (1C, TpA5), 137.3 (1C, TpB5), 123.3 (1C, C10), 122.7 (1C, C13), 119.7 (1C, C12), 119.0 (1C, C11), 112.1 (1C, C14), 107.5 (1C, TpB4), 107.3 (1C, TpC4), 106.8 (1C, TpA4), 62.3 (1C, C3), 51.2 (1C, C1), 49.7 (1C, C2), 42.00 (1C, C9), 39.4 (1C, C7), 33.0 (1C, C4), 28.1 (1C, C6), 28.1 (1C, C5), 24.6 (1C, C8), 13.7 (3C, PMe3).



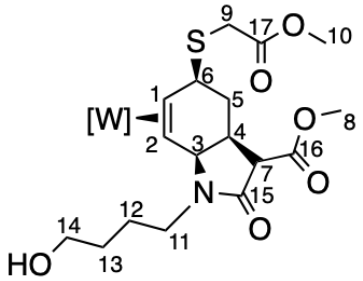
Compound 4.49:

Compound **29** (112 mg, 0.150 mmol) was placed in a test tube with THF (2 mL) and chilled to -60 °C. In a separate test tube, Methylamine (0.751 mL, 1.50 mmol) with THF (2 mL) was cooled at -60 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred cold for 10 min and then quenched with a solution of sodium tert-butoxide (0.260 mL, 0.451 mmol, 20%). The solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal THF and pipetted in 15 mL of cold stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **47** (85 mg, 0.110, 73%). **^{1}H NMR (800 MHz, THF) δ** 8.04 (d, *J* = 2.0 Hz, 1H, TpA3), 7.95 (d, *J* = 2.0 Hz, 1H, TpB3), 7.89 (d, *J* = 2.2 Hz, 1H, TpB5), 7.80 (d, *J* = 2.4 Hz, 1H, TpC5), 7.76 (d, *J* = 2.4 Hz, 1H, TpA5), 7.40 (d, *J* = 2.1 Hz, 1H, TpC3), 6.85 (td, *J* = 7.6, 1.7 Hz, 1H, H10), 6.59 (dd, *J* = 8.1, 1.3 Hz, 1H, H12), 6.28 (dt, *J* = 9.0, 2.2 Hz, 2H, TpB4/TpC4), 6.16 (td, *J* = 7.4, 1.4 Hz, 1H, H11), 6.13 (t, *J* = 2.1 Hz, 1H, TpA4), 5.86 (dd, *J* = 7.5, 1.8 Hz, 1H, H9), 4.77 (d, *J* = 5.0 Hz, 1H, H6), 4.14 (d, *J* = 14.8 Hz, 1H, H8A), 3.90 (d, *J* = 14.7 Hz, 1H, H8B), 3.48 (m, 1H, H3), 3.22 (d, *J* = 1.4 Hz, 3H, MeNH2), 2.51 (m, 3H, H7A/H5/H4), 2.32 (ddd, *J* = 13.4, 11.0, 2.8 Hz, 1H, H2), 2.27 (dd, *J* = 20.7, 6.2 Hz, 1H, H7B), 1.28 (d, *J* = 11.1 Hz, 1H, H1), 1.22 (d, *J* = 8.6 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, THF) δ** 176.3 (1C, C14), 144.4 (1C, TpA3), 141.8 (1C, TpB3), 137.3 (1C, TpB5), 136.9 (1C, TpC5), 136.7 (1C, TpA5), 129.0 (1C, C12), 128.5 (1C, C11), 122.8 (1C, C16), 121.2 (1C, C15), 119.5 (1C, C9) 106.8 (1C, TpB4), 106.7 (2C, TpB4/TpC4), 64.1 (1C, C6), 59.5 (1C, C3), 56.3 (1C, C2), 49.9 (2C, C1/MeNH2), 41.3 (2C, C7/C8), 31.8 (1C, C4), 29.9 (1C, C5), 14.1 (3C, PMe3).



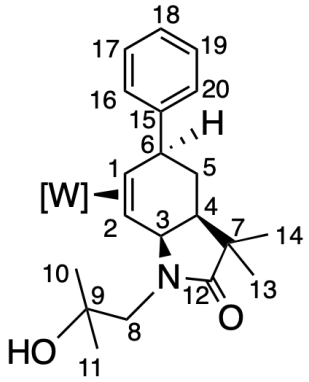
Compound 4.50:

Compound **29** (132 mg, 0.177 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Phenylmethanethiolate (109 mg, 0.886 mmol) with ACN (2 mL) was cooled in a separate test tube, at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **48** (105 mg, 0.121 mmol, 68%). **^{1}H NMR (800 MHz, CD_3CN) δ** 7.98 (dd, *J* = 4.6, 2.1 Hz, 2H, TpA3/TpB3), 7.89 (d, *J* = 2.3 Hz, 1H, TpA5), 7.85 (dd, *J* = 7.1, 2.4 Hz, 2H, TpB5/TpC5), 7.34 (m, 4H, H17/H18), 7.23 (m, 2H, TpC3/H19), 6.97 (m, 1H, H12), 6.68 (dd, *J* = 8.1, 1.2 Hz, 1H, H13), 6.34 (t, *J* = 2.2 Hz, 1H, TpA4), 6.25 (td, *J* = 2.3, 1.2 Hz, 3H, TpB4/TpC4/H11), 5.83 (m, 1H, H10), 4.81 (d, *J* = 7.3 Hz, 1H, H3), 4.25 (d, *J* = 15.1 Hz, 1H, H8A), 4.04 (d, *J* = 15.0 Hz, 1H, H8B), 3.81 (s, 2H, H15), 3.69 (s, 1H, H6), 2.80 (m, 1H, H7A), 2.67 (m, 1H, H4), 2.63 (dd, *J* = 16.7, 9.0 Hz, 1H, H7B), 2.32 (t, *J* = 11.9 Hz, 1H, H1), 2.25 (m, 1H, H5A), 1.73 (dd, *J* = 14.8, 4.2 Hz, 1H, H5B), 1.28 (m, 1H, H2), 0.92 (d, *J* = 8.4 Hz, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN) δ** 178.2 (1C, C20), 144.4 (1C, TpA3), 143.9 (1C, TpB3), 142.0 (1C, TpC5), 140.4 (1C, C16), 138.0 (1C, TpA5), 137.8 (1C, TpC3), 137.5 (1C, TpB5), 131.7 (1C, C10), 130.1 (1C, C12), 130.1 (1C, C18), 129.5 (1C, C17), 127.7 (1C, C19), 119.9 (1C, C13), 107.5 (1C, TpB4), 107.3 (1C, TpC4), 107.1 (1C, TpA4), 63.4 (1C, C3), 53.5 (1C, C1), 49.0 (1C, C2), 43.6 (1C, C6), 42.3 (1C, C8), 40.1 (1C, C7), 36.6 (1C, C15), 29.9 (1C, C5), 29.6 (1C, C4), 13.9 (3C, PMe3).



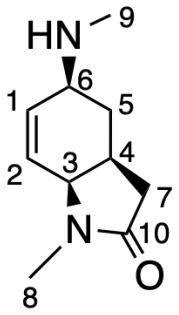
Compound 4.51:

Compound **30** (85 mg, 0.110 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30°C. 2-methoxy-2-oxoethyl-1-potassium thiolate (35 mg, 0.33 mmol) with ACN (2 mL) was cooled in a separate test tube, at -30 °C for 10 mins. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 10 min. The reaction was washed three times (H_2O/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **x** (61 mg, 0.070 mmol, 63 %). **^{1}H NMR (400 MHz, CD_3CN):** δ 8.05 (t, *J* = 2.7 Hz, 2H, TpA3/TpB3), 7.85 (dd, *J* = 4.8, 2.3 Hz, 2H, TpB5/TpC5), 7.82 (d, *J* = 2.5 Hz, 1H, TpA5), 7.45 (d, *J* = 2.3 Hz, 1H, TpC3), 6.37 (t, *J* = 2.2 Hz, 1H, TpB4), 6.32 (t, *J* = 2.3 Hz, 1H, TpA4), 6.28 (t, *J* = 2.3 Hz, 1H, TpC4), 4.91 (d, *J* = 7.3 Hz, 1H, H3), 4.18 (s, 1H, H6), 4.02 (d, *J* = 6.0 Hz, 1H, H7), 3.72 (s, 3H, H10), 3.70 (s, 3H, H8), 3.45 (d, *J* = 14.8 Hz, 1H, H9A), 3.36 (d, *J* = 14.8 Hz, 1H, H9B), 3.30 (s, 3H, H11A/H14A/H14B), 2.84 (m, 1H, H4), 2.62 (d, *J* = 14.1 Hz, 1H, H11), 2.50 (t, *J* = 11.6 Hz, 1H, H1), 2.42 (m, 1H, H5A), 1.79 (d, *J* = 15.4 Hz, 1H, H5B), 1.26 (t, *J* = 8.3 Hz, 4H, H12A/H12B/H13A/H13B), 1.17 (d, *J* = 8.5 Hz, 9H, PMe3), 1.05 (d, *J* = 11.0 Hz, 1H, H2). **^{13}C NMR (201 MHz, CD_3CN):** δ 172.4 (1C, C15), 172.1 (1C, C16), 170.2 (1C, C17), 144.2 (1C, TpA3), 143.2 (1C, TpB3), 142.0 (1C, TpC3), 138.0 (1C, TpA5), 137.9 (1C, TpB5), 137.4 (1C, TpC5), 107.5 (1C, TpB4), 107.2 (1C, TpA4), 107.0 (1C, TpC4), 62.1 (1C, C14), 59.2 (1C, C3), 56.5 (1C, C7), 53.0 (1C, C1), 52.8 (1C, C9), 52.7 (1C, C10), 48.9 (1C, C2), 45.7 (1C, C6), 40.5 (1C, C11), 34.6 (1C, C5), 34.2 (1C, C10), 30.5 (1C, C12), 27.8 (1C, C5), 24.9 (1C, C13), 13.6 (3C, PMe3).



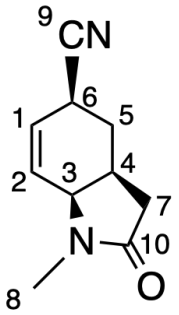
Compound 4.52:

Compound **31** (40 mg, 0.056 mmol) was placed in a test tube, with ACN (2 mL), and chilled to -30 °C. Phenyllithium (0.150 mL, 0.280 mmol, 2 M) was cooled in a separate test tube, at -30 °C for 30 min with CuI (32 mg, 0.170 mmol). After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 30 min. The reaction was washed three times (H_2O/DCM; 30 mL/30mL), and dried over anhydrous Na_2SO_4. The clear solution was evaporated in vacuo. The resulting clear film was dissolved in minimal DCM and pipetted in 100 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield **50** (32.0 mg, 0.041, 72.0%). **^{1}H NMR (800 MHz, CD_2Cl_2) δ** 8.03 (1H, d, TpB3), 7.99 (1H, TpA3), 7.77 (1H, d, TpB5), 7.75 (d, 1H, TpA5), 7.73 (1H, d, TpC5), 7.47 (2H, m, H16/H20), 7.47 (1H, d, TpC3), 7.38 (2H, m, H17/H19), 7.24 (1H, H18), 6.33 (t, 1H, TpB4), 6.27 (t, 1H, TpC4), 6.23 (t, 1H, TpA4), 4.95 (1H, d, H3), 3.90 (1H, m, H6), 3.23 (1H, d, H8), 2.93 (1H, dt, H1), 2.87 (1H, d, H8), 2.36 (1H, m, H4), 1.63 (1H, m, H5), 1.28 (5H, m, H2/H5/H10), 1.17 (3H, s, H11), 1.02 (3H, s, H13), 0.89 (3H, s, H14), 0.82 (9H, d, PMe_3). **^{13}C NMR (201 MHz, CD_2Cl_2) δ** 183.7 (1C, C12), 152.3 (1C, C15), 143.6 (1C, TpA3), 142.5 (1C, TpB3), 140.5 (1C, TpB5), 137.2 (1C, TpA5), 137.1 (1C, TpC5), 136.6 (1C, TpC3), 129.1 (2C, C16/C20), 128.4 (2C, C17/C19), 126.1 (1C, C18), 106.9 (1C, TpB4), 106.4 (1C, TpC4) , 106.1 (1C, TpA4), 71.7 (1C, C9), 60.7 (1C, C3), 55.4 (1C, C1), 53.7 (1C, C8), 50.3 (1C, C2), 45.5 (1C, C6), 44.5 (1C, C4), 44.4 (1C, C7), 36.8 (1C, C5), 28.5 (1C, C14), 28.3 (1C, C13), 23.8 (1C, C11), 19.7 (1C, C10), 14.3 (d, J = 29.7 Hz, 1C, PMe_3).



Compound 4.53:

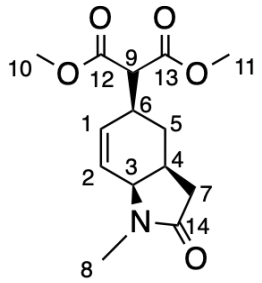
Compound **32** (70.0 mg, 0.100 mmol) was placed in a test tube with no solvent at -40 °C for 10 min. In a separate test tube, $NOPF_6$ (25 mg, 0.14 mmol) with ACN (2 mL) was cooled to -40°C for 10 min. The latter solution was added to the former dropwise, then allowed to react for 5 minutes. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in stirring cold pentane (50 mL). A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with cold pentane (2 x 30 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (13 mg, 0.072 mmol, 70%). **^{1}H NMR (800 MHz, CD_3CN) δ:** 6.21 (1H, m, H2), 6.07 (1H, m, H1), 5.30 (1H, m, H6), 3.92 (1H, bs, H3), 2.86 (3H, s, H10), 2.76 (3H, s, H8), 2.68 (1H, m, H4), 2.64 (1H, m, H7), 1.88 (2H, m, H5/H7), 1.56 (1H, q, H5). **^{13}C NMR (201 MHz, CD_3CN) δ:** 174.2 (1C, C9), 133.4 (1C, C2), 128.8 (1C, C1), 60.4 (1C, C6), 56.1 (1C, C3), 38.8 (1C, C7), 32.0 (1C, C5), 30.7 (1C, C4), 29.5 (1C, C10), 27.7 (1C, C8). **HRMS:** Expected = 180.1263 amu; Obtained = 180.1262 amu.



Compound 4.54:

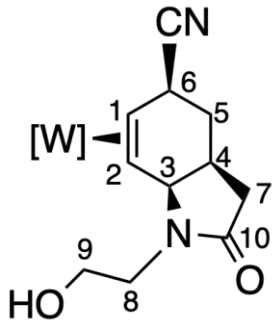
Compound **35** (80 mg, 0.12 mmol) was placed in a test tube with acetone (2 mL). $NOPF_6$ was added (29 mg. 0.17 mmol) and the reaction stirred at room temperature for 10 min. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over

anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (13 mg, 0.074 mmol, 62%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25°C):** 6.12 (1H, m, H2), 6.00 (1H, d, H1), 3.84 (1H, m, H3), 3.42 (1H, m, H6), 2.73 (1H, m, H8), 2.53 (1H, m, H7), 2.45 (1H, m, H4), 2.05 (2H, m, H5/H7), 1.57 (1H, m, H5). **^{13}C-NMR (201 MHz, CD_3CN, δ, 25ºC):** 173.6 (1C, C10), 127.6 (1C, C2),122.0 (1C, C1), 122.0 (1C, C9), 55.6 (1C, C3), 37.5 (1C, C7), 30.3 (1C, C4), 29.5 (1C, C5), 27.4 (1C, C8), 26.7 (1C, C6). **HRMS:** expected= 176.0950 amu; obtained= 199.0847 amu [+Na^+].



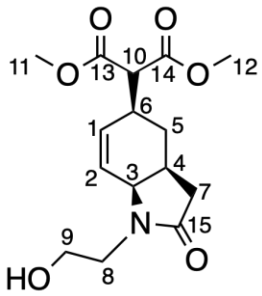
Compound 4.55:

Compound **36** (80 mg, 0.11 mmol) was placed in a test tube with acetone (2 mL). $NOPF_6$ was added (25 mg. 0.14 mmol) and the reaction stirred at room temperature for 10 min. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (20 mg, 0.071 mmol, 69%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25°C):** 5.96 (1H, m, H2), 5.90 (1H, m, H1), 3.82 (1H, m, H3), 3.68 (6H, s, H10/11), 3.33 (1H, d, H9) 2.83 (1H, m, H6), 2.69 (3H, s, H8), 2.56 (1H, m, H7), 2.43 (1H, m, H4), 1.89 (1H, d, H7), 1.63 (1H, m, H5), 1.10 (1H, m, H5). **^{13}C-NMR (201 MHz, CD_3CN, δ, 25ºC):** 174.0 (1C, C14), 169.6 (1C, C12), 169.5 (1C, C13), 134.7 (1C, C1), 125.6 (1C, C2), 56.5 (1C, C9), 56.3 (1C, C3), 53.1 (2C, C11/10), 38.7 (1C, C7), 36.2 (1C, C6), 31.3 (1C, C4), 30.7 (1C, C5), 27.2 (1C, C8). **HRMS:** expected= 281.1263 amu; obtained= 281.1265 amu.



Compound 4.56:

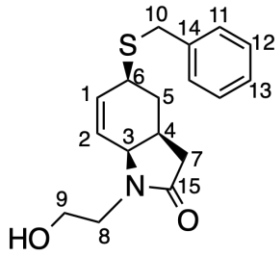
Compound **38** (70 mg, 0.98 mmol) was placed in a test tube with acetone (2 mL). $NOPF_6$ was added (24.0 mg. 0.138 mmol) and the reaction stirred at room temperature for 10 min. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (14 mg, 0.068 mmol, 69%). **^{1}H-NMR (800 MHz, $CDCl_3$, δ, 25°C):** 6.14 (1H, m, H2), 6.04 (1H, d, H1), 4.10 (1H, m, H3), 3.78 (2H, m, H9), 3.68 (1H, m, H8), 3.32 (1H, m, H6), 3.27 (1H, m, H8), 2.72 (1H, m, H7), 2.49 (1H, m, H4), 2.27 (1H, d, H7), 2.09 (1H, m, H5), 1.79 (1H, m, H5). **^{13}C-NMR (201 MHz, $CDCl_3$, δ, 25°C):** 174.6 (1C, C10), 127.1 (1C, C2), 126.5 (1C, C1), 120.0 (1C, C11), 61.8 (1C, C9), 54.5 (1C, C3), 43.6 (1C, C8), 37.0 (1C, C7), 30.4 (1C, C4), 28.4 (1C, C5), 26.4 (1C, C6). **HRMS:** expected= 206.1055 amu; obtained= 206.1057 amu.



Compound 4.57:

Compound **39** (100 mg, 0.123 mmol) was placed in a test tube with acetone (2 mL). $NOPF_6$ was added (30.0 mg. 0.172 mmol) and the reaction stirred at room temperature for 10 min. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried

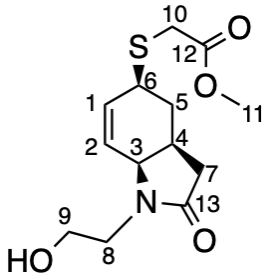
over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (25 mg, 0.080 mmol, 65%). **^{1}H-NMR (800 MHz, $CDCl_3$, δ, 25°C):** 5.98 (1H, m, H1), 5.90 (1H, m, H2), 4.02 (1H, m, H3), 3.68 (6H, s, H14/15), 3.56 (1H, m, H9), 3.51 (1H, m, H9), 3.45 (1H, m, H8), 3.35 (1H, d, H10), 3.14 (1H, m, H8), 2.84, 1H, m, H6), 2.62 (1H, m, H7), 2.43 (1H, m, H4), 1.89, (1H, d, H7), 1.62 (1H, m, H5), 1.11 (1H, m, H5). **^{13}C-NMR (201 MHz, $CDCl_3$, δ, 25°C):** 175.0 (1C, C13), 169.6 (1C, C11), 169.5 (1C, C12), 134.8 (1C, C1), 125.5 (1C, C2), 61.1 (1C, C9), 56.5 (1C, C10), 55.5 (1C, C3), 53.0 (2C, C14/15), 43.6 (1C, C8), 38.7 (1C, C7), 36.1 (1C, C6), 31.8 (1C, C4), 30.3 (1C, C5). **HRMS:** expected= 311.1369 amu; obtained= 311.1371 amu.



Compound 4.58:

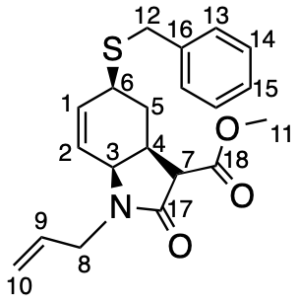
Compound **40** (80.0 mg, 0.099 mmol) with ACN (2 mL) was placed in a test tube. The solution was stirred at room temperature for 10 min. In a separate test tube, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (31.5 mg, 0.139 mmol) with ACN (2 mL) was cooled to -30°C for 10 min. The former solution was added to the later dropwise, then allowed to warm to room temperature over 10 minutes. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (24 mg, 0.079 mmol, 80%). **^{1}H NMR (800 MHz, CD_3CN) δ:** 7.33-7.30 (5H, phenyl ring), 6.05 (1H, m, H1), 5.88 (1H, m, H2), 4.01 (1H, m, H3), 3.77 (3H, s, H11), 3.76 (2H, m, H9), 3.59 (1H, m, H8), 3.31 (1H, m, H8), 3.21 (1H, m, H6), 2.67 (1H, dd, H7), 2.42 (1H, m, H4), 2.24 (1H, d, H7), 1.95 (1H, m, H5), 1.54 (1H, m, H5).**^{13}C NMR (800 MHz, CD_3CN) δ:** 175.7 (1C, C10), 138.1 (1C, C1), 135.5 (1C, C2), 129.0, 128.7, 127.3, 123.7 (6C, phenyl ring), 61.9 (1C, C9), 55.3 (1C, C3), 44.0 (1C, C8), 38.9

(1C, C6), 37.8 (1C, C7), 34.8 (1C, C11), 32.6 (1C, C5), 31.6 (1C, C4). **HRMS:** Expected = 303.1293 amu; Obtained = 303.1298 amu.



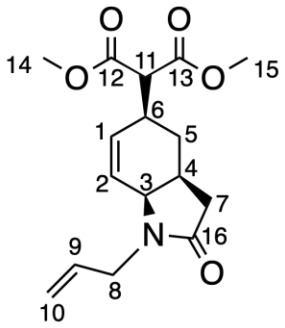
Compound 4.59:

Compound **41** (100.0 mg, 0.127 mmol) with ACN (2 mL) was placed in a test tube. The solution was stirred at room temperature for 10 min. In a separate test tube, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (57.6 mg, 0.254 mmol) with ACN (2 mL) was cooled to -30°C for 10 min. The former solution was added to the later dropwise, then allowed to warm to room temperature over 10 minutes. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (24 mg, 0.077 mmol, 61%). **^{1}H NMR (800 MHz, CD_3CN) δ:** 6.03 (2H, s, H1/H2), 4.02 (1H, d, H3), 3.66 (3H, s, H11), 3.58 (2H, m, H9), 3.48 (2H, m, H8/H6), 3.30 (2H, s, H10), 3.15 (1H, m, H8), 2.57 (1H, m, H7), 2.45 (1H, m, H4), 2.02 (1H, d, H7), 1.97 (1H, m, H5), 1.32 (1H, q, H5).**^{13}C NMR (800 MHz, CD_3CN) δ:** 174. 9 (1C, C13), 172.0 (1C, C12), 134.8 (1C, C2), 126.2 (1C, C1), 61.1 (1C, C9), 55.3 (1C, C3), 52.9 (1C C11), 43.8 (1C, C8), 40.8 (1C, C6), 38.3 (1C, C7), 33.0 (1C, C10), 32.4 (1C, C5), 32.0 (1C, C4). **HRMS:** Expected = 285.1035 amu; Obtained = 285.1038 amu.



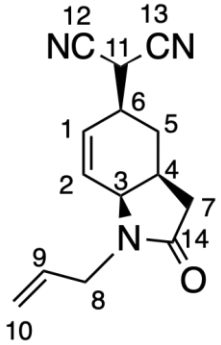
Compound 4.61:

Compound **43** (92 mg, 0.260 mmol) with ACN (2 mL) was placed in a test tube. The solution was stirred at room temperature for 10 min. In a separate test tube, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (120 mg, 0.510 mmol) with ACN (2 mL) was cooled to -30°C for 10 min. The former solution was added to the later dropwise, then allowed to warm to room temperature over 10 minutes. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (49 mg, 0.14 mmol, 53%). **^{1}H NMR (800 MHz, CD_3CN) δ** 7.37 – 7.23 (m, 5H, H13/H14/H15), 5.98 (m, 1H, H2), 5.85 (dt, *J* = 10.2, 3.1 Hz, 1H, H1), 5.74 (ddt, *J* = 16.7, 11.0, 5.7 Hz, 1H, H9), 5.20 (dt, *J* = 17.4, 1.6 Hz, 1H, H10A), 5.16 (dt, *J* = 10.4, 1.5 Hz, 1H, H10B), 4.14 (dt, *J* = 10.3, 4.8 Hz, 2H, H8A/H3), 3.81 (d, *J* = 1.5 Hz, 2H, H12), 3.70 (d, *J* = 1.2 Hz, 1H, H11), 3.61 (dd, *J* = 16.0, 6.4 Hz, 1H, H8B), 3.33 (s, 1H, H6), 2.74 (dq, *J* = 10.5, 4.6 Hz, 1H, H4), 2.27 (m, 1H, H7) 2.06 (dt, *J* = 13.5, 4.7 Hz, 1H, H5A), 1.53 (dt, *J* = 13.8, 9.2 Hz, 1H, H5B). **^{13}C NMR (201 MHz, CD_3CN) δ** 171.2, (1C, C17), 169.3 (1C, C18), 134.2 (1C, C2), 133.7 (1C, C9), 130.4 (1C, C16), 129.92 - 129.50 (3C, C13/C14/C15), 124.9 (1C, C1), 117.7 (1C, C10), 53.9 (1C, C3), 53.0 (1C, C11), 43.6 (2C, C7/C8), 39.3 (1C, C6), 36.3 (1C, C4), 35.5 (1C, C12), 31.3 (1C, C5). **HRMS:** Expected = 357.1399 amu; Found = 357.1399 amu.



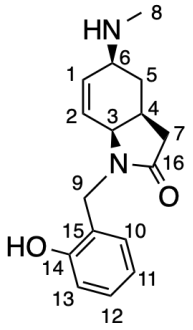
Compound 4.62:

Compound **44** (118.0 mg, 0.146 mmol) was placed in a test tube with acetone (2 mL). $NOPF_6$ was added (35.7 mg. 0.204 mmol) and the reaction stirred at room temperature for 10 min. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (32 mg, 0.10 mmol, 71%). **^{1}H-NMR (800 MHz, CD_3CN, δ, 25°C):** 5.89 (2H, m, H1/H2), 5.73 (1H, m, H9), 5.16 (1H, m, H10), 5.13 (1H, m, H10), 4.06 (1H, m, H8), 3.93 (1H, m, H3), 3.69 (6H, s, H15/H14), 3.57 (1H, m, H8), 3.35 (1H, s, H11), 2.83 (1H, m, H6), 2.60 (1H, dd, H7), 2.43 (1H, m, H4), 1.91 (1H, m, H7), 1.65 (1H, m, H5), 1.13 (1H, m, H5). **^{13}C-NMR (201 MHz, CD_3CN, δ, 25ºC):** 173.9 (1C, C16), 169.5 (2C, C13/C12), 134.5 (2C, C9/C1), 125.5 (1C, C2), 117.0 (1C, C10), 56.3 (1C, C11), 54.7 (1C, C3), 53.1(2C, C15/C14), 43.2 (1C, C8), 38.6 (1C, C7), 36.2 (1C, C6), 31.5 (1C, C4), 30.5 (1C, C5). **HRMS:** expected= 307.1420 amu; obtained = 308.1495 amu [$+H^+$].



Compound 4.63:

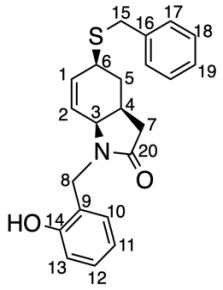
Compound **45** (93 mg, 0.12 mmol) was placed in a test tube with acetone (2 mL). $NOPF_6$ was added (26 mg. 0.15 mmol) and the reaction stirred at room temperature for 10 min. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (22 mg, 0.12 mmol, 73%). **^{1}H NMR (800 MHz, CD_3CN) δ** 6.14 (dt, *J* = 10.1, 3.3 Hz, 1H, H2), 5.94 (dq, *J* = 10.1, 1.5 Hz, 1H, H1), 5.74 (m, 1H, H9), 5.19 (dt, *J* = 17.3, 1.5 Hz, 1H, H10A), 5.13 (dt, *J* = 10.3, 1.4 Hz, 1H, H10B), 4.24 (dd, *J* = 5.2, 0.9 Hz, 1H, H11), 4.07 (ddt, *J* = 16.1, 4.5, 2.2 Hz, 1H, H8A), 3.98 (t, *J* = 5.1 Hz, 1H, H3), 3.64 (m, 1H, H8B), 2.91 (m, 1H, H6), 2.65 (dd, *J* = 16.8, 8.2 Hz, 1H, H7A), 2.51 (m, 1H, H4), 2.03 (d, *J* = 16.8 Hz, 1H, H7B), 1.92 (d, *J* = 1.4 Hz, 1H, H5A), 1.27 (s, 1H, H5B).**^{13}C NMR (201 MHz, CD_3CN) δ** 173.8 (1C, C140, 134.3 (1C, C9), 130.7 (1C, C1), 129.3 (1C, C2), 117.5 (1C, C10), 113.5 (1C, C12), 113.5 (1C, C13), 54.5 (1C, C3), 43.4 (1C, C8), 38.3 (1C, C7), 37.4 (1C, C6), 30.7 (1C, C4), 30.0 (1C, C5), 28.9 (1C, C11). **HRMS:** Expected = 241.1215 amu; Found = 241.1216.



Compound 4.64:

Compound **47** (81 mg, 0.10 mmol) was placed in a test tube with no solvent at -40 °C for 10 min. In a separate test tube, $NOPF_6$ (26 mg, 0.15 mmol) with ACN (2 mL) was cooled to -40°C for 10 min. The latter solution was added to the former dropwise, then allowed to react for 5 minutes. The reaction was washed three times (H_2O:NH4Cl/DCM; 30mL/30mL) and the DCM layers discarded. The aqueous layer was then washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL). The DCM layer was evaporated in vacuo to yield a clear oil (19 mg, 0.070 mmol, 67%). **^{1}H NMR (800 MHz, CD_3CN) δ** 7.21 (dd, *J* = 7.5, 1.7 Hz, 1H, H10), 7.17 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 1H, H12), 6.83 (dd, *J* = 8.1, 1.2 Hz, 1H, H13), 6.82 (dd, *J* = 7.4, 1.2 Hz, 1H, H11), 6.35 (m, 1H, H2), 6.19 (dd, *J* = 10.2, 1.7 Hz, 1H, H1), 4.48 (d, *J* = 15.3 Hz, 1H, H9A), 4.24 (d, *J* = 15.3 Hz, 1H, H9B), 3.97 (s, 1H, H3), 3.78 (m, 1H, H6),

2.71 (dd, *J* = 17.3, 8.2 Hz, 1H, H7A), 2.55 (m, 1H, H4), 2.50 (s, 3H, MeNH2), 2.15 (2H, H7B & H5B), 1.43 (m, 1H, H5A).**^{13}C NMR (201 MHz, CD_3CN) δ** 167.54 (1C, C16), 131.93 (1C, C10), 130.58 (1C, C12), 129.65 (1C, C1), 128.99 (1C, C2), 127.30 (2C, C14/C15), 120.55 (1C, C11), 55.18 (1C, C3), 54.97 (1C, C6), 41.43 (1C, C9), 37.92 (1C, C7), 30.19 (1C, C8), 29.74 (1C, C4), 28.04 (1C, C5). **HRMS:** [M-H+] expected = 273.1598 amu; [M-H+] found = 273.1599 amu



Compound 4.65:

Compound **48** (100 mg, 0.274 mmol) with ACN (2 mL) was placed in a test tube. The solution was stirred at room temperature for 10 min. In a separate test tube, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (124 mg, 0.547 mmol) with ACN (2 mL) was cooled to -30°C for 10 min. The former solution was added to the later dropwise, then allowed to warm to room temperature over 10 minutes. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (63 mg, 0.17 mmol, 63%). **^{1}H NMR (800 MHz, CD_3CN) δ** 7.27 (1H, dd, H17), 7.23 (1H, dd, H19/H10), 7.12 (1H, ddd, H12), 6.82 (2H, dd, H13/H11), 6.13 (m, 1H, H2), 6.03 (dd, 1H, H1), 4.44 (d, 1H, H8), 4.24 (d, 1H, H8), 3.95 (s, 1H, H3), 3.68 (s, 2H, H15), 3.27 (dd, 1H, 6), 2.61 (dd, 1H, H7), 2.42 (m, 1H, H4), 2.08 (1H, m, H7), 1.90 (m, 1H, H5) 1.32 (1H, m, H5).**^{13}C NMR (201 MHz, CD_3CN) δ** 176.9 (1C, C20), 156,8 (1C, C14), 139.8 (1C, C16), 136.2 (1C, C1), 132.2 (1C, C10), 130.7 (1C, C12), 129.9 (1C, C17), 129.5 (1C, C18), 129.5 (1C, C18), 127.9 (1C, C19), 125.0 (1C, C2), 124.0 (1C, C9), 120.6 (1C, C11), 118.0 (1C, C13), 55.9 (1C, C3), 41.7 (1C, C8), 40.0 (1C, C6), 38.1 (1C, C7), 34.5 (1C, C15), 32.9 (1C, C5), 31.9 (1C, C4). **HRMS:** [M-H+] expected = 365.1450 amu; [M-H+] found = 365.1453 amu

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Chapter 5 : An organometallic approach to the stereoselective synthesis of heteropolycyclic compounds through a benzene dearomatization

5.1 Introduction

Natural products and their derivatives continue to play a vital role in the discovery of new medicines, especially for treatments in cancer and infectious diseases.[1] Such structures have well-defined three-dimensional architectures, rich in carbon stereocenters, that are optimized for specific interactions with proteins. Molecules rich in stereogenic centers have greater ability to optimally fill space in a given receptor binding site, hence such complexity is strongly correlated with clinical success.[2] The overreliance on combinatorial methods featuring sp^2-sp^2 linkages has limited the effectiveness of current molecular libraries,[3-4] owing to generally poor binding specificities. This realization has brought a renewed focus on natural product-like motifs.[5] These pseudo-natural products, defined as natural product-like fragments, are not readily accessible through biosynthesis,[6] and are increasingly being recognized as valuable targets in drug discovery. This is particularly the case for polycyclic structures,[7-8] where incorporation into molecular libraries has been slower than expected.[9] The increased rigidity and complex structure of polycyclic compounds make them ideally suited for optimized and selective receptor interactions.[1]

The burgeoning field of dearomatization seeks to leverage the synthetic potential of aromatics through a number of diverse approaches including photoactivation,[10-11] high pressures,[12] enzymatic protocols,[13-14] and activation through transition metals.[15-16] The most common dearomatization strategy using metals is to coordinate the arene through all six of its carbons (η^6).[15, 17] Specifically, coordination to metals such as chromium,[18] manganese,[19] and iron[19] render the benzene electron-deficient thereby promoting the addition of nucleophiles to the aromatic core. While most of these reaction strategies result in substituted benzenes,[20] compounds such as cyclohexadienes[21] and cyclohexenones[20] can also be prepared under suitable conditions. It is also possible, however, to bind the benzene substrate through fewer carbons (e.g., η^2), enabling the remaining carbons of the ring to participate in conventional alkene reactions.[16]

Over the past three decades, our research group has endeavored to develop the chemistry of η^2-bound benzene complexes of osmium,[22] rhenium,[23] molybdenum,[16] and tungsten.[16] With the metal bound to only two carbons of the aromatic ring, the remaining four carbons are available for the addition of various chemical fragments. If such fragments can be linked together, before or after addition to the aromatic ring, the process would establish a blueprint for novel polycyclic architectures (**Figure 5.1, A, II, III**).[16] With the appropriate choices of "bridges", polycyclic structures could be designed to resemble natural products (**IV**-**VI**) and could find use in diversity-oriented synthesis (DOS),[24-26]

biological-oriented synthesis (BiOS),[27] and function-oriented synthesis (FOS)[28-31] approaches to drug discovery.

When a π-basic transition metal fragment binds to an arene (η^2), electron density flows from the metal into the arene π system. Correspondingly, early examples of the synthesis of polycyclic compounds from η^2-benzenes were initiated by addition of carbon electrophiles, as shown in **Figure 5.1 B**. Typically, these were Michael acceptors,[32-34] acetals,[35] and less commonly ketenes,[35] and carbenes.[36] In the present study complementary methods for the formation of polycyclic cores are investigated using nucleophilic bridges, primarily using those heteroatoms most commonly found in natural products (N, O, S). Given the highly electron-rich nature of the transition-metal-bound arene, each nucleophilic addition must be preceded by the addition of an electrophile to reverse the polarization of the metal-ligand interaction. In a recent study utilizing phenylsulfone complexes of tungsten,[37] the aromatic ring demonstrated the ability to accept up to three independent nucleophiles, thereby forming trisubstituted cyclohexene complexes.[37] We hypothesized that by tying these nucleophiles together, we could gain access to novel fused tricyclic or even tetracyclic cores. If such a reaction sequence could be developed, it would provide a highly modular approach to a class of polycyclic compounds, rich in carbon stereocenters and underrepresented in druggable chemical space **(Figure 5.1 C)**.

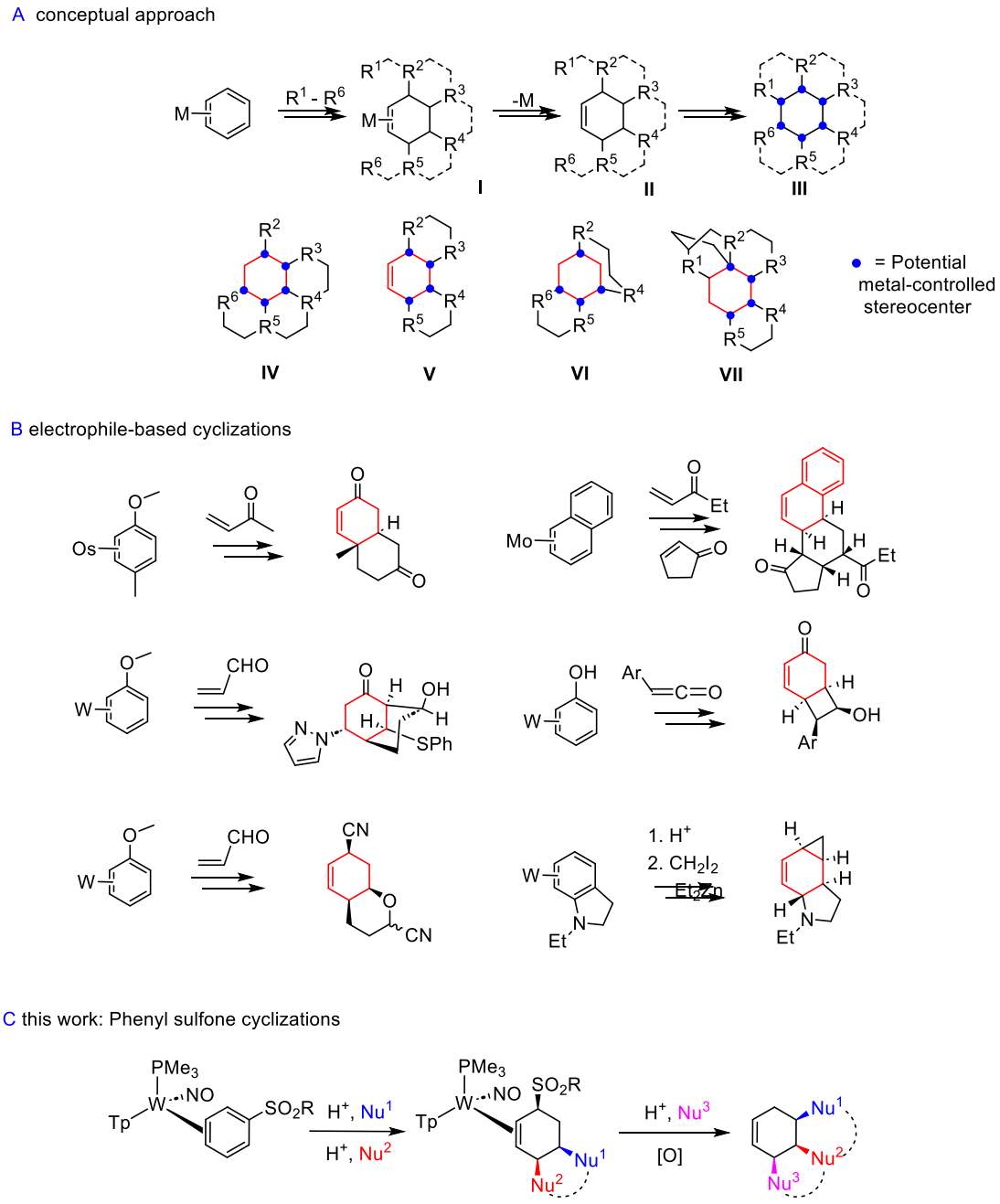

Figure 5.1 Panel **A** shows the conceptual approach to synthesis of polycyclic cores using benzene as the nucleus. Panel **B** shows previous examples of cyclizations with η^2-benzene complexes, all of which utilize carbon electrophiles and form a single new ring. Panel **C** shows this chemistry to the synthesis of tricyclic and tetracyclic molecules using "double nucleophile" bridges.

5.2 Results

5.2.1 Generation of Novel Polycyclic Cores from Diamines

Previously,[38] we demonstrated that protonation of the benzene ligand of WTp(NO)(PMe_3)(▪ ^{2}-benzene) followed by addition of an ester enolate produces a cyclohexadiene complex. Further protonation followed by the addition of an excess of a primary amine generates the tetrahydroindolone core. If similar chemistry was accessible for a phenyl sulfone derivative then the sulfinate group could serve as a leaving group to achieve an additional cyclization (**Figure 5.2 A**). Our study commenced with WTp(NO)(PMe_3)(3,4-η^2-$PhSO_2Me$) (**1**), which can be prepared on a multigram scale.[39] Diene complexes **2** - **4** were prepared in good yield via sequential addition of acid followed by an ester enolate. [37] We hoped to carry out the lactam formation with a primary amine connected to a second heteroatom nucleophile that could in turn displace the sulfinate group. For our strategy to be successful, following lactamization the addition of the tethered nucleophile (Nu^3) needed to occur faster than the competing elimination reaction, as described in **Figure 5.2 B**. Gratifyingly, when **2** – **4** were combined with 2 eq each of triflic acid (HOTf), excess ethylenediamine, and stirred at -30°C, the major product formed was a tricyclic (**5** – **7, Figure 5.2 A**). Several intermediates were observed by stopping the reaction early, but if the mixture was allowed to stir a full 72 hours the intermediates gave way to the desired products (**5** – **7**), provided that during the work up the product mixture was under basic conditions (vide infra). This one-pot reaction sequence was shown to be remarkably general, and was successful with a number of commercially available 1,2-diamines to give a triazaacenaphthylene core (**5** – **17**). In the case where steric interactions differentiated the two primary amine groups, the less encumbered nitrogen selectively formed the lactam ring (**8**-**11**). Ethanolamine also gave satisfactory results (**18**). When 1,3-diamines or 1,4-diamines were used, tricyclics containing seven- and eight-membered rings were formed, respectively (**19** – **122**). 2D NMR data techniques (COSY, NOSEY, HSQC, HMBC) were used to confirm the structure of every compound (**Figure 5.2 A**) along with SC-XRD data for complexes **5**-**16**, and **18**-**21**. These compounds were observed to be stable as solids, or in a basic solution, but partially underwent a ring-opening reaction under mild acidic conditions or long periods (3-7 days) in solution at ambient temperature, forming diene lactams analogous to **26** – **28** (**Figure 5.2 B**). Hence cold reaction temperatures and basic workup conditions were paramount in successfully running the reactions to completion with high purity. In the case of NH_2—Nu^3 = (±)-*trans*-1,2-diaminocyclohexane, a mixture of stereoisomers for **15**

resulted, owing to the racemic mixture of the phenylsulfone complex **1** used in the reaction. However, the stereoisomer *rel-(S,R,S,R,R)*-**15** could be separated from the others in pure form via recrystallization. When the reaction sequence described above was run under colder temperatures (-60 °C, 72 h), a new species was observed (**Figure 5.2 C**) typically as a mixture along with the fused tricyclic complexes. In one example (**23**), a single compound could be separated from its tricyclic analog **18.** Spectroscopic features for **20** were similar to those observed for **15**, but NOE data indicate that both allylic carbons of the bound alkene were connected to heteroatoms, with H6 oriented toward the PMe_3 ligand. A homologue of the 2-aminoethanol-derived (**24**) could also be prepared from 3-aminopropanol (**26**) that had no fused tricyclic counterpart observed. Meanwhile, whereas the bridged tricyclic **23** could be prepared as the dominant species at -60 °C, we were unable to separate **24** from its fused tricyclic isomer **5**. A full spectroscopic analysis revealed that this family of compounds **23**-**25** were rare examples of N-C6 bridged indolones. Regrettably, our attempts to grow single crystals of **23** or **24** species resulted in conversion to a mixture containing the fused tricyclic species (e.g. **5** or **18**) and diene complexes (**27** or the analog of **23**).

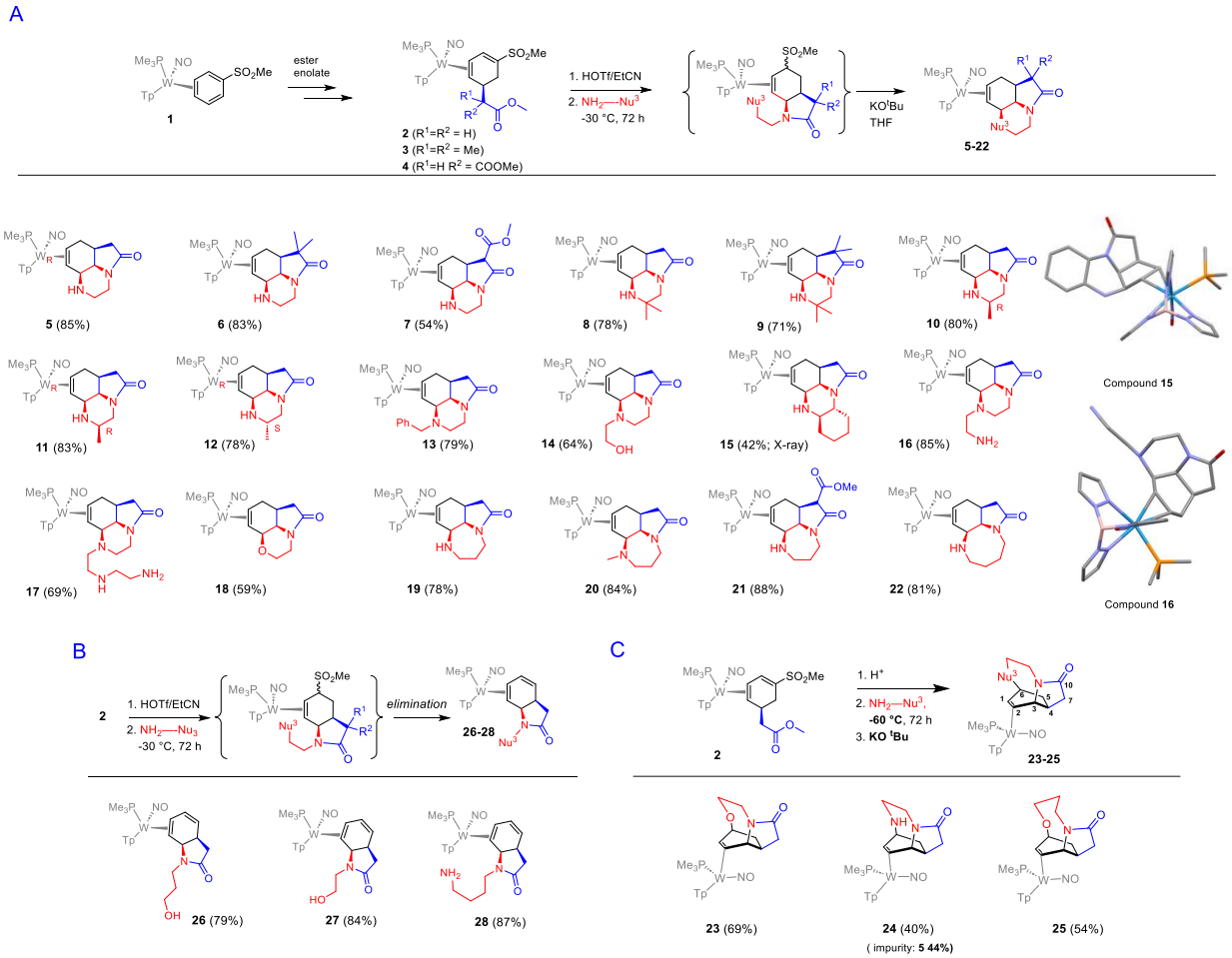

Figure 5.2 Multicyclic products obtained through the reaction with diamines. A) Fused tricyclic compounds, B) Diene lactam complexes produced as biproducts of tricyclic formation. C) Bridged tricyclic compounds.

5.2.2 Mechanistic Insight for the Novel Reactivity Pattern

The likely mechanism for the formation of the fused and bridged polycyclics starts with the protonation at the terminal position of the diene (C5 of **2**; **Figure 5.3**). The resulting ▪ ^{2}- allyl complex exists in two conformations (**IP** and **ID**) differing by the position of the carbenium carbon (C6 for proximal to the PMe_3 (**IP**) or C3 if distal to the PMe_3 (**ID**)). According to DFT calculations, the distal form is favored by 4.8 kcal/mol, influencing the amine to add to C3, adjacent to the ester group, thereby inducing the desired lactamization. This places the sulfone group in **IV** in an allylic position. Subsequent metal-stabilized loss of the sulfinate group forms a secondary allyl species (**III**), also present as two conformers. In contrast to the initial allyl (**I**), the distal conformer is roughly equal in free energy to the proximal form, owing to the electron-withdrawing nature of the amide nitrogen. This is consistent with the formation of an alternative tricyclic species that can

be formed at low temperatures, where the tethered nucleophile adds to C6 of **IIIP** rather than C3 of **IIID**. As described earlier, at cold temperatures (-60 °C) and basic reaction conditions (potassium tert-butoxide), we were able to trap and isolate the bridging tricyclics **23** – **25** (**Figure 5.2 C**). Calculations support the observation that the bridged tricyclics may be kinetically competitive, but that they are strongly thermodynamically disfavored compared to the fused tricyclics. For example, the ethylenediamine-derived bridged tricyclic **24** is 11.8 kcal less stable than its fused tricyclic isomer **5**. As shown in **Fig. 3**, in cases where the allyl species **III** fails to evolve into a tricyclic, elimination can occur to form the diene lactam **28**. Interestingly, even though the diene lactam **28** is roughly 4 kcal/mol less stable than its fused tricyclic isomer **5**, spectroscopic evidence confirms its formation as part of the decomposition of **24**. Meanwhile, there is no experimental indication of a purported dienamide isomer of type **V**, even though DFT calculations place such a species about 3 kcal/mol lower in energy than the diene **28**. Finally, calculations for the ethylene-derived tricyclic **5** indicate that the purported trans-fused isomer of **5** was only marginally disfavored (0.7 kcal/mol), although there was no sign of this species experimentally. Apparently, the kinetic barrier required for the allyl species **IIID** to bring the tethered amino group to C3, syn to the metal (**VI**) is too high to be competitive with addition anti to the metal.

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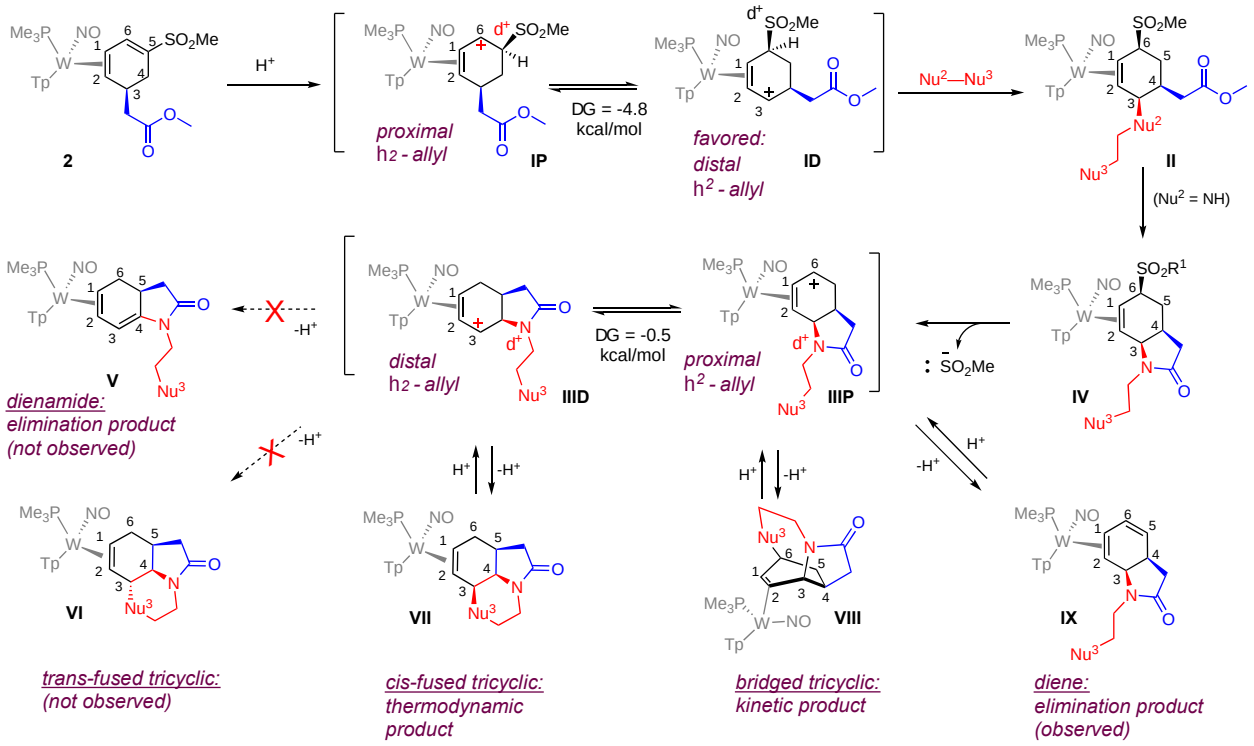


Figure 5.3 Mechanistic representation of the synthesis of fused and bridged tricyclic compounds.

5.3.3 Formation and Mechanism of Polycyclic Cores from Aniline Derivatives

Aniline derivatives were also considered as candidates for lactamization and subsequent ring closure. Encouraged by the reactivity displayed by ethylenediamine, we first explored *o*-phenylenediamine. Initially, results were puzzling, as the signals in the ^{1}HNMR spectrum revealed a mixture of two products, neither of which corresponding to the patterns observed for the fused or bridged tricyclics (**Figure 5.2 A** and **5.2 C**). In particular, an ester methoxy signal was present for both compounds. After thorough evaluation of 2D NMR data, it was posited that the two products formed were **29** and **31** (**Figure 5.4 A**), where the cyclization that occurred did not involve a lactamization. The scope for this reaction pattern was expanded using other aniline derivatives including *o*-aminothiophenol (**33**), *o*-aminophenol (**30**, **32**), and 2,3-diaminonapthalene (**34**), where Nu^2 is defined as the first of the two nucleophiles to add. We noticed similar behavior with thiols, including *o*-benzenedithiol (**39**), 2-mercaptophenol (**40**), and aliphatic variants such as ethanedithiol (**35**, **38**), and cysteamine (**36**, **37**). In addition to the methoxy signal, Compounds **29 - 41**, show a clear NOE interaction between the PMe_3 and the allylic methine proton H6. Further, a splitting pattern for H1 and H2 is observed to significantly differ from that seen for the fused and bridged lactam tricyclics (SI), indicating a different

cyclohexene ring conformation in these bi- and tricyclic esters: XRD data was successfully obtained for compounds **30**, **33**, **34**, **35**, **38**, **39, 40** and **41** demonstrating the half-chair nature of the cyclohexene ring as opposed to the boat conformation observed for the fused tricyclics. Particularly, compound **41** was purified through crystallization as, this was observed to be a biproduct toward the formation of **15**.

While the reactions forming the ester polycyclics **29**-**41** did not yield the originally desired products, they did provide some additional mechanistic insight. Whereas primary aliphatic amines were successful in forming the desired lactam ring, in the case of arylamines, lactamization is not as favorable, presumably due to the weaker nucleophilicity of the amine. Compounds of the type **II** could only be isolated when the nucleophile was ethanedithiol (SI, **42**). Indeed, loss of the sulfinate occurs readily (**II** → **X-P Figure 5.4 B**) followed by addition of a second arylamine (X**II**, **Figure 5.4 B**). Loss of the labile distal arylamine ligand in **XII** generates allyl **XIII-D**. An allyl shift to **XIII-P** then leads to the ring-closure that generates compounds of type **XIV**. In two cases (**29** and **30**), we observed a competing process in which loss of the sulfinate was immediately proceeded by a ring-closure to form compounds of type **XI** (formed as a mixture with **XIV**). This cyclization likely occurs for many of these complexes but is reversible. Indeed, whereas **29** could not be purified from **31**, **30** was successfully separated from **32** through recrystallization of **30** in a solution of acetonitrile (SI). When Nu^3 is an aliphatic nitrogen, the bond between the allylic carbon and Nu^3 is sufficiently inert that compounds of type **XI** can be isolated. Where Nu^3 is O or S, **XI** reopens, allowing the reaction to proceed to bicyclic compound of type **XIV**. An exception to this general trend occurs with cysteamine, where we speculate that the nitrogen is actually protonated (a zwitterionic form of cysteamine), thereby preventing the ring-closure from occurring to form **XI**. Parenthetically, the lack of an o-phenylenediamine lactam also led us to investigate aniline itself as a potential nucleophile toward lactamization. Consistent with our mechanistic hypothesis that aniline derivatives are not sufficiently nucleophilic to form the lactam, allyl formation was was observed when the parent complex **2** was added to aniline (SI, **80**).

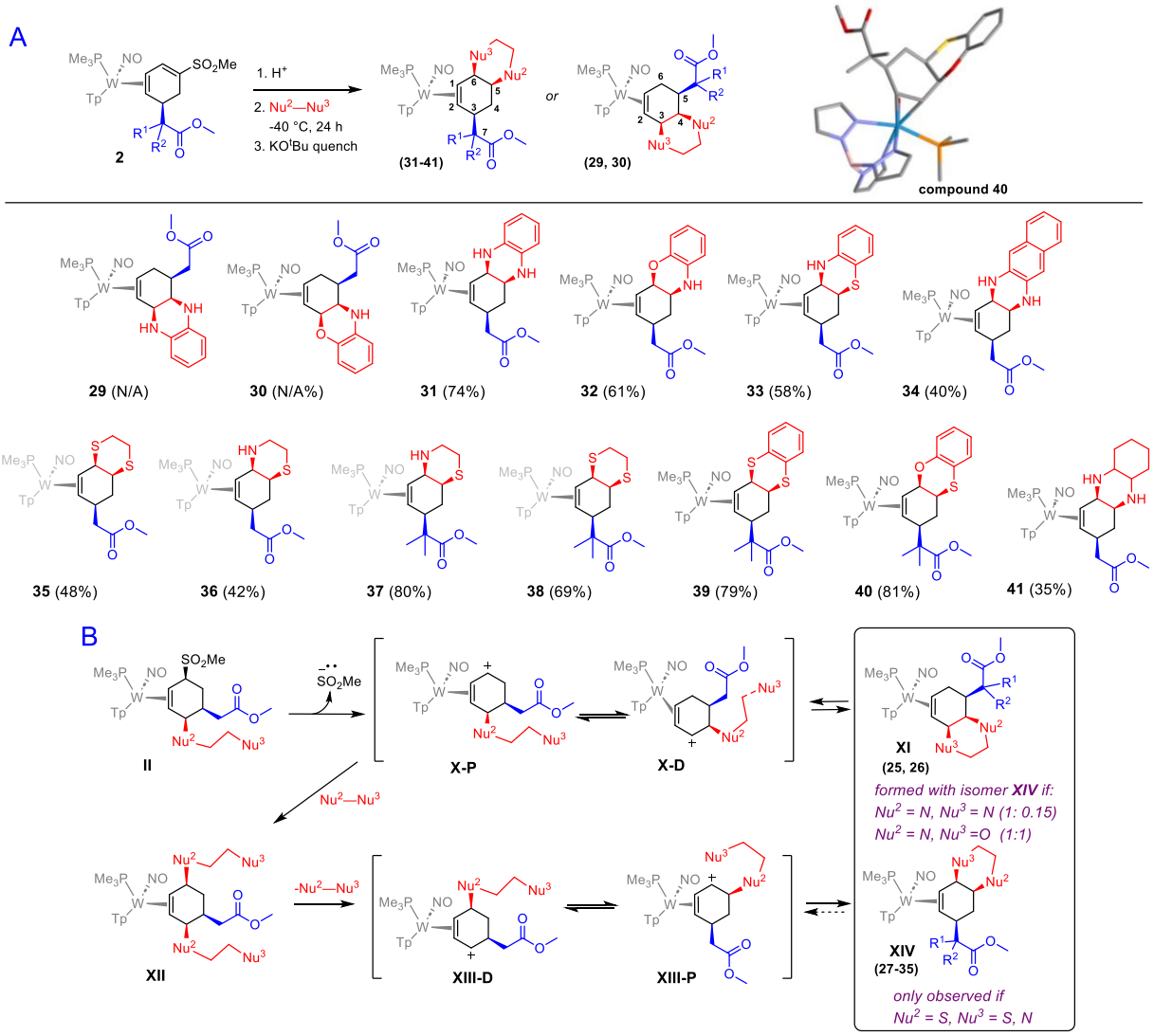


Figure 5.4 Formation of fused bi- and tricyclic esters. A) Range of heterocycles formed with pendant ester group. B) Proposed mechanism for the formation of bicyclic compounds 25-35, where loss of sulfinate group occurs prior to lactam formation.

5.3 Liberation of Novel Polycyclic cores

In an effort to liberate the synthesized polycyclic molecules from the {WTp(NO)(PMe_3)} fragment, several different approaches were employed. In most cases, 1-2 eq of Br_2 proved effective in liberating the organic product (e.g., **43-57** in **Figure 5.5**) with yields ranging from 58-73%. When the organic polycyclic contained sulfur, oxygen, or an aryl amine, this approach was generally unsuccessful, as the effect of the oxidant resulted in loss of the heteroatom and reformation of an allyl tungsten complex. In some of these cases, the use of DDQ was shown to be effective (e.g. **58, 59, 62-63, 65**) with yields ranging from 57%-74%. However, compounds of the type **64** was obtained by stirring the

parent complex **32** in acetonitrile over the course of a week. Unfortunately, the bridging tricyclics shown in **Figure 5.2 C** also proved elusive. **Figure 5.5 A** summarizes the successfully isolated organics.

Given the potential value of these polycyclic cores as precursors for novel pharmaceutical leads, we sought the ability to prepare such compounds in enantioenriched form. Complex **1** can be synthesized from a similar enrichment procedure published previously.[38] To demonstrate the successful synthesis of enantioenriched cores, we initially carried out the synthesis **44** from enantioenriched **5**. To our delight, the synthetic pathway worked cleanly on this precursor, leading us to seek more complex structures. We then explored compounds in the likes of **10** and **11**, which were then elaborated into their liberated organics (*R*)-**48** (77%), and (*S*)-**49** (72%). HPLC analysis using a Chiralpak IC-3 column determined that (*R*)-**48** and (*S*)-**49** were prepared with an er 20>1 for compounds 44, (*R*)-**48** and (*S*)-**49**.

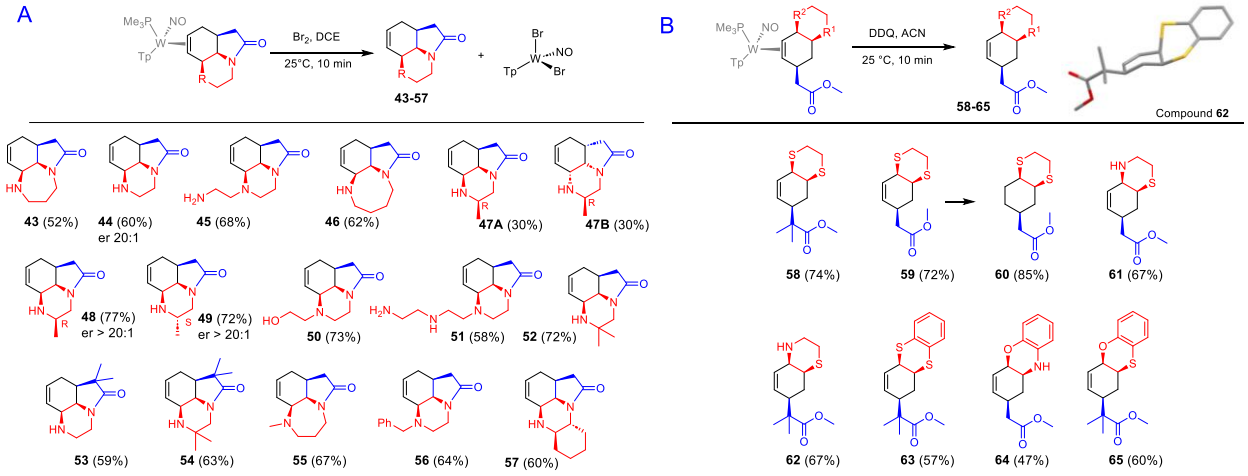


Figure 5.5 The oxidative decomplexation of heteropolycyclics. Panel A: oxidation via bromine. Panel B: oxidation via DDQ**.**

5.4 Expansion of Reactivity in Cycloaddition Chemistry

Although the emphasis on this study has been with heteroatom nucleophiles (Nu^2 and Nu^3), we recognize the hydroacenaphthene core is also prominent in natural products. To this end, we sought to demonstrate the methodology described in **Figure 5.1** where Nu^3 was a carbon. Selecting 2-(aminomethyl)indole as the bridging-nucleophile, we prepared the indolone **66** from ester **2**, in a similar manner to that shown in **Figure 5.2 A**. Upon standing for 1 day at -30 °C, then at room temperature for a day, this species slowly evolved cleanly into the pentacyclic **66**. Stirring **66** in acetonitrile for a week afforded the final organic **67** in 55% yield (one-pot from ester **2**).

Benzene offers a unique scaffold in providing a ring of six unsaturated carbons as potential stereocenters. Our focus is now shifting to methods that utilize the remaining ring carbons. One approach takes advantage of the ability of Selectfluor to oxidize η^2-diene complexes to biallylic ether complexes.[36, 40] Given the lability of alkoxy groups at the allylic positions of this tungsten system, such an oxidation could provide additional points of attachment for cyclizations. To demonstrate this, we treated the diene lactam **68** with Selectfluor in the presence of MeOH to generate the tricyclic **70**, an analogue of tricyclic **18** with an allylic methoxy group and an additional carbomethoxy tether (**Figure 5.6 B**). Exposing this material to acid followed by methylamine provided the tetracyclic bis-lactam **74** in good yield. A similar process delivers the seven-member ring analog **75**. A crystal structure of **75** confirms the all-cis stereochemistry of the tetracyclic ring system. Further action with DDQ provides the final tetracyclics, **76** and **77**, and an SC-XRD analysis of the organic **77** confirms its structure.

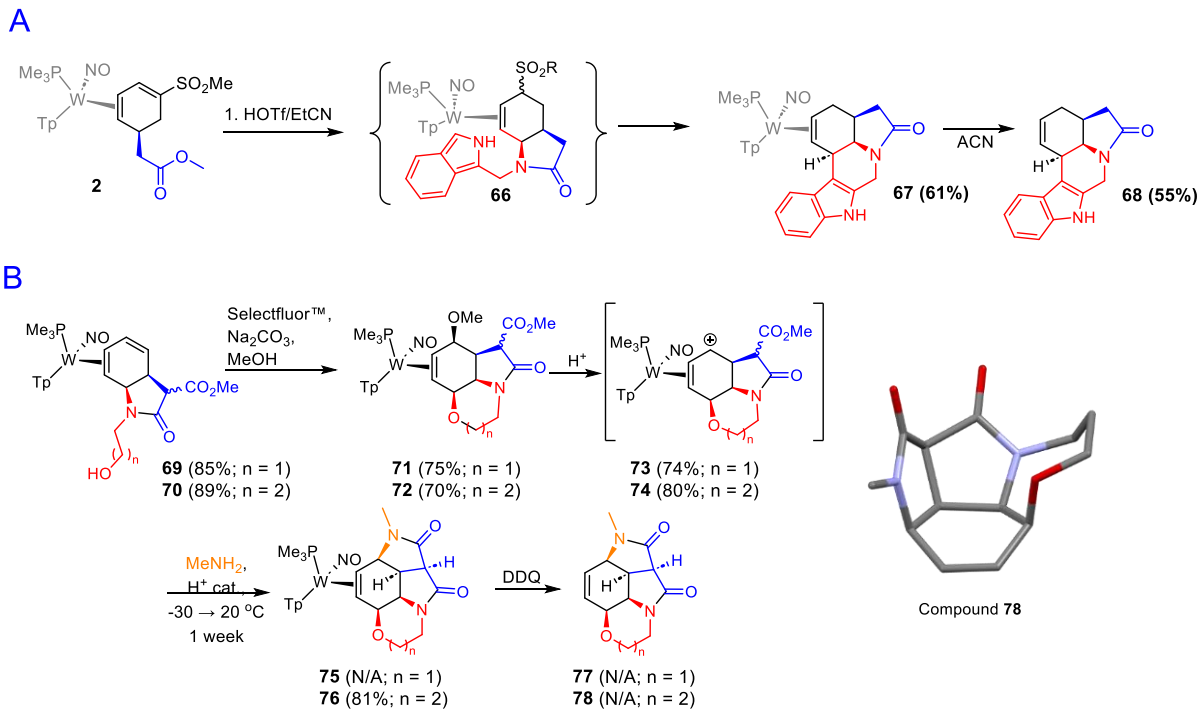


Figure 5.6. Preparations of more advanced heteropolycyclics. Panel A shows the preparation of an indolizidine pentacyclic via 2-(aminomethyl)indole. Panel B shows the preparation of bis-lactam polycyclics prepared from dimethylmalonate.

5.5 Discussion

The field of dearomatization is growing exponentially,[40-42] motivated by the ability to leverage multiple carbons of an aromatic ring in the synthesis of more complex products. Most of such reactions that result in a new ring involve only one or two carbons of the aromatic substrate, whereas polycyclizations of aromatics are virtually absent in the literature. One exception is recent synthesis of the pentacyclic core of the lycorine family carried out with tungsten, but this still represented only one new ring formed while the arene was bound to the metal.[43] Other examples include the photocyclization of phenylalkene derivatives in the synthesis of penifulven C [44] and ceratopicanol.[45] These examples all involve carbon-carbon linkages rather than heteroatoms.

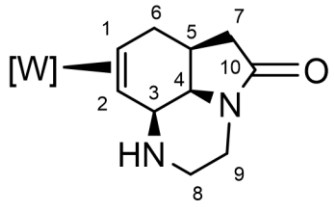
Many of the top selling pharmaceuticals contain tri-, or tetracyclic molecules with carbon stereocenters incorporated in the polycyclic core.[46] Examples include steroids (e.g., Symbicort, Trelegy, Relvar, Zytiga, Seretide, Mirena, Flixotide, Pulmicort, Premarin, Avodart, Breztri, Faslodex, and Medrol), tri- and tetracyclics incorporating nitrogen heterocycles (e.g., Biktarvy, Tivicay, Triumeq, Latuda, Dovato, Ingrezza, Austedo, Juluca, Cialis, Cabenuva), tetracycline antibiotics, (e.g., Vibramycin, Arestin, Xerava, Seysara, Nuzyra), taxol derivatives (e.g., Abraxane, Jevtana), and tri- and tetracyclic antidepressants (e.g., Ludiomil, Tolvan, Remeron, Coaxil). Other appearances of tricyclic nitrogen cores include the stemona[47] and lycorine[48] alkaloid families, many of which include the all-cis [6/6/5] core[48] analogous to **44** or the all-cis-[6/7/5] core[47] analogous to **43**. Yet remarkably, synthetic routes to the [6/6/5], [7/6/5], [8/6/5], [6/6/6], [6/6/5/5], [6/7/5/5], [6/6/6/5], and [6/6/6/6] cyclic skeletons (CSK) [9] (regardless of atom type) shown in **Figure 5.5** and **Figure 5.6** with all-cis ring junctures are practically absent in the chemical literature, likely owing in part to the lack of general methods to prepare them. An important exception is the lycorine family of compounds, for which numerous synthetic approaches have been reported. Baudoin et al have demonstrated an attractive synthesis of γ -lycorane in which a benzene precursor was hydrogenated to generate the required all-cis stereochemistry.[49] Over- and mis-hydrogenation were competing reactions, and the synthesis of the aromatic precursor required a challenging double Pd catalyzed C(sp^2)-H/C(sp^3)-H arylation. In comparison, the one-pot double cyclization methodology described herein is more modular and does not rely on precious metal catalysts.

Like γ-lycorane, tricyclic compounds (**43** – **57**) in **Figure 5.5** and tetracyclics (**68**, **77**-**78)** in **Fig. 5.6** meet all the criteria for Lipinski's rule of five[50] for evaluating drug likeliness, as well as the criteria of Ghose,[51] Veber,[52] Egan,[53] and Muegge,[54] and are in a molecular

weight range that is ideal for fragment libraries.[55-56] The same holds true for the tricyclic compounds **63-65** in **Figure 5.5**, none of which core is found in the literature. Even the cis-fused bicyclics in **Figure 5.5** (e.g., **58**-**62**) are not well represented (11 examples of *cis*-1,4-thiaazadecalins and 16 examples of *cis*-1,4-dithiadecalins). We believe the lack of conventional synthetic methods combined with the predicted bioavailability and drug likeliness of the compounds in **Figure 5.5** and **Figure 5.6** makes a strong case for this methodology providing access to an unexplored region of chemical space where there is a high chance of identifying new lead compounds.

Experimental:

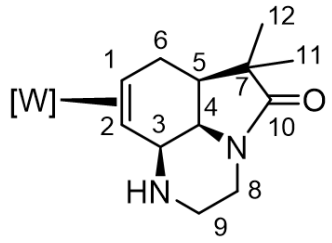
NMR spectra were obtained on 500, 600, or 800 MHz spectrometers. Chemical shifts are referenced to tetramethylsilane (TMS) utilizing residual ^{1}H signals of the deuterated solvents as internal standards. S46 Chemical Shifts are reported in ppm and coupling constants (J) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a solid on a spectrometer with an ATR crystal accessory, and peaks are reported in cm^{-1}. Electrochemical experiments were performed under a nitrogen atmosphere. Most cyclic voltammetric data were recorded at ambient temperature at 100 mV/ s, unless otherwise noted, with a standard three-electrode cell from +1.8 to −1.8 V with a platinum working electrode, acetonitrile or N,N-dimethylacetamide (DMA) solvent, and tetrabutylammonium (TBAH) electrolyte (∼1.0 M). All potentials are reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2}$= −0.78 V, −1.75 V) or ferrocene ($E_{1/2}$=0.55 V) as an internal standard. The peak separation of all reversible couples was less than 100 mV. All synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere unless otherwise noted. All solvents were purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes and were purged with nitrogen under an inert atmosphere. When possible, pyrazole protons of the tris(pyrazolyl)borate (Tp) ligand were uniquely assigned (e.g., "Tp3B") using two-dimensional NMR data. If unambiguous assignments were not possible, Tp protons were labeled as "Tp3/5 or Tp4". All J values for Tp protons are 2(±0.4) Hz. BH peaks (around 4−5 ppm) in the ^{1}H NMR spectra are not assigned due to their quadrupole broadening; However, confirmation of the BH group is provided by IR data (ca 2500 cm−1). Compounds **1**, **2**, **3**, **4** and **80** have been previously reported. Full characterization of compounds is provided in the SI. Ground-state structures were optimized at the M06 level of theory using the 6-31G**[LANL2DZ for W] basis set in Gaussian 16. Previous literature demonstrates that this functional and basis set choice accurately corroborates experimental results. Vibrational frequency analysis verified that optimized structures were minima, and rigid-rotorharmonic-oscillator thermochemical chemical corrections were applied at 298 K and 1 atm utilizing Gaussian's default implementation. When solvent corrections were applied to estimate DGsolv, optimization and frequency calculations were performed using the SMD continuum solvent model with the appropriate solvent's parameters from Gaussian.



Compound 5.5:

Compound **2** (500 mg, 0.682 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. After 10 min, a 1 M HOTf/EtCN (1.36 mL, 1.36 mmol) solution was added to the test tube and the solution was allowed to stir at -20 °C for 60 min. In a separate test tube, ethylene diamine (0.91 mL, 13.6 mmol) in EtCN was cooled at -20 °C for 20 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. A 20% KO^{t}Bu/THF solution (2.06 mL, 3.41 mmol) was added dropwise to quench the reaction. The reaction was washed three times (H_2O:Na_3PO_4/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **5** (396mg, 0.581 mmol, 85.3%, 50.1%-85.3%).

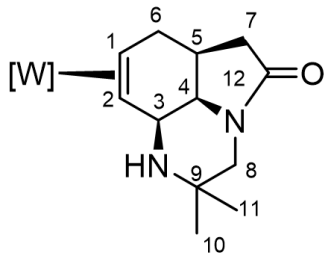
^{1}H-NMR (d_3-MeCN, δ, 25 C): 9.26 (1H, d, TpA3), 8.07 (1H, d, TpB3), 7.89 (1H, d, TpB5), 7.84 (1H, d, TpC5), 7.71 (1H, d, TpA5), 7.45 (1H, d, TpC3), 6.40 (1H, t, TpB4), 6.26 (1H, t, TpC4), 6.20 (1H, t, TpA4), 4.17 (1H, dd, H3), 3.78 (1H, m, H8), 3.80 (1H, m, H4), 2.84 (1H, m H5), 2.68 (2H, m, H1/H8), 2.68 (1H, m, H9), 2.53 (2H, m, H7), 25349 (1H, dd, H9), 2.30 (1H, m, H6), 2.12 (1H, m, H6), 1.21 (1H, m, H2), 1.17 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 173.4 (1C, C10), 144.9 (1C, TpA3), 142.1 (1C, TpB3), 137.9 (1C, TpB5), 137.3 (1C, TpC5), 136.6 (1C, TpA5), 136.1 (1C, TpC3), 107.4 (1C, TpB4), 106.8 (1C, TpC4), 106.1 (1C, TpA4), 65.4 (1C, C4), 57.0 (1C, C3), 50.8 (1C, C1), 47.9 (1C, C2), 41.8 (1C, C8), 40.3 (1C, C7), 34.0 (1C, C5), 38.5 (1C, C9), 32.1 (1C, C6), 13.7 (3C, d J= 29.9 Hz, PMe_3). **CV** (DMA): $E_{p,a}$= 0.82 V (NHE). **IR**: *ν*(NO) 1544 cm^{-1}, *ν*(CO) 1655 cm^{-1}, *ν*(BH) 2492 cm^{-1}.



Compound 5.6:

Compound **2** (104 mg, 0.137 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.274 mL, 0.274mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, ethylene diamine (0.09 mL, 1.37 mmol) in ACN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days and room temperature for 1 day. The reaction was washed three times (H_2O:Na_3PO_4/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **6** (81 mg, 0.110 mmol, 83%, 72-83%).

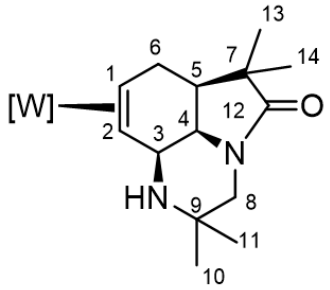
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.94 (1H, d, TpA3), 8.03 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.80 (1H, d, TpC5), 7.71 (1H, d, TpA5), 7.32 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.22 (1H, t, TpC4), 6.20 (1H, t, TpA4), 4.19 (1H, bs, H3), 3.76 (1H, d, H4), 3.73 (1H, d, H9), 2.74 (1H, m H8), 2.70 (1H, m, H9), 2.55 (2H, m, H1/H8), 2.44 (1H, m, H6), 2.35 (1H, m, H5), 2.31 (1H, m, H6), 1.33 (3H, s, H12), 1.20 (1H, m, H2), 1.10 (3H, s, H11), 1.15 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 179.0 (1C, C10), 146.8 (1C, TpA3), 144.8 (1C, TpB3), 142.0 (1C, TpB5), 137.9 (1C, TpC5), 137.0 (1C, TpA5), 136.7 (1C, TpC3), 107.5 (1C, TpB4), 106.9 (1C, TpC4), 106.3 (1C, TpA4), 61.4 (1C, C4), 57.5 (1C, C3), 52.2 (1C, C1), 48.5 (1C, C2), 46.2 (1C, C5), 43.9 (1C, C7), 41.2 (1C, C9), 38.4 (1C, C8), 30.3 (1C, C11), 29.3 (1C, C6), 20.8 (1C, C12), 13.7 (3C, d J= 29.4 Hz, PMe_3).



Compound 5.8:

Compound **2** (140 mg, 0.191 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.382 mL, 0.382 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-methylpropane-1,2-diamine (0.199 mL, 1.91 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and at room temperature for 4 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **8** (105 mg, 0.148 mmol, 77.5%).

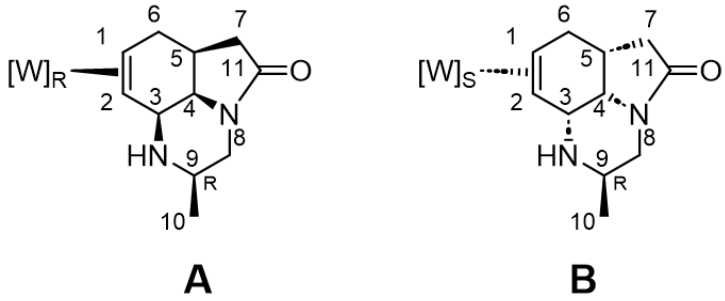
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.72 (1H, d, TpA3), 8.08 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.81 (1H, d, TpC5), 7.73 (1H, d, TpA5), 7.44 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.26 (1H, t, TpC4), 6.23 (1H, t, TpA4), 4.07 (1H, t, H3), 3.73 (1H, t, H4), 3.69 (1H, d, H8), 3.01 (1H, bs, H6), 2.76 (1H, m, H5), 2.60 (1H, m, H1), 2.55 (1H, m, H7), 2.50 (1H, m, H8), 2.36 (1H, m, H6), 2.30 (1H, dd, H7), 1.24 (1H, m, H2), 1.17 (9H, d, PMe3), 1.04 (3H, s, H11), 0.98 (3H, s, H10).
^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C): 174.3 (1C, C12), 144.6 (1C, TpA3), 142.1 (1C, TpB3), 142.1 (1C, TpB5), 137.9 (1C, TpC5), 137.8 (1C, TpC3), 137.1 (1C, TpA5), 107.4 (1C, TpB4), 106.9 (1C, TpC4), 106.4 (1C, TpA4), 60.6 (1C, C4), 54.6 (1C, C3), 52.7 (1C, C2), 52.1 (1C, C1), 50.7 (1C, C9), 49.7 (1C, C8), 37.6 (1C, C7), 32.6 (1C, C6), 31.6 (1C, C5), 30.1 (1C, 11), 29.6 (1C, C10), 13.6 (3C, PMe_3).



Compound 5.9:

Compound **3** (100 mg, 0.131 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.263 mL, 0.263 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-methylpropane-1,2-diamine (0.137 mL, 1.31 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and at room temperature for 4 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **9** (69 mg, 0.094 mmol, 71%).

^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.11 (1H, d, TpB3), 8.07 (1H, d, TpA3), 7.85 (1H, d, TpB5), 7.83 (1H, d, TpC5), 7.75 (1H, d, TpA5), 7.45 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.28 (1H, t, TpC4), 6.24 (1H, t, TpA4), 3.91 (1H, d, H3), 3.78 (1H, t, H4), 3.64 (1H, d, H8), 3.48 (1H, t, H6), 2.59 (1H, td, H1), 2.50 (1H, m, H8), 2.31 (1H, m, H5), 2.20 (1H, bs, H6), 1.23 (9H, d, PMe3), 1.18 (1H, m, H2), 1.09 (6H, d, H13/H14), 1.04 (3H, s, H10), 1.03 (3H, s, H11). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 179.6 (1C, C12), 144.8 (1C, TpB3), 144.3 (1C, TpA3), 142.1 (1C, TpB5), 138.0 (1C, TpC5), 137.1 (1C, TpC3), 136.9 (1C, TpA5), 107.3 (1C, TpB4), 106.9 (2C, TpC4/TpA4), 54.7 (2C, C4/C2), 52.9 (1C, C1), 51.8 (1C, C3), 52.7 (1C, C9), 47.9 (1C, C8), 44.5 (1C, C7), 42.6 (1C, C5), 28.3 (1C, C6), 30.5 (1C, 11), 27.9 (2C, C13/C14), 27.0 (1C, C10), 13.9 (3C, PMe_3).



Compound 5.10A+5.10B

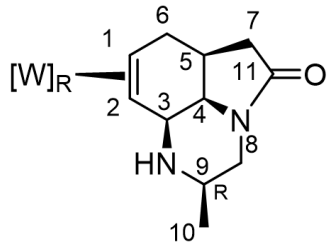
Compound **3** (100 mg, 0.136 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, (*R*)-Propane-1,2-diamine (101 mg, 1.36 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and at room temperature for 4 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **10A + 10B** (76 mg, 0.110 mmol, 80%).

10A

^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.46 (1H, d, TpA3), 8.06 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.82 (1H, d, TpA5), 7.73 (1H, d, TpC5), 7.41 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.25 (1H, t, TpC4), 6.24 (1H, t, TpA4), 4.11 (1H, t, H3), 3.89 (1H, t, H4), 3.23 (1H, dd, H8), 3.10 (1H, m, H9), 3.02 (1H, dd, H8), 2.85 (1H, m, H6), 2.75 (1H, m, H5), 2.61 (1H, m, H1), 2.48 (1H, m, H7), 2.33 (2H, m, H6/H7), 1.18 (9H, d, PMe3), 1.00 (3H, d, H10), 0.94 (1H, ddd, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 175.4 (1C, C11), 145.2 (1C, TpA3), 144.8 (1C, TpB3), 142.0 (1C, TpB5), 138.0 (1C, TpA5), 137.1 (1C, TpC5), 136.9 (1C, TpC3), 107.4 (1C, TpB4), 106.9 (1C, TpC4), 106.5 (1C, TpA4), 58.4 (1C, C4), 58.0 (1C, C3), 55.1 (1C, C2), 51.8 (1C, C1), 47.8 (1C, C9), 46.7 (1C, C8), 37.1 (1C, C7), 32.3 (1C, C6), 32.1 (1C, C5), 21.7 (1C, C10), 13.7 (3C, d J= 29.8 Hz, PMe_3).

10B

^{1}H-NMR (d_3-MeCN, δ, 25 C): 9.38 (1H, d, TpA3), 8.05 (1H, d, TpB3), 7.87 (1H, d, TpA5), 7.80 (1H, d, TpB5), 7.68 (1H, d, TpC5), 7.42 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.21 (1H, t, TpC4), 6.20 (1H, t, TpA4), 4.16 (1H, dd, H3), 3.85 (1H, dd, H8), 3.68 (1H, dd, H4), 2.85 (1H, m, H5), 2.71 (1H, m, H9), 2.65 (1H, m, H1), 2.55 (2H, m, H7), 2.28 (1H, m, H8), 2.15 (2H, m, H6), 1.12 (1H, td, H2), 1.14 (9H, d, PMe3), 0.89 (3H, d, H10). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 173.2 (1C, C11), 148.2 (1C, TpA3), 144.9 (1C, TpB3), 142.1 (1C, TpA5), 138.0 (1C, TpB5), 137.0 (1C, TpC5), 136.6 (1C, TpC3), 107.5 (1C, TpB4), 106.8 (1C, TpC4), 106.0 (1C, TpA4), 64.5 (1C, C4), 57.3 (1C, C3), 50.8 (1C, C1), 48.0 (1C, C8), 47.9 (1C, C2), 42.7 (1C, C9), 36.5 (1C, C7), 33.9 (1C, C5), 32.2 (1C, C6), 19.5 (1C, C10), 13.4 (3C, d J= 28.9 Hz, PMe_3).

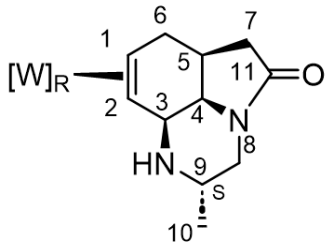


Compound 5.11:

Compound **3** (70 mg, 0.095 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.191 mL, 0.191 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, (*R*)-Propane-1,2-diamine (70.8 mg, 0.955 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and at room temperature for 4 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **11** (55 mg, 0.079 mmol, 82.9%).

^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.46 (1H, d, TpA3), 8.06 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.82 (1H, d, TpA5), 7.73 (1H, d, TpC5), 7.41 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.25 (1H, t, TpC4), 6.24 (1H, t, TpA4), 4.11 (1H, t, H3), 3.89 (1H, t, H4), 3.23 (1H, dd, H8), 3.10 (1H, m, H9), 3.02 (1H, dd, H8), 2.85 (1H, m, H6), 2.75 (1H, m, H5), 2.61 (1H, m, H1), 2.48 (1H, m, H7), 2.33 (2H, m, H6/H7), 1.18 (9H, d, PMe3), 1.00 (3H, d, H10), 0.94 (1H, ddd, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 175.4 (1C, C11), 145.2 (1C, TpA3), 144.8 (1C, TpB3), 142.0 (1C,

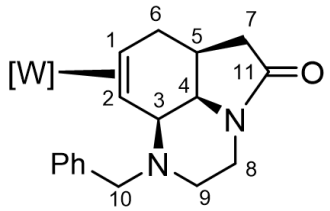
TpB5), 138.0 (1C, TpA5), 137.1 (1C, TpC5), 136.9 (1C, TpC3), 107.4 (1C, TpB4), 106.9 (1C, TpC4), 106.5 (1C, TpA4), 58.4 (1C, C4), 58.0 (1C, C3), 55.1 (1C, C2), 51.8 (1C, C1), 47.8 (1C, C9), 46.7 (1C, C8), 37.1 (1C, C7), 32.3 (1C, C6), 32.1 (1C, C5), 21.7 (1C, C10), 13.7 (3C, d J= 29.5 Hz, PMe_3).



Compound 5.12:

Compound **3** (70 mg, 0.095 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.191 mL, 0.191 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, (*S*)-Propane-1,2-diamine (70.8 mg, 0.955 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 h and at room temperature for 4 h. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **12** (52 mg, 0.075 mmol, 78%).

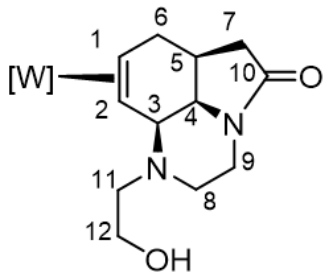
^{1}H-NMR (d_3-MeCN, δ, 25 C): 9.38 (1H, d, TpA3), 8.05 (1H, d, TpB3), 7.87 (1H, d, TpA5), 7.80 (1H, d, TpB5), 7.68 (1H, d, TpC5), 7.42 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.21 (1H, t, TpC4), 6.20 (1H, t, TpA4), 4.16 (1H, dd, H3), 3.85 (1H, dd, H8), 3.68 (1H, dd, H4), 2.85 (1H, m, H5), 2.71 (1H, m, H9), 2.65 (1H, m, H1), 2.55 (2H, m, H7), 2.28 (1H, m, H8), 2.15 (2H, m, H6), 1.12 (1H, td, H2), 1.14 (9H, d, PMe3), 0.89 (3H, d, H10). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 173.2 (1C, C11), 148.2 (1C, TpA3), 144.9 (1C, TpB3), 142.1 (1C, TpA5), 138.0 (1C, TpB5), 137.0 (1C, TpC5), 136.6 (1C, TpC3), 107.5 (1C, TpB4), 106.8 (1C, TpC4), 106.0 (1C, TpA4), 64.5 (1C, C4), 57.3 (1C, C3), 50.8 (1C, C1), 48.0 (1C, C8), 47.9 (1C, C2), 42.7 (1C, C9), 36.5 (1C, C7), 33.9 (1C, C5), 32.2 (1C, C6), 19.5 (1C, C10), 13.4 (3C, d J= 29.2 Hz, PMe_3).



Compound 5.13:

Compound **2** (120 mg, 0.164 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.327 mL, 0.327 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, *N1*-benzylethane-1,2-diamine (0.199 mL, 1.64 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. A 20% KO^{t}Bu in THF (0.297 mL, 0.491 mmol) was added to quench the reaction. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **13** (100 mg, 0.130 mmol, 79%).

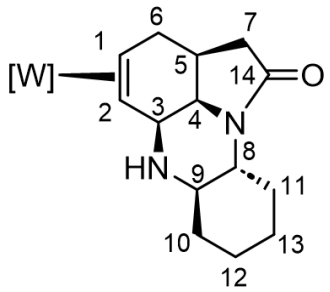
^{1}H-NMR (d_2-CH_2Cl_2, δ, 25 C): 9.41 (1H, d, TpA3), 8.08 (1H, d, TpB3), 7.79 (1H, d, TpB5), 7.70 (1H, d, TpC5), 7.55 (1H, d, TpA5), 7.44 (1H, d, TpC3), 7.32-7.24 (5H, m, Ph), 6.37 (1H, t, TpB4), 6.17 (1H, t, TpC4), 6.09 (1H, t, TpA4), 4.41 (1H, s, H3), 4.46 (1H, m, H8), 4.29 (1H, m, H8), 4.12 (1H, dd, H4), 3.57 (2H, m, H10/H9), 3.18 (1H, m, H6), 2.72 (1H, m, H1), 2.58 (2H, m, H6/H9), 2.49 (1H, d, H7), 2.40 (1H, m, H5), 2.35 (1H, d, H7), 2.17 (1H, d, H10), 1.53 (1H, td, H2), 1.14 (9H, d, PMe3). **^{13}C-NMR (d_2-CH_2Cl_2, δ, 25 C)**: 173.3 (1C, C11), 148.8 (1C, TpA3), 144.0 (1C, TpB3), 141.2 (1C, TpB5), 139.7 (1C, TpC5), 137.1 (1C, TpA5), 136.0 (1C, TpC3), 129.7, 128.6, 127.3 (6C, Ph), 106.9 (1C, TpB4), 105.9 (1C, TpC4), 105.3 (1C, TpA4), 64.4 (1C, C3), 56.7 (2C, C8/C4), 50.3 (1C, C1), 47.9 (1C, C2), 39.2 (1C, C10), 36.5 (1C, C9), 33.30 (1C, C7), 31.9 (1C, C5), 31.8 (1C, C6), 13.2 (3C, d J= 27.4 Hz, PMe_3).



Compound 5.14:

Compound **2** (300 mg, 0.409 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.818 mL, 0.818 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, N-(2-Hydroxyethyl)ethylenediamine (0.358 mL, 4.09 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. A 20% KO^{t}Bu/THF solution (0.741 mL, 1.23 mmol) was added to quench the reaction. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **14** (189 mg, 0.261 mmol, 63.7%).

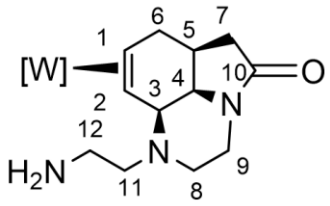
^{1}H-NMR (d_3-MeCN, δ, 25 C): 9.60 (1H, d, TpA3), 8.08 (1H, d, TpB3), 7.88 (1H, d, TpB5), 7.80 (1H, d, TpC5), 7.64 (1H, d, TpA5), 7.48 (1H, d, TpC3), 6.40 (1H, t, TpB4), 6.22 (1H, t, TpC4), 6.13 (1H, t, TpA4), 4.17 (1H, dd, H4), 4.06 (1H, m, H3), 3.77 (2H, m, H11), 3.52 (1H, m, H9), 3.42 (2H, m, H12), 3.14 (1H, m, H9), 3.02 (1H, m, H8), 2.83 (1H, m H5), 2.60 (1H, m, H1), 2.54 (2H, m, H7), 2.52 (1H, m, H8), 2.21 (1H, m, H6), 2.17 (1H, m, H6), 1.42 (1H, td, H2), 1.11 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 173.3 (1C, C10), 150.0 (1C, TpA3), 145.0 (1C, TpB3), 142.4 (1C, TpC5), 138.1 (1C, TpB5), 137.0 (1C, TpA5), 136.3 (1C, TpC3), 107.6 (1C, TpB4), 106.7 (1C, TpC4), 106.1 (1C, TpA4), 66.3 (1C, C12), 63.0 (1C, C3), 61.1 (1C, C4), 57.0 (1C, C11), 51.6 (1C, C1), 47.9 (1C, C2), 43.1 (1C, C8), 36.1 (1C, C7), 36 (1C, C9), 33.8 (1C, C5), 31.9 (1C, C6), 13.4 (3C, d J= 28.1 Hz, PMe_3).



Compound 5.15:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, (1S,2S)-(+)-Cyclohexane-1,2-diamine (0.200 mL, 1.36 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 1 days and at RT for 4 hours. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was loaded on a 60 mL medium-porosity frit filled two-thirds with basic alumina. Hexanes (150 mL) was eluted through the column, followed by diethyl ether (100 mL), ethyl acetate (150 mL) and methanol (200 mL). The methanol portion eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 100 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight to yield **15** (43 mg, 0.057 mmol, 41.9%).

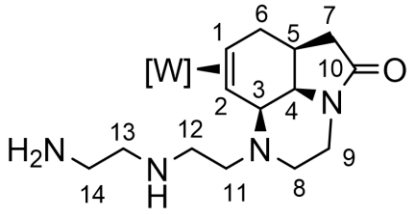
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.69 (1H, d, TpA3), 8.01 (1H, d, TpB3), 7.85 (1H, d, TpA5), 7.81 (1H, d, TpB5), 7.70 (1H, d, TpC5), 7.36 (1H, d, TpC3), 6.36 (1H, t, TpB4), 6.23 (1H, t, TpC4), 6.20 (1H, t, TpA4), 4.35 (1H, t, H3), 4.17 (1H, m, H4), 2.98 (1H, m, H8), 2.83 (1H, m, H5), 2.72 (1H, m, H9), 2.66 (1H, m, H1), 2.63 (1H, d, H7), 2.50 (1H, d, H7), 2.23 (1H, m, H6), 2.15 (3H, m, H10/H11), 1.66 (2H, m, H12/H13), 1.26 (2H, m, H12/H13), 1.17 (9H, d, PMe3), 1.14 (1H, m, H11), 0.68 (1H, m, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 176.1 (1C, C14), 146.1 (1C, TpA3), 145.0 (1C, TpB3), 141.9 (1C, TpA5), 137.9 (1C, TpB5), 137.1 (1C, TpC5), 136.7 (1C, TpC3), 107.4 (1C, TpB4), 106.9 (1C, TpC4), 106.1 (1C, TpA4), 61.3 (1C, C8), 59.6 (1C, C3), 58.8 (1C, C4), 56.8 (1C, C2), 55.4 (1C, C9), 51.1 (1C, C1), 36.2 (1C, C7), 33.7 (1C, C5), 31.5 (1C, C6), 31.3 (1C, C10), 30.3 (1C, C11), 26.3 (1C, C12), 25.4 (1C, C13), 13.7 (3C, d J= 28.4 Hz, PMe_3).



Compound 5.16:

Compound **2** (120 mg, 0.164 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. After 10 min, a 1 M HOTf/EtCN (0.327 mL, 0.327 mmol) solution was added to the test tube and the solution was allowed to stir at -20 °C for 60 min. In a separate test tube, N1-(aminomethyl)ethane-1,2-diamine (0.150 mL, 1.64 mmol) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. A 20% KO^{t}Bu/THF solution (0.297 mL, 0.491 mmol) was added to quench the reaction. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **16** (101.0 mg, 0.139 mmol, 85%).

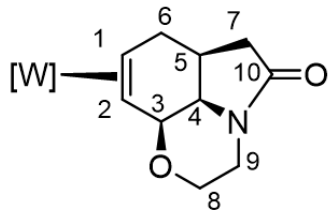
^{1}H-NMR (d_3-MeCN, δ, 25 C): 9.64 (1H, d, TpA3), 8.08 (1H, d, TpB3), 7.89 (1H, d, TpB5), 7.74 (1H, d, TpC5), 7.66 (1H, d, TpA5), 7.45 (1H, d, TpC3), 6.40 (1H, t, TpB4), 6.21 (1H, t, TpC4), 6.15 (1H, t, TpA4), 4.19 (1H, dd, H4), 4.04 (1H, m, H3), 3.51 (1H, m, H9), 3.12 (1H, m, H9), 3.02 (1H, m, H11), 3.01 (1H, m, H8), 2.95 (2H, m, H11/H12), 2.86 (1H, m, H12), 2.82 (1H, m H5), 2.60 (1H, m, H1), 2.54 (4H, m, H7/H8), 2.22 (1H, m, H6), 2.15 (1H, dd, H6), 1.40 (1H, m, H2), 1.10 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 C)**: 173.3 (1C, C10), 149.9 (1C, TpA3), 144.9 (1C, TpB3), 142.3 (1C, TpC3), 138.0 (1C, TpC5), 136.8 (1C, TpB5), 136.3 (1C, TpA5), 107.5 (1C, TpB4), 106.5 (1C, TpC4), 105.5 (1C, TpA4), 63.1 (1C, C3), 57.0 (1C, C4), 56.7 (1C, C11), 51.5 (1C, C1), 47.9 (1C, C2), 42.7 (1C, C8), 41.5 (1C, C12), 36.2 (1C, C7), 35.0 (1C, C9), 34.0 (1C, C5), 31.7 (1C, C6), 13.3 (3C, d J= 28.6 Hz, PMe_3). **CV (DMA):** $E_{p,a}$= 0.75 V (NHE). **IR:** ν(NO) 1542 cm^{-1}, ν(CO) 1661 cm^{-1}, ν(BH) 2486 cm^{-1}.



Compound 5.17:

Compound **2** (150 mg, 0.205 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. After 10 min, a 1 M HOTf/EtCN (0.410 mL, 0.410 mmol) solution was added to the test tube and the solution was allowed to stir at -20 °C for 60 min. In a separate test tube, N1,N1'-(ethane-1,2-diyl)bis(ethane-1,2-diamine) (0.610 mL, 4.09 mmol) was cooled at -30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. A 20% KO^{t}Bu/THF solution (0.354 mL, 0.614 mmol) was added to quench the reaction. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 150 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **17** (108.0 mg, 0.141 mmol, 68.8%).

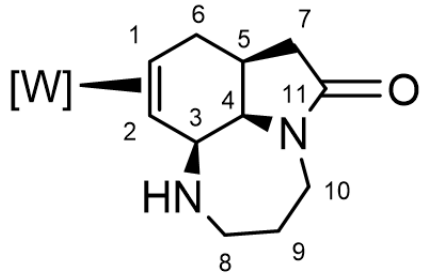
^{1}H-NMR (d_3-MeCN, δ, 25 C): 9.64 (1H, d, TpA3), 8.11 (1H, d, TpB3), 7.79 (1H, d, TpB5), 7.69 (1H, d, TpC5), 7.56 (1H, d, TpA5), 7.35 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.17 (1H, t, TpC4), 6.15 (1H, t, TpA4), 4.18 (1H, dd, H4), 4.10 (1H, dd, H3), 3.61 (1H, dd, H9), 3.18 (1H, m, H9), 3.15 (1H, m, H14), 3.12 (1H, m, H11), 2.90 (3H, m, H13/H5), 2.74 (3H, m, H8/H12), 2.63 (2H, m, H11/H14), 2.57 (2H, m, H7/H12), 2.55 (1H, m, H1), 2.52 (1H, m, H7), 2.28 (1H, td, H6), 2.14 (1H, dd, H6), 1.59 (1H, td, H2), 1.12 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 173.0 (1C, C10), 149.7 (1C, TpB3), 144.0 (1C, TpA3), 141.4 (1C, TpB5), 137.1 (1C, TpC5), 136.0 (1C, TpA5), 135.4 (1C, TpC3), 106.9 (1C, TpB4), 105.8 (1C, TpC4), 105.2 (1C, TpA4), 62.6 (1C, C3), 56.8 (1C, C4), 52.7 (1C, C11), 51.3 (1C, C1), 49.5 (1C, C8), 48.8 (1C, C13), 47.8 (1C, C2), 42.2 (1C, C14), 41.9 (1C, C12), 36.2 (1C, C7), 34.8 (1C, C9), 33.3 (1C, C5), 31.6 (1C, C6), 13.2 (3C, d J= 28.5 Hz, PMe_3).



Compound 5.18:

Compound **23** (80.0 mg, 0.120 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. In a separate test tube, adenine (0.470 mg, 0.350 mmol) was cooled at -30 °C for 20 min with KO^tB_u (0.140 mL, 0.203 mmol, 20% in THF). After 10 min, the former solution was added to the latter, dropwise. The reaction was worked up after 10 min. This was washed three times (H_2O:Na_3PO_4/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 30 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **18** (47 mg, 0.069 mmol, 59%).

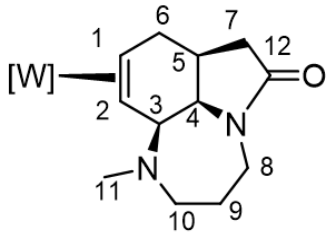
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.69 (1H, d, TpA3), 8.06 (1H, d, TpB3), 7.88 (1H, d, TpB5), 7.81 (1H, d, TpC5), 7.69 (1H, d, TpA5), 7.43 (1H, d, TpC3), 6.40 (1H, t, TpB4), 6.23 (1H, t, TpC4), 6.20 (1H, t, TpA4), 5.05 (1H, dt, H3), 3.74 (1H, m, H8), 3.54 (1H, m, H4), 3.33 (1H, m, H8), 3.17 (1H, m, H9), 2.93 (1H, m, H9), 2.70 (1H, , m, H1), 2.65 (1H, m, H5), 2.53 (1H, m, H6), 2.31 (1H, m, H7), 2.03 (1H, m, H6), 1.98 (1H, m, H7), 1.38 (1H, td, H2), 1.14 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C)**: 173.6 (1C, C10), 147.0 (1C, TpB3), 145.0 (1C, TpA3), 142.2 (1C, TpB5), 138.0 (1C, TpC5), 137.2 (1C, TpA5), 136.5 (1C, TpC3), 107.6 (1C, TpB4), 106.9 (1C, TpC4), 106.2 (1C, TpA4), 78.8 (1C, C3), 63.2 (1C, C4), 62.8 (1C, C1), 61.3 (1C, C2), 57.6 (1C, C8), 45.2 (1C, C9), 40.2 (1C, C7), 33.7 (1C, C5), 31.5 (1C, C6), 13.4 (3C, d J= 29.7 Hz, PMe_3).



Compound 5.19:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. After 10 min, a 1 M HOTf/EtCN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 60 min. In a separate test tube, diaminopropane (0.114 mL, 1.36 mmol) was cooled at -30 °C for 20 min in minimal EtCN. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. A 2M NaO^tBu/THF solution (0.205 mL, 0.409 mmol) was added to quench the reaction. The reaction was washed three times (H_2O:Na_3PO_4/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 30 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **19** (74 mg, 0.11 mmol, 78%; 78-79%).

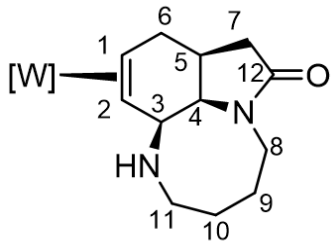
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.11 (1H, d, TpB3), 8.09 (1H, d, TpA3), 7.86 (1H, d, TpB5), 7.86 (1H, d, TpC5), 7.76 (1H, d, TpA5), 7.43 (1H, d, TpC3), 6.39 (1H, t, TpB4), 6.29 (1H, t, TpA4), 6.26 (1H, t, TpC4), 3.96 (1H, dd, H4), 3.89 (1H, m, H10), 3.66 (2H, m, H3/H6), 3.10 (1H, m, H8), 2.92 (1H, m, H10), 2.60 (4H, m, H1/H5/H6H8), 2.56 (1H, m, H7), 1.94 (1H, m, H7), 1.71 (1H, m, H9), 1.51 (1H, m, H9), 1.21 (9H, d, PMe3), 1.17 (1H, d, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 175.2 (1C, C11), 145.0 (1C, TpB3), 144.6 (1C, TpA3), 142.0 (1C, TpC3), 137.3 (2C, TpB5/C5), 136.7 (1C, TpA5), 107.4 (1C, TpB4), 107.1 (1C, TpA4), 107.0 (1C, TpC4), 66.1 (1C, C3), 62.2 (1C, C4), 54.4 (1C, C2), 52.0 (1C, C1), 51.8 (1C, C8), 42.1 (1C, C10), 38.6 (2C, C6/C7), 29.2 (1C, C9), 28.2 (1C, C5), 13.7 (3C, d J= 29.9 Hz, PMe_3). **CV (DMA):** $E_{p,a}$= 0.78 V (NHE).



Compound 5.20:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, N-Methyl-1,3-diaminopropane (0.064 mL, 061 mmol) was cooled at -30 °C for 30 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 2 days and room temperature for 1 day. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **20** (82 mg, 0.12 mmol, 84%).

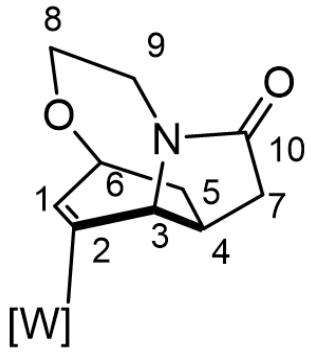
^{1}H NMR (800 MHz, CD_3CN): δ 9.16 (d, 1H, TpA3), 8.07 (d, *J* = 2.0 Hz, 1H, TpB3), 7.87 (d, *J* = 2.4 Hz, 1H, TpB5), 7.80 (d, *J* = 2.3 Hz, 1H, TpC5), 7.67 (d, *J* = 2.3 Hz, 1H, TpA5), 7.42 (d, *J* = 2.2 Hz, 1H, TpC3), 6.38 (t, *J* = 2.2 Hz, 1H, TpB4), 6.24 (t, *J* = 2.2 Hz, 1H, TpC4), 6.19 (t, *J* = 2.2 Hz, 1H, TpA4), 4.41 (dd, *J* = 9.1, 3.0 Hz, 1H, H4), 3.78 (dd, *J* = 7.7, 3.0 Hz, 1H, H3), 3.27 (m, 2H, H8A/H8B), 2.89 (m, 1H, H10A), 2.71 (m, 2H, H5/H10B), 2.61 (m, 5H, H1/H7A/H11), 2.52 (m, 1H, H6A), 2.43 (m, 1H, H6B), 2.24 (dd, *J* = 17.1, 4.0 Hz, 1H, H7B), 1.88 (d, *J* = 12.6 Hz, 1H, H9A), 1.54 (m, 1H, H9B), 1.24 (m, 1H, H2), 1.12 (d, *J* = 8.3 Hz, 9H, PMe3).**^{13}C NMR (201 MHz, CD_3CN):** δ 175.6 (1C, C12), 148.3 (1C, TpA3), 144.8 (1C, TpB3), 142.1 (1C, TpC3), 138.0 (1C, TpC5), 137.0 (1C, TpB5), 136.4 (1C, TpA5), 107.5 (1C, TpB4), 106.9 (1C, TpC4), 106.4 (1C, TpA4), 68.6 (1C, C3), 62.3 (1C, C4), 55.3 (1C, C10), 50.9 (1C, C1), 49.3 (1C, C2), 44.8 (1C, C8), 40.8 (1C, C11), 38.7 (1C, C7), 35.4 (1C, C6), 32.3 (1C, C5), 23.4 (1C, C9), 13.4 (3C, PMe3).



Compound 5.22:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 60 min. In a separate test tube, diaminobutane (0.137 mL, 1.36 mmol) was cooled at -30 °C for 60 min in minimal ACN. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 2 day and room temperature for 1 day. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 30 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **22** (78 mg, 0.110 mmol, 81%).

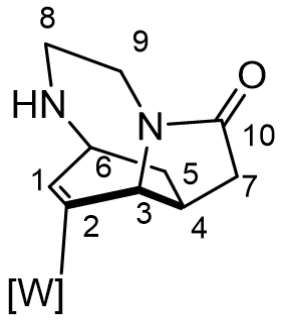
^{1}H NMR (800 MHz, CD_3CN): δ 8.09 (s, 1H, TpB3), 7.92 (s, 1H, TpA3), 7.86 (d, 1H, TpB5), 7.83 (d, 1H, TpC5) 7.76 (s, 1H, TpA5), 7.39 (s, 1H, TpC3), 6.38 (s, 1H, TpB4), 6.31 (d, 1H, TpA4), 6.26 (d, 1H, TpC4), 3.96 (m, 1H, H8A), 3.91 (dd, 1H, H4), 3.63 (t, 1H, H6A), 3.43 (t, 1H, H3), 2.90 (m, 2H, H8B/H11A), 2.75 (dd, 1H, 6B), 2.65 (t, 1H, H1), 2.52 (m, 3H, H5/H7A/H11B), 2.09 (dd, 1H, H7B), 1.90 (m, 1H, H9A), 1.67 (m, 1H, H9B), 1.61 (m, 1H, H10A), 1.42 (m, H10B), 1.22 (d, 1H, H2), 1.19 (d, 9H, PMe3). **^{13}C NMR (201 MHz, CD_3CN):** δ 175.6 (1C, C12), 144.8 (1C, TpB3), 144.4 (1C, TpA3), 141.7 (1C, TpC3), 137.9 (1C, TpB5), 137.2 (1C, TpC5), 136.8 (1C, TpA5), 107.4 (1C, TpA4), 107.1 (1C, TpB4), 107.1 (1C, TpC4), 63.3 (1C, C4), 60.5 (1C, C3), 56.8 (1C, C2), 50.9 (1C, C1), 50.8 (1C, C11), 41.4 (1C, C8), 41.0 (1C, C7), 37.3 (1C, C6), 29.3 (1C, C10), 28.4 (1C, C5), 28.1 (1C, C9), 13.4 (3C, PMe3).



Compound 5.23:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. After 10 min, a 1 M HOTf/EtCN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -60 °C for 60 min. In a separate test tube, 2-aminoethan-1-ol (0.165 mL, 2.73 mmol) with triethylamine (0.095 mL, 0.682 mmol) were cooled at -60 °C for 60 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -60 °C for 3 days. A pipette-full of 20% KO^{t}Bu/THF solution was added to quench the reaction. A distinct color change was observed from yellow to light brown. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **23** (72.0 mg, 0.110 mmol, 77.0%).

^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.06 (2H, d, TpB3/C5), 7.86 (2H, d, TpB5/C3), 7.78 (1H, d, TpA5), 7.49 (1H, d, TpA3), 6.28 (1H, t, TpB4), 6.29 (1H, t, TpA4), 6.26 (1H, t, TpC4), 4.69 (1H, d, H3), 3.60 (2H, m, H8), 3.58 (1H, t, H6), 3.17 (1H, m, H9), 3.03 (1H, m, H9), 2.61 (1H, m, H7), 2.52 (1H, m, H4), 2.47 (1H, m, H1), 2.20 (1H, d, H7), 2.05 (1H, m, H5), 1.23 (1H, m, H5), 1.19 (9H, d, PMe3), 1.15 (1H, d, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 177.5 (1C, C10), 144.5 (1C, TpB3), 144.1 (1C, TpB5), 143.5 (1C, TpC5), 142.2 (1C, TpA3), 137.7 (1C, TpA5), 137.4 (1C, TpC3), 107.5 (1C, TpB4), 107.2 (1C, TpA4), 106.8 (1C, TpC4), 63.3 (1C, C3), 62.6 (1C, C8), 58.4 (1C, C6), 57.3 (1C, C1), 49.0 (1C, C2), 44.1 (1C, C9), 41.6 (1C, C7), 33.5 (1C, C5), 30.3 (1C, C4), 13.8 (3C, d J= 28.4 Hz, PMe_3). **CV (DMA)**: $E_{p,a}$= 1.2 V (NHE). **IR:** *ν*(NO) 1546 cm^{-1}, *ν*(CO) 1649 cm^{-1}, *ν*(BH) 2361 cm^{-1}.

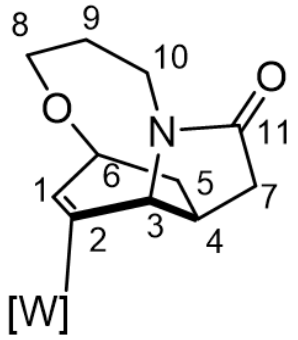


Compound 5.24:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with EtCN, and chilled to -20 °C. After 10 min, a 1 M HOTf/EtCN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -60 °C for 60 min. In a separate test tube, ethylenediamine (0.182 mL, 2.73 mmol) in proprionitrile at -60 °C for 60 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -60 °C for 3 days. A pipette-full of 20% KO^tBu/THF solution was added to quench the reaction. A distinct color change was observed from yellow to light brown. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **24** (37 mg, 0.054 mmol, 40%) and **5** (39 mg, 0.057 mmol, 44%) in 9:10 ratio.

Assignments for compound 24.

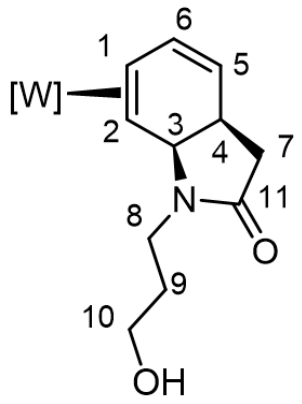
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.05 (2H, d, TpB3/C5), 7.85 (2H, d, TpB5/C3), 7.81 (1H, d, TpA5), 7.42 (1H, d, TpA3), 6.37 (1H, t, TpB4), 6.29 (1H, t, TpA4), 6.22 (1H, t, TpC4), 4.72 (1H, d, H3), 3.60 (1H, bs, H8), 3.15 (1H, m, H9), 2.88 (1H, m, H9), 2.65 (1H, m, H7), 2.51 (1H, m, H4), 2.33 (1H, m, H1), 2.19 (1H, d, H7), 1.23 (1H, m, H5), 1.19 (9H, d, PMe3), 1.09 (1H, d, H2).



Compound 5.25:

Compound **2** (110 mg, 0.150 mmol) was placed in a test tube, with ACN, and chilled to -60 °C. After 10 min, a 1 M HOTf/ACN (0.300 mL, 0.300 mmol) solution was added to the test tube and the solution was allowed to stir at -60 °C for 60 min. In a separate test tube, propanolamine (0.229 mL, 3.00 mmol) with triethylamine (0.083 mL, 0.600 mmol) were cooled at -60 °C for 60 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -60 °C for 3 days. A pipette-full of 20% KO^{t}Bu/THF solution was added to quench the reaction. A distinct color change was observed from yellow to light brown. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **25** (56 mg, 0.0.080 mmol, 54.0%).

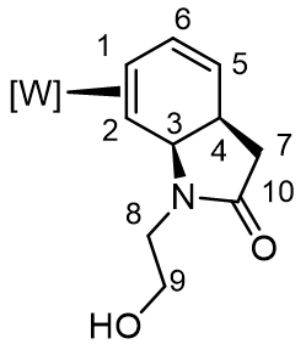
^{1}H NMR (800 MHz, CD_3CN): δ 8.08 (d, 1H, TpB3), 8.05 (d, 1H, TpA3), 7.86 (d, 1H, 7.85), 7.85 (d, 1H, TpC5), 7.79 (d, 1H, TpB5), 7.46 (d, 1H, TpC3), 6.37 (t, 1H, TpA4), 6.29 (t, 1H, TpC4), 6.25 (t, 1H, TpB4), 4.70 (d, 1H, C3), 3.63 (m, 2H, H8A/H8B), 3.60 (m, 1H, H6), 3.16 (m, 1H, H10A), 3.05 (m, 1H, H10B), 2.61 (dd, 1H, H7A) , 2.50 (t, 1H, H4), 2.46 (t, 1H, H1), 2.23 (d, 1H, H7B), 1.94 (m, 1H, H5A), 1.68 (m, 2H, H9A/H9B), 1.22 (d, 9H, PMe3), 1.17 (m, 1H, H5B), 1.09 (d, 1H, H2).**^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 177.4 (1C, C11), 144.6 (1C, TpB3), 143.4 (1C, TpB5), 142.1 (1C, TpC5), 138.0 (1C, TpA3), 137.8 (1C, TpA5), 137.4 (1C, TpC3), 107,5 (1C, TpB4), 107.2 (1C, TpA4), 106.8 (1C, TpC4), 62.7 (1C, C3), 62.1 (1C, C8), 58.9 (1C, C6), 57.0 (1C, C1), 48.7 (1C, C2), 40.6 (1C, C7), 36.8 (1C, C10), 34.2 (1C, C9), 33.5 (1C, C5), 31.6 (1C, C4), 14.0 (3C, PMe3).



Compound 5.26:

Compound **2** (100mg, 0.136 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, propanolamine (0.104 mL, 2.73 mmol) was cooled at -30 °C for 30 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 hrs and room temperature for 24 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **26** (75.0 mg, 0.108 mmol, 79.0%).

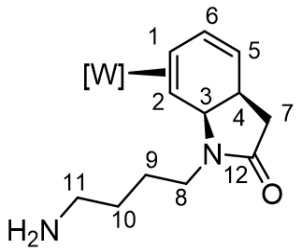
^{1}H NMR (800 MHz, CD_2Cl_2): δ 8.06 (d, *J* = 2.0 Hz, 1H, TpB3), 7.99 (d, *J* = 2.0 Hz, 1H, TpA5), 7.78 (d, *J* = 2.3 Hz, 1H, TpC5), 7.77 (d, *J* = 2.5 Hz, 1H, TpB5), 7.69 (d, *J* = 2.4 Hz, 1H, TpA3), 7.36 (d, *J* = 2.1 Hz, 1H, TpC3), 6.44 (ddd, *J* = 9.8, 5.2, 2.4 Hz, 1H, H6), 6.35 (t, *J* = 2.2 Hz, 1H, TpB4), 6.27 (t, *J* = 2.2 Hz, 1H, TpC4), 6.26 (t, *J* = 2.2 Hz, 1H, TpA4), 4.64 (m, 2H, H3/H5), 3.50 (ddd, *J* = 14.1, 11.1, 6.7 Hz, 2H, H8A/H10A), 3.41 (d, *J* = 9.9 Hz, 1H, H10B), 3.30 (t, *J* = 7.4 Hz, 1H, H4), 3.18 (ddd, *J* = 14.3, 6.3, 4.4 Hz, 1H, H8B), 2.71 (m, 2H, H1/H7A), 2.10 (d, *J* = 16.3 Hz, 1H, H7B), 1.60 (ddt, *J* = 13.7, 9.1, 4.4 Hz, 1H, H9A), 1.45 (tdd, *J* = 8.9, 7.4, 4.1 Hz, 1H, H9B), 1.41 (d, *J* = 9.5 Hz, 1H, H2), 1.21 (d, *J* = 8.4 Hz, 9H, PMe_3). **^{13}C NMR (201 MHz, CD_2Cl_2):** δ 177.2 (1C, C11), 143.8 (1C, TpB3), 142.7 (1C, TpA5), 140.8 (1C, TpC3), 137.2 (1C, TpC5), 136.5 (1C, TpA3), 136.3 (1C, TpB5), 131.3 (d, *J* = 3.5 Hz, 1C, C6), 120.0 (1C, C5), 106.9 (1C, TpB4), 106.5 (1C, TpC4), 106.1 (1C, TpA4), 64.1 (1C, C3), 58.2 (1C, C10), 49.6 (d, *J* = 10.1 Hz, 1C, C1), 47.9 (1C, C2), 39.9 (1C, C7), 36.4 (1C, C8), 33.0 (1C, C4), 32.1 (1C, C9), 13.8 (d, *J* = 28.2 Hz, 1C, PMe_3).



Compound 5.27:

Compound **2** (200mg, 0.273 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.546 mL, 0.546 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, ethanolamine (0.165 mL, 2.73 mmol) was cooled at -30 °C for 30 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 48 hrs and room temperature for 24 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **27** (157 mg, 0.230 mmol, 84.4%).

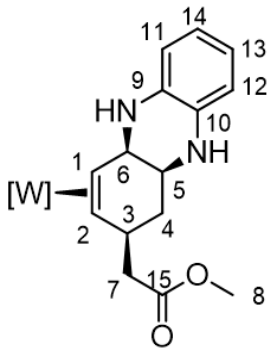
^{1}H NMR (800 MHz, CD_3CN): δ 8.07 (dd, *J* = 5.7, 2.1 Hz, 2H, TpA5/B3), 7.86 (m, 2H, TpA3/C5), 7.78 (d, *J* = 2.3 Hz, 1H, TpB5), 7.50 (d, *J* = 2.2 Hz, 1H, TpC3), 6.46 (ddd, *J* = 9.8, 4.7, 2.2 Hz, 1H, H6), 6.38 (t, 1H, TpA4), 6.31 (t, 1H, TpC4), 6.28 (t, 1H, TpB4), 4.71 (d, *J* = 6.1 Hz, 1H, H3), 4.52 (dd, *J* = 9.7, 2.0 Hz, 1H, H5), 3.40 (t, *J* = 6.1 Hz, 2H, H9A/9B), 3.32 (dt, *J* = 14.0, 5.8 Hz, 1H, H8A), 3.25 (m, 2H, H8B, H4), 2.80 (m, 1H, H1), 2.66 (t, *J* = 5.5 Hz, 1H, H7A), 1.92 (m, 1H, H7B), 1.33 (d, *J* = 9.6 Hz, 1H, H2), 1.18 (d, *J* = 8.6 Hz, 9H, PMe_3) . **^{13}C NMR (201 MHz, CD_3CN)**: δ 176.9 (1C, C10), 144.6 (1C, TpA5), 143.7 (1C, TpB3), 142.2 (1C, TpC3), 138.1 (1C, TpC5), 137.4 (1C, TpA3), 137.3 (1C, TpB5), 132.2 (1C, C6), 120.2 (1C, C5), 107.6 (1C, TpC4), 107.3 (1C, TpA4) , 106.8 (1C, TpB4) , 63.6 (1C, C3), 61.5 (1C, C9), 49.5 (d, *J* = 9.9 Hz, 1C, C1), 48.3 (1C, C2), 43.4 (1C, C8), 40.1 (1C, C7), 33.5 (1C, C4), 13.7 (d, *J* = 28.7 Hz, 1C, PMe_3).



Compound 5.28:

Compound **2** (50 mg, 0.068 mmol) was placed in a test tube, with CH_3CN, and chilled to -30 °C. After 10 min, a 1 M HOTf/CH_3CH_2CN (0.136 mL, 0.136 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 10 min. In a separate test tube, 1,4-diaminobutane (0.069 mL, 0.68 mmol) was cooled at -30 °C for 10 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with Na_2SO_4. The clear solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring pentane. An tan/white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield compound **28** (42.0 mg, 0.059 mmol, 87%).

^{1}H-NMR (d_6-$(D_3C)_2CO$, δ, 25°C): 8.18 (1H, d, TpA3), 8.15 (1H, d, TpB3), 7.97 (2H, t, TpB5/C5), 7.84 (1H, d, TpA5), 7.67 (1H, d, TpC3), 6.41 (2H, m, H6/TpB4), 6.35 (1H, t, TC4), 6.30 (1H, t, TpA4), 4.75 (1H, d, H3), 4.51 (1H, dd, H5), 3.38 (1H, d, H11), 3.32 (1H, t, H4), 3.20 (1H, m, H8), 3.11 (1H, m, H11), 3.07 (1H, m, H8), 2.85 (1H, m, H1), 2.62 (1H, m, H7), 1.92 (1H, d, H7), 1.62 (2H, m, H9), 1.44 (1H, d, H2), 1.41 (2H, m, H10), 1.27 (9H, d, PMe_3).**^{13}C-NMR (d_6-$(D_3C)_2CO$, δ, 25°C):** 174.7 (1C, C9), 144.5 (1C, TpB3) 143.4 (1C, TpA3), 142.0 (2C, TpB5/A5), 137.1 (1C, TpC3), 136.9 (1C, TpC5), 131.8 (1C, C6), 120.6 (1C, C5), 107.3 (1C, TpB4), 107.1 (1C, TpC4), 106.5 (1C, TpA4), 62.5 (1C, C3), 51.7 (1C, C8), 49.6 (1C, d, C1), 48.2 (1C, C2), 40.3 (1C, s, C7), 39.6 (1C, C11), 32.8 (1C, s, C4), 28.6 (1C, C9), 26.9 (1C, C10) 13.7 (3C, d, PMe_3).



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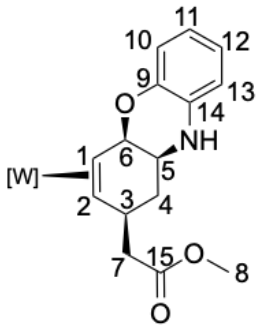
Compound 5.31:

Compound **2** (150 mg, 0.205 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.409 mL, 0.409 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, o-Phenylenediamine (221 mg, 2.05 mmol) was cooled at -30 °C for 30 min in minimal THF. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 72 hours. The reaction was washed three times (H_2O:Na_3PO_4/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 20 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **31** (112 mg, 0.147 mmol, 72%).

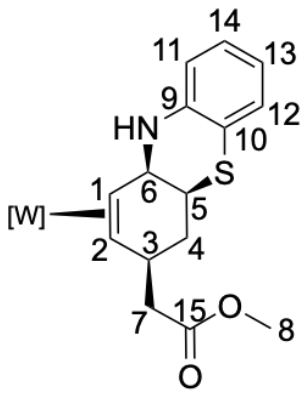
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.27 (1H, d, TpA5), 8.03 (1H, d, TpB3), 7.86 (1H, d, TpB5), 7.85 (1H, d, TpC5), 7.80 (1H, d, TpA3), 7.49 (1H, d, TpC3), 6.47 (1H, m, H11), 6.42 (2H, m, H12/H13), 6.40 (1H, m, H14), 6.38 (1H, t, TpB4), 6.30 (1H, t, TpC4), 6.27 (1H, t, TpA4), 4.22 (1H, d, H6), 3.67 (2H, m, H3/H5), 3.61 (3H, s, H8), 2.40 (1H, m, H1), 2.29 (1H, m, H7), 2.03 (1H, m, H7), 1.39 (2H, m, H4), 1.12 (9H, d, PMe3), 0.78 (1H, m, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 174.3 (1C, C15), 144.3 (1C, TpB3), 142.2 (1C, TpA5), 141.7 (1C, TpC3), 138.2 (1C, TpB5), 137.6 (1C, TpC5), 137.4 (1C, TpA3), 118.4 (2C, C13/C14), 114.2 (C10/C12), 113.9 (2C, C9/C11), 107.7 (1C, TpB4), 107.1 (1C, TpC4), 106.8 (1C, TpA4), 62.1 (1C, C1), 55.7 (1C, C4), 53.1 (1C, C2), 52.1 (1C, C8), 49.5 (1C, C3), 46.3 (1C, C7), 39.5 (1C, C5), 36.6 (1C, C6), 13.7 (3C, d J= 29.9 Hz, PMe_3). **CV (DMA):** $E_{p,a}$= 0.74 V (NHE). **IR:** ν(NO) 1558 cm^{-1}, ν(CO) 1732 cm^{-1}, ν(BH) 2503 cm^{-1}.



Compound 5.32:

Compound **2** (150mg, 0.205 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.410 mL, 0.410 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-Aminophenol (224 mg, 2.05 mmol) was cooled at -30 °C for 30 min in THF. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 72 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting brown film was desiccated for 1hr then dissolved in minimal acetonitrile. After 24 hrs, crystals were removed from the solution via vacuum filtration through a 15ml fine-porosity fitted-disk. The filtrate was evaporated to dryness, dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL overnight to yield compound **32** (96.0 mg, 0.130 mmol, 61%).

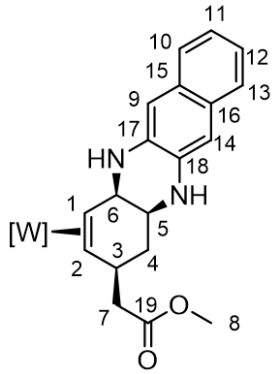
^{1}H NMR (800 MHz, CD_3CN): δ 8.25 (d, *J* = 2.1 Hz, 1H, TpA3), 8.04 (d, *J* = 2.0 Hz, 1H, TpB3), 7.88 (d, *J* = 2.3 Hz, 1H, TpC5), 7.86 (d, *J* = 2.3 Hz, 1H, TpB5), 7.82 (d, *J* = 2.3 Hz, 1H, TpA5), 7.50 (d, *J* = 2.2 Hz, 1H, TpC3), 6.73 (dd, *J* = 7.8, 1.4 Hz, 1H, H11), 6.39 (t, *J* = 2.2 Hz, 1H, TpB4), 6.29 (dt, *J* = 4.1, 2.2 Hz, 2H, TpA4/C4), 6.73 (d, 1H, H10), 6.68 (t, 1H, H12), 6.54 (M, 2H, H11/H13), 4.79 (d, *J* = 2.5 Hz, 1H, H6), 3.83 (d, *J* = 12.4 Hz, 1H, H5), 3.65 (m, 1H, H3), 3.61 (s, 3H, H8), 2.71 (t, *J* = 11.1 Hz, 1H, H1), 2.31 (dd, *J* = 14.7, 3.4 Hz, 1H, H7A), 2.06 (m, 1H, H7B), 1.54 (dt, *J* = 11.6, 4.0 Hz, 1H, H4A), 1.41 (m, 1H, H4B), 1.12 (d, *J* = 8.4 Hz, 9H, PMe_3), 0.84 (ddd, *J* = 11.3, 3.1, 2.3 Hz, 1H, H2). **^{13}C NMR (201 MHz, CD_3CN):** δ 174.2 (1C, C15), 143.3 (1C, TpB3), 141.3 (1C, TpA3), 140.9 (1C, TpC3), 137.2 (1C, TpA5), 136.7 (1C, TpC5), 136.4 (1C, TpB5), 133.8 (1C, C14), 121.0 (1C, C12), 116.5 (1C, C11), 115.6 (1C, C13), 113.9 (1C, C10), 79.0 (d, *J* = 4.5 Hz, 1C, C6), 58.5 (d, *J* = 10.8 Hz, 1C, C1), 53.3, (1C, C2) , 51.9 (1C, C8) , 49.3 (1C, C5), 46.0 (1C, C7), 38.8 (1C, C3), 36.1 (1C, C4), 12.9 (d, *J* = 28.8 Hz, 3C, PMe_3).



Compound 5.33:

Compound **2** (120 mg, 0.164 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.327 mL, 0.327 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-aminothiophenol (0.175 mL, 1.64 mmol) was cooled at -30 °C for 30 min in THF. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with $MgSO_4$. The solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield compound **33** (74.0 mg, 0.095 mmol, 58.0%).

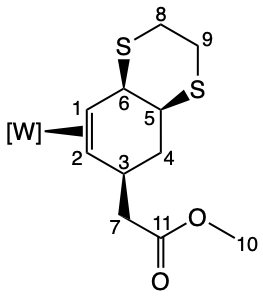
^{1}H NMR (600 MHz, CD_3CN): δ 8.26 (d, *J* = 2.1 Hz, 1H, TpA3), 8.05 (d, *J* = 2.0 Hz, 1H, TpB3), 7.88 (d, *J* = 2.3 Hz, 1H, TpB5), 7.86 (d, *J* = 2.3 Hz, 1H, TpC5), 7.81 (d, *J* = 2.4 Hz, 1H, TpA5), 7.52 (d, *J* = 2.2 Hz, 1H, TpC3), 6.94 (dd, *J* = 7.7, 1.5 Hz, 1H, H11), 6.89 (m, 1H, H13), 6.60 (dd, *J* = 8.1, 1.5 Hz, 1H, H14), 6.53 (m, 1H, H12), 6.40 (t, *J* = 2.2 Hz, 1H, TpB4), 6.33 (t, *J* = 2.2 Hz, 1H, TpC4), 6.29 (t, *J* = 2.2 Hz, 1H, TpA4), 4.43 (d, *J* = 3.7 Hz, 1H, H6), 3.78 (s, 1H, H3), 3.59 (s, 4H, H8/H5), 2.48 (t, *J* = 11.0 Hz, 1H, H1), 2.31 (d, *J* = 3.5 Hz, 1H, H7A), 2.07 (d, *J* = 3.1 Hz, 1H, H7B), 1.68 (m, 1H, H4A), 1.58 (q, *J* = 12.1 Hz, 1H, H4B), 1.12 (d, *J* = 8.4 Hz, 9H, PMe3), 0.82 (dt, *J* = 11.2, 2.5 Hz, 1H, H2). **^{13}C NMR (201 MHz, CD_3CN):** δ 174.0 (1C, C15), 144.4 (1C, TpB3), 142.3 (1C, TpA3), 141.7 (1C, TpC3), 138.2 (1C, C10), 137.7 (1C, TpA5), 137.4 (1C, TpC5), 137.1 (1C, TpB5), 128.0 (1C, C11), 126.2 (1C, C13), 118.3 (1C, C12), 115.0 (1C, C14), 107.7 (1C, TpA4), 107.3 (1C, TpB4), 106.8 (1C, TpC4), 66.3 (1C, C1), 55.3 (1C, C6), 52.0 (1C,C2), 51.9 (1C, C8), 46.4 (1C, C7), 39.9 (1C, C3), 36.6 (2C, C5/4), 13.1 (d, *J* = 28.6 Hz, 3C, PMe3).



Compound 5.34:

Compound **2** (150 mg, 0.205 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.409 mL, 0.409 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, naphthalene-2,3-diamine (324 mg, 2.05 mmol) in MeOH (2 mL) was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 3 days and at room temperature for a day. The reaction was removed from the glovebox and loaded onto a silica column with 2ml DCM. The column was eluted with 100ml hexanes, 400ml diethyl ether and 200ml ethyl acetate. The ethyl acetate portion was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. Precipitation was induced twice to collect all the material. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed pentane (2 × 10 mL) desiccated overnight to yield compound **34** (67.0 mg, 0.083 mmol, 40.0%).

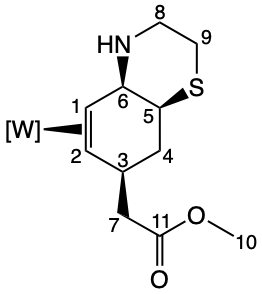
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.28 (1H, d, TpA3), 8.05 (1H, d, TpB3), 7.87 (1H, d, TpB5), 7.86 (1H, d, TpC5), 7.81 (1H, d, TpA3), 7.73 (1H, dd, H10), 7.64 (1H, d, H13), 7.52 (1H, d, TpC3), 7.43 (1H, dd, H12), 7.2408 (1H, dd, H11), 6.77 (1H, s, H9), 6.68 (1H, s, H14), 6.39 (1H, t, TpB4), 6.33 (1H, t, TpC4), 6.28 (1H, t, TpA4), 4.36 (1H, d, H6), 3.81 (1H, m, H5), 3.70 (1H, dd, H3), 3.60 (3H, s, H8), 2.45 (1H, t, H1), 2.33 (1H, m, H7), 2.05 (1H, d, H7), 1.55 (1H, m, H4), 1.45 (1H, m, H4), 1.16 (9H, d, PMe3), 0.82 (1H, m, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 174.3 (1C, C19), 142.2 (1C, TpB3), 142.3 (1C, TpA5), 140.5 (1C, TpC3), 137.1 (1C, TpB5), 136.4 (1C, TpC5), 137.4 (1C, TpA3), 136.7 (1C, C16), 136.1 (1C, C15), 128.7 (1C, C18), 128.1 (1C, C17), 126.9 (1C, C13), 125.7 (1C, C12), 124.6 (1C, C11), 128.0 (1C, C10), 107.8 (1C, TpB4), 107.2 (1C, TpC4), 106.7 (1C, TpA4), 106.5 (1C, C9), 105.5 (1C, C14), 61.2 (1C, C1), 53.7 (1C, C6), 52.8 (1C, C2), 49.1 (1C, C5), 46.0 (1C, C7), 39.1(1C, C3), 36.5 (1C, C4), 13.7 (3C, d J= 29.6 Hz, PMe_3).



Compound 5.35:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, Ethane-1,2-dithiol (0.115 ml, 1.37 mmol) and Triethylamine (0.076 ml, 0.545 mmol) were cooled at -30 °C for 30 min in MeOH. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 5 hrs and room temperature for 24 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **35** (49.0 mg, 0.066 mmol, 48%, 41-48%).

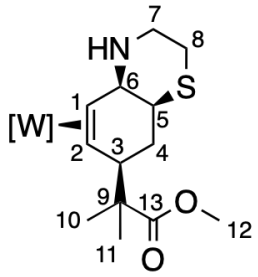
^{1}H NMR (800 MHz, CD_3CN): δ 8.25 (d, *J* = 2.1 Hz, 1H, TpA3), 8.03 (d, *J* = 2.0 Hz, 1H, TpB3), 7.86 (d, *J* = 2.4 Hz, 1H, TpB5), 7.83 (d, *J* = 2.3 Hz, 1H, TpC5), 7.79 (d, *J* = 2.4 Hz, 1H, TpA5), 7.34 (d, *J* = 2.2 Hz, 1H, TpC3), 6.38 (t, *J* = 2.2 Hz, 1H, TpB4), 6.27 (t, *J* = 2.3 Hz, 1H, TpA4), 6.24 (t, *J* = 2.3 Hz, 1H, TpC4), 4.44 (d, *J* = 3.0 Hz, 1H, H6), 3.82 (s, 1H, H3), 3.64 (s, 3H, H10), 3.27 (d, *J* = 12.5 Hz, 1H, H5), 3.16 (m, 1H, H8A), 2.99 (ddd, *J* = 14.3, 12.2, 2.4 Hz, 1H, H9A), 2.83 (d, *J* = 13.6 Hz, 1H, H8B), 2.50 (q, *J* = 12.0 Hz, 1H, H4A), 2.46 (ddd, *J* = 13.8, 4.1, 2.4 Hz, 1H, H9B), 2.31 (dd, *J* = 14.6, 3.5 Hz, 1H, H7A), 2.20 (t, *J* = 11.2 Hz, 1H, H1), 2.13 (Hidden, 1H, H7B), 1.74 (dt, *J* = 10.8, 3.2 Hz, 1H, H4B), 1.17 (d, *J* = 8.4 Hz, 9H, PMe3), 0.72 (dt, *J* = 11.3, 2.6 Hz, 1H, H2).**^{13}C NMR (201 MHz, CD_3CN)**: δ 174.1 (1C, C11), 144.3 (1C, TpB3), 142.3 (1C, TpA3), 141.9 (1C, TpC3), 138.1 (1C, TpC5), 137.6 (1C, TpA5), 137.3 (1C, TpB5), 107.7 (1C, TpB4), 107.2 (1C, TpA4), 106.7 (1C, TpC4), 61.4 (d, *J* = 10.9 Hz, 1C, C1), 52.3 (1C, C2), 51.9 (1C, C9), 47.8 (1C, C6), 46.5 (1C, C7), 40.2 (1C, C3), 36.6 (1C, C5), 34.8 (1C, C4), 34.2 (1C, C8), 23.8 (1C, C9), 13.5 (d, *J* = 28.2 Hz, 3C, PMe3).



Compound 5.36:

Compound **2** (125 mg, 0.170 mmol) was placed in a test tube, with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.341 mL, 0.341 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, cysteamine (132 mg, 1.70 mmol) in MeOH was cooled at -30 °C for 30 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 2 days and at room temperature for 1 day. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with $MgSO_4$. The solution was evaporated in vacuo. The resulting film was dissolved in minimal DCM and pipetted in 15 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fritted disk, washed hexane (2 × 10 mL) desiccated overnight to yield compound **36** (52.0 mg, 0.071mmol, 42%).

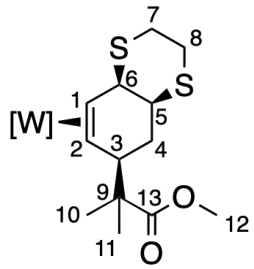
^{1}H NMR (600 MHz, CD_3CN): δ 8.24 (d, *J* = 2.1 Hz, 1H, TpA3), 8.03 (d, *J* = 2.0 Hz, 1H, TpB3), 7.86 (d, *J* = 2.4 Hz, 1H, TpB5), 7.83 (d, *J* = 2.3 Hz, 1H, TpC5), 7.79 (d, *J* = 2.4 Hz, 1H, TpA5), 7.39 (d, *J* = 2.2 Hz, 1H, TpC3), 6.38 (t, *J* = 2.2 Hz, 1H, TpB4), 6.27 (t, *J* = 2.3 Hz, 1H, TpA4), 6.25 (t, *J* = 2.3 Hz, 1H, TpC4), 4.02 (s, 1H, H6), 3.74 (s, 1H, H3), 3.64 (s, 3H, H10), 3.42 (m, 1H, H8A), 3.11 (t, *J* = 12.5 Hz, 1H, H8B), 2.98 (d, *J* = 13.4 Hz, 1H, H5), 2.84 (m, 1H, H9A), 2.33 (m, 1H, H7A), 2.25 (t, *J* = 11.1 Hz, 1H, H1), 2.15 (dd, *J* = 14.6, 11.2 Hz, 2H, H7B/H9B), 2.05 (m, 1H, H4A), 1.71 (m, 1H, H4B), 1.15 (d, *J* = 8.3 Hz, 9H, PMe3), 0.75 (dt, *J* = 11.4, 2.6 Hz, 1H, H2).**^{13}C NMR (201 MHz, CD_3CN):** δ 174.3 (1C, C11), 144.3 (1C, TpB3), 142.2 (1C, TpA3), 141.8 (1C, TpC3), 138.1 (1C, TpA5), 137.6 (1C, TpC5), 137.3 (1C, TpB5), 107.7 (1C, TpB4), 107.2 (1C, TpA4), 106.7 (1C, TpC4), 66.3 (1C, C1), 62.6 (1C, C6), 52.8 (1C, C2), 51.9 (1C, C10), 49.4 (1C, C8), 46.3 (1C, C7), 39.5 (1C, C3), 35.5 (1C, C5), 34.1 (1C, C4), 22.5 (1C, C9), 13.3 (d, *J* = 28.2 Hz, 3C, PMe3).



Compound 5.37:

Compound **3** (125 mg, 0.164 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.328 mL, 0.328 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, Cysteamine (0.127 ml, 1.64 mmol) was cooled at -30 °C for 30 min in MeOH. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 5 hrs and room temperature for 24 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **37** (100 mg, 0.132 mmol, 80%).

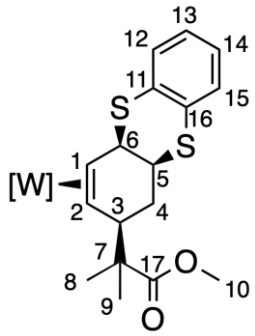
^{1}H NMR (800 MHz, CD_3CN): δ 8.01 (d, *J* = 2.1 Hz, 1H, TpA3), 7.97 (d, *J* = 2.0 Hz, 1H, TpB3), 7.83 (d, *J* = 2.4 Hz, 1H, TpB5), 7.80 (d, *J* = 2.3 Hz, 1H, TpC5), 7.79 (d, *J* = 2.4 Hz, 1H, TpA5), 7.36 (d, *J* = 2.2 Hz, 1H, TpC3), 6.32 (t, *J* = 2.2 Hz, 1H, TpB4), 6.28 (t, *J* = 2.3 Hz, 1H, TpA4), 6.26 (t, *J* = 2.3 Hz, 1H, TpC4), 3.88 (d, 1H, H6), 3.48 (s, 3H, H12), 3.40 (m, 1H, H3), 3.35 (d, 1H, H7), 3.04 (m, 1H, H5), 3.00 (m, 1H, H7), 2.81 (d, 1H, H8), 2.55 (m, 1H, H1), 2.33 (m, 1H, H4), 2.04 (m, 1H, H8), 1.43 (m, 1H, H4), 1.10 (d, *J* = 8.1 Hz, 9H, PMe3), 0.91 (s, 3H, H2) 0.72 (m, 1H, H2), 0.71 (s, 3H, H11).**^{13}C NMR (201 MHz, CD_3CN):** δ 179.2 (1C, C13), 144.0 (1C, TpB3), 143.6 (1C, TpA3), 141.5 (1C, TpC3), 138.1 (1C, TpC5), 137.5 (1C, TpA5), 137.2 (1C, TpB5), 107.3 (1C, TpB4), 107.3 (1C, TpA4), 106.8 (1C, TpC4), 61.8 (1C, C2), 61.5 (1C, C6), 51.9 (1C, C12), 51.2 (1C, C1), 49.8 (1C, C7), 46.0 (1C, C3), 34.4 (1C, C5), 28.4 (1C, C4), 24.0 (1C, C8), 23.1 (1C, C11), 20.9 (1C, C10), 13.40 (d, *J* = 28.1 Hz, 3C, PMe3).



Compound 5.38:

Compound **3** (100 mg, 0.144 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.289 mL, 0.289 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, Ethane-1,2-dithiol (0.122 ml, 1.45 mmol) and Triethylamine (0.806 ml, 0.578 mmol) were cooled at -30 °C for 30 min in MeOH. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 5 hrs and room temperature for 24 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **38** (77.0 mg, 0.990 mmol, 69%).

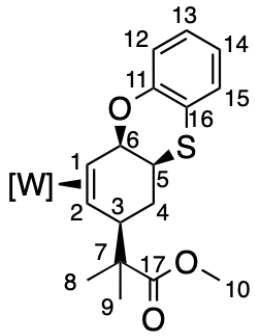
^{1}H NMR (800 MHz, CD_3CN): δ 8.02 (d, *J* = 2.1 Hz, 1H, TpA3), 7.97 (d, *J* = 2.1 Hz, 1H, TpB3), 7.84 (d, *J* = 2.3 Hz, 1H, TpC5), 7.80 (d, *J* = 2.4 Hz, 1H, TpB5), 7.80 (d, *J* = 2.5 Hz, 1H, TpA5), 7.35 (d, *J* = 2.3 Hz, 1H, TpC3), 6.32 (t, *J* = 2.2 Hz, 1H, TpB4), 6.28 (dt, *J* = 4.4, 2.1 Hz, 2H, TpA4/TpC4), 4.39 (d, *J* = 3.0 Hz, 1H, H6), 3.55 (m, 1H, H3), 3.47 (s, 3H, H12), 3.40 (d, *J* = 13.1 Hz, 1H, H5), 3.13 (ddd, *J* = 13.4, 12.3, 2.4 Hz, 1H, H7A), 3.00 (ddd, *J* = 14.3, 12.2, 2.4 Hz, 1H, H8A), 2.79 (m, 1H, H7B), 2.70 (td, *J* = 12.8, 11.0 Hz, 1H, H4A), 2.51 (dd, *J* = 14.0, 11.6 Hz, 1H, H1), 2.41 (ddd, *J* = 13.7, 4.1, 2.4 Hz, 1H, H8B), 1.48 (ddd, *J* = 12.3, 7.7, 3.4 Hz, 1H, H4B), 1.22 (d, *J* = 8.3 Hz, 9H, PMe3), 0.97 (s, 3H, H10), 0.74 (dt, *J* = 11.7, 1.7 Hz, 1H, H2), 0.67 (s, 3H, H11).**^{13}C NMR (201 MHz, CD_3CN):** δ 178.9 (1C, C13), 143.9 (1C, TpB3), 143.5 (1C, TpA3), 141.5 (1C, TpC3), 138.1 (1C, TpB5), 137.7 (1C, TpA5), 137.2 (1C, TpC5), 107.3 (2C, TpA4/TpB4), 106.7 (1C, TpC4), 59.7 (1C, C1), 51.9 (1C, C12), 50.1 (1C, C2), 49.8 (1C, C9), 49.7 (1C, C6), 45.9 (1C, C3), 35.0 (1C, C5), 34.0 (1C, C7), 28.7 (1C, C4), 23.8 (1C, C11), 23.7 (1C, C8), 20.6 (1C, C10), 13.6 (3C, PMe3).



Compound 5.39:

Compound **3** (100 mg, 0.131 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 15 min, a 1 M HOTf/ACN (0.262 mL, 0.262mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 1,2-benzenedithiol (187 mg, 1.31 mmol) and triethylamine (0.073 mL, 0.525 mmol) were cooled at -30 °C for 30 min in MeOH. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 5 hrs and for 24 hrs at RT. The reaction was washed three times (H_2O:NaOH/DCM; 30 mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting brown film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **39** (85.0 mg, 0.099 mmol, 79.0%).

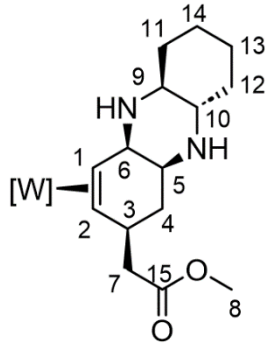
^{1}H NMR (600 MHz, CD_3CN): δ 8.04 (d, *J* = 2.1 Hz, 1H, TpA3), 7.97 (d, *J* = 2.0 Hz, 1H, TpB3), 7.86 (d, *J* = 2.4 Hz, 1H, TpB5), 7.82 (d, *J* = 2.3 Hz, 1H, TpC5), 7.81 (d, *J* = 2.4 Hz, 1H, TpA5), 7.43 (d, *J* = 2.2 Hz, 1H, TpC3), 7.21 (m, 1H, H11), 7.18 (m, 1H, H15), 7.01 (m, 1H, H12/H13), 6.32 (t, *J* = 2.2 Hz, 1H, TpB4), 6.31 (t, *J* = 2.3 Hz, 1H, TpA4), 6.28 (t, *J* = 2.3 Hz, 1H, TpC4), 4.41 (s, 1H, H6), 4.21 (s, 1H, H5), 3.54 (s, 3H, H3), 3.45 (s, 3H, H10), 2.85 (m, 1H, H1), 2.10 (m, 1H, H4), 1.55 (m, 1H, H4), 1.22 (d, *J* = 8.1 Hz, 9H, PMe3), 0.89 (s, 3H, H8), 0.85 (d, 1H, H2), 0.69 (s, 3H, H9).**^{13}C NMR (201 MHz, CD_3CN)**: δ 178.7 (1C, C17), 144.0 (1C, TpB3), 143.6 (1C, TpA3), 141.6 (1C, TpC3), 138.3 (1C, TpA5), 137.8 (1C, TpC5), 137.3 (1C, TpB5), 136.4 (1C, C16), 131.8 (1C, C15), 128.9 (1C, C14), 128.6 (1C, C11), 126.2 (1C, C13), 125.6 (1C, C12), 107.4 (1C, TpB4), 107.3 (1C, TpA4), 106.8 (1C, TpC4), 57.2 (1C, C2), 52.2 (1C, C6), 52.0 (1C, C10), 50.1 (1C, C7), 49.6 (1C, C1), 45.6 (1C, C3), 39.8 (1C, C5), 31.7 (1C, C4), 23.7 (1C, C9), 20.9 (1C, C8),13.4 (d, *J* = 27.3 Hz, 3C, PMe3).



Compound 5.40:

Compound **3** (70.0 mg, 0.092 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.180 mL, 0.180 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-mercaptophenol (0.10 mL, 0.92 mmol) and triethylamine (0.051 mL, 0.37 mmol) were cooled at -30 °C for 30 min in MeOH. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 5 hrs and for 24 hrs at RT. The reaction was washed three times (H_2O:NaOH/DCM; 30 mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting brown film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **40** (60.0 mg, 0.074 mmol, 81.0%).

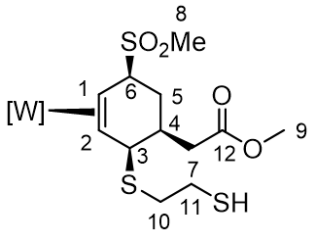
^{1}H NMR (600 MHz, CD_6CO): δ 8.10 (d, *J* = 2.1 Hz, 1H, TpA3), 8.08 (d, *J* = 2.0 Hz, 1H, TpB3), 7.99 (d, *J* = 2.4 Hz, 1H, TpB5), 7.93 (d, *J* = 2.3 Hz, 1H, TpC5), 7.89 (d, *J* = 2.4 Hz, 1H, TpA5), 7.65 (d, *J* = 2.2 Hz, 1H, TpC3), 7.04 (m, 1H, H15), 6.99 (m, 1H, H13), 6.90 (m, 1H, H12), 6.82 (m, 1H, H14), 6.40 (t, *J* = 2.2 Hz, 1H, TpB4), 6.38 (t, *J* = 2.3 Hz, 1H, TpA4), 6.32 (t, *J* = 2.3 Hz, 1H, TpC4), 4.86 (s, 1H, H6), 4.03 (s, 1H, H5), 3.56 (s, 3H, H3), 3.49 (s, 3H, H10), 3.09 (m, 1H, H1), 1.92 (m, 1H, H4), 1.55 (m, 1H, H4), 1.24(d, *J* = 8.3 Hz, 9H, PMe3), 0.95 (d, 1H, H2), 0.94 (s, 3H, H8), 0.68 (s, 3H, H9).**^{13}C NMR (201 MHz, CD_6CO):** δ 178.4 (1C, C11), 153.7 (1C, C11), 144.1 (1C, TpB3), 143.3 (1C, TpA3), 141.9 (1C, TpC3), 137.9 (1C, TpA5), 137.6 (1C, TpC5), 137.0 (1C, TpB5), 127.7 (1C, C15), 125.7 (1C, C13), 121.9 (1C, C14), 119.1 (1C, C16), 118.7 (1C, C12), 107.3 (1C, TpB4), 107.1 (1C, TpA4), 106.5 (1C, TpC4), 79.8 (1C, C6), 57.8 (1C, C1), 51.6 (1C, C10), 49.6 (1C, C2), 49.5 (1C, C7), 45.3 (1C, C3), 36.3 (1C, C5), 30.6 (1C, C4), 24.0 (1C, C9), 20.2 (1C, C8), 13.28 (d, *J* = 28.9 Hz, 3C, PMe3).



Compound 5.41:

Compound **2** (100 mg, 0.136 mmol) was placed in a test tube, with EtCN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.273 mL, 0.273 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, (1S,2S)-(+)-Cyclohexane-1,2-diamine (0.200 mL, 1.36 mmol) in EtCN was cooled at -30 °C for 30 min. Then, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 1 days and at RT for 4 hours. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 60 mL/60mL), and dried with golf-ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and added to a Filter Flask (250 mL). To this 200 mL of pentane were slowly added. Over the course of 3 days, crystals started forming, which were washed with pentane (2 x 20 mL) affording compound **41** (35.1 mg, 0.048 mmol, 34.8%).

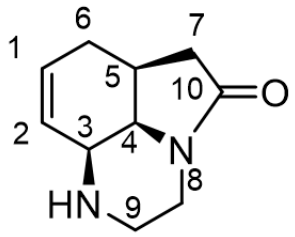
^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.27 (1H, d, TpA5), 8.02 (1H, d, TpB3), 7.84 (1H, d, TpB5), 7.82 (1H, d, TpC5), 7.79 (1H, d, TpA3), 7.39 (1H, d, TpC3), 6.37 (1H, t, TpB4), 6.26 (1H, t, TpC4), 6.24 (1H, t, TpA4), 3.82 (1H, d, H6), 3.64 (3H, s, H8), 3.56 (1H, m, H3), 3.16 (1H, dd, H9), 2.30 (2H, m, H7/H5), 2.24 (1H, m, H1), 2.05 (1H, t, H7), 1.96 (1H, m, H11), 1.72 (3H, m, H12/H14/H4), 1.53 (1H, m, H13), 1.33 (2H, m, H14/H3), 1.25 (2H, m, H11/H12), 1.14 (9H, d, PMe3), 1.05 (1H, m, H13), 0.72 (1H, dd, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 174.5 (1C, C15), 144.1 (1C, TpA3), 142.2 (1C, TpB3), 141.6 (1C, TpB5), 137.9 (1C, TpC5), 137.5 (1C, TpA5), 137.1 (1C, TpC3), 107.5 (1C, TpB4), 107.1 (1C, TpC4), 106.6 (1C, TpA4), 63.6 (1C, C5), 61.9 (1C, C1), 61.3 (1C, C6), 55.6 (1C, C10), 54.7 (1C, C2), 52.6 (1C, C9), 51.8 (1C, C8), 46.5 (1C, C7), 40.1 (1C, C3), 34.0 (1C, C1), 33.3 (1C, C13), 32.8 (1C, C12), 26.4 (1C, C11), 26.1 (1C, C14), 13.2 (3C, d J= 28.8 Hz, PMe_3).



Compound 5.42:

Compound **2** (75.0 mg, 0.10 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.200 mL, 0.200 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, ethane-1,2-dithiol (0.0690 mL, 0.820 mmol) and triethylamine (0.057 mL, 0.41 mmol) were cooled at -30 °C for 30 min in THF. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 12 hrs. A pipette-full of 20% KO^{t}Bu/THF solution was added to quench the reaction. A distinct color change was observed from yellow to light brown. The reaction was washed three times (H_2O:NaOH/DCM; 30 mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting brown film was dissolved in minimal DCM and pipetted in 50 mL of stirring pentane. A white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **42** (53.0 mg, 0.064 mmol, 63%).

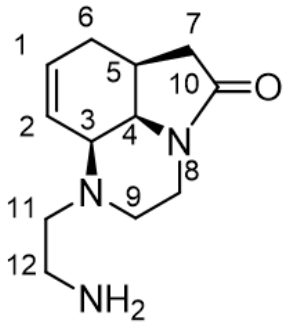
^{1}H NMR (800 MHz, CD_3CN): δ 8.11 (m, 1H), 8.05 (m, 1H), 7.88 (m, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.37 (m, 1H), 6.36 (dd, *J* = 2.4, 1.9 Hz, 1H), 6.31 (t, *J* = 2.3 Hz, 1H), 6.29 (t, *J* = 2.3 Hz, 1H), 4.37 (t, *J* = 9.3 Hz, 1H, H6), 3.92 (s, 1H, H3), 3.69 (s, 3H, H9), 3.00 (m, 3H, H8), 2.95 (m, 1H, H1), 2.77 (m, 1H, H7A), 2.50 (m, 2H, H10A/H10B), 2.45 (m, 1H, H7B), 2.25 (m, 2H, H11A/H11B), 1.74 (m, 1H, H5A), 1.68 (m, 1H, H5B), 1.39 (m, 1H, H2), 1.21 (d, *J* = 8.8 Hz, 9H, PMe3).



Compound 5.44:

In a glovebox, Compound **5** (70.0 mg, 0.103 mmol) was placed in a test tube with ~3ml dry MeCN (dried over sieves). A test tube was cooled to -30°C for 10 minutes. A 1M solution of bromine in DCE was added (123 uL, 0.123 mmol). Reaction mixture was stirred for 10 minutes at room temperature. Extraction with a 10% by weight sodium thiosulfate solution and DCM was carried out (3x50ml DCM). To the aqueous layer from this first extraction was added a 10% NaOH solution (50 mL). Another extraction with DCM was carried out (3x50 mL DCM). The second extraction was dried over sodium sulfate and evaporated in vacuo to yield a yellow oil (11.0 mg, 0.062 mmol, 60.0%).

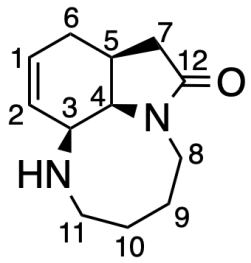
^{1}H-NMR ($CDCl_3$, δ, 25°C): 5.91 (1H, m, H1), 5.70 (1H, m, H2), 3.72 (1H, m, H9a), 3.72 (1H, td, H4), 3.40 (1H, m, H3), 2.85 (1H, m, H8a), 2.75 (2H, m, H9b, H8a), 2.68 (1H, m, H5), 2.57 (1H, m, H7a), 2.08 (1H, m, H6a), 2.02 (1H, dd, H7b), 1.83 (1H, dt, H6b). **^{13}C-NMR ($CDCl_3$, δ, 25ºC):** 174.1 (1C, s, C10), 131.8 (1C, s, C2), 129.6 (1C, s, C1), 58.3 (1C, s, C4), 50.7 (1C, s, C3), 41.4 (1C, s, C9), 40.2 (1C, s, C7), 40.0 (1C, s, C8), 29.4 (1C, s, C5), 28.2 (1C, s, C6). **HRMS:** expected =178.1106; obtained = 178.1106



Compound 5.45:

In a glovebox, Compound **16** (120 mg, 0.207 mmol) was placed in a test tube with ACN (2 mL). The solution was cooled to -30°C for 10 minutes. A solution of Br_2 in DCE was added (0.249 mL. 0.249 mmol, 1 molar). The reaction was stirred at -30°C for 10 minutes and then at room temperature for 10 more min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction was added 30ml saturated sodium hydroxide solution. Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (31.0 mg, 0.140 mmol, 68%).

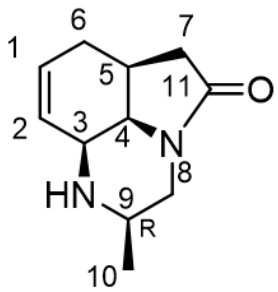
^{1}H-NMR ($CDCl_3$, δ, 25°C): 6.01 (1H, m, H1), 5.86 (1H, m, H2), 3.92 (1H, m, H4), 3.92 (1H, m, H8), 3.29 (1H, m, H3), 2.82 (3H, m, H9, H8), 2.73 (3H, m, H12, H5), 2.59 (1H, m, H11, H7), 2.49 (1H, t, H11), 2.10 (1H, m, H6), 1.99 (2H, t, H7, H6). **^{13}C-NMR ($CDCl_3$, δ, 25°C)**: 173.9 (1C, C10), 130.1 (1C, C1), 128.1 (1C, C2), 58.5 (1C, C4), 58.7 (1C, C3), 57.2 (1C, C12), 45.5 (1C, C11), 39.8 (1C, C8), 39.5 (1C, C7), 39.4 (1C, C9), 30.1 (1C, C5), 28.5 (1C, C6). **HRMS:** expected=221.1528; obtained= 221.1563



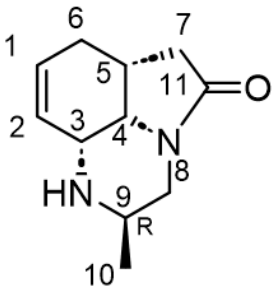
Compound 5.46:

In a glovebox, Compound **22** (105 mg, 0.148 mmol) was placed in a test tube with ACN (5 mL). A solution of Br_2 in DCE was added (0.185 mL, 0.185 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (19.0 mg, 0.920 mmol, 62.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 5.90 (ddt, *J* = 9.8, 5.6, 2.1 Hz, 1H, H1), 5.72 (dtd, *J* = 9.6, 3.9, 1.4 Hz, 1H, H2), 3.96 (ddd, *J* = 13.8, 10.0, 4.9 Hz, 1H, H8A), 3.52 (dd, *J* = 7.6, 5.7 Hz, 1H, H4), 3.42 (q, *J* = 7.0 Hz, 1H, H11A), 3.16 (t, *J* = 5.8 Hz, 1H, H3), 2.86 (ddd, *J* = 12.9, 6.4, 3.8 Hz, 1H, H6A), 2.81 (dt, *J* = 13.8, 4.8 Hz, 1H, H8B), 2.58 (dddd, *J* = 13.6, 7.5, 5.6, 2.7 Hz, 2H, H5/H11B), 2.25 (m, 1H, H7A), 2.10 (m, 2H, H6B/H7B), 1.85 (ttd, *J* = 9.9, 5.0, 1.2 Hz, 1H, H9A), 1.57 (m, 2H, H9B/H10A), 1.50 (m, 1H, H10B). **^{13}C NMR (201 MHz, CD_3CN):** δ 176.7 (1C, C12), 128.9 (1C, C2), 126.7 (1C, C1), 61.4 (1C, C4), 55.7 (1C, C3), 51.3 (1C, C11), 43.4 (1C, C8), 38.9 (1C, C7), 31.2 (1C, C5), 29.3 (1C, C10), 27.8 (1C, C9), 27.2 (1C, C6). **HRMS:** Expected = 206.1419; Obtained = 206.1422



A



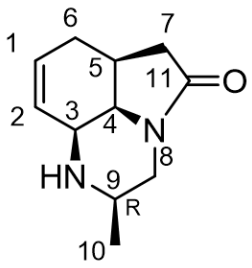
B

Compound 5.47:

Compounds **10A + 10B** (60.0 mg, 0.110 mmol) were placed in a test tube with ACN (2 mL). A solution of Br_2 in DCE was added (0.100 mL, 0.1300 mmol, 1M). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over anhydrous Na_2SO_4 and were evaporated in vacuo to yield a yellow oil (10.0 mg, 0.052 mmol, 60.0%).

47A: ^{1}H-NMR ($CDCl_3$, δ, 25°C): 5.83 (2H, s, H1/H2), 3.89 (1H, t, H4), 3.61 (1H, d, H3), 3.51 (1H, dd, H8), 3.20 (1H, m, H9), 3.07 (1H, dd, H8), 2.67 (1H, m, H5), 2.44 (1H, m, H7), 2.08 (1H, m, H6), 1.97 (2H, m, H6/H7), 1.06 (3H, d, H10). **^{13}C-NMR ($CDCl_3$, δ, 25ºC):** 175.2 (1C, C11), 129.8 (1C, C1), 128.4 (1C, C2), 55.6 (1C, C4), 51.0 (1C, C3), 47.5 (1C, C9), 46.9 (1C, C8), 38.9 (1C, C7), 29.8 (1C, C5), 26.9 (1C, C6), 19.7 (1C, C10). **HRMS:** expected =192.1263 amu; obtained = 192.1259 amu.

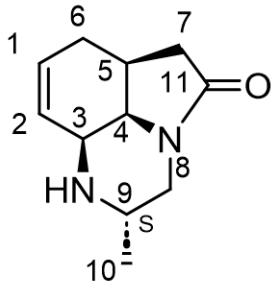
47B: ^{1}H-NMR ($CDCl_3$, δ, 25°C): 5.94 (1H, m, H2), 5.73 (1H, d, H1), 3.76 (2H, m, H8/H4), 3.45 (1H, bs, H3), 2.79 (1H, m, H5/H9), 2.50 (1H, m, H7), 2.32 (1H, t, H8), 2.08 (1H, m, H6), 1.86 (1H, m, H6/H7), 1.00 (3H, d, H10). **^{13}C-NMR ($CDCl_3$, δ, 25ºC):** 173.8 (1C, C11), 129.8 (1C, C1), 128.4 (1C, C2), 57.4 (1C, C4), 51.5 (1C, C3), 47.5 (1C, C9), 45.8 (1C, C8), 40.2 (1C, C7), 29.0 (1C, C5), 28.2 (1C, C6), 18.9 (1C, C10). **HRMS:** expected =192.1263 amu; obtained = 192.1259 amu.



Compound 5.48:

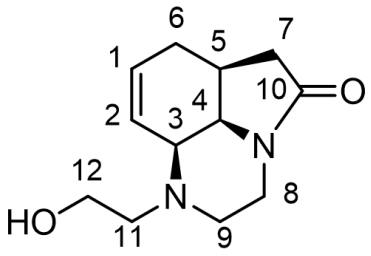
In a glovebox, Compound **11** (75.0 mg, 0.110 mmol) was placed in a test tube with ACN (2 mL). A solution of Br_2 in DCE was added (0.130 mL, 0.130 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (16.0 mg, 0.083 mmol, 77%).

^{1}H-NMR ($CDCl_3$, δ, 25°C): 5.81 (2H, s, H1/H2), 3.82 (1H, t, H4), 3.51 (1H, d, H3), 3.39 (1H, dd, H8), 3.09 (1H, m, H9), 3.01 (1H, dd, H8), 2.66 (1H, m, H5), 2.44 (1H, m, H7), 2.08 (1H, m, H6), 1.97 (2H, m, H6/H7), 1.08 (3H, d, H10). **^{13}C-NMR ($CDCl_3$, δ, 25ºC):** 175.2 (1C, C11), 132.9 (1C, C1), 127.4 (1C, C2), 56.2 (1C, C4), 51.0 (1C, C3), 47.2 (1C, C9), 46.5 (1C, C8), 38.9 (1C, C7), 30.0 (1C, C5), 26.9 (1C, C6), 20.3 (1C, C10). **HRMS:** expected =192.1263; obtained = 192.1262



Compound 5.49:

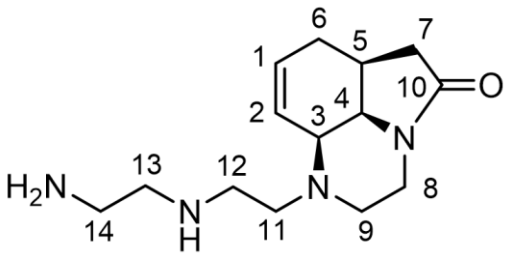
Compound **12** (75.0 mg, 0.110 mmol) was placed in a test tube with ACN (2 mL). A solution of Br_2 in DCE was added (0.130 mL, 0.130 mmol, 1M). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over anhydrous Na_2SO_4 and were evaporated in vacuo to yield a yellow oil (15.0 mg, 0.078 mmol, 72.0%).**^{1}H-NMR ($CDCl_3$, δ, 25°C):** 5.89 (1H, m, H2), 5.71 (1H, d, H1), 3.72 (2H, m, H8/H4), 3.41 (1H, bs, H3), 2.67 (1H, m, H5/H9), 2.49 (1H, m, H7), 2.22 (1H, t, H8), 2.08 (1H, m, H6), 1.87 (1H, m, H6), 1.85 (1H, m, H7), 1.00 (3H, d, H10). **^{13}C-NMR ($CDCl_3$, δ, 25°C):** 173.8 (1C, C11), 132.5 (1C, C1), 129.2 (1C, C2), 57.9 (1C, C4), 51.4 (1C, C3), 47.6 (1C, C9), 45.2 (1C, C8), 40.3 (1C, C7), 29.1 (1C, C5), 28.2 (1C, C6), 19.4 (1C, C10). **HRMS**: expected =192.1263 amu; obtained = 192.1258 amu.



Compound 5.50:

In a glovebox, Compound **14** (150 mg, 0.207 mmol) was placed in a test tube with ACN (5 mL). A solution of Br_2 in DCE was added (0.248 mL. 0.248 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (33.0 mg, 0.150 mmol, 73.0%).

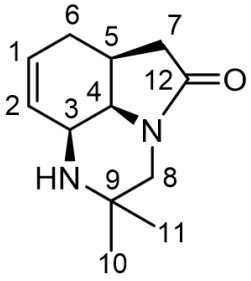
^{1}H NMR (800 MHz, CD_3CN): δ 6.00 (1H, ddd, H1), 5.91 (1H, m, H2), 3.87 (1H, m, H4), 3.74 (1H, dd, H8), 3.52 (2H, m, H12), 3.32 (1H, bs, H3), 2.79 (1H, m, H8), 2.75 (2H, m, H11), 2.72 (1H, m, H5), 2.65 (1H, m, H9), 2.51 (1H, m, H5), 2.48 (1H, m, H9), 2.11 (1H, m, H6), 1.98 (1H, m, H7), 1.84 (1H, dd, H7).**^{13}C NMR (201 MHz, CD_3CN):** δ 173.8 (1C, C10), 130.6 (1C, C1), 126.9 (1C, C2), 59.3 (1C, C12), 58.5 (1C, C4), 57.1 (1C, C11), 57.0 (1C, C3), 45.9 (1C, C9), 39.8 (1C, C7), 39.4 (1C, C8), 28.8 (1C, C5), 28.5 (1C, C6). **HRMS:** Expected = 222.1368; Obtained = 222.1370



Compound 5.51:

In a glovebox, Compound **17** (80.0 mg, 0.100 mmol) was placed in a test tube with ACN (2 mL). The solution was cooled to -30°C for 10 minutes. A solution of Br_2 in DCE was added (0.130 mL. 0.130 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (16.0 mg, 0.0610 mmol, 58.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 6.01 (1H, m, H1), 5.90 (1H, d, H2), 3.84 (1H, m, H4), 3.70 (1H, d, H8), 3.42 (2H, m, H14), 3.31 (1H, bs, H3), 2.74 (1H, m, H8), 2.74 (4H, m, H13/H11), 2.70 (1H, m, H5), 2.68 (1H, m, H9), 2.60 (2H, m, H12), 2.52 (1H, m, H7), 2.41 (1H, m, H9), 2.11 (1H, m, H6), 1.95 (1H, m, H6), 1.83 (1H, dd, H7).^{13}**C NMR (800 MHz, CD_3CN):** δ 172.9 (1C, C10), 129.5 (1C, C1), 126.1 (1C, C2), 65.3 (1C, C14), 57.3 (1C, C4), 55.6 (1C, C3), 53.8 (1C, C13), 53.6 (1C, C11), 52.1 (1C, C12), 45.0 (1C, C9), 38.9 (1C, C7), 38.6 (1C, C8), 27.9 (2C, C6/C5). **HRMS:** Expected = 264.1950; Obtained = 264.1954

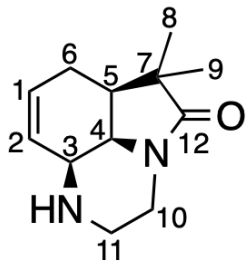


Compound 5.52:

In a glovebox, Compound **8** (100 mg, 0.141 mmol) was placed in a test tube with ACN (2 mL). The solution was cooled to -30°C for 10 minutes. A solution of Br_2 in DCE was added (0.176 mL. 0.176 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml).

To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (21.0 mg, 0.100 mmol, 72.0%).

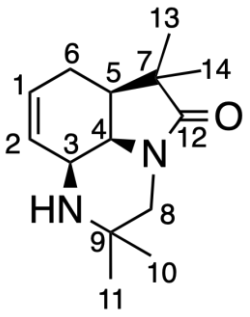
^{1}H NMR (800 MHz, CD_3CN): δ 5.82 (1H, m, H1), 5.72 (1H, m, H2), 3.69 (1H, m, H4), 3.62 (1H, m, H8), 3.49 (1H, m, H3), 3.37 (1H, m, H5), 2.71 (1H, d, H8), 2.49 (1H, m, H7), 2.44 (1H, m, H6), 2.01 (1H, m, H6), 1.98 (1H, m, H7), 1.13 (3H, s, H10), 1.05 (3H, s, H11).**^{13}C NMR (800 MHz, CD_3CN):** 174.5 (1C, C12), 132.3 (1C, C1), 129.7 (1C, C2), 55.2 (1C, C4), 49.4 (1C, C8), 49.3 (1C, C3), 49.0 (1C, C9), 38.8 (1C, C7), 28.6 (1C, C5), 26.7 (1C, C6), 13.3 (1C, C10), 10.4 (1C, C11). **HRMS:** Expected = 206.1419; Obtained = 206.1421



Compound 5.53:

In a glovebox, Compound **6** (98.0 mg, 0.140 mmol) was placed in a test tube with ACN (5 mL). A solution of Br_2 in DCE was added (0.180 mL. 0.180 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (19.0 mg, 0.093 mmol, 67.0%).

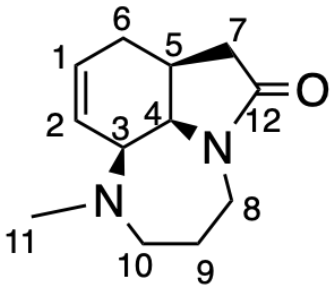
^{1}H-NMR (CD_3CN, δ, 25°C): 5.93 (1H, m, H1), 5.61 (1H, m, H2), 3.84 (1H, m, H10), 3.65 (1H, td, H4), 3.44 (1H, m, H3), 2.68 (1H, m, H10), 2.60 (2H, m, H11), 2.37 (1H, m, H5), 2.24 (1H, m, H6), 1.92 (1H, m, H6), 1.16 (s, 3H, H8), 1.08 (s, 3H, H9). **^{13}C-NMR (CD_3CN, δ, 25ºC):** 178.9 (1C, C12), 130.9 (1C, C2), 129.8 (1C, C1), 55.0 (1C, C4), 50.8 (1C, C3), 44.7 (1C, C7), 41.7 (1C, C11), 41.6 (1C, C10), 40.15 (1C, C5), 26.0 (1C, C6), 23.7 (1C, C8), 20.5 (1C, C9). **HRMS:** Expected = 206.1419; Obtained = 206.1423



Compound 5.54:

In a glovebox, Compound **9** (70.0 mg, 0.0950 mmol) was placed in a test tube with ACN (2 mL). The solution was cooled to -30°C for 10 minutes. A solution of Br_2 in DCE was added (0.114 mL. 0.114 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (14.0 mg, 0.060 mmol, 63.0%).

^{1}H NMR (800 MHz, $CDCCl_3$): δ 5.81 (2H, m, H1/H2), 3.80 (1H, m, H4), 3.76 (1H, d, H8), 3.74 (1H, m, H3), 2.30 (1H, d, H8), 2.28 (2H, q, H5/H6), 1.99 (1H, m, H6), 1.25 (3H, s, H10), 1.19 (3H, s, H11), 1.15 (3H, s, H13), 1.10 (3H, s, H14).**^{13}C NMR (800 MHz, $CDCCl_3$):** 179.3 (1C, C12), 126.9 (2C, C1/C2), 52.8 (1C, C4), 50.1 (1C, C8), 49.2 (1C, C3), 45.1 (1C, C9), 41.4 (1C, C7), 29.4 (1C, C5), 29.0 (1C, C6), 25.7 (1C, C10), 25.2 (1C, C11) 22.7 (1C, C13), 20.2 (1C, C14). **HRMS:** Expected = 234.1732; Obtained = 234.1737.

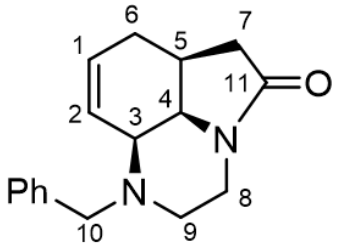


Compound 5.55:

In a glovebox, Compound **20** (112 mg, 0.158 mmol) was placed in a test tube with ACN (2 mL). A solution of Br_2 in DCE was added (0.205 mL, 0.205 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous

$Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (22.0 mg, 0.110 mmol, 67.0%).

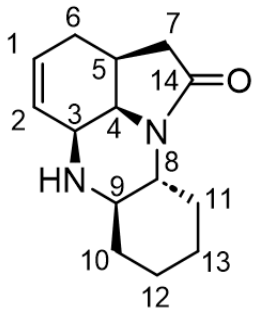
^{1}H NMR (800 MHz, CD_3CN): δ 5.91 (q, *J* = 2.4 Hz, 2H, H1/H2), 3.99 (dd, *J* = 7.4, 5.1 Hz, 1H, H4), 3.59 (ddd, *J* = 13.6, 6.6, 4.0 Hz, 1H, H8A), 3.34 (s, 1H, H3), 3.08 (ddd, *J* = 13.2, 9.0, 3.7 Hz, 1H, H8B), 2.86 (dt, *J* = 13.6, 5.9 Hz, 1H, H10A), 2.75 (ddd, *J* = 13.4, 7.9, 5.2 Hz, 1H, H10B), 2.65 (m, 1H, H5), 2.42 (s, 3H, H11), 2.39 (m, 1H, H7A), 2.16 (m, 1H, H6A), 1.91 (s, 2H, H6B/H7B), 1.69 (m, 2H, H9).**^{13}C NMR (201 MHz, CD_3CN):** δ 174.9 (1C, C12), 129.0 (1C, C2), 128.0 (1C, C1), 63.7 (1C, C4), 62.5 (1C, C3), 53.5 (1C, C10), 42.8 (1C, C11), 42.2 (1C, C8), 39.6 (1C, C7), 30.4 (1C, C5), 28.6 (1C, C6), 26.5 (1C, C9). **HRMS:** Expected = 206.1419 amu; Obtained = 206.1423 amu



Compound 5.56:

In a glovebox, Compound **13** (70.0 mg, 0.0910 mmol) was placed in a test tube with ACN (2 mL). A solution of Br_2 in DCE was added (0.109 mL, 0.109 mmol, 1 molar). The reaction was stirred at room temperature for 10 min.The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (15.0 mg, 0.0560 mmol, 62.0%).

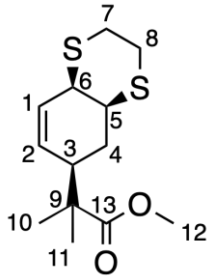
^{1}H NMR (800 MHz, d_2-CH_2Cl_2): δ 7.34-7.23 (5H, Ph), 5.95 (1H, m, H1), 5.68 (1H, dt, H2), 3.80 (4H, m, H3/H4/H8/H10), 2.74 (1H, m, H8), 2.68 (3H, m, H9/H10), 2.49 (2H, m, H5/H7), 2.24 (1H, m, H6), 2.09 (1H, m, H7), 2.16 (1H, m, H6).**^{13}C NMR (201 MHz, d_2-CH_2Cl_2):** δ 173.8 (1C, C11), 130.9 (2C, Ph), 129.3 (2C, Ph), 128.6 (1C, C2), 128.4 (1C, C1), 104.0 (1C, Ph), 41.3 (1C, C4), 39.4 (1C, C3), 39.9 (1C, C9), 39.8 (1C, C8), 32.3 (1C, C7), 30.1 (1C, C5), 29.2 (1C, C6) 27.9 (1C, C10). **HRMS**: Expected = 268.1576 amu; Obtained = 268.1577



Compound 5.57:

In a glovebox, Compound **15** (63.0 mg, 0.086 mmol) was placed in a test tube with ACN (2 mL). A solution of Br_2 in DCE was added (0.103 mL, 0.103 mmol, 1 molar). The reaction was stirred at room temperature for 10 min. The solution was extracted with an aqueous $Na_2S_2O_3$ (10% w/w) and DCM (3x 30ml). To the aqueous layer from this first extraction a 10% NaOH solution was added (30ml). Another extraction with DCM was carried out (3x40ml DCM). The layers from the second extraction were dried over sodium sulfate and were evaporated in vacuo to yield a yellow oil (12.0 mg, 0.052 mmol, 60.0%).

^{1}H-NMR ($CDCl_3$, δ, 25°C): 5.87 (1H, m, H1), 5.77 (1H, d, H2), 4.11 (1H, t, H4), 3.75 (1H, d, H3), 3.22 (1H, t, H8), 2.70 (1H, m, H5), 2.61 (1H, t, H9), 2.47 (1H, dd, H7), 2.21 (1H, m, H11), 1.99 (3H, m, H6/H7), 1.95 (1H, m, H10), 1.75 (1H, m, H10), 1.37 (2H, m, H12/H13), 1.25 (3H, H11/H12/H13). **^{13}C-NMR ($CDCl_3$, δ, 25ºC):** 175.4 (1C, C14), 131.4 (1C, C2), 127.8 (1C, C1), 61.1 (1C, C8), 56.5 (1C, C9), 54.0 (2C, C4/C3), 39.6 (1C, C7), 33.0 (1C, C11), 29.7 (1C, C5), 29.6 (1C, C10), 26.7 (1C, C6), 26.0 (1C, C12), 25.1 (1C, C13). **HRMS:** expected =232.1576; obtained = 232.1578

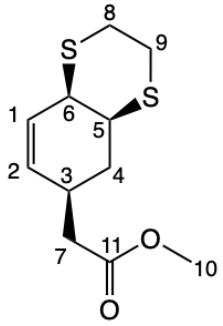


Compound 5.58:

In a glovebox, compound **38** (77.0 mg, 0.099 mmol) was placed in a test tube with ACN. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (45 mg, 0.20 mmol) in ACN was added dropwise, then the reaction allowed to stir at room temperature for 10 minutes The

reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 100 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (20.0 mg, 0.0730 mmol, 74.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 5.73 (ddd, *J* = 10.0, 5.5, 2.6 Hz, 1H, H1), 5.57 (ddt, *J* = 9.9, 2.4, 1.3 Hz, 1H, H2), 3.82 (ddq, *J* = 6.3, 3.1, 1.6 Hz, 1H, H6), 3.64 (s, 3H, H12), 2.99 (m, 2H, H7A/H8A), 2.87 (dtd, *J* = 12.8, 3.2, 1.4 Hz, 1H, H5), 2.74 (ddt, *J* = 13.1, 4.4, 2.4 Hz, 2H, H3/H7B), 2.61 (td, *J* = 12.6, 11.2 Hz, 1H, H4A), 2.48(m, 1H, H8B), 1.75 (m, 1H, H4B), 1.15 (s, 3H, H10), 1.13 (s, 3H, H11). **^{13}C NMR (201 MHz, CD_3CN):** δ 178.3 (1C, C13), 131.5 (1C, C2), 129.6 (1C, C1), 52.4 (1C, C12), 46.3 (1C, C3), 45.8 (1C, C9), 42.1 (1C, C6), 37.3 (1C, C5), 32.2 (1C, C7), 27.5 (1C, C4), 24.3 (1C, C8), 22.6 (1C, C10), 22.2 (1C, C11). **HRMS:** Expected = 272.0905 amu ; Obtained = 272.0895 amu

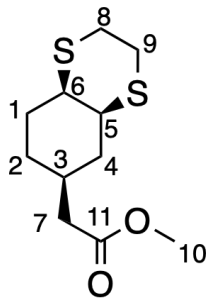


Compound 5.59:

In a glovebox, compound **35** (60.0 mg, 0.0800 mmol) was placed in a test tube with ACN. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (36 mg, 0.16 mmol) in ACN was added dropwise, then the reaction allowed to stir at room temperature over 10 minutes. The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (14.0 mg, 0.0570 mmol, 72.0%).

^{1}H NMR (800 MHz, CD_3CN) δ 5.65 (ddd, *J* = 9.9, 5.3, 2.5 Hz, 1H, H1), 5.60 (ddt, *J* = 9.8, 2.3, 1.2 Hz, 1H, H2), 3.84 (ddd, *J* = 6.4, 3.1, 1.4 Hz, 1H, H6), 3.63 (s, 3H, H10), 2.97 (m, 1H,

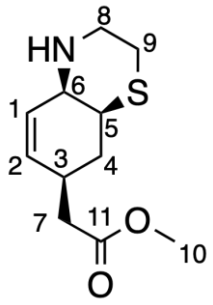
H8A), 2.96 (m, 1H, H9A), 2.89 (dtd, *J* = 12.7, 2.8, 1.2 Hz, 1H, H5), 2.78 (m, 1H, H3), 2.74 (m, 1H, H8B), 2.46 (m, 2H, H4A/H9B), 2.32 (dd, *J* = 15.5, 7.1 Hz, 1H, H7A), 2.30 (dd, *J* = 15.5, 7.7 Hz, 1H, H7B), 1.92 (ddd, *J* = 5.6, 2.7, 1.4 Hz, 1H, H4B).**^{13}C NMR (201 MHz, CD$_3$CN) δ** 173.3 (1C, C11), 133.7 (1C, C2), 128.5 (1C, C1), 52.1 (1C, C10), 41.9 (1C, C6), 40.6 (1C, C7), 36.9 (1C, C5), 35.9 (1C, C3), 32.2 (1C, C4), 32.1 (1C, C8), 24.3 (1C, C9). **HRMS:** Expected = 244.0592; Obtained = 244.0594



Compound 5.60:

35 was dissolved in methanol (2.00 mL) and added to a 4-dram vial. This solution was then circulated through a ThalesNano H-Cube flow hydrogenator for 4 hours. The temperature was set to 50 °C and the H2 pressure to 25 bars. The catalyst cartridge used contained 5%Pd on carbon. After circulation, the solution was collected and reduced to dryness (12 mg, 0.049 mmol, 85%).

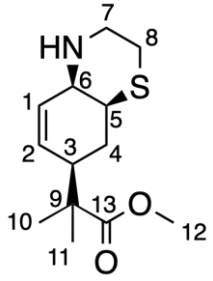
^{1}H NMR (800 MHz, CD$_3$CN) δ 3.61 (s, 2H, H10), 3.58 (s, 1H, H6), 3.02 (t, 1H, H8), 2.95 (t, 1H, H9), 2.81 (d, 1H, H8), 2.74 (d, 1H, H5), 2.42 (d, 1H, H9), 2.37 (q, 1H, H4), 2.26 (m, 2H, H7), 1.93 (m, 1H, H1), 1.87 (m, 1H, H3), 1.74 (m, 3H, H4/H1), 1.44 (m, 1H, H2), 1.23 (m, 1H, H2).**^{13}C NMR (201 MHz, CD$_3$CN) δ** 173.5 (1C, C11), 51.8 (1C, C10), 43.3 (1C, C6), 41.6 (1C, C7), 39.5 (1C, C5), 36.8 (1C, C3), 34.6 (1C, C4), 33.7 (1C, C1), 31.3 (1C, C8), 26.4 (1C, C2), 23.6 (1C, C9). **HRMS:** Expected = 246.0748 amu; Obtained = 246.0749 amu.



Compound 5.61:

In a glovebox, compound **36** (75.0 mg, 0.099 mmol) was placed in a test tube with ACN. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (45.0 mg, 0.210 mmol) in ACN was added dropwise, then the reaction allowed to stir at room temperature for 10 minutes The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 100 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (16.0 mg, 0.069 mmol, 67.0%).

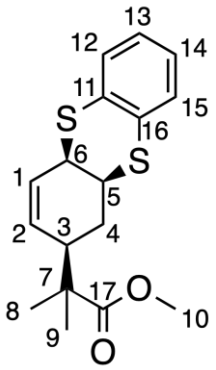
^{1}**H NMR (800 MHz, CD_3CN) δ** 5.65 (m, 1H, H1), 5.58 (d, 1H, H2), 3.64 (s, 3H, H10), 3.41 (d, 1H, H6), 3.22 (m, 1H, H8), 2.85 (t, 1H, H8), 2.72 (t, 1H, H9), 2.64 (m, 1H, H3), 2.53 (dd, 1H, H5), 2.33 (m, 1H, H7), 2.30 (m, 1H, H7), 2.09 (m, 1H, H9), 2.03 (m, 1H, H4), 1.86 (m, 1H, H4). **^{13}C NMR (201 MHz, CD_3CN) δ** 173.4 (1C, C11), 132.4 (1C, C2), 130.7 (1C, C1), 53.8 (1C, C6), 52.0 (1C, C12), 48.2 (1C, C8), 40.4 (1C, C7), 36.2 (1C, C5), 35.5 (1C, C3), 32.1 (1C, C4), 23.3 (1C, C9). **HRMS:** Expected = 227.0980; Obtained = 227.0983.



Compound 5.62:

In a glovebox, compound **37** (75.0 mg, 0.0990 mmol) was placed in a test tube with ACN. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (45.0 mg, 0.200 mmol) in ACN was added dropwise, then the reaction allowed to stir at room temperature for 10 minutes The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 100 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (17.0 mg, 0.0670 mmol, 67.0%).

^{1}H NMR (800 MHz, CD_3CN) δ 5.70 (m, 1H, H1), 5.53 (d, 1H, H2), 3.63 (s, 3H, H12), 3.37 (d, 1H, H6), 3.21 (m, 1H, H7), 2.84 (t, 1H, H7), 2.76 (t, 1H, H4), 2.58 (d, 1H, H5), 2.47 (d, 1H, H3), 2.12 (d, 1H, H8), 2.06 (d, 1H, H4), 1.63 (t, 1H, H8), 1.13 (s, 3H, H10), 1.11 (s, 3H, H11).**^{13}C NMR (201 MHz, CD_3CN) δ** 178.4 (1C, C13), 132.0 (1C, C1), 130.4 (1C, C2), 53.9 (1C, C6), 52.3 (1C, C12), 48.4 (1C, C7), 46.0 (1C, C9), 45.6 (1C, C5), 36.4 (1C, C3), 27.1 (1C, C8), 23.4 (1C, C4), 22.4 (1C, C10), 22.1 (1C, C11). **HRMS:** Expected = 256.1366 [H^+]; Obtained = 256.1361 [H^+]

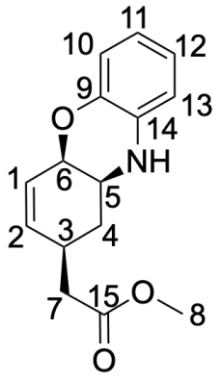


Compound 5.63:

In a glovebox, compound **39** (85.0 mg, 0.100 mmol) was placed in a test tube with ACN. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (47.0 mg, 0.210 mmol) in ACN was added dropwise, then the reaction allowed to stir at room temperature for 10 minutes The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 100 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl

ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (19.0 mg, 0.0590 mmol, 57.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 7.32 (dd, *J* = 7.8, 1.5 Hz, 1H, H13), 7.31 (dd, *J* = 7.7, 1.5 Hz, 1H, H12), 7.13 (td, *J* = 7.5, 1.4 Hz, 1H, H11), 7.09 (td, *J* = 7.5, 1.5 Hz, 1H, H14), 5.90 (ddd, *J* = 9.9, 5.1, 2.7 Hz, 1H, H1), 5.77 (dq, *J* = 10.0, 1.8 Hz, 1H, H2), 3.94 (m, 1H, H6), 3.65 (d, *J* = 0.9 Hz, 3H, H10), 3.41 (dtd, *J* = 6.4, 3.3, 1.4 Hz, 1H, H5), 2.64 (ddt, *J* = 12.2, 5.4, 2.1 Hz, 1H, H3), 2.07 (q, *J* = 12.5 Hz, 1H, H4A), 1.80 (dddt, *J* = 12.8, 5.6, 3.1, 1.5 Hz, 1H, H4B), 1.15 (s, 3H, H8), 1.13 (d, *J* = 2.1 Hz, 3H, H9). **^{13}C NMR (201 MHz, CD_3CN):** δ 178.0 (1C, C17), 137.5 (1C, C15), 135.3 (1C, C16), 133.2 (1C, C2), 130.6 (1C, C13), 129.2 (1C, C12), 127.8 (1C, C11), 126.2 (1C, C14), 125.9 (1C, C1), 52.4 (1C, C10), 45.9 (1C, C5), 45.6 (1C, C7), 45.1 (1C, C6), 44.3 (1C, C3), 29.1 (1C, C4), 22.6 (1C, C8), 22.1 (1C, C9).

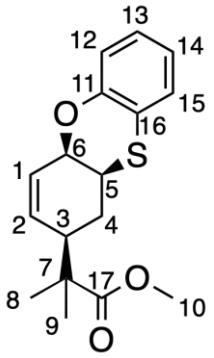


Compound 5.64:

Outside of a glovebox, compound **32** (96.0 mg, 0.130 mmol) was dissolved in acetonitrile and left to stir for 1 week. The solution was then evaporated in vacuo. The resulting brown oil was dissolved in minimal DCM and pipetted in 100ml of stirring hexanes. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5.00 ml). The resulting filtrate was evaporated to dryness to yield a clear oil (16.0 mg, 0.0480 mmol, 47.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 6.70 (td, *J* = 7.6, 1.5 Hz, 1H, H13), 6.67 (dd, *J* = 8.0, 1.4 Hz, 1H, H11), 6.56 (dd, *J* = 7.8, 1.6 Hz, 1H, H12), 6.49 (m, 1H, H10), 5.95 (ddd, *J* = 9.9, 5.0, 2.6 Hz, 1H, H2), 5.90 (d, *J* = 10.0 Hz, 1H, H1), 4.23 (s, 1H, H6), 3.63 (s, 3H, H8), 3.50 (dt, *J* = 12.4, 3.2 Hz, 1H, H5), 2.40 (dd, *J* = 16.0, 7.2 Hz, 1H, H7A), 2.32 (dd, *J* = 15.9, 7.7 Hz, 1H, H7B),

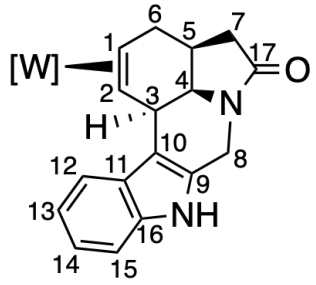
1.92 (m, 1H, H4A), 1.77 (m, 1H, H4B). **NMR (201 MHz, CD_3CN):** δ 183.0 (1C, C15), 137.3 (1C, C1), 126.1 (1C, C2), 122.6 (1C, C12), 117.6 (1C, C11), 117.0 (1C, C13), 115.0 (1C, C10), 68.7 (1C, C6), 52.0 (1C, C8), 49.9 (1C, C5), 40.2 (1C, C7), 34.3 (1C, C3), 33.1 (1C, C4). **HRMS:** Expected = 259.1208; Obtained = 259.1211



Compound 5.65:

In a glovebox, compound **40** (75.0 mg, 0.0930 mmol) was placed in a test tube with ACN. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (42.0 mg, 0.190 mmol) in ACN was added dropwise, then the reaction allowed to stir at room temperature for 10 minutes The reaction was washed three times (H_2O:$NaHCO_3$/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and pipetted in 100 mL of stirring hexane. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (17.0 mg, 0.0560 mmol, 60.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 7.07 (dd, *J* = 7.8, 1.8 Hz, 1H, H15), 6.99 (tdd, *J* = 7.3, 1.9, 0.7 Hz, 1H, H13), 6.88 (td, *J* = 7.5, 1.4 Hz, 1H, H14), 6.82 (dd, *J* = 8.0, 1.4 Hz, 1H, H12), 6.05 (ddd, *J* = 10.2, 5.3, 2.7 Hz, 1H, H1), 5.88 (dt, *J* = 10.2, 1.9 Hz, 1H, H2), 4.29 (m, 1H, H6), 3.64 (s, 3H, H10), 3.43 (dt, *J* = 13.2, 3.0 Hz, 1H, H5), 2.70 (m, 1H, H3), 1.84 (m, 1H, H4A), 1.77 (td, *J* = 12.9, 11.3 Hz, 1H, H4B), 1.13 (s, 3H, H8), 1.11 (s, 3H, H9). **^{13}C NMR (201 MHz, CD_3CN):** δ 178.1 (1C, C17), 153.0 (1C, C11), 134.9 (1C, C2), 127.5 (1C, C1), 127.4 (1C, C15), 126.1 (1C, C13), 123.1 (1C, C14), 119.3 (1C, C16), 119.2 (1C, C12), 69.9 (1C, C6), 52.4 (1C, C10), 45.6 (1C, C7), 45.5 (1C, C3), 39.4 (1C, C5), 29.0 (1C, C4), 22.5 (1C, C8), 22.0 (1C, C9). **HRMS:** Expected = 304.1133; Obtained = 304.1138

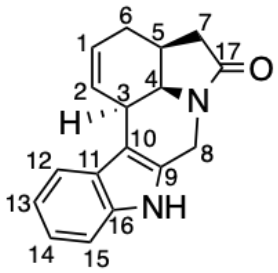


Compound 5.67:

Compound **2** (170 mg, 0.232 mmol) was placed in a test tube with ACN, and chilled to -30 °C. After 10 min, a 1 M HOTf/ACN (0.464 mL, 0.464 mmol) solution was added to the test tube and the solution was allowed to stir at -30 °C for 30 min. In a separate test tube, 2-(aminomethyl)indole (339 mg, 2.32 mmol) was cooled at -30 °C for 30 min in ACN. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 24 hrs and room temperature for 24 hrs. The reaction was washed three times (H_2O:Na_2CO_3/DCM; 30mL/30mL) and dried with Na_2SO_4. The organic layer was evaporated in vacuo. The resulting yellow film was dissolved in minimal DCM and loaded on a basic alumina column that was gradient eluded with hexane/ethyl acetate followed by ethyl acetate/Methanol. The band at 70:30 Ethyl acetate:Methanol was evaporated to dryness, dissolved in minimal DCM and pipetted in 25 mL of stirring hexane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed with hexane (2 × 10 mL) and desiccated overnight to yield compound **59** (105 mg, 0.137 mmol, 61.0%).

^{1}H NMR (800 MHz, CD_3CN): δ 8.23 (d, *J* = 2.4 Hz, 1H, TpB3), 7.94 (d, *J* = 2.4 Hz, 1H, TpA3), 7.87 (d, *J* = 2.5 Hz, 1H, TpB5), 7.74 (d, *J* = 2.4 Hz, 1H, TpC5), 7.53 (d, *J* = 2.3 Hz, 1H, TpC3), 7.51 (d, *J* = 2.4 Hz, 1H, TpA5), 7.47 (d, *J* = 7.8 Hz, 1H, H12), 7.35 (d, *J* = 8.2 Hz, 1H, H15), 7.03 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H, H14), 6.86 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H, H13), 6.43 (t, *J* = 2.2 Hz, 1H, TpB4), 6.16 (t, *J* = 2.3 Hz, 1H, TpC4), 5.47 (t, *J* = 2.3 Hz, 1H, TpA4), 4.86 (d, *J* = 17.1 Hz, 1H, H8A), 4.29 (dd, *J* = 7.0, 3.8 Hz, 1H, H3), 4.21 (dd, *J* = 17.0, 1.2 Hz, 1H, H8B), 3.98 (dd, *J* = 8.4, 3.9 Hz, 1H, H4), 3.02 (ddq, *J* = 13.8, 9.4, 4.2 Hz, 1H, H5), 2.64 (m, 2H, H7A/H7B), 2.57 (m, 2H, H1/H6A), 2.42 (ddd, *J* = 12.9, 8.3, 4.5 Hz, 1H, H6B), 1.45 (ddd, *J* = 9.8, 7.0, 2.9 Hz, 1H, H2), 1.15 (d, *J* = 8.4 Hz, 9H, PMe3).**^{13}C NMR (201 MHz, CD_3CN):** δ 175.67 (1C, C17), 147.64 (1C, TpA3), 144.86 (1C, TpB3), 142.79 (1C, TpC3), 138.02 (1C, C16), 137.57 (1C, TpC5), 136.95 (1C, TpB5), 136.79 (1C, TpA5), 131.29 (1C, C9), 128.68 (1C, C11), 122.08 (1C, C14), 120.38 (1C, C12), 119.84 (1C, C13), 117.26 (1C, C10), 111.90 (1C, C15),

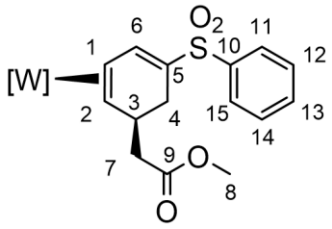
107.65 (1C, TpB4), 106.58 (1C, TpC4), 105.64 (1C, TpA4), 64.51 (1C, C4), 55.10 (1C, C2), 53.27 (1C, C1), 39.92 (1C, C8), 37.71 (1C, C7), 36.41 (1C, C3), 33.29 (1C, C6), 33.20 (1C, C5), 13.57 (3C, PMe3). **HRMS:** Expected = 767.2254 amu; Obtained = 767.2242 amu.



Compound 5.68:

Outside of a glovebox, compound **67** (105 mg, 0.137 mmol) was dissolved in acetonitrile and left to stir for 1 week. The solution was then evaporated in vacuo. The resulting brown oil was dissolved in minimal DCM and pipetted in 100ml of stirring hexanes. A brown solid precipitated out and was collected on a 15 mL fine-porosity fitted disk and washed two times with diethyl ether (5ml). The resulting filtrate was evaporated to dryness to yield a clear oil (20.0 mg, 0.137 mmol, 55.0%).

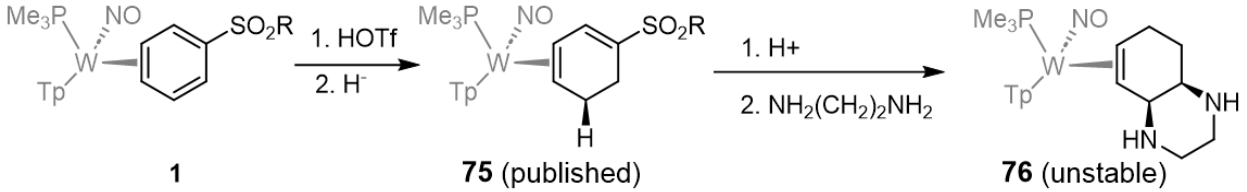
^{1}H NMR (800 MHz, CD_3CN): δ 7.51 (d, *J* = 7.8 Hz, 1H, H15), 7.37 (dt, *J* = 8.2, 0.9 Hz, 1H, H12), 7.14 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, H13), 7.06 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H, H14), 5.89 (m, 1H, H1), 5.85 (m, 1H, H2), 4.80 (d, *J* = 16.8 Hz, 1H, H8A), 4.15 (m, 2H, H3/H8B), 3.65 (s, 1H, H4), 2.88 (m, 1H, H5), 2.55 (ddd, *J* = 16.7, 9.0, 1.4 Hz, 1H, H7A), 2.26 (m, 1H, H6A), 2.05 (m, 2H, H6B/H7B). **^{13}C NMR (201 MHz, CD_3CN):** δ 175.06 (1C, C17), 137.92 (1C, C16), 131.96 (1C, C2), 130.63 (1C, C9), 127.37 (1C, C11), 126.64 (1C, C1), 122.58 (1C, C14), 120.20 (1C, C13), 118.69 (1C, C12), 112.18 (1C, C15), 111.23 (1C, C10), 57.89 (1C, C4), 39.57 (1C, C3), 38.80 (1C, C8), 32.48 (1C, C7), 29.81 (1C, C6), 27.48 (1C, C5). **HRMS:** Expected = 265.1335 amu [H^+]; Obtained = 265.1339 amu [H^+]



Compound 5.79:

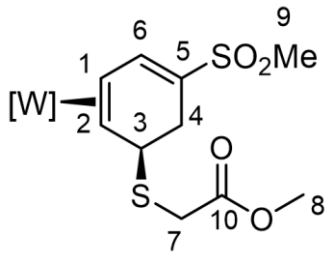
Compound **1** (1.00 g, 1.39 mmol) was placed in a test tube, with no solvent, and chilled to 0 °C. After 10 min, a 1 M HOTf/EtCN (2.10 mL, 2.10 mmol) solution was added to the test tube and the solution was allowed to stir at 0 °C for 10 min. In a separate test tube, 1-(*tert*-Butyldimethylsilyloxy)-1-methoxyethene (1.00 g, 1.20 mL, 5.50 mmol) was cooled at 0 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C overnight. The test tube was removed from the box and evaporated to dryness to form a dark oil, which was washed three times (H_2O/DCM: 60mL/60mL), and dried with golf ball size Na_2SO_4. A 60 mL medium-porosity frit was filled two-thirds with silica, and the previous mixture was placed on top. Hexanes (250 mL) was eluted through the column, followed by diethyl ether (200 mL) and by ethyl acetate (500 mL). The ethyl acetate portion eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 50 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight to yield compound **73** (444 mg, 558 mmol, 40%; 19%-44% yields).

^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.00 (1H, d, TpB3), 7.94 (1H, d, TpA3), 7.92 (1H, dd, H6), 7.86 (1H, d, TpC5), 7.85 (1H, d, TpB5), 7.85 (2H, m, H11, H15), 7.76 (1H, d, TpA5), 7.59 (H1, m, H13), 7.53 (2H, m, H12,14), 7.42 (1H, d, TpC3), 6.36 (1H, t, TpB4), 6.28 (1H, t, TpA4), 6.28 (1H, t, TpC4), 3.34 (3H, s, H8), 3.18 (1H, q, H3), 2.88 (1H, m, H1), 2.72 (1H, m, H4), 2.13 (1H, H4), 2.13 (2H, H7), 1.24 (9H, d, PMe3), 1.14 (1H, d, H2). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 174.3 (1C, C9), 147.2 (1C, C6), 144.7 (1C, TpB3), 143.3 (1C, C5), 143.2 (1C, TpA3), 142.2 (1C, TpC3), 142.0 (1C, C10), 138.3 (1C, TpB5), 137.6 (1C, TpC5), 137.3 (1C, TpA5), 129.7 (2C, C12/14), 128.4 (2C, C11,15), 126.6 (1C, C13), 107.8 (1C, TpB4), 107.1 (1C, TpC4), 106.9 (1C, TpA4), 62.3 (1C, C2) 51.8 (1C, C8), 48.5 (1C, C1), 44.3 (1C, C7), 34.3 (1C, C3), 27.8 (1C, C4), 13.7 (3C, d J= 29.9 Hz, PMe_3).



Compound 5.81:

Compound **75** (50.0 mg, 0.0760 mmol) was placed in a test tube, with CH_3CH_2CN, and chilled to -30 °C. After 10 min, a 1 M HOTf/EtCN (0.15 mL, 0.15 mmol) solution was added to the test tube and the solution was allowed to stir at -20 °C for 20 min. In a separate test tube, ethylene diamine (0.101 mL, 1.51 mmol) was cooled at -30 °C for 20 min, in minimal EtCN. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C overnight. A 2M NaO^tBu/THF solution (0.113 mL, 0.226 mmol) was added to quench the reaction, which was washed three times (H_2O:Na_2CO_3/DCM; 30 mL/30mL), and dried with golf ball size Na_2SO_4. The organic layer was evaporated in vacuo. The resulting brown film was dissolved in minimal DCM and pipetted in 15 mL of stirring pentane. An off-white solid precipitated out and was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL). Ungratifyingly, the precipitate turned from pale to dark in a matter of minutes in the box, and outside the box. The filtrate contained some desired product (yield not obtained). **^{1}H-NMR (d_2-CH_2Cl_2, δ, 25 C):** 8.26 (1H, d, TpA5), 8.03 (1H, d, TpB3), 7.76 (1H, d, TpB5), 7.71 (1H, d, TpC5), 7.68 (1H, d, TpA3), 7.31 (1H, d, TpC3), 6.33 (1H, t, TpB4), 6.25 (1H, t, TpA4), 6.19 (1H, t, TpC4), 4.16 (1H, s, H3), 3.34 (1H, m, H6), 3.02 (1H, m, H4), 2.91 (2H, m, H7/H8), 2.73 (1H, m, H8), 2.72 (1H, m, H1), 2.67 (1H, m, H6), 2.61 (1H, m, H7), 1.93 (1H, m, H5), 1.63 (1H, m, H5), 1.15 (9H, d, PMe3), 1.03 (1H, d, H2). **^{13}C-NMR (d_2-CH_2Cl_2, δ, 25 C):** 143.3 (1C, TpA5), 142.4 (1C, TpB3), 140.6 (1C, TpC3), 136.8 (1C, TpB5), 136.3 (1C, TpC5), 136.2 (1C, TpA3), 106.8 (1C, TpB4), 106.2 (1C, TpA4), 106.1 (1C, TpC4), 57.8 (1C, C3), 56.5 (1C, C2), 53.3 (1C, C4), 51.0 (1C, C1), 44.1 (1C, C8), 43.5 (1C, C7), 28.0 (1C, C6), 26.1 (1C, C5), 13.7 (3C, d J= 27.5 Hz, PMe_3).



Compound 5.82:

Compound **1** (200 g, 0.303 mmol) was placed in a test tube, with no solvent, and chilled to 0 °C. After 10 min, a 1 M HOTf/EtCN (0.364 mL, 0.364 mmol) solution was added to the test tube and the solution was allowed to stir at 0 °C for 10 min. In a separate test tube, potassium 2-methoxy-2-oxoethane-1-thiolate (219 mg, 1.52 mmol) was cooled at 30 °C for 20 min. After the time elapsed, the former solution was added to the latter, dropwise. The reaction stirred at -30 °C for 4 hours. The test tube was removed from the box and evaporated to dryness to form a dark oil, which was washed three times (H_2O/DCM: 60mL/60mL), and dried with golf ball size Na_2SO_4. A 60 mL medium-porosity frit was filled two-thirds with silica, and the previous mixture was placed on top. Hexanes (250 mL) was eluted through the column, followed by diethyl ether (200 mL) and by ethyl acetate (500 mL). The ethyl acetate portion eluted a yellow band, which was evaporated to dryness, redissolved in minimal DCM, and then added to 50 mL of stirred pentane. An off-white solid precipitated out of the pentane, which was collected on a 15 mL fine-porosity fitted disk, washed pentane (2 × 10 mL) and desiccated overnight to yield compound **77** (102 mg, 0.133 mmol, 44.0%).

^{1}H-NMR (d_3-MeCN, δ, 25 C): 8.03 (1H, d, TpB3), 7.90 (1H, d, TpA3), 7.88 (2H, s, TpC5/TpB5), 7.80 (1H, d, TpA5), 7.67 (1H, dd, H6), 7.46 (1H, d, TpC3), 6.38 (1H, t, TpB4), 6.33 (1H, t, TpA4), 6.31 (1H, t, TpC4), 4.38 (1H, d, H3), 3.55 (3H, s, H8), 3.33 (1H, d, H7), 3.26 (1H, d, H7), 2.98 (1H, m, H1), 2.92 (3H, s, H9), 2.66 (1H, m, H4), 2.15 (1H, m, H4), 1.41 (1H, d, H2), 1.24 (9H, d, PMe3). **^{13}C-NMR (d_3-MeCN, δ, 25 ^{0}C):** 172.4 (1C, C10), 145.2 (1C, C6), 144.6 (1C, TpB3), 142.8 (1C, C5), 142.1 (1C, TpA3), 138.3 (1C, TpB5), 137.8 (1C, TpC5), 137.4 (1C, TpA5), 107.8 (1C, TpB4), 107.5 (1C, TpC4), 107.2 (1C, TpA4), 59.5 (1C, C2) 52.7 (1C, C8), 48.1 (1C, C1), 47.4 (1C, C9), 44.8 (1C, C7), 34.6 (1C, C3), 28.6 (1C, C4), 13.7 (3C, d J= 29.2 Hz, PMe_3).

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Concluding Remarks

This thesis represents a significant contribution to the field of synthetic chemistry, addressing both fundamental challenges and practical applications with an innovative approach. Through a rigorous exploration of synthetic methodologies, this work has advanced our understanding of molecular design and reactivity, offering new insights and practical tools for future research. **Chapter 1** provides a comprehensive examination of novel synthetic strategies aimed at enhancing molecular three-dimensionality. By advocating for the use of alkene reactivity in aromatic systems and proposing dearomatization as a method to convert planar aromatic compounds into complex three-dimensional structures, this chapter establishes a foundational framework for further exploration. The detailed analysis of various dearomatization techniques—including enzymatic, photochemical/thermal, and transition metal-mediated—illustrates their respective strengths and limitations. The chapter's focus on transition-metal mediated reactions, particularly those involving dihapto-coordination of electron-deficient aromatic substrates, emphasizes the transformative potential of these methods in expanding the synthetic repertoire available for designing intricate molecular architectures. **Chapter 2** transitions from theoretical exploration to practical application, examining the synthesis of γ-lactams and hydroindolone cores—key structures found in pharmaceuticals and natural products. This chapter highlights how the advancements achieved using electron-deficient arenes have enabled the development of novel hydroindolone cores and innovative multicyclic molecules. By detailing these synthetic strategies, the chapter not only enhances the understanding of these core structures but also demonstrates their potential for further applications in drug discovery and development. **Chapter 3** introduces a novel and sophisticated process for synthesizing di- and trisubstituted cyclohexenes from electron deficient arenes. The method employs a series of nucleophilic addition reactions to a phenyl sulfone dihapto-coordinated to a tungsten complex, showcasing the methodology's ability to produce functionalized cyclohexenes with significant pharmaceutical potential. The detailed mechanistic insights and practical outcomes presented in this chapter underline the method's relevance and efficacy in advancing both synthetic methodology and pharmaceutical research. **Chapter 4** explores the synthesis of functionalized cis-hydro-2-oxindoles, employing a modular approach that involves the coordination of phenyl sulfones to a tungsten fragment. The chapter demonstrates how this method achieves high regio- and stereoselectivity through tandem protonation and nucleophilic additions, culminating in the formation of cis-

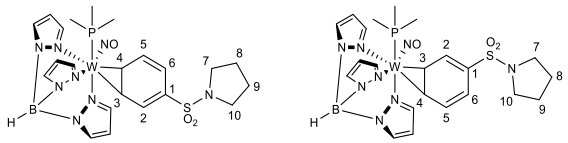
hydro-2-oxindoles via oxidative decomplexation. The approach described offers a versatile and robust alternative to existing methodologies, expanding the range of accessible compounds and providing a foundation for further functionalization and exploration. **Chapter 5** focuses on developing heteropolycyclic molecules from phenylsulfones highlights the potential for creating chemically diverse and biologically relevant polycyclic systems. By dihapto-coordinating the aromatic ring to a π-basic tungsten complex and performing a series of chemical transformations, this work illustrates the ability to synthesize compounds with novel structural features that mimic the skeletons of natural product. This advancement offers new possibilities for research and application in drug discovery and materials science.

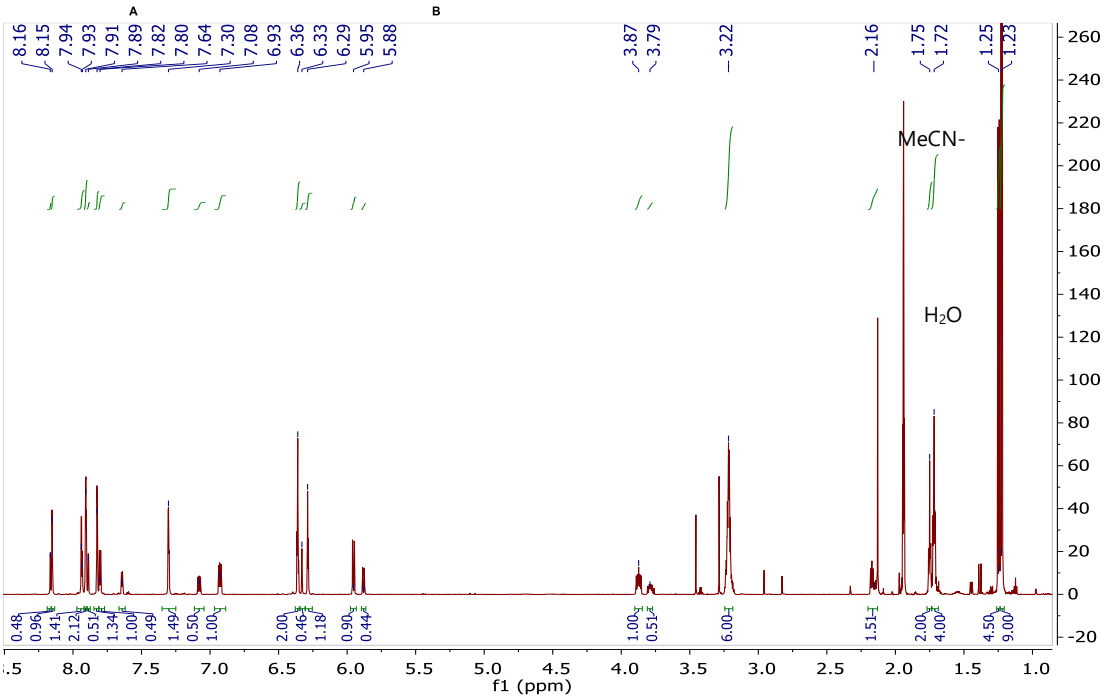
In conclusion, this thesis has made substantial contributions to synthetic chemistry by introducing and applying innovative methodologies that enhance molecular complexity and reactivity. The research presented not only advances theoretical understanding but also provides practical tools and strategies for drug development and materials science. The work underscores the importance of novel synthetic approaches in achieving complex molecular designs and sets the stage for future research endeavors. By addressing both fundamental and applied aspects of synthetic chemistry, this thesis paves the way for continued exploration and development in this dynamic and evolving field.

Appendix

NMR Data Chapter 3

^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.3a and 3.3b:





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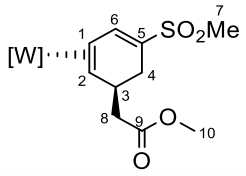
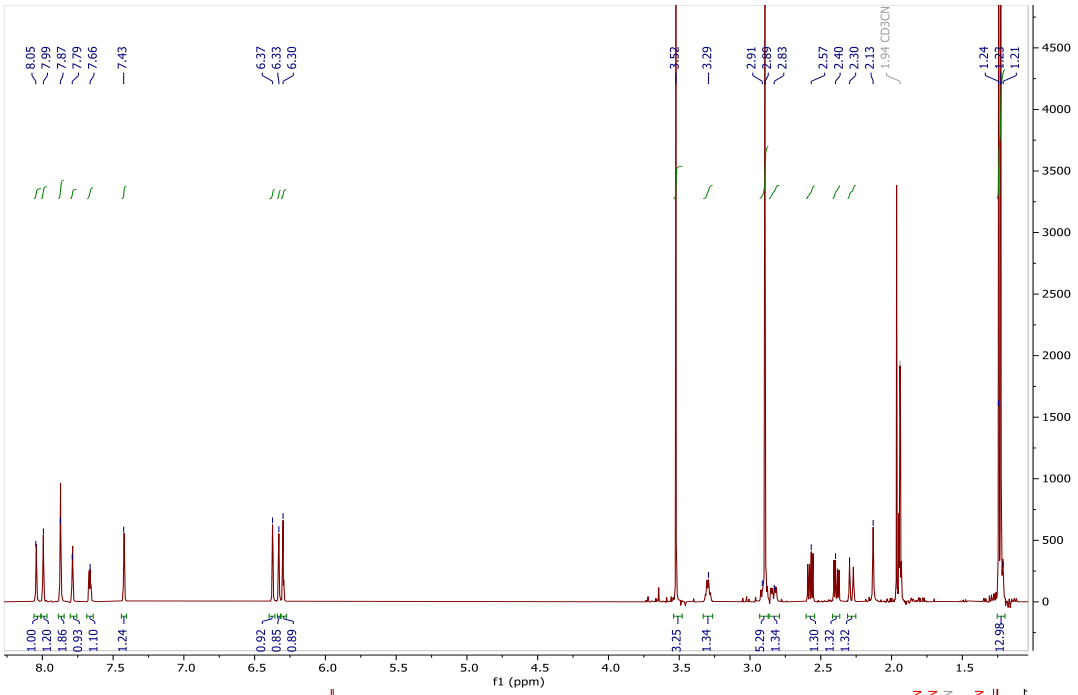
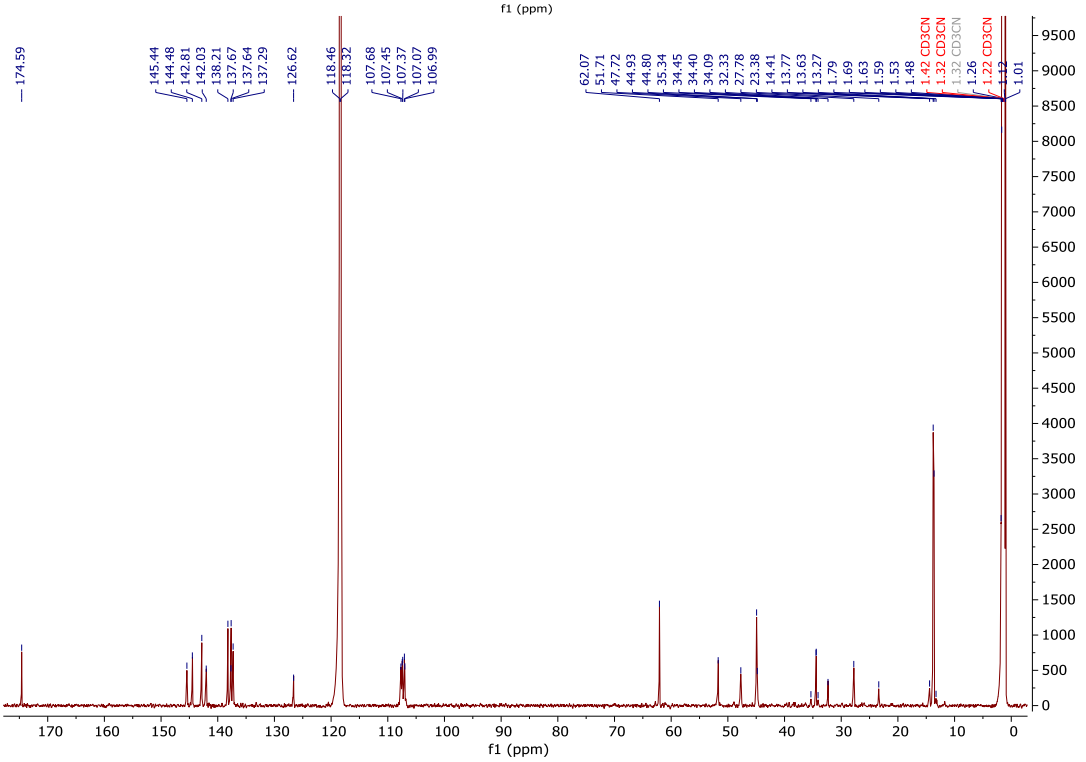
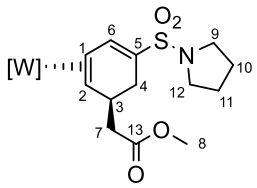
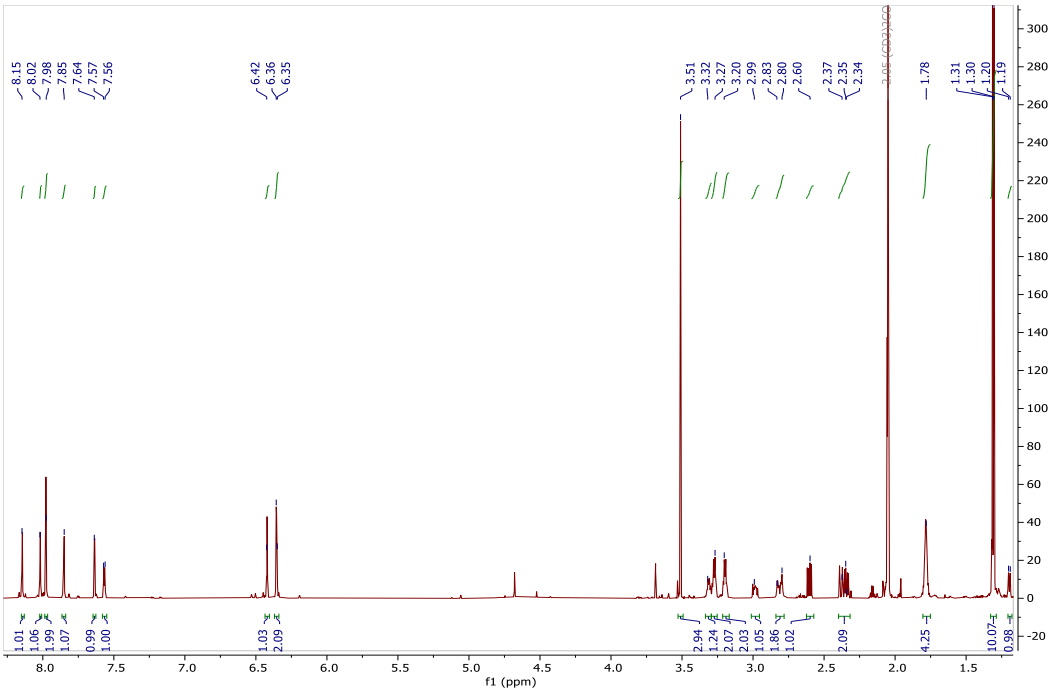


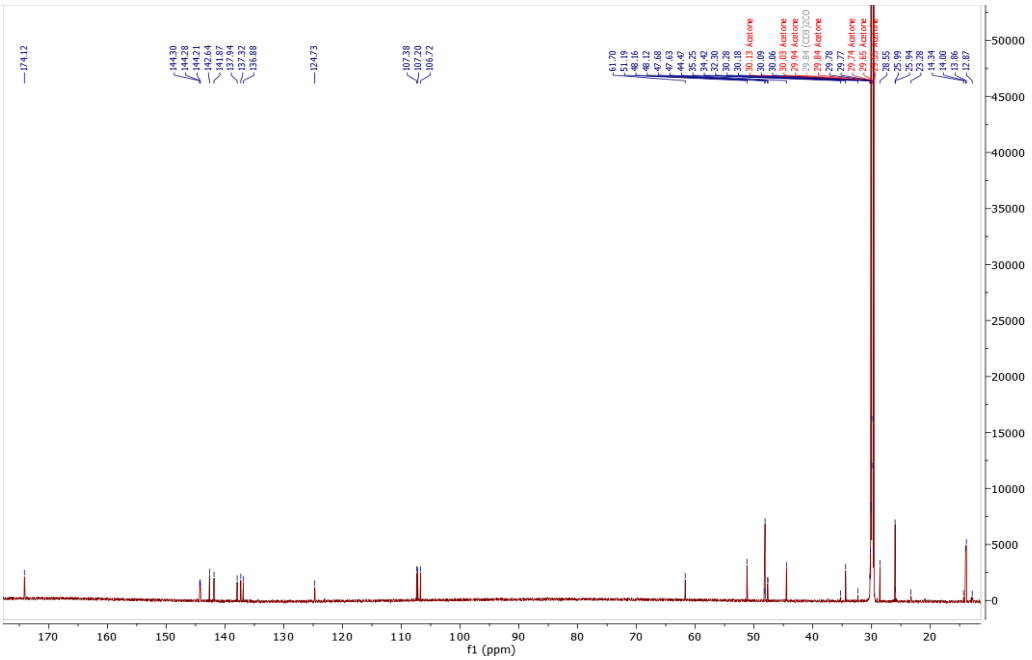




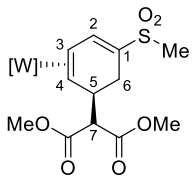
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.14:

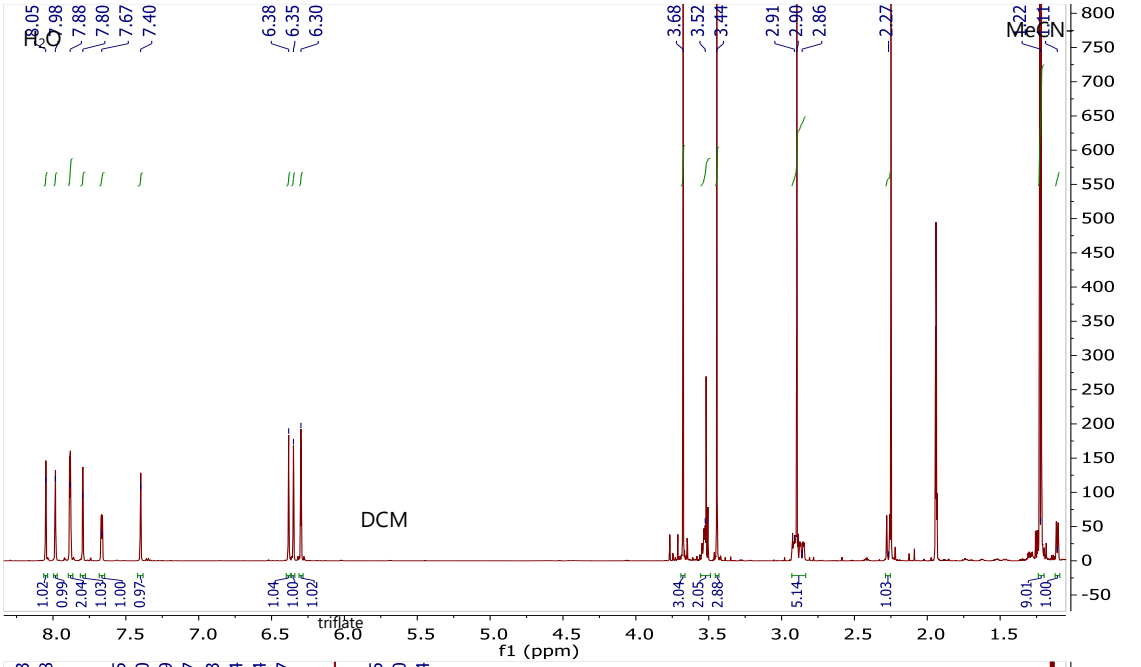


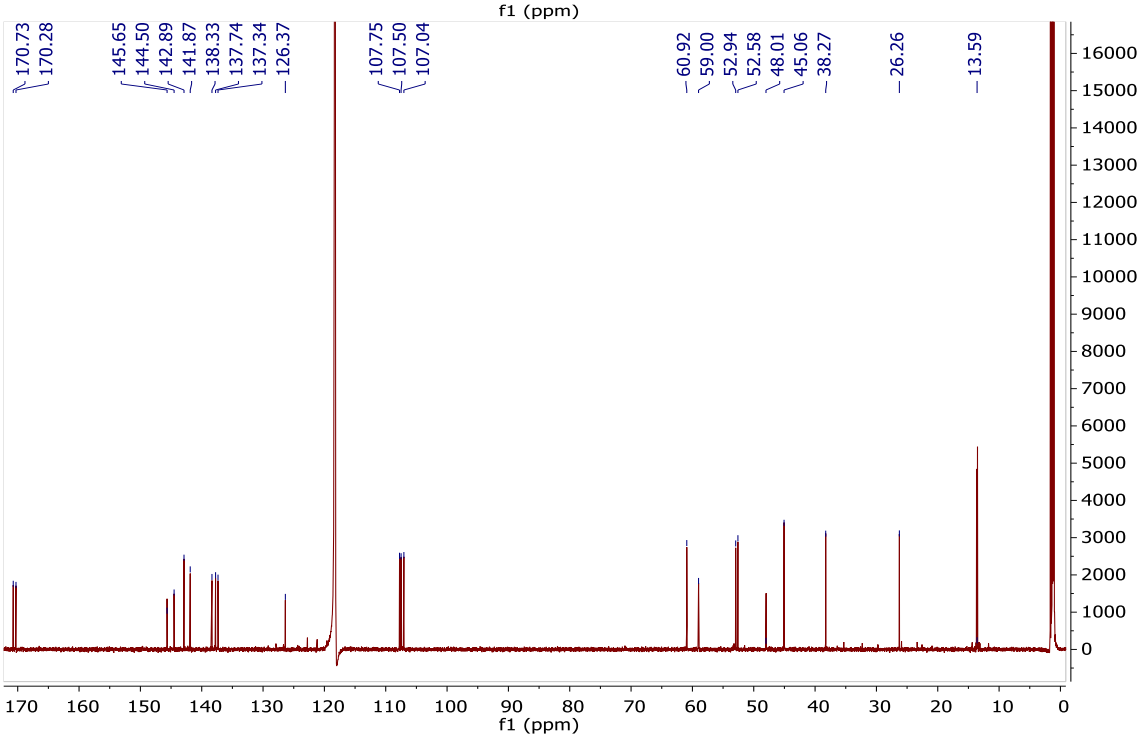




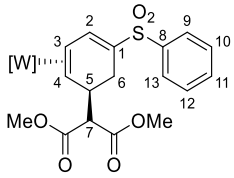
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.15:

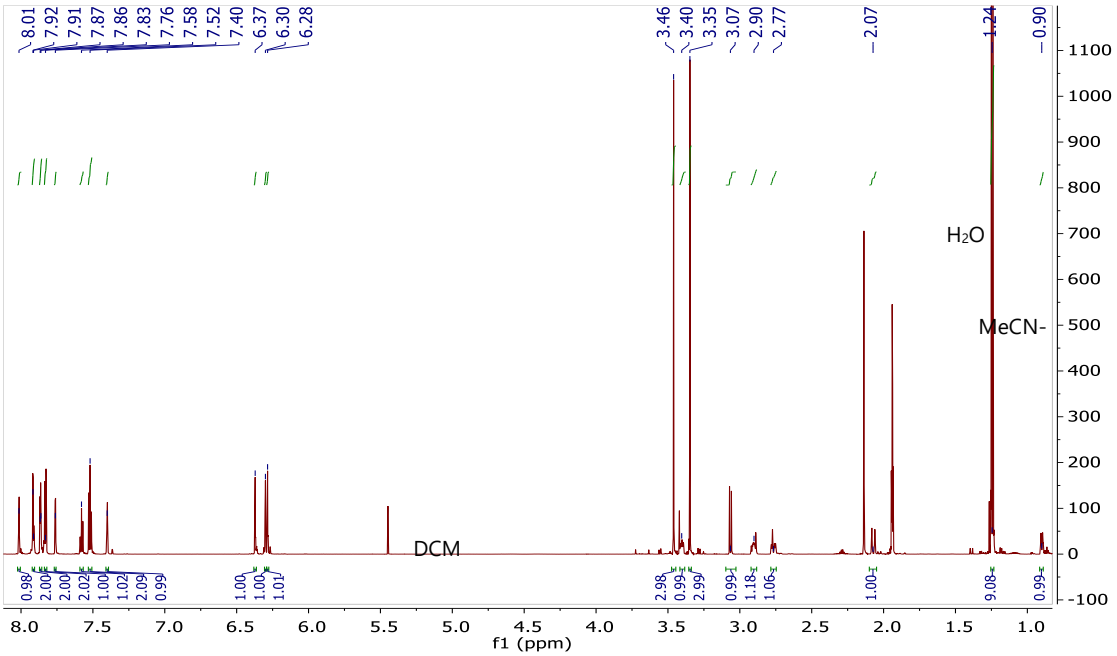


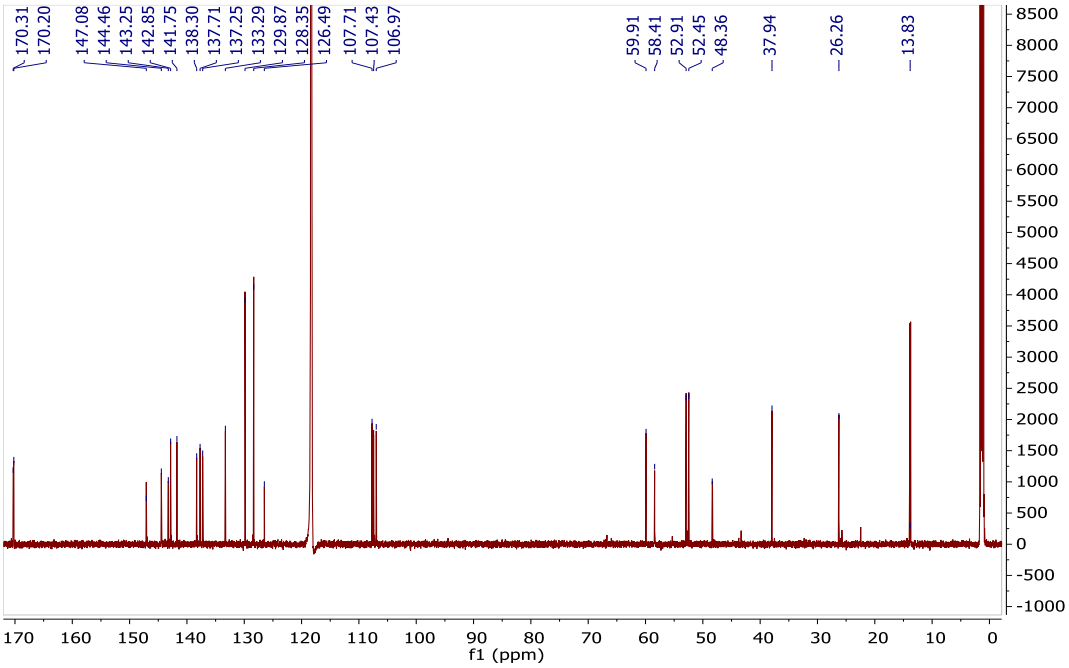




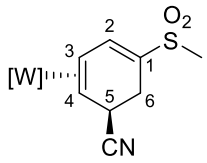
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.16:

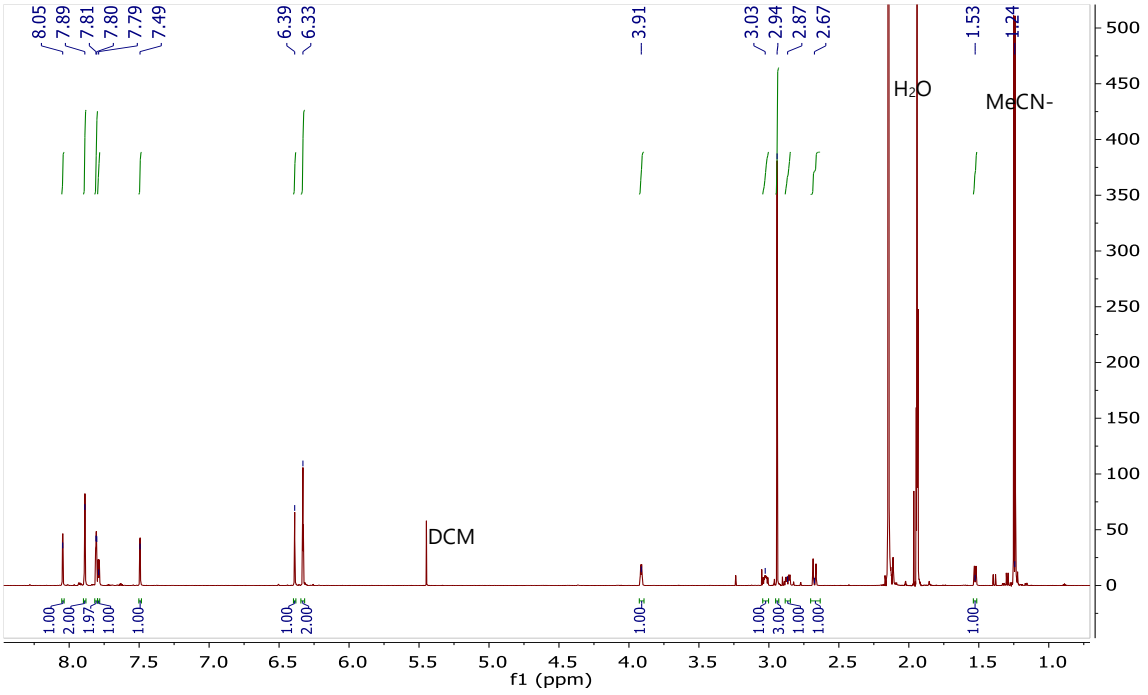


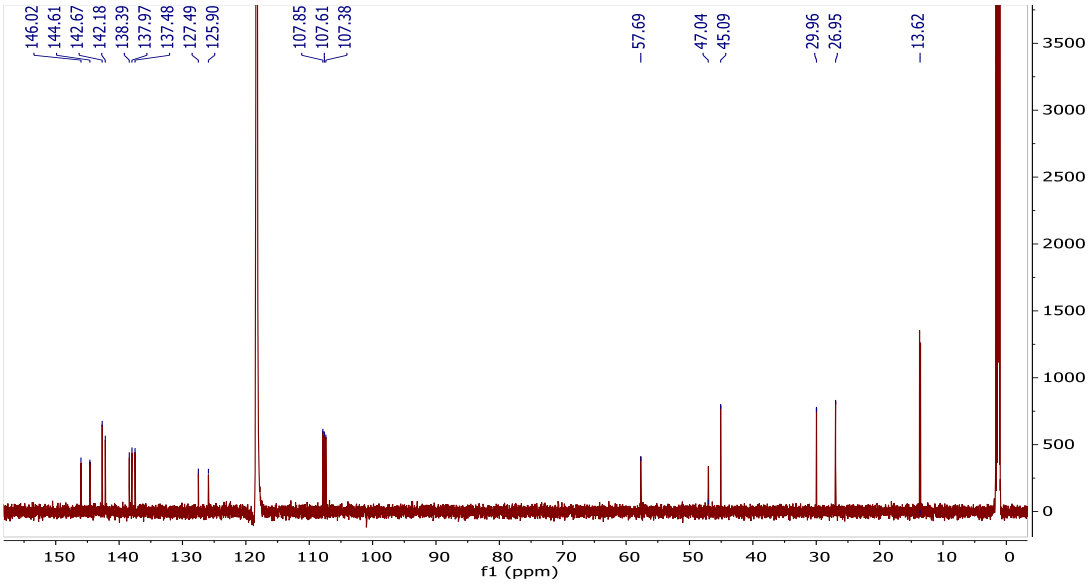




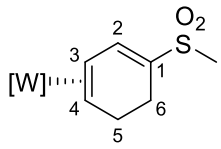
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.18:

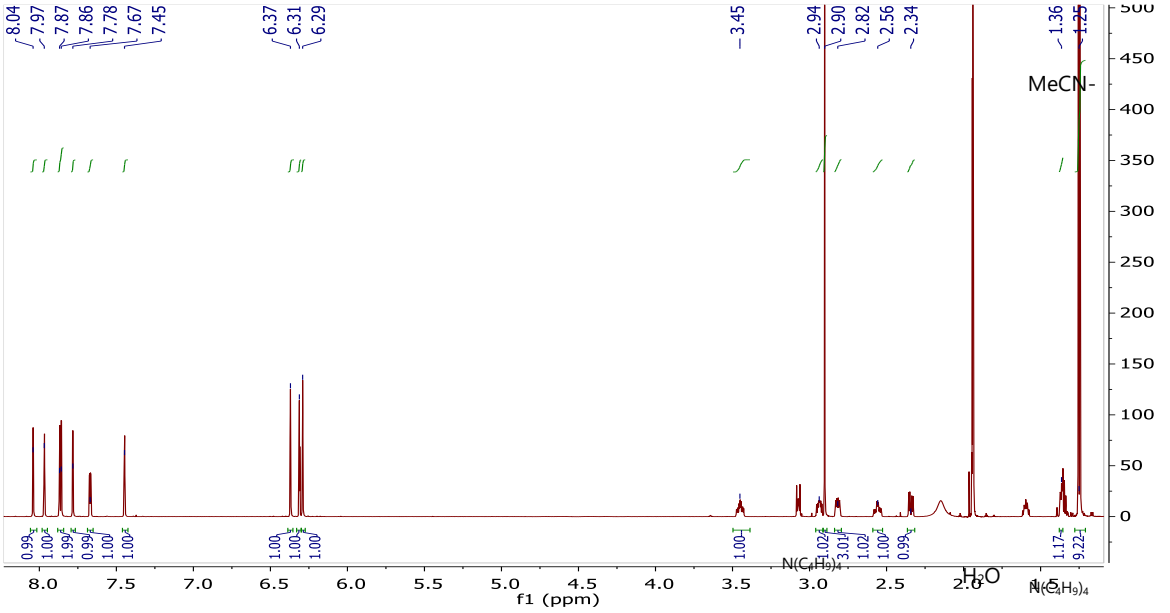


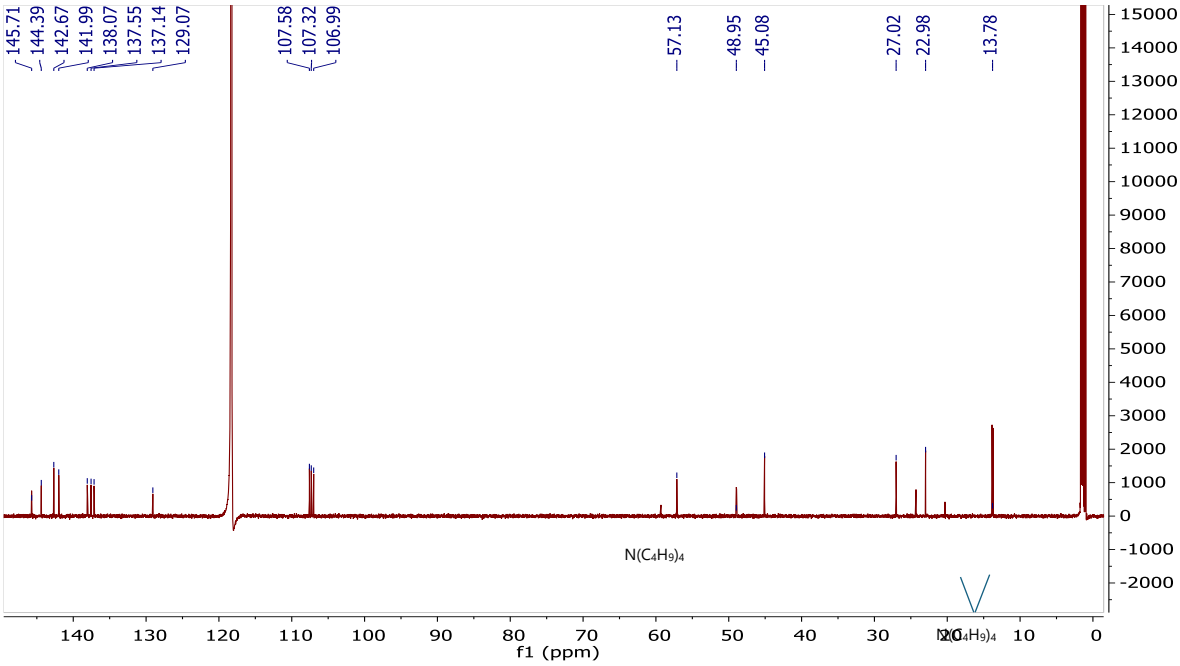




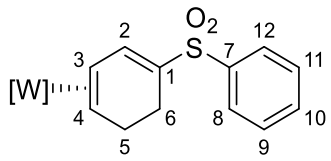
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.21:

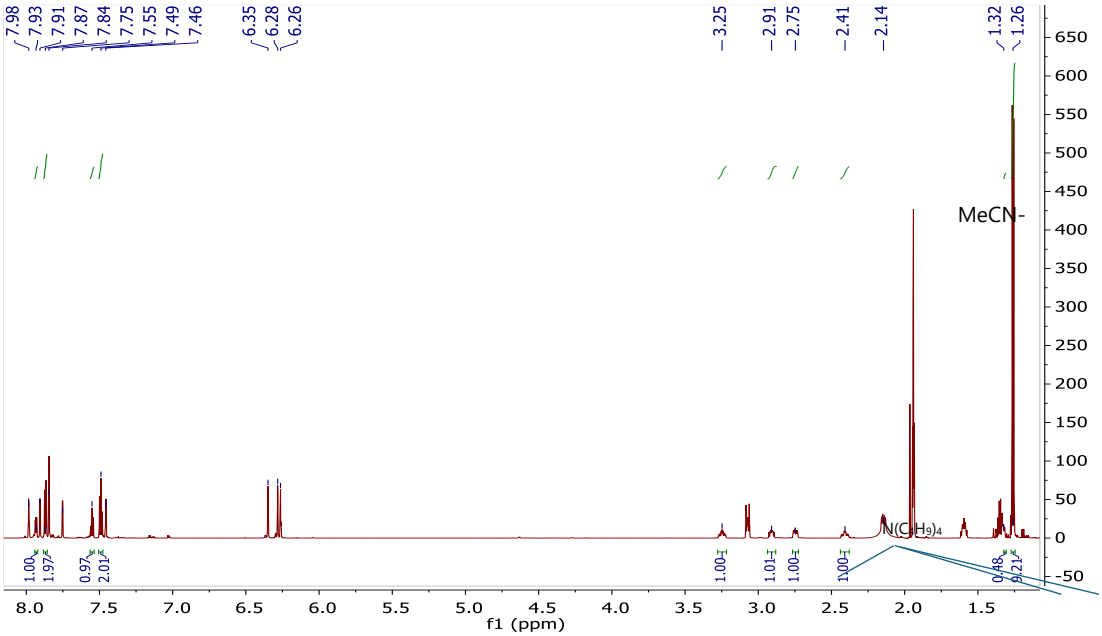


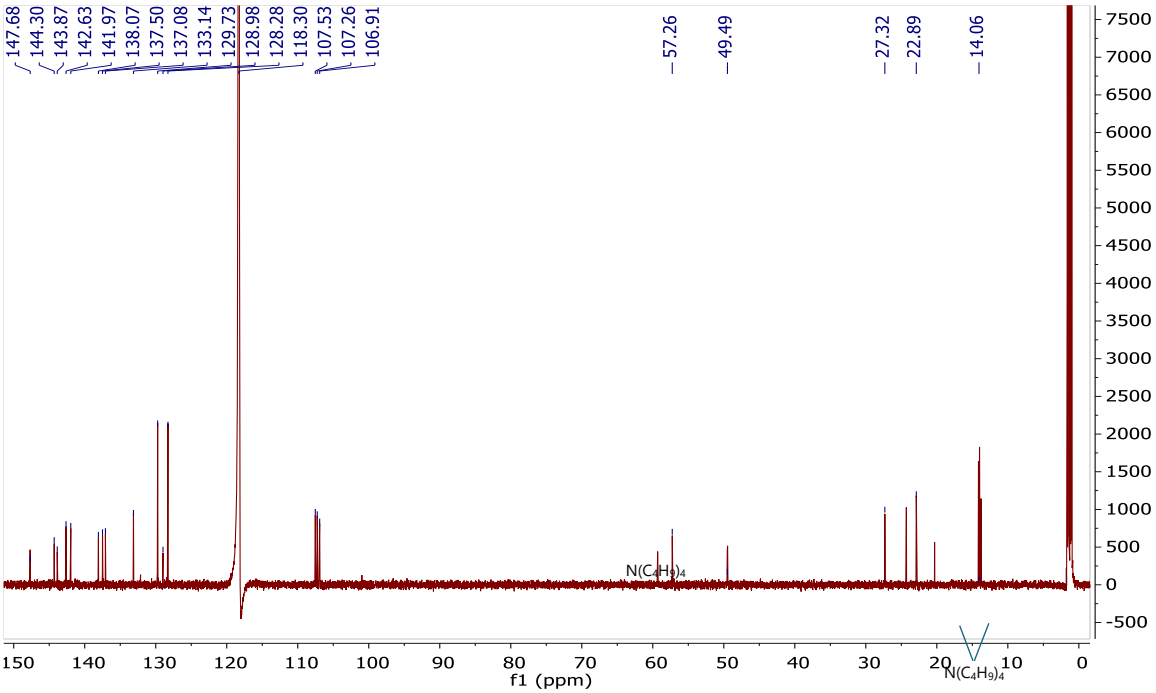




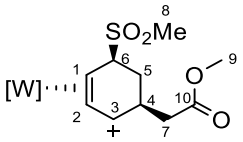
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.22:

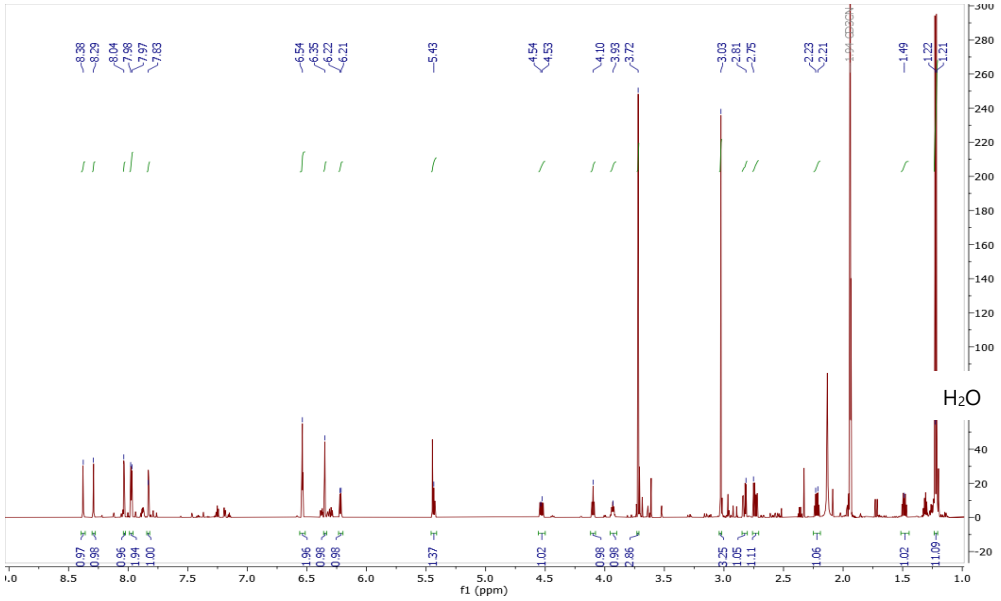


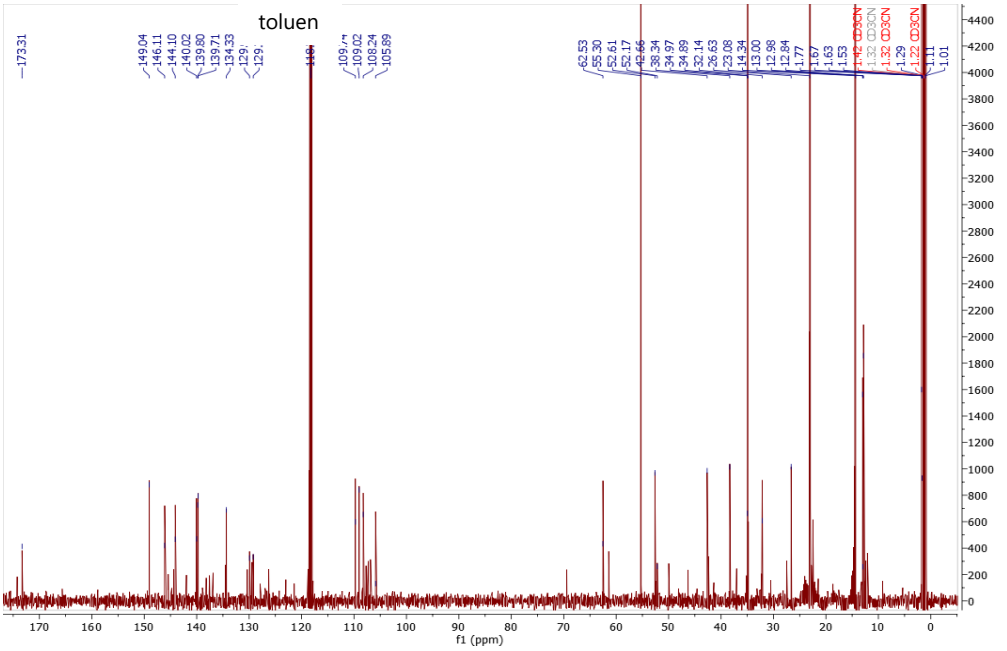




^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.28:

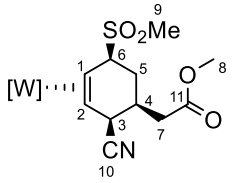


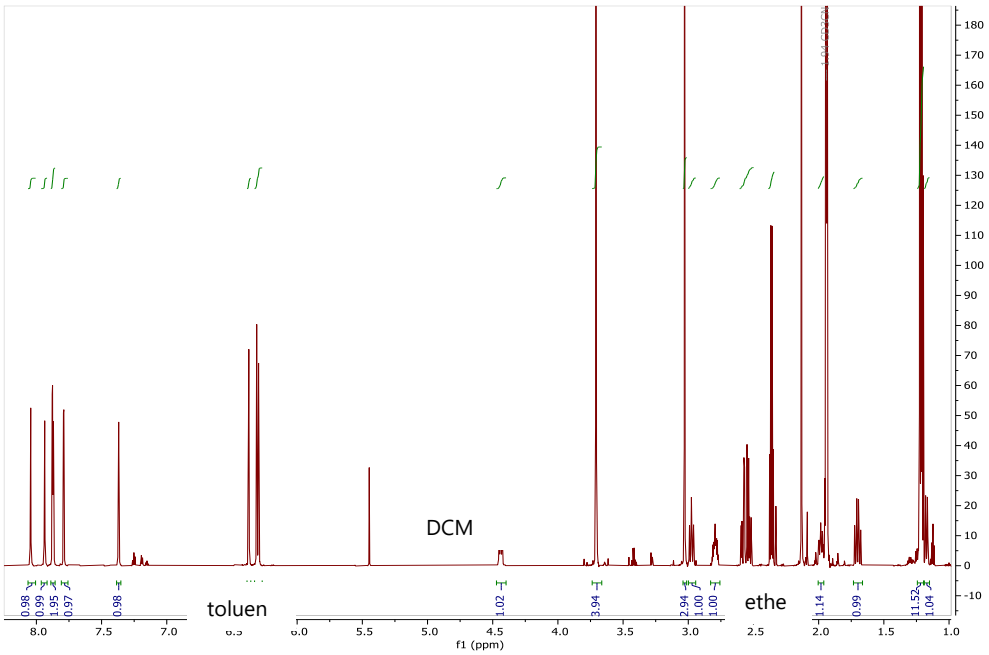


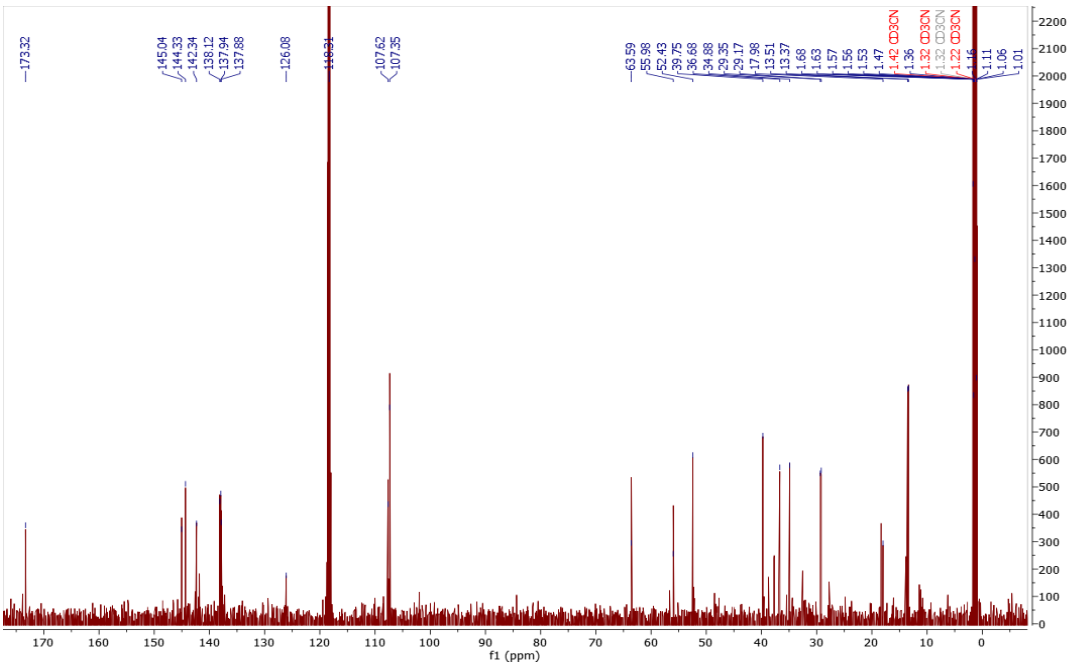


As the 2D experiment was run, the compound started to decompose.

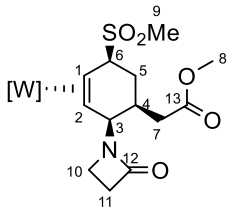
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.29:

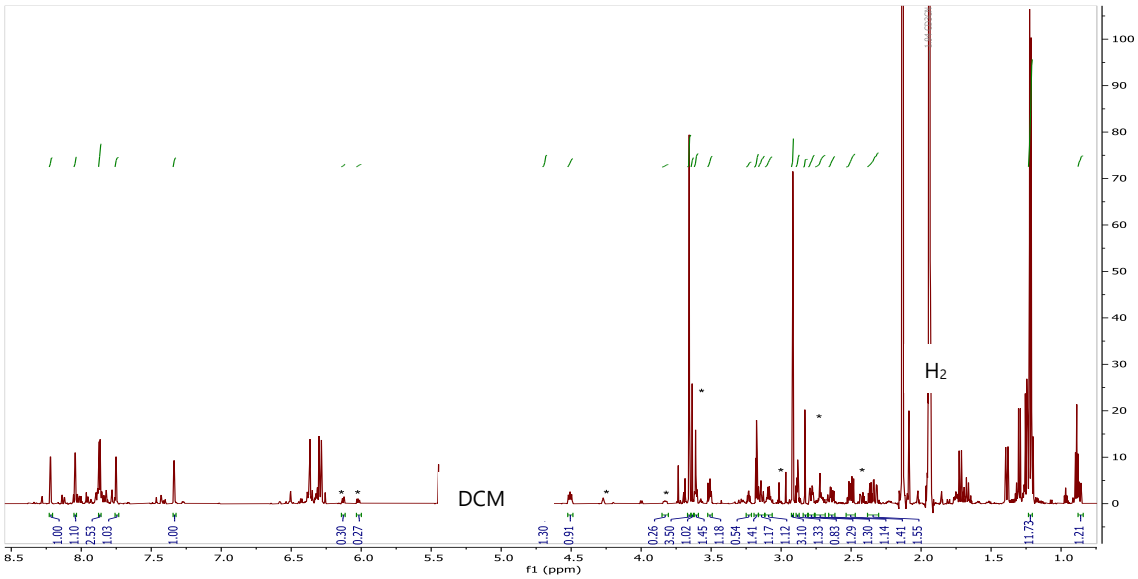


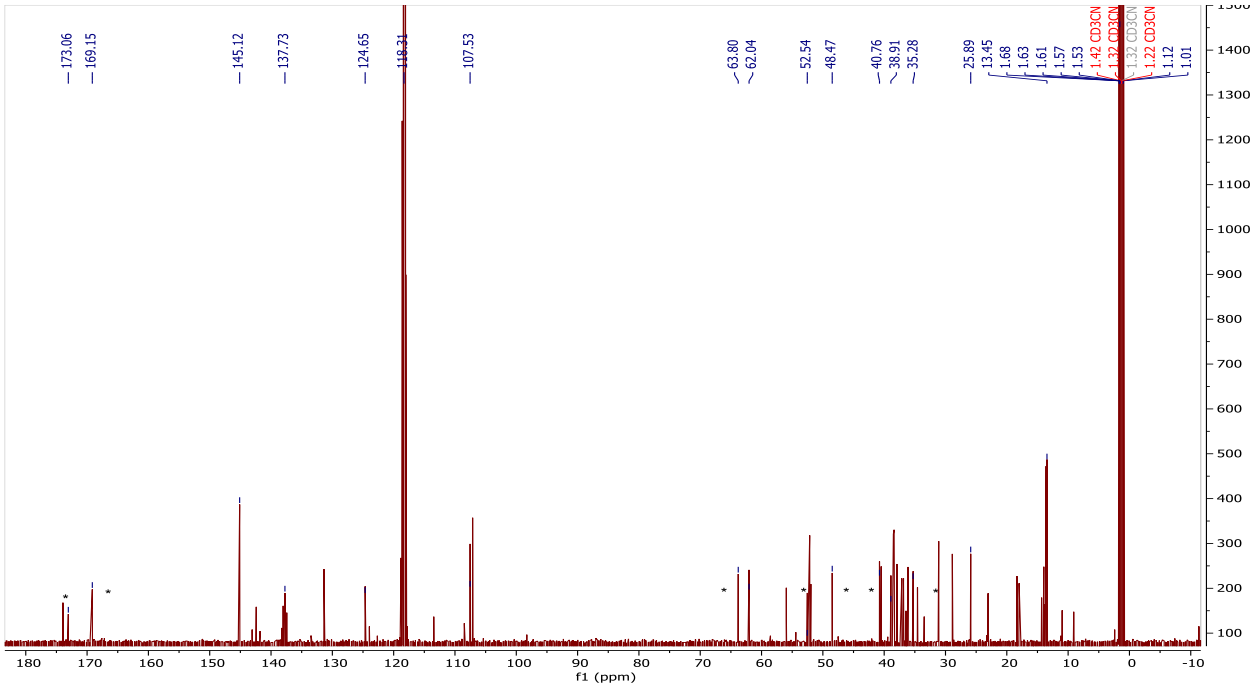




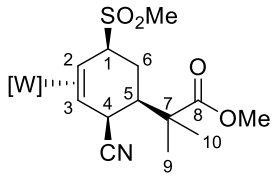
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.30:

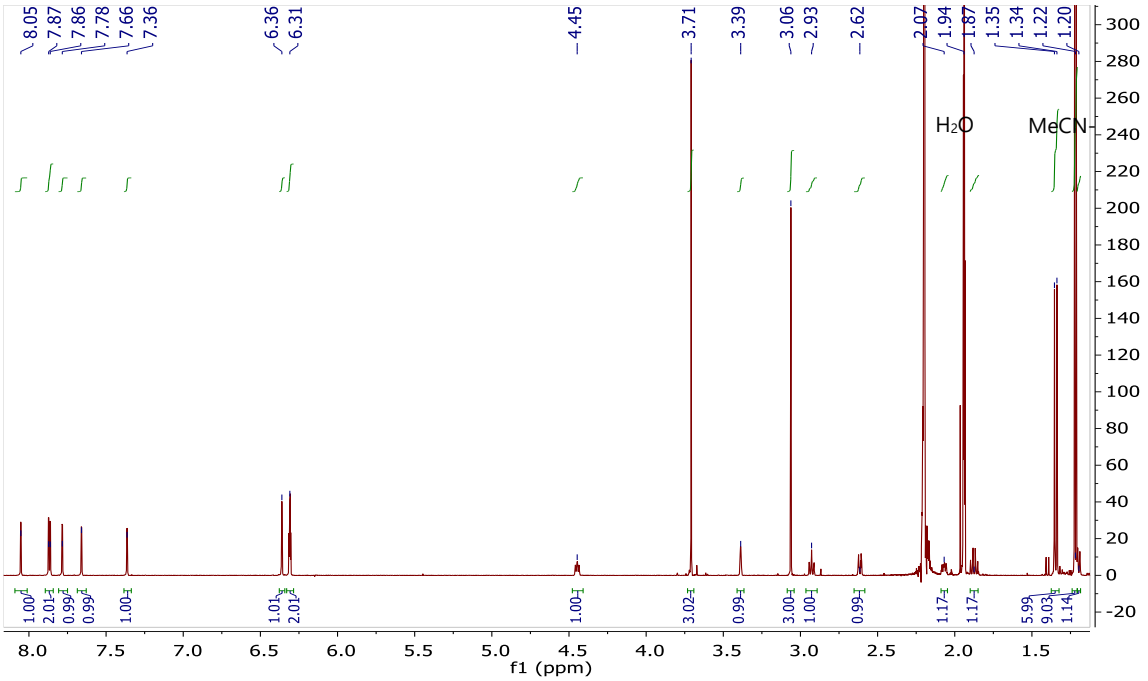


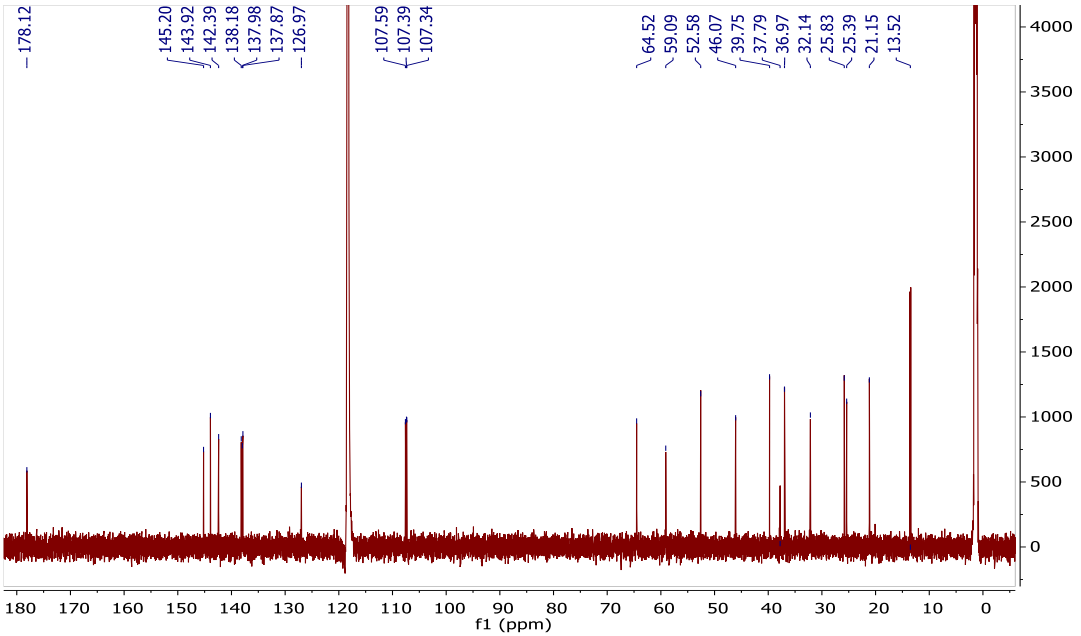




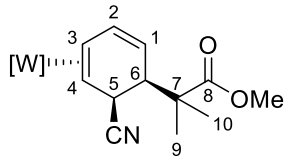
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.31:

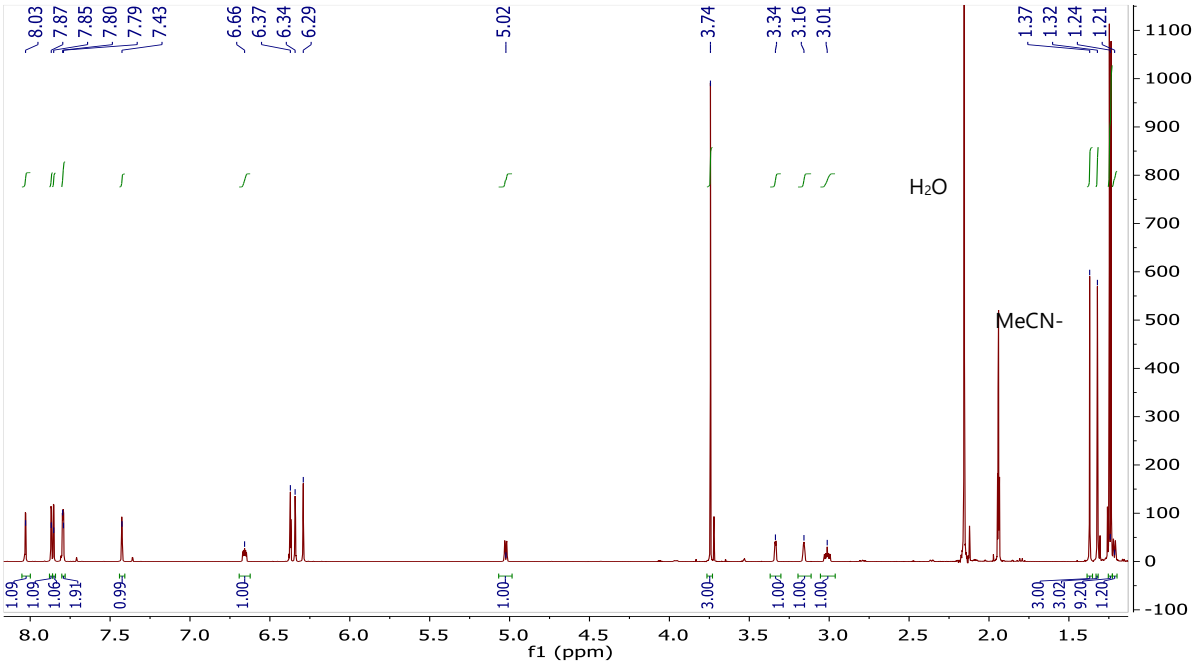


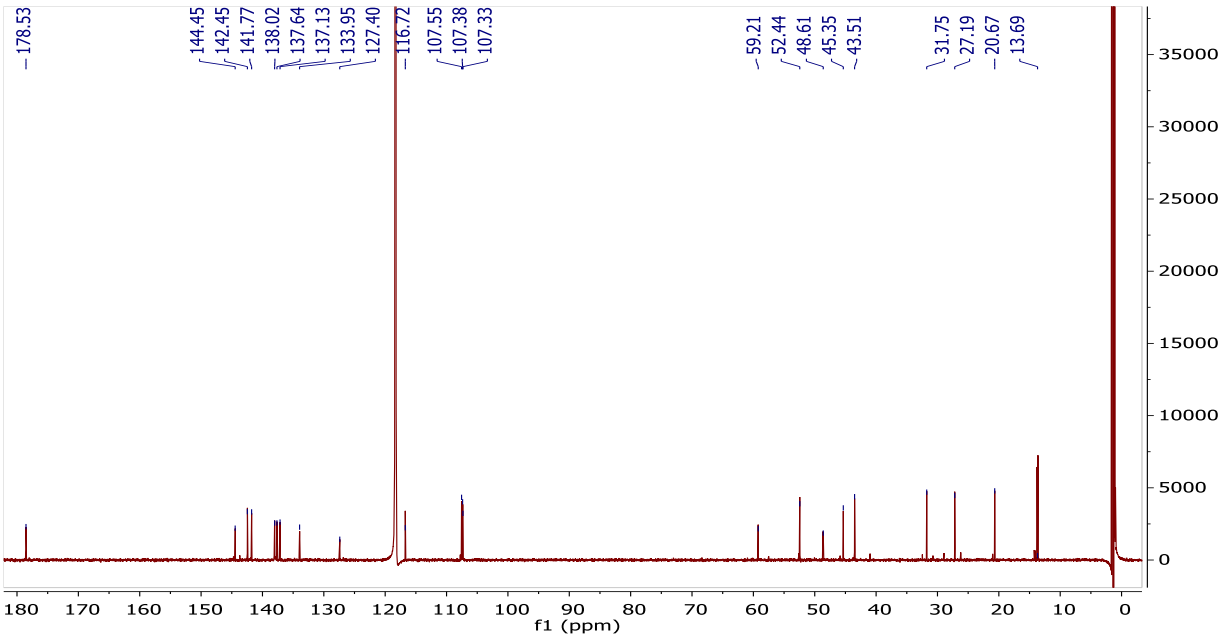




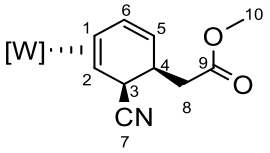
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.40:

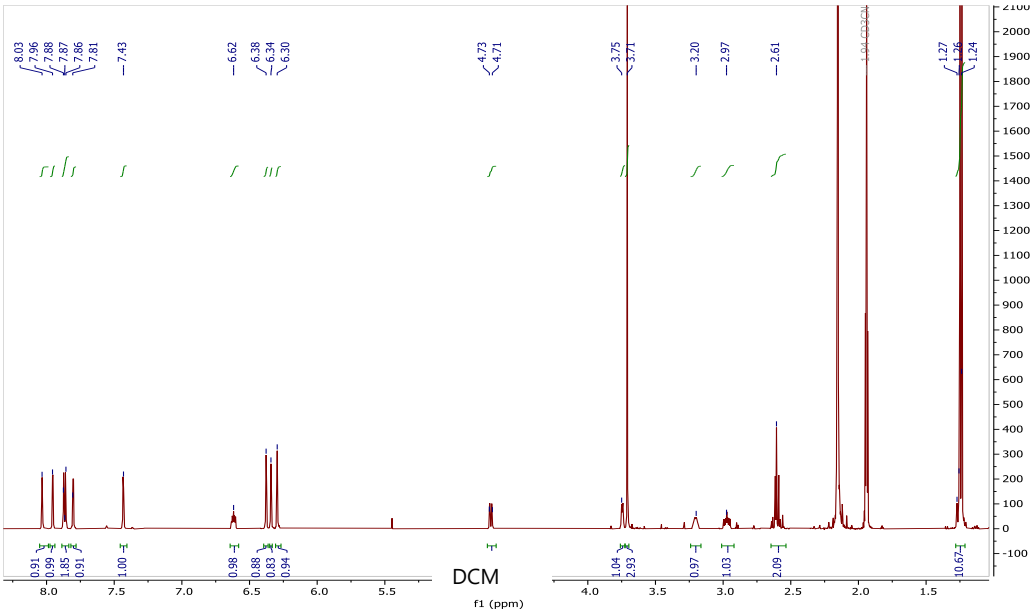


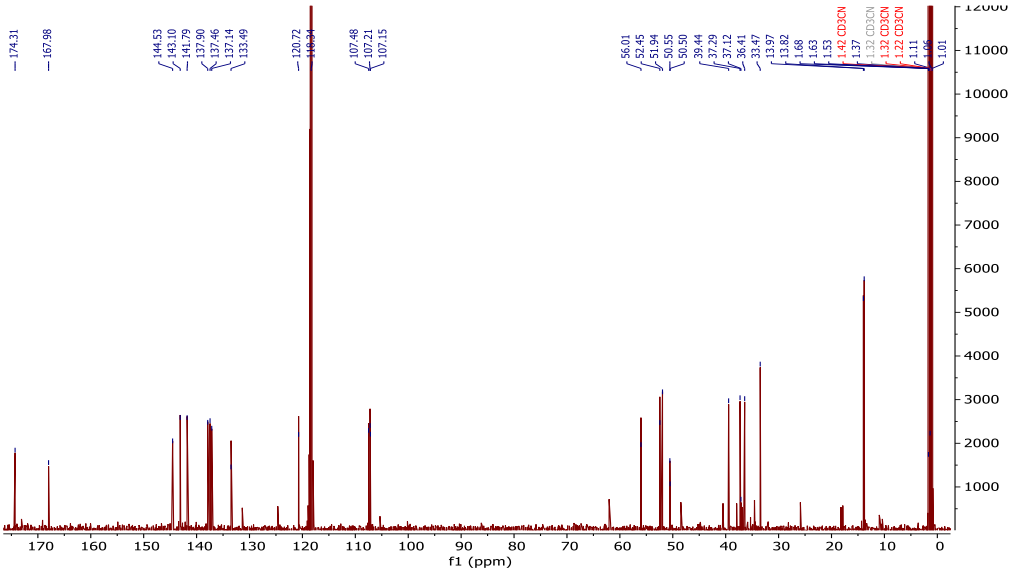




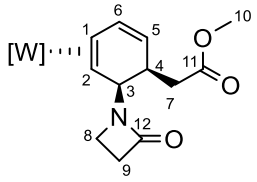
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.41:

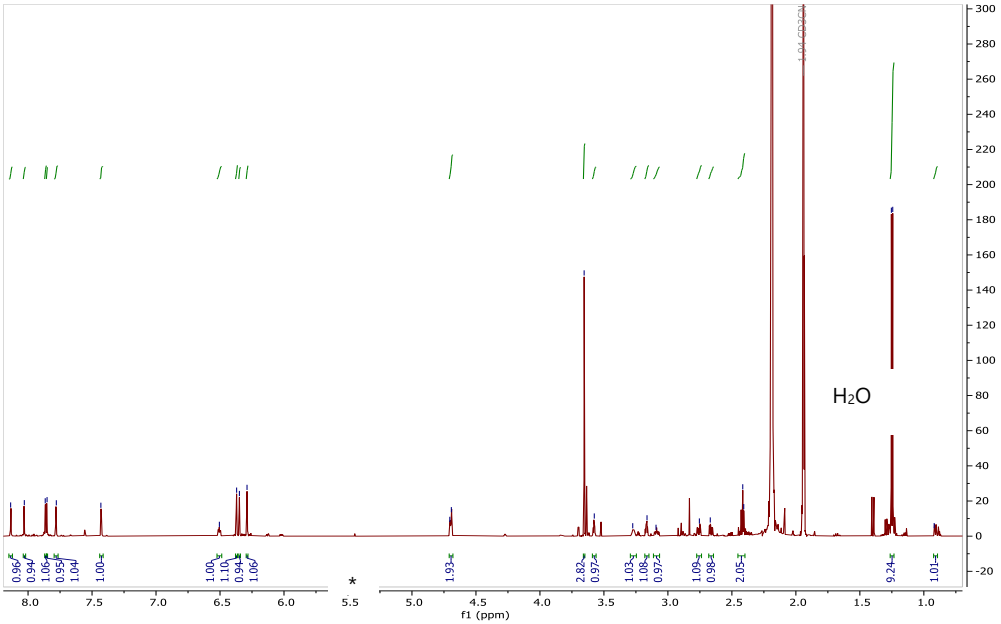


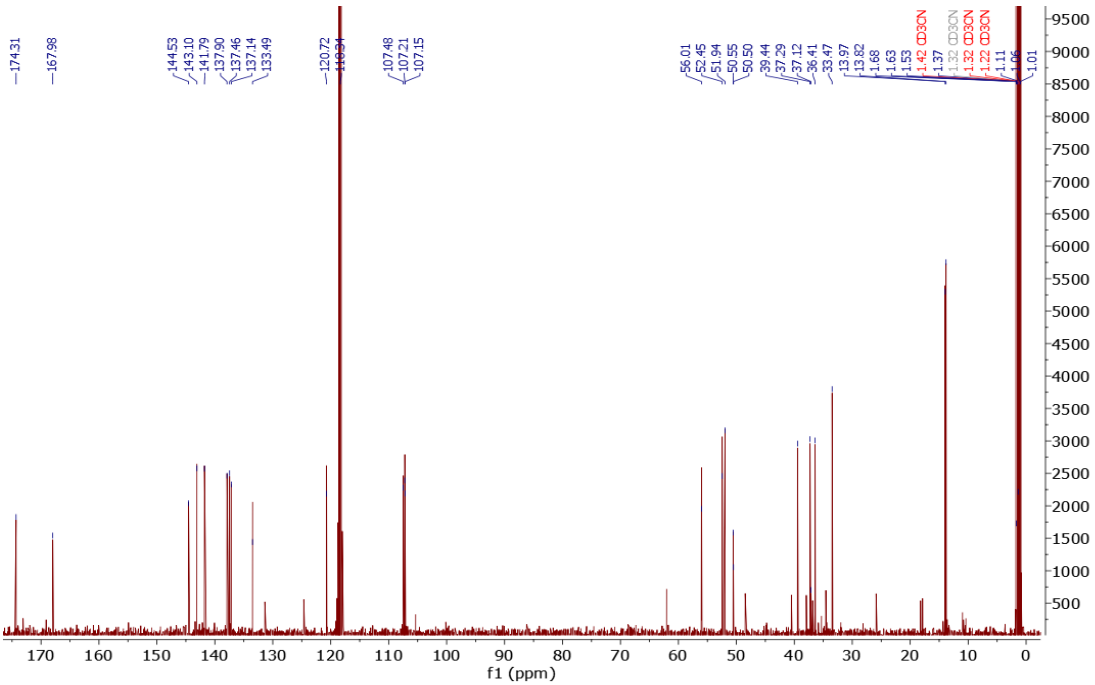




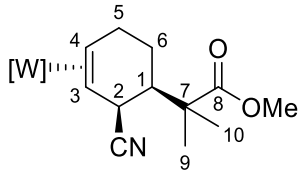
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.42:

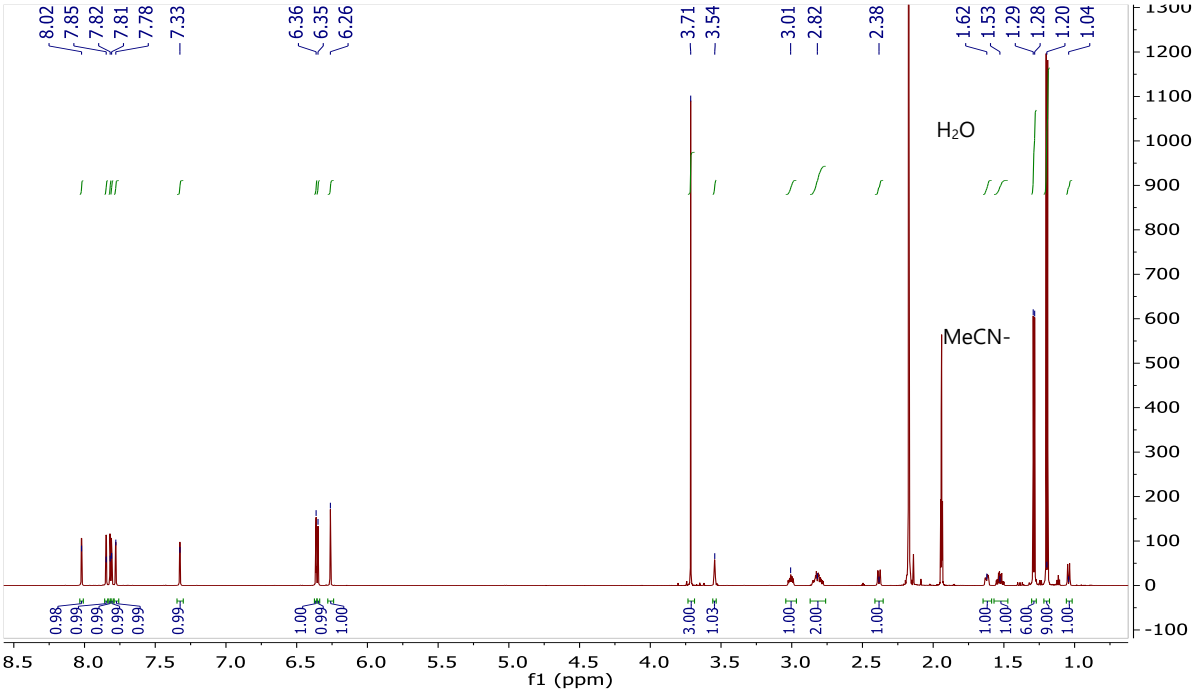


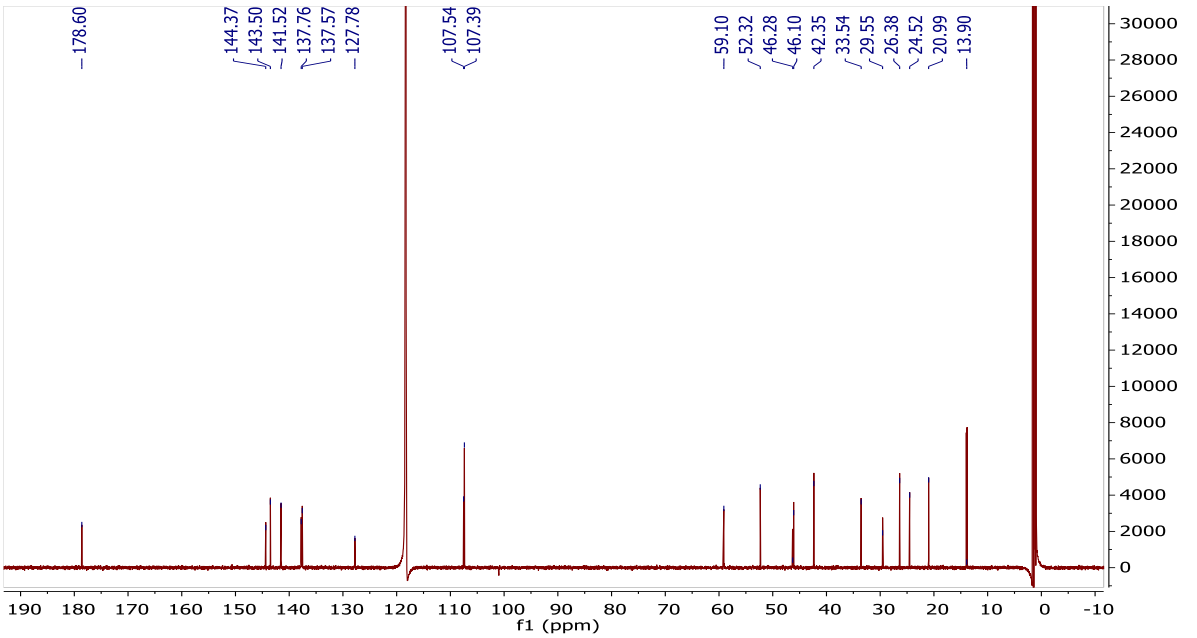




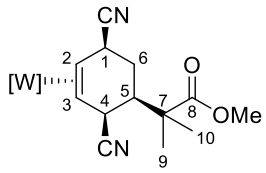
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.43:

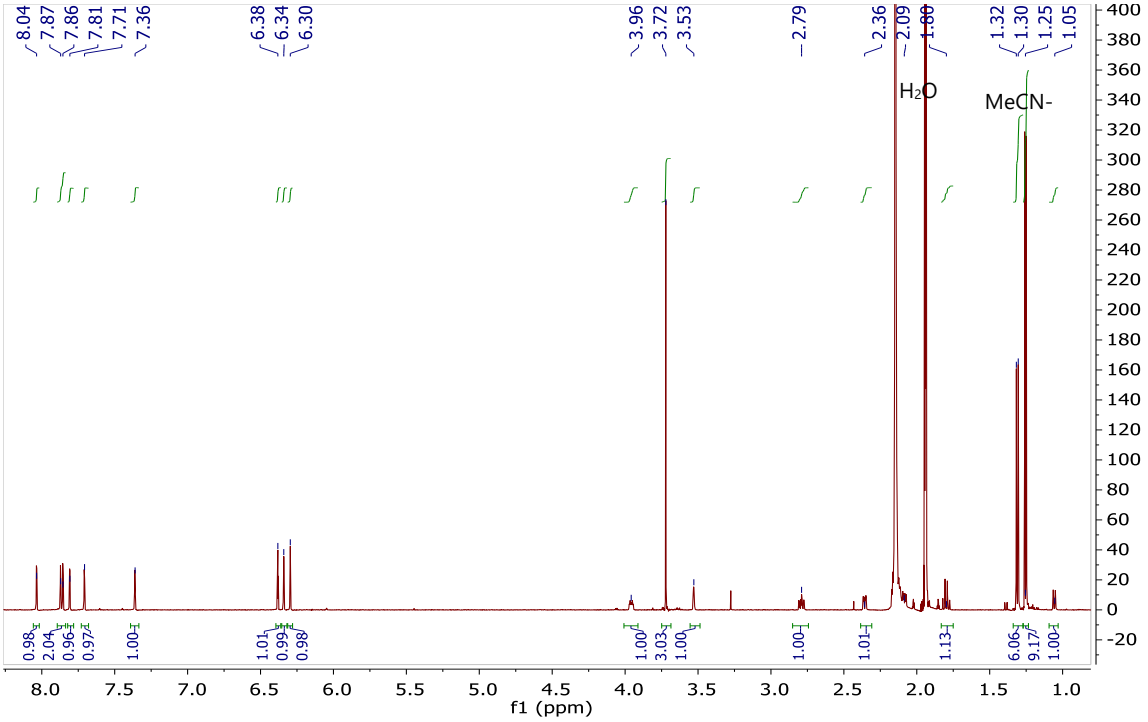


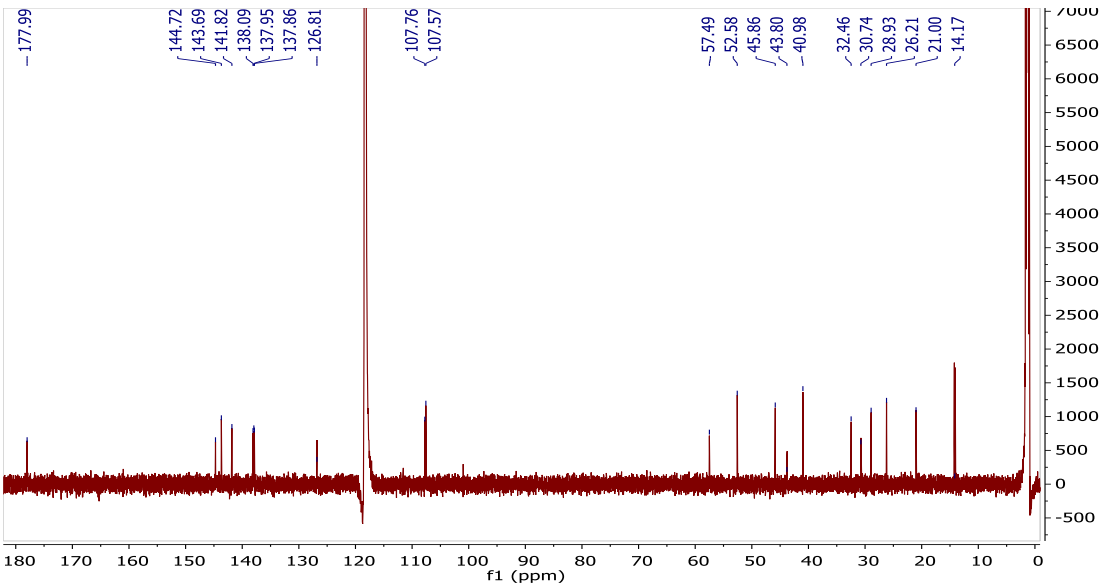




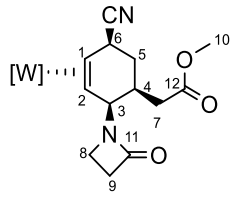
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.45:

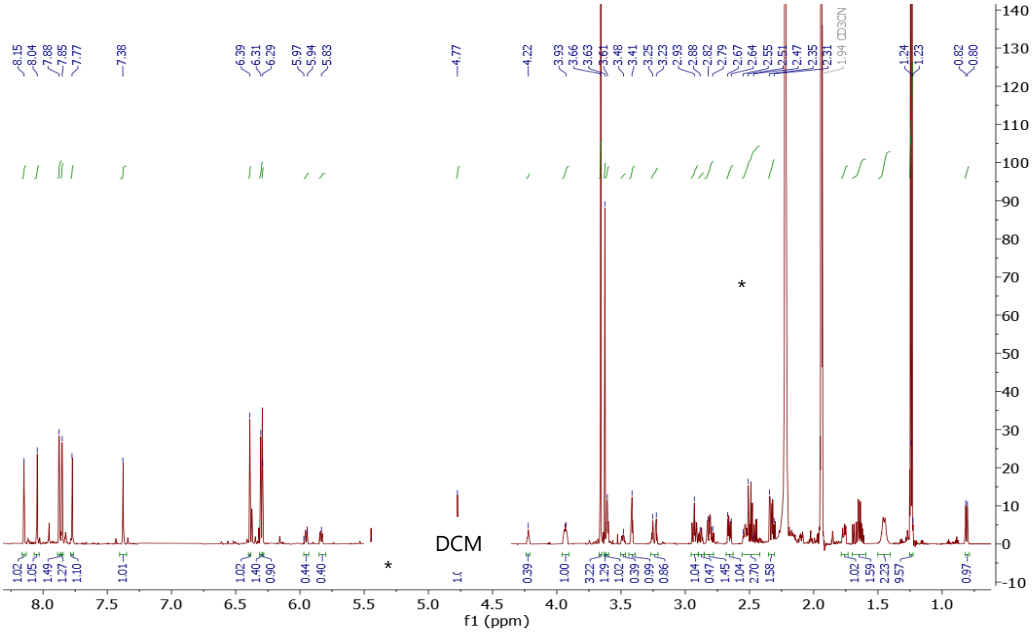


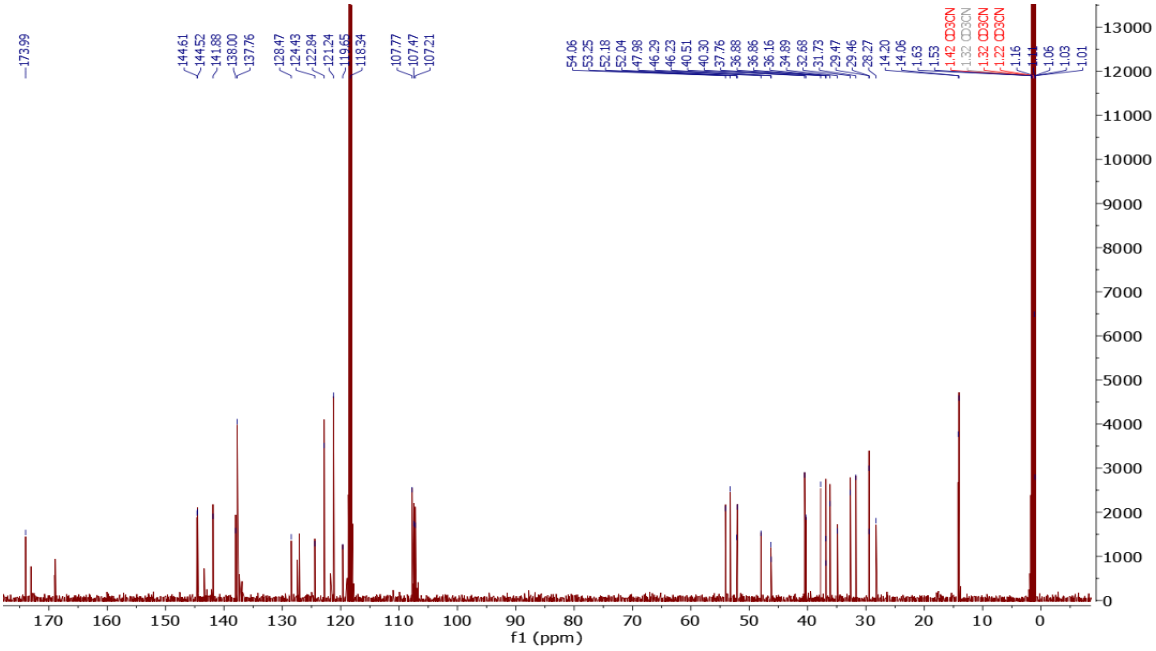




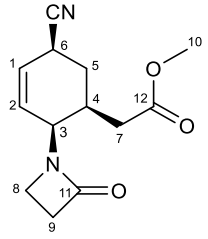
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.47:

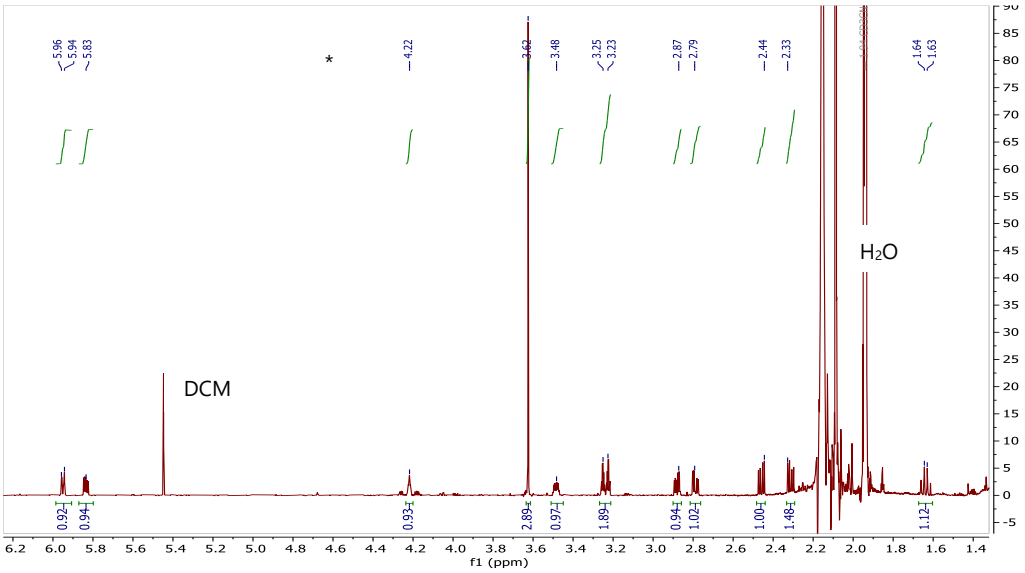


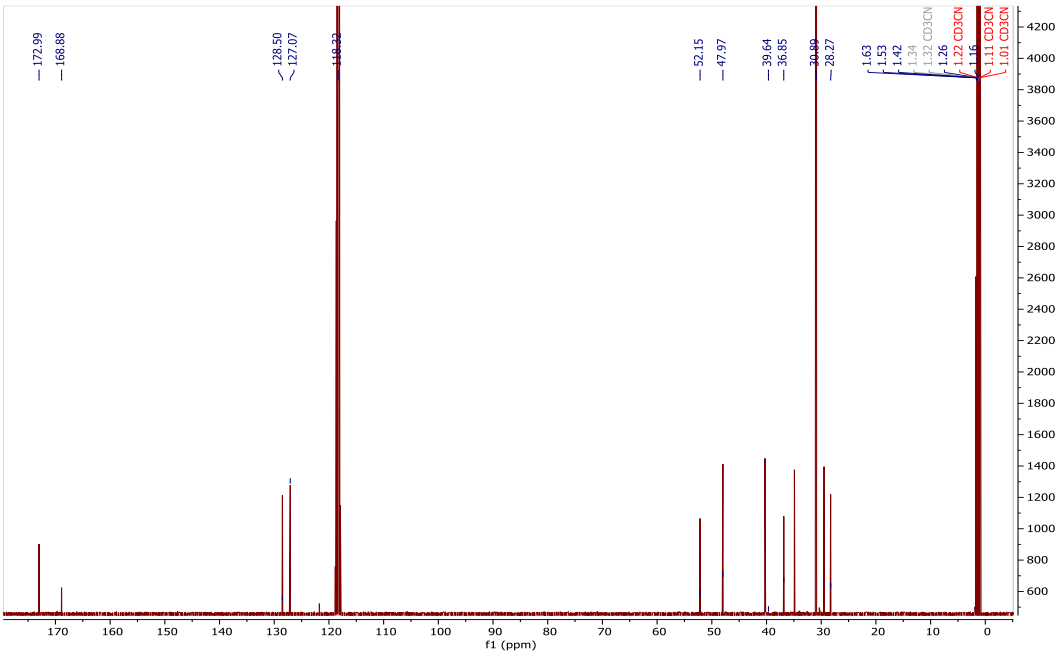




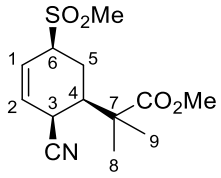
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.53:

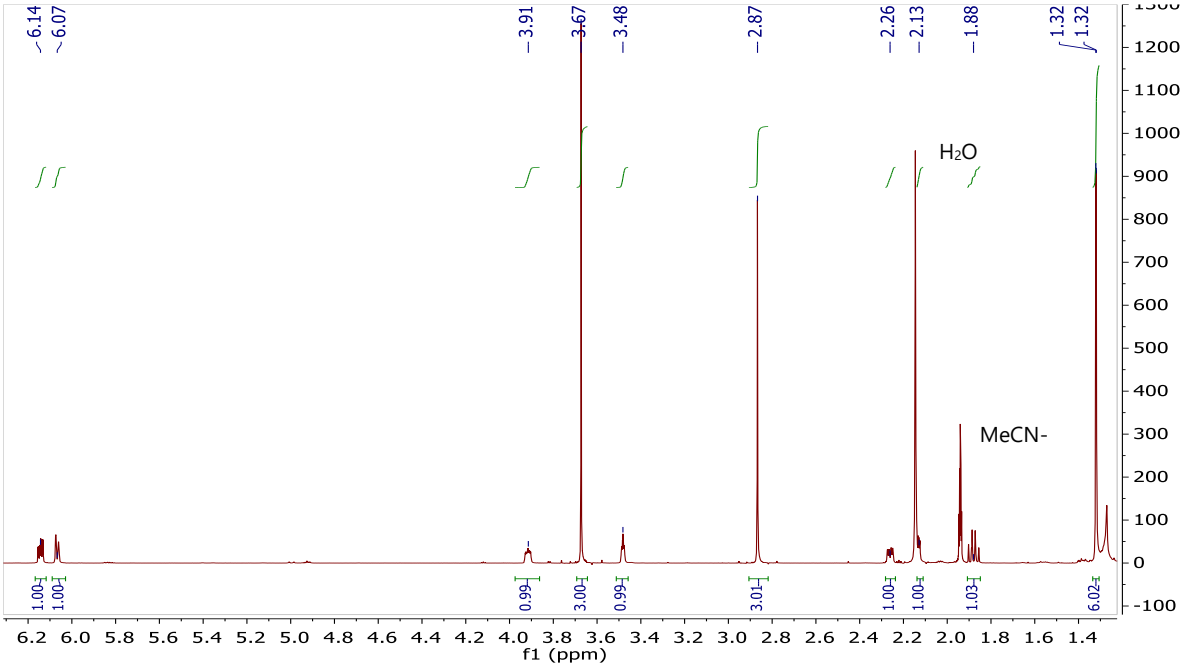


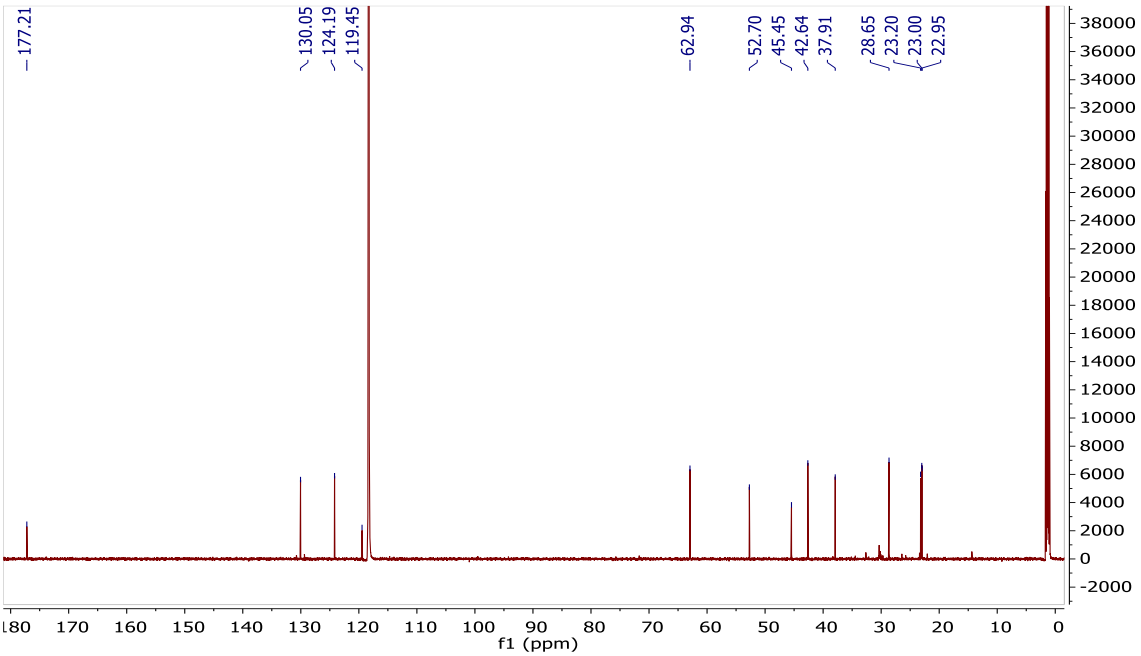




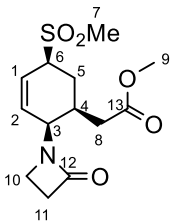
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.56:

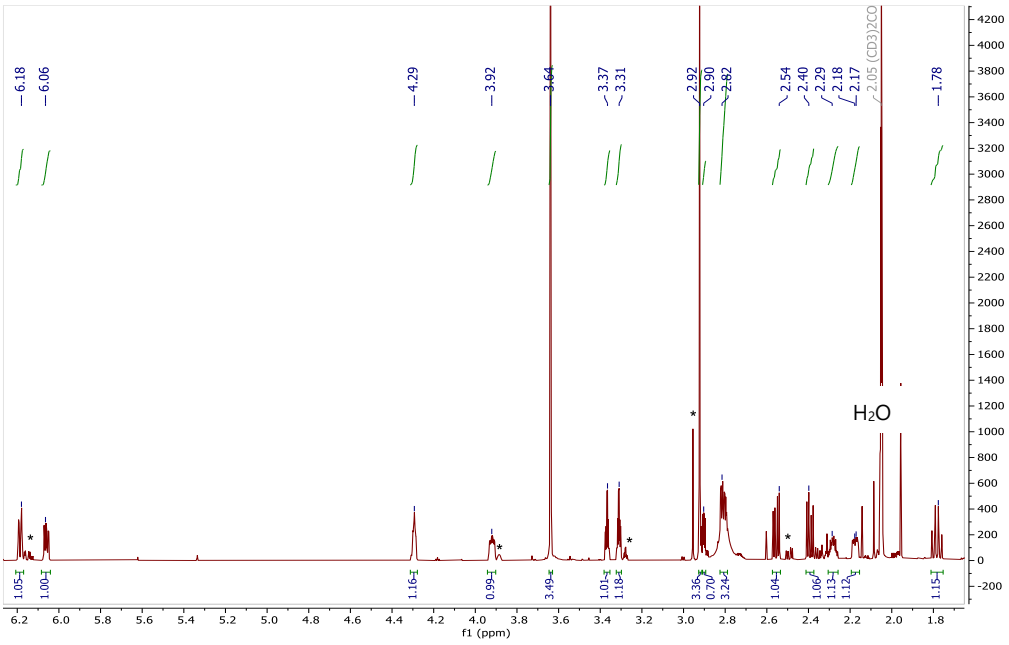


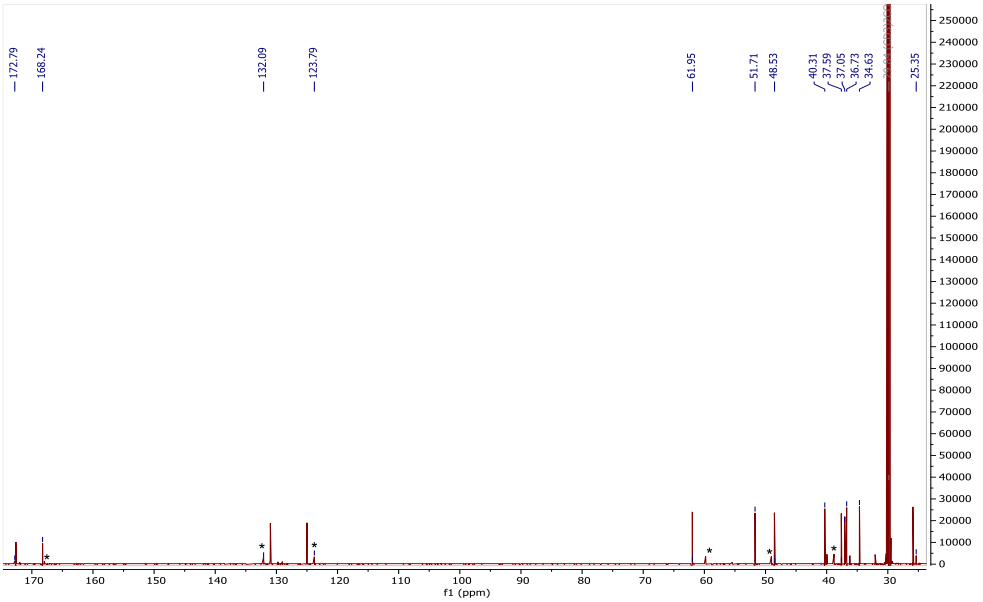




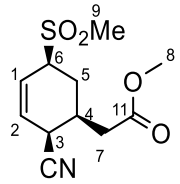
^{1}H-NMR (CD_3CN) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 3.57:



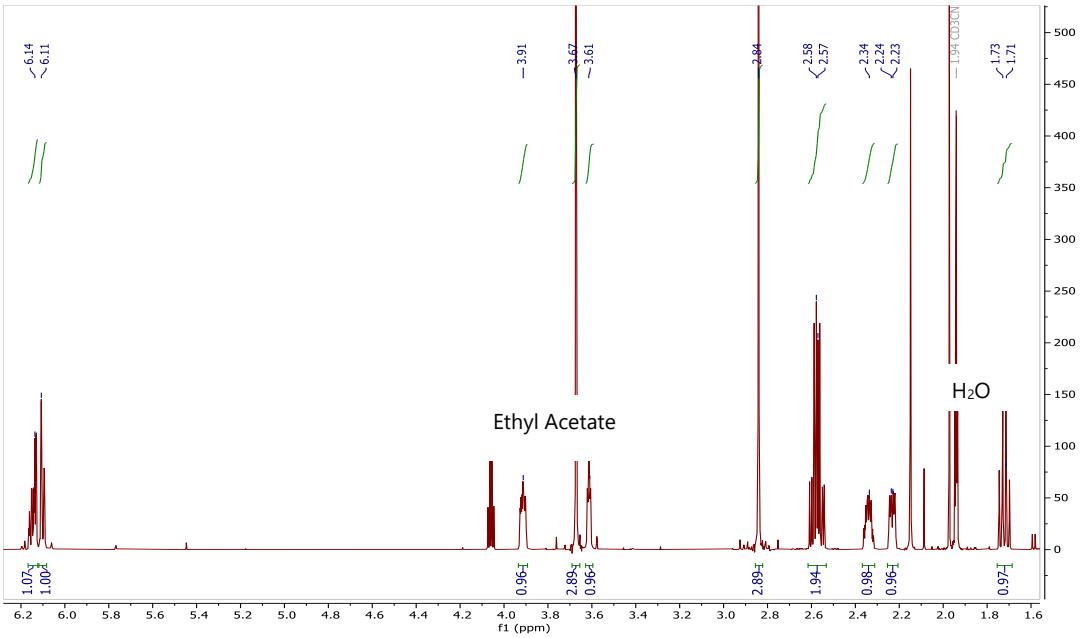


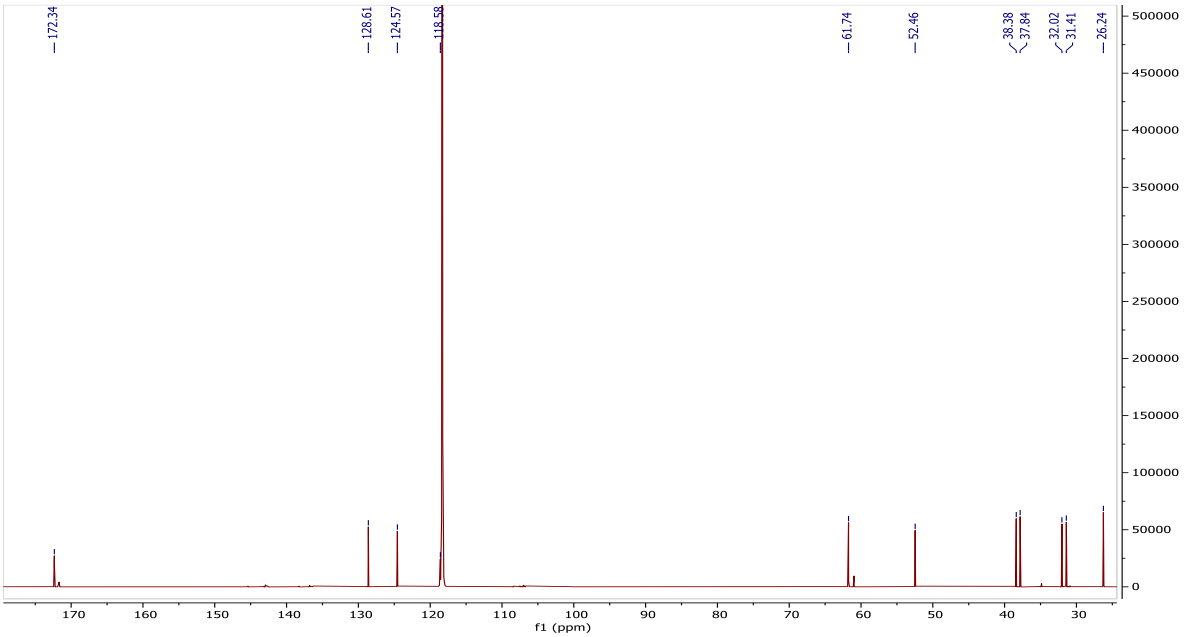


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.58:

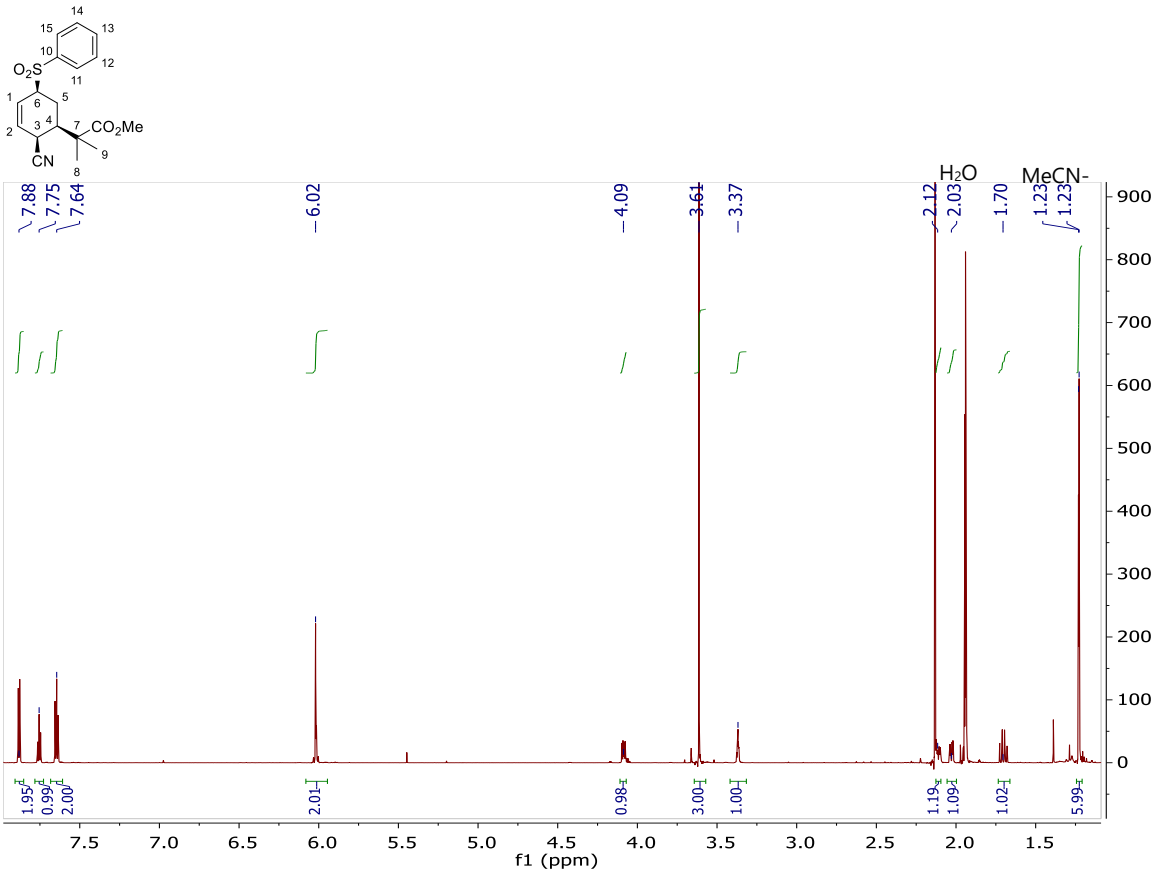


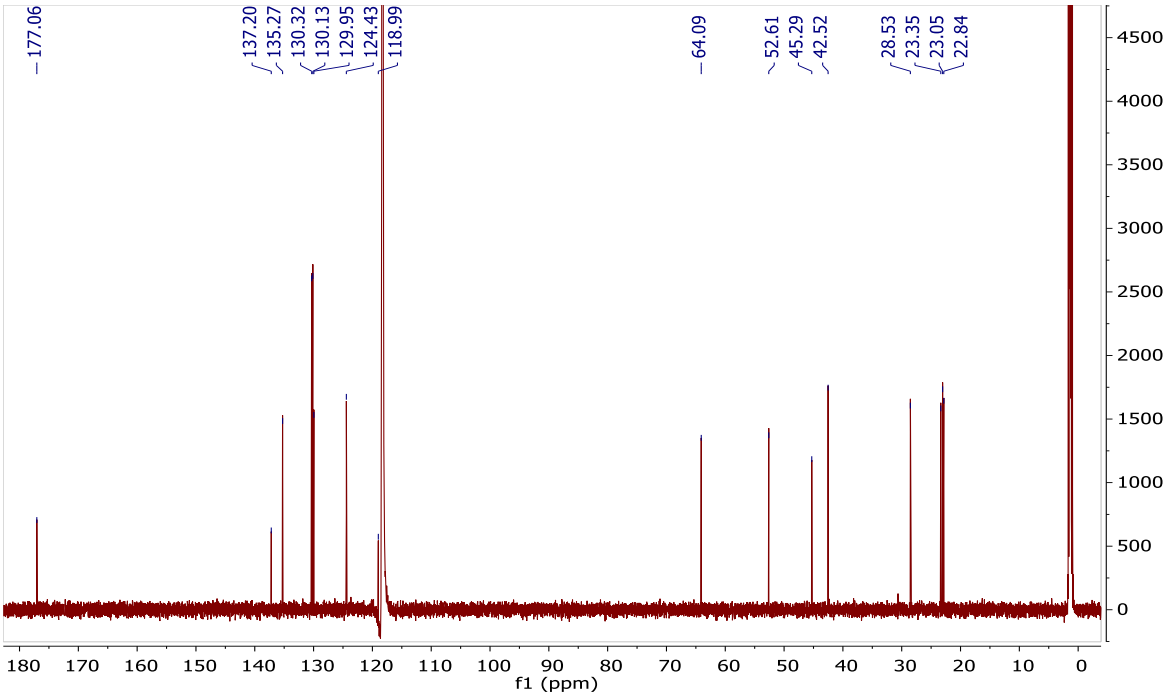
10





^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 3.59:

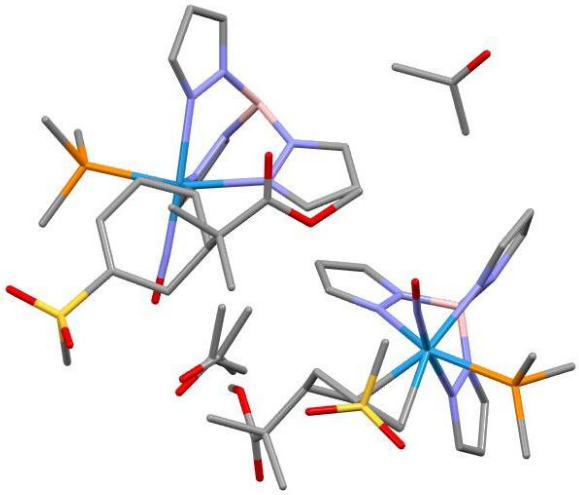




Crystallographic Data Chapter 3

Structure Report for Compound 10

A colourless, plate shaped crystal of **Compound 10** measuring 0.04×0.044×0.073 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_2_193_x2_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[1] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[2] and refined by full-matrix least-squares methods against F^2 using XL[3] within OLEX2.[4] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[5]



[1] *APEX5, Saint, SADABS*; Bruker AXS Inc. 2019.
[2] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[3] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[5] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for Compound 10.

