# The Reactivity of $\eta^2$-Aminoarenes Coordinated to Tungsten via Acid Trapping

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## ABSTRACT

PIENKOS, JARED A.

The Reactivity of $\eta^2$-Aminoarenes Coordinated to Tungsten via Acid Trapping

(Under the direction of Professor W. Dean Harman)

The Harman lab exploits π-basic metal fragments to functionalize arenes. Coordination of an aromatic molecule to a π-basic metal fragment usually occurs in an $\eta^2$-fashion. In the process of complexation, the arenes are dearomatized, and the resulting ligands are able to undergo synthetic transformations that are inaccessible to the unbound, organic analogs.[1] Currently, the [TpW(NO)($PMe_3$)] metal fragment is used as a dearomatization reagent because of its low cost, scalability, and accessibility to a TpW(NO)($PMe_3$)($\eta^2$-benzene) complex. The $\eta^2$-coordinated benzene can be substituted with a variety of aromatic ligands.[2]

For example, an aromatic ring with an amine moiety can be exchanged with tungsten-bound benzene and protonated *in situ*, forming its conjugate acid (Figure 1). This product, although cationic, is able to undergo a second electrophilic addition. Modifications of these bound arenes result in the formation of novel organometallic derivatives.

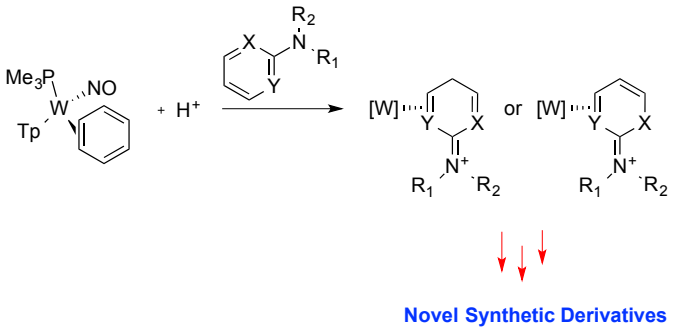


Figure 1: $\eta^2$-Dearomatization of Aromatic Compounds Containing an Amino Group

Friedel-Crafts,[3] hydroamination, and cyclopropanation[4] reactions have been performed on these coordinated $\eta^2$-aminoarenes. In some cases, after synthetic modifications, the functionalized ligand can be removed from the metal fragment. This strategy has been used to generate cyclohexenone, amidine, and hexahydroindole derivatives.

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(3) Pienkos, J. A.; Zottig, V. E.; Iovan, D. A.; Li, M.; Harrison, D. P.; Sabat, M.; Salomon, R. J.; Strausberg, L.; Teran, V. A.; Myers, W. H.; Harman, W. D. *Organometallics* **2013**, *32*, 691.
(4) Pienkos, J. A.; Knisely, A. T.; Liebov, B. K.; Teran, V.; Zottig, V. E.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2013**, *33*, 267.

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**Chapter 1** introduces the concept of aromaticity and describes modifications of arenes. **Chapters 2** and **3** are published works and have been reproduced in accordance with Section II.1 or American Chemical Society Journal Publishing Agreement. **Chapters 4** and **5** are outlines for papers. Proper citations for Chapters **2** and **3** are given and collaborative efforts describing the work in **Chapters 4** and **5** are listed. All chapters are presented as individual pieces. **Chapter 6** contains my concluding remarks and acknowledgements.

**Chapter 2:**

Pienkos, J. A.; Zottig, V. E.; Iovan, D. A.; Li, M.; Harrison, D. P.; Sabat, M.; Salomon, R. J.; Strausberg, L.; Teran, V. A.; Myers, W. H.; Harman, W. D. *Organometallics 2013*, 32, 691.

**Chapter 3:**

Pienkos, J. A.; Knisely, A. T.; Liebov, B. K.; Teran, V.; Zottig, V. E.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics 2013,* 3*3,* 267.

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**Chapter 6:**

Concluding Remarks and Acknowledgments

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## List of Abbreviations

| | |
|---|---|
| aq | Aqueous |
| br | Broad |
| CAN | Ceric Ammonium Nitrate |
| COSY | Correlation Spectroscopy |
| CV | Cyclic Voltammetry |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene |
| DCM | Dichloromethane |
| DDQ | 2,3-dichloro-5,6-dicyano-*p*-quinone |
| DFT | Density functional theory |
| DiPAT | *N,N*-Diisopropylammonium triflate |
| DMA | *N,N*-Dimethylacetamide |
| DME | 1,2-Dimethoxyethane |
| DMF | Dimethyformamide |
| DMSO | Dimethyl sulfoxide |
| DPhAT | Diphenylammonium Triflate |
| ee | Enantiomeric excess |
| ESI-MS | Electrospray Ionization Mass Spectrometry |
| EtOAc | Ethyl Acetate |
| HATR | Horizontal Attenuated Total Reflectance |
| HMBC | Heteronuclear Multiple Bond Coherence Spectroscopy |
| HRMS | High-Resolution Mass Spectroscopy |
| HSQC | Heteronuclear Single Quantum Correlation Spectroscopy |

| | |
|---|---|
| IR | Infrared |
| LRMS | Low-Resolution Mass Spectroscopy |
| *m*CPBA | *m*-Chloroperbenzoic Acid |
| MeIm | *N*-Methylimidazole |
| NBS | *N*-Bromosuccinimide |
| NCS | *N*-Chlorosuccinimide |
| NHE | Normal Hydrogen Electrode |
| NMR | Nuclear Magnetic Resonance |
| NOE | Nuclear Overhauser Effect |
| NOESY | Nuclear Overhauser Effect Spectroscopy |
| ORTEP | Oak Ridge Thermal Ellipsoid Program |
| OTf | Trifluoromethanesulfonate or triflate |
| ppm | Parts Per Million |
| sat | Saturated |
| TBAH | Tetrabutylammonium Hexafluorphosphate |
| TEA | Triethylamine |
| THF | Tetrahydrofuran |
| TLC | Thin layer chromatrography |
| Tp | Hydridotris(pyrazolyl)borate |
| UV | Ultraviolet |

## List of Figures

## List of Schemes

# Chapter 1

## An Overview of Dearomatization Chemistry

## 1.1 Introduction to Aromatic Molecules

Aromatic compounds are a unique class of molecules due to their innate stability.[1] Originally, these molecules were distinguished from their hydrocarbon congeners based on their reactivity, as they formed substitution products instead of addition products when treated with electrophiles. For example, bromination of cyclooctateraene yields the dibrominated species, while benzene, under similar reaction conditions, yields the substituted species (Figure 1).[2,3]

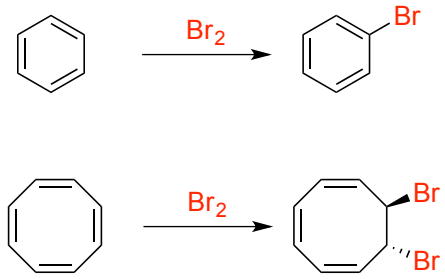


Figure 1: Bromination of Aromatic (above) and Non-aromatic Compounds (below)

Benzene, the archetype of aromatic molecules, contains all $sp^2$-hybridized carbons and exists in a planar arrangement. Its empirical formula, C:H, was known in 1825, but its structure was widely debated.[4-6] It was not until 1865 that Kekulé proposed a structure, which stood up to the test of time.[6] Since the discovery and characterization of benzene, many classes of aromatic molecules have been identified, some containing multicyclic ring systems and others containing heteroatoms.[7]

A general criterion to characterize aromatic molecules is Hückel's rule, which states that for a compound to be aromatic it must contain a cyclic array of 4n+2 π-

electrons. Although this principle breaks down with large annulene systems, it is consistent with the smaller systems that will be discussed in the remainder of this thesis.

Aromatic stability can be indirectly measured though a variety of experiments (e.g., magnetic susceptibility[8] and protonation equilibria[9]). One classic example compares the $\Delta H_{Hydrogenation}$ of 1,3-cyclohexadiene and cyclohexene to that of benzene. Although $\Delta H_{Hydrogenation}$ of benzene is expected to be -356 kJ/mole based on the $\Delta H_{Hydrogenation}$ of cyclohexene, it exhibits a $\Delta H_{Hydrogenation}$ of -206 kJ/mole, a 150 kJ/mole difference that cannot be solely accounted for based on resonance stabilization (Figure 2).[10,11] This energy difference is attributed to aromatic stabilization.

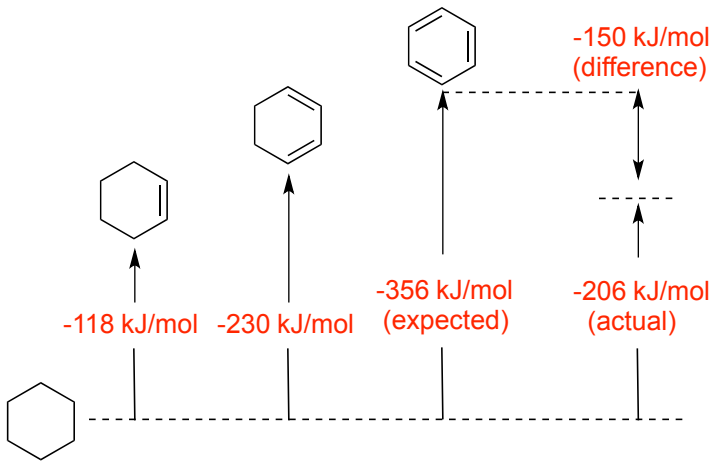


Figure 2: Hydrogenation of Benzene

## 1.2 Classic Reactivity of Aromatics

As implied by the hydrogenation experiment, which highlighted the stability of aromatic molecules, reactions to modify arenes usually require harsh conditions. Classic examples include the Birch reduction[12] and electrophilic aromatic substitution (EAS) reactions (Figure 3). The Birch reduction, although able to dearomatize arenes, requires $Na/NH_3$ in a protic solvent and these conditions are not tolerated by many functional groups. EAS reactions also require harsh reagents; either halogens promoted by a Lewis acid (e.g., $Br_2$ and $FeCl_3$)[7] or carbon electrophiles promoted by a Lewis acid (e.g., Friedel-Crafts Acylation and Friedel-Crafts Alkylation).[13]

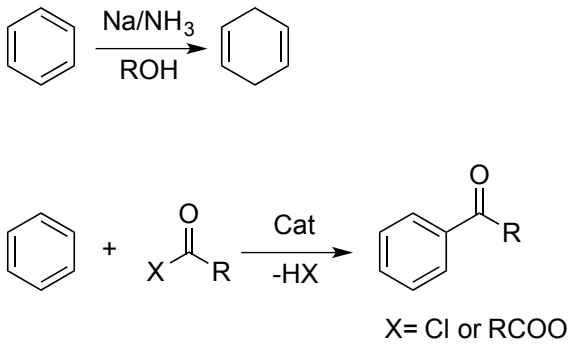


Figure 3: Classic Reactivity of Aromatic Molecules

## 1.3 Electrophilic Dearomatization *via* Hetereoatom Transfer Reagents

Less reactive electrophiles (e.g., Selectfluor™ and *m*-CPBA) cannot react with benzene, but they can react with other more nucleophilic arenes. For instance, polycyclic aromatic molecules (e.g., naphthalene and anthracene) can be directly modified under epoxidation conditions (Figure 4).[14] Selectfluor™, an electrophilic fluorine source, can modify *para*-cresol, an activated benzene molecule, to form a dearomatized product.[15,16] In a similar fashion, hypervalent iodine reagents can dearomatize phenolic compounds.[17] Exploiting asymmetric oxidants[18] or chiral organocatalytic compounds[19] allows for asymmetric iodine-catalyzed dearomatization; however, these conditions are only applicable to phenol compounds.

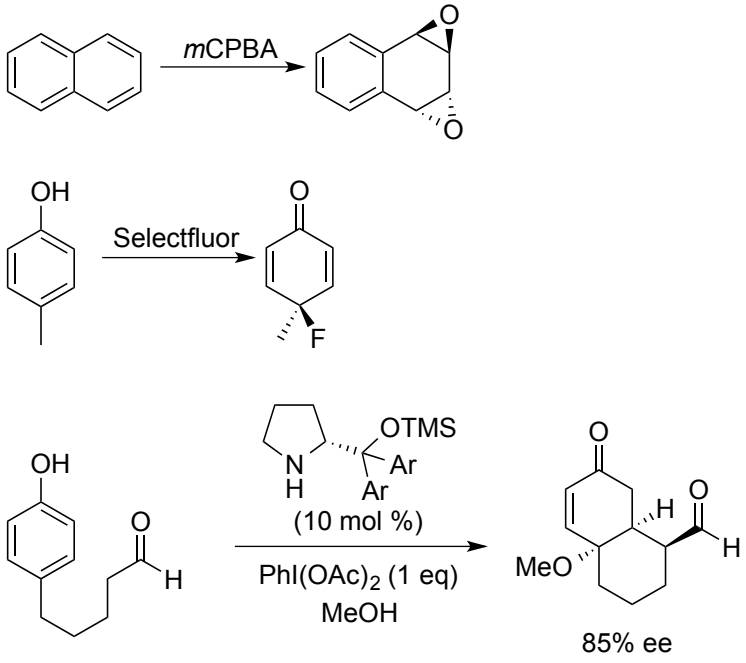


Figure 4: Electrophilic Dearomatization *via* Hetereoatom Transfer Reagents

## 1.4 Enzymatic Dearomatization

An elegant solution to modify benzene is found in nature, as certain types of bacteria are able to dearomatize this arene.[20] In certain cases these reactions occur enantioselectively, producing chiral building blocks.[21] These bacterial dearomatization reactions have been exploited in laboratory settings to synthesize natural products.[22] Although many substrates tolerate enzymatic dearomatization, these strategies are ineffective in forming C-C bonds.

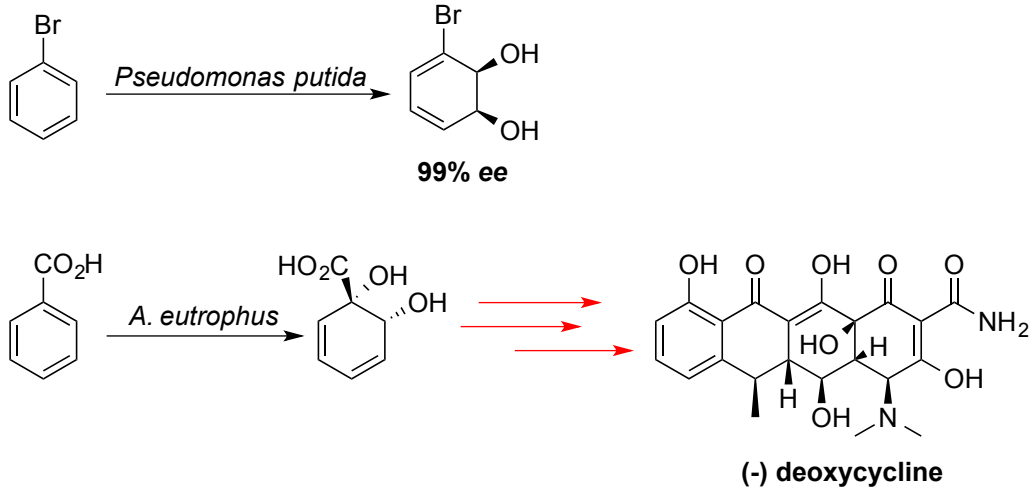


Figure 5: Enzymatic Dearomatization

## 1.5 Dearomatization *via* Cycloaddition Reactions

Benzene, despite containing a diene motif, is only able to undergo thermodynamic cycloadditons at very high temperatures and with very reactive dienophiles. An example can be seen in the reaction between benzene and the

activated alkyne, dicyanoacetylene.[23] Even with more activated arenes (1,4-benzenediol) and highly reactive dieneophiles (e.g., maleic anhydride), reactions still require elevated temperatures (250 °C).[24] However, when benzene is excited photochemically, [2+2] cycloadditions can take place at standard temperature and pressure (Figure 6).[25]

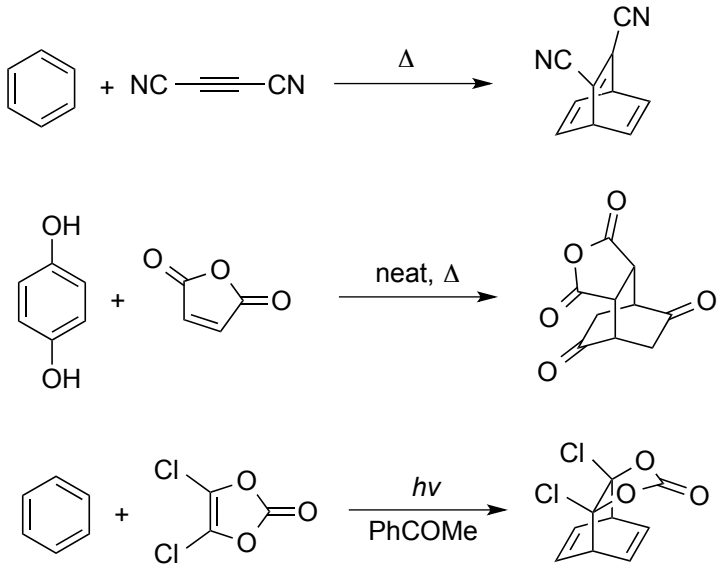


Figure 6: Cycloaddition Reactions with Aromatics

**1.6 Catalytic Dearomatization:**

In addition to promoting cycloaddition reactions, photochemical excitation allows for catalytic dearomatization of benzene with $OsO_4$ to form an acetoxy-derivatized cyclohexane (Figure 7).[26] Other catalytic dearomatization reactions exploit benzylic halides, forming $\eta^3$-allyic species with transition metals.[27-29] Following nucleophilic addition to these allyls, the arene substrate is effectively

dearomatized. Although this occurs catalytically, the methodology is only practical with a narrow range of substrates.

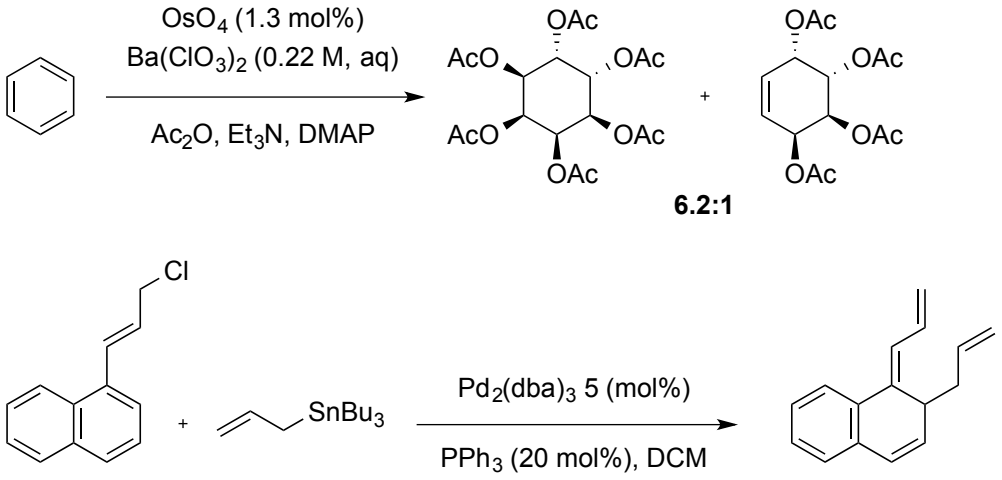


Figure 7: Catalytic Dearomatization Reactions

### 1.7 Dearomatization with π-Acidic Organometallic Fragments:

In contrast to catalytic dearomatization, using a stoichiometric amount of a transition metal allows for the generation of an organometallic scaffold. In some cases, the arene, once complexed to a metal system, becomes dearomatized and subsequent reactivity is dictated by the metal center. For instance, the π-acidic $[Cr(CO)_3]$ metal fragment is able to coordinate to benzene and form an $\eta^6$-arene.[30,31] This organometallic compound is then able to react with a variety of nucleophiles that, otherwise, would be inert to benzene. There have been a number of studies involving the regio-selectivity of additions to these $\eta^6$ arenes, in which the R group on the bound complex determines the electrophilic site on the bound arene.[32,33]

Complex modifications of these systems have been employed in the total synthesis of natural products such as (-)-acetoxytubifuran (Figure 8).[34]

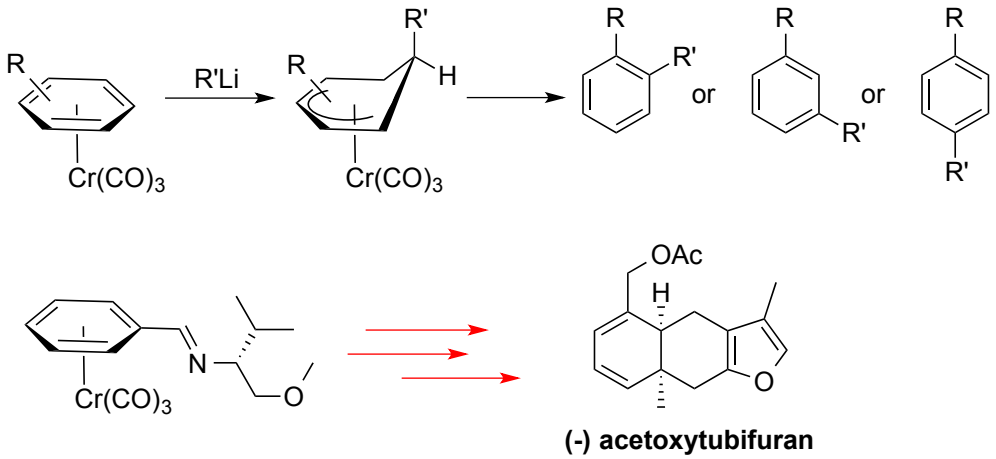


Figure 8: Dearomatization with [$Cr(CO)_3$] Metal Fragment

[$Mn^+(CO)_3$], parallel to the [$Cr(CO)_3$] analog, forms a stable "piano-stool" complex with benzene. Common reactivity patterns generally involve the reduction of the bound arene with $LiAlH_4$ followed by a second nucleophilic addition (Figure 9).[35]

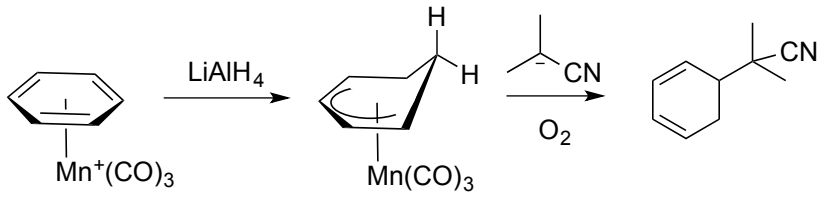


Figure 9: Dearomatization with [$Mn^+(CO)_3$] Metal Fragment

Reactions involving these π-acidic groups can be performed asymmetrically using bound chiral auxiliary groups[36] or a chiral nucleophile.[37]

### 1.8.a Dearomatization with π-Basic Organometallic Fragments

As a complement to the π-acidic strategy, electron rich metal fragments can also dearomatize arenes.[38] This strategy of π-basic dearomatization has proven successful in many cases and will be the focus of the remainder of this dissertation. There have been four generations of π-basic dearomatization reagents: an $[Os(NH_3)_5]^{2+}$ fragment, a $[TpRe(CO)(L)]^+$ fragment,[39] a [TpMo(NO)(L)] fragment,[40,41] and a [TpW(NO)(L)] system.[42] All of these metal fragments donate electron density into the empty π* orbital of the bound arene. This donation activates the bound arenes towards electrophilic additions and cycloadditions. In many cases, after addition of the electrophile ($E^+$), an allyl is formed that can react with a nucleophile ($Nu^-$), resulting in tandem $E^+/Nu^-$ additions.