CCDC number	
Empirical formula	$C_{27}H_{43}BN_7O_6PSW$
Formula weight	819.37
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.04×0.044×0.073
Crystal habit	colourless plate
Crystal system	triclinic
Space group	$P1$ (1)
a [Å]	11.7294(4)
b [Å]	12.2675(5)
c [Å]	12.9211(6)
α [°]	110.907(2)
β [°]	103.760(2)
γ [°]	94.8740(10)
Volume [$Å^3$]	1657.15(12)
Z	2
ρ_{calc} [gcm^{-3}]	1.642
μ [mm^{-1}]	3.647
F(000)	824
2θ range [°]	3.62 to 56.65 (0.75 Å)
Index ranges	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −17 ≤ l ≤ 17
Reflections collected	119521
Independent reflections	16484 [R_{int} = 0.0711]
Data / Restraints / Parameters	16484 / 10 / 816
Goodness-of-fit on F^2	1.026
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0284 wR_2 = 0.0571
Final *R* indexes [all data]	R_1 = 0.0362 wR_2 = 0.0598

Largest peak/hole [eÅ^{-3}]	1.20/−0.78
Flack X parameter	0.480(6)

Table 2 Atomic coordinates and Ueq [Å2] for **Compound 10**

Atom	***x***	***y***	***z***	U_{eq}
W1	0.23219(2)	0.33804(2)	0.26570(2)	0.01415(8)
S1	0.27829(15)	0.32515(14)	−0.13486(15)	0.0189(3)
P1	0.0445(2)	0.1922(2)	0.1385(2)	0.0181(5)
O1	0.1652(4)	0.5039(4)	0.1486(4)	0.0228(10)
O2	0.6819(5)	0.2357(5)	0.3027(5)	0.0286(11)
O3	0.6764(4)	0.4288(4)	0.3812(4)	0.0242(10)
O4	0.3816(4)	0.3706(4)	−0.1601(4)	0.0247(10)
O5	0.2055(5)	0.2137(4)	−0.2190(4)	0.0274(11)
N1	0.1091(5)	0.4115(5)	0.3652(5)	0.0172(11)
N2	0.1104(5)	0.4040(6)	0.4685(5)	0.0180(13)
N3	0.2480(5)	0.2107(5)	0.3546(4)	0.0156(11)
N4	0.2277(5)	0.2412(5)	0.4608(5)	0.0182(11)
N5	0.3538(5)	0.4556(5)	0.4400(5)	0.0172(11)
N6	0.3296(8)	0.4530(8)	0.5374(7)	0.0189(19)
N7	0.1994(5)	0.4373(5)	0.1967(5)	0.0170(11)
C1	0.0250(6)	0.4726(6)	0.3419(6)	0.0211(14)
H1	0.005381	0.490577	0.274830	0.025
C2	−0.0299(6)	0.5064(6)	0.4295(6)	0.0245(15)
H2	−0.092619	0.550506	0.434233	0.029
C3	0.0265(6)	0.4618(6)	0.5084(6)	0.0219(14)
H3	0.009343	0.470389	0.578809	0.026
C4	0.2651(6)	0.0972(6)	0.3233(6)	0.0205(13)
H4	0.282609	0.052580	0.253868	0.025
C5	0.2532(7)	0.0557(6)	0.4073(6)	0.0235(14)
H5	0.258386	−0.021757	0.405538	0.028
C6	0.2326(6)	0.1481(6)	0.4929(6)	0.0234(14)
H6	0.223145	0.147215	0.563606	0.028
C7	0.4495(6)	0.5416(6)	0.4763(6)	0.0218(14)
H7	0.486377	0.563573	0.426820	0.026
C8	0.4877(6)	0.5947(6)	0.5970(6)	0.0263(16)
H8	0.553287	0.657749	0.644653	0.032
C9	0.4093(6)	0.5355(6)	0.6315(6)	0.0233(15)

H9	0.411148	0.550620	0.709347	0.028
C10	0.3052(6)	0.2176(5)	0.1308(5)	0.0156(12)
H10	0.302843	0.134772	0.127550	0.019
C11	0.3995(5)	0.3068(5)	0.2242(5)	0.0143(12)
H11	0.447103	0.271053	0.274613	0.017
C12	0.4817(9)	0.3891(9)	0.1962(9)	0.019(2)
H12	0.509023	0.465240	0.266015	0.023
C13	0.4162(6)	0.4202(5)	0.0951(6)	0.0175(13)
H13A	0.376739	0.488064	0.125555	0.021
H13B	0.475784	0.445881	0.061532	0.021
C14	0.3237(6)	0.3188(6)	0.0005(6)	0.0167(14)
C15	0.2727(6)	0.2281(6)	0.0190(6)	0.0165(13)
H15	0.212891	0.168160	−0.043275	0.020
C16	0.5966(6)	0.3367(6)	0.1791(6)	0.0196(13)
C17	0.5708(6)	0.2170(6)	0.0796(6)	0.0237(14)
H17A	0.537560	0.225843	0.006538	0.036
H17B	0.513148	0.161623	0.089470	0.036
H17C	0.645064	0.186121	0.078450	0.036
C18	0.6881(6)	0.4239(6)	0.1645(6)	0.0237(14)
H18A	0.763830	0.395147	0.168156	0.036
H18B	0.701205	0.502473	0.226525	0.036
H18C	0.657473	0.429514	0.089407	0.036
C19	0.6561(5)	0.3240(6)	0.2917(6)	0.0198(14)
C20	0.7273(7)	0.4325(7)	0.4947(7)	0.0306(17)
H20A	0.787149	0.381321	0.492567	0.046
H20B	0.664253	0.404548	0.522252	0.046
H20C	0.765371	0.514341	0.547239	0.046
C21	0.1875(6)	0.4343(6)	−0.1186(6)	0.0256(15)
H21A	0.234338	0.510291	−0.059419	0.038
H21B	0.119333	0.410130	−0.094984	0.038
H21C	0.158430	0.442959	−0.192379	0.038
C22	0.0498(6)	0.0407(6)	0.0490(6)	0.0252(15)
H22A	0.094618	0.042099	−0.005726	0.038
H22B	−0.031730	−0.003495	0.006141	0.038
H22C	0.089297	0.002007	0.098353	0.038
C23	−0.0460(6)	0.2423(6)	0.0352(6)	0.0274(15)
H23A	−0.060369	0.321701	0.076271	0.041
H23B	−0.122518	0.186959	−0.005328	0.041
H23C	−0.003769	0.245276	−0.020999	0.041

C24	−0.0570(6)	0.1636(6)	0.2179(7)	0.0263(15)
H24A	−0.015928	0.133158	0.274300	0.040
H24B	−0.127598	0.104753	0.163499	0.040
H24C	−0.081733	0.237635	0.258414	0.040
B1	0.2193(7)	0.3697(7)	0.5326(6)	0.0196(15)
H1A	0.213(6)	0.379(6)	0.617(6)	0.014(17)
W2	0.66383(2)	0.90960(2)	0.47302(2)	0.01469(8)
S2	0.90771(15)	0.78791(15)	0.17038(16)	0.0211(3)
P2	0.8680(2)	1.0379(2)	0.5756(2)	0.0183(5)
O6	0.7861(5)	0.7000(4)	0.4193(5)	0.0287(11)
O7	0.3377(4)	0.9213(5)	0.0909(5)	0.0246(11)
O8	0.3075(4)	0.7384(4)	0.0881(4)	0.0229(10)
O9	1.0044(4)	0.8889(4)	0.2236(5)	0.0277(11)
O10	0.8719(5)	0.7308(5)	0.0457(5)	0.0337(13)
N8	0.6791(5)	0.8962(5)	0.6416(5)	0.0187(11)
N9	0.6090(6)	0.9445(6)	0.7099(5)	0.0225(14)
N10	0.5916(5)	1.0763(5)	0.5439(5)	0.0184(11)
N11	0.5336(5)	1.0895(5)	0.6262(5)	0.0222(12)
N12	0.4771(5)	0.8333(5)	0.4554(5)	0.0168(11)
N13	0.4275(7)	0.8787(8)	0.5450(8)	0.0196(18)
N14	0.7319(5)	0.7832(5)	0.4357(5)	0.0192(11)
C25	0.7549(6)	0.8484(7)	0.6986(6)	0.0262(15)
H25	0.814065	0.808284	0.670992	0.031
C26	0.7349(7)	0.8657(7)	0.8047(7)	0.0309(17)
H26	0.776643	0.840802	0.862416	0.037
C27	0.6422(7)	0.9262(7)	0.8083(7)	0.0306(17)
H27	0.607195	0.951031	0.870089	0.037
C28	0.5932(6)	1.1770(6)	0.5256(6)	0.0226(14)
H28	0.626648	1.192083	0.470831	0.027
C29	0.5395(7)	1.2568(7)	0.5968(7)	0.0292(17)
H29	0.531232	1.334762	0.601943	0.035
C30	0.5014(6)	1.1972(6)	0.6579(7)	0.0280(16)
H30	0.459195	1.226652	0.713324	0.034
C31	0.3927(6)	0.7463(6)	0.3718(6)	0.0211(14)
H31	0.402509	0.698109	0.299530	0.025
C32	0.2887(6)	0.7349(6)	0.4035(6)	0.0206(13)
H32	0.215888	0.680282	0.359107	0.025
C33	0.3145(6)	0.8203(6)	0.5134(6)	0.0232(14)
H33	0.261068	0.835591	0.559623	0.028

C34	0.6950(6)	0.9744(5)	0.3391(5)	0.0159(12)
H34	0.689312	1.059534	0.355637	0.019
C35	0.5812(5)	0.8929(6)	0.2947(5)	0.0153(12)
H35	0.512658	0.935969	0.290465	0.018
C36	0.5600(9)	0.7820(8)	0.1841(9)	0.016(2)
H36	0.502857	0.720001	0.189098	0.019
C37	0.6754(5)	0.7308(6)	0.1752(6)	0.0188(13)
H37A	0.687898	0.681829	0.222021	0.023
H37B	0.665085	0.678374	0.093661	0.023
C38	0.7835(6)	0.8259(6)	0.2160(7)	0.0165(14)
C39	0.7919(6)	0.9354(6)	0.2921(6)	0.0169(13)
H39	0.864506	0.990419	0.316689	0.020
C40	0.4966(5)	0.8056(6)	0.0753(6)	0.0181(13)
C41	0.5641(6)	0.9123(6)	0.0653(6)	0.0222(14)
H41A	0.576991	0.982810	0.136391	0.033
H41B	0.517051	0.926462	−0.000704	0.033
H41C	0.641445	0.895691	0.053738	0.033
C42	0.4765(6)	0.6968(6)	−0.0372(6)	0.0231(14)
H42A	0.552737	0.687553	−0.054907	0.035
H42B	0.420146	0.707712	−0.100587	0.035
H42C	0.443782	0.625698	−0.028154	0.035
C43	0.3739(6)	0.8318(6)	0.0862(5)	0.0172(12)
C44	0.1898(6)	0.7550(7)	0.1024(8)	0.0311(17)
H44A	0.146771	0.781393	0.043476	0.047
H44B	0.198742	0.815009	0.179500	0.047
H44C	0.144828	0.679625	0.093714	0.047
C45	0.9482(7)	0.6793(7)	0.2249(8)	0.0317(18)
H45A	1.017504	0.651280	0.201496	0.048
H45B	0.881108	0.612341	0.194051	0.048
H45C	0.968572	0.713971	0.309582	0.048
C46	0.9042(6)	1.1743(6)	0.5544(6)	0.0234(14)
H46A	0.890488	1.156100	0.471635	0.035
H46B	0.988197	1.210624	0.595698	0.035
H46C	0.853197	1.229723	0.584398	0.035
C47	0.9903(6)	0.9614(6)	0.5467(6)	0.0236(15)
H47A	0.980228	0.887164	0.558916	0.035
H47B	1.066381	1.012198	0.599244	0.035
H47C	0.990271	0.943553	0.466497	0.035
C48	0.9070(7)	1.0969(6)	0.7324(6)	0.0275(16)

H48A	0.842006	1.133304	0.757731	0.041
H48B	0.980485	1.156860	0.764789	0.041
H48C	0.919526	1.032345	0.759216	0.041
B2	0.4977(7)	0.9841(8)	0.6569(7)	0.0258(17)
H2A	0.447(7)	1.013(7)	0.719(7)	0.031
O11	0.0368(7)	0.8481(9)	0.7613(8)	0.079(3)
C49	0.2460(8)	0.9075(8)	0.8130(8)	0.042(2)
H49A	0.228026	0.965429	0.778195	0.063
H49B	0.305790	0.865292	0.782767	0.063
H49C	0.277206	0.948784	0.897201	0.063
C50	0.1348(9)	0.8207(9)	0.7838(8)	0.045(2)
C51	0.1482(9)	0.7046(8)	0.7835(8)	0.046(2)
H51A	0.196916	0.713074	0.859865	0.069
H51B	0.187402	0.665098	0.724969	0.069
H51C	0.069265	0.657003	0.765408	0.069
O54	0.917(2)	0.451(2)	0.7472(18)	0.0554(18)
C52	0.776(3)	0.581(2)	0.784(2)	0.0554(18)
H52A	0.772622	0.633079	0.860555	0.083
H52B	0.694983	0.546333	0.732509	0.083
H52C	0.819316	0.626522	0.752134	0.083
C53	0.840(4)	0.484(4)	0.795(4)	0.0554(18)
C54	0.810(3)	0.420(2)	0.866(2)	0.0554(18)
H54A	0.723494	0.392856	0.843179	0.083
H54B	0.837901	0.472792	0.948024	0.083
H54C	0.849690	0.350727	0.853623	0.083
O54A	0.898(2)	0.4753(18)	0.7433(17)	0.0554(18)
C12A	0.828(4)	0.480(4)	0.804(4)	0.0554(18)
C52A	0.729(3)	0.548(2)	0.7955(19)	0.0554(18)
H52D	0.749579	0.622983	0.863418	0.083
H52E	0.655547	0.500791	0.792492	0.083
H52F	0.716300	0.564616	0.725247	0.083
C53A	0.840(3)	0.427(2)	0.893(2)	0.0554(18)
H53A	0.763053	0.379995	0.880795	0.083
H53B	0.864661	0.491315	0.970067	0.083
H53C	0.900323	0.376638	0.885911	0.083

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for Compound 10 The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01377(17)	0.01305(18)	0.01591(19)	0.00609(15)	0.00370(15)	0.00365(14)
S1	0.0220(8)	0.0178(8)	0.0172(8)	0.0061(6)	0.0067(6)	0.0050(6)
P1	0.0154(10)	0.0176(10)	0.0207(12)	0.0078(9)	0.0038(8)	0.0019(7)
O1	0.033(3)	0.019(2)	0.026(3)	0.016(2)	0.011(2)	0.014(2)
O2	0.034(3)	0.027(3)	0.036(3)	0.022(2)	0.012(2)	0.015(2)
O3	0.024(2)	0.023(2)	0.024(3)	0.010(2)	0.001(2)	0.004(2)
O4	0.027(3)	0.027(3)	0.026(3)	0.012(2)	0.014(2)	0.008(2)
O5	0.033(3)	0.022(2)	0.019(3)	0.004(2)	0.002(2)	−0.002(2)
N1	0.019(3)	0.017(3)	0.017(3)	0.006(2)	0.008(2)	0.006(2)
N2	0.021(3)	0.020(3)	0.014(3)	0.005(3)	0.007(3)	0.005(2)
N3	0.019(3)	0.017(3)	0.014(3)	0.008(2)	0.006(2)	0.006(2)
N4	0.018(3)	0.022(3)	0.016(3)	0.007(2)	0.007(2)	0.005(2)
N5	0.016(3)	0.016(3)	0.017(3)	0.003(2)	0.002(2)	0.006(2)
N6	0.021(4)	0.023(4)	0.013(4)	0.008(3)	0.001(3)	0.008(3)
N7	0.015(3)	0.016(3)	0.016(3)	0.001(2)	0.006(2)	0.004(2)
C1	0.020(3)	0.022(3)	0.024(4)	0.011(3)	0.007(3)	0.005(3)
C2	0.022(3)	0.026(4)	0.027(4)	0.010(3)	0.007(3)	0.008(3)
C3	0.022(3)	0.025(3)	0.022(4)	0.008(3)	0.012(3)	0.008(3)
C4	0.022(3)	0.014(3)	0.023(4)	0.007(3)	0.002(3)	0.005(2)
C5	0.032(4)	0.015(3)	0.026(4)	0.012(3)	0.006(3)	0.007(3)
C6	0.028(4)	0.024(3)	0.022(4)	0.014(3)	0.006(3)	0.005(3)
C7	0.018(3)	0.015(3)	0.033(4)	0.010(3)	0.007(3)	0.005(2)
C8	0.023(3)	0.020(3)	0.021(4)	−0.002(3)	−0.004(3)	0.003(3)
C9	0.024(3)	0.021(3)	0.018(3)	0.001(3)	0.001(3)	0.011(3)
C10	0.021(3)	0.010(3)	0.018(3)	0.005(2)	0.010(3)	0.005(2)
C11	0.013(3)	0.016(3)	0.016(3)	0.007(2)	0.005(2)	0.005(2)
C12	0.021(5)	0.014(4)	0.018(4)	0.002(3)	0.005(3)	0.004(3)
C13	0.016(3)	0.014(3)	0.025(4)	0.012(3)	0.004(3)	0.003(2)
C14	0.018(3)	0.014(3)	0.018(4)	0.006(3)	0.005(3)	0.004(3)
C15	0.015(3)	0.015(3)	0.015(3)	0.000(3)	0.006(2)	0.004(2)
C16	0.017(3)	0.023(3)	0.023(4)	0.011(3)	0.008(3)	0.007(3)
C17	0.020(3)	0.022(3)	0.031(4)	0.010(3)	0.011(3)	0.010(3)
C18	0.022(3)	0.025(3)	0.032(4)	0.018(3)	0.009(3)	0.008(3)
C19	0.011(3)	0.021(3)	0.031(4)	0.012(3)	0.009(3)	0.001(2)
C20	0.027(4)	0.036(4)	0.032(4)	0.019(3)	0.006(3)	0.005(3)
C21	0.029(4)	0.031(4)	0.023(4)	0.012(3)	0.011(3)	0.016(3)
C22	0.024(4)	0.019(3)	0.025(4)	0.003(3)	0.006(3)	−0.003(3)

C23	0.025(4)	0.027(4)	0.025(4)	0.009(3)	0.000(3)	0.002(3)
C24	0.025(4)	0.024(4)	0.031(4)	0.012(3)	0.008(3)	−0.001(3)
B1	0.026(4)	0.022(4)	0.011(4)	0.006(3)	0.006(3)	0.008(3)
W2	0.01438(18)	0.01401(18)	0.01660(19)	0.00663(15)	0.00486(15)	0.00324(14)
S2	0.0212(8)	0.0200(8)	0.0257(9)	0.0086(7)	0.0123(7)	0.0074(6)
P2	0.0161(10)	0.0170(10)	0.0201(11)	0.0062(8)	0.0044(8)	0.0017(7)
O6	0.035(3)	0.022(2)	0.030(3)	0.010(2)	0.006(2)	0.016(2)
O7	0.025(3)	0.020(3)	0.035(3)	0.013(2)	0.013(2)	0.009(2)
O8	0.017(2)	0.023(2)	0.034(3)	0.015(2)	0.012(2)	0.0062(19)
O9	0.021(2)	0.024(3)	0.041(3)	0.011(2)	0.016(2)	0.005(2)
O10	0.035(3)	0.039(3)	0.029(3)	0.008(2)	0.017(2)	0.016(2)
N8	0.019(3)	0.024(3)	0.014(3)	0.011(2)	0.004(2)	0.000(2)
N9	0.027(4)	0.025(4)	0.016(3)	0.010(3)	0.007(3)	−0.001(3)
N10	0.021(3)	0.015(3)	0.019(3)	0.003(2)	0.011(2)	0.006(2)
N11	0.019(3)	0.025(3)	0.018(3)	0.001(2)	0.007(2)	0.004(2)
N12	0.016(3)	0.019(3)	0.019(3)	0.010(2)	0.005(2)	0.002(2)
N13	0.018(4)	0.024(4)	0.021(4)	0.012(3)	0.007(3)	0.007(3)
N14	0.017(3)	0.020(3)	0.018(3)	0.008(2)	0.000(2)	0.001(2)
C25	0.021(3)	0.031(4)	0.027(4)	0.016(3)	0.002(3)	−0.001(3)
C26	0.028(4)	0.035(4)	0.025(4)	0.017(3)	−0.004(3)	−0.007(3)
C27	0.033(4)	0.038(4)	0.015(4)	0.010(3)	0.003(3)	−0.009(3)
C28	0.025(3)	0.020(3)	0.025(4)	0.007(3)	0.011(3)	0.008(3)
C29	0.026(4)	0.021(4)	0.040(5)	0.008(3)	0.013(3)	0.007(3)
C30	0.025(4)	0.022(3)	0.033(4)	0.000(3)	0.017(3)	0.005(3)
C31	0.024(3)	0.016(3)	0.021(4)	0.007(3)	0.005(3)	0.003(3)
C32	0.017(3)	0.019(3)	0.026(4)	0.011(3)	0.005(3)	0.003(2)
C33	0.019(3)	0.028(4)	0.028(4)	0.015(3)	0.010(3)	0.005(3)
C34	0.021(3)	0.013(3)	0.017(3)	0.007(3)	0.009(3)	0.004(2)
C35	0.014(3)	0.020(3)	0.012(3)	0.007(2)	0.002(2)	0.005(2)
C36	0.018(4)	0.013(4)	0.017(4)	0.004(3)	0.009(4)	0.001(3)
C37	0.016(3)	0.015(3)	0.025(4)	0.008(3)	0.003(3)	0.006(2)
C38	0.019(3)	0.015(3)	0.017(4)	0.005(3)	0.009(3)	0.005(3)
C39	0.017(3)	0.018(3)	0.018(3)	0.010(3)	0.005(3)	0.001(2)
C40	0.014(3)	0.023(3)	0.021(3)	0.011(3)	0.007(2)	0.006(2)
C41	0.020(3)	0.032(4)	0.022(4)	0.018(3)	0.007(3)	0.004(3)
C42	0.020(3)	0.029(4)	0.017(3)	0.005(3)	0.003(3)	0.006(3)
C43	0.018(3)	0.019(3)	0.013(3)	0.006(2)	0.003(2)	0.004(2)
C44	0.021(4)	0.032(4)	0.051(5)	0.021(4)	0.019(3)	0.010(3)

C45	0.026(4)	0.033(4)	0.053(5)	0.027(4)	0.022(4)	0.015(3)
C46	0.024(3)	0.018(3)	0.028(4)	0.008(3)	0.008(3)	0.000(3)
C47	0.018(3)	0.027(4)	0.028(4)	0.012(3)	0.007(3)	0.006(3)
C48	0.029(4)	0.026(4)	0.025(4)	0.008(3)	0.008(3)	−0.003(3)
B2	0.022(4)	0.033(4)	0.021(4)	0.009(3)	0.008(3)	0.001(3)
O11	0.052(5)	0.121(7)	0.087(6)	0.061(6)	0.021(4)	0.046(5)
C49	0.045(5)	0.049(5)	0.034(5)	0.020(4)	0.011(4)	0.006(4)
C50	0.046(5)	0.065(6)	0.027(4)	0.018(4)	0.010(4)	0.021(5)
C51	0.044(5)	0.047(5)	0.036(5)	0.008(4)	0.006(4)	0.001(4)
O54	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C52	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C53	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C54	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
O54A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C12A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C52A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C53A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)

Table 4 Bond lengths and angles for **Compound 10Atom–Atom**	**Length [Å]**
W1–P1	2.502(3)
W1–N1	2.197(5)
W1–N3	2.241(5)
W1–N5	2.235(5)
W1–N7	1.765(6)
W1–C10	2.245(6)
W1–C11	2.184(6)
S1–O4	1.445(5)
S1–O5	1.442(5)
S1–C14	1.735(8)
S1–C21	1.766(7)
P1–C22	1.821(7)
P1–C23	1.818(8)
P1–C24	1.833(7)
O1–N7	1.231(7)

O2–C19	1.196(8)
O3–C19	1.343(8)
O3–C20	1.428(9)
N1–N2	1.367(8)
N1–C1	1.331(8)
N2–C3	1.355(9)
N2–B1	1.527(10)
N3–N4	1.373(7)
N3–C4	1.351(8)
N4–C6	1.347(9)
N4–B1	1.544(9)
N5–N6	1.364(10)
N5–C7	1.337(8)
N6–C9	1.341(11)
N6–B1	1.553(12)
C1–H1	0.9500
C1–C2	1.387(10)
C2–H2	0.9500
C2–C3	1.384(10)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.383(10)
C5–H5	0.9500
C5–C6	1.358(10)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.397(10)
C8–H8	0.9500
C8–C9	1.372(11)
C9–H9	0.9500
C10–H10	1.0000
C10–C11	1.447(9)
C10–C15	1.458(9)
C11–H11	1.0000
C11–C12	1.530(12)
C12–H12	1.0000
C12–C13	1.540(12)
C12–C16	1.571(12)
C13–H13A	0.9900

C13–H13B	0.9900
C13–C14	1.508(9)
C14–C15	1.340(9)
C15–H15	0.9500
C16–C17	1.514(9)
C16–C18	1.542(9)
C16–C19	1.526(10)
C17–H17A	0.9800
C17–H17B	0.9800
C17–H17C	0.9800
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
B1–H1A	1.08(7)
W2–P2	2.516(3)
W2–N8	2.209(5)
W2–N10	2.251(5)
W2–N12	2.233(5)
W2–N14	1.771(6)
W2–C34	2.235(6)
W2–C35	2.204(6)
S2–O9	1.441(5)
S2–O10	1.444(6)
S2–C38	1.737(7)

S2–C45	1.765(7)
P2–C46	1.822(7)
P2–C47	1.820(7)
P2–C48	1.815(8)
O6–N14	1.229(7)
O7–C43	1.198(8)
O8–C43	1.342(8)
O8–C44	1.457(8)
N8–N9	1.364(9)
N8–C25	1.327(9)
N9–C27	1.342(10)
N9–B2	1.525(11)
N10–N11	1.362(8)
N10–C28	1.337(9)
N11–C30	1.352(9)
N11–B2	1.537(11)
N12–N13	1.381(10)
N12–C31	1.333(8)
N13–C33	1.346(10)
N13–B2	1.536(12)
C25–H25	0.9500
C25–C26	1.391(11)
C26–H26	0.9500
C26–C27	1.368(12)
C27–H27	0.9500
C28–H28	0.9500
C28–C29	1.392(10)
C29–H29	0.9500
C29–C30	1.372(11)
C30–H30	0.9500
C31–H31	0.9500
C31–C32	1.388(9)
C32–H32	0.9500
C32–C33	1.373(10)
C33–H33	0.9500
C34–H34	1.0000
C34–C35	1.453(9)
C34–C39	1.450(9)
C35–H35	1.0000

C35–C36	1.530(11)
C36–H36	1.0000
C36–C37	1.551(11)
C36–C40	1.564(12)
C37–H37A	0.9900
C37–H37B	0.9900
C37–C38	1.496(9)
C38–C39	1.330(9)
C39–H39	0.9500
C40–C41	1.532(9)
C40–C42	1.533(9)
C40–C43	1.529(9)
C41–H41A	0.9800
C41–H41B	0.9800
C41–H41C	0.9800
C42–H42A	0.9800
C42–H42B	0.9800
C42–H42C	0.9800
C44–H44A	0.9800
C44–H44B	0.9800
C44–H44C	0.9800
C45–H45A	0.9800
C45–H45B	0.9800
C45–H45C	0.9800
C46–H46A	0.9800
C46–H46B	0.9800
C46–H46C	0.9800
C47–H47A	0.9800
C47–H47B	0.9800
C47–H47C	0.9800
C48–H48A	0.9800
C48–H48B	0.9800
C48–H48C	0.9800
B2–H2A	1.09(8)
O11–C50	1.222(11)
C49–H49A	0.9800
C49–H49B	0.9800
C49–H49C	0.9800
C49–C50	1.490(13)

C50–C51	1.444(14)
C51–H51A	0.9800
C51–H51B	0.9800
C51–H51C	0.9800
O54–C53	1.24(2)
C52–H52A	0.9800
C52–H52B	0.9800
C52–H52C	0.9800
C52–C53	1.48(2)
C53–C54	1.48(2)
C54–H54A	0.9800
C54–H54B	0.9800
C54–H54C	0.9800
O54A–C12A	1.24(2)
C12A–C52A	1.496(19)
C12A–C53A	1.496(19)
C52A–H52D	0.9800
C52A–H52E	0.9800
C52A–H52F	0.9800
C53A–H53A	0.9800
C53A–H53B	0.9800
C53A–H53C	0.9800
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	81.01(15)
N1–W1–N3	86.72(19)
N1–W1–N5	76.4(2)
N1–W1–C10	161.5(2)
N3–W1–P1	82.58(15)
N3–W1–C10	89.1(2)
N5–W1–P1	151.58(15)
N5–W1–N3	79.18(19)
N5–W1–C10	120.5(2)
N7–W1–P1	92.17(18)
N7–W1–N1	86.7(2)
N7–W1–N3	172.1(2)
N7–W1–N5	103.4(2)
N7–W1–C10	95.8(2)

N7–W1–C11	97.2(2)
C10–W1–P1	80.58(17)
C11–W1–P1	118.52(17)
C11–W1–N1	159.8(2)
C11–W1–N3	90.5(2)
C11–W1–N5	83.4(2)
C11–W1–C10	38.1(2)
O4–S1–C14	108.8(3)
O4–S1–C21	106.6(3)
O5–S1–O4	117.3(3)
O5–S1–C14	110.5(3)
O5–S1–C21	108.0(3)
C14–S1–C21	104.8(3)
C22–P1–W1	120.9(3)
C22–P1–C24	100.4(3)
C23–P1–W1	113.0(3)
C23–P1–C22	102.9(4)
C23–P1–C24	103.9(4)
C24–P1–W1	113.6(3)
C19–O3–C20	117.7(6)
N2–N1–W1	123.7(4)
C1–N1–W1	128.8(5)
C1–N1–N2	107.5(5)
N1–N2–B1	118.4(6)
C3–N2–N1	108.5(6)
C3–N2–B1	130.2(6)
N4–N3–W1	119.8(4)
C4–N3–W1	134.0(4)
C4–N3–N4	106.0(5)
N3–N4–B1	121.6(5)
C6–N4–N3	109.3(5)
C6–N4–B1	128.6(6)
N6–N5–W1	120.0(5)
C7–N5–W1	133.7(5)
C7–N5–N6	106.2(6)
N5–N6–B1	122.4(7)
C9–N6–N5	109.8(7)
C9–N6–B1	127.7(8)
O1–N7–W1	173.8(5)

N1–C1–H1	124.8
N1–C1–C2	110.4(6)
C2–C1–H1	124.8
C1–C2–H2	127.5
C3–C2–C1	104.9(6)
C3–C2–H2	127.5
N2–C3–C2	108.7(6)
N2–C3–H3	125.7
C2–C3–H3	125.7
N3–C4–H4	125.1
N3–C4–C5	109.8(6)
C5–C4–H4	125.1
C4–C5–H5	126.9
C6–C5–C4	106.1(6)
C6–C5–H5	126.9
N4–C6–C5	108.7(6)
N4–C6–H6	125.6
C5–C6–H6	125.6
N5–C7–H7	124.7
N5–C7–C8	110.5(6)
C8–C7–H7	124.7
C7–C8–H8	127.7
C9–C8–C7	104.6(6)
C9–C8–H8	127.7
N6–C9–C8	108.9(7)
N6–C9–H9	125.6
C8–C9–H9	125.6
W1–C10–H10	115.5
C11–C10–W1	68.6(3)
C11–C10–H10	115.5
C11–C10–C15	118.4(5)
C15–C10–W1	115.3(4)
C15–C10–H10	115.5
W1–C11–H11	110.9
C10–C11–W1	73.2(3)
C10–C11–H11	110.9
C10–C11–C12	119.0(6)
C12–C11–W1	126.7(5)
C12–C11–H11	110.9

C11–C12–H12	106.6
C11–C12–C13	112.6(7)
C11–C12–C16	110.2(7)
C13–C12–H12	106.6
C13–C12–C16	113.6(7)
C16–C12–H12	106.6
C12–C13–H13A	108.8
C12–C13–H13B	108.8
H13A–C13–H13B	107.7
C14–C13–C12	113.7(6)
C14–C13–H13A	108.8
C14–C13–H13B	108.8
C13–C14–S1	117.8(5)
C15–C14–S1	119.7(5)
C15–C14–C13	122.4(7)
C10–C15–H15	118.6
C14–C15–C10	122.8(6)
C14–C15–H15	118.6
C17–C16–C12	113.7(6)
C17–C16–C18	109.7(6)
C17–C16–C19	109.2(6)
C18–C16–C12	111.7(6)
C19–C16–C12	106.1(6)
C19–C16–C18	106.0(5)
C16–C17–H17A	109.5
C16–C17–H17B	109.5
C16–C17–H17C	109.5
H17A–C17–H17B	109.5
H17A–C17–H17C	109.5
H17B–C17–H17C	109.5
C16–C18–H18A	109.5
C16–C18–H18B	109.5
C16–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
O2–C19–O3	123.1(7)
O2–C19–C16	126.9(6)
O3–C19–C16	109.9(5)

O3–C20–H20A	109.5
O3–C20–H20B	109.5
O3–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
S1–C21–H21A	109.5
S1–C21–H21B	109.5
S1–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
N2–B1–N4	109.4(6)
N2–B1–N6	105.7(6)
N2–B1–H1A	110(4)
N4–B1–N6	107.5(6)
N4–B1–H1A	111(4)
N6–B1–H1A	113(4)
N8–W2–P2	83.57(15)
N8–W2–N10	86.2(2)
N8–W2–N12	77.0(2)

N8–W2–C34	161.3(2)
N10–W2–P2	86.33(15)
N12–W2–P2	156.34(15)
N12–W2–N10	79.11(19)
N12–W2–C34	118.4(2)
N14–W2–P2	89.11(18)
N14–W2–N8	87.6(2)
N14–W2–N10	172.7(2)
N14–W2–N12	103.3(2)
N14–W2–C34	98.2(2)
N14–W2–C35	96.5(2)
C34–W2–P2	78.81(17)
C34–W2–N10	86.6(2)
C35–W2–P2	117.00(17)
C35–W2–N8	159.0(2)
C35–W2–N10	90.7(2)
C35–W2–N12	82.0(2)
C35–W2–C34	38.2(2)
O9–S2–O10	117.3(3)
O9–S2–C38	110.0(3)
O9–S2–C45	108.3(4)
O10–S2–C38	109.1(3)
O10–S2–C45	107.3(4)
C38–S2–C45	104.0(3)
C46–P2–W2	119.7(3)
C47–P2–W2	114.2(3)
C47–P2–C46	103.4(3)
C48–P2–W2	115.0(3)
C48–P2–C46	99.6(3)
C48–P2–C47	102.4(4)
C43–O8–C44	115.5(5)
N9–N8–W2	122.9(4)
C25–N8–W2	130.1(5)
C25–N8–N9	106.9(6)
N8–N9–B2	118.3(6)
C27–N9–N8	109.2(7)
C27–N9–B2	131.1(7)
N11–N10–W2	120.2(4)
C28–N10–W2	134.1(4)

C28–N10–N11	105.7(5)
N10–N11–B2	120.7(5)
C30–N11–N10	109.9(6)
C30–N11–B2	128.8(6)
N13–N12–W2	120.2(5)
C31–N12–W2	134.1(5)
C31–N12–N13	105.7(6)
N12–N13–B2	121.0(7)
C33–N13–N12	109.2(7)
C33–N13–B2	129.7(8)
O6–N14–W2	174.4(5)
N8–C25–H25	125.0
N8–C25–C26	110.0(7)
C26–C25–H25	125.0
C25–C26–H26	127.4
C27–C26–C25	105.2(7)
C27–C26–H26	127.4
N9–C27–C26	108.6(7)
N9–C27–H27	125.7
C26–C27–H27	125.7
N10–C28–H28	124.3
N10–C28–C29	111.5(6)
C29–C28–H28	124.3
C28–C29–H29	127.9
C30–C29–C28	104.3(7)
C30–C29–H29	127.9
N11–C30–C29	108.7(6)
N11–C30–H30	125.6
C29–C30–H30	125.6
N12–C31–H31	124.3
N12–C31–C32	111.5(6)
C32–C31–H31	124.3
C31–C32–H32	127.7
C33–C32–C31	104.6(6)
C33–C32–H32	127.7
N13–C33–C32	109.1(7)
N13–C33–H33	125.5
C32–C33–H33	125.5
W2–C34–H34	115.1

C35–C34–W2	69.8(3)
C35–C34–H34	115.1
C39–C34–W2	116.0(4)
C39–C34–H34	115.1
C39–C34–C35	118.3(6)
W2–C35–H35	111.4
C34–C35–W2	72.0(3)
C34–C35–H35	111.4
C34–C35–C36	118.5(6)
C36–C35–W2	126.5(5)
C36–C35–H35	111.4
C35–C36–H36	106.5
C35–C36–C37	112.4(7)
C35–C36–C40	110.8(7)
C37–C36–H36	106.5
C37–C36–C40	113.6(7)
C40–C36–H36	106.5
C36–C37–H37A	109.1
C36–C37–H37B	109.1
H37A–C37–H37B	107.8
C38–C37–C36	112.4(6)
C38–C37–H37A	109.1
C38–C37–H37B	109.1
C37–C38–S2	118.2(5)
C39–C38–S2	118.6(5)
C39–C38–C37	123.1(6)
C34–C39–H39	118.6
C38–C39–C34	122.8(6)
C38–C39–H39	118.6
C41–C40–C36	113.3(6)
C41–C40–C42	108.5(6)
C42–C40–C36	112.0(6)
C43–C40–C36	107.3(6)
C43–C40–C41	107.9(5)
C43–C40–C42	107.6(5)
C40–C41–H41A	109.5
C40–C41–H41B	109.5
C40–C41–H41C	109.5
H41A–C41–H41B	109.5

H41A–C41–H41C	109.5
H41B–C41–H41C	109.5
C40–C42–H42A	109.5
C40–C42–H42B	109.5
C40–C42–H42C	109.5
H42A–C42–H42B	109.5
H42A–C42–H42C	109.5
H42B–C42–H42C	109.5
O7–C43–O8	122.6(6)
O7–C43–C40	126.6(6)
O8–C43–C40	110.8(5)
O8–C44–H44A	109.5
O8–C44–H44B	109.5
O8–C44–H44C	109.5
H44A–C44–H44B	109.5
H44A–C44–H44C	109.5
H44B–C44–H44C	109.5
S2–C45–H45A	109.5
S2–C45–H45B	109.5
S2–C45–H45C	109.5
H45A–C45–H45B	109.5
H45A–C45–H45C	109.5
H45B–C45–H45C	109.5
P2–C46–H46A	109.5
P2–C46–H46B	109.5
P2–C46–H46C	109.5
H46A–C46–H46B	109.5
H46A–C46–H46C	109.5
H46B–C46–H46C	109.5
P2–C47–H47A	109.5
P2–C47–H47B	109.5
P2–C47–H47C	109.5
H47A–C47–H47B	109.5
H47A–C47–H47C	109.5
H47B–C47–H47C	109.5
P2–C48–H48A	109.5
P2–C48–H48B	109.5
P2–C48–H48C	109.5
H48A–C48–H48B	109.5

H48A–C48–H48C	109.5
H48B–C48–H48C	109.5
N9–B2–N11	110.1(6)
N9–B2–N13	106.9(7)
N9–B2–H2A	110(4)
N11–B2–H2A	108(4)
N13–B2–N11	108.7(7)
N13–B2–H2A	114(4)
H49A–C49–H49B	109.5
H49A–C49–H49C	109.5
H49B–C49–H49C	109.5
C50–C49–H49A	109.5
C50–C49–H49B	109.5
C50–C49–H49C	109.5
O11–C50–C49	120.5(10)
O11–C50–C51	122.1(10)
C51–C50–C49	117.4(8)
C50–C51–H51A	109.5
C50–C51–H51B	109.5
C50–C51–H51C	109.5
H51A–C51–H51B	109.5
H51A–C51–H51C	109.5
H51B–C51–H51C	109.5
H52A–C52–H52B	109.5
H52A–C52–H52C	109.5
H52B–C52–H52C	109.5
C53–C52–H52A	109.5
C53–C52–H52B	109.5
C53–C52–H52C	109.5
O54–C53–C52	124(2)
O54–C53–C54	116(3)
C54–C53–C52	120(2)
C53–C54–H54A	109.5
C53–C54–H54B	109.5
C53–C54–H54C	109.5
H54A–C54–H54B	109.5
H54A–C54–H54C	109.5
H54B–C54–H54C	109.5

O54A–C12A–C52A	121(2)
O54A–C12A–C53A	125(3)
C53A–C12A–C52A	115(2)
C12A–C52A–H52D	109.5
C12A–C52A–H52E	109.5
C12A–C52A–H52F	109.5
H52D–C52A–H52E	109.5
H52D–C52A–H52F	109.5
H52E–C52A–H52F	109.5
C12A–C53A–H53A	109.5
C12A–C53A–H53B	109.5
C12A–C53A–H53C	109.5
H53A–C53A–H53B	109.5
H53A–C53A–H53C	109.5
H53B–C53A–H53C	109.5

Table 5 Torsion angles for **Compound 10Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	177.7(4)
W1–N1–N2–B1	14.9(8)
W1–N1–C1–C2	−177.8(5)
W1–N3–N4–C6	175.0(4)
W1–N3–N4–B1	−12.6(7)

W1–N3–C4–C5	−172.6(5)
W1–N5–N6–C9	−176.0(5)
W1–N5–N6–B1	0.3(10)
W1–N5–C7–C8	175.1(5)
W1–C10–C11–C12	−123.2(6)
W1–C10–C15–C14	76.0(7)
W1–C11–C12–C13	−55.4(9)
W1–C11–C12–C16	176.5(5)
S1–C14–C15–C10	−179.2(5)
O4–S1–C14–C13	40.4(6)
O4–S1–C14–C15	−142.4(5)
O5–S1–C14–C13	170.5(5)
O5–S1–C14–C15	−12.3(7)
N1–N2–C3–C2	0.4(8)
N1–N2–B1–N4	−65.4(8)
N1–N2–B1–N6	50.1(8)
N1–C1–C2–C3	0.1(8)
N2–N1–C1–C2	0.2(8)
N3–N4–C6–C5	−1.4(8)
N3–N4–B1–N2	64.8(8)
N3–N4–B1–N6	−49.6(8)
N3–C4–C5–C6	−2.1(8)
N4–N3–C4–C5	1.3(7)
N5–N6–C9–C8	0.2(9)
N5–N6–B1–N2	−59.5(9)
N5–N6–B1–N4	57.4(9)
N5–C7–C8–C9	0.0(8)
N6–N5–C7–C8	0.1(8)
C1–N1–N2–C3	−0.3(8)
C1–N1–N2–B1	−163.2(6)
C1–C2–C3–N2	−0.3(8)
C3–N2–B1–N4	136.1(7)
C3–N2–B1–N6	−108.4(8)
C4–N3–N4–C6	0.1(7)
C4–N3–N4–B1	172.4(6)
C4–C5–C6–N4	2.1(8)
C6–N4–B1–N2	−124.4(7)
C6–N4–B1–N6	121.2(7)
C7–N5–N6–C9	−0.2(8)

C7–N5–N6–B1	176.1(7)
C7–C8–C9–N6	−0.2(8)
C9–N6–B1–N2	116.2(9)
C9–N6–B1–N4	−127.0(8)
C10–C11–C12–C13	34.7(10)
C10–C11–C12–C16	−93.4(8)
C11–C10–C15–C14	−2.3(9)
C11–C12–C13–C14	−37.1(9)
C11–C12–C16–C17	61.7(9)
C11–C12–C16–C18	−173.5(6)
C11–C12–C16–C19	−58.4(8)
C12–C13–C14–S1	−160.1(6)
C12–C13–C14–C15	22.8(9)
C12–C16–C19–O2	124.5(8)
C12–C16–C19–O3	−55.2(7)
C13–C12–C16–C17	−65.8(9)
C13–C12–C16–C18	59.0(9)
C13–C12–C16–C19	174.1(6)
C13–C14–C15–C10	−2.2(10)
C15–C10–C11–W1	108.1(5)
C15–C10–C11–C12	−15.1(9)
C16–C12–C13–C14	89.2(8)
C17–C16–C19–O2	1.5(9)
C17–C16–C19–O3	−178.2(5)
C18–C16–C19–O2	−116.6(7)
C18–C16–C19–O3	63.7(6)
C20–O3–C19–O2	−2.4(9)
C20–O3–C19–C16	177.4(5)
C21–S1–C14–C13	−73.4(6)
C21–S1–C14–C15	103.8(6)
B1–N2–C3–C2	160.5(7)
B1–N4–C6–C5	−173.0(6)
B1–N6–C9–C8	−175.9(8)
W2–N8–N9–C27	−177.5(5)
W2–N8–N9–B2	14.4(9)
W2–N8–C25–C26	177.1(5)
W2–N10–N11–C30	178.3(5)
W2–N10–N11–B2	−10.5(8)
W2–N10–C28–C29	−177.1(5)

W2–N12–N13–C33	178.8(5)
W2–N12–N13–B2	1.5(10)
W2–N12–C31–C32	−178.9(5)
W2–C34–C35–C36	−122.4(6)
W2–C34–C39–C38	75.3(8)
W2–C35–C36–C37	−53.0(9)
W2–C35–C36–C40	178.8(4)
S2–C38–C39–C34	−177.4(5)
O9–S2–C38–C37	−176.7(5)
O9–S2–C38–C39	−1.7(7)
O10–S2–C38–C37	53.3(7)
O10–S2–C38–C39	−131.6(6)
N8–N9–C27–C26	0.2(8)
N8–N9–B2–N11	−66.4(8)
N8–N9–B2–N13	51.5(9)
N8–C25–C26–C27	0.3(8)
N9–N8–C25–C26	−0.2(8)
N10–N11–C30–C29	−0.7(8)
N10–N11–B2–N9	64.5(8)
N10–N11–B2–N13	−52.3(9)
N10–C28–C29–C30	−1.8(9)
N11–N10–C28–C29	1.4(8)
N12–N13–C33–C32	0.7(9)
N12–N13–B2–N9	−61.0(10)
N12–N13–B2–N11	57.9(10)
N12–C31–C32–C33	−0.6(8)
N13–N12–C31–C32	1.0(8)
C25–N8–N9–C27	0.0(8)
C25–N8–N9–B2	−168.1(6)
C25–C26–C27–N9	−0.3(8)
C27–N9–B2–N11	128.6(8)
C27–N9–B2–N13	−113.6(9)
C28–N10–N11–C30	−0.5(8)
C28–N10–N11–B2	170.8(6)
C28–C29–C30–N11	1.5(9)
C30–N11–B2–N9	−126.1(8)
C30–N11–B2–N13	117.1(8)
C31–N12–N13–C33	−1.0(9)
C31–N12–N13–B2	−178.3(7)

C31–C32–C33–N13	−0.1(8)
C33–N13–B2–N9	122.4(9)
C33–N13–B2–N11	−118.8(9)
C34–C35–C36–C37	35.0(10)
C34–C35–C36–C40	−93.2(8)
C35–C34–C39–C38	−4.6(10)
C35–C36–C37–C38	−39.7(9)
C35–C36–C40–C41	55.6(8)
C35–C36–C40–C42	178.8(6)
C35–C36–C40–C43	−63.4(8)
C36–C37–C38–S2	−159.6(6)
C36–C37–C38–C39	25.6(10)
C36–C40–C43–O7	119.7(8)
C36–C40–C43–O8	−61.4(7)
C37–C36–C40–C41	−71.9(8)
C37–C36–C40–C42	51.2(9)
C37–C36–C40–C43	169.1(6)
C37–C38–C39–C34	−2.7(11)
C39–C34–C35–W2	109.4(6)
C39–C34–C35–C36	−12.9(9)
C40–C36–C37–C38	87.0(8)
C41–C40–C43–O7	−2.7(9)
C41–C40–C43–O8	176.2(5)
C42–C40–C43–O7	−119.6(7)
C42–C40–C43–O8	59.3(7)
C44–O8–C43–O7	−3.1(9)
C44–O8–C43–C40	177.9(6)
C45–S2–C38–C37	−60.9(7)
C45–S2–C38–C39	114.2(7)
B2–N9–C27–C26	166.2(8)
B2–N11–C30–C29	−171.0(7)
B2–N13–C33–C32	177.7(8)

Crystal Structure Report for Compound 13

A colorless, block-like specimen of $C_{25}H_{39}BN_7O_6PSW$, approximate dimensions 0.051 mm x 0.060 mm x 0.147 mm, was coated with Paratone oil and mounted on a MiTeGen

MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 3.60 hours. The frames were integrated with the Bruker SAINT software package[6] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 40643 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 6926 were independent (average redundancy 5.868, completeness = 99.9%, R_{int} = 8.45%, R_{sig} = 6.17%) and 5383 (77.72%) were greater than 2σ(F^2). The final cell constants of a = 14.2707(7) Å, b = 15.3139(7) Å, c = 15.7164(9) Å, β = 113.803(2)°, volume = 3142.5(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 5809 reflections above 20 σ(I) with 5.320° < 2θ < 53.31°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[7] The ratio of minimum to maximum apparent transmission was 0.848. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6020 and 0.8280.

The structure was solved and refined using the Bruker SHELXTL Software Package[8] within APEX4 [1] and OLEX2,[9] using the space group P $2_1/n$, with Z = 4 for the formula unit, $C_{25}H_{39}BN_7O_6PSW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.2U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 397 variables converged at R1 = 3.40%, for the observed data and wR2 = 7.21% for all data. The goodness-of-fit was 1.016. The largest peak in the final difference electron density synthesis was 1.184 $e^-/Å^3$ and the largest hole was -0.726 $e^-/Å^3$ with an RMS deviation of 0.159 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.673 g/cm^3 and F(000), 1584 e^-.

[6] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

[7] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[8] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

[9] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

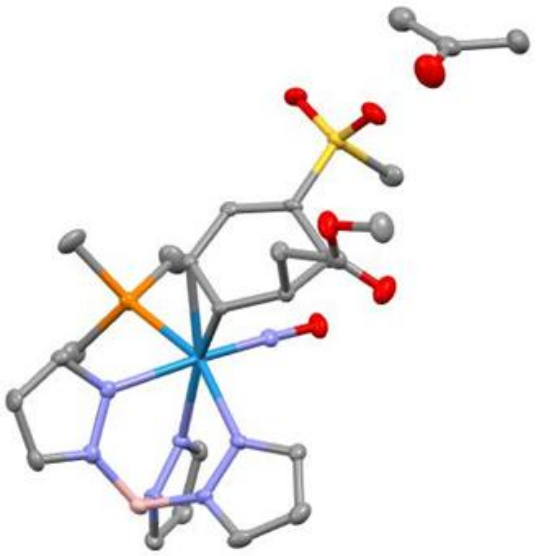


Table 1. Sample and crystal data for Compound 13.

Chemical formula	$C_{25}H_{39}BN_7O_6PSW$	
Formula weight	791.32 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.051 x 0.060 x 0.147 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.2707(7) Å	α = 90°
	b = 15.3139(7) Å	β = 113.803(2)°
	c = 15.7164(9) Å	γ = 90°
Volume	3142.5(3) Å3	
Z	4	
Density (calculated)	1.673 g/cm3	

Absorption coefficient	3.843 mm-1
F(000)	1584

Table 2. Data collection and structure refinement for Compound 13.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.94 to 27.10°
Index ranges	-18<=h<=18, -19<=k<=19, -20<=l<=20
Reflections collected	40643
Independent reflections	6926 [R(int) = 0.0845]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8280 and 0.6020
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)

Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	6926 / 0 / 397	
Goodness-of-fit on F2	1.016	
Final R indices	5383 data; I>2σ(I)	R1 = 0.0340, wR2 = 0.0655
	all data	R1 = 0.0548, wR2 = 0.0721
Weighting scheme	w=1/[σ2(Fo2)+(0.0284P)2] where P=(Fo2+2Fc2)/3	
Largest diff. peak and hole	1.184 and -0.726 eÅ-3	
R.M.S. deviation from mean	0.159 eÅ-3	

Table 2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å2) for Compound 13.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x/a	y/b	z/c	U(eq)
W1	0.62178(2)	0.26083(2)	0.36454(2)	0.01170(6)
S1	0.45660(9)	0.57962(7)	0.28531(9)	0.0184(3)
P1	0.44164(9)	0.20530(7)	0.29700(9)	0.0164(3)
O1	0.5863(3)	0.37128(19)	0.1965(2)	0.0222(8)
O2	0.4959(3)	0.66112(19)	0.3336(3)	0.0269(8)

	x/a	y/b	z/c	U(eq)
O3	0.3494(2)	0.5605(2)	0.2597(2)	0.0221(8)
O4	0.7977(3)	0.6189(2)	0.6542(2)	0.0270(8)
O5	0.8463(3)	0.5909(2)	0.5381(3)	0.0306(9)
N1	0.6495(3)	0.1669(2)	0.4829(3)	0.0145(8)
N2	0.7154(3)	0.0986(2)	0.4976(3)	0.0169(8)
N3	0.6490(3)	0.1461(2)	0.2932(3)	0.0154(8)
N4	0.7160(3)	0.0807(2)	0.3385(3)	0.0172(9)
N5	0.7906(3)	0.2532(2)	0.4159(3)	0.0154(8)
N6	0.8431(3)	0.1779(2)	0.4529(3)	0.0154(8)
N7	0.6007(3)	0.3275(2)	0.2668(3)	0.0154(8)
C1	0.6115(3)	0.1608(3)	0.5479(3)	0.0173(10)
C2	0.6524(4)	0.0894(3)	0.6037(3)	0.0213(11)
C3	0.7177(4)	0.0524(3)	0.5703(3)	0.0208(11)
C4	0.6152(4)	0.1286(3)	0.2030(3)	0.0175(10)
C5	0.6583(4)	0.0521(3)	0.1879(4)	0.0221(11)
C6	0.7223(4)	0.0247(3)	0.2757(4)	0.0217(11)
C7	0.8611(3)	0.3120(3)	0.4176(3)	0.0170(10)
C8	0.9596(4)	0.2759(3)	0.4573(4)	0.0236(11)
C9	0.9436(4)	0.1918(3)	0.4774(3)	0.0209(11)
C10	0.5482(4)	0.3538(3)	0.4302(3)	0.0155(10)
C11	0.6585(3)	0.3626(3)	0.4699(3)	0.0114(9)
C12	0.7050(3)	0.4516(3)	0.4681(3)	0.0156(10)
C13	0.6461(3)	0.5010(3)	0.3781(3)	0.0162(10)

	x/a	y/b	z/c	U(eq)
C14	0.5325(3)	0.4942(3)	0.3509(3)	0.0154(10)
C15	0.4884(3)	0.4253(3)	0.3722(3)	0.0135(9)
C16	0.4799(4)	0.5793(3)	0.1832(4)	0.0255(12)
C17	0.7098(4)	0.5065(3)	0.5516(3)	0.0167(10)
C18	0.7916(4)	0.5752(3)	0.5785(3)	0.0197(11)
C19	0.8730(4)	0.6887(3)	0.6839(4)	0.0312(13)
C20	0.4278(4)	0.0885(3)	0.2701(4)	0.0341(14)
C21	0.3637(4)	0.2121(3)	0.3626(4)	0.0333(14)
C22	0.3628(4)	0.2563(3)	0.1874(4)	0.0368(14)
B1	0.7832(4)	0.0912(3)	0.4428(4)	0.0184(12)
O6	0.2773(3)	0.6540(2)	0.0052(3)	0.0432(11)
C23	0.2352(4)	0.7358(3)	0.8665(4)	0.0385(14)
C24	0.2144(4)	0.6714(3)	0.9279(4)	0.0283(12)
C25	0.1120(4)	0.6282(3)	0.8898(4)	0.0342(14)

Table 3. Bond lengths (Å) for Compound 13.

W1-N7	1.766(4)	W1-C11	2.179(4)
W1-N3	2.201(3)	W1-N5	2.214(4)
W1-C10	2.252(4)	W1-N1	2.257(4)
W1-P1	2.5011(12)	S1-O3	1.446(3)
S1-O2	1.450(3)	S1-C14	1.745(4)
S1-C16	1.765(5)	P1-C21	1.799(5)

P1-C22	1.810(5)	P1-C20	1.831(5)
O1-N7	1.237(5)	O4-C18	1.338(6)
O4-C19	1.453(5)	O5-C18	1.212(5)
N1-C1	1.338(6)	N1-N2	1.362(5)
N2-C3	1.332(6)	N2-B1	1.537(6)
N3-C4	1.327(6)	N3-N4	1.370(5)
N4-C6	1.339(6)	N4-B1	1.537(7)
N5-C7	1.343(5)	N5-N6	1.371(5)
N6-C9	1.343(6)	N6-B1	1.552(6)
C1-C2	1.377(6)	C1-H1	0.950000
C2-C3	1.365(6)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.388(6)
C4-H4	0.950000	C5-C6	1.377(7)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.401(6)	C7-H7	0.950000
C8-C9	1.367(6)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.446(6)
C10-C15	1.459(6)	C10-H10	1.01(4)
C11-C12	1.521(6)	C11-H11	1.09(5)
C12-C13	1.523(6)	C12-C17	1.537(6)
C12-H12	1.000000	C13-C14	1.505(6)
C13-H13A	0.990000	C13-H13B	0.990000
C14-C15	1.338(6)	C15-H15	0.950000
C16-H16A	0.980000	C16-H16B	0.980000

C16-H16C	0.980000	C17-C18	1.499(6)
C17-H17A	0.990000	C17-H17B	0.990000
C19-H19A	0.980000	C19-H19B	0.980000
C19-H19C	0.980000	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
B1-H1A	0.98(5)	O6-C24	1.213(6)
C23-C24	1.492(7)	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
C24-C25	1.492(7)	C25-H25A	0.980000
C25-H25B	0.980000	C25-H25C	0.980000

Table 4. Bond angles (°) for Compound 13.

N7-W1-C11	98.73(16)	N7-W1-N3	91.22(15)
C11-W1-N3	157.02(15)	N7-W1-N5	97.24(15)
C11-W1-N5	82.44(14)	N3-W1-N5	75.76(13)
N7-W1-C10	94.94(16)	C11-W1-C10	38.06(16)
N3-W1-C10	161.59(15)	N5-W1-C10	120.44(15)
N7-W1-N1	175.65(14)	C11-W1-N1	85.47(15)
N3-W1-N1	84.45(14)	N5-W1-N1	82.11(13)
C10-W1-N1	89.08(15)	N7-W1-P1	92.43(12)

C11-W1-P1	117.14(11)	N3-W1-P1	82.81(10)
N5-W1-P1	156.60(9)	C10-W1-P1	79.62(12)
N1-W1-P1	86.63(10)	O3-S1-O2	117.5(2)
O3-S1-C14	110.3(2)	O2-S1-C14	108.7(2)
O3-S1-C16	108.2(2)	O2-S1-C16	107.6(2)
C14-S1-C16	103.6(2)	C21-P1-C22	103.3(3)
C21-P1-C20	98.9(2)	C22-P1-C20	103.5(3)
C21-P1-W1	120.28(18)	C22-P1-W1	113.24(18)
C20-P1-W1	115.28(17)	C18-O4-C19	115.3(4)
C1-N1-N2	106.4(4)	C1-N1-W1	133.0(3)
N2-N1-W1	120.5(3)	C3-N2-N1	109.2(4)
C3-N2-B1	129.6(4)	N1-N2-B1	120.6(4)
C4-N3-N4	106.6(3)	C4-N3-W1	130.0(3)
N4-N3-W1	123.2(3)	C6-N4-N3	109.0(4)
C6-N4-B1	130.9(4)	N3-N4-B1	118.9(4)
C7-N5-N6	106.2(3)	C7-N5-W1	131.9(3)
N6-N5-W1	121.8(3)	C9-N6-N5	109.0(4)
C9-N6-B1	130.2(4)	N5-N6-B1	119.4(4)
O1-N7-W1	177.5(3)	N1-C1-C2	110.1(4)
N1-C1-H1	125.000000	C2-C1-H1	125.000000
C3-C2-C1	105.3(4)	C3-C2-H2	127.300000
C1-C2-H2	127.300000	N2-C3-C2	109.0(4)
N2-C3-H3	125.500000	C2-C3-H3	125.500000
N3-C4-C5	111.0(4)	N3-C4-H4	124.500000

C5-C4-H4	124.500000	C6-C5-C4	104.3(4)
C6-C5-H5	127.900000	C4-C5-H5	127.900000
N4-C6-C5	109.2(4)	N4-C6-H6	125.400000
C5-C6-H6	125.400000	N5-C7-C8	110.6(4)
N5-C7-H7	124.700000	C8-C7-H7	124.700000
C9-C8-C7	104.1(4)	C9-C8-H8	127.900000
C7-C8-H8	127.900000	N6-C9-C8	110.0(4)
N6-C9-H9	125.000000	C8-C9-H9	125.000000
C11-C10-C15	117.3(4)	C11-C10-W1	68.2(2)
C15-C10-W1	116.8(3)	C11-C10-H10	116.(2)
C15-C10-H10	117.(2)	W1-C10-H10	112.(2)
C10-C11-C12	118.9(4)	C10-C11-W1	73.7(3)
C12-C11-W1	126.8(3)	C10-C11-H11	112.(2)
C12-C11-H11	111.(2)	W1-C11-H11	108.(2)
C11-C12-C13	112.4(4)	C11-C12-C17	110.1(4)
C13-C12-C17	109.8(3)	C11-C12-H12	108.100000
C13-C12-H12	108.100000	C17-C12-H12	108.100000
C14-C13-C12	110.9(4)	C14-C13-H13A	109.500000
C12-C13-H13A	109.500000	C14-C13-H13B	109.500000
C12-C13-H13B	109.500000	H13A-C13-H13B	108.000000
C15-C14-C13	123.0(4)	C15-C14-S1	119.8(3)
C13-C14-S1	117.1(3)	C14-C15-C10	122.2(4)

C14-C15-H15	118.900000	C10-C15-H15	118.900000
S1-C16-H16A	109.500000	S1-C16-H16B	109.500000
H16A-C16-H16B	109.500000	S1-C16-H16C	109.500000
H16A-C16-H16C	109.500000	H16B-C16-H16C	109.500000
C18-C17-C12	112.7(4)	C18-C17-H17A	109.100000
C12-C17-H17A	109.100000	C18-C17-H17B	109.100000
C12-C17-H17B	109.100000	H17A-C17-H17B	107.800000
O5-C18-O4	122.8(4)	O5-C18-C17	125.7(4)
O4-C18-C17	111.5(4)	O4-C19-H19A	109.500000
O4-C19-H19B	109.500000	H19A-C19-H19B	109.500000
O4-C19-H19C	109.500000	H19A-C19-H19C	109.500000
H19B-C19-H19C	109.500000	P1-C20-H20A	109.500000
P1-C20-H20B	109.500000	H20A-C20-H20B	109.500000
P1-C20-H20C	109.500000	H20A-C20-H20C	109.500000
H20B-C20-H20C	109.500000	P1-C21-H21A	109.500000
P1-C21-H21B	109.500000	H21A-C21-H21B	109.500000

P1-C21-H21C	109.500000	H21A-C21-H21C	109.500000
H21B-C21-H21C	109.500000	P1-C22-H22A	109.500000
P1-C22-H22B	109.500000	H22A-C22-H22B	109.500000
P1-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	N4-B1-N2	110.0(4)
N4-B1-N6	106.2(4)	N2-B1-N6	109.0(4)
N4-B1-H1A	112.(3)	N2-B1-H1A	110.(3)
N6-B1-H1A	110.(3)	C24-C23-H23A	109.500000
C24-C23-H23B	109.500000	H23A-C23-H23B	109.500000
C24-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	O6-C24-C23	122.2(5)
O6-C24-C25	120.9(5)	C23-C24-C25	116.9(5)
C24-C25-H25A	109.500000	C24-C25-H25B	109.500000
H25A-C25-H25B	109.500000	C24-C25-H25C	109.500000
H25A-C25-H25C	109.500000	H25B-C25-H25C	109.500000

Table 5. Torsion angles (°) for Compound 13.

C1-N1-N2-C3	-0.4(5)	W1-N1-N2-C3	-179.3(3)
C1-N1-N2-B1	-172.6(4)	W1-N1-N2-B1	8.5(5)
C4-N3-N4-C6	0.2(5)	W1-N3-N4-C6	-174.5(3)
C4-N3-N4-B1	168.9(4)	W1-N3-N4-B1	-5.9(5)
C7-N5-N6-C9	0.8(5)	W1-N5-N6-C9	179.5(3)
C7-N5-N6-B1	-167.4(4)	W1-N5-N6-B1	11.3(5)
N2-N1-C1-C2	-0.1(5)	W1-N1-C1-C2	178.7(3)
N1-C1-C2-C3	0.4(6)	N1-N2-C3-C2	0.7(5)
B1-N2-C3-C2	172.0(5)	C1-C2-C3-N2	-0.7(5)
N4-N3-C4-C5	0.4(5)	W1-N3-C4-C5	174.7(3)
N3-C4-C5-C6	-0.8(5)	N3-N4-C6-C5	-0.7(5)
B1-N4-C6-C5	-167.6(4)	C4-C5-C6-N4	1.0(5)
N6-N5-C7-C8	-1.2(5)	W1-N5-C7-C8	-179.7(3)
N5-C7-C8-C9	1.2(5)	N5-N6-C9-C8	-0.1(5)
B1-N6-C9-C8	166.5(5)	C7-C8-C9-N6	-0.6(5)
C15-C10-C11-C12	13.6(6)	W1-C10-C11-C12	123.5(4)
C15-C10-C11-W1	-109.9(4)	C10-C11-C12-C13	-38.4(6)

W1-C11-C12-C13	52.3(5)	C10-C11-C12-C17	84.4(5)
W1-C11-C12-C17	175.1(3)	C11-C12-C13-C14	44.0(5)
C17-C12-C13-C14	-78.9(4)	C12-C13-C14-C15	-29.8(6)
C12-C13-C14-S1	152.3(3)	O3-S1-C14-C15	-1.8(5)
O2-S1-C14-C15	128.3(4)	C16-S1-C14-C15	-117.4(4)
O3-S1-C14-C13	176.1(3)	O2-S1-C14-C13	-53.7(4)
C16-S1-C14-C13	60.5(4)	C13-C14-C15-C10	5.0(7)
S1-C14-C15-C10	-177.2(3)	C11-C10-C15-C14	4.2(7)
W1-C10-C15-C14	-73.9(5)	C11-C12-C17-C18	155.2(4)
C13-C12-C17-C18	-80.5(5)	C19-O4-C18-O5	1.6(7)
C19-O4-C18-C17	-178.2(4)	C12-C17-C18-O5	3.5(7)
C12-C17-C18-O4	-176.7(4)	C6-N4-B1-N2	-132.7(5)
N3-N4-B1-N2	61.5(5)	C6-N4-B1-N6	109.5(5)
N3-N4-B1-N6	-56.3(5)	C3-N2-B1-N4	126.4(5)
N1-N2-B1-N4	-63.1(5)	C3-N2-B1-N6	-117.5(5)
N1-N2-B1-N6	52.9(6)	C9-N6-B1-N4	-112.2(5)

N5-N6-B1-N4	53.2(5)	C9-N6-B1-N2	129.3(5)
N5-N6-B1-N2	-65.3(5)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 13.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01227(9)	0.01046(9)	0.01207(10)	0.00044(8)	0.00460(7)	-0.00004(7)
S1	0.0188(6)	0.0154(5)	0.0197(7)	0.0038(5)	0.0065(5)	0.0035(4)
P1	0.0143(6)	0.0148(5)	0.0183(7)	-0.0005(5)	0.0045(5)	-0.0007(4)
O1	0.033(2)	0.0182(16)	0.017(2)	0.0001(14)	0.0113(17)	-0.0029(14)
O2	0.031(2)	0.0166(16)	0.028(2)	0.0019(15)	0.0073(18)	0.0042(14)
O3	0.0155(18)	0.0253(17)	0.024(2)	0.0049(15)	0.0060(16)	0.0060(13)
O4	0.038(2)	0.0212(17)	0.023(2)	-0.0066(15)	0.0136(18)	-0.0104(15)
O5	0.031(2)	0.0319(19)	0.034(2)	-0.0104(17)	0.019(2)	-0.0131(16)
N1	0.013(2)	0.0145(18)	0.015(2)	-0.0019(15)	0.0048(18)	-0.0029(14)
N2	0.017(2)	0.0157(18)	0.017(2)	0.0005(16)	0.0062(18)	-0.0010(15)
N3	0.015(2)	0.0126(18)	0.020(2)	-0.0009(16)	0.0086(19)	0.0012(15)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N4	0.018(2)	0.0145(18)	0.021(2)	-0.0001(16)	0.0094(19)	0.0007(15)
N5	0.0157(19)	0.0130(19)	0.019(2)	0.0000(16)	0.0084(16)	0.0028(14)
N6	0.014(2)	0.0178(18)	0.015(2)	0.0032(16)	0.0070(18)	0.0037(15)
N7	0.018(2)	0.0117(17)	0.018(2)	-0.0031(16)	0.0081(18)	-0.0015(14)
C1	0.016(2)	0.020(2)	0.018(3)	-0.0004(19)	0.009(2)	0.0023(18)
C2	0.027(3)	0.023(2)	0.017(3)	0.005(2)	0.013(2)	0.000(2)
C3	0.023(3)	0.016(2)	0.022(3)	0.006(2)	0.008(2)	0.0003(19)
C4	0.019(3)	0.016(2)	0.016(3)	0.0012(19)	0.006(2)	-0.0019(18)
C5	0.029(3)	0.021(2)	0.021(3)	-0.006(2)	0.015(2)	-0.004(2)
C6	0.026(3)	0.013(2)	0.031(3)	-0.002(2)	0.017(3)	-0.0009(19)
C7	0.019(3)	0.014(2)	0.021(3)	-0.0030(19)	0.012(2)	-0.0012(18)
C8	0.020(3)	0.028(3)	0.026(3)	-0.007(2)	0.013(2)	-0.005(2)
C9	0.013(2)	0.030(3)	0.018(3)	-0.004(2)	0.004(2)	0.0036(19)
C10	0.018(2)	0.012(2)	0.021(3)	-0.0002(19)	0.012(2)	0.0014(17)
C11	0.011(2)	0.014(2)	0.009(3)	0.0000(18)	0.004(2)	0.0031(16)
C12	0.016(2)	0.015(2)	0.016(3)	-0.0009(18)	0.008(2)	-0.0008(17)
C13	0.017(3)	0.014(2)	0.018(3)	-0.0004(18)	0.007(2)	-0.0009(16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	0.014(2)	0.014(2)	0.017(3)	0.0012(18)	0.005(2)	0.0060(17)
C15	0.014(2)	0.014(2)	0.013(3)	-0.0030(18)	0.007(2)	0.0015(17)
C16	0.026(3)	0.029(3)	0.019(3)	0.007(2)	0.007(2)	0.008(2)
C17	0.020(3)	0.017(2)	0.012(3)	-0.0033(18)	0.006(2)	-0.0031(18)
C18	0.021(3)	0.018(2)	0.016(3)	0.002(2)	0.003(2)	0.0022(19)
C19	0.036(3)	0.026(3)	0.027(3)	-0.008(2)	0.008(3)	-0.012(2)
C20	0.024(3)	0.020(2)	0.062(4)	-0.005(3)	0.020(3)	-0.007(2)
C21	0.016(3)	0.042(3)	0.044(4)	-0.011(3)	0.015(3)	-0.008(2)
C22	0.026(3)	0.032(3)	0.037(3)	0.006(3)	-0.003(2)	0.000(2)
B1	0.017(3)	0.014(2)	0.023(3)	0.002(2)	0.008(3)	0.003(2)
O6	0.038(3)	0.043(2)	0.034(3)	0.0057(19)	-0.001(2)	-0.0019(18)
C23	0.038(3)	0.027(3)	0.057(4)	0.013(3)	0.026(3)	0.006(2)
C24	0.028(3)	0.021(3)	0.035(4)	0.000(2)	0.012(3)	0.006(2)
C25	0.032(3)	0.032(3)	0.039(4)	0.002(2)	0.014(3)	0.004(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 13.

	x/a	y/b	z/c	U(eq)
H1	0.5633	0.2001	0.5545	0.021000
H2	0.6381	0.0699	0.6547	0.026000

	x/a	y/b	z/c	U(eq)
H3	0.7583	0.0019	0.5949	0.025000
H4	0.5678	0.1638	0.1552	0.021000
H5	0.6464	0.0248	0.1302	0.027000
H6	0.7643	-0.0260	0.2895	0.026000
H7	0.8463	0.3701	0.3949	0.020000
H8	1.0229	0.3035	0.4677	0.028000
H9	0.9959	0.1495	0.5048	0.025000
H10	0.518(3)	0.323(3)	0.470(3)	0.010(11)
H11	0.694(3)	0.332(3)	0.538(3)	0.017(12)
H12	0.7766	0.4425	0.4736	0.019000
H13A	0.6667	0.5632	0.3863	0.019000
H13B	0.6633	0.4767	0.3278	0.019000
H15	0.4158	0.4228	0.3487	0.016000
H16A	0.4370	0.6236	0.1401	0.038000
H16B	0.4633	0.5217	0.1538	0.038000
H16C	0.5522	0.5925	0.1991	0.038000
H17A	0.6426	0.5350	0.5361	0.020000
H17B	0.7228	0.4675	0.6054	0.020000
H19A	0.8556	0.7327	0.6346	0.047000
H19B	0.9410	0.6647	0.6967	0.047000
H19C	0.8732	0.7158	0.7405	0.047000
H20A	0.4779	0.0557	0.3222	0.051000
H20B	0.4396	0.0776	0.2138	0.051000

	x/a	y/b	z/c	U(eq)
H20C	0.3584	0.0696	0.2599	0.051000
H21A	0.3502	0.2735	0.3710	0.050000
H21B	0.3998	0.1848	0.4236	0.050000
H21C	0.2988	0.1817	0.3290	0.050000
H22A	0.2921	0.2356	0.1671	0.055000
H22B	0.3891	0.2411	0.1406	0.055000
H22C	0.3646	0.3199	0.1954	0.055000
H1A	0.831(4)	0.043(3)	0.467(3)	0.022000
H23A	0.2833	0.7801	-0.0952	0.058000
H23B	0.1710	0.7639	-0.1741	0.058000
H23C	0.2651	0.7056	-0.1716	0.058000
H25A	0.1089	0.5847	-0.0656	0.051000
H25B	0.1013	0.5993	-0.1691	0.051000
H25C	0.0585	0.6721	-0.1209	0.051000

Crystal Structure Report for Compound 14

A colorless, block-like specimen of $C_{55}H_{88}B_2N_{16}O_{11}P_2S_2W_2$, approximate dimensions 0.086 mm x 0.104 mm x 0.124 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture PhotonIII Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 3.46 hours. The frames were integrated with the Bruker SAINT software package[10] using a narrow-frame algorithm. The integration of the data using a

[10] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

triclinic unit cell yielded a total of 132829 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 17061 were independent (average redundancy 7.786, completeness = 99.6%, R_{int} = 3.55%, R_{sig} = 2.05%) and 15621 (91.56%) were greater than 2σ(F^2). The final cell constants of a = 12.5014(17) Å, b = 15.955(2) Å, c = 19.452(2) Å, α = 72.833(4)°, β = 80.411(4)°, γ = 68.750(4)°, volume = 3447.2(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 9632 reflections above 20 σ(I) with 4.958° < 2θ < 56.49°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[11] The ratio of minimum to maximum apparent transmission was 0.890. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6700 and 0.7520.

The structure was solved and refined using the Bruker SHELXTL Software Package[12] within APEX4 [1] and OLEX2,[13] using the space group P -1, with Z = 2 for the formula unit, $C_{55}H_{88}B_2N_{16}O_{11}P_2S_2W_2$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atoms as well as H10, H11, H35 and H36 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). The relative occupancy of each set of disordered atoms was freely refined. Constraints and restraints were used on the anisotropic displacement parameters and/or bond lengths of many of the disordered atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 872 variables converged at R1 = 1.96%, for the observed data and wR2 = 4.36% for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was 0.981 $e^-/Å^3$ and the largest hole was -0.783 $e^-/Å^3$ with an RMS deviation of 0.078 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.604 g/cm^3 and F(000), 1676 e^-.

[11] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[12] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

[13] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

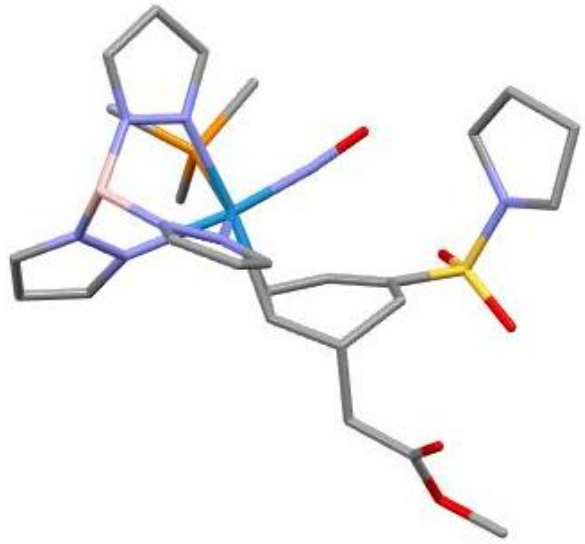


Table 1. Sample and crystal data for Compound 14.

Identification code	Harman_PS_2_153a_X3	
Chemical formula	$C_{55}H_{88}B_2N_{16}O_{11}P_2S_2W_2$	
Formula weight	1664.79 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.086 x 0.104 x 0.124 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.5014(17) Å	α = 72.833(4)°
	b = 15.955(2) Å	β = 80.411(4)°
	c = 19.452(2) Å	γ = 68.750(4)°
Volume	3447.2(8) $Å^3$	
Z	2	

Density (calculated)	1.604 g/cm^3
Absorption coefficient	3.507 mm^{-1}
F(000)	1676

Table 2. Data collection and structure refinement for Compound 14.

Diffractometer	Bruker D8 Venture PhotonIII Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.85 to 28.28°
Index ranges	-16<=h<=16, -21<=k<=21, -25<=l<=25
Reflections collected	132829
Independent reflections	17061 [R(int) = 0.0355]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7520 and 0.6700
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)

Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	17061 / 21 / 872	
Goodness-of-fit on F^2	1.040	
Δ/σ_{max}	0.004	
Final R indices	15621 data; I>2σ(I)	R1 = 0.0196, wR2 = 0.0424
	all data	R1 = 0.0229, wR2 = 0.0436
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0111P)^2+4.9954P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.981 and -0.783 eÅ^{-3}	
R.M.S. deviation from mean	0.078 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 14.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.72624(2)	0.64076(2)	0.15337(2)	0.01752(2)

	x/a	y/b	z/c	U(eq)
S1	0.15503(5)	0.62661(5)	0.04952(3)	0.03054(14)
P1	0.67619(5)	0.70424(5)	0.02412(3)	0.02708(13)
O1	0.82873(16)	0.78554(13)	0.14805(10)	0.0343(4)
O2	0.26022(15)	0.56541(15)	0.08240(11)	0.0390(5)
O3	0.14529(16)	0.63683(16)	0.97441(10)	0.0394(5)
O4	0.1700(2)	0.3978(2)	0.31032(13)	0.0683(8)
O5	0.26424(14)	0.32369(12)	0.22651(9)	0.0288(4)
N1	0.61902(16)	0.55178(14)	0.15956(10)	0.0215(4)
N2	0.51504(15)	0.56773(13)	0.19860(10)	0.0199(4)
N3	0.56098(16)	0.75243(13)	0.16554(10)	0.0200(4)
N4	0.46435(15)	0.73472(13)	0.19918(9)	0.0188(4)
N5	0.68352(15)	0.60727(12)	0.27036(9)	0.0174(4)
N6	0.57357(15)	0.61087(12)	0.29723(9)	0.0170(3)
N7	0.79314(16)	0.72255(14)	0.14944(10)	0.0227(4)
N8	0.13855(18)	0.72852(17)	0.05776(12)	0.0330(5)
C1	0.6241(2)	0.49014(17)	0.12369(13)	0.0269(5)
C2	0.5239(2)	0.46742(18)	0.13859(15)	0.0319(6)
C3	0.4573(2)	0.51816(17)	0.18582(13)	0.0264(5)
C4	0.5319(2)	0.84486(16)	0.14082(12)	0.0243(5)
C5	0.4154(2)	0.88756(17)	0.15750(12)	0.0252(5)
C6	0.37656(19)	0.81526(16)	0.19476(12)	0.0226(5)
C7	0.74237(18)	0.59174(15)	0.32648(11)	0.0181(4)
C8	0.67242(19)	0.58496(14)	0.39015(11)	0.0182(4)

	x/a	y/b	z/c	U(eq)
C9	0.56646(18)	0.59831(14)	0.36913(11)	0.0172(4)
C10	0.87477(19)	0.54184(17)	0.10402(12)	0.0226(5)
C11	0.87172(19)	0.51252(17)	0.18223(12)	0.0221(5)
C12	0.97958(19)	0.49825(17)	0.21751(12)	0.0234(5)
C13	0.0343(2)	0.57382(18)	0.17999(12)	0.0262(5)
C14	0.04200(19)	0.59065(18)	0.09936(12)	0.0253(5)
C15	0.96745(19)	0.57653(18)	0.06553(12)	0.0247(5)
C16	0.0392(2)	0.8093(2)	0.02789(15)	0.0383(6)
C17	0.0276(3)	0.8782(2)	0.0703(2)	0.0605(10)
C19	0.1793(3)	0.7420(2)	0.11956(16)	0.0398(7)
C20	0.0658(2)	0.40108(18)	0.21595(13)	0.0279(5)
C21	0.1702(2)	0.37577(19)	0.25641(13)	0.0307(6)
C22	0.3693(2)	0.2986(2)	0.26068(15)	0.0346(6)
C23	0.7352(2)	0.6334(2)	0.95983(14)	0.0406(7)
C24	0.7102(3)	0.8097(2)	0.97852(14)	0.0429(7)
C25	0.5232(2)	0.7361(2)	0.01444(14)	0.0360(6)
B1	0.4777(2)	0.63553(18)	0.24708(13)	0.0195(5)
C18	0.1363(5)	0.8497(4)	0.1056(3)	0.0395(17)
C18A	0.0847(7)	0.8248(5)	0.1326(4)	0.040(2)
W2	0.63354(2)	0.19871(2)	0.51602(2)	0.01076(2)
P2	0.73385(5)	0.24241(4)	0.39418(3)	0.01736(11)
O6	0.71083(13)	0.32272(11)	0.57099(10)	0.0247(4)
O9	0.8161(2)	0.93837(17)	0.81167(10)	0.0589(7)

	x/a	y/b	z/c	U(eq)
O10	0.94827(14)	0.82198(12)	0.77208(9)	0.0271(4)
N9	0.56449(14)	0.12345(11)	0.46207(9)	0.0136(3)
N10	0.44855(14)	0.15097(11)	0.45605(9)	0.0133(3)
N11	0.49105(14)	0.32236(11)	0.46791(9)	0.0130(3)
N12	0.38977(14)	0.31844(11)	0.45514(9)	0.0136(3)
N13	0.48414(14)	0.18959(11)	0.59374(9)	0.0132(3)
N14	0.38103(14)	0.20171(11)	0.57029(9)	0.0132(3)
N15	0.68088(14)	0.26889(12)	0.55080(10)	0.0151(3)
N16	0.02087(17)	0.22593(14)	0.61381(13)	0.0285(5)
C26	0.61309(18)	0.05383(14)	0.42919(11)	0.0156(4)
C27	0.52918(18)	0.03655(14)	0.40185(11)	0.0172(4)
C28	0.42676(18)	0.09909(14)	0.42046(11)	0.0166(4)
C29	0.48438(18)	0.41170(14)	0.44424(11)	0.0163(4)
C30	0.37918(18)	0.46580(14)	0.41514(11)	0.0178(4)
C31	0.32135(18)	0.40375(14)	0.42346(11)	0.0159(4)
C32	0.46856(17)	0.17595(14)	0.66523(11)	0.0159(4)
C33	0.35627(18)	0.17806(15)	0.68896(12)	0.0178(4)
C34	0.30426(17)	0.19429(14)	0.62717(11)	0.0171(4)
C35	0.79868(16)	0.07776(13)	0.52756(11)	0.0143(4)
C36	0.71756(17)	0.06435(14)	0.58870(11)	0.0149(4)
C37	0.75786(18)	0.04309(15)	0.66374(12)	0.0194(4)
C38	0.82913(19)	0.10305(16)	0.66555(12)	0.0225(5)
C39	0.91676(18)	0.10455(15)	0.60255(13)	0.0209(4)

	x/a	y/b	z/c	U(eq)
C40	0.90122(17)	0.09368(14)	0.53956(12)	0.0174(4)
C41	0.9879(2)	0.30079(18)	0.54792(16)	0.0324(6)
C42	0.9604(3)	0.3865(2)	0.5762(2)	0.0574(9)
C43	0.9155(4)	0.3605(2)	0.6515(2)	0.0688(13)
C44	0.9705(3)	0.2593(2)	0.67879(18)	0.0462(8)
C45	0.82735(19)	0.93865(15)	0.68639(12)	0.0221(4)
C46	0.8607(2)	0.90311(17)	0.76314(13)	0.0277(5)
C47	0.9891(2)	0.7808(2)	0.84361(14)	0.0378(6)
C48	0.8388(2)	0.15201(17)	0.35575(13)	0.0281(5)
C49	0.8129(3)	0.3201(2)	0.38826(15)	0.0378(6)
C50	0.6391(2)	0.3025(2)	0.32049(13)	0.0372(6)
B2	0.36246(19)	0.22731(15)	0.48954(12)	0.0137(4)
S2	0.0519(7)	0.1229(5)	0.5958(7)	0.0243(5)
O7	0.0962(18)	0.0656(14)	0.6624(10)	0.0408(12)
O8	0.1206(17)	0.1162(16)	0.5305(10)	0.0347(12)
S2A	0.04321(18)	0.11790(14)	0.6172(3)	0.0243(5)
O7A	0.0781(4)	0.0636(3)	0.6880(4)	0.0408(12)
O8A	0.1217(4)	0.1016(4)	0.5559(4)	0.0347(12)
O11	0.6008(3)	0.1885(2)	0.1403(2)	0.0520(10)
C51	0.5252(5)	0.0673(4)	0.1915(4)	0.0570(6)
C52	0.6356(5)	0.0876(4)	0.1653(3)	0.0570(6)
C53	0.6905(5)	0.0413(4)	0.1055(3)	0.0570(6)
C54	0.7054(5)	0.0694(4)	0.2274(3)	0.0570(6)

	x/a	y/b	z/c	U(eq)
C55	0.6875(7)	0.2293(5)	0.1123(4)	0.0570(6)
O11A	0.5402(6)	0.1488(5)	0.1612(4)	0.0473(19)
C51A	0.7198(11)	0.0649(9)	0.0893(7)	0.0570(6)
C52A	0.6703(10)	0.1177(7)	0.1523(6)	0.0570(6)
C53A	0.6990(15)	0.2083(8)	0.1239(9)	0.0570(6)
C54A	0.7305(11)	0.0397(8)	0.2129(7)	0.0570(6)
C55A	0.4795(10)	0.0882(9)	0.1928(7)	0.0570(6)

Table 4. Bond lengths (Å) for Compound 14.

W1-N7	1.766(2)	W1-C11	2.185(2)
W1-N5	2.1985(17)	W1-N3	2.2173(18)
W1-C10	2.244(2)	W1-N1	2.2475(19)
W1-P1	2.5101(7)	S1-O2	1.440(2)
S1-O3	1.4423(19)	S1-N8	1.616(2)
S1-C14	1.752(2)	P1-C23	1.819(3)
P1-C24	1.819(3)	P1-C25	1.820(3)
O1-N7	1.230(3)	O4-C21	1.200(3)
O5-C21	1.326(3)	O5-C22	1.443(3)
N1-C1	1.343(3)	N1-N2	1.370(2)
N2-C3	1.341(3)	N2-B1	1.538(3)
N3-C4	1.338(3)	N3-N4	1.357(2)
N4-C6	1.344(3)	N4-B1	1.546(3)

N5-C7	1.330(3)	N5-N6	1.374(2)
N6-C9	1.346(3)	N6-B1	1.537(3)
N8-C16	1.476(3)	N8-C19	1.478(3)
C1-C2	1.390(3)	C1-H1	0.950000
C2-C3	1.374(3)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.395(3)
C4-H4	0.950000	C5-C6	1.373(3)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.392(3)	C7-H7	0.950000
C8-C9	1.375(3)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.452(3)
C10-C15	1.463(3)	C10-H10	0.89(3)
C11-C12	1.528(3)	C11-H11	0.97(3)
C12-C13	1.538(3)	C12-C20	1.540(3)
C12-H12	1.000000	C13-C14	1.504(3)
C13-H13A	0.990000	C13-H13B	0.990000
C14-C15	1.340(3)	C15-H15	0.950000
C16-C17	1.513(5)	C16-H16A	0.990000
C16-H16B	0.990000	C17-C18A	1.394(8)
C17-C18	1.483(6)	C17-H17A	0.990000
C17-H17B	0.990000	C17-H17C	0.990000
C17-H17D	0.990000	C19-C18A	1.474(8)
C19-C18	1.555(6)	C19-H19A	0.990000
C19-H19B	0.990000	C19-H19C	0.990000

C19-H19D	0.990000	C20-C21	1.503(3)
C20-H20A	0.990000	C20-H20B	0.990000
C22-H22A	0.980000	C22-H22B	0.980000
C22-H22C	0.980000	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
C24-H24A	0.980000	C24-H24B	0.980000
C24-H24C	0.980000	C25-H25A	0.980000
C25-H25B	0.980000	C25-H25C	0.980000
B1-H1A	1.09(2)	C18-H18A	0.990000
C18-H18B	0.990000	C18A-H18C	0.990000
C18A-H18D	0.990000	W2-N15	1.7672(17)
W2-C36	2.184(2)	W2-N11	2.2043(17)
W2-N13	2.2185(16)	W2-C35	2.2466(19)
W2-N9	2.2549(17)	W2-P2	2.5187(6)
P2-C49	1.814(3)	P2-C48	1.816(2)
P2-C50	1.819(3)	O6-N15	1.230(2)
O9-C46	1.196(3)	O10-C46	1.345(3)
O10-C47	1.443(3)	N9-C26	1.346(2)
N9-N10	1.368(2)	N10-C28	1.343(3)
N10-B2	1.533(3)	N11-C29	1.338(2)
N11-N12	1.357(2)	N12-C31	1.342(3)
N12-B2	1.545(3)	N13-C32	1.335(3)

N13-N14	1.368(2)	N14-C34	1.346(3)
N14-B2	1.537(3)	N16-C41	1.468(4)
N16-C44	1.472(3)	N16-S2A	1.626(3)
N16-S2	1.676(8)	C26-C27	1.393(3)
C26-H26	0.950000	C27-C28	1.378(3)
C27-H27	0.950000	C28-H28	0.950000
C29-C30	1.390(3)	C29-H29	0.950000
C30-C31	1.384(3)	C30-H30	0.950000
C31-H31	0.950000	C32-C33	1.394(3)
C32-H32	0.950000	C33-C34	1.375(3)
C33-H33	0.950000	C34-H34	0.950000
C35-C36	1.447(3)	C35-C40	1.460(3)
C35-H35	0.94(3)	C36-C37	1.526(3)
C36-H36	0.95(2)	C37-C38	1.536(3)
C37-C45	1.539(3)	C37-H37	1.000000
C38-C39	1.502(3)	C38-H38A	0.990000
C38-H38B	0.990000	C39-C40	1.341(3)
C39-S2A	1.748(3)	C39-S2	1.794(8)
C40-H40	0.950000	C41-C42	1.528(4)
C41-H41A	0.990000	C41-H41B	0.990000
C42-C43	1.472(6)	C42-H42A	0.990000
C42-H42B	0.990000	C43-C44	1.474(4)
C43-H43A	0.990000	C43-H43B	0.990000
C44-H44A	0.990000	C44-H44B	0.990000

C45-C46	1.504(3)	C45-H45A	0.990000
C45-H45B	0.990000	C47-H47A	0.980000
C47-H47B	0.980000	C47-H47C	0.980000
C48-H48A	0.980000	C48-H48B	0.980000
C48-H48C	0.980000	C49-H49A	0.980000
C49-H49B	0.980000	C49-H49C	0.980000
C50-H50A	0.980000	C50-H50B	0.980000
C50-H50C	0.980000	B2-H2A	1.08(2)
S2-O7	1.412(12)	S2-O8	1.420(12)
S2A-O7A	1.435(3)	S2A-O8A	1.435(3)
O11-C55	1.413(9)	O11-C52	1.455(7)
C51-C52	1.505(7)	C51-H51A	0.980000
C51-H51B	0.980000	C51-H51C	0.980000
C52-C53	1.499(7)	C52-C54	1.505(7)
C53-H53A	0.980000	C53-H53B	0.980000
C53-H53C	0.980000	C54-H54A	0.980000
C54-H54B	0.980000	C54-H54C	0.980000
C55-H55A	0.980000	C55-H55B	0.980000
C55-H55C	0.980000	O11A-C55A	1.383(14)
O11A-C52A	1.514(13)	C51A-C52A	1.604(11)
C51A-H51D	0.980000	C51A-H51E	0.980000

C51A-H51F	0.980000	C52A-C54A	1.502(11)
C52A-C53A	1.537(12)	C53A-H53D	0.980000
C53A-H53E	0.980000	C53A-H53F	0.980000
C54A-H54D	0.980000	C54A-H54E	0.980000
C54A-H54F	0.980000	C55A-H55D	0.980000
C55A-H55E	0.980000	C55A-H55F	0.980000

Table 5. Bond angles (°) for Compound 14.

N7-W1-C11	99.46(9)	N7-W1-N5	97.70(8)
C11-W1-N5	82.58(7)	N7-W1-N3	86.31(8)
C11-W1-N3	159.32(8)	N5-W1-N3	76.95(7)
N7-W1-C10	97.61(9)	C11-W1-C10	38.25(8)
N5-W1-C10	120.53(8)	N3-W1-C10	161.03(7)
N7-W1-N1	172.44(8)	C11-W1-N1	87.72(8)
N5-W1-N1	80.78(7)	N3-W1-N1	86.14(7)
C10-W1-N1	89.49(8)	N7-W1-P1	94.29(6)
C11-W1-P1	118.59(6)	N5-W1-P1	153.54(5)
N3-W1-P1	80.39(5)	C10-W1-P1	80.81(6)
N1-W1-P1	84.24(5)	O2-S1-O3	119.24(12)
O2-S1-N8	105.82(12)	O3-S1-N8	106.82(12)

O2-S1-C14	107.95(12)	O3-S1-C14	107.93(11)
N8-S1-C14	108.73(12)	C23-P1-C24	102.65(15)
C23-P1-C25	100.09(13)	C24-P1-C25	104.66(14)
C23-P1-W1	121.00(10)	C24-P1-W1	113.81(10)
C25-P1-W1	112.59(9)	C21-O5-C22	115.8(2)
C1-N1-N2	106.01(18)	C1-N1-W1	133.73(16)
N2-N1-W1	119.44(14)	C3-N2-N1	109.76(18)
C3-N2-B1	128.91(19)	N1-N2-B1	121.31(18)
C4-N3-N4	106.61(18)	C4-N3-W1	130.51(15)
N4-N3-W1	122.80(14)	C6-N4-N3	109.50(19)
C6-N4-B1	131.20(19)	N3-N4-B1	117.78(17)
C7-N5-N6	106.59(17)	C7-N5-W1	132.40(14)
N6-N5-W1	120.58(13)	C9-N6-N5	109.10(17)
C9-N6-B1	129.18(18)	N5-N6-B1	121.45(17)
O1-N7-W1	173.48(17)	C16-N8-C19	111.2(2)
C16-N8-S1	120.15(18)	C19-N8-S1	122.40(19)
N1-C1-C2	110.4(2)	N1-C1-H1	124.800000
C2-C1-H1	124.800000	C3-C2-C1	105.1(2)
C3-C2-H2	127.500000	C1-C2-H2	127.500000
N2-C3-C2	108.7(2)	N2-C3-H3	125.700000
C2-C3-H3	125.700000	N3-C4-C5	110.4(2)
N3-C4-H4	124.800000	C5-C4-H4	124.800000
C6-C5-C4	104.5(2)	C6-C5-H5	127.800000
C4-C5-H5	127.800000	N4-C6-C5	109.0(2)

N4-C6-H6	125.500000	C5-C6-H6	125.500000
N5-C7-C8	110.62(19)	N5-C7-H7	124.700000
C8-C7-H7	124.700000	C9-C8-C7	104.84(19)
C9-C8-H8	127.600000	C7-C8-H8	127.600000
N6-C9-C8	108.84(18)	N6-C9-H9	125.600000
C8-C9-H9	125.600000	C11-C10-C15	118.0(2)
C11-C10-W1	68.66(12)	C15-C10-W1	116.82(17)
C11-C10-H10	118.4(18)	C15-C10-H10	113.9(18)
W1-C10-H10	113.6(18)	C10-C11-C12	117.20(19)
C10-C11-W1	73.09(13)	C12-C11-W1	127.57(17)
C10-C11-H11	116.4(16)	C12-C11-H11	110.8(16)
W1-C11-H11	107.4(16)	C11-C12-C13	112.17(19)
C11-C12-C20	108.42(19)	C13-C12-C20	110.63(19)
C11-C12-H12	108.500000	C13-C12-H12	108.500000
C20-C12-H12	108.500000	C14-C13-C12	111.22(19)
C14-C13-H13A	109.400000	C12-C13-H13A	109.400000
C14-C13-H13B	109.400000	C12-C13-H13B	109.400000
H13A-C13-H13B	108.000000	C15-C14-C13	122.0(2)
C15-C14-S1	119.85(18)	C13-C14-S1	118.13(17)
C14-C15-C10	122.8(2)	C14-C15-H15	118.600000
C10-C15-H15	118.600000	N8-C16-C17	103.5(2)

N8-C16-H16A	111.100000	C17-C16-H16A	111.100000
N8-C16-H16B	111.100000	C17-C16-H16B	111.100000
H16A-C16-H16B	109.000000	C18A-C17-C16	104.9(4)
C18-C17-C16	108.6(3)	C18-C17-H17A	110.000000
C16-C17-H17A	110.000000	C18-C17-H17B	110.000000
C16-C17-H17B	110.000000	H17A-C17-H17B	108.300000
C18A-C17-H17C	110.800000	C16-C17-H17C	110.800000
C18A-C17-H17D	110.800000	C16-C17-H17D	110.800000
H17C-C17-H17D	108.800000	C18A-C19-N8	100.8(3)
N8-C19-C18	102.7(3)	N8-C19-H19A	111.200000
C18-C19-H19A	111.200000	N8-C19-H19B	111.200000
C18-C19-H19B	111.200000	H19A-C19-H19B	109.100000
C18A-C19-H19C	111.600000	N8-C19-H19C	111.600000
C18A-C19-H19D	111.600000	N8-C19-H19D	111.600000
H19C-C19-H19D	109.400000	C21-C20-C12	112.8(2)

C21-C20-H20A	109.000000	C12-C20-H20A	109.000000
C21-C20-H20B	109.000000	C12-C20-H20B	109.000000
H20A-C20-H20B	107.800000	O4-C21-O5	123.0(2)
O4-C21-C20	124.8(2)	O5-C21-C20	112.1(2)
O5-C22-H22A	109.500000	O5-C22-H22B	109.500000
H22A-C22-H22B	109.500000	O5-C22-H22C	109.500000
H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
P1-C23-H23A	109.500000	P1-C23-H23B	109.500000
H23A-C23-H23B	109.500000	P1-C23-H23C	109.500000
H23A-C23-H23C	109.500000	H23B-C23-H23C	109.500000
P1-C24-H24A	109.500000	P1-C24-H24B	109.500000
H24A-C24-H24B	109.500000	P1-C24-H24C	109.500000
H24A-C24-H24C	109.500000	H24B-C24-H24C	109.500000
P1-C25-H25A	109.500000	P1-C25-H25B	109.500000
H25A-C25-H25B	109.500000	P1-C25-H25C	109.500000
H25A-C25-H25C	109.500000	H25B-C25-H25C	109.500000

N6-B1-N2	109.41(18)	N6-B1-N4	106.37(18)
N2-B1-N4	108.82(18)	N6-B1-H1A	111.7(13)
N2-B1-H1A	111.0(13)	N4-B1-H1A	109.3(13)
C17-C18-C19	102.6(4)	C17-C18-H18A	111.300000
C19-C18-H18A	111.300000	C17-C18-H18B	111.300000
C19-C18-H18B	111.300000	H18A-C18-H18B	109.200000
C17-C18A-C19	111.5(5)	C17-C18A-H18C	109.300000
C19-C18A-H18C	109.300000	C17-C18A-H18D	109.300000
C19-C18A-H18D	109.300000	H18C-C18A-H18D	108.000000
N15-W2-C36	98.32(8)	N15-W2-N11	89.80(7)
C36-W2-N11	157.74(7)	N15-W2-N13	99.18(7)
C36-W2-N13	81.80(7)	N11-W2-N13	76.44(6)
N15-W2-C35	96.06(7)	C36-W2-C35	38.09(7)
N11-W2-C35	161.54(7)	N13-W2-C35	119.56(7)
N15-W2-N9	173.67(7)	C36-W2-N9	87.99(7)
N11-W2-N9	84.52(6)	N13-W2-N9	82.22(6)
C35-W2-N9	88.53(7)	N15-W2-P2	92.04(6)
C36-W2-P2	117.80(6)	N11-W2-P2	82.33(4)
N13-W2-P2	155.86(4)	C35-W2-P2	79.98(6)
N9-W2-P2	84.45(4)	C49-P2-C48	102.38(13)

C49-P2-C50	103.60(15)	C48-P2-C50	99.71(12)
C49-P2-W2	114.35(9)	C48-P2-W2	119.73(8)
C50-P2-W2	114.75(9)	C46-O10-C47	116.1(2)
C26-N9-N10	106.24(16)	C26-N9-W2	134.29(14)
N10-N9-W2	119.43(12)	C28-N10-N9	109.57(16)
C28-N10-B2	128.33(17)	N9-N10-B2	122.05(16)
C29-N11-N12	106.54(16)	C29-N11-W2	130.10(14)
N12-N11-W2	123.33(12)	C31-N12-N11	110.01(16)
C31-N12-B2	130.41(17)	N11-N12-B2	118.47(16)
C32-N13-N14	106.32(16)	C32-N13-W2	132.94(14)
N14-N13-W2	120.72(12)	C34-N14-N13	109.42(16)
C34-N14-B2	128.92(17)	N13-N14-B2	121.49(16)
O6-N15-W2	175.58(16)	C41-N16-C44	111.3(2)
C41-N16-S2A	122.1(3)	C44-N16-S2A	118.6(3)
C41-N16-S2	109.5(4)	C44-N16-S2	132.4(5)
N9-C26-C27	110.43(18)	N9-C26-H26	124.800000
C27-C26-H26	124.800000	C28-C27-C26	104.74(18)
C28-C27-H27	127.600000	C26-C27-H27	127.600000
N10-C28-C27	109.02(18)	N10-C28-H28	125.500000
C27-C28-H28	125.500000	N11-C29-C30	110.42(18)

N11-C29-H29	124.800000	C30-C29-H29	124.800000
C31-C30-C29	104.75(18)	C31-C30-H30	127.600000
C29-C30-H30	127.600000	N12-C31-C30	108.27(18)
N12-C31-H31	125.900000	C30-C31-H31	125.900000
N13-C32-C33	110.78(18)	N13-C32-H32	124.600000
C33-C32-H32	124.600000	C34-C33-C32	104.55(18)
C34-C33-H33	127.700000	C32-C33-H33	127.700000
N14-C34-C33	108.93(18)	N14-C34-H34	125.500000
C33-C34-H34	125.500000	C36-C35-C40	117.64(18)
C36-C35-W2	68.62(11)	C40-C35-W2	117.49(13)
C36-C35-H35	120.0(15)	C40-C35-H35	113.2(15)
W2-C35-H35	112.6(15)	C35-C36-C37	117.67(17)
C35-C36-W2	73.29(11)	C37-C36-W2	129.25(14)
C35-C36-H36	115.3(14)	C37-C36-H36	110.1(14)
W2-C36-H36	107.0(14)	C36-C37-C38	111.77(18)
C36-C37-C45	107.89(17)	C38-C37-C45	111.43(18)
C36-C37-H37	108.600000	C38-C37-H37	108.600000
C45-C37-H37	108.600000	C39-C38-C37	110.88(18)
C39-C38-H38A	109.500000	C37-C38-H38A	109.500000
C39-C38-H38B	109.500000	C37-C38-H38B	109.500000

H38A-C38-H38B	108.100000	C40-C39-C38	122.56(19)
C40-C39-S2A	121.7(3)	C38-C39-S2A	115.7(2)
C40-C39-S2	109.0(4)	C38-C39-S2	128.4(4)
C39-C40-C35	122.4(2)	C39-C40-H40	118.800000
C35-C40-H40	118.800000	N16-C41-C42	101.0(2)
N16-C41-H41A	111.600000	C42-C41-H41A	111.600000
N16-C41-H41B	111.600000	C42-C41-H41B	111.600000
H41A-C41-H41B	109.400000	C43-C42-C41	105.3(3)
C43-C42-H42A	110.700000	C41-C42-H42A	110.700000
C43-C42-H42B	110.700000	C41-C42-H42B	110.700000
H42A-C42-H42B	108.800000	C42-C43-C44	107.2(3)
C42-C43-H43A	110.300000	C44-C43-H43A	110.300000
C42-C43-H43B	110.300000	C44-C43-H43B	110.300000
H43A-C43-H43B	108.500000	N16-C44-C43	104.7(3)
N16-C44-H44A	110.800000	C43-C44-H44A	110.800000
N16-C44-H44B	110.800000	C43-C44-H44B	110.800000

H44A-C44-H44B	108.900000	C46-C45-C37	114.87(19)
C46-C45-H45A	108.600000	C37-C45-H45A	108.600000
C46-C45-H45B	108.600000	C37-C45-H45B	108.600000
H45A-C45-H45B	107.500000	O9-C46-O10	122.6(2)
O9-C46-C45	126.7(2)	O10-C46-C45	110.7(2)
O10-C47-H47A	109.500000	O10-C47-H47B	109.500000
H47A-C47-H47B	109.500000	O10-C47-H47C	109.500000
H47A-C47-H47C	109.500000	H47B-C47-H47C	109.500000
P2-C48-H48A	109.500000	P2-C48-H48B	109.500000
H48A-C48-H48B	109.500000	P2-C48-H48C	109.500000
H48A-C48-H48C	109.500000	H48B-C48-H48C	109.500000
P2-C49-H49A	109.500000	P2-C49-H49B	109.500000
H49A-C49-H49B	109.500000	P2-C49-H49C	109.500000
H49A-C49-H49C	109.500000	H49B-C49-H49C	109.500000
P2-C50-H50A	109.500000	P2-C50-H50B	109.500000
H50A-C50-H50B	109.500000	P2-C50-H50C	109.500000

H50A-C50-H50C	109.500000	H50B-C50-H50C	109.500000
N10-B2-N14	109.02(16)	N10-B2-N12	108.38(16)
N14-B2-N12	106.53(16)	N10-B2-H2A	110.7(12)
N14-B2-H2A	110.8(12)	N12-B2-H2A	111.4(12)
O7-S2-O8	120.2(12)	O7-S2-N16	97.9(10)
O8-S2-N16	112.9(10)	O7-S2-C39	101.3(10)
O8-S2-C39	116.4(10)	N16-S2-C39	105.8(5)
O7A-S2A-O8A	119.0(2)	O7A-S2A-N16	107.4(3)
O8A-S2A-N16	103.9(3)	O7A-S2A-C39	109.4(3)
O8A-S2A-C39	106.7(3)	N16-S2A-C39	110.24(13)
C55-O11-C52	118.1(4)	C52-C51-H51A	109.500000
C52-C51-H51B	109.500000	H51A-C51-H51B	109.500000
C52-C51-H51C	109.500000	H51A-C51-H51C	109.500000
H51B-C51-H51C	109.500000	O11-C52-C53	112.1(5)
O11-C52-C54	101.2(5)	C53-C52-C54	119.0(5)
O11-C52-C51	104.8(4)	C53-C52-C51	107.6(5)
C54-C52-C51	111.1(5)	C52-C53-H53A	109.500000
C52-C53-H53B	109.500000	H53A-C53-H53B	109.500000

C52-C53-H53C	109.500000	H53A-C53-H53C	109.500000
H53B-C53-H53C	109.500000	C52-C54-H54A	109.500000
C52-C54-H54B	109.500000	H54A-C54-H54B	109.500000
C52-C54-H54C	109.500000	H54A-C54-H54C	109.500000
H54B-C54-H54C	109.500000	O11-C55-H55A	109.500000
O11-C55-H55B	109.500000	H55A-C55-H55B	109.500000
O11-C55-H55C	109.500000	H55A-C55-H55C	109.500000
H55B-C55-H55C	109.500000	C55A-O11A-C52A	123.2(8)
C52A-C51A-H51D	109.500000	C52A-C51A-H51E	109.500000
H51D-C51A-H51E	109.500000	C52A-C51A-H51F	109.500000
H51D-C51A-H51F	109.500000	H51E-C51A-H51F	109.500000
C54A-C52A-O11A	114.9(9)	C54A-C52A-C53A	122.5(11)
O11A-C52A-C53A	104.9(9)	C54A-C52A-C51A	97.5(9)
O11A-C52A-C51A	111.8(9)	C53A-C52A-C51A	104.6(11)
C52A-C53A-H53D	109.500000	C52A-C53A-H53E	109.500000

H53D-C53A-H53E	109.500000	C52A-C53A-H53F	109.500000
H53D-C53A-H53F	109.500000	H53E-C53A-H53F	109.500000
C52A-C54A-H54D	109.500000	C52A-C54A-H54E	109.500000
H54D-C54A-H54E	109.500000	C52A-C54A-H54F	109.500000
H54D-C54A-H54F	109.500000	H54E-C54A-H54F	109.500000
O11A-C55A-H55D	109.500000	O11A-C55A-H55E	109.500000
H55D-C55A-H55E	109.500000	O11A-C55A-H55F	109.500000
H55D-C55A-H55F	109.500000	H55E-C55A-H55F	109.500000

Table 6. Torsion angles (°) for Compound 14.

C1-N1-N2-C3	-1.0(3)	W1-N1-N2-C3	169.98(15)
C1-N1-N2-B1	-179.9(2)	W1-N1-N2-B1	-8.9(3)
C4-N3-N4-C6	0.5(2)	W1-N3-N4-C6	-176.53(14)
C4-N3-N4-B1	-167.09(18)	W1-N3-N4-B1	15.9(2)
C7-N5-N6-C9	0.5(2)	W1-N5-N6-C9	-172.85(13)
C7-N5-N6-B1	175.11(19)	W1-N5-N6-B1	1.7(2)

O2-S1-N8-C16	178.56(19)	O3-S1-N8-C16	50.5(2)
C14-S1-N8-C16	-65.7(2)	O2-S1-N8-C19	-31.6(2)
O3-S1-N8-C19	-159.6(2)	C14-S1-N8-C19	84.2(2)
N2-N1-C1-C2	0.8(3)	W1-N1-C1-C2	-168.36(18)
N1-C1-C2-C3	-0.3(3)	N1-N2-C3-C2	0.9(3)
B1-N2-C3-C2	179.6(2)	C1-C2-C3-N2	-0.4(3)
N4-N3-C4-C5	-0.9(2)	W1-N3-C4-C5	175.81(15)
N3-C4-C5-C6	0.9(3)	N3-N4-C6-C5	0.1(2)
B1-N4-C6-C5	165.4(2)	C4-C5-C6-N4	-0.6(3)
N6-N5-C7-C8	0.1(2)	W1-N5-C7-C8	172.32(15)
N5-C7-C8-C9	-0.6(2)	N5-N6-C9-C8	-0.9(2)
B1-N6-C9-C8	-174.9(2)	C7-C8-C9-N6	0.9(2)
C15-C10-C11-C12	-14.1(3)	W1-C10-C11-C12	-124.1(2)
C15-C10-C11-W1	109.9(2)	C10-C11-C12-C13	40.5(3)
W1-C11-C12-C13	-48.5(3)	C10-C11-C12-C20	-81.9(3)
W1-C11-C12-C20	-170.94(16)	C11-C12-C13-C14	-46.0(3)
C20-C12-C13-C14	75.2(2)	C12-C13-C14-C15	28.4(3)
C12-C13-C14-S1	-149.80(17)	O2-S1-C14-C15	-129.1(2)

O3-S1-C14-C15	1.0(3)	N8-S1-C14-C15	116.5(2)
O2-S1-C14-C13	49.1(2)	O3-S1-C14-C13	179.21(19)
N8-S1-C14-C13	-65.3(2)	C13-C14-C15-C10	-1.4(4)
S1-C14-C15-C10	176.70(19)	C11-C10-C15-C14	-6.6(4)
W1-C10-C15-C14	72.2(3)	C19-N8-C16-C17	5.3(3)
S1-N8-C16-C17	158.3(2)	N8-C16-C17-C18A	-20.6(5)
N8-C16-C17-C18	16.9(4)	C16-N8-C19-C18A	11.0(5)
S1-N8-C19-C18A	-141.3(4)	C16-N8-C19-C18	-23.9(4)
S1-N8-C19-C18	-176.2(3)	C11-C12-C20-C21	-173.9(2)
C13-C12-C20-C21	62.7(3)	C22-O5-C21-O4	-3.3(4)
C22-O5-C21-C20	178.1(2)	C12-C20-C21-O4	35.0(4)
C12-C20-C21-O5	-146.4(2)	C9-N6-B1-N2	-130.2(2)
N5-N6-B1-N2	56.4(3)	C9-N6-B1-N4	112.4(2)
N5-N6-B1-N4	-61.0(2)	C3-N2-B1-N6	130.0(2)
N1-N2-B1-N6	-51.4(3)	C3-N2-B1-N4	-114.2(2)
N1-N2-B1-N4	64.5(2)	C6-N4-B1-N6	-114.6(2)

N3-N4-B1-N6	49.7(2)	C6-N4-B1-N2	127.6(2)
N3-N4-B1-N2	-68.1(2)	C16-C17-C18-C19	-31.1(5)
N8-C19-C18-C17	32.7(5)	C16-C17-C18A-C19	29.8(8)
N8-C19-C18A-C17	-25.6(7)	C26-N9-N10-C28	0.2(2)
W2-N9-N10-C28	178.08(13)	C26-N9-N10-B2	177.75(17)
W2-N9-N10-B2	-4.4(2)	C29-N11-N12-C31	0.5(2)
W2-N11-N12-C31	-177.93(13)	C29-N11-N12-B2	-168.64(17)
W2-N11-N12-B2	12.9(2)	C32-N13-N14-C34	-0.8(2)
W2-N13-N14-C34	-179.10(13)	C32-N13-N14-B2	174.91(17)
W2-N13-N14-B2	-3.4(2)	N10-N9-C26-C27	0.2(2)
W2-N9-C26-C27	-177.26(14)	N9-C26-C27-C28	-0.5(2)
N9-N10-C28-C27	-0.5(2)	B2-N10-C28-C27	-177.85(18)
C26-C27-C28-N10	0.6(2)	N12-N11-C29-C30	-0.8(2)
W2-N11-C29-C30	177.51(14)	N11-C29-C30-C31	0.8(2)
N11-N12-C31-C30	-0.1(2)	B2-N12-C31-C30	167.40(19)

C29-C30-C31-N12	-0.4(2)	N14-N13-C32-C33	0.6(2)
W2-N13-C32-C33	178.66(14)	N13-C32-C33-C34	-0.3(2)
N13-N14-C34-C33	0.6(2)	B2-N14-C34-C33	-174.64(18)
C32-C33-C34-N14	-0.2(2)	C40-C35-C36-C37	-15.3(3)
W2-C35-C36-C37	-126.05(18)	C40-C35-C36-W2	110.77(17)
C35-C36-C37-C38	41.7(2)	W2-C36-C37-C38	-48.9(2)
C35-C36-C37-C45	-81.2(2)	W2-C36-C37-C45	-171.69(15)
C36-C37-C38-C39	-46.0(2)	C45-C37-C38-C39	74.8(2)
C37-C38-C39-C40	28.1(3)	C37-C38-C39-S2A	-150.07(17)
C37-C38-C39-S2	-153.6(4)	C38-C39-C40-C35	-1.2(3)
S2A-C39-C40-C35	176.85(17)	S2-C39-C40-C35	-179.8(3)
C36-C35-C40-C39	-6.2(3)	W2-C35-C40-C39	72.8(2)
C44-N16-C41-C42	23.5(3)	S2A-N16-C41-C42	171.8(2)
S2-N16-C41-C42	178.4(4)	N16-C41-C42-C43	-31.8(3)
C41-C42-C43-C44	29.7(4)	C41-N16-C44-C43	-6.3(3)

S2A-N16-C44-C43	-155.8(2)	S2-N16-C44-C43	-153.5(4)
C42-C43-C44-N16	-14.8(4)	C36-C37-C45-C46	-172.39(19)
C38-C37-C45-C46	64.6(3)	C47-O10-C46-O9	-2.3(4)
C47-O10-C46-C45	179.5(2)	C37-C45-C46-O9	21.0(4)
C37-C45-C46-O10	-160.9(2)	C28-N10-B2-N14	122.5(2)
N9-N10-B2-N14	-54.5(2)	C28-N10-B2-N12	-121.9(2)
N9-N10-B2-N12	61.0(2)	C34-N14-B2-N10	-125.5(2)
N13-N14-B2-N10	59.7(2)	C34-N14-B2-N12	117.7(2)
N13-N14-B2-N12	-57.1(2)	C31-N12-B2-N10	127.5(2)
N11-N12-B2-N10	-65.9(2)	C31-N12-B2-N14	-115.3(2)
N11-N12-B2-N14	51.3(2)	C41-N16-S2-O7	171.6(9)
C44-N16-S2-O7	-40.8(10)	C41-N16-S2-O8	44.1(10)
C44-N16-S2-O8	-168.3(10)	C41-N16-S2-C39	-84.3(6)
C44-N16-S2-C39	63.3(7)	C40-C39-S2-O7	-136.6(9)
C38-C39-S2-O7	44.9(10)	C40-C39-S2-O8	-4.5(11)

C38-C39-S2-O8	177.0(10)	C40-C39-S2-N16	121.7(5)
C38-C39-S2-N16	-56.8(7)	C41-N16-S2A-O7A	177.7(3)
C44-N16-S2A-O7A	-36.2(3)	C41-N16-S2A-O8A	50.7(3)
C44-N16-S2A-O8A	-163.2(3)	C41-N16-S2A-C39	-63.2(4)
C44-N16-S2A-C39	82.8(4)	C40-C39-S2A-O7A	-137.8(2)
C38-C39-S2A-O7A	40.4(3)	C40-C39-S2A-O8A	-7.8(3)
C38-C39-S2A-O8A	170.3(3)	C40-C39-S2A-N16	104.4(3)
C38-C39-S2A-N16	-77.5(4)	C55-O11-C52-C53	-63.8(7)
C55-O11-C52-C54	64.1(6)	C55-O11-C52-C51	179.7(6)
C55A-O11A-C52A-C54A	-35.8(14)	C55A-O11A-C52A-C53A	-173.2(11)
C55A-O11A-C52A-C51A	74.1(12)		

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for Compound 14.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01316(4)	0.02555(5)	0.01341(4)	-0.00782(3)	0.00112(3)	-0.00453(3)
S1	0.0168(3)	0.0499(4)	0.0276(3)	-0.0159(3)	0.0022(2)	-0.0111(3)
P1	0.0192(3)	0.0425(4)	0.0150(3)	-0.0087(3)	-0.0001(2)	-0.0044(3)
O1	0.0333(10)	0.0376(10)	0.0391(10)	-0.0130(8)	0.0045(8)	-0.0202(8)
O2	0.0167(8)	0.0537(12)	0.0480(12)	-0.0214(10)	-0.0025(8)	-0.0067(8)
O3	0.0286(10)	0.0695(14)	0.0262(9)	-0.0196(9)	0.0083(8)	-0.0219(10)
O4	0.0424(13)	0.100(2)	0.0570(14)	-0.0565(15)	-0.0295(11)	0.0224(13)
O5	0.0194(8)	0.0373(10)	0.0245(8)	-0.0107(7)	-0.0040(7)	0.0001(7)
N1	0.0157(9)	0.0282(10)	0.0215(9)	-0.0110(8)	-0.0019(7)	-0.0044(8)
N2	0.0141(8)	0.0251(10)	0.0218(9)	-0.0085(8)	-0.0018(7)	-0.0057(7)
N3	0.0173(9)	0.0251(10)	0.0157(8)	-0.0066(7)	0.0023(7)	-0.0052(7)
N4	0.0138(8)	0.0248(10)	0.0166(8)	-0.0075(7)	0.0000(7)	-0.0037(7)
N5	0.0145(8)	0.0209(9)	0.0161(8)	-0.0070(7)	0.0026(7)	-0.0051(7)
N6	0.0152(8)	0.0199(9)	0.0159(8)	-0.0061(7)	0.0021(7)	-0.0060(7)
N7	0.0184(9)	0.0307(11)	0.0176(9)	-0.0074(8)	0.0030(7)	-0.0074(8)
N8	0.0256(11)	0.0455(13)	0.0300(11)	-0.0084(10)	-0.0053(9)	-0.0137(10)
C1	0.0221(11)	0.0321(13)	0.0291(12)	-0.0174(10)	-0.0041(9)	-0.0035(10)
C2	0.0286(13)	0.0332(14)	0.0417(15)	-0.0195(12)	-0.0085(11)	-0.0086(11)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	0.0210(11)	0.0291(12)	0.0329(13)	-0.0106(10)	-0.0067(9)	-0.0085(10)
C4	0.0280(12)	0.0245(11)	0.0188(11)	-0.0041(9)	-0.0016(9)	-0.0080(10)
C5	0.0258(12)	0.0233(11)	0.0213(11)	-0.0064(9)	-0.0063(9)	0.0004(9)
C6	0.0165(10)	0.0284(12)	0.0205(11)	-0.0114(9)	-0.0022(8)	0.0000(9)
C7	0.0163(10)	0.0191(10)	0.0194(10)	-0.0083(8)	-0.0010(8)	-0.0039(8)
C8	0.0222(10)	0.0169(10)	0.0160(10)	-0.0072(8)	0.0001(8)	-0.0053(8)
C9	0.0196(10)	0.0142(9)	0.0166(10)	-0.0050(8)	0.0035(8)	-0.0057(8)
C10	0.0148(10)	0.0352(13)	0.0203(11)	-0.0157(10)	-0.0015(8)	-0.0040(9)
C11	0.0161(10)	0.0294(12)	0.0197(11)	-0.0106(9)	-0.0002(8)	-0.0031(9)
C12	0.0177(10)	0.0333(13)	0.0177(10)	-0.0138(9)	-0.0024(8)	-0.0007(9)
C13	0.0175(11)	0.0395(14)	0.0234(11)	-0.0151(10)	-0.0042(9)	-0.0047(10)
C14	0.0150(10)	0.0390(14)	0.0212(11)	-0.0125(10)	0.0006(8)	-0.0053(10)
C15	0.0156(10)	0.0386(14)	0.0192(11)	-0.0141(10)	0.0010(8)	-0.0038(9)
C16	0.0312(14)	0.0477(17)	0.0299(14)	0.0048(12)	-0.0082(11)	-0.0151(13)
C17	0.058(2)	0.0383(18)	0.086(3)	-0.0043(18)	-0.033(2)	-0.0145(16)
C19	0.0339(15)	0.0471(17)	0.0431(16)	-0.0140(13)	-0.0140(12)	-0.0117(13)
C20	0.0202(11)	0.0384(14)	0.0225(11)	-0.0163(10)	-0.0047(9)	0.0014(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	0.0266(12)	0.0355(14)	0.0250(12)	-0.0129(10)	-0.0087(10)	0.0027(10)
C22	0.0216(12)	0.0379(15)	0.0371(14)	-0.0044(12)	-0.0096(10)	-0.0024(11)
C23	0.0294(14)	0.068(2)	0.0191(12)	-0.0222(13)	-0.0040(10)	-0.0003(13)
C24	0.0451(17)	0.0566(19)	0.0213(13)	0.0002(12)	0.0003(12)	-0.0193(15)
C25	0.0226(12)	0.0544(18)	0.0237(12)	-0.0118(12)	-0.0052(10)	-0.0012(12)
B1	0.0159(11)	0.0233(12)	0.0196(11)	-0.0071(10)	-0.0006(9)	-0.0059(9)
C18	0.033(3)	0.044(3)	0.045(3)	-0.008(2)	-0.007(2)	-0.016(2)
C18A	0.036(4)	0.044(4)	0.042(4)	-0.013(3)	-0.003(3)	-0.015(3)
W2	0.00812(4)	0.00925(4)	0.01593(4)	-0.00505(3)	0.00004(3)	-0.00298(3)
P2	0.0146(2)	0.0166(3)	0.0191(3)	-0.0049(2)	0.0032(2)	-0.0048(2)
O6	0.0177(8)	0.0221(8)	0.0445(10)	-0.0215(7)	0.0010(7)	-0.0095(6)
O9	0.0558(14)	0.0599(14)	0.0233(10)	-0.0106(10)	-0.0045(9)	0.0254(11)
O10	0.0209(8)	0.0295(9)	0.0205(8)	0.0023(7)	-0.0048(6)	-0.0016(7)
N9	0.0121(8)	0.0119(8)	0.0178(8)	-0.0050(6)	-0.0014(6)	-0.0039(6)
N10	0.0118(8)	0.0111(8)	0.0184(8)	-0.0036(6)	-0.0026(6)	-0.0047(6)
N11	0.0107(7)	0.0113(8)	0.0176(8)	-0.0039(6)	-0.0007(6)	-0.0043(6)
N12	0.0118(8)	0.0125(8)	0.0172(8)	-0.0054(6)	-0.0013(6)	-0.0034(6)
N13	0.0095(7)	0.0129(8)	0.0176(8)	-0.0046(6)	-0.0017(6)	-0.0033(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N14	0.0087(7)	0.0127(8)	0.0193(8)	-0.0055(6)	-0.0013(6)	-0.0035(6)
N15	0.0087(7)	0.0131(8)	0.0243(9)	-0.0079(7)	0.0016(6)	-0.0033(6)
N16	0.0181(9)	0.0216(10)	0.0532(14)	-0.0213(9)	-0.0057(9)	-0.0044(8)
C26	0.0174(10)	0.0114(9)	0.0166(9)	-0.0046(7)	0.0000(8)	-0.0028(8)
C27	0.0234(11)	0.0125(9)	0.0178(10)	-0.0059(8)	-0.0030(8)	-0.0059(8)
C28	0.0196(10)	0.0144(9)	0.0197(10)	-0.0043(8)	-0.0051(8)	-0.0084(8)
C29	0.0169(10)	0.0127(9)	0.0197(10)	-0.0049(8)	0.0019(8)	-0.0062(8)
C30	0.0218(10)	0.0114(9)	0.0184(10)	-0.0040(8)	-0.0017(8)	-0.0033(8)
C31	0.0156(9)	0.0140(9)	0.0162(9)	-0.0043(8)	-0.0038(8)	-0.0009(8)
C32	0.0153(9)	0.0151(9)	0.0169(10)	-0.0052(8)	-0.0027(8)	-0.0029(8)
C33	0.0152(10)	0.0182(10)	0.0189(10)	-0.0055(8)	0.0021(8)	-0.0050(8)
C34	0.0121(9)	0.0159(10)	0.0234(10)	-0.0061(8)	0.0026(8)	-0.0056(8)
C35	0.0105(9)	0.0109(9)	0.0221(10)	-0.0084(8)	-0.0028(7)	-0.0004(7)
C36	0.0113(9)	0.0122(9)	0.0219(10)	-0.0042(8)	-0.0042(8)	-0.0036(7)
C37	0.0131(9)	0.0210(10)	0.0215(10)	-0.0064(8)	-0.0036(8)	-0.0008(8)
C38	0.0187(10)	0.0221(11)	0.0285(12)	-0.0133(9)	-0.0100(9)	0.0003(9)
C39	0.0123(9)	0.0149(10)	0.0386(13)	-0.0122(9)	-0.0070(9)	-0.0016(8)
C40	0.0095(9)	0.0112(9)	0.0311(11)	-0.0082(8)	-0.0003(8)	-0.0011(7)
C41	0.0190(11)	0.0309(13)	0.0506(16)	-0.0169(12)	-0.0005(11)	-0.0077(10)
C42	0.059(2)	0.0239(15)	0.088(3)	-0.0220(16)	-0.0070(19)	-0.0061(14)
C43	0.079(3)	0.046(2)	0.075(3)	-0.0432(19)	-0.039(2)	0.0237(18)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C44	0.0530(19)	0.0453(17)	0.059(2)	-0.0352(16)	0.0020(15)	-0.0231(15)
C45	0.0187(10)	0.0213(11)	0.0216(11)	-0.0021(9)	-0.0048(8)	-0.0024(9)
C46	0.0198(11)	0.0300(13)	0.0227(11)	0.0008(10)	-0.0024(9)	-0.0017(10)
C47	0.0318(14)	0.0439(16)	0.0225(12)	0.0043(11)	-0.0094(10)	-0.0020(12)
C48	0.0228(12)	0.0283(12)	0.0251(12)	-0.0079(10)	0.0097(9)	-0.0031(10)
C49	0.0476(16)	0.0394(15)	0.0363(14)	-0.0106(12)	0.0145(12)	-0.0328(14)
C50	0.0306(14)	0.0454(16)	0.0199(12)	-0.0077(11)	0.0001(10)	0.0043(12)
B2	0.0127(10)	0.0115(10)	0.0182(11)	-0.0040(8)	-0.0026(8)	-0.0045(8)
S2	0.0125(4)	0.0198(4)	0.0466(16)	-0.0193(7)	-0.0088(7)	-0.0007(3)
O7	0.0371(19)	0.0297(11)	0.060(3)	-0.006(2)	-0.033(2)	-0.0082(12)
O8	0.0103(8)	0.035(2)	0.071(3)	-0.037(3)	0.008(2)	-0.0066(11)
S2A	0.0125(4)	0.0198(4)	0.0466(16)	-0.0193(7)	-0.0088(7)	-0.0007(3)
O7A	0.0371(19)	0.0297(11)	0.060(3)	-0.006(2)	-0.033(2)	-0.0082(12)
O8A	0.0103(8)	0.035(2)	0.071(3)	-0.037(3)	0.008(2)	-0.0066(11)
O11	0.048(2)	0.0391(19)	0.067(2)	-0.0175(17)	0.0132(17)	-0.0177(16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C51	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C52	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C53	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C54	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C55	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
O11A	0.036(4)	0.058(4)	0.052(4)	-0.014(3)	0.008(3)	-0.025(3)
C51A	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C52A	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C53A	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C54A	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)
C55A	0.0496(14)	0.0450(15)	0.0685(15)	-0.0090(11)	-0.0028(11)	-0.0115(11)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 14.

	x/a	y/b	z/c	U(eq)
H1	0.6873	0.4655	0.0925	0.032000

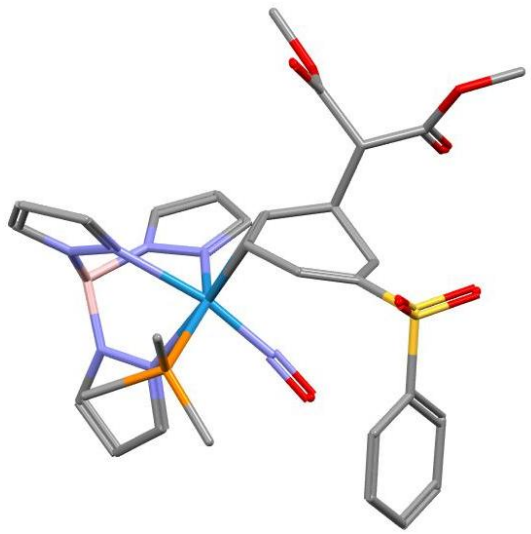
	x/a	y/b	z/c	U(eq)
H2	0.5054	0.4258	0.1201	0.038000
H3	0.3827	0.5181	0.2061	0.032000
H4	0.5834	0.8769	0.1155	0.029000
H5	0.3725	0.9521	0.1457	0.030000
H6	0.3000	0.8212	0.2142	0.027000
H7	0.8212	0.5861	0.3235	0.022000
H8	0.6933	0.5736	0.4377	0.022000
H9	0.4992	0.5986	0.4003	0.021000
H10	0.854(2)	0.5104(19)	0.0809(15)	0.028(7)
H11	0.841(2)	0.4626(19)	0.2053(14)	0.027(7)
H12	0.9578	0.5005	0.2690	0.028000
H13A	0.9875	0.6324	0.1934	0.031000
H13B	1.1123	0.5543	0.1967	0.031000
H15	0.9751	0.5896	0.0144	0.030000
H16A	0.9689	0.7920	0.0353	0.046000
H16B	1.0542	0.8350	-0.0243	0.046000
H17A	1.0124	0.9414	0.0376	0.073000
H17B	0.9625	0.8793	0.1072	0.073000
H17C	1.0636	0.9251	0.0424	0.073000
H17D	0.9457	0.9105	0.0824	0.073000
H19A	1.2641	0.7159	0.1199	0.048000
H19B	1.1451	0.7128	0.1659	0.048000
H19C	1.1875	0.6877	0.1619	0.048000

	x/a	y/b	z/c	U(eq)
H19D	1.2533	0.7540	0.1068	0.048000
H20A	1.0269	0.3542	0.2373	0.033000
H20B	1.0905	0.3992	0.1652	0.033000
H22A	1.4343	0.2648	0.2325	0.052000
H22B	1.3642	0.2590	0.3095	0.052000
H22C	1.3810	0.3551	0.2633	0.052000
H23A	0.8193	0.6148	-0.0437	0.061000
H23B	0.7060	0.6695	-0.0876	0.061000
H23C	0.7121	0.5778	-0.0239	0.061000
H24A	0.6629	0.8598	0.0011	0.064000
H24B	0.6943	0.8277	-0.0724	0.064000
H24C	0.7918	0.7982	-0.0177	0.064000
H25A	0.4995	0.6810	0.0345	0.054000
H25B	0.5080	0.7608	-0.0368	0.054000
H25C	0.4797	0.7835	0.0404	0.054000
H1A	0.396(2)	0.6349(17)	0.2774(13)	0.019(6)
H18A	1.1221	0.8686	0.1513	0.047000
H18B	1.1923	0.8766	0.0734	0.047000
H18C	1.0293	0.8049	0.1708	0.048000
H18D	1.1161	0.8631	0.1499	0.048000
H26	0.6933	0.0211	0.4252	0.019000
H27	0.5402	-0.0084	0.3761	0.021000
H28	0.3527	0.1046	0.4098	0.020000

	x/a	y/b	z/c	U(eq)
H29	0.5432	0.4349	0.4469	0.020000
H30	0.3528	0.5310	0.3942	0.021000
H31	0.2461	0.4189	0.4092	0.019000
H32	0.5262	0.1661	0.6958	0.019000
H33	0.3231	0.1701	0.7371	0.021000
H34	0.2267	0.1994	0.6250	0.021000
H35	0.812(2)	0.0450(17)	0.4923(13)	0.019(6)
H36	0.677(2)	0.0237(16)	0.5884(12)	0.012(6)
H37	0.6887	0.0564	0.6982	0.023000
H38A	0.7774	0.1673	0.6643	0.027000
H38B	0.8687	0.0778	0.7110	0.027000
H40	0.9591	0.0964	0.5013	0.021000
H41A	0.9198	0.3003	0.5286	0.039000
H41B	1.0521	0.2967	0.5102	0.039000
H42A	1.0305	0.4027	0.5739	0.069000
H42B	0.9021	0.4405	0.5476	0.069000
H43A	0.8309	0.3767	0.6539	0.083000
H43B	0.9341	0.3940	0.6809	0.083000
H44A	1.0308	0.2454	0.7115	0.055000
H44B	0.9130	0.2298	0.7051	0.055000
H45A	0.7814	-0.0969	0.6792	0.027000
H45B	0.8982	-0.0739	0.6541	0.027000
H47A	1.0578	-0.2740	0.8430	0.057000

	x/a	y/b	z/c	U(eq)
H47B	0.9289	-0.2378	0.8770	0.057000
H47C	1.0083	-0.1737	0.8594	0.057000
H48A	0.9016	0.1167	0.3879	0.042000
H48B	0.8696	0.1805	0.3086	0.042000
H48C	0.8017	0.1100	0.3501	0.042000
H49A	0.7628	0.3736	0.4063	0.057000
H49B	0.8388	0.3418	0.3379	0.057000
H49C	0.8797	0.2869	0.4174	0.057000
H50A	0.5916	0.2655	0.3198	0.056000
H50B	0.6853	0.3109	0.2747	0.056000
H50C	0.5892	0.3634	0.3273	0.056000
H2A	0.2757(19)	0.2358(15)	0.4816(12)	0.011(5)
H51A	0.4758	0.0893	0.1512	0.085000
H51B	0.4855	0.0992	0.2293	0.085000
H51C	0.5423	0.0001	0.2111	0.085000
H53A	0.6336	0.0575	0.0705	0.085000
H53B	0.7186	-0.0263	0.1253	0.085000
H53C	0.7550	0.0624	0.0816	0.085000
H54A	0.6650	0.1144	0.2561	0.085000
H54B	0.7806	0.0758	0.2088	0.085000
H54C	0.7160	0.0062	0.2578	0.085000
H55A	0.7323	0.2225	0.1516	0.085000
H55B	0.6518	0.2955	0.0893	0.085000

	x/a	y/b	z/c	U(eq)
H55C	0.7383	0.1982	0.0766	0.085000
H51D	0.6644	0.0380	0.0826	0.085000
H51E	0.7928	0.0153	0.1025	0.085000
H51F	0.7325	0.1092	0.0443	0.085000
H53D	0.6664	0.2468	0.1583	0.085000
H53E	0.6662	0.2423	0.0772	0.085000
H53F	0.7827	0.1935	0.1182	0.085000
H54D	0.7284	-0.0192	0.2083	0.085000
H54E	0.6917	0.0507	0.2591	0.085000
H54F	0.8106	0.0367	0.2108	0.085000
H55D	0.3969	0.1222	0.1895	0.085000
H55E	0.4964	0.0607	0.2437	0.085000
H55F	0.5022	0.0387	0.1677	0.085000



Crystal Structure Report for Compound 16

A yellow plate-like specimen of $C_{20}H_{31}BCl_2N_7O_3PSW$, approximate dimensions 0.079 mm x 0.144 mm x 0.223 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with a fine-focus sealed tube (Mo K_α, λ = 0.71073 Å) and a graphite monochromator.

The total exposure time was 3.56 hours. The frames were integrated with the Bruker SAINT software package[14] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 37280 reflections to a maximum θ angle of 28.33° (0.75 Å resolution), of which 6837 were independent (average redundancy 5.453, completeness = 99.8%, R_{int} = 3.83%, R_{sig} = 2.79%) and 6005 (87.83%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.4005(6) Å, b = 12.5289(9) Å, c = 26.2545(17) Å, β = 95.218(2)°, volume = 2751.8(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9938 reflections above 20 σ(I) with 4.503° < 2θ < 56.44°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[1] The ratio of minimum to maximum apparent transmission was 0.814. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4007 and 0.4920.

The structure was solved and refined using the Bruker SHELXTL Software Package[15] within APEX3 [1] and OLEX2,[16] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{20}H_{31}BCl_2N_7O_3PSW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 341 variables converged at R1 = 2.76%, for the observed data and wR2 = 5.84% for all data. The goodness-of-fit was 1.076. The largest peak in the final difference electron density synthesis was 2.123 $e^-/Å^3$ and the largest hole was -1.183 $e^-/Å^3$ with an RMS deviation of 0.113 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.801 g/cm^3 and F(000), 1472 e^-.

[14] Bruker (2012). *Saint; SADABS; APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
[15] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.
[16] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Table 1. Sample and crystal data for Compound 16.

Identification code	Harman_SS7_198_3_X1	
Chemical formula	$C_{20}H_{31}BCl_2N_7O_3PSW$	
Formula weight	746.11 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.079 x 0.144 x 0.223 mm	
Crystal habit	yellow plate	
Crystal system	monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 8.4005(6) Å	α = 90°
	b = 12.5289(9) Å	β = 95.218(2)°
	c = 26.2545(17) Å	γ = 90°
Volume	2751.8(3) $Å^3$	
Z	4	
Density (calculated)	1.801 g/cm^3	
Absorption coefficient	4.563 mm^{-1}	
F(000)	1472	

Table 2. Data collection and structure refinement for Compound 16.

Diffractometer	Bruker Kappa APEXII Duo

Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)	
Theta range for data collection	1.56 to 28.33°	
Index ranges	-11<=h<=11, -16<=k<=16, -33<=l<=34	
Reflections collected	37280	
Independent reflections	6837 [R(int) = 0.0383]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.4920 and 0.4007	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6837 / 0 / 341	
Goodness-of-fit on F^2	1.076	
Δ/σ_{max}	0.002	
Final R indices	6005 data; I>2σ(I)	R1 = 0.0276, wR2 = 0.0562
	all data	R1 = 0.0348, wR2 = 0.0584

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0182P)^2+6.9716P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.123 and -1.183 eÅ^{-3}
R.M.S. deviation from mean	0.113 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 16.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.34589(2)	0.69785(2)	0.39085(2)	0.01502(4)
Cl1	0.74593(18)	0.79483(10)	0.63040(5)	0.0577(4)
Cl2	0.82830(14)	0.97932(9)	0.69460(4)	0.0407(2)
S1	0.21809(11)	0.82372(7)	0.57469(3)	0.02406(19)
P1	0.12030(11)	0.56752(8)	0.39641(3)	0.02144(19)
O1	0.1446(3)	0.8797(2)	0.42275(10)	0.0282(6)
O2	0.1235(3)	0.7361(2)	0.59110(11)	0.0329(6)
O3	0.3196(3)	0.8789(2)	0.61359(10)	0.0304(6)
N1	0.4726(3)	0.5566(2)	0.36044(10)	0.0192(6)
N2	0.5127(3)	0.5551(2)	0.31113(11)	0.0208(6)
N3	0.2331(3)	0.7143(2)	0.31217(10)	0.0179(6)
N4	0.3049(3)	0.6807(2)	0.27036(10)	0.0198(6)

	x/a	y/b	z/c	U(eq)
N5	0.5279(3)	0.7847(2)	0.35055(11)	0.0197(6)
N6	0.5686(3)	0.7503(2)	0.30401(11)	0.0218(6)
N7	0.2318(3)	0.8071(2)	0.41044(10)	0.0194(6)
C1	0.5167(5)	0.4612(3)	0.38015(14)	0.0264(8)
C2	0.5837(5)	0.3988(3)	0.34427(16)	0.0343(9)
C3	0.5797(5)	0.4613(3)	0.30131(15)	0.0285(8)
C4	0.0902(4)	0.7535(3)	0.29437(14)	0.0221(7)
C5	0.0699(5)	0.7455(3)	0.24144(14)	0.0262(8)
C6	0.2078(4)	0.6996(3)	0.22764(13)	0.0245(7)
C7	0.6105(4)	0.8754(3)	0.36046(14)	0.0243(7)
C8	0.7040(4)	0.8986(3)	0.32093(15)	0.0290(8)
C9	0.6748(4)	0.8185(3)	0.28634(15)	0.0273(8)
C10	0.4106(4)	0.6368(3)	0.46998(13)	0.0232(7)
C11	0.5378(4)	0.7010(3)	0.45355(13)	0.0252(7)
C12	0.5936(4)	0.7960(3)	0.48671(14)	0.0290(8)
C13	0.4557(5)	0.8568(3)	0.50854(14)	0.0274(8)
C14	0.3370(4)	0.7796(3)	0.52755(13)	0.0217(7)
C15	0.3164(4)	0.6795(3)	0.50983(13)	0.0214(7)
C16	0.0887(5)	0.9189(4)	0.54439(16)	0.0386(10)
C17	0.9315(5)	0.6286(4)	0.40946(18)	0.0373(10)
C18	0.1390(5)	0.4590(3)	0.44305(15)	0.0319(9)
C19	0.0698(5)	0.4928(3)	0.33746(16)	0.0354(9)
C20	0.7011(5)	0.9279(3)	0.64311(16)	0.0338(9)

	x/a	y/b	z/c	U(eq)
B1	0.4847(5)	0.6540(3)	0.27679(15)	0.0227(8)

Table 4. Bond lengths (Å) for Compound 16.

W1-N7	1.774(3)	W1-C11	2.197(3)
W1-N3	2.203(3)	W1-N5	2.222(3)
W1-C10	2.234(4)	W1-N1	2.249(3)
W1-P1	2.5158(9)	Cl1-C20	1.748(4)
Cl2-C20	1.767(4)	S1-O2	1.444(3)
S1-O3	1.446(3)	S1-C14	1.749(4)
S1-C16	1.754(4)	P1-C17	1.822(4)
P1-C19	1.825(4)	P1-C18	1.827(4)
O1-N7	1.230(4)	N1-C1	1.341(4)
N1-N2	1.367(4)	N2-C3	1.339(5)
N2-B1	1.537(5)	N3-C4	1.341(4)
N3-N4	1.366(4)	N4-C6	1.346(4)
N4-B1	1.541(5)	N5-C7	1.345(5)
N5-N6	1.368(4)	N6-C9	1.349(5)
N6-B1	1.540(5)	C1-C2	1.383(5)
C1-H1	0.95	C2-C3	1.371(6)
C2-H2	0.95	C3-H3	0.95
C4-C5	1.388(5)	C4-H4	0.95
C5-C6	1.371(5)	C5-H5	0.95

C6-H6	0.95	C7-C8	1.388(5)
C7-H7	0.95	C8-C9	1.360(6)
C8-H8	0.95	C9-H9	0.95
C10-C11	1.435(5)	C10-C15	1.469(5)
C10-H10	0.85(5)	C11-C12	1.524(5)
C11-H11	0.97(4)	C12-C13	1.540(5)
C12-H12A	0.99	C12-H12B	0.99
C13-C14	1.506(5)	C13-H13A	0.99
C13-H13B	0.99	C14-C15	1.343(5)
C15-H15	0.95	C16-H16A	0.98
C16-H16B	0.98	C16-H16C	0.98
C17-H17A	0.98	C17-H17B	0.98
C17-H17C	0.98	C18-H18A	0.98
C18-H18B	0.98	C18-H18C	0.98
C19-H19A	0.98	C19-H19B	0.98
C19-H19C	0.98	C20-H20A	0.99
C20-H20B	0.99	B1-H1A	1.11(3)

Table 5. Bond angles (°) for Compound 16.

N7-W1-C11	98.50(14)	N7-W1-N3	90.12(11)
C11-W1-N3	157.62(12)	N7-W1-N5	100.01(12)
C11-W1-N5	81.84(12)	N3-W1-N5	76.33(10)
N7-W1-C10	94.99(13)	C11-W1-C10	37.77(14)

N3-W1-C10	162.11(13)	N5-W1-C10	119.38(12)
N7-W1-N1	174.82(12)	C11-W1-N1	86.64(12)
N3-W1-N1	85.28(10)	N5-W1-N1	81.24(10)
C10-W1-N1	88.71(12)	N7-W1-P1	93.11(10)
C11-W1-P1	118.26(11)	N3-W1-P1	81.55(8)
N5-W1-P1	154.19(8)	C10-W1-P1	81.07(10)
N1-W1-P1	83.87(8)	O2-S1-O3	117.28(17)
O2-S1-C14	109.63(17)	O3-S1-C14	108.24(17)
O2-S1-C16	108.5(2)	O3-S1-C16	107.2(2)
C14-S1-C16	105.30(18)	C17-P1-C19	103.7(2)
C17-P1-C18	102.1(2)	C19-P1-C18	100.72(19)
C17-P1-W1	114.29(15)	C19-P1-W1	113.68(14)
C18-P1-W1	120.16(14)	C1-N1-N2	105.7(3)
C1-N1-W1	133.4(2)	N2-N1-W1	120.8(2)
C3-N2-N1	109.8(3)	C3-N2-B1	129.7(3)
N1-N2-B1	120.5(3)	C4-N3-N4	106.2(3)
C4-N3-W1	131.0(2)	N4-N3-W1	122.7(2)
C6-N4-N3	109.7(3)	C6-N4-B1	130.0(3)
N3-N4-B1	118.6(3)	C7-N5-N6	105.8(3)
C7-N5-W1	133.4(2)	N6-N5-W1	120.6(2)
C9-N6-N5	109.5(3)	C9-N6-B1	128.8(3)
N5-N6-B1	121.4(3)	O1-N7-W1	176.1(3)
N1-C1-C2	110.9(3)	N1-C1-H1	124.6
C2-C1-H1	124.6	C3-C2-C1	104.8(3)

C3-C2-H2	127.6	C1-C2-H2	127.6
N2-C3-C2	108.8(3)	N2-C3-H3	125.6
C2-C3-H3	125.6	N3-C4-C5	110.3(3)
N3-C4-H4	124.8	C5-C4-H4	124.8
C6-C5-C4	105.4(3)	C6-C5-H5	127.3
C4-C5-H5	127.3	N4-C6-C5	108.4(3)
N4-C6-H6	125.8	C5-C6-H6	125.8
N5-C7-C8	110.4(3)	N5-C7-H7	124.8
C8-C7-H7	124.8	C9-C8-C7	105.4(3)
C9-C8-H8	127.3	C7-C8-H8	127.3
N6-C9-C8	108.8(3)	N6-C9-H9	125.6
C8-C9-H9	125.6	C11-C10-C15	118.3(3)
C11-C10-W1	69.7(2)	C15-C10-W1	115.8(2)
C11-C10-H10	119.(3)	C15-C10-H10	112.(3)
W1-C10-H10	115.(3)	C10-C11-C12	117.7(3)
C10-C11-W1	72.5(2)	C12-C11-W1	127.5(3)
C10-C11-H11	113.(3)	C12-C11-H11	113.(3)
W1-C11-H11	107.(3)	C11-C12-C13	113.4(3)
C11-C12-H12A	108.9	C13-C12-H12A	108.9
C11-C12-H12B	108.9	C13-C12-H12B	108.9
H12A-C12-H12B	107.7	C14-C13-C12	110.4(3)

C14-C13-H13A	109.6	C12-C13-H13A	109.6
C14-C13-H13B	109.6	C12-C13-H13B	109.6
H13A-C13-H13B	108.1	C15-C14-C13	123.6(3)
C15-C14-S1	118.4(3)	C13-C14-S1	118.0(3)
C14-C15-C10	121.8(3)	C14-C15-H15	119.1
C10-C15-H15	119.1	S1-C16-H16A	109.5
S1-C16-H16B	109.5	H16A-C16-H16B	109.5
S1-C16-H16C	109.5	H16A-C16-H16C	109.5
H16B-C16-H16C	109.5	P1-C17-H17A	109.5
P1-C17-H17B	109.5	H17A-C17-H17B	109.5
P1-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	P1-C18-H18A	109.5
P1-C18-H18B	109.5	H18A-C18-H18B	109.5
P1-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	P1-C19-H19A	109.5
P1-C19-H19B	109.5	H19A-C19-H19B	109.5

P1-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5	Cl1-C20-Cl2	111.6(2)
Cl1-C20-H20A	109.3	Cl2-C20-H20A	109.3
Cl1-C20-H20B	109.3	Cl2-C20-H20B	109.3
H20A-C20-H20B	108.0	N2-B1-N6	108.7(3)
N2-B1-N4	109.6(3)	N6-B1-N4	106.4(3)
N2-B1-H1A	110.3(19)	N6-B1-H1A	113.1(19)
N4-B1-H1A	108.8(19)		

Table 6. Torsion angles (°) for Compound 16.

C1-N1-N2-C3	-0.1(4)	W1-N1-N2-C3	-177.1(2)
C1-N1-N2-B1	-177.9(3)	W1-N1-N2-B1	5.2(4)
C4-N3-N4-C6	0.3(4)	W1-N3-N4-C6	179.2(2)
C4-N3-N4-B1	167.0(3)	W1-N3-N4-B1	-14.2(4)
C7-N5-N6-C9	0.5(4)	W1-N5-N6-C9	177.0(2)
C7-N5-N6-B1	-173.6(3)	W1-N5-N6-B1	2.9(4)
N2-N1-C1-C2	-0.2(4)	W1-N1-C1-C2	176.2(3)
N1-C1-C2-C3	0.4(5)	N1-N2-C3-C2	0.4(4)
B1-N2-C3-C2	177.9(4)	C1-C2-C3-N2	-0.5(5)

N4-N3-C4-C5	-0.1(4)	W1-N3-C4-C5	-178.9(2)
N3-C4-C5-C6	-0.1(4)	N3-N4-C6-C5	-0.4(4)
B1-N4-C6-C5	-165.0(3)	C4-C5-C6-N4	0.3(4)
N6-N5-C7-C8	-0.4(4)	W1-N5-C7-C8	-176.3(3)
N5-C7-C8-C9	0.2(4)	N5-N6-C9-C8	-0.4(4)
B1-N6-C9-C8	173.2(3)	C7-C8-C9-N6	0.1(4)
C15-C10-C11-C12	14.6(5)	W1-C10-C11-C12	123.7(3)
C15-C10-C11-W1	-109.2(3)	C10-C11-C12-C13	-39.7(5)
W1-C11-C12-C13	48.9(4)	C11-C12-C13-C14	43.0(4)
C12-C13-C14-C15	-25.3(5)	C12-C13-C14-S1	155.5(3)
O2-S1-C14-C15	6.0(3)	O3-S1-C14-C15	135.1(3)
C16-S1-C14-C15	-110.5(3)	O2-S1-C14-C13	-174.7(3)
O3-S1-C14-C13	-45.7(3)	C16-S1-C14-C13	68.7(3)
C13-C14-C15-C10	0.3(5)	S1-C14-C15-C10	179.5(3)
C11-C10-C15-C14	6.1(5)	W1-C10-C15-C14	-73.7(4)
C3-N2-B1-N6	-122.4(4)	N1-N2-B1-N6	54.8(4)

C3-N2-B1-N4	121.7(4)	N1-N2-B1-N4	-61.1(4)
C9-N6-B1-N2	126.7(4)	N5-N6-B1-N2	-60.4(4)
C9-N6-B1-N4	-115.3(4)	N5-N6-B1-N4	57.5(4)
C6-N4-B1-N2	-129.9(4)	N3-N4-B1-N2	66.6(4)
C6-N4-B1-N6	112.7(4)	N3-N4-B1-N6	-50.7(4)

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for Compound 16.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01482(6)	0.01780(7)	0.01235(6)	-0.00013(5)	0.00071(4)	0.00220(5)
Cl1	0.0766(9)	0.0460(7)	0.0452(7)	-0.0168(6)	-0.0237(6)	0.0237(7)
Cl2	0.0425(6)	0.0364(6)	0.0426(6)	-0.0044(5)	0.0011(5)	-0.0078(5)
S1	0.0274(4)	0.0269(5)	0.0179(4)	-0.0018(3)	0.0021(3)	0.0008(4)
P1	0.0194(4)	0.0236(5)	0.0220(4)	-0.0010(4)	0.0055(3)	-0.0039(4)
O1	0.0326(15)	0.0271(14)	0.0256(13)	-0.0012(11)	0.0061(11)	0.0098(11)
O2	0.0327(15)	0.0378(16)	0.0295(14)	-0.0007(12)	0.0100(12)	-0.0053(12)
O3	0.0344(15)	0.0358(16)	0.0210(13)	-0.0045(11)	0.0021(11)	-0.0036(12)
N1	0.0198(14)	0.0219(15)	0.0161(13)	0.0016(11)	0.0026(11)	0.0044(11)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	0.0212(14)	0.0243(15)	0.0178(14)	-0.0027(12)	0.0059(11)	0.0015(12)
N3	0.0197(14)	0.0198(15)	0.0139(13)	0.0002(11)	0.0006(10)	0.0003(11)
N4	0.0240(14)	0.0219(15)	0.0136(13)	0.0010(11)	0.0025(11)	0.0006(12)
N5	0.0177(13)	0.0196(15)	0.0218(14)	-0.0020(11)	0.0008(11)	0.0021(11)
N6	0.0198(14)	0.0246(16)	0.0216(15)	-0.0004(12)	0.0055(12)	0.0009(12)
N7	0.0190(13)	0.0232(15)	0.0158(13)	0.0011(12)	0.0010(10)	0.0022(12)
C1	0.032(2)	0.0253(19)	0.0223(18)	0.0038(15)	0.0023(15)	0.0098(16)
C2	0.041(2)	0.030(2)	0.033(2)	0.0000(17)	0.0062(18)	0.0179(18)
C3	0.032(2)	0.027(2)	0.027(2)	-0.0045(16)	0.0068(16)	0.0070(16)
C4	0.0204(17)	0.0219(18)	0.0237(18)	-0.0024(14)	0.0008(14)	0.0028(14)
C5	0.0282(19)	0.028(2)	0.0206(18)	0.0047(15)	-0.0063(14)	0.0017(16)
C6	0.0311(19)	0.0276(18)	0.0139(15)	0.0032(15)	-0.0022(13)	-0.0058(16)
C7	0.0222(17)	0.0214(18)	0.0291(19)	-0.0021(15)	0.0010(14)	-0.0004(14)
C8	0.0218(18)	0.027(2)	0.038(2)	0.0027(17)	0.0048(16)	-0.0038(15)
C9	0.0201(17)	0.031(2)	0.032(2)	0.0062(16)	0.0077(15)	0.0003(15)
C10	0.0272(19)	0.0234(19)	0.0186(17)	-0.0020(14)	0.0010(14)	0.0050(15)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	0.0203(16)	0.036(2)	0.0189(16)	0.0016(16)	-0.0020(13)	0.0064(16)
C12	0.0219(17)	0.043(2)	0.0218(18)	-0.0008(17)	-0.0015(14)	-0.0084(17)
C13	0.033(2)	0.029(2)	0.0198(18)	-0.0017(15)	-0.0011(15)	-0.0075(16)
C14	0.0245(17)	0.0270(19)	0.0131(15)	0.0016(13)	-0.0005(13)	0.0014(14)
C15	0.0242(17)	0.0231(18)	0.0165(16)	0.0045(13)	0.0000(13)	-0.0005(14)
C16	0.039(2)	0.045(3)	0.031(2)	-0.0004(19)	0.0044(18)	0.016(2)
C17	0.0210(19)	0.040(2)	0.053(3)	0.002(2)	0.0148(18)	-0.0004(17)
C18	0.043(2)	0.0235(19)	0.031(2)	-0.0005(16)	0.0111(18)	-0.0106(17)
C19	0.041(2)	0.034(2)	0.031(2)	-0.0078(18)	0.0029(18)	-0.0131(19)
C20	0.033(2)	0.035(2)	0.033(2)	0.0075(18)	0.0001(17)	0.0018(17)
B1	0.025(2)	0.025(2)	0.0188(19)	-0.0004(16)	0.0059(16)	0.0019(16)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 16.

	x/a	y/b	z/c	U(eq)
H1	0.5037	0.4394	0.4142	0.032

	x/a	y/b	z/c	U(eq)
H2	0.6238	0.3281	0.3485	0.041
H3	0.6181	0.4413	0.2697	0.034
H4	0.0138	0.7825	0.3150	0.026
H5	-0.0203	0.7672	0.2195	0.031
H6	0.2309	0.6838	0.1937	0.029
H7	0.6056	0.9176	0.3903	0.029
H8	0.7735	0.9578	0.3185	0.035
H9	0.7217	0.8118	0.2549	0.033
H10	0.423(5)	0.569(4)	0.4722(16)	0.034(12)
H11	0.625(5)	0.659(3)	0.4424(16)	0.034(12)
H12A	0.6528	0.8459	0.4661	0.035
H12B	0.6685	0.7705	0.5154	0.035
H13A	0.4989	0.9032	0.5370	0.033
H13B	0.4015	0.9028	0.4816	0.033
H15	0.2389	0.6352	0.5234	0.026
H16A	0.0150	0.8836	0.5186	0.058
H16B	0.1512	0.9726	0.5278	0.058
H16C	0.0276	0.9535	0.5698	0.058
H17A	-0.1531	0.5746	0.4066	0.056
H17B	-0.0953	0.6857	0.3846	0.056
H17C	-0.0586	0.6585	0.4441	0.056
H18A	0.1454	0.4887	0.4777	0.048
H18B	0.2361	0.4180	0.4387	0.048

	x/a	y/b	z/c	U(eq)
H18C	0.0456	0.4121	0.4378	0.048
H19A	0.1637	0.4528	0.3286	0.053
H19B	0.0362	0.5425	0.3097	0.053
H19C	-0.0175	0.4431	0.3424	0.053
H20A	0.5887	0.9331	0.6514	0.041
H20B	0.7123	0.9714	0.6122	0.041
H1A	0.526(4)	0.638(3)	0.2385(13)	0.016(9)

Crystal Structure Report for Compound 3.17

Single crystals of $C_{27}H_{35}BN_7O_5PSW$ **[mo_Harman_PS_3_89_0m]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker D8 Venture** diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

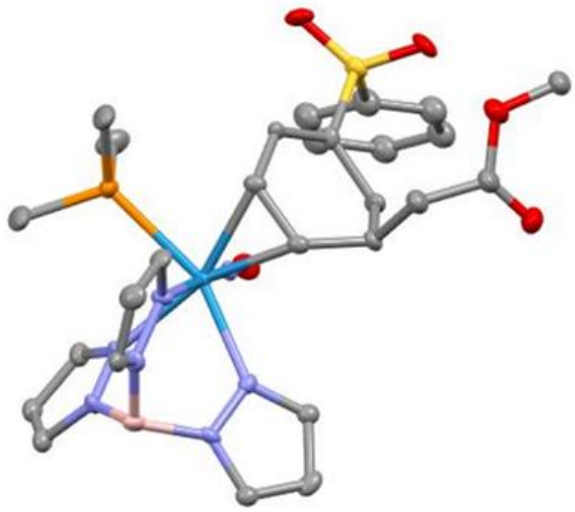


Table 1 Crystal data and structure refinement for 3.17.

Identification code	mo_Harman_PS_3_89_0m

Empirical formula	$C_{27}H_{35}BN_7O_5PSW$
Formula weight	795.31
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.7699(7)
b/Å	15.4292(7)
c/Å	15.4711(7)
α/°	90
β/°	90.283(2)
γ/°	90
Volume/Å^3	3048.2(3)
Z	4
ρ_{calc}g/cm^3	1.733
μ/mm^{-1}	3.960
F(000)	1584.0
Crystal size/mm^3	0.05 × 0.035 × 0.023
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.14 to 51.472
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	41294
Independent reflections	5807 [R_{int} = 0.1653, R_{sigma} = 0.1007]
Data/restraints/parameters	5807/0/317
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.0778
Final R indexes [all data]	R_1 = 0.0880, wR_2 = 0.0920
Largest diff. peak/hole / e Å^{-3}	1.39/-1.02

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_Harman_PS_3_89_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	5732.3(2)	2194.1(2)	3306.6(2)	14.24(9)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_Harman_PS_3_89_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	9892.2(16)	2384.1(12)	3851.0(12)	21.1(5)
P1	6331.5(17)	911.8(12)	2451.6(13)	21.6(5)
O1	6833(4)	1563(3)	4900(3)	24.8(13)
O2	10163(4)	1669(3)	3288(3)	26.7(13)
O3	10538(4)	3150(3)	3847(3)	27.5(13)
O4	9594(4)	4979(3)	3276(4)	31.7(14)
O5	8556(5)	5476(4)	4334(4)	40.6(17)
N00D	6402(5)	1836(3)	4238(4)	15.4(14)
N1	4630(5)	3078(3)	3964(4)	16.9(14)
N2	3582(5)	3077(3)	3770(4)	16.1(14)
N3	4395(5)	1334(3)	3605(4)	16.3(10)
N4	3386(5)	1544(4)	3397(4)	16.3(10)
N5	4767(5)	2612(3)	2156(4)	16.1(14)
N6	3702(5)	2636(4)	2222(4)	17.9(14)
C1	4735(6)	3623(4)	4635(5)	18.0(12)
C2	3793(6)	3966(4)	4876(5)	22.2(19)
C3	3073(6)	3606(4)	4320(5)	18.0(12)
C4	4356(7)	578(4)	4018(5)	21.8(11)
C5	3327(6)	293(5)	4080(5)	21.8(11)
C6	2735(7)	924(4)	3686(5)	21.8(11)
C7	4988(6)	2892(5)	1362(4)	19.8(17)
C8	4090(7)	3098(5)	919(5)	25.5(19)
C9	3298(6)	2942(4)	1489(5)	20.9(18)
C10	6609(6)	3378(4)	3119(4)	17.4(12)
C11	7120(6)	2725(4)	2624(4)	17.4(12)
C12	8149(6)	2440(4)	2896(5)	14.6(17)
C15	7278(6)	3900(4)	3752(5)	19.1(17)
C16	8076(6)	3320(5)	4236(5)	20.8(18)
C17	8605(6)	2702(4)	3624(4)	17.1(16)
C18	7826(7)	4612(5)	3204(5)	28.7(12)
C19	8674(7)	5081(5)	3678(6)	28.7(12)
C20	10489(6)	5335(5)	3691(5)	28.7(12)
C21	9893(7)	1996(5)	4924(5)	31.7(9)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo_Harman_PS_3_89_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C22	9487(7)	1191(5)	5101(5)	31.7(9)
C23	9542(7)	877(5)	5936(5)	31.7(9)
C24	9998(7)	1377(5)	6587(5)	31.7(9)
C25	10402(6)	2173(6)	6400(5)	31.7(9)
C26	10348(7)	2490(5)	5565(5)	31.7(9)
C27	6924(7)	1101(5)	1400(5)	36.6(17)
C28	7290(7)	247(5)	3007(6)	36(2)
C29	5343(7)	136(5)	2159(5)	36.6(17)
B1	3138(8)	2463(5)	3081(6)	19(2)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for mo_Harman_PS_3_89_0m. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	13.08(17)	14.53(14)	15.12(15)	-0.45(15)	1.02(11)	0.20(16)
S1	14.7(11)	25.5(11)	23.0(10)	-0.1(8)	-1.6(8)	-1.0(8)
P1	19.1(13)	18.8(10)	26.8(12)	-7.3(9)	5.2(9)	-2.1(9)
O1	22(3)	27(3)	25(3)	8(2)	-4(3)	2(2)
O2	16(3)	37(3)	26(3)	-8(3)	2(2)	10(3)
O3	13(3)	34(3)	36(3)	0(3)	1(3)	-10(2)
O4	21(4)	30(3)	44(4)	-4(3)	5(3)	-7(3)
O5	33(4)	36(3)	52(4)	-24(3)	10(3)	-10(3)
N00D	14(4)	14(3)	18(3)	-2(3)	0(3)	-3(3)
N1	20(4)	14(3)	16(3)	-1(2)	3(3)	-1(3)
N2	9(4)	18(3)	21(3)	5(3)	1(3)	0(3)
N3	11(3)	15(2)	23(2)	-2.9(19)	-1(2)	-3(2)
N4	11(3)	15(2)	23(2)	-2.9(19)	-1(2)	-3(2)
N5	12(4)	21(3)	15(3)	1(3)	2(3)	2(3)
N6	15(4)	20(3)	19(3)	2(3)	-4(3)	1(3)
C1	18(3)	18(3)	18(3)	2(2)	2(2)	1(2)
C2	35(6)	18(4)	14(4)	0(3)	3(4)	3(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for mo_Harman_PS_3_89_0m. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	18(3)	18(3)	18(3)	2(2)	2(2)	1(2)
C4	26(3)	17(2)	22(3)	-1.5(19)	4(2)	-5(2)
C5	26(3)	17(2)	22(3)	-1.5(19)	4(2)	-5(2)
C6	26(3)	17(2)	22(3)	-1.5(19)	4(2)	-5(2)
C7	26(5)	21(4)	13(4)	-3(3)	5(3)	-1(4)
C8	28(5)	31(4)	17(4)	0(3)	-3(4)	4(4)
C9	21(5)	13(4)	28(4)	-4(3)	5(4)	-3(3)
C10	14(3)	20(3)	17(3)	2(2)	1(2)	2(2)
C11	14(3)	20(3)	17(3)	2(2)	1(2)	2(2)
C12	12(4)	12(3)	20(4)	-2(3)	0(3)	0(3)
C15	13(5)	17(4)	27(5)	-2(3)	2(3)	-4(3)
C16	13(5)	26(4)	23(4)	-7(3)	-3(3)	1(3)
C17	18(4)	15(4)	18(4)	2(3)	-4(3)	-2(3)
C18	23(3)	26(2)	38(3)	-7(2)	6(2)	-7(2)
C19	23(3)	26(2)	38(3)	-7(2)	6(2)	-7(2)
C20	23(3)	26(2)	38(3)	-7(2)	6(2)	-7(2)
C21	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C22	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C23	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C24	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C25	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C26	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C27	35(4)	41(4)	34(4)	-23(3)	11(3)	-11(3)
C28	45(7)	25(4)	38(6)	5(4)	12(5)	12(4)
C29	35(4)	41(4)	34(4)	-23(3)	11(3)	-11(3)
B1	15(5)	16(4)	27(5)	1(4)	7(4)	3(4)

Table 4 Bond Lengths for mo_Harman_PS_3_89_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	P1	2.5019(19)	N4	B1	1.533(10)
W1	N00D	1.761(6)	N5	N6	1.365(8)

Table 4 Bond Lengths for mo_Harman_PS_3_89_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	N1	2.211(6)	N5	C7	1.334(8)
W1	N3	2.213(6)	N6	C9	1.330(9)
W1	N5	2.254(6)	N6	B1	1.538(10)
W1	C10	2.163(7)	C1	C2	1.367(10)
W1	C11	2.223(7)	C2	C3	1.374(10)
S1	O2	1.448(5)	C4	C5	1.390(11)
S1	O3	1.441(5)	C5	C6	1.373(10)
S1	C17	1.750(8)	C7	C8	1.371(10)
S1	C21	1.764(8)	C8	C9	1.367(10)
P1	C27	1.822(8)	C10	C11	1.425(9)
P1	C28	1.810(8)	C10	C15	1.526(10)
P1	C29	1.796(8)	C11	C12	1.447(10)
O1	N00D	1.234(7)	C12	C17	1.328(9)
O4	C19	1.341(9)	C15	C16	1.547(10)
O4	C20	1.418(9)	C15	C18	1.557(10)
O5	C19	1.194(9)	C16	C17	1.506(10)
N1	N2	1.370(8)	C18	C19	1.492(11)
N1	C1	1.343(9)	C21	C22	1.374(11)
N2	C3	1.349(9)	C21	C26	1.377(11)
N2	B1	1.533(11)	C22	C23	1.381(11)
N3	N4	1.365(8)	C23	C24	1.393(11)
N3	C4	1.331(8)	C24	C25	1.364(11)
N4	C6	1.345(9)	C25	C26	1.382(11)

Table 5 Bond Angles for mo_Harman_PS_3_89_0m.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N00D	W1	P1	92.05(18)	C6	N4	B1	129.5(7)
N00D	W1	N1	97.2(2)	N6	N5	W1	119.3(4)
N00D	W1	N3	90.7(2)	C7	N5	W1	134.7(5)
N00D	W1	N5	175.8(2)	C7	N5	N6	106.0(6)
N00D	W1	C10	97.2(3)	N5	N6	B1	122.1(6)
N00D	W1	C11	96.9(3)	C9	N6	N5	109.1(6)
N1	W1	P1	158.12(17)	C9	N6	B1	128.1(7)

Table 5 Bond Angles for mo_Harman_PS_3_89_0m.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	W1	N3	77.3(2)	N1	C1	C2	111.6(7)
N1	W1	N5	80.8(2)	C1	C2	C3	105.1(7)
N1	W1	C11	120.1(2)	N2	C3	C2	108.4(7)
N3	W1	P1	82.79(15)	N3	C4	C5	110.3(7)
N3	W1	N5	85.2(2)	C6	C5	C4	105.3(7)
N3	W1	C11	159.6(2)	N4	C6	C5	108.1(7)
N5	W1	P1	88.64(15)	N5	C7	C8	110.8(7)
C10	W1	P1	115.92(19)	C9	C8	C7	104.8(7)
C10	W1	N1	82.6(2)	N6	C9	C8	109.2(7)
C10	W1	N3	159.2(2)	C11	C10	W1	73.3(4)
C10	W1	N5	86.2(2)	C11	C10	C15	117.5(6)
C10	W1	C11	37.9(2)	C15	C10	W1	130.4(5)
C11	W1	P1	78.11(18)	C10	C11	W1	68.8(4)
C11	W1	N5	87.3(2)	C10	C11	C12	118.5(6)
O2	S1	C17	108.6(3)	C12	C11	W1	118.4(5)
O2	S1	C21	108.0(3)	C17	C12	C11	123.2(7)
O3	S1	O2	118.9(3)	C10	C15	C16	111.8(6)
O3	S1	C17	107.8(3)	C10	C15	C18	105.9(6)
O3	S1	C21	106.5(4)	C16	C15	C18	112.0(6)
C17	S1	C21	106.3(4)	C17	C16	C15	111.0(6)
C27	P1	W1	118.4(3)	C12	C17	S1	119.4(6)
C28	P1	W1	113.9(3)	C12	C17	C16	122.0(7)
C28	P1	C27	103.4(4)	C16	C17	S1	118.4(5)
C29	P1	W1	116.3(3)	C19	C18	C15	113.7(7)
C29	P1	C27	100.1(4)	O4	C19	C18	110.5(7)
C29	P1	C28	102.4(4)	O5	C19	O4	124.6(8)
C19	O4	C20	116.8(6)	O5	C19	C18	124.9(8)
O1	N00D	W1	177.2(5)	C22	C21	S1	119.7(6)
N2	N1	W1	121.4(4)	C22	C21	C26	120.9(8)
C1	N1	W1	132.9(5)	C26	C21	S1	119.3(6)
C1	N1	N2	105.3(6)	C21	C22	C23	119.1(8)
N1	N2	B1	120.7(6)	C22	C23	C24	120.1(8)
C3	N2	N1	109.6(6)	C25	C24	C23	120.1(8)
C3	N2	B1	129.4(7)	C24	C25	C26	120.0(8)
N4	N3	W1	122.5(4)	C21	C26	C25	119.7(8)

Table 5 Bond Angles for mo_Harman_PS_3_89_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N3	W1	131.0(5)	N2	B1	N6	108.7(6)
C4	N3	N4	106.5(6)	N4	B1	N2	105.9(7)
N3	N4	B1	119.2(6)	N4	B1	N6	109.9(6)
C6	N4	N3	109.7(6)				

Table 6 Torsion Angles for mo_Harman_PS_3_89_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
W1	N1	N2	C3	173.7(4)	C3	N2	B1	N6	129.5(7)
W1	N1	N2	B1	-0.5(8)	C4	N3	N4	C6	0.4(8)
W1	N1	C1	C2	-173.0(5)	C4	N3	N4	B1	167.6(6)
W1	N3	N4	C6	-177.4(4)	C4	C5	C6	N4	0.8(8)
W1	N3	N4	B1	-10.2(8)	C6	N4	B1	N2	110.6(8)
W1	N3	C4	C5	177.6(5)	C6	N4	B1	N6	-132.2(8)
W1	N5	N6	C9	176.8(4)	C7	N5	N6	C9	-1.3(7)
W1	N5	N6	B1	5.4(8)	C7	N5	N6	B1	-172.7(6)
W1	N5	C7	C8	-177.4(5)	C7	C8	C9	N6	-1.6(8)
W1	C10	C11	C12	-111.7(6)	C9	N6	B1	N2	-115.2(8)
W1	C10	C15	C16	50.1(9)	C9	N6	B1	N4	129.3(7)
W1	C10	C15	C18	172.4(5)	C10	C11	C12	C17	6.0(10)
W1	C11	C12	C17	-73.9(8)	C10	C15	C16	C17	44.4(8)
S1	C21	C22	C23	176.7(6)	C10	C15	C18	C19	-168.7(7)
S1	C21	C26	C25	-176.6(6)	C11	C10	C15	C16	-40.9(9)
O2	S1	C17	C12	-15.7(7)	C11	C10	C15	C18	81.3(8)
O2	S1	C17	C16	168.7(5)	C11	C12	C17	S1	-175.0(5)
O2	S1	C21	C22	-40.3(8)	C11	C12	C17	C16	0.4(11)
O2	S1	C21	C26	136.6(7)	C15	C10	C11	W1	127.4(6)
O3	S1	C17	C12	114.4(6)	C15	C10	C11	C12	15.7(9)
O3	S1	C17	C16	-61.2(6)	C15	C16	C17	S1	149.2(5)
O3	S1	C21	C22	-169.1(7)	C15	C16	C17	C12	-26.3(9)
O3	S1	C21	C26	7.8(8)	C15	C18	C19	O4	119.8(7)
N1	N2	C3	C2	0.6(7)	C15	C18	C19	O5	-58.7(11)
N1	N2	B1	N4	60.4(8)	C16	C15	C18	C19	-46.6(9)
N1	N2	B1	N6	-57.6(8)	C17	S1	C21	C22	76.1(8)

Table 6 Torsion Angles for mo_Harman_PS_3_89_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	0.2(8)	C17	S1	C21	C26	-107.0(7)
N2	N1	C1	C2	0.2(7)	C18	C15	C16	C17	-74.3(8)
N3	N4	C6	C5	-0.7(8)	C20	O4	C19	O5	3.2(12)
N3	N4	B1	N2	-53.7(8)	C20	O4	C19	C18	-175.3(6)
N3	N4	B1	N6	63.5(9)	C21	S1	C17	C12	-131.6(6)
N3	C4	C5	C6	-0.5(8)	C21	S1	C17	C16	52.7(6)
N4	N3	C4	C5	0.1(8)	C21	C22	C23	C24	0.4(13)
N5	N6	C9	C8	1.9(8)	C22	C21	C26	C25	0.2(13)
N5	N6	B1	N2	54.4(8)	C22	C23	C24	C25	-0.7(13)
N5	N6	B1	N4	-61.0(9)	C23	C24	C25	C26	0.8(13)
N5	C7	C8	C9	0.8(8)	C24	C25	C26	C21	-0.6(13)
N6	N5	C7	C8	0.3(8)	C26	C21	C22	C23	-0.2(13)
C1	N1	N2	C3	-0.5(7)	B1	N2	C3	C2	174.1(7)
C1	N1	N2	B1	-174.6(6)	B1	N4	C6	C5	-166.2(7)
C1	C2	C3	N2	-0.5(8)	B1	N6	C9	C8	172.6(7)
C3	N2	B1	N4	-112.5(8)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_Harman_PS_3_89_0m.

Atom	*x*	*y*	*z*	U(eq)
H1	5383.48	3754.9	4909.05	22
H2	3664.76	4367.08	5329.52	27
H3	2339.95	3712.36	4321.8	22
H4	4947.86	276.46	4239.82	26
H5	3084.44	-227.28	4338.71	26
H6	1993.91	922.97	3627.33	26
H7	5674.74	2941.71	1133.76	24
H8	4030.55	3304.77	342.05	31
H9	2574.46	3035.78	1379.63	25
H10	6213.59	3778.18	2727.71	21
H11	7029.36	2784.85	1984.83	21
H12	8517.32	2046.23	2536.35	17
H15	6809.67	4184.56	4183.67	23

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_Harman_PS_3_89_0m.

Atom	*x*	*y*	*z*	U(eq)
H16A	8611.2	3689.34	4519.62	25
H16B	7711.56	2987.26	4691.73	25
H18A	8127.92	4339.94	2681.64	34
H18B	7294.14	5037.59	3010.13	34
H20A	11120.96	5152.23	3383.51	43
H20B	10522.04	5129.11	4289.41	43
H20C	10442.02	5968.77	3685.41	43
H22	9172.9	855.54	4655.82	38
H23	9268.4	320.24	6066.93	38
H24	10027.73	1162.53	7162.68	38
H25	10721.09	2509.27	6842.6	38
H26	10623.67	3046.46	5434.65	38
H27A	6440.87	1436.17	1036.76	55
H27B	7072.53	544.17	1121.9	55
H27C	7578.43	1425.3	1475.31	55
H28A	7923.17	589.17	3117.29	54
H28B	7464.53	-254.47	2647.65	54
H28C	6999.55	47.83	3557.78	54
H29A	5042.84	-116.63	2683.05	55
H29B	5656.22	-323.27	1807.37	55
H29C	4789.53	425.61	1825.37	55
H1A	2320(60)	2570(40)	3030(50)	29

Experimental

Single crystals of $C_{27}H_{35}BN_7O_5PSW$ **[mo_Harman_PS_3_89_0m]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker D8 Venture** diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [mo_Harman_PS_3_89_0m]

Crystal Data for $C_{27}H_{35}BN_7O_5PSW$ (*M* =795.31 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.7699(7) Å, *b* = 15.4292(7) Å, *c* = 15.4711(7) Å, *β* = 90.283(2)°, *V* = 3048.2(3) $Å^3$, *Z* = 4, *T* = 100.00 K, μ(Mo Kα) = 3.960 mm^{-1}, *Dcalc* = 1.733 g/cm^3, 41294 reflections measured (4.14° ≤ 2Θ ≤ 51.472°), 5807 unique (R_{int} = 0.1653, R_{sigma} = 0.1007) which were used in all calculations. The final R_1 was 0.0444 (I > 2σ(I)) and wR_2 was 0.0920 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All B(H) groups, All C(H,H,H) groups
2. Uiso/Uaniso restraints and constraints
Uanis(C21) = Uanis(C22) = Uanis(C23) = Uanis(C24) = Uanis(C25) = Uanis(C26)
Uanis(C6) = Uanis(C5) = Uanis(C4)
Uanis(C11) = Uanis(C10)
Uanis(N4) = Uanis(N3)
Uanis(C19) = Uanis(C18)
Uanis(C19) = Uanis(C20)
Uanis(C1) = Uanis(C3)
Uanis(C29) = Uanis(C27)
3.a Ternary CH refined with riding coordinates:
C10(H10), C11(H11), C15(H15)
3.b Secondary CH2 refined with riding coordinates:
C16(H16A,H16B), C18(H18A,H18B)
3.c Aromatic/amide H refined with riding coordinates:
C1(H1), C2(H2), C3(H3), C4(H4), C5(H5), C6(H6), C7(H7), C8(H8), C9(H9), C12(H12), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26)
3.d Idealised Me refined as rotating group:
C20(H20A,H20B,H20C), C27(H27A,H27B,H27C), C28(H28A,H28B,H28C), C29(H29A,H29B, H29C)

Crystal Structure Report for Compound 21

A yellow blocks-like specimen of $C_{29}H_{37}BN_7O_7PSW$, approximate dimensions 0.075 mm x 0.081 mm x 0.244 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with a fine-focus sealed tube (Mo K_α, λ = 0.71073 Å) and a graphite monochromator.

The total exposure time was 3.08 hours. The frames were integrated with the Bruker SAINT software package[17] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 53711 reflections to a maximum θ angle of 28.34° (0.75 Å resolution), of which 8375 were independent (average redundancy 6.413, completeness = 99.8%, R_{int} = 7.89%, R_{sig} = 5.82%) and 6486 (77.44%) were greater than 2σ(F^2). The final cell constants of a = 12.5334(8) Å, b = 22.9625(17) Å, c = 12.6358(9) Å, β = 112.263(2)°, volume = 3365.5(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 8009 reflections above 20 σ(I) with 4.972° < 2θ < 49.28°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[1] The ratio of minimum to maximum apparent transmission was 0.805. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4740 and 0.7740.

The structure was solved and refined using the Bruker SHELXTL Software Package[18] within APEX3 [1] and OLEX2,[19] using the space group P $2_1/n$, with Z = 4 for the formula unit, $C_{29}H_{37}BN_7O_7PSW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 440 variables converged at R1 = 4.31%, for the observed data and wR2 = 7.60% for all data. The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was 1.008 $e^-/Å^3$ and the largest hole was -1.311 $e^-/Å^3$ with an RMS deviation of 0.153 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.684 g/cm^3 and F(000), 1704 e^-.

[17] Bruker (2012). *Saint; SADABS; APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
[18] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.
[19] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

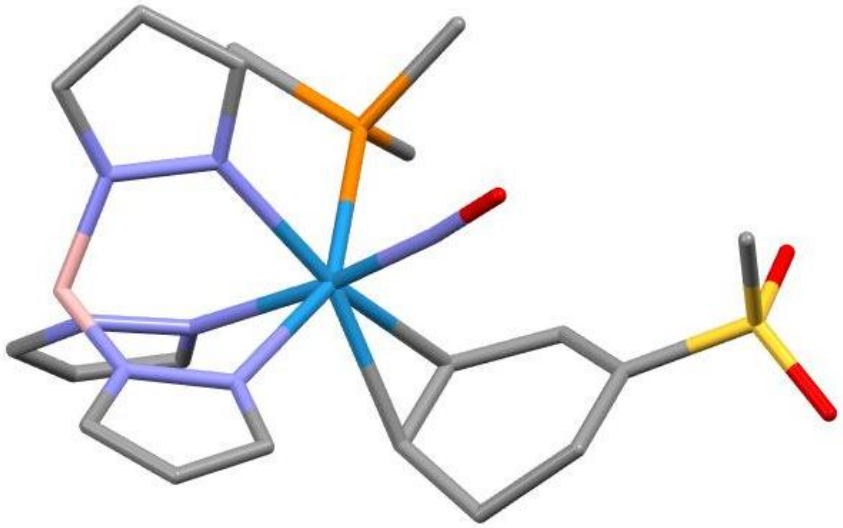


Table 1. Sample and crystal data for Compound 21.

Identification code	Harman_PS_3_55
Chemical formula	$C_{21}H_{34}BN_7O_4PSW$
Formula weight	706.24 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.078 x 0.112 x 0.132 mm
Crystal habit	translucent intense colourless plate
Crystal system	monoclinic
Space group	P 2_1/n
Unit cell dimensions	a = 10.8707(4) Å α = 90°
	b = 19.7711(7) Å β = 96.5960(10)°
	c = 12.6847(4) Å γ = 90°
Volume	2708.22(16) $Å^3$
Z	4

Density (calculated)	1.732 g/cm^3
Absorption coefficient	4.443 mm^{-1}
F(000)	1404

Table 2. Data collection and structure refinement for Harman_PS_3_55.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.06 to 27.50°
Index ranges	-14<=h<=12, -25<=k<=24, -15<=l<=16
Reflections collected	38883
Independent reflections	6232 [R(int) = 0.0391]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7230 and 0.5920
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)

Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6232 / 0 / 342	
Goodness-of-fit on F^2	1.035	
Δ/σ_{max}	0.003	
Final R indices	5429 data; I>2σ(I)	R1 = 0.0232, wR2 = 0.0510
	all data	R1 = 0.0301, wR2 = 0.0540
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0235P)^2+3.0103P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.517 and -0.508 eÅ^{-3}	
R.M.S. deviation from mean	0.099 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Harman_PS_3_55.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.51852(2)	0.27478(2)	0.52884(2)	0.01763(4)

	x/a	y/b	z/c	U(eq)
S1	0.80128(8)	0.46995(4)	0.43554(7)	0.02807(17)
P1	0.51366(7)	0.33230(4)	0.70436(6)	0.02286(16)
O1	0.7945(2)	0.28164(11)	0.5406(2)	0.0326(5)
O2	0.8283(2)	0.49890(11)	0.33599(19)	0.0355(6)
O3	0.7889(2)	0.51695(12)	0.52077(19)	0.0360(6)
N1	0.3173(2)	0.25688(13)	0.53856(19)	0.0209(5)
N2	0.2742(2)	0.19234(12)	0.54685(18)	0.0197(5)
N3	0.5497(2)	0.18636(13)	0.63370(19)	0.0219(5)
N4	0.4656(2)	0.13573(13)	0.63637(19)	0.0223(5)
N5	0.4917(2)	0.18863(13)	0.41766(19)	0.0223(5)
N6	0.4245(2)	0.13365(13)	0.44144(19)	0.0222(5)
N7	0.6807(2)	0.28120(12)	0.5318(2)	0.0229(5)
C1	0.2188(3)	0.29742(16)	0.5408(2)	0.0226(6)
C2	0.1123(3)	0.26004(16)	0.5512(2)	0.0237(6)
C3	0.1520(3)	0.19371(16)	0.5547(2)	0.0233(6)
C4	0.6449(3)	0.17102(16)	0.7061(2)	0.0265(7)
C5	0.6228(3)	0.11032(17)	0.7564(3)	0.0304(7)
C6	0.5088(3)	0.08940(16)	0.7096(2)	0.0285(7)
C7	0.5450(3)	0.17234(17)	0.3312(2)	0.0280(7)
C8	0.5131(3)	0.10731(17)	0.2986(3)	0.0319(7)
C9	0.4375(3)	0.08437(17)	0.3707(2)	0.0286(7)
C10	0.4755(3)	0.38084(16)	0.4732(2)	0.0228(6)
C11	0.4592(3)	0.33342(16)	0.3857(2)	0.0238(6)

	x/a	y/b	z/c	U(eq)
C12	0.5308(3)	0.34689(17)	0.2920(2)	0.0275(7)
C13	0.6648(3)	0.36881(16)	0.3252(2)	0.0278(7)
C14	0.6702(3)	0.41955(15)	0.4140(2)	0.0237(6)
C15	0.5835(3)	0.42429(15)	0.4806(2)	0.0222(6)
C16	0.9216(3)	0.41285(17)	0.4775(3)	0.0329(7)
C17	0.6648(3)	0.3522(2)	0.7717(3)	0.0365(8)
C18	0.4321(3)	0.41161(17)	0.7152(3)	0.0326(8)
C19	0.4403(3)	0.28107(18)	0.7993(3)	0.0331(8)
B1	0.3607(3)	0.13102(18)	0.5440(3)	0.0238(7)
O4	0.9265(2)	0.08058(11)	0.50273(19)	0.0321(5)
C20	0.9330(3)	0.00973(16)	0.4982(3)	0.0309(7)
C21	0.8036(4)	0.1033(2)	0.5031(4)	0.0554(12)

Table 4. Bond lengths (Å) for Harman_PS_3_55.

W1-N7	1.764(3)	W1-C11	2.189(3)
W1-N3	2.199(2)	W1-N5	2.209(2)
W1-N1	2.233(3)	W1-C10	2.245(3)
W1-P1	2.5061(8)	S1-O3	1.444(2)
S1-O2	1.447(2)	S1-C14	1.735(3)
S1-C16	1.763(3)	P1-C17	1.805(3)
P1-C18	1.814(3)	P1-C19	1.826(3)
O1-N7	1.229(3)	N1-C1	1.340(4)

N1-N2	1.367(3)	N2-C3	1.344(4)
N2-B1	1.537(4)	N3-C4	1.337(4)
N3-N4	1.359(3)	N4-C6	1.350(4)
N4-B1	1.541(4)	N5-C7	1.337(4)
N5-N6	1.362(4)	N6-C9	1.343(4)
N6-B1	1.544(4)	C1-C2	1.393(4)
C1-H1	0.950000	C2-C3	1.380(4)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.393(4)	C4-H4	0.950000
C5-C6	1.375(5)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.383(5)
C7-H7	0.950000	C8-C9	1.374(5)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.448(4)	C10-C15	1.449(4)
C10-H10	0.98(3)	C11-C12	1.517(4)
C11-H11	1.01(3)	C12-C13	1.532(5)
C12-H12A	0.990000	C12-H12B	0.990000
C13-C14	1.504(4)	C13-H13A	0.990000
C13-H13B	0.990000	C14-C15	1.339(4)
C15-H15	0.950000	C16-H16A	0.980000
C16-H16B	0.980000	C16-H16C	0.980000
C17-H17A	0.980000	C17-H17B	0.980000
C17-H17C	0.980000	C18-H18A	0.980000
C18-H18B	0.980000	C18-H18C	0.980000

C19-H19A	0.980000	C19-H19B	0.980000
C19-H19C	0.980000	B1-H1A	1.08(3)
O4-C20	1.404(4)	O4-C21	1.409(4)
C20-C20#1	1.503(7)	C20-H20A	0.990000
C20-H20B	0.990000	C21-H21A	0.980000
C21-H21B	0.980000	C21-H21C	0.980000

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1

Table 5. Bond angles (°) for Harman_PS_3_55.

N7-W1-C11	100.26(12)	N7-W1-N3	87.71(10)
C11-W1-N3	158.95(11)	N7-W1-N5	97.33(10)
C11-W1-N5	82.76(10)	N3-W1-N5	76.88(9)
N7-W1-N1	173.36(10)	C11-W1-N1	86.14(10)
N3-W1-N1	85.67(9)	N5-W1-N1	81.65(9)
N7-W1-C10	96.39(11)	C11-W1-C10	38.10(11)
N3-W1-C10	160.90(10)	N5-W1-C10	120.79(10)
N1-W1-C10	89.73(10)	N7-W1-P1	94.09(8)
C11-W1-P1	117.55(8)	N3-W1-P1	80.85(6)
N5-W1-P1	154.46(7)	N1-W1-P1	84.38(6)
C10-W1-P1	80.25(8)	O3-S1-O2	116.41(15)
O3-S1-C14	110.00(15)	O2-S1-C14	109.57(15)
O3-S1-C16	108.40(16)	O2-S1-C16	107.41(16)

C14-S1-C16	104.32(16)	C17-P1-C18	101.67(17)
C17-P1-C19	104.56(17)	C18-P1-C19	100.08(16)
C17-P1-W1	114.09(12)	C18-P1-W1	121.32(11)
C19-P1-W1	112.93(12)	C1-N1-N2	106.0(2)
C1-N1-W1	134.1(2)	N2-N1-W1	119.89(18)
C3-N2-N1	109.7(2)	C3-N2-B1	129.0(3)
N1-N2-B1	121.2(2)	C4-N3-N4	106.6(2)
C4-N3-W1	130.5(2)	N4-N3-W1	122.90(18)
C6-N4-N3	109.6(3)	C6-N4-B1	130.6(3)
N3-N4-B1	117.8(2)	C7-N5-N6	106.5(2)
C7-N5-W1	132.2(2)	N6-N5-W1	120.57(17)
C9-N6-N5	109.3(2)	C9-N6-B1	129.1(3)
N5-N6-B1	121.2(2)	O1-N7-W1	174.6(2)
N1-C1-C2	111.1(3)	N1-C1-H1	124.500000
C2-C1-H1	124.500000	C3-C2-C1	104.3(3)
C3-C2-H2	127.800000	C1-C2-H2	127.800000
N2-C3-C2	109.0(3)	N2-C3-H3	125.500000
C2-C3-H3	125.500000	N3-C4-C5	110.5(3)
N3-C4-H4	124.800000	C5-C4-H4	124.800000
C6-C5-C4	104.8(3)	C6-C5-H5	127.600000
C4-C5-H5	127.600000	N4-C6-C5	108.5(3)
N4-C6-H6	125.700000	C5-C6-H6	125.700000
N5-C7-C8	110.6(3)	N5-C7-H7	124.700000
C8-C7-H7	124.700000	C9-C8-C7	104.8(3)

C9-C8-H8	127.600000	C7-C8-H8	127.600000
N6-C9-C8	108.8(3)	N6-C9-H9	125.600000
C8-C9-H9	125.600000	C11-C10-C15	117.4(3)
C11-C10-W1	68.84(17)	C15-C10-W1	113.3(2)
C11-C10-H10	121.3(19)	C15-C10-H10	114.4(19)
W1-C10-H10	112.8(18)	C10-C11-C12	117.3(3)
C10-C11-W1	73.05(17)	C12-C11-W1	127.9(2)
C10-C11-H11	113.1(19)	C12-C11-H11	109.3(18)
W1-C11-H11	111.7(19)	C11-C12-C13	113.0(3)
C11-C12-H12A	109.000000	C13-C12-H12A	109.000000
C11-C12-H12B	109.000000	C13-C12-H12B	109.000000
H12A-C12-H12B	107.800000	C14-C13-C12	110.4(3)
C14-C13-H13A	109.600000	C12-C13-H13A	109.600000
C14-C13-H13B	109.600000	C12-C13-H13B	109.600000
H13A-C13-H13B	108.100000	C15-C14-C13	123.3(3)
C15-C14-S1	119.0(2)	C13-C14-S1	117.5(2)

C14-C15-C10	122.7(3)	C14-C15-H15	118.600000
C10-C15-H15	118.600000	S1-C16-H16A	109.500000
S1-C16-H16B	109.500000	H16A-C16-H16B	109.500000
S1-C16-H16C	109.500000	H16A-C16-H16C	109.500000
H16B-C16-H16C	109.500000	P1-C17-H17A	109.500000
P1-C17-H17B	109.500000	H17A-C17-H17B	109.500000
P1-C17-H17C	109.500000	H17A-C17-H17C	109.500000
H17B-C17-H17C	109.500000	P1-C18-H18A	109.500000
P1-C18-H18B	109.500000	H18A-C18-H18B	109.500000
P1-C18-H18C	109.500000	H18A-C18-H18C	109.500000
H18B-C18-H18C	109.500000	P1-C19-H19A	109.500000
P1-C19-H19B	109.500000	H19A-C19-H19B	109.500000
P1-C19-H19C	109.500000	H19A-C19-H19C	109.500000
H19B-C19-H19C	109.500000	N2-B1-N4	109.6(2)
N2-B1-N6	109.2(3)	N4-B1-N6	105.9(3)

N2-B1-H1A	110.1(16)	N4-B1-H1A	112.2(16)
N6-B1-H1A	109.7(16)	C20-O4-C21	111.7(3)
O4-C20-C20#1	107.9(3)	O4-C20-H20A	110.100000
C20#1-C20-H20A	110.100000	O4-C20-H20B	110.100000
C20#1-C20-H20B	110.100000	H20A-C20-H20B	108.400000
O4-C21-H21A	109.500000	O4-C21-H21B	109.500000
H21A-C21-H21B	109.500000	O4-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1

Table 6. Torsion angles (°) for Harman_PS_3_55.

C1-N1-N2-C3	-0.4(3)	W1-N1-N2-C3	178.19(18)
C1-N1-N2-B1	178.2(2)	W1-N1-N2-B1	-3.1(3)
C4-N3-N4-C6	-0.2(3)	W1-N3-N4-C6	-178.59(19)
C4-N3-N4-B1	-165.9(3)	W1-N3-N4-B1	15.8(3)
C7-N5-N6-C9	0.4(3)	W1-N5-N6-C9	-170.49(19)
C7-N5-N6-B1	173.5(3)	W1-N5-N6-B1	2.6(3)

N2-N1-C1-C2	0.5(3)	W1-N1-C1-C2	-177.9(2)
N1-C1-C2-C3	-0.3(3)	N1-N2-C3-C2	0.2(3)
B1-N2-C3-C2	-178.3(3)	C1-C2-C3-N2	0.1(3)
N4-N3-C4-C5	-0.2(3)	W1-N3-C4-C5	178.0(2)
N3-C4-C5-C6	0.5(4)	N3-N4-C6-C5	0.5(3)
B1-N4-C6-C5	163.7(3)	C4-C5-C6-N4	-0.6(4)
N6-N5-C7-C8	0.0(4)	W1-N5-C7-C8	169.4(2)
N5-C7-C8-C9	-0.4(4)	N5-N6-C9-C8	-0.7(4)
B1-N6-C9-C8	-173.1(3)	C7-C8-C9-N6	0.7(4)
C15-C10-C11-C12	-18.4(4)	W1-C10-C11-C12	-124.4(3)
C15-C10-C11-W1	106.0(3)	C10-C11-C12-C13	42.6(4)
W1-C11-C12-C13	-46.6(4)	C11-C12-C13-C14	-43.4(4)
C12-C13-C14-C15	24.3(4)	C12-C13-C14-S1	-160.4(2)
O3-S1-C14-C15	-6.4(3)	O2-S1-C14-C15	-135.6(2)
C16-S1-C14-C15	109.7(3)	O3-S1-C14-C13	178.0(2)
O2-S1-C14-C13	48.9(3)	C16-S1-C14-C13	-65.9(3)
C13-C14-C15-C10	-0.2(5)	S1-C14-C15-C10	-175.5(2)

C11-C10-C15-C14	-3.6(4)	W1-C10-C15-C14	73.7(3)
C3-N2-B1-N4	-121.5(3)	N1-N2-B1-N4	60.1(3)
C3-N2-B1-N6	122.9(3)	N1-N2-B1-N6	-55.5(3)
C6-N4-B1-N2	130.6(3)	N3-N4-B1-N2	-67.3(3)
C6-N4-B1-N6	-111.7(3)	N3-N4-B1-N6	50.4(3)
C9-N6-B1-N2	-132.2(3)	N5-N6-B1-N2	56.2(4)
C9-N6-B1-N4	109.9(3)	N5-N6-B1-N4	-61.7(3)
C21-O4-C20-C20#1	-178.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1

Table 7. Anisotropic atomic displacement parameters (Å^2) for Harman_PS_3_55.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.01630(6)	0.01889(7)	0.01756(6)	0.00023(4)	0.00133(4)	-0.00051(5)
S1	0.0233(4)	0.0217(4)	0.0407(4)	0.0003(3)	0.0098(3)	-0.0011(3)
P1	0.0230(4)	0.0255(4)	0.0197(4)	-0.0021(3)	0.0009(3)	-0.0003(3)
O1	0.0173(12)	0.0302(13)	0.0500(14)	0.0044(11)	0.0027(10)	0.0012(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.0329(14)	0.0256(12)	0.0512(14)	0.0109(11)	0.0186(11)	0.0022(10)
O3	0.0273(13)	0.0285(13)	0.0538(15)	-0.0124(11)	0.0112(11)	-0.0063(10)
N1	0.0203(13)	0.0206(13)	0.0215(12)	-0.0003(10)	0.0013(10)	-0.0020(10)
N2	0.0188(13)	0.0197(13)	0.0204(11)	-0.0026(10)	0.0017(9)	-0.0013(10)
N3	0.0203(13)	0.0222(13)	0.0230(12)	0.0003(10)	0.0025(10)	0.0012(10)
N4	0.0220(13)	0.0190(12)	0.0264(13)	-0.0002(10)	0.0051(10)	-0.0008(10)
N5	0.0216(13)	0.0225(13)	0.0225(12)	-0.0015(10)	0.0021(10)	0.0030(10)
N6	0.0208(13)	0.0214(13)	0.0243(12)	-0.0050(10)	0.0023(10)	0.0012(10)
N7	0.0197(13)	0.0207(13)	0.0279(13)	0.0012(10)	0.0009(10)	-0.0011(10)
C1	0.0229(16)	0.0244(15)	0.0201(14)	-0.0007(12)	-0.0002(11)	0.0008(12)
C2	0.0165(15)	0.0308(17)	0.0240(15)	-0.0009(12)	0.0034(11)	0.0017(12)
C3	0.0191(15)	0.0284(17)	0.0224(14)	-0.0023(12)	0.0026(11)	-0.0027(13)
C4	0.0226(16)	0.0273(16)	0.0279(15)	0.0019(13)	-0.0042(12)	0.0034(13)
C5	0.0342(19)	0.0298(17)	0.0267(16)	0.0074(13)	0.0013(13)	0.0085(15)
C6	0.0332(19)	0.0226(16)	0.0311(16)	0.0037(13)	0.0098(14)	0.0047(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	0.0307(18)	0.0300(17)	0.0244(15)	-0.0009(13)	0.0075(12)	0.0050(14)
C8	0.036(2)	0.0319(18)	0.0276(16)	-0.0067(14)	0.0050(14)	0.0077(15)
C9	0.0291(18)	0.0245(16)	0.0307(16)	-0.0069(13)	-0.0024(13)	0.0040(14)
C10	0.0218(16)	0.0249(16)	0.0218(14)	0.0019(12)	0.0031(11)	0.0026(13)
C11	0.0219(16)	0.0273(16)	0.0218(14)	0.0038(12)	0.0005(11)	0.0003(13)
C12	0.0310(18)	0.0302(17)	0.0214(15)	0.0028(13)	0.0035(12)	0.0000(14)
C13	0.0298(18)	0.0268(17)	0.0284(16)	0.0015(13)	0.0105(13)	0.0004(14)
C14	0.0231(16)	0.0205(15)	0.0278(15)	0.0023(12)	0.0038(12)	0.0007(12)
C15	0.0232(16)	0.0199(15)	0.0233(14)	0.0019(12)	0.0019(11)	0.0024(12)
C16	0.0249(18)	0.0281(18)	0.046(2)	0.0013(15)	0.0063(14)	-0.0010(14)
C17	0.0298(19)	0.046(2)	0.0323(18)	-0.0104(16)	-0.0047(14)	-0.0026(16)
C18	0.041(2)	0.0303(18)	0.0265(16)	-0.0062(14)	0.0045(14)	0.0062(15)
C19	0.036(2)	0.040(2)	0.0246(16)	0.0002(14)	0.0087(13)	-0.0003(16)
B1	0.0213(18)	0.0218(17)	0.0286(17)	-0.0031(14)	0.0037(13)	-0.0005(14)
O4	0.0311(13)	0.0220(12)	0.0443(13)	0.0041(10)	0.0094(10)	0.0019(10)
C20	0.0289(19)	0.0244(17)	0.0400(18)	0.0064(14)	0.0065(14)	-0.0017(14)
C21	0.043(2)	0.034(2)	0.095(3)	0.017(2)	0.033(2)	0.0141(18)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for Harman_PS_3_55.

	x/a	y/b	z/c	U(eq)
H1	0.2213	0.3453	0.5358	0.027000
H2	0.0309	0.2765	0.5551	0.028000
H3	0.1012	0.1552	0.5615	0.028000
H4	0.7174	0.1978	0.7211	0.032000
H5	0.6750	0.0882	0.8111	0.036000
H6	0.4673	0.0491	0.7261	0.034000
H7	0.5976	0.2014	0.2970	0.034000
H8	0.5379	0.0837	0.2393	0.038000
H9	0.4006	0.0408	0.3705	0.034000
H10	0.405(3)	0.4002(16)	0.503(2)	0.020(8)
H11	0.370(3)	0.3249(17)	0.359(3)	0.029(9)
H12A	0.4880	0.3827	0.2472	0.033000
H12B	0.5310	0.3053	0.2484	0.033000
H13A	0.7154	0.3288	0.3487	0.033000
H13B	0.6996	0.3890	0.2637	0.033000
H15	0.5932	0.4575	0.5350	0.027000
H16A	0.9209	0.3755	0.4266	0.049000
H16B	0.9095	0.3949	0.5476	0.049000
H16C	1.0014	0.4364	0.4818	0.049000
H17A	0.7122	0.3103	0.7856	0.055000

	x/a	y/b	z/c	U(eq)
H17B	0.6555	0.3748	0.8391	0.055000
H17C	0.7085	0.3821	0.7270	0.055000
H18A	0.4706	0.4468	0.6756	0.049000
H18B	0.4363	0.4247	0.7900	0.049000
H18C	0.3452	0.4061	0.6858	0.049000
H19A	0.3558	0.2695	0.7692	0.050000
H19B	0.4375	0.3067	0.8651	0.050000
H19C	0.4881	0.2395	0.8145	0.050000
H1A	0.308(3)	0.0845(16)	0.546(2)	0.019(8)
H20A	-0.1140	-0.0070	0.4318	0.037000
H20B	-0.1033	-0.0105	0.5590	0.037000
H21A	-0.2463	0.0880	0.4382	0.083000
H21B	-0.1974	0.1528	0.5061	0.083000
H21C	-0.2308	0.0848	0.5651	0.083000

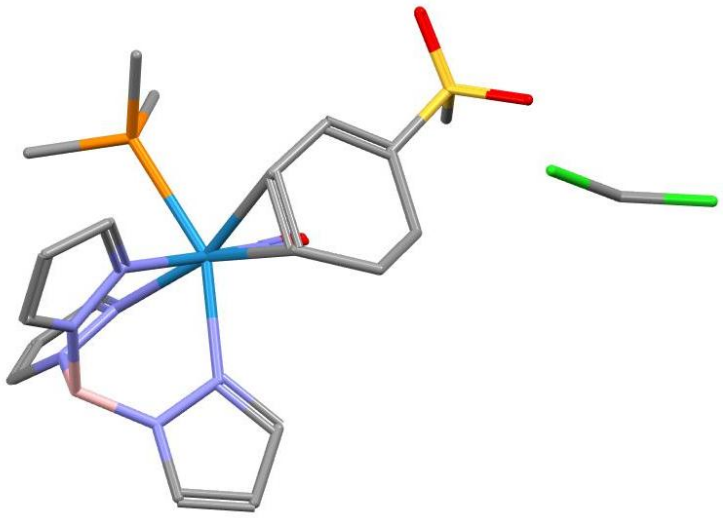


Table 1. Sample and crystal data for Compound 21.

Chemical formula	$C_{29}H_{37}BN_7O_7PSW$	
Formula weight	853.34 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.075 x 0.081 x 0.244 mm	
Crystal habit	yellow blocks	
Crystal system	monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 12.5334(8) Å	α = 90°
	b = 22.9625(17) Å	β = 112.263(2)°
	c = 12.6358(9) Å	γ = 90°
Volume	3365.5(4) $Å^3$	
Z	4	
Density (calculated)	1.684 g/cm^3	
Absorption coefficient	3.598 mm^{-1}	
F(000)	1704	

Table 2. Data collection and structure refinement for Compound 21.

Diffractometer	Bruker Kappa APEXII Duo
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)
Theta range for data collection	1.77 to 28.34°

Index ranges	-16<=h<=16, -30<=k<=30, -16<=l<=16	
Reflections collected	53711	
Independent reflections	8375 [R(int) = 0.0789]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7740 and 0.4740	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8375 / 0 / 440	
Goodness-of-fit on F^2	1.072	
Δ/σ_{max}	0.002	
Final R indices	6486 data; I>2σ(I)	R1 = 0.0431, wR2 = 0.0702
	all data	R1 = 0.0681, wR2 = 0.0760
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+15.7645P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.008 and -1.311 eÅ^{-3}	

R.M.S. deviation from mean	0.153 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 21.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.44433(2)	0.63752(2)	0.22078(2)	0.01447(5)
S1	0.37858(12)	0.61056(6)	0.61261(10)	0.0216(3)
P1	0.64745(12)	0.65170(6)	0.36032(10)	0.0200(3)
O1	0.3778(3)	0.73421(15)	0.3419(3)	0.0265(9)
O2	0.4652(4)	0.57333(17)	0.6898(3)	0.0374(10)
O3	0.2635(3)	0.60975(17)	0.6146(3)	0.0323(10)
O4	0.0004(3)	0.55914(19)	0.2532(4)	0.0416(11)
O5	0.0391(3)	0.47737(17)	0.3541(3)	0.0299(9)
O6	0.2555(4)	0.4231(2)	0.2560(4)	0.0537(13)
O7	0.1153(4)	0.4727(2)	0.1187(4)	0.0501(12)
N1	0.3024(3)	0.63719(19)	0.0474(3)	0.0169(8)
N2	0.3293(3)	0.63925(18)	0.9517(3)	0.0165(8)
N3	0.4904(3)	0.71006(18)	0.1313(3)	0.0157(9)
N4	0.4966(3)	0.70436(18)	0.0259(3)	0.0184(9)
N5	0.5282(3)	0.57984(18)	0.1287(3)	0.0168(9)

	x/a	y/b	z/c	U(eq)
N6	0.5273(3)	0.59689(18)	0.0248(3)	0.0186(9)
N7	0.3989(4)	0.69204(18)	0.2928(3)	0.0186(9)
C1	0.1886(4)	0.6311(2)	0.0097(4)	0.0227(11)
C2	0.1409(4)	0.6291(2)	0.8908(4)	0.0252(12)
C3	0.2321(4)	0.6343(2)	0.8575(4)	0.0208(10)
C4	0.5129(4)	0.7655(2)	0.1609(4)	0.0221(11)
C5	0.5349(4)	0.7965(2)	0.0771(4)	0.0263(12)
C6	0.5234(4)	0.7561(2)	0.9930(4)	0.0226(11)
C7	0.5980(4)	0.5330(2)	0.1596(4)	0.0213(11)
C8	0.6431(4)	0.5205(2)	0.0771(4)	0.0241(12)
C9	0.5953(4)	0.5614(2)	0.9933(4)	0.0243(12)
C10	0.4525(4)	0.5629(2)	0.3397(4)	0.0150(10)
C11	0.3421(4)	0.5655(2)	0.2466(4)	0.0176(10)
C12	0.2342(4)	0.5726(2)	0.2743(4)	0.0207(11)
C13	0.2553(4)	0.6128(2)	0.3779(4)	0.0209(11)
C14	0.3662(4)	0.5969(2)	0.4732(4)	0.0179(10)
C15	0.4558(4)	0.5748(2)	0.4536(4)	0.0171(10)
C16	0.4312(4)	0.6827(2)	0.6412(4)	0.0170(10)
C17	0.3524(5)	0.7281(2)	0.6053(5)	0.0299(13)
C18	0.3928(7)	0.7856(3)	0.6244(6)	0.0442(17)
C19	0.5083(7)	0.7954(3)	0.6796(6)	0.0457(18)
C20	0.5870(6)	0.7502(3)	0.7144(5)	0.0422(17)
C21	0.5477(5)	0.6931(3)	0.6940(5)	0.0314(13)

	x/a	y/b	z/c	U(eq)
C22	0.1893(4)	0.5140(2)	0.3023(4)	0.0221(11)
C23	0.0670(5)	0.5207(2)	0.2983(4)	0.0249(12)
C24	0.9228(5)	0.4807(3)	0.3543(5)	0.0344(14)
C25	0.1919(5)	0.4643(3)	0.2251(5)	0.0314(13)
C26	0.1089(6)	0.4261(3)	0.0387(6)	0.059(2)
C27	0.6661(5)	0.7102(3)	0.4611(5)	0.0346(14)
C28	0.7462(5)	0.6703(3)	0.2899(5)	0.0371(15)
C29	0.7271(5)	0.5927(3)	0.4525(5)	0.0331(14)
B1	0.4535(5)	0.6478(2)	0.9593(4)	0.0190(12)

Table 4. Bond lengths (Å) for Compound 21.

W1-N7	1.764(4)	W1-C11	2.191(5)
W1-N3	2.210(4)	W1-N1	2.238(4)
W1-C10	2.256(4)	W1-N5	2.267(4)
W1-P1	2.5089(13)	S1-O2	1.435(4)
S1-O3	1.452(4)	S1-C14	1.737(5)
S1-C16	1.768(5)	P1-C27	1.804(6)
P1-C29	1.818(5)	P1-C28	1.828(5)
O1-N7	1.232(5)	O4-C23	1.200(6)
O5-C23	1.339(6)	O5-C24	1.461(6)
O6-C25	1.203(7)	O7-C25	1.337(7)
O7-C26	1.453(7)	N1-C1	1.329(6)

N1-N2	1.374(5)	N2-C3	1.346(6)
N2-B1	1.536(7)	N3-C4	1.328(6)
N3-N4	1.369(5)	N4-C6	1.343(6)
N4-B1	1.531(7)	N5-C7	1.348(6)
N5-N6	1.366(5)	N6-C9	1.345(6)
N6-B1	1.525(7)	C1-C2	1.392(6)
C1-H1	0.95	C2-C3	1.365(7)
C2-H2	0.95	C3-H3	0.95
C4-C5	1.388(7)	C4-H4	0.95
C5-C6	1.377(7)	C5-H5	0.95
C6-H6	0.95	C7-C8	1.390(7)
C7-H7	0.95	C8-C9	1.372(7)
C8-H8	0.95	C9-H9	0.95
C10-C11	1.438(7)	C10-C15	1.451(6)
C10-H10	0.88(5)	C11-C12	1.528(7)
C11-H11	0.81(5)	C12-C13	1.541(7)
C12-C22	1.551(7)	C12-H12	1.0
C13-C14	1.500(7)	C13-H13A	0.99
C13-H13B	0.99	C14-C15	1.338(7)
C15-H15	0.95	C16-C21	1.377(7)
C16-C17	1.389(7)	C17-C18	1.402(8)
C17-H17	0.95	C18-C19	1.367(10)
C18-H18	0.95	C19-C20	1.384(10)
C19-H19	0.95	C20-C21	1.392(8)

C20-H20	0.95	C21-H21	0.95
C22-C25	1.509(8)	C22-C23	1.523(7)
C22-H22	1.0	C24-H24A	0.98
C24-H24B	0.98	C24-H24C	0.98
C26-H26A	0.98	C26-H26B	0.98
C26-H26C	0.98	C27-H27A	0.98
C27-H27B	0.98	C27-H27C	0.98
C28-H28A	0.98	C28-H28B	0.98
C28-H28C	0.98	C29-H29A	0.98
C29-H29B	0.98	C29-H29C	0.98
B1-H1A	1.11(5)		

Table 5. Bond angles (°) for Compound 21.

N7-W1-C11	97.90(18)	N7-W1-N3	85.82(16)
C11-W1-N3	157.87(16)	N7-W1-N1	102.42(17)
C11-W1-N1	81.40(16)	N3-W1-N1	76.50(14)
N7-W1-C10	97.92(17)	C11-W1-C10	37.70(17)
N3-W1-C10	163.53(16)	N1-W1-C10	117.90(17)
N7-W1-N5	169.20(17)	C11-W1-N5	92.68(17)
N3-W1-N5	85.17(15)	N1-W1-N5	81.21(14)
C10-W1-N5	89.14(16)	N7-W1-P1	89.15(13)
C11-W1-P1	119.23(13)	N3-W1-P1	82.50(11)
N1-W1-P1	155.06(10)	C10-W1-P1	81.53(13)

N5-W1-P1	83.80(10)	O2-S1-O3	118.8(2)
O2-S1-C14	109.6(2)	O3-S1-C14	107.9(2)
O2-S1-C16	106.9(2)	O3-S1-C16	107.7(2)
C14-S1-C16	105.0(2)	C27-P1-C29	102.1(3)
C27-P1-C28	103.8(3)	C29-P1-C28	100.2(3)
C27-P1-W1	114.7(2)	C29-P1-W1	121.2(2)
C28-P1-W1	112.47(18)	C23-O5-C24	114.9(4)
C25-O7-C26	115.1(5)	C1-N1-N2	106.0(3)
C1-N1-W1	134.3(3)	N2-N1-W1	119.5(3)
C3-N2-N1	109.5(4)	C3-N2-B1	128.4(4)
N1-N2-B1	122.0(4)	C4-N3-N4	106.4(4)
C4-N3-W1	130.4(3)	N4-N3-W1	123.2(3)
C6-N4-N3	109.3(4)	C6-N4-B1	131.2(4)
N3-N4-B1	118.5(4)	C7-N5-N6	106.0(4)
C7-N5-W1	134.0(3)	N6-N5-W1	119.3(3)
C9-N6-N5	109.6(4)	C9-N6-B1	128.7(4)
N5-N6-B1	121.6(4)	O1-N7-W1	172.2(4)
N1-C1-C2	110.8(4)	N1-C1-H1	124.6
C2-C1-H1	124.6	C3-C2-C1	105.2(4)
C3-C2-H2	127.4	C1-C2-H2	127.4
N2-C3-C2	108.5(4)	N2-C3-H3	125.7
C2-C3-H3	125.7	N3-C4-C5	111.0(5)
N3-C4-H4	124.5	C5-C4-H4	124.5
C6-C5-C4	104.6(5)	C6-C5-H5	127.7

C4-C5-H5	127.7	N4-C6-C5	108.8(4)
N4-C6-H6	125.6	C5-C6-H6	125.6
N5-C7-C8	110.6(4)	N5-C7-H7	124.7
C8-C7-H7	124.7	C9-C8-C7	104.8(5)
C9-C8-H8	127.6	C7-C8-H8	127.6
N6-C9-C8	109.1(4)	N6-C9-H9	125.5
C8-C9-H9	125.5	C11-C10-C15	117.4(4)
C11-C10-W1	68.7(3)	C15-C10-W1	119.7(3)
C11-C10-H10	119.(3)	C15-C10-H10	115.(3)
W1-C10-H10	110.(3)	C10-C11-C12	118.6(4)
C10-C11-W1	73.6(3)	C12-C11-W1	124.9(3)
C10-C11-H11	112.(4)	C12-C11-H11	115.(4)
W1-C11-H11	105.(4)	C11-C12-C13	112.1(4)
C11-C12-C22	112.9(4)	C13-C12-C22	106.6(4)
C11-C12-H12	108.4	C13-C12-H12	108.4
C22-C12-H12	108.4	C14-C13-C12	110.2(4)
C14-C13-H13A	109.6	C12-C13-H13A	109.6
C14-C13-H13B	109.6	C12-C13-H13B	109.6
H13A-C13-H13B	108.1	C15-C14-C13	122.1(4)
C15-C14-S1	119.8(4)	C13-C14-S1	118.0(4)
C14-C15-C10	123.0(4)	C14-C15-H15	118.5
C10-C15-H15	118.5	C21-C16-C17	121.4(5)

C21-C16-S1	120.4(4)	C17-C16-S1	118.2(4)
C16-C17-C18	119.0(6)	C16-C17-H17	120.5
C18-C17-H17	120.5	C19-C18-C17	119.2(6)
C19-C18-H18	120.4	C17-C18-H18	120.4
C18-C19-C20	121.9(6)	C18-C19-H19	119.1
C20-C19-H19	119.1	C19-C20-C21	119.3(6)
C19-C20-H20	120.4	C21-C20-H20	120.4
C16-C21-C20	119.3(6)	C16-C21-H21	120.3
C20-C21-H21	120.3	C25-C22-C23	108.8(4)
C25-C22-C12	114.2(4)	C23-C22-C12	110.7(4)
C25-C22-H22	107.6	C23-C22-H22	107.6
C12-C22-H22	107.6	O4-C23-O5	121.6(5)
O4-C23-C22	126.9(5)	O5-C23-C22	111.5(4)
O5-C24-H24A	109.5	O5-C24-H24B	109.5
H24A-C24-H24B	109.5	O5-C24-H24C	109.5
H24A-C24-H24C	109.5	H24B-C24-H24C	109.5
O6-C25-O7	125.1(6)	O6-C25-C22	123.9(6)
O7-C25-C22	111.0(5)	O7-C26-H26A	109.5
O7-C26-H26B	109.5	H26A-C26-H26B	109.5
O7-C26-H26C	109.5	H26A-C26-H26C	109.5
H26B-C26-H26C	109.5	P1-C27-H27A	109.5

P1-C27-H27B	109.5	H27A-C27-H27B	109.5
P1-C27-H27C	109.5	H27A-C27-H27C	109.5
H27B-C27-H27C	109.5	P1-C28-H28A	109.5
P1-C28-H28B	109.5	H28A-C28-H28B	109.5
P1-C28-H28C	109.5	H28A-C28-H28C	109.5
H28B-C28-H28C	109.5	P1-C29-H29A	109.5
P1-C29-H29B	109.5	H29A-C29-H29B	109.5
P1-C29-H29C	109.5	H29A-C29-H29C	109.5
H29B-C29-H29C	109.5	N6-B1-N4	109.7(4)
N6-B1-N2	109.2(4)	N4-B1-N2	106.3(4)
N6-B1-H1A	108.(3)	N4-B1-H1A	110.(3)
N2-B1-H1A	114.(3)		

Table 6. Torsion angles (°) for Compound 21.

C1-N1-N2-C3	-0.1(6)	W1-N1-N2-C3	175.5(3)
C1-N1-N2-B1	178.3(4)	W1-N1-N2-B1	-6.1(6)
C4-N3-N4-C6	0.4(5)	W1-N3-N4-C6	178.4(3)

C4-N3-N4-B1	-169.2(4)	W1-N3-N4-B1	8.8(6)
C7-N5-N6-C9	-0.3(5)	W1-N5-N6-C9	171.0(3)
C7-N5-N6-B1	177.7(4)	W1-N5-N6-B1	-11.1(6)
N2-N1-C1-C2	0.1(6)	W1-N1-C1-C2	-174.6(4)
N1-C1-C2-C3	0.0(6)	N1-N2-C3-C2	0.1(6)
B1-N2-C3-C2	-178.2(5)	C1-C2-C3-N2	-0.1(6)
N4-N3-C4-C5	-0.5(6)	W1-N3-C4-C5	-178.3(3)
N3-C4-C5-C6	0.4(6)	N3-N4-C6-C5	-0.2(6)
B1-N4-C6-C5	167.6(5)	C4-C5-C6-N4	-0.1(6)
N6-N5-C7-C8	0.9(6)	W1-N5-C7-C8	-168.5(4)
N5-C7-C8-C9	-1.2(6)	N5-N6-C9-C8	-0.5(6)
B1-N6-C9-C8	-178.2(5)	C7-C8-C9-N6	1.0(6)
C15-C10-C11-C12	-7.9(7)	W1-C10-C11-C12	-121.2(4)
C15-C10-C11-W1	113.3(4)	C10-C11-C12-C13	36.7(6)
W1-C11-C12-C13	-52.6(5)	C10-C11-C12-C22	-83.6(5)
W1-C11-C12-C22	-173.0(3)	C11-C12-C13-C14	-46.0(5)
C22-C12-C13-C14	78.0(5)	C12-C13-C14-C15	30.9(6)

C12-C13-C14-S1	-151.6(3)	O2-S1-C14-C15	-25.3(5)
O3-S1-C14-C15	-156.0(4)	C16-S1-C14-C15	89.3(4)
O2-S1-C14-C13	157.1(4)	O3-S1-C14-C13	26.4(4)
C16-S1-C14-C13	-88.3(4)	C13-C14-C15-C10	-1.7(7)
S1-C14-C15-C10	-179.3(4)	C11-C10-C15-C14	-11.1(7)
W1-C10-C15-C14	68.8(6)	O2-S1-C16-C21	22.1(5)
O3-S1-C16-C21	150.9(4)	C14-S1-C16-C21	-94.3(4)
O2-S1-C16-C17	-160.2(4)	O3-S1-C16-C17	-31.4(4)
C14-S1-C16-C17	83.4(4)	C21-C16-C17-C18	-0.6(8)
S1-C16-C17-C18	-178.2(4)	C16-C17-C18-C19	-1.2(8)
C17-C18-C19-C20	1.9(9)	C18-C19-C20-C21	-0.9(9)
C17-C16-C21-C20	1.6(8)	S1-C16-C21-C20	179.2(4)
C19-C20-C21-C16	-0.9(8)	C11-C12-C22-C25	-42.0(6)
C13-C12-C22-C25	-165.5(4)	C11-C12-C22-C23	-165.2(4)
C13-C12-C22-C23	71.3(5)	C24-O5-C23-O4	0.4(7)

C24-O5-C23-C22	179.9(4)	C25-C22-C23-O4	-108.2(6)
C12-C22-C23-O4	18.1(7)	C25-C22-C23-O5	72.4(5)
C12-C22-C23-O5	-161.4(4)	C26-O7-C25-O6	2.4(9)
C26-O7-C25-C22	-178.2(5)	C23-C22-C25-O6	-124.5(6)
C12-C22-C25-O6	111.3(6)	C23-C22-C25-O7	56.0(6)
C12-C22-C25-O7	-68.1(6)	C9-N6-B1-N4	-117.2(5)
N5-N6-B1-N4	65.3(6)	C9-N6-B1-N2	126.7(5)
N5-N6-B1-N2	-50.8(6)	C6-N4-B1-N6	129.7(5)
N3-N4-B1-N6	-63.4(5)	C6-N4-B1-N2	-112.4(5)
N3-N4-B1-N2	54.5(5)	C3-N2-B1-N6	-120.0(5)
N1-N2-B1-N6	61.8(6)	C3-N2-B1-N4	121.7(5)
N1-N2-B1-N4	-56.4(6)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 21.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01856(10)	0.01692(9)	0.00925(8)	0.00221(8)	0.00676(6)	0.00036(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0392(8)	0.0149(6)	0.0172(6)	0.0003(5)	0.0180(6)	-0.0032(6)
P1	0.0227(7)	0.0257(7)	0.0126(6)	0.0023(5)	0.0080(5)	0.0011(5)
O1	0.038(2)	0.0194(19)	0.027(2)	-0.0105(15)	0.0183(17)	-0.0019(17)
O2	0.072(3)	0.027(2)	0.0161(19)	0.0062(15)	0.0192(19)	0.017(2)
O3	0.044(2)	0.036(2)	0.032(2)	-0.0146(17)	0.0323(19)	-0.023(2)
O4	0.027(2)	0.038(3)	0.060(3)	0.024(2)	0.017(2)	0.004(2)
O5	0.027(2)	0.030(2)	0.036(2)	0.0073(17)	0.0167(18)	-0.0028(18)
O6	0.068(3)	0.034(3)	0.068(3)	0.005(2)	0.036(3)	0.018(3)
O7	0.057(3)	0.046(3)	0.037(3)	-0.021(2)	0.006(2)	-0.003(2)
N1	0.021(2)	0.020(2)	0.0113(17)	0.0033(17)	0.0084(15)	0.004(2)
N2	0.023(2)	0.0159(19)	0.0125(17)	-0.0013(16)	0.0089(15)	-0.0005(19)
N3	0.020(2)	0.018(2)	0.0111(18)	0.0042(15)	0.0080(16)	-0.0012(18)
N4	0.021(2)	0.021(2)	0.0147(19)	0.0049(16)	0.0081(17)	0.0010(18)
N5	0.022(2)	0.020(2)	0.0102(18)	0.0015(15)	0.0077(16)	0.0010(18)
N6	0.020(2)	0.026(2)	0.0128(19)	0.0023(16)	0.0094(17)	0.0014(19)
N7	0.021(2)	0.019(2)	0.015(2)	0.0020(16)	0.0052(17)	-0.0048(18)
C1	0.021(3)	0.031(3)	0.018(2)	0.007(2)	0.010(2)	0.002(2)
C2	0.021(3)	0.031(3)	0.020(2)	0.008(2)	0.003(2)	-0.004(2)
C3	0.026(3)	0.020(2)	0.015(2)	0.008(2)	0.0055(19)	0.000(2)
C4	0.024(3)	0.023(3)	0.017(2)	0.0004(19)	0.005(2)	-0.005(2)
C5	0.024(3)	0.024(3)	0.028(3)	0.005(2)	0.006(2)	-0.011(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	0.017(3)	0.033(3)	0.021(2)	0.011(2)	0.009(2)	-0.003(2)
C7	0.025(3)	0.023(3)	0.016(2)	0.0037(19)	0.008(2)	0.004(2)
C8	0.023(3)	0.029(3)	0.020(3)	0.006(2)	0.008(2)	0.009(2)
C9	0.021(3)	0.038(3)	0.018(2)	0.002(2)	0.012(2)	0.004(2)
C10	0.023(3)	0.012(2)	0.015(2)	0.0042(17)	0.013(2)	0.004(2)
C11	0.028(3)	0.014(2)	0.013(2)	0.0009(18)	0.009(2)	-0.001(2)
C12	0.024(3)	0.019(3)	0.018(2)	0.0066(19)	0.007(2)	-0.001(2)
C13	0.023(3)	0.024(3)	0.020(2)	0.004(2)	0.013(2)	0.001(2)
C14	0.028(3)	0.015(2)	0.015(2)	-0.0016(18)	0.014(2)	-0.002(2)
C15	0.025(3)	0.011(2)	0.017(2)	0.0008(17)	0.009(2)	-0.002(2)
C16	0.021(3)	0.018(2)	0.014(2)	-0.0043(18)	0.0097(19)	-0.010(2)
C17	0.036(3)	0.025(3)	0.040(3)	0.000(2)	0.027(3)	-0.001(3)
C18	0.072(5)	0.025(3)	0.057(4)	0.002(3)	0.048(4)	0.006(3)
C19	0.077(5)	0.031(4)	0.051(4)	-0.017(3)	0.049(4)	-0.025(4)
C20	0.041(4)	0.055(4)	0.039(3)	-0.018(3)	0.024(3)	-0.027(4)
C21	0.029(3)	0.044(4)	0.025(3)	-0.005(2)	0.015(2)	-0.006(3)
C22	0.020(3)	0.023(3)	0.022(3)	0.005(2)	0.006(2)	0.003(2)
C23	0.028(3)	0.024(3)	0.022(3)	0.000(2)	0.008(2)	-0.009(2)
C24	0.027(3)	0.036(3)	0.047(4)	-0.002(3)	0.022(3)	-0.008(3)
C25	0.028(3)	0.031(3)	0.039(3)	0.000(3)	0.017(3)	-0.003(3)
C26	0.055(5)	0.072(6)	0.051(4)	-0.037(4)	0.021(4)	-0.012(4)

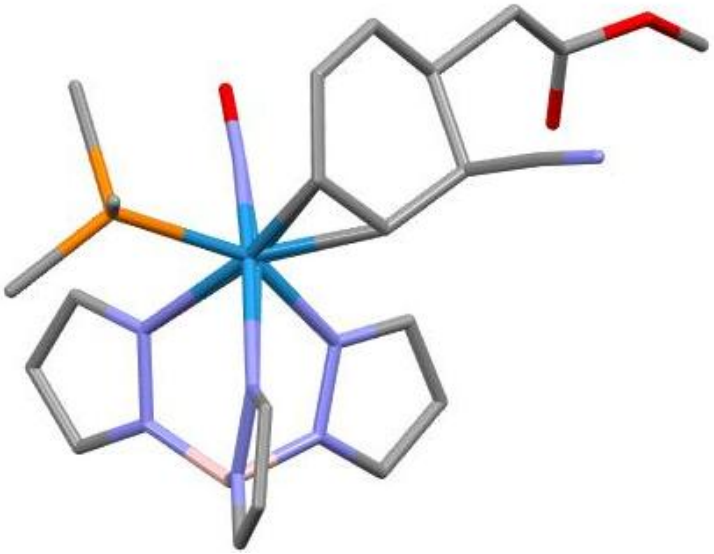
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	0.033(3)	0.039(3)	0.021(3)	-0.008(2)	-0.002(2)	-0.006(3)
C28	0.020(3)	0.063(4)	0.025(3)	0.012(3)	0.006(2)	-0.007(3)
C29	0.025(3)	0.041(4)	0.030(3)	0.015(3)	0.006(2)	0.008(3)
B1	0.021(3)	0.021(3)	0.015(2)	0.003(2)	0.007(2)	0.001(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 21.

	x/a	y/b	z/c	U(eq)
H1	0.1457	0.6284	0.0574	0.027
H2	0.0618	0.6249	-0.1570	0.03
H3	0.2278	0.6344	-0.2192	0.025
H4	0.5139	0.7819	0.2304	0.027
H5	0.5536	0.8366	0.0776	0.032
H6	0.5330	0.7636	-0.0769	0.027
H7	0.6142	0.5115	0.2281	0.026
H8	0.6953	0.4902	0.0784	0.029
H9	0.6082	0.5642	-0.0760	0.029
H10	0.503(4)	0.537(2)	0.337(4)	0.018
H11	0.337(4)	0.542(2)	0.197(4)	0.013(13)
H12	0.1721	0.5902	0.2063	0.025
H13A	0.2586	0.6538	0.3552	0.025
H13B	0.1906	0.6090	0.4044	0.025

	x/a	y/b	z/c	U(eq)
H15	0.5248	0.5665	0.5173	0.021
H17	0.2723	0.7203	0.5684	0.036
H18	0.3406	0.8173	0.5992	0.053
H19	0.5353	0.8344	0.6945	0.055
H20	0.6670	0.7582	0.7517	0.051
H21	0.6007	0.6615	0.7163	0.038
H22	0.2399	0.5031	0.3823	0.027
H24A	-0.1337	0.4787	0.2755	0.052
H24B	-0.0864	0.5176	0.3890	0.052
H24C	-0.0895	0.4481	0.3984	0.052
H26A	0.0345	0.4279	-0.0259	0.089
H26B	0.1164	0.3884	0.0773	0.089
H26C	0.1714	0.4305	0.0107	0.089
H27A	0.6391	0.7467	0.4196	0.052
H27B	0.7479	0.7137	0.5102	0.052
H27C	0.6214	0.7018	0.5084	0.052
H28A	0.7427	0.6402	0.2338	0.056
H28B	0.8250	0.6729	0.3472	0.056
H28C	0.7239	0.7079	0.2509	0.056
H29A	0.6968	0.5860	0.5125	0.05
H29B	0.8089	0.6032	0.4876	0.05
H29C	0.7186	0.5572	0.4070	0.05
H1A	0.462(4)	0.650(2)	-0.125(4)	0.024(14)

x/a y/b z/c U(eq)



Crystal Structure Report for Compound 41

A colorless, plate-like specimen of $C_{23.13}H_{32.81}BN_8O_{3.51}PW$, approximate dimensions 0.021 mm x 0.059 mm x 0.059 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 5.49 hours. The frames were integrated with the Bruker SAINT software package[20] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 32253 reflections to a maximum θ angle of 25.71° (0.82 Å resolution), of which 5370 were independent (average redundancy 6.006, completeness = 99.9%, R_{int} = 5.44%, R_{sig} = 3.68%) and 4433 (82.55%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.3629(8) Å, b = 12.0832(6) Å, c = 16.0072(7) Å, β = 117.1630(10)°, volume = 2815.8(2) $Å^3$, are based upon the refinement of the XYZ-

[20] Bruker (2012). *Saint; SADABS; APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.

centroids of 9495 reflections above 20 σ(I) with 4.380° < 2θ < 51.34°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[1] The ratio of minimum to maximum apparent transmission was 0.451. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0152 and 0.0337.

The structure was solved and refined using the Bruker SHELXTL Software Package[21] within APEX3 [1] and OLEX2,[22] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{23.13}H_{32.81}BN_8O_{3.51}PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom was located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The relative occupancy of each set of disordered atoms was freely refined, with constraints and restraints on the anisotropic displacement parameters and/or bonds of most of the disordered atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 398 variables converged at R1 = 4.76%, for the observed data and wR2 = 9.75% for all data. The goodness-of-fit was 1.128. The largest peak in the final difference electron density synthesis was 1.071 $e^-/Å^3$ and the largest hole was -2.312 $e^-/Å^3$ with an RMS deviation of 0.123 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.662 g/cm^3 and F(000), 1399 e^-.

Table 1. Sample and crystal data for Compound 41.

Chemical formula	$C_{23.13}H_{32.81}BN_8O_{3.51}PW$
Formula weight	704.73 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.021 x 0.059 x 0.059 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P $2_1/c$

[21] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.
[22] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Unit cell dimensions	a = 16.3629(8) Å α = 90°
	b = 12.0832(6) Å β = 117.1630(10)°
	c = 16.0072(7) Å γ = 90°
Volume	2815.8(2) $Å^3$
Z	4
Density (calculated)	1.662 g/cm^3
Absorption coefficient	4.201 mm^{-1}
F(000)	1399

Table 2. Data collection and structure refinement for Compound 41.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.19 to 25.71°
Index ranges	-19<=h<=19, -13<=k<=14, -19<=l<=19
Reflections collected	32253
Independent reflections	5370 [R(int) = 0.0544]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan

Max. and min. transmission	0.0337 and 0.0152	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5370 / 17 / 398	
Goodness-of-fit on F^2	1.128	
Final R indices	4433 data; $I>2\sigma(I)$	R1 = 0.0476, wR2 = 0.0927
	all data	R1 = 0.0611, wR2 = 0.0975
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0130P)^2+21.6194P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.071 and -2.312 eÅ^{-3}	
R.M.S. deviation from mean	0.123 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 41.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
O1	0.1143(4)	0.6876(5)	0.5949(4)	0.0533(14)
N1	0.4251(4)	0.6872(5)	0.5757(4)	0.0406(14)
N2	0.4995(4)	0.7351(5)	0.6493(4)	0.0422(15)
N3	0.3313(4)	0.8323(5)	0.6580(5)	0.0460(15)
N4	0.4204(4)	0.8559(5)	0.7192(4)	0.0432(16)
N5	0.3797(4)	0.6204(5)	0.7258(4)	0.0393(14)
N6	0.4649(4)	0.6657(5)	0.7771(4)	0.0382(14)
N7	0.1875(4)	0.6781(5)	0.5880(4)	0.0418(14)
N8	0.2752(5)	0.2237(6)	0.5017(5)	0.0563(19)
C00S	0.1400(6)	0.5276(7)	0.4111(6)	0.057(2)
C1	0.4542(6)	0.6578(7)	0.5135(6)	0.050(2)
C2	0.5466(6)	0.6864(7)	0.5456(6)	0.054(2)
C3	0.5706(5)	0.7354(7)	0.6305(6)	0.047(2)
C4	0.2805(6)	0.9125(7)	0.6664(6)	0.054(2)
C5	0.3364(6)	0.9907(7)	0.7321(6)	0.055(2)
C6	0.4241(6)	0.9523(6)	0.7635(6)	0.047(2)
C7	0.3689(5)	0.5438(6)	0.7788(5)	0.0440(19)
C8	0.4479(6)	0.5371(7)	0.8656(5)	0.0463(19)
C9	0.5061(5)	0.6162(6)	0.8611(5)	0.0428(18)
C10	0.2401(6)	0.5525(7)	0.4617(6)	0.050(2)
C11	0.2948(5)	0.5008(6)	0.5503(5)	0.0399(18)

	x/a	y/b	z/c	U(eq)
C12	0.2507(5)	0.4041(6)	0.5773(5)	0.0425(18)
C13	0.1477(5)	0.4252(7)	0.5489(6)	0.0454(19)
C14	0.0977(6)	0.4641(7)	0.4486(6)	0.056(2)
C15	0.2612(5)	0.3023(7)	0.5334(6)	0.047(2)
C16	0.1025(5)	0.3234(8)	0.5670(6)	0.053(2)
C17	0.1412(7)	0.2968(9)	0.6676(7)	0.065(3)
B1	0.4943(6)	0.7684(8)	0.7394(7)	0.043(2)
W1	0.28918(6)	0.67602(8)	0.57699(9)	0.0270(5)
P1	0.221(2)	0.802(3)	0.4274(19)	0.0559(12)
O2	0.185(2)	0.365(3)	0.731(2)	0.086(7)
O3	0.1282(7)	0.1924(8)	0.6779(7)	0.057(3)
C18	0.1568(13)	0.1550(16)	0.7733(11)	0.077(5)
C19	0.251(3)	0.748(4)	0.337(3)	0.063(2)
C20	0.258(3)	0.946(3)	0.441(3)	0.063(2)
C21	0.118(2)	0.863(3)	0.429(2)	0.063(2)
W1A	0.2909(4)	0.6720(5)	0.5921(9)	0.100(3)
P1A	0.2287(9)	0.7994(12)	0.4415(8)	0.0559(12)
O2A	0.211(3)	0.241(4)	0.717(3)	0.086(7)
O3A	0.090(3)	0.348(3)	0.705(2)	0.057(3)
C18A	0.122(4)	0.321(6)	0.805(4)	0.077(5)
C19A	0.2303(15)	0.7678(17)	0.3308(11)	0.063(2)
C20A	0.2831(13)	0.9365(15)	0.4637(13)	0.063(2)
C21A	0.1012(8)	0.8119(13)	0.3783(10)	0.063(2)

	x/a	y/b	z/c	U(eq)
O2B	0.205(8)	0.337(11)	0.746(8)	0.086(7)
O3B	0.064(2)	0.302(3)	0.710(2)	0.057(3)
C18B	0.071(4)	0.302(5)	0.799(4)	0.077(5)
O4	0.0710(6)	0.4418(8)	0.9533(7)	0.055(3)
C22	0.9878(9)	0.4658(12)	0.9559(9)	0.047(3)
C23	0.0530(11)	0.3845(13)	0.8664(10)	0.059(4)

Table 4. Bond lengths (Å) for Compound 41.

O1-N7	1.258(8)	N1-C1	1.333(10)
N1-N2	1.376(8)	N1-W1	2.238(6)
N1-W1A	2.334(11)	N2-C3	1.328(10)
N2-B1	1.536(11)	N3-C4	1.323(10)
N3-N4	1.364(8)	N3-W1A	2.160(9)
N3-W1	2.216(7)	N4-C6	1.351(9)
N4-B1	1.525(11)	N5-C7	1.320(9)
N5-N6	1.369(8)	N5-W1A	2.060(12)
N5-W1	2.258(6)	N6-C9	1.338(9)
N6-B1	1.550(11)	N7-W1A	1.666(9)
N7-W1	1.752(6)	N8-C15	1.147(10)
C00S-C14	1.343(12)	C00S-C10	1.490(12)
C00S-H00S	0.950000	C1-C2	1.400(11)
C1-H1	0.950000	C2-C3	1.365(12)

C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.399(11)	C4-H4	0.950000
C5-C6	1.367(11)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.403(10)
C7-H7	0.950000	C8-C9	1.375(11)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.430(11)	C10-W1	2.219(8)
C10-W1A	2.356(12)	C10-H10	1.000000
C10-H10A	1.000000	C11-C12	1.536(10)
C11-W1	2.170(7)	C11-W1A	2.184(9)
C11-H11	1.000000	C11-H11A	1.000000
C12-C15	1.466(11)	C12-C13	1.553(11)
C12-H12	1.000000	C13-C14	1.506(11)
C13-C16	1.528(11)	C13-H13	1.000000
C14-H14	0.950000	C16-C17	1.472(12)
C16-H16A	0.990000	C16-H16B	0.990000
C17-O2	1.24(4)	C17-O2A	1.25(5)
C17-O3	1.302(13)	C17-O2B	1.31(13)
C17-O3A	1.37(4)	C17-O3B	1.69(4)
B1-H1A	1.00(7)	W1-P1	2.615(17)
P1-C20	1.831(16)	P1-C19	1.847(15)
P1-C21	1.852(16)	O3-C18	1.450(17)
C18-H18A	0.980000	C18-H18B	0.980000
C18-H18C	0.980000	C19-H19A	0.980000

C19-H19B	0.980000	C19-H19C	0.980000
C20-H20A	0.980000	C20-H20B	0.980000
C20-H20C	0.980000	C21-H21A	0.980000
C21-H21B	0.980000	C21-H21C	0.980000
W1A-P1A	2.640(11)	P1A-C19A	1.825(11)
P1A-C20A	1.837(11)	P1A-C21A	1.862(13)
O3A-C18A	1.48(6)	C18A-H18D	0.980000
C18A-H18E	0.980000	C18A-H18F	0.980000
C19A-H19F	0.980000	C19A-H19E	0.980000
C19A-H19D	0.980000	C20A-H20D	0.980000
C20A-H20E	0.980000	C20A-H20F	0.980000
C21A-H21D	0.980000	C21A-H21E	0.980000
C21A-H21F	0.980000	O3B-C18B	1.38(6)
C18B-H18G	0.980000	C18B-H18H	0.980000
C18B-H18I	0.980000	O4-C22	1.411(15)
O4-C23	1.458(17)	C22-C22#1	1.52(3)
C22-H22A	0.990000	C22-H22B	0.990000
C23-H23A	0.980000	C23-H23B	0.980000
C23-H23C	0.980000		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+1, -z+2

Table 5. Bond angles (°) for Compound 41.

C1-N1-N2	105.9(6)	C1-N1-W1	133.3(6)
N2-N1-W1	120.7(5)	C1-N1-W1A	137.5(6)
N2-N1-W1A	116.5(5)	C3-N2-N1	109.3(7)
C3-N2-B1	129.8(7)	N1-N2-B1	120.5(6)
C4-N3-N4	106.9(6)	C4-N3-W1A	129.8(6)
N4-N3-W1A	121.7(5)	C4-N3-W1	129.9(5)
N4-N3-W1	122.9(5)	C6-N4-N3	109.5(6)
C6-N4-B1	130.2(7)	N3-N4-B1	119.5(6)
C7-N5-N6	107.1(6)	C7-N5-W1A	129.9(6)
N6-N5-W1A	123.0(5)	C7-N5-W1	132.1(5)
N6-N5-W1	120.8(4)	C9-N6-N5	109.4(6)
C9-N6-B1	130.2(6)	N5-N6-B1	120.0(6)
O1-N7-W1A	172.9(7)	O1-N7-W1	175.6(6)
C14-C00S-C10	122.4(8)	C14-C00S-H00S	118.800000
C10-C00S-H00S	118.800000	N1-C1-C2	110.7(8)
N1-C1-H1	124.700000	C2-C1-H1	124.700000
C3-C2-C1	104.2(7)	C3-C2-H2	127.900000
C1-C2-H2	127.900000	N2-C3-C2	109.9(7)
N2-C3-H3	125.100000	C2-C3-H3	125.100000
N3-C4-C5	110.2(7)	N3-C4-H4	124.900000

C5-C4-H4	124.900000	C6-C5-C4	105.3(7)
C6-C5-H5	127.300000	C4-C5-H5	127.300000
N4-C6-C5	108.2(7)	N4-C6-H6	125.900000
C5-C6-H6	125.900000	N5-C7-C8	110.1(7)
N5-C7-H7	125.000000	C8-C7-H7	125.000000
C9-C8-C7	104.8(7)	C9-C8-H8	127.600000
C7-C8-H8	127.600000	N6-C9-C8	108.7(7)
N6-C9-H9	125.700000	C8-C9-H9	125.700000
C11-C10-C00S	119.0(8)	C11-C10-W1	69.1(4)
C00S-C10-W1	118.6(6)	C11-C10-W1A	65.2(5)
C00S-C10-W1A	117.4(6)	C11-C10-H10	114.300000
C00S-C10-H10	114.300000	W1-C10-H10	114.300000
C11-C10-H10A	115.300000	C00S-C10-H10A	115.300000
W1A-C10-H10A	115.300000	C10-C11-C12	116.7(7)
C10-C11-W1	72.9(5)	C12-C11-W1	128.2(5)
C10-C11-W1A	78.3(6)	C12-C11-W1A	123.5(6)
C10-C11-H11	111.100000	C12-C11-H11	111.100000
W1-C11-H11	111.100000	C10-C11-H11A	111.400000

C12-C11-H11A	111.400000	W1A-C11-H11A	111.400000
C15-C12-C11	109.3(7)	C15-C12-C13	110.2(6)
C11-C12-C13	112.3(6)	C15-C12-H12	108.300000
C11-C12-H12	108.300000	C13-C12-H12	108.300000
C14-C13-C16	112.3(7)	C14-C13-C12	110.6(7)
C16-C13-C12	111.5(7)	C14-C13-H13	107.400000
C16-C13-H13	107.400000	C12-C13-H13	107.400000
C00S-C14-C13	120.9(8)	C00S-C14-H14	119.500000
C13-C14-H14	119.500000	N8-C15-C12	175.8(9)
C17-C16-C13	112.3(7)	C17-C16-H16A	109.100000
C13-C16-H16A	109.100000	C17-C16-H16B	109.100000
C13-C16-H16B	109.100000	H16A-C16-H16B	107.900000
O2-C17-O3	127.1(14)	O2A-C17-O3A	122.(3)
O2-C17-C16	123.0(13)	O2A-C17-C16	128.(2)
O3-C17-C16	109.7(9)	O2B-C17-C16	137.(5)
O3A-C17-C16	109.3(16)	O2B-C17-O3B	91.(6)
C16-C17-O3B	114.0(13)	N4-B1-N2	111.1(7)
N4-B1-N6	106.2(7)	N2-B1-N6	108.4(6)

N4-B1-H1A	116.(4)	N2-B1-H1A	107.(4)
N6-B1-H1A	108.(4)	N7-W1-C11	99.3(3)
N7-W1-N3	89.1(3)	C11-W1-N3	156.5(3)
N7-W1-C10	95.4(3)	C11-W1-C10	38.0(3)
N3-W1-C10	163.3(3)	N7-W1-N1	173.7(3)
C11-W1-N1	85.7(3)	N3-W1-N1	84.8(2)
C10-W1-N1	90.9(3)	N7-W1-N5	95.4(3)
C11-W1-N5	81.4(2)	N3-W1-N5	75.9(2)
C10-W1-N5	119.4(3)	N1-W1-N5	81.5(2)
N7-W1-P1	93.3(7)	C11-W1-P1	115.1(9)
N3-W1-P1	86.0(9)	C10-W1-P1	77.7(9)
N1-W1-P1	88.0(7)	N5-W1-P1	159.8(9)
C20-P1-C19	104.(3)	C20-P1-C21	82.(2)
C19-P1-C21	136.(3)	C20-P1-W1	117.9(19)
C19-P1-W1	111.1(19)	C21-P1-W1	103.2(13)
C17-O3-C18	116.2(12)	O3-C18-H18A	109.500000
O3-C18-H18B	109.500000	H18A-C18-H18B	109.500000
O3-C18-H18C	109.500000	H18A-C18-H18C	109.500000
H18B-C18-H18C	109.500000	P1-C19-H19A	109.500000
P1-C19-H19B	109.500000	H19A-C19-H19B	109.500000

P1-C19-H19C	109.500000	H19A-C19-H19C	109.500000
H19B-C19-H19C	109.500000	P1-C20-H20A	109.500000
P1-C20-H20B	109.500000	H20A-C20-H20B	109.500000
P1-C20-H20C	109.500000	H20A-C20-H20C	109.500000
H20B-C20-H20C	109.500000	P1-C21-H21A	109.500000
P1-C21-H21B	109.500000	H21A-C21-H21B	109.500000
P1-C21-H21C	109.500000	H21A-C21-H21C	109.500000
H21B-C21-H21C	109.500000	N7-W1A-N5	106.0(8)
N7-W1A-N3	93.4(4)	N5-W1A-N3	81.4(4)
N7-W1A-C11	101.6(4)	N5-W1A-C11	85.8(4)
N3-W1A-C11	162.5(4)	N7-W1A-N1	169.5(7)
N5-W1A-N1	83.5(3)	N3-W1A-N1	83.7(3)
C11-W1A-N1	83.1(4)	N7-W1A-C10	92.9(4)
N5-W1A-C10	122.1(4)	N3-W1A-C10	152.7(7)
C11-W1A-C10	36.5(3)	N1-W1A-C10	85.3(5)
N7-W1A-P1A	88.6(5)	N5-W1A-P1A	157.0(5)
N3-W1A-P1A	80.1(5)	C11-W1A-P1A	109.0(6)

N1-W1A-P1A	80.9(5)	C10-W1A-P1A	73.5(5)
C19A-P1A-C20A	99.0(12)	C19A-P1A-C21A	89.9(11)
C20A-P1A-C21A	110.8(9)	C19A-P1A-W1A	126.4(9)
C20A-P1A-W1A	113.5(8)	C21A-P1A-W1A	114.4(7)
C17-O3A-C18A	113.(3)	O3A-C18A-H18D	109.500000
O3A-C18A-H18E	109.500000	H18D-C18A-H18E	109.500000
O3A-C18A-H18F	109.500000	H18D-C18A-H18F	109.500000
H18E-C18A-H18F	109.500000	P1A-C19A-H19F	109.500000
P1A-C19A-H19E	109.500000	H19F-C19A-H19E	109.500000
P1A-C19A-H19D	109.500000	H19F-C19A-H19D	109.500000
H19E-C19A-H19D	109.500000	P1A-C20A-H20D	109.500000
P1A-C20A-H20E	109.500000	H20D-C20A-H20E	109.500000
P1A-C20A-H20F	109.500000	H20D-C20A-H20F	109.500000
H20E-C20A-H20F	109.500000	P1A-C21A-H21D	109.500000
P1A-C21A-H21E	109.500000	H21D-C21A-H21E	109.500000

P1A-C21A-H21F	109.500000	H21D-C21A-H21F	109.500000
H21E-C21A-H21F	109.500000	C18B-O3B-C17	134.(4)
O3B-C18B-H18G	109.500000	O3B-C18B-H18H	109.500000
H18G-C18B-H18H	109.500000	O3B-C18B-H18I	109.500000
H18G-C18B-H18I	109.500000	H18H-C18B-H18I	109.500000
C22-O4-C23	110.3(11)	O4-C22-C22#1	106.9(13)
O4-C22-H22A	110.300000	C22#1-C22-H22A	110.300000
O4-C22-H22B	110.300000	C22#1-C22-H22B	110.300000
H22A-C22-H22B	108.600000	O4-C23-H23A	109.500000
O4-C23-H23B	109.500000	H23A-C23-H23B	109.500000
O4-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+1, -z+2

Table 6. Torsion angles (°) for Compound 41.

C1-N1-N2-C3	0.8(8)	W1-N1-N2-C3	-177.7(5)
W1A-N1-N2-C3	178.5(5)	C1-N1-N2-B1	-173.6(7)
W1-N1-N2-B1	7.9(9)	W1A-N1-N2-B1	4.2(9)
C4-N3-N4-C6	-1.4(9)	W1A-N3-N4-C6	-168.2(7)
W1-N3-N4-C6	-175.1(5)	C4-N3-N4-B1	168.9(7)
W1A-N3-N4-B1	2.1(10)	W1-N3-N4-B1	-4.8(10)
C7-N5-N6-C9	0.3(8)	W1A-N5-N6-C9	179.5(6)
W1-N5-N6-C9	-177.5(5)	C7-N5-N6-B1	-172.6(7)
W1A-N5-N6-B1	6.6(9)	W1-N5-N6-B1	9.5(9)
N2-N1-C1-C2	-0.2(9)	W1-N1-C1-C2	178.1(5)
W1A-N1-C1-C2	-177.2(6)	N1-C1-C2-C3	-0.4(9)
N1-N2-C3-C2	-1.1(9)	B1-N2-C3-C2	172.6(8)
C1-C2-C3-N2	1.0(9)	N4-N3-C4-C5	1.2(10)
W1A-N3-C4-C5	166.5(8)	W1-N3-C4-C5	174.3(6)
N3-C4-C5-C6	-0.5(11)	N3-N4-C6-C5	1.1(9)
B1-N4-C6-C5	-167.8(8)	C4-C5-C6-N4	-0.4(10)
N6-N5-C7-C8	-0.7(8)	W1A-N5-C7-C8	-179.7(6)
W1-N5-C7-C8	176.9(5)	N5-C7-C8-C9	0.7(9)

N5-N6-C9-C8	0.1(9)	B1-N6-C9-C8	172.1(7)
C7-C8-C9-N6	-0.5(9)	C14-C00S-C10-C11	4.7(13)
C14-C00S-C10-W1	-76.0(10)	C14-C00S-C10-W1A	-70.7(11)
C00S-C10-C11-C12	12.8(11)	W1-C10-C11-C12	124.8(6)
W1A-C10-C11-C12	121.7(7)	C00S-C10-C11-W1	-111.9(8)
C00S-C10-C11-W1A	-108.9(8)	C10-C11-C12-C15	83.1(9)
W1-C11-C12-C15	171.9(5)	W1A-C11-C12-C15	176.7(6)
C10-C11-C12-C13	-39.5(9)	W1-C11-C12-C13	49.2(9)
W1A-C11-C12-C13	54.0(8)	C15-C12-C13-C14	-73.8(8)
C11-C12-C13-C14	48.4(9)	C15-C12-C13-C16	51.9(9)
C11-C12-C13-C16	174.1(6)	C10-C00S-C14-C13	7.1(14)
C16-C13-C14-C00S	-158.9(9)	C12-C13-C14-C00S	-33.7(11)
C14-C13-C16-C17	-170.2(8)	C12-C13-C16-C17	65.0(10)
C13-C16-C17-O2	19.(3)	C13-C16-C17-O2A	-85.(3)
C13-C16-C17-O3	-156.1(9)	C13-C16-C17-O2B	-1.(9)

C13-C16-C17-O3A	92.4(19)	C13-C16-C17-O3B	118.9(15)
C6-N4-B1-N2	-132.1(8)	N3-N4-B1-N2	59.9(9)
C6-N4-B1-N6	110.2(9)	N3-N4-B1-N6	-57.8(9)
C3-N2-B1-N4	125.0(8)	N1-N2-B1-N4	-61.9(9)
C3-N2-B1-N6	-118.6(8)	N1-N2-B1-N6	54.5(9)
C9-N6-B1-N4	-116.7(8)	N5-N6-B1-N4	54.6(9)
C9-N6-B1-N2	123.8(8)	N5-N6-B1-N2	-64.9(9)
O2-C17-O3-C18	9.(3)	C16-C17-O3-C18	-175.7(11)
O2A-C17-O3A-C18A	-5.(5)	C16-C17-O3A-C18A	177.(3)
O2B-C17-O3B-C18B	-24.(7)	C16-C17-O3B-C18B	-167.(5)
C23-O4-C22-C22#1	-175.0(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y+1, -z+2

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 41.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.037(3)	0.050(3)	0.067(4)	-0.010(3)	0.019(3)	-0.005(3)
N1	0.041(3)	0.034(3)	0.043(3)	0.002(3)	0.017(3)	0.000(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	0.038(4)	0.032(3)	0.050(4)	0.004(3)	0.014(3)	-0.002(3)
N3	0.037(3)	0.033(3)	0.063(4)	-0.003(3)	0.019(3)	0.003(3)
N4	0.039(4)	0.034(4)	0.047(4)	-0.009(3)	0.013(3)	-0.005(3)
N5	0.041(4)	0.033(3)	0.040(3)	-0.003(3)	0.016(3)	-0.004(3)
N6	0.033(3)	0.036(3)	0.040(3)	-0.001(3)	0.012(3)	-0.002(3)
N7	0.038(4)	0.031(3)	0.048(4)	-0.004(3)	0.012(3)	0.001(3)
N8	0.051(4)	0.036(4)	0.067(5)	-0.013(4)	0.014(4)	-0.003(3)
C00S	0.061(6)	0.049(5)	0.040(5)	-0.003(4)	0.006(4)	-0.013(5)
C1	0.056(5)	0.043(5)	0.050(5)	0.001(4)	0.025(4)	0.007(4)
C2	0.051(5)	0.050(5)	0.069(6)	0.018(5)	0.035(4)	0.011(4)
C3	0.037(4)	0.039(4)	0.064(5)	0.013(4)	0.023(4)	0.005(4)
C4	0.036(4)	0.046(5)	0.071(6)	-0.015(4)	0.016(4)	-0.002(4)
C5	0.057(5)	0.038(5)	0.074(6)	-0.016(4)	0.031(5)	-0.002(4)
C6	0.049(5)	0.033(4)	0.054(5)	-0.010(4)	0.019(4)	-0.007(4)
C7	0.044(5)	0.038(4)	0.048(5)	-0.008(4)	0.019(4)	-0.009(4)
C8	0.059(5)	0.039(4)	0.038(4)	-0.006(4)	0.019(4)	-0.009(4)
C9	0.046(5)	0.034(4)	0.037(4)	-0.003(3)	0.010(4)	0.001(4)
C10	0.051(5)	0.045(5)	0.044(4)	-0.005(4)	0.012(4)	-0.007(4)
C11	0.039(4)	0.038(4)	0.040(4)	-0.010(3)	0.016(3)	-0.005(3)
C12	0.046(4)	0.034(4)	0.033(4)	-0.004(3)	0.006(3)	-0.008(3)
C13	0.040(4)	0.039(4)	0.052(5)	-0.003(4)	0.016(4)	-0.006(4)
C14	0.040(5)	0.053(5)	0.052(5)	0.007(4)	0.001(4)	0.001(4)
C15	0.034(4)	0.037(5)	0.052(5)	0.001(4)	0.004(4)	0.001(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	0.036(4)	0.053(5)	0.055(5)	0.001(4)	0.009(4)	-0.005(4)
C17	0.051(6)	0.074(7)	0.059(6)	0.000(5)	0.017(5)	-0.014(5)
B1	0.031(5)	0.040(5)	0.048(5)	-0.002(4)	0.011(4)	-0.003(4)
W1	0.0235(5)	0.0244(4)	0.0302(5)	-0.0028(3)	0.0098(2)	-0.0013(3)
P1	0.047(2)	0.0498(15)	0.059(4)	0.018(2)	0.014(3)	0.0057(15)
O2	0.098(18)	0.097(19)	0.050(12)	0.010(9)	0.023(11)	-0.041(13)
O3	0.072(7)	0.046(6)	0.048(5)	0.016(4)	0.023(5)	-0.007(5)
C18	0.086(12)	0.089(13)	0.064(9)	0.026(9)	0.041(9)	0.009(10)
C19	0.070(7)	0.050(5)	0.059(5)	0.012(4)	0.020(4)	0.003(4)
C20	0.070(7)	0.050(5)	0.059(5)	0.012(4)	0.020(4)	0.003(4)
C21	0.070(7)	0.050(5)	0.059(5)	0.012(4)	0.020(4)	0.003(4)
W1A	0.099(5)	0.057(2)	0.088(3)	0.001(2)	-0.007(2)	-0.001(2)
P1A	0.047(2)	0.0498(15)	0.059(4)	0.018(2)	0.014(3)	0.0057(15)
O2A	0.098(18)	0.097(19)	0.050(12)	0.010(9)	0.023(11)	-0.041(13)
O3A	0.072(7)	0.046(6)	0.048(5)	0.016(4)	0.023(5)	-0.007(5)
C18A	0.086(12)	0.089(13)	0.064(9)	0.026(9)	0.041(9)	0.009(10)
C19A	0.070(7)	0.050(5)	0.059(5)	0.012(4)	0.020(4)	0.003(4)
C20A	0.070(7)	0.050(5)	0.059(5)	0.012(4)	0.020(4)	0.003(4)
C21A	0.070(7)	0.050(5)	0.059(5)	0.012(4)	0.020(4)	0.003(4)
O2B	0.098(18)	0.097(19)	0.050(12)	0.010(9)	0.023(11)	-0.041(13)
O3B	0.072(7)	0.046(6)	0.048(5)	0.016(4)	0.023(5)	-0.007(5)
C18B	0.086(12)	0.089(13)	0.064(9)	0.026(9)	0.041(9)	0.009(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	0.044(6)	0.051(6)	0.068(7)	0.010(5)	0.023(5)	0.002(5)
C22	0.028(7)	0.052(9)	0.050(8)	0.009(7)	0.009(6)	0.005(6)
C23	0.068(11)	0.051(9)	0.054(9)	-0.001(8)	0.024(8)	-0.001(8)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 41.

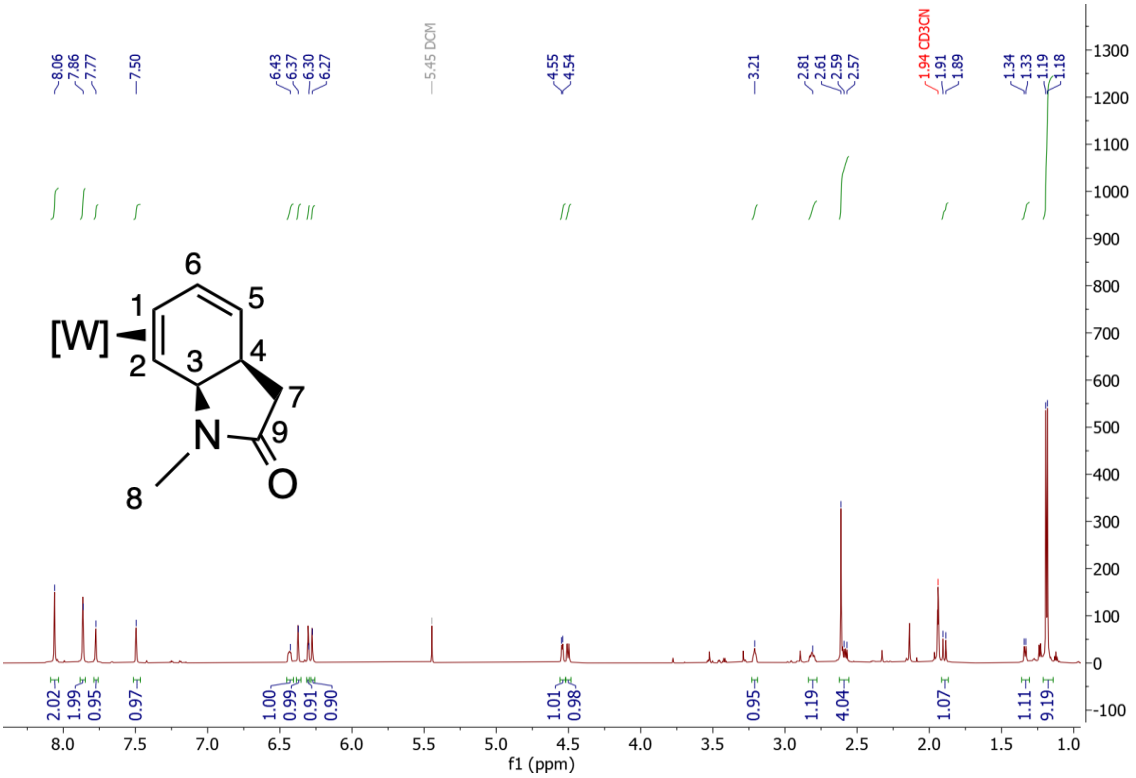
	x/a	y/b	z/c	U(eq)
H00S	0.1047	0.5577	0.3502	0.068000
H1	0.4173	0.6223	0.4553	0.059000
H2	0.5840	0.6745	0.5153	0.065000
H3	0.6294	0.7653	0.6703	0.056000
H4	0.2154	0.9164	0.6326	0.065000
H5	0.3174	1.0565	0.7508	0.067000
H6	0.4783	0.9873	0.8087	0.056000
H7	0.3154	0.4996	0.7607	0.053000
H8	0.4587	0.4886	0.9163	0.056000
H9	0.5657	0.6329	0.9095	0.051000
H10	0.2707	0.5576	0.4201	0.060000
H10A	0.2710	0.5624	0.4208	0.060000
H11	0.3566	0.4798	0.5568	0.048000
H11A	0.3570	0.4806	0.5577	0.048000
H12	0.2841	0.3946	0.6470	0.051000

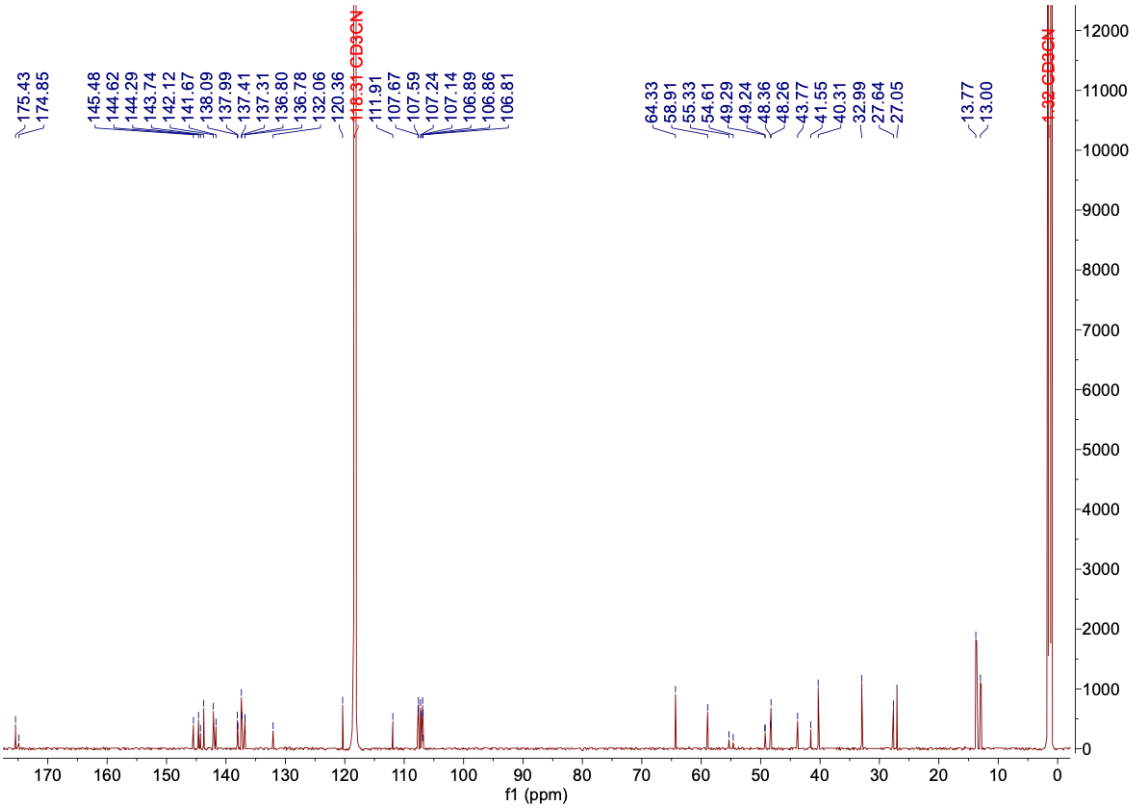
	x/a	y/b	z/c	U(eq)
H13	0.1447	0.4863	0.5895	0.054000
H14	0.0354	0.4435	0.4113	0.067000
H16A	0.0358	0.3370	0.5416	0.063000
H16B	0.1109	0.2592	0.5332	0.063000
H1A	0.558(5)	0.790(6)	0.787(5)	0.034(19)
H18A	0.1596	0.0740	0.7753	0.115000
H18B	0.1126	0.1805	0.7945	0.115000
H18C	0.2177	0.1853	0.8145	0.115000
H19A	0.2255	0.7961	0.2818	0.095000
H19B	0.2264	0.6728	0.3188	0.095000
H19C	0.3184	0.7452	0.3623	0.095000
H20A	0.3254	0.9498	0.4725	0.095000
H20B	0.2338	0.9859	0.4778	0.095000
H20C	0.2349	0.9807	0.3785	0.095000
H21A	0.0823	0.9025	0.3698	0.095000
H21B	0.1375	0.9150	0.4815	0.095000
H21C	0.0808	0.8043	0.4361	0.095000
H18D	0.0791	0.3509	0.8256	0.115000
H18E	0.1832	0.3531	0.8421	0.115000
H18F	0.1258	0.2402	0.8128	0.115000
H19F	0.2055	0.6933	0.3101	0.095000
H19E	0.2936	0.7712	0.3397	0.095000
H19D	0.1925	0.8219	0.2831	0.095000

	x/a	y/b	z/c	U(eq)
H20D	0.2643	0.9793	0.5041	0.095000
H20E	0.2639	0.9754	0.4040	0.095000
H20F	0.3500	0.9279	0.4950	0.095000
H21D	0.0738	0.7379	0.3626	0.095000
H21E	0.0834	0.8545	0.3205	0.095000
H21F	0.0795	0.8498	0.4185	0.095000
H18G	0.0096	0.3144	0.7948	0.115000
H18H	0.1125	0.3602	0.8367	0.115000
H18I	0.0939	0.2297	0.8289	0.115000
H22A	-0.0434	0.3964	0.9581	0.056000
H22B	-0.0537	0.5080	0.8993	0.056000
H23A	0.0098	0.4280	0.8127	0.089000
H23B	0.0263	0.3117	0.8657	0.089000
H23C	0.1106	0.3753	0.8625	0.089000

NMR Data Chapter 4

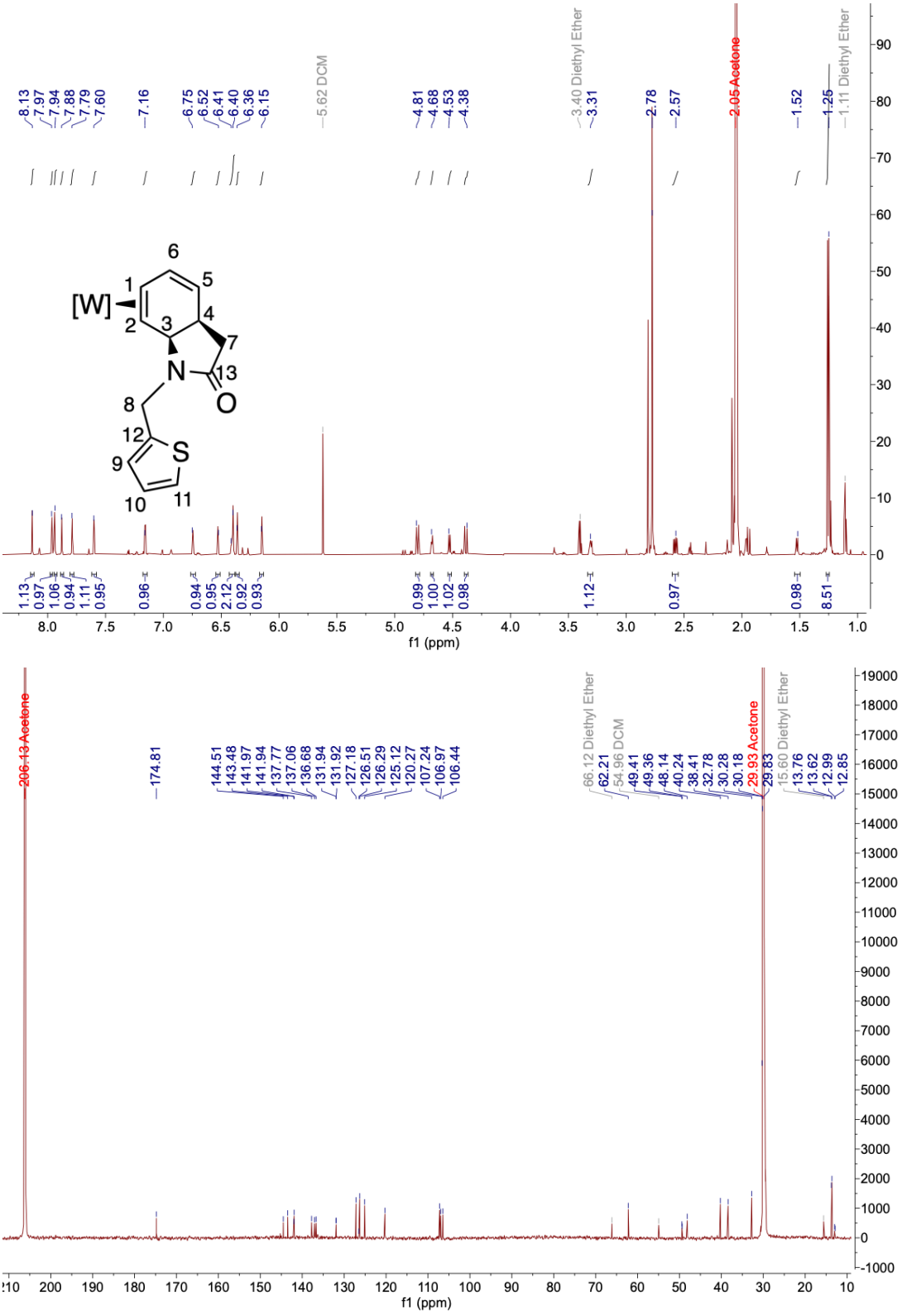
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.4:



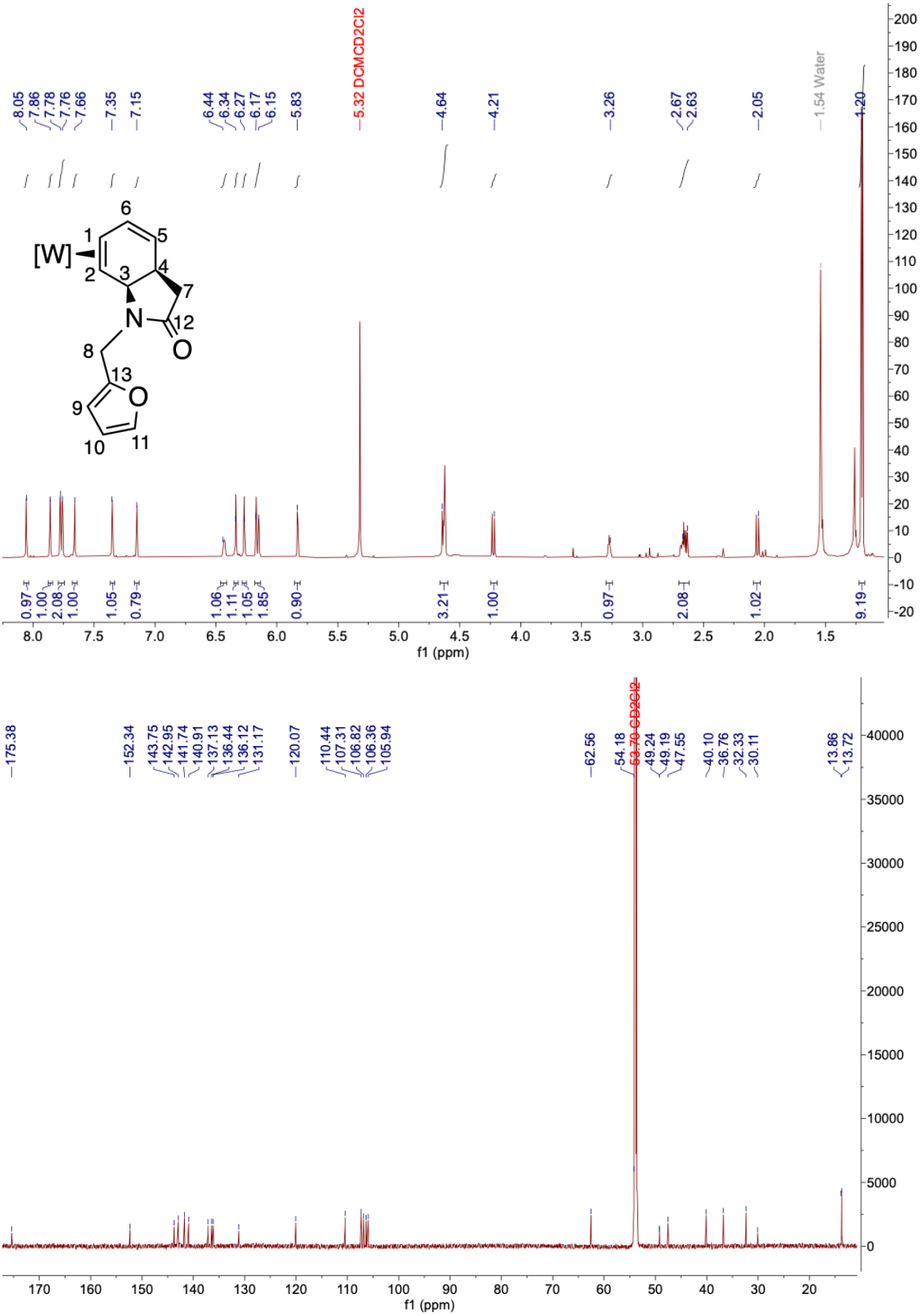


Compound ring-walks during the course of the 2D NMR experiment

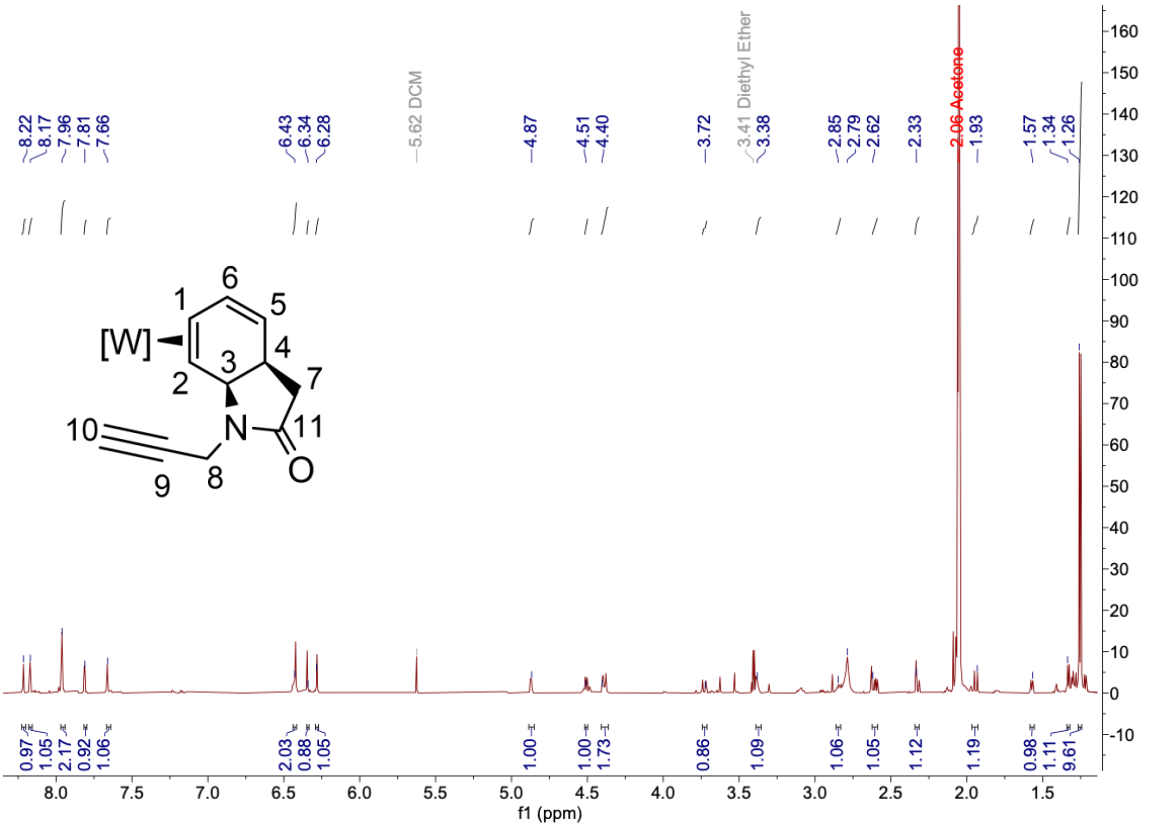
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.7:

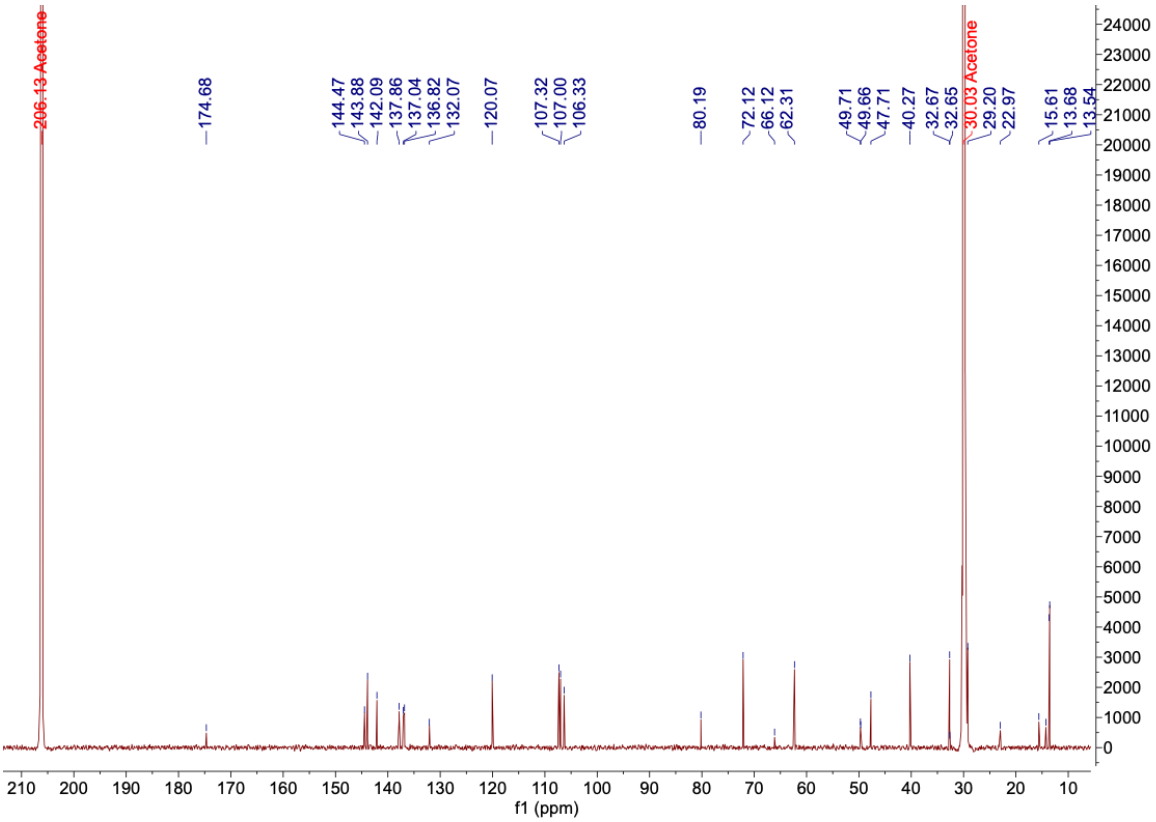


^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 4.8:

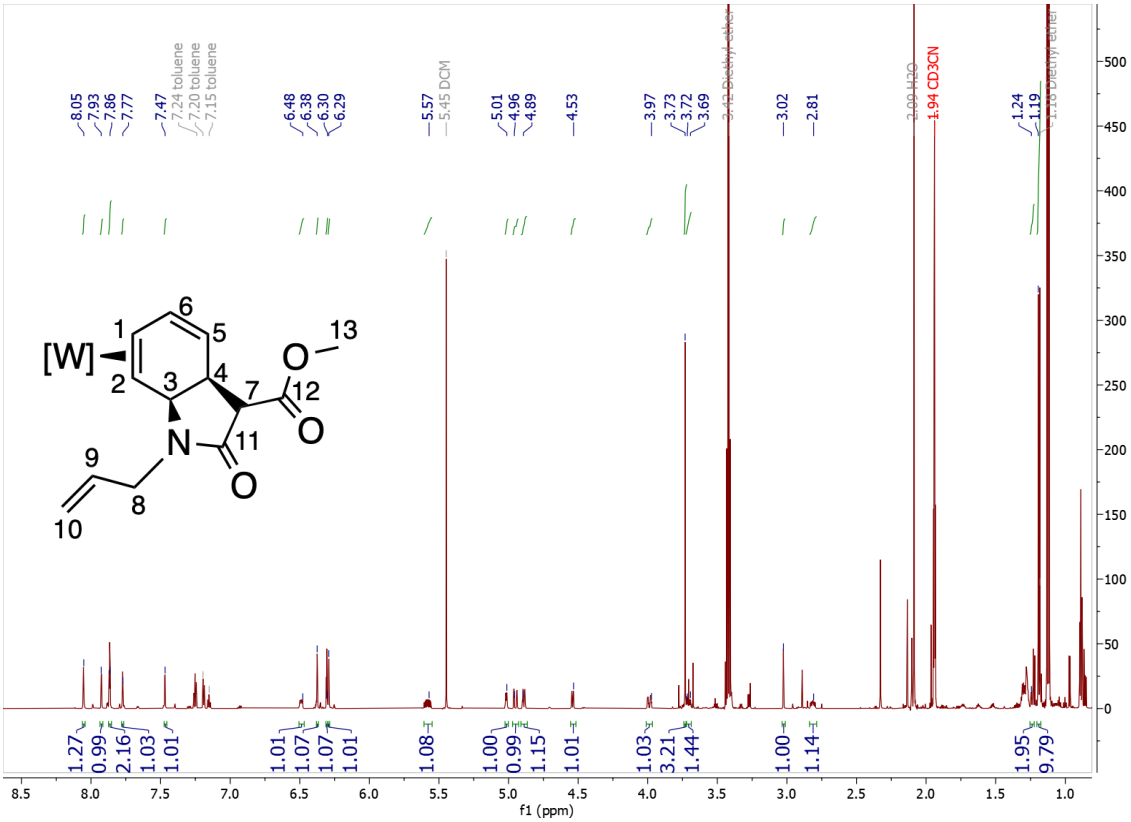


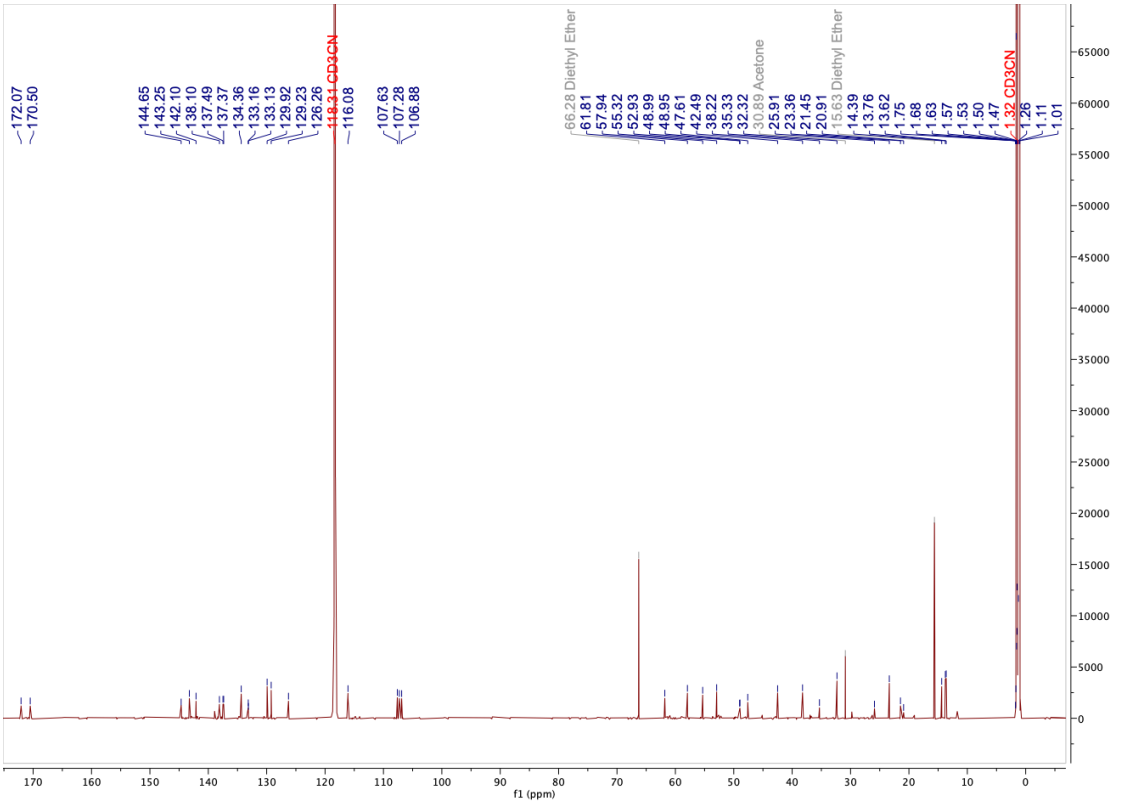
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.9:



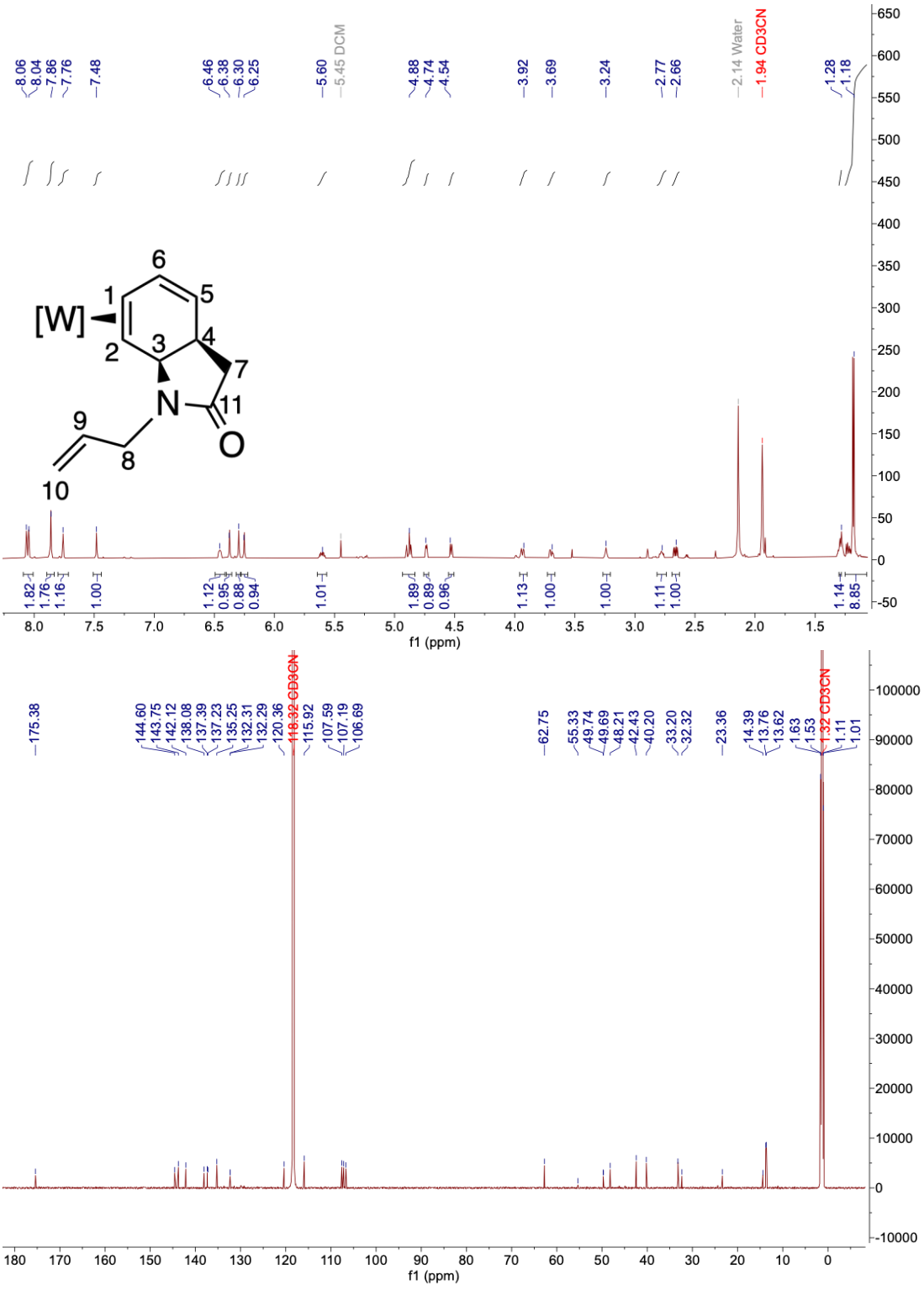


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.10:

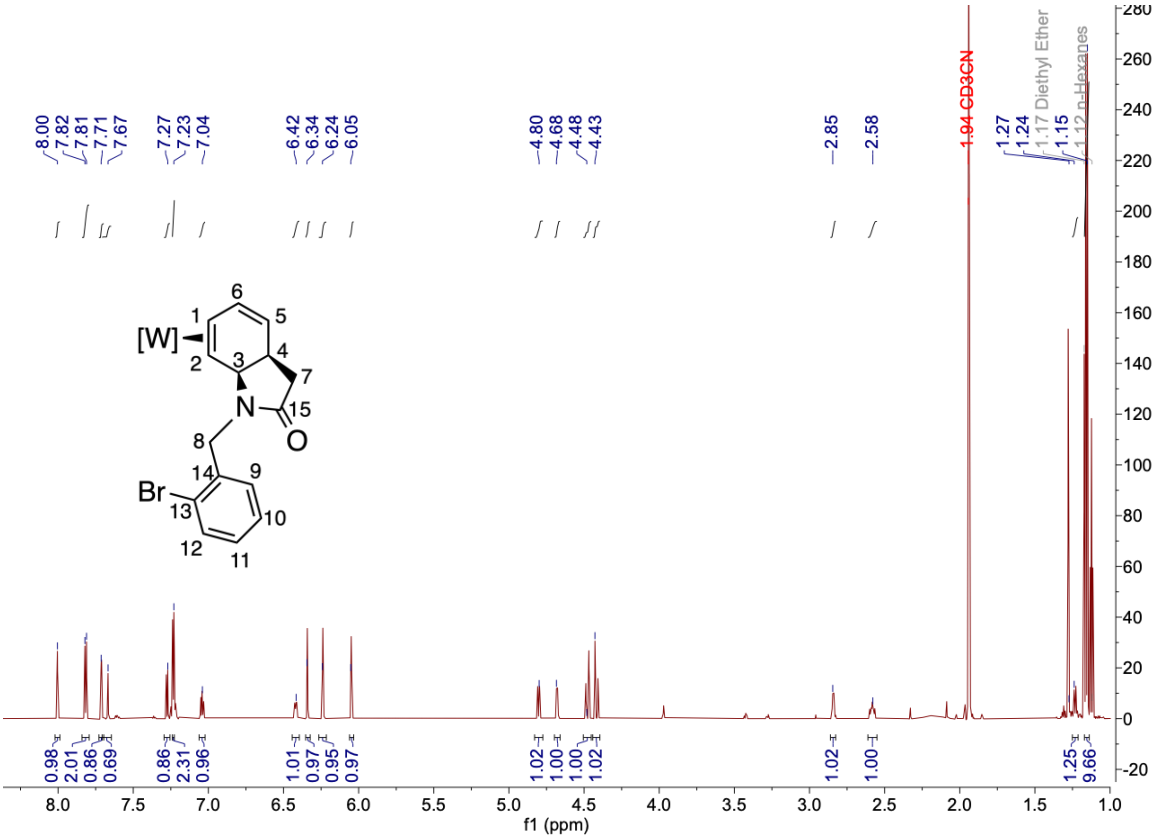


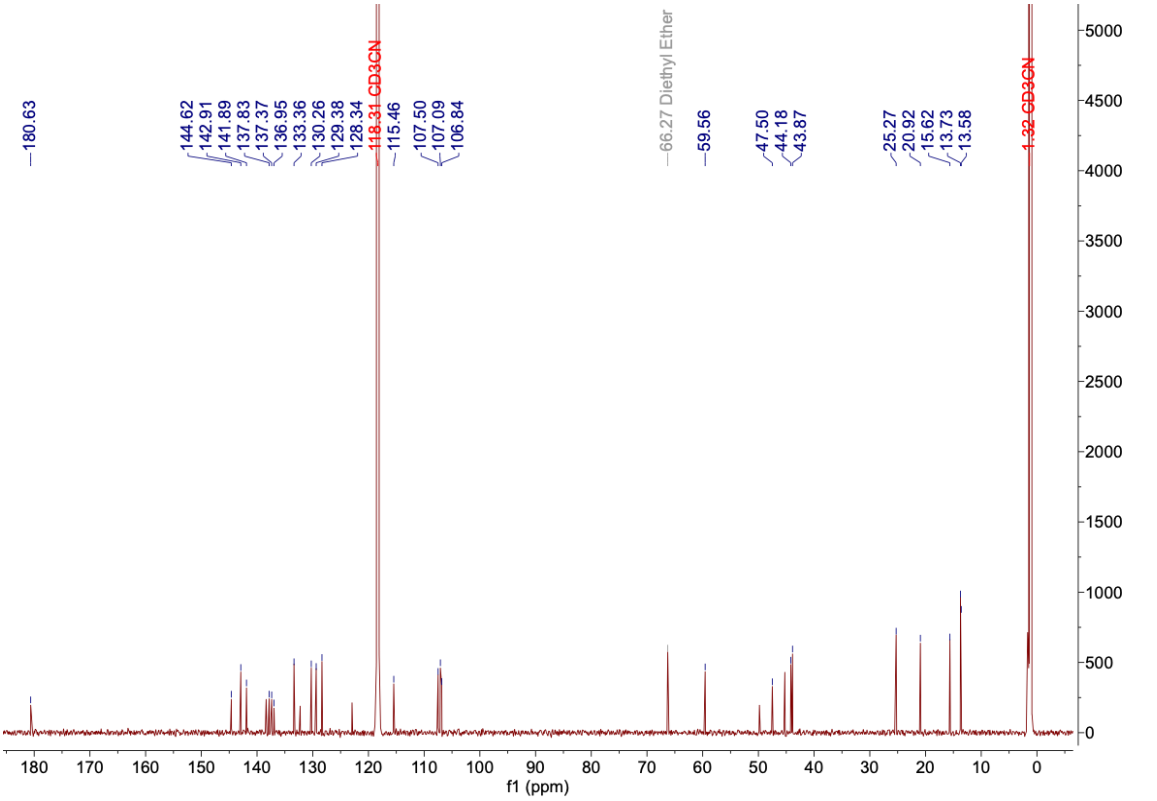


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.11:

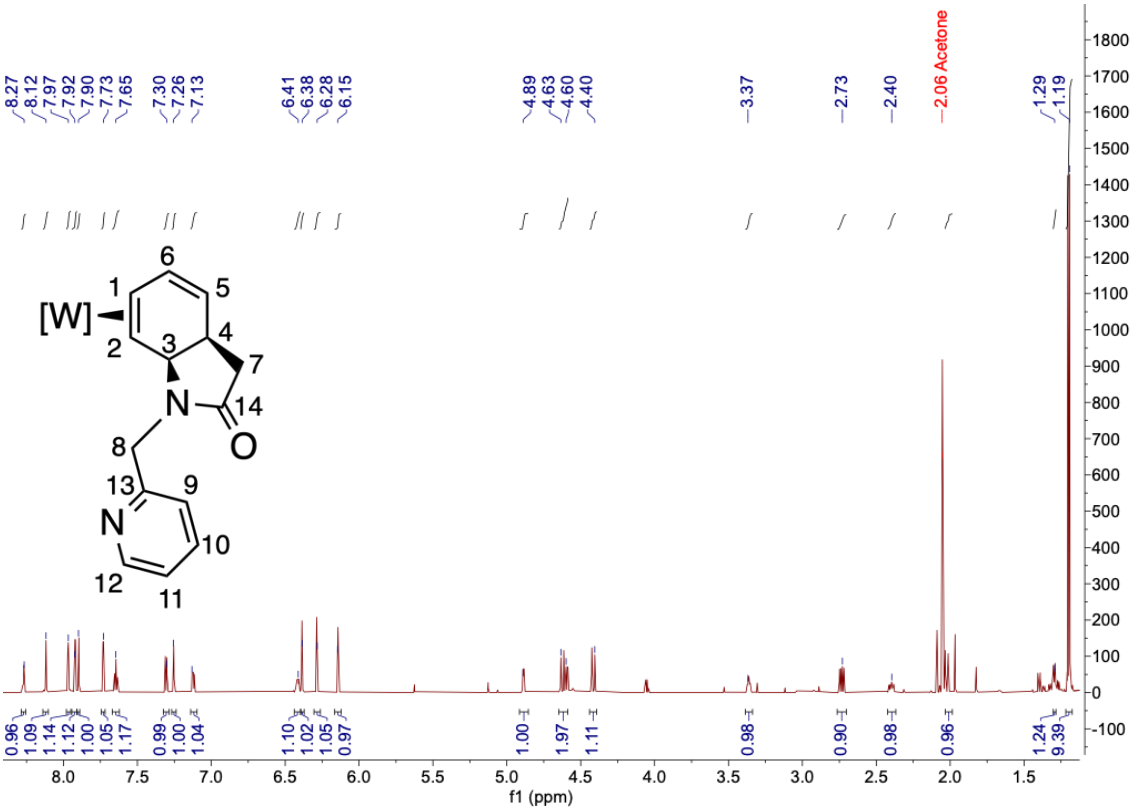

8.06
8.04
7.86
7.76
7.48
6.46
6.38
6.30
6.25
5.60
5.45 DCM
4.88
4.74
4.54
3.92
3.69
3.24
2.77
2.66
2.14 Water
1.94 CD3CN
1.28
1.18
[W]
1
2
3
4
5
6
7
N
9
8
10
11
O
1.82
1.76
1.16
1.00
1.12
0.95
0.88
0.94
1.01
1.89
0.89
0.96
1.13
1.00
1.00
1.11
1.00
1.14
8.85
f1 (ppm)
175.38
144.60
143.75
142.12
138.08
137.39
137.23
135.25
132.31
132.29
120.36
118.32 CD3CN
115.92
107.59
107.19
106.69
62.75
55.33
49.74
49.69
48.21
42.43
40.20
33.20
32.32
23.36
14.39
13.76
13.62
1.63
1.53
1.32 CD3CN
1.11
1.01
f1 (ppm)

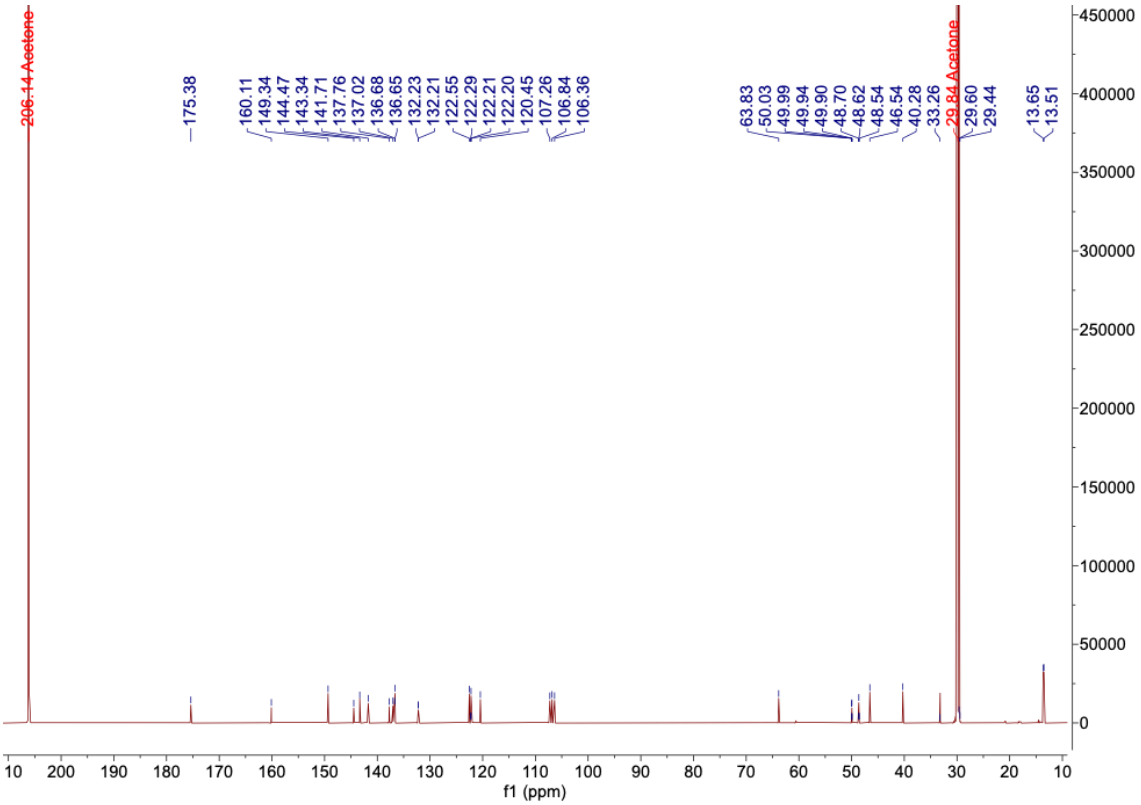
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.12:



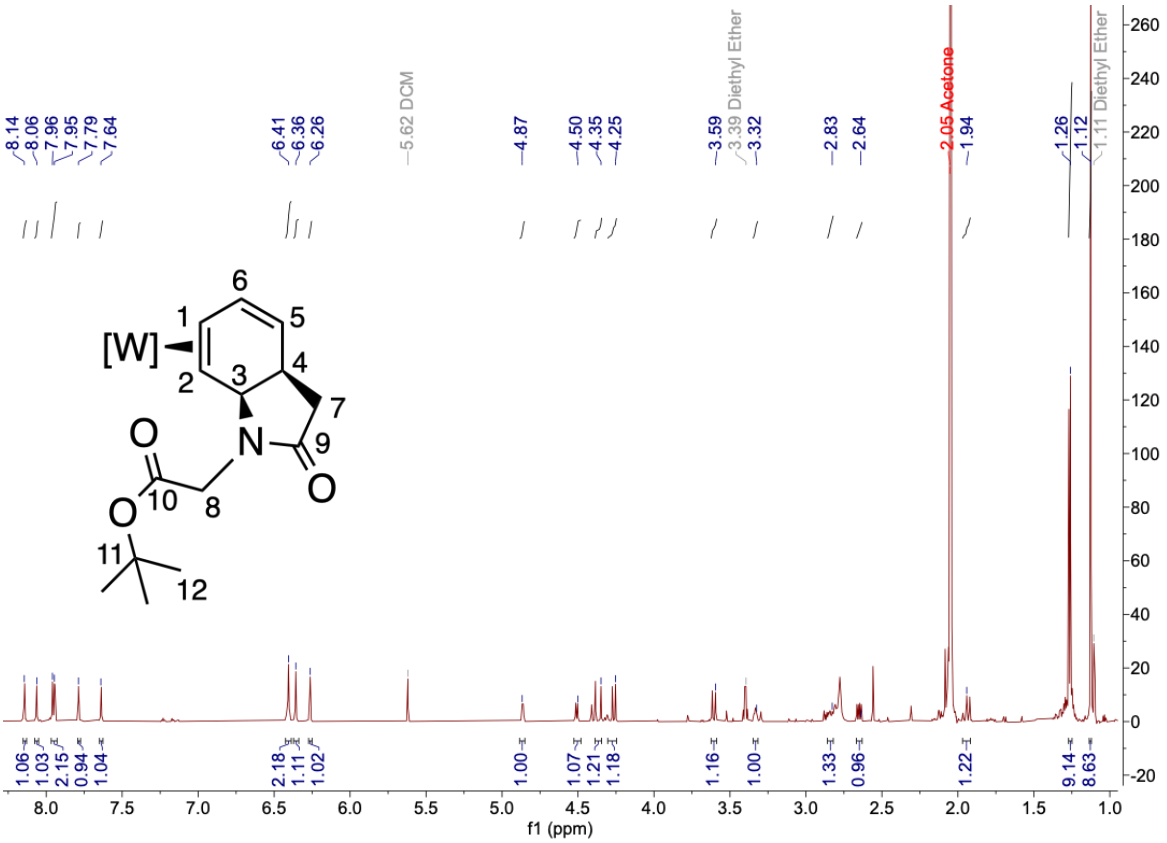


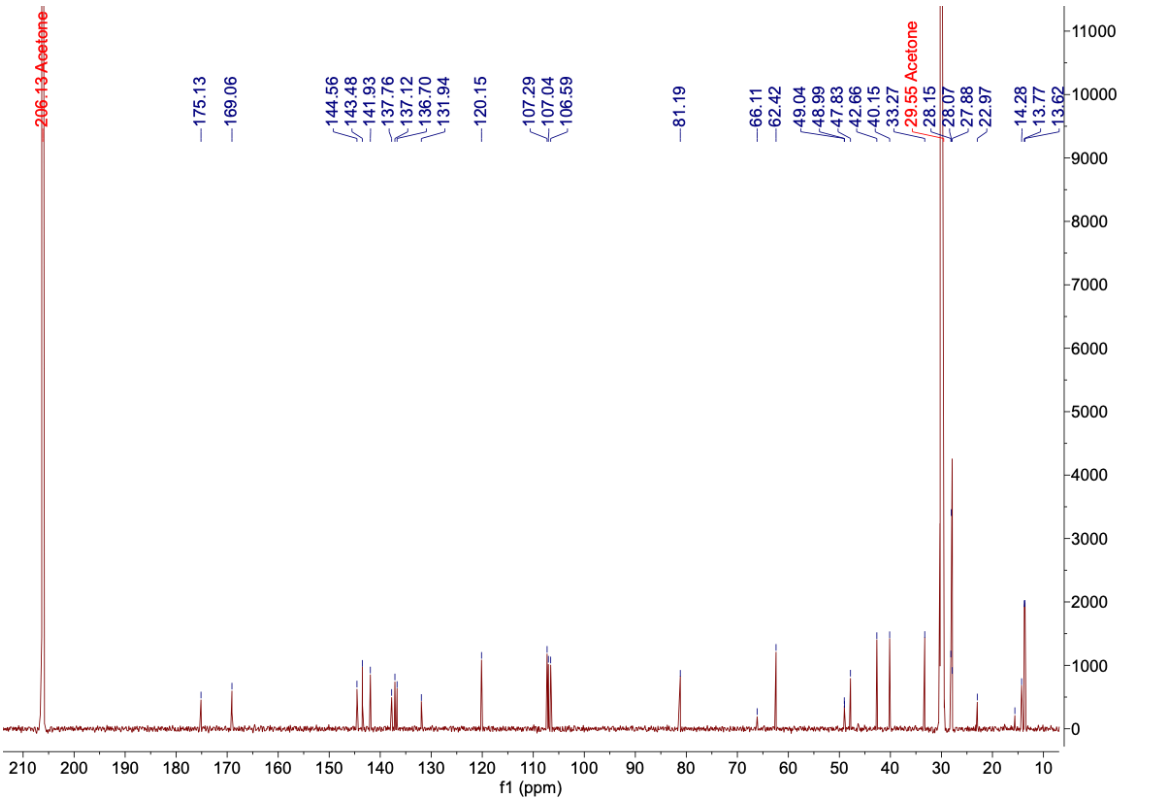
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.13:



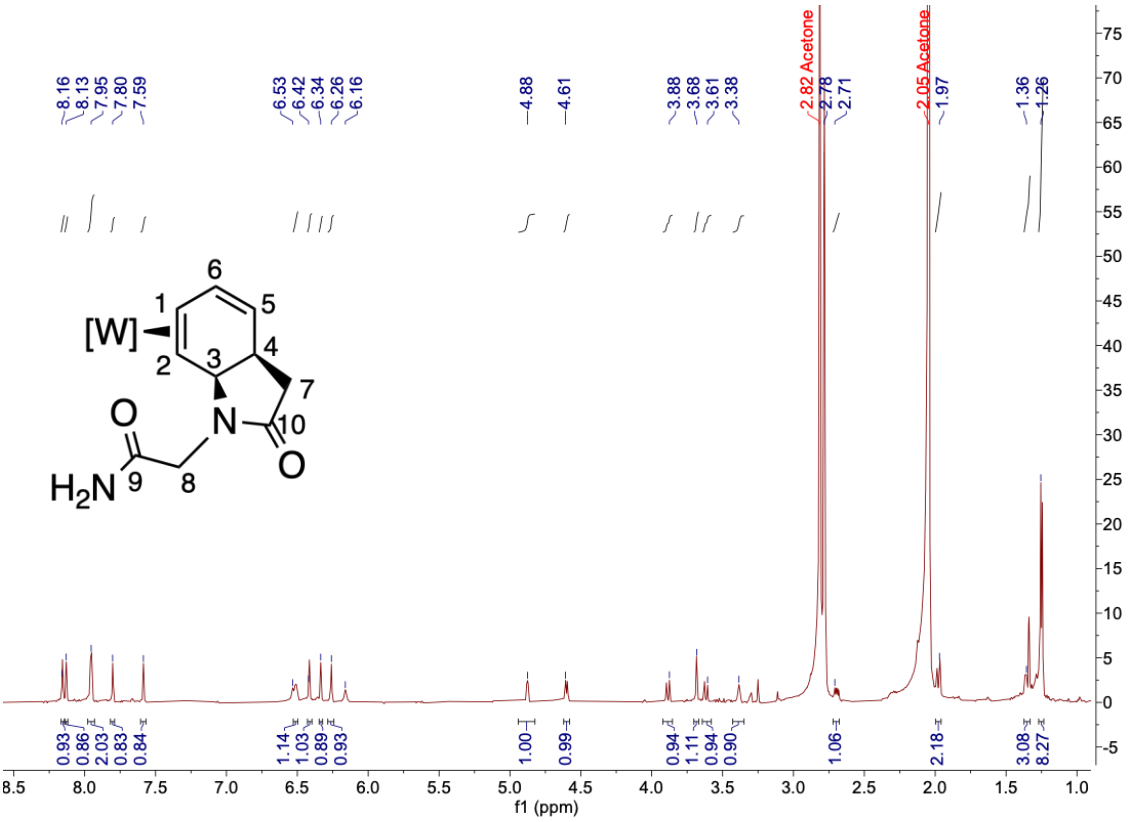


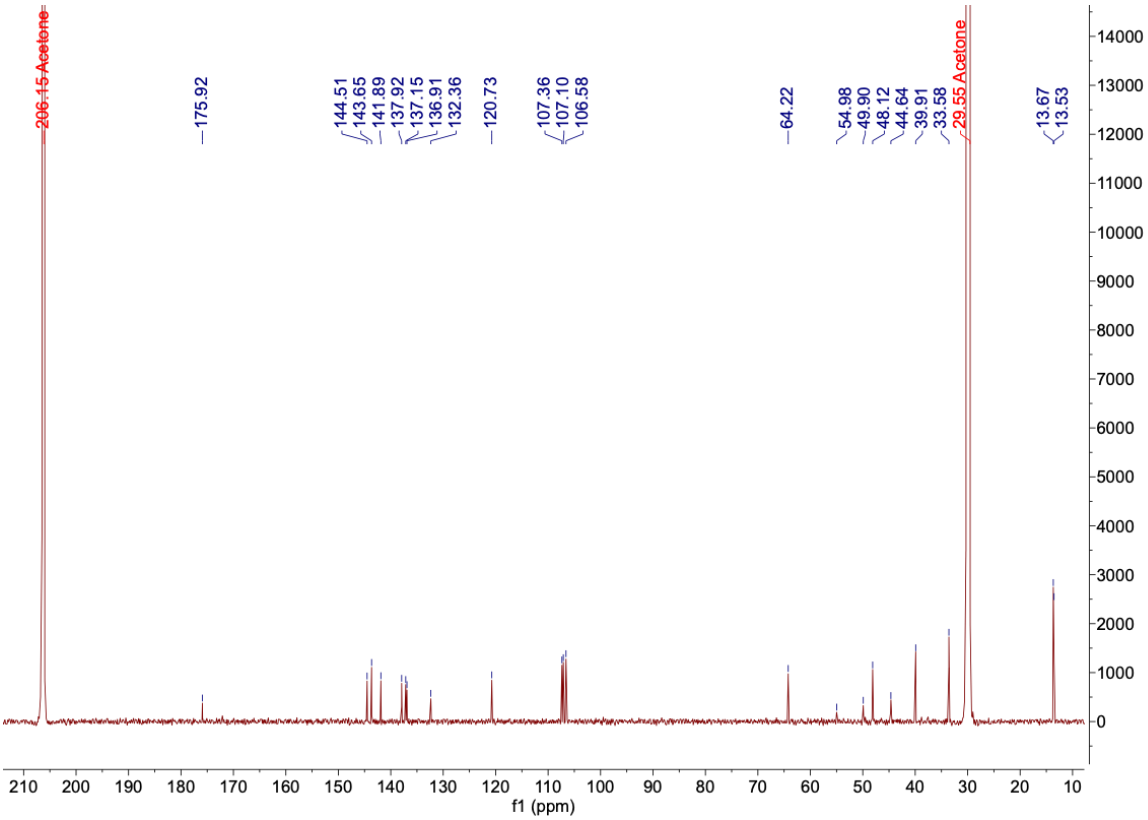
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.14:



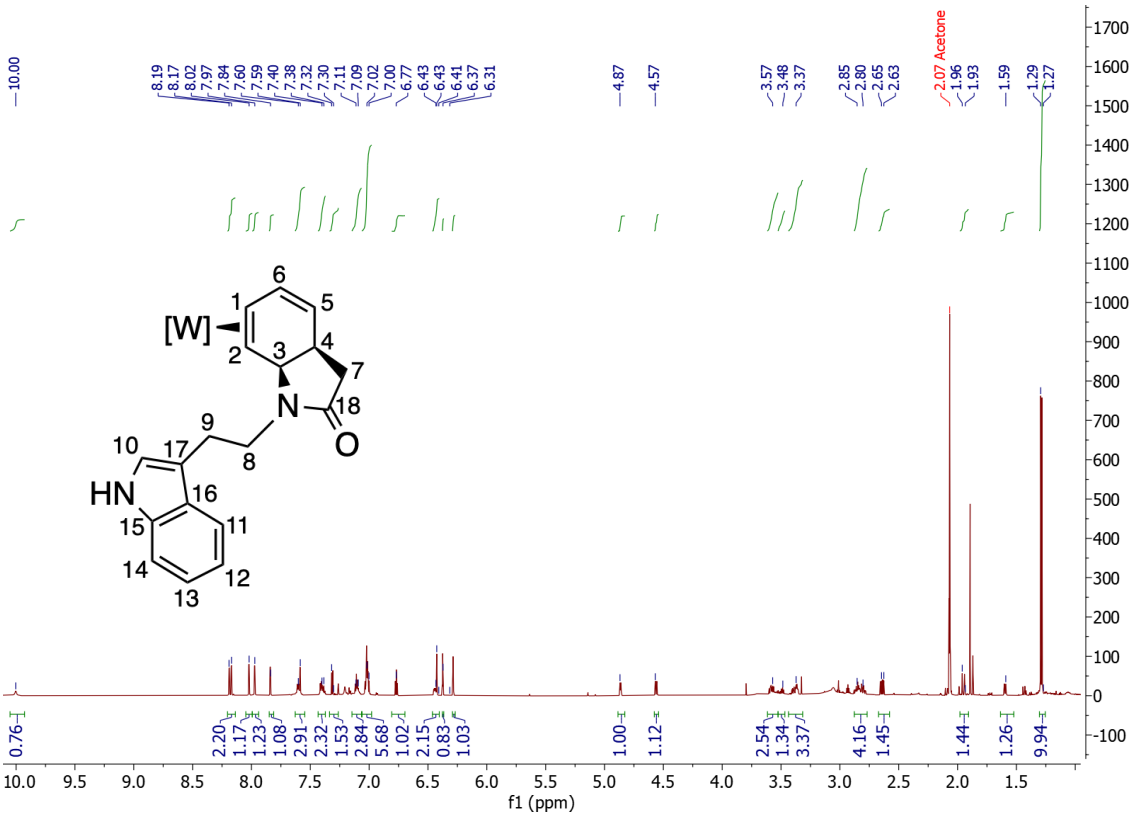


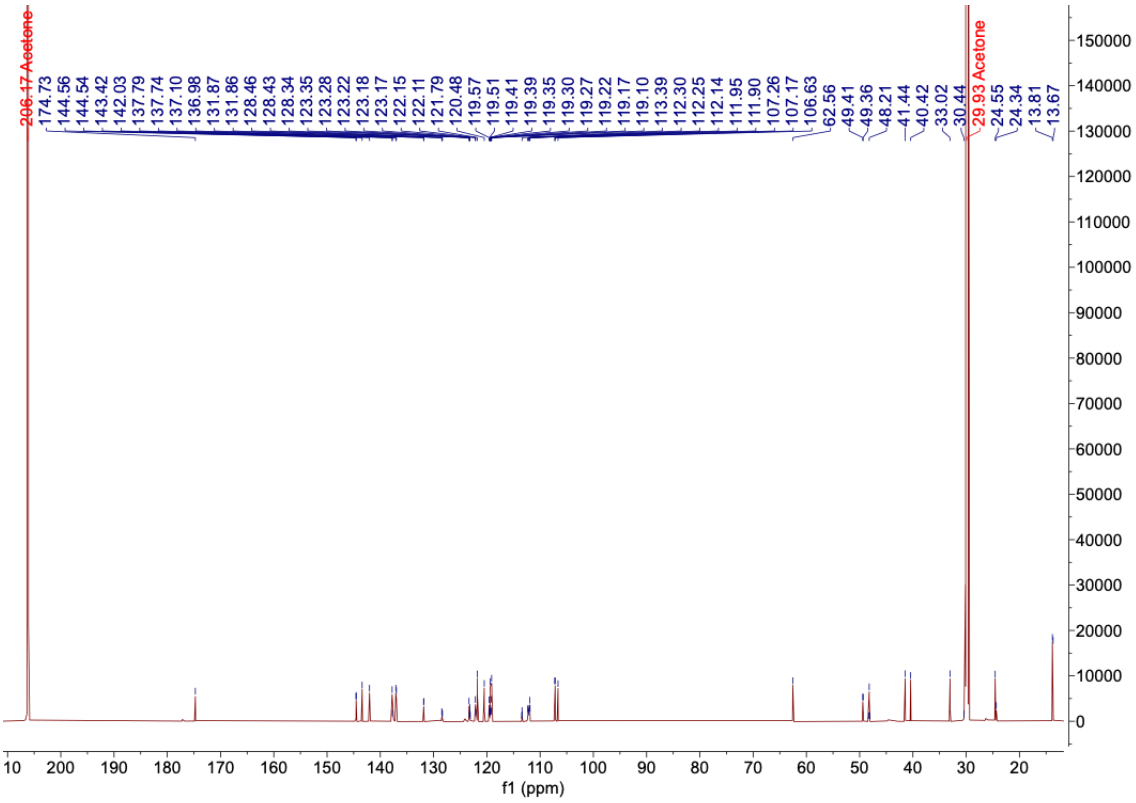
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.15:



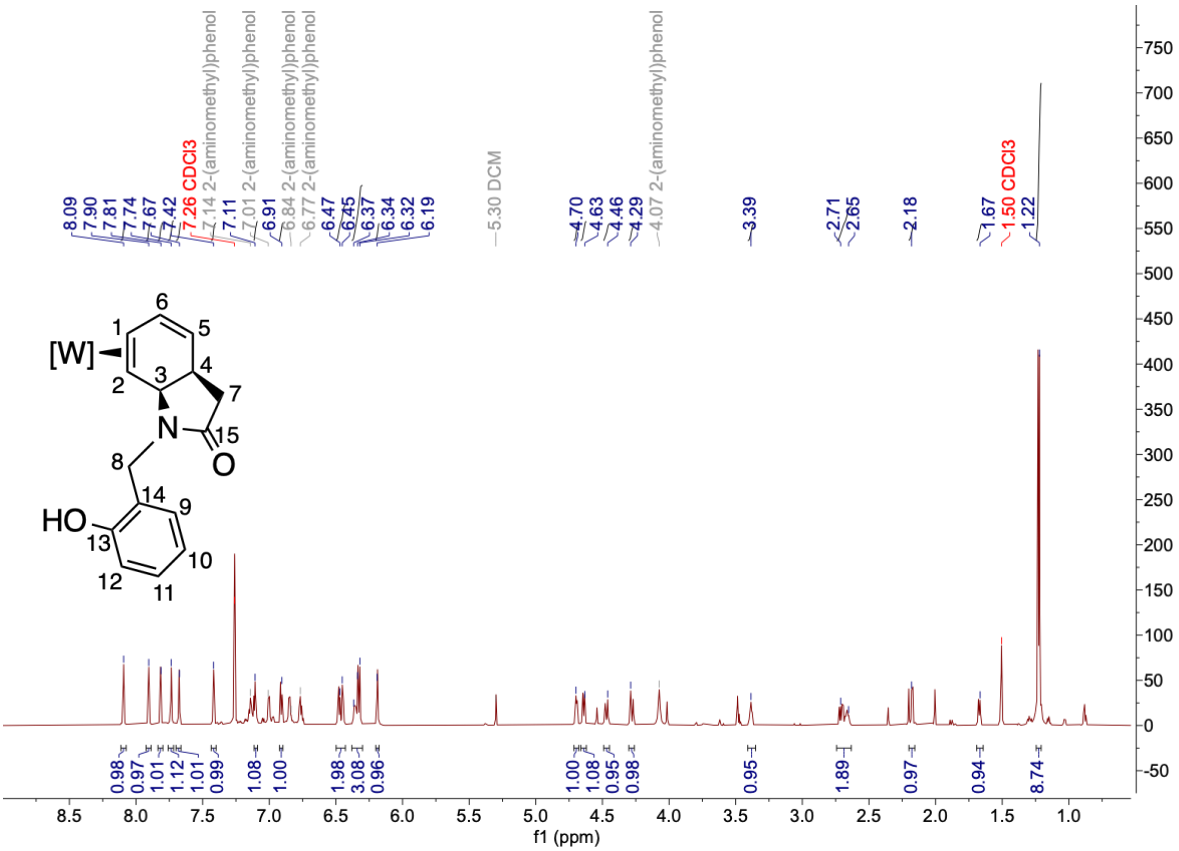


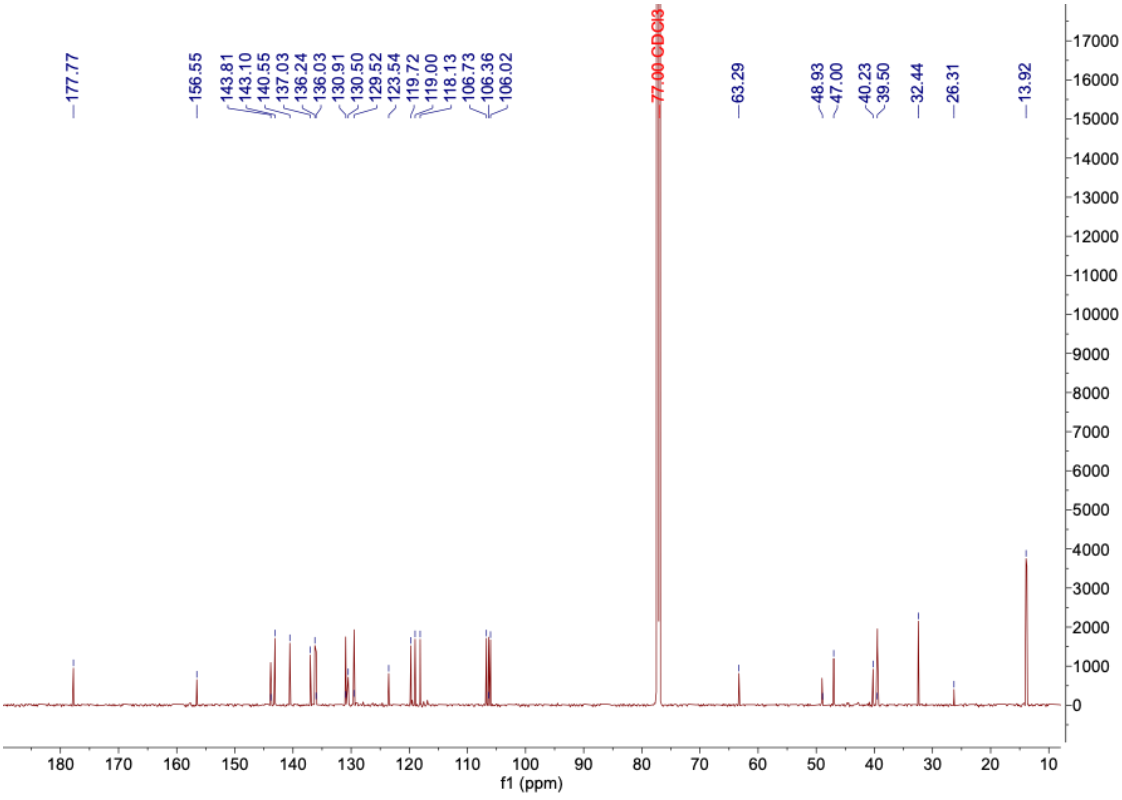
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.16:



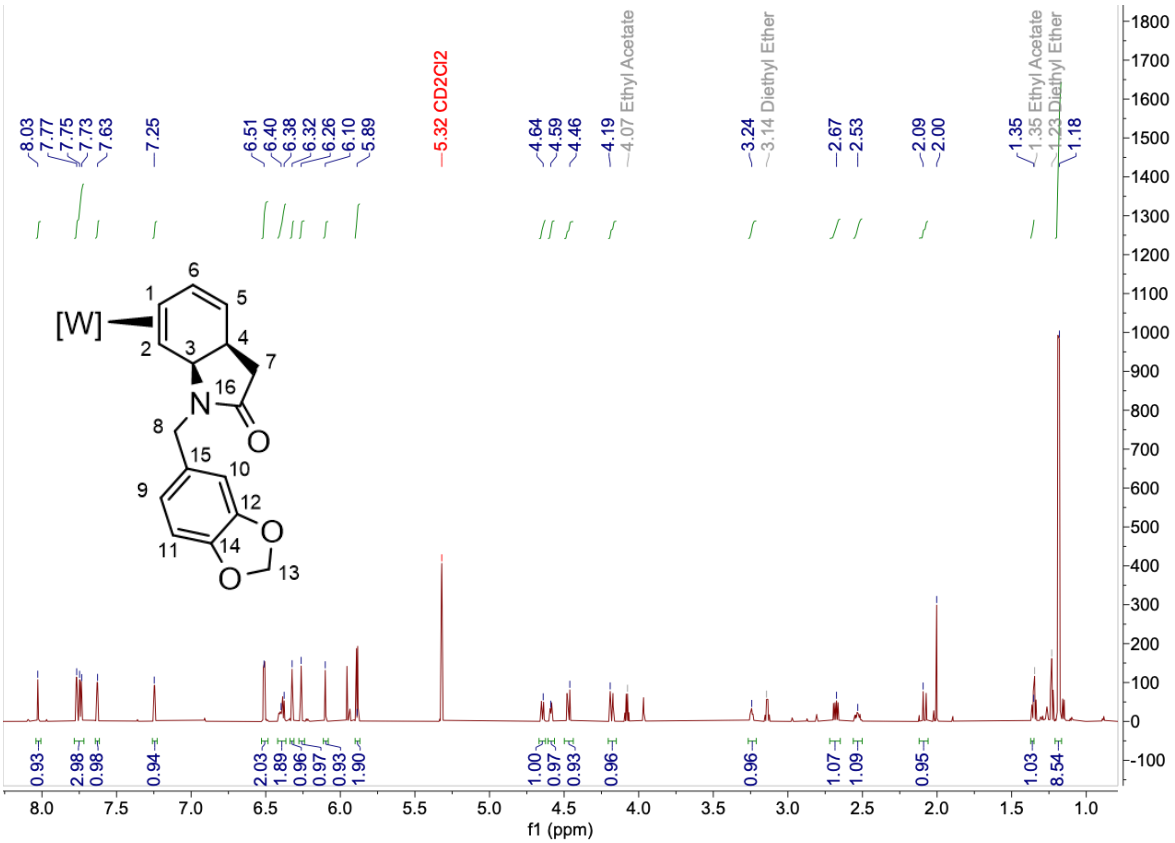


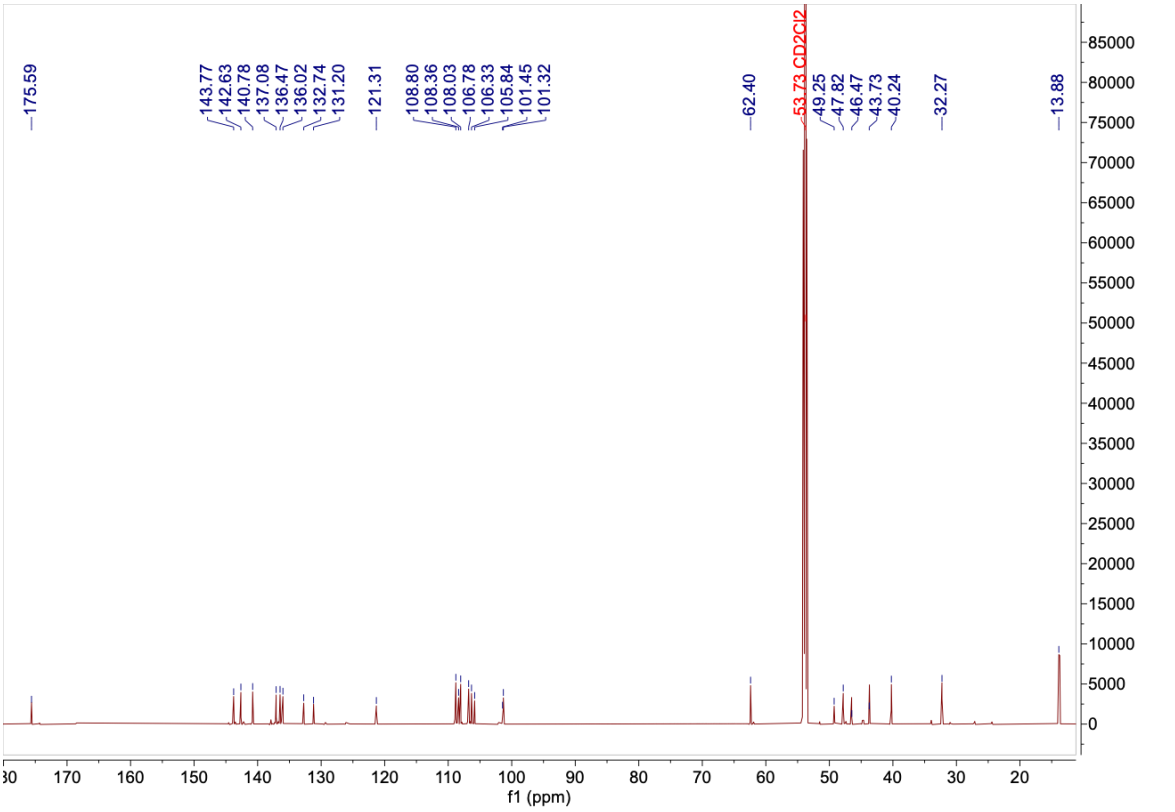
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.17:



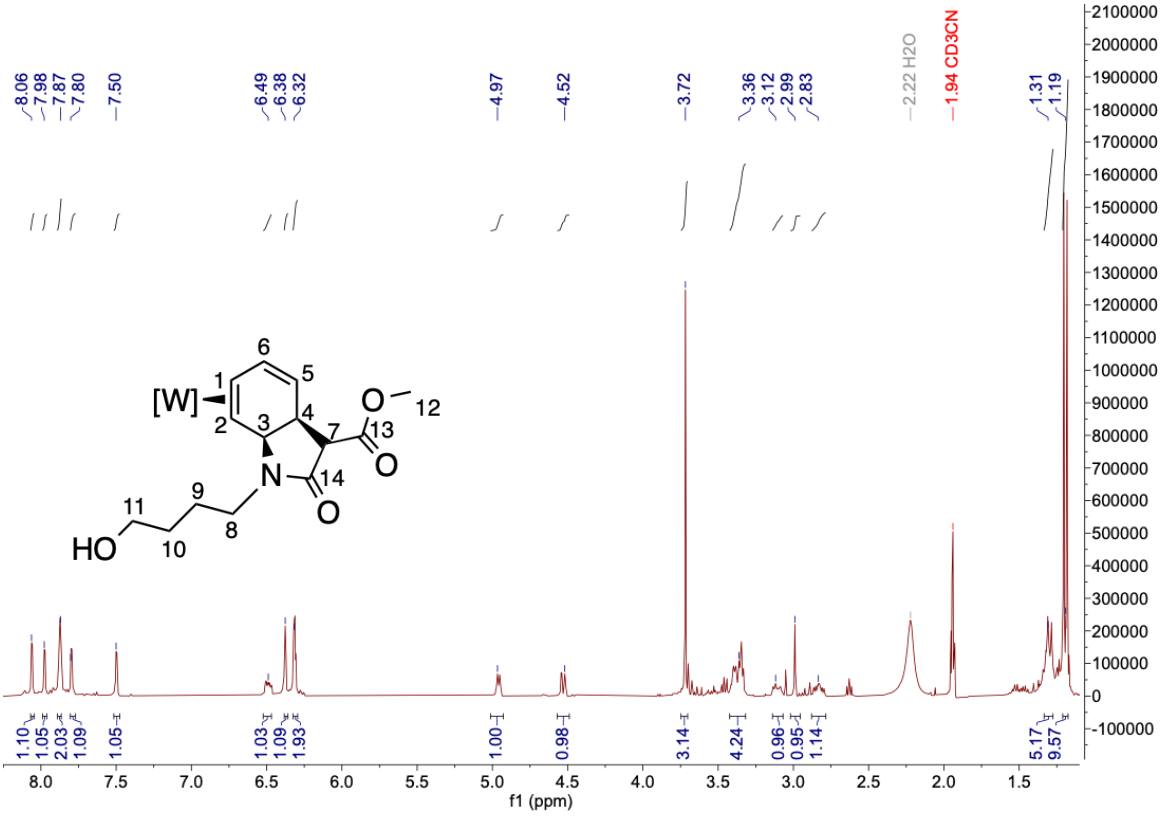


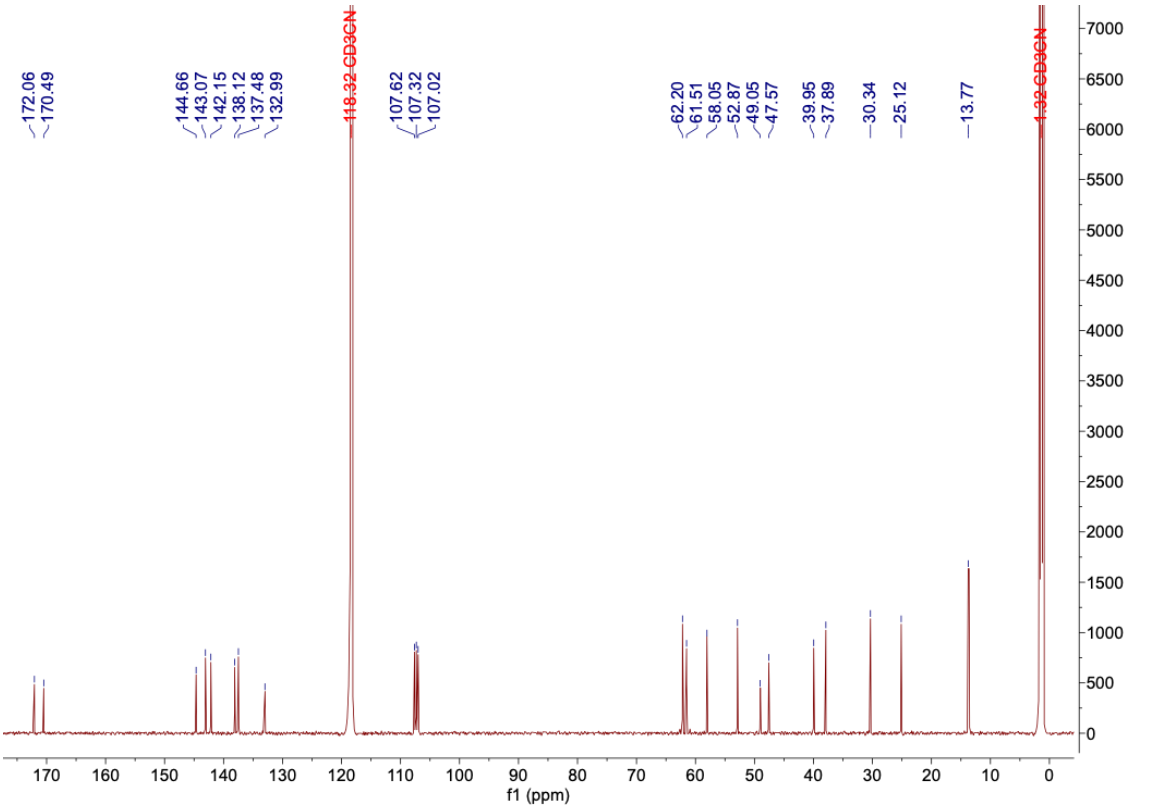
^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 4.19:



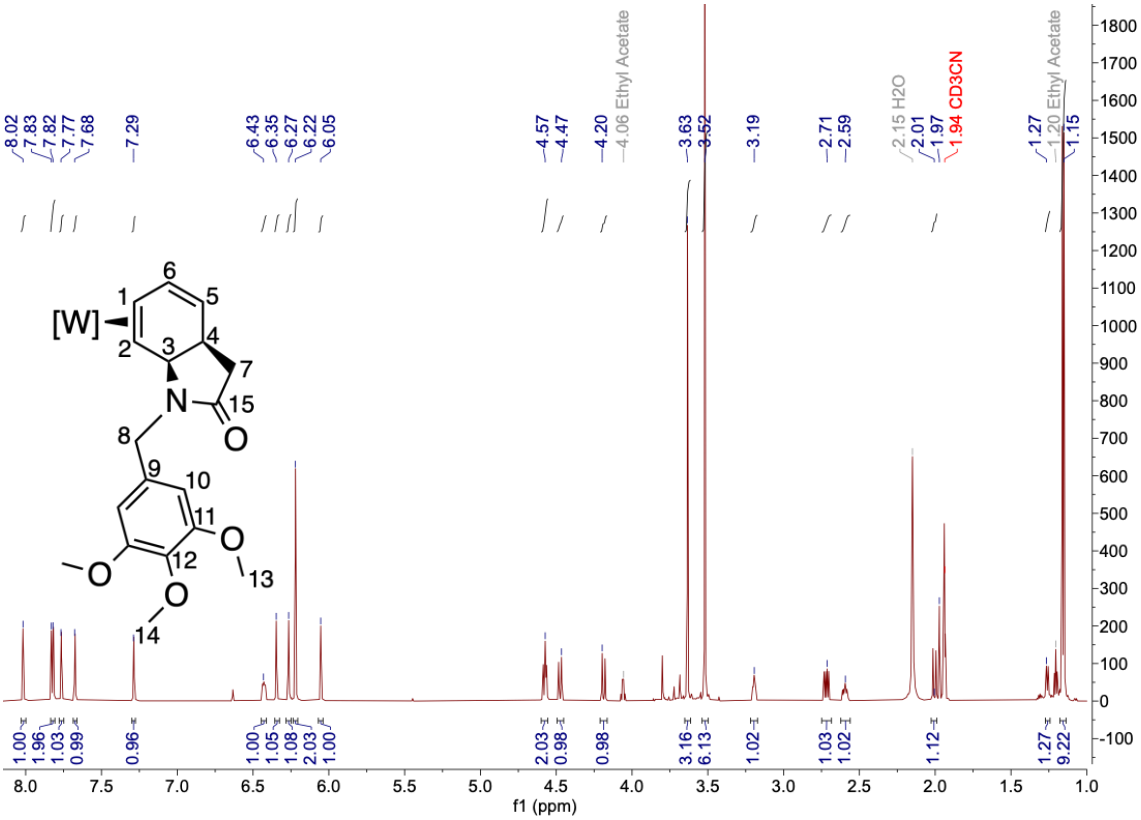


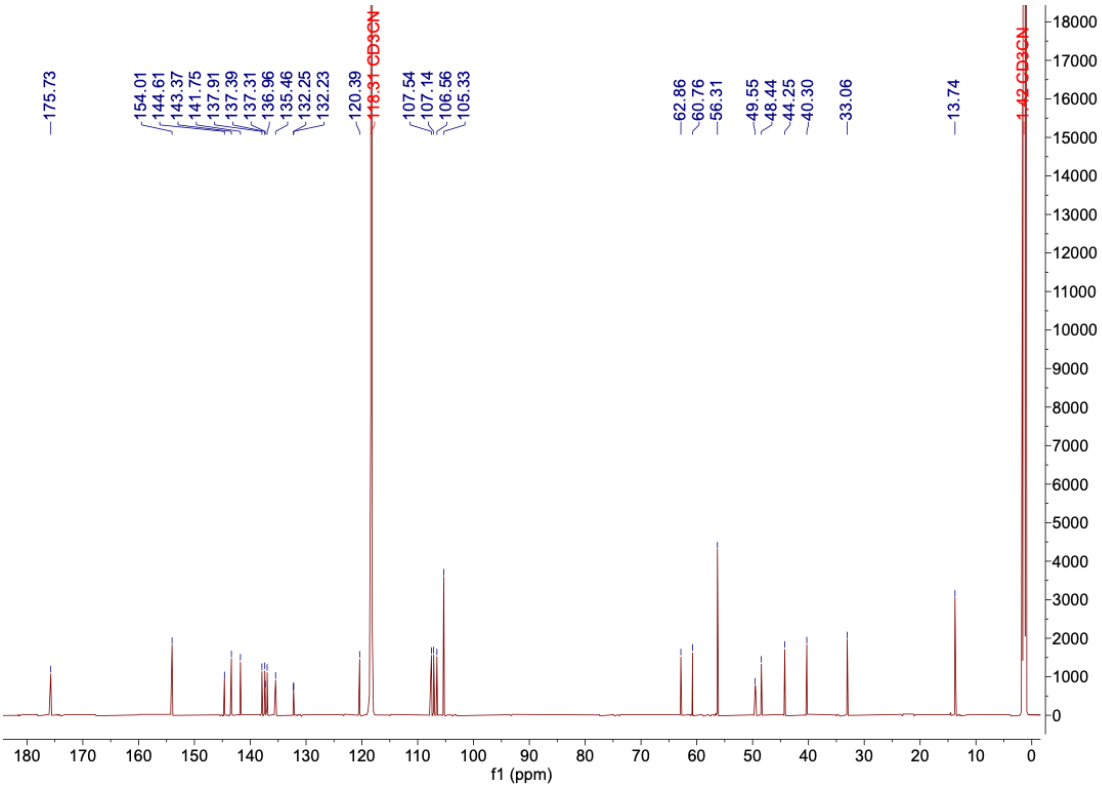
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.20:



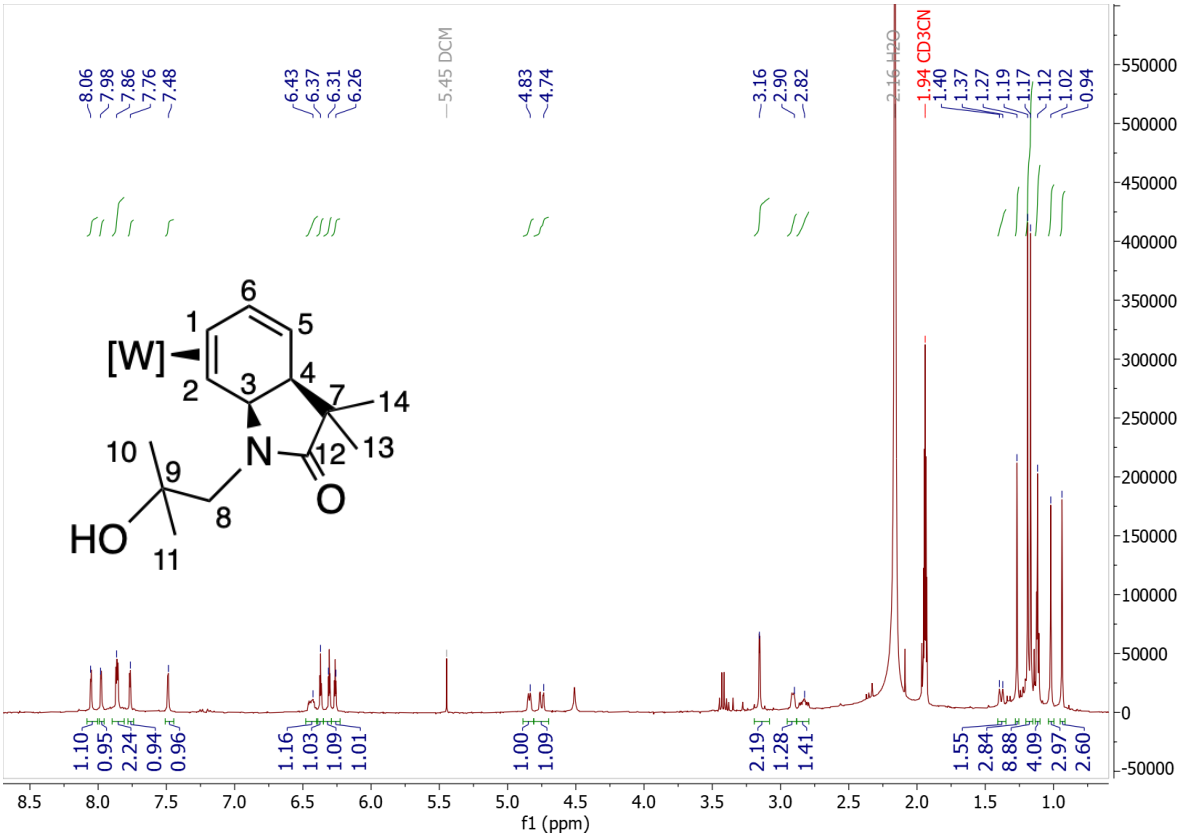


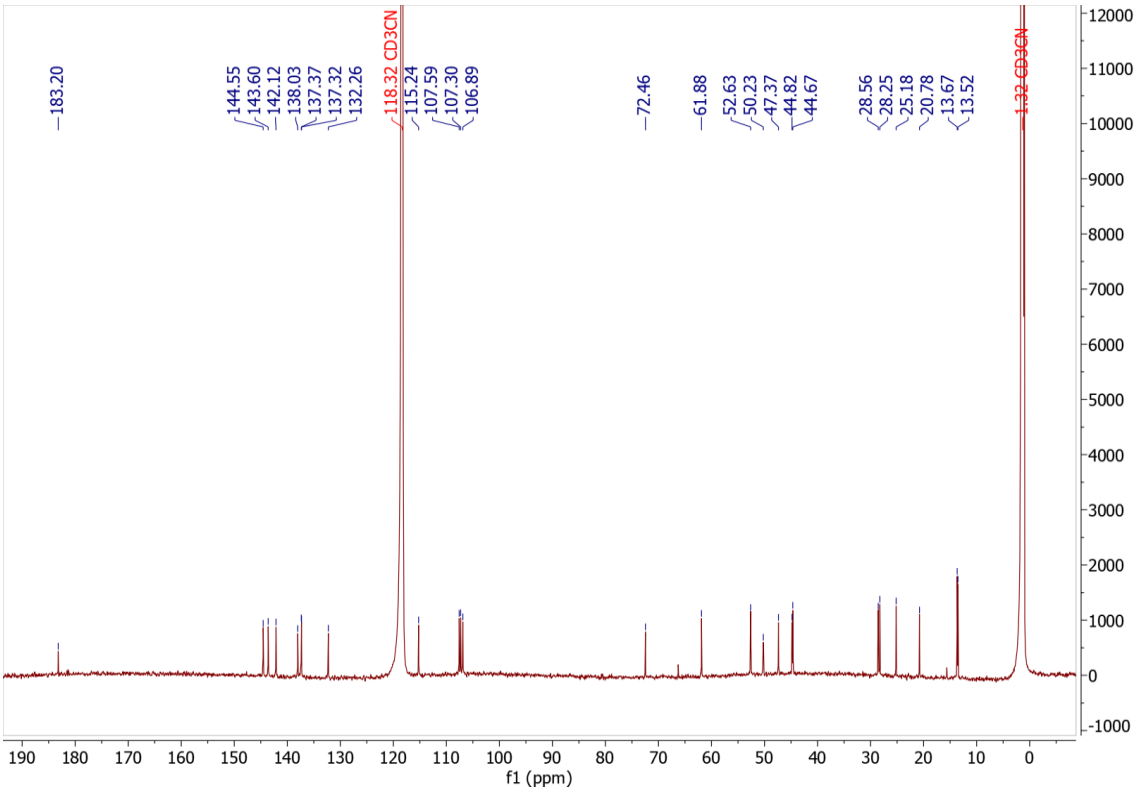
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.21:



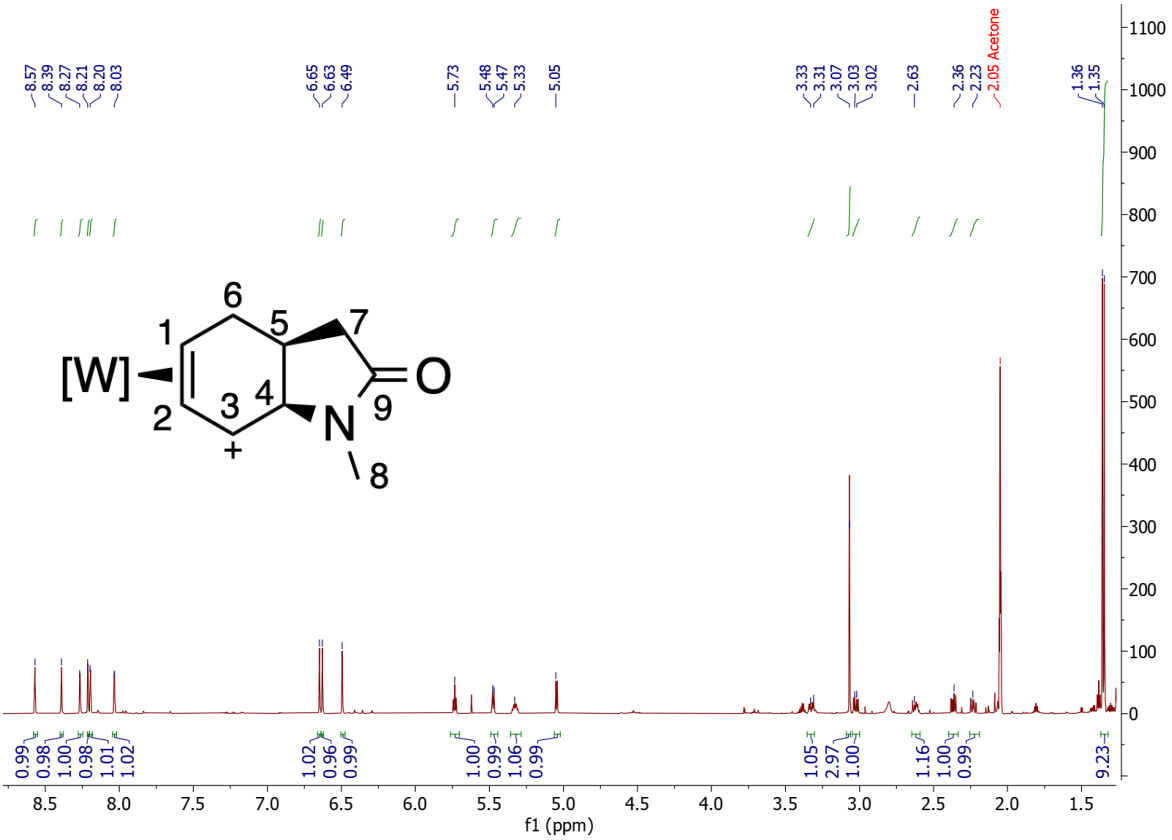


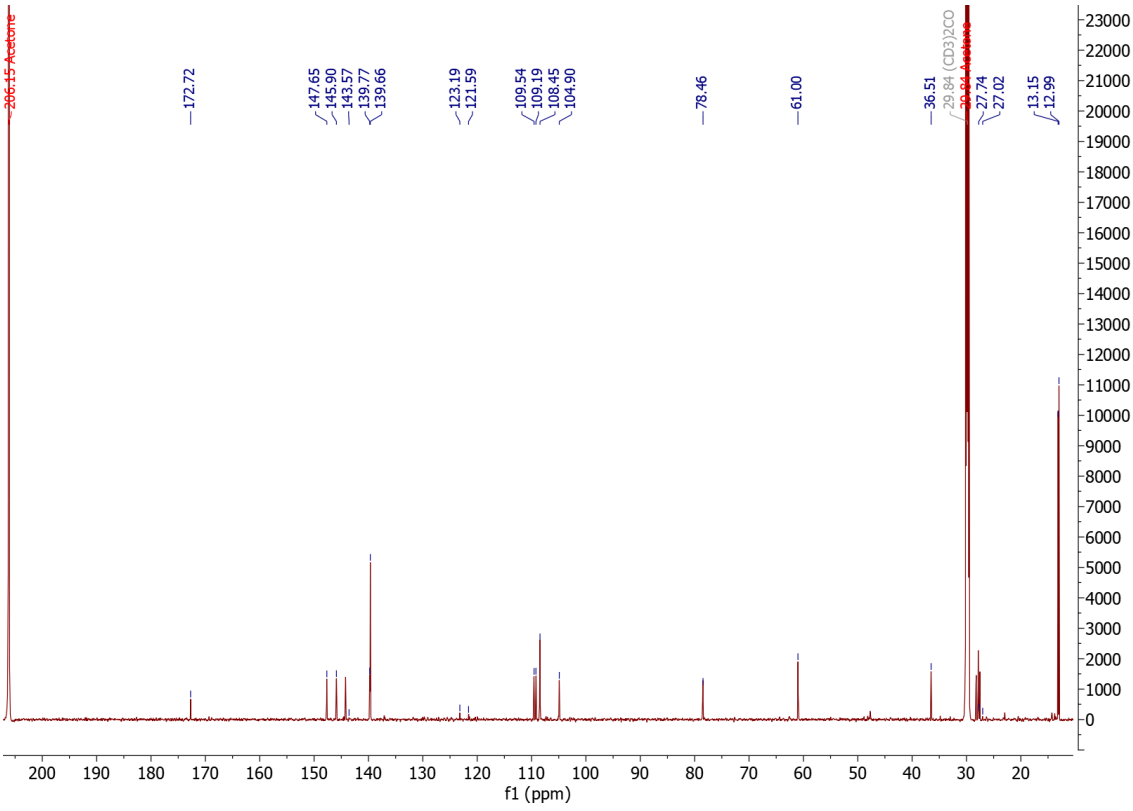
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.23:



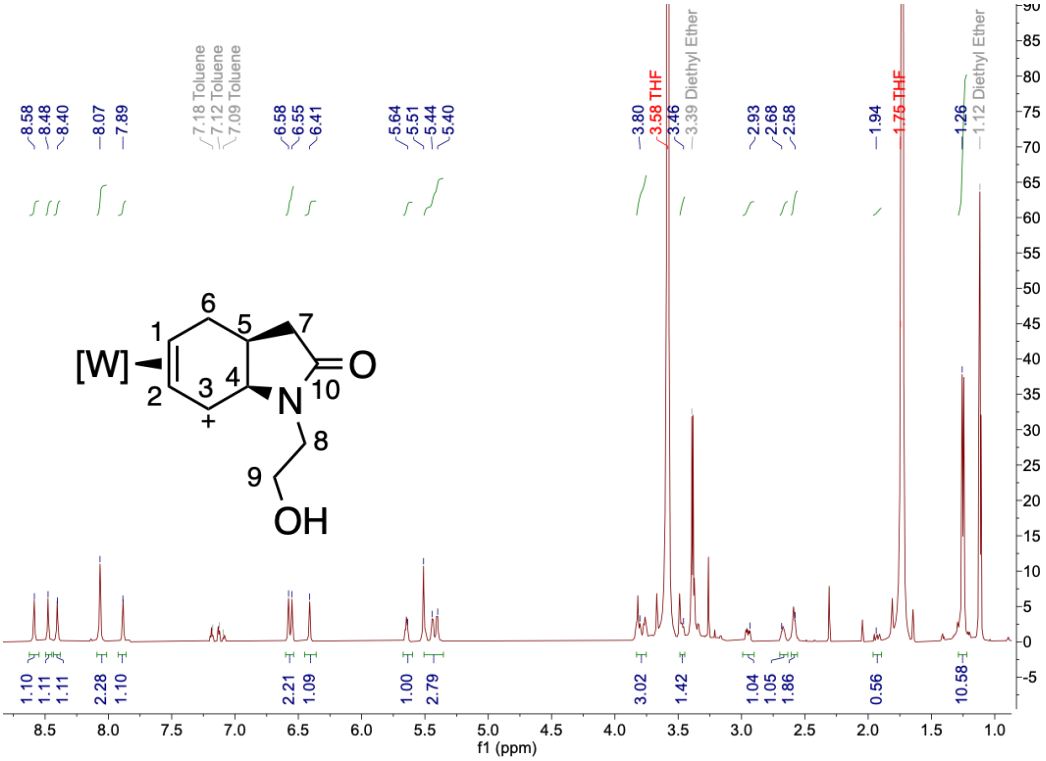


^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.24:



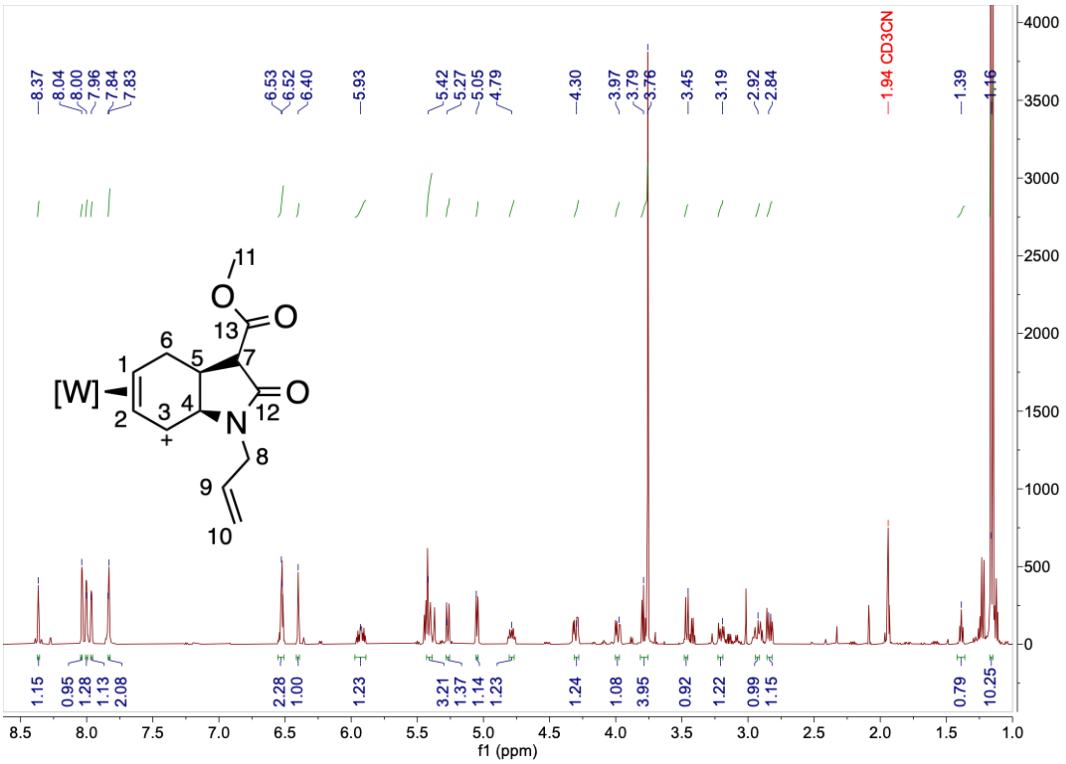


^{1}H-NMR (D_8-THF) of Compound 4.25:



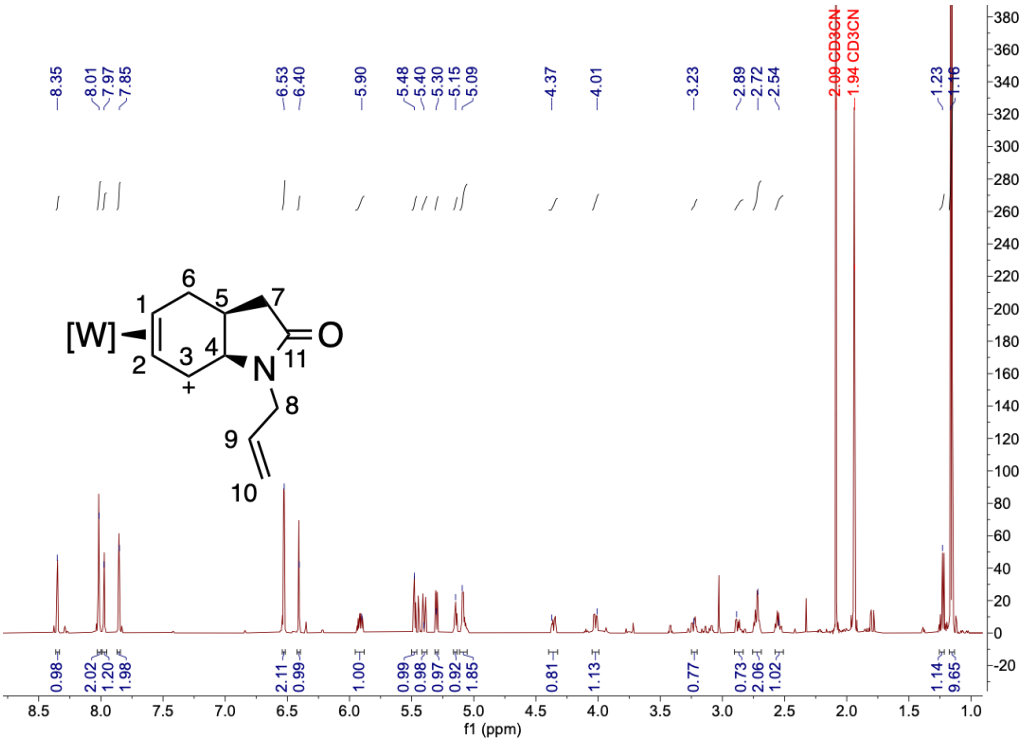
Complex is unstable in solution. Partial Characterization

^{1}H-NMR (CD_3CN) of Compound 4.28:



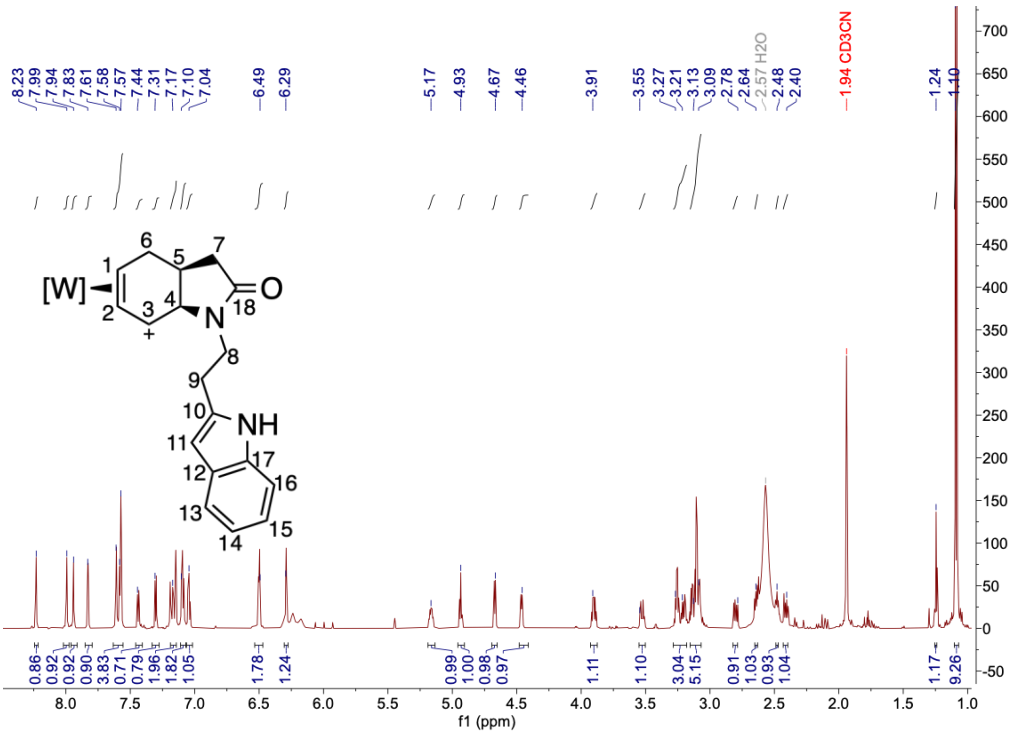
Complex is unstable in solution. Partial Characterization

^{1}H-NMR (CD_3CN) of Compound 4.29:



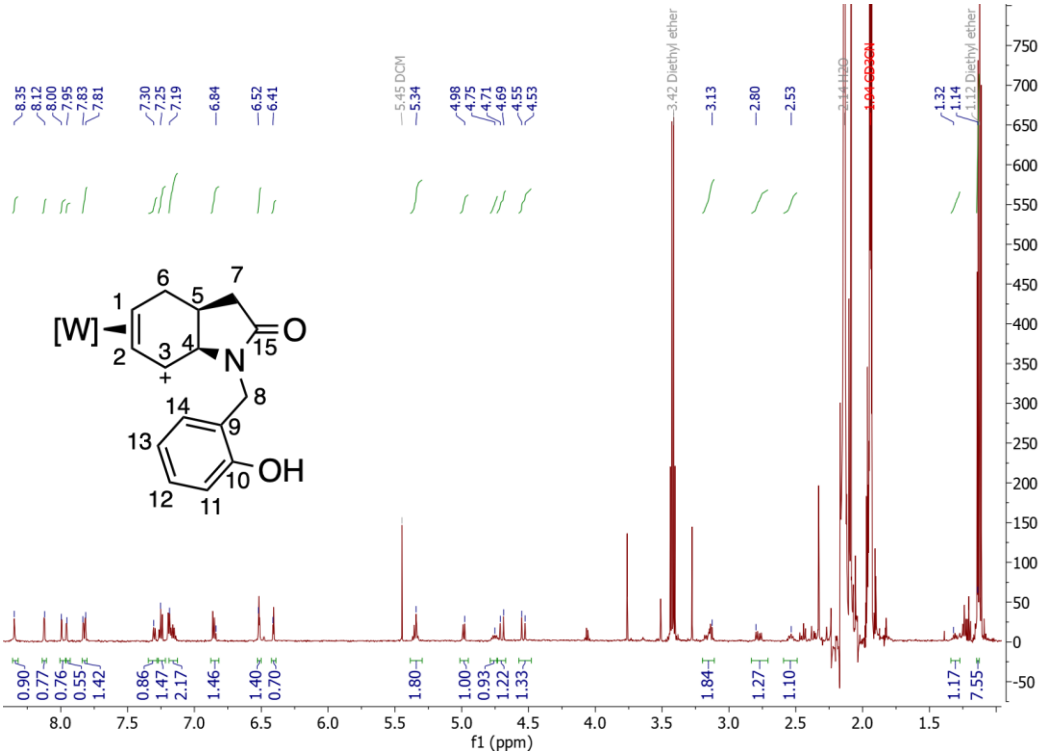
Complex is unstable in solution. Partial Characterization

^{1}H-NMR (CD_3CN) of Compound 4.31:



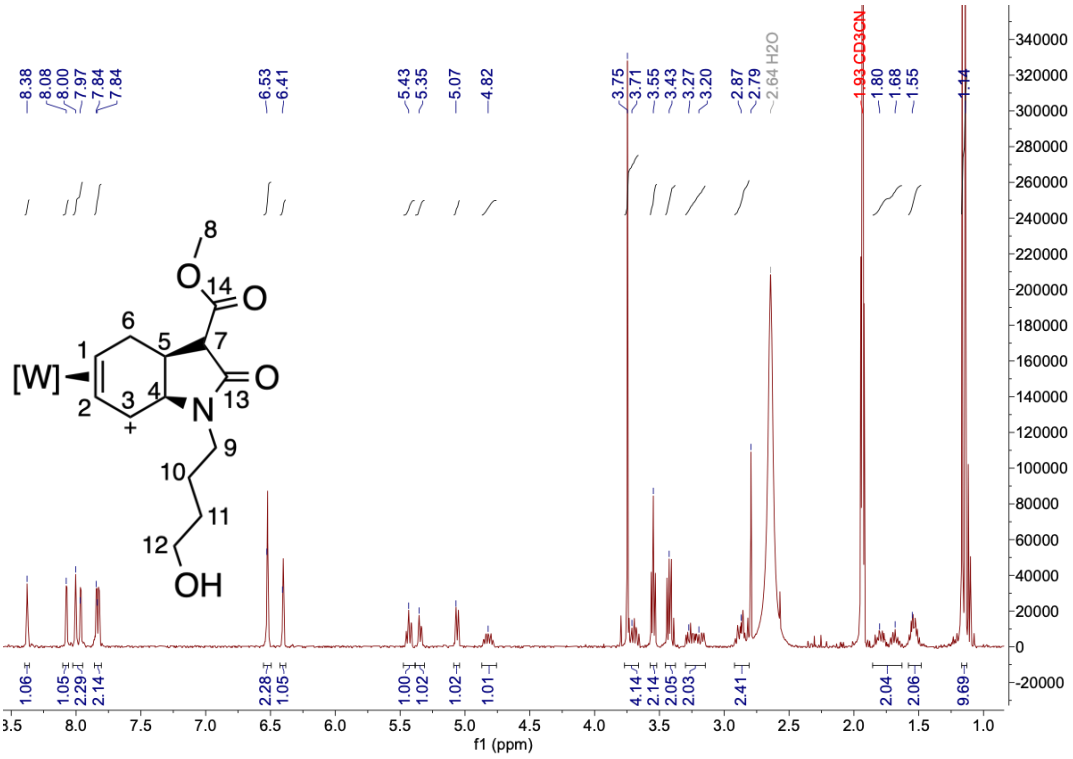
Complex is unstable in solution. Partial Characterization

^{1}H-NMR (CD_3CN) of Compound 4.32:



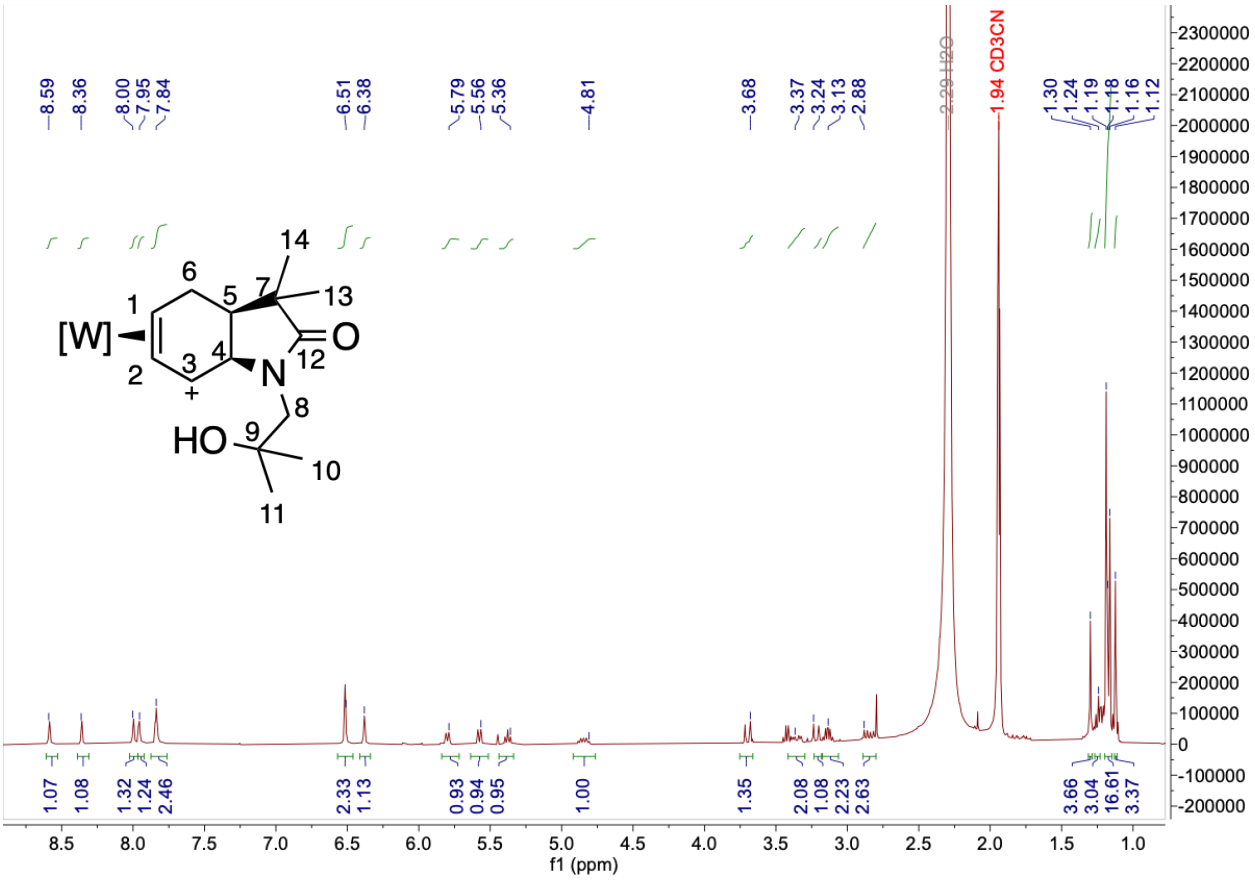
Complex is unstable in solution. Partial Characterization

^{1}H-NMR (CD_3CN) of Compound 4.33:



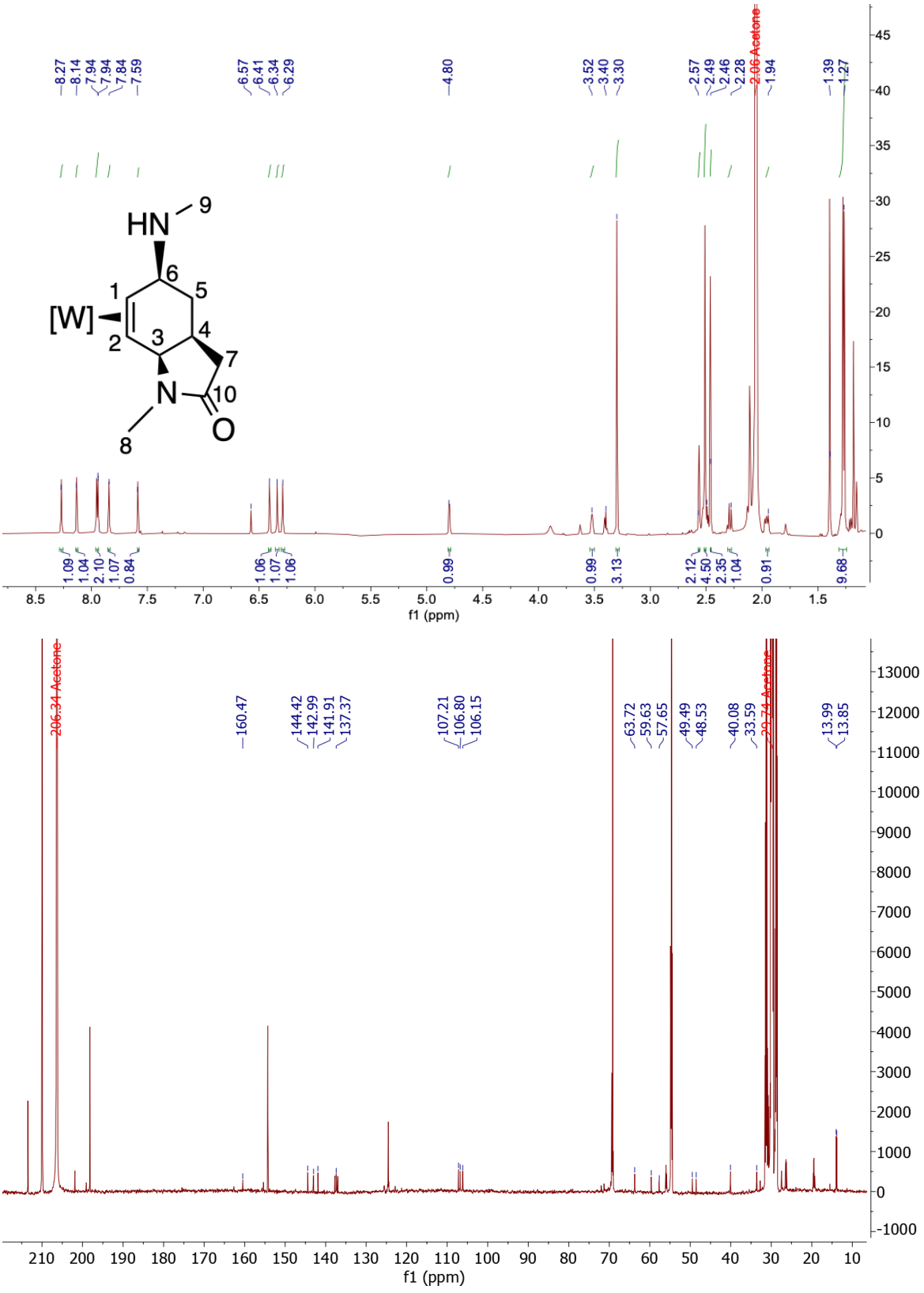
Complex is unstable in solution. Partial Characterization

^{1}H-NMR (CD_3CN) of Compound 4.34:

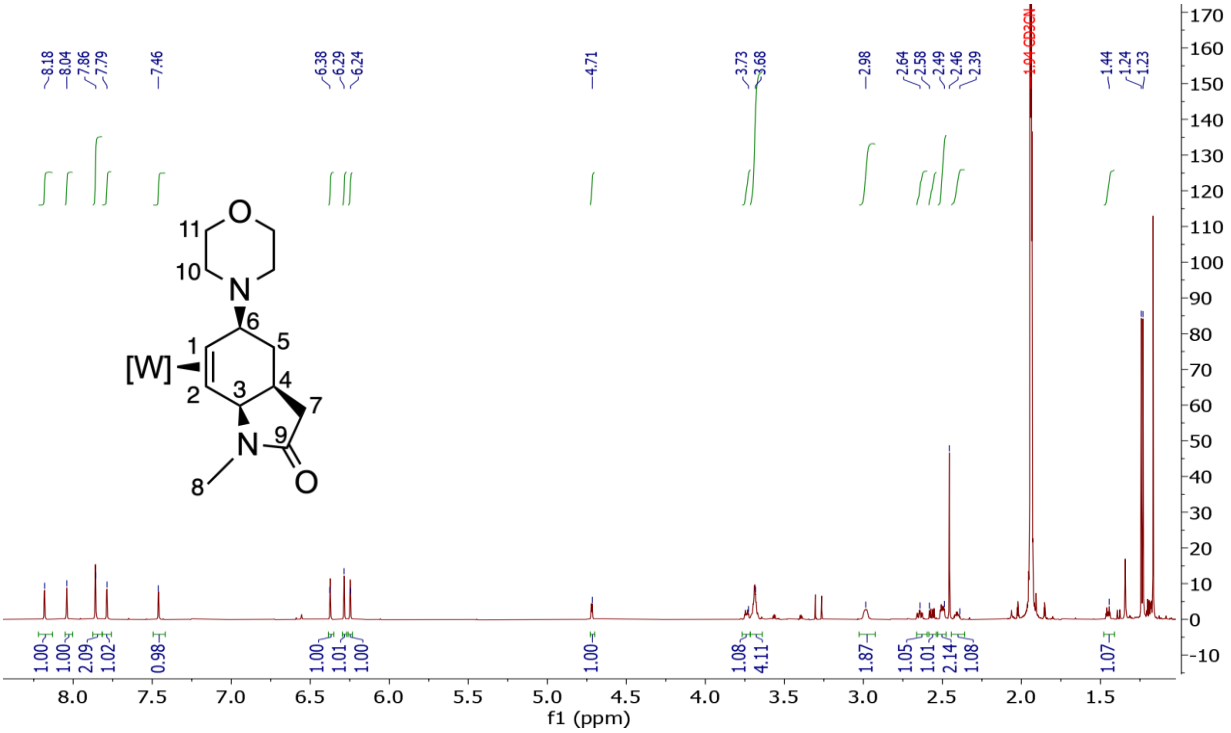


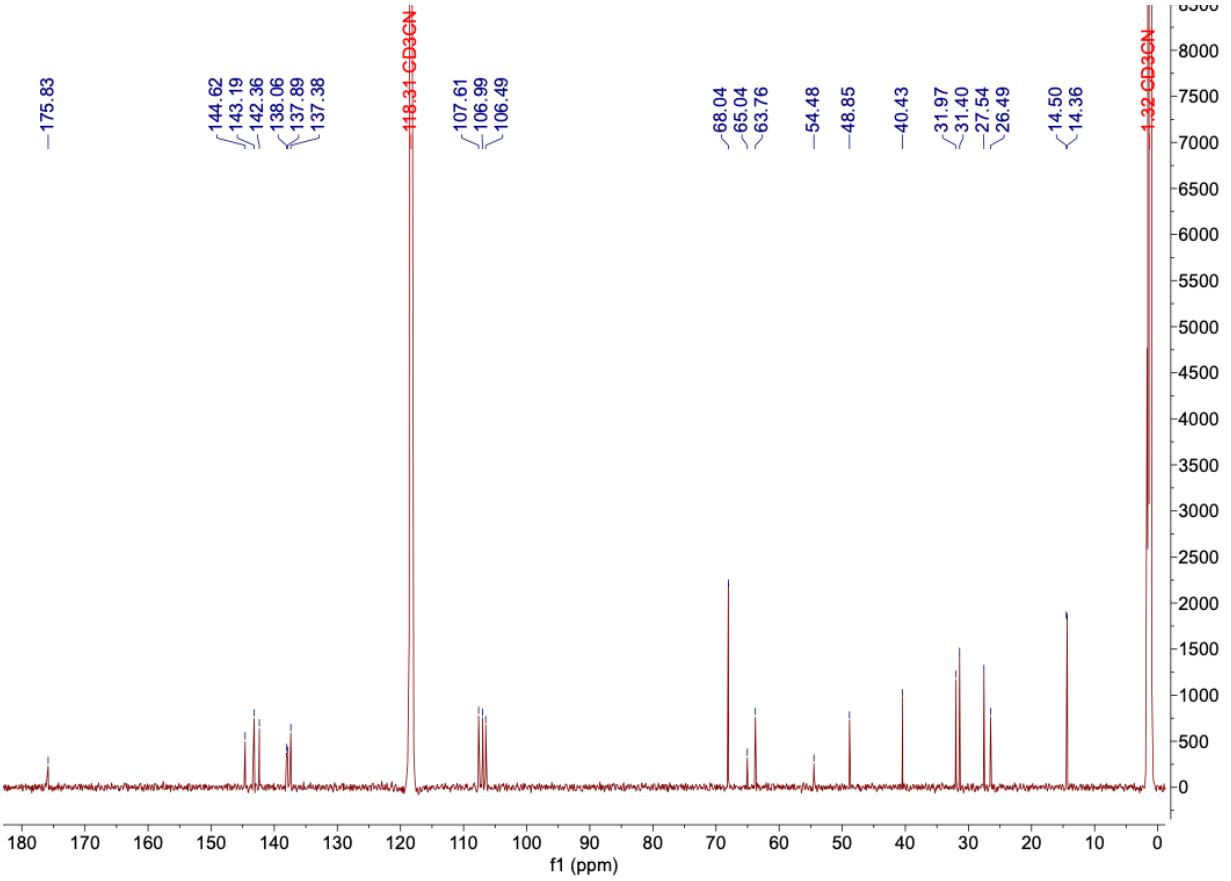
Complex is unstable in solution. Partial Characterization

^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 4.34:

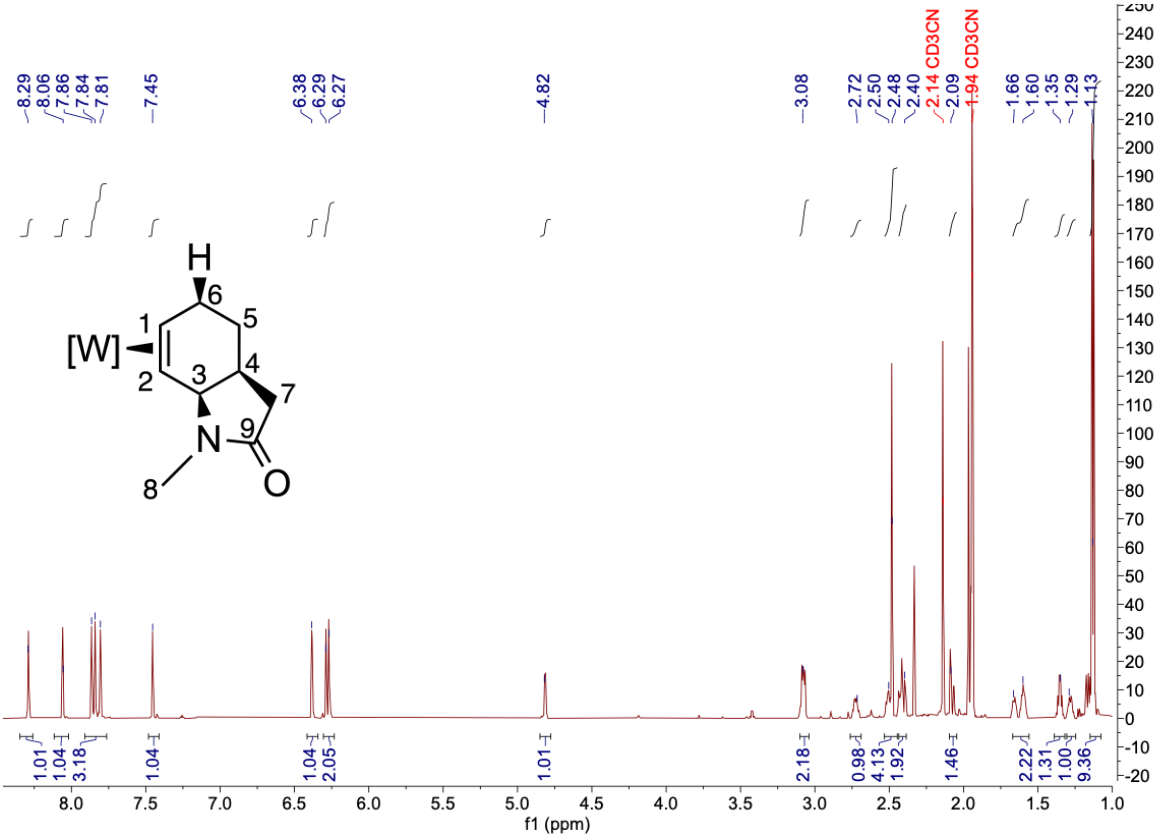


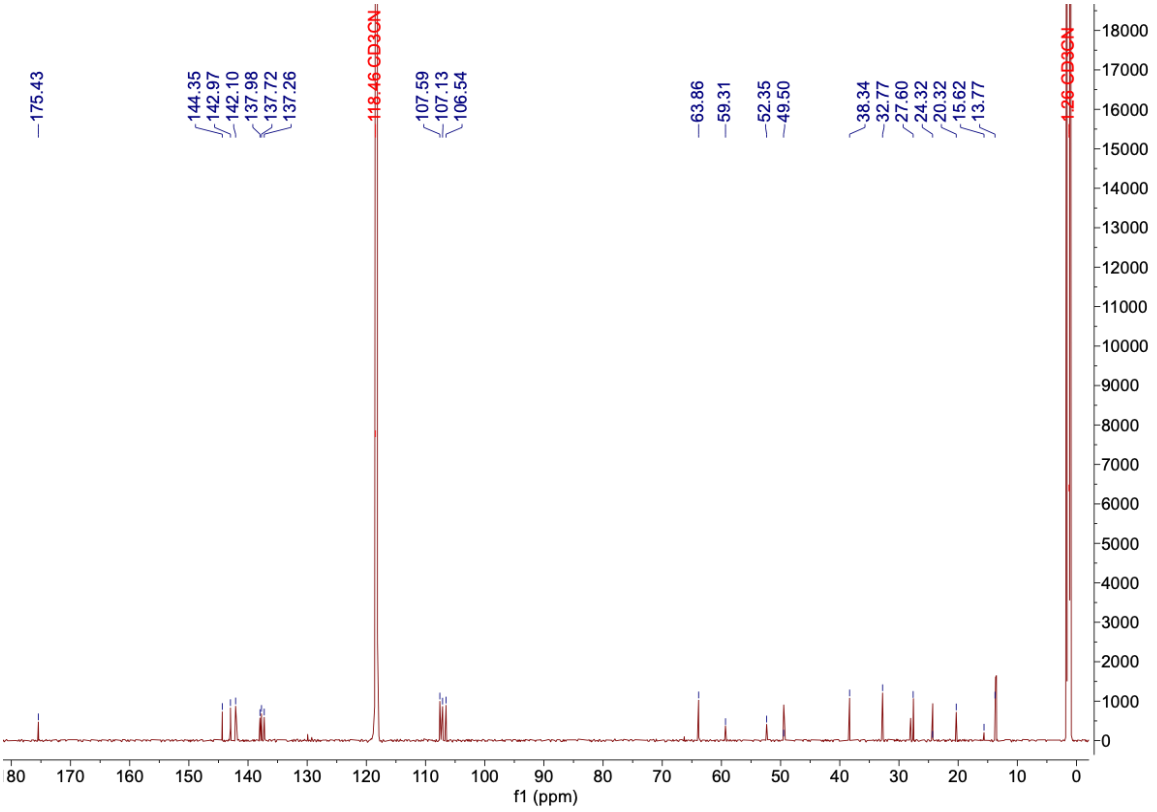
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.35:



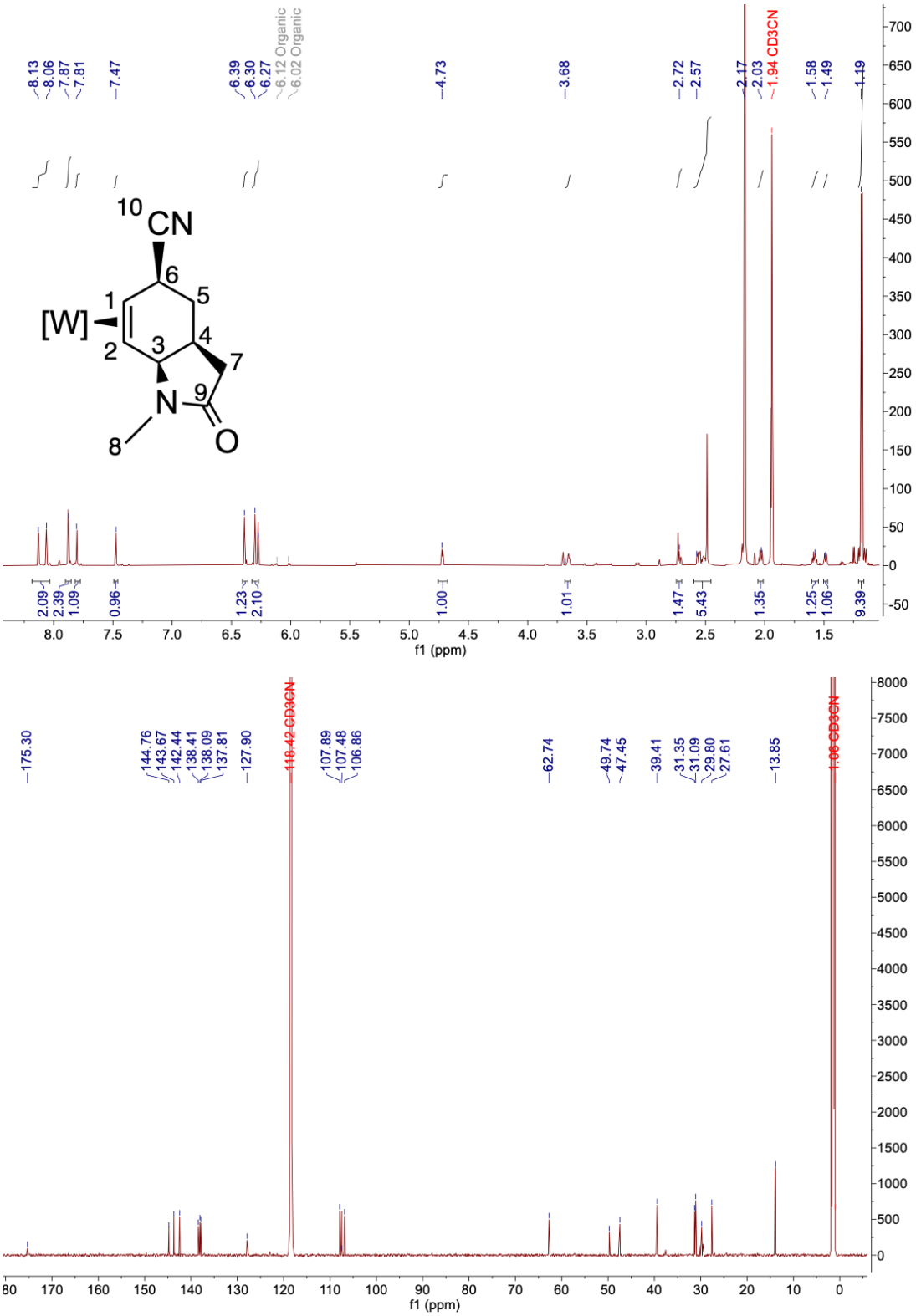


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.36:



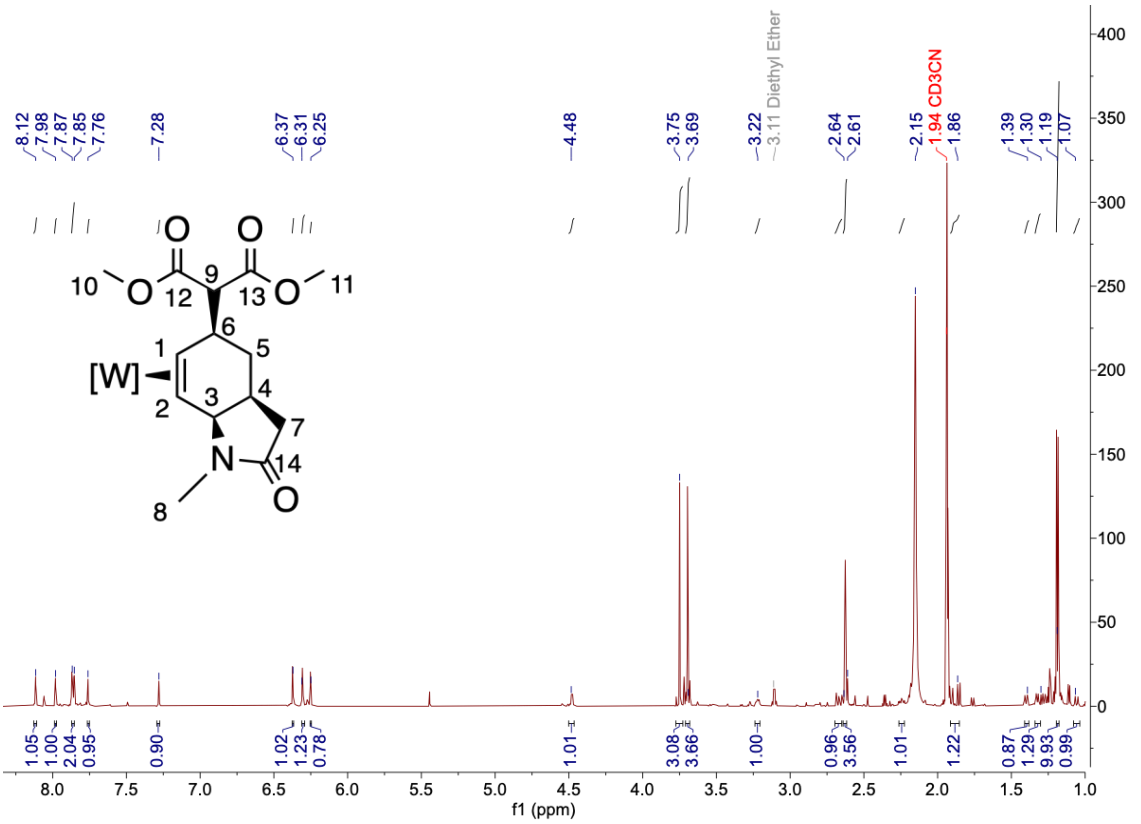


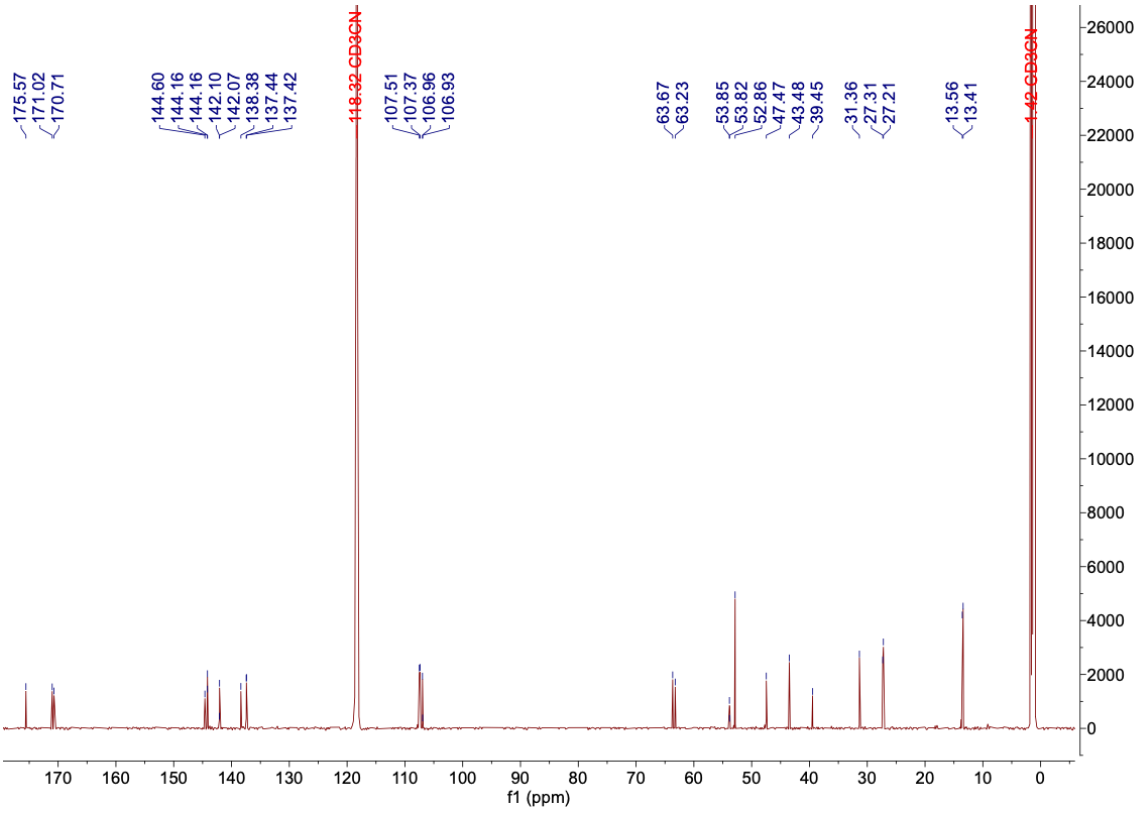
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.37:



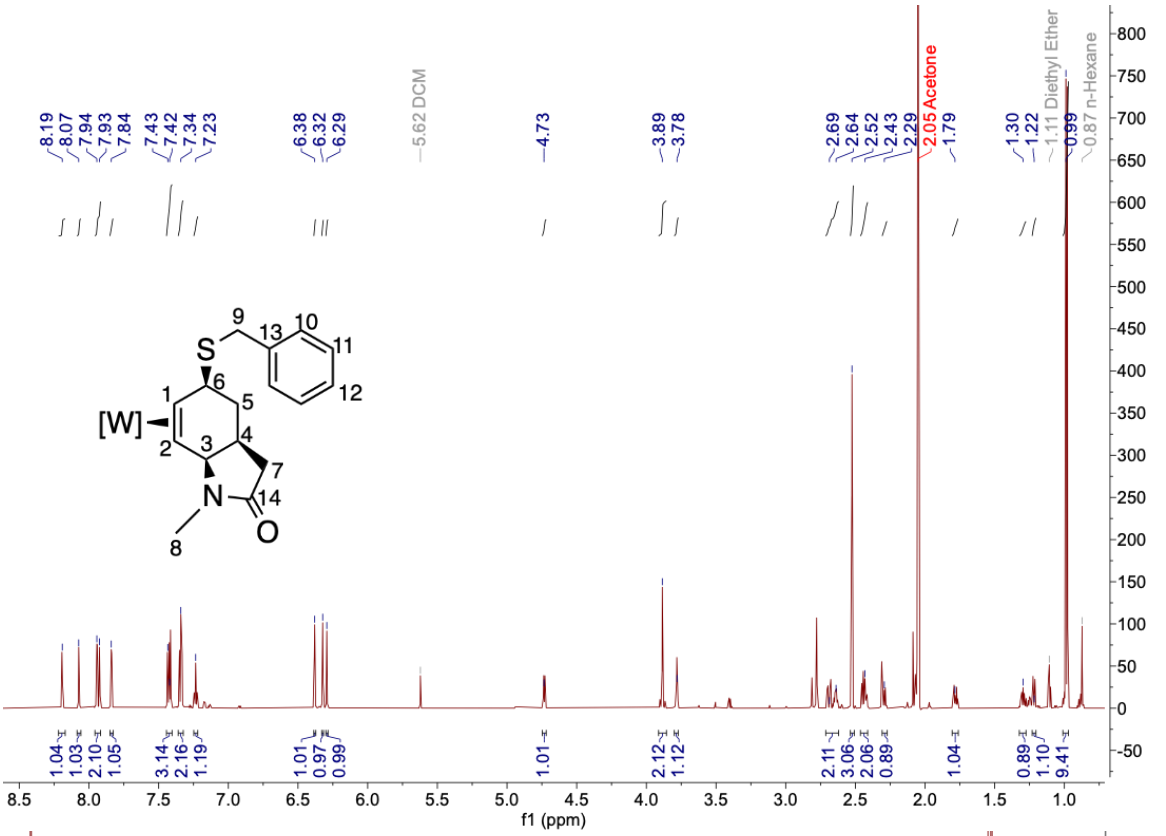
Whilst in solution, the metal started to decomplex liberating the free organic.