### 1.8.b Dearomatization with $[Os(NH_3)_5]^{2+}$ Fragment

The pentaamineosmium system is able to bind a variety of arenes, including benzenes,[43] anisoles,[44] and pyrroles.[45] These molecules, once coordinated, are activated towards hydrogenation,[43] electrophilic addition,[46] and cycloaddition reactions.[47] An important initial study indicated that an $\eta^2$-coordinated benzene

could be subjected to hydrogenation under mild temperatures and pressures (Figure 10).[43]

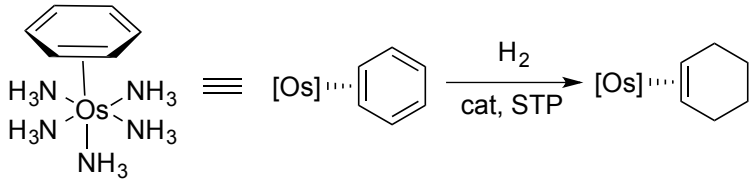


Figure 10: Hydrogenation of Benzene Promoted by an $[Os(NH_3)^5]^{2+}$ Fragment

The reactivity of the coordination of aniline molecules was also surveyed with the $[Os(NH_3)_5]^{2+}$ system. A brief overview of the reactivity of coordinated aniline is presented below (Figure 11).[48,49]

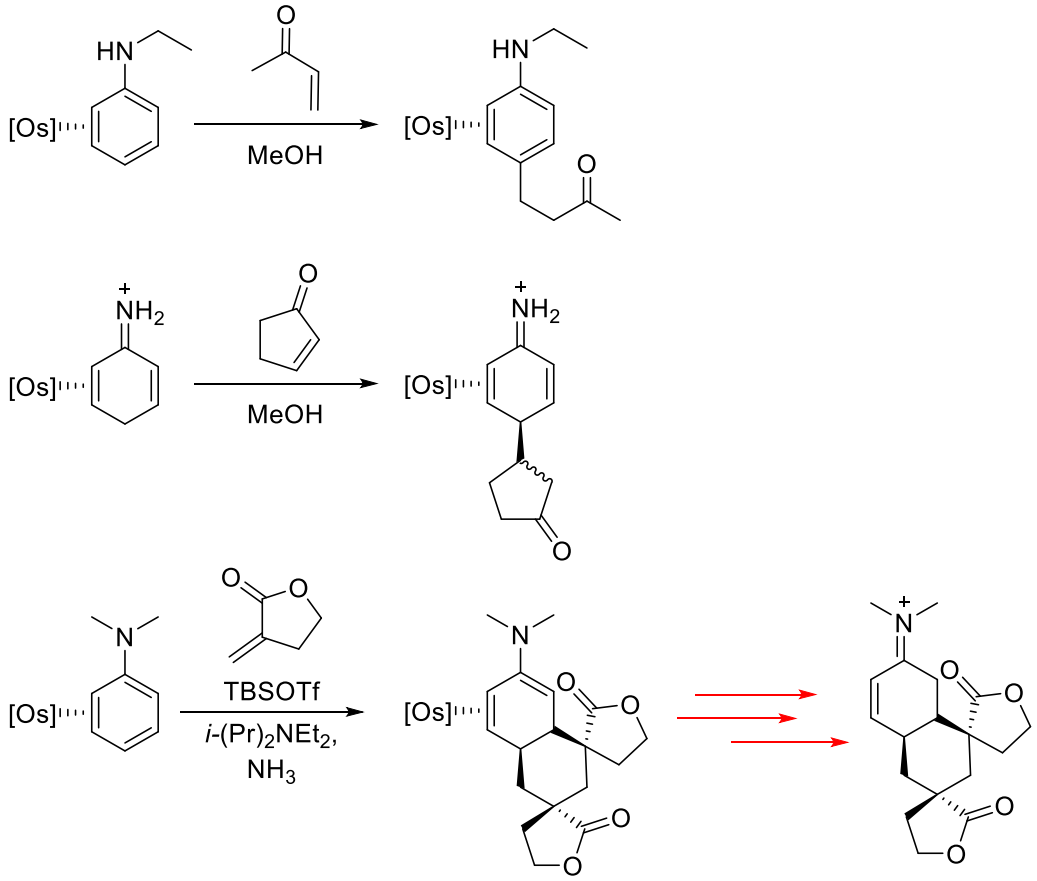


Figure 11: $[Os(NH_3)_5]^{2+}$ Promoted Aniline Reactivity

One limitation of the $[Os(NH_3)_5]^{2+}$ system is that the metal is achiral. In order to access chiral compounds, asymmetric auxiliary groups must be utilized. In the case of bound anisole derivatives, a chiral acetate group is able to dictate the facial selectivity of the initial electrophilic addition (Figure 12).[50,51]

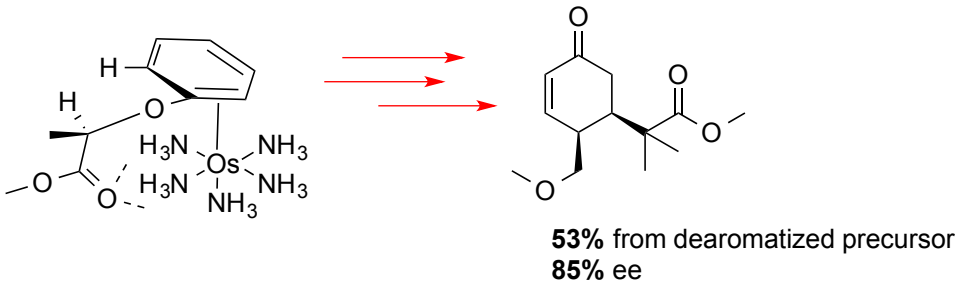


Figure 12: Promoting Enantioselectivity with a Chiral Anisole Derivative

### 1.8.c Dearomatization with [TpRe(CO)(L)] and [TpMo(NO)(L)]

Like the $[Os(NH_3)^5]^{2+}$ system, both the Re(I) and the Mo(0) dearomatization reagents can bind a variety of arenes. However, the Mo(0) system is unable to coordinate benzene in the $\eta^2$ fashion. Both compounds have an auxiliary ligand (L), which, when changed, can modify the reactivity of the bound arene. Enantioselectivity can be achieved in the case of the [TpRe(CO)(1-methylimidizole)]$^+$ reagent by first binding a sacrificial chiral ligand, α-pinene (Figure 13).[52] This process is currently being investigated in the [TpMo(NO)(4-dimethylaminopyridine)] system.

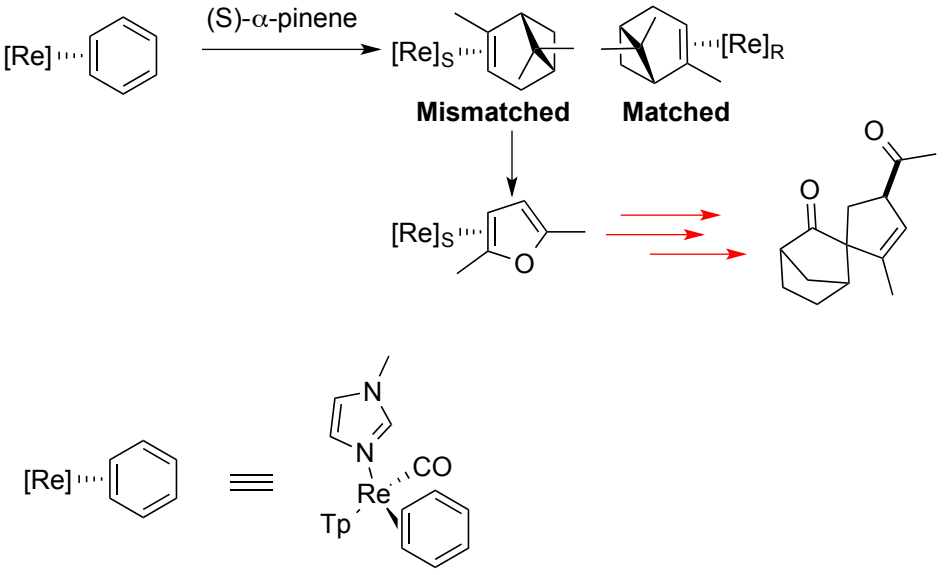


Figure 13: Chiral Resolution of a [TpRe(CO)(1-methylimidizole)] Dearomatization Reagent

### 1.8.d Dearomatization with [TpW(NO)($PMe_3$)]

Because of its cost, scalability, and ability to promote reactivity, [TpW(NO)($PMe_3$)] has proven to be extremely valuable as a dearomatization reagent.[53] The tungsten system is the most π-basic of the four aforementioned reagents. This can be demonstrated through its capability of promoting cycloadditions with benzene (Figure 14).[38,42] One disadvantage of this system is that the ancillary ligand, $PMe_3$, cannot be easily changed.[54] Previous work has shown that pyridine compounds (e.g., 4-picoline) are able to replace the $PMe_3$ and the resulting metal fragment can complex benzene; however, these procedures have unacceptably low yields and cannot be performed on a multi-gram scale.

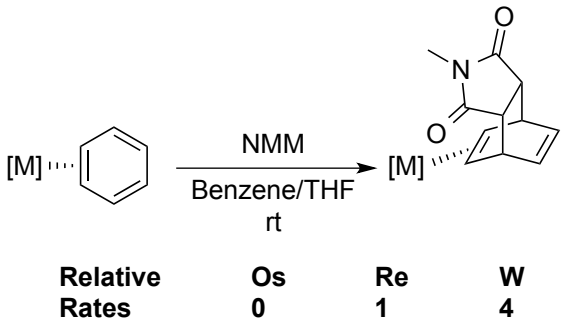


Figure 14: Relative Rates of Cycloadditions with Various $\eta^2$-Dearomatization Reagents

The $\eta^2$-benzene in the TpW(NO)($PMe_3$)($\eta^2$-benzene) complex can be exchanged with a variety of arenes. This allows access to ligands that cannot tolerate the reduction conditions of the [TpW(NO)($PMe_3$)] precursor, TpW(NO)($PMe_3$)(Br). This strategy has been used to synthesize various phenol derivatives, which, in the presence of sodium, would not be able to complex to the metal due to the generation of phenoxide in solution.

Once coordinated to the [TpW(NO)($PMe_3$)] metal fragment, the phenol molecule tautomerizes to the keto-form.[55] Now an enone, the coordinated phenol molecule demonstrates reactivity that is different from the free, unbound ligand. When subjected to electrophiles, the coordinated compound reacts at the *meta*-position, showing umpolung reactivity.[56] Upon deprotonation with a stong base (e.g., DBU), mild alkylations can be performed, which mimic the uncoordinated ligand's reactivity.[55] Ultimately, these compounds can be decomplexed from the metal center to generate cyclohexenones (Figure 15).

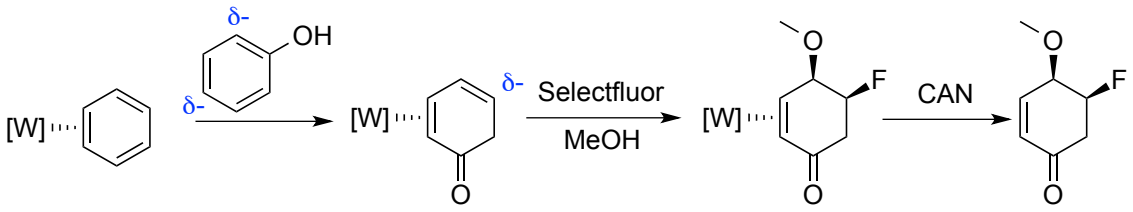


Figure 15: Dearomatization of Phenol and Reactivity of the Coordinated Compound

Although the coordinated phenol can be synthetically modified under various conditions (e.g., [2+2] cycloadditions,[57] tandem additions,[56] and mild alkylations), it is not stable to harsh conditions. In the presence of strongly coordinating Lewis acids or Brønstead acids, decomposition can occur.[58] It is believed that this is caused, to some extent, by initial coordination to the Lewis basic site on the ketone.

As a second generation to the phenol chemistry, *N*,*N*-dimethylaniline was used as a ligand. Exchange reactions between TpW(NO)($PMe_3$)($\eta^2$-benzene) and *N*,*N*-dimethylaniline do not produce a stable compound. However, protonating *N*,*N*-dimethylaniline with diisopropylammonium triflate (DiPAT) after it coordinates to the [TpW(NO)($PMe_3$)] complex produces the corresponding conjugate acid, which precipitates out of solution.[59] Nitrogen substitution on the aniline molecules proved to be necessary, as aniline molecules that contain unsubstituted nitrogen atoms form N-H insertion species in the presence of the dearomatization reagent (Figure 16).

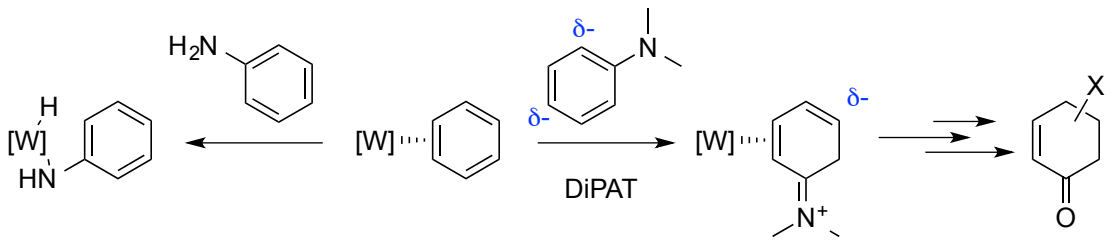


Figure 16: Dearomatization of *N*,*N*-dimethylaniline

The TpW(NO)($PMe_3$)($\eta^2$-*N*,*N*-dimethylanilinium) derivative serves as a synthon to α,β-unsaturated enones. Upon liberation of the molecule from the metal center and following a water work up, it was anticipated that hydrolysis would convert the iminium into a ketone. The presence of a positive charge on the nitrogen eliminates Lewis basic sites on the coordinated ligand and allows reactions to take place in the presence of stronger Lewis acids (e.g., $AlCl_3$). Unlike the $\eta^2$-phenol compounds, the aniline species quantitatively generates an allylic species upon protonation, and even after extended periods of time, minimal degradation is observed. An initial publication reported that this compound is indeed stable to harsh electrophilic additions. Additionally, upon deprotonation, the resulting enamine is able to react with alkyl bromides (Figure 17).[59]

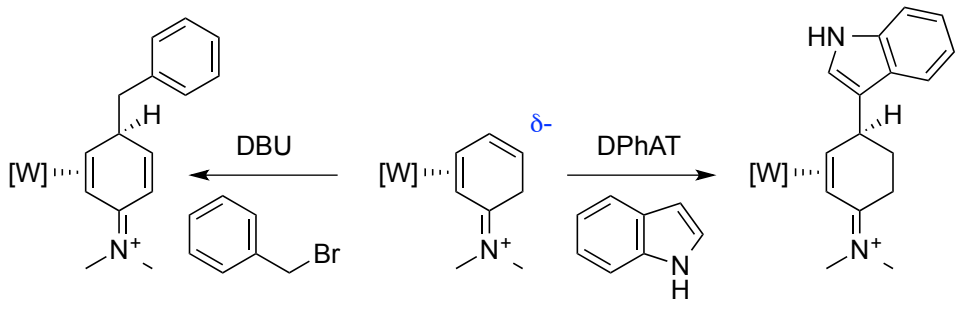


Figure 17: Preliminary Reactivity of Metal-bound *N*,*N*-dimethylaniline

The remaining chapters of this work will describe reactions with the aniline system. Each chapter highlights a portion of research, starting with the initial screening of allyl reactivity and how that compares to other $\eta^2$-coordinated arenes. The second chapter focuses on the selective opening of cyclopropane ring systems within the coordinated aniline system. Chapter three addresses the exploitation of coordinated aniline species with pyridine motifs, and the final chapter describes the complexation of larger hetereocyclic molecules that contain an aniline core.

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# Chapter 2

## Friedel–Crafts Ring-Coupling Reactions Promoted by Tungsten Dearomatization Agent

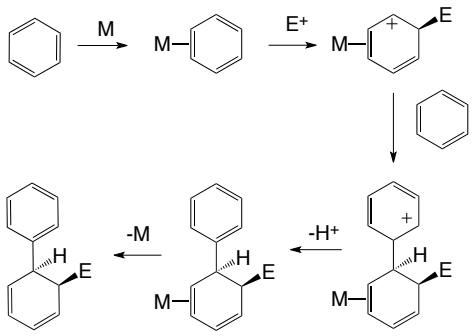
**Abstract:** The complexes TpW(NO)($PMe_3$)(L), where L=phenol, *N,N*-dimethylanilinium, or naphthalene, undergo protonation followed by addition of an aromatic nucleophile. The addition of aromatic molecules occurs at the para carbon of the phenol or aniline ring, or the beta carbon of the naphthalene. The addition occurs anti to the metal fragment, as determined by X-ray crystallography. In the case where L=phenol or *N,N*-dimethylanilinium, treatment of the bound arene with an electrophilic heteroatom followed by an aromatic nucleophile sets two stereocenters, with both additions occurring anti to the metal. The resultant ligands have been removed from the metal by oxidative decomplexation using ceric ammonium nitrate (CAN).

**Introduction.**

The Suzuki,[1,2] Negishi,[3-5] and Heck[6-8] reactions have become valuable methods for the coupling of two aromatic rings. Such cross-coupling reactions typically result in the formation of a new bond between two $sp^2$ carbons.[9,10] Cross-coupling reactions that form an $C_{sp2}$-$C_{sp3}$ bonds are also known, but can be more difficult to perform,[11,12,13] owing to undesired eliminations and hydrodehalogenation reactions.[14] A complementary ring-coupling procedure was envisioned between two aromatic rings in which one was first activated (dearomatized) via its dihapto-coordination to a π-basic metal. Protonation of such an arene complex would create an electrophilic arenium species that could react with a second aromatic molecule through a Friedel-Crafts type reaction mechanism, and a subsequent deprotonation would regenerate the acid. The product, after

removal of the metal, would be a hydroarylated arene. Alternatively, other electrophiles (E+) could be used in place of protons if substituted cyclohexadienes were desired. The general reaction sequence is proposed in Scheme 1, using benzene for both arenes.

Scheme 1: Proposed Aromatic Coupling with $\eta^2$–Coordinated Arenes.




**Results and Discussion:**

Of the dihapto-coordinate dearomatization reagents available, [TpW(NO)($PMe_3$)] is most economical,[15] provides the greatest degree of activation, and has a commercially available precursor, TpW(NO)$(Br)_2$. Several different types of $\eta^2$-coordinated arene complexes were considered as precursors to the electrophilic partner of the coupling reaction, including complexes of benzene (**1**), naphthalene (**2**), and anisole (**3**). Complexes of phenol (**4**) and *p*-cresol (**5**) were included since these arenes exist bound to the tungsten as their non-aromatic 2H-tautomers.[16] Finally, 2H-arenium complexes derived from anisole (**6**) and *N*,*N*-

dimethylaniline (**7**) were also included in the study, as these non-aromatic systems are structurally similar to the phenol analogs. The seven arene-derived tungsten complexes investigated are summarized in Figure 1.[17-22]

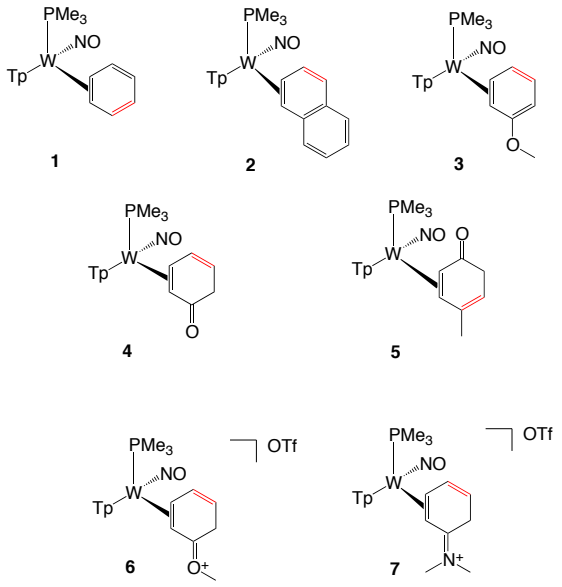
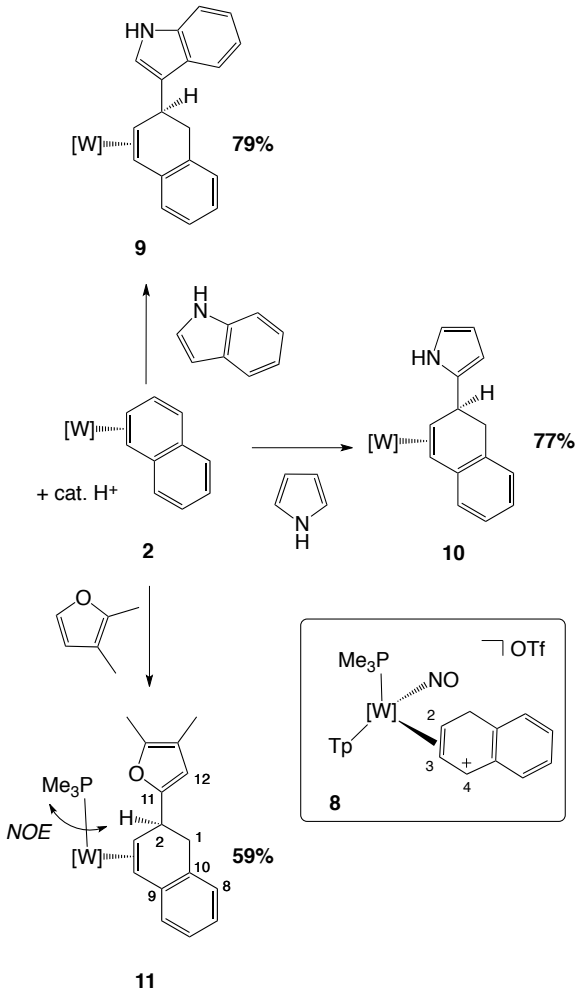



Figure 1: $\eta^2$–Arene-derived Complexes for Consideration as Partners for Friedel-Crafts Reactions.

Solvents and Brønsted acid catalysts were varied to optimize the addition of aromatic nucleophiles across the highlighted double bond of **1-7**. For the case of the benzene complex **1**, exposure to strong acids (e.g. $CH_3CN$•HOTf) resulted in significant decomposition judging from the appearance of multiple peaks in $^{31}P$ NMR spectra. The use of weaker acids as catalysts (e.g. diphenylammonium triflate (DPhAT), camphorsulfonic acid, and 2,6-lutidinium triflate) resulted in no reaction other than eventual ligand substitution. Attempts to quantitatively protonate the benzene complex **1** in the presence of an aromatic nucleophile either led to

intractable mixtures of products or decomposition, as indicated by $^{31}P$ NMR data. The naphthalene complex **2** was more tolerant of acids, and the naphthalenium complex **8** could even be isolated at ambient temperatures. Proton NMR data for the naphthalenium ligand of complex **8** generally match that of the Re analog,[23] with the exception of H4, which appears considerably more downfield for the W system owing to its "$\eta^2$-allyl" character.[21] When naphthalene complex **2** was stirred in a $CHCl_3$ solution of indole along with 0.1 equiv of the acid catalyst $[Ph_2NH_2]OTf$ (DPhAT), the addition product **9** was obtained. Similar results were observed with pyrrole to yield compound **10**. While furan failed to react with naphthalene complex **2** under the conditions tested, 2-methyl- and 2,3-dimethylfuran were both sufficiently nucleophilic to undergo ring-coupling. We chose the 2,3-dimethylfuran product **11** as an example for full characterization. Parallel reactions with nucleophilic benzenes such as anisole and aniline were not observed. Successful ring-coupling reactions with naphthalene complex **2** are summarized in Scheme 2.

Scheme 2: Reactions with Naphthalene Complex **2** and Various Aromatic Nucleophiles. [W]= $TpW(NO)(PMe_3)$.




With regard to characterization of **9**-**11**, H2 showed a strong NOE interaction with the $PMe_3$ ligand, which supports the assignment of nucleophilic addition *anti* to the metal fragment. Data from multi-dimensional NMR experiments indicated that the addition reactions to naphthalene **2** occurred in a 1,2-fashion, rather than the 1,4-addition occasionally observed with rhenium

complexes.[24] In the case of the pyrrole-derived product **10**, as well as the dimethylfuran analog **11**, HMBC and NOE data, along with chemical shifts of the aromatic protons, confirm that the electrophilic addition occurs at the alpha-carbon of these heterocycles. HMBC, COSY, and NOE data further support the given structural and stereochemical assignments in Scheme **2**.[18] A crystal structure determination for the indolyldihydronaphthalene **9** confirms that the addition of the indole occurs anti to the tungsten metal fragment (Figure 2).