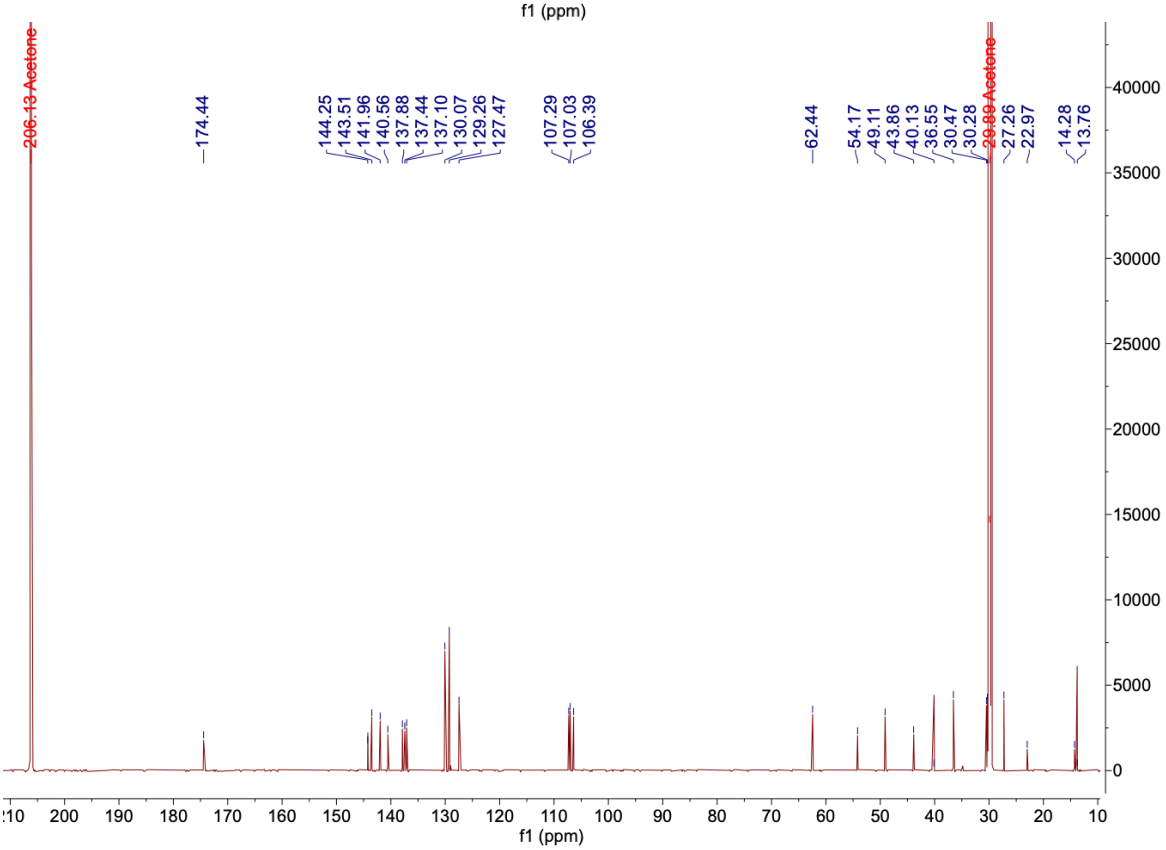
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.38:



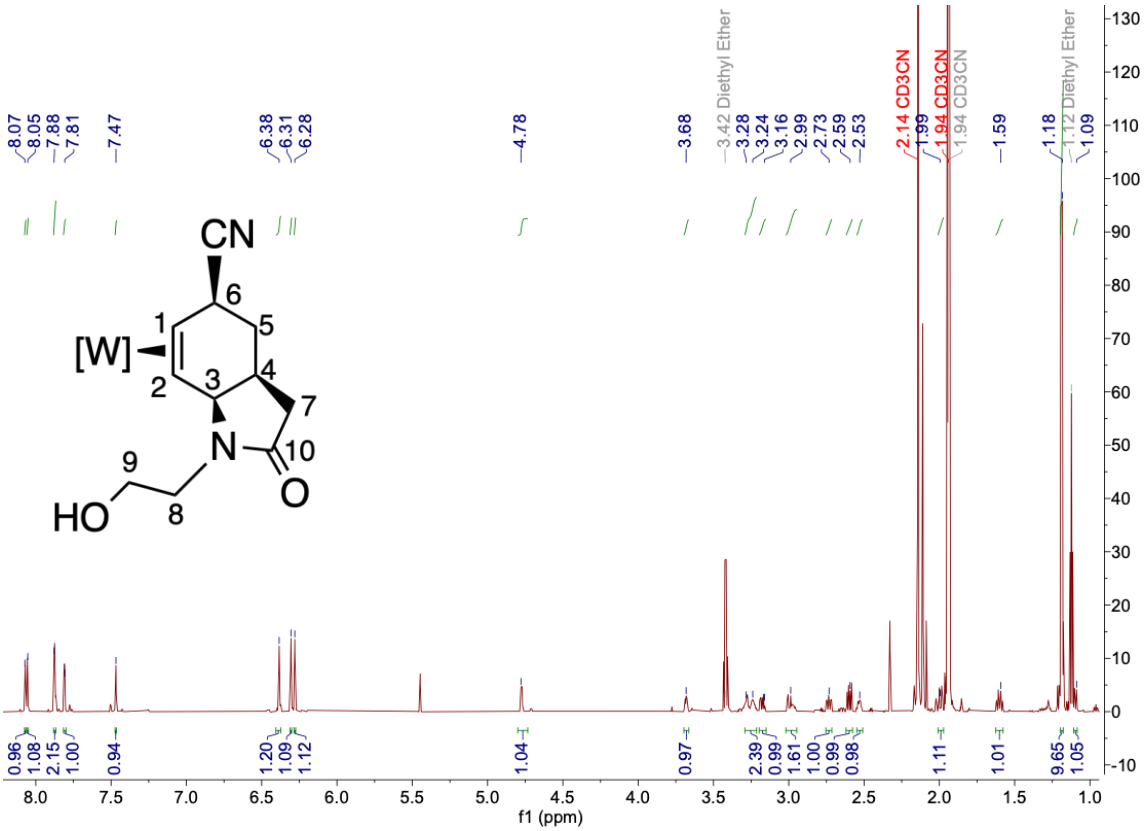


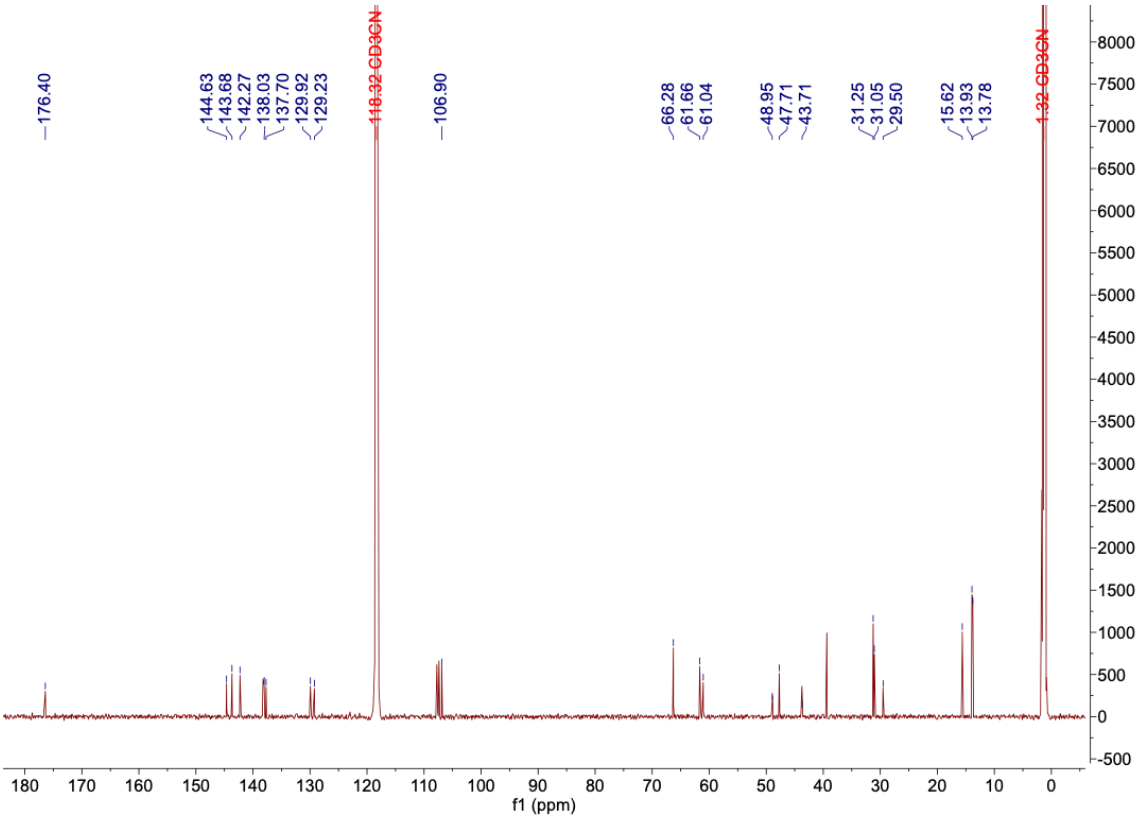
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.39:



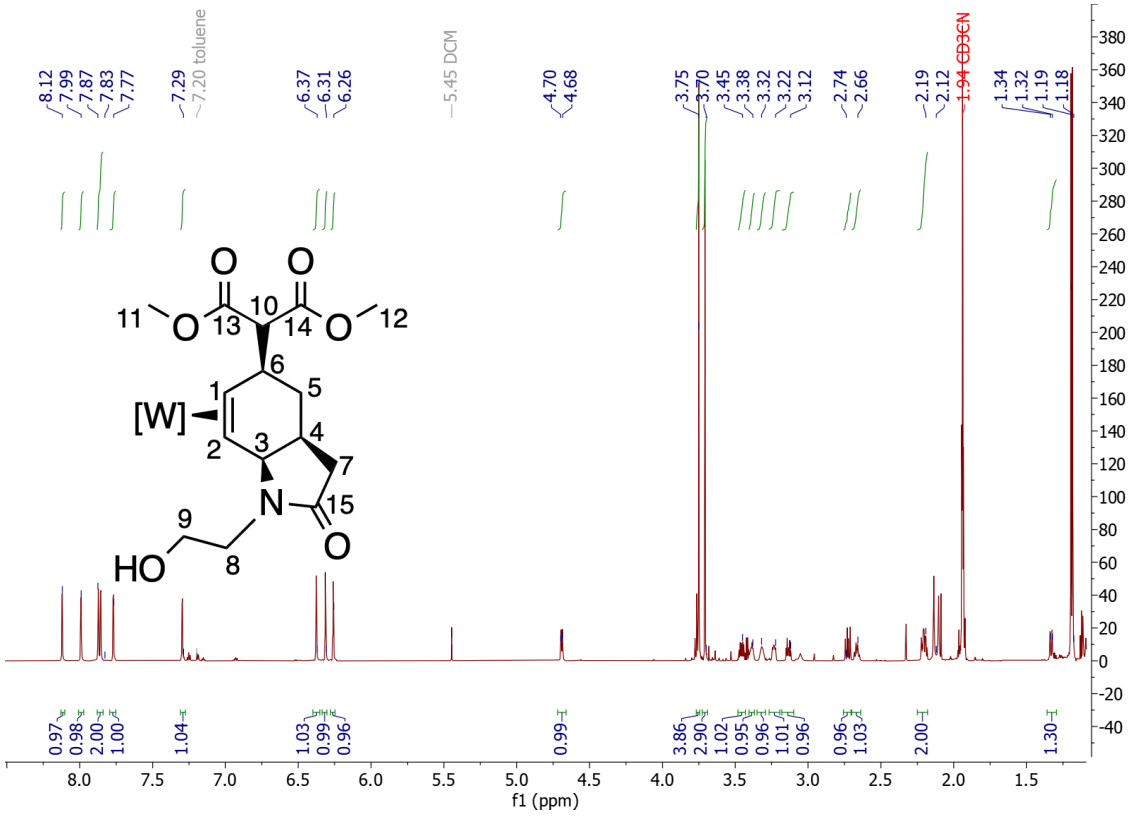


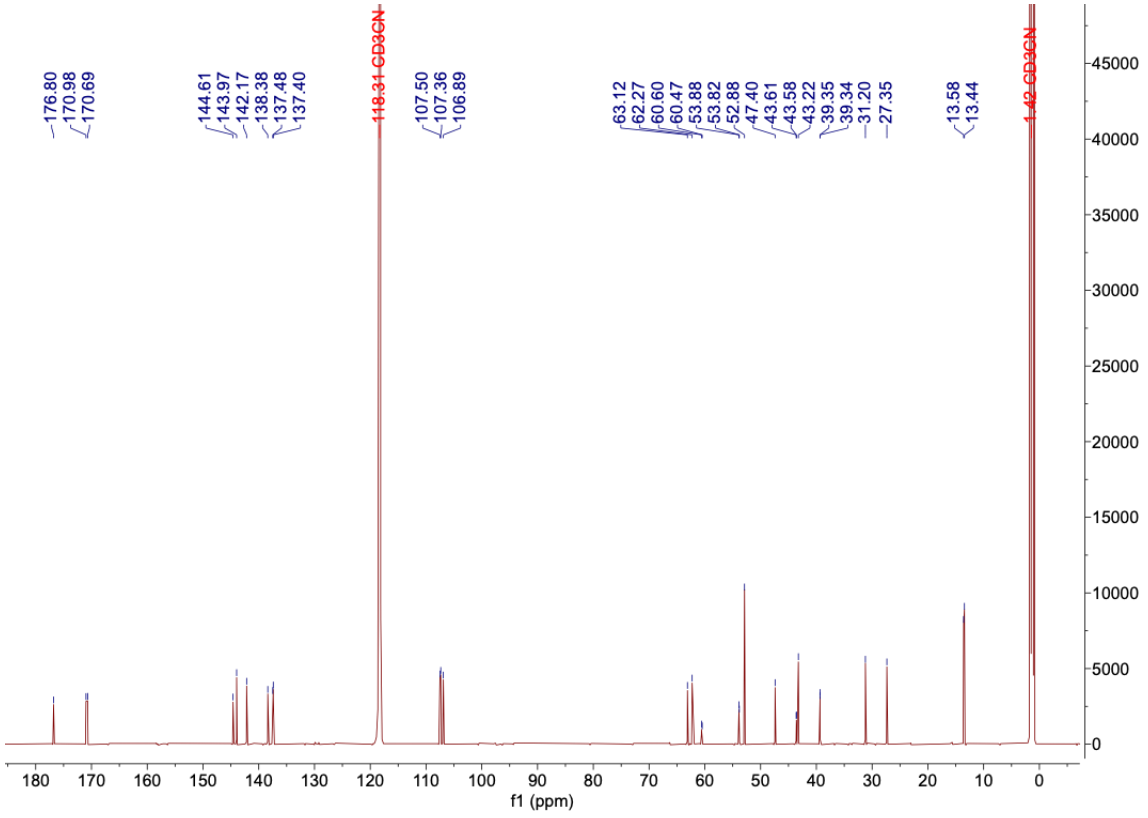
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.40:



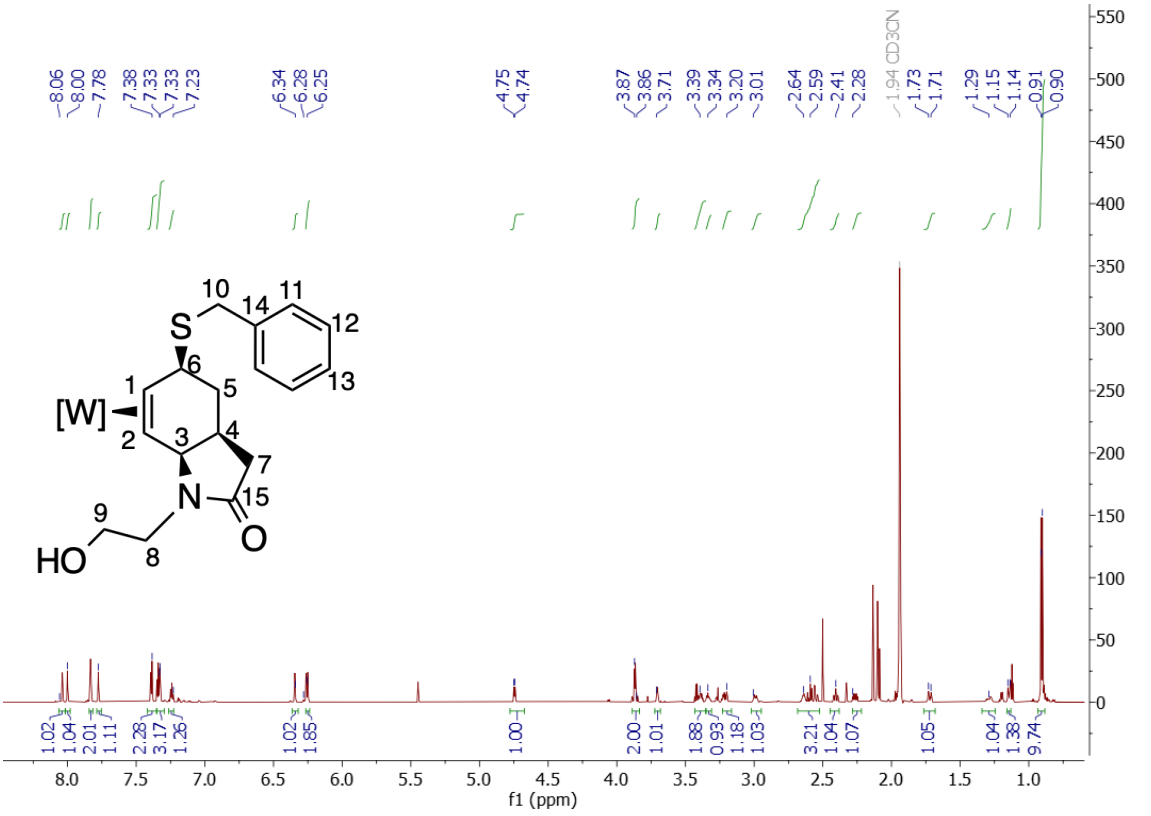


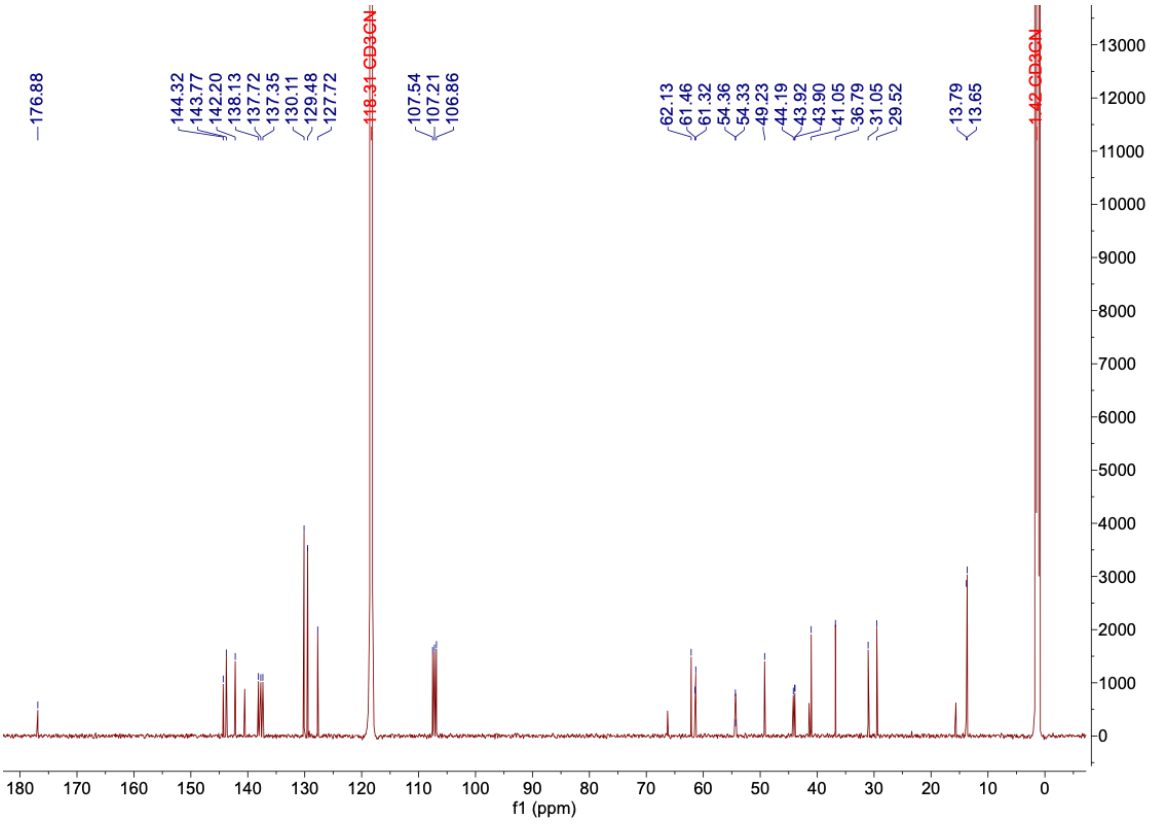
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.41:



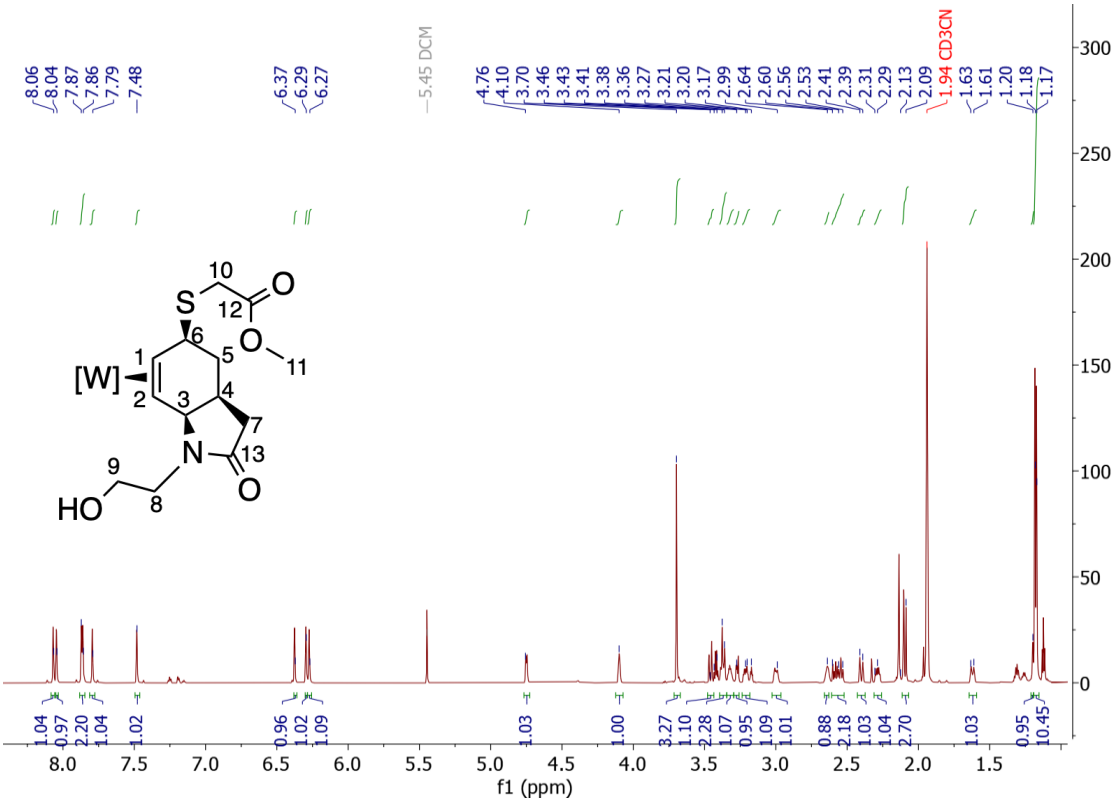


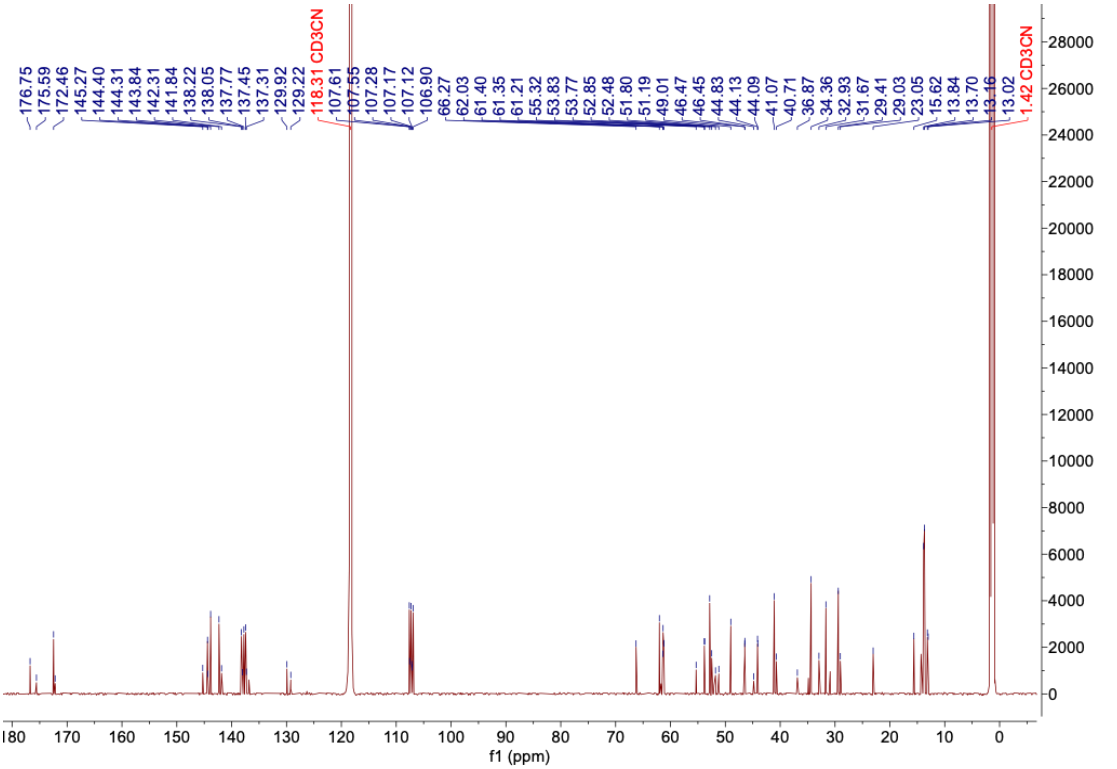
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.42:





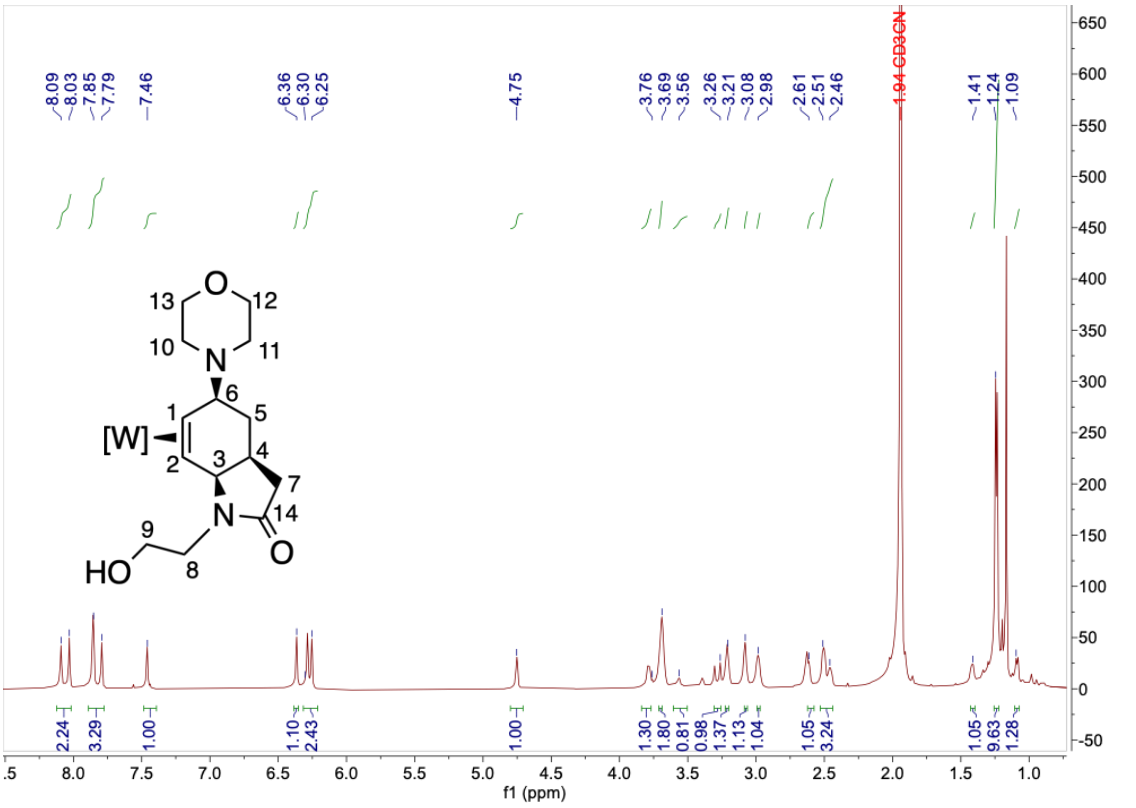
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.43:

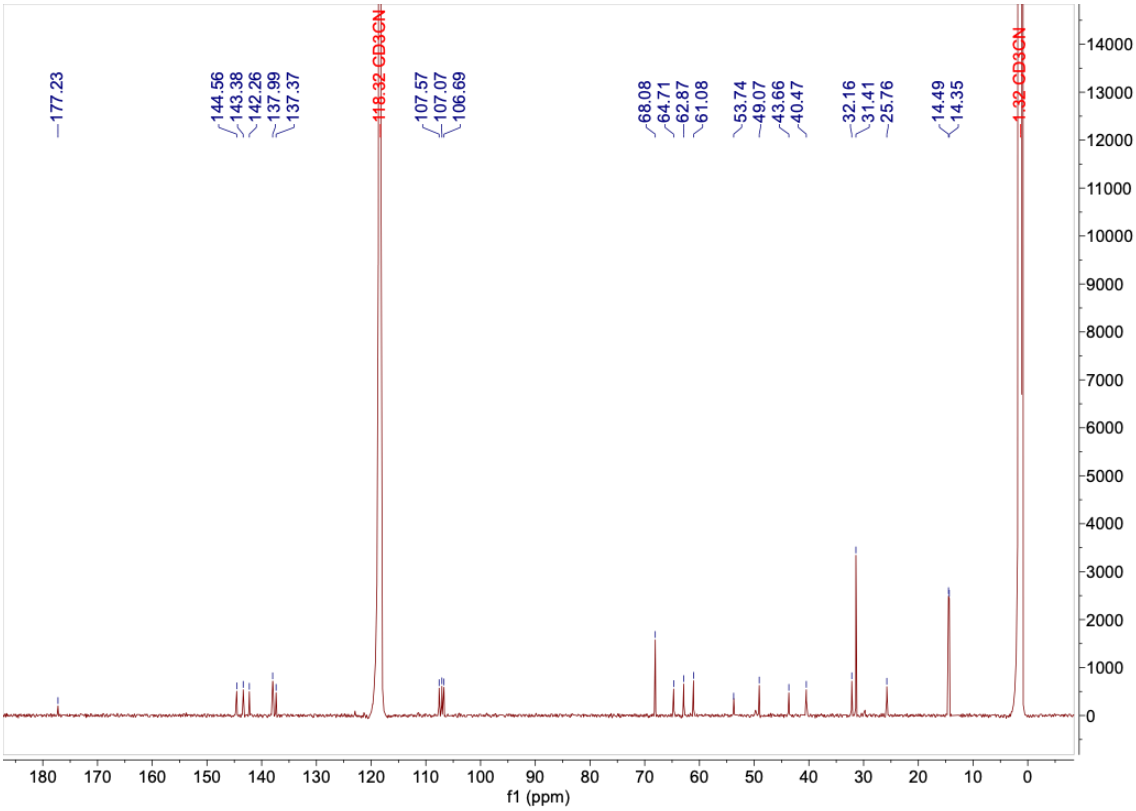




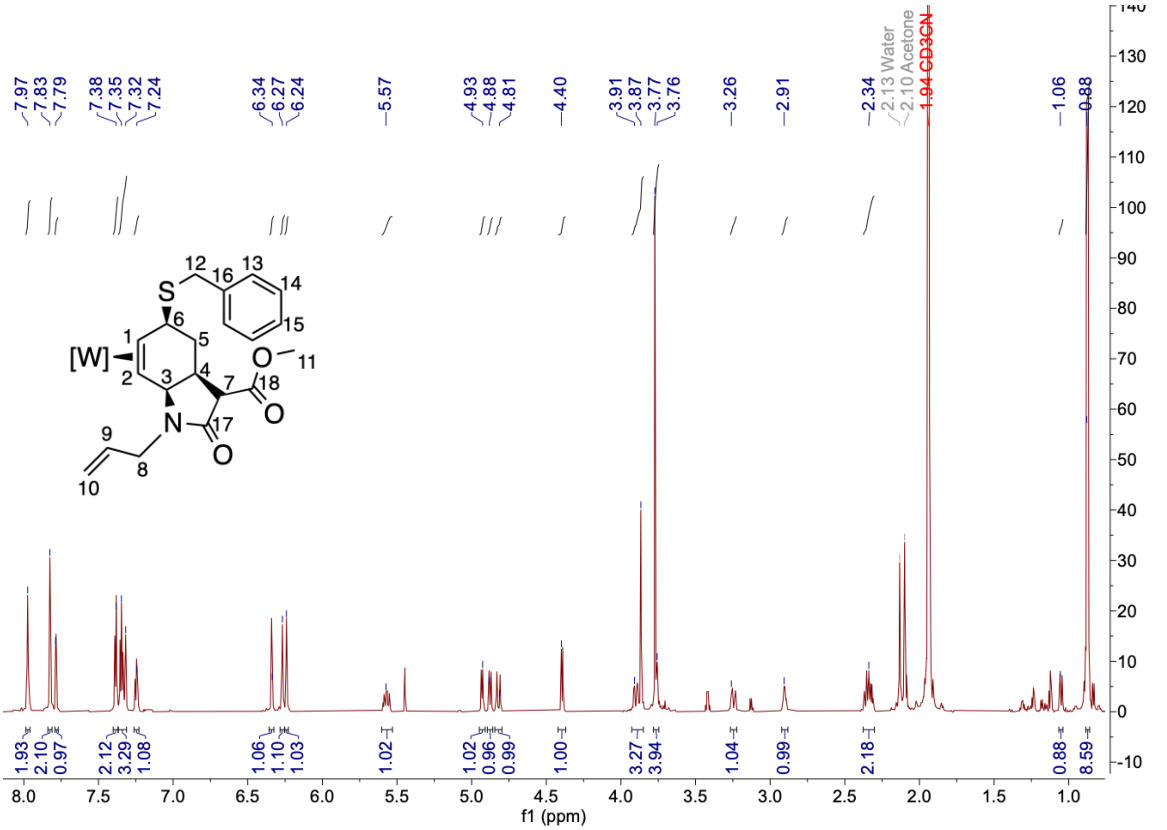
While in solution the other isomer was also generated.

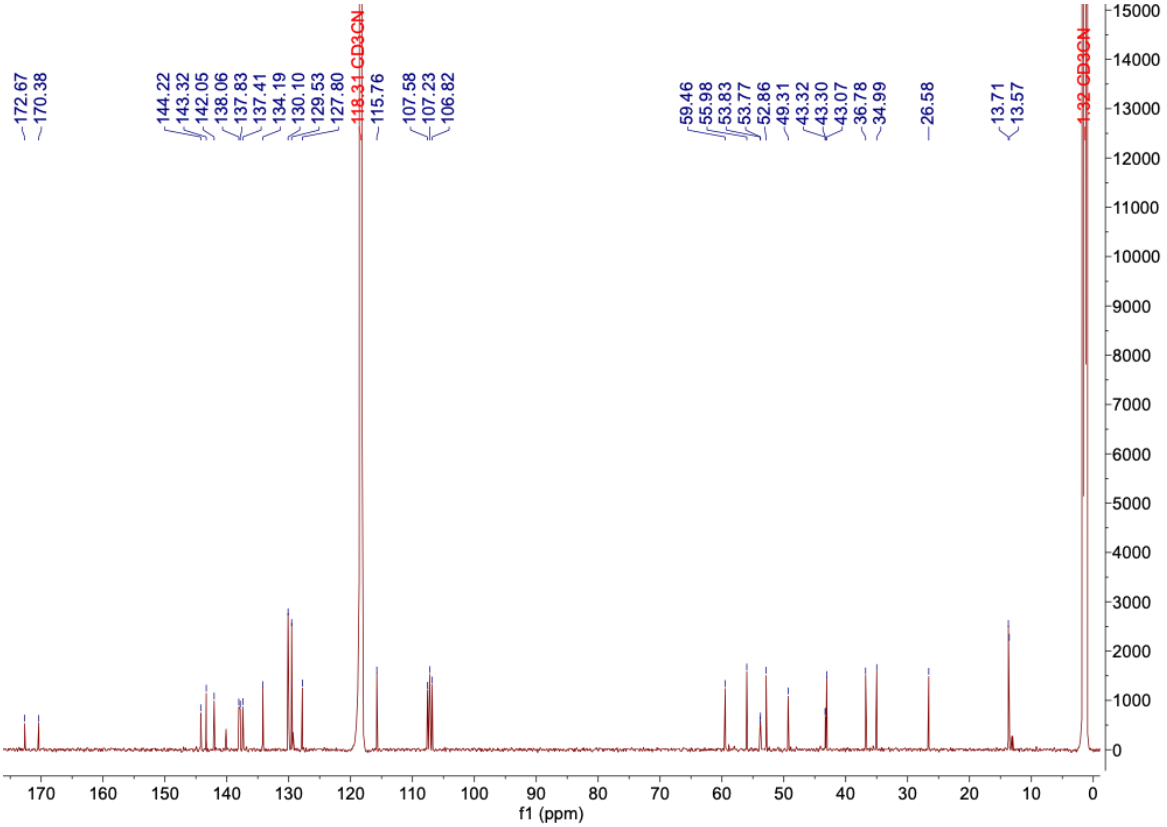
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.44:



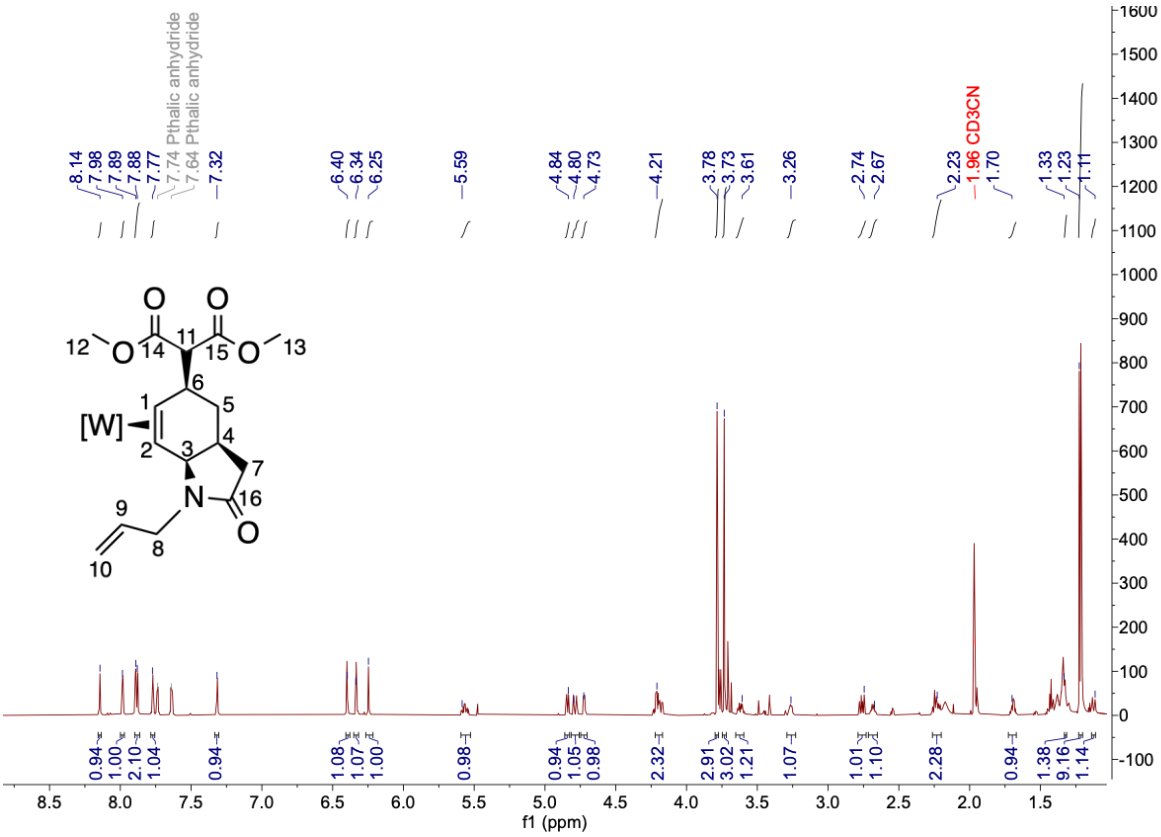


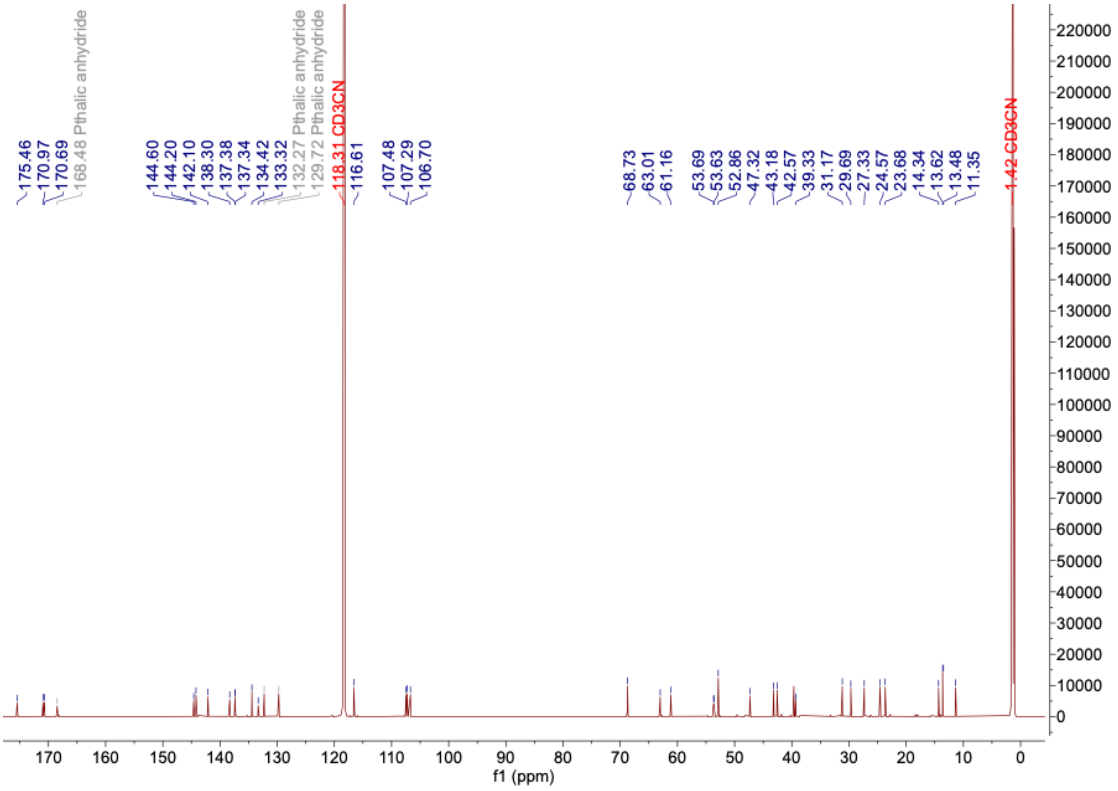
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.45:



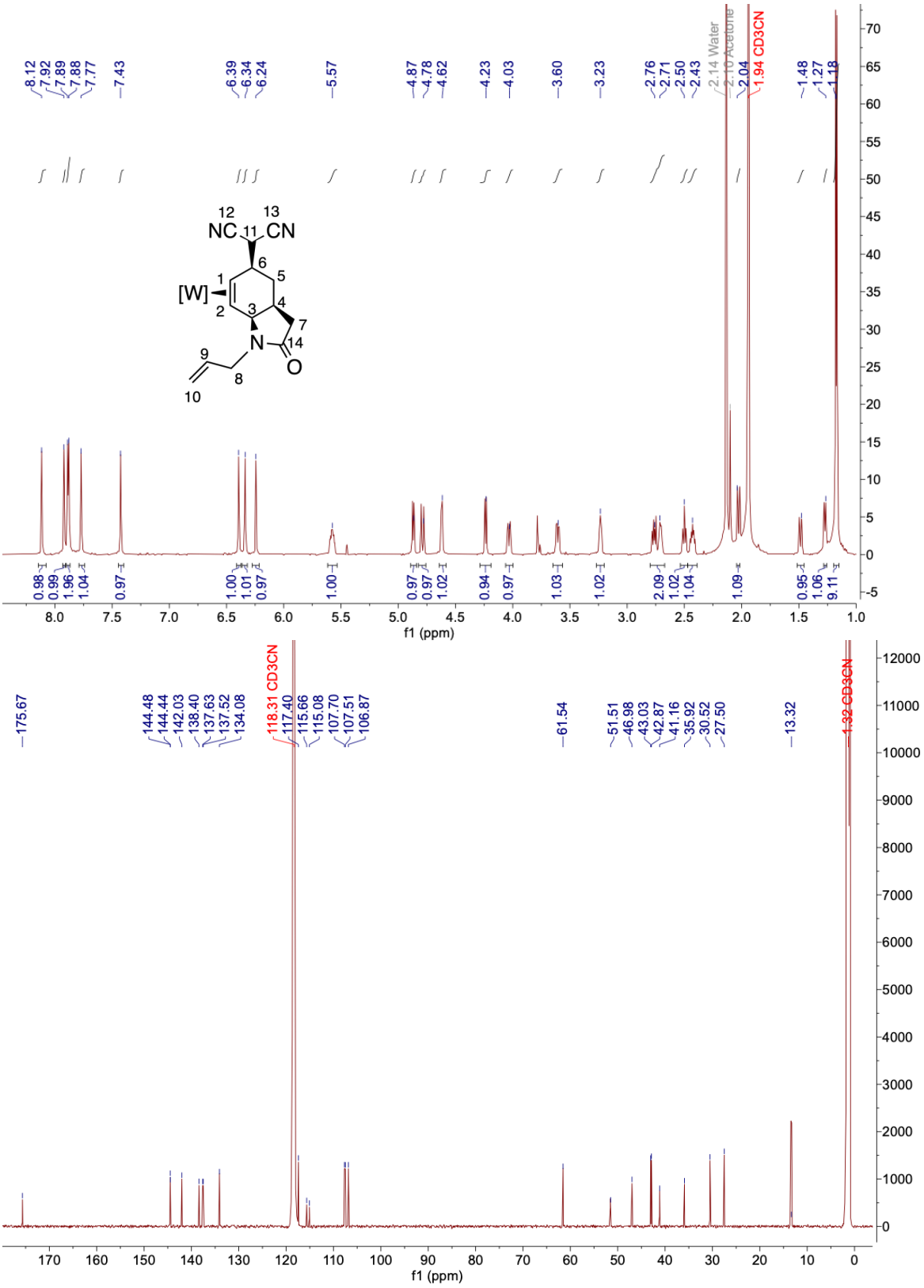


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.46:

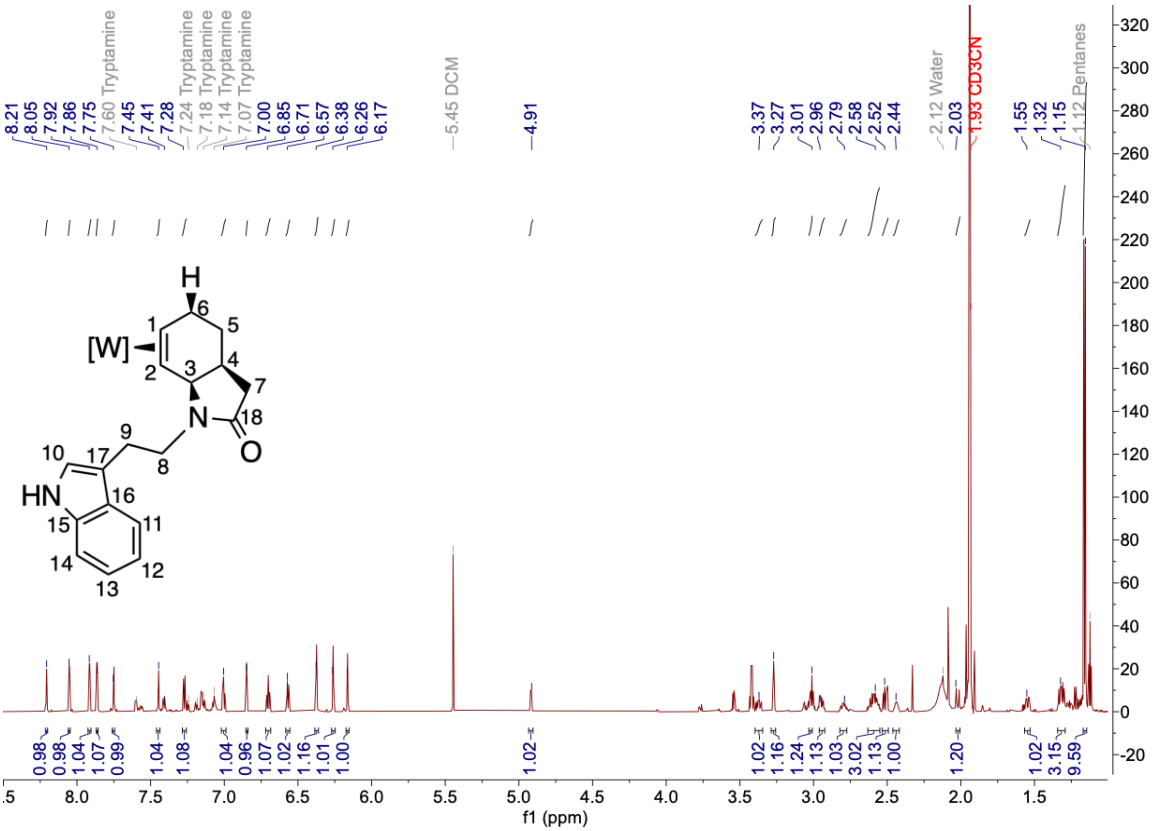


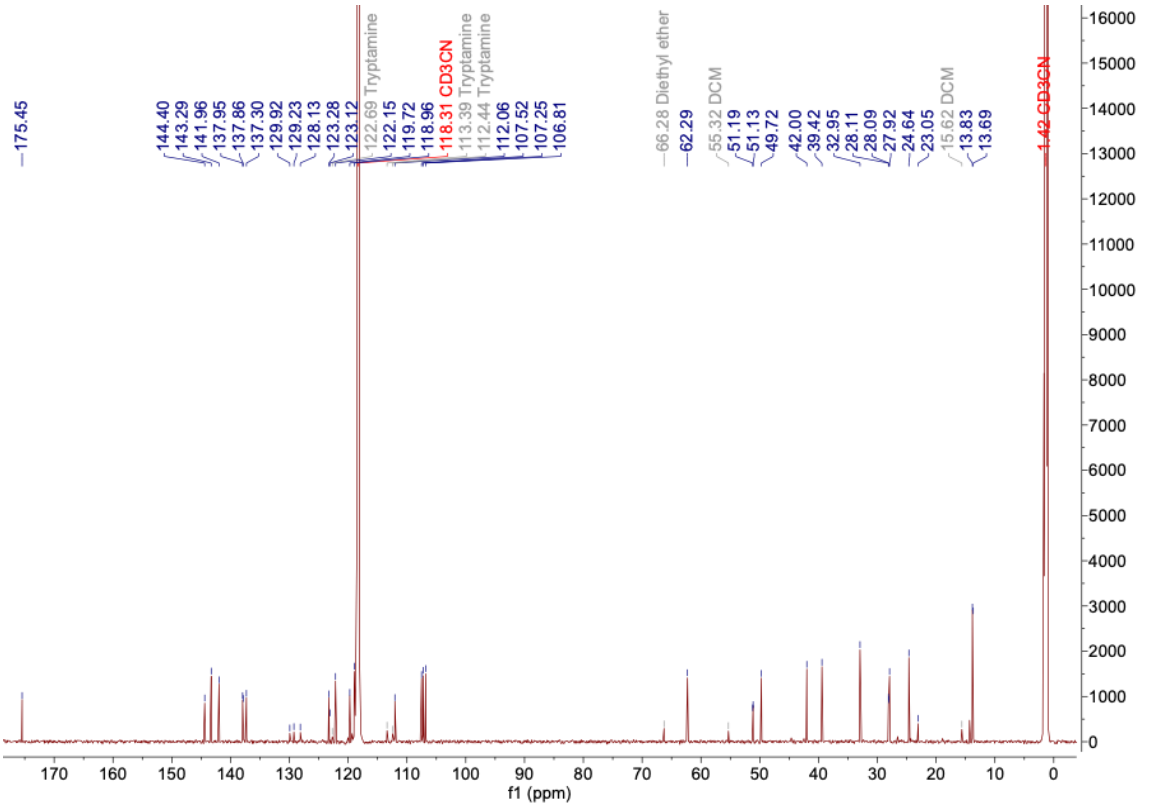


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.47:

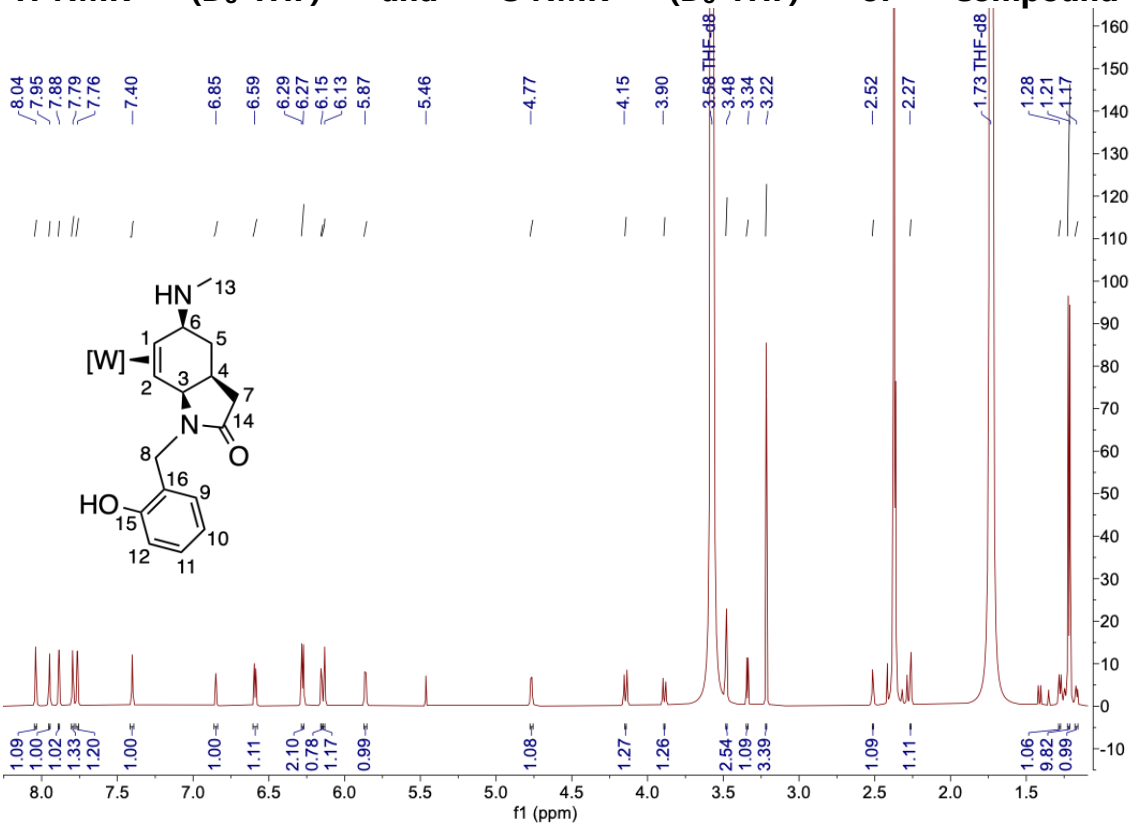


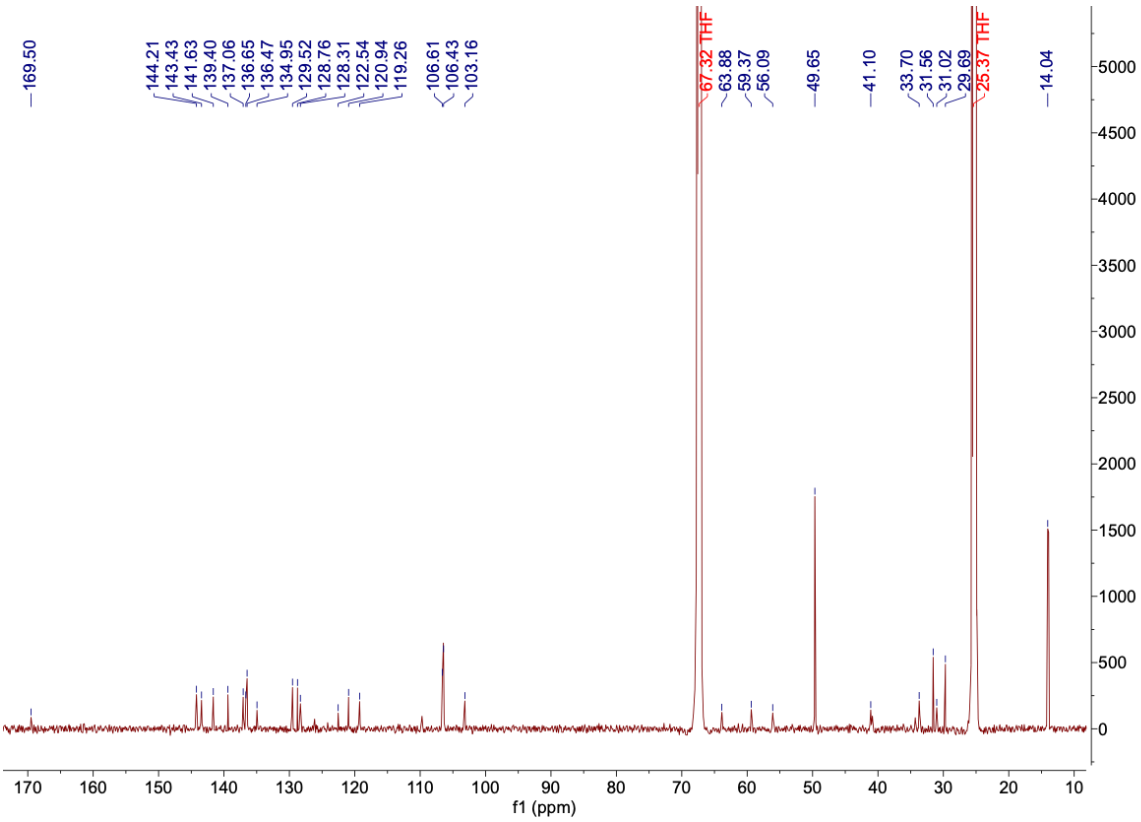
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.48:



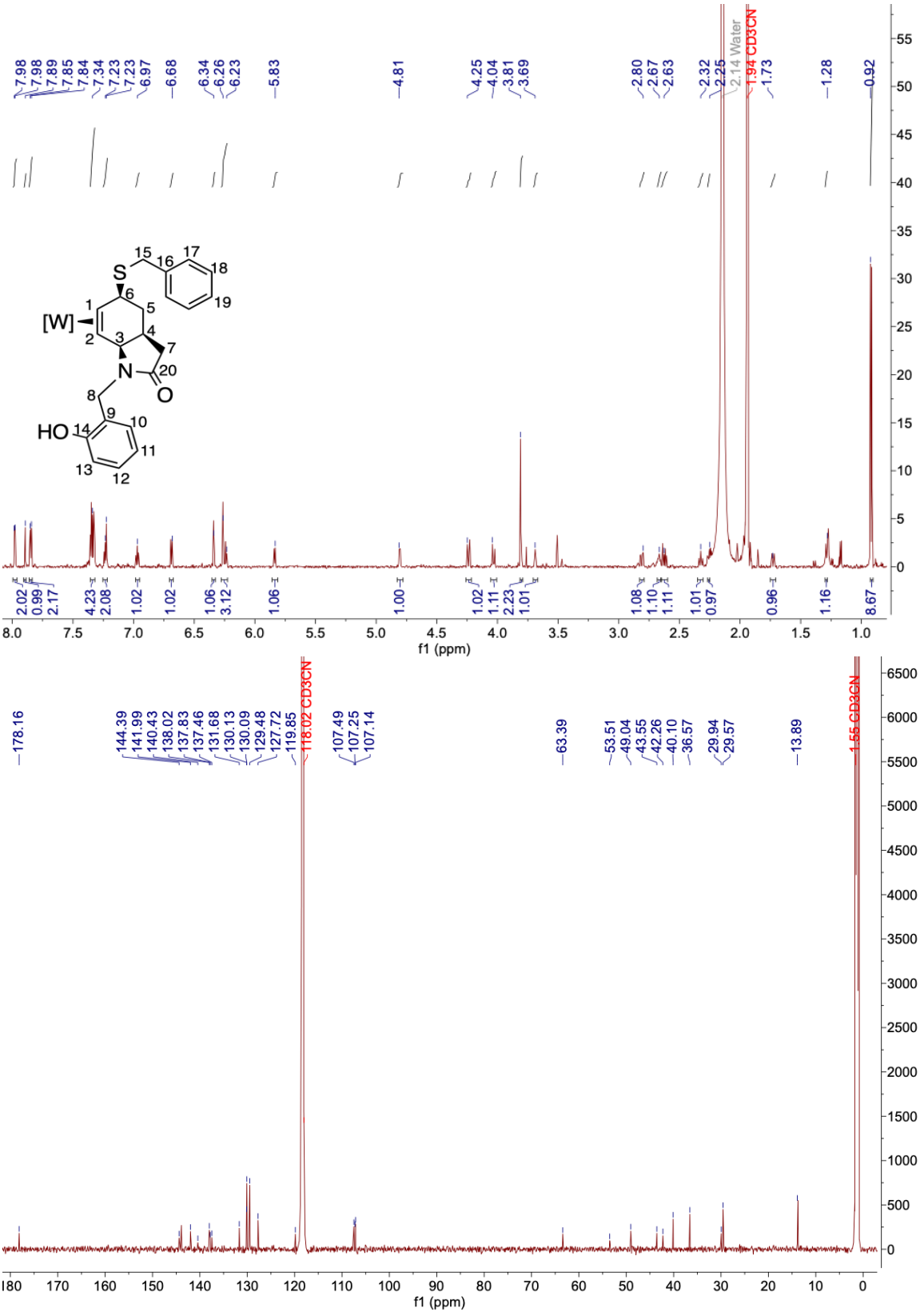


^{1}H-NMR (D_8-THF) and C-NMR (D_8-THF) of Compound 4.49:

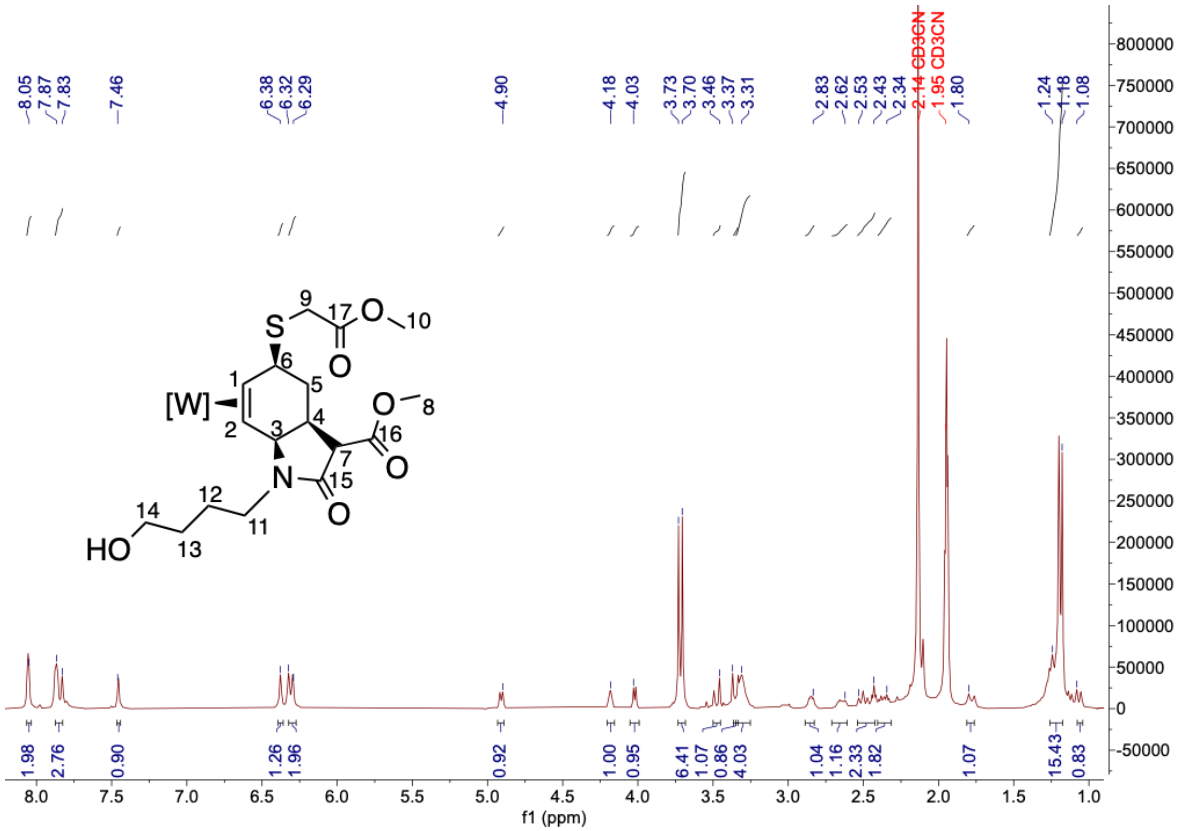


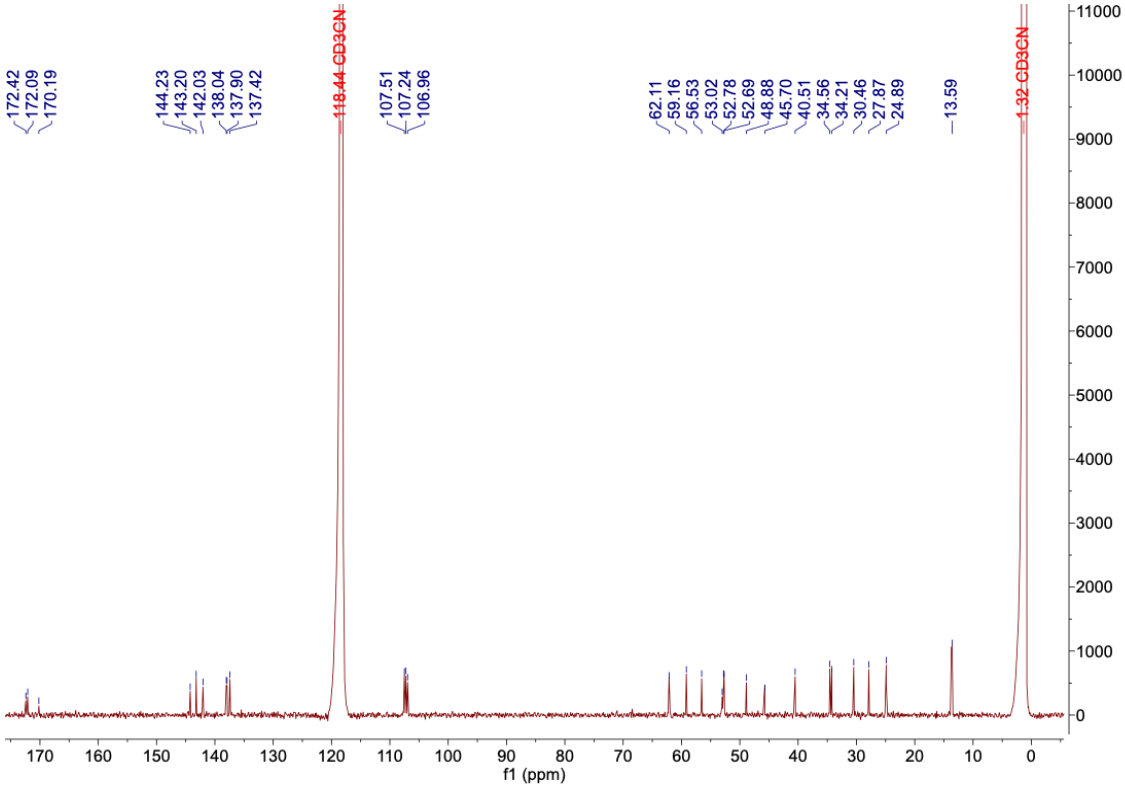


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.50:

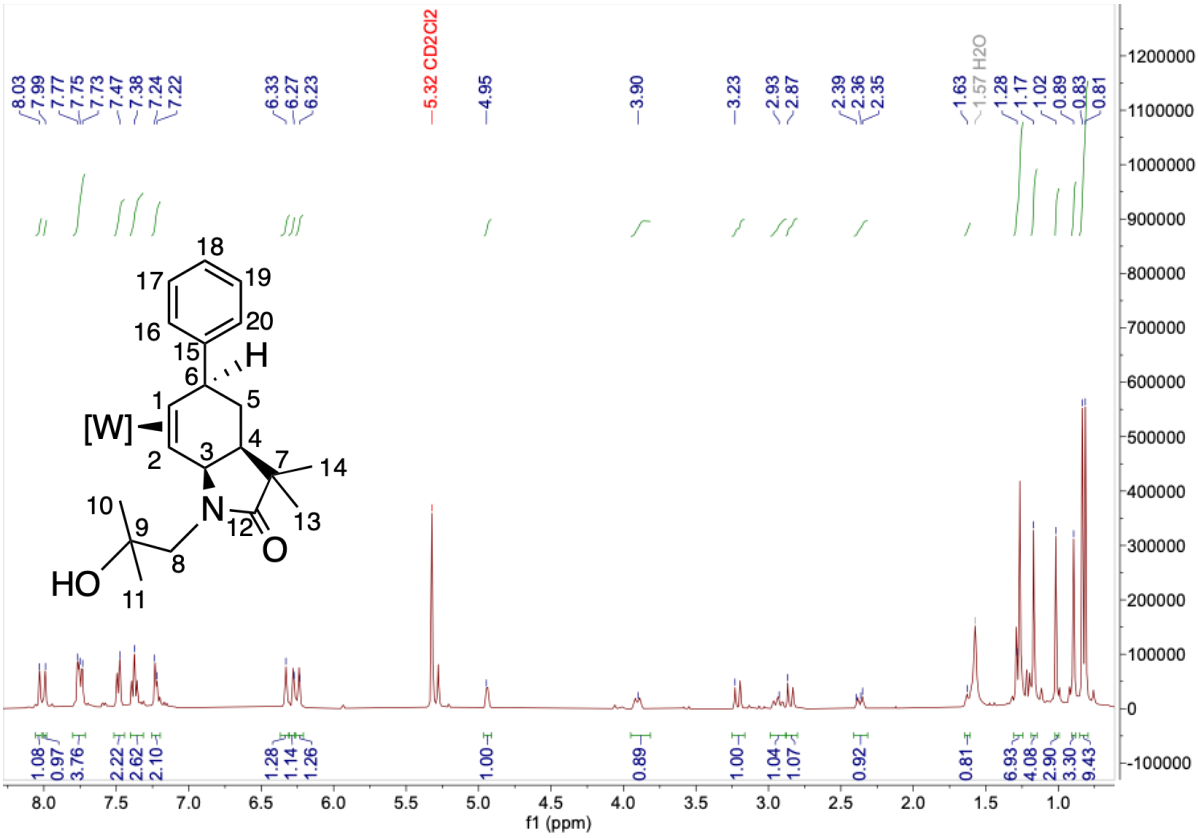


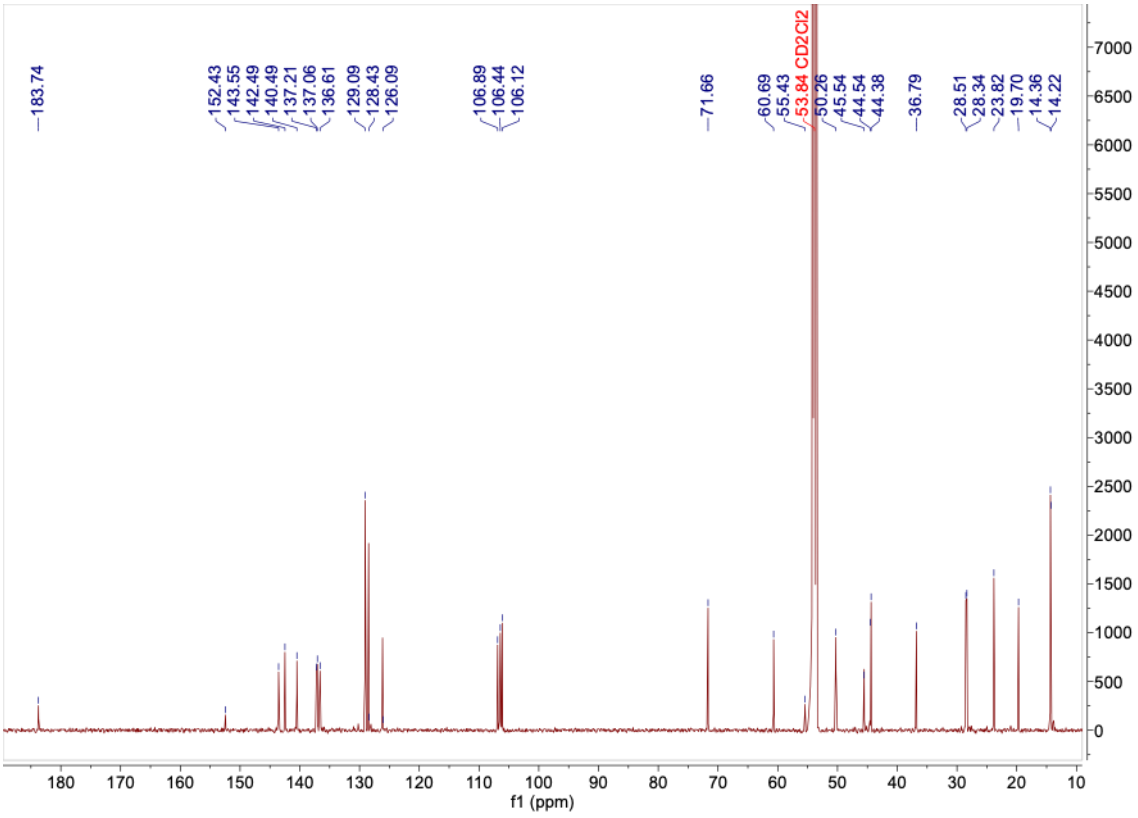
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.51:



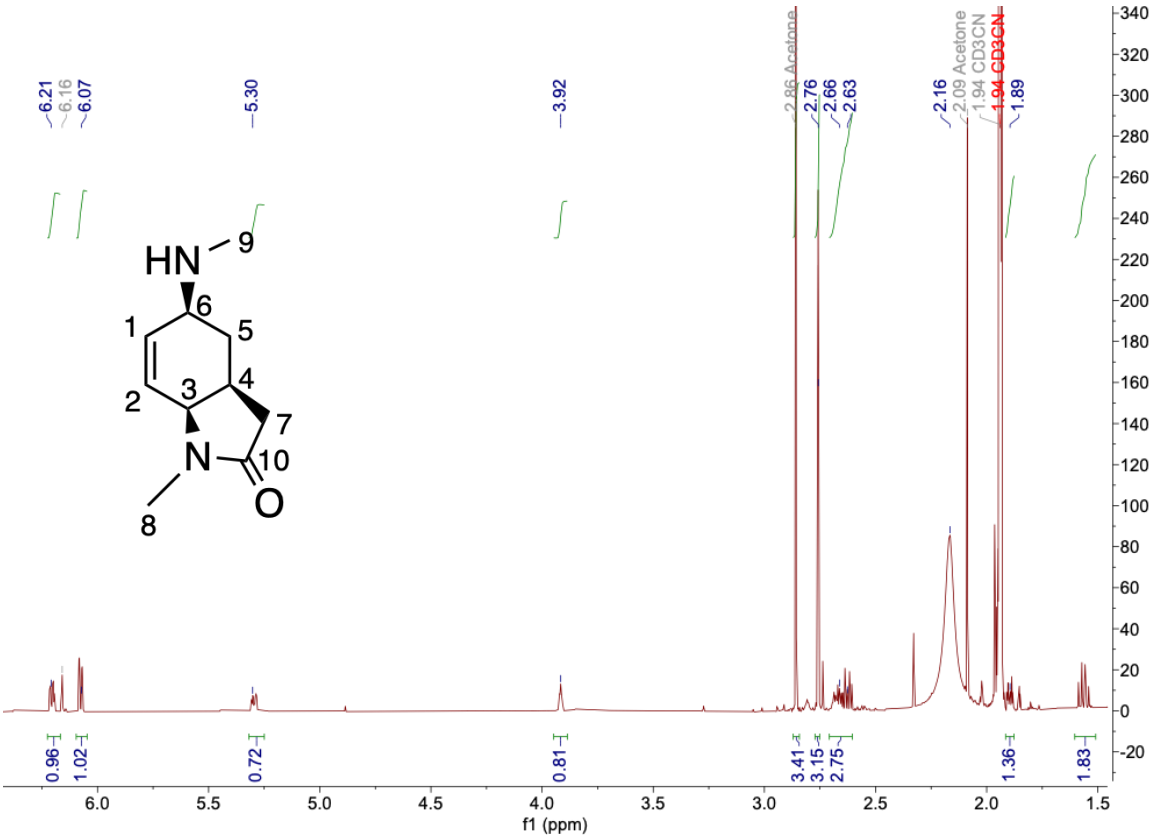


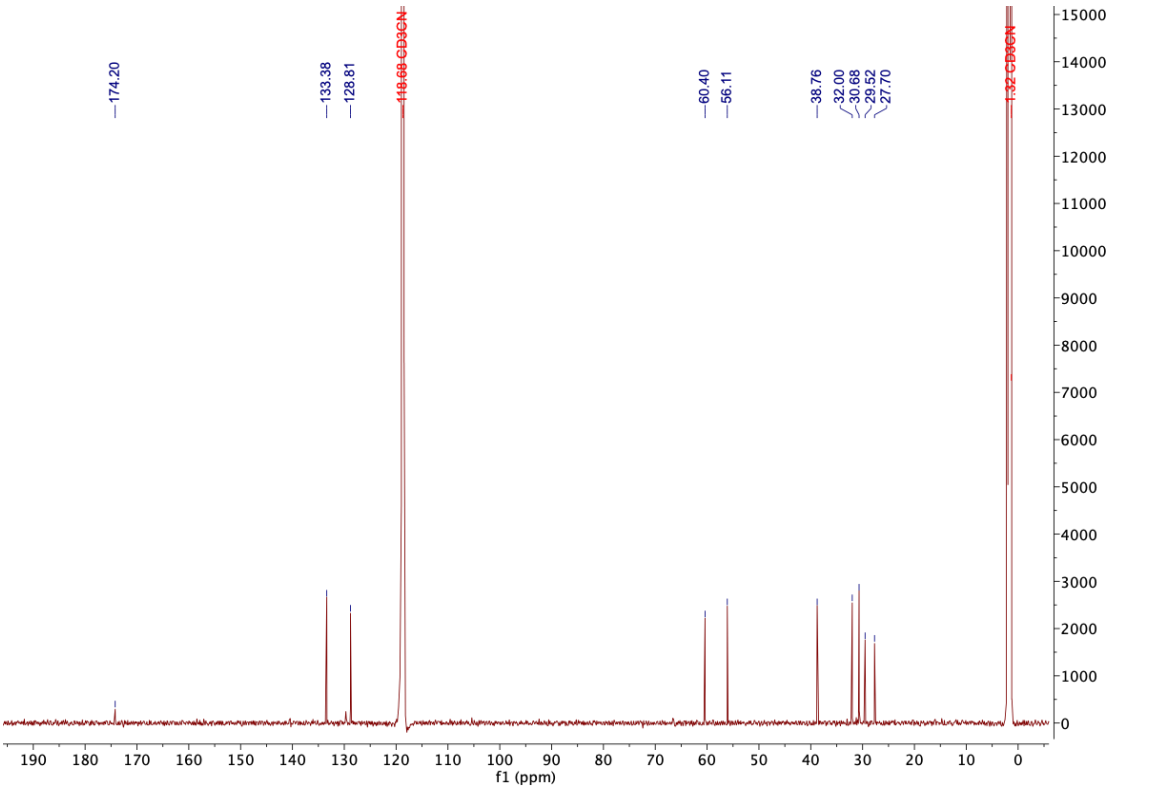
^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 4.52:



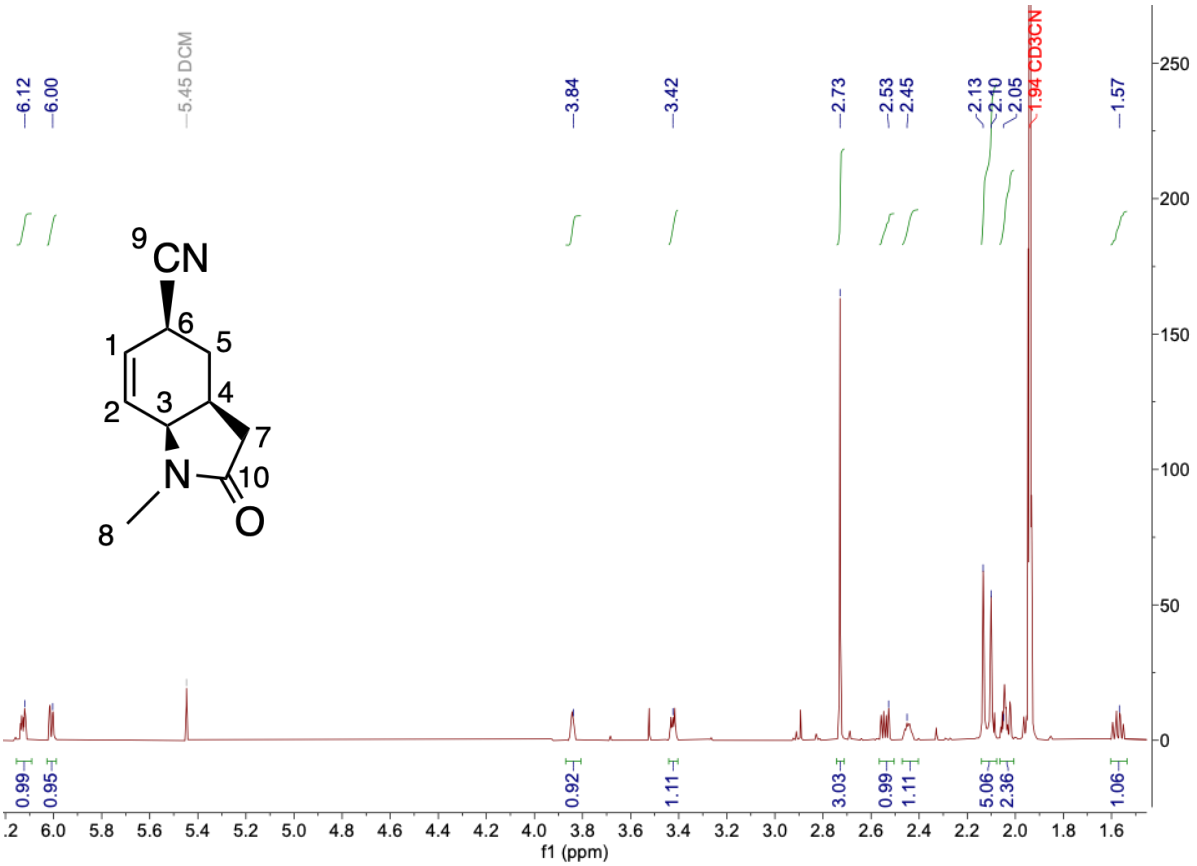


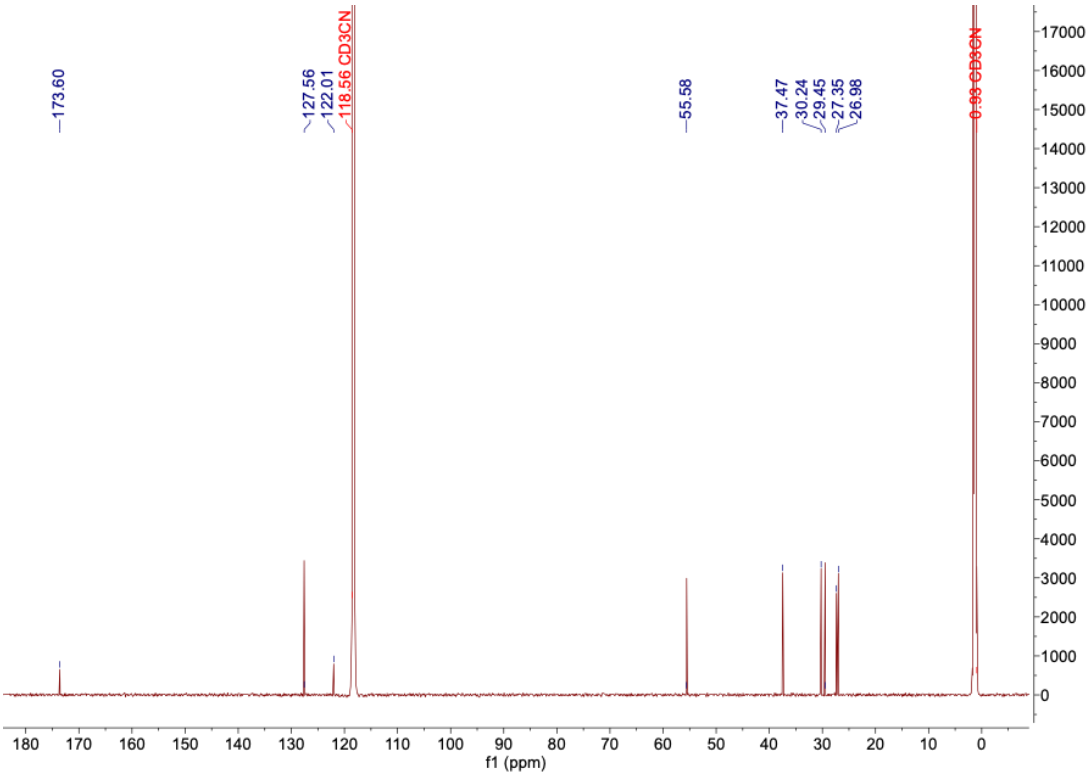
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.53:



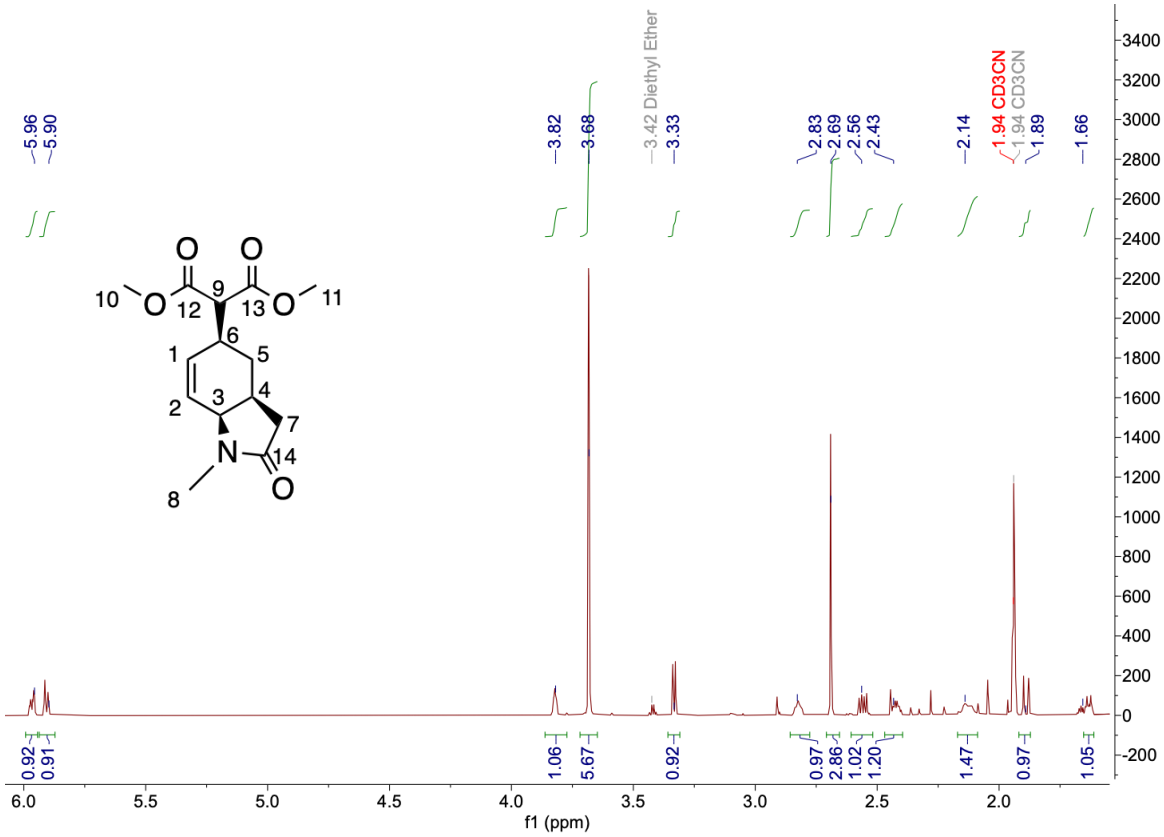


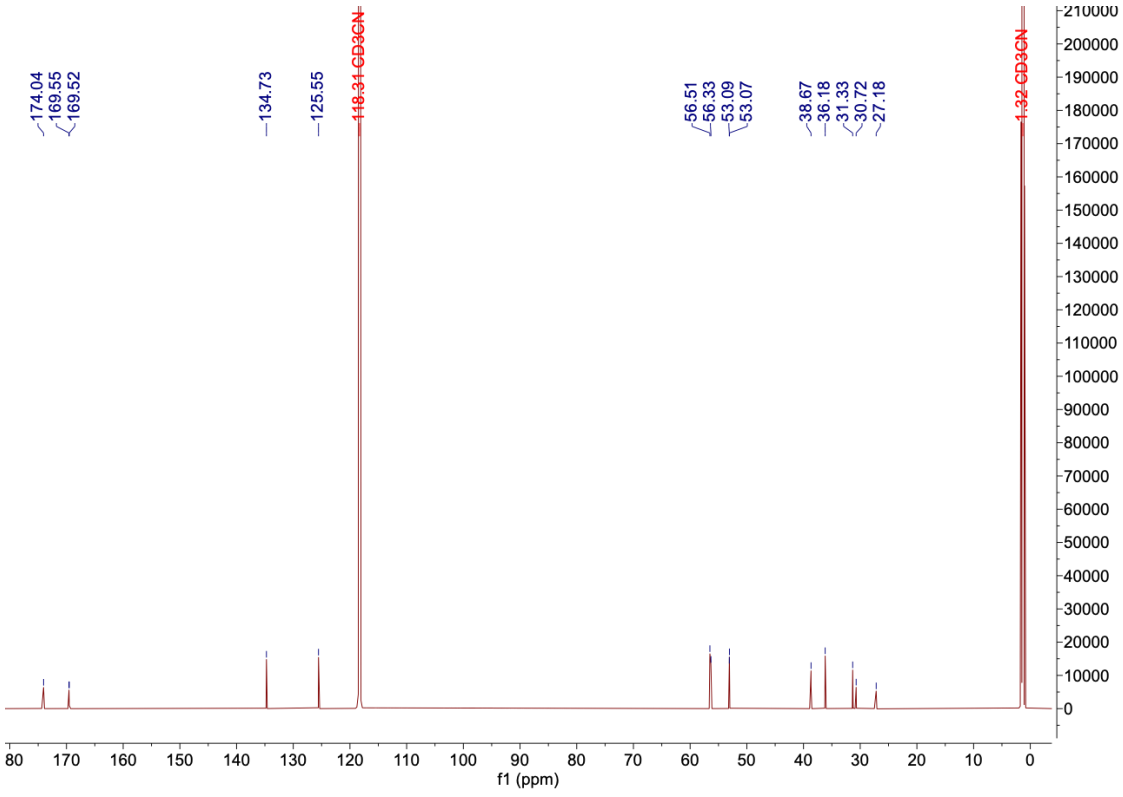
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.54:



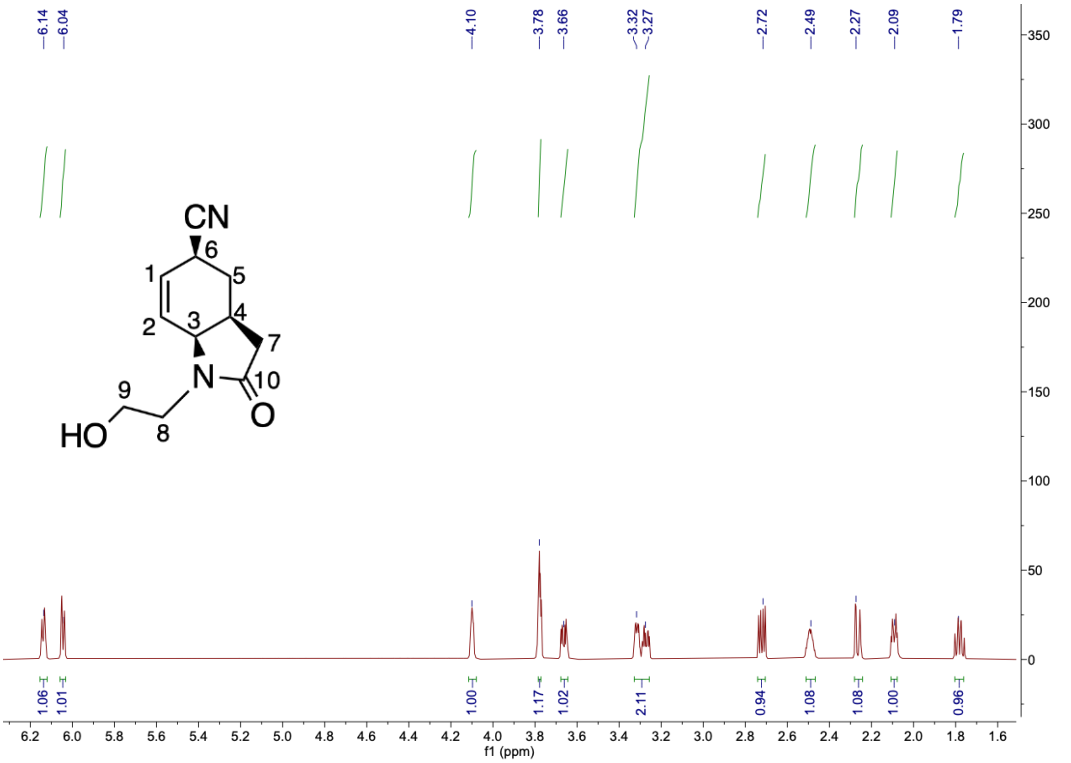


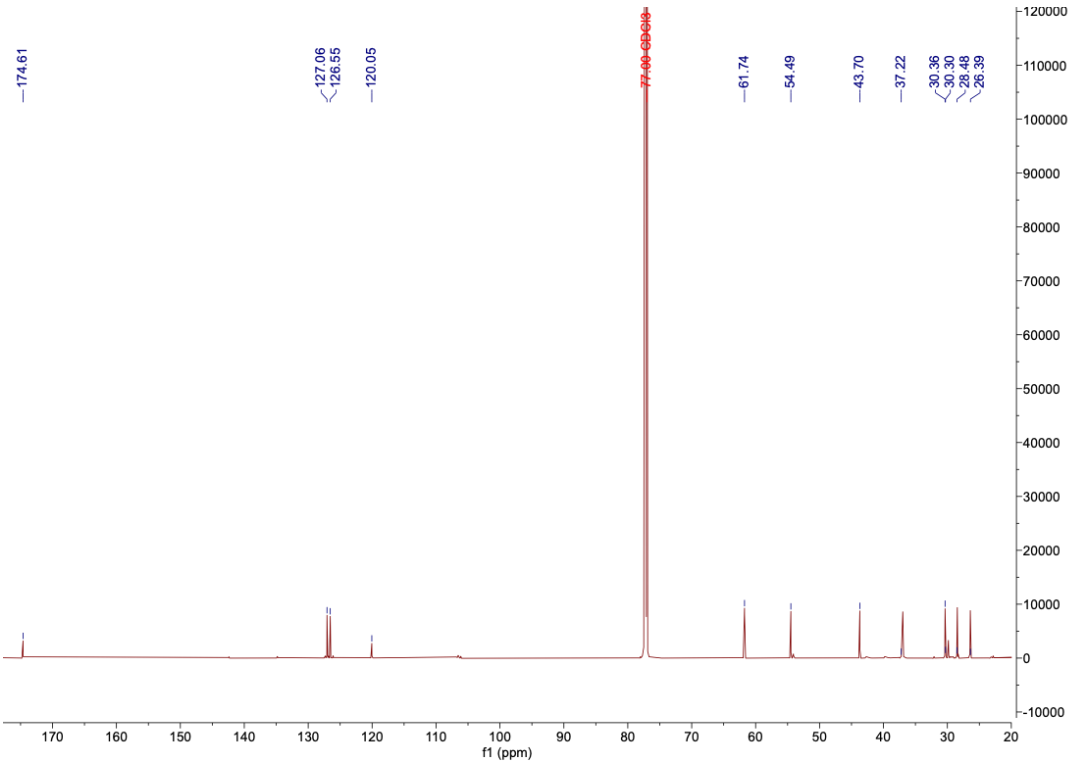
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.55:



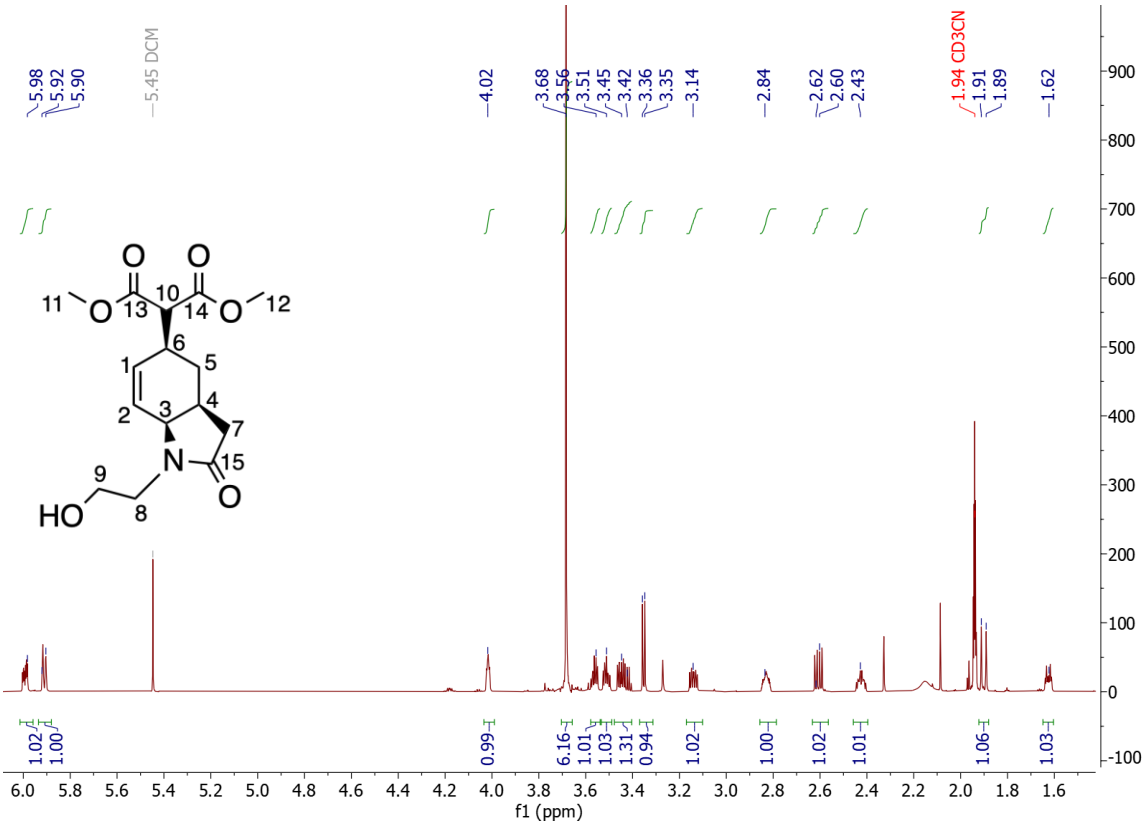


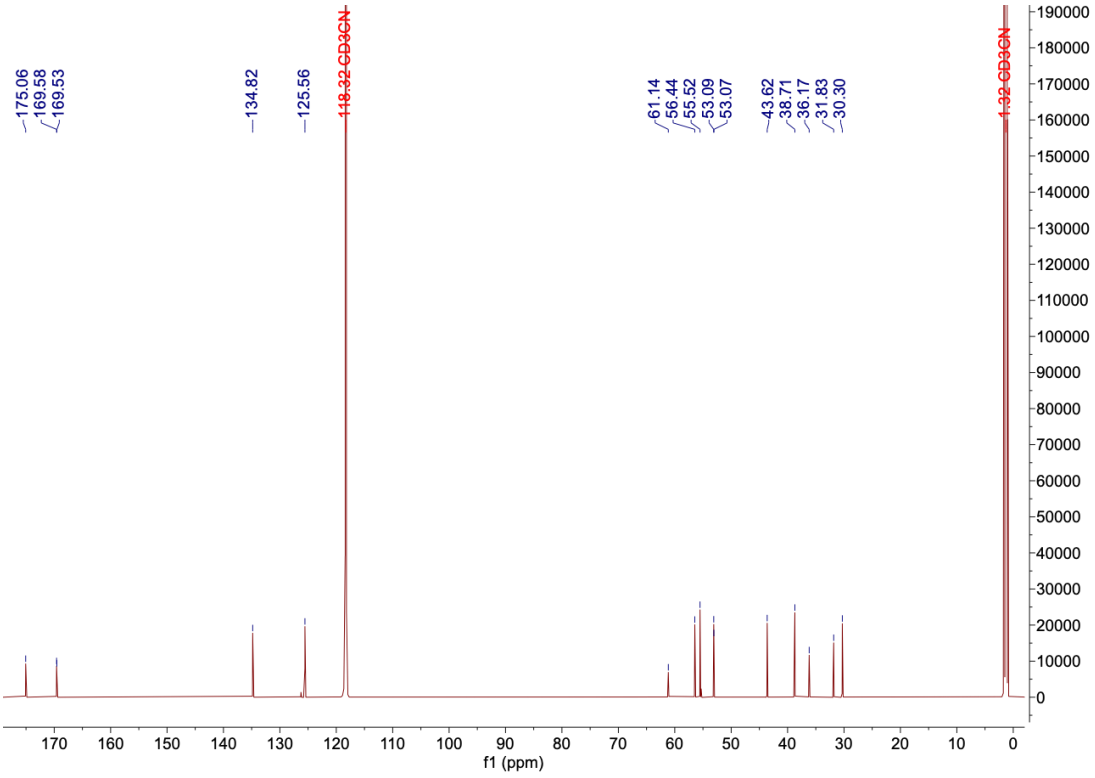
^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR ($CDCl_3$) of Compound 4.56:



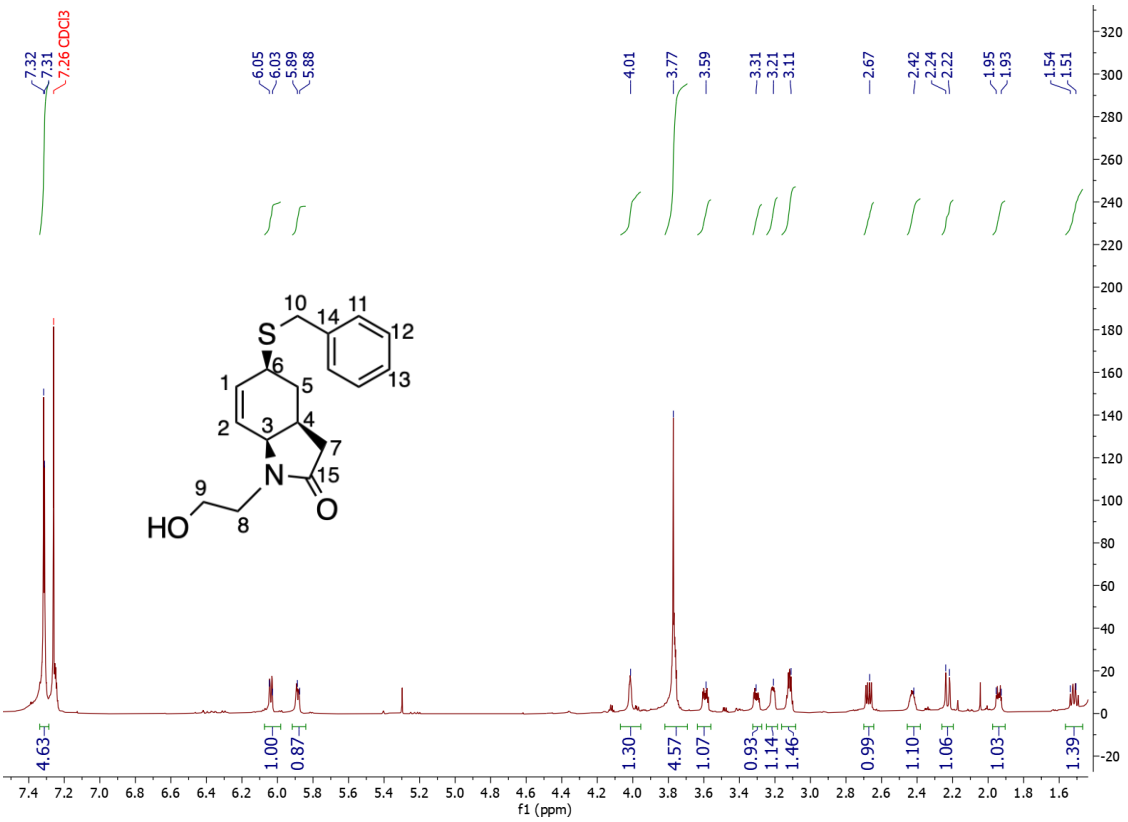


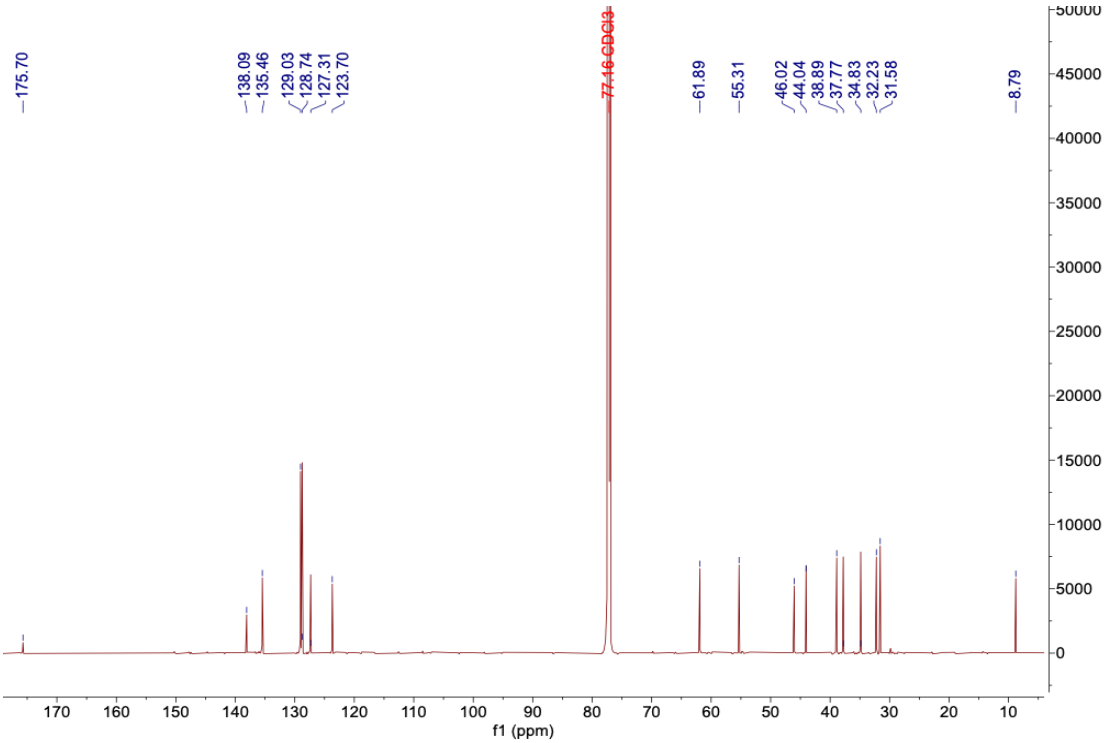
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.57:



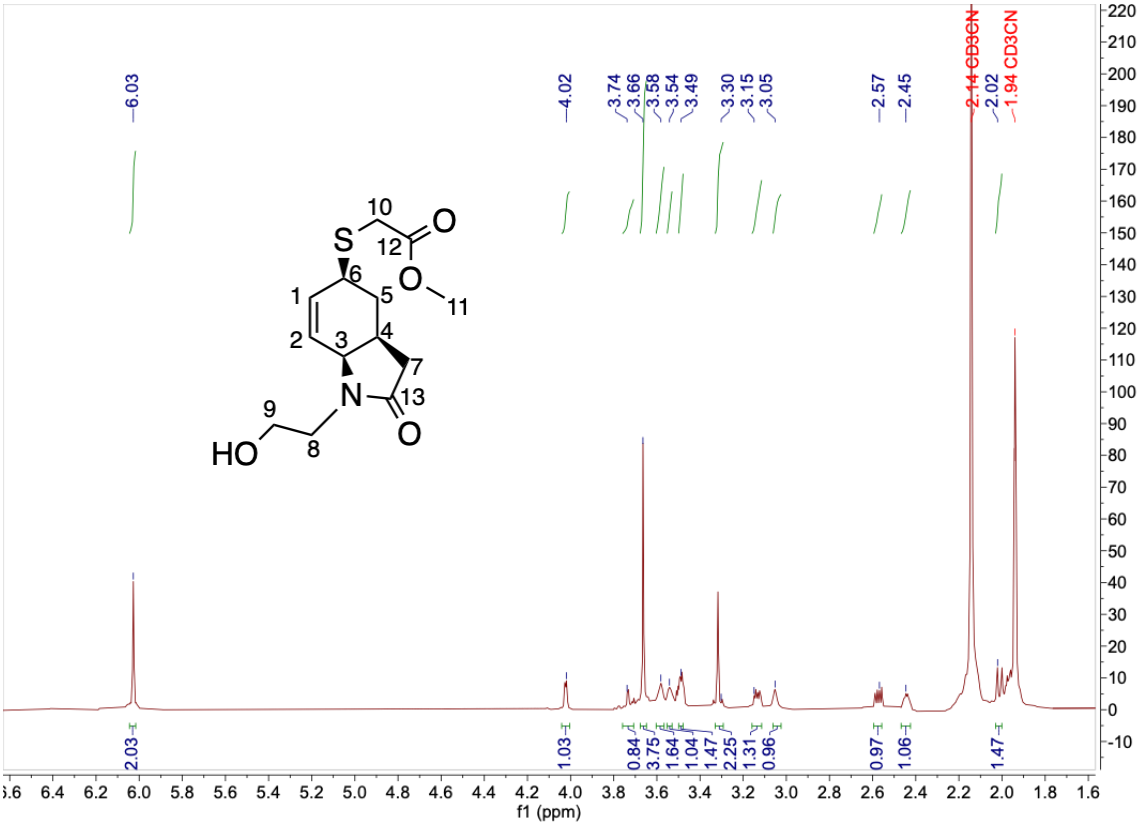


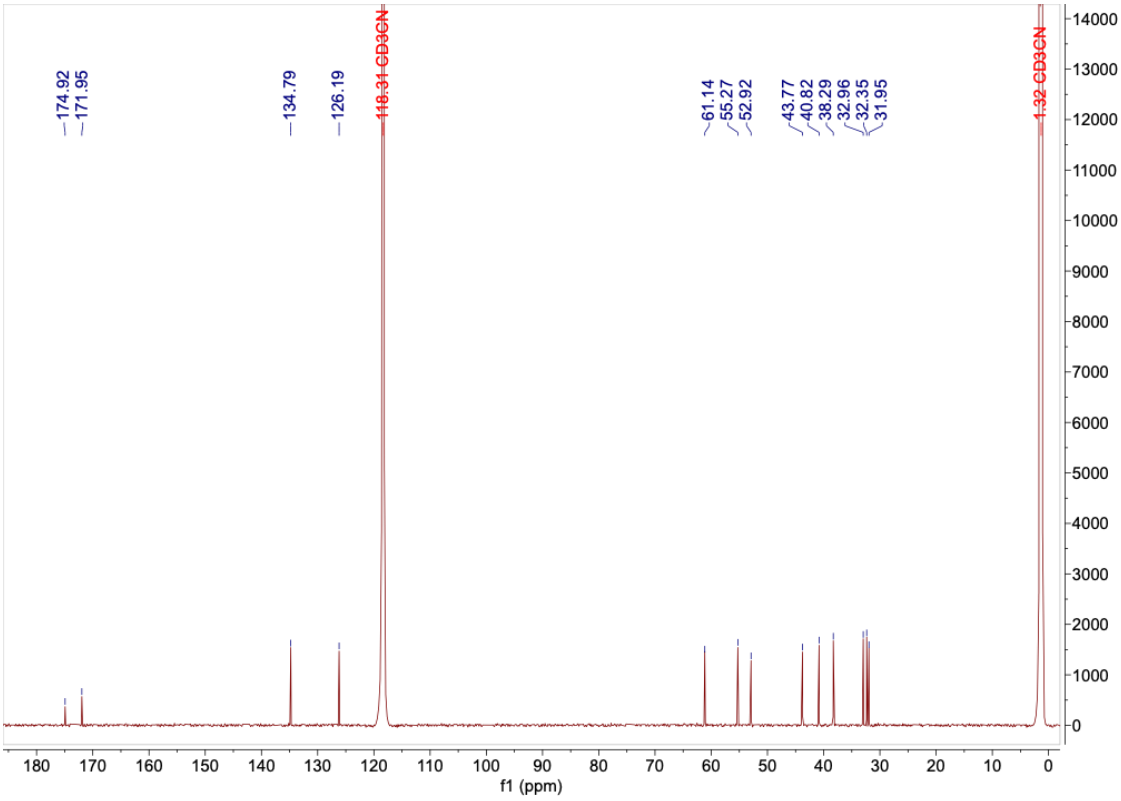
^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR ($CDCl_3$) of Compound 4.58:



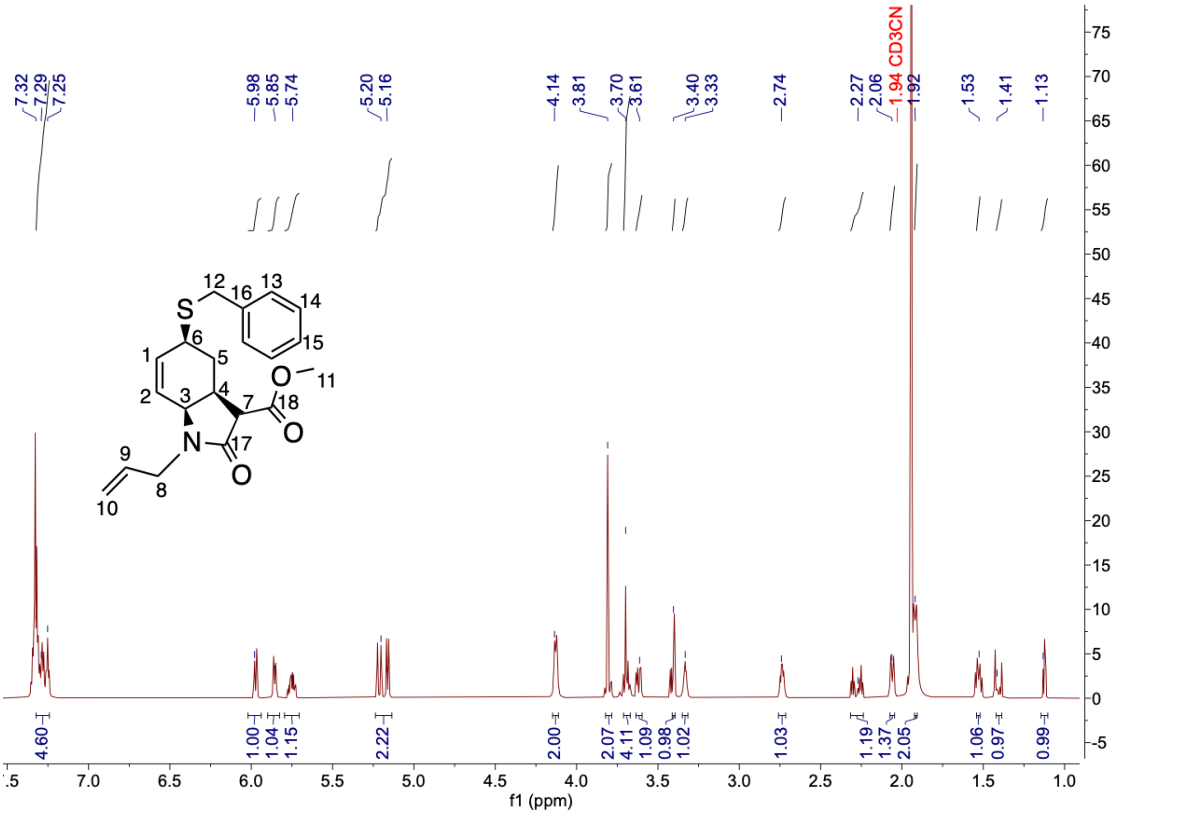


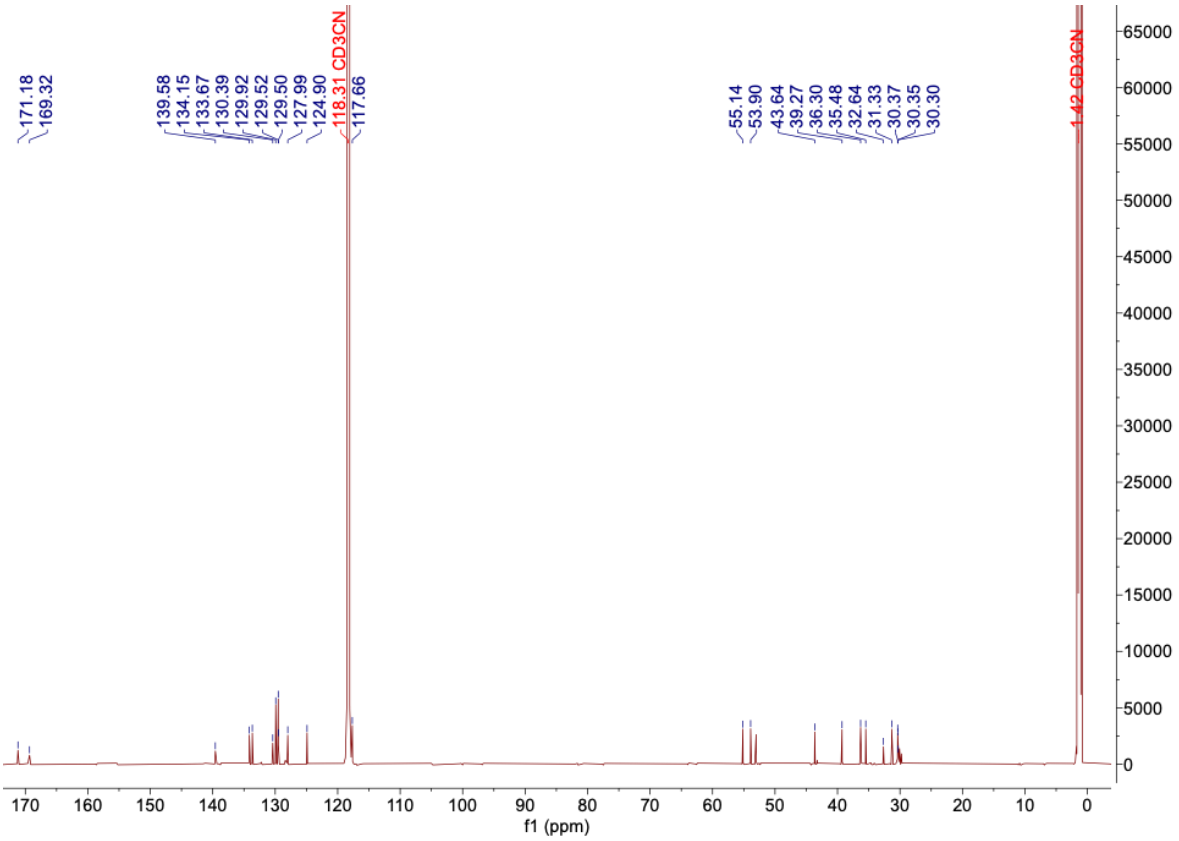
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.59:



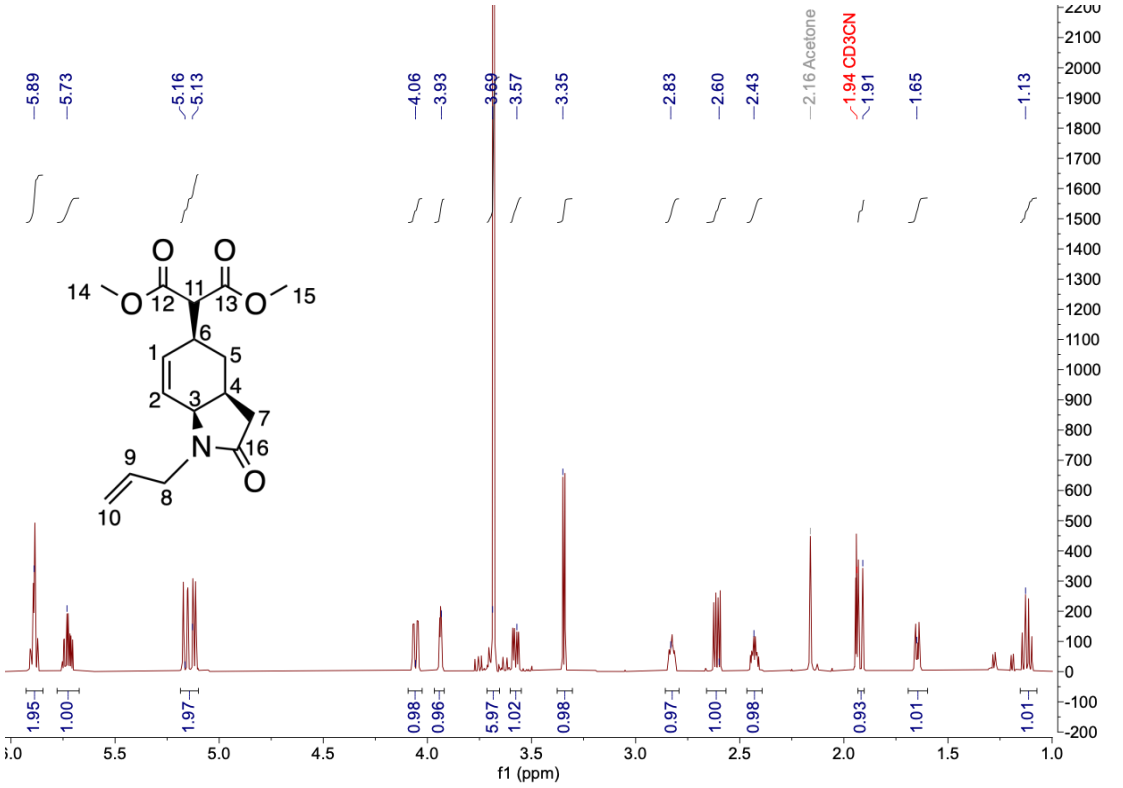


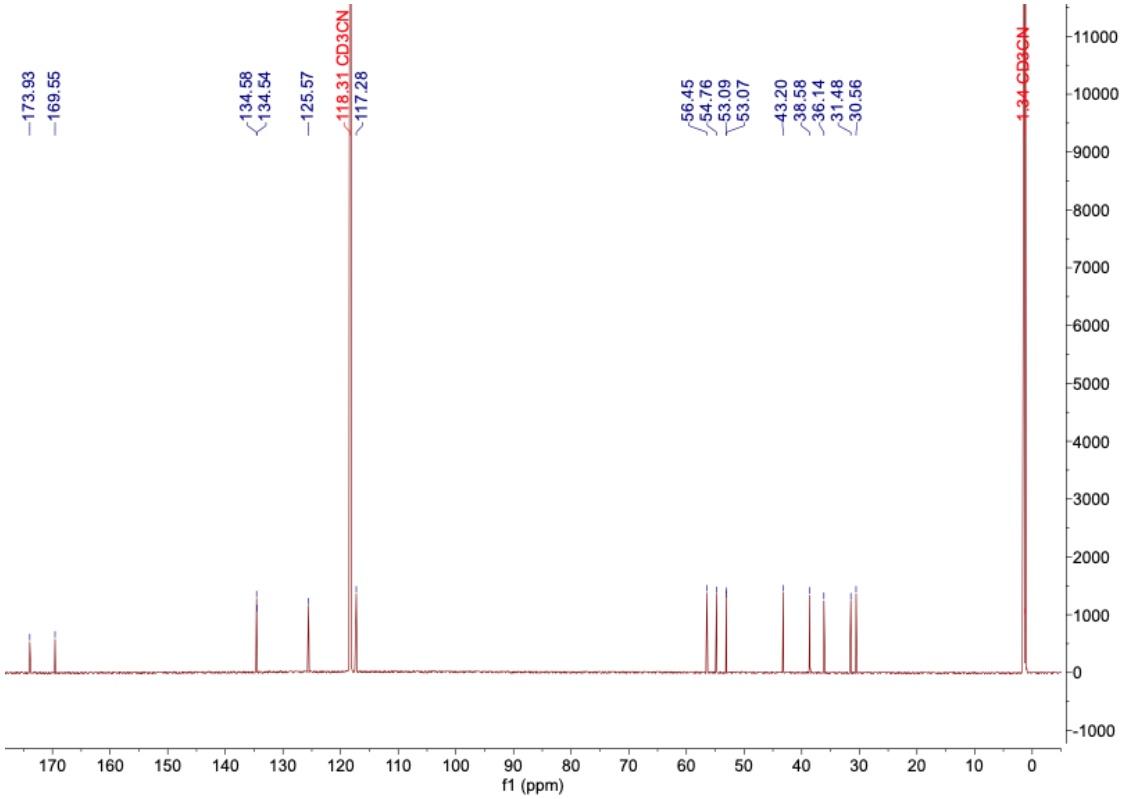
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.61:



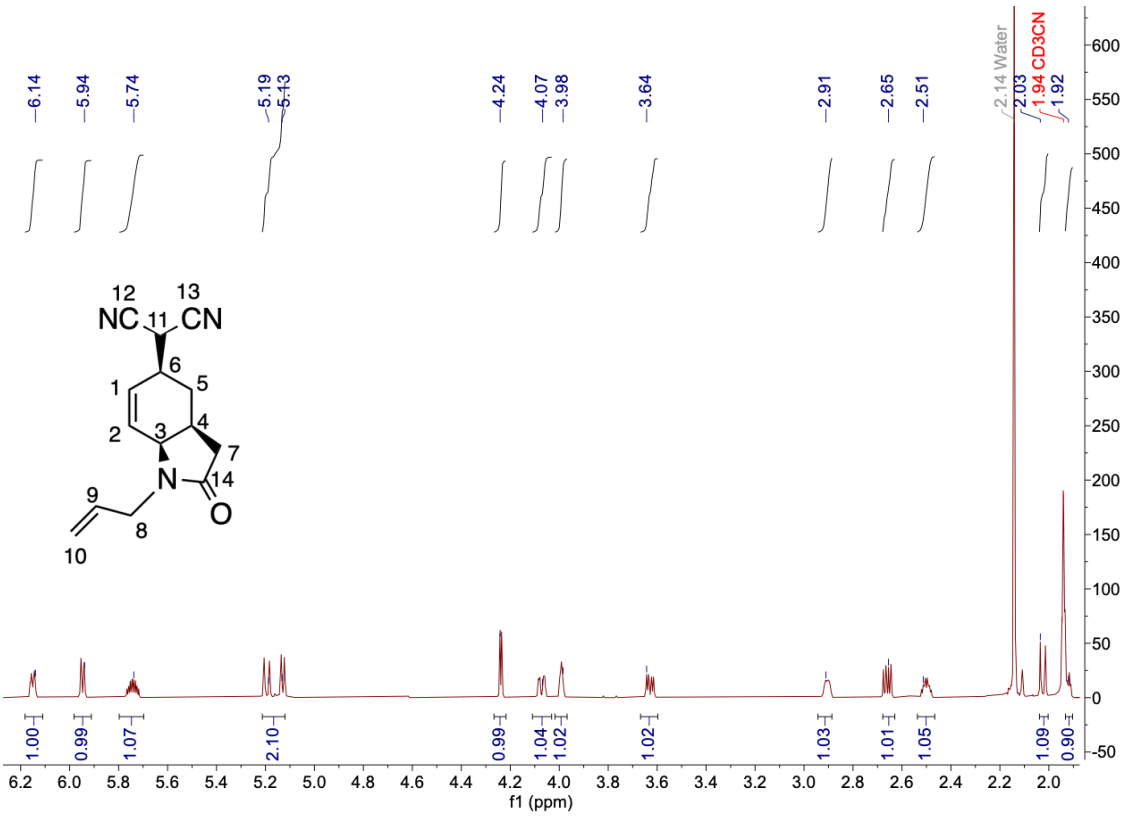


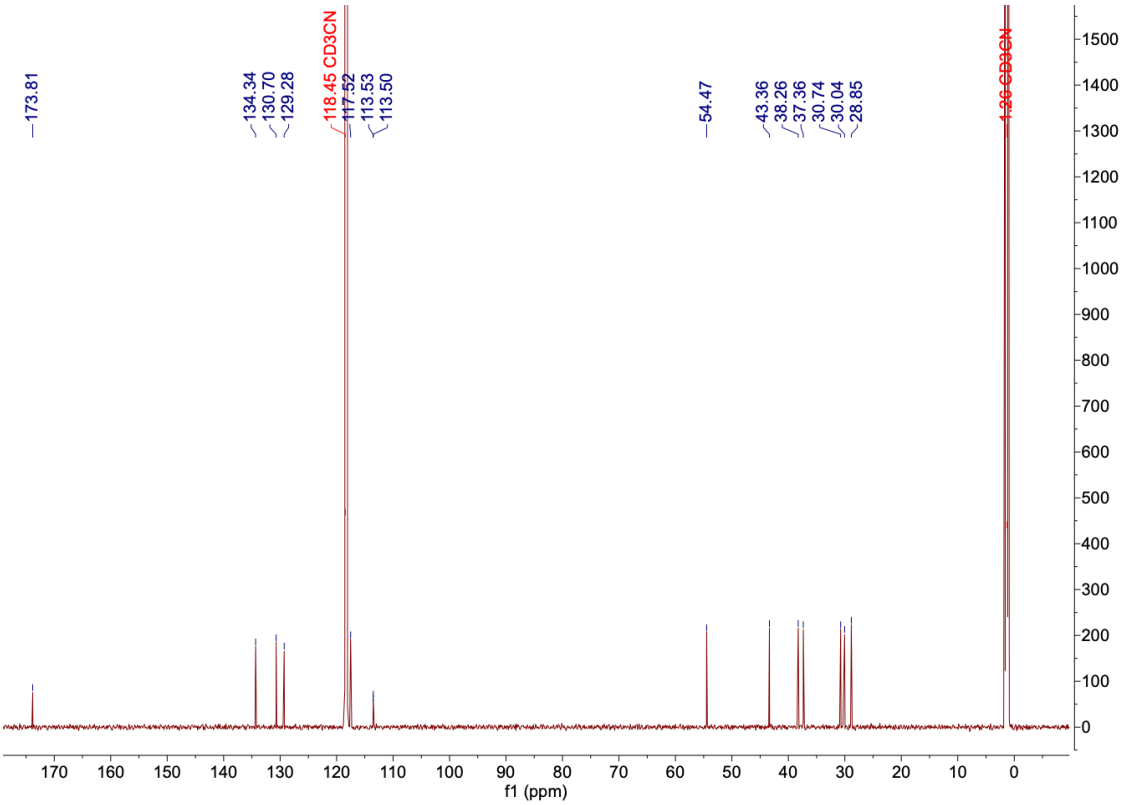
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.62:



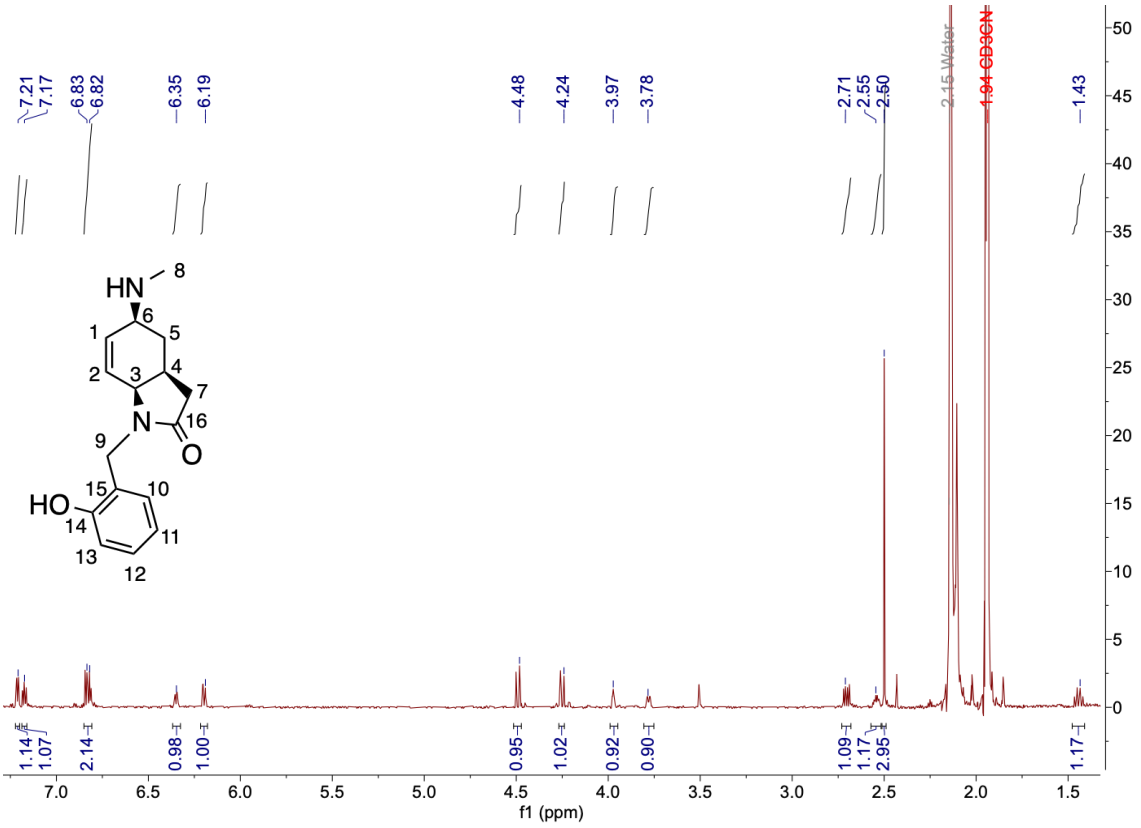


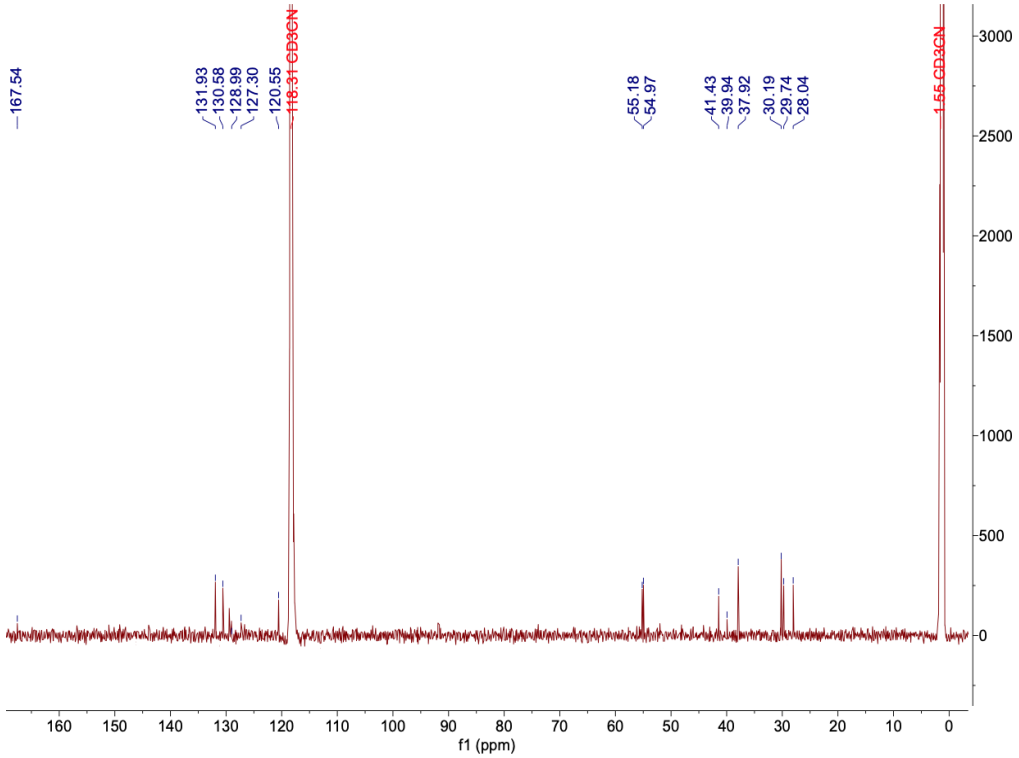
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.63:



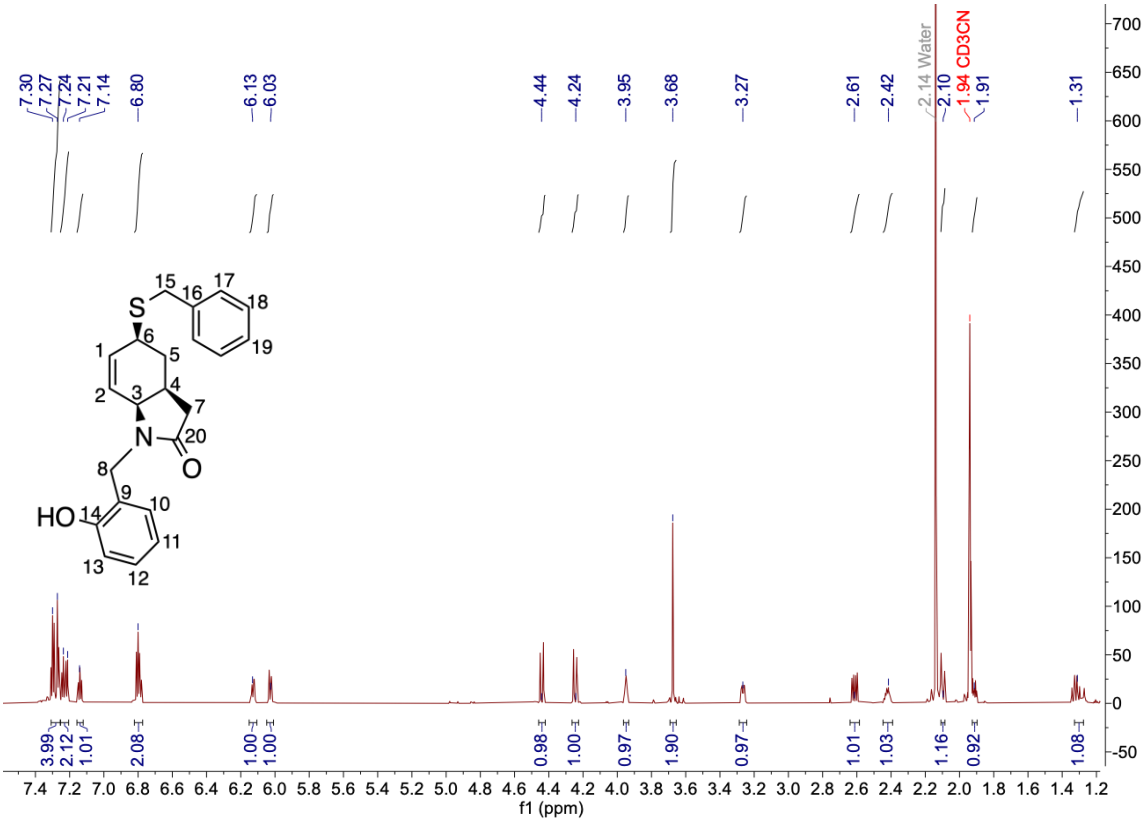


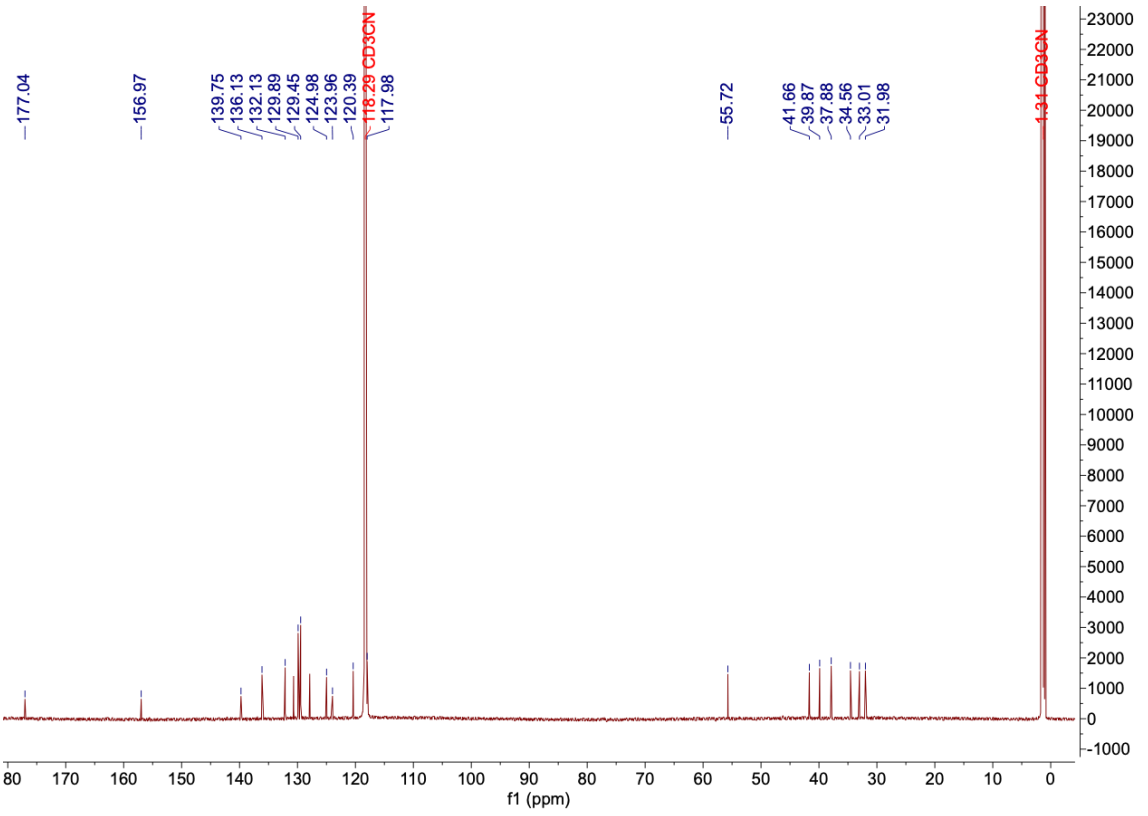
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.64:





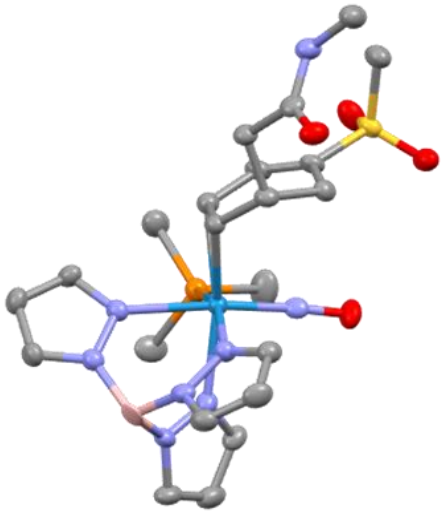
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 4.65:





Crystallographic Data Chapter 4

Crystal Structure Report for 4.3



Structure Report for 4.3

A colourless, plate shaped crystal of 4.3 measuring 0.07×0.07×0.104 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_1_187_x2_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800 low temperature device. Data collection and processing were done within the Bruker APEX4 software suite.[23] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[24] and refined by full-matrix least-squares methods against F^2 using XL[25] within OLEX2.[26] All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[27]

[23] *APEX4*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[24] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[25] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[26] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[27] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for 4.3

CCDC number	
Empirical formula	$C_{25}H_{40}BN_8O_5PSW$
Formula weight	790.34
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.07×0.07×0.104
Crystal habit	colourless plate
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
a [Å]	10.7683(6)
b [Å]	31.8429(18)
c [Å]	9.4093(5)
α [°]	90
β [°]	103.957(2)
γ [°]	90
Volume [$Å^3$]	3131.1(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.677
μ [mm^{-1}]	3.856
F(000)	1584
2θ range [°]	3.90 to 56.62 (0.75 Å)
Index ranges	−14 ≤ h ≤ 14 −42 ≤ k ≤ 42 −12 ≤ l ≤ 12
Reflections collected	53770
Independent reflections	7804 [R_{int} = 0.0759]
Data / Restraints / Parameters	7804 / 0 / 401
Goodness-of-fit on F^2	1.089
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0443 wR_2 = 0.0889
Final *R* indexes [all data]	R_1 = 0.0647 wR_2 = 0.0953

Largest peak/hole [eÅ^{-3}]	1.99/−1.60

Table 2 Atomic coordinates and Ueq [Å^2] for 4.3

Atom	***x***	***y***	***z***	U_{eq}
W1	0.29823(2)	0.40839(2)	0.56300(2)	0.02102(7)
S1	0.71779(13)	0.37654(4)	0.96625(14)	0.0272(3)
P1	0.28985(14)	0.46892(4)	0.73215(15)	0.0262(3)
O1	0.5677(4)	0.42850(12)	0.5551(5)	0.0361(10)
O2	0.5441(4)	0.22939(12)	0.6568(4)	0.0342(9)
O3	0.7006(4)	0.40876(13)	1.0678(4)	0.0391(10)
O4	0.8101(4)	0.38389(13)	0.8802(4)	0.0344(9)
O5	−0.0345(7)	0.2393(2)	0.4868(8)	0.097(2)
N1	0.2669(4)	0.37173(14)	0.3577(5)	0.0254(9)
N2	0.1546(5)	0.37426(14)	0.2533(5)	0.0271(10)
N3	0.2263(4)	0.45521(13)	0.3881(5)	0.0255(9)
N4	0.1154(4)	0.44897(14)	0.2849(5)	0.0250(9)
N5	0.0887(4)	0.39797(13)	0.5435(5)	0.0237(9)
N6	0.0049(4)	0.39675(13)	0.4081(5)	0.0246(9)
N7	0.4591(4)	0.41948(13)	0.5632(5)	0.0240(9)
N8	0.5932(5)	0.23405(15)	0.9024(5)	0.0326(11)
H8	0.568(6)	0.2433(19)	0.981(7)	0.039
C1	0.3476(6)	0.34932(16)	0.3013(6)	0.0282(12)
H1	0.432903	0.342530	0.351143	0.034
C2	0.2890(6)	0.33728(18)	0.1589(6)	0.0346(14)
H2	0.324766	0.320982	0.094068	0.042
C3	0.1703(6)	0.35382(18)	0.1328(6)	0.0325(13)
H3	0.107136	0.351453	0.043217	0.039
C4	0.2721(6)	0.49245(16)	0.3614(6)	0.0286(12)
H4	0.348986	0.504654	0.417274	0.034
C5	0.1906(6)	0.51096(19)	0.2392(6)	0.0363(14)
H5	0.200031	0.537480	0.196777	0.044
C6	0.0951(6)	0.48267(17)	0.1946(6)	0.0329(13)
H6	0.024538	0.485988	0.112450	0.039
C7	0.0150(5)	0.39326(17)	0.6384(6)	0.0273(12)
H7	0.046655	0.393073	0.741818	0.033
C8	−0.1109(6)	0.38877(18)	0.5691(6)	0.0309(12)
H8A	−0.180734	0.384823	0.613042	0.037
C9	−0.1152(5)	0.39117(18)	0.4220(6)	0.0292(12)
H9	−0.189843	0.389217	0.344208	0.035

C10	0.3258(5)	0.34582(16)	0.6600(6)	0.0227(11)
H10	0.252(5)	0.3321(17)	0.638(6)	0.024(15)
C11	0.3375(5)	0.37492(17)	0.7793(6)	0.0252(11)
H11	0.278(5)	0.3811(17)	0.831(6)	0.025(15)
C12	0.4640(5)	0.38153(17)	0.8762(6)	0.0281(12)
H12	0.471281	0.398288	0.961344	0.034
C13	0.5705(5)	0.36477(17)	0.8494(5)	0.0263(11)
C14	0.5669(5)	0.33759(16)	0.7178(6)	0.0256(11)
H14A	0.635362	0.316188	0.743021	0.031
H14B	0.583800	0.355134	0.637687	0.031
C15	0.4375(5)	0.31557(16)	0.6646(6)	0.0262(11)
H15	0.431195	0.304606	0.563500	0.031
C16	0.4238(5)	0.27828(16)	0.7651(6)	0.0266(11)
H16A	0.430064	0.288844	0.865564	0.032
H16B	0.338186	0.265447	0.729487	0.032
C17	0.5251(5)	0.24519(16)	0.7695(6)	0.0273(12)
C18	0.6932(6)	0.2030(2)	0.9210(7)	0.0385(14)
H18A	0.758074	0.212259	0.870556	0.058
H18B	0.656771	0.176191	0.879605	0.058
H18C	0.732779	0.199413	1.025586	0.058
C19	0.7647(6)	0.33001(19)	1.0655(6)	0.0351(13)
H19A	0.848849	0.334058	1.132527	0.053
H19B	0.769333	0.307102	0.997413	0.053
H19C	0.701938	0.322947	1.121810	0.053
C20	0.2504(6)	0.4610(2)	0.9078(6)	0.0373(14)
H20A	0.313950	0.442394	0.968905	0.056
H20B	0.165337	0.448263	0.891978	0.056
H20C	0.250702	0.488134	0.957160	0.056
C21	0.4380(6)	0.4983(2)	0.7836(8)	0.0488(18)
H21A	0.426765	0.522280	0.844809	0.073
H21B	0.461253	0.508569	0.695248	0.073
H21C	0.506144	0.480110	0.838657	0.073
C22	0.1722(7)	0.50899(19)	0.6585(7)	0.0421(16)
H22A	0.086349	0.496621	0.637026	0.063
H22B	0.189091	0.520408	0.568298	0.063
H22C	0.177572	0.531593	0.730438	0.063
C23	0.0205(8)	0.2397(2)	0.3878(9)	0.0546(19)
C24	0.0181(9)	0.2036(3)	0.2943(9)	0.070(2)
H24A	−0.037928	0.181968	0.319226	0.105

H24B	0.104942	0.192280	0.308356	0.105
H24C	−0.014181	0.211912	0.191755	0.105
C25	0.1001(11)	0.2752(3)	0.3751(10)	0.095(4)
H25A	0.189862	0.268297	0.418976	0.143
H25B	0.074785	0.299386	0.426235	0.143
H25C	0.089872	0.282199	0.271454	0.143
B1	0.0496(6)	0.4057(2)	0.2669(6)	0.0295(13)
H1A	−0.026(5)	0.4018(16)	0.175(6)	0.023(14)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for 4.3 The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02301(11)	0.01863(10)	0.02101(10)	0.00018(9)	0.00451(8)	0.00058(9)
S1	0.0275(7)	0.0261(7)	0.0240(7)	0.0005(5)	−0.0017(6)	0.0013(5)
P1	0.0276(7)	0.0246(7)	0.0263(7)	−0.0045(5)	0.0062(6)	0.0012(6)
O1	0.029(2)	0.029(2)	0.054(3)	0.0026(19)	0.015(2)	−0.0054(17)
O2	0.049(3)	0.028(2)	0.027(2)	−0.0003(16)	0.0122(19)	0.0046(19)
O3	0.035(2)	0.040(2)	0.037(2)	−0.016(2)	−0.0013(19)	0.005(2)
O4	0.034(2)	0.036(2)	0.030(2)	0.0050(17)	0.0030(18)	−0.0059(18)
O5	0.127(6)	0.068(4)	0.122(6)	−0.022(4)	0.082(5)	−0.015(4)
N1	0.027(2)	0.026(2)	0.023(2)	0.0000(18)	0.0048(19)	0.0013(19)
N2	0.033(3)	0.025(2)	0.022(2)	0.0039(18)	0.004(2)	−0.005(2)
N3	0.027(2)	0.020(2)	0.032(2)	0.0020(18)	0.010(2)	0.0020(18)
N4	0.024(2)	0.028(2)	0.022(2)	0.0042(18)	0.0041(19)	0.0053(19)
N5	0.025(2)	0.021(2)	0.024(2)	−0.0010(16)	0.0026(19)	−0.0007(17)
N6	0.026(2)	0.022(2)	0.025(2)	−0.0006(17)	0.0045(19)	0.0009(18)
N7	0.033(3)	0.014(2)	0.024(2)	−0.0019(16)	0.004(2)	−0.0003(18)
N8	0.039(3)	0.031(3)	0.028(2)	0.005(2)	0.011(2)	0.006(2)
C1	0.034(3)	0.025(3)	0.027(3)	0.001(2)	0.010(2)	0.005(2)
C2	0.053(4)	0.028(3)	0.026(3)	−0.007(2)	0.016(3)	0.003(3)

C3	0.041(4)	0.029(3)	0.025(3)	0.000(2)	0.004(3)	−0.002(3)
C4	0.037(3)	0.018(3)	0.035(3)	−0.001(2)	0.017(3)	0.000(2)
C5	0.052(4)	0.031(3)	0.032(3)	0.006(2)	0.021(3)	0.010(3)
C6	0.045(4)	0.027(3)	0.028(3)	0.008(2)	0.013(3)	0.010(3)
C7	0.032(3)	0.029(3)	0.022(3)	−0.001(2)	0.008(2)	−0.005(2)
C8	0.028(3)	0.033(3)	0.034(3)	−0.003(2)	0.013(3)	−0.004(2)
C9	0.023(3)	0.034(3)	0.030(3)	0.000(2)	0.003(2)	−0.003(2)
C10	0.024(3)	0.021(3)	0.022(2)	0.001(2)	0.005(2)	0.000(2)
C11	0.027(3)	0.024(3)	0.025(3)	0.001(2)	0.007(2)	0.001(2)
C12	0.034(3)	0.027(3)	0.020(3)	−0.001(2)	0.000(2)	0.003(2)
C13	0.030(3)	0.029(3)	0.017(2)	0.001(2)	0.000(2)	0.003(2)
C14	0.026(3)	0.025(3)	0.025(3)	0.000(2)	0.006(2)	0.006(2)
C15	0.034(3)	0.020(3)	0.024(3)	0.002(2)	0.006(2)	0.003(2)
C16	0.033(3)	0.022(3)	0.026(3)	0.002(2)	0.009(2)	0.002(2)
C17	0.036(3)	0.017(2)	0.031(3)	0.003(2)	0.011(3)	−0.003(2)
C18	0.041(4)	0.042(3)	0.033(3)	0.007(3)	0.011(3)	0.010(3)
C19	0.033(3)	0.035(3)	0.034(3)	0.007(3)	0.000(3)	0.000(3)
C20	0.041(4)	0.043(4)	0.029(3)	−0.006(3)	0.011(3)	0.006(3)
C21	0.044(4)	0.051(4)	0.054(4)	−0.028(3)	0.014(3)	−0.017(3)
C22	0.061(4)	0.034(3)	0.036(3)	−0.003(3)	0.020(3)	0.022(3)
C23	0.072(5)	0.037(4)	0.061(5)	0.002(3)	0.028(4)	−0.004(4)
C24	0.101(7)	0.054(5)	0.056(5)	−0.002(4)	0.024(5)	0.006(5)
C25	0.132(9)	0.088(7)	0.070(6)	−0.012(5)	0.034(6)	−0.062(7)
B1	0.018(3)	0.047(4)	0.016(3)	−0.003(3)	−0.010(2)	−0.002(3)

Table 4 Bond lengths and angles for 4.3

Atom–Atom	Length [Å]
W1–P1	2.5152(14)
W1–N1	2.212(4)
W1–N3	2.218(4)
W1–N5	2.244(4)
W1–N7	1.768(5)
W1–C10	2.182(5)
W1–C11	2.245(5)
S1–O3	1.444(4)
S1–O4	1.445(4)
S1–C13	1.739(6)
S1–C19	1.759(6)
P1–C20	1.821(6)

P1–C21	1.813(6)
P1–C22	1.814(6)
O1–N7	1.224(6)
O2–C17	1.234(6)
O5–C23	1.218(9)
N1–N2	1.364(6)
N1–C1	1.330(7)
N2–C3	1.353(7)
N2–B1	1.538(8)
N3–N4	1.359(6)
N3–C4	1.331(6)
N4–C6	1.353(7)
N4–B1	1.540(8)
N5–N6	1.373(6)
N5–C7	1.339(6)
N6–C9	1.343(7)
N6–B1	1.544(7)
N8–H8	0.90(6)
N8–C17	1.336(7)
N8–C18	1.441(7)
C1–H1	0.9500
C1–C2	1.391(8)
C2–H2	0.9500
C2–C3	1.349(8)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.398(8)
C5–H5	0.9500
C5–C6	1.356(9)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.362(8)
C8–H8A	0.9500
C8–C9	1.376(8)
C9–H9	0.9500
C10–H10	0.88(6)
C10–C11	1.437(7)
C10–C15	1.534(7)
C11–H11	0.91(5)
C11–C12	1.461(8)

C12–H12	0.9500
C12–C13	1.342(8)
C13–C14	1.503(7)
C14–H14A	0.9900
C14–H14B	0.9900
C14–C15	1.532(8)
C15–H15	1.0000
C15–C16	1.547(7)
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.510(7)
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C19–H19A	0.9800
C19–H19B	0.9800
C19–H19C	0.9800
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–C24	1.445(10)
C23–C25	1.443(10)
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
B1–H1A	1.05(6)

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	159.35(12)
N1–W1–N3	75.77(16)

N1–W1–N5	84.94(16)
N1–W1–C11	119.78(18)
N3–W1–P1	83.97(12)
N3–W1–N5	82.80(16)
N3–W1–C11	161.39(18)
N5–W1–P1	88.63(11)
N5–W1–C11	88.26(18)
N7–W1–P1	91.78(13)
N7–W1–N1	92.84(18)
N7–W1–N3	91.89(18)
N7–W1–N5	174.61(17)
N7–W1–C10	98.5(2)
N7–W1–C11	97.1(2)
C10–W1–P1	117.21(14)
C10–W1–N1	81.95(17)
C10–W1–N3	155.84(19)
C10–W1–N5	86.09(18)
C10–W1–C11	37.86(19)
C11–W1–P1	79.51(14)
O3–S1–O4	118.1(3)
O3–S1–C13	109.2(3)
O3–S1–C19	108.3(3)
O4–S1–C13	109.0(2)
O4–S1–C19	106.6(3)
C13–S1–C19	104.8(3)
C20–P1–W1	121.4(2)
C21–P1–W1	113.7(2)
C21–P1–C20	102.2(3)
C21–P1–C22	103.1(3)
C22–P1–W1	115.2(2)
C22–P1–C20	98.6(3)
N2–N1–W1	121.3(3)
C1–N1–W1	130.9(4)
C1–N1–N2	107.2(4)
N1–N2–B1	121.4(4)
C3–N2–N1	107.9(5)
C3–N2–B1	128.7(5)
N4–N3–W1	121.4(3)
C4–N3–W1	131.3(4)
C4–N3–N4	107.3(4)

N3–N4–B1	120.8(4)
C6–N4–N3	108.3(5)
C6–N4–B1	129.8(5)
N6–N5–W1	120.2(3)
C7–N5–W1	135.1(4)
C7–N5–N6	104.7(4)
N5–N6–B1	121.5(4)
C9–N6–N5	110.2(4)
C9–N6–B1	128.0(5)
O1–N7–W1	175.9(4)
C17–N8–H8	119(4)
C17–N8–C18	121.4(5)
C18–N8–H8	119(4)
N1–C1–H1	124.9
N1–C1–C2	110.1(5)
C2–C1–H1	124.9
C1–C2–H2	127.6
C3–C2–C1	104.9(5)
C3–C2–H2	127.6
N2–C3–H3	125.1
C2–C3–N2	109.9(5)
C2–C3–H3	125.1
N3–C4–H4	125.0
N3–C4–C5	110.1(5)
C5–C4–H4	125.0
C4–C5–H5	127.7
C6–C5–C4	104.7(5)
C6–C5–H5	127.7
N4–C6–C5	109.7(5)
N4–C6–H6	125.2
C5–C6–H6	125.2
N5–C7–H7	124.0
N5–C7–C8	112.0(5)
C8–C7–H7	124.0
C7–C8–H8A	127.3
C7–C8–C9	105.3(5)
C9–C8–H8A	127.3
N6–C9–C8	107.8(5)
N6–C9–H9	126.1
C8–C9–H9	126.1

W1–C10–H10	109(4)
C11–C10–W1	73.5(3)
C11–C10–H10	114(4)
C11–C10–C15	117.5(5)
C15–C10–W1	127.8(4)
C15–C10–H10	110(4)
W1–C11–H11	112(3)
C10–C11–W1	68.7(3)
C10–C11–H11	128(4)
C10–C11–C12	118.2(5)
C12–C11–W1	116.2(4)
C12–C11–H11	108(4)
C11–C12–H12	118.8
C13–C12–C11	122.4(5)
C13–C12–H12	118.8
C12–C13–S1	119.0(4)
C12–C13–C14	122.0(5)
C14–C13–S1	118.9(4)
C13–C14–H14A	109.2
C13–C14–H14B	109.2
C13–C14–C15	111.9(4)
H14A–C14–H14B	107.9
C15–C14–H14A	109.2
C15–C14–H14B	109.2
C10–C15–H15	108.6
C10–C15–C16	108.0(4)
C14–C15–C10	111.5(4)
C14–C15–H15	108.6
C14–C15–C16	111.4(4)
C16–C15–H15	108.6
C15–C16–H16A	109.2
C15–C16–H16B	109.2
H16A–C16–H16B	107.9
C17–C16–C15	112.2(4)
C17–C16–H16A	109.2
C17–C16–H16B	109.2
O2–C17–N8	121.9(5)
O2–C17–C16	122.0(5)
N8–C17–C16	116.1(5)
N8–C18–H18A	109.5

N8–C18–H18B	109.5
N8–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
S1–C19–H19A	109.5
S1–C19–H19B	109.5
S1–C19–H19C	109.5
H19A–C19–H19B	109.5
H19A–C19–H19C	109.5
H19B–C19–H19C	109.5
P1–C20–H20A	109.5
P1–C20–H20B	109.5
P1–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
P1–C21–H21A	109.5
P1–C21–H21B	109.5
P1–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
O5–C23–C24	121.2(7)
O5–C23–C25	118.7(8)
C25–C23–C24	119.8(8)
C23–C24–H24A	109.5
C23–C24–H24B	109.5
C23–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
C23–C25–H25A	109.5
C23–C25–H25B	109.5

C23–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
N2–B1–N4	105.3(4)
N2–B1–N6	109.8(5)
N2–B1–H1A	107(3)
N4–B1–N6	107.5(4)
N4–B1–H1A	116(3)
N6–B1–H1A	110(3)

Table 5 Torsion angles for 4.3

Atom–Atom–Atom–Atom	Torsion Angle [°]
W1–N1–N2–C3	170.8(3)
W1–N1–N2–B1	5.7(6)
W1–N1–C1–C2	−170.5(4)
W1–N3–N4–C6	179.2(3)
W1–N3–N4–B1	−12.2(6)
W1–N3–C4–C5	−178.5(4)
W1–N5–N6–C9	−178.6(3)
W1–N5–N6–B1	−4.6(6)
W1–N5–C7–C8	178.3(4)
W1–C10–C11–C12	−109.1(5)
W1–C10–C15–C14	48.8(6)
W1–C10–C15–C16	171.5(4)
W1–C11–C12–C13	−71.9(6)
S1–C13–C14–C15	156.3(4)
O3–S1–C13–C12	−7.9(5)
O3–S1–C13–C14	169.6(4)
O4–S1–C13–C12	−138.3(4)
O4–S1–C13–C14	39.2(5)
N1–N2–C3–C2	1.6(6)
N1–N2–B1–N4	55.4(6)
N1–N2–B1–N6	−60.1(6)
N1–C1–C2–C3	0.5(7)
N2–N1–C1–C2	0.5(6)
N3–N4–C6–C5	−0.8(6)
N3–N4–B1–N2	−51.5(6)
N3–N4–B1–N6	65.6(6)
N3–C4–C5–C6	−0.4(6)

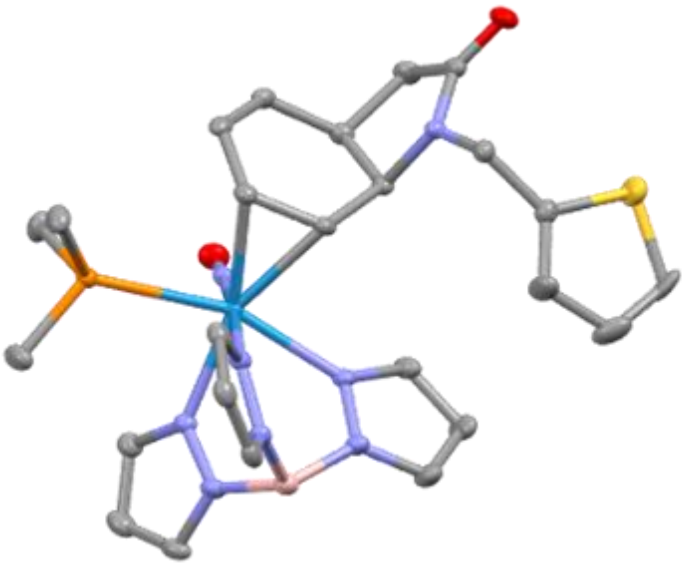
N4–N3–C4–C5	−0.1(6)
N5–N6–C9–C8	0.2(6)
N5–N6–B1–N2	59.0(6)
N5–N6–B1–N4	−55.0(6)
N5–C7–C8–C9	−0.5(7)
N6–N5–C7–C8	0.6(6)
C1–N1–N2–C3	−1.3(6)
C1–N1–N2–B1	−166.3(5)
C1–C2–C3–N2	−1.3(7)
C3–N2–B1–N4	−106.3(6)
C3–N2–B1–N6	138.3(5)
C4–N3–N4–C6	0.5(5)
C4–N3–N4–B1	169.1(4)
C4–C5–C6–N4	0.8(6)
C6–N4–B1–N2	114.4(6)
C6–N4–B1–N6	−128.6(5)
C7–N5–N6–C9	−0.4(6)
C7–N5–N6–B1	173.6(5)
C7–C8–C9–N6	0.2(6)
C9–N6–B1–N2	−128.1(5)
C9–N6–B1–N4	117.9(6)
C10–C11–C12–C13	6.8(8)
C10–C15–C16–C17	176.4(4)
C11–C10–C15–C14	−41.1(6)
C11–C10–C15–C16	81.6(6)
C11–C12–C13–S1	176.8(4)
C11–C12–C13–C14	−0.6(8)
C12–C13–C14–C15	−26.3(7)
C13–C14–C15–C10	44.9(6)
C13–C14–C15–C16	−75.9(5)
C14–C15–C16–C17	−60.8(6)
C15–C10–C11–W1	124.4(4)
C15–C10–C11–C12	15.3(7)
C15–C16–C17–O2	−53.1(7)
C15–C16–C17–N8	126.8(5)
C18–N8–C17–O2	0.3(8)
C18–N8–C17–C16	−179.6(5)
C19–S1–C13–C12	107.9(5)
C19–S1–C13–C14	−74.6(5)
B1–N2–C3–C2	165.2(5)

B1–N4–C6–C5	−168.1(5)
B1–N6–C9–C8	−173.3(5)

Table 6 Hydrogen bonds for compound 4.3

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N8–H8···O2#1	0.90(6)	1.94(6)	2.825(6)	168(6)

Symmetry transformations used to generate equivalent atoms: #1: +X, 0.5-Y, 0.5+Z;



A colorless, plate-like specimen of $C_{28}H_{38}BN_8O_3PSW$, approximate dimensions 0.050 mm x 0.080 mm x 0.127 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture PhotonIII Kappa four-circle diffractometer system equipped with a Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 2.74 hours. The frames were integrated with the Bruker SAINT software package[28] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 95376 reflections to a maximum θ angle of 28.31°

[28] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

(0.75 Å resolution), of which 7821 were independent (average redundancy 12.195, completeness = 99.7%, R_{int} = 5.34%, R_{sig} = 2.49%) and 6957 (88.95%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.3843(6) Å, b = 23.9895(10) Å, c = 9.8282(4) Å, β = 93.3370(10)°, volume = 3150.3(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9807 reflections above 20 σ(I) with 5.937° < 2θ < 56.50°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[29] The ratio of minimum to maximum apparent transmission was 0.924. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6420 and 0.8320.

The structure was solved and refined using the Bruker SHELXTL Software Package[30] within APEX4 [1] and OLEX2,[31] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{28}H_{38}BN_8O_3PSW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). The relative occupancy of the disordered atoms was freely refined, with constraints on the anisotropic displacement parameters of the disordered atoms and restraints on some of the disordered bond. The final anisotropic full-matrix least-squares refinement on F^2 with 416 variables converged at R1 = 1.95%, for the observed data and wR2 = 4.48% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 0.916 $e^-/Å^3$ and the largest hole was -0.343 $e^-/Å^3$ with an RMS deviation of 0.086 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.671 g/cm^3 and F(000), 1584 e^-.

Table 1. Sample and crystal data for compound 4.7

Chemical formula	$C_{28}H_{38}BN_8O_3PSW$
Formula weight	792.35 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.050 x 0.080 x 0.127 mm

[29] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[30] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

[31] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 13.3843(6) Å	α = 90°
	b = 23.9895(10) Å	β = 93.3370(10)°
	c = 9.8282(4) Å	γ = 90°
Volume	3150.3(2) $Å^3$	
Z	4	
Density (calculated)	1.671 g/cm^3	
Absorption coefficient	3.828 mm^{-1}	
F(000)	1584	

Table 2. Data collection and structure refinement for compound 4.7

Diffractometer	Bruker D8 Venture PhotonIII Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.24 to 28.31°
Index ranges	-17<=h<=17, -31<=k<=31, -13<=l<=12
Reflections collected	95376
Independent reflections	7821 [R(int) = 0.0534]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8320 and 0.6420
Structure solution technique	direct methods

Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7821 / 2 / 416	
Goodness-of-fit on F^2	1.025	
Δ/σ_{max}	0.003	
Final R indices	6957 data; I>2σ(I)	R1 = 0.0195, wR2 = 0.0426
	all data	R1 = 0.0247, wR2 = 0.0448
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0191P)^2+2.2905P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.916 and -0.343 eÅ^{-3}	
R.M.S. deviation from mean	0.086 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.7.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.75097(2)	0.43730(2)	0.71698(2)	0.01228(3)
P1	0.76978(4)	0.53633(2)	0.64285(5)	0.01484(11)
O1	0.72315(12)	0.47474(7)	0.00345(15)	0.0212(3)
O2	0.28050(12)	0.34362(7)	0.78438(17)	0.0237(3)
N1	0.78917(13)	0.41168(7)	0.50539(18)	0.0156(4)
N2	0.87000(13)	0.37809(7)	0.48796(18)	0.0154(4)

	x/a	y/b	z/c	U(eq)
N3	0.91570(13)	0.43960(7)	0.75411(18)	0.0154(4)
N4	0.97723(13)	0.40233(8)	0.69660(18)	0.0167(4)
N5	0.79153(13)	0.35089(7)	0.77208(18)	0.0161(4)
N6	0.86105(14)	0.32225(7)	0.70454(19)	0.0182(4)
N7	0.73190(13)	0.45867(7)	0.88539(18)	0.0147(3)
N8	0.44132(13)	0.35563(7)	0.72090(18)	0.0150(4)
C1	0.75554(17)	0.42702(9)	0.3794(2)	0.0187(4)
C2	0.81391(17)	0.40413(9)	0.2819(2)	0.0199(5)
C3	0.88550(17)	0.37339(9)	0.3546(2)	0.0177(4)
C4	0.97461(17)	0.47213(9)	0.8352(2)	0.0197(5)
C5	0.07419(18)	0.45686(10)	0.8293(2)	0.0238(5)
C6	0.07251(17)	0.41204(10)	0.7416(2)	0.0209(5)
C7	0.76025(17)	0.31681(10)	0.8676(2)	0.0213(5)
C8	0.80794(19)	0.26536(10)	0.8611(3)	0.0290(6)
C9	0.87139(18)	0.27069(10)	0.7574(3)	0.0261(5)
C10	0.59578(16)	0.45633(9)	0.6299(2)	0.0159(4)
C11	0.60427(15)	0.39895(9)	0.6721(2)	0.0143(4)
C12	0.53863(15)	0.37695(9)	0.7793(2)	0.0146(4)
C13	0.50418(16)	0.42051(9)	0.8828(2)	0.0167(4)
C14	0.48953(16)	0.47728(9)	0.8204(2)	0.0177(4)
C15	0.53131(16)	0.49303(9)	0.7075(2)	0.0177(4)
C16	0.40446(17)	0.39635(10)	0.9253(2)	0.0205(5)
C17	0.36527(16)	0.36273(9)	0.8043(2)	0.0178(4)
C18	0.43552(16)	0.31475(9)	0.6114(2)	0.0169(4)
C19	0.48594(17)	0.26071(9)	0.6504(2)	0.0187(4)
C23	0.89375(18)	0.55726(10)	0.5975(3)	0.0265(5)
C24	0.69708(18)	0.56429(9)	0.4953(2)	0.0236(5)
C25	0.74160(19)	0.58518(10)	0.7758(2)	0.0244(5)
B1	0.93132(19)	0.35364(10)	0.6112(3)	0.0174(5)
S1	0.43233(9)	0.21421(5)	0.75559(12)	0.0291(3)
C20	0.5769(8)	0.2410(6)	0.6184(13)	0.0319(16)
C21	0.6042(6)	0.1885(4)	0.6750(7)	0.0327(12)
C22	0.5337(4)	0.16946(17)	0.7543(6)	0.0284(9)

	x/a	y/b	z/c	U(eq)
S1A	0.5962(13)	0.2447(8)	0.599(2)	0.0319(16)
C20A	0.448(3)	0.2209(12)	0.732(3)	0.0291(3)
C21A	0.511(3)	0.1792(13)	0.755(4)	0.0284(9)
C22A	0.598(4)	0.191(3)	0.700(5)	0.0327(12)
O3	0.08394(14)	0.20053(8)	0.73977(19)	0.0340(4)
C26	0.0474(4)	0.16872(18)	0.5166(4)	0.0805(14)
C27	0.10184(19)	0.20355(10)	0.6204(3)	0.0273(5)
C28	0.1797(2)	0.24124(14)	0.5703(3)	0.0432(7)

Table 4. Bond lengths (Å) for compound 4.7

W1-N7	1.7654(18)	W1-C11	2.190(2)
W1-N5	2.2025(17)	W1-N3	2.2144(18)
W1-C10	2.247(2)	W1-N1	2.2555(18)
W1-P1	2.5018(6)	P1-C25	1.811(2)
P1-C23	1.814(2)	P1-C24	1.826(2)
O1-N7	1.235(2)	O2-C17	1.229(3)
N1-C1	1.344(3)	N1-N2	1.368(2)
N2-C3	1.344(3)	N2-B1	1.539(3)
N3-C4	1.339(3)	N3-N4	1.360(2)
N4-C6	1.346(3)	N4-B1	1.545(3)
N5-C7	1.331(3)	N5-N6	1.360(2)
N6-C9	1.346(3)	N6-B1	1.547(3)
N8-C17	1.354(3)	N8-C18	1.455(3)
N8-C12	1.483(3)	C1-C2	1.385(3)
C1-H1	0.950000	C2-C3	1.376(3)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.387(3)	C4-H4	0.950000
C5-C6	1.377(3)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.393(3)
C7-H7	0.950000	C8-C9	1.370(3)
C8-H8	0.950000	C9-H9	0.950000

C10-C11	1.440(3)	C10-C15	1.476(3)
C10-H10	0.92(3)	C11-C12	1.506(3)
C11-H11	1.00(2)	C12-C13	1.547(3)
C12-H12	1.000000	C13-C14	1.502(3)
C13-C16	1.535(3)	C13-H13	1.000000
C14-C15	1.326(3)	C14-H14	0.950000
C15-H15	0.950000	C16-C17	1.505(3)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.501(3)	C18-H18A	0.990000
C18-H18B	0.990000	C19-C20	1.359(10)
C19-C20A	1.367(17)	C19-S1A	1.634(16)
C19-S1	1.707(2)	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
C24-H24A	0.980000	C24-H24B	0.980000
C24-H24C	0.980000	C25-H25A	0.980000
C25-H25B	0.980000	C25-H25C	0.980000
B1-H1A	1.12(2)	S1-C22	1.731(3)
C20-C21	1.417(17)	C20-H20	0.950000
C21-C22	1.338(6)	C21-H21	0.950000
C22-H22	0.950000	S1A-C22A	1.63(7)
C20A-C21A	1.32(4)	C20A-H20A	0.950000
C21A-C22A	1.336(18)	C21A-H21A	0.950000
C22A-H22A	0.950000	O3-C27	1.213(3)
C26-C27	1.478(4)	C26-H26A	0.980000
C26-H26B	0.980000	C26-H26C	0.980000
C27-C28	1.485(4)	C28-H28A	0.980000
C28-H28B	0.980000	C28-H28C	0.980000

Table 5. Bond angles (°) for compound 4.7.

N7-W1-C11	97.70(8)	N7-W1-N5	95.15(7)

C11-W1-N5	81.92(7)	N7-W1-N3	92.02(7)
C11-W1-N3	156.36(7)	N5-W1-N3	75.76(6)
N7-W1-C10	96.74(8)	C11-W1-C10	37.85(8)
N5-W1-C10	119.60(7)	N3-W1-C10	161.30(7)
N7-W1-N1	175.15(7)	C11-W1-N1	87.04(7)
N5-W1-N1	84.51(6)	N3-W1-N1	83.21(6)
C10-W1-N1	87.60(7)	N7-W1-P1	91.13(6)
C11-W1-P1	116.39(6)	N5-W1-P1	159.68(5)
N3-W1-P1	84.74(5)	C10-W1-P1	78.62(6)
N1-W1-P1	87.61(5)	C25-P1-C23	103.31(12)
C25-P1-C24	102.20(11)	C23-P1-C24	98.97(11)
C25-P1-W1	112.07(8)	C23-P1-W1	116.32(8)
C24-P1-W1	121.46(8)	C1-N1-N2	105.71(17)
C1-N1-W1	133.88(15)	N2-N1-W1	119.96(12)
C3-N2-N1	109.86(17)	C3-N2-B1	129.08(19)
N1-N2-B1	121.01(17)	C4-N3-N4	106.29(18)
C4-N3-W1	131.21(15)	N4-N3-W1	122.42(13)
C6-N4-N3	109.56(18)	C6-N4-B1	130.46(19)
N3-N4-B1	119.42(17)	C7-N5-N6	106.63(17)
C7-N5-W1	131.96(15)	N6-N5-W1	121.41(13)
C9-N6-N5	109.50(18)	C9-N6-B1	128.60(19)
N5-N6-B1	120.01(17)	O1-N7-W1	176.89(16)
C17-N8-C18	121.53(18)	C17-N8-C12	113.34(17)
C18-N8-C12	121.78(17)	N1-C1-C2	110.9(2)
N1-C1-H1	124.500000	C2-C1-H1	124.500000
C3-C2-C1	104.89(19)	C3-C2-H2	127.600000
C1-C2-H2	127.600000	N2-C3-C2	108.6(2)
N2-C3-H3	125.700000	C2-C3-H3	125.700000
N3-C4-C5	110.8(2)	N3-C4-H4	124.600000
C5-C4-H4	124.600000	C6-C5-C4	104.6(2)
C6-C5-H5	127.700000	C4-C5-H5	127.700000
N4-C6-C5	108.8(2)	N4-C6-H6	125.600000
C5-C6-H6	125.600000	N5-C7-C8	110.4(2)
N5-C7-H7	124.800000	C8-C7-H7	124.800000

C9-C8-C7	104.9(2)	C9-C8-H8	127.600000
C7-C8-H8	127.600000	N6-C9-C8	108.6(2)
N6-C9-H9	125.700000	C8-C9-H9	125.700000
C11-C10-C15	117.37(19)	C11-C10-W1	68.93(12)
C15-C10-W1	118.64(14)	C11-C10-H10	118.6(16)
C15-C10-H10	115.1(16)	W1-C10-H10	110.0(15)
C10-C11-C12	119.81(19)	C10-C11-W1	73.22(12)
C12-C11-W1	123.97(14)	C10-C11-H11	114.9(13)
C12-C11-H11	113.1(14)	W1-C11-H11	105.9(14)
N8-C12-C11	112.61(17)	N8-C12-C13	101.46(16)
C11-C12-C13	115.56(17)	N8-C12-H12	109.000000
C11-C12-H12	109.000000	C13-C12-H12	109.000000
C14-C13-C16	111.02(18)	C14-C13-C12	112.42(18)
C16-C13-C12	102.76(17)	C14-C13-H13	110.100000
C16-C13-H13	110.100000	C12-C13-H13	110.100000
C15-C14-C13	123.3(2)	C15-C14-H14	118.400000
C13-C14-H14	118.400000	C14-C15-C10	123.4(2)
C14-C15-H15	118.300000	C10-C15-H15	118.300000
C17-C16-C13	104.83(17)	C17-C16-H16A	110.800000
C13-C16-H16A	110.800000	C17-C16-H16B	110.800000
C13-C16-H16B	110.800000	H16A-C16-H16B	108.900000
O2-C17-N8	125.2(2)	O2-C17-C16	127.0(2)
N8-C17-C16	107.80(18)	N8-C18-C19	112.91(17)
N8-C18-H18A	109.000000	C19-C18-H18A	109.000000
N8-C18-H18B	109.000000	C19-C18-H18B	109.000000
H18A-C18-H18B	107.800000	C20-C19-C18	129.5(5)
C20A-C19-C18	125.3(15)	C20A-C19-S1A	113.0(17)
C18-C19-S1A	121.7(7)	C20-C19-S1	109.1(5)

C18-C19-S1	121.37(17)	P1-C23-H23A	109.500000
P1-C23-H23B	109.500000	H23A-C23-H23B	109.500000
P1-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	P1-C24-H24A	109.500000
P1-C24-H24B	109.500000	H24A-C24-H24B	109.500000
P1-C24-H24C	109.500000	H24A-C24-H24C	109.500000
H24B-C24-H24C	109.500000	P1-C25-H25A	109.500000
P1-C25-H25B	109.500000	H25A-C25-H25B	109.500000
P1-C25-H25C	109.500000	H25A-C25-H25C	109.500000
H25B-C25-H25C	109.500000	N2-B1-N4	108.44(18)
N2-B1-N6	109.72(18)	N4-B1-N6	106.41(18)
N2-B1-H1A	108.9(12)	N4-B1-H1A	111.0(13)
N6-B1-H1A	112.3(13)	C19-S1-C22	92.5(2)
C19-C20-C21	115.6(6)	C19-C20-H20	122.200000
C21-C20-H20	122.200000	C22-C21-C20	110.9(7)
C22-C21-H21	124.500000	C20-C21-H21	124.500000
C21-C22-S1	111.9(5)	C21-C22-H22	124.100000
S1-C22-H22	124.100000	C22A-S1A-C19	88.8(17)
C21A-C20A-C19	112.(3)	C21A-C20A-H20A	124.100000
C19-C20A-H20A	124.100000	C20A-C21A-C22A	110.(4)
C20A-C21A-H21A	125.200000	C22A-C21A-H21A	125.200000
C21A-C22A-S1A	116.(4)	C21A-C22A-H22A	122.200000

S1A-C22A-H22A	122.200000	C27-C26-H26A	109.500000
C27-C26-H26B	109.500000	H26A-C26-H26B	109.500000
C27-C26-H26C	109.500000	H26A-C26-H26C	109.500000
H26B-C26-H26C	109.500000	O3-C27-C26	121.1(3)
O3-C27-C28	122.6(2)	C26-C27-C28	116.2(3)
C27-C28-H28A	109.500000	C27-C28-H28B	109.500000
H28A-C28-H28B	109.500000	C27-C28-H28C	109.500000
H28A-C28-H28C	109.500000	H28B-C28-H28C	109.500000

Table 6. Torsion angles (°) for compound 4.7.

C1-N1-N2-C3	0.4(2)	W1-N1-N2-C3	-172.98(13)
C1-N1-N2-B1	177.98(18)	W1-N1-N2-B1	4.7(2)
C4-N3-N4-C6	-0.2(2)	W1-N3-N4-C6	-177.23(14)
C4-N3-N4-B1	172.11(18)	W1-N3-N4-B1	-5.0(2)
C7-N5-N6-C9	0.7(2)	W1-N5-N6-C9	-179.67(15)
C7-N5-N6-B1	-164.96(19)	W1-N5-N6-B1	14.7(2)
N2-N1-C1-C2	-0.4(2)	W1-N1-C1-C2	171.56(15)
N1-C1-C2-C3	0.3(2)	N1-N2-C3-C2	-0.2(2)
B1-N2-C3-C2	-177.5(2)	C1-C2-C3-N2	-0.1(2)
N4-N3-C4-C5	0.9(2)	W1-N3-C4-C5	177.63(15)
N3-C4-C5-C6	-1.3(3)	N3-N4-C6-C5	-0.6(3)
B1-N4-C6-C5	-171.8(2)	C4-C5-C6-N4	1.1(3)

N6-N5-C7-C8	-1.1(3)	W1-N5-C7-C8	179.34(16)
N5-C7-C8-C9	1.1(3)	N5-N6-C9-C8	-0.1(3)
B1-N6-C9-C8	164.0(2)	C7-C8-C9-N6	-0.6(3)
C15-C10-C11-C12	7.7(3)	W1-C10-C11-C12	119.99(18)
C15-C10-C11-W1	-112.27(18)	C17-N8-C12-C11	-147.72(18)
C18-N8-C12-C11	52.7(2)	C17-N8-C12-C13	-23.6(2)
C18-N8-C12-C13	176.83(17)	C10-C11-C12-N8	88.1(2)
W1-C11-C12-N8	177.27(13)	C10-C11-C12-C13	-27.8(3)
W1-C11-C12-C13	61.3(2)	N8-C12-C13-C14	-89.2(2)
C11-C12-C13-C14	32.9(3)	N8-C12-C13-C16	30.2(2)
C11-C12-C13-C16	152.30(18)	C16-C13-C14-C15	-135.2(2)
C12-C13-C14-C15	-20.7(3)	C13-C14-C15-C10	0.7(3)
C11-C10-C15-C14	6.8(3)	W1-C10-C15-C14	-72.9(3)
C14-C13-C16-C17	92.6(2)	C12-C13-C16-C17	-27.8(2)
C18-N8-C17-O2	-12.7(3)	C12-N8-C17-O2	-172.3(2)
C18-N8-C17-C16	165.76(18)	C12-N8-C17-C16	6.1(2)
C13-C16-C17-O2	-167.2(2)	C13-C16-C17-N8	14.4(2)
C17-N8-C18-C19	-96.8(2)	C12-N8-C18-C19	61.2(2)
N8-C18-C19-C20	-102.0(8)	N8-C18-C19-C20A	75.8(19)

N8-C18-C19-S1A	-102.7(10)	N8-C18-C19-S1	75.0(2)
C3-N2-B1-N4	115.3(2)	N1-N2-B1-N4	-61.8(2)
C3-N2-B1-N6	-128.9(2)	N1-N2-B1-N6	54.0(2)
C6-N4-B1-N2	-127.5(2)	N3-N4-B1-N2	62.1(2)
C6-N4-B1-N6	114.5(2)	N3-N4-B1-N6	-55.9(2)
C9-N6-B1-N2	130.9(2)	N5-N6-B1-N2	-66.5(2)
C9-N6-B1-N4	-112.0(2)	N5-N6-B1-N4	50.7(2)
C20-C19-S1-C22	0.1(7)	C18-C19-S1-C22	-177.4(3)
C18-C19-C20-C21	178.3(6)	S1-C19-C20-C21	1.0(12)
C19-C20-C21-C22	-2.0(14)	C20-C21-C22-S1	2.0(9)
C19-S1-C22-C21	-1.3(5)	C20A-C19-S1A-C22A	-7.(3)
C18-C19-S1A-C22A	172.(2)	C18-C19-C20A-C21A	-176.(2)
S1A-C19-C20A-C21A	2.(4)	C19-C20A-C21A-C22A	5.(5)
C20A-C21A-C22A-S1A	-11.(6)	C19-S1A-C22A-C21A	10.(4)

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.7.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.01103(5)	0.01293(4)	0.01287(5)	0.00080(3)	0.00048(3)	0.00042(3)
P1	0.0138(3)	0.0151(3)	0.0156(3)	0.0013(2)	0.0009(2)	-0.0010(2)
O1	0.0232(8)	0.0282(9)	0.0124(7)	-0.0050(6)	0.0016(6)	0.0004(7)
O2	0.0140(8)	0.0265(9)	0.0309(9)	0.0027(7)	0.0042(7)	-0.0009(7)
N1	0.0138(9)	0.0161(9)	0.0171(9)	-0.0012(7)	0.0009(7)	-0.0007(7)
N2	0.0147(9)	0.0147(8)	0.0171(9)	-0.0015(7)	0.0036(7)	-0.0008(7)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N3	0.0137(9)	0.0168(9)	0.0156(8)	0.0008(7)	0.0008(7)	0.0003(7)
N4	0.0130(9)	0.0214(9)	0.0161(9)	0.0022(7)	0.0030(7)	0.0018(7)
N5	0.0124(9)	0.0167(9)	0.0193(9)	0.0028(7)	0.0022(7)	0.0022(7)
N6	0.0161(9)	0.0168(9)	0.0220(9)	0.0024(7)	0.0050(7)	0.0037(7)
N7	0.0124(9)	0.0155(8)	0.0160(9)	0.0036(7)	-0.0011(7)	-0.0019(7)
N8	0.0124(9)	0.0143(8)	0.0183(9)	-0.0008(7)	0.0017(7)	0.0005(7)
C1	0.0181(11)	0.0196(11)	0.0180(10)	0.0000(8)	-0.0014(9)	-0.0049(8)
C2	0.0241(12)	0.0207(11)	0.0148(10)	-0.0016(8)	0.0002(9)	-0.0079(9)
C3	0.0191(11)	0.0157(10)	0.0190(10)	-0.0051(8)	0.0064(9)	-0.0052(8)
C4	0.0190(11)	0.0209(11)	0.0187(11)	0.0000(9)	-0.0027(9)	-0.0014(9)
C5	0.0182(12)	0.0310(13)	0.0218(11)	0.0039(10)	-0.0029(9)	-0.0052(10)
C6	0.0131(11)	0.0295(12)	0.0201(11)	0.0056(9)	0.0006(8)	0.0009(9)
C7	0.0165(11)	0.0248(11)	0.0229(11)	0.0094(9)	0.0043(9)	0.0034(9)
C8	0.0276(13)	0.0227(12)	0.0374(14)	0.0164(11)	0.0082(11)	0.0068(10)
C9	0.0241(13)	0.0198(11)	0.0352(13)	0.0077(10)	0.0078(10)	0.0080(9)
C10	0.0135(10)	0.0184(10)	0.0156(10)	0.0005(8)	-0.0007(8)	-0.0010(8)
C11	0.0110(10)	0.0152(10)	0.0167(10)	-0.0021(8)	0.0012(8)	-0.0004(8)
C12	0.0123(10)	0.0156(10)	0.0156(10)	0.0011(8)	-0.0005(8)	0.0001(8)
C13	0.0161(11)	0.0189(10)	0.0153(10)	-0.0009(8)	0.0024(8)	0.0005(8)
C14	0.0147(10)	0.0167(10)	0.0214(11)	-0.0044(8)	0.0001(8)	0.0010(8)
C15	0.0139(10)	0.0154(10)	0.0233(11)	-0.0006(8)	-0.0041(8)	0.0015(8)
C16	0.0194(11)	0.0245(11)	0.0181(10)	0.0010(9)	0.0068(9)	0.0011(9)
C17	0.0157(11)	0.0166(10)	0.0213(11)	0.0054(8)	0.0036(8)	0.0025(8)
C18	0.0170(10)	0.0147(10)	0.0190(10)	0.0008(8)	0.0004(8)	-0.0010(8)
C19	0.0216(11)	0.0161(10)	0.0183(10)	-0.0005(8)	0.0006(9)	-0.0009(9)
C23	0.0197(12)	0.0288(13)	0.0312(13)	0.0116(10)	0.0043(10)	-0.0015(10)
C24	0.0247(12)	0.0199(11)	0.0253(12)	0.0067(9)	-0.0066(10)	-0.0028(9)
C25	0.0346(14)	0.0153(10)	0.0237(12)	-0.0024(9)	0.0051(10)	-0.0010(10)
B1	0.0161(12)	0.0177(12)	0.0186(12)	-0.0003(9)	0.0039(9)	0.0011(9)

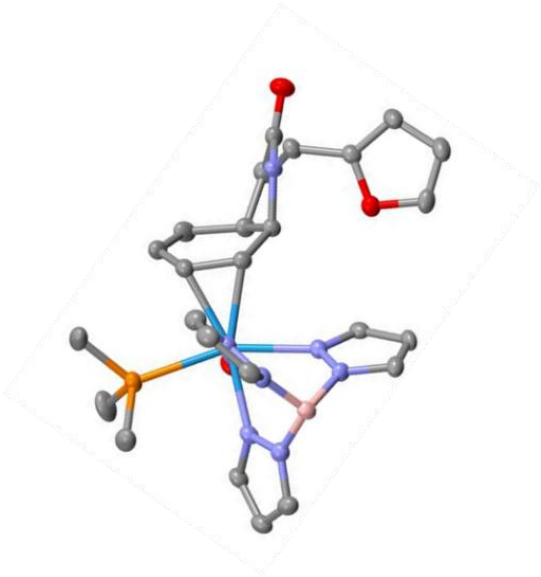
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0331(6)	0.0219(5)	0.0331(6)	0.0122(3)	0.0094(4)	0.0026(4)
C20	0.028(4)	0.0271(19)	0.043(4)	0.010(2)	0.020(2)	0.006(3)
C21	0.041(2)	0.0331(18)	0.024(4)	-0.001(3)	0.0050(18)	0.0197(16)
C22	0.049(3)	0.013(2)	0.0235(13)	0.0037(15)	0.0020(19)	0.0141(14)
S1A	0.028(4)	0.0271(19)	0.043(4)	0.010(2)	0.020(2)	0.006(3)
C20A	0.0331(6)	0.0219(5)	0.0331(6)	0.0122(3)	0.0094(4)	0.0026(4)
C21A	0.049(3)	0.013(2)	0.0235(13)	0.0037(15)	0.0020(19)	0.0141(14)
C22A	0.041(2)	0.0331(18)	0.024(4)	-0.001(3)	0.0050(18)	0.0197(16)
O3	0.0290(10)	0.0387(11)	0.0349(10)	-0.0019(8)	0.0071(8)	0.0020(8)
C26	0.110(4)	0.072(3)	0.056(2)	-0.025(2)	-0.024(2)	-0.018(3)
C27	0.0249(13)	0.0280(13)	0.0284(13)	-0.0048(10)	-0.0027(10)	0.0104(10)
C28	0.0329(16)	0.058(2)	0.0395(16)	0.0059(14)	0.0112(13)	0.0052(14)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.7.

	x/a	y/b	z/c	U(eq)
H1	0.6993	0.4504	0.3598	0.022000
H2	0.8062	0.4087	0.1858	0.024000
H3	0.9373	0.3524	0.3168	0.021000
H4	0.9513	0.5017	0.8894	0.024000
H5	1.1309	0.4736	0.8754	0.029000
H6	1.1293	0.3914	0.7170	0.025000
H7	0.7122	0.3262	0.9312	0.026000
H8	0.7985	0.2335	0.9165	0.035000
H9	0.9153	0.2427	0.7278	0.031000
H10	0.5974(18)	0.4646(10)	0.538(3)	0.019000
H11	0.6136(17)	0.3718(10)	0.597(2)	0.015(6)
H12	0.5746	0.3461	0.8301	0.017000
H13	0.5533	0.4225	0.9633	0.020000
H14	0.4483	0.5032	0.8640	0.021000

	x/a	y/b	z/c	U(eq)
H15	0.5191	0.5298	0.6749	0.021000
H16A	0.4150	0.3724	1.0068	0.025000
H16B	0.3572	0.4265	0.9457	0.025000
H18A	0.4671	0.3305	0.5312	0.020000
H18B	0.3643	0.3074	0.5846	0.020000
H23A	0.9409	0.5533	0.6770	0.040000
H23B	0.8921	0.5962	0.5675	0.040000
H23C	0.9152	0.5335	0.5234	0.040000
H24A	0.7157	0.5449	0.4128	0.035000
H24B	0.7109	0.6042	0.4866	0.035000
H24C	0.6256	0.5588	0.5074	0.035000
H25A	0.6715	0.5809	0.7978	0.037000
H25B	0.7527	0.6233	0.7441	0.037000
H25C	0.7853	0.5778	0.8573	0.037000
H1A	0.9912(18)	0.3260(10)	0.574(2)	0.021000
H20	0.6193	0.2612	0.5617	0.038000
H21	0.6645	0.1693	0.6589	0.039000
H22	0.5388	0.1355	0.8039	0.034000
H20A	0.3839	0.2229	0.7686	0.035000
H21A	0.4977	0.1460	0.8035	0.034000
H22A	0.6565	0.1691	0.7185	0.039000
H26A	0.0052	0.1418	0.5617	0.121000
H26B	0.0955	0.1487	0.4633	0.121000
H26C	0.0053	0.1925	0.4559	0.121000
H28A	0.2080	0.2639	0.6460	0.065000
H28B	0.1496	0.2657	0.4993	0.065000
H28C	0.2329	0.2190	0.5325	0.065000

Crystal Structure Report for compound 4.8



A yellow block-like specimen of $C_{25}H_{32}BN_8O_3PW$, approximate dimensions 0.078 mm x 0.197 mm x 0.201 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with a fine-focus sealed tube (Mo K_α, λ = 0.71073 Å) and a graphite monochromator.

The total exposure time was 1.04 hours. The frames were integrated with the Bruker SAINT software package[32] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 41505 reflections to a maximum θ angle of 27.56° (0.77 Å resolution), of which 6416 were independent (average redundancy 6.469, completeness = 99.5%, R_{int} = 6.26%, R_{sig} = 4.01%) and 5154 (80.33%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.5287(7) Å, b = 16.8147(12) Å, c = 17.3887(13) Å, β = 92.706(2)°, volume = 2782.9(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 8548 reflections above 20 σ(I) with 4.69° < 2θ < 52.04°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[33] The ratio of minimum to maximum apparent transmission was 0.460. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0296 and 0.0644.

The structure was solved and refined using the Bruker SHELXTL Software Package[34] within

[32] Bruker (2019). *Saint; APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
[33] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985
[34] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

APEX3 [1] and OLEX2,[35] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{25}H_{32}BN_8O_3PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atoms, as well as H10 and H11were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 367 variables converged at R1 = 3.47%, for the observed data and wR2 = 8.73% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 2.294 $e^-/Å^3$ and the largest hole was -0.896 $e^-/Å^3$ with an RMS deviation of 0.141 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.714 g/cm^3 and F(000), 1424 e^-.

Table 1. Sample and crystal data for compound 4.8

Chemical formula	$C_{25}H_{32}BN_8O_3PW$	
Formula weight	718.21 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.078 x 0.197 x 0.201 mm	
Crystal habit	yellow block	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 9.5287(7) Å	α = 90°
	b = 16.8147(12) Å	β = 92.706(2)°
	c = 17.3887(13) Å	γ = 90°
Volume	2782.9(4) $Å^3$	
Z	4	
Density (calculated)	1.714 g/cm^3	
Absorption coefficient	4.251 mm^{-1}	
F(000)	1424	

[35] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Table 2. Data collection and structure refinement for compound 4.8.

Diffractometer	Bruker Kappa APEXII Duo	
Radiation source	fine-focus sealed tube (Mo K_α, λ = 0.71073 Å)	
Theta range for data collection	1.69 to 27.56°	
Index ranges	-12<=h<=12, -21<=k<=21, -19<=l<=22	
Reflections collected	41505	
Independent reflections	6416 [R(int) = 0.0626]	
Coverage of independent reflections	99.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.0644 and 0.0296	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6416 / 0 / 367	
Goodness-of-fit on F^2	1.046	
Δ/σ_{max}	0.001	
Final R indices	5154 data; I>2σ(I)	R1 = 0.0347, wR2 = 0.0813
	all data	R1 = 0.0480, wR2 = 0.0873
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0401P)^2+7.2080P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.294 and -0.896 $eÅ^{-3}$	

R.M.S. deviation from mean	0.141 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.8

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.72032(2)	0.41671(2)	0.76843(2)	0.02067(7)
P1	0.57678(15)	0.30198(8)	0.81405(8)	0.0283(3)
O1	0.9747(4)	0.3160(2)	0.7461(2)	0.0385(9)
O2	0.7822(4)	0.4867(2)	0.3879(2)	0.0358(9)
O3	0.7662(4)	0.6568(2)	0.5960(2)	0.0279(8)
N1	0.5364(4)	0.4923(2)	0.7979(2)	0.0241(9)
N2	0.5516(4)	0.5493(2)	0.8545(2)	0.0243(8)
N3	0.7813(4)	0.4273(2)	0.8924(2)	0.0239(9)
N4	0.7554(4)	0.4953(2)	0.9335(2)	0.0251(9)
N5	0.8381(4)	0.5298(2)	0.7777(2)	0.0223(8)
N6	0.7982(4)	0.5880(2)	0.8265(2)	0.0226(8)
N7	0.8691(5)	0.3575(2)	0.7527(2)	0.0262(9)
N8	0.7283(4)	0.4935(2)	0.5153(2)	0.0228(8)
C1	0.3997(6)	0.4927(3)	0.7756(3)	0.0315(11)
C2	0.3259(6)	0.5473(3)	0.8177(3)	0.0315(11)
C3	0.4256(5)	0.5812(3)	0.8667(3)	0.0291(11)
C4	0.8511(5)	0.3781(3)	0.9406(3)	0.0274(11)
C5	0.8702(5)	0.4123(3)	0.0126(3)	0.0295(11)
C6	0.8097(5)	0.4865(3)	0.0052(3)	0.0291(11)
C7	0.9502(5)	0.5568(3)	0.7427(3)	0.0238(10)
C8	0.9825(5)	0.6340(3)	0.7676(3)	0.0249(10)
C9	0.8843(5)	0.6512(3)	0.8204(3)	0.0258(10)
C10	0.6007(6)	0.3858(3)	0.6579(3)	0.0266(11)

	x/a	y/b	z/c	U(eq)
C11	0.6773(5)	0.4590(3)	0.6508(3)	0.0228(10)
C12	0.7875(5)	0.4652(3)	0.5916(3)	0.0218(10)
C13	0.8582(5)	0.3864(3)	0.5693(3)	0.0249(10)
C14	0.7615(6)	0.3164(3)	0.5735(3)	0.0321(12)
C15	0.6465(6)	0.3165(3)	0.6132(3)	0.0305(12)
C16	0.9005(6)	0.4025(3)	0.4860(3)	0.0290(11)
C17	0.7979(5)	0.4648(3)	0.4550(3)	0.0268(11)
C18	0.6417(5)	0.5652(3)	0.5077(3)	0.0258(10)
C19	0.7225(5)	0.6400(3)	0.5211(3)	0.0238(10)
C20	0.7669(6)	0.6973(3)	0.4739(3)	0.0316(12)
C21	0.8425(5)	0.7535(3)	0.5210(3)	0.0343(12)
C22	0.8401(5)	0.7271(3)	0.5932(3)	0.0286(11)
C23	0.4189(7)	0.2694(4)	0.7612(3)	0.0447(16)
C24	0.5113(6)	0.3164(4)	0.9100(3)	0.0371(13)
C25	0.6739(7)	0.2098(3)	0.8230(4)	0.0492(16)
B1	0.6964(6)	0.5690(3)	0.8907(3)	0.0236(11)

Table 4. Bond lengths (Å) for compound 4.8.

W1-N7	1.765(4)	W1-C11	2.186(5)
W1-N5	2.211(4)	W1-N3	2.213(4)
W1-N1	2.244(4)	W1-C10	2.249(5)
W1-P1	2.5148(13)	P1-C25	1.808(6)
P1-C23	1.811(6)	P1-C24	1.825(5)
O1-N7	1.233(5)	O2-C17	1.225(6)
O3-C19	1.378(6)	O3-C22	1.378(6)
N1-C1	1.341(6)	N1-N2	1.377(6)
N2-C3	1.341(6)	N2-B1	1.526(7)
N3-C4	1.334(6)	N3-N4	1.376(6)
N4-C6	1.336(6)	N4-B1	1.538(7)
N5-C7	1.334(6)	N5-N6	1.360(5)
N6-C9	1.350(6)	N6-B1	1.546(7)

N8-C17	1.356(6)	N8-C18	1.463(6)
N8-C12	1.496(6)	C1-C2	1.387(8)
C1-H1	0.95	C2-C3	1.370(8)
C2-H2	0.95	C3-H3	0.95
C4-C5	1.383(7)	C4-H4	0.95
C5-C6	1.378(7)	C5-H5	0.95
C6-H6	0.95	C7-C8	1.397(7)
C7-H7	0.95	C8-C9	1.372(7)
C8-H8	0.95	C9-H9	0.95
C10-C11	1.440(7)	C10-C15	1.478(7)
C10-H10	0.96(6)	C11-C12	1.507(7)
C11-H11	0.86(5)	C12-C13	1.544(6)
C12-H12	1.0	C13-C14	1.498(7)
C13-C16	1.544(7)	C13-H13	1.0
C14-C15	1.322(8)	C14-H14	0.95
C15-H15	0.95	C16-C17	1.516(7)
C16-H16A	0.99	C16-H16B	0.99
C18-C19	1.487(7)	C18-H18A	0.99
C18-H18B	0.99	C19-C20	1.346(7)
C20-C21	1.424(8)	C20-H20	0.95
C21-C22	1.333(8)	C21-H21	0.95
C22-H22	0.95	C23-H23A	0.98
C23-H23B	0.98	C23-H23C	0.98
C24-H24A	0.98	C24-H24B	0.98
C24-H24C	0.98	C25-H25A	0.98
C25-H25B	0.98	C25-H25C	0.98
B1-H1A	1.10(5)		

Table 5. Bond angles (°) for compound 4.8.

N7-W1-C11	98.93(19)	N7-W1-N5	95.05(17)
C11-W1-N5	81.99(16)	N7-W1-N3	91.16(17)
C11-W1-N3	156.08(16)	N5-W1-N3	75.53(14)
N7-W1-N1	175.66(16)	C11-W1-N1	85.14(17)

N5-W1-N1	84.00(14)	N3-W1-N1	84.50(14)
N7-W1-C10	96.65(19)	C11-W1-C10	37.85(18)
N5-W1-C10	119.78(16)	N3-W1-C10	161.88(17)
N1-W1-C10	87.48(17)	N7-W1-P1	93.94(14)
C11-W1-P1	117.65(13)	N5-W1-P1	156.75(11)
N3-W1-P1	82.91(11)	N1-W1-P1	85.43(11)
C10-W1-P1	80.27(13)	C25-P1-C23	101.2(3)
C25-P1-C24	103.4(3)	C23-P1-C24	101.1(3)
C25-P1-W1	113.6(2)	C23-P1-W1	121.5(2)
C24-P1-W1	113.65(19)	C19-O3-C22	106.0(4)
C1-N1-N2	105.8(4)	C1-N1-W1	134.0(3)
N2-N1-W1	120.0(3)	C3-N2-N1	109.0(4)
C3-N2-B1	130.3(4)	N1-N2-B1	120.6(4)
C4-N3-N4	106.6(4)	C4-N3-W1	131.5(3)
N4-N3-W1	121.8(3)	C6-N4-N3	108.8(4)
C6-N4-B1	131.0(4)	N3-N4-B1	119.2(4)
C7-N5-N6	107.1(4)	C7-N5-W1	132.4(3)
N6-N5-W1	120.5(3)	C9-N6-N5	109.1(4)
C9-N6-B1	128.6(4)	N5-N6-B1	120.4(4)
O1-N7-W1	176.5(4)	C17-N8-C18	121.2(4)
C17-N8-C12	113.3(4)	C18-N8-C12	122.0(4)
N1-C1-C2	111.1(5)	N1-C1-H1	124.4
C2-C1-H1	124.4	C3-C2-C1	104.5(5)
C3-C2-H2	127.8	C1-C2-H2	127.8
N2-C3-C2	109.6(5)	N2-C3-H3	125.2
C2-C3-H3	125.2	N3-C4-C5	110.5(5)
N3-C4-H4	124.7	C5-C4-H4	124.7
C6-C5-C4	104.8(4)	C6-C5-H5	127.6
C4-C5-H5	127.6	N4-C6-C5	109.2(5)
N4-C6-H6	125.4	C5-C6-H6	125.4
N5-C7-C8	110.1(4)	N5-C7-H7	125.0
C8-C7-H7	125.0	C9-C8-C7	104.9(4)
C9-C8-H8	127.6	C7-C8-H8	127.6
N6-C9-C8	108.8(4)	N6-C9-H9	125.6

C8-C9-H9	125.6	C11-C10-C15	117.8(5)
C11-C10-W1	68.7(3)	C15-C10-W1	118.7(4)
C11-C10-H10	115.(3)	C15-C10-H10	117.(3)
W1-C10-H10	111.(3)	C10-C11-C12	119.3(4)
C10-C11-W1	73.5(3)	C12-C11-W1	123.7(3)
C10-C11-H11	116.(4)	C12-C11-H11	115.(4)
W1-C11-H11	103.(3)	N8-C12-C11	112.5(4)
N8-C12-C13	101.6(4)	C11-C12-C13	116.0(4)
N8-C12-H12	108.8	C11-C12-H12	108.8
C13-C12-H12	108.8	C14-C13-C16	111.9(4)
C14-C13-C12	112.6(4)	C16-C13-C12	102.9(4)
C14-C13-H13	109.8	C16-C13-H13	109.8
C12-C13-H13	109.8	C15-C14-C13	123.6(5)
C15-C14-H14	118.2	C13-C14-H14	118.2
C14-C15-C10	123.2(5)	C14-C15-H15	118.4
C10-C15-H15	118.4	C17-C16-C13	105.2(4)
C17-C16-H16A	110.7	C13-C16-H16A	110.7
C17-C16-H16B	110.7	C13-C16-H16B	110.7
H16A-C16-H16B	108.8	O2-C17-N8	125.9(5)
O2-C17-C16	126.5(5)	N8-C17-C16	107.5(4)
N8-C18-C19	113.4(4)	N8-C18-H18A	108.9
C19-C18-H18A	108.9	N8-C18-H18B	108.9
C19-C18-H18B	108.9	H18A-C18-H18B	107.7
C20-C19-O3	109.8(4)	C20-C19-C18	133.2(5)
O3-C19-C18	117.0(4)	C19-C20-C21	106.8(5)
C19-C20-H20	126.6	C21-C20-H20	126.6
C22-C21-C20	106.9(5)	C22-C21-H21	126.6
C20-C21-H21	126.6	C21-C22-O3	110.5(5)
C21-C22-H22	124.8	O3-C22-H22	124.8

P1-C23-H23A	109.5	P1-C23-H23B	109.5
H23A-C23-H23B	109.5	P1-C23-H23C	109.5
H23A-C23-H23C	109.5	H23B-C23-H23C	109.5
P1-C24-H24A	109.5	P1-C24-H24B	109.5
H24A-C24-H24B	109.5	P1-C24-H24C	109.5
H24A-C24-H24C	109.5	H24B-C24-H24C	109.5
P1-C25-H25A	109.5	P1-C25-H25B	109.5
H25A-C25-H25B	109.5	P1-C25-H25C	109.5
H25A-C25-H25C	109.5	H25B-C25-H25C	109.5
N2-B1-N4	109.1(4)	N2-B1-N6	109.4(4)
N4-B1-N6	106.7(4)	N2-B1-H1A	111.(3)
N4-B1-H1A	107.(3)	N6-B1-H1A	114.(3)

Table 6. Torsion angles (°) for compound 4.8.

C1-N1-N2-C3	1.5(5)	W1-N1-N2-C3	-174.2(3)
C1-N1-N2-B1	-176.6(4)	W1-N1-N2-B1	7.7(5)
C4-N3-N4-C6	0.2(5)	W1-N3-N4-C6	-176.8(3)
C4-N3-N4-B1	170.6(4)	W1-N3-N4-B1	-6.5(6)
C7-N5-N6-C9	1.1(5)	W1-N5-N6-C9	-178.7(3)
C7-N5-N6-B1	-164.4(4)	W1-N5-N6-B1	15.8(5)
N2-N1-C1-C2	-1.3(6)	W1-N1-C1-C2	173.5(4)
N1-C1-C2-C3	0.6(6)	N1-N2-C3-C2	-1.2(6)
B1-N2-C3-C2	176.7(5)	C1-C2-C3-N2	0.4(6)
N4-N3-C4-C5	0.5(6)	W1-N3-C4-C5	177.1(3)

N3-C4-C5-C6	-1.0(6)	N3-N4-C6-C5	-0.9(6)
B1-N4-C6-C5	-169.7(5)	C4-C5-C6-N4	1.2(6)
N6-N5-C7-C8	-1.1(5)	W1-N5-C7-C8	178.5(3)
N5-C7-C8-C9	0.8(5)	N5-N6-C9-C8	-0.6(5)
B1-N6-C9-C8	163.4(5)	C7-C8-C9-N6	-0.1(5)
C15-C10-C11-C12	7.6(7)	W1-C10-C11-C12	119.8(4)
C15-C10-C11-W1	-112.2(4)	C17-N8-C12-C11	-149.9(4)
C18-N8-C12-C11	51.1(6)	C17-N8-C12-C13	-25.2(5)
C18-N8-C12-C13	175.8(4)	C10-C11-C12-N8	89.3(5)
W1-C11-C12-N8	178.2(3)	C10-C11-C12-C13	-27.1(6)
W1-C11-C12-C13	61.9(5)	N8-C12-C13-C14	-90.6(5)
C11-C12-C13-C14	31.7(6)	N8-C12-C13-C16	29.9(5)
C11-C12-C13-C16	152.2(4)	C16-C13-C14-C15	-134.6(5)
C12-C13-C14-C15	-19.4(7)	C13-C14-C15-C10	0.0(8)
C11-C10-C15-C14	6.7(8)	W1-C10-C15-C14	-72.9(6)
C14-C13-C16-C17	94.8(5)	C12-C13-C16-C17	-26.2(5)
C18-N8-C17-O2	-10.8(8)	C12-N8-C17-O2	-170.0(5)
C18-N8-C17-C16	167.9(4)	C12-N8-C17-C16	8.7(5)
C13-C16-C17-O2	-169.5(5)	C13-C16-C17-N8	11.8(5)
C17-N8-C18-C19	-86.2(6)	C12-N8-C18-C19	71.2(6)

C22-O3-C19-C20	-0.1(5)	C22-O3-C19-C18	178.8(4)
N8-C18-C19-C20	105.7(7)	N8-C18-C19-O3	-72.9(6)
O3-C19-C20-C21	-0.1(6)	C18-C19-C20-C21	-178.8(5)
C19-C20-C21-C22	0.3(6)	C20-C21-C22-O3	-0.3(6)
C19-O3-C22-C21	0.3(6)	C3-N2-B1-N4	118.5(5)
N1-N2-B1-N4	-63.9(5)	C3-N2-B1-N6	-125.1(5)
N1-N2-B1-N6	52.5(5)	C6-N4-B1-N2	-129.1(5)
N3-N4-B1-N2	63.1(6)	C6-N4-B1-N6	112.8(6)
N3-N4-B1-N6	-55.1(5)	C9-N6-B1-N2	129.8(5)
N5-N6-B1-N2	-67.8(5)	C9-N6-B1-N4	-112.3(5)
N5-N6-B1-N4	50.1(5)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.8.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02602(11)	0.01542(9)	0.02066(10)	0.00064(8)	0.00190(7)	-0.00127(8)
P1	0.0365(7)	0.0221(6)	0.0266(7)	-0.0006(5)	0.0053(6)	-0.0070(5)
O1	0.042(2)	0.029(2)	0.045(2)	0.0019(17)	0.0037(18)	0.0163(17)
O2	0.050(2)	0.036(2)	0.0223(18)	0.0022(16)	0.0042(16)	0.0002(18)
O3	0.0323(19)	0.0231(17)	0.0286(19)	-0.0007(14)	0.0043(15)	-0.0024(14)
N1	0.030(2)	0.0199(19)	0.022(2)	0.0005(16)	0.0022(17)	-0.0027(16)
N2	0.025(2)	0.0188(19)	0.029(2)	0.0002(17)	0.0024(17)	0.0010(16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N3	0.028(2)	0.019(2)	0.025(2)	0.0033(16)	0.0030(17)	0.0012(16)
N4	0.025(2)	0.025(2)	0.025(2)	-0.0007(17)	0.0025(17)	-0.0019(17)
N5	0.022(2)	0.0195(19)	0.025(2)	0.0011(16)	0.0011(16)	0.0004(15)
N6	0.027(2)	0.0171(18)	0.023(2)	-0.0028(16)	0.0008(16)	0.0004(16)
N7	0.036(2)	0.0181(19)	0.024(2)	0.0021(16)	0.0024(18)	0.0007(17)
N8	0.031(2)	0.0184(18)	0.0195(19)	0.0006(16)	0.0006(16)	-0.0004(16)
C1	0.030(3)	0.034(3)	0.030(3)	0.001(2)	-0.001(2)	-0.001(2)
C2	0.025(3)	0.036(3)	0.034(3)	0.003(2)	0.004(2)	0.004(2)
C3	0.035(3)	0.023(2)	0.030(3)	0.002(2)	0.007(2)	0.007(2)
C4	0.032(3)	0.020(2)	0.030(3)	0.006(2)	0.002(2)	0.000(2)
C5	0.031(3)	0.031(3)	0.027(3)	0.008(2)	0.001(2)	-0.001(2)
C6	0.029(3)	0.034(3)	0.024(3)	0.000(2)	0.001(2)	-0.003(2)
C7	0.023(2)	0.026(2)	0.022(2)	0.0039(19)	-0.0021(19)	0.0022(19)
C8	0.020(2)	0.022(2)	0.032(3)	0.006(2)	0.000(2)	-0.0043(18)
C9	0.024(2)	0.020(2)	0.033(3)	0.002(2)	-0.004(2)	-0.0018(19)
C10	0.030(3)	0.025(2)	0.025(3)	0.003(2)	-0.001(2)	-0.004(2)
C11	0.027(3)	0.018(2)	0.023(2)	-0.0004(19)	0.0000(19)	0.0020(19)
C12	0.026(2)	0.018(2)	0.022(2)	-0.0003(18)	0.0015(19)	0.0015(18)
C13	0.033(3)	0.018(2)	0.024(2)	-0.0029(19)	0.002(2)	0.0020(19)
C14	0.053(3)	0.018(2)	0.026(3)	-0.003(2)	0.002(2)	0.001(2)
C15	0.047(3)	0.021(2)	0.024(3)	-0.001(2)	-0.001(2)	-0.007(2)
C16	0.034(3)	0.026(3)	0.028(3)	-0.003(2)	0.007(2)	0.000(2)
C17	0.033(3)	0.021(2)	0.026(3)	-0.003(2)	0.003(2)	-0.005(2)
C18	0.030(3)	0.020(2)	0.028(3)	0.0034(19)	0.004(2)	-0.0001(19)

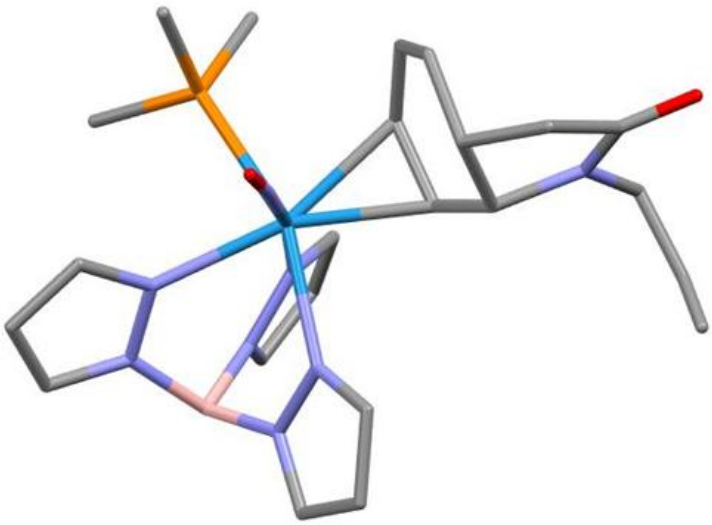
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	0.025(2)	0.020(2)	0.026(2)	0.0025(19)	0.0014(19)	0.0036(19)
C20	0.031(3)	0.030(3)	0.033(3)	0.010(2)	-0.005(2)	-0.005(2)
C21	0.031(3)	0.024(2)	0.047(3)	0.010(2)	-0.005(2)	-0.005(2)
C22	0.027(3)	0.019(2)	0.040(3)	-0.006(2)	0.002(2)	-0.0021(19)
C23	0.053(4)	0.050(4)	0.032(3)	-0.003(3)	0.006(3)	-0.030(3)
C24	0.039(3)	0.044(3)	0.030(3)	-0.003(2)	0.009(2)	-0.014(3)
C25	0.066(4)	0.020(3)	0.062(4)	0.002(3)	0.014(3)	-0.006(3)
B1	0.030(3)	0.019(3)	0.022(3)	0.000(2)	0.003(2)	0.001(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.8.

	x/a	y/b	z/c	U(eq)
H1	0.3588	0.4598	0.7362	0.038
H2	0.2282	0.5587	0.8135	0.038
H3	0.4081	0.6212	0.9036	0.035
H4	0.8832	0.3266	0.9273	0.033
H5	0.9151	0.3897	1.0574	0.035
H6	0.8070	0.5253	1.0449	0.035
H7	1.0007	0.5278	0.7061	0.029
H8	1.0562	0.6672	0.7515	0.03
H9	0.8780	0.6996	0.8481	0.031
H10	0.502(6)	0.392(3)	0.663(3)	0.026(14)
H11	0.630(5)	0.502(3)	0.657(3)	0.023(14)
H12	0.8618	0.5033	0.6107	0.026
H13	0.9442	0.3772	0.6033	0.03
H14	0.7840	0.2696	0.5462	0.039
H15	0.5907	0.2696	0.6130	0.037
H16A	0.9982	0.4224	0.4856	0.035
H16B	0.8931	0.3533	0.4548	0.035
H18A	0.5664	0.5624	0.5449	0.031

	x/a	y/b	z/c	U(eq)
H18B	0.5962	0.5667	0.4553	0.031
H20	0.7508	0.6997	0.4196	0.038
H21	0.8863	0.8007	0.5042	0.041
H22	0.8833	0.7531	0.6367	0.034
H23A	0.3481	0.3117	0.7615	0.067
H23B	0.3823	0.2216	0.7855	0.067
H23C	0.4408	0.2574	0.7079	0.067
H24A	0.5908	0.3216	0.9475	0.056
H24B	0.4540	0.2705	0.9236	0.056
H24C	0.4539	0.3647	0.9105	0.056
H25A	0.6939	0.1901	0.7716	0.074
H25B	0.6179	0.1703	0.8495	0.074
H25C	0.7624	0.2190	0.8526	0.074
H1A	0.689(5)	0.616(3)	0.934(3)	0.024(13)

Crystal Structure Report for compound 4.11



A colorless, plate-like specimen of $C_{25}H_{37}BN_8O_3PW$, approximate dimensions 0.039 mm x 0.116 mm x 0.121 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with a Incoatec IμS 3.0 micro-focus sealed X-ray

tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 1.43 hours. The frames were integrated with the Bruker SAINT software package[36] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38094 reflections to a maximum θ angle of 25.69° (0.82 Å resolution), of which 5478 were independent (average redundancy 6.954, completeness = 99.8%, R_{int} = 6.29%, R_{sig} = 3.85%) and 4483 (81.84%) were greater than 2σ(F^2). The final cell constants of a = 11.6179(7) Å, b = 15.6672(8) Å, c = 15.8765(7) Å, β = 91.465(2)°, volume = 2888.9(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 7311 reflections above 20 σ(I) with 5.018° < 2θ < 51.14°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[37] The ratio of minimum to maximum apparent transmission was 0.488. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6370 and 0.8570.

The structure was solved and refined using the Bruker SHELXTL Software Package[38] within APEX4 [1] and OLEX2,[39] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{25}H_{37}BN_8O_3PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 368 variables converged at R1 = 3.98%, for the observed data and wR2 = 9.14% for all data. The goodness-of-fit was 1.102. The largest peak in the final difference electron density synthesis was 2.557 $e^-/Å^3$ and the largest hole was -1.213 $e^-/Å^3$ with an RMS deviation of 0.113 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.663 g/cm^3 and F(000), 1444 e^-.

Table 1. Sample and crystal data for compound 4.11.

Chemical formula	$C_{25}H_{37}BN_8O_3PW$

[36] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

[37] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[38] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

[39] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Formula weight	723.25 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.039 x 0.116 x 0.121 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P $2_1/c$
Unit cell dimensions	a = 11.6179(7) Å α = 90°
	b = 15.6672(8) Å β = 91.465(2)°
	c = 15.8765(7) Å γ = 90°
Volume	2888.9(3) $Å^3$
Z	4
Density (calculated)	1.663 g/cm^3
Absorption coefficient	4.096 mm^{-1}
F(000)	1444

Table 2. Data collection and structure refinement for compound 4.11

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.51 to 25.69°
Index ranges	-14<=h<=13, -19<=k<=19, -19<=l<=19
Reflections collected	38094
Independent reflections	5478 [R(int) = 0.0629]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan

Max. and min. transmission	0.8570 and 0.6370	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5478 / 0 / 368	
Goodness-of-fit on F^2	1.102	
Δ/σ_{max}	0.002	
Final R indices	4483 data; $I>2\sigma(I)$	R1 = 0.0398, wR2 = 0.0851
	all data	R1 = 0.0534, wR2 = 0.0914
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0309P)^2+9.5909P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	2.557 and -1.213 eÅ^{-3}	
R.M.S. deviation from mean	0.113 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.11.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.61662(2)	0.21912(2)	0.66337(2)	0.03629(9)
P1	0.66184(17)	0.09154(11)	0.75271(10)	0.0452(4)

	x/a	y/b	z/c	U(eq)
O1	0.7212(4)	0.1415(3)	0.5101(3)	0.0525(12)
O2	0.0848(4)	0.4634(4)	0.6143(4)	0.0658(14)
N1	0.5143(6)	0.2664(3)	0.7719(3)	0.0460(14)
N2	0.3970(5)	0.2720(3)	0.7643(3)	0.0451(13)
N3	0.4615(4)	0.1431(3)	0.6309(3)	0.0347(11)
N4	0.3527(5)	0.1688(3)	0.6452(3)	0.0414(12)
N5	0.5034(4)	0.3130(3)	0.5963(3)	0.0350(11)
N6	0.3907(4)	0.3201(3)	0.6146(3)	0.0373(11)
N7	0.6819(5)	0.1753(3)	0.5738(3)	0.0424(13)
N8	0.9024(5)	0.4215(4)	0.6460(4)	0.0488(14)
C1	0.5410(8)	0.2910(4)	0.8511(4)	0.058(2)
C2	0.4434(9)	0.3111(5)	0.8935(5)	0.071(3)
C3	0.3537(8)	0.2994(4)	0.8375(4)	0.057(2)
C4	0.4538(6)	0.0681(4)	0.5898(3)	0.0392(14)
C5	0.3388(6)	0.0472(4)	0.5759(4)	0.0485(16)
C6	0.2782(6)	0.1122(4)	0.6111(5)	0.0515(17)
C7	0.5209(6)	0.3658(4)	0.5328(3)	0.0365(14)
C8	0.4194(6)	0.4077(4)	0.5085(4)	0.0415(15)
C9	0.3387(6)	0.3759(4)	0.5625(4)	0.0395(14)
C10	0.7813(7)	0.2584(4)	0.7298(4)	0.0502(17)
C11	0.7354(6)	0.3282(4)	0.6791(4)	0.0444(15)
C12	0.8107(5)	0.3640(4)	0.6113(4)	0.0431(15)
C13	0.8849(6)	0.2981(4)	0.5665(5)	0.0502(17)
C14	0.9332(6)	0.2325(5)	0.6263(5)	0.061(2)
C15	0.8865(7)	0.2169(5)	0.7009(5)	0.0573(19)
C16	0.9822(7)	0.3528(5)	0.5332(5)	0.063(2)
C17	0.9987(7)	0.4189(5)	0.6019(5)	0.0556(18)
C18	0.8846(7)	0.4849(4)	0.7116(5)	0.0556(19)
C19	0.8293(9)	0.5643(6)	0.6829(6)	0.085(3)
C20	0.8189(8)	0.5951(8)	0.6169(8)	0.109(4)
C21	0.7516(7)	0.0129(5)	0.7025(5)	0.0577(19)
C22	0.7347(7)	0.1077(5)	0.8551(4)	0.0557(19)
C23	0.5363(7)	0.0304(5)	0.7840(5)	0.060(2)

	x/a	y/b	z/c	U(eq)
B1	0.3342(8)	0.2599(5)	0.6786(5)	0.0465(19)
O3	0.0510(6)	0.0995(6)	0.4600(5)	0.106(3)
C24	0.0126(10)	0.1557(9)	0.3938(8)	0.118(4)
C25	0.9780(8)	0.0279(7)	0.4636(7)	0.105(4)

Table 4. Bond lengths (Å) for compound 4.11.

W1-N7	1.767(6)	W1-C11	2.206(7)
W1-N3	2.210(5)	W1-N5	2.225(5)
W1-N1	2.245(5)	W1-C10	2.247(7)
W1-P1	2.4991(17)	P1-C21	1.812(7)
P1-C23	1.824(8)	P1-C22	1.831(7)
O1-N7	1.239(6)	O2-C17	1.231(8)
N1-C1	1.344(8)	N1-N2	1.368(8)
N2-C3	1.349(8)	N2-B1	1.538(10)
N3-C4	1.345(7)	N3-N4	1.352(7)
N4-C6	1.343(8)	N4-B1	1.540(9)
N5-C7	1.325(7)	N5-N6	1.354(7)
N6-C9	1.338(8)	N6-B1	1.545(9)
N8-C17	1.335(9)	N8-C18	1.457(9)
N8-C12	1.490(8)	C1-C2	1.370(11)
C1-H1	0.950000	C2-C3	1.364(12)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.388(9)	C4-H4	0.950000
C5-C6	1.366(10)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.395(9)
C7-H7	0.950000	C8-C9	1.380(9)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.450(9)	C10-C15	1.468(11)
C10-H10	1.05(7)	C11-C12	1.513(9)
C11-H11	1.02(5)	C12-C13	1.531(9)
C12-H12	1.000000	C13-C14	1.498(11)

C13-C16	1.523(10)	C13-H13	1.000000
C14-C15	1.339(11)	C14-H14	0.950000
C15-H15	0.950000	C16-C17	1.513(10)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.467(11)	C18-H18A	0.990000
C18-H18B	0.990000	C19-C20	1.157(12)
C19-H19	0.950000	C20-H20A	0.950000
C20-H20B	0.950000	C21-H21A	0.980000
C21-H21B	0.980000	C21-H21C	0.980000
C22-H22A	0.980000	C22-H22B	0.980000
C22-H22C	0.980000	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
B1-H1A	1.06(6)	O3-C25	1.407(13)
O3-C24	1.434(14)	C24-H24A	0.980000
C24-H24B	0.980000	C24-H24C	0.980000
C25-C25#1	1.53(2)	C25-H25A	0.990000
C25-H25B	0.990000		

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y, -z+1

Table 5. Bond angles (°) for compound 4.11**.**

N7-W1-C11	96.4(2)	N7-W1-N3	88.1(2)
C11-W1-N3	161.4(2)	N7-W1-N5	97.6(2)
C11-W1-N5	84.4(2)	N3-W1-N5	77.08(18)
N7-W1-N1	173.1(2)	C11-W1-N1	90.0(2)
N3-W1-N1	84.97(19)	N5-W1-N1	80.26(18)
N7-W1-C10	96.1(3)	C11-W1-C10	38.0(2)
N3-W1-C10	159.5(2)	N5-W1-C10	121.9(2)
N1-W1-C10	90.6(3)	N7-W1-P1	93.29(17)
C11-W1-P1	115.69(18)	N3-W1-P1	81.92(13)
N5-W1-P1	155.92(14)	N1-W1-P1	86.33(14)
C10-W1-P1	77.81(18)	C21-P1-C23	103.6(4)

C21-P1-C22	103.1(3)	C23-P1-C22	100.7(4)
C21-P1-W1	114.2(2)	C23-P1-W1	114.6(2)
C22-P1-W1	118.6(2)	C1-N1-N2	105.7(6)
C1-N1-W1	134.3(6)	N2-N1-W1	119.9(4)
C3-N2-N1	109.6(6)	C3-N2-B1	128.5(7)
N1-N2-B1	121.3(5)	C4-N3-N4	106.9(5)
C4-N3-W1	128.9(4)	N4-N3-W1	124.1(4)
C6-N4-N3	109.3(5)	C6-N4-B1	131.0(6)
N3-N4-B1	118.3(5)	C7-N5-N6	106.2(5)
C7-N5-W1	132.6(4)	N6-N5-W1	121.0(3)
C9-N6-N5	110.2(5)	C9-N6-B1	127.8(6)
N5-N6-B1	121.3(5)	O1-N7-W1	175.8(5)
C17-N8-C18	122.1(6)	C17-N8-C12	112.8(6)
C18-N8-C12	124.3(6)	N1-C1-C2	110.5(8)
N1-C1-H1	124.700000	C2-C1-H1	124.700000
C3-C2-C1	106.1(7)	C3-C2-H2	126.900000
C1-C2-H2	126.900000	N2-C3-C2	108.0(7)
N2-C3-H3	126.000000	C2-C3-H3	126.000000
N3-C4-C5	109.6(6)	N3-C4-H4	125.200000
C5-C4-H4	125.200000	C6-C5-C4	105.3(6)
C6-C5-H5	127.400000	C4-C5-H5	127.400000
N4-C6-C5	108.9(6)	N4-C6-H6	125.600000
C5-C6-H6	125.600000	N5-C7-C8	111.1(6)
N5-C7-H7	124.500000	C8-C7-H7	124.500000
C9-C8-C7	104.0(6)	C9-C8-H8	128.000000
C7-C8-H8	128.000000	N6-C9-C8	108.5(6)
N6-C9-H9	125.800000	C8-C9-H9	125.800000
C11-C10-C15	117.3(7)	C11-C10-W1	69.5(4)
C15-C10-W1	116.0(5)	C11-C10-H10	111.(4)
C15-C10-H10	124.(4)	W1-C10-H10	106.(4)
C10-C11-C12	117.6(6)	C10-C11-W1	72.5(4)
C12-C11-W1	125.3(4)	C10-C11-H11	118.(3)

C12-C11-H11	115.(3)	W1-C11-H11	102.(3)
N8-C12-C11	112.4(5)	N8-C12-C13	100.0(5)
C11-C12-C13	115.0(5)	N8-C12-H12	109.700000
C11-C12-H12	109.700000	C13-C12-H12	109.700000
C14-C13-C16	109.7(6)	C14-C13-C12	112.0(6)
C16-C13-C12	102.3(6)	C14-C13-H13	110.800000
C16-C13-H13	110.800000	C12-C13-H13	110.800000
C15-C14-C13	122.2(7)	C15-C14-H14	118.900000
C13-C14-H14	118.900000	C14-C15-C10	123.7(7)
C14-C15-H15	118.200000	C10-C15-H15	118.200000
C17-C16-C13	102.5(6)	C17-C16-H16A	111.300000
C13-C16-H16A	111.300000	C17-C16-H16B	111.300000
C13-C16-H16B	111.300000	H16A-C16-H16B	109.200000
O2-C17-N8	125.9(7)	O2-C17-C16	126.2(7)
N8-C17-C16	107.9(6)	N8-C18-C19	115.2(7)
N8-C18-H18A	108.500000	C19-C18-H18A	108.500000
N8-C18-H18B	108.500000	C19-C18-H18B	108.500000
H18A-C18-H18B	107.500000	C20-C19-C18	132.0(11)
C20-C19-H19	114.000000	C18-C19-H19	114.000000
C19-C20-H20A	120.000000	C19-C20-H20B	120.000000

H20A-C20-H20B	120.000000	P1-C21-H21A	109.500000
P1-C21-H21B	109.500000	H21A-C21-H21B	109.500000
P1-C21-H21C	109.500000	H21A-C21-H21C	109.500000
H21B-C21-H21C	109.500000	P1-C22-H22A	109.500000
P1-C22-H22B	109.500000	H22A-C22-H22B	109.500000
P1-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	P1-C23-H23A	109.500000
P1-C23-H23B	109.500000	H23A-C23-H23B	109.500000
P1-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	N2-B1-N4	110.6(6)
N2-B1-N6	107.9(6)	N4-B1-N6	105.9(5)
N2-B1-H1A	112.(3)	N4-B1-H1A	110.(3)
N6-B1-H1A	111.(3)	C25-O3-C24	110.0(8)
O3-C24-H24A	109.500000	O3-C24-H24B	109.500000
H24A-C24-H24B	109.500000	O3-C24-H24C	109.500000
H24A-C24-H24C	109.500000	H24B-C24-H24C	109.500000
O3-C25-C25#1	107.3(10)	O3-C25-H25A	110.300000
C25#1-C25-H25A	110.300000	O3-C25-H25B	110.300000
C25#1-C25-H25B	110.300000	H25A-C25-H25B	108.500000

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y, -z+1

Table 6. Torsion angles (°) for compound 4.11**.**

C1-N1-N2-C3	0.0(7)	W1-N1-N2-C3	178.2(4)
C1-N1-N2-B1	172.1(6)	W1-N1-N2-B1	-9.7(7)
C4-N3-N4-C6	-2.0(6)	W1-N3-N4-C6	174.1(4)
C4-N3-N4-B1	-170.3(5)	W1-N3-N4-B1	5.8(7)
C7-N5-N6-C9	0.7(6)	W1-N5-N6-C9	-175.6(4)
C7-N5-N6-B1	172.5(5)	W1-N5-N6-B1	-3.8(7)
N2-N1-C1-C2	0.6(8)	W1-N1-C1-C2	-177.3(5)
N1-C1-C2-C3	-0.9(9)	N1-N2-C3-C2	-0.5(8)
B1-N2-C3-C2	-171.9(6)	C1-C2-C3-N2	0.8(8)
N4-N3-C4-C5	1.6(6)	W1-N3-C4-C5	-174.2(4)
N3-C4-C5-C6	-0.6(7)	N3-N4-C6-C5	1.6(7)
B1-N4-C6-C5	167.9(6)	C4-C5-C6-N4	-0.6(8)
N6-N5-C7-C8	-0.4(6)	W1-N5-C7-C8	175.3(4)
N5-C7-C8-C9	-0.1(7)	N5-N6-C9-C8	-0.8(7)
B1-N6-C9-C8	-171.9(6)	C7-C8-C9-N6	0.5(7)
C15-C10-C11-C12	-11.9(9)	W1-C10-C11-C12	-121.3(5)
C15-C10-C11-W1	109.4(6)	C17-N8-C12-C11	147.8(6)
C18-N8-C12-C11	-42.2(9)	C17-N8-C12-C13	25.4(7)
C18-N8-C12-C13	-164.7(6)	C10-C11-C12-N8	-77.6(7)
W1-C11-C12-N8	-165.0(4)	C10-C11-C12-C13	36.0(8)
W1-C11-C12-C13	-51.4(8)	N8-C12-C13-C14	81.3(6)

C11-C12-C13-C14	-39.3(8)	N8-C12-C13-C16	-36.1(7)
C11-C12-C13-C16	-156.7(6)	C16-C13-C14-C15	133.8(7)
C12-C13-C14-C15	20.9(10)	C13-C14-C15-C10	3.4(12)
C11-C10-C15-C14	-8.6(11)	W1-C10-C15-C14	70.6(9)
C14-C13-C16-C17	-83.9(7)	C12-C13-C16-C17	35.2(7)
C18-N8-C17-O2	5.5(12)	C12-N8-C17-O2	175.7(7)
C18-N8-C17-C16	-173.4(6)	C12-N8-C17-C16	-3.2(8)
C13-C16-C17-O2	160.4(8)	C13-C16-C17-N8	-20.7(8)
C17-N8-C18-C19	90.2(9)	C12-N8-C18-C19	-78.8(9)
N8-C18-C19-C20	-19.4(17)	C3-N2-B1-N4	-126.1(7)
N1-N2-B1-N4	63.4(8)	C3-N2-B1-N6	118.5(7)
N1-N2-B1-N6	-52.0(8)	C6-N4-B1-N2	134.2(7)
N3-N4-B1-N2	-60.5(7)	C6-N4-B1-N6	-109.2(7)
N3-N4-B1-N6	56.1(7)	C9-N6-B1-N2	-129.2(6)
N5-N6-B1-N2	60.6(7)	C9-N6-B1-N4	112.4(7)
N5-N6-B1-N4	-57.8(8)	C24-O3-C25-C25#1	-178.8(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y, -z+1

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.11**.**

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.04330(16)	0.03362(14)	0.03167(13)	0.00133(11)	-0.00439(9)	-0.00256(12)
P1	0.0560(11)	0.0395(9)	0.0396(9)	0.0051(7)	-0.0064(8)	0.0054(8)
O1	0.052(3)	0.061(3)	0.045(3)	-0.014(2)	0.011(2)	-0.004(2)
O2	0.043(3)	0.065(3)	0.089(4)	-0.008(3)	-0.006(3)	-0.014(3)
N1	0.072(4)	0.033(3)	0.033(3)	0.001(2)	-0.001(3)	0.000(3)
N2	0.066(4)	0.033(3)	0.037(3)	0.002(2)	0.014(3)	0.000(3)
N3	0.039(3)	0.034(3)	0.031(2)	0.001(2)	0.001(2)	-0.004(2)
N4	0.044(3)	0.035(3)	0.046(3)	0.002(2)	0.009(2)	-0.010(2)
N5	0.041(3)	0.029(2)	0.035(3)	0.001(2)	0.001(2)	-0.004(2)
N6	0.038(3)	0.033(3)	0.040(3)	0.003(2)	-0.002(2)	-0.008(2)
N7	0.040(3)	0.038(3)	0.049(3)	0.005(2)	-0.008(2)	-0.007(2)
N8	0.039(3)	0.048(3)	0.059(3)	-0.002(3)	-0.006(3)	-0.007(3)
C1	0.102(6)	0.039(4)	0.031(3)	-0.001(3)	-0.005(4)	0.009(4)
C2	0.123(8)	0.051(4)	0.039(4)	-0.003(3)	0.015(5)	0.022(5)
C3	0.084(6)	0.039(4)	0.051(4)	0.007(3)	0.025(4)	0.015(4)
C4	0.055(4)	0.033(3)	0.029(3)	0.001(2)	0.004(3)	-0.001(3)
C5	0.048(4)	0.041(4)	0.057(4)	0.001(3)	0.004(3)	-0.009(3)
C6	0.041(4)	0.045(4)	0.068(5)	0.001(3)	0.006(3)	-0.012(3)
C7	0.044(4)	0.031(3)	0.035(3)	-0.001(2)	0.002(3)	-0.009(3)
C8	0.048(4)	0.036(3)	0.039(3)	0.000(3)	-0.009(3)	-0.005(3)
C9	0.037(4)	0.035(3)	0.046(3)	-0.003(3)	-0.002(3)	0.000(3)
C10	0.060(5)	0.046(4)	0.044(4)	-0.001(3)	-0.019(3)	-0.003(3)
C11	0.048(4)	0.038(4)	0.046(4)	-0.011(3)	-0.008(3)	-0.002(3)
C12	0.035(4)	0.040(4)	0.055(4)	-0.002(3)	-0.008(3)	-0.007(3)
C13	0.037(4)	0.054(4)	0.059(4)	-0.007(3)	0.001(3)	-0.007(3)
C14	0.039(4)	0.055(5)	0.088(6)	-0.006(4)	0.000(4)	0.001(4)
C15	0.053(5)	0.046(4)	0.072(5)	0.005(4)	-0.018(4)	-0.002(4)
C16	0.055(5)	0.064(5)	0.071(5)	-0.012(4)	0.004(4)	-0.010(4)
C17	0.047(5)	0.057(5)	0.063(4)	-0.002(4)	-0.008(4)	-0.011(4)
C18	0.063(5)	0.044(4)	0.060(4)	-0.006(3)	-0.003(4)	-0.005(4)
C19	0.101(8)	0.078(6)	0.078(6)	0.021(5)	0.038(6)	0.021(6)
C20	0.053(6)	0.129(10)	0.145(10)	0.059(9)	0.013(6)	0.014(6)

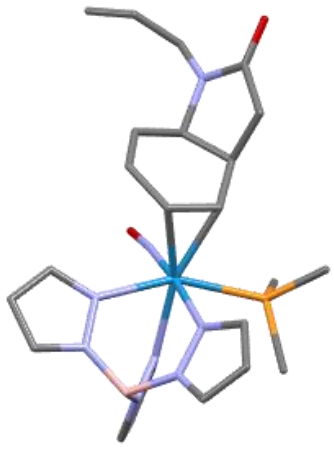
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	0.071(5)	0.045(4)	0.057(4)	0.000(3)	-0.010(4)	0.009(4)
C22	0.069(5)	0.055(4)	0.043(4)	0.010(3)	-0.013(3)	0.015(4)
C23	0.078(6)	0.053(4)	0.050(4)	0.022(3)	-0.003(4)	-0.003(4)
B1	0.052(5)	0.040(4)	0.048(4)	0.003(3)	0.014(4)	0.006(4)
O3	0.061(4)	0.130(7)	0.127(6)	-0.064(5)	-0.018(4)	0.006(4)
C24	0.083(8)	0.134(11)	0.134(10)	-0.034(9)	-0.017(7)	0.020(8)
C25	0.044(6)	0.113(9)	0.156(11)	-0.062(8)	-0.018(6)	0.010(6)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.11.

	x/a	y/b	z/c	U(eq)
H1	0.6170	0.2941	0.8745	0.069000
H2	0.4390	0.3294	0.9503	0.085000
H3	0.2746	0.3089	0.8483	0.069000
H4	0.5173	0.0346	0.5729	0.047000
H5	0.3087	-0.0018	0.5480	0.058000
H6	0.1966	0.1167	0.6114	0.062000
H7	0.5930	0.3741	0.5071	0.044000
H8	0.4085	0.4487	0.4649	0.050000
H9	0.2595	0.3911	0.5625	0.047000
H10	0.761(6)	0.266(4)	0.793(4)	0.051(19)
H11	0.685(4)	0.372(3)	0.708(3)	0.017(13)
H12	0.7621	0.3957	0.5688	0.052000
H13	0.8405	0.2704	0.5192	0.060000
H14	0.9991	0.2009	0.6106	0.073000
H15	0.9235	0.1767	0.7373	0.069000
H16A	1.0530	0.3187	0.5260	0.076000
H16B	0.9599	0.3798	0.4788	0.076000
H18A	0.9602	0.4991	0.7381	0.067000
H18B	0.8368	0.4590	0.7555	0.067000
H19	0.7959	0.5964	0.7267	0.102000

	x/a	y/b	z/c	U(eq)
H20A	0.8497	0.5675	0.5692	0.131000
H20B	0.7796	0.6479	0.6105	0.131000
H21A	0.7102	-0.0110	0.6534	0.087000
H21B	0.7704	-0.0329	0.7426	0.087000
H21C	0.8228	0.0400	0.6844	0.087000
H22A	0.8148	0.1246	0.8465	0.084000
H22B	0.7331	0.0545	0.8875	0.084000
H22C	0.6954	0.1528	0.8860	0.084000
H23A	0.4808	0.0687	0.8100	0.090000
H23B	0.5603	-0.0137	0.8245	0.090000
H23C	0.5004	0.0035	0.7342	0.090000
H1A	0.245(6)	0.273(4)	0.682(4)	0.042(17)
H24A	0.0288	0.1299	0.3391	0.176000
H24B	0.0533	0.2103	0.3991	0.176000
H24C	-0.0704	0.1653	0.3979	0.176000
H25A	-0.0204	-0.0042	0.4100	0.126000
H25B	-0.1021	0.0462	0.4733	0.126000

Structure Report for compound 4.11_2



A yellow, needle shaped crystal of compound 4.11_2 measuring 0.029×0.053×0.055 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_2_azetidinone_x3_ were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800 low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[40] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[41] and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/1[42] within OLEX2.[43] All non-hydrogen atoms were refined with anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[44]

Refinement details for compound 4.11_2

The structure was refined as a two-component twin on HKLF5 data, with the BASF for the twin domains refining to 0.358. The relative occupancy of the disordered atoms was freely refined. Constraints and restraints were used as needed on the anisotropic displacement parameters and/or bond lengths of the disordered atoms.

[40] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[41] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[42] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[43] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[44] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1. Crystal data and structure refinement for compound 4.11_2

CCDC number	
Empirical formula	$C_{23}H_{32}BN_8O_2PW$
Formula weight	678.19
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.029×0.053×0.055
Crystal habit	yellow needle
Crystal system	monoclinic
Space group	$P2_1/n$ (14)
a [Å]	9.5016(8)
b [Å]	9.0422(7)
c [Å]	30.722(3)
α [°]	90
β [°]	96.066(2)
γ [°]	90
Volume [$Å^3$]	2624.7(4)
Z	4
ρ_{calc} [gcm^{-3}]	1.716
μ [mm^{-1}]	4.499
F(000)	1344
2θ range [°]	4.38 to 50.74 (0.83 Å)
Index ranges	−11 ≤ h ≤ 11 0 ≤ k ≤ 10 0 ≤ l ≤ 37
Reflections collected	4807
Independent reflections	4807 [R_{int} = 0.1672]
Data / Restraints / Parameters	4807 / 5 / 349
Goodness-of-fit on F^2	1.083
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0477 wR_2 = 0.0858
Final *R* indexes [all data]	R_1 = 0.0711 wR_2 = 0.0934

Largest peak/hole [eÅ^{-3}]	1.58/−0.74

Table 2. Atomic coordinates and Ueq [Å^2] for compound 4.11_2

Atom	***x***	***y***	***z***	U_{eq}
W1	0.39659(3)	0.76680(3)	0.38657(2)	0.02473(12)
P1	0.4260(2)	0.9628(2)	0.33051(7)	0.0289(5)
O1	0.6971(5)	0.7755(6)	0.42728(17)	0.0376(13)
O2	0.7850(6)	0.3556(7)	0.25538(19)	0.0498(16)
N1	0.3074(6)	0.6639(7)	0.4435(2)	0.0291(14)
N2	0.1902(7)	0.7209(7)	0.4598(2)	0.0335(15)
N3	0.3655(6)	0.9615(6)	0.4282(2)	0.0296(15)
N4	0.2432(7)	0.9828(7)	0.4474(2)	0.0330(15)
N5	0.1682(6)	0.7920(6)	0.3642(2)	0.0284(14)
N6	0.0752(6)	0.8433(7)	0.3923(2)	0.0283(14)
N7	0.5750(6)	0.7657(7)	0.40864(19)	0.0300(14)
N8	0.7848(7)	0.4600(9)	0.3231(2)	0.0430(18)
C	0.3475(9)	0.5496(9)	0.4692(3)	0.0353(19)
H1	0.427619	0.489575	0.465722	0.042
C2	0.2588(10)	0.5289(9)	0.5015(3)	0.042(2)
H2	0.264280	0.454569	0.523453	0.050
C3	0.1614(10)	0.6399(9)	0.4946(3)	0.043(2)
H3	0.085217	0.657185	0.511671	0.051
C4	0.4570(9)	1.0618(8)	0.4450(2)	0.0356(19)
H4	0.551371	1.071861	0.437820	0.043
C5	0.3958(10)	1.1498(9)	0.4746(3)	0.039(2)
H5	0.437815	1.230611	0.490874	0.047
C6	0.2628(9)	1.0960(9)	0.4753(3)	0.038(2)
H6	0.194290	1.133121	0.492847	0.045
C7	0.0895(7)	0.7778(8)	0.3251(3)	0.0310(17)
H7	0.124634	0.743944	0.299055	0.037
C8	−0.0476(8)	0.8191(9)	0.3282(3)	0.0335(18)
H8	−0.123434	0.819787	0.305448	0.040
C9	−0.0530(8)	0.8593(8)	0.3714(3)	0.0322(18)
H9	−0.134582	0.892783	0.383872	0.039
C10	0.3862(7)	0.5350(7)	0.3631(2)	0.0263(16)
H10	0.287688	0.495903	0.356674	0.032
C11	0.4304(8)	0.6283(8)	0.3294(3)	0.0285(17)
Chapter 5 11	**Chapter 6** 0.355750	**Chapter 7** 0.642047	**Chapter 8** 0.304277	**Chapter 9** 0.034

Chapter 10	**Chapter 11**	**Chapter 12**	**Chapter 13**	**Chapter 14**
12	.5783(8)	.6015(8)	.3151(2)	.0255(16)
Chapter 15	**Chapter 16**	**Chapter 17**	**Chapter 18**	**Chapter 19**
12	.616771	.698698	.306345	.031
Chapter 20	**Chapter 21**	**Chapter 22**	**Chapter 23**	**Chapter 24**
13	.6863(8)	.5323(9)	.3505(3)	.0360(19)
Chapter 25	**Chapter 26**	**Chapter 27**	**Chapter 28**	**Chapter 29**
13	.736414	.611801	.368711	.043
Chapter 30	**Chapter 31**	**Chapter 32**	**Chapter 33**	**Chapter 34**
14	.6228(9)	.4249(9)	.3788(3)	.037(2)
Chapter 35	**Chapter 36**	**Chapter 37**	**Chapter 38**	**Chapter 39**
14	.681297	.351171	.393451	.044
Chapter 40	**Chapter 41**	**Chapter 42**	**Chapter 43**	**Chapter 44**
15	.4864(9)	.4282(8)	.3845(3)	.0349(19)
Chapter 45	**Chapter 46**	**Chapter 47**	**Chapter 48**	**Chapter 49**
15	.451849	.357205	.403498	.042
Chapter 50	**Chapter 51**	**Chapter 52**	**Chapter 53**	**Chapter 54**
16	.5810(8)	.4945(9)	.2766(2)	.0322(18)
Chapter 55	**Chapter 56**	**Chapter 57**	**Chapter 58**	**Chapter 59**
16A	.507989	.416799	.277657	.039
Chapter 60	**Chapter 61**	**Chapter 62**	**Chapter 63**	**Chapter 64**
16B	.564155	.547711	.248409	.039
Chapter 65	**Chapter 66**	**Chapter 67**	**Chapter 68**	**Chapter 69**
17	.7258(8)	.4292(9)	.2823(2)	.0331(18)
Chapter 70	**Chapter 71**	**Chapter 72**	**Chapter 73**	**Chapter 74**
24	.6018(8)	.0465(8)	.3338(3)	.0364(19)
Chapter 75	**Chapter 76**	**Chapter 77**	**Chapter 78**	**Chapter 79**
24A	.628093	.083072	.363625	.055
Chapter 80	**Chapter 81**	**Chapter 82**	**Chapter 83**	**Chapter 84**
24B	.600811	.129093	.313139	.055
Chapter 85	**Chapter 86**	**Chapter 87**	**Chapter 88**	**Chapter 89**
24C	.670809	.972420	.326547	.055
Chapter 90	**Chapter 91**	**Chapter 92**	**Chapter 93**	**Chapter 94**
25	.3917(9)	.9254(9)	.2722(3)	.0375(19)
Chapter 95	**Chapter 96**	**Chapter 97**	**Chapter 98**	**Chapter 99**
25A	.460348	.852838	.263706	.056
Chapter 100	**Chapter 101**	**Chapter 102**	**Chapter 103**	**Chapter 104**
25B	.400586	.017211	.255825	.056

Chapter 10 25C	**Chapter 106** .295730	**Chapter 107** .885879	**Chapter 108** .265791	**Chapter 109** .056
Chapter 11 26	**Chapter 111** .3070(9)	**Chapter 112** .1212(9)	**Chapter 113** .3343(3)	**Chapter 114** .038(2)
Chapter 11 26A	**Chapter 116** .208590	**Chapter 117** .088662	**Chapter 118** .327902	**Chapter 119** .057
Chapter 12 26B	**Chapter 121** .327971	**Chapter 122** .197033	**Chapter 123** .313147	**Chapter 124** .057
Chapter 12 26C	**Chapter 126** .320842	**Chapter 127** .162532	**Chapter 128** .363958	**Chapter 129** .057
Chapter 13 1	**Chapter 131** .1233(11)	**Chapter 132** .8656(10)	**Chapter 133** .4413(3)	**Chapter 134** .036(2)
Chapter 13 1A	**Chapter 136** .031(9)	**Chapter 137** .904(9)	**Chapter 138** .461(3)	**Chapter 139** .05(3)
Chapter 14 21	**Chapter 141** .9332(10)	**Chapter 142** .4302(12)	**Chapter 143** .3399(4)	**Chapter 144** .032(3)
Chapter 14 21A	**Chapter 146** .992356	**Chapter 147** .428051	**Chapter 148** .315285	**Chapter 149** .038
Chapter 15 21B	**Chapter 151** .968458	**Chapter 152** .510672	**Chapter 153** .360063	**Chapter 154** .038
Chapter 15 22	**Chapter 156** .9452(12)	**Chapter 157** .2894(12)	**Chapter 158** .3630(4)	**Chapter 159** .043(3)
Chapter 16 22	**Chapter 161** .899546	**Chapter 162** .206272	**Chapter 163** .348927	**Chapter 164** .051
Chapter 16 23	**Chapter 166** .0136(14)	**Chapter 167** .2687(17)	**Chapter 168** .4014(4)	**Chapter 169** .048(3)
Chapter 17 23A	**Chapter 171** .060681	**Chapter 172** .349109	**Chapter 173** .416614	**Chapter 174** .058
Chapter 17 23B	**Chapter 176** .016460	**Chapter 177** .173123	**Chapter 178** .414326	**Chapter 179** .058
Chapter 18 18	**Chapter 181** .896(2)	**Chapter 182** .345(3)	**Chapter 183** .3389(8)	**Chapter 184** .032(3)
Chapter 18 18A	**Chapter 186** .850087	**Chapter 187** .256759	**Chapter 188** .350376	**Chapter 189** .038
Chapter 19 18B	**Chapter 191** .948953	**Chapter 192** .313027	**Chapter 193** .314401	**Chapter 194** .038
Chapter 19 19	**Chapter 196** .992(2)	**Chapter 197** .413(3)	**Chapter 198** .3733(8)	**Chapter 199** .037(8)

Chapter 2(19	**Chapter 201** .020180	**Chapter 202** .510979	**Chapter 203** .367511	**Chapter 204** .044
Chapter 2(20	**Chapter 206** .044(4)	**Chapter 207** .359(4)	**Chapter 208** .4105(9)	**Chapter 209** .048(3)
Chapter 2' 20A	**Chapter 211** .019704	**Chapter 212** .261617	**Chapter 213** .418580	**Chapter 214** .058
Chapter 2' 20B	**Chapter 216** .105405	**Chapter 217** .417351	**Chapter 218** .429922	**Chapter 219** .058

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters (Å^2) for compound 4.11_2

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02450(18)	0.02845(18)	0.02195(16)	0.00382(14)	0.00582(11)	0.00099(13)
P1	0.0278(11)	0.0314(10)	0.0282(12)	0.0071(8)	0.0064(9)	0.0004(8)
O1	0.027(3)	0.057(3)	0.029(3)	0.000(3)	0.002(2)	0.001(3)
O2	0.041(4)	0.082(4)	0.027(3)	−0.003(3)	0.007(3)	0.022(3)
N1	0.030(4)	0.033(3)	0.025(4)	0.004(3)	0.009(3)	0.007(3)
N2	0.038(4)	0.040(4)	0.024(3)	0.010(3)	0.012(3)	0.006(3)
N3	0.031(4)	0.030(3)	0.028(4)	0.007(3)	0.001(3)	0.002(3)
N4	0.046(4)	0.033(3)	0.020(4)	−0.001(3)	0.002(3)	0.010(3)
N5	0.031(3)	0.026(3)	0.031(4)	0.003(3)	0.014(3)	−0.002(3)
N6	0.021(3)	0.037(3)	0.030(4)	0.006(3)	0.012(3)	0.004(2)
N7	0.031(3)	0.035(3)	0.024(3)	0.008(3)	0.005(3)	0.007(3)
N8	0.030(4)	0.075(5)	0.024(4)	0.004(4)	0.006(3)	0.011(3)
C1	0.042(5)	0.038(4)	0.026(5)	0.003(4)	0.006(4)	0.005(4)
C2	0.061(6)	0.035(4)	0.032(5)	0.010(4)	0.017(4)	0.002(4)
C3	0.059(6)	0.050(5)	0.022(5)	0.010(4)	0.021(4)	0.008(4)
C4	0.053(5)	0.032(4)	0.020(4)	0.009(3)	0.000(4)	0.001(4)
C5	0.059(6)	0.030(4)	0.027(5)	−0.001(3)	−0.003(4)	0.002(4)
C6	0.049(6)	0.038(4)	0.024(5)	0.005(4)	−0.002(4)	0.010(4)
C7	0.025(4)	0.029(4)	0.040(5)	0.002(4)	0.005(3)	−0.006(3)
C8	0.021(4)	0.047(5)	0.032(5)	0.007(4)	−0.002(3)	−0.004(3)
C9	0.022(4)	0.039(4)	0.037(5)	0.003(4)	0.010(4)	0.003(3)
C10	0.022(4)	0.025(4)	0.034(5)	0.001(3)	0.007(3)	0.001(3)
C11	0.023(4)	0.037(4)	0.027(5)	0.002(3)	0.008(3)	0.003(3)
C12	0.028(4)	0.035(4)	0.013(4)	0.007(3)	0.001(3)	−0.003(3)
C13	0.028(4)	0.056(5)	0.025(5)	0.002(4)	0.008(4)	0.011(4)

C14	0.037(5)	0.045(5)	0.029(5)	0.005(4)	0.011(4)	0.016(4)
C15	0.047(5)	0.037(4)	0.023(4)	0.005(3)	0.013(4)	0.005(4)
C16	0.025(4)	0.049(5)	0.023(4)	0.002(4)	0.006(3)	0.006(3)
C17	0.030(4)	0.051(5)	0.020(4)	0.008(4)	0.008(4)	0.009(4)
C24	0.030(5)	0.036(4)	0.045(5)	0.008(4)	0.012(4)	−0.001(3)
C25	0.041(5)	0.044(5)	0.029(5)	0.008(4)	0.009(4)	0.003(4)
C26	0.031(5)	0.044(5)	0.040(5)	0.004(4)	0.004(4)	0.004(4)
B1	0.042(6)	0.040(5)	0.027(5)	0.011(4)	0.014(5)	0.004(4)
C21	0.018(6)	0.047(7)	0.029(6)	−0.008(6)	0.001(5)	0.001(5)
C22	0.031(6)	0.035(6)	0.063(9)	0.009(6)	0.007(6)	0.016(5)
C23	0.043(7)	0.062(9)	0.039(7)	0.009(7)	0.002(5)	0.025(7)
C18	0.018(6)	0.047(7)	0.029(6)	−0.008(6)	0.001(5)	0.001(5)
C19	0.025(16)	0.042(17)	0.05(2)	−0.032(15)	0.026(15)	−0.016(12)
C20	0.043(7)	0.062(9)	0.039(7)	0.009(7)	0.002(5)	0.025(7)

Table 4. Bond lengths and angles for compound 4.11_2

Atom–Atom	Length [Å]
W1–N7	1.758(6)
W1–C11	2.207(7)
W1–N3	2.214(6)
W1–C10	2.216(7)
W1–N5	2.218(6)
W1–N1	2.227(6)
W1–P1	2.5071(19)
P1–C25	1.817(8)
P1–C24	1.827(8)
P1–C26	1.837(8)
O1–N7	1.242(7)
O2–C17	1.242(9)
N1–C1	1.331(10)
N1–N2	1.369(8)
N2–C3	1.347(9)
N2–B1	1.538(11)
N3–C4	1.324(10)
N3–N4	1.373(9)
N4–C6	1.334(10)
N4–B1	1.552(12)
N5–C7	1.350(9)

N5–N6	1.381(8)
N6–C9	1.325(10)
N6–B1	1.539(12)
N8–C17	1.347(10)
N8–C21	1.474(11)
N8–C13	1.478(10)
N8–C18	1.527(18)
C1–C2	1.381(11)
C1–H1	0.9500
C2–C3	1.367(12)
C2–H2	0.9500
C3–H3	0.9500
C4–C5	1.380(11)
C4–H4	0.9500
C5–C6	1.357(12)
C5–H5	0.9500
C6–H6	0.9500
C7–C8	1.369(10)
C7–H7	0.9500
C8–C9	1.381(11)
C8–H8	0.9500
C9–H9	0.9500
C10–C11	1.430(10)
C10–C15	1.463(10)
C10–H10	1.0000
C11–C12	1.536(10)
C11–H11	1.0000
C12–C16	1.530(10)
C12–C13	1.546(10)
C12–H12	1.0000
C13–C14	1.475(11)
C13–H13	1.0000
C14–C15	1.325(11)
C14–H14	0.9500
C15–H15	0.9500
C16–C17	1.491(10)
C16–H16A	0.9900
C16–H16B	0.9900
C24–H24A	0.9800
C24–H24B	0.9800

C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
B1–H1A	1.17(9)
C21–C22	1.456(14)
C21–H21A	0.9900
C21–H21B	0.9900
C22–C23	1.298(15)
C22–H22	0.9500
C23–H23A	0.9500
C23–H23B	0.9500
C18–C19	1.457(19)
C18–H18A	0.9900
C18–H18B	0.9900
C19–C20	1.29(2)
C19–H19	0.9500
C20–H20A	0.9500
C20–H20B	0.9500

Atom–Atom–Atom	**Angle [°]**
N7–W1–C11	95.1(3)
N7–W1–N3	87.9(3)
C11–W1–N3	161.8(2)
N7–W1–C10	97.4(3)
C11–W1–C10	37.7(3)
N3–W1–C10	159.5(2)
N7–W1–N5	172.9(3)
C11–W1–N5	91.8(3)
N3–W1–N5	84.9(2)
C10–W1–N5	89.3(2)
N7–W1–N1	97.2(2)
C11–W1–N1	119.1(2)
N3–W1–N1	78.1(2)
C10–W1–N1	81.5(2)
N5–W1–N1	81.1(2)

N7–W1–P1	95.52(19)
C11–W1–P1	79.56(19)
N3–W1–P1	82.30(16)
C10–W1–P1	116.68(19)
N5–W1–P1	83.72(15)
N1–W1–P1	156.12(16)
C25–P1–C24	101.5(4)
C25–P1–C26	99.2(4)
C24–P1–C26	103.8(4)
C25–P1–W1	121.6(3)
C24–P1–W1	115.0(3)
C26–P1–W1	113.2(3)
C1–N1–N2	105.6(6)
C1–N1–W1	132.9(5)
N2–N1–W1	121.5(4)
C3–N2–N1	109.1(6)
C3–N2–B1	130.2(7)
N1–N2–B1	120.4(6)
C4–N3–N4	106.7(6)
C4–N3–W1	130.4(5)
N4–N3–W1	122.1(5)
C6–N4–N3	108.5(7)
C6–N4–B1	130.7(7)
N3–N4–B1	119.7(6)
C7–N5–N6	105.0(6)
C7–N5–W1	134.2(5)
N6–N5–W1	120.6(5)
C9–N6–N5	110.4(6)
C9–N6–B1	128.6(6)
N5–N6–B1	120.9(6)
O1–N7–W1	173.5(5)
C17–N8–C21	125.3(7)
C17–N8–C13	113.3(6)
C21–N8–C13	121.3(7)
C17–N8–C18	111.2(10)
C13–N8–C18	125.4(12)
N1–C1–C2	111.9(7)
N1–C1–H1	124.1
C2–C1–H1	124.1
C3–C2–C1	104.1(7)

C3–C2–H2	127.9
C1–C2–H2	127.9
N2–C3–C2	109.3(7)
N2–C3–H3	125.4
C2–C3–H3	125.4
N3–C4–C5	110.3(8)
N3–C4–H4	124.9
C5–C4–H4	124.9
C6–C5–C4	105.2(8)
C6–C5–H5	127.4
C4–C5–H5	127.4
N4–C6–C5	109.4(8)
N4–C6–H6	125.3
C5–C6–H6	125.3
N5–C7–C8	110.7(7)
N5–C7–H7	124.7
C8–C7–H7	124.7
C7–C8–C9	105.7(7)
C7–C8–H8	127.1
C9–C8–H8	127.1
N6–C9–C8	108.2(7)
N6–C9–H9	125.9
C8–C9–H9	125.9
C11–C10–C15	119.1(6)
C11–C10–W1	70.8(4)
C15–C10–W1	118.2(5)
C11–C10–H10	114.0
C15–C10–H10	114.0
W1–C10–H10	114.0
C10–C11–C12	117.5(6)
C10–C11–W1	71.5(4)
C12–C11–W1	122.1(5)
C10–C11–H11	113.2
C12–C11–H11	113.2
W1–C11–H11	113.2
C16–C12–C11	114.3(6)
C16–C12–C13	102.9(6)
C11–C12–C13	115.0(6)
C16–C12–H12	108.1
C11–C12–H12	108.1

C13–C12–H12	108.1
C14–C13–N8	111.6(7)
C14–C13–C12	113.5(7)
N8–C13–C12	101.0(6)
C14–C13–H13	110.1
N8–C13–H13	110.1
C12–C13–H13	110.1
C15–C14–C13	121.9(7)
C15–C14–H14	119.0
C13–C14–H14	119.0
C14–C15–C10	123.7(7)
C14–C15–H15	118.1
C10–C15–H15	118.1
C17–C16–C12	104.6(6)
C17–C16–H16A	110.8
C12–C16–H16A	110.8
C17–C16–H16B	110.8
C12–C16–H16B	110.8
H16A–C16–H16B	108.9
O2–C17–N8	123.8(7)
O2–C17–C16	127.8(7)
N8–C17–C16	108.3(6)
P1–C24–H24A	109.5
P1–C24–H24B	109.5
H24A–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
H25A–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
H26A–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5

N2–B1–N6	108.6(7)
N2–B1–N4	105.5(7)
N6–B1–N4	110.3(6)
N2–B1–H1A	111(4)
N6–B1–H1A	112(4)
N4–B1–H1A	109(4)
C22–C21–N8	110.7(9)
C22–C21–H21A	109.5
N8–C21–H21A	109.5
C22–C21–H21B	109.5
N8–C21–H21B	109.5
H21A–C21–H21B	108.1
C23–C22–C21	125.1(12)
C23–C22–H22	117.4
C21–C22–H22	117.4
C22–C23–H23A	120.0
C22–C23–H23B	120.0
H23A–C23–H23B	120.0
C19–C18–N8	107.5(17)
C19–C18–H18A	110.2
N8–C18–H18A	110.2
C19–C18–H18B	110.2
N8–C18–H18B	110.2
H18A–C18–H18B	108.5
C20–C19–C18	129(3)
C20–C19–H19	115.3
C18–C19–H19	115.3
C19–C20–H20A	120.0
C19–C20–H20B	120.0
H20A–C20–H20B	120.0

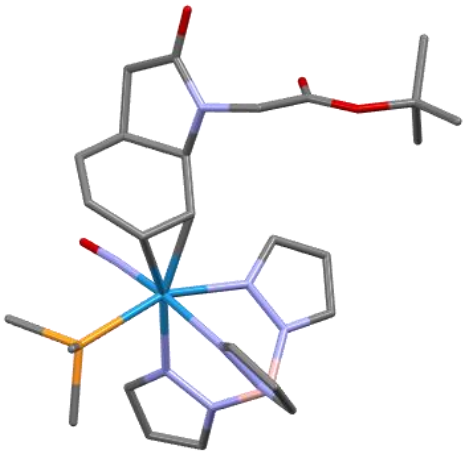
Table 5. Torsion angles for compound 4.11_2

Atom–Atom–Atom–Atom	Torsion Angle [°]
C1–N1–N2–C3	−0.5(9)
W1–N1–N2–C3	−178.6(5)
C1–N1–N2–B1	173.4(7)
W1–N1–N2–B1	−4.7(9)
C4–N3–N4–C6	0.4(8)

W1–N3–N4–C6	171.1(5)
C4–N3–N4–B1	−168.9(7)
W1–N3–N4–B1	1.8(9)
C7–N5–N6–C9	0.0(7)
W1–N5–N6–C9	175.6(5)
C7–N5–N6–B1	176.6(6)
W1–N5–N6–B1	−7.8(8)
N2–N1–C1–C2	0.9(9)
W1–N1–C1–C2	178.6(6)
N1–C1–C2–C3	−0.9(10)
N1–N2–C3–C2	−0.1(10)
B1–N2–C3–C2	−173.2(8)
C1–C2–C3–N2	0.6(10)
N4–N3–C4–C5	−0.9(8)
W1–N3–C4–C5	−170.4(5)
N3–C4–C5–C6	0.9(9)
N3–N4–C6–C5	0.2(9)
B1–N4–C6–C5	167.9(8)
C4–C5–C6–N4	−0.7(9)
N6–N5–C7–C8	0.2(8)
W1–N5–C7–C8	−174.5(5)
N5–C7–C8–C9	−0.4(8)
N5–N6–C9–C8	−0.3(8)
B1–N6–C9–C8	−176.5(7)
C7–C8–C9–N6	0.4(8)
C15–C10–C11–C12	5.0(10)
W1–C10–C11–C12	117.2(7)
C15–C10–C11–W1	−112.3(7)
C10–C11–C12–C16	91.8(8)
W1–C11–C12–C16	176.3(5)
C10–C11–C12–C13	−26.9(10)
W1–C11–C12–C13	57.5(8)
C17–N8–C13–C14	97.4(8)
C21–N8–C13–C14	−83.9(10)
C18–N8–C13–C14	−44.7(15)
C17–N8–C13–C12	−23.5(9)
C21–N8–C13–C12	155.1(8)
C18–N8–C13–C12	−165.6(13)
C16–C12–C13–C14	−89.5(7)
C11–C12–C13–C14	35.5(9)

C16–C12–C13–N8	30.2(7)
C11–C12–C13–N8	155.1(6)
N8–C13–C14–C15	−137.0(8)
C12–C13–C14–C15	−23.6(11)
C13–C14–C15–C10	1.1(13)
C11–C10–C15–C14	9.2(12)
W1–C10–C15–C14	−73.4(9)
C11–C12–C16–C17	−153.2(6)
C13–C12–C16–C17	−27.8(7)
C21–N8–C17–O2	8.9(14)
C13–N8–C17–O2	−172.5(8)
C18–N8–C17–O2	−25.0(16)
C21–N8–C17–C16	−172.4(8)
C13–N8–C17–C16	6.1(10)
C18–N8–C17–C16	153.7(13)
C12–C16–C17–O2	−167.0(8)
C12–C16–C17–N8	14.4(8)
C3–N2–B1–N6	−126.8(9)
N1–N2–B1–N6	60.7(9)
C3–N2–B1–N4	115.0(9)
N1–N2–B1–N4	−57.4(9)
C9–N6–B1–N2	122.4(8)
N5–N6–B1–N2	−53.4(9)
C9–N6–B1–N4	−122.5(8)
N5–N6–B1–N4	61.7(8)
C6–N4–B1–N2	−107.3(8)
N3–N4–B1–N2	59.3(8)
C6–N4–B1–N6	135.6(8)
N3–N4–B1–N6	−57.8(9)
C17–N8–C21–C22	−95.4(11)
C13–N8–C21–C22	86.2(11)
N8–C21–C22–C23	−131.8(12)
C17–N8–C18–C19	157.4(17)
C13–N8–C18–C19	−60(3)
N8–C18–C19–C20	136(3)

Structure Report for compound 4.14



A colourless, plate shaped crystal of compound 4.14 measuring 0.037×0.04×0.063 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for cu_harman_ld_2_135_trial2_x3_0 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Cu K_α, λ=1.54178 Å) using a HELIOS MX double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[45] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[46] and refined by full-matrix least-squares methods against F^2 using XL[47] within OLEX2.[48] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atom was located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[49]

[45] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
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[47] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[48] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[49] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for compound 4.14

CCDC number	
Empirical formula	$C_{26}H_{38}BN_8O_4PW$
Formula weight	752.27
Temperature [K]	100.00
Wavelength [Å]	1.54178
Crystal size [mm^3]	0.037×0.04×0.063
Crystal habit	colourless plate
Crystal system	orthorhombic
Space group	$Pbca$ (61)
a [Å]	20.0579(6)
b [Å]	13.1448(4)
c [Å]	22.9346(7)
α [°]	90
β [°]	90
γ [°]	90
Volume [$Å^3$]	6046.9(3)
Z	8
ρ_{calc} [gcm^{-3}]	1.653
μ [mm^{-1}]	7.962
F(000)	3008
2θ range [°]	7.71 to 136.83 (0.83 Å)
Index ranges	−21 ≤ h ≤ 24 −15 ≤ k ≤ 15 −27 ≤ l ≤ 22
Reflections collected	36472
Independent reflections	5512 [R_{int} = 0.0906]
Data / Restraints / Parameters	5512 / 0 / 380
Goodness-of-fit on F^2	1.038
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0364 wR_2 = 0.0713
Final *R* indexes [all data]	R_1 = 0.0586 wR_2 = 0.0788

Largest peak/hole [eÅ^{-3}]	1.11/−1.23

Table 2 Atomic coordinates and Ueq [Å^2] for compound 4.14

Atom	***x***	***y***	***z***	U_{eq}
W1	0.45607(2)	0.78161(2)	0.64867(2)	0.01745(8)
P1	0.33527(6)	0.82057(11)	0.63509(7)	0.0278(3)
O1	0.4915(2)	0.9861(3)	0.60063(18)	0.0320(9)
O2	0.6230(2)	0.6471(3)	0.40362(19)	0.0412(11)
O3	0.6996(2)	0.6178(4)	0.5413(2)	0.0507(13)
O4	0.6722(2)	0.4550(3)	0.56334(19)	0.0399(11)
N1	0.5507(2)	0.7471(3)	0.6964(2)	0.0192(9)
N2	0.55015(19)	0.7188(3)	0.75358(18)	0.0177(8)
N3	0.44211(19)	0.8591(3)	0.7328(2)	0.0214(10)
N4	0.4519(2)	0.8152(3)	0.7862(2)	0.0217(9)
N5	0.4252(2)	0.6411(3)	0.6974(2)	0.0201(9)
N6	0.43947(19)	0.6319(3)	0.75595(19)	0.0188(9)
N7	0.4778(2)	0.9002(3)	0.6180(2)	0.0208(9)
N8	0.5738(2)	0.6495(3)	0.4941(2)	0.0298(11)
C1	0.6149(2)	0.7495(4)	0.6809(3)	0.0229(12)
H1	0.630605	0.767034	0.643187	0.027
C2	0.6557(2)	0.7227(4)	0.7278(3)	0.0254(12)
H2	0.702933	0.718023	0.728336	0.030
C3	0.6128(2)	0.7049(4)	0.7727(2)	0.0212(11)
H3	0.625118	0.685708	0.811121	0.025
C4	0.4301(2)	0.9575(4)	0.7434(3)	0.0255(13)
H4	0.421729	1.007182	0.714279	0.031
C5	0.4316(3)	0.9771(4)	0.8031(3)	0.0296(14)
H5	0.424138	1.040183	0.822174	0.036
C6	0.4461(2)	0.8853(4)	0.8280(3)	0.0259(12)
H6	0.451284	0.873318	0.868586	0.031
C7	0.3949(2)	0.5520(4)	0.6827(3)	0.0239(12)
H7	0.379422	0.535493	0.644727	0.029
C8	0.3896(3)	0.4893(4)	0.7304(3)	0.0283(13)
H8	0.369783	0.423689	0.731544	0.034
C9	0.4187(2)	0.5399(4)	0.7757(3)	0.0260(13)
H9	0.423468	0.514980	0.814365	0.031
C10	0.2790(3)	0.7252(5)	0.6069(4)	0.0516(19)
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H10B	0.233955	0.753628	0.604342	0.077
H10C	0.278818	0.666213	0.632967	0.077
C11	0.3193(3)	0.9298(5)	0.5892(3)	0.0432(17)
H11A	0.341312	0.989791	0.605842	0.065
H11B	0.271200	0.941901	0.586982	0.065
H11C	0.336893	0.917001	0.550043	0.065
C12	0.2902(3)	0.8552(6)	0.7013(3)	0.0522(19)
H12A	0.295635	0.801439	0.730495	0.078
H12B	0.242769	0.863632	0.692275	0.078
H12C	0.308022	0.919267	0.716675	0.078
C13	0.5021(3)	0.6872(4)	0.5805(2)	0.0224(12)
H13	0.511413	0.616569	0.594507	0.027
C14	0.4330(3)	0.7006(4)	0.5648(2)	0.0261(12)
H14	0.405177	0.638110	0.569729	0.031
C15	0.4181(3)	0.7591(4)	0.5115(3)	0.0326(14)
H15	0.373558	0.759219	0.497536	0.039
C16	0.4635(3)	0.8115(4)	0.4819(3)	0.0284(13)
H16	0.450111	0.846984	0.447802	0.034
C17	0.5354(3)	0.8167(4)	0.5005(2)	0.0243(12)
H17	0.544508	0.881991	0.521357	0.029
C18	0.5549(3)	0.7245(4)	0.5392(2)	0.0240(11)
H18	0.595540	0.742725	0.562238	0.029
C19	0.5825(3)	0.8049(4)	0.4477(3)	0.0299(13)
H19A	0.560796	0.829114	0.411494	0.036
H19B	0.624260	0.843607	0.453754	0.036
C20	0.5962(3)	0.6926(4)	0.4446(3)	0.0305(14)
C21	0.5944(3)	0.5480(4)	0.5105(3)	0.0356(15)
H21A	0.596425	0.504675	0.475235	0.043
H21B	0.560830	0.518362	0.537216	0.043
C22	0.6622(3)	0.5476(5)	0.5403(3)	0.0367(15)
C23	0.7353(3)	0.4297(6)	0.5953(3)	0.0475(18)
C24	0.7938(4)	0.4366(7)	0.5526(4)	0.071(3)
H24A	0.784072	0.395489	0.517969	0.107
H24B	0.834319	0.410960	0.571441	0.107
H24C	0.800477	0.507623	0.541049	0.107
C25	0.7439(3)	0.4997(6)	0.6463(3)	0.055(2)
H25A	0.752081	0.569015	0.632290	0.082
H25B	0.781811	0.477048	0.669901	0.082
H25C	0.703317	0.498867	0.670156	0.082

C26	0.7223(4)	0.3220(6)	0.6136(4)	0.062(2)
H26A	0.682243	0.319552	0.638007	0.093
H26B	0.760552	0.296530	0.635897	0.093
H26	0.715762	0.279579	0.578975	0.093
B1	0.4832(3)	0.7099(4)	0.7875(3)	0.0223(13)
H1A	0.493(3)	0.680(4)	0.832(3)	0.030(15)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 4.14. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02093(11)	0.01280(10)	0.01863(14)	0.00132(10)	−0.00115(11)	−0.00180(9)
P1	0.0229(6)	0.0280(6)	0.0326(10)	0.0074(6)	−0.0031(6)	−0.0018(5)
O1	0.051(2)	0.0177(17)	0.027(2)	0.0055(16)	0.0022(19)	−0.0042(17)
O2	0.045(2)	0.052(3)	0.026(3)	−0.014(2)	0.003(2)	0.010(2)
O3	0.039(2)	0.049(3)	0.064(4)	0.001(2)	−0.006(2)	0.007(2)
O4	0.045(2)	0.043(2)	0.032(3)	0.002(2)	−0.007(2)	0.019(2)
N1	0.0230(19)	0.0161(18)	0.019(3)	−0.0019(16)	−0.0020(19)	−0.0040(16)
N2	0.0209(19)	0.0149(17)	0.017(2)	0.0022(18)	0.0021(18)	0.0020(17)
N3	0.025(2)	0.0174(19)	0.022(3)	0.0024(19)	0.0026(18)	0.0026(17)
N4	0.021(2)	0.021(2)	0.023(3)	−0.0019(18)	0.002(2)	−0.0015(17)
N5	0.023(2)	0.019(2)	0.019(3)	−0.0009(18)	0.0002(19)	−0.0001(17)
N6	0.022(2)	0.021(2)	0.014(3)	0.0034(18)	0.0032(17)	0.0001(16)
N7	0.027(2)	0.021(2)	0.015(3)	−0.0009(19)	0.0013(18)	−0.0050(17)
N8	0.037(2)	0.028(2)	0.024(3)	−0.008(2)	−0.003(2)	0.013(2)
C1	0.023(2)	0.029(3)	0.017(3)	−0.003(2)	0.003(2)	−0.006(2)
C2	0.018(2)	0.029(3)	0.029(3)	−0.006(3)	−0.002(2)	−0.001(2)
C3	0.027(2)	0.018(2)	0.019(3)	0.001(2)	−0.005(2)	0.002(2)
C4	0.023(2)	0.014(2)	0.039(4)	0.002(2)	0.001(2)	0.001(2)
C5	0.033(3)	0.022(3)	0.034(4)	−0.010(2)	0.009(3)	0.001(2)
C6	0.028(3)	0.027(3)	0.023(3)	−0.009(2)	0.008(2)	−0.002(2)
C7	0.023(2)	0.020(2)	0.029(4)	−0.001(2)	−0.003(2)	−0.011(2)
C8	0.026(3)	0.021(2)	0.038(4)	0.009(2)	−0.003(3)	−0.007(2)

C9	0.022(3)	0.022(3)	0.033(4)	0.009(2)	0.010(2)	−0.003(2)
C10	0.032(3)	0.049(4)	0.074(6)	−0.003(4)	−0.016(3)	−0.009(3)
C11	0.037(3)	0.042(3)	0.051(5)	0.014(3)	−0.005(3)	0.009(3)
C12	0.026(3)	0.086(6)	0.044(5)	−0.003(4)	0.008(3)	−0.004(3)
C13	0.033(3)	0.015(2)	0.019(3)	0.000(2)	−0.005(2)	0.005(2)
C14	0.039(3)	0.027(3)	0.012(3)	−0.005(2)	−0.003(2)	−0.009(2)
C15	0.035(3)	0.039(3)	0.024(4)	−0.009(3)	−0.012(3)	0.000(3)
C16	0.038(3)	0.028(3)	0.019(3)	0.002(2)	−0.004(3)	0.004(2)
C17	0.032(3)	0.023(2)	0.018(3)	−0.004(2)	0.000(2)	−0.001(2)
C18	0.030(3)	0.025(2)	0.017(3)	−0.001(2)	0.001(2)	0.002(2)
C19	0.035(3)	0.034(3)	0.021(3)	0.004(3)	−0.003(3)	0.000(2)
C20	0.032(3)	0.042(3)	0.018(3)	−0.008(3)	−0.008(3)	0.006(2)
C21	0.050(4)	0.027(3)	0.031(4)	−0.012(3)	−0.009(3)	0.016(3)
C22	0.044(4)	0.038(3)	0.028(4)	−0.006(3)	−0.002(3)	0.018(3)
C23	0.038(4)	0.068(5)	0.036(4)	0.010(4)	0.000(3)	0.023(3)
C24	0.054(4)	0.110(7)	0.049(6)	0.035(5)	0.024(4)	0.043(5)
C25	0.031(3)	0.094(6)	0.039(5)	0.005(4)	−0.004(3)	0.003(3)
C26	0.050(4)	0.074(5)	0.062(6)	0.022(4)	−0.006(4)	0.026(4)
B1	0.027(3)	0.019(3)	0.021(4)	0.000(3)	0.007(3)	−0.002(2)

Table 4 Bond lengths and angles for compound 4.14

Atom–Atom	Length [Å]
W1–P1	2.4962(13)
W1–N1	2.237(4)
W1–N3	2.200(4)
W1–N5	2.246(4)
W1–N7	1.766(4)
W1–C13	2.200(5)
W1–C14	2.246(5)
P1–C10	1.806(6)
P1–C11	1.808(6)
P1–C12	1.825(7)
O1–N7	1.228(5)
O2–C20	1.238(7)
O3–C22	1.190(8)
O4–C22	1.344(7)
O4–C23	1.499(7)
N1–N2	1.363(6)
N1–C1	1.335(6)

N2–C3	1.343(6)
N2–B1	1.557(7)
N3–N4	1.369(6)
N3–C4	1.338(6)
N4–C6	1.334(7)
N4–B1	1.520(7)
N5–N6	1.378(6)
N5–C7	1.363(6)
N6–C9	1.358(6)
N6–B1	1.531(7)
N8–C18	1.479(7)
N8–C20	1.344(8)
N8–C21	1.448(7)
C1–H1	0.9500
C1–C2	1.397(8)
C2–H2	0.9500
C2–C3	1.361(8)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.392(9)
C5–H5	0.9500
C5–C6	1.367(8)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.373(8)
C8–H8	0.9500
C8–C9	1.364(8)
C9–H9	0.9500
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800
C13–H13	1.0000
C13–C14	1.442(7)
C13–C18	1.503(7)

C14–H14	1.0000
C14–C15	1.475(8)
C15–H15	0.9500
C15–C16	1.328(8)
C16–H16	0.9500
C16–C17	1.505(7)
C17–H17	1.0000
C17–C18	1.553(7)
C17–C19	1.543(8)
C18–H18	1.0000
C19–H19A	0.9900
C19–H19B	0.9900
C19–C20	1.503(8)
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.521(8)
C23–C24	1.531(9)
C23–C25	1.498(11)
C23–C26	1.500(11)
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
B1–H1A	1.11(6)

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	157.83(12)
N1–W1–N5	79.85(15)
N1–W1–C14	119.83(18)
N3–W1–P1	83.73(11)
N3–W1–N1	76.86(15)
N3–W1–N5	84.78(15)
N3–W1–C14	160.78(18)
N5–W1–P1	87.88(11)

N7–W1–P1	90.49(14)
N7–W1–N1	99.49(17)
N7–W1–N3	88.42(18)
N7–W1–N5	173.14(18)
N7–W1–C13	96.38(19)
N7–W1–C14	97.3(2)
C13–W1–P1	115.75(14)
C13–W1–N1	82.97(18)
C13–W1–N3	159.78(17)
C13–W1–N5	90.33(17)
C13–W1–C14	37.83(19)
C14–W1–P1	77.92(15)
C14–W1–N5	88.84(18)
C10–P1–W1	120.6(2)
C10–P1–C11	103.4(3)
C10–P1–C12	99.3(3)
C11–P1–W1	114.0(2)
C11–P1–C12	101.4(4)
C12–P1–W1	115.4(2)
C22–O4–C23	121.3(5)
N2–N1–W1	121.3(3)
C1–N1–W1	133.1(4)
C1–N1–N2	105.6(4)
N1–N2–B1	120.6(4)
C3–N2–N1	110.1(4)
C3–N2–B1	129.3(5)
N4–N3–W1	124.9(3)
C4–N3–W1	129.1(4)
C4–N3–N4	105.7(4)
N3–N4–B1	117.5(4)
C6–N4–N3	109.8(4)
C6–N4–B1	130.6(5)
N6–N5–W1	120.0(3)
C7–N5–W1	135.0(4)
C7–N5–N6	105.0(4)
N5–N6–B1	121.4(4)
C9–N6–N5	109.8(4)
C9–N6–B1	127.9(5)
O1–N7–W1	175.0(4)
C20–N8–C18	113.3(5)

C20–N8–C21	120.8(5)
C21–N8–C18	120.4(5)
N1–C1–H1	124.6
N1–C1–C2	110.8(5)
C2–C1–H1	124.6
C1–C2–H2	127.6
C3–C2–C1	104.8(4)
C3–C2–H2	127.6
N2–C3–C2	108.8(5)
N2–C3–H3	125.6
C2–C3–H3	125.6
N3–C4–H4	124.6
N3–C4–C5	110.7(5)
C5–C4–H4	124.6
C4–C5–H5	127.7
C6–C5–C4	104.6(5)
C6–C5–H5	127.7
N4–C6–C5	109.2(5)
N4–C6–H6	125.4
C5–C6–H6	125.4
N5–C7–H7	124.6
N5–C7–C8	110.7(5)
C8–C7–H7	124.6
C7–C8–H8	126.8
C9–C8–C7	106.3(5)
C9–C8–H8	126.8
N6–C9–C8	108.1(5)
N6–C9–H9	125.9
C8–C9–H9	125.9
P1–C10–H10A	109.5
P1–C10–H10B	109.5
P1–C10–H10C	109.5
H10A–C10–H10B	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
P1–C11–H11A	109.5
P1–C11–H11B	109.5
P1–C11–H11C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5

H11B–C11–H11C	109.5
P1–C12–H12A	109.5
P1–C12–H12B	109.5
P1–C12–H12C	109.5
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
W1–C13–H13	111.9
C14–C13–W1	72.8(3)
C14–C13–H13	111.9
C14–C13–C18	118.7(5)
C18–C13–W1	124.0(3)
C18–C13–H13	111.9
W1–C14–H14	114.1
C13–C14–W1	69.3(3)
C13–C14–H14	114.1
C13–C14–C15	117.7(5)
C15–C14–W1	120.3(4)
C15–C14–H14	114.1
C14–C15–H15	118.1
C16–C15–C14	123.7(5)
C16–C15–H15	118.1
C15–C16–H16	118.8
C15–C16–C17	122.4(5)
C17–C16–H16	118.8
C16–C17–H17	110.5
C16–C17–C18	111.6(4)
C16–C17–C19	111.1(5)
C18–C17–H17	110.5
C19–C17–H17	110.5
C19–C17–C18	102.5(4)
N8–C18–C13	113.8(4)
N8–C18–C17	100.6(4)
N8–C18–H18	108.7
C13–C18–C17	115.9(4)
C13–C18–H18	108.7
C17–C18–H18	108.7
C17–C19–H19A	110.9
C17–C19–H19B	110.9
H19A–C19–H19B	108.9

C20–C19–C17	104.3(4)
C20–C19–H19A	110.9
C20–C19–H19B	110.9
O2–C20–N8	125.6(5)
O2–C20–C19	126.1(6)
N8–C20–C19	108.3(5)
N8–C21–H21A	109.2
N8–C21–H21B	109.2
N8–C21–C22	112.0(5)
H21A–C21–H21B	107.9
C22–C21–H21A	109.2
C22–C21–H21B	109.2
O3–C22–O4	126.9(6)
O3–C22–C21	124.8(6)
O4–C22–C21	108.3(5)
O4–C23–C24	108.7(6)
O4–C23–C26	101.5(6)
C25–C23–O4	110.1(5)
C25–C23–C24	112.1(7)
C25–C23–C26	112.4(7)
C26–C23–C24	111.6(6)
C23–C24–H24A	109.5
C23–C24–H24B	109.5
C23–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
C23–C25–H25A	109.5
C23–C25–H25B	109.5
C23–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
C23–C26–H26A	109.5
C23–C26–H26B	109.5
C23–C26–H26C	109.5
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
N2–B1–H1A	109(3)

N4–B1–N2	106.1(4)
N4–B1–N6	111.3(4)
N4–B1–H1A	115(3)
N6–B1–N2	107.9(4)
N6–B1–H1A	107(3)

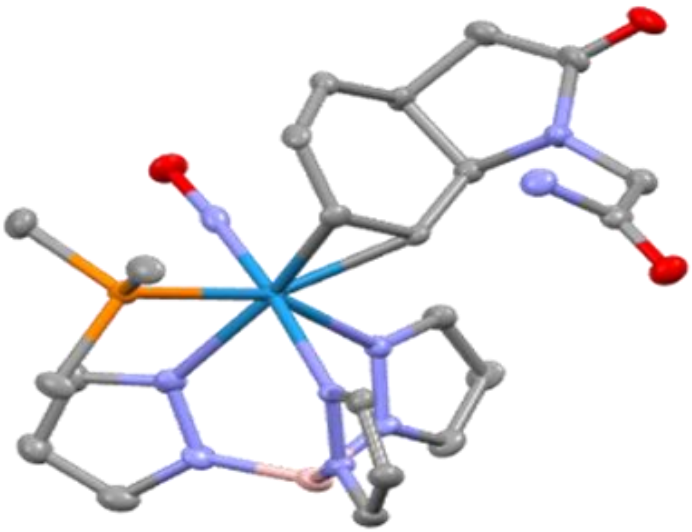
Table 5 Torsion angles for compound 4.14

Atom–Atom–Atom–Atom	Torsion Angle [°]
W1–N1–N2–C3	−178.5(3)
W1–N1–N2–B1	−0.1(5)
W1–N1–C1–C2	178.7(3)
W1–N3–N4–C6	173.4(3)
W1–N3–N4–B1	8.3(6)
W1–N3–C4–C5	−173.7(3)
W1–N5–N6–C9	−177.6(3)
W1–N5–N6–B1	−7.2(5)
W1–N5–C7–C8	178.0(4)
W1–C13–C14–C15	114.3(5)
W1–C13–C18–N8	−175.0(3)
W1–C13–C18–C17	−59.0(6)
W1–C14–C15–C16	71.3(7)
N1–N2–C3–C2	−0.7(5)
N1–N2–B1–N4	−60.7(6)
N1–N2–B1–N6	58.7(6)
N1–C1–C2–C3	−0.5(6)
N2–N1–C1–C2	0.1(5)
N3–N4–C6–C5	0.7(6)
N3–N4–B1–N2	55.4(6)
N3–N4–B1–N6	−61.8(6)
N3–C4–C5–C6	0.9(6)
N4–N3–C4–C5	−0.5(6)
N5–N6–C9–C8	−1.1(6)
N5–N6–B1–N2	−54.1(6)
N5–N6–B1–N4	61.9(6)
N5–C7–C8–C9	−1.2(6)
N6–N5–C7–C8	0.5(6)
N8–C21–C22–O3	−12.4(9)
N8–C21–C22–O4	169.1(5)
C1–N1–N2–C3	0.4(5)

C1–N1–N2–B1	178.7(4)
C1–C2–C3–N2	0.7(6)
C3–N2–B1–N4	117.3(5)
C3–N2–B1–N6	−123.3(5)
C4–N3–N4–C6	−0.1(5)
C4–N3–N4–B1	−165.3(4)
C4–C5–C6–N4	−0.9(6)
C6–N4–B1–N2	−106.0(6)
C6–N4–B1–N6	136.8(5)
C7–N5–N6–C9	0.3(5)
C7–N5–N6–B1	170.7(4)
C7–C8–C9–N6	1.3(6)
C9–N6–B1–N2	114.4(5)
C9–N6–B1–N4	−129.5(5)
C13–C14–C15–C16	−9.8(8)
C14–C13–C18–N8	−87.1(6)
C14–C13–C18–C17	28.9(7)
C14–C15–C16–C17	−0.3(9)
C15–C16–C17–C18	23.2(7)
C15–C16–C17–C19	136.9(6)
C16–C17–C18–N8	86.8(5)
C16–C17–C18–C13	−36.4(6)
C16–C17–C19–C20	−91.8(5)
C17–C19–C20–O2	167.8(5)
C17–C19–C20–N8	−11.8(6)
C18–N8–C20–O2	170.0(5)
C18–N8–C20–C19	−10.5(6)
C18–N8–C21–C22	−70.0(7)
C18–C13–C14–W1	−119.9(4)
C18–C13–C14–C15	−5.6(7)
C18–C17–C19–C20	27.5(5)
C19–C17–C18–N8	−32.2(5)
C19–C17–C18–C13	−155.4(4)
C20–N8–C18–C13	152.3(5)
C20–N8–C18–C17	27.7(6)
C20–N8–C21–C22	82.0(7)
C21–N8–C18–C13	−53.7(7)
C21–N8–C18–C17	−178.3(5)
C21–N8–C20–O2	16.1(9)
C21–N8–C20–C19	−164.3(5)

C22–O4–C23–C24	−63.9(8)
C22–O4–C23–C25	59.2(8)
C22–O4–C23–C26	178.4(6)
C23–O4–C22–O3	0.9(10)
C23–O4–C22–C21	179.3(5)
B1–N2–C3–C2	−178.9(5)
B1–N4–C6–C5	163.2(5)
B1–N6–C9–C8	−170.7(5)

Crystal Structure Report for compound 4.15



A colorless, plate-like specimen of $C_{22}H_{31}BN_9O_3PW$, approximate dimensions 0.029 mm x 0.032 mm x 0.106 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with a Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 3.09 hours. The frames were integrated with the Bruker SAINT software package[50] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 45385 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 5983 were independent (average redundancy 7.586, completeness = 99.9%, R_{int} = 10.60%, R_{sig} = 6.36%) and 4452 (74.41%) were greater than

[50] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

2σ(F^2). The final cell constants of a = 8.3014(5) Å, b = 22.8434(13) Å, c = 13.9364(8) Å, β = 99.836(2)°, volume = 2603.9(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 4947 reflections above 20 σ(I) with 4.638° < 2θ < 54.91°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[51] The ratio of minimum to maximum apparent transmission was 0.880. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6450 and 0.8800.

The structure was solved and refined using the Bruker SHELXTL Software Package[52] within APEX4 [1] and OLEX2,[53] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{22}H_{31}BN_9O_3PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom. The final anisotropic full-matrix least-squares refinement on F^2 with 357 variables converged at R1 = 3.50%, for the observed data and wR2 = 7.80% for all data. The goodness-of-fit was 1.012. The largest peak in the final difference electron density synthesis was 0.937 $e^-/Å^3$ and the largest hole was -0.897 $e^-/Å^3$ with an RMS deviation of 0.168 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.773 g/cm^3 and F(000), 1376 e^-.

Table 1. Sample and crystal data for compound 4.15

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Chemical formula	$C_{22}H_{31}BN_9O_3PW$
Formula weight	695.19 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.029 x 0.032 x 0.106 mm
Crystal habit	colorless plate
Crystal system	monoclinic

[51] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[52] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

[53] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Space group	P $2_1/c$	
Unit cell dimensions	a = 8.3014(5) Å	α = 90°
	b = 22.8434(13) Å	β = 99.836(2)°
	c = 13.9364(8) Å	γ = 90°
Volume	2603.9(3) $Å^3$	
Z	4	
Density (calculated)	1.773 g/cm^3	
Absorption coefficient	4.541 mm^{-1}	
F(000)	1376	

Table 2. Data collection and structure refinement for Harman_LD_PS201_X2.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.32 to 27.50°
Index ranges	-10<=h<=10, -29<=k<=29, -18<=l<=18
Reflections collected	45385
Independent reflections	5983 [R(int) = 0.1060]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8800 and 0.6450
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)

Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5983 / 0 / 357	
Goodness-of-fit on F^2	1.012	
Δ/σ_{max}	0.003	
Final R indices	4452 data; $I>2\sigma(I)$	R1 = 0.0350, wR2 = 0.0694
	all data	R1 = 0.0607, wR2 = 0.0780
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0330P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.937 and -0.897 eÅ^{-3}	
R.M.S. deviation from mean	0.168 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.15

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.57560(2)	0.40420(2)	0.70514(2)	0.01340(7)
P1	0.38582(16)	0.38090(6)	0.82117(10)	0.0164(3)
O1	0.2973(4)	0.45822(17)	0.5689(3)	0.0247(9)
O2	0.8643(5)	0.68106(16)	0.7125(3)	0.0293(9)
O3	0.1459(4)	0.52738(16)	0.9213(3)	0.0245(9)
N1	0.7624(5)	0.35668(16)	0.8120(3)	0.0126(9)
N2	0.8305(5)	0.30562(18)	0.7862(3)	0.0164(9)
N3	0.4975(5)	0.31593(18)	0.6513(3)	0.0173(9)
N4	0.6045(5)	0.27023(18)	0.6583(3)	0.0187(10)
N5	0.7500(5)	0.38348(17)	0.6056(3)	0.0147(9)
N6	0.8247(5)	0.32981(18)	0.6115(3)	0.0167(9)

	x/a	y/b	z/c	U(eq)
N7	0.4164(5)	0.43735(18)	0.6227(3)	0.0172(9)
N8	0.8417(5)	0.58145(17)	0.7237(3)	0.0184(10)
N9	0.8895(6)	0.5597(2)	0.9215(4)	0.0208(10)
C1	0.8261(6)	0.3651(2)	0.9066(4)	0.0169(11)
C2	0.9322(6)	0.3207(2)	0.9412(4)	0.0205(12)
C3	0.9311(6)	0.2836(2)	0.8630(4)	0.0217(12)
C4	0.3514(7)	0.2943(2)	0.6163(4)	0.0222(12)
C5	0.3585(7)	0.2345(2)	0.6023(4)	0.0252(13)
C6	0.5222(7)	0.2207(2)	0.6297(4)	0.0243(12)
C7	0.7986(6)	0.4123(2)	0.5322(4)	0.0194(11)
C8	0.9047(6)	0.3785(2)	0.4902(4)	0.0214(12)
C9	0.9183(6)	0.3269(2)	0.5412(4)	0.0211(12)
C10	0.6137(6)	0.4811(2)	0.8053(4)	0.0158(11)
C11	0.7315(6)	0.4811(2)	0.7391(4)	0.0142(10)
C12	0.7387(6)	0.5329(2)	0.6737(4)	0.0186(11)
C13	0.5756(6)	0.5653(2)	0.6407(4)	0.0180(11)
C14	0.4693(6)	0.5647(2)	0.7175(4)	0.0178(11)
C15	0.4883(6)	0.5271(2)	0.7913(4)	0.0162(11)
C16	0.6307(7)	0.6279(2)	0.6210(4)	0.0232(12)
C17	0.7908(7)	0.6355(2)	0.6900(4)	0.0199(12)
C18	0.0065(6)	0.5719(2)	0.7755(4)	0.0195(11)
C19	0.0197(6)	0.5497(2)	0.8797(4)	0.0185(11)
C20	0.4194(7)	0.4112(2)	0.9432(4)	0.0220(12)
C21	0.3764(7)	0.3029(2)	0.8510(4)	0.0215(12)
C22	0.1756(6)	0.4025(2)	0.7749(4)	0.0255(12)
B1	0.7890(8)	0.2821(3)	0.6818(4)	0.0202(13)

Table 4. Bond lengths (Å) for compound 4.15

.

W1-N7	1.767(4)	W1-C11	2.185(5)
W1-N3	2.210(4)	W1-N5	2.221(4)

W1-C10	2.233(5)	W1-N1	2.239(4)
W1-P1	2.5001(14)	P1-C20	1.813(5)
P1-C22	1.821(5)	P1-C21	1.834(5)
O1-N7	1.230(5)	O2-C17	1.220(6)
O3-C19	1.219(6)	N1-C1	1.348(6)
N1-N2	1.371(5)	N2-C3	1.338(6)
N2-B1	1.534(7)	N3-C4	1.323(6)
N3-N4	1.363(6)	N4-C6	1.347(7)
N4-B1	1.535(7)	N5-C7	1.335(6)
N5-N6	1.370(5)	N6-C9	1.352(6)
N6-B1	1.527(7)	N8-C17	1.362(6)
N8-C18	1.450(6)	N8-C12	1.498(6)
N9-C19	1.333(7)	N9-H9A	0.77(6)
N9-H9B	0.85(7)	C1-C2	1.376(7)
C1-H1	0.950000	C2-C3	1.379(7)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.381(7)	C4-H4	0.950000
C5-C6	1.384(8)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.374(7)
C7-H7	0.950000	C8-C9	1.372(7)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.454(7)	C10-C15	1.468(7)
C10-H10	0.92(5)	C11-C12	1.501(7)
C11-H11	0.90(6)	C12-C13	1.542(7)
C12-H12	1.000000	C13-C14	1.498(7)
C13-C16	1.541(7)	C13-H13	1.000000
C14-C15	1.330(7)	C14-H14	0.950000
C15-H15	0.950000	C16-C17	1.512(7)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.524(7)	C18-H18A	0.990000
C18-H18B	0.990000	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000

C22-H22B 0.980000 C22-H22C 0.980000
B1-H1A 1.14(5)

Table 5. Bond angles (°) for compound 4.15

.

N7-W1-C11	98.38(19)	N7-W1-N3	91.52(17)
C11-W1-N3	159.32(17)	N7-W1-N5	100.36(17)
C11-W1-N5	83.19(16)	N3-W1-N5	77.17(15)
N7-W1-C10	94.58(18)	C11-W1-C10	38.42(18)
N3-W1-C10	158.83(17)	N5-W1-C10	121.36(17)
N7-W1-N1	175.31(16)	C11-W1-N1	85.89(16)
N3-W1-N1	85.03(14)	N5-W1-N1	82.00(15)
C10-W1-N1	87.57(16)	N7-W1-P1	91.62(14)
C11-W1-P1	116.51(13)	N3-W1-P1	81.07(11)
N5-W1-P1	155.34(11)	C10-W1-P1	78.51(14)
N1-W1-P1	84.72(11)	C20-P1-C22	102.3(3)
C20-P1-C21	99.4(2)	C22-P1-C21	105.5(3)
C20-P1-W1	120.84(18)	C22-P1-W1	112.64(19)
C21-P1-W1	114.17(18)	C1-N1-N2	105.6(4)
C1-N1-W1	133.9(3)	N2-N1-W1	120.5(3)
C3-N2-N1	109.8(4)	C3-N2-B1	129.5(4)
N1-N2-B1	120.7(4)	C4-N3-N4	106.6(4)
C4-N3-W1	131.5(4)	N4-N3-W1	121.6(3)
C6-N4-N3	109.3(4)	C6-N4-B1	130.5(5)
N3-N4-B1	119.6(4)	C7-N5-N6	107.1(4)
C7-N5-W1	133.5(3)	N6-N5-W1	119.3(3)
C9-N6-N5	108.1(4)	C9-N6-B1	128.9(4)
N5-N6-B1	122.8(4)	O1-N7-W1	175.1(4)
C17-N8-C18	121.2(4)	C17-N8-C12	113.1(4)
C18-N8-C12	122.4(4)	C19-N9-H9A	122.(4)
C19-N9-H9B	123.(5)	H9A-N9-H9B	113.(6)
N1-C1-C2	111.0(5)	N1-C1-H1	124.500000

C2-C1-H1	124.500000	C1-C2-C3	105.0(5)
C1-C2-H2	127.500000	C3-C2-H2	127.500000
N2-C3-C2	108.8(5)	N2-C3-H3	125.600000
C2-C3-H3	125.600000	N3-C4-C5	111.3(5)
N3-C4-H4	124.400000	C5-C4-H4	124.400000
C4-C5-C6	104.5(5)	C4-C5-H5	127.800000
C6-C5-H5	127.800000	N4-C6-C5	108.3(5)
N4-C6-H6	125.800000	C5-C6-H6	125.800000
N5-C7-C8	110.4(5)	N5-C7-H7	124.800000
C8-C7-H7	124.800000	C9-C8-C7	105.3(5)
C9-C8-H8	127.300000	C7-C8-H8	127.300000
N6-C9-C8	109.0(5)	N6-C9-H9	125.500000
C8-C9-H9	125.500000	C11-C10-C15	117.0(4)
C11-C10-W1	69.0(3)	C15-C10-W1	117.3(3)
C11-C10-H10	113.(3)	C15-C10-H10	119.(3)
W1-C10-H10	112.(3)	C10-C11-C12	119.0(4)
C10-C11-W1	72.6(3)	C12-C11-W1	125.9(3)
C10-C11-H11	115.(4)	C12-C11-H11	109.(4)
W1-C11-H11	111.(4)	N8-C12-C11	112.4(4)
N8-C12-C13	100.7(4)	C11-C12-C13	115.8(4)
N8-C12-H12	109.200000	C11-C12-H12	109.200000
C13-C12-H12	109.200000	C14-C13-C16	111.3(4)
C14-C13-C12	112.2(4)	C16-C13-C12	103.1(4)
C14-C13-H13	110.000000	C16-C13-H13	110.000000
C12-C13-H13	110.000000	C15-C14-C13	123.5(5)
C15-C14-H14	118.300000	C13-C14-H14	118.300000
C14-C15-C10	123.6(5)	C14-C15-H15	118.200000
C10-C15-H15	118.200000	C17-C16-C13	104.4(4)
C17-C16-H16A	110.900000	C13-C16-H16A	110.900000
C17-C16-H16B	110.900000	C13-C16-H16B	110.900000
H16A-C16-H16B	108.900000	O2-C17-N8	125.0(5)

O2-C17-C16	127.4(5)	N8-C17-C16	107.6(4)
N8-C18-C19	115.7(4)	N8-C18-H18A	108.400000
C19-C18-H18A	108.400000	N8-C18-H18B	108.400000
C19-C18-H18B	108.400000	H18A-C18-H18B	107.400000
O3-C19-N9	124.1(5)	O3-C19-C18	120.6(5)
N9-C19-C18	115.3(5)	P1-C20-H20A	109.500000
P1-C20-H20B	109.500000	H20A-C20-H20B	109.500000
P1-C20-H20C	109.500000	H20A-C20-H20C	109.500000
H20B-C20-H20C	109.500000	P1-C21-H21A	109.500000
P1-C21-H21B	109.500000	H21A-C21-H21B	109.500000
P1-C21-H21C	109.500000	H21A-C21-H21C	109.500000
H21B-C21-H21C	109.500000	P1-C22-H22A	109.500000
P1-C22-H22B	109.500000	H22A-C22-H22B	109.500000
P1-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	N6-B1-N2	108.8(4)
N6-B1-N4	106.6(4)	N2-B1-N4	108.5(4)
N6-B1-H1A	111.(3)	N2-B1-H1A	110.(3)
N4-B1-H1A	112.(3)		

Table 6. Torsion angles (°) for compound 4.15

.