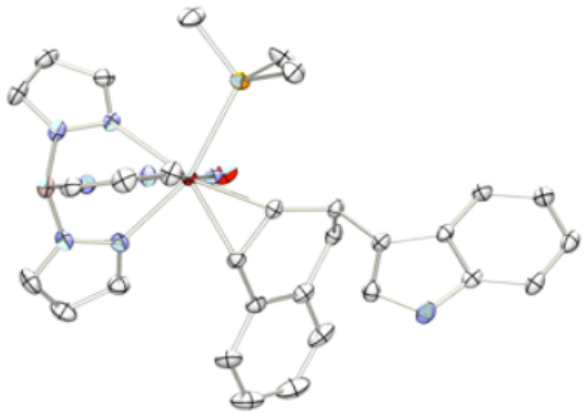
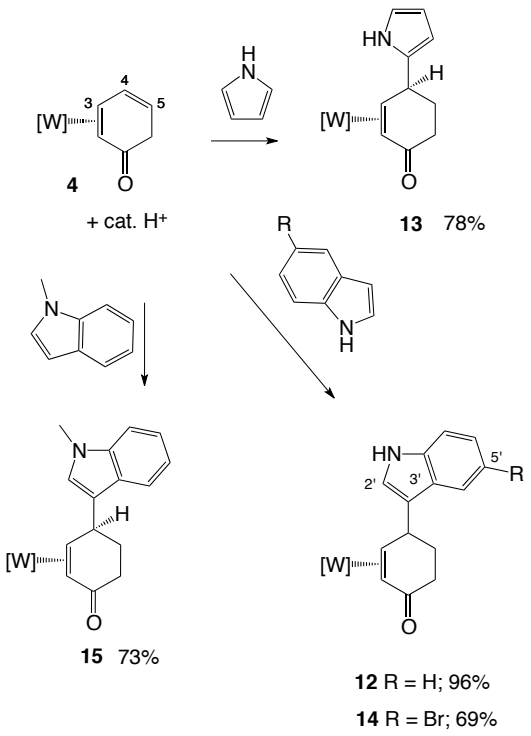


Figure 2: Crystal Structure of the Indolyldihydronapthalene Product **9**.

Coordinated anisole, **3**, exists as two coordination diastereomers in which the methoxy group is either proximal or distal to the $PMe_3$ ligand. Treating **3** with catalytic acid (e.g., DPhAT or $CH_3CN$•HOTf) in the presence of an aromatic nucleophile resulted in the decomposing the starting material: the $^{31}P$ signal

observed for **3** was replaced with a new signal that showed no $^{183}W$-$^{31}P$ coupling. Weaker acids failed to alter the starting material. However, for the dearomatized 2H-phenol complex (**4**), indole and pyrrole derivatives were found to add across the C4-C5 double bond. A screen of substituted indole complexes showed that substitution on the indolyl 3'-position prevented this reaction, but substitution on the nitrogen or bio-relevant 5'-position was well tolerated (Scheme 3).

**Scheme 3:** Reactions of Phenol Complex **4** with Various Aromatic Nucleophiles. [W]= $TpW(NO)(PMe_3)$.



As shown in the crystal structures of **12** and **13**, the additions occurred both regio- and stereoselectively, with the orientation of the nucleophile *anti* to the metal complex (Figure 3).

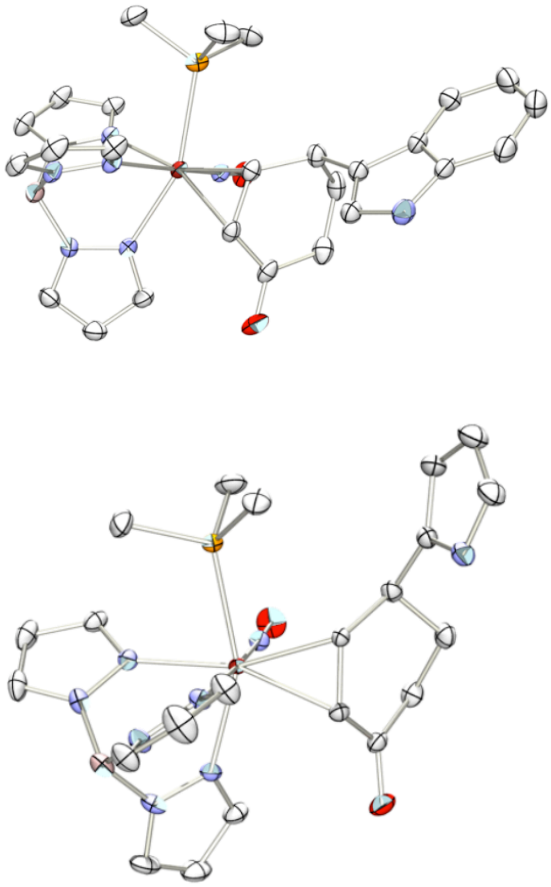
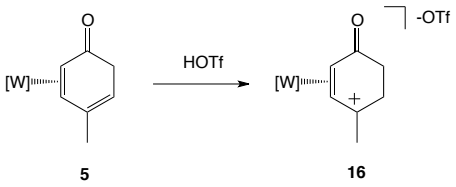


Figure 3: Crystal Structure of Indole (**12**; top) and Pyrrole (**13**; bottom) Addition Products. Co-crystallized $CHCl_3$ Omitted for Clarity from **12**.

In contrast to the phenol complex (**4**), the *p*-cresol analog **5** undergoes quantitative protonation with DPhAT or $CH_3CN$•HOTf. However, this allylic species failed to react with any aromatic nucleophiles (Scheme 4). Likely reasons for this

include an increased steric repulsion between the methyl group and the Tp ligand upon the addition of a nucleophile and the decreased electrophilicity of the allyl species due to the donor methyl group.[21]

Scheme 4: Attempted Reactions with p-Cresol Complex **5** [W]= TpW(NO)($PMe_3$).



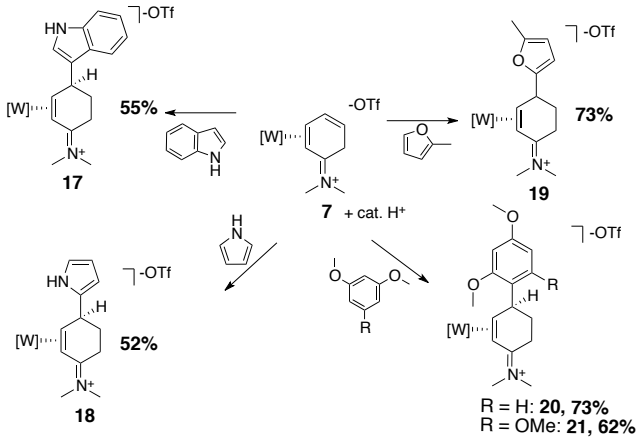

**5** **16**

Quantitative protonation of anisole complex **3** forms **6**, an isolable, cationic species.[25] Under the conditions tested, compound **6** did not react cleanly with any aromatic nucleophiles. Monitoring reactions between **6** and an aromatic compound in different solvents showed in each case a substantial amount of decomposition. Attempts to quantitatively protonate complex **6** with $CH_3CN$•HOTf showed no reaction, as indicated by $^{31}P$ NMR spectra. Conditions involving catalytic acid, **6**, and an excess of an aromatic nucleophile were also unsuccessful in generating clean product complexes.

The TpW(NO)($PMe_3$) complex of *N*,*N*-dimethylaniline is not sufficiently stable to be isolated, but its conjugate acid **7** is easily handled, even in air. While the bound 2H-anilinium ligand is formally a cation, strong backbonding from the tungsten renders it capable of additional protonation.[17] In the presence of acid, **7** reacts with indole,

pyrrole, activated furans, and even 1,3-dimethoxybenzene and 1,3,5-trimethoxybenzene. Of the nucleophiles that successfully reacted with anilinium complex **7**, 1,3-dimethoxybenzene appeared to be the least activated.[26] Various anisole derivatives and thiophenes showed no reactivity with **7**, as indicated by $^{31}$P-NMR experiments. These results are summarized in Scheme 5.

Scheme 5: Reactions with Anilinium **7** and Various Aromatic Nucleophiles [W]= TpW(NO)($PMe_3$).

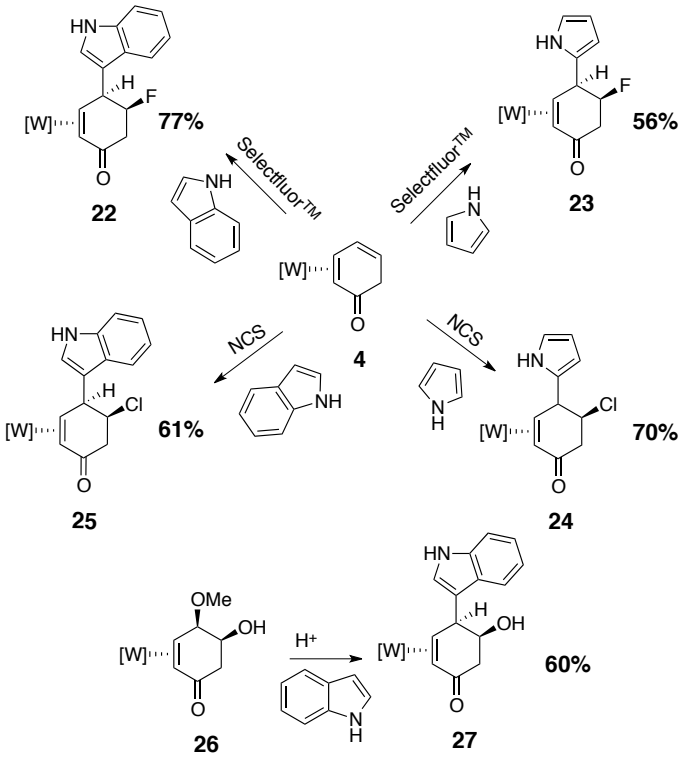



Electrophiles other than $H^+$ are capable of reacting with arene or arenium derivatives,[17,27] and we next explored combining these reactions with the Friedel-Crafts reaction to form more functionalized ring-coupling products.

Phenol complex **4** and anilinium complex **7** were both found to react with heteroatom electrophiles followed by the stereospecific addition of aromatic nucleophiles to form *cis*-γ,δ-disubstituted cyclohexenone derivatives. This reaction

sequence seemed to work best for the phenol complexes (Scheme 6). Whereas the byproducts from Selectfluor™ and NCS did not seem to interfere with the Friedel-Crafts reaction step, we found that 3-chlorobenzoate (from mCPBA) was apparently competitive.[27] However, the oxygenated derivative **26** could be generated from phenol **4** using mCPBA, and subsequent treatment with acid in the presence of indole formed the desired 5-hydroxy-4-indolyl-substituted product **27** in 60% yield.

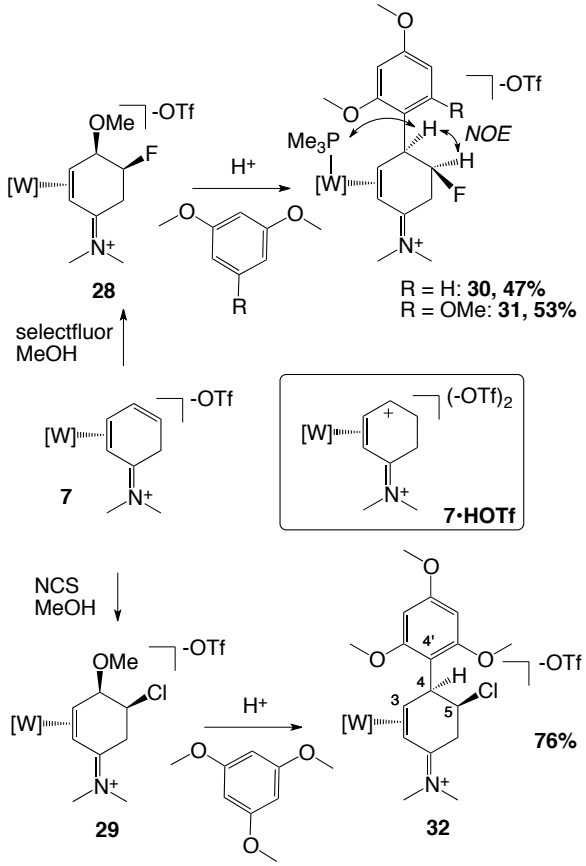
Scheme 6: Electrophilic Heteroatom Addition Followed by Aromatic Nucleophilic Addition to Phenol Complex **4** [W]= TpW(NO)($PMe_3$).




Similar to the reaction with the hydroxylated enone **26**, we found that by starting with the previously reported 5-halo-4-methoxy analog of the anilinium

system, **28** or **29**, one could generate clean ring-coupled products via a π-allyl intermediate (Scheme 7). This strategy prevented any complications that could occur from the electrophile reacting with the aromatic nucleophile. Indeed a one-pot, sequential addition of an electrophilic reagent (e.g. Selectfluor™), followed by an aromatic carbon nucleophile, led to impurities in the isolated product.

Scheme 7: Electrophilic Hetereoatom Addition Followed by Aromatic Nucleophilic Addition to Anilinium **7** [W]= TpW(NO)($PMe_3$).



A crystal structure of compound **32** confirms the relative stereochemistry of the hetereoatom electrophile and carbon nucleophile (Figure 4). Complexes **30**-**31** have NOE interactions between H4 and H5, and the methine proton *anti* to the aromatic nucleophile (H4) has a strong NOE interaction with the $PMe_3$ ligand.

Interestingly, the methoxy groups in **32** are all non-equivalent, an observation suggesting slow rotation of the bulky aryl ring about the C4-C4' axis on the NMR timescale.

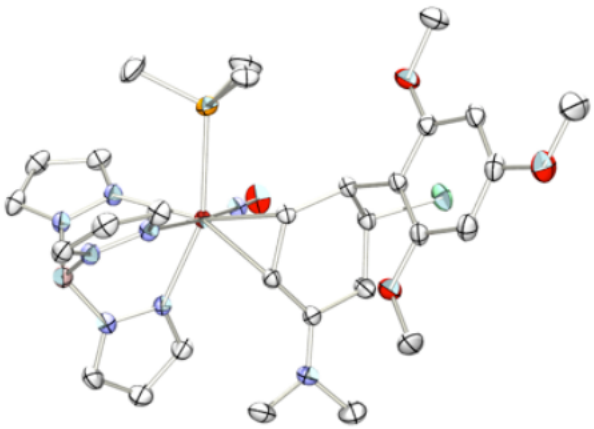
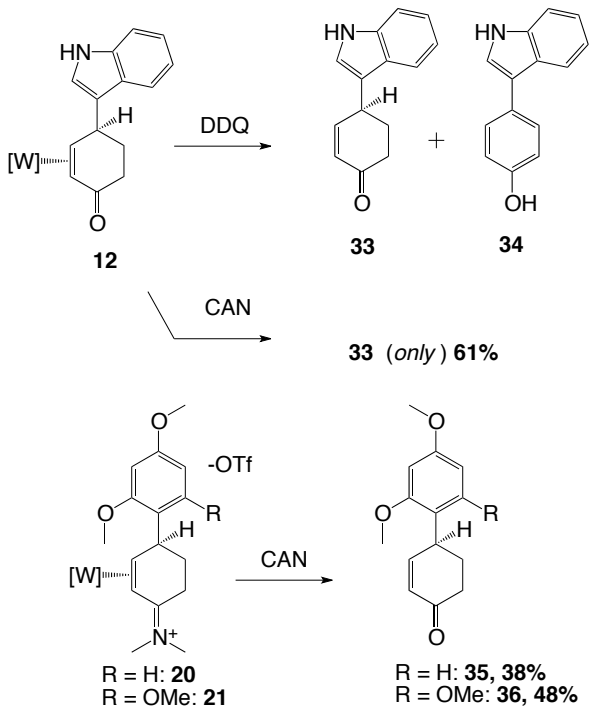


Figure 4: Crystal Structure of the 5-Chloro-4-arylated Derivative **32**. Triflate Counterion Omitted for Clarity.

In order to liberate the ring-coupled organic products, various complexes described above were treated with a reagent capable of oxidizing the tungsten. For enone complexes, we found that either ceric ammonium nitrate (CAN) or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) were sufficient, but for the iminium analogs, the stronger oxidant CAN was required. In addition, DDQ sometimes rearomatized the liberated product back to a phenol. For example, the oxidation of

**12** by DDQ afforded two organic products, both the enone, **33**, and the rearomatized *para*-substituted phenol, **34**, in a 1:1 ratio. Varying equivalents of DDQ, concentration, temperature, solvent, and addition of base to the reaction failed to prevent the formation of the *p*-indol-3-ylphenol impurity. In contrast, oxidation of **12** with CAN did not produce any of the aromatic side product. However, we note that purification of **33** using basic alumina in the presence of $O_2$ effected its conversion to **34**. Rearomatization was avoided using silica, and **33** could be isolated in a 61% yield. $^1$H-NMR resonances from the uncoordinated double bond of **33**, shifted downfield from 3.42 and 2.31 ppm in **12** to 7.13 ppm and 6.16 ppm in **33**. Multidimensional NMR data, along with HRMS, confirmed the structural assignment of **33** as 4-(indol-3-yl)-cyclohex-2-enone (Scheme 8).

Scheme 8: Oxidative Decomplexation of Enones.

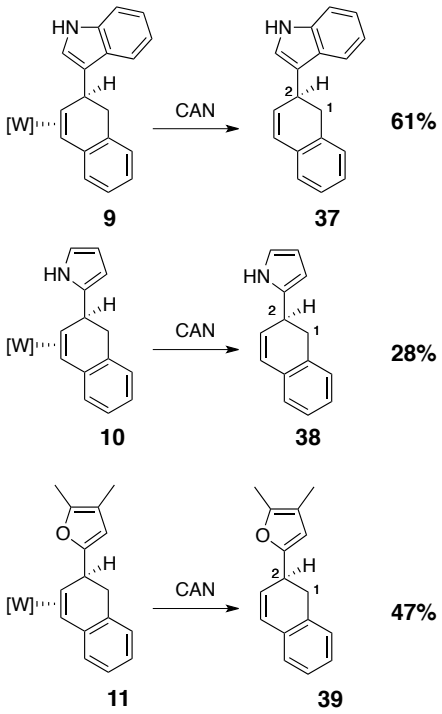


Unfortunately, the decomplexation conditions used for **33** did not work for the pyrrole analog, and only phenol and pyrrole were recovered. Further, using these conditions with products containing halogens did not yield any clean organic compounds.

Compared to enone complexes, iminium compounds **17**-**21**, are oxidized at higher potentials. For these complexes, DDQ fails to oxidize the tungsten, and CAN was employed. Thus, compounds **20** and **21** were oxidized with CAN and the liberated iminiums were hydrolyzed *in situ* to form the 4-arylated enones **35** and **36** in yields of 38% and 48%, respectively (Scheme 9). Oxidative decomplexation failed to generate clean organic products from the halide derivatives (**22**-**25** or **30**-**32**).

Dihydronaphthalene derivatives **9**-**11**, having lower W(I/0) reduction potentials than the enone or eniminium complexes, readily oxidized in the presence of CAN as shown in (Scheme 9). Treating **9**-**11** with one equivalent of CAN produced the organic products **37**-**39** with yields of 61%, 28%, and 47%, respectively. NOE and COSY interactions between H1 and H2 of compounds **37**-**39** confirmed 1,2 addition in the liberated dihydronapthalenes.

Scheme 9: Oxidative Decomplexation of Dihydronaphthalenes **9-11**. [W]=TpW(NO)($PMe_3$).




Whereas organic anilines and phenols react with electrophiles at the ortho and para positions, coordination to the TpW(NO)($PMe_3$) metal fragment allows the initial electrophilic attack to occur at the *meta* position. The subsequent addition of the aromatic nucleophile occurs at the *para* position, reactivity that is not seen in the parent complex. To our knowledge, none of the organic γ-substituted cyclohexenones reported in this paper has been previously synthesized. However, we note that **33** closely resembles an advanced synthetic intermediate patented for use as an anti-depressant.[28] In most cases, naphthalene undergoes electrophilic addition reactions preferentially at the 1-position. However, under thermodynamic control or in the presence of a bulky electrophile, 2-substitution is preferred.[29] $\eta^2$-

coordination of naphthalene with the TpW(NO)($PMe_3$) metal fragment allows for selective protonation at the 1-position, followed by nucleophilic addition to the 2-position. Of the organic complexes made through this strategy, only **38** has been previously synthesized: under photochemical conditions, pyrrole and naphthalene are reported to combine to produce **38** as one component of a complex mixture of products.[30]

Pioneering work by Yamamoto,[31] Maier,[32] Miura[33] and Buchwald[34] groups demonstrated the ability to arylate the γ-position of enones, generating products similar to some of those synthesized in this report. This was accomplished by using Pd-catalyzed coupling of the enone to an aryl bromide, or by trapping Sn-masked dienolates.[31] In particular, Buchwald et al. have generated compounds similar to compounds herein with a quaternary center in the γ-position.[12] However, most of the reports involving palladium-mediated arylation of carbonyl functional groups focus on α-arylation.[35-37] γ-Substituted cyclohexenones that do not contain a quaternary carbon in the γ-position have also been synthesized directly through conjugate addition to cyclohexenones, followed by ring expansion,[38] or by dehydrogenation of cyclohexenones.[39,40] However, in no other cases are $sp^2$-$sp^3$ ring-coupled products formed from aromatic precursors.

**Conclusion.**

We have explored a new method for coupling aromatic rings in which the bicyclic product is partially dearomatized. The method utilizes a tungsten-activated

arene prepared from a commercially available precursor $TpW(NO)Br_2$ (Sigma-Aldrich) that, upon electrophilic activation, undergoes a Friedel-Crafts type addition of various electron-rich aromatic rings. In all cases, the arylation is regio- and stereoselective. Additionally, in the case of phenol and aniline-derived examples, the new C-C bond occurs with a reversal of the natural polarization for these arenes.

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**Experimental Section.**

**General Methods.** NMR spectra were obtained on either a 300, 500, or 600 MHz spectrometer (Varian INOVA or Bruker Avance). All chemical shifts are reported in ppm. Proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual $^{1}H$ or $^{13}C$ signals of the deuterated solvent as an internal standard. Phosphorus NMR signals are referenced to 85% $H_3PO_4$ (δ) 0.00 ppm using a triphenylphosphate external standard in acetone (δ = -16.58 ppm). Coupling constants (*J*) are reported in hertz (Hz). Infrared (IR) spectra were recorded on a MIDAC Prospect Series (model PRS) spectrometer as a glaze on a horizontal attenuated total reflectance (HATR) accessory (Pike Industries). Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data were taken at ambient temperature at 100 mV/s in a standard three-electrode cell with a glassy carbon working electrode using tetrabutylammonium hexafluorophosphate (TBAH) as an electrolyte [approximately 0.5 M in dimethylacetamide (DMA)] unless otherwise noted. All

potentials are reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = -0.78 V), ferrocene ($E_{1/2}$ = +0.55 V), or decamethylferrocene ($E_{1/2}$ = +0.04 V) as an internal standard. The peak-to-peak separation was 100 mV or less for all reversible couples. High-resolution electrospray ionization mass spectrometry (ESI-MS) analyses were obtained on a Bruker BioTOF-Q instrument running in ESI mode from samples dissolved in 1:3 water/acetonitrile solution containing sodium trifluoroacetate (NaTFA), and using $[Na(NaTFA)_x]^+$ clusters as an internal standard. For metal complexes, these data are reported using the five most intense peaks from the isotopic envelope for either $M^+$ (for monocationic complexes) or for $[M + H]^+$ or $[M + Na]^+$ (for neutral complexes). The data are listed as *m/z* with the intensity relative to the most abundant peak of the isotopic envelope given in parentheses for both the calculated and observed peaks. The difference between calculated and observed peaks is reported in ppm. For organic species, the calculated and observed peaks for $[M + H]^+$ or $[M + Na]^+$ are reported, with the difference between them reported in ppm. LRMS data was acquired on a Shimadzu G-17A/QP-5050 GC-MS instrument operating either in GC-MS or in direct inlet/MS mode. Mass spectra are reported as $M^+$ for neutral or monocationic samples. In all cases, observed isotopic envelopes were consistent with the molecular composition reported. The data are listed as *m/z* with the intensity relative to the most abundant peak of the isotopic envelope given in parentheses for both the calculated and observed peaks.