C1-N1-N2-C3	0.5(5)	W1-N1-N2-C3	-176.5(3)

C1-N1-N2-B1	-178.8(4)	W1-N1-N2-B1	4.2(6)
C4-N3-N4-C6	-1.4(6)	W1-N3-N4-C6	173.6(3)
C4-N3-N4-B1	170.6(4)	W1-N3-N4-B1	-14.4(6)
C7-N5-N6-C9	0.1(5)	W1-N5-N6-C9	177.3(3)
C7-N5-N6-B1	-175.0(4)	W1-N5-N6-B1	2.2(6)
N2-N1-C1-C2	-0.1(6)	W1-N1-C1-C2	176.3(3)
N1-C1-C2-C3	-0.3(6)	N1-N2-C3-C2	-0.7(6)
B1-N2-C3-C2	178.6(5)	C1-C2-C3-N2	0.6(6)
N4-N3-C4-C5	1.6(6)	W1-N3-C4-C5	-172.7(4)
N3-C4-C5-C6	-1.2(6)	N3-N4-C6-C5	0.7(6)
B1-N4-C6-C5	-170.2(5)	C4-C5-C6-N4	0.3(6)
N6-N5-C7-C8	-0.4(6)	W1-N5-C7-C8	-177.0(4)
N5-C7-C8-C9	0.5(6)	N5-N6-C9-C8	0.2(6)
B1-N6-C9-C8	174.9(5)	C7-C8-C9-N6	-0.5(6)
C15-C10-C11-C12	11.1(7)	W1-C10-C11-C12	121.9(4)
C15-C10-C11-W1	-110.8(4)	C17-N8-C12-C11	-149.4(4)
C18-N8-C12-C11	50.8(6)	C17-N8-C12-C13	-25.6(5)
C18-N8-C12-C13	174.7(4)	C10-C11-C12-N8	83.8(6)
W1-C11-C12-N8	172.6(3)	C10-C11-C12-C13	-31.2(7)
W1-C11-C12-C13	57.6(6)	N8-C12-C13-C14	-87.7(5)
C11-C12-C13-C14	33.8(6)	N8-C12-C13-C16	32.1(5)
C11-C12-C13-C16	153.6(4)	C16-C13-C14-C15	-133.9(5)

C12-C13-C14-C15	-19.0(7)	C13-C14-C15-C10	-1.0(8)
C11-C10-C15-C14	5.8(7)	W1-C10-C15-C14	-73.3(6)
C14-C13-C16-C17	91.1(5)	C12-C13-C16-C17	-29.3(5)
C18-N8-C17-O2	-12.4(8)	C12-N8-C17-O2	-172.4(5)
C18-N8-C17-C16	167.3(4)	C12-N8-C17-C16	7.3(6)
C13-C16-C17-O2	-165.9(5)	C13-C16-C17-N8	14.4(6)
C17-N8-C18-C19	119.0(5)	C12-N8-C18-C19	-82.9(6)
N8-C18-C19-O3	162.5(5)	N8-C18-C19-N9	-21.3(7)
C9-N6-B1-N2	126.6(5)	N5-N6-B1-N2	-59.4(6)
C9-N6-B1-N4	-116.6(5)	N5-N6-B1-N4	57.4(6)
C3-N2-B1-N6	-124.4(5)	N1-N2-B1-N6	54.7(6)
C3-N2-B1-N4	120.0(6)	N1-N2-B1-N4	-60.9(6)
C6-N4-B1-N6	120.3(6)	N3-N4-B1-N6	-49.8(6)
C6-N4-B1-N2	-122.6(6)	N3-N4-B1-N2	67.3(6)

Table 7. Anisotropic atomic displacement parameters (Å^2)
for compound 4.15

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The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.01414(10)	0.01532(10)	0.01115(10)	0.00015(9)	0.00333(7)	0.00012(9)
P1	0.0179(7)	0.0171(7)	0.0152(7)	0.0011(6)	0.0054(5)	0.0001(5)
O1	0.021(2)	0.032(2)	0.019(2)	0.0053(17)	-0.0036(16)	0.0022(17)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.033(2)	0.016(2)	0.038(2)	0.0002(18)	0.0051(19)	-0.0057(17)
O3	0.021(2)	0.033(2)	0.019(2)	0.0022(17)	0.0020(16)	0.0031(17)
N1	0.013(2)	0.012(2)	0.011(2)	-0.0020(16)	0.0006(17)	-0.0003(16)
N2	0.016(2)	0.017(2)	0.017(2)	0.0013(18)	0.0059(18)	0.0034(17)
N3	0.019(2)	0.020(2)	0.013(2)	0.0017(18)	0.0006(18)	0.0004(18)
N4	0.023(2)	0.017(2)	0.015(2)	-0.0071(18)	0.0009(19)	-0.0021(18)
N5	0.015(2)	0.016(2)	0.014(2)	-0.0015(17)	0.0037(18)	-0.0017(17)
N6	0.021(2)	0.018(2)	0.011(2)	-0.0046(18)	0.0030(18)	0.0050(18)
N7	0.020(2)	0.020(2)	0.013(2)	-0.0055(18)	0.0070(19)	-0.0056(18)
N8	0.016(2)	0.016(2)	0.023(2)	0.0012(18)	0.0017(19)	-0.0017(17)
N9	0.023(3)	0.026(3)	0.014(3)	-0.004(2)	0.006(2)	0.001(2)
C1	0.014(2)	0.022(3)	0.015(3)	0.000(2)	0.004(2)	0.000(2)
C2	0.021(3)	0.021(3)	0.018(3)	0.003(2)	0.000(2)	0.002(2)
C3	0.021(3)	0.017(3)	0.027(3)	0.003(2)	0.003(2)	0.003(2)
C4	0.022(3)	0.027(3)	0.018(3)	-0.003(2)	0.004(2)	-0.005(2)
C5	0.027(3)	0.025(3)	0.024(3)	-0.005(2)	0.006(2)	-0.006(2)
C6	0.034(3)	0.021(3)	0.018(3)	-0.002(2)	0.006(2)	0.002(2)
C7	0.021(3)	0.022(3)	0.017(3)	0.006(2)	0.007(2)	0.002(2)
C8	0.023(3)	0.033(3)	0.010(3)	0.002(2)	0.009(2)	0.004(2)
C9	0.020(3)	0.030(3)	0.015(3)	-0.005(2)	0.006(2)	0.004(2)
C10	0.015(3)	0.019(3)	0.011(3)	0.000(2)	-0.002(2)	0.001(2)
C11	0.012(2)	0.017(3)	0.015(3)	0.000(2)	0.005(2)	0.002(2)
C12	0.017(3)	0.021(3)	0.019(3)	-0.002(2)	0.004(2)	0.000(2)
C13	0.013(3)	0.020(3)	0.020(3)	0.005(2)	0.001(2)	0.000(2)
C14	0.018(3)	0.015(3)	0.021(3)	-0.002(2)	0.007(2)	-0.002(2)
C15	0.017(2)	0.019(3)	0.015(3)	-0.005(2)	0.009(2)	-0.001(2)
C16	0.027(3)	0.020(3)	0.024(3)	0.005(2)	0.009(2)	0.001(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C17	0.025(3)	0.020(3)	0.018(3)	0.004(2)	0.011(2)	-0.003(2)
C18	0.020(3)	0.020(3)	0.019(3)	0.001(2)	0.005(2)	-0.002(2)
C19	0.020(3)	0.017(3)	0.019(3)	-0.005(2)	0.002(2)	-0.001(2)
C20	0.029(3)	0.025(3)	0.014(3)	-0.001(2)	0.012(2)	0.000(2)
C21	0.034(3)	0.020(3)	0.012(3)	0.000(2)	0.011(2)	-0.002(2)
C22	0.018(3)	0.031(3)	0.029(3)	0.001(3)	0.007(2)	-0.001(2)
B1	0.025(3)	0.017(3)	0.018(3)	-0.001(3)	0.003(3)	0.000(3)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.15

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	x/a	y/b	z/c	U(eq)
H9A	0.805(7)	0.567(2)	0.891(4)	0.022(18)
H9B	0.883(8)	0.548(3)	0.979(5)	0.05(2)
H1	0.8011	0.3974	0.9444	0.020000
H2	0.9929	0.3164	1.0051	0.025000
H3	0.9917	0.2483	0.8636	0.026000
H4	0.2541	0.3169	0.6026	0.027000
H5	0.2707	0.2087	0.5792	0.030000
H6	0.5686	0.1827	0.6284	0.029000
H7	0.7645	0.4507	0.5118	0.023000
H8	0.9575	0.3888	0.4373	0.026000
H9	0.9830	0.2943	0.5291	0.025000
H10	0.659(6)	0.471(2)	0.868(4)	0.012(13)
H11	0.834(7)	0.471(2)	0.766(4)	0.034(17)
H12	0.7841	0.5203	0.6150	0.022000
H13	0.5159	0.5475	0.5792	0.022000
H14	0.3839	0.5928	0.7132	0.021000
H15	0.4167	0.5301	0.8375	0.019000
H16A	0.6462	0.6322	0.5525	0.028000
H16B	0.5492	0.6570	0.6347	0.028000

	x/a	y/b	z/c	U(eq)
H18A	1.0673	0.6093	0.7770	0.023000
H18B	1.0611	0.5434	0.7383	0.023000
H20A	0.5306	0.4020	0.9758	0.033000
H20B	0.3405	0.3942	0.9802	0.033000
H20C	0.4051	0.4538	0.9396	0.033000
H21A	0.3281	0.2811	0.7926	0.032000
H21B	0.3091	0.2977	0.9017	0.032000
H21C	0.4871	0.2883	0.8747	0.032000
H22A	0.1695	0.4451	0.7685	0.038000
H22B	0.1049	0.3894	0.8203	0.038000
H22C	0.1395	0.3844	0.7111	0.038000
H1A	0.864(6)	0.241(2)	0.674(4)	0.020(14)

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 4.15

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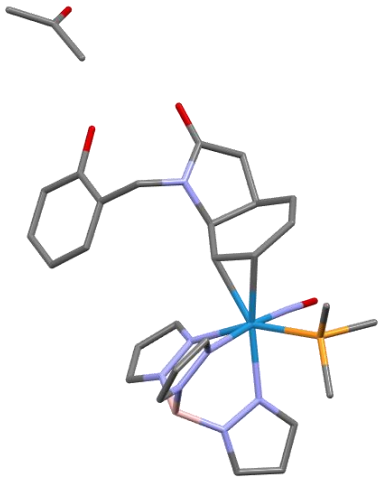
	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N9-H9B···O3#1	0.85(7)	2.26(7)	3.011(7)	148.(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2, -y+1, -z+2

Structure Report for compound 4.17



A colourless, plate shaped crystal of compound 4.17

measuring 0.035×0.104×0.147 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for cu_harman_ld_2_137acetone2_x3_ were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Cu K_α, λ=1.54178 Å) using a HELIOS EF double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Plus low temperature device. Data collection and processing were done within the Bruker APEX4 software suite.[54] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with SHELXT[55] and refined by full-matrix least-squares methods against F^2 using XL[56] within OLEX2.[57] All non-hydrogen atoms were refined with anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[58]

[54] *APEX4, Saint, SADABS*; Bruker AXS Inc. 2019.
[55] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[56] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[57] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[58] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for compound 4.17

CCDC number	
Empirical formula	$C_{30}H_{40}BN_8O_4PW$
Formula weight	802.33
Temperature [K]	100.00
Wavelength [Å]	1.54178
Crystal size [mm^3]	0.035×0.104×0.147
Crystal habit	colourless plate
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
a [Å]	13.4760(5)
b [Å]	24.0325(9)
c [Å]	9.8450(4)
α [°]	90
β [°]	93.390(2)
γ [°]	90
Volume [$Å^3$]	3182.8(2)
Z	4
ρ_{calc} [gcm^{-3}]	1.674
μ [mm^{-1}]	7.609
F(000)	1608
2θ range [°]	6.57 to 136.97 (0.83 Å)
Index ranges	−16 ≤ h ≤ 16 −28 ≤ k ≤ 28 −11 ≤ l ≤ 11
Reflections collected	37329
Independent reflections	5821 [R_{int} = 0.0576]
Data / Restraints / Parameters	5821 / 0 / 419
Goodness-of-fit on F^2	1.057
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0387 wR_2 = 0.0994

Final *R* indexes [all data]	R_1 = 0.0473 wR_2 = 0.1056
Largest peak/hole [eÅ^{-3}]	1.27/−0.99

Table 2 Atomic coordinates and Ueq [Å^2] for compound 4.17

Atom	***x***	***y***	***z***	U_{eq}
W1	0.75338(2)	0.56224(2)	0.71687(2)	0.02605(10)
P1	0.77445(10)	0.46313(5)	0.64566(15)	0.0296(3)
O1	0.7239(3)	0.52567(17)	1.0028(4)	0.0383(9)
O2	0.2893()	0.66186(17)	0.7871(5)	0.0466(11)
O3	0.3365(4)	0.77237(19)	0.7762(6)	0.0617(15)
H3	0.319(6)	0.739(4)	0.772(9)	0.07(3)
N1	0.7923(3)	0.64878(19)	0.7706(5)	0.0320(10)
N2	0.8623(3)	0.67732(18)	0.7047(5)	0.0337(10)
N3	0.9176(3)	0.56061(17)	0.7555(5)	0.0290(9)
N4	0.9784(3)	0.59803(19)	0.6986(5)	0.0323(10)
N5	0.7943(3)	0.58603(18)	0.5060(5)	0.0306(10)
N6	0.8717(3)	0.62129(17)	0.4891(5)	0.0317(10)
N7	0.7339(3)	0.54196(18)	0.8825(5)	0.0290(10)
N8	0.4468(3)	0.64688(17)	0.7219(5)	0.0308(10)
C1	0.7623(5)	0.6820(3)	0.8686(7)	0.0458(16)
H1	0.713802	0.672363	0.930787	0.055
C2	0.8118(5)	0.7326(3)	0.8672(8)	0.0492(17)
H2	0.804406	0.763427	0.926161	0.059
C3	0.8739(5)	0.7283(2)	0.7621(7)	0.0435(15)
H3A	0.917787	0.756506	0.734167	0.052
C4	0.9766(4)	0.5285(2)	0.8382(6)	0.0385(13)
H4	0.954047	0.499017	0.892663	0.046
C5	1.0745(4)	0.5446(3)	0.8327(7)	0.0434(14)
H5	1.131138	0.528506	0.879394	0.052
C6	1.0723(4)	0.5889(3)	0.7453(6)	0.0393(13)
H6	1.128453	0.609839	0.721552	0.047
C7	0.7640(4)	0.5691(2)	0.3808(6)	0.0312(12)
H7	0.710607	0.543945	0.361833	0.037
C8	0.8199(5)	0.5929(2)	0.2821(6)	0.0378(13)
H8	0.812926	0.587825	0.186286	0.045
C9	0.8877(5)	0.6256(2)	0.3553(6)	0.0367(13)

H9	0.937828	0.647619	0.317789	0.044
C10	0.7002(4)	0.4323(2)	0.5043(7)	0.0370(13)
H10A	0.712449	0.392179	0.501768	0.055
H10B	0.718548	0.449200	0.418719	0.055
H10C	0.629512	0.439106	0.516464	0.05
C11	0.7552(5)	0.4152(3)	0.7840(7)	0.0461(15)
H11A	0.687812	0.420002	0.814611	0.069
H11B	0.803760	0.422863	0.859682	0.069
H11C	0.763504	0.376941	0.752351	0.069
C12	0.8970(5)	0.4439(3)	0.5934(8)	0.0511(18)
H12A	0.946508	0.450775	0.668482	0.077
H12B	0.913133	0.466309	0.514433	0.077
H12C	0.897400	0.404405	0.569072	0.077
C13	0.6073(4)	0.6008(2)	0.6692(6)	0.0281(11)
H13	0.608018	0.626722	0.589926	0.034
C14	0.5996(4)	0.5430(2)	0.6273(6)	0.0278(11)
H14	0.595278	0.537224	0.526521	0.033
C15	0.5354(4)	0.5062(2)	0.7027(6)	0.0316(12)
H15	0.524965	0.469381	0.669715	0.038
C16	0.4911(4)	0.5210(2)	0.8140(6)	0.0330(12)
H16	0.449065	0.494923	0.854773	0.040
C17	0.5052(4)	0.5782(2)	0.8787(6)	0.0315(12)
H17	0.552328	0.575595	0.960793	0.038
C18	0.5429(4)	0.6219(2)	0.7784(	0.0295(11)
H18	0.580749	0.651168	0.832003	0.035
C19	0.450(4)	0.6017(2)	0.9190(6)	0.0387(13)
H19A	0.356381	0.571382	0.930332	0.046
H19B	0.413157	0.622894	1.005162	0.046
C20	0.3716(4)	0.6390(2)	0.8038(6)	0.0350(13)
C21	0.4433(4)	0.6890(2)	0.6163(6)	0.0325(12)
H21A	0.373487	0.693905	0.581427	0.039
H21B	0.481659	0.675608	0.539971	0.039
C22	0.4845(4)	0.7450(2)	0.6635(6)	0.0329(12)
C23	0.429(4)	0.7826(2)	0.7364(7)	0.0376(13)
C24	0.4686(5)	0.8343(2)	0.7716(7)	0.0425(15)
H24	0.429568	0.860335	0.817908	0.051
C25	0.5637(5)	0.8482(2)	0.7398(7)	0.0416(14)
H25	0.589802	0.883841	0.763819	0.050
C26	0.6207(5)	0.8112(3)	0.6741(7)	0.0418(14)

H26	0.687306	0.820081	0.655910	0.050
C27	0.5800(5)	0.7600(2)	0.6339(6)	0.0375(13)
H27	0.618734	0.734803	0.584856	0.045
B1	0.9322(5)	0.6462(3)	0.6126(7)	0.0338(14)
H1A	0.989(4)	0.673(2)	0.580(6)	0.026(14)
O4	0.0766(5)	0.7912(3)	0.7208(7)	0.091(2)
C28	0.1677(9)	0.7473(6)	0.5443(13)	0.125(5)
H28A	0.231108	0.764587	0.524518	0.188
H28B	0.136514	0.731418	0.460641	0.18
H28C	0.179515	0.717779	0.611982	0.188
C29	0.0988(8)	0.7914(5)	0.6004(10)	0.089(3)
C30	0.0613(16)	0.8341(7)	0.5063(18)	0.204(11)
H30A	0.006232	0.818960	0.448222	0.306
H30B	0.114710	0.846129	0.449651	0.306
H30C	0.037825	0.865898	0.557699	0.306

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 4.17

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02753(15)	0.02218(14)	0.02841(15)	−0.00177(9)	0.00133(10)	0.00137(9)
P1	0.0310(7)	0.0242(6)	0.0336(7)	−0.0018(5)	0.0018(6)	0.0039(5)
O1	0.048(2)	0.040(2)	0.026(2)	0.0035(17)	0.0009(17)	0.0015(18)
O2	0.034(2)	0.032(2)	0.076(3)	−0.005(2)	0.016(2)	−0.0001(18)
O3	0.049(3)	0.029(2)	0.110(5)	−0.010(3)	0.035(3)	−0.005(2)
N1	0.026(2)	0.031(2)	0.040(3)	−0.003(2)	0.005(2)	0.0017(18)
N2	0.038(2)	0.022(2)	0.042(3)	−0.0037(19)	0.003(2)	0.0000(18)
N3	0.027(2)	0.027(2)	0.033(2)	0.0002(18)	0.0001(19)	0.0015(17)
N4	0.030(2)	0.031(2)	0.037(3)	−0.0040(19)	0.006(2)	−0.0020(19)
N5	0.034(2)	0.022(2)	0.036(3)	−0.0017(19)	0.002(2)	0.0039(18)
N6	0.038(2)	0.021(2)	0.037(3)	0.0024(18)	0.008(2)	0.0034(18)

N7	0.018(2)	0.033(2)	0.034(3)	−0.0161(19)	−0.0093(18)	0.0041(17)
N8	0.032(2)	0.022(2)	0.038(3)	0.0001(18)	0.005(2)	0.0001(18)
C1	0.038(3)	0.049(4)	0.051(4)	−0.024(3)	0.006(3)	−0.003(3)
C2	0.040(3)	0.040(3)	0.068(5)	−0.029(3)	0.008(3)	−0.004(3)
C3	0.044(3)	0.027(3)	0.060(4)	−0.015(3)	0.002(3)	−0.008(2)
C4	0.036(3)	0.034(3)	0.044(3)	0.005(3)	−0.007(3)	0.001(2)
C5	0.031(3)	0.046(3)	0.052(4)	−0.001(3)	−0.003(3)	0.006(3)
C6	0.033(3)	0.041(3)	0.045(4)	−0.004(3)	0.005(3)	0.003(2)
C7	0.036(3)	0.028(3)	0.030(3)	−0.002(2)	−0.002(2)	0.009(2)
C8	0.048(3)	0.030(3)	0.035(3)	0.001(2)	0.000(3)	0.011(3)
C9	0.045(3)	0.028(3)	0.038(3)	0.006(2)	0.012(3)	0.009(2)
C10	0.042(3)	0.025(3)	0.044(3)	−0.005(2)	0.000(3)	0.003(2)
C11	0.061(4)	0.030(3)	0.047(4)	0.004(3)	−0.002(3)	0.004(3)
C12	0.034(3)	0.052(4)	0.068(5)	−0.024(3)	0.009(3)	0.005(3)
C13	0.027(3)	0.024(2)	0.034(3)	0.002(2)	0.004(2)	0.001(2)
C14	0.025(3)	0.029(3)	0.029(3)	−0.002(2)	−0.003(2)	0.002(2)
C15	0.028(3)	0.021(2)	0.045(3)	−0.002(2)	−0.005(2)	0.003(2)
C16	0.031(3)	0.021(2)	0.047(3)	0.003(2)	0.003(2)	0.002(2)
C17	0.035(3)	0.030(3)	0.030(3)	−0.002(2)	0.005(2)	−0.002(2)
C18	0.027(3)	0.024(2)	0.038(3)	0.001(2)	0.004(2)	−0.001(2)
C19	0.042(3)	0.032(3)	0.044(3)	−0.005(2)	0.016(3)	−0.007(2)
C20	0.037(3)	0.023(3)	0.047(3)	−0.007(2)	0.012(3)	−0.005(2)
C21	0.028(3)	0.027(3)	0.042(3)	−0.003(2)	0.004(2)	0.003(2)
C22	0.033(3)	0.027(3)	0.038(3)	0.004(2)	0.005(2)	−0.003(2)
C23	0.034(3)	0.025(3)	0.054(4)	0.000(2)	0.007(3)	0.002(2)
C24	0.055(4)	0.025(3)	0.049(4)	0.002(3)	0.016(3)	0.001(3)
C25	0.049(4)	0.029(3)	0.046(4)	0.001(3)	0.000(3)	−0.007(3)
C26	0.037(3)	0.039(3)	0.051(4)	0.004(3)	0.010(3)	−0.007(3)
C27	0.044(3)	0.027(3)	0.042(3)	0.003(2)	0.007(3)	−0.002(2)
B1	0.039(3)	0.028(3)	0.036(4)	−0.003(3)	0.009(3)	−0.001(3)
O4	0.084(4)	0.122(6)	0.068(4)	0.004(4)	0.018(3)	−0.018(4)
C28	0.087(8)	0.188(14)	0.104(9)	−0.029(9)	0.040(7)	−0.029(9)
C29	0.096(7)	0.109(8)	0.062(6)	0.010(5)	0.006(5)	−0.043(6)
C30	0.31(3)	0.140(14)	0.144(15)	0.071(12)	−0.104(16)	−0.095(16)

Table 4 Bond lengths and angles for compound 4.17

_Atom–Atom	Length [Å]
W1–P1	2.5039(13)
W1–N1	2.202(4)
W1–N3	2.224(4)
W1–N5	2.253(5)
W1–N7	1.737(5)
W1–C13	2.201(5)
W1–C14	2.251(5)
P1–C10	1.822(6)
P1–C11	1.813(6)
P1–C12	1.818(6)
O1–N7	1.262(6)
O2–C20	1.240(7)
O3–H3	0.84(9)
O3–C23	1.362(7)
N1–N2	1.361(6)
N1–C1	1.334(7)
N2–C3	1.355(7)
N2–B1	1.539(8)
N3–N4	1.359(6)
N3–C4	1.347(7)
N4–C6	1.339(7)
N4–B1	1.543(8)
N5–N6	1.361(6)
N5–C7	1.339(7)
N6–C9	1.352(7)
N6–B1	1.544(8)
N8–C18	1.503(7)
N8–C20	1.346(7)
N8–C21	1.449(7)
C1–H1	0.9500
C1–C2	1.387(9)
C2–H2	0.9500
C2–C3	1.373(9)
C3–H3A	0.9500

C4–H4	0.9500
C4–C5	1.379(9)
C5–H5	0.9500
C5–C6	1.367(9)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.387(8)
C8–H8	0.9500
C8–C9	1.376(9)
C9–H9	0.9500
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800
C13–H13	1.0000
C13–C14	1.449(7)
C13–C18	1.508(7)
C14–H14	1.0000
C14–C15	1.470(8)
C15–H15	0.9500
C15–C16	1.326(8)
C16–H16	0.9500
C16–C17	1.522(7)
C17–H17	1.0000
C17–C18	1.550(7)
C17–C19	1.538(8)
C18–H18	1.0000
C19–H19A	0.9900
C19–H19B	0.9900
C19–C20	1.493(9)
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.520(7)
C22–C23	1.392(8)
C22–C27	1.383(8)

C23–C24	1.385(8)
C24–H24	0.9500
C24–C25	1.379(9)
C25–H25	0.9500
C25–C26	1.364(9)
C26–H26	0.9500
C26–C27	1.394(8)
C27–H27	0.9500
B1–H1A	1.07(6)
O4–C29	1.240(11)
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
C28–C29	1.533(17)
C29–C30	1.452(17)
C30–H30A	0.9800
C30–H30B	0.9800
C30–H30C	0.9800

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	159.47(12)
N1–W1–N3	75.81(16)
N1–W1–N5	85.04(17)
N1–W1–C14	119.24(18)
N3–W1–P1	84.43(11)
N3–W1–N5	82.33(17)
N3–W1–C14	161.28(18)
N5–W1–P1	86.87(11)
N7–W1–P1	91.26(14)
N7–W1–N1	94.98(19)
N7–W1–N3	92.22(18)
N7–W1–N5	174.38(17)
N7–W1–C13	97.8(2)
N7–W1–C14	97.10(19)
C13–W1–P1	117.08(14)
C13–W1–N1	81.45(18)
C13–W1–N3	155.87(17)
C13–W1–N5	87.81(18)
C13–W1–C14	37.97(19)

C14–W1–P1	79.18(13)
C14–W1–N5	87.76(18)
C10–P1–W1	122.25(18)
C11–P1–W1	111.7(2)
C11–P1–C10	102.6(3)
C11–P1–C12	103.0(3)
C12–P1–W1	116.1(2)
C12–P1–C10	98.5(3)
C23–O3–H3	115(6)
N2–N1–W1	121.6(3)
C1–N1–W1	131.4(4)
C1–N1–N2	106.9(5)
N1–N2–B1	120.1(4)
C3–N2–N1	108.9(5)
C3–N2–B1	128.7(5)
N4–N3–W1	122.4(3)
C4–N3–W1	131.3(4)
C4–N3–N4	106.2(4)
N3–N4–B1	119.3(4)
C6–N4–N3	109.3(5)
C6–N4–B1	130.9(5)
N6–N5–W1	120.1(3)
C7–N5–W1	133.9(4)
C7–N5–N6	105.7(5)
N5–N6–B1	121.2(4)
C9–N6–N5	109.5(5)
C9–N6–B1	129.1(5)
O1–N7–W1	176.9(4)
C20–N8–C18	112.6(5)
C20–N8–C21	122.3(5)
C21–N8–C18	122.3(4)
N1–C1–H1	124.7
N1–C1–C2	110.5(6)
C2–C1–H1	124.7
C1–C2–H2	127.5
C3–C2–C1	104.9(5)
C3–C2–H2	127.5
N2–C3–C2	108.7(5)
N2–C3–H3A	125.6
C2–C3–H3A	125.6

N3–C4–H4	124.8
N3–C4–C5	110.3(5)
C5–C4–H4	124.8
C4–C5–H5	127.5
C6–C5–C4	104.9(5)
C6–C5–H5	127.5
N4–C6–C5	109.2(5)
N4–C6–H6	125.4
C5–C6–H6	125.4
N5–C7–H7	124.1
N5–C7–C8	111.8(5)
C8–C7–H7	124.1
C7–C8–H8	128.1
C9–C8–C7	103.8(5)
C9–C8–H8	128.1
N6–C9–C8	109.1(5)
N6–C9–H9	125.4
C8–C9–H9	125.4
P1–C10–H10A	109.5
P1–C10–H10B	109.5
P1–C10–H10C	109.5
H10A–C10–H10B	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
P1–C11–H11A	109.5
P1–C11–H11B	109.5
P1–C11–H11C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
P1–C12–H12A	109.5
P1–C12–H12B	109.5
P1–C12–H12C	109.5
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
W1–C13–H13	112.2
C14–C13–W1	72.9(3)
C14–C13–H13	112.2
C14–C13–C18	119.5(4)

C18–C13–W1	122.3(4)
C18–C13–H13	112.2
W1–C14–H14	114.6
C13–C14–W1	69.1(3)
C13–C14–H14	114.6
C13–C14–C15	117.8(5)
C15–C14–W1	118.7(4)
C15–C14–H14	114.6
C14–C15–H15	117.9
C16–C15–C14	124.2(5)
C16–C15–H15	117.9
C15–C16–H16	118.7
C15–C16–C17	122.5(5)
C17–C16–H16	118.7
C16–C17–H17	109.9
C16–C17–C18	112.5(5)
C16–C17–C19	110.5(5)
C18–C17–H17	109.9
C19–C17–H17	109.9
C19–C17–C18	104.0(4)
N8–C18–C13	112.9(5)
N8–C18–C17	101.4(4)
N8–C18–H18	108.5
C13–C18–C17	116.7(4)
C13–C18–H18	108.5
C17–C18–H18	108.5
C17–C19–H19A	110.8
C17–C19–H19B	110.8
H19A–C19–H19B	108.9
C20–C19–C17	104.7(5)
C20–C19–H19A	110.8
C20–C19–H19B	110.8
O2–C20–N8	123.9(6)
O2–C20–C19	126.4(5)
N8–C20–C19	109.6(5)
N8–C21–H21A	108.8
N8–C21–H21B	108.8
N8–C21–C22	113.8(5)
H21A–C21–H21B	107.7
C22–C21–H21A	108.8

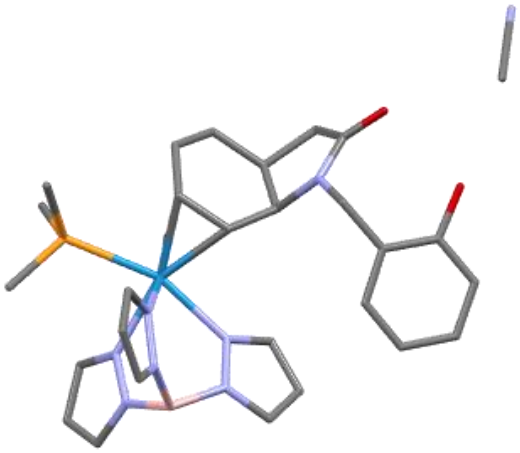
C22–C21–H21B	108.8
C23–C22–C21	122.5(5)
C27–C22–C21	119.6(5)
C27–C22–C23	117.9(5)
O3–C23–C22	123.9(5)
O3–C23–C24	115.6(5)
C24–C23–C22	120.5(5)
C23–C24–H24	119.9
C25–C24–C23	120.2(6)
C25–C24–H24	119.9
C24–C25–H25	119.8
C26–C25–C24	120.5(6)
C26–C25–H25	119.8
C25–C26–H26	120.4
C25–C26–C27	119.2(6)
C27–C26–H26	120.4
C22–C27–C26	121.7(6)
C22–C27–H27	119.2
C26–C27–H27	119.2
N2–B1–N4	106.4(5)
N2–B1–N6	109.8(5)
N2–B1–H1A	111(3)
N4–B1–N6	108.6(4)
N4–B1–H1A	110(3)
N6–B1–H1A	111(3)
H28A–C28–H28B	109.5
H28A–C28–H28C	109.5
H28B–C28–H28C	109.5
C29–C28–H28A	109.5
C29–C28–H28B	109.5
C29–C28–H28C	109.5
O4–C29–C28	121.8(11)
O4–C29–C30	121.2(14)
C30–C29–C28	117.0(13)
C29–C30–H30A	109.5
C29–C30–H30B	109.5
C29–C30–H30C	109.5
H30A–C30–H30B	109.5
H30A–C30–H30C	109.5
H30B–C30–H30C	109.5

Table 5 Torsion angles for cu_harman_ld_2_137acetone2_x3_**Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	−177.5(4)
W1–N1–N2–B1	−13.4(7)
W1–N1–C1–C2	176.7(4)
W1–N3–N4–C6	176.7(4)
W1–N3–N4–B1	4.7(6)
W1–N3–C4–C5	−177.2(4)
W1–N5–N6–C9	174.7(3)
W1–N5–N6–B1	−0.7(6)
W1–N5–C7–C8	−173.8(4)
W1–C13–C14–C15	112.4(4)
W1–C13–C18–N8	179.6(3)
W1–C13–C18–C17	−63.4(6)
W1–C14–C15–C16	73.9(6)
O3–C23–C24–C25	178.0(6)
N1–N2–C3–C2	0.8(7)
N1–N2–B1–N4	−51.9(7)
N1–N2–B1–N6	65.5(6)
N1–C1–C2–C3	0.1(8)
N2–N1–C1–C2	0.4(7)
N3–N4–C6–C5	0.8(7)
N3–N4–B1–N2	56.3(6)
N3–N4–B1–N6	−61.8(6)
N3–C4–C5–C6	1.4(7)
N4–N3–C4–C5	−1.0(7)
N5–N6–C9–C8	0.2(6)
N5–N6–B1–N2	−56.5(6)
N5–N6–B1–N4	59.5(6)
N5–C7–C8–C9	0.4(6)
N6–N5–C7–C8	−0.2(6)
N8–C21–C22–C23	−79.7(7)
N8–C21–C22–C27	100.3(6)
C1–N1–N2–C3	−0.7(7)
C1–N1–N2–B1	163.4(5)
C1–C2–C3–N2	−0.5(8)
C3–N2–B1–N4	108.7(7)
C3–N2–B1–N6	−134.0(6)

C4–N3–N4–C6	0.1(6)
C4–N3–N4–B1	−171.9(5)
C4–C5–C6–N4	−1.3(7)
C6–N4–B1–N2	−113.7(6)
C6–N4–B1–N6	128.2(6)
C7–N5–N6–C9	0.0(5)
C7–N5–N6–B1	−175.3(5)
C7–C8–C9–N6	−0.4(6)
C9–N6–B1–N2	129.2(5)
C9–N6–B1–N4	−114.8(6)
C13–C14–C15–C16	−6.3(8)
C14–C13–C18–N8	−92.8(6)
C14–C13–C18–C17	24.2(7)
C14–C15–C16–C17	−2.0(9)
C15–C16–C17–C18	20.2(8)
C15–C16–C17–C19	136.0(6)
C16–C17–C18–N8	92.9(5)
C16–C17–C18–C13	−30.2(7)
C16–C17–C19–C20	−97.0(5)
C17–C19–C20–O2	171.7(5)
C17–C19–C20–N8	−11.6(6)
C18–N8–C20–O2	170.3(5)
C18–N8–C20–C19	−6.6(6)
C18–N8–C21–C22	−69.9(6)
C18–C13–C14–W1	−118.0(5)
C18–C13–C14–C15	−5.6(7)
C18–C17–C19–C20	24.0(6)
C19–C17–C18–N8	−26.7(5)
C19–C17–C18–C13	−149.9(5)
C20–N8–C18–C13	147.2(5)
C20–N8–C18–C17	21.5(6)
C20–N8–C21–C22	90.0(6)
C21–N8–C18–C13	−51.2(6)
C21–N8–C18–C17	−176.9(5)
C21–N8–C20–O2	8.6(8)
C21–N8–C20–C19	−168.2(5)
C21–C22–C23–O3	2.3(10)
C21–C22–C23–C24	−176.9(6)
C21–C22–C27–C26	179.5(6)
C22–C23–C24–C25	−2.7(10)

C23–C22–C27–C26	−0.5(9)
C23–C24–C25–C26	−0.4(10)
C24–C25–C26–C27	2.9(10)
C25–C26–C27–C22	−2.5(10)
C27–C22–C23–O3	−177.7(6)
C27–C22–C23–C24	3.1(9)
B1–N2–C3–C2	−161.5(6)
B1–N4–C6–C5	171.5(6)
B1–N6–C9–C8	175.1(5)

Structure Report for compound 4.17



A ?, plate shaped crystal of harman_ld_2_137_x2 measuring 0.058×0.096×0.149 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for harman_ld_2_137_x2 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800 low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[59] All data were integrated with the Bruker

[59] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.

SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[60] and refined by full-matrix least-squares methods against F^2 using XL[61] within OLEX2.[62] All non-hydrogen atoms were refined with anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.

[60] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[61] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[62] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table 1 Crystal data and structure refinement for compound 4.17

CCDC number	
Empirical formula	$C_{29}H_{37}BN_9O_3PW$
Formula weight	785.30
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.058×0.096×0.149
Crystal habit	? plate
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
a [Å]	13.3840(4)
b [Å]	24.2740(6)
c [Å]	9.6958(3)
α [°]	90
β [°]	94.5760(10)
γ [°]	90
Volume [$Å^3$]	3139.96(16)
Z	4
ρ_{calc} [gcm^{-3}]	1.661
μ [mm^{-1}]	3.777
F(000)	1568
2θ range [°]	4.54 to 50.74 (0.83 Å)
Index ranges	−16 ≤ h ≤ 16 −27 ≤ k ≤ 29 −11 ≤ l ≤ 11
Reflections collected	128682
Independent reflections	5760 [R_{int} = 0.0824]
Data / Restraints / Parameters	5760 / 0 / 409
Goodness-of-fit on F^2	1.108
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0257 wR_2 = 0.0548

Final *R* indexes [all data]	R_1 = 0.0320 wR_2 = 0.0571
Largest peak/hole [eÅ^{-3}]	0.96/−1.12

Table 2 Atomic coordinates and Ueq [Å^2] for compound 4.17

Atom	***x***	***y***	***z***	U_{eq}
W1	0.75455(2)	0.43760(2)	0.71954(2)	0.01013(5)
P1	0.77764(7)	0.53565(4)	0.64828(10)	0.01426(19)
O1	0.7188(2)	0.47473(11)	1.0063(3)	0.0197(6)
O2	0.28738(19)	0.33496(10)	0.7585(3)	0.0205(6)
O3	0.3272(2)	0.22690(12)	0.7304(3)	0.0268(7)
H3	0.312(4)	0.262(2)	0.724(5)	0.034(13)
N1	0.9198(2)	0.43835(12)	0.7591(3)	0.0141(6)
N2	0.9794(2)	0.39919(12)	0.7062(3)	0.0140(6)
N3	0.7924(2)	0.35176(12)	0.7773(3)	0.0131(6)
N4	0.8601(2)	0.32224(12)	0.7099(3)	0.0149(6)
N5	0.7942(2)	0.41366(12)	0.5073(3)	0.0142(6
N6	0.8710(2)	0.37734(11)	0.4908(3)	0.0141(6)
N7	0.7319(2)	0.45894(11)	0.8899(3)	0.0120(6)
N8	0.4481(2)	0.35165(11)	0.7075(3)	0.0136(6)
C1	0.9812(3)	0.46986(15)	0.8413(4)	0.0179(8)
H1	0.960194	0.500481	0.892777	0.021
C2	1.0795(3)	0.45185(15)	0.8414(4)	0.0204(8)
H2	1.137270	0.467283	0.890034	0.024
C3	1.0749(3)	0.40668(15)	0.7553(4)	0.0177(8)
H3A	1.130207	0.384515	0.734274	0.021
C4	0.7654(3)	0.32047(15)	0.8807(4)	0.0177(8)
H4	0.719695	0.331308	0.945742	0.0
C5	0.8136(3)	0.2695(16)	0.8804(4)	0.0213(8)
H5	0.806694	0.239552	0.941698	0.026
C6	0.8733(3)	0.27241(15)	0.7719(4)	0.0194(8)
H6	0.916670	0.244128	0.744734	0.023
C7	0.7648(3)	0.43148(14)	0.3802(4)	0.0174(8)
H7	0.712303	0.457304	0.360020	0.021
C8	0.8204(3)	0.40758(15)	0.2815(4)	0.0197(8)
H8	0.813835	0.413265	0.184291	0.024
C9	0.8872(3)	0.37372(15)	0.3561(4)	0.0174(8)

H9	0.936747	0.351459	0.318521	0.021
C10	0.8988(3)	0.55258(16)	0.5864(5)	0.0272(10)
H10A	0.951925	0.544744	0.659218	0.041
H10B	0.900236	0.591759	0.562257	0.041
H10C	0.909374	0.530360	0.504472	0.04
C11	0.7671(3)	0.58292(15)	0.7917(4)	0.0230(9)
H11A	0.70122	0.578575	0.827955	0.034
H11B	0.774576	0.62088	0.759546	0.034
H11C	0.819701	0.574834	0.865068	0.034
C12	0.6977(3)	0.56753(15)	0.5091(4)	0.0195(8
H12A	0.706983	0.548645	0.421752	0.029
H12B	0.715773	0.606454	0.501144	0.029
H12C	0.627410	0.564597	0.529861	0.029
C13	0.5999(3)	0.4575(15)	0.6258(4)	0.0144(7)
H13	0.594999	0.463817	0.523617	0.017
C14	0.6077(3)	0.40002(14)	0.6663(4)	0.0129(7)
H14	0.608931	0.375249	0.584051	0.015
C15	0.5427(3)	0.37706(14)	0.7716(4)	0.0126(7)
H15	0.581483	0.348185	0.826455	0.015
C16	0.5014(3)	0.41918(15)	0.8737()	0.0162(8)
H16	0.54629	0.420163	0.961199	0.019
C17	0.4908(3)	0.47636(15)	0.8138(4)	0.0164(8)
H17	0.449818	0.501904	0.857511	0.020
C18	0.5352(3)	0.49316(14)	0.7042(4)	0.0152(8)
H18	0.524996	0.530139	0.674252	0.018
C19	0.3988(3)	0.39516(16)	0.9029(4)	0.0195(8)
H19A	0.403842	0.374025	0.990545	0.023
H19B	0.348794	0.424907	0.909597	0.023
C20	0.3698(3)	0.35817(14)	0.7825(4)	0.0168(8)
C21	0.4485(3)	0.30982(14)	0.5990(4)	0.0157(7)
H21A	0.490403	0.323068	0.526108	0.019
H21B	0.379313	0.305141	0.556386	0.019
C22	0.4873(3)	0.25480(15)	0.6500(4)	0.0158(7)
C23	0.5870(3)	0.24035(16)	0.6387(4)	0.0222(8)
H23	0.630359	0.265867	0.599156	0.027
C24	0.6247(3)	0.18974(16)	0.6838(4)	0.0222(8)
H24	0.693328	0.181048	0.677127	0.027
C25	0.5615(3)	0.15212(16)	0.7383(4)	0.0222(9)
H25	0.586235	0.116920	0.766954	0.027

C26	0.4623(3)	0.16532(15)	0.7515(4)	0.0206(8)
H26	0.419147	0.139129	0.788771	0.025
C27	0.4255(3)	0.21681(15)	0.7104(4)	0.0171(8)
B1	0.9310(3)	0.35234(17)	0.6171(4)	0.0153(8)
H1A	0.990(3)	0.3244(14)	0.584(4)	0.010(9)
N9	0.0566(3)	0.31011(17)	1.1622(5)	0.0429(10)
C28	0.1476(4)	0.2663(2)	0.9636(5)	0.0440(13)
H28A	0.098295	0.253644	0.890235	0.066
H28B	0.187418	0.234936	1.000104	0.066
H28C	0.191842	0.293658	0.925808	0.066
C29	0.0955(3)	0.29128(19)	1.0748(5)	0.0315(10)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 4.17

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.00949(8)	0.01025(7)	0.01051(8)	0.00061(6)	−0.00016(5)	0.00062(6)
P1	0.0136(5)	0.0132(4)	0.0157(5)	0.0014(4)	−0.0005(4)	−0.0009(4)
O1	0.0215(14)	0.0255(14)	0.0121(13)	−0.0047(11)	0.0014(11)	0.0010(11)
O2	0.0116(13)	0.0205(13)	0.0299(15)	0.0017(11)	0.0055(11)	−0.0003(11)
O3	0.0171(15)	0.0206(15)	0.0436(19)	0.0029(13)	0.0079(13)	−0.0027(12)
N1	0.0127(15)	0.0151(14)	0.0142(15)	−0.0026(12)	0.0005(12)	0.0026(12)
N2	0.0130(15)	0.0146(14)	0.0148(15)	0.0023(12)	0.0027(12)	0.0021(12)
N3	0.0107(15)	0.0161(15)	0.0129(15)	−0.0002(12)	0.0029(12)	0.0037(12)
N4	0.0139(15)	0.0125(14)	0.0183(16)	0.0004(12)	0.0022(12)	0.0022(12)
N5	0.0134(15)	0.0134(14)	0.0157(16)	0.0011(12)	0.0010(12)	−0.0009(12)
N6	0.0138(15)	0.0117(14)	0.0174(16)	−0.0023(12)	0.0041(12)	−0.0024(12)
N7	0.0150(15)	0.0108(13)	0.0100(15)	−0.0028(11)	−0.0001(12)	−0.0002(12)

N8	0.0127(15)	0.0094(14)	0.0184(16)	0.0002(12)	−0.0003(12)	0.0003(11)
C1	0.018(2)	0.0194(19)	0.0153(19)	−0.0027(15)	−0.0018(15)	−0.0010(15)
C2	0.0148(19)	0.023(2)	0.022(2)	0.0019(16)	−0.0064(16)	−0.0036(15)
C3	0.0085(18)	0.025(2)	0.020(2)	0.0020(16)	0.0007(15)	0.0005(15)
C4	0.0105(18)	0.027(2)	0.0159(19)	0.0040(16)	0.0008(14)	0.0002(15)
C5	0.018(2)	0.0209(19)	0.025(2)	0.0123(16)	0.0012(16)	0.0038(16)
C6	0.019(2)	0.0137(17)	0.025(2)	0.0032(15)	0.0013(16)	0.0045(15)
C7	0.0182(19)	0.0148(17)	0.0185(19)	0.0028(15)	−0.0026(15)	−0.0043(15)
C8	0.024(2)	0.0215(19)	0.0132(19)	−0.0031(15)	0.0010(16)	−0.0079(16)
C9	0.021(2)	0.0159(18)	0.0164(19)	−0.0050(15)	0.0062(15)	−0.0063(15)
C10	0.016(2)	0.026(2)	0.040(3)	0.0152(19)	0.0040(18)	−0.0043(16)
C11	0.033(2)	0.0130(17)	0.022(2)	−0.0025(16)	−0.0045(18)	0.0034(16)
C12	0.021(2)	0.0167(18)	0.020(2)	0.0058(15)	−0.0031(16)	0.0002(15)
C13	0.0141(18)	0.0187(18)	0.0099(17)	0.0025(14)	−0.0021(14)	−0.0012(14)
C14	0.0118(18)	0.0150(17)	0.0117(17)	−0.0037(14)	−0.0004(14)	0.0008(14)
C15	0.0112(18)	0.0140(17)	0.0123(17)	0.0013(14)	−0.0008(14)	0.0018(14)
C16	0.0175(19)	0.0178(18)	0.0133(18)	−0.0028(14)	0.0019(15)	0.0028(15)
C17	0.0119(18)	0.0161(18)	0.0208(19)	−0.0045(15)	−0.0007(15)	0.0047(14)
C18	0.0119(18)	0.0120(17)	0.021(2)	−0.0016(14)	−0.0036(15)	−0.0009(14)
C19	0.020(2)	0.0218(19)	0.0168(19)	0.0023(16)	0.0043(16)	0.0022(16)
C20	0.017(2)	0.0163(18)	0.0181(19)	0.0080(15)	0.0055(15)	0.0054(15)
C21	0.0168(18)	0.0167(17)	0.0138(18)	0.0007(15)	0.0021(14)	−0.0029(15)

C22	0.0183(19)	0.0172(18)	0.0115(18)	0.0001(14)	−0.0010(14)	−0.0012(15)
C23	0.018(2)	0.025(2)	0.024(2)	−0.0026(17)	0.0050(16)	−0.0024(16)
C24	0.019(2)	0.023(2)	0.024(2)	−0.0032(17)	0.0009(16)	0.0052(16)
C25	0.033(2)	0.0179(19)	0.0148(19)	−0.0026(15)	−0.0020(17)	0.0041(17)
C26	0.027(2)	0.0174(18)	0.018(2)	−0.0018(15)	0.0012(16)	−0.0060(16)
C27	0.0171(19)	0.0179(18)	0.0155(19)	−0.0026(15)	−0.0027(15)	−0.0010(15)
B1	0.013(2)	0.016(2)	0.017(2)	−0.0028(16)	0.0010(17)	0.0035(16)
N9	0.040(2)	0.040(2)	0.051(3)	−0.011(2)	0.021(2)	−0.011(2)
C28	0.036(3)	0.064(3)	0.033(3)	−0.005(2)	0.014(2)	−0.014(2)
C29	0.029(2)	0.034(2)	0.032(2)	0.001(2)	0.011(2)	−0.0115(19)

Table 4 Bond lengths and angles compound 4.17

Atom–Atom	**Length [Å]**
W1–P1	2.5042(9)
W1–N1	2.214(3)
W1–N3	2.206(3)
W1–N5	2.243(3)
W1–N7	1.780(3)
W1–C13	2.245(4)
W1–C14	2.191(3)
P1–C10	1.820(4)
P1–C11	1.817(4)
P1–C12	1.826(4)
O1–N7	1.218(4)
O2–C20	1.244(5)
O3–H3	0.87(5)
O3–C27	1.368(5)
N1–N2	1.367(4)

N1–C1	1.338(5)
N2–C3	1.341(5)
N2–B1	1.539(5)
N3–N4	1.362(4)
N3–C4	1.331(5)
N4–C6	1.356(5)
N4–B1	1.543(5)
N5–N6	1.373(4)
N5–C7	1.335(5)
N6–C9	1.343(5)
N6–B1	1.536(5)
N8–C15	1.498(4)
N8–C20	1.332(5)
N8–C21	1.463(4)
C1–H1	0.9500
C1–C2	1.387(5)
C2–H2	0.9500
C2–C3	1.376(5)
C3–H3A	0.9500
C4–H4	0.9500
C4–C5	1.394(5)
C5–H5	0.9500
C5–C6	1.372(5)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.386(5)
C8–H8	0.9500
C8–C9	1.377(5)
C9–H9	0.9500
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800
C13–H13	1.0000
C13–C14	1.445(5)

C13–C18	1.481(5)
C14–H14	1.0000
C14–C15	1.500(5)
C15–H15	1.0000
C15–C16	1.555(5)
C16–H16	1.0000
C16–C17	1.507(5)
C16–C19	1.540(5)
C17–H17	0.9500
C17–C18	1.322(5)
C18–H18	0.9500
C19–H19A	0.9900
C19–H19B	0.9900
C19–C20	1.499(5)
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.503(5)
C22–C23	1.392(5)
C22–C27	1.398(5)
C23–H23	0.9500
C23–C24	1.385(5)
C24–H24	0.9500
C24–C25	1.379(6)
C25–H25	0.9500
C25–C26	1.380(6)
C26–H26	0.9500
C26–C27	1.390(5)
B1–H1A	1.11(4)
N9–C29	1.126(6)
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
C28–C29	1.461(6)

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	84.06(8)
N1–W1–N5	81.67(11)
N1–W1–C13	160.81(12)
N3–W1–P1	159.51(8)

N3–W1–N1	75.98(11)
N3–W1–N5	85.50(10)
N3–W1–C13	119.29(12)
N5–W1–P1	87.12(8)
N5–W1–C13	87.79(12)
N7–W1–P1	90.76(9)
N7–W1–N1	94.52(12)
N7–W1–N3	95.29(12)
N7–W1–N5	175.80(12)
N7–W1–C13	95.39(13)
N7–W1–C14	97.09(13)
C13–W1–P1	79.42(9)
C14–W1–P1	117.31(9)
C14–W1–N1	155.38(12)
C14–W1–N3	81.38(12)
C14–W1–N5	87.10(12)
C14–W1–C13	38.00(13)
C10–P1–W1	116.00(13)
C10–P1–C12	98.38(19)
C11–P1–W1	111.72(13)
C11–P1–C10	103.6(2)
C11–P1–C12	102.77(18)
C12–P1–W1	121.92(12)
C27–O3–H3	112(3)
N2–N1–W1	122.3(2)
C1–N1–W1	131.7(2)
C1–N1–N2	105.8(3)
N1–N2–B1	119.5(3)
C3–N2–N1	109.9(3)
C3–N2–B1	130.2(3)
N4–N3–W1	121.6(2)
C4–N3–W1	131.3(2)
C4–N3–N4	107.0(3)
N3–N4–B1	119.6(3)
C6–N4–N3	108.9(3)
C6–N4–B1	128.1(3)
N6–N5–W1	120.5(2)
C7–N5–W1	133.5(3)
C7–N5–N6	105.6(3)
N5–N6–B1	120.6(3)

C9–N6–N5	109.6(3)
C9–N6–B1	129.4(3)
O1–N7–W1	177.9(3)
C20–N8–C15	113.6(3)
C20–N8–C21	121.6(3)
C21–N8–C15	122.2(3)
N1–C1–H1	124.5
N1–C1–C2	111.0(3)
C2–C1–H1	124.5
C1–C2–H2	127.6
C3–C2–C1	104.8(3)
C3–C2–H2	127.6
N2–C3–C2	108.6(3)
N2–C3–H3A	125.7
C2–C3–H3A	125.7
N3–C4–H4	124.8
N3–C4–C5	110.5(3)
C5–C4–H4	124.8
C4–C5–H5	127.6
C6–C5–C4	104.8(3)
C6–C5–H5	127.6
N4–C6–C5	108.8(3)
N4–C6–H6	125.6
C5–C6–H6	125.6
N5–C7–H7	124.3
N5–C7–C8	111.5(3)
C8–C7–H7	124.3
C7–C8–H8	127.8
C9–C8–C7	104.5(3)
C9–C8–H8	127.8
N6–C9–C8	108.8(3)
N6–C9–H9	125.6
C8–C9–H9	125.6
P1–C10–H10A	109.5
P1–C10–H10B	109.5
P1–C10–H10C	109.5
H10A–C10–H10B	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
P1–C11–H11A	109.5

P1–C11–H11B	109.5
P1–C11–H11C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
P1–C12–H12A	109.5
P1–C12–H12B	109.5
P1–C12–H12C	109.5
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
W1–C13–H13	114.8
C14–C13–W1	68.98(19)
C14–C13–H13	114.8
C14–C13–C18	117.3(3)
C18–C13–W1	118.4(2)
C18–C13–H13	114.8
W1–C14–H14	111.5
C13–C14–W1	73.0(2)
C13–C14–H14	111.5
C13–C14–C15	120.6(3)
C15–C14–W1	123.5(2)
C15–C14–H14	111.5
N8–C15–C14	112.8(3)
N8–C15–H15	108.5
N8–C15–C16	101.7(3)
C14–C15–H15	108.5
C14–C15–C16	116.3(3)
C16–C15–H15	108.5
C15–C16–H16	109.7
C17–C16–C15	112.8(3)
C17–C16–H16	109.7
C17–C16–C19	111.2(3)
C19–C16–C15	103.6(3)
C19–C16–H16	109.7
C16–C17–H17	118.0
C18–C17–C16	124.0(3)
C18–C17–H17	118.0
C13–C18–H18	118.3
C17–C18–C13	123.3(3)

C17–C18–H18	118.3
C16–C19–H19A	110.7
C16–C19–H19B	110.7
H19A–C19–H19B	108.8
C20–C19–C16	105.2(3)
C20–C19–H19A	110.7
C20–C19–H19B	110.7
O2–C20–N8	124.6(4)
O2–C20–C19	126.0(3)
N8–C20–C19	109.3(3)
N8–C21–H21A	108.8
N8–C21–H21B	108.8
N8–C21–C22	113.7(3)
H21A–C21–H21B	107.7
C22–C21–H21A	108.8
C22–C21–H21B	108.8
C23–C22–C21	120.4(3)
C23–C22–C27	118.0(3)
C27–C22–C21	121.6(3)
C22–C23–H23	119.2
C24–C23–C22	121.7(4)
C24–C23–H23	119.2
C23–C24–H24	120.3
C25–C24–C23	119.3(4)
C25–C24–H24	120.3
C24–C25–H25	119.8
C24–C25–C26	120.4(4)
C26–C25–H25	119.8
C25–C26–H26	119.9
C25–C26–C27	120.2(4)
C27–C26–H26	119.9
O3–C27–C22	123.3(3)
O3–C27–C26	116.3(3)
C26–C27–C22	120.3(4)
N2–B1–N4	105.9(3)
N2–B1–H1A	109.7(19)
N4–B1–H1A	111.4(18)
N6–B1–N2	109.0(3)
N6–B1–N4	110.2(3)
N6–B1–H1A	110.5(19)

H28A–C28–H28B	109.5
H28A–C28–H28C	109.5
H28B–C28–H28C	109.5
C29–C28–H28A	109.5
C29–C28–H28B	109.5
C29–C28–H28C	109.5
N9–C29–C28	178.8(6)

Table 1 Torsion angles for compound 4.17 2

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
W1–N1–N2–C3	−174.8(2)
W1–N1–N2–B1	−0.7(4)
W1–N1–C1–C2	174.7(3)
W1–N3–N4–C6	176.3(2)
W1–N3–N4–B1	15.4(4)
W1–N3–C4–C5	−176.2(3)
W1–N5–N6–C9	−173.8(2)
W1–N5–N6–B1	0.1(4)
W1–N5–C7–C8	172.9(2)
W1–C13–C14–C15	119.4(3)
W1–C13–C18–C17	−74.7(4)
W1–C14–C15–N8	−177.6(2)
W1–C14–C15–C16	65.4(4)
N1–N2–C3–C2	−0.6(4)
N1–N2–B1–N4	−59.1(4)
N1–N2–B1–N6	59.4(4)
N1–C1–C2–C3	−0.8(4)
N2–N1–C1–C2	0.4(4)
N3–N4–C6–C5	0.0(4)
N3–N4–B1–N2	50.9(4)
N3–N4–B1–N6	−66.8(4)
N3–C4–C5–C6	1.3(4)
N4–N3–C4–C5	−1.3(4)
N5–N6–C9–C8	−0.4(4)
N5–N6–B1–N2	−58.9(4)
N5–N6–B1–N4	56.9(4)

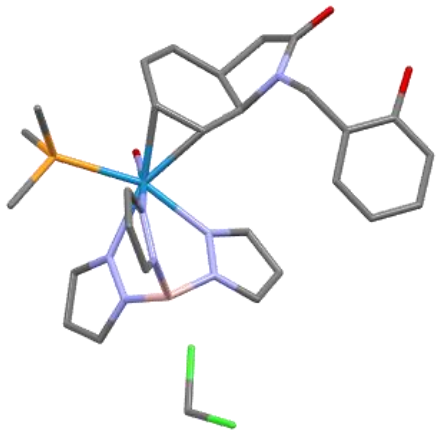
N5–C7–C8–C9	−0.4(4)
N6–N5–C7–C8	0.1(4)
N8–C15–C16–C17	−95.7(3)
N8–C15–C16–C19	24.7(3)
N8–C21–C22–C23	−96.3(4)
N8–C21–C22–C27	83.4(4)
C1–N1–N2–C3	0.1(4)
C1–N1–N2–B1	174.2(3)
C1–C2–C3–N2	0.8(4)
C3–N2–B1–N4	113.6(4)
C3–N2–B1–N6	−127.9(4)
C4–N3–N4–C6	0.7(4)
C4–N3–N4–B1	−160.1(3)
C4–C5–C6–N4	−0.8(4)
C6–N4–B1–N2	−105.9(4)
C6–N4–B1–N6	136.4(4)
C7–N5–N6–C9	0.2(4)
C7–N5–N6–B1	174.1(3)
C7–C8–C9–N6	0.5(4)
C9–N6–B1–N2	113.7(4)
C9–N6–B1–N4	−130.5(3)
C13–C14–C15–N8	93.3(4)
C13–C14–C15–C16	−23.7(5)
C14–C13–C18–C17	4.9(5)
C14–C15–C16–C17	27.3(4)
C14–C15–C16–C19	147.7(3)
C15–N8–C20–O2	−170.8(3)
C15–N8–C20–C19	6.4(4)
C15–N8–C21–C22	71.7(4)
C15–C16–C17–C18	−17.0(5)
C15–C16–C19–C20	−22.1(4)
C16–C17–C18–C13	0.8(6)
C16–C19–C20–O2	−172.3(3)
C16–C19–C20–N8	10.6(4)
C17–C16–C19–C20	99.4(3)
C18–C13–C14–W1	−112.0(3)
C18–C13–C14–C15	7.4(5)
C19–C16–C17–C18	−133.0(4)
C20–N8–C15–C14	−145.5(3)
C20–N8–C15–C16	−20.2(4)

C20–N8–C21–C22	−88.7(4)
C21–N8–C15–C14	52.6(4)
C21–N8–C15–C16	178.0(3)
C21–N8–C20–O2	−8.8(5)
C21–N8–C20–C19	168.3(3)
C21–C22–C23–C24	−179.4(3)
C21–C22–C27–O3	−1.4(5)
C21–C22–C27–C26	177.3(3)
C22–C23–C24–C25	1.5(6)
C23–C22–C27–O3	178.2(3)
C23–C22–C27–C26	−3.0(5)
C23–C24–C25–C26	−1.8(6)
C24–C25–C26–C27	−0.3(6)
C25–C26–C27–O3	−178.4(3)
C25–C26–C27–C22	2.8(6)
C27–C22–C23–C24	0.9(6)
B1–N2–C3–C2	−173.9(3)
B1–N4–C6–C5	158.8(4)
B1–N6–C9–C8	−173.6(3)

Table 5 Hydrogen bonds for compound 4.17

D–H···A [Å]	**d(D–H) [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(DHA) [°]**
O3–H3···O2	0.87(5)	1.84(5)	2.695(4)	166(5)

Structure Report for compound 4.17



A ?, block shaped crystal of compound 4.17
measuring 0.048×0.091×0.153 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for harman_ld_2_137 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_{α}, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[63] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[64] and refined by full-matrix least-squares methods against F^2 using XL[65] within OLEX2.[66] All non-hydrogen atoms were refined with anisotropically. The B-H and O-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[67]

[63] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[64] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[65] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[66] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[67] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for compound 4.17

CCDC number	
Empirical formula	$C_{28}H_{36}BCl_2N_8O_3PW$
Formula weight	829.18
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.048×0.091×0.153
Crystal habit	? block
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
a [Å]	13.4697(4)
b [Å]	24.0362(6)
c [Å]	9.7338(2)
α [°]	90
β [°]	94.3460(10)
γ [°]	90
Volume [$Å^3$]	3142.36(14)
Z	4
ρ_{calc} [gcm^{-3}]	1.753
μ [mm^{-1}]	3.942
F(000)	1648
2θ range [°]	4.53 to 56.62 (0.75 Å)
Index ranges	−17 ≤ h ≤ 17 −32 ≤ k ≤ 32 −12 ≤ l ≤ 12
Reflections collected	171781
Independent reflections	7806 [R_{int} = 0.0471]
Data / Restraints / Parameters	7806 / 0 / 408
Goodness-of-fit on F^2	1.052
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0204 wR_2 = 0.0509
Final *R* indexes [all data]	R_1 = 0.0235 wR_2 = 0.0529

Largest peak/hole [eÅ^{-3}]	0.95/−1.32

Table 2 Atomic coordinates and Ueq [Å^2] for compound 4.17

Atom	***x***	***y***	***z***	U_{eq}
B1	0.9305(2)	0.35142(11)	0.6156(3)	0.0161(5)
H1	0.990(2)	0.3226(12)	0.583(3)	0.016(7)
C1	0.7645(2)	0.43094(10)	0.3784(3)	0.0175(5)
H1A	0.711692	0.456518	0.358012	0.021
C2	0.8211(2)	0.40691(11)	0.2801(3)	0.0198(5)
H2	0.814983	0.412348	0.183140	0.024
C3	0.88826(19)	0.37331()	0.350(3)	0.0180(5)
H3	0.938267	0.351085	0.319350	0.022
C4	0.76110(19)	0.31729(11)	0.8728(3)	0.0187(5)
H4	0.714628	0.327568	0.936955	0.022
C5	0.8063(2)	0.26549(11)	0.8678(3)	0.0226(5)
H5	0.79697	0.234228	0.925120	0.027
C6	0.8680(2)	0.26945(11)	0.7611(3)	0.0219(5)
H6	0.909969	0.240804	0.731319	0.026
C7	0.97987(19)	0.46971(11)	0.8412(3)	0.0177(5)
H7	0.958772	0.500246	0.893703	0.021
C8	1.07839(19)	0.45191(11)	0.8388(3)	0.0201(5)
H8	1.135933	0.467564	0.886325	0.024
C9	1.07351(18)	0.40665(11)	0.7521(3)	0.0182(5)
H9	1.128559	0.384643	0.729524	0.022
C10	0.9002(2)	0.55238(12)	0.5847(3)	0.0263(6)
H10A	0.952385	0.545225	0.658312	0.039
H10B	0.901857	0.591669	0.558056	0.039
H10C	0.911524	0.529047	0.504843	0.039
C11	0.7691(2)	0.58417(11)	0.7882(3)	0.0242(6)
H11A	0.704773	0.578952	0.827289	0.036
H11B	0.773984	0.622445	0.754699	0.036
H11C	0.823025	0.577069	0.859323	0.036
C12	0.7010(2)	0.56819(10)	0.5063(3)	0.0189(5)
H12A	0.710873	0.548934	0.419587	0.028
H12B	0.719366	0.607441	0.498068	0.028
H12C	0.630953	0.565446	0.526130	0.028
C13	0.60105(17)	0.45798(10)	0.6250(2)	0.0143(4)

H13	0.596562	0.464438	0.523188	0.017
C14	0.60802(17)	0.40011(10)	0.6659(2)	0.0136(4)
H14	0.608738	0.374805	0.584434	0.016
C15	0.54277(17)	0.37776(10)	0.7727(2)	0.0131(4)
H15	0.580366	0.348205	0.827021	0.016
C16	0.50472(18)	0.4219(10)	0.8744(2)	0.0152(4)
H16	0.551218	0.422659	0.959448	0.018
C17	0.49320(18)	0.47840(10)	0.8133(3)	0.0166(5
H17	0.452051	0.504343	0.855849	0.020
C18	0.53775(18)	0.49467(10)	0.7023(3)	0.0158(5)
H18	0.528132	0.531912	0.671423	0.019
C19	0.40394(19)	0.39742(11)	0.9100(3)	0.0183(5)
H19A	0.411202	0.376072	0.997130	0.022
H19B	0.355009	0.427641	0.919556	0.02
C20	0.37152(18)	0.36008(10)	0.7912(3)	0.0161(5)
C21	0.44490(18)	0.31148(10)	0.6022(2)	0.0150(4)
H21A	0.484712	0.324844	0.527381	0.018
H21B	0.375306	0.306912	0.563319	0.018
C22	0.48458(18)	0.25552(10)	0.6516(2)	0.0152(4)
C23	0.5828(2)	0.24066(11)	0.6342(3)	0.0199(5)
H23	0.624634	0.266329	0.591977	0.024
C24	0.6210(2)	0.18933(11)	0.6768(3)	0.0218(5)
H24	0.688654	0.180354	0.665662	0.026
C25	0.5595(2)	0.15130(11)	0.7357(3)	0.0210(5)
H25	0.584495	0.115733	0.763323	0.025
C26	0.4619(2)	0.16511(11)	0.7544(3)	0.0197(5)
H26	0.419994	0.138812	0.794302	0.024
C27	0.42416(19)	0.21733(10)	0.7151(3)	0.0168(5)
N1	0.79439(15)	0.41327(9)	0.5057(2)	0.0146(4)
N2	0.87123(15)	0.37722(8)	0.4900(2)	0.0150(4)
N3	0.79191(15)	0.35067(9)	0.7750(2)	0.0151(4)
N	0.85853(16)	0.32093(8)	0.7064(2)	0.0162(4)
N5	0.91907(15)	0.43766(8)	0.7591(2)	0.0139(4
N6	0.97822(15)	0.39856(9)	0.7044(2)	0.0155(4)
N7	0.73314(15)	0.45885(8)	0.8877(2)	0.0139(4)
N8	0.44763(15)	0.35345(8)	0.7113(2)	0.0134(4)
O1	0.72149(14)	0.47511(8)	1.00531(18)	0.0204(4)
O2	0.28934(14)	0.33668(8)	0.7716(2)	0.0208(4)
O3	0.32757(15)	0.22728(9)	0.7387(2)	0.0245(4)

H3A	0.317(3	0.2585(17)	0.742(4)	0.032(10)
P1	0.779115)	0.53604(3)	0.64598(6)	0.01392(12)
W1	0.75480(2)	0.43735(2)	0.71858(2)	0.01115(3)
C28	1.1399(3)	0.29719(18)	1.0035(4)	0.0427(8)
H28A	1.178183	0.284592	1.088644	0.051
H28B	1.179855	0.325804	0.959534	0.051
Cl1	1.02603(7)	0.32680(4)	1.04626(9)	0.0394(18)
Cl2	1.11983(8)	0.24008(5)	0.88985(13)	0.0581(3)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 4.17

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0166(13)	0.0145(12)	0.0173(12)	0.0006(10)	0.0018(10)	0.0008(10)
C1	0.0197(12)	0.0155(11)	0.0169(11)	0.0017(9)	−0.0018(9)	−0.0029(9)
C2	0.0251(13)	0.0198(12)	0.0144(11)	−0.0009(9)	0.0012(10)	−0.0062(10)
C3	0.0204(12)	0.0164(11)	0.0176(11)	−0.0042(9)	0.0051(9)	−0.0058(9)
C4	0.0158(11)	0.0214(12)	0.0187(11)	0.0056(10)	−0.0005(9)	−0.0003(9)
C5	0.0226(13)	0.0182(12)	0.0271(13)	0.0092(10)	0.0024(10)	0.0017(10)
C6	0.0249(13)	0.0143(11)	0.0265(13)	0.0041(10)	0.0017(10)	0.0037(10)
C7	0.0173(12)	0.0173(11)	0.0181(11)	0.0002(9)	−0.0020(9)	−0.0006(9)
C8	0.0142(12)	0.0241(12)	0.0212(12)	0.0046(10)	−0.0037(9)	−0.0023(10)
C9	0.0118(11)	0.0236(12)	0.0191(11)	0.0050(10)	0.0011(9)	0.0025(9)
C10	0.0181(13)	0.0274(14)	0.0337(15)	0.0126(12)	0.0037(11)	−0.0024(11)
C11	0.0368(16)	0.0145(12)	0.0204(12)	−0.0020(10)	−0.0030(11)	0.0023(11)
C12	0.0216(12)	0.0158(11)	0.0186(12)	0.0054(9)	−0.0023(10)	−0.0002(9)
C13	0.0122(11)	0.0164(11)	0.0140(10)	0.0008(9)	−0.0006(8)	−0.0002(9)
C14	0.0125(10)	0.0143(10)	0.0139(10)	−0.0015(8)	0.0002(8)	−0.0005(8)
C15	0.0121(10)	0.0131(10)	0.0138(10)	−0.0005(8)	0.0001(8)	0.0005(8)
C16	0.0155(11)	0.0164(11)	0.0138(10)	−0.0017(9)	0.0019(9)	0.0019(9)
C17	0.0148(11)	0.0145(11)	0.0200(12)	−0.0031(9)	−0.0009(9)	0.0016(9)
C18	0.0122(11)	0.0141(11)	0.0205(11)	0.0000(9)	−0.0036(9)	0.0009(8)
C19	0.0189(12)	0.0203(12)	0.0164(11)	0.0000(9)	0.0059(9)	0.0003(10)

C20	0.0141(11)	0.0145(11)	0.0200(11)	0.0030(9)	0.0025(9)	0.0021(9)
C21	0.0159(11)	0.0136(10)	0.0154(10)	−0.0002(9)	0.0000(8)	−0.0005(9)
C22	0.0155(11)	0.0157(11)	0.0140(10)	−0.0025(9)	−0.0002(8)	−0.0008(9)
C23	0.0194(12)	0.0199(12)	0.0210(12)	−0.0005(10)	0.0052(10)	−0.0014(10)
C24	0.0188(12)	0.0221(12)	0.0246(13)	−0.0036(11)	0.0028(10)	0.0039(10)
C25	0.0268(14)	0.0152(11)	0.0203(12)	−0.0012(9)	−0.0022(10)	0.0045(10)
C26	0.0249(13)	0.0168(11)	0.0171(11)	0.0001(9)	0.0008(10)	−0.0031(10)
C27	0.0171(12)	0.0167(11)	0.0165(11)	−0.0031(9)	0.0007(9)	−0.0029(9)
N1	0.0147(9)	0.0144(9)	0.0147(9)	−0.0009(8)	0.0009(7)	−0.0014(8)
N2	0.0158(10)	0.0139(9)	0.0156(9)	−0.0024(8)	0.0031(8)	−0.0009(8)
N3	0.0125(9)	0.0148(9)	0.0180(10)	0.0024(8)	0.0012(8)	0.0000(7)
N4	0.0179(10)	0.0129(9)	0.0182(10)	0.0009(8)	0.0035(8)	0.0022(8)
N5	0.0130(9)	0.0136(9)	0.0151(9)	0.0007(7)	0.0002(7)	0.0006(7)
N6	0.0135(9)	0.0157(9)	0.0174(10)	0.0008(8)	0.0022(8)	0.0018(8)
N7	0.0116(9)	0.0144(9)	0.0153(9)	0.0026(8)	−0.0014(7)	−0.0002(7)
N8	0.0128(9)	0.0133(9)	0.0140(9)	−0.0005(7)	0.0009(7)	−0.0002(7)
O1	0.0225(9)	0.0254(9)	0.0133(8)	−0.0041(7)	0.0013(7)	0.0000(7)
O2	0.0148(9)	0.0200(9)	0.0282(10)	0.0004(8)	0.0056(7)	−0.0015(7)
O3	0.0172(9)	0.0167(9)	0.0403(12)	0.0010(8)	0.0069(8)	−0.0021(7)
P1	0.0137(3)	0.0126(3)	0.0153(3)	0.0018(2)	−0.0002(2)	−0.0009(2)
W1	0.01081(5)	0.01070(5)	0.01179(5)	0.00054(3)	−0.00011(3)	0.00031(3)
C28	0.0312(17)	0.062(2)	0.0351(17)	−0.0020(17)	0.0016(14)	−0.0028(16)
Cl1	0.0378(4)	0.0437(4)	0.0375(4)	0.0020(3)	0.0081(3)	−0.0069(3)
Cl2	0.0483(6)	0.0577(6)	0.0725(7)	−0.0155(5)	0.0315(5)	−0.0139(5)

Table 4 Bond lengths and angles for compound 4.17

Atom–Atom	Length [Å]
B1–H1	1.13(3)
B1–N2	1.539(3)
B1–N4	1.545(3)
B1–N6	1.536(3)

C1–H1A	0.9500
C1–C2	1.393(4)
C1–N1	1.343(3)
C2–H2	0.9500
C2–C3	1.384(4)
C3–H3	0.9500
C3–N2	1.345(3)
C4–H4	0.9500
C4–C5	1.389(4)
C4–N3	1.335(3)
C5–H5	0.9500
C5–C6	1.382(4)
C6–H6	0.9500
C6–N4	1.349(3)
C7–H7	0.9500
C7–C8	1.396(4)
C7–N5	1.343(3)
C8–H8	0.9500
C8–C9	1.375(4)
C9–H9	0.9500
C9–N6	1.346(3)
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C10–P1	1.821(3)
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C11–P1	1.817(3)
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800
C12–P1	1.827(3)
C13–H13	1.0000
C13–C14	1.448(3)
C13–C18	1.472(3)
C13–W1	2.254(2)
C14–H14	1.0000
C14–C15	1.510(3)
C14–W1	2.195(2)

C15–H15	1.0000
C15–C16	1.552(3)
C15–N8	1.492(3)
C16–H16	1.0000
C16–C17	1.502(3)
C16–C19	1.536(3)
C17–H17	0.9500
C17–C18	1.334(4)
C18–H18	0.9500
C19–H19A	0.9900
C19–H19B	0.9900
C19–C20	1.502(3)
C20–N8	1.342(3)
C20–O2	1.243(3)
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.512(3)
C21–N8	1.463(3)
C22–C23	1.392(3)
C22–C27	1.401(3)
C23–H23	0.9500
C23–C24	1.389(4)
C24–H24	0.9500
C24–C25	1.387(4)
C25–H25	0.9500
C25–C26	1.381(4)
C26–H26	0.9500
C26–C27	1.397(4)
C27–O3	1.360(3)
N1–N2	1.367(3)
N1–W1	2.254(2)
N3–N4	1.361(3)
N3–W1	2.202(2)
N5–N6	1.366(3)
N5–W1	2.218(2)
N7–O1	1.231(3)
N7–W1	1.770(2)
O3–H3A	0.76(4)
P1–W1	2.5039(6)
C28–H28A	0.9900

C28–H28B	0.9900
C28–Cl1	1.769(4)
C28–Cl2	1.770(4)

Atom–Atom–Atom	**Angle [°]**
N2–B1–H1	111.2(15)
N2–B1–N4	109.6(2)
N4–B1–H1	111.3(16)
N6–B1–H1	109.6(16)
N6–B1–N2	108.6(2)
N6–B1–N4	106.4(2)
C2–C1–H1A	124.4
N1–C1–H1A	124.4
N1–C1–C2	111.2(2)
C1–C2–H2	127.9
C3–C2–C1	104.2(2)
C3–C2–H2	127.9
C2–C3–H3	125.5
N2–C3–C2	108.9(2)
N2–C3–H3	125.5
C5–C4–H4	124.7
N3–C4–H4	124.7
N3–C4–C5	110.7(2)
C4–C5–H5	127.6
C6–C5–C4	104.8(2)
C6–C5–H5	127.6
C5–C6–H6	125.8
N4–C6–C5	108.4(2)
N4–C6–H6	125.8
C8–C7–H7	124.7
N5–C7–H7	124.7
N5–C7–C8	110.6(2)
C7–C8–H8	127.7
C9–C8–C7	104.6(2)
C9–C8–H8	127.7
C8–C9–H9	125.5
N6–C9–C8	109.0(2)
N6–C9–H9	125.5
H10A–C10–H10B	109.5

H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
P1–C10–H10A	109.5
P1–C10–H10B	109.5
P1–C10–H10C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
P1–C11–H11A	109.5
P1–C11–H11B	109.5
P1–C11–H11C	109.5
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
P1–C12–H12A	109.5
P1–C12–H12B	109.5
P1–C12–H12C	109.5
C14–C13–H13	114.8
C14–C13–C18	117.6(2)
C14–C13–W1	68.83(13)
C18–C13–H13	114.8
C18–C13–W1	118.37(16)
W1–C13–H13	114.8
C13–C14–H14	111.7
C13–C14–C15	120.2(2)
C13–C14–W1	73.21(13)
C15–C14–H14	111.7
C15–C14–W1	123.03(16)
W1–C14–H14	111.7
C14–C15–H15	108.6
C14–C15–C16	115.9(2)
C16–C15–H15	108.6
N8–C15–C14	112.98(19)
N8–C15–H15	108.6
N8–C15–C16	101.77(18)
C15–C16–H16	109.6
C17–C16–C15	113.1(2)
C17–C16–H16	109.6
C17–C16–C19	111.3(2)
C19–C16–C15	103.51(19)

C19–C16–H16	109.6
C16–C17–H17	118.3
C18–C17–C16	123.4(2)
C18–C17–H17	118.3
C13–C18–H18	118.2
C17–C18–C13	123.5(2)
C17–C18–H18	118.2
C16–C19–H19A	110.7
C16–C19–H19B	110.7
H19A–C19–H19B	108.8
C20–C19–C16	105.0(2)
C20–C19–H19A	110.7
C20–C19–H19B	110.7
N8–C20–C19	109.1(2)
O2–C20–C19	126.3(2)
O2–C20–N8	124.6(2)
H21A–C21–H21B	107.8
C22–C21–H21A	108.9
C22–C21–H21B	108.9
N8–C21–H21A	108.9
N8–C21–H21B	108.9
N8–C21–C22	113.16(19)
C23–C22–C21	120.3(2)
C23–C22–C27	118.3(2)
C27–C22–C21	121.3(2)
C22–C23–H23	119.1
C24–C23–C22	121.7(2)
C24–C23–H23	119.1
C23–C24–H24	120.4
C25–C24–C23	119.3(2)
C25–C24–H24	120.4
C24–C25–H25	120.0
C26–C25–C24	120.0(2)
C26–C25–H25	120.0
C25–C26–H26	119.7
C25–C26–C27	120.7(2)
C27–C26–H26	119.7
C26–C27–C22	119.9(2)
O3–C27–C22	123.7(2)
O3–C27–C26	116.4(2)

C1–N1–N2	105.9(2)
C1–N1–W1	133.80(17)
N2–N1–W1	119.96(15)
C3–N2–B1	128.8(2)
C3–N2–N1	109.8(2)
N1–N2–B1	121.2(2)
C4–N3–N4	106.6(2)
C4–N3–W1	132.01(18)
N4–N3–W1	121.36(15)
C6–N4–B1	128.0(2)
C6–N4–N3	109.5(2)
N3–N4–B1	119.79(19)
C7–N5–N6	106.2(2)
C7–N5–W1	131.51(17)
N6–N5–W1	122.14(15)
C9–N6–B1	130.4(2)
C9–N6–N5	109.6(2)
N5–N6–B1	119.7(2)
O1–N7–W1	177.41(19)
C20–N8–C15	113.06(19)
C20–N8–C21	121.6(2)
C21–N8–C15	122.32(19)
C27–O3–H3A	111(3)
C10–P1–C12	98.30(13)
C10–P1–W1	115.86(10)
C11–P1–C10	103.44(15)
C11–P1–C12	103.07(13)
C11–P1–W1	111.67(9)
C12–P1–W1	122.06(9)
C13–W1–N1	87.65(8)
C13–W1–P1	79.23(6)
C14–W1–C13	37.96(8)
C14–W1–N1	87.26(8)
C14–W1–N3	81.72(8)
C14–W1–N5	155.73(8)
C14–W1–P1	117.06(6)
N1–W1–P1	86.49(5)
N3–W1–C13	119.55(8)
N3–W1–N1	85.47(8)
N3–W1–N5	75.78(7)

N3–W1–P1	159.16(6)
N5–W1–C13	160.89(8)
N5–W1–N1	82.06(7)
N5–W1–P1	84.08(5)
N7–W1–C13	95.77(9)
N7–W1–C14	97.31(9)
N7–W1–N1	175.42(8)
N7–W1–N3	95.44(8)
N7–W1–N5	93.80(8)
N7–W1–P1	91.15(7)
H28A–C28–H28B	108.0
Cl1–C28–H28A	109.3
Cl1–C28–H28B	109.3
Cl1–C28–Cl2	111.4(2)
Cl2–C28–H28A	109.3
Cl2–C28–H28B	109.3

Table 5 Torsion angles for compound 4.17

–Atom–Atom–Atom	**Torsion Angle [°]**
C1–C2–C3–N2	0.5(3)
C1–N1–N2–B1	175.4(2)
C1–N1–N2–C3	0.4(3)
C2–C1–N1–N2	−0.1(3)
C2–C1–N1–W1	172.73(17)
C2–C3–N2–B1	−175.1(2)
C2–C3–N2–N1	−0.6(3)
C4–C5–C6–N4	−0.3(3)
C4–N3–N4–B1	−162.5(2)
C4–N3–N4–C6	0.5(3)
C5–C4–N3–N4	−0.7(3)
C5–C4–N3–W1	−179.94(18)
C5–C6–N4–B1	161.1(2)
C5–C6–N4–N3	−0.1(3)
C7–C8–C9–N6	0.9(3)
C7–N5–N6–B1	174.1(2)
C7–N5–N6–C9	−0.1(3)
C8–C7–N5–N6	0.7(3)

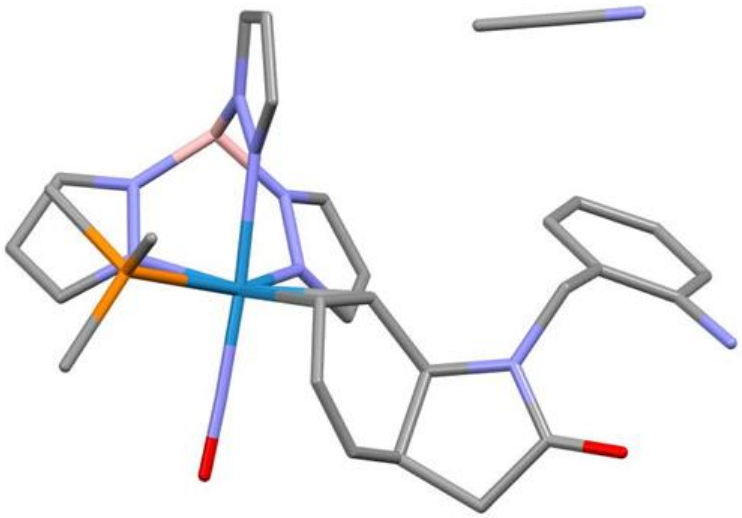
C8–C7–N5–W1	176.40(17)
C8–C9–N6–B1	−173.9(2)
C8–C9–N6–N5	−0.5(3)
C13–C14–C15–C16	−24.5(3)
C13–C14–C15–N8	92.5(3)
C14–C13–C18–C17	5.2(4)
C14–C15–C16–C17	29.2(3)
C14–C15–C16–C19	149.8(2)
C14–C15–N8–C20	−147.4(2)
C14–C15–N8–C21	52.0(3)
C15–C16–C17–C18	−19.1(3)
C15–C16–C19–C20	−23.3(2)
C16–C15–N8–C20	−22.4(2)
C16–C15–N8–C21	177.0(2)
C16–C17–C18–C13	1.7(4)
C16–C19–C20–N8	10.5(3)
C16–C19–C20–O2	−172.5(2)
C17–C16–C19–C20	98.5(2)
C18–C13–C14–C15	7.0(3)
C18–C13–C14–W1	−111.9(2)
C19–C16–C17–C18	−135.1(2)
C19–C20–N8–C15	7.9(3)
C19–C20–N8–C21	168.6(2)
C21–C22–C23–C24	−179.1(2)
C21–C22–C27–C26	177.3(2)
C21–C22–C27–O3	−0.9(4)
C22–C21–N8–C15	70.3(3)
C22–C21–N8–C20	−88.7(3)
C22–C23–C24–C25	1.4(4)
C23–C22–C27–C26	−2.3(4)
C23–C22–C27–O3	179.5(2)
C23–C24–C25–C26	−1.4(4)
C24–C25–C26–C27	−0.4(4)
C25–C26–C27–C22	2.3(4)
C25–C26–C27–O3	−179.4(2)
C27–C22–C23–C24	0.5(4)
N1–C1–C2–C3	−0.2(3)
N2–B1–N4–C6	132.8(3)
N2–B1–N4–N3	−67.7(3)
N2–B1–N6–C9	−126.9(3)

N2–B1–N6–N5	60.3(3)
N3–C4–C5–C6	0.6(3)
N4–B1–N2–C3	−130.0(2)
N4–B1–N2–N1	56.1(3)
N4–B1–N6–C9	115.3(3)
N4–B1–N6–N5	−57.6(3)
N5–C7–C8–C9	−1.0(3)
N6–B1–N2–C3	114.2(3)
N6–B1–N2–N1	−59.8(3)
N6–B1–N4–C6	−109.9(3)
N6–B1–N4–N3	49.5(3)
N8–C15–C16–C17	−93.8(2)
N8–C15–C16–C19	26.8(2)
N8–C21–C22–C23	−96.9(3)
N8–C21–C22–C27	83.5(3)
O2–C20–N8–C15	−169.2(2)
O2–C20–N8–C21	−8.4(4)
W1–C13–C14–C15	118.9(2)
W1–C13–C18–C17	−74.3(3)
W1–C14–C15–C16	64.3(3)
W1–C14–C15–N8	−178.74(15)
W1–N1–N2–B1	1.4(3)
W1–N1–N2–C3	−173.63(15)
W1–N3–N4–B1	16.8(3)
W1–N3–N4–C6	179.81(17)
W1–N5–N6–B1	−2.1(3)
W1–N5–N6–C9	−176.34(16)

Table 6 Hydrogen bonds for compound 4.17

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O3–H3A···O2	0.76(4)	1.94(4)	2.703(3)	174(4)

Crystal Structure Report for compound 4.18



A yellow, block-like specimen of $C_{31}H_{41}BN_{11}O_2PW$, approximate dimensions 0.290 mm x 0.296 mm x 0.327 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 0.34 hours. The frames were integrated with the Bruker SAINT software package[68] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 48388 reflections to a maximum θ angle of 29.60° (0.72 Å resolution), of which 9753 were independent (average redundancy 4.961, completeness = 99.9%, R_{int} = 4.04%, R_{sig} = 3.09%) and 8888 (91.13%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.1865(3) Å, b = 24.5060(8) Å, c = 14.3046(5) Å, β = 103.6740(10)°, volume = 3469.7(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9450 reflections above 20 σ(I) with 5.555° < 2θ < 59.17°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[69] The ratio of minimum to maximum apparent transmission was 0.501. The calculated minimum and maximum

[68] Bruker (2012). *Saint; SADABS; APEX5*. Bruker AXS Inc., Madison, Wisconsin, USA.

[69] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

transmission coefficients (based on crystal size) are 0.4010 and 0.4370.

The structure was solved and refined using the Bruker SHELXTL Software Package[70] within APEX5 [1] and OLEX2,[71] using the space group P $2_1/n$, with Z = 4 for the formula unit, $C_{31}H_{41}BN_{11}O_2PW$. The B-H and N-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 449 variables converged at R1 = 3.09%, for the observed data and wR2 = 6.83% for all data. The goodness-of-fit was 1.246. The largest peak in the final difference electron density synthesis was 1.338 $e^-/Å^3$ and the largest hole was -1.921 $e^-/Å^3$ with an RMS deviation of 0.107 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.580 g/cm^3 and F(000), 1656 e^-.

Table 1. Sample and crystal data for compound 4.18

Chemical formula	$C_{31}H_{41}BN_{11}O_2PW$	
Formula weight	825.38 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.290 x 0.296 x 0.327 mm	
Crystal habit	yellow block	
Crystal system	monoclinic	
Space group	P $2_1/n$	
Unit cell dimensions	a = 10.1865(3) Å	α = 90°
	b = 24.5060(8) Å	β = 103.6740(10)°
	c = 14.3046(5) Å	γ = 90°
Volume	3469.7(2) $Å^3$	
Z	4	
Density (calculated)	1.580 g/cm^3	
Absorption coefficient	3.422 mm^{-1}	
F(000)	1656	

[70] Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.
[71] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Table 2. Data collection and structure refinement for compound 4.18		
Diffractometer	Bruker D8 Venture Photon III Kappa four-circle diffractometer	
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)	
Theta range for data collection	2.22 to 29.60°	
Index ranges	-14<=h<=14, -34<=k<=34, -19<=l<=19	
Reflections collected	48388	
Independent reflections	9753 [R(int) = 0.0404]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.4370 and 0.4010	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9753 / 0 / 449	
Goodness-of-fit on F^2	1.246	
Δ/σ_{max}	0.002	
Final R indices	8888 data; I>2σ(I)	R1 = 0.0309, wR2 = 0.0673
	all data	R1 = 0.0346, wR2 = 0.0683
Weighting scheme	$w=1/[\sigma^2(F_o^2)+8.1488P]$ where $P=(F_o^2+2F_c^2)/3$	

Largest diff. peak and hole	1.338 and -1.921 eÅ^{-3}
R.M.S. deviation from mean	0.107 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.18

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.47351(2)	0.29903(2)	0.32881(2)	0.01585(4)
P1	0.29840(9)	0.22986(4)	0.25625(6)	0.02209(17)
O1	0.3827(2)	0.29998(10)	0.51374(16)	0.0223(5)
O2	0.3214(3)	0.56504(11)	0.36171(18)	0.0300(6)
N1	0.5331(3)	0.29137(11)	0.18843(18)	0.0196(5)
N2	0.6571(3)	0.27154(12)	0.1842(2)	0.0218(6)
N3	0.5951(3)	0.22448(12)	0.3696(2)	0.0213(5)
N4	0.7031(3)	0.21259(12)	0.3318(2)	0.0219(6)
N5	0.6832(3)	0.32845(11)	0.38200(19)	0.0182(5)
N6	0.7844(3)	0.30770(11)	0.34420(19)	0.0202(5)
N7	0.4219(3)	0.30066(11)	0.43819(18)	0.0172(5)
N8	0.4074(3)	0.48403(11)	0.32192(18)	0.0193(5)
N9	0.5633(4)	0.61525(13)	0.3139(2)	0.0292(7)
C1	0.4653(3)	0.29862(15)	0.0967(2)	0.0222(6)
C2	0.5448(4)	0.28316(16)	0.0351(2)	0.0272(8)
C3	0.6652(4)	0.26642(15)	0.0919(2)	0.0257(7)
C4	0.5829(4)	0.18243(14)	0.4273(2)	0.0248(7)
C5	0.6798(4)	0.14274(15)	0.4246(3)	0.0284(7)
C6	0.7544(4)	0.16374(15)	0.3637(3)	0.0273(7)
C7	0.7411(3)	0.36275(14)	0.4518(2)	0.0204(6)
C8	0.8801(3)	0.36490(14)	0.4602(2)	0.0237(7)
C9	0.9026(3)	0.32954(15)	0.3907(2)	0.0243(7)
C10	0.4344(3)	0.38453(13)	0.2896(2)	0.0187(6)
C11	0.3102(3)	0.35604(14)	0.2521(2)	0.0199(6)
C12	0.1959(3)	0.36646(14)	0.2959(2)	0.0221(6)

	x/a	y/b	z/c	U(eq)
C13	0.2070(3)	0.39674(15)	0.3746(2)	0.0224(6)
C14	0.3366(3)	0.42274(14)	0.4274(2)	0.0198(6)
C15	0.4393(3)	0.42859(13)	0.3642(2)	0.0165(6)
C16	0.3448(3)	0.51592(14)	0.3751(2)	0.0226(6)
C17	0.3127(3)	0.48187(14)	0.4546(2)	0.0223(6)
C18	0.4682(3)	0.50635(14)	0.2473(2)	0.0219(6)
C19	0.6165(3)	0.52078(14)	0.2823(2)	0.0221(6)
C20	0.7146(4)	0.48154(15)	0.2821(3)	0.0267(7)
C21	0.8513(4)	0.49294(16)	0.3119(3)	0.0304(8)
C22	0.8908(4)	0.54563(17)	0.3417(3)	0.0319(8)
C23	0.7954(4)	0.58512(16)	0.3431(3)	0.0288(7)
C24	0.6577(4)	0.57375(14)	0.3148(2)	0.0236(7)
C25	0.2085(4)	0.20397(19)	0.3426(3)	0.0376(10)
C26	0.1618(4)	0.24580(18)	0.1531(3)	0.0340(8)
C27	0.3694(4)	0.17014(16)	0.2108(3)	0.0323(8)
B1	0.7606(4)	0.25754(16)	0.2772(3)	0.0225(7)
N10	0.6902(6)	0.5162(2)	0.0050(3)	0.0694(14)
C28	0.6522(6)	0.4726(2)	0.0124(4)	0.0600(14)
C29	0.6102(8)	0.4176(2)	0.0231(5)	0.078(2)
N11	0.4350(7)	0.1064(3)	0.5688(4)	0.093(2)
C30	0.4958(7)	0.0651(3)	0.5991(4)	0.0715(19)
C31	0.5709(6)	0.0130(3)	0.6416(4)	0.073(2)

Table 4. Bond lengths (Å) for compound 4.18
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W1-N7	1.765(2)	W1-C10	2.181(3)
W1-N3	2.207(3)	W1-N5	2.212(3)
W1-N1	2.239(2)	W1-C11	2.249(3)
W1-P1	2.5014(9)	P1-C26	1.816(4)
P1-C25	1.817(4)	P1-C27	1.819(4)
O1-N7	1.238(3)	O2-C16	1.233(4)
N1-C1	1.342(4)	N1-N2	1.368(4)
N2-C3	1.349(4)	N2-B1	1.528(5)
N3-C4	1.344(4)	N3-N4	1.367(4)

N4-C6	1.342(4)	N4-B1	1.544(5)
N5-C7	1.331(4)	N5-N6	1.370(4)
N6-C9	1.342(4)	N6-B1	1.542(5)
N8-C16	1.352(4)	N8-C18	1.461(4)
N8-C15	1.491(4)	N9-C24	1.398(5)
N9-H9A	0.84(5)	N9-H9B	0.89(5)
C1-C2	1.384(4)	C1-H1	0.950000
C2-C3	1.364(5)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.393(5)
C4-H4	0.950000	C5-C6	1.384(5)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.393(4)	C7-H7	0.950000
C8-C9	1.379(5)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.433(4)
C10-C15	1.511(4)	C10-H10	0.92(4)
C11-C12	1.469(4)	C11-H11	0.97(4)
C12-C13	1.331(5)	C12-H12	0.950000
C13-C14	1.500(5)	C13-H13	0.950000
C14-C17	1.534(5)	C14-C15	1.543(4)
C14-H14	1.000000	C15-H15	1.000000
C16-C17	1.506(5)	C17-H17A	0.990000
C17-H17B	0.990000	C18-C19	1.517(5)
C18-H18A	0.990000	C18-H18B	0.990000
C19-C20	1.387(5)	C19-C24	1.409(5)
C20-C21	1.385(5)	C20-H20	0.950000
C21-C22	1.389(5)	C21-H21	0.950000
C22-C23	1.375(6)	C22-H22	0.950000
C23-C24	1.394(5)	C23-H23	0.950000
C25-H25A	0.980000	C25-H25B	0.980000
C25-H25C	0.980000	C26-H26A	0.980000
C26-H26B	0.980000	C26-H26C	0.980000
C27-H27A	0.980000	C27-H27B	0.980000
C27-H27C	0.980000	B1-H1A	1.04(4)
N10-C28	1.149(7)	C28-C29	1.433(7)
C29-H29A	0.980000	C29-H29B	0.980000
C29-H29C	0.980000	N11-C30	1.212(10)

C30-C31	1.538(10)	C31-H31A	0.980000
C31-H31B	0.980000	C31-H31C	0.980000

Table 5. Bond angles (°) for compound 4.18.			
N7-W1-C10	97.57(12)	N7-W1-N3	92.89(11)
C10-W1-N3	156.95(11)	N7-W1-N5	98.81(11)
C10-W1-N5	83.01(11)	N3-W1-N5	75.10(10)
N7-W1-N1	176.19(11)	C10-W1-N1	85.51(11)
N3-W1-N1	85.04(10)	N5-W1-N1	83.76(10)
N7-W1-C11	94.45(12)	C10-W1-C11	37.71(12)
N3-W1-C11	161.30(11)	N5-W1-C11	120.54(11)
N1-W1-C11	86.60(11)	N7-W1-P1	92.91(9)
C10-W1-P1	118.37(9)	N3-W1-P1	81.34(8)
N5-W1-P1	154.09(7)	N1-W1-P1	83.63(7)
C11-W1-P1	81.13(9)	C26-P1-C25	102.40(19)
C26-P1-C27	100.10(19)	C25-P1-C27	105.6(2)
C26-P1-W1	121.73(14)	C25-P1-W1	112.28(13)
C27-P1-W1	112.88(13)	C1-N1-N2	105.8(3)
C1-N1-W1	132.8(2)	N2-N1-W1	121.2(2)
C3-N2-N1	110.3(3)	C3-N2-B1	130.0(3)
N1-N2-B1	119.7(3)	C4-N3-N4	106.2(3)
C4-N3-W1	132.0(2)	N4-N3-W1	121.7(2)
C6-N4-N3	109.9(3)	C6-N4-B1	130.1(3)
N3-N4-B1	119.0(3)	C7-N5-N6	106.8(3)
C7-N5-W1	133.2(2)	N6-N5-W1	119.9(2)
C9-N6-N5	109.1(3)	C9-N6-B1	128.1(3)
N5-N6-B1	121.2(3)	O1-N7-W1	177.5(2)
C16-N8-C18	122.2(3)	C16-N8-C15	112.6(3)
C18-N8-C15	123.2(3)	C24-N9-H9A	117.(3)
C24-N9-H9B	113.(3)	H9A-N9-H9B	112.(4)
N1-C1-C2	110.0(3)	N1-C1-H1	125.000000
C2-C1-H1	125.000000	C3-C2-C1	106.4(3)
C3-C2-H2	126.800000	C1-C2-H2	126.800000
N2-C3-C2	107.5(3)	N2-C3-H3	126.300000
C2-C3-H3	126.300000	N3-C4-C5	110.5(3)

N3-C4-H4	124.800000	C5-C4-H4	124.800000
C6-C5-C4	104.8(3)	C6-C5-H5	127.600000
C4-C5-H5	127.600000	N4-C6-C5	108.6(3)
N4-C6-H6	125.700000	C5-C6-H6	125.700000
N5-C7-C8	110.5(3)	N5-C7-H7	124.800000
C8-C7-H7	124.800000	C9-C8-C7	104.6(3)
C9-C8-H8	127.700000	C7-C8-H8	127.700000
N6-C9-C8	109.0(3)	N6-C9-H9	125.500000
C8-C9-H9	125.500000	C11-C10-C15	119.4(3)
C11-C10-W1	73.72(19)	C15-C10-W1	122.1(2)
C11-C10-H10	116.(2)	C15-C10-H10	115.(2)
W1-C10-H10	103.(2)	C10-C11-C12	118.3(3)
C10-C11-W1	68.57(18)	C12-C11-W1	118.0(2)
C10-C11-H11	115.(2)	C12-C11-H11	116.(2)
W1-C11-H11	112.(2)	C13-C12-C11	122.7(3)
C13-C12-H12	118.700000	C11-C12-H12	118.700000
C12-C13-C14	123.5(3)	C12-C13-H13	118.200000
C14-C13-H13	118.200000	C13-C14-C17	110.8(3)
C13-C14-C15	112.5(3)	C17-C14-C15	103.3(3)
C13-C14-H14	110.000000	C17-C14-H14	110.000000
C15-C14-H14	110.000000	N8-C15-C10	113.4(2)
N8-C15-C14	102.1(2)	C10-C15-C14	115.7(3)
N8-C15-H15	108.400000	C10-C15-H15	108.400000
C14-C15-H15	108.400000	O2-C16-N8	125.2(3)
O2-C16-C17	126.1(3)	N8-C16-C17	108.7(3)
C16-C17-C14	104.9(3)	C16-C17-H17A	110.800000
C14-C17-H17A	110.800000	C16-C17-H17B	110.800000
C14-C17-H17B	110.800000	H17A-C17-H17B	108.800000
N8-C18-C19	114.0(3)	N8-C18-H18A	108.700000
C19-C18-H18A	108.700000	N8-C18-H18B	108.700000
C19-C18-H18B	108.700000	H18A-C18-H18B	107.600000
C20-C19-C24	118.8(3)	C20-C19-C18	120.0(3)

C24-C19-C18	121.3(3)	C21-C20-C19	122.1(4)
C21-C20-H20	118.900000	C19-C20-H20	118.900000
C20-C21-C22	118.6(4)	C20-C21-H21	120.700000
C22-C21-H21	120.700000	C23-C22-C21	120.3(4)
C23-C22-H22	119.900000	C21-C22-H22	119.900000
C22-C23-C24	121.4(4)	C22-C23-H23	119.300000
C24-C23-H23	119.300000	C23-C24-N9	120.0(3)
C23-C24-C19	118.7(3)	N9-C24-C19	121.1(3)
P1-C25-H25A	109.500000	P1-C25-H25B	109.500000
H25A-C25-H25B	109.500000	P1-C25-H25C	109.500000
H25A-C25-H25C	109.500000	H25B-C25-H25C	109.500000
P1-C26-H26A	109.500000	P1-C26-H26B	109.500000
H26A-C26-H26B	109.500000	P1-C26-H26C	109.500000
H26A-C26-H26C	109.500000	H26B-C26-H26C	109.500000
P1-C27-H27A	109.500000	P1-C27-H27B	109.500000
H27A-C27-H27B	109.500000	P1-C27-H27C	109.500000
H27A-C27-H27C	109.500000	H27B-C27-H27C	109.500000
N2-B1-N6	109.7(3)	N2-B1-N4	109.5(3)
N6-B1-N4	106.1(3)	N2-B1-H1A	112.(2)
N6-B1-H1A	111.(2)	N4-B1-H1A	108.(2)
N10-C28-C29	177.7(8)	C28-C29-H29A	109.500000
C28-C29-H29B	109.500000	H29A-C29-H29B	109.500000
C28-C29-H29C	109.500000	H29A-C29-H29C	109.500000
H29B-C29-H29C	109.500000	N11-C30-C31	177.5(7)
C30-C31-H31A	109.500000	C30-C31-H31B	109.500000

H31A-C31-H31B	109.500000	C30-C31-H31C	109.500000
H31A-C31-H31C	109.500000	H31B-C31-H31C	109.500000

Table 6. Torsion angles (°) for compound 4.18			
C1-N1-N2-C3	-0.3(4)	W1-N1-N2-C3	174.8(2)
C1-N1-N2-B1	-178.9(3)	W1-N1-N2-B1	-3.8(4)
C4-N3-N4-C6	1.4(4)	W1-N3-N4-C6	-176.3(2)
C4-N3-N4-B1	-168.7(3)	W1-N3-N4-B1	13.6(4)
C7-N5-N6-C9	-0.2(4)	W1-N5-N6-C9	-176.9(2)
C7-N5-N6-B1	166.5(3)	W1-N5-N6-B1	-10.2(4)
N2-N1-C1-C2	0.5(4)	W1-N1-C1-C2	-173.8(2)
N1-C1-C2-C3	-0.5(4)	N1-N2-C3-C2	0.0(4)
B1-N2-C3-C2	178.4(3)	C1-C2-C3-N2	0.3(4)
N4-N3-C4-C5	-1.8(4)	W1-N3-C4-C5	175.6(2)
N3-C4-C5-C6	1.5(4)	N3-N4-C6-C5	-0.4(4)
B1-N4-C6-C5	168.2(3)	C4-C5-C6-N4	-0.6(4)
N6-N5-C7-C8	0.1(4)	W1-N5-C7-C8	176.2(2)
N5-C7-C8-C9	0.0(4)	N5-N6-C9-C8	0.3(4)
B1-N6-C9-C8	-165.4(3)	C7-C8-C9-N6	-0.2(4)
C15-C10-C11-C12	-6.9(5)	W1-C10-C11-C12	111.2(3)
C15-C10-C11-W1	-118.1(3)	C10-C11-C12-C13	-7.1(5)
W1-C11-C12-C13	72.4(4)	C11-C12-C13-C14	-0.8(6)
C12-C13-C14-C17	135.7(3)	C12-C13-C14-C15	20.6(5)
C16-N8-C15-C10	147.8(3)	C18-N8-C15-C10	-47.7(4)

C16-N8-C15-C14	22.7(3)	C18-N8-C15-C14	-172.8(3)
C11-C10-C15-N8	-90.6(3)	W1-C10-C15-N8	-179.1(2)
C11-C10-C15-C14	26.9(4)	W1-C10-C15-C14	-61.6(3)
C13-C14-C15-N8	91.3(3)	C17-C14-C15-N8	-28.2(3)
C13-C14-C15-C10	-32.3(4)	C17-C14-C15-C10	-151.8(3)
C18-N8-C16-O2	6.9(5)	C15-N8-C16-O2	171.5(3)
C18-N8-C16-C17	-171.5(3)	C15-N8-C16-C17	-6.8(4)
O2-C16-C17-C14	169.4(3)	N8-C16-C17-C14	-12.2(4)
C13-C14-C17-C16	-95.5(3)	C15-C14-C17-C16	25.2(3)
C16-N8-C18-C19	92.1(4)	C15-N8-C18-C19	-71.0(4)
N8-C18-C19-C20	87.7(4)	N8-C18-C19-C24	-92.7(4)
C24-C19-C20-C21	-0.7(5)	C18-C19-C20-C21	178.9(3)
C19-C20-C21-C22	-0.8(5)	C20-C21-C22-C23	1.3(6)
C21-C22-C23-C24	-0.2(6)	C22-C23-C24-N9	-177.8(3)
C22-C23-C24-C19	-1.3(5)	C20-C19-C24-C23	1.7(5)
C18-C19-C24-C23	-177.9(3)	C20-C19-C24-N9	178.2(3)
C18-C19-C24-N9	-1.5(5)	C3-N2-B1-N6	126.5(4)
N1-N2-B1-N6	-55.2(4)	C3-N2-B1-N4	-117.4(4)
N1-N2-B1-N4	60.8(4)	C9-N6-B1-N2	-131.2(3)
N5-N6-B1-N2	64.8(4)	C9-N6-B1-N4	110.6(4)

N5-N6-B1-N4	-53.4(4)	C6-N4-B1-N2	125.0(4)
N3-N4-B1-N2	-67.2(4)	C6-N4-B1-N6	-116.7(4)
N3-N4-B1-N6	51.1(4)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.18.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.01570(6)	0.01550(6)	0.01667(6)	-0.00214(5)	0.00448(4)	-0.00163(5)
P1	0.0225(4)	0.0243(4)	0.0199(4)	-0.0043(3)	0.0060(3)	-0.0079(3)
O1	0.0247(11)	0.0246(12)	0.0186(10)	-0.0003(9)	0.0070(9)	-0.0023(10)
O2	0.0378(14)	0.0217(13)	0.0306(13)	0.0029(10)	0.0082(11)	0.0107(11)
N1	0.0205(12)	0.0203(14)	0.0187(12)	-0.0015(10)	0.0060(10)	-0.0008(11)
N2	0.0214(13)	0.0233(15)	0.0230(13)	-0.0045(11)	0.0097(11)	0.0006(11)
N3	0.0237(13)	0.0174(13)	0.0230(13)	-0.0020(10)	0.0060(11)	-0.0007(11)
N4	0.0210(13)	0.0205(14)	0.0236(13)	-0.0035(10)	0.0041(11)	0.0009(11)
N5	0.0169(12)	0.0168(13)	0.0214(12)	-0.0010(10)	0.0054(10)	0.0007(10)
N6	0.0191(12)	0.0195(14)	0.0229(13)	-0.0012(10)	0.0069(10)	0.0002(11)
N7	0.0173(11)	0.0156(12)	0.0184(12)	-0.0006(10)	0.0039(9)	-0.0026(10)
N8	0.0235(13)	0.0175(13)	0.0173(12)	0.0013(10)	0.0059(10)	0.0048(11)
N9	0.0370(18)	0.0191(15)	0.0306(16)	-0.0003(12)	0.0062(14)	0.0007(14)
C1	0.0239(15)	0.0250(16)	0.0184(14)	-0.0019(12)	0.0066(12)	-0.0003(14)
C2	0.0369(19)	0.0337(19)	0.0176(14)	0.0087(13)	0.0194(14)	0.0046(16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	0.0281(17)	0.0256(18)	0.0241(16)	-0.0026(13)	0.0074(13)	0.0024(14)
C4	0.0312(17)	0.0198(16)	0.0218(15)	-0.0018(12)	0.0029(13)	-0.0049(14)
C5	0.0362(19)	0.0180(17)	0.0275(17)	-0.0010(13)	0.0005(15)	0.0005(15)
C6	0.0291(17)	0.0207(17)	0.0286(17)	-0.0063(13)	0.0001(14)	0.0064(14)
C7	0.0218(15)	0.0186(15)	0.0201(14)	0.0017(11)	0.0036(12)	0.0015(12)
C8	0.0209(15)	0.0212(16)	0.0273(16)	-0.0017(13)	0.0022(13)	-0.0023(13)
C9	0.0177(14)	0.0261(18)	0.0290(17)	0.0001(13)	0.0055(13)	-0.0014(13)
C10	0.0189(14)	0.0187(15)	0.0191(14)	0.0006(11)	0.0060(12)	0.0007(12)
C11	0.0185(14)	0.0226(16)	0.0182(14)	-0.0019(12)	0.0037(12)	-0.0005(12)
C12	0.0169(14)	0.0257(17)	0.0227(15)	-0.0005(12)	0.0027(12)	-0.0020(13)
C13	0.0178(14)	0.0263(17)	0.0241(15)	0.0014(13)	0.0069(12)	0.0021(13)
C14	0.0199(14)	0.0204(16)	0.0201(14)	-0.0008(11)	0.0067(12)	0.0009(12)
C15	0.0180(13)	0.0151(14)	0.0161(13)	0.0005(10)	0.0036(11)	0.0018(11)
C16	0.0228(15)	0.0216(17)	0.0225(15)	-0.0008(12)	0.0038(13)	0.0042(13)
C17	0.0233(15)	0.0223(16)	0.0222(15)	-0.0028(12)	0.0072(12)	0.0014(13)
C18	0.0302(17)	0.0184(16)	0.0171(14)	0.0023(11)	0.0057(12)	0.0011(13)
C19	0.0267(16)	0.0217(16)	0.0184(14)	0.0026(12)	0.0061(12)	-0.0005(13)
C20	0.0321(18)	0.0205(17)	0.0301(17)	0.0023(13)	0.0125(15)	-0.0012(14)
C21	0.0318(18)	0.0266(19)	0.0346(19)	0.0025(15)	0.0116(16)	0.0025(15)
C22	0.0313(19)	0.032(2)	0.0323(19)	0.0025(15)	0.0070(15)	-0.0048(16)
C23	0.0356(19)	0.0243(18)	0.0249(16)	0.0001(13)	0.0040(15)	-0.0048(15)
C24	0.0314(17)	0.0224(17)	0.0169(14)	0.0035(12)	0.0052(13)	0.0008(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C25	0.034(2)	0.051(3)	0.0289(18)	-0.0041(18)	0.0112(16)	-0.023(2)
C26	0.0301(19)	0.038(2)	0.0311(19)	-0.0044(16)	0.0017(15)	-0.0101(17)
C27	0.037(2)	0.0249(19)	0.0342(19)	-0.0107(15)	0.0058(16)	-0.0072(16)
B1	0.0205(16)	0.0221(19)	0.0255(17)	-0.0034(14)	0.0069(14)	0.0022(15)
N10	0.092(4)	0.054(3)	0.058(3)	-0.004(2)	0.010(3)	-0.028(3)
C28	0.076(4)	0.051(3)	0.055(3)	-0.008(2)	0.018(3)	-0.020(3)
C29	0.109(5)	0.042(3)	0.099(5)	-0.007(3)	0.058(4)	-0.023(3)
N11	0.100(5)	0.105(5)	0.066(4)	0.032(3)	0.003(3)	-0.037(4)
C30	0.069(4)	0.104(6)	0.044(3)	-0.004(3)	0.017(3)	-0.035(4)
C31	0.054(3)	0.114(6)	0.051(3)	-0.029(3)	0.011(3)	-0.005(4)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.18

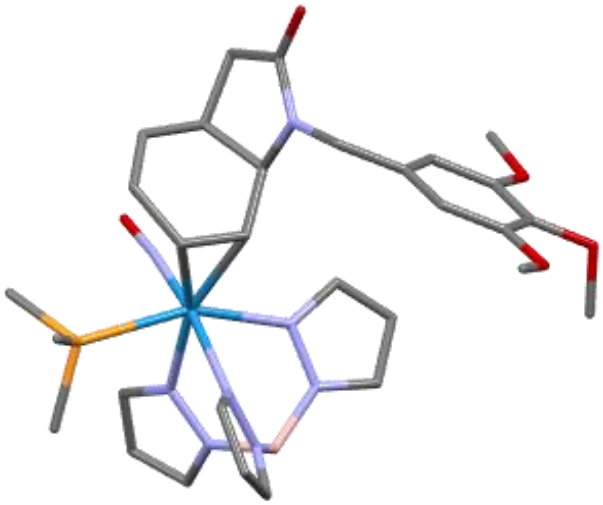
	x/a	y/b	z/c	U(eq)
H9A	0.487(5)	0.606(2)	0.322(3)	0.037(13)
H9B	0.597(4)	0.644(2)	0.351(3)	0.035(12)
H1	0.3758	0.3123	0.0770	0.027000
H2	0.5204	0.2840	-0.0332	0.033000
H3	0.7410	0.2535	0.0703	0.031000
H4	0.5174	0.1801	0.4646	0.030000
H5	0.6920	0.1087	0.4574	0.034000
H6	0.8293	0.1465	0.3472	0.033000
H7	0.6942	0.3829	0.4904	0.024000
H8	0.9449	0.3860	0.5042	0.028000
H9	0.9881	0.3219	0.3778	0.029000
H10	0.487(4)	0.3907(15)	0.246(2)	0.015(9)
H11	0.288(4)	0.3505(15)	0.183(3)	0.016(9)
H12	0.1105	0.3510	0.2668	0.027000
H13	0.1287	0.4022	0.3986	0.027000
H14	0.3773	0.4012	0.4866	0.024000

	x/a	y/b	z/c	U(eq)
H15	0.5323	0.4294	0.4072	0.020000
H17A	0.2177	0.4873	0.4582	0.027000
H17B	0.3729	0.4915	0.5174	0.027000
H18A	0.4178	0.5395	0.2204	0.026000
H18B	0.4583	0.4793	0.1946	0.026000
H20	0.6871	0.4457	0.2609	0.032000
H21	0.9167	0.4653	0.3120	0.036000
H22	0.9841	0.5544	0.3611	0.038000
H23	0.8241	0.6209	0.3639	0.035000
H25A	0.2722	0.1855	0.3952	0.056000
H25B	0.1390	0.1780	0.3106	0.056000
H25C	0.1657	0.2344	0.3686	0.056000
H26A	0.1072	0.2756	0.1697	0.051000
H26B	0.1049	0.2135	0.1349	0.051000
H26C	0.1994	0.2570	0.0990	0.051000
H27A	0.4163	0.1814	0.1615	0.049000
H27B	0.2966	0.1447	0.1826	0.049000
H27C	0.4335	0.1522	0.2637	0.049000
H1A	0.851(4)	0.2437(15)	0.264(3)	0.018(9)
H29A	0.5957	0.3987	-0.0388	0.116000
H29B	0.5259	0.4179	0.0448	0.116000
H29C	0.6804	0.3986	0.0707	0.116000
H31A	0.6399	0.0041	0.6065	0.110000
H31B	0.5065	-0.0172	0.6358	0.110000
H31C	0.6143	0.0190	0.7096	0.110000

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 4.18

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N9-H9A···O2	0.84(5)	2.15(5)	2.975(5)	165.(4)
N9-H9B···O1#1	0.89(5)	2.35(5)	3.171(4)	153.(4)

Structure Report for compound 4.19



A colourless, block shaped crystal of compound 4.19
measuring 0.087×0.11×0.125 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_2_245_x3_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[72] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[73] and refined by full-matrix least-squares methods against F^2 using XL[74] within OLEX2.[75] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atom, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.

[72] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[73] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[74] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[75] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table 1 Crystal data and structure refinement for compound 4.19

CCDC number	
Empirical formula	$C_{33}H_{46}BN_8O_6PW$
Formula weight	876.41
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.087×0.11×0.125
Crystal habit	colourless block
Crystal system	triclinic
Space group	$P\overline{1}$ (2)
a [Å]	12.9069(5)
b [Å]	13.1092(6)
c [Å]	13.8406(6)
α [°]	110.281(2)
β [°]	116.2650(10)
γ [°]	96.791(2)
Volume [$Å^3$]	1864.30(14)
Z	2
ρ_{calc} [gcm^{-3}]	1.561
μ [mm^{-1}]	3.194
F(000)	884
2θ range [°]	4.72 to 56.57 (0.75 Å)
Index ranges	−16 ≤ h ≤ 17 −17 ≤ k ≤ 17 −18 ≤ l ≤ 18
Reflections collected	81614
Independent reflections	9234 [R_{int} = 0.0448]
Data / Restraints / Parameters	9234 / 0 / 471
Goodness-of-fit on F^2	1.032
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0179 wR_2 = 0.0379
Final *R* indexes [all data]	R_1 = 0.0203 wR_2 = 0.0388

Largest peak/hole [eÅ^{-3}]	0.43/−0.50

Table 2 Atomic coordinates and Ueq [Å^2] for compound 4.19

Atom	***x***	***y***	***z***	U_{eq}
B1	0.76109(19)	0.99567(18)	0.26666(19)	0.0146(4)
H1	0.7582(19)	1.0815(18)	0.3112(19)	0.013(5)
C1	0.63754(17)	0.83978(17)	−0.0538817)	0.0157(4)
H1A	0.617737	0.772949	−0.123317	0.019
C2	0.60479(17)	0.93675(17)	−0.05522(18)	0.0176(4)
H2	0.559841	0.949179	−0.123613	0.021
C3	0.65156(16)	1.01114(17)	0.06414(18)	0.0159(4)
H3	0.644019	1.085281	0.093371	0.019
C4	0.58445(17)	0.73382(17)	0.23112(18)	0.0163(4)
H4	0.555418	0.652719	0.200224	0.020
C5	0.54764(19)	0.81048(18)	0.29691(19)	0.0211(4)
H5	0.490931	0.793013	0.319703	0.025
C6	0.61107(18)	0.91720(18)	0.32191(18)	0.0196(4)
H6	0.605902	0.988315	0.366016	0.024
C7	1.04244(17)	0.92470(17)	0.36277(17)	0.0170(4)
H7	1.087528	0.872529	0.360754	0.020
C8	1.09339(18)	1.04193(18)	0.43875(18)	0.0196(4)
H8	1.177132	1.084665	0.496423	0.023
C9	0.99587(18)	1.08232(17)	0.41200(17)	0.0178(4)
H9	1.000336	1.160021	0.449260	0.021
C10	0.81288(16)	0.63517(16)	0.23333(16)	0.0125(3)
H10	0.847(2)	0.687(2)	0.316(2)	0.021(6)
C11	0.89336(17)	0.62993(16)	0.18677(17)	0.0147(4)
H11	0.973(2)	0.6771(18)	0.2395(19)	0.012(5)
C12	0.87166(18)	0.51825(17)	0.09285(18)	0.0179(4)
H12	0.930979	0.510759	0.07021	0.021
C13	0.77329(19)	0.42742(17)	0.03815(18)	0.0180(4)
H13	0.765121	0.358613	−0.022419	0.022
C14	0.67460(17)	0.42874(16)	0.06780(17)	0.0149(4)
H14	0.602813	0.437757	0.005900	0.018
C15	0.72154(16)	0.52439(15)	0.19451(16)	0.0128(3)

H15	0.650127	0.541746	0.199382	0.015
C16	0.63549(17)	0.31929(16)	0.07765(18)	0.0169(4)
H16A	0.549879	0.301110	0.058199	0.020
H16B	0.643770	0.252913	0.02248	0.020
C17	0.72268(17)	0.34893(16)	0.2089(18)	0.0157(4)
C18	0.86131(17)	0.52082(17)	0.39708(16)	0.0151(4)
H18A	0.933087	0.574385	0.411227	0.018
H18B	0.888884	0.462150	0.422244	0.018
C19	0.81778(17)	0.58747(16)	0.47701(17)	0.0136(4)
C20	0.69501(17)	0.57150(16)	0.43635(17)	0.0148(4)
H2	0.634562	0.517770	0.355873	0.018
C21	0.66108(17)	0.63546(17)	0.51524(17)	0.0165(4)
C22	0.74994(17)	0.71328(17)	0.63319(17)	0.0157(4)
C23	0.87285(17)	0.72630(16)	0.67369(17)	0.0152(4
C24	0.90698(17)	0.66390(16)	0.59580(17)	0.0140(4)
H24	0.990788	0.673159	0.623241	0.017
C25	0.44914(18)	0.5425(2)	0.36779(19)	0.0276(5)
H25A	0.456495	0.558527	0.306589	0.041
H25B	0.369425	0.543815	0.358086	0.041
H25C	0.456634	0.46657	0.35849	0.041
C26	0.7209(2)	0.8874(19)	0.7156(2)	0.0279(5)
H26A	0.661698	0.879719	0.636210	0.042
H26B	0.803214	0.928211	0.738831	0.04
H26C	0.701478	0.931380	0.775144	0.042
C27	1.07711(17)	0.80875(19)	0.83870(19)	0.0219(4)
H27A	1.107362	0.827406	0.791209	0.033
H27B	1.083080	0.733763	0.834864	0.033
H27C	1.126329	0.867716	0.922733	0.033
C28	0.83587(19)	0.64367(17)	−0.11090(18)	0.0195(4)
H28A	0.819302	0.567526	−0.113567	0.029
H28B	0.892201	0.6518	−0.139395	0.029
H28C	0.759270	0.652321	−0.162760	0.029
C29	1.06040(18)	0.74980(19)	0.1133(2)	0.0219(4)
H29A	1.108939	0.812670	0.195333	0.033
H29B	1.096191	0.758661	0.066116	0.033
H29C	1.059938	0.676178	0.116353	0.033
C30	0.93141(18)	0.88866(17)	0.03417(19)	0.0186(4)
H30A	0.854605	0.891707	−0.024242	0.028

H30B	0.990664	0.894256	0.008565	0.028
H30C	0.963720	0.952805	0.113616	0.028
N1	0.70129(14)	0.85447(1)	0.06002(14)	0.0129(3)
N	0.70957(14)	0.96058(13)	0.13179(14)	0.0136()
N3	0.66645(14)	0.78979(13)	0.21715(14)	0.0130(3)
N4	0.68168(14)	0.90402(13)	0.27343(14)	0.0147(3)
N5	0.92075(14)	0.89504(13)	0.29250(14)	0.0137(3)
N6	0.89306(14)	0.99433(13)	0.3246(14)	0.0143(3)
N7	0.65588(14)	0.62104(13)	−0.00949(14)	0.0128(3)
N8	0.77272(14)	0.46421(13)	0.26982(14)	0.0135(3)
O1	0.57367(12)	0.54924(11)	−0.11139(12)	0.0177(3)
O2	0.74490(13)	0.28094(12)	0.25160(13)	0.0204(3)
O3	0.541(12)	0.62792(13)	0.48506(12)	0.0228(3)
O4	0.71547(12)	0.77640(12)	0.71052(12)	0.0202(3
O5	0.9526(2)	0.80492(12)	0.79112(12)	0.0184(3)
P1	0.90399(4)	0.75333(4)	0.04265(4)	0.01364(9)
W1	0.77353(2)	0.73438(2)	0.12978(2)	0.01023(2)
C31	0.1891(2)	0.6264(3)	0.4223(3)	0.0545(9)
H31A	0.226488	0.567056	0.432132	0.082
H31B	0.138864	0.605446	0.336310	0.0
H31C	0.137696	0.632694	0.457766	0.082
C32	0.2868(2)	0.7390(2)	0.4843(2)	0.028(5)
C33	0.3957(2)	0.7651(2)	0.6030(2)	0.0323(5)
H33A	0.368749	0.759208	0.657445	0.049
H33B	0.450296	0.843214	0.638454	0.049
H33C	0.439210	0.710076	0.590826	0.049
O6	0.27617(18)	0.80527(15)	0.44042(17)	0.0423(4)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 4.19

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0180(10)	0.0101(10)	0.0149(10)	0.0048(8)	0.0086(8)	0.0044(8)
C1	0.0157(8)	0.0174(9)	0.0133(9)	0.0069(8)	0.0071(7)	0.0047(7)
C2	0.0152(9)	0.0198(10)	0.0183(10)	0.0108(8)	0.0071(8)	0.0065(8)
C3	0.0131(8)	0.0149(9)	0.0224(10)	0.0107(8)	0.0092(8)	0.0058(7)

C4	0.0150(8)	0.0150(9)	0.0195(10)	0.0084(8)	0.0089(8)	0.0049(7)
C5	0.0220(10)	0.0226(11)	0.0280(11)	0.0126(9)	0.0186(9)	0.0098(8)
C6	0.0237(10)	0.0187(10)	0.0210(10)	0.0077(8)	0.0152(9)	0.0101(8)
C7	0.0153(9)	0.0209(10)	0.0145(9)	0.0090(8)	0.0071(7)	0.0041(7)
C8	0.0163(9)	0.0206(10)	0.0141(9)	0.0077(8)	0.0040(8)	−0.0019(8)
C9	0.0208(9)	0.0126(9)	0.0128(9)	0.0039(8)	0.0061(8)	−0.0017(7)
C10	0.0158(8)	0.0107(9)	0.0096(8)	0.0044(7)	0.0055(7)	0.0047(7)
C11	0.0131(8)	0.0135(9)	0.0177(9)	0.0080(8)	0.0070(8)	0.0053(7)
C12	0.0242(10)	0.0201(10)	0.0222(10)	0.0134(9)	0.0173(8)	0.0136(8)
C13	0.0276(10)	0.0148(9)	0.0172(9)	0.0077(8)	0.0149(8)	0.0098(8)
C14	0.0186(9)	0.0120(9)	0.0126(9)	0.0057(7)	0.0068(7)	0.0045(7)
C15	0.0156(8)	0.0119(9)	0.0136(9)	0.0066(7)	0.0084(7)	0.0065(7)
C16	0.0191(9)	0.0107(9)	0.0189(10)	0.0058(8)	0.0093(8)	0.0035(7)
C17	0.0182(9)	0.0150(9)	0.0207(10)	0.0088(8)	0.0141(8)	0.0083(7)
C18	0.0177(9)	0.0175(9)	0.0137(9)	0.0077(8)	0.0097(8)	0.0085(7)
C19	0.0189(9)	0.0120(9)	0.0165(9)	0.0088(8)	0.0120(8)	0.0069(7)
C20	0.0160(9)	0.0159(9)	0.0122(9)	0.0061(8)	0.0073(7)	0.0044(7)
C21	0.0136(8)	0.0193(10)	0.0172(9)	0.0081(8)	0.0087(8)	0.0048(7)
C22	0.0181(9)	0.0170(9)	0.0140(9)	0.0059(8)	0.0106(8)	0.0055(7)
C23	0.0151(8)	0.0139(9)	0.0150(9)	0.0062(8)	0.0077(7)	0.0014(7)
C24	0.0152(8)	0.0132(9)	0.0167(9)	0.0080(8)	0.0094(7)	0.0056(7)
C25	0.0149(9)	0.0401(13)	0.0162(10)	0.0036(10)	0.0067(8)	0.0056(9)
C26	0.0297(11)	0.0234(11)	0.0331(12)	0.0080(10)	0.0212(10)	0.0113(9)
C27	0.0143(9)	0.0255(11)	0.0172(10)	0.0031(9)	0.0072(8)	0.0025(8)
C28	0.0238(10)	0.0170(10)	0.0164(9)	0.0046(8)	0.0123(8)	0.0031(8)
C29	0.0169(9)	0.0279(11)	0.0264(11)	0.0140(9)	0.0140(9)	0.0080(8)
C30	0.0214(9)	0.0157(10)	0.0212(10)	0.0082(8)	0.0135(8)	0.0038(8)
N1	0.0152(7)	0.0102(7)	0.0123(7)	0.0035(6)	0.0076(6)	0.0040(6)
N2	0.0138(7)	0.0106(7)	0.0156(8)	0.0052(6)	0.0077(6)	0.0038(6)
N3	0.0155(7)	0.0095(7)	0.0144(8)	0.0049(6)	0.0083(6)	0.0046(6)
N4	0.0183(8)	0.0108(8)	0.0144(8)	0.0040(6)	0.0093(6)	0.0046(6)
N5	0.0146(7)	0.0114(8)	0.0115(7)	0.0036(6)	0.0055(6)	0.0022(6)
N6	0.0176(8)	0.0102(7)	0.0122(7)	0.0037(6)	0.0072(6)	0.0023(6)
N7	0.0142(7)	0.0127(8)	0.0147(8)	0.0072(6)	0.0089(6)	0.0054(6)
N8	0.0165(7)	0.0141(8)	0.0134(8)	0.0075(6)	0.0088(6)	0.0080(6)
O1	0.0169(6)	0.0151(7)	0.0107(6)	0.0018(5)	0.0032(5)	−0.0001(5)
O2	0.0286(8)	0.0159(7)	0.0254(8)	0.0131(6)	0.0168(7)	0.0113(6)
O3	0.0131(6)	0.0329(9)	0.0140(7)	0.0023(6)	0.0072(6)	0.0056(6)
O4	0.0201(7)	0.0216(7)	0.0168(7)	0.0030(6)	0.0123(6)	0.0063(6)

O5	0.0135(6)	0.0197(7)	0.0145(7)	0.0021(6)	0.0065(5)	0.0025(5)
P1	0.0141(2)	0.0128(2)	0.0138(2)	0.00503(19)	0.00807(19)	0.00316(18)
W1	0.01078(3)	0.00908(4)	0.01009(4)	0.00375(3)	0.00533(3)	0.00291(2)
C31	0.0278(13)	0.0589(19)	0.081(2)	0.0547(19)	0.0149(14)	0.0122(13)
C32	0.0316(12)	0.0335(13)	0.0365(13)	0.0215(11)	0.0235(11)	0.0188(10)
C33	0.0353(13)	0.0395(14)	0.0328(13)	0.0168(11)	0.0229(11)	0.0224(11)
O6	0.0586(12)	0.0326(10)	0.0434(11)	0.0242(9)	0.0258(10)	0.0195(9)

Table 4 Bond lengths and angles for compound 4.19

Atom–Atom	**Length [Å]**
B1–H1	1.09(2)
B1–N2	1.540(3)
B1–N4	1.541(3)
B1–N6	1.534(3)
C1–H1A	0.9500
C1–C2	1.390(3)
C1–N1	1.343(2)
C2–H2	0.9500
C2–C3	1.380(3)
C3–H3	0.9500
C3–N2	1.343(2)
C4–H4	0.9500
C4–C5	1.388(3)
C4–N3	1.339(2)
C5–H5	0.9500
C5–C6	1.375(3)
C6–H6	0.9500
C6–N4	1.345(2)
C7–H7	0.9500
C7–C8	1.389(3)
C7–N5	1.344(2)
C8–H8	0.9500
C8–C9	1.372(3)
C9–H9	0.9500
C9–N6	1.343(2)
C10–H10	0.95(2)

C10–C11	1.441(3)
C10–C15	1.510(2)
C10–W1	2.1927(17)
C11–H11	0.92(2)
C11–C12	1.474(3)
C11–W1	2.2492(18)
C12–H12	0.9500
C12–C13	1.330(3)
C13–H13	0.9500
C13–C14	1.501(3)
C14–H14	1.0000
C14–C15	1.540(3)
C14–C16	1.535(3)
C15–H15	1.0000
C15–N8	1.493(2)
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.513(3)
C17–N8	1.348(2)
C17–O2	1.232(2)
C18–H18A	0.9900
C18–H18B	0.9900
C18–C19	1.516(3)
C18–N8	1.439(2)
C19–C20	1.386(3)
C19–C24	1.394(3)
C20–H20	0.9500
C20–C21	1.401(3)
C21–C22	1.390(3)
C21–O3	1.362(2)
C22–C23	1.394(3)
C22–O4	1.387(2)
C23–C24	1.385(3)
C23–O5	1.368(2)
C24–H24	0.9500
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C25–O3	1.429(2)
C26–H26A	0.9800

C26–H26B	0.9800
C26–H26C	0.9800
C26–O4	1.427(3)
C27–H27A	0.9800
C27–H27B	0.9800
C27–H27C	0.9800
C27–O5	1.426(2)
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
C28–P1	1.813(2)
C29–H29A	0.9800
C29–H29B	0.9800
C29–H29C	0.9800
C29–P1	1.828(2)
C30–H30A	0.9800
C30–H30B	0.9800
C30–H30C	0.9800
C30–P1	1.8217(19)
N1–N2	1.359(2)
N1–W1	2.2100(15)
N3–N4	1.369(2)
N3–W1	2.2378(15)
N5–N6	1.367(2)
N5–W1	2.2575(15)
N7–O1	1.233(2)
N7–W1	1.7662(16)
P1–W1	2.5014(5)
C31–H31A	0.9800
C31–H31B	0.9800
C31–H31C	0.9800
C31–C32	1.494(4)
C32–C33	1.498(3)
C32–O6	1.209(3)
C33–H33A	0.9800
C33–H33B	0.9800
C33–H33C	0.9800

Atom–Atom–Atom	**Angle [°]**

N2–B1–H1	110.2(11)
N2–B1–N4	106.46(15)
N4–B1–H1	111.7(11)
N6–B1–H1	110.1(11)
N6–B1–N2	109.07(16)
N6–B1–N4	109.30(15)
C2–C1–H1A	125.0
N1–C1–H1A	125.0
N1–C1–C2	109.99(17)
C1–C2–H2	127.4
C3–C2–C1	105.24(17)
C3–C2–H2	127.4
C2–C3–H3	125.9
N2–C3–C2	108.20(17)
N2–C3–H3	125.9
C5–C4–H4	124.6
N3–C4–H4	124.6
N3–C4–C5	110.73(17)
C4–C5–H5	127.5
C6–C5–C4	105.00(17)
C6–C5–H5	127.5
C5–C6–H6	125.7
N4–C6–C5	108.54(18)
N4–C6–H6	125.7
C8–C7–H7	124.6
N5–C7–H7	124.6
N5–C7–C8	110.84(18)
C7–C8–H8	127.7
C9–C8–C7	104.65(17)
C9–C8–H8	127.7
C8–C9–H9	125.5
N6–C9–C8	109.05(18)
N6–C9–H9	125.5
C11–C10–H10	117.4(14)
C11–C10–C15	118.42(16)
C11–C10–W1	73.21(10)
C15–C10–H10	112.3(14)
C15–C10–W1	122.38(12)
W1–C10–H10	107.9(14)
C10–C11–H11	117.1(13)

C10–C11–C12	117.61(17)
C10–C11–W1	68.95(10)
C12–C11–H11	116.7(13)
C12–C11–W1	117.66(13)
W1–C11–H11	109.6(13)
C11–C12–H12	118.3
C13–C12–C11	123.37(18)
C13–C12–H12	118.3
C12–C13–H13	118.5
C12–C13–C14	122.97(18)
C14–C13–H13	118.5
C13–C14–H14	110.4
C13–C14–C15	111.49(16)
C13–C14–C16	111.13(16)
C15–C14–H14	110.4
C16–C14–H14	110.4
C16–C14–C15	102.71(15)
C10–C15–C14	116.11(15)
C10–C15–H15	108.8
C14–C15–H15	108.8
N8–C15–C10	113.22(15)
N8–C15–C14	100.84(14)
N8–C15–H15	108.8
C14–C16–H16A	111.0
C14–C16–H16B	111.0
H16A–C16–H16B	109.0
C17–C16–C14	103.68(15)
C17–C16–H16A	111.0
C17–C16–H16B	111.0
N8–C17–C16	107.81(16)
O2–C17–C16	126.78(18)
O2–C17–N8	125.41(18)
H18A–C18–H18B	107.4
C19–C18–H18A	108.4
C19–C18–H18B	108.4
N8–C18–H18A	108.4
N8–C18–H18B	108.4
N8–C18–C19	115.69(15)
C20–C19–C18	122.23(17)
C20–C19–C24	120.77(17)

C24–C19–C18	116.97(16)
C19–C20–H20	120.4
C19–C20–C21	119.27(17)
C21–C20–H20	120.4
C22–C21–C20	120.09(17)
O3–C21–C20	124.45(17)
O3–C21–C22	115.46(17)
C21–C22–C23	120.00(18)
O4–C22–C21	119.67(17)
O4–C22–C23	120.33(17)
C24–C23–C22	120.14(17)
O5–C23–C22	115.33(17)
O5–C23–C24	124.50(17)
C19–C24–H24	120.2
C23–C24–C19	119.69(17)
C23–C24–H24	120.2
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
O3–C25–H25A	109.5
O3–C25–H25B	109.5
O3–C25–H25C	109.5
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
O4–C26–H26A	109.5
O4–C26–H26B	109.5
O4–C26–H26C	109.5
H27A–C27–H27B	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
O5–C27–H27A	109.5
O5–C27–H27B	109.5
O5–C27–H27C	109.5
H28A–C28–H28B	109.5
H28A–C28–H28C	109.5
H28B–C28–H28C	109.5
P1–C28–H28A	109.5
P1–C28–H28B	109.5
P1–C28–H28C	109.5

H29A–C29–H29B	109.5
H29A–C29–H29C	109.5
H29B–C29–H29C	109.5
P1–C29–H29A	109.5
P1–C29–H29B	109.5
P1–C29–H29C	109.5
H30A–C30–H30B	109.5
H30A–C30–H30C	109.5
H30B–C30–H30C	109.5
P1–C30–H30A	109.5
P1–C30–H30B	109.5
P1–C30–H30C	109.5
C1–N1–N2	106.60(15)
C1–N1–W1	130.11(13)
N2–N1–W1	123.18(11)
C3–N2–B1	130.30(16)
C3–N2–N1	109.97(15)
N1–N2–B1	118.89(15)
C4–N3–N4	106.02(15)
C4–N3–W1	133.93(13)
N4–N3–W1	120.04(11)
C6–N4–B1	128.73(16)
C6–N4–N3	109.70(15)
N3–N4–B1	121.34(15)
C7–N5–N6	105.86(15)
C7–N5–W1	134.30(13)
N6–N5–W1	119.12(11)
C9–N6–B1	128.57(17)
C9–N6–N5	109.60(16)
N5–N6–B1	121.81(15)
O1–N7–W1	173.82(13)
C17–N8–C15	113.20(15)
C17–N8–C18	121.92(16)
C18–N8–C15	124.78(15)
C21–O3–C25	117.26(16)
C22–O4–C26	111.95(15)
C23–O5–C27	116.06(15)
C28–P1–C29	102.48(10)
C28–P1–C30	104.59(9)
C28–P1–W1	112.48(7)

C29–P1–W1	121.72(7)
C30–P1–C29	99.60(9)
C30–P1–W1	113.85(7)
C10–W1–C11	37.84(7)
C10–W1–N1	159.94(6)
C10–W1–N3	82.75(6)
C10–W1–N5	91.42(6)
C10–W1–P1	116.14(5)
C11–W1–N5	89.52(6)
C11–W1–P1	78.34(5)
N1–W1–C11	161.02(6)
N1–W1–N3	77.22(6)
N1–W1–N5	84.65(6)
N1–W1–P1	83.12(4)
N3–W1–C11	119.84(6)
N3–W1–N5	81.82(6)
N3–W1–P1	156.88(4)
N5–W1–P1	84.37(4)
N7–W1–C10	97.13(7)
N7–W1–C11	96.77(7)
N7–W1–N1	87.54(6)
N7–W1–N3	99.94(6)
N7–W1–N5	171.42(6)
N7–W1–P1	91.17(5)
H31A–C31–H31B	109.5
H31A–C31–H31C	109.5
H31B–C31–H31C	109.5
C32–C31–H31A	109.5
C32–C31–H31B	109.5
C32–C31–H31C	109.5
C31–C32–C33	116.5(2)
O6–C32–C31	120.9(2)
O6–C32–C33	122.7(2)
C32–C33–H33A	109.5
C32–C33–H33B	109.5
C32–C33–H33C	109.5
H33A–C33–H33B	109.5
H33A–C33–H33C	109.5
H33B–C33–H33C	109.5

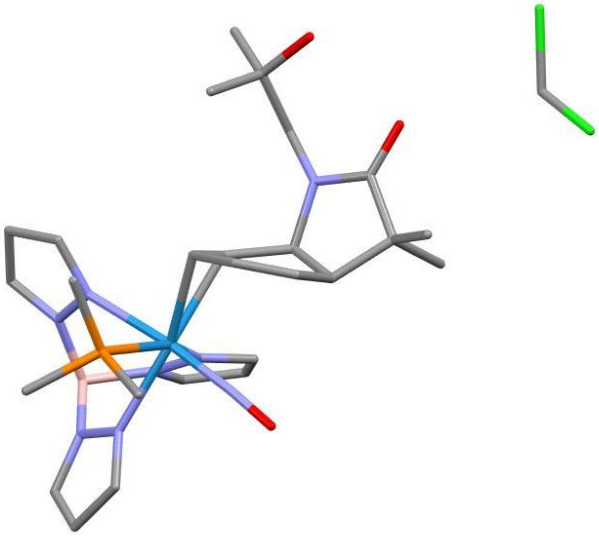
Table 5 Torsion angles for compound 4.19

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C1–C2–C3–N2	0.5(2)
C1–N1–N2–B1	170.90(16)
C1–N1–N2–C3	0.3(2)
C2–C1–N1–N2	0.0(2)
C2–C1–N1–W1	176.27(12)
C2–C3–N2–B1	−169.68(18)
C2–C3–N2–N1	−0.5(2)
C4–C5–C6–N4	−0.1(2)
C4–N3–N4–B1	−174.31(16)
C4–N3–N4–C6	0.7(2)
C5–C4–N3–N4	−0.7(2)
C5–C4–N3–W1	178.09(14)
C5–C6–N4–B1	174.12(18)
C5–C6–N4–N3	−0.4(2)
C7–C8–C9–N6	−0.4(2)
C7–N5–N6–B1	−178.20(16)
C7–N5–N6–C9	0.4(2)
C8–C7–N5–N6	−0.6(2)
C8–C7–N5–W1	169.16(13)
C8–C9–N6–B1	178.46(17)
C8–C9–N6–N5	0.0(2)
C10–C11–C12–C13	9.4(3)
C10–C15–N8–C17	−148.53(16)
C10–C15–N8–C18	34.9(2)
C11–C10–C15–C14	−30.3(2)
C11–C10–C15–N8	85.6(2)
C11–C12–C13–C14	−0.9(3)
C12–C13–C14–C15	−21.9(3)
C12–C13–C14–C16	−135.81(19)
C13–C14–C15–C10	36.3(2)
C13–C14–C15–N8	−86.41(17)
C13–C14–C16–C17	87.88(18)
C14–C15–N8–C17	−23.81(19)
C14–C15–N8–C18	159.63(16)
C14–C16–C17–N8	17.8(2)

C14–C16–C17–O2	−162.25(19)
C15–C10–C11–C12	7.1(2)
C15–C10–C11–W1	118.21(15)
C15–C14–C16–C17	−31.44(18)
C16–C14–C15–C10	155.40(15)
C16–C14–C15–N8	32.66(17)
C16–C17–N8–C15	4.0(2)
C16–C17–N8–C18	−179.33(16)
C18–C19–C20–C21	179.60(17)
C18–C19–C24–C23	−179.23(16)
C19–C18–N8–C15	66.6(2)
C19–C18–N8–C17	−109.7(2)
C19–C20–C21–C22	−0.5(3)
C19–C20–C21–O3	179.30(18)
C20–C19–C24–C23	−1.2(3)
C20–C21–C22–C23	−1.1(3)
C20–C21–C22–O4	179.84(17)
C20–C21–O3–C25	5.0(3)
C21–C22–C23–C24	1.6(3)
C21–C22–C23–O5	−179.93(17)
C21–C22–O4–C26	−96.2(2)
C22–C21–O3–C25	−175.13(18)
C22–C23–C24–C19	−0.4(3)
C22–C23–O5–C27	172.16(17)
C23–C22–O4–C26	84.8(2)
C24–C19–C20–C21	1.7(3)
C24–C23–O5–C27	−9.4(3)
N1–C1–C2–C3	−0.3(2)
N2–B1–N4–C6	−118.2(2)
N2–B1–N4–N3	55.8(2)
N2–B1–N6–C9	117.0(2)
N2–B1–N6–N5	−64.7(2)
N3–C4–C5–C6	0.5(2)
N4–B1–N2–C3	112.1(2)
N4–B1–N2–N1	−56.3(2)
N4–B1–N6–C9	−126.96(19)
N4–B1–N6–N5	51.3(2)
N5–C7–C8–C9	0.6(2)
N6–B1–N2–C3	−130.11(19)
N6–B1–N2–N1	61.5(2)

N6–B1–N4–C6	124.2(2)
N6–B1–N4–N3	−61.9(2)
N8–C18–C19–C20	16.3(3)
N8–C18–C19–C24	−165.71(16)
O2–C17–N8–C15	−175.93(17)
O2–C17–N8–C18	0.7(3)
O3–C21–C22–C23	179.06(17)
O3–C21–C22–O4	0.0(3)
O4–C22–C23–C24	−179.37(17)
O4–C22–C23–O5	−0.9(3)
O5–C23–C24–C19	−178.78(17)
W1–C10–C11–C12	−111.10(16)
W1–C10–C15–C14	57.0(2)
W1–C10–C15–N8	173.01(12)
W1–C11–C12–C13	−70.1(2)
W1–N1–N2–B1	−5.7(2)
W1–N1–N2–C3	−176.27(12)
W1–N3–N4–B1	6.7(2)
W1–N3–N4–C6	−178.33(12)
W1–N5–N6–B1	10.2(2)
W1–N5–N6–C9	−171.28(12)

Structure Report for compound 4.23



A colourless, needle shaped crystal of compound 4.23

measuring 0.064×0.067×0.073 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ps_7_185_x2_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_{α}, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[76] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with SHELXT[77] and refined by full-matrix least-squares methods against F^2 using SHELXL--2019/1[78] within OLEX2.[79] All non-hydrogen atoms were refined with anisotropically. The B-H and O-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[80]

[76] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[77] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[78] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[79] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[80] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for compound 4.23

CCDC number	
Empirical formula	$C_{27}H_{42}BCl_2N_8O_3PW$
Formula weight	823.21
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.064×0.067×0.073
Crystal habit	colourless needle
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
a [Å]	10.0201(5)
b [Å]	13.1562(6)
c [Å]	13.6352(7)
α [°]	112.735(2)
β [°]	94.796(2)
γ [°]	92.148(2)
Volume [$Å^3$]	1647.24(14)
Z	2
ρ_{calc} [gcm^{-3}]	1.660
μ [mm^{-1}]	3.759
F(000)	824
2θ range [°]	4.09 to 56.63 (0.75 Å)
Index ranges	−13 ≤ h ≤ 13 −17 ≤ k ≤ 15 −18 ≤ l ≤ 18
Reflections collected	56394
Independent reflections	8214 [R_{int} = 0.0849]
Data / Restraints / Parameters	8214 / 0 / 410
Goodness-of-fit on F^2	1.021
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0350 wR_2 = 0.0720

Final *R* indexes [all data]	R_1 = 0.0494 wR_2 = 0.0770
Largest peak/hole [eÅ^{-3}]	1.15/−1.02

Table Atomic coordinates and Ueq [Å^2] for compound 4.23

Atom	***x***	***y***	***z***	U_{eq}
W1	0.72911(2)	0.40570(2)	0.69272(2)	0.01446(5)
P1	0.69977(11)	0.34486(9)	0.84293(9)	0.0197(2)
O1	0.4455(3)	0.4684(3)	0.6825(3)	0.0285(7)
O2	0.4993(3)	0.0160(2)	0.2104(2)	0.0244(7)
O3	0.7162(3)	−0.0926(2)	0.2257(3)	0.0291(7)
H3	0.630(6)	−0.059(5)	0.214(5)	0.058(18)
N1	0.9483(3)	0.3796(3)	0.7168(3)	0.0176(7)
N2	1.0430(3)	0.4655(3)	0.7477(3)	0.0179(7)
N3	0.7823(3)	0.5682(3)	0.8255(3)	0.0185(7)
N4	0.9055(3)	0.6221(3)	0.8438(3)	0.0206(7)
N5	0.8099(3)	0.5069(3)	0.6115(3)	0.0166(7)
N6	0.9270(3)	0.5715(3)	0.6516(3)	0.0177(7)
N7	0.5604(3)	0.4387(3)	0.6839(3)	0.0184(7)
N8	0.6356(3)	0.1446(3)	0.3488(3)	0.0178(7)
C1	1.0140(4)	0.298(3)	0.7087(3)	0.0212(9)
H1	0.972614	0.218381	0.688161	0.025
C2	1.1507(4)	0.3187(4)	0.7344(3)	0.0241(9)
H2	1.219400	0.271233	0.735441	0.029
C3	1.16494)	0.4289(4)	0.7579(3)	0.0231(9)
H3A	1.247605	0.473044	0.778317	0.028
C4	0.7107(4)	0.6299(3)	0.9018(3)	0.0213(9)
H4	0.619938	0.611931	0.9077	0.026
C5	0.7877(5)	0.7244(3)	0.9711(3)	0.0253(9)
H5	0.761516	0.781802	1.032427	0.030
C6	0.9089(5)	0.7163(3)	0.9314(4)	0.0263(10)
H6	0.984072	0.768847	0.960935	0.032
C7	0.7642(4)	0.5263(3)	0.5253(3)	0.0210(9)
H7	0.683153	0.492928	0.481081	0.025
C8	0.8505(5)	0.601(3)	0.5100(4)	0.0263(10)
H8	0.841785	0.628158	0.454671	0.032
C9	0.9517(5)	0.6280(3)	0.5914(4)	0.0257(10)
H9	1.027197	0.678688	0.603175	0.031
C10	0.7233(4)	0.2704(3)	0.5353(3)	0.0170(8)

H10	0.804(5)	0.259(4)	0.521(4)	0.020
C1	0.6875(4)	0.2223(3)	0.6083(3)	0.0179(8)
H11	0.742(5)	0.179(4)	0.626(4)	0.025(12)
C12	0.5461(4)	0.1817(3)	0.5981(3)	0.0218(9)
H12	0.521721	0.144310	0.642004	0.026
C13	0.4504(4)	0.1945(3)	0.5311(3)	0.0230(9)
H13	0.360893	0.168683	0.531974	0.028
C14	0.4760(4)	0.2473(3)	0.4542(3)	0.0188(8)
H14	0.443173	0.323157	0.480453	0.023
C15	0.6267(4)	0.2540(3)	0.4385(3)	0.0167(8)
H15	0.645750	0.314524	0.413380	0.020
C16	0.4087(4)	0.1785(3)	0.3397(3)	0.0204(9)
C17	0.5179(4)	0.1027(3)	0.2919(3)	0.0196(8)
C18	0.2774(4)	0.1126(3)	0.3314(4)	0.0258(10)
H18A	0.293423	0.057497	0.362231	0.039
H18B	0.241660	0.075138	0.256078	0.039
H18C	0.212514	0.162636	0.370607	0.039
C19	0.3871(4)	0.2513(3)	0.2753(4)	0.0253(9)
H19A	0.311078	0.296040	0.299330	0.038
H19B	0.368211	0.204196	0.199128	0.0
H19C	0.46829	0.300048	0.286599	0.038
C20	0.7621(4)	0.1079(3)	0.3057(3)	0.0189(8)
H20A	0.834627	0.164668	0.348822	0.023
H20B	0.756689	0.105531	0.232016	0.023
C21	0.8035(4)	−0.0036(3	0.3020(3)	0.0200(8)
C22	0.9418(4)	−0.0206(4)	0.2627(4)	0.0316(11)
H22A	0.963222	−0.096968	0.247124	0.047
H22B	1.009005	0.030176	0.317972	0.047
H22C	0.9422	−0.005848	0.197507	0.047
C23	0.8048(5)	−0.0096(4)	0.4114(4)	0.0276(10)
H23A	0.714767	0.001078	0.435120	0.041
H23	0.868821	0.048333	0.462921	0.041
H23C	0.831501	−0.02145	0.406670	0.041
C24	0.7383(5)	0.2073(3)	0.8329(4)	0.0266(10)
H24A	0.679261	0.15125	0.774308	0.040
H24B	0.724361	0.19855	0.900216	0.040
H24C	0.832156	0.196181	0.818900	0.040
C25	0.5290(5)	0.3503(4)	0.872(4)	0.0322(11)
H25A	0.500166	0.425084	0.896177	0.048

H25B	0.525640	0.331452	0.941872	0.048
H25C	0.469030	0.297467	0.819267	0.048
C26	0.8016(5)	0.4252(4)	0.9678(4)	0.0352(11)
H26A	0.896286	0.4272	0.954900	0.053
H26B	0.790531	0.391086	1.019285	0.053
H26C	0.773130	0.500695	0.99562	0.053
B1	1.0047(5)	0.5817(4)	0.7587(4)	0.0212(10)
H1A	1.094(4)	0.635(3)	0.775(3)	0.014(10)
Cl1	0.37232(14)	−0.17836(12)	−0.07847(11)	0.0466(3)
Cl2	0.15833(13)	−0.03384(11)	0.00321(11)	0.0418(3)
C27	0.3311(5)	−0.0401(4)	−0.0086(4)	0.0402(12)
H27A	0.381330	−0.00954	0.063621	0.048
H27B	0.358681	0.006018	−0.047231	0.048

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 4.23

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01250(8)	0.01471(8)	0.01524(9)	0.00471(6)	0.00205(5)	0.00111(5)
P1	0.0215(5)	0.0202(5)	0.0181(6)	0.0080(4)	0.0035(4)	0.0016(4)
O1	0.0147(14)	0.0363(18)	0.0333(19)	0.0113(15)	0.0051(13)	0.0084(13)
O2	0.0211(15)	0.0203(15)	0.0245(17)	0.0013(13)	0.0000(12)	0.0003(12)
O3	0.0273(17)	0.0170(15)	0.0327(19)	−0.0002(14)	−0.0033(14)	0.0035(13)
N1	0.0150(16)	0.0182(16)	0.0200(18)	0.0076(14)	0.0033(13)	0.0032(13)
N2	0.0127(15)	0.0222(17)	0.0172(18)	0.0058(14)	0.0025(13)	−0.0010(13)
N3	0.0191(17)	0.0195(17)	0.0148(18)	0.0047(14)	0.0017(14)	0.0005(13)
N4	0.0197(17)	0.0190(17)	0.0198(19)	0.0043(15)	0.0001(14)	−0.0004(13)
N5	0.0184(16)	0.0147(16)	0.0131(17)	0.0013(13)	0.0013(13)	0.0047(13)
N6	0.0148(16)	0.0179(16)	0.0207(19)	0.0070(14)	0.0058(13)	0.0002(13)
N7	0.0195(17)	0.0176(16)	0.0151(18)	0.0025(14)	0.0040(14)	0.0027(13)
N8	0.0169(16)	0.0157(16)	0.0178(18)	0.0037(14)	0.0007(14)	0.0013(13)
C1	0.023(2)	0.020(2)	0.022(2)	0.0091(18)	0.0013(17)	0.0062(16)
C2	0.021(2)	0.028(2)	0.023(2)	0.0099(19)	0.0010(17)	0.0075(17)

C3	0.0145(19)	0.031(2)	0.020(2)	0.0059(19)	0.0025(16)	0.0032(17)
C4	0.024(2)	0.020(2)	0.021(2)	0.0085(18)	0.0091(17)	0.0058(16)
C5	0.037(3)	0.019(2)	0.018(2)	0.0045(18)	0.0035(19)	0.0069(18)
C6	0.032(2)	0.017(2)	0.022(2)	0.0012(18)	−0.0038(19)	−0.0043(17)
C7	0.027(2)	0.0169(19)	0.018(2)	0.0053(17)	0.0019(17)	0.0044(16)
C8	0.039(3)	0.019(2)	0.023(2)	0.0090(18)	0.011(2)	0.0061(18)
C9	0.030(2)	0.020(2)	0.029(3)	0.0089(19)	0.013(2)	0.0035(17)
C10	0.0163(19)	0.0149(18)	0.018(2)	0.0050(16)	0.0034(16)	0.0012(15)
C11	0.020(2)	0.0136(18)	0.017(2)	0.0039(16)	−0.0007(16)	0.0010(15)
C12	0.025(2)	0.017(2)	0.021(2)	0.0058(17)	0.0055(17)	−0.0037(16)
C13	0.017(2)	0.018(2)	0.028(2)	0.0035(18)	0.0034(17)	−0.0050(16)
C14	0.0164(19)	0.0188(19)	0.020(2)	0.0067(17)	0.0003(16)	0.0006(15)
C15	0.0185(19)	0.0131(18)	0.018(2)	0.0058(16)	0.0023(16)	0.0000(14)
C16	0.019(2)	0.021(2)	0.020(2)	0.0062(17)	0.0011(16)	0.0028(16)
C17	0.022(2)	0.0159(19)	0.020(2)	0.0061(17)	0.0022(17)	0.0020(15)
C18	0.017(2)	0.028(2)	0.025(2)	0.0019(19)	0.0003(18)	0.0024(17)
C19	0.026(2)	0.024(2)	0.022(2)	0.0034(18)	0.0005(18)	0.0057(17)
C20	0.0182(19)	0.0165(19)	0.022(2)	0.0068(17)	0.0048(16)	0.0012(15)
C21	0.018(2)	0.022(2)	0.019(2)	0.0067(17)	0.0037(16)	0.0013(16)
C22	0.022(2)	0.037(3)	0.043(3)	0.020(2)	0.012(2)	0.0085(19)
C23	0.030(2)	0.024(2)	0.029(3)	0.010(2)	0.007(2)	0.0062(18)
C24	0.034(2)	0.023(2)	0.027(2)	0.0135(19)	0.005(2)	0.0058(18)
C25	0.037(3)	0.035(3)	0.034(3)	0.020(2)	0.019(2)	0.011(2)
C26	0.045(3)	0.035(3)	0.026(3)	0.015(2)	−0.007(2)	−0.001(2)
B1	0.016(2)	0.020(2)	0.024(3)	0.005(2)	0.0007(19)	−0.0009(18)
Cl1	0.0497(8)	0.0602(9)	0.0401(8)	0.0278(7)	0.0151(6)	0.0167(7)
Cl2	0.0350(7)	0.0469(7)	0.0484(8)	0.0240(7)	0.0045(6)	0.0028(6)
C27	0.037(3)	0.049(3)	0.031(3)	0.015(2)	−0.005(2)	−0.013(2)

Table 4 Bond lengths and angles for compound 4.23	Length [Å]
Atom–Atom	
W1–P1	2.5045(11)
W1–N1	2.252(3)
W1–N3	2.212(3)
W1–N5	2.205(3)
W1–N7	1.767(3)
W1–C10	2.190(4)
W1–C11	2.241(4)
P1–C24	1.821(4)
P1–C25	1.817(5)
P1–C26	1.815(5)
O1–N7	1.230(4)
O2–C17	1.241(5)
O3–H3	1.01(6)
O3–C21	1.431(5)
N1–N2	1.356(4)
N1–C1	1.334(5)
N2–C3	1.345(5)
N2–B1	1.544(6)
N3–N4	1.355(5)
N3–C4	1.330(5)
N4–C6	1.345(5)
N4–B1	1.540(6)
N5–N6	1.363(4)
N5–C7	1.345(5)
N6–C9	1.334(5)
N6–B1	1.552(6)
N8–C15	1.498(5)
N8–C17	1.328(5)
N8–C20	1.462(5)
C1–H1	0.9500
C1–C2	1.384(6)
C2–H2	0.9500
C2–C3	1.357(6)
C3–H3A	0.9500

C4–H4	0.9500
C4–C5	1.389(6)
C5–H5	0.9500
C5–C6	1.362(6)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.373(6)
C8–H8	0.9500
C8–C9	1.366(6)
C9–H9	0.9500
C10–H10	0.85(4)
C10–C11	1.431(6)
C10–C15	1.509(5)
C11–H11	0.89(5)
C11–C12	1.472(6)
C12–H12	0.9500
C12–C13	1.329(6)
C13–H13	0.9500
C13–C14	1.497(6)
C14–H14	1.0000
C14–C15	1.547(5)
C14–C16	1.549(6)
C15–H15	1.0000
C16–C17	1.521(5)
C16–C18	1.520(6)
C16–C19	1.539(6)
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C19–H19A	0.9800
C19–H19B	0.9800
C19–H19C	0.9800
C20–H20A	0.9900
C20–H20B	0.9900
C20–C21	1.523(5)
C21–C22	1.521(6)
C21–C23	1.523(6)
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800

C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
B1–H1A	1.07(4)
Cl1–C27	1.781(6)
Cl2–C27	1.754(5)
C27–H27A	0.9900
C27–H27B	0.9900

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	86.26(9)
N3–W1–P1	82.71(9)
N3–W1–N1	84.44(12)
N3–W1–C11	159.07(14)
N5–W1–P1	157.30(9)
N5–W1–N1	81.62(12)
N5–W1–N3	77.09(12)
N5–W1–C11	121.51(13)
N7–W1–P1	93.07(11)
N7–W1–N1	174.54(13)
N7–W1–N3	90.10(14)
N7–W1–N5	97.16(14)
N7–W1–C10	98.25(15)
N7–W1–C11	96.33(15)
C10–W1–P1	114.47(11)
C10–W1–N1	86.94(13)
C10–W1–N3	160.24(14)
C10–W1–N5	84.09(13)
C10–W1–C11	37.66(15)
C11–W1–P1	77.09(11)
C11–W1–N1	88.81(13)

C24–P1–W1	121.30(15)
C25–P1–W1	113.44(16)
C25–P1–C24	101.5(2)
C26–P1–W1	115.25(17)
C26–P1–C24	98.6(2)
C26–P1–C25	104.2(2)
C21–O3–H3	106(3)
N2–N1–W1	120.8(2)
C1–N1–W1	133.0(3)
C1–N1–N2	106.2(3)
N1–N2–B1	120.9(3)
C3–N2–N1	109.3(3)
C3–N2–B1	129.7(4)
N4–N3–W1	122.5(2)
C4–N3–W1	130.6(3)
C4–N3–N4	106.9(3)
N3–N4–B1	119.5(3)
C6–N4–N3	108.9(3)
C6–N4–B1	130.7(4)
N6–N5–W1	121.0(2)
C7–N5–W1	133.4(3)
C7–N5–N6	105.5(3)
N5–N6–B1	121.6(3)
C9–N6–N5	109.8(3)
C9–N6–B1	128.3(4)
O1–N7–W1	175.9(3)
C17–N8–C15	112.7(3)
C17–N8–C20	121.5(3)
C20–N8–C15	122.5(3)
N1–C1–H1	124.7
N1–C1–C2	110.6(4)
C2–C1–H1	124.7
C1–C2–H2	127.6
C3–C2–C1	104.8(4)
C3–C2–H2	127.6
N2–C3–C2	109.1(4)
N2–C3–H3A	125.5
C2–C3–H3A	125.5
N3–C4–H4	124.8
N3–C4–C5	110.3(4)

C5–C4–H4	124.8
C4–C5–H5	127.7
C6–C5–C4	104.6(4)
C6–C5–H5	127.7
N4–C6–C5	109.2(4)
N4–C6–H6	125.4
C5–C6–H6	125.4
N5–C7–H7	124.6
N5–C7–C8	110.8(4)
C8–C7–H7	124.6
C7–C8–H8	127.4
C9–C8–C7	105.1(4)
C9–C8–H8	127.4
N6–C9–C8	108.9(4)
N6–C9–H9	125.6
C8–C9–H9	125.6
W1–C10–H10	108(3)
C11–C10–W1	73.1(2)
C11–C10–H10	111(3)
C11–C10–C15	119.2(3)
C15–C10–W1	125.9(3)
C15–C10–H10	113(3)
W1–C11–H11	118(3)
C10–C11–W1	69.3(2)
C10–C11–H11	121(3)
C10–C11–C12	116.9(4)
C12–C11–W1	115.0(3)
C12–C11–H11	111(3)
C11–C12–H12	118.1
C13–C12–C11	123.7(4)
C13–C12–H12	118.1
C12–C13–H13	118.2
C12–C13–C14	123.6(4)
C14–C13–H13	118.2
C13–C14–H14	109.7
C13–C14–C15	111.8(3)
C13–C14–C16	112.5(3)
C15–C14–H14	109.7
C15–C14–C16	103.2(3)
C16–C14–H14	109.7

N8–C15–C10	112.5(3)
N8–C15–C14	100.7(3)
N8–C15–H15	109.2
C10–C15–C14	115.6(3)
C10–C15–H15	109.2
C14–C15–H15	109.2
C17–C16–C14	101.6(3)
C17–C16–C19	107.3(3)
C18–C16–C14	116.2(4)
C18–C16–C17	111.2(3)
C18–C16–C19	108.9(3)
C19–C16–C14	111.1(3)
O2–C17–N8	125.4(4)
O2–C17–C16	124.7(4)
N8–C17–C16	109.9(3)
C16–C18–H18A	109.5
C16–C18–H18B	109.5
C16–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
C16–C19–H19A	109.5
C16–C19–H19B	109.5
C16–C19–H19C	109.5
H19A–C19–H19B	109.5
H19A–C19–H19C	109.5
H19B–C19–H19C	109.5
N8–C20–H20A	108.0
N8–C20–H20B	108.0
N8–C20–C21	117.4(3)
H20A–C20–H20B	107.2
C21–C20–H20A	108.0
C21–C20–H20B	108.0
O3–C21–C20	111.4(3)
O3–C21–C22	105.7(3)
O3–C21–C23	109.3(3)
C22–C21–C20	108.2(3)
C22–C21–C23	110.8(4)
C23–C21–C20	111.2(3)
C21–C22–H22A	109.5

C21–C22–H22B	109.5
C21–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
C21–C23–H23A	109.5
C21–C23–H23B	109.5
C21–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
N2–B1–N6	108.2(3)
N2–B1–H1A	109(2)
N4–B1–N2	108.8(4)
N4–B1–N6	106.2(3)
N4–B1–H1A	114(2)
N6–B1–H1A	110(2)
Cl1–C27–H27A	109.4
Cl1–C27–H27B	109.4
Cl2–C27–Cl1	111.3(3)
Cl2–C27–H27A	109.4
Cl2–C27–H27B	109.4

H27A–C27–H27B 108.0

Table 6 Torsion angles for compound 4.23	Torsion Angle [°]
Atom–Atom–Atom–Atom	
W1–N1–N2–C3	179.1(3)
W1–N1–N2–B1	−4.9(5)
W1–N1–C1–C2	−178.6(3)
W1–N3–N4–C6	−178.0(3)
W1–N3–N4–B1	11.8(5)
W1–N3–C4–C5	177.6(3)
W1–N5–N6–C9	−177.3(3)
W1–N5–N6–B1	−3.4(4)
W1–N5–C7–C8	177.1(3)
W1–C10–C11–C12	108.3(3)
W1–C10–C15–N8	−171.2(3)
W1–C10–C15–C14	−56.3(4)
W1–C11–C12–C13	73.5(5)
N1–N2–C3–C2	−0.4(5)
N1–N2–B1–N4	60.9(5)
N1–N2–B1–N6	−54.2(5)
N1–C1–C2–C3	−0.3(5)
N2–N1–C1–C2	0.1(5)
N3–N4–C6–C5	0.1(5)
N3–N4–B1–N2	−65.2(4)
N3–N4–B1–N6	51.2(5)
N3–C4–C5–C6	0.6(5)
N4–N3–C4–C5	−0.5(5)
N5–N6–C9–C8	−0.2(5)
N5–N6–B1–N2	60.0(4)
N5–N6–B1–N4	−56.7(4)
N5–C7–C8–C9	−0.5(5)
N6–N5–C7–C8	0.4(4)
N8–C20–C21–O3	68.4(5)
N8–C20–C21–C22	−175.8(4)
N8–C20–C21–C23	−53.9(5)
C1–N1–N2–C3	0.2(4)
C1–N1–N2–B1	176.3(4)
C1–C2–C3–N2	0.5(5)
C3–N2–B1–N4	−124.0(4)

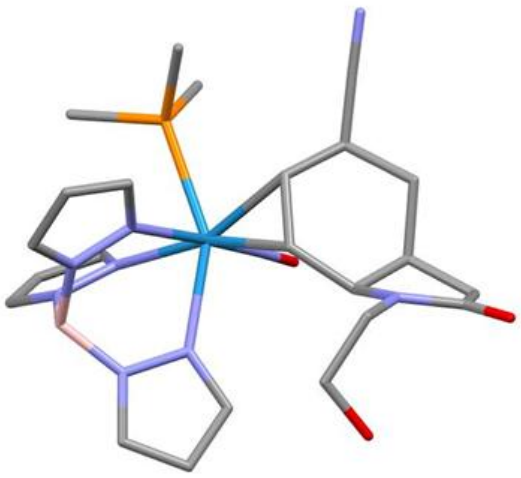
C3–N2–B1–N6	121.0(4)
C4–N3–N4–C6	0.3(4)
C4–N3–N4–B1	−169.9(4)
C4–C5–C6–N4	−0.4(5)
C6–N4–B1–N2	127.2(4)
C6–N4–B1–N6	−116.5(4)
C7–N5–N6–C9	−0.1(4)
C7–N5–N6–B1	173.8(3)
C7–C8–C9–N6	0.4(5)
C9–N6–B1–N2	−127.2(4)
C9–N6–B1–N4	116.1(4)
C10–C11–C12–C13	−4.9(6)
C11–C10–C15–N8	−81.6(4)
C11–C10–C15–C14	33.3(5)
C11–C12–C13–C14	2.8(7)
C12–C13–C14–C15	16.5(6)
C12–C13–C14–C16	132.1(4)
C13–C14–C15–N8	88.4(4)
C13–C14–C15–C10	−33.0(5)
C13–C14–C16–C17	−88.8(4)
C13–C14–C16–C18	32.1(5)
C13–C14–C16–C19	157.3(3)
C14–C16–C17–O2	162.3(4)
C14–C16–C17–N8	−19.2(4)
C15–N8–C17–O2	176.3(4)
C15–N8–C17–C16	−2.2(5)
C15–N8–C20–C21	125.6(4)
C15–C10–C11–W1	−122.2(3)
C15–C10–C11–C12	−13.9(5)
C15–C14–C16–C17	31.9(4)
C15–C14–C16–C18	152.8(3)
C15–C14–C16–C19	−82.0(4)
C16–C14–C15–N8	−32.8(4)
C16–C14–C15–C10	−154.2(3)
C17–N8–C15–C10	146.3(4)
C17–N8–C15–C14	22.6(4)
C17–N8–C20–C21	−76.4(5)
C18–C16–C17–O2	38.0(6)
C18–C16–C17–N8	−143.5(4)
C19–C16–C17–O2	−81.0(5)

C19–C16–C17–N8	97.5(4)
C20–N8–C15–C10	−54.0(5)
C20–N8–C15–C14	−177.6(3)
C20–N8–C17–O2	16.2(6)
C20–N8–C17–C16	−162.2(3)
B1–N2–C3–C2	−176.0(4)
B1–N4–C6–C5	168.8(4)
B1–N6–C9–C8	−173.6(4)

Table 7 Hydrogen bonds for compound 4.23

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O3–H3···O2	1.01(6)	1.68(6)	2.682(4)	171(5)

Crystal Structure Report for compound 4.40



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A yellow, block-like specimen of $C_{23}H_{33}BN_9O_3PW$, approximate dimensions 0.106 mm x 0.264 mm x 0.437 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 0.50 hours. The frames were integrated with the Bruker SAINT software package[81] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 83221 reflections to a maximum θ angle of 33.17° (0.65 Å resolution), of which 10677 were independent (average redundancy 7.794, completeness = 99.9%, R_{int} = 4.06%, R_{sig} = 2.44%) and 9561 (89.55%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.1605(4) Å, b = 11.5282(3) Å, c = 19.0565(6) Å, β = 104.5070(10)°, volume = 2799.01(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 9810 reflections above 20 σ(I) with 4.903° < 2θ < 66.22°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[82] The ratio of minimum to maximum apparent transmission was 0.601. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2600 and 0.6630.

The structure was solved and refined using the Bruker SHELXTL Software Package[83] within APEX5 [1] and OLEX2,[84] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{23}H_{33}BN_9O_3PW$. Non-hydrogen atoms were refined anisotropically. The B-H and O-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 362 variables converged at R1 = 2.25%, for the observed data and wR2 = 4.27% for all data. The goodness-of-fit was 1.074. The largest peak in the final difference electron density synthesis was 0.712 $e^-/Å^3$ and the largest hole was -1.123 $e^-/Å^3$ with an RMS deviation of 0.102 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.683 g/cm^3 and F(000), 1408 e^-.

[81] Bruker (2012). *Saint; SADABS; APEX5*. Bruker AXS Inc., Madison, Wisconsin, USA.

[82] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[83] Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.

[84] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Table 1. Sample and crystal data for compound 4.40**.**		
Chemical formula	$C_{23}H_{33}BN_9O_3PW$	
Formula weight	709.21 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.106 x 0.264 x 0.437 mm	
Crystal habit	yellow block	
Crystal system	monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 13.1605(4) Å	α = 90°
	b = 11.5282(3) Å	β = 104.5070(10)°
	c = 19.0565(6) Å	γ = 90°
Volume	2799.01(14) $Å^3$	
Z	4	
Density (calculated)	1.683 g/cm^3	
Absorption coefficient	4.227 mm^{-1}	
F(000)	1408	

Table 2. Data collection and structure refinement for compound 4.40	
Diffractometer	Bruker D8 Venture Photon III Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.08 to 33.17°
Index ranges	-20<=h<=20, -17<=k<=17, -28<=l<=29
Reflections collected	83221
Independent reflections	10677 [R(int) = 0.0406]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan

Max. and min. transmission	0.6630 and 0.2600	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	10677 / 0 / 362	
Goodness-of-fit on F^2	1.074	
Δ/σ_{max}	0.001	
Final R indices	9561 data; I>2σ(I)	R1 = 0.0225, wR2 = 0.0415
	all data	R1 = 0.0276, wR2 = 0.0427
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0033P)^2+3.5943P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.712 and -1.123 eÅ^{-3}	
R.M.S. deviation from mean	0.102 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.40

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.19024(2)	0.74493(2)	0.46586(2)	0.00904(2)
P1	0.09363(4)	0.69684(4)	0.33743(3)	0.01541(9)
O1	0.02870(11)	0.65118(13)	0.53739(9)	0.0232(3)
O2	0.50356(11)	0.37785(11)	0.70390(7)	0.0189(3)
O3	0.54040(14)	0.68415(13)	0.72642(8)	0.0259(3)

	x/a	y/b	z/c	U(eq)
N1	0.30060(11)	0.83254(13)	0.41001(8)	0.0128(3)
N2	0.30644(12)	0.95064(13)	0.40914(9)	0.0153(3)
N3	0.09260(11)	0.90086(13)	0.43763(8)	0.0131(3)
N4	0.13196(12)	0.00731(13)	0.42976(8)	0.0156(3)
N5	0.26640(11)	0.87018(12)	0.55279(8)	0.0119(3)
N6	0.28476(12)	0.98133(13)	0.53417(8)	0.0146(3)
N7	0.09618(11)	0.68657(13)	0.50834(8)	0.0131(3)
N8	0.18133(15)	0.31991(16)	0.35268(10)	0.0268(4)
N9	0.43482(11)	0.52059(12)	0.62180(8)	0.0133(3)
C1	0.36270(14)	0.79456(17)	0.36888(10)	0.0166(3)
C2	0.40748(16)	0.88682(18)	0.34075(11)	0.0223(4)
C3	0.37006(16)	0.98416(18)	0.36800(11)	0.0222(4)
C4	0.98827(14)	0.91242(17)	0.42352(10)	0.0173(3)
C5	0.95978(16)	0.02647(19)	0.40590(10)	0.0226(4)
C6	0.05271(16)	0.08471(18)	0.41106(10)	0.0215(4)
C7	0.29638(14)	0.86645(16)	0.62538(10)	0.0152(3)
C8	0.33466(15)	0.97386(17)	0.65394(10)	0.0197(4)
C9	0.32540(15)	0.04357(17)	0.59442(11)	0.0200(4)
C10	0.25829(13)	0.57287(15)	0.45241(10)	0.0131(3)
C11	0.31973(13)	0.62921(14)	0.51776(9)	0.0120(3)
C12	0.33117(13)	0.57761(14)	0.59190(9)	0.0124(3)
C13	0.25549(14)	0.47775(16)	0.59646(10)	0.0153(3)
C14	0.24115(14)	0.39763(16)	0.53099(10)	0.0167(3)
C15	0.19385(14)	0.46376(15)	0.46058(10)	0.0150(3)
C16	0.18586(15)	0.38406(16)	0.39948(11)	0.0192(4)
C17	0.31426(15)	0.41449(16)	0.66539(10)	0.0175(3)
C18	0.42835(14)	0.43309(15)	0.66700(10)	0.0148(3)
C19	0.53376(13)	0.57512(15)	0.62049(10)	0.0137(3)
C20	0.54588(14)	0.69503(15)	0.65387(10)	0.0160(3)
C21	0.15539(17)	0.60873(18)	0.28063(11)	0.0231(4)
C22	0.06307(18)	0.82437(19)	0.27892(11)	0.0257(4)
C23	0.96760(17)	0.6249(2)	0.32703(13)	0.0312(5)
B1	0.25152(17)	0.02498(18)	0.45539(12)	0.0166(4)

Table 4. Bond lengths (Å) for compound 4.40			
W1-N7	1.7726(15)	W1-C11	2.1949(16)
W1-N3	2.1967(14)	W1-C10	2.2174(17)
W1-N5	2.2365(14)	W1-N1	2.2444(15)
W1-P1	2.5209(5)	P1-C21	1.818(2)
P1-C23	1.820(2)	P1-C22	1.828(2)
O1-N7	1.2280(19)	O2-C18	1.237(2)
O3-C20	1.408(2)	O3-H3	0.79(3)
N1-C1	1.340(2)	N1-N2	1.364(2)
N2-C3	1.339(2)	N2-B1	1.534(3)
N3-C4	1.338(2)	N3-N4	1.355(2)
N4-C6	1.351(2)	N4-B1	1.540(3)
N5-C7	1.341(2)	N5-N6	1.367(2)
N6-C9	1.346(2)	N6-B1	1.539(3)
N8-C16	1.149(3)	N9-C18	1.343(2)
N9-C19	1.452(2)	N9-C12	1.493(2)
C1-C2	1.387(3)	C1-H1	0.950000
C2-C3	1.378(3)	C2-H2	0.950000
C3-H3A	0.950000	C4-C5	1.385(3)
C4-H4	0.950000	C5-C6	1.377(3)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.395(3)	C7-H7	0.950000
C8-C9	1.370(3)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.457(2)
C10-C15	1.547(2)	C10-H10	0.93(3)
C11-C12	1.505(2)	C11-H11	0.95(2)
C12-C13	1.539(2)	C12-H12	1.000000
C13-C14	1.526(3)	C13-C17	1.532(2)
C13-H13	1.000000	C14-C15	1.533(2)
C14-H14A	0.990000	C14-H14B	0.990000
C15-C16	1.466(3)	C15-H15	1.000000
C17-C18	1.509(3)	C17-H17A	0.990000
C17-H17B	0.990000	C19-C20	1.513(2)
C19-H19A	0.990000	C19-H19B	0.990000
C20-H20A	0.990000	C20-H20B	0.990000

C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
C23-H23A	0.980000	C23-H23B	0.980000
C23-H23C	0.980000	B1-H1A	1.09(2)

Table 5. Bond angles (°) for compound 4.40.			
N7-W1-C11	96.65(7)	N7-W1-N3	89.42(6)
C11-W1-N3	161.48(6)	N7-W1-C10	93.54(7)
C11-W1-C10	38.55(6)	N3-W1-C10	158.76(6)
N7-W1-N5	98.13(6)	C11-W1-N5	84.57(6)
N3-W1-N5	77.24(5)	C10-W1-N5	122.96(6)
N7-W1-N1	175.06(6)	C11-W1-N1	88.02(6)
N3-W1-N1	85.64(5)	C10-W1-N1	91.13(6)
N5-W1-N1	80.65(6)	N7-W1-P1	96.88(5)
C11-W1-P1	116.72(5)	N3-W1-P1	79.65(4)
C10-W1-P1	79.11(5)	N5-W1-P1	152.20(4)
N1-W1-P1	82.38(4)	C21-P1-C23	102.22(11)
C21-P1-C22	98.57(10)	C23-P1-C22	104.17(11)
C21-P1-W1	120.59(7)	C23-P1-W1	115.48(8)
C22-P1-W1	113.31(7)	C20-O3-H3	110.(2)
C1-N1-N2	105.95(15)	C1-N1-W1	133.82(12)
N2-N1-W1	120.00(11)	C3-N2-N1	109.90(16)
C3-N2-B1	128.96(16)	N1-N2-B1	120.98(15)
C4-N3-N4	106.80(15)	C4-N3-W1	129.69(13)
N4-N3-W1	123.50(11)	C6-N4-N3	109.65(16)
C6-N4-B1	131.02(17)	N3-N4-B1	118.26(14)
C7-N5-N6	105.81(14)	C7-N5-W1	134.82(12)
N6-N5-W1	119.24(11)	C9-N6-N5	109.67(15)
C9-N6-B1	127.79(16)	N5-N6-B1	122.28(14)
O1-N7-W1	176.95(14)	C18-N9-C19	122.52(14)
C18-N9-C12	112.14(15)	C19-N9-C12	122.72(13)
N1-C1-C2	110.85(17)	N1-C1-H1	124.600000
C2-C1-H1	124.600000	C3-C2-C1	104.61(17)
C3-C2-H2	127.700000	C1-C2-H2	127.700000

N2-C3-C2	108.68(17)	N2-C3-H3A	125.700000
C2-C3-H3A	125.700000	N3-C4-C5	110.19(18)
N3-C4-H4	124.900000	C5-C4-H4	124.900000
C6-C5-C4	105.30(16)	C6-C5-H5	127.400000
C4-C5-H5	127.400000	N4-C6-C5	108.06(18)
N4-C6-H6	126.000000	C5-C6-H6	126.000000
N5-C7-C8	111.00(17)	N5-C7-H7	124.500000
C8-C7-H7	124.500000	C9-C8-C7	104.41(16)
C9-C8-H8	127.800000	C7-C8-H8	127.800000
N6-C9-C8	109.11(17)	N6-C9-H9	125.400000
C8-C9-H9	125.400000	C11-C10-C15	118.53(15)
C11-C10-W1	69.89(9)	C15-C10-W1	117.93(12)
C11-C10-H10	118.1(15)	C15-C10-H10	112.2(15)
W1-C10-H10	114.1(15)	C10-C11-C12	121.98(15)
C10-C11-W1	71.56(9)	C12-C11-W1	123.15(12)
C10-C11-H11	116.0(13)	C12-C11-H11	112.2(13)
W1-C11-H11	105.7(13)	N9-C12-C11	113.53(14)
N9-C12-C13	101.04(13)	C11-C12-C13	115.76(14)
N9-C12-H12	108.700000	C11-C12-H12	108.700000
C13-C12-H12	108.700000	C14-C13-C17	110.21(15)
C14-C13-C12	110.85(15)	C17-C13-C12	102.10(14)
C14-C13-H13	111.100000	C17-C13-H13	111.100000
C12-C13-H13	111.100000	C13-C14-C15	110.77(15)
C13-C14-H14A	109.500000	C15-C14-H14A	109.500000
C13-C14-H14B	109.500000	C15-C14-H14B	109.500000
H14A-C14-H14B	108.100000	C16-C15-C14	108.43(15)
C16-C15-C10	111.21(16)	C14-C15-C10	112.32(14)
C16-C15-H15	108.300000	C14-C15-H15	108.300000
C10-C15-H15	108.300000	N8-C16-C15	178.3(2)
C18-C17-C13	103.63(14)	C18-C17-H17A	111.000000
C13-C17-H17A	111.000000	C18-C17-H17B	111.000000

C13-C17-H17B	111.000000	H17A-C17-H17B	109.000000
O2-C18-N9	125.51(18)	O2-C18-C17	126.04(17)
N9-C18-C17	108.45(15)	N9-C19-C20	112.89(14)
N9-C19-H19A	109.000000	C20-C19-H19A	109.000000
N9-C19-H19B	109.000000	C20-C19-H19B	109.000000
H19A-C19-H19B	107.800000	O3-C20-C19	107.79(15)
O3-C20-H20A	110.100000	C19-C20-H20A	110.100000
O3-C20-H20B	110.100000	C19-C20-H20B	110.100000
H20A-C20-H20B	108.500000	P1-C21-H21A	109.500000
P1-C21-H21B	109.500000	H21A-C21-H21B	109.500000
P1-C21-H21C	109.500000	H21A-C21-H21C	109.500000
H21B-C21-H21C	109.500000	P1-C22-H22A	109.500000
P1-C22-H22B	109.500000	H22A-C22-H22B	109.500000
P1-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	P1-C23-H23A	109.500000
P1-C23-H23B	109.500000	H23A-C23-H23B	109.500000
P1-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	N2-B1-N6	108.54(15)
N2-B1-N4	109.58(15)	N6-B1-N4	106.51(16)
N2-B1-H1A	110.9(12)	N6-B1-H1A	109.8(12)
N4-B1-H1A	111.4(12)		

Table 6. Torsion angles (°) for compound 4.40			
C1-N1-N2-C3	0.4(2)	W1-N1-N2-C3	-174.80(12)
C1-N1-N2-B1	-175.35(16)	W1-N1-N2-B1	9.4(2)
C4-N3-N4-C6	0.1(2)	W1-N3-N4-C6	178.84(12)
C4-N3-N4-B1	169.60(16)	W1-N3-N4-B1	-11.7(2)
C7-N5-N6-C9	0.2(2)	W1-N5-N6-C9	176.60(12)
C7-N5-N6-B1	-174.37(16)	W1-N5-N6-B1	2.0(2)
N2-N1-C1-C2	-0.8(2)	W1-N1-C1-C2	173.52(13)
N1-C1-C2-C3	0.8(2)	N1-N2-C3-C2	0.0(2)
B1-N2-C3-C2	175.40(18)	C1-C2-C3-N2	-0.5(2)
N4-N3-C4-C5	0.5(2)	W1-N3-C4-C5	-178.12(13)
N3-C4-C5-C6	-0.9(2)	N3-N4-C6-C5	-0.7(2)
B1-N4-C6-C5	-168.36(19)	C4-C5-C6-N4	0.9(2)
N6-N5-C7-C8	-0.4(2)	W1-N5-C7-C8	-176.01(13)
N5-C7-C8-C9	0.5(2)	N5-N6-C9-C8	0.1(2)
B1-N6-C9-C8	174.29(18)	C7-C8-C9-N6	-0.4(2)
C15-C10-C11-C12	6.5(2)	W1-C10-C11-C12	118.13(15)
C15-C10-C11-W1	-111.64(15)	C18-N9-C12-C11	-150.74(15)
C19-N9-C12-C11	47.2(2)	C18-N9-C12-C13	-26.12(18)
C19-N9-C12-C13	171.84(15)	C10-C11-C12-N9	103.16(18)
W1-C11-C12-N9	-168.99(11)	C10-C11-C12-C13	-13.1(2)
W1-C11-C12-C13	74.77(18)	N9-C12-C13-C14	-83.20(16)
C11-C12-C13-C14	39.9(2)	N9-C12-C13-C17	34.17(17)

C11-C12-C13-C17	157.26(15)	C17-C13-C14-C15	-173.49(15)
C12-C13-C14-C15	-61.20(19)	C13-C14-C15-C16	177.71(15)
C13-C14-C15-C10	54.4(2)	C11-C10-C15-C16	-148.66(16)
W1-C10-C15-C16	130.25(14)	C11-C10-C15-C14	-26.9(2)
W1-C10-C15-C14	-108.02(15)	C14-C13-C17-C18	86.21(17)
C12-C13-C17-C18	-31.61(18)	C19-N9-C18-O2	-11.4(3)
C12-N9-C18-O2	-173.48(17)	C19-N9-C18-C17	168.21(16)
C12-N9-C18-C17	6.1(2)	C13-C17-C18-O2	-163.61(18)
C13-C17-C18-N9	16.78(19)	C18-N9-C19-C20	-106.79(19)
C12-N9-C19-C20	53.4(2)	N9-C19-C20-O3	59.82(19)
C3-N2-B1-N6	-122.7(2)	N1-N2-B1-N6	52.2(2)
C3-N2-B1-N4	121.3(2)	N1-N2-B1-N4	-63.8(2)
C9-N6-B1-N2	126.85(19)	N5-N6-B1-N2	-59.6(2)
C9-N6-B1-N4	-115.2(2)	N5-N6-B1-N4	58.3(2)
C6-N4-B1-N2	-128.4(2)	N3-N4-B1-N2	64.8(2)
C6-N4-B1-N6	114.4(2)	N3-N4-B1-N6	-52.4(2)

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.40.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.00882(3)	0.00948(3)	0.00875(3)	0.00022(2)	0.00204(2)	0.00013(2)
P1	0.0150(2)	0.0194(2)	0.01089(19)	-0.00247(16)	0.00150(15)	-0.00184(16)
O1	0.0191(7)	0.0233(7)	0.0327(8)	0.0018(6)	0.0171(6)	-0.0029(5)
O2	0.0218(6)	0.0152(6)	0.0171(6)	0.0042(5)	0.0000(5)	0.0029(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	0.0437(9)	0.0162(7)	0.0186(7)	-0.0024(6)	0.0095(6)	0.0018(6)
N1	0.0123(6)	0.0121(6)	0.0143(7)	0.0013(5)	0.0037(5)	-0.0002(5)
N2	0.0177(7)	0.0124(6)	0.0160(7)	0.0029(5)	0.0048(5)	-0.0025(5)
N3	0.0133(6)	0.0144(6)	0.0109(6)	0.0003(5)	0.0015(5)	0.0024(5)
N4	0.0190(7)	0.0134(7)	0.0132(7)	0.0018(5)	0.0018(5)	0.0046(5)
N5	0.0115(6)	0.0118(6)	0.0114(6)	0.0001(5)	0.0008(5)	0.0016(5)
N6	0.0169(7)	0.0109(6)	0.0148(7)	-0.0016(5)	0.0018(5)	-0.0011(5)
N7	0.0111(6)	0.0132(6)	0.0160(7)	-0.0016(5)	0.0049(5)	-0.0004(5)
N8	0.0327(10)	0.0211(8)	0.0251(9)	-0.0045(7)	0.0046(7)	-0.0037(7)
N9	0.0123(6)	0.0116(6)	0.0147(7)	0.0019(5)	0.0011(5)	0.0008(5)
C1	0.0146(7)	0.0191(8)	0.0176(8)	0.0020(7)	0.0069(6)	-0.0007(6)
C2	0.0211(9)	0.0274(10)	0.0223(9)	0.0023(8)	0.0128(7)	-0.0055(7)
C3	0.0265(10)	0.0204(9)	0.0216(9)	0.0049(7)	0.0098(8)	-0.0074(7)
C4	0.0136(7)	0.0266(9)	0.0113(7)	0.0004(7)	0.0021(6)	0.0060(6)
C5	0.0219(9)	0.0319(10)	0.0139(8)	0.0039(7)	0.0042(7)	0.0160(8)
C6	0.0286(10)	0.0203(9)	0.0150(8)	0.0040(7)	0.0041(7)	0.0140(7)
C7	0.0157(8)	0.0178(8)	0.0110(7)	-0.0009(6)	0.0016(6)	0.0048(6)
C8	0.0199(8)	0.0217(9)	0.0145(8)	-0.0050(7)	-0.0015(6)	0.0010(7)
C9	0.0198(9)	0.0154(8)	0.0221(9)	-0.0055(7)	0.0004(7)	-0.0016(6)
C10	0.0143(7)	0.0120(7)	0.0140(8)	0.0000(6)	0.0054(6)	0.0018(6)
C11	0.0117(7)	0.0109(7)	0.0137(7)	0.0023(6)	0.0038(6)	0.0020(5)
C12	0.0128(7)	0.0117(7)	0.0128(7)	0.0017(6)	0.0031(6)	0.0028(5)
C13	0.0142(7)	0.0165(8)	0.0158(8)	0.0041(6)	0.0048(6)	-0.0006(6)
C14	0.0168(8)	0.0150(8)	0.0173(8)	0.0028(6)	0.0024(6)	-0.0038(6)
C15	0.0172(8)	0.0125(7)	0.0158(8)	-0.0002(6)	0.0049(6)	-0.0003(6)
C16	0.0198(8)	0.0152(8)	0.0210(9)	0.0008(7)	0.0018(7)	-0.0029(6)
C17	0.0212(8)	0.0172(8)	0.0146(8)	0.0045(6)	0.0057(6)	-0.0010(6)
C18	0.0205(8)	0.0108(7)	0.0121(7)	-0.0008(6)	0.0020(6)	0.0000(6)
C19	0.0118(7)	0.0148(7)	0.0151(8)	0.0012(6)	0.0042(6)	0.0024(6)
C20	0.0160(8)	0.0129(7)	0.0194(8)	0.0003(6)	0.0049(6)	-0.0014(6)
C21	0.0317(10)	0.0256(10)	0.0122(8)	-0.0051(7)	0.0059(7)	0.0019(8)
C22	0.0344(11)	0.0271(10)	0.0129(8)	0.0026(8)	0.0006(8)	0.0071(8)
C23	0.0208(10)	0.0442(13)	0.0265(11)	-0.0114(10)	0.0018(8)	-0.0134(9)
B1	0.0194(9)	0.0121(8)	0.0177(9)	0.0009(7)	0.0033(7)	-0.0005(7)

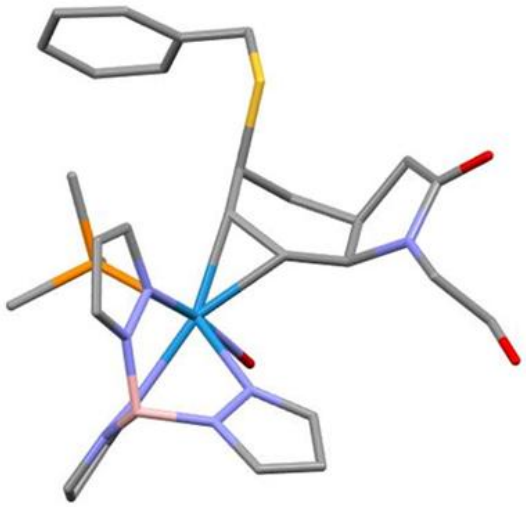
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for compound 4.40

	x/a	y/b	z/c	U(eq)
H3	0.525(2)	0.745(2)	0.7406(17)	0.035(8)
H1	0.3745	0.7152	0.3602	0.020000
H2	0.4536	0.8836	0.3096	0.027000
H3A	0.3866	1.0621	0.3591	0.027000
H4	-0.0594	0.8513	0.4253	0.021000
H5	-0.1092	1.0578	0.3930	0.027000
H6	0.0598	1.1653	0.4029	0.026000
H7	0.2921	0.7995	0.6536	0.018000
H8	0.3612	0.9941	0.7035	0.024000
H9	0.3446	1.1231	0.5955	0.024000
H10	0.2871(19)	0.568(2)	0.4129(13)	0.022(6)
H11	0.3817(17)	0.6670(19)	0.5135(12)	0.011(5)
H12	0.3219	0.6406	0.6259	0.015000
H13	0.1865	0.5081	0.6015	0.018000
H14A	0.1943	0.3326	0.5359	0.020000
H14B	0.3099	0.3648	0.5292	0.020000
H15	0.1214	0.4890	0.4612	0.018000
H17A	0.2973	0.4483	0.7089	0.021000
H17B	0.2966	0.3309	0.6628	0.021000
H19A	0.5388	0.5808	0.5696	0.016000
H19B	0.5922	0.5255	0.6471	0.016000
H20A	0.6142	0.7289	0.6518	0.019000
H20B	0.4892	0.7466	0.6270	0.019000
H21A	0.1676	0.5304	0.3009	0.035000
H21B	0.2226	0.6437	0.2788	0.035000
H21C	0.1093	0.6047	0.2315	0.035000
H22A	0.1278	0.8672	0.2801	0.039000
H22B	0.0143	0.8746	0.2961	0.039000
H22C	0.0307	0.7997	0.2291	0.039000
H23A	-0.0655	0.6136	0.2754	0.047000
H23B	-0.0779	0.6729	0.3487	0.047000
H23C	-0.0216	0.5494	0.3514	0.047000

	x/a	y/b	z/c	U(eq)
H1A	0.2726(17)	1.1162(19)	0.4532(12)	0.014(5)

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 4.40				
	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3-H3···O2#1	0.79(3)	1.95(3)	2.733(2)	168.(3)

Crystal Structure Report for compound 4.42



A colorless, needle-like specimen of $C_{29}H_{40}BN_8O_3PSW$, approximate dimensions 0.031 mm x 0.045 mm x 0.098 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture PhotonIII Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Cu Kα, λ = 1.54178 Å) and a HELIOS EF double bounce multilayer mirror monochromator.

The total exposure time was 6.57 hours. The frames were integrated with the Bruker SAINT software package[85] using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 26983 reflections to a maximum θ angle of 68.31° (0.83 Å resolution), of which 5844 were independent (average redundancy 4.617,

[85] Bruker (2012). *Saint; SADABS; APEX5*. Bruker AXS Inc., Madison, Wisconsin, USA.

completeness = 99.6%, R_{int} = 8.73%, R_{sig} = 6.55%) and 4163 (71.24%) were greater than 2σ(F^2). The final cell constants of a = 15.9236(5) Å, b = 16.8347(5) Å, c = 23.8830(6) Å, volume = 6402.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 4993 reflections above 20 σ(I) with 7.403° < 2θ < 136.6°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[86] The ratio of minimum to maximum apparent transmission was 0.820. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5030 and 0.7870.

The structure was solved and refined using the Bruker SHELXTL Software Package[87] within APEX5 [1] and OLEX2,[88] using the space group P b c a, with Z = 8 for the formula unit, $C_{29}H_{40}BN_8O_3PSW$. The B-H and O-H hydrogen atoms, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The relative occupancy of the disordered atoms was freely refined, with constraints on the anisotropic displacement parameters and bond lengths of the disordered atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 381 variables converged at R1 = 4.37%, for the observed data and wR2 = 9.09% for all data. The goodness-of-fit was 1.018. The largest peak in the final difference electron density synthesis was 1.299 $e^-/Å^3$ and the largest hole was -1.116 $e^-/Å^3$ with an RMS deviation of 0.125 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.673 g/cm^3 and F(000), 3232 e^-.

Table 1. Sample and crystal data for compound 4.42	
Chemical formula	$C_{29}H_{40}BN_8O_3PSW$
Formula weight	806.38 g/mol
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal size	0.031 x 0.045 x 0.098 mm
Crystal habit	colorless needle

[86] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[87] Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.

[88] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 15.9236(5) Å	α = 90°
	b = 16.8347(5) Å	β = 90°
	c = 23.8830(6) Å	γ = 90°
Volume	6402.3(3) $Å^3$	
Z	8	
Density (calculated)	1.673 g/cm^3	
Absorption coefficient	8.137 mm^{-1}	
F(000)	3232	

Table 2. Data collection and structure refinement for compound 4.42	
Diffractometer	Bruker D8 Venture PhotonIII Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Cu Kα, λ = 1.54178 Å)
Theta range for data collection	3.70 to 68.31°
Index ranges	-19<=h<=18, -20<=k<=15, -28<=l<=22
Reflections collected	26983
Independent reflections	5844 [R(int) = 0.0873]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7870 and 0.5030
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5844 / 1 / 381	
Goodness-of-fit on F^2	1.018	
Δ/σ_{max}	0.002	
Final R indices	4163 data; I>2σ(I)	R1 = 0.0437, wR2 = 0.0820
	all data	R1 = 0.0722, wR2 = 0.0909
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0245P)^2+16.3601P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.299 and -1.116 eÅ^{-3}	
R.M.S. deviation from mean	0.125 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.42.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.72422(2)	0.54089(2)	0.43286(2)	0.02022(8)
S1	0.68108(15)	0.57901(13)	0.23237(6)	0.0458(5)
P1	0.82898(11)	0.64368(10)	0.40309(6)	0.0241(3)
O1	0.6029(3)	0.6687(3)	0.46663(19)	0.0369(12)
O2	0.4296(3)	0.4148(4)	0.2596(2)	0.0521(16)
O3	0.3936(4)	0.2861(3)	0.4214(2)	0.0465(14)
N1	0.8271(3)	0.4514(3)	0.41513(19)	0.0244(11)
N2	0.8589(3)	0.4054(3)	0.4579(2)	0.0266(12)
N3	0.7869(3)	0.5543(3)	0.51420(18)	0.0228(11)
N4	0.8313(4)	0.4960(3)	0.5401(2)	0.0259(12)
N5	0.6744(3)	0.4394(3)	0.48411(19)	0.0228(11)

	x/a	y/b	z/c	U(eq)
N6	0.7281(4)	0.3931(3)	0.51471(18)	0.0229(11)
N7	0.6515(3)	0.6151(4)	0.45118(19)	0.0284(13)
N8	0.5014(4)	0.4415(4)	0.3397(2)	0.0340(15)
C1	0.8696(4)	0.4282(4)	0.3690(3)	0.0294(15)
C2	0.9276(4)	0.3707(4)	0.3815(3)	0.0344(16)
C3	0.9186(4)	0.3572(4)	0.4379(3)	0.0331(15)
C4	0.7869(4)	0.6170(4)	0.5492(2)	0.0263(14)
C5	0.8319(5)	0.5979(4)	0.5975(3)	0.0342(16)
C6	0.8584(5)	0.5216(4)	0.5906(3)	0.0332(17)
C7	0.5964(4)	0.4144(4)	0.4964(2)	0.0257(14)
C8	0.6000(5)	0.3523(4)	0.5342(2)	0.0293(15)
C9	0.6832(4)	0.3412(4)	0.5449(2)	0.0267(14)
C10	0.7019(4)	0.5404(5)	0.3407(2)	0.0282(14)
C11	0.6425(4)	0.4885(4)	0.3680(2)	0.0230(13)
C12	0.5483(4)	0.5057(4)	0.3676(2)	0.0285(15)
C13	0.5213(5)	0.5811(5)	0.3336(3)	0.042(2)
C14	0.5890(6)	0.6430(5)	0.3245(3)	0.044(2)
C15	0.6740(5)	0.6116(4)	0.3060(2)	0.0329(16)
C16	0.6727(6)	0.6731(6)	0.1954(3)	0.055(2)
C23	0.4836(5)	0.5476(6)	0.2793(3)	0.047(2)
C24	0.4664(4)	0.4613(6)	0.2903(3)	0.0415(19)
C25	0.4893(4)	0.3640(5)	0.3653(3)	0.0352(17)
C26	0.4066(5)	0.3608(5)	0.3955(3)	0.0367(17)
C27	0.7872(5)	0.7446(4)	0.4023(3)	0.0334(16)
C28	0.9211(4)	0.6521(5)	0.4492(3)	0.0373(17)
C29	0.8838(5)	0.6341(5)	0.3366(3)	0.0401(19)
B1	0.8222(5)	0.4107(5)	0.5171(3)	0.0266(16)
C17	0.7427(5)	0.7328(6)	0.2104(4)	0.0310(9)
C18	0.8190(6)	0.7074(4)	0.1885(4)	0.0310(9)
C19	0.8918(4)	0.7505(6)	0.1990(4)	0.0310(9)
C20	0.8883(6)	0.8190(6)	0.2314(4)	0.0310(9)
C21	0.8120(8)	0.8444(5)	0.2534(3)	0.0310(9)
C22	0.7392(6)	0.8013(6)	0.2428(4)	0.0310(9)
C17A	0.7441(6)	0.7255(6)	0.2073(4)	0.0310(9)
C18A	0.8299(7)	0.7123(5)	0.2016(4)	0.0310(9)

	x/a	y/b	z/c	U(eq)
C19A	0.8868(5)	0.7700(7)	0.2187(5)	0.0310(9)
C20A	0.8580(8)	0.8409(6)	0.2415(4)	0.0310(9)
C21A	0.7722(8)	0.8541(5)	0.2472(4)	0.0310(9)
C22A	0.7153(6)	0.7964(7)	0.2301(5)	0.0310(9)

Table 4. Bond lengths (Å) for compound 4.42			
W1-N7	1.759(6)	W1-N3	2.196(5)
W1-C11	2.207(6)	W1-C10	2.229(6)
W1-N5	2.247(5)	W1-N1	2.266(5)
W1-P1	2.5065(17)	S1-C16	1.818(9)
S1-C15	1.845(6)	P1-C29	1.819(6)
P1-C27	1.824(7)	P1-C28	1.839(7)
O1-N7	1.245(7)	O2-C24	1.222(9)
O3-C26	1.417(9)	O3-H3	0.94(9)
N1-C1	1.350(8)	N1-N2	1.377(7)
N2-C3	1.338(8)	N2-B1	1.533(9)
N3-C4	1.347(8)	N3-N4	1.360(7)
N4-C6	1.351(8)	N4-B1	1.545(9)
N5-C7	1.343(8)	N5-N6	1.368(7)
N6-C9	1.339(8)	N6-B1	1.529(9)
N8-C24	1.346(8)	N8-C25	1.453(9)
N8-C12	1.474(9)	C1-C2	1.371(10)
C1-H1	0.950000	C2-C3	1.375(10)
C2-H2	0.950000	C3-H3A	0.950000
C4-C5	1.396(9)	C4-H4	0.950000
C5-C6	1.362(10)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.382(9)
C7-H7	0.950000	C8-C9	1.361(10)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.444(10)	C10-C15	1.523(9)
C10-H10	0.85(6)	C11-C12	1.528(9)
C11-H11	0.90(6)	C12-C13	1.567(9)
C12-H12	1.000000	C13-C14	1.516(12)
C13-C23	1.537(10)	C13-H13	1.000000

C14-C15	1.519(11)	C14-H14A	0.990000
C14-H14B	0.990000	C15-H15	1.000000
C16-C17A	1.467(11)	C16-C17	1.543(11)
C16-H16A	0.990000	C16-H16B	0.990000
C16-H16C	0.990000	C16-H16D	0.990000
C23-C24	1.501(12)	C23-H23A	0.990000
C23-H23B	0.990000	C25-C26	1.502(9)
C25-H25A	0.990000	C25-H25B	0.990000
C26-H26A	0.990000	C26-H26B	0.990000
C27-H27A	0.980000	C27-H27B	0.980000
C27-H27C	0.980000	C28-H28A	0.980000
C28-H28B	0.980000	C28-H28C	0.980000
C29-H29A	0.980000	C29-H29B	0.980000
C29-H29C	0.980000	B1-H1A	0.94(6)
C17-C18	1.390000	C17-C22	1.390000
C18-C19	1.390000	C18-H18	0.950000
C19-C20	1.390000	C19-H19	0.950000
C20-C21	1.390000	C20-H20	0.950000
C21-C22	1.390000	C21-H21	0.950000
C22-H22	0.950000	C17A-C18A	1.390000
C17A-C22A	1.390000	C18A-C19A	1.390000
C18A-H18A	0.950000	C19A-C20A	1.390000
C19A-H19A	0.950000	C20A-C21A	1.390000
C20A-H20A	0.950000	C21A-C22A	1.390000
C21A-H21A	0.950000	C22A-H22A	0.950000

Table 5. Bond angles (°) for compound 4.42			
N7-W1-N3	90.3(2)	N7-W1-C11	94.0(2)
N3-W1-C11	158.4(2)	N7-W1-C10	98.2(2)
N3-W1-C10	161.1(2)	C11-W1-C10	38.0(2)
N7-W1-N5	99.9(2)	N3-W1-N5	75.93(18)
C11-W1-N5	82.5(2)	C10-W1-N5	118.6(2)

N7-W1-N1	174.2(2)	N3-W1-N1	84.57(18)
C11-W1-N1	91.7(2)	C10-W1-N1	85.9(2)
N5-W1-N1	81.45(19)	N7-W1-P1	91.05(19)
N3-W1-P1	82.95(14)	C11-W1-P1	118.00(18)
C10-W1-P1	80.13(19)	N5-W1-P1	156.15(14)
N1-W1-P1	85.68(14)	C16-S1-C15	101.5(4)
C29-P1-C27	104.3(3)	C29-P1-C28	98.4(3)
C27-P1-C28	103.0(4)	C29-P1-W1	120.4(3)
C27-P1-W1	113.8(3)	C28-P1-W1	114.5(2)
C26-O3-H3	99.(6)	C1-N1-N2	105.0(5)
C1-N1-W1	135.0(4)	N2-N1-W1	120.0(4)
C3-N2-N1	109.7(5)	C3-N2-B1	129.3(6)
N1-N2-B1	120.8(5)	C4-N3-N4	106.4(5)
C4-N3-W1	129.1(4)	N4-N3-W1	124.4(4)
C6-N4-N3	110.0(6)	C6-N4-B1	130.1(6)
N3-N4-B1	117.4(5)	C7-N5-N6	106.4(5)
C7-N5-W1	133.1(4)	N6-N5-W1	120.2(4)
C9-N6-N5	109.0(6)	C9-N6-B1	129.0(6)
N5-N6-B1	121.5(5)	O1-N7-W1	176.5(5)
C24-N8-C25	122.5(7)	C24-N8-C12	115.1(7)
C25-N8-C12	122.3(5)	N1-C1-C2	111.4(6)
N1-C1-H1	124.300000	C2-C1-H1	124.300000
C1-C2-C3	105.0(6)	C1-C2-H2	127.500000
C3-C2-H2	127.500000	N2-C3-C2	108.9(6)
N2-C3-H3A	125.600000	C2-C3-H3A	125.600000
N3-C4-C5	109.4(6)	N3-C4-H4	125.300000
C5-C4-H4	125.300000	C6-C5-C4	106.1(6)
C6-C5-H5	127.000000	C4-C5-H5	127.000000
N4-C6-C5	108.1(6)	N4-C6-H6	126.000000
C5-C6-H6	126.000000	N5-C7-C8	109.9(6)
N5-C7-H7	125.000000	C8-C7-H7	125.000000
C9-C8-C7	105.5(6)	C9-C8-H8	127.300000
C7-C8-H8	127.300000	N6-C9-C8	109.2(6)
N6-C9-H9	125.400000	C8-C9-H9	125.400000
C11-C10-C15	122.1(6)	C11-C10-W1	70.2(3)
C15-C10-W1	125.5(5)	C11-C10-H10	110.(4)

C15-C10-H10	115.(4)	W1-C10-H10	106.(4)
C10-C11-C12	121.7(6)	C10-C11-W1	71.9(3)
C12-C11-W1	120.5(4)	C10-C11-H11	112.(4)
C12-C11-H11	114.(4)	W1-C11-H11	111.(4)
N8-C12-C11	111.2(5)	N8-C12-C13	102.7(5)
C11-C12-C13	115.2(6)	N8-C12-H12	109.200000
C11-C12-H12	109.200000	C13-C12-H12	109.200000
C14-C13-C23	114.1(6)	C14-C13-C12	115.8(6)
C23-C13-C12	104.3(6)	C14-C13-H13	107.400000
C23-C13-H13	107.400000	C12-C13-H13	107.400000
C13-C14-C15	115.9(7)	C13-C14-H14A	108.300000
C15-C14-H14A	108.300000	C13-C14-H14B	108.300000
C15-C14-H14B	108.300000	H14A-C14-H14B	107.400000
C14-C15-C10	112.0(6)	C14-C15-S1	115.8(5)
C10-C15-S1	105.5(5)	C14-C15-H15	107.700000
C10-C15-H15	107.700000	S1-C15-H15	107.700000
C17A-C16-S1	112.0(7)	C17-C16-S1	113.8(6)
C17-C16-H16A	108.800000	S1-C16-H16A	108.800000
C17-C16-H16B	108.800000	S1-C16-H16B	108.800000
H16A-C16-H16B	107.700000	C17A-C16-H16C	109.200000
S1-C16-H16C	109.200000	C17A-C16-H16D	109.200000
S1-C16-H16D	109.200000	H16C-C16-H16D	107.900000
C24-C23-C13	106.2(6)	C24-C23-H23A	110.500000
C13-C23-H23A	110.500000	C24-C23-H23B	110.500000
C13-C23-H23B	110.500000	H23A-C23-H23B	108.700000
O2-C24-N8	124.4(9)	O2-C24-C23	127.0(7)

N8-C24-C23	108.5(6)	N8-C25-C26	110.5(6)
N8-C25-H25A	109.500000	C26-C25-H25A	109.500000
N8-C25-H25B	109.500000	C26-C25-H25B	109.500000
H25A-C25-H25B	108.100000	O3-C26-C25	111.7(6)
O3-C26-H26A	109.300000	C25-C26-H26A	109.300000
O3-C26-H26B	109.300000	C25-C26-H26B	109.300000
H26A-C26-H26B	107.900000	P1-C27-H27A	109.500000
P1-C27-H27B	109.500000	H27A-C27-H27B	109.500000
P1-C27-H27C	109.500000	H27A-C27-H27C	109.500000
H27B-C27-H27C	109.500000	P1-C28-H28A	109.500000
P1-C28-H28B	109.500000	H28A-C28-H28B	109.500000
P1-C28-H28C	109.500000	H28A-C28-H28C	109.500000
H28B-C28-H28C	109.500000	P1-C29-H29A	109.500000
P1-C29-H29B	109.500000	H29A-C29-H29B	109.500000
P1-C29-H29C	109.500000	H29A-C29-H29C	109.500000
H29B-C29-H29C	109.500000	N6-B1-N2	109.1(5)
N6-B1-N4	106.6(6)	N2-B1-N4	110.2(6)
N6-B1-H1A	114.(3)	N2-B1-H1A	106.(3)
N4-B1-H1A	110.(3)	C18-C17-C22	120.000000
C18-C17-C16	110.1(8)	C22-C17-C16	129.8(8)
C17-C18-C19	120.000000	C17-C18-H18	120.000000
C19-C18-H18	120.000000	C18-C19-C20	120.000000
C18-C19-H19	120.000000	C20-C19-H19	120.000000

C21-C20-C19	120.000000	C21-C20-H20	120.000000
C19-C20-H20	120.000000	C20-C21-C22	120.000000
C20-C21-H21	120.000000	C22-C21-H21	120.000000
C21-C22-C17	120.000000	C21-C22-H22	120.000000
C17-C22-H22	120.000000	C18A-C17A-C22A	120.000000
C18A-C17A-C16	130.2(9)	C22A-C17A-C16	109.7(9)
C19A-C18A-C17A	120.000000	C19A-C18A-H18A	120.000000
C17A-C18A-H18A	120.000000	C18A-C19A-C20A	120.000000
C18A-C19A-H19A	120.000000	C20A-C19A-H19A	120.000000
C21A-C20A-C19A	120.000000	C21A-C20A-H20A	120.000000
C19A-C20A-H20A	120.000000	C20A-C21A-C22A	120.000000
C20A-C21A-H21A	120.000000	C22A-C21A-H21A	120.000000
C21A-C22A-C17A	120.000000	C21A-C22A-H22A	120.000000
C17A-C22A-H22A	120.000000		

Table 6. Torsion angles (°) for compound 4.42			
C1-N1-N2-C3	0.5(7)	W1-N1-N2-C3	180.0(4)
C1-N1-N2-B1	-176.1(6)	W1-N1-N2-B1	3.3(8)
C4-N3-N4-C6	0.2(7)	W1-N3-N4-C6	-177.0(4)
C4-N3-N4-B1	164.2(6)	W1-N3-N4-B1	-13.0(7)
C7-N5-N6-C9	-0.1(6)	W1-N5-N6-C9	175.0(4)
C7-N5-N6-B1	-172.5(5)	W1-N5-N6-B1	2.6(7)
N2-N1-C1-C2	-1.1(8)	W1-N1-C1-C2	179.5(5)
N1-C1-C2-C3	1.3(8)	N1-N2-C3-C2	0.2(8)
B1-N2-C3-C2	176.5(7)	C1-C2-C3-N2	-0.9(8)
N4-N3-C4-C5	0.2(7)	W1-N3-C4-C5	177.2(4)

N3-C4-C5-C6	-0.5(8)	N3-N4-C6-C5	-0.6(8)
B1-N4-C6-C5	-161.9(7)	C4-C5-C6-N4	0.6(8)
N6-N5-C7-C8	-0.4(7)	W1-N5-C7-C8	-174.6(4)
N5-C7-C8-C9	0.8(7)	N5-N6-C9-C8	0.6(7)
B1-N6-C9-C8	172.2(6)	C7-C8-C9-N6	-0.8(7)
C15-C10-C11-C12	-5.1(9)	W1-C10-C11-C12	115.1(5)
C15-C10-C11-W1	-120.2(6)	C24-N8-C12-C11	-111.2(6)
C25-N8-C12-C11	72.6(7)	C24-N8-C12-C13	12.6(8)
C25-N8-C12-C13	-163.6(6)	C10-C11-C12-N8	118.8(6)
W1-C11-C12-N8	-154.7(4)	C10-C11-C12-C13	2.5(8)
W1-C11-C12-C13	88.9(6)	N8-C12-C13-C14	-143.3(6)
C11-C12-C13-C14	-22.2(8)	N8-C12-C13-C23	-17.0(7)
C11-C12-C13-C23	104.1(7)	C23-C13-C14-C15	-75.6(8)
C12-C13-C14-C15	45.6(8)	C13-C14-C15-C10	-46.4(8)
C13-C14-C15-S1	74.7(7)	C11-C10-C15-C14	26.4(9)
W1-C10-C15-C14	-61.1(8)	C11-C10-C15-S1	-100.4(6)
W1-C10-C15-S1	172.1(4)	C16-S1-C15-C14	69.2(6)
C16-S1-C15-C10	-166.4(5)	C15-S1-C16-C17A	64.6(8)
C15-S1-C16-C17	59.9(7)	C14-C13-C23-C24	143.7(7)
C12-C13-C23-C24	16.3(8)	C25-N8-C24-O2	-8.5(11)
C12-N8-C24-O2	175.3(7)	C25-N8-C24-C23	173.8(6)

C12-N8-C24-C23	-2.3(8)	C13-C23-C24-O2	173.1(7)
C13-C23-C24-N8	-9.4(8)	C24-N8-C25-C26	-81.1(8)
C12-N8-C25-C26	94.8(7)	N8-C25-C26-O3	-179.4(6)
C9-N6-B1-N2	128.5(6)	N5-N6-B1-N2	-60.8(7)
C9-N6-B1-N4	-112.5(7)	N5-N6-B1-N4	58.3(6)
C3-N2-B1-N6	-119.3(7)	N1-N2-B1-N6	56.6(8)
C3-N2-B1-N4	123.9(7)	N1-N2-B1-N4	-60.2(8)
C6-N4-B1-N6	107.8(8)	N3-N4-B1-N6	-52.4(7)
C6-N4-B1-N2	-133.9(7)	N3-N4-B1-N2	65.9(8)
S1-C16-C17-C18	70.5(7)	S1-C16-C17-C22	-106.2(8)
C22-C17-C18-C19	0.000000	C16-C17-C18-C19	-177.1(7)
C17-C18-C19-C20	0.000000	C18-C19-C20-C21	0.000000
C19-C20-C21-C22	0.000000	C20-C21-C22-C17	0.000000
C18-C17-C22-C21	0.000000	C16-C17-C22-C21	176.4(9)
S1-C16-C17A-C18A	55.0(10)	S1-C16-C17A-C22A	-121.5(6)
C22A-C17A-C18A-C19A	0.000000	C16-C17A-C18A-C19A	-176.3(11)
C17A-C18A-C19A-C20A	0.000000	C18A-C19A-C20A-C21A	0.000000
C19A-C20A-C21A-C22A	0.000000	C20A-C21A-C22A-C17A	0.000000
C18A-C17A-C22A-C21A	0.000000	C16-C17A-C22A-C21A	177.0(9)

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for compound 4.42
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02732(14)	0.02085(13)	0.01249(11)	-0.00159(11)	0.00100(12)	0.00085(14)
S1	0.0716(14)	0.0508(11)	0.0150(7)	-0.0013(7)	-0.0038(8)	-0.0232(11)
P1	0.0299(9)	0.0238(8)	0.0186(7)	-0.0001(6)	0.0043(7)	-0.0002(7)
O1	0.049(3)	0.033(3)	0.029(2)	-0.006(2)	-0.001(2)	0.013(2)
O2	0.035(3)	0.095(5)	0.026(3)	-0.004(3)	-0.006(2)	-0.015(3)
O3	0.060(4)	0.039(3)	0.040(3)	-0.005(2)	0.006(3)	-0.001(3)
N1	0.026(3)	0.027(3)	0.020(2)	-0.005(2)	0.000(2)	-0.002(3)
N2	0.029(3)	0.026(3)	0.025(3)	0.002(2)	0.000(2)	-0.003(2)
N3	0.031(3)	0.021(3)	0.017(2)	-0.0010(18)	-0.001(2)	-0.003(2)
N4	0.026(3)	0.033(3)	0.019(2)	0.000(2)	-0.003(2)	-0.005(3)
N5	0.030(3)	0.021(3)	0.017(2)	-0.0008(18)	-0.001(2)	-0.001(2)
N6	0.031(3)	0.020(3)	0.018(2)	-0.0016(18)	0.000(2)	-0.001(3)
N7	0.031(3)	0.039(3)	0.015(2)	-0.001(2)	-0.001(2)	0.001(3)
N8	0.028(3)	0.052(4)	0.022(3)	-0.001(2)	-0.003(2)	0.002(3)
C1	0.035(4)	0.032(4)	0.021(3)	-0.007(3)	0.007(3)	-0.005(3)
C2	0.022(4)	0.036(4)	0.045(4)	-0.009(3)	0.009(3)	0.005(3)
C3	0.027(3)	0.029(4)	0.043(4)	-0.003(3)	0.003(3)	0.005(3)
C4	0.026(3)	0.029(3)	0.023(3)	-0.007(2)	0.003(3)	-0.003(3)
C5	0.040(4)	0.042(4)	0.020(3)	-0.009(3)	-0.002(3)	-0.009(4)
C6	0.037(4)	0.042(4)	0.021(3)	0.002(3)	-0.008(3)	-0.013(3)
C7	0.025(4)	0.029(4)	0.023(3)	-0.006(3)	0.005(3)	-0.001(3)
C8	0.039(4)	0.029(4)	0.020(3)	-0.002(3)	0.009(3)	-0.009(3)
C9	0.038(4)	0.022(3)	0.020(3)	-0.002(2)	0.003(3)	-0.003(3)
C10	0.038(4)	0.030(3)	0.016(3)	-0.004(3)	0.002(3)	0.005(3)
C11	0.028(4)	0.027(3)	0.014(3)	-0.006(2)	-0.008(2)	0.001(3)
C12	0.036(4)	0.031(4)	0.019(3)	-0.001(3)	-0.003(3)	0.005(3)
C13	0.050(5)	0.052(5)	0.025(3)	0.004(3)	-0.005(3)	0.025(4)
C14	0.070(6)	0.038(4)	0.025(3)	0.005(3)	-0.011(4)	0.016(4)
C15	0.051(4)	0.029(4)	0.018(3)	-0.001(3)	-0.006(3)	-0.004(3)
C16	0.053(5)	0.084(7)	0.028(4)	0.024(4)	-0.010(4)	-0.007(5)
C23	0.045(5)	0.066(6)	0.031(4)	0.010(4)	-0.016(3)	0.009(5)
C24	0.024(3)	0.082(6)	0.019(3)	-0.005(4)	-0.002(3)	-0.004(4)
C25	0.027(4)	0.049(5)	0.030(3)	-0.011(3)	-0.002(3)	0.000(3)
C26	0.038(4)	0.041(4)	0.031(4)	0.005(3)	0.005(3)	0.002(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	0.048(5)	0.020(3)	0.032(3)	0.003(3)	0.000(3)	0.001(3)
C28	0.030(4)	0.044(4)	0.037(4)	0.004(3)	0.005(3)	-0.003(3)
C29	0.049(5)	0.041(4)	0.031(4)	-0.004(3)	0.020(3)	-0.014(4)
B1	0.031(4)	0.028(4)	0.021(3)	0.009(3)	-0.002(3)	0.004(4)
C17	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C18	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C19	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C20	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C21	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C22	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C17A	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C18A	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C19A	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C20A	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C21A	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)
C22A	0.042(2)	0.0344(19)	0.0162(16)	0.0016(14)	-0.0012(16)	0.0078(18)

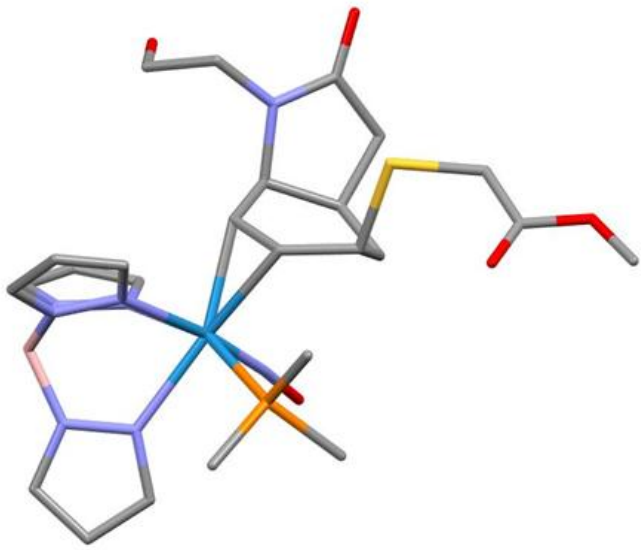
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.42

	x/a	y/b	z/c	U(eq)
H3	0.410(6)	0.300(6)	0.458(4)	0.07(3)
H1	0.8605	0.4491	0.3326	0.035000
H2	0.9657	0.3456	0.3565	0.041000
H3A	0.9496	0.3198	0.4593	0.040000
H4	0.7603	0.6666	0.5422	0.032000
H5	0.8421	0.6313	0.6289	0.041000
H6	0.8904	0.4916	0.6167	0.040000
H7	0.5462	0.4361	0.4813	0.031000
H8	0.5542	0.3234	0.5494	0.035000
H9	0.7058	0.3028	0.5699	0.032000
H10	0.741(4)	0.513(3)	0.327(2)	0.007(15)
H11	0.655(4)	0.437(4)	0.362(2)	0.015(16)
H12	0.5281	0.5109	0.4071	0.034000
H13	0.4747	0.6072	0.3548	0.050000

	x/a	y/b	z/c	U(eq)
H14A	0.5968	0.6728	0.3599	0.053000
H14B	0.5689	0.6811	0.2960	0.053000
H15	0.7162	0.6549	0.3116	0.039000
H16A	0.6744	0.6627	0.1546	0.066000
H16B	0.6176	0.6974	0.2041	0.066000
H16C	0.6700	0.6629	0.1546	0.066000
H16D	0.6201	0.7000	0.2066	0.066000
H23A	0.4310	0.5758	0.2697	0.057000
H23B	0.5236	0.5537	0.2479	0.057000
H25A	0.5355	0.3535	0.3920	0.042000
H25B	0.4908	0.3224	0.3360	0.042000
H26A	0.4051	0.4030	0.4243	0.044000
H26B	0.3606	0.3711	0.3686	0.044000
H27A	0.7402	0.7476	0.3760	0.050000
H27B	0.8314	0.7816	0.3906	0.050000
H27C	0.7678	0.7588	0.4399	0.050000
H28A	0.9035	0.6725	0.4858	0.056000
H28B	0.9619	0.6886	0.4324	0.056000
H28C	0.9469	0.5996	0.4538	0.056000
H29A	0.9186	0.5862	0.3371	0.060000
H29B	0.9195	0.6808	0.3307	0.060000
H29C	0.8427	0.6303	0.3062	0.060000
H1A	0.853(3)	0.375(4)	0.539(2)	0.005(13)
H18	0.8214	0.6607	0.1663	0.037000
H19	0.9439	0.7332	0.1840	0.037000
H20	0.9380	0.8484	0.2387	0.037000
H21	0.8096	0.8911	0.2756	0.037000
H22	0.6871	0.8186	0.2578	0.037000
H18A	0.8496	0.6638	0.1861	0.037000
H19A	0.9454	0.7610	0.2149	0.037000
H20A	0.8969	0.8804	0.2532	0.037000
H21A	0.7525	0.9026	0.2627	0.037000
H22A	0.6567	0.8055	0.2339	0.037000

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 4.42				
	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3-H3···O1#1	0.94(9)	1.89(9)	2.782(7)	157.(8)

Crystal Structure Report for compound 4.43



A yellow, block-like specimen of $C_{25}H_{38}BN_8O_5PSW$, approximate dimensions 0.058 mm x 0.061 mm x 0.106 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with a Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 4.70 hours. The frames were integrated with the Bruker SAINT software package[89] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 44728 reflections to a maximum θ angle of 28.29° (0.75 Å resolution), of which 7565 were independent (average redundancy 5.912, completeness = 99.6%, R_{int} = 5.25%, R_{sig} = 3.74%) and 6822 (90.18%) were greater than $2\sigma(F^2)$. The final

[89] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

cell constants of a = 10.1532(4) Å, b = 12.5345(6) Å, c = 13.0332(6) Å, α = 82.3060(10)°, β = 77.6650(10)°, γ = 70.7070(10)°, volume = 1525.78(12) Å^3, are based upon the refinement of the XYZ-centroids of 9918 reflections above 20 σ(I) with 5.003° < 2θ < 56.43°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[90] The ratio of minimum to maximum apparent transmission was 0.926. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6790 and 0.8030.

The structure was solved and refined using the Bruker SHELXTL Software Package[91] within APEX4 [1] and OLEX2,[92] using the space group P -1, with Z = 2 for the formula unit, $C_{25}H_{38}BN_8O_5PSW$. Non-hydrogen atoms were refined anisotropically. The B-H and O-H hydrogen atoms, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 399 variables converged at R1 = 2.56%, for the observed data and wR2 = 6.18% for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 1.156 e$^-$/Å^3 and the largest hole was -0.805 e$^-$/Å^3 with an RMS deviation of 0.122 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.716 g/cm^3 and F(000), 788 e$^-$.

Table 1. Sample and crystal data for compound 4.43

Chemical formula	$C_{25}H_{38}BN_8O_5PSW$
Formula weight	788.32 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.058 x 0.061 x 0.106 mm
Crystal habit	yellow block
Crystal system	triclinic
Space group	P -1

[90] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[91] Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.

[92] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Unit cell dimensions	a = 10.1532(4) Å	α = 82.3060(10)°
	b = 12.5345(6) Å	β = 77.6650(10)°
	c = 13.0332(6) Å	γ = 70.7070(10)°
Volume	1525.78(12) $Å^3$	
Z	2	
Density (calculated)	1.716 g/cm^3	
Absorption coefficient	3.956 mm^{-1}	
F(000)	788	

Table 2. Data collection and structure refinement for compound 4.43

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.73 to 28.29°
Index ranges	-13<=h<=12, -16<=k<=16, -17<=l<=17
Reflections collected	44728
Independent reflections	7565 [R(int) = 0.0525]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8030 and 0.6790
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7565 / 0 / 399	
Goodness-of-fit on F^2	1.049	
Δ/σ_{max}	0.002	
Final R indices	6822 data; $I>2\sigma(I)$	R1 = 0.0256, wR2 = 0.0597
	all data	R1 = 0.0311, wR2 = 0.0618
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0321P)^2+0.7189P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.156 and -0.805 eÅ^{-3}	
R.M.S. deviation from mean	0.122 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.43

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.72172(2)	0.23529(2)	0.24159(2)	0.01256(4)
S1	0.49058(9)	0.63732(7)	0.29181(7)	0.02422(18)
P1	0.92889(9)	0.31025(7)	0.19728(6)	0.01734(16)
O1	0.6787(3)	0.2594(2)	0.01861(17)	0.0245(5)
O2	0.1068(3)	0.3148(2)	0.4611(2)	0.0252(5)
O3	0.0890(2)	0.63515(19)	0.35742(19)	0.0235(5)
O4	0.7246(3)	0.7365(3)	0.1697(4)	0.0707(12)
O5	0.5787(3)	0.8808(2)	0.0884(2)	0.0384(7)
N1	0.7683(3)	0.1829(2)	0.40473(19)	0.0164(5)

	x/a	y/b	z/c	U(eq)
N2	0.7907(3)	0.0730(2)	0.4433(2)	0.0184(5)
N3	0.8823(3)	0.0674(2)	0.2103(2)	0.0155(5)
N4	0.8832(3)	0.9739(2)	0.2778(2)	0.0179(5)
N5	0.5960(3)	0.1176(2)	0.2801(2)	0.0170(5)
N6	0.6269(3)	0.0254(2)	0.3494(2)	0.0188(5)
N7	0.6939(3)	0.2559(2)	0.11034(19)	0.0149(5)
N8	0.2708(3)	0.4672(2)	0.35579(19)	0.0152(5)
C1	0.7866(3)	0.2373(3)	0.4794(2)	0.0195(6)
C2	0.8222(4)	0.1630(3)	0.5655(2)	0.0240(7)
C3	0.8236(3)	0.0607(3)	0.5395(2)	0.0226(7)
C4	0.9808(3)	0.0309(3)	0.1262(2)	0.0187(6)
C5	0.0467(4)	0.9147(3)	0.1376(3)	0.0232(7)
C6	0.9810(4)	0.8815(3)	0.2340(3)	0.0237(7)
C7	0.4823(3)	0.1181(3)	0.2438(3)	0.0199(6)
C8	0.4377(4)	0.0261(3)	0.2909(3)	0.0257(7)
C9	0.5324(4)	0.9696(3)	0.3558(3)	0.0245(7)
C10	0.5227(3)	0.3517(2)	0.3191(2)	0.0152(6)
C11	0.6231(3)	0.4139(3)	0.2892(2)	0.0146(6)
C12	0.5900(3)	0.5159(3)	0.2113(2)	0.0165(6)
C13	0.5088(3)	0.5036(3)	0.1312(2)	0.0194(6)
C14	0.3787(3)	0.4640(3)	0.1743(2)	0.0168(6)
C15	0.3825(3)	0.3914(2)	0.2810(2)	0.0139(6)
C16	0.2477(3)	0.4373(3)	0.4683(2)	0.0181(6)
C17	0.2274(3)	0.3218(3)	0.4953(2)	0.0201(7)
C18	0.1901(3)	0.5613(3)	0.3111(2)	0.0175(6)
C19	0.2396(3)	0.5626(3)	0.1943(2)	0.0204(7)
C20	0.4742(4)	0.7550(3)	0.1953(3)	0.0264(7)
C21	0.6090(4)	0.7848(3)	0.1518(3)	0.0365(9)
C22	0.6937(5)	0.9274(4)	0.0485(4)	0.0481(11)
C23	0.9628(4)	0.3539(3)	0.0578(3)	0.0276(8)
C24	0.9326(4)	0.4313(3)	0.2591(3)	0.0260(7)
C25	0.0990(4)	0.2125(3)	0.2218(3)	0.0269(7)
B1	0.7749(4)	0.9844(3)	0.3811(3)	0.0204(7)

Table 4. Bond lengths (Å) for compound 4.43

W1-N7	1.764(2)	W1-C10	2.192(3)
W1-N5	2.198(3)	W1-N3	2.220(2)
W1-N1	2.242(2)	W1-C11	2.242(3)
W1-P1	2.5065(8)	S1-C20	1.794(4)
S1-C12	1.843(3)	P1-C23	1.820(3)
P1-C25	1.822(3)	P1-C24	1.825(3)
O1-N7	1.231(3)	O2-C17	1.421(4)
O2-H2	0.77(4)	O3-C18	1.237(4)
O4-C21	1.186(5)	O5-C21	1.350(5)
O5-C22	1.444(5)	N1-C1	1.337(4)
N1-N2	1.364(3)	N2-C3	1.342(4)
N2-B1	1.526(5)	N3-C4	1.332(4)
N3-N4	1.367(3)	N4-C6	1.352(4)
N4-B1	1.536(4)	N5-C7	1.337(4)
N5-N6	1.361(3)	N6-C9	1.346(4)
N6-B1	1.546(5)	N8-C18	1.335(4)
N8-C16	1.452(4)	N8-C15	1.484(4)
C1-C2	1.388(4)	C1-H1	0.950000
C2-C3	1.365(5)	C2-H2A	0.950000
C3-H3	0.950000	C4-C5	1.390(4)
C4-H4	0.950000	C5-C6	1.372(5)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.395(5)	C7-H7	0.950000
C8-C9	1.370(5)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.440(4)
C10-C15	1.513(4)	C10-H10	0.96(3)
C11-C12	1.514(4)	C11-H11	0.98(3)
C12-C13	1.512(4)	C12-H12	1.000000
C13-C14	1.532(4)	C13-H13A	0.990000
C13-H13B	0.990000	C14-C19	1.538(4)

C14-C15	1.556(4)	C14-H14	1.000000
C15-H15	1.000000	C16-C17	1.514(4)
C16-H16A	0.990000	C16-H16B	0.990000
C17-H17A	0.990000	C17-H17B	0.990000
C18-C19	1.498(4)	C19-H19A	0.990000
C19-H19B	0.990000	C20-C21	1.511(5)
C20-H20A	0.990000	C20-H20B	0.990000
C22-H22A	0.980000	C22-H22B	0.980000
C22-H22C	0.980000	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
C24-H24A	0.980000	C24-H24B	0.980000
C24-H24C	0.980000	C25-H25A	0.980000
C25-H25B	0.980000	C25-H25C	0.980000
B1-H1A	1.04(3)		

Table 5. Bond angles (°) for compound 4.43

N7-W1-C10	100.59(11)	N7-W1-N5	90.88(11)
C10-W1-N5	81.54(10)	N7-W1-N3	91.09(10)
C10-W1-N3	155.28(11)	N5-W1-N3	76.54(9)
N7-W1-N1	171.91(10)	C10-W1-N1	85.20(10)
N5-W1-N1	84.35(9)	N3-W1-N1	81.45(9)
N7-W1-C11	99.59(11)	C10-W1-C11	37.89(11)
N5-W1-C11	119.41(10)	N3-W1-C11	160.32(11)
N1-W1-C11	88.46(10)	N7-W1-P1	93.11(8)
C10-W1-P1	115.42(8)	N5-W1-P1	161.44(7)
N3-W1-P1	85.26(7)	N1-W1-P1	89.43(7)
C11-W1-P1	77.75(8)	C20-S1-C12	102.28(15)
C23-P1-C25	104.13(17)	C23-P1-C24	102.28(17)
C25-P1-C24	97.84(16)	C23-P1-W1	111.15(12)
C25-P1-W1	116.63(12)	C24-P1-W1	122.34(12)
C17-O2-H2	103.(3)	C21-O5-C22	116.1(3)
C1-N1-N2	106.2(2)	C1-N1-W1	133.7(2)
N2-N1-W1	120.08(19)	C3-N2-N1	109.4(3)

C3-N2-B1	128.8(3)	N1-N2-B1	121.7(2)
C4-N3-N4	106.0(2)	C4-N3-W1	131.6(2)
N4-N3-W1	121.97(19)	C6-N4-N3	109.4(3)
C6-N4-B1	130.5(3)	N3-N4-B1	119.9(2)
C7-N5-N6	107.2(3)	C7-N5-W1	130.0(2)
N6-N5-W1	122.9(2)	C9-N6-N5	109.1(3)
C9-N6-B1	129.9(3)	N5-N6-B1	118.4(3)
O1-N7-W1	174.0(2)	C18-N8-C16	123.2(3)
C18-N8-C15	114.9(2)	C16-N8-C15	121.9(2)
N1-C1-C2	110.5(3)	N1-C1-H1	124.800000
C2-C1-H1	124.800000	C3-C2-C1	105.0(3)
C3-C2-H2A	127.500000	C1-C2-H2A	127.500000
N2-C3-C2	108.9(3)	N2-C3-H3	125.500000
C2-C3-H3	125.500000	N3-C4-C5	111.3(3)
N3-C4-H4	124.400000	C5-C4-H4	124.400000
C6-C5-C4	104.5(3)	C6-C5-H5	127.700000
C4-C5-H5	127.700000	N4-C6-C5	108.7(3)
N4-C6-H6	125.600000	C5-C6-H6	125.600000
N5-C7-C8	109.8(3)	N5-C7-H7	125.100000
C8-C7-H7	125.100000	C9-C8-C7	105.1(3)
C9-C8-H8	127.500000	C7-C8-H8	127.500000
N6-C9-C8	108.9(3)	N6-C9-H9	125.600000
C8-C9-H9	125.600000	C11-C10-C15	121.4(3)
C11-C10-W1	72.94(17)	C15-C10-W1	126.3(2)
C11-C10-H10	117.(2)	C15-C10-H10	109.6(19)
W1-C10-H10	104.7(19)	C10-C11-C12	118.1(3)
C10-C11-W1	69.17(16)	C12-C11-W1	123.4(2)
C10-C11-H11	110.(2)	C12-C11-H11	115.(2)
W1-C11-H11	112.(2)	C13-C12-C11	113.4(3)
C13-C12-S1	112.3(2)	C11-C12-S1	105.3(2)
C13-C12-H12	108.600000	C11-C12-H12	108.600000
S1-C12-H12	108.600000	C12-C13-C14	116.5(3)
C12-C13-H13A	108.200000	C14-C13-H13A	108.200000

C12-C13-H13B	108.200000	C14-C13-H13B	108.200000
H13A-C13-H13B	107.300000	C13-C14-C19	113.0(3)
C13-C14-C15	115.5(3)	C19-C14-C15	104.4(2)
C13-C14-H14	107.900000	C19-C14-H14	107.900000
C15-C14-H14	107.900000	N8-C15-C10	110.7(2)
N8-C15-C14	103.3(2)	C10-C15-C14	116.1(2)
N8-C15-H15	108.800000	C10-C15-H15	108.800000
C14-C15-H15	108.800000	N8-C16-C17	113.1(3)
N8-C16-H16A	109.000000	C17-C16-H16A	109.000000
N8-C16-H16B	109.000000	C17-C16-H16B	109.000000
H16A-C16-H16B	107.800000	O2-C17-C16	112.5(3)
O2-C17-H17A	109.100000	C16-C17-H17A	109.100000
O2-C17-H17B	109.100000	C16-C17-H17B	109.100000
H17A-C17-H17B	107.800000	O3-C18-N8	126.2(3)
O3-C18-C19	124.9(3)	N8-C18-C19	108.9(3)
C18-C19-C14	106.4(2)	C18-C19-H19A	110.400000
C14-C19-H19A	110.400000	C18-C19-H19B	110.400000
C14-C19-H19B	110.400000	H19A-C19-H19B	108.600000
C21-C20-S1	115.4(3)	C21-C20-H20A	108.400000
S1-C20-H20A	108.400000	C21-C20-H20B	108.400000
S1-C20-H20B	108.400000	H20A-C20-H20B	107.500000
O4-C21-O5	123.0(4)	O4-C21-C20	127.9(4)

O5-C21-C20	109.0(3)	O5-C22-H22A	109.500000
O5-C22-H22B	109.500000	H22A-C22-H22B	109.500000
O5-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	P1-C23-H23A	109.500000
P1-C23-H23B	109.500000	H23A-C23-H23B	109.500000
P1-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	P1-C24-H24A	109.500000
P1-C24-H24B	109.500000	H24A-C24-H24B	109.500000
P1-C24-H24C	109.500000	H24A-C24-H24C	109.500000
H24B-C24-H24C	109.500000	P1-C25-H25A	109.500000
P1-C25-H25B	109.500000	H25A-C25-H25B	109.500000
P1-C25-H25C	109.500000	H25A-C25-H25C	109.500000
H25B-C25-H25C	109.500000	N2-B1-N4	108.3(3)
N2-B1-N6	110.0(3)	N4-B1-N6	106.2(3)
N2-B1-H1A	106.9(18)	N4-B1-H1A	113.9(18)
N6-B1-H1A	111.4(18)		

Table 6. Torsion angles (°) for compound 4.43

C1-N1-N2-C3	-0.7(3)	W1-N1-N2-C3	176.8(2)
C1-N1-N2-B1	178.2(3)	W1-N1-N2-B1	-4.3(4)
C4-N3-N4-C6	-0.4(3)	W1-N3-N4-C6	173.0(2)
C4-N3-N4-B1	-176.2(3)	W1-N3-N4-B1	-2.8(4)

C7-N5-N6-C9	-0.1(3)	W1-N5-N6-C9	-179.5(2)
C7-N5-N6-B1	163.6(3)	W1-N5-N6-B1	-15.7(3)
N2-N1-C1-C2	0.7(4)	W1-N1-C1-C2	-176.3(2)
N1-C1-C2-C3	-0.5(4)	N1-N2-C3-C2	0.4(4)
B1-N2-C3-C2	-178.4(3)	C1-C2-C3-N2	0.0(4)
N4-N3-C4-C5	-0.2(4)	W1-N3-C4-C5	-172.8(2)
N3-C4-C5-C6	0.8(4)	N3-N4-C6-C5	0.9(4)
B1-N4-C6-C5	176.1(3)	C4-C5-C6-N4	-1.0(4)
N6-N5-C7-C8	0.7(3)	W1-N5-C7-C8	-180.0(2)
N5-C7-C8-C9	-1.1(4)	N5-N6-C9-C8	-0.6(4)
B1-N6-C9-C8	-161.9(3)	C7-C8-C9-N6	1.0(4)
C15-C10-C11-C12	-4.8(4)	W1-C10-C11-C12	117.7(2)
C15-C10-C11-W1	-122.5(3)	C10-C11-C12-C13	-32.7(4)
W1-C11-C12-C13	49.8(3)	C10-C11-C12-S1	90.4(3)
W1-C11-C12-S1	172.89(15)	C20-S1-C12-C13	-62.7(3)
C20-S1-C12-C11	173.5(2)	C11-C12-C13-C14	48.5(4)
S1-C12-C13-C14	-70.7(3)	C12-C13-C14-C19	93.7(3)
C12-C13-C14-C15	-26.4(4)	C18-N8-C15-C10	134.5(3)
C16-N8-C15-C10	-48.7(4)	C18-N8-C15-C14	9.5(3)
C16-N8-C15-C14	-173.6(3)	C11-C10-C15-N8	-90.4(3)
W1-C10-C15-N8	178.35(19)	C11-C10-C15-C14	26.9(4)

W1-C10-C15-C14	-64.3(3)	C13-C14-C15-N8	111.0(3)
C19-C14-C15-N8	-13.7(3)	C13-C14-C15-C10	-10.4(4)
C19-C14-C15-C10	-135.2(3)	C18-N8-C16-C17	123.7(3)
C15-N8-C16-C17	-52.9(4)	N8-C16-C17-O2	-61.4(3)
C16-N8-C18-O3	1.4(5)	C15-N8-C18-O3	178.2(3)
C16-N8-C18-C19	-177.5(3)	C15-N8-C18-C19	-0.7(4)
O3-C18-C19-C14	172.4(3)	N8-C18-C19-C14	-8.7(4)
C13-C14-C19-C18	-112.4(3)	C15-C14-C19-C18	13.9(3)
C12-S1-C20-C21	-72.7(3)	C22-O5-C21-O4	-4.4(6)
C22-O5-C21-C20	174.1(3)	S1-C20-C21-O4	4.3(6)
S1-C20-C21-O5	-174.1(3)	C3-N2-B1-N4	-119.9(3)
N1-N2-B1-N4	61.4(4)	C3-N2-B1-N6	124.3(3)
N1-N2-B1-N6	-54.3(4)	C6-N4-B1-N2	128.3(3)
N3-N4-B1-N2	-56.9(4)	C6-N4-B1-N6	-113.5(4)
N3-N4-B1-N6	61.3(4)	C9-N6-B1-N2	-134.0(3)
N5-N6-B1-N2	66.3(3)	C9-N6-B1-N4	109.0(4)
N5-N6-B1-N4	-50.8(3)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.43

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01267(7)	0.01169(6)	0.01142(6)	-0.00020(4)	-0.00177(4)	-0.00177(4)
S1	0.0262(4)	0.0183(4)	0.0267(4)	-0.0049(3)	-0.0046(3)	-0.0038(3)
P1	0.0159(4)	0.0180(4)	0.0179(4)	0.0010(3)	-0.0043(3)	-0.0051(3)
O1	0.0289(13)	0.0270(13)	0.0136(11)	-0.0014(9)	-0.0071(9)	-0.0015(10)
O2	0.0244(13)	0.0293(14)	0.0209(12)	0.0010(10)	-0.0011(10)	-0.0100(11)
O3	0.0173(11)	0.0156(11)	0.0297(13)	0.0029(9)	0.0003(9)	0.0009(9)
O4	0.0290(18)	0.0367(19)	0.138(4)	0.020(2)	-0.019(2)	-0.0065(15)
O5	0.0422(16)	0.0365(16)	0.0361(15)	0.0024(12)	0.0003(12)	-0.0183(13)
N1	0.0185(13)	0.0157(13)	0.0136(12)	-0.0004(10)	-0.0020(10)	-0.0043(10)
N2	0.0204(14)	0.0157(13)	0.0149(12)	0.0036(10)	-0.0007(10)	-0.0035(11)
N3	0.0149(13)	0.0153(13)	0.0144(12)	0.0010(10)	-0.0030(10)	-0.0026(10)
N4	0.0206(14)	0.0121(12)	0.0166(13)	0.0020(10)	-0.0050(10)	0.0003(10)
N5	0.0196(13)	0.0122(12)	0.0190(13)	-0.0031(10)	-0.0022(10)	-0.0048(10)
N6	0.0219(14)	0.0139(13)	0.0182(13)	0.0009(10)	0.0017(10)	-0.0064(11)
N7	0.0154(12)	0.0121(12)	0.0156(12)	0.0001(9)	-0.0033(10)	-0.0022(10)
N8	0.0136(12)	0.0142(12)	0.0141(12)	-0.0008(9)	0.0002(9)	-0.0011(10)
C1	0.0192(16)	0.0204(16)	0.0179(15)	-0.0018(12)	-0.0031(12)	-0.0049(13)
C2	0.0257(17)	0.0310(19)	0.0130(15)	-0.0010(13)	-0.0062(13)	-0.0041(15)
C3	0.0210(16)	0.0259(17)	0.0154(15)	0.0037(13)	-0.0017(12)	-0.0027(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C4	0.0177(15)	0.0242(16)	0.0131(14)	-0.0030(12)	-0.0033(11)	-0.0038(13)
C5	0.0215(17)	0.0212(17)	0.0217(16)	-0.0058(13)	-0.0046(13)	0.0021(13)
C6	0.0279(18)	0.0157(16)	0.0206(16)	-0.0043(12)	-0.0088(13)	0.0061(13)
C7	0.0141(15)	0.0169(15)	0.0276(17)	-0.0082(13)	-0.0016(12)	-0.0022(12)
C8	0.0177(16)	0.0215(17)	0.039(2)	-0.0091(15)	0.0024(14)	-0.0091(14)
C9	0.0302(19)	0.0160(16)	0.0269(17)	-0.0028(13)	0.0048(14)	-0.0125(14)
C10	0.0171(15)	0.0123(14)	0.0128(14)	0.0005(11)	-0.0014(11)	0.0015(12)
C11	0.0146(14)	0.0145(14)	0.0132(14)	-0.0041(11)	-0.0017(11)	-0.0019(11)
C12	0.0172(15)	0.0133(14)	0.0171(15)	-0.0020(11)	-0.0008(11)	-0.0032(12)
C13	0.0215(16)	0.0150(15)	0.0177(15)	0.0042(12)	-0.0020(12)	0.0033(13)
C14	0.0219(16)	0.0150(14)	0.0127(14)	0.0013(11)	-0.0030(11)	0.0054(12)
C15	0.0138(14)	0.0125(14)	0.0129(13)	-0.0015(11)	-0.0003(11)	0.0020(11)
C16	0.0175(15)	0.0182(15)	0.0140(14)	-0.0022(11)	-0.0015(11)	-0.0001(12)
C17	0.0167(15)	0.0219(16)	0.0164(15)	0.0049(12)	-0.0023(12)	-0.0017(13)
C18	0.0147(15)	0.0152(15)	0.0227(16)	0.0029(12)	-0.0027(12)	-0.0070(12)
C19	0.0145(15)	0.0224(16)	0.0203(16)	0.0074(13)	-0.0035(12)	-0.0035(13)
C20	0.0236(18)	0.0151(16)	0.041(2)	-0.0032(14)	-0.0070(15)	-0.0053(13)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	0.033(2)	0.026(2)	0.047(2)	-0.0032(17)	-0.0008(18)	-0.0077(17)
C22	0.048(3)	0.046(3)	0.048(3)	-0.003(2)	0.013(2)	-0.025(2)
C23	0.0289(19)	0.034(2)	0.0211(17)	0.0049(14)	-0.0005(14)	-0.0160(16)
C24	0.0248(18)	0.0247(18)	0.0330(19)	-0.0044(14)	-0.0098(15)	-0.0098(15)
C25	0.0190(17)	0.0258(18)	0.035(2)	-0.0029(15)	-0.0082(14)	-0.0043(14)
B1	0.0262(19)	0.0156(17)	0.0169(17)	0.0008(13)	-0.0044(14)	-0.0036(15)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.43

	x/a	y/b	z/c	U(eq)
H2	0.046(4)	0.335(3)	0.508(3)	0.022(10)
H1	0.7767	0.3158	0.4744	0.023000
H2A	0.8415	0.1798	0.6286	0.029000
H3	0.8444	-0.0081	0.5825	0.027000
H4	1.0030	0.0781	0.0662	0.022000
H5	1.1207	-0.1315	0.0893	0.028000
H6	1.0010	-0.1939	0.2649	0.028000
H7	0.4383	0.1728	0.1934	0.024000
H8	0.3589	0.0069	0.2803	0.031000
H9	0.5315	-0.0980	0.3983	0.029000
H10	0.510(3)	0.321(3)	0.391(3)	0.011(8)
H11	0.655(4)	0.426(3)	0.351(3)	0.018(9)
H12	0.6813	0.5273	0.1731	0.020000
H13A	0.5749	0.4492	0.0805	0.023000
H13B	0.4774	0.5778	0.0914	0.023000
H14	0.3701	0.4175	0.1209	0.020000
H15	0.3534	0.3239	0.2756	0.017000

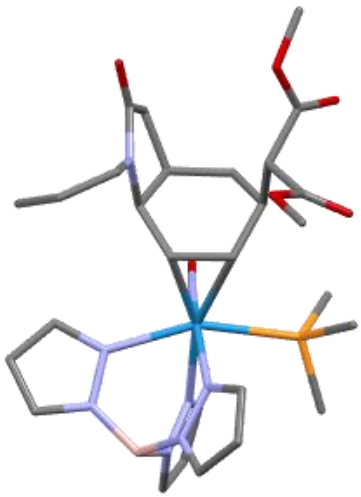
	x/a	y/b	z/c	U(eq)
H16A	0.1628	0.4951	0.5028	0.022000
H16B	0.3301	0.4383	0.4969	0.022000
H17A	0.3131	0.2637	0.4620	0.024000
H17B	0.2167	0.3050	0.5725	0.024000
H19A	0.2562	0.6355	0.1668	0.025000
H19B	0.1678	0.5524	0.1590	0.025000
H20A	0.4393	0.7380	0.1360	0.032000
H20B	0.4015	0.8223	0.2272	0.032000
H22A	0.7712	0.8725	0.0057	0.072000
H22B	0.7280	0.9438	0.1075	0.072000
H22C	0.6599	0.9975	0.0050	0.072000
H23A	0.9767	0.2903	0.0161	0.041000
H23B	1.0483	0.3775	0.0417	0.041000
H23C	0.8817	0.4174	0.0406	0.041000
H24A	0.8509	0.4969	0.2470	0.039000
H24B	1.0204	0.4492	0.2285	0.039000
H24C	0.9285	0.4128	0.3350	0.039000
H25A	1.0979	0.2007	0.2978	0.040000
H25B	1.1749	0.2443	0.1877	0.040000
H25C	1.1155	0.1399	0.1931	0.040000
H1A	0.789(3)	-0.090(3)	0.429(3)	0.012(8)

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 4.43

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O2-H2···O3#1	0.77(4)	1.97(4)	2.739(3)	170.(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y+1, -z+1

Structure Report for compound 4.46



A white, plate shaped crystal of compound 4.46 measuring 0.031×0.046×0.053 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for cu_harman_ld_2_169trial2_x2_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Cu K_α, λ=1.54178 Å) using a HELIOS MX double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[93] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with XT[94] and refined by full-matrix least-squares methods against F^2 using XL[95] within OLEX2.[96] All non-hydrogen atoms were refined with anisotropically. The B-H atom was located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[97]

[93] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[94] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[95] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[96] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[97] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for compound 4.46

CCDC number	
Empirical formula	$C_{28}H_{40}BN_8O_6PW$
Formula weight	810.31
Temperature [K]	101.00
Wavelength [Å]	1.54178
Crystal size [mm^3]	0.031×0.046×0.053
Crystal habit	white plate
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
a [Å]	11.3380(2)
b [Å]	13.0368(2)
c [Å]	13.8181(2)
α [°]	63.3890(10)
β [°]	88.9180(10)
γ [°]	68.6850(10)
Volume [$Å^3$]	1675.60(5)
Z	2
ρ_{calc} [gcm^{-3}]	1.606
μ [mm^{-1}]	7.278
F(000)	812
2θ range [°]	7.26 to 136.90 (0.83 Å)
Index ranges	−13 ≤ h ≤ 13 −15 ≤ k ≤ 15 −16 ≤ l ≤ 16
Reflections collected	37279
Independent reflections	6142 [R_{int} = 0.0835]
Data / Restraints / Parameters	6142 / 0 / 415
Goodness-of-fit on F^2	1.043
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0321 wR_2 = 0.0734
Final *R* indexes [all data]	R_1 = 0.0418 wR_2 = 0.0771

Largest peak/hole [eÅ^{-3}]	1.28/−1.45

Table 2 Atomic coordinates and Ueq [Å^2] for compound 4.46

Atom	***x***	***y***	***z***	U_{eq}
W1	0.34067(2)	0.61351(2)	0.17990(2)	0.01726(7)
P1	0.10510(10)	0.72452(10)	0.16095(9)	0.0203(2)
O1	0.2940(3)	0.6732(3)	−0.0555(3)	0.0272(7)
O2	0.5287(4)	0.0317(3)	0.2415(3)	0.0348(8)
O3	0.2463(4)	0.2003(3)	0.4884(3)	0.0394(9)
O4	0.0552(3)	0.3562(3)	0.3969(3)	0.0391(9)
O5	0.0354(4)	0.2930(4)	0.1879(4)	0.0504(11)
O6	0.1941(4)	0.1085(3)	0.2983(3)	0.0490(11)
N1	0.5496(3)	0.5777(3)	0.2049(3)	0.0189(7)
N2	0.5884(3)	0.6404(3)	0.2467(3)	0.0217(8)
N3	0.3390(3)	0.8042(3)	0.1078(3)	0.0210(8)
N4	0.3997(4)	0.8421(3)	0.1605(3)	0.0235(8)
N5	0.3529(3)	0.6179(3)	0.342(3)	0.0206(8)
N6	0.4145(4)	0.6850(3)	0.3542(3)	0.0229(8)
N7	0.3176(3)	0.6398(3)	0.0428(3)	0.0198(8)
N	0.5109(4)	0.1975(3)	0.2698(3)	0.0245(8)
C1	0.6563(4)	0.5057()	0.1859(4)	0.0208(9)
H1	0.658309	0.452104	0.156226	0.025
C2	0.7631(4)	0.5198(4)	0.2151(4)	0.02830)
H2	0.849849	0.479146	0.210442	0.034
C3	0.7153(4)	0.6059(4)	0.2524(4)	0.0284(10)
H3	0.765113	0.636328	0.278357	0.03
C4	0.2927(4)	0.8983(4)	0.0054(4)	0.0241(10)
H4	0.245820	0.897524	−0.050370	0.029
C5	0.3230(4)	0.9974(4)	−0.0079(4)	0.0285(10)
H5	0.300596	1.075778	−0.072095	0.034
C6	0.3924(4)	0.9577(4)	0.0916(4)	0.0280(10)
H6	0.428929	1.003866	0.108848	0.034
C7	0.3000(4)	0.5795(4)	0.4318(4)	0.0258(10)
H7	0.251564	0.52965	0.44615	0.031
C	0.3249(5)	0.6219(4)	0.5013(4)	0.0297(11)
H8	0.297528	0.608393	0.569792	0.036
C9	0.3980(5)	0.6878(4)	0.4497(4)	0.0278(10)
H9	0.431405	0.728661	0.476922	0.033

C10	0.0148(5)	0.7607(5)	0.0349(4)	0.0318(11)
H10A	0.053134	0.801544	−0.027653	0.048
H10B	−0.074504	0.816918	0.025784	0.048
H10C	0.016890	0.683367	0.038261	0.048
C11	0.0575(5)	0.8772(4)	0.1565(4)	0.0302(11)
H11A	0.099514	0.866426	0.223709	0.04
H11B	−0.035998	0.914465	0.150822	0.045
H11C	0.083551	0.932375	0.092522	0.045
C12	0.0134(4)	0.6625(4)	0.2654(4)	0.0291(11)
H12A	0.022323	0.580412	0.275633	0.04
H12	−0.077484	0.719686	0.241734	0.04
H12C	0.046047	0.653916	0.334929	0.044
C13	0.4179(4)	0.4077(4)	0.2644(3	0.0184(9)
H13	0.469698	0.369484	0.338678	0.022
C14	0.2806(4)	0.4525(4)	0.2643(4)	0.0201(9)
H14	0.260337	0.439973	0.338564	0.024
C15	0.2005(4)	0.4143(4)	0.2101(4)	0.0238(10)
H15	0.108797	0.474280	0.192723	0.029
C1	0.2419(4	0.4173(4)	0.1029(4)	0.0248(10)
H16A	0.201408	0.504758	0.043449	0.030
H	0.20637	0.36753	0.08510	0.030
C17	0.38664)	0.3691(4)	0.1003(4)	0.0223(9)
H17	0.403172	0.434354	0.03464	0.027
C18	0.4746(4)	0.3357(4)	0.2029(4)	0.0198(9
H18	0.553943	0.349495	0.179529	0.02
C19	0.4375(5)	0.2465(4)	0.0925(4)	0.0272(10)
H19	0.366374	0.235076	0.063903	0.033
H19B	0.502243	0.246780	0.043448	0.03
C20	0.4971(4)	0.1445(4)	0.2081(4)	0.0259(10)
C21	0.5670(5)	0.1241(4)	0.3850(4)	0.0309(11)
H21A	0.56740	0.039658	0.411913	0.03
H21B	0.511141	0.162938	0.425608	0.037
C22	0.7007(6)	0.1103(5)	0.4123(5	0.0455(14)
H22	0.734865	0.073114	0.48794	0.05
C23	0.7748(6)	0.1446(6)	0.3420(5)	0.0521(16)
H23A	0.74420	0.18228	0.265405	0.062
H23B	0.858776	0.131944	0.367315	0.062
C24	0.2101(5)	0.2820(4)	0.2963(4)	0.0272(10)
H24	0.302340	0.222458	0.318326	0.033

C25	0.1334(5)	0.2327()	0.2535(4)	0.0313(1)
C	0.1349(7	0.0466(6)	0.2633	0.0578()
H26A	0.150133	0.060998	0.189147	0.0
H26B	0.042140	0.08026	0.262950	0.087
H26C	0.172151	−0.043331	0.314165	0.087
C27	0.1590(5)	0.2861()	0.3976(4	0.0284(10)
C28	0.2055(6)	0.1967(6)	0.5896(5)	0.0473(15)
H28	0.18114	0.279425	0584597	0.071
H28B	0.27619	0.135116	0.651386	0.071
H28C	0.131480	0.173272	0.601204	0.071
B1	0.4914(5)	0.7417(5)	0.2696(5)	0.0266(12)
H1A	0.546(5)	0.779(5)	0.299(4)	0.034(14)

U_{eq} is defined as 1/3 of the trace ofthe orthogonlized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å²) for compound 4.46 . The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02175(11)	0.01608(10)	0.01621(11)	−0.00831(8)	0.00426(7)	−0.00906(7)
P1	0.0210(5)	0.0196(5)	0.0224(6)	−0.0113(5)	0.0058(4)	−0.0086(4)
O1	0.0347(18)	0.0314(18)	0.0141(17)	−0.0098(15)	0.0051(14)	−0.0131(15)
O2	0.052(2)	0.0211(17)	0.032(2)	−0.0145(16)	0.0021(16)	−0.0118(15)
O3	0.046(2)	0.036(2)	0.029(2)	−0.0160(17)	0.0030(17)	−0.0070(17)
O4	0.033(2)	0.040(2)	0.036(2)	−0.0149(18)	0.0100(16)	−0.0099(17)
O5	0.039(2)	0.043(2)	0.077(3)	−0.035(2)	−0.002(2)	−0.0165(19)
O6	0.084(3)	0.028(2)	0.035(2)	−0.0125(18)	−0.009(2)	−0.025(2)
N1	0.0200(17)	0.0186(18)	0.018(2)	−0.0076(16)	0.0025(15)	−0.0096(15)
N2	0.0221(18)	0.0227(19)	0.026(2)	−0.0127(17)	0.0037(16)	−0.0138(16)
N3	0.0243(19)	0.0190(18)	0.020(2)	−0.0085(17)	0.0046(16)	−0.0092(15)

N4	0.0264(19)	0.0229(19)	0.030(2)	−0.0162(18)	0.0076(16)	−0.0148(16)
N5	0.0238(18)	0.0194(18)	0.020(2)	−0.0103(16)	0.0032(15)	−0.0094(15)
N6	0.031(2)	0.0236(19)	0.023(2)	−0.0162(17)	0.0030(16)	−0.0131(16)
N7	0.0243(19)	0.0170(18)	0.018(2)	−0.0084(16)	0.0034(15)	−0.0085(15)
N8	0.033(2)	0.0176(18)	0.023(2)	−0.0104(17)	0.0038(17)	−0.0082(16)
C1	0.018(2)	0.022(2)	0.021(2)	−0.0076(19)	0.0077(17)	−0.0102(17)
C2	0.025(2)	0.031(3)	0.031(3)	−0.015(2)	0.008(2)	−0.013(2)
C3	0.025(2)	0.030(3)	0.030(3)	−0.012(2)	0.002(2)	−0.013(2)
C4	0.021(2)	0.023(2)	0.025(3)	−0.010(2)	0.0067(19)	−0.0080(18)
C5	0.029(2)	0.019(2)	0.032(3)	−0.008(2)	0.010(2)	−0.0085(19)
C6	0.026(2)	0.023(2)	0.040(3)	−0.018(2)	0.013(2)	−0.0116(19)
C7	0.030(2)	0.028(2)	0.021(3)	−0.011(2)	0.006(2)	−0.014(2)
C8	0.043(3)	0.029(3)	0.017(2)	−0.013(2)	0.004(2)	−0.012(2)
C9	0.036(3)	0.026(2)	0.023(3)	−0.013(2)	−0.002(2)	−0.011(2)
C10	0.027(2)	0.036(3)	0.030(3)	−0.017(2)	0.003(2)	−0.008(2)
C11	0.031(3)	0.026(2)	0.036(3)	−0.016(2)	0.011(2)	−0.012(2)
C12	0.024(2)	0.029(3)	0.037(3)	−0.017(2)	0.013(2)	−0.011(2)
C13	0.029(2)	0.013(2)	0.012(2)	−0.0035(18)	0.0007(17)	−0.0105(17)
C14	0.027(2)	0.016(2)	0.018(2)	−0.0074(19)	0.0056(18)	−0.0103(18)
C15	0.025(2)	0.023(2)	0.030(3)	−0.017(2)	0.0030(19)	−0.0108(19)
C16	0.032(2)	0.021(2)	0.018(2)	−0.008(2)	−0.0005(19)	−0.0102(19)
C17	0.030(2)	0.020(2)	0.018(2)	−0.0101(19)	0.0063(19)	−0.0103(19)
C18	0.024(2)	0.014(2)	0.018(2)	−0.0067(19)	0.0036(18)	−0.0061(17)
C19	0.036(3)	0.024(2)	0.022(3)	−0.013(2)	0.004(2)	−0.010(2)

C20	0.033(2)	0.024(2)	0.027(3)	−0.015(2)	0.009(2)	−0.014(2)
C21	0.043(3)	0.022(2)	0.022(3)	−0.008(2)	0.001(2)	−0.009(2)
C22	0.042(3)	0.039(3)	0.039(3)	−0.013(3)	−0.012(3)	−0.004(3)
C23	0.033(3)	0.053(4)	0.048(4)	−0.011(3)	−0.005(3)	−0.010(3)
C24	0.028(2)	0.022(2)	0.032(3)	−0.012(2)	0.008(2)	−0.0108(19)
C25	0.036(3)	0.031(3)	0.033(3)	−0.017(2)	0.012(2)	−0.018(2)
C26	0.099(5)	0.037(3)	0.047(4)	−0.021(3)	−0.007(4)	−0.035(3)
C27	0.030(3)	0.023(2)	0.031(3)	−0.010(2)	0.005(2)	−0.013(2)
C28	0.055(4)	0.046(3)	0.030(3)	−0.020(3)	0.003(3)	−0.006(3)
B1	0.031(3)	0.025(3)	0.030(3)	−0.016(3)	0.003(2)	−0.013(2)

Table 4 Bond lengths and angles for compound 4.46

Atom–Atom	**Length [Å]**
W1–P1	2.4847(11)
W1–N1	2.243(3)
W1–N3	2.217(3)
W1–N5	2.263(4)
W1–N7	1.773(4)
W1–C13	2.203(4)
W1–C14	2.247(4)
P1–C10	1.813(5)
P1–C11	1.836(5)
P1–C12	1.824(5)
O1–N7	1.228(5)
O2–C20	1.232(5)
O3–C27	1.338(6)
O3–C28	1.451(6)
O4–C27	1.197(6)
O5–C25	1.199(6)
O6–C25	1.337(6)
O6–C26	1.445(6)
N1–N2	1.375(5)
N1–C1	1.341(5)
N2–C3	1.334(6)
N2–B1	1.536(6)
N3–N4	1.357(5)

N3–C4	1.337(6)
N4–C6	1.346(6)
N4–B1	1.539(7)
N5–N6	1.369(5)
N5–C7	1.344(6)
N6–C9	1.344(6)
N6–B1	1.526(7)
N8–C18	1.502(5)
N8–C20	1.356(6)
N8–C21	1.444(6)
C1–H1	0.9500
C1–C2	1.381(6)
C2–H2	0.9500
C2–C3	1.373(7)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.389(6)
C5–H5	0.9500
C5–C6	1.374(7)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.381(6)
C8–H8	0.9500
C8–C9	1.370(7)
C9–H9	0.9500
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800
C13–H13	1.0000
C13–C14	1.450(6)
C13–C18	1.507(6)
C14–H14	1.0000
C14–C15	1.524(6)
C15–H15	1.0000

C15–C16	1.535(6)
C15–C24	1.559(6)
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.535(6)
C17–H17	1.0000
C17–C18	1.542(6)
C17–C19	1.544(6)
C18–H18	1.0000
C19–H19A	0.9900
C19–H19B	0.9900
C19–C20	1.503(7)
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.494(8)
C22–H22	0.9500
C22–C23	1.306(9)
C23–H23A	0.9500
C23–H23B	0.9500
C24–H24	1.0000
C24–C25	1.511(7)
C24–C27	1.520(7)
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
B1–H1A	1.09(5)

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	157.36(9)
N1–W1–N5	81.59(13)
N1–W1–C14	119.00(14)
N3–W1–P1	83.76(9)
N3–W1–N1	76.74(13)
N3–W1–N5	84.33(13)
N3–W1–C14	161.31(14)
N5–W1–P1	85.20(9)

N7–W1–P1	89.36(12)
N7–W1–N1	100.61(14)
N7–W1–N3	86.33(14)
N7–W1–N5	169.65(14)
N7–W1–C13	98.50(15)
N7–W1–C14	99.51(16)
C13–W1–P1	116.61(11)
C13–W1–N1	82.23(14)
C13–W1–N3	158.95(14)
C13–W1–N5	91.81(14)
C13–W1–C14	38.01(15)
C14–W1–P1	78.61(11)
C14–W1–N5	88.05(14)
C10–P1–W1	113.36(16)
C10–P1–C11	103.6(2)
C10–P1–C12	103.4(2)
C11–P1–W1	113.99(16)
C12–P1–W1	122.42(16)
C12–P1–C11	97.5(2)
C27–O3–C28	114.6(4)
C25–O6–C26	116.2(4)
N2–N1–W1	119.6(3)
C1–N1–W1	134.5(3)
C1–N1–N2	105.9(3)
N1–N2–B1	121.7(3)
C3–N2–N1	109.0(4)
C3–N2–B1	129.0(4)
N4–N3–W1	124.1(3)
C4–N3–W1	129.3(3)
C4–N3–N4	106.3(4)
N3–N4–B1	117.6(3)
C6–N4–N3	110.0(4)
C6–N4–B1	129.9(4)
N6–N5–W1	119.2(3)
C7–N5–W1	135.0(3)
C7–N5–N6	105.3(3)
N5–N6–B1	121.8(3)
C9–N6–N5	109.8(4)
C9–N6–B1	128.4(4)
O1–N7–W1	172.2(3)

C20–N8–C18	112.6(4)
C20–N8–C21	122.2(4)
C21–N8–C18	124.9(3)
N1–C1–H1	124.5
N1–C1–C2	111.1(4)
C2–C1–H1	124.5
C1–C2–H2	127.8
C3–C2–C1	104.3(4)
C3–C2–H2	127.8
N2–C3–C2	109.7(4)
N2–C3–H3	125.1
C2–C3–H3	125.1
N3–C4–H4	124.8
N3–C4–C5	110.4(4)
C5–C4–H4	124.8
C4–C5–H5	127.4
C6–C5–C4	105.2(4)
C6–C5–H5	127.4
N4–C6–C5	108.1(4)
N4–C6–H6	125.9
C5–C6–H6	125.9
N5–C7–H7	124.4
N5–C7–C8	111.3(4)
C8–C7–H7	124.4
C7–C8–H8	127.6
C9–C8–C7	104.8(4)
C9–C8–H8	127.6
N6–C9–C8	108.9(4)
N6–C9–H9	125.6
C8–C9–H9	125.6
P1–C10–H10A	109.5
P1–C10–H10B	109.5
P1–C10–H10C	109.5
H10A–C10–H10B	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
P1–C11–H11A	109.5
P1–C11–H11B	109.5
P1–C11–H11C	109.5
H11A–C11–H11B	109.5

H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
P1–C12–H12A	109.5
P1–C12–H12B	109.5
P1–C12–H12C	109.5
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
W1–C13–H13	112.8
C14–C13–W1	72.6(2)
C14–C13–H13	112.8
C14–C13–C18	119.6(4)
C18–C13–W1	120.7(3)
C18–C13–H13	112.8
W1–C14–H14	112.0
C13–C14–W1	69.4(2)
C13–C14–H14	112.0
C13–C14–C15	118.0(4)
C15–C14–W1	126.6(3)
C15–C14–H14	112.0
C14–C15–H15	108.2
C14–C15–C16	112.7(4)
C14–C15–C24	107.4(4)
C16–C15–H15	108.2
C16–C15–C24	112.1(3)
C24–C15–H15	108.2
C15–C16–H16A	107.9
C15–C16–H16B	107.9
C15–C16–C17	117.4(4)
H16A–C16–H16B	107.2
C17–C16–H16A	107.9
C17–C16–H16B	107.9
C16–C17–H17	108.4
C16–C17–C18	115.6(4)
C16–C17–C19	112.9(4)
C18–C17–H17	108.4
C18–C17–C19	102.9(3)
C19–C17–H17	108.4
N8–C18–C13	113.7(3)
N8–C18–C17	102.2(3)

N8–C18–H18	108.1
C13–C18–C17	116.1(3)
C13–C18–H18	108.1
C17–C18–H18	108.1
C17–C19–H19A	110.7
C17–C19–H19B	110.7
H19A–C19–H19B	108.8
C20–C19–C17	105.2(4)
C20–C19–H19A	110.7
C20–C19–H19B	110.7
O2–C20–N8	125.5(4)
O2–C20–C19	126.1(4)
N8–C20–C19	108.5(4)
N8–C21–H21A	108.4
N8–C21–H21B	108.4
N8–C21–C22	115.5(5)
H21A–C21–H21B	107.5
C22–C21–H21A	108.4
C22–C21–H21B	108.4
C21–C22–H22	116.9
C23–C22–C21	126.1(5)
C23–C22–H22	116.9
C22–C23–H23A	120.0
C22–C23–H23B	120.0
H23A–C23–H23B	120.0
C15–C24–H24	108.9
C25–C24–C15	113.1(4)
C25–C24–H24	108.9
C25–C24–C27	107.0(4)
C27–C24–C15	110.1(4)
C27–C24–H24	108.9
O5–C25–O6	124.0(5)
O5–C25–C24	126.9(5)
O6–C25–C24	109.1(4)
O6–C26–H26A	109.5
O6–C26–H26B	109.5
O6–C26–H26C	109.5
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5

O3–C27–C24	110.8(4)
O4–C27–O3	124.2(5)
O4–C27–C24	125.0(5)
O3–C28–H28A	109.5
O3–C28–H28B	109.5
O3–C28–H28C	109.5
H28A–C28–H28B	109.5
H28A–C28–H28C	109.5
H28B–C28–H28C	109.5
N2–B1–N4	107.0(4)
N2–B1–H1A	107(3)
N4–B1–H1A	112(3)
N6–B1–N2	109.6(4)
N6–B1–N4	109.2(4)
N6–B1–H1A	112(3)

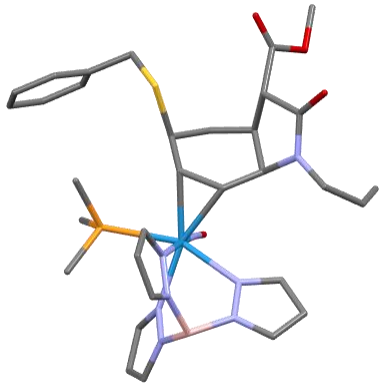
Table 5 Torsion angles for compound 4.46

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
W1–N1–N2–C3	−178.9(3)
W1–N1–N2–B1	−4.2(5)
W1–N1–C1–C2	178.9(3)
W1–N3–N4–C6	173.5(3)
W1–N3–N4–B1	9.5(5)
W1–N3–C4–C5	−174.0(3)
W1–N5–N6–C9	172.7(3)
W1–N5–N6–B1	−8.8(5)
W1–N5–C7–C8	−170.9(3)
W1–C13–C14–C15	121.4(4)
W1–C13–C18–N8	−174.4(3)
W1–C13–C18–C17	−56.1(5)
W1–C14–C15–C16	43.7(5)
W1–C14–C15–C24	167.6(3)
N1–N2–C3–C2	−0.2(5)
N1–N2–B1–N4	−57.7(5)
N1–N2–B1–N6	60.6(5)
N1–C1–C2–C3	−0.6(5)
N2–N1–C1–C2	0.5(5)

N3–N4–C6–C5	1.2(5)
N3–N4–B1–N2	54.2(5)
N3–N4–B1–N6	−64.3(5)
N3–C4–C5–C6	1.0(5)
N4–N3–C4–C5	−0.3(5)
N5–N6–C9–C8	0.1(5)
N5–N6–B1–N2	−52.2(5)
N5–N6–B1–N4	64.7(5)
N5–C7–C8–C9	−0.7(5)
N6–N5–C7–C8	0.8(5)
N8–C21–C22–C23	−8.9(8)
C1–N1–N2–C3	−0.2(5)
C1–N1–N2–B1	174.5(4)
C1–C2–C3–N2	0.4(6)
C3–N2–B1–N4	115.8(5)
C3–N2–B1–N6	−125.9(5)
C4–N3–N4–C6	−0.6(5)
C4–N3–N4–B1	−164.6(4)
C4–C5–C6–N4	−1.3(5)
C6–N4–B1–N2	−106.0(5)
C6–N4–B1–N6	135.4(4)
C7–N5–N6–C9	−0.5(5)
C7–N5–N6–B1	177.9(4)
C7–C8–C9–N6	0.4(5)
C9–N6–B1–N2	125.9(5)
C9–N6–B1–N4	−117.2(5)
C13–C14–C15–C16	−40.5(5)
C13–C14–C15–C24	83.4(5)
C14–C13–C18–N8	−88.0(5)
C14–C13–C18–C17	30.3(6)
C14–C15–C16–C17	40.3(5)
C14–C15–C24–C25	179.4(4)
C14–C15–C24–C27	59.8(5)
C15–C16–C17–C18	−6.3(6)
C15–C16–C17–C19	111.9(4)
C15–C24–C25–O5	−31.5(7)
C15–C24–C25–O6	146.8(4)
C15–C24–C27–O3	−125.7(4)
C15–C24–C27–O4	54.1(6)
C16–C15–C24–C25	−56.3(5)

C16–C15–C24–C27	−175.9(4)
C16–C17–C18–N8	95.4(4)
C16–C17–C18–C13	−29.0(5)
C16–C17–C19–C20	−99.1(4)
C17–C19–C20–O2	166.4(5)
C17–C19–C20–N8	−13.8(5)
C18–N8–C20–O2	174.6(4)
C18–N8–C20–C19	−5.1(5)
C18–N8–C21–C22	−67.9(6)
C18–C13–C14–W1	−115.9(4)
C18–C13–C14–C15	5.5(6)
C18–C17–C19–C20	26.2(5)
C19–C17–C18–N8	−28.2(4)
C19–C17–C18–C13	−152.5(4)
C20–N8–C18–C13	147.7(4)
C20–N8–C18–C17	21.7(5)
C20–N8–C21–C22	105.5(5)
C21–N8–C18–C13	−38.3(6)
C21–N8–C18–C17	−164.3(4)
C21–N8–C20–O2	0.5(7)
C21–N8–C20–C19	−179.3(4)
C24–C15–C16–C17	−80.9(5)
C25–C24–C27–O3	111.0(4)
C25–C24–C27–O4	−69.1(6)
C26–O6–C25–O5	0.1(8)
C26–O6–C25–C24	−178.3(5)
C27–C24–C25–O5	89.9(6)
C27–C24–C25–O6	−91.8(5)
C28–O3–C27–O4	0.5(7)
C28–O3–C27–C24	−179.6(4)
B1–N2–C3–C2	−174.3(5)
B1–N4–C6–C5	162.7(4)
B1–N6–C9–C8	−178.2(4)

Structure Report for compound 4.45



A colourless, plate shaped crystal of compound 4.45 measuring 0.055×0.065×0.192 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for ld-2-61 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[98] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with SHELXT[99] and refined by full-matrix least-squares methods against F^2 using XL[100] within OLEX2.[101] All non-hydrogen atoms were refined with anisotropically. The B-H atom was located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[102]

[98] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[99] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[100] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[101] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[102] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Refinement details for compound 4.45 The relative occupancy of the disordered atoms was freely refined. Constraints and restraints were used as needed on the anisotropic displacement parameters and/or bond lengths of the disordered atoms.

Table 1 Crystal data and structure refinement for ld-2-61CCDC number	
Empirical formula	$C_{32}H_{42}BN_8O_4PSW$
Formula weight	860.42
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.055×0.065×0.192
Crystal habit	colourless plate
Crystal system	triclinic
Space group	$P\overline{1}$ (2)
a [Å]	11.1724(6)
b [Å]	12.0571(6)
c [Å]	13.6472(7)
α [°]	74.847(2)
β [°]	78.374(2)
γ [°]	88.142(2)
Volume [$Å^3$]	1737.65(16)
Z	2
ρ_{calc} [gcm^{-3}]	1.644
μ [mm^{-1}]	3.479
F(000)	864
2θ range [°]	4.06 to 56.67 (0.75 Å)
Index ranges	−14 ≤ h ≤ 14 −16 ≤ k ≤ 14 −18 ≤ l ≤ 18
Reflections collected	55445
Independent reflections	8639 [R_{int} = 0.1109]
Data / Restraints / Parameters	8639 / 0 / 455

Goodness-of-fit on F^2	1.015
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0428 wR_2 = 0.0864
Final R indexes [all data]	R_1 = 0.0658 wR_2 = 0.0954
Largest peak/hole [eÅ^{-3}]	1.78/−1.44

Table Atomic coordinates and Ueq [Å^2] for compound 4.45

Atom	***x***	***y***	***z***	U_{eq}
W1	0.74410(2)	0.70191(2)	0.16533(2)	0.020357)
S1	0.63077(13)	0.53487(11)	0.53627(10)	0.0311(
P1	0.6686(14)	0.85668(11)	0.25449(11)	0.0293(3)
O1	1.006(3)	0.7156(3)	0.1816(3)	0.0366(9)
O2	0.6946(4)	0.1512(3)	0.3977(3)	0.0388(10)
N1	0.5514(4)	0.7081(3)	0.1368(3)	0.0247(9)
N2	0.5312(4)	0.7421(4)	0.0379(3)	0.0268(9)
	0.7763(4)	0.6231(3)	0.0320(3)	0.0225(9)
N4	0.7195(4)	0.6633(4)	−0.0491(3)	0.0274(10)
N5	0.7763(4)	0.8523(4)	0.0300(3)	0.0248(9)
N6	0.7161(4)	0.8687(4)	−0.0498(3)	0.0254(9)
N7	0.8961(4)	0.7074(3)	0.1782(3)	0.0255(9)
N8	0.7642(4)	0.3181(4)	0.2752(3)	0.0269(10)
C1	0.4407(5)	0.6901(4)	0.1989(4)	0.0266(11)
H1	0.426908	0.665936	0.272425	0.032
C2	0.3498(5)	0.7112(5)	0.1425(4)	0.0321(12)
H2	0.263930	0.704550	0.167851	0.039
C3	0.4109(5)	0.7441(5)	0.0411(4)	0.0310(12)
H3	0.373394	0.765071	−0.017593	0.037
C4	0.8473(5)	0.5378(4)	0.0100(4)	0.0294(12)
H4	0.898547	0.494769	0.053228	0.035
C	0.8360(5)	0.5207(5)	−0.0843(4)	0.0342(13)
H5	0.875893	0.465527	−0.117476	0.041
C6	0.7536(5)	0.6019(5)	−0.1191(4)	0.0354(14)
H6	0.725627	0.612747	−0.182145	0.043
C7	0.8509(5)	0.9448(4)	0.0069(4)	0.0255(11)
H	0.90517	0.956549	0.048567	0.031
C8	0.8377(5)	1.0201(5)	−0.0852(4)	0.0330(13)
H8	0.878755	1.092031	−0.117792	0.040

C9	0.7529(5)	0.9692(5)	−0.1197(4)	0.0314(12)
H9	0.724620	0.999452	−0.182342	0.038
C10	0.5508(6)	0.8249(5)	0.3718(4)	0.0430(16)
H10A	0.473599	0.806580	0.355271	0.064
H10B	0.540330	0.891996	0.400358	0.064
H10C	0.574916	0.759115	0.422806	0.064
C11	0.7858(7)	0.9283(5)	0.2916(5)	0.0508(18)
H11A	0.820076	0.873513	0.345134	0.076
H11B	0.749777	0.992064	0.318923	0.076
H11C	0.850741	0.958116	0.230998	0.076
C12	0.5960(5)	0.9734(5)	0.1735(4)	0.0368(14)
H12A	0.658073	1.017532	0.116361	0.055
H12B	0.555867	1.02404	0.215289	0.055
H12C	0.535117	0.941298	0.145383	0.055
C13	0.6741(5)	0.5957(4)	0.3251(4)	0.0241(11)
H13	0.583535	0.600708	0.346700	0.029
C14	0.7076(4)	0.5226(4)	0.2558(4)	0.0221(10)
H14	0.634017	0.489504	0.241427	0.027
C15	0.8084(5)	0.4344(4)	0.2695(4)	0.0248(11)
H15	0.880470	0.457759	0.211195	0.030
C16	0.8489(5)	0.4140(4)	0.3739(4)	0.0284(12)
H16	0.932179	0.380414	0.365953	0.034
C17	0.8576(5)	0.5248(5)	0.4067(4)	0.0317(12)
H17A	0.881494	0.505425	0.475096	0.038
H17B	0.923285	0.574586	0.356358	0.038
C18	0.7406(5)	0.5919(4)	0.4137(4)	0.0269(11)
H18	0.762450	0.672745	0.410388	0.032
C9	0.7591(5)	0.3193(4)	0.4454(4)	0.0315(12)
H1	0.680635	0.357430	0.465822	0.038
H19A	0.685834	0.343638	0.489708	0.038
C20	0.7369(5)	0.2495(5)	0.3722(5)	0.0314(13)
C2	0.7443(5)	0.2849(5)	0.1860(5)	0.0352(13)
H21A	0.710222	0.350521	0.140082	0.042
H21B	0.683383	0.220872	0.208599	0.042
C22	0.8613(6)	0.2476(5)	0.1251(5)	0.0421(16)
H22	0.858689	0.237650	0.058780	0.050
C23	0.9638(6)	0.2282(5)	0.1562(6)	0.0489(18)
H23A	0.970349	0.237075	0.222073	0.059
H23B	1.032506	0.205061	0.113149	0.059

C26	0.7051(6)	0.5734(5)	0.6299(4)	0.0341(13)
H26A	0.663392	0.532011	0.700632	0.04
H26	0.790877	0.548025	0.619672	0.041
C27	0.7041(5)	0.7005(4)	0.6213(4)	0.0263(11)
C28	0.5954(5)	0.7564(5)	0.6315(4)	0.0357(13)
H28	0.521079	0.713989	0.644916	0.043
C29	0.5917(6)	0.8727(5)	0.6226(5)	0.0413(15)
H29	0.515576	0.910079	0.630609	0.050
C30	0.6975(7)	0.9332(5)	0.6023(5)	0.0482(17)
H30	0.695093	1.014018	0.593303	0.058
C31	0.8088(6)	0.8803(6)	0.5945(6)	0.0536(18)
H31	0.882572	0.923042	0.582756	0.064
C32	0.8104(6)	0.762(6)	0.6043(5)	0.0455(16)
H32	0.886230	0.72844	0.599032	0.055
B1	0.6364(6)	0.7689(6)	−0.0555(5)	0.0291(13)
H1A	0.605(4)	0.790(4)	−0.132(4)	0.026(14)
O3	0.7395(6)	0.2343(5)	0.6286(4)	0.0593(18)
O4	0.9067(5)	0.2080(5)	0.5252(4)	0.0499(15)
C24	0.7968(7)	0.2516(6)	0.5452(6)	0.0318(16)
C25	0.9507(8)	0.1454(8)	0.6160(6)	0.053(2)
H25A	1.029026	0.110851	0.594940	0.079
H25B	0.891145	0.084817	0.657456	0.079
H25C	0.96178	0.198172	0.657471	0.079
O3A	0.907(3)	0.157(3)	0.472(2)	0.0593(18)
O4A	0.836(3)	0.258(3)	0.589(2)	0.0499(15)
C24A	0.842(4)	0.229(3)	0.500(3)	0.0318(16)
C25A	0.871(4)	0.189(4)	0.671(3)	0.053(2)
H25D	0.957886	0.201846	0.666775	0.079
H25E	0.855870	0.108821	0.672771	0.079
H25F	0.823688	0.205577	0.734386	0.079

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å²) for compound 4.45. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02507(11)	0.01916(10)	0.01795(11)	−0.00728(7)	−0.00361(7)	−0.00027(7)
S1	0.0447(8)	0.0281(7)	0.0203(7)	−0.0061(6)	−0.0054(6)	−0.0068(6)
P1	0.0467(9)	0.0208(6)	0.0216(7)	−0.0086(6)	−0.0061(6)	0.0046(6)

O1	0.025(2)	0.033(2)	0.053(3)	−0.0068(19)	−0.0152(19)	−0.0042(16)
O2	0.040(2)	0.0211(19)	0.047(3)	−0.0035(18)	0.0060(19)	−0.0090(17)
N1	0.031(2)	0.023(2)	0.017(2)	−0.0025(18)	0.0001(18)	−0.0033(18)
N2	0.029(2)	0.029(2)	0.021(2)	−0.0024(19)	−0.0076(18)	−0.0019(19)
N3	0.026(2)	0.023(2)	0.018(2)	−0.0065(18)	−0.0007(17)	−0.0013(17)
N4	0.034(2)	0.031(2)	0.017(2)	−0.0082(19)	−0.0023(19)	−0.0023(19)
N5	0.027(2)	0.024(2)	0.024(2)	−0.0083(19)	−0.0062(18)	−0.0010(18)
N6	0.029(2)	0.028(2)	0.017(2)	−0.0025(18)	−0.0043(18)	−0.0018(18)
N7	0.039(3)	0.017(2)	0.020(2)	−0.0059(17)	−0.0052(19)	0.0014(18)
N8	0.027(2)	0.021(2)	0.030(3)	−0.0083(19)	0.0025(19)	0.0001(18)
C1	0.028(3)	0.026(3)	0.022(3)	−0.002(2)	0.000(2)	−0.002(2)
C2	0.027(3)	0.030(3)	0.035(3)	−0.003(2)	−0.003(2)	−0.002(2)
C3	0.029(3)	0.032(3)	0.029(3)	0.000(2)	−0.010(2)	−0.001(2)
C4	0.033(3)	0.027(3)	0.024(3)	−0.008(2)	0.005(2)	−0.003(2)
C5	0.043(3)	0.030(3)	0.031(3)	−0.017(3)	0.003(3)	−0.010(3)
C6	0.043(3)	0.045(3)	0.021(3)	−0.018(3)	0.001(2)	−0.010(3)
C7	0.024(3)	0.020(2)	0.030(3)	−0.006(2)	0.000(2)	−0.002(2)
C8	0.034(3)	0.024(3)	0.033(3)	−0.001(2)	0.002(2)	0.001(2)
C9	0.031(3)	0.031(3)	0.025(3)	−0.001(2)	0.002(2)	0.000(2)
C10	0.073(5)	0.031(3)	0.021(3)	−0.010(2)	0.003(3)	0.018(3)
C11	0.082(5)	0.035(3)	0.049(4)	−0.024(3)	−0.028(4)	0.003(3)
C12	0.045(3)	0.031(3)	0.029(3)	−0.005(2)	0.001(3)	0.011(3)
C13	0.032(3)	0.020(2)	0.022(3)	−0.008(2)	−0.005(2)	−0.001(2)
C14	0.024(3)	0.022(2)	0.023(3)	−0.008(2)	−0.007(2)	0.000(2)
C15	0.029(3)	0.017(2)	0.026(3)	−0.004(2)	−0.001(2)	−0.002(2)
C16	0.022(3)	0.022(3)	0.038(3)	−0.003(2)	−0.005(2)	−0.001(2)
C17	0.039(3)	0.028(3)	0.028(3)	−0.001(2)	−0.013(2)	−0.003(2)
C18	0.037(3)	0.022(3)	0.020(3)	−0.001(2)	−0.007(2)	−0.004(2)
C19	0.033(3)	0.022(3)	0.036(3)	−0.001(2)	−0.005(2)	−0.001(2)

C20	0.024(3)	0.023(3)	0.041(3)	−0.007(3)	0.002(2)	0.004(2)
C21	0.042(3)	0.024(3)	0.039(3)	−0.014(3)	0.001(3)	−0.004(2)
C22	0.050(4)	0.027(3)	0.047(4)	−0.019(3)	0.012(3)	−0.009(3)
C23	0.039(4)	0.035(3)	0.062(5)	−0.016(3)	0.017(3)	0.005(3)
C26	0.053(4)	0.032(3)	0.019(3)	−0.002(2)	−0.015(3)	−0.008(3)
C27	0.034(3)	0.028(3)	0.017(3)	−0.004(2)	−0.006(2)	−0.002(2)
C28	0.042(3)	0.042(3)	0.029(3)	−0.021(3)	−0.003(3)	0.000(3)
C29	0.052(4)	0.049(4)	0.033(3)	−0.024(3)	−0.016(3)	0.016(3)
C30	0.077(5)	0.025(3)	0.041(4)	−0.002(3)	−0.015(4)	0.001(3)
C31	0.050(4)	0.045(4)	0.062(5)	−0.016(4)	0.001(4)	−0.016(3)
C32	0.039(4)	0.048(4)	0.047(4)	−0.011(3)	−0.006(3)	0.007(3)
B1	0.031(3)	0.035(3)	0.018(3)	−0.002(3)	−0.003(3)	−0.004(3)
O3	0.068(4)	0.072(4)	0.027(3)	−0.002(3)	−0.004(3)	0.034(3)
O4	0.037(3)	0.073(4)	0.029(3)	0.004(3)	−0.006(2)	0.016(3)
C24	0.029(4)	0.030(3)	0.031(4)	−0.008(3)	0.007(3)	0.001(3)
C25	0.045(5)	0.075(6)	0.031(4)	0.003(4)	−0.015(4)	0.006(4)
O3A	0.068(4)	0.072(4)	0.027(3)	−0.002(3)	−0.004(3)	0.034(3)
O4A	0.037(3)	0.073(4)	0.029(3)	0.004(3)	−0.006(2)	0.016(3)
C24A	0.029(4)	0.030(3)	0.031(4)	−0.008(3)	0.007(3)	0.001(3)
C25A	0.045(5)	0.075(6)	0.031(4)	0.003(4)	−0.015(4)	0.006(4)

Table 4 Bond lengths and angles for compound 4.45

Atom–Atom	**Length [Å]**
W1–P1	2.5185(12)
W1–N1	2.260(4)
W1–N3	2.228(4)
W1–N5	2.202(4)
W1–N7	1.747(5)
W1–C13	2.219(5)
W1–C14	2.196(5)
S1–C18	1.845(5)
S1–C26	1.817(5)
P1–C10	1.819(6)
P1–C11	1.811(6)
P1–C12	1.828(6)
O1–N7	1.252(5)

O2–C20	1.227(6)
N1–N2	1.366(6)
N1–C1	1.339(6)
N2–C3	1.336(7)
N2–B1	1.522(7)
N3–N4	1.358(6)
N3–C4	1.337(6)
N4–C6	1.346(6)
N4–B1	1.545(8)
N5–N6	1.361(6)
N5–C7	1.345(6)
N6–C9	1.348(7)
N6–B1	1.547(7)
N8–C15	1.479(6)
N8–C20	1.345(7)
N8–C21	1.436(7)
C1–H1	0.9500
C1–C2	1.374(7)
C2–H2	0.9500
C2–C3	1.374(8)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.386(7)
C5–H5	0.9500
C5–C6	1.381(8)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.377(8)
C8–H8	0.9500
C8–C9	1.365(8)
C9–H9	0.9500
C10–H10A	0.9800
C10–H10B	0.9800
C10–H10C	0.9800
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800

C13–H13	1.0000
C13–C14	1.444(6)
C13–C18	1.532(7)
C14–H14	1.0000
C14–C15	1.529(7)
C15–H15	1.0000
C15–C16	1.537(7)
C16–H16	1.0000
C16–C17	1.527(7)
C16–C19	1.535(7)
C17–H17A	0.9900
C17–H17B	0.9900
C17–C18	1.515(7)
C18–H18	1.0000
C19–H19	1.0000
C19–H19A	1.0000
C19–C20	1.523(8)
C19–C24	1.526(10)
C19–C24A	1.55(4)
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.523(8)
C22–H22	0.9500
C22–C23	1.293(9)
C23–H23A	0.9500
C23–H23B	0.9500
C26–H26A	0.9900
C26–H26B	0.9900
C26–C27	1.506(7)
C27–C28	1.369(7)
C27–C32	1.367(8)
C28–H28	0.9500
C28–C29	1.376(8)
C29–H29	0.9500
C29–C30	1.351(9)
C30–H30	0.9500
C30–C31	1.376(9)
C31–H31	0.9500
C31–C32	1.397(9)
C32–H32	0.9500

B1–H1A	1.12(5)
O3–C24	1.157(9)
O4–C24	1.325(9)
O4–C25	1.442(9)
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
O3A–C24A	1.21(4)
O4A–C24A	1.33(5)
O4A–C25A	1.34(4)
C25A–H25D	0.9800
C25A–H25E	0.9800
C25A–H25F	0.9800

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	82.78(10)
N3–W1–P1	153.86(11)
N3–W1–N1	81.40(15)
N5–W1–P1	80.83(11)
N5–W1–N1	84.15(15)
N5–W1–N3	76.97(15)
N5–W1–C13	159.90(16)
N7–W1–P1	96.47(13)
N7–W1–N1	175.05(17)
N7–W1–N3	97.50(16)
N7–W1–N5	90.91(18)
N7–W1–C13	95.99(19)
N7–W1–C14	96.12(18)
C13–W1–P1	79.65(12)
C13–W1–N1	88.69(17)
C13–W1–N3	120.53(16)
C14–W1–P1	117.46(12)
C14–W1–N1	88.54(17)
C14–W1–N3	82.83(16)
C14–W1–N5	159.32(16)
C14–W1–C13	38.17(16)
C26–S1–C18	102.0(3)
C10–P1–W1	120.67(19)
C10–P1–C12	99.6(3)

C11–P1–W1	115.2(2)
C11–P1–C10	102.2(3)
C11–P1–C12	104.1(3)
C12–P1–W1	112.67(18)
N2–N1–W1	120.1(3)
C1–N1–W1	133.8(4)
C1–N1–N2	106.0(4)
N1–N2–B1	121.6(4)
C3–N2–N1	109.1(4)
C3–N2–B1	129.3(5)
N4–N3–W1	120.7(3)
C4–N3–W1	132.8(4)
C4–N3–N4	106.5(4)
N3–N4–B1	121.7(4)
C6–N4–N3	109.4(4)
C6–N4–B1	128.8(5)
N6–N5–W1	123.4(3)
C7–N5–W1	131.0(4)
C7–N5–N6	105.5(4)
N5–N6–B1	118.7(4)
C9–N6–N5	109.9(4)
C9–N6–B1	130.8(5)
O1–N7–W1	176.3(4)
C20–N8–C15	113.8(4)
C20–N8–C21	123.4(5)
C21–N8–C15	122.7(4)
N1–C1–H1	124.4
N1–C1–C2	111.1(5)
C2–C1–H1	124.4
C1–C2–H2	127.8
C1–C2–C3	104.5(5)
C3–C2–H2	127.8
N2–C3–C2	109.3(5)
N2–C3–H3	125.3
C2–C3–H3	125.3
N3–C4–H4	124.5
N3–C4–C5	110.9(5)
C5–C4–H4	124.5
C4–C5–H5	127.8
C6–C5–C4	104.3(5)

C6–C5–H5	127.8
N4–C6–C5	108.8(5)
N4–C6–H6	125.6
C5–C6–H6	125.6
N5–C7–H7	124.5
N5–C7–C8	110.9(5)
C8–C7–H7	124.5
C7–C8–H8	127.4
C9–C8–C7	105.2(5)
C9–C8–H8	127.4
N6–C9–C8	108.5(5)
N6–C9–H9	125.8
C8–C9–H9	125.8
P1–C10–H10A	109.5
P1–C10–H10B	109.5
P1–C10–H10C	109.5
H10A–C10–H10B	109.5
H10A–C10–H10C	109.5
H10B–C10–H10C	109.5
P1–C11–H11A	109.5
P1–C11–H11B	109.5
P1–C11–H11C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
P1–C12–H12A	109.5
P1–C12–H12B	109.5
P1–C12–H12C	109.5
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
W1–C13–H13	112.3
C14–C13–W1	70.1(3)
C14–C13–H13	112.3
C14–C13–C18	121.8(4)
C18–C13–W1	121.8(3)
C18–C13–H13	112.3
W1–C14–H14	111.7
C13–C14–W1	71.7(3)
C13–C14–H14	111.7

C13–C14–C15	121.6(4)
C15–C14–W1	122.9(3)
C15–C14–H14	111.7
N8–C15–C14	111.3(4)
N8–C15–H15	110.1
N8–C15–C16	101.3(4)
C14–C15–H15	110.1
C14–C15–C16	113.7(4)
C16–C15–H15	110.1
C15–C16–H16	107.6
C17–C16–C15	112.8(4)
C17–C16–H16	107.6
C17–C16–C19	117.9(5)
C19–C16–C15	102.8(4)
C19–C16–H16	107.6
C16–C17–H17A	108.7
C16–C17–H17B	108.7
H17A–C17–H17B	107.6
C18–C17–C16	114.3(4)
C18–C17–H17A	108.7
C18–C17–H17B	108.7
S1–C18–H18	107.7
C13–C18–S1	107.4(4)
C13–C18–H18	107.7
C17–C18–S1	112.7(4)
C17–C18–C13	113.4(4)
C17–C18–H18	107.7
C16–C19–H19	107.0
C16–C19–H19A	117.5
C16–C19–C24A	103.9(14)
C20–C19–C16	102.6(4)
C20–C19–H19	107.0
C20–C19–H19A	117.5
C20–C19–C24	116.1(5)
C20–C19–C24A	94.4(14)
C24–C19–C16	116.4(5)
C24–C19–H19	107.0
C24A–C19–H19A	117.5
O2–C20–N8	126.3(5)
O2–C20–C19	126.1(5)

N8–C20–C19	107.4(4)
N8–C21–H21A	109.1
N8–C21–H21B	109.1
N8–C21–C22	112.4(5)
H21A–C21–H21B	107.8
C22–C21–H21A	109.1
C22–C21–H21B	109.1
C21–C22–H22	117.2
C23–C22–C21	125.5(6)
C23–C22–H22	117.2
C22–C23–H23A	120.0
C22–C23–H23B	120.0
H23A–C23–H23B	120.0
S1–C26–H26A	109.0
S1–C26–H26B	109.0
26A–C26–H26B	107.8

C27–C26–S1	113.0(4)
C27–C26–H26A	109.0
C27–C26–H26B	109.0
C28–C27–C26	120.1(5)
C32–C27–C26	121.2(5)
C32–C27–C28	118.8(5)
C27–C28–H28	119.3
C27–C28–C29	121.4(6)
C29–C28–H28	119.3
C28–C29–H29	120.4
C30–C29–C28	119.3(6)
C30–C29–H29	120.4
C29–C30–H30	119.3
C29–C30–C31	121.4(6)
C31–C30–H30	119.3
C30–C31–H31	120.9
C30–C31–C32	118.3(6)
C32–C31–H31	120.9
C27–C32–C31	120.8(6)
C27–C32–H32	119.6
C31–C32–H32	119.6
N2–B1–N4	108.4(5)
N2–B1–N6	109.6(4)

N2–B1–H1A	113(3)
N4–B1–N6	106.1(4)
N4–B1–H1A	109(2)
N6–B1–H1A	110(3)
C24–O4–C25	114.3(6)
O3–C24–C19	127.3(7)
O3–C24–O4	121.8(8)
O4–C24–C19	110.8(6)
O4–C25–H25A	109.5
O4–C25–H25B	109.5
O4–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
C24A–O4A–C25A	123(4)
O3A–C24A–C19	132(3)
O3A–C24A–O4A	126(4)
O4A–C24A–C19	101(3)
O4A–C25A–H25D	109.5
O4A–C25A–H25E	109.5
O4A–C25A–H25F	109.5
H25D–C25A–H25E	109.5
H25D–C25A–H25F	109.5
H25E–C25A–H25F	109.5

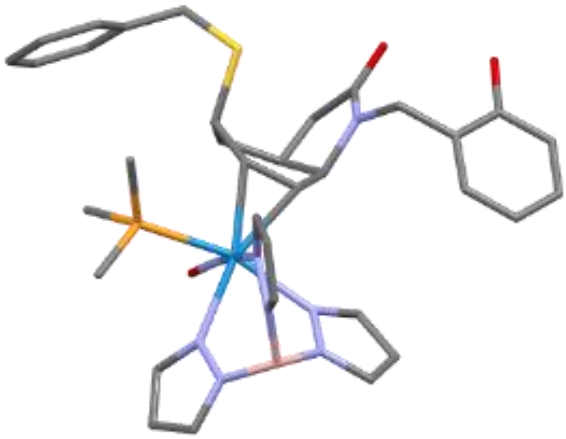
Table 5 Torsion angles for compound 4.45

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
W1–N1–N2–C3	−177.0(3)
W1–N1–N2–B1	4.1(6)
W1–N1–C1–C2	176.6(3)
W1–N3–N4–C6	−180.0(3)
W1–N3–N4–B1	3.4(6)
W1–N3–C4–C5	−179.6(4)
W1–N5–N6–C9	178.5(3)

W1–N5–N6–B1	−10.0(6)
W1–N5–C7–C8	−177.8(3)
W1–C13–C14–C15	117.9(5)
W1–C13–C18–S1	162.0(2)
W1–C13–C18–C17	−72.9(5)
W1–C14–C15–N8	−146.3(3)
W1–C14–C15–C16	100.0(4)
S1–C26–C27–C28	57.9(6)
S1–C26–C27–C32	−122.7(5)
N1–N2–C3–C2	−0.1(6)
N1–N2–B1–N4	55.1(6)
N1–N2–B1–N6	−60.3(6)
N1–C1–C2–C3	−0.3(6)
N2–N1–C1–C2	0.3(6)
N3–N4–C6–C5	−0.9(6)
N3–N4–B1–N2	−60.5(6)
N3–N4–B1–N6	57.2(6)
N3–C4–C5–C6	0.4(6)
N4–N3–C4–C5	−0.9(6)
N5–N6–C9–C8	−0.4(6)
N5–N6–B1–N2	63.9(6)
N5–N6–B1–N4	−53.0(5)
N5–C7–C8–C9	−1.2(6)
N6–N5–C7–C8	1.0(5)
N8–C15–C16–C17	−160.1(4)
N8–C15–C16–C19	−32.1(5)
N8–C21–C22–C23	11.0(8)
C1–N1–N2–C3	−0.1(5)
C1–N1–N2–B1	−179.0(5)
C1–C2–C3–N2	0.2(6)
C3–N2–B1–N4	−123.5(6)
C3–N2–B1–N6	121.1(6)
C4–N3–N4–C6	1.1(6)
C4–N3–N4–B1	−175.5(4)
C4–C5–C6–N4	0.3(6)
C6–N4–B1–N2	123.6(6)
C6–N4–B1–N6	−118.7(6)
C7–N5–N6–C9	−0.3(5)
C7–N5–N6–B1	171.1(4)
C7–C8–C9–N6	1.0(6)

C9–N6–B1–N2	−126.8(5)
C9–N6–B1–N4	116.3(6)
C13–C14–C15–N8	126.0(5)
C13–C14–C15–C16	12.4(7)
C14–C13–C18–S1	−113.0(5)
C14–C13–C18–C17	12.1(7)
C14–C15–C16–C17	−40.5(6)
C14–C15–C16–C19	87.5(5)
C15–N8–C20–O2	177.2(5)
C15–N8–C20–C19	1.4(6)
C15–N8–C21–C22	83.5(6)
C15–C16–C17–C18	56.7(6)
C15–C16–C19–C20	33.3(5)
C15–C16–C19–C24	161.2(5)
C15–C16–C19–C24A	131.2(15)
C16–C17–C18–S1	81.1(5)
C16–C17–C18–C13	−41.1(6)
C16–C19–C20–O2	161.9(5)
C16–C19–C20–N8	−22.3(5)
C16–C19–C24–O3	128.8(8)
C16–C19–C24–O4	−53.9(8)
C16–C19–C24A–O3A	−78(4)
C16–C19–C24A–O4A	96(2)
C17–C16–C19–C20	158.1(5)
C17–C16–C19–C24	−74.1(6)
C17–C16–C19–C24A	−104.1(15)
C18–S1–C26–C27	71.2(5)
C18–C13–C14–W1	−115.8(5)
C18–C13–C14–C15	2.1(7)
C19–C16–C17–C18	−62.9(6)
C20–N8–C15–C14	−101.3(5)
C20–N8–C15–C16	19.9(5)
C20–N8–C21–C22	−101.0(6)
C20–C19–C24–O3	−110.3(8)
C20–C19–C24–O4	67.0(7)
C20–C19–C24A–O3A	27(4)

C20–C19–C24A–O4A	−160(2)
C21–N8–C15–C14	74.6(6)
C21–N8–C15–C16	−164.2(5)
C21–N8–C20–O2	1.4(8)
C21–N8–C20–C19	−174.5(5)
C26–S1–C18–C13	−164.4(3)
C26–S1–C18–C17	70.1(4)
C26–C27–C28–C29	−179.1(5)
C26–C27–C32–C31	178.8(6)
C27–C28–C29–C30	0.7(9)
C28–C27–C32–C31	−1.8(9)
C28–C29–C30–C31	−2.6(10)
C29–C30–C31–C32	2.3(11)
C30–C31–C32–C27	−0.1(10)
C32–C27–C28–C29	1.5(8)
B1–N2–C3–C2	178.7(5)
B1–N4–C6–C5	175.4(5)
B1–N6–C9–C8	−170.5(5)
C24–C19–C20–O2	33.8(8)
C24–C19–C20–N8	−150.3(5)
C25–O4–C24–C19	178.2(6)
C25–O4–C24–O3	−4.3(12)
C24A–C19–C20–O2	56.6(15)
C24A–C19–C20–N8	−127.6(14)
C25A–O4A–C24A–C19	164(3)
C25A–O4A–C24A–O3A	−21(6)



Structure Report for compound 4.50 A colourless, plate shaped crystal of compound 4.50 measuring 0.035×0.076×0.107 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_2_155_x3_0m_sq were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[103] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by direct methods with SHELXT[104] and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/1[105] within OLEX2.[106] All non-hydrogen atoms were refined with anisotropically. The B-H and O-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions wit

[103] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[104] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[105] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[106] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

h U_{iso} =

CCDC number	
Empirical formula	C34H42BN8O3PSW
Formula weight	868.44
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal size [mm3]	0.035×0.076×0.107
Crystal habit	colourless plate
Crystal system	triclinic
Space group	$P\overline{1}$ (2)
a [Å]	10.9432(4)
b [Å]	13.3828(5)
c [Å]	14.6510(6)
α [°]	110.6030(10)
β [°]	93.8430(10)
γ [°]	113.0670(10)
Volume [Å3]	1794.77(12)
Z	2
ρcalc [gcm−3]	1.607
μ [mm−1]	3.368
F(000)	872
2θ range [°]	4.13 to 56.57 (0.75 Å)
Index ranges	−14 ≤ h ≤ 13 −17 ≤ k ≤ 17 −19 ≤ l ≤ 19
Reflections collected	64453
Independent reflections	8909 [Rint = 0.0797]
Data / Restraints / Parameters	8909 / 0 / 461
Goodness-of-fit on F2	1.013
Final R indexes [I≥2σ(I)]	R1 = 0.0303 wR2 = 0.0608
Final R indexes [all data]	R1 = 0.0418 wR2 = 0.0647
Largest peak/hole [eÅ−3]	0.85/−0.62

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1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[107]

Refinement details for compound 4.50

[1] Disordered solvent located in the crystal lattice could not be adequately modeled with or without restraints. Therefore, the solvent was accounted for using the Platon SQUEEZE method. A void space of 98 A3 containing 35 electrons was found. This corresponds to approximately one molecule of dichloromethane.

[2]

[3] **Table 1 Crystal data and structure refinement for** compound 4.50

[4] **Table 2 Atomic coordinates and Ueq [Å²] for** compound 4.50

Atom	x	y	z		Ueq
W1	0.63211(2)	0.38781(2)	0.77151(2)		0.01595(4)
S1	0.29876(9)	−0.03076(8)	0.59005(7)		0.02510(18)
P1	0.63962(9)	0.29737(8)	0.89349(7)		0.01995(18)
O1	0.4151(2)	0.4520(2)	0.85002(18)		0.0242(5)

[107] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

O2	0.1097(2)	0.0171(2)	0.36386(18)		0.0295(6)
O3	0.2138(4)	0.0531(3)	0.2068(2)		0.0453(8)
H3	0.179(4)	0.024(3)	0.242(3)		0.019(11)
N1	0.7123(3)	0.5123(2)	0.6977(2)		0.0198(6)
N2	0.8488(3)	0.5866(2)	0.7210(2)		0.0227(6)
N3	0.7769(3)	0.5547(2)	0.8998(2)		0.0190(6)
N4	0.9066(3)	0.6242(2)	0.8985(2)		0.0212(6)
N5	0.8222(3)	0.3654(2)	0.7403(2)		0.0209(6)
N6	0.9444(3)	0.4654(3)	0.7671(2)		0.0224(6)
N7	0.4996(3)	0.4216(2)	0.8127(2)		0.0189(6)
N8	0.3224(3)	0.1464(2)	0.4670(2)		0.0193(6)
C1	0.6523(4)	0.5363(3)	0.6309(3)		0.0248(7)
H1	0.556909	0.498165	0.601577		0.030
C2	0.7497(4)	0.6251(3)	0.6106(3)		0.0315(9)
H2	0.734709	0.658425	0.565985		0.038
C3	0.8714(4)	0.6540(3)	0.6687(3)		0.0293(8)
H3A	0.958155	0.712379	0.671696		0.035
C4	0.7550(4)	0.6133(3)	0.9870(3)		0.0231(7)
H4	0.672713	0.585642	1.008183		0.028
C5	0.8700(4)	0.7206(3)	1.0420(3)		0.0285(8)
H5	0.882396	0.778595	1.106683		0.034
C6	0.9618(4)	0.7245(3)	0.9826(3)		0.0267(8)
H6	1.050407	0.788176	0.998544		0.032
C7	0.8501(4)	0.2723(3)	0.7081(3)		0.0266(8)
H7	0.783793	0.191508	0.683979		0.032
C8	0.9891(4)	0.3093(4)	0.7145(3)		0.0309(8)
H8	1.035418	0.260742	0.696899		0.037
C9	1.0450(4)	0.4312(4)	0.7517(3)		0.0307(8)
H9	1.139167	0.483217	0.764538		0.037
C10	0.5184(3)	0.2612(3)	0.6168(2)		0.0178(6)
H10	0.583(4)	0.265(3)	0.576(3)		0.025(10)
C11	0.5079(3)	0.1937(3)	0.6760(2)		0.0175(6)
H11	0.567(3)	0.156(3)	0.669(2)		0.012(8)
C12	0.3693(3)	0.1222(3)	0.6888(2)		0.0200(7)
H12	0.384732	0.116727	0.754605		0.024
C13	0.2715(3)	0.1780(3)	0.6928(3)		0.0210(7)
H13A	0.293868	0.239157	0.761817		0.025
H13B	0.177698	0.115401	0.680048		0.025
C14	0.2709(3)	0.2365(3)	0.6189(2)		0.0194(7)
H14	0.275202	0.316708	0.656856		0.023
C15	0.3888(3)	0.2524(3)	0.5646(2)		0.0176(6)
H15	0.411934	0.325489	0.551653		0.021
C16	0.1432(3)	0.1640(3)	0.5328(3)		0.0239(7)

H16A	0.068952	0.107279	0.549979		0.029
H16B	0.110711	0.217099	0.517479		0.029
C17	0.1858(3)	0.0988(3)	0.4452(3)		0.0221(7)
C18	0.3960(4)	0.1109(3)	0.3918(3)		0.0228(7)
H18A	0.340298	0.025925	0.345922		0.027
H18B	0.482724	0.118906	0.425926		0.027
C19	0.4276(4)	0.1848(3)	0.3309(3)		0.0302(9)
C20	0.5495(5)	0.2883(4)	0.3626(3)		0.0410(11)
H20	0.611558	0.312547	0.423434		0.049
C21	0.5828(6)	0.3568(4)	0.3081(4)		0.0617(16)
H21	0.667014	0.427003	0.330792		0.074
C22	0.4928(8)	0.3223(5)	0.2209(4)		0.072(2)
H22	0.515274	0.369153	0.183023		0.086
C23	0.3707(7)	0.2212(5)	0.1872(3)		0.0600(16)
H23	0.309367	0.198051	0.126350		0.072
C24	0.3369(5)	0.1519(4)	0.2437(3)		0.0399(10)
C25	0.1589(4)	−0.1061(3)	0.6400(3)		0.0311(8)
H25A	0.086230	−0.081243	0.631794		0.037
H25B	0.119555	−0.193098	0.599342		0.037
C26	0.1982(3)	−0.0825(3)	0.7481(3)		0.0254(8)
C27	0.1341(4)	−0.0337(3)	0.8172(3)		0.0301(8)
H27	0.064717	−0.015822	0.794969		0.036
C28	0.1686(4)	−0.0108(3)	0.9163(3)		0.0350(9)
H28	0.123565	0.023092	0.961954		0.042
C29	0.2692(4)	−0.0367(3)	0.9510(3)		0.0351(9)
H29	0.293583	−0.020190	1.019960		0.042
C30	0.3325(4)	−0.0864(3)	0.8839(3)		0.0338(9)
H30	0.400586	−0.105242	0.906673		0.041
C31	0.2985(4)	−0.1096(3)	0.7836(3)		0.0306(8)
H31	0.343336	−0.144121	0.738188		0.037
C32	0.5021(4)	0.2786(3)	0.9582(3)		0.0266(8)
H32A	0.507245	0.356818	0.998424		0.040
H32B	0.510763	0.239937	1.002314		0.040
H32C	0.413959	0.229035	0.908888		0.040
C33	0.7895(4)	0.3838(4)	0.9981(3)		0.0376(10)
H33A	0.872202	0.397329	0.972342		0.056
H33B	0.785651	0.340044	1.040051		0.056
H33C	0.791296	0.460640	1.038261		0.056
C34	0.6427(4)	0.1530(3)	0.8523(3)		0.0250(7)
H34A	0.563700	0.093734	0.796263		0.038
H34B	0.638835	0.128461	0.908106		0.038
H34C	0.727148	0.159433	0.830565		0.038
B1	0.9513(4)	0.5902(4)	0.7991(3)		0.0245(8)
H1A	1.054(4)	0.652(3)	0.806(3)		0.032(10)

Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

Table 1 Anisotropic displacement parameters (Å2) for compound 4.50

. The anisotropic displacement factor exponent takes the form:
−2π2[h2(a*)2U11 + k2(b*)2U22 + … + 2hka*b*U12]

Atom	U11	U22	U33	U23	U13	U12
W1	0.01451(7)	0.01611(7)	0.01836(7)	0.00936(5)	0.00433(5)	0.00582(5)
S1	0.0250(4)	0.0186(4)	0.0269(5)	0.0090(4)	0.0044(4)	0.0057(4)
P1	0.0209(4)	0.0195(4)	0.0209(4)	0.0107(4)	0.0029(3)	0.0085(4)
O1	0.0222(12)	0.0272(13)	0.0276(13)	0.0119(11)	0.0119(10)	0.0137(11)
O2	0.0251(13)	0.0299(14)	0.0231(13)	0.0052(11)	−0.0003(11)	0.0082(11)
O3	0.060(2)	0.065(2)	0.0234(16)	0.0178(16)	0.0099(15)	0.0400(19)
N1	0.0167(13)	0.0189(14)	0.0211(15)	0.0093(12)	0.0030(11)	0.0046(11)
N2	0.0168(14)	0.0215(16)	0.0247(16)	0.0108(13)	0.0058(12)	0.0023(12)
N3	0.0149(13)	0.0179(14)	0.0218(15)	0.0097(12)	0.0033(11)	0.0039(11)
N4	0.0167(13)	0.0184(14)	0.0241(15)	0.0088(12)	0.0024(12)	0.0037(11)
N5	0.0161(13)	0.0235(15)	0.0210(15)	0.0089(12)	0.0057(11)	0.0069(12)
N6	0.0139(13)	0.0258(16)	0.0240(15)	0.0087(13)	0.0047(12)	0.0070(12)
N7	0.0194(13)	0.0177(14)	0.0189(14)	0.0107(12)	0.0023(11)	0.0051(11)
N8	0.0208(14)	0.0205(14)	0.0162(14)	0.0076(12)	0.0044(11)	0.0088(12)
C1	0.0246(17)	0.0249(19)	0.0266(19)	0.0142(16)	0.0032(15)	0.0100(15)
C2	0.034(2)	0.027(2)	0.036(2)	0.0214(18)	0.0081(17)	0.0077(17)
C3	0.0277(19)	0.0252(19)	0.032(2)	0.0179(17)	0.0088(16)	0.0037(15)
C4	0.0261(17)	0.0247(18)	0.0248(18)	0.0125(15)	0.0089(15)	0.0146(15)
C5	0.035(2)	0.0259(19)	0.0224(19)	0.0061(16)	0.0052(16)	0.0152(17)
C6	0.0239(18)	0.0185(18)	0.028(2)	0.0078(15)	−0.0003(15)	0.0028(14)
C7	0.0286(19)	0.0270(19)	0.028(2)	0.0105(16)	0.0103(16)	0.0165(16)
C8	0.0295(19)	0.038(2)	0.032(2)	0.0116(18)	0.0121(17)	0.0228(18)
C9	0.0188(17)	0.039(2)	0.031(2)	0.0120(18)	0.0082(15)	0.0111(16)
C10	0.0144(15)	0.0191(16)	0.0182(16)	0.0083(14)	0.0047(13)	0.0053(13)
C11	0.0172(15)	0.0127(15)	0.0199(17)	0.0044(13)	0.0028(13)	0.0065(13)
C12	0.0202(16)	0.0194(17)	0.0172(16)	0.0087(14)	0.0025(13)	0.0051(14)
C13	0.0193(16)	0.0209(17)	0.0217(17)	0.0116(14)	0.0062(14)	0.0053(14)
C14	0.0156(15)	0.0215(17)	0.0215(17)	0.0098(14)	0.0036(13)	0.0079(13)
C15	0.0174(15)	0.0167(16)	0.0190(16)	0.0098(14)	0.0053(13)	0.0055(13)
C16	0.0189(16)	0.0275(19)	0.0245(18)	0.0106(16)	0.0051(14)	0.0095(15)
C17	0.0212(17)	0.0224(18)	0.0237(18)	0.0118(15)	0.0031(14)	0.0088(14)
C18	0.0259(17)	0.0226(18)	0.0208(17)	0.0073(15)	0.0073(14)	0.0126(15)
C19	0.051(2)	0.027(2)	0.0235(19)	0.0125(16)	0.0204(18)	0.0245(19)
C20	0.058(3)	0.032(2)	0.041(2)	0.018(2)	0.035(2)	0.021(2)
C21	0.102(4)	0.039(3)	0.060(3)	0.028(3)	0.063(3)	0.033(3)

C22	0.152(6)	0.046(3)	0.051(3)	0.032(3)	0.068(4)	0.059(4)
C23	0.130(5)	0.059(3)	0.029(2)	0.026(2)	0.036(3)	0.068(4)
C24	0.069(3)	0.038(2)	0.028(2)	0.0147(19)	0.021(2)	0.036(2)
C25	0.0209(17)	0.0218(19)	0.039(2)	0.0129(17)	0.0015(16)	−0.0011(15)
C26	0.0190(16)	0.0194(18)	0.034(2)	0.0160(16)	0.0045(15)	0.0009(14)
C27	0.0230(18)	0.0241(19)	0.042(2)	0.0171(18)	0.0071(17)	0.0067(15)
C28	0.034(2)	0.030(2)	0.043(2)	0.0192(19)	0.0143(19)	0.0119(18)
C29	0.035(2)	0.032(2)	0.038(2)	0.0249(19)	0.0065(18)	0.0067(18)
C30	0.0268(19)	0.033(2)	0.046(2)	0.027(2)	0.0036(18)	0.0092(17)
C31	0.0240(18)	0.026(2)	0.046(2)	0.0199(18)	0.0105(17)	0.0102(16)
C32	0.035(2)	0.0251(19)	0.0278(19)	0.0168(16)	0.0140(16)	0.0146(16)
C33	0.041(2)	0.028(2)	0.036(2)	0.0142(18)	−0.0109(18)	0.0107(18)
C34	0.0331(19)	0.0261(19)	0.0244(18)	0.0158(16)	0.0068(15)	0.0167(16)
B1	0.0182(19)	0.024(2)	0.027(2)	0.0111(18)	0.0068(16)	0.0039(16)

Table 3v Bond lengths and angles for compound 4.50Atom–Atom	Length [Å]
W1–N7	1.764(3)
W1–C10	2.196(3)
W1–N3	2.215(3)
W1–N1	2.228(3)
W1–C11	2.230(3)
W1–N5	2.268(3)
W1–P1	2.4992(9)
S1–C25	1.833(4)
S1–C12	1.846(3)
P1–C32	1.814(3)
P1–C33	1.818(4)
P1–C34	1.825(3)
O1–N7	1.235(3)
O2–C17	1.244(4)
O3–C24	1.363(6)
O3–H3	0.78(4)
N1–C1	1.339(4)
N1–N2	1.365(4)
N2–C3	1.341(4)
N2–B1	1.522(5)
N3–C4	1.337(4)
N3–N4	1.364(4)
N4–C6	1.336(4)
N4–B1	1.540(5)
N5–C7	1.331(4)
N5–N6	1.374(4)
N6–C9	1.352(4)
N6–B1	1.536(5)
N8–C17	1.338(4)

N8–C18	1.463(4)
N8–C15	1.486(4)
C1–C2	1.391(5)
C1–H1	0.9500
C2–C3	1.364(5)
C2–H2	0.9500
C3–H3A	0.9500
C4–C5	1.389(5)
C4–H4	0.9500
C5–C6	1.370(5)
C5–H5	0.9500
C6–H6	0.9500
C7–C8	1.388(5)
C7–H7	0.9500
C8–C9	1.371(5)
C8–H8	0.9500
C9–H9	0.9500
C10–C11	1.437(4)
C10–C15	1.507(4)
C10–H10	0.95(3)
C11–C12	1.510(4)
C11–H11	0.96(3)
C12–C13	1.520(4)
C12–H12	1.0000
C13–C14	1.544(4)
C13–H13A	0.9900
C13–H13B	0.9900
C14–C16	1.525(5)
C14–C15	1.545(4)
C14–H14	1.0000
C15–H15	1.0000
C16–C17	1.495(5)
C16–H16A	0.9900
C16–H16B	0.9900
C18–C19	1.513(5)
C18–H18A	0.9900
C18–H18B	0.9900
C19–C24	1.379(6)
C19–C20	1.389(6)
C20–C21	1.380(6)
C20–H20	0.9500
C21–C22	1.370(8)
C21–H21	0.9500
C22–C23	1.373(8)
C22–H22	0.9500
C23–C24	1.413(6)
C23–H23	0.9500
C25–C26	1.497(5)
C25–H25A	0.9900
C25–H25B	0.9900
C26–C27	1.390(5)
C26–C31	1.405(5)
C27–C28	1.367(6)
C27–H27	0.9500
C28–C29	1.392(6)

C28–H28	0.9500
C29–C30	1.371(6)
C29–H29	0.9500
C30–C31	1.382(5)
C30–H30	0.9500
C31–H31	0.9500
C32–H32A	0.9800
C32–H32B	0.9800
C32–H32C	0.9800
C33–H33A	0.9800
C33–H33B	0.9800
C33–H33C	0.9800
C34–H34A	0.9800
C34–H34B	0.9800
C34–H34C	0.9800
B1–H1A	1.07(4)

Atom–Atom–Atom	Angle [°]
N7–W1–C10	97.73(12)
N7–W1–N3	87.36(11)
C10–W1–N3	160.18(11)
N7–W1–N1	100.30(11)
C10–W1–N1	82.28(11)
N3–W1–N1	77.96(10)
N7–W1–C11	98.64(12)
C10–W1–C11	37.87(12)
N3–W1–C11	160.15(11)
N1–W1–C11	119.03(11)
N7–W1–N5	171.70(11)
C10–W1–N5	90.51(11)
N3–W1–N5	84.54(10)
N1–W1–N5	79.77(10)
C11–W1–N5	88.45(11)
N7–W1–P1	91.91(9)
C10–W1–P1	115.66(9)
N3–W1–P1	83.12(7)
N1–W1–P1	156.88(7)
C11–W1–P1	77.80(9)
N5–W1–P1	85.35(7)
C25–S1–C12	99.47(16)
C32–P1–C33	101.58(19)
C32–P1–C34	103.01(16)
C33–P1–C34	99.15(18)
C32–P1–W1	114.86(12)
C33–P1–W1	115.20(13)
C34–P1–W1	120.26(11)
C24–O3–H3	121(3)
C1–N1–N2	106.2(3)
C1–N1–W1	133.2(2)
N2–N1–W1	120.6(2)
C3–N2–N1	109.5(3)
C3–N2–B1	128.4(3)
N1–N2–B1	122.0(3)
C4–N3–N4	106.5(3)
C4–N3–W1	129.1(2)

N4–N3–W1	124.1(2)
C6–N4–N3	109.4(3)
C6–N4–B1	131.2(3)
N3–N4–B1	118.0(3)
C7–N5–N6	106.6(3)
C7–N5–W1	134.1(2)
N6–N5–W1	119.0(2)
C9–N6–N5	108.7(3)
C9–N6–B1	129.4(3)
N5–N6–B1	121.7(3)
O1–N7–W1	174.1(2)
C17–N8–C18	121.4(3)
C17–N8–C15	113.6(3)
C18–N8–C15	123.9(3)
N1–C1–C2	110.2(3)
N1–C1–H1	124.9
C2–C1–H1	124.9
C3–C2–C1	105.1(3)
C3–C2–H2	127.4
C1–C2–H2	127.4
N2–C3–C2	108.9(3)
N2–C3–H3A	125.5
C2–C3–H3A	125.5
N3–C4–C5	110.2(3)
N3–C4–H4	124.9
C5–C4–H4	124.9
C6–C5–C4	105.0(3)
C6–C5–H5	127.5
C4–C5–H5	127.5
N4–C6–C5	108.9(3)
N4–C6–H6	125.5
C5–C6–H6	125.5
N5–C7–C8	110.8(3)
N5–C7–H7	124.6
C8–C7–H7	124.6
C9–C8–C7	104.9(3)
C9–C8–H8	127.6
C7–C8–H8	127.6
N6–C9–C8	109.0(3)
N6–C9–H9	125.5
C8–C9–H9	125.5
C11–C10–C15	118.5(3)
C11–C10–W1	72.36(18)
C15–C10–W1	124.5(2)
C11–C10–H10	118(2)
C15–C10–H10	112(2)
W1–C10–H10	107(2)
C10–C11–C12	119.3(3)
C10–C11–W1	69.76(18)
C12–C11–W1	122.4(2)
C10–C11–H11	115.3(19)
C12–C11–H11	114.2(19)
W1–C11–H11	108.6(19)
C11–C12–C13	114.5(3)
C11–C12–S1	108.0(2)

C13–C12–S1	113.0(2)
C11–C12–H12	107.0
C13–C12–H12	107.0
S1–C12–H12	107.0
C12–C13–C14	116.6(3)
C12–C13–H13A	108.1
C14–C13–H13A	108.1
C12–C13–H13B	108.1
C14–C13–H13B	108.1
H13A–C13–H13B	107.3
C16–C14–C13	113.0(3)
C16–C14–C15	103.2(3)
C13–C14–C15	115.3(3)
C16–C14–H14	108.4
C13–C14–H14	108.4
C15–C14–H14	108.4
N8–C15–C10	112.5(3)
N8–C15–C14	101.9(2)
C10–C15–C14	116.9(3)
N8–C15–H15	108.4
C10–C15–H15	108.4
C14–C15–H15	108.4
C17–C16–C14	105.5(3)
C17–C16–H16A	110.7
C14–C16–H16A	110.7
C17–C16–H16B	110.7
C14–C16–H16B	110.7
H16A–C16–H16B	108.8
O2–C17–N8	124.7(3)
O2–C17–C16	126.9(3)
N8–C17–C16	108.4(3)
N8–C18–C19	112.6(3)
N8–C18–H18A	109.1
C19–C18–H18A	109.1
N8–C18–H18B	109.1
C19–C18–H18B	109.1
H18A–C18–H18B	107.8
C24–C19–C20	118.7(4)
C24–C19–C18	121.2(4)
C20–C19–C18	120.1(4)
C21–C20–C19	121.7(5)
C21–C20–H20	119.1
C19–C20–H20	119.1
C22–C21–C20	119.1(5)
C22–C21–H21	120.4
C20–C21–H21	120.4
C21–C22–C23	121.1(5)
C21–C22–H22	119.4
C23–C22–H22	119.4
C22–C23–C24	119.4(5)
C22–C23–H23	120.3
C24–C23–H23	120.3
O3–C24–C19	123.4(4)
O3–C24–C23	116.7(4)
C19–C24–C23	120.0(5)

C26–C25–S1	115.1(2)
C26–C25–H25A	108.5
S1–C25–H25A	108.5
C26–C25–H25B	108.5
S1–C25–H25B	108.5
H25A–C25–H25B	107.5
C27–C26–C31	117.5(4)
C27–C26–C25	120.3(3)
C31–C26–C25	122.1(3)
C28–C27–C26	121.4(4)
C28–C27–H27	119.3
C26–C27–H27	119.3
C27–C28–C29	120.6(4)
C27–C28–H28	119.7
C29–C28–H28	119.7
C30–C29–C28	118.9(4)
C30–C29–H29	120.5
C28–C29–H29	120.5
C29–C30–C31	120.8(4)
C29–C30–H30	119.6
C31–C30–H30	119.6
C30–C31–C26	120.6(4)
C30–C31–H31	119.7
C26–C31–H31	119.7
P1–C32–H32A	109.5
P1–C32–H32B	109.5
H32A–C32–H32B	109.5
P1–C32–H32C	109.5
H32A–C32–H32C	109.5
H32B–C32–H32C	109.5
P1–C33–H33A	109.5
P1–C33–H33B	109.5
H33A–C33–H33B	109.5
P1–C33–H33C	109.5
H33A–C33–H33C	109.5
H33B–C33–H33C	109.5
P1–C34–H34A	109.5
P1–C34–H34B	109.5
H34A–C34–H34B	109.5
P1–C34–H34C	109.5
H34A–C34–H34C	109.5
H34B–C34–H34C	109.5
N2–B1–N6	108.9(3)
N2–B1–N4	106.6(3)
N6–B1–N4	109.5(3)
N2–B1–H1A	112(2)
N6–B1–H1A	109(2)
N4–B1–H1A	112(2)

Table 5 Torsion angles for compound 4.50

Atom–Atom–Atom–Atom	Torsion Angle [°]
C1–N1–N2–C3	−0.4(4)
W1–N1–N2–C3	−178.8(2)
C1–N1–N2–B1	177.0(3)
W1–N1–N2–B1	−1.4(4)

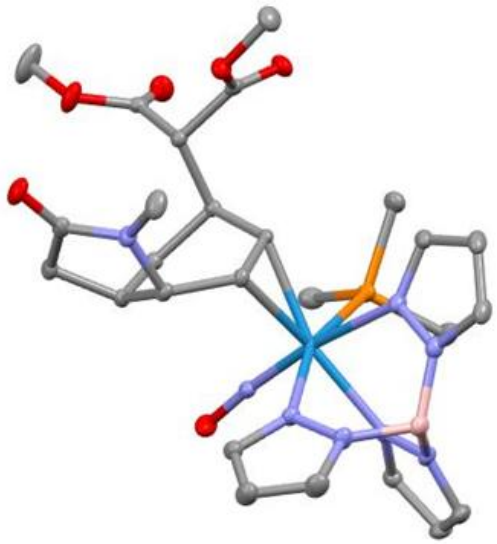
C4–N3–N4–C6	−1.1(4)
W1–N3–N4–C6	173.1(2)
C4–N3–N4–B1	−169.1(3)
W1–N3–N4–B1	5.1(4)
C7–N5–N6–C9	−0.6(4)
W1–N5–N6–C9	173.4(2)
C7–N5–N6–B1	174.3(3)
W1–N5–N6–B1	−11.6(4)
N2–N1–C1–C2	0.4(4)
W1–N1–C1–C2	178.5(2)
N1–C1–C2–C3	−0.2(4)
N1–N2–C3–C2	0.2(4)
B1–N2–C3–C2	−177.0(3)
C1–C2–C3–N2	0.0(4)
N4–N3–C4–C5	0.1(4)
W1–N3–C4–C5	−173.8(2)
N3–C4–C5–C6	1.0(4)
N3–N4–C6–C5	1.8(4)
B1–N4–C6–C5	167.7(3)
C4–C5–C6–N4	−1.7(4)
N6–N5–C7–C8	0.8(4)
W1–N5–C7–C8	−172.0(2)
N5–C7–C8–C9	−0.6(4)
N5–N6–C9–C8	0.3(4)
B1–N6–C9–C8	−174.2(3)
C7–C8–C9–N6	0.2(4)
C15–C10–C11–C12	−3.6(4)
W1–C10–C11–C12	116.6(3)
C15–C10–C11–W1	−120.2(3)
C10–C11–C12–C13	−33.9(4)
W1–C11–C12–C13	49.6(4)
C10–C11–C12–S1	93.0(3)
W1–C11–C12–S1	176.52(16)
C25–S1–C12–C11	166.0(2)
C25–S1–C12–C13	−66.2(3)
C11–C12–C13–C14	40.6(4)
S1–C12–C13–C14	−83.6(3)
C12–C13–C14–C16	107.1(3)
C12–C13–C14–C15	−11.2(4)
C17–N8–C15–C10	146.1(3)
C18–N8–C15–C10	−45.9(4)
C17–N8–C15–C14	20.1(3)
C18–N8–C15–C14	−171.9(3)
C11–C10–C15–N8	−83.2(3)
W1–C10–C15–N8	−170.6(2)
C11–C10–C15–C14	34.1(4)
W1–C10–C15–C14	−53.3(4)
C16–C14–C15–N8	−26.3(3)
C13–C14–C15–N8	97.3(3)
C16–C14–C15–C10	−149.3(3)
C13–C14–C15–C10	−25.7(4)
C13–C14–C16–C17	−100.4(3)
C15–C14–C16–C17	24.7(3)
C18–N8–C17–O2	4.6(5)
C15–N8–C17–O2	172.9(3)

C18–N8–C17–C16	−172.9(3)
C15–N8–C17–C16	−4.6(4)
C14–C16–C17–O2	169.2(3)
C14–C16–C17–N8	−13.4(4)
C17–N8–C18–C19	88.6(4)
C15–N8–C18–C19	−78.5(4)
N8–C18–C19–C24	−89.3(4)
N8–C18–C19–C20	90.4(4)
C24–C19–C20–C21	−1.4(6)
C18–C19–C20–C21	178.8(3)
C19–C20–C21–C22	0.5(6)
C20–C21–C22–C23	0.1(7)
C21–C22–C23–C24	0.3(7)
C20–C19–C24–O3	−179.0(3)
C18–C19–C24–O3	0.7(6)
C20–C19–C24–C23	1.8(6)
C18–C19–C24–C23	−178.5(3)
C22–C23–C24–O3	179.5(4)
C22–C23–C24–C19	−1.3(6)
C12–S1–C25–C26	−49.7(3)
S1–C25–C26–C27	122.0(3)
S1–C25–C26–C31	−58.9(4)
C31–C26–C27–C28	1.1(5)
C25–C26–C27–C28	−179.7(3)
C26–C27–C28–C29	−0.4(6)
C27–C28–C29–C30	−0.5(6)
C28–C29–C30–C31	0.7(6)
C29–C30–C31–C26	0.0(6)
C27–C26–C31–C30	−0.9(5)
C25–C26–C31–C30	179.9(3)
C3–N2–B1–N6	−124.3(4)
N1–N2–B1–N6	58.8(4)
C3–N2–B1–N4	117.7(4)
N1–N2–B1–N4	−59.2(4)
C9–N6–B1–N2	123.6(4)
N5–N6–B1–N2	−50.2(4)
C9–N6–B1–N4	−120.3(4)
N5–N6–B1–N4	65.9(4)
C6–N4–B1–N2	−108.6(4)
N3–N4–B1–N2	56.3(4)
C6–N4–B1–N6	133.8(4)
N3–N4–B1–N6	−61.3(4)

Table 1 Hydrogen bonds for compound 4.50

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O3–H3···O2	0.78(4)	2.01(4)	2.743(4)	157(4)

Crystal Structure Report for compound 4.38



A colorless, block-like specimen of $C_{26}H_{38}BN_8O_6PW$, approximate dimensions 0.056 mm x 0.065 mm x 0.097 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 1.73 hours. The frames were integrated with the Bruker SAINT software package[108] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 63243 reflections to a maximum θ angle of 29.59° (0.72 Å resolution), of which 8614 were independent (average redundancy 7.342, completeness = 99.6%, R_{int} = 4.98%, R_{sig} = 3.32%) and 6400 (74.30%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.0031(3) Å, b = 15.3108(5) Å, c = 17.4537(5) Å, β = 106.1490(10)°, volume = 3081.02(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 9887 reflections above 20 σ(I) with 4.548° < 2θ < 59.03°. Data were corrected

[108] Bruker (2019). *Saint; APEX4*. Bruker AXS Inc., Madison, Wisconsin, USA.

for absorption effects using the Multi-Scan method (SADABS).[109] The ratio of minimum to maximum apparent transmission was 0.940. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7060 and 0.8130.

The structure was solved and refined using the Bruker SHELXTL Software Package[110] within APEX4 [1] and OLEX2,[111] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{26}H_{38}BN_8O_6PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 406 variables converged at R1 = 2.28%, for the observed data and wR2 = 5.12% for all data. The goodness-of-fit was 1.008. The largest peak in the final difference electron density synthesis was 1.393 $e^-/Å^3$ and the largest hole was -0.482 $e^-/Å^3$ with an RMS deviation of 0.108 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.691 g/cm^3 and F(000), 1568 e^-.