**Allyl compound 8.**

Triflic acid (22 mg, 0.147 mmol) in $CHCl_3$ (1.52 g) was added to **2** (51 mg, 0.081 mmol). The resulting orange solution was precipitated over stirring ether (16 mL) and filtered through a 15 mL medium porosity fritted funnel to give **8** as an orange solid (53 mg, 84%).

$^1$H NMR ($CDCl_3$): δ 8.24 (d, J = 2.0, 1H, Pz3C), 8.06 (d, J = 2.0, 1H, Pz3B), 8.04 (d, J = 2.0, 1H, Pz3A), 7.89 (d, J = 2.0, 1H, Pz5C), 7.81 (d, J = 2.0, 1H, Pz5B), 7.72 (d, J = 2.0, 1H, Pz5A), 7.39 (d, J = 7.5, 1H, H5), 7.29 (m, 1H, H6), 7.17 (m, 1H, H7), 7.16 (m, 1H, H8), 6.71 (d, J = 7.2, 1H, H4), 6.59 (t, J = 2.0, 1H, Pz4C), 6.39 (t, J = 2.0, 1H, Pz4B), 6.34 (t, J = 2.0, 1H, Pz4A), 5.12 (dd, J = 20.7, 5.6, 1H, H1), 5.04 (m, 1H, H2), 4.95 (t, J = 7.3, 1H, H3), 3.83 (d, J = 20.5, 1H, H1'), 1.23 (d, J = 9.4, 9H, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 147.09 (Pz3A), 144.56 (Pz3B), 143.20 (Pz3C), 138.38 (Pz5C), 138.35 (Pz5A), 138.17 (Pz5B), 136.61 (C9 or C10), 132.86 (C9 or C10), 131.25 (C7), 130.46 (C4), 129.73 (C5), 128.10 (C8), 126.88 (C6), 109.02 (Pz4C), 108.47 (Pz4B), 107.39 (Pz4A), 96.55 (C3), 72.15 (C2), 33.17 (C1), 12.85 (d, J = 32, $PMe_3$).

**TpW(NO)($PMe_3$)(3,4-η$^2$-(3-(1,2-dihydronaphthalen-2-yl)-1*H*-indole)) (9)**

Compound **2** (201 mg, 0.319 mmol), indole (178 mg, 1.521 mmol), and diphenylammonium triflate (DPhAT) (10 mg, 0.031 mmol) were weighed into a 4-dram vial. $CHCl_3$ (4.982 g) was added to the vial, and the reaction mixture was stirred for a week. $Et_2O$ (5 mL) was added to precipitate a light beige precipitate,

which was filtered on a 15 mL fine-porosity fritted funnel as **9** (188 mg, 0.252 mmol, 79%).

$^{1}$H NMR (d$^{6}$-acetone): δ 9.67 (s, 1H, NH), 8.15 (d, 1H, *J* = 2.0, Pz3B), 8.01 (d, 1H, *J* = 2.0, Pz5C), 7.96 (d, 1H, *J* = 2.0, Pz5B), 7.86 (d, 1H, *J* = 2.0, Pz5A), 7.79 (d, 1H, *J* = 7.6, H11), 7.71 (d, 1H, *J* = 2.0, Pz3C), 7.39 (d, 1H, *J* = Pz3A), 7.35 (d, 1H, *J* = 7.9, H14), 7.08 (m, 1H, H15), 7.05 (m, 1H, H17), 7.02 (m, 1H, H16), 6.95 (t, 1H, *J* = 7.5, H6), 6.76 (d, 1H, *J* = 7.3, H8), 6.68 (t, 1H, *J* = 7.3, H7), 6.61 (d, 1H, *J* = 7.6, H5), 6.41 (t, 1H, *J* = 2.0, Pz4B), 6.36 (t, 1H, *J* = 2.0, Pz4C), 6.21 (t, 1H, *J* = 2.0, Pz4A), 4.59 (d, 1H, *J* = 6.1, H2), 3.74 (dd, 1H, *J* = 6.2, 15.4 H1), 3.30 (dd, 1H, *J* = 10.2, 12.6, H3), 2.66 (d, 1H, *J* = 15.8, H1'), 2.24 (dd, 1H, *J* = 1.8, 10.2, H4), 1.39 (d, 9H, *J* = 8.3, $PMe_3$). $^{13}$C NMR (d$^{6}$-acetone): δ 146.7 (s, C9), 144.5 (s, Pz3A), 144.3 (s, Pz3B), 142.0 (s, Pz3C), 138.0 (s, Pz5C), 137.8 (s, C18), 137.6 (s, C13), 137.2 (s, Pz5B), 136.7 (s, Pz5A), 133.9 (s, C10), 129.6 (s, C12), 129.6 (s, C8), 129.5 (s, C5), 124.7 (s, C6), 123.4 (s, C16), 123.2 (s, C7), 121.8 (s, C15), 119.5 (s, C11), 119.4 (s, C17), 112.2 (s, C14), 107.4 (s, Pz4B), 107.2 (s, Pz4C), 106.0 (s, Pz4A), 63.9 (s, C3), 55.1 (s, C4), 37.9 (s, C2), 36.0 (s, C1), 13.5 (d, *J* = 28, $PMe_3$). $^{31}$P NMR (d$^{6}$-acetone): δ -8.62 ($J_{P\text{-}W}$ = 281 Hz). CV (DMA): $E_{p,a}$ = +0.488 V. IR: $\nu_{NO}$ = 1550 cm$^{-1}$. HRMS (M+Na)$^{+}$ obs'd (%), calc'd (%), ppm: 769.20481 (83.1), 769.20715 (80.1), -3; 770.2098 (81.3), 770.20965 (81.8), 0.2; 771.20731 (100), 771.20967 (100), -3.1; 772.21193 (50.7), 772.21345 (48.7), -2; 773.20883 (76.2), 773.21287 (81.9), -5.2.

**TpW(NO)($PMe_3$)(3,4-η$^2$-(2-(1,2-dihydronaphthalen-2-yl)-1*H*-pyrrole)) (10)**

Compound **2** (150 mg, 0.238 mmol) and camphorsulfonic acid (15 mg, 0.065 mmol) were weighed into a 4-dram vial. $CHCl_3$ (1.531 g) and pyrrole (102 mg, 1.52 mmol) were added and after stirring, the solution was allowed to stand 2.5 hours. The vial was removed from the glovebox, and the solution was diluted with 30 mL DCM and extracted with 10 mL of sat. aq. $NaHCO_3$ solution. The aqueous layer was back-extracted with 5 mL DCM. The organic layer was extracted twice with 10 mL portions of water, each of which was back-extracted with DCM (5 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered on a 60 mL medium-porosity fritted funnel. The filtrate was concentrated *in vacuo*. The brown oil was re-dissolved in minimal DCM and added to a stirring solution of hexanes (30 mL). The pale tan solid that precipitated was collected on a 15 mL fine-porosity fritted funnel to give **10** (128 mg, 0.183 mmol, 77%).

$^1$H NMR ($CDCl_3$): δ 8.05 (d, 1H, *J* = 2.0, Pz3B), 7.87 (broad s, 1H, NH), 7.75 (d, 1H, *J* = 2.0, Pz5C), 7.71 (d, 1H, *J* = 2.0, pz5B), 7.63 (d, 1H, *J* = 2.0, Pz5A), 7.39 (d, 1H, *J* = 2.0, Pz3C), 7.33 (d, 1H, *J* = 2.0, pz3A), 7.07 (m, 2H, H6 and H8), 6.88 (t, 1H, *J* = 7.5, H7), 6.66 (d, 1H, *J* = 7.5, H5), 6.46 (m, 1H, H14), 6.29 (t, 1H, *J* = 2.0, Pz4B), 6.20 (t, 1H, *J* = 2.0, Pz4C), 6.12 (t, 1H, *J* = 2.0, Pz4A), 6.08 (m, 1H, H13), 5.99 (m, 1H, H12), 4.17 (d, 1H, *J* = 6.5, H2), 3.59 (dd, 1H, *J* = 6.7, 15.9, H1), 3.03 (dd, 1H, *J* = 10.3, 12.5, H3), 2.71 (dd, 1H, *J* = 6.7, 15.9, H1'), 2.14 (dd, 1H, *J* = 1.8, 10.3, H4), 1.33 (d, 9H, *J* = 8.1, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 144.7 (s, C9), 144.0 (s, pz3A), 143.4 (s, C11), 143.1 (s, Pz3B), 140.6 (s, Pz3C), 136.7 (s, Pz5C), 136.1 (s, Pz5B), 135.4 (s, Pz5A), 132.4 (s, C10), 129.1 (s, C5), 129.1 (s, C8), 124.5 (s, C6), 123.5 (s, C7), 116.6 (s, C14), 106.9 (s, C13),

106.9 (s, Pz4B), 106.0 (s, Pz4C), 105.4 (s, Pz4A), 102.5 (s, C12), 62.5 (s, C3), 53.5 (s, C4), 39.3 (s, C2), 34.5 (s, C1), 13.6 (d, $J$ = 28, $PMe_3$). $^{31}P$ NMR ($CDCl_3$): δ -9.36 ($J_{P\text{-}W}$ = 280 Hz). CV (DMA): $E_{p,a}$ = +0.533 V. IR: $\nu_{NO}$ = 1535 $cm^{-1}$. HRMS $(M+Na)^+$ obs'd (%), calc'd (%), ppm: 719.19051 (65.1), 719.19144 (82.2), -1.3; 720.19459 (67.6), 720.19397 (81.2), 0.9; 721.19485 (100), 721.1939 (100), 1.3; 722.19681 (47.3), 722.19785 (46), -1.4; 723.19812 (81.5), 723.19712 (82.7), 1.4.

**TpW(NO)($PMe_3$)(3,4-η²-(5-(1,2-dihydronaphthalen-2-yl)-2,3-dimethylfuran)) (11)**

Compound **2** (101 mg, 0.160 mmol) and camphorsulfonic acid (16 mg, 0.070 mmol) were weighed into a vial and dissolved in $CHCl_3$ (1.006 g). 2,3-dimethylfuran (59 mg, 0.615 mmol) was added to the solution and the reaction was allowed to stand for 3 hours. The vial was removed from the glovebox, and the solution was diluted with DCM (20mL) and extracted with 5 mL of a sat. aq. $NaHCO_3$ solution. The aqueous layer was back-extracted with 5 mL DCM. The DCM solution was extracted twice with 10 mL portions of water, each of which was back-extracted with DCM (5mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered on a 60 mL medium-porosity fritted funnel, and concentrated *in vacuo*. The brown residue was taken into a glovebox, dissolved in minimal DCM and precipitated in stirring hexanes (30 mL). The mixture was filtered on a 15 mL fine-porosity fritted funnel to give **11** as a light tan solid (68 mg, 0.094 mmol, 59%).