Table 1. Sample and crystal data for compound 4.38

Chemical formula	$C_{26}H_{38}BN_8O_6PW$	
Formula weight	784.27 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.056 x 0.065 x 0.097 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 12.0031(3) Å	α = 90°
	b = 15.3108(5) Å	β = 106.1490(10)°
	c = 17.4537(5) Å	γ = 90°

[109] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[110] Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

[111] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Volume	3081.02(16) $Å^3$
Z	4
Density (calculated)	1.691 g/cm^3
Absorption coefficient	3.855 mm^{-1}
F(000)	1568

Table 2. Data collection and structure refinement for compound 4.38.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.21 to 29.59°
Index ranges	-16<=h<=16, -21<=k<=21, -24<=l<=22
Reflections collected	63243
Independent reflections	8614 [R(int) = 0.0498]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8130 and 0.7060
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$

Data / restraints / parameters	8614 / 0 / 406	
Goodness-of-fit on F^2	1.008	
Δ/σ_{max}	0.001	
Final R indices	6400 data; I>2σ(I)	R1 = 0.0228, wR2 = 0.0449
	all data	R1 = 0.0397, wR2 = 0.0512
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0155P)^2+2.8816P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.393 and -0.482 eÅ^{-3}	
R.M.S. deviation from mean	0.108 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.38

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.31685(2)	0.24844(2)	0.30758(2)	0.01065(3)
P1	0.32131(5)	0.10309(4)	0.37316(4)	0.01515(13)
O1	0.39740(15)	0.17572(13)	0.17300(11)	0.0249(4)
O2	0.82540(15)	0.46243(12)	0.37493(12)	0.0226(4)
O3	0.63624(16)	0.20781(13)	0.59291(11)	0.0212(4)
O4	0.68890(15)	0.34632(12)	0.57802(10)	0.0186(4)
O5	0.79904(16)	0.11103(12)	0.51169(11)	0.0233(4)
O6	0.89215(15)	0.22375(13)	0.47616(13)	0.0256(5)
N1	0.22684(17)	0.30717(14)	0.39298(12)	0.0159(4)
N2	0.12380(17)	0.35028(14)	0.36420(13)	0.0171(4)
N3	0.13707(17)	0.21375(14)	0.23981(12)	0.0144(4)
N4	0.04534(17)	0.26763(13)	0.23712(13)	0.0158(4)

	x/a	y/b	z/c	U(eq)
N5	0.25173(17)	0.36537(14)	0.23414(12)	0.0154(4)
N6	0.15034(18)	0.40527(14)	0.23474(13)	0.0177(4)
N7	0.36995(17)	0.20423(14)	0.23116(12)	0.0151(4)
N8	0.63864(17)	0.42272(13)	0.36715(13)	0.0152(4)
C1	0.2519(2)	0.31274(17)	0.47287(15)	0.0173(5)
C2	0.1663(2)	0.35884(18)	0.49514(16)	0.0220(6)
C3	0.0872(2)	0.38155(17)	0.42502(16)	0.0202(6)
C4	0.0959(2)	0.14794(17)	0.18933(15)	0.0166(5)
C5	0.9773(2)	0.15862(18)	0.15410(16)	0.0219(6)
C6	0.9495(2)	0.23539(18)	0.18542(15)	0.0206(6)
C7	0.2895(2)	0.40518(17)	0.17812(15)	0.0187(5)
C8	0.2146(2)	0.47204(19)	0.14266(17)	0.0246(6)
C9	0.1276(2)	0.46949(18)	0.17961(17)	0.0235(6)
C10	0.4600(2)	0.33740(16)	0.36072(14)	0.0134(5)
C11	0.48239(19)	0.25853(16)	0.40706(14)	0.0121(5)
C12	0.5935(2)	0.20865(16)	0.41192(14)	0.0126(5)
C13	0.6221(2)	0.20688(16)	0.33196(14)	0.0134(5)
C14	0.6130(2)	0.29498(16)	0.28690(14)	0.0135(5)
C15	0.5451(2)	0.36757(16)	0.31706(15)	0.0139(5)
C16	0.6165(2)	0.49088(17)	0.41872(18)	0.0238(6)
C17	0.7404(2)	0.41482(16)	0.34954(15)	0.0157(5)
C18	0.7313(2)	0.33873(17)	0.29326(15)	0.0169(5)
C19	0.69871(19)	0.24847(16)	0.47734(14)	0.0127(4)
C20	0.6701(2)	0.26263(16)	0.55554(15)	0.0159(5)
C21	0.6662(2)	0.36946(19)	0.65273(16)	0.0236(6)
C22	0.8006(2)	0.18581(17)	0.49132(14)	0.0156(5)
C23	0.9948(2)	0.1691(2)	0.4901(2)	0.0398(9)
C24	0.3724(2)	0.09344(18)	0.48150(15)	0.0207(6)
C25	0.4074(2)	0.02243(17)	0.33854(16)	0.0222(6)
C26	0.1825(2)	0.04713(19)	0.35562(18)	0.0281(7)
B1	0.0668(2)	0.3598(2)	0.27494(18)	0.0179(6)

Table 4. Bond lengths (Å) for compound 4.38

W1-N7	1.765(2)	W1-C10	2.187(2)
W1-N5	2.214(2)	W1-N3	2.2177(19)
W1-C11	2.251(2)	W1-N1	2.257(2)
W1-P1	2.4963(7)	P1-C25	1.818(3)
P1-C26	1.822(3)	P1-C24	1.825(3)
O1-N7	1.231(3)	O2-C17	1.231(3)
O3-C20	1.201(3)	O4-C20	1.341(3)
O4-C21	1.449(3)	O5-C22	1.201(3)
O6-C22	1.333(3)	O6-C23	1.452(3)
N1-C1	1.345(3)	N1-N2	1.368(3)
N2-C3	1.345(3)	N2-B1	1.524(4)
N3-C4	1.339(3)	N3-N4	1.366(3)
N4-C6	1.343(3)	N4-B1	1.548(4)
N5-C7	1.334(3)	N5-N6	1.364(3)
N6-C9	1.350(3)	N6-B1	1.541(4)
N8-C17	1.346(3)	N8-C16	1.450(3)
N8-C15	1.481(3)	C1-C2	1.388(4)
C1-H1	0.950000	C2-C3	1.369(4)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.395(3)	C4-H4	0.950000
C5-C6	1.376(4)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.389(4)
C7-H7	0.950000	C8-C9	1.372(4)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.437(3)	C10-C15	1.506(3)
C10-H10	0.95(3)	C11-C12	1.518(3)
C11-H11	0.92(3)	C12-C13	1.528(3)
C12-C19	1.571(3)	C12-H12	1.000000
C13-C14	1.550(3)	C13-H13A	0.990000
C13-H13B	0.990000	C14-C18	1.546(3)
C14-C15	1.554(3)	C14-H14	1.000000
C15-H15	1.000000	C16-H16A	0.980000

C16-H16B	0.980000	C16-H16C	0.980000
C17-C18	1.508(4)	C18-H18A	0.990000
C18-H18B	0.990000	C19-C20	1.513(3)
C19-C22	1.520(3)	C19-H19	1.000000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
C24-H24A	0.980000	C24-H24B	0.980000
C24-H24C	0.980000	C25-H25A	0.980000
C25-H25B	0.980000	C25-H25C	0.980000
C26-H26A	0.980000	C26-H26B	0.980000
C26-H26C	0.980000	B1-H1A	1.06(3)

Table 5. Bond angles (°) for compound 4.38

N7-W1-C10	98.80(9)	N7-W1-N5	90.92(9)
C10-W1-N5	81.44(8)	N7-W1-N3	90.42(8)
C10-W1-N3	155.33(9)	N5-W1-N3	75.55(8)
N7-W1-C11	100.51(9)	C10-W1-C11	37.74(9)
N5-W1-C11	119.00(8)	N3-W1-C11	161.27(8)
N7-W1-N1	172.55(8)	C10-W1-N1	86.33(8)
N5-W1-N1	84.46(8)	N3-W1-N1	82.77(7)
C11-W1-N1	86.86(8)	N7-W1-P1	92.20(7)
C10-W1-P1	116.53(6)	N5-W1-P1	160.99(5)
N3-W1-P1	85.68(6)	C11-W1-P1	78.80(6)
N1-W1-P1	90.32(6)	C25-P1-C26	101.68(14)
C25-P1-C24	103.36(13)	C26-P1-C24	99.45(13)
C25-P1-W1	113.26(9)	C26-P1-W1	116.12(9)
C24-P1-W1	120.37(9)	C20-O4-C21	116.0(2)
C22-O6-C23	115.0(2)	C1-N1-N2	105.6(2)
C1-N1-W1	134.44(17)	N2-N1-W1	119.98(15)
C3-N2-N1	110.0(2)	C3-N2-B1	128.4(2)
N1-N2-B1	121.6(2)	C4-N3-N4	106.59(19)
C4-N3-W1	131.10(17)	N4-N3-W1	121.94(15)

C6-N4-N3	109.4(2)	C6-N4-B1	129.1(2)
N3-N4-B1	119.90(19)	C7-N5-N6	106.7(2)
C7-N5-W1	131.04(17)	N6-N5-W1	121.98(16)
C9-N6-N5	109.0(2)	C9-N6-B1	128.7(2)
N5-N6-B1	119.7(2)	O1-N7-W1	174.06(18)
C17-N8-C16	122.8(2)	C17-N8-C15	113.7(2)
C16-N8-C15	122.5(2)	N1-C1-C2	110.7(2)
N1-C1-H1	124.700000	C2-C1-H1	124.700000
C3-C2-C1	105.2(2)	C3-C2-H2	127.400000
C1-C2-H2	127.400000	N2-C3-C2	108.5(2)
N2-C3-H3	125.700000	C2-C3-H3	125.700000
N3-C4-C5	110.3(2)	N3-C4-H4	124.900000
C5-C4-H4	124.900000	C6-C5-C4	104.8(2)
C6-C5-H5	127.600000	C4-C5-H5	127.600000
N4-C6-C5	108.9(2)	N4-C6-H6	125.600000
C5-C6-H6	125.600000	N5-C7-C8	110.7(2)
N5-C7-H7	124.700000	C8-C7-H7	124.700000
C9-C8-C7	104.6(2)	C9-C8-H8	127.700000
C7-C8-H8	127.700000	N6-C9-C8	109.0(2)
N6-C9-H9	125.500000	C8-C9-H9	125.500000
C11-C10-C15	119.7(2)	C11-C10-W1	73.55(13)
C15-C10-W1	122.66(17)	C11-C10-H10	117.9(15)
C15-C10-H10	111.2(15)	W1-C10-H10	106.8(15)
C10-C11-C12	118.5(2)	C10-C11-W1	68.70(13)
C12-C11-W1	125.56(16)	C10-C11-H11	115.6(17)
C12-C11-H11	111.7(17)	W1-C11-H11	110.5(17)
C11-C12-C13	112.05(19)	C11-C12-C19	111.19(19)
C13-C12-C19	109.32(19)	C11-C12-H12	108.000000
C13-C12-H12	108.000000	C19-C12-H12	108.000000
C12-C13-C14	116.5(2)	C12-C13-H13A	108.200000
C14-C13-H13A	108.200000	C12-C13-H13B	108.200000

C14-C13-H13B	108.200000	H13A-C13-H13B	107.300000
C18-C14-C13	113.97(19)	C18-C14-C15	102.92(19)
C13-C14-C15	114.9(2)	C18-C14-H14	108.200000
C13-C14-H14	108.200000	C15-C14-H14	108.200000
N8-C15-C10	112.7(2)	N8-C15-C14	103.00(18)
C10-C15-C14	116.4(2)	N8-C15-H15	108.100000
C10-C15-H15	108.100000	C14-C15-H15	108.100000
N8-C16-H16A	109.500000	N8-C16-H16B	109.500000
H16A-C16-H16B	109.500000	N8-C16-H16C	109.500000
H16A-C16-H16C	109.500000	H16B-C16-H16C	109.500000
O2-C17-N8	125.3(2)	O2-C17-C18	126.5(2)
N8-C17-C18	108.2(2)	C17-C18-C14	106.3(2)
C17-C18-H18A	110.500000	C14-C18-H18A	110.500000
C17-C18-H18B	110.500000	C14-C18-H18B	110.500000
H18A-C18-H18B	108.700000	C20-C19-C22	108.67(19)
C20-C19-C12	111.88(19)	C22-C19-C12	108.7(2)
C20-C19-H19	109.200000	C22-C19-H19	109.200000
C12-C19-H19	109.200000	O3-C20-O4	124.3(2)
O3-C20-C19	125.9(2)	O4-C20-C19	109.8(2)
O4-C21-H21A	109.500000	O4-C21-H21B	109.500000
H21A-C21-H21B	109.500000	O4-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
O5-C22-O6	123.8(2)	O5-C22-C19	124.8(2)
O6-C22-C19	111.3(2)	O6-C23-H23A	109.500000

O6-C23-H23B	109.500000	H23A-C23-H23B	109.500000
O6-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	P1-C24-H24A	109.500000
P1-C24-H24B	109.500000	H24A-C24-H24B	109.500000
P1-C24-H24C	109.500000	H24A-C24-H24C	109.500000
H24B-C24-H24C	109.500000	P1-C25-H25A	109.500000
P1-C25-H25B	109.500000	H25A-C25-H25B	109.500000
P1-C25-H25C	109.500000	H25A-C25-H25C	109.500000
H25B-C25-H25C	109.500000	P1-C26-H26A	109.500000
P1-C26-H26B	109.500000	H26A-C26-H26B	109.500000
P1-C26-H26C	109.500000	H26A-C26-H26C	109.500000
H26B-C26-H26C	109.500000	N2-B1-N6	110.2(2)
N2-B1-N4	108.9(2)	N6-B1-N4	105.7(2)
N2-B1-H1A	111.9(14)	N6-B1-H1A	111.3(14)
N4-B1-H1A	108.7(14)		

Table 6. Torsion angles (°) for compound 4.38

C1-N1-N2-C3	0.2(3)	W1-N1-N2-C3	-178.57(16)
C1-N1-N2-B1	179.0(2)	W1-N1-N2-B1	0.2(3)
C4-N3-N4-C6	-0.3(3)	W1-N3-N4-C6	173.40(17)

C4-N3-N4-B1	-167.4(2)	W1-N3-N4-B1	6.3(3)
C7-N5-N6-C9	-0.5(3)	W1-N5-N6-C9	-174.70(17)
C7-N5-N6-B1	162.8(2)	W1-N5-N6-B1	-11.4(3)
N2-N1-C1-C2	-0.1(3)	W1-N1-C1-C2	178.41(18)
N1-C1-C2-C3	0.0(3)	N1-N2-C3-C2	-0.2(3)
B1-N2-C3-C2	-178.9(2)	C1-C2-C3-N2	0.2(3)
N4-N3-C4-C5	-0.3(3)	W1-N3-C4-C5	-173.21(18)
N3-C4-C5-C6	0.8(3)	N3-N4-C6-C5	0.8(3)
B1-N4-C6-C5	166.4(3)	C4-C5-C6-N4	-1.0(3)
N6-N5-C7-C8	1.0(3)	W1-N5-C7-C8	174.45(18)
N5-C7-C8-C9	-1.0(3)	N5-N6-C9-C8	-0.2(3)
B1-N6-C9-C8	-161.6(3)	C7-C8-C9-N6	0.7(3)
C15-C10-C11-C12	1.3(3)	W1-C10-C11-C12	119.9(2)
C15-C10-C11-W1	-118.7(2)	C10-C11-C12-C13	-39.9(3)
W1-C11-C12-C13	43.2(3)	C10-C11-C12-C19	82.8(3)
W1-C11-C12-C19	165.90(16)	C11-C12-C13-C14	46.5(3)
C19-C12-C13-C14	-77.2(2)	C12-C13-C14-C18	102.8(2)
C12-C13-C14-C15	-15.6(3)	C17-N8-C15-C10	148.4(2)
C16-N8-C15-C10	-43.2(3)	C17-N8-C15-C14	22.1(3)
C16-N8-C15-C14	-169.5(2)	C11-C10-C15-N8	-87.4(3)
W1-C10-C15-N8	-176.18(15)	C11-C10-C15-C14	31.3(3)

W1-C10-C15-C14	-57.5(3)	C18-C14-C15-N8	-23.6(2)
C13-C14-C15-N8	100.9(2)	C18-C14-C15-C10	-147.4(2)
C13-C14-C15-C10	-22.9(3)	C16-N8-C17-O2	0.8(4)
C15-N8-C17-O2	169.3(2)	C16-N8-C17-C18	-178.6(2)
C15-N8-C17-C18	-10.2(3)	O2-C17-C18-C14	174.2(2)
N8-C17-C18-C14	-6.3(3)	C13-C14-C18-C17	-106.3(2)
C15-C14-C18-C17	18.8(2)	C11-C12-C19-C20	48.6(3)
C13-C12-C19-C20	172.8(2)	C11-C12-C19-C22	168.5(2)
C13-C12-C19-C22	-67.2(2)	C21-O4-C20-O3	0.2(3)
C21-O4-C20-C19	-179.40(19)	C22-C19-C20-O3	-63.9(3)
C12-C19-C20-O3	56.1(3)	C22-C19-C20-O4	115.6(2)
C12-C19-C20-O4	-124.4(2)	C23-O6-C22-O5	-3.1(4)
C23-O6-C22-C19	178.4(2)	C20-C19-C22-O5	64.1(3)
C12-C19-C22-O5	-57.9(3)	C20-C19-C22-O6	-117.5(2)
C12-C19-C22-O6	120.6(2)	C3-N2-B1-N6	121.2(3)
N1-N2-B1-N6	-57.3(3)	C3-N2-B1-N4	-123.4(3)
N1-N2-B1-N4	58.1(3)	C9-N6-B1-N2	-136.0(3)
N5-N6-B1-N2	64.3(3)	C9-N6-B1-N4	106.6(3)
N5-N6-B1-N4	-53.1(3)	C6-N4-B1-N2	133.4(3)
N3-N4-B1-N2	-62.3(3)	C6-N4-B1-N6	-108.3(3)
N3-N4-B1-N6	56.0(3)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.38

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.00902(4)	0.01249(5)	0.01036(5)	0.00041(4)	0.00259(3)	-0.00013(4)
P1	0.0143(3)	0.0144(3)	0.0155(3)	0.0021(3)	0.0021(2)	-0.0025(2)
O1	0.0188(9)	0.0377(12)	0.0190(10)	-0.0116(9)	0.0067(8)	-0.0022(8)
O2	0.0132(9)	0.0197(10)	0.0346(11)	0.0006(8)	0.0059(8)	-0.0032(7)
O3	0.0247(10)	0.0244(10)	0.0160(9)	0.0032(8)	0.0079(8)	-0.0035(8)
O4	0.0186(9)	0.0208(10)	0.0179(9)	-0.0041(8)	0.0075(7)	0.0002(7)
O5	0.0244(10)	0.0183(10)	0.0282(11)	0.0065(8)	0.0090(8)	0.0052(8)
O6	0.0126(9)	0.0216(10)	0.0437(13)	0.0005(9)	0.0094(8)	0.0004(7)
N1	0.0129(10)	0.0180(11)	0.0168(10)	-0.0028(9)	0.0042(8)	-0.0006(8)
N2	0.0136(10)	0.0182(11)	0.0205(11)	-0.0022(9)	0.0063(8)	0.0008(8)
N3	0.0113(10)	0.0183(11)	0.0129(10)	0.0001(8)	0.0023(8)	0.0002(8)
N4	0.0099(9)	0.0197(12)	0.0171(10)	-0.0004(8)	0.0027(8)	0.0004(8)
N5	0.0121(10)	0.0168(11)	0.0165(11)	0.0013(8)	0.0029(8)	0.0021(8)
N6	0.0140(10)	0.0170(11)	0.0220(11)	0.0034(9)	0.0048(9)	0.0035(8)
N7	0.0116(10)	0.0190(11)	0.0142(10)	-0.0001(9)	0.0025(8)	-0.0012(8)
N8	0.0143(10)	0.0121(10)	0.0196(11)	-0.0011(8)	0.0052(8)	-0.0015(8)
C1	0.0143(12)	0.0226(14)	0.0149(12)	-0.0025(10)	0.0040(10)	-0.0053(10)
C2	0.0194(13)	0.0292(15)	0.0198(13)	-0.0100(11)	0.0094(11)	-0.0073(11)
C3	0.0165(12)	0.0208(14)	0.0259(14)	-0.0081(11)	0.0104(11)	-0.0017(10)
C4	0.0182(12)	0.0171(13)	0.0150(12)	-0.0005(10)	0.0052(10)	-0.0018(10)
C5	0.0168(13)	0.0287(15)	0.0172(13)	-0.0047(11)	-0.0003(10)	-0.0037(11)
C6	0.0114(11)	0.0301(16)	0.0187(13)	-0.0002(11)	0.0016(9)	-0.0007(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	0.0148(12)	0.0234(14)	0.0170(13)	0.0041(11)	0.0029(10)	-0.0018(10)
C8	0.0196(13)	0.0271(15)	0.0251(14)	0.0094(12)	0.0032(11)	-0.0009(11)
C9	0.0200(13)	0.0193(14)	0.0288(15)	0.0075(11)	0.0028(11)	0.0032(11)
C10	0.0114(11)	0.0131(12)	0.0160(12)	0.0006(10)	0.0045(9)	0.0000(9)
C11	0.0101(10)	0.0158(12)	0.0101(10)	-0.0001(10)	0.0020(8)	-0.0024(9)
C12	0.0117(11)	0.0118(12)	0.0135(11)	0.0011(9)	0.0019(9)	-0.0021(9)
C13	0.0122(11)	0.0152(12)	0.0129(11)	-0.0007(10)	0.0040(9)	0.0008(9)
C14	0.0118(11)	0.0160(13)	0.0134(11)	0.0014(10)	0.0045(9)	0.0003(9)
C15	0.0104(11)	0.0141(12)	0.0164(12)	0.0021(9)	0.0020(9)	-0.0013(9)
C16	0.0211(13)	0.0160(13)	0.0366(16)	-0.0067(12)	0.0119(12)	-0.0032(10)
C17	0.0133(11)	0.0151(12)	0.0188(13)	0.0053(10)	0.0047(10)	0.0014(9)
C18	0.0138(12)	0.0186(13)	0.0192(13)	0.0029(10)	0.0063(10)	-0.0019(10)
C19	0.0109(10)	0.0131(11)	0.0138(11)	-0.0004(10)	0.0029(8)	-0.0006(10)
C20	0.0103(10)	0.0209(14)	0.0146(11)	-0.0003(10)	0.0002(9)	0.0003(9)
C21	0.0257(14)	0.0254(15)	0.0224(14)	-0.0066(12)	0.0110(11)	0.0011(11)
C22	0.0154(12)	0.0185(13)	0.0111(11)	-0.0004(10)	0.0004(9)	-0.0008(10)
C23	0.0142(14)	0.0299(18)	0.076(3)	-0.0005(17)	0.0136(15)	0.0049(12)
C24	0.0211(13)	0.0226(14)	0.0182(13)	0.0051(11)	0.0051(10)	-0.0025(11)
C25	0.0260(14)	0.0173(13)	0.0207(13)	-0.0013(11)	0.0024(11)	0.0019(11)
C26	0.0218(14)	0.0267(16)	0.0306(16)	0.0108(13)	-0.0011(12)	-0.0113(12)

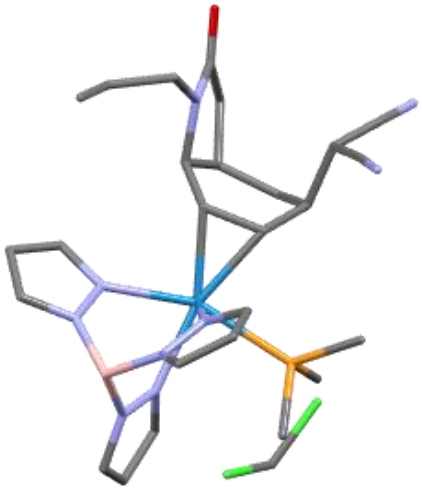
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.0129(13)	0.0221(15)	0.0192(14)	-0.0007(12)	0.0050(11)	0.0029(11)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for compound 4.38

	x/a	y/b	z/c	U(eq)
H1	0.3189	0.2884	0.5091	0.021000
H2	0.1633	0.3718	0.5477	0.026000
H3	0.0180	0.4139	0.4201	0.024000
H4	0.1411	0.1007	0.1790	0.020000
H5	-0.0732	0.1211	0.1167	0.026000
H6	-0.1253	0.2614	0.1726	0.025000
H7	0.3582	0.3899	0.1644	0.022000
H8	0.2219	0.5109	0.1019	0.029000
H9	0.0619	0.5069	0.1682	0.028000
H10	0.428(2)	0.3856(17)	0.3816(15)	0.008(6)
H11	0.467(2)	0.2609(17)	0.4556(17)	0.015(7)
H12	0.5825	0.1470	0.4274	0.015000
H13A	0.5696	0.1645	0.2968	0.016000
H13B	0.7022	0.1846	0.3412	0.016000
H14	0.5734	0.2841	0.2292	0.016000
H15	0.5018	0.4030	0.2700	0.017000
H16A	0.5664	0.5356	0.3863	0.036000
H16B	0.6901	0.5175	0.4484	0.036000
H16C	0.5780	0.4657	0.4563	0.036000
H18A	0.7954	0.2969	0.3143	0.020000
H18B	0.7350	0.3592	0.2402	0.020000
H19	0.7208	0.3056	0.4579	0.015000
H21A	0.5876	0.3510	0.6516	0.035000
H21B	0.6731	0.4329	0.6603	0.035000
H21C	0.7225	0.3401	0.6968	0.035000

	x/a	y/b	z/c	U(eq)
H23A	0.9747	0.1142	0.4606	0.060000
H23B	1.0244	0.1566	0.5472	0.060000
H23C	1.0544	0.1996	0.4718	0.060000
H24A	0.4522	0.1151	0.5002	0.031000
H24B	0.3701	0.0320	0.4968	0.031000
H24C	0.3223	0.1280	0.5057	0.031000
H25A	0.3811	0.0189	0.2802	0.033000
H25B	0.3983	-0.0347	0.3614	0.033000
H25C	0.4893	0.0396	0.3554	0.033000
H26A	0.1258	0.0864	0.3685	0.042000
H26B	0.1921	-0.0049	0.3895	0.042000
H26C	0.1550	0.0298	0.2995	0.042000
H1A	-0.013(2)	0.3931(17)	0.2630(15)	0.013(7)

Structure Report for compound 4.47



A colourless, block shaped crystal of **compound** 47 measuring 0.07×0.079×0.128 mm was coated with Paratone oil and mounted on a . Data for mo_harman_ld_2_189_x2_0m were measured on a Bruker APEX-II CCD [No _diffrn_measurement_device given] equipped with a [No _diffrn_detector_type given] detector and an Incoatec IμS 3.0 [No _diffrn_source

given] (MoK_α, λ=0.71073 Å) using a [No _diffrn_radiation_monochromator given] as monochromator. The crystal temperature was controlled with. Data collection and processing were done within the Bruker APEX5 software suite.[112] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a multi-scan method (SADABS).
The structure was solved by dual methods with SHELXT[113] and refined by full-matrix least-squares methods against F^2 using XL[114] within OLEX2.[115] All non-hydrogen atoms were refined with anisotropically. The B-H and H11 atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[116]

Table 1 Crystal data and structure refinement for compound 4.47

CCDC number	
Empirical formula	$C_{27}H_{36}BCl_2N_{10}O_2PW$
Formula weight	829.19
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.07×0.079×0.128
Crystal habit	colourless block
Crystal system	monoclinic
Space group	$P2_1/n$ (14)
a [Å]	11.7873(5)
b [Å]	12.3160(5)
c [Å]	23.2393(8)
α [°]	90
β [°]	102.6230(10)
γ [°]	90
Volume [$Å^3$]	3292.2(2)
Z	4
ρ_{calc} [gcm^{-3}]	1.673
μ [mm^{-1}]	3.762
F(000)	1648

[112] *APEX5, Saint, SADABS*; Bruker AXS Inc. 2019.
[113] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[114] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[115] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[116] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

2θ range [°]	4.31 to 56.63 (0.75 Å)
Index ranges	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −30 ≤ l ≤ 26
Reflections collected	66790
Independent reflections	8185 [R_{int} = 0.0707]
Data / Restraints / Parameters	8185 / 0 / 408
Goodness-of-fit on F^2	1.024
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0300 wR_2 = 0.0648
Final *R* indexes [all data]	R_1 = 0.0403 wR_2 = 0.0688
Largest peak/hole [eÅ^{-3}]	0.87/−1.31

Table 2 Atomic coordinates and Ueq [Å2] for compound 4.47

Atom	x	y	z	Ueq
W1	0.51554(2)	0.45217(2)	0.65563(2)	0.01373(4)
P1	0.34672(9)	0.45673(8)	0.70493(4)	0.0217(2)
O1	0.3693(2)	0.5698(2)	0.55284(12)	0.0242(6)
O2	0.5154(3)	0.0799(2)	0.44245(12)	0.0308(7)
N1	0.6965(3)	0.4918(2)	0.64728(13)	0.0155(6)
N2	0.7778(3)	0.5219(2)	0.69622(13)	0.0159(6)
N3	0.5499(3)	0.6126(2)	0.69738(13)	0.0164(6)
N4	0.6447(3)	0.6349(2)	0.74084(13)	0.0167(6)
N5	0.6104(3)	0.3886(2)	0.74463(13)	0.0164(6)
N6	0.6985(3)	0.4469(2)	0.77918(13)	0.0167(6)
N7	0.4318(3)	0.5174(2)	0.59276(13)	0.0176(6)

N8	0.5651(3)	0.1843(2)	0.52639(13)	0.0194(6)
N9	0.3935(3)	0.0271(3)	0.68902(15)	0.0250(7)
N10	0.1552(3)	0.0548(3)	0.51764(18)	0.0383(9)
C1	0.7532(3)	0.4846(3)	0.60348(16)	0.0196(7)
H1	0.717898	0.466415	0.563887	0.023
C2	0.8703(3)	0.5073(3)	0.62362(18)	0.0220(8)
H2	0.929236	0.507101	0.601531	0.026
C3	0.8825(3)	0.5303(3)	0.68268(17)	0.0196(7)
H3	0.953031	0.548936	0.709311	0.024
C4	0.4889(3)	0.7045(3)	0.68661(17)	0.0198(7)
H4	0.419008	0.712790	0.657500	0.024
C5	0.5423(3)	0.7866(3)	0.72416(17)	0.0214(8)
H5	0.516322	0.859159	0.726337	0.026
C6	0.6410(3)	0.7396(3)	0.75739(17)	0.0208(8)
H6	0.697132	0.774989	0.787031	0.025
C7	0.5932(3)	0.3032(3)	0.77771(16)	0.0187(7)
H7	0.536367	0.248428	0.765215	0.022
C8	0.6693(3)	0.3055(3)	0.83257(16)	0.0214(8)
H8	0.674990	0.254664	0.863839	0.026
C9	0.7345(3)	0.3976(3)	0.83145(16)	0.0209(8)
H9	0.795121	0.422348	0.862619	0.025
C10	0.4529(3)	0.2832(3)	0.63694(15)	0.0164(7)
H10	0.472036	0.236373	0.672915	0.020
C11	0.5530(3)	0.3024(3)	0.61230(15)	0.0153(7)
H11	0.623(4)	0.280(3)	0.6326(17)	0.015(10)
C12	0.5427(3)	0.2956(3)	0.54668(15)	0.0186(7)
H12	0.601052	0.346145	0.535822	0.022
C13	0.4217(3)	0.3221(3)	0.50709(16)	0.0204(8)

H13	0.422968	0.399191	0.493718	0.024
C14	0.3181(3)	0.3087(3)	0.53705(17)	0.0227(8)
H14A	0.289174	0.381916	0.544028	0.027
H14B	0.254925	0.270932	0.509180	0.027
C15	0.3417(3)	0.2471(3)	0.59512(16)	0.0193(7)
H15	0.275585	0.261362	0.614701	0.023
C16	0.4150(4)	0.2486(3)	0.45332(17)	0.0284(9)
H16A	0.336102	0.217396	0.440722	0.034
H16B	0.433015	0.290453	0.420042	0.034
C17	0.5029(4)	0.1602(3)	0.47171(16)	0.0248(8)
C18	0.6702(4)	0.1256(3)	0.55280(18)	0.0264(9)
H18A	0.671183	0.055532	0.532008	0.032
H18B	0.669862	0.109513	0.594503	0.032
C19	0.7783(4)	0.1882(4)	0.5502(2)	0.0341(10)
H19	0.777704	0.231136	0.516131	0.041
C20	0.8724(5)	0.1876(5)	0.5913(2)	0.0494(14)
H20A	0.875879	0.145584	0.625932	0.059
H20B	0.937773	0.229200	0.586845	0.059
C21	0.3490(3)	0.1208(3)	0.58582(16)	0.0189(7)
H21	0.414024	0.105777	0.565601	0.023
C22	0.2401(4)	0.0801(3)	0.54829(18)	0.0241(8)
C23	0.3734(3)	0.0638(3)	0.64305(17)	0.0202(7)
C24	0.2876(4)	0.3347(3)	0.7318(2)	0.0321(10)
H24A	0.262965	0.283655	0.699135	0.048
H24B	0.220682	0.354150	0.748378	0.048
H24C	0.347468	0.300640	0.762463	0.048
C25	0.2175(4)	0.5189(5)	0.6611(2)	0.0465(14)
H25A	0.236552	0.591507	0.648683	0.070
H25B	0.158146	0.524822	0.684570	0.070
H25C	0.187781	0.474178	0.626157	0.070
C26	0.3782(5)	0.5351(4)	0.7734(2)	0.0395(12)
H26A	0.446411	0.504429	0.800267	0.059
H26B	0.311134	0.532064	0.791947	0.059
H26C	0.393775	0.610777	0.764652	0.059
B1	0.7438(4)	0.5507(3)	0.75511(17)	0.0170(8)

Cl1	0.19571(14)	0.82742(13)	0.61048(6)	0.0578(4)
Cl2	0.01123(15)	0.69832(14)	0.53811(10)	0.0852(6)
C27	0.0562(5)	0.8286(5)	0.5624(3)	0.0515(14)
H27A	−0.000771	0.860260	0.583218	0.062
H27B	0.058430	0.875058	0.527917	0.062
H1A	0.821(3)	0.584(3)	0.7902(17)	0.016(10)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å²) for compound 4.47. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01541(7)	0.01356(7)	0.01176(7)	0.00069(5)	0.00196(5)	−0.00035(6)
P1	0.0193(5)	0.0218(5)	0.0257(5)	0.0016(4)	0.0085(4)	−0.0009(4)
O1	0.0269(15)	0.0222(14)	0.0201(13)	0.0077(11)	−0.0018(11)	0.0025(11)
O2	0.0477(19)	0.0244(15)	0.0216(14)	−0.0098(11)	0.0105(13)	−0.0057(13)
N1	0.0144(14)	0.0173(14)	0.0147(14)	−0.0001(11)	0.0029(11)	0.0001(11)
N2	0.0176(15)	0.0126(14)	0.0166(14)	0.0003(11)	0.0021(12)	0.0003(11)
N3	0.0177(15)	0.0141(14)	0.0164(14)	−0.0024(11)	0.0015(12)	−0.0021(12)
N4	0.0172(15)	0.0161(14)	0.0166(14)	0.0012(12)	0.0033(12)	−0.0011(12)
N5	0.0210(16)	0.0132(14)	0.0149(14)	−0.0015(11)	0.0034(12)	−0.0006(12)
N6	0.0193(15)	0.0157(14)	0.0140(13)	−0.0017(12)	0.0016(11)	0.0003(12)
N7	0.0185(15)	0.0154(14)	0.0191(15)	0.0019(11)	0.0048(12)	0.0001(12)
N8	0.0246(17)	0.0172(15)	0.0169(15)	−0.0038(12)	0.0056(13)	−0.0006(12)
N9	0.0237(17)	0.0242(17)	0.0260(18)	0.0018(14)	0.0031(14)	0.0008(13)
N10	0.035(2)	0.029(2)	0.043(2)	−0.0018(17)	−0.0084(18)	−0.0031(17)
C1	0.028(2)	0.0169(17)	0.0145(16)	0.0011(13)	0.0061(15)	−0.0024(15)

C2	0.0225(19)	0.0186(18)	0.028(2)	−0.0028(15)	0.0122(16)	−0.0038(15)
C3	0.0162(17)	0.0160(17)	0.0263(19)	0.0001(14)	0.0038(14)	−0.0004(14)
C4	0.0181(18)	0.0182(18)	0.0215(18)	0.0025(14)	0.0009(15)	−0.0003(14)
C5	0.026(2)	0.0121(16)	0.0257(19)	−0.0016(14)	0.0054(16)	0.0029(14)
C6	0.028(2)	0.0133(17)	0.0218(18)	−0.0022(14)	0.0068(16)	−0.0013(15)
C7	0.0220(19)	0.0163(17)	0.0175(17)	−0.0011(14)	0.0034(15)	−0.0029(14)
C8	0.028(2)	0.0198(18)	0.0145(17)	0.0046(14)	0.0006(15)	−0.0002(15)
C9	0.027(2)	0.0207(18)	0.0129(16)	0.0008(14)	−0.0009(14)	0.0015(15)
C10	0.0209(18)	0.0113(15)	0.0167(17)	−0.0013(13)	0.0035(14)	−0.0027(13)
C11	0.0199(18)	0.0125(16)	0.0128(16)	0.0002(12)	0.0021(14)	0.0007(13)
C12	0.0231(19)	0.0169(17)	0.0151(17)	0.0001(13)	0.0026(14)	−0.0029(14)
C13	0.026(2)	0.0179(17)	0.0135(16)	−0.0012(14)	−0.0033(15)	0.0017(15)
C14	0.0215(19)	0.0207(19)	0.0224(19)	0.0006(15)	−0.0028(15)	−0.0015(15)
C15	0.0194(18)	0.0214(18)	0.0170(17)	−0.0010(14)	0.0036(14)	−0.0010(15)
C16	0.037(2)	0.029(2)	0.0173(18)	−0.0015(16)	0.0022(17)	−0.0029(18)
C17	0.033(2)	0.026(2)	0.0163(17)	−0.0026(15)	0.0073(16)	−0.0081(17)
C18	0.034(2)	0.0205(19)	0.025(2)	−0.0044(16)	0.0062(17)	0.0042(17)
C19	0.031(2)	0.040(3)	0.034(2)	−0.007(2)	0.0122(19)	0.001(2)
C20	0.037(3)	0.070(4)	0.041(3)	−0.015(3)	0.008(2)	0.000(3)
C21	0.0192(18)	0.0191(18)	0.0179(17)	−0.0008(14)	0.0031(14)	−0.0018(14)
C22	0.026(2)	0.0194(18)	0.0236(19)	0.0015(15)	−0.0011(16)	−0.0020(15)

C23	0.0204(18)	0.0160(18)	0.0236(19)	−0.0018(14)	0.0039(15)	−0.0013(14)
C24	0.038(3)	0.027(2)	0.036(2)	−0.0040(18)	0.019(2)	−0.0086(18)
C25	0.023(2)	0.065(4)	0.053(3)	0.028(3)	0.011(2)	0.012(2)
C26	0.051(3)	0.035(3)	0.043(3)	−0.014(2)	0.033(2)	−0.012(2)
B1	0.022(2)	0.0140(18)	0.0140(17)	0.0002(15)	0.0027(15)	0.0013(16)
Cl1	0.0631(9)	0.0583(9)	0.0449(8)	0.0062(6)	−0.0036(7)	0.0081(7)
Cl2	0.0568(10)	0.0617(10)	0.1228(17)	0.0397(10)	−0.0118(10)	−0.0255(8)
C27	0.043(3)	0.056(3)	0.057(4)	0.019(3)	0.016(3)	0.008(3)

Table 4 Bond lengths and angles for compound 4.47

Atom–Atom	Length [Å]
W1–P1	2.5044(10)
W1–N1	2.238(3)
W1–N3	2.199(3)
W1–N5	2.265(3)
W1–N7	1.767(3)
W1–C10	2.219(3)
W1–C11	2.192(3)
P1–C24	1.824(4)
P1–C25	1.807(5)
P1–C26	1.828(5)
O1–N7	1.234(4)
O2–C17	1.228(5)
N1–N2	1.369(4)
N1–C1	1.337(5)
N2–C3	1.342(5)
N2–B1	1.549(5)
N3–N4	1.361(4)
N3–C4	1.335(5)
N4–C6	1.349(5)
N4–B1	1.543(5)
N5–N6	1.369(4)
N5–C7	1.344(5)
N6–C9	1.341(4)
N6–B1	1.538(5)
N8–C12	1.492(5)

N8–C17	1.354(5)
N8–C18	1.450(5)
N9–C23	1.136(5)
N10–C22	1.137(5)
C1–H1	0.9500
C1–C2	1.386(5)
C2–H2	0.9500
C2–C3	1.378(5)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.393(5)
C5–H5	0.9500
C5–C6	1.375(5)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.390(5)
C8–H8	0.9500
C8–C9	1.374(5)
C9–H9	0.9500
C10–H10	1.0000
C10–C11	1.440(5)
C10–C15	1.517(5)
C11–H11	0.90(4)
C11–C12	1.505(5)
C12–H12	1.0000
C12–C13	1.554(5)
C13–H13	1.0000
C13–C14	1.541(5)
C13–C16	1.531(5)
C14–H14A	0.9900
C14–H14B	0.9900
C14–C15	1.520(5)
C15–H15	1.0000
C15–C21	1.576(5)
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.499(6)
C18–H18A	0.9900
C18–H18B	0.9900
C18–C19	1.502(6)

C19–H19	0.9500
C19–C20	1.296(7)
C20–H20A	0.9500
C20–H20B	0.9500
C21–H21	1.0000
C21–C22	1.473(5)
C21–C23	1.475(5)
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
B1–H1A	1.15(4)
Cl1–C27	1.774(6)
Cl2–C27	1.744(6)
C27–H27A	0.9900
C27–H27B	0.9900

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	154.51(8)
N1–W1–N5	82.24(11)
N3–W1–P1	82.30(8)
N3–W1–N1	75.85(11)
N3–W1–N5	84.34(11)
N3–W1–C10	161.81(12)
N5–W1–P1	82.70(8)
N7–W1–P1	90.68(10)
N7–W1–N1	101.55(12)
N7–W1–N3	88.41(12)
N7–W1–N5	170.77(12)
N7–W1–C10	99.34(14)
N7–W1–C11	97.74(13)
C10–W1–P1	81.19(10)
C10–W1–N1	118.05(12)
C10–W1–N5	86.06(12)

C11–W1–P1	119.28(10)
C11–W1–N1	81.48(12)
C11–W1–N3	157.28(13)
C11–W1–N5	91.13(12)
C11–W1–C10	38.09(13)
C24–P1–W1	122.65(15)
C24–P1–C26	99.0(2)
C25–P1–W1	114.04(17)
C25–P1–C24	101.8(2)
C25–P1–C26	104.6(3)
C26–P1–W1	112.32(15)
N2–N1–W1	119.7(2)
C1–N1–W1	134.1(3)
C1–N1–N2	106.0(3)
N1–N2–B1	121.8(3)
C3–N2–N1	109.8(3)
C3–N2–B1	128.2(3)
N4–N3–W1	123.4(2)
C4–N3–W1	129.8(2)
C4–N3–N4	106.8(3)
N3–N4–B1	119.0(3)
C6–N4–N3	109.4(3)
C6–N4–B1	130.7(3)
N6–N5–W1	120.9(2)
C7–N5–W1	133.4(2)
C7–N5–N6	105.4(3)
N5–N6–B1	120.1(3)
C9–N6–N5	110.1(3)
C9–N6–B1	129.8(3)
O1–N7–W1	173.4(3)
C17–N8–C12	113.6(3)
C17–N8–C18	121.7(3)
C18–N8–C12	121.2(3)
N1–C1–H1	124.6
N1–C1–C2	110.8(3)
C2–C1–H1	124.6
C1–C2–H2	127.5
C3–C2–C1	104.9(3)
C3–C2–H2	127.5
N2–C3–C2	108.5(3)

N2–C3–H3	125.8
C2–C3–H3	125.8
N3–C4–H4	124.9
N3–C4–C5	110.3(3)
C5–C4–H4	124.9
C4–C5–H5	127.5
C6–C5–C4	105.0(3)
C6–C5–H5	127.5
N4–C6–C5	108.5(3)
N4–C6–H6	125.7
C5–C6–H6	125.7
N5–C7–H7	124.4
N5–C7–C8	111.2(3)
C8–C7–H7	124.4
C7–C8–H8	127.7
C9–C8–C7	104.5(3)
C9–C8–H8	127.7
N6–C9–C8	108.9(3)
N6–C9–H9	125.6
C8–C9–H9	125.6
W1–C10–H10	111.9
C11–C10–W1	69.93(19)
C11–C10–H10	111.9
C11–C10–C15	117.5(3)
C15–C10–W1	127.1(2)
C15–C10–H10	111.9
W1–C11–H11	106(3)
C10–C11–W1	71.98(19)
C10–C11–H11	118(3)
C10–C11–C12	120.1(3)
C12–C11–W1	122.2(2)
C12–C11–H11	112(3)
N8–C12–C11	113.0(3)
N8–C12–H12	108.2
N8–C12–C13	102.1(3)
C11–C12–H12	108.2
C11–C12–C13	116.7(3)
C13–C12–H12	108.2
C12–C13–H13	108.0
C14–C13–C12	115.2(3)

C14–C13–H13	108.0
C16–C13–C12	103.6(3)
C16–C13–H13	108.0
C16–C13–C14	113.6(3)
C13–C14–H14A	108.2
C13–C14–H14B	108.2
H14A–C14–H14B	107.3
C15–C14–C13	116.5(3)
C15–C14–H14A	108.2
C15–C14–H14B	108.2
C10–C15–C14	112.8(3)
C10–C15–H15	107.9
C10–C15–C21	108.2(3)
C14–C15–H15	107.9
C14–C15–C21	112.1(3)
C21–C15–H15	107.9
C13–C16–H16A	110.4
C13–C16–H16B	110.4
H16A–C16–H16B	108.6
C17–C16–C13	106.7(3)
C17–C16–H16A	110.4
C17–C16–H16B	110.4
O2–C17–N8	126.2(4)
O2–C17–C16	125.9(4)
N8–C17–C16	107.9(3)
N8–C18–H18A	109.1
N8–C18–H18B	109.1
N8–C18–C19	112.3(3)
H18A–C18–H18B	107.9
C19–C18–H18A	109.1
C19–C18–H18B	109.1
C18–C19–H19	117.9
C20–C19–C18	124.3(5)
C20–C19–H19	117.9
C19–C20–H20A	120.0
C19–C20–H20B	120.0
H20A–C20–H20B	120.0
C15–C21–H21	108.5
C22–C21–C15	110.5(3)
C22–C21–H21	108.5

C22–C21–C23	110.2(3)
C23–C21–C15	110.6(3)
C23–C21–H21	108.5
N10–C22–C21	175.8(4)
N9–C23–C21	175.0(4)
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
N2–B1–H1A	113(2)
N4–B1–N2	107.1(3)
N4–B1–H1A	110(2)
N6–B1–N2	107.9(3)
N6–B1–N4	109.3(3)
N6–B1–H1A	109(2)
Cl1–C27–H27A	109.3
Cl1–C27–H27B	109.3
Cl2–C27–Cl1	111.8(3)
Cl2–C27–H27A	109.3
Cl2–C27–H27B	109.3
H27A–C27–H27B	107.9

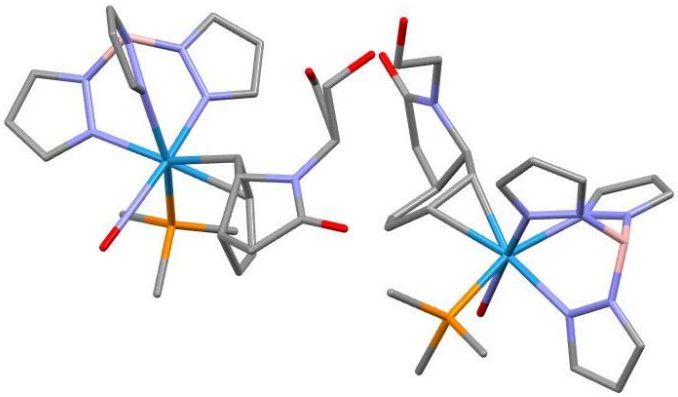
Table 5 Torsion angles for compound 4.47

Atom–Atom–Atom–Atom	Torsion Angle [°]
W1–N1–N2–C3	173.3(2)

W1–N1–N2–B1	−11.8(4)
W1–N1–C1–C2	−172.4(3)
W1–N3–N4–C6	−179.8(2)
W1–N3–N4–B1	10.4(4)
W1–N3–C4–C5	179.4(3)
W1–N5–N6–C9	174.9(2)
W1–N5–N6–B1	−6.8(4)
W1–N5–C7–C8	−173.6(3)
W1–C10–C11–C12	−117.3(3)
W1–C10–C15–C14	42.8(4)
W1–C10–C15–C21	167.3(2)
W1–C11–C12–N8	−176.4(2)
W1–C11–C12–C13	−58.5(4)
N1–N2–C3–C2	1.1(4)
N1–N2–B1–N4	−51.0(4)
N1–N2–B1–N6	66.6(4)
N1–C1–C2–C3	−0.7(4)
N2–N1–C1–C2	1.3(4)
N3–N4–C6–C5	−0.1(4)
N3–N4–B1–N2	52.0(4)
N3–N4–B1–N6	−64.7(4)
N3–C4–C5–C6	1.4(4)
N4–N3–C4–C5	−1.5(4)
N5–N6–C9–C8	−0.6(4)
N5–N6–B1–N2	−54.1(4)
N5–N6–B1–N4	62.1(4)
N5–C7–C8–C9	0.1(4)
N6–N5–C7–C8	−0.4(4)
N8–C12–C13–C14	100.9(3)
N8–C12–C13–C16	−23.8(4)
N8–C18–C19–C20	143.6(5)
C1–N1–N2–C3	−1.5(4)
C1–N1–N2–B1	173.4(3)
C1–C2–C3–N2	−0.3(4)
C3–N2–B1–N4	122.8(4)
C3–N2–B1–N6	−119.6(4)
C4–N3–N4–C6	1.0(4)
C4–N3–N4–B1	−168.8(3)
C4–C5–C6–N4	−0.8(4)
C6–N4–B1–N2	−115.3(4)

C6–N4–B1–N6	128.0(4)
C7–N5–N6–C9	0.6(4)
C7–N5–N6–B1	178.9(3)
C7–C8–C9–N6	0.3(4)
C9–N6–B1–N2	123.9(4)
C9–N6–B1–N4	−119.9(4)
C10–C11–C12–N8	−89.7(4)
C10–C11–C12–C13	28.2(5)
C10–C15–C21–C22	176.6(3)
C10–C15–C21–C23	54.4(4)
C11–C10–C15–C14	−42.0(4)
C11–C10–C15–C21	82.5(4)
C11–C12–C13–C14	−22.7(5)
C11–C12–C13–C16	−147.5(3)
C12–N8–C17–O2	170.8(4)
C12–N8–C17–C16	−9.6(4)
C12–N8–C18–C19	−55.7(5)
C12–C13–C14–C15	−14.0(5)
C12–C13–C16–C17	19.6(4)
C13–C14–C15–C10	46.0(4)
C13–C14–C15–C21	−76.3(4)
C13–C16–C17–O2	172.5(4)
C13–C16–C17–N8	−7.0(4)
C14–C13–C16–C17	−106.2(4)
C14–C15–C21–C22	−58.5(4)
C14–C15–C21–C23	179.3(3)
C15–C10–C11–W1	122.3(3)
C15–C10–C11–C12	5.0(5)
C16–C13–C14–C15	105.4(4)
C17–N8–C12–C11	147.8(3)
C17–N8–C12–C13	21.7(4)
C17–N8–C18–C19	102.1(4)
C18–N8–C12–C11	−52.8(5)
C18–N8–C12–C13	−178.9(3)
C18–N8–C17–O2	11.5(6)
C18–N8–C17–C16	−169.0(3)
B1–N2–C3–C2	−173.4(3)
B1–N4–C6–C5	168.1(3)
B1–N6–C9–C8	−178.7(3)

Crystal Structure Report for compound 4.5



A colorless, plate-like specimen of $C_{22}H_{32}BN_8O_3PW$, approximate dimensions 0.044 mm x 0.087 mm x 0.134 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 5.82 hours. The frames were integrated with the Bruker SAINT software package[117] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 114708 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 13137 were independent (average redundancy 8.732, completeness = 99.8%, R_{int} = 6.25%, R_{sig} = 3.56%) and 10636 (80.96%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.2055(5) Å, b = 17.2321(5) Å, c = 23.6985(8) Å, β = 100.4770(10)°, volume = 5302.9(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9855 reflections above 20 σ(I) with 5.753° < 2θ < 56.52°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[118] The ratio of minimum to maximum apparent transmission was 0.752. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5870 and 0.8280.

[117] Bruker (2012). *Saint; SADABS; APEX5*. Bruker AXS Inc., Madison, Wisconsin, USA.

[118] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

The structure was solved and refined using the Bruker SHELXTL Software Package[119] within APEX5 [1] and OLEX2,[120] using the space group P $2_1/c$, with Z = 8 for the formula unit, $C_{22}H_{32}BN_8O_3PW$. The B-H and O-H hydrogen atoms (except H6A), as well as H10,H11, H32 and H33 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The relative occupancy of the disordered atoms was freely refined, with constraints on the anisotropic displacement parameters of the disordered C atoms and restraints on the disordered C-C and C-O bonds. The final anisotropic full-matrix least-squares refinement on F^2 with 699 variables converged at R1 = 2.91%, for the observed data and wR2 = 6.81% for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was 1.977 $e^-/Å^3$ and the largest hole was -0.649 $e^-/Å^3$ with an RMS deviation of 0.126 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.709 g/cm^3 and F(000), 2704 e^-.

Table 1. Sample and crystal data for compound 4.5		
Chemical formula	$C_{22}H_{32}BN_8O_3PW$	
Formula weight	682.18 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.044 x 0.087 x 0.134 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 13.2055(5) Å	α = 90°
	b = 17.2321(5) Å	β = 100.4770(10)°
	c = 23.6985(8) Å	γ = 90°
Volume	5302.9(3) $Å^3$	
Z	8	
Density (calculated)	1.709 g/cm^3	
Absorption coefficient	4.457 mm^{-1}	
F(000)	2704	

[119] Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.
[120] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Table 2. Data collection and structure refinement for compound 4.5		
Diffractometer	Bruker D8 Venture Photon III Kappa four-circle diffractometer	
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)	
Theta range for data collection	1.96 to 28.28°	
Index ranges	-17<=h<=17, -22<=k<=18, -31<=l<=31	
Reflections collected	114708	
Independent reflections	13137 [R(int) = 0.0625]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8280 and 0.5870	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13137 / 3 / 699	
Goodness-of-fit on F^2	1.026	
Δ/σ_{max}	0.002	
Final R indices	10636 data; I>2σ(I)	R1 = 0.0291, wR2 = 0.0612
	all data	R1 = 0.0455, wR2 = 0.0681

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0282P)^2+8.7391P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.977 and -0.649 eÅ^{-3}
R.M.S. deviation from mean	0.126 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound 4.5

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.48585(2)	0.33182(2)	0.22559(2)	0.02009(4)
P1	0.55995(8)	0.23615(6)	0.30181(4)	0.0255(2)
O1	0.3745(2)	0.20466(15)	0.15329(11)	0.0302(6)
O2	0.9916(2)	0.44208(18)	0.21610(13)	0.0390(7)
O3	0.2261(3)	0.5666(2)	0.35419(16)	0.0568(10)
N1	0.5778(3)	0.42277(18)	0.28120(15)	0.0296(7)
N2	0.6495(3)	0.46549(19)	0.26059(16)	0.0343(8)
N3	0.6315(2)	0.30719(18)	0.19600(14)	0.0272(7)
N4	0.7049(3)	0.3625(2)	0.19633(16)	0.0335(8)
N5	0.4878(2)	0.42119(17)	0.15790(14)	0.0245(7)
N6	0.5765(3)	0.46096(18)	0.15562(15)	0.0301(8)
N7	0.4187(2)	0.25813(17)	0.18215(13)	0.0224(6)
N8	0.1679(3)	0.44088(19)	0.22713(14)	0.0276(7)
C1	0.5677(4)	0.4559(2)	0.33138(19)	0.0375(10)
C2	0.6296(4)	0.5201(3)	0.3426(2)	0.0461(13)
C3	0.6804(4)	0.5245(2)	0.2980(2)	0.0425(12)
C4	0.6708(3)	0.2413(2)	0.17845(17)	0.0317(9)
C5	0.7688(4)	0.2541(3)	0.1678(2)	0.0419(11)
C6	0.7880(3)	0.3316(3)	0.1799(2)	0.0418(11)
C7	0.4192(3)	0.4426(2)	0.11192(15)	0.0241(8)
C8	0.4637(3)	0.4956(2)	0.07919(18)	0.0321(9)
C9	0.5620(3)	0.5053(2)	0.10847(19)	0.0343(10)
C10	0.3515(3)	0.3980(2)	0.24068(16)	0.0247(8)

	x/a	y/b	z/c	U(eq)
C11	0.3686(3)	0.3371(2)	0.28315(17)	0.0279(8)
C12	0.2933(3)	0.2736(2)	0.27697(17)	0.0297(9)
C13	0.2170(3)	0.2664(2)	0.23220(17)	0.0294(9)
C14	0.1971(3)	0.3233(2)	0.18355(17)	0.0267(8)
C15	0.2487(3)	0.4016(2)	0.20070(16)	0.0245(8)
C16	0.0828(3)	0.3449(2)	0.16890(18)	0.0315(9)
C17	0.0725(3)	0.4135(2)	0.20663(17)	0.0320(9)
C18	0.1856(3)	0.5114(2)	0.26111(17)	0.0323(9)
C19	0.2124(4)	0.4952(3)	0.32454(18)	0.0381(10)
C20	0.5324(4)	0.2433(3)	0.37409(17)	0.0375(10)
C21	0.5260(4)	0.1363(2)	0.2830(2)	0.0425(12)
C22	0.7000(3)	0.2353(3)	0.3190(2)	0.0426(11)
B1	0.6756(4)	0.4489(3)	0.2019(2)	0.0353(11)
W2	0.08021(2)	0.22745(2)	0.46951(2)	0.01984(4)
P2	0.03717(8)	0.12352(5)	0.39518(4)	0.0237(2)
O4	0.1756(2)	0.10116(15)	0.54896(11)	0.0302(6)
O5	0.5761(2)	0.33217(19)	0.50121(14)	0.0440(8)
N9	0.9900(2)	0.31270(17)	0.40799(13)	0.0222(6)
N10	0.9102(2)	0.35231(18)	0.42367(14)	0.0250(7)
N11	0.9297(2)	0.20024(18)	0.49148(14)	0.0249(7)
N12	0.8527(3)	0.25397(19)	0.48892(14)	0.0268(7)
N13	0.0604(2)	0.31663(17)	0.53438(13)	0.0233(6)
N14	0.9708(3)	0.35763(18)	0.53007(14)	0.0271(7)
N15	0.1398(2)	0.15526(17)	0.51728(13)	0.0229(6)
N16	0.4000(3)	0.33810(19)	0.48980(14)	0.0282(7)
C23	0.9975(3)	0.3387(2)	0.35557(17)	0.0264(8)
C24	0.9236(3)	0.3947(2)	0.33717(18)	0.0331(9)
C25	0.8702(3)	0.4016(2)	0.38144(18)	0.0326(9)
C26	0.8969(3)	0.1356(2)	0.51286(18)	0.0334(9)
C27	0.7983(4)	0.1459(3)	0.5239(2)	0.0391(10)
C28	0.7725(3)	0.2212(3)	0.50877(18)	0.0334(9)
C29	0.1180(3)	0.3367(2)	0.58481(17)	0.0285(8)
C30	0.0666(3)	0.3899(3)	0.61317(18)	0.0370(10)
C31	0.9740(4)	0.4008(2)	0.5776(2)	0.0377(10)
C32	0.2169(3)	0.2965(2)	0.46487(15)	0.0216(7)

	x/a	y/b	z/c	U(eq)
C33	0.2075(3)	0.2405(2)	0.41853(16)	0.0229(7)
C34	0.2847(3)	0.1793(2)	0.42374(16)	0.0256(8)
C35	0.3539(3)	0.1664(2)	0.47060(17)	0.0281(8)
C36	0.3646(3)	0.2163(2)	0.52337(17)	0.0284(8)
C37	0.3137(3)	0.2958(2)	0.50933(16)	0.0246(8)
C38	0.4781(3)	0.2365(3)	0.54386(19)	0.0347(10)
C39	0.4924(3)	0.3068(3)	0.50981(18)	0.0338(10)
C40	0.3862(4)	0.4078(3)	0.45597(18)	0.0369(10)
C42	0.0506(4)	0.1416(2)	0.32118(17)	0.0363(10)
C43	0.1133(3)	0.0361(2)	0.41345(19)	0.0340(9)
C44	0.9075(3)	0.0839(3)	0.3848(2)	0.0369(10)
B2	0.8780(4)	0.3400(3)	0.4823(2)	0.0283(9)
O6	0.3565(4)	0.5399(2)	0.45081(18)	0.0519(15)
C41	0.3621(5)	0.4769(4)	0.4893(3)	0.0406(16)
O6A	0.3871(14)	0.4987(9)	0.5359(7)	0.046(6)
C41A	0.3260(19)	0.469(2)	0.4850(15)	0.0406(16)

Table 4. Bond lengths (Å) for compound 4.5			
W1-N7	1.768(3)	W1-C10	2.192(4)
W1-N3	2.205(3)	W1-N5	2.227(3)
W1-C11	2.244(4)	W1-N1	2.255(3)
W1-P1	2.5090(10)	P1-C21	1.814(4)
P1-C20	1.819(4)	P1-C22	1.820(5)
O1-N7	1.230(4)	O2-C17	1.234(5)
O3-C19	1.413(5)	O3-H3	0.86(7)
N1-C1	1.348(5)	N1-N2	1.358(5)
N2-C3	1.362(5)	N2-B1	1.521(7)
N3-C4	1.346(5)	N3-N4	1.359(4)
N4-C6	1.340(6)	N4-B1	1.550(6)
N5-C7	1.336(5)	N5-N6	1.367(4)
N6-C9	1.338(5)	N6-B1	1.561(6)
N8-C17	1.350(5)	N8-C18	1.454(5)
N8-C15	1.494(5)	C1-C2	1.373(6)
C1-H1	0.950000	C2-C3	1.354(7)

C2-H2A	0.950000	C3-H3A	0.950000
C4-C5	1.381(6)	C4-H4	0.950000
C5-C6	1.381(7)	C5-H5	0.950000
C6-H6B	0.950000	C7-C8	1.396(5)
C7-H7	0.950000	C8-C9	1.366(6)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.442(5)	C10-C15	1.509(5)
C10-H10	0.91(4)	C11-C12	1.468(6)
C11-H11	0.83(5)	C12-C13	1.329(6)
C12-H12	0.950000	C13-C14	1.500(5)
C13-H13	0.950000	C14-C16	1.532(5)
C14-C15	1.533(5)	C14-H14	1.000000
C15-H15	1.000000	C16-C17	1.503(6)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.507(6)	C18-H18A	0.990000
C18-H18B	0.990000	C19-H19A	0.990000
C19-H19B	0.990000	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
B1-H1A	1.13(4)	W2-N15	1.768(3)
W2-C32	2.181(4)	W2-N11	2.195(3)
W2-N13	2.222(3)	W2-N9	2.252(3)
W2-C33	2.252(4)	W2-P2	2.5039(10)
P2-C44	1.818(4)	P2-C43	1.819(4)
P2-C42	1.821(4)	O4-N15	1.236(4)
O5-C39	1.240(5)	N9-C23	1.341(5)
N9-N10	1.362(4)	N10-C25	1.346(5)
N10-B2	1.540(6)	N11-C26	1.328(5)
N11-N12	1.368(4)	N12-C28	1.357(5)
N12-B2	1.534(5)	N13-C29	1.340(5)
N13-N14	1.366(4)	N14-C31	1.345(5)
N14-B2	1.540(6)	N16-C39	1.339(5)
N16-C40	1.436(5)	N16-C37	1.495(5)
C23-C24	1.385(5)	C23-H23	0.950000

C24-C25	1.372(6)	C24-H24	0.950000
C25-H25	0.950000	C26-C27	1.385(6)
C26-H26	0.950000	C27-C28	1.372(6)
C27-H27	0.950000	C28-H28	0.950000
C29-C30	1.386(6)	C29-H29	0.950000
C30-C31	1.366(6)	C30-H30	0.950000
C31-H31	0.950000	C32-C33	1.451(5)
C32-C37	1.502(5)	C32-H32	0.95(4)
C33-C34	1.457(5)	C33-H33	0.92(4)
C34-C35	1.322(5)	C34-H34	0.950000
C35-C36	1.503(5)	C35-H35	0.950000
C36-C38	1.529(6)	C36-C37	1.535(5)
C36-H36	1.000000	C37-H37	1.000000
C38-C39	1.487(6)	C38-H38A	0.990000
C38-H38B	0.990000	C40-C41	1.497(7)
C40-C41A	1.551(18)	C40-H40A	0.990000
C40-H40B	0.990000	C40-H40C	0.990000
C40-H40D	0.990000	C42-H42A	0.980000
C42-H42B	0.980000	C42-H42C	0.980000
C43-H43A	0.980000	C43-H43B	0.980000
C43-H43C	0.980000	C44-H44A	0.980000
C44-H44B	0.980000	C44-H44C	0.980000
B2-H2	1.10(4)	O6-C41	1.412(9)
O6-H6	1.03(8)	C41-H41A	0.990000
C41-H41B	0.990000	O6A-C41A	1.42(2)
O6A-H6A	0.840000	C41A-H41C	0.990000
C41A-H41D	0.990000		

Table 5. Bond angles (°) for compound 4.5			
N7-W1-C10	97.68(14)	N7-W1-N3	92.89(13)
C10-W1-N3	158.54(13)	N7-W1-N5	98.48(12)
C10-W1-N5	82.74(13)	N3-W1-N5	77.24(12)
N7-W1-C11	93.16(15)	C10-W1-C11	37.92(14)
N3-W1-C11	159.96(13)	N5-W1-C11	120.62(13)

N7-W1-N1	177.49(13)	C10-W1-N1	84.79(13)
N3-W1-N1	84.92(13)	N5-W1-N1	82.23(12)
C11-W1-N1	88.52(14)	N7-W1-P1	92.05(10)
C10-W1-P1	116.45(10)	N3-W1-P1	81.60(9)
N5-W1-P1	156.75(9)	C11-W1-P1	79.11(10)
N1-W1-P1	86.43(8)	C21-P1-C20	102.3(2)
C21-P1-C22	104.0(2)	C20-P1-C22	99.1(2)
C21-P1-W1	113.59(15)	C20-P1-W1	120.97(15)
C22-P1-W1	114.48(16)	C19-O3-H3	105.(5)
C1-N1-N2	106.0(3)	C1-N1-W1	132.9(3)
N2-N1-W1	120.2(3)	N1-N2-C3	108.5(4)
N1-N2-B1	121.1(3)	C3-N2-B1	130.1(4)
C4-N3-N4	106.2(3)	C4-N3-W1	132.0(3)
N4-N3-W1	121.7(3)	C6-N4-N3	109.9(4)
C6-N4-B1	129.5(4)	N3-N4-B1	119.1(3)
C7-N5-N6	106.7(3)	C7-N5-W1	133.1(3)
N6-N5-W1	119.8(2)	C9-N6-N5	109.0(3)
C9-N6-B1	129.5(3)	N5-N6-B1	121.4(3)
O1-N7-W1	177.4(3)	C17-N8-C18	122.5(3)
C17-N8-C15	112.4(3)	C18-N8-C15	123.8(3)
N1-C1-C2	111.2(5)	N1-C1-H1	124.400000
C2-C1-H1	124.400000	C3-C2-C1	104.8(4)
C3-C2-H2A	127.600000	C1-C2-H2A	127.600000
C2-C3-N2	109.5(4)	C2-C3-H3A	125.200000
N2-C3-H3A	125.200000	N3-C4-C5	110.4(4)
N3-C4-H4	124.800000	C5-C4-H4	124.800000
C4-C5-C6	105.0(4)	C4-C5-H5	127.500000
C6-C5-H5	127.500000	N4-C6-C5	108.4(4)
N4-C6-H6B	125.800000	C5-C6-H6B	125.800000
N5-C7-C8	110.0(4)	N5-C7-H7	125.000000
C8-C7-H7	125.000000	C9-C8-C7	104.7(4)
C9-C8-H8	127.600000	C7-C8-H8	127.600000
N6-C9-C8	109.5(4)	N6-C9-H9	125.300000
C8-C9-H9	125.300000	C11-C10-C15	118.5(4)
C11-C10-W1	73.0(2)	C15-C10-W1	125.6(3)
C11-C10-H10	116.(2)	C15-C10-H10	113.(2)

W1-C10-H10	105.(2)	C10-C11-C12	117.1(4)
C10-C11-W1	69.1(2)	C12-C11-W1	116.0(3)
C10-C11-H11	120.(3)	C12-C11-H11	115.(3)
W1-C11-H11	111.(3)	C13-C12-C11	123.4(4)
C13-C12-H12	118.300000	C11-C12-H12	118.300000
C12-C13-C14	123.6(4)	C12-C13-H13	118.200000
C14-C13-H13	118.200000	C13-C14-C16	111.2(3)
C13-C14-C15	111.4(3)	C16-C14-C15	102.6(3)
C13-C14-H14	110.500000	C16-C14-H14	110.500000
C15-C14-H14	110.500000	N8-C15-C10	112.6(3)
N8-C15-C14	101.2(3)	C10-C15-C14	115.8(3)
N8-C15-H15	109.000000	C10-C15-H15	109.000000
C14-C15-H15	109.000000	C17-C16-C14	104.4(3)
C17-C16-H16A	110.900000	C14-C16-H16A	110.900000
C17-C16-H16B	110.900000	C14-C16-H16B	110.900000
H16A-C16-H16B	108.900000	O2-C17-N8	125.3(4)
O2-C17-C16	126.7(4)	N8-C17-C16	108.0(3)
N8-C18-C19	112.5(3)	N8-C18-H18A	109.100000
C19-C18-H18A	109.100000	N8-C18-H18B	109.100000
C19-C18-H18B	109.100000	H18A-C18-H18B	107.800000
O3-C19-C18	108.6(4)	O3-C19-H19A	110.000000
C18-C19-H19A	110.000000	O3-C19-H19B	110.000000
C18-C19-H19B	110.000000	H19A-C19-H19B	108.300000
P1-C20-H20A	109.500000	P1-C20-H20B	109.500000
H20A-C20-H20B	109.500000	P1-C20-H20C	109.500000
H20A-C20-H20C	109.500000	H20B-C20-H20C	109.500000

P1-C21-H21A	109.500000	P1-C21-H21B	109.500000
H21A-C21-H21B	109.500000	P1-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
P1-C22-H22A	109.500000	P1-C22-H22B	109.500000
H22A-C22-H22B	109.500000	P1-C22-H22C	109.500000
H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
N2-B1-N4	111.1(4)	N2-B1-N6	108.5(4)
N4-B1-N6	105.0(4)	N2-B1-H1A	114.(2)
N4-B1-H1A	112.(2)	N6-B1-H1A	105.(2)
N15-W2-C32	98.07(14)	N15-W2-N11	90.83(13)
C32-W2-N11	157.18(12)	N15-W2-N13	97.94(12)
C32-W2-N13	81.95(12)	N11-W2-N13	76.01(11)
N15-W2-N9	174.39(13)	C32-W2-N9	87.52(12)
N11-W2-N9	84.11(11)	N13-W2-N9	83.22(11)
N15-W2-C33	97.19(14)	C32-W2-C33	38.15(13)
N11-W2-C33	160.86(13)	N13-W2-C33	119.67(12)
N9-W2-C33	86.92(12)	N15-W2-P2	87.99(10)
C32-W2-P2	116.03(10)	N11-W2-P2	85.10(9)
N13-W2-P2	160.23(8)	N9-W2-P2	89.16(8)
C33-W2-P2	77.88(10)	C44-P2-C43	100.8(2)
C44-P2-C42	100.8(2)	C43-P2-C42	103.0(2)
C44-P2-W2	116.86(14)	C43-P2-W2	112.34(14)
C42-P2-W2	120.38(14)	C23-N9-N10	106.0(3)
C23-N9-W2	134.3(3)	N10-N9-W2	119.6(2)
C25-N10-N9	109.4(3)	C25-N10-B2	128.5(3)
N9-N10-B2	122.1(3)	C26-N11-N12	107.1(3)
C26-N11-W2	129.9(3)	N12-N11-W2	122.8(2)
C28-N12-N11	108.9(3)	C28-N12-B2	129.4(3)
N11-N12-B2	119.0(3)	C29-N13-N14	106.1(3)
C29-N13-W2	132.5(3)	N14-N13-W2	121.0(2)
C31-N14-N13	109.2(3)	C31-N14-B2	128.6(4)

N13-N14-B2	121.1(3)	O4-N15-W2	175.3(3)
C39-N16-C40	123.3(4)	C39-N16-C37	113.0(3)
C40-N16-C37	123.7(3)	N9-C23-C24	111.0(4)
N9-C23-H23	124.500000	C24-C23-H23	124.500000
C25-C24-C23	104.5(4)	C25-C24-H24	127.800000
C23-C24-H24	127.800000	N10-C25-C24	109.1(4)
N10-C25-H25	125.500000	C24-C25-H25	125.500000
N11-C26-C27	110.3(4)	N11-C26-H26	124.900000
C27-C26-H26	124.900000	C28-C27-C26	105.6(4)
C28-C27-H27	127.200000	C26-C27-H27	127.200000
N12-C28-C27	108.1(4)	N12-C28-H28	125.900000
C27-C28-H28	125.900000	N13-C29-C30	110.8(4)
N13-C29-H29	124.600000	C30-C29-H29	124.600000
C31-C30-C29	104.8(4)	C31-C30-H30	127.600000
C29-C30-H30	127.600000	N14-C31-C30	109.2(4)
N14-C31-H31	125.400000	C30-C31-H31	125.400000
C33-C32-C37	118.0(3)	C33-C32-W2	73.6(2)
C37-C32-W2	124.5(3)	C33-C32-H32	118.(2)
C37-C32-H32	112.(2)	W2-C32-H32	107.(2)
C32-C33-C34	117.1(3)	C32-C33-W2	68.3(2)
C34-C33-W2	117.5(3)	C32-C33-H33	118.(2)
C34-C33-H33	116.(2)	W2-C33-H33	112.(2)
C35-C34-C33	124.0(4)	C35-C34-H34	118.000000
C33-C34-H34	118.000000	C34-C35-C36	123.3(3)
C34-C35-H35	118.300000	C36-C35-H35	118.300000
C35-C36-C38	109.5(3)	C35-C36-C37	111.0(3)
C38-C36-C37	103.3(3)	C35-C36-H36	110.900000
C38-C36-H36	110.900000	C37-C36-H36	110.900000
N16-C37-C32	112.2(3)	N16-C37-C36	100.1(3)
C32-C37-C36	116.3(3)	N16-C37-H37	109.300000
C32-C37-H37	109.300000	C36-C37-H37	109.300000
C39-C38-C36	103.1(3)	C39-C38-H38A	111.100000
C36-C38-H38A	111.100000	C39-C38-H38B	111.100000

C36-C38-H38B	111.100000	H38A-C38-H38B	109.100000
O5-C39-N16	125.6(4)	O5-C39-C38	125.5(4)
N16-C39-C38	108.9(4)	N16-C40-C41	112.8(4)
N16-C40-C41A	109.9(18)	N16-C40-H40A	109.000000
C41-C40-H40A	109.000000	N16-C40-H40B	109.000000
C41-C40-H40B	109.000000	H40A-C40-H40B	107.800000
N16-C40-H40C	109.700000	C41A-C40-H40C	109.700000
N16-C40-H40D	109.700000	C41A-C40-H40D	109.700000
H40C-C40-H40D	108.200000	P2-C42-H42A	109.500000
P2-C42-H42B	109.500000	H42A-C42-H42B	109.500000
P2-C42-H42C	109.500000	H42A-C42-H42C	109.500000
H42B-C42-H42C	109.500000	P2-C43-H43A	109.500000
P2-C43-H43B	109.500000	H43A-C43-H43B	109.500000
P2-C43-H43C	109.500000	H43A-C43-H43C	109.500000
H43B-C43-H43C	109.500000	P2-C44-H44A	109.500000
P2-C44-H44B	109.500000	H44A-C44-H44B	109.500000
P2-C44-H44C	109.500000	H44A-C44-H44C	109.500000
H44B-C44-H44C	109.500000	N12-B2-N10	109.0(3)
N12-B2-N14	105.9(3)	N10-B2-N14	108.8(3)
N12-B2-H2	109.(2)	N10-B2-H2	109.(2)
N14-B2-H2	115.(2)	C41-O6-H6	113.(4)

O6-C41-C40	105.1(5)	O6-C41-H41A	110.700000
C40-C41-H41A	110.700000	O6-C41-H41B	110.700000
C40-C41-H41B	110.700000	H41A-C41-H41B	108.800000
C41A-O6A-H6A	109.500000	O6A-C41A-C40	111.4(17)
O6A-C41A-H41C	109.300000	C40-C41A-H41C	109.300000
O6A-C41A-H41D	109.300000	C40-C41A-H41D	109.300000
H41C-C41A-H41D	108.000000		

Table 6. Torsion angles (°) for compound 4.5			
C1-N1-N2-C3	-1.0(4)	W1-N1-N2-C3	169.3(2)
C1-N1-N2-B1	-175.3(3)	W1-N1-N2-B1	-5.0(5)
C4-N3-N4-C6	-0.5(5)	W1-N3-N4-C6	176.1(3)
C4-N3-N4-B1	166.9(4)	W1-N3-N4-B1	-16.5(5)
C7-N5-N6-C9	-0.6(4)	W1-N5-N6-C9	173.8(3)
C7-N5-N6-B1	-178.2(4)	W1-N5-N6-B1	-3.8(5)
N2-N1-C1-C2	1.4(5)	W1-N1-C1-C2	-167.2(3)
N1-C1-C2-C3	-1.3(5)	C1-C2-C3-N2	0.6(5)
N1-N2-C3-C2	0.3(5)	B1-N2-C3-C2	173.9(4)
N4-N3-C4-C5	0.2(5)	W1-N3-C4-C5	-175.8(3)
N3-C4-C5-C6	0.1(5)	N3-N4-C6-C5	0.6(5)
B1-N4-C6-C5	-165.1(4)	C4-C5-C6-N4	-0.4(5)
N6-N5-C7-C8	0.8(4)	W1-N5-C7-C8	-172.6(3)
N5-C7-C8-C9	-0.6(5)	N5-N6-C9-C8	0.3(5)
B1-N6-C9-C8	177.6(4)	C7-C8-C9-N6	0.2(5)
C15-C10-C11-C12	12.3(5)	W1-C10-C11-C12	-109.4(3)

C15-C10-C11-W1	121.7(3)	C10-C11-C12-C13	6.1(6)
W1-C11-C12-C13	-72.6(5)	C11-C12-C13-C14	-1.7(6)
C12-C13-C14-C16	-133.1(4)	C12-C13-C14-C15	-19.4(6)
C17-N8-C15-C10	-150.0(3)	C18-N8-C15-C10	42.8(5)
C17-N8-C15-C14	-25.7(4)	C18-N8-C15-C14	167.1(3)
C11-C10-C15-N8	82.0(4)	W1-C10-C15-N8	170.7(2)
C11-C10-C15-C14	-33.8(5)	W1-C10-C15-C14	54.9(4)
C13-C14-C15-N8	-86.4(4)	C16-C14-C15-N8	32.6(4)
C13-C14-C15-C10	35.7(5)	C16-C14-C15-C10	154.7(3)
C13-C14-C16-C17	89.3(4)	C15-C14-C16-C17	-29.8(4)
C18-N8-C17-O2	-3.4(6)	C15-N8-C17-O2	-170.8(4)
C18-N8-C17-C16	174.4(3)	C15-N8-C17-C16	7.0(4)
C14-C16-C17-O2	-167.2(4)	C14-C16-C17-N8	15.0(4)
C17-N8-C18-C19	99.1(4)	C15-N8-C18-C19	-94.9(4)
N8-C18-C19-O3	-178.8(4)	N1-N2-B1-N4	-53.5(5)
C3-N2-B1-N4	133.5(4)	N1-N2-B1-N6	61.3(4)
C3-N2-B1-N6	-111.6(4)	C6-N4-B1-N2	-128.3(5)
N3-N4-B1-N2	67.1(5)	C6-N4-B1-N6	114.6(5)
N3-N4-B1-N6	-50.0(5)	C9-N6-B1-N2	126.4(4)
N5-N6-B1-N2	-56.6(5)	C9-N6-B1-N4	-114.8(5)
N5-N6-B1-N4	62.2(5)	C23-N9-N10-C25	0.0(4)
W2-N9-N10-C25	177.8(3)	C23-N9-N10-B2	-178.8(3)

W2-N9-N10-B2	-0.9(4)	C26-N11-N12-C28	-0.2(4)
W2-N11-N12-C28	-175.8(3)	C26-N11-N12-B2	162.9(4)
W2-N11-N12-B2	-12.6(5)	C29-N13-N14-C31	-0.9(4)
W2-N13-N14-C31	172.9(3)	C29-N13-N14-B2	-169.9(3)
W2-N13-N14-B2	3.9(4)	N10-N9-C23-C24	0.0(4)
W2-N9-C23-C24	-177.4(3)	N9-C23-C24-C25	0.1(5)
N9-N10-C25-C24	0.1(5)	B2-N10-C25-C24	178.7(4)
C23-C24-C25-N10	-0.1(5)	N12-N11-C26-C27	0.7(5)
W2-N11-C26-C27	175.8(3)	N11-C26-C27-C28	-0.8(5)
N11-N12-C28-C27	-0.3(5)	B2-N12-C28-C27	-161.1(4)
C26-C27-C28-N12	0.7(5)	N14-N13-C29-C30	0.2(5)
W2-N13-C29-C30	-172.6(3)	N13-C29-C30-C31	0.6(5)
N13-N14-C31-C30	1.3(5)	B2-N14-C31-C30	169.2(4)
C29-C30-C31-N14	-1.2(5)	C37-C32-C33-C34	10.1(5)
W2-C32-C33-C34	-110.7(3)	C37-C32-C33-W2	120.8(3)
C32-C33-C34-C35	8.7(6)	W2-C33-C34-C35	-69.6(5)
C33-C34-C35-C36	-3.3(6)	C34-C35-C36-C38	-132.6(4)
C34-C35-C36-C37	-19.2(6)	C39-N16-C37-C32	-146.3(3)
C40-N16-C37-C32	37.2(5)	C39-N16-C37-C36	-22.4(4)

C40-N16-C37-C36	161.2(3)	C33-C32-C37-N16	81.4(4)
W2-C32-C37-N16	170.1(2)	C33-C32-C37-C36	-32.9(5)
W2-C32-C37-C36	55.8(4)	C35-C36-C37-N16	-85.0(4)
C38-C36-C37-N16	32.2(4)	C35-C36-C37-C32	36.0(5)
C38-C36-C37-C32	153.2(3)	C35-C36-C38-C39	86.3(4)
C37-C36-C38-C39	-32.0(4)	C40-N16-C39-O5	-1.4(6)
C37-N16-C39-O5	-177.9(4)	C40-N16-C39-C38	178.8(3)
C37-N16-C39-C38	2.3(4)	C36-C38-C39-O5	-160.7(4)
C36-C38-C39-N16	19.0(4)	C39-N16-C40-C41	-104.1(5)
C37-N16-C40-C41	71.9(5)	C39-N16-C40-C41A	-123.6(10)
C37-N16-C40-C41A	52.4(11)	C28-N12-B2-N10	-135.8(4)
N11-N12-B2-N10	64.9(4)	C28-N12-B2-N14	107.2(4)
N11-N12-B2-N14	-52.0(4)	C25-N10-B2-N12	124.6(4)
N9-N10-B2-N12	-56.9(5)	C25-N10-B2-N14	-120.4(4)
N9-N10-B2-N14	58.1(4)	C31-N14-B2-N12	-109.6(4)
N13-N14-B2-N12	57.1(4)	C31-N14-B2-N10	133.3(4)
N13-N14-B2-N10	-60.0(4)	N16-C40-C41-O6	177.0(4)
N16-C40-C41A-O6A	71.(3)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for compound 4.5

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01997(8)	0.01936(7)	0.01986(7)	0.00037(5)	0.00070(6)	-0.00083(5)
P1	0.0275(5)	0.0256(5)	0.0216(5)	0.0018(4)	0.0000(4)	0.0012(4)
O1	0.0384(17)	0.0232(13)	0.0264(14)	-0.0035(11)	-0.0012(12)	-0.0089(12)
O2	0.0269(16)	0.0472(18)	0.0442(18)	0.0144(14)	0.0101(14)	0.0082(13)
O3	0.076(3)	0.0462(19)	0.045(2)	-0.0082(17)	0.0040(19)	0.0205(19)
N1	0.0262(18)	0.0221(15)	0.0354(19)	0.0007(13)	-0.0078(15)	-0.0012(13)
N2	0.0286(19)	0.0248(16)	0.043(2)	0.0044(15)	-0.0100(16)	-0.0011(14)
N3	0.0219(17)	0.0258(15)	0.0339(18)	0.0066(14)	0.0051(14)	0.0002(13)
N4	0.0218(18)	0.0327(18)	0.046(2)	0.0106(16)	0.0070(16)	-0.0024(14)
N5	0.0231(17)	0.0216(15)	0.0288(17)	0.0013(12)	0.0046(14)	-0.0044(12)
N6	0.0225(18)	0.0262(16)	0.040(2)	0.0088(14)	0.0023(15)	-0.0053(13)
N7	0.0242(17)	0.0228(15)	0.0200(15)	0.0035(12)	0.0037(13)	-0.0008(12)
N8	0.0233(18)	0.0361(17)	0.0237(16)	0.0029(14)	0.0050(14)	0.0057(14)
C1	0.045(3)	0.031(2)	0.030(2)	-0.0073(17)	-0.010(2)	0.0045(19)
C2	0.067(4)	0.030(2)	0.032(2)	-0.0029(18)	-0.016(2)	0.003(2)
C3	0.039(3)	0.0227(19)	0.054(3)	0.0057(19)	-0.024(2)	-0.0029(18)
C4	0.033(2)	0.034(2)	0.030(2)	0.0052(17)	0.0088(18)	0.0074(17)
C5	0.032(3)	0.053(3)	0.044(3)	0.005(2)	0.015(2)	0.013(2)
C6	0.024(2)	0.050(3)	0.052(3)	0.016(2)	0.011(2)	0.003(2)
C7	0.025(2)	0.0248(17)	0.0208(18)	-0.0010(14)	0.0007(15)	-0.0028(15)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	0.040(3)	0.030(2)	0.027(2)	0.0063(16)	0.0066(18)	-0.0039(18)
C9	0.033(2)	0.029(2)	0.039(2)	0.0091(18)	0.0042(19)	-0.0095(17)
C10	0.024(2)	0.0276(19)	0.0215(18)	-0.0028(15)	0.0021(15)	0.0027(15)
C11	0.028(2)	0.036(2)	0.0188(19)	-0.0011(16)	0.0007(16)	0.0052(17)
C12	0.028(2)	0.038(2)	0.026(2)	0.0104(17)	0.0098(17)	0.0052(17)
C13	0.027(2)	0.032(2)	0.029(2)	0.0064(16)	0.0065(17)	-0.0024(16)
C14	0.021(2)	0.034(2)	0.0242(19)	0.0019(16)	0.0014(15)	-0.0020(16)
C15	0.023(2)	0.0300(19)	0.0205(18)	0.0047(15)	0.0039(15)	0.0031(15)
C16	0.021(2)	0.040(2)	0.032(2)	0.0056(17)	0.0016(17)	-0.0017(17)
C17	0.027(2)	0.042(2)	0.028(2)	0.0152(17)	0.0063(17)	0.0053(18)
C18	0.034(2)	0.033(2)	0.029(2)	0.0034(17)	0.0036(18)	0.0126(18)
C19	0.047(3)	0.038(2)	0.030(2)	0.0009(18)	0.008(2)	0.012(2)
C20	0.039(3)	0.049(3)	0.023(2)	0.0073(18)	0.0009(18)	0.009(2)
C21	0.059(3)	0.026(2)	0.039(3)	0.0087(18)	-0.004(2)	-0.007(2)
C22	0.031(3)	0.053(3)	0.040(3)	0.009(2)	-0.002(2)	0.007(2)
B1	0.021(2)	0.026(2)	0.057(3)	0.013(2)	0.000(2)	-0.0025(18)
W2	0.02005(8)	0.02051(7)	0.01853(7)	0.00038(5)	0.00237(5)	0.00286(5)
P2	0.0264(5)	0.0231(4)	0.0214(5)	-0.0008(4)	0.0039(4)	0.0002(4)
O4	0.0394(17)	0.0284(14)	0.0210(14)	0.0064(11)	0.0004(12)	0.0075(12)
O5	0.0245(16)	0.061(2)	0.047(2)	-0.0215(16)	0.0089(14)	-0.0081(14)
N9	0.0190(16)	0.0235(15)	0.0239(16)	0.0000(12)	0.0031(13)	0.0035(12)
N10	0.0192(16)	0.0269(15)	0.0283(17)	0.0024(13)	0.0026(13)	0.0036(13)
N11	0.0220(17)	0.0264(15)	0.0270(17)	0.0000(13)	0.0065(13)	0.0001(13)
N12	0.0239(18)	0.0309(16)	0.0259(17)	-0.0025(13)	0.0053(14)	0.0033(13)
N13	0.0195(16)	0.0271(15)	0.0230(16)	-0.0008(12)	0.0033(13)	0.0028(12)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N14	0.0233(18)	0.0282(16)	0.0296(18)	-0.0031(13)	0.0044(14)	0.0031(13)
N15	0.0267(17)	0.0241(15)	0.0179(15)	0.0001(12)	0.0047(13)	0.0023(13)
N16	0.0253(18)	0.0346(17)	0.0250(17)	-0.0040(14)	0.0055(14)	-0.0029(14)
C23	0.024(2)	0.0282(19)	0.0258(19)	0.0047(15)	0.0022(16)	-0.0002(15)
C24	0.033(2)	0.033(2)	0.031(2)	0.0120(17)	0.0003(18)	0.0017(17)
C25	0.026(2)	0.030(2)	0.040(2)	0.0093(17)	-0.0002(18)	0.0060(16)
C26	0.039(3)	0.030(2)	0.034(2)	0.0021(17)	0.0145(19)	-0.0012(18)
C27	0.038(3)	0.037(2)	0.044(3)	0.005(2)	0.013(2)	-0.0080(19)
C28	0.024(2)	0.046(2)	0.032(2)	-0.0007(18)	0.0093(17)	-0.0021(18)
C29	0.027(2)	0.032(2)	0.025(2)	-0.0047(16)	0.0004(16)	0.0027(16)
C30	0.036(3)	0.045(2)	0.029(2)	-0.0147(19)	0.0034(19)	0.001(2)
C31	0.035(3)	0.035(2)	0.045(3)	-0.0110(19)	0.013(2)	0.0081(18)
C32	0.0206(19)	0.0217(17)	0.0224(18)	0.0003(14)	0.0032(15)	0.0002(14)
C33	0.0217(19)	0.0281(18)	0.0181(18)	0.0008(14)	0.0016(15)	0.0021(15)
C34	0.026(2)	0.0275(18)	0.0244(19)	-0.0015(15)	0.0065(16)	0.0011(15)
C35	0.025(2)	0.0291(19)	0.029(2)	-0.0038(16)	0.0016(16)	0.0074(16)
C36	0.026(2)	0.033(2)	0.0252(19)	-0.0023(16)	0.0011(16)	0.0076(16)
C37	0.022(2)	0.0290(19)	0.0232(19)	-0.0038(15)	0.0048(15)	0.0017(15)
C38	0.023(2)	0.046(2)	0.032(2)	-0.0075(18)	-0.0032(17)	0.0091(18)
C39	0.024(2)	0.047(2)	0.030(2)	-0.0183(18)	0.0051(17)	-0.0023(18)
C40	0.038(3)	0.046(2)	0.025(2)	0.0013(18)	0.0017(18)	-0.014(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C42	0.053(3)	0.036(2)	0.0199(19)	-0.0002(16)	0.0062(19)	-0.008(2)
C43	0.039(3)	0.0235(18)	0.038(2)	-0.0028(17)	0.004(2)	0.0046(17)
C44	0.027(2)	0.041(2)	0.041(3)	-0.0118(19)	0.0008(19)	-0.0032(18)
B2	0.023(2)	0.028(2)	0.035(2)	-0.0006(18)	0.0057(19)	0.0060(18)
O6	0.074(3)	0.029(2)	0.042(2)	0.0030(17)	-0.016(2)	-0.005(2)
C41	0.052(4)	0.028(3)	0.033(3)	-0.002(2)	-0.013(4)	-0.014(3)
O6A	0.036(11)	0.040(11)	0.055(14)	0.016(9)	-0.007(9)	0.007(8)
C41A	0.052(4)	0.028(3)	0.033(3)	-0.002(2)	-0.013(4)	-0.014(3)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for compound 4.5

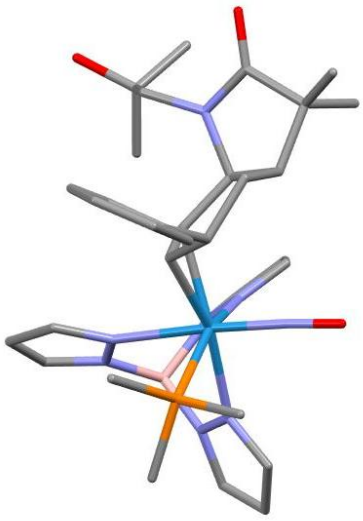
	x/a	y/b	z/c	U(eq)
H3	0.279(5)	0.560(4)	0.381(3)	0.085000
H1	0.5234	0.4373	0.3558	0.045000
H2A	0.6356	0.5540	0.3747	0.055000
H3A	0.7299	0.5629	0.2934	0.051000
H4	0.6360	0.1928	0.1740	0.038000
H5	0.8133	0.2174	0.1549	0.050000
H6B	0.8496	0.3586	0.1770	0.050000
H7	0.3503	0.4244	0.1028	0.029000
H8	0.4325	0.5197	0.0443	0.039000
H9	0.6123	0.5383	0.0971	0.041000
H10	0.376(3)	0.445(2)	0.2527(16)	0.020(10)
H11	0.396(4)	0.347(3)	0.316(2)	0.037(13)
H12	0.2994	0.2357	0.3065	0.036000
H13	0.1727	0.2228	0.2310	0.035000
H14	0.2211	0.3019	0.1490	0.032000
H15	0.2570	0.4303	0.1652	0.029000
H16A	0.0630	0.3589	0.1279	0.038000
H16B	0.0391	0.3013	0.1774	0.038000

	x/a	y/b	z/c	U(eq)
H18A	0.1229	0.5441	0.2534	0.039000
H18B	0.2425	0.5410	0.2492	0.039000
H19A	0.1563	0.4652	0.3370	0.046000
H19B	0.2764	0.4641	0.3331	0.046000
H20A	0.5575	0.2932	0.3910	0.056000
H20B	0.5668	0.2009	0.3976	0.056000
H20C	0.4579	0.2398	0.3726	0.056000
H21A	0.4512	0.1298	0.2786	0.064000
H21B	0.5604	0.1018	0.3134	0.064000
H21C	0.5480	0.1232	0.2468	0.064000
H22A	0.7275	0.2148	0.2863	0.064000
H22B	0.7225	0.2023	0.3527	0.064000
H22C	0.7253	0.2882	0.3274	0.064000
H1A	0.735(3)	0.489(2)	0.1893(17)	0.029(11)
H23	0.0469	0.3211	0.3339	0.032000
H24	-0.0876	0.4222	0.3018	0.040000
H25	-0.1861	0.4357	0.3822	0.039000
H26	-0.0644	0.0890	0.5196	0.040000
H27	-0.2428	0.1087	0.5388	0.047000
H28	-0.2905	0.2461	0.5117	0.040000
H29	0.1850	0.3170	0.5992	0.034000
H30	0.0905	0.4136	0.6493	0.044000
H31	-0.0797	0.4337	0.5853	0.045000
H32	0.194(3)	0.348(2)	0.4556(16)	0.018(10)
H33	0.183(3)	0.258(2)	0.3817(18)	0.022(10)
H34	0.2854	0.1466	0.3915	0.031000
H35	0.3991	0.1235	0.4709	0.034000
H36	0.3355	0.1896	0.5543	0.034000
H37	0.2997	0.3201	0.5454	0.030000
H38A	0.4925	0.2478	0.5855	0.042000
H38B	0.5234	0.1937	0.5357	0.042000
H40A	0.3295	0.3998	0.4229	0.044000
H40B	0.4498	0.4182	0.4407	0.044000
H40C	0.3478	0.3958	0.4171	0.044000
H40D	0.4542	0.4291	0.4521	0.044000

	x/a	y/b	z/c	U(eq)
H42A	0.0005	0.1810	0.3044	0.055000
H42B	0.0381	0.0934	0.2991	0.055000
H42C	0.1204	0.1602	0.3203	0.055000
H43A	0.1840	0.0453	0.4079	0.051000
H43B	0.0832	-0.0066	0.3886	0.051000
H43C	0.1135	0.0225	0.4536	0.051000
H44A	-0.1018	0.0554	0.4193	0.055000
H44B	-0.1029	0.0486	0.3518	0.055000
H44C	-0.1426	0.1263	0.3777	0.055000
H2	-0.191(3)	0.375(2)	0.4839(17)	0.028(11)
H6	0.388(6)	0.590(4)	0.470(3)	0.078000
H41A	0.2956	0.4698	0.5025	0.049000
H41B	0.4169	0.4856	0.5232	0.049000
H6A	0.3510	0.5281	0.5525	0.069000
H41C	0.3042	0.5118	0.4579	0.049000
H41D	0.2633	0.4443	0.4945	0.049000

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 4.5

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3-H3···O6^a	0.86(7)	1.82(7)	2.644(5)	161.(7)
$O6^{a-H6}$a···O5#1	1.03(8)	1.54(8)	2.564(5)	174.(7)



Structure Tables

A colourless, plate-shaped crystal of **compound** 4.52 measuring 0.089×0.084×0.042 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data were collected from a shock-cooled single crystal at 100.00 K on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer with a microfocus sealed X-ray tube using a HELIOS double bounce multilayer mirror as monochromator and a PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used Mo K_α radiation (λ = 0.71073 Å). Data collection and processing were done within the Bruker APEX5 software suite.[121] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[122] and refined by full-matrix least-squares methods against F^2 using XL[123] within OLEX2.[124] All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms as well as the H atoms on the carbons bound directly to W were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[125]

[121] *APEX5, Saint, SADABS*; Bruker AXS Inc. 2019.
[122] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[123] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[124] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[125] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1. Crystal data and structure refinement for compound 4.52

CCDC number	
Empirical formula	$C_{32}H_{46}BN_8O_3PW$
Formula weight	816.40
Temperature [K]	100.00
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	15.8125(4)
b [Å]	11.4375(3)
c [Å]	19.7702(5)
α [°]	90
β [°]	95.1980(10)
γ [°]	90
Volume [Å^3]	3560.84(16)
Z	4
ρ_{calc} [gcm^{-3}]	1.523
μ [mm^{-1}]	3.333
F(000)	1648
Crystal size [mm^3]	0.089×0.084×0.042
Crystal colour	colourless
Crystal shape	plate
Radiation	Mo K_α (λ=0.71073 Å)
2θ range [°]	4.12 to 56.61 (0.75 Å)
Index ranges	−18 ≤ h ≤ 21 −15 ≤ k ≤ 15 −26 ≤ l ≤ 26
Reflections collected	65080
Independent reflections	8840 R_{int} = 0.0602 R_{sigma} = 0.0385
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	8840/1/437
Absorption correction	0.6600/0.7457
T_{min}/T_{max} (method)	(Multi-Scan)
Goodness-of-fit on F^2	0.995
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0256 wR_2 = 0.0510
Final *R* indexes [all data]	R_1 = 0.0520 wR_2 = 0.0596

Largest peak/hole [eÅ^{-3}]	1.17/−0.53

Table 2. Atomic coordinates and U_{eq} [Å^2] compound 4.52

Atom	*x*	*y*	*z*	U_{eq}
W1	0.19678(2)	0.49967(2)	0.35044(2)	0.01379(4)
P1	0.10676(5)	0.35348(7)	0.28358(5)	0.01846(17)
O1	0.05468(14)	0.6740(2)	0.33526(13)	0.0270(6)
O2	0.40779(14)	0.9393(2)	0.21106(12)	0.0258(5)
O3	0.59668(14)	0.6821(2)	0.31305(13)	0.0247(5)
H3	0.599(3)	0.6144(18)	0.304(2)	0.050(15)
N1	0.29770(16)	0.3606(2)	0.36856(13)	0.0166(5)
N2	0.32779(16)	0.3323(2)	0.43347(13)	0.0187(6)
N3	0.14446(16)	0.4169(2)	0.43886(13)	0.0182(6)
N4	0.19698(17)	0.3717(2)	0.49117(13)	0.0204(6)
N5	0.26275(16)	0.5875(2)	0.43998(13)	0.0183(6)
N6	0.30721(17)	0.5250(2)	0.49034(13)	0.0199(6)
N7	0.11451(16)	0.6043(2)	0.34041(13)	0.0166(5)
N8	0.37308(16)	0.7702(2)	0.26481(13)	0.0174(6)
C1	0.34173(19)	0.2948(3)	0.32795(17)	0.0192(7)
H1	0.334333	0.296365	0.279729	0.023
C2	0.3994(2)	0.2245(3)	0.36572(17)	0.0223(7)
H2	0.437734	0.169652	0.349310	0.027
C3	0.3890(2)	0.2513(3)	0.43189(18)	0.0231(7)
H3A	0.420140	0.217907	0.470503	0.028
C4	0.0652(2)	0.4058(3)	0.45705(18)	0.0236(7)
H4	0.015423	0.431197	0.430554	0.028
C5	0.0660(2)	0.3519(3)	0.52026(18)	0.0296(8)
H5	0.018695	0.332866	0.544491	0.035
C6	0.1502(2)	0.3323(3)	0.53982(18)	0.0268(8)
H6	0.171922	0.296487	0.581154	0.032
C7	0.2663(2)	0.6989(3)	0.46000(17)	0.0248(8)
H7	0.239635	0.762088	0.435233	0.030
C8	0.3144(2)	0.7097(3)	0.52206(18)	0.0292(8)
H8	0.327539	0.779571	0.546822	0.035
C9	0.3386(2)	0.5985(3)	0.53984(17)	0.0270(8)
H9	0.371939	0.576493	0.580231	0.032
C10	0.2925(2)	0.5899(3)	0.29513(16)	0.0164(6)
H10	0.345(2)	0.558(3)	0.3094(17)	0.020
C11	0.23830(19)	0.5267(2)	0.24544(16)	0.0148(7)
H11	0.264(2)	0.464(3)	0.2276(16)	0.013(8)
C12	0.1812(2)	0.5930(3)	0.19186(16)	0.0190(7)

H12	0.121468	0.588013	0.204388	0.023
C13	0.2049(2)	0.7223(3)	0.18718(17)	0.0225(7)
H13A	0.255062	0.728713	0.160829	0.027
H13B	0.157410	0.763784	0.161430	0.027
C14	0.22496(19)	0.7845(3)	0.25518(16)	0.0160(6)
H14	0.173661	0.789297	0.281144	0.019
C15	0.29806(19)	0.7208(3)	0.29602(16)	0.0168(6)
H15	0.300303	0.747689	0.344271	0.020
C16	0.3561(2)	0.8766(3)	0.23727(16)	0.0199(7)
C17	0.26343(19)	0.9070(3)	0.24493(17)	0.0189(7)
C18	0.2593(2)	0.9805(3)	0.30945(18)	0.0262(8)
H18A	0.199876	0.992614	0.317948	0.039
H18B	0.286502	1.056381	0.303477	0.039
H18C	0.289058	0.939518	0.348131	0.039
C19	0.2247(2)	0.9764(3)	0.18392(18)	0.0249(8)
H19A	0.227904	0.930296	0.142469	0.037
H19B	0.256173	1.049655	0.180256	0.037
H19C	0.165171	0.994017	0.189853	0.037
C20	0.45601(19)	0.7156(3)	0.26403(16)	0.0187(7)
H20A	0.485827	0.753007	0.227801	0.022
H20B	0.447284	0.632393	0.251365	0.022
C21	0.51457(19)	0.7205(3)	0.33016(17)	0.0212(7)
C22	0.4852(2)	0.6425(3)	0.38573(17)	0.0256(8)
H22A	0.477411	0.562475	0.368492	0.038
H22B	0.431182	0.671839	0.399688	0.038
H22C	0.527948	0.642763	0.424829	0.038
C23	0.5270(2)	0.8458(3)	0.3543(2)	0.0319(8)
H23A	0.569193	0.848029	0.393705	0.048
H23B	0.472888	0.876958	0.367029	0.048
H23C	0.546769	0.893420	0.317623	0.048
C24	0.1837(2)	0.5434(3)	0.12009(18)	0.0257(8)
C25	0.1133(3)	0.5515(5)	0.0733(2)	0.0499(12)
H25	0.061666	0.581551	0.087243	0.060
C26	0.1168(3)	0.5163(5)	0.0057(2)	0.0666(17)
H26	0.068301	0.523758	-0.026030	0.080
C27	0.1903(3)	0.4713(4)	-0.0140(2)	0.0537(14)
H27	0.192767	0.445434	-0.059426	0.064
C28	0.2605(3)	0.4632(4)	0.0312(2)	0.0458(11)
H28	0.311764	0.432334	0.016927	0.055
C29	0.2576(2)	0.4995(3)	0.09742(18)	0.0346(8)

H29	0.307290	0.494299	0.128090	0.042
C30	0.0031(2)	0.4111(3)	0.2532(2)	0.0375(10)
H30A	-0.031009	0.349021	0.230016	0.056
H30B	0.010118	0.475380	0.221357	0.056
H30C	-0.025655	0.440061	0.291724	0.056
C31	0.1411(2)	0.2861(3)	0.20753(17)	0.0256(8)
H31A	0.098691	0.228675	0.189870	0.038
H31B	0.195707	0.246910	0.218567	0.038
H31C	0.147389	0.346370	0.173110	0.038
C32	0.0801(3)	0.2226(3)	0.32954(19)	0.0351(9)
H32A	0.044802	0.244070	0.365887	0.053
H32B	0.132333	0.185110	0.349253	0.053
H32C	0.048734	0.168238	0.298217	0.053
B1	0.2937(2)	0.3915(4)	0.4946(2)	0.0225(8)
H1A	0.3255(19)	0.355(3)	0.5426(16)	0.020(9)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters [Å^2] for compound 4.52
The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01429(6)	0.01216(6)	0.01519(6)	−0.00021(6)	0.00280(4)	0.00056(6)
P1	0.0170(4)	0.0146(4)	0.0242(4)	−0.0028(4)	0.0036(3)	−0.0014(3)
O1	0.0212(12)	0.0240(13)	0.0365(15)	0.0068(11)	0.0058(11)	0.0096(10)
O2	0.0216(12)	0.0209(13)	0.0356(14)	0.0096(11)	0.0057(11)	−0.0017(10)
O3	0.0156(11)	0.0229(14)	0.0361(15)	0.0022(12)	0.0043(10)	0.0022(10)
N1	0.0185(13)	0.0160(13)	0.0155(13)	0.0024(11)	0.0026(11)	0.0003(11)
N2	0.0218(14)	0.0174(14)	0.0167(14)	0.0024(11)	0.0005(11)	0.0013(11)
N3	0.0199(13)	0.0174(14)	0.0178(14)	0.0028(11)	0.0044(11)	0.0022(11)
N4	0.0257(14)	0.0177(14)	0.0183(14)	0.0016(11)	0.0051(12)	0.0016(11)
N5	0.0231(14)	0.0152(13)	0.0168(14)	−0.0015(11)	0.0020(11)	0.0003(11)
N6	0.0235(14)	0.0204(17)	0.0159(13)	0.0002(11)	0.0024(11)	−0.0011(11)
N7	0.0180(13)	0.0157(13)	0.0163(14)	0.0000(11)	0.0021(11)	0.0006(11)
N8	0.0149(13)	0.0150(13)	0.0228(14)	0.0022(11)	0.0040(11)	−0.0009(10)
C1	0.0194(16)	0.0171(16)	0.0213(17)	−0.0007(13)	0.0033(13)	0.0005(13)
C2	0.0194(16)	0.0182(17)	0.0298(19)	0.0011(14)	0.0048(14)	0.0040(13)
C3	0.0208(17)	0.0212(17)	0.0264(18)	0.0068(14)	−0.0019(14)	0.0055(13)
C4	0.0209(16)	0.0207(17)	0.031(2)	−0.0018(15)	0.0094(15)	0.0013(14)
C5	0.035(2)	0.0250(19)	0.031(2)	0.0033(16)	0.0189(17)	0.0001(16)
C6	0.037(2)	0.0226(18)	0.0227(18)	0.0039(15)	0.0140(16)	−0.0005(15)

C7	0.0344(19)	0.0190(17)	0.0224(18)	−0.0019(14)	0.0101(15)	−0.0019(15)
C8	0.038(2)	0.027(2)	0.0237(19)	−0.0098(16)	0.0075(16)	−0.0072(16)
C9	0.0270(18)	0.037(2)	0.0168(17)	−0.0046(15)	0.0012(14)	−0.0038(16)
C10	0.0178(15)	0.0142(15)	0.0175(16)	0.0011(13)	0.0029(13)	−0.0026(12)
C11	0.0159(14)	0.0145(17)	0.0148(15)	−0.0007(11)	0.0054(12)	0.0009(11)
C12	0.0185(15)	0.0197(17)	0.0195(17)	0.0017(13)	0.0044(13)	−0.0016(13)
C13	0.0213(17)	0.0190(17)	0.0264(18)	0.0005(14)	−0.0012(14)	0.0016(13)
C14	0.0158(15)	0.0134(15)	0.0189(16)	−0.0008(13)	0.0024(12)	−0.0003(12)
C15	0.0188(15)	0.0148(15)	0.0172(16)	0.0018(13)	0.0036(13)	−0.0015(12)
C16	0.0203(16)	0.0210(17)	0.0185(17)	−0.0005(14)	0.0019(13)	−0.0020(13)
C17	0.0184(15)	0.0142(16)	0.0247(18)	−0.0002(13)	0.0045(13)	−0.0005(12)
C18	0.0319(18)	0.015(2)	0.0318(19)	−0.0040(14)	0.0052(15)	0.0008(13)
C19	0.0222(16)	0.021(2)	0.0316(19)	0.0054(14)	0.0027(14)	0.0033(13)
C20	0.0171(15)	0.0177(16)	0.0222(17)	−0.0004(13)	0.0061(13)	0.0005(12)
C21	0.0139(15)	0.0203(17)	0.0294(19)	−0.0004(14)	0.0019(14)	0.0006(13)
C22	0.0220(17)	0.032(2)	0.0225(18)	0.0041(16)	0.0014(14)	−0.0004(15)
C23	0.0291(19)	0.0253(19)	0.040(2)	−0.0054(17)	−0.0032(17)	−0.0008(15)
C24	0.033(2)	0.0213(16)	0.0229(18)	0.0015(15)	0.0030(15)	−0.0065(15)
C25	0.036(2)	0.084(4)	0.029(2)	−0.008(2)	0.0002(19)	−0.008(2)
C26	0.054(3)	0.118(5)	0.026(2)	−0.016(3)	−0.004(2)	−0.031(3)
C27	0.078(4)	0.059(3)	0.027(2)	−0.014(2)	0.014(2)	−0.027(3)
C28	0.072(3)	0.029(2)	0.040(3)	−0.0037(18)	0.019(2)	0.003(2)
C29	0.045(2)	0.0324(19)	0.0266(18)	−0.001(2)	0.0044(16)	0.007(2)
C30	0.0169(17)	0.034(2)	0.059(3)	−0.018(2)	−0.0086(17)	0.0024(15)
C31	0.0288(18)	0.0218(18)	0.0263(19)	−0.0073(15)	0.0030(15)	−0.0045(15)
C32	0.055(2)	0.0170(18)	0.036(2)	−0.0055(16)	0.0178(19)	−0.0170(17)
B1	0.026(2)	0.024(2)	0.018(2)	0.0021(16)	0.0036(16)	0.0029(16)

Table 4. Bond lengths and angles for compound 4.52

Atom–Atom	Length [Å]
W1–P1	2.4957(9)
W1–N1	2.259(3)
W1–N3	2.213(3)
W1–N5	2.213(3)
W1–N7	1.765(3)
W1–C10	2.203(3)
W1–C11	2.255(3)
P1–C30	1.818(4)
P1–C31	1.816(3)
P1–C32	1.820(3)

O1–N7	1.235(3)
O2–C16	1.236(4)
O3–H3	0.794(19)
O3–C21	1.440(4)
N1–N2	1.366(3)
N1–C1	1.340(4)
N2–C3	1.343(4)
N2–B1	1.526(4)
N3–N4	1.368(4)
N3–C4	1.341(4)
N4–C6	1.344(4)
N4–B1	1.541(5)
N5–N6	1.367(4)
N5–C7	1.333(4)
N6–C9	1.350(4)
N6–B1	1.546(5)
N8–C15	1.497(4)
N8–C16	1.350(4)
N8–C20	1.454(4)
C1–H1	0.9500
C1–C2	1.383(4)
C2–H2	0.9500
C2–C3	1.368(5)
C3–H3A	0.9500
C4–H4	0.9500
C4–C5	1.393(5)
C5–H5	0.9500
C5–C6	1.370(5)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.389(5)
C8–H8	0.9500
C8–C9	1.366(5)
C9–H9	0.9500
C10–H10	0.93(3)
C10–C11	1.439(4)
C10–C15	1.499(4)
C11–H11	0.91(3)
C11–C12	1.529(4)
C12–H12	1.0000

C12–C13	1.530(4)
C12–C24	1.532(5)
C13–H13A	0.9900
C13–H13B	0.9900
C13–C14	1.529(4)
C14–H14	1.0000
C14–C15	1.533(4)
C14–C17	1.548(4)
C15–H15	1.0000
C16–C17	1.527(4)
C17–C18	1.534(4)
C17–C19	1.525(4)
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C19–H19A	0.9800
C19–H19B	0.9800
C19–H19C	0.9800
C20–H20A	0.9900
C20–H20B	0.9900
C20–C21	1.533(4)
C21–C22	1.521(4)
C21–C23	1.518(5)
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–C25	1.384(5)
C24–C29	1.383(5)
C25–H25	0.9500
C25–C26	1.401(6)
C26–H26	0.9500
C26–C27	1.360(7)
C27–H27	0.9500
C27–C28	1.363(7)
C28–H28	0.9500
C28–C29	1.379(5)
C29–H29	0.9500

C30–H30A	0.9800
C30–H30B	0.9800
C30–H30C	0.9800
C31–H31A	0.9800
C31–H31B	0.9800
C31–H31C	0.9800
C32–H32A	0.9800
C32–H32B	0.9800
C32–H32C	0.9800
B1–H1A	1.11(3)

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	88.46(7)
N3–W1–P1	84.02(7)
N3–W1–N1	83.28(9)
N3–W1–C11	161.24(10)
N5–W1–P1	158.89(7)
N5–W1–N1	85.29(9)
N5–W1–N3	75.24(10)
N5–W1–C11	121.25(10)
N7–W1–P1	90.87(9)
N7–W1–N1	176.36(10)
N7–W1–N3	93.10(10)
N7–W1–N5	94.09(11)
N7–W1–C10	99.17(12)
N7–W1–C11	94.39(11)
C10–W1–P1	115.83(8)
C10–W1–N1	84.33(10)
C10–W1–N3	156.25(11)
C10–W1–N5	83.62(11)
C10–W1–C11	37.64(11)
C11–W1–P1	78.69(8)
C11–W1–N1	88.98(10)
C30–P1–W1	112.71(12)
C30–P1–C32	102.7(2)
C31–P1–W1	121.60(11)
C31–P1–C30	102.02(18)
C31–P1–C32	99.47(17)
C32–P1–W1	115.68(13)

C21–O3–H3	114(3)
N2–N1–W1	119.77(18)
C1–N1–W1	134.3(2)
C1–N1–N2	105.9(2)
N1–N2–B1	121.4(3)
C3–N2–N1	109.4(3)
C3–N2–B1	129.2(3)
N4–N3–W1	120.93(19)
C4–N3–W1	132.7(2)
C4–N3–N4	106.2(3)
N3–N4–B1	120.7(3)
C6–N4–N3	109.4(3)
C6–N4–B1	128.8(3)
N6–N5–W1	121.27(19)
C7–N5–W1	132.5(2)
C7–N5–N6	106.2(3)
N5–N6–B1	119.5(3)
C9–N6–N5	109.5(3)
C9–N6–B1	128.2(3)
O1–N7–W1	176.9(2)
C16–N8–C15	111.8(2)
C16–N8–C20	122.0(3)
C20–N8–C15	126.2(2)
N1–C1–H1	124.6
N1–C1–C2	110.8(3)
C2–C1–H1	124.6
C1–C2–H2	127.6
C3–C2–C1	104.8(3)
C3–C2–H2	127.6
N2–C3–C2	109.0(3)
N2–C3–H3A	125.5
C2–C3–H3A	125.5
N3–C4–H4	124.8
N3–C4–C5	110.4(3)
C5–C4–H4	124.8
C4–C5–H5	127.6
C6–C5–C4	104.9(3)
C6–C5–H5	127.6
N4–C6–C5	109.1(3)
N4–C6–H6	125.5

C5–C6–H6	125.5
N5–C7–H7	124.7
N5–C7–C8	110.6(3)
C8–C7–H7	124.7
C7–C8–H8	127.4
C9–C8–C7	105.2(3)
C9–C8–H8	127.4
N6–C9–C8	108.5(3)
N6–C9–H9	125.8
C8–C9–H9	125.8
W1–C10–H10	107(2)
C11–C10–W1	73.11(17)
C11–C10–H10	118(2)
C11–C10–C15	122.7(3)
C15–C10–W1	120.2(2)
C15–C10–H10	110(2)
W1–C11–H11	115(2)
C10–C11–W1	69.25(17)
C10–C11–H11	113(2)
C10–C11–C12	120.1(3)
C12–C11–W1	120.2(2)
C12–C11–H11	112(2)
C11–C12–H12	108.2
C11–C12–C13	112.9(3)
C11–C12–C24	113.3(3)
C13–C12–H12	108.2
C13–C12–C24	105.9(3)
C24–C12–H12	108.2
C12–C13–H13A	108.4
C12–C13–H13B	108.4
H13A–C13–H13B	107.5
C14–C13–C12	115.4(3)
C14–C13–H13A	108.4
C14–C13–H13B	108.4
C13–C14–H14	111.3
C13–C14–C15	109.2(3)
C13–C14–C17	111.0(3)
C15–C14–H14	111.3
C15–C14–C17	102.3(2)
C17–C14–H14	111.3

N8–C15–C10	114.8(2)
N8–C15–C14	101.0(2)
N8–C15–H15	108.4
C10–C15–C14	115.4(3)
C10–C15–H15	108.4
C14–C15–H15	108.4
O2–C16–N8	125.3(3)
O2–C16–C17	125.9(3)
N8–C16–C17	108.8(3)
C16–C17–C14	101.5(2)
C16–C17–C18	108.7(3)
C18–C17–C14	109.9(3)
C19–C17–C14	116.1(3)
C19–C17–C16	111.1(3)
C19–C17–C18	109.1(3)
C17–C18–H18A	109.5
C17–C18–H18B	109.5
C17–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
C17–C19–H19A	109.5
C17–C19–H19B	109.5
C17–C19–H19C	109.5
H19A–C19–H19B	109.5
H19A–C19–H19C	109.5
H19B–C19–H19C	109.5
N8–C20–H20A	108.1
N8–C20–H20B	108.1
N8–C20–C21	116.8(3)
H20A–C20–H20B	107.3
C21–C20–H20A	108.1
C21–C20–H20B	108.1
O3–C21–C20	106.0(3)
O3–C21–C22	109.4(3)
O3–C21–C23	105.6(3)
C22–C21–C20	113.2(3)
C23–C21–C20	110.7(3)
C23–C21–C22	111.5(3)
C21–C22–H22A	109.5

C21–C22–H22B	109.5
C21–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
C21–C23–H23A	109.5
C21–C23–H23B	109.5
C21–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
C25–C24–C12	120.6(3)
C29–C24–C12	121.8(3)
C29–C24–C25	117.3(3)
C24–C25–H25	119.4
C24–C25–C26	121.3(4)
C26–C25–H25	119.4
C25–C26–H26	120.3
C27–C26–C25	119.4(4)
C27–C26–H26	120.3
C26–C27–H27	119.9
C26–C27–C28	120.3(4)
C28–C27–H27	119.9
C27–C28–H28	119.8
C27–C28–C29	120.4(4)
C29–C28–H28	119.8
C24–C29–H29	119.4
C28–C29–C24	121.3(4)
C28–C29–H29	119.4
P1–C30–H30A	109.5
P1–C30–H30B	109.5
P1–C30–H30C	109.5
H30A–C30–H30B	109.5
H30A–C30–H30C	109.5
H30B–C30–H30C	109.5
P1–C31–H31A	109.5
P1–C31–H31B	109.5
P1–C31–H31C	109.5
H31A–C31–H31B	109.5
H31A–C31–H31C	109.5

H31B–C31–H31C	109.5
P1–C32–H32A	109.5
P1–C32–H32B	109.5
P1–C32–H32C	109.5
H32A–C32–H32B	109.5
H32A–C32–H32C	109.5
H32B–C32–H32C	109.5
N2–B1–N4	108.7(3)
N2–B1–N6	109.5(3)
N2–B1–H1A	110.1(16)
N4–B1–N6	106.5(3)
N4–B1–H1A	110.6(16)
N6–B1–H1A	111.3(17)

Table 5. Torsion angles for compound 4.52

Atom–Atom–Atom–Atom	Torsion Angle [°]
W1–N1–N2–C3	−177.8(2)
W1–N1–N2–B1	0.9(4)
W1–N1–C1–C2	177.8(2)
W1–N3–N4–C6	176.9(2)
W1–N3–N4–B1	8.2(4)
W1–N3–C4–C5	−176.3(2)
W1–N5–N6–C9	−177.9(2)
W1–N5–N6–B1	−15.3(4)
W1–N5–C7–C8	177.8(2)
W1–C10–C11–C12	113.7(3)
W1–C10–C15–N8	171.9(2)
W1–C10–C15–C14	−71.3(3)
W1–C11–C12–C13	96.2(3)
W1–C11–C12–C24	−143.4(2)
O2–C16–C17–C14	160.0(3)
O2–C16–C17–C18	−84.2(4)
O2–C16–C17–C19	35.9(5)
N1–N2–C3–C2	−0.6(4)
N1–N2–B1–N4	57.6(4)
N1–N2–B1–N6	−58.4(4)
N1–C1–C2–C3	−0.5(4)
N2–N1–C1–C2	0.2(3)
N3–N4–C6–C5	−0.4(4)

N3–N4–B1–N2	−63.7(4)
N3–N4–B1–N6	54.2(4)
N3–C4–C5–C6	0.8(4)
N4–N3–C4–C5	−1.0(4)
N5–N6–C9–C8	0.3(4)
N5–N6–B1–N2	67.5(4)
N5–N6–B1–N4	−49.9(4)
N5–C7–C8–C9	−1.3(4)
N6–N5–C7–C8	1.5(4)
N8–C16–C17–C14	−20.9(3)
N8–C16–C17–C18	94.9(3)
N8–C16–C17–C19	−145.0(3)
N8–C20–C21–O3	−169.1(3)
N8–C20–C21–C22	70.9(4)
N8–C20–C21–C23	−55.1(4)
C1–N1–N2–C3	0.2(3)
C1–N1–N2–B1	178.9(3)
C1–C2–C3–N2	0.7(4)
C3–N2–B1–N4	−124.0(3)
C3–N2–B1–N6	120.1(3)
C4–N3–N4–C6	0.9(3)
C4–N3–N4–B1	−167.8(3)
C4–C5–C6–N4	−0.2(4)
C6–N4–B1–N2	130.0(3)
C6–N4–B1–N6	−112.1(4)
C7–N5–N6–C9	−1.1(3)
C7–N5–N6–B1	161.5(3)
C7–C8–C9–N6	0.6(4)
C9–N6–B1–N2	−133.6(3)
C9–N6–B1–N4	109.1(4)
C10–C11–C12–C13	14.0(4)
C10–C11–C12–C24	134.5(3)
C11–C10–C15–N8	−99.6(3)
C11–C10–C15–C14	17.3(4)
C11–C12–C13–C14	−43.1(4)
C11–C12–C24–C25	149.8(4)
C11–C12–C24–C29	−36.5(4)
C12–C13–C14–C15	57.8(3)
C12–C13–C14–C17	169.8(3)
C12–C24–C25–C26	174.1(4)

C12–C24–C29–C28	−175.1(3)
C13–C12–C24–C25	−85.9(4)
C13–C12–C24–C29	87.7(4)
C13–C14–C15–N8	81.3(3)
C13–C14–C15–C10	−43.2(3)
C13–C14–C17–C16	−81.2(3)
C13–C14–C17–C18	163.9(3)
C13–C14–C17–C19	39.4(4)
C15–N8–C16–O2	176.5(3)
C15–N8–C16–C17	−2.6(4)
C15–N8–C20–C21	−76.8(4)
C15–C10–C11–W1	−115.5(3)
C15–C10–C11–C12	−1.8(4)
C15–C14–C17–C16	35.1(3)
C15–C14–C17–C18	−79.8(3)
C15–C14–C17–C19	155.7(3)
C16–N8–C15–C10	150.0(3)
C16–N8–C15–C14	25.2(3)
C16–N8–C20–C21	101.8(3)
C17–C14–C15–N8	−36.4(3)
C17–C14–C15–C10	−160.8(3)
C20–N8–C15–C10	−31.2(4)
C20–N8–C15–C14	−156.0(3)
C20–N8–C16–O2	−2.3(5)
C20–N8–C16–C17	178.6(3)
C24–C12–C13–C14	−167.7(3)
C24–C25–C26–C27	1.2(8)
C25–C24–C29–C28	−1.2(6)
C25–C26–C27–C28	−1.6(8)
C26–C27–C28–C29	0.6(7)
C27–C28–C29–C24	0.9(6)
C29–C24–C25–C26	0.2(7)
B1–N2–C3–C2	−179.1(3)
B1–N4–C6–C5	167.1(3)
B1–N6–C9–C8	−160.4(3)

Table 6. Hydrogen bonds for compound 4.52

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O3–H3···O2$^{\#1}$	0.794(19)	2.03(2)	2.817(3)	173(4)

Symmetry transformations used to generate equivalent atoms: #1: 1-X, -0.5+Y, 0.5-Z;

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[1] Bruker, *SAINT*, *8.40B*, Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Unknown Reference, please add.
[3] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3–8, doi:10.1107/S2053273314026370.
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[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341, doi:10.1107/S0021889808042726.
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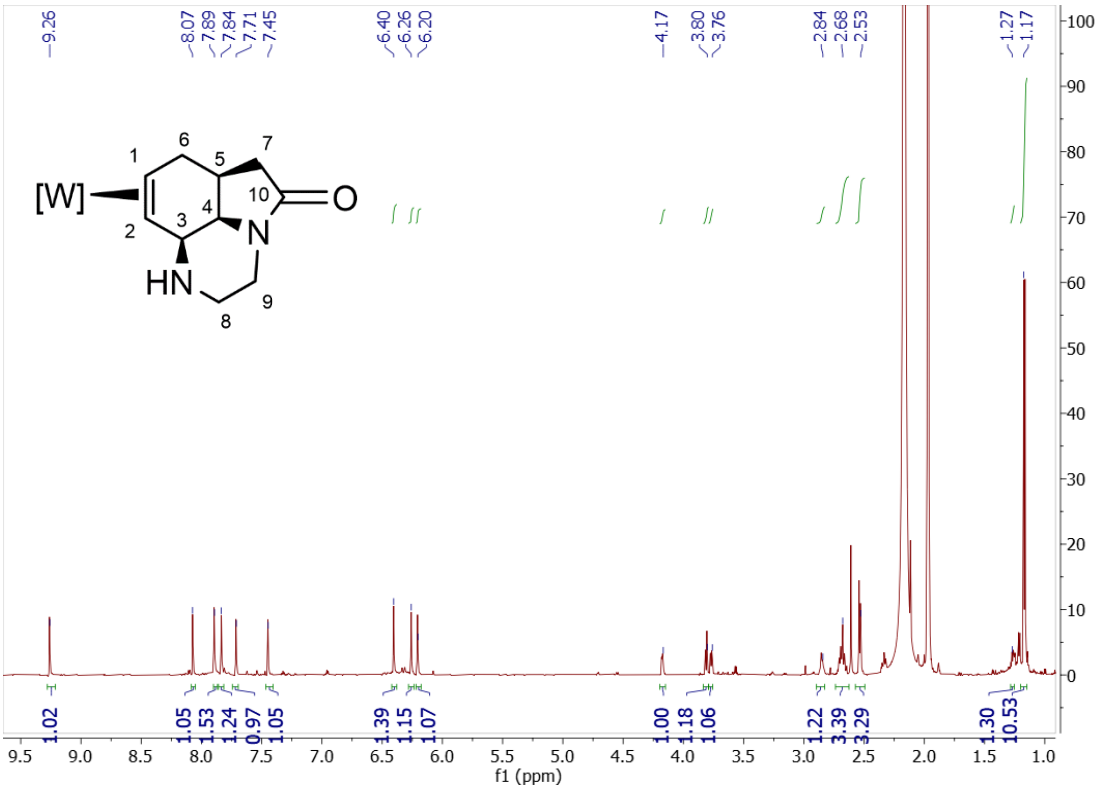
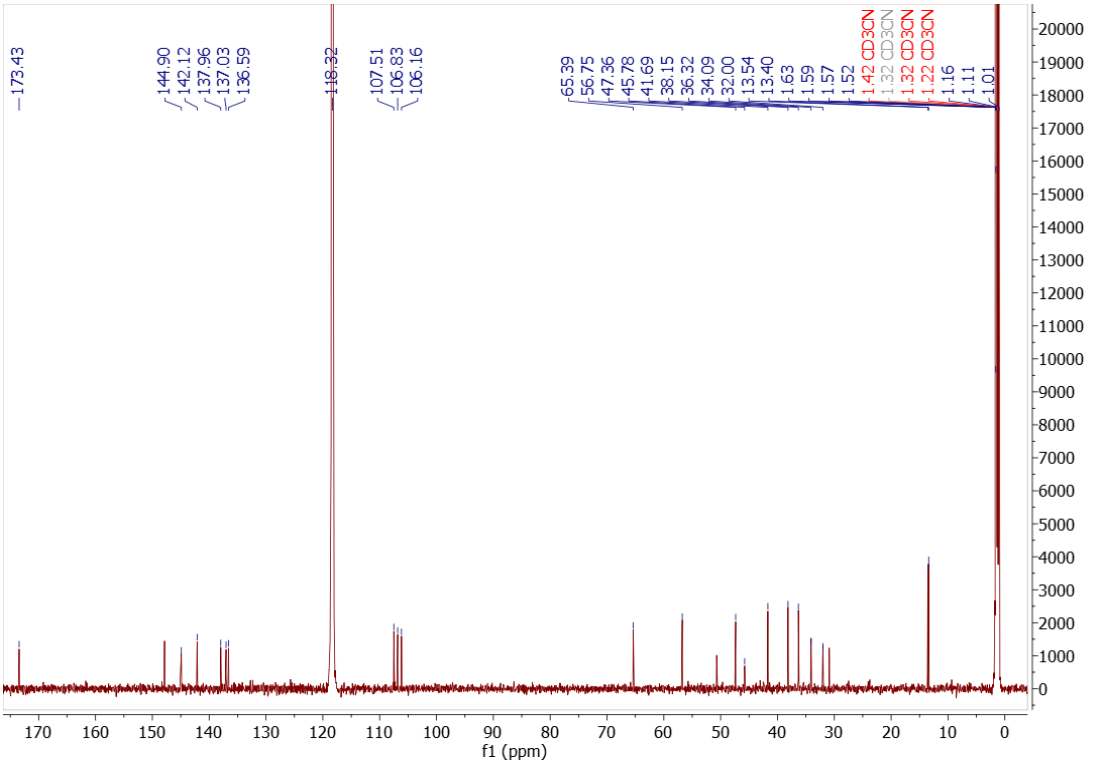
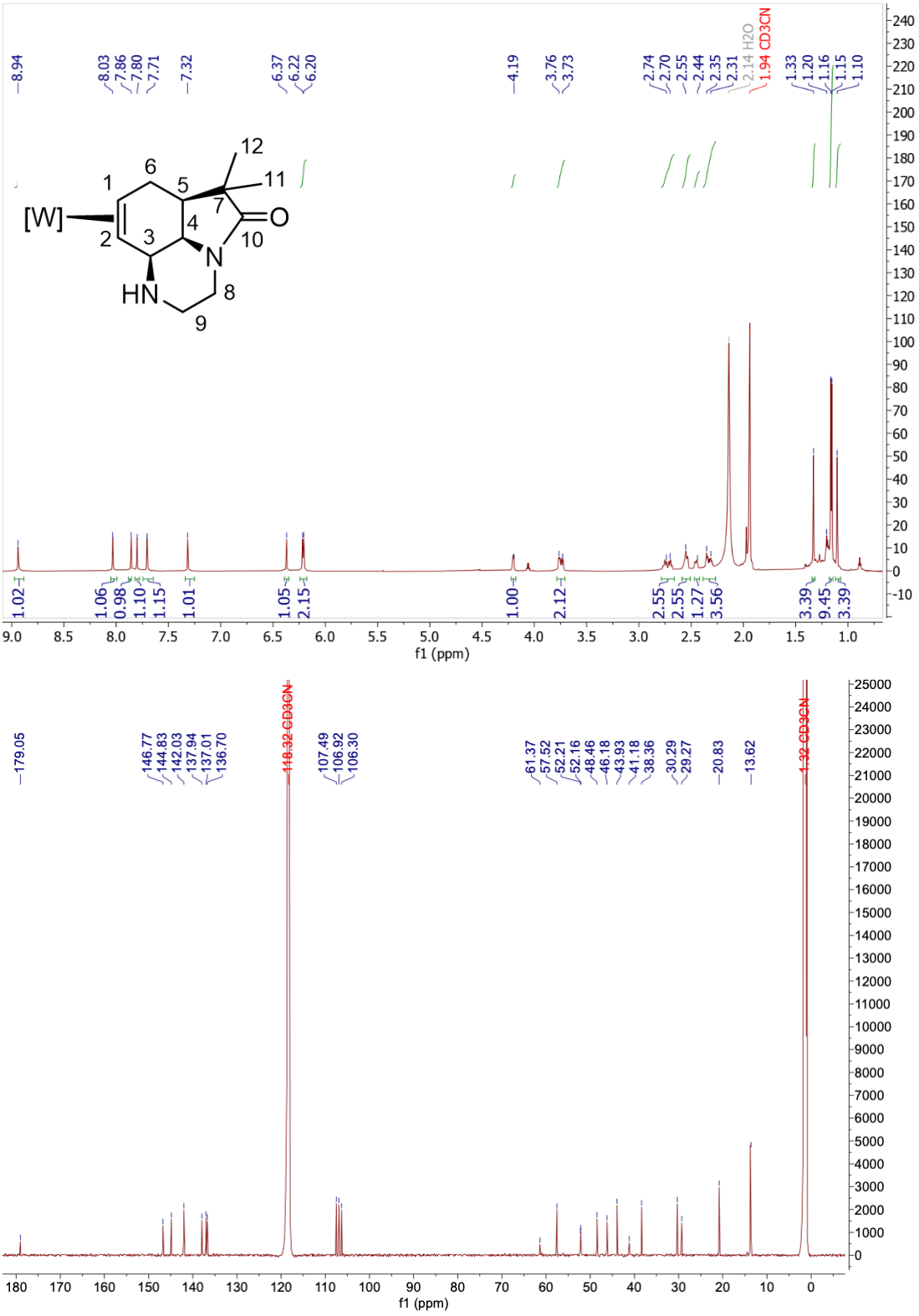
NMR Data Chapter 5

^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.5:

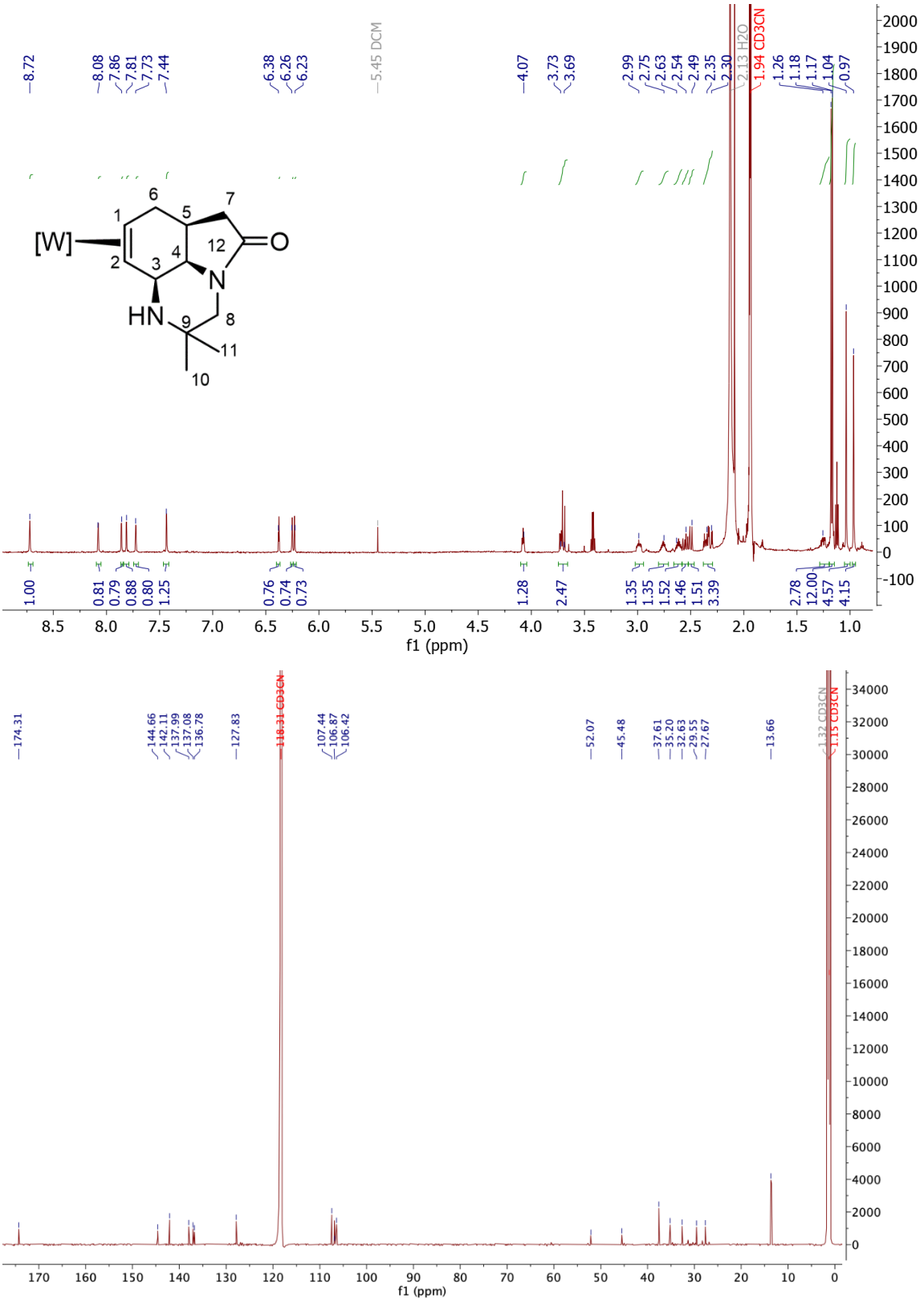




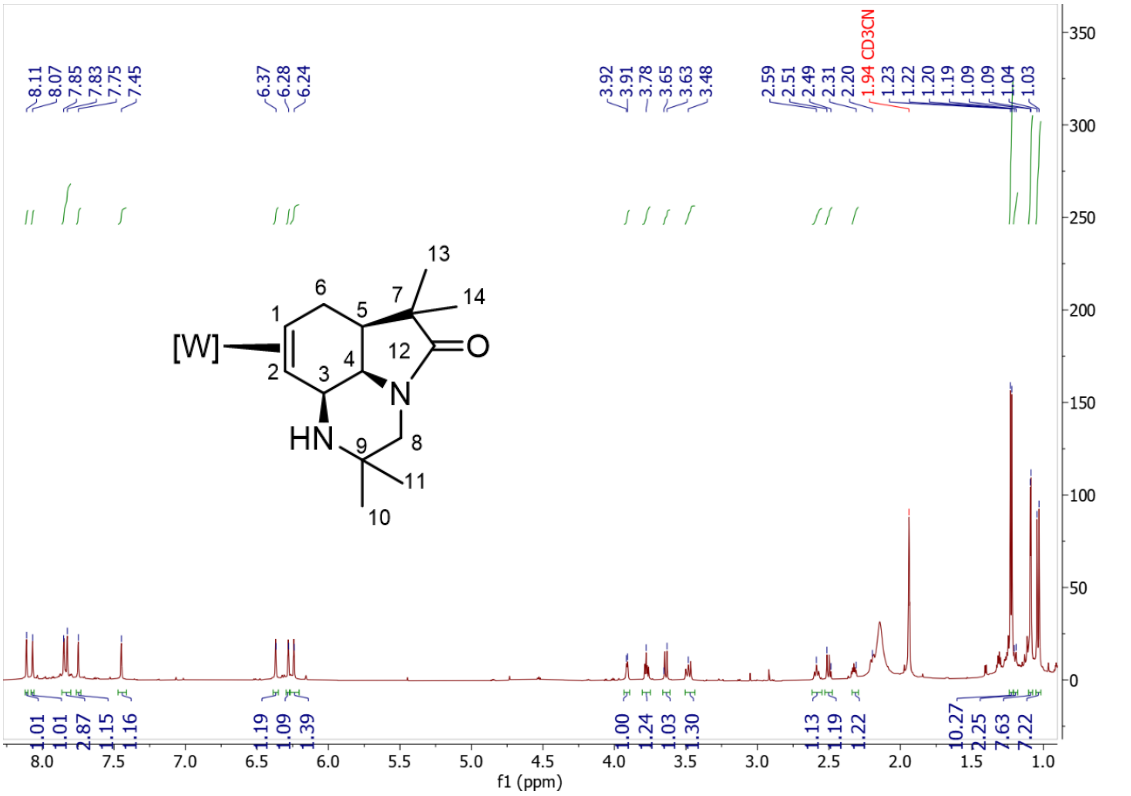
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.6:

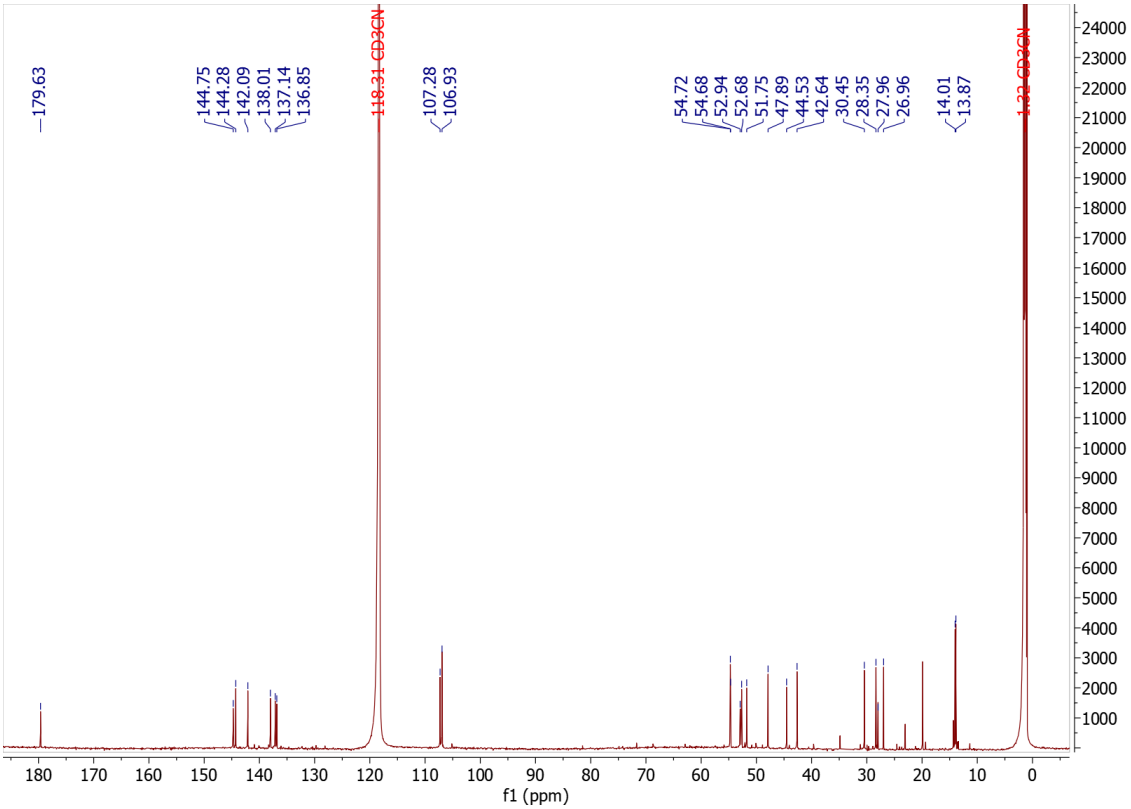


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.8:

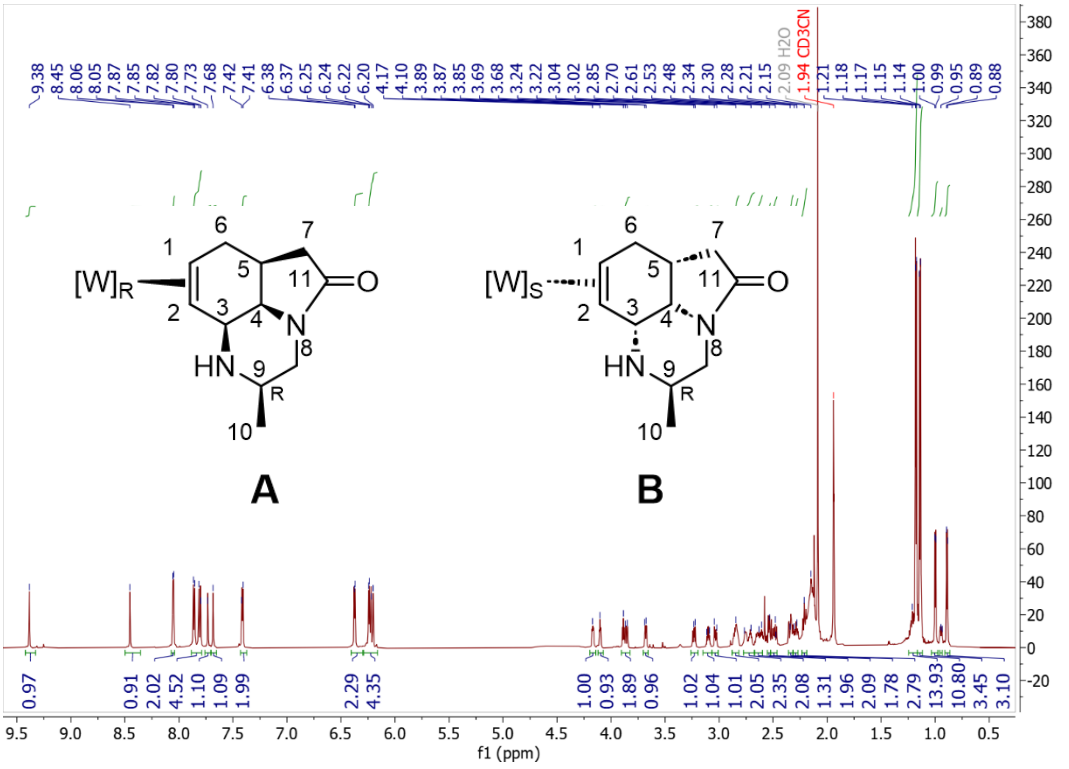


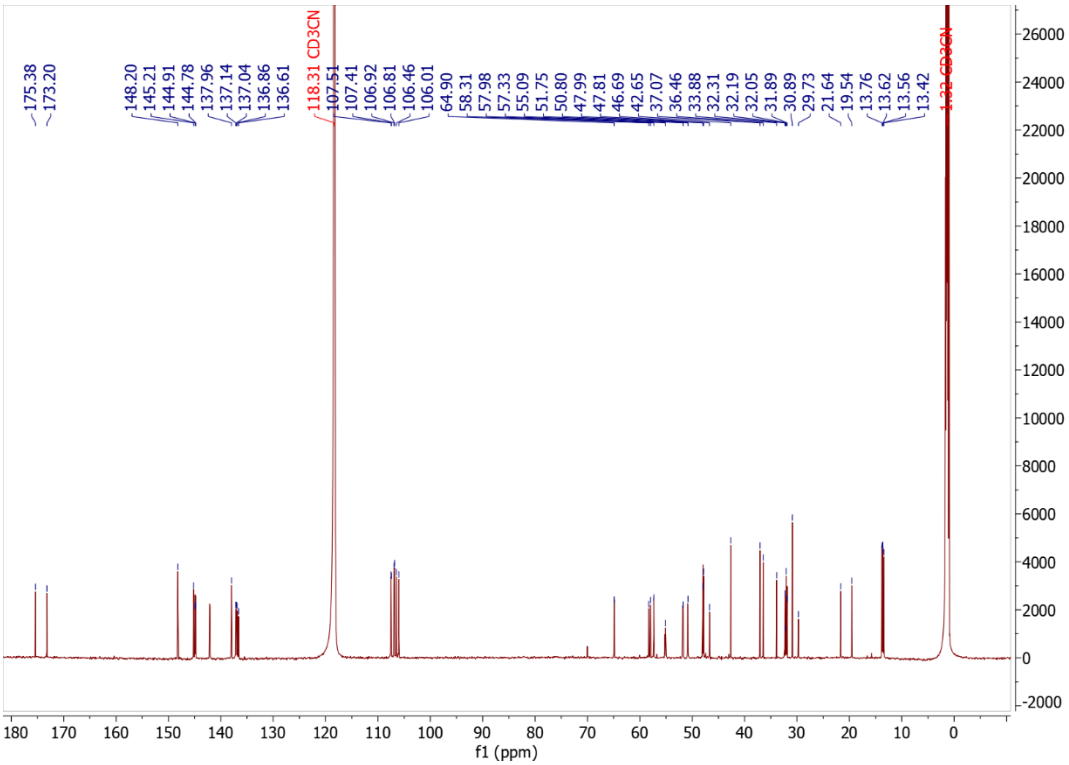
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.9:



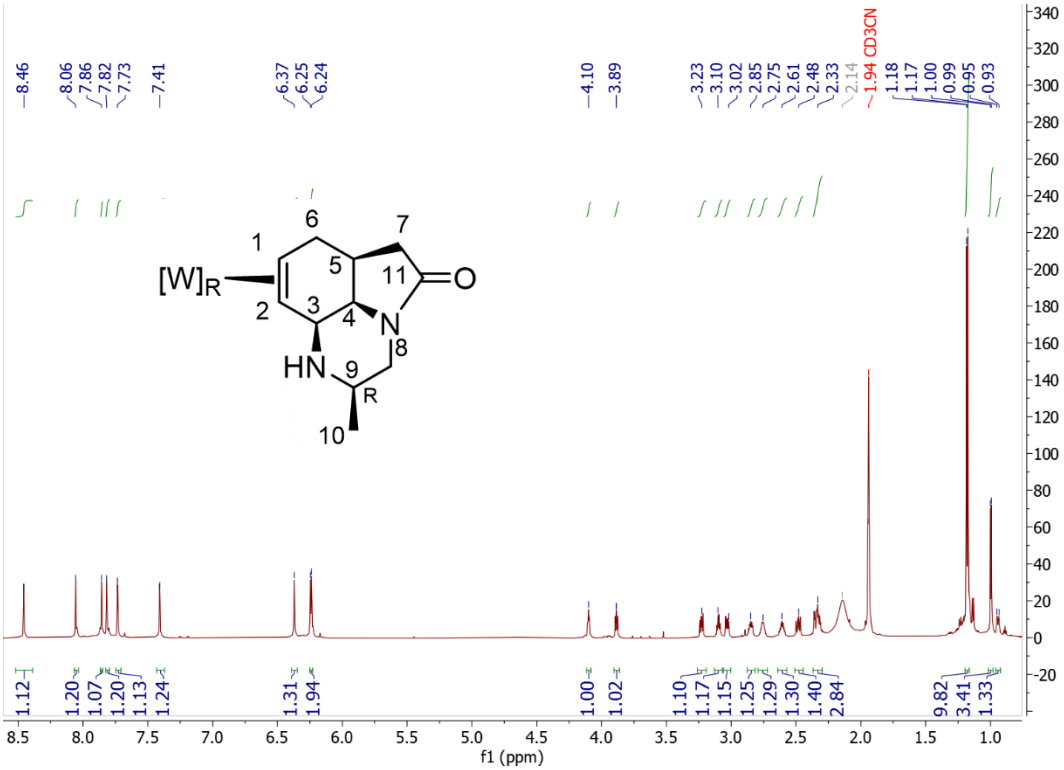


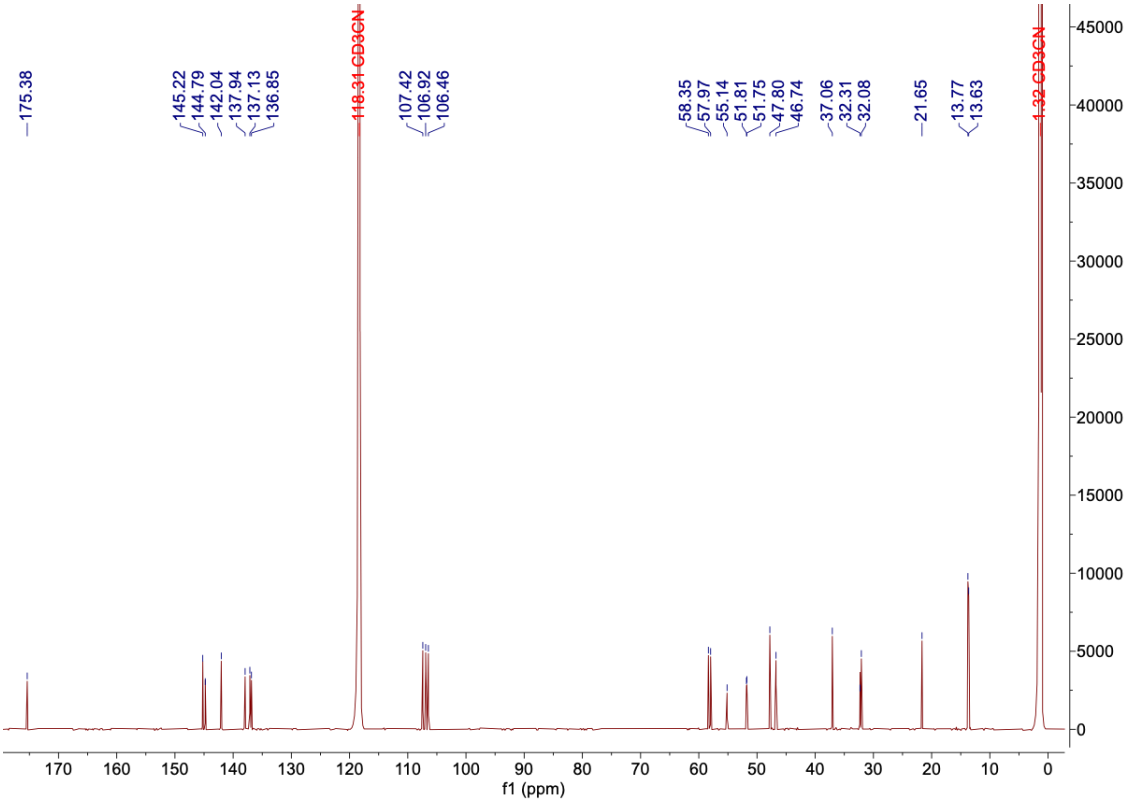
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.10:



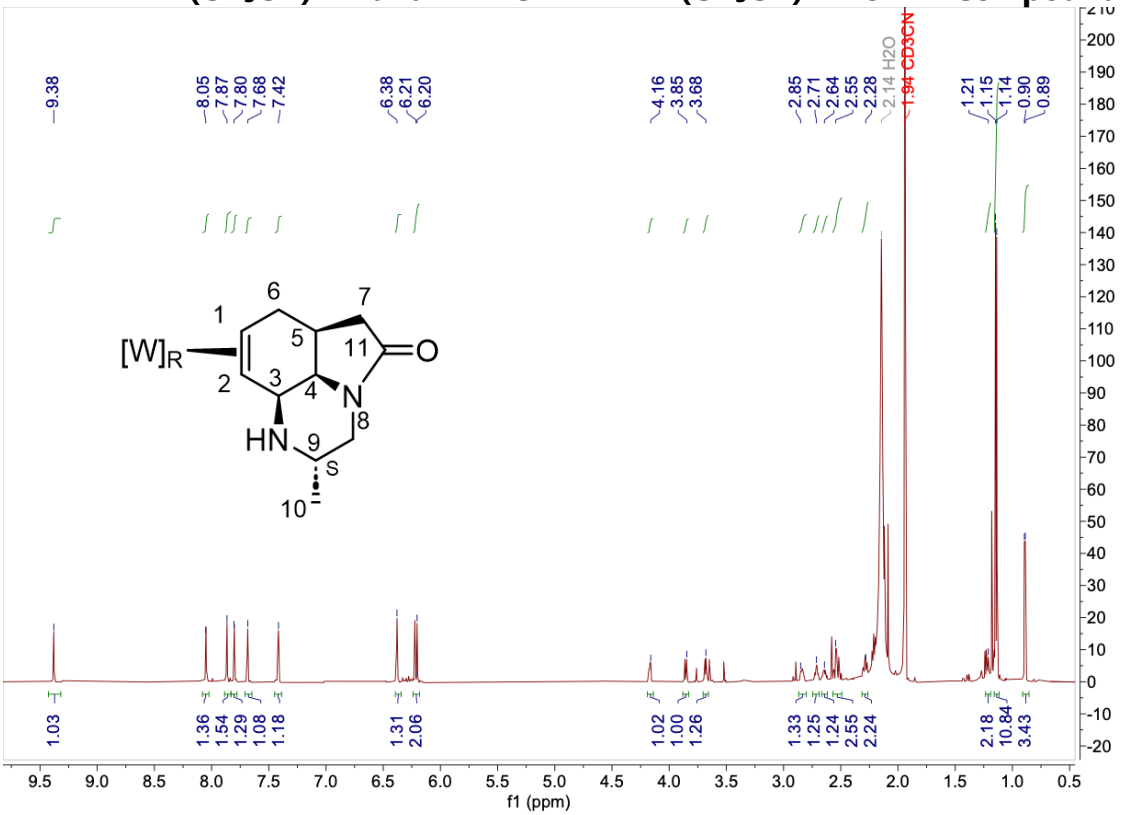


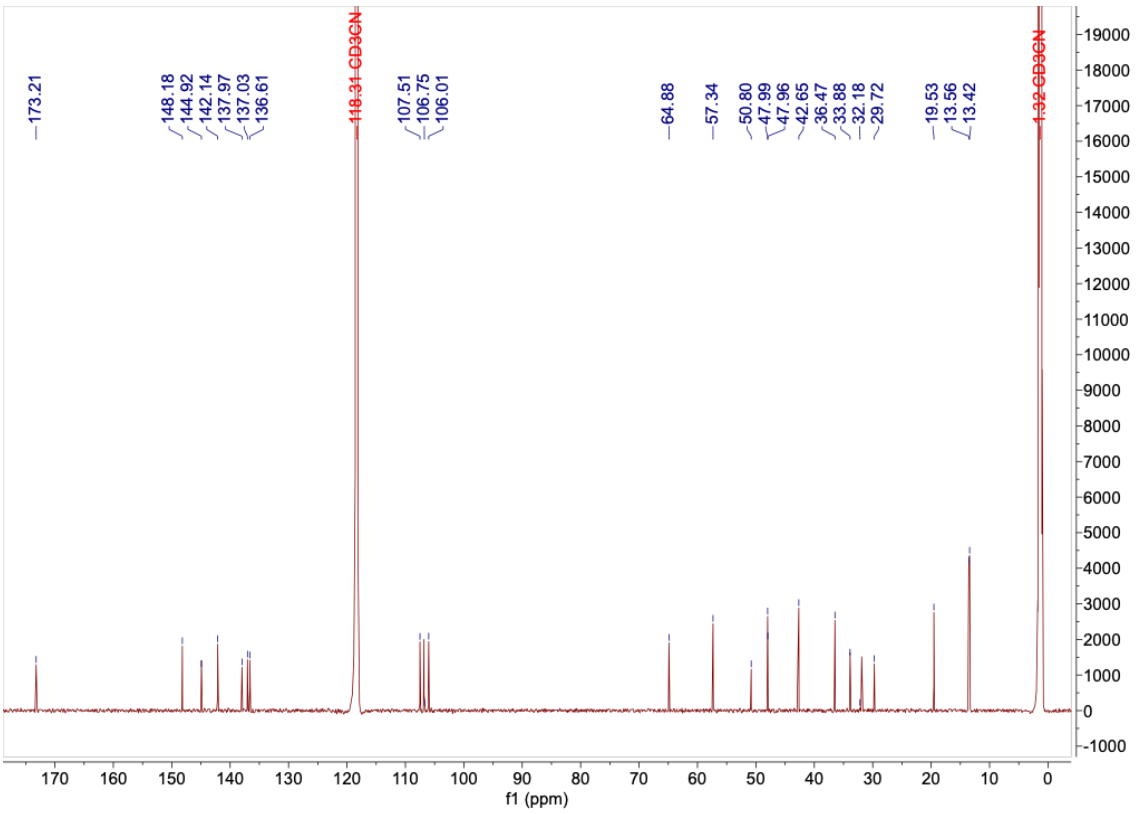
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.11:



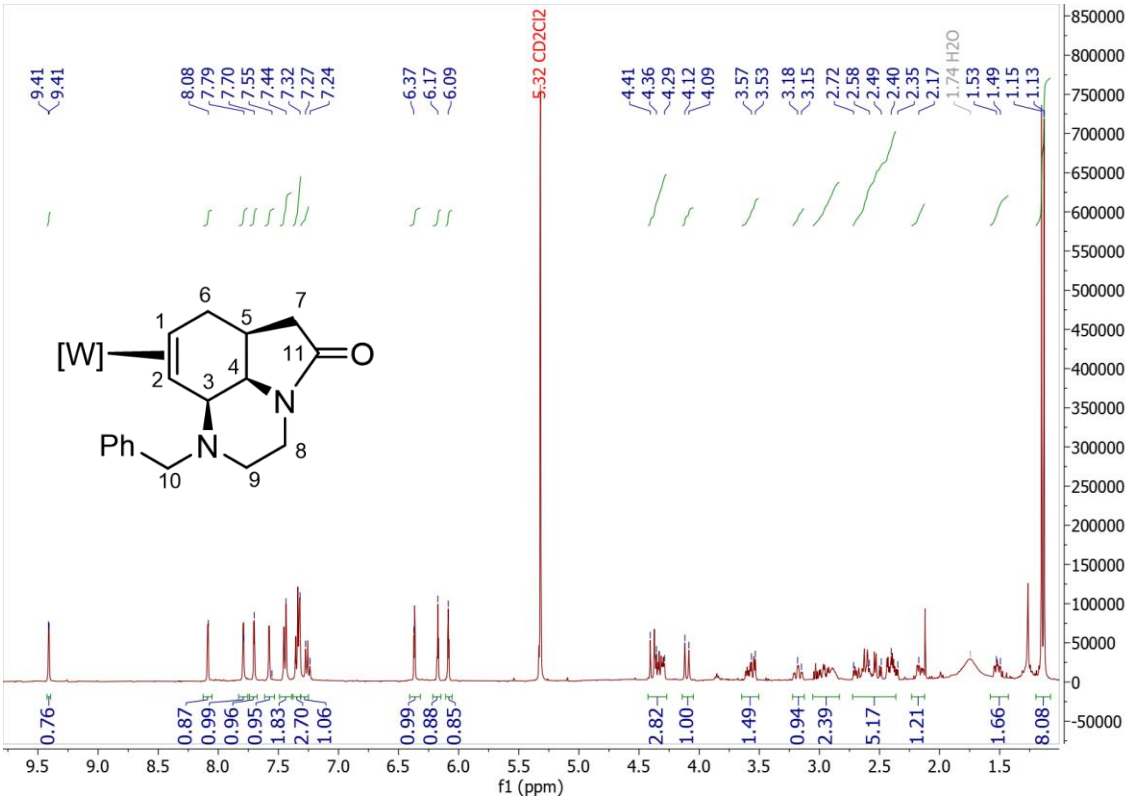


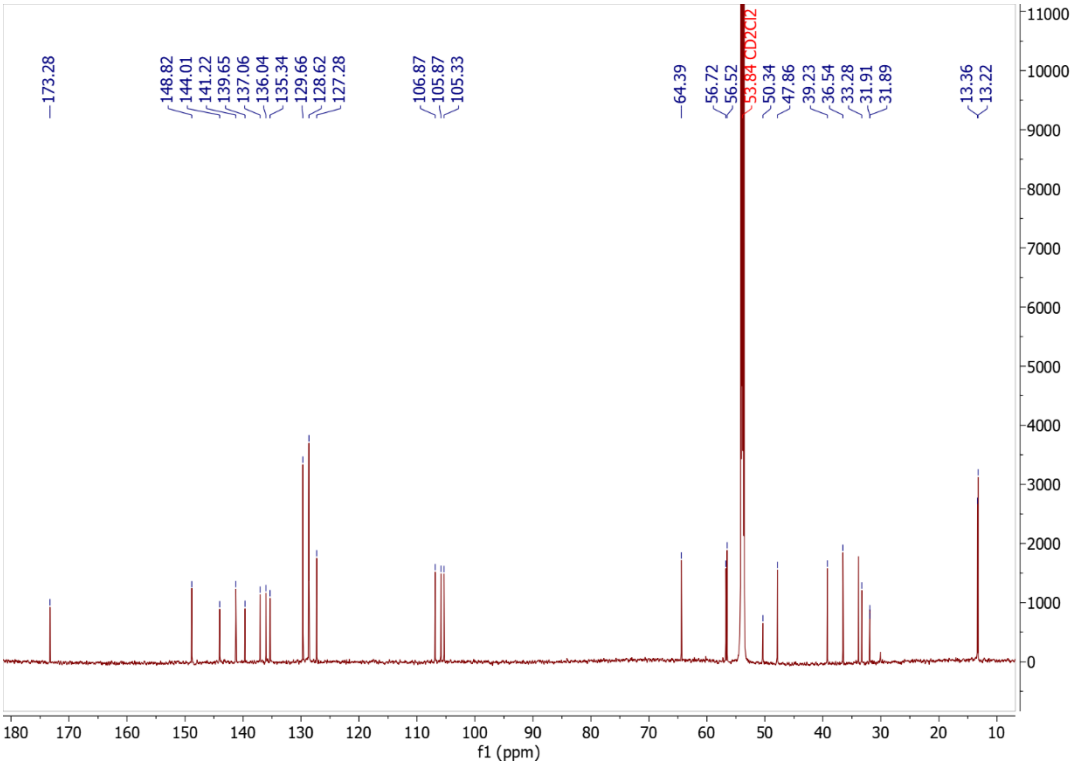
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.12:



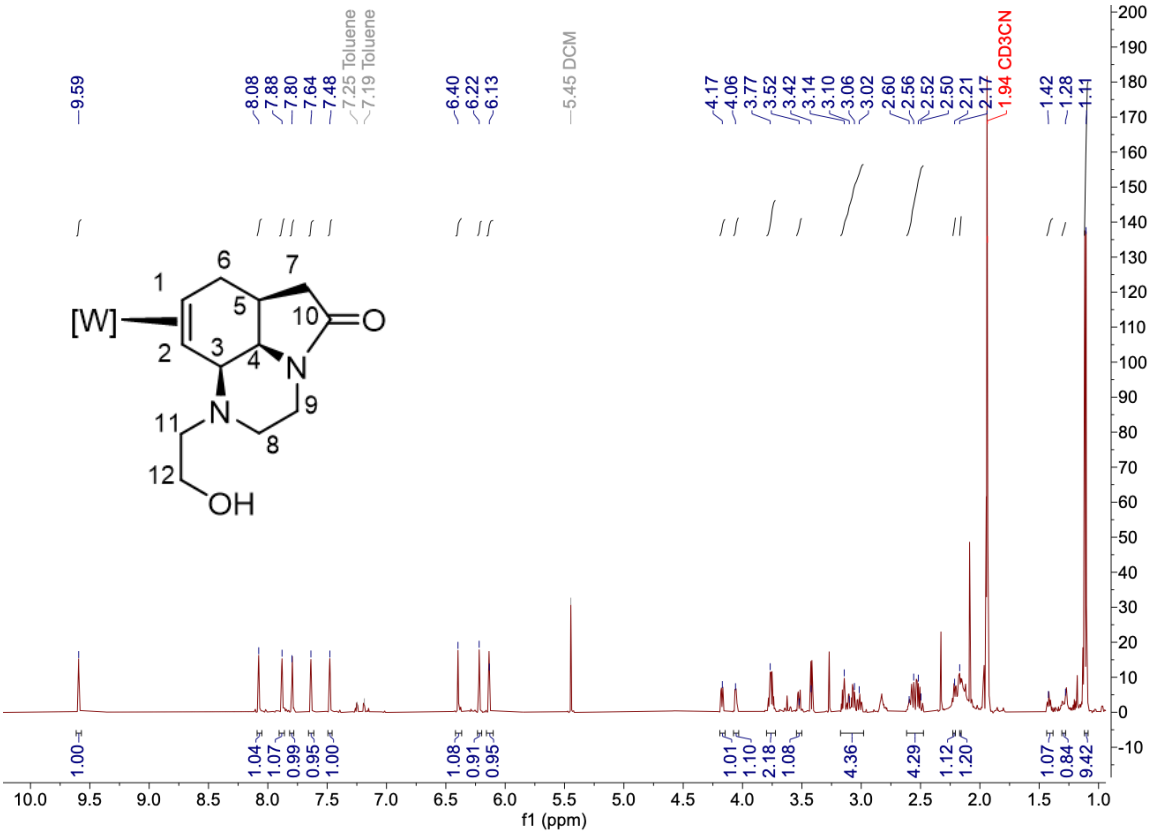


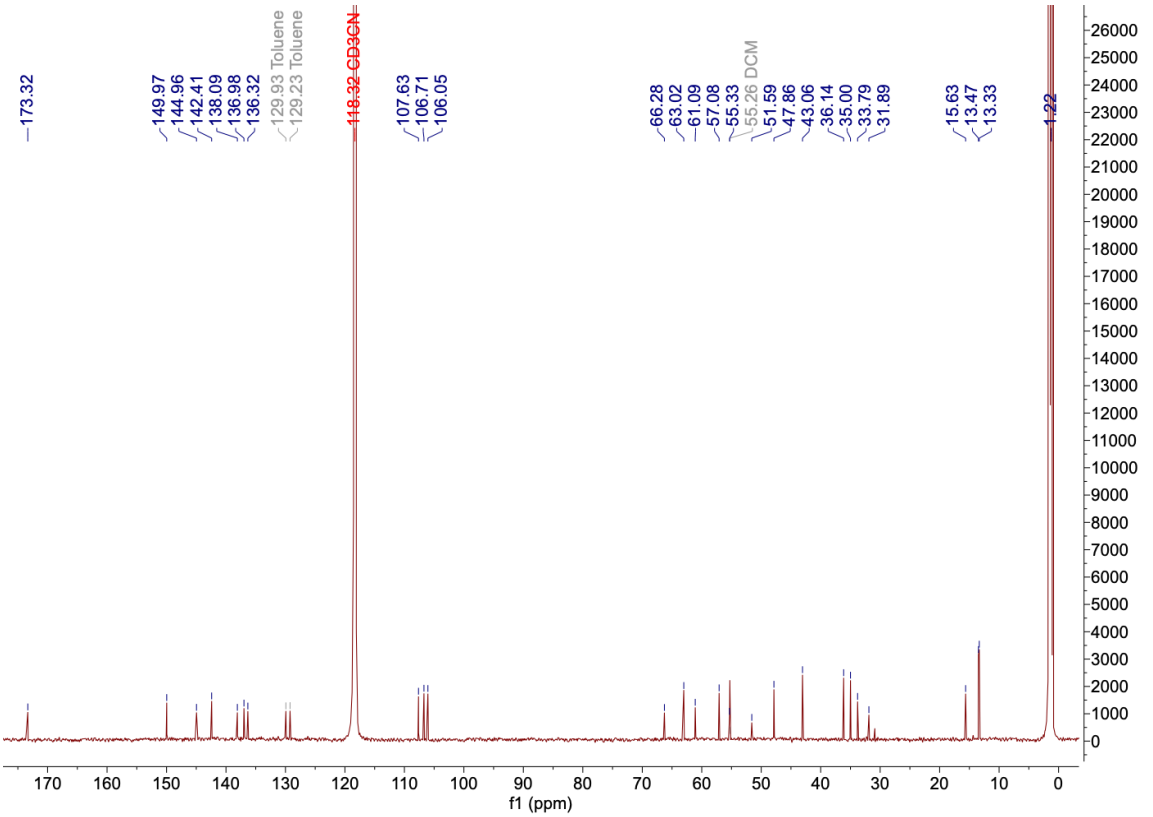
^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 5.13:



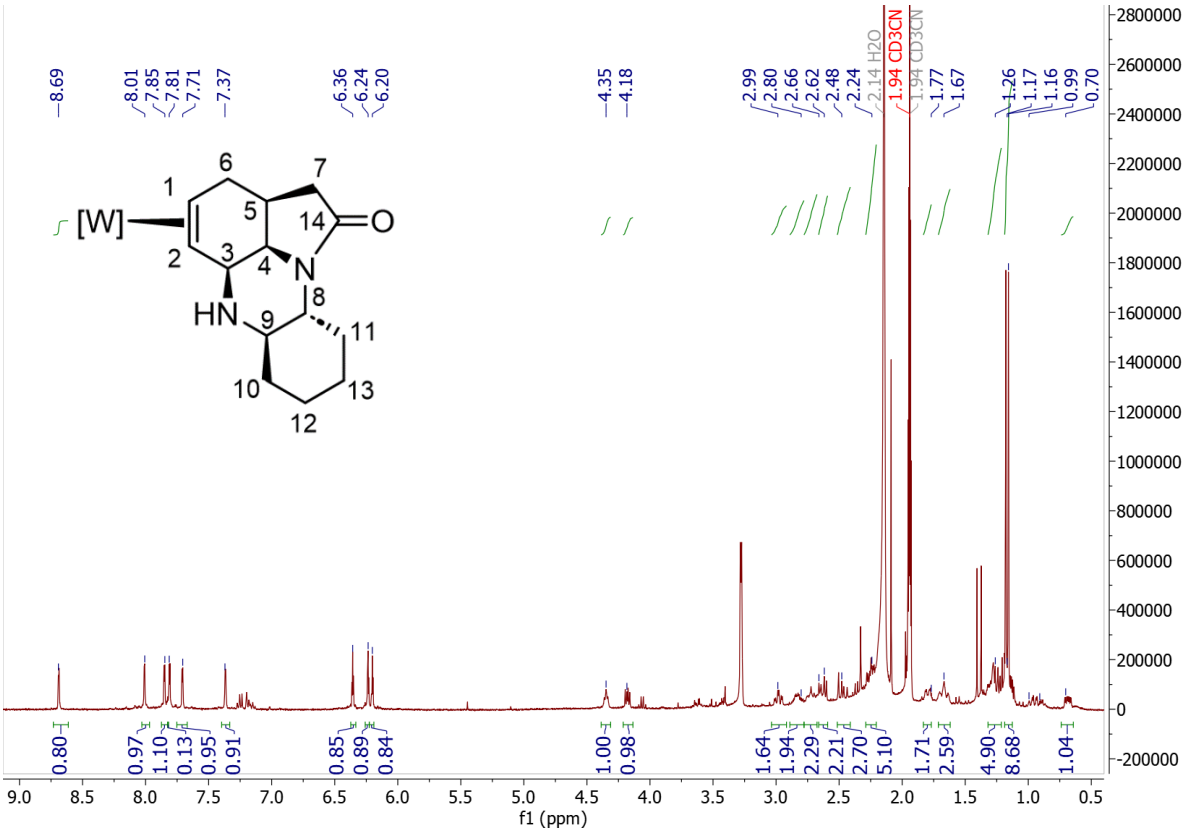


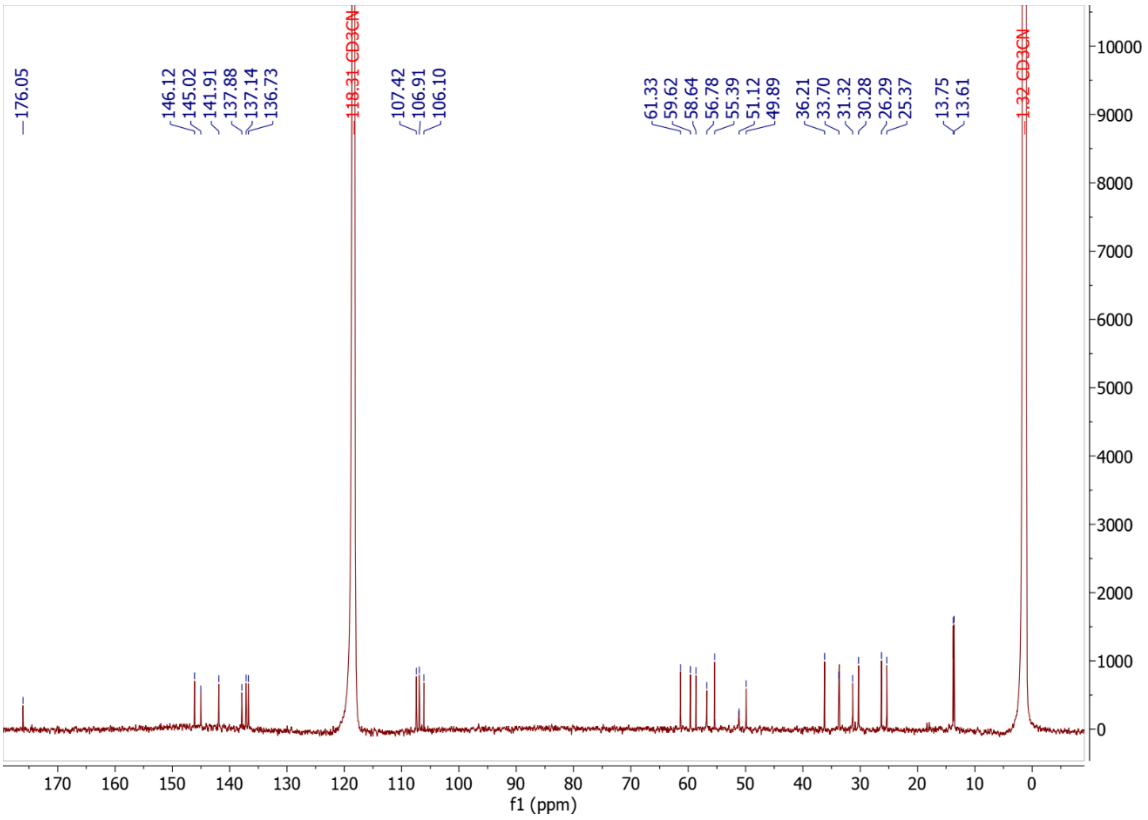
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.14:



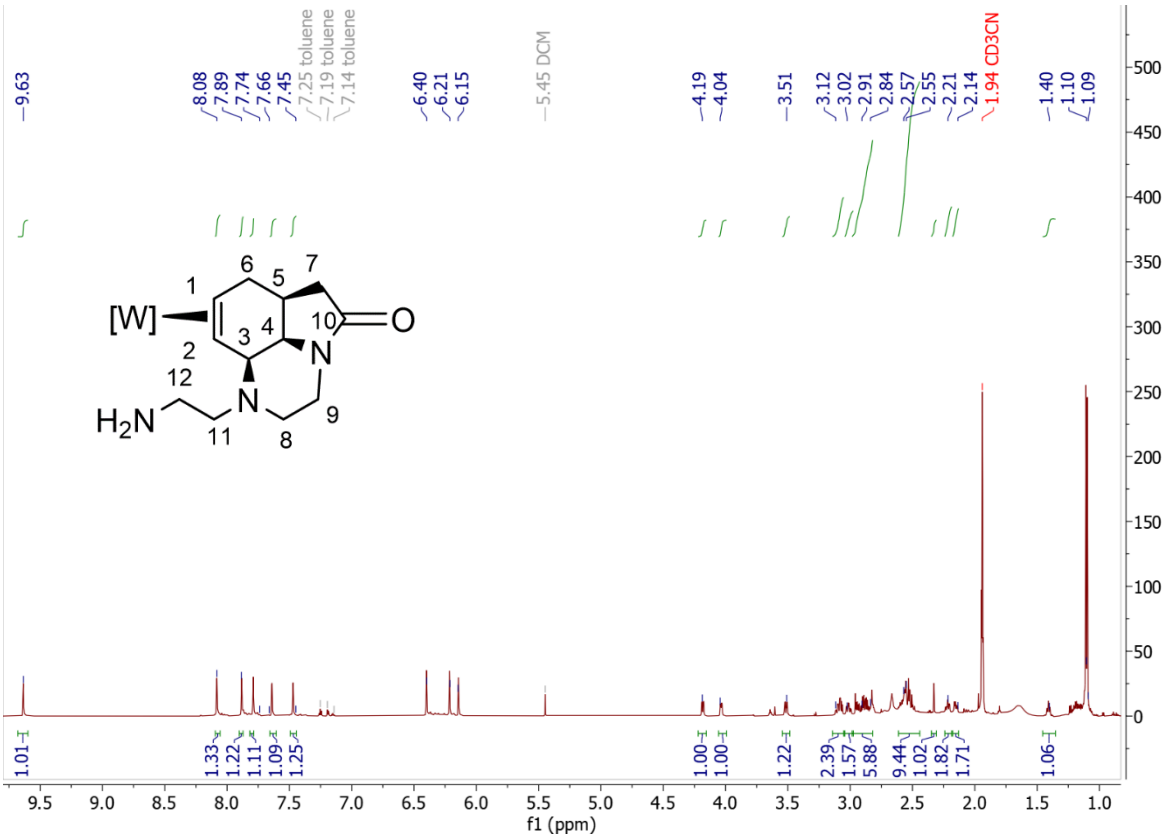


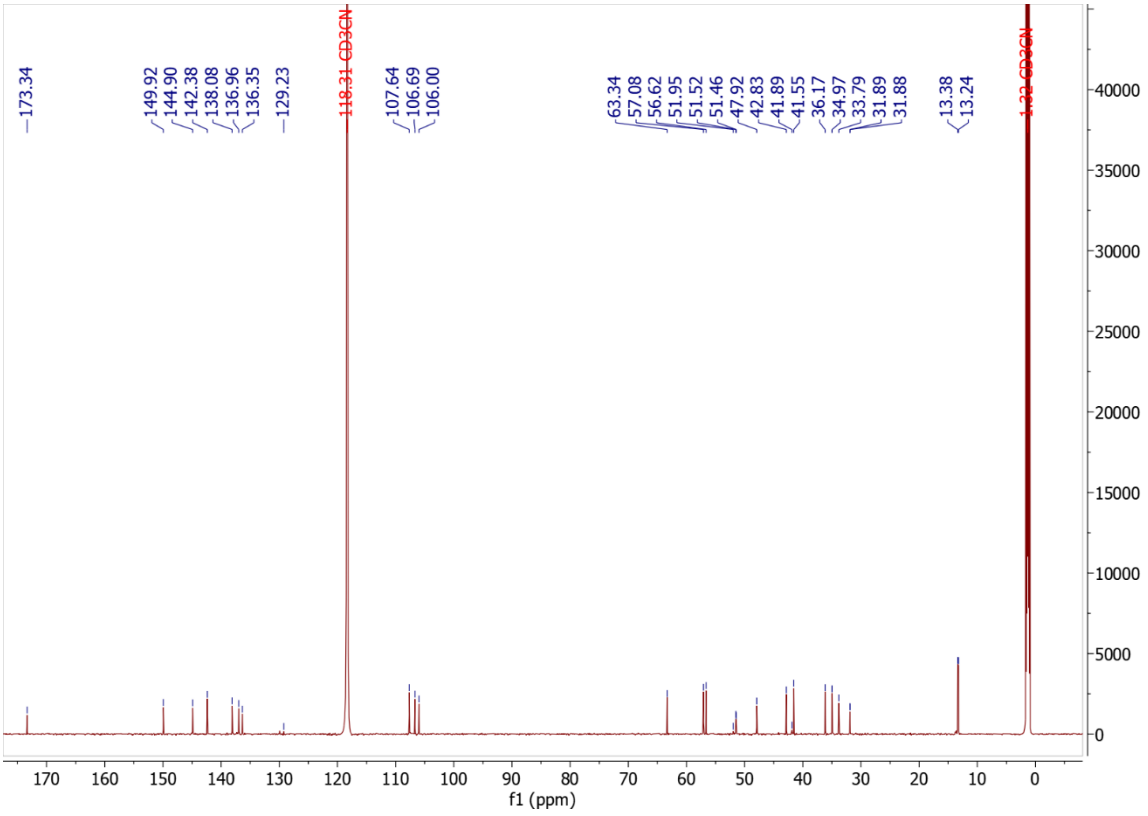
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.15:



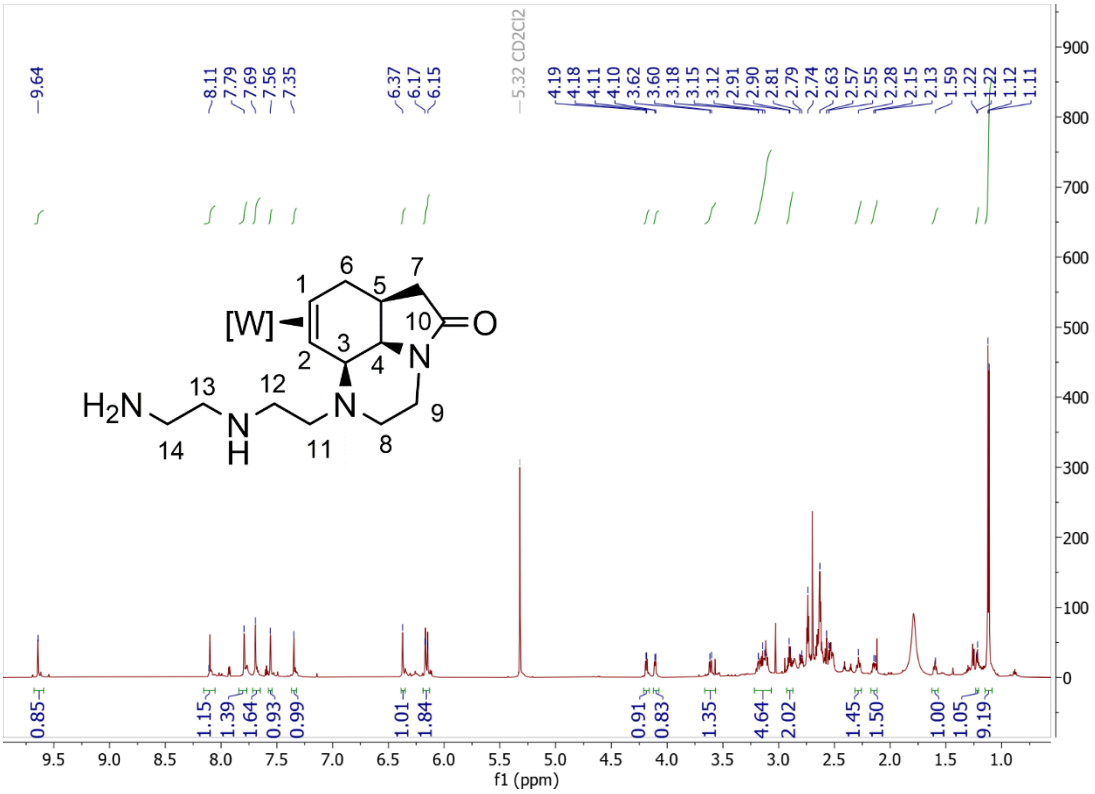


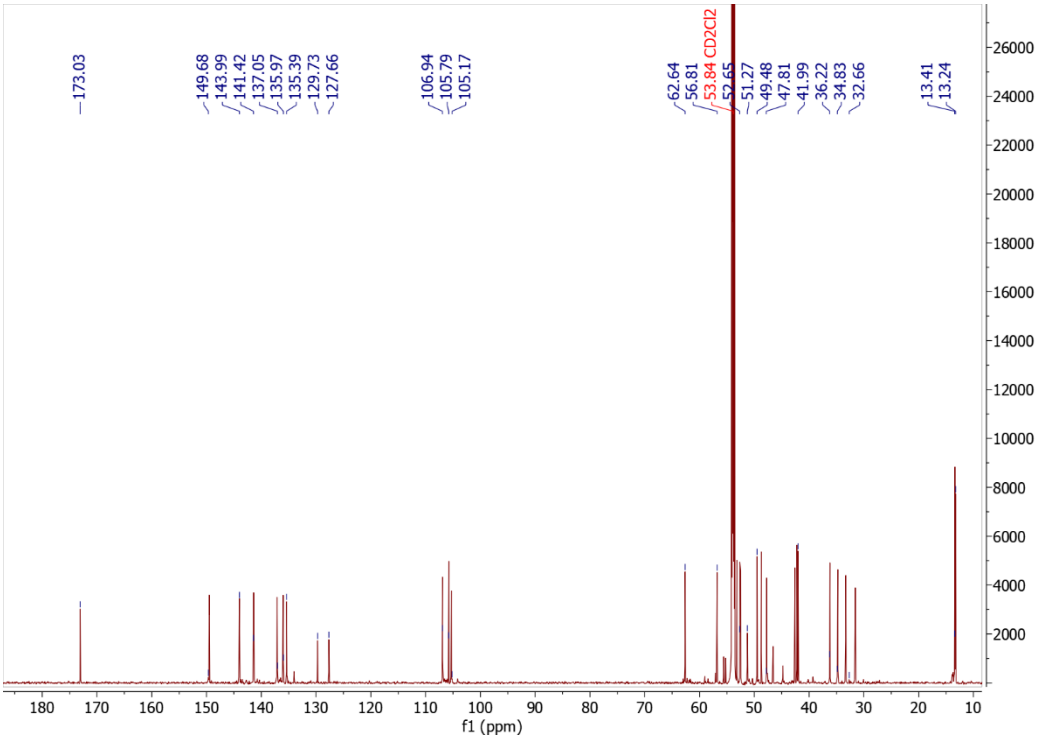
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.16:



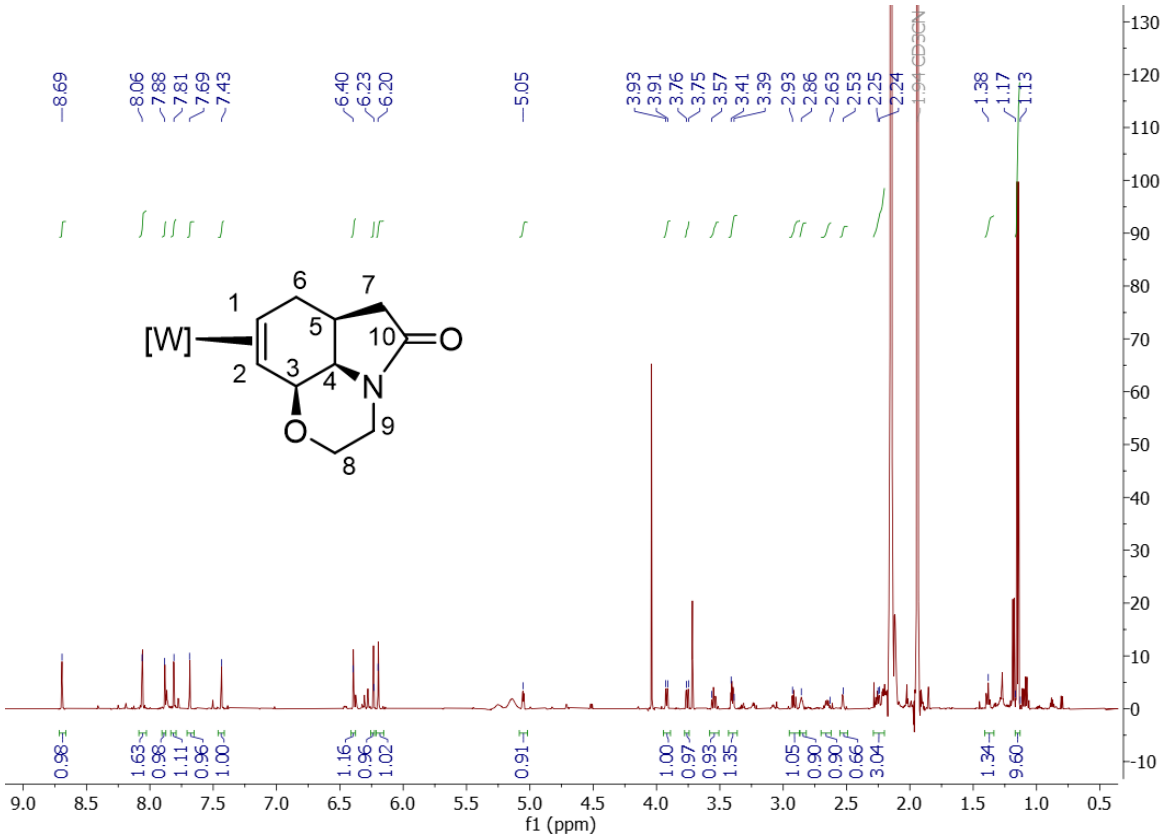


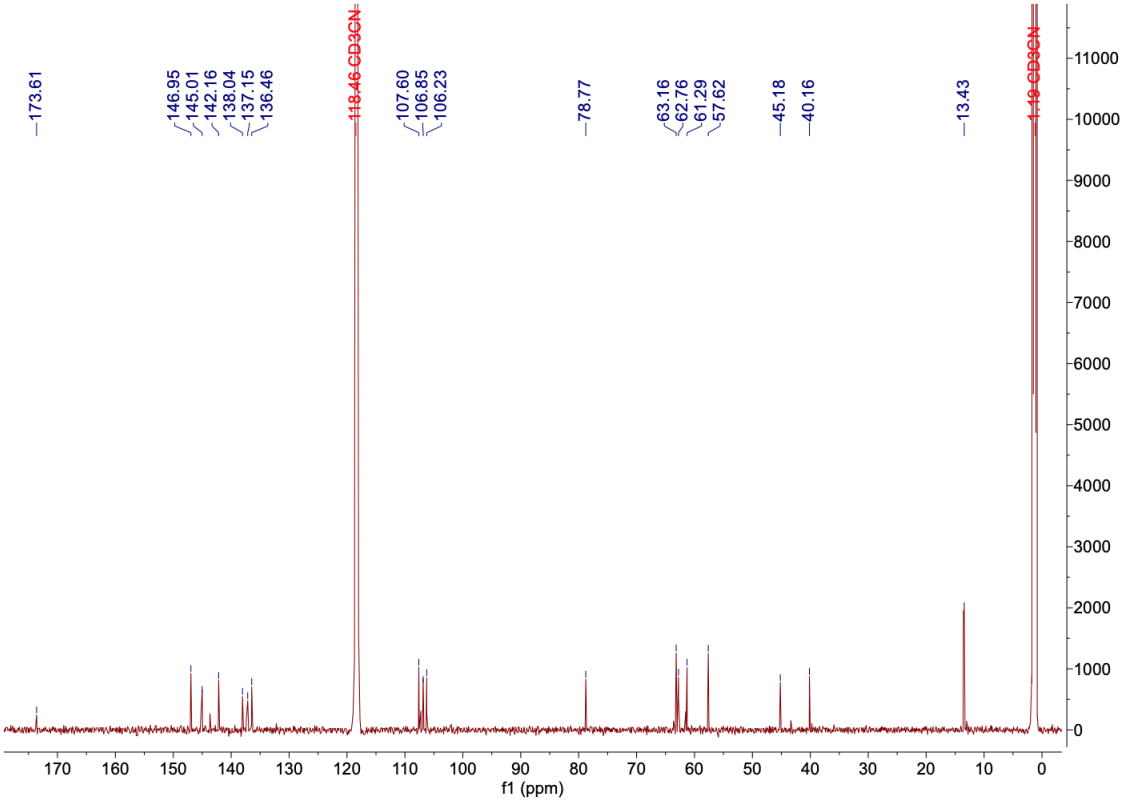
^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 5.17:



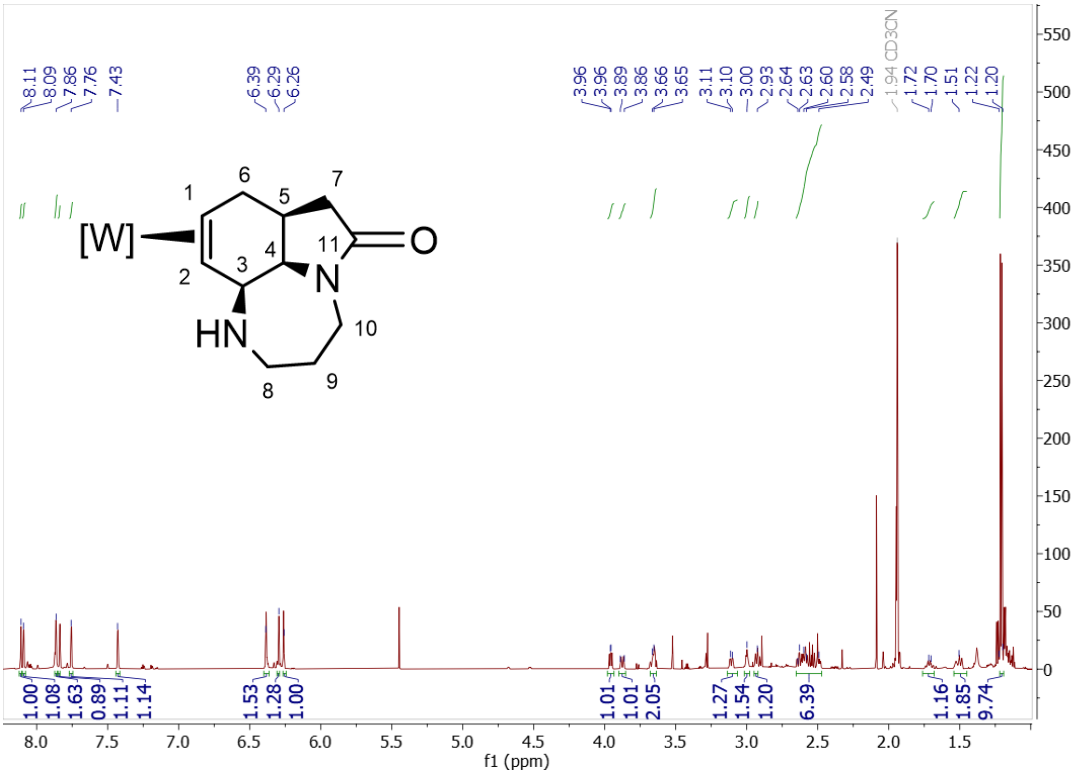


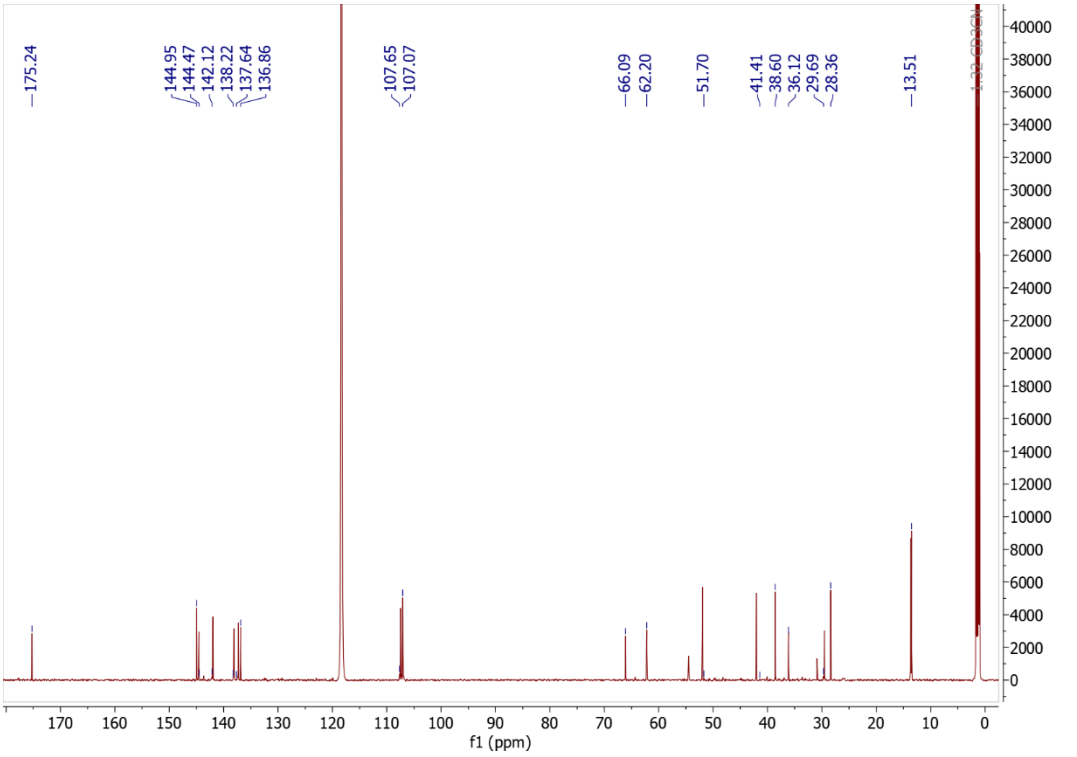
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.18:



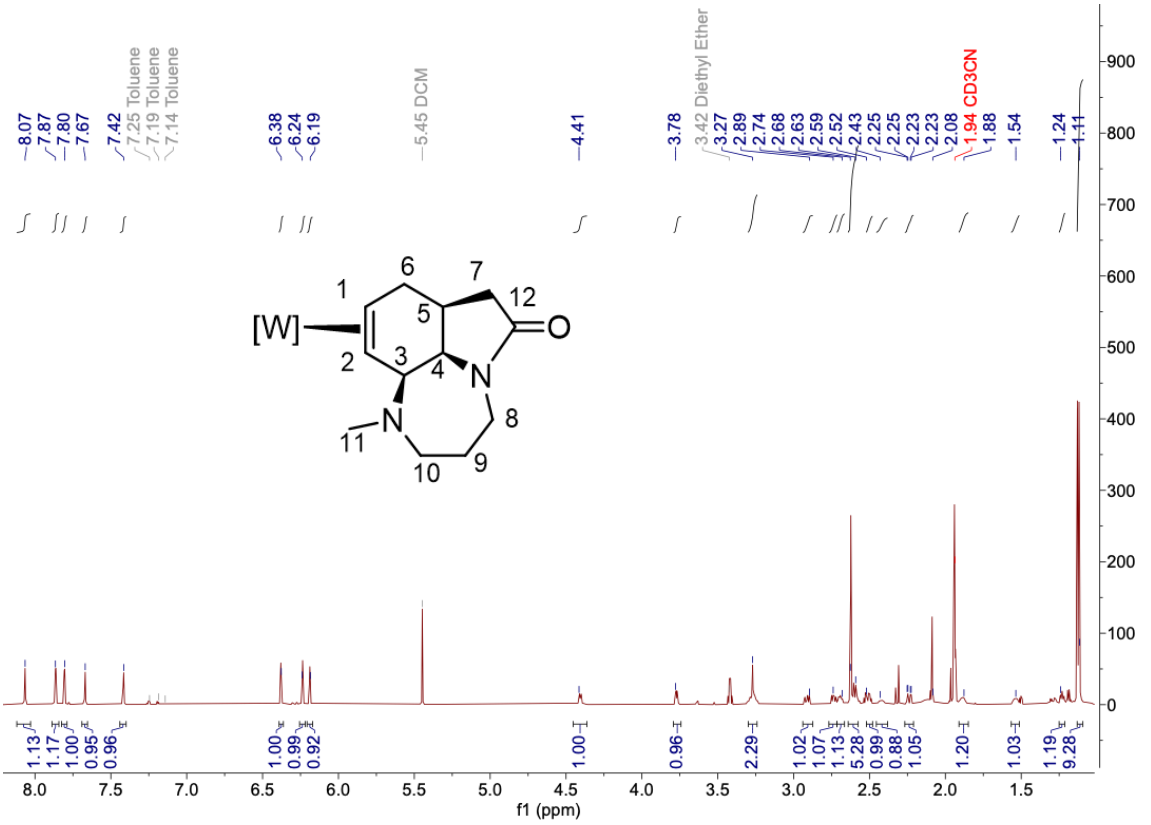


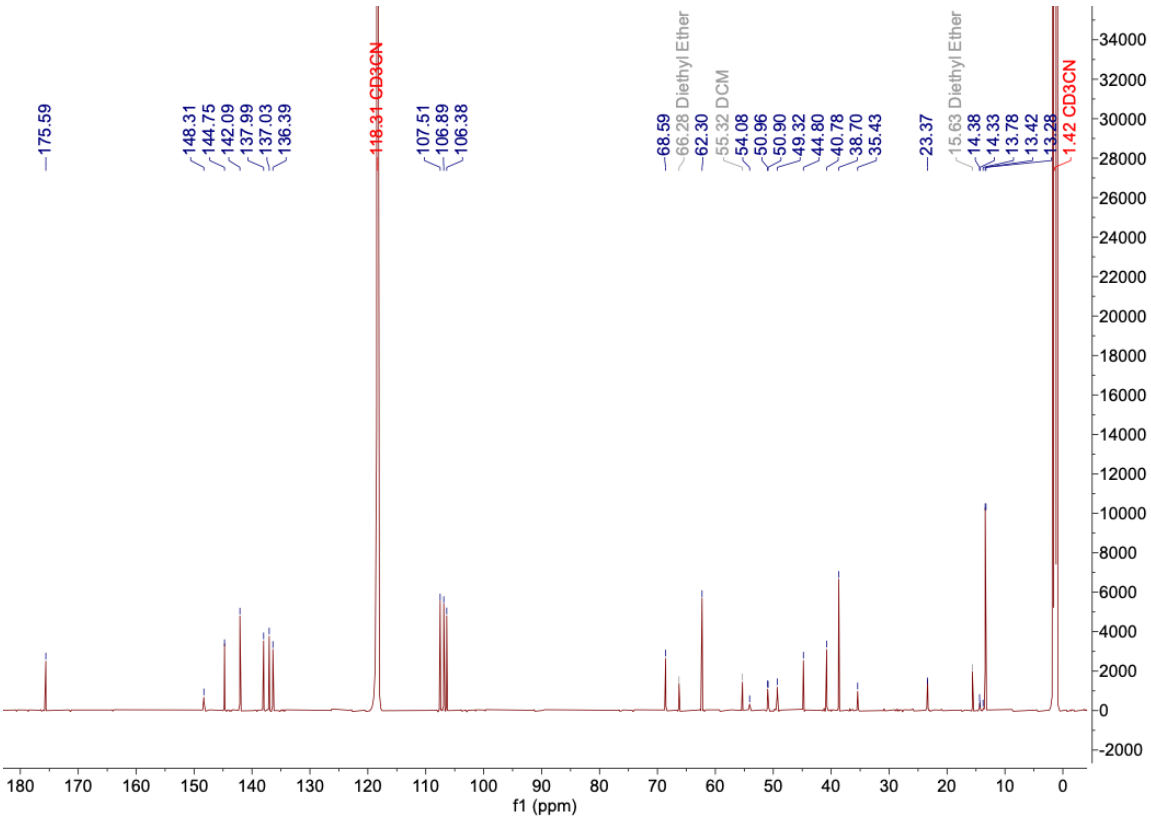
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.19:



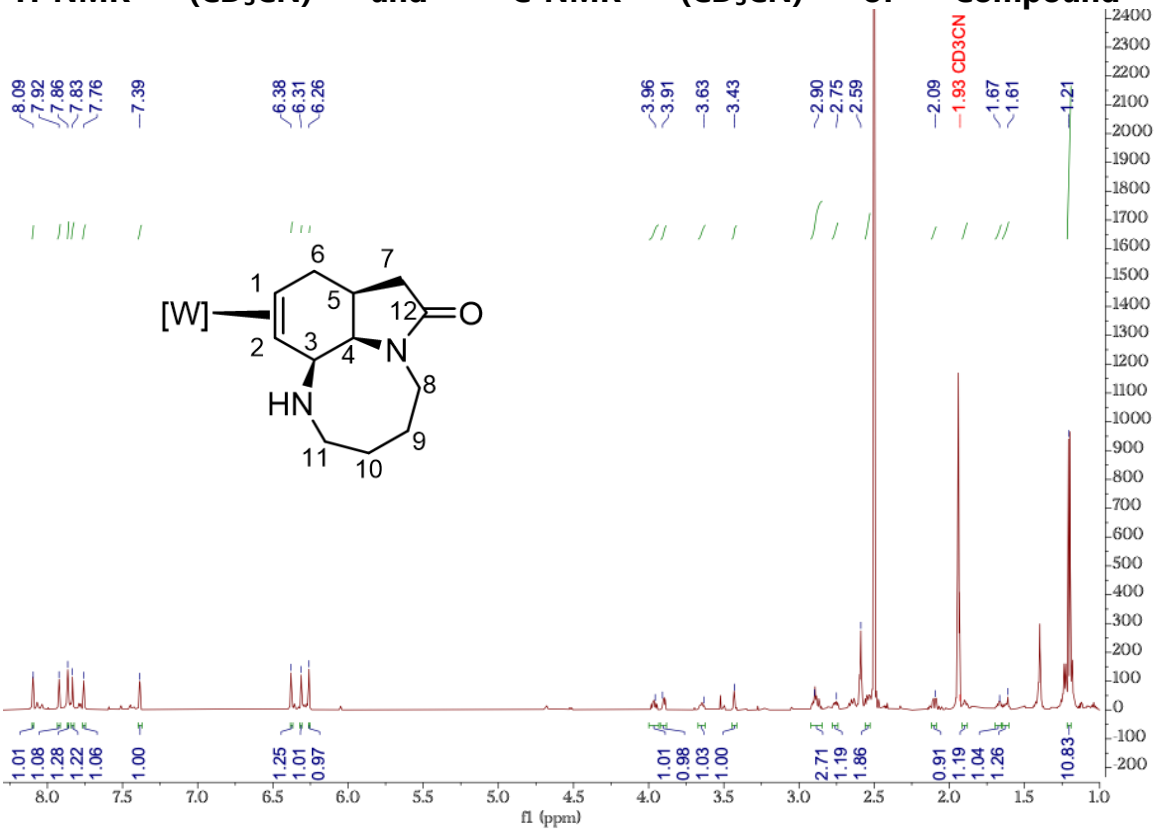


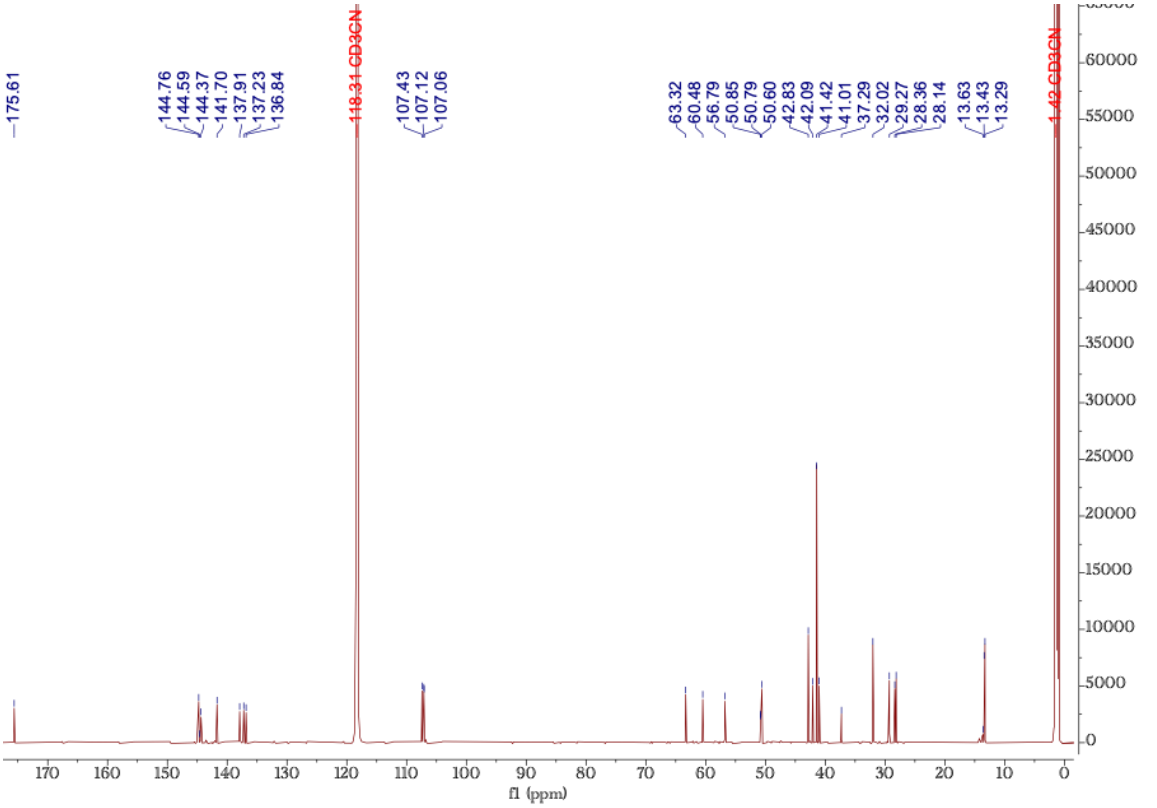
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.20:



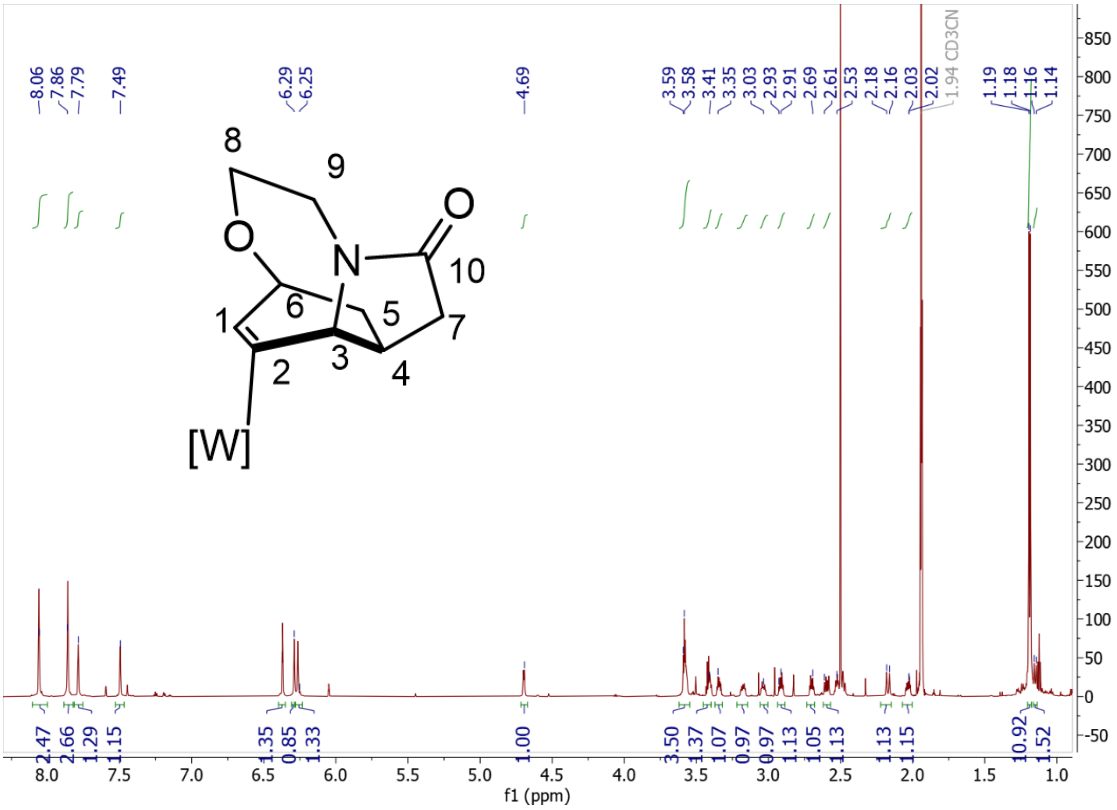


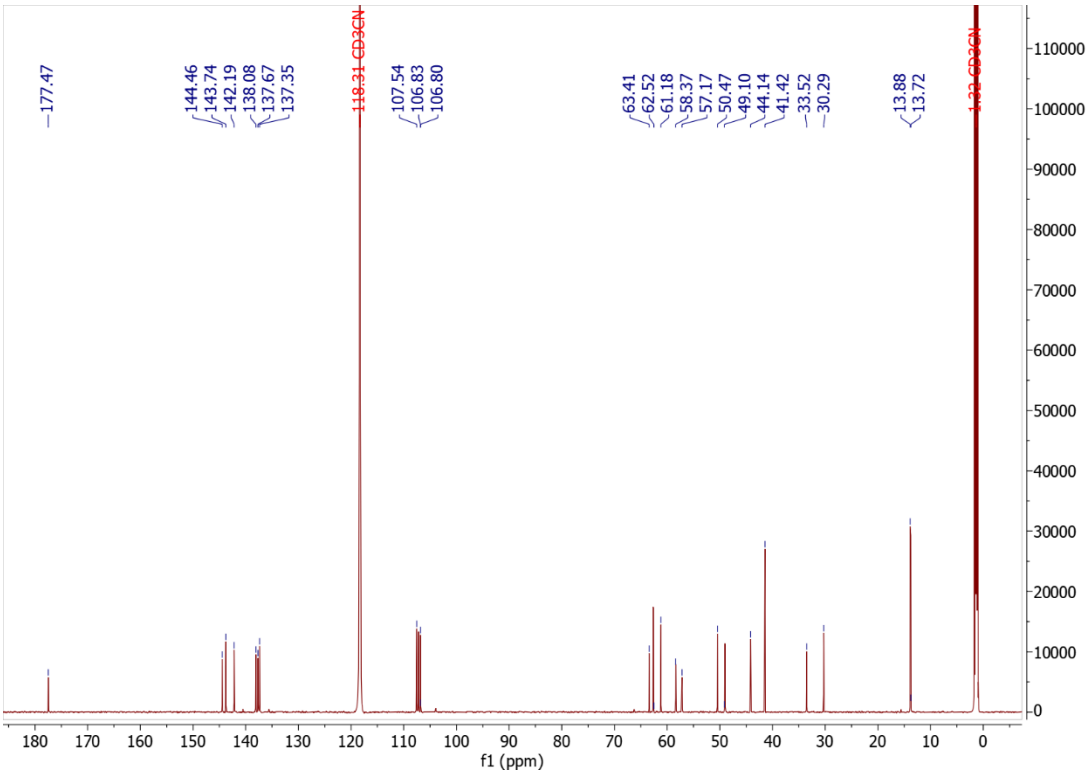
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.22:





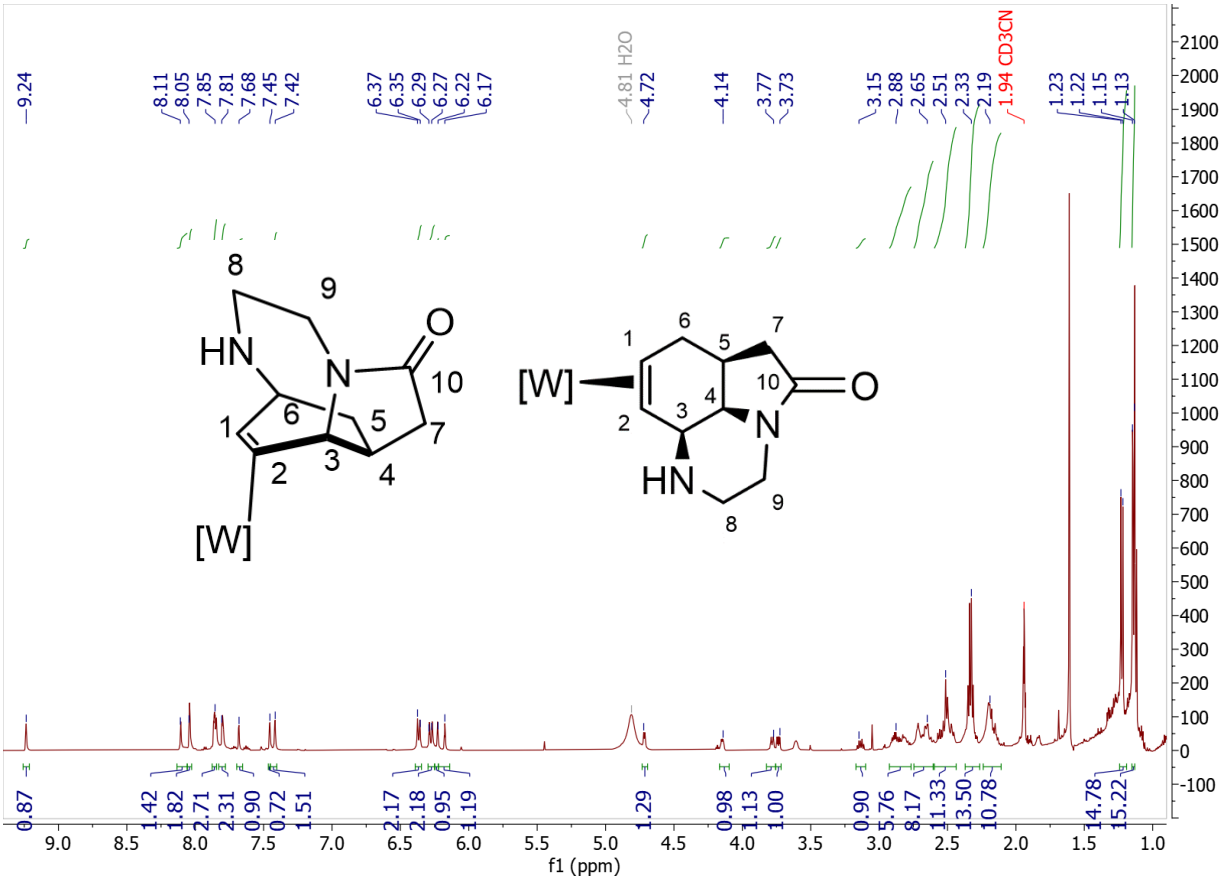
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.23:





Multiple crystallization experiments were attempted. However, none proved successful in isolating 20.

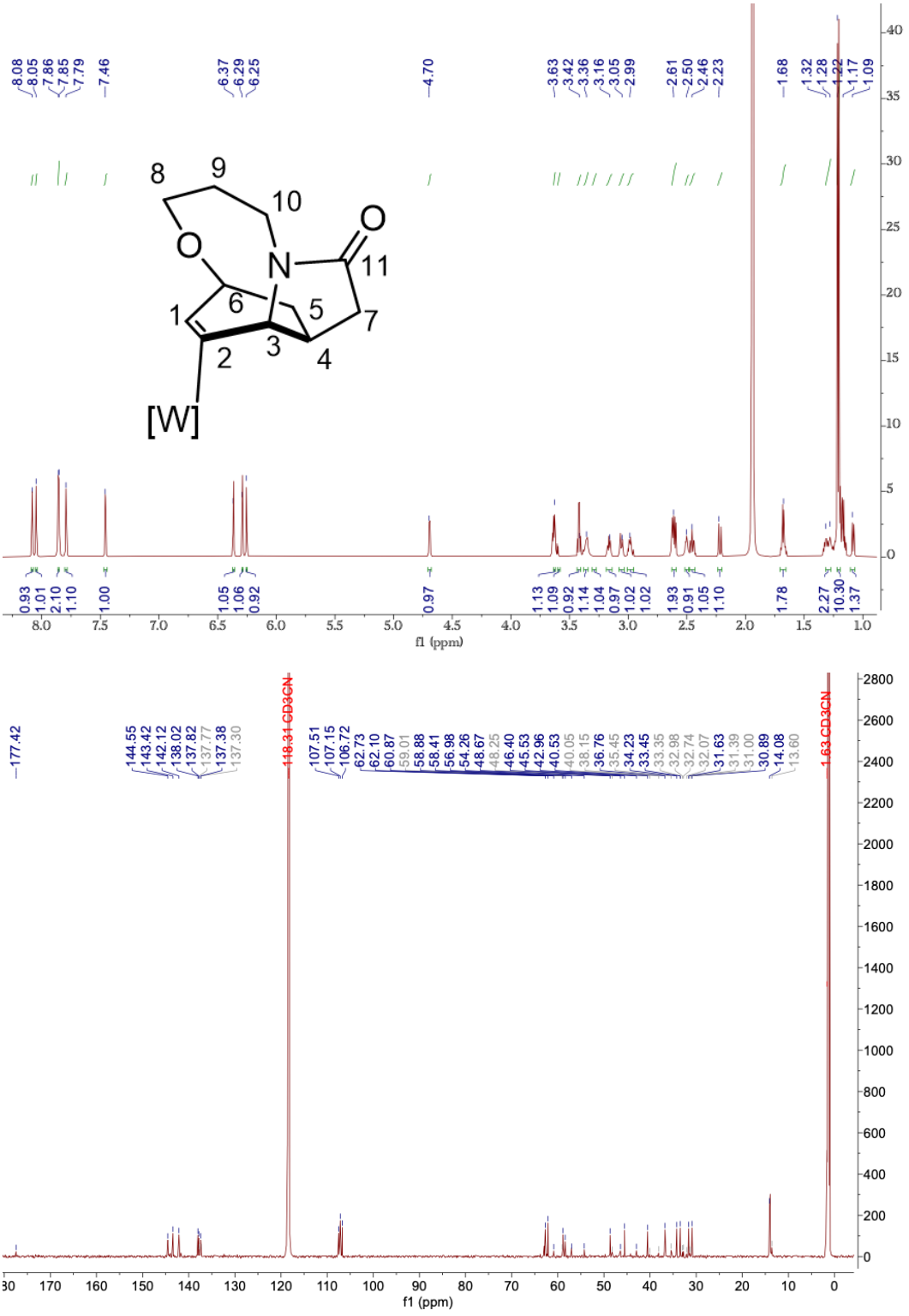
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.24 + 5.5:



Different reaction and separation conditions were employed to purify 21, but the mixture never resolved to a single isomer of 21.

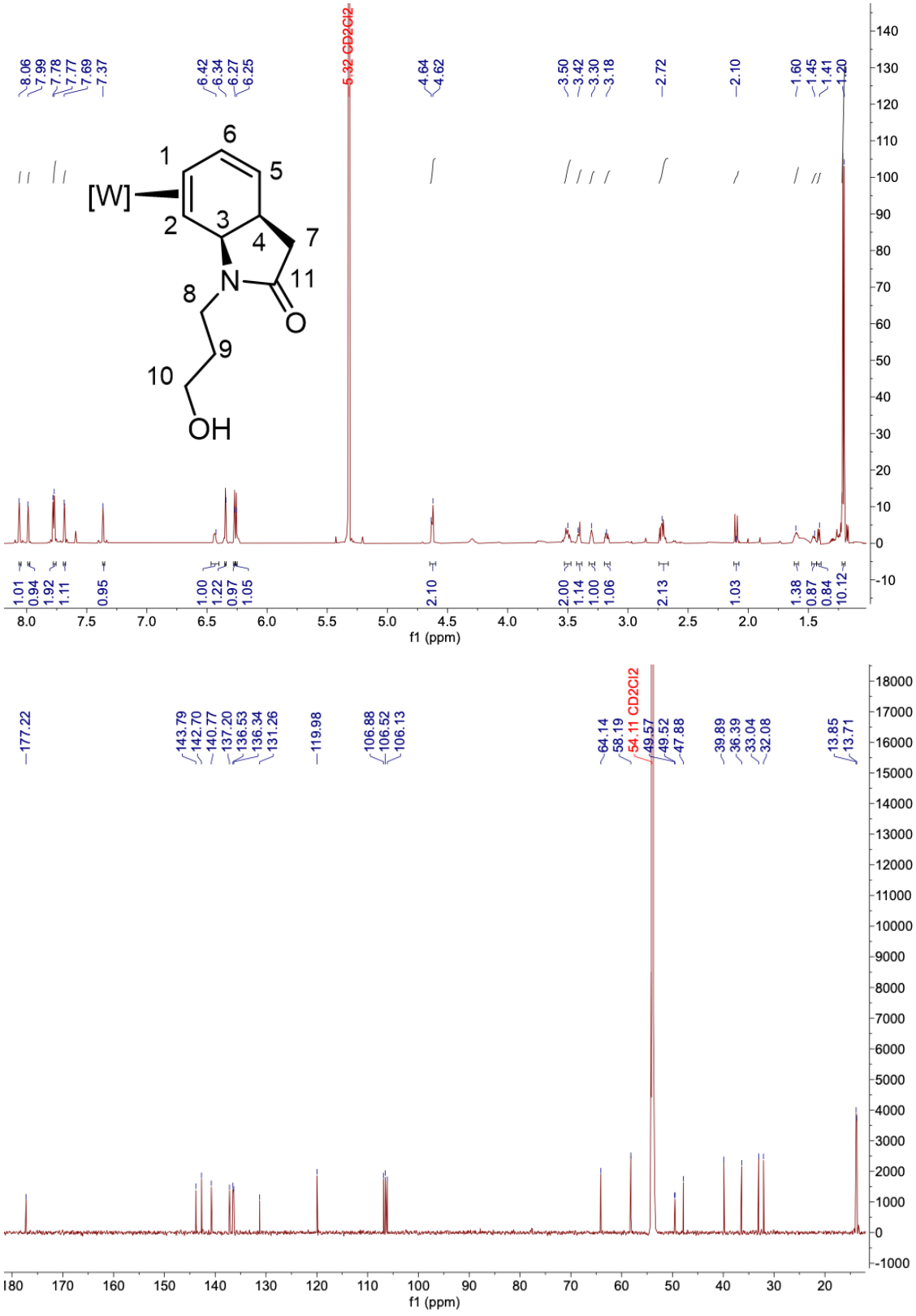
Multiple crystallization experiments were attempted. However, none proved successful in isolating 21.

^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.25:

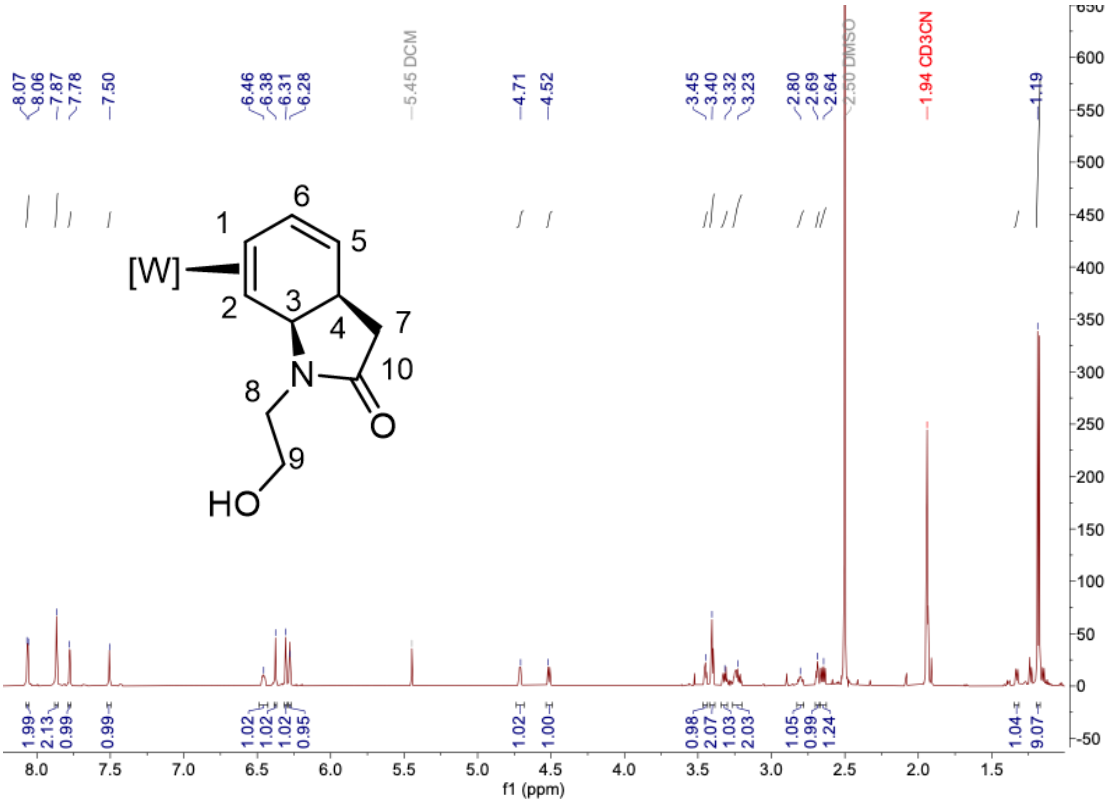


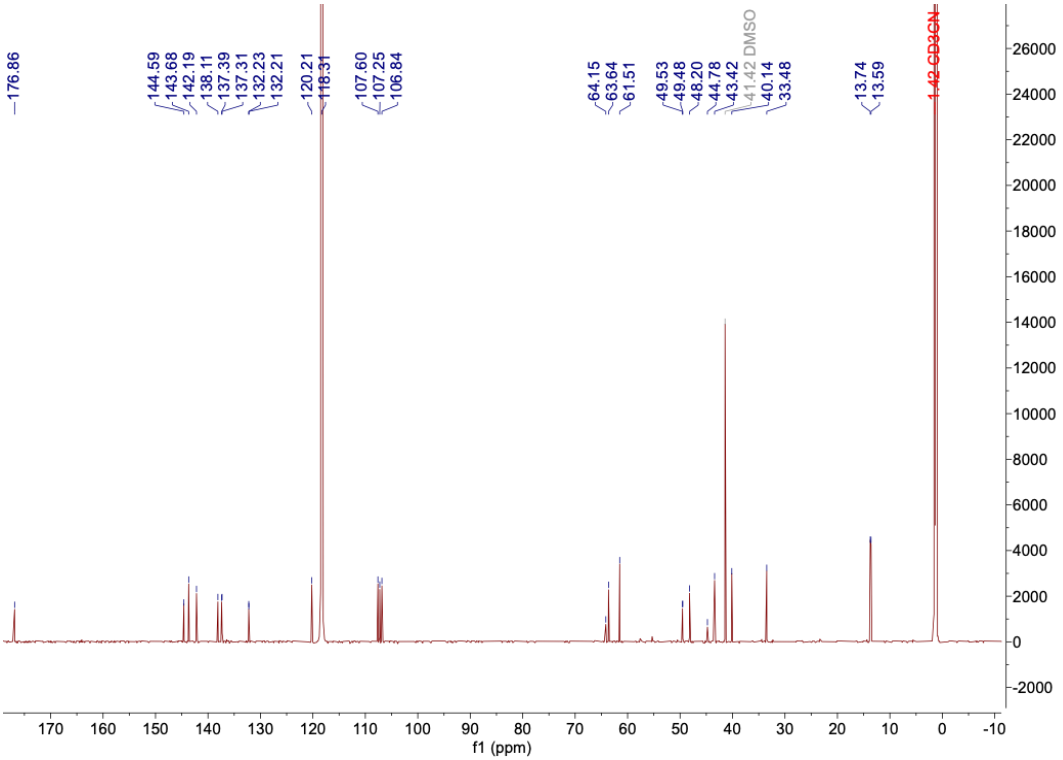
Multiple crystallization experiments were attempted. However, none proved successful in isolating 24.

^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 5.26:

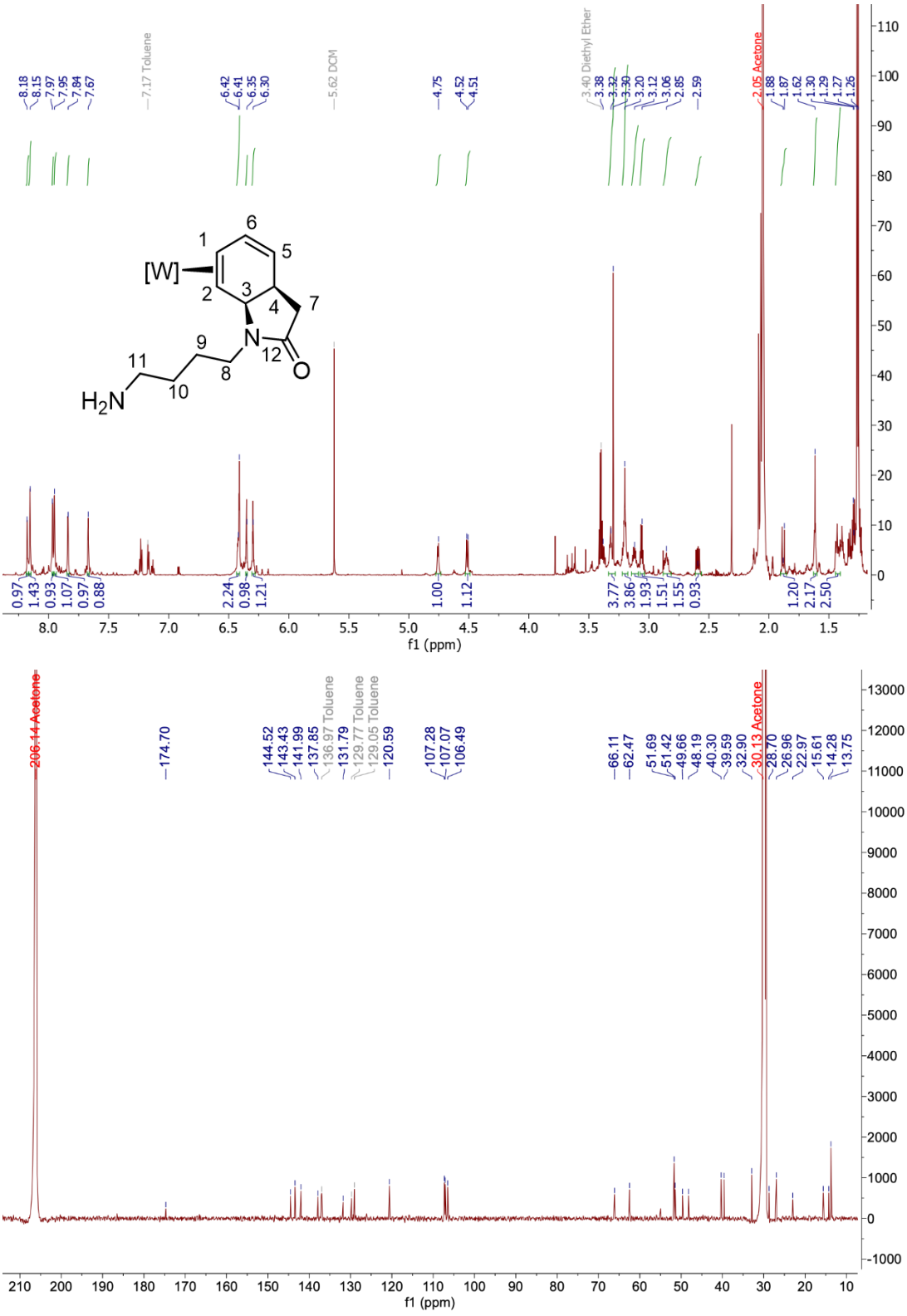


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.27:

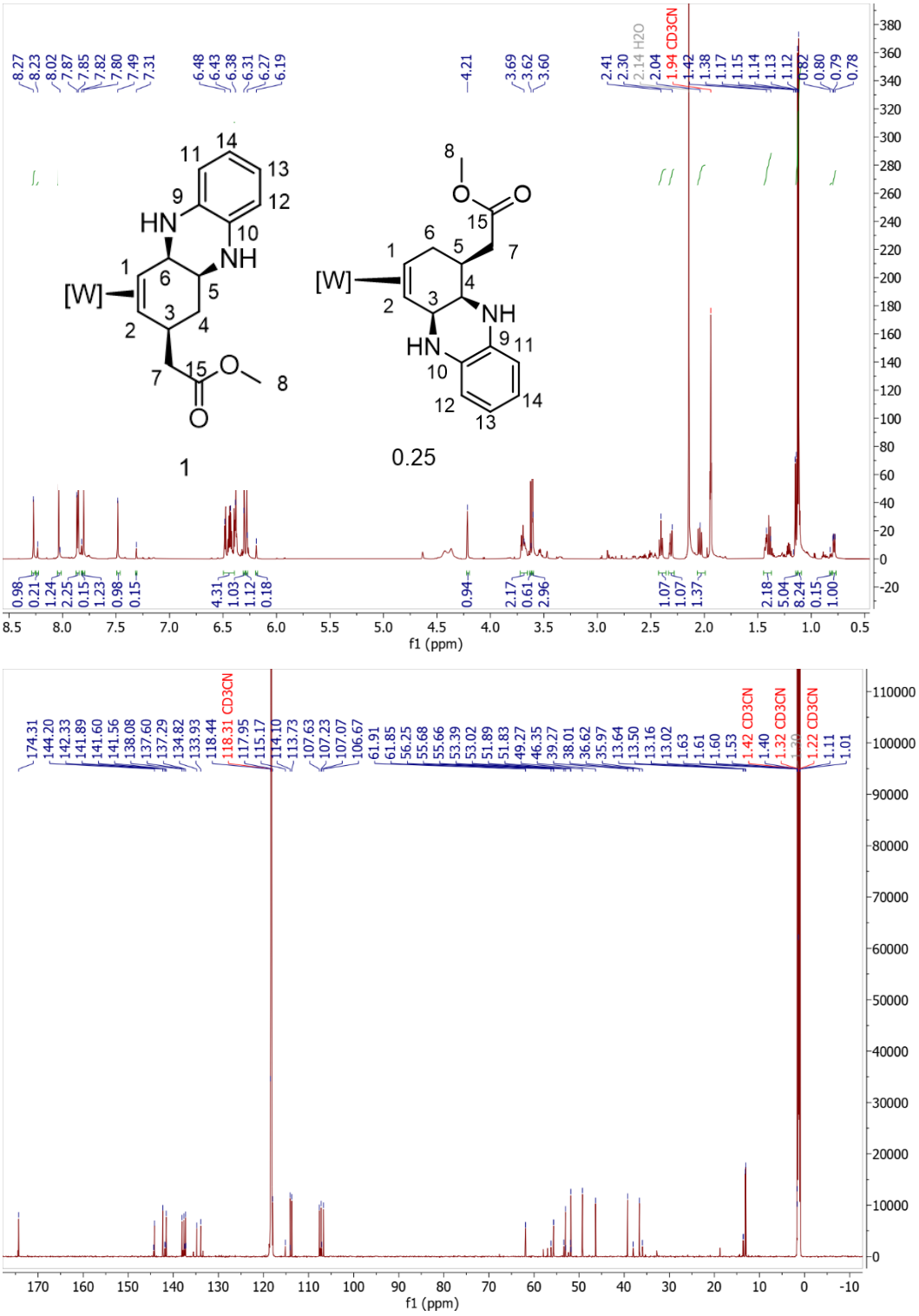




^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.28:

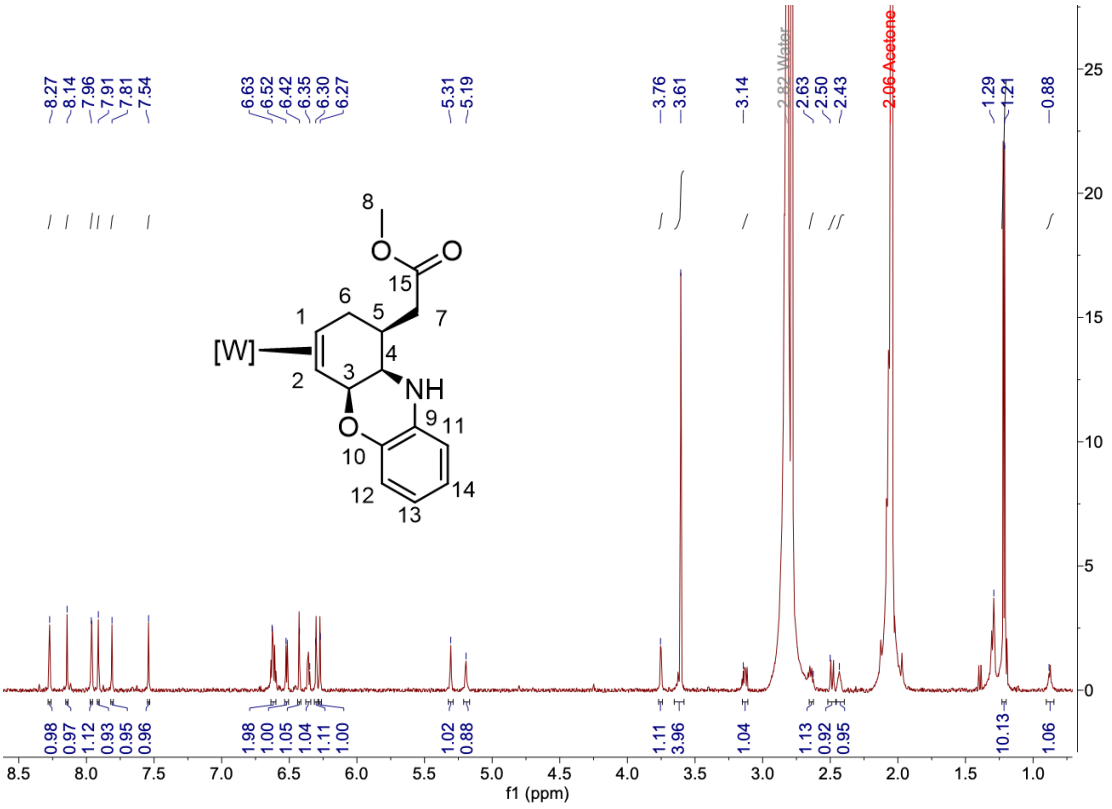


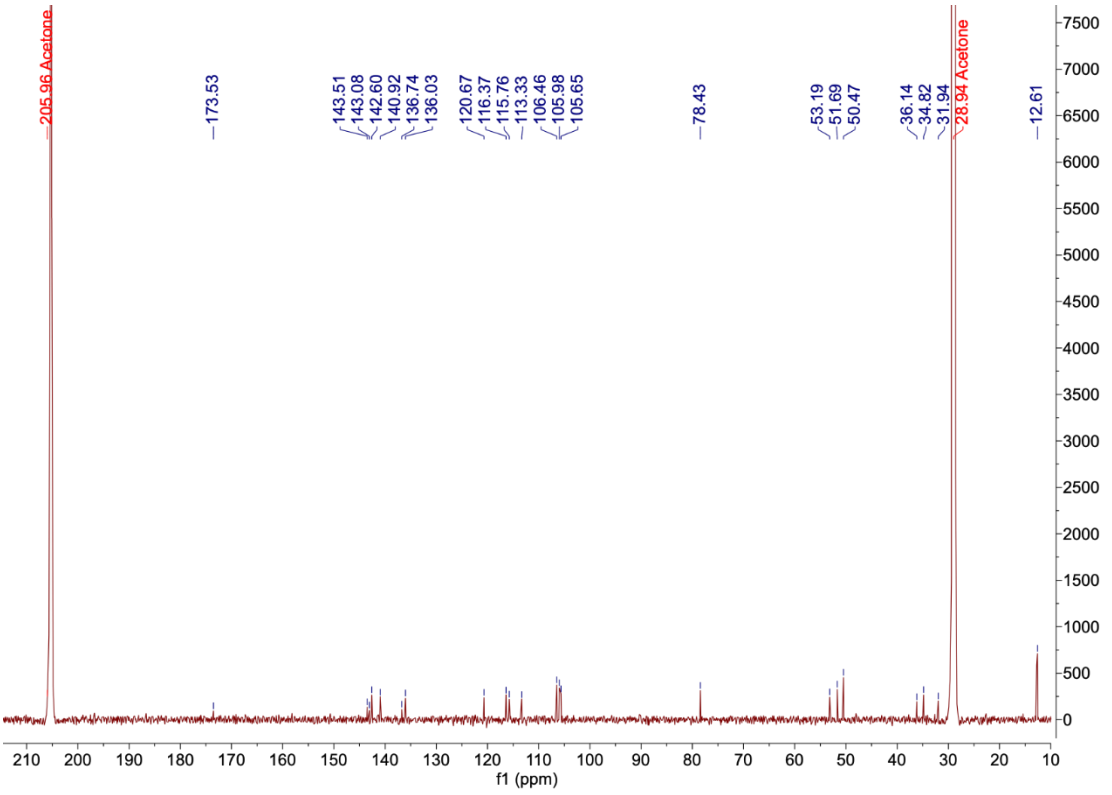
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.29 + 5.31:



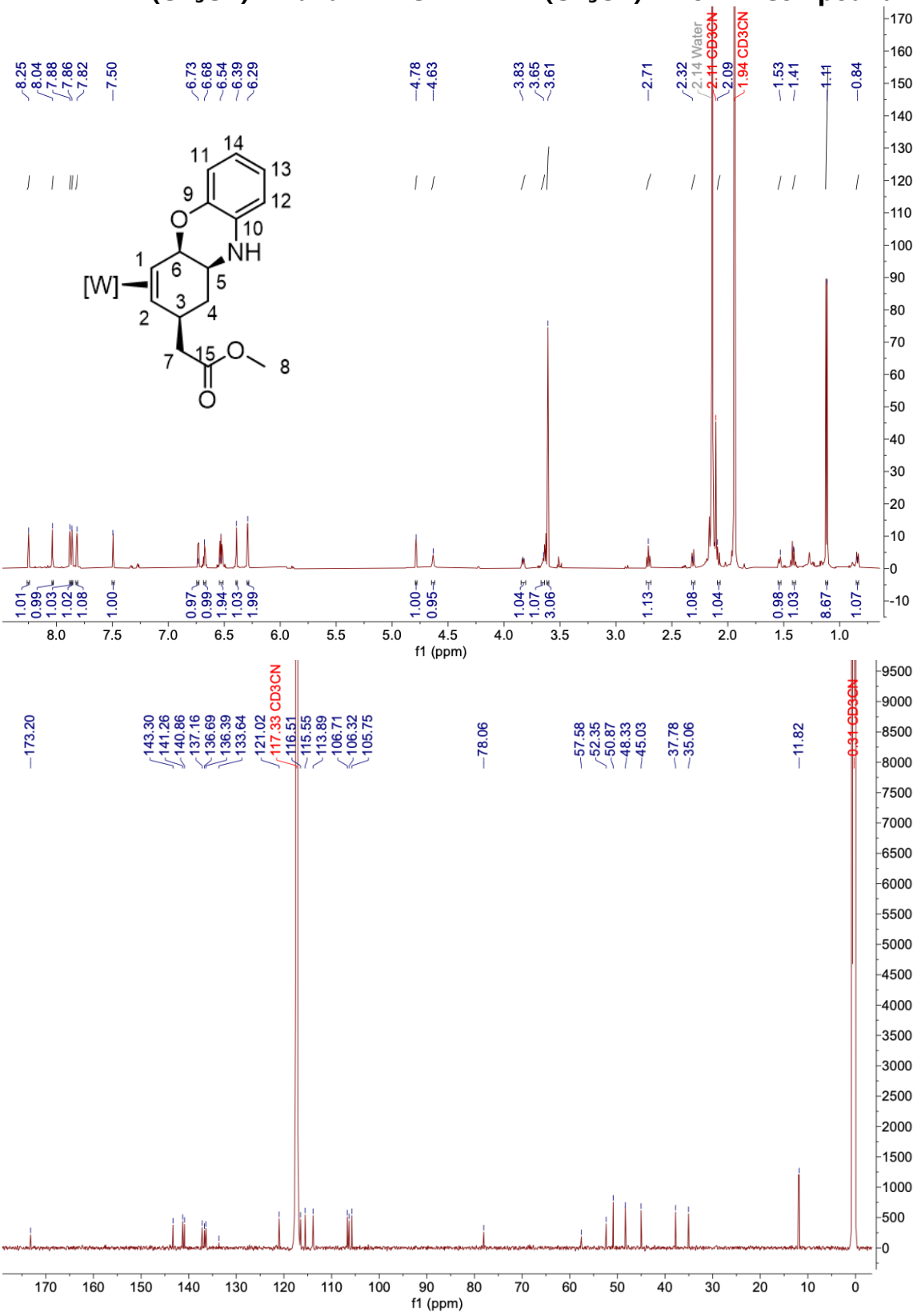
Different reaction and separation conditions were employed to purify 28 from 26, but the mixture never resolved to a single isomer of 28. Multiple crystallization.

^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 5.30:

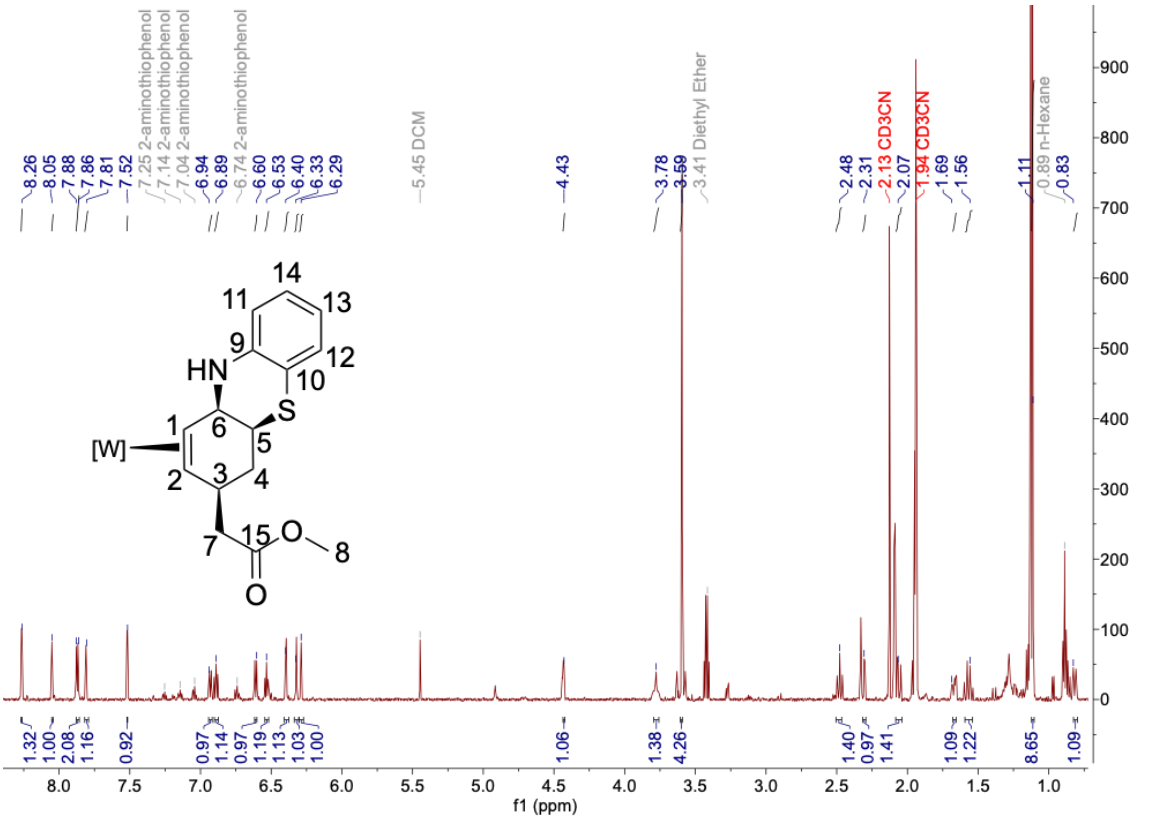


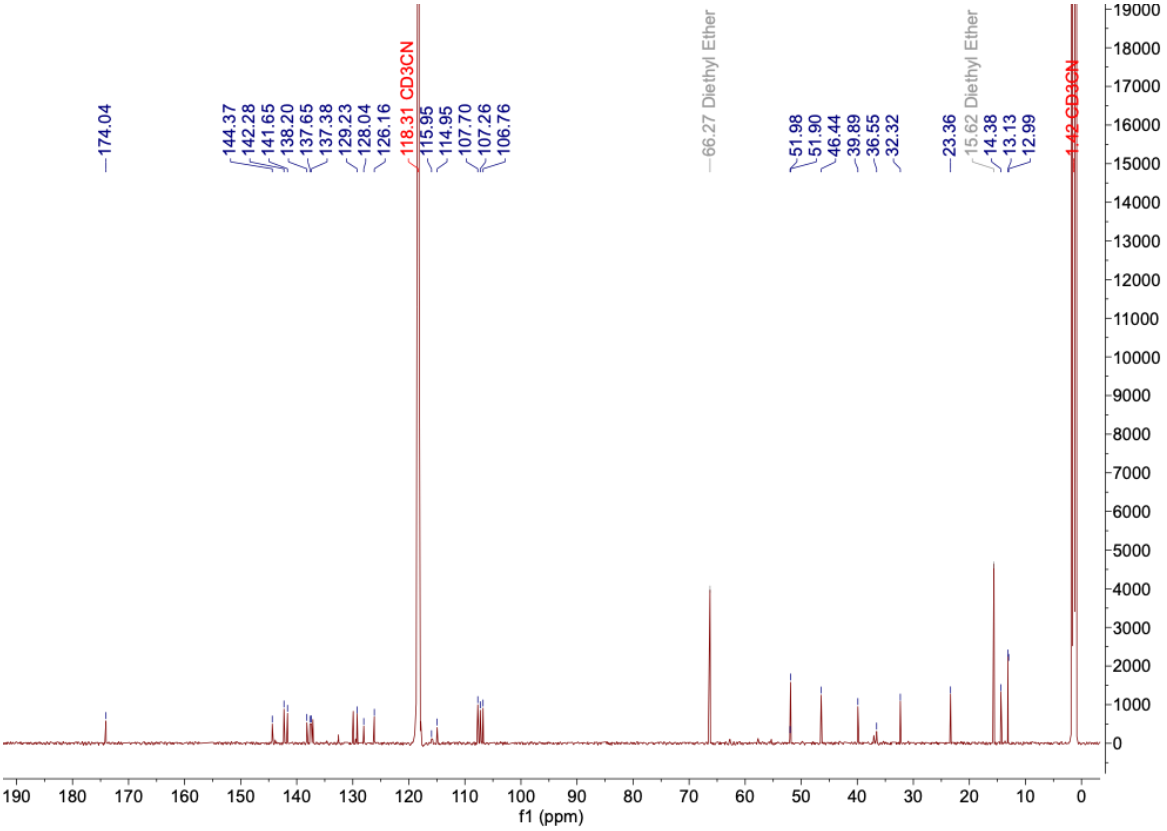


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.32:

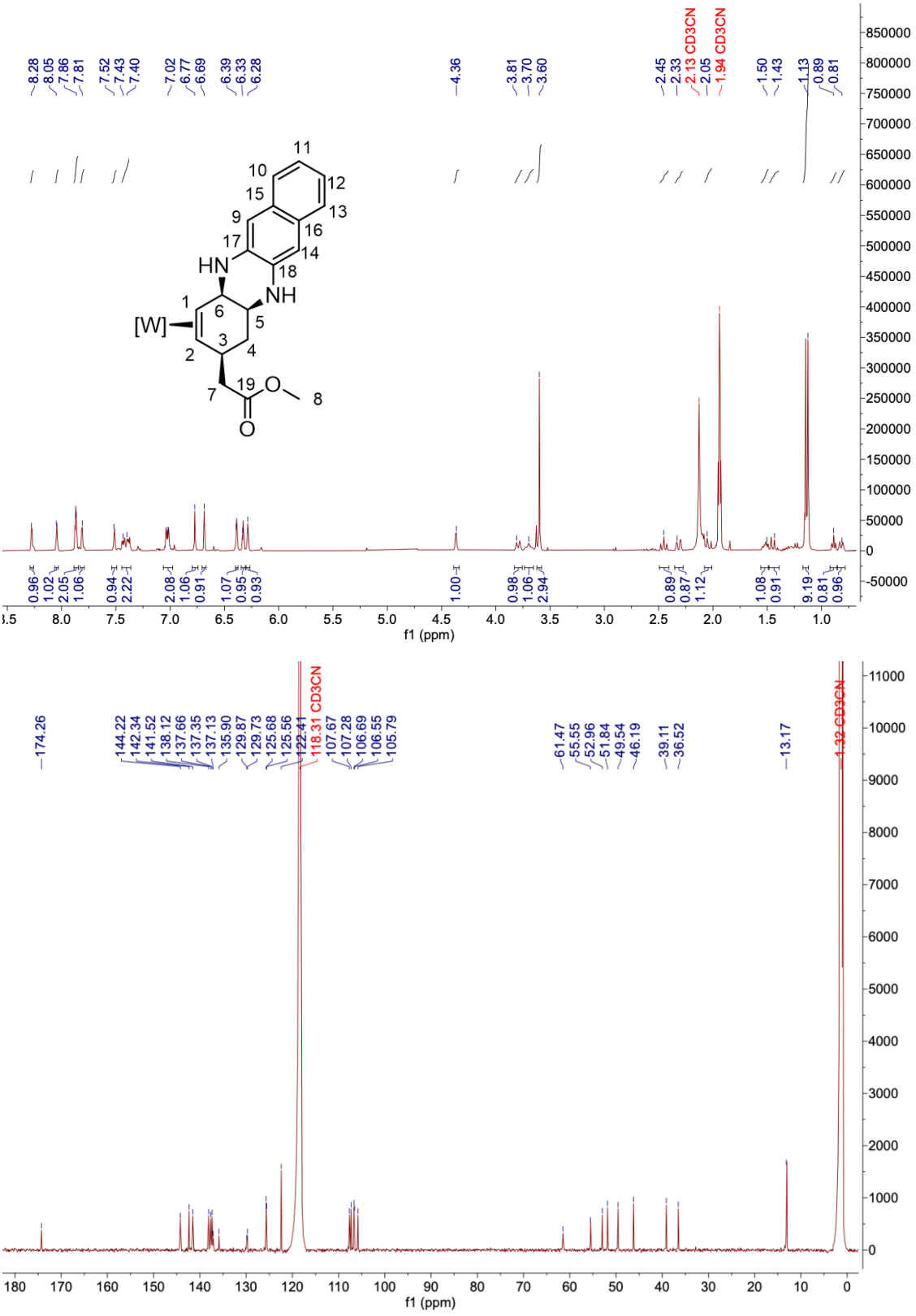


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.33:

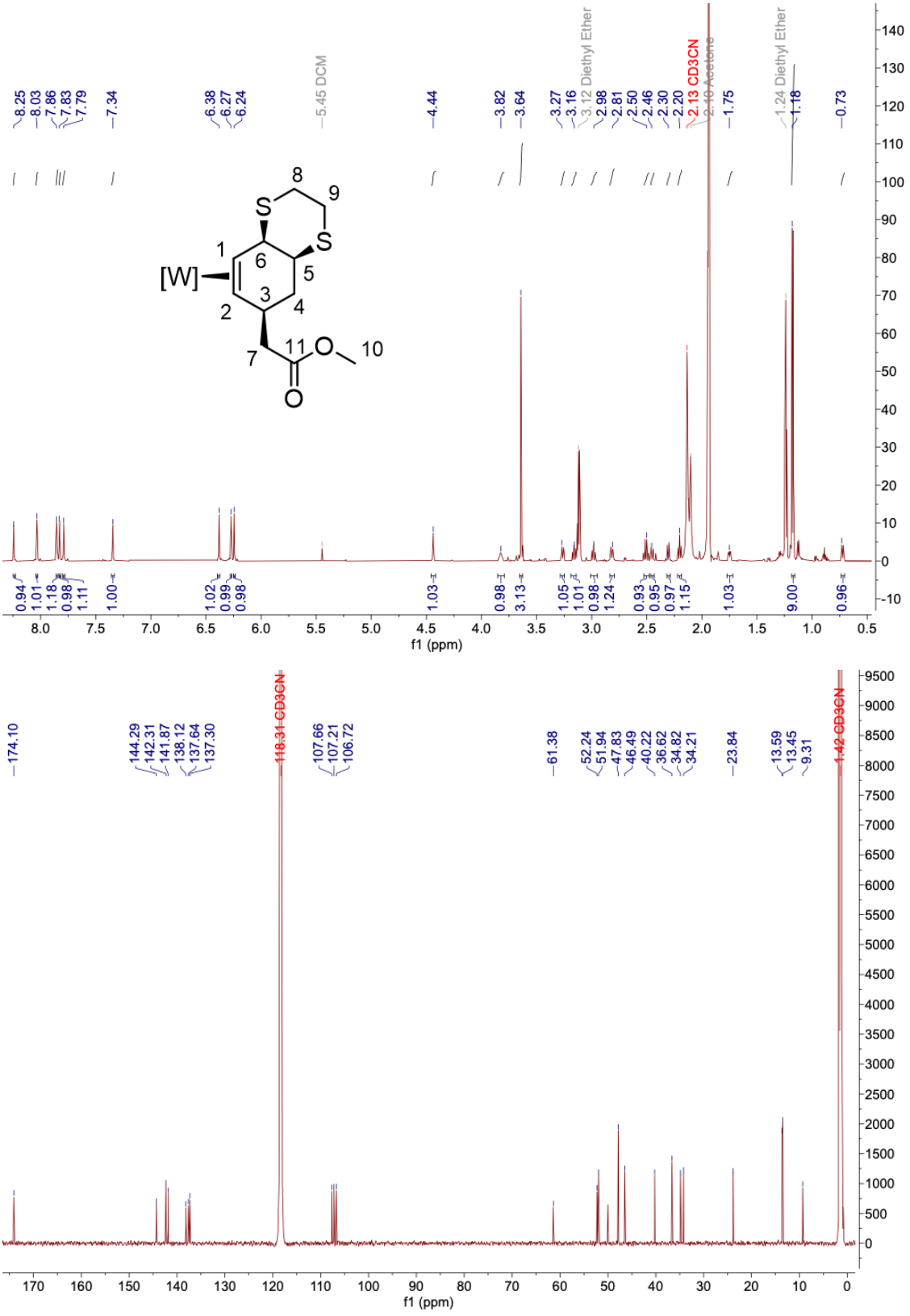




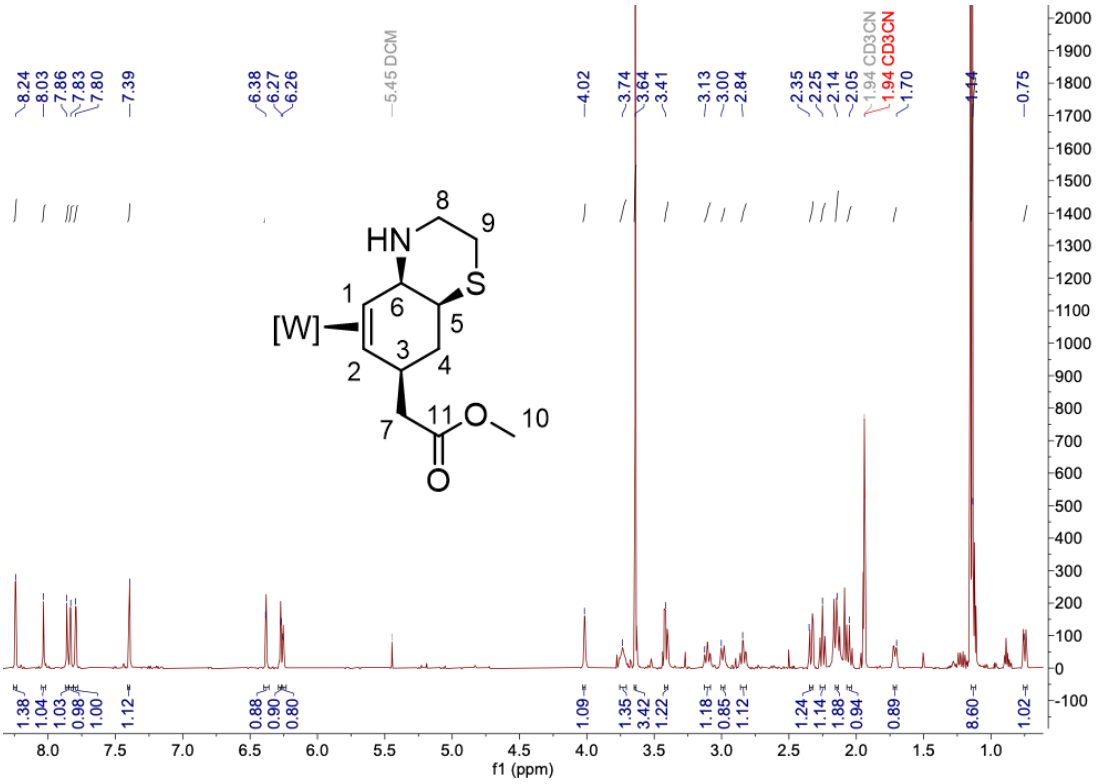
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.34:

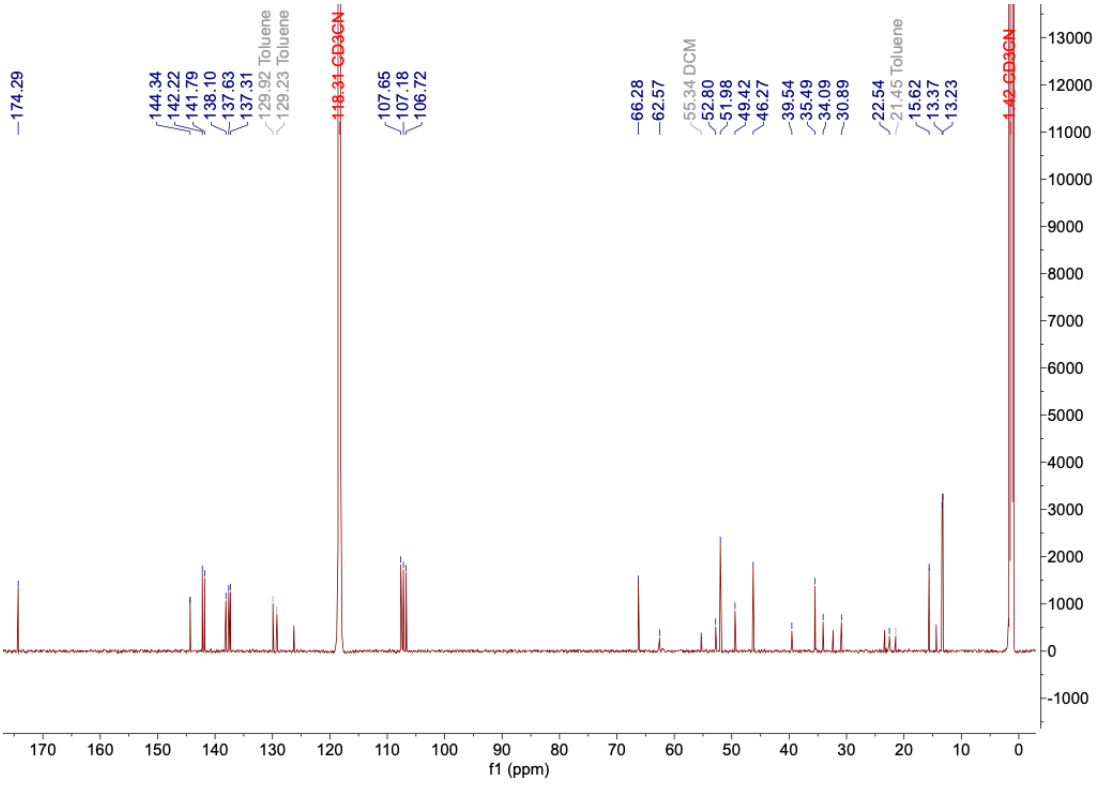


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.35:

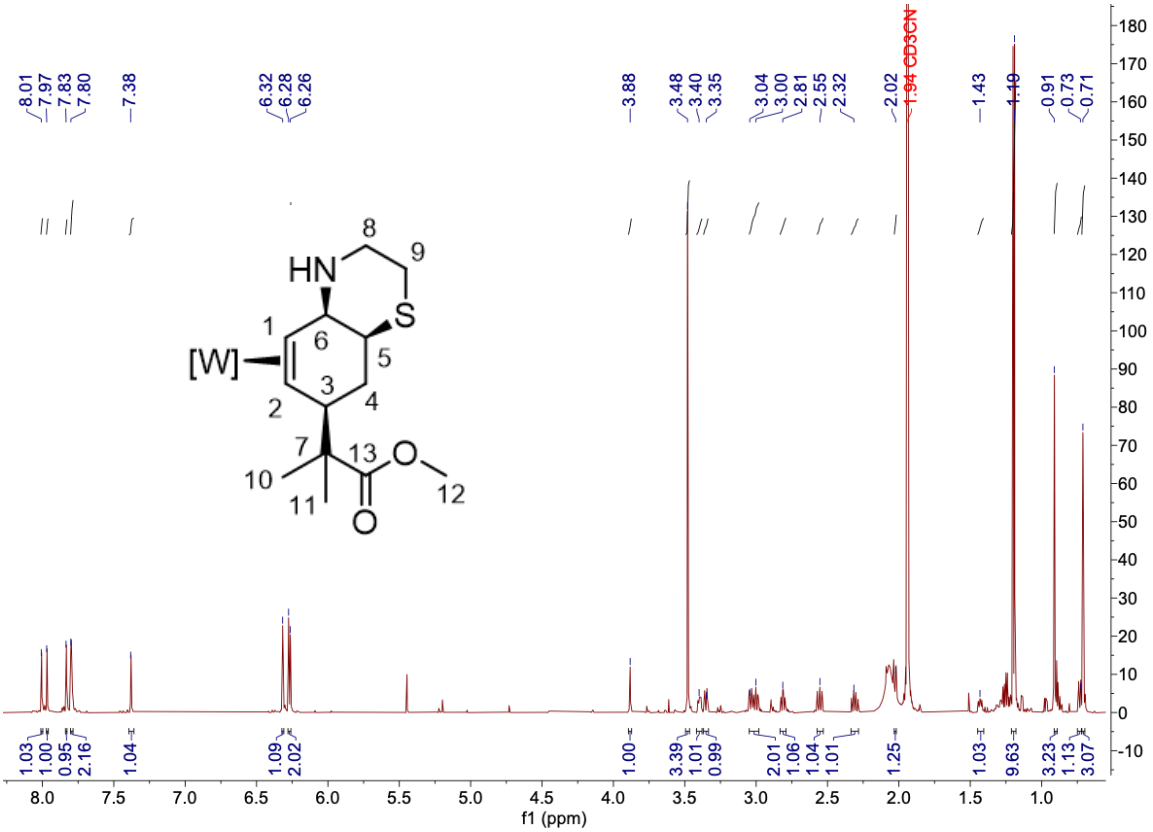


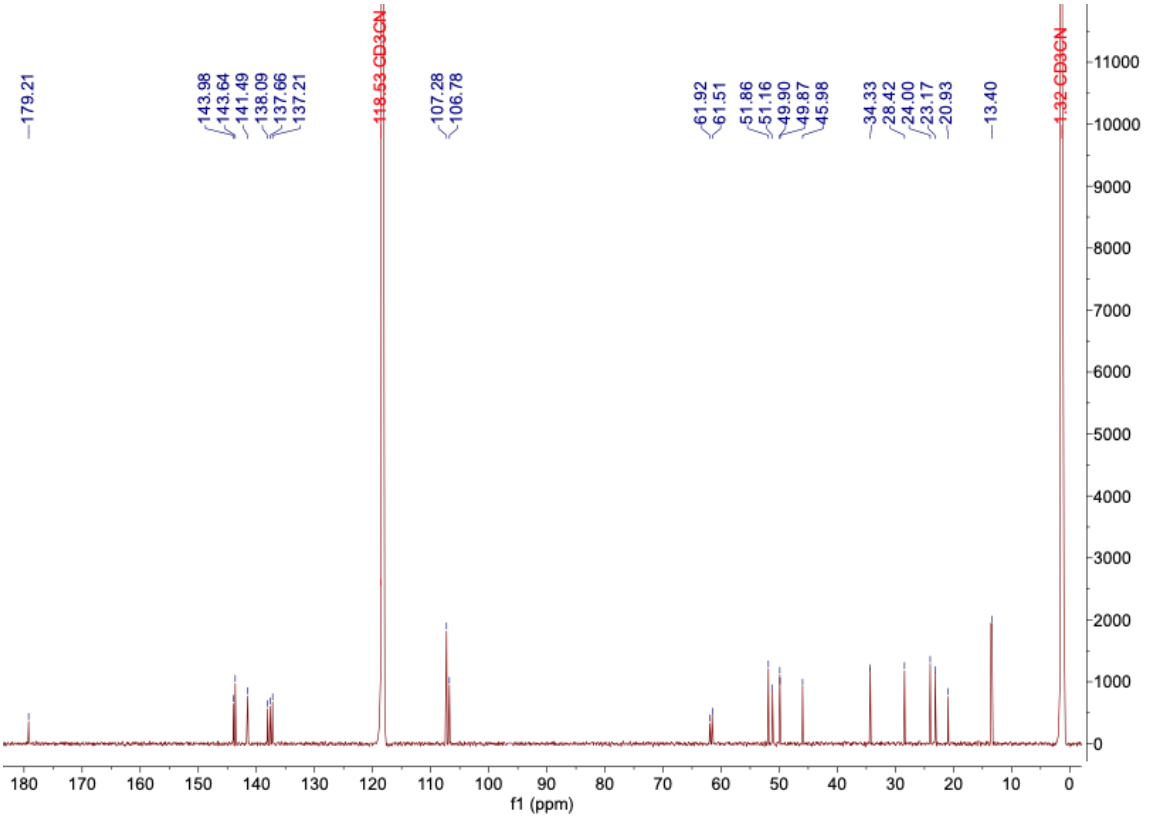
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.36:



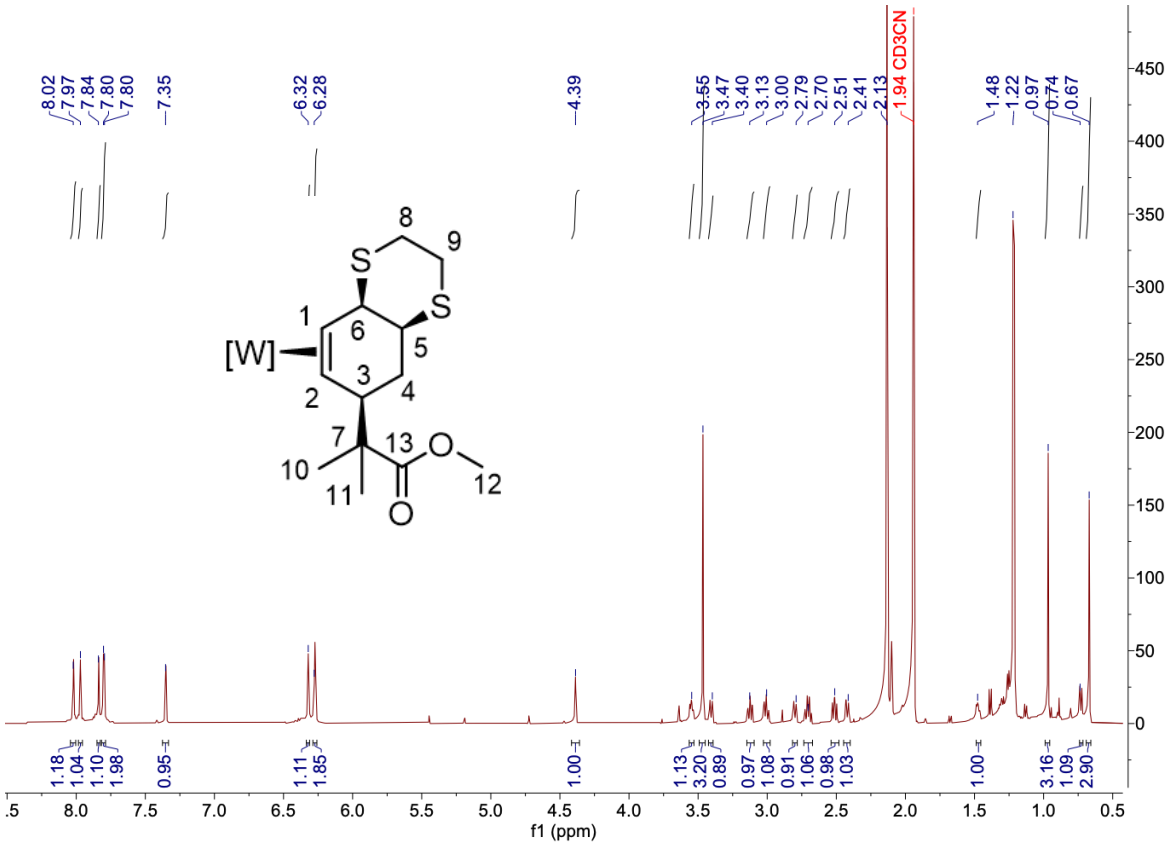


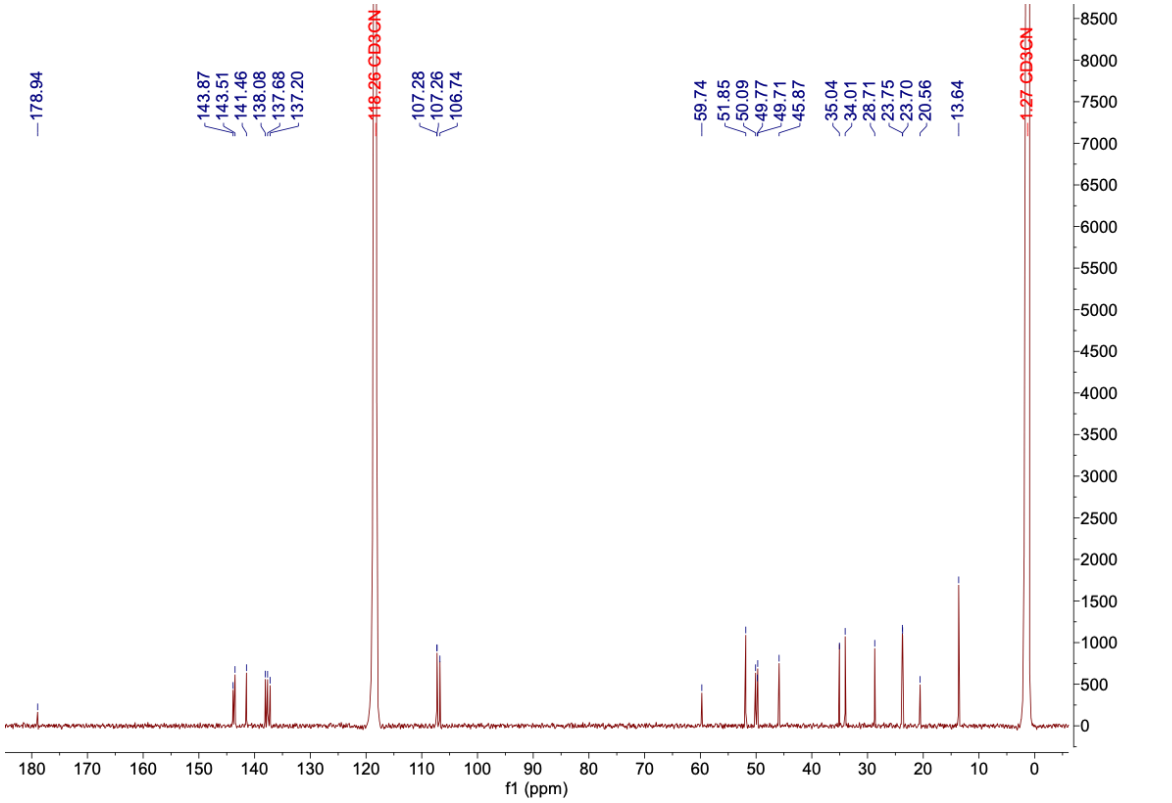
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.37:



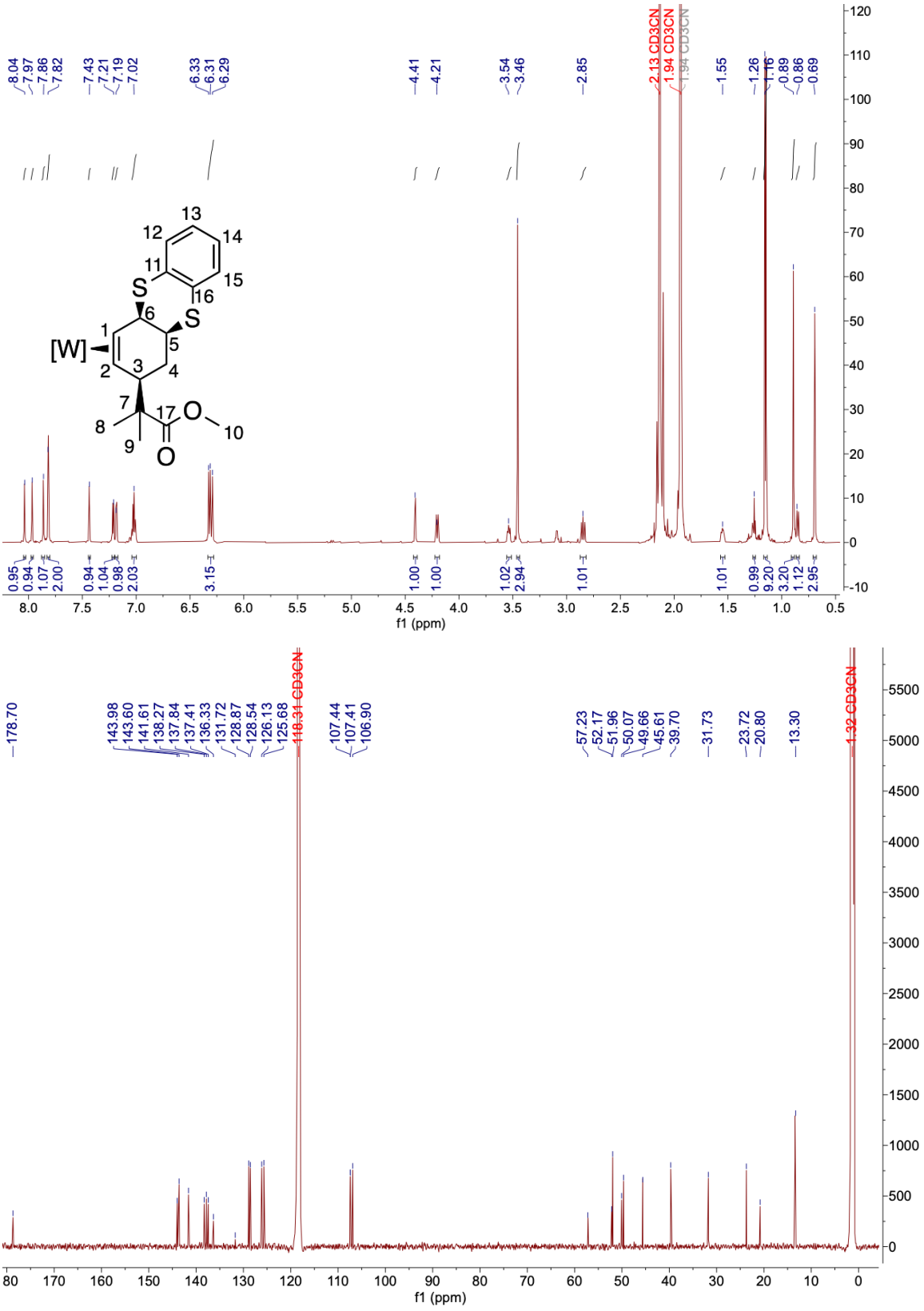


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.38:

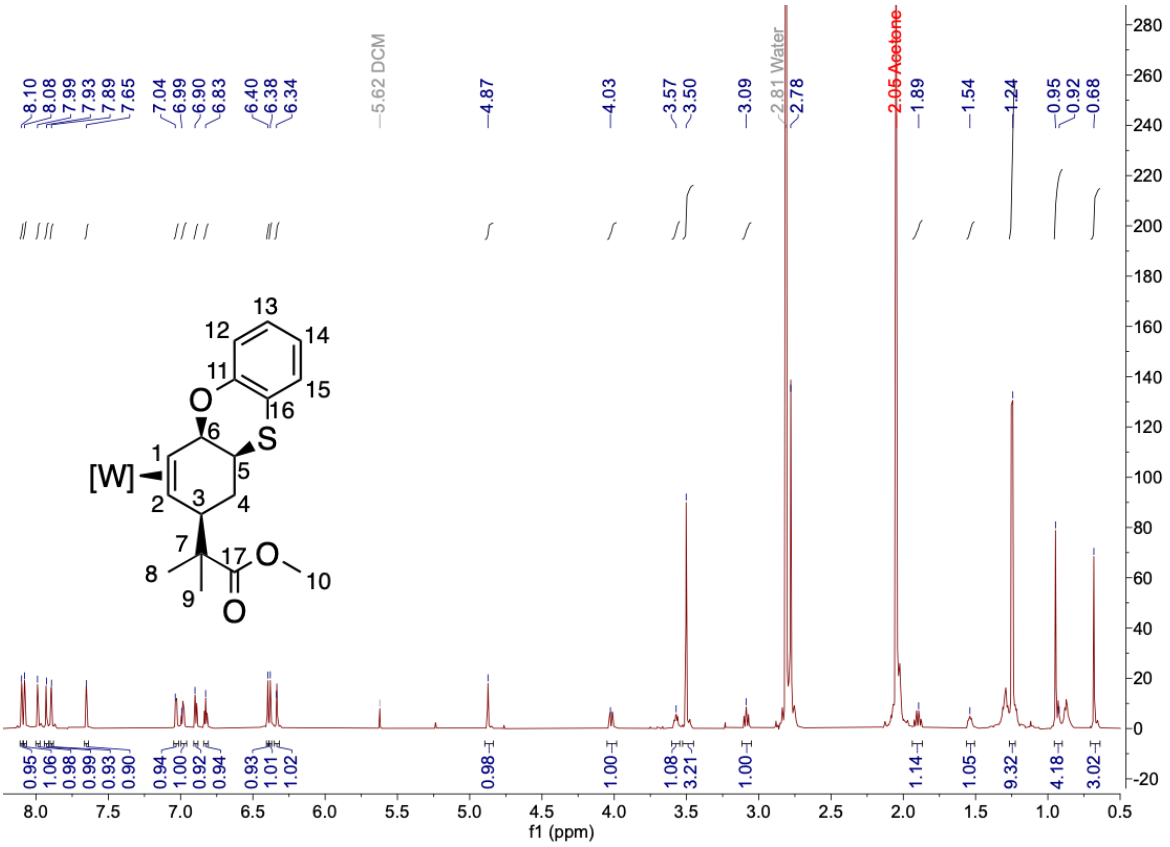


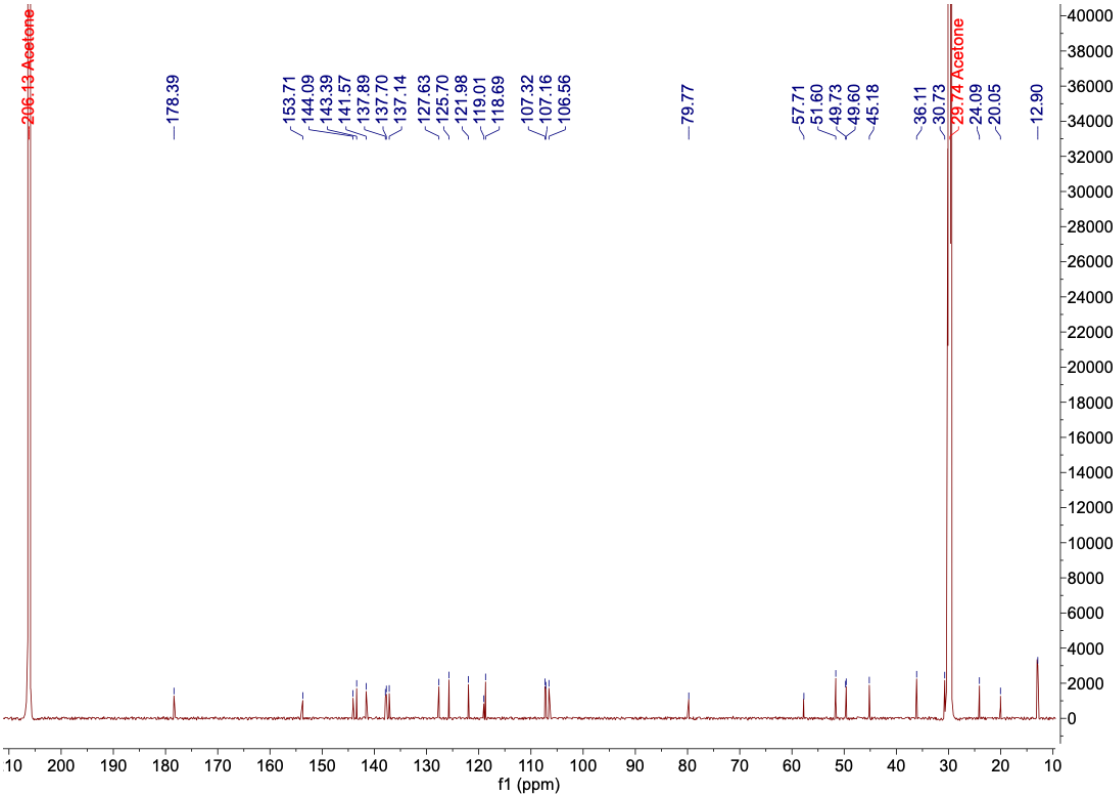


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.39:

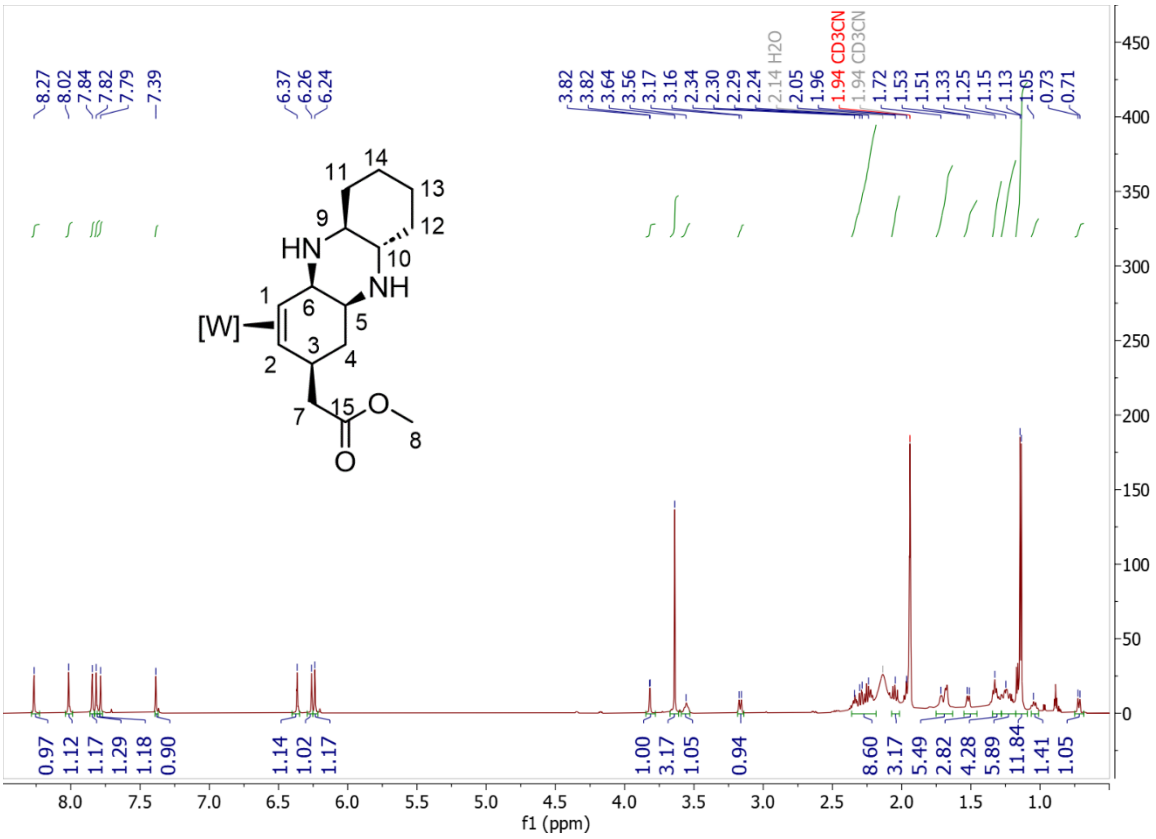


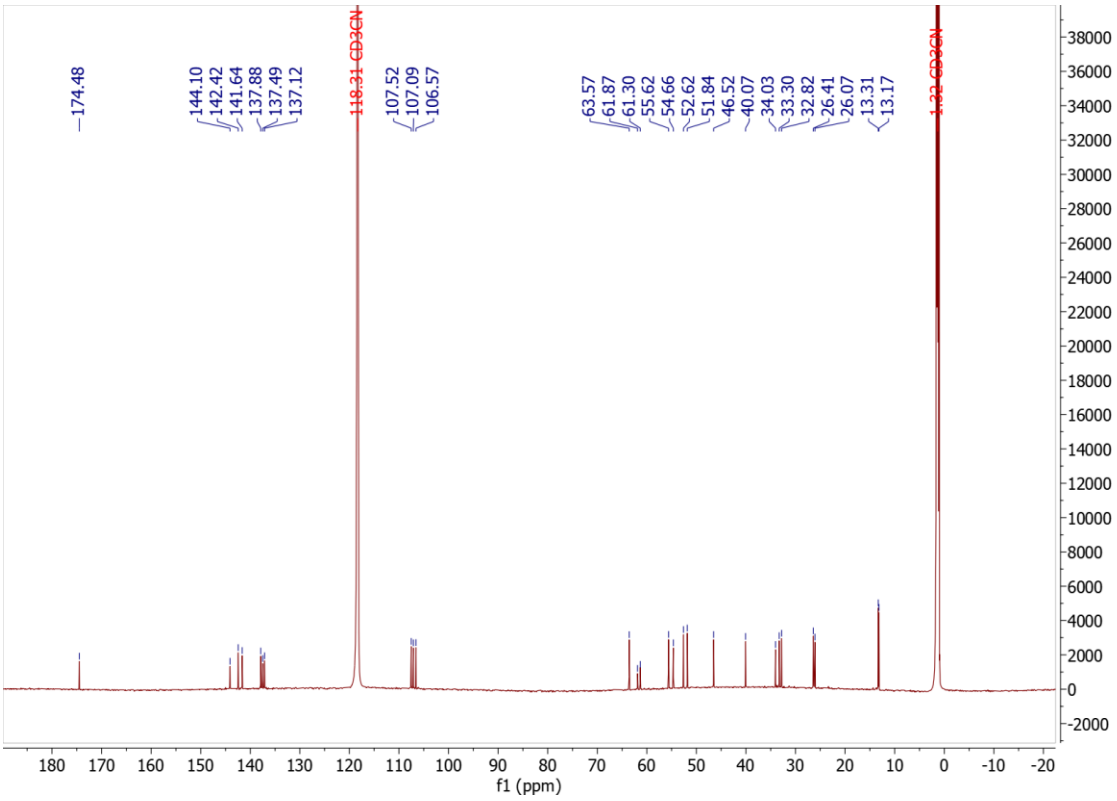
^{1}H-NMR ($(CD_3)_2CO$) and ^{13}C-NMR ($(CD_3)_2CO$) of Compound 5.40:



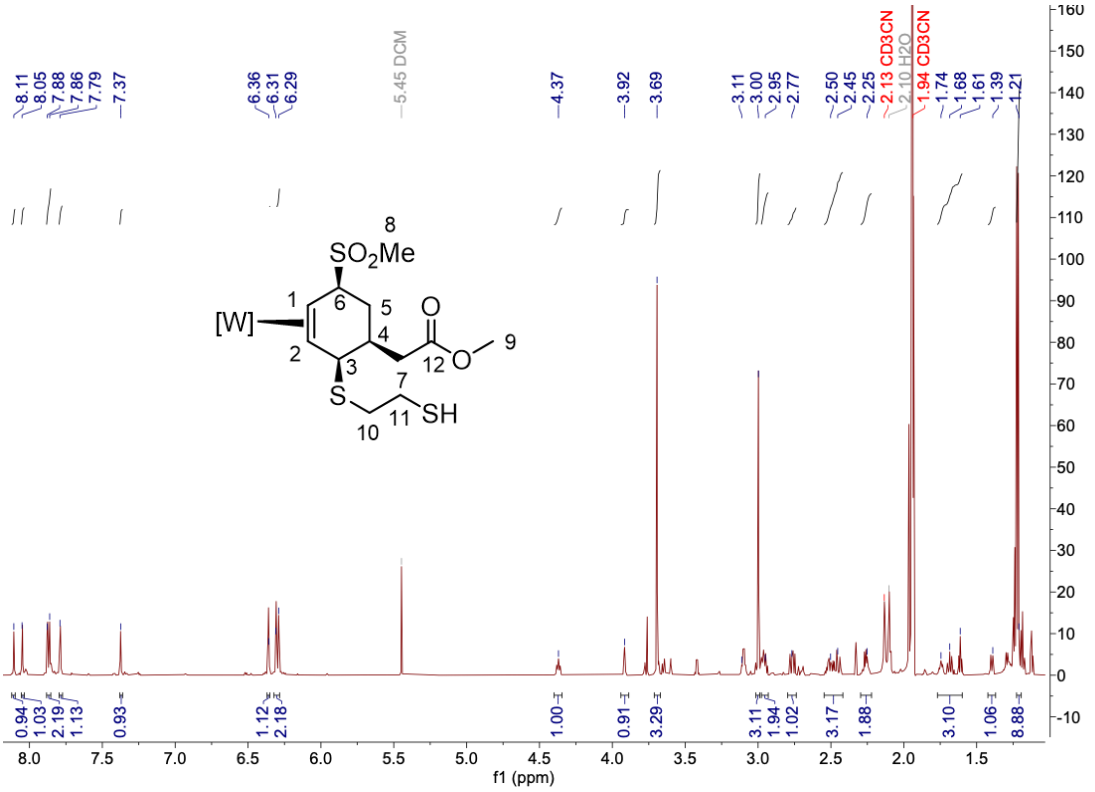


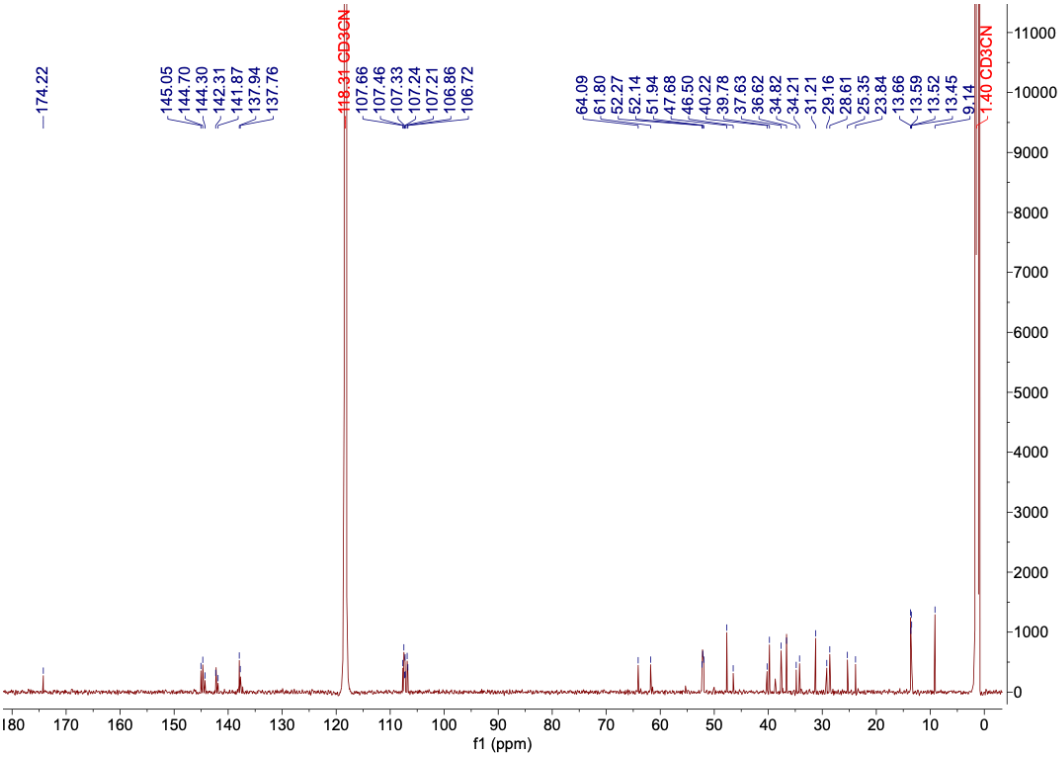
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.41:





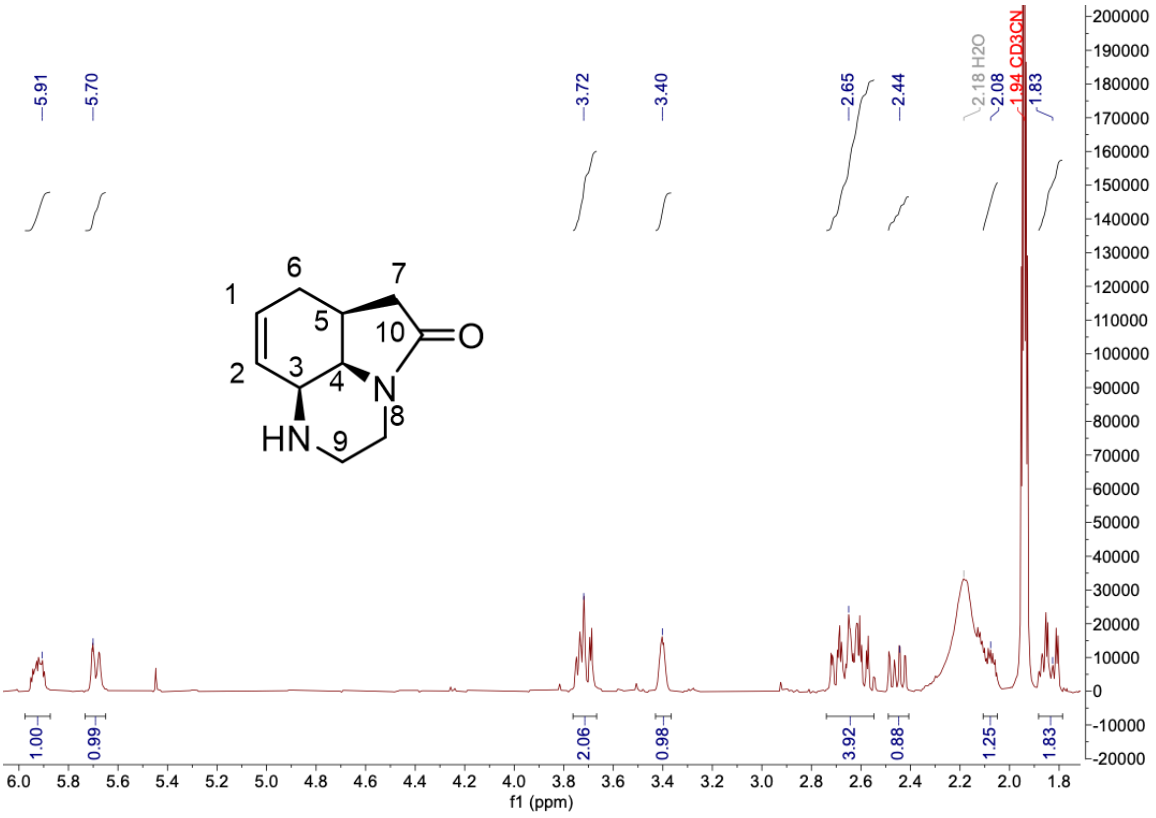
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.42:

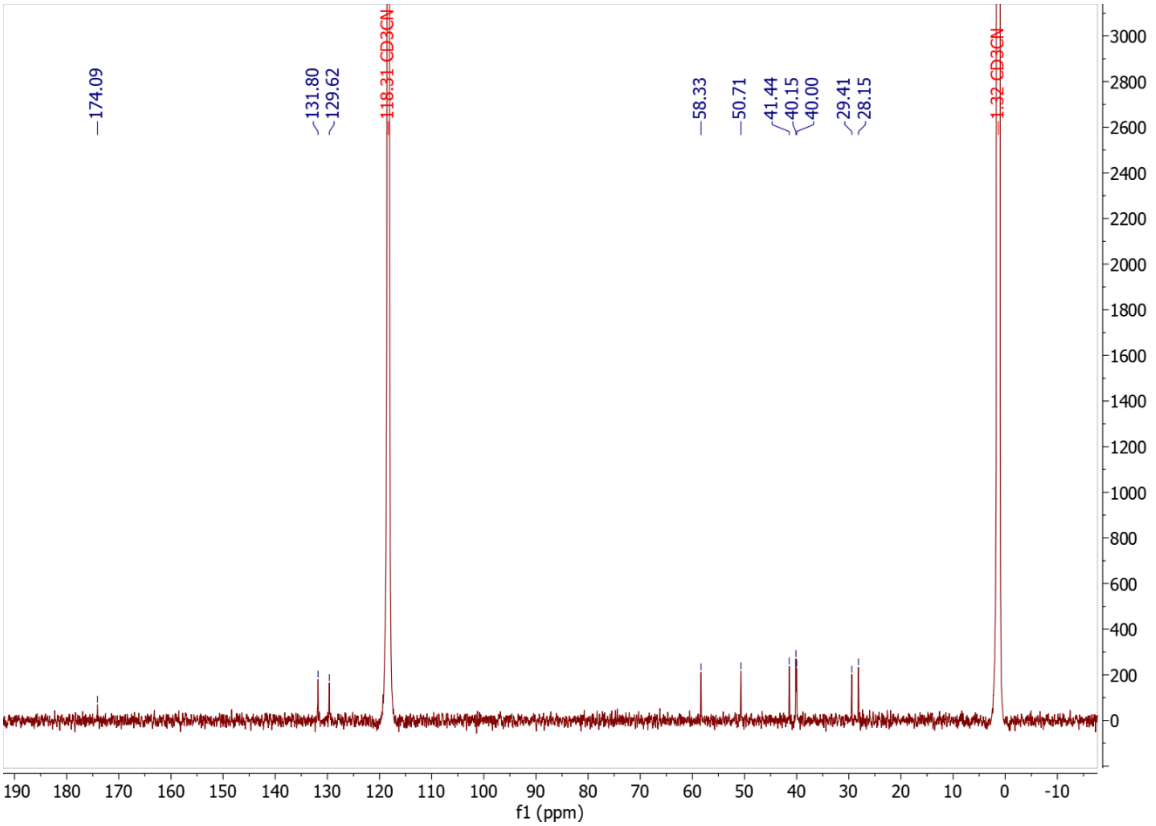




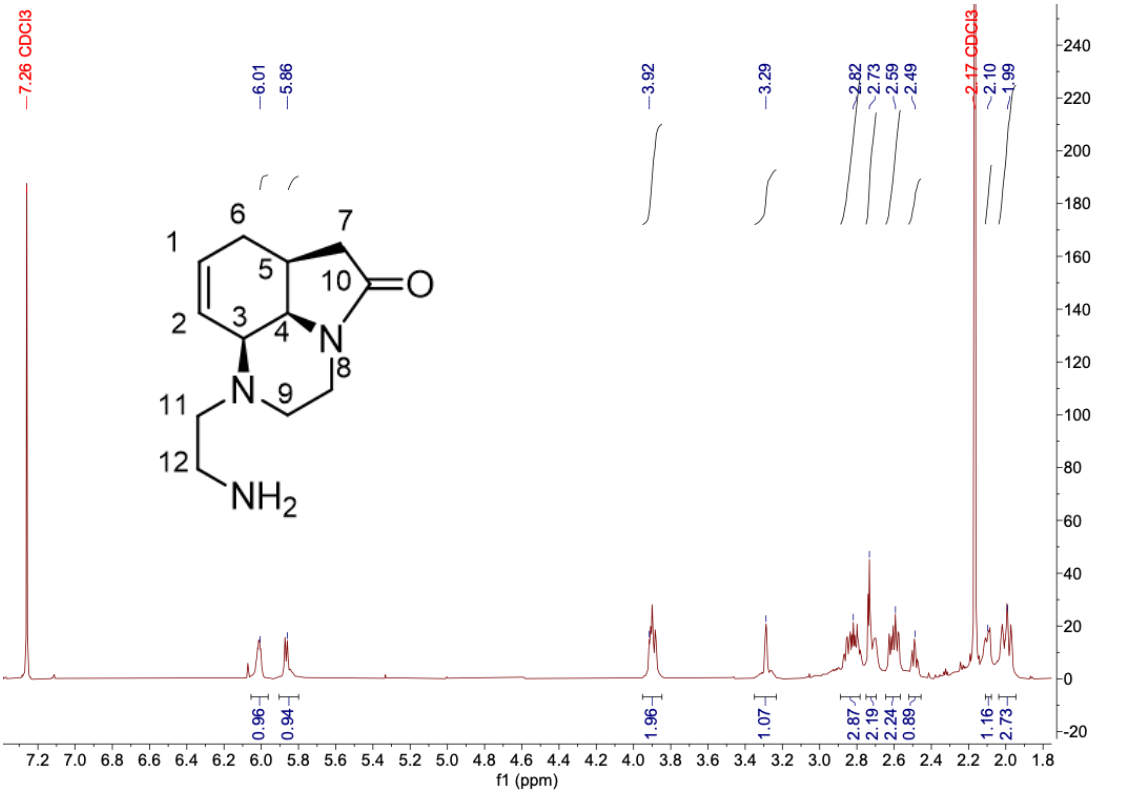
Over the course of the 2D NMR experiments 38 partially converts into 32.

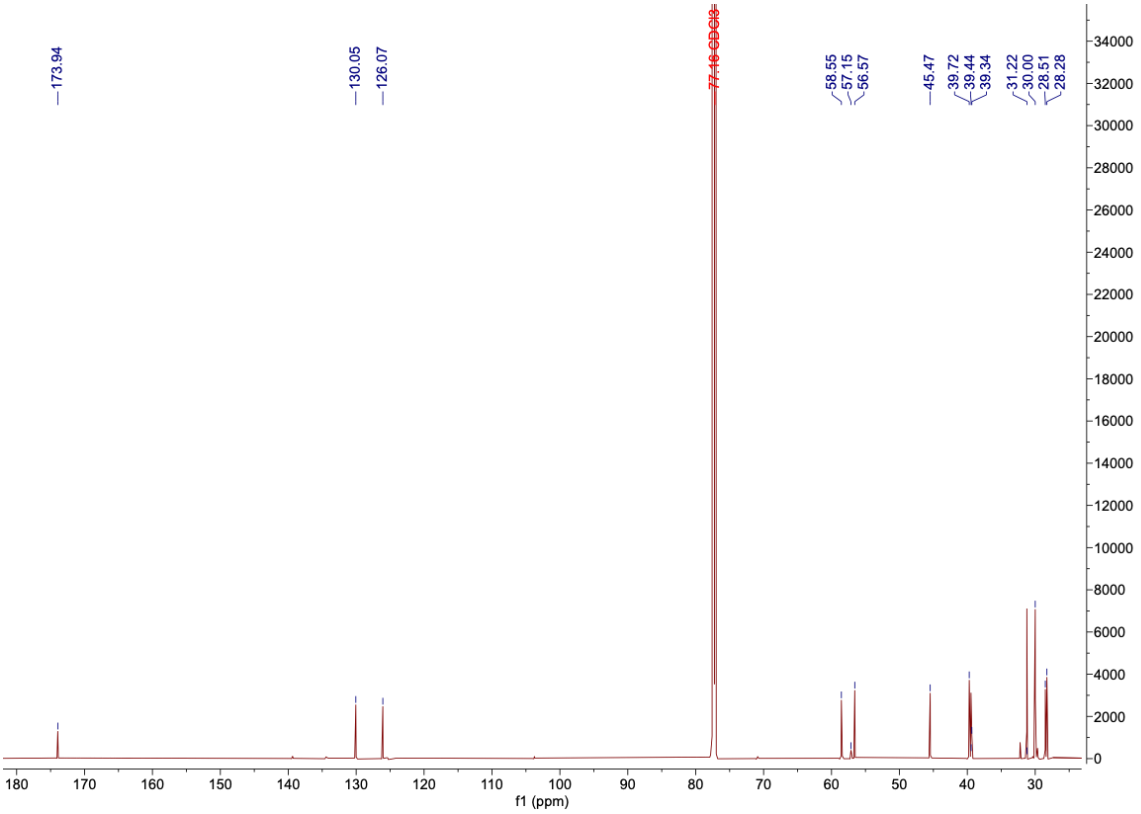
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.44:



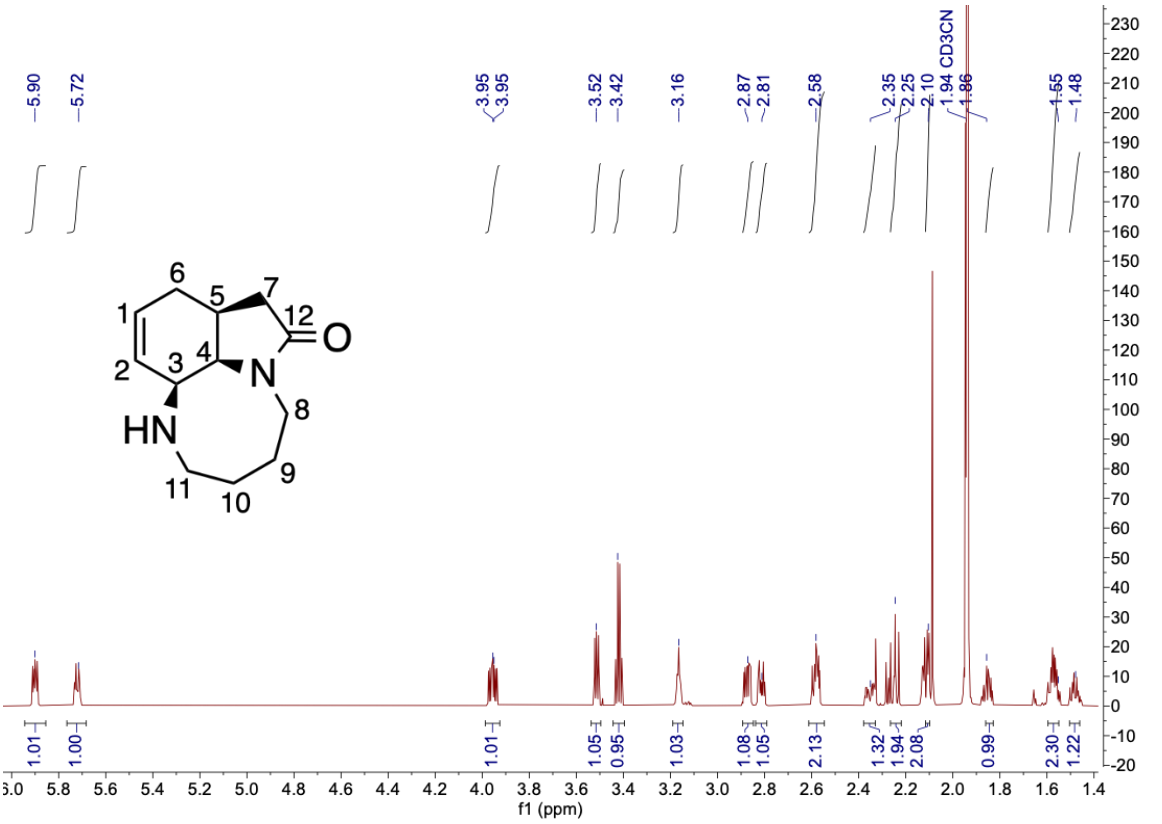


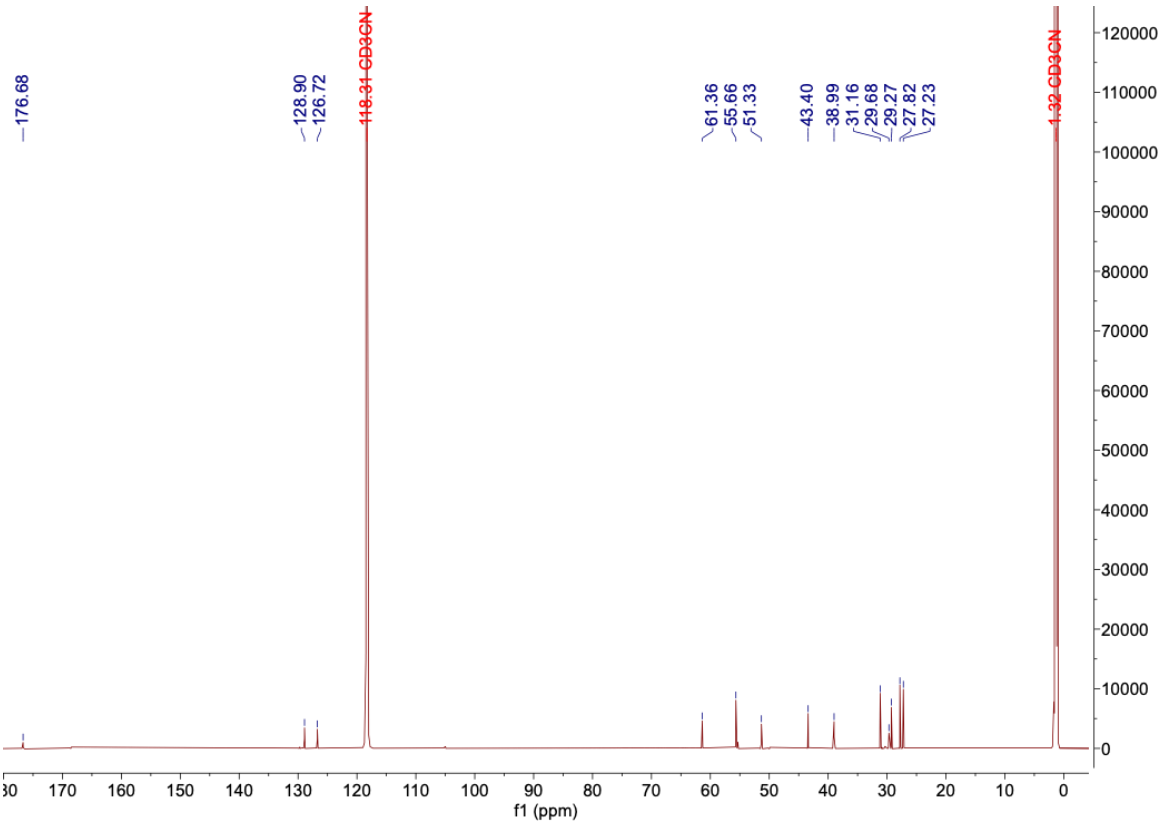
^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR ($CDCl_3$) of Compound 5.45:



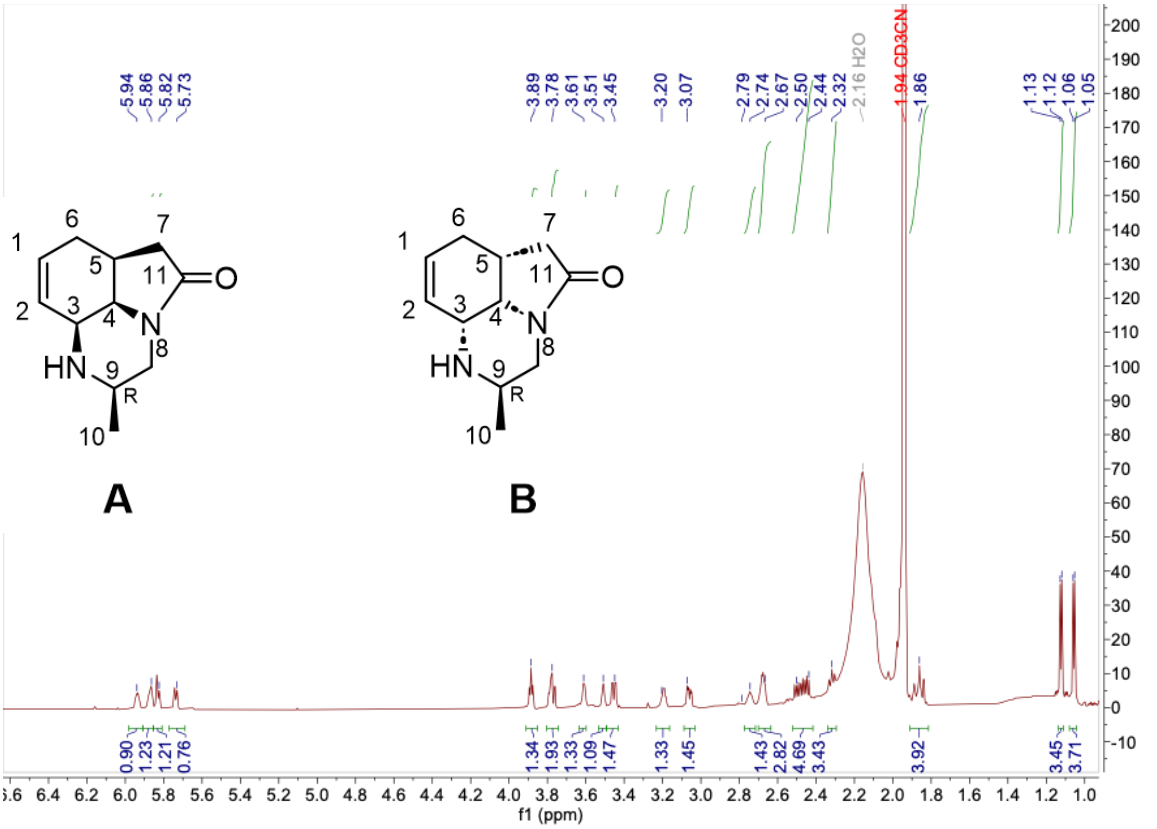


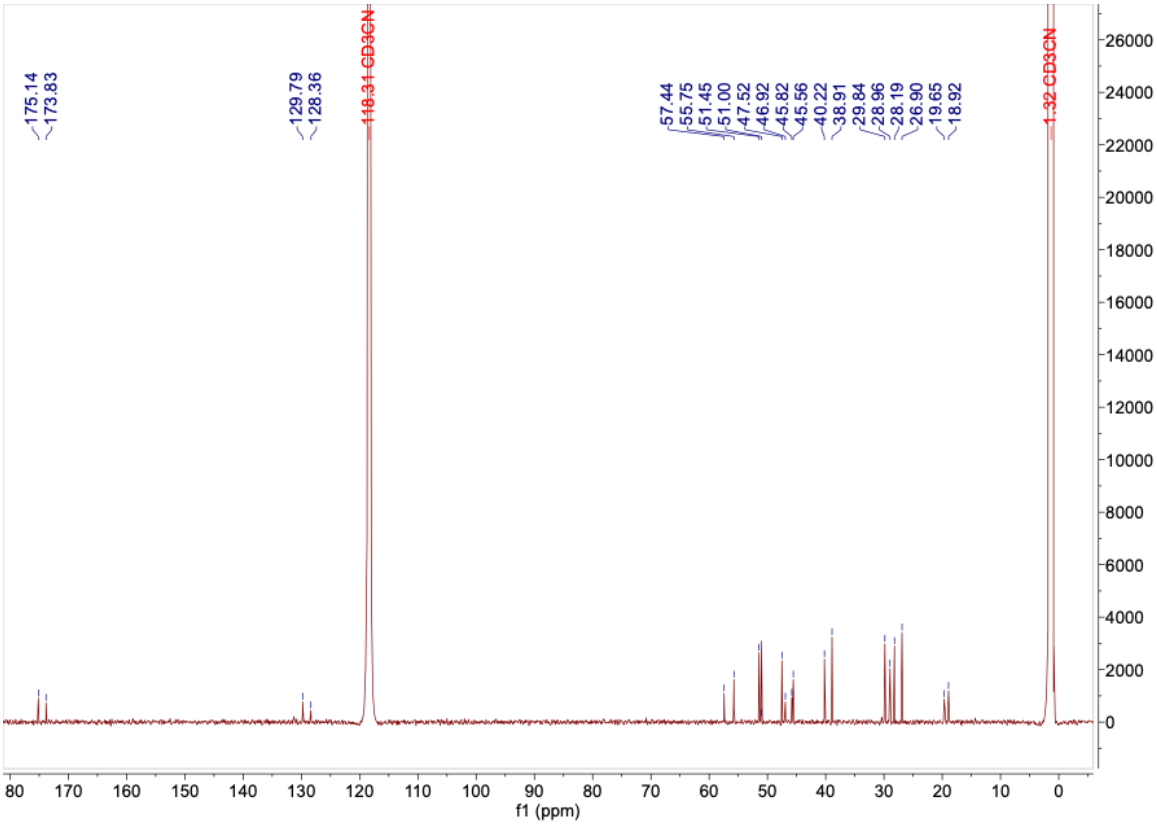
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.46:



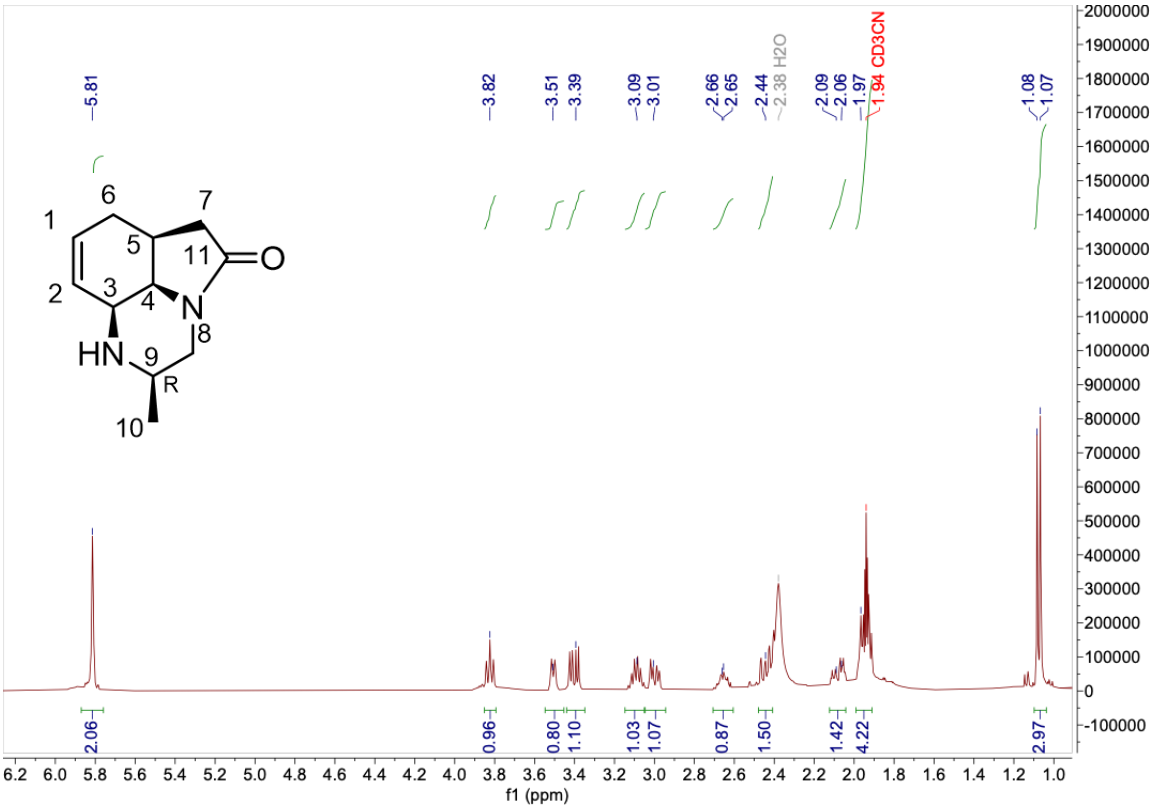


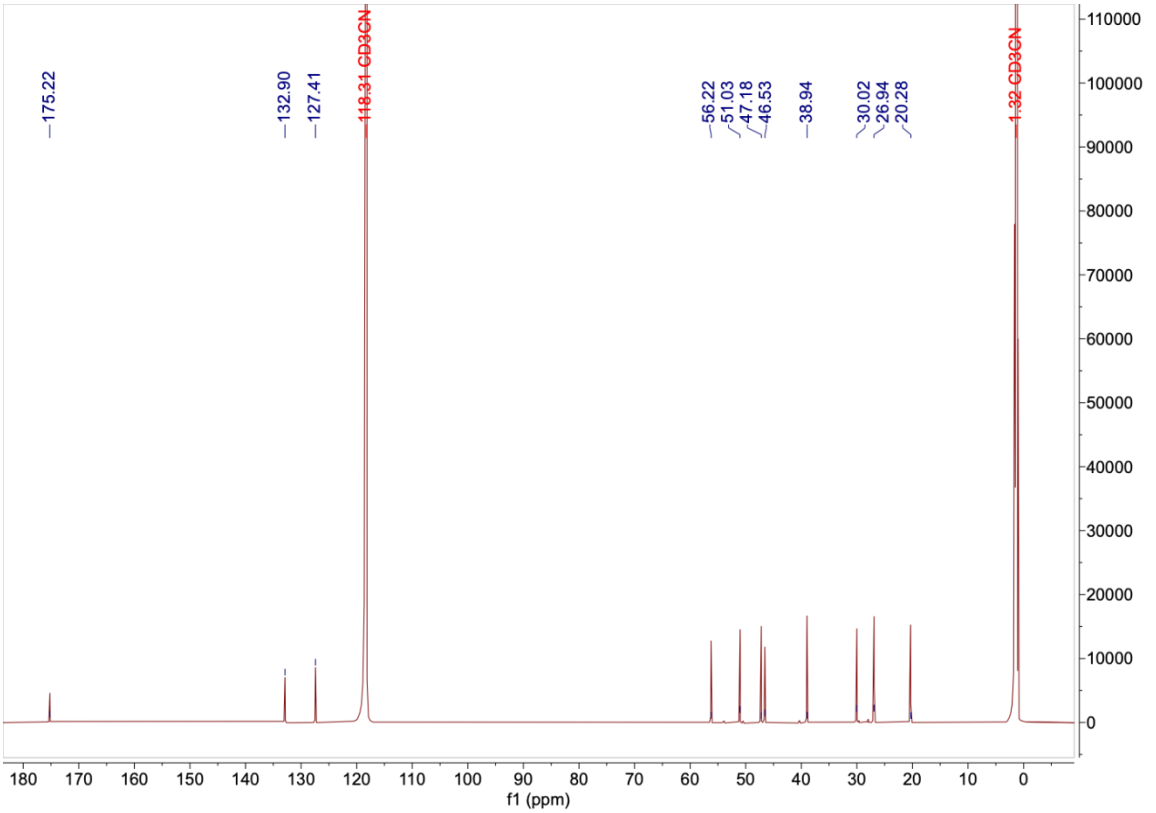
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.47:



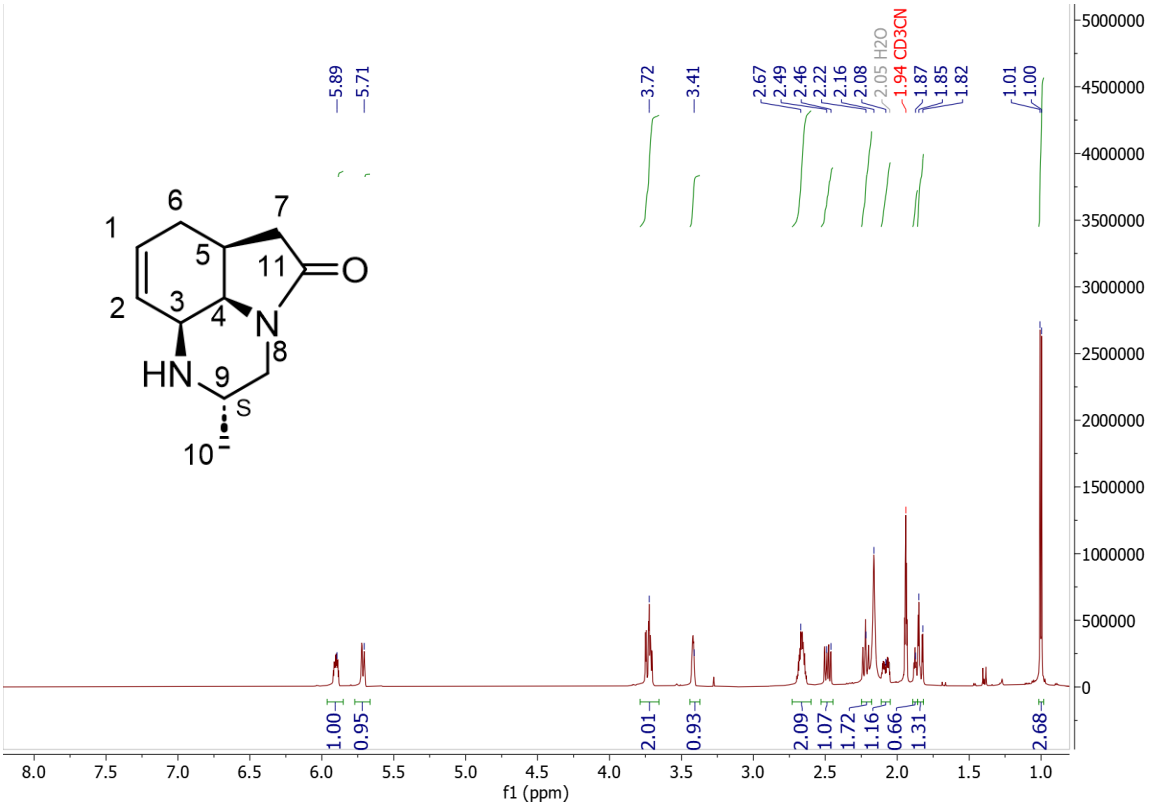


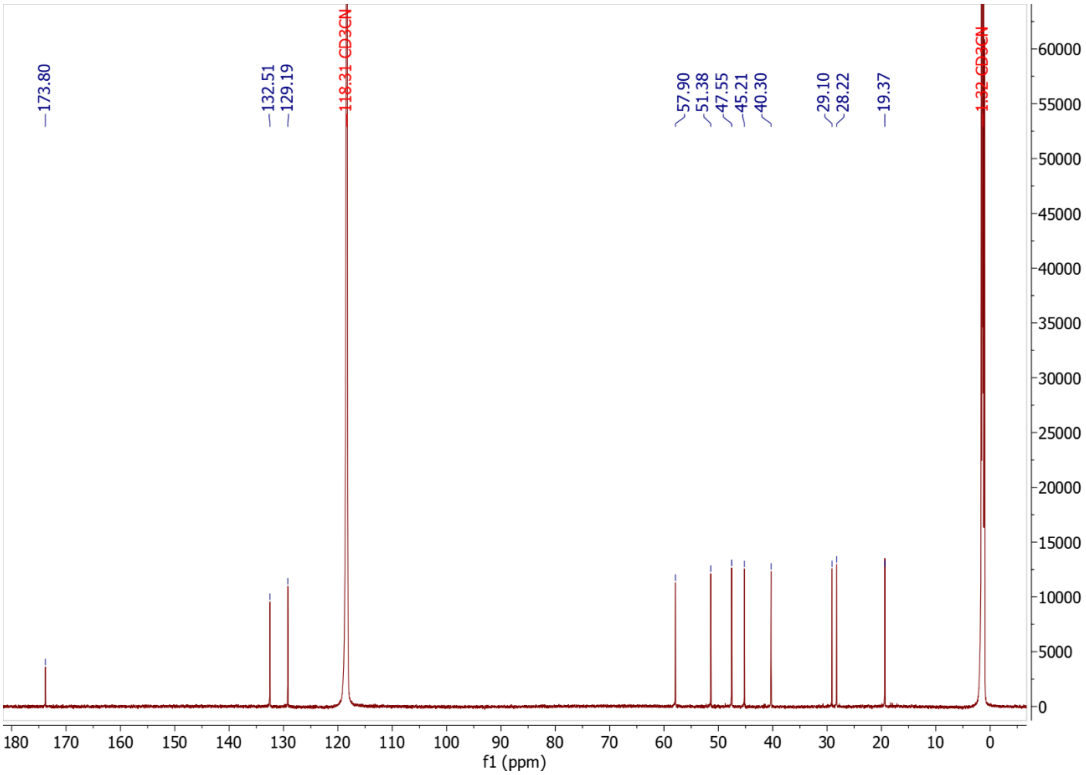
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.48:



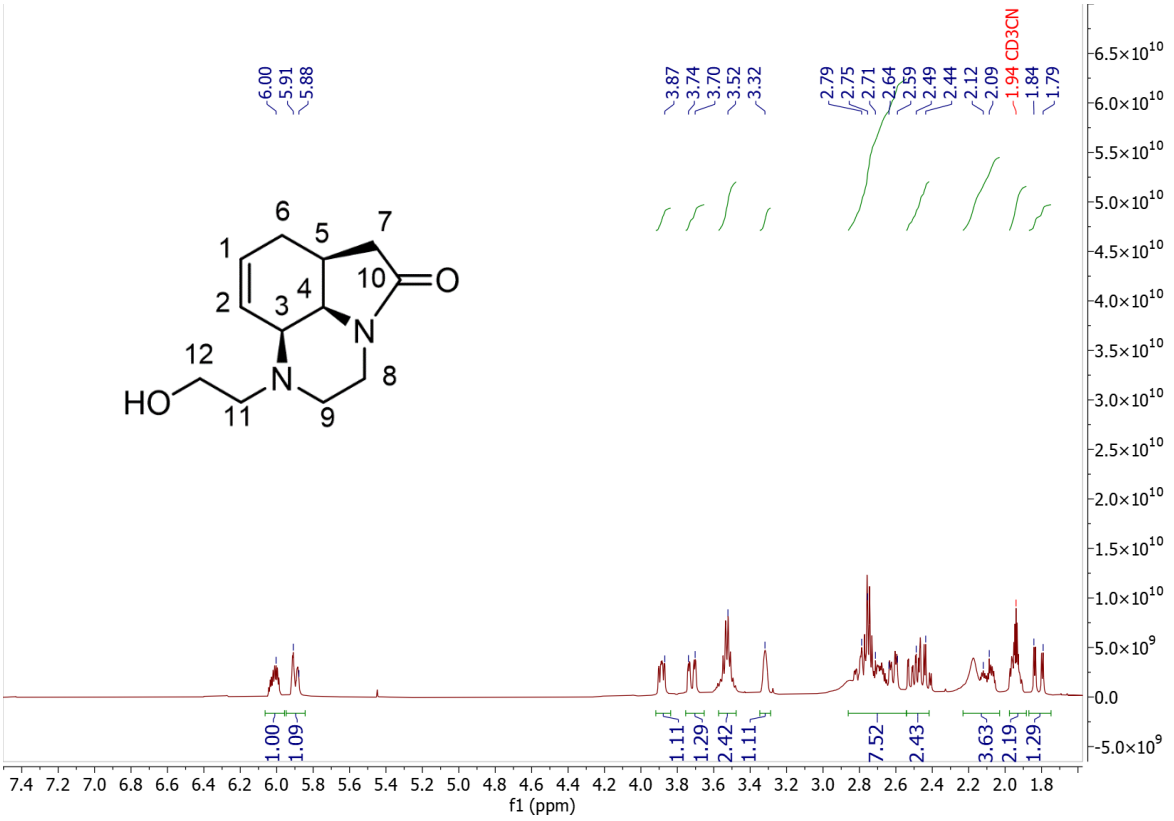


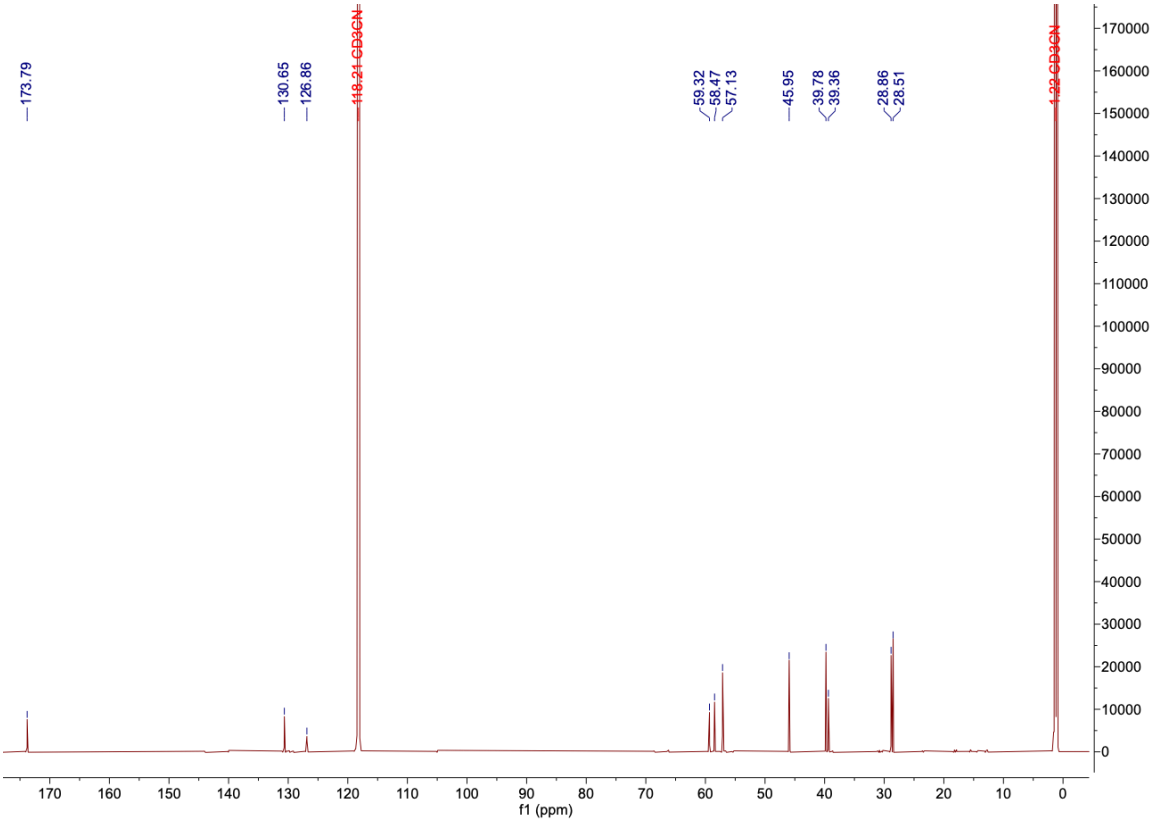
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.49:



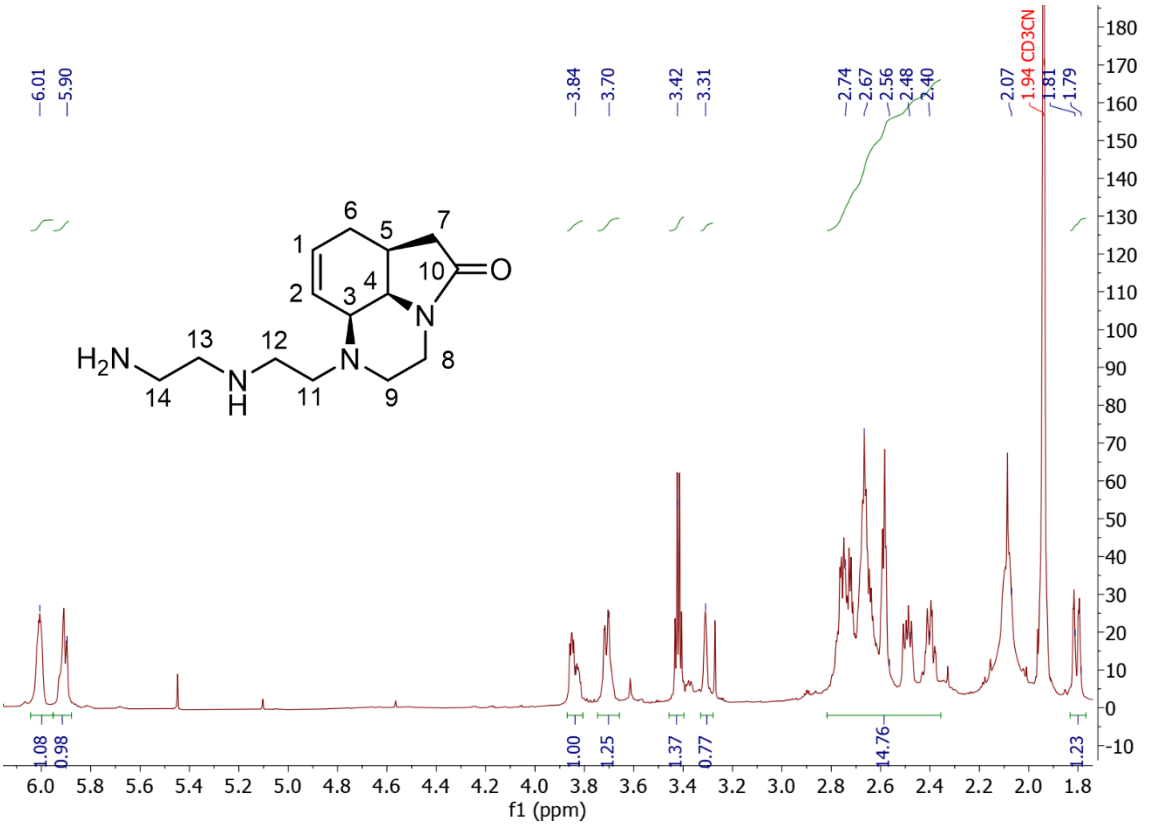


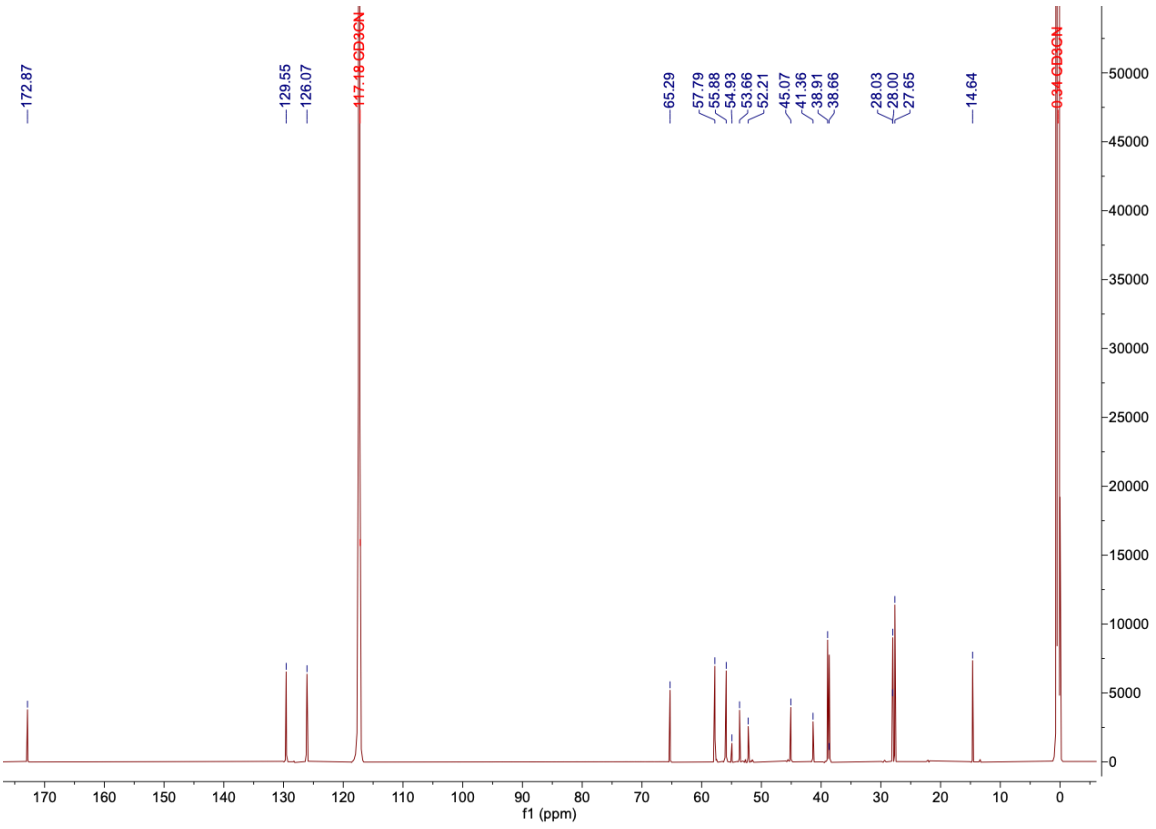
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.50:



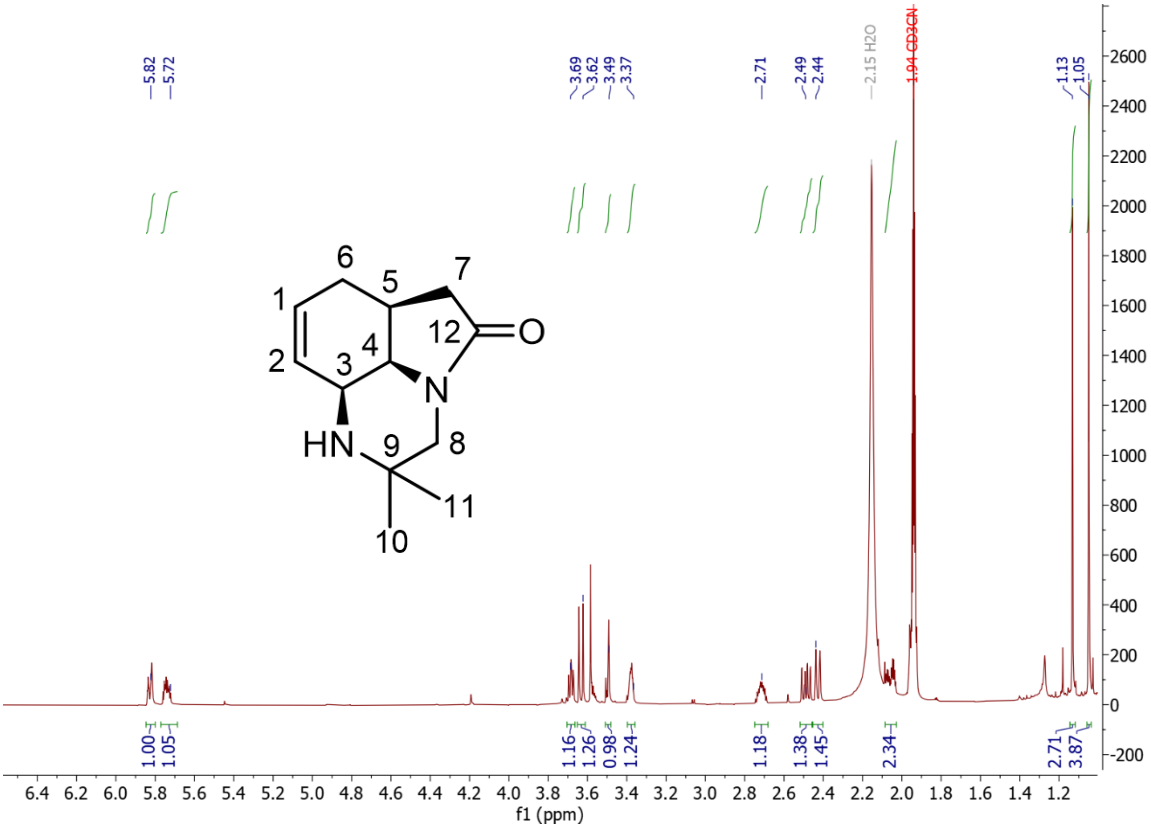


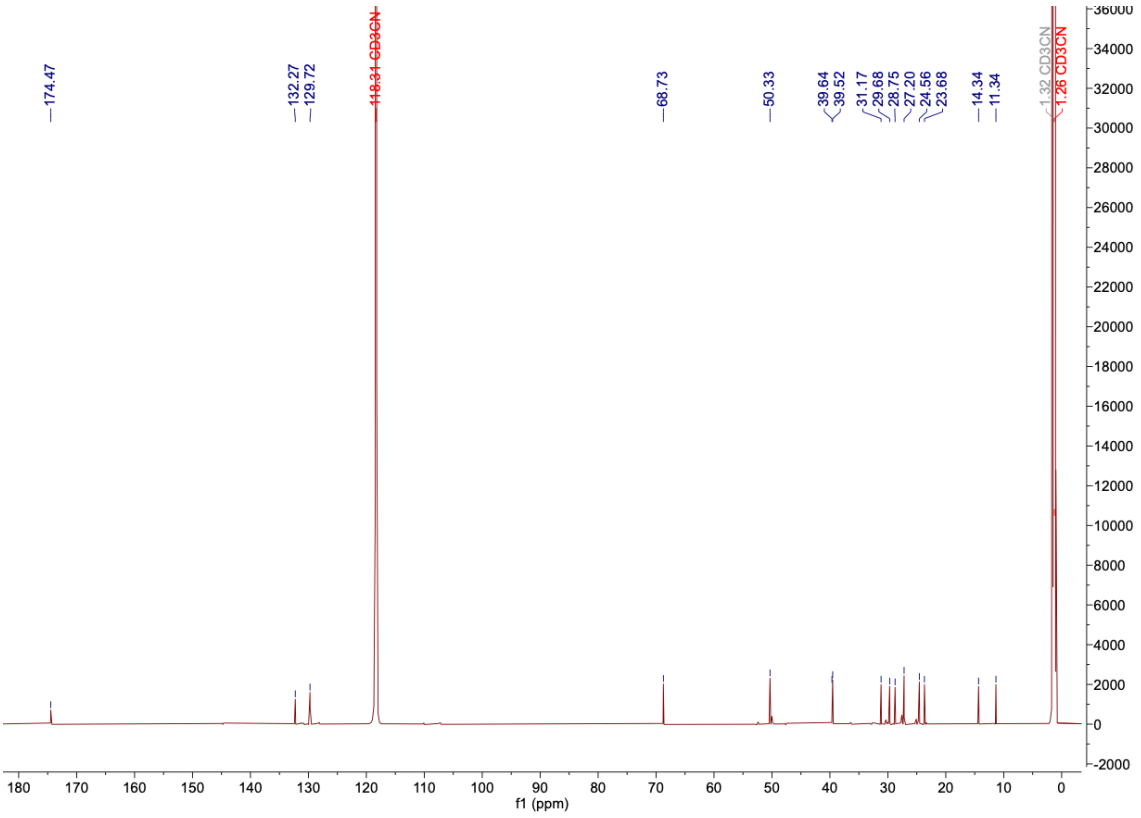
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.51:



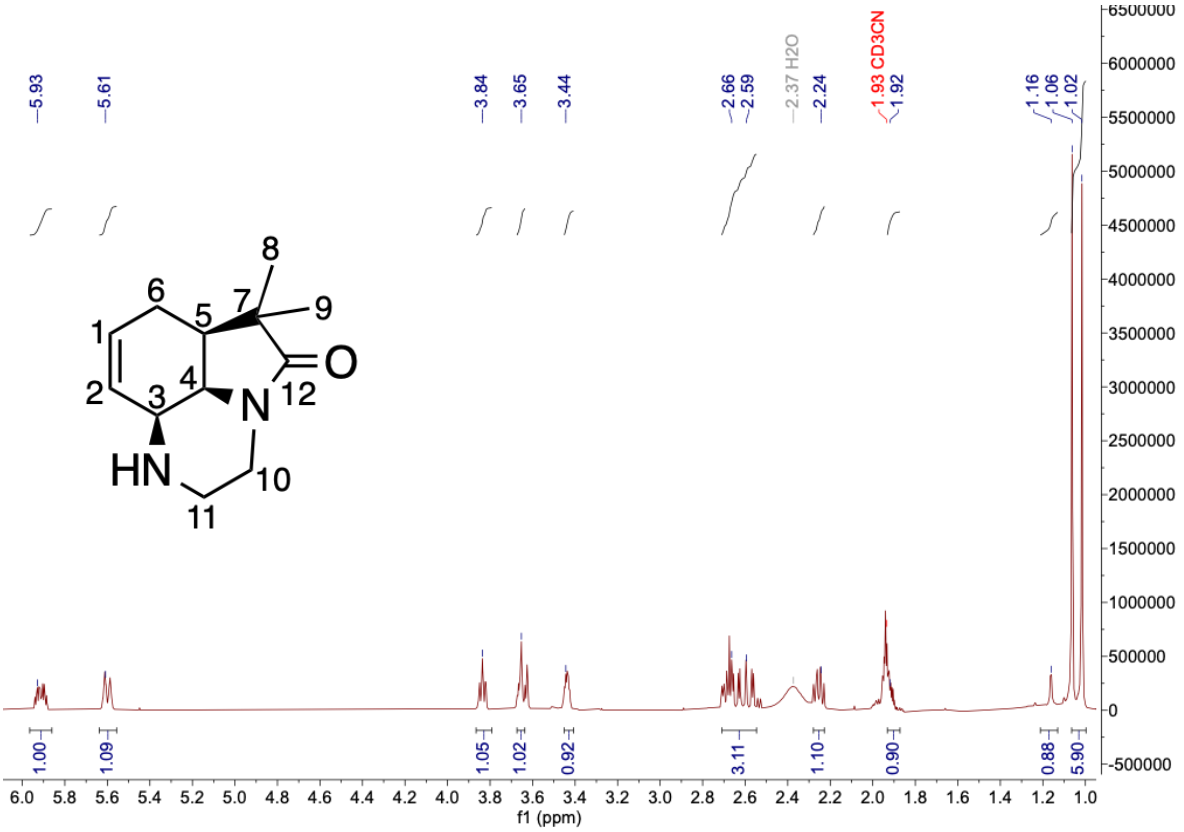


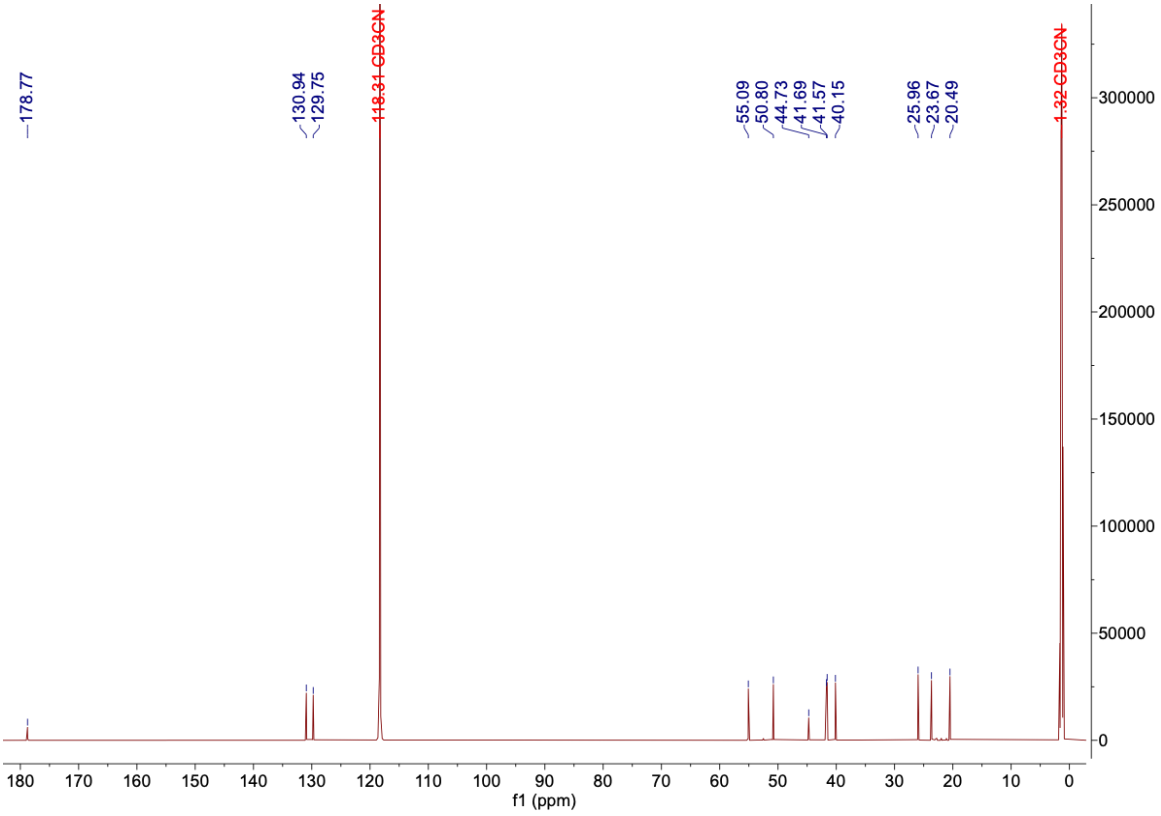
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.52:



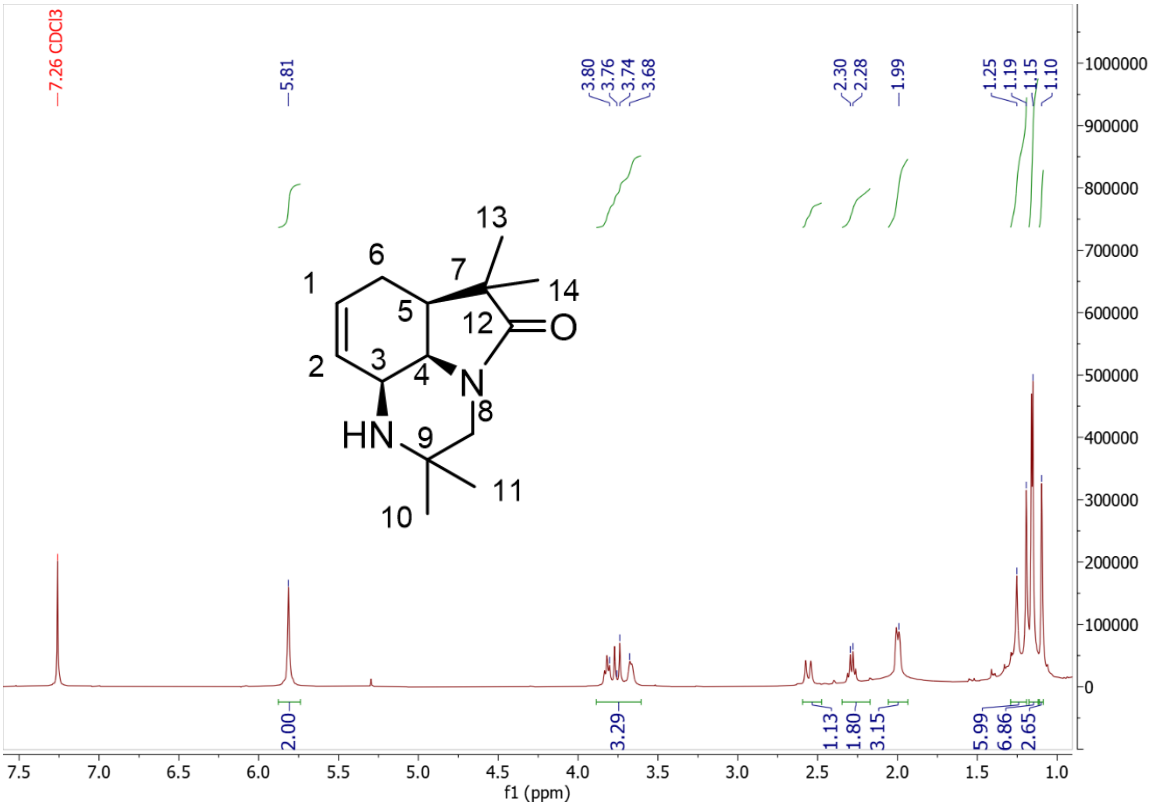


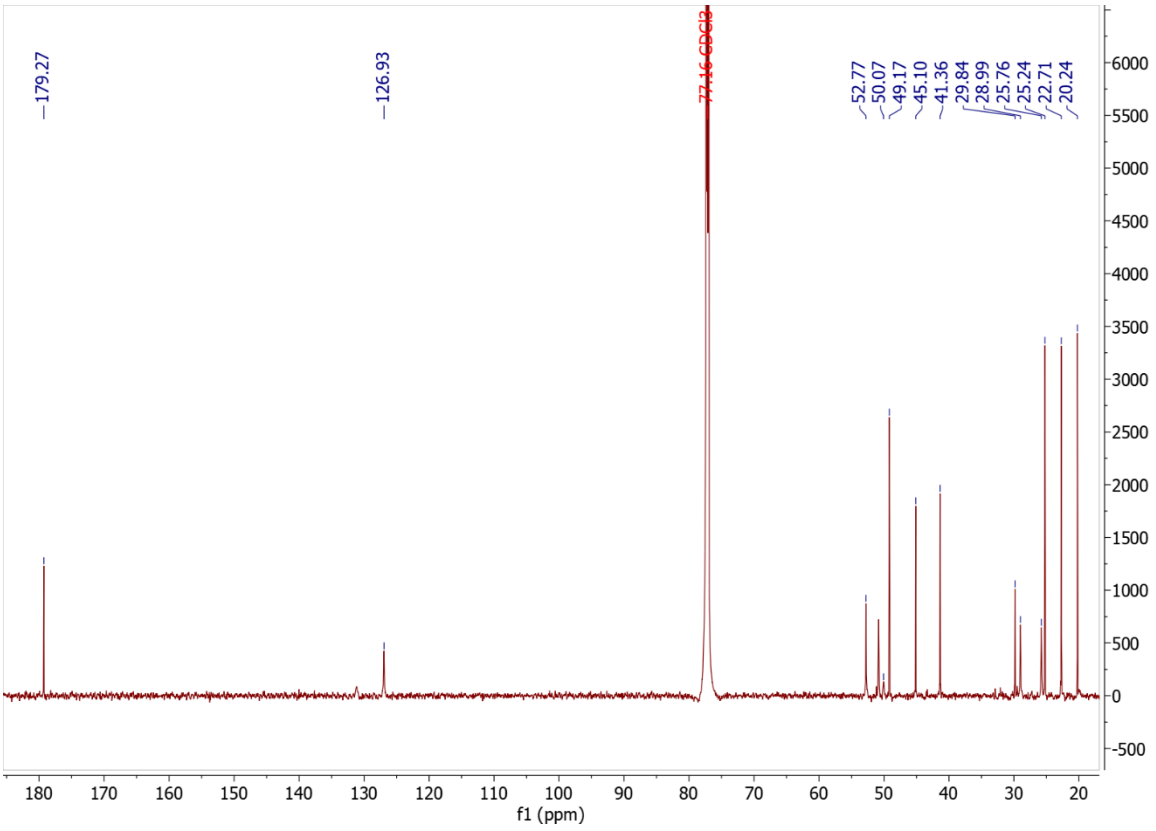
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.53:



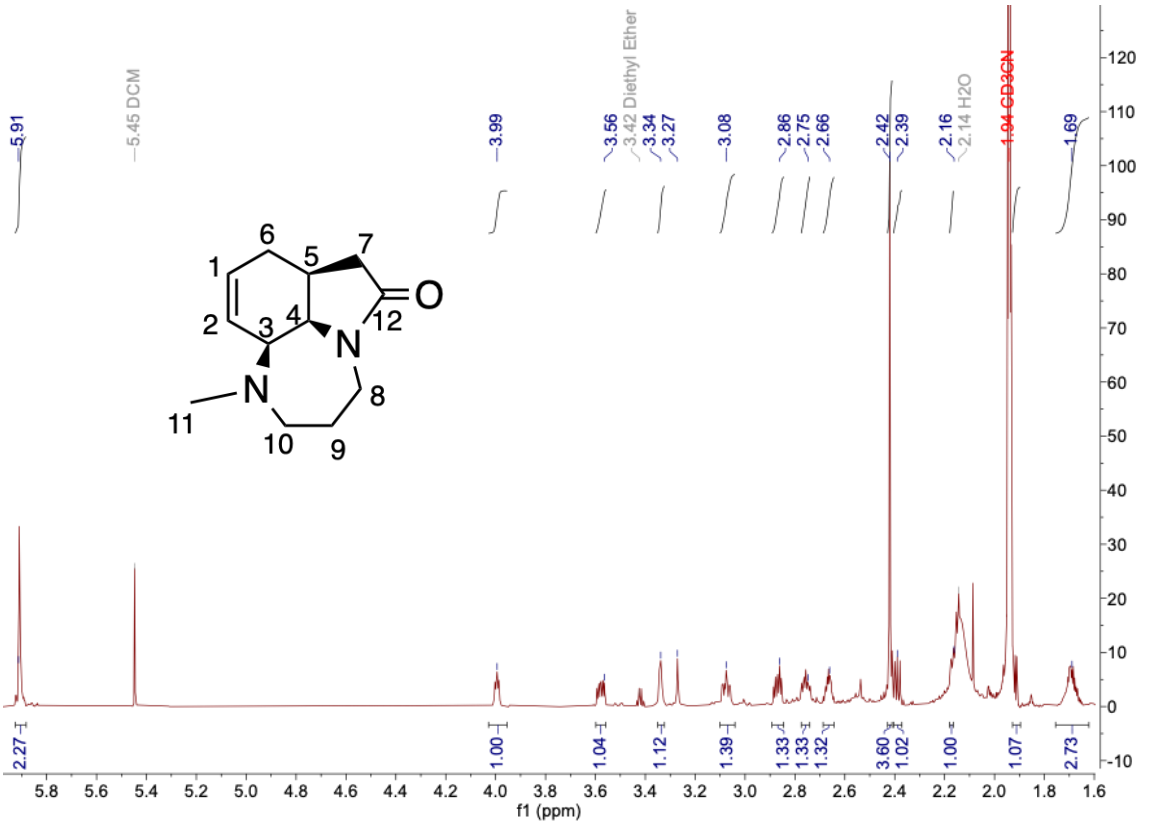


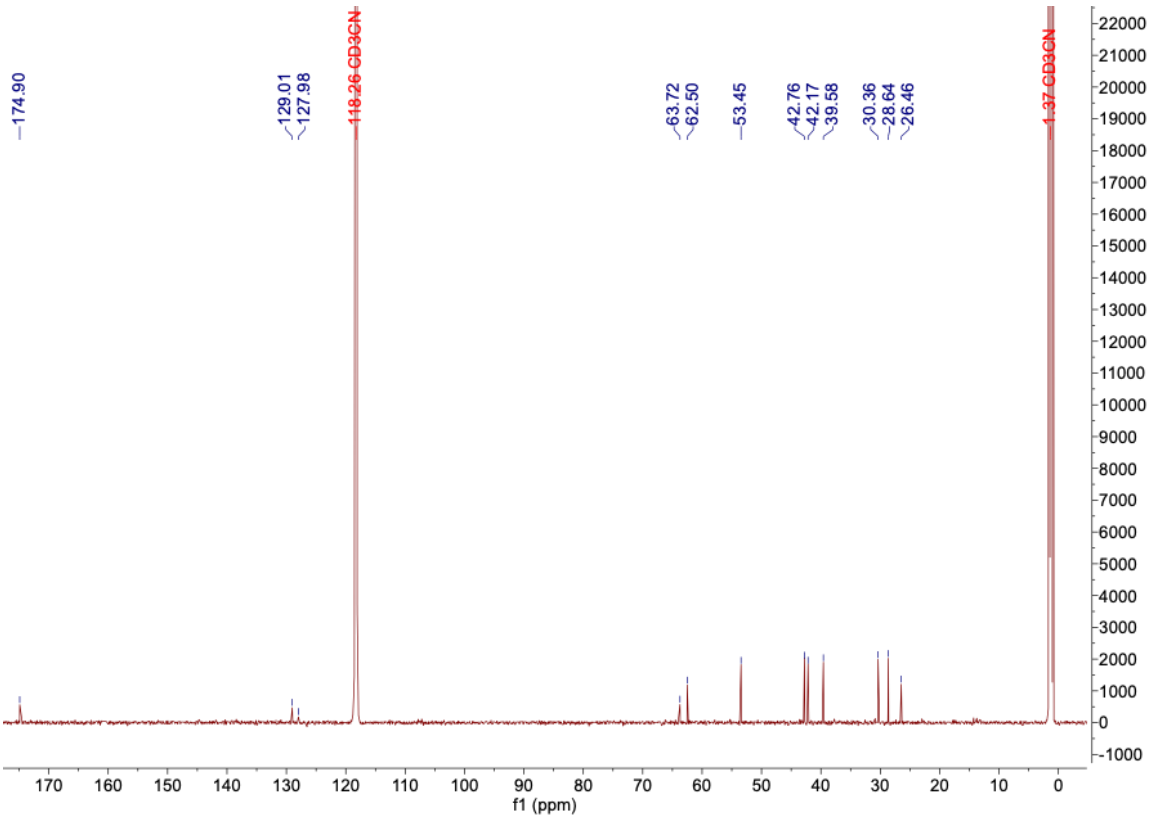
^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR ($CDCl_3$) of Compound 5.54:



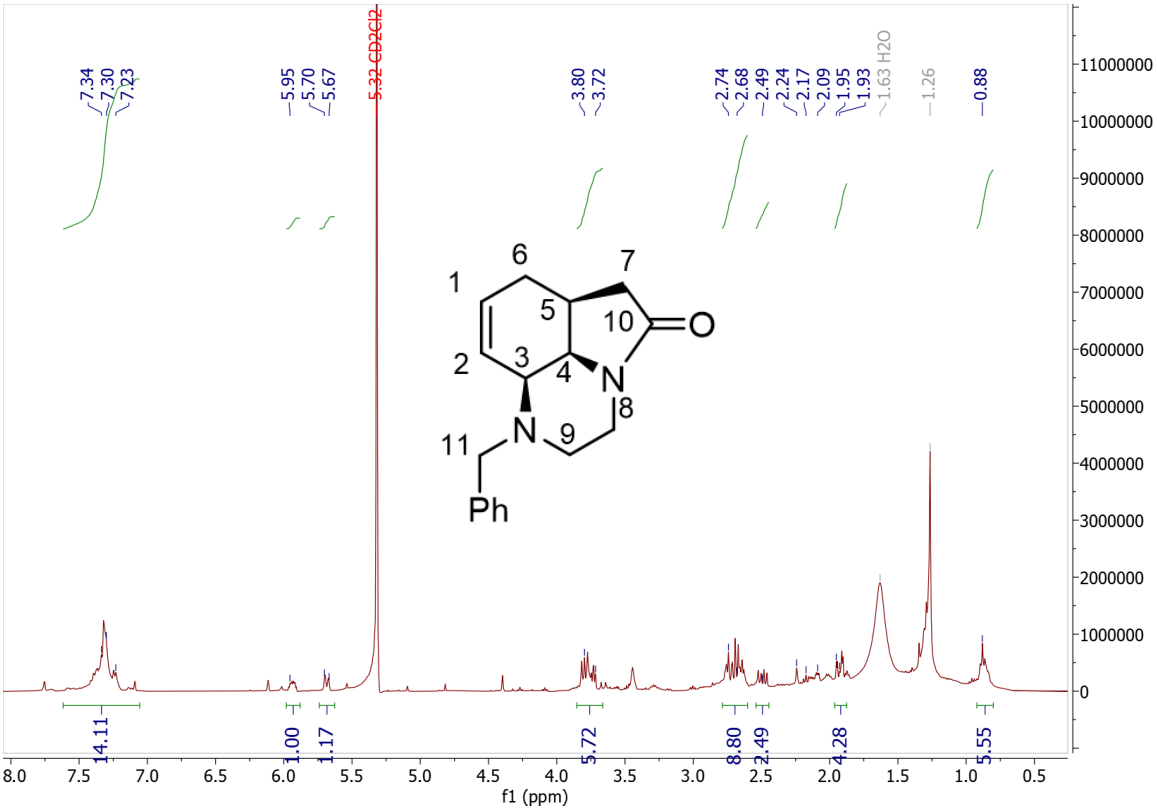


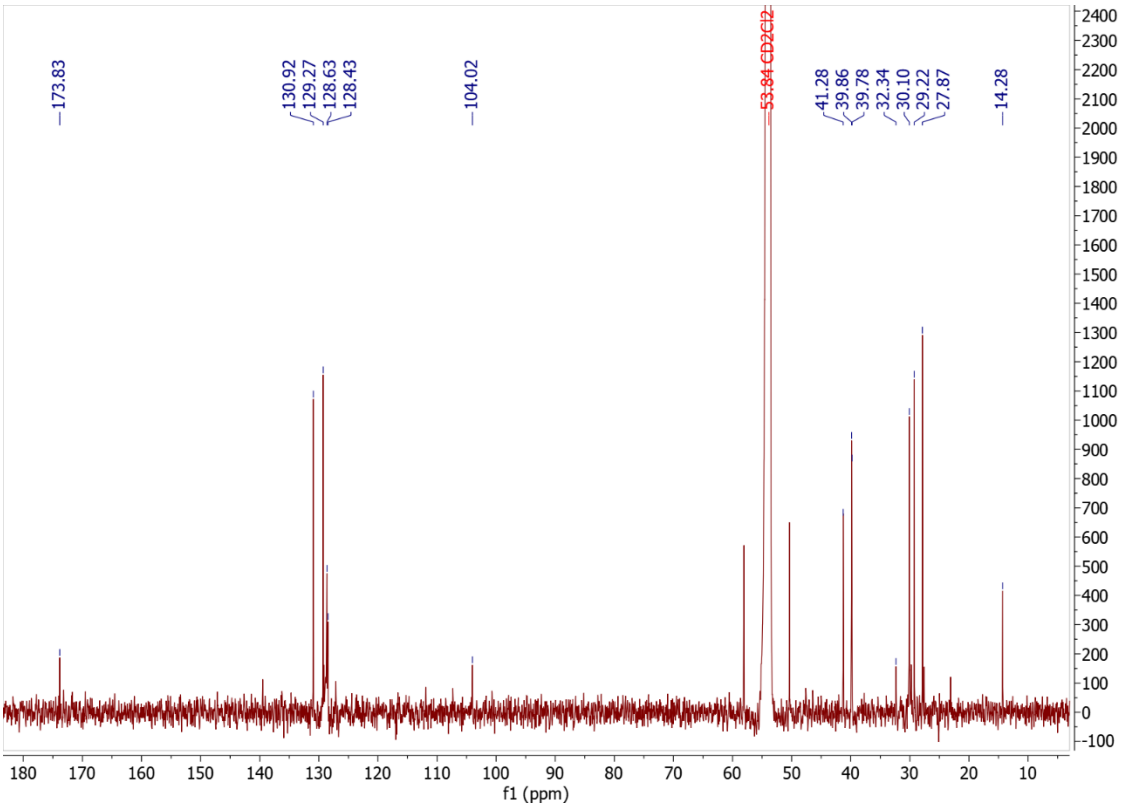
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.55:



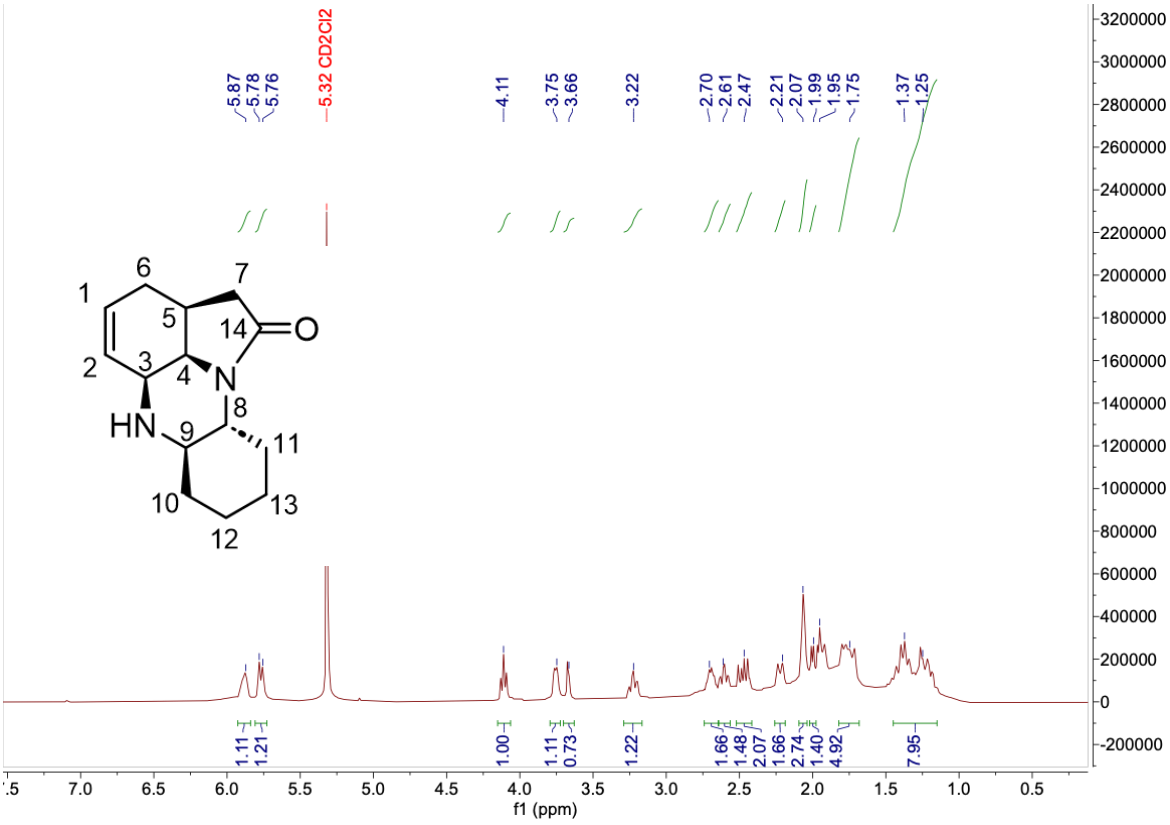


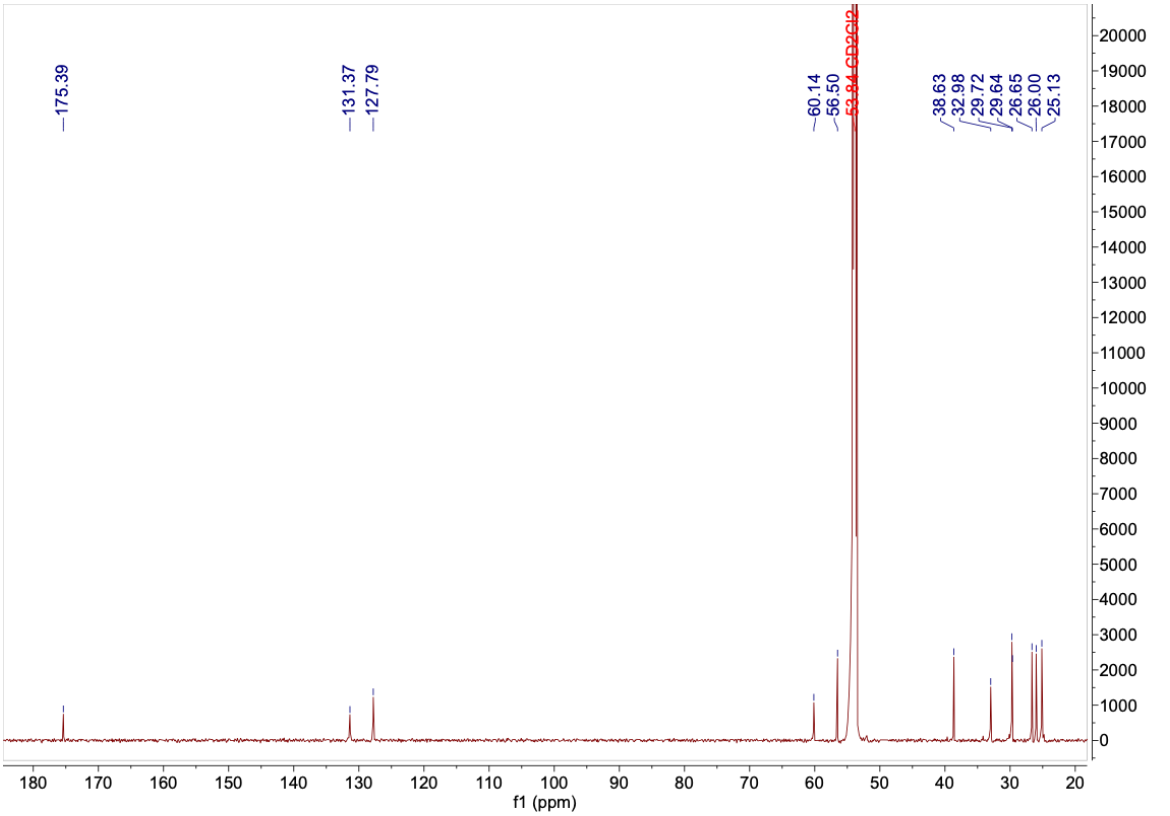
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.56:



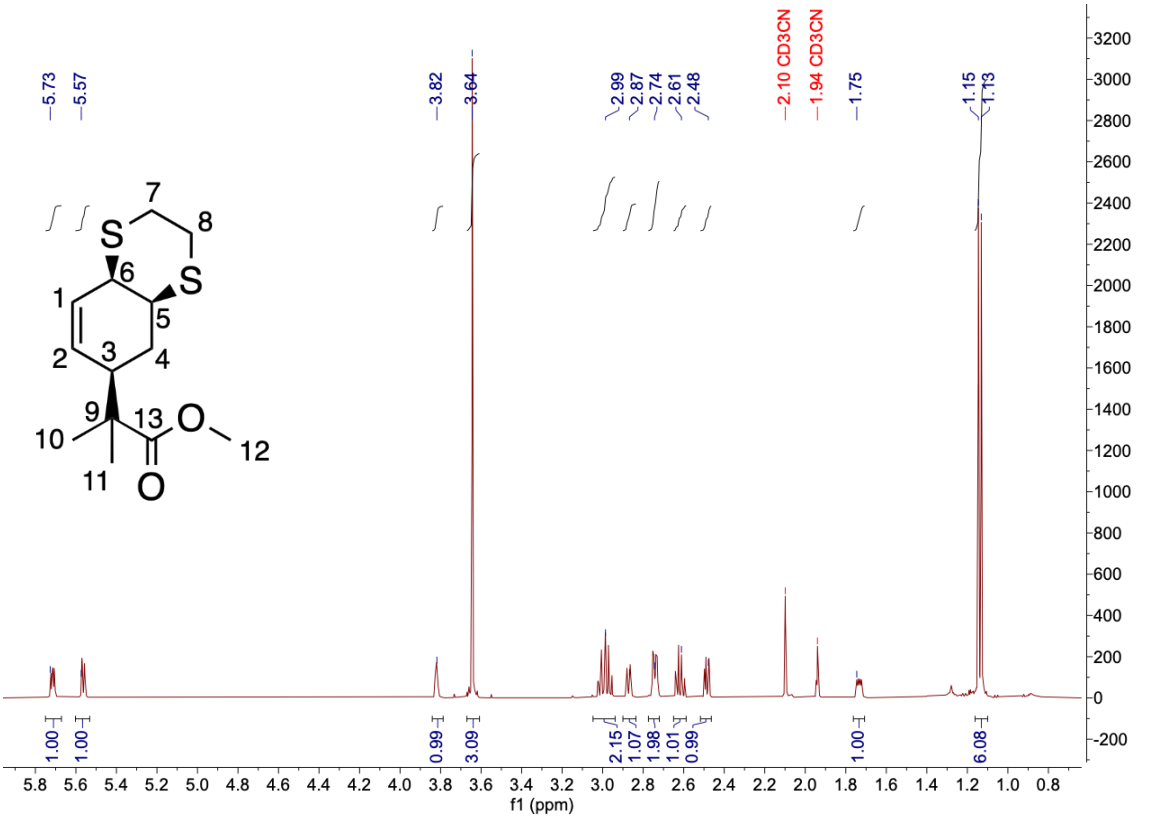


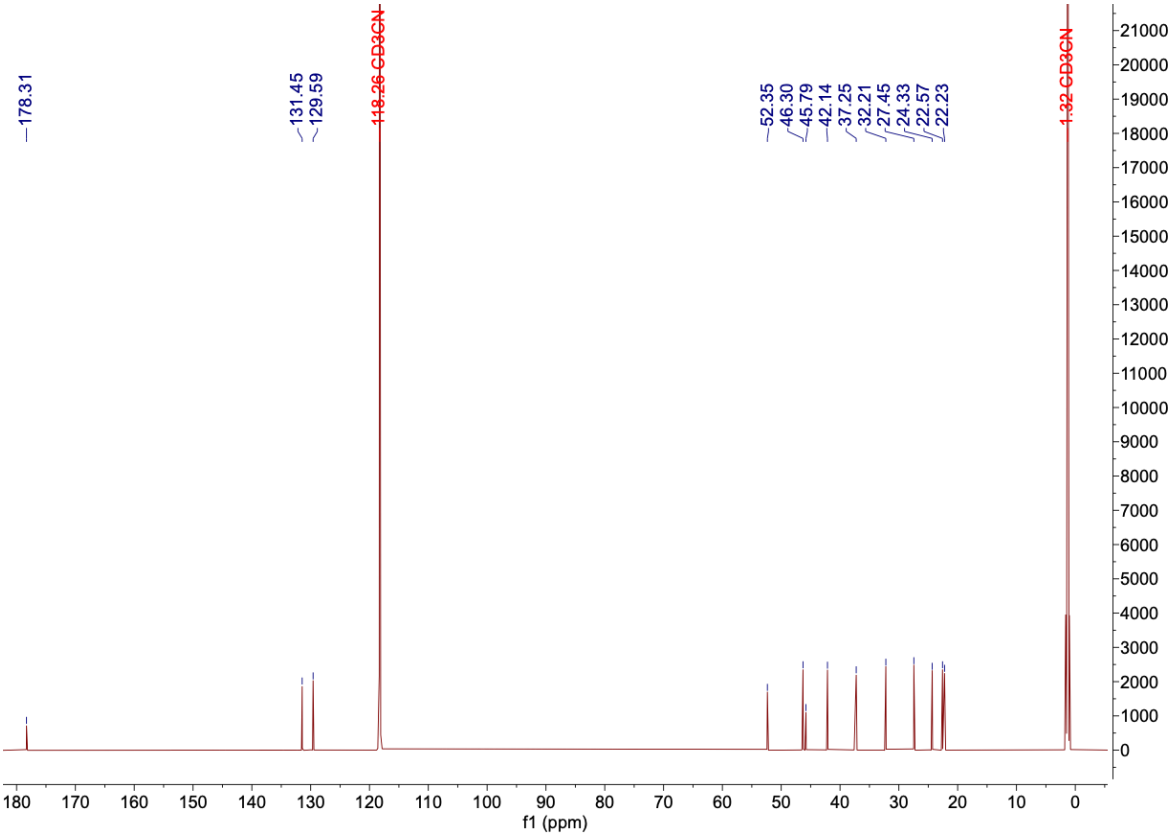
^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 5.57:



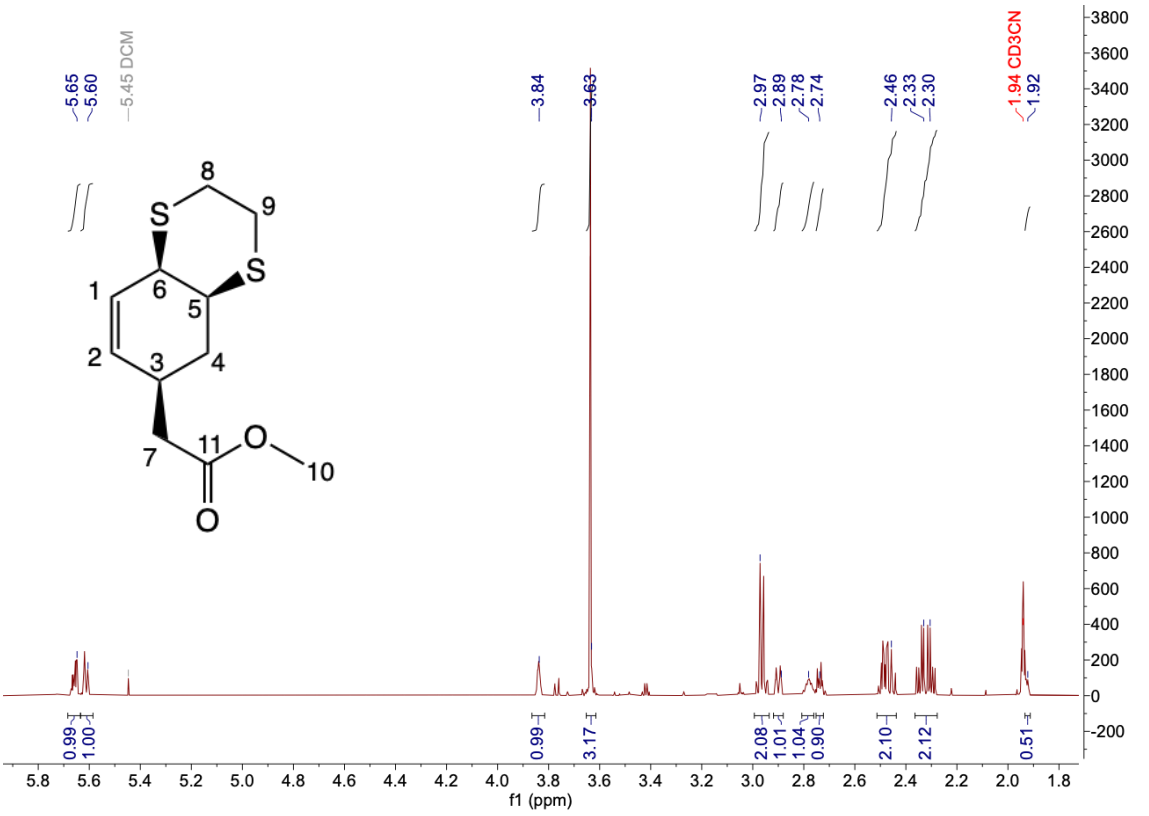


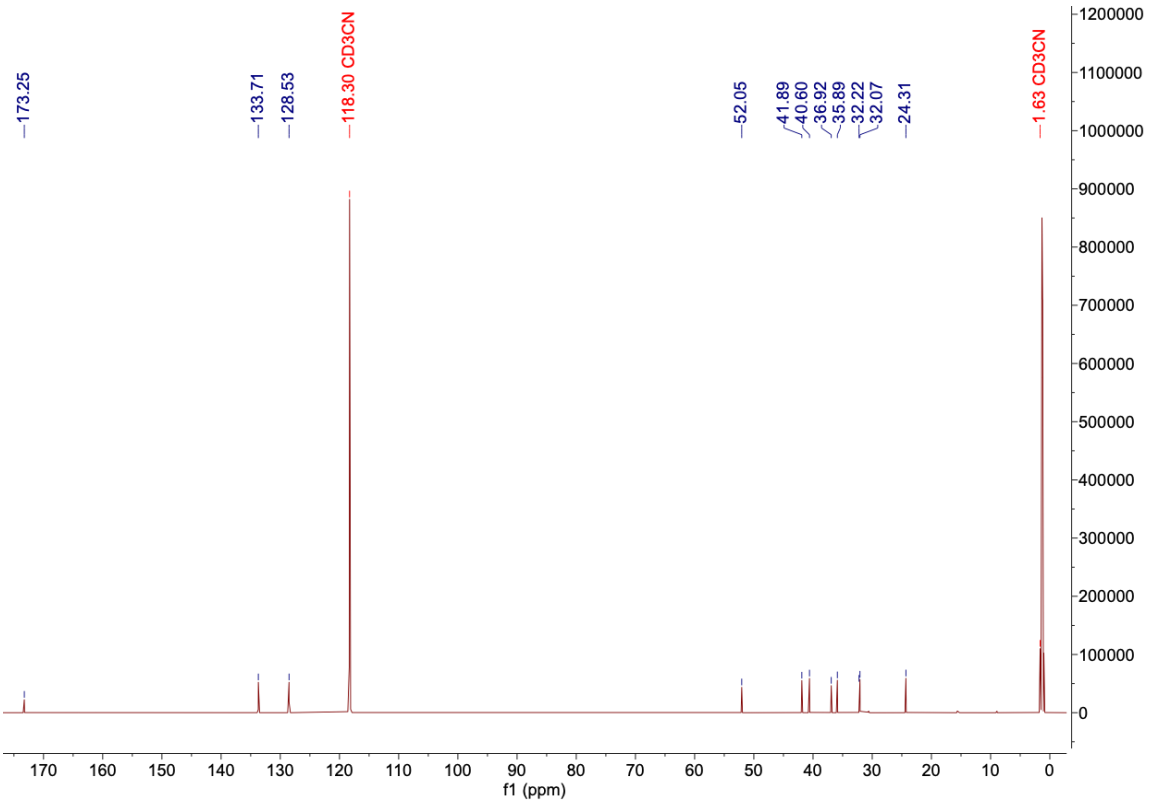
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.58:



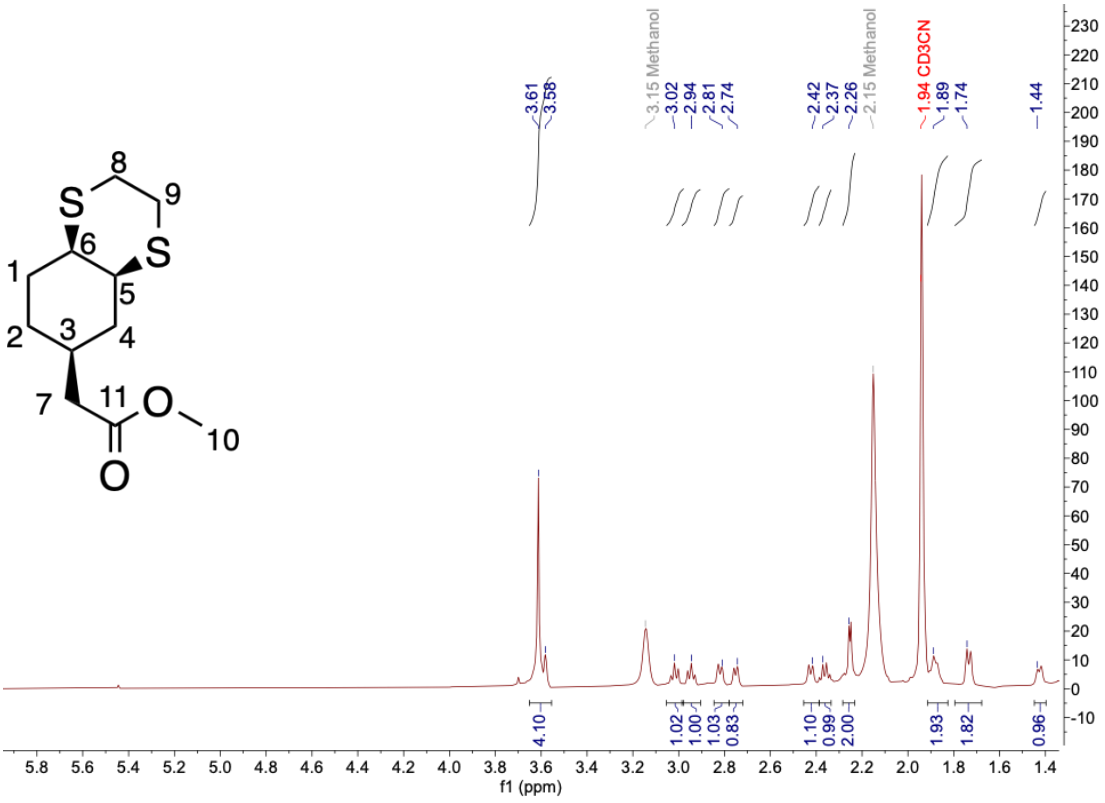


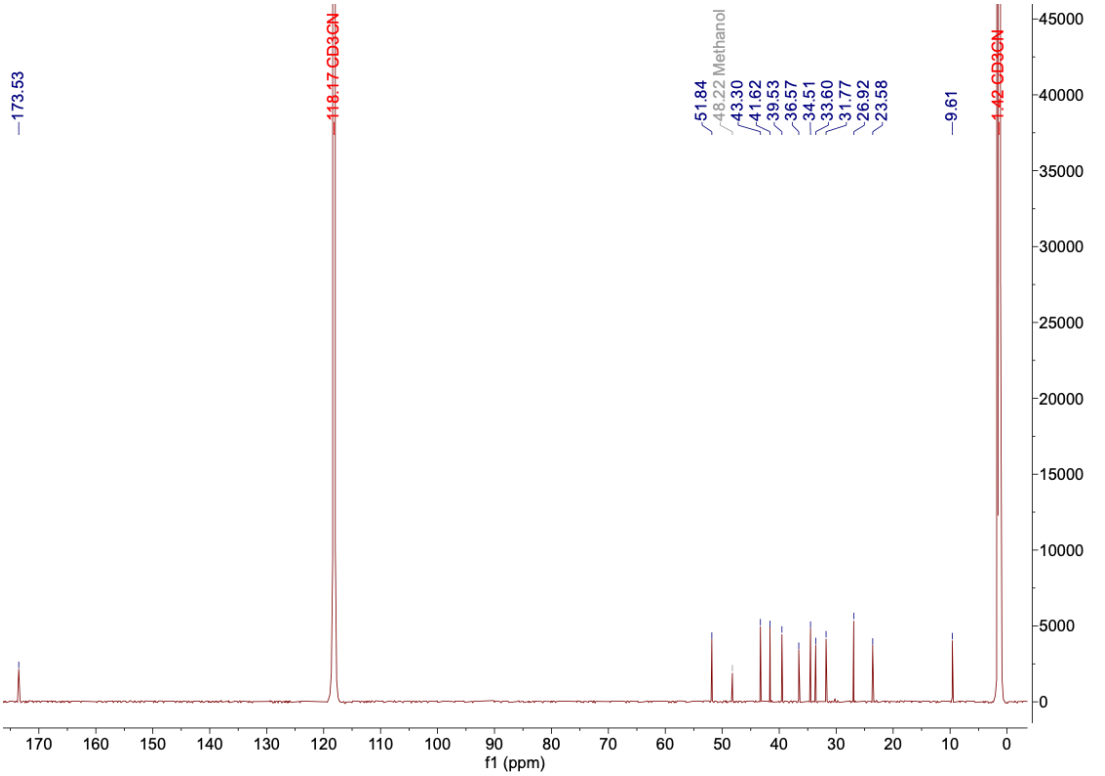
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.59:



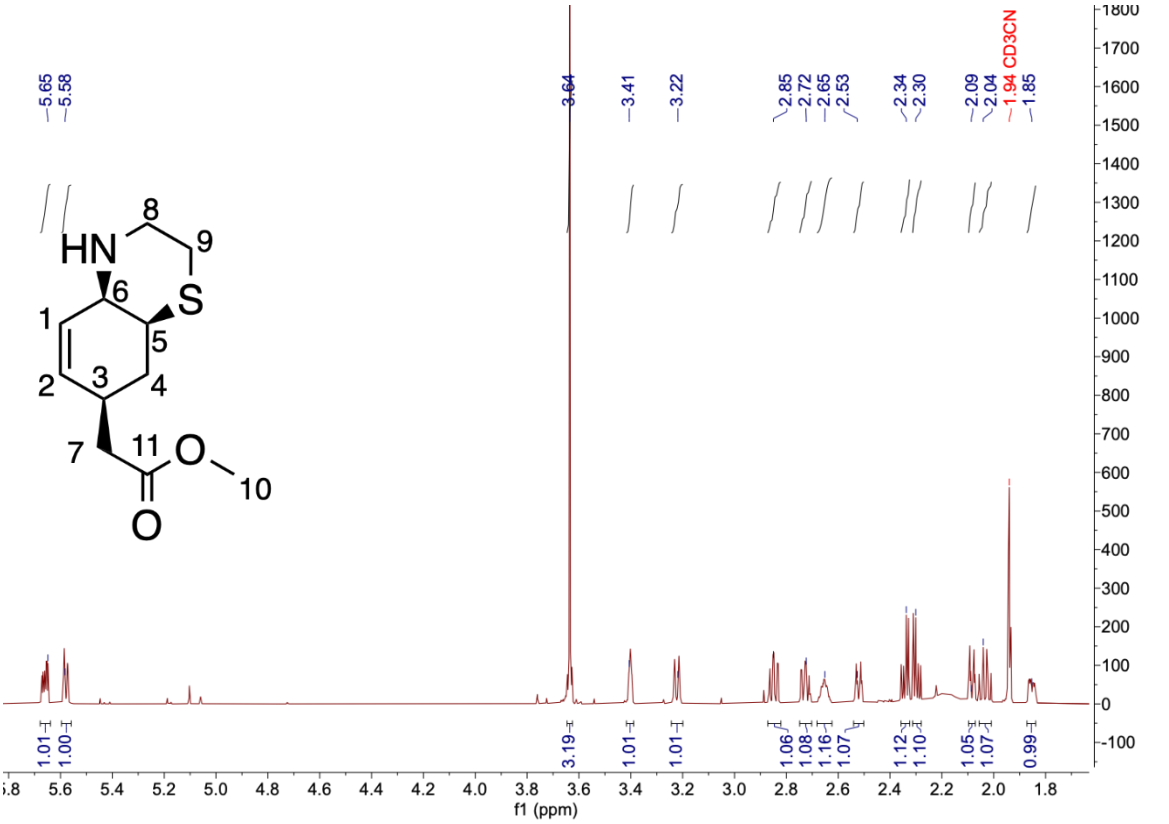


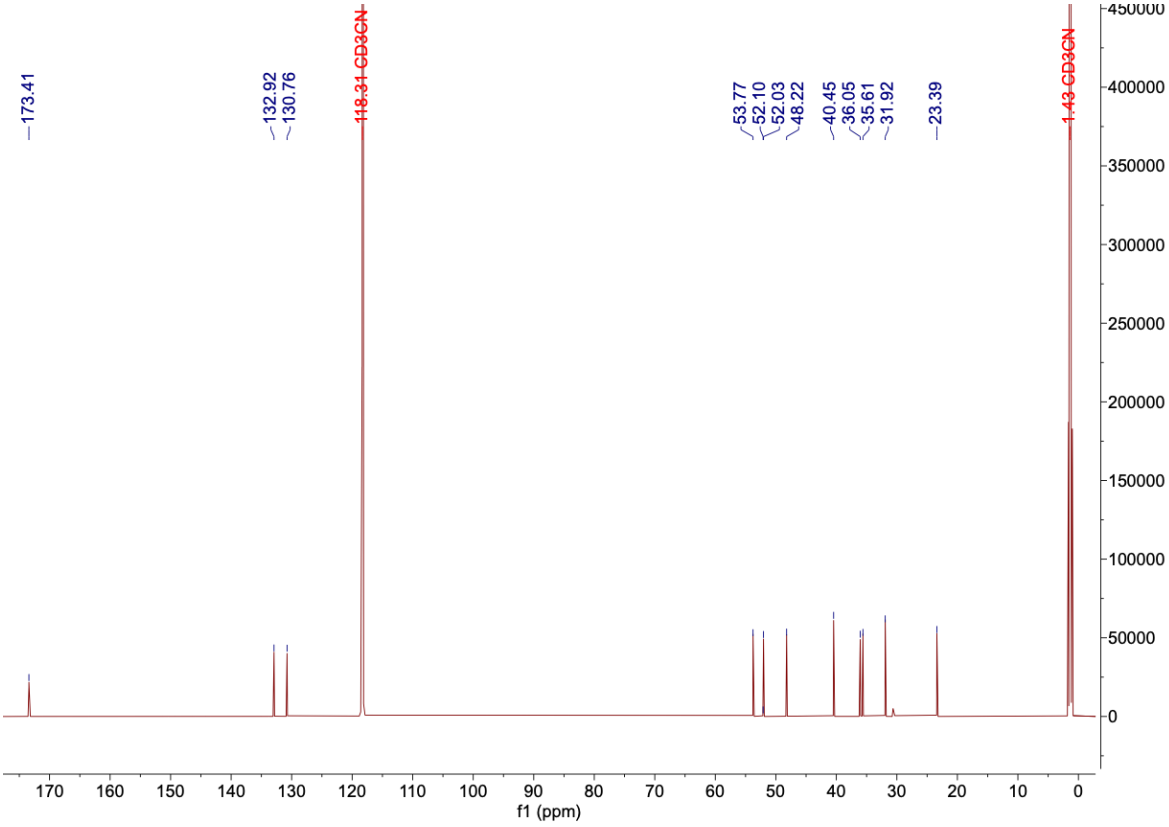
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.60:



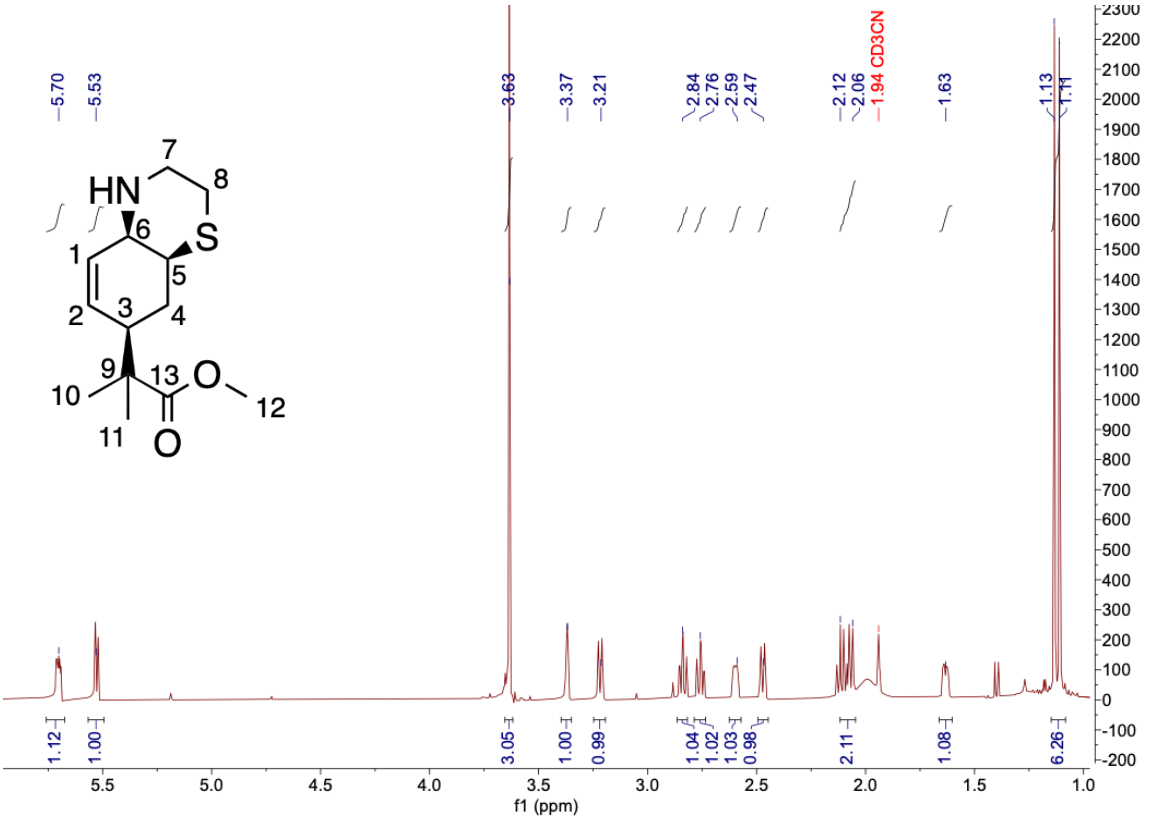


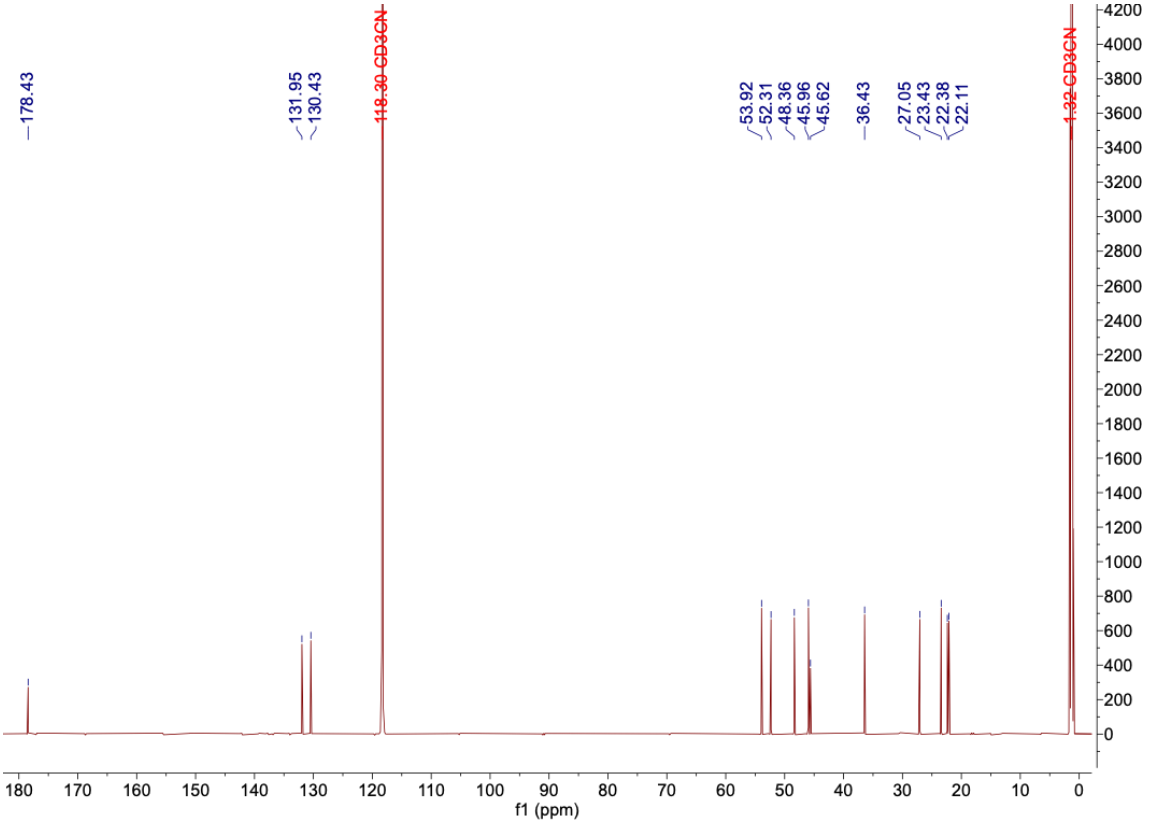
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.61:



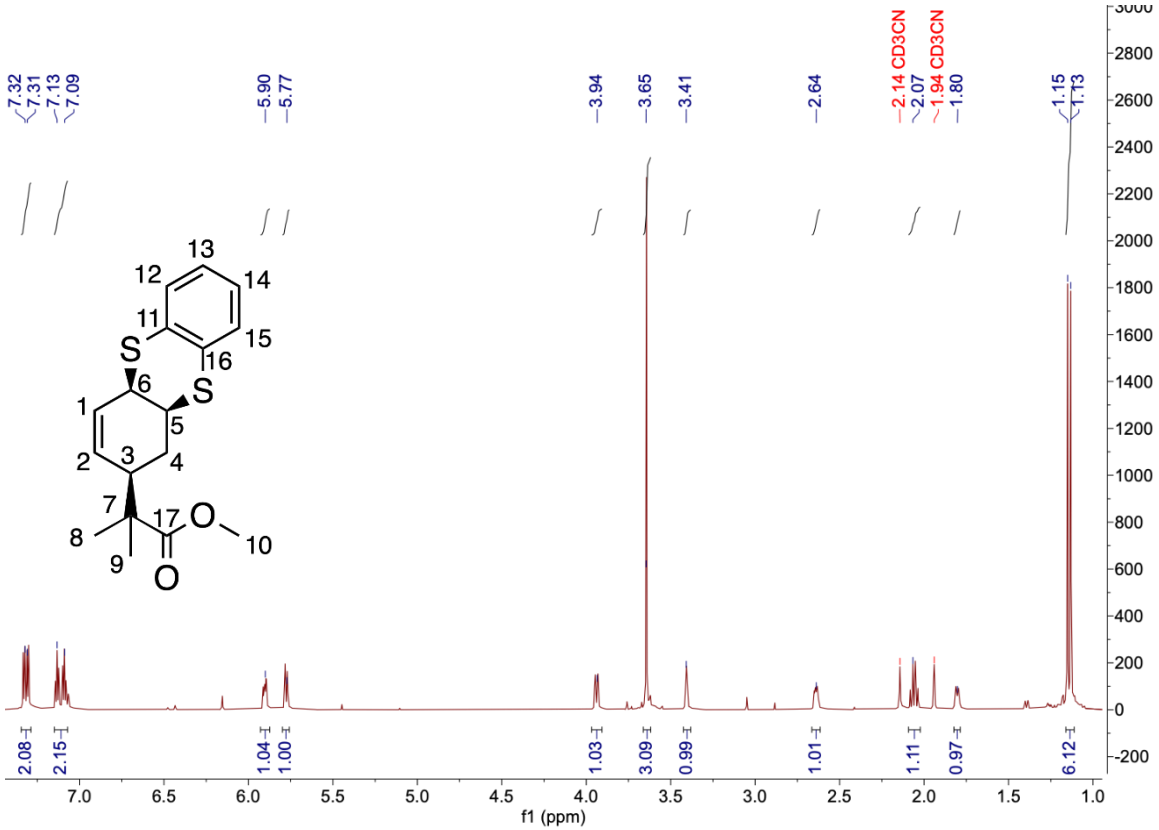


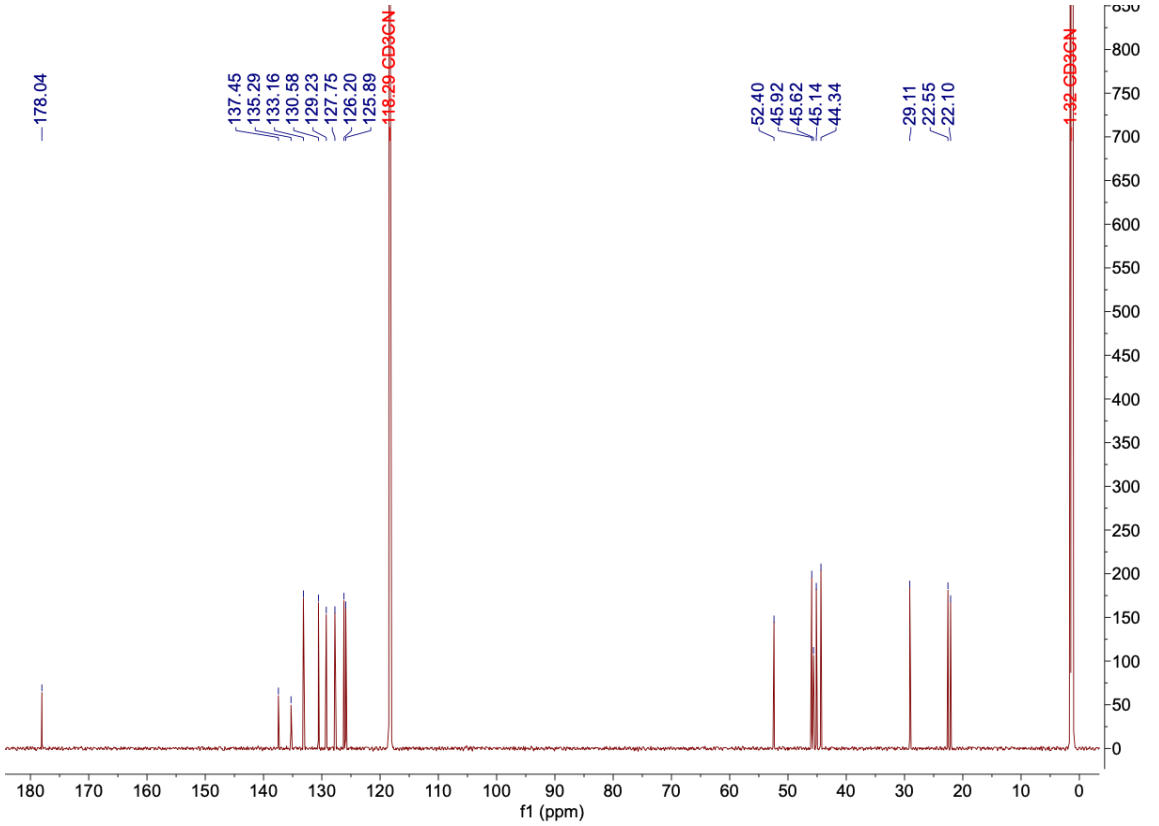
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.62:



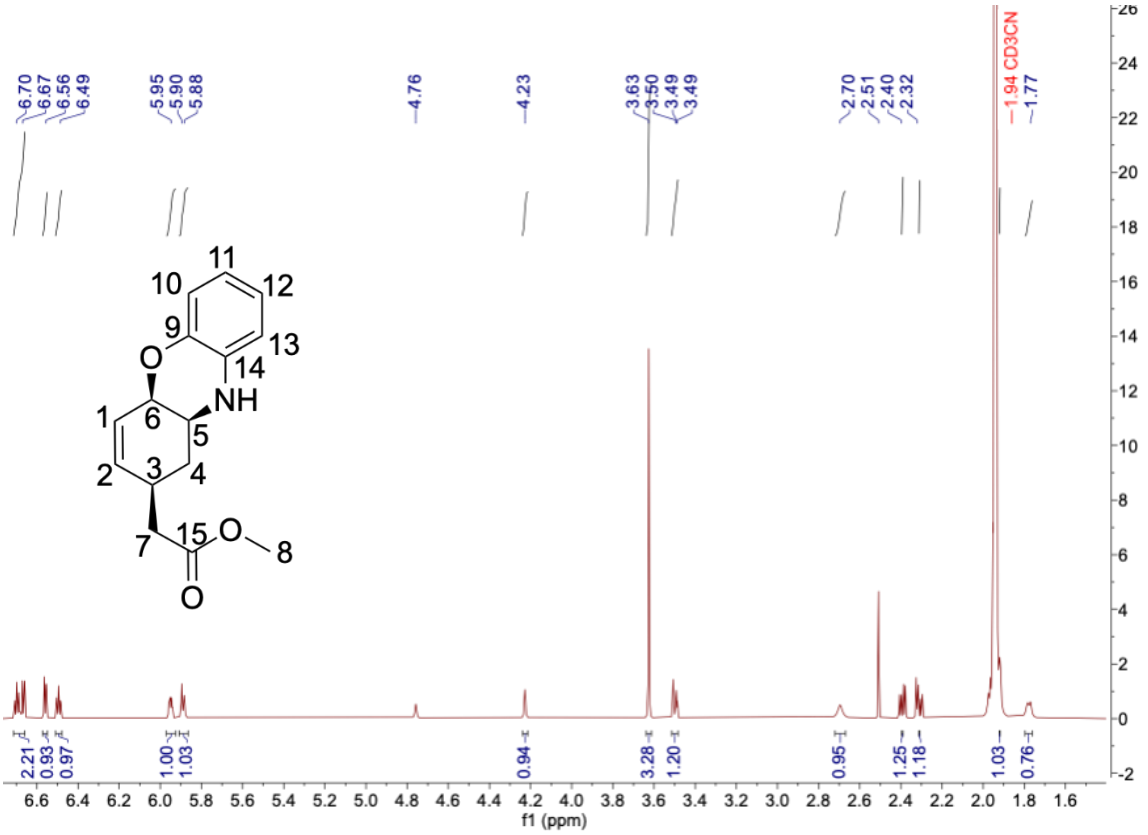


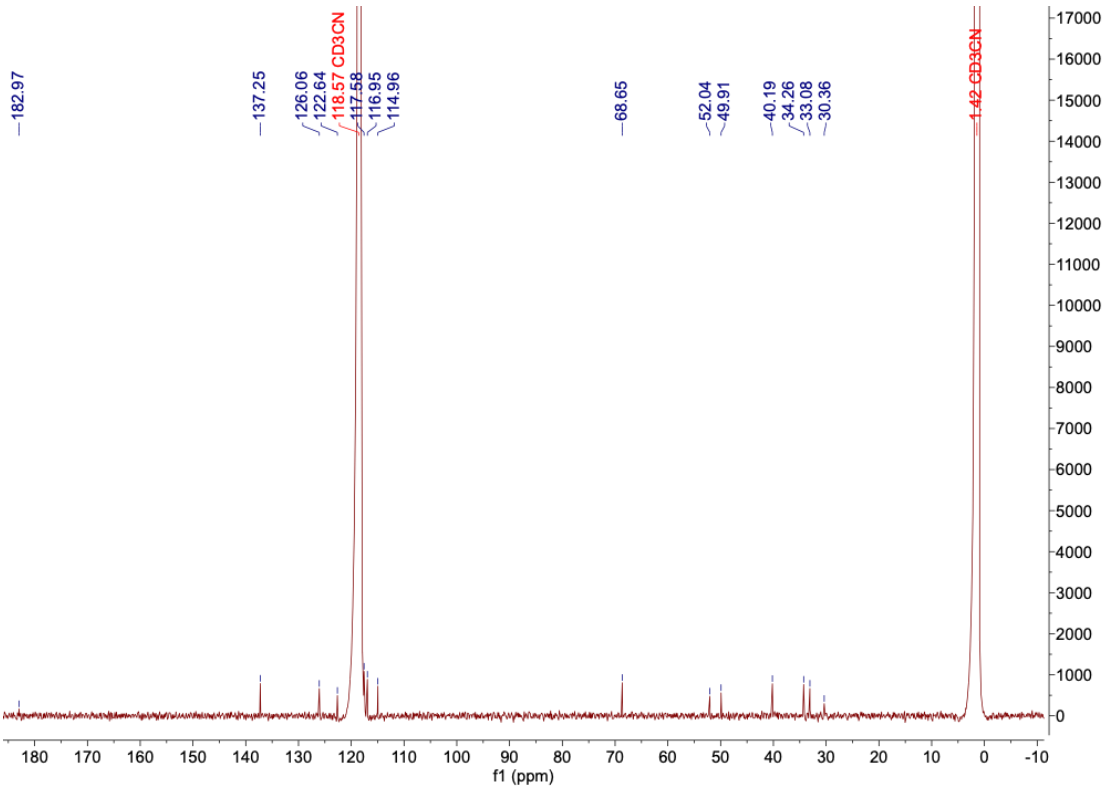
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.63:



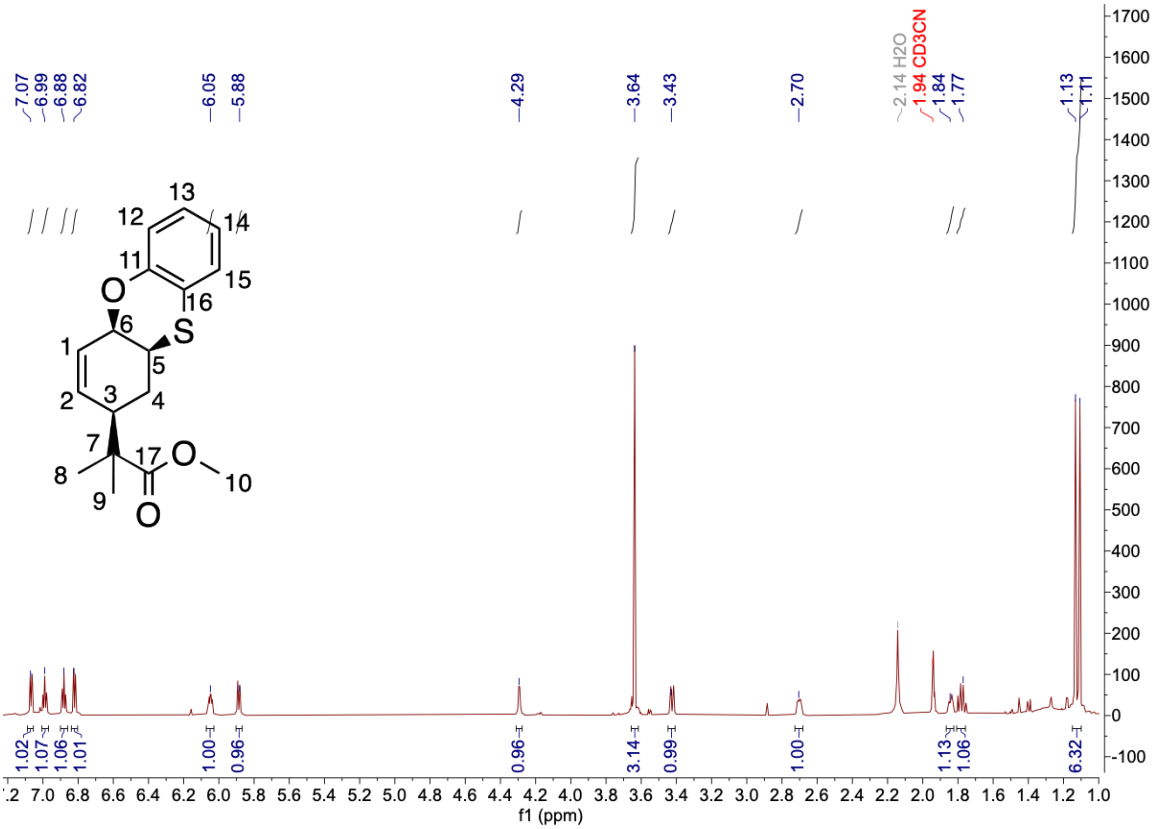


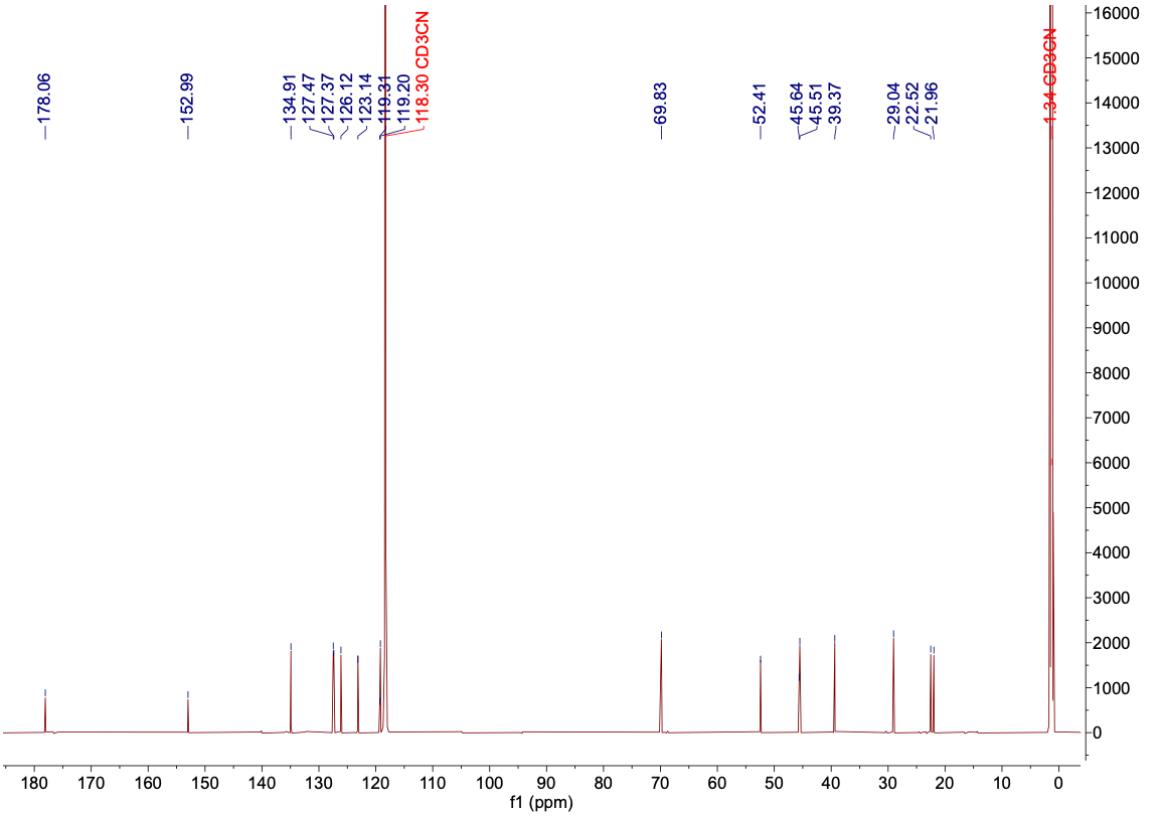
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.64:



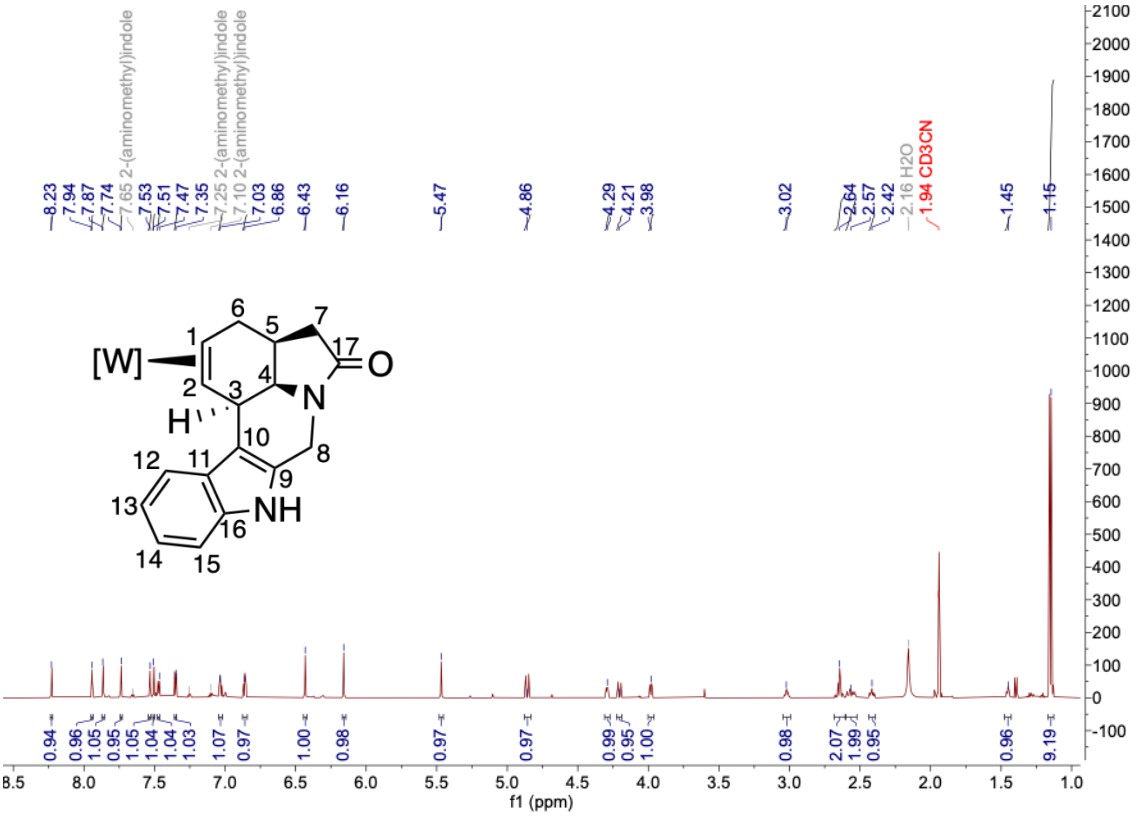


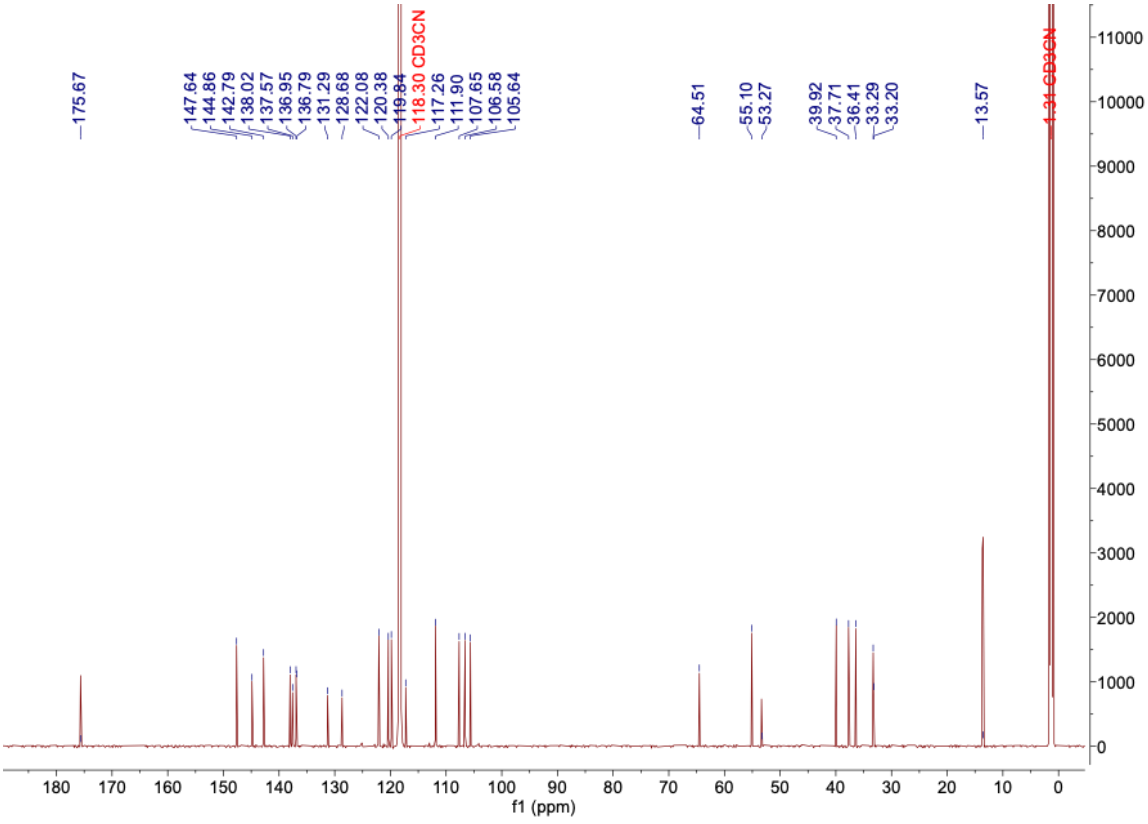
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.65:



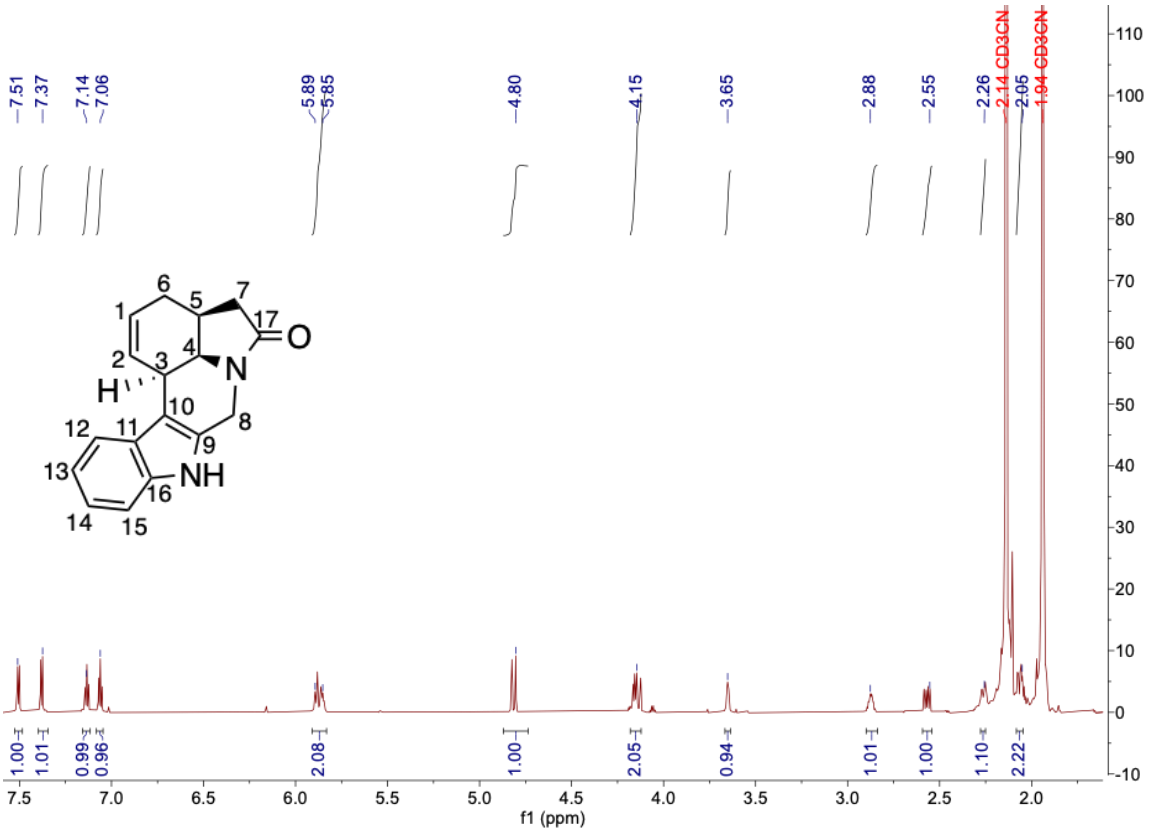


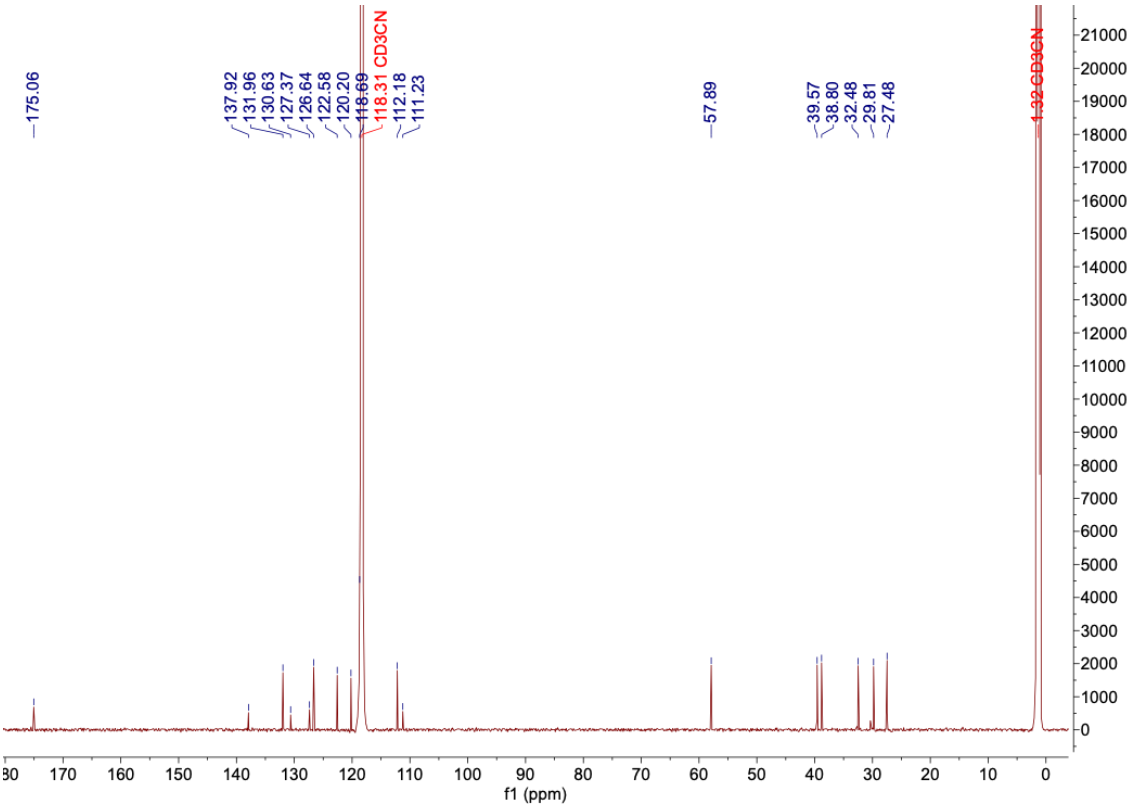
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.67:



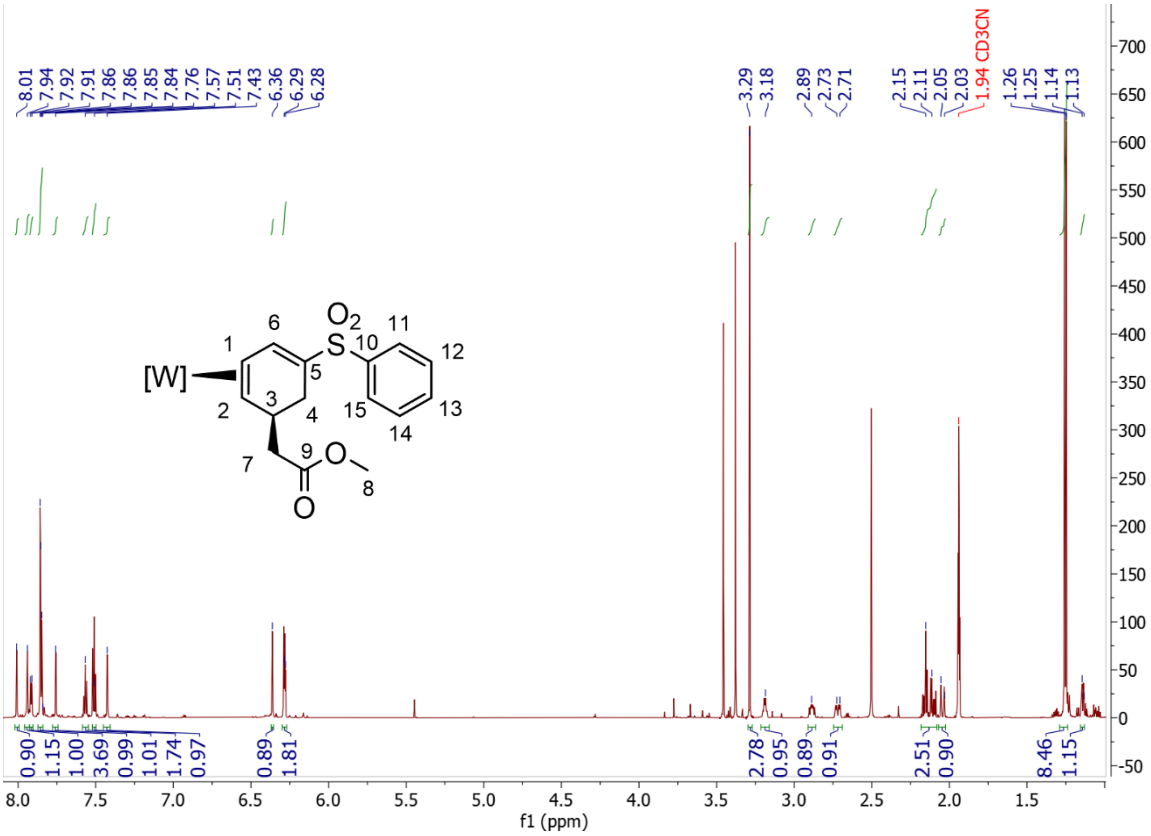


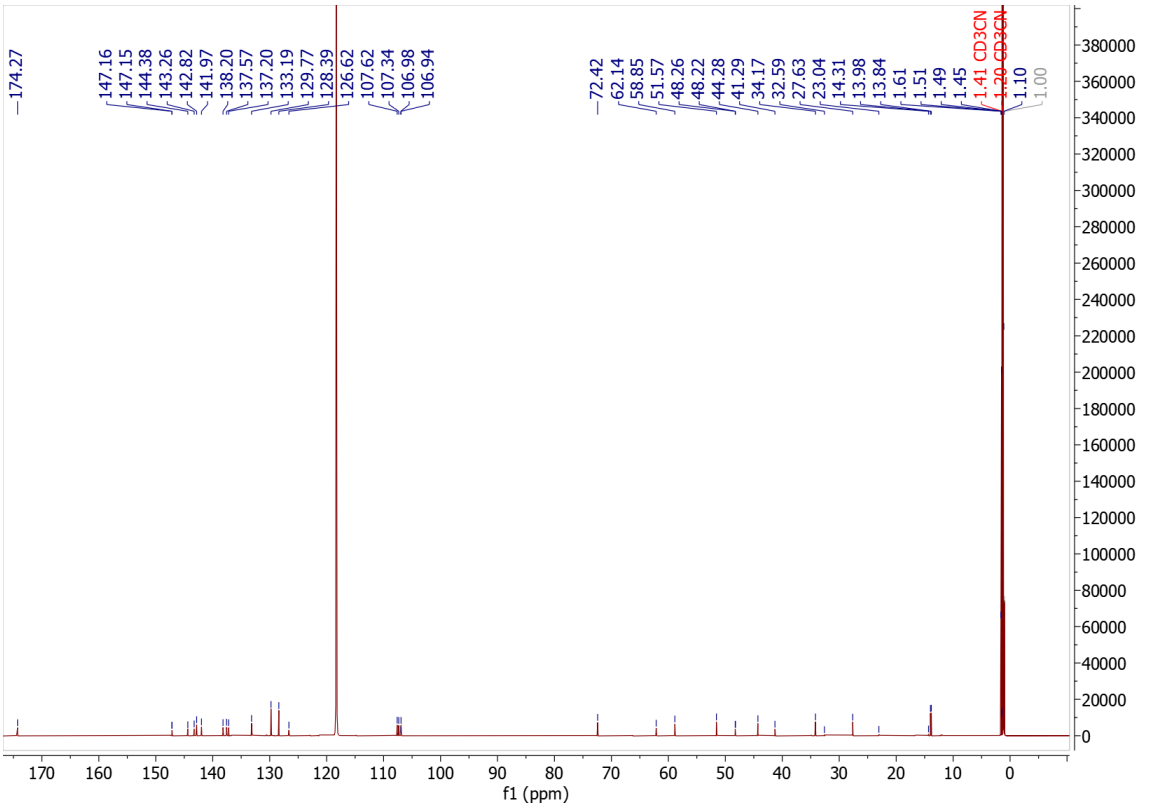
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 5.68:



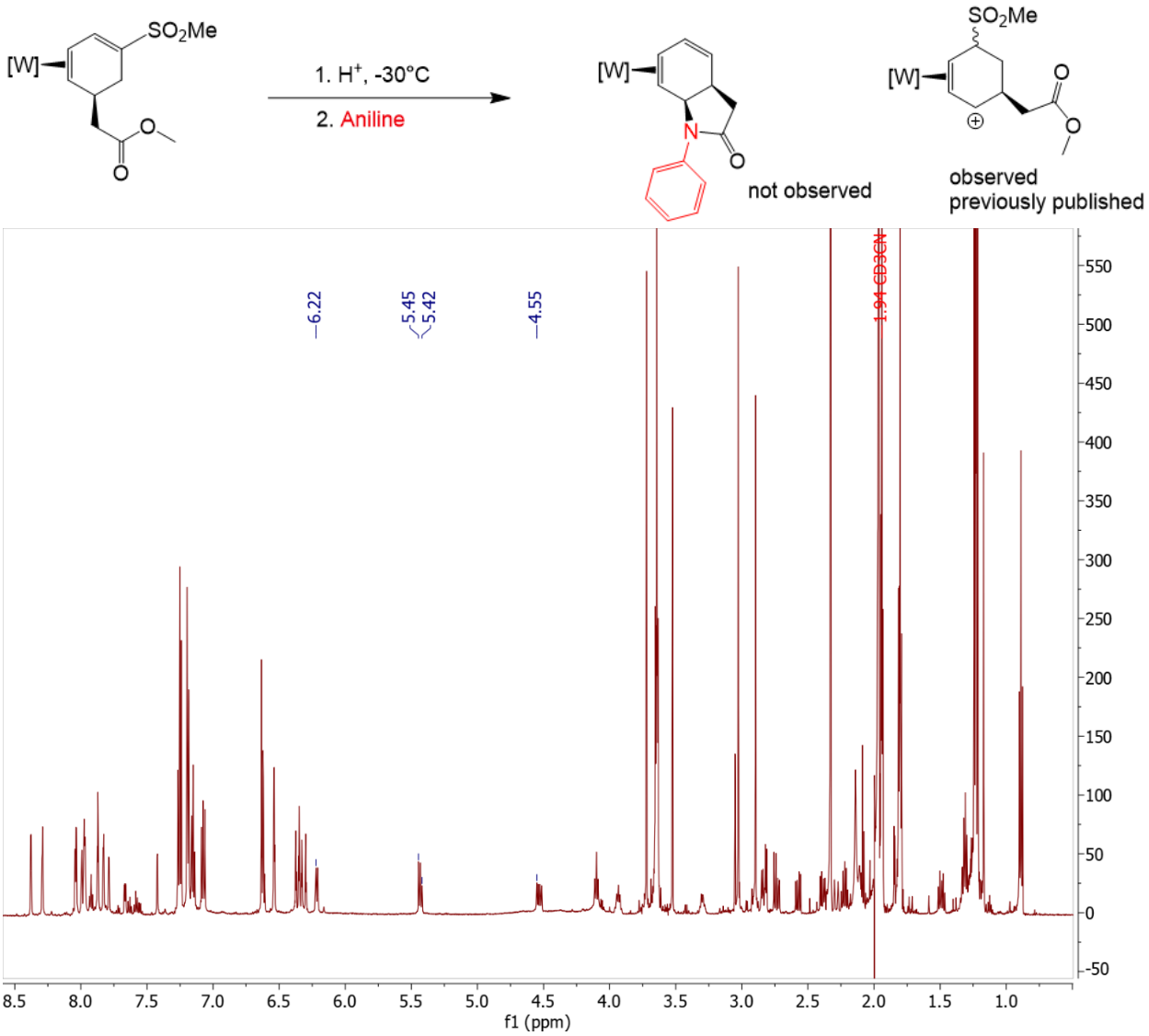


^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 79:





^{1}H-NMR (CD_3CN) for Reaction of 2 with Aniline:



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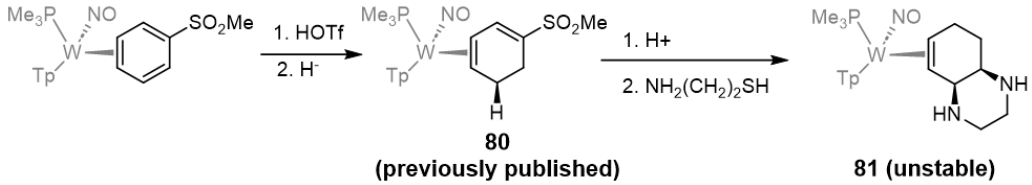
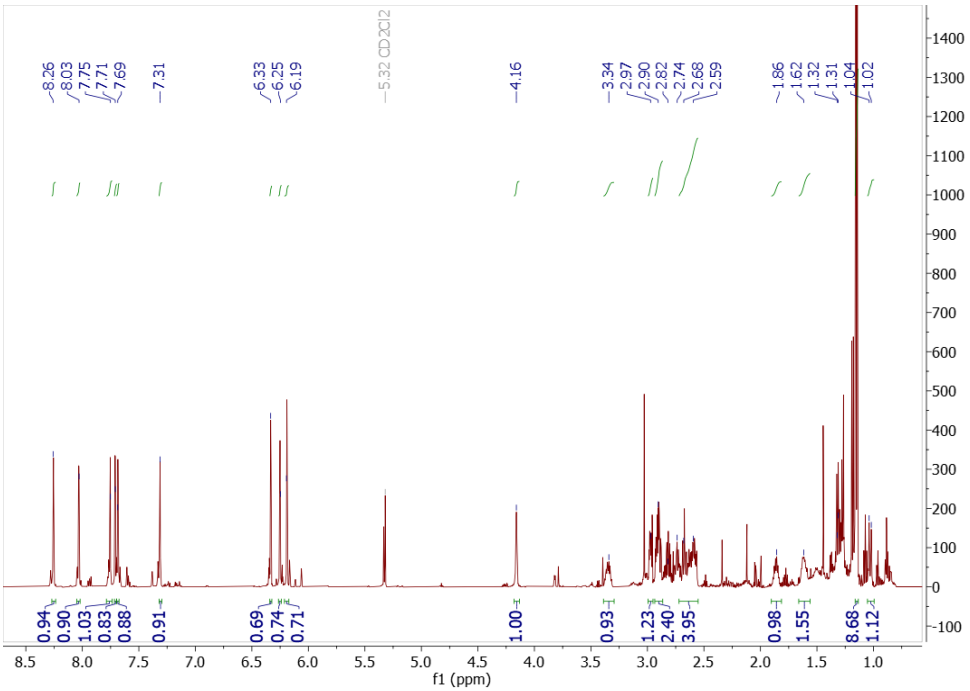
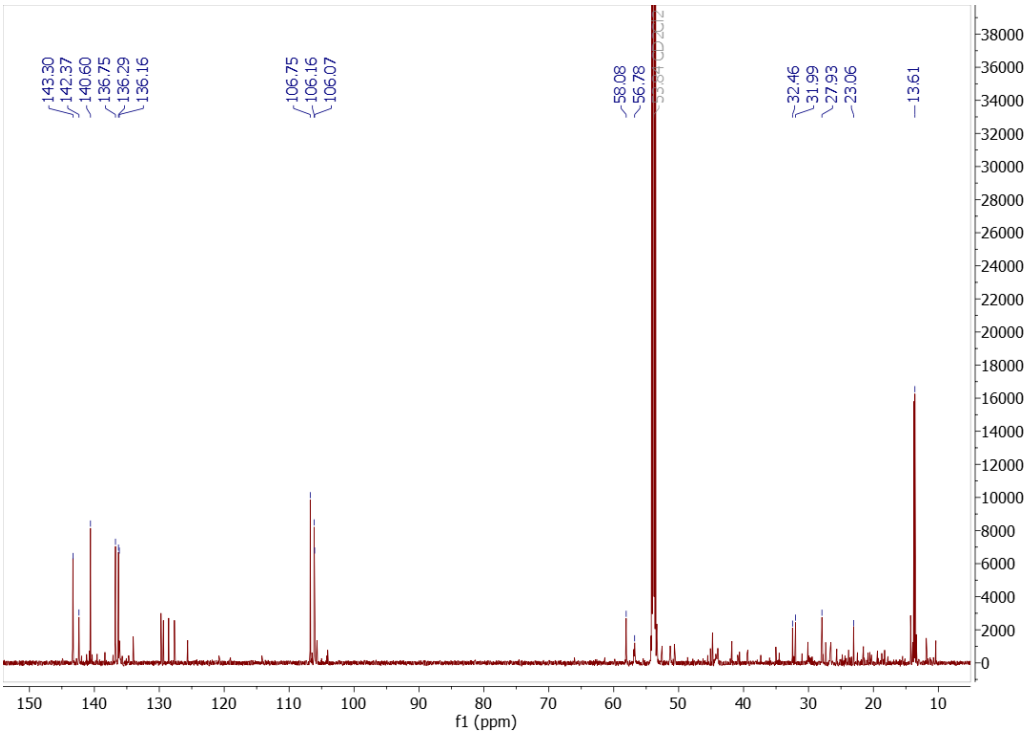
^{1}H-NMR (CD_2Cl_2) and ^{13}C-NMR (CD_2Cl_2) of Compound 81:



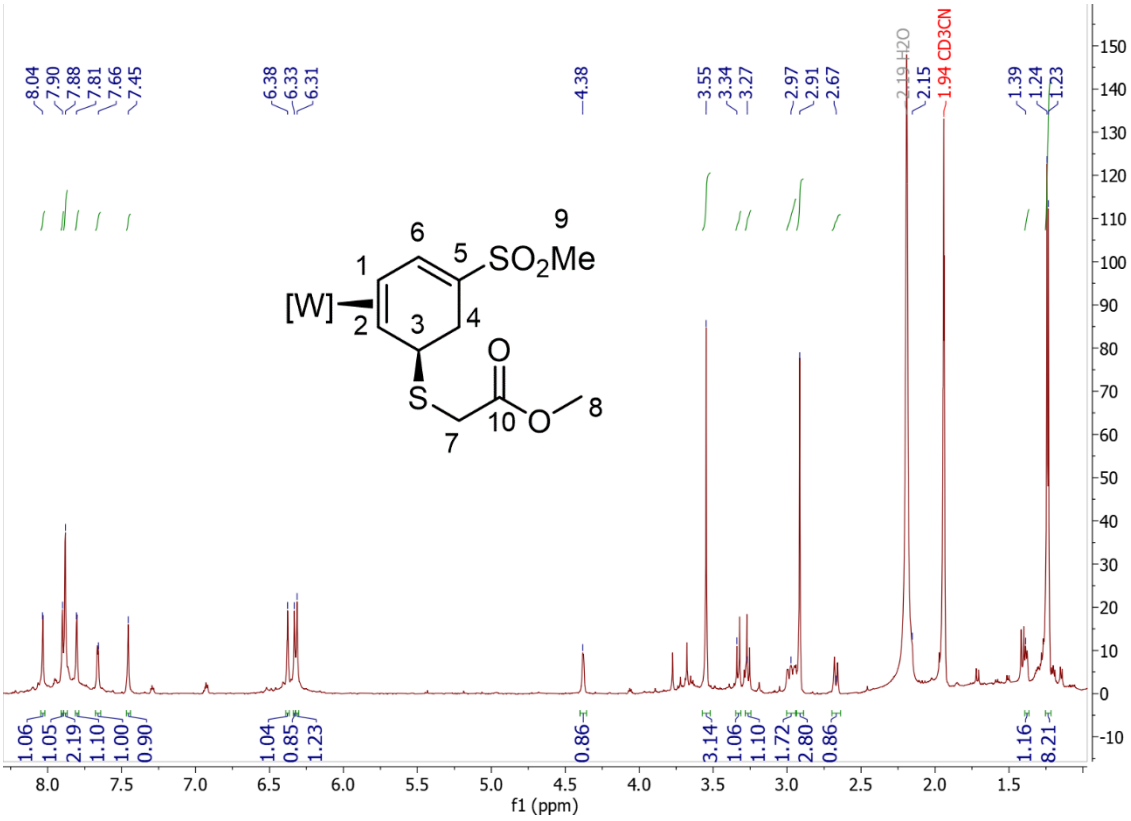
80
(previously published)

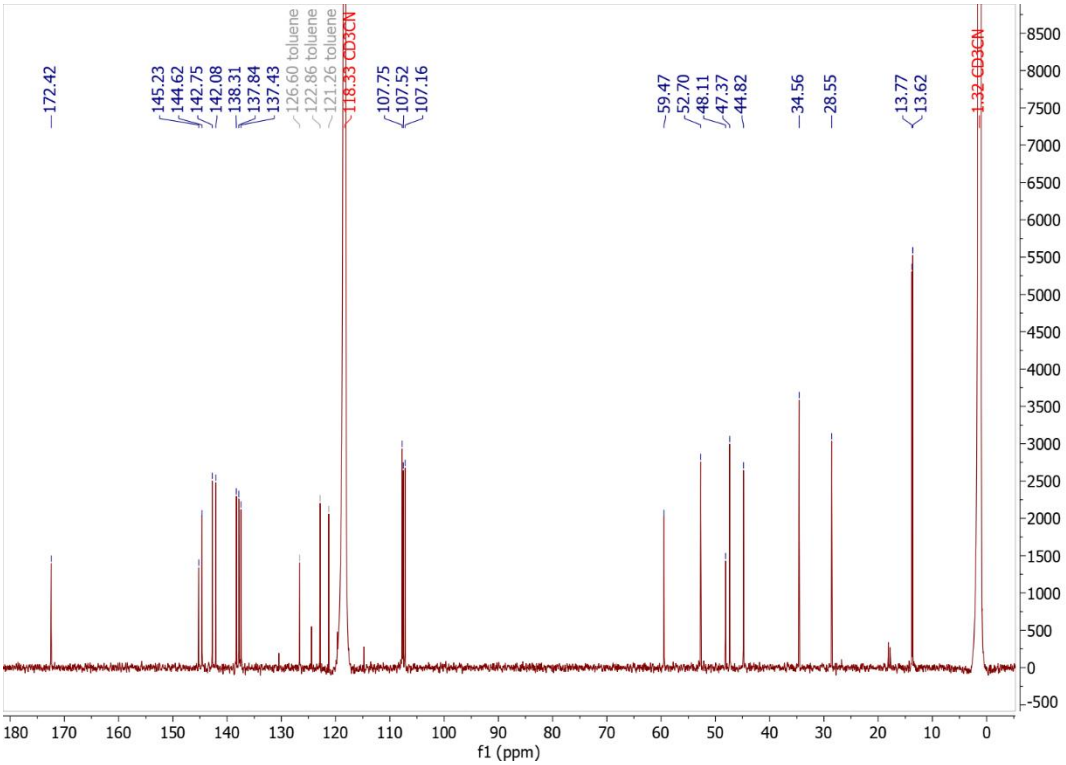
81 (unstable)





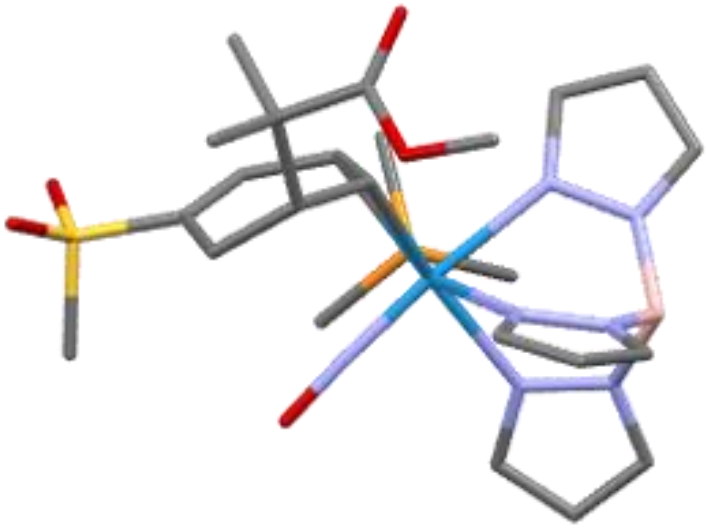
^{1}H-NMR (CD_3CN) and ^{13}C-NMR (CD_3CN) of Compound 82:





Crystallographic Data Chapter 5

Structure Report for Compound 5.3



A colourless, plate shaped crystal of **Compound 5.3**
measuring 0.04×0.044×0.073 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_2_193_x2_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[126] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[127] and refined by full-matrix least-squares methods against F^2 using XL[128] within OLEX2.[129] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically

[126] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[127] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[128] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[129] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[130]

Refinement details for Compound 5.3

Refined as a 2-component inversion twin.

Table 1 Crystal data and structure refinement for Compound 5.3

CCDC number	
Empirical formula	$C_{27}H_{43}BN_7O_6PSW$
Formula weight	819.37
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.04×0.044×0.073
Crystal habit	colourless plate
Crystal system	triclinic
Space group	$P1$ (1)
a [Å]	11.7294(4)
b [Å]	12.2675(5)
c [Å]	12.9211(6)
α [°]	110.907(2)
β [°]	103.760(2)
γ [°]	94.8740(10)
Volume [$Å^3$]	1657.15(12)
Z	2
ρ_{calc} [gcm^{-3}]	1.642
μ [mm^{-1}]	3.647
F(000)	824
2θ range [°]	3.62 to 56.65 (0.75 Å)
Index ranges	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −17 ≤ l ≤ 17
Reflections collected	119521

[130] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Independent reflections	16484 [R_{int} = 0.0711]
Data / Restraints / Parameters	16484 / 10 / 816
Goodness-of-fit on F^2	1.026
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0284 wR_2 = 0.0571
Final R indexes [all data]	R_1 = 0.0362 wR_2 = 0.0598
Largest peak/hole [eÅ^{-3}]	1.20/−0.78
Flack X parameter	0.480(6)

Table 2 Atomic coordinates and Ueq [Å2] for Compound 5.3

Atom	***x***	***y***	***z***	U_{eq}
W1	0.23219(2)	0.33804(2)	0.26570(2)	0.01415(8)
S1	0.27829(15)	0.32515(14)	−0.13486(15)	0.0189(3)
P1	0.0445(2)	0.1922(2)	0.1385(2)	0.0181(5)
O1	0.1652(4)	0.5039(4)	0.1486(4)	0.0228(10)
O2	0.6819(5)	0.2357(5)	0.3027(5)	0.0286(11)
O3	0.6764(4)	0.4288(4)	0.3812(4)	0.0242(10)
O4	0.3816(4)	0.3706(4)	−0.1601(4)	0.0247(10)
O5	0.2055(5)	0.2137(4)	−0.2190(4)	0.0274(11)
N1	0.1091(5)	0.4115(5)	0.3652(5)	0.0172(11)
N2	0.1104(5)	0.4040(6)	0.4685(5)	0.0180(13)
N3	0.2480(5)	0.2107(5)	0.3546(4)	0.0156(11)
N4	0.2277(5)	0.2412(5)	0.4608(5)	0.0182(11)
N5	0.3538(5)	0.4556(5)	0.4400(5)	0.0172(11)
N6	0.3296(8)	0.4530(8)	0.5374(7)	0.0189(19)
N7	0.1994(5)	0.4373(5)	0.1967(5)	0.0170(11)
C1	0.0250(6)	0.4726(6)	0.3419(6)	0.0211(14)
H1	0.005381	0.490577	0.274830	0.025
C2	−0.0299(6)	0.5064(6)	0.4295(6)	0.0245(15)
H2	−0.092619	0.550506	0.434233	0.029
C3	0.0265(6)	0.4618(6)	0.5084(6)	0.0219(14)
H3	0.009343	0.470389	0.578809	0.026
C4	0.2651(6)	0.0972(6)	0.3233(6)	0.0205(13)

H4	0.282609	0.052580	0.253868	0.025
C5	0.2532(7)	0.0557(6)	0.4073(6)	0.0235(14)
H5	0.258386	−0.021757	0.405538	0.028
C6	0.2326(6)	0.1481(6)	0.4929(6)	0.0234(14)
H6	0.223145	0.147215	0.563606	0.028
C7	0.4495(6)	0.5416(6)	0.4763(6)	0.0218(14)
H7	0.486377	0.563573	0.426820	0.026
C8	0.4877(6)	0.5947(6)	0.5970(6)	0.0263(16)
H8	0.553287	0.657749	0.644653	0.032
C9	0.4093(6)	0.5355(6)	0.6315(6)	0.0233(15)
H9	0.411148	0.550620	0.709347	0.028
C10	0.3052(6)	0.2176(5)	0.1308(5)	0.0156(12)
H10	0.302843	0.134772	0.127550	0.019
C11	0.3995(5)	0.3068(5)	0.2242(5)	0.0143(12)
H11	0.447103	0.271053	0.274613	0.017
C12	0.4817(9)	0.3891(9)	0.1962(9)	0.019(2)
H12	0.509023	0.465240	0.266015	0.023
C13	0.4162(6)	0.4202(5)	0.0951(6)	0.0175(13)
H13A	0.376739	0.488064	0.125555	0.021
H13B	0.475784	0.445881	0.061532	0.021
C14	0.3237(6)	0.3188(6)	0.0005(6)	0.0167(14)
C15	0.2727(6)	0.2281(6)	0.0190(6)	0.0165(13)
H15	0.212891	0.168160	−0.043275	0.020
C16	0.5966(6)	0.3367(6)	0.1791(6)	0.0196(13)
C17	0.5708(6)	0.2170(6)	0.0796(6)	0.0237(14)
H17A	0.537560	0.225843	0.006538	0.036
H17B	0.513148	0.161623	0.089470	0.036
H17C	0.645064	0.186121	0.078450	0.036
C18	0.6881(6)	0.4239(6)	0.1645(6)	0.0237(14)
H18A	0.763830	0.395147	0.168156	0.036
H18B	0.701205	0.502473	0.226525	0.036
H18C	0.657473	0.429514	0.089407	0.036
C19	0.6561(5)	0.3240(6)	0.2917(6)	0.0198(14)
C20	0.7273(7)	0.4325(7)	0.4947(7)	0.0306(17)
H20A	0.787149	0.381321	0.492567	0.046
H20B	0.664253	0.404548	0.522252	0.046
H20C	0.765371	0.514341	0.547239	0.046
C21	0.1875(6)	0.4343(6)	−0.1186(6)	0.0256(15)
H21A	0.234338	0.510291	−0.059419	0.038

H21B	0.119333	0.410130	−0.094984	0.038
H21C	0.158430	0.442959	−0.192379	0.038
C22	0.0498(6)	0.0407(6)	0.0490(6)	0.0252(15)
H22A	0.094618	0.042099	−0.005726	0.038
H22B	−0.031730	−0.003495	0.006141	0.038
H22C	0.089297	0.002007	0.098353	0.038
C23	−0.0460(6)	0.2423(6)	0.0352(6)	0.0274(15)
H23A	−0.060369	0.321701	0.076271	0.041
H23B	−0.122518	0.186959	−0.005328	0.041
H23C	−0.003769	0.245276	−0.020999	0.041
C24	−0.0570(6)	0.1636(6)	0.2179(7)	0.0263(15)
H24A	−0.015928	0.133158	0.274300	0.040
H24B	−0.127598	0.104753	0.163499	0.040
H24C	−0.081733	0.237635	0.258414	0.040
B1	0.2193(7)	0.3697(7)	0.5326(6)	0.0196(15)
H1A	0.213(6)	0.379(6)	0.617(6)	0.014(17)
W2	0.66383(2)	0.90960(2)	0.47302(2)	0.01469(8)
S2	0.90771(15)	0.78791(15)	0.17038(16)	0.0211(3)
P2	0.8680(2)	1.0379(2)	0.5756(2)	0.0183(5)
O6	0.7861(5)	0.7000(4)	0.4193(5)	0.0287(11)
O7	0.3377(4)	0.9213(5)	0.0909(5)	0.0246(11)
O8	0.3075(4)	0.7384(4)	0.0881(4)	0.0229(10)
O9	1.0044(4)	0.8889(4)	0.2236(5)	0.0277(11)
O10	0.8719(5)	0.7308(5)	0.0457(5)	0.0337(13)
N8	0.6791(5)	0.8962(5)	0.6416(5)	0.0187(11)
N9	0.6090(6)	0.9445(6)	0.7099(5)	0.0225(14)
N10	0.5916(5)	1.0763(5)	0.5439(5)	0.0184(11)
N11	0.5336(5)	1.0895(5)	0.6262(5)	0.0222(12)
N12	0.4771(5)	0.8333(5)	0.4554(5)	0.0168(11)
N13	0.4275(7)	0.8787(8)	0.5450(8)	0.0196(18)
N14	0.7319(5)	0.7832(5)	0.4357(5)	0.0192(11)
C25	0.7549(6)	0.8484(7)	0.6986(6)	0.0262(15)
H25	0.814065	0.808284	0.670992	0.031
C26	0.7349(7)	0.8657(7)	0.8047(7)	0.0309(17)
H26	0.776643	0.840802	0.862416	0.037
C27	0.6422(7)	0.9262(7)	0.8083(7)	0.0306(17)
H27	0.607195	0.951031	0.870089	0.037
C28	0.5932(6)	1.1770(6)	0.5256(6)	0.0226(14)
H28	0.626648	1.192083	0.470831	0.027

C29	0.5395(7)	1.2568(7)	0.5968(7)	0.0292(17)
H29	0.531232	1.334762	0.601943	0.035
C30	0.5014(6)	1.1972(6)	0.6579(7)	0.0280(16)
H30	0.459195	1.226652	0.713324	0.034
C31	0.3927(6)	0.7463(6)	0.3718(6)	0.0211(14)
H31	0.402509	0.698109	0.299530	0.025
C32	0.2887(6)	0.7349(6)	0.4035(6)	0.0206(13)
H32	0.215888	0.680282	0.359107	0.025
C33	0.3145(6)	0.8203(6)	0.5134(6)	0.0232(14)
H33	0.261068	0.835591	0.559623	0.028
C34	0.6950(6)	0.9744(5)	0.3391(5)	0.0159(12)
H34	0.689312	1.059534	0.355637	0.019
C35	0.5812(5)	0.8929(6)	0.2947(5)	0.0153(12)
H35	0.512658	0.935969	0.290465	0.018
C36	0.5600(9)	0.7820(8)	0.1841(9)	0.016(2)
H36	0.502857	0.720001	0.189098	0.019
C37	0.6754(5)	0.7308(6)	0.1752(6)	0.0188(13)
H37A	0.687898	0.681829	0.222021	0.023
H37B	0.665085	0.678374	0.093661	0.023
C38	0.7835(6)	0.8259(6)	0.2160(7)	0.0165(14)
C39	0.7919(6)	0.9354(6)	0.2921(6)	0.0169(13)
H39	0.864506	0.990419	0.316689	0.020
C40	0.4966(5)	0.8056(6)	0.0753(6)	0.0181(13)
C41	0.5641(6)	0.9123(6)	0.0653(6)	0.0222(14)
H41A	0.576991	0.982810	0.136391	0.033
H41B	0.517051	0.926462	−0.000704	0.033
H41C	0.641445	0.895691	0.053738	0.033
C42	0.4765(6)	0.6968(6)	−0.0372(6)	0.0231(14)
H42A	0.552737	0.687553	−0.054907	0.035
H42B	0.420146	0.707712	−0.100587	0.035
H42C	0.443782	0.625698	−0.028154	0.035
C43	0.3739(6)	0.8318(6)	0.0862(5)	0.0172(12)
C44	0.1898(6)	0.7550(7)	0.1024(8)	0.0311(17)
H44A	0.146771	0.781393	0.043476	0.047
H44B	0.198742	0.815009	0.179500	0.047
H44C	0.144828	0.679625	0.093714	0.047
C45	0.9482(7)	0.6793(7)	0.2249(8)	0.0317(18)
H45A	1.017504	0.651280	0.201496	0.048
H45B	0.881108	0.612341	0.194051	0.048

H45C	0.968572	0.713971	0.309582	0.048
C46	0.9042(6)	1.1743(6)	0.5544(6)	0.0234(14)
H46A	0.890488	1.156100	0.471635	0.035
H46B	0.988197	1.210624	0.595698	0.035
H46C	0.853197	1.229723	0.584398	0.035
C47	0.9903(6)	0.9614(6)	0.5467(6)	0.0236(15)
H47A	0.980228	0.887164	0.558916	0.035
H47B	1.066381	1.012198	0.599244	0.035
H47C	0.990271	0.943553	0.466497	0.035
C48	0.9070(7)	1.0969(6)	0.7324(6)	0.0275(16)
H48A	0.842006	1.133304	0.757731	0.041
H48B	0.980485	1.156860	0.764789	0.041
H48C	0.919526	1.032345	0.759216	0.041
B2	0.4977(7)	0.9841(8)	0.6569(7)	0.0258(17)
H2A	0.447(7)	1.013(7)	0.719(7)	0.031
O11	0.0368(7)	0.8481(9)	0.7613(8)	0.079(3)
C49	0.2460(8)	0.9075(8)	0.8130(8)	0.042(2)
H49A	0.228026	0.965429	0.778195	0.063
H49B	0.305790	0.865292	0.782767	0.063
H49C	0.277206	0.948784	0.897201	0.063
C50	0.1348(9)	0.8207(9)	0.7838(8)	0.045(2)
C51	0.1482(9)	0.7046(8)	0.7835(8)	0.046(2)
H51A	0.196916	0.713074	0.859865	0.069
H51B	0.187402	0.665098	0.724969	0.069
H51C	0.069265	0.657003	0.765408	0.069
O54	0.917(2)	0.451(2)	0.7472(18)	0.0554(18)
C52	0.776(3)	0.581(2)	0.784(2)	0.0554(18)
H52A	0.772622	0.633079	0.860555	0.083
H52B	0.694983	0.546333	0.732509	0.083
H52C	0.819316	0.626522	0.752134	0.083
C53	0.840(4)	0.484(4)	0.795(4)	0.0554(18)
C54	0.810(3)	0.420(2)	0.866(2)	0.0554(18)
H54A	0.723494	0.392856	0.843179	0.083
H54B	0.837901	0.472792	0.948024	0.083
H54C	0.849690	0.350727	0.853623	0.083
O54A	0.898(2)	0.4753(18)	0.7433(17)	0.0554(18)
C12A	0.828(4)	0.480(4)	0.804(4)	0.0554(18)
C52A	0.729(3)	0.548(2)	0.7955(19)	0.0554(18)
H52D	0.749579	0.622983	0.863418	0.083

H52E	0.655547	0.500791	0.792492	0.083
H52F	0.716300	0.564616	0.725247	0.083
C53A	0.840(3)	0.427(2)	0.893(2)	0.0554(18)
H53A	0.763053	0.379995	0.880795	0.083
H53B	0.864661	0.491315	0.970067	0.083
H53C	0.900323	0.376638	0.885911	0.083

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for **Compound 5.3**

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01377(17)	0.01305(18)	0.01591(19)	0.00609(15)	0.00370(15)	0.00365(14)
S1	0.0220(8)	0.0178(8)	0.0172(8)	0.0061(6)	0.0067(6)	0.0050(6)
P1	0.0154(10)	0.0176(10)	0.0207(12)	0.0078(9)	0.0038(8)	0.0019(7)
O1	0.033(3)	0.019(2)	0.026(3)	0.016(2)	0.011(2)	0.014(2)
O2	0.034(3)	0.027(3)	0.036(3)	0.022(2)	0.012(2)	0.015(2)
O3	0.024(2)	0.023(2)	0.024(3)	0.010(2)	0.001(2)	0.004(2)
O4	0.027(3)	0.027(3)	0.026(3)	0.012(2)	0.014(2)	0.008(2)
O5	0.033(3)	0.022(2)	0.019(3)	0.004(2)	0.002(2)	−0.002(2)
N1	0.019(3)	0.017(3)	0.017(3)	0.006(2)	0.008(2)	0.006(2)
N2	0.021(3)	0.020(3)	0.014(3)	0.005(3)	0.007(3)	0.005(2)
N3	0.019(3)	0.017(3)	0.014(3)	0.008(2)	0.006(2)	0.006(2)
N4	0.018(3)	0.022(3)	0.016(3)	0.007(2)	0.007(2)	0.005(2)
N5	0.016(3)	0.016(3)	0.017(3)	0.003(2)	0.002(2)	0.006(2)
N6	0.021(4)	0.023(4)	0.013(4)	0.008(3)	0.001(3)	0.008(3)
N7	0.015(3)	0.016(3)	0.016(3)	0.001(2)	0.006(2)	0.004(2)
C1	0.020(3)	0.022(3)	0.024(4)	0.011(3)	0.007(3)	0.005(3)
C2	0.022(3)	0.026(4)	0.027(4)	0.010(3)	0.007(3)	0.008(3)
C3	0.022(3)	0.025(3)	0.022(4)	0.008(3)	0.012(3)	0.008(3)
C4	0.022(3)	0.014(3)	0.023(4)	0.007(3)	0.002(3)	0.005(2)
C5	0.032(4)	0.015(3)	0.026(4)	0.012(3)	0.006(3)	0.007(3)
C6	0.028(4)	0.024(3)	0.022(4)	0.014(3)	0.006(3)	0.005(3)
C7	0.018(3)	0.015(3)	0.033(4)	0.010(3)	0.007(3)	0.005(2)
C8	0.023(3)	0.020(3)	0.021(4)	−0.002(3)	−0.004(3)	0.003(3)
C9	0.024(3)	0.021(3)	0.018(3)	0.001(3)	0.001(3)	0.011(3)
C10	0.021(3)	0.010(3)	0.018(3)	0.005(2)	0.010(3)	0.005(2)
C11	0.013(3)	0.016(3)	0.016(3)	0.007(2)	0.005(2)	0.005(2)

C12	0.021(5)	0.014(4)	0.018(4)	0.002(3)	0.005(3)	0.004(3)
C13	0.016(3)	0.014(3)	0.025(4)	0.012(3)	0.004(3)	0.003(2)
C14	0.018(3)	0.014(3)	0.018(4)	0.006(3)	0.005(3)	0.004(3)
C15	0.015(3)	0.015(3)	0.015(3)	0.000(3)	0.006(2)	0.004(2)
C16	0.017(3)	0.023(3)	0.023(4)	0.011(3)	0.008(3)	0.007(3)
C17	0.020(3)	0.022(3)	0.031(4)	0.010(3)	0.011(3)	0.010(3)
C18	0.022(3)	0.025(3)	0.032(4)	0.018(3)	0.009(3)	0.008(3)
C19	0.011(3)	0.021(3)	0.031(4)	0.012(3)	0.009(3)	0.001(2)
C20	0.027(4)	0.036(4)	0.032(4)	0.019(3)	0.006(3)	0.005(3)
C21	0.029(4)	0.031(4)	0.023(4)	0.012(3)	0.011(3)	0.016(3)
C22	0.024(4)	0.019(3)	0.025(4)	0.003(3)	0.006(3)	−0.003(3)
C23	0.025(4)	0.027(4)	0.025(4)	0.009(3)	0.000(3)	0.002(3)
C24	0.025(4)	0.024(4)	0.031(4)	0.012(3)	0.008(3)	−0.001(3)
B1	0.026(4)	0.022(4)	0.011(4)	0.006(3)	0.006(3)	0.008(3)
W2	0.01438(18)	0.01401(18)	0.01660(19)	0.00663(15)	0.00486(15)	0.00324(14)
S2	0.0212(8)	0.0200(8)	0.0257(9)	0.0086(7)	0.0123(7)	0.0074(6)
P2	0.0161(10)	0.0170(10)	0.0201(11)	0.0062(8)	0.0044(8)	0.0017(7)
O6	0.035(3)	0.022(2)	0.030(3)	0.010(2)	0.006(2)	0.016(2)
O7	0.025(3)	0.020(3)	0.035(3)	0.013(2)	0.013(2)	0.009(2)
O8	0.017(2)	0.023(2)	0.034(3)	0.015(2)	0.012(2)	0.0062(19)
O9	0.021(2)	0.024(3)	0.041(3)	0.011(2)	0.016(2)	0.005(2)
O10	0.035(3)	0.039(3)	0.029(3)	0.008(2)	0.017(2)	0.016(2)
N8	0.019(3)	0.024(3)	0.014(3)	0.011(2)	0.004(2)	0.000(2)
N9	0.027(4)	0.025(4)	0.016(3)	0.010(3)	0.007(3)	−0.001(3)
N10	0.021(3)	0.015(3)	0.019(3)	0.003(2)	0.011(2)	0.006(2)
N11	0.019(3)	0.025(3)	0.018(3)	0.001(2)	0.007(2)	0.004(2)
N12	0.016(3)	0.019(3)	0.019(3)	0.010(2)	0.005(2)	0.002(2)
N13	0.018(4)	0.024(4)	0.021(4)	0.012(3)	0.007(3)	0.007(3)
N14	0.017(3)	0.020(3)	0.018(3)	0.008(2)	0.000(2)	0.001(2)
C25	0.021(3)	0.031(4)	0.027(4)	0.016(3)	0.002(3)	−0.001(3)
C26	0.028(4)	0.035(4)	0.025(4)	0.017(3)	−0.004(3)	−0.007(3)
C27	0.033(4)	0.038(4)	0.015(4)	0.010(3)	0.003(3)	−0.009(3)
C28	0.025(3)	0.020(3)	0.025(4)	0.007(3)	0.011(3)	0.008(3)
C29	0.026(4)	0.021(4)	0.040(5)	0.008(3)	0.013(3)	0.007(3)
C30	0.025(4)	0.022(3)	0.033(4)	0.000(3)	0.017(3)	0.005(3)
C31	0.024(3)	0.016(3)	0.021(4)	0.007(3)	0.005(3)	0.003(3)
C32	0.017(3)	0.019(3)	0.026(4)	0.011(3)	0.005(3)	0.003(2)
C33	0.019(3)	0.028(4)	0.028(4)	0.015(3)	0.010(3)	0.005(3)

C34	0.021(3)	0.013(3)	0.017(3)	0.007(3)	0.009(3)	0.004(2)
C35	0.014(3)	0.020(3)	0.012(3)	0.007(2)	0.002(2)	0.005(2)
C36	0.018(4)	0.013(4)	0.017(4)	0.004(3)	0.009(4)	0.001(3)
C37	0.016(3)	0.015(3)	0.025(4)	0.008(3)	0.003(3)	0.006(2)
C38	0.019(3)	0.015(3)	0.017(4)	0.005(3)	0.009(3)	0.005(3)
C39	0.017(3)	0.018(3)	0.018(3)	0.010(3)	0.005(3)	0.001(2)
C40	0.014(3)	0.023(3)	0.021(3)	0.011(3)	0.007(2)	0.006(2)
C41	0.020(3)	0.032(4)	0.022(4)	0.018(3)	0.007(3)	0.004(3)
C42	0.020(3)	0.029(4)	0.017(3)	0.005(3)	0.003(3)	0.006(3)
C43	0.018(3)	0.019(3)	0.013(3)	0.006(2)	0.003(2)	0.004(2)
C44	0.021(4)	0.032(4)	0.051(5)	0.021(4)	0.019(3)	0.010(3)
C45	0.026(4)	0.033(4)	0.053(5)	0.027(4)	0.022(4)	0.015(3)
C46	0.024(3)	0.018(3)	0.028(4)	0.008(3)	0.008(3)	0.000(3)
C47	0.018(3)	0.027(4)	0.028(4)	0.012(3)	0.007(3)	0.006(3)
C48	0.029(4)	0.026(4)	0.025(4)	0.008(3)	0.008(3)	−0.003(3)
B2	0.022(4)	0.033(4)	0.021(4)	0.009(3)	0.008(3)	0.001(3)
O11	0.052(5)	0.121(7)	0.087(6)	0.061(6)	0.021(4)	0.046(5)
C49	0.045(5)	0.049(5)	0.034(5)	0.020(4)	0.011(4)	0.006(4)
C50	0.046(5)	0.065(6)	0.027(4)	0.018(4)	0.010(4)	0.021(5)
C51	0.044(5)	0.047(5)	0.036(5)	0.008(4)	0.006(4)	0.001(4)
O54	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C52	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C53	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C54	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
O54A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C12A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C52A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)
C53A	0.072(6)	0.046(4)	0.039(3)	0.014(3)	0.000(3)	0.027(3)

Table 4 Bond lengths and angles for **Compound 5.3** **Atom–Atom**	**Length [Å]**
W1–P1	2.502(3)
W1–N1	2.197(5)
W1–N3	2.241(5)
W1–N5	2.235(5)

W1–N7	1.765(6)
W1–C10	2.245(6)
W1–C11	2.184(6)
S1–O4	1.445(5)
S1–O5	1.442(5)
S1–C14	1.735(8)
S1–C21	1.766(7)
P1–C22	1.821(7)
P1–C23	1.818(8)
P1–C24	1.833(7)
O1–N7	1.231(7)
O2–C19	1.196(8)
O3–C19	1.343(8)
O3–C20	1.428(9)
N1–N2	1.367(8)
N1–C1	1.331(8)
N2–C3	1.355(9)
N2–B1	1.527(10)
N3–N4	1.373(7)
N3–C4	1.351(8)
N4–C6	1.347(9)
N4–B1	1.544(9)
N5–N6	1.364(10)
N5–C7	1.337(8)
N6–C9	1.341(11)
N6–B1	1.553(12)
C1–H1	0.9500
C1–C2	1.387(10)
C2–H2	0.9500
C2–C3	1.384(10)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.383(10)
C5–H5	0.9500
C5–C6	1.358(10)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.397(10)
C8–H8	0.9500

C8–C9	1.372(11)
C9–H9	0.9500
C10–H10	1.0000
C10–C11	1.447(9)
C10–C15	1.458(9)
C11–H11	1.0000
C11–C12	1.530(12)
C12–H12	1.0000
C12–C13	1.540(12)
C12–C16	1.571(12)
C13–H13A	0.9900
C13–H13B	0.9900
C13–C14	1.508(9)
C14–C15	1.340(9)
C15–H15	0.9500
C16–C17	1.514(9)
C16–C18	1.542(9)
C16–C19	1.526(10)
C17–H17A	0.9800
C17–H17B	0.9800
C17–H17C	0.9800
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800

B1–H1A	1.08(7)
W2–P2	2.516(3)
W2–N8	2.209(5)
W2–N10	2.251(5)
W2–N12	2.233(5)
W2–N14	1.771(6)
W2–C34	2.235(6)
W2–C35	2.204(6)
S2–O9	1.441(5)
S2–O10	1.444(6)
S2–C38	1.737(7)
S2–C45	1.765(7)
P2–C46	1.822(7)
P2–C47	1.820(7)
P2–C48	1.815(8)
O6–N14	1.229(7)
O7–C43	1.198(8)
O8–C43	1.342(8)
O8–C44	1.457(8)
N8–N9	1.364(9)
N8–C25	1.327(9)
N9–C27	1.342(10)
N9–B2	1.525(11)
N10–N11	1.362(8)
N10–C28	1.337(9)
N11–C30	1.352(9)
N11–B2	1.537(11)
N12–N13	1.381(10)
N12–C31	1.333(8)
N13–C33	1.346(10)
N13–B2	1.536(12)
C25–H25	0.9500
C25–C26	1.391(11)
C26–H26	0.9500
C26–C27	1.368(12)
C27–H27	0.9500
C28–H28	0.9500
C28–C29	1.392(10)
C29–H29	0.9500

C29–C30	1.372(11)
C30–H30	0.9500
C31–H31	0.9500
C31–C32	1.388(9)
C32–H32	0.9500
C32–C33	1.373(10)
C33–H33	0.9500
C34–H34	1.0000
C34–C35	1.453(9)
C34–C39	1.450(9)
C35–H35	1.0000
C35–C36	1.530(11)
C36–H36	1.0000
C36–C37	1.551(11)
C36–C40	1.564(12)
C37–H37A	0.9900
C37–H37B	0.9900
C37–C38	1.496(9)
C38–C39	1.330(9)
C39–H39	0.9500
C40–C41	1.532(9)
C40–C42	1.533(9)
C40–C43	1.529(9)
C41–H41A	0.9800
C41–H41B	0.9800
C41–H41C	0.9800
C42–H42A	0.9800
C42–H42B	0.9800
C42–H42C	0.9800
C44–H44A	0.9800
C44–H44B	0.9800
C44–H44C	0.9800
C45–H45A	0.9800
C45–H45B	0.9800
C45–H45C	0.9800
C46–H46A	0.9800
C46–H46B	0.9800
C46–H46C	0.9800
C47–H47A	0.9800

C47–H47B	0.9800
C47–H47C	0.9800
C48–H48A	0.9800
C48–H48B	0.9800
C48–H48C	0.9800
B2–H2A	1.09(8)
O11–C50	1.222(11)
C49–H49A	0.9800
C49–H49B	0.9800
C49–H49C	0.9800
C49–C50	1.490(13)
C50–C51	1.444(14)
C51–H51A	0.9800
C51–H51B	0.9800
C51–H51C	0.9800
O54–C53	1.24(2)
C52–H52A	0.9800
C52–H52B	0.9800
C52–H52C	0.9800
C52–C53	1.48(2)
C53–C54	1.48(2)
C54–H54A	0.9800
C54–H54B	0.9800
C54–H54C	0.9800
O54A–C12A	1.24(2)
C12A–C52A	1.496(19)
C12A–C53A	1.496(19)
C52A–H52D	0.9800
C52A–H52E	0.9800
C52A–H52F	0.9800
C53A–H53A	0.9800
C53A–H53B	0.9800
C53A–H53C	0.9800
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	81.01(15)
N1–W1–N3	86.72(19)
N1–W1–N5	76.4(2)

N1–W1–C10	161.5(2)
N3–W1–P1	82.58(15)
N3–W1–C10	89.1(2)
N5–W1–P1	151.58(15)
N5–W1–N3	79.18(19)
N5–W1–C10	120.5(2)
N7–W1–P1	92.17(18)
N7–W1–N1	86.7(2)
N7–W1–N3	172.1(2)
N7–W1–N5	103.4(2)
N7–W1–C10	95.8(2)
N7–W1–C11	97.2(2)
C10–W1–P1	80.58(17)
C11–W1–P1	118.52(17)
C11–W1–N1	159.8(2)
C11–W1–N3	90.5(2)
C11–W1–N5	83.4(2)
C11–W1–C10	38.1(2)
O4–S1–C14	108.8(3)
O4–S1–C21	106.6(3)
O5–S1–O4	117.3(3)
O5–S1–C14	110.5(3)
O5–S1–C21	108.0(3)
C14–S1–C21	104.8(3)
C22–P1–W1	120.9(3)
C22–P1–C24	100.4(3)
C23–P1–W1	113.0(3)
C23–P1–C22	102.9(4)
C23–P1–C24	103.9(4)
C24–P1–W1	113.6(3)
C19–O3–C20	117.7(6)
N2–N1–W1	123.7(4)
C1–N1–W1	128.8(5)
C1–N1–N2	107.5(5)
N1–N2–B1	118.4(6)
C3–N2–N1	108.5(6)
C3–N2–B1	130.2(6)
N4–N3–W1	119.8(4)
C4–N3–W1	134.0(4)

C4–N3–N4	106.0(5)
N3–N4–B1	121.6(5)
C6–N4–N3	109.3(5)
C6–N4–B1	128.6(6)
N6–N5–W1	120.0(5)
C7–N5–W1	133.7(5)
C7–N5–N6	106.2(6)
N5–N6–B1	122.4(7)
C9–N6–N5	109.8(7)
C9–N6–B1	127.7(8)
O1–N7–W1	173.8(5)
N1–C1–H1	124.8
N1–C1–C2	110.4(6)
C2–C1–H1	124.8
C1–C2–H2	127.5
C3–C2–C1	104.9(6)
C3–C2–H2	127.5
N2–C3–C2	108.7(6)
N2–C3–H3	125.7
C2–C3–H3	125.7
N3–C4–H4	125.1
N3–C4–C5	109.8(6)
C5–C4–H4	125.1
C4–C5–H5	126.9
C6–C5–C4	106.1(6)
C6–C5–H5	126.9
N4–C6–C5	108.7(6)
N4–C6–H6	125.6
C5–C6–H6	125.6
N5–C7–H7	124.7
N5–C7–C8	110.5(6)
C8–C7–H7	124.7
C7–C8–H8	127.7
C9–C8–C7	104.6(6)
C9–C8–H8	127.7
N6–C9–C8	108.9(7)
N6–C9–H9	125.6
C8–C9–H9	125.6
W1–C10–H10	115.5

C11–C10–W1	68.6(3)
C11–C10–H10	115.5
C11–C10–C15	118.4(5)
C15–C10–W1	115.3(4)
C15–C10–H10	115.5
W1–C11–H11	110.9
C10–C11–W1	73.2(3)
C10–C11–H11	110.9
C10–C11–C12	119.0(6)
C12–C11–W1	126.7(5)
C12–C11–H11	110.9
C11–C12–H12	106.6
C11–C12–C13	112.6(7)
C11–C12–C16	110.2(7)
C13–C12–H12	106.6
C13–C12–C16	113.6(7)
C16–C12–H12	106.6
C12–C13–H13A	108.8
C12–C13–H13B	108.8
H13A–C13–H13B	107.7
C14–C13–C12	113.7(6)
C14–C13–H13A	108.8
C14–C13–H13B	108.8
C13–C14–S1	117.8(5)
C15–C14–S1	119.7(5)
C15–C14–C13	122.4(7)
C10–C15–H15	118.6
C14–C15–C10	122.8(6)
C14–C15–H15	118.6
C17–C16–C12	113.7(6)
C17–C16–C18	109.7(6)
C17–C16–C19	109.2(6)
C18–C16–C12	111.7(6)
C19–C16–C12	106.1(6)
C19–C16–C18	106.0(5)
C16–C17–H17A	109.5
C16–C17–H17B	109.5
C16–C17–H17C	109.5
H17A–C17–H17B	109.5

H17A–C17–H17C	109.5
H17B–C17–H17C	109.5
C16–C18–H18A	109.5
C16–C18–H18B	109.5
C16–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
O2–C19–O3	123.1(7)
O2–C19–C16	126.9(6)
O3–C19–C16	109.9(5)
O3–C20–H20A	109.5
O3–C20–H20B	109.5
O3–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
S1–C21–H21A	109.5
S1–C21–H21B	109.5
S1–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5

H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
N2–B1–N4	109.4(6)
N2–B1–N6	105.7(6)
N2–B1–H1A	110(4)
N4–B1–N6	107.5(6)
N4–B1–H1A	111(4)
N6–B1–H1A	113(4)
N8–W2–P2	83.57(15)
N8–W2–N10	86.2(2)
N8–W2–N12	77.0(2)
N8–W2–C34	161.3(2)
N10–W2–P2	86.33(15)
N12–W2–P2	156.34(15)
N12–W2–N10	79.11(19)
N12–W2–C34	118.4(2)
N14–W2–P2	89.11(18)
N14–W2–N8	87.6(2)
N14–W2–N10	172.7(2)
N14–W2–N12	103.3(2)
N14–W2–C34	98.2(2)
N14–W2–C35	96.5(2)
C34–W2–P2	78.81(17)
C34–W2–N10	86.6(2)
C35–W2–P2	117.00(17)
C35–W2–N8	159.0(2)
C35–W2–N10	90.7(2)
C35–W2–N12	82.0(2)
C35–W2–C34	38.2(2)
O9–S2–O10	117.3(3)
O9–S2–C38	110.0(3)
O9–S2–C45	108.3(4)
O10–S2–C38	109.1(3)
O10–S2–C45	107.3(4)
C38–S2–C45	104.0(3)
C46–P2–W2	119.7(3)
C47–P2–W2	114.2(3)
C47–P2–C46	103.4(3)
C48–P2–W2	115.0(3)

C48–P2–C46	99.6(3)
C48–P2–C47	102.4(4)
C43–O8–C44	115.5(5)
N9–N8–W2	122.9(4)
C25–N8–W2	130.1(5)
C25–N8–N9	106.9(6)
N8–N9–B2	118.3(6)
C27–N9–N8	109.2(7)
C27–N9–B2	131.1(7)
N11–N10–W2	120.2(4)
C28–N10–W2	134.1(4)
C28–N10–N11	105.7(5)
N10–N11–B2	120.7(5)
C30–N11–N10	109.9(6)
C30–N11–B2	128.8(6)
N13–N12–W2	120.2(5)
C31–N12–W2	134.1(5)
C31–N12–N13	105.7(6)
N12–N13–B2	121.0(7)
C33–N13–N12	109.2(7)
C33–N13–B2	129.7(8)
O6–N14–W2	174.4(5)
N8–C25–H25	125.0
N8–C25–C26	110.0(7)
C26–C25–H25	125.0
C25–C26–H26	127.4
C27–C26–C25	105.2(7)
C27–C26–H26	127.4
N9–C27–C26	108.6(7)
N9–C27–H27	125.7
C26–C27–H27	125.7
N10–C28–H28	124.3
N10–C28–C29	111.5(6)
C29–C28–H28	124.3
C28–C29–H29	127.9
C30–C29–C28	104.3(7)
C30–C29–H29	127.9
N11–C30–C29	108.7(6)
N11–C30–H30	125.6

C29–C30–H30	125.6
N12–C31–H31	124.3
N12–C31–C32	111.5(6)
C32–C31–H31	124.3
C31–C32–H32	127.7
C33–C32–C31	104.6(6)
C33–C32–H32	127.7
N13–C33–C32	109.1(7)
N13–C33–H33	125.5
C32–C33–H33	125.5
W2–C34–H34	115.1
C35–C34–W2	69.8(3)
C35–C34–H34	115.1
C39–C34–W2	116.0(4)
C39–C34–H34	115.1
C39–C34–C35	118.3(6)
W2–C35–H35	111.4
C34–C35–W2	72.0(3)
C34–C35–H35	111.4
C34–C35–C36	118.5(6)
C36–C35–W2	126.5(5)
C36–C35–H35	111.4
C35–C36–H36	106.5
C35–C36–C37	112.4(7)
C35–C36–C40	110.8(7)
C37–C36–H36	106.5
C37–C36–C40	113.6(7)
C40–C36–H36	106.5
C36–C37–H37A	109.1
C36–C37–H37B	109.1
H37A–C37–H37B	107.8
C38–C37–C36	112.4(6)
C38–C37–H37A	109.1
C38–C37–H37B	109.1
C37–C38–S2	118.2(5)
C39–C38–S2	118.6(5)
C39–C38–C37	123.1(6)
C34–C39–H39	118.6
C38–C39–C34	122.8(6)

C38–C39–H39	118.6
C41–C40–C36	113.3(6)
C41–C40–C42	108.5(6)
C42–C40–C36	112.0(6)
C43–C40–C36	107.3(6)
C43–C40–C41	107.9(5)
C43–C40–C42	107.6(5)
C40–C41–H41A	109.5
C40–C41–H41B	109.5
C40–C41–H41C	109.5
H41A–C41–H41B	109.5
H41A–C41–H41C	109.5
H41B–C41–H41C	109.5
C40–C42–H42A	109.5
C40–C42–H42B	109.5
C40–C42–H42C	109.5
H42A–C42–H42B	109.5
H42A–C42–H42C	109.5
H42B–C42–H42C	109.5
O7–C43–O8	122.6(6)
O7–C43–C40	126.6(6)
O8–C43–C40	110.8(5)
O8–C44–H44A	109.5
O8–C44–H44B	109.5
O8–C44–H44C	109.5
H44A–C44–H44B	109.5
H44A–C44–H44C	109.5
H44B–C44–H44C	109.5
S2–C45–H45A	109.5
S2–C45–H45B	109.5
S2–C45–H45C	109.5
H45A–C45–H45B	109.5
H45A–C45–H45C	109.5
H45B–C45–H45C	109.5
P2–C46–H46A	109.5
P2–C46–H46B	109.5
P2–C46–H46C	109.5
H46A–C46–H46B	109.5
H46A–C46–H46C	109.5

H46B–C46–H46C	109.5
P2–C47–H47A	109.5
P2–C47–H47B	109.5
P2–C47–H47C	109.5
H47A–C47–H47B	109.5
H47A–C47–H47C	109.5
H47B–C47–H47C	109.5
P2–C48–H48A	109.5
P2–C48–H48B	109.5
P2–C48–H48C	109.5
H48A–C48–H48B	109.5
H48A–C48–H48C	109.5
H48B–C48–H48C	109.5
N9–B2–N11	110.1(6)
N9–B2–N13	106.9(7)
N9–B2–H2A	110(4)
N11–B2–H2A	108(4)
N13–B2–N11	108.7(7)
N13–B2–H2A	114(4)
H49A–C49–H49B	109.5
H49A–C49–H49C	109.5
H49B–C49–H49C	109.5
C50–C49–H49A	109.5
C50–C49–H49B	109.5
C50–C49–H49C	109.5
O11–C50–C49	120.5(10)
O11–C50–C51	122.1(10)
C51–C50–C49	117.4(8)
C50–C51–H51A	109.5
C50–C51–H51B	109.5
C50–C51–H51C	109.5
H51A–C51–H51B	109.5
H51A–C51–H51C	109.5
H51B–C51–H51C	109.5
H52A–C52–H52B	109.5
H52A–C52–H52C	109.5
H52B–C52–H52C	109.5
C53–C52–H52A	109.5
C53–C52–H52B	109.5

C53–C52–H52C	109.5
O54–C53–C52	124(2)
O54–C53–C54	116(3)
C54–C53–C52	120(2)
C53–C54–H54A	109.5
C53–C54–H54B	109.5
C53–C54–H54C	109.5
H54A–C54–H54B	109.5
H54A–C54–H54C	109.5
H54B–C54–H54C	109.5
O54A–C12A–C52A	121(2)
O54A–C12A–C53A	125(3)
C53A–C12A–C52A	115(2)
C12A–C52A–H52D	109.5
C12A–C52A–H52E	109.5
C12A–C52A–H52F	109.5
H52D–C52A–H52E	109.5
H52D–C52A–H52F	109.5
H52E–C52A–H52F	109.5
C12A–C53A–H53A	109.5
C12A–C53A–H53B	109.5
C12A–C53A–H53C	109.5
H53A–C53A–H53B	109.5
H53A–C53A–H53C	109.5

H53B–C53A–H53C	109.5

Table 5 Torsion angles for **Compound 5.3** **Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	177.7(4)
W1–N1–N2–B1	14.9(8)
W1–N1–C1–C2	−177.8(5)
W1–N3–N4–C6	175.0(4)
W1–N3–N4–B1	−12.6(7)
W1–N3–C4–C5	−172.6(5)
W1–N5–N6–C9	−176.0(5)
W1–N5–N6–B1	0.3(10)
W1–N5–C7–C8	175.1(5)
W1–C10–C11–C12	−123.2(6)
W1–C10–C15–C14	76.0(7)
W1–C11–C12–C13	−55.4(9)
W1–C11–C12–C16	176.5(5)
S1–C14–C15–C10	−179.2(5)
O4–S1–C14–C13	40.4(6)
O4–S1–C14–C15	−142.4(5)
O5–S1–C14–C13	170.5(5)
O5–S1–C14–C15	−12.3(7)
N1–N2–C3–C2	0.4(8)
N1–N2–B1–N4	−65.4(8)
N1–N2–B1–N6	50.1(8)
N1–C1–C2–C3	0.1(8)
N2–N1–C1–C2	0.2(8)
N3–N4–C6–C5	−1.4(8)
N3–N4–B1–N2	64.8(8)
N3–N4–B1–N6	−49.6(8)
N3–C4–C5–C6	−2.1(8)
N4–N3–C4–C5	1.3(7)
N5–N6–C9–C8	0.2(9)
N5–N6–B1–N2	−59.5(9)

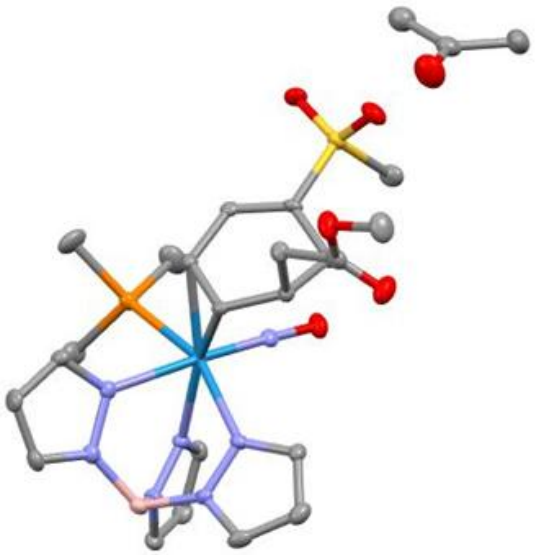
N5–N6–B1–N4	57.4(9)
N5–C7–C8–C9	0.0(8)
N6–N5–C7–C8	0.1(8)
C1–N1–N2–C3	−0.3(8)
C1–N1–N2–B1	−163.2(6)
C1–C2–C3–N2	−0.3(8)
C3–N2–B1–N4	136.1(7)
C3–N2–B1–N6	−108.4(8)
C4–N3–N4–C6	0.1(7)
C4–N3–N4–B1	172.4(6)
C4–C5–C6–N4	2.1(8)
C6–N4–B1–N2	−124.4(7)
C6–N4–B1–N6	121.2(7)
C7–N5–N6–C9	−0.2(8)
C7–N5–N6–B1	176.1(7)
C7–C8–C9–N6	−0.2(8)
C9–N6–B1–N2	116.2(9)
C9–N6–B1–N4	−127.0(8)
C10–C11–C12–C13	34.7(10)
C10–C11–C12–C16	−93.4(8)
C11–C10–C15–C14	−2.3(9)
C11–C12–C13–C14	−37.1(9)
C11–C12–C16–C17	61.7(9)
C11–C12–C16–C18	−173.5(6)
C11–C12–C16–C19	−58.4(8)
C12–C13–C14–S1	−160.1(6)
C12–C13–C14–C15	22.8(9)
C12–C16–C19–O2	124.5(8)
C12–C16–C19–O3	−55.2(7)
C13–C12–C16–C17	−65.8(9)
C13–C12–C16–C18	59.0(9)
C13–C12–C16–C19	174.1(6)
C13–C14–C15–C10	−2.2(10)
C15–C10–C11–W1	108.1(5)
C15–C10–C11–C12	−15.1(9)
C16–C12–C13–C14	89.2(8)
C17–C16–C19–O2	1.5(9)
C17–C16–C19–O3	−178.2(5)
C18–C16–C19–O2	−116.6(7)

C18–C16–C19–O3	63.7(6)
C20–O3–C19–O2	−2.4(9)
C20–O3–C19–C16	177.4(5)
C21–S1–C14–C13	−73.4(6)
C21–S1–C14–C15	103.8(6)
B1–N2–C3–C2	160.5(7)
B1–N4–C6–C5	−173.0(6)
B1–N6–C9–C8	−175.9(8)
W2–N8–N9–C27	−177.5(5)
W2–N8–N9–B2	14.4(9)
W2–N8–C25–C26	177.1(5)
W2–N10–N11–C30	178.3(5)
W2–N10–N11–B2	−10.5(8)
W2–N10–C28–C29	−177.1(5)
W2–N12–N13–C33	178.8(5)
W2–N12–N13–B2	1.5(10)
W2–N12–C31–C32	−178.9(5)
W2–C34–C35–C36	−122.4(6)
W2–C34–C39–C38	75.3(8)
W2–C35–C36–C37	−53.0(9)
W2–C35–C36–C40	178.8(4)
S2–C38–C39–C34	−177.4(5)
O9–S2–C38–C37	−176.7(5)
O9–S2–C38–C39	−1.7(7)
O10–S2–C38–C37	53.3(7)
O10–S2–C38–C39	−131.6(6)
N8–N9–C27–C26	0.2(8)
N8–N9–B2–N11	−66.4(8)
N8–N9–B2–N13	51.5(9)
N8–C25–C26–C27	0.3(8)
N9–N8–C25–C26	−0.2(8)
N10–N11–C30–C29	−0.7(8)
N10–N11–B2–N9	64.5(8)
N10–N11–B2–N13	−52.3(9)
N10–C28–C29–C30	−1.8(9)
N11–N10–C28–C29	1.4(8)
N12–N13–C33–C32	0.7(9)
N12–N13–B2–N9	−61.0(10)
N12–N13–B2–N11	57.9(10)

N12–C31–C32–C33	−0.6(8)
N13–N12–C31–C32	1.0(8)
C25–N8–N9–C27	0.0(8)
C25–N8–N9–B2	−168.1(6)
C25–C26–C27–N9	−0.3(8)
C27–N9–B2–N11	128.6(8)
C27–N9–B2–N13	−113.6(9)
C28–N10–N11–C30	−0.5(8)
C28–N10–N11–B2	170.8(6)
C28–C29–C30–N11	1.5(9)
C30–N11–B2–N9	−126.1(8)
C30–N11–B2–N13	117.1(8)
C31–N12–N13–C33	−1.0(9)
C31–N12–N13–B2	−178.3(7)
C31–C32–C33–N13	−0.1(8)
C33–N13–B2–N9	122.4(9)
C33–N13–B2–N11	−118.8(9)
C34–C35–C36–C37	35.0(10)
C34–C35–C36–C40	−93.2(8)
C35–C34–C39–C38	−4.6(10)
C35–C36–C37–C38	−39.7(9)
C35–C36–C40–C41	55.6(8)
C35–C36–C40–C42	178.8(6)
C35–C36–C40–C43	−63.4(8)
C36–C37–C38–S2	−159.6(6)
C36–C37–C38–C39	25.6(10)
C36–C40–C43–O7	119.7(8)
C36–C40–C43–O8	−61.4(7)
C37–C36–C40–C41	−71.9(8)
C37–C36–C40–C42	51.2(9)
C37–C36–C40–C43	169.1(6)
C37–C38–C39–C34	−2.7(11)
C39–C34–C35–W2	109.4(6)
C39–C34–C35–C36	−12.9(9)
C40–C36–C37–C38	87.0(8)
C41–C40–C43–O7	−2.7(9)
C41–C40–C43–O8	176.2(5)
C42–C40–C43–O7	−119.6(7)
C42–C40–C43–O8	59.3(7)

C44–O8–C43–O7	−3.1(9)
C44–O8–C43–C40	177.9(6)
C45–S2–C38–C37	−60.9(7)
C45–S2–C38–C39	114.2(7)
B2–N9–C27–C26	166.2(8)
B2–N11–C30–C29	−171.0(7)
B2–N13–C33–C32	177.7(8)

Crystal Structure Report for Compound 5.2



A colorless, block-like specimen of $C_{25}H_{39}BN_7O_6PSW$, approximate dimensions 0.051 mm x 0.060 mm x 0.147 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 3.60 hours. The frames were integrated with the Bruker SAINT software package[131] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 40643 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 6926 were independent (average redundancy 5.868, completeness = 99.9%, R_{int} = 8.45%, R_{sig} = 6.17%) and 5383 (77.72%) were greater than 2σ(F^2). The final cell constants of a = 14.2707(7) Å, b = 15.3139(7) Å, c = 15.7164(9) Å, β = 113.803(2)°, volume = 3142.5(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 5809 reflections above 20 σ(I) with 5.320° < 2θ < 53.31°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[132] The ratio of minimum to maximum apparent transmission was 0.848. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6020 and 0.8280.

The structure was solved and refined using the Bruker SHELXTL Software Package[133] within APEX4 [1] and OLEX2,[134] using the space group P $2_1/n$, with Z = 4 for the formula unit, $C_{25}H_{39}BN_7O_6PSW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.2U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 397 variables converged at R1 = 3.40%, for the observed data and wR2 = 7.21% for all data. The goodness-of-fit was 1.016. The largest peak in the final difference electron density synthesis was 1.184 $e^-/Å^3$ and the largest hole was -0.726 $e^-/Å^3$ with an RMS deviation of 0.159 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.673 g/cm^3 and F(000), 1584 e^-.

Table 1. Sample and crystal data for Compound 5.2

Chemical formula	$C_{25}H_{39}BN_7O_6PSW$
Formula weight	791.32 g/mol

[131] Bruker (2019). Saint; APEX4. Bruker AXS Inc., Madison, Wisconsin, USA.
[132] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985
[133] Sheldrick, G. M. (2015). Acta Cryst. A**71**, 3-8.
[134] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.051 x 0.060 x 0.147 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 2_1/n
Unit cell dimensions	a = 14.2707(7) Å α = 90°
	b = 15.3139(7) Å β = 113.803(2)°
	c = 15.7164(9) Å γ = 90°
Volume	3142.5(3) $Å^3$
Z	4
Density (calculated)	1.673 g/cm^3
Absorption coefficient	3.843 mm^{-1}
F(000)	1584

Table 2. Data collection and structure refinement for Compound 5.2

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.94 to 27.10°
Index ranges	-18<=h<=18, -19<=k<=19, -20<=l<=20

Reflections collected	40643	
Independent reflections	6926 [R(int) = 0.0845]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8280 and 0.6020	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6926 / 0 / 397	
Goodness-of-fit on F^2	1.016	
Final R indices	5383 data; $I>2\sigma(I)$	R1 = 0.0340, wR2 = 0.0655
	all data	R1 = 0.0548, wR2 = 0.0721
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0284P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.184 and -0.726 eÅ^{-3}	

R.M.S. deviation from mean	0.159 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 5.2

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.62178(2)	0.26083(2)	0.36454(2)	0.01170(6)
S1	0.45660(9)	0.57962(7)	0.28531(9)	0.0184(3)
P1	0.44164(9)	0.20530(7)	0.29700(9)	0.0164(3)
O1	0.5863(3)	0.37128(19)	0.1965(2)	0.0222(8)
O2	0.4959(3)	0.66112(19)	0.3336(3)	0.0269(8)
O3	0.3494(2)	0.5605(2)	0.2597(2)	0.0221(8)
O4	0.7977(3)	0.6189(2)	0.6542(2)	0.0270(8)
O5	0.8463(3)	0.5909(2)	0.5381(3)	0.0306(9)
N1	0.6495(3)	0.1669(2)	0.4829(3)	0.0145(8)
N2	0.7154(3)	0.0986(2)	0.4976(3)	0.0169(8)
N3	0.6490(3)	0.1461(2)	0.2932(3)	0.0154(8)
N4	0.7160(3)	0.0807(2)	0.3385(3)	0.0172(9)
N5	0.7906(3)	0.2532(2)	0.4159(3)	0.0154(8)
N6	0.8431(3)	0.1779(2)	0.4529(3)	0.0154(8)
N7	0.6007(3)	0.3275(2)	0.2668(3)	0.0154(8)

	x/a	y/b	z/c	U(eq)
C1	0.6115(3)	0.1608(3)	0.5479(3)	0.0173(10)
C2	0.6524(4)	0.0894(3)	0.6037(3)	0.0213(11)
C3	0.7177(4)	0.0524(3)	0.5703(3)	0.0208(11)
C4	0.6152(4)	0.1286(3)	0.2030(3)	0.0175(10)
C5	0.6583(4)	0.0521(3)	0.1879(4)	0.0221(11)
C6	0.7223(4)	0.0247(3)	0.2757(4)	0.0217(11)
C7	0.8611(3)	0.3120(3)	0.4176(3)	0.0170(10)
C8	0.9596(4)	0.2759(3)	0.4573(4)	0.0236(11)
C9	0.9436(4)	0.1918(3)	0.4774(3)	0.0209(11)
C10	0.5482(4)	0.3538(3)	0.4302(3)	0.0155(10)
C11	0.6585(3)	0.3626(3)	0.4699(3)	0.0114(9)
C12	0.7050(3)	0.4516(3)	0.4681(3)	0.0156(10)
C13	0.6461(3)	0.5010(3)	0.3781(3)	0.0162(10)
C14	0.5325(3)	0.4942(3)	0.3509(3)	0.0154(10)
C15	0.4884(3)	0.4253(3)	0.3722(3)	0.0135(9)
C16	0.4799(4)	0.5793(3)	0.1832(4)	0.0255(12)
C17	0.7098(4)	0.5065(3)	0.5516(3)	0.0167(10)
C18	0.7916(4)	0.5752(3)	0.5785(3)	0.0197(11)
C19	0.8730(4)	0.6887(3)	0.6839(4)	0.0312(13)
C20	0.4278(4)	0.0885(3)	0.2701(4)	0.0341(14)
C21	0.3637(4)	0.2121(3)	0.3626(4)	0.0333(14)
C22	0.3628(4)	0.2563(3)	0.1874(4)	0.0368(14)
B1	0.7832(4)	0.0912(3)	0.4428(4)	0.0184(12)

	x/a	y/b	z/c	U(eq)
O6	0.2773(3)	0.6540(2)	0.0052(3)	0.0432(11)
C23	0.2352(4)	0.7358(3)	0.8665(4)	0.0385(14)
C24	0.2144(4)	0.6714(3)	0.9279(4)	0.0283(12)
C25	0.1120(4)	0.6282(3)	0.8898(4)	0.0342(14)

Table 4. Bond lengths (Å) for Compound 5.2

W1-N7	1.766(4)	W1-C11	2.179(4)
W1-N3	2.201(3)	W1-N5	2.214(4)
W1-C10	2.252(4)	W1-N1	2.257(4)
W1-P1	2.5011(12)	S1-O3	1.446(3)
S1-O2	1.450(3)	S1-C14	1.745(4)
S1-C16	1.765(5)	P1-C21	1.799(5)
P1-C22	1.810(5)	P1-C20	1.831(5)
O1-N7	1.237(5)	O4-C18	1.338(6)
O4-C19	1.453(5)	O5-C18	1.212(5)
N1-C1	1.338(6)	N1-N2	1.362(5)
N2-C3	1.332(6)	N2-B1	1.537(6)
N3-C4	1.327(6)	N3-N4	1.370(5)
N4-C6	1.339(6)	N4-B1	1.537(7)
N5-C7	1.343(5)	N5-N6	1.371(5)
N6-C9	1.343(6)	N6-B1	1.552(6)
C1-C2	1.377(6)	C1-H1	0.950000

C2-C3	1.365(6)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.388(6)
C4-H4	0.950000	C5-C6	1.377(7)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.401(6)	C7-H7	0.950000
C8-C9	1.367(6)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.446(6)
C10-C15	1.459(6)	C10-H10	1.01(4)
C11-C12	1.521(6)	C11-H11	1.09(5)
C12-C13	1.523(6)	C12-C17	1.537(6)
C12-H12	1.000000	C13-C14	1.505(6)
C13-H13A	0.990000	C13-H13B	0.990000
C14-C15	1.338(6)	C15-H15	0.950000
C16-H16A	0.980000	C16-H16B	0.980000
C16-H16C	0.980000	C17-C18	1.499(6)
C17-H17A	0.990000	C17-H17B	0.990000
C19-H19A	0.980000	C19-H19B	0.980000
C19-H19C	0.980000	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
B1-H1A	0.98(5)	O6-C24	1.213(6)
C23-C24	1.492(7)	C23-H23A	0.980000

C23-H23B	0.980000	C23-H23C	0.980000
C24-C25	1.492(7)	C25-H25A	0.980000
C25-H25B	0.980000	C25-H25C	0.980000

Table 5. Bond angles (°) for Compound 5.2

N7-W1-C11	98.73(16)	N7-W1-N3	91.22(15)
C11-W1-N3	157.02(15)	N7-W1-N5	97.24(15)
C11-W1-N5	82.44(14)	N3-W1-N5	75.76(13)
N7-W1-C10	94.94(16)	C11-W1-C10	38.06(16)
N3-W1-C10	161.59(15)	N5-W1-C10	120.44(15)
N7-W1-N1	175.65(14)	C11-W1-N1	85.47(15)
N3-W1-N1	84.45(14)	N5-W1-N1	82.11(13)
C10-W1-N1	89.08(15)	N7-W1-P1	92.43(12)
C11-W1-P1	117.14(11)	N3-W1-P1	82.81(10)
N5-W1-P1	156.60(9)	C10-W1-P1	79.62(12)
N1-W1-P1	86.63(10)	O3-S1-O2	117.5(2)
O3-S1-C14	110.3(2)	O2-S1-C14	108.7(2)
O3-S1-C16	108.2(2)	O2-S1-C16	107.6(2)
C14-S1-C16	103.6(2)	C21-P1-C22	103.3(3)
C21-P1-C20	98.9(2)	C22-P1-C20	103.5(3)
C21-P1-W1	120.28(18)	C22-P1-W1	113.24(18)
C20-P1-W1	115.28(17)	C18-O4-C19	115.3(4)
C1-N1-N2	106.4(4)	C1-N1-W1	133.0(3)

N2-N1-W1	120.5(3)	C3-N2-N1	109.2(4)
C3-N2-B1	129.6(4)	N1-N2-B1	120.6(4)
C4-N3-N4	106.6(3)	C4-N3-W1	130.0(3)
N4-N3-W1	123.2(3)	C6-N4-N3	109.0(4)
C6-N4-B1	130.9(4)	N3-N4-B1	118.9(4)
C7-N5-N6	106.2(3)	C7-N5-W1	131.9(3)
N6-N5-W1	121.8(3)	C9-N6-N5	109.0(4)
C9-N6-B1	130.2(4)	N5-N6-B1	119.4(4)
O1-N7-W1	177.5(3)	N1-C1-C2	110.1(4)
N1-C1-H1	125.000000	C2-C1-H1	125.000000
C3-C2-C1	105.3(4)	C3-C2-H2	127.300000
C1-C2-H2	127.300000	N2-C3-C2	109.0(4)
N2-C3-H3	125.500000	C2-C3-H3	125.500000
N3-C4-C5	111.0(4)	N3-C4-H4	124.500000
C5-C4-H4	124.500000	C6-C5-C4	104.3(4)
C6-C5-H5	127.900000	C4-C5-H5	127.900000
N4-C6-C5	109.2(4)	N4-C6-H6	125.400000
C5-C6-H6	125.400000	N5-C7-C8	110.6(4)
N5-C7-H7	124.700000	C8-C7-H7	124.700000
C9-C8-C7	104.1(4)	C9-C8-H8	127.900000
C7-C8-H8	127.900000	N6-C9-C8	110.0(4)
N6-C9-H9	125.000000	C8-C9-H9	125.000000
C11-C10-C15	117.3(4)	C11-C10-W1	68.2(2)
C15-C10-W1	116.8(3)	C11-C10-H10	116.(2)

C15-C10-H10	117.(2)	W1-C10-H10	112.(2)
C10-C11-C12	118.9(4)	C10-C11-W1	73.7(3)
C12-C11-W1	126.8(3)	C10-C11-H11	112.(2)
C12-C11-H11	111.(2)	W1-C11-H11	108.(2)
C11-C12-C13	112.4(4)	C11-C12-C17	110.1(4)
C13-C12-C17	109.8(3)	C11-C12-H12	108.100000
C13-C12-H12	108.100000	C17-C12-H12	108.100000
C14-C13-C12	110.9(4)	C14-C13-H13A	109.500000
C12-C13-H13A	109.500000	C14-C13-H13B	109.500000
C12-C13-H13B	109.500000	H13A-C13-H13B	108.000000
C15-C14-C13	123.0(4)	C15-C14-S1	119.8(3)
C13-C14-S1	117.1(3)	C14-C15-C10	122.2(4)
C14-C15-H15	118.900000	C10-C15-H15	118.900000
S1-C16-H16A	109.500000	S1-C16-H16B	109.500000
H16A-C16-H16B	109.500000	S1-C16-H16C	109.500000
H16A-C16-H16C	109.500000	H16B-C16-H16C	109.500000
C18-C17-C12	112.7(4)	C18-C17-H17A	109.100000
C12-C17-H17A	109.100000	C18-C17-H17B	109.100000
C12-C17-H17B	109.100000	H17A-C17-H17B	107.800000

O5-C18-O4	122.8(4)	O5-C18-C17	125.7(4)
O4-C18-C17	111.5(4)	O4-C19-H19A	109.500000
O4-C19-H19B	109.500000	H19A-C19-H19B	109.500000
O4-C19-H19C	109.500000	H19A-C19-H19C	109.500000
H19B-C19-H19C	109.500000	P1-C20-H20A	109.500000
P1-C20-H20B	109.500000	H20A-C20-H20B	109.500000
P1-C20-H20C	109.500000	H20A-C20-H20C	109.500000
H20B-C20-H20C	109.500000	P1-C21-H21A	109.500000
P1-C21-H21B	109.500000	H21A-C21-H21B	109.500000
P1-C21-H21C	109.500000	H21A-C21-H21C	109.500000
H21B-C21-H21C	109.500000	P1-C22-H22A	109.500000
P1-C22-H22B	109.500000	H22A-C22-H22B	109.500000
P1-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	N4-B1-N2	110.0(4)
N4-B1-N6	106.2(4)	N2-B1-N6	109.0(4)
N4-B1-H1A	112.(3)	N2-B1-H1A	110.(3)

N6-B1-H1A	110.(3)	C24-C23-H23A	109.500000
C24-C23-H23B	109.500000	H23A-C23-H23B	109.500000
C24-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	O6-C24-C23	122.2(5)
O6-C24-C25	120.9(5)	C23-C24-C25	116.9(5)
C24-C25-H25A	109.500000	C24-C25-H25B	109.500000
H25A-C25-H25B	109.500000	C24-C25-H25C	109.500000
H25A-C25-H25C	109.500000	H25B-C25-H25C	109.500000

Table 6. Torsion angles (°) for Compound 5.2 .

C1-N1-N2-C3	-0.4(5)	W1-N1-N2-C3	-179.3(3)
C1-N1-N2-B1	-172.6(4)	W1-N1-N2-B1	8.5(5)
C4-N3-N4-C6	0.2(5)	W1-N3-N4-C6	-174.5(3)
C4-N3-N4-B1	168.9(4)	W1-N3-N4-B1	-5.9(5)
C7-N5-N6-C9	0.8(5)	W1-N5-N6-C9	179.5(3)
C7-N5-N6-B1	-167.4(4)	W1-N5-N6-B1	11.3(5)
N2-N1-C1-C2	-0.1(5)	W1-N1-C1-C2	178.7(3)

N1-C1-C2-C3	0.4(6)	N1-N2-C3-C2	0.7(5)
B1-N2-C3-C2	172.0(5)	C1-C2-C3-N2	-0.7(5)
N4-N3-C4-C5	0.4(5)	W1-N3-C4-C5	174.7(3)
N3-C4-C5-C6	-0.8(5)	N3-N4-C6-C5	-0.7(5)
B1-N4-C6-C5	-167.6(4)	C4-C5-C6-N4	1.0(5)
N6-N5-C7-C8	-1.2(5)	W1-N5-C7-C8	-179.7(3)
N5-C7-C8-C9	1.2(5)	N5-N6-C9-C8	-0.1(5)
B1-N6-C9-C8	166.5(5)	C7-C8-C9-N6	-0.6(5)
C15-C10-C11-C12	13.6(6)	W1-C10-C11-C12	123.5(4)
C15-C10-C11-W1	-109.9(4)	C10-C11-C12-C13	-38.4(6)
W1-C11-C12-C13	52.3(5)	C10-C11-C12-C17	84.4(5)
W1-C11-C12-C17	175.1(3)	C11-C12-C13-C14	44.0(5)
C17-C12-C13-C14	-78.9(4)	C12-C13-C14-C15	-29.8(6)
C12-C13-C14-S1	152.3(3)	O3-S1-C14-C15	-1.8(5)
O2-S1-C14-C15	128.3(4)	C16-S1-C14-C15	-117.4(4)
O3-S1-C14-C13	176.1(3)	O2-S1-C14-C13	-53.7(4)
C16-S1-C14-C13	60.5(4)	C13-C14-C15-C10	5.0(7)

S1-C14-C15-C10	-177.2(3)	C11-C10-C15-C14	4.2(7)
W1-C10-C15-C14	-73.9(5)	C11-C12-C17-C18	155.2(4)
C13-C12-C17-C18	-80.5(5)	C19-O4-C18-O5	1.6(7)
C19-O4-C18-C17	-178.2(4)	C12-C17-C18-O5	3.5(7)
C12-C17-C18-O4	-176.7(4)	C6-N4-B1-N2	-132.7(5)
N3-N4-B1-N2	61.5(5)	C6-N4-B1-N6	109.5(5)
N3-N4-B1-N6	-56.3(5)	C3-N2-B1-N4	126.4(5)
N1-N2-B1-N4	-63.1(5)	C3-N2-B1-N6	-117.5(5)
N1-N2-B1-N6	52.9(6)	C9-N6-B1-N4	-112.2(5)
N5-N6-B1-N4	53.2(5)	C9-N6-B1-N2	129.3(5)
N5-N6-B1-N2	-65.3(5)		

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for Compound 5.2

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01227(9)	0.01046(9)	0.01207(10)	0.00044(8)	0.00460(7)	-0.00004(7)
S1	0.0188(6)	0.0154(5)	0.0197(7)	0.0038(5)	0.0065(5)	0.0035(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	0.0143(6)	0.0148(5)	0.0183(7)	-0.0005(5)	0.0045(5)	-0.0007(4)
O1	0.033(2)	0.0182(16)	0.017(2)	0.0001(14)	0.0113(17)	-0.0029(14)
O2	0.031(2)	0.0166(16)	0.028(2)	0.0019(15)	0.0073(18)	0.0042(14)
O3	0.0155(18)	0.0253(17)	0.024(2)	0.0049(15)	0.0060(16)	0.0060(13)
O4	0.038(2)	0.0212(17)	0.023(2)	-0.0066(15)	0.0136(18)	-0.0104(15)
O5	0.031(2)	0.0319(19)	0.034(2)	-0.0104(17)	0.019(2)	-0.0131(16)
N1	0.013(2)	0.0145(18)	0.015(2)	-0.0019(15)	0.0048(18)	-0.0029(14)
N2	0.017(2)	0.0157(18)	0.017(2)	0.0005(16)	0.0062(18)	-0.0010(15)
N3	0.015(2)	0.0126(18)	0.020(2)	-0.0009(16)	0.0086(19)	0.0012(15)
N4	0.018(2)	0.0145(18)	0.021(2)	-0.0001(16)	0.0094(19)	0.0007(15)
N5	0.0157(19)	0.0130(19)	0.019(2)	0.0000(16)	0.0084(16)	0.0028(14)
N6	0.014(2)	0.0178(18)	0.015(2)	0.0032(16)	0.0070(18)	0.0037(15)
N7	0.018(2)	0.0117(17)	0.018(2)	-0.0031(16)	0.0081(18)	-0.0015(14)
C1	0.016(2)	0.020(2)	0.018(3)	-0.0004(19)	0.009(2)	0.0023(18)
C2	0.027(3)	0.023(2)	0.017(3)	0.005(2)	0.013(2)	0.000(2)
C3	0.023(3)	0.016(2)	0.022(3)	0.006(2)	0.008(2)	0.0003(19)
C4	0.019(3)	0.016(2)	0.016(3)	0.0012(19)	0.006(2)	-0.0019(18)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C5	0.029(3)	0.021(2)	0.021(3)	-0.006(2)	0.015(2)	-0.004(2)
C6	0.026(3)	0.013(2)	0.031(3)	-0.002(2)	0.017(3)	-0.0009(19)
C7	0.019(3)	0.014(2)	0.021(3)	-0.0030(19)	0.012(2)	-0.0012(18)
C8	0.020(3)	0.028(3)	0.026(3)	-0.007(2)	0.013(2)	-0.005(2)
C9	0.013(2)	0.030(3)	0.018(3)	-0.004(2)	0.004(2)	0.0036(19)
C10	0.018(2)	0.012(2)	0.021(3)	-0.0002(19)	0.012(2)	0.0014(17)
C11	0.011(2)	0.014(2)	0.009(3)	0.0000(18)	0.004(2)	0.0031(16)
C12	0.016(2)	0.015(2)	0.016(3)	-0.0009(18)	0.008(2)	-0.0008(17)
C13	0.017(3)	0.014(2)	0.018(3)	-0.0004(18)	0.007(2)	-0.0009(16)
C14	0.014(2)	0.014(2)	0.017(3)	0.0012(18)	0.005(2)	0.0060(17)
C15	0.014(2)	0.014(2)	0.013(3)	-0.0030(18)	0.007(2)	0.0015(17)
C16	0.026(3)	0.029(3)	0.019(3)	0.007(2)	0.007(2)	0.008(2)
C17	0.020(3)	0.017(2)	0.012(3)	-0.0033(18)	0.006(2)	-0.0031(18)
C18	0.021(3)	0.018(2)	0.016(3)	0.002(2)	0.003(2)	0.0022(19)
C19	0.036(3)	0.026(3)	0.027(3)	-0.008(2)	0.008(3)	-0.012(2)
C20	0.024(3)	0.020(2)	0.062(4)	-0.005(3)	0.020(3)	-0.007(2)
C21	0.016(3)	0.042(3)	0.044(4)	-0.011(3)	0.015(3)	-0.008(2)
C22	0.026(3)	0.032(3)	0.037(3)	0.006(3)	-0.003(2)	0.000(2)

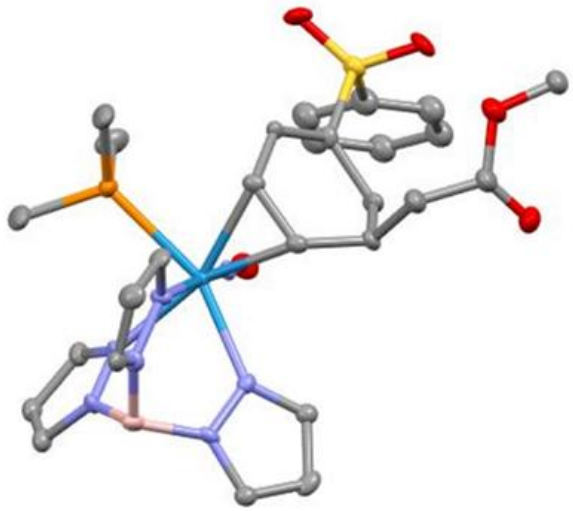
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.017(3)	0.014(2)	0.023(3)	0.002(2)	0.008(3)	0.003(2)
O6	0.038(3)	0.043(2)	0.034(3)	0.0057(19)	-0.001(2)	-0.0019(18)
C23	0.038(3)	0.027(3)	0.057(4)	0.013(3)	0.026(3)	0.006(2)
C24	0.028(3)	0.021(3)	0.035(4)	0.000(2)	0.012(3)	0.006(2)
C25	0.032(3)	0.032(3)	0.039(4)	0.002(2)	0.014(3)	0.004(2)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for Compound 5.2

	x/a	y/b	z/c	U(eq)
H1	0.5633	0.2001	0.5545	0.021000
H2	0.6381	0.0699	0.6547	0.026000
H3	0.7583	0.0019	0.5949	0.025000
H4	0.5678	0.1638	0.1552	0.021000
H5	0.6464	0.0248	0.1302	0.027000
H6	0.7643	-0.0260	0.2895	0.026000
H7	0.8463	0.3701	0.3949	0.020000
H8	1.0229	0.3035	0.4677	0.028000
H9	0.9959	0.1495	0.5048	0.025000
H10	0.518(3)	0.323(3)	0.470(3)	0.010(11)
H11	0.694(3)	0.332(3)	0.538(3)	0.017(12)
H12	0.7766	0.4425	0.4736	0.019000

	x/a	y/b	z/c	U(eq)
H13A	0.6667	0.5632	0.3863	0.019000
H13B	0.6633	0.4767	0.3278	0.019000
H15	0.4158	0.4228	0.3487	0.016000
H16A	0.4370	0.6236	0.1401	0.038000
H16B	0.4633	0.5217	0.1538	0.038000
H16C	0.5522	0.5925	0.1991	0.038000
H17A	0.6426	0.5350	0.5361	0.020000
H17B	0.7228	0.4675	0.6054	0.020000
H19A	0.8556	0.7327	0.6346	0.047000
H19B	0.9410	0.6647	0.6967	0.047000
H19C	0.8732	0.7158	0.7405	0.047000
H20A	0.4779	0.0557	0.3222	0.051000
H20B	0.4396	0.0776	0.2138	0.051000
H20C	0.3584	0.0696	0.2599	0.051000
H21A	0.3502	0.2735	0.3710	0.050000
H21B	0.3998	0.1848	0.4236	0.050000
H21C	0.2988	0.1817	0.3290	0.050000
H22A	0.2921	0.2356	0.1671	0.055000
H22B	0.3891	0.2411	0.1406	0.055000
H22C	0.3646	0.3199	0.1954	0.055000
H1A	0.831(4)	0.043(3)	0.467(3)	0.022000
H23A	0.2833	0.7801	-0.0952	0.058000
H23B	0.1710	0.7639	-0.1741	0.058000

	x/a	y/b	z/c	U(eq)
H23C	0.2651	0.7056	-0.1716	0.058000
H25A	0.1089	0.5847	-0.0656	0.051000
H25B	0.1013	0.5993	-0.1691	0.051000
H25C	0.0585	0.6721	-0.1209	0.051000



Compound 5_79

Table 1 Crystal data and structure refinement for Compound 5_79.

Empirical formula	**$C_{27}H_{35}BN_7O_5PSW$**
Formula weight	**795.31**
Temperature/K	**100.00**
Crystal system	**monoclinic**
Space group	**$P2_1/c$**
a/Å	**12.7699(7)**
b/Å	**15.4292(7)**
c/Å	**15.4711(7)**
α/°	**90**
β/°	**90.283(2)**
γ/°	**90**

Volume/Å^3	**3048.2(3)**
Z	**4**
ρ_{calc}g/cm^3	**1.733**
μ/mm^{-1}	**3.960**
F(000)	**1584.0**
Crystal size/mm^3	**0.05 × 0.035 × 0.023**
Radiation	**Mo Kα (λ = 0.71073)**
2Θ range for data collection/°	**4.14 to 51.472**
Index ranges	**-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18**
Reflections collected	**41294**
Independent reflections	**5807 [R_{int} = 0.1653, R_{sigma} = 0.1007]**
Data/restraints/parameters	**5807/0/317**
Goodness-of-fit on F^2	**1.002**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0444, wR_2 = 0.0778**
Final R indexes [all data]	**R_1 = 0.0880, wR_2 = 0.0920**
Largest diff. peak/hole / e Å^{-3}	**1.39/-1.02**

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_79. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	5732.3(2)	2194.1(2)	3306.6(2)	14.24(9)
S1	9892.2(16)	2384.1(12)	3851.0(12)	21.1(5)
P1	6331.5(17)	911.8(12)	2451.6(13)	21.6(5)
O1	6833(4)	1563(3)	4900(3)	24.8(13)
O2	10163(4)	1669(3)	3288(3)	26.7(13)
O3	10538(4)	3150(3)	3847(3)	27.5(13)
O4	9594(4)	4979(3)	3276(4)	31.7(14)
O5	8556(5)	5476(4)	4334(4)	40.6(17)
N00D	6402(5)	1836(3)	4238(4)	15.4(14)
N1	4630(5)	3078(3)	3964(4)	16.9(14)
N2	3582(5)	3077(3)	3770(4)	16.1(14)
N3	4395(5)	1334(3)	3605(4)	16.3(10)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_79. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N4	3386(5)	1544(4)	3397(4)	16.3(10)
N5	4767(5)	2612(3)	2156(4)	16.1(14)
N6	3702(5)	2636(4)	2222(4)	17.9(14)
C1	4735(6)	3623(4)	4635(5)	18.0(12)
C2	3793(6)	3966(4)	4876(5)	22.2(19)
C3	3073(6)	3606(4)	4320(5)	18.0(12)
C4	4356(7)	578(4)	4018(5)	21.8(11)
C5	3327(6)	293(5)	4080(5)	21.8(11)
C6	2735(7)	924(4)	3686(5)	21.8(11)
C7	4988(6)	2892(5)	1362(4)	19.8(17)
C8	4090(7)	3098(5)	919(5)	25.5(19)
C9	3298(6)	2942(4)	1489(5)	20.9(18)
C10	6609(6)	3378(4)	3119(4)	17.4(12)
C11	7120(6)	2725(4)	2624(4)	17.4(12)
C12	8149(6)	2440(4)	2896(5)	14.6(17)
C15	7278(6)	3900(4)	3752(5)	19.1(17)
C16	8076(6)	3320(5)	4236(5)	20.8(18)
C17	8605(6)	2702(4)	3624(4)	17.1(16)
C18	7826(7)	4612(5)	3204(5)	28.7(12)
C19	8674(7)	5081(5)	3678(6)	28.7(12)
C20	10489(6)	5335(5)	3691(5)	28.7(12)
C21	9893(7)	1996(5)	4924(5)	31.7(9)
C22	9487(7)	1191(5)	5101(5)	31.7(9)
C23	9542(7)	877(5)	5936(5)	31.7(9)
C24	9998(7)	1377(5)	6587(5)	31.7(9)
C25	10402(6)	2173(6)	6400(5)	31.7(9)
C26	10348(7)	2490(5)	5565(5)	31.7(9)
C27	6924(7)	1101(5)	1400(5)	36.6(17)
C28	7290(7)	247(5)	3007(6)	36(2)
C29	5343(7)	136(5)	2159(5)	36.6(17)
B1	3138(8)	2463(5)	3081(6)	19(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound 5_79. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	13.08(17)	14.53(14)	15.12(15)	-0.45(15)	1.02(11)	0.20(16)
S1	14.7(11)	25.5(11)	23.0(10)	-0.1(8)	-1.6(8)	-1.0(8)
P1	19.1(13)	18.8(10)	26.8(12)	-7.3(9)	5.2(9)	-2.1(9)
O1	22(3)	27(3)	25(3)	8(2)	-4(3)	2(2)
O2	16(3)	37(3)	26(3)	-8(3)	2(2)	10(3)
O3	13(3)	34(3)	36(3)	0(3)	1(3)	-10(2)
O4	21(4)	30(3)	44(4)	-4(3)	5(3)	-7(3)
O5	33(4)	36(3)	52(4)	-24(3)	10(3)	-10(3)
N00D	14(4)	14(3)	18(3)	-2(3)	0(3)	-3(3)
N1	20(4)	14(3)	16(3)	-1(2)	3(3)	-1(3)
N2	9(4)	18(3)	21(3)	5(3)	1(3)	0(3)
N3	11(3)	15(2)	23(2)	-2.9(19)	-1(2)	-3(2)
N4	11(3)	15(2)	23(2)	-2.9(19)	-1(2)	-3(2)
N5	12(4)	21(3)	15(3)	1(3)	2(3)	2(3)
N6	15(4)	20(3)	19(3)	2(3)	-4(3)	1(3)
C1	18(3)	18(3)	18(3)	2(2)	2(2)	1(2)
C2	35(6)	18(4)	14(4)	0(3)	3(4)	3(4)
C3	18(3)	18(3)	18(3)	2(2)	2(2)	1(2)
C4	26(3)	17(2)	22(3)	-1.5(19)	4(2)	-5(2)
C5	26(3)	17(2)	22(3)	-1.5(19)	4(2)	-5(2)
C6	26(3)	17(2)	22(3)	-1.5(19)	4(2)	-5(2)
C7	26(5)	21(4)	13(4)	-3(3)	5(3)	-1(4)
C8	28(5)	31(4)	17(4)	0(3)	-3(4)	4(4)
C9	21(5)	13(4)	28(4)	-4(3)	5(4)	-3(3)
C10	14(3)	20(3)	17(3)	2(2)	1(2)	2(2)
C11	14(3)	20(3)	17(3)	2(2)	1(2)	2(2)
C12	12(4)	12(3)	20(4)	-2(3)	0(3)	0(3)
C15	13(5)	17(4)	27(5)	-2(3)	2(3)	-4(3)
C16	13(5)	26(4)	23(4)	-7(3)	-3(3)	1(3)
C17	18(4)	15(4)	18(4)	2(3)	-4(3)	-2(3)
C18	23(3)	26(2)	38(3)	-7(2)	6(2)	-7(2)
C19	23(3)	26(2)	38(3)	-7(2)	6(2)	-7(2)
C20	23(3)	26(2)	38(3)	-7(2)	6(2)	-7(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound 5_79. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C22	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C23	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C24	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C25	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C26	27(2)	38(2)	29.3(19)	0.6(16)	-2.9(16)	-2.3(17)
C27	35(4)	41(4)	34(4)	-23(3)	11(3)	-11(3)
C28	45(7)	25(4)	38(6)	5(4)	12(5)	12(4)
C29	35(4)	41(4)	34(4)	-23(3)	11(3)	-11(3)
B1	15(5)	16(4)	27(5)	1(4)	7(4)	3(4)

Table 4 Bond Lengths for Compound 5_79.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	P1	2.5019(19)	N4	B1	1.533(10)
W1	N00D	1.761(6)	N5	N6	1.365(8)
W1	N1	2.211(6)	N5	C7	1.334(8)
W1	N3	2.213(6)	N6	C9	1.330(9)
W1	N5	2.254(6)	N6	B1	1.538(10)
W1	C10	2.163(7)	C1	C2	1.367(10)
W1	C11	2.223(7)	C2	C3	1.374(10)
S1	O2	1.448(5)	C4	C5	1.390(11)
S1	O3	1.441(5)	C5	C6	1.373(10)
S1	C17	1.750(8)	C7	C8	1.371(10)
S1	C21	1.764(8)	C8	C9	1.367(10)
P1	C27	1.822(8)	C10	C11	1.425(9)
P1	C28	1.810(8)	C10	C15	1.526(10)
P1	C29	1.796(8)	C11	C12	1.447(10)
O1	N00D	1.234(7)	C12	C17	1.328(9)
O4	C19	1.341(9)	C15	C16	1.547(10)
O4	C20	1.418(9)	C15	C18	1.557(10)
O5	C19	1.194(9)	C16	C17	1.506(10)

Table 4 Bond Lengths for Compound 5_79.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	N2	1.370(8)	C18	C19	1.492(11)
N1	C1	1.343(9)	C21	C22	1.374(11)
N2	C3	1.349(9)	C21	C26	1.377(11)
N2	B1	1.533(11)	C22	C23	1.381(11)
N3	N4	1.365(8)	C23	C24	1.393(11)
N3	C4	1.331(8)	C24	C25	1.364(11)
N4	C6	1.345(9)	C25	C26	1.382(11)

Table 5 Bond Angles for Compound 5_79.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N00D	W1	P1	92.05(18)	C6	N4	B1	129.5(7)
N00D	W1	N1	97.2(2)	N6	N5	W1	119.3(4)
N00D	W1	N3	90.7(2)	C7	N5	W1	134.7(5)
N00D	W1	N5	175.8(2)	C7	N5	N6	106.0(6)
N00D	W1	C10	97.2(3)	N5	N6	B1	122.1(6)
N00D	W1	C11	96.9(3)	C9	N6	N5	109.1(6)
N1	W1	P1	158.12(17)	C9	N6	B1	128.1(7)
N1	W1	N3	77.3(2)	N1	C1	C2	111.6(7)
N1	W1	N5	80.8(2)	C1	C2	C3	105.1(7)
N1	W1	C11	120.1(2)	N2	C3	C2	108.4(7)
N3	W1	P1	82.79(15)	N3	C4	C5	110.3(7)
N3	W1	N5	85.2(2)	C6	C5	C4	105.3(7)
N3	W1	C11	159.6(2)	N4	C6	C5	108.1(7)
N5	W1	P1	88.64(15)	N5	C7	C8	110.8(7)
C10	W1	P1	115.92(19)	C9	C8	C7	104.8(7)
C10	W1	N1	82.6(2)	N6	C9	C8	109.2(7)
C10	W1	N3	159.2(2)	C11	C10	W1	73.3(4)
C10	W1	N5	86.2(2)	C11	C10	C15	117.5(6)
C10	W1	C11	37.9(2)	C15	C10	W1	130.4(5)
C11	W1	P1	78.11(18)	C10	C11	W1	68.8(4)
C11	W1	N5	87.3(2)	C10	C11	C12	118.5(6)
O2	S1	C17	108.6(3)	C12	C11	W1	118.4(5)
O2	S1	C21	108.0(3)	C17	C12	C11	123.2(7)

Table 5 Bond Angles for Compound 5_79.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	S1	O2	118.9(3)	C10	C15	C16	111.8(6)
O3	S1	C17	107.8(3)	C10	C15	C18	105.9(6)
O3	S1	C21	106.5(4)	C16	C15	C18	112.0(6)
C17	S1	C21	106.3(4)	C17	C16	C15	111.0(6)
C27	P1	W1	118.4(3)	C12	C17	S1	119.4(6)
C28	P1	W1	113.9(3)	C12	C17	C16	122.0(7)
C28	P1	C27	103.4(4)	C16	C17	S1	118.4(5)
C29	P1	W1	116.3(3)	C19	C18	C15	113.7(7)
C29	P1	C27	100.1(4)	O4	C19	C18	110.5(7)
C29	P1	C28	102.4(4)	O5	C19	O4	124.6(8)
C19	O4	C20	116.8(6)	O5	C19	C18	124.9(8)
O1	N00D	W1	177.2(5)	C22	C21	S1	119.7(6)
N2	N1	W1	121.4(4)	C22	C21	C26	120.9(8)
C1	N1	W1	132.9(5)	C26	C21	S1	119.3(6)
C1	N1	N2	105.3(6)	C21	C22	C23	119.1(8)
N1	N2	B1	120.7(6)	C22	C23	C24	120.1(8)
C3	N2	N1	109.6(6)	C25	C24	C23	120.1(8)
C3	N2	B1	129.4(7)	C24	C25	C26	120.0(8)
N4	N3	W1	122.5(4)	C21	C26	C25	119.7(8)
C4	N3	W1	131.0(5)	N2	B1	N6	108.7(6)
C4	N3	N4	106.5(6)	N4	B1	N2	105.9(7)
N3	N4	B1	119.2(6)	N4	B1	N6	109.9(6)
C6	N4	N3	109.7(6)				

Table 6 Torsion Angles for Compound 5_79.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
W1	N1	N2	C3	173.7(4)	C3	N2	B1	N6	129.5(7)
W1	N1	N2	B1	-0.5(8)	C4	N3	N4	C6	0.4(8)
W1	N1	C1	C2	-173.0(5)	C4	N3	N4	B1	167.6(6)
W1	N3	N4	C6	-177.4(4)	C4	C5	C6	N4	0.8(8)
W1	N3	N4	B1	-10.2(8)	C6	N4	B1	N2	110.6(8)
W1	N3	C4	C5	177.6(5)	C6	N4	B1	N6	-132.2(8)
W1	N5	N6	C9	176.8(4)	C7	N5	N6	C9	-1.3(7)

Table 6 Torsion Angles for Compound 5_79.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
W1	N5	N6	B1	5.4(8)	C7	N5	N6	B1	-172.7(6)
W1	N5	C7	C8	-177.4(5)	C7	C8	C9	N6	-1.6(8)
W1	C10	C11	C12	-111.7(6)	C9	N6	B1	N2	-115.2(8)
W1	C10	C15	C16	50.1(9)	C9	N6	B1	N4	129.3(7)
W1	C10	C15	C18	172.4(5)	C10	C11	C12	C17	6.0(10)
W1	C11	C12	C17	-73.9(8)	C10	C15	C16	C17	44.4(8)
S1	C21	C22	C23	176.7(6)	C10	C15	C18	C19	-168.7(7)
S1	C21	C26	C25	-176.6(6)	C11	C10	C15	C16	-40.9(9)
O2	S1	C17	C12	-15.7(7)	C11	C10	C15	C18	81.3(8)
O2	S1	C17	C16	168.7(5)	C11	C12	C17	S1	-175.0(5)
O2	S1	C21	C22	-40.3(8)	C11	C12	C17	C16	0.4(11)
O2	S1	C21	C26	136.6(7)	C15	C10	C11	W1	127.4(6)
O3	S1	C17	C12	114.4(6)	C15	C10	C11	C12	15.7(9)
O3	S1	C17	C16	-61.2(6)	C15	C16	C17	S1	149.2(5)
O3	S1	C21	C22	-169.1(7)	C15	C16	C17	C12	-26.3(9)
O3	S1	C21	C26	7.8(8)	C15	C18	C19	O4	119.8(7)
N1	N2	C3	C2	0.6(7)	C15	C18	C19	O5	-58.7(11)
N1	N2	B1	N4	60.4(8)	C16	C15	C18	C19	-46.6(9)
N1	N2	B1	N6	-57.6(8)	C17	S1	C21	C22	76.1(8)
N1	C1	C2	C3	0.2(8)	C17	S1	C21	C26	-107.0(7)
N2	N1	C1	C2	0.2(7)	C18	C15	C16	C17	-74.3(8)
N3	N4	C6	C5	-0.7(8)	C20	O4	C19	O5	3.2(12)
N3	N4	B1	N2	-53.7(8)	C20	O4	C19	C18	-175.3(6)
N3	N4	B1	N6	63.5(9)	C21	S1	C17	C12	-131.6(6)
N3	C4	C5	C6	-0.5(8)	C21	S1	C17	C16	52.7(6)
N4	N3	C4	C5	0.1(8)	C21	C22	C23	C24	0.4(13)
N5	N6	C9	C8	1.9(8)	C22	C21	C26	C25	0.2(13)
N5	N6	B1	N2	54.4(8)	C22	C23	C24	C25	-0.7(13)
N5	N6	B1	N4	-61.0(9)	C23	C24	C25	C26	0.8(13)
N5	C7	C8	C9	0.8(8)	C24	C25	C26	C21	-0.6(13)
N6	N5	C7	C8	0.3(8)	C26	C21	C22	C23	-0.2(13)
C1	N1	N2	C3	-0.5(7)	B1	N2	C3	C2	174.1(7)
C1	N1	N2	B1	-174.6(6)	B1	N4	C6	C5	-166.2(7)
C1	C2	C3	N2	-0.5(8)	B1	N6	C9	C8	172.6(7)
C3	N2	B1	N4	-112.5(8)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_79.

Atom	*x*	*y*	*z*	U(eq)
H1	5383.48	3754.9	4909.05	22
H2	3664.76	4367.08	5329.52	27
H3	2339.95	3712.36	4321.8	22
H4	4947.86	276.46	4239.82	26
H5	3084.44	-227.28	4338.71	26
H6	1993.91	922.97	3627.33	26
H7	5674.74	2941.71	1133.76	24
H8	4030.55	3304.77	342.05	31
H9	2574.46	3035.78	1379.63	25
H10	6213.59	3778.18	2727.71	21
H11	7029.36	2784.85	1984.83	21
H12	8517.32	2046.23	2536.35	17
H15	6809.67	4184.56	4183.67	23
H16A	8611.2	3689.34	4519.62	25
H16B	7711.56	2987.26	4691.73	25
H18A	8127.92	4339.94	2681.64	34
H18B	7294.14	5037.59	3010.13	34
H20A	11120.96	5152.23	3383.51	43
H20B	10522.04	5129.11	4289.41	43
H20C	10442.02	5968.77	3685.41	43
H22	9172.9	855.54	4655.82	38
H23	9268.4	320.24	6066.93	38
H24	10027.73	1162.53	7162.68	38
H25	10721.09	2509.27	6842.6	38
H26	10623.67	3046.46	5434.65	38
H27A	6440.87	1436.17	1036.76	55
H27B	7072.53	544.17	1121.9	55
H27C	7578.43	1425.3	1475.31	55
H28A	7923.17	589.17	3117.29	54
H28B	7464.53	-254.47	2647.65	54
H28C	6999.55	47.83	3557.78	54
H29A	5042.84	-116.63	2683.05	55

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_79.

Atom	*x*	*y*	*z*	U(eq)
H29B	5656.22	-323.27	1807.37	55
H29C	4789.53	425.61	1825.37	55
H1A	2320(60)	2570(40)	3030(50)	29

Experimental

Single crystals of $C_{27}H_{35}BN_7O_5PSW$ [mo_Harman_PS_3_89_0m] were []. A suitable crystal was selected and [] on a Bruker D8 Venture diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. **Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.**
2. **Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.**
3. **Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.**

Crystal structure determination of [mo_Harman_PS_3_89_0m]

Crystal Data for $C_{27}H_{35}BN_7O_5PSW$ (*M* =795.31 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.7699(7) Å, *b* = 15.4292(7) Å, *c* = 15.4711(7) Å, *β* = 90.283(2)°, *V* = 3048.2(3) Å^3, *Z* = 4, *T* = 100.00 K, μ(Mo Kα) = 3.960 mm^{-1}, *Dcalc* = 1.733 g/cm^3, 41294 reflections measured (4.14° ≤ 2Θ ≤ 51.472°), 5807 unique (R_{int} = 0.1653, R_{sigma} = 0.1007) which were used in all calculations. The final R_1 was 0.0444 (I > 2σ(I)) and wR_2 was 0.0920 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

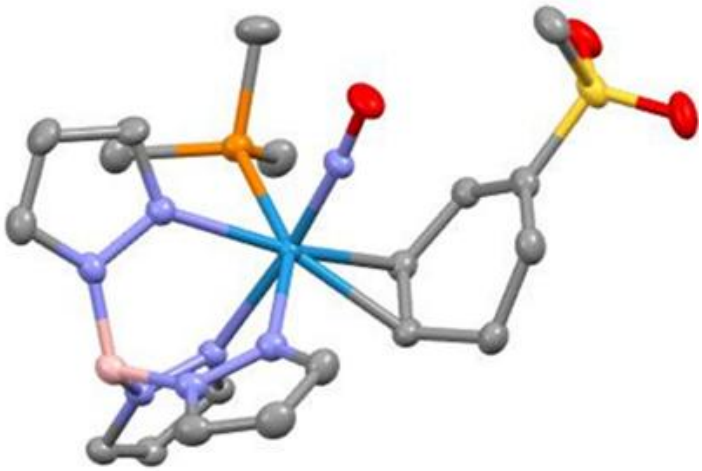
Details:

1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All B(H) groups, All C(H,H,H) groups
2. Uiso/Uaniso restraints and constraints

Uanis(C21) = Uanis(C22) = Uanis(C23) = Uanis(C24) = Uanis(C25) = Uanis(C26)
Uanis(C6) = Uanis(C5) = Uanis(C4)
Uanis(C11) = Uanis(C10)
Uanis(N4) = Uanis(N3)
Uanis(C19) = Uanis(C18)
Uanis(C19) = Uanis(C20)
Uanis(C1) = Uanis(C3)
Uanis(C29) = Uanis(C27)
3.a Ternary CH refined with riding coordinates: C10(H10), C11(H11), C15(H15)
3.b Secondary CH2 refined with riding coordinates: C16(H16A,H16B), C18(H18A,H18B)
3.c Aromatic/amide H refined with riding coordinates: C1(H1), C2(H2), C3(H3), C4(H4), C5(H5), C6(H6), C7(H7), C8(H8), C9(H9), C12(H12), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26)
3.d Idealised Me refined as rotating group: C20(H20A,H20B,H20C), C27(H27A,H27B,H27C), C28(H28A,H28B,H28C), C29(H29A,H29B, H29C)

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Crystal Structure Report for Harman_PS_3_55



A colourless, plate-like specimen of $C_{21}H_{34}BN_7O_4PSW$, approximate dimensions 0.078 mm x 0.112 mm x 0.132 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 1.42 hours. The frames were integrated with the Bruker SAINT software package[135] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38883 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 6232 were independent (average redundancy 6.239, completeness = 99.9%, R_{int} = 3.91%, R_{sig} = 2.71%) and 5429 (87.11%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.8707(4) Å, b = 19.7711(7) Å, c = 12.6847(4) Å, β = 96.5960(10)°, volume = 2708.22(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 9898 reflections above 20 σ(I) with 5.111° < 2θ < 54.99°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[136] The ratio of minimum to maximum apparent transmission was 0.660. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5920 and 0.7230.

[135] Bruker (2019). Saint; APEX4. Bruker AXS Inc., Madison, Wisconsin, USA.

[136] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

The structure was solved and refined using the Bruker SHELXTL Software Package[137] within APEX4 [1] and OLEX2,[138] using the space group P $2_1/n$, with Z = 4 for the formula unit, $C_{21}H_{34}BN_7O_4PSW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 342 variables converged at R1 = 2.32%, for the observed data and wR2 = 5.40% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 1.517 $e^-/Å^3$ and the largest hole was -0.508 $e^-/Å^3$ with an RMS deviation of 0.099 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.732 g/cm^3 and F(000), 1404 e^-.

Table 1. Sample and crystal data for Harman_PS_3_55.

Identification code	Harman_PS_3_55
Chemical formula	$C_{21}H_{34}BN_7O_4PSW$
Formula weight	706.24 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.078 x 0.112 x 0.132 mm
Crystal habit	translucent intense colourless plate
Crystal system	monoclinic
Space group	P $2_1/n$
Unit cell dimensions	a = 10.8707(4) Å α = 90°
	b = 19.7711(7) Å β = 96.5960(10)°

[137] Sheldrick, G. M. (2015). Acta Cryst. A**71**, 3-8.
[138] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

	c = 12.6847(4) Å γ = 90°
Volume	2708.22(16) $Å^3$
Z	4
Density (calculated)	1.732 g/cm^3
Absorption coefficient	4.443 mm^{-1}
F(000)	1404

Table 2. Data collection and structure refinement for Harman_PS_3_55.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.06 to 27.50°
Index ranges	-14<=h<=12, -25<=k<=24, -15<=l<=16
Reflections collected	38883
Independent reflections	6232 [R(int) = 0.0391]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7230 and 0.5920

Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6232 / 0 / 342	
Goodness-of-fit on F^2	1.035	
Δ/σ_{max}	0.003	
Final R indices	5429 data; I>2σ(I)	R1 = 0.0232, wR2 = 0.0510
	all data	R1 = 0.0301, wR2 = 0.0540
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0235P)^2+3.0103P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.517 and -0.508 eÅ^{-3}	
R.M.S. deviation from mean	0.099 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Harman_PS_3_55.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.51852(2)	0.27478(2)	0.52884(2)	0.01763(4)
S1	0.80128(8)	0.46995(4)	0.43554(7)	0.02807(17)
P1	0.51366(7)	0.33230(4)	0.70436(6)	0.02286(16)
O1	0.7945(2)	0.28164(11)	0.5406(2)	0.0326(5)
O2	0.8283(2)	0.49890(11)	0.33599(19)	0.0355(6)
O3	0.7889(2)	0.51695(12)	0.52077(19)	0.0360(6)
N1	0.3173(2)	0.25688(13)	0.53856(19)	0.0209(5)
N2	0.2742(2)	0.19234(12)	0.54685(18)	0.0197(5)
N3	0.5497(2)	0.18636(13)	0.63370(19)	0.0219(5)
N4	0.4656(2)	0.13573(13)	0.63637(19)	0.0223(5)
N5	0.4917(2)	0.18863(13)	0.41766(19)	0.0223(5)
N6	0.4245(2)	0.13365(13)	0.44144(19)	0.0222(5)
N7	0.6807(2)	0.28120(12)	0.5318(2)	0.0229(5)
C1	0.2188(3)	0.29742(16)	0.5408(2)	0.0226(6)
C2	0.1123(3)	0.26004(16)	0.5512(2)	0.0237(6)
C3	0.1520(3)	0.19371(16)	0.5547(2)	0.0233(6)
C4	0.6449(3)	0.17102(16)	0.7061(2)	0.0265(7)
C5	0.6228(3)	0.11032(17)	0.7564(3)	0.0304(7)
C6	0.5088(3)	0.08940(16)	0.7096(2)	0.0285(7)
C7	0.5450(3)	0.17234(17)	0.3312(2)	0.0280(7)
C8	0.5131(3)	0.10731(17)	0.2986(3)	0.0319(7)

	x/a	y/b	z/c	U(eq)
C9	0.4375(3)	0.08437(17)	0.3707(2)	0.0286(7)
C10	0.4755(3)	0.38084(16)	0.4732(2)	0.0228(6)
C11	0.4592(3)	0.33342(16)	0.3857(2)	0.0238(6)
C12	0.5308(3)	0.34689(17)	0.2920(2)	0.0275(7)
C13	0.6648(3)	0.36881(16)	0.3252(2)	0.0278(7)
C14	0.6702(3)	0.41955(15)	0.4140(2)	0.0237(6)
C15	0.5835(3)	0.42429(15)	0.4806(2)	0.0222(6)
C16	0.9216(3)	0.41285(17)	0.4775(3)	0.0329(7)
C17	0.6648(3)	0.3522(2)	0.7717(3)	0.0365(8)
C18	0.4321(3)	0.41161(17)	0.7152(3)	0.0326(8)
C19	0.4403(3)	0.28107(18)	0.7993(3)	0.0331(8)
B1	0.3607(3)	0.13102(18)	0.5440(3)	0.0238(7)
O4	0.9265(2)	0.08058(11)	0.50273(19)	0.0321(5)
C20	0.9330(3)	0.00973(16)	0.4982(3)	0.0309(7)
C21	0.8036(4)	0.1033(2)	0.5031(4)	0.0554(12)

Table 4. Bond lengths (Å) for Harman_PS_3_55.

W1-N7	1.764(3)	W1-C11	2.189(3)
W1-N3	2.199(2)	W1-N5	2.209(2)
W1-N1	2.233(3)	W1-C10	2.245(3)
W1-P1	2.5061(8)	S1-O3	1.444(2)
S1-O2	1.447(2)	S1-C14	1.735(3)

S1-C16	1.763(3)	P1-C17	1.805(3)
P1-C18	1.814(3)	P1-C19	1.826(3)
O1-N7	1.229(3)	N1-C1	1.340(4)
N1-N2	1.367(3)	N2-C3	1.344(4)
N2-B1	1.537(4)	N3-C4	1.337(4)
N3-N4	1.359(3)	N4-C6	1.350(4)
N4-B1	1.541(4)	N5-C7	1.337(4)
N5-N6	1.362(4)	N6-C9	1.343(4)
N6-B1	1.544(4)	C1-C2	1.393(4)
C1-H1	0.950000	C2-C3	1.380(4)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.393(4)	C4-H4	0.950000
C5-C6	1.375(5)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.383(5)
C7-H7	0.950000	C8-C9	1.374(5)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.448(4)	C10-C15	1.449(4)
C10-H10	0.98(3)	C11-C12	1.517(4)
C11-H11	1.01(3)	C12-C13	1.532(5)
C12-H12A	0.990000	C12-H12B	0.990000
C13-C14	1.504(4)	C13-H13A	0.990000
C13-H13B	0.990000	C14-C15	1.339(4)
C15-H15	0.950000	C16-H16A	0.980000
C16-H16B	0.980000	C16-H16C	0.980000

C17-H17A	0.980000	C17-H17B	0.980000
C17-H17C	0.980000	C18-H18A	0.980000
C18-H18B	0.980000	C18-H18C	0.980000
C19-H19A	0.980000	C19-H19B	0.980000
C19-H19C	0.980000	B1-H1A	1.08(3)
O4-C20	1.404(4)	O4-C21	1.409(4)
C20-C20#1	1.503(7)	C20-H20A	0.990000
C20-H20B	0.990000	C21-H21A	0.980000
C21-H21B	0.980000	C21-H21C	0.980000

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1

Table 5. Bond angles (°) for Harman_PS_3_55.

N7-W1-C11	100.26(12)	N7-W1-N3	87.71(10)
C11-W1-N3	158.95(11)	N7-W1-N5	97.33(10)
C11-W1-N5	82.76(10)	N3-W1-N5	76.88(9)
N7-W1-N1	173.36(10)	C11-W1-N1	86.14(10)
N3-W1-N1	85.67(9)	N5-W1-N1	81.65(9)
N7-W1-C10	96.39(11)	C11-W1-C10	38.10(11)
N3-W1-C10	160.90(10)	N5-W1-C10	120.79(10)
N1-W1-C10	89.73(10)	N7-W1-P1	94.09(8)
C11-W1-P1	117.55(8)	N3-W1-P1	80.85(6)
N5-W1-P1	154.46(7)	N1-W1-P1	84.38(6)

C10-W1-P1	80.25(8)	O3-S1-O2	116.41(15)
O3-S1-C14	110.00(15)	O2-S1-C14	109.57(15)
O3-S1-C16	108.40(16)	O2-S1-C16	107.41(16)
C14-S1-C16	104.32(16)	C17-P1-C18	101.67(17)
C17-P1-C19	104.56(17)	C18-P1-C19	100.08(16)
C17-P1-W1	114.09(12)	C18-P1-W1	121.32(11)
C19-P1-W1	112.93(12)	C1-N1-N2	106.0(2)
C1-N1-W1	134.1(2)	N2-N1-W1	119.89(18)
C3-N2-N1	109.7(2)	C3-N2-B1	129.0(3)
N1-N2-B1	121.2(2)	C4-N3-N4	106.6(2)
C4-N3-W1	130.5(2)	N4-N3-W1	122.90(18)
C6-N4-N3	109.6(3)	C6-N4-B1	130.6(3)
N3-N4-B1	117.8(2)	C7-N5-N6	106.5(2)
C7-N5-W1	132.2(2)	N6-N5-W1	120.57(17)
C9-N6-N5	109.3(2)	C9-N6-B1	129.1(3)
N5-N6-B1	121.2(2)	O1-N7-W1	174.6(2)
N1-C1-C2	111.1(3)	N1-C1-H1	124.500000
C2-C1-H1	124.500000	C3-C2-C1	104.3(3)
C3-C2-H2	127.800000	C1-C2-H2	127.800000
N2-C3-C2	109.0(3)	N2-C3-H3	125.500000
C2-C3-H3	125.500000	N3-C4-C5	110.5(3)
N3-C4-H4	124.800000	C5-C4-H4	124.800000
C6-C5-C4	104.8(3)	C6-C5-H5	127.600000
C4-C5-H5	127.600000	N4-C6-C5	108.5(3)

N4-C6-H6	125.700000	C5-C6-H6	125.700000
N5-C7-C8	110.6(3)	N5-C7-H7	124.700000
C8-C7-H7	124.700000	C9-C8-C7	104.8(3)
C9-C8-H8	127.600000	C7-C8-H8	127.600000
N6-C9-C8	108.8(3)	N6-C9-H9	125.600000
C8-C9-H9	125.600000	C11-C10-C15	117.4(3)
C11-C10-W1	68.84(17)	C15-C10-W1	113.3(2)
C11-C10-H10	121.3(19)	C15-C10-H10	114.4(19)
W1-C10-H10	112.8(18)	C10-C11-C12	117.3(3)
C10-C11-W1	73.05(17)	C12-C11-W1	127.9(2)
C10-C11-H11	113.1(19)	C12-C11-H11	109.3(18)
W1-C11-H11	111.7(19)	C11-C12-C13	113.0(3)
C11-C12-H12A	109.000000	C13-C12-H12A	109.000000
C11-C12-H12B	109.000000	C13-C12-H12B	109.000000
H12A-C12-H12B	107.800000	C14-C13-C12	110.4(3)
C14-C13-H13A	109.600000	C12-C13-H13A	109.600000
C14-C13-H13B	109.600000	C12-C13-H13B	109.600000

H13A-C13-H13B	108.100000	C15-C14-C13	123.3(3)
C15-C14-S1	119.0(2)	C13-C14-S1	117.5(2)
C14-C15-C10	122.7(3)	C14-C15-H15	118.600000
C10-C15-H15	118.600000	S1-C16-H16A	109.500000
S1-C16-H16B	109.500000	H16A-C16-H16B	109.500000
S1-C16-H16C	109.500000	H16A-C16-H16C	109.500000
H16B-C16-H16C	109.500000	P1-C17-H17A	109.500000
P1-C17-H17B	109.500000	H17A-C17-H17B	109.500000
P1-C17-H17C	109.500000	H17A-C17-H17C	109.500000
H17B-C17-H17C	109.500000	P1-C18-H18A	109.500000
P1-C18-H18B	109.500000	H18A-C18-H18B	109.500000
P1-C18-H18C	109.500000	H18A-C18-H18C	109.500000
H18B-C18-H18C	109.500000	P1-C19-H19A	109.500000
P1-C19-H19B	109.500000	H19A-C19-H19B	109.500000
P1-C19-H19C	109.500000	H19A-C19-H19C	109.500000

H19B-C19-H19C	109.500000	N2-B1-N4	109.6(2)
N2-B1-N6	109.2(3)	N4-B1-N6	105.9(3)
N2-B1-H1A	110.1(16)	N4-B1-H1A	112.2(16)
N6-B1-H1A	109.7(16)	C20-O4-C21	111.7(3)
O4-C20-C20#1	107.9(3)	O4-C20-H20A	110.100000
C20#1-C20-H20A	110.100000	O4-C20-H20B	110.100000
C20#1-C20-H20B	110.100000	H20A-C20-H20B	108.400000
O4-C21-H21A	109.500000	O4-C21-H21B	109.500000
H21A-C21-H21B	109.500000	O4-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1

Table 6. Torsion angles (°) for Harman_PS_3_55.

C1-N1-N2-C3	-0.4(3)	W1-N1-N2-C3	178.19(18)
C1-N1-N2-B1	178.2(2)	W1-N1-N2-B1	-3.1(3)
C4-N3-N4-C6	-0.2(3)	W1-N3-N4-C6	-178.59(19)
C4-N3-N4-B1	-165.9(3)	W1-N3-N4-B1	15.8(3)

C7-N5-N6-C9	0.4(3)	W1-N5-N6-C9	-170.49(19)
C7-N5-N6-B1	173.5(3)	W1-N5-N6-B1	2.6(3)
N2-N1-C1-C2	0.5(3)	W1-N1-C1-C2	-177.9(2)
N1-C1-C2-C3	-0.3(3)	N1-N2-C3-C2	0.2(3)
B1-N2-C3-C2	-178.3(3)	C1-C2-C3-N2	0.1(3)
N4-N3-C4-C5	-0.2(3)	W1-N3-C4-C5	178.0(2)
N3-C4-C5-C6	0.5(4)	N3-N4-C6-C5	0.5(3)
B1-N4-C6-C5	163.7(3)	C4-C5-C6-N4	-0.6(4)
N6-N5-C7-C8	0.0(4)	W1-N5-C7-C8	169.4(2)
N5-C7-C8-C9	-0.4(4)	N5-N6-C9-C8	-0.7(4)
B1-N6-C9-C8	-173.1(3)	C7-C8-C9-N6	0.7(4)
C15-C10-C11-C12	-18.4(4)	W1-C10-C11-C12	-124.4(3)
C15-C10-C11-W1	106.0(3)	C10-C11-C12-C13	42.6(4)
W1-C11-C12-C13	-46.6(4)	C11-C12-C13-C14	-43.4(4)
C12-C13-C14-C15	24.3(4)	C12-C13-C14-S1	-160.4(2)
O3-S1-C14-C15	-6.4(3)	O2-S1-C14-C15	-135.6(2)
C16-S1-C14-C15	109.7(3)	O3-S1-C14-C13	178.0(2)
O2-S1-C14-C13	48.9(3)	C16-S1-C14-C13	-65.9(3)

C13-C14-C15-C10	-0.2(5)	S1-C14-C15-C10	-175.5(2)
C11-C10-C15-C14	-3.6(4)	W1-C10-C15-C14	73.7(3)
C3-N2-B1-N4	-121.5(3)	N1-N2-B1-N4	60.1(3)
C3-N2-B1-N6	122.9(3)	N1-N2-B1-N6	-55.5(3)
C6-N4-B1-N2	130.6(3)	N3-N4-B1-N2	-67.3(3)
C6-N4-B1-N6	-111.7(3)	N3-N4-B1-N6	50.4(3)
C9-N6-B1-N2	-132.2(3)	N5-N6-B1-N2	56.2(4)
C9-N6-B1-N4	109.9(3)	N5-N6-B1-N4	-61.7(3)
C21-O4-C20-C20#1	-178.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1

Table 7. Anisotropic atomic displacement parameters (Å^2) for Harman_PS_3_55.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.01630(6)	0.01889(7)	0.01756(6)	0.00023(4)	0.00133(4)	-0.00051(5)
S1	0.0233(4)	0.0217(4)	0.0407(4)	0.0003(3)	0.0098(3)	-0.0011(3)
P1	0.0230(4)	0.0255(4)	0.0197(4)	-0.0021(3)	0.0009(3)	-0.0003(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0173(12)	0.0302(13)	0.0500(14)	0.0044(11)	0.0027(10)	0.0012(9)
O2	0.0329(14)	0.0256(12)	0.0512(14)	0.0109(11)	0.0186(11)	0.0022(10)
O3	0.0273(13)	0.0285(13)	0.0538(15)	-0.0124(11)	0.0112(11)	-0.0063(10)
N1	0.0203(13)	0.0206(13)	0.0215(12)	-0.0003(10)	0.0013(10)	-0.0020(10)
N2	0.0188(13)	0.0197(13)	0.0204(11)	-0.0026(10)	0.0017(9)	-0.0013(10)
N3	0.0203(13)	0.0222(13)	0.0230(12)	0.0003(10)	0.0025(10)	0.0012(10)
N4	0.0220(13)	0.0190(12)	0.0264(13)	-0.0002(10)	0.0051(10)	-0.0008(10)
N5	0.0216(13)	0.0225(13)	0.0225(12)	-0.0015(10)	0.0021(10)	0.0030(10)
N6	0.0208(13)	0.0214(13)	0.0243(12)	-0.0050(10)	0.0023(10)	0.0012(10)
N7	0.0197(13)	0.0207(13)	0.0279(13)	0.0012(10)	0.0009(10)	-0.0011(10)
C1	0.0229(16)	0.0244(15)	0.0201(14)	-0.0007(12)	-0.0002(11)	0.0008(12)
C2	0.0165(15)	0.0308(17)	0.0240(15)	-0.0009(12)	0.0034(11)	0.0017(12)
C3	0.0191(15)	0.0284(17)	0.0224(14)	-0.0023(12)	0.0026(11)	-0.0027(13)
C4	0.0226(16)	0.0273(16)	0.0279(15)	0.0019(13)	-0.0042(12)	0.0034(13)
C5	0.0342(19)	0.0298(17)	0.0267(16)	0.0074(13)	0.0013(13)	0.0085(15)
C6	0.0332(19)	0.0226(16)	0.0311(16)	0.0037(13)	0.0098(14)	0.0047(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	0.0307(18)	0.0300(17)	0.0244(15)	-0.0009(13)	0.0075(12)	0.0050(14)
C8	0.036(2)	0.0319(18)	0.0276(16)	-0.0067(14)	0.0050(14)	0.0077(15)
C9	0.0291(18)	0.0245(16)	0.0307(16)	-0.0069(13)	-0.0024(13)	0.0040(14)
C10	0.0218(16)	0.0249(16)	0.0218(14)	0.0019(12)	0.0031(11)	0.0026(13)
C11	0.0219(16)	0.0273(16)	0.0218(14)	0.0038(12)	0.0005(11)	0.0003(13)
C12	0.0310(18)	0.0302(17)	0.0214(15)	0.0028(13)	0.0035(12)	0.0000(14)
C13	0.0298(18)	0.0268(17)	0.0284(16)	0.0015(13)	0.0105(13)	0.0004(14)
C14	0.0231(16)	0.0205(15)	0.0278(15)	0.0023(12)	0.0038(12)	0.0007(12)
C15	0.0232(16)	0.0199(15)	0.0233(14)	0.0019(12)	0.0019(11)	0.0024(12)
C16	0.0249(18)	0.0281(18)	0.046(2)	0.0013(15)	0.0063(14)	-0.0010(14)
C17	0.0298(19)	0.046(2)	0.0323(18)	-0.0104(16)	-0.0047(14)	-0.0026(16)
C18	0.041(2)	0.0303(18)	0.0265(16)	-0.0062(14)	0.0045(14)	0.0062(15)
C19	0.036(2)	0.040(2)	0.0246(16)	0.0002(14)	0.0087(13)	-0.0003(16)
B1	0.0213(18)	0.0218(17)	0.0286(17)	-0.0031(14)	0.0037(13)	-0.0005(14)
O4	0.0311(13)	0.0220(12)	0.0443(13)	0.0041(10)	0.0094(10)	0.0019(10)
C20	0.0289(19)	0.0244(17)	0.0400(18)	0.0064(14)	0.0065(14)	-0.0017(14)
C21	0.043(2)	0.034(2)	0.095(3)	0.017(2)	0.033(2)	0.0141(18)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for Harman_PS_3_55.

	x/a	y/b	z/c	U(eq)
H1	0.2213	0.3453	0.5358	0.027000
H2	0.0309	0.2765	0.5551	0.028000
H3	0.1012	0.1552	0.5615	0.028000
H4	0.7174	0.1978	0.7211	0.032000
H5	0.6750	0.0882	0.8111	0.036000
H6	0.4673	0.0491	0.7261	0.034000
H7	0.5976	0.2014	0.2970	0.034000
H8	0.5379	0.0837	0.2393	0.038000
H9	0.4006	0.0408	0.3705	0.034000
H10	0.405(3)	0.4002(16)	0.503(2)	0.020(8)
H11	0.370(3)	0.3249(17)	0.359(3)	0.029(9)
H12A	0.4880	0.3827	0.2472	0.033000
H12B	0.5310	0.3053	0.2484	0.033000
H13A	0.7154	0.3288	0.3487	0.033000
H13B	0.6996	0.3890	0.2637	0.033000
H15	0.5932	0.4575	0.5350	0.027000
H16A	0.9209	0.3755	0.4266	0.049000
H16B	0.9095	0.3949	0.5476	0.049000
H16C	1.0014	0.4364	0.4818	0.049000
H17A	0.7122	0.3103	0.7856	0.055000

	x/a	y/b	z/c	U(eq)
H17B	0.6555	0.3748	0.8391	0.055000
H17C	0.7085	0.3821	0.7270	0.055000
H18A	0.4706	0.4468	0.6756	0.049000
H18B	0.4363	0.4247	0.7900	0.049000
H18C	0.3452	0.4061	0.6858	0.049000
H19A	0.3558	0.2695	0.7692	0.050000
H19B	0.4375	0.3067	0.8651	0.050000
H19C	0.4881	0.2395	0.8145	0.050000
H1A	0.308(3)	0.0845(16)	0.546(2)	0.019(8)
H20A	-0.1140	-0.0070	0.4318	0.037000
H20B	-0.1033	-0.0105	0.5590	0.037000
H21A	-0.2463	0.0880	0.4382	0.083000
H21B	-0.1974	0.1528	0.5061	0.083000
H21C	-0.2308	0.0848	0.5651	0.083000

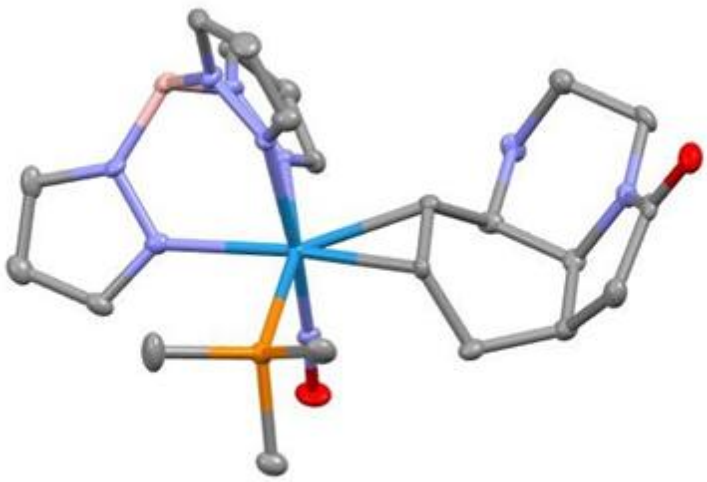


Table 1 Crystal data and structure refinement for Compound 5_5.

Empirical formula	$C_{22}H_{33}BN_9O_2PW$
Formula weight	681.20
Temperature/K	108.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2784(5)
b/Å	17.4183(10)
c/Å	14.9222(8)
α/°	90
β/°	106.847(2)
γ/°	90
Volume/Å^3	2556.9(2)
Z	4
ρ_{calc}g/cm^3	1.770
μ/mm^{-1}	4.620
F(000)	1352.0
Crystal size/mm^3	0.04 × 0.02 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.294 to 56.578
Index ranges	-13 ≤ h ≤ 13, -23 ≤ k ≤ 23, -19 ≤ l ≤ 18
Reflections collected	36954
Independent reflections	6337 [R_{int} = 0.0905, R_{sigma} = 0.0665]
Data/restraints/parameters	6337/1/335
Goodness-of-fit on F^2	1.000

Final R indexes [I>=2σ (I)] R_1 = 0.0345, wR_2 = 0.0623

Final R indexes [all data] R_1 = 0.0619, wR_2 = 0.0706

Largest diff. peak/hole / e $Å^{-3}$ 1.36/-0.79

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for Compound 5_5. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	2185.2(2)	7328.0(2)	4389.3(2)	11.27(6)
P1	2076.9(13)	8556.5(7)	5245.4(9)	14.8(3)
O1	-851(3)	7189.9(19)	3800(3)	24.2(8)
O2	4372(3)	5088.7(18)	8135(2)	19.9(8)
N1	4439(4)	7478(2)	4633(3)	13.9(9)
N2	4973(4)	7427(2)	3896(3)	15.9(9)
N3	2119(4)	8059(2)	3165(3)	14.1(8)
N4	3030(4)	7977(2)	2655(3)	14.1(8)
N5	2295(4)	6502(2)	3298(3)	13.9(8)
N6	3242(4)	6561(2)	2815(3)	16.1(9)
N7	398(4)	7239(2)	4075(3)	13.2(8)
N8	2695(4)	5006(2)	6736(3)	15.7(9)
N9	2111(4)	4900(2)	4819(3)	16.8(9)
C1	5457(5)	7664(3)	5372(4)	19.1(10)
C2	6657(5)	7745(3)	5127(4)	22.3(11)
C3	6314(5)	7588(3)	4193(4)	18.2(11)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 5_5. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C4	1241(5)	8599(3)	2729(3)	16.3(10)
C5	1566(5)	8875(3)	1953(4)	20.4(11)
C6	2695(5)	8467(3)	1916(3)	18.2(11)
C7	1484(5)	5924(2)	2917(3)	15.0(10)
C8	1891(5)	5586(3)	2203(4)	21.1(11)
C9	2997(5)	6010(3)	2155(3)	17.4(11)
C10	2685(5)	6295(3)	5287(3)	15.0(10)
C11	2535(4)	6932(2)	5863(3)	12.8(9)
C12	1332(4)	6872(3)	6261(3)	16.6(10)
C13	1353(5)	6105(3)	6772(3)	16.2(10)
C14	1507(4)	5412(3)	6153(3)	14.6(10)
C15	1712(5)	5620(3)	5208(3)	15.6(10)
C16	3364(5)	4547(3)	5422(4)	19.4(11)
C17	3161(5)	4332(2)	6351(3)	17.0(10)
C18	2547(5)	6033(3)	7684(4)	20.3(11)
C19	3331(5)	5329(3)	7565(4)	16.4(10)
C20	3065(5)	8678(3)	6466(4)	22.5(12)
C21	2563(6)	9442(3)	4769(4)	27.7(13)
C22	340(4)	8769(3)	5245(4)	20.3(11)
B1	4074(5)	7311(3)	2897(4)	16.0(11)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 5_5. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	9.99(9)	12.28(9)	12.14(10)	-0.19(9)	4.13(7)	0.81(9)
P1	16.1(6)	13.8(6)	14.9(7)	-0.6(5)	5.1(5)	0.5(5)
O1	8.8(16)	26(2)	35(2)	-3.3(16)	2.3(16)	-1.5(14)
O2	17.6(17)	22.1(18)	18(2)	3.6(15)	2.2(16)	-4.4(15)
N1	9.8(18)	17(2)	15(2)	1.4(15)	2.9(16)	-1.6(15)
N2	12.2(18)	21(2)	15(2)	2.8(17)	5.4(17)	0.4(16)
N3	12.8(19)	14(2)	16(2)	-4.2(17)	5.1(17)	-2.0(16)
N4	10.6(18)	16.8(19)	17(2)	0.4(17)	7.6(17)	-1.2(16)
N5	13.4(19)	16(2)	14(2)	0.8(16)	6.9(17)	1.6(16)
N6	18(2)	18(2)	14(2)	-2.5(17)	7.3(18)	2.4(17)
N7	11.5(18)	16(2)	13(2)	-1.6(16)	5.3(16)	0.6(16)
N8	17(2)	15(2)	14(2)	2.1(17)	4.0(18)	0.7(16)
N9	23(2)	14(2)	11(2)	-4.3(17)	1.0(19)	0.0(17)
C1	16(2)	20(2)	21(3)	-5(2)	5(2)	-1(2)
C2	10(2)	27(3)	27(3)	0(2)	1(2)	-1(2)
C3	14(2)	18(2)	25(3)	8(2)	8(2)	2(2)
C4	14(2)	15(2)	17(3)	-3(2)	0(2)	2.8(19)
C5	20(3)	19(3)	18(3)	0(2)	-1(2)	0(2)
C6	25(3)	16(2)	10(3)	-0.3(19)	0(2)	-6(2)
C7	17(2)	14(2)	13(3)	0.2(19)	2(2)	1.6(19)
C8	22(3)	19(3)	20(3)	-5(2)	3(2)	2(2)
C9	19(2)	22(3)	11(3)	-2(2)	4(2)	6(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound 5_5. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	13(2)	14(2)	20(3)	1.6(19)	9(2)	1.4(19)
C11	15(2)	10(2)	14(3)	2.7(19)	5(2)	0.3(19)
C12	11(2)	23(3)	17(3)	-1(2)	5(2)	0(2)
C13	15(2)	18(2)	17(3)	-1(2)	7(2)	0(2)
C14	11(2)	18(2)	13(3)	0.5(19)	0.6(19)	-1.7(19)
C15	13(2)	16(2)	18(3)	-4(2)	3(2)	-0.8(19)
C16	20(2)	17(2)	22(3)	1(2)	7(2)	2(2)
C17	18(2)	10(2)	21(3)	2.7(19)	2(2)	2.0(19)
C18	27(3)	16(2)	19(3)	0(2)	10(2)	-3(2)
C19	14(2)	18(2)	17(3)	7(2)	4(2)	-3.6(19)
C20	25(3)	21(3)	21(3)	-6(2)	7(2)	4(2)
C21	43(3)	20(3)	21(3)	4(2)	9(3)	-5(2)
C22	16(2)	22(3)	21(3)	-4(2)	2(2)	2(2)
B1	15(2)	18(3)	18(3)	0(2)	9(2)	-1(2)

Table 4 Bond Lengths for Compound 5_5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	P1	2.5111(12)	N6	C9	1.347(6)
W1	N1	2.254(4)	N6	B1	1.547(7)
W1	N3	2.211(4)	N8	C14	1.460(6)
W1	N5	2.200(4)	N8	C17	1.447(5)

Table 4 Bond Lengths for Compound 5_5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	N7	1.766(4)	N8	C19	1.343(6)
W1	C10	2.212(5)	N9	C15	1.489(6)
W1	C11	2.232(4)	N9	C16	1.475(6)
P1	C20	1.823(5)	C1	C2	1.390(6)
P1	C21	1.827(5)	C2	C3	1.363(7)
P1	C22	1.823(4)	C4	C5	1.381(7)
O1	N7	1.232(4)	C5	C6	1.375(6)
O2	C19	1.232(5)	C7	C8	1.384(6)
N1	N2	1.367(5)	C8	C9	1.374(6)
N1	C1	1.322(6)	C10	C11	1.438(6)
N2	C3	1.350(6)	C10	C15	1.526(6)
N2	B1	1.522(7)	C11	C12	1.523(6)
N3	N4	1.375(5)	C12	C13	1.536(6)
N3	C4	1.335(6)	C13	C14	1.555(6)
N4	C6	1.358(6)	C13	C18	1.551(7)
N4	B1	1.549(7)	C14	C15	1.529(6)
N5	N6	1.372(5)	C16	C17	1.507(6)
N5	C7	1.326(6)	C18	C19	1.507(6)

Table 5 Bond Angles for Compound 5_5.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	W1	P1	90.81(10)	N5	N6	B1	118.8(4)

Table 5 Bond Angles for Compound 5_5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	W1	P1	86.25(10)	C9	N6	N5	108.7(4)
N3	W1	N1	81.40(13)	C9	N6	B1	129.9(4)
N3	W1	C10	156.10(15)	O1	N7	W1	176.0(4)
N3	W1	C11	161.69(15)	C17	N8	C14	118.2(4)
N5	W1	P1	162.40(10)	C19	N8	C14	116.4(4)
N5	W1	N1	85.66(13)	C19	N8	C17	125.2(4)
N5	W1	N3	76.17(14)	C16	N9	C15	113.8(4)
N5	W1	C10	82.15(16)	N1	C1	C2	110.7(4)
N5	W1	C11	119.91(15)	C3	C2	C1	105.2(4)
N7	W1	P1	90.77(12)	N2	C3	C2	108.3(4)
N7	W1	N1	173.98(16)	N3	C4	C5	111.1(4)
N7	W1	N3	92.91(15)	C6	C5	C4	105.4(5)
N7	W1	N5	91.10(15)	N4	C6	C5	108.1(4)
N7	W1	C10	97.49(16)	N5	C7	C8	111.1(4)
N7	W1	C11	95.29(16)	C9	C8	C7	104.5(4)
C10	W1	P1	114.94(13)	N6	C9	C8	109.1(4)
C10	W1	N1	87.11(15)	C11	C10	W1	71.8(3)
C10	W1	C11	37.77(16)	C11	C10	C15	117.3(4)
C11	W1	P1	77.31(11)	C15	C10	W1	123.3(3)
C11	W1	N1	90.72(15)	C10	C11	W1	70.4(3)
C20	P1	W1	120.90(16)	C10	C11	C12	114.8(4)
C20	P1	C21	98.9(2)	C12	C11	W1	119.2(3)
C21	P1	W1	117.63(18)	C11	C12	C13	110.9(4)

Table 5 Bond Angles for Compound 5_5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	P1	W1	111.14(16)	C12	C13	C14	111.8(4)
C22	P1	C20	103.8(2)	C12	C13	C18	113.6(4)
C22	P1	C21	101.9(2)	C18	C13	C14	105.5(4)
N2	N1	W1	119.7(3)	N8	C14	C13	103.5(4)
C1	N1	W1	133.7(3)	N8	C14	C15	110.4(4)
C1	N1	N2	106.4(3)	C15	C14	C13	115.3(4)
N1	N2	B1	121.7(3)	N9	C15	C10	115.6(4)
C3	N2	N1	109.4(4)	N9	C15	C14	106.7(4)
C3	N2	B1	128.5(4)	C10	C15	C14	112.0(4)
N4	N3	W1	122.3(3)	N9	C16	C17	109.6(4)
C4	N3	W1	131.5(3)	N8	C17	C16	108.3(4)
C4	N3	N4	106.0(4)	C19	C18	C13	106.0(4)
N3	N4	B1	119.0(4)	O2	C19	N8	125.9(5)
C6	N4	N3	109.3(4)	O2	C19	C18	125.6(5)
C6	N4	B1	130.9(4)	N8	C19	C18	108.4(4)
N6	N5	W1	122.4(3)	N2	B1	N4	108.2(4)
C7	N5	W1	130.8(3)	N2	B1	N6	110.7(4)
C7	N5	N6	106.6(4)	N6	B1	N4	106.5(4)

Table 6 Torsion Angles for Compound 5_5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
W1	N1	N2	C3	175.8(3)	C6	N4	B1	N6	-112.5(5)

Table 6 Torsion Angles for Compound 5_5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
W1	N1	N2	B1	3.2(5)	C7	N5	N6	C9	-0.8(5)
W1	N1	C1	C2	-174.7(3)	C7	N5	N6	B1	162.8(4)
W1	N3	N4	C6	176.3(3)	C7	C8	C9	N6	1.0(6)
W1	N3	N4	B1	4.7(5)	C9	N6	B1	N2	-136.0(5)
W1	N3	C4	C5	-176.4(3)	C9	N6	B1	N4	106.6(5)
W1	N5	N6	C9	-175.7(3)	C10	C11	C12	C13	52.8(6)
W1	N5	N6	B1	-12.2(5)	C11	C10	C15	N9	-164.9(4)
W1	N5	C7	C8	175.8(3)	C11	C10	C15	C14	-42.5(6)
W1	C10	C11	C12	114.0(4)	C11	C12	C13	C14	-51.2(5)
W1	C10	C15	N9	109.7(4)	C11	C12	C13	C18	68.1(5)
W1	C10	C15	C14	-127.9(4)	C12	C13	C14	N8	125.1(4)
W1	C11	C12	C13	133.3(3)	C12	C13	C14	C15	4.4(5)
N1	N2	C3	C2	0.0(5)	C12	C13	C18	C19	-122.3(4)
N1	N2	B1	N4	57.3(5)	C13	C14	C15	N9	168.9(4)
N1	N2	B1	N6	-59.1(5)	C13	C14	C15	C10	41.5(5)
N1	C1	C2	C3	-0.7(6)	C13	C18	C19	O2	178.3(4)
N2	N1	C1	C2	0.7(5)	C13	C18	C19	N8	-2.1(5)
N3	N4	C6	C5	0.6(5)	C14	N8	C17	C16	53.2(5)
N3	N4	B1	N2	-62.1(5)	C14	N8	C19	O2	-177.2(4)
N3	N4	B1	N6	57.0(5)	C14	N8	C19	C18	3.2(5)
N3	C4	C5	C6	0.9(6)	C14	C13	C18	C19	0.4(5)
N4	N3	C4	C5	-0.6(5)	C15	N9	C16	C17	61.4(5)
N5	N6	C9	C8	-0.2(5)	C15	C10	C11	W1	-118.7(4)

Table 6 Torsion Angles for Compound 5_5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N5	N6	B1	N2	64.5(5)	C15	C10	C11	C12	-4.7(6)
N5	N6	B1	N4	-52.9(5)	C16	N9	C15	C10	65.9(5)
N5	C7	C8	C9	-1.5(6)	C16	N9	C15	C14	-59.3(5)
N6	N5	C7	C8	1.4(5)	C17	N8	C14	C13	-177.7(4)
N8	C14	C15	N9	52.0(5)	C17	N8	C14	C15	-53.7(5)
N8	C14	C15	C10	-75.4(5)	C17	N8	C19	O2	-2.8(7)
N9	C16	C17	N8	-53.5(5)	C17	N8	C19	C18	177.7(4)
C1	N1	N2	C3	-0.4(5)	C18	C13	C14	N8	1.2(4)
C1	N1	N2	B1	-173.0(4)	C18	C13	C14	C15	-119.5(4)
C1	C2	C3	N2	0.4(5)	C19	N8	C14	C13	-2.9(5)
C3	N2	B1	N4	-113.7(5)	C19	N8	C14	C15	121.1(4)
C3	N2	B1	N6	129.9(5)	C19	N8	C17	C16	-121.2(5)
C4	N3	N4	C6	0.0(5)	B1	N2	C3	C2	171.9(5)
C4	N3	N4	B1	-171.6(4)	B1	N4	C6	C5	170.8(5)
C4	C5	C6	N4	-0.9(5)	B1	N6	C9	C8	-161.3(5)
C6	N4	B1	N2	128.5(5)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_5.

Atom	*x*	*y*	*z*	U(eq)
H9	2240(50)	5030(30)	4300(20)	20
H1	5380.31	7733.23	5985.92	23
H2	7527.8	7880.21	5526.03	27

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_5.

Atom	*x*	*y*	*z*	U(eq)
H3	6916.94	7591.22	3816.13	22
H4	490.63	8770.68	2926.15	20
H5	1107.66	9263.72	1533.4	25
H6	3159.89	8518.55	1453.87	22
H7	722.13	5763.33	3108.37	18
H8	1495.64	5156.71	1830.3	25
H9A	3506.08	5926.87	1724.1	21
H10	3652.01	6130.25	5407.5	18
H11	3399.31	7116.76	6314.14	15
H12A	474.13	6915.68	5746.02	20
H12B	1364.58	7300.94	6702.37	20
H13	478.51	6049	6932.08	19
H14	690.04	5073.12	6046.91	18
H15	809.46	5780.88	4784.11	19
H16A	4129.4	4912.97	5521.25	23
H16B	3589.8	4082.54	5114.51	23
H17A	2480.95	3915.89	6265.18	20
H17B	4027.95	4148.3	6784.56	20
H18A	3134.08	6494.15	7775.02	24
H18B	2197.81	5976.31	8233.22	24
H20A	2851.99	8260.98	6841.92	34
H20B	2836.89	9171.73	6697.89	34

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 5_5.

Atom	*x*	*y*	*z*	U(eq)
H20C	4036.37	8666.77	6516.07	34
H21A	3496.73	9394.93	4733.09	42
H21B	2506.7	9873.49	5177.43	42
H21C	1946.34	9532.09	4140.97	42
H22A	-229.71	8842.5	4599.18	30
H22B	332.11	9238.29	5605.5	30
H22C	-15.55	8340.77	5529.19	30
H1A	4620(40)	7270(20)	2370(30)	17(12)

Experimental

Single crystals of $C_{22}H_{33}BN_9O_2PW$ **[Compound 5_5]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker APEX-II CCD** diffractometer. The crystal was kept at 108.00 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [Compound 5_5]

Crystal Data for $C_{22}H_{33}BN_9O_2PW$ (M =681.20 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.2784(5) Å, b = 17.4183(10) Å, c = 14.9222(8) Å, β = 106.847(2)°, V = 2556.9(2) Å^3, Z = 4, T = 108.00 K, μ(Mo Kα) = 4.620 mm^{-1}, *Dcalc* = 1.770 g/cm^3, 36954 reflections measured (4.294° ≤ 2Θ ≤ 56.578°), 6337 unique (R_{int} = 0.0905, R_{sigma} = 0.0665) which were used in all calculations. The final R_1 was 0.0345 (I > 2σ(I)) and wR_2 was 0.0706 (all data).

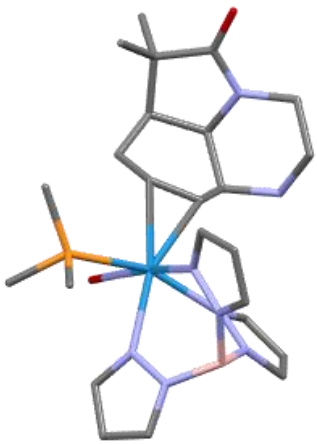
Refinement model description

Number of restraints - 1, number of constraints - unknown.
Details:

1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups, All N(H) groups
At 1.5 times of:
All C(H,H,H) groups
2. Restrained distances
N9-H9
0.87 with sigma of 0.02
3.a Ternary CH refined with riding coordinates:
C10(H10), C11(H11), C13(H13), C14(H14), C15(H15)
3.b Secondary CH2 refined with riding coordinates:
C12(H12A,H12B), C16(H16A,H16B), C17(H17A,H17B), C18(H18A,H18B)
3.c Aromatic/amide H refined with riding coordinates:
C1(H1), C2(H2), C3(H3), C4(H4), C5(H5), C6(H6), C7(H7), C8(H8), C9(H9A)
3.d Idealised Me refined as rotating group:
C20(H20A,H20B,H20C), C21(H21A,H21B,H21C), C22(H22A,H22B,H22C)

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Structure Report for Compound 5_6



A colourless, needle shaped crystal of Compound 5_6 measuring 0.04×0.059×0.169 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ld_217_x2_0m_4 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an

Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[139] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (TWINABS).
The structure was solved by dual methods with XT[140] and refined by full-matrix least-squares methods against F^2 using XL[141] within OLEX2.[142] All non-hydrogen atoms were refined with anisotropically. The N-H and B-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[143]

Refinement details for Compound 5_6
Refined as a 2-component twin on HKLF 5 data. The BASF parameter for the twin domains refined to 0.4908.

[139] *APEX5*, *Saint*, *TWINABS*; Bruker AXS Inc. 2019.
[140] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[141] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[142] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[143] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for Compound 5_6

CCDC number	
Empirical formula	$C_{24}H_{37}BN_9O_2PW$
Formula weight	709.25
Temperature [K]	106.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.04×0.059×0.169
Crystal habit	colourless needle
Crystal system	monoclinic
Space group	$P2_1/n$ (14)
a [Å]	10.3764(3)
b [Å]	22.9111(7)
c [Å]	11.7392(3)
α [°]	90
β [°]	95.6140(10)
γ [°]	90
Volume [$Å^3$]	2777.43(14)
Z	4
ρ_{calc} [gcm^{-3}]	1.696
μ [mm^{-1}]	4.257
F(000)	1416
2θ range [°]	4.33 to 54.98 (0.77 Å)
Index ranges	−13 ≤ h ≤ 13 0 ≤ k ≤ 29 0 ≤ l ≤ 15
Reflections collected	6407
Independent reflections	6407 [R_{int} = 0.0701]
Data / Restraints / Parameters	6407 / 0 / 364
Goodness-of-fit on F^2	1.042
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0313 wR_2 = 0.0655
Final *R* indexes [all data]	R_1 = 0.0374 wR_2 = 0.0679

Largest peak/hole [eÅ^{-3}]	1.67/−0.66

Table 1 Atomic coordinates and Ueq [Å2] for Compound 5_6

Atom	*x*	*y*	*z*	U_{eq}
W1	0.71588(2)	0.65421(2)	0.82498(2)	0.01183(5)
P1	0.74699(12)	0.56574(5)	0.94757(9)	0.0157(2)
O1	1.0014(3)	0.66831(17)	0.8053(3)	0.0275(9)
O2	0.5435(3)	0.51851(15)	0.3095(3)	0.0203(7)
N1	0.5065(3)	0.64873(17)	0.8516(3)	0.0122(8)
N2	0.4478(4)	0.69278(17)	0.9057(3)	0.0138(8)
N3	0.7373(4)	0.69880(16)	0.9930(3)	0.0150(8)
N4	0.6410(4)	0.73247(17)	1.0311(3)	0.0158(8)
N5	0.6664(4)	0.74664(17)	0.7833(3)	0.0152(8)
N6	0.5822(4)	0.77647(17)	0.8424(3)	0.0163(8)
N7	0.8829(4)	0.66227(17)	0.8111(3)	0.0160(8)
N8	0.6310(4)	0.60212(17)	0.3898(3)	0.0163(8)
N9	0.6258(4)	0.71267(17)	0.4818(3)	0.0172(8)
H9	0.602(5)	0.738(2)	0.536(4)	0.011(13)
C1	0.4140(4)	0.6091(2)	0.8234(4)	0.0173(9)
H1	0.427734	0.572744	0.787439	0.021
C2	0.2949(5)	0.62837(19)	0.8539(4)	0.0170(9)
H2	0.213819	0.608964	0.841954	0.020
C3	0.3204(5)	0.6819(2)	0.9053(4)	0.0152(9)
H3	0.258644	0.706768	0.935160	0.018
C4	0.8416(5)	0.7069(2)	1.0665(4)	0.0190(10)
H4	0.923603	0.689340	1.060538	0.023
C5	0.8137(5)	0.7449(2)	1.1534(4)	0.0217(11)
H5	0.870831	0.757343	1.216928	0.026
C6	0.6857(5)	0.7606(2)	1.1278(4)	0.0202(10)
H6	0.637848	0.786593	1.170673	0.024
C7	0.7194(5)	0.7858(2)	0.7165(4)	0.0186(10)
H7	0.783173	0.777060	0.666222	0.022
C8	0.6676(5)	0.8406(2)	0.7313(4)	0.0233(10)
H8	0.686663	0.875664	0.693277	0.028
C9	0.5831(5)	0.8333(2)	0.8123(4)	0.0207(10)
H9A	0.533245	0.863331	0.842542	0.025
C10	0.6462(5)	0.64016(19)	0.6451(4)	0.0132(9)
H10	0.556(5)	0.646(2)	0.640(4)	0.016
C11	0.6917(5)	0.5852(2)	0.6873(4)	0.0174(9)

H11	0.627(6)	0.559(2)	0.692(4)	0.021(14)
C12	0.8151(5)	0.5638(2)	0.6404(4)	0.0178(10)
H12A	0.830504	0.522838	0.664709	0.021
H12B	0.888729	0.587371	0.675124	0.021
C13	0.8133(5)	0.56704(19)	0.5085(3)	0.0149(9)
H13	0.905499	0.568310	0.490516	0.018
C14	0.7466(4)	0.62308(19)	0.4575(4)	0.0148(9)
H14	0.804660	0.642267	0.405566	0.018
C15	0.7073(5)	0.66853(18)	0.5461(4)	0.0152(10)
H15	0.788237	0.688557	0.578787	0.018
C16	0.5433(5)	0.6451(2)	0.3320(4)	0.0210(10)
H16A	0.464514	0.625523	0.295972	0.025
H16B	0.586286	0.665242	0.271368	0.025
C17	0.5073(5)	0.6888(2)	0.4204(4)	0.0179(10)
H17A	0.455345	0.720750	0.382235	0.021
H17B	0.454390	0.669431	0.475137	0.021
C18	0.6274(5)	0.5444(2)	0.3712(4)	0.0158(9)
C19	0.7461(5)	0.5163(2)	0.4368(4)	0.0174(10)
C20	0.7047(6)	0.4635(2)	0.5035(4)	0.0261(12)
H20A	0.781660	0.444172	0.541348	0.039
H20B	0.657293	0.436061	0.450815	0.039
H20C	0.648742	0.476271	0.561292	0.039
C21	0.8333(5)	0.4963(2)	0.3455(4)	0.0260(12)
H21A	0.856518	0.530030	0.300411	0.039
H21B	0.786861	0.467635	0.294941	0.039
H21C	0.912221	0.478480	0.383081	0.039
C22	0.7306(6)	0.4924(2)	0.8899(4)	0.0240(11)
H22A	0.647625	0.488828	0.842862	0.036
H22B	0.733945	0.464245	0.952875	0.036
H22C	0.801545	0.484586	0.842651	0.036
C23	0.9033(6)	0.5619(3)	1.0323(5)	0.0330(14)
H23A	0.972648	0.565501	0.981763	0.050
H23B	0.911145	0.524429	1.072526	0.050
H23C	0.910183	0.593808	1.088223	0.050
C24	0.6362(6)	0.5633(3)	1.0589(4)	0.0306(13)
H24A	0.643396	0.599586	1.103213	0.046
H24B	0.658538	0.530124	1.109846	0.046
H24C	0.547246	0.558773	1.023584	0.046
B1	0.5237(5)	0.7476(2)	0.9459(4)	0.0150(11)

H1A	0.465(5)	0.778(2)	0.991(4)	0.020(14)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 1 Anisotropic displacement parameters (Å^2) for Compound 5_6. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01085(8)	0.01294(8)	0.01156(8)	−0.00077(7)	0.00052(6)	0.00032(9)
P1	0.0180(6)	0.0154(6)	0.0136(5)	0.0004(4)	0.0009(5)	0.0023(5)
O1	0.0091(16)	0.037(2)	0.037(2)	−0.0042(17)	0.0076(15)	−0.0053(15)
O2	0.0191(17)	0.0198(18)	0.0214(18)	−0.0050(14)	−0.0007(14)	−0.0029(15)
N1	0.0086(18)	0.0085(18)	0.020(2)	−0.0082(16)	0.0031(14)	0.0025(15)
N2	0.016(2)	0.0137(19)	0.0113(18)	0.0003(15)	−0.0025(15)	−0.0025(16)
N3	0.0150(19)	0.0150(18)	0.0146(17)	−0.0007(14)	0.0001(15)	0.0013(17)
N4	0.017(2)	0.0152(19)	0.0156(18)	−0.0004(15)	0.0011(16)	0.0020(17)
N5	0.0128(19)	0.020(2)	0.0128(17)	−0.0009(15)	0.0002(15)	0.0002(17)
N6	0.016(2)	0.0146(19)	0.018(2)	−0.0002(15)	0.0002(16)	0.0004(16)
N7	0.028(2)	0.010(2)	0.0106(17)	−0.0049(14)	0.0052(16)	−0.0021(17)
N8	0.015(2)	0.017(2)	0.0164(18)	0.0004(15)	−0.0040(16)	0.0017(17)
N9	0.019(2)	0.0127(19)	0.0195(19)	−0.0003(16)	0.0008(17)	−0.0001(17)
C1	0.017(2)	0.015(2)	0.019(2)	0.0000(18)	0.000(2)	−0.0021(19)
C2	0.018(2)	0.009(2)	0.024(2)	0.0000(18)	0.0033(19)	−0.0017(19)
C3	0.012(2)	0.020(2)	0.014(2)	−0.0017(17)	0.0003(18)	0.005(2)
C4	0.017(2)	0.020(2)	0.020(2)	0.0000(18)	−0.002(2)	0.002(2)

C5	0.021(3)	0.028(3)	0.015(2)	−0.0103(19)	−0.0053(19)	0.000(2)
C6	0.023(3)	0.021(2)	0.016(2)	−0.0059(18)	0.001(2)	0.002(2)
C7	0.021(3)	0.022(2)	0.013(2)	0.0006(17)	−0.0019(18)	−0.003(2)
C8	0.026(3)	0.014(2)	0.029(2)	0.001(2)	−0.001(2)	−0.003(2)
C9	0.021(2)	0.012(2)	0.028(3)	−0.0004(19)	−0.005(2)	0.0012(19)
C10	0.012(2)	0.014(2)	0.014(2)	−0.0025(16)	0.0016(17)	−0.0029(17)
C11	0.016(2)	0.020(2)	0.016(2)	−0.0009(18)	0.002(2)	−0.003(2)
C12	0.019(3)	0.016(2)	0.018(2)	−0.0059(18)	−0.0003(18)	0.004(2)
C13	0.015(2)	0.014(2)	0.015(2)	−0.0046(17)	0.0002(18)	−0.0001(19)
C14	0.014(2)	0.017(2)	0.013(2)	−0.0021(16)	0.0020(18)	−0.0038(19)
C15	0.018(3)	0.012(2)	0.016(2)	−0.0006(16)	0.0003(18)	−0.0031(18)
C16	0.026(2)	0.016(2)	0.019(2)	0.001(2)	−0.005(2)	0.003(2)
C17	0.021(3)	0.015(2)	0.017(2)	0.0028(19)	−0.0003(19)	0.004(2)
C18	0.013(2)	0.022(2)	0.014(2)	−0.0006(18)	0.0069(17)	−0.004(2)
C19	0.017(2)	0.017(2)	0.018(2)	−0.0045(17)	0.0016(19)	0.000(2)
C20	0.035(3)	0.017(2)	0.025(2)	0.0030(19)	−0.005(2)	0.000(2)
C21	0.024(3)	0.033(3)	0.021(2)	−0.013(2)	0.004(2)	0.004(2)
C22	0.036(3)	0.016(2)	0.020(2)	0.0000(18)	−0.002(2)	−0.001(2)
C23	0.029(3)	0.026(3)	0.041(3)	0.003(3)	−0.013(3)	0.001(3)
C24	0.039(3)	0.032(3)	0.023(3)	0.009(2)	0.014(2)	0.011(3)
B1	0.015(2)	0.013(3)	0.017(3)	−0.004(2)	0.000(2)	−0.004(2)

Table 1 Bond lengths and angles for	**Length [Å]**

Compound 5_6**Atom–Atom**	
W1–P1	2.4885(12)
W1–N1	2.229(4)
W1–N3	2.213(3)
W1–N5	2.222(4)
W1–N7	1.766(4)
W1–C10	2.188(4)
W1–C11	2.258(5)
P1–C22	1.813(5)
P1–C23	1.820(6)
P1–C24	1.824(5)
O1–N7	1.246(5)
O2–C18	1.229(6)
N1–N2	1.367(5)
N1–C1	1.340(6)
N2–C3	1.344(6)
N2–B1	1.533(6)
N3–N4	1.372(5)
N3–C4	1.330(6)
N4–C6	1.348(6)
N4–B1	1.538(7)
N5–N6	1.353(5)
N5–C7	1.344(6)
N6–C9	1.350(6)
N6–B1	1.557(6)
N8–C14	1.453(6)
N8–C16	1.463(6)
N8–C18	1.341(6)
N9–H9	0.91(5)
N9–C15	1.477(6)
N9–C17	1.469(6)
C1–H1	0.9500
C1–C2	1.391(7)
C2–H2	0.9500
C2–C3	1.381(6)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.392(7)

C5–H5	0.9500
C5–C6	1.381(7)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.383(7)
C8–H8	0.9500
C8–C9	1.365(7)
C9–H9A	0.9500
C10–H10	0.94(5)
C10–C11	1.418(6)
C10–C15	1.523(6)
C11–H11	0.91(6)
C11–C12	1.522(7)
C12–H12A	0.9900
C12–H12B	0.9900
C12–C13	1.549(6)
C13–H13	1.0000
C13–C14	1.551(6)
C13–C19	1.559(6)
C14–H14	1.0000
C14–C15	1.554(6)
C15–H15	1.0000
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.514(7)
C17–H17A	0.9900
C17–H17B	0.9900
C18–C19	1.529(7)
C19–C20	1.526(7)
C19–C21	1.539(6)
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800

C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
B1–H1A	1.10(5)
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	86.90(11)
N1–W1–C11	91.13(16)
N3–W1–P1	82.22(10)
N3–W1–N1	85.14(14)
N3–W1–N5	75.93(13)
N3–W1–C11	162.92(15)
N5–W1–P1	156.57(10)
N5–W1–N1	82.95(15)
N5–W1–C11	120.21(15)
N7–W1–P1	93.76(13)
N7–W1–N1	176.11(15)
N7–W1–N3	91.15(16)
N7–W1–N5	95.03(16)
N7–W1–C10	99.25(17)
N7–W1–C11	92.77(17)
C10–W1–P1	116.76(12)
C10–W1–N1	83.84(16)
C10–W1–N3	157.37(16)
C10–W1–N5	83.13(15)
C10–W1–C11	37.15(16)
C11–W1–P1	80.93(12)
C22–P1–W1	122.44(16)
C22–P1–C23	101.9(3)
C22–P1–C24	101.3(3)
C23–P1–W1	114.4(2)
C23–P1–C24	101.4(3)
C24–P1–W1	112.62(18)
N2–N1–W1	120.6(3)
C1–N1–W1	133.5(3)

C1–N1–N2	105.9(4)
N1–N2–B1	120.6(4)
C3–N2–N1	110.1(4)
C3–N2–B1	128.9(4)
N4–N3–W1	122.5(3)
C4–N3–W1	130.4(3)
C4–N3–N4	106.4(4)
N3–N4–B1	118.0(4)
C6–N4–N3	110.0(4)
C6–N4–B1	128.7(4)
N6–N5–W1	121.0(3)
C7–N5–W1	131.7(3)
C7–N5–N6	106.5(4)
N5–N6–B1	120.4(4)
C9–N6–N5	109.4(4)
C9–N6–B1	128.8(4)
O1–N7–W1	177.8(3)
C14–N8–C16	118.3(4)
C18–N8–C14	115.1(4)
C18–N8–C16	125.6(4)
C15–N9–H9	105(3)
C17–N9–H9	108(3)
C17–N9–C15	113.9(4)
N1–C1–H1	124.7
N1–C1–C2	110.7(4)
C2–C1–H1	124.7
C1–C2–H2	127.5
C3–C2–C1	104.9(4)
C3–C2–H2	127.5
N2–C3–C2	108.2(4)
N2–C3–H3	125.9
C2–C3–H3	125.9
N3–C4–H4	124.8
N3–C4–C5	110.4(4)
C5–C4–H4	124.8
C4–C5–H5	127.2
C6–C5–C4	105.6(4)
C6–C5–H5	127.2
N4–C6–C5	107.6(4)

N4–C6–H6	126.2
C5–C6–H6	126.2
N5–C7–H7	124.9
N5–C7–C8	110.2(4)
C8–C7–H7	124.9
C7–C8–H8	127.4
C9–C8–C7	105.1(4)
C9–C8–H8	127.4
N6–C9–C8	108.7(4)
N6–C9–H9A	125.6
C8–C9–H9A	125.6
W1–C10–H10	106(3)
C11–C10–W1	74.1(3)
C11–C10–H10	116(3)
C11–C10–C15	119.8(4)
C15–C10–W1	123.4(3)
C15–C10–H10	112(3)
W1–C11–H11	117(3)
C10–C11–W1	68.7(3)
C10–C11–H11	113(4)
C10–C11–C12	115.0(4)
C12–C11–W1	116.5(3)
C12–C11–H11	117(3)
C11–C12–H12A	108.6
C11–C12–H12B	108.6
C11–C12–C13	114.7(4)
H12A–C12–H12B	107.6
C13–C12–H12A	108.6
C13–C12–H12B	108.6
C12–C13–H13	107.1
C12–C13–C14	112.7(4)
C12–C13–C19	117.7(4)
C14–C13–H13	107.1
C14–C13–C19	104.4(3)
C19–C13–H13	107.1
N8–C14–C13	104.5(3)
N8–C14–H14	109.0
N8–C14–C15	109.3(4)
C13–C14–H14	109.0

C13–C14–C15	115.6(3)
C15–C14–H14	109.0
N9–C15–C10	115.0(4)
N9–C15–C14	106.9(3)
N9–C15–H15	107.4
C10–C15–C14	112.4(3)
C10–C15–H15	107.4
C14–C15–H15	107.4
N8–C16–H16A	110.1
N8–C16–H16B	110.1
N8–C16–C17	108.1(4)
H16A–C16–H16B	108.4
C17–C16–H16A	110.1
C17–C16–H16B	110.1
N9–C17–C16	109.4(4)
N9–C17–H17A	109.8
N9–C17–H17B	109.8
C16–C17–H17A	109.8
C16–C17–H17B	109.8
H17A–C17–H17B	108.2
O2–C18–N8	125.4(5)
O2–C18–C19	125.7(4)
N8–C18–C19	108.9(4)
C18–C19–C13	104.7(4)
C18–C19–C21	106.0(4)
C20–C19–C13	116.6(4)
C20–C19–C18	109.8(4)
C20–C19–C21	109.6(4)
C21–C19–C13	109.6(4)
C19–C20–H20A	109.5
C19–C20–H20B	109.5
C19–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
C19–C21–H21A	109.5
C19–C21–H21B	109.5
C19–C21–H21C	109.5
H21A–C21–H21B	109.5

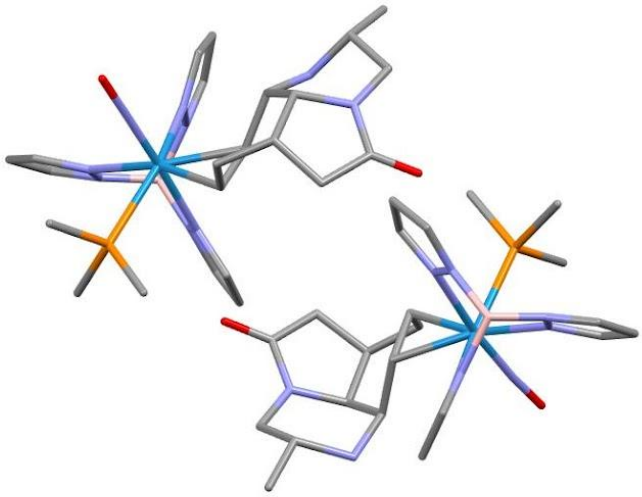
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
N2–B1–N4	111.4(4)
N2–B1–N6	109.6(4)
N2–B1–H1A	112(3)
N4–B1–N6	105.0(4)
N4–B1–H1A	106(3)
N6–B1–H1A	112(3)

Table 1 Torsion angles for Compound 5_6 **Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	175.9(3)
W1–N1–N2–B1	1.8(5)
W1–N1–C1–C2	−176.1(3)
W1–N3–N4–C6	−171.6(3)
W1–N3–N4–B1	−10.2(5)
W1–N3–C4–C5	171.1(3)

W1–N5–N6–C9	171.1(3)
W1–N5–N6–B1	3.4(5)
W1–N5–C7–C8	−170.7(3)
W1–C10–C11–C12	−110.3(4)
W1–C10–C15–N9	−111.6(4)
W1–C10–C15–C14	125.8(4)
W1–C11–C12–C13	−126.7(3)
O2–C18–C19–C13	−175.5(4)
O2–C18–C19–C20	−49.6(6)
O2–C18–C19–C21	68.7(6)
N1–N2–C3–C2	2.4(5)
N1–N2–B1–N4	−59.2(5)
N1–N2–B1–N6	56.7(5)
N1–C1–C2–C3	−1.4(5)
N2–N1–C1–C2	2.8(5)
N3–N4–C6–C5	−0.1(6)
N3–N4–B1–N2	63.7(5)
N3–N4–B1–N6	−54.9(5)
N3–C4–C5–C6	−1.0(6)
N4–N3–C4–C5	1.0(5)
N5–N6–C9–C8	0.9(5)
N5–N6–B1–N2	−60.2(5)
N5–N6–B1–N4	59.6(5)
N5–C7–C8–C9	1.5(5)
N6–N5–C7–C8	−1.0(5)
N8–C14–C15–N9	−52.5(5)
N8–C14–C15–C10	74.5(5)
N8–C16–C17–N9	53.5(5)
N8–C18–C19–C13	6.0(5)
N8–C18–C19–C20	131.9(4)
N8–C18–C19–C21	−109.9(4)
C1–N1–N2–C3	−3.2(5)
C1–N1–N2–B1	−177.3(4)
C1–C2–C3–N2	−0.6(5)
C3–N2–B1–N4	128.0(5)
C3–N2–B1–N6	−116.1(5)
C4–N3–N4–C6	−0.5(5)
C4–N3–N4–B1	160.9(4)
C4–C5–C6–N4	0.7(6)

C6–N4–B1–N2	−138.9(5)
C6–N4–B1–N6	102.5(5)
C7–N5–N6–C9	0.0(5)
C7–N5–N6–B1	−167.7(4)
C7–C8–C9–N6	−1.4(5)
C9–N6–B1–N2	134.7(5)
C9–N6–B1–N4	−105.4(5)
C10–C11–C12–C13	−49.1(6)
C11–C10–C15–N9	158.4(4)
C11–C10–C15–C14	35.8(6)
C11–C12–C13–C14	39.4(6)
C11–C12–C13–C19	−82.3(5)
C12–C13–C14–N8	−113.9(4)
C12–C13–C14–C15	6.3(6)
C12–C13–C19–C18	113.0(4)
C12–C13–C19–C20	−8.5(6)
C12–C13–C19–C21	−133.7(4)
C13–C14–C15–N9	−170.1(4)
C13–C14–C15–C10	−43.0(5)
C14–N8–C16–C17	−53.8(6)
C14–N8–C18–O2	−174.3(4)
C14–N8–C18–C19	4.2(5)
C14–C13–C19–C18	−12.9(4)
C14–C13–C19–C20	−134.4(4)
C14–C13–C19–C21	100.4(4)
C15–N9–C17–C16	−62.1(5)
C15–C10–C11–W1	119.8(4)
C15–C10–C11–C12	9.5(6)
C16–N8–C14–C13	178.3(4)
C16–N8–C14–C15	53.9(5)
C16–N8–C18–O2	−6.1(8)
C16–N8–C18–C19	172.4(4)
C17–N9–C15–C10	−65.3(5)
C17–N9–C15–C14	60.2(5)
C18–N8–C14–C13	−12.6(5)
C18–N8–C14–C15	−137.0(4)
C18–N8–C16–C17	138.4(5)
C19–C13–C14–N8	15.0(4)
C19–C13–C14–C15	135.3(4)

B1–N2–C3–C2	175.8(4)
B1–N4–C6–C5	−159.0(5)
B1–N6–C9–C8	167.3(4)



Structure Report for Compound 5.8

A colourless, needle shaped crystal of Compound 5.8

measuring 0.052×0.096×0.115 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ps_7_229_x2_0m were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo Kα, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.144 All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

[144] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.

The structure was solved by dual methods with SHELXT145 and refined by full-matrix least-squares methods against F2 using XL146 within OLEX2.147 All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms as well as the H atoms on the carbons bound directly to W were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[148]

[145] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[146] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[147] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[148] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for Compound 5.8

CCDC number	
Empirical formula	C23H35BN9O2PW
Formula weight	695.23
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm3]	0.052×0.096×0.115
Crystal habit	colourless needle
Crystal system	monoclinic
Space group	$P2_1$ (4)
a [Å]	8.5048(4)
b [Å]	28.6885(10)
c [Å]	11.0890(3)
α [°]	90
β [°]	94.1170(10)
γ [°]	90
Volume [Å3]	2698.62(17)
Z	4
ρcalc [gcm−3]	1.711
μ [mm−1]	4.379
F(000)	1384
2θ range [°]	3.95 to 56.67 (0.75 Å)
Index ranges	−11 ≤ h ≤ 11 −38 ≤ k ≤ 38 −14 ≤ l ≤ 14
Reflections collected	86623
Independent reflections	13427 [Rint = 0.0691]
Data / Restraints / Parameters	13427 / 1 / 705
Goodness-of-fit on F2	1.025
Final R indexes [I≥2σ(I)]	R1 = 0.0319 wR2 = 0.0682

Final R indexes [all data]	R1 = 0.0368 wR2 = 0.0702
Largest peak/hole [eÅ−3]	1.35/−0.55
Flack X parameter	-0.002(5)

Table 2 Atomic coordinates and Ueq [Å2] for Compound 5.8

Atom	x	y	z	Ueq
W1	0.95938(3)	0.35506(2)	0.80255(2)	0.01631(7)
P1	0.7697(3)	0.31200(8)	0.92429(18)	0.0228(4)
O1	1.0906(8)	0.2674(2)	0.7028(6)	0.0337(15)
O2	0.5024(8)	0.4362(2)	0.3209(6)	0.0392(16)
N1	0.8674(8)	0.4197(2)	0.8864(6)	0.0214(14)
N2	0.9667(8)	0.4489(2)	0.9521(5)	0.0203(13)
N3	1.1137(7)	0.3527(3)	0.9718(5)	0.0182(12)
N4	1.1733(8)	0.3924(2)	1.0262(6)	0.0212(15)
N5	1.1627(8)	0.3996(2)	0.7655(6)	0.0206(14)
N6	1.2082(7)	0.4358(2)	0.8399(6)	0.0208(13)
N7	1.0367(8)	0.3037(3)	0.7434(6)	0.0224(14)
N8	0.9915(9)	0.4240(2)	0.4700(6)	0.0272(15)
H8	1.094(11)	0.423(3)	0.493(8)	0.02(2)
N9	0.7371(9)	0.3979(3)	0.3448(6)	0.0246(15)
C1	0.7243(10)	0.4372(3)	0.8892(8)	0.031(2)
H1	0.631303	0.423667	0.851544	0.038
C2	0.7298(12)	0.4786(3)	0.9557(8)	0.034(2)
H2	0.643865	0.498450	0.970631	0.041
C3	0.8814(11)	0.4846(3)	0.9939(8)	0.0270(18)
H3	0.922482	0.509676	1.042413	0.032
C4	1.1846(11)	0.3172(3)	1.0311(8)	0.027(2)
H4	1.166323	0.285222	1.012608	0.032
C5	1.2894(11)	0.3336(4)	1.1241(8)	0.028(2)
H5	1.353426	0.315476	1.179999	0.034
C6	1.2809(11)	0.3810(3)	1.1179(8)	0.027(2)
H6	1.339817	0.402300	1.168835	0.032
C7	1.2608(10)	0.3996(3)	0.6773(8)	0.0242(18)
H7	1.258244	0.377572	0.613114	0.029
C8	1.3672(10)	0.4362(3)	0.6919(8)	0.0292(19)
H8A	1.448294	0.444127	0.641053	0.035

C9	1.3301(9)	0.4583(3)	0.7958(8)	0.0274(18)
H9	1.381736	0.484986	0.830459	0.033
C10	0.8646(10)	0.3859(3)	0.6309(7)	0.0239(17)
H10	0.852(11)	0.421(3)	0.637(8)	0.029
C11	0.7479(9)	0.3547(3)	0.6716(6)	0.0213(14)
H11	0.665(11)	0.365(3)	0.704(8)	0.03(3)
C12	0.7092(11)	0.3137(3)	0.5872(7)	0.0252(19)
H12A	0.616639	0.296697	0.614084	0.030
H12B	0.799542	0.291895	0.589744	0.030
C13	0.6732(10)	0.3315(3)	0.4565(7)	0.0252(19)
H13	0.652698	0.304048	0.402261	0.030
C14	0.8129(9)	0.3594(3)	0.4114(6)	0.0225(15)
H14	0.869590	0.339522	0.354355	0.027
C15	0.9337(10)	0.3787(3)	0.5111(7)	0.0234(16)
H15	1.024495	0.356578	0.522252	0.028
C16	1.0016(10)	0.4275(3)	0.3389(7)	0.0267(17)
H16	1.051583	0.398848	0.307194	0.032
C17	0.8320(11)	0.4319(3)	0.2867(8)	0.035(2)
H17A	0.792185	0.463682	0.300907	0.042
H17B	0.826216	0.426242	0.198373	0.042
C18	0.5838(10)	0.4038(3)	0.3623(7)	0.0271(18)
C19	0.5322(10)	0.3647(3)	0.4400(7)	0.030(2)
H19A	0.439819	0.348462	0.400144	0.036
H19B	0.503484	0.376702	0.519166	0.036
C20	1.0973(11)	0.4708(3)	0.3109(8)	0.036(2)
H20A	1.093843	0.475445	0.223194	0.054
H20B	1.206877	0.466633	0.342691	0.054
H20C	1.052370	0.498134	0.348877	0.054
C21	0.5585(11)	0.3117(4)	0.8847(9)	0.043(2)
H21A	0.504949	0.294920	0.946942	0.065
H21B	0.537121	0.296106	0.806544	0.065
H21C	0.519613	0.343811	0.879175	0.065
C22	0.7727(12)	0.3311(4)	1.0805(7)	0.036(2)
H22A	0.736994	0.363554	1.083183	0.054
H22B	0.880261	0.328787	1.118013	0.054
H22C	0.702355	0.311326	1.124495	0.054
C23	0.8078(12)	0.2501(3)	0.9384(9)	0.042(3)
H23A	0.919194	0.245043	0.964017	0.064
H23B	0.782908	0.234917	0.860222	0.064

H23C	0.741902	0.236808	0.998746	0.064
B1	1.1419(11)	0.4397(3)	0.9658(8)	0.0227(18)
H1A	1.210(9)	0.466(3)	1.017(7)	0.02(2)
W2	0.51297(3)	0.64975(2)	0.71330(2)	0.01667(7)
P2	0.7239(2)	0.68611(7)	0.59872(17)	0.0214(4)
O3	0.4091(9)	0.7447(2)	0.7890(6)	0.0353(15)
O4	0.9612(8)	0.5719(2)	1.1753(6)	0.0373(15)
N10	0.5893(7)	0.5822(2)	0.6323(5)	0.0183(13)
N11	0.4919(8)	0.5589(2)	0.5493(5)	0.0199(13)
N12	0.3666(8)	0.6579(2)	0.5416(6)	0.0188(14)
N13	0.3016(8)	0.6218(2)	0.4752(6)	0.0211(14)
N14	0.3049(8)	0.6049(2)	0.7401(5)	0.0187(13)
N15	0.2468(7)	0.5744(2)	0.6529(6)	0.0212(13)
N16	0.4500(8)	0.7049(2)	0.7621(6)	0.0218(14)
N17	0.4147(8)	0.6178(2)	1.0726(6)	0.0245(14)
H17	0.383(12)	0.634(4)	1.134(9)	0.05(3)
N18	0.7334(9)	0.6135(2)	1.1544(6)	0.0244(15)
C24	0.7259(9)	0.5588(3)	0.6373(7)	0.0244(17)
H24	0.816932	0.567019	0.687450	0.029
C25	0.7166(11)	0.5208(3)	0.5590(8)	0.0289(19)
H25	0.796580	0.498601	0.545846	0.035
C26	0.5675(10)	0.5224(3)	0.5054(7)	0.0246(17)
H26	0.524134	0.501012	0.446561	0.029
C27	0.3093(10)	0.6972(3)	0.4894(7)	0.0208(17)
H27	0.334521	0.727955	0.515957	0.025
C28	0.2050(11)	0.6855(3)	0.3882(7)	0.0271(19)
H28	0.148345	0.706387	0.334609	0.033
C29	0.2034(10)	0.6384(3)	0.3844(7)	0.0247(19)
H29	0.142901	0.619975	0.326985	0.030
C30	0.2155(10)	0.5977(3)	0.8341(8)	0.0285(19)
H30	0.227796	0.613996	0.908810	0.034
C31	0.1043(9)	0.5638(3)	0.8076(8)	0.0291(18)
H31	0.027585	0.552344	0.858318	0.035
C32	0.1282(9)	0.5503(3)	0.6929(7)	0.0249(17)
H32	0.069015	0.527183	0.648342	0.030
C33	0.5845(9)	0.6255(3)	0.8970(7)	0.0205(16)
H33	0.594(10)	0.590(3)	0.892(7)	0.02(2)
C34	0.7186(8)	0.6476(3)	0.8486(6)	0.0190(14)
H34	0.806(12)	0.631(4)	0.832(9)	0.05(3)

C35	0.7763(10)	0.6911(3)	0.9163(7)	0.0229(18)
H35A	0.872438	0.702800	0.881124	0.027
H35B	0.694534	0.715631	0.906416	0.027
C36	0.8127(10)	0.6814(3)	1.0501(7)	0.0232(17)
H36	0.835339	0.711564	1.093123	0.028
C37	0.6697(9)	0.6575(3)	1.1040(6)	0.0228(17)
H37	0.633155	0.677240	1.170886	0.027
C38	0.5291(8)	0.6470(3)	1.0129(6)	0.0205(14)
H38	0.476348	0.677297	0.990756	0.025
C39	0.4851(10)	0.5726(3)	1.1203(7)	0.0252(18)
H39	0.517842	0.554044	1.049947	0.030
C40	0.6292(11)	0.5806(3)	1.2055(7)	0.0286(18)
H40A	0.596648	0.592653	1.283551	0.034
H40B	0.685113	0.550710	1.221031	0.034
C41	0.8868(10)	0.6066(3)	1.1400(7)	0.0246(17)
C42	0.9508(9)	0.6478(4)	1.0783(7)	0.0288(16)
H42A	0.996957	0.638169	1.002718	0.035
H42B	1.034004	0.663115	1.131437	0.035
C43	0.3596(11)	0.5453(3)	1.1798(8)	0.0304(19)
H43A	0.332459	0.561418	1.253377	0.046
H43B	0.399553	0.514034	1.200808	0.046
H43C	0.265446	0.542607	1.123865	0.046
C44	0.7032(12)	0.6763(4)	0.4363(7)	0.043(3)
H44A	0.704834	0.642752	0.419982	0.064
H44B	0.790496	0.691408	0.398462	0.064
H44C	0.602962	0.689499	0.403050	0.064
C45	0.9304(10)	0.6707(3)	0.6293(8)	0.034(2)
H45A	0.962651	0.677235	0.714306	0.052
H45B	0.994954	0.689217	0.577319	0.052
H45C	0.944865	0.637519	0.612904	0.052
C46	0.7310(12)	0.7497(3)	0.6087(9)	0.038(2)
H46A	0.626617	0.762579	0.584575	0.057
H46B	0.807918	0.761721	0.554718	0.057
H46C	0.762125	0.759027	0.692024	0.057
B2	0.3174(11)	0.5725(3)	0.5289(8)	0.0222(18)
H2A	0.257(10)	0.551(3)	0.464(7)	0.027

Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

Table 3 Anisotropic displacement parameters (Å2) for Compound 5.8

. The anisotropic displacement factor exponent takes the form:
−2π2[h2(a*)2U11 + k2(b*)2U22 + ... + 2hka*b*U12]

Atom	U11	U22	U33	U23	U13	U12
W1	0.01894(14)	0.01468(14)	0.01513(12)	−0.00039(11)	0.00001(10)	0.00054(12)
P1	0.0247(11)	0.0225(11)	0.0217(9)	−0.0033(8)	0.0052(8)	−0.0034(8)
O1	0.040(4)	0.018(3)	0.043(4)	−0.011(3)	0.005(3)	0.010(3)
O2	0.039(4)	0.024(4)	0.052(4)	−0.007(3)	−0.011(3)	0.007(3)
N1	0.022(3)	0.018(3)	0.025(3)	−0.004(3)	−0.001(3)	0.004(3)
N2	0.023(3)	0.016(3)	0.022(3)	−0.002(3)	0.000(2)	0.000(3)
N3	0.023(3)	0.013(3)	0.018(3)	−0.002(3)	−0.002(2)	0.001(3)
N4	0.018(3)	0.022(4)	0.022(3)	−0.003(3)	−0.006(3)	−0.003(3)
N5	0.026(4)	0.016(3)	0.020(3)	−0.002(3)	0.002(3)	0.001(3)
N6	0.017(3)	0.015(3)	0.029(3)	0.003(3)	−0.005(3)	−0.004(2)
N7	0.021(3)	0.029(4)	0.017(3)	0.003(3)	−0.002(2)	−0.003(3)
N8	0.030(4)	0.028(4)	0.023(3)	0.000(3)	−0.003(3)	−0.004(3)
N9	0.029(4)	0.020(4)	0.024(3)	−0.001(3)	−0.001(3)	0.000(3)
C1	0.024(4)	0.033(5)	0.036(5)	−0.009(4)	−0.006(4)	0.007(4)
C2	0.039(5)	0.024(5)	0.039(5)	−0.010(4)	−0.003(4)	0.015(4)
C3	0.037(5)	0.015(4)	0.030(4)	−0.004(3)	0.003(4)	0.001(3)
C4	0.028(5)	0.024(5)	0.028(4)	0.002(4)	0.001(4)	−0.002(4)
C5	0.029(5)	0.033(5)	0.022(4)	0.009(4)	−0.004(3)	0.003(4)
C6	0.031(5)	0.029(5)	0.021(4)	−0.001(3)	−0.003(3)	−0.002(4)
C7	0.024(4)	0.026(4)	0.023(4)	0.007(3)	0.001(3)	0.005(3)
C8	0.019(4)	0.036(5)	0.033(4)	0.009(4)	0.004(3)	0.001(3)
C9	0.017(4)	0.024(4)	0.041(5)	0.005(3)	−0.001(3)	0.001(3)
C10	0.034(5)	0.020(4)	0.017(3)	−0.003(3)	−0.005(3)	−0.002(3)
C11	0.024(4)	0.018(3)	0.022(3)	0.000(4)	0.001(3)	0.003(4)
C12	0.028(5)	0.023(5)	0.025(4)	−0.001(3)	0.001(3)	−0.004(4)
C13	0.027(5)	0.024(4)	0.024(4)	−0.005(3)	−0.004(3)	−0.010(3)
C14	0.028(4)	0.018(4)	0.020(3)	−0.001(3)	−0.001(3)	0.001(3)
C15	0.023(4)	0.021(4)	0.025(4)	0.005(3)	−0.004(3)	0.000(3)
C16	0.033(5)	0.022(4)	0.026(4)	−0.003(3)	0.007(3)	−0.002(3)
C17	0.034(5)	0.034(5)	0.037(5)	0.007(4)	−0.007(4)	−0.006(4)
C18	0.030(4)	0.025(4)	0.025(4)	−0.010(3)	−0.005(3)	0.001(4)
C19	0.026(4)	0.038(6)	0.025(4)	0.001(3)	−0.005(3)	−0.003(4)
C20	0.041(5)	0.032(5)	0.034(4)	0.011(4)	0.001(4)	−0.007(4)
C21	0.027(5)	0.056(7)	0.048(5)	0.004(5)	0.006(4)	−0.007(4)

C22	0.046(6)	0.042(6)	0.020(4)	−0.003(4)	0.007(4)	−0.016(4)
C23	0.055(7)	0.022(5)	0.052(6)	−0.003(4)	0.017(5)	−0.007(5)
B1	0.022(4)	0.017(4)	0.029(4)	−0.004(4)	−0.001(4)	−0.004(3)
W2	0.01830(14)	0.01537(15)	0.01614(12)	−0.00028(12)	−0.00007(10)	0.00071(12)
P2	0.0251(11)	0.0204(10)	0.0190(9)	−0.0026(8)	0.0022(8)	−0.0044(8)
O3	0.052(4)	0.018(3)	0.036(3)	−0.008(3)	0.004(3)	0.011(3)
O4	0.032(4)	0.032(4)	0.045(4)	0.001(3)	−0.012(3)	0.006(3)
N10	0.018(3)	0.019(3)	0.018(3)	−0.002(2)	0.000(2)	−0.002(3)
N11	0.020(3)	0.017(3)	0.023(3)	−0.002(3)	0.000(2)	−0.002(3)
N12	0.023(3)	0.011(4)	0.022(3)	0.001(2)	0.002(3)	−0.001(3)
N13	0.026(4)	0.016(3)	0.021(3)	0.002(3)	−0.001(3)	0.003(3)
N14	0.017(3)	0.022(4)	0.017(3)	0.003(3)	0.001(2)	0.001(3)
N15	0.019(3)	0.019(3)	0.026(3)	0.002(3)	0.000(3)	0.003(3)
N16	0.026(4)	0.019(4)	0.020(3)	0.000(3)	0.001(3)	0.004(3)
N17	0.027(4)	0.028(4)	0.019(3)	0.001(3)	0.003(3)	0.001(3)
N18	0.028(4)	0.021(4)	0.024(3)	0.006(3)	−0.002(3)	−0.001(3)
C24	0.015(4)	0.028(4)	0.030(4)	−0.001(4)	−0.004(3)	−0.003(3)
C25	0.029(5)	0.020(4)	0.037(5)	−0.007(4)	0.001(4)	0.004(3)
C26	0.026(4)	0.019(4)	0.028(4)	−0.004(3)	0.001(3)	0.002(3)
C27	0.025(4)	0.018(4)	0.019(4)	0.006(3)	−0.003(3)	0.009(3)
C28	0.031(5)	0.032(5)	0.019(4)	0.002(3)	−0.001(3)	0.000(4)
C29	0.026(4)	0.028(5)	0.019(3)	−0.002(3)	−0.009(3)	0.005(3)
C30	0.024(4)	0.040(5)	0.022(4)	0.001(4)	0.001(3)	0.005(4)
C31	0.016(4)	0.034(5)	0.037(4)	0.008(4)	0.001(3)	0.003(3)
C32	0.016(4)	0.018(4)	0.039(4)	0.006(3)	−0.005(3)	0.003(3)
C33	0.026(4)	0.017(4)	0.019(3)	−0.003(3)	0.000(3)	−0.001(3)
C34	0.020(3)	0.019(4)	0.018(3)	0.001(4)	−0.001(3)	−0.002(4)
C35	0.026(4)	0.024(5)	0.018(4)	−0.001(3)	−0.004(3)	−0.005(3)
C36	0.030(5)	0.016(4)	0.023(4)	−0.002(3)	−0.005(3)	0.001(3)
C37	0.033(4)	0.019(4)	0.016(3)	−0.003(3)	−0.002(3)	0.003(3)
C38	0.025(4)	0.021(4)	0.016(3)	0.003(3)	0.000(3)	0.004(4)
C39	0.035(5)	0.023(4)	0.018(3)	0.002(3)	0.003(3)	−0.007(3)
C40	0.042(5)	0.019(4)	0.023(4)	0.004(3)	−0.005(4)	−0.004(4)
C41	0.025(4)	0.022(4)	0.026(4)	−0.007(3)	−0.008(3)	−0.002(3)
C42	0.028(4)	0.032(4)	0.026(3)	0.001(4)	−0.003(3)	−0.003(4)
C43	0.036(5)	0.024(4)	0.032(4)	−0.001(3)	0.003(4)	−0.002(4)
C44	0.043(6)	0.060(7)	0.026(4)	−0.003(4)	0.013(4)	−0.020(5)
C45	0.029(5)	0.037(5)	0.038(5)	0.006(4)	0.007(4)	−0.005(4)

C46	0.048(6)	0.019(5)	0.048(5)	0.005(4)	0.011(5)	−0.004(4)
B2	0.019(4)	0.022(5)	0.025(4)	0.002(3)	−0.006(3)	−0.006(3)

Table 4 Bond lengths and angles for Compound 5.8 –Atom	Length [Å]
W1–P1	2.503(2)
W1–N1	2.240(6)
W1–N3	2.213(6)
W1–N5	2.212(7)
W1–N7	1.760(7)
W1–C10	2.199(8)
W1–C11	2.229(7)
P1–C21	1.819(10)
P1–C22	1.815(8)
P1–C23	1.810(10)
O1–N7	1.235(9)
O2–C18	1.229(11)
N1–N2	1.364(9)
N1–C1	1.320(11)
N2–C3	1.354(10)
N2–B1	1.511(11)
N3–N4	1.369(10)
N3–C4	1.333(12)
N4–C6	1.358(11)
N4–B1	1.527(11)
N5–N6	1.366(9)
N5–C7	1.330(10)
N6–C9	1.343(10)
N6–B1	1.547(11)
N8–H8	0.89(9)
N8–C15	1.473(10)
N8–C16	1.465(10)
N9–C14	1.454(11)
N9–C17	1.446(11)
N9–C18	1.342(11)
C1–H1	0.9500
C1–C2	1.398(12)
C2–H2	0.9500
C2–C3	1.339(13)
C3–H3	0.9500

C4–H4	0.9500
C4–C5	1.395(13)
C5–H5	0.9500
C5–C6	1.364(12)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.388(12)
C8–H8A	0.9500
C8–C9	1.372(12)
C9–H9	0.9500
C10–H10	1.01(10)
C10–C11	1.435(12)
C10–C15	1.505(11)
C11–H11	0.87(9)
C11–C12	1.523(12)
C12–H12A	0.9900
C12–H12B	0.9900
C12–C13	1.546(12)
C13–H13	1.0000
C13–C14	1.544(11)
C13–C19	1.531(13)
C14–H14	1.0000
C14–C15	1.557(11)
C15–H15	1.0000
C16–H16	1.0000
C16–C17	1.521(12)
C16–C20	1.531(12)
C17–H17A	0.9900
C17–H17B	0.9900
C18–C19	1.499(12)
C19–H19A	0.9900
C19–H19B	0.9900
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800

C23–H23B	0.9800
C23–H23C	0.9800
B1–H1A	1.09(8)
W2–P2	2.500(2)
W2–N10	2.252(6)
W2–N12	2.211(7)
W2–N14	2.224(7)
W2–N16	1.768(7)
W2–C33	2.197(8)
W2–C34	2.222(7)
P2–C44	1.819(8)
P2–C45	1.819(9)
P2–C46	1.830(9)
O3–N16	1.236(9)
O4–C41	1.229(10)
N10–N11	1.367(9)
N10–C24	1.339(10)
N11–C26	1.340(10)
N11–B2	1.536(11)
N12–N13	1.364(9)
N12–C27	1.342(10)
N13–C29	1.348(10)
N13–B2	1.536(11)
N14–N15	1.372(9)
N14–C30	1.349(10)
N15–C32	1.325(10)
N15–B2	1.541(10)
N17–H17	0.89(10)
N17–C38	1.476(10)
N17–C39	1.509(10)
N18–C37	1.470(10)
N18–C40	1.437(10)
N18–C41	1.340(11)
C24–H24	0.9500
C24–C25	1.393(12)
C25–H25	0.9500
C25–C26	1.362(12)
C26–H26	0.9500
C27–H27	0.9500
C27–C28	1.419(12)
C28–H28	0.9500
C28–C29	1.353(13)

C29–H29	0.9500
C30–H30	0.9500
C30–C31	1.374(13)
C31–H31	0.9500
C31–C32	1.359(12)
C32–H32	0.9500
C33–H33	1.01(9)
C33–C34	1.443(11)
C33–C38	1.530(10)
C34–H34	0.91(10)
C34–C35	1.519(12)
C35–H35A	0.9900
C35–H35B	0.9900
C35–C36	1.519(11)
C36–H36	1.0000
C36–C37	1.553(11)
C36–C42	1.534(12)
C37–H37	1.0000
C37–C38	1.539(10)
C38–H38	1.0000
C39–H39	1.0000
C39–C40	1.511(12)
C39–C43	1.514(11)
C40–H40A	0.9900
C40–H40B	0.9900
C41–C42	1.489(12)
C42–H42A	0.9900
C42–H42B	0.9900
C43–H43A	0.9800
C43–H43B	0.9800
C43–H43C	0.9800
C44–H44A	0.9800
C44–H44B	0.9800
C44–H44C	0.9800
C45–H45A	0.9800
C45–H45B	0.9800
C45–H45C	0.9800
C46–H46A	0.9800
C46–H46B	0.9800
C46–H46C	0.9800
B2–H2A	1.05(8)

Atom–Atom–Atom	Angle [°]
N1–W1–P1	85.80(18)
N3–W1–P1	83.89(17)
N3–W1–N1	82.9(3)
N3–W1–C11	162.6(2)
N5–W1–P1	158.12(17)
N5–W1–N1	84.3(2)
N5–W1–N3	75.6(2)
N5–W1–C11	119.1(3)
N7–W1–P1	93.4(2)
N7–W1–N1	177.2(3)
N7–W1–N3	94.4(3)
N7–W1–N5	95.5(3)
N7–W1–C10	97.9(3)
N7–W1–C11	93.3(3)
C10–W1–P1	117.1(2)
C10–W1–N1	84.8(3)
C10–W1–N3	154.8(3)
C10–W1–N5	81.3(3)
C10–W1–C11	37.8(3)
C11–W1–P1	80.1(2)
C11–W1–N1	89.2(3)
C21–P1–W1	122.4(3)
C22–P1–W1	113.6(3)
C22–P1–C21	100.2(5)
C23–P1–W1	114.4(3)
C23–P1–C21	100.6(5)
C23–P1–C22	102.9(5)
N2–N1–W1	120.7(5)
C1–N1–W1	132.5(6)
C1–N1–N2	106.8(7)
N1–N2–B1	120.9(6)
C3–N2–N1	108.8(7)
C3–N2–B1	130.3(7)
N4–N3–W1	121.8(5)
C4–N3–W1	131.4(6)
C4–N3–N4	106.2(6)
N3–N4–B1	119.8(6)
C6–N4–N3	109.7(7)
C6–N4–B1	129.0(7)
N6–N5–W1	121.2(4)
C7–N5–W1	132.5(6)

C7–N5–N6	106.3(7)
N5–N6–B1	119.6(6)
C9–N6–N5	109.7(6)
C9–N6–B1	129.5(7)
O1–N7–W1	179.4(6)
C15–N8–H8	103(6)
C16–N8–H8	99(6)
C16–N8–C15	114.3(6)
C17–N9–C14	119.8(7)
C18–N9–C14	114.9(7)
C18–N9–C17	124.0(8)
N1–C1–H1	125.1
N1–C1–C2	109.9(8)
C2–C1–H1	125.1
C1–C2–H2	127.2
C3–C2–C1	105.7(8)
C3–C2–H2	127.2
N2–C3–H3	125.6
C2–C3–N2	108.8(8)
C2–C3–H3	125.6
N3–C4–H4	124.8
N3–C4–C5	110.4(8)
C5–C4–H4	124.8
C4–C5–H5	127.2
C6–C5–C4	105.7(9)
C6–C5–H5	127.2
N4–C6–C5	108.0(9)
N4–C6–H6	126.0
C5–C6–H6	126.0
N5–C7–H7	124.7
N5–C7–C8	110.6(8)
C8–C7–H7	124.7
C7–C8–H8A	127.4
C9–C8–C7	105.2(7)
C9–C8–H8A	127.4
N6–C9–C8	108.3(8)
N6–C9–H9	125.9
C8–C9–H9	125.9
W1–C10–H10	112(5)
C11–C10–W1	72.2(4)
C11–C10–H10	121(5)
C11–C10–C15	120.9(7)

C15–C10–W1	124.5(6)
C15–C10–H10	104(5)
W1–C11–H11	112(6)
C10–C11–W1	70.0(4)
C10–C11–H11	121(6)
C10–C11–C12	114.4(6)
C12–C11–W1	122.2(6)
C12–C11–H11	112(6)
C11–C12–H12A	109.7
C11–C12–H12B	109.7
C11–C12–C13	109.9(7)
H12A–C12–H12B	108.2
C13–C12–H12A	109.7
C13–C12–H12B	109.7
C12–C13–H13	108.5
C14–C13–C12	111.7(7)
C14–C13–H13	108.5
C19–C13–C12	114.7(7)
C19–C13–H13	108.5
C19–C13–C14	104.7(7)
N9–C14–C13	103.5(6)
N9–C14–H14	109.2
N9–C14–C15	109.6(7)
C13–C14–H14	109.2
C13–C14–C15	116.0(6)
C15–C14–H14	109.2
N8–C15–C10	108.2(7)
N8–C15–C14	108.2(6)
N8–C15–H15	109.0
C10–C15–C14	113.4(7)
C10–C15–H15	109.0
C14–C15–H15	109.0
N8–C16–H16	110.5
N8–C16–C17	105.2(7)
N8–C16–C20	109.1(7)
C17–C16–H16	110.5
C17–C16–C20	111.0(7)
C20–C16–H16	110.5
N9–C17–C16	108.6(7)
N9–C17–H17A	110.0
N9–C17–H17B	110.0
C16–C17–H17A	110.0

C16–C17–H17B	110.0
H17A–C17–H17B	108.4
O2–C18–N9	124.6(8)
O2–C18–C19	126.9(8)
N9–C18–C19	108.5(7)
C13–C19–H19A	110.5
C13–C19–H19B	110.5
C18–C19–C13	105.9(7)
C18–C19–H19A	110.5
C18–C19–H19B	110.5
H19A–C19–H19B	108.7
C16–C20–H20A	109.5
C16–C20–H20B	109.5
C16–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
P1–C21–H21A	109.5
P1–C21–H21B	109.5
P1–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
N2–B1–N4	109.9(7)
N2–B1–N6	110.0(7)
N2–B1–H1A	114(4)
N4–B1–N6	105.6(6)
N4–B1–H1A	109(4)
N6–B1–H1A	108(4)
N10–W2–P2	85.31(16)

N12–W2–P2	84.16(17)
N12–W2–N10	84.7(2)
N12–W2–N14	76.8(2)
N12–W2–C34	162.1(2)
N14–W2–P2	156.36(17)
N14–W2–N10	79.1(2)
N16–W2–P2	91.5(2)
N16–W2–N10	174.3(3)
N16–W2–N12	90.3(3)
N16–W2–N14	102.4(3)
N16–W2–C33	94.0(3)
N16–W2–C34	93.4(3)
C33–W2–P2	116.3(2)
C33–W2–N10	91.6(3)
C33–W2–N12	158.9(3)
C33–W2–N14	82.1(3)
C33–W2–C34	38.1(3)
C34–W2–P2	78.22(19)
C34–W2–N10	90.6(3)
C34–W2–N14	119.3(3)
C44–P2–W2	114.6(3)
C44–P2–C46	102.4(5)
C45–P2–W2	121.5(3)
C45–P2–C44	99.9(5)
C45–P2–C46	101.7(5)
C46–P2–W2	114.0(3)
N11–N10–W2	120.7(5)
C24–N10–W2	133.5(5)
C24–N10–N11	105.4(6)
N10–N11–B2	120.5(6)
C26–N11–N10	110.1(6)
C26–N11–B2	129.0(7)
N13–N12–W2	124.4(5)
C27–N12–W2	128.7(6)
C27–N12–N13	106.5(7)
N12–N13–B2	118.0(6)
C29–N13–N12	109.9(7)
C29–N13–B2	130.2(7)
N15–N14–W2	121.7(4)
C30–N14–W2	133.6(6)
C30–N14–N15	104.6(7)
N14–N15–B2	120.5(6)

C32–N15–N14	109.9(6)
C32–N15–B2	129.5(7)
O3–N16–W2	175.6(6)
C38–N17–H17	107(7)
C38–N17–C39	112.8(6)
C39–N17–H17	109(7)
C40–N18–C37	119.5(7)
C41–N18–C37	114.6(7)
C41–N18–C40	125.7(7)
N10–C24–H24	124.6
N10–C24–C25	110.9(7)
C25–C24–H24	124.6
C24–C25–H25	127.6
C26–C25–C24	104.8(8)
C26–C25–H25	127.6
N11–C26–C25	108.9(7)
N11–C26–H26	125.6
C25–C26–H26	125.6
N12–C27–H27	125.4
N12–C27–C28	109.3(8)
C28–C27–H27	125.4
C27–C28–H28	127.3
C29–C28–C27	105.4(8)
C29–C28–H28	127.3
N13–C29–C28	108.9(8)
N13–C29–H29	125.5
C28–C29–H29	125.5
N14–C30–H30	124.4
N14–C30–C31	111.2(8)
C31–C30–H30	124.4
C30–C31–H31	127.6
C32–C31–C30	104.8(7)
C32–C31–H31	127.6
N15–C32–C31	109.5(8)
N15–C32–H32	125.2
C31–C32–H32	125.2
W2–C33–H33	107(5)
C34–C33–W2	71.9(4)
C34–C33–H33	111(5)
C34–C33–C38	115.7(7)
C38–C33–W2	124.7(5)
C38–C33–H33	118(5)

W2–C34–H34	119(6)
C33–C34–W2	70.0(4)
C33–C34–H34	121(7)
C33–C34–C35	114.4(6)
C35–C34–W2	121.4(6)
C35–C34–H34	107(7)
C34–C35–H35A	109.3
C34–C35–H35B	109.3
H35A–C35–H35B	108.0
C36–C35–C34	111.6(7)
C36–C35–H35A	109.3
C36–C35–H35B	109.3
C35–C36–H36	109.1
C35–C36–C37	110.2(7)
C35–C36–C42	114.4(7)
C37–C36–H36	109.1
C42–C36–H36	109.1
C42–C36–C37	104.7(7)
N18–C37–C36	104.4(6)
N18–C37–H37	109.3
N18–C37–C38	109.2(7)
C36–C37–H37	109.3
C38–C37–C36	115.3(6)
C38–C37–H37	109.3
N17–C38–C33	113.6(7)
N17–C38–C37	108.8(6)
N17–C38–H38	107.7
C33–C38–C37	111.0(6)
C33–C38–H38	107.7
C37–C38–H38	107.7
N17–C39–H39	108.0
N17–C39–C40	111.8(7)
N17–C39–C43	108.9(7)
C40–C39–H39	108.0
C40–C39–C43	111.9(7)
C43–C39–H39	108.0
N18–C40–C39	110.4(6)
N18–C40–H40A	109.6
N18–C40–H40B	109.6
C39–C40–H40A	109.6
C39–C40–H40B	109.6
H40A–C40–H40B	108.1

O4–C41–N18	124.3(8)
O4–C41–C42	126.4(8)
N18–C41–C42	109.3(7)
C36–C42–H42A	110.3
C36–C42–H42B	110.3
C41–C42–C36	107.0(7)
C41–C42–H42A	110.3
C41–C42–H42B	110.3
H42A–C42–H42B	108.6
C39–C43–H43A	109.5
C39–C43–H43B	109.5
C39–C43–H43C	109.5
H43A–C43–H43B	109.5
H43A–C43–H43C	109.5
H43B–C43–H43C	109.5
P2–C44–H44A	109.5
P2–C44–H44B	109.5
P2–C44–H44C	109.5
H44A–C44–H44B	109.5
H44A–C44–H44C	109.5
H44B–C44–H44C	109.5
P2–C45–H45A	109.5
P2–C45–H45B	109.5
P2–C45–H45C	109.5
H45A–C45–H45B	109.5
H45A–C45–H45C	109.5
H45B–C45–H45C	109.5
P2–C46–H46A	109.5
P2–C46–H46B	109.5
P2–C46–H46C	109.5
H46A–C46–H46B	109.5
H46A–C46–H46C	109.5
H46B–C46–H46C	109.5
N11–B2–N13	110.4(7)
N11–B2–N15	108.2(6)
N11–B2–H2A	112(5)
N13–B2–N15	106.6(7)
N13–B2–H2A	104(5)
N15–B2–H2A	115(4)

Table 5 Torsion angles for Compound 5.8 Atom–Atom–Atom–Atom	Torsion Angle [°]
W1–N1–N2–C3	−179.0(5)
W1–N1–N2–B1	2.5(9)
W1–N1–C1–C2	179.3(6)
W1–N3–N4–C6	−171.5(5)
W1–N3–N4–B1	−3.9(9)
W1–N3–C4–C5	171.0(5)
W1–N5–N6–C9	−177.8(5)
W1–N5–N6–B1	13.5(9)
W1–N5–C7–C8	177.8(6)
W1–C10–C11–C12	−117.2(7)
W1–C10–C15–N8	−115.5(7)
W1–C10–C15–C14	124.5(7)
W1–C11–C12–C13	−131.2(6)
O2–C18–C19–C13	174.8(8)
N1–N2–C3–C2	−0.3(9)
N1–N2–B1–N4	−59.8(9)
N1–N2–B1–N6	56.1(9)
N1–C1–C2–C3	−1.0(11)
N2–N1–C1–C2	0.8(10)
N3–N4–C6–C5	−0.9(11)
N3–N4–B1–N2	60.7(9)
N3–N4–B1–N6	−57.9(9)
N3–C4–C5–C6	−0.8(11)
N4–N3–C4–C5	0.2(8)
N5–N6–C9–C8	−1.0(9)
N5–N6–B1–N2	−66.1(9)
N5–N6–B1–N4	52.4(9)
N5–C7–C8–C9	0.9(10)
N6–N5–C7–C8	−1.4(9)
N8–C16–C17–N9	−45.1(9)
N9–C14–C15–N8	−28.4(8)
N9–C14–C15–C10	91.5(8)
N9–C18–C19–C13	−5.6(9)
C1–N1–N2–C3	−0.4(9)
C1–N1–N2–B1	−178.9(7)
C1–C2–C3–N2	0.7(10)

C3–N2–B1–N4	122.1(8)
C3–N2–B1–N6	−122.1(8)
C4–N3–N4–C6	0.4(8)
C4–N3–N4–B1	168.0(8)
C4–C5–C6–N4	1.0(12)
C6–N4–B1–N2	−134.3(9)
C6–N4–B1–N6	107.1(9)
C7–N5–N6–C9	1.5(9)
C7–N5–N6–B1	−167.2(7)
C7–C8–C9–N6	0.1(10)
C9–N6–B1–N2	127.7(8)
C9–N6–B1–N4	−113.8(9)
C10–C11–C12–C13	−50.3(10)
C11–C10–C15–N8	155.7(8)
C11–C10–C15–C14	35.7(11)
C11–C12–C13–C14	58.1(9)
C11–C12–C13–C19	−60.9(9)
C12–C13–C14–N9	−139.9(7)
C12–C13–C14–C15	−19.9(10)
C12–C13–C19–C18	135.7(7)
C13–C14–C15–N8	−145.2(7)
C13–C14–C15–C10	−25.2(10)
C14–N9–C17–C16	−16.4(11)
C14–N9–C18–O2	174.7(8)
C14–N9–C18–C19	−4.9(9)
C14–C13–C19–C18	12.9(8)
C15–N8–C16–C17	73.8(9)
C15–N8–C16–C20	−167.0(7)
C15–C10–C11–W1	120.1(8)
C15–C10–C11–C12	2.8(11)
C16–N8–C15–C10	−156.1(7)
C16–N8–C15–C14	−33.0(9)
C17–N9–C14–C13	−179.2(7)
C17–N9–C14–C15	56.5(9)
C17–N9–C18–O2	7.5(13)
C17–N9–C18–C19	−172.1(8)
C18–N9–C14–C13	13.0(9)
C18–N9–C14–C15	−111.3(8)
C18–N9–C17–C16	150.2(8)
C19–C13–C14–N9	−15.1(8)
C19–C13–C14–C15	104.9(8)
C20–C16–C17–N9	−162.9(7)

B1–N2–C3–C2	178.1(8)
B1–N4–C6–C5	−167.0(8)
B1–N6–C9–C8	166.3(8)
W2–N10–N11–C26	174.1(5)
W2–N10–N11–B2	−12.7(9)
W2–N10–C24–C25	−173.1(6)
W2–N12–N13–C29	172.2(5)
W2–N12–N13–B2	6.2(9)
W2–N12–C27–C28	−172.5(5)
W2–N14–N15–C32	176.9(5)
W2–N14–N15–B2	−4.3(9)
W2–N14–C30–C31	−176.2(6)
W2–C33–C34–C35	116.4(7)
W2–C33–C38–N17	107.1(7)
W2–C33–C38–C37	−129.9(6)
W2–C34–C35–C36	135.7(6)
O4–C41–C42–C36	178.9(8)
N10–N11–C26–C25	0.1(9)
N10–N11–B2–N13	65.6(9)
N10–N11–B2–N15	−50.6(9)
N10–C24–C25–C26	0.4(10)
N11–N10–C24–C25	−0.3(9)
N12–N13–C29–C28	1.3(10)
N12–N13–B2–N11	−61.1(9)
N12–N13–B2–N15	56.1(9)
N12–C27–C28–C29	0.4(10)
N13–N12–C27–C28	0.4(8)
N14–N15–C32–C31	−0.3(9)
N14–N15–B2–N11	61.1(9)
N14–N15–B2–N13	−57.5(9)
N14–C30–C31–C32	−0.1(10)
N15–N14–C30–C31	0.0(10)
N17–C39–C40–N18	−47.2(9)
N18–C37–C38–N17	53.8(8)
N18–C37–C38–C33	−71.9(8)
N18–C41–C42–C36	−2.4(9)
C24–N10–N11–C26	0.1(8)
C24–N10–N11–B2	173.4(7)
C24–C25–C26–N11	−0.3(9)
C26–N11–B2–N13	−122.5(8)
C26–N11–B2–N15	121.2(8)
C27–N12–N13–C29	−1.0(8)

C27–N12–N13–B2	−167.1(7)
C27–C28–C29–N13	−1.0(10)
C29–N13–B2–N11	136.1(8)
C29–N13–B2–N15	−106.7(9)
C30–N14–N15–C32	0.2(9)
C30–N14–N15–B2	179.0(7)
C30–C31–C32–N15	0.3(10)
C32–N15–B2–N11	−120.4(8)
C32–N15–B2–N13	121.0(8)
C33–C34–C35–C36	55.1(10)
C34–C33–C38–N17	−167.9(7)
C34–C33–C38–C37	−44.9(10)
C34–C35–C36–C37	−52.3(9)
C34–C35–C36–C42	65.4(9)
C35–C36–C37–N18	122.3(7)
C35–C36–C37–C38	2.6(10)
C35–C36–C42–C41	−118.7(8)
C36–C37–C38–N17	170.9(6)
C36–C37–C38–C33	45.2(9)
C37–N18–C40–C39	48.6(10)
C37–N18–C41–O4	−179.6(7)
C37–N18–C41–C42	1.7(9)
C37–C36–C42–C41	2.2(8)
C38–N17–C39–C40	55.8(8)
C38–N17–C39–C43	179.9(6)
C38–C33–C34–W2	−120.5(7)
C38–C33–C34–C35	−4.1(10)
C39–N17–C38–C33	65.8(8)
C39–N17–C38–C37	−58.4(8)
C40–N18–C37–C36	−176.0(7)
C40–N18–C37–C38	−52.2(9)
C40–N18–C41–O4	−4.2(13)
C40–N18–C41–C42	177.1(7)
C41–N18–C37–C36	−0.3(9)
C41–N18–C37–C38	123.5(7)
C41–N18–C40–C39	−126.5(9)
C42–C36–C37–N18	−1.2(8)
C42–C36–C37–C38	−121.0(7)
C43–C39–C40–N18	−169.6(7)
B2–N11–C26–C25	−172.4(8)
B2–N13–C29–C28	165.1(8)
B2–N15–C32–C31	−179.0(8)

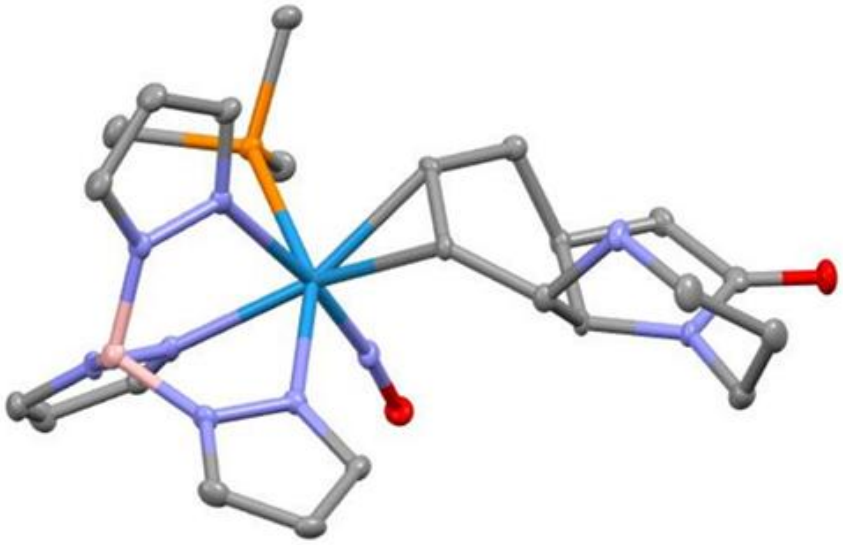


Table 1 Crystal data and structure refinement for Compound 5.19.

Empirical formula	$C_{25}H_{38}BN_{10}O_2PW$
Formula weight	736.28
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	9.7805(3)
b/Å	12.4416(4)
c/Å	12.9471(5)
α/°	96.8520(10)

β/°	106.2720(10)
γ/°	104.6560(10)
Volume/Å^3	1432.14(8)
Z	2
ρ_{calc}g/cm^3	1.707
μ/mm^{-1}	4.132
F(000)	736.0
Crystal size/mm^3	0.132 × 0.061 × 0.043
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.292 to 56.576
Index ranges	-10 ≤ h ≤ 13, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	43181
Independent reflections	7101 [R_{int} = 0.0559, R_{sigma} = 0.0375]
Data/restraints/parameters	7101/0/379
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0251, wR_2 = 0.0568
Final R indexes [all data]	R_1 = 0.0296, wR_2 = 0.0582
Largest diff. peak/hole / e Å^{-3}	1.01/-1.18

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound 19. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	3454.5(2)	7488.8(2)	6452.4(2)	8.38(4)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 19. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P1	4087.6(8)	9460.4(6)	7534.2(6)	11.91(15)
O1	376(2)	6659.4(19)	6601.7(18)	16.1(4)
O2	-2897(2)	7237(2)	2054.4(18)	19.2(5)
N1	3747(3)	5786(2)	6122(2)	12.1(5)
N2	4981(3)	5553(2)	6758(2)	12.8(5)
N3	4195(3)	7162(2)	8124(2)	12.3(5)
N4	5432(3)	6831(2)	8522(2)	12.6(5)
N5	5906(3)	8001(2)	6635(2)	11.8(5)
N6	6826(3)	7464(2)	7227(2)	13.3(5)
N7	1607(3)	7029(2)	6488(2)	12.4(5)
N8	-1117(3)	6492(2)	2978(2)	12.7(5)
N9	1614(3)	6962(2)	2693(2)	14.9(5)
C1	2948(3)	4843(2)	5374(2)	13.4(6)
C2	3648(3)	3996(3)	5505(3)	15.4(6)
C3	4916(3)	4486(3)	6389(3)	16.7(6)
C4	3601(3)	7235(3)	8934(2)	14.6(6)
C5	4459(4)	6965(3)	9859(3)	18.6(6)
C6	5597(3)	6706(3)	9561(3)	16.7(6)
C7	6764(3)	8771(3)	6258(3)	14.6(6)
C8	8231(3)	8725(3)	6598(3)	16.9(6)
C9	8213(3)	7896(3)	7205(3)	16.8(6)
C10	2975(3)	7309(2)	4669(2)	10.9(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound 19. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C11	3091(3)	8457(2)	5113(2)	10.7(5)
C12	1714(3)	8838(2)	4680(3)	12.9(6)
C13	242(3)	7956(2)	4554(2)	12.1(6)
C14	148(3)	6751(3)	3989(2)	11.8(6)
C15	1564(3)	6624(3)	3748(2)	13.1(6)
C16	964(4)	6006(3)	1743(3)	20.5(7)
C17	-739(4)	5686(3)	1289(3)	19.8(7)
C18	-1519(3)	5475(3)	2145(3)	17.7(6)
C19	-1834(3)	7278(3)	2847(3)	15.5(6)
C20	-1114(3)	8236(3)	3837(3)	14.8(6)
C21	4691(3)	10704(3)	6971(3)	16.4(6)
C22	2610(3)	9758(3)	7993(3)	18.4(6)
C23	5676(3)	9799(3)	8795(3)	19.2(7)
B1	6193(4)	6453(3)	7714(3)	13.3(7)
N10	10827(4)	8078(3)	9647(3)	36.9(8)
C24	10379(4)	8385(3)	10304(3)	24.6(7)
C25	9854(5)	8763(4)	11190(4)	40.4(10)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 19. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	7.85(6)	8.94(6)	7.99(6)	0.44(4)	2.04(4)	3.03(4)
P1	11.7(3)	11.3(4)	11.7(4)	0.2(3)	3.3(3)	3.2(3)
O1	11.3(10)	21.1(12)	18.2(12)	6.7(9)	7.3(9)	4.6(8)
O2	16.6(11)	24.0(12)	13.7(11)	4.1(9)	-1.6(9)	7.4(9)
N1	13.6(11)	13.2(12)	10.7(12)	3.0(10)	4.7(10)	5.0(9)
N2	14.4(12)	12.1(12)	13.1(13)	2.8(10)	3.8(10)	6.9(10)
N3	12.4(11)	10.7(12)	11.5(13)	-0.7(10)	1.4(10)	3.9(9)
N4	10.6(11)	15.3(13)	11.1(13)	3.0(10)	0.5(10)	5.6(9)
N5	12.4(11)	11.1(12)	11.3(12)	0.0(10)	2.1(10)	5.4(9)
N6	10.4(11)	14.9(13)	14.4(13)	1.9(10)	2.0(10)	6.3(10)
N7	11.1(11)	17.0(13)	9.4(12)	2.1(10)	3.4(9)	5.2(10)
N8	10.7(11)	13.4(12)	10.0(12)	1.3(10)	-0.6(9)	1.9(9)
N9	12.9(13)	21.2(14)	8.5(13)	1.2(11)	3.1(10)	3.1(11)
C1	13.4(13)	13.7(14)	10.8(14)	0.6(12)	4.3(11)	0.6(11)
C2	21.5(15)	9.2(14)	15.8(16)	0.8(12)	9.1(12)	2.3(11)
C3	22.2(15)	14.2(15)	18.3(16)	4.8(13)	9.6(13)	9.4(12)
C4	14.9(14)	14.0(15)	12.6(15)	0.0(12)	4.1(12)	2.1(11)
C5	25.0(16)	19.7(16)	11.2(15)	3.4(13)	5.6(13)	6.9(13)
C6	16.5(14)	17.1(15)	12.4(15)	3.2(12)	-1.1(12)	4.1(12)
C7	12.2(13)	13.1(14)	15.8(16)	-0.2(12)	3.7(12)	1.7(11)
C8	11.7(13)	17.8(16)	20.2(17)	1.7(13)	6.0(12)	2.8(11)
C9	9.9(13)	19.5(16)	18.9(16)	0.4(13)	2.8(12)	4.9(11)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 19. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	9.4(12)	14.7(14)	8.4(14)	2.3(11)	1.6(11)	4.7(11)
C11	10.0(13)	10.7(14)	12.6(14)	5.3(11)	3.5(11)	3.9(11)
C12	13.6(13)	12.5(14)	12.9(15)	1.4(12)	4.9(11)	4.5(11)
C13	11.1(13)	14.1(14)	10.7(14)	2.5(12)	1.7(11)	5.3(11)
C14	10.1(13)	14.6(14)	8.0(14)	2.2(11)	-0.5(11)	3.0(11)
C15	15.0(14)	13.5(14)	9.7(14)	-0.4(12)	2.7(11)	5.1(11)
C16	24.3(16)	26.2(18)	11.5(16)	-0.1(13)	6.0(13)	10.2(14)
C17	26.1(16)	18.4(16)	10.9(15)	-1.7(13)	1.5(13)	7.2(13)
C18	17.2(15)	13.7(15)	17.5(16)	0.6(13)	0.7(12)	3.1(12)
C19	14.5(14)	17.9(15)	14.3(15)	6.1(12)	5.9(12)	2.5(12)
C20	13.2(13)	17.0(15)	16.0(16)	4.8(12)	4.1(12)	7.7(11)
C21	18.3(14)	11.5(14)	17.1(16)	0.6(12)	5.1(12)	2.4(11)
C22	19.5(15)	16.3(15)	23.8(18)	1.8(13)	11.1(13)	9.5(12)
C23	16.9(15)	18.9(16)	15.4(16)	-2.5(13)	0.1(12)	2.8(12)
B1	9.7(14)	15.3(16)	14.7(17)	2.0(14)	2.6(13)	5.4(12)
N10	29.7(17)	53(2)	29.0(19)	3.4(16)	14.0(15)	10.6(15)
C24	21.6(16)	28.2(19)	20.5(18)	4.4(15)	4.1(14)	4.8(14)
C25	47(2)	35(2)	41(3)	-0.5(19)	27(2)	6.2(19)

Table 4 Bond Lengths for Compound 19.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	P1	2.5076(8)	N8	C14	1.463(3)
W1	N1	2.217(2)	N8	C18	1.450(4)
W1	N3	2.203(2)	N8	C19	1.340(4)
W1	N5	2.255(2)	N9	C15	1.487(4)
W1	N7	1.767(2)	N9	C16	1.470(4)
W1	C10	2.195(3)	C1	C2	1.396(4)
W1	C11	2.226(3)	C2	C3	1.370(4)
P1	C21	1.823(3)	C4	C5	1.388(4)
P1	C22	1.810(3)	C5	C6	1.372(4)
P1	C23	1.827(3)	C7	C8	1.396(4)
O1	N7	1.232(3)	C8	C9	1.369(4)
O2	C19	1.225(4)	C10	C11	1.438(4)
N1	N2	1.377(3)	C10	C15	1.514(4)
N1	C1	1.329(4)	C11	C12	1.521(4)
N2	C3	1.335(4)	C12	C13	1.527(4)
N2	B1	1.538(4)	C13	C14	1.557(4)
N3	N4	1.361(3)	C13	C20	1.538(4)
N3	C4	1.338(4)	C14	C15	1.543(4)
N4	C6	1.343(4)	C16	C17	1.529(4)
N4	B1	1.538(4)	C17	C18	1.524(5)
N5	N6	1.372(3)	C19	C20	1.504(4)
N5	C7	1.339(4)	N10	C24	1.130(5)
N6	C9	1.337(4)	C24	C25	1.457(5)

Table 4 Bond Lengths for Compound 19.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N6	B1	1.543(4)			

Table 5 Bond Angles for Compound 19.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	W1	P1	154.68(7)	C9	N6	N5	109.5(2)
N1	W1	N5	80.40(9)	C9	N6	B1	129.3(3)
N1	W1	C11	120.05(10)	O1	N7	W1	173.4(2)
N3	W1	P1	80.93(7)	C18	N8	C14	121.8(2)
N3	W1	N1	78.18(9)	C19	N8	C14	115.8(3)
N3	W1	N5	84.63(9)	C19	N8	C18	122.3(3)
N3	W1	C11	159.23(10)	C16	N9	C15	113.5(3)
N5	W1	P1	83.56(6)	N1	C1	C2	110.7(3)
N7	W1	P1	96.00(8)	C3	C2	C1	104.5(3)
N7	W1	N1	97.18(10)	N2	C3	C2	109.3(3)
N7	W1	N3	87.38(10)	N3	C4	C5	110.4(3)
N7	W1	N5	171.97(10)	C6	C5	C4	105.0(3)
N7	W1	C10	99.19(11)	N4	C6	C5	108.7(3)
N7	W1	C11	99.14(11)	N5	C7	C8	110.0(3)
C10	W1	P1	116.42(8)	C9	C8	C7	105.1(3)
C10	W1	N1	82.60(10)	N6	C9	C8	109.0(3)
C10	W1	N3	160.34(10)	C11	C10	W1	72.20(16)
C10	W1	N5	88.12(10)	C11	C10	C15	117.7(2)

Table 5 Bond Angles for Compound 19.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	W1	C11	37.97(11)	C15	C10	W1	129.1(2)
C11	W1	P1	78.80(8)	C10	C11	W1	69.83(16)
C11	W1	N5	88.65(9)	C10	C11	C12	116.4(2)
C21	P1	W1	121.39(11)	C12	C11	W1	125.0(2)
C21	P1	C23	98.82(15)	C11	C12	C13	114.3(2)
C22	P1	W1	114.91(11)	C12	C13	C14	112.3(2)
C22	P1	C21	101.80(15)	C12	C13	C20	112.2(2)
C22	P1	C23	104.13(15)	C20	C13	C14	105.7(2)
C23	P1	W1	113.28(11)	N8	C14	C13	103.4(2)
N2	N1	W1	120.44(18)	N8	C14	C15	111.6(2)
C1	N1	W1	133.3(2)	C15	C14	C13	116.3(2)
C1	N1	N2	106.2(2)	N9	C15	C10	110.0(2)
N1	N2	B1	121.7(2)	N9	C15	C14	110.5(2)
C3	N2	N1	109.2(2)	C10	C15	C14	112.0(2)
C3	N2	B1	129.1(3)	N9	C16	C17	112.8(3)
N4	N3	W1	123.44(19)	C18	C17	C16	114.4(3)
C4	N3	W1	130.2(2)	N8	C18	C17	111.4(3)
C4	N3	N4	106.4(2)	O2	C19	N8	126.2(3)
N3	N4	B1	118.6(2)	O2	C19	C20	124.9(3)
C6	N4	N3	109.6(2)	N8	C19	C20	108.9(2)
C6	N4	B1	130.6(2)	C19	C20	C13	105.8(2)
N6	N5	W1	120.27(18)	N2	B1	N6	107.2(2)
C7	N5	W1	133.4(2)	N4	B1	N2	107.5(2)

Table 5 Bond Angles for Compound 19.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N5	N6	106.4(2)	N4	B1	N6	109.7(2)
N5	N6	B1	120.9(2)	N10	C24	C25	177.2(4)

Table 6 Torsion Angles for Compound 19.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
W1	N1	N2	C3	-178.99(19)	C4	C5	C6	N4	0.8(4)
W1	N1	N2	B1	0.1(3)	C6	N4	B1	N2	114.5(3)
W1	N1	C1	C2	178.6(2)	C6	N4	B1	N6	-129.3(3)
W1	N3	N4	C6	179.7(2)	C7	N5	N6	C9	-0.3(3)
W1	N3	N4	B1	-11.7(3)	C7	N5	N6	B1	-175.3(3)
W1	N3	C4	C5	-179.1(2)	C7	C8	C9	N6	0.3(4)
W1	N5	N6	C9	179.0(2)	C9	N6	B1	N2	-117.8(3)
W1	N5	N6	B1	4.0(3)	C9	N6	B1	N4	125.8(3)
W1	N5	C7	C8	-178.7(2)	C10	C11	C12	C13	41.9(4)
W1	C10	C11	C12	-120.0(2)	C11	C10	C15	N9	77.9(3)
W1	C10	C15	N9	166.9(2)	C11	C10	C15	C14	-45.4(4)
W1	C10	C15	C14	43.6(3)	C11	C12	C13	C14	-45.7(3)
W1	C11	C12	C13	-41.1(3)	C11	C12	C13	C20	-164.6(3)
O2	C19	C20	C13	-175.2(3)	C12	C13	C14	N8	-117.5(3)
N1	N2	C3	C2	0.2(3)	C12	C13	C14	C15	5.2(3)
N1	N2	B1	N4	58.5(3)	C12	C13	C20	C19	116.8(3)
N1	N2	B1	N6	-59.4(3)	C13	C14	C15	N9	-84.1(3)

Table 6 Torsion Angles for Compound 19.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	0.5(3)	C13	C14	C15	C10	38.9(3)
N2	N1	C1	C2	-0.4(3)	C14	N8	C18	C17	-91.0(3)
N3	N4	C6	C5	-0.4(4)	C14	N8	C19	O2	178.5(3)
N3	N4	B1	N2	-51.4(3)	C14	N8	C19	C20	-1.2(3)
N3	N4	B1	N6	64.8(3)	C14	C13	C20	C19	-5.9(3)
N3	C4	C5	C6	-1.0(4)	C15	N9	C16	C17	81.6(3)
N4	N3	C4	C5	0.7(3)	C15	C10	C11	W1	125.4(3)
N5	N6	C9	C8	0.0(4)	C15	C10	C11	C12	5.4(4)
N5	N6	B1	N2	56.1(3)	C16	N9	C15	C10	142.4(2)
N5	N6	B1	N4	-60.3(3)	C16	N9	C15	C14	-93.5(3)
N5	C7	C8	C9	-0.5(4)	C16	C17	C18	N8	63.3(4)
N6	N5	C7	C8	0.5(3)	C18	N8	C14	C13	174.4(2)
N8	C14	C15	N9	34.2(3)	C18	N8	C14	C15	48.6(4)
N8	C14	C15	C10	157.2(2)	C18	N8	C19	O2	1.5(5)
N8	C19	C20	C13	4.5(3)	C18	N8	C19	C20	-178.1(3)
N9	C16	C17	C18	-52.6(4)	C19	N8	C14	C13	-2.6(3)
C1	N1	N2	C3	0.1(3)	C19	N8	C14	C15	-128.4(3)
C1	N1	N2	B1	179.3(3)	C19	N8	C18	C17	85.7(3)
C1	C2	C3	N2	-0.4(3)	C20	C13	C14	N8	5.1(3)
C3	N2	B1	N4	-122.6(3)	C20	C13	C14	C15	127.8(3)
C3	N2	B1	N6	119.6(3)	B1	N2	C3	C2	-178.8(3)
C4	N3	N4	C6	-0.2(3)	B1	N4	C6	C5	-167.3(3)
C4	N3	N4	B1	168.5(3)	B1	N6	C9	C8	174.4(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 19.

Atom	*x*	*y*	*z*	U(eq)
H9	2490(40)	7190(30)	2780(30)	15(9)
H1	2027.31	4756.75	4824.07	16
H2	3317.81	3247.66	5077.86	19
H3	5637.1	4124.09	6692.97	20
H4	2717.31	7441.21	8883.12	18
H5	4295.05	6960.76	10548.04	22
H6	6372.3	6475.63	10015.39	20
H7	6424.77	9273.48	5823.87	17
H8	9062.76	9173.08	6441.89	20
H9A	9051.91	7665.43	7554.9	20
H10	3800(40)	7180(30)	4520(30)	13
H11	4000(40)	9030(30)	5180(30)	13
H12A	1679.87	9031.65	3954.91	15
H12B	1812.94	9536.16	5185.48	15
H13	144.27	7924.93	5299.57	14
H14	-115.93	6205.47	4461.4	14
H15	1520.4	5805.67	3675.5	16
H16A	1252.6	5339.19	1963.23	25
H16B	1382.27	6209.06	1154.33	25
H17A	-1016.85	6303.23	946.01	24
H17B	-1110.86	4992.22	705.04	24

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 19.

Atom	*x*	*y*	*z*	U(eq)
H18A	-2613.73	5216.51	1778.37	21
H18B	-1238.61	4864.68	2500.37	21
H20A	-1821.78	8288.51	4244.31	18
H20B	-793.55	8967.25	3612.62	18
H21A	5624.97	10717.02	6824.88	25
H21B	4852.27	11393	7500.85	25
H21C	3920.62	10671.81	6284.28	25
H22A	1705.31	9595.23	7359.88	28
H22B	2920.68	10558.73	8354.51	28
H22C	2405.53	9279.62	8514.71	28
H23A	5421.36	9307.2	9294.16	29
H23B	5915.3	10594.52	9152.05	29
H23C	6541.4	9677.13	8616.63	29
H1A	7100(40)	6120(30)	8120(30)	18(9)
H25A	8776.97	8396.13	10991.48	61
H25B	10055.94	9588.21	11308.66	61
H25C	10375.21	8557.11	11865.91	61

Experimental

Single crystals of $C_{25}H_{38}BN_{10}O_2PW$ **[Compound 19]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker D8 Venture** diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [Compound 19]

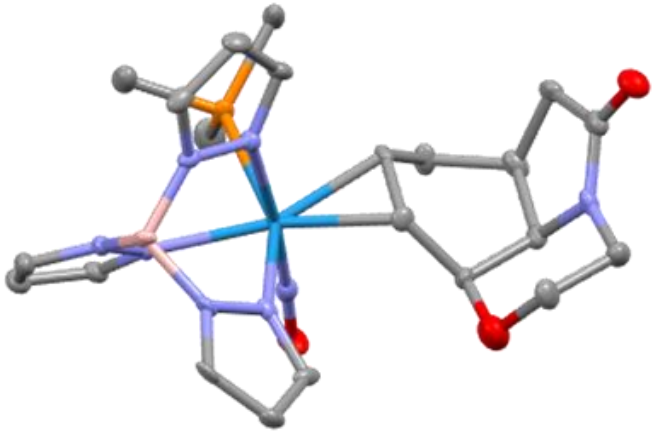
Crystal Data for $C_{25}H_{38}BN_{10}O_2PW$ (M =736.28 g/mol): triclinic, space group P-1 (no. 2), a = 9.7805(3) Å, b = 12.4416(4) Å, c = 12.9471(5) Å, α = 96.8520(10)°, β = 106.2720(10)°, γ = 104.6560(10)°, V = 1432.14(8) Å^3, Z = 2, T = 100.00 K, μ(Mo Kα) = 4.132 mm^{-1}, *Dcalc* = 1.707 g/cm^3, 43181 reflections measured (4.292° ≤ 2Θ ≤ 56.576°), 7101 unique (R_{int} = 0.0559, R_{sigma} = 0.0375) which were used in all calculations. The final R_1 was 0.0251 (I > 2σ(I)) and wR_2 was 0.0582 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
C13(H13), C14(H14), C15(H15)
2.b Secondary CH2 refined with riding coordinates:
C12(H12A,H12B), C16(H16A,H16B), C17(H17A,H17B), C18(H18A,H18B), C20(H20A,H20B)
2.c Aromatic/amide H refined with riding coordinates:
C1(H1), C2(H2), C3(H3), C4(H4), C5(H5), C6(H6), C7(H7), C8(H8), C9(H9A)
2.d Idealised Me refined as rotating group:
C21(H21A,H21B,H21C), C22(H22A,H22B,H22C), C23(H23A,H23B,H23C), C25(H25A,H25B, H25C)

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Crystal Structure Report for Compound 5.18



A colorless, plate-like specimen of $C_{24}H_{35}BN_9O_3PW$, approximate dimensions 0.058 mm x 0.091 mm x 0.117 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture PhotonIII Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 2.30 hours. The frames were integrated with the Bruker SAINT software package[149] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 37138 reflections to a maximum θ angle of 27.49° (0.77 Å resolution), of which 6358 were independent (average redundancy 5.841, completeness = 99.8%, R_{int} = 9.67%, R_{sig} = 7.41%) and 4590 (72.19%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.6632(6) Å, b = 15.0807(6) Å, c = 15.8438(7) Å, β = 95.127(2)°, volume = 2775.6(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 4975 reflections above 20 σ(I) with 5.827° < 2θ < 54.73°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[1] The ratio of minimum to maximum apparent transmission was 0.889. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6350 and 0.7900.

The structure was solved and refined using the Bruker SHELXTL Software Package[150]

[149] Bruker (2012). Saint; SADABS; APEX3. Bruker AXS Inc., Madison, Wisconsin, USA.
[150] Sheldrick, G. M. (2015). Acta Cryst. A**71**, 3-8.

within APEX3 [1] and OLEX2,[151] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{24}H_{35}BN_9O_3PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5 for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 365 variables converged at R1 = 3.95%, for the observed data and wR2 = 8.49% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 1.327 $e^-/Å^3$ and the largest hole was -0.966 $e^-/Å^3$ with an RMS deviation of 0.194 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.731 g/cm^3 and F(000), 1440 e^-.

Table 1. Sample and crystal data for Compound 18.

Chemical formula	$C_{24}H_{35}BN_9O_3PW$	
Formula weight	723.24 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.058 x 0.091 x 0.117 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 11.6632(6) Å	α = 90°
	b = 15.0807(6) Å	β = 95.127(2)°
	c = 15.8438(7) Å	γ = 90°
Volume	2775.6(2) $Å^3$	

[151] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Z	4
Density (calculated)	1.731 g/cm^3
Absorption coefficient	4.264 mm^{-1}
F(000)	1440

Table 2. Data collection and structure refinement for Compound 18.

Diffractometer	Bruker D8 Venture PhotonIII Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.87 to 27.49°
Index ranges	-14<=h<=15, -19<=k<=18, -20<=l<=20
Reflections collected	37138
Independent reflections	6358 [R(int) = 0.0967]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7900 and 0.6350
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)

Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6358 / 0 / 365	
Goodness-of-fit on F^2	1.033	
Final R indices	4590 data; $I>2\sigma(I)$	R1 = 0.0395, wR2 = 0.0756
	all data	R1 = 0.0681, wR2 = 0.0849
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0346P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.327 and -0.966 eÅ^{-3}	
R.M.S. deviation from mean	0.194 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 18.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.37861(2)	0.22336(2)	0.16091(2)	0.01114(7)
P1	0.33307(14)	0.09093(9)	0.24644(10)	0.0170(3)
O1	0.2553(4)	0.1617(3)	0.9963(2)	0.0280(10)

	x/a	y/b	z/c	U(eq)
O2	0.2271(4)	0.4643(3)	0.0673(3)	0.0405(13)
O3	0.0335(4)	0.5110(3)	0.3197(3)	0.0257(10)
N1	0.4882(4)	0.2655(3)	0.2784(3)	0.0145(10)
N2	0.6051(4)	0.2639(3)	0.2785(3)	0.0136(10)
N3	0.5251(4)	0.1358(3)	0.1349(3)	0.0125(10)
N4	0.6364(4)	0.1539(3)	0.1632(3)	0.0141(10)
N5	0.4981(4)	0.3167(3)	0.1055(3)	0.0144(10)
N6	0.6137(4)	0.3118(3)	0.1279(3)	0.0150(10)
N7	0.3040(4)	0.1872(3)	0.0661(3)	0.0172(10)
N8	0.0578(4)	0.4695(3)	0.1833(3)	0.0193(11)
C1	0.4651(5)	0.2884(3)	0.3570(3)	0.0177(12)
C2	0.5679(6)	0.3004(3)	0.4080(4)	0.0199(13)
C3	0.6542(6)	0.2844(3)	0.3561(3)	0.0202(13)
C4	0.5275(5)	0.0580(3)	0.0947(3)	0.0176(13)
C5	0.6390(5)	0.0251(4)	0.0965(3)	0.0210(13)
C6	0.7063(6)	0.0886(4)	0.1401(3)	0.0196(13)
C7	0.4820(6)	0.3733(3)	0.0413(3)	0.0174(13)
C8	0.5860(5)	0.4057(3)	0.0201(4)	0.0177(13)
C9	0.6680(5)	0.3656(3)	0.0751(3)	0.0160(12)
C10	0.2713(5)	0.3425(3)	0.1734(4)	0.0153(12)
C11	0.2241(5)	0.2684(3)	0.2201(3)	0.0135(11)
C12	0.1059(5)	0.2374(3)	0.1881(4)	0.0197(13)
C13	0.0195(6)	0.3147(4)	0.1849(4)	0.0219(14)

	x/a	y/b	z/c	U(eq)
C14	0.0628(5)	0.3914(3)	0.1295(4)	0.0174(12)
C15	0.1871(5)	0.3796(3)	0.1020(3)	0.0163(12)
C16	0.2171(6)	0.5403(4)	0.1249(4)	0.0241(14)
C17	0.0971(5)	0.5533(4)	0.1515(4)	0.0221(14)
C18	0.0343(5)	0.4547(4)	0.2636(4)	0.0201(13)
C19	0.0081(5)	0.3571(4)	0.2733(4)	0.0201(13)
C20	0.2558(6)	0.1018(4)	0.3401(4)	0.0248(15)
C21	0.2523(6)	0.0054(4)	0.1873(4)	0.0293(16)
C22	0.4615(6)	0.0337(4)	0.2908(4)	0.0271(15)
B1	0.6649(6)	0.2479(4)	0.1966(4)	0.0159(14)
N9	0.0936(5)	0.7706(4)	0.5208(4)	0.0349(14)
C23	0.0621(6)	0.7004(4)	0.5130(4)	0.0292(16)
C24	0.0190(6)	0.6094(4)	0.5039(4)	0.0295(16)

Table 4. Bond lengths (Å) for Compound 18.

W1-N7	1.754(5)	W1-C10	2.208(5)
W1-C11	2.211(5)	W1-N5	2.216(4)
W1-N3	2.227(4)	W1-N1	2.254(5)
W1-P1	2.4971(14)	P1-C21	1.809(6)
P1-C20	1.811(6)	P1-C22	1.815(6)
O1-N7	1.258(6)	O2-C16	1.476(7)
O2-C15	1.482(7)	O3-C18	1.230(7)

N1-C1	1.342(7)	N1-N2	1.364(6)
N2-C3	1.345(7)	N2-B1	1.546(7)
N3-C4	1.337(7)	N3-N4	1.363(6)
N4-C6	1.350(7)	N4-B1	1.538(7)
N5-C7	1.329(7)	N5-N6	1.366(7)
N6-C9	1.361(6)	N6-B1	1.535(8)
N8-C18	1.344(7)	N8-C17	1.450(7)
N8-C14	1.458(7)	C1-C2	1.397(8)
C1-H1	0.950000	C2-C3	1.377(8)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.390(8)	C4-H4	0.950000
C5-C6	1.382(8)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.378(8)
C7-H7	0.950000	C8-C9	1.375(8)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.473(7)	C10-C15	1.536(8)
C10-H10	0.86(6)	C11-C12	1.501(8)
C11-H11	0.96(6)	C12-C13	1.540(8)
C12-H12A	0.990000	C12-H12B	0.990000
C13-C19	1.555(8)	C13-C14	1.563(8)
C13-H13	1.000000	C14-C15	1.560(8)
C14-H14	1.000000	C15-H15	1.000000
C16-C17	1.510(8)	C16-H16A	0.990000
C16-H16B	0.990000	C17-H17A	0.990000

C17-H17B	0.990000	C18-C19	1.513(8)
C19-H19A	0.990000	C19-H19B	0.990000
C20-H20A	0.980000	C20-H20B	0.980000
C20-H20C	0.980000	C21-H21A	0.980000
C21-H21B	0.980000	C21-H21C	0.980000
C22-H22A	0.980000	C22-H22B	0.980000
C22-H22C	0.980000	B1-H1A	1.09(6)
N9-C23	1.124(8)	C23-C24	1.464(9)
C24-H24A	0.980000	C24-H24B	0.980000
C24-H24C	0.980000		

Table 5. Bond angles (°) for Compound 18.

N7-W1-C10	95.0(2)	N7-W1-C11	95.6(2)
C10-W1-C11	38.93(19)	N7-W1-N5	98.02(19)
C10-W1-N5	84.28(18)	C11-W1-N5	122.53(18)
N7-W1-N3	89.30(19)	C10-W1-N3	161.69(18)
C11-W1-N3	158.20(17)	N5-W1-N3	77.50(16)
N7-W1-N1	175.18(19)	C10-W1-N1	88.86(19)
C11-W1-N1	89.23(18)	N5-W1-N1	79.51(16)
N3-W1-N1	86.13(16)	N7-W1-P1	95.91(14)
C10-W1-P1	116.88(15)	C11-W1-P1	78.16(14)
N5-W1-P1	153.46(13)	N3-W1-P1	80.21(11)
N1-W1-P1	84.83(11)	C21-P1-C20	102.4(3)

C21-P1-C22	103.6(3)	C20-P1-C22	100.3(3)
C21-P1-W1	114.6(2)	C20-P1-W1	121.20(19)
C22-P1-W1	112.5(2)	C16-O2-C15	113.3(4)
C1-N1-N2	106.7(5)	C1-N1-W1	133.9(4)
N2-N1-W1	119.3(3)	C3-N2-N1	109.9(4)
C3-N2-B1	128.0(5)	N1-N2-B1	121.9(5)
C4-N3-N4	105.8(4)	C4-N3-W1	131.1(4)
N4-N3-W1	123.0(3)	C6-N4-N3	110.2(4)
C6-N4-B1	130.4(5)	N3-N4-B1	117.9(4)
C7-N5-N6	107.6(5)	C7-N5-W1	131.3(4)
N6-N5-W1	120.3(3)	C9-N6-N5	108.1(5)
C9-N6-B1	129.6(5)	N5-N6-B1	122.0(4)
O1-N7-W1	177.0(4)	C18-N8-C17	124.9(5)
C18-N8-C14	116.2(4)	C17-N8-C14	118.1(5)
N1-C1-C2	109.7(5)	N1-C1-H1	125.100000
C2-C1-H1	125.100000	C3-C2-C1	105.5(5)
C3-C2-H2	127.300000	C1-C2-H2	127.300000
N2-C3-C2	108.2(5)	N2-C3-H3	125.900000
C2-C3-H3	125.900000	N3-C4-C5	111.2(5)
N3-C4-H4	124.400000	C5-C4-H4	124.400000
C6-C5-C4	104.6(5)	C6-C5-H5	127.700000
C4-C5-H5	127.700000	N4-C6-C5	108.1(5)
N4-C6-H6	125.900000	C5-C6-H6	125.900000
N5-C7-C8	110.3(6)	N5-C7-H7	124.800000

C8-C7-H7	124.800000	C9-C8-C7	105.5(5)
C9-C8-H8	127.300000	C7-C8-H8	127.300000
N6-C9-C8	108.5(5)	N6-C9-H9	125.800000
C8-C9-H9	125.800000	C11-C10-C15	113.7(5)
C11-C10-W1	70.6(3)	C15-C10-W1	124.1(4)
C11-C10-H10	121.(4)	C15-C10-H10	110.(4)
W1-C10-H10	113.(4)	C10-C11-C12	116.2(5)
C10-C11-W1	70.4(3)	C12-C11-W1	121.3(4)
C10-C11-H11	114.(3)	C12-C11-H11	114.(3)
W1-C11-H11	114.(4)	C11-C12-C13	110.7(4)
C11-C12-H12A	109.500000	C13-C12-H12A	109.500000
C11-C12-H12B	109.500000	C13-C12-H12B	109.500000
H12A-C12-H12B	108.100000	C12-C13-C19	113.0(5)
C12-C13-C14	109.6(5)	C19-C13-C14	105.0(4)
C12-C13-H13	109.700000	C19-C13-H13	109.700000
C14-C13-H13	109.700000	N8-C14-C15	110.0(5)
N8-C14-C13	103.7(4)	C15-C14-C13	115.3(5)
N8-C14-H14	109.200000	C15-C14-H14	109.200000
C13-C14-H14	109.200000	O2-C15-C10	112.7(5)
O2-C15-C14	109.7(4)	C10-C15-C14	112.7(4)
O2-C15-H15	107.200000	C10-C15-H15	107.200000
C14-C15-H15	107.200000	O2-C16-C17	113.6(5)

O2-C16-H16A	108.900000	C17-C16-H16A	108.900000
O2-C16-H16B	108.900000	C17-C16-H16B	108.900000
H16A-C16-H16B	107.700000	N8-C17-C16	108.3(5)
N8-C17-H17A	110.000000	C16-C17-H17A	110.000000
N8-C17-H17B	110.000000	C16-C17-H17B	110.000000
H17A-C17-H17B	108.400000	O3-C18-N8	125.7(5)
O3-C18-C19	125.7(5)	N8-C18-C19	108.6(5)
C18-C19-C13	105.9(4)	C18-C19-H19A	110.600000
C13-C19-H19A	110.600000	C18-C19-H19B	110.600000
C13-C19-H19B	110.600000	H19A-C19-H19B	108.700000
P1-C20-H20A	109.500000	P1-C20-H20B	109.500000
H20A-C20-H20B	109.500000	P1-C20-H20C	109.500000
H20A-C20-H20C	109.500000	H20B-C20-H20C	109.500000
P1-C21-H21A	109.500000	P1-C21-H21B	109.500000
H21A-C21-H21B	109.500000	P1-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000

P1-C22-H22A	109.500000	P1-C22-H22B	109.500000
H22A-C22-H22B	109.500000	P1-C22-H22C	109.500000
H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
N6-B1-N4	106.1(5)	N6-B1-N2	108.7(5)
N4-B1-N2	109.4(4)	N6-B1-H1A	109.(3)
N4-B1-H1A	111.(3)	N2-B1-H1A	113.(3)
N9-C23-C24	178.8(8)	C23-C24-H24A	109.500000
C23-C24-H24B	109.500000	H24A-C24-H24B	109.500000
C23-C24-H24C	109.500000	H24A-C24-H24C	109.500000
H24B-C24-H24C	109.500000		

Table 6. Torsion angles (°) for Compound 18.

C1-N1-N2-C3	0.6(5)	W1-N1-N2-C3	-175.1(3)
C1-N1-N2-B1	-174.7(4)	W1-N1-N2-B1	9.6(6)
C4-N3-N4-C6	0.6(6)	W1-N3-N4-C6	178.4(3)
C4-N3-N4-B1	168.0(4)	W1-N3-N4-B1	-14.1(6)
C7-N5-N6-C9	-1.0(5)	W1-N5-N6-C9	170.1(3)

C7-N5-N6-B1	-176.1(4)	W1-N5-N6-B1	-5.0(6)
N2-N1-C1-C2	-0.7(6)	W1-N1-C1-C2	174.1(3)
N1-C1-C2-C3	0.5(6)	N1-N2-C3-C2	-0.3(6)
B1-N2-C3-C2	174.6(5)	C1-C2-C3-N2	-0.1(6)
N4-N3-C4-C5	0.0(6)	W1-N3-C4-C5	-177.6(4)
N3-C4-C5-C6	-0.6(6)	N3-N4-C6-C5	-0.9(6)
B1-N4-C6-C5	-166.3(5)	C4-C5-C6-N4	0.9(6)
N6-N5-C7-C8	0.6(6)	W1-N5-C7-C8	-169.1(4)
N5-C7-C8-C9	0.0(6)	N5-N6-C9-C8	1.0(5)
B1-N6-C9-C8	175.6(5)	C7-C8-C9-N6	-0.6(6)
C15-C10-C11-C12	3.6(7)	W1-C10-C11-C12	-116.1(4)
C15-C10-C11-W1	119.7(4)	C10-C11-C12-C13	-55.7(6)
W1-C11-C12-C13	-137.7(4)	C11-C12-C13-C19	-60.8(6)
C11-C12-C13-C14	56.0(6)	C18-N8-C14-C15	-115.9(5)
C17-N8-C14-C15	53.9(7)	C18-N8-C14-C13	8.0(7)
C17-N8-C14-C13	177.7(5)	C12-C13-C14-N8	-128.8(5)
C19-C13-C14-N8	-7.2(6)	C12-C13-C14-C15	-8.5(7)

C19-C13-C14-C15	113.1(5)	C16-O2-C15-C10	-73.3(6)
C16-O2-C15-C14	53.0(7)	C11-C10-C15-O2	168.8(4)
W1-C10-C15-O2	-109.2(5)	C11-C10-C15-C14	44.1(6)
W1-C10-C15-C14	126.0(4)	N8-C14-C15-O2	-50.5(6)
C13-C14-C15-O2	-167.3(5)	N8-C14-C15-C10	75.9(6)
C13-C14-C15-C10	-40.9(6)	C15-O2-C16-C17	-55.2(7)
C18-N8-C17-C16	115.6(6)	C14-N8-C17-C16	-53.2(7)
O2-C16-C17-N8	51.4(7)	C17-N8-C18-O3	6.2(10)
C14-N8-C18-O3	175.2(6)	C17-N8-C18-C19	-174.1(5)
C14-N8-C18-C19	-5.2(7)	O3-C18-C19-C13	179.6(6)
N8-C18-C19-C13	-0.1(7)	C12-C13-C19-C18	124.1(5)
C14-C13-C19-C18	4.6(6)	C9-N6-B1-N4	-110.5(6)
N5-N6-B1-N4	63.4(6)	C9-N6-B1-N2	131.9(5)
N5-N6-B1-N2	-54.2(6)	C6-N4-B1-N6	113.6(6)
N3-N4-B1-N6	-50.9(6)	C6-N4-B1-N2	-129.3(6)
N3-N4-B1-N2	66.2(6)	C3-N2-B1-N6	-123.5(6)

N1-N2-B1-N6	50.8(6)	C3-N2-B1-N4	121.1(6)			
N1-N2-B1-N4	-64.6(6)					

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 18.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01248(12)	0.00969(10)	0.01157(11)	0.00030(10)	0.00277(8)	-0.00044(10)
P1	0.0156(9)	0.0131(6)	0.0231(8)	0.0050(6)	0.0054(7)	-0.0008(6)
O1	0.028(3)	0.037(2)	0.018(2)	-0.0147(19)	-0.002(2)	0.000(2)
O2	0.039(3)	0.039(3)	0.045(3)	0.003(2)	0.016(3)	0.007(2)
O3	0.028(3)	0.026(2)	0.024(2)	-0.0073(19)	0.005(2)	-0.0054(19)
N1	0.012(3)	0.014(2)	0.017(2)	0.0009(19)	0.0024(19)	-0.0009(19)
N2	0.018(3)	0.011(2)	0.011(2)	0.0000(18)	-0.0015(19)	-0.0022(19)
N3	0.013(3)	0.012(2)	0.012(2)	0.0012(18)	0.003(2)	0.0026(18)
N4	0.015(3)	0.015(2)	0.013(2)	0.0009(19)	0.003(2)	0.0031(19)
N5	0.016(3)	0.012(2)	0.017(2)	-0.005(2)	0.005(2)	-0.0004(19)
N6	0.016(3)	0.015(2)	0.016(2)	-0.0008(19)	0.010(2)	-0.0003(19)
N7	0.017(3)	0.013(2)	0.021(3)	0.003(2)	0.004(2)	0.0008(19)
N8	0.017(3)	0.016(2)	0.026(3)	-0.002(2)	0.009(2)	0.003(2)
C1	0.025(4)	0.016(3)	0.013(3)	0.001(2)	0.008(2)	-0.001(2)
C2	0.033(4)	0.015(3)	0.012(3)	-0.004(2)	0.004(3)	-0.004(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	0.030(4)	0.011(2)	0.018(3)	-0.001(2)	-0.006(3)	-0.002(2)
C4	0.021(4)	0.018(3)	0.014(3)	-0.002(2)	0.005(3)	-0.001(2)
C5	0.027(4)	0.019(3)	0.018(3)	-0.004(2)	0.003(3)	0.002(3)
C6	0.022(4)	0.021(3)	0.018(3)	0.002(2)	0.006(3)	0.008(3)
C7	0.034(4)	0.008(2)	0.011(3)	0.000(2)	0.004(3)	0.000(2)
C8	0.024(4)	0.014(3)	0.016(3)	0.002(2)	0.010(3)	-0.002(2)
C9	0.016(3)	0.015(2)	0.019(3)	-0.005(2)	0.013(3)	-0.004(2)
C10	0.018(3)	0.008(2)	0.020(3)	-0.001(2)	0.001(3)	-0.003(2)
C11	0.012(3)	0.019(3)	0.009(3)	-0.003(2)	0.002(2)	0.003(2)
C12	0.012(3)	0.013(3)	0.035(3)	0.002(3)	0.005(3)	-0.003(2)
C13	0.022(4)	0.018(3)	0.027(3)	-0.005(3)	0.009(3)	-0.003(3)
C14	0.018(3)	0.017(3)	0.017(3)	-0.002(2)	-0.001(2)	0.003(2)
C15	0.018(3)	0.015(2)	0.017(3)	0.004(2)	0.004(2)	0.005(2)
C16	0.028(4)	0.014(3)	0.031(4)	-0.001(3)	0.008(3)	0.002(3)
C17	0.026(4)	0.018(3)	0.023(3)	0.005(2)	0.007(3)	0.004(3)
C18	0.015(3)	0.025(3)	0.020(3)	-0.002(3)	0.002(3)	0.001(2)
C19	0.017(3)	0.026(3)	0.019(3)	0.004(3)	0.008(3)	0.002(2)
C20	0.023(4)	0.024(3)	0.029(3)	0.013(3)	0.013(3)	0.009(3)
C21	0.026(4)	0.017(3)	0.045(4)	0.001(3)	0.007(3)	-0.010(3)
C22	0.023(4)	0.029(3)	0.031(4)	0.011(3)	0.010(3)	0.006(3)
B1	0.016(4)	0.019(3)	0.013(3)	0.005(2)	0.005(3)	0.000(2)
N9	0.041(4)	0.029(3)	0.032(3)	-0.001(3)	-0.008(3)	-0.003(3)
C23	0.027(4)	0.037(4)	0.022(3)	-0.007(3)	-0.006(3)	0.006(3)

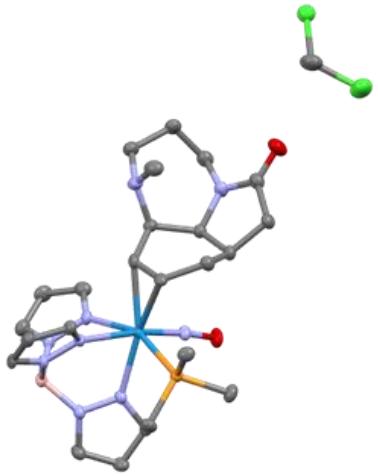
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C24	0.037(4)	0.026(3)	0.026(3)	-0.003(3)	0.008(3)	-0.004(3)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 18.

	x/a	y/b	z/c	U(eq)
H1	0.3902	0.2953	0.3751	0.021000
H2	0.5765	0.3163	0.4662	0.024000
H3	0.7345	0.2874	0.3723	0.024000
H4	0.4615	0.0288	0.0684	0.021000
H5	0.6636	-0.0289	0.0730	0.025000
H6	0.7876	0.0866	0.1517	0.024000
H7	0.4091	0.3893	0.0139	0.021000
H8	0.5986	0.4470	-0.0234	0.021000
H9	0.7488	0.3740	0.0761	0.019000
H10	0.308(5)	0.385(4)	0.200(4)	0.018000
H11	0.235(5)	0.275(3)	0.281(4)	0.016000
H12A	0.0807	0.1903	0.2258	0.024000
H12B	0.1080	0.2119	0.1307	0.024000
H13	-0.0576	0.2938	0.1601	0.026000
H14	0.0079	0.3991	0.0779	0.021000
H15	0.1825	0.3354	0.0549	0.020000
H16A	0.2408	0.5949	0.0964	0.029000

	x/a	y/b	z/c	U(eq)
H16B	0.2709	0.5314	0.1762	0.029000
H17A	0.0978	0.5992	0.1963	0.026000
H17B	0.0447	0.5731	0.1026	0.026000
H19A	-0.0707	0.3489	0.2904	0.024000
H19B	0.0635	0.3298	0.3167	0.024000
H20A	0.2900	0.1497	0.3758	0.037000
H20B	0.2608	0.0460	0.3719	0.037000
H20C	0.1749	0.1156	0.3232	0.037000
H21A	0.1737	0.0262	0.1718	0.044000
H21B	0.2500	-0.0481	0.2223	0.044000
H21C	0.2895	-0.0084	0.1358	0.044000
H22A	0.5037	0.0105	0.2448	0.041000
H22B	0.4395	-0.0155	0.3265	0.041000
H22C	0.5107	0.0752	0.3252	0.041000
H1A	0.758(5)	0.258(3)	0.206(4)	0.019000
H24A	0.0418	0.5840	0.4509	0.044000
H24B	-0.0651	0.6096	0.5027	0.044000
H24C	0.0515	0.5737	0.5519	0.044000

Structure Report for Compound 20



A ?, needle shaped crystal of Compound 20 measuring 0.04×0.091×0.166 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for harman_ld_2_87_x2 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[152] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with XT[153] and refined by full-matrix least-squares methods against F^2 using XL[154] within OLEX2.[155] All non-hydrogen atoms were refined with anisotropically. The B-H atom was located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[156]

[152] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[153] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[154] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[155] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[156] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for Compound 20

CCDC number	
Empirical formula	$C_{25}H_{39}BCl_2N_9O_2PW$
Formula weight	794.18
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.04×0.091×0.166
Crystal habit	? needle
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
a [Å]	10.2091(6)
b [Å]	12.4991(7)
c [Å]	12.5035(6)
α [°]	106.427(2)
β [°]	101.778(2)
γ [°]	94.072(2)
Volume [$Å^3$]	1484.01(14)
Z	2
ρ_{calc} [gcm^{-3}]	1.777
μ [mm^{-1}]	4.168
F(000)	792
2θ range [°]	4.08 to 52.75 (0.80 Å)
Index ranges	−12 ≤ h ≤ 12 −15 ≤ k ≤ 15 −14 ≤ l ≤ 15
Reflections collected	44707
Independent reflections	6011 [R_{int} = 0.0416]
Data / Restraints / Parameters	6011 / 0 / 378
Goodness-of-fit on F^2	1.105
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0336 wR_2 = 0.0972
Final *R* indexes [all data]	R_1 = 0.0367 wR_2 = 0.0998

Largest peak/hole [eÅ^{-3}]	2.50/−0.93

Table 2 Atomic coordinates and Ueq [Å2] for Compound 20

Atom	*x*	*y*	*z*	U_{eq}
W1	0.23000(2)	0.65410(2)	0.32458(2)	0.02266(8)
P1	0.23001(13)	0.75429(11)	0.17675(12)	0.0265(3)
O1	0.5323(4)	0.6920(4)	0.3931(3)	0.0367(9)
O2	0.5771(5)	0.1942(4)	0.1161(4)	0.0457(11)
N1	0.0048(4)	0.6589(3)	0.2824(4)	0.0253(8)
N2	−0.0566(4)	0.7151(4)	0.3658(4)	0.0268(9)
N3	0.2374(4)	0.8275(4)	0.4377(4)	0.0260(9)
N4	0.1380(4)	0.8627(4)	0.4893(4)	0.0271(9)
N5	0.1834(4)	0.6266(4)	0.4828(4)	0.0282(9)
N6	0.0948(4)	0.6861(4)	0.5350(4)	0.0284(9)
N7	0.4084(4)	0.6705(4)	0.3636(4)	0.0275(9)
N8	0.4842(5)	0.3041(4)	0.2515(4)	0.0308(9)
N9	0.2034(5)	0.2716(4)	0.2463(4)	0.0336(10)
C1	−0.0944(5)	0.6149(4)	0.1881(5)	0.0284(10)
H1	−0.081428	0.572504	0.115886	0.034
C2	−0.2185(5)	0.6393(5)	0.2094(5)	0.0312(11)
H2	−0.304440	0.617032	0.157128	0.037
C3	−0.1898(5)	0.7030(4)	0.3234(5)	0.0265(10)
H3	−0.254017	0.733225	0.364724	0.032
C4	0.3354(5)	0.9154(4)	0.4699(5)	0.0298(11)
H4	0.418469	0.914193	0.446760	0.036
C5	0.2974(6)	1.0084(5)	0.5421(5)	0.0350(12)
H5	0.346889	1.081780	0.576358	0.042
C6	0.1719(6)	0.9707(5)	0.5529(5)	0.0324(11)
H6	0.118581	1.014086	0.598023	0.039
C7	0.2288(6)	0.5621(5)	0.5477(5)	0.0327(11)
H7	0.294533	0.513121	0.533464	0.039
C8	0.1665(6)	0.5768(5)	0.6390(5)	0.0363(12)
H8	0.179383	0.539979	0.696482	0.044
C9	0.0825(6)	0.6556(5)	0.6280(5)	0.0335(12)
H9	0.025302	0.684027	0.677553	0.040
C10	0.1881(5)	0.4691(4)	0.2622(4)	0.0273(10)
H10	0.091571	0.443587	0.257982	0.033
C11	0.1981(5)	0.5092(4)	0.1655(4)	0.0270(10)
H11	0.108329	0.502421	0.112013	0.032

C12	0.3066(6)	0.4702(5)	0.1030(5)	0.0308(11)
H12A	0.327275	0.525012	0.063021	0.037
H12B	0.269963	0.397088	0.043758	0.037
C13	0.4373(5)	0.4566(5)	0.1778(5)	0.0291(11)
H13	0.493426	0.532192	0.212686	0.035
C14	0.4214(5)	0.4074(4)	0.2764(4)	0.0282(10)
H14	0.478392	0.460715	0.349423	0.034
C15	0.2768(5)	0.3865(4)	0.2952(4)	0.0280(10)
H15	0.289087	0.404096	0.380056	0.034
C16	0.5181(6)	0.3768(5)	0.1070(5)	0.0321(11)
H16A	0.470018	0.349661	0.025078	0.038
H16B	0.608510	0.416077	0.113623	0.038
C17	0.5309(6)	0.2798(5)	0.1561(5)	0.0344(12)
C18	0.4964(6)	0.2331(5)	0.3262(5)	0.0355(12)
H18A	0.504925	0.280462	0.406189	0.043
H18B	0.579450	0.197218	0.323164	0.043
C19	0.3757(6)	0.1427(5)	0.2921(5)	0.0374(12)
H19A	0.393163	0.090921	0.338944	0.045
H19B	0.363844	0.098328	0.210670	0.045
C20	0.2460(6)	0.1920(5)	0.3085(5)	0.0379(13)
H20A	0.171826	0.128755	0.285850	0.045
H20B	0.257094	0.230453	0.391413	0.045
C21	0.1740(6)	0.2228(5)	0.1219(5)	0.0405(13)
H21A	0.123391	0.272094	0.085632	0.061
H21B	0.120078	0.148529	0.099376	0.061
H21C	0.258888	0.214974	0.097129	0.061
C22	0.1533(6)	0.6847(5)	0.0238(4)	0.0312(11)
H22A	0.197400	0.618650	−0.003995	0.047
H22B	0.164689	0.737404	−0.019650	0.047
H22C	0.056763	0.660998	0.013603	0.047
C23	0.3971(6)	0.8086(5)	0.1724(5)	0.0363(12)
H23A	0.437806	0.868520	0.243988	0.054
H23B	0.390670	0.838930	0.107558	0.054
H23C	0.453298	0.747756	0.163166	0.054
C24	0.1403(6)	0.8768(5)	0.1988(5)	0.0361(12)
H24A	0.044885	0.852822	0.192776	0.054
H24B	0.147753	0.913639	0.140307	0.054
H24C	0.180051	0.929812	0.275100	0.054
B1	0.0246(6)	0.7739(5)	0.4893(5)	0.0287(12)

Cl1	0.8580(2)	0.06154(17)	0.1055(2)	0.0710(6)
Cl2	0.73556(16)	−0.13147(13)	0.15165(13)	0.0425(3)
C25	0.7037(8)	−0.0125(6)	0.1060(7)	0.0543(17)
H25A	0.657286	0.037477	0.158300	0.065
H25B	0.644032	−0.036705	0.027936	0.065
H1A	−0.041(6)	0.813(5)	0.540(5)	0.037(17)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å2) for Compound 20. The anisotropic displacement factor exponent takes the form: −2π2[h2(a*)2U11 + k2(b*)2U22 + ... + 2hka*b*U12]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01956(12)	0.02352(12)	0.02550(12)	0.00693(8)	0.00751(8)	0.00250(7)
P1	0.0250(6)	0.0251(6)	0.0302(6)	0.0088(5)	0.0079(5)	0.0021(5)
O1	0.0198(18)	0.047(2)	0.039(2)	0.0062(18)	0.0066(16)	0.0008(16)
O2	0.055(3)	0.042(2)	0.047(2)	0.014(2)	0.021(2)	0.021(2)
N1	0.023(2)	0.023(2)	0.030(2)	0.0073(17)	0.0082(17)	0.0039(16)
N2	0.025(2)	0.026(2)	0.031(2)	0.0090(17)	0.0107(17)	0.0035(16)
N3	0.023(2)	0.027(2)	0.027(2)	0.0073(17)	0.0047(16)	0.0038(16)
N4	0.024(2)	0.027(2)	0.029(2)	0.0052(17)	0.0102(17)	0.0034(17)
N5	0.025(2)	0.027(2)	0.033(2)	0.0079(18)	0.0116(18)	0.0012(17)
N6	0.027(2)	0.035(2)	0.027(2)	0.0118(18)	0.0106(17)	0.0014(18)
N7	0.023(2)	0.029(2)	0.028(2)	0.0047(17)	0.0069(17)	0.0023(17)
N8	0.030(2)	0.033(2)	0.035(2)	0.0164(19)	0.0101(19)	0.0074(18)
N9	0.035(2)	0.027(2)	0.039(3)	0.0103(19)	0.010(2)	0.0029(19)
C1	0.025(2)	0.027(3)	0.033(3)	0.010(2)	0.006(2)	0.0017(19)
C2	0.023(2)	0.034(3)	0.039(3)	0.016(2)	0.007(2)	0.005(2)
C3	0.019(2)	0.027(2)	0.035(3)	0.010(2)	0.010(2)	0.0026(18)
C4	0.024(2)	0.027(3)	0.037(3)	0.006(2)	0.010(2)	0.0000(19)
C5	0.032(3)	0.027(3)	0.041(3)	0.003(2)	0.009(2)	0.003(2)
C6	0.031(3)	0.033(3)	0.030(3)	0.003(2)	0.009(2)	0.005(2)
C7	0.032(3)	0.026(3)	0.035(3)	0.008(2)	0.000(2)	0.003(2)
C8	0.048(3)	0.038(3)	0.026(3)	0.014(2)	0.010(2)	0.003(3)
C9	0.034(3)	0.037(3)	0.032(3)	0.013(2)	0.014(2)	0.000(2)
C10	0.020(2)	0.031(3)	0.032(3)	0.008(2)	0.0102(19)	0.0021(19)
C11	0.028(2)	0.022(2)	0.030(3)	0.0058(19)	0.009(2)	0.0009(19)
C12	0.034(3)	0.031(3)	0.028(3)	0.009(2)	0.008(2)	0.008(2)
C13	0.027(3)	0.031(3)	0.032(3)	0.010(2)	0.011(2)	0.004(2)

C14	0.027(2)	0.029(3)	0.030(3)	0.009(2)	0.009(2)	0.004(2)
C15	0.030(3)	0.025(2)	0.027(2)	0.007(2)	0.007(2)	0.002(2)
C16	0.033(3)	0.032(3)	0.034(3)	0.010(2)	0.014(2)	0.007(2)
C17	0.035(3)	0.035(3)	0.036(3)	0.012(2)	0.012(2)	0.011(2)
C18	0.039(3)	0.037(3)	0.035(3)	0.015(2)	0.011(2)	0.011(2)
C19	0.042(3)	0.035(3)	0.044(3)	0.020(3)	0.016(3)	0.009(2)
C20	0.043(3)	0.029(3)	0.046(3)	0.013(2)	0.017(3)	0.006(2)
C21	0.039(3)	0.034(3)	0.046(3)	0.011(3)	0.005(3)	0.005(2)
C22	0.033(3)	0.030(3)	0.028(3)	0.010(2)	0.002(2)	0.002(2)
C23	0.028(3)	0.042(3)	0.037(3)	0.011(2)	0.009(2)	−0.003(2)
C24	0.042(3)	0.029(3)	0.042(3)	0.013(2)	0.012(3)	0.010(2)
B1	0.028(3)	0.031(3)	0.029(3)	0.007(2)	0.013(2)	0.005(2)
Cl1	0.0726(13)	0.0515(11)	0.1068(17)	0.0388(11)	0.0384(12)	0.0122(9)
Cl2	0.0453(8)	0.0408(8)	0.0438(8)	0.0149(6)	0.0124(6)	0.0066(6)
C25	0.060(4)	0.039(4)	0.066(5)	0.018(3)	0.013(4)	0.014(3)

Table 4 Bond lengths and angles for harman_ld_2_87_x2**tom–Atom**	**Length [Å]**
W1–P1	2.5087(13)
W1–N1	2.260(4)
W1–N3	2.215(4)
W1–N5	2.237(4)
W1–N7	1.767(4)
W1–C10	2.201(5)
W1–C11	2.226(5)
P1–C22	1.838(5)
P1–C23	1.808(6)
P1–C24	1.823(6)
O1–N7	1.231(6)
O2–C17	1.218(7)
N1–N2	1.374(6)
N1–C1	1.336(7)
N2–C3	1.336(6)
N2–B1	1.537(7)
N3–N4	1.345(6)
N3–C4	1.341(7)

N4–C6	1.338(7)
N4–B1	1.545(7)
N5–N6	1.364(6)
N5–C7	1.339(7)
N6–C9	1.349(7)
N6–B1	1.531(8)
N8–C14	1.466(7)
N8–C17	1.338(7)
N8–C18	1.452(7)
N9–C15	1.470(7)
N9–C20	1.464(7)
N9–C21	1.459(8)
C1–H1	0.9500
C1–C2	1.384(7)
C2–H2	0.9500
C2–C3	1.381(8)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.390(8)
C5–H5	0.9500
C5–C6	1.380(8)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.391(8)
C8–H8	0.9500
C8–C9	1.369(8)
C9–H9	0.9500
C10–H10	1.0000
C10–C11	1.453(7)
C10–C15	1.509(7)
C11–H11	1.0000
C11–C12	1.513(7)
C12–H12A	0.9900
C12–H12B	0.9900
C12–C13	1.516(7)
C13–H13	1.0000
C13–C14	1.555(7)
C13–C16	1.541(7)
C14–H14	1.0000

C14–C15	1.558(7)
C15–H15	1.0000
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.509(8)
C18–H18A	0.9900
C18–H18B	0.9900
C18–C19	1.514(8)
C19–H19A	0.9900
C19–H19B	0.9900
C19–C20	1.527(8)
C20–H20A	0.9900
C20–H20B	0.9900
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
B1–H1A	1.06(6)
Cl1–C25	1.772(8)
Cl2–C25	1.765(7)
C25–H25A	0.9900
C25–H25B	0.9900
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	83.89(11)
N3–W1–P1	82.20(12)
N3–W1–N1	83.86(15)
N3–W1–N5	76.89(16)
N3–W1–C11	160.06(18)
N5–W1–P1	155.46(12)
N5–W1–N1	81.26(16)

N7–W1–P1	92.41(15)
N7–W1–N1	172.24(17)
N7–W1–N3	88.88(18)
N7–W1–N5	99.81(18)
N7–W1–C10	99.35(19)
N7–W1–C11	98.19(19)
C10–W1–P1	117.04(14)
C10–W1–N1	88.41(17)
C10–W1–N3	158.42(18)
C10–W1–N5	82.04(17)
C10–W1–C11	38.31(19)
C11–W1–P1	78.91(14)
C11–W1–N1	87.82(17)
C11–W1–N5	119.72(17)
C22–P1–W1	121.98(18)
C23–P1–W1	113.6(2)
C23–P1–C22	101.6(3)
C23–P1–C24	104.3(3)
C24–P1–W1	113.8(2)
C24–P1–C22	99.1(3)
N2–N1–W1	120.2(3)
C1–N1–W1	134.3(4)
C1–N1–N2	105.6(4)
N1–N2–B1	121.2(4)
C3–N2–N1	110.0(4)
C3–N2–B1	128.7(4)
N4–N3–W1	123.7(3)
C4–N3–W1	129.4(4)
C4–N3–N4	106.9(4)
N3–N4–B1	118.7(4)
C6–N4–N3	110.0(4)
C6–N4–B1	129.8(4)
N6–N5–W1	120.4(3)
C7–N5–W1	133.7(4)
C7–N5–N6	105.9(4)
N5–N6–B1	122.1(4)
C9–N6–N5	110.0(4)
C9–N6–B1	127.9(5)
O1–N7–W1	174.3(4)

C17–N8–C14	115.7(4)
C17–N8–C18	122.1(5)
C18–N8–C14	122.2(4)
C20–N9–C15	115.8(5)
C21–N9–C15	117.0(5)
C21–N9–C20	113.6(5)
N1–C1–H1	124.4
N1–C1–C2	111.2(5)
C2–C1–H1	124.4
C1–C2–H2	127.6
C3–C2–C1	104.7(5)
C3–C2–H2	127.6
N2–C3–C2	108.5(4)
N2–C3–H3	125.7
C2–C3–H3	125.7
N3–C4–H4	125.0
N3–C4–C5	109.9(5)
C5–C4–H4	125.0
C4–C5–H5	127.7
C6–C5–C4	104.7(5)
C6–C5–H5	127.7
N4–C6–C5	108.5(5)
N4–C6–H6	125.8
C5–C6–H6	125.8
N5–C7–H7	124.7
N5–C7–C8	110.7(5)
C8–C7–H7	124.7
C7–C8–H8	127.4
C9–C8–C7	105.1(5)
C9–C8–H8	127.4
N6–C9–C8	108.3(5)
N6–C9–H9	125.8
C8–C9–H9	125.8
W1–C10–H10	110.3
C11–C10–W1	71.8(3)
C11–C10–H10	110.3
C11–C10–C15	121.5(4)
C15–C10–W1	127.4(4)
C15–C10–H10	110.3

W1–C11–H11	112.6
C10–C11–W1	69.9(3)
C10–C11–H11	112.6
C10–C11–C12	117.3(4)
C12–C11–W1	125.0(4)
C12–C11–H11	112.6
C11–C12–H12A	108.4
C11–C12–H12B	108.4
C11–C12–C13	115.4(4)
H12A–C12–H12B	107.5
C13–C12–H12A	108.4
C13–C12–H12B	108.4
C12–C13–H13	108.1
C12–C13–C14	115.5(4)
C12–C13–C16	111.4(4)
C14–C13–H13	108.1
C16–C13–H13	108.1
C16–C13–C14	105.3(4)
N8–C14–C13	103.8(4)
N8–C14–H14	107.4
N8–C14–C15	112.3(4)
C13–C14–H14	107.4
C13–C14–C15	117.9(4)
C15–C14–H14	107.4
N9–C15–C10	109.9(4)
N9–C15–C14	118.0(4)
N9–C15–H15	105.3
C10–C15–C14	112.0(4)
C10–C15–H15	105.3
C14–C15–H15	105.3
C13–C16–H16A	110.5
C13–C16–H16B	110.5
H16A–C16–H16B	108.7
C17–C16–C13	106.0(4)
C17–C16–H16A	110.5
C17–C16–H16B	110.5
O2–C17–N8	125.7(5)
O2–C17–C16	125.7(5)
N8–C17–C16	108.6(5)

N8–C18–H18A	109.2
N8–C18–H18B	109.2
N8–C18–C19	111.9(5)
H18A–C18–H18B	107.9
C19–C18–H18A	109.2
C19–C18–H18B	109.2
C18–C19–H19A	109.2
C18–C19–H19B	109.2
C18–C19–C20	112.1(5)
H19A–C19–H19B	107.9
C20–C19–H19A	109.2
C20–C19–H19B	109.2
N9–C20–C19	117.4(5)
N9–C20–H20A	108.0
N9–C20–H20B	108.0
C19–C20–H20A	108.0
C19–C20–H20B	108.0
H20A–C20–H20B	107.2
N9–C21–H21A	109.5
N9–C21–H21B	109.5
N9–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5

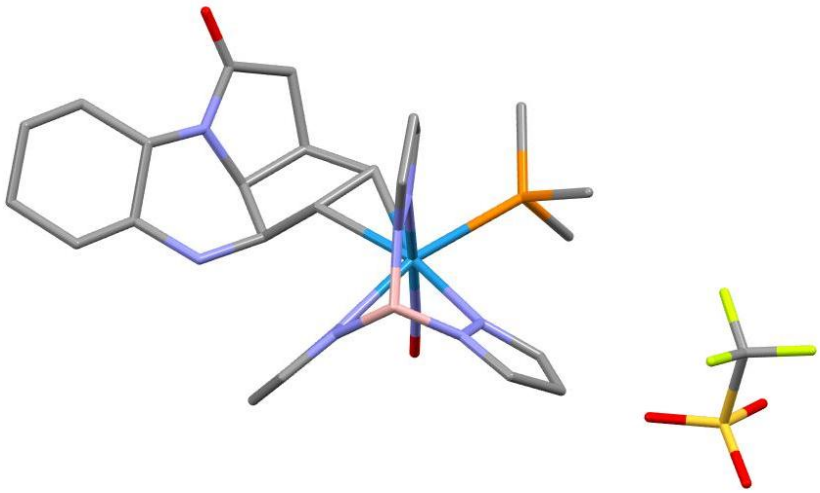
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
N2–B1–N4	109.7(4)
N2–B1–H1A	110(4)
N4–B1–H1A	110(3)
N6–B1–N2	108.2(4)
N6–B1–N4	106.4(4)
N6–B1–H1A	113(4)
Cl1–C25–H25A	109.7
Cl1–C25–H25B	109.7
Cl2–C25–Cl1	109.8(4)
Cl2–C25–H25A	109.7
Cl2–C25–H25B	109.7
H25A–C25–H25B	108.2

Table 5 Torsion angles for Compound 20 **Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	−177.4(3)
W1–N1–N2–B1	−1.1(6)
W1–N1–C1–C2	177.2(4)
W1–N3–N4–C6	179.3(4)
W1–N3–N4–B1	12.0(6)
W1–N3–C4–C5	−179.8(4)
W1–N5–N6–C9	180.0(3)
W1–N5–N6–B1	−0.5(6)
W1–N5–C7–C8	179.6(4)
W1–C10–C11–C12	119.8(4)
W1–C10–C15–N9	172.2(3)
W1–C10–C15–C14	−54.5(6)
W1–C11–C12–C13	48.3(6)
N1–N2–C3–C2	−1.0(6)
N1–N2–B1–N4	58.3(6)
N1–N2–B1–N6	−57.4(6)
N1–C1–C2–C3	0.8(6)

N2–N1–C1–C2	−1.4(6)
N3–N4–C6–C5	0.6(6)
N3–N4–B1–N2	−64.9(6)
N3–N4–B1–N6	51.9(6)
N3–C4–C5–C6	1.0(7)
N4–N3–C4–C5	−0.7(6)
N5–N6–C9–C8	1.4(6)
N5–N6–B1–N2	59.0(6)
N5–N6–B1–N4	−58.8(6)
N5–C7–C8–C9	−1.3(7)
N6–N5–C7–C8	2.1(6)
N8–C14–C15–N9	−22.2(6)
N8–C14–C15–C10	−151.3(4)
N8–C18–C19–C20	−65.7(6)
C1–N1–N2–C3	1.4(5)
C1–N1–N2–B1	177.7(4)
C1–C2–C3–N2	0.1(6)
C3–N2–B1–N4	−126.2(5)
C3–N2–B1–N6	118.1(5)
C4–N3–N4–C6	0.0(6)
C4–N3–N4–B1	−167.3(5)
C4–C5–C6–N4	−1.0(7)
C6–N4–B1–N2	130.7(6)
C6–N4–B1–N6	−112.5(6)
C7–N5–N6–C9	−2.1(6)
C7–N5–N6–B1	177.4(5)
C7–C8–C9–N6	−0.1(6)
C9–N6–B1–N2	−121.5(6)
C9–N6–B1–N4	120.7(5)
C10–C11–C12–C13	−35.3(7)
C11–C10–C15–N9	−97.3(6)
C11–C10–C15–C14	35.9(7)
C11–C12–C13–C14	38.4(7)
C11–C12–C13–C16	158.4(4)
C12–C13–C14–N8	120.1(5)
C12–C13–C14–C15	−4.9(7)
C12–C13–C16–C17	−119.2(5)
C13–C14–C15–N9	98.4(6)
C13–C14–C15–C10	−30.7(6)

C13–C16–C17–O2	172.6(6)
C13–C16–C17–N8	−8.0(6)
C14–N8–C17–O2	−174.3(6)
C14–N8–C17–C16	6.3(7)
C14–N8–C18–C19	90.8(6)
C14–C13–C16–C17	6.7(6)
C15–N9–C20–C19	−77.7(6)
C15–C10–C11–W1	−123.3(5)
C15–C10–C11–C12	−3.4(7)
C16–C13–C14–N8	−3.3(5)
C16–C13–C14–C15	−128.2(5)
C17–N8–C14–C13	−1.9(6)
C17–N8–C14–C15	126.6(5)
C17–N8–C18–C19	−89.9(6)
C18–N8–C14–C13	177.5(5)
C18–N8–C14–C15	−54.1(6)
C18–N8–C17–O2	6.4(9)
C18–N8–C17–C16	−173.0(5)
C18–C19–C20–N9	58.6(7)
C20–N9–C15–C10	−153.4(5)
C20–N9–C15–C14	76.5(6)
C21–N9–C15–C10	68.4(6)
C21–N9–C15–C14	−61.7(6)
C21–N9–C20–C19	61.9(7)
B1–N2–C3–C2	−176.9(5)
B1–N4–C6–C5	166.1(5)
B1–N6–C9–C8	−178.2(5)

Structure Report for Compound 5.15



A colourless, plate shaped crystal of Compound 5.15 measuring 0.046×0.079×0.109 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 5.15 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[157] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by dual methods with SHELXT[158] and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/1[159] within OLEX2.[160] All non-hydrogen atoms were refined with anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[161]

[157] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[158] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[159] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[160] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[161] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for Compound 5.15

CCDC number	
Empirical formula	$C_{27}H_{40}BF_3N_9O_5PSW$
Formula weight	885.37
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.046×0.079×0.109
Crystal habit	colourless plate
Crystal system	monoclinic
Space group	Pn (7)
a [Å]	12.2532(6)
b [Å]	7.4647(4)
c [Å]	17.8039(9)
α [°]	90
β [°]	100.779(2)
γ [°]	90
Volume [$Å^3$]	1599.73(14)
Z	2
ρ_{calc} [gcm^{-3}]	1.838
μ [mm^{-1}]	3.798
F(000)	884
2θ range [°]	4.45 to 52.76 (0.80 Å)
Index ranges	−15 ≤ h ≤ 15 −9 ≤ k ≤ 9 −22 ≤ l ≤ 22
Reflections collected	37253
Independent reflections	6536 [R_{int} = 0.0374]
Data / Restraints / Parameters	6536 / 2 / 436
Goodness-of-fit on F^2	1.080
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0313 wR_2 = 0.0770
Final *R* indexes [all data]	R_1 = 0.0319 wR_2 = 0.0773

Largest peak/hole [eÅ^{-3}]	7.19/−0.84
Flack X parameter	-0.019(2)

Table 2 Atomic coordinates and Ueq [Å2] for Compound 5.15

Atom	***x***	***y***	***z***	U_{eq}
S1	0.14245(18)	0.2543(3)	0.72095(12)	0.0229(4)
F1	0.0426(5)	0.3978(7)	0.5913(3)	0.0297(13)
F2	−0.0366(4)	0.4553(8)	0.6863(3)	0.0280(11)
F3	0.1155(6)	0.5882(8)	0.6756(4)	0.0341(15)
O3	0.1548(5)	0.3211(12)	0.7984(4)	0.0325(15)
O4	0.2439(5)	0.2538(10)	0.6911(4)	0.0310(15)
O5	0.0737(7)	0.1000(9)	0.7032(5)	0.0394(19)
C27	0.0616(7)	0.4353(13)	0.6663(5)	0.0217(17)
W1	0.49812(2)	0.60208(3)	0.50363(2)	0.01339(9)
P1	0.39455(17)	0.7919(3)	0.58347(11)	0.0169(4)
O1	0.6119(6)	0.3739(8)	0.6335(4)	0.0245(14)
O2	0.8668(5)	1.2047(8)	0.4659(3)	0.0199(12)
N1	0.4126(5)	0.7509(9)	0.3990(3)	0.0127(13)
N2	0.3596(6)	0.6594(9)	0.3361(4)	0.0154(13)
N3	0.3399(6)	0.4444(10)	0.4764(4)	0.0162(13)
N4	0.2963(6)	0.3985(8)	0.4022(4)	0.0162(14)
N5	0.5340(6)	0.3990(8)	0.4225(4)	0.0173(14)
N6	0.4703(6)	0.3736(9)	0.3517(4)	0.0159(14)
N7	0.5634(5)	0.4684(9)	0.5820(4)	0.0149(13)
N8	0.8072(6)	0.5553(9)	0.4355(4)	0.0151(13)
H8A	0.821402	0.436608	0.443976	0.018
H8B	0.751217	0.564682	0.394186	0.018
N9	0.8738(6)	0.9028(8)	0.4889(4)	0.0158(14)
C1	0.3934(7)	0.9246(11)	0.3840(5)	0.0177(16)
H1	0.421725	1.020027	0.417297	0.021
C2	0.3254(7)	0.9457(12)	0.3120(5)	0.0188(16)
H2	0.298034	1.054592	0.287976	0.023
C3	0.3067(6)	0.7740(11)	0.2833(4)	0.0159(15)
H3	0.263943	0.742659	0.234925	0.019
C4	0.2732(8)	0.3723(11)	0.5196(5)	0.0205(17)
H4	0.284381	0.381390	0.573677	0.025
C5	0.1855(7)	0.2822(12)	0.4747(5)	0.0212(17)
H5	0.126293	0.220542	0.491038	0.025
C6	0.2035(7)	0.3021(12)	0.4015(5)	0.0209(17)

H6	0.157338	0.254869	0.357087	0.025
C7	0.6186(6)	0.2851(11)	0.4287(5)	0.0170(15)
H7	0.674391	0.271017	0.473189	0.020
C8	0.6142(7)	0.1900(12)	0.3615(5)	0.0209(17)
H8	0.665638	0.103196	0.350438	0.025
C9	0.5187(6)	0.2487(10)	0.3141(4)	0.0135(15)
H9	0.491561	0.207986	0.263544	0.016
C10	0.6151(7)	0.8306(11)	0.5367(4)	0.0160(15)
H10	0.586080	0.950582	0.517533	0.019
C11	0.6528(6)	0.7190(10)	0.4810(4)	0.0139(14)
H11	0.643242	0.776903	0.429556	0.017
C12	0.7669(7)	0.6335(11)	0.5052(5)	0.0154(15)
H12	0.760796	0.533968	0.541857	0.018
C13	0.8526(6)	0.7693(10)	0.5449(4)	0.0145(15)
H13	0.923304	0.706207	0.567066	0.017
C14	0.8123(7)	0.8819(10)	0.6078(5)	0.0176(17)
H14	0.862337	0.857883	0.657945	0.021
C15	0.6930(7)	0.8322(12)	0.6145(4)	0.0176(16)
H15A	0.692937	0.712196	0.638186	0.021
H15B	0.665223	0.919383	0.648334	0.021
C16	0.9096(7)	0.6427(10)	0.4164(5)	0.0158(15)
H16	0.973663	0.614201	0.458325	0.019
C17	0.9334(8)	0.5632(14)	0.3428(5)	0.0183(18)
H17A	0.867192	0.576149	0.301789	0.022
H17B	0.949837	0.433802	0.350158	0.022
C18	1.0329(7)	0.6583(12)	0.3191(5)	0.0227(17)
H18A	1.101098	0.631966	0.356991	0.027
H18B	1.043551	0.612321	0.268853	0.027
C19	1.0148(8)	0.8581(12)	0.3142(5)	0.0234(18)
H19A	0.950130	0.884727	0.273365	0.028
H19B	1.080877	0.916311	0.300273	0.028
C20	0.9945(7)	0.9350(12)	0.3896(5)	0.0200(17)
H20A	0.981249	1.065608	0.384001	0.024
H20B	1.061191	0.916147	0.429720	0.024
C21	0.8946(7)	0.8456(10)	0.4134(4)	0.0144(15)
H21	0.827184	0.874080	0.374152	0.017
C22	0.8577(7)	1.0723(11)	0.5076(5)	0.0173(16)
C23	0.8267(7)	1.0770(11)	0.5854(5)	0.0182(16)
H23A	0.756721	1.144416	0.583728	0.022

H23B	0.886040	1.135381	0.622841	0.022
C24	0.4286(7)	1.0271(11)	0.6001(5)	0.0195(16)
H24A	0.508030	1.039219	0.621293	0.029
H24B	0.385268	1.076318	0.636298	0.029
H24C	0.410891	1.092705	0.551662	0.029
C25	0.4060(9)	0.7091(13)	0.6810(5)	0.0271(19)
H25A	0.377694	0.586146	0.679864	0.041
H25B	0.362290	0.785777	0.708954	0.041
H25C	0.484027	0.710968	0.706684	0.041
C26	0.2447(7)	0.8108(13)	0.5488(5)	0.0249(18)
H26A	0.230886	0.864017	0.497570	0.037
H26B	0.212137	0.887119	0.583616	0.037
H26C	0.210901	0.691543	0.546648	0.037
B1	0.3542(8)	0.4543(12)	0.3361(5)	0.0146(16)
H1A	0.311403	0.409773	0.286193	0.018

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for Compound 5.15. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0217(10)	0.0297(11)	0.0165(10)	0.0038(8)	0.0020(8)	0.0019(8)
F1	0.037(3)	0.033(3)	0.019(3)	0.001(2)	0.004(2)	0.010(2)
F2	0.025(3)	0.033(3)	0.027(3)	−0.004(2)	0.008(2)	0.001(2)
F3	0.038(4)	0.028(3)	0.038(4)	0.001(2)	0.012(3)	−0.007(3)
O3	0.024(3)	0.057(5)	0.016(3)	0.002(3)	0.003(3)	−0.002(3)
O4	0.026(3)	0.044(4)	0.024(3)	0.002(3)	0.004(3)	0.008(3)
O5	0.042(5)	0.031(4)	0.040(4)	0.006(3)	−0.005(4)	−0.001(3)
C27	0.021(4)	0.029(5)	0.015(4)	−0.003(4)	0.003(3)	0.000(4)
W1	0.01501(13)	0.01354(14)	0.01135(13)	0.00016(16)	0.00178(8)	−0.00087(17)
P1	0.0176(9)	0.0196(10)	0.0134(9)	0.0009(8)	0.0029(7)	0.0007(8)
O1	0.029(4)	0.022(3)	0.019(3)	0.007(3)	−0.005(3)	0.004(3)
O2	0.019(3)	0.019(3)	0.022(3)	0.001(2)	0.006(2)	0.000(2)
N1	0.014(3)	0.016(3)	0.007(3)	−0.001(2)	0.000(2)	−0.003(2)
N2	0.017(3)	0.017(3)	0.010(3)	−0.002(3)	−0.003(2)	−0.002(3)
N3	0.016(3)	0.019(3)	0.014(3)	0.002(3)	0.004(3)	0.000(3)
N4	0.012(3)	0.019(4)	0.017(3)	0.002(3)	0.000(3)	−0.001(2)
N5	0.018(3)	0.018(4)	0.015(3)	−0.003(2)	0.001(3)	−0.002(3)

N6	0.017(3)	0.018(3)	0.013(3)	0.000(3)	0.003(3)	−0.001(3)
N7	0.016(3)	0.013(3)	0.016(3)	−0.001(3)	0.003(3)	0.001(3)
N8	0.020(3)	0.011(3)	0.015(3)	0.000(3)	0.003(3)	−0.001(3)
N9	0.018(3)	0.017(4)	0.013(3)	0.000(2)	0.004(3)	−0.002(2)
C1	0.021(4)	0.015(4)	0.018(4)	0.000(3)	0.006(3)	−0.001(3)
C2	0.019(4)	0.022(4)	0.015(4)	0.004(3)	0.001(3)	−0.002(3)
C3	0.015(4)	0.020(4)	0.012(3)	0.003(3)	0.000(3)	−0.001(3)
C4	0.024(4)	0.020(4)	0.018(4)	0.002(3)	0.005(3)	0.002(3)
C5	0.017(4)	0.024(4)	0.025(4)	−0.001(3)	0.008(3)	−0.002(3)
C6	0.016(4)	0.021(4)	0.024(4)	−0.006(4)	0.001(3)	−0.003(3)
C7	0.013(3)	0.016(4)	0.022(4)	0.002(3)	0.001(3)	0.000(3)
C8	0.018(4)	0.020(4)	0.025(4)	−0.001(3)	0.006(3)	0.000(3)
C9	0.017(4)	0.013(3)	0.012(3)	−0.002(3)	0.005(3)	−0.003(3)
C10	0.021(4)	0.017(4)	0.010(3)	0.001(3)	0.003(3)	−0.006(3)
C11	0.017(4)	0.015(4)	0.010(3)	0.000(3)	0.001(3)	−0.002(3)
C12	0.019(4)	0.015(4)	0.013(4)	−0.002(3)	0.004(3)	−0.001(3)
C13	0.017(4)	0.014(4)	0.012(3)	0.001(3)	0.000(3)	0.000(3)
C14	0.020(4)	0.019(4)	0.013(4)	0.000(3)	0.001(3)	0.000(3)
C15	0.018(4)	0.021(4)	0.013(4)	−0.002(3)	0.001(3)	−0.003(3)
C16	0.016(4)	0.009(3)	0.023(4)	0.000(3)	0.003(3)	−0.002(3)
C17	0.018(4)	0.017(4)	0.020(4)	−0.002(3)	0.004(4)	−0.002(4)
C18	0.024(4)	0.022(4)	0.025(4)	−0.003(4)	0.012(3)	−0.002(4)
C19	0.028(5)	0.020(4)	0.026(5)	−0.002(3)	0.013(4)	−0.001(4)
C20	0.021(4)	0.019(4)	0.021(4)	−0.004(3)	0.008(3)	−0.003(3)
C21	0.019(4)	0.007(3)	0.017(4)	−0.003(3)	0.005(3)	−0.001(3)
C22	0.011(4)	0.017(4)	0.023(4)	−0.003(3)	0.002(3)	0.000(3)
C23	0.021(4)	0.016(4)	0.017(4)	−0.004(3)	0.001(3)	0.001(3)
C24	0.021(4)	0.017(4)	0.021(4)	−0.002(3)	0.005(3)	0.004(3)
C25	0.039(5)	0.027(5)	0.015(4)	0.004(4)	0.006(4)	0.006(4)
C26	0.021(4)	0.030(5)	0.024(4)	0.003(4)	0.005(3)	0.006(4)
B1	0.018(4)	0.013(4)	0.013(4)	−0.003(4)	0.003(3)	−0.004(3)

Table 4 Bond lengths and angles for Compound 5.15 **Atom–Atom**	**Length [Å]**
S1–O5	1.427(8)
S1–O4	1.441(7)
S1–O3	1.448(7)

S1–C27	1.842(10)
F1–C27	1.341(10)
F2–C27	1.326(10)
F3–C27	1.313(11)
W1–N7	1.779(7)
W1–C11	2.191(8)
W1–N5	2.195(7)
W1–C10	2.235(8)
W1–N3	2.243(7)
W1–N1	2.253(6)
W1–P1	2.513(2)
P1–C24	1.816(9)
P1–C25	1.824(9)
P1–C26	1.830(9)
O1–N7	1.220(9)
O2–C22	1.253(11)
N1–C1	1.336(10)
N1–N2	1.367(9)
N2–C3	1.345(10)
N2–B1	1.532(11)
N3–C4	1.335(11)
N3–N4	1.372(10)
N4–C6	1.345(11)
N4–B1	1.541(11)
N5–C7	1.329(11)
N5–N6	1.366(10)
N6–C9	1.347(10)
N6–B1	1.522(12)
N8–C16	1.508(10)
N8–C12	1.535(10)
N8–H8A	0.9100
N8–H8B	0.9100
N9–C22	1.333(10)
N9–C13	1.466(10)
N9–C21	1.477(10)
C1–C2	1.401(12)
C1–H1	0.9500
C2–C3	1.382(12)
C2–H2	0.9500

C3–H3	0.9500
C4–C5	1.387(12)
C4–H4	0.9500
C5–C6	1.369(12)
C5–H5	0.9500
C6–H6	0.9500
C7–C8	1.384(12)
C7–H7	0.9500
C8–C9	1.380(11)
C8–H8	0.9500
C9–H9	0.9500
C10–C11	1.435(11)
C10–C15	1.528(10)
C10–H10	1.0000
C11–C12	1.524(11)
C11–H11	1.0000
C12–C13	1.534(11)
C12–H12	1.0000
C13–C14	1.554(11)
C13–H13	1.0000
C14–C23	1.529(11)
C14–C15	1.534(11)
C14–H14	1.0000
C15–H15A	0.9900
C15–H15B	0.9900
C16–C17	1.516(12)
C16–C21	1.525(11)
C16–H16	1.0000
C17–C18	1.537(12)
C17–H17A	0.9900
C17–H17B	0.9900
C18–C19	1.508(12)
C18–H18A	0.9900
C18–H18B	0.9900
C19–C20	1.523(12)
C19–H19A	0.9900
C19–H19B	0.9900
C20–C21	1.523(11)
C20–H20A	0.9900

C20–H20B	0.9900
C21–H21	1.0000
C22–C23	1.505(12)
C23–H23A	0.9900
C23–H23B	0.9900
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
B1–H1A	1.0000
Atom–Atom–Atom	**Angle [°]**
O5–S1–O4	115.5(5)
O5–S1–O3	116.2(5)
O4–S1–O3	114.1(4)
O5–S1–C27	103.8(4)
O4–S1–C27	102.9(4)
O3–S1–C27	101.6(4)
F3–C27–F2	109.2(8)
F3–C27–F1	107.3(8)
F2–C27–F1	107.1(7)
F3–C27–S1	111.2(6)
F2–C27–S1	111.5(6)
F1–C27–S1	110.4(6)
N7–W1–C11	95.2(3)
N7–W1–N5	90.7(3)
C11–W1–N5	82.4(3)
N7–W1–C10	92.8(3)
C11–W1–C10	37.8(3)
N5–W1–C10	120.2(3)
N7–W1–N3	96.8(3)
C11–W1–N3	155.8(3)
N5–W1–N3	76.5(3)
C10–W1–N3	160.7(3)

N7–W1–N1	175.4(3)
C11–W1–N1	86.3(3)
N5–W1–N1	85.2(2)
C10–W1–N1	91.0(3)
N3–W1–N1	80.2(2)
N7–W1–P1	94.2(2)
C11–W1–P1	115.2(2)
N5–W1–P1	161.2(2)
C10–W1–P1	77.7(2)
N3–W1–P1	84.88(18)
N1–W1–P1	89.07(17)
C24–P1–C25	101.4(4)
C24–P1–C26	99.5(4)
C25–P1–C26	103.9(4)
C24–P1–W1	120.8(3)
C25–P1–W1	113.0(3)
C26–P1–W1	115.7(3)
C1–N1–N2	106.4(6)
C1–N1–W1	132.9(5)
N2–N1–W1	120.5(5)
C3–N2–N1	110.3(7)
C3–N2–B1	128.4(7)
N1–N2–B1	120.9(6)
C4–N3–N4	106.5(7)
C4–N3–W1	133.2(6)
N4–N3–W1	120.3(5)
C6–N4–N3	108.5(7)
C6–N4–B1	130.4(7)
N3–N4–B1	121.1(6)
C7–N5–N6	106.9(7)
C7–N5–W1	129.5(6)
N6–N5–W1	123.6(5)
C9–N6–N5	109.0(7)
C9–N6–B1	131.8(7)
N5–N6–B1	117.9(7)
O1–N7–W1	176.7(6)
C16–N8–C12	115.2(6)
C16–N8–H8A	108.5
C12–N8–H8A	108.5

C16–N8–H8B	108.5
C12–N8–H8B	108.5
H8A–N8–H8B	107.5
C22–N9–C13	115.0(7)
C22–N9–C21	124.1(7)
C13–N9–C21	120.3(6)
N1–C1–C2	110.1(7)
N1–C1–H1	124.9
C2–C1–H1	124.9
C3–C2–C1	105.3(8)
C3–C2–H2	127.4
C1–C2–H2	127.4
N2–C3–C2	107.9(7)
N2–C3–H3	126.1
C2–C3–H3	126.1
N3–C4–C5	110.8(8)
N3–C4–H4	124.6
C5–C4–H4	124.6
C6–C5–C4	104.5(7)
C6–C5–H5	127.7
C4–C5–H5	127.7
N4–C6–C5	109.7(7)
N4–C6–H6	125.2
C5–C6–H6	125.2
N5–C7–C8	110.6(7)
N5–C7–H7	124.7
C8–C7–H7	124.7
C9–C8–C7	104.9(7)
C9–C8–H8	127.6
C7–C8–H8	127.6
N6–C9–C8	108.5(7)
N6–C9–H9	125.7
C8–C9–H9	125.7
C11–C10–C15	113.8(7)
C11–C10–W1	69.4(4)
C15–C10–W1	120.4(5)
C11–C10–H10	115.1
C15–C10–H10	115.1
W1–C10–H10	115.1

C10–C11–C12	116.3(6)
C10–C11–W1	72.8(4)
C12–C11–W1	124.1(5)
C10–C11–H11	112.6
C12–C11–H11	112.6
W1–C11–H11	112.6
C11–C12–C13	111.5(6)
C11–C12–N8	110.3(6)
C13–C12–N8	109.1(6)
C11–C12–H12	108.6
C13–C12–H12	108.6
N8–C12–H12	108.6
N9–C13–C12	109.3(6)
N9–C13–C14	104.1(6)
C12–C13–C14	114.0(7)
N9–C13–H13	109.8
C12–C13–H13	109.8
C14–C13–H13	109.8
C23–C14–C15	114.2(7)
C23–C14–C13	105.0(6)
C15–C14–C13	111.2(7)
C23–C14–H14	108.8
C15–C14–H14	108.8
C13–C14–H14	108.8
C10–C15–C14	112.0(6)
C10–C15–H15A	109.2
C14–C15–H15A	109.2
C10–C15–H15B	109.2
C14–C15–H15B	109.2
H15A–C15–H15B	107.9
N8–C16–C17	109.2(6)
N8–C16–C21	109.8(6)
C17–C16–C21	113.6(7)
N8–C16–H16	108.1
C17–C16–H16	108.1
C21–C16–H16	108.1
C16–C17–C18	110.3(7)
C16–C17–H17A	109.6
C18–C17–H17A	109.6

C16–C17–H17B	109.6
C18–C17–H17B	109.6
H17A–C17–H17B	108.1
C19–C18–C17	111.0(8)
C19–C18–H18A	109.4
C17–C18–H18A	109.4
C19–C18–H18B	109.4
C17–C18–H18B	109.4
H18A–C18–H18B	108.0
C18–C19–C20	111.6(7)
C18–C19–H19A	109.3
C20–C19–H19A	109.3
C18–C19–H19B	109.3
C20–C19–H19B	109.3
H19A–C19–H19B	108.0
C19–C20–C21	110.6(7)
C19–C20–H20A	109.5
C21–C20–H20A	109.5
C19–C20–H20B	109.5
C21–C20–H20B	109.5
H20A–C20–H20B	108.1
N9–C21–C20	114.3(7)
N9–C21–C16	107.2(6)
C20–C21–C16	110.3(7)
N9–C21–H21	108.3
C20–C21–H21	108.3
C16–C21–H21	108.3
O2–C22–N9	124.6(8)
O2–C22–C23	126.4(8)
N9–C22–C23	109.1(7)
C22–C23–C14	106.2(7)
C22–C23–H23A	110.5
C14–C23–H23A	110.5
C22–C23–H23B	110.5
C14–C23–H23B	110.5
H23A–C23–H23B	108.7
P1–C24–H24A	109.5
P1–C24–H24B	109.5
H24A–C24–H24B	109.5

P1–C24–H24C	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
H25A–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
H26A–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
N6–B1–N2	110.9(6)
N6–B1–N4	107.5(7)
N2–B1–N4	107.2(6)
N6–B1–H1A	110.4
N2–B1–H1A	110.4
N4–B1–H1A	110.4

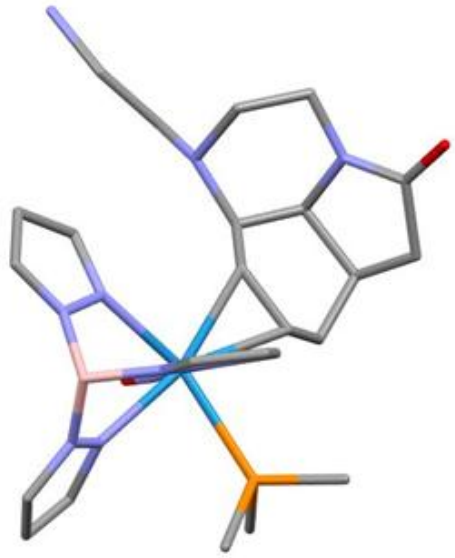
Table 5 Torsion angles for Compound 5.15 **Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
O5–S1–C27–F3	−178.8(7)
O4–S1–C27–F3	−58.1(7)
O3–S1–C27–F3	60.3(7)
O5–S1–C27–F2	59.1(8)
O4–S1–C27–F2	179.8(6)
O3–S1–C27–F2	−61.9(7)
O5–S1–C27–F1	−59.8(7)
O4–S1–C27–F1	60.9(7)
O3–S1–C27–F1	179.3(6)
C1–N1–N2–C3	−1.1(9)
W1–N1–N2–C3	174.7(5)
C1–N1–N2–B1	−174.0(7)
W1–N1–N2–B1	1.8(9)
C4–N3–N4–C6	0.9(9)
W1–N3–N4–C6	178.7(5)

C4–N3–N4–B1	−178.0(7)
W1–N3–N4–B1	−0.2(9)
C7–N5–N6–C9	−2.2(9)
W1–N5–N6–C9	175.6(5)
C7–N5–N6–B1	165.9(7)
W1–N5–N6–B1	−16.3(9)
N2–N1–C1–C2	1.5(9)
W1–N1–C1–C2	−173.5(6)
N1–C1–C2–C3	−1.4(9)
N1–N2–C3–C2	0.2(9)
B1–N2–C3–C2	172.4(7)
C1–C2–C3–N2	0.7(9)
N4–N3–C4–C5	−1.0(10)
W1–N3–C4–C5	−178.4(6)
N3–C4–C5–C6	0.7(10)
N3–N4–C6–C5	−0.5(9)
B1–N4–C6–C5	178.3(8)
C4–C5–C6–N4	−0.1(10)
N6–N5–C7–C8	2.6(9)
W1–N5–C7–C8	−175.0(6)
N5–C7–C8–C9	−2.0(10)
N5–N6–C9–C8	0.9(9)
B1–N6–C9–C8	−164.9(8)
C7–C8–C9–N6	0.6(9)
C15–C10–C11–C12	−4.9(10)
W1–C10–C11–C12	−120.1(7)
C15–C10–C11–W1	115.1(6)
C10–C11–C12–C13	−45.6(9)
W1–C11–C12–C13	−131.9(6)
C10–C11–C12–N8	−167.0(6)
W1–C11–C12–N8	106.7(6)
C16–N8–C12–C11	115.5(7)
C16–N8–C12–C13	−7.3(9)
C22–N9–C13–C12	124.3(7)
C21–N9–C13–C12	−47.0(9)
C22–N9–C13–C14	2.2(9)
C21–N9–C13–C14	−169.1(7)
C11–C12–C13–N9	−68.1(8)
N8–C12–C13–N9	54.0(8)

C11–C12–C13–C14	47.9(9)
N8–C12–C13–C14	170.0(6)
N9–C13–C14–C23	−6.2(8)
C12–C13–C14–C23	−125.1(7)
N9–C13–C14–C15	117.8(7)
C12–C13–C14–C15	−1.2(9)
C11–C10–C15–C14	54.1(9)
W1–C10–C15–C14	133.3(6)
C23–C14–C15–C10	69.3(9)
C13–C14–C15–C10	−49.3(9)
C12–N8–C16–C17	−175.1(7)
C12–N8–C16–C21	−50.0(9)
N8–C16–C17–C18	176.3(7)
C21–C16–C17–C18	53.5(10)
C16–C17–C18–C19	−54.3(10)
C17–C18–C19–C20	57.4(10)
C18–C19–C20–C21	−57.9(10)
C22–N9–C21–C20	56.8(11)
C13–N9–C21–C20	−132.7(8)
C22–N9–C21–C16	179.4(7)
C13–N9–C21–C16	−10.1(10)
C19–C20–C21–N9	175.7(7)
C19–C20–C21–C16	54.9(9)
N8–C16–C21–N9	58.3(8)
C17–C16–C21–N9	−179.1(7)
N8–C16–C21–C20	−176.7(7)
C17–C16–C21–C20	−54.2(9)
C13–N9–C22–O2	−176.8(7)
C21–N9–C22–O2	−5.9(13)
C13–N9–C22–C23	2.9(10)
C21–N9–C22–C23	173.8(7)
O2–C22–C23–C14	172.9(8)
N9–C22–C23–C14	−6.8(9)
C15–C14–C23–C22	−114.2(7)
C13–C14–C23–C22	7.8(9)
C9–N6–B1–N2	−128.2(8)
N5–N6–B1–N2	67.0(9)
C9–N6–B1–N4	114.9(9)
N5–N6–B1–N4	−49.9(9)

C3–N2–B1–N6	130.0(8)
N1–N2–B1–N6	−58.5(9)
C3–N2–B1–N4	−112.9(9)
N1–N2–B1–N4	58.7(9)
C6–N4–B1–N6	−119.2(9)
N3–N4–B1–N6	59.5(9)
C6–N4–B1–N2	121.5(9)
N3–N4–B1–N2	−59.8(9)

Crystal Structure Report for Compound 16



A colorless, needle-like specimen of $C_{24}H_{38}BN_{10}O_2PW$, approximate dimensions 0.007 mm x 0.073 mm x 0.108 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture PhotonIII Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Cu Kα, λ = 1.54178 Å) and a HELIOS EF double bounce multilayer mirror monochromator.

The total exposure time was 9.23 hours. The frames were integrated with the Bruker SAINT software package[162] using a narrow-frame algorithm. The integration of the data using a

[162] Bruker (2012). Saint; SADABS; APEX5. Bruker AXS Inc., Madison, Wisconsin, USA.

monoclinic unit cell yielded a total of 57045 reflections to a maximum θ angle of 68.45° (0.83 Å resolution), of which 13688 were independent (average redundancy 4.168, completeness = 99.6%, R_{int} = 11.17%, R_{sig} = 7.88%) and 10917 (79.76%) were greater than 2σ(F^2). The final cell constants of a = 22.7017(8) Å, b = 14.4788(4) Å, c = 22.8425(14) Å, β = 93.093(2)°, volume = 7497.2(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 9838 reflections above 20 σ(I) with 5.346° < 2θ < 136.3°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[163] The ratio of minimum to maximum apparent transmission was 0.697. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5460 and 0.9570.

The structure was solved and refined using the Bruker SHELXTL Software Package[164] within APEX5 [1] and OLEX2,[165] using the space group I 2, with Z = 8 for the formula unit, $C_{24}H_{38}BN_{10}O_2PW$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The relative occupancy of the disordered atoms was freely refined, with constraints and restraints on the anisotropic displacement parameters and bond lengths of the disordered atoms. A global RIGU restraint was used due to the weak diffraction data. A mixture of CH_2Cl_2 and Et_2O solvent located in the crystal lattice was severely disordered and could not be adequately modeled with or without restraints. Thus, the structure factors were modified using the PLATON SQUEEZE[166] technique, in order to produce a "solvate-free" structure factor set. PLATON reported a total electron density of 1003 e^- and total solvent accessible volume of 2228 $Å^3$. The final anisotropic full-matrix least-squares refinement on F^2 with 716 variables converged at R1 = 5.35%, for the observed data and wR2 = 14.86% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 1.104 $e^-/Å^3$ and the largest hole was -0.884 $e^-/Å^3$ with an RMS deviation of 0.103 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.283 g/cm^3 and F(000), 2896 e^-.

Table 1. Sample and crystal data for **Compound 16**	
Chemical formula	$C_{24}H_{38}BN_{10}O_2PW$

[163] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[164] Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

[165] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

[166] Spek, A. L. *Acta Crystallogr. Sect C: Struct. Chem.* **2015**, *C71*, 9-18.

Formula weight	724.27 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.007 x 0.073 x 0.108 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	I 2	
Unit cell dimensions	a = 22.7017(8) Å	α = 90°
	b = 14.4788(4) Å	β = 93.093(2)°
	c = 22.8425(14) Å	γ = 90°
Volume	7497.2(6) $Å^3$	
Z	8	
Density (calculated)	1.283 g/cm^3	
Absorption coefficient	6.375 mm^{-1}	
F(000)	2896	

Table 2. Data collection and structure refinement for Compound 16.	
Diffractometer	Bruker D8 Venture PhotonIII Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Cu Kα, λ = 1.54178 Å)
Theta range for data collection	2.67 to 68.45°
Index ranges	-27<=h<=27, -17<=k<=17, -27<=l<=26
Reflections collected	57045

Independent reflections	13688 [R(int) = 0.1117]	
Coverage of independent reflections	99.6%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9570 and 0.5460	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13688 / 755 / 716	
Goodness-of-fit on F^2	1.035	
Δ/σ_{max}	0.003	
Final R indices	10917 data; I>2σ(I)	R1 = 0.0535, wR2 = 0.1355
	all data	R1 = 0.0705, wR2 = 0.1486
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0824P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.009(13)	
Largest diff. peak and hole	1.104 and -0.884 eÅ^{-3}	

R.M.S. deviation from mean	0.103 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 16.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.67888(2)	0.59419(3)	0.30990(3)	0.05511(18)
P1	0.65460(18)	0.7317(3)	0.2466(2)	0.0678(10)
O1	0.5981(8)	0.6541(14)	0.4022(9)	0.131(6)
O2	0.5267(7)	0.2819(13)	0.1539(8)	0.117(5)
N1	0.7467(5)	0.5634(7)	0.2412(6)	0.058(2)
N2	0.8053(5)	0.5675(7)	0.2576(6)	0.060(2)
N3	0.7441(5)	0.6911(7)	0.3477(5)	0.051(2)
N4	0.8029(5)	0.6820(7)	0.3417(6)	0.057(2)
N5	0.7409(5)	0.4986(8)	0.3594(5)	0.054(2)
N6	0.7999(5)	0.5148(8)	0.3613(6)	0.063(3)
N7	0.6306(6)	0.6278(9)	0.3629(7)	0.073(3)
N8	0.6044(6)	0.3393(9)	0.3547(7)	0.077(3)
N9	0.5342(5)	0.3260(9)	0.2491(8)	0.074(3)
C1	0.7425(8)	0.5375(11)	0.1850(8)	0.072(3)
C2	0.7974(8)	0.5238(11)	0.1659(9)	0.077(4)
C3	0.8360(8)	0.5407(11)	0.2130(8)	0.073(4)
C4	0.7371(8)	0.7706(10)	0.3775(7)	0.065(3)

	x/a	**y/b**	**z/c**	**U(eq)**
C5	0.7920(8)	0.8131(10)	0.3888(7)	0.067(3)
C6	0.8321(8)	0.7560(10)	0.3652(7)	0.066(3)
C7	0.7320(7)	0.4251(9)	0.3928(7)	0.061(3)
C8	0.7848(7)	0.3969(11)	0.4170(7)	0.069(3)
C9	0.8258(7)	0.4513(10)	0.3978(7)	0.065(3)
C10	0.6313(6)	0.4627(9)	0.2866(7)	0.061(3)
C11	0.6094(7)	0.5389(10)	0.2488(8)	0.067(3)
C12	0.5461(7)	0.5657(11)	0.2513(11)	0.084(5)
C13	0.5046(6)	0.4815(11)	0.2450(9)	0.077(4)
C14	0.5258(7)	0.4042(10)	0.2871(8)	0.071(3)
C15	0.5834(6)	0.4221(10)	0.3236(8)	0.067(3)
C16	0.6107(9)	0.2610(12)	0.3172(10)	0.088(5)
C17	0.5556(9)	0.2386(11)	0.2785(11)	0.091(5)
C18	0.5232(8)	0.3428(14)	0.1936(11)	0.086(4)
C19	0.5055(8)	0.4369(15)	0.1835(10)	0.094(4)
C20	0.5674(12)	0.3167(18)	0.4036(11)	0.115(6)
C22	0.6302(10)	0.7156(15)	0.1704(10)	0.102(6)
C23	0.7174(7)	0.8075(10)	0.2353(8)	0.068(4)
C24	0.5971(9)	0.8041(12)	0.2766(10)	0.090(5)
B1	0.8273(7)	0.5872(12)	0.3204(7)	0.061(3)
N10	0.572(5)	0.244(9)	0.524(4)	0.142(11)
C21	0.593(4)	0.272(9)	0.462(3)	0.124(8)
N10A	0.5610(14)	0.327(3)	0.5113(15)	0.142(11)
C21A	0.5938(16)	0.369(3)	0.4585(14)	0.124(8)

	x/a	**y/b**	**z/c**	**U(eq)**
W2	0.68077(3)	0.49117(4)	0.67722(3)	0.05836(19)
P2	0.7407(2)	0.3518(3)	0.6541(2)	0.0711(10)
O3	0.5738(9)	0.4446(15)	0.6016(9)	0.132(6)
O4	0.8286(9)	0.7921(13)	0.5315(6)	0.116(5)
N11	0.7578(5)	0.5219(7)	0.7441(6)	0.061(3)
N12	0.7489(6)	0.5195(7)	0.8020(6)	0.063(3)
N13	0.6493(5)	0.3967(7)	0.7447(6)	0.058(2)
N14	0.6624(6)	0.4076(8)	0.8018(6)	0.063(3)
N15	0.6398(5)	0.5884(8)	0.7368(6)	0.061(2)
N16	0.6443(5)	0.5752(8)	0.7974(6)	0.064(3)
N17	0.6199(7)	0.4611(9)	0.6314(7)	0.076(3)
N18	0.6318(9)	0.7477(10)	0.6018(8)	0.096(4)
N19	0.7310(9)	0.7574(10)	0.5337(7)	0.085(4)
N20	0.491(2)	0.917(4)	0.613(4)	0.38(4)
C25	0.8152(8)	0.5450(11)	0.7387(9)	0.074(4)
C26	0.8428(8)	0.5578(11)	0.7938(9)	0.077(4)
C27	0.7982(8)	0.5437(11)	0.8308(8)	0.072(3)
C28	0.6188(6)	0.3162(9)	0.7386(8)	0.060(3)
C29	0.6141(7)	0.2756(11)	0.7914(9)	0.073(4)
C30	0.6418(7)	0.3349(10)	0.8319(8)	0.069(3)
C31	0.6028(7)	0.6610(10)	0.7278(9)	0.069(3)
C32	0.5841(7)	0.6938(11)	0.7816(8)	0.076(4)
C33	0.6128(7)	0.6364(10)	0.8234(8)	0.068(3)
C34	0.7007(7)	0.6192(10)	0.6278(8)	0.069(3)

	x/a	y/b	z/c	U(eq)
C35	0.7352(9)	0.5423(11)	0.6079(8)	0.075(4)
C36	0.7218(13)	0.5179(13)	0.5434(9)	0.106(6)
C37	0.7275(12)	0.5970(15)	0.5036(8)	0.102(5)
C38	0.6878(11)	0.6806(12)	0.5243(9)	0.094(4)
C39	0.6614(9)	0.6633(11)	0.5816(8)	0.078(4)
C40	0.6765(11)	0.8231(11)	0.6094(10)	0.095(5)
C41	0.7103(13)	0.8416(14)	0.5561(11)	0.107(6)
C42	0.7870(12)	0.7364(15)	0.5250(8)	0.092(4)
C43	0.7867(13)	0.6346(16)	0.5044(8)	0.104(5)
C44	0.5785(14)	0.7778(19)	0.5767(17)	0.153(10)
C45	0.544(2)	0.847(4)	0.616(3)	0.26(2)
C46	0.8129(10)	0.3630(12)	0.6286(10)	0.097(6)
C47	0.7036(12)	0.2738(14)	0.6029(9)	0.099(6)
C48	0.7591(7)	0.2763(11)	0.7164(8)	0.068(4)
B2	0.6875(8)	0.5003(13)	0.8256(9)	0.068(3)

Table 4. Bond lengths (Å) for Compound 16.

W1-N7	1.744(13)	W1-N3	2.184(11)
W1-C11	2.199(16)	W1-N5	2.238(11)
W1-C10	2.239(13)	W1-N1	2.300(12)
W1-P1	2.504(4)	P1-C22	1.81(2)
P1-C23	1.829(14)	P1-C24	1.84(2)
O1-N7	1.25(2)	O2-C18	1.27(3)

N1-C1	1.34(2)	N1-N2	1.364(17)
N2-C3	1.32(2)	N2-B1	1.52(2)
N3-C4	1.351(18)	N3-N4	1.356(15)
N4-C6	1.355(18)	N4-B1	1.57(2)
N5-C7	1.330(18)	N5-N6	1.358(17)
N6-C9	1.35(2)	N6-B1	1.56(2)
N8-C16	1.43(2)	N8-C15	1.46(2)
N8-C20	1.47(3)	N9-C18	1.30(3)
N9-C14	1.45(2)	N9-C17	1.50(2)
C1-C2	1.36(2)	C1-H1	0.950000
C2-C3	1.37(3)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.40(2)
C4-H4	0.950000	C5-C6	1.36(2)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.36(2)	C7-H7	0.950000
C8-C9	1.31(2)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.47(2)
C10-C15	1.531(19)	C10-H10	1.000000
C11-C12	1.49(2)	C11-H11	1.000000
C12-C13	1.54(2)	C12-H12A	0.990000
C12-H12B	0.990000	C13-C14	1.54(2)
C13-C19	1.55(3)	C13-H13	1.000000
C14-C15	1.53(2)	C14-H14	1.000000
C15-H15	1.000000	C16-C17	1.53(3)
C16-H16A	0.990000	C16-H16B	0.990000

C17-H17A	0.990000	C17-H17B	0.990000
C18-C19	1.44(3)	C19-H19A	0.990000
C19-H19B	0.990000	C20-C21A	1.55(3)
C20-C21	1.57(4)	C20-H20A	0.990000
C20-H20B	0.990000	C20-H20C	0.990000
C20-H20D	0.990000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
C23-H23A	0.980000	C23-H23B	0.980000
C23-H23C	0.980000	C24-H24A	0.980000
C24-H24B	0.980000	C24-H24C	0.980000
B1-H1A	1.000000	N10-C21	1.58(4)
N10-H10A	0.880000	N10-H10B	0.880000
C21-H21A	0.990000	C21-H21B	0.990000
N10A-C21A	1.57(3)	N10A-H10C	0.880000
N10A-H10D	0.880000	C21A-H21C	0.990000
C21A-H21D	0.990000	W2-N17	1.742(16)
W2-C35	2.189(17)	W2-N15	2.200(12)
W2-N13	2.208(12)	W2-C34	2.230(14)
W2-N11	2.303(13)	W2-P2	2.505(4)
P2-C46	1.78(2)	P2-C47	1.80(2)
P2-C48	1.824(16)	O3-N17	1.24(2)
O4-C42	1.24(3)	N11-N12	1.349(18)
N11-C25	1.36(2)	N12-C27	1.31(2)
N12-B2	1.55(2)	N13-N14	1.331(18)
N13-C28	1.359(18)	N14-C30	1.354(19)

N14-B2	1.55(2)	N15-C31	1.354(19)
N15-N16	1.394(18)	N16-C33	1.302(19)
N16-B2	1.58(2)	N18-C44	1.38(3)
N18-C39	1.48(2)	N18-C40	1.49(3)
N19-C42	1.33(3)	N19-C41	1.41(2)
N19-C38	1.49(3)	N20-C45	1.58(4)
N20-H20E	0.880000	N20-H20F	0.880000
C25-C26	1.39(3)	C25-H25	0.950000
C26-C27	1.37(3)	C26-H26	0.950000
C27-H27	0.950000	C28-C29	1.35(2)
C28-H28	0.950000	C29-C30	1.39(3)
C29-H29	0.950000	C30-H30	0.950000
C31-C32	1.41(3)	C31-H31	0.950000
C32-C33	1.40(2)	C32-H32	0.950000
C33-H33	0.950000	C34-C35	1.45(2)
C34-C39	1.49(2)	C34-H34	1.000000
C35-C36	1.53(3)	C35-H35	1.000000
C36-C37	1.47(3)	C36-H36A	0.990000
C36-H36B	0.990000	C37-C43	1.45(4)
C37-C38	1.60(3)	C37-H37	1.000000
C38-C39	1.49(3)	C38-H38	1.000000
C39-H39	1.000000	C40-C41	1.50(3)
C40-H40A	0.990000	C40-H40B	0.990000
C41-H41A	0.990000	C41-H41B	0.990000
C42-C43	1.55(3)	C43-H43A	0.990000

C43-H43B	0.990000	C44-C45	1.58(4)
C44-H44A	0.990000	C44-H44B	0.990000
C45-H45A	0.990000	C45-H45B	0.990000
C46-H46A	0.980000	C46-H46B	0.980000
C46-H46C	0.980000	C47-H47A	0.980000
C47-H47B	0.980000	C47-H47C	0.980000
C48-H48A	0.980000	C48-H48B	0.980000
C48-H48C	0.980000	B2-H2A	1.000000

Table 5. Bond angles (°) for Compound 16.

N7-W1-N3	89.1(5)	N7-W1-C11	95.0(7)
N3-W1-C11	158.8(5)	N7-W1-N5	102.9(6)
N3-W1-N5	78.6(4)	C11-W1-N5	120.4(5)
N7-W1-C10	95.1(5)	N3-W1-C10	161.5(5)
C11-W1-C10	38.7(6)	N5-W1-C10	82.9(5)
N7-W1-N1	174.6(5)	N3-W1-N1	86.0(4)
C11-W1-N1	88.8(5)	N5-W1-N1	78.4(4)
C10-W1-N1	90.3(4)	N7-W1-P1	93.0(5)
N3-W1-P1	80.8(3)	C11-W1-P1	78.2(4)
N5-W1-P1	153.7(3)	C10-W1-P1	116.8(4)
N1-W1-P1	84.0(3)	C22-P1-C23	98.1(9)
C22-P1-C24	104.2(11)	C23-P1-C24	106.6(9)
C22-P1-W1	119.9(7)	C23-P1-W1	114.2(5)
C24-P1-W1	112.2(6)	C1-N1-N2	107.2(12)
C1-N1-W1	134.0(11)	N2-N1-W1	118.8(9)

C3-N2-N1	108.7(13)	C3-N2-B1	128.4(14)
N1-N2-B1	122.3(11)	C4-N3-N4	106.1(11)
C4-N3-W1	130.7(10)	N4-N3-W1	123.2(8)
C6-N4-N3	110.3(12)	C6-N4-B1	129.9(12)
N3-N4-B1	118.9(10)	C7-N5-N6	107.5(11)
C7-N5-W1	132.2(10)	N6-N5-W1	120.1(8)
C9-N6-N5	107.3(12)	C9-N6-B1	130.7(13)
N5-N6-B1	121.5(11)	O1-N7-W1	177.1(15)
C16-N8-C15	113.5(15)	C16-N8-C20	111.0(16)
C15-N8-C20	111.6(16)	C18-N9-C14	114.4(15)
C18-N9-C17	129.4(16)	C14-N9-C17	116.2(16)
N1-C1-C2	109.3(16)	N1-C1-H1	125.300000
C2-C1-H1	125.300000	C1-C2-C3	106.2(16)
C1-C2-H2	126.900000	C3-C2-H2	126.900000
N2-C3-C2	108.5(15)	N2-C3-H3	125.800000
C2-C3-H3	125.800000	N3-C4-C5	109.8(14)
N3-C4-H4	125.100000	C5-C4-H4	125.100000
C6-C5-C4	105.6(14)	C6-C5-H5	127.200000
C4-C5-H5	127.200000	N4-C6-C5	108.2(14)
N4-C6-H6	125.900000	C5-C6-H6	125.900000
N5-C7-C8	108.4(14)	N5-C7-H7	125.800000
C8-C7-H7	125.800000	C9-C8-C7	108.1(15)
C9-C8-H8	126.000000	C7-C8-H8	126.000000
C8-C9-N6	108.7(14)	C8-C9-H9	125.700000
N6-C9-H9	125.700000	C11-C10-C15	112.6(12)

C11-C10-W1	69.2(8)	C15-C10-W1	122.9(10)
C11-C10-H10	114.700000	C15-C10-H10	114.700000
W1-C10-H10	114.700000	C10-C11-C12	118.0(14)
C10-C11-W1	72.1(8)	C12-C11-W1	122.7(13)
C10-C11-H11	112.700000	C12-C11-H11	112.700000
W1-C11-H11	112.700000	C11-C12-C13	112.0(13)
C11-C12-H12A	109.200000	C13-C12-H12A	109.200000
C11-C12-H12B	109.200000	C13-C12-H12B	109.200000
H12A-C12-H12B	107.900000	C14-C13-C12	110.5(14)
C14-C13-C19	104.2(15)	C12-C13-C19	112.1(16)
C14-C13-H13	110.000000	C12-C13-H13	110.000000
C19-C13-H13	110.000000	N9-C14-C15	108.9(12)
N9-C14-C13	104.1(15)	C15-C14-C13	116.5(12)
N9-C14-H14	109.100000	C15-C14-H14	109.100000
C13-C14-H14	109.100000	N8-C15-C10	111.2(12)
N8-C15-C14	111.9(12)	C10-C15-C14	112.0(14)
N8-C15-H15	107.200000	C10-C15-H15	107.200000
C14-C15-H15	107.200000	N8-C16-C17	114.1(15)
N8-C16-H16A	108.700000	C17-C16-H16A	108.700000
N8-C16-H16B	108.700000	C17-C16-H16B	108.700000
H16A-C16-H16B	107.600000	N9-C17-C16	108.4(14)

N9-C17-H17A	110.000000	C16-C17-H17A	110.000000
N9-C17-H17B	110.000000	C16-C17-H17B	110.000000
H17A-C17-H17B	108.400000	O2-C18-N9	123.(2)
O2-C18-C19	125.(2)	N9-C18-C19	111.8(19)
C18-C19-C13	105.5(19)	C18-C19-H19A	110.600000
C13-C19-H19A	110.600000	C18-C19-H19B	110.600000
C13-C19-H19B	110.600000	H19A-C19-H19B	108.800000
N8-C20-C21A	107.1(19)	N8-C20-C21	122.(4)
N8-C20-H20A	106.800000	C21-C20-H20A	106.800000
N8-C20-H20B	106.800000	C21-C20-H20B	106.800000
H20A-C20-H20B	106.600000	N8-C20-H20C	110.300000
C21A-C20-H20C	110.300000	N8-C20-H20D	110.300000
C21A-C20-H20D	110.300000	H20C-C20-H20D	108.600000
P1-C22-H22A	109.500000	P1-C22-H22B	109.500000
H22A-C22-H22B	109.500000	P1-C22-H22C	109.500000
H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
P1-C23-H23A	109.500000	P1-C23-H23B	109.500000

H23A-C23-H23B	109.500000	P1-C23-H23C	109.500000
H23A-C23-H23C	109.500000	H23B-C23-H23C	109.500000
P1-C24-H24A	109.500000	P1-C24-H24B	109.500000
H24A-C24-H24B	109.500000	P1-C24-H24C	109.500000
H24A-C24-H24C	109.500000	H24B-C24-H24C	109.500000
N2-B1-N6	108.6(11)	N2-B1-N4	110.6(12)
N6-B1-N4	104.1(11)	N2-B1-H1A	111.100000
N6-B1-H1A	111.100000	N4-B1-H1A	111.100000
C21-N10-H10A	120.000000	C21-N10-H10B	120.000000
H10A-N10-H10B	120.000000	C20-C21-N10	138.(8)
C20-C21-H21A	102.600000	N10-C21-H21A	102.600000
C20-C21-H21B	102.600000	N10-C21-H21B	102.600000
H21A-C21-H21B	104.900000	C21A-N10A-H10C	120.000000
C21A-N10A-H10D	120.000000	H10C-N10A-H10D	120.000000
C20-C21A-N10A	105.(3)	C20-C21A-H21C	110.800000
N10A-C21A-H21C	110.800000	C20-C21A-H21D	110.800000
N10A-C21A-H21D	110.800000	H21C-C21A-H21D	108.900000

N17-W2-C35	96.4(7)	N17-W2-N15	100.6(6)
C35-W2-N15	120.4(5)	N17-W2-N13	89.4(5)
C35-W2-N13	158.5(5)	N15-W2-N13	78.5(4)
N17-W2-C34	94.6(6)	C35-W2-C34	38.3(6)
N15-W2-C34	83.4(5)	N13-W2-C34	161.9(5)
N17-W2-N11	174.7(5)	C35-W2-N11	88.6(6)
N15-W2-N11	78.3(4)	N13-W2-N11	85.3(4)
C34-W2-N11	90.5(5)	N17-W2-P2	95.4(5)
C35-W2-P2	77.6(4)	N15-W2-P2	153.9(3)
N13-W2-P2	81.2(3)	C34-W2-P2	115.8(4)
N11-W2-P2	83.9(3)	C46-P2-C47	104.5(11)
C46-P2-C48	97.6(9)	C47-P2-C48	102.2(9)
C46-P2-W2	121.1(6)	C47-P2-W2	113.7(8)
C48-P2-W2	115.0(5)	N12-N11-C25	106.9(14)
N12-N11-W2	119.8(9)	C25-N11-W2	133.2(12)
C27-N12-N11	108.4(14)	C27-N12-B2	129.3(15)
N11-N12-B2	122.1(13)	N14-N13-C28	106.7(12)
N14-N13-W2	123.2(8)	C28-N13-W2	129.9(11)
N13-N14-C30	110.0(13)	N13-N14-B2	120.4(12)
C30-N14-B2	128.8(14)	C31-N15-N16	105.7(13)
C31-N15-W2	133.0(12)	N16-N15-W2	121.0(8)
C33-N16-N15	110.2(13)	C33-N16-B2	128.8(15)
N15-N16-B2	120.7(12)	O3-N17-W2	174.6(16)
C44-N18-C39	122.(2)	C44-N18-C40	113.0(18)
C39-N18-C40	108.9(16)	C42-N19-C41	126.(2)

C42-N19-C38	115.8(17)	C41-N19-C38	117.8(19)
C45-N20-H20E	120.000000	C45-N20-H20F	120.000000
H20E-N20-H20F	120.000000	N11-C25-C26	109.7(16)
N11-C25-H25	125.100000	C26-C25-H25	125.100000
C27-C26-C25	103.2(15)	C27-C26-H26	128.400000
C25-C26-H26	128.400000	N12-C27-C26	111.6(17)
N12-C27-H27	124.200000	C26-C27-H27	124.200000
C29-C28-N13	110.2(15)	C29-C28-H28	124.900000
N13-C28-H28	124.900000	C28-C29-C30	105.7(14)
C28-C29-H29	127.100000	C30-C29-H29	127.100000
N14-C30-C29	107.4(16)	N14-C30-H30	126.300000
C29-C30-H30	126.300000	N15-C31-C32	110.1(16)
N15-C31-H31	125.000000	C32-C31-H31	125.000000
C33-C32-C31	104.1(14)	C33-C32-H32	127.900000
C31-C32-H32	127.900000	N16-C33-C32	109.9(16)
N16-C33-H33	125.100000	C32-C33-H33	125.100000
C35-C34-C39	114.9(15)	C35-C34-W2	69.3(8)
C39-C34-W2	125.8(12)	C35-C34-H34	113.100000
C39-C34-H34	113.100000	W2-C34-H34	113.100000
C34-C35-C36	113.3(16)	C34-C35-W2	72.4(9)
C36-C35-W2	121.8(15)	C34-C35-H35	114.200000
C36-C35-H35	114.200000	W2-C35-H35	114.200000
C37-C36-C35	113.4(17)	C37-C36-H36A	108.900000

C35-C36-H36A	108.900000	C37-C36-H36B	108.900000
C35-C36-H36B	108.900000	H36A-C36-H36B	107.700000
C43-C37-C36	113.(2)	C43-C37-C38	104.5(19)
C36-C37-C38	109.7(17)	C43-C37-H37	109.700000
C36-C37-H37	109.700000	C38-C37-H37	109.700000
C39-C38-N19	107.0(16)	C39-C38-C37	113.2(15)
N19-C38-C37	103.3(19)	C39-C38-H38	111.000000
N19-C38-H38	111.000000	C37-C38-H38	111.000000
N18-C39-C34	113.4(16)	N18-C39-C38	110.3(14)
C34-C39-C38	116.1(17)	N18-C39-H39	105.300000
C34-C39-H39	105.300000	C38-C39-H39	105.300000
N18-C40-C41	114.2(19)	N18-C40-H40A	108.700000
C41-C40-H40A	108.700000	N18-C40-H40B	108.700000
C41-C40-H40B	108.700000	H40A-C40-H40B	107.600000
N19-C41-C40	109.6(16)	N19-C41-H41A	109.700000
C40-C41-H41A	109.700000	N19-C41-H41B	109.700000
C40-C41-H41B	109.700000	H41A-C41-H41B	108.200000
O4-C42-N19	124.(2)	O4-C42-C43	130.(2)
N19-C42-C43	106.(2)	C37-C43-C42	110.(2)

C37-C43-H43A	109.600000	C42-C43-H43A	109.600000
C37-C43-H43B	109.600000	C42-C43-H43B	109.600000
H43A-C43-H43B	108.100000	N18-C44-C45	114.(3)
N18-C44-H44A	108.700000	C45-C44-H44A	108.700000
N18-C44-H44B	108.700000	C45-C44-H44B	108.700000
H44A-C44-H44B	107.600000	C44-C45-N20	142.(5)
C44-C45-H45A	101.500000	N20-C45-H45A	101.500000
C44-C45-H45B	101.500000	N20-C45-H45B	101.500000
H45A-C45-H45B	104.600000	P2-C46-H46A	109.500000
P2-C46-H46B	109.500000	H46A-C46-H46B	109.500000
P2-C46-H46C	109.500000	H46A-C46-H46C	109.500000
H46B-C46-H46C	109.500000	P2-C47-H47A	109.500000
P2-C47-H47B	109.500000	H47A-C47-H47B	109.500000
P2-C47-H47C	109.500000	H47A-C47-H47C	109.500000
H47B-C47-H47C	109.500000	P2-C48-H48A	109.500000

P2-C48-H48B	109.500000	H48A-C48-H48B	109.500000
P2-C48-H48C	109.500000	H48A-C48-H48C	109.500000
H48B-C48-H48C	109.500000	N14-B2-N12	110.9(13)
N14-B2-N16	104.1(13)	N12-B2-N16	106.6(13)
N14-B2-H2A	111.600000	N12-B2-H2A	111.600000
N16-B2-H2A	111.600000		

Table 6. Torsion angles (°) for Compound 16.			
C1-N1-N2-C3	-2.7(15)	W1-N1-N2-C3	175.2(9)
C1-N1-N2-B1	-174.9(13)	W1-N1-N2-B1	3.0(15)
C4-N3-N4-C6	-2.4(16)	W1-N3-N4-C6	174.7(9)
C4-N3-N4-B1	167.6(13)	W1-N3-N4-B1	-15.3(16)
C7-N5-N6-C9	-1.8(16)	W1-N5-N6-C9	175.0(9)
C7-N5-N6-B1	171.3(13)	W1-N5-N6-B1	-11.9(17)
N2-N1-C1-C2	0.9(17)	W1-N1-C1-C2	-176.6(10)
N1-C1-C2-C3	1.1(19)	N1-N2-C3-C2	3.4(16)
B1-N2-C3-C2	175.0(13)	C1-C2-C3-N2	-2.8(18)
N4-N3-C4-C5	1.8(16)	W1-N3-C4-C5	-175.0(10)
N3-C4-C5-C6	-0.6(18)	N3-N4-C6-C5	2.1(17)
B1-N4-C6-C5	-166.5(14)	C4-C5-C6-N4	-0.9(17)

N6-N5-C7-C8	1.8(17)	W1-N5-C7-C8	-174.4(10)
N5-C7-C8-C9	-1.2(18)	C7-C8-C9-N6	0.0(18)
N5-N6-C9-C8	1.1(17)	B1-N6-C9-C8	-171.1(15)
C15-C10-C11-C12	0.(2)	W1-C10-C11-C12	-118.1(16)
C15-C10-C11-W1	118.1(12)	C10-C11-C12-C13	-50.(2)
W1-C11-C12-C13	-135.6(14)	C11-C12-C13-C14	49.(2)
C11-C12-C13-C19	-66.(2)	C18-N9-C14-C15	-123.5(15)
C17-N9-C14-C15	54.8(18)	C18-N9-C14-C13	1.3(17)
C17-N9-C14-C13	179.6(13)	C12-C13-C14-N9	-122.7(15)
C19-C13-C14-N9	-2.1(15)	C12-C13-C14-C15	-3.(2)
C19-C13-C14-C15	117.7(14)	C16-N8-C15-C10	-71.8(18)
C20-N8-C15-C10	162.0(16)	C16-N8-C15-C14	54.3(18)
C20-N8-C15-C14	-72.0(19)	C11-C10-C15-N8	172.7(14)
W1-C10-C15-N8	-108.2(14)	C11-C10-C15-C14	46.7(17)
W1-C10-C15-C14	125.8(12)	N9-C14-C15-N8	-53.7(18)

C13-C14-C15-N8	-170.8(14)	N9-C14-C15-C10	71.9(16)
C13-C14-C15-C10	-45.2(18)	C15-N8-C16-C17	-53.(2)
C20-N8-C16-C17	74.(2)	C18-N9-C17-C16	126.(2)
C14-N9-C17-C16	-52.(2)	N8-C16-C17-N9	49.(2)
C14-N9-C18-O2	-178.2(16)	C17-N9-C18-O2	4.(3)
C14-N9-C18-C19	0.(2)	C17-N9-C18-C19	-177.8(16)
O2-C18-C19-C13	176.7(16)	N9-C18-C19-C13	-1.6(19)
C14-C13-C19-C18	2.3(17)	C12-C13-C19-C18	121.8(15)
C16-N8-C20-C21A	143.(2)	C15-N8-C20-C21A	-89.(3)
C16-N8-C20-C21	86.(6)	C15-N8-C20-C21	-147.(6)
C3-N2-B1-N6	-114.7(15)	N1-N2-B1-N6	55.8(16)
C3-N2-B1-N4	131.6(14)	N1-N2-B1-N4	-57.9(15)
C9-N6-B1-N2	119.8(16)	N5-N6-B1-N2	-51.5(17)
C9-N6-B1-N4	-122.3(15)	N5-N6-B1-N4	66.4(15)
C6-N4-B1-N2	-126.2(15)	N3-N4-B1-N2	66.0(15)
C6-N4-B1-N6	117.3(15)	N3-N4-B1-N6	-50.4(16)

N8-C20-C21-N10	174.(12)	N8-C20-C21A-N10A	-169.(2)
C25-N11-N12-C27	2.3(15)	W2-N11-N12-C27	-176.9(9)
C25-N11-N12-B2	176.9(13)	W2-N11-N12-B2	-2.3(16)
C28-N13-N14-C30	1.1(15)	W2-N13-N14-C30	-174.3(10)
C28-N13-N14-B2	-169.3(12)	W2-N13-N14-B2	15.3(17)
C31-N15-N16-C33	-0.8(15)	W2-N15-N16-C33	-174.8(9)
C31-N15-N16-B2	-175.8(13)	W2-N15-N16-B2	10.3(16)
N12-N11-C25-C26	-0.3(17)	W2-N11-C25-C26	178.8(10)
N11-C25-C26-C27	-1.8(18)	N11-N12-C27-C26	-3.6(17)
B2-N12-C27-C26	-177.7(14)	C25-C26-C27-N12	3.3(18)
N14-N13-C28-C29	-1.5(15)	W2-N13-C28-C29	173.5(10)
N13-C28-C29-C30	1.3(17)	N13-N14-C30-C29	-0.3(17)
B2-N14-C30-C29	169.0(14)	C28-C29-C30-N14	-0.6(17)
N16-N15-C31-C32	0.1(16)	W2-N15-C31-C32	173.1(10)
N15-C31-C32-C33	0.5(17)	N15-N16-C33-C32	1.1(16)

B2-N16-C33-C32	175.6(14)	C31-C32-C33-N16	-1.0(17)
C39-C34-C35-C36	-3.(2)	W2-C34-C35-C36	117.8(17)
C39-C34-C35-W2	-121.0(14)	C34-C35-C36-C37	54.(3)
W2-C35-C36-C37	137.2(19)	C35-C36-C37-C43	62.(3)
C35-C36-C37-C38	-54.(3)	C42-N19-C38-C39	117.5(18)
C41-N19-C38-C39	-56.(2)	C42-N19-C38-C37	-2.(2)
C41-N19-C38-C37	-176.1(18)	C43-C37-C38-C39	-115.(2)
C36-C37-C38-C39	7.(3)	C43-C37-C38-N19	1.(2)
C36-C37-C38-N19	123.(2)	C44-N18-C39-C34	-154.(2)
C40-N18-C39-C34	72.(2)	C44-N18-C39-C38	74.(3)
C40-N18-C39-C38	-61.(2)	C35-C34-C39-N18	-173.7(15)
W2-C34-C39-N18	104.6(16)	C35-C34-C39-C38	-44.(2)
W2-C34-C39-C38	-126.1(15)	N19-C38-C39-N18	60.(2)
C37-C38-C39-N18	172.6(18)	N19-C38-C39-C34	-71.(2)
C37-C38-C39-C34	42.(2)	C44-N18-C40-C41	-85.(3)

C39-N18-C40-C41	55.(2)	C42-N19-C41-C40	-123.(2)
C38-N19-C41-C40	50.(3)	N18-C40-C41-N19	-48.(3)
C41-N19-C42-O4	-6.(3)	C38-N19-C42-O4	-179.3(18)
C41-N19-C42-C43	176.0(19)	C38-N19-C42-C43	3.(2)
C36-C37-C43-C42	-118.7(19)	C38-C37-C43-C42	1.(2)
O4-C42-C43-C37	180.(2)	N19-C42-C43-C37	-2.(2)
C39-N18-C44-C45	161.(3)	C40-N18-C44-C45	-66.(4)
N18-C44-C45-N20	167.(8)	N13-N14-B2-N12	-64.9(17)
C30-N14-B2-N12	126.7(16)	N13-N14-B2-N16	49.5(17)
C30-N14-B2-N16	-119.0(16)	C27-N12-B2-N14	-130.5(16)
N11-N12-B2-N14	56.2(18)	C27-N12-B2-N16	116.8(16)
N11-N12-B2-N16	-56.6(18)	C33-N16-B2-N14	121.7(16)
N15-N16-B2-N14	-64.3(15)	C33-N16-B2-N12	-121.0(16)
N15-N16-B2-N12	53.0(17)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 16.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.0534(3)	0.0376(3)	0.0750(4)	0.0046(3)	0.0096(3)	-0.0005(2)
P1	0.064(2)	0.0479(18)	0.092(3)	0.0145(17)	0.0016(19)	-0.0036(15)
O1	0.118(11)	0.131(13)	0.148(13)	-0.026(10)	0.049(10)	-0.003(10)
O2	0.087(9)	0.129(11)	0.137(11)	-0.045(9)	0.011(8)	-0.013(8)
N1	0.060(5)	0.043(5)	0.072(6)	-0.001(4)	0.019(4)	-0.003(4)
N2	0.062(5)	0.044(5)	0.076(5)	-0.001(4)	0.020(4)	-0.005(4)
N3	0.049(4)	0.041(4)	0.062(6)	0.005(4)	0.007(4)	0.000(4)
N4	0.055(5)	0.044(5)	0.073(7)	-0.001(4)	0.001(4)	-0.006(4)
N5	0.060(5)	0.039(4)	0.063(5)	0.008(4)	0.013(4)	0.004(4)
N6	0.056(5)	0.050(5)	0.084(7)	0.001(4)	0.008(5)	0.003(4)
N7	0.061(6)	0.051(6)	0.109(8)	0.002(5)	0.026(6)	-0.001(5)
N8	0.072(7)	0.056(6)	0.104(8)	0.012(5)	0.016(6)	-0.010(5)
N9	0.050(6)	0.055(5)	0.118(7)	-0.017(5)	0.014(6)	0.002(4)
C1	0.078(7)	0.059(8)	0.080(7)	-0.006(6)	0.016(6)	-0.007(6)
C2	0.081(8)	0.062(8)	0.092(8)	-0.017(6)	0.025(6)	-0.012(6)
C3	0.074(7)	0.057(8)	0.092(8)	-0.007(6)	0.025(6)	-0.011(6)
C4	0.077(7)	0.045(6)	0.074(9)	-0.002(5)	0.008(6)	-0.002(5)
C5	0.090(8)	0.049(6)	0.062(8)	0.005(5)	0.000(6)	-0.011(5)
C6	0.076(7)	0.049(6)	0.072(8)	0.004(5)	0.004(6)	-0.013(5)
C7	0.065(6)	0.048(6)	0.070(8)	0.006(5)	0.012(5)	0.003(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	0.080(7)	0.056(7)	0.071(8)	0.000(6)	0.006(6)	0.008(5)
C9	0.072(7)	0.049(6)	0.075(8)	-0.007(5)	0.009(6)	0.012(5)
C10	0.054(6)	0.055(6)	0.077(7)	-0.008(5)	0.024(5)	-0.008(4)
C11	0.057(6)	0.054(6)	0.089(8)	0.004(6)	0.012(5)	-0.014(5)
C12	0.061(7)	0.053(7)	0.137(14)	0.008(7)	0.002(7)	-0.013(5)
C13	0.048(6)	0.057(6)	0.126(9)	0.005(6)	0.005(6)	-0.009(5)
C14	0.057(6)	0.052(6)	0.107(8)	-0.005(5)	0.020(5)	0.002(5)
C15	0.051(6)	0.057(6)	0.095(8)	-0.004(5)	0.028(5)	-0.003(5)
C16	0.079(9)	0.054(7)	0.131(11)	-0.004(7)	0.004(8)	-0.001(6)
C17	0.086(10)	0.044(6)	0.143(12)	-0.013(7)	0.001(9)	0.006(6)
C18	0.056(8)	0.086(8)	0.115(8)	-0.011(6)	0.013(7)	-0.012(6)
C19	0.062(9)	0.095(8)	0.126(10)	0.000(7)	0.007(8)	-0.015(7)
C20	0.119(14)	0.105(13)	0.123(10)	0.017(8)	0.037(9)	-0.026(10)
C22	0.110(14)	0.079(11)	0.112(12)	0.029(8)	-0.027(9)	-0.026(10)
C23	0.068(8)	0.052(7)	0.083(10)	0.026(7)	-0.003(7)	-0.013(6)
C24	0.082(10)	0.059(8)	0.129(13)	0.032(8)	-0.001(9)	0.014(8)
B1	0.051(6)	0.050(6)	0.083(7)	-0.001(5)	0.012(5)	-0.007(5)
N10	0.121(19)	0.18(3)	0.128(13)	0.030(14)	0.047(12)	-0.002(19)
C21	0.121(17)	0.137(18)	0.117(11)	0.010(9)	0.043(10)	-0.009(14)
N10A	0.121(19)	0.18(3)	0.128(13)	0.030(14)	0.047(12)	-0.002(19)
C21A	0.121(17)	0.137(18)	0.117(11)	0.010(9)	0.043(10)	-0.009(14)
W2	0.0688(4)	0.0379(3)	0.0688(4)	0.0013(3)	0.0070(3)	0.0048(3)
P2	0.086(3)	0.0475(18)	0.081(3)	0.0025(17)	0.017(2)	0.0130(17)
O3	0.119(10)	0.149(15)	0.127(12)	0.021(11)	-0.002(9)	-0.036(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	0.154(11)	0.128(11)	0.069(8)	-0.009(7)	0.031(8)	-0.029(9)
N11	0.056(5)	0.045(5)	0.082(6)	0.004(4)	0.005(4)	-0.004(4)
N12	0.069(5)	0.043(5)	0.077(6)	0.002(4)	0.004(4)	0.000(4)
N13	0.057(6)	0.039(4)	0.078(6)	0.006(4)	0.005(4)	0.003(4)
N14	0.063(6)	0.049(5)	0.076(6)	0.007(4)	0.011(5)	-0.001(4)
N15	0.058(5)	0.038(4)	0.086(6)	0.001(4)	0.007(4)	-0.003(4)
N16	0.058(5)	0.050(5)	0.086(6)	0.001(4)	0.009(5)	-0.004(4)
N17	0.090(7)	0.058(7)	0.079(7)	0.011(5)	0.011(6)	-0.002(5)
N18	0.118(9)	0.056(6)	0.115(11)	0.018(6)	0.019(7)	0.012(6)
N19	0.130(9)	0.056(6)	0.070(8)	-0.006(5)	0.020(7)	-0.004(5)
N20	0.27(5)	0.28(5)	0.59(9)	0.10(6)	0.15(5)	0.12(5)
C25	0.068(7)	0.059(8)	0.095(8)	0.009(7)	0.010(6)	-0.004(6)
C26	0.069(7)	0.059(8)	0.102(9)	0.014(7)	-0.004(6)	-0.010(6)
C27	0.074(7)	0.056(8)	0.083(8)	0.010(6)	-0.010(5)	-0.008(6)
C28	0.047(6)	0.039(5)	0.094(8)	0.010(5)	0.007(6)	0.005(4)
C29	0.059(8)	0.055(7)	0.106(9)	0.012(6)	0.014(6)	0.003(5)
C30	0.063(8)	0.053(6)	0.091(8)	0.017(5)	0.010(6)	-0.002(5)
C31	0.063(7)	0.042(6)	0.103(8)	0.002(5)	0.013(6)	0.004(5)
C32	0.071(8)	0.051(7)	0.106(9)	-0.009(6)	0.011(7)	0.004(6)
C33	0.064(7)	0.045(6)	0.098(8)	-0.008(5)	0.014(6)	-0.003(5)
C34	0.076(8)	0.048(6)	0.082(7)	0.010(5)	0.008(6)	-0.001(5)
C35	0.100(9)	0.052(7)	0.075(7)	0.014(5)	0.019(7)	0.012(6)
C36	0.178(18)	0.063(8)	0.078(8)	0.008(6)	0.024(9)	0.023(8)
C37	0.167(12)	0.072(7)	0.069(8)	0.005(6)	0.016(8)	0.011(7)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C38	0.143(10)	0.053(7)	0.086(9)	0.005(6)	0.014(7)	-0.007(6)
C39	0.102(9)	0.054(6)	0.079(8)	0.020(5)	-0.001(6)	0.006(6)
C40	0.139(12)	0.046(7)	0.103(11)	0.007(7)	0.039(9)	0.005(7)
C41	0.152(15)	0.059(8)	0.114(13)	-0.006(7)	0.045(12)	-0.003(8)
C42	0.133(9)	0.092(9)	0.052(9)	-0.001(7)	0.023(7)	0.002(6)
C43	0.162(12)	0.095(9)	0.057(9)	0.002(7)	0.023(9)	0.014(7)
C44	0.132(12)	0.094(14)	0.23(3)	0.062(14)	0.000(12)	0.020(10)
C45	0.21(3)	0.21(4)	0.36(5)	-0.02(3)	0.03(3)	0.08(3)
C46	0.123(12)	0.050(8)	0.121(14)	0.012(8)	0.044(10)	0.035(7)
C47	0.135(14)	0.071(10)	0.091(11)	-0.009(9)	0.011(10)	0.020(9)
C48	0.061(8)	0.058(8)	0.088(9)	0.010(7)	0.020(7)	0.015(6)
B2	0.074(7)	0.057(6)	0.072(8)	0.002(6)	0.009(5)	0.002(5)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 16.

	x/a	y/b	z/c	U(eq)
H1	0.7067	0.5298	0.1621	0.086000
H2	0.8072	0.5061	0.1276	0.093000
H3	0.8776	0.5343	0.2136	0.088000
H4	0.7004	0.7942	0.3891	0.078000
H5	0.7996	0.8698	0.4087	0.081000
H6	0.8734	0.7663	0.3652	0.079000
H7	0.6949	0.3972	0.3986	0.073000

	x/a	y/b	z/c	U(eq)
H8	0.7910	0.3465	0.4432	0.083000
H9	0.8669	0.4469	0.4079	0.078000
H10	0.6555	0.4158	0.2665	0.074000
H11	0.6223	0.5337	0.2078	0.080000
H12A	0.5359	0.6102	0.2194	0.101000
H12B	0.5401	0.5969	0.2891	0.101000
H13	0.4635	0.5001	0.2533	0.093000
H14	0.4938	0.3895	0.3140	0.086000
H15	0.5746	0.4692	0.3539	0.080000
H16A	0.6211	0.2065	0.3418	0.106000
H16B	0.6439	0.2727	0.2918	0.106000
H17A	0.5650	0.1920	0.2487	0.109000
H17B	0.5245	0.2130	0.3027	0.109000
H19A	0.4658	0.4396	0.1632	0.113000
H19B	0.5338	0.4692	0.1591	0.113000
H20A	0.5358	0.2750	0.3877	0.137000
H20B	0.5478	0.3747	0.4148	0.137000
H20C	0.5675	0.2492	0.4107	0.137000
H20D	0.5262	0.3368	0.3945	0.137000
H22A	0.6558	0.6706	0.1523	0.153000
H22B	0.6322	0.7747	0.1497	0.153000
H22C	0.5895	0.6930	0.1681	0.153000
H23A	0.7291	0.8389	0.2722	0.102000
H23B	0.7063	0.8535	0.2053	0.102000

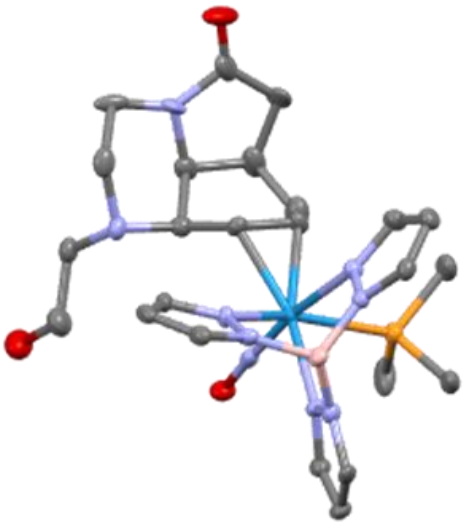
	x/a	y/b	z/c	U(eq)
H23C	0.7506	0.7707	0.2225	0.102000
H24A	0.5600	0.7695	0.2763	0.135000
H24B	0.5916	0.8598	0.2526	0.135000
H24C	0.6091	0.8216	0.3170	0.135000
H1A	0.8714	0.5856	0.3245	0.073000
H10A	0.5347	0.2546	0.5325	0.170000
H10B	0.5961	0.2184	0.5503	0.170000
H21A	0.6280	0.3110	0.4720	0.148000
H21B	0.6100	0.2129	0.4478	0.148000
H10C	0.5342	0.2837	0.5051	0.170000
H10D	0.5695	0.3470	0.5472	0.170000
H21C	0.5866	0.4358	0.4551	0.148000
H21D	0.6369	0.3577	0.4636	0.148000
H20E	0.4699	0.9257	0.5801	0.455000
H20F	0.4820	0.9479	0.6449	0.455000
H25	0.8337	0.5514	0.7026	0.089000
H26	0.8829	0.5727	0.8035	0.092000
H27	0.8024	0.5506	0.8722	0.086000
H28	0.6032	0.2919	0.7024	0.072000
H29	0.5956	0.2184	0.7992	0.088000
H30	0.6457	0.3261	0.8732	0.082000
H31	0.5912	0.6860	0.6905	0.083000
H32	0.5579	0.7435	0.7881	0.091000
H33	0.6098	0.6414	0.8646	0.082000

	x/a	y/b	z/c	U(eq)
H34	0.7247	0.6649	0.6517	0.083000
H35	0.7783	0.5462	0.6195	0.090000
H36A	0.7490	0.4684	0.5321	0.127000
H36B	0.6811	0.4935	0.5387	0.127000
H37	0.7146	0.5785	0.4627	0.123000
H38	0.6567	0.6970	0.4933	0.112000
H39	0.6290	0.6178	0.5730	0.094000
H40A	0.7047	0.8068	0.6423	0.114000
H40B	0.6561	0.8806	0.6203	0.114000
H41A	0.6845	0.8729	0.5259	0.128000
H41B	0.7441	0.8828	0.5665	0.128000
H43A	0.8018	0.6310	0.4646	0.125000
H43B	0.8131	0.5976	0.5311	0.125000
H44A	0.5530	0.7234	0.5681	0.184000
H44B	0.5856	0.8083	0.5390	0.184000
H45A	0.5768	0.8865	0.6324	0.310000
H45B	0.5341	0.8068	0.6491	0.310000
H46A	0.8114	0.3996	0.5925	0.145000
H46B	0.8289	0.3016	0.6208	0.145000
H46C	0.8384	0.3940	0.6585	0.145000
H47A	0.6694	0.2467	0.6208	0.148000
H47B	0.7308	0.2247	0.5925	0.148000
H47C	0.6905	0.3078	0.5674	0.148000
H48A	0.7806	0.3116	0.7473	0.102000

	x/a	y/b	z/c	U(eq)
H48B	0.7840	0.2254	0.7038	0.102000
H48C	0.7228	0.2513	0.7315	0.102000
H2A	0.6886	0.5025	0.8694	0.081000

Table 9. Hydrogen bond distances (Å) and angles (°) for Compound 16.				
	Donor-H	**Acceptor-H**	**Donor-Acceptor**	**Angle**
$N10^{a}$-$H10A^{a}$···N10^a#1	0.88	2.68	3.4(2)	136.5
$N10A^{b}$-$H10C^{b}$···N10A^b#1	0.88	2.26	2.79(7)	118.5
$N10A^{b}$-$H10D^{b}$···O3	0.88	1.88	2.68(5)	149.7

Crystal Structure Report for Compound 14



A colorless, plate-like specimen of $C_{24}H_{37}BN_9O_3PW$, approximate dimensions 0.029 mm x 0.092 mm x 0.145 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 2.32 hours. The frames were integrated with the Bruker SAINT software package[167] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 49232 reflections to a maximum θ angle of 28.31° (0.75 Å resolution), of which 6751 were independent (average redundancy 7.293, completeness = 99.8%, R_{int} = 8.32%, R_{sig} = 5.39%) and 5059 (74.94%) were greater than $2\sigma(F^2)$. The final cell constants of a = 14.5623(4) Å, b = 12.1588(4) Å, c = 15.6697(4) Å, β = 102.0340(10)°, volume = 2713.51(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 8709 reflections above 20 σ(I) with 4.404° < 2θ < 54.34°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[168] The ratio of minimum to maximum apparent transmission was 0.889. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5700 and 0.8840.

The structure was solved and refined using the Bruker SHELXTL Software Package[169] within APEX4 [1] and OLEX2,[170] using the space group P $2_1/c$, with Z = 4 for the formula unit, $C_{24}H_{37}BN_9O_3PW$. Non-hydrogen atoms were refined anisotropically. The B-H and O-H hydrogen atoms, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). The relative occupancy of the disordered sites was freely refined, with constraints and restraints on the anisotropic displacement parameters and bond lengths of most of the disordered atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 423 variables converged at R1 = 3.44%, for the observed data and wR2 = 7.98% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 1.061 $e^-/Å^3$ and the largest hole was -0.969 $e^-/Å^3$ with an RMS deviation of 0.156 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.775 g/cm^3 and F(000), 1448 e^-.

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Table 1. Sample and crystal data for Compound 14.

Chemical formula	$C_{24}H_{37}BN_9O_3PW$
Formula weight	725.25 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.029 x 0.092 x 0.145 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 14.5623(4) Å α = 90°
	b = 12.1588(4) Å β = 102.0340(10)°
	c = 15.6697(4) Å γ = 90°
Volume	2713.51(14) $Å^3$
Z	4
Density (calculated)	1.775 g/cm^3
Absorption coefficient	4.362 mm^{-1}
F(000)	1448

Table 2. Data collection and structure refinement for Compound 14.

Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer

Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.41 to 28.31°
Index ranges	-19<=h<=19, -16<=k<=14, -17<=l<=20
Reflections collected	49232
Independent reflections	6751 [R(int) = 0.0832]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8840 and 0.5700
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6751 / 161 / 423
Goodness-of-fit on F^2	1.036
Δ/σ_{max}	0.001

Final R indices	5059 data; I>2σ(I)	R1 = 0.0344, wR2 = 0.0712
	all data	R1 = 0.0584, wR2 = 0.0798
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0355P)^2+1.7619P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.061 and -0.969 eÅ^{-3}	
R.M.S. deviation from mean	0.156 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 14.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.72776(2)	0.33246(2)	0.36804(2)	0.01732(6)
P1	0.76814(9)	0.19338(10)	0.48818(8)	0.0231(3)
O1	0.9176(2)	0.2972(3)	0.3259(2)	0.0269(8)
O2	0.0302(3)	0.5759(4)	0.1989(3)	0.0471(11)
N1	0.5840(3)	0.3316(3)	0.4031(2)	0.0207(8)
N2	0.5092(3)	0.2877(3)	0.3459(2)	0.0175(8)
N3	0.6788(3)	0.1845(3)	0.2887(2)	0.0189(8)
N4	0.5870(3)	0.1653(3)	0.2533(2)	0.0203(8)
N5	0.6392(3)	0.4055(3)	0.2485(2)	0.0174(8)

	x/a	y/b	z/c	U(eq)
N6	0.5542(3)	0.3585(3)	0.2111(2)	0.0204(8)
N7	0.8388(3)	0.3149(3)	0.3427(2)	0.0216(8)
N8	0.8300(3)	0.6323(3)	0.3062(3)	0.0249(9)
C1	0.5528(3)	0.3526(4)	0.4766(3)	0.0257(11)
C2	0.4606(3)	0.3213(4)	0.4674(3)	0.0257(10)
C3	0.4353(3)	0.2817(4)	0.3842(3)	0.0219(10)
C4	0.7278(4)	0.0991(4)	0.2672(3)	0.0229(10)
C5	0.6665(3)	0.0228(4)	0.2198(3)	0.0259(11)
C6	0.5784(3)	0.0676(4)	0.2125(3)	0.0215(10)
C7	0.6501(3)	0.4916(4)	0.1983(3)	0.0216(10)
C8	0.5739(3)	0.4995(4)	0.1286(3)	0.0241(10)
C9	0.5156(3)	0.4151(4)	0.1388(3)	0.0218(10)
C10	0.7549(3)	0.5072(4)	0.4012(3)	0.0206(9)
C11	0.7699(3)	0.4443(4)	0.4811(3)	0.0225(10)
C12	0.8665(4)	0.4542(5)	0.5387(3)	0.0365(13)
C14	0.8884(4)	0.6330(4)	0.4656(3)	0.0274(11)
C15	0.8426(3)	0.5639(4)	0.3853(3)	0.0226(10)
C20	0.9192(3)	0.6515(4)	0.2790(3)	0.0274(11)
C21	0.9381(4)	0.5658(5)	0.2154(4)	0.0387(14)
C22	0.8872(4)	0.1400(5)	0.5025(4)	0.0469(17)
C23	0.7577(5)	0.2232(5)	0.5991(3)	0.0394(14)
C24	0.6957(4)	0.0709(4)	0.4698(3)	0.0360(13)
B1	0.5166(4)	0.2577(5)	0.2515(4)	0.0212(11)

	x/a	y/b	z/c	U(eq)
O3	0.7535(16)	0.804(2)	0.5674(16)	0.045(5)
N9	0.836(3)	0.731(2)	0.479(2)	0.029(3)
C13	0.898(4)	0.567(4)	0.552(2)	0.035(3)
C16	0.782(3)	0.736(4)	0.324(2)	0.027(6)
C17	0.8229(18)	0.804(2)	0.4064(19)	0.030(5)
C18	0.8027(18)	0.727(3)	0.5543(18)	0.035(5)
C19	0.835(2)	0.627(2)	0.6035(16)	0.034(5)
O3A	0.725(3)	0.821(2)	0.536(3)	0.076(9)
N9A	0.831(3)	0.733(2)	0.460(2)	0.029(3)
C13A	0.886(5)	0.583(4)	0.556(2)	0.035(3)
C16A	0.770(3)	0.729(4)	0.303(3)	0.028(6)
C17A	0.808(2)	0.799(2)	0.382(2)	0.032(6)
C18A	0.787(2)	0.748(2)	0.528(2)	0.037(5)
C19A	0.814(2)	0.656(2)	0.588(2)	0.038(5)

Table 4. Bond lengths (Å) for Compound 14.

W1-N7	1.756(4)	W1-C10	2.203(5)
W1-C11	2.216(5)	W1-N3	2.218(4)
W1-N5	2.225(4)	W1-N1	2.272(4)
W1-P1	2.5076(12)	P1-C23	1.813(5)
P1-C24	1.813(5)	P1-C22	1.821(6)
O1-N7	1.250(5)	O2-C21	1.423(7)

O2-H2	0.89(8)	N1-C1	1.347(6)
N1-N2	1.367(5)	N2-C3	1.339(6)
N2-B1	1.549(6)	N3-C4	1.342(6)
N3-N4	1.357(5)	N4-C6	1.342(6)
N4-B1	1.518(7)	N5-C7	1.338(6)
N5-N6	1.378(5)	N6-C9	1.344(6)
N6-B1	1.533(7)	N8-C16A	1.46(4)
N8-C20	1.467(6)	N8-C15	1.471(6)
N8-C16	1.50(5)	C1-C2	1.375(7)
C1-H1	0.950000	C2-C3	1.367(6)
C2-H2A	0.950000	C3-H3	0.950000
C4-C5	1.390(7)	C4-H4	0.950000
C5-C6	1.376(7)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.388(6)
C7-H7	0.950000	C8-C9	1.362(7)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.444(6)	C10-C15	1.517(6)
C10-H10	1.00(5)	C11-C12	1.510(7)
C11-H11	0.94(5)	C12-C13	1.45(6)
C12-C13A	1.60(6)	C12-H12A	0.990000
C12-H12B	0.990000	C12-H12C	0.990000
C12-H12D	0.990000	C14-N9	1.456(12)
C14-N9A	1.463(13)	C14-C15	1.544(6)
C14-C13	1.552(13)	C14-C13A	1.554(13)

C14-H14	1.000000	C14-H14A	1.000000
C15-H15	1.000000	C20-C21	1.508(7)
C20-H20A	0.990000	C20-H20B	0.990000
C21-H21A	0.990000	C21-H21B	0.990000
C22-H22A	0.980000	C22-H22B	0.980000
C22-H22C	0.980000	C23-H23A	0.980000
C23-H23B	0.980000	C23-H23C	0.980000
C24-H24A	0.980000	C24-H24B	0.980000
C24-H24C	0.980000	B1-H1A	1.14(4)
O3-C18	1.22(3)	N9-C18	1.361(14)
N9-C17	1.430(14)	C13-C19	1.535(14)
C13-H13	1.000000	C16-C17	1.54(3)
C16-H16A	0.990000	C16-H16B	0.990000
C17-H17A	0.990000	C17-H17B	0.990000
C18-C19	1.46(2)	C19-H19A	0.990000
C19-H19B	0.990000	O3A-C18A	1.30(4)
N9A-C18A	1.370(15)	N9A-C17A	1.436(14)
C13A-C19A	1.535(15)	C13A-H13A	1.000000
C16A-C17A	1.51(4)	C16A-H16C	0.990000
C16A-H16D	0.990000	C17A-H17C	0.990000
C17A-H17D	0.990000	C18A-C19A	1.45(2)

C19A-H19C	0.990000	C19A-H19D	0.990000

Table 5. Bond angles (°) for Compound 14.

N7-W1-C10	92.39(17)	N7-W1-C11	98.09(18)
C10-W1-C11	38.15(17)	N7-W1-N3	88.74(15)
C10-W1-N3	159.24(15)	C11-W1-N3	161.59(16)
N7-W1-N5	104.91(15)	C10-W1-N5	81.83(15)
C11-W1-N5	116.31(16)	N3-W1-N5	77.86(13)
N7-W1-N1	172.73(15)	C10-W1-N1	94.39(16)
C11-W1-N1	85.68(16)	N3-W1-N1	85.86(14)
N5-W1-N1	78.72(13)	N7-W1-P1	90.28(12)
C10-W1-P1	118.08(12)	C11-W1-P1	80.29(13)
N3-W1-P1	82.62(10)	N5-W1-P1	154.83(10)
N1-W1-P1	84.20(10)	C23-P1-C24	98.9(2)
C23-P1-C22	102.8(3)	C24-P1-C22	103.6(3)
C23-P1-W1	122.1(2)	C24-P1-W1	113.38(19)
C22-P1-W1	113.64(18)	C21-O2-H2	99.(6)
C1-N1-N2	105.6(4)	C1-N1-W1	134.3(3)
N2-N1-W1	119.4(3)	C3-N2-N1	109.5(4)
C3-N2-B1	129.5(4)	N1-N2-B1	120.9(4)
C4-N3-N4	107.1(4)	C4-N3-W1	130.0(3)
N4-N3-W1	122.9(3)	C6-N4-N3	109.5(4)
C6-N4-B1	130.6(4)	N3-N4-B1	119.0(4)

C7-N5-N6	106.2(4)	C7-N5-W1	133.5(3)
N6-N5-W1	120.3(3)	C9-N6-N5	109.1(4)
C9-N6-B1	129.4(4)	N5-N6-B1	121.5(4)
O1-N7-W1	177.0(3)	C16A-N8-C20	115.0(19)
C16A-N8-C15	116.7(18)	C20-N8-C15	111.8(4)
C20-N8-C16	113.4(16)	C15-N8-C16	107.2(15)
N1-C1-C2	110.8(4)	N1-C1-H1	124.600000
C2-C1-H1	124.600000	C3-C2-C1	105.0(4)
C3-C2-H2A	127.500000	C1-C2-H2A	127.500000
N2-C3-C2	109.1(4)	N2-C3-H3	125.500000
C2-C3-H3	125.500000	N3-C4-C5	109.6(4)
N3-C4-H4	125.200000	C5-C4-H4	125.200000
C6-C5-C4	105.3(4)	C6-C5-H5	127.300000
C4-C5-H5	127.300000	N4-C6-C5	108.5(4)
N4-C6-H6	125.800000	C5-C6-H6	125.800000
N5-C7-C8	110.1(4)	N5-C7-H7	125.000000
C8-C7-H7	125.000000	C9-C8-C7	105.7(4)
C9-C8-H8	127.100000	C7-C8-H8	127.100000
N6-C9-C8	108.8(4)	N6-C9-H9	125.600000
C8-C9-H9	125.600000	C11-C10-C15	113.8(4)
C11-C10-W1	71.4(3)	C15-C10-W1	121.1(3)
C11-C10-H10	115.(3)	C15-C10-H10	118.(3)

W1-C10-H10	109.(3)	C10-C11-C12	115.4(4)
C10-C11-W1	70.4(3)	C12-C11-W1	126.5(4)
C10-C11-H11	119.(3)	C12-C11-H11	111.(3)
W1-C11-H11	110.(3)	C13-C12-C11	113.1(19)
C11-C12-C13A	107.(2)	C13-C12-H12A	109.000000
C11-C12-H12A	109.000000	C13-C12-H12B	109.000000
C11-C12-H12B	109.000000	H12A-C12-H12B	107.800000
C11-C12-H12C	110.400000	C13A-C12-H12C	110.400000
C11-C12-H12D	110.400000	C13A-C12-H12D	110.400000
H12C-C12-H12D	108.600000	N9-C14-C15	114.5(18)
N9A-C14-C15	104.8(18)	N9-C14-C13	104.5(15)
C15-C14-C13	112.(3)	N9A-C14-C13A	105.3(16)
C15-C14-C13A	116.(3)	N9-C14-H14	108.500000
C15-C14-H14	108.500000	C13-C14-H14	108.500000
N9A-C14-H14A	110.100000	C15-C14-H14A	110.100000
C13A-C14-H14A	110.100000	N8-C15-C10	115.7(4)
N8-C15-C14	109.6(4)	C10-C15-C14	110.4(4)

N8-C15-H15	106.900000	C10-C15-H15	106.900000
C14-C15-H15	106.900000	N8-C20-C21	112.1(4)
N8-C20-H20A	109.200000	C21-C20-H20A	109.200000
N8-C20-H20B	109.200000	C21-C20-H20B	109.200000
H20A-C20-H20B	107.900000	O2-C21-C20	111.7(5)
O2-C21-H21A	109.300000	C20-C21-H21A	109.300000
O2-C21-H21B	109.300000	C20-C21-H21B	109.300000
H21A-C21-H21B	107.900000	P1-C22-H22A	109.500000
P1-C22-H22B	109.500000	H22A-C22-H22B	109.500000
P1-C22-H22C	109.500000	H22A-C22-H22C	109.500000
H22B-C22-H22C	109.500000	P1-C23-H23A	109.500000
P1-C23-H23B	109.500000	H23A-C23-H23B	109.500000
P1-C23-H23C	109.500000	H23A-C23-H23C	109.500000
H23B-C23-H23C	109.500000	P1-C24-H24A	109.500000
P1-C24-H24B	109.500000	H24A-C24-H24B	109.500000

P1-C24-H24C	109.500000	H24A-C24-H24C	109.500000
H24B-C24-H24C	109.500000	N4-B1-N6	107.5(4)
N4-B1-N2	109.8(4)	N6-B1-N2	108.0(4)
N4-B1-H1A	111.(2)	N6-B1-H1A	109.(2)
N2-B1-H1A	111.(2)	C18-N9-C17	134.6(18)
C18-N9-C14	112.9(19)	C17-N9-C14	112.1(19)
C12-C13-C19	108.(3)	C12-C13-C14	113.(3)
C19-C13-C14	104.7(18)	C12-C13-H13	110.100000
C19-C13-H13	110.100000	C14-C13-H13	110.100000
N8-C16-C17	120.(2)	N8-C16-H16A	107.400000
C17-C16-H16A	107.400000	N8-C16-H16B	107.400000
C17-C16-H16B	107.400000	H16A-C16-H16B	106.900000
N9-C17-C16	107.(3)	N9-C17-H17A	110.300000
C16-C17-H17A	110.300000	N9-C17-H17B	110.300000
C16-C17-H17B	110.300000	H17A-C17-H17B	108.500000
O3-C18-N9	116.(2)	O3-C18-C19	133.(2)
N9-C18-C19	111.(2)	C18-C19-C13	106.(2)
C18-C19-H19A	110.500000	C13-C19-H19A	110.500000

C18-C19-H19B	110.500000	C13-C19-H19B	110.500000
H19A-C19-H19B	108.700000	C18A-N9A-C17A	121.(2)
C18A-N9A-C14	114.(2)	C17A-N9A-C14	124.(2)
C19A-C13A-C14	102.3(18)	C19A-C13A-C12	121.(4)
C14-C13A-C12	105.(3)	C19A-C13A-H13A	109.100000
C14-C13A-H13A	109.100000	C12-C13A-H13A	109.100000
N8-C16A-C17A	108.(2)	N8-C16A-H16C	110.000000
C17A-C16A-H16C	110.000000	N8-C16A-H16D	110.000000
C17A-C16A-H16D	110.000000	H16C-C16A-H16D	108.400000
N9A-C17A-C16A	111.(3)	N9A-C17A-H17C	109.500000
C16A-C17A-H17C	109.500000	N9A-C17A-H17D	109.500000
C16A-C17A-H17D	109.500000	H17C-C17A-H17D	108.000000
O3A-C18A-N9A	128.(2)	O3A-C18A-C19A	124.(2)
N9A-C18A-C19A	107.(2)	C18A-C19A-C13A	110.(2)
C18A-C19A-H19C	109.600000	C13A-C19A-H19C	109.600000

C18A-C19A-H19D	109.600000	C13A-C19A-H19D	109.600000
H19C-C19A-H19D	108.100000		

Table 6. Torsion angles (°) for Compound 14.

C1-N1-N2-C3	-0.4(5)	W1-N1-N2-C3	171.5(3)
C1-N1-N2-B1	177.1(4)	W1-N1-N2-B1	-11.0(5)
C4-N3-N4-C6	1.9(5)	W1-N3-N4-C6	-177.1(3)
C4-N3-N4-B1	-168.2(4)	W1-N3-N4-B1	12.8(5)
C7-N5-N6-C9	0.8(5)	W1-N5-N6-C9	-178.2(3)
C7-N5-N6-B1	-179.0(4)	W1-N5-N6-B1	2.0(5)
N2-N1-C1-C2	1.0(5)	W1-N1-C1-C2	-169.2(3)
N1-C1-C2-C3	-1.1(6)	N1-N2-C3-C2	-0.3(5)
B1-N2-C3-C2	-177.5(4)	C1-C2-C3-N2	0.8(6)
N4-N3-C4-C5	-1.8(5)	W1-N3-C4-C5	177.0(3)
N3-C4-C5-C6	1.1(5)	N3-N4-C6-C5	-1.2(5)
B1-N4-C6-C5	167.4(4)	C4-C5-C6-N4	0.0(5)
N6-N5-C7-C8	-0.8(5)	W1-N5-C7-C8	178.0(3)
N5-C7-C8-C9	0.5(5)	N5-N6-C9-C8	-0.5(5)
B1-N6-C9-C8	179.3(4)	C7-C8-C9-N6	0.0(5)
C15-C10-C11-C12	5.5(6)	W1-C10-C11-C12	122.0(4)
C15-C10-C11-W1	-116.5(4)	C10-C11-C12-C13	47.6(11)

W1-C11-C12-C13	131.3(10)	C10-C11-C12-C13A	54.5(10)
W1-C11-C12-C13A	138.2(9)	C16A-N8-C15-C10	65.(2)
C20-N8-C15-C10	-159.8(4)	C16-N8-C15-C10	75.2(16)
C16A-N8-C15-C14	-61.(2)	C20-N8-C15-C14	74.6(5)
C16-N8-C15-C14	-50.4(16)	C11-C10-C15-N8	-177.8(4)
W1-C10-C15-N8	100.3(4)	C11-C10-C15-C14	-52.6(5)
W1-C10-C15-C14	-134.5(4)	N9-C14-C15-N8	58.0(17)
N9A-C14-C15-N8	50.6(17)	C13-C14-C15-N8	176.8(17)
C13A-C14-C15-N8	166.3(18)	N9-C14-C15-C10	-70.6(17)
N9A-C14-C15-C10	-78.0(17)	C13-C14-C15-C10	48.2(18)
C13A-C14-C15-C10	37.7(19)	C16A-N8-C20-C21	-132.7(18)
C15-N8-C20-C21	91.2(5)	C16-N8-C20-C21	-147.3(15)
N8-C20-C21-O2	-171.8(4)	C6-N4-B1-N6	-116.3(5)
N3-N4-B1-N6	51.3(5)	C6-N4-B1-N2	126.5(5)
N3-N4-B1-N2	-65.9(5)	C9-N6-B1-N4	119.8(5)
N5-N6-B1-N4	-60.5(5)	C9-N6-B1-N2	-121.9(5)

N5-N6-B1-N2	57.9(5)	C3-N2-B1-N4	-117.9(5)
N1-N2-B1-N4	65.1(5)	C3-N2-B1-N6	125.2(5)
N1-N2-B1-N6	-51.8(5)	C15-C14-N9-C18	115.(3)
C13-C14-N9-C18	-8.(5)	C15-C14-N9-C17	-59.(3)
C13-C14-N9-C17	178.(4)	C11-C12-C13-C19	66.(2)
C11-C12-C13-C14	-50.(3)	N9-C14-C13-C12	127.(3)
C15-C14-C13-C12	2.(3)	N9-C14-C13-C19	9.(5)
C15-C14-C13-C19	-116.(3)	C20-N8-C16-C17	-71.(3)
C15-N8-C16-C17	53.(3)	C18-N9-C17-C16	-121.(5)
C14-N9-C17-C16	51.(4)	N8-C16-C17-N9	-52.(3)
C17-N9-C18-O3	-4.(6)	C14-N9-C18-O3	-176.(3)
C17-N9-C18-C19	176.(4)	C14-N9-C18-C19	4.(4)
O3-C18-C19-C13	-178.(4)	N9-C18-C19-C13	2.(4)
C12-C13-C19-C18	-128.(2)	C14-C13-C19-C18	-7.(4)
C15-C14-N9A-C18A	118.(3)	C13A-C14-N9A-C18A	-5.(5)

C15-C14-N9A-C17A	-51.(4)	C13A-C14-N9A-C17A	-174.(5)
N9A-C14-C13A-C19A	7.(5)	C15-C14-C13A-C19A	-108.(3)
N9A-C14-C13A-C12	135.(3)	C15-C14-C13A-C12	19.(4)
C11-C12-C13A-C19A	50.(3)	C11-C12-C13A-C14	-65.(3)
C20-N8-C16A-C17A	-78.(3)	C15-N8-C16A-C17A	56.(3)
C18A-N9A-C17A-C16A	-119.(4)	C14-N9A-C17A-C16A	49.(5)
N8-C16A-C17A-N9A	-45.(4)	C17A-N9A-C18A-O3A	-3.(6)
C14-N9A-C18A-O3A	-172.(3)	C17A-N9A-C18A-C19A	169.(4)
C14-N9A-C18A-C19A	1.(4)	O3A-C18A-C19A-C13A	177.(4)
N9A-C18A-C19A-C13A	4.(4)	C14-C13A-C19A-C18A	-7.(5)
C12-C13A-C19A-C18A	-124.(2)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 14.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01976(9)	0.01539(10)	0.01769(9)	-0.00023(8)	0.00589(6)	-0.00110(8)
P1	0.0291(7)	0.0199(7)	0.0213(6)	0.0025(5)	0.0080(5)	-0.0002(5)
O1	0.0226(18)	0.0241(19)	0.037(2)	-0.0041(15)	0.0117(15)	0.0034(14)
O2	0.046(3)	0.039(3)	0.066(3)	0.004(2)	0.033(2)	0.004(2)
N1	0.0216(19)	0.019(2)	0.0230(18)	-0.0018(17)	0.0090(15)	-0.0014(17)
N2	0.0185(19)	0.0149(19)	0.0195(18)	0.0007(15)	0.0048(15)	0.0003(15)
N3	0.0218(19)	0.014(2)	0.0220(19)	-0.0028(15)	0.0065(15)	-0.0021(16)
N4	0.0215(19)	0.018(2)	0.0222(18)	0.0009(17)	0.0063(15)	-0.0033(17)
N5	0.0185(19)	0.017(2)	0.0170(18)	0.0031(15)	0.0036(15)	-0.0021(16)
N6	0.024(2)	0.018(2)	0.0180(18)	-0.0034(15)	0.0034(15)	0.0024(16)
N7	0.031(2)	0.014(2)	0.0194(19)	-0.0005(15)	0.0040(16)	-0.0044(17)
N8	0.026(2)	0.021(2)	0.030(2)	0.0051(17)	0.0110(18)	-0.0026(17)
C1	0.029(3)	0.026(3)	0.023(2)	-0.005(2)	0.007(2)	-0.001(2)
C2	0.028(3)	0.026(3)	0.027(2)	-0.001(2)	0.015(2)	-0.001(2)
C3	0.021(2)	0.019(2)	0.027(2)	0.0035(19)	0.0059(19)	-0.001(2)
C4	0.028(3)	0.018(2)	0.026(2)	0.0004(19)	0.011(2)	0.003(2)
C5	0.035(3)	0.014(2)	0.032(3)	-0.0016(19)	0.014(2)	0.001(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	0.031(3)	0.014(2)	0.021(2)	-0.0021(18)	0.008(2)	-0.008(2)
C7	0.029(2)	0.016(2)	0.024(2)	0.0019(19)	0.0138(19)	0.000(2)
C8	0.036(3)	0.021(2)	0.018(2)	0.003(2)	0.0105(19)	0.010(2)
C9	0.026(2)	0.021(3)	0.019(2)	0.0003(18)	0.0039(19)	0.005(2)
C10	0.023(2)	0.016(2)	0.022(2)	-0.0024(19)	0.0035(18)	-0.002(2)
C11	0.025(3)	0.026(3)	0.018(2)	-0.0028(19)	0.006(2)	-0.008(2)
C12	0.036(3)	0.042(3)	0.030(3)	0.007(2)	0.002(2)	-0.008(3)
C14	0.027(3)	0.029(3)	0.029(3)	-0.007(2)	0.010(2)	-0.011(2)
C15	0.023(2)	0.022(3)	0.024(2)	-0.0016(19)	0.0060(19)	0.000(2)
C20	0.029(3)	0.024(3)	0.031(3)	0.005(2)	0.011(2)	-0.005(2)
C21	0.040(3)	0.040(3)	0.042(3)	0.000(3)	0.021(3)	-0.006(3)
C22	0.039(3)	0.050(4)	0.055(4)	0.033(3)	0.018(3)	0.013(3)
C23	0.067(4)	0.032(3)	0.024(2)	0.003(2)	0.018(3)	-0.005(3)
C24	0.063(4)	0.024(3)	0.027(3)	0.000(2)	0.022(3)	-0.007(3)
B1	0.025(3)	0.015(3)	0.024(2)	0.002(2)	0.006(2)	0.002(2)
O3	0.035(8)	0.034(9)	0.074(10)	-0.027(7)	0.032(7)	-0.006(6)
N9	0.036(4)	0.027(3)	0.031(10)	-0.014(5)	0.022(8)	-0.005(2)
C13	0.038(12)	0.042(10)	0.023(3)	-0.002(5)	0.003(3)	-0.017(5)
C16	0.015(10)	0.033(9)	0.031(13)	0.007(10)	0.001(9)	-0.006(7)
C17	0.012(7)	0.028(7)	0.049(12)	-0.024(8)	0.002(7)	-0.001(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	0.036(9)	0.039(12)	0.035(10)	-0.008(8)	0.020(8)	-0.020(8)
C19	0.059(11)	0.030(11)	0.016(7)	-0.010(7)	0.011(7)	-0.007(8)
O3A	0.069(17)	0.039(9)	0.15(3)	-0.013(13)	0.085(17)	-0.003(11)
N9A	0.036(4)	0.027(3)	0.031(10)	-0.014(5)	0.022(8)	-0.005(2)
C13A	0.038(12)	0.042(10)	0.023(3)	-0.002(5)	0.003(3)	-0.017(5)
C16A	0.018(10)	0.021(8)	0.040(16)	0.005(11)	-0.001(10)	0.005(8)
C17A	0.036(12)	0.016(8)	0.043(12)	0.002(9)	0.008(9)	0.001(7)
C18A	0.057(11)	0.014(8)	0.044(12)	-0.003(8)	0.021(10)	-0.012(7)
C19A	0.061(13)	0.023(12)	0.034(11)	-0.006(8)	0.019(9)	-0.017(10)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 14.

	x/a	y/b	z/c	U(eq)
H2	1.026(6)	0.644(7)	0.177(6)	0.10(3)
H1	0.5896	0.3847	0.5278	0.031000
H2A	0.4226	0.3260	0.5098	0.031000
H3	0.3750	0.2544	0.3577	0.026000
H4	0.7942	0.0919	0.2820	0.027000
H5	0.6821	-0.0457	0.1973	0.031000
H6	0.5211	0.0349	0.1835	0.026000
H7	0.7024	0.5402	0.2089	0.026000
H8	0.5645	0.5527	0.0832	0.029000

	x/a	y/b	z/c	U(eq)
H9	0.4572	0.3989	0.1010	0.026000
H10	0.694(3)	0.548(4)	0.387(3)	0.020(13)
H11	0.723(3)	0.445(4)	0.514(3)	0.017(12)
H12A	0.8658	0.4206	0.5961	0.044000
H12B	0.9117	0.4123	0.5121	0.044000
H12C	0.9143	0.4222	0.5094	0.044000
H12D	0.8691	0.4148	0.5945	0.044000
H14	0.9524	0.6560	0.4587	0.033000
H14A	0.9544	0.6521	0.4626	0.033000
H15	0.8884	0.5047	0.3788	0.027000
H20A	0.9711	0.6511	0.3311	0.033000
H20B	0.9177	0.7251	0.2516	0.033000
H21A	0.9306	0.4917	0.2392	0.046000
H21B	0.8916	0.5735	0.1598	0.046000
H22A	0.8960	0.1070	0.4477	0.070000
H22B	0.8975	0.0841	0.5485	0.070000
H22C	0.9322	0.2002	0.5190	0.070000
H23A	0.7950	0.2886	0.6201	0.059000
H23B	0.7808	0.1604	0.6367	0.059000
H23C	0.6917	0.2368	0.6004	0.059000
H24A	0.6301	0.0908	0.4679	0.054000
H24B	0.7168	0.0185	0.5173	0.054000
H24C	0.7010	0.0372	0.4142	0.054000

	x/a	y/b	z/c	U(eq)
H1A	0.445(3)	0.234(4)	0.211(3)	0.010(11)
H13	0.9651	0.5689	0.5848	0.042000
H16A	0.7167	0.7164	0.3273	0.032000
H16B	0.7784	0.7847	0.2732	0.032000
H17A	0.8836	0.8372	0.4012	0.036000
H17B	0.7792	0.8641	0.4137	0.036000
H19A	0.7811	0.5806	0.6093	0.041000
H19B	0.8707	0.6466	0.6626	0.041000
H13A	0.9484	0.5925	0.5959	0.042000
H16C	0.7046	0.7064	0.3036	0.033000
H16D	0.7695	0.7718	0.2495	0.033000
H17C	0.8640	0.8392	0.3735	0.038000
H17D	0.7597	0.8542	0.3897	0.038000
H19C	0.7570	0.6122	0.5907	0.046000
H19D	0.8406	0.6841	0.6467	0.046000

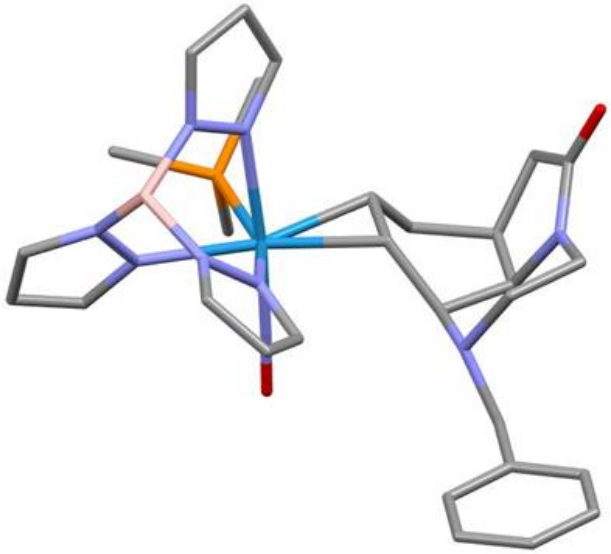
Table 9. Hydrogen bond distances (Å) and angles (°) for Compound 14.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O2-H2···O1#1	0.89(8)	2.04(9)	2.844(6)	149.(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, y+1/2, -z+1/2

Crystal Structure Report for Compound 13



A colorless, plate-like specimen of $C_{29}H_{39}BN_9O_2PW$, approximate dimensions 0.048 mm x 0.068 mm x 0.094 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 2.99 hours. The frames were integrated with the Bruker SAINT software package[171] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 58132 reflections to a maximum θ angle of 29.60° (0.72 Å resolution), of which 8652 were independent (average redundancy 6.719, completeness = 99.6%, R_{int} = 8.88%, R_{sig} = 6.51%) and 6395 (73.91%) were greater than 2σ(F^2). The final cell constants of a = 9.8388(4) Å, b = 13.1493(5) Å, c = 23.9472(11) Å, β = 94.483(2)°, volume = 3088.7(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9100 reflections above 20 σ(I) with 4.608° < 2θ < 58.94°. Data were corrected for

[171] Bruker (2012). Saint; SADABS; APEX5. Bruker AXS Inc., Madison, Wisconsin, USA.

absorption effects using the Multi-Scan method (SADABS).[172] The ratio of minimum to maximum apparent transmission was 0.877. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7140 and 0.8370.

The structure was solved and refined using the Bruker SHELXTL Software Package[173] within APEX5 [1] and OLEX2, using the space group P $2_1/n$, with Z = 4 for the formula unit, $C_{29}H_{39}BN_9O_2PW$. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom, as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 400 variables converged at R1 = 3.70%, for the observed data and wR2 = 7.72% for all data. The goodness-of-fit was 1.010. The largest peak in the final difference electron density synthesis was 1.447 $e^-/Å^3$ and the largest hole was -1.201 $e^-/Å^3$ with an RMS deviation of 0.169 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.659 g/cm^3 and F(000), 1544 e^-.

Table 1. Sample and crystal data for Compound 13.		
Chemical formula	$C_{29}H_{39}BN_9O_2PW$	
Formula weight	771.32 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.048 x 0.068 x 0.094 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P $2_1/n$	
Unit cell dimensions	a = 9.8388(4) Å	α = 90°

[172] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[173] Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

	b = 13.1493(5) Å	β = 94.483(2)°
	c = 23.9472(11) Å	γ = 90°
Volume	3088.7(2) $Å^3$	
Z	4	
Density (calculated)	1.659 g/cm^3	
Absorption coefficient	3.835 mm^{-1}	
F(000)	1544	

Table 2. Data collection and structure refinement for Compound 13.	
Diffractometer	Bruker D8 Venture Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.18 to 29.60°
Index ranges	-13<=h<=13, -18<=k<=17, -33<=l<=32
Reflections collected	58132
Independent reflections	8652 [R(int) = 0.0888]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8370 and 0.7140

Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8652 / 0 / 400	
Goodness-of-fit on F^2	1.010	
Δ/σ_{max}	0.003	
Final R indices	6395 data; I>2σ(I)	R1 = 0.0370, wR2 = 0.0683
	all data	R1 = 0.0646, wR2 = 0.0772
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0264P)^2+3.6923P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.447 and -1.201 eÅ^{-3}	
R.M.S. deviation from mean	0.169 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 13.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.40800(2)	0.78192(2)	0.68416(2)	0.01402(5)
P1	0.36274(11)	0.95211(8)	0.72480(5)	0.0169(2)
O1	0.1240(3)	0.7197(2)	0.70621(14)	0.0282(7)
O2	0.4196(4)	0.8981(2)	0.42858(14)	0.0329(8)
N1	0.6232(3)	0.8367(3)	0.67726(14)	0.0197(7)
N2	0.7289(3)	0.7879(3)	0.70693(15)	0.0220(7)
N3	0.4783(3)	0.7427(2)	0.77187(14)	0.0184(7)
N4	0.6104(4)	0.7165(3)	0.78768(15)	0.0210(7)
N5	0.5130(3)	0.6340(2)	0.67374(14)	0.0178(7)
N6	0.6325(3)	0.6121(3)	0.70455(15)	0.0198(7)
N7	0.2414(4)	0.7428(2)	0.69612(14)	0.0185(7)
N8	0.2868(3)	0.6122(2)	0.54033(14)	0.0168(7)
N9	0.2820(4)	0.7863(3)	0.47068(14)	0.0219(7)
C1	0.6801(4)	0.9106(3)	0.64872(18)	0.0211(9)
C2	0.8200(4)	0.9106(3)	0.65952(19)	0.0235(9)
C3	0.8478(4)	0.8314(3)	0.69606(19)	0.0248(10)
C4	0.4095(5)	0.7342(3)	0.81740(18)	0.0217(9)
C5	0.4958(5)	0.7037(3)	0.86340(19)	0.0297(11)
C6	0.6214(5)	0.6929(3)	0.84236(19)	0.0264(10)
C7	0.4754(5)	0.5490(3)	0.64645(17)	0.0210(9)
C8	0.5673(5)	0.4709(3)	0.66042(19)	0.0268(10)
C9	0.6648(5)	0.5133(3)	0.69684(19)	0.0257(10)
C10	0.3724(4)	0.7688(3)	0.59247(16)	0.0156(8)
C11	0.3455(4)	0.8725(3)	0.60828(16)	0.0151(8)

	x/a	y/b	z/c	U(eq)
C12	0.2010(4)	0.9096(3)	0.59377(17)	0.0195(9)
C13	0.1646(5)	0.8939(3)	0.53109(18)	0.0226(9)
C14	0.1868(4)	0.7816(3)	0.51491(17)	0.0200(8)
C15	0.2511(4)	0.7133(3)	0.56300(17)	0.0175(8)
C16	0.3824(4)	0.6211(3)	0.49620(17)	0.0195(9)
C17	0.3328(5)	0.6929(3)	0.44881(19)	0.0249(10)
C18	0.3309(5)	0.8795(3)	0.46085(19)	0.0253(10)
C19	0.2563(5)	0.9558(3)	0.49457(18)	0.0246(10)
C20	0.1673(4)	0.5502(3)	0.52401(19)	0.0225(9)
C21	0.2043(4)	0.4423(3)	0.5103(2)	0.0241(9)
C22	0.2496(5)	0.3752(3)	0.5523(2)	0.0300(11)
C23	0.2857(5)	0.2760(4)	0.5397(2)	0.0351(11)
C24	0.2769(5)	0.2440(4)	0.4847(2)	0.0390(13)
C25	0.2322(5)	0.3100(4)	0.4423(2)	0.0377(13)
C26	0.1963(5)	0.4081(3)	0.4548(2)	0.0289(10)
C27	0.1847(4)	0.9776(3)	0.73345(19)	0.0236(9)
C28	0.4174(4)	0.0651(3)	0.68911(18)	0.0212(9)
C29	0.4399(5)	0.9750(3)	0.79546(18)	0.0261(10)
B1	0.7062(5)	0.6928(4)	0.7425(2)	0.0236(11)

Table 4. Bond lengths (Å) for Compound 13.

W1-N7	1.763(4)	W1-C10	2.203(4)
W1-C11	2.219(4)	W1-N3	2.220(3)

W1-N5	2.226(3)	W1-N1	2.254(3)
W1-P1	2.4943(10)	P1-C27	1.812(4)
P1-C28	1.816(4)	P1-C29	1.825(4)
O1-N7	1.236(4)	O2-C18	1.234(6)
N1-C1	1.336(5)	N1-N2	1.372(4)
N2-C3	1.346(5)	N2-B1	1.539(6)
N3-C4	1.332(5)	N3-N4	1.369(5)
N4-C6	1.342(6)	N4-B1	1.522(7)
N5-C7	1.332(5)	N5-N6	1.369(4)
N6-C9	1.353(5)	N6-B1	1.541(6)
N8-C20	1.459(5)	N8-C16	1.473(5)
N8-C15	1.488(5)	N9-C18	1.344(5)
N9-C17	1.440(5)	N9-C14	1.469(6)
C1-C2	1.381(6)	C1-H1	0.950000
C2-C3	1.373(6)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.396(6)
C4-H4	0.950000	C5-C6	1.378(7)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.392(6)	C7-H7	0.950000
C8-C9	1.364(6)	C8-H8	0.950000
C9-H9	0.950000	C10-C11	1.446(5)
C10-C15	1.524(5)	C10-H10	1.00(5)
C11-C12	1.517(5)	C11-H11	0.89(4)
C12-C13	1.530(6)	C12-H12A	0.990000
C12-H12B	0.990000	C13-C19	1.538(6)

C13-C14	1.547(5)	C13-H13	1.000000
C14-C15	1.555(5)	C14-H14	1.000000
C15-H15	1.000000	C16-C17	1.527(6)
C16-H16A	0.990000	C16-H16B	0.990000
C17-H17A	0.990000	C17-H17B	0.990000
C18-C19	1.514(6)	C19-H19A	0.990000
C19-H19B	0.990000	C20-C21	1.508(6)
C20-H20A	0.990000	C20-H20B	0.990000
C21-C22	1.385(6)	C21-C26	1.398(6)
C22-C23	1.392(6)	C22-H22	0.950000
C23-C24	1.379(8)	C23-H23	0.950000
C24-C25	1.382(8)	C24-H24	0.950000
C25-C26	1.378(6)	C25-H25	0.950000
C26-H26	0.950000	C27-H27A	0.980000
C27-H27B	0.980000	C27-H27C	0.980000
C28-H28A	0.980000	C28-H28B	0.980000
C28-H28C	0.980000	C29-H29A	0.980000
C29-H29B	0.980000	C29-H29C	0.980000
B1-H1A	1.08(4)		

Table 5. Bond angles (°) for Compound 13.			
N7-W1-C10	93.53(16)	N7-W1-C11	95.04(15)
C10-W1-C11	38.16(13)	N7-W1-N3	90.19(14)
C10-W1-N3	159.75(13)	C11-W1-N3	160.96(13)
N7-W1-N5	102.07(14)	C10-W1-N5	81.89(13)

C11-W1-N5	118.61(13)	N3-W1-N5	77.87(12)
N7-W1-N1	174.66(14)	C10-W1-N1	91.67(14)
C11-W1-N1	88.30(14)	N3-W1-N1	85.33(12)
N5-W1-N1	79.86(12)	N7-W1-P1	90.09(11)
C10-W1-P1	116.09(10)	C11-W1-P1	77.95(11)
N3-W1-P1	83.76(9)	N5-W1-P1	157.89(9)
N1-W1-P1	86.53(9)	C27-P1-C28	103.1(2)
C27-P1-C29	101.5(2)	C28-P1-C29	100.6(2)
C27-P1-W1	114.48(14)	C28-P1-W1	118.81(14)
C29-P1-W1	115.84(14)	C1-N1-N2	105.9(3)
C1-N1-W1	134.7(3)	N2-N1-W1	119.4(3)
C3-N2-N1	109.7(3)	C3-N2-B1	128.2(3)
N1-N2-B1	121.9(3)	C4-N3-N4	106.5(3)
C4-N3-W1	130.8(3)	N4-N3-W1	122.6(3)
C6-N4-N3	109.3(4)	C6-N4-B1	129.7(4)
N3-N4-B1	118.8(3)	C7-N5-N6	106.4(3)
C7-N5-W1	132.4(3)	N6-N5-W1	120.7(2)
C9-N6-N5	109.2(3)	C9-N6-B1	129.6(3)
N5-N6-B1	121.2(3)	O1-N7-W1	176.8(3)
C20-N8-C16	113.5(3)	C20-N8-C15	112.9(3)
C16-N8-C15	111.9(3)	C18-N9-C17	125.1(4)
C18-N9-C14	114.9(4)	C17-N9-C14	119.0(4)
N1-C1-C2	110.9(4)	N1-C1-H1	124.600000
C2-C1-H1	124.600000	C3-C2-C1	105.4(4)
C3-C2-H2	127.300000	C1-C2-H2	127.300000

N2-C3-C2	108.2(4)	N2-C3-H3	125.900000
C2-C3-H3	125.900000	N3-C4-C5	110.7(4)
N3-C4-H4	124.600000	C5-C4-H4	124.600000
C6-C5-C4	104.4(4)	C6-C5-H5	127.800000
C4-C5-H5	127.800000	N4-C6-C5	109.1(4)
N4-C6-H6	125.500000	C5-C6-H6	125.500000
N5-C7-C8	110.5(4)	N5-C7-H7	124.700000
C8-C7-H7	124.700000	C9-C8-C7	105.2(4)
C9-C8-H8	127.400000	C7-C8-H8	127.400000
N6-C9-C8	108.6(4)	N6-C9-H9	125.700000
C8-C9-H9	125.700000	C11-C10-C15	114.9(3)
C11-C10-W1	71.5(2)	C15-C10-W1	123.9(3)
C11-C10-H10	120.(2)	C15-C10-H10	113.(2)
W1-C10-H10	109.(2)	C10-C11-C12	115.5(3)
C10-C11-W1	70.3(2)	C12-C11-W1	123.7(3)
C10-C11-H11	117.(3)	C12-C11-H11	115.(3)
W1-C11-H11	109.(3)	C11-C12-C13	109.0(3)
C11-C12-H12A	109.900000	C13-C12-H12A	109.900000
C11-C12-H12B	109.900000	C13-C12-H12B	109.900000
H12A-C12-H12B	108.300000	C12-C13-C19	112.5(4)
C12-C13-C14	110.4(3)	C19-C13-C14	105.2(4)
C12-C13-H13	109.500000	C19-C13-H13	109.500000
C14-C13-H13	109.500000	N9-C14-C13	104.5(3)

N9-C14-C15	108.2(3)	C13-C14-C15	115.0(3)
N9-C14-H14	109.600000	C13-C14-H14	109.600000
C15-C14-H14	109.600000	N8-C15-C10	113.4(3)
N8-C15-C14	109.8(3)	C10-C15-C14	109.0(3)
N8-C15-H15	108.100000	C10-C15-H15	108.100000
C14-C15-H15	108.100000	N8-C16-C17	113.4(3)
N8-C16-H16A	108.900000	C17-C16-H16A	108.900000
N8-C16-H16B	108.900000	C17-C16-H16B	108.900000
H16A-C16-H16B	107.700000	N9-C17-C16	110.9(4)
N9-C17-H17A	109.500000	C16-C17-H17A	109.500000
N9-C17-H17B	109.500000	C16-C17-H17B	109.500000
H17A-C17-H17B	108.000000	O2-C18-N9	124.8(4)
O2-C18-C19	126.8(4)	N9-C18-C19	108.4(4)
C18-C19-C13	106.4(4)	C18-C19-H19A	110.400000
C13-C19-H19A	110.400000	C18-C19-H19B	110.400000
C13-C19-H19B	110.400000	H19A-C19-H19B	108.600000
N8-C20-C21	112.4(3)	N8-C20-H20A	109.100000
C21-C20-H20A	109.100000	N8-C20-H20B	109.100000

C21-C20-H20B	109.100000	H20A-C20-H20B	107.900000
C22-C21-C26	118.5(4)	C22-C21-C20	120.6(4)
C26-C21-C20	120.9(4)	C21-C22-C23	120.8(5)
C21-C22-H22	119.600000	C23-C22-H22	119.600000
C24-C23-C22	119.6(5)	C24-C23-H23	120.200000
C22-C23-H23	120.200000	C23-C24-C25	120.3(5)
C23-C24-H24	119.800000	C25-C24-H24	119.800000
C26-C25-C24	120.0(5)	C26-C25-H25	120.000000
C24-C25-H25	120.000000	C25-C26-C21	120.8(5)
C25-C26-H26	119.600000	C21-C26-H26	119.600000
P1-C27-H27A	109.500000	P1-C27-H27B	109.500000
H27A-C27-H27B	109.500000	P1-C27-H27C	109.500000
H27A-C27-H27C	109.500000	H27B-C27-H27C	109.500000
P1-C28-H28A	109.500000	P1-C28-H28B	109.500000
H28A-C28-H28B	109.500000	P1-C28-H28C	109.500000
H28A-C28-H28C	109.500000	H28B-C28-H28C	109.500000
P1-C29-H29A	109.500000	P1-C29-H29B	109.500000
H29A-C29-H29B	109.500000	P1-C29-H29C	109.500000
H29A-C29-H29C	109.500000	H29B-C29-H29C	109.500000
N4-B1-N2	110.6(4)	N4-B1-N6	105.8(4)

N2-B1-N6	108.4(4)	N4-B1-H1A	113.(2)
N2-B1-H1A	111.(3)	N6-B1-H1A	108.(2)

Table 6. Torsion angles (°) for Compound 13.			
C1-N1-N2-C3	-0.4(5)	W1-N1-N2-C3	178.9(3)
C1-N1-N2-B1	-175.9(4)	W1-N1-N2-B1	3.5(5)
C4-N3-N4-C6	-0.3(4)	W1-N3-N4-C6	-177.5(3)
C4-N3-N4-B1	164.7(4)	W1-N3-N4-B1	-12.5(5)
C7-N5-N6-C9	-1.5(5)	W1-N5-N6-C9	171.0(3)
C7-N5-N6-B1	-179.2(4)	W1-N5-N6-B1	-6.7(5)
N2-N1-C1-C2	-0.2(5)	W1-N1-C1-C2	-179.4(3)
N1-C1-C2-C3	0.7(5)	N1-N2-C3-C2	0.9(5)
B1-N2-C3-C2	176.0(4)	C1-C2-C3-N2	-0.9(5)
N4-N3-C4-C5	0.7(4)	W1-N3-C4-C5	177.6(3)
N3-C4-C5-C6	-0.8(5)	N3-N4-C6-C5	-0.2(5)
B1-N4-C6-C5	-163.1(4)	C4-C5-C6-N4	0.6(5)
N6-N5-C7-C8	1.7(5)	W1-N5-C7-C8	-169.6(3)
N5-C7-C8-C9	-1.3(5)	N5-N6-C9-C8	0.8(5)
B1-N6-C9-C8	178.2(4)	C7-C8-C9-N6	0.3(5)
C15-C10-C11-C12	0.7(5)	W1-C10-C11-C12	-118.8(3)

C15-C10-C11-W1	119.5(3)	C10-C11-C12-C13	-54.9(5)
W1-C11-C12-C13	-137.4(3)	C11-C12-C13-C19	-62.4(4)
C11-C12-C13-C14	54.8(5)	C18-N9-C14-C13	5.9(4)
C17-N9-C14-C13	175.4(3)	C18-N9-C14-C15	-117.2(4)
C17-N9-C14-C15	52.3(5)	C12-C13-C14-N9	-123.5(4)
C19-C13-C14-N9	-1.8(4)	C12-C13-C14-C15	-4.9(5)
C19-C13-C14-C15	116.7(4)	C20-N8-C15-C10	166.6(3)
C16-N8-C15-C10	-63.9(4)	C20-N8-C15-C14	-71.1(4)
C16-N8-C15-C14	58.3(4)	C11-C10-C15-N8	172.0(3)
W1-C10-C15-N8	-104.3(4)	C11-C10-C15-C14	49.3(5)
W1-C10-C15-C14	133.0(3)	N9-C14-C15-N8	-54.9(4)
C13-C14-C15-N8	-171.4(3)	N9-C14-C15-C10	69.9(4)
C13-C14-C15-C10	-46.5(5)	C20-N8-C16-C17	75.1(4)
C15-N8-C16-C17	-54.0(4)	C18-N9-C17-C16	120.8(4)
C14-N9-C17-C16	-47.6(5)	N8-C16-C17-N9	46.1(5)

C17-N9-C18-O2	5.4(7)	C14-N9-C18-O2	174.1(4)
C17-N9-C18-C19	-176.1(4)	C14-N9-C18-C19	-7.3(5)
O2-C18-C19-C13	-175.9(4)	N9-C18-C19-C13	5.6(5)
C12-C13-C19-C18	118.2(4)	C14-C13-C19-C18	-2.0(4)
C16-N8-C20-C21	60.9(5)	C15-N8-C20-C21	-170.5(4)
N8-C20-C21-C22	72.5(5)	N8-C20-C21-C26	-106.3(5)
C26-C21-C22-C23	-0.3(7)	C20-C21-C22-C23	-179.1(4)
C21-C22-C23-C24	0.3(7)	C22-C23-C24-C25	-0.2(8)
C23-C24-C25-C26	0.1(8)	C24-C25-C26-C21	-0.1(7)
C22-C21-C26-C25	0.2(7)	C20-C21-C26-C25	179.0(4)
C6-N4-B1-N2	-133.8(4)	N3-N4-B1-N2	64.6(5)
C6-N4-B1-N6	109.0(5)	N3-N4-B1-N6	-52.5(5)
C3-N2-B1-N4	125.7(4)	N1-N2-B1-N4	-59.7(5)
C3-N2-B1-N6	-118.8(4)	N1-N2-B1-N6	55.8(5)
C9-N6-B1-N4	-112.6(5)	N5-N6-B1-N4	64.5(5)
C9-N6-B1-N2	128.7(4)	N5-N6-B1-N2	-54.1(5)

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 13.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01368(7)	0.01429(7)	0.01401(8)	-0.00011(7)	0.00065(5)	0.00154(7)
P1	0.0164(5)	0.0162(5)	0.0182(5)	-0.0015(4)	0.0015(4)	-0.0001(4)
O1	0.0168(14)	0.0242(15)	0.045(2)	0.0077(15)	0.0089(14)	-0.0027(13)
O2	0.047(2)	0.0267(17)	0.0261(18)	0.0065(14)	0.0106(16)	0.0015(15)
N1	0.0171(17)	0.0223(17)	0.0192(18)	0.0004(15)	-0.0017(14)	0.0037(14)
N2	0.0153(16)	0.0226(17)	0.0270(19)	0.0008(16)	-0.0047(15)	0.0018(15)
N3	0.0192(17)	0.0165(16)	0.0193(18)	0.0004(14)	-0.0010(15)	0.0025(13)
N4	0.0232(18)	0.0186(16)	0.0202(18)	0.0025(15)	-0.0055(15)	0.0046(15)
N5	0.0201(17)	0.0175(16)	0.0157(17)	0.0000(13)	0.0014(14)	0.0075(13)
N6	0.0162(17)	0.0220(17)	0.0210(19)	-0.0001(15)	0.0013(15)	0.0075(14)
N7	0.0239(18)	0.0125(15)	0.0186(18)	0.0019(13)	-0.0008(15)	0.0026(13)
N8	0.0180(17)	0.0152(15)	0.0173(18)	-0.0037(13)	0.0021(14)	-0.0011(13)
N9	0.032(2)	0.0171(16)	0.0162(17)	-0.0056(15)	-0.0007(15)	0.0031(16)
C1	0.019(2)	0.023(2)	0.022(2)	0.0016(17)	0.0055(18)	0.0008(17)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	0.016(2)	0.024(2)	0.030(2)	-0.0051(19)	0.0019(18)	-0.0023(17)
C3	0.0133(19)	0.032(2)	0.029(2)	-0.003(2)	-0.0002(18)	0.0004(18)
C4	0.029(2)	0.018(2)	0.018(2)	-0.0016(16)	0.0033(18)	0.0001(17)
C5	0.046(3)	0.029(2)	0.014(2)	0.0013(18)	0.000(2)	-0.002(2)
C6	0.033(3)	0.025(2)	0.019(2)	0.0036(17)	-0.011(2)	-0.0009(19)
C7	0.031(2)	0.0180(19)	0.014(2)	-0.0004(16)	0.0026(18)	0.0004(17)
C8	0.041(3)	0.018(2)	0.022(2)	-0.0027(18)	0.006(2)	0.0054(19)
C9	0.027(2)	0.025(2)	0.026(2)	0.0048(19)	0.004(2)	0.0098(18)
C10	0.0191(19)	0.0173(19)	0.0110(18)	-0.0011(15)	0.0044(15)	0.0052(16)
C11	0.0153(19)	0.0180(19)	0.0119(19)	0.0039(15)	0.0013(16)	0.0009(15)
C12	0.020(2)	0.0190(19)	0.019(2)	-0.0006(16)	-0.0021(17)	0.0062(16)
C13	0.028(2)	0.019(2)	0.020(2)	0.0004(17)	-0.0050(19)	0.0057(17)
C14	0.022(2)	0.0213(19)	0.016(2)	-0.0004(18)	-0.0006(16)	0.0035(18)
C15	0.0179(19)	0.0176(18)	0.017(2)	-0.0005(17)	0.0011(16)	0.0044(17)
C16	0.022(2)	0.0182(19)	0.019(2)	-0.0047(16)	0.0037(17)	0.0041(16)
C17	0.034(2)	0.020(2)	0.020(2)	-0.0024(17)	-0.001(2)	0.0020(18)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	0.031(2)	0.025(2)	0.018(2)	0.0017(18)	-0.005(2)	0.0024(19)
C19	0.037(3)	0.019(2)	0.017(2)	-0.0009(17)	-0.0013(19)	0.0044(19)
C20	0.017(2)	0.022(2)	0.029(2)	-0.0040(18)	-0.0003(18)	-0.0024(17)
C21	0.019(2)	0.020(2)	0.033(3)	-0.0037(19)	0.0032(19)	-0.0028(17)
C22	0.025(2)	0.027(2)	0.039(3)	-0.004(2)	0.011(2)	-0.0054(19)
C23	0.035(3)	0.024(2)	0.047(3)	0.004(2)	0.013(2)	-0.002(2)
C24	0.039(3)	0.021(2)	0.060(4)	-0.008(2)	0.019(3)	-0.006(2)
C25	0.040(3)	0.028(2)	0.046(3)	-0.019(2)	0.011(3)	-0.007(2)
C26	0.027(2)	0.028(2)	0.032(3)	-0.005(2)	0.005(2)	-0.0072(19)
C27	0.023(2)	0.025(2)	0.024(2)	-0.0011(18)	0.0088(19)	0.0001(17)
C28	0.026(2)	0.0133(17)	0.024(2)	-0.0026(17)	0.0030(18)	-0.0037(17)
C29	0.035(3)	0.021(2)	0.022(2)	-0.0032(18)	0.000(2)	0.0004(19)
B1	0.018(2)	0.027(2)	0.024(3)	0.003(2)	-0.007(2)	0.0099(19)

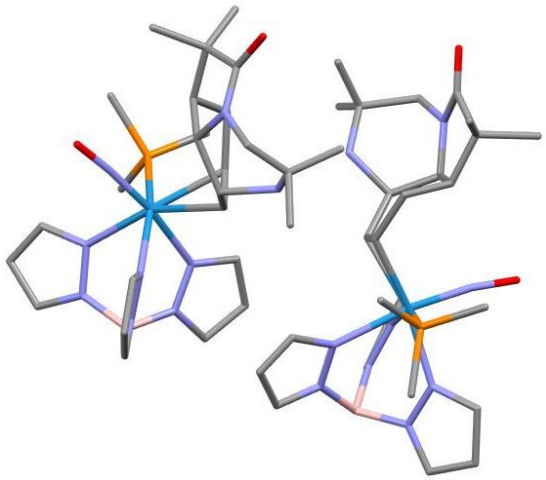
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 13.

	x/a	y/b	z/c	U(eq)
H1	0.6309	0.9569	0.6243	0.025000

	x/a	y/b	z/c	U(eq)
H2	0.8835	0.9557	0.6448	0.028000
H3	0.9358	0.8110	0.7111	0.030000
H4	0.3148	0.7471	0.8184	0.026000
H5	0.4730	0.6929	0.9008	0.036000
H6	0.7028	0.6722	0.8632	0.032000
H7	0.3969	0.5426	0.6210	0.025000
H8	0.5631	0.4026	0.6474	0.032000
H9	0.7424	0.4792	0.7139	0.031000
H10	0.460(4)	0.752(3)	0.5763(18)	0.019000
H11	0.410(4)	0.918(3)	0.6029(18)	0.018000
H12A	0.1940	0.9826	0.6032	0.023000
H12B	0.1368	0.8712	0.6157	0.023000
H13	0.0671	0.9129	0.5217	0.027000
H14	0.0985	0.7514	0.4995	0.024000
H15	0.1815	0.7028	0.5907	0.021000
H16A	0.3971	0.5528	0.4804	0.023000
H16B	0.4713	0.6458	0.5132	0.023000
H17A	0.4090	0.7081	0.4254	0.030000
H17B	0.2596	0.6594	0.4248	0.030000
H19A	0.2005	1.0019	0.4694	0.030000
H19B	0.3219	0.9972	0.5184	0.030000
H20A	0.1168	0.5812	0.4909	0.027000
H20B	0.1062	0.5497	0.5550	0.027000
H22	0.2561	0.3973	0.5902	0.036000

	x/a	y/b	z/c	U(eq)
H23	0.3163	0.2305	0.5689	0.042000
H24	0.3018	0.1764	0.4760	0.047000
H25	0.2262	0.2876	0.4044	0.045000
H26	0.1657	0.4532	0.4255	0.035000
H27A	0.1340	0.9808	0.6966	0.035000
H27B	0.1763	1.0427	0.7528	0.035000
H27C	0.1474	0.9231	0.7556	0.035000
H28A	0.5163	1.0626	0.6866	0.032000
H28B	0.3939	1.1257	0.7101	0.032000
H28C	0.3714	1.0679	0.6513	0.032000
H29A	0.3897	0.9371	0.8225	0.039000
H29B	0.4363	1.0478	0.8039	0.039000
H29C	0.5351	0.9524	0.7980	0.039000
H1A	0.803(5)	0.661(3)	0.7592(19)	0.028000

Structure Report for Compound 10



A colourless, needle shaped crystal of Compound 10 measuring 0.026×0.042×0.107 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for mo_harman_ps_7_137_x3_0m_sq were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[174] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by direct methods with SHELXT[175] and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/1[176] within OLEX2.[177] All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms were located in the electron density map and were refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[178]

Refinement details for Compound 10 Disordered solvent located in the crystal lattice could not be adequately modeled with or without restraints. Therefore, the solvent was accounted for using the Platon SQUEEZE method. A void space of 327 A3 containing 15 electrons was found.

Table 1 Crystal data and structure refinement for Compound 10

CCDC number	
Empirical formula	$C_{26}H_{41}BN_9O_2PW$
Formula weight	737.31
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.026×0.042×0.107
Crystal habit	colourless needle
Crystal system	monoclinic
Space group	$P2_1/c$ (14)

[174] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[175] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
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a [Å]	12.3484(9)
b [Å]	25.111(2)
c [Å]	20.0032(18)
α [°]	90
β [°]	91.104(2)
γ [°]	90
Volume [Å^3]	6201.5(9)
Z	8
ρ_{calc} [gcm^{-3}]	1.579
μ [mm^{-1}]	3.816
F(000)	2960
2θ range [°]	4.17 to 50.10 (0.84 Å)
Index ranges	−14 ≤ h ≤ 13 −29 ≤ k ≤ 29 −23 ≤ l ≤ 23
Reflections collected	74891
Independent reflections	10958 [R_{int} = 0.1215]
Data / Restraints / Parameters	10958 / 0 / 751
Goodness-of-fit on F^2	1.021
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0444 wR_2 = 0.0954
Final *R* indexes [all data]	R_1 = 0.0734 wR_2 = 0.1075
Largest peak/hole [eÅ^{-3}]	1.71/−0.94

Table 2 Atomic coordinates and Ueq [Å2] for Compound 10

Atom	***x***	***y***	***z***	U_{eq}
B1	0.6187(8)	0.8392(3)	0.3359(5)	0.031(2)
H1	0.611(5)	0.880(3)	0.328(3)	0.019(18)
C1	0.3776(6)	0.7583(3)	0.3554(4)	0.0281(17)
H1A	0.340879	0.725411	0.360702	0.034
C2	0.3263(6)	0.8077(3)	0.3511(4)	0.0307(18)
H2	0.250964	0.815069	0.352800	0.037
C3	0.4098(6)	0.8432(3)	0.3440(4)	0.0315(18)

H3	0.401819	0.880714	0.339669	0.038
C4	0.7615(6)	0.7745(3)	0.4732(4)	0.0262(16)
H4	0.784842	0.743483	0.496518	0.031
C5	0.7876(6)	0.8268(3)	0.4926(4)	0.0294(17)
H5	0.830570	0.838063	0.529843	0.035
C6	0.7360(6)	0.8580(3)	0.4445(4)	0.0325(19)
H6	0.737782	0.895840	0.443081	0.039
C7	0.7508(6)	0.7439(3)	0.2281(4)	0.0274(17)
H7	0.772803	0.708990	0.216249	0.033
C8	0.7784(6)	0.7894(3)	0.1934(4)	0.0304(17)
H8	0.821504	0.791865	0.154665	0.037
C9	0.7294(6)	0.8306(3)	0.2273(4)	0.0301(18)
H9	0.732286	0.867240	0.215895	0.036
C10	0.5577(5)	0.6613(3)	0.2783(4)	0.0246(16)
H10	0.505136	0.683595	0.252021	0.030
C11	0.5076(6)	0.6403(3)	0.3375(4)	0.0297(18)
H11	0.430196	0.651330	0.341560	0.036
C12	0.5263(6)	0.5819(3)	0.3534(4)	0.0282(17)
H12A	0.508414	0.575452	0.400796	0.034
H12B	0.476238	0.560165	0.325406	0.034
C13	0.6412(6)	0.5636(3)	0.3419(4)	0.0280(17)
H13	0.689206	0.580073	0.377034	0.034
C14	0.6830(6)	0.5809(3)	0.2723(4)	0.0246(16)
H14	0.759407	0.593799	0.276854	0.030
C15	0.6143(6)	0.6224(3)	0.2330(4)	0.0255(17)
H15	0.664630	0.643242	0.204501	0.031
C16	0.5713(6)	0.5601(3)	0.1385(4)	0.0269(17)
C17	0.6779(6)	0.5348(3)	0.1627(4)	0.0276(17)
H17A	0.685421	0.499037	0.142627	0.033
H17B	0.739525	0.556936	0.148167	0.033
C18	0.5910(7)	0.5896(3)	0.0724(4)	0.037(2)
H18A	0.641436	0.619098	0.080365	0.056
H18B	0.522085	0.603519	0.054619	0.056
H18C	0.621830	0.564814	0.040003	0.056
C19	0.4844(6)	0.5162(3)	0.1280(4)	0.0344(19)
H19A	0.506359	0.492424	0.091800	0.052
H19B	0.414758	0.532716	0.116122	0.052
H19C	0.477234	0.495663	0.169306	0.052
C20	0.6560(6)	0.4869(3)	0.2703(4)	0.0291(18)

C21	0.6603(6)	0.5016(3)	0.3431(4)	0.0286(17)
C22	0.5794(7)	0.4701(3)	0.3828(5)	0.040(2)
H22A	0.583528	0.481067	0.429787	0.060
H22B	0.595978	0.432019	0.379434	0.060
H22C	0.506192	0.476714	0.364895	0.060
C23	0.7764(6)	0.4899(3)	0.3678(4)	0.036(2)
H23A	0.826897	0.513515	0.344928	0.054
H23B	0.794522	0.452763	0.358138	0.054
H23C	0.781863	0.496079	0.416148	0.054
C24	0.4148(6)	0.6577(3)	0.4830(4)	0.0334(19)
H24A	0.413042	0.622362	0.462151	0.050
H24B	0.361088	0.680747	0.460873	0.050
H24C	0.397899	0.654379	0.530512	0.050
C25	0.6296(7)	0.6412(3)	0.5270(5)	0.045(2)
H25A	0.592118	0.634430	0.568895	0.068
H25B	0.700262	0.657479	0.536891	0.068
H25C	0.640020	0.607518	0.503244	0.068
C26	0.5297(7)	0.7448(3)	0.5278(4)	0.046(2)
H26A	0.489431	0.772073	0.502707	0.069
H26B	0.600655	0.758897	0.541639	0.069
H26C	0.489153	0.734615	0.567428	0.069
N1	0.4855(5)	0.7633(2)	0.3509(3)	0.0234(13)
N2	0.5043(5)	0.8170(2)	0.3440(3)	0.0259(14)
N3	0.6997(5)	0.7740(2)	0.4177(3)	0.0249(14)
N4	0.6832(5)	0.8267(2)	0.4005(3)	0.0275(14)
N5	0.6896(5)	0.7554(2)	0.2802(3)	0.0277(14)
N6	0.6771(5)	0.8096(2)	0.2794(3)	0.0251(14)
N7	0.7443(5)	0.6694(2)	0.3789(3)	0.0271(14)
N8	0.5308(5)	0.5981(2)	0.1881(3)	0.0288(15)
H8A	0.484(7)	0.584(3)	0.213(4)	0.03(2)
N9	0.6803(5)	0.5304(2)	0.2346(3)	0.0263(14)
O1	0.8321(4)	0.64714(19)	0.3937(3)	0.0329(13)
O2	0.6410(4)	0.44232(19)	0.2469(3)	0.0366(14)
P1	0.54838(16)	0.68634(7)	0.47475(11)	0.0291(4)
W1	0.62533(2)	0.70635(2)	0.36293(2)	0.02367(9)
B2	0.8741(7)	0.3266(3)	0.2977(5)	0.030(2)
H2A	0.861(5)	0.369(2)	0.292(3)	0.015(17)
C27	0.6404(6)	0.2409(3)	0.3206(4)	0.0242(16)
H27	0.606919	0.207239	0.326540	0.029

C28	0.5849(6)	0.2890(3)	0.3147(4)	0.0271(17)
H28	0.508862	0.294521	0.315758	0.033
C29	0.6642(6)	0.3266(3)	0.3068(4)	0.0278(17)
H29	0.652552	0.363753	0.301732	0.033
C30	1.0250(6)	0.2671(3)	0.4363(4)	0.0249(16)
H30	1.050452	0.237132	0.460957	0.030
C31	1.0485(6)	0.3195(3)	0.4519(4)	0.0295(17)
H31	1.092239	0.332300	0.488051	0.035
C32	0.9951(6)	0.3493(3)	0.4038(4)	0.0287(18)
H32	0.995694	0.387076	0.400571	0.034
C33	1.0145(6)	0.2331(3)	0.1923(4)	0.0277(17)
H33	1.041942	0.198774	0.182010	0.033
C34	1.0335(6)	0.2789(3)	0.1552(4)	0.0319(18)
H34	1.075048	0.281855	0.115934	0.038
C35	0.9800(6)	0.3183(3)	0.1869(4)	0.0300(18)
H35	0.977679	0.354580	0.173596	0.036
C36	0.8209(6)	0.1506(3)	0.2423(4)	0.0271(17)
H36	0.764128	0.172240	0.218546	0.033
C37	0.7791(6)	0.1274(3)	0.3026(4)	0.0266(17)
H37	0.701547	0.136930	0.309690	0.032
C38	0.8010(6)	0.0683(3)	0.3144(4)	0.0281(17)
H38A	0.785334	0.059467	0.361425	0.034
H38B	0.751393	0.047100	0.285403	0.034
C39	0.9165(6)	0.0528(2)	0.3000(4)	0.0241(16)
H39	0.965393	0.069166	0.334717	0.029
C40	0.9523(6)	0.0720(3)	0.2297(4)	0.0281(17)
H40	1.028109	0.085911	0.233096	0.034
C41	0.8793(6)	0.1140(3)	0.1935(4)	0.0267(17)
H41	0.926642	0.136662	0.165125	0.032
C42	0.8369(6)	0.0556(3)	0.0955(4)	0.0313(18)
C43	0.9459(7)	0.0297(3)	0.1174(4)	0.037(2)
H43A	0.952784	−0.005740	0.096192	0.044
H43B	1.006841	0.052136	0.102593	0.044
C44	0.7535(6)	0.0121(3)	0.0821(4)	0.038(2)
H44A	0.774667	−0.008754	0.043056	0.057
H44B	0.682420	0.028273	0.073555	0.057
H44C	0.749819	−0.011353	0.121212	0.057
C45	0.8554(7)	0.0887(3)	0.0334(4)	0.037(2)
H45A	0.900841	0.119441	0.044960	0.056

H45B	0.785598	0.101043	0.015165	0.056
H45C	0.891744	0.066920	−0.000116	0.056
C46	0.9320(6)	−0.0213(3)	0.2229(5)	0.035(2)
C47	0.9387(6)	−0.0086(3)	0.2974(4)	0.0329(19)
C48	0.8627(7)	−0.0433(3)	0.3373(5)	0.041(2)
H48A	0.872781	−0.035790	0.385068	0.061
H48B	0.878782	−0.080928	0.328784	0.061
H48C	0.787619	−0.035733	0.323741	0.061
C49	1.0579(6)	−0.0194(3)	0.3187(5)	0.042(2)
H49A	1.105006	0.006950	0.297832	0.062
H49B	1.078657	−0.055208	0.304399	0.062
H49C	1.065326	−0.016729	0.367482	0.062
C50	0.6900(6)	0.1417(3)	0.4506(4)	0.0335(19)
H50A	0.692529	0.105673	0.431806	0.050
H50B	0.633551	0.162340	0.427234	0.050
H50C	0.673475	0.139606	0.498271	0.050
C51	0.9071(7)	0.1320(3)	0.4920(5)	0.044(2)
H51A	0.877349	0.129434	0.536937	0.067
H51B	0.979828	0.147570	0.494778	0.067
H51C	0.911019	0.096440	0.472121	0.067
C52	0.7981(8)	0.2324(3)	0.4931(5)	0.048(2)
H52A	0.749678	0.222901	0.529487	0.072
H52B	0.765243	0.260864	0.466134	0.072
H52C	0.867634	0.244598	0.511960	0.072
N10	0.7471(5)	0.2486(2)	0.3170(3)	0.0247(14)
N11	0.7609(5)	0.3023(2)	0.3076(3)	0.0253(14)
N12	0.9614(5)	0.2646(2)	0.3817(3)	0.0243(14)
N13	0.9419(5)	0.3158(2)	0.3620(3)	0.0269(14)
N14	0.9529(5)	0.2441(2)	0.2441(3)	0.0275(14)
N15	0.9305(5)	0.2975(2)	0.2408(3)	0.0247(14)
N16	1.0136(5)	0.1597(2)	0.3405(3)	0.0262(14)
N17	0.7949(5)	0.0897(2)	0.1496(3)	0.0291(15)
H17	0.752(6)	0.070(3)	0.178(4)	0.019(19)
N18	0.9510(5)	0.0240(2)	0.1892(3)	0.0301(15)
O3	1.1045(4)	0.13941(19)	0.3516(3)	0.0341(13)
O4	0.9162(5)	−0.06553(19)	0.1982(3)	0.0449(16)
P2	0.82028(16)	0.17396(7)	0.44046(11)	0.0278(4)
W2	0.89183(2)	0.19482(2)	0.32714(2)	0.02323(9)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 2 Anisotropic displacement parameters (Å^2) for Compound 10. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.043(6)	0.018(4)	0.031(5)	0.005(4)	−0.002(4)	0.001(4)
C1	0.032(5)	0.028(4)	0.024(4)	−0.001(3)	0.001(3)	0.005(3)
C2	0.028(4)	0.035(4)	0.029(5)	−0.001(3)	−0.003(3)	0.011(3)
C3	0.037(5)	0.024(4)	0.033(5)	0.001(3)	0.002(4)	0.003(3)
C4	0.027(4)	0.024(4)	0.028(4)	0.003(3)	0.005(3)	−0.006(3)
C5	0.029(4)	0.029(4)	0.030(5)	−0.006(3)	0.000(3)	−0.003(3)
C6	0.035(5)	0.017(4)	0.045(5)	−0.012(3)	0.001(4)	−0.004(3)
C7	0.022(4)	0.025(4)	0.035(5)	−0.007(3)	−0.003(3)	−0.004(3)
C8	0.030(4)	0.032(4)	0.029(5)	0.002(3)	0.006(3)	−0.004(3)
C9	0.032(4)	0.023(4)	0.036(5)	0.006(3)	0.002(4)	0.001(3)
C10	0.018(4)	0.019(3)	0.037(5)	−0.003(3)	−0.008(3)	0.000(3)
C11	0.025(4)	0.020(4)	0.044(5)	−0.003(3)	0.002(4)	−0.001(3)
C12	0.029(4)	0.021(4)	0.035(5)	0.004(3)	−0.002(4)	−0.004(3)
C13	0.029(4)	0.017(3)	0.038(5)	−0.003(3)	−0.002(4)	0.000(3)
C14	0.026(4)	0.021(4)	0.027(4)	0.001(3)	0.001(3)	0.000(3)
C15	0.030(4)	0.020(4)	0.026(4)	−0.002(3)	−0.003(3)	0.001(3)
C16	0.027(4)	0.020(3)	0.034(5)	−0.002(3)	0.000(3)	0.007(3)
C17	0.035(4)	0.025(4)	0.023(4)	−0.011(3)	−0.004(3)	0.000(3)
C18	0.040(5)	0.034(4)	0.037(5)	0.005(4)	−0.002(4)	0.008(4)
C19	0.034(5)	0.027(4)	0.042(5)	−0.009(3)	−0.006(4)	−0.004(3)
C20	0.029(4)	0.020(4)	0.039(5)	0.004(3)	−0.003(4)	0.006(3)
C21	0.032(4)	0.017(3)	0.037(5)	−0.002(3)	0.005(4)	0.003(3)
C22	0.047(5)	0.025(4)	0.047(6)	0.003(4)	0.004(4)	0.002(3)
C23	0.045(5)	0.026(4)	0.037(5)	−0.005(3)	−0.006(4)	0.012(3)
C24	0.028(4)	0.026(4)	0.046(5)	−0.009(3)	0.005(4)	0.001(3)
C25	0.038(5)	0.053(5)	0.045(6)	0.025(4)	−0.003(4)	0.002(4)
C26	0.050(6)	0.054(5)	0.035(5)	−0.017(4)	0.011(4)	−0.016(4)
N1	0.029(4)	0.019(3)	0.022(3)	−0.004(2)	−0.001(3)	0.002(2)
N2	0.034(4)	0.016(3)	0.028(4)	−0.003(2)	−0.002(3)	0.008(2)
N3	0.024(3)	0.023(3)	0.027(4)	0.001(3)	0.002(3)	−0.002(2)
N4	0.031(4)	0.015(3)	0.036(4)	0.005(3)	0.004(3)	0.002(2)
N5	0.028(4)	0.023(3)	0.033(4)	−0.001(3)	0.003(3)	0.001(2)
N6	0.032(4)	0.016(3)	0.027(4)	0.003(2)	−0.001(3)	0.000(2)

N7	0.035(4)	0.018(3)	0.028(4)	−0.003(3)	0.006(3)	−0.004(3)
N8	0.027(4)	0.025(3)	0.034(4)	0.004(3)	−0.002(3)	0.004(3)
N9	0.028(3)	0.019(3)	0.032(4)	−0.004(3)	−0.001(3)	0.003(2)
O1	0.026(3)	0.028(3)	0.045(4)	0.004(2)	−0.005(3)	0.007(2)
O2	0.051(4)	0.016(3)	0.042(4)	−0.002(2)	−0.008(3)	−0.003(2)
P1	0.0311(11)	0.0237(9)	0.0326(12)	−0.0006(8)	0.0000(9)	−0.0019(8)
W1	0.02521(17)	0.01711(14)	0.02866(18)	−0.00015(12)	−0.00043(13)	0.00063(11)
B2	0.038(5)	0.022(4)	0.029(5)	−0.001(4)	0.001(4)	0.006(4)
C27	0.025(4)	0.024(4)	0.024(4)	−0.003(3)	−0.002(3)	−0.005(3)
C28	0.027(4)	0.029(4)	0.025(4)	−0.003(3)	0.000(3)	0.005(3)
C29	0.037(5)	0.017(3)	0.029(4)	0.004(3)	−0.003(3)	0.002(3)
C30	0.022(4)	0.021(4)	0.031(5)	0.001(3)	0.000(3)	−0.001(3)
C31	0.032(4)	0.025(4)	0.032(5)	−0.002(3)	−0.006(4)	0.001(3)
C32	0.030(4)	0.016(3)	0.040(5)	−0.005(3)	−0.001(4)	−0.004(3)
C33	0.024(4)	0.022(4)	0.037(5)	−0.010(3)	0.002(3)	−0.001(3)
C34	0.031(4)	0.035(4)	0.029(5)	0.003(3)	0.005(4)	−0.007(3)
C35	0.034(4)	0.025(4)	0.031(5)	0.012(3)	0.004(4)	0.002(3)
C36	0.024(4)	0.017(3)	0.039(5)	−0.004(3)	−0.004(3)	0.003(3)
C37	0.023(4)	0.018(3)	0.039(5)	0.001(3)	0.002(3)	−0.006(3)
C38	0.035(5)	0.022(4)	0.027(4)	−0.006(3)	0.003(3)	−0.001(3)
C39	0.031(4)	0.015(3)	0.026(4)	0.001(3)	0.000(3)	−0.003(3)
C40	0.025(4)	0.018(3)	0.041(5)	−0.002(3)	−0.002(4)	−0.005(3)
C41	0.026(4)	0.020(3)	0.034(5)	−0.004(3)	0.002(3)	−0.001(3)
C42	0.030(4)	0.030(4)	0.034(5)	−0.003(3)	0.001(4)	0.001(3)
C43	0.034(5)	0.031(4)	0.047(6)	−0.012(4)	0.002(4)	0.004(3)
C44	0.038(5)	0.032(4)	0.044(6)	−0.012(4)	0.002(4)	−0.004(3)
C45	0.032(5)	0.039(5)	0.041(5)	−0.004(4)	0.004(4)	−0.002(3)
C46	0.030(5)	0.021(4)	0.055(6)	−0.008(4)	0.003(4)	0.004(3)
C47	0.034(5)	0.018(4)	0.047(5)	0.004(3)	0.010(4)	0.007(3)
C48	0.039(5)	0.023(4)	0.060(6)	0.002(4)	0.011(4)	0.004(3)
C49	0.036(5)	0.021(4)	0.068(7)	0.003(4)	0.000(4)	0.009(3)
C50	0.038(5)	0.031(4)	0.032(5)	−0.002(3)	0.001(4)	−0.004(3)
C51	0.041(5)	0.049(5)	0.043(6)	0.019(4)	−0.003(4)	−0.008(4)
C52	0.064(6)	0.035(5)	0.046(6)	−0.016(4)	0.018(5)	−0.011(4)
N10	0.027(4)	0.016(3)	0.031(4)	−0.006(2)	0.003(3)	−0.003(2)
N11	0.032(4)	0.018(3)	0.026(4)	0.003(2)	−0.002(3)	0.006(2)
N12	0.026(3)	0.015(3)	0.032(4)	−0.003(2)	0.002(3)	0.003(2)
N13	0.028(3)	0.017(3)	0.036(4)	0.002(3)	0.001(3)	0.000(2)

N14	0.032(4)	0.018(3)	0.033(4)	−0.005(3)	0.000(3)	0.000(2)
N15	0.033(4)	0.019(3)	0.022(3)	0.005(2)	−0.004(3)	0.000(2)
N16	0.030(4)	0.018(3)	0.031(4)	−0.002(3)	0.001(3)	−0.004(2)
N17	0.027(4)	0.025(3)	0.035(4)	−0.004(3)	0.002(3)	0.002(3)
N18	0.033(4)	0.021(3)	0.036(4)	−0.007(3)	0.001(3)	0.001(3)
O3	0.029(3)	0.027(3)	0.046(4)	−0.001(2)	−0.005(3)	0.001(2)
O4	0.048(4)	0.019(3)	0.067(4)	−0.011(3)	−0.001(3)	0.001(2)
P2	0.0286(11)	0.0227(9)	0.0319(12)	−0.0007(8)	0.0003(9)	−0.0030(8)
W2	0.02506(17)	0.01601(14)	0.02857(18)	−0.00057(12)	−0.00066(13)	0.00042(11)

Table 3 Bond lengths and angles for Compound 10 **Atom–Atom**	**Length [Å]**
B1–N2	1.530(11)
B1–N4	1.537(11)
B1–N6	1.543(11)
B1–H1	1.04(6)
C1–N1	1.343(9)
C1–C2	1.393(10)
C1–H1A	0.9500
C2–C3	1.373(11)
C2–H2	0.9500
C3–N2	1.340(9)
C3–H3	0.9500
C4–N3	1.334(9)
C4–C5	1.405(10)
C4–H4	0.9500
C5–C6	1.386(11)
C5–H5	0.9500
C6–N4	1.341(9)
C6–H6	0.9500
C7–N5	1.331(10)
C7–C8	1.382(10)
C7–H7	0.9500
C8–C9	1.382(11)
C8–H8	0.9500

C9–N6	1.344(10)
C9–H9	0.9500
C10–C11	1.445(11)
C10–C15	1.512(10)
C10–W1	2.189(7)
C10–H10	1.0000
C11–C12	1.518(9)
C11–W1	2.257(7)
C11–H11	1.0000
C12–C13	1.514(10)
C12–H12A	0.9900
C12–H12B	0.9900
C13–C14	1.556(11)
C13–C21	1.575(9)
C13–H13	1.0000
C14–N9	1.475(9)
C14–C15	1.546(9)
C14–H14	1.0000
C15–N8	1.485(9)
C15–H15	1.0000
C16–N8	1.470(10)
C16–C17	1.532(10)
C16–C18	1.538(11)
C16–C19	1.551(10)
C17–N9	1.441(10)
C17–H17A	0.9900
C17–H17B	0.9900
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C19–H19A	0.9800
C19–H19B	0.9800
C19–H19C	0.9800
C20–O2	1.227(8)
C20–N9	1.343(9)
C20–C21	1.503(11)
C21–C22	1.511(11)
C21–C23	1.536(10)
C22–H22A	0.9800

C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–P1	1.810(8)
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–P1	1.828(8)
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–P1	1.827(8)
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
N1–N2	1.376(8)
N1–W1	2.252(6)
N3–N4	1.382(8)
N3–W1	2.212(6)
N5–N6	1.370(7)
N5–W1	2.222(6)
N7–O1	1.251(7)
N7–W1	1.761(6)
N8–H8A	0.85(8)
P1–W1	2.498(2)
B2–N15	1.531(11)
B2–N11	1.541(11)
B2–N13	1.545(11)
B2–H2A	1.08(6)
C27–N10	1.334(9)
C27–C28	1.392(9)
C27–H27	0.9500
C28–C29	1.372(10)
C28–H28	0.9500
C29–N11	1.339(9)
C29–H29	0.9500
C30–N12	1.335(9)

C30–C31	1.383(9)
C30–H30	0.9500
C31–C32	1.377(10)
C31–H31	0.9500
C32–N13	1.349(9)
C32–H32	0.9500
C33–N14	1.326(10)
C33–C34	1.390(10)
C33–H33	0.9500
C34–C35	1.354(11)
C34–H34	0.9500
C35–N15	1.354(10)
C35–H35	0.9500
C36–C37	1.445(11)
C36–C41	1.530(10)
C36–W2	2.196(7)
C36–H36	1.0000
C37–C38	1.525(9)
C37–W2	2.241(7)
C37–H37	1.0000
C38–C39	1.510(10)
C38–H38A	0.9900
C38–H38B	0.9900
C39–C40	1.558(11)
C39–C47	1.568(9)
C39–H39	1.0000
C40–N18	1.452(9)
C40–C41	1.557(10)
C40–H40	1.0000
C41–N17	1.482(9)
C41–H41	1.0000
C42–N17	1.483(10)
C42–C45	1.515(11)
C42–C44	1.522(10)
C42–C43	1.551(11)
C43–N18	1.443(11)
C43–H43A	0.9900
C43–H43B	0.9900
C44–H44A	0.9800

C44–H44B	0.9800
C44–H44C	0.9800
C45–H45A	0.9800
C45–H45B	0.9800
C45–H45C	0.9800
C46–O4	1.231(9)
C46–N18	1.345(10)
C46–C47	1.524(12)
C47–C48	1.519(11)
C47–C49	1.548(11)
C48–H48A	0.9800
C48–H48B	0.9800
C48–H48C	0.9800
C49–H49A	0.9800
C49–H49B	0.9800
C49–H49C	0.9800
C50–P2	1.817(8)
C50–H50A	0.9800
C50–H50B	0.9800
C50–H50C	0.9800
C51–P2	1.810(8)
C51–H51A	0.9800
C51–H51B	0.9800
C51–H51C	0.9800
C52–P2	1.829(8)
C52–H52A	0.9800
C52–H52B	0.9800
C52–H52C	0.9800
N10–N11	1.375(7)
N10–W2	2.246(6)
N12–N13	1.365(7)
N12–W2	2.228(5)
N14–N15	1.369(7)
N14–W2	2.216(6)
N16–O3	1.249(7)
N16–W2	1.759(6)
N17–H17	0.93(7)
P2–W2	2.504(2)

Atom–Atom–Atom	**Angle [°]**
N2–B1–N4	107.5(6)
N2–B1–N6	110.4(6)
N4–B1–N6	106.0(6)
N2–B1–H1	107(4)
N4–B1–H1	112(4)
N6–B1–H1	113(4)
N1–C1–C2	111.3(7)
N1–C1–H1A	124.3
C2–C1–H1A	124.3
C3–C2–C1	104.1(7)
C3–C2–H2	128.0
C1–C2–H2	128.0
N2–C3–C2	109.6(6)
N2–C3–H3	125.2
C2–C3–H3	125.2
N3–C4–C5	111.3(6)
N3–C4–H4	124.4
C5–C4–H4	124.4
C6–C5–C4	103.8(6)
C6–C5–H5	128.1
C4–C5–H5	128.1
N4–C6–C5	109.6(6)
N4–C6–H6	125.2
C5–C6–H6	125.2
N5–C7–C8	111.3(7)
N5–C7–H7	124.3
C8–C7–H7	124.3
C9–C8–C7	104.8(7)
C9–C8–H8	127.6
C7–C8–H8	127.6
N6–C9–C8	108.0(6)
N6–C9–H9	126.0
C8–C9–H9	126.0
C11–C10–C15	117.8(6)
C11–C10–W1	73.6(4)
C15–C10–W1	128.6(5)
C11–C10–H10	110.5

C15–C10–H10	110.5
W1–C10–H10	110.5
C10–C11–C12	117.3(6)
C10–C11–W1	68.5(4)
C12–C11–W1	124.6(5)
C10–C11–H11	113.0
C12–C11–H11	113.0
W1–C11–H11	113.0
C13–C12–C11	113.6(6)
C13–C12–H12A	108.9
C11–C12–H12A	108.9
C13–C12–H12B	108.9
C11–C12–H12B	108.9
H12A–C12–H12B	107.7
C12–C13–C14	112.3(6)
C12–C13–C21	115.9(6)
C14–C13–C21	103.8(6)
C12–C13–H13	108.2
C14–C13–H13	108.2
C21–C13–H13	108.2
N9–C14–C15	108.2(6)
N9–C14–C13	102.3(5)
C15–C14–C13	117.0(6)
N9–C14–H14	109.7
C15–C14–H14	109.7
C13–C14–H14	109.7
N8–C15–C10	107.7(6)
N8–C15–C14	113.5(5)
C10–C15–C14	112.7(6)
N8–C15–H15	107.6
C10–C15–H15	107.6
C14–C15–H15	107.6
N8–C16–C17	110.9(6)
N8–C16–C18	109.3(6)
C17–C16–C18	108.8(6)
N8–C16–C19	108.0(6)
C17–C16–C19	109.6(6)
C18–C16–C19	110.2(6)
N9–C17–C16	110.4(6)

N9–C17–H17A	109.6
C16–C17–H17A	109.6
N9–C17–H17B	109.6
C16–C17–H17B	109.6
H17A–C17–H17B	108.1
C16–C18–H18A	109.5
C16–C18–H18B	109.5
H18A–C18–H18B	109.5
C16–C18–H18C	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
C16–C19–H19A	109.5
C16–C19–H19B	109.5
H19A–C19–H19B	109.5
C16–C19–H19C	109.5
H19A–C19–H19C	109.5
H19B–C19–H19C	109.5
O2–C20–N9	125.0(8)
O2–C20–C21	126.6(7)
N9–C20–C21	108.2(6)
C20–C21–C22	111.7(6)
C20–C21–C23	106.3(6)
C22–C21–C23	110.7(7)
C20–C21–C13	103.0(6)
C22–C21–C13	115.2(6)
C23–C21–C13	109.4(6)
C21–C22–H22A	109.5
C21–C22–H22B	109.5
H22A–C22–H22B	109.5
C21–C22–H22C	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
C21–C23–H23A	109.5
C21–C23–H23B	109.5
H23A–C23–H23B	109.5
C21–C23–H23C	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5

P1–C24–H24B	109.5
H24A–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
H25A–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
H26A–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
C1–N1–N2	105.5(5)
C1–N1–W1	134.0(5)
N2–N1–W1	120.1(4)
C3–N2–N1	109.4(6)
C3–N2–B1	128.8(6)
N1–N2–B1	121.7(5)
C4–N3–N4	106.1(5)
C4–N3–W1	130.1(5)
N4–N3–W1	123.7(4)
C6–N4–N3	109.3(6)
C6–N4–B1	132.1(6)
N3–N4–B1	118.5(6)
C7–N5–N6	105.7(6)
C7–N5–W1	132.9(5)
N6–N5–W1	121.2(5)
C9–N6–N5	110.0(6)
C9–N6–B1	128.1(6)
N5–N6–B1	121.7(6)
O1–N7–W1	174.2(5)
C16–N8–C15	115.6(6)
C16–N8–H8A	112(6)
C15–N8–H8A	107(6)

C20–N9–C17	126.3(6)
C20–N9–C14	115.5(6)
C17–N9–C14	116.3(5)
C24–P1–C26	98.1(4)
C24–P1–C25	101.1(4)
C26–P1–C25	103.9(5)
C24–P1–W1	121.7(3)
C26–P1–W1	114.4(3)
C25–P1–W1	115.0(3)
N7–W1–C10	99.9(3)
N7–W1–N3	88.7(2)
C10–W1–N3	158.3(2)
N7–W1–N5	96.8(2)
C10–W1–N5	81.2(2)
N3–W1–N5	78.0(2)
N7–W1–N1	171.6(2)
C10–W1–N1	88.0(2)
N3–W1–N1	82.8(2)
N5–W1–N1	81.5(2)
N7–W1–C11	100.7(3)
C10–W1–C11	37.9(3)
N3–W1–C11	159.3(3)
N5–W1–C11	118.5(3)
N1–W1–C11	87.3(2)
N7–W1–P1	93.5(2)
C10–W1–P1	116.3(2)
N3–W1–P1	82.67(16)
N5–W1–P1	157.82(16)
N1–W1–P1	85.36(16)
C11–W1–P1	78.4(2)
N15–B2–N11	109.5(6)
N15–B2–N13	106.7(6)
N11–B2–N13	107.6(6)
N15–B2–H2A	117(4)
N11–B2–H2A	106(3)
N13–B2–H2A	110(3)
N10–C27–C28	110.8(6)
N10–C27–H27	124.6
C28–C27–H27	124.6

C29–C28–C27	104.8(7)
C29–C28–H28	127.6
C27–C28–H28	127.6
N11–C29–C28	108.9(6)
N11–C29–H29	125.5
C28–C29–H29	125.5
N12–C30–C31	110.3(6)
N12–C30–H30	124.9
C31–C30–H30	124.9
C32–C31–C30	105.3(6)
C32–C31–H31	127.3
C30–C31–H31	127.3
N13–C32–C31	108.4(6)
N13–C32–H32	125.8
C31–C32–H32	125.8
N14–C33–C34	110.4(6)
N14–C33–H33	124.8
C34–C33–H33	124.8
C35–C34–C33	105.4(7)
C35–C34–H34	127.3
C33–C34–H34	127.3
C34–C35–N15	108.8(6)
C34–C35–H35	125.6
N15–C35–H35	125.6
C37–C36–C41	118.1(6)
C37–C36–W2	72.7(4)
C41–C36–W2	127.6(5)
C37–C36–H36	111.0
C41–C36–H36	111.0
W2–C36–H36	111.0
C36–C37–C38	117.1(6)
C36–C37–W2	69.3(4)
C38–C37–W2	126.4(5)
C36–C37–H37	112.3
C38–C37–H37	112.3
W2–C37–H37	112.3
C39–C38–C37	112.7(6)
C39–C38–H38A	109.1
C37–C38–H38A	109.1

C39–C38–H38B	109.1
C37–C38–H38B	109.1
H38A–C38–H38B	107.8
C38–C39–C40	112.2(6)
C38–C39–C47	115.2(6)
C40–C39–C47	102.8(6)
C38–C39–H39	108.8
C40–C39–H39	108.8
C47–C39–H39	108.8
N18–C40–C41	107.7(6)
N18–C40–C39	104.3(5)
C41–C40–C39	117.2(6)
N18–C40–H40	109.2
C41–C40–H40	109.2
C39–C40–H40	109.2
N17–C41–C36	106.9(6)
N17–C41–C40	113.0(5)
C36–C41–C40	112.7(6)
N17–C41–H41	108.0
C36–C41–H41	108.0
C40–C41–H41	108.0
N17–C42–C45	110.0(6)
N17–C42–C44	107.3(7)
C45–C42–C44	111.3(7)
N17–C42–C43	110.5(6)
C45–C42–C43	108.6(7)
C44–C42–C43	109.2(6)
N18–C43–C42	110.1(7)
N18–C43–H43A	109.6
C42–C43–H43A	109.6
N18–C43–H43B	109.6
C42–C43–H43B	109.6
H43A–C43–H43B	108.2
C42–C44–H44A	109.5
C42–C44–H44B	109.5
H44A–C44–H44B	109.5
C42–C44–H44C	109.5
H44A–C44–H44C	109.5
H44B–C44–H44C	109.5

C42–C45–H45A	109.5
C42–C45–H45B	109.5
H45A–C45–H45B	109.5
C42–C45–H45C	109.5
H45A–C45–H45C	109.5
H45B–C45–H45C	109.5
O4–C46–N18	126.2(8)
O4–C46–C47	125.9(8)
N18–C46–C47	107.8(6)
C48–C47–C46	111.8(7)
C48–C47–C49	110.3(7)
C46–C47–C49	105.5(7)
C48–C47–C39	116.0(6)
C46–C47–C39	103.4(6)
C49–C47–C39	109.2(6)
C47–C48–H48A	109.5
C47–C48–H48B	109.5
H48A–C48–H48B	109.5
C47–C48–H48C	109.5
H48A–C48–H48C	109.5
H48B–C48–H48C	109.5
C47–C49–H49A	109.5
C47–C49–H49B	109.5
H49A–C49–H49B	109.5
C47–C49–H49C	109.5
H49A–C49–H49C	109.5
H49B–C49–H49C	109.5
P2–C50–H50A	109.5
P2–C50–H50B	109.5
H50A–C50–H50B	109.5
P2–C50–H50C	109.5
H50A–C50–H50C	109.5
H50B–C50–H50C	109.5
P2–C51–H51A	109.5
P2–C51–H51B	109.5
H51A–C51–H51B	109.5
P2–C51–H51C	109.5
H51A–C51–H51C	109.5
H51B–C51–H51C	109.5

P2–C52–H52A	109.5
P2–C52–H52B	109.5
H52A–C52–H52B	109.5
P2–C52–H52C	109.5
H52A–C52–H52C	109.5
H52B–C52–H52C	109.5
C27–N10–N11	105.9(5)
C27–N10–W2	133.9(4)
N11–N10–W2	120.1(4)
C29–N11–N10	109.6(6)
C29–N11–B2	129.0(6)
N10–N11–B2	121.4(5)
C30–N12–N13	106.9(5)
C30–N12–W2	130.8(4)
N13–N12–W2	122.4(4)
C32–N13–N12	109.1(6)
C32–N13–B2	131.0(6)
N12–N13–B2	119.7(6)
C33–N14–N15	106.6(6)
C33–N14–W2	132.7(5)
N15–N14–W2	120.7(5)
C35–N15–N14	108.8(6)
C35–N15–B2	128.7(6)
N14–N15–B2	121.8(6)
O3–N16–W2	173.8(5)
C41–N17–C42	114.8(6)
C41–N17–H17	105(4)
C42–N17–H17	111(4)
C46–N18–C43	125.3(6)
C46–N18–C40	115.0(7)
C43–N18–C40	118.2(6)
C51–P2–C50	101.1(4)
C51–P2–C52	103.4(5)
C50–P2–C52	98.7(4)
C51–P2–W2	114.9(3)
C50–P2–W2	121.5(3)
C52–P2–W2	114.4(3)
N16–W2–C36	101.0(3)
N16–W2–N14	95.3(3)

C36–W2–N14	80.7(2)
N16–W2–N12	90.0(2)
C36–W2–N12	157.0(2)
N14–W2–N12	78.1(2)
N16–W2–C37	100.3(3)
C36–W2–C37	38.0(3)
N14–W2–C37	118.5(2)
N12–W2–C37	159.1(3)
N16–W2–N10	172.5(2)
C36–W2–N10	85.9(2)
N14–W2–N10	83.0(2)
N12–W2–N10	82.5(2)
C37–W2–N10	86.8(2)
N16–W2–P2	94.2(2)
C36–W2–P2	116.8(2)
N14–W2–P2	157.95(15)
N12–W2–P2	82.00(17)
C37–W2–P2	79.1(2)
N10–W2–P2	85.04(17)

Table 4 Torsion angles for Compound 10 **Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
N1–C1–C2–C3	−0.2(9)
C1–C2–C3–N2	−0.1(9)
N3–C4–C5–C6	0.4(9)
C4–C5–C6–N4	0.3(9)
N5–C7–C8–C9	−0.3(9)
C7–C8–C9–N6	0.5(9)
C15–C10–C11–C12	6.5(10)
W1–C10–C11–C12	−119.0(6)
C15–C10–C11–W1	125.4(6)
C10–C11–C12–C13	41.0(9)
W1–C11–C12–C13	−40.7(9)
C11–C12–C13–C14	−48.8(8)
C11–C12–C13–C21	−167.9(6)
C12–C13–C14–N9	−105.8(6)
C21–C13–C14–N9	20.2(7)

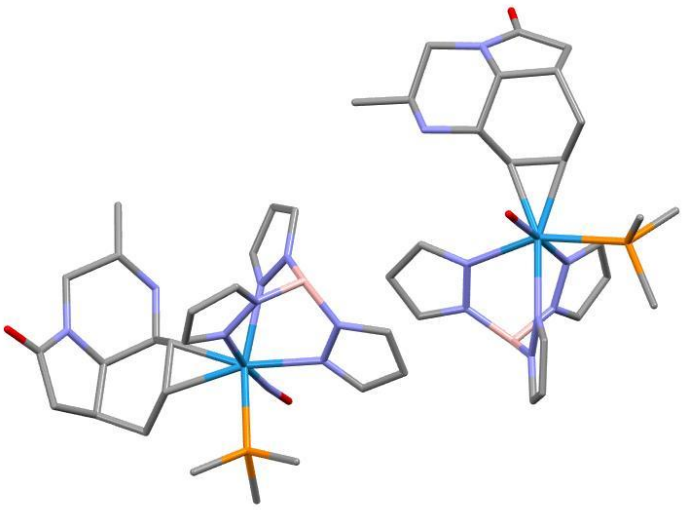
C12–C13–C14–C15	12.2(8)
C21–C13–C14–C15	138.2(6)
C11–C10–C15–N8	83.3(8)
W1–C10–C15–N8	173.9(5)
C11–C10–C15–C14	−42.6(9)
W1–C10–C15–C14	48.0(9)
N9–C14–C15–N8	24.3(9)
C13–C14–C15–N8	−90.5(8)
N9–C14–C15–C10	147.0(6)
C13–C14–C15–C10	32.2(9)
N8–C16–C17–N9	31.4(8)
C18–C16–C17–N9	151.7(6)
C19–C16–C17–N9	−87.7(7)
O2–C20–C21–C22	−37.2(10)
N9–C20–C21–C22	147.8(6)
O2–C20–C21–C23	83.6(9)
N9–C20–C21–C23	−91.3(7)
O2–C20–C21–C13	−161.4(7)
N9–C20–C21–C13	23.6(8)
C12–C13–C21–C20	97.1(8)
C14–C13–C21–C20	−26.5(7)
C12–C13–C21–C22	−24.7(10)
C14–C13–C21–C22	−148.4(7)
C12–C13–C21–C23	−150.2(7)
C14–C13–C21–C23	86.2(7)
C2–C1–N1–N2	0.3(8)
C2–C1–N1–W1	173.0(5)
C2–C3–N2–N1	0.3(9)
C2–C3–N2–B1	178.5(7)
C1–N1–N2–C3	−0.3(8)
W1–N1–N2–C3	−174.2(5)
C1–N1–N2–B1	−178.7(7)
W1–N1–N2–B1	7.4(8)
N4–B1–N2–C3	118.0(8)
N6–B1–N2–C3	−126.8(8)
N4–B1–N2–N1	−63.9(8)
N6–B1–N2–N1	51.2(9)
C5–C4–N3–N4	−0.8(8)
C5–C4–N3–W1	−177.4(5)

C5–C6–N4–N3	−0.8(9)
C5–C6–N4–B1	−176.1(8)
C4–N3–N4–C6	1.0(8)
W1–N3–N4–C6	177.8(5)
C4–N3–N4–B1	177.0(7)
W1–N3–N4–B1	−6.2(8)
N2–B1–N4–C6	−122.5(8)
N6–B1–N4–C6	119.4(8)
N2–B1–N4–N3	62.6(8)
N6–B1–N4–N3	−55.5(8)
C8–C7–N5–N6	−0.1(8)
C8–C7–N5–W1	−174.3(5)
C8–C9–N6–N5	−0.6(8)
C8–C9–N6–B1	174.1(7)
C7–N5–N6–C9	0.4(8)
W1–N5–N6–C9	175.4(5)
C7–N5–N6–B1	−174.7(7)
W1–N5–N6–B1	0.3(8)
N2–B1–N6–C9	129.5(7)
N4–B1–N6–C9	−114.4(8)
N2–B1–N6–N5	−56.4(9)
N4–B1–N6–N5	59.7(8)
C17–C16–N8–C15	25.9(9)
C18–C16–N8–C15	−94.1(7)
C19–C16–N8–C15	146.0(6)
C10–C15–N8–C16	178.0(6)
C14–C15–N8–C16	−56.6(9)
O2–C20–N9–C17	9.7(12)
C21–C20–N9–C17	−175.3(6)
O2–C20–N9–C14	173.6(7)
C21–C20–N9–C14	−11.3(8)
C16–C17–N9–C20	97.6(8)
C16–C17–N9–C14	−66.2(8)
C15–C14–N9–C20	−130.5(7)
C13–C14–N9–C20	−6.4(8)
C15–C14–N9–C17	35.1(8)
C13–C14–N9–C17	159.2(6)
N10–C27–C28–C29	0.2(8)
C27–C28–C29–N11	0.5(8)

N12–C30–C31–C32	0.3(9)
C30–C31–C32–N13	0.4(9)
N14–C33–C34–C35	−0.1(9)
C33–C34–C35–N15	−0.2(9)
C41–C36–C37–C38	2.6(10)
W2–C36–C37–C38	−121.3(6)
C41–C36–C37–W2	123.9(6)
C36–C37–C38–C39	44.5(9)
W2–C37–C38–C39	−38.9(9)
C37–C38–C39–C40	−51.4(8)
C37–C38–C39–C47	−168.6(6)
C38–C39–C40–N18	−104.6(6)
C47–C39–C40–N18	19.8(7)
C38–C39–C40–C41	14.3(8)
C47–C39–C40–C41	138.6(6)
C37–C36–C41–N17	85.5(8)
W2–C36–C41–N17	174.6(5)
C37–C36–C41–C40	−39.2(9)
W2–C36–C41–C40	49.9(8)
N18–C40–C41–N17	25.5(9)
C39–C40–C41–N17	−91.4(8)
N18–C40–C41–C36	146.9(6)
C39–C40–C41–C36	29.9(8)
N17–C42–C43–N18	27.4(8)
C45–C42–C43–N18	148.1(6)
C44–C42–C43–N18	−90.4(8)
O4–C46–C47–C48	−34.4(11)
N18–C46–C47–C48	148.2(6)
O4–C46–C47–C49	85.5(9)
N18–C46–C47–C49	−91.9(7)
O4–C46–C47–C39	−159.8(7)
N18–C46–C47–C39	22.7(8)
C38–C39–C47–C48	−25.7(10)
C40–C39–C47–C48	−148.0(7)
C38–C39–C47–C46	97.0(7)
C40–C39–C47–C46	−25.3(7)
C38–C39–C47–C49	−151.1(7)
C40–C39–C47–C49	86.6(8)
C28–C27–N10–N11	−0.8(8)

C28–C27–N10–W2	176.2(5)
C28–C29–N11–N10	−1.0(8)
C28–C29–N11–B2	177.1(7)
C27–N10–N11–C29	1.1(8)
W2–N10–N11–C29	−176.4(5)
C27–N10–N11–B2	−177.2(6)
W2–N10–N11–B2	5.3(8)
N15–B2–N11–C29	−124.7(8)
N13–B2–N11–C29	119.7(8)
N15–B2–N11–N10	53.2(9)
N13–B2–N11–N10	−62.4(8)
C31–C30–N12–N13	−0.9(8)
C31–C30–N12–W2	179.7(5)
C31–C32–N13–N12	−0.9(8)
C31–C32–N13–B2	−176.6(8)
C30–N12–N13–C32	1.1(8)
W2–N12–N13–C32	−179.4(5)
C30–N12–N13–B2	177.4(6)
W2–N12–N13–B2	−3.1(8)
N15–B2–N13–C32	118.7(8)
N11–B2–N13–C32	−123.9(8)
N15–B2–N13–N12	−56.6(8)
N11–B2–N13–N12	60.8(8)
C34–C33–N14–N15	0.3(8)
C34–C33–N14–W2	−177.7(5)
C34–C35–N15–N14	0.4(8)
C34–C35–N15–B2	170.5(7)
C33–N14–N15–C35	−0.5(8)
W2–N14–N15–C35	177.9(5)
C33–N14–N15–B2	−171.4(7)
W2–N14–N15–B2	7.0(8)
N11–B2–N15–C35	129.8(7)
N13–B2–N15–C35	−114.0(8)
N11–B2–N15–N14	−61.2(8)
N13–B2–N15–N14	54.9(8)
C36–C41–N17–C42	175.9(6)
C40–C41–N17–C42	−59.5(9)

C45–C42–N17–C41	−90.1(7)
C44–C42–N17–C41	148.7(6)
C43–C42–N17–C41	29.7(9)
O4–C46–N18–C43	6.3(13)
C47–C46–N18–C43	−176.3(7)
O4–C46–N18–C40	172.0(7)
C47–C46–N18–C40	−10.6(9)
C42–C43–N18–C46	100.5(8)
C42–C43–N18–C40	−64.8(8)
C41–C40–N18–C46	−131.5(7)
C39–C40–N18–C46	−6.4(8)
C41–C40–N18–C43	35.2(9)
C39–C40–N18–C43	160.3(6)



Structure Report for compound 9

A colourless, needle-shaped crystal of compound 9

measuring 0.035×0.076×0.107 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for compound 9

were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the

Bruker APEX5 software suite.[179] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with SHELXT[180] and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/1[181] within OLEX2.[182] All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms, as well as the hydrogen atoms on carbons directly bound to W were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[183]

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[183] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Table 1 Crystal data and structure refinement for compound 9

CCDC number	
Empirical formula	$C_{23}H_{35}BN_9O_2PW$
Formula weight	695.23
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1$ (4)
a [Å]	10.5222(8)
b [Å]	13.6741(9)
c [Å]	19.3241(15)
α [°]	90
β [°]	103.811(2)
γ [°]	90
Volume [Å^3]	2700.0(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.710
μ [mm^{-1}]	4.377
F(000)	1384
Crystal size [mm^3]	0.032×0.065×0.364
Crystal colour	colourless
Crystal shape	needle
Radiation	Mo K_α (λ=0.71073 Å)
2θ range [°]	3.69 to 56.59 (0.75 Å)
Index ranges	−14 ≤ h ≤ 14 −18 ≤ k ≤ 18 −25 ≤ l ≤ 25
Reflections collected	82479
Independent reflections	13362 R_{int} = 0.0541 R_{sigma} = 0.0374
Completeness to θ = 25.242°	99.9
Data / Restraints / Parameters	13362 / 1 / 705

Goodness-of-fit on F^2	1.031
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0273 wR_2 = 0.0601
Final R indexes [all data]	R_1 = 0.0304 wR_2 = 0.0616
Largest peak/hole [eÅ^{-3}]	1.02/−0.57
Flack X parameter	-0.011(4)

Table 2 Atomic coordinates and Ueq [Å^2] for compound 9

Atom	***x***	***y***	***z***	U_{eq}
W1	0.30482(2)	0.37099(2)	0.08984(2)	0.01323(6)
P1	0.19128(16)	0.35826(13)	−0.03874(9)	0.0171(3)
O1	0.5626(4)	0.3712(4)	0.0492(2)	0.0241(9)
O2	0.2631(5)	0.8404(3)	0.1723(3)	0.0266(10)
N1	0.1006(5)	0.3558(4)	0.1100(3)	0.0177(11)
N2	0.0717(5)	0.2735(4)	0.1438(3)	0.0195(11)
N3	0.3027(5)	0.2093(4)	0.0847(3)	0.0167(12)
N4	0.2346(5)	0.1511(4)	0.1205(3)	0.0165(11)
N5	0.3533(5)	0.3293(4)	0.2045(3)	0.0174(11)
N6	0.2882(5)	0.2551(4)	0.2284(3)	0.0162(10)
N7	0.4575(4)	0.3715(4)	0.0675(3)	0.0161(9)
N8	0.4332(5)	0.7428(4)	0.1610(3)	0.0199(11)
N9	0.5521(5)	0.5685(4)	0.2203(3)	0.0168(11)
H9	0.635(7)	0.578(5)	0.220(4)	0.009(16)
C1	−0.0114(6)	0.4072(5)	0.0912(4)	0.0210(13)
H1	−0.020297	0.468046	0.066805	0.025
C2	−0.1121(6)	0.3594(6)	0.1124(3)	0.0252(14)
H2	−0.200341	0.380268	0.105593	0.030
C3	−0.0566(6)	0.2756(5)	0.1452(4)	0.0232(14)
H3	−0.100774	0.226858	0.165544	0.028
C4	0.3633(6)	0.1490(5)	0.0483(4)	0.0200(13)
H4	0.418939	0.169617	0.018909	0.024
C5	0.3337(7)	0.0520(5)	0.0594(4)	0.0224(14)
H5	0.362128	−0.004774	0.039157	0.027
C6	0.2534(7)	0.0567(5)	0.1066(4)	0.0232(14)
H6	0.217607	0.002245	0.125993	0.028
C7	0.4410(5)	0.3635(5)	0.2607(3)	0.0188(11)

H7	0.499934	0.415729	0.259413	0.023
C8	0.4338(7)	0.3108(5)	0.3222(4)	0.0211(13)
H8	0.484741	0.320027	0.369439	0.025
C9	0.3364(6)	0.2430(5)	0.2987(3)	0.0200(13)
H9A	0.308017	0.195451	0.327492	0.024
C10	0.2599(6)	0.5268(4)	0.0624(3)	0.0157(12)
H10	0.163(7)	0.541(5)	0.056(4)	0.019
C11	0.3406(6)	0.5207(4)	0.1348(3)	0.0165(12)
H11	0.301(7)	0.537(5)	0.180(4)	0.015(17)
C12	0.4765(6)	0.5670(4)	0.1451(3)	0.0172(12)
H12	0.526694	0.525584	0.118292	0.021
C13	0.4690(6)	0.6710(4)	0.1124(3)	0.0170(12)
H13	0.556480	0.688586	0.104209	0.020
C14	0.3639(6)	0.6851(5)	0.0426(4)	0.0197(13)
H14	0.403373	0.721531	0.008022	0.024
C15	0.3151(6)	0.5855(4)	0.0104(4)	0.0202(13)
H15A	0.246597	0.595404	−0.034083	0.024
H15B	0.388379	0.549271	−0.001640	0.024
C16	0.2582(6)	0.7495(5)	0.0626(4)	0.0233(14)
H16A	0.236086	0.805423	0.029334	0.028
H16B	0.177680	0.711091	0.060757	0.028
C17	0.3155(6)	0.7851(4)	0.1371(4)	0.0204(13)
C18	0.5089(6)	0.7447(5)	0.2337(4)	0.0216(13)
H18A	0.470064	0.791626	0.261794	0.026
H18B	0.599673	0.765668	0.235401	0.026
C19	0.5092(6)	0.6421(4)	0.2648(3)	0.0188(12)
H19	0.416927	0.626100	0.265826	0.023
C20	0.5904(7)	0.6367(5)	0.3404(4)	0.0244(14)
H20A	0.576564	0.573381	0.361106	0.037
H20B	0.564367	0.689359	0.368554	0.037
H20C	0.683202	0.644034	0.340626	0.037
C21	0.2949(6)	0.3798(6)	−0.1008(3)	0.0251(13)
H21A	0.249621	0.357124	−0.148416	0.038
H21B	0.377263	0.343872	−0.084760	0.038
H21C	0.313296	0.449869	−0.102486	0.038
C22	0.0495(6)	0.4350(5)	−0.0751(4)	0.0235(13)
H22A	0.070971	0.503402	−0.062229	0.035
H22B	−0.024032	0.414294	−0.055629	0.035
H22C	0.025276	0.428696	−0.127161	0.035

C23	0.1198(7)	0.2381(5)	−0.0668(4)	0.0255(14)
H23A	0.057486	0.244048	−0.113188	0.038
H23B	0.074353	0.213679	−0.031516	0.038
H23C	0.189491	0.192308	−0.070616	0.038
B1	0.1768(7)	0.1979(5)	0.1783(4)	0.0200(14)
H1A	0.147(7)	0.149(5)	0.206(4)	0.03(2)
W2	0.75339(2)	0.11095(2)	0.47177(2)	0.01500(6)
P2	0.78244(17)	−0.06627(12)	0.44956(10)	0.0206(3)
O3	0.4803(5)	0.0840(4)	0.4886(3)	0.0349(13)
O4	1.1835(5)	0.1655(5)	0.7641(3)	0.0440(15)
N10	0.9436(5)	0.1377(4)	0.4394(3)	0.0164(11)
N11	0.9446(5)	0.1941(4)	0.3816(3)	0.0180(10)
N12	0.6660(5)	0.1149(5)	0.3545(3)	0.0172(11)
N13	0.7156(5)	0.1703(4)	0.3089(3)	0.0221(11)
N14	0.7386(5)	0.2703(4)	0.4508(3)	0.0151(11)
N15	0.7677(5)	0.3106(4)	0.3920(3)	0.0169(11)
N16	0.5949(6)	0.0935(4)	0.4856(3)	0.0222(12)
N17	0.9626(5)	0.1916(4)	0.7339(3)	0.0222(12)
N18	0.7510(6)	0.2926(4)	0.6478(3)	0.0234(12)
H18	0.710(8)	0.304(6)	0.677(4)	0.02(2)
C24	1.0687(5)	0.1107(5)	0.4668(3)	0.0181(11)
H24	1.097552	0.070569	0.507713	0.022
C25	1.1496(6)	0.1504(5)	0.4264(4)	0.0194(13)
H25	1.241622	0.142702	0.433805	0.023
C26	1.0677(6)	0.2029(5)	0.3736(4)	0.0205(13)
H26	1.093459	0.239318	0.337369	0.025
C27	0.5617(7)	0.0685(5)	0.3166(4)	0.0279(16)
H27	0.507384	0.025932	0.335744	0.033
C28	0.5438(7)	0.0914(6)	0.2451(4)	0.0355(19)
H28	0.478319	0.067014	0.206226	0.043
C29	0.6405(7)	0.1566(6)	0.2426(4)	0.0300(17)
H29	0.653125	0.187546	0.200714	0.036
C30	0.6957(6)	0.3434(4)	0.4855(3)	0.0168(12)
H30	0.668914	0.336249	0.528841	0.020
C31	0.6959(6)	0.4304(4)	0.4494(3)	0.0174(12)
H31	0.670203	0.493115	0.462346	0.021
C32	0.7420(6)	0.4062(4)	0.3901(4)	0.0194(13)
H32	0.753333	0.450316	0.354106	0.023

C33	0.8700(7)	0.0581(5)	0.5766(3)	0.0189(13)
H33	0.956(7)	0.041(5)	0.572(4)	0.023
C34	0.8409(6)	0.1610(5)	0.5807(3)	0.0164(12)
H34	0.908(8)	0.208(6)	0.581(4)	0.03(2)
C35	0.7673(6)	0.1870(4)	0.6377(3)	0.0190(12)
H35	0.678115	0.157229	0.623055	0.023
C36	0.8383(6)	0.1400(5)	0.7089(3)	0.0181(13)
H36	0.783907	0.148248	0.744490	0.022
C37	0.8750(7)	0.0321(5)	0.7054(4)	0.0255(14)
H37	0.837017	−0.006757	0.739393	0.031
C38	0.8228(7)	−0.0066(5)	0.6293(4)	0.0243(14)
H38A	0.853871	−0.074426	0.625961	0.029
H38B	0.725935	−0.007492	0.617531	0.029
C39	1.0259(8)	0.0309(6)	0.7296(4)	0.0333(18)
H39A	1.054627	−0.009778	0.772948	0.040
H39B	1.063919	0.003471	0.691648	0.040
C40	1.0696(7)	0.1350(6)	0.7451(4)	0.0285(16)
C41	0.9611(7)	0.2971(5)	0.7403(4)	0.0268(14)
H41A	1.051514	0.322389	0.748039	0.032
H41B	0.927435	0.315005	0.782279	0.032
C42	0.8762(7)	0.3441(5)	0.6743(4)	0.0274(16)
H42	0.925326	0.343400	0.635905	0.033
C43	0.8470(10)	0.4499(5)	0.6895(4)	0.040(2)
H43A	0.793012	0.451675	0.724366	0.059
H43B	0.799784	0.481408	0.645228	0.059
H43C	0.929270	0.484695	0.708591	0.059
C44	0.9371(6)	−0.1256(5)	0.4914(3)	0.0224(12)
H44A	0.955576	−0.116269	0.543138	0.034
H44B	1.007715	−0.096662	0.473066	0.034
H44C	0.930946	−0.195660	0.480500	0.034
C45	0.7745(7)	−0.1022(5)	0.3579(4)	0.0318(17)
H45A	0.836161	−0.062601	0.338982	0.048
H45B	0.685540	−0.091754	0.328875	0.048
H45C	0.797533	−0.171457	0.356496	0.048
C46	0.6596(7)	−0.1424(5)	0.4747(4)	0.0335(17)
H46A	0.672974	−0.210738	0.462890	0.050
H46B	0.572251	−0.121129	0.448716	0.050
H46C	0.667071	−0.136476	0.526054	0.050
B2	0.8203(7)	0.2469(5)	0.3390(4)	0.0205(14)

H2A	0.845(7)	0.285(5)	0.293(4)	0.019(18)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for compound 9

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01083(10)	0.01417(12)	0.01440(12)	−0.00051(10)	0.00245(8)	−0.00027(10)
P1	0.0174(7)	0.0188(9)	0.0140(7)	−0.0011(7)	0.0016(6)	0.0013(7)
O1	0.0150(19)	0.027(2)	0.033(2)	−0.010(2)	0.0122(18)	−0.003(2)
O2	0.030(3)	0.020(2)	0.032(3)	0.0004(19)	0.011(2)	0.0085(19)
N1	0.014(2)	0.021(3)	0.018(3)	−0.001(2)	0.0043(19)	−0.001(2)
N2	0.012(2)	0.026(3)	0.021(3)	−0.004(2)	0.005(2)	−0.006(2)
N3	0.015(3)	0.019(3)	0.015(3)	0.001(2)	0.002(2)	−0.003(2)
N4	0.014(2)	0.015(2)	0.020(3)	0.001(2)	0.003(2)	−0.0062(19)
N5	0.018(3)	0.017(2)	0.018(3)	0.003(2)	0.004(2)	0.002(2)
N6	0.014(2)	0.017(2)	0.017(3)	0.001(2)	0.005(2)	−0.0011(19)
N7	0.017(2)	0.013(2)	0.017(2)	−0.001(2)	0.0023(18)	−0.001(2)
N8	0.020(3)	0.014(2)	0.026(3)	0.001(2)	0.006(2)	0.002(2)
N9	0.010(2)	0.015(2)	0.022(3)	−0.001(2)	−0.002(2)	−0.0008(19)
C1	0.017(3)	0.027(3)	0.018(3)	−0.004(2)	0.002(2)	0.006(2)
C2	0.012(3)	0.037(4)	0.025(3)	−0.006(3)	0.001(2)	0.002(3)
C3	0.013(3)	0.033(4)	0.025(4)	−0.007(3)	0.007(3)	−0.007(3)
C4	0.020(3)	0.020(3)	0.019(3)	−0.001(2)	0.004(3)	0.003(2)
C5	0.026(4)	0.018(3)	0.021(4)	−0.003(3)	0.000(3)	0.002(3)
C6	0.025(3)	0.019(3)	0.025(4)	0.000(3)	0.003(3)	−0.007(3)
C7	0.016(3)	0.016(3)	0.024(3)	−0.001(3)	0.004(2)	−0.002(2)
C8	0.021(3)	0.024(3)	0.018(3)	−0.001(3)	0.003(3)	0.001(3)
C9	0.016(3)	0.027(3)	0.018(3)	0.003(2)	0.006(2)	0.000(2)
C10	0.013(3)	0.014(3)	0.019(3)	−0.002(2)	0.002(2)	0.003(2)
C11	0.017(3)	0.014(3)	0.018(3)	−0.002(2)	0.004(2)	0.000(2)
C12	0.014(3)	0.016(3)	0.022(3)	0.001(2)	0.006(2)	0.002(2)
C13	0.016(3)	0.016(3)	0.020(3)	0.000(2)	0.006(2)	−0.001(2)
C14	0.018(3)	0.020(3)	0.021(3)	0.003(2)	0.006(3)	0.001(2)
C15	0.022(3)	0.021(3)	0.018(3)	0.002(2)	0.005(3)	0.002(2)
C16	0.020(3)	0.017(3)	0.032(4)	0.003(3)	0.004(3)	0.003(2)

C17	0.017(3)	0.012(3)	0.032(4)	0.002(2)	0.007(3)	0.003(2)
C18	0.023(3)	0.018(3)	0.024(4)	−0.003(3)	0.006(3)	−0.001(3)
C19	0.015(3)	0.021(3)	0.020(3)	−0.003(2)	0.002(2)	−0.002(2)
C20	0.024(3)	0.025(3)	0.024(4)	−0.004(3)	0.004(3)	−0.001(3)
C21	0.030(3)	0.031(3)	0.018(3)	−0.003(3)	0.013(3)	0.005(3)
C22	0.017(3)	0.028(3)	0.021(3)	−0.002(3)	−0.004(3)	0.003(3)
C23	0.025(3)	0.024(3)	0.024(4)	−0.002(3)	0.000(3)	−0.002(3)
B1	0.016(3)	0.021(3)	0.022(4)	0.001(3)	0.003(3)	−0.003(3)
W2	0.01317(11)	0.01486(12)	0.01652(13)	−0.00186(10)	0.00264(9)	−0.00055(10)
P2	0.0193(8)	0.0160(7)	0.0257(9)	−0.0030(6)	0.0038(7)	−0.0013(6)
O3	0.015(2)	0.047(3)	0.045(3)	0.002(3)	0.012(2)	−0.007(2)
O4	0.019(3)	0.072(4)	0.039(4)	−0.006(3)	0.002(2)	0.003(3)
N10	0.014(2)	0.017(3)	0.018(3)	−0.0016(19)	0.002(2)	0.0012(19)
N11	0.018(3)	0.020(2)	0.017(3)	0.001(2)	0.005(2)	0.001(2)
N12	0.020(2)	0.022(3)	0.007(2)	0.000(2)	−0.0025(19)	0.009(3)
N13	0.018(3)	0.030(3)	0.016(3)	−0.005(2)	−0.002(2)	0.007(2)
N14	0.013(3)	0.020(3)	0.011(3)	0.001(2)	0.002(2)	0.0044(19)
N15	0.021(3)	0.018(2)	0.011(3)	0.0001(19)	0.003(2)	0.002(2)
N16	0.026(3)	0.019(3)	0.021(3)	0.001(2)	0.004(2)	−0.001(2)
N17	0.016(3)	0.032(3)	0.020(3)	0.002(2)	0.006(2)	−0.001(2)
N18	0.026(3)	0.025(3)	0.019(3)	0.000(2)	0.005(2)	0.005(2)
C24	0.019(3)	0.016(3)	0.018(3)	0.001(3)	0.001(2)	0.005(3)
C25	0.012(3)	0.020(3)	0.027(4)	−0.003(3)	0.006(3)	0.003(2)
C26	0.021(3)	0.021(3)	0.022(3)	−0.001(2)	0.010(3)	0.002(2)
C27	0.018(3)	0.029(3)	0.032(4)	−0.012(3)	−0.004(3)	0.004(3)
C28	0.028(4)	0.049(5)	0.021(4)	−0.016(3)	−0.012(3)	0.011(3)
C29	0.031(4)	0.043(4)	0.013(3)	−0.006(3)	−0.001(3)	0.012(3)
C30	0.014(3)	0.021(3)	0.015(3)	−0.002(2)	0.001(2)	0.001(2)
C31	0.016(3)	0.017(3)	0.018(3)	−0.002(2)	0.001(2)	0.003(2)
C32	0.015(3)	0.021(3)	0.022(3)	0.003(2)	0.004(2)	0.002(2)
C33	0.020(3)	0.025(3)	0.013(3)	0.003(2)	0.005(3)	0.001(3)
C34	0.016(3)	0.021(3)	0.010(3)	−0.001(2)	−0.001(2)	−0.001(2)
C35	0.016(3)	0.020(3)	0.020(3)	0.002(2)	0.003(2)	0.002(2)
C36	0.018(3)	0.026(3)	0.010(3)	0.005(2)	0.003(2)	−0.004(2)
C37	0.033(4)	0.024(3)	0.023(4)	0.004(3)	0.013(3)	0.001(3)
C38	0.031(4)	0.019(3)	0.026(4)	0.002(3)	0.013(3)	0.001(3)

C39	0.037(4)	0.038(4)	0.023(4)	0.006(3)	0.005(3)	0.020(3)
C40	0.022(3)	0.047(4)	0.018(3)	0.004(3)	0.008(3)	0.008(3)
C41	0.023(3)	0.033(4)	0.025(4)	−0.005(3)	0.006(3)	−0.007(3)
C42	0.039(4)	0.023(3)	0.023(4)	0.000(3)	0.013(3)	−0.005(3)
C43	0.072(6)	0.023(4)	0.024(4)	−0.002(3)	0.013(4)	0.000(4)
C44	0.026(3)	0.017(3)	0.026(3)	−0.002(3)	0.008(2)	0.000(3)
C45	0.035(4)	0.026(4)	0.031(4)	−0.008(3)	0.003(3)	0.004(3)
C46	0.029(4)	0.026(4)	0.047(5)	−0.007(3)	0.010(3)	−0.009(3)
B2	0.018(3)	0.022(3)	0.021(4)	0.003(3)	0.004(3)	0.007(3)

Table 4 Bond lengths and angles for **compound 9** **Atom–Atom**	**Length [Å]**
W1–N7	1.761(5)
W1–N3	2.214(6)
W1–C10	2.219(6)
W1–C11	2.221(6)
W1–N5	2.226(5)
W1–N1	2.283(5)
W1–P1	2.4927(17)
P1–C22	1.823(7)
P1–C21	1.827(6)
P1–C23	1.834(7)
O1–N7	1.238(6)
O2–C17	1.231(7)
N1–C1	1.346(8)
N1–N2	1.372(7)
N2–C3	1.356(8)
N2–B1	1.544(9)
N3–C4	1.340(8)
N3–N4	1.364(7)
N4–C6	1.343(8)
N4–B1	1.533(9)
N5–C7	1.331(8)
N5–N6	1.365(7)
N6–C9	1.342(8)
N6–B1	1.543(9)

N8–C17	1.345(8)
N8–C18	1.440(9)
N8–C13	1.468(8)
N9–C19	1.464(8)
N9–C12	1.480(8)
N9–H9	0.88(7)
C1–C2	1.386(9)
C1–H1	0.9500
C2–C3	1.372(10)
C2–H2	0.9500
C3–H3	0.9500
C4–C5	1.390(9)
C4–H4	0.9500
C5–C6	1.385(10)
C5–H5	0.9500
C6–H6	0.9500
C7–C8	1.408(9)
C7–H7	0.9500
C8–C9	1.376(9)
C8–H8	0.9500
C9–H9A	0.9500
C10–C11	1.455(9)
C10–C15	1.507(9)
C10–H10	1.02(7)
C11–C12	1.533(8)
C11–H11	1.08(7)
C12–C13	1.550(8)
C12–H12	1.0000
C13–C14	1.538(9)
C13–H13	1.0000
C14–C15	1.534(9)
C14–C16	1.539(9)
C14–H14	1.0000
C15–H15A	0.9900
C15–H15B	0.9900
C16–C17	1.504(10)
C16–H16A	0.9900
C16–H16B	0.9900
C18–C19	1.526(9)

C18–H18A	0.9900
C18–H18B	0.9900
C19–C20	1.508(9)
C19–H19	1.0000
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
B1–H1A	0.96(7)
W2–N16	1.767(6)
W2–C34	2.196(6)
W2–N14	2.215(5)
W2–C33	2.224(7)
W2–N12	2.234(5)
W2–N10	2.265(5)
W2–P2	2.4926(16)
P2–C46	1.814(7)
P2–C45	1.821(8)
P2–C44	1.825(6)
O3–N16	1.228(7)
O4–C40	1.239(9)
N10–C24	1.347(7)
N10–N11	1.360(7)
N11–C26	1.345(8)
N11–B2	1.548(9)
N12–C27	1.326(9)
N12–N13	1.356(8)
N13–C29	1.348(9)
N13–B2	1.531(9)
N14–C30	1.340(8)
N14–N15	1.362(7)

N15–C32	1.333(8)
N15–B2	1.545(9)
N17–C40	1.340(9)
N17–C41	1.448(9)
N17–C36	1.464(8)
N18–C35	1.473(8)
N18–C42	1.474(9)
N18–H18	0.81(8)
C24–C25	1.396(9)
C24–H24	0.9500
C25–C26	1.371(9)
C25–H25	0.9500
C26–H26	0.9500
C27–C28	1.387(11)
C27–H27	0.9500
C28–C29	1.362(12)
C28–H28	0.9500
C29–H29	0.9500
C30–C31	1.380(9)
C30–H30	0.9500
C31–C32	1.387(9)
C31–H31	0.9500
C32–H32	0.9500
C33–C34	1.445(9)
C33–C38	1.519(9)
C33–H33	0.97(7)
C34–C35	1.531(9)
C34–H34	0.96(8)
C35–C36	1.541(9)
C35–H35	1.0000
C36–C37	1.530(9)
C36–H36	1.0000
C37–C38	1.536(10)
C37–C39	1.544(11)
C37–H37	1.0000
C38–H38A	0.9900
C38–H38B	0.9900
C39–C40	1.504(12)
C39–H39A	0.9900

C39–H39B	0.9900
C41–C42	1.515(10)
C41–H41A	0.9900
C41–H41B	0.9900
C42–C43	1.523(10)
C42–H42	1.0000
C43–H43A	0.9800
C43–H43B	0.9800
C43–H43C	0.9800
C44–H44A	0.9800
C44–H44B	0.9800
C44–H44C	0.9800
C45–H45A	0.9800
C45–H45B	0.9800
C45–H45C	0.9800
C46–H46A	0.9800
C46–H46B	0.9800
C46–H46C	0.9800
B2–H2A	1.12(7)
Atom–Atom–Atom	**Angle [°]**
N7–W1–N3	89.6(2)
N7–W1–C10	95.3(3)
N3–W1–C10	161.7(2)
N7–W1–C11	90.7(2)
N3–W1–C11	159.6(2)
C10–W1–C11	38.3(2)
N7–W1–N5	103.9(2)
N3–W1–N5	77.67(19)
C10–W1–N5	118.0(2)
C11–W1–N5	82.5(2)
N7–W1–N1	173.5(2)
N3–W1–N1	85.23(19)
C10–W1–N1	88.5(2)
C11–W1–N1	95.5(2)
N5–W1–N1	78.94(19)
N7–W1–P1	90.21(16)
N3–W1–P1	83.56(15)

C10–W1–P1	78.76(17)
C11–W1–P1	116.79(17)
N5–W1–P1	156.29(14)
N1–W1–P1	85.24(13)
C22–P1–C21	102.4(3)
C22–P1–C23	99.3(3)
C21–P1–C23	102.5(3)
C22–P1–W1	119.9(2)
C21–P1–W1	115.1(2)
C23–P1–W1	115.0(2)
C1–N1–N2	106.1(5)
C1–N1–W1	134.9(4)
N2–N1–W1	118.8(4)
C3–N2–N1	109.1(5)
C3–N2–B1	128.3(6)
N1–N2–B1	122.5(5)
C4–N3–N4	106.3(5)
C4–N3–W1	129.6(4)
N4–N3–W1	124.1(4)
C6–N4–N3	109.9(5)
C6–N4–B1	130.4(5)
N3–N4–B1	118.3(5)
C7–N5–N6	107.0(5)
C7–N5–W1	132.2(4)
N6–N5–W1	120.9(4)
C9–N6–N5	109.5(5)
C9–N6–B1	128.3(5)
N5–N6–B1	122.1(5)
O1–N7–W1	177.7(4)
C17–N8–C18	125.2(6)
C17–N8–C13	115.1(5)
C18–N8–C13	118.0(5)
C19–N9–C12	114.6(5)
C19–N9–H9	110(4)
C12–N9–H9	107(4)
N1–C1–C2	110.9(6)
N1–C1–H1	124.6
C2–C1–H1	124.6
C3–C2–C1	105.0(6)

C3–C2–H2	127.5
C1–C2–H2	127.5
N2–C3–C2	109.0(6)
N2–C3–H3	125.5
C2–C3–H3	125.5
N3–C4–C5	110.6(6)
N3–C4–H4	124.7
C5–C4–H4	124.7
C6–C5–C4	104.7(6)
C6–C5–H5	127.7
C4–C5–H5	127.7
N4–C6–C5	108.5(6)
N4–C6–H6	125.8
C5–C6–H6	125.8
N5–C7–C8	110.0(5)
N5–C7–H7	125.0
C8–C7–H7	125.0
C9–C8–C7	104.6(6)
C9–C8–H8	127.7
C7–C8–H8	127.7
N6–C9–C8	108.9(6)
N6–C9–H9A	125.5
C8–C9–H9A	125.5
C11–C10–C15	116.3(5)
C11–C10–W1	70.9(3)
C15–C10–W1	125.2(4)
C11–C10–H10	118(4)
C15–C10–H10	110(4)
W1–C10–H10	112(4)
C10–C11–C12	114.4(5)
C10–C11–W1	70.8(3)
C12–C11–W1	119.8(4)
C10–C11–H11	122(4)
C12–C11–H11	110(4)
W1–C11–H11	116(4)
N9–C12–C11	113.5(5)
N9–C12–C13	110.6(5)
C11–C12–C13	111.8(5)
N9–C12–H12	106.9

C11–C12–H12	106.9
C13–C12–H12	106.9
N8–C13–C14	103.7(5)
N8–C13–C12	110.4(5)
C14–C13–C12	115.4(5)
N8–C13–H13	109.1
C14–C13–H13	109.1
C12–C13–H13	109.1
C15–C14–C13	110.2(5)
C15–C14–C16	114.7(5)
C13–C14–C16	105.3(5)
C15–C14–H14	108.8
C13–C14–H14	108.8
C16–C14–H14	108.8
C10–C15–C14	110.3(5)
C10–C15–H15A	109.6
C14–C15–H15A	109.6
C10–C15–H15B	109.6
C14–C15–H15B	109.6
H15A–C15–H15B	108.1
C17–C16–C14	106.0(5)
C17–C16–H16A	110.5
C14–C16–H16A	110.5
C17–C16–H16B	110.5
C14–C16–H16B	110.5
H16A–C16–H16B	108.7
O2–C17–N8	124.9(6)
O2–C17–C16	126.6(6)
N8–C17–C16	108.4(5)
N8–C18–C19	108.4(5)
N8–C18–H18A	110.0
C19–C18–H18A	110.0
N8–C18–H18B	110.0
C19–C18–H18B	110.0
H18A–C18–H18B	108.4
N9–C19–C20	110.7(5)
N9–C19–C18	111.9(5)
C20–C19–C18	111.9(5)
N9–C19–H19	107.4

C20–C19–H19	107.4
C18–C19–H19	107.4
C19–C20–H20A	109.5
C19–C20–H20B	109.5
H20A–C20–H20B	109.5
C19–C20–H20C	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
P1–C21–H21A	109.5
P1–C21–H21B	109.5
H21A–C21–H21B	109.5
P1–C21–H21C	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
H22A–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
H23A–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
N4–B1–N6	107.1(5)
N4–B1–N2	109.5(6)
N6–B1–N2	106.8(5)
N4–B1–H1A	111(4)
N6–B1–H1A	107(5)
N2–B1–H1A	114(4)
N16–W2–C34	95.3(2)
N16–W2–N14	97.7(2)
C34–W2–N14	82.2(2)
N16–W2–C33	98.8(2)
C34–W2–C33	38.2(2)
N14–W2–C33	119.0(2)
N16–W2–N12	89.0(2)

C34–W2–N12	160.4(2)
N14–W2–N12	78.3(2)
C33–W2–N12	159.4(2)
N16–W2–N10	172.7(2)
C34–W2–N10	91.1(2)
N14–W2–N10	79.57(18)
C33–W2–N10	88.4(2)
N12–W2–N10	83.85(19)
N16–W2–P2	93.06(18)
C34–W2–P2	115.30(18)
N14–W2–P2	158.62(14)
C33–W2–P2	77.14(18)
N12–W2–P2	83.49(17)
N10–W2–P2	87.51(13)
C46–P2–C45	103.6(4)
C46–P2–C44	104.1(3)
C45–P2–C44	98.1(3)
C46–P2–W2	112.8(2)
C45–P2–W2	116.8(2)
C44–P2–W2	119.3(2)
C24–N10–N11	106.3(5)
C24–N10–W2	133.8(4)
N11–N10–W2	119.9(4)
C26–N11–N10	109.9(5)
C26–N11–B2	127.7(6)
N10–N11–B2	122.0(5)
C27–N12–N13	107.8(5)
C27–N12–W2	129.3(5)
N13–N12–W2	122.9(4)
C29–N13–N12	108.1(6)
C29–N13–B2	131.4(6)
N12–N13–B2	119.2(5)
C30–N14–N15	106.6(5)
C30–N14–W2	131.3(4)
N15–N14–W2	122.0(4)
C32–N15–N14	109.6(5)
C32–N15–B2	129.6(6)
N14–N15–B2	120.9(5)
O3–N16–W2	173.9(5)

C40–N17–C41	126.0(6)
C40–N17–C36	115.2(6)
C41–N17–C36	118.8(5)
C35–N18–C42	113.0(5)
C35–N18–H18	112(6)
C42–N18–H18	104(6)
N10–C24–C25	110.0(5)
N10–C24–H24	125.0
C25–C24–H24	125.0
C26–C25–C24	105.1(5)
C26–C25–H25	127.4
C24–C25–H25	127.4
N11–C26–C25	108.6(6)
N11–C26–H26	125.7
C25–C26–H26	125.7
N12–C27–C28	109.8(7)
N12–C27–H27	125.1
C28–C27–H27	125.1
C29–C28–C27	105.0(6)
C29–C28–H28	127.5
C27–C28–H28	127.5
N13–C29–C28	109.3(7)
N13–C29–H29	125.4
C28–C29–H29	125.4
N14–C30–C31	110.4(5)
N14–C30–H30	124.8
C31–C30–H30	124.8
C30–C31–C32	104.7(5)
C30–C31–H31	127.6
C32–C31–H31	127.6
N15–C32–C31	108.7(6)
N15–C32–H32	125.7
C31–C32–H32	125.7
C34–C33–C38	115.0(6)
C34–C33–W2	69.9(4)
C38–C33–W2	127.0(5)
C34–C33–H33	118(4)
C38–C33–H33	113(4)
W2–C33–H33	109(4)

C33–C34–C35	114.6(5)
C33–C34–W2	72.0(4)
C35–C34–W2	126.4(4)
C33–C34–H34	120(5)
C35–C34–H34	109(5)
W2–C34–H34	111(5)
N18–C35–C34	114.7(5)
N18–C35–C36	109.7(5)
C34–C35–C36	109.0(5)
N18–C35–H35	107.7
C34–C35–H35	107.7
C36–C35–H35	107.7
N17–C36–C37	105.3(5)
N17–C36–C35	107.3(5)
C37–C36–C35	115.8(5)
N17–C36–H36	109.4
C37–C36–H36	109.4
C35–C36–H36	109.4
C36–C37–C38	109.8(6)
C36–C37–C39	104.4(6)
C38–C37–C39	113.2(6)
C36–C37–H37	109.8
C38–C37–H37	109.8
C39–C37–H37	109.8
C33–C38–C37	109.9(6)
C33–C38–H38A	109.7
C37–C38–H38A	109.7
C33–C38–H38B	109.7
C37–C38–H38B	109.7
H38A–C38–H38B	108.2
C40–C39–C37	107.1(6)
C40–C39–H39A	110.3
C37–C39–H39A	110.3
C40–C39–H39B	110.3
C37–C39–H39B	110.3
H39A–C39–H39B	108.6
O4–C40–N17	124.7(8)
O4–C40–C39	127.3(7)
N17–C40–C39	108.0(6)

N17–C41–C42	111.5(6)
N17–C41–H41A	109.3
C42–C41–H41A	109.3
N17–C41–H41B	109.3
C42–C41–H41B	109.3
H41A–C41–H41B	108.0
N18–C42–C41	112.9(6)
N18–C42–C43	108.4(7)
C41–C42–C43	110.3(6)
N18–C42–H42	108.4
C41–C42–H42	108.4
C43–C42–H42	108.4
C42–C43–H43A	109.5
C42–C43–H43B	109.5
H43A–C43–H43B	109.5
C42–C43–H43C	109.5
H43A–C43–H43C	109.5
H43B–C43–H43C	109.5
P2–C44–H44A	109.5
P2–C44–H44B	109.5
H44A–C44–H44B	109.5
P2–C44–H44C	109.5
H44A–C44–H44C	109.5
H44B–C44–H44C	109.5
P2–C45–H45A	109.5
P2–C45–H45B	109.5
H45A–C45–H45B	109.5
P2–C45–H45C	109.5
H45A–C45–H45C	109.5
H45B–C45–H45C	109.5
P2–C46–H46A	109.5
P2–C46–H46B	109.5
H46A–C46–H46B	109.5
P2–C46–H46C	109.5
H46A–C46–H46C	109.5
H46B–C46–H46C	109.5
N13–B2–N15	107.4(5)
N13–B2–N11	108.9(5)
N15–B2–N11	107.5(5)

N13–B2–H2A	108(4)
N15–B2–H2A	117(4)
N11–B2–H2A	108(4)

Table 5 Torsion angles for compound 9

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C1–N1–N2–C3	0.1(7)
W1–N1–N2–C3	−175.1(4)
C1–N1–N2–B1	−175.9(6)
W1–N1–N2–B1	8.9(7)
C4–N3–N4–C6	0.3(7)
W1–N3–N4–C6	−179.8(4)
C4–N3–N4–B1	168.2(5)
W1–N3–N4–B1	−11.9(7)
C7–N5–N6–C9	−0.6(7)
W1–N5–N6–C9	178.9(4)
C7–N5–N6–B1	179.2(5)
W1–N5–N6–B1	−1.2(7)
N2–N1–C1–C2	0.0(7)
W1–N1–C1–C2	174.0(4)
N1–C1–C2–C3	−0.1(8)
N1–N2–C3–C2	−0.2(7)
B1–N2–C3–C2	175.5(6)
C1–C2–C3–N2	0.1(8)
N4–N3–C4–C5	0.8(7)
W1–N3–C4–C5	−179.1(5)
N3–C4–C5–C6	−1.5(8)
N3–N4–C6–C5	−1.2(8)
B1–N4–C6–C5	−167.2(6)
C4–C5–C6–N4	1.6(8)
N6–N5–C7–C8	0.2(7)
W1–N5–C7–C8	−179.3(4)
N5–C7–C8–C9	0.2(7)
N5–N6–C9–C8	0.8(7)
B1–N6–C9–C8	−179.0(6)

C7–C8–C9–N6	−0.6(7)
C15–C10–C11–C12	−5.8(7)
W1–C10–C11–C12	114.9(5)
C15–C10–C11–W1	−120.7(5)
C19–N9–C12–C11	−75.1(6)
C19–N9–C12–C13	51.5(7)
C10–C11–C12–N9	174.5(5)
W1–C11–C12–N9	−104.5(5)
C10–C11–C12–C13	48.6(7)
W1–C11–C12–C13	129.6(4)
C17–N8–C13–C14	10.6(7)
C18–N8–C13–C14	176.3(5)
C17–N8–C13–C12	−113.6(6)
C18–N8–C13–C12	52.2(7)
N9–C12–C13–N8	−47.0(7)
C11–C12–C13–N8	80.5(6)
N9–C12–C13–C14	−164.1(5)
C11–C12–C13–C14	−36.6(7)
N8–C13–C14–C15	−136.3(5)
C12–C13–C14–C15	−15.5(7)
N8–C13–C14–C16	−12.1(6)
C12–C13–C14–C16	108.7(6)
C11–C10–C15–C14	−48.7(7)
W1–C10–C15–C14	−133.1(5)
C13–C14–C15–C10	58.4(7)
C16–C14–C15–C10	−60.2(7)
C15–C14–C16–C17	131.6(6)
C13–C14–C16–C17	10.3(6)
C18–N8–C17–O2	8.7(10)
C13–N8–C17–O2	173.3(6)
C18–N8–C17–C16	−168.7(6)
C13–N8–C17–C16	−4.1(7)
C14–C16–C17–O2	178.4(6)
C14–C16–C17–N8	−4.3(7)
C17–N8–C18–C19	109.9(6)
C13–N8–C18–C19	−54.4(7)
C12–N9–C19–C20	179.1(5)
C12–N9–C19–C18	−55.3(7)
N8–C18–C19–N9	53.2(7)

N8–C18–C19–C20	178.1(5)
C6–N4–B1–N6	114.0(7)
N3–N4–B1–N6	−51.0(7)
C6–N4–B1–N2	−130.6(7)
N3–N4–B1–N2	64.4(7)
C9–N6–B1–N4	−120.8(6)
N5–N6–B1–N4	59.4(7)
C9–N6–B1–N2	122.0(6)
N5–N6–B1–N2	−57.8(7)
C3–N2–B1–N4	121.4(7)
N1–N2–B1–N4	−63.4(7)
C3–N2–B1–N6	−122.9(7)
N1–N2–B1–N6	52.3(7)
C24–N10–N11–C26	−0.6(7)
W2–N10–N11–C26	178.0(4)
C24–N10–N11–B2	−174.7(6)
W2–N10–N11–B2	3.8(7)
C27–N12–N13–C29	−0.3(7)
W2–N12–N13–C29	−179.7(4)
C27–N12–N13–B2	168.3(5)
W2–N12–N13–B2	−11.1(7)
C30–N14–N15–C32	−0.6(7)
W2–N14–N15–C32	175.8(4)
C30–N14–N15–B2	−179.9(6)
W2–N14–N15–B2	−3.5(8)
N11–N10–C24–C25	0.1(7)
W2–N10–C24–C25	−178.1(4)
N10–C24–C25–C26	0.3(7)
N10–N11–C26–C25	0.8(7)
B2–N11–C26–C25	174.5(6)
C24–C25–C26–N11	−0.6(7)
N13–N12–C27–C28	1.5(8)
W2–N12–C27–C28	−179.2(5)
N12–C27–C28–C29	−2.0(8)
N12–N13–C29–C28	−0.9(8)
B2–N13–C29–C28	−167.7(6)
C27–C28–C29–N13	1.7(8)
N15–N14–C30–C31	0.4(7)
W2–N14–C30–C31	−175.5(4)

N14–C30–C31–C32	0.0(7)
N14–N15–C32–C31	0.6(7)
B2–N15–C32–C31	179.8(6)
C30–C31–C32–N15	−0.3(7)
C38–C33–C34–C35	0.1(9)
W2–C33–C34–C35	122.5(5)
C38–C33–C34–W2	−122.4(6)
C42–N18–C35–C34	−64.0(7)
C42–N18–C35–C36	59.1(7)
C33–C34–C35–N18	173.2(6)
W2–C34–C35–N18	−101.7(6)
C33–C34–C35–C36	49.7(7)
W2–C34–C35–C36	134.8(5)
C40–N17–C36–C37	1.2(7)
C41–N17–C36–C37	177.7(6)
C40–N17–C36–C35	−122.8(6)
C41–N17–C36–C35	53.8(7)
N18–C35–C36–N17	−56.7(7)
C34–C35–C36–N17	69.7(6)
N18–C35–C36–C37	−174.0(5)
C34–C35–C36–C37	−47.6(7)
N17–C36–C37–C38	−121.9(6)
C35–C36–C37–C38	−3.6(8)
N17–C36–C37–C39	−0.2(7)
C35–C36–C37–C39	118.1(6)
C34–C33–C38–C37	−54.1(8)
W2–C33–C38–C37	−136.9(5)
C36–C37–C38–C33	53.9(7)
C39–C37–C38–C33	−62.3(7)
C36–C37–C39–C40	−0.6(7)
C38–C37–C39–C40	118.8(6)
C41–N17–C40–O4	1.4(11)
C36–N17–C40–O4	177.7(6)
C41–N17–C40–C39	−177.8(6)
C36–N17–C40–C39	−1.6(8)
C37–C39–C40–O4	−177.9(7)
C37–C39–C40–N17	1.3(8)
C40–N17–C41–C42	128.5(7)
C36–N17–C41–C42	−47.6(8)

C35–N18–C42–C41	−52.1(8)
C35–N18–C42–C43	−174.6(6)
N17–C41–C42–N18	43.6(8)
N17–C41–C42–C43	165.1(6)
C29–N13–B2–N15	113.9(7)
N12–N13–B2–N15	−51.7(7)
C29–N13–B2–N11	−130.0(7)
N12–N13–B2–N11	64.4(7)
C32–N15–B2–N13	−118.2(7)
N14–N15–B2–N13	61.0(7)
C32–N15–B2–N11	124.8(7)
N14–N15–B2–N11	−56.0(7)
C26–N11–B2–N13	126.4(7)
N10–N11–B2–N13	−60.6(7)
C26–N11–B2–N15	−117.6(7)
N10–N11–B2–N15	55.4(7)

Table 6 Hydrogen bonds for compound 9

D–H···A [Å]	**d(D–H) [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(DHA) [°]**
N9–H9···O4$^{\#1}$	0.88(7)	2.21(7)	3.031(8)	154(6)

Symmetry transformations used to generate equivalent atoms:
#1: 2-X, 0.5+Y, 1-Z;

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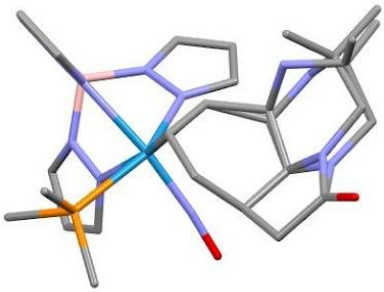

Structure Report for Compound 6 colourless, plate-shaped crystal of Compound 6 measuring 0.098×0.081×0.032 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data were collected from a single crystal at 300.00 K on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo Kα, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.184 All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods using SHELXT185 and refined by full-matrix least-squares methods against F2 using SHELXL--2019/1186 within OLEX2.187 All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with Uiso = 1.2Uequiv of the parent atom (1.5Uequiv for methyl). This report and the CIF file were generated using FinalCif.188

Refinement details for Compound 6

[184] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
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[187] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
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'The relative occupancy of the disordered atoms was freely refined. Constraints and restraints were used as needed on the anisotropic displacement parameters and/or bond lengths of the disordered atoms .'

Table 1. Crystal data and structure refinement for Compound 6

CCDC number	
Empirical formula	C24H37BN9O2PW
Formula weight	709.25
Temperature [K]	300.00
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	9.9748(3)
b [Å]	12.9649(5)
c [Å]	13.1464(5)
α [°]	60.4930(10)
β [°]	84.9820(10)
γ [°]	74.5230(10)
Volume [Å3]	1424.00(9)
Z	2
ρcalc [gcm−3]	1.654
μ [mm−1]	4.151
F(000)	708
Crystal size [mm3]	0.098×0.081×0.032
Crystal colour	colourless
Crystal shape	plate
Radiation	Mo Kα (λ=0.71073 Å)
2θ range [°]	4.24 to 52.75 (0.80 Å)

Index ranges	−12 ≤ h ≤ 12 −16 ≤ k ≤ 16 −16 ≤ l ≤ 16
Reflections collected	56583
Independent reflections	5833 Rint = 0.0903 Rsigma = 0.0422
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	5833/97/426
Absorption correction Tmin/Tmax (method)	0.5773/0.7454 (Multi-Scan)
Goodness-of-fit on F2	1.017
Final R indexes [I≥2σ(I)]	R1 = 0.0283 wR2 = 0.0574
Final R indexes [all data]	R1 = 0.0390 wR2 = 0.0622
Largest peak/hole [eÅ−3]	1.00/−0.60

Table 2. Atomic coordinates and Ueq [Å2] for Compound 6

Atom	x	y	z	Ueq
W1	0.73488(2)	0.62788(2)	0.65293(2)	0.03161(6)
P1	0.74522(12)	0.72547(12)	0.77379(11)	0.0437(3)
O1	1.0452(3)	0.5351(3)	0.6722(3)	0.0555(9)
O2	1.0557(5)	1.0285(4)	0.1725(4)	0.0895(15)
N1	0.5027(3)	0.6727(3)	0.6749(3)	0.0367(8)
N2	0.4381(3)	0.5795(3)	0.7349(3)	0.0390(8)
N3	0.7439(4)	0.4645(3)	0.8262(3)	0.0389(8)
N4	0.6376(4)	0.4091(3)	0.8672(3)	0.0414(9)
N5	0.6793(3)	0.4963(3)	0.6115(3)	0.0337(8)
N6	0.5860(4)	0.4312(3)	0.6769(3)	0.0389(8)
N7	0.9176(4)	0.5786(3)	0.6571(3)	0.0366(8)
C1	0.4026(5)	0.7751(5)	0.6439(4)	0.0471(11)
H1	0.416737	0.853404	0.602741	0.057
C2	0.2755(5)	0.7516(5)	0.6801(5)	0.0582(14)
H2	0.190061	0.808167	0.668129	0.070

C3	0.3021(5)	0.6273(5)	0.7374(4)	0.0514(12)
H3	0.236377	0.582626	0.772582	0.062
C4	0.8498(5)	0.3957(5)	0.9060(4)	0.0479(11)
H4	0.936272	0.412086	0.899755	0.057
C5	0.8129(6)	0.2971(5)	0.9987(4)	0.0617(14)
H5	0.867087	0.236358	1.065995	0.074
C6	0.6792(5)	0.3076(5)	0.9707(4)	0.0551(13)
H6	0.625883	0.253271	1.015945	0.066
C7	0.7218(5)	0.4580(4)	0.5338(4)	0.0415(10)
H7	0.785504	0.486942	0.477450	0.050
C8	0.6575(5)	0.3689(4)	0.5490(4)	0.0514(12)
H8	0.669751	0.327399	0.506485	0.062
C9	0.5731(5)	0.3554(4)	0.6388(4)	0.0470(11)
H9	0.515645	0.302147	0.669230	0.056
C10	0.7049(5)	0.8235(4)	0.5122(4)	0.0446(11)
H10	0.621(5)	0.874(4)	0.529(4)	0.040(12)
C11	0.6997(5)	0.7475(4)	0.4627(4)	0.0431(11)
H11	0.610(5)	0.753(4)	0.443(4)	0.051(14)
C13	0.9397(5)	0.7699(4)	0.3774(4)	0.0453(11)
H13	1.008740	0.690561	0.405378	0.054
H13A	1.025976	0.706104	0.390262	0.054
C14	0.9548(6)	0.8255(5)	0.4540(4)	0.0519(13)
H14	1.002342	0.760997	0.529350	0.062
C15	0.8155(6)	0.8939(5)	0.4735(5)	0.0541(13)
H15A	0.781895	0.969782	0.401261	0.065
H15B	0.828935	0.915334	0.532224	0.065
C16	1.0479(6)	0.9124(5)	0.3829(4)	0.0553(13)
H16A	1.021734	0.985218	0.391503	0.066
H16B	1.145097	0.871660	0.408436	0.066
C17	1.0238(5)	0.9445(5)	0.2604(5)	0.0553(13)
C22	0.9201(6)	0.7220(7)	0.8041(6)	0.080(2)
H22A	0.970189	0.638937	0.855600	0.120
H22B	0.916212	0.771116	0.840527	0.120
H22C	0.966664	0.754024	0.732170	0.120
C23	0.6518(6)	0.8835(6)	0.7300(6)	0.0748(17)
H23A	0.674269	0.936442	0.651956	0.112
H23B	0.678372	0.906607	0.782776	0.112
H23C	0.553333	0.890888	0.732018	0.112
C24	0.6800(8)	0.6492(7)	0.9192(5)	0.088(2)
H24A	0.588158	0.642263	0.912420	0.132
H24B	0.676614	0.696345	0.957697	0.132
H24C	0.740875	0.568867	0.964039	0.132

B1	0.5180(5)	0.4459(5)	0.7798(5)	0.0405(11)
H1A	0.452(4)	0.390(4)	0.815(4)	0.043(12)
N8	0.976(3)	0.8554(18)	0.2647(9)	0.063(6)
N9	0.7120(7)	0.8527(7)	0.2562(6)	0.0498(19)
H9A	0.679(9)	0.920(9)	0.263(8)	0.060
C12	0.7941(9)	0.7538(9)	0.3649(6)	0.050(2)
H12	0.808973	0.676522	0.363786	0.060
C18	0.9459(11)	0.8321(12)	0.1732(9)	0.062(3)
H18A	0.983338	0.745867	0.197124	0.075
H18B	0.989443	0.879398	0.102411	0.075
C19	0.7874(13)	0.8684(9)	0.1494(9)	0.053(3)
C20	0.7568(17)	0.7867(12)	0.1061(11)	0.070(4)
H20A	0.784255	0.702484	0.166477	0.105
H20B	0.808053	0.796827	0.037906	0.105
H20C	0.658902	0.809407	0.086669	0.105
C21	0.7367(13)	1.0021(9)	0.0566(8)	0.088(3)
H21A	0.771069	1.052213	0.077167	0.133
H21B	0.636663	1.026015	0.051749	0.133
H21C	0.770150	1.012503	-0.017701	0.133
N8A	0.944(5)	0.874(3)	0.2611(11)	0.051(7)
N9A	0.7787(11)	0.7272(9)	0.2789(8)	0.040(3)
H9B	0.845(12)	0.688(11)	0.240(11)	0.047
C12A	0.8196(14)	0.7124(15)	0.3923(12)	0.050(2)
H12A	0.859264	0.624017	0.441690	0.060
C18A	0.8973(17)	0.8910(16)	0.1492(13)	0.049(4)
H18C	0.967613	0.842089	0.123483	0.059
H18D	0.880739	0.976489	0.089452	0.059
C19A	0.7619(15)	0.8497(15)	0.1708(15)	0.042(4)
C20A	0.724(3)	0.8392(19)	0.0674(17)	0.068(5)
H20D	0.791919	0.773503	0.063250	0.102
H20E	0.721000	0.914728	-0.003595	0.102
H20F	0.633730	0.822576	0.077294	0.102
C21A	0.6443(14)	0.9433(13)	0.1836(13)	0.055(4)
H21D	0.561971	0.913671	0.203822	0.082
H21E	0.626259	1.019154	0.111016	0.082
H21F	0.669868	0.956516	0.244178	0.082

Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

Table 3. Anisotropic displacement parameters [Å2] for Compound 6.

The anisotropic displacement factor exponent takes the form:

−2π2[h2(a*)2U11 + k2(b*)2U22 + … + 2hka*b*U12]

Atom	U11	U22	U33	U23	U13	U12
W1	0.02926(9)	0.03870(10)	0.03441(9)	−0.02178(8)	0.00330(6)	−0.01270(7)
P1	0.0404(6)	0.0593(8)	0.0525(7)	−0.0402(7)	0.0086(5)	−0.0204(6)
O1	0.0306(17)	0.064(2)	0.066(2)	−0.0299(19)	0.0062(15)	−0.0098(16)
O2	0.107(3)	0.107(4)	0.061(3)	−0.024(3)	0.019(2)	−0.077(3)
N1	0.0289(17)	0.040(2)	0.045(2)	−0.0235(18)	0.0024(15)	−0.0099(16)
N2	0.0324(18)	0.044(2)	0.042(2)	−0.0213(18)	0.0046(15)	−0.0130(17)
N3	0.0390(19)	0.046(2)	0.0356(19)	−0.0206(18)	0.0034(15)	−0.0148(17)
N4	0.043(2)	0.040(2)	0.039(2)	−0.0158(18)	0.0068(16)	−0.0144(18)
N5	0.0342(18)	0.037(2)	0.0367(19)	−0.0219(17)	0.0039(14)	−0.0119(15)
N6	0.0350(19)	0.041(2)	0.044(2)	−0.0218(18)	0.0001(16)	−0.0132(17)
N7	0.0362(19)	0.046(2)	0.0361(19)	−0.0247(17)	0.0054(15)	−0.0144(17)
C1	0.040(2)	0.044(3)	0.060(3)	−0.029(2)	0.004(2)	−0.006(2)
C2	0.032(2)	0.058(3)	0.083(4)	−0.038(3)	0.004(2)	−0.002(2)
C3	0.028(2)	0.062(3)	0.061(3)	−0.029(3)	0.011(2)	−0.011(2)
C4	0.040(2)	0.056(3)	0.044(3)	−0.022(2)	−0.004(2)	−0.009(2)
C5	0.061(3)	0.058(3)	0.043(3)	−0.010(3)	−0.013(2)	−0.003(3)
C6	0.061(3)	0.043(3)	0.043(3)	−0.009(2)	0.006(2)	−0.012(2)
C7	0.047(3)	0.042(3)	0.038(2)	−0.025(2)	0.0029(19)	−0.004(2)
C8	0.065(3)	0.046(3)	0.054(3)	−0.034(3)	−0.007(2)	−0.007(2)
C9	0.050(3)	0.041(3)	0.060(3)	−0.029(2)	−0.005(2)	−0.016(2)
C10	0.051(3)	0.044(3)	0.043(3)	−0.021(2)	−0.002(2)	−0.017(2)
C11	0.052(3)	0.043(3)	0.036(2)	−0.016(2)	−0.004(2)	−0.021(2)
C13	0.046(3)	0.033(2)	0.056(3)	−0.022(2)	−0.007(2)	−0.005(2)
C14	0.072(3)	0.046(3)	0.041(3)	−0.014(2)	−0.004(2)	−0.034(3)
C15	0.078(4)	0.048(3)	0.051(3)	−0.028(3)	0.015(3)	−0.036(3)
C16	0.061(3)	0.053(3)	0.057(3)	−0.022(3)	0.002(2)	−0.031(3)
C17	0.050(3)	0.061(3)	0.060(3)	−0.027(3)	0.014(2)	−0.029(3)
C22	0.051(3)	0.122(6)	0.115(5)	−0.090(5)	0.000(3)	−0.030(4)
C23	0.082(4)	0.076(4)	0.094(5)	−0.065(4)	0.003(3)	−0.014(3)
C24	0.131(6)	0.106(5)	0.069(4)	−0.066(4)	0.048(4)	−0.059(5)
B1	0.040(3)	0.041(3)	0.043(3)	−0.020(2)	0.011(2)	−0.018(2)
N8	0.061(13)	0.096(11)	0.061(6)	−0.050(6)	0.031(4)	−0.050(9)
N9	0.058(4)	0.049(4)	0.035(3)	−0.013(3)	0.004(3)	−0.015(3)
C12	0.093(5)	0.038(6)	0.023(3)	−0.005(4)	0.010(3)	−0.047(4)
C18	0.074(6)	0.077(8)	0.053(5)	−0.038(6)	0.026(4)	−0.040(5)
C19	0.073(6)	0.056(5)	0.038(4)	−0.021(4)	0.016(3)	−0.036(4)
C20	0.087(9)	0.081(8)	0.063(8)	−0.044(7)	0.008(6)	−0.038(8)
C21	0.121(9)	0.072(6)	0.051(5)	−0.010(4)	0.009(5)	−0.034(5)
N8A	0.041(13)	0.080(14)	0.049(8)	−0.036(8)	0.022(5)	−0.040(11)
N9A	0.051(6)	0.041(5)	0.036(4)	−0.022(4)	0.007(4)	−0.021(4)
C12A	0.093(5)	0.038(6)	0.023(3)	−0.005(4)	0.010(3)	−0.047(4)

C18A	0.053(7)	0.051(9)	0.046(7)	−0.022(7)	0.012(5)	−0.024(6)
C19A	0.045(6)	0.038(6)	0.034(6)	−0.008(5)	0.002(4)	−0.017(5)
C20A	0.085(12)	0.068(12)	0.050(8)	−0.026(8)	−0.006(7)	−0.021(10)
C21A	0.058(7)	0.050(7)	0.054(8)	−0.019(6)	0.003(5)	−0.023(5)

Table 4. Bond lengths and angles for Compound 6 0mAtom–Atom	Length [Å]
W1–P1	2.4929(11)
W1–N1	2.262(3)
W1–N3	2.206(4)
W1–N5	2.233(3)
W1–N7	1.759(3)
W1–C10	2.239(5)
W1–C11	2.197(4)
P1–C22	1.806(5)
P1–C23	1.820(6)
P1–C24	1.822(6)
O1–N7	1.236(4)
O2–C17	1.227(6)
N1–N2	1.373(5)
N1–C1	1.325(6)
N2–C3	1.338(5)
N2–B1	1.524(6)
N3–N4	1.362(5)
N3–C4	1.334(6)
N4–C6	1.341(6)
N4–B1	1.539(6)
N5–N6	1.372(5)
N5–C7	1.334(5)
N6–C9	1.339(5)
N6–B1	1.534(6)
C1–H1	0.9300
C1–C2	1.373(6)
C2–H2	0.9300
C2–C3	1.358(7)
C3–H3	0.9300
C4–H4	0.9300
C4–C5	1.376(7)
C5–H5	0.9300
C5–C6	1.368(7)
C6–H6	0.9300
C7–H7	0.9300

C7–C8	1.391(6)
C8–H8	0.9300
C8–C9	1.355(7)
C9–H9	0.9300
C10–H10	1.00(4)
C10–C11	1.435(6)
C10–C15	1.514(6)
C11–H11	0.93(5)
C11–C12	1.508(9)
C11–C12A	1.557(14)
C13–H13	0.9800
C13–H13A	0.9800
C13–C14	1.535(6)
C13–N8	1.434(11)
C13–C12	1.555(9)
C13–N8A	1.464(14)
C13–C12A	1.523(13)
C14–H14	0.9800
C14–C15	1.512(7)
C14–C16	1.540(6)
C15–H15A	0.9700
C15–H15B	0.9700
C16–H16A	0.9700
C16–H16B	0.9700
C16–C17	1.476(7)
C17–N8	1.339(11)
C17–N8A	1.363(14)
C22–H22A	0.9600
C22–H22B	0.9600
C22–H22C	0.9600
C23–H23A	0.9600
C23–H23B	0.9600
C23–H23C	0.9600
C24–H24A	0.9600
C24–H24B	0.9600
C24–H24C	0.9600
B1–H1A	1.02(4)
N8–C18	1.447(11)
N9–H9A	0.89(9)
N9–C12	1.482(10)
N9–C19	1.481(12)
C12–H12	0.9800

C18–H18A	0.9700
C18–H18B	0.9700
C18–C19	1.537(12)
C19–C20	1.529(11)
C19–C21	1.518(11)
C20–H20A	0.9600
C20–H20B	0.9600
C20–H20C	0.9600
C21–H21A	0.9600
C21–H21B	0.9600
C21–H21C	0.9600
N8A–C18A	1.473(14)
N9A–H9B	0.99(13)
N9A–C12A	1.487(14)
N9A–C19A	1.50(2)
C12A–H12A	0.9800
C18A–H18C	0.9700
C18A–H18D	0.9700
C18A–C19A	1.536(15)
C19A–C20A	1.521(14)
C19A–C21A	1.511(14)
C20A–H20D	0.9600
C20A–H20E	0.9600
C20A–H20F	0.9600
C21A–H21D	0.9600
C21A–H21E	0.9600
C21A–H21F	0.9600
Atom–Atom–Atom	Angle [°]
N1–W1–P1	84.86(9)
N3–W1–P1	82.53(10)
N3–W1–N1	85.01(13)
N3–W1–N5	76.67(12)
N3–W1–C10	161.44(15)
N5–W1–P1	155.64(9)
N5–W1–N1	80.86(12)
N5–W1–C10	118.85(14)
N7–W1–P1	91.93(11)
N7–W1–N1	171.96(14)
N7–W1–N3	87.26(15)
N7–W1–N5	99.52(14)
N7–W1–C10	99.18(17)

N7–W1–C11	97.81(17)
C10–W1–P1	79.89(12)
C10–W1–N1	87.54(16)
C11–W1–P1	117.62(12)
C11–W1–N1	90.20(16)
C11–W1–N3	158.84(15)
C11–W1–N5	82.22(15)
C11–W1–C10	37.74(16)
C22–P1–W1	113.57(19)
C22–P1–C23	102.1(3)
C22–P1–C24	103.1(3)
C23–P1–W1	122.4(2)
C23–P1–C24	99.4(3)
C24–P1–W1	113.6(2)
N2–N1–W1	119.8(3)
C1–N1–W1	135.0(3)
C1–N1–N2	105.2(3)
N1–N2–B1	121.2(3)
C3–N2–N1	109.3(4)
C3–N2–B1	129.3(4)
N4–N3–W1	123.6(3)
C4–N3–W1	129.6(3)
C4–N3–N4	106.6(4)
N3–N4–B1	117.9(3)
C6–N4–N3	109.0(4)
C6–N4–B1	130.2(4)
N6–N5–W1	120.3(2)
C7–N5–W1	134.0(3)
C7–N5–N6	105.7(3)
N5–N6–B1	121.4(3)
C9–N6–N5	109.6(4)
C9–N6–B1	129.0(4)
O1–N7–W1	173.3(3)
N1–C1–H1	124.1
N1–C1–C2	111.8(4)
C2–C1–H1	124.1
C1–C2–H2	127.6
C3–C2–C1	104.7(4)
C3–C2–H2	127.6
N2–C3–C2	109.0(4)
N2–C3–H3	125.5
C2–C3–H3	125.5

N3–C4–H4	124.8
N3–C4–C5	110.4(4)
C5–C4–H4	124.8
C4–C5–H5	127.4
C6–C5–C4	105.1(4)
C6–C5–H5	127.4
N4–C6–C5	108.9(4)
N4–C6–H6	125.6
C5–C6–H6	125.6
N5–C7–H7	124.7
N5–C7–C8	110.5(4)
C8–C7–H7	124.7
C7–C8–H8	127.4
C9–C8–C7	105.2(4)
C9–C8–H8	127.4
N6–C9–C8	109.0(4)
N6–C9–H9	125.5
C8–C9–H9	125.5
W1–C10–H10	108(3)
C11–C10–W1	69.5(3)
C11–C10–H10	124(3)
C11–C10–C15	118.4(4)
C15–C10–W1	125.5(4)
C15–C10–H10	107(2)
W1–C11–H11	107(3)
C10–C11–W1	72.7(3)
C10–C11–H11	114(3)
C10–C11–C12	117.8(5)
C10–C11–C12A	122.8(6)
C12–C11–W1	130.3(5)
C12–C11–H11	110(3)
C12A–C11–W1	113.2(6)
C12A–C11–H11	117(3)
C14–C13–H13	109.0
C14–C13–H13A	106.9
C14–C13–C12	117.8(5)
N8–C13–H13	109.0
N8–C13–C14	102.8(6)
N8–C13–C12	108.7(8)
C12–C13–H13	109.0
N8A–C13–H13A	106.9
N8A–C13–C14	100.0(10)

N8A–C13–C12A	114.9(12)
C12A–C13–H13A	106.9
C12A–C13–C14	120.4(6)
C13–C14–H14	110.0
C13–C14–C16	103.0(4)
C15–C14–C13	112.0(4)
C15–C14–H14	110.0
C15–C14–C16	111.7(4)
C16–C14–H14	110.0
C10–C15–H15A	108.6
C10–C15–H15B	108.6
C14–C15–C10	114.6(4)
C14–C15–H15A	108.6
C14–C15–H15B	108.6
H15A–C15–H15B	107.6
C14–C16–H16A	110.8
C14–C16–H16B	110.8
H16A–C16–H16B	108.8
C17–C16–C14	104.9(4)
C17–C16–H16A	110.8
C17–C16–H16B	110.8
O2–C17–C16	126.7(5)
O2–C17–N8	126.4(7)
O2–C17–N8A	125.2(7)
N8–C17–C16	106.4(6)
N8A–C17–C16	107.6(7)
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5

H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
N2–B1–N4	110.6(4)
N2–B1–N6	108.9(4)
N2–B1–H1A	111(2)
N4–B1–H1A	112(2)
N6–B1–N4	106.4(4)
N6–B1–H1A	108(2)
C13–N8–C18	112.3(8)
C17–N8–C13	116.4(9)
C17–N8–C18	131.3(9)
C12–N9–H9A	110(6)
C19–N9–H9A	116(6)
C19–N9–C12	112.5(7)
C11–C12–C13	114.8(6)
C11–C12–H12	107.5
C13–C12–H12	107.5
N9–C12–C11	105.0(7)
N9–C12–C13	114.1(6)
N9–C12–H12	107.5
N8–C18–H18A	109.8
N8–C18–H18B	109.8
N8–C18–C19	109.4(13)
H18A–C18–H18B	108.2
C19–C18–H18A	109.8
C19–C18–H18B	109.8
N9–C19–C18	111.3(8)
N9–C19–C20	110.7(9)
N9–C19–C21	107.2(8)
C20–C19–C18	107.1(10)
C21–C19–C18	111.0(9)
C21–C19–C20	109.5(10)
C19–C20–H20A	109.5
C19–C20–H20B	109.5
C19–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
C19–C21–H21A	109.5
C19–C21–H21B	109.5
C19–C21–H21C	109.5
H21A–C21–H21B	109.5

H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
C13–N8A–C18A	126.4(12)
C17–N8A–C13	112.8(11)
C17–N8A–C18A	119.4(11)
C12A–N9A–H9B	120(7)
C12A–N9A–C19A	119.0(11)
C19A–N9A–H9B	90(7)
C11–C12A–H12A	104.9
C13–C12A–C11	113.7(9)
C13–C12A–H12A	104.9
N9A–C12A–C11	116.7(10)
N9A–C12A–C13	110.4(9)
N9A–C12A–H12A	104.9
N8A–C18A–H18C	110.3
N8A–C18A–H18D	110.3
N8A–C18A–C19A	106.9(15)
H18C–C18A–H18D	108.6
C19A–C18A–H18C	110.3
C19A–C18A–H18D	110.3
N9A–C19A–C18A	110.7(12)
N9A–C19A–C20A	108.4(13)
N9A–C19A–C21A	109.6(12)
C20A–C19A–C18A	109.9(16)
C21A–C19A–C18A	109.9(13)
C21A–C19A–C20A	108.2(15)
C19A–C20A–H20D	109.5
C19A–C20A–H20E	109.5
C19A–C20A–H20F	109.5
H20D–C20A–H20E	109.5
H20D–C20A–H20F	109.5
H20E–C20A–H20F	109.5
C19A–C21A–H21D	109.5
C19A–C21A–H21E	109.5
C19A–C21A–H21F	109.5
H21D–C21A–H21E	109.5
H21D–C21A–H21F	109.5
H21E–C21A–H21F	109.5

Table 5. Torsion angles for Compound 6 Atom–Atom–Atom–Atom	Torsion Angle [°]
W1–N1–N2–C3	179.6(3)
W1–N1–N2–B1	−4.4(5)

W1–N1–C1–C2	−179.5(3)
W1–N3–N4–C6	175.4(3)
W1–N3–N4–B1	12.7(5)
W1–N3–C4–C5	−175.8(3)
W1–N5–N6–C9	−177.7(3)
W1–N5–N6–B1	−0.3(5)
W1–N5–C7–C8	177.0(3)
W1–C10–C11–C12	−127.1(5)
W1–C10–C11–C12A	−106.8(8)
W1–C10–C15–C14	46.5(6)
W1–C11–C12–C13	−53.8(9)
W1–C11–C12–N9	−180.0(4)
W1–C11–C12A–C13	−85.9(10)
W1–C11–C12A–N9A	143.8(9)
O2–C17–N8–C13	−177.3(12)
O2–C17–N8–C18	−1(4)
O2–C17–N8A–C13	171.9(16)
O2–C17–N8A–C18A	4(5)
N1–N2–C3–C2	−0.4(6)
N1–N2–B1–N4	60.8(5)
N1–N2–B1–N6	−55.8(5)
N1–C1–C2–C3	0.7(6)
N2–N1–C1–C2	−0.9(5)
N3–N4–C6–C5	0.9(6)
N3–N4–B1–N2	−65.6(5)
N3–N4–B1–N6	52.5(5)
N3–C4–C5–C6	1.1(6)
N4–N3–C4–C5	−0.6(5)
N5–N6–C9–C8	0.3(5)
N5–N6–B1–N2	59.2(5)
N5–N6–B1–N4	−60.0(5)
N5–C7–C8–C9	0.4(5)
N6–N5–C7–C8	−0.3(5)
C1–N1–N2–C3	0.8(5)
C1–N1–N2–B1	176.7(4)
C1–C2–C3–N2	−0.2(6)
C3–N2–B1–N4	−124.2(5)
C3–N2–B1–N6	119.3(5)
C4–N3–N4–C6	−0.2(5)
C4–N3–N4–B1	−162.9(4)
C4–C5–C6–N4	−1.2(6)
C6–N4–B1–N2	136.1(5)

C6–N4–B1–N6	−105.9(5)
C7–N5–N6–C9	0.0(5)
C7–N5–N6–B1	177.4(4)
C7–C8–C9–N6	−0.4(5)
C9–N6–B1–N2	−124.0(5)
C9–N6–B1–N4	116.8(5)
C10–C11–C12–C13	36.6(9)
C10–C11–C12–N9	−89.5(7)
C10–C11–C12A–C13	−2.1(14)
C10–C11–C12A–N9A	−132.4(9)
C11–C10–C15–C14	−37.6(6)
C13–C14–C15–C10	49.0(6)
C13–C14–C16–C17	25.5(5)
C13–N8–C18–C19	72(2)
C13–N8A–C18A–C19A	41(5)
C14–C13–N8–C17	7(2)
C14–C13–N8–C18	−170.1(16)
C14–C13–C12–C11	−22.8(9)
C14–C13–C12–N9	98.5(7)
C14–C13–N8A–C17	31(3)
C14–C13–N8A–C18A	−162(4)
C14–C13–C12A–C11	15.8(14)
C14–C13–C12A–N9A	149.1(8)
C14–C16–C17–O2	165.1(6)
C14–C16–C17–N8	−22.1(15)
C14–C16–C17–N8A	−7(2)
C15–C10–C11–W1	120.2(4)
C15–C10–C11–C12	−6.9(8)
C15–C10–C11–C12A	13.3(10)
C15–C14–C16–C17	−94.8(5)
C16–C14–C15–C10	163.9(4)
C16–C17–N8–C13	10(2)
C16–C17–N8–C18	−174(2)
C16–C17–N8A–C13	−16(4)
C16–C17–N8A–C18A	177(3)
C17–N8–C18–C19	−105(3)
C17–N8A–C18A–C19A	−154(3)
B1–N2–C3–C2	−175.9(5)
B1–N4–C6–C5	160.7(5)
B1–N6–C9–C8	−176.9(4)
N8–C13–C14–C15	100.7(13)
N8–C13–C14–C16	−19.5(13)

N8–C13–C12–C11	−139.1(12)
N8–C13–C12–N9	−17.8(14)
N8–C18–C19–N9	−30.1(13)
N8–C18–C19–C20	−151.2(10)
N8–C18–C19–C21	89.3(11)
C12–C13–C14–C15	−18.8(6)
C12–C13–C14–C16	−138.9(5)
C12–C13–N8–C17	132.4(18)
C12–C13–N8–C18	−44(2)
C12–N9–C19–C18	−29.2(11)
C12–N9–C19–C20	89.7(10)
C12–N9–C19–C21	−150.8(8)
C19–N9–C12–C11	−177.6(6)
C19–N9–C12–C13	55.8(10)
N8A–C13–C14–C15	87.5(19)
N8A–C13–C14–C16	−32.6(19)
N8A–C13–C12A–C11	−104(2)
N8A–C13–C12A–N9A	29(2)
N8A–C18A–C19A–N9A	−48(2)
N8A–C18A–C19A–C20A	−168(2)
N8A–C18A–C19A–C21A	73(2)
C12A–C13–C14–C15	−39.4(9)
C12A–C13–C14–C16	−159.5(8)
C12A–C13–N8A–C17	162(2)
C12A–C13–N8A–C18A	−32(5)
C12A–N9A–C19A–C18A	57.9(16)
C12A–N9A–C19A–C20A	178.6(15)
C12A–N9A–C19A–C21A	−63.5(15)
C19A–N9A–C12A–C11	85.8(13)
C19A–N9A–C12A–C13	−46.0(16)

Table 6. Hydrogen bonds for Compound 6

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N9A–H9B···O1#1	0.99(13)	2.48(12)	3.149(11)	125(9)

Symmetry transformations used to generate equivalent atoms:

#1: 2-X, 1-Y, 1-Z;

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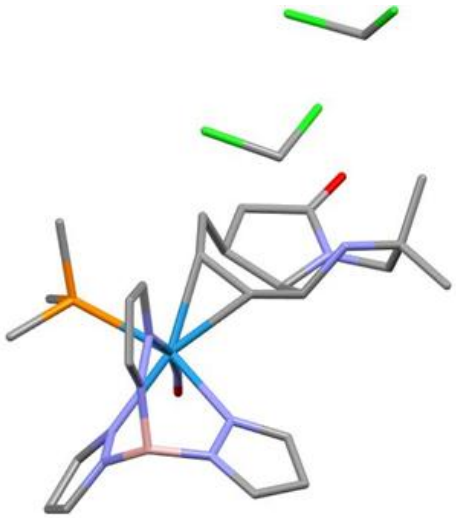
Crystal Structure Report for Compound 5.8



A colorless, needle-like specimen of $C_{26}H_{41}BCl_4N_9O_2PW$, approximate dimensions 0.023 mm x 0.037 mm x 0.074 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 11.03 hours. The frames were integrated with the Bruker SAINT software package[189] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 71345 reflections to a maximum θ angle of 28.36° (0.75 Å resolution), of which 8515 were independent (average redundancy 8.379, completeness = 99.5%, R_{int} = 8.49%, R_{sig} = 4.97%) and 7357 (86.40%) were greater than 2σ(F^2). The final cell constants of a = 9.8458(4) Å, b = 13.1319(7) Å, c = 14.4525(8) Å, α = 109.749(2)°, β = 100.603(2)°, γ = 94.134(2)°, volume = 1710.38(15) $Å^3$, are based upon the refinement of the XYZ-centroids of 9988 reflections above 20 σ(I) with 5.008° < 2θ < 55.63°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[190] The ratio of minimum to maximum apparent transmission was 0.809. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7670 and 0.9180.

The structure was solved and refined using the Bruker SHELXTL Software Package[191] within APEX5 [1] and OLEX2,[192] using the space group P -1, with Z = 2 for the formula unit, $C_{26}H_{41}BCl_4N_9O_2PW$. Non-hydrogen atoms were refined anisotropically. The B-H and N-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The final anisotropic full-matrix least-squares refinement on F^2 with 417 variables converged at R1 = 3.32%, for the observed data and wR2 = 7.63% for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was 1.744 $e^-/Å^3$ and the largest hole was -0.960 $e^-/Å^3$ with an RMS deviation of 0.128 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.707 g/cm^3 and F(000), 876 e^-.

Table 1. Sample and crystal data for Compound 5.8.

Chemical formula	$C_{26}H_{41}BCl_4N_9O_2PW$
Formula weight	879.11 g/mol

[189] Bruker (2012). Saint; SADABS; APEX5. Bruker AXS Inc., Madison, Wisconsin, USA.

[190] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[191] Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

[192] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.023 x 0.037 x 0.074 mm	
Crystal habit	colorless needle	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.8458(4) Å	α = 109.749(2)°
	b = 13.1319(7) Å	β = 100.603(2)°
	c = 14.4525(8) Å	γ = 94.134(2)°
Volume	1710.38(15) $Å^3$	
Z	2	
Density (calculated)	1.707 g/cm^3	
Absorption coefficient	3.776 mm^{-1}	
F(000)	876	

Table 2. Data collection and structure refinement for Compound 5.8.	
Diffractometer	Bruker D8 Venture Photon III Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.82 to 28.36°
Index ranges	-11<=h<=13, -17<=k<=17, -19<=l<=19
Reflections collected	71345

Independent reflections	8515 [R(int) = 0.0849]	
Coverage of independent reflections	99.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9180 and 0.7670	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8515 / 0 / 417	
Goodness-of-fit on F^2	1.047	
Δ/σ_{max}	0.002	
Final R indices	7357 data; I>2σ(I)	R1 = 0.0332, wR2 = 0.0736
	all data	R1 = 0.0427, wR2 = 0.0763
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0321P)^2+1.7234P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.744 and -0.960 eÅ^{-3}	

R.M.S. deviation from mean	0.128 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 5.8.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.68571(2)	0.64317(2)	0.86566(2)	0.01881(5)
P1	0.61963(10)	0.75141(9)	0.75653(8)	0.0234(2)
O1	0.4198(3)	0.6616(2)	0.9380(2)	0.0285(6)
O2	0.1279(3)	0.2069(3)	0.6274(2)	0.0376(8)
N1	0.8191(3)	0.6093(3)	0.9915(2)	0.0195(6)
N2	0.9434(3)	0.6746(3)	0.0437(3)	0.0232(7)
N3	0.7528(3)	0.8081(3)	0.9814(3)	0.0225(7)
N4	0.8880(3)	0.8492(3)	0.0278(3)	0.0248(7)
N5	0.8968(3)	0.6665(3)	0.8302(3)	0.0218(7)
N6	0.0098(3)	0.7255(3)	0.9061(3)	0.0248(7)
N7	0.5260(3)	0.6477(3)	0.9051(2)	0.0214(7)
N8	0.3222(3)	0.3005(3)	0.7504(3)	0.0245(7)
N9	0.5804(4)	0.2717(3)	0.7364(3)	0.0265(8)
C1	0.8048(4)	0.5343(3)	0.0340(3)	0.0229(8)
C2	0.9192(4)	0.5498(3)	0.1133(3)	0.0267(9)
C3	0.0035(4)	0.6397(3)	0.1166(3)	0.0265(9)
C4	0.6764(4)	0.8850(3)	0.0208(3)	0.0271(9)

	x/a	**y/b**	**z/c**	**U(eq)**
C5	0.7613(5)	0.9765(4)	0.0933(4)	0.0327(10)
C6	0.8939(5)	0.9495(4)	0.0957(3)	0.0314(10)
C7	0.9453(4)	0.6342(3)	0.7454(3)	0.0258(9)
C8	0.0873(4)	0.6708(3)	0.7652(3)	0.0286(9)
C9	0.1239(4)	0.7270(3)	0.8673(3)	0.0283(9)
C10	0.6178(4)	0.5102(3)	0.7140(3)	0.0248(8)
C11	0.6668(4)	0.4652(3)	0.7903(3)	0.0224(8)
C12	0.5673(4)	0.3810(3)	0.8053(3)	0.0235(8)
C13	0.4141(4)	0.4050(3)	0.7912(3)	0.0230(8)
C14	0.3641(4)	0.4632(3)	0.7172(3)	0.0243(8)
C15	0.4679(4)	0.4690(4)	0.6530(3)	0.0284(9)
C16	0.2220(4)	0.3951(4)	0.6530(3)	0.0290(9)
C17	0.2166(4)	0.2898(4)	0.6728(3)	0.0300(9)
C18	0.3652(4)	0.2162(3)	0.7859(3)	0.0282(9)
C19	0.4990(4)	0.1802(3)	0.7489(3)	0.0277(9)
C20	0.5895(5)	0.1443(4)	0.8259(4)	0.0351(10)
C21	0.4582(5)	0.0875(4)	0.6460(4)	0.0378(11)
C22	0.6315(5)	0.7051(4)	0.6255(3)	0.0334(10)
C23	0.4431(4)	0.7837(4)	0.7516(4)	0.0359(11)
C24	0.7277(5)	0.8851(4)	0.7999(4)	0.0371(11)
B1	0.9972(5)	0.7703(4)	0.0160(4)	0.0253(10)
Cl1	0.84398(15)	0.39726(11)	0.50749(10)	0.0504(3)
Cl2	0.69065(13)	0.19528(11)	0.50017(9)	0.0443(3)
C25	0.8279(5)	0.3024(4)	0.5691(4)	0.0407(12)

	x/a	y/b	z/c	U(eq)
Cl3	0.97398(13)	0.14652(10)	0.34745(9)	0.0419(3)
Cl4	0.14542(17)	0.97924(16)	0.36638(16)	0.0742(5)
C26	0.0065(5)	0.0450(4)	0.4018(4)	0.0372(11)

Table 4. Bond lengths (Å) for Compound 5.8.

W1-N7	1.767(3)	W1-C11	2.197(4)
W1-N3	2.206(3)	W1-N1	2.232(3)
W1-C10	2.238(4)	W1-N5	2.254(3)
W1-P1	2.4904(11)	P1-C22	1.812(5)
P1-C23	1.813(4)	P1-C24	1.830(5)
O1-N7	1.227(4)	O2-C17	1.244(5)
N1-C1	1.337(5)	N1-N2	1.368(4)
N2-C3	1.344(5)	N2-B1	1.530(6)
N3-C4	1.337(5)	N3-N4	1.354(4)
N4-C6	1.340(5)	N4-B1	1.538(6)
N5-C7	1.343(5)	N5-N6	1.377(4)
N6-C9	1.347(5)	N6-B1	1.529(6)
N8-C17	1.343(5)	N8-C18	1.428(5)
N8-C13	1.458(5)	N9-C12	1.475(5)
N9-C19	1.477(5)	N9-H9	0.90(6)
C1-C2	1.399(6)	C1-H1	0.950000
C2-C3	1.375(6)	C2-H2	0.950000
C3-H3	0.950000	C4-C5	1.387(6)

C4-H4	0.950000	C5-C6	1.375(6)
C5-H5	0.950000	C6-H6	0.950000
C7-C8	1.390(5)	C7-H7	0.950000
C8-C9	1.372(6)	C8-H8	0.950000
C9-H9A	0.950000	C10-C11	1.443(6)
C10-C15	1.527(5)	C10-H10	0.86(5)
C11-C12	1.520(5)	C11-H11	1.04(4)
C12-C13	1.554(5)	C12-H12	1.000000
C13-C14	1.542(6)	C13-H13	1.000000
C14-C15	1.516(6)	C14-C16	1.548(5)
C14-H14	1.000000	C15-H15A	0.990000
C15-H15B	0.990000	C16-C17	1.504(6)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.557(6)	C18-H18A	0.990000
C18-H18B	0.990000	C19-C20	1.518(6)
C19-C21	1.530(6)	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
C23-H23A	0.980000	C23-H23B	0.980000
C23-H23C	0.980000	C24-H24A	0.980000
C24-H24B	0.980000	C24-H24C	0.980000
B1-H1A	1.16(4)	Cl1-C25	1.773(5)
Cl2-C25	1.756(5)	C25-H25A	0.990000

C25-H25B	0.990000	Cl3-C26	1.781(5)
Cl4-C26	1.735(5)	C26-H26A	0.990000
C26-H26B	0.990000		

Table 5. Bond angles (°) for Compound 5.8.			
N7-W1-C11	98.20(14)	N7-W1-N3	86.32(13)
C11-W1-N3	160.21(13)	N7-W1-N1	99.83(13)
C11-W1-N1	82.66(13)	N3-W1-N1	77.58(12)
N7-W1-C10	99.91(15)	C11-W1-C10	37.97(15)
N3-W1-C10	160.10(14)	N1-W1-C10	119.33(14)
N7-W1-N5	170.76(13)	C11-W1-N5	90.97(13)
N3-W1-N5	84.64(12)	N1-W1-N5	80.13(12)
C10-W1-N5	88.01(14)	N7-W1-P1	93.38(11)
C11-W1-P1	116.96(11)	N3-W1-P1	81.77(9)
N1-W1-P1	154.60(9)	C10-W1-P1	79.02(11)
N5-W1-P1	83.41(9)	C22-P1-C23	103.3(2)
C22-P1-C24	98.5(2)	C23-P1-C24	103.9(2)
C22-P1-W1	122.09(16)	C23-P1-W1	113.38(15)
C24-P1-W1	113.34(16)	C1-N1-N2	106.0(3)
C1-N1-W1	133.5(2)	N2-N1-W1	120.5(2)
C3-N2-N1	109.7(3)	C3-N2-B1	128.8(3)
N1-N2-B1	121.5(3)	C4-N3-N4	106.8(3)
C4-N3-W1	129.8(3)	N4-N3-W1	123.5(2)
C6-N4-N3	109.0(3)	C6-N4-B1	130.5(3)
N3-N4-B1	118.4(3)	C7-N5-N6	105.8(3)

C7-N5-W1	134.2(3)	N6-N5-W1	120.0(2)
C9-N6-N5	109.3(3)	C9-N6-B1	129.4(3)
N5-N6-B1	121.1(3)	O1-N7-W1	173.6(3)
C17-N8-C18	126.8(4)	C17-N8-C13	115.2(4)
C18-N8-C13	117.2(3)	C12-N9-C19	114.4(3)
C12-N9-H9	102.(4)	C19-N9-H9	113.(4)
N1-C1-C2	110.9(3)	N1-C1-H1	124.500000
C2-C1-H1	124.500000	C3-C2-C1	104.3(4)
C3-C2-H2	127.800000	C1-C2-H2	127.800000
N2-C3-C2	109.0(4)	N2-C3-H3	125.500000
C2-C3-H3	125.500000	N3-C4-C5	110.6(4)
N3-C4-H4	124.700000	C5-C4-H4	124.700000
C6-C5-C4	104.1(4)	C6-C5-H5	128.000000
C4-C5-H5	128.000000	N4-C6-C5	109.5(4)
N4-C6-H6	125.300000	C5-C6-H6	125.300000
N5-C7-C8	111.0(4)	N5-C7-H7	124.500000
C8-C7-H7	124.500000	C9-C8-C7	104.7(4)
C9-C8-H8	127.600000	C7-C8-H8	127.600000
N6-C9-C8	109.2(4)	N6-C9-H9A	125.400000
C8-C9-H9A	125.400000	C11-C10-C15	117.2(4)
C11-C10-W1	69.5(2)	C15-C10-W1	126.4(3)
C11-C10-H10	111.(3)	C15-C10-H10	112.(3)
W1-C10-H10	113.(3)	C10-C11-C12	118.6(3)
C10-C11-W1	72.5(2)	C12-C11-W1	125.2(3)
C10-C11-H11	120.(3)	C12-C11-H11	111.(2)

W1-C11-H11	104.(2)	N9-C12-C11	108.2(3)
N9-C12-C13	112.2(3)	C11-C12-C13	112.7(3)
N9-C12-H12	107.800000	C11-C12-H12	107.800000
C13-C12-H12	107.800000	N8-C13-C14	104.1(3)
N8-C13-C12	107.8(3)	C14-C13-C12	118.6(3)
N8-C13-H13	108.700000	C14-C13-H13	108.700000
C12-C13-H13	108.700000	C15-C14-C13	112.1(3)
C15-C14-C16	112.1(3)	C13-C14-C16	104.6(3)
C15-C14-H14	109.300000	C13-C14-H14	109.300000
C16-C14-H14	109.300000	C14-C15-C10	113.3(3)
C14-C15-H15A	108.900000	C10-C15-H15A	108.900000
C14-C15-H15B	108.900000	C10-C15-H15B	108.900000
H15A-C15-H15B	107.700000	C17-C16-C14	105.4(3)
C17-C16-H16A	110.700000	C14-C16-H16A	110.700000
C17-C16-H16B	110.700000	C14-C16-H16B	110.700000
H16A-C16-H16B	108.800000	O2-C17-N8	125.0(4)
O2-C17-C16	126.5(4)	N8-C17-C16	108.6(3)
N8-C18-C19	109.1(3)	N8-C18-H18A	109.900000
C19-C18-H18A	109.900000	N8-C18-H18B	109.900000
C19-C18-H18B	109.900000	H18A-C18-H18B	108.300000

N9-C19-C20	108.7(3)	N9-C19-C21	107.4(4)
C20-C19-C21	110.9(4)	N9-C19-C18	110.6(3)
C20-C19-C18	109.5(4)	C21-C19-C18	109.8(3)
C19-C20-H20A	109.500000	C19-C20-H20B	109.500000
H20A-C20-H20B	109.500000	C19-C20-H20C	109.500000
H20A-C20-H20C	109.500000	H20B-C20-H20C	109.500000
C19-C21-H21A	109.500000	C19-C21-H21B	109.500000
H21A-C21-H21B	109.500000	C19-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
P1-C22-H22A	109.500000	P1-C22-H22B	109.500000
H22A-C22-H22B	109.500000	P1-C22-H22C	109.500000
H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
P1-C23-H23A	109.500000	P1-C23-H23B	109.500000
H23A-C23-H23B	109.500000	P1-C23-H23C	109.500000
H23A-C23-H23C	109.500000	H23B-C23-H23C	109.500000
P1-C24-H24A	109.500000	P1-C24-H24B	109.500000
H24A-C24-H24B	109.500000	P1-C24-H24C	109.500000

H24A-C24-H24C	109.500000	H24B-C24-H24C	109.500000
N6-B1-N2	108.2(3)	N6-B1-N4	109.9(3)
N2-B1-N4	107.1(3)	N6-B1-H1A	100.(2)
N2-B1-H1A	114.(2)	N4-B1-H1A	117.(2)
Cl2-C25-Cl1	111.4(3)	Cl2-C25-H25A	109.300000
Cl1-C25-H25A	109.300000	Cl2-C25-H25B	109.300000
Cl1-C25-H25B	109.300000	H25A-C25-H25B	108.000000
Cl4-C26-Cl3	112.2(3)	Cl4-C26-H26A	109.200000
Cl3-C26-H26A	109.200000	Cl4-C26-H26B	109.200000
Cl3-C26-H26B	109.200000	H26A-C26-H26B	107.900000

Table 6. Torsion angles (°) for Compound 5.8.			
C1-N1-N2-C3	0.1(4)	W1-N1-N2-C3	178.9(3)
C1-N1-N2-B1	179.3(4)	W1-N1-N2-B1	-1.9(5)
C4-N3-N4-C6	0.7(5)	W1-N3-N4-C6	-178.4(3)
C4-N3-N4-B1	166.2(4)	W1-N3-N4-B1	-12.9(5)
C7-N5-N6-C9	-0.8(4)	W1-N5-N6-C9	179.2(3)
C7-N5-N6-B1	-176.3(3)	W1-N5-N6-B1	3.6(5)
N2-N1-C1-C2	-0.3(4)	W1-N1-C1-C2	-178.8(3)
N1-C1-C2-C3	0.4(5)	N1-N2-C3-C2	0.2(5)

B1-N2-C3-C2	-179.0(4)	C1-C2-C3-N2	-0.3(5)
N4-N3-C4-C5	-0.2(5)	W1-N3-C4-C5	178.9(3)
N3-C4-C5-C6	-0.4(5)	N3-N4-C6-C5	-1.0(5)
B1-N4-C6-C5	-164.2(4)	C4-C5-C6-N4	0.9(5)
N6-N5-C7-C8	0.2(4)	W1-N5-C7-C8	-179.7(3)
N5-C7-C8-C9	0.4(5)	N5-N6-C9-C8	1.1(5)
B1-N6-C9-C8	176.1(4)	C7-C8-C9-N6	-0.9(5)
C15-C10-C11-C12	-0.2(5)	W1-C10-C11-C12	121.1(3)
C15-C10-C11-W1	-121.3(4)	C19-N9-C12-C11	174.7(3)
C19-N9-C12-C13	-60.3(5)	C10-C11-C12-N9	88.3(4)
W1-C11-C12-N9	176.4(3)	C10-C11-C12-C13	-36.4(5)
W1-C11-C12-C13	51.7(4)	C17-N8-C13-C14	-7.2(5)
C18-N8-C13-C14	163.5(3)	C17-N8-C13-C12	-134.0(4)
C18-N8-C13-C12	36.8(5)	N9-C12-C13-N8	25.7(5)
C11-C12-C13-N8	148.2(3)	N9-C12-C13-C14	-92.1(4)
C11-C12-C13-C14	30.4(5)	N8-C13-C14-C15	-108.6(4)
C12-C13-C14-C15	11.1(5)	N8-C13-C14-C16	13.1(4)

C12-C13-C14-C16	132.8(4)	C13-C14-C15-C10	-48.4(5)
C16-C14-C15-C10	-165.7(3)	C11-C10-C15-C14	44.7(5)
W1-C10-C15-C14	-38.9(5)	C15-C14-C16-C17	107.2(4)
C13-C14-C16-C17	-14.5(4)	C18-N8-C17-O2	9.8(7)
C13-N8-C17-O2	179.5(4)	C18-N8-C17-C16	-171.9(4)
C13-N8-C17-C16	-2.2(5)	C14-C16-C17-O2	-171.0(4)
C14-C16-C17-N8	10.7(5)	C17-N8-C18-C19	102.8(5)
C13-N8-C18-C19	-66.7(4)	C12-N9-C19-C20	-90.0(4)
C12-N9-C19-C21	150.0(4)	C12-N9-C19-C18	30.2(5)
N8-C18-C19-N9	28.7(5)	N8-C18-C19-C20	148.5(3)
N8-C18-C19-C21	-89.6(4)	C9-N6-B1-N2	-118.1(4)
N5-N6-B1-N2	56.4(4)	C9-N6-B1-N4	125.3(4)
N5-N6-B1-N4	-60.1(5)	C3-N2-B1-N6	121.1(4)
N1-N2-B1-N6	-58.0(5)	C3-N2-B1-N4	-120.6(4)
N1-N2-B1-N4	60.3(5)	C6-N4-B1-N6	-132.4(4)
N3-N4-B1-N6	65.8(5)	C6-N4-B1-N2	110.3(5)
N3-N4-B1-N2	-51.5(5)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 5.8.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01616(7)	0.01837(8)	0.02153(8)	0.00726(6)	0.00318(5)	0.00216(5)
P1	0.0212(5)	0.0266(5)	0.0266(5)	0.0137(4)	0.0064(4)	0.0058(4)
O1	0.0180(13)	0.0293(16)	0.0362(17)	0.0081(13)	0.0086(12)	0.0028(11)
O2	0.0300(16)	0.0342(18)	0.0374(19)	0.0049(15)	-0.0008(13)	-0.0056(13)
N1	0.0179(14)	0.0183(16)	0.0207(16)	0.0061(13)	0.0022(12)	0.0033(12)
N2	0.0159(14)	0.0254(18)	0.0277(18)	0.0118(15)	0.0000(13)	0.0002(13)
N3	0.0204(15)	0.0207(17)	0.0258(18)	0.0088(14)	0.0033(13)	0.0018(13)
N4	0.0217(16)	0.0228(17)	0.0265(18)	0.0074(15)	0.0016(13)	-0.0008(13)
N5	0.0172(15)	0.0205(16)	0.0281(18)	0.0092(14)	0.0045(13)	0.0041(12)
N6	0.0174(15)	0.0247(17)	0.0321(19)	0.0121(15)	0.0023(13)	0.0012(13)
N7	0.0209(15)	0.0166(16)	0.0235(17)	0.0053(13)	0.0011(13)	0.0027(12)
N8	0.0216(16)	0.0209(17)	0.0275(18)	0.0057(14)	0.0036(13)	0.0000(13)
N9	0.0279(17)	0.0171(17)	0.030(2)	0.0034(15)	0.0070(15)	0.0018(13)
C1	0.0262(19)	0.0180(18)	0.025(2)	0.0073(16)	0.0075(16)	0.0041(15)
C2	0.033(2)	0.027(2)	0.024(2)	0.0118(18)	0.0087(17)	0.0108(17)
C3	0.0244(19)	0.030(2)	0.024(2)	0.0087(18)	0.0026(16)	0.0068(16)
C4	0.029(2)	0.024(2)	0.029(2)	0.0073(18)	0.0104(17)	0.0059(16)
C5	0.038(2)	0.020(2)	0.036(3)	0.0038(19)	0.0110(19)	0.0020(17)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	0.032(2)	0.024(2)	0.031(2)	0.0042(18)	0.0018(18)	0.0005(17)
C7	0.0234(19)	0.028(2)	0.031(2)	0.0130(18)	0.0089(16)	0.0104(16)
C8	0.0237(19)	0.029(2)	0.040(3)	0.017(2)	0.0131(18)	0.0081(16)
C9	0.0155(17)	0.030(2)	0.045(3)	0.020(2)	0.0061(17)	0.0048(15)
C10	0.026(2)	0.024(2)	0.021(2)	0.0034(17)	0.0061(16)	0.0020(16)
C11	0.0184(17)	0.023(2)	0.024(2)	0.0054(16)	0.0056(15)	0.0043(15)
C12	0.0201(18)	0.0192(19)	0.026(2)	0.0025(16)	0.0040(15)	0.0027(15)
C13	0.0220(18)	0.0182(19)	0.026(2)	0.0049(16)	0.0058(15)	0.0005(14)
C14	0.0215(18)	0.023(2)	0.025(2)	0.0070(17)	0.0017(15)	0.0032(15)
C15	0.026(2)	0.030(2)	0.027(2)	0.0101(18)	0.0026(17)	0.0004(17)
C16	0.0230(19)	0.034(2)	0.027(2)	0.0087(19)	0.0021(16)	0.0015(17)
C17	0.0236(19)	0.031(2)	0.030(2)	0.0053(19)	0.0034(17)	0.0015(17)
C18	0.029(2)	0.022(2)	0.031(2)	0.0074(18)	0.0055(17)	0.0017(16)
C19	0.027(2)	0.0186(19)	0.033(2)	0.0045(17)	0.0052(17)	0.0030(15)
C20	0.034(2)	0.025(2)	0.040(3)	0.007(2)	0.0030(19)	0.0077(18)
C21	0.042(3)	0.020(2)	0.040(3)	-0.0005(19)	0.007(2)	-0.0036(18)
C22	0.036(2)	0.039(3)	0.032(2)	0.020(2)	0.0099(19)	0.0080(19)
C23	0.027(2)	0.052(3)	0.043(3)	0.030(2)	0.0132(19)	0.017(2)
C24	0.044(3)	0.027(2)	0.045(3)	0.018(2)	0.012(2)	0.0032(19)
B1	0.021(2)	0.023(2)	0.031(3)	0.011(2)	0.0024(18)	0.0017(17)
Cl1	0.0646(8)	0.0380(7)	0.0421(7)	0.0066(6)	0.0121(6)	0.0047(6)
Cl2	0.0401(6)	0.0516(8)	0.0367(7)	0.0143(6)	0.0032(5)	-0.0001(5)
C25	0.037(2)	0.039(3)	0.037(3)	0.005(2)	0.003(2)	0.008(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl3	0.0531(7)	0.0388(6)	0.0375(7)	0.0154(5)	0.0132(5)	0.0132(5)
Cl4	0.0625(9)	0.0912(13)	0.1188(15)	0.0802(12)	0.0478(10)	0.0415(9)
C26	0.038(2)	0.038(3)	0.042(3)	0.021(2)	0.011(2)	0.006(2)

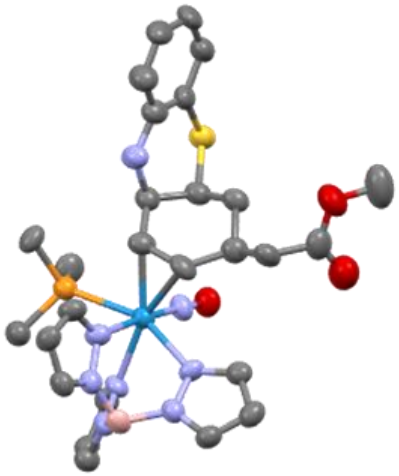
Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 5.8.

	x/a	y/b	z/c	U(eq)
H9	0.552(6)	0.277(5)	0.675(4)	0.052(17)
H1	0.7274	0.4780	1.0131	0.028000
H2	0.9350	0.5078	1.1554	0.032000
H3	1.0902	0.6719	1.1629	0.032000
H4	0.5775	0.8779	1.0018	0.032000
H5	0.7341	1.0426	1.1324	0.039000
H6	0.9769	0.9949	1.1387	0.038000
H7	0.8898	0.5920	0.6805	0.031000
H8	1.1460	0.6595	0.7184	0.034000
H9A	1.2153	0.7614	0.9047	0.034000
H10	0.677(5)	0.507(4)	0.676(4)	0.029(12)
H11	0.769(5)	0.448(4)	0.802(3)	0.029(12)
H12	0.5984	0.3833	0.8759	0.028000
H13	0.3970	0.4479	0.8587	0.028000
H14	0.3492	0.5389	0.7561	0.029000
H15A	0.4400	0.5183	0.6162	0.034000

	x/a	y/b	z/c	U(eq)
H15B	0.4642	0.3953	0.6023	0.034000
H16A	0.1439	0.4341	0.6735	0.035000
H16B	0.2164	0.3810	0.5805	0.035000
H18A	0.2898	0.1530	0.7600	0.034000
H18B	0.3849	0.2436	0.8605	0.034000
H20A	0.6681	0.1137	0.7992	0.053000
H20B	0.5338	0.0887	0.8400	0.053000
H20C	0.6251	0.2075	0.8883	0.053000
H21A	0.3908	0.1093	0.5999	0.057000
H21B	0.4159	0.0217	0.6536	0.057000
H21C	0.5416	0.0722	0.6187	0.057000
H22A	0.5769	0.6323	0.5896	0.050000
H22B	0.7294	0.7016	0.6214	0.050000
H22C	0.5947	0.7563	0.5947	0.050000
H23A	0.4321	0.8426	0.7247	0.054000
H23B	0.4251	0.8073	0.8196	0.054000
H23C	0.3766	0.7186	0.7078	0.054000
H24A	0.6987	0.9226	0.7529	0.056000
H24B	0.8259	0.8753	0.8030	0.056000
H24C	0.7162	0.9291	0.8672	0.056000
H1A	1.112(5)	0.807(4)	1.055(3)	0.030000
H25A	0.9165	0.2719	0.5778	0.049000
H25B	0.8109	0.3406	0.6369	0.049000
H26A	0.0267	0.0798	0.4762	0.045000

	x/a	y/b	z/c	U(eq)
H26B	-0.0785	-0.0097	0.3807	0.045000

Crystal Structure Report for Compound 33



A colorless, needle-like specimen of $C_{27}H_{36}BN_8O_3PSW$, approximate dimensions 0.032 mm x 0.033 mm x 0.136 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Cu K_α, λ = 1.54178 Å) and a HELIOS MX double bounce multilayer mirror monochromator.

The total exposure time was 17.36 hours. A two-domain twin was identified with the "Domains" plugin of APEX4. The frames were integrated with the Bruker SAINT software package[193] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 121269 reflections to a maximum θ angle of 68.38° (0.83 Å resolution), of which 11577 were independent (average redundancy 10.475, completeness = 99.7%, R_{int} = 10.35%, R_{sig} = 8.86%) and 9367 (80.91%) were greater than 2σ(F^2). The final cell constants of a = 7.6301(4) Å, b = 13.8917(6) Å, c = 29.8378(13) Å, α = 88.409(2)°, β =

[193] Bruker (2012). Saint; TWINABS; APEX3. Bruker AXS Inc., Madison, Wisconsin, USA.

89.470(2)°, γ = 88.564(2)°, volume = 3160.3(3) Å^3, are based upon the refinement of the XYZ-centroids of 9728 reflections above 20 σ(I) with 5.926° < 2θ < 136.6°. Data were corrected for absorption effects using the Multi-Scan method (TWINABS).[194] The ratio of minimum to maximum apparent transmission was 0.726. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4010 and 0.7790.

The structure was solved using the Bruker SHELXTL Software Package[195] within APEX4 [1] and OLEX2, [196] using the space group P -1, with Z = 4 for the formula unit, $C_{27}H_{36}BN_8O_3PSW$. Refinement was done on HKLF5 data. The BASF of the twin refined to 0.51261. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The data was not good enough to identify the positions of the B-H or N-H hydrogen atoms in the electron density map. The final anisotropic full-matrix least-squares refinement on F^2 with 766 variables converged at R1 = 8.75%, for the observed data and wR2 = 24.39% for all data. The goodness-of-fit was 1.064. The largest peak in the final difference electron density synthesis was 3.591 e$^-$/Å^3 and the largest hole was -2.457 e$^-$/Å^3 with an RMS deviation of 0.243 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.636 g/cm^3 and F(000), 1552 e$^-$.

Table 1. Sample and crystal data for Compound 33.

Chemical formula	$C_{27}H_{36}BN_8O_3PSW$
Formula weight	778.33 g/mol
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal size	0.032 x 0.033 x 0.136 mm

[194] Sevvana, M., Ruf, M., Us\'on, I., Sheldrick, G. M., and Herbst-Irmer, R. (2019). "Non-merohedral twinning: from minerals to proteins", Acta. Cryst. D75, 1040-1050.doi:10.1107/S2059798319010179

[195] Sheldrick, G. M. (2015). Acta Cryst. A**71**, 3-8.
[196] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Crystal habit	colorless needle	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6301(4) Å	α = 88.409(2)°
	b = 13.8917(6) Å	β = 89.470(2)°
	c = 29.8378(13) Å	γ = 88.564(2)°
Volume	3160.3(3) $Å^3$	
Z	4	
Density (calculated)	1.636 g/cm^3	
Absorption coefficient	8.219 mm^{-1}	
F(000)	1552	

Table 2. Data collection and structure refinement for Compound 33.

Diffractometer	Bruker D8 Venture Photon III Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Cu K_α, λ = 1.54178 Å)
Theta range for data collection	2.96 to 68.38°
Reflections collected	121269
Independent reflections	11577 [R(int) = 0.1035]
Coverage of independent reflections	99.7%

Absorption correction	Multi-Scan	
Max. and min. transmission	0.7790 and 0.4010	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11577 / 0 / 766	
Goodness-of-fit on F^2	1.064	
Δ/σ_{max}	0.001	
Final R indices	9367 data; I>2σ(I)	R1 = 0.0875, wR2 = 0.2286
	all data	R1 = 0.1031, wR2 = 0.2439
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1183P)^2+21.9211P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	3.591 and -2.457 eÅ^{-3}	
R.M.S. deviation from mean	0.243 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 33.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.36581(8)	0.31488(4)	0.60893(2)	0.0432(2)
S1	0.2958(5)	0.7151(3)	0.57844(13)	0.0545(8)
P1	0.2332(5)	0.3165(2)	0.53200(12)	0.0478(8)
O1	0.6777(14)	0.4332(8)	0.5860(4)	0.061(3)
O2	0.6632(18)	0.5454(9)	0.7353(4)	0.073(3)
O3	0.447(2)	0.6228(10)	0.7728(4)	0.086(4)
N1	0.1422(15)	0.2168(7)	0.6287(4)	0.043(2)
N2	0.1767(15)	0.1262(8)	0.6444(4)	0.049(3)
N3	0.4905(15)	0.1842(8)	0.5864(4)	0.046(2)
N4	0.4618(16)	0.0949(8)	0.6049(4)	0.048(3)
N5	0.4846(14)	0.2491(8)	0.6709(4)	0.043(2)
N6	0.4582(15)	0.1562(8)	0.6825(4)	0.048(3)
N7	0.5511(16)	0.3884(8)	0.5931(4)	0.052(3)
N8	0.9974(16)	0.5775(8)	0.5961(5)	0.053(3)
C1	0.965(2)	0.2269(12)	0.6295(5)	0.054(3)
C2	0.8901(19)	0.1444(10)	0.6463(5)	0.049(3)
C3	0.030(2)	0.0828(11)	0.6564(5)	0.053(3)
C4	0.6043(19)	0.1651(10)	0.5512(5)	0.052(3)

	x/a	y/b	z/c	U(eq)
C5	0.638(2)	0.0667(11)	0.5474(6)	0.061(4)
C6	0.5488(19)	0.0263(10)	0.5828(5)	0.050(3)
C7	0.579(2)	0.2856(11)	0.7042(5)	0.054(3)
C8	0.609(2)	0.2177(12)	0.7375(5)	0.057(4)
C9	0.5289(18)	0.1367(11)	0.7236(5)	0.051(3)
C10	0.2559(18)	0.4183(10)	0.6566(5)	0.048(3)
C11	0.1731(19)	0.4360(8)	0.6139(5)	0.045(3)
C12	0.1719(19)	0.5306(10)	0.5890(5)	0.050(3)
C13	0.318(2)	0.5948(10)	0.6040(5)	0.054(3)
C14	0.3256(19)	0.5962(10)	0.6556(5)	0.049(3)
C15	0.374(2)	0.4976(11)	0.6743(5)	0.056(3)
C16	0.368(2)	0.4967(11)	0.7266(5)	0.054(3)
C17	0.514(3)	0.5568(12)	0.7440(5)	0.063(4)
C18	0.574(4)	0.687(2)	0.7906(10)	0.125(10)
C19	0.084(2)	0.7423(10)	0.5980(5)	0.055(3)
C20	0.9616(19)	0.6724(10)	0.6054(5)	0.051(3)
C21	0.794(2)	0.6967(11)	0.6223(6)	0.059(4)
C22	0.747(3)	0.7913(14)	0.6292(7)	0.076(5)
C23	0.869(2)	0.8618(13)	0.6212(8)	0.081(6)
C24	0.032(3)	0.8390(11)	0.6082(6)	0.068(5)
C25	0.011(2)	0.3604(11)	0.5226(5)	0.056(3)
C26	0.217(3)	0.1981(12)	0.5070(7)	0.074(5)
C27	0.357(2)	0.3838(12)	0.4901(5)	0.061(4)

	x/a	y/b	z/c	U(eq)
B1	0.367(2)	0.0889(11)	0.6500(6)	0.045(3)
W2	0.85361(8)	0.16146(4)	0.88412(2)	0.0435(2)
S2	0.8377(5)	0.7713(3)	0.92783(13)	0.0546(8)
P2	0.7113(5)	0.1715(3)	0.96029(12)	0.0485(8)
O4	0.1750(14)	0.0450(8)	0.9086(4)	0.061(3)
O5	0.138(2)	0.9097(11)	0.7467(6)	0.097(4)
O6	0.913(2)	0.8068(10)	0.7441(5)	0.086(4)
N9	0.6239(15)	0.2573(8)	0.8620(4)	0.047(2)
N10	0.6509(15)	0.3501(8)	0.8469(4)	0.047(2)
N11	0.9734(15)	0.2963(7)	0.9059(4)	0.046(2)
N12	0.9377(15)	0.3820(8)	0.8853(4)	0.050(3)
N13	0.9670(14)	0.2208(8)	0.8209(3)	0.044(2)
N14	0.9362(15)	0.3156(8)	0.8079(4)	0.048(3)
N15	0.0455(15)	0.0902(8)	0.8992(4)	0.050(3)
N16	0.5152(15)	0.8988(9)	0.9043(5)	0.054(3)
C28	0.449(2)	0.2496(11)	0.8599(5)	0.055(3)
C29	0.3659(19)	0.3321(11)	0.8460(5)	0.051(3)
C30	0.4992(19)	0.3935(11)	0.8375(5)	0.051(3)
C31	0.0789(19)	0.3142(11)	0.9396(5)	0.053(3)
C32	0.108(2)	0.4123(11)	0.9417(5)	0.057(4)
C33	0.016(2)	0.4523(11)	0.9061(5)	0.055(3)
C34	0.0655(18)	0.1825(10)	0.7886(5)	0.049(3)
C35	0.0955(19)	0.2514(11)	0.7536(5)	0.056(4)

	x/a	y/b	z/c	U(eq)
C36	0.0113(19)	0.3349(11)	0.7676(5)	0.051(3)
C37	0.756(2)	0.0523(10)	0.8400(5)	0.053(3)
C38	0.670(2)	0.0431(10)	0.8826(5)	0.051(3)
C39	0.6851(19)	0.9488(10)	0.9100(5)	0.050(3)
C40	0.841(2)	0.8849(10)	0.8962(5)	0.051(3)
C41	0.8475(19)	0.8745(9)	0.8462(4)	0.048(3)
C42	0.877(2)	0.9697(11)	0.8226(5)	0.057(3)
C43	0.855(2)	0.9633(10)	0.7718(5)	0.060(4)
C44	0.984(3)	0.8911(14)	0.7525(5)	0.069(4)
C45	0.030(4)	0.7338(19)	0.7289(8)	0.111(9)
C46	0.625(2)	0.7349(11)	0.9147(6)	0.062(4)
C47	0.495(2)	0.8003(11)	0.9044(5)	0.060(4)
C48	0.330(2)	0.7647(13)	0.8931(6)	0.070(4)
C49	0.293(3)	0.6707(12)	0.8928(6)	0.073(5)
C50	0.422(3)	0.6032(11)	0.9032(7)	0.074(5)
C51	0.592(3)	0.6346(11)	0.9151(6)	0.067(4)
C52	0.4891(17)	0.1272(12)	0.9704(5)	0.055(3)
C53	0.837(2)	0.1117(13)	0.0050(5)	0.064(4)
C54	0.680(2)	0.2941(11)	0.9797(6)	0.062(4)
B2	0.838(2)	0.3844(12)	0.8400(5)	0.049(4)

Table 4. Bond lengths (Å) for Compound 33.

W1-N7	1.816(12)	W1-N3	2.150(11)
W1-C10	2.195(13)	W1-C11	2.214(12)
W1-N5	2.230(10)	W1-N1	2.274(11)
W1-P1	2.516(4)	S1-C19	1.749(17)
S1-C13	1.821(13)	P1-C25	1.808(15)
P1-C27	1.812(15)	P1-C26	1.832(16)
O1-N7	1.176(16)	O2-C17	1.17(2)
O3-C17	1.36(2)	O3-C18	1.45(3)
N1-N2	1.351(15)	N1-C1	1.353(19)
N2-C3	1.327(19)	N2-B1	1.54(2)
N3-N4	1.367(16)	N3-C4	1.383(19)
N4-C6	1.334(18)	N4-B1	1.53(2)
N5-C7	1.347(19)	N5-N6	1.347(16)
N6-C9	1.361(18)	N6-B1	1.548(19)
N8-C20	1.376(18)	N8-C12	1.484(19)
N8-H8	0.880000	C1-C2	1.38(2)
C1-H1	0.950000	C2-C3	1.38(2)
C2-H2	0.950000	C3-H3	0.950000
C4-C5	1.39(2)	C4-H4	0.950000
C5-C6	1.37(2)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.37(2)
C7-H7	0.950000	C8-C9	1.37(2)
C8-H8A	0.950000	C9-H9	0.950000
C10-C11	1.44(2)	C10-C15	1.55(2)

C10-H10	1.000000	C11-C12	1.491(17)
C11-H11	1.000000	C12-C13	1.52(2)
C12-H12	1.000000	C13-C14	1.54(2)
C13-H13	1.000000	C14-C15	1.502(19)
C14-H14A	0.990000	C14-H14B	0.990000
C15-C16	1.561(19)	C15-H15	1.000000
C16-C17	1.51(2)	C16-H16A	0.990000
C16-H16B	0.990000	C18-H18A	0.980000
C18-H18B	0.980000	C18-H18C	0.980000
C19-C20	1.38(2)	C19-C24	1.43(2)
C20-C21	1.41(2)	C21-C22	1.37(2)
C21-H21	0.950000	C22-C23	1.38(3)
C22-H22	0.950000	C23-C24	1.33(3)
C23-H23	0.950000	C24-H24	0.950000
C25-H25A	0.980000	C25-H25B	0.980000
C25-H25C	0.980000	C26-H26A	0.980000
C26-H26B	0.980000	C26-H26C	0.980000
C27-H27A	0.980000	C27-H27B	0.980000
C27-H27C	0.980000	B1-H1A	1.000000
W2-N15	1.801(11)	W2-C37	2.185(13)
W2-C38	2.186(14)	W2-N13	2.215(10)
W2-N11	2.221(10)	W2-N9	2.266(11)
W2-P2	2.516(4)	S2-C46	1.760(19)
S2-C40	1.817(14)	P2-C53	1.822(15)

P2-C54	1.824(16)	P2-C52	1.838(14)
O4-N15	1.189(15)	O5-C44	1.21(2)
O6-C44	1.33(2)	O6-C45	1.42(3)
N9-C28	1.346(19)	N9-N10	1.373(16)
N10-C30	1.321(18)	N10-B2	1.53(2)
N11-C31	1.325(19)	N11-N12	1.348(16)
N12-C33	1.328(19)	N12-B2	1.56(2)
N13-C34	1.332(19)	N13-N14	1.377(15)
N14-C36	1.352(19)	N14-B2	1.55(2)
N16-C47	1.38(2)	N16-C39	1.500(19)
N16-H16	0.880000	C28-C29	1.35(2)
C28-H28	0.950000	C29-C30	1.36(2)
C29-H29	0.950000	C30-H30	0.950000
C31-C32	1.39(2)	C31-H31	0.950000
C32-C33	1.38(2)	C32-H32	0.950000
C33-H33	0.950000	C34-C35	1.42(2)
C34-H34	0.950000	C35-C36	1.38(2)
C35-H35	0.950000	C36-H36	0.950000
C37-C38	1.43(2)	C37-C42	1.55(2)
C37-H37	1.000000	C38-C39	1.527(19)
C38-H38	1.000000	C39-C40	1.53(2)
C39-H39	1.000000	C40-C41	1.50(2)
C40-H40	1.000000	C41-C42	1.504(19)
C41-H41A	0.990000	C41-H41B	0.990000

C42-C43	1.53(2)	C42-H42	1.000000
C43-C44	1.51(2)	C43-H43A	0.990000
C43-H43B	0.990000	C45-H45A	0.980000
C45-H45B	0.980000	C45-H45C	0.980000
C46-C47	1.36(2)	C46-C51	1.42(2)
C47-C48	1.41(2)	C48-C49	1.34(2)
C48-H48	0.950000	C49-C50	1.37(3)
C49-H49	0.950000	C50-C51	1.43(3)
C50-H50	0.950000	C51-H51	0.950000
C52-H52A	0.980000	C52-H52B	0.980000
C52-H52C	0.980000	C53-H53A	0.980000
C53-H53B	0.980000	C53-H53C	0.980000
C54-H54A	0.980000	C54-H54B	0.980000
C54-H54C	0.980000	B2-H2A	1.000000

Table 5. Bond angles (°) for Compound 33.

N7-W1-N3	93.5(5)	N7-W1-C10	94.5(5)
N3-W1-C10	157.8(5)	N7-W1-C11	96.0(5)
N3-W1-C11	160.0(5)	C10-W1-C11	38.1(5)
N7-W1-N5	96.3(5)	N3-W1-N5	76.2(4)
C10-W1-N5	82.5(5)	C11-W1-N5	120.0(4)
N7-W1-N1	177.4(5)	N3-W1-N1	84.0(4)
C10-W1-N1	87.4(5)	C11-W1-N1	86.7(5)

N5-W1-N1	82.2(4)	N7-W1-P1	95.6(4)
N3-W1-P1	82.7(3)	C10-W1-P1	117.0(4)
C11-W1-P1	79.0(4)	N5-W1-P1	156.3(3)
N1-W1-P1	85.1(3)	C19-S1-C13	97.5(7)
C25-P1-C27	102.6(7)	C25-P1-C26	98.7(8)
C27-P1-C26	102.7(9)	C25-P1-W1	121.2(5)
C27-P1-W1	113.9(5)	C26-P1-W1	115.1(6)
C17-O3-C18	114.7(18)	N2-N1-C1	105.3(12)
N2-N1-W1	120.1(8)	C1-N1-W1	134.5(10)
C3-N2-N1	110.8(11)	C3-N2-B1	128.3(12)
N1-N2-B1	120.6(11)	N4-N3-C4	103.1(11)
N4-N3-W1	124.3(9)	C4-N3-W1	132.6(9)
C6-N4-N3	111.5(12)	C6-N4-B1	129.7(12)
N3-N4-B1	117.9(11)	C7-N5-N6	106.4(11)
C7-N5-W1	132.8(10)	N6-N5-W1	120.8(8)
N5-N6-C9	109.1(11)	N5-N6-B1	120.7(11)
C9-N6-B1	130.1(12)	O1-N7-W1	174.6(12)
C20-N8-C12	127.5(12)	C20-N8-H8	116.300000
C12-N8-H8	116.300000	N1-C1-C2	110.6(14)
N1-C1-H1	124.700000	C2-C1-H1	124.700000
C1-C2-C3	104.8(13)	C1-C2-H2	127.600000
C3-C2-H2	127.600000	N2-C3-C2	108.3(13)
N2-C3-H3	125.800000	C2-C3-H3	125.800000
N3-C4-C5	111.8(14)	N3-C4-H4	124.100000

C5-C4-H4	124.100000	C6-C5-C4	103.8(15)
C6-C5-H5	128.100000	C4-C5-H5	128.100000
N4-C6-C5	109.8(13)	N4-C6-H6	125.100000
C5-C6-H6	125.100000	N5-C7-C8	110.9(14)
N5-C7-H7	124.500000	C8-C7-H7	124.500000
C7-C8-C9	105.1(13)	C7-C8-H8A	127.500000
C9-C8-H8A	127.500000	N6-C9-C8	108.4(13)
N6-C9-H9	125.800000	C8-C9-H9	125.800000
C11-C10-C15	117.6(12)	C11-C10-W1	71.7(8)
C15-C10-W1	119.2(10)	C11-C10-H10	114.000000
C15-C10-H10	114.000000	W1-C10-H10	114.000000
C10-C11-C12	124.2(12)	C10-C11-W1	70.2(7)
C12-C11-W1	128.3(11)	C10-C11-H11	109.500000
C12-C11-H11	109.500000	W1-C11-H11	109.500000
N8-C12-C11	107.6(12)	N8-C12-C13	110.9(11)
C11-C12-C13	112.2(12)	N8-C12-H12	108.700000
C11-C12-H12	108.700000	C13-C12-H12	108.700000
C12-C13-C14	110.7(12)	C12-C13-S1	111.2(10)
C14-C13-S1	112.6(10)	C12-C13-H13	107.400000
C14-C13-H13	107.400000	S1-C13-H13	107.400000
C15-C14-C13	110.1(11)	C15-C14-H14A	109.600000
C13-C14-H14A	109.600000	C15-C14-H14B	109.600000

C13-C14-H14B	109.600000	H14A-C14-H14B	108.100000
C14-C15-C10	112.7(12)	C14-C15-C16	110.4(12)
C10-C15-C16	110.1(13)	C14-C15-H15	107.800000
C10-C15-H15	107.800000	C16-C15-H15	107.800000
C17-C16-C15	109.8(13)	C17-C16-H16A	109.700000
C15-C16-H16A	109.700000	C17-C16-H16B	109.700000
C15-C16-H16B	109.700000	H16A-C16-H16B	108.200000
O2-C17-O3	125.3(16)	O2-C17-C16	124.9(16)
O3-C17-C16	109.7(16)	O3-C18-H18A	109.500000
O3-C18-H18B	109.500000	H18A-C18-H18B	109.500000
O3-C18-H18C	109.500000	H18A-C18-H18C	109.500000
H18B-C18-H18C	109.500000	C20-C19-C24	116.8(15)
C20-C19-S1	122.2(12)	C24-C19-S1	121.0(13)
N8-C20-C19	121.5(14)	N8-C20-C21	117.9(13)
C19-C20-C21	120.6(14)	C22-C21-C20	120.3(16)
C22-C21-H21	119.900000	C20-C21-H21	119.900000
C21-C22-C23	119.1(18)	C21-C22-H22	120.400000
C23-C22-H22	120.400000	C24-C23-C22	120.9(17)
C24-C23-H23	119.500000	C22-C23-H23	119.500000

C23-C24-C19	122.0(17)	C23-C24-H24	119.000000
C19-C24-H24	119.000000	P1-C25-H25A	109.500000
P1-C25-H25B	109.500000	H25A-C25-H25B	109.500000
P1-C25-H25C	109.500000	H25A-C25-H25C	109.500000
H25B-C25-H25C	109.500000	P1-C26-H26A	109.500000
P1-C26-H26B	109.500000	H26A-C26-H26B	109.500000
P1-C26-H26C	109.500000	H26A-C26-H26C	109.500000
H26B-C26-H26C	109.500000	P1-C27-H27A	109.500000
P1-C27-H27B	109.500000	H27A-C27-H27B	109.500000
P1-C27-H27C	109.500000	H27A-C27-H27C	109.500000
H27B-C27-H27C	109.500000	N4-B1-N2	109.5(12)
N4-B1-N6	108.2(11)	N2-B1-N6	107.7(11)
N4-B1-H1A	110.500000	N2-B1-H1A	110.500000
N6-B1-H1A	110.500000	N15-W2-C37	93.3(5)
N15-W2-C38	97.2(6)	C37-W2-C38	38.1(6)
N15-W2-N13	95.1(5)	C37-W2-N13	83.0(5)
C38-W2-N13	120.2(5)	N15-W2-N11	92.3(5)
C37-W2-N11	160.0(5)	C38-W2-N11	158.9(5)

N13-W2-N11	77.4(4)	N15-W2-N9	176.1(5)
C37-W2-N9	87.7(5)	C38-W2-N9	85.9(5)
N13-W2-N9	81.3(4)	N11-W2-N9	85.6(4)
N15-W2-P2	98.9(4)	C37-W2-P2	116.6(4)
C38-W2-P2	78.5(4)	N13-W2-P2	155.0(3)
N11-W2-P2	81.4(3)	N9-W2-P2	84.0(3)
C46-S2-C40	99.5(8)	C53-P2-C54	103.5(8)
C53-P2-C52	102.9(8)	C54-P2-C52	99.2(8)
C53-P2-W2	113.9(6)	C54-P2-W2	114.0(5)
C52-P2-W2	120.9(5)	C44-O6-C45	116.(2)
C28-N9-N10	103.2(11)	C28-N9-W2	136.5(10)
N10-N9-W2	120.2(8)	C30-N10-N9	109.9(12)
C30-N10-B2	130.4(12)	N9-N10-B2	119.5(11)
C31-N11-N12	106.1(11)	C31-N11-W2	132.0(10)
N12-N11-W2	121.8(8)	C33-N12-N11	110.5(12)
C33-N12-B2	129.9(13)	N11-N12-B2	119.1(11)
C34-N13-N14	106.0(10)	C34-N13-W2	133.2(9)
N14-N13-W2	120.8(8)	C36-N14-N13	110.7(11)
C36-N14-B2	129.4(12)	N13-N14-B2	119.8(11)
O4-N15-W2	178.1(12)	C47-N16-C39	125.6(13)
C47-N16-H16	117.200000	C39-N16-H16	117.200000

N9-C28-C29	113.2(13)	N9-C28-H28	123.400000
C29-C28-H28	123.400000	C28-C29-C30	103.7(13)
C28-C29-H29	128.200000	C30-C29-H29	128.200000
N10-C30-C29	109.9(13)	N10-C30-H30	125.000000
C29-C30-H30	125.000000	N11-C31-C32	110.8(14)
N11-C31-H31	124.600000	C32-C31-H31	124.600000
C33-C32-C31	104.2(14)	C33-C32-H32	127.900000
C31-C32-H32	127.900000	N12-C33-C32	108.3(13)
N12-C33-H33	125.800000	C32-C33-H33	125.800000
N13-C34-C35	110.6(13)	N13-C34-H34	124.700000
C35-C34-H34	124.700000	C36-C35-C34	105.0(13)
C36-C35-H35	127.500000	C34-C35-H35	127.500000
N14-C36-C35	107.8(12)	N14-C36-H36	126.100000
C35-C36-H36	126.100000	C38-C37-C42	120.6(13)
C38-C37-W2	71.0(8)	C42-C37-W2	121.6(10)
C38-C37-H37	112.600000	C42-C37-H37	112.600000
W2-C37-H37	112.600000	C37-C38-C39	120.3(13)
C37-C38-W2	70.9(8)	C39-C38-W2	125.8(10)
C37-C38-H38	111.300000	C39-C38-H38	111.300000
W2-C38-H38	111.300000	N16-C39-C38	106.4(11)
N16-C39-C40	111.3(11)	C38-C39-C40	113.2(12)

N16-C39-H39	108.600000	C38-C39-H39	108.600000
C40-C39-H39	108.600000	C41-C40-C39	110.9(12)
C41-C40-S2	114.3(10)	C39-C40-S2	109.7(10)
C41-C40-H40	107.200000	C39-C40-H40	107.200000
S2-C40-H40	107.200000	C40-C41-C42	111.2(12)
C40-C41-H41A	109.400000	C42-C41-H41A	109.400000
C40-C41-H41B	109.400000	C42-C41-H41B	109.400000
H41A-C41-H41B	108.000000	C41-C42-C43	111.7(12)
C41-C42-C37	113.3(13)	C43-C42-C37	109.0(12)
C41-C42-H42	107.500000	C43-C42-H42	107.500000
C37-C42-H42	107.500000	C44-C43-C42	111.0(13)
C44-C43-H43A	109.400000	C42-C43-H43A	109.400000
C44-C43-H43B	109.400000	C42-C43-H43B	109.400000
H43A-C43-H43B	108.000000	O5-C44-O6	125.1(18)
O5-C44-C43	121.7(19)	O6-C44-C43	113.2(17)
O6-C45-H45A	109.500000	O6-C45-H45B	109.500000
H45A-C45-H45B	109.500000	O6-C45-H45C	109.500000
H45A-C45-H45C	109.500000	H45B-C45-H45C	109.500000

C47-C46-C51	120.1(17)	C47-C46-S2	121.5(12)
C51-C46-S2	118.4(14)	C46-C47-N16	123.8(15)
C46-C47-C48	117.6(15)	N16-C47-C48	118.6(16)
C49-C48-C47	124.2(19)	C49-C48-H48	117.900000
C47-C48-H48	117.900000	C48-C49-C50	119.6(18)
C48-C49-H49	120.200000	C50-C49-H49	120.200000
C49-C50-C51	119.1(15)	C49-C50-H50	120.400000
C51-C50-H50	120.400000	C46-C51-C50	119.4(17)
C46-C51-H51	120.300000	C50-C51-H51	120.300000
P2-C52-H52A	109.500000	P2-C52-H52B	109.500000
H52A-C52-H52B	109.500000	P2-C52-H52C	109.500000
H52A-C52-H52C	109.500000	H52B-C52-H52C	109.500000
P2-C53-H53A	109.500000	P2-C53-H53B	109.500000
H53A-C53-H53B	109.500000	P2-C53-H53C	109.500000
H53A-C53-H53C	109.500000	H53B-C53-H53C	109.500000
P2-C54-H54A	109.500000	P2-C54-H54B	109.500000
H54A-C54-H54B	109.500000	P2-C54-H54C	109.500000
H54A-C54-H54C	109.500000	H54B-C54-H54C	109.500000
N10-B2-N14	108.9(12)	N10-B2-N12	110.4(12)
N14-B2-N12	108.0(12)	N10-B2-H2A	109.800000

N14-B2-H2A	109.800000	N12-B2-H2A	109.800000

Table 6. Torsion angles (°) for Compound 33.

C1-N1-N2-C3	-2.8(15)	W1-N1-N2-C3	176.5(9)
C1-N1-N2-B1	-177.9(12)	W1-N1-N2-B1	1.4(16)
C4-N3-N4-C6	-0.7(15)	W1-N3-N4-C6	176.5(9)
C4-N3-N4-B1	169.4(12)	W1-N3-N4-B1	-13.3(16)
C7-N5-N6-C9	2.7(15)	W1-N5-N6-C9	-173.8(9)
C7-N5-N6-B1	-175.0(12)	W1-N5-N6-B1	8.5(15)
N2-N1-C1-C2	1.3(16)	W1-N1-C1-C2	-177.8(9)
N1-C1-C2-C3	0.5(17)	N1-N2-C3-C2	3.2(16)
B1-N2-C3-C2	177.8(14)	C1-C2-C3-N2	-2.2(16)
N4-N3-C4-C5	2.3(15)	W1-N3-C4-C5	-174.6(10)
N3-C4-C5-C6	-3.0(17)	N3-N4-C6-C5	-1.2(17)
B1-N4-C6-C5	-169.8(14)	C4-C5-C6-N4	2.5(17)
N6-N5-C7-C8	-1.6(16)	W1-N5-C7-C8	174.3(10)
N5-C7-C8-C9	-0.1(17)	N5-N6-C9-C8	-2.8(16)
B1-N6-C9-C8	174.6(14)	C7-C8-C9-N6	1.7(17)
C15-C10-C11-C12	-9.(2)	W1-C10-C11-C12	-123.5(15)
C15-C10-C11-W1	114.0(12)	C20-N8-C12-C11	136.5(15)

C20-N8-C12-C13	13.(2)	C10-C11-C12-N8	-101.7(16)
W1-C11-C12-N8	167.4(9)	C10-C11-C12-C13	21.(2)
W1-C11-C12-C13	-70.4(15)	N8-C12-C13-C14	73.8(14)
C11-C12-C13-C14	-46.5(16)	N8-C12-C13-S1	-52.2(14)
C11-C12-C13-S1	-172.5(10)	C19-S1-C13-C12	57.2(12)
C19-S1-C13-C14	-67.7(12)	C12-C13-C14-C15	64.4(15)
S1-C13-C14-C15	-170.4(11)	C13-C14-C15-C10	-52.1(17)
C13-C14-C15-C16	-175.7(13)	C11-C10-C15-C14	25.3(18)
W1-C10-C15-C14	108.8(12)	C11-C10-C15-C16	149.1(13)
W1-C10-C15-C16	-127.5(11)	C14-C15-C16-C17	-68.2(17)
C10-C15-C16-C17	166.7(13)	C18-O3-C17-O2	5.(3)
C18-O3-C17-C16	-177.9(18)	C15-C16-C17-O2	-56.(2)
C15-C16-C17-O3	127.3(14)	C13-S1-C19-C20	-30.7(14)
C13-S1-C19-C24	147.5(13)	C12-N8-C20-C19	17.(2)
C12-N8-C20-C21	-163.9(14)	C24-C19-C20-N8	178.9(14)

S1-C19-C20-N8	-3.(2)	C24-C19-C20-C21	0.(2)
S1-C19-C20-C21	178.4(12)	N8-C20-C21-C22	-175.4(16)
C19-C20-C21-C22	4.(2)	C20-C21-C22-C23	-3.(3)
C21-C22-C23-C24	-2.(3)	C22-C23-C24-C19	6.(3)
C20-C19-C24-C23	-5.(2)	S1-C19-C24-C23	177.0(15)
C6-N4-B1-N2	-125.5(15)	N3-N4-B1-N2	66.5(15)
C6-N4-B1-N6	117.5(15)	N3-N4-B1-N6	-50.5(16)
C3-N2-B1-N4	127.0(15)	N1-N2-B1-N4	-58.8(16)
C3-N2-B1-N6	-115.7(16)	N1-N2-B1-N6	58.5(16)
N5-N6-B1-N4	52.7(16)	C9-N6-B1-N4	-124.4(15)
N5-N6-B1-N2	-65.4(16)	C9-N6-B1-N2	117.4(15)
C28-N9-N10-C30	1.0(16)	W2-N9-N10-C30	-177.7(9)
C28-N9-N10-B2	-174.0(12)	W2-N9-N10-B2	7.2(16)
C31-N11-N12-C33	-1.4(15)	W2-N11-N12-C33	176.0(9)
C31-N11-N12-B2	171.2(12)	W2-N11-N12-B2	-11.4(16)
C34-N13-N14-C36	1.4(15)	W2-N13-N14-C36	-177.3(9)

C34-N13-N14-B2	-174.8(12)	W2-N13-N14-B2	6.5(16)
N10-N9-C28-C29	-2.2(18)	W2-N9-C28-C29	176.3(10)
N9-C28-C29-C30	2.4(19)	N9-N10-C30-C29	0.4(16)
B2-N10-C30-C29	174.7(14)	C28-C29-C30-N10	-1.6(17)
N12-N11-C31-C32	1.7(16)	W2-N11-C31-C32	-175.3(10)
N11-C31-C32-C33	-1.4(17)	N11-N12-C33-C32	0.5(17)
B2-N12-C33-C32	-171.0(14)	C31-C32-C33-N12	0.5(17)
N14-N13-C34-C35	-1.6(15)	W2-N13-C34-C35	176.9(10)
N13-C34-C35-C36	1.3(16)	N13-N14-C36-C35	-0.7(16)
B2-N14-C36-C35	175.1(14)	C34-C35-C36-N14	-0.3(16)
C42-C37-C38-C39	-5.(2)	W2-C37-C38-C39	-121.0(13)
C42-C37-C38-W2	116.1(13)	C47-N16-C39-C38	148.3(14)
C47-N16-C39-C40	25.(2)	C37-C38-C39-N16	-102.7(15)
W2-C38-C39-N16	169.9(10)	C37-C38-C39-C40	19.9(19)
W2-C38-C39-C40	-67.5(16)	N16-C39-C40-C41	71.0(15)

C38-C39-C40-C41	-48.8(16)	N16-C39-C40-S2	-56.1(14)
C38-C39-C40-S2	-175.8(10)	C46-S2-C40-C41	-70.1(12)
C46-S2-C40-C39	55.1(11)	C39-C40-C41-C42	63.9(16)
S2-C40-C41-C42	-171.6(11)	C40-C41-C42-C43	-171.1(13)
C40-C41-C42-C37	-47.6(17)	C38-C37-C42-C41	18.6(19)
W2-C37-C42-C41	103.9(14)	C38-C37-C42-C43	143.6(14)
W2-C37-C42-C43	-131.1(12)	C41-C42-C43-C44	-60.1(19)
C37-C42-C43-C44	174.0(14)	C45-O6-C44-O5	3.(3)
C45-O6-C44-C43	-175.8(16)	C42-C43-C44-O5	-77.(2)
C42-C43-C44-O6	101.5(17)	C40-S2-C46-C47	-27.7(15)
C40-S2-C46-C51	152.2(13)	C51-C46-C47-N16	178.4(15)
S2-C46-C47-N16	-2.(2)	C51-C46-C47-C48	-2.(2)
S2-C46-C47-C48	178.2(13)	C39-N16-C47-C46	8.(3)
C39-N16-C47-C48	-172.3(15)	C46-C47-C48-C49	1.(3)
N16-C47-C48-C49	-178.6(17)	C47-C48-C49-C50	-1.(3)

C48-C49-C50-C51	1.(3)	C47-C46-C51-C50	2.(2)
S2-C46-C51-C50	-178.1(13)	C49-C50-C51-C46	-2.(3)
C30-N10-B2-N14	-118.6(15)	N9-N10-B2-N14	55.3(15)
C30-N10-B2-N12	123.0(15)	N9-N10-B2-N12	-63.1(16)
C36-N14-B2-N10	120.0(15)	N13-N14-B2-N10	-64.7(15)
C36-N14-B2-N12	-120.1(15)	N13-N14-B2-N12	55.3(16)
C33-N12-B2-N10	-122.5(15)	N11-N12-B2-N10	66.5(15)
C33-N12-B2-N14	118.5(15)	N11-N12-B2-N14	-52.5(16)

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for Compound 33.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.0498(4)	0.0418(3)	0.0380(3)	-0.0015(2)	-0.0036(2)	0.0002(2)
S1	0.065(2)	0.0465(18)	0.053(2)	0.0019(15)	-0.0076(16)	-0.0031(15)
P1	0.0554(19)	0.0459(17)	0.0420(18)	-0.0021(14)	-0.0055(14)	0.0005(14)
O1	0.059(6)	0.071(7)	0.052(6)	-0.003(5)	0.005(5)	-0.006(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.076(8)	0.072(8)	0.072(8)	-0.001(6)	-0.013(6)	-0.007(6)
O3	0.112(10)	0.085(9)	0.063(8)	-0.019(7)	0.008(7)	-0.037(8)
N1	0.055(6)	0.036(5)	0.039(6)	-0.003(4)	-0.003(5)	0.002(4)
N2	0.053(6)	0.047(6)	0.047(6)	0.007(5)	-0.006(5)	-0.001(5)
N3	0.053(6)	0.044(6)	0.042(6)	-0.003(5)	-0.001(5)	0.000(5)
N4	0.057(7)	0.042(6)	0.046(6)	-0.003(5)	-0.005(5)	-0.002(5)
N5	0.047(6)	0.045(6)	0.037(6)	0.002(4)	-0.001(4)	0.003(4)
N6	0.056(6)	0.044(6)	0.044(6)	-0.010(5)	-0.002(5)	-0.003(5)
N7	0.053(7)	0.044(6)	0.060(7)	-0.005(5)	0.004(6)	-0.007(5)
N8	0.053(6)	0.035(6)	0.070(8)	-0.005(5)	-0.005(6)	0.004(5)
C1	0.060(8)	0.069(9)	0.035(7)	-0.009(6)	-0.007(6)	-0.007(7)
C2	0.054(8)	0.044(7)	0.051(8)	-0.008(6)	0.006(6)	-0.014(6)
C3	0.061(8)	0.056(8)	0.040(7)	0.004(6)	-0.001(6)	-0.006(7)
C4	0.054(8)	0.051(8)	0.051(8)	-0.008(6)	-0.009(6)	0.006(6)
C5	0.068(9)	0.057(9)	0.058(9)	0.001(7)	-0.012(8)	0.008(7)
C6	0.058(8)	0.038(6)	0.056(8)	-0.010(6)	-0.014(6)	0.008(6)
C7	0.062(8)	0.055(8)	0.046(8)	-0.010(6)	0.002(6)	0.003(7)
C8	0.056(8)	0.073(10)	0.042(8)	0.010(7)	-0.010(6)	-0.005(7)
C9	0.045(7)	0.061(8)	0.047(8)	0.002(6)	-0.005(6)	-0.005(6)
C10	0.050(7)	0.047(7)	0.048(7)	-0.012(6)	0.000(6)	0.003(6)
C11	0.062(8)	0.024(5)	0.049(7)	0.000(5)	-0.014(6)	0.007(5)
C12	0.064(8)	0.048(7)	0.038(7)	0.001(6)	-0.001(6)	-0.001(6)
C13	0.069(9)	0.036(7)	0.055(8)	0.010(6)	0.000(7)	0.013(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	0.050(7)	0.048(7)	0.050(8)	-0.011(6)	-0.007(6)	0.005(6)
C15	0.063(9)	0.058(8)	0.046(8)	0.004(6)	-0.007(7)	0.007(7)
C16	0.073(9)	0.054(8)	0.035(7)	-0.009(6)	-0.001(6)	-0.003(7)
C17	0.083(12)	0.062(9)	0.043(8)	0.000(7)	-0.015(8)	-0.006(8)
C18	0.15(2)	0.13(2)	0.11(2)	-0.043(17)	0.013(18)	-0.063(19)
C19	0.064(9)	0.047(8)	0.054(8)	0.000(6)	-0.014(7)	0.006(6)
C20	0.055(8)	0.051(8)	0.048(8)	-0.004(6)	-0.014(6)	-0.004(6)
C21	0.053(8)	0.050(8)	0.075(11)	0.001(7)	-0.004(7)	0.006(6)
C22	0.068(11)	0.077(12)	0.086(13)	-0.026(10)	-0.015(9)	0.003(9)
C23	0.070(11)	0.060(10)	0.114(16)	-0.027(10)	-0.044(11)	0.019(9)
C24	0.086(12)	0.046(8)	0.073(11)	-0.003(7)	-0.038(9)	-0.006(8)
C25	0.059(8)	0.063(9)	0.045(8)	0.008(7)	-0.010(6)	-0.002(7)
C26	0.085(12)	0.059(9)	0.080(12)	-0.020(8)	-0.035(10)	0.018(8)
C27	0.069(9)	0.073(10)	0.040(7)	0.009(7)	-0.002(7)	-0.007(8)
B1	0.050(8)	0.039(7)	0.048(9)	-0.005(6)	0.001(7)	0.000(6)
W2	0.0492(4)	0.0431(3)	0.0383(3)	-0.0010(2)	-0.0020(2)	-0.0041(2)
S2	0.066(2)	0.0479(18)	0.0498(19)	0.0021(15)	-0.0002(16)	-0.0042(15)
P2	0.0534(19)	0.0474(18)	0.0448(18)	-0.0020(14)	-0.0001(15)	-0.0039(14)
O4	0.056(6)	0.068(7)	0.059(6)	0.003(5)	-0.006(5)	0.013(5)
O5	0.097(11)	0.089(10)	0.104(12)	0.003(8)	0.016(9)	0.015(8)
O6	0.102(10)	0.067(8)	0.090(10)	-0.020(7)	0.001(8)	0.005(7)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N9	0.050(6)	0.046(6)	0.044(6)	0.007(5)	-0.005(5)	-0.007(5)
N10	0.051(6)	0.047(6)	0.042(6)	-0.006(5)	-0.001(5)	0.000(5)
N11	0.054(6)	0.035(5)	0.048(6)	-0.010(5)	-0.002(5)	-0.004(4)
N12	0.049(6)	0.050(6)	0.051(7)	-0.012(5)	0.004(5)	-0.004(5)
N13	0.048(6)	0.051(6)	0.032(5)	0.010(4)	-0.001(4)	-0.009(5)
N14	0.050(6)	0.045(6)	0.049(6)	-0.005(5)	-0.001(5)	0.000(5)
N15	0.051(6)	0.048(6)	0.051(7)	-0.009(5)	-0.005(5)	0.006(5)
N16	0.047(6)	0.049(6)	0.065(8)	0.005(6)	-0.004(5)	-0.001(5)
C28	0.064(9)	0.053(8)	0.049(8)	0.011(6)	-0.001(7)	-0.013(7)
C29	0.049(7)	0.057(8)	0.045(7)	0.011(6)	0.000(6)	0.003(6)
C30	0.059(8)	0.045(7)	0.050(8)	-0.003(6)	-0.003(6)	0.006(6)
C31	0.050(7)	0.054(8)	0.056(8)	-0.009(7)	-0.001(6)	-0.003(6)
C32	0.059(8)	0.057(8)	0.057(9)	-0.012(7)	0.012(7)	-0.023(7)
C33	0.071(9)	0.050(8)	0.044(8)	-0.003(6)	0.004(7)	-0.007(7)
C34	0.046(7)	0.049(7)	0.053(8)	0.003(6)	-0.004(6)	-0.005(6)
C35	0.053(8)	0.071(10)	0.045(8)	0.001(7)	0.003(6)	-0.010(7)
C36	0.057(8)	0.052(8)	0.045(7)	0.007(6)	0.003(6)	-0.008(6)
C37	0.068(9)	0.042(7)	0.050(8)	-0.013(6)	-0.016(7)	-0.001(6)
C38	0.062(8)	0.047(7)	0.044(7)	0.000(6)	-0.009(6)	-0.012(6)
C39	0.054(8)	0.048(7)	0.047(7)	-0.006(6)	-0.003(6)	-0.005(6)
C40	0.057(8)	0.043(7)	0.051(8)	0.000(6)	-0.008(6)	-0.004(6)
C41	0.059(8)	0.042(7)	0.043(7)	0.001(5)	-0.012(6)	-0.001(6)
C42	0.065(9)	0.057(8)	0.049(8)	0.003(7)	-0.005(7)	-0.002(7)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C43	0.086(11)	0.038(7)	0.055(9)	0.000(6)	0.005(8)	-0.004(7)
C44	0.085(12)	0.077(11)	0.043(8)	0.003(8)	0.007(8)	0.009(9)
C45	0.13(2)	0.12(2)	0.081(15)	-0.008(14)	0.006(14)	0.049(17)
C46	0.076(10)	0.050(8)	0.061(9)	-0.017(7)	0.025(8)	-0.007(7)
C47	0.077(10)	0.055(9)	0.049(8)	-0.009(7)	0.004(7)	-0.016(8)
C48	0.071(10)	0.064(10)	0.075(11)	-0.009(8)	-0.002(9)	-0.010(8)
C49	0.087(12)	0.061(10)	0.073(11)	-0.025(9)	0.020(9)	-0.029(9)
C50	0.097(13)	0.040(8)	0.085(13)	-0.023(8)	0.023(10)	-0.011(8)
C51	0.085(11)	0.046(8)	0.071(11)	-0.007(7)	0.023(9)	-0.003(8)
C52	0.041(7)	0.080(10)	0.043(8)	0.000(7)	0.003(6)	-0.009(6)
C53	0.076(10)	0.081(11)	0.035(7)	0.005(7)	-0.009(7)	-0.001(8)
C54	0.070(10)	0.051(8)	0.065(10)	-0.004(7)	0.013(8)	-0.002(7)
B2	0.071(10)	0.042(8)	0.035(8)	0.008(6)	-0.002(7)	0.004(7)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 33.

	x/a	y/b	z/c	U(eq)
H8	-0.0938	0.5403	0.5941	0.063000
H1	-0.0982	0.2833	0.6197	0.065000
H2	-0.2313	0.1324	0.6502	0.059000
H3	0.0221	0.0200	0.6696	0.063000
H4	0.6533	0.2132	0.5320	0.062000

	x/a	y/b	z/c	U(eq)
H5	0.7076	0.0350	0.5253	0.074000
H6	0.5486	-0.0405	0.5904	0.061000
H7	0.6188	0.3498	0.7044	0.065000
H8A	0.6718	0.2252	0.7645	0.068000
H9	0.5236	0.0771	0.7399	0.061000
H10	0.1774	0.3890	0.6799	0.057000
H11	0.0517	0.4104	0.6149	0.054000
H12	0.1877	0.5187	0.5563	0.060000
H13	0.4311	0.5659	0.5931	0.064000
H14A	0.4135	0.6428	0.6648	0.059000
H14B	0.2100	0.6170	0.6678	0.059000
H15	0.4974	0.4822	0.6647	0.067000
H16A	0.2536	0.5229	0.7370	0.065000
H16B	0.3820	0.4296	0.7384	0.065000
H18A	0.5860	0.7434	0.7701	0.187000
H18B	0.6880	0.6535	0.7934	0.187000
H18C	0.5352	0.7089	0.8201	0.187000
H21	-0.2872	0.6474	0.6289	0.071000
H22	-0.3678	0.8081	0.6393	0.092000
H23	-0.1632	0.9275	0.6251	0.097000
H24	0.1156	0.8882	0.6056	0.082000
H25A	-0.0042	0.4246	0.5350	0.084000
H25B	-0.0712	0.3163	0.5373	0.084000

	x/a	y/b	z/c	U(eq)
H25C	-0.0118	0.3639	0.4903	0.084000
H26A	0.1559	0.2050	0.4783	0.111000
H26B	0.1514	0.1553	0.5274	0.111000
H26C	0.3349	0.1707	0.5021	0.111000
H27A	0.3111	0.3713	0.4602	0.091000
H27B	0.4805	0.3636	0.4915	0.091000
H27C	0.3451	0.4527	0.4958	0.091000
H1A	0.3690	0.0211	0.6623	0.055000
H16	0.4203	0.9354	0.9006	0.065000
H28	0.3893	1.1920	0.8673	0.066000
H29	0.2434	1.3444	0.8430	0.061000
H30	0.4851	1.4579	0.8264	0.062000
H31	1.1278	1.2666	0.9595	0.064000
H32	1.1764	1.4444	0.9628	0.069000
H33	1.0089	1.5188	0.8979	0.066000
H34	1.1095	1.1179	0.7889	0.059000
H35	1.1595	1.2423	0.7266	0.067000
H36	1.0070	1.3950	0.7516	0.062000
H37	0.6768	1.0802	0.8162	0.064000
H38	0.5462	1.0677	0.8812	0.061000
H39	0.6976	0.9643	0.9424	0.060000
H40	0.9501	0.9183	0.9048	0.061000
H41A	0.7357	0.8481	0.8361	0.057000

	x/a	y/b	z/c	U(eq)
H41B	0.9433	0.8285	0.8383	0.057000
H42	1.0010	0.9877	0.8282	0.068000
H43A	0.7342	0.9441	0.7652	0.072000
H43B	0.8735	1.0275	0.7574	0.072000
H45A	1.0378	0.7374	0.6961	0.167000
H45B	0.9874	0.6705	0.7385	0.167000
H45C	1.1466	0.7428	0.7415	0.167000
H48	0.2398	0.8100	0.8852	0.084000
H49	0.1789	0.6512	0.8854	0.088000
H50	0.3977	0.5365	0.9026	0.089000
H51	0.6814	0.5888	0.9231	0.081000
H52A	0.4084	1.1580	0.9486	0.082000
H52B	0.4509	1.1428	1.0008	0.082000
H52C	0.4894	1.0573	0.9670	0.082000
H53A	0.8354	1.0418	1.0015	0.096000
H53B	0.7856	1.1280	1.0341	0.096000
H53C	0.9587	1.1330	1.0035	0.096000
H54A	0.7940	1.3231	0.9838	0.093000
H54B	0.6155	1.2928	1.0083	0.093000
H54C	0.6124	1.3324	0.9574	0.093000
H2A	0.8358	1.4514	0.8267	0.059000

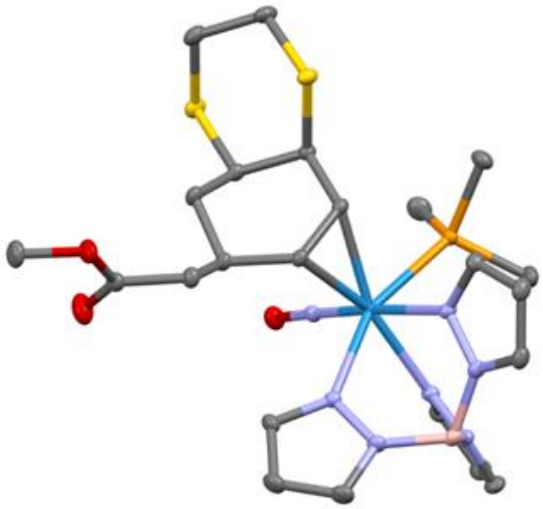
Table 9. Hydrogen bond distances (Å) and angles (°) for Compound 33.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N8-H8···O1#1	0.88	2.34	3.217(17)	175.7
N16-H16···O4#1	0.88	2.40	3.259(16)	166.2

Symmetry transformations used to generate equivalent atoms:

#1 x-1, y, z

Structure Report for Compound 35



A colourless, block shaped crystal of Compound 35 measuring 0.091×0.143×0.293 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 35 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800 low temperature device. Data collection and processing were

done within the Bruker APEX5 software suite.[197] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).
The structure was solved by direct methods with SHELXT[198] and refined by full-matrix least-squares methods against F^2 using XL[199] within OLEX2.[200] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atom as well as H10 and H11 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[201]

Table 1 Crystal data and structure refinement for Compound 35

CCDC number	
Empirical formula	$C_{23}H_{35}BN_7O_3PS_2W$
Formula weight	747.33
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.091×0.143×0.293
Crystal habit	colourless block
Crystal system	triclinic
Space group	$P\overline{1}$ (2)
a [Å]	10.9448(5)
b [Å]	11.7132(6)
c [Å]	12.6725(6)
α [°]	113.7540(10)
β [°]	101.3110(10)
γ [°]	94.751(2)
Volume [$Å^3$]	1434.19(12)
Z	2
ρ_{calc} [gcm^{-3}]	1.731
μ [mm^{-1}]	4.267
F(000)	744

[197] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[198] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[199] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[200] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[201] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

2θ range [°]	3.63 to 59.19 (0.72 Å)
Index ranges	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −17 ≤ l ≤ 17
Reflections collected	47593
Independent reflections	8034 [R_{int} = 0.0312]
Data / Restraints / Parameters	8034 / 0 / 359
Goodness-of-fit on F^2	1.067
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0155 wR_2 = 0.0340
Final R indexes [all data]	R_1 = 0.0163 wR_2 = 0.0343
Largest peak/hole [eÅ^{-3}]	1.48/−0.54

Table 1 Atomic coordinates and Ueq [Å2] for Compound 35

Atom	***x***	***y***	***z***	U_{eq}
W1	0.75916(2)	0.60842(2)	0.33479(2)	0.01029(2)
S1	0.71117(4)	0.10407(3)	0.02827(3)	0.01738(7)
S2	0.67636(4)	0.32356(3)	−0.08570(3)	0.01684(7)
P1	0.96707(4)	0.61510(4)	0.28176(3)	0.01324(7)
O1	0.80501(11)	0.39925(11)	0.40873(11)	0.0191(2)
O2	0.29195(13)	0.23710(13)	0.21203(13)	0.0290(3)
O3	0.17719(11)	0.25325(11)	0.05297(11)	0.0207(2)
N1	0.73686(12)	0.77880(12)	0.29578(11)	0.0135(2)
N2	0.72822(12)	0.89125(12)	0.38299(11)	0.0139(2)
N3	0.86961(12)	0.75193(12)	0.51211(11)	0.0135(2)
N4	0.84493(12)	0.87115(12)	0.56419(11)	0.0149(2)
N5	0.61049(12)	0.67687(12)	0.43132(11)	0.0136(2)
N6	0.61299(12)	0.80328(12)	0.49304(12)	0.0155(2)
N7	0.78439(11)	0.48366(12)	0.37650(11)	0.0124(2)
C1	0.72821(15)	0.79810(14)	0.19722(14)	0.0162(3)
H1	0.731339	0.735426	0.121965	0.019
C2	0.71405(15)	0.92216(15)	0.22013(15)	0.0185(3)
H2	0.705776	0.959961	0.165966	0.022

C3	0.71474(14)	0.97796(14)	0.33908(14)	0.0170(3)
H3	0.706974	1.063445	0.382794	0.020
C4	0.96545(14)	0.74205(15)	0.58939(14)	0.0167(3)
H4	1.001786	0.668106	0.576123	0.020
C5	1.00470(15)	0.85565(17)	0.69235(14)	0.0207(3)
H5	1.071537	0.874610	0.760596	0.025
C6	0.92495(15)	0.93439(16)	0.67314(14)	0.0195(3)
H6	0.926223	1.019052	0.727608	0.023
C7	0.51083(14)	0.61698(15)	0.44687(14)	0.0168(3)
H7	0.486411	0.527446	0.413879	0.020
C8	0.44765(15)	0.70350(17)	0.51792(15)	0.0213(3)
H8	0.374067	0.685825	0.541871	0.026
C9	0.51589(15)	0.82044(16)	0.54562(15)	0.0202(3)
H9	0.497583	0.900032	0.593805	0.024
C10	0.69938(14)	0.48915(13)	0.13861(13)	0.0128(2)
C11	0.59008(13)	0.50045(13)	0.18817(13)	0.0126(2)
C12	0.50905(13)	0.38471(13)	0.18389(13)	0.0134(3)
H12	0.531238	0.384920	0.264374	0.016
C13	0.53101(14)	0.25927(14)	0.09195(14)	0.0160(3)
H13A	0.491980	0.187479	0.103843	0.019
H13B	0.490421	0.248035	0.010540	0.019
C14	0.67222(14)	0.25980(13)	0.10534(13)	0.0145(3)
H14	0.710563	0.287307	0.192102	0.017
C15	0.73306(14)	0.35969(13)	0.07309(13)	0.0132(3)
H15	0.827186	0.366460	0.093655	0.016
C16	0.71389(17)	0.16764(15)	−0.15883(14)	0.0210(3)
H16A	0.686854	0.138884	−0.246138	0.025
H16B	0.806858	0.173342	−0.136706	0.025
C17	0.65100(17)	0.06988(15)	−0.12684(14)	0.0204(3)
H17A	0.665811	−0.015057	−0.177351	0.025
H17B	0.558453	0.068097	−0.143623	0.025
C18	0.36923(14)	0.39688(14)	0.15423(14)	0.0156(3)
H18A	0.356622	0.476455	0.216341	0.019
H18B	0.348763	0.403266	0.077382	0.019
C19	0.27865(14)	0.28775(15)	0.14591(14)	0.0163(3)
C20	0.08225(16)	0.15143(17)	0.03813(17)	0.0254(3)
H20A	0.010194	0.136926	−0.028226	0.038

H20B	0.053586	0.174085	0.111389	0.038
H20C	0.118377	0.074020	0.021114	0.038
C21	1.08695(17)	0.75525(18)	0.38000(16)	0.0271(4)
H21A	1.050827	0.831640	0.389889	0.041
H21B	1.159310	0.755385	0.345122	0.041
H21C	1.115153	0.754062	0.457827	0.041
C22	0.97232(16)	0.61369(17)	0.13830(14)	0.0203(3)
H22A	0.917600	0.536879	0.074042	0.030
H22B	1.059543	0.614804	0.130080	0.030
H22C	0.942638	0.688615	0.133680	0.030
C23	1.05197(16)	0.48933(17)	0.28640(16)	0.0231(3)
H23A	1.081799	0.502246	0.369215	0.035
H23B	1.124665	0.490900	0.252203	0.035
H23C	0.995163	0.407110	0.240276	0.035
B1	0.72307(16)	0.90303(16)	0.50722(15)	0.0154(3)
H1A	0.708(2)	0.993(2)	0.5589(19)	0.022(5)
H11	0.5388(19)	0.5620(19)	0.1768(18)	0.013(5)
H10	0.711(2)	0.542(2)	0.0966(19)	0.018(5)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 1 Anisotropic displacement parameters (Å^2) for Compound 35. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01049(3)	0.00967(3)	0.01005(3)	0.00358(2)	0.00248(2)	0.00203(2)
S1	0.02209(18)	0.01199(15)	0.01832(17)	0.00637(13)	0.00451(14)	0.00653(13)
S2	0.02441(18)	0.01330(16)	0.01191(15)	0.00441(13)	0.00420(13)	0.00480(13)
P1	0.01285(16)	0.01296(16)	0.01314(16)	0.00448(13)	0.00451(13)	0.00117(13)
O1	0.0188(5)	0.0208(5)	0.0237(6)	0.0151(5)	0.0053(4)	0.0063(4)
O2	0.0242(6)	0.0341(7)	0.0347(7)	0.0245(6)	0.0015(5)	−0.0007(5)
O3	0.0146(5)	0.0236(6)	0.0210(6)	0.0099(5)	0.0006(4)	−0.0036(4)
N1	0.0148(6)	0.0119(5)	0.0108(5)	0.0024(4)	0.0018(4)	0.0023(4)
N2	0.0140(6)	0.0106(5)	0.0158(6)	0.0043(5)	0.0038(4)	0.0036(4)
N3	0.0127(5)	0.0148(6)	0.0121(5)	0.0043(5)	0.0037(4)	0.0030(4)
N4	0.0148(6)	0.0135(6)	0.0129(6)	0.0025(5)	0.0029(4)	0.0017(4)
N5	0.0129(5)	0.0138(5)	0.0121(5)	0.0037(5)	0.0030(4)	0.0022(4)
N6	0.0143(6)	0.0153(6)	0.0161(6)	0.0044(5)	0.0065(5)	0.0052(5)

N7	0.0092(5)	0.0143(5)	0.0133(5)	0.0051(5)	0.0035(4)	0.0026(4)
C1	0.0179(7)	0.0150(7)	0.0143(7)	0.0065(5)	0.0014(5)	0.0017(5)
C2	0.0188(7)	0.0154(7)	0.0210(7)	0.0097(6)	0.0005(6)	0.0017(5)
C3	0.0149(7)	0.0122(6)	0.0226(7)	0.0074(6)	0.0019(5)	0.0028(5)
C4	0.0134(6)	0.0213(7)	0.0160(7)	0.0091(6)	0.0030(5)	0.0029(5)
C5	0.0170(7)	0.0260(8)	0.0150(7)	0.0077(6)	−0.0005(6)	−0.0012(6)
C6	0.0202(7)	0.0189(7)	0.0126(7)	0.0019(6)	0.0021(6)	−0.0010(6)
C7	0.0151(7)	0.0204(7)	0.0150(7)	0.0077(6)	0.0047(5)	0.0012(5)
C8	0.0167(7)	0.0284(8)	0.0207(8)	0.0103(7)	0.0093(6)	0.0047(6)
C9	0.0173(7)	0.0243(8)	0.0194(7)	0.0067(6)	0.0092(6)	0.0080(6)
C10	0.0156(6)	0.0102(6)	0.0116(6)	0.0046(5)	0.0016(5)	0.0019(5)
C11	0.0123(6)	0.0107(6)	0.0127(6)	0.0039(5)	0.0011(5)	0.0019(5)
C12	0.0126(6)	0.0118(6)	0.0140(6)	0.0042(5)	0.0021(5)	0.0018(5)
C13	0.0160(7)	0.0104(6)	0.0189(7)	0.0039(5)	0.0044(5)	0.0013(5)
C14	0.0169(7)	0.0111(6)	0.0144(6)	0.0046(5)	0.0031(5)	0.0035(5)
C15	0.0145(6)	0.0119(6)	0.0125(6)	0.0044(5)	0.0032(5)	0.0031(5)
C16	0.0311(9)	0.0155(7)	0.0147(7)	0.0032(6)	0.0082(6)	0.0071(6)
C17	0.0259(8)	0.0131(7)	0.0175(7)	0.0027(6)	0.0032(6)	0.0038(6)
C18	0.0134(6)	0.0148(6)	0.0177(7)	0.0069(5)	0.0022(5)	0.0021(5)
C19	0.0128(6)	0.0174(7)	0.0180(7)	0.0064(6)	0.0046(5)	0.0033(5)
C20	0.0155(7)	0.0245(8)	0.0317(9)	0.0106(7)	0.0024(6)	−0.0048(6)
C21	0.0246(8)	0.0253(8)	0.0226(8)	0.0026(7)	0.0089(7)	−0.0093(7)
C22	0.0199(7)	0.0258(8)	0.0182(7)	0.0108(6)	0.0087(6)	0.0038(6)
C23	0.0197(8)	0.0267(8)	0.0281(8)	0.0141(7)	0.0093(6)	0.0107(6)
B1	0.0160(7)	0.0129(7)	0.0146(7)	0.0032(6)	0.0040(6)	0.0031(6)

Table 1 Bond lengths and angles for Compound 35 **Atom–Atom**	**Length [Å]**
W1–P1	2.4998(4)
W1–N1	2.2616(13)
W1–N3	2.2116(13)
W1–N5	2.2346(12)
W1–N7	1.7672(13)
W1–C10	2.2300(14)
W1–C11	2.2015(14)

S1–C14	1.8220(15)
S1–C17	1.8089(17)
S2–C15	1.8422(15)
S2–C16	1.8091(16)
P1–C21	1.8227(17)
P1–C22	1.8236(16)
P1–C23	1.8200(17)
O1–N7	1.2335(17)
O2–C19	1.201(2)
O3–C19	1.3464(19)
O3–C20	1.440(2)
N1–N2	1.3617(17)
N1–C1	1.3434(19)
N2–C3	1.346(2)
N2–B1	1.537(2)
N3–N4	1.3597(17)
N3–C4	1.3346(19)
N4–C6	1.348(2)
N4–B1	1.537(2)
N5–N6	1.3625(17)
N5–C7	1.3378(19)
N6–C9	1.349(2)
N6–B1	1.537(2)
C1–H1	0.9500
C1–C2	1.391(2)
C2–H2	0.9500
C2–C3	1.379(2)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.394(2)
C5–H5	0.9500
C5–C6	1.379(2)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.393(2)
C8–H8	0.9500
C8–C9	1.378(2)
C9–H9	0.9500
C10–C11	1.448(2)

C10–C15	1.5242(19)
C10–H10	0.98(2)
C11–C12	1.533(2)
C11–H11	0.99(2)
C12–H12	1.0000
C12–C13	1.537(2)
C12–C18	1.535(2)
C13–H13A	0.9900
C13–H13B	0.9900
C13–C14	1.521(2)
C14–H14	1.0000
C14–C15	1.530(2)
C15–H15	1.0000
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.517(2)
C17–H17A	0.9900
C17–H17B	0.9900
C18–H18A	0.9900
C18–H18B	0.9900
C18–C19	1.506(2)
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9800
C21–H21B	0.9800
C21–H21C	0.9800
C22–H22A	0.9800
C22–H22B	0.9800
C22–H22C	0.9800
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
B1–H1A	1.04(2)
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	86.93(3)
N3–W1–P1	83.89(3)

N3–W1–N1	83.85(5)
N3–W1–N5	76.56(5)
N3–W1–C10	161.21(5)
N5–W1–P1	158.15(3)
N5–W1–N1	81.41(5)
N7–W1–P1	92.33(4)
N7–W1–N1	175.44(5)
N7–W1–N3	91.60(5)
N7–W1–N5	97.83(5)
N7–W1–C10	96.76(5)
N7–W1–C11	95.49(5)
C10–W1–P1	79.00(4)
C10–W1–N1	87.52(5)
C10–W1–N5	118.62(5)
C11–W1–P1	117.13(4)
C11–W1–N1	88.85(5)
C11–W1–N3	157.40(5)
C11–W1–N5	81.22(5)
C11–W1–C10	38.14(5)
C17–S1–C14	102.63(7)
C16–S2–C15	102.38(7)
C21–P1–W1	115.78(6)
C21–P1–C22	99.65(8)
C22–P1–W1	119.23(6)
C23–P1–W1	115.06(6)
C23–P1–C21	101.02(9)
C23–P1–C22	103.39(8)
C19–O3–C20	115.52(13)
N2–N1–W1	120.55(9)
C1–N1–W1	133.52(10)
C1–N1–N2	105.93(12)
N1–N2–B1	121.03(12)
C3–N2–N1	109.96(12)
C3–N2–B1	128.77(13)
N4–N3–W1	123.36(9)
C4–N3–W1	129.74(11)
C4–N3–N4	106.87(12)
N3–N4–B1	118.88(12)
C6–N4–N3	109.47(13)

C6–N4–B1	130.34(13)
N6–N5–W1	120.77(9)
C7–N5–W1	132.97(10)
C7–N5–N6	106.23(12)
N5–N6–B1	121.43(12)
C9–N6–N5	109.66(13)
C9–N6–B1	128.53(13)
O1–N7–W1	177.95(12)
N1–C1–H1	124.5
N1–C1–C2	110.91(14)
C2–C1–H1	124.5
C1–C2–H2	127.7
C3–C2–C1	104.51(14)
C3–C2–H2	127.7
N2–C3–C2	108.70(13)
N2–C3–H3	125.7
C2–C3–H3	125.7
N3–C4–H4	124.8
N3–C4–C5	110.38(14)
C5–C4–H4	124.8
C4–C5–H5	127.7
C6–C5–C4	104.69(14)
C6–C5–H5	127.7
N4–C6–C5	108.60(14)
N4–C6–H6	125.7
C5–C6–H6	125.7
N5–C7–H7	124.5
N5–C7–C8	110.91(14)
C8–C7–H7	124.5
C7–C8–H8	127.8
C9–C8–C7	104.46(14)
C9–C8–H8	127.8
N6–C9–C8	108.74(14)
N6–C9–H9	125.6
C8–C9–H9	125.6
W1–C10–H10	109.7(12)
C11–C10–W1	69.87(8)
C11–C10–C15	120.79(12)
C11–C10–H10	115.5(12)

C15–C10–W1	125.83(10)
C15–C10–H10	110.1(12)
W1–C11–H11	107.6(12)
C10–C11–W1	72.00(8)
C10–C11–C12	121.66(12)
C10–C11–H11	115.5(12)
C12–C11–W1	121.64(10)
C12–C11–H11	112.3(12)
C11–C12–H12	108.7
C11–C12–C13	112.26(12)
C11–C12–C18	108.30(12)
C13–C12–H12	108.7
C18–C12–H12	108.7
C18–C12–C13	110.22(12)
C12–C13–H13A	109.7
C12–C13–H13B	109.7
H13A–C13–H13B	108.2
C14–C13–C12	110.04(12)
C14–C13–H13A	109.7
C14–C13–H13B	109.7
S1–C14–H14	106.2
C13–C14–S1	113.94(10)
C13–C14–H14	106.2
C13–C14–C15	111.15(12)
C15–C14–S1	112.57(10)
C15–C14–H14	106.2
S2–C15–H15	109.3
C10–C15–S2	104.28(10)
C10–C15–C14	111.68(12)
C10–C15–H15	109.3
C14–C15–S2	112.73(10)
C14–C15–H15	109.3
S2–C16–H16A	108.9
S2–C16–H16B	108.9
H16A–C16–H16B	107.8
C17–C16–S2	113.19(11)
C17–C16–H16A	108.9
C17–C16–H16B	108.9
S1–C17–H17A	109.2

S1–C17–H17B	109.2
C16–C17–S1	111.92(11)
C16–C17–H17A	109.2
C16–C17–H17B	109.2
H17A–C17–H17B	107.9
C12–C18–H18A	108.8
C12–C18–H18B	108.8
H18A–C18–H18B	107.7
C19–C18–C12	113.77(12)
C19–C18–H18A	108.8
C19–C18–H18B	108.8
O2–C19–O3	123.29(15)
O2–C19–C18	126.06(15)
O3–C19–C18	110.65(13)
O3–C20–H20A	109.5
O3–C20–H20B	109.5
O3–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
P1–C21–H21A	109.5
P1–C21–H21B	109.5
P1–C21–H21C	109.5
H21A–C21–H21B	109.5
H21A–C21–H21C	109.5
H21B–C21–H21C	109.5
P1–C22–H22A	109.5
P1–C22–H22B	109.5
P1–C22–H22C	109.5
H22A–C22–H22B	109.5
H22A–C22–H22C	109.5
H22B–C22–H22C	109.5
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
N2–B1–N6	108.60(12)

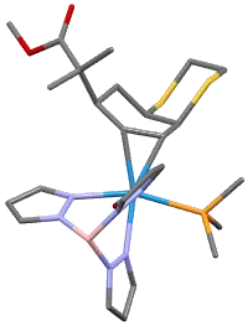
N2–B1–H1A	109.9(12)
N4–B1–N2	109.43(12)
N4–B1–N6	106.69(12)
N4–B1–H1A	112.9(12)
N6–B1–H1A	109.2(12)

Table 5 Torsion angles for mo_harman_ld_1_291_x3_0m**Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	−179.60(10)
W1–N1–N2–B1	−4.74(17)
W1–N1–C1–C2	179.42(11)
W1–N3–N4–C6	177.77(10)
W1–N3–N4–B1	9.54(18)
W1–N3–C4–C5	−178.24(11)
W1–N5–N6–C9	−178.49(10)
W1–N5–N6–B1	−4.98(18)
W1–N5–C7–C8	178.48(11)
W1–C10–C11–C12	−116.60(13)
W1–C10–C15–S2	−171.79(8)
W1–C10–C15–C14	66.19(15)
W1–C11–C12–C13	−104.71(13)
W1–C11–C12–C18	133.36(11)
S1–C14–C15–S2	63.04(12)
S1–C14–C15–C10	−179.94(10)
S2–C16–C17–S1	−66.33(14)
N1–N2–C3–C2	0.15(17)
N1–N2–B1–N4	61.00(17)
N1–N2–B1–N6	−55.11(17)
N1–C1–C2–C3	0.09(18)
N2–N1–C1–C2	0.00(17)
N3–N4–C6–C5	0.73(18)
N3–N4–B1–N2	−63.84(17)
N3–N4–B1–N6	53.47(17)
N3–C4–C5–C6	0.93(18)
N4–N3–C4–C5	−0.51(17)
N5–N6–C9–C8	−0.23(18)
N5–N6–B1–N2	61.55(17)

N5–N6–B1–N4	−56.31(17)
N5–C7–C8–C9	−0.45(19)
N6–N5–C7–C8	0.32(17)
C1–N1–N2–C3	−0.09(16)
C1–N1–N2–B1	174.78(13)
C1–C2–C3–N2	−0.14(17)
C3–N2–B1–N4	−125.19(16)
C3–N2–B1–N6	118.70(16)
C4–N3–N4–C6	−0.14(17)
C4–N3–N4–B1	−168.37(13)
C4–C5–C6–N4	−0.99(18)
C6–N4–B1–N2	130.77(16)
C6–N4–B1–N6	−111.92(17)
C7–N5–N6–C9	−0.06(17)
C7–N5–N6–B1	173.46(13)
C7–C8–C9–N6	0.40(19)
C9–N6–B1–N2	−126.26(16)
C9–N6–B1–N4	115.88(17)
C10–C11–C12–C13	−17.38(19)
C10–C11–C12–C18	−139.31(13)
C11–C10–C15–S2	101.88(13)
C11–C10–C15–C14	−20.14(18)
C11–C12–C13–C14	47.16(16)
C11–C12–C18–C19	179.36(12)
C12–C13–C14–S1	165.51(10)
C12–C13–C14–C15	−66.03(16)
C12–C18–C19–O2	42.1(2)
C12–C18–C19–O3	−138.39(13)
C13–C12–C18–C19	56.19(17)
C13–C14–C15–S2	−66.14(14)
C13–C14–C15–C10	50.88(16)
C14–S1–C17–C16	60.22(13)
C15–S2–C16–C17	58.69(14)
C15–C10–C11–W1	120.48(13)
C15–C10–C11–C12	3.9(2)
C16–S2–C15–C10	−178.21(10)
C16–S2–C15–C14	−56.88(12)
C17–S1–C14–C13	68.57(13)
C17–S1–C14–C15	−59.16(12)

C18–C12–C13–C14	167.99(12)
C20–O3–C19–O2	1.1(2)
C20–O3–C19–C18	−178.45(13)
B1–N2–C3–C2	−174.21(14)
B1–N4–C6–C5	167.18(15)
B1–N6–C9–C8	−173.15(15)

Structure Report for Compound 5.38



A colourless, plate shaped crystal of Compound 5.38 measuring 0.046×0.061×0.079 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 5.38 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Cu K_α, λ=1.54178 Å) using a HELIOS MX double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[202] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

[202] *APEX5, Saint, SADABS*; Bruker AXS Inc. 2019.

The structure was solved by dual methods with SHELXT[203] and refined by full-matrix least-squares methods against F^2 using XL[204] within OLEX2.[205] All non-hydrogen atoms were refined with anisotropically. The B-H, H10 and H11 atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[206]

Table 1 Crystal data and structure refinement for Compound 5.38

CCDC number	
Empirical formula	$C_{25}H_{39}BN_7O_3PS_2W$
Formula weight	775.38
Temperature [K]	100.00
Wavelength [Å]	1.54178
Crystal size [mm^3]	0.046×0.061×0.079
Crystal habit	colourless plate
Crystal system	triclinic
Space group	$P\overline{1}$ (2)
a [Å]	8.5618(2)
b [Å]	11.0656(4)
c [Å]	17.2112(5)
α [°]	89.714(2)
β [°]	76.786(2)
γ [°]	74.931(2)
Volume [$Å^3$]	1530.28(8)
Z	2
ρ_{calc} [gcm^{-3}]	1.683
μ [mm^{-1}]	9.091
F(000)	776
2θ range [°]	5.28 to 137.08 (0.83 Å)
Index ranges	−10 ≤ h ≤ 9 −13 ≤ k ≤ 13 −20 ≤ l ≤ 20

[203] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[204] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[205] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[206] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Reflections collected	31042
Independent reflections	5623 [R_{int} = 0.1001]
Data / Restraints / Parameters	5623 / 0 / 379
Goodness-of-fit on F^2	1.044
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0458 wR_2 = 0.1043
Final R indexes [all data]	R_1 = 0.0601 wR_2 = 0.1109
Largest peak/hole [eÅ^{-3}]	1.50/−0.87

Table 2 Atomic coordinates and Ueq [Å2] for Compound 5.38

Atom	***x***	***y***	***z***	U_{eq}
W1	0.35678(4)	0.45679(3)	0.71516(2)	0.02928(11)
S1	0.7930(3)	0.01835(19)	0.60631(11)	0.0480(5)
S2	0.4128(3)	0.01234(18)	0.72590(12)	0.0469(5)
P1	0.1752(2)	0.40076(18)	0.63251(10)	0.0352(4)
O1	0.6685(6)	0.4037(5)	0.5840(3)	0.0443(13)
O2	0.7883(7)	0.0418(6)	0.9365(4)	0.0595(16)
O3	0.8909(6)	0.2014(5)	0.8944(3)	0.0457(12)
N1	0.4538(7)	0.5801(5)	0.7825(3)	0.0369(14)
N2	0.3567(8)	0.6926(6)	0.8178(3)	0.0386(14)
N3	0.2692(7)	0.6429(5)	0.6699(3)	0.0327(12)
N4	0.1819(7)	0.7468(5)	0.7198(3)	0.0377(14)
N5	0.1216(7)	0.5260(6)	0.8142(3)	0.0363(14)
N6	0.0801(8)	0.6458(6)	0.8450(3)	0.0402(14)
N7	0.5404(7)	0.4203(5)	0.6377(3)	0.0347(13)
C1	0.6094(9)	0.5757(8)	0.7837(4)	0.0450(19)
H1	0.703330	0.507767	0.762100	0.054
C2	0.6153(10)	0.6848(8)	0.8210(5)	0.048(2)
H2	0.710368	0.705500	0.830707	0.057
C3	0.4566(11)	0.7544(8)	0.8404(4)	0.049(2)
H3	0.420026	0.835843	0.866337	0.059
C4	0.2864(9)	0.6837(7)	0.5959(4)	0.0413(17)
H4	0.345930	0.632733	0.548695	0.050
C5	0.2081(10)	0.8066(8)	0.5970(5)	0.048(2)

H5	0.198772	0.855752	0.552039	0.058
C6	0.1452(9)	0.8462(7)	0.6751(5)	0.0436(18)
H6	0.085778	0.929414	0.694844	0.052
C7	0.0211(8)	0.4672(7)	0.8597(4)	0.0380(17)
H7	0.022518	0.382151	0.851083	0.046
C8	−0.0865(10)	0.5483(9)	0.9217(5)	0.050(2)
H8	−0.170494	0.530095	0.962952	0.060
C9	−0.0464(10)	0.6597(9)	0.9109(4)	0.049(2)
H9	−0.098281	0.734319	0.943941	0.058
C10	0.3630(9)	0.2611(6)	0.7469(4)	0.0325(15)
H10	0.251(9)	0.242(6)	0.774(4)	0.035(19)
C11	0.4381(8)	0.3149(6)	0.8007(4)	0.0315(15)
H11	0.370(10)	0.352(8)	0.852(5)	0.05(2)
C12	0.6123(8)	0.2550(7)	0.8132(4)	0.0340(15)
H12	0.680753	0.315806	0.797601	0.041
C13	0.6991(9)	0.1332(7)	0.7608(4)	0.0394(17)
H13A	0.821087	0.116973	0.753230	0.047
H13B	0.665169	0.062374	0.788636	0.047
C14	0.6566(9)	0.1398(7)	0.6791(4)	0.0402(17)
H14	0.676170	0.220257	0.657890	0.048
C15	0.4738(9)	0.1536(7)	0.6878(4)	0.0392(17)
H15	0.447408	0.168738	0.634309	0.047
C16	0.6015(9)	0.2315(7)	0.9049(4)	0.0355(16)
C17	0.5661(10)	0.3560(7)	0.9506(4)	0.0431(18)
H17A	0.657230	0.394831	0.930662	0.065
H17B	0.556693	0.342369	1.007564	0.065
H17C	0.461623	0.411449	0.943048	0.065
C18	0.4692(10)	0.1643(8)	0.9393(4)	0.0433(18)
H18A	0.359512	0.217081	0.936551	0.065
H18B	0.470390	0.147520	0.995154	0.065
H18C	0.492488	0.084845	0.908363	0.065
C19	0.7678(10)	0.1472(8)	0.9139(4)	0.0448(18)
C20	1.0496(10)	0.1260(8)	0.9068(5)	0.054(2)
H20A	1.093908	0.054633	0.867367	0.081
H20B	1.032911	0.095246	0.960784	0.081
H20C	1.128599	0.177507	0.900670	0.081
C21	0.7337(10)	−0.1166(8)	0.6449(5)	0.050(2)
H21A	0.802750	−0.191139	0.609927	0.060
H21B	0.756393	−0.128716	0.698668	0.060

C22	0.5507(11)	−0.1077(8)	0.6509(5)	0.056(2)
H22A	0.529481	−0.189907	0.664642	0.068
H22B	0.525244	−0.088201	0.598166	0.068
C23	0.0665(10)	0.2804(8)	0.6640(5)	0.0477(19)
H23A	0.147950	0.198988	0.661460	0.072
H23B	−0.006786	0.276350	0.628425	0.072
H23C	−0.000086	0.301422	0.718947	0.072
C24	0.2803(11)	0.3474(8)	0.5298(4)	0.048(2)
H24A	0.377594	0.276815	0.528946	0.072
H24B	0.316201	0.416047	0.501364	0.072
H24C	0.203782	0.320396	0.503521	0.072
C25	0.0024(9)	0.5306(8)	0.6203(5)	0.0464(19)
H25A	0.044904	0.587852	0.582657	0.070
H25B	−0.053650	0.575852	0.672084	0.070
H25C	−0.076864	0.497867	0.599437	0.070
B1	0.1756(12)	0.7406(9)	0.8101(5)	0.043(2)
H1A	0.118(8)	0.822(6)	0.840(4)	0.023(16)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for Compound 5.38. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.02506(17)	0.03691(18)	0.02332(16)	0.00648(11)	−0.00493(11)	−0.00454(12)
S1	0.0487(11)	0.0487(11)	0.0343(9)	0.0017(8)	−0.0056(8)	0.0047(9)
S2	0.0493(11)	0.0378(10)	0.0517(11)	0.0036(8)	−0.0110(9)	−0.0091(9)
P1	0.0301(9)	0.0445(10)	0.0315(9)	0.0070(7)	−0.0097(7)	−0.0083(8)
O1	0.034(3)	0.060(3)	0.030(2)	0.009(2)	0.005(2)	−0.008(2)
O2	0.052(4)	0.051(4)	0.076(4)	0.029(3)	−0.022(3)	−0.010(3)
O3	0.035(3)	0.043(3)	0.057(3)	0.001(2)	−0.016(2)	−0.002(2)
N1	0.039(4)	0.039(3)	0.033(3)	0.010(2)	−0.015(3)	−0.006(3)
N2	0.046(4)	0.041(3)	0.029(3)	0.005(2)	−0.012(3)	−0.011(3)
N3	0.031(3)	0.035(3)	0.032(3)	0.003(2)	−0.009(2)	−0.007(2)

N4	0.042(4)	0.031(3)	0.041(3)	0.007(3)	−0.017(3)	−0.005(3)
N5	0.032(3)	0.045(4)	0.027(3)	0.007(2)	−0.003(2)	−0.005(3)
N6	0.040(4)	0.048(4)	0.027(3)	0.000(3)	−0.008(2)	−0.003(3)
N7	0.027(3)	0.038(3)	0.033(3)	0.005(2)	−0.006(2)	0.002(2)
C1	0.035(4)	0.059(5)	0.048(4)	0.025(4)	−0.021(3)	−0.015(4)
C2	0.046(5)	0.054(5)	0.060(5)	0.024(4)	−0.038(4)	−0.021(4)
C3	0.071(6)	0.049(5)	0.041(4)	0.014(3)	−0.030(4)	−0.027(4)
C4	0.042(4)	0.052(5)	0.032(4)	0.013(3)	−0.014(3)	−0.012(4)
C5	0.041(4)	0.059(5)	0.050(5)	0.028(4)	−0.024(4)	−0.010(4)
C6	0.038(4)	0.036(4)	0.058(5)	0.011(3)	−0.024(4)	−0.002(3)
C7	0.029(4)	0.049(4)	0.029(3)	0.006(3)	−0.002(3)	−0.002(3)
C8	0.037(4)	0.075(6)	0.037(4)	0.002(4)	−0.004(3)	−0.017(4)
C9	0.037(4)	0.070(6)	0.033(4)	−0.006(4)	−0.008(3)	−0.004(4)
C10	0.034(4)	0.032(4)	0.027(3)	0.004(3)	−0.002(3)	−0.003(3)
C11	0.028(4)	0.035(4)	0.027(3)	0.009(3)	−0.008(3)	0.000(3)
C12	0.030(4)	0.040(4)	0.029(3)	0.002(3)	−0.002(3)	−0.008(3)
C13	0.034(4)	0.047(4)	0.035(4)	0.005(3)	−0.007(3)	−0.008(3)
C14	0.047(4)	0.041(4)	0.029(3)	0.003(3)	−0.009(3)	−0.006(3)
C15	0.045(4)	0.037(4)	0.034(4)	0.008(3)	−0.013(3)	−0.005(3)
C16	0.038(4)	0.038(4)	0.034(4)	0.005(3)	−0.012(3)	−0.013(3)
C17	0.040(4)	0.051(5)	0.035(4)	0.002(3)	−0.006(3)	−0.008(4)
C18	0.043(4)	0.053(5)	0.038(4)	0.016(3)	−0.014(3)	−0.017(4)
C19	0.040(4)	0.055(5)	0.040(4)	−0.001(4)	−0.012(3)	−0.013(4)
C20	0.039(5)	0.057(5)	0.064(5)	0.002(4)	−0.021(4)	−0.005(4)
C21	0.045(5)	0.048(5)	0.053(5)	−0.002(4)	−0.016(4)	0.003(4)
C22	0.062(6)	0.048(5)	0.056(5)	−0.005(4)	−0.016(4)	−0.007(4)

C23	0.047(5)	0.056(5)	0.049(4)	0.016(4)	−0.018(4)	−0.022(4)
C24	0.058(5)	0.060(5)	0.029(4)	0.006(3)	−0.013(3)	−0.018(4)
C25	0.034(4)	0.054(5)	0.056(5)	0.014(4)	−0.020(3)	−0.011(4)
B1	0.047(5)	0.046(5)	0.034(4)	−0.004(4)	−0.011(4)	−0.010(4)

Table 4 Bond lengths and angles for Compound 5.38 **Atom–Atom**	**Length [Å]**
W1–P1	2.5190(19)
W1–N1	2.222(6)
W1–N3	2.204(6)
W1–N5	2.278(5)
W1–N7	1.769(5)
W1–C10	2.221(7)
W1–C11	2.235(6)
S1–C14	1.809(7)
S1–C21	1.778(9)
S2–C15	1.845(7)
S2–C22	1.825(8)
P1–C23	1.828(8)
P1–C24	1.814(7)
P1–C25	1.826(8)
O1–N7	1.234(7)
O2–C19	1.209(10)
O3–C19	1.322(9)
O3–C20	1.459(9)
N1–N2	1.360(8)
N1–C1	1.325(9)
N2–C3	1.345(10)
N2–B1	1.540(11)
N3–N4	1.373(8)
N3–C4	1.339(9)
N4–C6	1.350(9)
N4–B1	1.544(10)
N5–N6	1.357(8)
N5–C7	1.325(9)

N6–C9	1.355(9)
N6–B1	1.531(11)
C1–H1	0.9500
C1–C2	1.388(12)
C2–H2	0.9500
C2–C3	1.343(12)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.349(11)
C5–H5	0.9500
C5–C6	1.356(11)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.387(10)
C8–H8	0.9500
C8–C9	1.364(12)
C9–H9	0.9500
C10–H10	1.04(7)
C10–C11	1.451(10)
C10–C15	1.527(9)
C11–H11	0.97(8)
C11–C12	1.530(9)
C12–H12	1.0000
C12–C13	1.538(10)
C12–C16	1.583(9)
C13–H13A	0.9900
C13–H13B	0.9900
C13–C14	1.528(10)
C14–H14	1.0000
C14–C15	1.505(11)
C15–H15	1.0000
C16–C17	1.514(10)
C16–C18	1.522(10)
C16–C19	1.527(11)
C17–H17A	0.9800
C17–H17B	0.9800
C17–H17C	0.9800
C18–H18A	0.9800
C18–H18B	0.9800

C18–H18C	0.9800
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C21–H21A	0.9900
C21–H21B	0.9900
C21–C22	1.524(12)
C22–H22A	0.9900
C22–H22B	0.9900
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
B1–H1A	0.98(6)

Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	157.34(15)
N1–W1–N5	83.1(2)
N1–W1–C11	84.0(2)
N3–W1–P1	81.79(16)
N3–W1–N1	76.7(2)
N3–W1–N5	83.0(2)
N3–W1–C10	158.8(2)
N3–W1–C11	158.3(2)
N5–W1–P1	87.17(16)
N7–W1–P1	95.4(2)
N7–W1–N1	92.4(2)
N7–W1–N3	91.7(2)
N7–W1–N5	173.7(2)
N7–W1–C10	96.8(2)
N7–W1–C11	99.1(2)
C10–W1–P1	78.11(19)
C10–W1–N1	122.0(2)
C10–W1–N5	89.3(2)

C10–W1–C11	38.0(3)
C11–W1–P1	115.52(19)
C11–W1–N5	84.9(2)
C21–S1–C14	101.4(4)
C22–S2–C15	101.2(4)
C23–P1–W1	120.1(3)
C24–P1–W1	114.9(3)
C24–P1–C23	101.8(4)
C24–P1–C25	102.2(4)
C25–P1–W1	114.6(3)
C25–P1–C23	100.7(4)
C19–O3–C20	114.3(6)
N2–N1–W1	121.8(4)
C1–N1–W1	129.8(5)
C1–N1–N2	107.1(6)
N1–N2–B1	120.5(6)
C3–N2–N1	107.7(6)
C3–N2–B1	130.2(7)
N4–N3–W1	122.5(4)
C4–N3–W1	132.1(5)
C4–N3–N4	105.4(6)
N3–N4–B1	118.9(6)
C6–N4–N3	108.9(6)
C6–N4–B1	130.6(7)
N6–N5–W1	119.1(4)
C7–N5–W1	132.5(5)
C7–N5–N6	107.6(6)
N5–N6–B1	122.4(6)
C9–N6–N5	108.6(6)
C9–N6–B1	128.9(7)
O1–N7–W1	175.5(5)
N1–C1–H1	124.9
N1–C1–C2	110.2(7)
C2–C1–H1	124.9
C1–C2–H2	127.7
C3–C2–C1	104.5(7)
C3–C2–H2	127.7
N2–C3–H3	124.8
C2–C3–N2	110.4(7)

C2–C3–H3	124.8
N3–C4–H4	124.5
N3–C4–C5	111.1(7)
C5–C4–H4	124.5
C4–C5–H5	126.8
C4–C5–C6	106.4(7)
C6–C5–H5	126.8
N4–C6–C5	108.1(7)
N4–C6–H6	126.0
C5–C6–H6	126.0
N5–C7–H7	125.1
N5–C7–C8	109.9(7)
C8–C7–H7	125.1
C7–C8–H8	127.3
C9–C8–C7	105.5(7)
C9–C8–H8	127.3
N6–C9–C8	108.5(7)
N6–C9–H9	125.8
C8–C9–H9	125.8
W1–C10–H10	118(4)
C11–C10–W1	71.5(4)
C11–C10–H10	115(4)
C11–C10–C15	118.3(6)
C15–C10–W1	118.8(4)
C15–C10–H10	111(4)
W1–C11–H11	104(5)
C10–C11–W1	70.5(4)
C10–C11–H11	119(5)
C10–C11–C12	123.6(6)
C12–C11–W1	130.0(5)
C12–C11–H11	106(5)
C11–C12–H12	107.9
C11–C12–C13	112.2(6)
C11–C12–C16	109.7(5)
C13–C12–H12	107.9
C13–C12–C16	111.2(6)
C16–C12–H12	107.9
C12–C13–H13A	109.2
C12–C13–H13B	109.2

H13A–C13–H13B	107.9
C14–C13–C12	112.2(6)
C14–C13–H13A	109.2
C14–C13–H13B	109.2
S1–C14–H14	105.4
C13–C14–S1	114.0(5)
C13–C14–H14	105.4
C15–C14–S1	114.8(5)
C15–C14–C13	110.8(6)
C15–C14–H14	105.4
S2–C15–H15	108.8
C10–C15–S2	105.2(5)
C10–C15–H15	108.8
C14–C15–S2	112.0(5)
C14–C15–C10	113.1(6)
C14–C15–H15	108.8
C17–C16–C12	109.1(6)
C17–C16–C18	110.5(6)
C17–C16–C19	109.4(6)
C18–C16–C12	111.9(6)
C18–C16–C19	107.0(6)
C19–C16–C12	109.0(6)
C16–C17–H17A	109.5
C16–C17–H17B	109.5
C16–C17–H17C	109.5
H17A–C17–H17B	109.5
H17A–C17–H17C	109.5
H17B–C17–H17C	109.5
C16–C18–H18A	109.5
C16–C18–H18B	109.5
C16–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
O2–C19–O3	122.3(7)
O2–C19–C16	124.8(7)
O3–C19–C16	112.9(7)
O3–C20–H20A	109.5
O3–C20–H20B	109.5

O3–C20–H20C	109.5
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
S1–C21–H21A	109.0
S1–C21–H21B	109.0
H21A–C21–H21B	107.8
C22–C21–S1	113.1(6)
C22–C21–H21A	109.0
C22–C21–H21B	109.0
S2–C22–H22A	109.2
S2–C22–H22B	109.2
C21–C22–S2	112.2(6)
C21–C22–H22A	109.2
C21–C22–H22B	109.2
H22A–C22–H22B	107.9
P1–C23–H23A	109.5
P1–C23–H23B	109.5
P1–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
P1–C24–H24A	109.5
P1–C24–H24B	109.5
P1–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
N2–B1–N4	106.7(6)
N2–B1–H1A	112(4)
N4–B1–H1A	112(4)
N6–B1–N2	108.7(7)
N6–B1–N4	109.1(6)

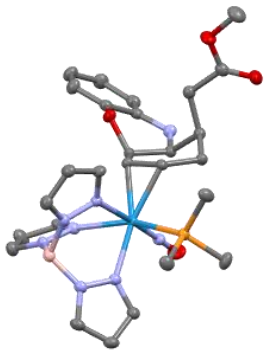
N6–B1–H1A	108(4)

Table 5 Torsion angles for Compound 5.38 **Atom–Atom–Atom–Atom**	**Torsion Angle [°]**
W1–N1–N2–C3	−168.7(4)
W1–N1–N2–B1	−1.8(8)
W1–N1–C1–C2	168.0(5)
W1–N3–N4–C6	−179.9(5)
W1–N3–N4–B1	13.0(8)
W1–N3–C4–C5	178.9(5)
W1–N5–N6–C9	−170.0(5)
W1–N5–N6–B1	6.3(8)
W1–N5–C7–C8	168.3(5)
W1–C10–C11–C12	−125.6(6)
W1–C10–C15–S2	−169.0(3)
W1–C10–C15–C14	68.5(7)
W1–C11–C12–C13	−90.6(7)
W1–C11–C12–C16	145.2(5)
S1–C14–C15–S2	64.0(6)
S1–C14–C15–C10	−177.3(5)
S1–C21–C22–S2	−67.4(7)
N1–N2–C3–C2	−0.3(8)
N1–N2–B1–N4	−58.1(8)
N1–N2–B1–N6	59.4(8)
N1–C1–C2–C3	−1.1(8)
N2–N1–C1–C2	1.0(8)
N3–N4–C6–C5	0.1(9)
N3–N4–B1–N2	51.5(9)
N3–N4–B1–N6	−65.7(8)
N3–C4–C5–C6	2.7(9)
N4–N3–C4–C5	−2.6(8)
N5–N6–C9–C8	−0.5(9)
N5–N6–B1–N2	−62.0(8)
N5–N6–B1–N4	53.9(9)
N5–C7–C8–C9	0.4(9)
N6–N5–C7–C8	−0.8(8)
C1–N1–N2–C3	−0.4(7)
C1–N1–N2–B1	166.5(6)
C1–C2–C3–N2	0.9(8)

C3–N2–B1–N4	105.4(8)
C3–N2–B1–N6	−137.1(7)
C4–N3–N4–C6	1.5(8)
C4–N3–N4–B1	−165.7(7)
C4–C5–C6–N4	−1.7(9)
C6–N4–B1–N2	−112.4(8)
C6–N4–B1–N6	130.3(8)
C7–N5–N6–C9	0.8(8)
C7–N5–N6–B1	177.1(7)
C7–C8–C9–N6	0.1(9)
C9–N6–B1–N2	113.5(8)
C9–N6–B1–N4	−130.5(8)
C10–C11–C12–C13	1.2(9)
C10–C11–C12–C16	−122.9(7)
C11–C10–C15–S2	107.6(6)
C11–C10–C15–C14	−14.9(9)
C11–C12–C13–C14	35.7(8)
C11–C12–C16–C17	−72.7(7)
C11–C12–C16–C18	49.9(8)
C11–C12–C16–C19	168.0(6)
C12–C13–C14–S1	165.0(5)
C12–C13–C14–C15	−63.6(8)
C12–C16–C19–O2	−114.1(8)
C12–C16–C19–O3	66.0(8)
C13–C12–C16–C17	162.6(6)
C13–C12–C16–C18	−74.8(8)
C13–C12–C16–C19	43.2(8)
C13–C14–C15–S2	−66.9(7)
C13–C14–C15–C10	51.8(8)
C14–S1–C21–C22	59.7(7)
C15–S2–C22–C21	59.1(7)
C15–C10–C11–W1	113.4(6)
C15–C10–C11–C12	−12.2(9)
C16–C12–C13–C14	159.0(6)
C17–C16–C19–O2	126.8(8)
C17–C16–C19–O3	−53.2(8)
C18–C16–C19–O2	7.1(10)
C18–C16–C19–O3	−172.9(6)
C20–O3–C19–O2	−3.4(11)

C20–O3–C19–C16	176.6(6)
C21–S1–C14–C13	70.2(6)
C21–S1–C14–C15	−59.2(6)
C22–S2–C15–C10	179.5(5)
C22–S2–C15–C14	−57.2(6)
B1–N2–C3–C2	−165.5(7)
B1–N4–C6–C5	165.3(8)
B1–N6–C9–C8	−176.5(7)

Structure Report for Compound 30



A colourless, block shaped crystal of Compound 30

measuring 0.032×0.078×0.086 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 30

were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[207] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

[207] *APEX5, Saint, SADABS*; Bruker AXS Inc. 2019.

The structure was solved by direct methods with XS[208] and refined by full-matrix least-squares methods against F^2 using XL[209] within OLEX2.[210] All non-hydrogen atoms were refined with anisotropically. The N-H and B-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[211]

Table 1 Crystal data and structure refinement for Compound 30

CCDC number	
Empirical formula	$C_{29}H_{39}BN_9O_4PW$
Formula weight	803.32
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.032×0.078×0.086
Crystal habit	colourless block
Crystal system	triclinic
Space group	*P*1 (1)
a [Å]	8.3069(3)
b [Å]	8.9205(3)
c [Å]	12.2685(4)
α [°]	109.8177(12)
β [°]	97.1550(12)
γ [°]	105.0904(12)
Volume [$Å^3$]	802.80(5)
Z	1
ρ_{calc} [gcm^{-3}]	1.662
μ [mm^{-1}]	3.697
F(000)	402
2θ range [°]	5.01 to 56.58 (0.75 Å)

[208] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[209] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[210] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[211] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Index ranges	−11 ≤ h ≤ 11 −11 ≤ k ≤ 11 −16 ≤ l ≤ 16
Reflections collected	49695
Independent reflections	7958 [R_{int} = 0.0486]
Data / Restraints / Parameters	7958 / 3 / 415
Goodness-of-fit on F^2	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0218 wR_2 = 0.0485
Final R indexes [all data]	R_1 = 0.0218 wR_2 = 0.0485
Largest peak/hole [eÅ^{-3}]	1.17/−0.37
Flack X parameter	-0.024(3)

Table 2 Atomic coordinates and Ueq [Å2] for Compound 30

Atom	***x***	***y***	***z***	U_{eq}
W1	0.29891(2)	0.51571(2)	0.45206(2)	0.01554(5)
P1	0.49295(16)	0.35489(16)	0.48691(11)	0.0200(2)
O1	0.5791(6)	0.8254(6)	0.4829(5)	0.0361(11)
O2	0.0830(4)	0.8488(4)	0.7082(3)	0.0202(7)
O3	0.5763(5)	0.8453(6)	1.0401(4)	0.0331(9)
O4	0.3052(6)	0.7417(6)	1.0481(4)	0.0312(10)
N1	0.0941(5)	0.5620(5)	0.3447(4)	0.0190(8)
N2	−0.0190(5)	0.4311(5)	0.2459(4)	0.0205(8)
N3	0.3146(7)	0.3854(6)	0.2678(4)	0.0195(8)
N4	0.1746(6)	0.2683(5)	0.1810(4)	0.0207(8)
N5	0.0848(8)	0.2793(8)	0.4183(5)	0.0189(12)
N6	−0.0229(5)	0.1911(5)	0.3083(4)	0.0203(8)
N7	0.4665(8)	0.6996(7)	0.4715(6)	0.0207(13)
N8	0.3878(6)	1.1095(5)	0.7983(4)	0.0207(8)
C1	0.0603(8)	0.6997(7)	0.3437(5)	0.0267(11)
H1	0.119326	0.810320	0.401317	0.032
C2	−0.0728(8)	0.6605(8)	0.2471(5)	0.0335(13)
H2	−0.121775	0.735536	0.227167	0.040

C3	−0.1176(7)	0.4893(7)	0.1872(5)	0.0260(11)
H3	−0.204239	0.423287	0.115922	0.031
C4	0.4462(7)	0.3948(7)	0.2165(5)	0.0241(10)
H4	0.560410	0.466281	0.256110	0.029
C5	0.3946(7)	0.2860(7)	0.0968(5)	0.0276(11)
H5	0.463932	0.267681	0.040714	0.033
C6	0.2199(8)	0.2106(7)	0.0779(5)	0.0246(11)
H6	0.145019	0.131267	0.004178	0.030
C7	0.0277(6)	0.1964(6)	0.4867(5)	0.0200(9)
H7	0.078877	0.229371	0.568436	0.024
C8	−0.1156(7)	0.0568(7)	0.4222(5)	0.0238(10)
H8A	−0.179860	−0.022281	0.449418	0.029
C9	−0.1437(7)	0.0585(6)	0.3094(5)	0.0238(10)
H9	−0.233802	−0.021121	0.243427	0.029
C10	0.3234(6)	0.5780(7)	0.6454(4)	0.0180(9)
H10	0.270621	0.478508	0.664599	0.022
C11	0.1991(7)	0.6429(6)	0.6006(5)	0.0165(9)
H11	0.079562	0.574765	0.594788	0.020
C12	0.2215(6)	0.8281(6)	0.6471(4)	0.0182(9)
H12	0.205349	0.861832	0.577687	0.022
C13	0.3965(6)	0.9419(6)	0.7311(4)	0.0186(9)
H13	0.480024	0.956037	0.680421	0.022
C14	0.4639(7)	0.8658(7)	0.8139(5)	0.0201(10)
H14	0.578300	0.945813	0.864894	0.024
C15	0.4886(6)	0.7019(6)	0.7364(4)	0.0198(9)
H15A	0.578756	0.728387	0.693702	0.024
H15B	0.528209	0.648153	0.788243	0.024
C16	0.0805(7)	1.0127(6)	0.7462(4)	0.0211(9)
C17	−0.0755(7)	1.0415(7)	0.7424(5)	0.0260(11)
H17	−0.179452	0.949395	0.709635	0.031
C18	−0.0798(7)	1.2055(7)	0.7867(5)	0.0286(11)
H18	−0.186321	1.226295	0.785949	0.034
C19	0.0731(7)	1.3386(7)	0.8321(5)	0.0283(11)
H19	0.071068	1.451008	0.863517	0.034
C20	0.2294(8)	1.3089(7)	0.8321(5)	0.0233(12)
H20	0.332867	1.401408	0.860381	0.028
C21	0.2358(6)	1.1450(6)	0.7909(4)	0.0199(9)
C22	0.3449(6)	0.8374(6)	0.8949(5)	0.0218(10)
H22A	0.305441	0.936238	0.924359	0.026

H22B	0.242730	0.738021	0.847501	0.026
C23	0.4263(7)	0.8098(6)	1.0005(5)	0.0236(10)
C24	0.3658(9)	0.7033(8)	1.1480(6)	0.0381(14)
H24A	0.449235	0.644192	1.128854	0.057
H24B	0.268693	0.631447	1.164460	0.057
H24C	0.420441	0.808107	1.218436	0.057
C25	0.4984(8)	0.2906(7)	0.6120(5)	0.0285(11)
H25A	0.545765	0.390540	0.686501	0.043
H25B	0.570590	0.218399	0.606179	0.043
H25C	0.381785	0.228116	0.610964	0.043
C26	0.7196(7)	0.4563(7)	0.5010(6)	0.0316(12)
H26A	0.734548	0.477426	0.428942	0.047
H26B	0.784397	0.382714	0.511236	0.047
H26C	0.761659	0.563448	0.570399	0.047
C27	0.4427(7)	0.1482(7)	0.3664(5)	0.0271(11)
H27A	0.321227	0.084349	0.351698	0.041
H27B	0.513625	0.086573	0.389285	0.041
H27C	0.466261	0.163076	0.293765	0.041
B1	−0.0055(7)	0.2512(7)	0.2056(5)	0.0215(11)
H1A	−0.096422	0.172605	0.132203	0.026
N9	0.6931(6)	0.4697(6)	0.9206(4)	0.0309(10)
C28	0.7845(7)	0.5965(7)	0.9332(5)	0.0280(11)
C29	0.9016(7)	0.7604(8)	0.9491(6)	0.0355(13)
H29A	0.925680	0.757162	0.872319	0.053
H29B	1.008955	0.786310	1.005737	0.053
H29C	0.848636	0.847455	0.979997	0.053
H8	0.479(9)	1.199(9)	0.815(6)	0.036(18)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for Compound 30

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01491(7)	0.01568(7)	0.01570(7)	0.00633(5)	0.00391(5)	0.00396(5)
P1	0.0197(6)	0.0219(6)	0.0195(6)	0.0081(5)	0.0045(5)	0.0085(5)
O1	0.033(3)	0.029(2)	0.041(3)	0.016(2)	0.014(2)	−0.005(2)
O2	0.0181(16)	0.0163(16)	0.0239(17)	0.0048(13)	0.0069(13)	0.0051(13)
O3	0.028(2)	0.048(3)	0.024(2)	0.0162(18)	0.0036(16)	0.0137(19)
O4	0.035(3)	0.038(2)	0.026(2)	0.0217(19)	0.0085(19)	0.008(2)

N1	0.024(2)	0.0174(19)	0.020(2)	0.0093(17)	0.0065(16)	0.0097(16)
N2	0.0203(19)	0.022(2)	0.0176(19)	0.0069(16)	0.0026(16)	0.0072(16)
N3	0.022(2)	0.021(2)	0.018(2)	0.0078(18)	0.0055(18)	0.009(2)
N4	0.023(2)	0.019(2)	0.018(2)	0.0053(17)	0.0044(16)	0.0064(17)
N5	0.018(3)	0.021(3)	0.019(3)	0.008(3)	0.006(2)	0.007(3)
N6	0.0190(19)	0.020(2)	0.019(2)	0.0058(16)	0.0026(16)	0.0052(16)
N7	0.020(3)	0.021(3)	0.019(2)	0.008(2)	0.005(2)	0.004(2)
N8	0.021(2)	0.017(2)	0.025(2)	0.0084(17)	0.0066(17)	0.0060(17)
C1	0.042(3)	0.021(2)	0.019(3)	0.008(2)	0.007(2)	0.014(2)
C2	0.047(3)	0.033(3)	0.025(3)	0.011(2)	0.002(2)	0.024(3)
C3	0.025(2)	0.030(3)	0.024(3)	0.010(2)	0.002(2)	0.012(2)
C4	0.023(2)	0.030(3)	0.020(2)	0.011(2)	0.0057(19)	0.010(2)
C5	0.033(3)	0.032(3)	0.023(3)	0.011(2)	0.013(2)	0.013(2)
C6	0.032(3)	0.024(3)	0.017(3)	0.006(2)	0.007(2)	0.009(2)
C7	0.021(2)	0.019(2)	0.023(3)	0.011(2)	0.010(2)	0.0074(19)
C8	0.023(2)	0.021(2)	0.025(3)	0.008(2)	0.008(2)	0.005(2)
C9	0.021(2)	0.020(2)	0.027(3)	0.007(2)	0.003(2)	0.0045(19)
C10	0.020(2)	0.021(2)	0.015(2)	0.0080(19)	0.0046(18)	0.008(2)
C11	0.015(2)	0.017(2)	0.018(2)	0.0057(18)	0.0055(19)	0.0058(19)
C12	0.016(2)	0.023(2)	0.017(2)	0.0080(18)	0.0034(17)	0.0069(18)
C13	0.018(2)	0.019(2)	0.017(2)	0.0061(18)	0.0033(17)	0.0051(18)
C14	0.019(2)	0.021(2)	0.019(2)	0.007(2)	0.004(2)	0.007(2)
C15	0.020(2)	0.021(2)	0.018(2)	0.0056(19)	0.0049(18)	0.008(2)
C16	0.026(2)	0.022(2)	0.018(2)	0.0083(19)	0.0063(19)	0.010(2)
C17	0.021(2)	0.021(2)	0.032(3)	0.007(2)	0.006(2)	0.005(2)
C18	0.024(3)	0.030(3)	0.034(3)	0.011(2)	0.011(2)	0.014(2)
C19	0.032(3)	0.024(3)	0.031(3)	0.009(2)	0.009(2)	0.015(2)
C20	0.029(3)	0.020(3)	0.021(3)	0.009(2)	0.006(2)	0.007(2)
C21	0.024(2)	0.021(2)	0.017(2)	0.0091(19)	0.0069(18)	0.0094(19)
C22	0.022(2)	0.021(2)	0.022(3)	0.007(2)	0.004(2)	0.0077(19)
C23	0.029(3)	0.021(2)	0.021(2)	0.0069(19)	0.004(2)	0.009(2)
C24	0.050(4)	0.039(3)	0.030(3)	0.021(3)	0.008(3)	0.014(3)
C25	0.040(3)	0.030(3)	0.023(3)	0.012(2)	0.009(2)	0.021(2)
C26	0.017(2)	0.032(3)	0.043(3)	0.012(3)	0.005(2)	0.008(2)
C27	0.035(3)	0.023(3)	0.026(3)	0.008(2)	0.006(2)	0.015(2)
B1	0.021(3)	0.021(3)	0.021(3)	0.008(2)	0.003(2)	0.006(2)
N9	0.031(2)	0.029(3)	0.030(3)	0.011(2)	0.001(2)	0.009(2)
C28	0.026(3)	0.033(3)	0.027(3)	0.012(2)	0.004(2)	0.014(2)
C29	0.026(3)	0.033(3)	0.047(4)	0.015(3)	0.009(3)	0.009(2)

Table 4 Bond lengths and angles for Compound 30

Atom–Atom	Length [Å]
W1–P1	2.5074(12)
W1–N1	2.230(4)
W1–N3	2.202(4)
W1–N5	2.248(7)
W1–N7	1.775(6)
W1–C10	2.214(5)
W1–C11	2.181(5)
P1–C25	1.811(6)
P1–C26	1.822(6)
P1–C27	1.832(5)
O1–N7	1.211(7)
O2–C12	1.467(6)
O2–C16	1.382(6)
O3–C23	1.195(7)
O4–C23	1.338(7)
O4–C24	1.447(7)
N1–N2	1.379(6)
N1–C1	1.334(6)
N2–C3	1.337(6)
N2–B1	1.550(7)
N3–N4	1.372(6)
N3–C4	1.326(7)
N4–C6	1.336(7)
N4–B1	1.542(7)
N5–N6	1.361(7)
N5–C7	1.346(8)
N6–C9	1.343(7)
N6–B1	1.535(7)
N8–C13	1.468(6)
N8–C21	1.379(6)
N8–H8	0.89(7)
C1–H1	0.9500
C1–C2	1.392(8)
C2–H2	0.9500

C2–C3	1.373(8)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.395(7)
C5–H5	0.9500
C5–C6	1.384(9)
C6–H6	0.9500
C7–H7	0.9500
C7–C8	1.385(7)
C8–H8A	0.9500
C8–C9	1.380(8)
C9–H9	0.9500
C10–H10	1.0000
C10–C11	1.446(7)
C10–C15	1.530(7)
C11–H11	1.0000
C11–C12	1.505(7)
C12–H12	1.0000
C12–C13	1.535(6)
C13–H13	1.0000
C13–C14	1.526(7)
C14–H14	1.0000
C14–C15	1.532(7)
C14–C22	1.521(8)
C15–H15A	0.9900
C15–H15B	0.9900
C16–C17	1.384(7)
C16–C21	1.397(7)
C17–H17	0.9500
C17–C18	1.389(8)
C18–H18	0.9500
C18–C19	1.387(8)
C19–H19	0.9500
C19–C20	1.391(8)
C20–H20	0.9500
C20–C21	1.394(7)
C22–H22A	0.9900
C22–H22B	0.9900
C22–C23	1.510(7)

C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
C27–H27A	0.9800
C27–H27B	0.9800
C27–H27C	0.9800
B1–H1A	1.0000
N9–C28	1.134(8)
C28–C29	1.463(8)
C29–H29A	0.9800
C29–H29B	0.9800
C29–H29C	0.9800
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	154.59(11)
N1–W1–N5	82.04(19)
N3–W1–P1	79.94(15)
N3–W1–N1	77.23(18)
N3–W1–N5	85.2(2)
N3–W1–C10	159.21(16)
N5–W1–P1	85.07(15)
N7–W1–P1	95.4(2)
N7–W1–N1	96.5(2)
N7–W1–N3	92.3(2)
N7–W1–N5	177.4(3)
N7–W1–C10	94.5(2)
N7–W1–C11	94.6(2)
C10–W1–P1	79.89(14)
C10–W1–N1	121.28(17)
C10–W1–N5	88.1(2)
C11–W1–P1	118.04(15)
C11–W1–N1	83.23(18)

C11–W1–N3	159.88(15)
C11–W1–N5	87.4(2)
C11–W1–C10	38.40(19)
C25–P1–W1	120.85(18)
C25–P1–C26	102.2(3)
C25–P1–C27	98.9(3)
C26–P1–W1	115.3(2)
C26–P1–C27	103.7(3)
C27–P1–W1	113.40(18)
C16–O2–C12	111.7(4)
C23–O4–C24	115.9(5)
N2–N1–W1	119.9(3)
C1–N1–W1	134.3(4)
C1–N1–N2	105.2(4)
N1–N2–B1	121.4(4)
C3–N2–N1	110.2(4)
C3–N2–B1	127.9(4)
N4–N3–W1	122.5(3)
C4–N3–W1	131.4(4)
C4–N3–N4	106.1(4)
N3–N4–B1	118.9(4)
C6–N4–N3	110.0(4)
C6–N4–B1	129.7(5)
N6–N5–W1	120.0(4)
C7–N5–W1	134.2(4)
C7–N5–N6	105.7(5)
N5–N6–B1	121.7(5)
C9–N6–N5	109.9(5)
C9–N6–B1	128.3(4)
O1–N7–W1	178.8(6)
C13–N8–H8	119(5)
C21–N8–C13	122.0(4)
C21–N8–H8	113(5)
N1–C1–H1	124.4
N1–C1–C2	111.2(5)
C2–C1–H1	124.4
C1–C2–H2	127.6
C3–C2–C1	104.8(5)
C3–C2–H2	127.6

N2–C3–C2	108.6(5)
N2–C3–H3	125.7
C2–C3–H3	125.7
N3–C4–H4	124.5
N3–C4–C5	111.0(5)
C5–C4–H4	124.5
C4–C5–H5	127.7
C6–C5–C4	104.5(5)
C6–C5–H5	127.7
N4–C6–C5	108.4(5)
N4–C6–H6	125.8
C5–C6–H6	125.8
N5–C7–H7	124.4
N5–C7–C8	111.2(5)
C8–C7–H7	124.4
C7–C8–H8A	127.8
C9–C8–C7	104.4(5)
C9–C8–H8A	127.8
N6–C9–C8	108.8(4)
N6–C9–H9	125.6
C8–C9–H9	125.6
W1–C10–H10	113.4
C11–C10–W1	69.6(3)
C11–C10–H10	113.4
C11–C10–C15	119.1(4)
C15–C10–W1	121.1(3)
C15–C10–H10	113.4
W1–C11–H11	111.2
C10–C11–W1	72.0(3)
C10–C11–H11	111.2
C10–C11–C12	121.9(4)
C12–C11–W1	124.1(3)
C12–C11–H11	111.2
O2–C12–C11	106.2(4)
O2–C12–H12	108.5
O2–C12–C13	110.5(4)
C11–C12–H12	108.5
C11–C12–C13	114.6(4)
C13–C12–H12	108.5

N8–C13–C12	110.0(4)
N8–C13–H13	107.4
N8–C13–C14	111.6(4)
C12–C13–H13	107.4
C14–C13–C12	112.9(4)
C14–C13–H13	107.4
C13–C14–H14	108.4
C13–C14–C15	107.8(4)
C15–C14–H14	108.4
C22–C14–C13	111.8(4)
C22–C14–H14	108.4
C22–C14–C15	112.0(5)
C10–C15–C14	112.3(4)
C10–C15–H15A	109.1
C10–C15–H15B	109.1
C14–C15–H15A	109.1
C14–C15–H15B	109.1
H15A–C15–H15B	107.9
O2–C16–C17	119.2(5)
O2–C16–C21	119.1(4)
C17–C16–C21	121.7(5)
C16–C17–H17	120.1
C16–C17–C18	119.8(5)
C18–C17–H17	120.1
C17–C18–H18	120.3
C19–C18–C17	119.3(5)
C19–C18–H18	120.3
C18–C19–H19	119.7
C18–C19–C20	120.5(5)
C20–C19–H19	119.7
C19–C20–H20	119.6
C19–C20–C21	120.7(5)
C21–C20–H20	119.6
N8–C21–C16	119.4(4)
N8–C21–C20	122.7(5)
C20–C21–C16	117.8(5)
C14–C22–H22A	108.8
C14–C22–H22B	108.8
H22A–C22–H22B	107.6

C23–C22–C14	114.0(4)
C23–C22–H22A	108.8
C23–C22–H22B	108.8
O3–C23–O4	123.2(5)
O3–C23–C22	126.6(5)
O4–C23–C22	110.2(5)
O4–C24–H24A	109.5
O4–C24–H24B	109.5
O4–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
P1–C25–H25A	109.5
P1–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25B	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
P1–C27–H27A	109.5
P1–C27–H27B	109.5
P1–C27–H27C	109.5
H27A–C27–H27B	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
N2–B1–H1A	110.8
N4–B1–N2	105.8(4)
N4–B1–H1A	110.8
N6–B1–N2	108.3(4)
N6–B1–N4	110.4(4)
N6–B1–H1A	110.8
N9–C28–C29	179.7(6)
C28–C29–H29A	109.5
C28–C29–H29B	109.5

C28–C29–H29C	109.5
H29A–C29–H29B	109.5
H29A–C29–H29C	109.5
H29B–C29–H29C	109.5

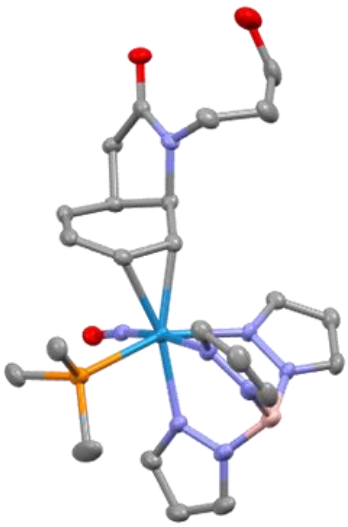
Table 5 Torsion angles for Compound 30

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
W1–N1–N2–C3	−172.9(3)
W1–N1–N2–B1	−1.1(6)
W1–N1–C1–C2	172.0(4)
W1–N3–N4–C6	179.5(4)
W1–N3–N4–B1	11.9(6)
W1–N3–C4–C5	179.3(4)
W1–N5–N6–C9	−178.0(4)
W1–N5–N6–B1	−1.6(7)
W1–N5–C7–C8	177.9(4)
W1–C10–C11–C12	−119.5(4)
W1–C10–C15–C14	111.7(4)
W1–C11–C12–O2	157.2(3)
W1–C11–C12–C13	−80.6(5)
O2–C12–C13–N8	−43.3(5)
O2–C12–C13–C14	82.0(5)
O2–C16–C17–C18	176.3(5)
O2–C16–C21–N8	−1.2(7)
O2–C16–C21–C20	−178.0(5)
N1–N2–C3–C2	−0.7(6)
N1–N2–B1–N4	−59.3(6)
N1–N2–B1–N6	59.0(6)
N1–C1–C2–C3	−0.9(7)
N2–N1–C1–C2	0.5(7)
N3–N4–C6–C5	2.0(6)
N3–N4–B1–N2	52.8(6)
N3–N4–B1–N6	−64.1(6)
N3–C4–C5–C6	0.9(6)
N4–N3–C4–C5	0.2(6)

N5–N6–C9–C8	−0.6(6)
N5–N6–B1–N2	−57.2(6)
N5–N6–B1–N4	58.1(6)
N5–C7–C8–C9	−0.1(6)
N6–N5–C7–C8	−0.3(6)
N8–C13–C14–C15	−173.4(4)
N8–C13–C14–C22	63.1(5)
C1–N1–N2–C3	0.1(6)
C1–N1–N2–B1	171.9(5)
C1–C2–C3–N2	1.0(7)
C3–N2–B1–N4	111.0(6)
C3–N2–B1–N6	−130.7(5)
C4–N3–N4–C6	−1.4(6)
C4–N3–N4–B1	−169.0(4)
C4–C5–C6–N4	−1.8(6)
C6–N4–B1–N2	−112.0(6)
C6–N4–B1–N6	131.1(5)
C7–N5–N6–C9	0.5(6)
C7–N5–N6–B1	176.8(4)
C7–C8–C9–N6	0.4(6)
C9–N6–B1–N2	118.4(5)
C9–N6–B1–N4	−126.3(5)
C10–C11–C12–O2	−113.8(5)
C10–C11–C12–C13	8.4(7)
C11–C10–C15–C14	29.3(6)
C11–C12–C13–N8	−163.2(4)
C11–C12–C13–C14	−37.9(6)
C12–O2–C16–C17	143.9(5)
C12–O2–C16–C21	−38.1(6)
C12–C13–C14–C15	62.1(6)
C12–C13–C14–C22	−61.4(5)
C13–N8–C21–C16	17.8(7)
C13–N8–C21–C20	−165.6(5)
C13–C14–C15–C10	−56.7(6)
C13–C14–C22–C23	−163.6(4)
C14–C22–C23–O3	18.2(8)
C14–C22–C23–O4	−163.3(5)
C15–C10–C11–W1	115.1(4)
C15–C10–C11–C12	−4.4(7)

C15–C14–C22–C23	75.3(5)
C16–O2–C12–C11	−174.7(4)
C16–O2–C12–C13	60.5(5)
C16–C17–C18–C19	1.3(9)
C17–C16–C21–N8	176.7(5)
C17–C16–C21–C20	0.0(8)
C17–C18–C19–C20	0.8(9)
C18–C19–C20–C21	−2.6(9)
C19–C20–C21–N8	−174.5(5)
C19–C20–C21–C16	2.2(8)
C21–N8–C13–C12	5.8(6)
C21–N8–C13–C14	−120.3(5)
C21–C16–C17–C18	−1.7(8)
C22–C14–C15–C10	66.7(5)
C24–O4–C23–O3	−3.5(8)
C24–O4–C23–C22	177.9(5)
B1–N2–C3–C2	−171.8(5)
B1–N4–C6–C5	167.8(5)
B1–N6–C9–C8	−176.6(5)

Crystal Structure Report for Compound 26



A colorless, block-like specimen of $C_{26}H_{40}BN_8O_4PW$, approximate dimensions 0.055 mm x 0.082 mm x 0.179 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture PhotonIII Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 1.43 hours. The frames were integrated with the Bruker SAINT software package[212] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 89355 reflections to a maximum θ angle of 27.56° (0.77 Å resolution), of which 13963 were independent (average redundancy 6.399, completeness = 99.4%, R_{int} = 7.04%, R_{sig} = 4.91%) and 10442 (74.78%) were greater than $2\sigma(F^2)$. The final cell constants of a = 21.1853(9) Å, b = 15.0978(6) Å, c = 20.4456(8) Å, β = 111.7050(10)°, volume = 6075.9(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9052 reflections above 20 σ(I) with 4.836° < 2θ < 54.82°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[213] The ratio of minimum to maximum apparent transmission was 0.869. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5420 and 0.8140.

The structure was solved and refined using the Bruker SHELXTL Software Package[214] within APEX4 [1] and OLEX2,[215] using the space group P $2_1/c$, with Z = 8 for the formula unit, $C_{26}H_{40}BN_8O_4PW$. Non-hydrogen atoms were refined anisotropically. The B-H and O-H hydrogen atoms were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = $1.2U_{equiv}$ of the parent atom ($1.5U_{equiv}$ for methyl). The relative occupancy of the two sites of the disordered acetone solvent was freely refined, with constraints and restraints used as needed on the anisotropic displacement parameters and bond lengths of the disordered atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 805 variables converged at R1 = 3.46%, for the observed data and wR2 = 7.42% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 1.165 $e^-/Å^3$ and the largest hole was -0.795 $e^-/Å^3$ with an RMS deviation of 0.125 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.649 g/cm^3 and F(000), 3024 e^-.

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Table 1. Sample and crystal data for Compound 26.

Chemical formula	$C_{26}H_{40}BN_8O_4PW$
Formula weight	754.29 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.055 x 0.082 x 0.179 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 21.1853(9) Å α = 90°
	b = 15.0978(6) Å β = 111.7050(10)°
	c = 20.4456(8) Å γ = 90°
Volume	6075.9(4) $Å^3$
Z	8
Density (calculated)	1.649 g/cm^3
Absorption coefficient	3.901 mm^{-1}
F(000)	3024

Table 2. Data collection and structure refinement for Compound 26.

Diffractometer	Bruker D8 Venture PhotonIII Kappa four-circle diffractometer

Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	2.01 to 27.56°
Index ranges	-27<=h<=27, -19<=k<=19, -25<=l<=26
Reflections collected	89355
Independent reflections	13963 [R(int) = 0.0704]
Coverage of independent reflections	99.4%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8140 and 0.5420
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13963 / 114 / 805
Goodness-of-fit on F^2	1.025
Δ/σ_{max}	0.003

Final R indices	10442 data; I>2σ(I)	R1 = 0.0346, wR2 = 0.0667
	all data	R1 = 0.0566, wR2 = 0.0742
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0227P)^2+10.0889P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.165 and -0.795 eÅ^{-3}	
R.M.S. deviation from mean	0.125 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 26.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
W1	0.90405(2)	0.01633(2)	0.72626(2)	0.01680(5)
P1	0.92238(6)	0.14262(8)	0.65677(6)	0.0214(2)
O1	0.78065(15)	0.1121(2)	0.72665(16)	0.0280(7)
O2	0.6652(2)	0.7144(3)	0.5575(2)	0.0628(14)
O3	0.7171(2)	0.5726(3)	0.6511(3)	0.0646(15)
N1	0.00590(17)	0.9654(2)	0.73144(18)	0.0209(8)
N2	0.05928(18)	0.9637(2)	0.79503(19)	0.0236(8)
N3	0.96179(17)	0.1012(2)	0.81638(18)	0.0200(8)
N4	0.02396(17)	0.0804(2)	0.86300(18)	0.0212(8)

	x/a	y/b	z/c	U(eq)
N5	0.92852(17)	0.9255(2)	0.81912(18)	0.0193(8)
N6	0.99320(17)	0.9250(2)	0.86991(18)	0.0194(8)
N7	0.82876(17)	0.0680(2)	0.72522(18)	0.0198(8)
N8	0.7650(2)	0.7849(3)	0.6191(2)	0.0353(10)
C1	0.0303(2)	0.9353(3)	0.6843(3)	0.0260(10)
C2	0.0988(2)	0.9136(3)	0.7162(3)	0.0307(11)
C3	0.1148(2)	0.9331(3)	0.7860(3)	0.0286(11)
C4	0.9431(2)	0.1776(3)	0.8369(2)	0.0239(10)
C5	0.9943(2)	0.2063(3)	0.8981(2)	0.0311(11)
C6	0.0442(2)	0.1434(3)	0.9129(2)	0.0266(10)
C7	0.8925(2)	0.8703(3)	0.8425(2)	0.0178(9)
C8	0.9320(2)	0.8342(3)	0.9070(2)	0.0218(9)
C9	0.9954(2)	0.8706(3)	0.9229(2)	0.0224(10)
C10	0.8568(2)	0.8980(3)	0.6674(2)	0.0214(9)
C11	0.8607(2)	0.9612(3)	0.6167(2)	0.0249(10)
C12	0.7975(2)	0.9983(3)	0.5657(2)	0.0328(12)
C13	0.7372(2)	0.9856(3)	0.5716(2)	0.0315(12)
C14	0.7281(2)	0.9290(3)	0.6278(2)	0.0271(11)
C15	0.7881(2)	0.8655(3)	0.6631(2)	0.0228(10)
C16	0.6674(2)	0.8666(4)	0.5987(3)	0.0413(14)
C17	0.6973(3)	0.7810(4)	0.5872(3)	0.0453(16)
C18	0.8079(3)	0.7069(4)	0.6286(4)	0.062(2)
C19	0.8206(3)	0.6601(4)	0.6982(4)	0.063(2)

	x/a	y/b	z/c	U(eq)
C20	0.7569(3)	0.6284(4)	0.7074(3)	0.0515(16)
C21	0.9428(2)	0.1233(3)	0.5789(2)	0.0310(11)
C22	0.8507(2)	0.2164(3)	0.6252(2)	0.0298(11)
C23	0.9919(2)	0.2159(3)	0.7063(3)	0.0352(12)
B1	0.0492(2)	0.9846(4)	0.8644(3)	0.0224(11)
W2	0.40718(2)	0.08088(2)	0.22509(2)	0.01794(5)
P2	0.43752(6)	0.20328(8)	0.15974(6)	0.0242(3)
O4	0.28354(15)	0.1845(2)	0.21610(15)	0.0241(7)
O5	0.15496(15)	0.8117(2)	0.02554(16)	0.0290(8)
O6	0.1968(2)	0.6485(3)	0.0859(2)	0.0547(12)
N9	0.51022(18)	0.0249(3)	0.23949(19)	0.0237(8)
N10	0.56009(18)	0.0231(3)	0.3049(2)	0.0264(9)
N11	0.46168(17)	0.1653(3)	0.31636(18)	0.0226(8)
N12	0.52216(18)	0.1417(3)	0.36784(18)	0.0249(9)
N13	0.42326(17)	0.9901(2)	0.31624(18)	0.0195(8)
N14	0.48493(17)	0.9872(2)	0.37069(18)	0.0214(8)
N15	0.33236(17)	0.1378(2)	0.21911(17)	0.0195(8)
N16	0.25880(18)	0.8638(2)	0.09935(18)	0.0203(8)
C24	0.5388(2)	0.9981(3)	0.1946(3)	0.0288(11)
C25	0.6072(2)	0.9786(3)	0.2305(3)	0.0345(12)
C26	0.6181(2)	0.9954(3)	0.2990(3)	0.0319(12)
C27	0.4450(2)	0.2436(3)	0.3354(2)	0.0280(11)
C28	0.4938(3)	0.2721(3)	0.3986(2)	0.0336(12)

	x/a	y/b	z/c	U(eq)
C29	0.5410(2)	0.2053(3)	0.4171(2)	0.0310(12)
C30	0.3832(2)	0.9355(3)	0.3340(2)	0.0199(9)
C31	0.4173(2)	0.8982(3)	0.3998(2)	0.0240(10)
C32	0.4814(2)	0.9322(3)	0.4210(2)	0.0260(10)
C33	0.3571(2)	0.9643(3)	0.1634(2)	0.0189(9)
C34	0.3670(2)	0.0278(3)	0.1150(2)	0.0205(9)
C35	0.3060(2)	0.0704(3)	0.0643(2)	0.0233(10)
C36	0.2448(2)	0.0626(3)	0.0674(2)	0.0236(10)
C37	0.2309(2)	0.0071(3)	0.1218(2)	0.0204(9)
C38	0.2860(2)	0.9359(3)	0.1524(2)	0.0184(9)
C39	0.1666(2)	0.9518(3)	0.0889(2)	0.0229(10)
C40	0.1914(2)	0.8683(3)	0.0667(2)	0.0207(9)
C41	0.2978(2)	0.7863(3)	0.0956(3)	0.0288(11)
C42	0.3055(2)	0.7192(3)	0.1526(3)	0.0353(12)
C43	0.2385(3)	0.6834(4)	0.1517(3)	0.0424(14)
C44	0.4653(2)	0.1793(3)	0.0874(2)	0.0309(11)
C45	0.3700(3)	0.2821(3)	0.1215(3)	0.0339(12)
C46	0.5080(3)	0.2720(4)	0.2147(3)	0.0485(16)
B2	0.5447(3)	0.0454(4)	0.3708(3)	0.0281(12)
O8	0.0713(10)	0.3829(16)	0.0062(14)	0.052(5)
C50	0.1672(15)	0.428(2)	0.1082(11)	0.102(9)
C51	0.135(6)	0.378(13)	0.044(9)	0.049(7)
C52	0.1770(9)	0.3134(12)	0.0261(12)	0.046(5)

	x/a	y/b	z/c	U(eq)
O8A	0.0775(12)	0.3529(16)	0.9940(12)	0.109(8)
C50A	0.1231(7)	0.4603(8)	0.0841(7)	0.045(4)
C51A	0.125(4)	0.379(10)	0.042(7)	0.049(7)
C52A	0.1959(10)	0.3355(12)	0.0622(10)	0.072(5)
O7A	0.6711(7)	0.2539(9)	0.5544(7)	0.039(4)
C47A	0.6364(11)	0.4063(12)	0.5483(11)	0.0439(12)
C48A	0.6707(16)	0.3211(14)	0.5805(14)	0.0439(12)
C49A	0.6925(17)	0.3080(16)	0.6580(14)	0.0439(12)
O7	0.6104(4)	0.3216(6)	0.5472(3)	0.096(3)
C47	0.7109(4)	0.3970(5)	0.5575(4)	0.0439(12)
C48	0.6655(6)	0.3489(5)	0.5850(5)	0.0439(12)
C49	0.6948(6)	0.3340(6)	0.6631(5)	0.0439(12)

Table 4. Bond lengths (Å) for Compound 26.

W1-N7	1.768(4)	W1-C10	2.181(4)
W1-N3	2.206(4)	W1-N5	2.242(3)
W1-C11	2.243(4)	W1-N1	2.256(3)
W1-P1	2.4926(12)	P1-C22	1.800(5)
P1-C21	1.820(5)	P1-C23	1.821(5)
O1-N7	1.227(4)	O2-C17	1.239(6)
O3-C20	1.423(7)	O3-H3	0.94(8)
N1-C1	1.332(6)	N1-N2	1.372(5)

N2-C3	1.338(6)	N2-B1	1.543(6)
N3-C4	1.336(6)	N3-N4	1.347(5)
N4-C6	1.344(6)	N4-B1	1.538(6)
N5-C7	1.333(5)	N5-N6	1.380(5)
N6-C9	1.346(5)	N6-B1	1.527(6)
N8-C17	1.339(6)	N8-C18	1.456(7)
N8-C15	1.484(6)	C1-C2	1.392(6)
C1-H1	0.950000	C2-C3	1.371(7)
C2-H2	0.950000	C3-H3A	0.950000
C4-C5	1.388(6)	C4-H4	0.950000
C5-C6	1.368(7)	C5-H5	0.950000
C6-H6	0.950000	C7-C8	1.386(6)
C7-H7	0.950000	C8-C9	1.375(6)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.433(6)	C10-C15	1.508(6)
C10-H10	1.000000	C11-C12	1.470(6)
C11-H11	1.000000	C12-C13	1.341(7)
C12-H12	0.950000	C13-C14	1.501(7)
C13-H13	0.950000	C14-C16	1.526(7)
C14-C15	1.541(6)	C14-H14	1.000000
C15-H15	1.000000	C16-C17	1.495(8)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.520(10)	C18-H18A	0.990000
C18-H18B	0.990000	C19-C20	1.510(8)

C19-H19A	0.990000	C19-H19B	0.990000
C20-H20A	0.990000	C20-H20B	0.990000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
C23-H23A	0.980000	C23-H23B	0.980000
C23-H23C	0.980000	B1-H1A	1.05(4)
W2-N15	1.767(4)	W2-C33	2.197(4)
W2-N11	2.201(4)	W2-N13	2.236(3)
W2-C34	2.239(4)	W2-N9	2.256(4)
W2-P2	2.4997(12)	P2-C45	1.801(5)
P2-C44	1.818(5)	P2-C46	1.823(5)
O4-N15	1.235(4)	O5-C40	1.246(5)
O6-C43	1.411(6)	O6-H6A	0.99(7)
N9-C24	1.335(6)	N9-N10	1.364(5)
N10-C26	1.344(6)	N10-B2	1.536(7)
N11-C27	1.333(6)	N11-N12	1.371(5)
N12-C29	1.342(6)	N12-B2	1.524(7)
N13-C30	1.327(5)	N13-N14	1.368(5)
N14-C32	1.345(6)	N14-B2	1.541(6)
N16-C40	1.336(5)	N16-C41	1.452(5)
N16-C38	1.493(5)	C24-C25	1.392(6)
C24-H24	0.950000	C25-C26	1.358(7)
C25-H25	0.950000	C26-H26	0.950000

C27-C28	1.392(6)	C27-H27	0.950000
C28-C29	1.371(7)	C28-H28	0.950000
C29-H29	0.950000	C30-C31	1.388(6)
C30-H30	0.950000	C31-C32	1.365(6)
C31-H31	0.950000	C32-H32	0.950000
C33-C34	1.447(6)	C33-C38	1.501(6)
C33-H33	1.000000	C34-C35	1.471(6)
C34-H34	1.000000	C35-C36	1.327(6)
C35-H35	0.950000	C36-C37	1.506(6)
C36-H36	0.950000	C37-C39	1.526(6)
C37-C38	1.538(6)	C37-H37	1.000000
C38-H38	1.000000	C39-C40	1.499(6)
C39-H39A	0.990000	C39-H39B	0.990000
C41-C42	1.506(7)	C41-H41A	0.990000
C41-H41B	0.990000	C42-C43	1.513(7)
C42-H42A	0.990000	C42-H42B	0.990000
C43-H43A	0.990000	C43-H43B	0.990000
C44-H44A	0.980000	C44-H44B	0.980000
C44-H44C	0.980000	C45-H45A	0.980000
C45-H45B	0.980000	C45-H45C	0.980000
C46-H46A	0.980000	C46-H46B	0.980000
C46-H46C	0.980000	B2-H2A	1.06(5)
O8-C51	1.28(11)	C50-C51	1.44(17)
C50-H50A	0.980000	C50-H50B	0.980000

C50-H50C	0.980000	C51-C52	1.46(18)
C52-H52A	0.980000	C52-H52B	0.980000
C52-H52C	0.980000	O8A-C51A	1.19(10)
C50A-C51A	1.51(15)	C50A-H50D	0.980000
C50A-H50E	0.980000	C50A-H50F	0.980000
C51A-C52A	1.55(10)	C52A-H52D	0.980000
C52A-H52E	0.980000	C52A-H52F	0.980000
O7A-C48A	1.15(3)	C47A-C48A	1.504(16)
C47A-H47A	0.980000	C47A-H47B	0.980000
C47A-H47C	0.980000	C48A-C49A	1.490(15)
C49A-H49A	0.980000	C49A-H49B	0.980000
C49A-H49C	0.980000	O7-C48	1.209(12)
C47-C48	1.472(11)	C47-H47D	0.980000
C47-H47E	0.980000	C47-H47F	0.980000
C48-C49	1.501(9)	C49-H49D	0.980000
C49-H49E	0.980000	C49-H49F	0.980000

Table 5. Bond angles (°) for Compound 26.

N7-W1-C10	97.28(16)	N7-W1-N3	88.46(15)
C10-W1-N3	159.54(15)	N7-W1-N5	101.82(14)
C10-W1-N5	83.19(15)	N3-W1-N5	76.40(13)
N7-W1-C11	96.72(16)	C10-W1-C11	37.78(16)
N3-W1-C11	160.97(15)	N5-W1-C11	119.98(15)
N7-W1-N1	173.52(15)	C10-W1-N1	89.00(14)
N3-W1-N1	86.18(13)	N5-W1-N1	80.46(13)
C11-W1-N1	87.24(15)	N7-W1-P1	89.20(12)
C10-W1-P1	116.65(12)	N3-W1-P1	82.91(9)
N5-W1-P1	156.16(9)	C11-W1-P1	78.88(12)
N1-W1-P1	86.53(9)	C22-P1-C21	103.1(2)
C22-P1-C23	103.0(2)	C21-P1-C23	100.3(2)
C22-P1-W1	112.91(16)	C21-P1-W1	120.89(17)
C23-P1-W1	114.34(16)	C20-O3-H3	102.(5)
C1-N1-N2	106.0(3)	C1-N1-W1	134.7(3)
N2-N1-W1	119.3(3)	C3-N2-N1	109.6(4)
C3-N2-B1	128.6(4)	N1-N2-B1	121.4(3)
C4-N3-N4	107.7(4)	C4-N3-W1	128.8(3)
N4-N3-W1	123.4(3)	C6-N4-N3	109.0(4)
C6-N4-B1	129.8(4)	N3-N4-B1	118.4(3)
C7-N5-N6	105.5(3)	C7-N5-W1	134.7(3)
N6-N5-W1	119.7(3)	C9-N6-N5	109.8(3)
C9-N6-B1	128.5(4)	N5-N6-B1	121.6(3)
O1-N7-W1	173.0(3)	C17-N8-C18	122.1(5)

C17-N8-C15	112.6(4)	C18-N8-C15	122.2(4)
N1-C1-C2	110.9(4)	N1-C1-H1	124.600000
C2-C1-H1	124.600000	C3-C2-C1	104.6(4)
C3-C2-H2	127.700000	C1-C2-H2	127.700000
N2-C3-C2	109.0(4)	N2-C3-H3A	125.500000
C2-C3-H3A	125.500000	N3-C4-C5	109.3(4)
N3-C4-H4	125.400000	C5-C4-H4	125.400000
C6-C5-C4	105.3(4)	C6-C5-H5	127.300000
C4-C5-H5	127.300000	N4-C6-C5	108.7(4)
N4-C6-H6	125.700000	C5-C6-H6	125.700000
N5-C7-C8	111.3(4)	N5-C7-H7	124.400000
C8-C7-H7	124.400000	C9-C8-C7	105.1(4)
C9-C8-H8	127.400000	C7-C8-H8	127.400000
N6-C9-C8	108.3(4)	N6-C9-H9	125.800000
C8-C9-H9	125.900000	C11-C10-C15	119.2(4)
C11-C10-W1	73.5(3)	C15-C10-W1	122.3(3)
C11-C10-H10	112.200000	C15-C10-H10	112.200000
W1-C10-H10	112.200000	C10-C11-C12	119.1(4)
C10-C11-W1	68.8(2)	C12-C11-W1	119.8(3)
C10-C11-H11	114.000000	C12-C11-H11	114.000000
W1-C11-H11	114.000000	C13-C12-C11	122.0(5)
C13-C12-H12	119.000000	C11-C12-H12	119.000000
C12-C13-C14	123.1(4)	C12-C13-H13	118.500000
C14-C13-H13	118.500000	C13-C14-C16	112.4(4)

C13-C14-C15	113.3(4)	C16-C14-C15	103.2(4)
C13-C14-H14	109.300000	C16-C14-H14	109.300000
C15-C14-H14	109.300000	N8-C15-C10	113.4(4)
N8-C15-C14	101.4(3)	C10-C15-C14	115.8(4)
N8-C15-H15	108.600000	C10-C15-H15	108.600000
C14-C15-H15	108.600000	C17-C16-C14	104.5(4)
C17-C16-H16A	110.800000	C14-C16-H16A	110.800000
C17-C16-H16B	110.800000	C14-C16-H16B	110.800000
H16A-C16-H16B	108.900000	O2-C17-N8	124.7(6)
O2-C17-C16	126.2(5)	N8-C17-C16	108.9(4)
N8-C18-C19	112.7(5)	N8-C18-H18A	109.000000
C19-C18-H18A	109.000000	N8-C18-H18B	109.000000
C19-C18-H18B	109.000000	H18A-C18-H18B	107.800000
C20-C19-C18	114.0(5)	C20-C19-H19A	108.800000
C18-C19-H19A	108.800000	C20-C19-H19B	108.800000
C18-C19-H19B	108.800000	H19A-C19-H19B	107.600000
O3-C20-C19	112.1(5)	O3-C20-H20A	109.200000

C19-C20-H20A	109.200000	O3-C20-H20B	109.200000
C19-C20-H20B	109.200000	H20A-C20-H20B	107.900000
P1-C21-H21A	109.500000	P1-C21-H21B	109.500000
H21A-C21-H21B	109.500000	P1-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
P1-C22-H22A	109.500000	P1-C22-H22B	109.500000
H22A-C22-H22B	109.500000	P1-C22-H22C	109.500000
H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
P1-C23-H23A	109.500000	P1-C23-H23B	109.500000
H23A-C23-H23B	109.500000	P1-C23-H23C	109.500000
H23A-C23-H23C	109.500000	H23B-C23-H23C	109.500000
N6-B1-N4	106.3(4)	N6-B1-N2	108.8(4)
N4-B1-N2	109.9(4)	N6-B1-H1A	111.(2)
N4-B1-H1A	111.(2)	N2-B1-H1A	110.(2)
N15-W2-C33	96.88(15)	N15-W2-N11	87.31(14)
C33-W2-N11	160.26(15)	N15-W2-N13	102.25(14)
C33-W2-N13	83.10(14)	N11-W2-N13	77.16(13)
N15-W2-C34	96.09(15)	C33-W2-C34	38.06(15)
N11-W2-C34	160.81(15)	N13-W2-C34	120.16(14)

N15-W2-N9	172.31(15)	C33-W2-N9	90.74(14)
N11-W2-N9	85.84(13)	N13-W2-N9	79.61(13)
C34-W2-N9	89.27(14)	N15-W2-P2	90.27(12)
C33-W2-P2	116.76(11)	N11-W2-P2	82.37(10)
N13-W2-P2	155.34(9)	C34-W2-P2	78.74(11)
N9-W2-P2	85.36(10)	C45-P2-C44	102.8(2)
C45-P2-C46	103.3(3)	C44-P2-C46	100.2(2)
C45-P2-W2	113.61(17)	C44-P2-W2	120.80(17)
C46-P2-W2	113.90(17)	C43-O6-H6A	106.(4)
C24-N9-N10	106.5(4)	C24-N9-W2	133.4(3)
N10-N9-W2	119.8(3)	C26-N10-N9	108.7(4)
C26-N10-B2	130.0(4)	N9-N10-B2	121.1(4)
C27-N11-N12	106.3(4)	C27-N11-W2	130.4(3)
N12-N11-W2	123.3(3)	C29-N12-N11	109.0(4)
C29-N12-B2	130.6(4)	N11-N12-B2	118.0(4)
C30-N13-N14	105.8(3)	C30-N13-W2	133.9(3)
N14-N13-W2	120.2(3)	C32-N14-N13	109.6(4)
C32-N14-B2	129.0(4)	N13-N14-B2	121.3(3)
O4-N15-W2	174.2(3)	C40-N16-C41	122.6(4)
C40-N16-C38	112.4(3)	C41-N16-C38	123.5(3)
N9-C24-C25	110.5(5)	N9-C24-H24	124.700000

C25-C24-H24	124.700000	C26-C25-C24	104.5(4)
C26-C25-H25	127.800000	C24-C25-H25	127.800000
N10-C26-C25	109.8(4)	N10-C26-H26	125.100000
C25-C26-H26	125.100000	N11-C27-C28	111.1(4)
N11-C27-H27	124.500000	C28-C27-H27	124.500000
C29-C28-C27	104.2(4)	C29-C28-H28	127.900000
C27-C28-H28	127.900000	N12-C29-C28	109.6(4)
N12-C29-H29	125.200000	C28-C29-H29	125.200000
N13-C30-C31	111.1(4)	N13-C30-H30	124.400000
C31-C30-H30	124.400000	C32-C31-C30	104.8(4)
C32-C31-H31	127.600000	C30-C31-H31	127.600000
N14-C32-C31	108.6(4)	N14-C32-H32	125.700000
C31-C32-H32	125.700000	C34-C33-C38	118.5(4)
C34-C33-W2	72.5(2)	C38-C33-W2	124.0(3)
C34-C33-H33	112.100000	C38-C33-H33	112.100000
W2-C33-H33	112.100000	C33-C34-C35	117.4(4)
C33-C34-W2	69.4(2)	C35-C34-W2	117.4(3)
C33-C34-H34	115.000000	C35-C34-H34	115.000000
W2-C34-H34	115.000000	C36-C35-C34	123.1(4)
C36-C35-H35	118.500000	C34-C35-H35	118.500000
C35-C36-C37	123.1(4)	C35-C36-H36	118.500000

C37-C36-H36	118.500000	C36-C37-C39	111.4(4)
C36-C37-C38	111.3(4)	C39-C37-C38	102.5(3)
C36-C37-H37	110.500000	C39-C37-H37	110.500000
C38-C37-H37	110.500000	N16-C38-C33	114.4(3)
N16-C38-C37	100.6(3)	C33-C38-C37	115.5(4)
N16-C38-H38	108.700000	C33-C38-H38	108.700000
C37-C38-H38	108.700000	C40-C39-C37	103.7(3)
C40-C39-H39A	111.000000	C37-C39-H39A	111.000000
C40-C39-H39B	111.000000	C37-C39-H39B	111.000000
H39A-C39-H39B	109.000000	O5-C40-N16	125.7(4)
O5-C40-C39	125.6(4)	N16-C40-C39	108.7(4)
N16-C41-C42	113.7(4)	N16-C41-H41A	108.800000
C42-C41-H41A	108.800000	N16-C41-H41B	108.800000
C42-C41-H41B	108.800000	H41A-C41-H41B	107.700000
C41-C42-C43	113.5(4)	C41-C42-H42A	108.900000
C43-C42-H42A	108.900000	C41-C42-H42B	108.900000
C43-C42-H42B	108.900000	H42A-C42-H42B	107.700000

O6-C43-C42	113.4(5)	O6-C43-H43A	108.900000
C42-C43-H43A	108.900000	O6-C43-H43B	108.900000
C42-C43-H43B	108.900000	H43A-C43-H43B	107.700000
P2-C44-H44A	109.500000	P2-C44-H44B	109.500000
H44A-C44-H44B	109.500000	P2-C44-H44C	109.500000
H44A-C44-H44C	109.500000	H44B-C44-H44C	109.500000
P2-C45-H45A	109.500000	P2-C45-H45B	109.500000
H45A-C45-H45B	109.500000	P2-C45-H45C	109.500000
H45A-C45-H45C	109.500000	H45B-C45-H45C	109.500000
P2-C46-H46A	109.500000	P2-C46-H46B	109.500000
H46A-C46-H46B	109.500000	P2-C46-H46C	109.500000
H46A-C46-H46C	109.500000	H46B-C46-H46C	109.500000
N12-B2-N10	109.8(4)	N12-B2-N14	107.4(4)
N10-B2-N14	108.3(4)	N12-B2-H2A	111.(3)
N10-B2-H2A	110.(3)	N14-B2-H2A	110.(3)
C51-C50-H50A	109.500000	C51-C50-H50B	109.500000
H50A-C50-H50B	109.500000	C51-C50-H50C	109.500000

H50A-C50-H50C	109.500000	H50B-C50-H50C	109.500000
O8-C51-C50	124.(10)	O8-C51-C52	119.(10)
C50-C51-C52	117.(8)	C51-C52-H52A	109.500000
C51-C52-H52B	109.500000	H52A-C52-H52B	109.500000
C51-C52-H52C	109.500000	H52A-C52-H52C	109.500000
H52B-C52-H52C	109.500000	C51A-C50A-H50D	109.500000
C51A-C50A-H50E	109.500000	H50D-C50A-H50E	109.500000
C51A-C50A-H50F	109.500000	H50D-C50A-H50F	109.500000
H50E-C50A-H50F	109.500000	O8A-C51A-C50A	123.(8)
O8A-C51A-C52A	121.(10)	C50A-C51A-C52A	115.(6)
C51A-C52A-H52D	109.500000	C51A-C52A-H52E	109.500000
H52D-C52A-H52E	109.500000	C51A-C52A-H52F	109.500000
H52D-C52A-H52F	109.500000	H52E-C52A-H52F	109.500000
C48A-C47A-H47A	109.500000	C48A-C47A-H47B	109.500000
H47A-C47A-H47B	109.500000	C48A-C47A-H47C	109.500000

H47A-C47A-H47C	109.500000	H47B-C47A-H47C	109.500000
O7A-C48A-C49A	108.9(18)	O7A-C48A-C47A	130.(2)
C49A-C48A-C47A	119.(2)	C48A-C49A-H49A	109.500000
C48A-C49A-H49B	109.500000	H49A-C49A-H49B	109.500000
C48A-C49A-H49C	109.500000	H49A-C49A-H49C	109.500000
H49B-C49A-H49C	109.500000	C48-C47-H47D	109.500000
C48-C47-H47E	109.500000	H47D-C47-H47E	109.500000
C48-C47-H47F	109.500000	H47D-C47-H47F	109.500000
H47E-C47-H47F	109.500000	O7-C48-C47	122.5(8)
O7-C48-C49	123.4(8)	C47-C48-C49	114.1(8)
C48-C49-H49D	109.500000	C48-C49-H49E	109.500000
H49D-C49-H49E	109.500000	C48-C49-H49F	109.500000
H49D-C49-H49F	109.500000	H49E-C49-H49F	109.500000

Table 6. Torsion angles (°) for Compound 26.

C1-N1-N2-C3	0.1(5)	W1-N1-N2-C3	-178.7(3)

C1-N1-N2-B1	-173.5(4)	W1-N1-N2-B1	7.7(5)
C4-N3-N4-C6	0.2(5)	W1-N3-N4-C6	-177.6(3)
C4-N3-N4-B1	163.1(4)	W1-N3-N4-B1	-14.7(5)
C7-N5-N6-C9	-0.3(5)	W1-N5-N6-C9	175.8(3)
C7-N5-N6-B1	-176.5(4)	W1-N5-N6-B1	-0.4(5)
N2-N1-C1-C2	0.2(5)	W1-N1-C1-C2	178.8(3)
N1-C1-C2-C3	-0.4(5)	N1-N2-C3-C2	-0.3(5)
B1-N2-C3-C2	172.6(4)	C1-C2-C3-N2	0.5(5)
N4-N3-C4-C5	-0.1(5)	W1-N3-C4-C5	177.6(3)
N3-C4-C5-C6	0.0(5)	N3-N4-C6-C5	-0.2(5)
B1-N4-C6-C5	-160.5(4)	C4-C5-C6-N4	0.1(5)
N6-N5-C7-C8	0.0(5)	W1-N5-C7-C8	-175.2(3)
N5-C7-C8-C9	0.3(5)	N5-N6-C9-C8	0.5(5)
B1-N6-C9-C8	176.3(4)	C7-C8-C9-N6	-0.5(5)
C15-C10-C11-C12	5.1(6)	W1-C10-C11-C12	-113.2(4)
C15-C10-C11-W1	118.2(4)	C10-C11-C12-C13	10.5(7)
W1-C11-C12-C13	-70.3(6)	C11-C12-C13-C14	-3.4(8)
C12-C13-C14-C16	-134.0(5)	C12-C13-C14-C15	-17.5(7)

C17-N8-C15-C10	-149.1(4)	C18-N8-C15-C10	50.1(6)
C17-N8-C15-C14	-24.3(5)	C18-N8-C15-C14	174.9(5)
C11-C10-C15-N8	90.7(5)	W1-C10-C15-N8	178.9(3)
C11-C10-C15-C14	-25.9(6)	W1-C10-C15-C14	62.3(5)
C13-C14-C15-N8	-92.0(4)	C16-C14-C15-N8	29.7(4)
C13-C14-C15-C10	31.1(5)	C16-C14-C15-C10	152.9(4)
C13-C14-C16-C17	96.1(5)	C15-C14-C16-C17	-26.3(5)
C18-N8-C17-O2	-6.6(9)	C15-N8-C17-O2	-167.5(5)
C18-N8-C17-C16	168.7(5)	C15-N8-C17-C16	7.9(6)
C14-C16-C17-O2	-172.4(5)	C14-C16-C17-N8	12.4(6)
C17-N8-C18-C19	-91.3(6)	C15-N8-C18-C19	67.7(6)
N8-C18-C19-C20	59.5(6)	C18-C19-C20-O3	55.3(7)
C9-N6-B1-N4	-115.4(5)	N5-N6-B1-N4	60.0(5)
C9-N6-B1-N2	126.3(4)	N5-N6-B1-N2	-58.3(5)
C6-N4-B1-N6	107.4(5)	N3-N4-B1-N6	-51.4(5)

C6-N4-B1-N2	-135.0(4)	N3-N4-B1-N2	66.3(5)
C3-N2-B1-N6	-118.4(5)	N1-N2-B1-N6	53.8(5)
C3-N2-B1-N4	125.5(5)	N1-N2-B1-N4	-62.3(5)
C24-N9-N10-C26	0.0(5)	W2-N9-N10-C26	-173.9(3)
C24-N9-N10-B2	-176.8(4)	W2-N9-N10-B2	9.3(5)
C27-N11-N12-C29	0.2(5)	W2-N11-N12-C29	-177.9(3)
C27-N11-N12-B2	164.3(4)	W2-N11-N12-B2	-13.8(5)
C30-N13-N14-C32	-0.9(5)	W2-N13-N14-C32	176.3(3)
C30-N13-N14-B2	-177.5(4)	W2-N13-N14-B2	-0.3(5)
N10-N9-C24-C25	0.1(5)	W2-N9-C24-C25	172.8(3)
N9-C24-C25-C26	-0.2(6)	N9-N10-C26-C25	-0.1(5)
B2-N10-C26-C25	176.3(5)	C24-C25-C26-N10	0.2(6)
N12-N11-C27-C28	0.3(5)	W2-N11-C27-C28	178.2(3)
N11-C27-C28-C29	-0.7(5)	N11-N12-C29-C28	-0.7(5)
B2-N12-C29-C28	-162.0(5)	C27-C28-C29-N12	0.8(5)

N14-N13-C30-C31	1.1(5)	W2-N13-C30-C31	-175.5(3)
N13-C30-C31-C32	-1.0(5)	N13-N14-C32-C31	0.3(5)
B2-N14-C32-C31	176.6(5)	C30-C31-C32-N14	0.4(5)
C38-C33-C34-C35	8.7(6)	W2-C33-C34-C35	-111.0(4)
C38-C33-C34-W2	119.8(4)	C33-C34-C35-C36	9.6(6)
W2-C34-C35-C36	-70.2(5)	C34-C35-C36-C37	-1.9(7)
C35-C36-C37-C39	-135.6(4)	C35-C36-C37-C38	-21.9(6)
C40-N16-C38-C33	-150.3(4)	C41-N16-C38-C33	43.6(5)
C40-N16-C38-C37	-25.9(4)	C41-N16-C38-C37	168.0(4)
C34-C33-C38-N16	83.2(5)	W2-C33-C38-N16	170.6(3)
C34-C33-C38-C37	-32.9(5)	W2-C33-C38-C37	54.5(5)
C36-C37-C38-N16	-85.7(4)	C39-C37-C38-N16	33.4(4)
C36-C37-C38-C33	38.0(5)	C39-C37-C38-C33	157.1(4)
C36-C37-C39-C40	88.3(4)	C38-C37-C39-C40	-30.8(4)
C41-N16-C40-O5	-6.1(7)	C38-N16-C40-O5	-172.3(4)

C41-N16-C40-C39	172.9(4)	C38-N16-C40-C39	6.7(5)
C37-C39-C40-O5	-165.1(4)	C37-C39-C40-N16	15.9(5)
C40-N16-C41-C42	-89.5(5)	C38-N16-C41-C42	75.2(5)
N16-C41-C42-C43	59.9(6)	C41-C42-C43-O6	53.9(6)
C29-N12-B2-N10	-133.8(5)	N11-N12-B2-N10	66.3(5)
C29-N12-B2-N14	108.6(5)	N11-N12-B2-N14	-51.3(5)
C26-N10-B2-N12	119.8(5)	N9-N10-B2-N12	-64.2(5)
C26-N10-B2-N14	-123.2(5)	N9-N10-B2-N14	52.8(6)
C32-N14-B2-N12	-116.0(5)	N13-N14-B2-N12	59.9(5)
C32-N14-B2-N10	125.4(5)	N13-N14-B2-N10	-58.7(6)

Table 7. Anisotropic atomic displacement parameters (Å^2) for Compound 26.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01604(8)	0.01720(9)	0.01690(9)	0.00136(7)	0.00579(6)	0.00046(7)
P1	0.0228(6)	0.0211(6)	0.0207(6)	0.0043(5)	0.0084(5)	0.0011(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0194(16)	0.0320(19)	0.0352(18)	0.0024(15)	0.0132(14)	0.0085(14)
O2	0.053(2)	0.089(4)	0.055(3)	-0.049(3)	0.030(2)	-0.045(2)
O3	0.064(3)	0.052(3)	0.099(4)	-0.046(3)	0.054(3)	-0.038(2)
N1	0.0152(17)	0.020(2)	0.0254(19)	0.0035(16)	0.0050(15)	0.0022(15)
N2	0.0190(18)	0.021(2)	0.030(2)	0.0026(17)	0.0082(16)	-0.0013(16)
N3	0.0221(18)	0.018(2)	0.0201(18)	0.0063(15)	0.0079(15)	-0.0006(15)
N4	0.0194(18)	0.022(2)	0.0201(18)	0.0035(16)	0.0042(15)	-0.0035(15)
N5	0.0168(17)	0.020(2)	0.0192(18)	0.0002(15)	0.0043(14)	-0.0017(15)
N6	0.0181(18)	0.0154(19)	0.0232(19)	0.0030(15)	0.0058(15)	-0.0009(14)
N7	0.0200(18)	0.020(2)	0.0180(18)	0.0026(15)	0.0057(14)	-0.0031(15)
N8	0.033(2)	0.036(3)	0.046(3)	-0.025(2)	0.024(2)	-0.015(2)
C1	0.029(2)	0.023(3)	0.032(3)	0.002(2)	0.017(2)	0.003(2)
C2	0.028(3)	0.023(3)	0.047(3)	0.000(2)	0.022(2)	0.005(2)
C3	0.017(2)	0.019(3)	0.050(3)	0.007(2)	0.013(2)	0.0005(18)
C4	0.033(2)	0.018(2)	0.026(2)	0.0007(19)	0.016(2)	-0.001(2)
C5	0.042(3)	0.030(3)	0.026(2)	-0.007(2)	0.018(2)	-0.007(2)
C6	0.031(2)	0.026(3)	0.021(2)	-0.003(2)	0.0077(19)	-0.011(2)
C7	0.016(2)	0.017(2)	0.020(2)	-0.0020(17)	0.0064(16)	-0.0012(17)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	0.027(2)	0.018(2)	0.023(2)	0.0018(18)	0.0118(18)	-0.0016(19)
C9	0.026(2)	0.023(3)	0.016(2)	-0.0004(18)	0.0044(17)	0.0012(19)
C10	0.019(2)	0.022(2)	0.024(2)	-0.0045(19)	0.0078(17)	0.0006(18)
C11	0.024(2)	0.031(3)	0.019(2)	-0.005(2)	0.0079(18)	-0.006(2)
C12	0.028(3)	0.043(3)	0.020(2)	0.004(2)	-0.0014(19)	-0.007(2)
C13	0.027(2)	0.038(3)	0.023(2)	0.002(2)	0.001(2)	0.004(2)
C14	0.022(2)	0.038(3)	0.019(2)	0.003(2)	0.0062(18)	0.000(2)
C15	0.023(2)	0.022(3)	0.023(2)	-0.0069(19)	0.0076(18)	-0.0043(18)
C16	0.023(3)	0.058(4)	0.036(3)	0.000(3)	0.003(2)	-0.006(3)
C17	0.037(3)	0.074(4)	0.032(3)	-0.024(3)	0.021(2)	-0.032(3)
C18	0.049(4)	0.047(4)	0.117(6)	-0.051(4)	0.062(4)	-0.026(3)
C19	0.037(3)	0.026(3)	0.130(7)	-0.027(4)	0.035(4)	-0.008(3)
C20	0.046(3)	0.036(3)	0.078(4)	-0.020(3)	0.029(3)	-0.008(3)
C21	0.039(3)	0.027(3)	0.033(3)	0.006(2)	0.021(2)	0.001(2)
C22	0.037(3)	0.026(3)	0.029(2)	0.008(2)	0.014(2)	0.006(2)
C23	0.038(3)	0.034(3)	0.032(3)	0.005(2)	0.012(2)	-0.015(2)
B1	0.016(2)	0.021(3)	0.028(3)	0.003(2)	0.006(2)	-0.003(2)
W2	0.01676(9)	0.02016(10)	0.01610(9)	0.00098(7)	0.00515(6)	-0.00096(7)
P2	0.0253(6)	0.0263(7)	0.0200(6)	0.0012(5)	0.0070(5)	-0.0077(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	0.0245(16)	0.0214(17)	0.0265(16)	-0.0031(14)	0.0096(13)	0.0033(13)
O5	0.0273(17)	0.0260(19)	0.0291(17)	-0.0088(15)	0.0049(14)	-0.0048(14)
O6	0.045(2)	0.032(2)	0.069(3)	0.001(2)	0.000(2)	-0.0093(19)
N9	0.0201(18)	0.028(2)	0.0226(19)	0.0039(17)	0.0078(15)	0.0008(16)
N10	0.0188(18)	0.028(2)	0.030(2)	0.0063(18)	0.0058(16)	-0.0034(16)
N11	0.0211(18)	0.025(2)	0.0181(18)	0.0012(16)	0.0028(15)	-0.0033(16)
N12	0.0217(19)	0.031(2)	0.0186(18)	0.0001(17)	0.0032(15)	-0.0082(17)
N13	0.0149(17)	0.022(2)	0.0190(18)	0.0031(15)	0.0026(14)	0.0013(15)
N14	0.0184(18)	0.025(2)	0.0162(18)	0.0034(16)	0.0016(14)	-0.0004(16)
N15	0.0226(18)	0.022(2)	0.0135(17)	-0.0007(15)	0.0060(14)	-0.0047(16)
N16	0.0237(18)	0.017(2)	0.0211(18)	-0.0026(15)	0.0095(15)	-0.0002(15)
C24	0.026(2)	0.025(3)	0.037(3)	0.001(2)	0.013(2)	0.000(2)
C25	0.028(3)	0.034(3)	0.048(3)	0.005(3)	0.021(2)	0.005(2)
C26	0.016(2)	0.030(3)	0.047(3)	0.010(2)	0.010(2)	0.000(2)
C27	0.036(3)	0.023(3)	0.026(2)	-0.002(2)	0.011(2)	-0.005(2)
C28	0.045(3)	0.029(3)	0.025(2)	-0.006(2)	0.011(2)	-0.011(2)
C29	0.035(3)	0.039(3)	0.018(2)	-0.001(2)	0.007(2)	-0.015(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C30	0.021(2)	0.020(2)	0.022(2)	-0.0027(18)	0.0118(18)	-0.0007(18)
C31	0.028(2)	0.024(3)	0.024(2)	0.004(2)	0.0141(19)	0.003(2)
C32	0.029(2)	0.026(3)	0.019(2)	0.0061(19)	0.0048(19)	0.003(2)
C33	0.021(2)	0.018(2)	0.020(2)	-0.0015(18)	0.0090(17)	0.0024(18)
C34	0.019(2)	0.017(2)	0.025(2)	-0.0036(18)	0.0086(18)	-0.0001(17)
C35	0.031(2)	0.020(2)	0.018(2)	-0.0017(18)	0.0083(19)	-0.0027(19)
C36	0.024(2)	0.017(2)	0.023(2)	0.0014(19)	0.0023(18)	0.0020(18)
C37	0.018(2)	0.018(2)	0.024(2)	-0.0050(18)	0.0073(18)	-0.0014(18)
C38	0.020(2)	0.021(2)	0.015(2)	-0.0004(17)	0.0073(16)	0.0002(18)
C39	0.017(2)	0.024(2)	0.024(2)	-0.003(2)	0.0030(17)	-0.0015(19)
C40	0.024(2)	0.020(2)	0.019(2)	0.0016(18)	0.0092(18)	-0.0011(18)
C41	0.027(2)	0.021(3)	0.040(3)	-0.005(2)	0.015(2)	0.002(2)
C42	0.028(3)	0.021(3)	0.052(3)	0.002(2)	0.009(2)	0.003(2)
C43	0.045(3)	0.029(3)	0.048(3)	0.020(3)	0.010(3)	-0.001(2)
C44	0.034(3)	0.033(3)	0.029(2)	0.007(2)	0.015(2)	-0.003(2)
C45	0.047(3)	0.022(3)	0.035(3)	0.005(2)	0.018(2)	-0.002(2)
C46	0.052(3)	0.060(4)	0.032(3)	0.000(3)	0.015(3)	-0.038(3)
B2	0.026(3)	0.031(3)	0.021(3)	0.001(2)	0.002(2)	-0.006(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O8	0.040(8)	0.061(12)	0.055(12)	0.005(8)	0.019(7)	-0.009(8)
C50	0.094(18)	0.13(2)	0.053(11)	-0.024(12)	-0.007(11)	-0.038(16)
C51	0.069(19)	0.045(5)	0.034(7)	-0.002(4)	0.023(15)	-0.029(16)
C52	0.038(9)	0.036(9)	0.063(12)	0.004(9)	0.016(8)	-0.014(7)
O8A	0.144(15)	0.111(17)	0.050(8)	-0.005(10)	0.011(9)	-0.092(12)
C50A	0.051(8)	0.039(7)	0.045(7)	-0.009(5)	0.019(6)	-0.016(5)
C51A	0.069(19)	0.045(5)	0.034(7)	-0.002(4)	0.023(15)	-0.029(16)
C52A	0.081(12)	0.053(10)	0.076(11)	0.004(9)	0.021(9)	0.011(8)
O7A	0.043(9)	0.040(9)	0.033(7)	0.001(6)	0.012(6)	-0.016(7)
C47A	0.060(3)	0.033(3)	0.040(2)	-0.009(2)	0.0198(19)	-0.008(3)
C48A	0.060(3)	0.033(3)	0.040(2)	-0.009(2)	0.0198(19)	-0.008(3)
C49A	0.060(3)	0.033(3)	0.040(2)	-0.009(2)	0.0198(19)	-0.008(3)
O7	0.067(5)	0.145(8)	0.058(4)	-0.002(5)	0.003(4)	-0.056(5)
C47	0.060(3)	0.033(3)	0.040(2)	-0.009(2)	0.0198(19)	-0.008(3)
C48	0.060(3)	0.033(3)	0.040(2)	-0.009(2)	0.0198(19)	-0.008(3)
C49	0.060(3)	0.033(3)	0.040(2)	-0.009(2)	0.0198(19)	-0.008(3)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for Compound 26.

	x/a	y/b	z/c	U(eq)
H3	0.694(4)	0.614(5)	0.616(4)	0.097000
H1	1.0044	0.9295	0.6353	0.031000

	x/a	y/b	z/c	U(eq)
H2	1.1279	0.8905	0.6945	0.037000
H3A	1.1583	0.9259	0.8222	0.034000
H4	0.9014	1.2075	0.8133	0.029000
H5	0.9946	1.2585	0.9241	0.037000
H6	1.0861	1.1442	0.9519	0.032000
H7	0.8457	0.8575	0.8182	0.021000
H8	0.9183	0.7931	0.9344	0.026000
H9	1.0342	0.8594	0.9642	0.027000
H10	0.8900	0.8484	0.6745	0.026000
H11	0.8956	0.9467	0.5962	0.030000
H12	0.7995	1.0323	0.5274	0.039000
H13	0.6984	1.0138	0.5386	0.038000
H14	0.7219	0.9680	0.6645	0.033000
H15	0.7903	0.8520	0.7118	0.027000
H16A	0.6446	0.8591	0.6327	0.050000
H16B	0.6341	0.8895	0.5538	0.050000
H18A	0.8520	0.7248	0.6263	0.075000
H18B	0.7860	0.6650	0.5895	0.075000
H19A	0.8507	0.6086	0.7017	0.076000
H19B	0.8450	0.7011	0.7371	0.076000
H20A	0.7694	0.5955	0.7523	0.062000
H20B	0.7293	0.6803	0.7101	0.062000
H21A	0.9835	1.0862	0.5915	0.046000

	x/a	y/b	z/c	U(eq)
H21B	0.9512	1.1801	0.5605	0.046000
H21C	0.9046	1.0933	0.5430	0.046000
H22A	0.8104	1.1833	0.5957	0.045000
H22B	0.8601	1.2637	0.5973	0.045000
H22C	0.8425	1.2422	0.6653	0.045000
H23A	0.9789	1.2502	0.7401	0.053000
H23B	1.0017	1.2564	0.6738	0.053000
H23C	1.0324	1.1806	0.7316	0.053000
H1A	1.095(2)	0.975(3)	0.907(2)	0.015(11)
H6A	0.168(3)	-0.302(5)	0.060(4)	0.082000
H24	0.5157	-0.0070	0.1451	0.035000
H25	0.6392	-0.0418	0.2113	0.041000
H26	0.6603	-0.0113	0.3371	0.038000
H27	0.4050	0.2757	0.3093	0.034000
H28	0.4943	0.3256	0.4233	0.040000
H29	0.5810	0.2042	0.4585	0.037000
H30	0.3372	-0.0766	0.3055	0.024000
H31	0.3998	-0.1421	0.4245	0.029000
H32	0.5175	-0.0808	0.4641	0.031000
H33	0.3887	-0.0873	0.1717	0.023000
H34	0.4024	0.0113	0.0958	0.025000
H35	0.3108	0.1052	0.0277	0.028000
H36	0.2080	0.0935	0.0337	0.028000

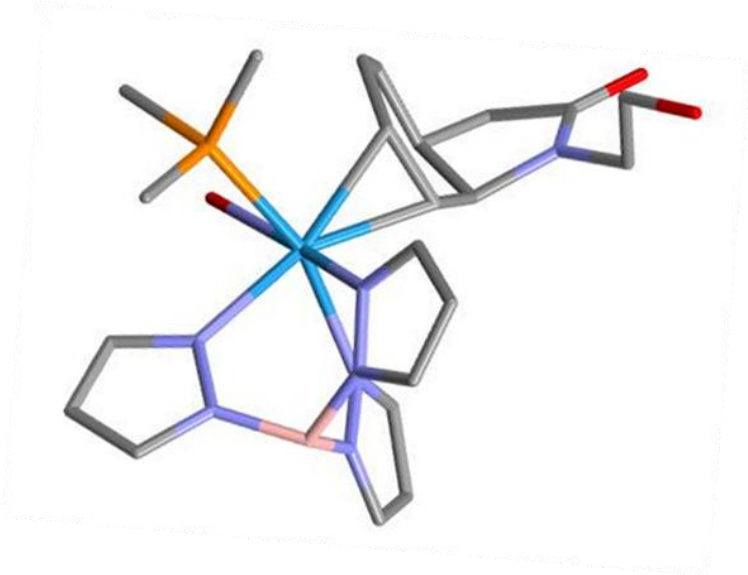
	x/a	y/b	z/c	U(eq)
H37	0.2275	0.0454	0.1603	0.025000
H38	0.2849	-0.0846	0.1984	0.022000
H39A	0.1452	-0.0608	0.1235	0.028000
H39B	0.1333	-0.0174	0.0478	0.028000
H41A	0.3436	-0.1945	0.0988	0.035000
H41B	0.2754	-0.2424	0.0492	0.035000
H42A	0.3301	-0.2530	0.1989	0.042000
H42B	0.3334	-0.3307	0.1471	0.042000
H43A	0.2476	-0.3636	0.1878	0.051000
H43B	0.2136	-0.2684	0.1647	0.051000
H44A	0.5082	0.1464	0.1052	0.046000
H44B	0.4719	0.2350	0.0661	0.046000
H44C	0.4307	0.1437	0.0519	0.046000
H45A	0.3335	0.2543	0.0821	0.051000
H45B	0.3875	0.3335	0.1043	0.051000
H45C	0.3522	0.3012	0.1571	0.051000
H46A	0.4931	0.3084	0.2460	0.073000
H46B	0.5230	0.3105	0.1846	0.073000
H46C	0.5457	0.2339	0.2429	0.073000
H2A	0.588(2)	0.033(3)	0.417(2)	0.031(13)
H50A	0.1995	0.3898	0.1438	0.154000
H50B	0.1327	0.4493	0.1258	0.154000
H50C	0.1913	0.4785	0.0985	0.154000

	x/a	y/b	z/c	U(eq)
H52A	0.2075	0.3444	0.0076	0.069000
H52B	0.1478	0.2728	-0.0098	0.069000
H52C	0.2039	0.2797	0.0682	0.069000
H50D	0.0804	0.4922	0.0603	0.067000
H50E	0.1614	0.4990	0.0879	0.067000
H50F	0.1261	0.4428	0.1313	0.067000
H52D	0.2201	0.3627	0.0347	0.108000
H52E	0.1904	0.2719	0.0520	0.108000
H52F	0.2220	0.3443	0.1125	0.108000
H47A	0.6250	0.4046	0.4972	0.066000
H47B	0.6671	0.4561	0.5685	0.066000
H47C	0.5947	0.4137	0.5580	0.066000
H49A	0.6830	0.2469	0.6677	0.066000
H49B	0.6674	0.3489	0.6768	0.066000
H49C	0.7413	0.3196	0.6805	0.066000
H47D	0.7486	0.3584	0.5590	0.066000
H47E	0.7288	0.4497	0.5864	0.066000
H47F	0.6854	0.4150	0.5088	0.066000
H49D	0.7205	0.3865	0.6864	0.066000
H49E	0.7252	0.2825	0.6737	0.066000
H49F	0.6580	0.3231	0.6802	0.066000

Table 9. Hydrogen bond distances (Å) and angles (°) for Compound 26.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3-H3···O2	0.94(8)	1.89(8)	2.810(7)	166.(7)
O6-H6A···O5	0.99(7)	1.84(7)	2.752(5)	152.(6)

Crystal Structure Report for Compound 5.27



A colorless, plate-like specimen of $C_{22}H_{32}BN_8O_3PW$, approximate dimensions 0.044 mm x 0.087 mm x 0.134 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The total exposure time was 5.82 hours. The frames were integrated with the Bruker SAINT software package[216] using a narrow-frame algorithm. The integration of the data using a

[216] Bruker (2012). Saint; SADABS; APEX5. Bruker AXS Inc., Madison, Wisconsin, USA.

monoclinic unit cell yielded a total of 114708 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 13137 were independent (average redundancy 8.732, completeness = 99.8%, R_{int} = 6.25%, R_{sig} = 3.56%) and 10636 (80.96%) were greater than 2σ(F^2). The final cell constants of a = 13.2055(5) Å, b = 17.2321(5) Å, c = 23.6985(8) Å, β = 100.4770(10)°, volume = 5302.9(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9855 reflections above 20 σ(I) with 5.753° < 2θ < 56.52°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[217] The ratio of minimum to maximum apparent transmission was 0.752. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5870 and 0.8280.

The structure was solved and refined using the Bruker SHELXTL Software Package[218] within APEX5 [1] and OLEX2,[219] using the space group P $2_1/c$, with Z = 8 for the formula unit, $C_{22}H_{32}BN_8O_3PW$. The B-H and O-H hydrogen atoms (except H6A), as well as H10,H11, H32 and H33 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The relative occupancy of the disordered atoms was freely refined, with constraints on the anisotropic displacement parameters of the disordered C atoms and restraints on the disordered C-C and C-O bonds. The final anisotropic full-matrix least-squares refinement on F^2 with 699 variables converged at R1 = 2.91%, for the observed data and wR2 = 6.81% for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was 1.977 $e^-/Å^3$ and the largest hole was -0.649 $e^-/Å^3$ with an RMS deviation of 0.126 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.709 g/cm^3 and F(000), 2704 e^-.

Table 1. Sample and crystal data for Compound 5.27	
Chemical formula	$C_{22}H_{32}BN_8O_3PW$
Formula weight	682.18 g/mol
Temperature	100(2) K

[217] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. "Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination"J. Appl. Cryst. (2015) 48, 3-10. doi:10.1107/S1600576714022985

[218] Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

[219] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

Wavelength	0.71073 Å	
Crystal size	0.044 x 0.087 x 0.134 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P $2_1/c$	
Unit cell dimensions	a = 13.2055(5) Å	α = 90°
	b = 17.2321(5) Å	β = 100.4770(10)°
	c = 23.6985(8) Å	γ = 90°
Volume	5302.9(3) $Å^3$	
Z	8	
Density (calculated)	1.709 g/cm^3	
Absorption coefficient	4.457 mm^{-1}	
F(000)	2704	

Table 2. Data collection and structure refinement for Compound 5.27.	
Diffractometer	Bruker D8 Venture Photon III Kappa four-circle diffractometer
Radiation source	Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å)
Theta range for data collection	1.96 to 28.28°
Index ranges	-17<=h<=17, -22<=k<=18, -31<=l<=31
Reflections collected	114708
Independent reflections	13137 [R(int) = 0.0625]

Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8280 and 0.5870	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13137 / 3 / 699	
Goodness-of-fit on F^2	1.026	
Δ/σ_{max}	0.002	
Final R indices	10636 data; $I>2\sigma(I)$	R1 = 0.0291, wR2 = 0.0612
	all data	R1 = 0.0455, wR2 = 0.0681
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0282P)^2+8.7391P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.977 and -0.649 eÅ^{-3}	
R.M.S. deviation from mean	0.126 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Compound 5.27.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
W1	0.48585(2)	0.33182(2)	0.22559(2)	0.02009(4)
P1	0.55995(8)	0.23615(6)	0.30181(4)	0.0255(2)
O1	0.3745(2)	0.20466(15)	0.15329(11)	0.0302(6)
O2	0.9916(2)	0.44208(18)	0.21610(13)	0.0390(7)
O3	0.2261(3)	0.5666(2)	0.35419(16)	0.0568(10)
N1	0.5778(3)	0.42277(18)	0.28120(15)	0.0296(7)
N2	0.6495(3)	0.46549(19)	0.26059(16)	0.0343(8)
N3	0.6315(2)	0.30719(18)	0.19600(14)	0.0272(7)
N4	0.7049(3)	0.3625(2)	0.19633(16)	0.0335(8)
N5	0.4878(2)	0.42119(17)	0.15790(14)	0.0245(7)
N6	0.5765(3)	0.46096(18)	0.15562(15)	0.0301(8)
N7	0.4187(2)	0.25813(17)	0.18215(13)	0.0224(6)
N8	0.1679(3)	0.44088(19)	0.22713(14)	0.0276(7)
C1	0.5677(4)	0.4559(2)	0.33138(19)	0.0375(10)
C2	0.6296(4)	0.5201(3)	0.3426(2)	0.0461(13)
C3	0.6804(4)	0.5245(2)	0.2980(2)	0.0425(12)
C4	0.6708(3)	0.2413(2)	0.17845(17)	0.0317(9)
C5	0.7688(4)	0.2541(3)	0.1678(2)	0.0419(11)
C6	0.7880(3)	0.3316(3)	0.1799(2)	0.0418(11)

	x/a	**y/b**	**z/c**	**U(eq)**
C7	0.4192(3)	0.4426(2)	0.11192(15)	0.0241(8)
C8	0.4637(3)	0.4956(2)	0.07919(18)	0.0321(9)
C9	0.5620(3)	0.5053(2)	0.10847(19)	0.0343(10)
C10	0.3515(3)	0.3980(2)	0.24068(16)	0.0247(8)
C11	0.3686(3)	0.3371(2)	0.28315(17)	0.0279(8)
C12	0.2933(3)	0.2736(2)	0.27697(17)	0.0297(9)
C13	0.2170(3)	0.2664(2)	0.23220(17)	0.0294(9)
C14	0.1971(3)	0.3233(2)	0.18355(17)	0.0267(8)
C15	0.2487(3)	0.4016(2)	0.20070(16)	0.0245(8)
C16	0.0828(3)	0.3449(2)	0.16890(18)	0.0315(9)
C17	0.0725(3)	0.4135(2)	0.20663(17)	0.0320(9)
C18	0.1856(3)	0.5114(2)	0.26111(17)	0.0323(9)
C19	0.2124(4)	0.4952(3)	0.32454(18)	0.0381(10)
C20	0.5324(4)	0.2433(3)	0.37409(17)	0.0375(10)
C21	0.5260(4)	0.1363(2)	0.2830(2)	0.0425(12)
C22	0.7000(3)	0.2353(3)	0.3190(2)	0.0426(11)
B1	0.6756(4)	0.4489(3)	0.2019(2)	0.0353(11)
W2	0.08021(2)	0.22745(2)	0.46951(2)	0.01984(4)
P2	0.03717(8)	0.12352(5)	0.39518(4)	0.0237(2)
O4	0.1756(2)	0.10116(15)	0.54896(11)	0.0302(6)
O5	0.5761(2)	0.33217(19)	0.50121(14)	0.0440(8)
N9	0.9900(2)	0.31270(17)	0.40799(13)	0.0222(6)
N10	0.9102(2)	0.35231(18)	0.42367(14)	0.0250(7)
N11	0.9297(2)	0.20024(18)	0.49148(14)	0.0249(7)

	x/a	y/b	z/c	U(eq)
N12	0.8527(3)	0.25397(19)	0.48892(14)	0.0268(7)
N13	0.0604(2)	0.31663(17)	0.53438(13)	0.0233(6)
N14	0.9708(3)	0.35763(18)	0.53007(14)	0.0271(7)
N15	0.1398(2)	0.15526(17)	0.51728(13)	0.0229(6)
N16	0.4000(3)	0.33810(19)	0.48980(14)	0.0282(7)
C23	0.9975(3)	0.3387(2)	0.35557(17)	0.0264(8)
C24	0.9236(3)	0.3947(2)	0.33717(18)	0.0331(9)
C25	0.8702(3)	0.4016(2)	0.38144(18)	0.0326(9)
C26	0.8969(3)	0.1356(2)	0.51286(18)	0.0334(9)
C27	0.7983(4)	0.1459(3)	0.5239(2)	0.0391(10)
C28	0.7725(3)	0.2212(3)	0.50877(18)	0.0334(9)
C29	0.1180(3)	0.3367(2)	0.58481(17)	0.0285(8)
C30	0.0666(3)	0.3899(3)	0.61317(18)	0.0370(10)
C31	0.9740(4)	0.4008(2)	0.5776(2)	0.0377(10)
C32	0.2169(3)	0.2965(2)	0.46487(15)	0.0216(7)
C33	0.2075(3)	0.2405(2)	0.41853(16)	0.0229(7)
C34	0.2847(3)	0.1793(2)	0.42374(16)	0.0256(8)
C35	0.3539(3)	0.1664(2)	0.47060(17)	0.0281(8)
C36	0.3646(3)	0.2163(2)	0.52337(17)	0.0284(8)
C37	0.3137(3)	0.2958(2)	0.50933(16)	0.0246(8)
C38	0.4781(3)	0.2365(3)	0.54386(19)	0.0347(10)
C39	0.4924(3)	0.3068(3)	0.50981(18)	0.0338(10)
C40	0.3862(4)	0.4078(3)	0.45597(18)	0.0369(10)
C42	0.0506(4)	0.1416(2)	0.32118(17)	0.0363(10)

	x/a	y/b	z/c	U(eq)
C43	0.1133(3)	0.0361(2)	0.41345(19)	0.0340(9)
C44	0.9075(3)	0.0839(3)	0.3848(2)	0.0369(10)
B2	0.8780(4)	0.3400(3)	0.4823(2)	0.0283(9)
O6	0.3565(4)	0.5399(2)	0.45081(18)	0.0519(15)
C41	0.3621(5)	0.4769(4)	0.4893(3)	0.0406(16)
O6A	0.3871(14)	0.4987(9)	0.5359(7)	0.046(6)
C41A	0.3260(19)	0.469(2)	0.4850(15)	0.0406(16)

Table 4. Bond lengths (Å) for Compound 5.27.

W1-N7	1.768(3)	W1-C10	2.192(4)
W1-N3	2.205(3)	W1-N5	2.227(3)
W1-C11	2.244(4)	W1-N1	2.255(3)
W1-P1	2.5090(10)	P1-C21	1.814(4)
P1-C20	1.819(4)	P1-C22	1.820(5)
O1-N7	1.230(4)	O2-C17	1.234(5)
O3-C19	1.413(5)	O3-H3	0.86(7)
N1-C1	1.348(5)	N1-N2	1.358(5)
N2-C3	1.362(5)	N2-B1	1.521(7)
N3-C4	1.346(5)	N3-N4	1.359(4)
N4-C6	1.340(6)	N4-B1	1.550(6)
N5-C7	1.336(5)	N5-N6	1.367(4)
N6-C9	1.338(5)	N6-B1	1.561(6)
N8-C17	1.350(5)	N8-C18	1.454(5)

N8-C15	1.494(5)	C1-C2	1.373(6)
C1-H1	0.950000	C2-C3	1.354(7)
C2-H2A	0.950000	C3-H3A	0.950000
C4-C5	1.381(6)	C4-H4	0.950000
C5-C6	1.381(7)	C5-H5	0.950000
C6-H6B	0.950000	C7-C8	1.396(5)
C7-H7	0.950000	C8-C9	1.366(6)
C8-H8	0.950000	C9-H9	0.950000
C10-C11	1.442(5)	C10-C15	1.509(5)
C10-H10	0.91(4)	C11-C12	1.468(6)
C11-H11	0.83(5)	C12-C13	1.329(6)
C12-H12	0.950000	C13-C14	1.500(5)
C13-H13	0.950000	C14-C16	1.532(5)
C14-C15	1.533(5)	C14-H14	1.000000
C15-H15	1.000000	C16-C17	1.503(6)
C16-H16A	0.990000	C16-H16B	0.990000
C18-C19	1.507(6)	C18-H18A	0.990000
C18-H18B	0.990000	C19-H19A	0.990000
C19-H19B	0.990000	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
B1-H1A	1.13(4)	W2-N15	1.768(3)
W2-C32	2.181(4)	W2-N11	2.195(3)

W2-N13	2.222(3)	W2-N9	2.252(3)
W2-C33	2.252(4)	W2-P2	2.5039(10)
P2-C44	1.818(4)	P2-C43	1.819(4)
P2-C42	1.821(4)	O4-N15	1.236(4)
O5-C39	1.240(5)	N9-C23	1.341(5)
N9-N10	1.362(4)	N10-C25	1.346(5)
N10-B2	1.540(6)	N11-C26	1.328(5)
N11-N12	1.368(4)	N12-C28	1.357(5)
N12-B2	1.534(5)	N13-C29	1.340(5)
N13-N14	1.366(4)	N14-C31	1.345(5)
N14-B2	1.540(6)	N16-C39	1.339(5)
N16-C40	1.436(5)	N16-C37	1.495(5)
C23-C24	1.385(5)	C23-H23	0.950000
C24-C25	1.372(6)	C24-H24	0.950000
C25-H25	0.950000	C26-C27	1.385(6)
C26-H26	0.950000	C27-C28	1.372(6)
C27-H27	0.950000	C28-H28	0.950000
C29-C30	1.386(6)	C29-H29	0.950000
C30-C31	1.366(6)	C30-H30	0.950000
C31-H31	0.950000	C32-C33	1.451(5)
C32-C37	1.502(5)	C32-H32	0.95(4)
C33-C34	1.457(5)	C33-H33	0.92(4)
C34-C35	1.322(5)	C34-H34	0.950000
C35-C36	1.503(5)	C35-H35	0.950000
C36-C38	1.529(6)	C36-C37	1.535(5)

C36-H36	1.000000	C37-H37	1.000000
C38-C39	1.487(6)	C38-H38A	0.990000
C38-H38B	0.990000	C40-C41	1.497(7)
C40-C41A	1.551(18)	C40-H40A	0.990000
C40-H40B	0.990000	C40-H40C	0.990000
C40-H40D	0.990000	C42-H42A	0.980000
C42-H42B	0.980000	C42-H42C	0.980000
C43-H43A	0.980000	C43-H43B	0.980000
C43-H43C	0.980000	C44-H44A	0.980000
C44-H44B	0.980000	C44-H44C	0.980000
B2-H2	1.10(4)	O6-C41	1.412(9)
O6-H6	1.03(8)	C41-H41A	0.990000
C41-H41B	0.990000	O6A-C41A	1.42(2)
O6A-H6A	0.840000	C41A-H41C	0.990000
C41A-H41D	0.990000		

Table 5. Bond angles (°) for Compound 5.27.			
N7-W1-C10	97.68(14)	N7-W1-N3	92.89(13)
C10-W1-N3	158.54(13)	N7-W1-N5	98.48(12)
C10-W1-N5	82.74(13)	N3-W1-N5	77.24(12)
N7-W1-C11	93.16(15)	C10-W1-C11	37.92(14)
N3-W1-C11	159.96(13)	N5-W1-C11	120.62(13)
N7-W1-N1	177.49(13)	C10-W1-N1	84.79(13)

N3-W1-N1	84.92(13)	N5-W1-N1	82.23(12)
C11-W1-N1	88.52(14)	N7-W1-P1	92.05(10)
C10-W1-P1	116.45(10)	N3-W1-P1	81.60(9)
N5-W1-P1	156.75(9)	C11-W1-P1	79.11(10)
N1-W1-P1	86.43(8)	C21-P1-C20	102.3(2)
C21-P1-C22	104.0(2)	C20-P1-C22	99.1(2)
C21-P1-W1	113.59(15)	C20-P1-W1	120.97(15)
C22-P1-W1	114.48(16)	C19-O3-H3	105.(5)
C1-N1-N2	106.0(3)	C1-N1-W1	132.9(3)
N2-N1-W1	120.2(3)	N1-N2-C3	108.5(4)
N1-N2-B1	121.1(3)	C3-N2-B1	130.1(4)
C4-N3-N4	106.2(3)	C4-N3-W1	132.0(3)
N4-N3-W1	121.7(3)	C6-N4-N3	109.9(4)
C6-N4-B1	129.5(4)	N3-N4-B1	119.1(3)
C7-N5-N6	106.7(3)	C7-N5-W1	133.1(3)
N6-N5-W1	119.8(2)	C9-N6-N5	109.0(3)
C9-N6-B1	129.5(3)	N5-N6-B1	121.4(3)
O1-N7-W1	177.4(3)	C17-N8-C18	122.5(3)
C17-N8-C15	112.4(3)	C18-N8-C15	123.8(3)
N1-C1-C2	111.2(5)	N1-C1-H1	124.400000
C2-C1-H1	124.400000	C3-C2-C1	104.8(4)
C3-C2-H2A	127.600000	C1-C2-H2A	127.600000
C2-C3-N2	109.5(4)	C2-C3-H3A	125.200000
N2-C3-H3A	125.200000	N3-C4-C5	110.4(4)
N3-C4-H4	124.800000	C5-C4-H4	124.800000

C4-C5-C6	105.0(4)	C4-C5-H5	127.500000
C6-C5-H5	127.500000	N4-C6-C5	108.4(4)
N4-C6-H6B	125.800000	C5-C6-H6B	125.800000
N5-C7-C8	110.0(4)	N5-C7-H7	125.000000
C8-C7-H7	125.000000	C9-C8-C7	104.7(4)
C9-C8-H8	127.600000	C7-C8-H8	127.600000
N6-C9-C8	109.5(4)	N6-C9-H9	125.300000
C8-C9-H9	125.300000	C11-C10-C15	118.5(4)
C11-C10-W1	73.0(2)	C15-C10-W1	125.6(3)
C11-C10-H10	116.(2)	C15-C10-H10	113.(2)
W1-C10-H10	105.(2)	C10-C11-C12	117.1(4)
C10-C11-W1	69.1(2)	C12-C11-W1	116.0(3)
C10-C11-H11	120.(3)	C12-C11-H11	115.(3)
W1-C11-H11	111.(3)	C13-C12-C11	123.4(4)
C13-C12-H12	118.300000	C11-C12-H12	118.300000
C12-C13-C14	123.6(4)	C12-C13-H13	118.200000
C14-C13-H13	118.200000	C13-C14-C16	111.2(3)
C13-C14-C15	111.4(3)	C16-C14-C15	102.6(3)
C13-C14-H14	110.500000	C16-C14-H14	110.500000
C15-C14-H14	110.500000	N8-C15-C10	112.6(3)
N8-C15-C14	101.2(3)	C10-C15-C14	115.8(3)
N8-C15-H15	109.000000	C10-C15-H15	109.000000
C14-C15-H15	109.000000	C17-C16-C14	104.4(3)
C17-C16-H16A	110.900000	C14-C16-H16A	110.900000

C17-C16-H16B	110.900000	C14-C16-H16B	110.900000
H16A-C16-H16B	108.900000	O2-C17-N8	125.3(4)
O2-C17-C16	126.7(4)	N8-C17-C16	108.0(3)
N8-C18-C19	112.5(3)	N8-C18-H18A	109.100000
C19-C18-H18A	109.100000	N8-C18-H18B	109.100000
C19-C18-H18B	109.100000	H18A-C18-H18B	107.800000
O3-C19-C18	108.6(4)	O3-C19-H19A	110.000000
C18-C19-H19A	110.000000	O3-C19-H19B	110.000000
C18-C19-H19B	110.000000	H19A-C19-H19B	108.300000
P1-C20-H20A	109.500000	P1-C20-H20B	109.500000
H20A-C20-H20B	109.500000	P1-C20-H20C	109.500000
H20A-C20-H20C	109.500000	H20B-C20-H20C	109.500000
P1-C21-H21A	109.500000	P1-C21-H21B	109.500000
H21A-C21-H21B	109.500000	P1-C21-H21C	109.500000
H21A-C21-H21C	109.500000	H21B-C21-H21C	109.500000
P1-C22-H22A	109.500000	P1-C22-H22B	109.500000
H22A-C22-H22B	109.500000	P1-C22-H22C	109.500000

H22A-C22-H22C	109.500000	H22B-C22-H22C	109.500000
N2-B1-N4	111.1(4)	N2-B1-N6	108.5(4)
N4-B1-N6	105.0(4)	N2-B1-H1A	114.(2)
N4-B1-H1A	112.(2)	N6-B1-H1A	105.(2)
N15-W2-C32	98.07(14)	N15-W2-N11	90.83(13)
C32-W2-N11	157.18(12)	N15-W2-N13	97.94(12)
C32-W2-N13	81.95(12)	N11-W2-N13	76.01(11)
N15-W2-N9	174.39(13)	C32-W2-N9	87.52(12)
N11-W2-N9	84.11(11)	N13-W2-N9	83.22(11)
N15-W2-C33	97.19(14)	C32-W2-C33	38.15(13)
N11-W2-C33	160.86(13)	N13-W2-C33	119.67(12)
N9-W2-C33	86.92(12)	N15-W2-P2	87.99(10)
C32-W2-P2	116.03(10)	N11-W2-P2	85.10(9)
N13-W2-P2	160.23(8)	N9-W2-P2	89.16(8)
C33-W2-P2	77.88(10)	C44-P2-C43	100.8(2)
C44-P2-C42	100.8(2)	C43-P2-C42	103.0(2)
C44-P2-W2	116.86(14)	C43-P2-W2	112.34(14)
C42-P2-W2	120.38(14)	C23-N9-N10	106.0(3)
C23-N9-W2	134.3(3)	N10-N9-W2	119.6(2)
C25-N10-N9	109.4(3)	C25-N10-B2	128.5(3)
N9-N10-B2	122.1(3)	C26-N11-N12	107.1(3)
C26-N11-W2	129.9(3)	N12-N11-W2	122.8(2)
C28-N12-N11	108.9(3)	C28-N12-B2	129.4(3)

N11-N12-B2	119.0(3)	C29-N13-N14	106.1(3)
C29-N13-W2	132.5(3)	N14-N13-W2	121.0(2)
C31-N14-N13	109.2(3)	C31-N14-B2	128.6(4)
N13-N14-B2	121.1(3)	O4-N15-W2	175.3(3)
C39-N16-C40	123.3(4)	C39-N16-C37	113.0(3)
C40-N16-C37	123.7(3)	N9-C23-C24	111.0(4)
N9-C23-H23	124.500000	C24-C23-H23	124.500000
C25-C24-C23	104.5(4)	C25-C24-H24	127.800000
C23-C24-H24	127.800000	N10-C25-C24	109.1(4)
N10-C25-H25	125.500000	C24-C25-H25	125.500000
N11-C26-C27	110.3(4)	N11-C26-H26	124.900000
C27-C26-H26	124.900000	C28-C27-C26	105.6(4)
C28-C27-H27	127.200000	C26-C27-H27	127.200000
N12-C28-C27	108.1(4)	N12-C28-H28	125.900000
C27-C28-H28	125.900000	N13-C29-C30	110.8(4)
N13-C29-H29	124.600000	C30-C29-H29	124.600000
C31-C30-C29	104.8(4)	C31-C30-H30	127.600000
C29-C30-H30	127.600000	N14-C31-C30	109.2(4)
N14-C31-H31	125.400000	C30-C31-H31	125.400000
C33-C32-C37	118.0(3)	C33-C32-W2	73.6(2)
C37-C32-W2	124.5(3)	C33-C32-H32	118.(2)
C37-C32-H32	112.(2)	W2-C32-H32	107.(2)
C32-C33-C34	117.1(3)	C32-C33-W2	68.3(2)
C34-C33-W2	117.5(3)	C32-C33-H33	118.(2)

C34-C33-H33	116.(2)	W2-C33-H33	112.(2)
C35-C34-C33	124.0(4)	C35-C34-H34	118.000000
C33-C34-H34	118.000000	C34-C35-C36	123.3(3)
C34-C35-H35	118.300000	C36-C35-H35	118.300000
C35-C36-C38	109.5(3)	C35-C36-C37	111.0(3)
C38-C36-C37	103.3(3)	C35-C36-H36	110.900000
C38-C36-H36	110.900000	C37-C36-H36	110.900000
N16-C37-C32	112.2(3)	N16-C37-C36	100.1(3)
C32-C37-C36	116.3(3)	N16-C37-H37	109.300000
C32-C37-H37	109.300000	C36-C37-H37	109.300000
C39-C38-C36	103.1(3)	C39-C38-H38A	111.100000
C36-C38-H38A	111.100000	C39-C38-H38B	111.100000
C36-C38-H38B	111.100000	H38A-C38-H38B	109.100000
O5-C39-N16	125.6(4)	O5-C39-C38	125.5(4)
N16-C39-C38	108.9(4)	N16-C40-C41	112.8(4)
N16-C40-C41A	109.9(18)	N16-C40-H40A	109.000000
C41-C40-H40A	109.000000	N16-C40-H40B	109.000000
C41-C40-H40B	109.000000	H40A-C40-H40B	107.800000
N16-C40-H40C	109.700000	C41A-C40-H40C	109.700000
N16-C40-H40D	109.700000	C41A-C40-H40D	109.700000

H40C-C40-H40D	108.200000	P2-C42-H42A	109.500000
P2-C42-H42B	109.500000	H42A-C42-H42B	109.500000
P2-C42-H42C	109.500000	H42A-C42-H42C	109.500000
H42B-C42-H42C	109.500000	P2-C43-H43A	109.500000
P2-C43-H43B	109.500000	H43A-C43-H43B	109.500000
P2-C43-H43C	109.500000	H43A-C43-H43C	109.500000
H43B-C43-H43C	109.500000	P2-C44-H44A	109.500000
P2-C44-H44B	109.500000	H44A-C44-H44B	109.500000
P2-C44-H44C	109.500000	H44A-C44-H44C	109.500000
H44B-C44-H44C	109.500000	N12-B2-N10	109.0(3)
N12-B2-N14	105.9(3)	N10-B2-N14	108.8(3)
N12-B2-H2	109.(2)	N10-B2-H2	109.(2)
N14-B2-H2	115.(2)	C41-O6-H6	113.(4)
O6-C41-C40	105.1(5)	O6-C41-H41A	110.700000
C40-C41-H41A	110.700000	O6-C41-H41B	110.700000
C40-C41-H41B	110.700000	H41A-C41-H41B	108.800000

C41A-O6A-H6A	109.500000	O6A-C41A-C40	111.4(17)
O6A-C41A-H41C	109.300000	C40-C41A-H41C	109.300000
O6A-C41A-H41D	109.300000	C40-C41A-H41D	109.300000
H41C-C41A-H41D	108.000000		

Table 6. Torsion angles (°) for Compound 5.27.			
C1-N1-N2-C3	-1.0(4)	W1-N1-N2-C3	169.3(2)
C1-N1-N2-B1	-175.3(3)	W1-N1-N2-B1	-5.0(5)
C4-N3-N4-C6	-0.5(5)	W1-N3-N4-C6	176.1(3)
C4-N3-N4-B1	166.9(4)	W1-N3-N4-B1	-16.5(5)
C7-N5-N6-C9	-0.6(4)	W1-N5-N6-C9	173.8(3)
C7-N5-N6-B1	-178.2(4)	W1-N5-N6-B1	-3.8(5)
N2-N1-C1-C2	1.4(5)	W1-N1-C1-C2	-167.2(3)
N1-C1-C2-C3	-1.3(5)	C1-C2-C3-N2	0.6(5)
N1-N2-C3-C2	0.3(5)	B1-N2-C3-C2	173.9(4)
N4-N3-C4-C5	0.2(5)	W1-N3-C4-C5	-175.8(3)
N3-C4-C5-C6	0.1(5)	N3-N4-C6-C5	0.6(5)
B1-N4-C6-C5	-165.1(4)	C4-C5-C6-N4	-0.4(5)
N6-N5-C7-C8	0.8(4)	W1-N5-C7-C8	-172.6(3)
N5-C7-C8-C9	-0.6(5)	N5-N6-C9-C8	0.3(5)

B1-N6-C9-C8	177.6(4)	C7-C8-C9-N6	0.2(5)
C15-C10-C11-C12	12.3(5)	W1-C10-C11-C12	-109.4(3)
C15-C10-C11-W1	121.7(3)	C10-C11-C12-C13	6.1(6)
W1-C11-C12-C13	-72.6(5)	C11-C12-C13-C14	-1.7(6)
C12-C13-C14-C16	-133.1(4)	C12-C13-C14-C15	-19.4(6)
C17-N8-C15-C10	-150.0(3)	C18-N8-C15-C10	42.8(5)
C17-N8-C15-C14	-25.7(4)	C18-N8-C15-C14	167.1(3)
C11-C10-C15-N8	82.0(4)	W1-C10-C15-N8	170.7(2)
C11-C10-C15-C14	-33.8(5)	W1-C10-C15-C14	54.9(4)
C13-C14-C15-N8	-86.4(4)	C16-C14-C15-N8	32.6(4)
C13-C14-C15-C10	35.7(5)	C16-C14-C15-C10	154.7(3)
C13-C14-C16-C17	89.3(4)	C15-C14-C16-C17	-29.8(4)
C18-N8-C17-O2	-3.4(6)	C15-N8-C17-O2	-170.8(4)
C18-N8-C17-C16	174.4(3)	C15-N8-C17-C16	7.0(4)
C14-C16-C17-O2	-167.2(4)	C14-C16-C17-N8	15.0(4)
C17-N8-C18-C19	99.1(4)	C15-N8-C18-C19	-94.9(4)

N8-C18-C19-O3	-178.8(4)	N1-N2-B1-N4	-53.5(5)
C3-N2-B1-N4	133.5(4)	N1-N2-B1-N6	61.3(4)
C3-N2-B1-N6	-111.6(4)	C6-N4-B1-N2	-128.3(5)
N3-N4-B1-N2	67.1(5)	C6-N4-B1-N6	114.6(5)
N3-N4-B1-N6	-50.0(5)	C9-N6-B1-N2	126.4(4)
N5-N6-B1-N2	-56.6(5)	C9-N6-B1-N4	-114.8(5)
N5-N6-B1-N4	62.2(5)	C23-N9-N10-C25	0.0(4)
W2-N9-N10-C25	177.8(3)	C23-N9-N10-B2	-178.8(3)
W2-N9-N10-B2	-0.9(4)	C26-N11-N12-C28	-0.2(4)
W2-N11-N12-C28	-175.8(3)	C26-N11-N12-B2	162.9(4)
W2-N11-N12-B2	-12.6(5)	C29-N13-N14-C31	-0.9(4)
W2-N13-N14-C31	172.9(3)	C29-N13-N14-B2	-169.9(3)
W2-N13-N14-B2	3.9(4)	N10-N9-C23-C24	0.0(4)
W2-N9-C23-C24	-177.4(3)	N9-C23-C24-C25	0.1(5)
N9-N10-C25-C24	0.1(5)	B2-N10-C25-C24	178.7(4)
C23-C24-C25-N10	-0.1(5)	N12-N11-C26-C27	0.7(5)
W2-N11-C26-C27	175.8(3)	N11-C26-C27-C28	-0.8(5)

N11-N12-C28-C27	-0.3(5)	B2-N12-C28-C27	-161.1(4)
C26-C27-C28-N12	0.7(5)	N14-N13-C29-C30	0.2(5)
W2-N13-C29-C30	-172.6(3)	N13-C29-C30-C31	0.6(5)
N13-N14-C31-C30	1.3(5)	B2-N14-C31-C30	169.2(4)
C29-C30-C31-N14	-1.2(5)	C37-C32-C33-C34	10.1(5)
W2-C32-C33-C34	-110.7(3)	C37-C32-C33-W2	120.8(3)
C32-C33-C34-C35	8.7(6)	W2-C33-C34-C35	-69.6(5)
C33-C34-C35-C36	-3.3(6)	C34-C35-C36-C38	-132.6(4)
C34-C35-C36-C37	-19.2(6)	C39-N16-C37-C32	-146.3(3)
C40-N16-C37-C32	37.2(5)	C39-N16-C37-C36	-22.4(4)
C40-N16-C37-C36	161.2(3)	C33-C32-C37-N16	81.4(4)
W2-C32-C37-N16	170.1(2)	C33-C32-C37-C36	-32.9(5)
W2-C32-C37-C36	55.8(4)	C35-C36-C37-N16	-85.0(4)
C38-C36-C37-N16	32.2(4)	C35-C36-C37-C32	36.0(5)
C38-C36-C37-C32	153.2(3)	C35-C36-C38-C39	86.3(4)

C37-C36-C38-C39	-32.0(4)	C40-N16-C39-O5	-1.4(6)
C37-N16-C39-O5	-177.9(4)	C40-N16-C39-C38	178.8(3)
C37-N16-C39-C38	2.3(4)	C36-C38-C39-O5	-160.7(4)
C36-C38-C39-N16	19.0(4)	C39-N16-C40-C41	-104.1(5)
C37-N16-C40-C41	71.9(5)	C39-N16-C40-C41A	-123.6(10)
C37-N16-C40-C41A	52.4(11)	C28-N12-B2-N10	-135.8(4)
N11-N12-B2-N10	64.9(4)	C28-N12-B2-N14	107.2(4)
N11-N12-B2-N14	-52.0(4)	C25-N10-B2-N12	124.6(4)
N9-N10-B2-N12	-56.9(5)	C25-N10-B2-N14	-120.4(4)
N9-N10-B2-N14	58.1(4)	C31-N14-B2-N12	-109.6(4)
N13-N14-B2-N12	57.1(4)	C31-N14-B2-N10	133.3(4)
N13-N14-B2-N10	-60.0(4)	N16-C40-C41-O6	177.0(4)
N16-C40-C41A-O6A	71.(3)		

Table 7. Anisotropic atomic displacement parameters ($Å^2$) for Compound 5.27.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
W1	0.01997(8)	0.01936(7)	0.01986(7)	0.00037(5)	0.00070(6)	-0.00083(5)
P1	0.0275(5)	0.0256(5)	0.0216(5)	0.0018(4)	0.0000(4)	0.0012(4)
O1	0.0384(17)	0.0232(13)	0.0264(14)	-0.0035(11)	-0.0012(12)	-0.0089(12)
O2	0.0269(16)	0.0472(18)	0.0442(18)	0.0144(14)	0.0101(14)	0.0082(13)
O3	0.076(3)	0.0462(19)	0.045(2)	-0.0082(17)	0.0040(19)	0.0205(19)
N1	0.0262(18)	0.0221(15)	0.0354(19)	0.0007(13)	-0.0078(15)	-0.0012(13)
N2	0.0286(19)	0.0248(16)	0.043(2)	0.0044(15)	-0.0100(16)	-0.0011(14)
N3	0.0219(17)	0.0258(15)	0.0339(18)	0.0066(14)	0.0051(14)	0.0002(13)
N4	0.0218(18)	0.0327(18)	0.046(2)	0.0106(16)	0.0070(16)	-0.0024(14)
N5	0.0231(17)	0.0216(15)	0.0288(17)	0.0013(12)	0.0046(14)	-0.0044(12)
N6	0.0225(18)	0.0262(16)	0.040(2)	0.0088(14)	0.0023(15)	-0.0053(13)
N7	0.0242(17)	0.0228(15)	0.0200(15)	0.0035(12)	0.0037(13)	-0.0008(12)
N8	0.0233(18)	0.0361(17)	0.0237(16)	0.0029(14)	0.0050(14)	0.0057(14)
C1	0.045(3)	0.031(2)	0.030(2)	-0.0073(17)	-0.010(2)	0.0045(19)
C2	0.067(4)	0.030(2)	0.032(2)	-0.0029(18)	-0.016(2)	0.003(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	0.039(3)	0.0227(19)	0.054(3)	0.0057(19)	-0.024(2)	-0.0029(18)
C4	0.033(2)	0.034(2)	0.030(2)	0.0052(17)	0.0088(18)	0.0074(17)
C5	0.032(3)	0.053(3)	0.044(3)	0.005(2)	0.015(2)	0.013(2)
C6	0.024(2)	0.050(3)	0.052(3)	0.016(2)	0.011(2)	0.003(2)
C7	0.025(2)	0.0248(17)	0.0208(18)	-0.0010(14)	0.0007(15)	-0.0028(15)
C8	0.040(3)	0.030(2)	0.027(2)	0.0063(16)	0.0066(18)	-0.0039(18)
C9	0.033(2)	0.029(2)	0.039(2)	0.0091(18)	0.0042(19)	-0.0095(17)
C10	0.024(2)	0.0276(19)	0.0215(18)	-0.0028(15)	0.0021(15)	0.0027(15)
C11	0.028(2)	0.036(2)	0.0188(19)	-0.0011(16)	0.0007(16)	0.0052(17)
C12	0.028(2)	0.038(2)	0.026(2)	0.0104(17)	0.0098(17)	0.0052(17)
C13	0.027(2)	0.032(2)	0.029(2)	0.0064(16)	0.0065(17)	-0.0024(16)
C14	0.021(2)	0.034(2)	0.0242(19)	0.0019(16)	0.0014(15)	-0.0020(16)
C15	0.023(2)	0.0300(19)	0.0205(18)	0.0047(15)	0.0039(15)	0.0031(15)
C16	0.021(2)	0.040(2)	0.032(2)	0.0056(17)	0.0016(17)	-0.0017(17)
C17	0.027(2)	0.042(2)	0.028(2)	0.0152(17)	0.0063(17)	0.0053(18)
C18	0.034(2)	0.033(2)	0.029(2)	0.0034(17)	0.0036(18)	0.0126(18)
C19	0.047(3)	0.038(2)	0.030(2)	0.0009(18)	0.008(2)	0.012(2)
C20	0.039(3)	0.049(3)	0.023(2)	0.0073(18)	0.0009(18)	0.009(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C21	0.059(3)	0.026(2)	0.039(3)	0.0087(18)	-0.004(2)	-0.007(2)
C22	0.031(3)	0.053(3)	0.040(3)	0.009(2)	-0.002(2)	0.007(2)
B1	0.021(2)	0.026(2)	0.057(3)	0.013(2)	0.000(2)	-0.0025(18)
W2	0.02005(8)	0.02051(7)	0.01853(7)	0.00038(5)	0.00237(5)	0.00286(5)
P2	0.0264(5)	0.0231(4)	0.0214(5)	-0.0008(4)	0.0039(4)	0.0002(4)
O4	0.0394(17)	0.0284(14)	0.0210(14)	0.0064(11)	0.0004(12)	0.0075(12)
O5	0.0245(16)	0.061(2)	0.047(2)	-0.0215(16)	0.0089(14)	-0.0081(14)
N9	0.0190(16)	0.0235(15)	0.0239(16)	0.0000(12)	0.0031(13)	0.0035(12)
N10	0.0192(16)	0.0269(15)	0.0283(17)	0.0024(13)	0.0026(13)	0.0036(13)
N11	0.0220(17)	0.0264(15)	0.0270(17)	0.0000(13)	0.0065(13)	0.0001(13)
N12	0.0239(18)	0.0309(16)	0.0259(17)	-0.0025(13)	0.0053(14)	0.0033(13)
N13	0.0195(16)	0.0271(15)	0.0230(16)	-0.0008(12)	0.0033(13)	0.0028(12)
N14	0.0233(18)	0.0282(16)	0.0296(18)	-0.0031(13)	0.0044(14)	0.0031(13)
N15	0.0267(17)	0.0241(15)	0.0179(15)	0.0001(12)	0.0047(13)	0.0023(13)
N16	0.0253(18)	0.0346(17)	0.0250(17)	-0.0040(14)	0.0055(14)	-0.0029(14)
C23	0.024(2)	0.0282(19)	0.0258(19)	0.0047(15)	0.0022(16)	-0.0002(15)
C24	0.033(2)	0.033(2)	0.031(2)	0.0120(17)	0.0003(18)	0.0017(17)
C25	0.026(2)	0.030(2)	0.040(2)	0.0093(17)	-0.0002(18)	0.0060(16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C26	0.039(3)	0.030(2)	0.034(2)	0.0021(17)	0.0145(19)	-0.0012(18)
C27	0.038(3)	0.037(2)	0.044(3)	0.005(2)	0.013(2)	-0.0080(19)
C28	0.024(2)	0.046(2)	0.032(2)	-0.0007(18)	0.0093(17)	-0.0021(18)
C29	0.027(2)	0.032(2)	0.025(2)	-0.0047(16)	0.0004(16)	0.0027(16)
C30	0.036(3)	0.045(2)	0.029(2)	-0.0147(19)	0.0034(19)	0.001(2)
C31	0.035(3)	0.035(2)	0.045(3)	-0.0110(19)	0.013(2)	0.0081(18)
C32	0.0206(19)	0.0217(17)	0.0224(18)	0.0003(14)	0.0032(15)	0.0002(14)
C33	0.0217(19)	0.0281(18)	0.0181(18)	0.0008(14)	0.0016(15)	0.0021(15)
C34	0.026(2)	0.0275(18)	0.0244(19)	-0.0015(15)	0.0065(16)	0.0011(15)
C35	0.025(2)	0.0291(19)	0.029(2)	-0.0038(16)	0.0016(16)	0.0074(16)
C36	0.026(2)	0.033(2)	0.0252(19)	-0.0023(16)	0.0011(16)	0.0076(16)
C37	0.022(2)	0.0290(19)	0.0232(19)	-0.0038(15)	0.0048(15)	0.0017(15)
C38	0.023(2)	0.046(2)	0.032(2)	-0.0075(18)	-0.0032(17)	0.0091(18)
C39	0.024(2)	0.047(2)	0.030(2)	-0.0183(18)	0.0051(17)	-0.0023(18)
C40	0.038(3)	0.046(2)	0.025(2)	0.0013(18)	0.0017(18)	-0.014(2)
C42	0.053(3)	0.036(2)	0.0199(19)	-0.0002(16)	0.0062(19)	-0.008(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C43	0.039(3)	0.0235(18)	0.038(2)	-0.0028(17)	0.004(2)	0.0046(17)
C44	0.027(2)	0.041(2)	0.041(3)	-0.0118(19)	0.0008(19)	-0.0032(18)
B2	0.023(2)	0.028(2)	0.035(2)	-0.0006(18)	0.0057(19)	0.0060(18)
O6	0.074(3)	0.029(2)	0.042(2)	0.0030(17)	-0.016(2)	-0.005(2)
C41	0.052(4)	0.028(3)	0.033(3)	-0.002(2)	-0.013(4)	-0.014(3)
O6A	0.036(11)	0.040(11)	0.055(14)	0.016(9)	-0.007(9)	0.007(8)
C41A	0.052(4)	0.028(3)	0.033(3)	-0.002(2)	-0.013(4)	-0.014(3)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for Compound 5.27.

	x/a	y/b	z/c	U(eq)
H3	0.279(5)	0.560(4)	0.381(3)	0.085000
H1	0.5234	0.4373	0.3558	0.045000
H2A	0.6356	0.5540	0.3747	0.055000
H3A	0.7299	0.5629	0.2934	0.051000
H4	0.6360	0.1928	0.1740	0.038000
H5	0.8133	0.2174	0.1549	0.050000
H6B	0.8496	0.3586	0.1770	0.050000
H7	0.3503	0.4244	0.1028	0.029000
H8	0.4325	0.5197	0.0443	0.039000
H9	0.6123	0.5383	0.0971	0.041000

	x/a	y/b	z/c	U(eq)
H10	0.376(3)	0.445(2)	0.2527(16)	0.020(10)
H11	0.396(4)	0.347(3)	0.316(2)	0.037(13)
H12	0.2994	0.2357	0.3065	0.036000
H13	0.1727	0.2228	0.2310	0.035000
H14	0.2211	0.3019	0.1490	0.032000
H15	0.2570	0.4303	0.1652	0.029000
H16A	0.0630	0.3589	0.1279	0.038000
H16B	0.0391	0.3013	0.1774	0.038000
H18A	0.1229	0.5441	0.2534	0.039000
H18B	0.2425	0.5410	0.2492	0.039000
H19A	0.1563	0.4652	0.3370	0.046000
H19B	0.2764	0.4641	0.3331	0.046000
H20A	0.5575	0.2932	0.3910	0.056000
H20B	0.5668	0.2009	0.3976	0.056000
H20C	0.4579	0.2398	0.3726	0.056000
H21A	0.4512	0.1298	0.2786	0.064000
H21B	0.5604	0.1018	0.3134	0.064000
H21C	0.5480	0.1232	0.2468	0.064000
H22A	0.7275	0.2148	0.2863	0.064000
H22B	0.7225	0.2023	0.3527	0.064000
H22C	0.7253	0.2882	0.3274	0.064000
H1A	0.735(3)	0.489(2)	0.1893(17)	0.029(11)
H23	0.0469	0.3211	0.3339	0.032000
H24	-0.0876	0.4222	0.3018	0.040000

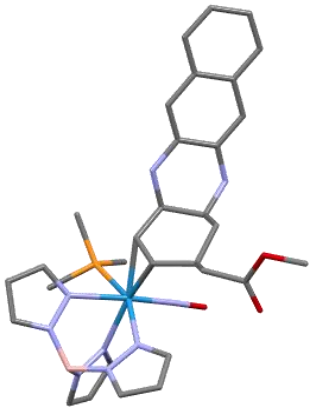
	x/a	y/b	z/c	U(eq)
H25	-0.1861	0.4357	0.3822	0.039000
H26	-0.0644	0.0890	0.5196	0.040000
H27	-0.2428	0.1087	0.5388	0.047000
H28	-0.2905	0.2461	0.5117	0.040000
H29	0.1850	0.3170	0.5992	0.034000
H30	0.0905	0.4136	0.6493	0.044000
H31	-0.0797	0.4337	0.5853	0.045000
H32	0.194(3)	0.348(2)	0.4556(16)	0.018(10)
H33	0.183(3)	0.258(2)	0.3817(18)	0.022(10)
H34	0.2854	0.1466	0.3915	0.031000
H35	0.3991	0.1235	0.4709	0.034000
H36	0.3355	0.1896	0.5543	0.034000
H37	0.2997	0.3201	0.5454	0.030000
H38A	0.4925	0.2478	0.5855	0.042000
H38B	0.5234	0.1937	0.5357	0.042000
H40A	0.3295	0.3998	0.4229	0.044000
H40B	0.4498	0.4182	0.4407	0.044000
H40C	0.3478	0.3958	0.4171	0.044000
H40D	0.4542	0.4291	0.4521	0.044000
H42A	0.0005	0.1810	0.3044	0.055000
H42B	0.0381	0.0934	0.2991	0.055000
H42C	0.1204	0.1602	0.3203	0.055000
H43A	0.1840	0.0453	0.4079	0.051000
H43B	0.0832	-0.0066	0.3886	0.051000

	x/a	y/b	z/c	U(eq)
H43C	0.1135	0.0225	0.4536	0.051000
H44A	-0.1018	0.0554	0.4193	0.055000
H44B	-0.1029	0.0486	0.3518	0.055000
H44C	-0.1426	0.1263	0.3777	0.055000
H2	-0.191(3)	0.375(2)	0.4839(17)	0.028(11)
H6	0.388(6)	0.590(4)	0.470(3)	0.078000
H41A	0.2956	0.4698	0.5025	0.049000
H41B	0.4169	0.4856	0.5232	0.049000
H6A	0.3510	0.5281	0.5525	0.069000
H41C	0.3042	0.5118	0.4579	0.049000
H41D	0.2633	0.4443	0.4945	0.049000

Table 9. Hydrogen bond distances (Å) and angles (°) for Harman_PS_4_225_X2.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O3-H3···O6^a	0.86(7)	1.82(7)	2.644(5)	161.(7)
O6^{a}-^{H6}a···O5#1	1.03(8)	1.54(8)	2.564(5)	174.(7)

Structure Report for Compound 5.34



A colourless, needle shaped crystal of Compound 5.34 measuring 0.067×0.07×0.134 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for **Compound 5.34** were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800 low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[220] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by direct methods with SHELXT[221] and refined by full-matrix least-squares methods against F^2 using XL[222] within OLEX2.[223] All non-hydrogen atoms were refined with anisotropically. The N-H and B-Hy hydrogen atoms, as well as H10 and H15 were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[224]

[220] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[221] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[222] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[223] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[224] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Refinement details for Compound 5.34

'Disordered solvent located in the crystal lattice could not be adequately modeled with or without restraints. Therefore, the solvent was accounted for using the Platon SQUEEZE method. A void space of 948 A3 containing 211 electrons was found. This corresponds to a mixture of acetone and pentanes.'

Table 1 Crystal data and structure refinement for Compound 5.34

CCDC number	
Empirical formula	$C_{31}H_{39}BN_9O_3PW$
Formula weight	811.34
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.067×0.07×0.134
Crystal habit	colourless needle
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
a [Å]	17.0566(9)
b [Å]	17.6280(11)
c [Å]	14.1011(7)
α [°]	90
β [°]	111.951(2)
γ [°]	90
Volume [$Å^3$]	3932.5(4)
Z	4
ρ_{calc} [gcm^{-3}]	1.370
μ [mm^{-1}]	3.018
F(000)	1624
2θ range [°]	3.88 to 56.59 (0.75 Å)
Index ranges	−22 ≤ h ≤ 21 −23 ≤ k ≤ 23 −18 ≤ l ≤ 17
Reflections collected	60914
Independent reflections	9741 [R_{int} = 0.0553]

Data / Restraints / Parameters	9741 / 0 / 439
Goodness-of-fit on F^2	1.020
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0236 wR_2 = 0.0478
Final R indexes [all data]	R_1 = 0.0357 wR_2 = 0.0524
Largest peak/hole [eÅ^{-3}]	0.82/−0.59

Table 2 Atomic coordinates and Ueq [Å2] for Compound 5.34

Atom	***x***	***y***	***z***	U_{eq}
W1	0.14297(2)	0.74385(2)	0.44299(2)	0.01519(3)
P1	0.20167(5)	0.87552(4)	0.46679(5)	0.02439(15)
O1	0.24911(12)	0.68982(11)	0.32730(14)	0.0259(4)
O2	0.20818(16)	0.43065(13)	0.46897(18)	0.0529(7)
O3	0.28202(16)	0.40555(12)	0.63274(17)	0.0435(6)
N1	0.05639(13)	0.79030(11)	0.51768(15)	0.0181(4)
N2	−0.02916(13)	0.79130(11)	0.46411(15)	0.0191(4)
N3	0.04894(13)	0.79437(11)	0.30301(16)	0.0190(4)
N4	−0.03529(14)	0.79724(11)	0.28404(16)	0.0197(4)
N5	0.04406(13)	0.65464(11)	0.38847(15)	0.0177(4)
N6	−0.03929(13)	0.67283(11)	0.36203(15)	0.0172(4)
N7	0.20627(13)	0.71238(12)	0.37689(15)	0.0183(4)
N8	0.37380(15)	0.74107(14)	0.73965(18)	0.0294(5)
H8	0.3465(19)	0.7554(16)	0.766(2)	0.025(8)
N9	0.46374(14)	0.67434(13)	0.63804(18)	0.0239(5)
H9	0.488(2)	0.6426(18)	0.619(2)	0.034(9)
C1	0.06848(17)	0.82741(14)	0.60583(19)	0.0213(5)
H1	0.122064	0.835367	0.658799	0.026
C2	−0.00771(18)	0.85238(15)	0.6088(2)	0.0259(6)
H2	−0.016500	0.880164	0.661669	0.031
C3	−0.06755(18)	0.82800(15)	0.5182(2)	0.0251(6)

H3	−0.126741	0.835838	0.497114	0.030
C4	0.05890(18)	0.82410(14)	0.22153(19)	0.0227(5)
H4	0.111601	0.828943	0.213629	0.027
C5	−0.01872(19)	0.84722(15)	0.1492(2)	0.0282(6)
H5	−0.029105	0.870512	0.084892	0.034
C6	−0.07660(18)	0.82887(14)	0.19158(19)	0.0242(6)
H6	−0.135858	0.837043	0.160996	0.029
C7	0.04681(17)	0.57981(14)	0.37393(19)	0.0218(5)
H7	0.096998	0.551494	0.385864	0.026
C8	−0.03466(17)	0.54933(14)	0.3387(2)	0.0237(6)
H8A	−0.050379	0.497804	0.322708	0.028
C9	−0.08696(17)	0.60958(14)	0.33213(19)	0.0231(5)
H9A	−0.146780	0.607342	0.310226	0.028
C10	0.23998(16)	0.73327(14)	0.59893(18)	0.0181(5)
H10	0.2251(17)	0.7652(14)	0.645(2)	0.015(7)
C11	0.33526(16)	0.73713(14)	0.62814(19)	0.0203(5)
H11	0.349463	0.784420	0.598783	0.024
C12	0.37167(16)	0.66921(14)	0.59195(19)	0.0207(5)
H12	0.354296	0.673009	0.516076	0.025
C13	0.33658(16)	0.59515(14)	0.6160(2)	0.0212(5)
H13A	0.348888	0.592315	0.690344	0.025
H13B	0.364733	0.551718	0.597407	0.025
C14	0.24081(16)	0.58993(13)	0.55696(19)	0.0180(5)
H14	0.230063	0.582988	0.482758	0.022
C15	0.19568(16)	0.66225(13)	0.56928(18)	0.0165(5)
H15	0.1506(16)	0.6504(14)	0.5923(19)	0.016(7)
C16	0.20551(17)	0.52047(13)	0.5942(2)	0.0226(5)
H16A	0.226987	0.520450	0.669827	0.027
H16B	0.143070	0.523704	0.568395	0.027
C17	0.23106(18)	0.44789(15)	0.5574(2)	0.0279(6)
C18	0.3118(3)	0.33602(19)	0.6016(3)	0.0619(12)
H18A	0.338228	0.348160	0.552548	0.093
H18B	0.263957	0.301722	0.569627	0.093
H18C	0.353365	0.311379	0.661751	0.093
C19	0.45378(17)	0.71603(15)	0.7967(2)	0.0228(5)

C20	0.48919(17)	0.72383(15)	0.9013(2)	0.0247(6)
H20	0.457431	0.747765	0.935642	0.030
C21	0.57182(17)	0.69717(14)	0.9593(2)	0.0234(5)
C22	0.60992(19)	0.70666(17)	1.0672(2)	0.0318(6)
H22	0.579304	0.730832	1.102827	0.038
C23	0.69041(19)	0.68120(18)	1.1201(2)	0.0354(7)
H23	0.715384	0.688160	1.192033	0.043
C24	0.73632(18)	0.64481(17)	1.0685(2)	0.0319(7)
H24	0.792010	0.627083	1.105688	0.038
C25	0.70083(18)	0.63490(15)	0.9647(2)	0.0272(6)
H25	0.732152	0.609639	0.930855	0.033
C26	0.61883(17)	0.66141(15)	0.9072(2)	0.0240(6)
C27	0.58097(17)	0.65318(14)	0.7994(2)	0.0235(5)
H27	0.612044	0.628935	0.764457	0.028
C28	0.50106(17)	0.67904(14)	0.7441(2)	0.0227(5)
C29	0.25854(19)	0.91507(15)	0.5932(2)	0.0313(7)
H29A	0.221652	0.915229	0.632307	0.047
H29B	0.275898	0.967141	0.586375	0.047
H29C	0.308700	0.884158	0.628846	0.047
C30	0.2717(2)	0.89361(19)	0.3991(3)	0.0468(9)
H30A	0.322992	0.862915	0.429075	0.070
H30B	0.286917	0.947491	0.404825	0.070
H30C	0.243010	0.880194	0.326869	0.070
C31	0.1196(2)	0.94885(16)	0.4186(2)	0.0380(8)
H31A	0.087744	0.940824	0.345461	0.057
H31B	0.146184	0.999042	0.429195	0.057
H31C	0.081103	0.945749	0.455536	0.057
B1	−0.06927(18)	0.75574(16)	0.3570(2)	0.0193(5)
H1A	−0.1375(16)	0.7590(13)	0.3306(19)	0.013(6)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for **Compound 5.34**

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	0.01482(5)	0.01516(5)	0.01391(5)	0.00073(4)	0.00345(4)	−0.00031(4)
P1	0.0267(4)	0.0178(3)	0.0246(4)	0.0010(3)	0.0049(3)	−0.0048(3)

O1	0.0228(10)	0.0357(11)	0.0218(10)	0.0014(8)	0.0112(8)	0.0037(8)
O2	0.0566(16)	0.0371(13)	0.0409(14)	−0.0199(10)	−0.0094(12)	0.0101(11)
O3	0.0618(16)	0.0306(11)	0.0418(13)	0.0145(9)	0.0236(12)	0.0238(11)
N1	0.0172(11)	0.0178(10)	0.0164(10)	0.0023(8)	0.0028(9)	0.0031(8)
N2	0.0171(11)	0.0206(10)	0.0166(10)	0.0001(8)	0.0031(9)	0.0032(8)
N3	0.0199(11)	0.0169(10)	0.0178(10)	0.0011(8)	0.0041(9)	−0.0008(8)
N4	0.0203(11)	0.0173(10)	0.0174(10)	0.0015(8)	0.0023(9)	0.0010(8)
N5	0.0168(11)	0.0174(10)	0.0172(10)	0.0008(8)	0.0043(9)	−0.0004(8)
N6	0.0148(11)	0.0198(10)	0.0148(10)	0.0019(8)	0.0031(8)	−0.0011(8)
N7	0.0159(11)	0.0221(11)	0.0139(10)	0.0021(8)	0.0023(9)	0.0002(8)
N8	0.0189(12)	0.0417(15)	0.0207(11)	−0.0099(10)	−0.0006(10)	0.0099(11)
N9	0.0150(12)	0.0299(13)	0.0244(12)	−0.0044(9)	0.0046(10)	0.0009(9)
C1	0.0248(14)	0.0190(12)	0.0158(12)	−0.0014(9)	0.0025(11)	0.0017(10)
C2	0.0273(15)	0.0287(14)	0.0192(13)	−0.0032(10)	0.0060(12)	0.0072(11)
C3	0.0219(14)	0.0285(14)	0.0264(14)	0.0003(11)	0.0108(12)	0.0078(11)
C4	0.0297(15)	0.0184(12)	0.0197(13)	0.0017(9)	0.0087(12)	−0.0034(11)
C5	0.0411(18)	0.0215(13)	0.0166(13)	0.0033(10)	0.0048(12)	−0.0018(12)
C6	0.0257(15)	0.0225(13)	0.0173(13)	0.0030(10)	0.0000(11)	0.0016(11)
C7	0.0236(14)	0.0197(12)	0.0191(13)	0.0015(9)	0.0044(11)	−0.0001(10)
C8	0.0260(15)	0.0205(13)	0.0216(13)	−0.0009(10)	0.0053(11)	−0.0049(11)
C9	0.0214(14)	0.0249(13)	0.0182(12)	0.0000(10)	0.0018(11)	−0.0072(11)
C10	0.0175(12)	0.0197(12)	0.0143(11)	−0.0004(9)	0.0025(10)	0.0014(10)
C11	0.0165(12)	0.0201(12)	0.0190(12)	−0.0002(9)	0.0006(10)	0.0017(10)
C12	0.0166(13)	0.0248(13)	0.0166(12)	−0.0017(9)	0.0016(10)	0.0008(10)
C13	0.0197(14)	0.0193(12)	0.0228(13)	−0.0004(10)	0.0057(11)	0.0031(10)
C14	0.0176(13)	0.0187(12)	0.0168(12)	0.0002(9)	0.0056(10)	0.0008(10)
C15	0.0149(12)	0.0185(12)	0.0159(12)	0.0023(9)	0.0056(10)	0.0010(9)
C16	0.0226(14)	0.0175(12)	0.0277(14)	0.0037(10)	0.0093(12)	0.0027(10)
C17	0.0236(15)	0.0185(13)	0.0368(16)	0.0013(11)	0.0059(13)	−0.0012(11)

C18	0.090(3)	0.0349(19)	0.067(3)	0.0137(18)	0.036(2)	0.036(2)
C19	0.0179(13)	0.0227(13)	0.0231(13)	−0.0028(10)	0.0021(11)	−0.0012(10)
C20	0.0188(13)	0.0276(14)	0.0237(13)	−0.0035(10)	0.0034(11)	0.0018(11)
C21	0.0184(13)	0.0217(13)	0.0261(14)	0.0024(10)	0.0037(11)	−0.0023(10)
C22	0.0253(16)	0.0389(17)	0.0274(15)	0.0019(12)	0.0056(13)	0.0050(13)
C23	0.0272(17)	0.0502(19)	0.0225(15)	0.0045(13)	0.0018(13)	0.0056(14)
C24	0.0168(14)	0.0413(17)	0.0303(16)	0.0077(12)	0.0004(12)	0.0057(12)
C25	0.0208(14)	0.0253(14)	0.0313(15)	0.0009(11)	0.0049(12)	0.0000(11)
C26	0.0169(13)	0.0230(13)	0.0273(14)	0.0038(10)	0.0028(11)	−0.0022(10)
C27	0.0191(14)	0.0236(13)	0.0276(14)	−0.0027(10)	0.0085(12)	−0.0021(10)
C28	0.0190(14)	0.0206(13)	0.0252(14)	−0.0029(10)	0.0045(11)	−0.0032(10)
C29	0.0336(17)	0.0188(13)	0.0326(16)	−0.0046(11)	0.0021(13)	−0.0055(12)
C30	0.057(2)	0.0409(19)	0.052(2)	−0.0056(15)	0.0311(19)	−0.0242(17)
C31	0.047(2)	0.0199(14)	0.0327(17)	0.0021(11)	−0.0011(15)	0.0027(13)
B1	0.0164(13)	0.0234(14)	0.0158(12)	0.0012(11)	0.0033(11)	0.0004(11)

C2–C3	1.372(4)
C3–H3	0.9500
C4–H4	0.9500
C4–C5	1.396(4)
C5–H5	0.9500
C5–C6	1.370(4)
C6–H6	0.9500

C7–H7	0.9500
C7–C8	1.397(4)
C8–H8A	0.9500
C8–C9	1.368(4)
C9–H9A	0.9500
C10–H10	0.96(3)
C10–C11	1.522(3)
C10–C15	1.441(3)
C11–H11	1.0000
C11–C12	1.522(3)
C12–H12	1.0000
C12–C13	1.526(3)
C13–H13A	0.9900
C13–H13B	0.9900
C13–C14	1.534(3)
C14–H14	1.0000
C14–C15	1.532(3)
C14–C16	1.541(3)
C15–H15	0.96(3)
C16–H16A	0.9900
C16–H16B	0.9900
C16–C17	1.505(4)
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C19–C20	1.375(4)
C19–C28	1.440(4)
C20–H20	0.9500
C20–C21	1.419(4)
C21–C22	1.423(4)
C21–C26	1.422(4)
C22–H22	0.9500
C22–C23	1.370(4)
C23–H23	0.9500
C23–C24	1.407(4)
C24–H24	0.9500
C24–C25	1.370(4)
C25–H25	0.9500
C25–C26	1.409(4)

C26–C27	1.418(4)
C27–H27	0.9500
C27–C28	1.371(4)
C29–H29A	0.9800
C29–H29B	0.9800
C29–H29C	0.9800
C30–H30A	0.9800
C30–H30B	0.9800
C30–H30C	0.9800
C31–H31A	0.9800
C31–H31B	0.9800
C31–H31C	0.9800
B1–H1A	1.08(2)
Atom–Atom–Atom	**Angle [°]**
N1–W1–P1	84.26(5)
N3–W1–P1	82.33(6)
N3–W1–N1	83.57(7)
N3–W1–N5	76.87(7)
N5–W1–P1	156.53(6)
N5–W1–N1	82.76(7)
N7–W1–P1	93.99(7)
N7–W1–N1	175.58(8)
N7–W1–N3	92.18(8)
N7–W1–N5	97.49(8)
N7–W1–C10	96.95(9)
N7–W1–C15	94.39(9)
C10–W1–P1	80.30(6)
C10–W1–N1	86.77(8)
C10–W1–N3	160.87(8)
C10–W1–N5	118.26(8)
C15–W1–P1	118.41(7)
C15–W1–N1	90.01(8)
C15–W1–N3	157.65(8)
C15–W1–N5	81.10(8)
C15–W1–C10	38.12(9)
C29–P1–W1	121.83(9)
C29–P1–C31	98.39(14)

C30–P1–W1	113.70(11)
C30–P1–C29	103.48(15)
C30–P1–C31	104.01(16)
C31–P1–W1	113.05(10)
C17–O3–C18	115.6(3)
N2–N1–W1	119.60(15)
C1–N1–W1	134.57(17)
C1–N1–N2	105.4(2)
N1–N2–B1	121.80(19)
C3–N2–N1	109.8(2)
C3–N2–B1	128.4(2)
N4–N3–W1	123.40(15)
C4–N3–W1	130.17(18)
C4–N3–N4	106.4(2)
N3–N4–B1	118.95(19)
C6–N4–N3	109.7(2)
C6–N4–B1	130.6(2)
N6–N5–W1	120.41(14)
C7–N5–W1	133.21(18)
C7–N5–N6	106.4(2)
N5–N6–B1	121.91(19)
C9–N6–N5	109.6(2)
C9–N6–B1	128.1(2)
O1–N7–W1	178.11(19)
C11–N8–H8	116(3)
C19–N8–H8	119(3)
C19–N8–C11	124.4(2)
C12–N9–H9	114(2)
C28–N9–H9	109(2)
C28–N9–C12	117.7(2)
N1–C1–H1	124.5
N1–C1–C2	111.0(2)
C2–C1–H1	124.5
C1–C2–H2	127.7
C3–C2–C1	104.6(2)
C3–C2–H2	127.7
N2–C3–C2	109.2(2)
N2–C3–H3	125.4
C2–C3–H3	125.4

N3–C4–H4	124.7
N3–C4–C5	110.7(2)
C5–C4–H4	124.7
C4–C5–H5	127.7
C6–C5–C4	104.7(2)
C6–C5–H5	127.7
N4–C6–C5	108.5(2)
N4–C6–H6	125.7
C5–C6–H6	125.7
N5–C7–H7	124.9
N5–C7–C8	110.3(2)
C8–C7–H7	124.9
C7–C8–H8A	127.4
C9–C8–C7	105.2(2)
C9–C8–H8A	127.4
N6–C9–C8	108.6(2)
N6–C9–H9A	125.7
C8–C9–H9A	125.7
W1–C10–H10	109.4(16)
C11–C10–W1	126.30(17)
C11–C10–H10	108.4(16)
C15–C10–W1	70.64(13)
C15–C10–H10	117.5(15)
C15–C10–C11	120.6(2)
N8–C11–C10	107.4(2)
N8–C11–H11	108.9
N8–C11–C12	108.8(2)
C10–C11–H11	108.9
C10–C11–C12	113.7(2)
C12–C11–H11	108.9
N9–C12–C11	107.9(2)
N9–C12–H12	108.1
N9–C12–C13	113.6(2)
C11–C12–H12	108.1
C11–C12–C13	110.8(2)
C13–C12–H12	108.1
C12–C13–H13A	109.5
C12–C13–H13B	109.5
C12–C13–C14	110.9(2)

H13A–C13–H13B	108.0
C14–C13–H13A	109.5
C14–C13–H13B	109.5
C13–C14–H14	108.5
C13–C14–C16	109.6(2)
C15–C14–C13	111.5(2)
C15–C14–H14	108.5
C15–C14–C16	110.23(19)
C16–C14–H14	108.5
W1–C15–H15	106.2(15)
C10–C15–W1	71.24(13)
C10–C15–C14	121.6(2)
C10–C15–H15	119.3(15)
C14–C15–W1	121.48(16)
C14–C15–H15	110.8(15)
C14–C16–H16A	109.4
C14–C16–H16B	109.4
H16A–C16–H16B	108.0
C17–C16–C14	111.0(2)
C17–C16–H16A	109.4
C17–C16–H16B	109.4
O2–C17–O3	123.6(3)
O2–C17–C16	123.4(3)
O3–C17–C16	113.0(2)
O3–C18–H18A	109.5
O3–C18–H18B	109.5
O3–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
N8–C19–C20	122.6(2)
N8–C19–C28	118.0(2)
C20–C19–C28	119.4(2)
C19–C20–H20	119.0
C19–C20–C21	121.9(3)
C21–C20–H20	119.0
C20–C21–C22	122.4(3)
C20–C21–C26	118.6(2)
C26–C21–C22	119.0(3)

C21–C22–H22	119.8
C23–C22–C21	120.5(3)
C23–C22–H22	119.8
C22–C23–H23	119.8
C22–C23–C24	120.4(3)
C24–C23–H23	119.8
C23–C24–H24	120.0
C25–C24–C23	120.1(3)
C25–C24–H24	120.0
C24–C25–H25	119.3
C24–C25–C26	121.4(3)
C26–C25–H25	119.3
C25–C26–C21	118.7(3)
C25–C26–C27	122.6(3)
C27–C26–C21	118.7(2)
C26–C27–H27	118.9
C28–C27–C26	122.2(2)
C28–C27–H27	118.9
N9–C28–C19	117.5(2)
C27–C28–N9	123.3(2)
C27–C28–C19	119.1(2)
P1–C29–H29A	109.5
P1–C29–H29B	109.5
P1–C29–H29C	109.5
H29A–C29–H29B	109.5
H29A–C29–H29C	109.5
H29B–C29–H29C	109.5
P1–C30–H30A	109.5
P1–C30–H30B	109.5
P1–C30–H30C	109.5
H30A–C30–H30B	109.5
H30A–C30–H30C	109.5
H30B–C30–H30C	109.5
P1–C31–H31A	109.5
P1–C31–H31B	109.5
P1–C31–H31C	109.5
H31A–C31–H31B	109.5
H31A–C31–H31C	109.5
H31B–C31–H31C	109.5

N2–B1–N4	108.8(2)
N2–B1–N6	108.8(2)
N2–B1–H1A	110.0(13)
N4–B1–N6	106.26(19)
N4–B1–H1A	111.7(13)
N6–B1–H1A	111.2(13)

Table 4 Torsion angles for Compound 5.34

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
W1–N1–N2–C3	−173.63(16)
W1–N1–N2–B1	5.0(3)
W1–N1–C1–C2	171.88(18)
W1–N3–N4–C6	−177.95(16)
W1–N3–N4–B1	−7.1(3)
W1–N3–C4–C5	178.03(17)
W1–N5–N6–C9	−179.62(15)
W1–N5–N6–B1	7.0(3)
W1–N5–C7–C8	179.55(17)
W1–C10–C11–N8	170.04(17)
W1–C10–C11–C12	−69.5(3)
W1–C10–C15–C14	116.0(2)
N1–N2–C3–C2	0.3(3)
N1–N2–B1–N4	−61.5(3)
N1–N2–B1–N6	53.9(3)
N1–C1–C2–C3	0.6(3)
N2–N1–C1–C2	−0.4(3)
N3–N4–C6–C5	−0.1(3)
N3–N4–B1–N2	62.5(3)
N3–N4–B1–N6	−54.5(3)
N3–C4–C5–C6	−0.6(3)
N4–N3–C4–C5	0.5(3)
N5–N6–C9–C8	−0.1(3)
N5–N6–B1–N2	−61.9(3)
N5–N6–B1–N4	55.0(3)
N5–C7–C8–C9	0.3(3)
N6–N5–C7–C8	−0.4(3)

N8–C11–C12–N9	−51.8(3)
N8–C11–C12–C13	73.1(3)
N8–C19–C20–C21	179.6(3)
N8–C19–C28–N9	2.9(4)
N8–C19–C28–C27	−179.7(2)
N9–C12–C13–C14	−174.3(2)
C1–N1–N2–C3	0.1(3)
C1–N1–N2–B1	178.7(2)
C1–C2–C3–N2	−0.5(3)
C3–N2–B1–N4	116.9(3)
C3–N2–B1–N6	−127.8(3)
C4–N3–N4–C6	−0.2(3)
C4–N3–N4–B1	170.7(2)
C4–C5–C6–N4	0.4(3)
C6–N4–B1–N2	−128.8(3)
C6–N4–B1–N6	114.2(3)
C7–N5–N6–C9	0.3(3)
C7–N5–N6–B1	−173.1(2)
C7–C8–C9–N6	−0.1(3)
C9–N6–B1–N2	126.0(2)
C9–N6–B1–N4	−117.0(3)
C10–C11–C12–N9	−171.4(2)
C10–C11–C12–C13	−46.5(3)
C11–N8–C19–C20	177.0(3)
C11–N8–C19–C28	−4.1(4)
C11–C10–C15–W1	−121.4(2)
C11–C10–C15–C14	−5.4(3)
C11–C12–C13–C14	64.0(3)
C12–N9–C28–C19	−30.9(3)
C12–N9–C28–C27	151.8(2)
C12–C13–C14–C15	−49.7(3)
C12–C13–C14–C16	−172.0(2)
C13–C14–C15–W1	107.5(2)
C13–C14–C15–C10	21.2(3)
C13–C14–C16–C17	−72.2(3)
C14–C16–C17–O2	−64.7(4)
C14–C16–C17–O3	114.7(3)
C15–C10–C11–N8	−102.5(3)
C15–C10–C11–C12	17.9(3)

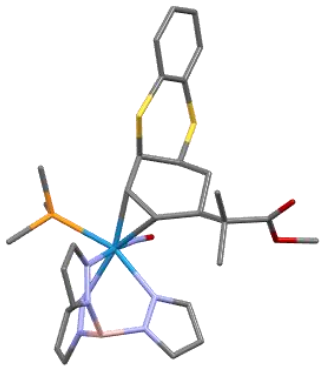
C15–C14–C16–C17	164.7(2)
C16–C14–C15–W1	−130.57(19)
C16–C14–C15–C10	143.2(2)
C18–O3–C17–O2	1.9(5)
C18–O3–C17–C16	−177.5(3)
C19–N8–C11–C10	153.2(3)
C19–N8–C11–C12	29.7(4)
C19–C20–C21–C22	178.4(3)
C19–C20–C21–C26	0.0(4)
C20–C19–C28–N9	−178.2(2)
C20–C19–C28–C27	−0.8(4)
C20–C21–C22–C23	−178.9(3)
C20–C21–C26–C25	−180.0(2)
C20–C21–C26–C27	−0.6(4)
C21–C22–C23–C24	−0.5(5)
C21–C26–C27–C28	0.5(4)
C22–C21–C26–C25	1.6(4)
C22–C21–C26–C27	−179.0(2)
C22–C23–C24–C25	0.3(5)
C23–C24–C25–C26	0.8(4)
C24–C25–C26–C21	−1.8(4)
C24–C25–C26–C27	178.9(3)
C25–C26–C27–C28	179.9(2)
C26–C21–C22–C23	−0.5(4)
C26–C27–C28–N9	177.4(2)
C26–C27–C28–C19	0.2(4)
C28–N9–C12–C11	56.0(3)
C28–N9–C12–C13	−67.2(3)
C28–C19–C20–C21	0.7(4)
B1–N2–C3–C2	−178.2(2)
B1–N4–C6–C5	−169.6(2)
B1–N6–C9–C8	172.7(2)

Table 5 Hydrogen bonds for Compound 5.34

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N8–H8···O1$^{\#1}$	0.74(3)	2.35(3)	3.082(3)	172(3)

Symmetry transformations used to generate equivalent atoms: #1: +X, 1.5-Y, 0.5+Z;

Structure Report for Compound 5.39



A colourless, plate shaped crystal of **Compound 5.39**
measuring 0.035×0.053×0.067 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for **Compound 5.39**
were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Cu K_α, λ=1.54178 Å) using a HELIOS EF double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[225] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

[225] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.

The structure was solved by direct methods with SHELXT[226] and refined by full-matrix least-squares methods against F^2 using XL[227] within OLEX2.[228] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atom, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[229]

Refinement details for Compound 5.39

Disordered solvent located in the crystal lattice could not be adequately modeled with or without restraints. Therefore, the solvent was accounted for using the Platon SQUEEZE method. A void space of 843 A3 containing 167 electrons was found. This corresponds to a disordered mixture Acetone and Pentanes.

Table 1 Crystal data and structure refinement for Compound 5.39

CCDC number	
Empirical formula	$C_{29}H_{39}BN_7O_3PS_2W$
Formula weight	823.42
Temperature [K]	100.00
Wavelength [Å]	1.54178
Crystal size [mm^3]	0.035×0.053×0.067
Crystal habit	colourless plate
Crystal system	orthorhombic
Space group	$Pbca$ (61)
a [Å]	16.6203(5)
b [Å]	13.9359(4)
c [Å]	30.5898(10)
α [°]	90
β [°]	90
γ [°]	90
Volume [$Å^3$]	7085.2(4)
Z	8
ρ_{calc} [gcm^{-3}]	1.544

[226] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[227] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[228] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[229] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

μ [mm^{-1}]	7.894
F(000)	3296
2θ range [°]	5.78 to 141.89 (0.82 Å)
Index ranges	−20 ≤ h ≤ 19 −17 ≤ k ≤ 16 −36 ≤ l ≤ 37
Reflections collected	71009
Independent reflections	6778 [R_{int} = 0.1019]
Data / Restraints / Parameters	6778 / 0 / 415
Goodness-of-fit on F^2	1.047
Final R indexes [I≥2σ(I)]	R_1 = 0.0379 wR_2 = 0.0837
Final R indexes [all data]	R_1 = 0.0540 wR_2 = 0.0910
Largest peak/hole [eÅ^{-3}]	2.12/−1.09

Table 2 Atomic coordinates and Ueq [Å2] for Compound 5.39

Atom	***x***	***y***	***z***	U_{eq}
B1	0.3487(4)	0.6625(4)	0.3380(2)	0.0350(14)
H1	0.324(3)	0.727(4)	0.3417(16)	0.024(13)
C1	0.5538(3)	0.6169(4)	0.37175(17)	0.0343(12)
H1A	0.600349	0.577497	0.373563	0.041
C2	0.5482(4)	0.7092(4)	0.38806(19)	0.0428(14)
H2	0.588539	0.744714	0.402970	0.051
C3	0.4714(4)	0.7382(4)	0.37793(18)	0.0397(13)
H3	0.448834	0.799036	0.384721	0.048
C4	0.2600(3)	0.4353(4)	0.36359(17)	0.0335(11)
H4	0.259419	0.367172	0.362077	0.040
C5	0.1941(3)	0.4922(4)	0.3750(2)	0.0420(14)
H5	0.141505	0.471363	0.382572	0.050
C6	0.2218(3)	0.5839(4)	0.37284(18)	0.0384(13)
H6	0.191044	0.639919	0.378666	0.046
C7	0.3611(3)	0.5349(4)	0.23610(17)	0.0309(11)

H7	0.375001	0.480548	0.218912	0.037
C8	0.3152(3)	0.6117(4)	0.22109(18)	0.0357(12)
H8	0.293077	0.620466	0.192722	0.043
C9	0.3090(3)	0.6720(4)	0.25638(17)	0.0329(11)
H9	0.279842	0.730662	0.257065	0.039
C10	0.4651(3)	0.3981(4)	0.39370(17)	0.0280(10)
H10	0.472(3)	0.454(4)	0.4086(18)	0.033(15)
C11	0.5325(3)	0.3744(3)	0.36631(16)	0.0266(10)
H11	0.579(3)	0.412(4)	0.3704(16)	0.020(12)
C12	0.5545(3)	0.2692(3)	0.35884(17)	0.0285(10)
H12	0.570206	0.259249	0.327609	0.034
C13	0.4848(3)	0.2024(3)	0.37056(17)	0.0276(10)
H13	0.440080	0.219226	0.350069	0.033
C14	0.4530(3)	0.2229(3)	0.41618(16)	0.0262(10)
H14A	0.497705	0.219728	0.437517	0.031
H14B	0.412642	0.173828	0.424318	0.031
C15	0.4142(3)	0.3232(3)	0.41764(16)	0.0278(10)
H15	0.361461	0.318813	0.402022	0.033
C16	0.3959(3)	0.3533(4)	0.46590(16)	0.0307(11)
C17	0.4719(4)	0.3630(4)	0.49413(18)	0.0393(13)
H17A	0.509618	0.407209	0.479997	0.059
H17B	0.497317	0.299918	0.497409	0.059
H17C	0.457208	0.387921	0.522996	0.059
C18	0.3496(3)	0.4490(4)	0.46729(17)	0.0364(12)
H18A	0.384488	0.500852	0.456933	0.055
H18B	0.332667	0.462294	0.497376	0.055
H18C	0.302016	0.444590	0.448442	0.055
C19	0.3397(3)	0.2789(4)	0.48664(17)	0.0356(12)
C20	0.2205(5)	0.1896(6)	0.4793(2)	0.072(2)
H20A	0.179618	0.174242	0.457301	0.108
H20B	0.194324	0.216955	0.505201	0.108
H20C	0.249347	0.131057	0.487542	0.108
C21	0.6592(3)	0.1254(4)	0.39478(16)	0.0278(10)
C22	0.7348(3)	0.0968(4)	0.41115(17)	0.0332(11)
H22	0.772513	0.143597	0.420606	0.040
C23	0.7539(3)	0.0004(4)	0.41341(17)	0.0354(12)
H23	0.804716	−0.018803	0.424619	0.043
C24	0.6995(3)	−0.0686(4)	0.39946(19)	0.0397(13)
H24	0.713596	−0.134593	0.400436	0.048

C25	0.6253(3)	−0.0411(4)	0.38423(19)	0.0354(12)
H25	0.587875	−0.088630	0.375151	0.042
C26	0.6041(3)	0.0559(4)	0.38191(16)	0.0274(10)
C27	0.6588(3)	0.4255(4)	0.29197(19)	0.0374(12)
H27A	0.674116	0.467263	0.316372	0.056
H27B	0.696451	0.434739	0.267688	0.056
H27C	0.660359	0.358399	0.301495	0.056
C28	0.5748(3)	0.5734(4)	0.24999(19)	0.0378(12)
H28A	0.524573	0.597429	0.237244	0.057
H28B	0.615832	0.568337	0.227106	0.057
H28C	0.593297	0.617922	0.272678	0.057
C29	0.5452(3)	0.3764(4)	0.22719(19)	0.0405(13)
H29A	0.497172	0.395428	0.210705	0.061
H29B	0.539083	0.310125	0.237317	0.061
H29C	0.592619	0.381224	0.208305	0.061
N1	0.4845(3)	0.5910(3)	0.35311(14)	0.0305(9)
N2	0.4340(3)	0.6676(3)	0.35715(14)	0.0349(10)
N3	0.3232(2)	0.4895(3)	0.35521(13)	0.0279(9)
N4	0.3001(3)	0.5824(3)	0.36108(15)	0.0327(9)
N5	0.3830(2)	0.5470(3)	0.27730(13)	0.0285(9)
N6	0.3510(2)	0.6342(3)	0.28995(14)	0.0294(9)
N7	0.3966(2)	0.3459(3)	0.30379(13)	0.0288(9)
O1	0.3611(2)	0.2768(3)	0.28799(14)	0.0434(9)
O2	0.3487(3)	0.2437(3)	0.52234(13)	0.0505(11)
O3	0.2768(2)	0.2587(3)	0.46144(13)	0.0475(10)
P1	0.55743(7)	0.45551(9)	0.27409(4)	0.0279(3)
S1	0.64180(7)	0.25026(9)	0.39413(5)	0.0345(3)
S2	0.50758(7)	0.07727(8)	0.36033(4)	0.0300(3)
W1	0.44041(2)	0.45034(2)	0.32634(2)	0.02334(8)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for **Compound 5.39**

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.043(3)	0.019(3)	0.043(4)	0.001(2)	0.001(3)	0.008(3)
C1	0.040(3)	0.025(2)	0.038(3)	0.004(2)	−0.010(2)	−0.005(2)
C2	0.057(4)	0.028(3)	0.044(3)	0.003(2)	−0.020(3)	−0.003(3)
C3	0.055(3)	0.023(3)	0.041(3)	−0.003(2)	−0.010(3)	0.000(2)

C4	0.030(3)	0.034(3)	0.037(3)	0.007(2)	−0.001(2)	−0.002(2)
C5	0.024(3)	0.049(3)	0.052(3)	0.005(3)	0.001(2)	0.004(2)
C6	0.033(3)	0.042(3)	0.040(3)	−0.003(2)	0.006(2)	0.014(2)
C7	0.026(2)	0.033(3)	0.034(3)	−0.002(2)	0.000(2)	−0.001(2)
C8	0.028(3)	0.047(3)	0.033(3)	0.005(2)	−0.001(2)	0.000(2)
C9	0.028(2)	0.030(3)	0.041(3)	0.008(2)	0.000(2)	0.000(2)
C10	0.038(3)	0.017(2)	0.029(3)	0.006(2)	−0.004(2)	−0.004(2)
C11	0.024(2)	0.022(2)	0.033(3)	0.003(2)	−0.005(2)	−0.003(2)
C12	0.025(2)	0.026(2)	0.034(3)	0.003(2)	−0.003(2)	0.000(2)
C13	0.028(3)	0.017(2)	0.037(3)	0.0020(19)	−0.003(2)	0.0033(19)
C14	0.028(2)	0.019(2)	0.031(2)	0.0019(19)	0.000(2)	−0.0048(19)
C15	0.029(2)	0.022(2)	0.033(3)	0.002(2)	−0.002(2)	−0.0003(19)
C16	0.036(3)	0.028(3)	0.028(3)	0.002(2)	0.000(2)	−0.006(2)
C17	0.049(3)	0.031(3)	0.038(3)	−0.004(2)	−0.008(2)	−0.005(2)
C18	0.044(3)	0.031(3)	0.035(3)	−0.006(2)	0.006(2)	0.003(2)
C19	0.046(3)	0.030(3)	0.031(3)	−0.004(2)	0.004(2)	−0.006(2)
C20	0.072(5)	0.096(6)	0.049(4)	−0.009(4)	0.022(4)	−0.048(4)
C21	0.025(2)	0.027(2)	0.032(3)	0.002(2)	0.003(2)	0.003(2)
C22	0.023(2)	0.041(3)	0.036(3)	0.001(2)	0.000(2)	−0.001(2)
C23	0.026(3)	0.043(3)	0.038(3)	0.004(2)	0.000(2)	0.010(2)
C24	0.035(3)	0.034(3)	0.050(3)	0.009(2)	0.002(2)	0.007(2)
C25	0.029(3)	0.025(3)	0.052(3)	0.003(2)	0.000(2)	−0.003(2)
C26	0.025(2)	0.024(2)	0.033(3)	0.001(2)	0.001(2)	0.003(2)
C27	0.028(3)	0.046(3)	0.039(3)	−0.001(2)	−0.003(2)	−0.009(2)
C28	0.037(3)	0.038(3)	0.039(3)	0.011(2)	−0.002(2)	−0.007(2)
C29	0.038(3)	0.041(3)	0.043(3)	−0.004(2)	0.008(2)	0.004(2)
N1	0.033(2)	0.021(2)	0.037(2)	0.0034(18)	−0.0018(19)	−0.0046(17)
N2	0.052(3)	0.023(2)	0.030(2)	−0.0024(17)	0.005(2)	0.005(2)
N3	0.027(2)	0.026(2)	0.031(2)	0.0043(17)	0.0014(18)	0.0034(17)
N4	0.033(2)	0.025(2)	0.039(2)	0.0022(18)	−0.0012(19)	0.0063(18)
N5	0.026(2)	0.031(2)	0.028(2)	−0.0012(18)	0.0035(16)	−0.0048(18)
N6	0.028(2)	0.025(2)	0.034(2)	0.0050(18)	−0.0018(17)	0.0013(17)

N7	0.029(2)	0.023(2)	0.034(2)	0.0010(18)	−0.0058(18)	0.0048(18)
O1	0.042(2)	0.030(2)	0.058(3)	−0.0062(18)	−0.0096(19)	−0.0081(17)
O2	0.069(3)	0.047(2)	0.035(2)	0.0069(19)	0.000(2)	−0.017(2)
O3	0.043(2)	0.060(3)	0.039(2)	−0.0020(19)	0.0042(18)	−0.025(2)
P1	0.0245(6)	0.0275(6)	0.0317(6)	0.0025(5)	0.0029(5)	−0.0017(5)
S1	0.0270(6)	0.0243(6)	0.0520(8)	0.0006(5)	−0.0100(6)	−0.0026(5)
S2	0.0256(6)	0.0206(5)	0.0438(7)	−0.0019(5)	−0.0035(5)	0.0002(5)
W1	0.02216(12)	0.01894(11)	0.02893(13)	0.00093(9)	0.00034(9)	−0.00037(8)

Table 4 Bond lengths and angles for Compound 5.39

Atom–Atom	**Length [Å]**
B1–H1	0.99(5)
B1–N2	1.536(8)
B1–N4	1.548(8)
B1–N6	1.522(8)
C1–H1A	0.9500
C1–C2	1.383(8)
C1–N1	1.334(7)
C2–H2	0.9500
C2–C3	1.374(9)
C3–H3	0.9500
C3–N2	1.327(7)
C4–H4	0.9500
C4–C5	1.396(8)
C4–N3	1.320(7)
C5–H5	0.9500
C5–C6	1.360(9)
C6–H6	0.9500
C6–N4	1.351(7)
C7–H7	0.9500
C7–C8	1.394(8)
C7–N5	1.323(6)

C8–H8	0.9500
C8–C9	1.372(8)
C9–H9	0.9500
C9–N6	1.349(7)
C10–H10	0.91(6)
C10–C11	1.438(7)
C10–C15	1.530(7)
C10–W1	2.224(5)
C11–H11	0.94(5)
C11–C12	1.529(7)
C11–W1	2.226(5)
C12–H12	1.0000
C12–C13	1.529(7)
C12–S1	1.827(5)
C13–H13	1.0000
C13–C14	1.519(7)
C13–S2	1.811(5)
C14–H14A	0.9900
C14–H14B	0.9900
C14–C15	1.540(7)
C15–H15	1.0000
C15–C16	1.564(7)
C16–C17	1.535(7)
C16–C18	1.541(7)
C16–C19	1.533(7)
C17–H17A	0.9800
C17–H17B	0.9800
C17–H17C	0.9800
C18–H18A	0.9800
C18–H18B	0.9800
C18–H18C	0.9800
C19–O2	1.206(7)
C19–O3	1.329(7)
C20–H20A	0.9800
C20–H20B	0.9800
C20–H20C	0.9800
C20–O3	1.450(8)
C21–C22	1.410(7)
C21–C26	1.390(7)

C21–S1	1.764(5)
C22–H22	0.9500
C22–C23	1.382(8)
C23–H23	0.9500
C23–C24	1.386(8)
C24–H24	0.9500
C24–C25	1.373(8)
C25–H25	0.9500
C25–C26	1.398(7)
C26–S2	1.760(5)
C27–H27A	0.9800
C27–H27B	0.9800
C27–H27C	0.9800
C27–P1	1.820(5)
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
C28–P1	1.824(5)
C29–H29A	0.9800
C29–H29B	0.9800
C29–H29C	0.9800
C29–P1	1.820(6)
N1–N2	1.364(6)
N1–W1	2.248(4)
N3–N4	1.362(6)
N3–W1	2.207(4)
N5–N6	1.382(6)
N5–W1	2.231(4)
N7–O1	1.229(5)
N7–W1	1.768(4)
P1–W1	2.5184(12)
Atom–Atom–Atom	**Angle [°]**
N2–B1–H1	108(3)
N2–B1–N4	109.9(4)
N4–B1–H1	112(3)
N6–B1–H1	111(3)
N6–B1–N2	110.9(5)

N6–B1–N4	105.5(4)
C2–C1–H1A	124.8
N1–C1–H1A	124.8
N1–C1–C2	110.3(5)
C1–C2–H2	127.6
C3–C2–C1	104.8(5)
C3–C2–H2	127.6
C2–C3–H3	125.5
N2–C3–C2	109.0(5)
N2–C3–H3	125.5
C5–C4–H4	124.8
N3–C4–H4	124.8
N3–C4–C5	110.3(5)
C4–C5–H5	127.6
C6–C5–C4	104.9(5)
C6–C5–H5	127.6
C5–C6–H6	125.5
N4–C6–C5	108.9(5)
N4–C6–H6	125.5
C8–C7–H7	124.3
N5–C7–H7	124.3
N5–C7–C8	111.5(5)
C7–C8–H8	127.7
C9–C8–C7	104.6(5)
C9–C8–H8	127.7
C8–C9–H9	125.6
N6–C9–C8	108.7(5)
N6–C9–H9	125.6
C11–C10–H10	113(4)
C11–C10–C15	123.6(4)
C11–C10–W1	71.3(3)
C15–C10–H10	114(4)
C15–C10–W1	124.4(3)
W1–C10–H10	102(4)
C10–C11–H11	116(3)
C10–C11–C12	119.6(4)
C10–C11–W1	71.0(3)
C12–C11–H11	111(3)
C12–C11–W1	122.6(3)

W1–C11–H11	112(3)
C11–C12–H12	109.7
C11–C12–C13	111.6(4)
C11–C12–S1	103.9(3)
C13–C12–H12	109.7
C13–C12–S1	112.1(3)
S1–C12–H12	109.7
C12–C13–H13	105.9
C12–C13–S2	112.7(3)
C14–C13–C12	111.3(4)
C14–C13–H13	105.9
C14–C13–S2	114.4(3)
S2–C13–H13	105.9
C13–C14–H14A	109.6
C13–C14–H14B	109.6
C13–C14–C15	110.1(4)
H14A–C14–H14B	108.2
C15–C14–H14A	109.6
C15–C14–H14B	109.6
C10–C15–C14	111.9(4)
C10–C15–H15	107.3
C10–C15–C16	112.1(4)
C14–C15–H15	107.3
C14–C15–C16	110.6(4)
C16–C15–H15	107.3
C17–C16–C15	113.3(4)
C17–C16–C18	108.6(4)
C18–C16–C15	110.8(4)
C19–C16–C15	109.1(4)
C19–C16–C17	109.2(4)
C19–C16–C18	105.5(4)
C16–C17–H17A	109.5
C16–C17–H17B	109.5
C16–C17–H17C	109.5
H17A–C17–H17B	109.5
H17A–C17–H17C	109.5
H17B–C17–H17C	109.5
C16–C18–H18A	109.5
C16–C18–H18B	109.5

C16–C18–H18C	109.5
H18A–C18–H18B	109.5
H18A–C18–H18C	109.5
H18B–C18–H18C	109.5
O2–C19–C16	125.0(5)
O2–C19–O3	122.4(5)
O3–C19–C16	112.5(4)
H20A–C20–H20B	109.5
H20A–C20–H20C	109.5
H20B–C20–H20C	109.5
O3–C20–H20A	109.5
O3–C20–H20B	109.5
O3–C20–H20C	109.5
C22–C21–S1	115.4(4)
C26–C21–C22	119.3(5)
C26–C21–S1	125.2(4)
C21–C22–H22	120.1
C23–C22–C21	119.8(5)
C23–C22–H22	120.1
C22–C23–H23	119.7
C22–C23–C24	120.6(5)
C24–C23–H23	119.7
C23–C24–H24	120.1
C25–C24–C23	119.8(5)
C25–C24–H24	120.1
C24–C25–H25	119.6
C24–C25–C26	120.8(5)
C26–C25–H25	119.6
C21–C26–C25	119.6(5)
C21–C26–S2	126.0(4)
C25–C26–S2	114.4(4)
H27A–C27–H27B	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
P1–C27–H27A	109.5
P1–C27–H27B	109.5
P1–C27–H27C	109.5
H28A–C28–H28B	109.5
H28A–C28–H28C	109.5

H28B–C28–H28C	109.5
P1–C28–H28A	109.5
P1–C28–H28B	109.5
P1–C28–H28C	109.5
H29A–C29–H29B	109.5
H29A–C29–H29C	109.5
H29B–C29–H29C	109.5
P1–C29–H29A	109.5
P1–C29–H29B	109.5
P1–C29–H29C	109.5
C1–N1–N2	106.4(4)
C1–N1–W1	132.3(4)
N2–N1–W1	121.0(3)
C3–N2–B1	130.6(5)
C3–N2–N1	109.5(5)
N1–N2–B1	119.9(4)
C4–N3–N4	107.1(4)
C4–N3–W1	129.7(4)
N4–N3–W1	122.5(3)
C6–N4–B1	127.7(5)
C6–N4–N3	108.8(4)
N3–N4–B1	118.6(4)
C7–N5–N6	105.9(4)
C7–N5–W1	132.9(4)
N6–N5–W1	120.5(3)
C9–N6–B1	128.4(4)
C9–N6–N5	109.2(4)
N5–N6–B1	120.5(4)
O1–N7–W1	175.5(4)
C19–O3–C20	115.5(5)
C27–P1–C28	100.5(3)
C27–P1–C29	101.6(3)
C27–P1–W1	121.16(19)
C28–P1–W1	113.86(19)
C29–P1–C28	104.2(3)
C29–P1–W1	113.35(19)
C21–S1–C12	106.2(2)
C26–S2–C13	106.8(2)
C10–W1–C11	37.69(19)

C10–W1–N1	83.57(17)
C10–W1–N5	154.15(17)
C10–W1–P1	117.08(14)
C11–W1–N1	89.44(17)
C11–W1–N5	161.86(16)
C11–W1–P1	80.29(13)
N1–W1–P1	87.38(11)
N3–W1–C10	82.70(17)
N3–W1–C11	120.29(17)
N3–W1–N1	85.77(15)
N3–W1–N5	75.07(14)
N3–W1–P1	158.17(11)
N5–W1–N1	81.81(15)
N5–W1–P1	83.45(10)
N7–W1–C10	99.66(18)
N7–W1–C11	96.10(18)
N7–W1–N1	174.15(17)
N7–W1–N3	89.79(17)
N7–W1–N5	93.37(17)
N7–W1–P1	95.39(14)

Table 5 Torsion angles for Compound 5.39

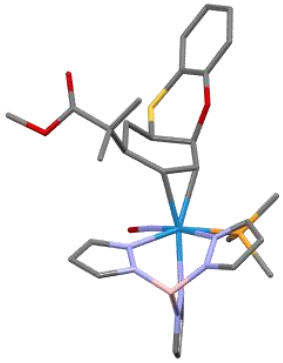
Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C1–C2–C3–N2	0.2(7)
C1–N1–N2–B1	178.7(5)
C1–N1–N2–C3	−0.3(6)
C2–C1–N1–N2	0.4(6)
C2–C1–N1–W1	−172.1(4)
C2–C3–N2–B1	−178.8(5)
C2–C3–N2–N1	0.0(6)
C4–C5–C6–N4	−0.4(7)
C4–N3–N4–B1	−157.6(5)
C4–N3–N4–C6	−0.4(6)
C5–C4–N3–N4	0.2(6)
C5–C4–N3–W1	−170.0(4)
C5–C6–N4–B1	155.0(5)

C5–C6–N4–N3	0.5(6)
C7–C8–C9–N6	1.8(6)
C7–N5–N6–B1	167.0(5)
C7–N5–N6–C9	1.3(5)
C8–C7–N5–N6	−0.1(5)
C8–C7–N5–W1	169.9(3)
C8–C9–N6–B1	−166.2(5)
C8–C9–N6–N5	−2.0(6)
C10–C11–C12–C13	18.0(6)
C10–C11–C12–S1	−102.9(4)
C10–C15–C16–C17	−62.4(6)
C10–C15–C16–C18	59.9(5)
C10–C15–C16–C19	175.7(4)
C11–C10–C15–C14	11.0(7)
C11–C10–C15–C16	135.9(5)
C11–C12–C13–C14	−51.8(5)
C11–C12–C13–S2	178.0(3)
C11–C12–S1–C21	169.6(3)
C12–C13–C14–C15	66.2(5)
C12–C13–S2–C26	46.1(4)
C13–C12–S1–C21	49.0(4)
C13–C14–C15–C10	−43.5(5)
C13–C14–C15–C16	−169.3(4)
C14–C13–S2–C26	−82.4(4)
C14–C15–C16–C17	63.2(5)
C14–C15–C16–C18	−174.4(4)
C14–C15–C16–C19	−58.6(5)
C15–C10–C11–C12	2.0(7)
C15–C10–C11–W1	119.4(5)
C15–C16–C19–O2	133.5(6)
C15–C16–C19–O3	−48.5(6)
C16–C19–O3–C20	−179.3(5)
C17–C16–C19–O2	9.2(8)
C17–C16–C19–O3	−172.8(5)
C18–C16–C19–O2	−107.4(6)
C18–C16–C19–O3	70.6(5)
C21–C22–C23–C24	0.4(8)
C21–C26–S2–C13	−13.7(5)
C22–C21–C26–C25	−1.8(7)

C22–C21–C26–S2	−179.4(4)
C22–C21–S1–C12	165.1(4)
C22–C23–C24–C25	−1.6(8)
C23–C24–C25–C26	1.0(8)
C24–C25–C26–C21	0.6(8)
C24–C25–C26–S2	178.5(4)
C25–C26–S2–C13	168.6(4)
C26–C21–C22–C23	1.3(8)
C26–C21–S1–C12	−17.0(5)
N1–C1–C2–C3	−0.4(7)
N2–B1–N4–C6	141.2(5)
N2–B1–N4–N3	−66.5(6)
N2–B1–N6–C9	−136.3(5)
N2–B1–N6–N5	61.1(6)
N3–C4–C5–C6	0.1(6)
N4–B1–N2–C3	−118.4(6)
N4–B1–N2–N1	62.9(6)
N4–B1–N6–C9	104.8(5)
N4–B1–N6–N5	−57.9(6)
N5–C7–C8–C9	−1.0(6)
N6–B1–N2–C3	125.4(6)
N6–B1–N2–N1	−53.3(6)
N6–B1–N4–C6	−99.3(6)
N6–B1–N4–N3	53.1(6)
O2–C19–O3–C20	−1.3(9)
S1–C12–C13–C14	64.2(5)
S1–C12–C13–S2	−66.0(4)
S1–C21–C22–C23	179.4(4)
S1–C21–C26–C25	−179.7(4)
S1–C21–C26–S2	2.7(7)
S2–C13–C14–C15	−164.5(3)
W1–C10–C11–C12	−117.4(4)
W1–C10–C15–C14	100.3(5)
W1–C10–C15–C16	−134.8(4)
W1–C11–C12–C13	−67.4(5)
W1–C11–C12–S1	171.7(3)
W1–N1–N2–B1	−7.8(6)
W1–N1–N2–C3	173.3(4)
W1–N3–N4–B1	13.4(6)

W1–N3–N4–C6	170.6(3)
W1–N5–N6–B1	−4.6(6)
W1–N5–N6–C9	−170.3(3)

Structure Report for Compound 40



A colourless, prism shaped crystal of Compound 40 measuring 0.044×0.044×0.081 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 40 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Cu K_α, λ=1.54178 Å) using a HELIOS EF double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[230] All data were integrated with the Bruker SAINT V8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

[230] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.

The structure was solved by dual methods with XT[231] and refined by full-matrix least-squares methods against F^2 using XL[232] within OLEX2.[233] All non-hydrogen atoms were refined with anisotropically. The B-H hydrogen atom was located in the electron density map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[234]

Table 6. Crystal data and structure refinement for Compound 40

CCDC number	
Empirical formula	$C_{29}H_{39}BN_7O_4PSW$
Formula weight	807.36
Temperature [K]	100.00
Wavelength [Å]	1.54178
Crystal size [mm^3]	0.044×0.044×0.081
Crystal habit	colourless prism
Crystal system	monoclinic
Space group	$P2_1/n$ (14)
a [Å]	18.5399(9)
b [Å]	7.9462(3)
c [Å]	22.9289(11)
α [°]	90
β [°]	107.818(3)
γ [°]	90
Volume [$Å^3$]	3215.9(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.668
μ [mm^{-1}]	8.116
F(000)	1616
2θ range [°]	5.39 to 137.48 (0.83 Å)
Index ranges	−22 ≤ h ≤ 22 −9 ≤ k ≤ 9 −27 ≤ l ≤ 27

[231] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[232] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[233] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[234] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

Reflections collected	33065
Independent reflections	5936 [R_{int} = 0.1169]
Data / Restraints / Parameters	5936 / 0 / 407
Goodness-of-fit on F^2	1.040
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0610 wR_2 = 0.1567
Final R indexes [all data]	R_1 = 0.0843 wR_2 = 0.1773
Largest peak/hole [eÅ^{-3}]	2.60/−1.29

Table 7. Atomic coordinates and Ueq [Å2] for Compound 40

Atom	***x***	***y***	***z***	U_{eq}
B1	0.2553(7)	0.2605(12)	0.4479(5)	0.043(2)
H1	0.240(5)	0.219(11)	0.401(4)	0.03(2)
C1	0.4008(6)	0.0792(11)	0.5727(5)	0.045(2)
H1A	0.423632	0.059964	0.615279	0.054
C2	0.4139(6)	−0.0173(11)	0.5257(4)	0.044(2)
H2	0.446515	−0.111652	0.529570	0.053
C3	0.3695(6)	0.0551(11)	0.4736(5)	0.047(2)
H3	0.366704	0.019236	0.433447	0.056
C4	0.1500(5)	0.1653(12)	0.5538(5)	0.046(2)
H4	0.142721	0.168245	0.593010	0.055
C5	0.1070(6)	0.0734(12)	0.5049(6)	0.054(3)
H5	0.064718	0.004394	0.503634	0.065
C6	0.1370(6)	0.1007(11)	0.4583(5)	0.048(2)
H6	0.119680	0.052245	0.418592	0.058
C7	0.2684(5)	0.7022(11)	0.4892(4)	0.0430(19)
H7	0.278665	0.790958	0.518332	0.052
C8	0.2434(6)	0.7256(12)	0.4259(4)	0.047(2)
H8	0.232313	0.828602	0.403887	0.056
C9	0.2385(5)	0.5653(12)	0.4028(4)	0.041(2)
H9	0.223871	0.536802	0.360526	0.049
C10	0.3726(5)	0.6154(10)	0.6390(4)	0.0407(19)
H10	0.359180	0.722136	0.614991	0.049
C11	0.4184(5)	0.5035(11)	0.6146(4)	0.0382(18)

H11	0.427260	0.552892	0.577312	0.046
C12	0.4901(5)	0.4144(10)	0.6550(4)	0.0372(18)
H12	0.478685	0.291220	0.653309	0.045
C13	0.5112(5)	0.4678(12)	0.7233(4)	0.0412(19)
H13A	0.542330	0.378381	0.749103	0.049
H13B	0.542095	0.571654	0.729436	0.049
C14	0.4418(5)	0.4993(11)	0.7438(4)	0.0404(19)
H14	0.409555	0.395849	0.734632	0.048
C15	0.3960(6)	0.6444(11)	0.7065(4)	0.045(2)
H15	0.349944	0.664643	0.719555	0.054
C16	0.4775(5)	0.8531(11)	0.7746(4)	0.0395(19)
C17	0.5028(6)	1.0214(12)	0.7789(5)	0.052(2)
H17	0.495074	1.087004	0.742861	0.062
C18	0.5384(6)	1.0901(11)	0.8352(5)	0.048(2)
H18	0.555050	1.203736	0.837838	0.057
C19	0.5506(5)	0.9955(12)	0.8886(4)	0.045(2)
H19	0.574151	1.044662	0.927527	0.054
C20	0.5275(6)	0.8278(12)	0.8839(4)	0.047(2)
H20	0.536566	0.762011	0.919986	0.057
C21	0.4914(5)	0.7545(11)	0.8271(4)	0.042(2)
C22	0.5588(5)	0.4384(11)	0.6301(4)	0.0389(18)
C23	0.5436(6)	0.3518(13)	0.5683(4)	0.048(2)
H23A	0.534064	0.231851	0.572649	0.071
H23B	0.587857	0.364790	0.553801	0.071
H23C	0.499276	0.402907	0.538743	0.071
C24	0.5769(6)	0.6229(12)	0.6238(5)	0.051(2)
H24A	0.533300	0.677601	0.594543	0.076
H24B	0.621091	0.631694	0.609120	0.076
H24C	0.587843	0.678241	0.663792	0.076
C25	0.6272(5)	0.3548(13)	0.6752(4)	0.045(2)
C26	0.6800(8)	0.0963(16)	0.7199(6)	0.069(3)
H26A	0.726511	0.117453	0.709328	0.104
H26B	0.668958	−0.024596	0.717114	0.104
H26C	0.686585	0.135020	0.761817	0.104
C27	0.2176(7)	0.8017(12)	0.6359(5)	0.057(3)
H27A	0.176658	0.842491	0.650889	0.085
H27B	0.216830	0.863429	0.598679	0.085
H27C	0.266430	0.819610	0.667369	0.085
C28	0.1797(7)	0.4933(15)	0.6835(5)	0.059(3)

H28A	0.223474	0.501366	0.720511	0.089
H28B	0.164827	0.375062	0.675713	0.089
H28C	0.137351	0.557642	0.689417	0.089
C29	0.1121(6)	0.5908(13)	0.5587(4)	0.048(2)
H29A	0.093010	0.476961	0.546650	0.073
H29B	0.117894	0.650523	0.523032	0.073
H29C	0.076120	0.651706	0.574641	0.073
N1	0.3516(4)	0.2014(9)	0.5490(3)	0.0375(15)
N2	0.3298(4)	0.1849(9)	0.4863(3)	0.0411(16)
N3	0.2032(5)	0.2496(9)	0.5382(3)	0.0424(17)
N4	0.1942(4)	0.2059(9)	0.4779(3)	0.0409(16)
N5	0.2761(4)	0.5409(9)	0.5033(3)	0.0385(15)
N6	0.2578(4)	0.4551(9)	0.4495(3)	0.0386(15)
N7	0.3136(5)	0.2737(9)	0.6581(3)	0.0429(17)
O1	0.3176(5)	0.1816(10)	0.7013(3)	0.063(2)
O2	0.4421(4)	0.7977(8)	0.7162(3)	0.0475(15)
O3	0.6829(4)	0.4232(10)	0.7065(3)	0.0577(18)
O4	0.6167(4)	0.1877(8)	0.6772(3)	0.0530(16)
P1	0.20457(15)	0.5782(3)	0.61860(11)	0.0434(5)
S1	0.46420(14)	0.5427(3)	0.82515(10)	0.0437(5)
W1	0.30211(2)	0.39930(4)	0.59289(2)	0.03547(17)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 1. Anisotropic displacement parameters (Å^2) for Compound 40. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	0.054(6)	0.034(5)	0.037(5)	−0.004(4)	0.010(4)	−0.005(5)
C1	0.047(5)	0.033(4)	0.048(5)	0.005(4)	0.005(4)	0.006(4)
C2	0.045(5)	0.027(4)	0.057(5)	−0.002(4)	0.011(4)	0.001(4)
C3	0.051(6)	0.033(4)	0.058(6)	−0.008(4)	0.020(5)	−0.005(4)
C4	0.039(5)	0.037(5)	0.061(5)	0.000(4)	0.016(4)	−0.011(4)
C5	0.036(5)	0.040(5)	0.082(7)	0.000(5)	0.011(5)	−0.002(4)
C6	0.047(5)	0.037(5)	0.051(5)	−0.004(4)	0.001(4)	−0.005(4)
C7	0.042(5)	0.033(4)	0.052(5)	−0.007(4)	0.012(4)	−0.002(4)
C8	0.055(6)	0.037(5)	0.049(5)	0.008(4)	0.017(4)	0.001(4)
C9	0.047(5)	0.044(5)	0.028(4)	−0.003(3)	0.004(4)	−0.006(4)
C10	0.045(5)	0.033(4)	0.038(4)	−0.001(3)	0.003(4)	−0.007(4)
C11	0.043(5)	0.039(4)	0.031(4)	0.004(3)	0.010(3)	−0.004(4)

C12	0.048(5)	0.027(4)	0.039(4)	−0.003(3)	0.016(4)	−0.001(4)
C13	0.038(5)	0.040(5)	0.041(4)	0.001(4)	0.006(4)	0.002(4)
C14	0.046(5)	0.039(4)	0.035(4)	−0.003(3)	0.010(4)	0.001(4)
C15	0.057(6)	0.032(4)	0.042(5)	−0.005(3)	0.010(4)	−0.001(4)
C16	0.043(5)	0.039(4)	0.036(4)	0.001(3)	0.010(4)	0.005(4)
C17	0.064(6)	0.035(5)	0.048(5)	0.000(4)	0.005(5)	−0.002(5)
C18	0.050(6)	0.031(4)	0.058(6)	−0.001(4)	0.010(5)	−0.004(4)
C19	0.043(5)	0.048(5)	0.039(4)	−0.007(4)	0.005(4)	−0.004(4)
C20	0.055(6)	0.043(5)	0.038(4)	0.001(4)	0.008(4)	0.001(4)
C21	0.037(5)	0.037(4)	0.048(5)	0.001(4)	0.005(4)	0.004(4)
C22	0.035(5)	0.040(4)	0.038(4)	−0.004(3)	0.005(4)	−0.001(4)
C23	0.046(5)	0.052(5)	0.042(5)	0.006(4)	0.010(4)	0.004(4)
C24	0.050(6)	0.041(5)	0.061(6)	0.006(4)	0.016(5)	−0.011(4)
C25	0.039(5)	0.051(5)	0.045(5)	0.003(4)	0.013(4)	−0.004(4)
C26	0.062(7)	0.068(7)	0.071(7)	0.017(6)	0.012(6)	0.022(6)
C27	0.067(7)	0.038(5)	0.059(6)	−0.004(4)	0.011(5)	0.008(5)
C28	0.073(7)	0.062(6)	0.041(5)	−0.002(4)	0.015(5)	0.006(6)
C29	0.044(5)	0.053(6)	0.042(5)	−0.001(4)	0.005(4)	0.007(4)
N1	0.034(4)	0.034(3)	0.043(4)	−0.001(3)	0.010(3)	−0.003(3)
N2	0.050(4)	0.031(3)	0.041(4)	−0.006(3)	0.011(3)	−0.004(3)
N3	0.048(4)	0.036(4)	0.045(4)	−0.002(3)	0.016(3)	0.000(3)
N4	0.043(4)	0.033(4)	0.042(4)	0.001(3)	0.005(3)	0.000(3)
N5	0.037(4)	0.035(4)	0.041(4)	−0.003(3)	0.008(3)	0.001(3)
N6	0.043(4)	0.032(3)	0.037(3)	−0.001(3)	0.006(3)	−0.004(3)
N7	0.053(5)	0.038(4)	0.034(3)	0.003(3)	0.009(3)	−0.007(3)
O1	0.077(5)	0.053(4)	0.051(4)	0.015(3)	0.007(4)	−0.009(4)
O2	0.060(4)	0.034(3)	0.041(3)	−0.001(2)	0.004(3)	0.003(3)
O3	0.041(4)	0.071(5)	0.050(4)	0.000(3)	−0.001(3)	−0.006(3)
O4	0.054(4)	0.042(3)	0.054(4)	0.012(3)	0.002(3)	0.003(3)
P1	0.0463(13)	0.0424(12)	0.0394(11)	−0.0020(9)	0.0097(10)	0.0039(10)
S1	0.0543(14)	0.0361(10)	0.0371(10)	0.0000(8)	0.0087(9)	−0.0009(10)
W1	0.0375(3)	0.0303(2)	0.0361(2)	−0.00066(14)	0.00769(16)	−0.00063(16)

Table 8. Bond lengths and angles for Compound 40

Atom–Atom	Length [Å]

B1–H1	1.08(9)
B1–N2	1.516(14)
B1–N4	1.556(14)
B1–N6	1.547(12)
C1–H1A	0.9500
C1–C2	1.404(14)
C1–N1	1.328(12)
C2–H2	0.9500
C2–C3	1.354(14)
C3–H3	0.9500
C3–N2	1.350(13)
C4–H4	0.9500
C4–C5	1.370(15)
C4–N3	1.330(12)
C5–H5	0.9500
C5–C6	1.364(16)
C6–H6	0.9500
C6–N4	1.316(12)
C7–H7	0.9500
C7–C8	1.394(14)
C7–N5	1.319(12)
C8–H8	0.9500
C8–C9	1.372(13)
C9–H9	0.9500
C9–N6	1.344(11)
C10–H10	1.0000
C10–C11	1.454(13)
C10–C15	1.492(12)
C10–W1	2.219(8)
C11–H11	1.0000
C11–C12	1.541(13)
C11–W1	2.219(9)
C12–H12	1.0000
C12–C13	1.552(12)
C12–C22	1.559(13)
C13–H13A	0.9900
C13–H13B	0.9900
C13–C14	1.519(13)
C14–H14	1.0000

C14–C15	1.530(13)
C14–S1	1.815(9)
C15–H15	1.0000
C15–O2	1.466(12)
C16–C17	1.411(13)
C16–C21	1.392(13)
C16–O2	1.370(10)
C17–H17	0.9500
C17–C18	1.370(14)
C18–H18	0.9500
C18–C19	1.395(14)
C19–H19	0.9500
C19–C20	1.394(15)
C20–H20	0.9500
C20–C21	1.396(13)
C21–S1	1.754(9)
C22–C23	1.522(13)
C22–C24	1.520(13)
C22–C25	1.522(13)
C23–H23A	0.9800
C23–H23B	0.9800
C23–H23C	0.9800
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
C25–O3	1.193(12)
C25–O4	1.345(12)
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800
C26–O4	1.469(13)
C27–H27A	0.9800
C27–H27B	0.9800
C27–H27C	0.9800
C27–P1	1.819(10)
C28–H28A	0.9800
C28–H28B	0.9800
C28–H28C	0.9800
C28–P1	1.818(11)

C29–H29A	0.9800
C29–H29B	0.9800
C29–H29C	0.9800
C29–P1	1.843(10)
N1–N2	1.376(10)
N1–W1	2.212(7)
N3–N4	1.384(10)
N3–W1	2.223(8)
N5–N6	1.360(10)
N5–W1	2.260(7)
N7–O1	1.216(10)
N7–W1	1.755(7)
P1–W1	2.508(2)
Atom–Atom–Atom	**Angle [°]**
N2–B1–H1	112(5)
N2–B1–N4	106.9(7)
N2–B1–N6	111.5(8)
N4–B1–H1	111(5)
N6–B1–H1	109(5)
N6–B1–N4	106.8(8)
C2–C1–H1A	124.9
N1–C1–H1A	124.9
N1–C1–C2	110.1(8)
C1–C2–H2	127.9
C3–C2–C1	104.1(8)
C3–C2–H2	127.9
C2–C3–H3	124.5
N2–C3–C2	111.0(9)
N2–C3–H3	124.5
C5–C4–H4	125.0
N3–C4–H4	125.0
N3–C4–C5	110.0(9)
C4–C5–H5	126.8
C6–C5–C4	106.3(9)
C6–C5–H5	126.8
C5–C6–H6	125.9
N4–C6–C5	108.2(9)

N4–C6–H6	125.9
C8–C7–H7	124.4
N5–C7–H7	124.4
N5–C7–C8	111.2(8)
C7–C8–H8	128.1
C9–C8–C7	103.9(8)
C9–C8–H8	128.1
C8–C9–H9	125.4
N6–C9–C8	109.1(7)
N6–C9–H9	125.4
C11–C10–H10	112.6
C11–C10–C15	118.3(8)
C11–C10–W1	70.9(5)
C15–C10–H10	112.6
C15–C10–W1	123.7(6)
W1–C10–H10	112.6
C10–C11–H11	110.9
C10–C11–C12	123.3(7)
C10–C11–W1	70.9(5)
C12–C11–H11	110.9
C12–C11–W1	124.4(6)
W1–C11–H11	110.9
C11–C12–H12	107.0
C11–C12–C13	112.6(7)
C11–C12–C22	112.0(7)
C13–C12–H12	107.0
C13–C12–C22	110.8(7)
C22–C12–H12	107.0
C12–C13–H13A	109.1
C12–C13–H13B	109.1
H13A–C13–H13B	107.8
C14–C13–C12	112.5(7)
C14–C13–H13A	109.1
C14–C13–H13B	109.1
C13–C14–H14	107.9
C13–C14–C15	109.2(8)
C13–C14–S1	113.6(6)
C15–C14–H14	107.9
C15–C14–S1	110.2(6)

S1–C14–H14	107.9
C10–C15–C14	113.6(7)
C10–C15–H15	109.4
C14–C15–H15	109.4
O2–C15–C10	104.9(7)
O2–C15–C14	110.0(8)
O2–C15–H15	109.4
C21–C16–C17	120.2(8)
O2–C16–C17	115.0(8)
O2–C16–C21	124.8(8)
C16–C17–H17	120.1
C18–C17–C16	119.9(9)
C18–C17–H17	120.1
C17–C18–H18	119.5
C17–C18–C19	120.9(9)
C19–C18–H18	119.5
C18–C19–H19	120.5
C20–C19–C18	118.9(8)
C20–C19–H19	120.5
C19–C20–H20	119.4
C19–C20–C21	121.3(9)
C21–C20–H20	119.4
C16–C21–C20	118.7(9)
C16–C21–S1	122.8(7)
C20–C21–S1	118.4(7)
C23–C22–C12	110.3(7)
C23–C22–C25	108.3(8)
C24–C22–C12	112.4(8)
C24–C22–C23	109.4(8)
C24–C22–C25	108.9(8)
C25–C22–C12	107.5(7)
C22–C23–H23A	109.5
C22–C23–H23B	109.5
C22–C23–H23C	109.5
H23A–C23–H23B	109.5
H23A–C23–H23C	109.5
H23B–C23–H23C	109.5
C22–C24–H24A	109.5
C22–C24–H24B	109.5

C22–C24–H24C	109.5
H24A–C24–H24B	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
O3–C25–C22	126.7(9)
O3–C25–O4	122.4(9)
O4–C25–C22	110.8(8)
H26A–C26–H26B	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
O4–C26–H26A	109.5
O4–C26–H26B	109.5
O4–C26–H26C	109.5
H27A–C27–H27B	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
P1–C27–H27A	109.5
P1–C27–H27B	109.5
P1–C27–H27C	109.5
H28A–C28–H28B	109.5
H28A–C28–H28C	109.5
H28B–C28–H28C	109.5
P1–C28–H28A	109.5
P1–C28–H28B	109.5
P1–C28–H28C	109.5
H29A–C29–H29B	109.5
H29A–C29–H29C	109.5
H29B–C29–H29C	109.5
P1–C29–H29A	109.5
P1–C29–H29B	109.5
P1–C29–H29C	109.5
C1–N1–N2	107.7(7)
C1–N1–W1	131.4(6)
N2–N1–W1	120.8(5)
C3–N2–B1	129.7(8)
C3–N2–N1	107.0(7)
N1–N2–B1	119.6(7)
C4–N3–N4	105.6(8)
C4–N3–W1	132.1(7)

N4–N3–W1	121.6(6)
C6–N4–B1	130.1(8)
C6–N4–N3	109.8(8)
N3–N4–B1	119.3(7)
C7–N5–N6	106.6(7)
C7–N5–W1	133.2(6)
N6–N5–W1	120.0(5)
C9–N6–B1	129.4(7)
C9–N6–N5	109.2(7)
N5–N6–B1	121.3(7)
O1–N7–W1	176.1(7)
C16–O2–C15	119.9(7)
C25–O4–C26	114.7(8)
C27–P1–C29	98.1(5)
C27–P1–W1	123.2(4)
C28–P1–C27	103.5(5)
C28–P1–C29	102.6(5)
C28–P1–W1	111.3(4)
C29–P1–W1	115.4(3)
C21–S1–C14	100.5(4)
C10–W1–N3	161.1(3)
C10–W1–N5	88.8(3)
C10–W1–P1	79.1(3)
C11–W1–C10	38.2(3)
C11–W1–N3	154.6(3)
C11–W1–N5	86.6(3)
C11–W1–P1	117.1(2)
N1–W1–C10	120.1(3)
N1–W1–C11	81.8(3)
N1–W1–N3	75.4(3)
N1–W1–N5	86.8(3)
N1–W1–P1	159.93(19)
N3–W1–N5	81.0(3)
N3–W1–P1	84.6(2)
N5–W1–P1	87.84(19)
N7–W1–C10	97.7(3)
N7–W1–C11	99.5(3)
N7–W1–N1	91.4(3)
N7–W1–N3	92.3(3)

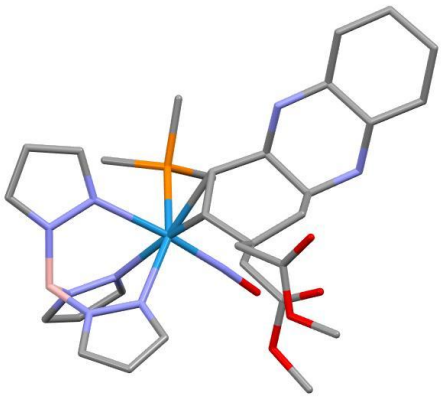
N7–W1–N5	173.3(3)
N7–W1–P1	91.7(3)

Table 9. Torsion angles for Compound 40

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C1–C2–C3–N2	−1.4(11)
C1–N1–N2–B1	157.6(8)
C1–N1–N2–C3	−2.6(10)
C2–C1–N1–N2	1.8(10)
C2–C1–N1–W1	179.0(6)
C2–C3–N2–B1	−155.0(9)
C2–C3–N2–N1	2.5(11)
C4–C5–C6–N4	−1.1(11)
C4–N3–N4–B1	−170.6(8)
C4–N3–N4–C6	0.6(10)
C5–C4–N3–N4	−1.3(10)
C5–C4–N3–W1	−171.6(7)
C5–C6–N4–B1	170.3(9)
C5–C6–N4–N3	0.3(11)
C7–C8–C9–N6	1.3(11)
C7–N5–N6–B1	−176.0(8)
C7–N5–N6–C9	−0.5(10)
C8–C7–N5–N6	1.4(11)
C8–C7–N5–W1	−173.1(7)
C8–C9–N6–B1	174.5(9)
C8–C9–N6–N5	−0.5(11)
C10–C11–C12–C13	−4.4(11)
C10–C11–C12–C22	−130.1(8)
C10–C15–O2–C16	−175.2(8)
C11–C10–C15–C14	−26.0(12)
C11–C10–C15–O2	94.2(9)
C11–C12–C13–C14	35.6(10)

C11–C12–C22–C23	−65.4(9)
C11–C12–C22–C24	56.9(10)
C11–C12–C22–C25	176.7(7)
C12–C13–C14–C15	−62.0(9)
C12–C13–C14–S1	174.6(6)
C12–C22–C25–O3	−113.9(10)
C12–C22–C25–O4	64.6(9)
C13–C12–C22–C23	167.8(7)
C13–C12–C22–C24	−69.8(10)
C13–C12–C22–C25	50.0(9)
C13–C14–C15–C10	56.9(11)
C13–C14–C15–O2	−60.4(9)
C13–C14–S1–C21	79.0(7)
C14–C15–O2–C16	−52.7(11)
C15–C10–C11–C12	−0.4(12)
C15–C10–C11–W1	118.7(8)
C15–C14–S1–C21	−43.8(8)
C16–C17–C18–C19	0.3(17)
C16–C21–S1–C14	13.5(9)
C17–C16–C21–C20	2.9(14)
C17–C16–C21–S1	−178.1(8)
C17–C16–O2–C15	−163.6(9)
C17–C18–C19–C20	1.6(16)
C18–C19–C20–C21	−1.3(15)
C19–C20–C21–C16	−0.9(15)
C19–C20–C21–S1	−180.0(8)
C20–C21–S1–C14	−167.5(8)
C21–C16–C17–C18	−2.6(16)
C21–C16–O2–C15	18.6(13)
C22–C12–C13–C14	162.0(7)
C22–C25–O4–C26	−179.8(9)
C23–C22–C25–O3	126.9(11)
C23–C22–C25–O4	−54.6(10)
C24–C22–C25–O3	8.1(14)
C24–C22–C25–O4	−173.4(8)
N1–C1–C2–C3	−0.3(11)
N2–B1–N4–C6	−110.4(10)
N2–B1–N4–N3	58.8(9)
N2–B1–N6–C9	129.8(10)

N2–B1–N6–N5	−55.7(11)
N3–C4–C5–C6	1.5(12)
N4–B1–N2–C3	107.1(10)
N4–B1–N2–N1	−48.0(10)
N4–B1–N6–C9	−113.8(10)
N4–B1–N6–N5	60.7(11)
N5–C7–C8–C9	−1.7(11)
N6–B1–N2–C3	−136.5(9)
N6–B1–N2–N1	68.4(10)
N6–B1–N4–C6	130.1(9)
N6–B1–N4–N3	−60.7(10)
O2–C16–C17–C18	179.5(10)
O2–C16–C21–C20	−179.5(9)
O2–C16–C21–S1	−0.5(14)
O3–C25–O4–C26	−1.1(14)
S1–C14–C15–C10	−177.7(7)
S1–C14–C15–O2	65.0(9)
W1–C10–C11–C12	−119.1(8)
W1–C10–C15–C14	58.9(11)
W1–C10–C15–O2	179.1(6)
W1–C11–C12–C13	−92.9(8)
W1–C11–C12–C22	141.4(6)
W1–N1–N2–B1	−20.0(10)
W1–N1–N2–C3	179.9(6)
W1–N3–N4–B1	0.9(10)
W1–N3–N4–C6	172.2(6)
W1–N5–N6–B1	−0.7(11)
W1–N5–N6–C9	174.8(6)



Structure Report for Compound 41

A colourless, needle shaped crystal of Compound 41 measuring 0.044×0.079×0.352 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 41 were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo Kα, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800Pluslow temperature device. Data collection and processing were done within the Bruker APEX5 software suite.235 All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by direct methods with SHELXT236 and refined by full-matrix least-squares methods against F2 using SHELXL-2019/1237 within OLEX2.238 All non-hydrogen atoms were refined with anisotropically. The B-H and N-H hydrogen atoms, as well as H10 and H11, were located in the electron density map and refined isotropically. All other hydrogen atoms, including the O-H hydrogen atoms, were placed in geometrically calculated positions with Uiso = 1.2Uequiv of the parent atom (1.5Uequiv for methyl). This report and the CIF file were generated using FinalCif.239

Refinement details for Compound 41

[235] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[236] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[237] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[238] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[239] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

The relative occupancy of the disordered atoms was freely refined. Constraints and restraints were used as needed on the anisotropic displacement parameters and/or bond lengths of the disordered atoms.

Table 1 Crystal data and structure refinement for Compound 41

CCDC number	
Empirical formula	C27H45BN9O4PW
Formula weight	785.35
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal size [mm3]	0.044×0.079×0.352
Crystal habit	colourless needle
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (19)
a [Å]	7.8278(2)
b [Å]	17.0738(6)
c [Å]	23.1515(8)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å3]	3094.20(17)
Z	4
ρcalc [gcm−3]	1.686
μ [mm−1]	3.834
F(000)	1584
2θ range [°]	4.25 to 56.59 (0.75 Å)
Index ranges	−9 ≤ h ≤ 10 −22 ≤ k ≤ 22 −29 ≤ l ≤ 30
Reflections collected	54423
Independent reflections	7680 [Rint = 0.0428]
Data / Restraints / Parameters	7680 / 3 / 474
Goodness-of-fit on F2	1.100

Final R indexes [I≥2σ(I)]	R1 = 0.0211 wR2 = 0.0404
Final R indexes [all data]	R1 = 0.0226 wR2 = 0.0409
Largest peak/hole [eÅ−3]	0.47/−0.77
Flack X parameter	-0.012(3)

Table 2 Atomic coordinates and Ueq [Å2] for Compound 41

Atom	x	y	z	Ueq
W1	0.38164(2)	0.56480(2)	0.26622(2)	0.01349(4)
P1	0.57715(13)	0.47654(7)	0.21082(5)	0.0176(2)
O1	0.1661(3)	0.42993(18)	0.30647(12)	0.0215(6)
N1	0.5197(4)	0.6635(2)	0.22124(15)	0.0176(8)
N2	0.4326(4)	0.7129(2)	0.18519(16)	0.0167(8)
N3	0.2308(4)	0.5627(2)	0.18472(14)	0.0156(6)
N4	0.1861(4)	0.6298(2)	0.15606(16)	0.0164(8)
N5	0.1847(4)	0.6576(2)	0.28129(15)	0.0178(8)
N6	0.1593(4)	0.71558(19)	0.24194(16)	0.0178(7)
N7	0.2586(4)	0.48526(19)	0.29270(15)	0.0143(7)
N8	0.8156(5)	0.4959(2)	0.38949(17)	0.0175(8)
H8	0.882(7)	0.505(3)	0.366(2)	0.018(12)
N9	0.5809(4)	0.39295(19)	0.43966(15)	0.0128(7)
H9	0.498(6)	0.378(3)	0.465(2)	0.012(12)
C1	0.6853(5)	0.6819(3)	0.2148(2)	0.0212(10)
H1	0.776569	0.657234	0.234781	0.025
C2	0.7052(6)	0.7418(3)	0.1749(2)	0.0200(9)
H2	0.808982	0.765202	0.162436	0.024
C3	0.5418(6)	0.7602(3)	0.1572(2)	0.0181(10)
H3	0.511790	0.799544	0.130038	0.022
C4	0.1627(5)	0.5036(3)	0.1549(2)	0.0194(10)
H4	0.173868	0.449914	0.165008	0.023
C5	0.0735(5)	0.5310(3)	0.1073(2)	0.0219(10)
H5	0.013584	0.501047	0.079293	0.026
C6	0.0908(5)	0.6112(3)	0.10956(19)	0.0200(9)
H6	0.043482	0.647332	0.082790	0.024
C7	0.0833(5)	0.6752(3)	0.32609(19)	0.0203(9)
H7	0.073087	0.644266	0.360018	0.024
C8	−0.0046(6)	0.7444(3)	0.3164(2)	0.0261(10)

H8A	−0.082302	0.769997	0.341688	0.031
C9	0.0457(5)	0.7679(2)	0.2622(2)	0.0214(9)
H9A	0.006798	0.813281	0.242412	0.026
C10	0.6013(5)	0.5555(2)	0.32738(16)	0.0159(8)
H10	0.698(5)	0.576(2)	0.3109(17)	0.009(10)
C11	0.4780(6)	0.6101(2)	0.3497(2)	0.0181(9)
H11	0.498(5)	0.664(3)	0.3433(19)	0.012(11)
C12	0.3852(7)	0.5952(2)	0.40664(17)	0.0198(8)
H12	0.271414	0.572763	0.396136	0.024
H12A	0.262047	0.582248	0.400363	0.024
C13	0.4753(6)	0.5329(2)	0.44312(19)	0.0183(9)
H13A	0.581772	0.554995	0.459434	0.022
H13B	0.400472	0.517391	0.475648	0.022
C14	0.5179(5)	0.4610(2)	0.40696(17)	0.0125(8)
H14	0.410959	0.444604	0.386668	0.015
C15	0.6496(5)	0.4823(2)	0.36062(17)	0.0144(8)
H15	0.661226	0.437540	0.333009	0.017
C16	0.8760(5)	0.4254(2)	0.41903(16)	0.0157(7)
H16	0.880772	0.381353	0.390569	0.019
C17	0.7502(5)	0.4043(2)	0.46640(18)	0.0128(8)
H17	0.744316	0.447728	0.495296	0.015
C18	0.8065(5)	0.3285(2)	0.49634(19)	0.0153(9)
H18A	0.803017	0.284735	0.468313	0.018
H18B	0.726299	0.316193	0.528132	0.018
C19	0.9879(5)	0.3364(3)	0.52068(19)	0.0173(9)
H19A	0.987572	0.374803	0.552721	0.021
H19B	1.025274	0.285294	0.536420	0.021
C20	1.1138(6)	0.3631(2)	0.47433(18)	0.0209(8)
H20A	1.226665	0.372808	0.492273	0.025
H20B	1.127726	0.320962	0.445316	0.025
C21	1.0529(5)	0.4372(3)	0.44450(18)	0.0204(8)
H21A	1.133947	0.451405	0.413387	0.024
H21B	1.049916	0.480770	0.472685	0.024
C25	0.8046(5)	0.4703(3)	0.2268(2)	0.0263(10)
H25A	0.856554	0.522223	0.222895	0.039
H25B	0.859204	0.433934	0.199703	0.039
H25C	0.820535	0.451246	0.266368	0.039
C26	0.5149(6)	0.3737(3)	0.2104(2)	0.0258(10)
H26A	0.519703	0.352889	0.249825	0.039

H26B	0.593238	0.344016	0.185660	0.039
H26C	0.398198	0.368759	0.195480	0.039
C27	0.5931(6)	0.5013(3)	0.13444(19)	0.0268(11)
H27A	0.479232	0.499598	0.116888	0.040
H27B	0.667797	0.463470	0.115026	0.040
H27C	0.640840	0.554035	0.130331	0.040
B1	0.2373(6)	0.7100(3)	0.1807(2)	0.0200(10)
H1A	0.183(5)	0.758(3)	0.155(2)	0.017(12)
O2	0.0674(8)	0.6547(4)	0.4709(3)	0.0314(16)
O3	0.2658(11)	0.6492(5)	0.5407(3)	0.052(2)
C22	0.3479(16)	0.6700(12)	0.4423(11)	0.022(3)
H22A	0.457261	0.690981	0.457228	0.027
H22B	0.297961	0.710065	0.416431	0.027
C23	0.2310(18)	0.6578(8)	0.4914(6)	0.022(3)
C24	−0.0662(13)	0.6370(5)	0.5116(5)	0.044(3)
H24A	−0.168142	0.667785	0.502253	0.066
H24B	−0.027623	0.649963	0.550710	0.066
H24C	−0.093781	0.581037	0.509552	0.066
O2A	0.184(2)	0.6644(12)	0.5050(8)	0.042(5)
O3A	0.4513(13)	0.6686(6)	0.5422(5)	0.042(3)
C22A	0.408(2)	0.6761(18)	0.4398(15)	0.024(5)
H22C	0.529116	0.692424	0.437771	0.029
H22D	0.338588	0.716804	0.420289	0.029
C23A	0.355(2)	0.6710(7)	0.5012(5)	0.033(3)
C24A	0.130(2)	0.6540(10)	0.5654(6)	0.057(5)
H24D	0.004829	0.649463	0.567021	0.085
H24E	0.166151	0.699358	0.588212	0.085
H24F	0.181557	0.606391	0.581114	0.085
O5	0.8325(12)	0.6453(6)	0.4571(5)	0.046(3)
H5A	0.731132	0.645198	0.472488	0.069
H5B	0.834778	0.603477	0.435652	0.069
O4	0.6614(19)	0.6391(6)	0.5648(7)	0.117(5)
H4A	0.557098	0.651160	0.555317	0.176
H4B	0.668680	0.589001	0.558227	0.176

Ueq is defined as 1/3 of the trace of the orthogonalized Uij tensor.

Table 3 Anisotropic displacement parameters (Å2) for Compound 41. The anisotropic displacement factor exponent takes the form: −2π2[h2(a*)2U11 + k2(b*)2U22 + … + 2hka*b*U12]

Atom	U11	U22	U33	U23	U13	U12

W1	0.01285(6)	0.01435(6)	0.01328(7)	0.00434(7)	−0.00201(7)	−0.00134(6)
P1	0.0152(5)	0.0231(6)	0.0146(5)	0.0070(4)	0.0015(4)	0.0029(4)
O1	0.0201(14)	0.0201(14)	0.0243(16)	0.0029(14)	−0.0012(11)	−0.0079(13)
N1	0.0192(17)	0.0178(17)	0.016(2)	0.0067(14)	−0.0071(14)	−0.0012(14)
N2	0.0196(18)	0.0152(17)	0.0154(19)	0.0045(14)	−0.0029(14)	−0.0011(13)
N3	0.0151(14)	0.0163(15)	0.0155(17)	0.0057(16)	−0.0027(12)	−0.0012(15)
N4	0.0159(17)	0.0190(18)	0.0142(19)	0.0046(15)	−0.0057(14)	−0.0003(13)
N5	0.0198(17)	0.0173(17)	0.016(2)	0.0048(14)	−0.0044(13)	0.0013(13)
N6	0.0185(16)	0.0181(16)	0.0169(19)	0.0032(14)	−0.0041(14)	0.0005(12)
N7	0.0143(16)	0.0176(17)	0.0110(17)	−0.0003(14)	−0.0005(14)	0.0009(13)
N8	0.0130(16)	0.0208(19)	0.019(2)	0.0088(16)	−0.0019(15)	−0.0045(14)
N9	0.0100(17)	0.0148(16)	0.0135(18)	0.0035(13)	−0.0001(13)	−0.0028(12)
C1	0.018(2)	0.023(2)	0.022(3)	0.0090(18)	−0.0059(17)	−0.0054(17)
C2	0.025(2)	0.019(2)	0.015(2)	0.0047(18)	−0.0003(18)	−0.0096(17)
C3	0.027(2)	0.015(2)	0.012(2)	0.0052(17)	−0.0024(18)	−0.0022(17)
C4	0.017(2)	0.020(2)	0.022(2)	−0.0016(18)	0.0029(17)	−0.0026(16)
C5	0.017(2)	0.033(2)	0.015(2)	−0.0055(19)	−0.0023(16)	−0.0045(17)
C6	0.016(2)	0.030(2)	0.014(2)	0.0029(17)	−0.0023(17)	0.0014(17)
C7	0.020(2)	0.025(2)	0.016(2)	0.0004(17)	−0.0005(17)	0.0005(16)
C8	0.023(2)	0.031(3)	0.024(3)	−0.007(2)	−0.002(2)	0.0074(19)
C9	0.0205(18)	0.0152(18)	0.028(3)	−0.004(2)	−0.008(2)	0.0020(15)

C10	0.0143(18)	0.021(2)	0.0129(18)	0.0056(16)	−0.0059(16)	−0.0043(18)
C11	0.022(2)	0.012(2)	0.020(2)	0.0044(17)	−0.0073(18)	−0.0038(16)
C12	0.032(2)	0.0129(17)	0.015(2)	0.0007(14)	−0.002(2)	0.005(2)
C13	0.024(2)	0.0154(19)	0.015(2)	−0.0004(17)	−0.0003(17)	0.0024(16)
C14	0.0118(18)	0.0125(18)	0.013(2)	0.0017(14)	−0.0012(15)	−0.0016(14)
C15	0.013(2)	0.0188(19)	0.0117(19)	0.0025(15)	−0.0022(15)	−0.0012(15)
C16	0.0153(16)	0.0175(18)	0.0143(18)	0.0021(15)	−0.0005(17)	0.0003(19)
C17	0.0163(19)	0.0131(18)	0.009(2)	0.0009(15)	−0.0022(16)	0.0000(15)
C18	0.019(2)	0.013(2)	0.014(2)	0.0032(16)	0.0032(16)	0.0015(16)
C19	0.015(2)	0.023(2)	0.014(2)	0.0028(18)	0.0012(17)	0.0056(16)
C20	0.0156(18)	0.030(2)	0.018(2)	0.0050(17)	0.001(2)	0.003(2)
C21	0.0128(17)	0.030(2)	0.019(2)	0.008(2)	0.0001(15)	−0.0036(19)
C25	0.0178(19)	0.041(3)	0.020(3)	0.011(2)	0.0039(19)	0.0054(18)
C26	0.027(2)	0.023(2)	0.028(3)	0.002(2)	0.003(2)	0.0050(19)
C27	0.022(2)	0.043(3)	0.016(2)	0.006(2)	0.0031(19)	0.007(2)
B1	0.022(2)	0.019(2)	0.019(3)	0.004(2)	−0.006(2)	0.0002(19)
O2	0.026(4)	0.039(4)	0.029(4)	0.003(3)	0.007(3)	−0.007(3)
O3	0.061(5)	0.082(6)	0.015(4)	−0.004(4)	0.008(4)	0.024(4)
C22	0.019(6)	0.016(5)	0.031(7)	−0.005(4)	−0.004(8)	0.006(6)
C23	0.022(8)	0.009(4)	0.035(7)	−0.006(4)	−0.008(6)	0.006(5)
C24	0.054(6)	0.025(5)	0.054(7)	−0.005(4)	0.031(5)	−0.013(4)
O2A	0.030(8)	0.040(8)	0.055(12)	0.014(7)	0.019(7)	0.010(6)
O3A	0.046(6)	0.045(6)	0.035(6)	−0.006(5)	−0.014(5)	0.011(5)
C22A	0.030(11)	0.020(8)	0.022(8)	0.002(6)	0.000(12)	0.007(11)
C23A	0.051(10)	0.015(5)	0.031(7)	−0.005(5)	−0.007(7)	0.009(6)
C24A	0.056(10)	0.087(12)	0.028(7)	0.025(7)	−0.002(8)	0.038(10)
O5	0.035(6)	0.047(6)	0.057(8)	−0.010(5)	0.001(5)	−0.011(4)
O4	0.133(12)	0.079(8)	0.141(11)	0.011(8)	−0.051(9)	0.003(7)

Table 4 Bond lengths and angles for Compound 41

tom–Atom	Length [Å]
W1–N7	1.774(3)
W1–C11	2.215(5)
W1–N3	2.226(3)
W1–C10	2.233(4)
W1–N5	2.238(3)
W1–N1	2.257(3)
W1–P1	2.5015(11)
P1–C25	1.822(4)
P1–C27	1.822(4)
P1–C26	1.823(5)
O1–N7	1.232(4)
N1–C1	1.342(5)
N1–N2	1.368(5)
N2–C3	1.343(5)
N2–B1	1.533(6)
N3–C4	1.333(5)
N3–N4	1.370(5)
N4–C6	1.348(5)
N4–B1	1.536(6)
N5–C7	1.340(5)
N5–N6	1.360(5)
N6–C9	1.345(5)
N6–B1	1.547(6)
N8–C16	1.463(5)
N8–C15	1.480(5)
N8–H8	0.77(5)
N9–C14	1.472(5)
N9–C17	1.475(5)
N9–H9	0.91(5)
C1–C2	1.387(6)
C1–H1	0.9500
C2–C3	1.378(6)
C2–H2	0.9500
C3–H3	0.9500
C4–C5	1.387(6)
C4–H4	0.9500
C5–C6	1.376(6)
C5–H5	0.9500
C6–H6	0.9500
C7–C8	1.386(6)

C7–H7	0.9500
C8–C9	1.376(7)
C8–H8A	0.9500
C9–H9A	0.9500
C10–C11	1.438(6)
C10–C15	1.516(5)
C10–H10	0.92(4)
C11–C12	1.526(6)
C11–H11	0.94(4)
C12–C13	1.531(6)
C12–C22	1.55(2)
C12–C22A	1.59(3)
C12–H12	1.0000
C12–H12A	1.0000
C13–C14	1.522(5)
C13–H13A	0.9900
C13–H13B	0.9900
C14–C15	1.531(5)
C14–H14	1.0000
C15–H15	1.0000
C16–C17	1.518(5)
C16–C21	1.518(5)
C16–H16	1.0000
C17–C18	1.533(6)
C17–H17	1.0000
C18–C19	1.534(6)
C18–H18A	0.9900
C18–H18B	0.9900
C19–C20	1.526(6)
C19–H19A	0.9900
C19–H19B	0.9900
C20–C21	1.518(6)
C20–H20A	0.9900
C20–H20B	0.9900
C21–H21A	0.9900
C21–H21B	0.9900
C25–H25A	0.9800
C25–H25B	0.9800
C25–H25C	0.9800
C26–H26A	0.9800
C26–H26B	0.9800
C26–H26C	0.9800

C27–H27A	0.9800
C27–H27B	0.9800
C27–H27C	0.9800
B1–H1A	1.10(5)
O2–C23	1.367(16)
O2–C24	1.441(10)
O3–C23	1.183(17)
C22–C23	1.47(2)
C22–H22A	0.9900
C22–H22B	0.9900
C24–H24A	0.9800
C24–H24B	0.9800
C24–H24C	0.9800
O2A–C23A	1.35(2)
O2A–C24A	1.470(18)
O3A–C23A	1.211(15)
C22A–C23A	1.48(4)
C22A–H22C	0.9900
C22A–H22D	0.9900
C24A–H24D	0.9800
C24A–H24E	0.9800
C24A–H24F	0.9800
O5–H5A	0.8699
O5–H5B	0.8702
O4–H4A	0.8702
O4–H4B	0.8713
Atom–Atom–Atom	Angle [°]
N7–W1–C11	98.66(16)
N7–W1–N3	89.59(14)
C11–W1–N3	157.83(15)
N7–W1–C10	98.31(15)
C11–W1–C10	37.73(15)
N3–W1–C10	160.87(13)
N7–W1–N5	96.56(14)
C11–W1–N5	81.43(15)
N3–W1–N5	77.19(13)
C10–W1–N5	118.79(14)
N7–W1–N1	172.34(14)
C11–W1–N1	88.78(14)
N3–W1–N1	82.82(12)
C10–W1–N1	88.67(14)

N5–W1–N1	82.71(13)
N7–W1–P1	92.77(11)
C11–W1–P1	116.73(12)
N3–W1–P1	83.13(9)
C10–W1–P1	79.13(11)
N5–W1–P1	158.10(9)
N1–W1–P1	85.43(10)
C25–P1–C27	98.3(2)
C25–P1–C26	101.9(2)
C27–P1–C26	103.7(2)
C25–P1–W1	121.96(17)
C27–P1–W1	113.57(16)
C26–P1–W1	114.81(16)
C1–N1–N2	105.6(3)
C1–N1–W1	133.6(3)
N2–N1–W1	120.2(2)
C3–N2–N1	110.3(3)
C3–N2–B1	128.4(4)
N1–N2–B1	121.3(3)
C4–N3–N4	106.3(3)
C4–N3–W1	131.5(3)
N4–N3–W1	122.2(3)
C6–N4–N3	109.3(3)
C6–N4–B1	130.6(4)
N3–N4–B1	120.0(3)
C7–N5–N6	105.6(3)
C7–N5–W1	133.4(3)
N6–N5–W1	120.8(3)
C9–N6–N5	110.3(4)
C9–N6–B1	128.4(4)
N5–N6–B1	120.8(3)
O1–N7–W1	174.4(3)
C16–N8–C15	111.5(3)
C16–N8–H8	106(4)
C15–N8–H8	107(4)
C14–N9–C17	114.4(3)
C14–N9–H9	108(3)
C17–N9–H9	114(3)
N1–C1–C2	110.8(4)
N1–C1–H1	124.6
C2–C1–H1	124.6
C3–C2–C1	105.2(4)

C3–C2–H2	127.4
C1–C2–H2	127.4
N2–C3–C2	108.1(4)
N2–C3–H3	126.0
C2–C3–H3	126.0
N3–C4–C5	110.9(4)
N3–C4–H4	124.5
C5–C4–H4	124.5
C6–C5–C4	104.8(4)
C6–C5–H5	127.6
C4–C5–H5	127.6
N4–C6–C5	108.6(4)
N4–C6–H6	125.7
C5–C6–H6	125.7
N5–C7–C8	111.1(4)
N5–C7–H7	124.4
C8–C7–H7	124.4
C9–C8–C7	104.7(4)
C9–C8–H8A	127.7
C7–C8–H8A	127.7
N6–C9–C8	108.3(4)
N6–C9–H9A	125.9
C8–C9–H9A	125.9
C11–C10–C15	121.3(4)
C11–C10–W1	70.4(2)
C15–C10–W1	124.9(3)
C11–C10–H10	118(3)
C15–C10–H10	108(3)
W1–C10–H10	110(2)
C10–C11–C12	121.5(4)
C10–C11–W1	71.8(2)
C12–C11–W1	122.3(3)
C10–C11–H11	118(3)
C12–C11–H11	112(3)
W1–C11–H11	105(3)
C11–C12–C13	111.9(4)
C11–C12–C22	114.4(8)
C13–C12–C22	111.5(9)
C11–C12–C22A	102.7(11)
C13–C12–C22A	106.6(11)
C11–C12–H12	106.1
C13–C12–H12	106.1

C22–C12–H12	106.1
C11–C12–H12A	111.7
C13–C12–H12A	111.7
C22A–C12–H12A	111.7
C14–C13–C12	111.0(3)
C14–C13–H13A	109.4
C12–C13–H13A	109.4
C14–C13–H13B	109.4
C12–C13–H13B	109.4
H13A–C13–H13B	108.0
N9–C14–C13	115.3(3)
N9–C14–C15	108.8(3)
C13–C14–C15	110.0(3)
N9–C14–H14	107.5
C13–C14–H14	107.5
C15–C14–H14	107.5
N8–C15–C10	108.6(3)
N8–C15–C14	108.2(3)
C10–C15–C14	112.5(3)
N8–C15–H15	109.2
C10–C15–H15	109.2
C14–C15–H15	109.2
N8–C16–C17	108.9(3)
N8–C16–C21	111.5(3)
C17–C16–C21	110.1(3)
N8–C16–H16	108.8
C17–C16–H16	108.8
C21–C16–H16	108.8
N9–C17–C16	108.1(3)
N9–C17–C18	109.7(3)
C16–C17–C18	109.9(3)
N9–C17–H17	109.7
C16–C17–H17	109.7
C18–C17–H17	109.7
C17–C18–C19	111.0(3)
C17–C18–H18A	109.4
C19–C18–H18A	109.4
C17–C18–H18B	109.4
C19–C18–H18B	109.4
H18A–C18–H18B	108.0
C20–C19–C18	111.5(3)
C20–C19–H19A	109.3

C18–C19–H19A	109.3
C20–C19–H19B	109.3
C18–C19–H19B	109.3
H19A–C19–H19B	108.0
C21–C20–C19	111.4(4)
C21–C20–H20A	109.3
C19–C20–H20A	109.3
C21–C20–H20B	109.3
C19–C20–H20B	109.3
H20A–C20–H20B	108.0
C20–C21–C16	110.6(4)
C20–C21–H21A	109.5
C16–C21–H21A	109.5
C20–C21–H21B	109.5
C16–C21–H21B	109.5
H21A–C21–H21B	108.1
P1–C25–H25A	109.5
P1–C25–H25B	109.5
H25A–C25–H25B	109.5
P1–C25–H25C	109.5
H25A–C25–H25C	109.5
H25B–C25–H25C	109.5
P1–C26–H26A	109.5
P1–C26–H26B	109.5
H26A–C26–H26B	109.5
P1–C26–H26C	109.5
H26A–C26–H26C	109.5
H26B–C26–H26C	109.5
P1–C27–H27A	109.5
P1–C27–H27B	109.5
H27A–C27–H27B	109.5
P1–C27–H27C	109.5
H27A–C27–H27C	109.5
H27B–C27–H27C	109.5
N2–B1–N4	108.3(4)
N2–B1–N6	109.2(4)
N4–B1–N6	107.0(4)
N2–B1–H1A	114(2)
N4–B1–H1A	111(2)
N6–B1–H1A	108(2)
C23–O2–C24	117.4(9)
C23–C22–C12	114.3(13)

C23–C22–H22A	108.7
C12–C22–H22A	108.7
C23–C22–H22B	108.7
C12–C22–H22B	108.7
H22A–C22–H22B	107.6
O3–C23–O2	123.2(13)
O3–C23–C22	128.2(14)
O2–C23–C22	108.6(12)
O2–C24–H24A	109.5
O2–C24–H24B	109.5
H24A–C24–H24B	109.5
O2–C24–H24C	109.5
H24A–C24–H24C	109.5
H24B–C24–H24C	109.5
C23A–O2A–C24A	111.0(18)
C23A–C22A–C12	112.3(18)
C23A–C22A–H22C	109.1
C12–C22A–H22C	109.1
C23A–C22A–H22D	109.1
C12–C22A–H22D	109.1
H22C–C22A–H22D	107.9
O3A–C23A–O2A	124.3(16)
O3A–C23A–C22A	125.6(16)
O2A–C23A–C22A	110.0(15)
O2A–C24A–H24D	109.5
O2A–C24A–H24E	109.5
H24D–C24A–H24E	109.5
O2A–C24A–H24F	109.5
H24D–C24A–H24F	109.5
H24E–C24A–H24F	109.5
H5A–O5–H5B	104.5
H4A–O4–H4B	104.4

Table 5 Torsion angles for Compound 41

Atom–Atom–Atom–Atom	Torsion Angle [°]
C1–N1–N2–C3	0.1(5)
W1–N1–N2–C3	−171.8(3)
C1–N1–N2–B1	−179.7(4)
W1–N1–N2–B1	8.5(5)

C4–N3–N4–C6	0.4(4)
W1–N3–N4–C6	−177.9(3)
C4–N3–N4–B1	177.1(4)
W1–N3–N4–B1	−1.2(5)
C7–N5–N6–C9	0.4(4)
W1–N5–N6–C9	−174.9(3)
C7–N5–N6–B1	−172.0(4)
W1–N5–N6–B1	12.7(5)
N2–N1–C1–C2	−0.4(5)
W1–N1–C1–C2	169.9(3)
N1–C1–C2–C3	0.5(6)
N1–N2–C3–C2	0.2(5)
B1–N2–C3–C2	180.0(4)
C1–C2–C3–N2	−0.4(6)
N4–N3–C4–C5	−0.2(4)
W1–N3–C4–C5	177.8(3)
N3–C4–C5–C6	0.0(5)
N3–N4–C6–C5	−0.4(5)
B1–N4–C6–C5	−176.6(4)
C4–C5–C6–N4	0.3(5)
N6–N5–C7–C8	−1.1(5)
W1–N5–C7–C8	173.4(3)
N5–C7–C8–C9	1.3(5)
N5–N6–C9–C8	0.5(5)
B1–N6–C9–C8	172.1(4)
C7–C8–C9–N6	−1.0(5)
C15–C10–C11–C12	−2.4(6)
W1–C10–C11–C12	117.2(4)
C15–C10–C11–W1	−119.7(4)
C10–C11–C12–C13	17.1(6)
W1–C11–C12–C13	104.5(4)
C10–C11–C12–C22	145.1(8)
W1–C11–C12–C22	−127.5(8)
C10–C11–C12–C22A	131.1(10)
W1–C11–C12–C22A	−141.5(9)
C11–C12–C13–C14	−48.1(5)
C22–C12–C13–C14	−177.7(6)
C22A–C12–C13–C14	−159.6(9)
C17–N9–C14–C13	−67.4(4)
C17–N9–C14–C15	56.6(4)
C12–C13–C14–N9	−171.1(3)
C12–C13–C14–C15	65.5(4)

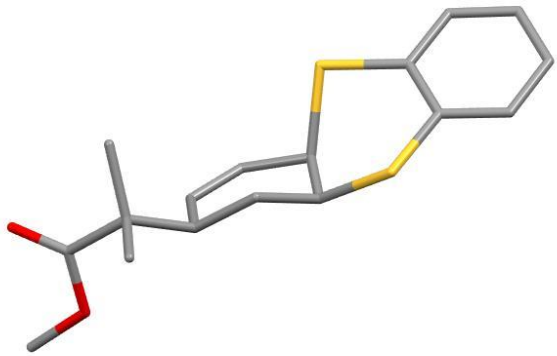
C16–N8–C15–C10	−175.9(3)
C16–N8–C15–C14	61.7(4)
C11–C10–C15–N8	−101.4(4)
W1–C10–C15–N8	171.7(3)
C11–C10–C15–C14	18.3(5)
W1–C10–C15–C14	−68.6(4)
N9–C14–C15–N8	−56.0(4)
C13–C14–C15–N8	71.1(4)
N9–C14–C15–C10	−176.0(3)
C13–C14–C15–C10	−48.8(4)
C15–N8–C16–C17	−63.0(4)
C15–N8–C16–C21	175.3(3)
C14–N9–C17–C16	−57.1(4)
C14–N9–C17–C18	−177.0(3)
N8–C16–C17–N9	57.8(4)
C21–C16–C17–N9	−179.7(3)
N8–C16–C17–C18	177.6(3)
C21–C16–C17–C18	−59.9(4)
N9–C17–C18–C19	175.7(3)
C16–C17–C18–C19	57.0(4)
C17–C18–C19–C20	−53.7(5)
C18–C19–C20–C21	53.3(5)
C19–C20–C21–C16	−56.2(5)
N8–C16–C21–C20	−179.4(3)
C17–C16–C21–C20	59.7(4)
C3–N2–B1–N4	116.3(5)
N1–N2–B1–N4	−64.0(5)
C3–N2–B1–N6	−127.6(5)
N1–N2–B1–N6	52.1(5)
C6–N4–B1–N2	−124.6(5)
N3–N4–B1–N2	59.5(5)
C6–N4–B1–N6	117.8(5)
N3–N4–B1–N6	−58.1(5)
C9–N6–B1–N2	123.7(4)
N5–N6–B1–N2	−65.4(5)
C9–N6–B1–N4	−119.4(4)
N5–N6–B1–N4	51.5(5)
C11–C12–C22–C23	169.0(11)
C13–C12–C22–C23	−62.7(14)
C24–O2–C23–O3	−2.7(17)
C24–O2–C23–C22	175.3(11)
C12–C22–C23–O3	99.3(18)

C12–C22–C23–O2	−78.6(15)
C11–C12–C22A–C23A	−169.3(13)
C13–C12–C22A–C23A	−51.5(15)
C24A–O2A–C23A–O3A	0(2)
C24A–O2A–C23A–C22A	176.3(18)
C12–C22A–C23A–O3A	105.2(16)
C12–C22A–C23A–O2A	−71.1(19)

Table 6 Hydrogen bonds for Compound 41

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O4^a–H4A^a···O3^a	0.87	2.31	3.152(16)	164.1
O5^b–H5B^b···H8	0.87	2.37	3.22(5)	168.2
O5^b–H5A^b···O3A^b	0.87	2.75	3.598(15)	165.2

Structure Report for Compound 63



A colourless, plate shaped crystal of Compound 63

measuring 0.157×0.201×0.371 mm was coated with Paratone oil and mounted on a MiTeGen micromount. Data for Compound 63

were measured on a Bruker D8 VENTURE dual wavelength Mo/Cu Kappa four-circle diffractometer equipped with a PHOTON III detector and an Incoatec IμS 3.0 microfocus sealed X-ray tube (Mo K_α, λ=0.71073 Å) using a HELIOS double bounce multilayer mirror as monochromator. The crystal temperature was controlled with an Oxford Cryostream 800low temperature device. Data collection and processing were done within the Bruker APEX5 software suite.[240] All data were integrated with the Bruker SAINT 8.40B software using a narrow-frame algorithm. Data were corrected for absorption effects using a Multi-Scan method (SADABS).

The structure was solved by dual methods with SHELXT[241] and refined by full-matrix least-squares methods against F^2 using XL[242] within OLEX2.[243] All non-hydrogen atoms were refined with anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl). This report and the CIF file were generated using FinalCif.[244]

Table 1 Crystal data and structure refinement for Compound 63

CCDC number	
Empirical formula	$C_{17}H_{20}O_2S_2$
Formula weight	320.45
Temperature [K]	100.00
Wavelength [Å]	0.71073
Crystal size [mm^3]	0.157×0.201×0.371
Crystal habit	colourless plate
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
a [Å]	13.5314(7)
b [Å]	10.2355(4)
c [Å]	12.7533(5)
α [°]	90

[240] *APEX5*, *Saint*, *SADABS*; Bruker AXS Inc. 2019.
[241] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst. Sect. A Found. Adv.* **2015**, *71*, 3-8.
[242] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst. Sect. C Struct. Chem.* **2015**, *71*, 3-8.
[243] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a completed structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
[244] Kratzert, D. FinalCif, https://dkratzert.de/finalcif.html.

β [°]	117.304(2)
γ [°]	90
Volume [Å^3]	1569.54(12)
Z	4
ρ_{calc} [gcm^{-3}]	1.356
μ [mm^{-1}]	0.341
F(000)	680
2θ range [°]	5.23 to 56.57 (0.75 Å)
Index ranges	−18 ≤ h ≤ 18 −13 ≤ k ≤ 11 −16 ≤ l ≤ 17
Reflections collected	23870
Independent reflections	3885 [R_{int} = 0.0757]
Data / Restraints / Parameters	3885 / 0 / 193
Goodness-of-fit on F^2	1.068
Final R indexes [I≥2σ(I)]	R_1 = 0.0416 wR_2 = 0.0911
Final R indexes [all data]	R_1 = 0.0580 wR_2 = 0.1013
Largest peak/hole [eÅ^{-3}]	0.50/−0.29

Table 2 Atomic coordinates and Ueq [Å2] for Compound 63

Atom	***x***	***y***	***z***	U_{eq}
S1	0.43691(4)	0.66239(4)	0.75764(4)	0.01225(12)
S2	0.37115(4)	0.87432(4)	0.54635(4)	0.01197(12)
O1	0.94854(12)	0.58124(14)	0.76938(12)	0.0190(3)
O2	0.82757(12)	0.56970(14)	0.57731(12)	0.0170(3)
C1	0.54487(16)	0.52580(17)	0.66105(16)	0.0124(4)
H1	0.537439	0.441461	0.687737	0.015
C2	0.63962(16)	0.55464(18)	0.65917(16)	0.0125(4)
H2	0.696068	0.489726	0.685001	0.015
C3	0.66351(15)	0.68424(17)	0.61854(16)	0.0108(4)
H3	0.649527	0.672976	0.534970	0.013

C4	0.58211(16)	0.78859(18)	0.61895(17)	0.0129(4)
H4A	0.602425	0.813845	0.701285	0.016
H4B	0.587264	0.867349	0.576659	0.016
C5	0.46325(15)	0.73675(17)	0.55953(16)	0.0111(4)
H5	0.446276	0.708484	0.477933	0.013
C6	0.44837(16)	0.61895(17)	0.62335(16)	0.0106(4)
H6	0.379023	0.572038	0.568252	0.013
C7	0.78744(16)	0.72479(18)	0.69214(16)	0.0120(4)
C8	0.81778(18)	0.7499(2)	0.82184(17)	0.0185(4)
H8A	0.799594	0.672523	0.854901	0.028
H8B	0.775568	0.825040	0.827405	0.028
H8C	0.897581	0.768104	0.866163	0.028
C9	0.81272(18)	0.84728(18)	0.63833(19)	0.0182(4)
H9A	0.892426	0.866802	0.680695	0.027
H9B	0.770364	0.921581	0.645160	0.027
H9C	0.791461	0.831329	0.554910	0.027
C10	0.86390(16)	0.61727(18)	0.68746(17)	0.0124(4)
C11	0.89837(18)	0.4718(2)	0.56508(19)	0.0214(4)
H11A	0.868023	0.446091	0.482039	0.032
H11B	0.901860	0.395239	0.612800	0.032
H11C	0.973293	0.507602	0.592085	0.032
C12	0.30327(16)	0.73299(17)	0.68831(16)	0.0115(4)
C13	0.22573(17)	0.70534(18)	0.72913(17)	0.0147(4)
H13	0.244698	0.646804	0.793330	0.018
C14	0.12161(17)	0.76259(19)	0.67671(18)	0.0166(4)
H14	0.070690	0.746637	0.707428	0.020
C15	0.09114(17)	0.84371(19)	0.57886(18)	0.0166(4)
H15	0.019024	0.881540	0.541825	0.020
C16	0.16644(16)	0.86887(18)	0.53593(17)	0.0142(4)
H16	0.144796	0.922160	0.467922	0.017
C17	0.27374(16)	0.81699(17)	0.59124(16)	0.0108(4)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters (Å^2) for Compound 63

. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0136(2)	0.0129(2)	0.0104(2)	0.00238(17)	0.00564(18)	0.00301(17)

S2	0.0125(2)	0.0103(2)	0.0142(2)	0.00347(17)	0.00707(18)	0.00240(16)
O1	0.0144(7)	0.0211(7)	0.0184(7)	0.0015(6)	0.0049(6)	0.0047(6)
O2	0.0172(7)	0.0198(7)	0.0150(7)	−0.0019(6)	0.0082(6)	0.0056(6)
C1	0.0160(10)	0.0083(8)	0.0134(9)	−0.0002(7)	0.0071(8)	0.0009(7)
C2	0.0161(10)	0.0091(8)	0.0126(9)	−0.0003(7)	0.0068(8)	0.0033(7)
C3	0.0113(9)	0.0105(8)	0.0108(8)	0.0003(7)	0.0052(7)	0.0005(7)
C4	0.0133(9)	0.0100(8)	0.0162(9)	0.0004(7)	0.0073(8)	0.0012(7)
C5	0.0124(9)	0.0100(8)	0.0121(9)	0.0015(7)	0.0067(7)	0.0028(7)
C6	0.0124(9)	0.0093(8)	0.0106(8)	−0.0004(7)	0.0056(7)	0.0002(7)
C7	0.0115(9)	0.0113(8)	0.0127(9)	−0.0008(7)	0.0051(7)	0.0005(7)
C8	0.0171(10)	0.0227(10)	0.0151(9)	−0.0041(8)	0.0069(8)	0.0016(8)
C9	0.0172(10)	0.0116(8)	0.0264(11)	0.0014(8)	0.0105(9)	−0.0011(7)
C10	0.0135(9)	0.0107(8)	0.0149(9)	0.0013(7)	0.0082(8)	−0.0027(7)
C11	0.0201(11)	0.0204(10)	0.0262(11)	−0.0049(9)	0.0127(9)	0.0032(8)
C12	0.0123(9)	0.0097(8)	0.0118(9)	−0.0014(7)	0.0050(7)	0.0005(7)
C13	0.0195(10)	0.0114(8)	0.0152(9)	0.0002(7)	0.0096(8)	−0.0005(7)
C14	0.0159(10)	0.0158(9)	0.0217(10)	−0.0033(8)	0.0118(8)	−0.0027(7)
C15	0.0120(9)	0.0133(9)	0.0226(10)	−0.0031(8)	0.0062(8)	0.0011(7)
C16	0.0137(10)	0.0118(8)	0.0147(9)	−0.0002(7)	0.0045(8)	0.0008(7)
C17	0.0119(9)	0.0102(8)	0.0110(8)	−0.0032(7)	0.0058(7)	−0.0010(7)

Table 4 Bond lengths and angles for Compound 63

Atom–Atom	**Length [Å]**
S1–C6	1.8435(18)
S1–C12	1.7628(19)
S2–C5	1.8363(18)
S2–C17	1.7613(19)
O1–C10	1.201(2)
O2–C10	1.349(2)
O2–C11	1.443(2)
C1–H1	0.9500
C1–C2	1.327(3)

C1–C6	1.506(2)
C2–H2	0.9500
C2–C3	1.512(2)
C3–H3	1.0000
C3–C4	1.536(2)
C3–C7	1.556(3)
C4–H4A	0.9900
C4–H4B	0.9900
C4–C5	1.525(3)
C5–H5	1.0000
C5–C6	1.519(2)
C6–H6	1.0000
C7–C8	1.532(3)
C7–C9	1.541(3)
C7–C10	1.530(3)
C8–H8A	0.9800
C8–H8B	0.9800
C8–H8C	0.9800
C9–H9A	0.9800
C9–H9B	0.9800
C9–H9C	0.9800
C11–H11A	0.9800
C11–H11B	0.9800
C11–H11C	0.9800
C12–C13	1.397(3)
C12–C17	1.406(3)
C13–H13	0.9500
C13–C14	1.382(3)
C14–H14	0.9500
C14–C15	1.395(3)
C15–H15	0.9500
C15–C16	1.384(3)
C16–H16	0.9500
C16–C17	1.396(3)
Atom–Atom–Atom	**Angle [°]**
C12–S1–C6	97.87(9)
C17–S2–C5	107.01(8)

C10–O2–C11	114.86(15)
C2–C1–H1	118.1
C2–C1–C6	123.84(17)
C6–C1–H1	118.1
C1–C2–H2	117.9
C1–C2–C3	124.18(17)
C3–C2–H2	117.9
C2–C3–H3	107.4
C2–C3–C4	110.03(15)
C2–C3–C7	111.59(15)
C4–C3–H3	107.4
C4–C3–C7	112.86(15)
C7–C3–H3	107.4
C3–C4–H4A	109.5
C3–C4–H4B	109.5
H4A–C4–H4B	108.1
C5–C4–C3	110.54(15)
C5–C4–H4A	109.5
C5–C4–H4B	109.5
S2–C5–H5	107.7
C4–C5–S2	107.19(12)
C4–C5–H5	107.7
C6–C5–S2	113.99(13)
C6–C5–C4	112.26(15)
C6–C5–H5	107.7
S1–C6–H6	108.5
C1–C6–S1	106.62(12)
C1–C6–C5	111.40(15)
C1–C6–H6	108.5
C5–C6–S1	113.25(12)
C5–C6–H6	108.5
C8–C7–C3	112.14(16)
C8–C7–C9	109.89(16)
C9–C7–C3	110.26(15)
C10–C7–C3	110.21(15)
C10–C7–C8	108.15(15)
C10–C7–C9	105.99(15)
C7–C8–H8A	109.5
C7–C8–H8B	109.5

C7–C8–H8C	109.5
H8A–C8–H8B	109.5
H8A–C8–H8C	109.5
H8B–C8–H8C	109.5
C7–C9–H9A	109.5
C7–C9–H9B	109.5
C7–C9–H9C	109.5
H9A–C9–H9B	109.5
H9A–C9–H9C	109.5
H9B–C9–H9C	109.5
O1–C10–O2	122.82(17)
O1–C10–C7	125.39(17)
O2–C10–C7	111.74(16)
O2–C11–H11A	109.5
O2–C11–H11B	109.5
O2–C11–H11C	109.5
H11A–C11–H11B	109.5
H11A–C11–H11C	109.5
H11B–C11–H11C	109.5
C13–C12–S1	120.19(14)
C13–C12–C17	119.54(17)
C17–C12–S1	120.27(14)
C12–C13–H13	119.8
C14–C13–C12	120.45(18)
C14–C13–H13	119.8
C13–C14–H14	119.9
C13–C14–C15	120.16(19)
C15–C14–H14	119.9
C14–C15–H15	120.1
C16–C15–C14	119.71(18)
C16–C15–H15	120.1
C15–C16–H16	119.6
C15–C16–C17	120.87(18)
C17–C16–H16	119.6
C12–C17–S2	122.48(14)
C16–C17–S2	117.98(14)
C16–C17–C12	119.15(17)

Table 5 Torsion angles for Compound 63

Atom–Atom–Atom–Atom	Torsion Angle [°]
S1–C12–C13–C14	178.62(15)
S1–C12–C17–S2	−9.0(2)
S1–C12–C17–C16	178.30(14)
S2–C5–C6–S1	−44.07(17)
S2–C5–C6–C1	−164.26(13)
C1–C2–C3–C4	18.2(3)
C1–C2–C3–C7	144.31(18)
C2–C1–C6–S1	−111.96(18)
C2–C1–C6–C5	12.1(3)
C2–C3–C4–C5	−47.2(2)
C2–C3–C7–C8	−64.7(2)
C2–C3–C7–C9	172.50(15)
C2–C3–C7–C10	55.8(2)
C3–C4–C5–S2	−172.45(12)
C3–C4–C5–C6	61.7(2)
C3–C7–C10–O1	−138.94(19)
C3–C7–C10–O2	43.8(2)
C4–C3–C7–C8	59.8(2)
C4–C3–C7–C9	−63.0(2)
C4–C3–C7–C10	−179.65(15)
C4–C5–C6–S1	78.04(17)
C4–C5–C6–C1	−42.1(2)
C5–S2–C17–C12	40.51(17)
C5–S2–C17–C16	−146.69(14)
C6–S1–C12–C13	136.96(16)
C6–S1–C12–C17	−42.73(16)
C6–C1–C2–C3	−0.3(3)
C7–C3–C4–C5	−172.56(15)
C8–C7–C10–O1	−16.0(3)
C8–C7–C10–O2	166.66(16)
C9–C7–C10–O1	101.8(2)
C9–C7–C10–O2	−75.54(19)
C11–O2–C10–O1	0.0(3)

C11–O2–C10–C7	177.35(15)
C12–S1–C6–C1	−165.75(13)
C12–S1–C6–C5	71.38(14)
C12–C13–C14–C15	3.1(3)
C13–C12–C17–S2	171.33(14)
C13–C12–C17–C16	−1.4(3)
C13–C14–C15–C16	−1.4(3)
C14–C15–C16–C17	−1.8(3)
C15–C16–C17–S2	−169.92(15)
C15–C16–C17–C12	3.1(3)
C17–S2–C5–C4	−134.84(13)
C17–S2–C5–C6	−9.97(16)
C17–C12–C13–C14	−1.7(3)
Atom–Atom–Atom–Atom	**Torsion Angle [°]**
S1–C12–C13–C14	178.62(15)
S1–C12–C17–S2	−9.0(2)
S1–C12–C17–C16	178.30(14)
S2–C5–C6–S1	−44.07(17)
S2–C5–C6–C1	−164.26(13)
C1–C2–C3–C4	18.2(3)
C1–C2–C3–C7	144.31(18)
C2–C1–C6–S1	−111.96(18)
C2–C1–C6–C5	12.1(3)
C2–C3–C4–C5	−47.2(2)
C2–C3–C7–C8	−64.7(2)
C2–C3–C7–C9	172.50(15)
C2–C3–C7–C10	55.8(2)
C3–C4–C5–S2	−172.45(12)
C3–C4–C5–C6	61.7(2)
C3–C7–C10–O1	−138.94(19)
C3–C7–C10–O2	43.8(2)
C4–C3–C7–C8	59.8(2)
C4–C3–C7–C9	−63.0(2)
C4–C3–C7–C10	−179.65(15)
C4–C5–C6–S1	78.04(17)
C4–C5–C6–C1	−42.1(2)
C5–S2–C17–C12	40.51(17)
C5–S2–C17–C16	−146.69(14)

C6–S1–C12–C13	136.96(16)
C6–S1–C12–C17	−42.73(16)
C6–C1–C2–C3	−0.3(3)
C7–C3–C4–C5	−172.56(15)
C8–C7–C10–O1	−16.0(3)
C8–C7–C10–O2	166.66(16)
C9–C7–C10–O1	101.8(2)
C9–C7–C10–O2	−75.54(19)
C11–O2–C10–O1	0.0(3)
C11–O2–C10–C7	177.35(15)
C12–S1–C6–C1	−165.75(13)
C12–S1–C6–C5	71.38(14)
C12–C13–C14–C15	3.1(3)
C13–C12–C17–S2	171.33(14)
C13–C12–C17–C16	−1.4(3)
C13–C14–C15–C16	−1.4(3)
C14–C15–C16–C17	−1.8(3)
C15–C16–C17–S2	−169.92(15)
C15–C16–C17–C12	3.1(3)
C17–S2–C5–C4	−134.84(13)
C17–S2–C5–C6	−9.97(16)
C17–C12–C13–C14	−1.7(3)