$^{1}$H NMR ($CDCl_3$): δ 8.09 (d, 1H, *J* = 2.0, Pz3B), 8.00 (d, 1H, *J* = 2.0, Pz5C), 7.94 (d, 1H, *J* = 2.0, Pz5B), 7.82 (d, 1H, *J* = 2.0, Pz5A), 7.68 (d, 1H, *J* = 2.0, Pz3C), 7.27 (d, 1H, *J* = 2.0, Pz3A), 6.96 (d, 1H, *J* = 7.5, H8), 6.93 (dd, 1H, *J* = 7.5, 8.4, H6), 6.75 (dd, 1H, *J* = 7.5, 8.4, H7), 6.48 (d, 1H, *J* = 7.6, H5), 6.38 (t, 1H, *J* = 2.0, Pz4B), 6.37 (t, 1H, *J* = 2.0, Pz4C), 6.17 (t, 1H, *J* = 2.0, Pz4A), 5.66 (s, 1H, H12), 4.05 (d, 1H, *J* = 6.7, H2), 3.57 (dd, 1H, *J* = 7.1, 16.0, H1), 3.22 (dd, 1H, *J* = 10.4, 11.5, H3), 2.73 (d, 1H, *J* = 16.0, H1'), 2.13 (s, 3H, H15), 2.00 (dd, 1H, *J* = 1.9, 10.3, H4), 1.75 (s, 3H, H16), 1.36 (d, 9H, *J* = 8.3, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 162.9 (s, C11), 146.0 (s, C9), 144.8 (s, C14), 144.2 (s, Pz3B), 144.2 (s, Pz3A), 141.8 (s, Pz3C), 138.0 (s, Pz5C), 137.2 (s, Pz5B), 136.7 (s, Pz5A), 133.1 (s, C10), 129.6 (s, C5), 128.9 (s, C8), 124.6 (s, C6), 123.2 (s, C7), 115.0 (s, C13), 108.3 (s, C12), 107.3 (s, Pz4B), 107.2 (s, Pz4C), 105.9 (s, Pz4A), 60.1 (s, C3), 54.2 (s, C4), 40.4 (s, C2), 33.1 (s, C1), 13.2 (d, *J* = 28.1, $PMe_3$), 11.5 (s, C15), 10.1 (s, C16). $^{31}$P NMR ($CDCl_3$): δ -9.36 ($J_{P\text{-}W}$ = 280 Hz). CV (DMA): $E_{p,a}$ = +0.543 V. IR: $\nu_{NO}$ = 1552 cm$^{-1}$. HRMS $(M+Na)^+$ obs'd (%), calc'd (%), ppm: 748.20465 (100), 748.20679 (81.2), -2.9; 749.21042 (95.3), 749.20933 (81.4), 1.5; 750.20893 (95.9), 750.20929 (100), -0.5; 751.2124 (54.6), 751.21319 (47.3), -1.1; 752.21027 (86.6), 752.2125 (82.4), -3.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(-4-(1H-indol-3-yl)cyclohex-2-enone)) (12)**

In a 4-dram vial charged with a stir bar, in a fume hood, **4** (0.755 g, 1.265 mmol) was added and dissolved in $CHCl_3$ (2 mL), followed by the addition of indole (0.527 g, 4.501 mmol). The solution was yellow and homogeneous. After 1 min, 0.72 mL of 0.17 M TfOH/MeOH solution was added to the reaction solution and the resulting mixture was stirred for 3 hrs. To the reaction solution 2 mL of 0.5M aq. $NaHCO_3$ was

added and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5M aqueous $NaHCO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug then the solvent was removed *in vacuo*. The residue was dissolved in 1 mL $CHCl_3$ and added to 50 mL of stirring hexanes to induce a precipitate. The white precipitate was collected on a 15 mL fine-porosity fritted disk, then rinsed with hexanes (3 x 5 mL) and dried *in vacuo*, giving **12** (0.867 g, 1.214 mmol, 96%).

$^1$H NMR ($CDCl_3$): δ 8.37 (br s, 1H, NH), 8.21 (d, 1H, *J* = 2.0, Pz3B), 7.89 (d, 1H, *J* = 2.0, Pz3A), 7.81 (d, 1H, *J* = 7.8, Ph4'), 7.77 (d, 1H, *J* = 2.0, Pz5B), 7.71 (d, 1H, *J* = 2.0, Pz5C), 7.58 (d, 1H, *J* = 2.0, Pz5A), 7.38 (d, 1H, *J* = 8.0, Ph7'), 7.31 (br s, 1H, indole alkene), 7.30 (d, 1H, *J* = 2.0, Pz3C), 7.17 (t, 1H, *J* = 8.0, Ph6'), 7.14 (t, 1H, *J* = 7.8, Ph5'), 6.37 (t, 1H, *J* = 2.0, Pz4B), 6.20 (t, 1H, *J* = 2.0, Pz4A), 6.18 (t, 1H, *J* = 2.0, Pz4C), 4.40 (br m, 1H, H4), 3.42 (ddd, 1H, *J* = 2.2, 10.2, 12.5, H3), 2.61 (dt, 1H, *J* = 5.8, 17.3, H6), 2.49 (dq, 1H, *J* = 5.8, 5.8, 7.9, 13.1, H5), 2.31 (d, 1H, *J* = 10.2, H2), 2.25 (dt, 1H, *J* = 5.8, 17.3, H6 overlaps with H2), 2.09 (dq, 1H, *J* = 5.8, 5.8, 6.5, 13.1, H5), 1.14 (d, 9H, *J* = 8.4, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 210.9 (s, C1), 143.8 (s, Pz3A), 143.7 (s, Pz3B), 140.2 (s, indole alkene C2'), 136.8 (s, Pz5C), 136.8 (s, C7'a), 136.6 (s, Pz5B), 135.8 (s, Pz5A), 126.6 (s, C3'a), 125.7 (s, indole alkene C3'), 122.2 (s, Pz3C), 121.8 (s, C6'), 119.2 (s, C4' or C5'), 119.1 (s C4' or C5'), 111.5 (s, C7'), 107.0 (s, Pz4B), 106.2 (s, Pz4C), 106.0 (s, Pz4CA), 68.0 (d, *J* = 13.0, C3), 59.7 (s, C2), 35.5 (s, C4), 34.2 (s, C6), 30.2 (s, C5), 13.8 (d, *J* = 28.8, $PMe_3$). $^{31}$P NMR ($CDCl_3$): δ -7.99 ($J_{P\text{-}W}$ = 284 Hz). CV: $E_{p,a}$ = + 0.84 V. IR: $\nu_{BH}$ = 2484 $cm^{-1}$, $\nu_{CO}$ = 1601 $cm^{-1}$, $\nu_{NO}$ = 1562 $cm^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%),

ppm: 713.20422 (89.3), 713.20441 (82.1), -0.3; 714.20582 (89.2), 714.20694 (81.1), -1.6; 715.20631 (92.2), 715.20688 (100), -0.8; 716.20988 (44.6), 716.21082 (46.1), -1.3; 717.21011 (100), 717.2101 (82.8), 0.0.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(4-(1H-pyrrol-2-yl)cyclohex-2-enone)) (13)**

To a 4-dram vial charged with a stir bar, **4** (0.050 g, 0.084 mmol) and pyrrole (0.079 g, 1.190 mmol) were added and dissolved in $CHCl_3$ (1 mL). After 1 min, a 0.17 M DPhAT/EtOH solution (0.5 mL) was added to the reaction solution and stirred for 3 hrs. To the reaction solution 2 mL of 0.5M aqueous $NaHCO_3$ was added and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5M aq. $NaHCO_3$ then dried over anhydrous $MgSO_4$. The organic layer was filtered through a celite plug and the solvent was removed from the filtrate *in vacuo.* The residue was dissolved in $CHCl_3$ and added to stirring hexanes (50 mL). A white precipitate was collected on a 15 mL fine-porosity fritted disk under vacuum, then rinsed with hexanes (3 x 5 mL), giving **13** (0.043 g, 0.0655 mmol, 78 %).

$^1$H NMR ($CDCl_3$): δ 9.21 (s, 1H, NH), 8.16 (d, 1H, *J* = 2.0, Pz3B), 7.79 (d, 1H, *J* = 2.0, Pz3A), 7.75 (d, 1H, *J* = 2.0, Pz5B), 7.68 (d, 1H, *J* = 2.0, Pz5C), 7.56 (d, 1H, *J* = 2.0, Pz5A), 7.38 (d, 1H, *J* = 2.0, Pz3C), 6.69 (ddd, 1H, *J* = 1.7, 2.7, 2.7, pyrrole H5'), 6.36 (t, 1H, *J* = 2.0, Pz4B), 6.21 (t, 1H, *J* = 2.0, Pz4A), 6.19 (t, 1H, *J* = 2.0, Pz4C), 6.09 (q, 1H, *J* = 2.7, pyrrole H4'), 6.01 (ddd, 1H, *J* = 1.7, 2.7, 2.7, pyrrole H3'), 4.23 (br m, 1H, H4), 3.34 (ddd, 1H, *J* = 2.8, 9.7, 12.8, H3), 2.75 (ddd, 1H, *J* = 6.0, 9.2, 16.2, H6), 2.27 (dddd,

1H, *J* = 1.2, 5.3, 5.4, 16.2, H6), 2.22 (d, 1H, *J* = 9.7, H2), 2.18 (dddd, 1H, *J* = 2.0, 5.4, 6.0, 17.7, H5), 1.65 (ddd, 1H, *J* = 5.3, 9.2, 17.7, H5), 1.04 (d, 9H, *J* = 8.6, $PMe_3$). $^{13}C$ NMR ($CDCl_3$): δ 210.9 (s, C1), 143.8 (s, 2C, Pz3A and Pz3B), 140.5 (s, Pz3C), 140.3 (s, C2'), 136.9 (s, Pz5C), 136.6 (s, Pz5B), 136.0 (s, Pz5A), 117.1 (s, C5'), 107.5 (s, C4'), 107.1 (s, Pz4B), 106.2 (s, Pz4C), 105.9 (s, Pz4A), 104.9 (s, C3'), 66.4 (d, *J* = 12.9, C3), 60.1 (s, C2), 38.0 (s, C4), 35.6 (s, C6), 34.8 (s, C5), 13.7 (d, *J* = 28.7, $PMe_3$). $^{31}P$ NMR ($CDCl_3$): δ -8.96 ($J_{P\text{-}W}$ = 280 Hz). CV: $E_{p,a}$ = + 0.82 V. IR: $\nu_{BH}$ = 2493 $cm^{-1}$, $\nu_{CO}$ = 1603 $cm^{-1}$, $\nu_{NO}$ = 1563 $cm^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), ppm: 663.19145 (97.2), 663.18871 (84.2), 4.1; 664.19264 (107.2), 664.19125 (80.3), 2.1; 665.19054 (100), 665.19111 (100), -0.9; 666.19417 (34.7), 666.19523 (43.4), -1.6; 667.19559 (94.1), 667.19435 (83.8), 1.9.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(4-(5-bromo-1H-indol-3-yl)cyclohex-2-enone)) (14)**

To a 4-dram vial charged with a stir bar, in a fume hood, **4** (0.050 g, 0.084 mmol) and 5-bromoindole (0.067 g, 0.346 mmol) were added and dissolved in $CHCl_3$ (1 mL). After 1 min, a 0.17 M TfOH/MeOH solution (0.05 mL) was added to the reaction solution and stirred for 3 hrs. To the reaction solution, 2 mL of 0.5M aq. $NaHCO_3$ was added and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5M aq. $NaHCO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug, and solvent was removed from the filtrate *in vacuo.* The residue was dissolved in $CHCl_3$ and added to hexanes (50 mL). A white precipitate was collected on a 15 mL fine-porosity fritted disk under

vacuum, and then rinsed with hexanes (3 x 5 mL), giving **14** (0.046 g, 0.0579 mmol, 69%).

$^{1}$H NMR ($CDCl_3$): δ 8.83 (s, 1H, NH), 8.22 (d, 1H, *J* = 2.0, Pz3B), 7.92 (d, 1H, *J* = 2.0, Pz3A), 7.85 (d, 1H, *J* = 1.7, Ph4'), 7.78 (d, 1H, *J* = 2.0, Pz5B), 7.73 (d, 1H, *J* = 2.0, Pz5C), 7.59 (d, 1H, *J* = 2.0, Pz5A), 7.33 (d, 1H, *J* = 2.0, Pz3C), 7.31 (d, 1H, *J* = 2.2, indole alkene H2'), 7.22 (dd, 1H, *J* = 1.7, 8.5 Ph), 7.15 (d, 1H, *J* = 8.5, Ph), 6.38 (t, 1H, *J* = 2.0, Pz4B), 6.20 (t, 1H, *J* = 2.0, Pz4A), 6.19 (t, 1H, *J* = 2.0, Pz4C), 4.25 (br m, 1H, H4), 3.31 (ddd 1H, *J* = 1.0, 9.7, 11.4, H3), 2.59-2.54 (m, 1H, H5), 2.54-2.49 (m, 1H, H6), 2.34 (d, 1H, *J* = 9.7, H2), 2.24-2.17 (m, 1H, H6), 2.04-1.97 (m, 1H, H5), 1.17 (d, 9H, *J* = 8.4, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 211.0 (s, C1), 143.9 (s, Pz3A), 143.7 (s, Pz3B), 140.3 (s, Pz3C), 137.0 (s, Pz5C), 136.6 (s, Pz5B), 135.8 (s, Pz5A), 135.4 (s, C7'a), 128.4 (s,C3a'), 125.5 (s, indole alkene C3'), 123.8 (s, indole alkene C2'), 121.4 (s, C4'), 113.0 (s, Ph), 112.6 (s, Ph), 112.4 (s, C5'), 107.1 (s, Pz4B), 106.3 (s, Pz4A or Pz4C), 106.0 (s, Pz4A or Pz4C), 68.1 (d, *J* = 13.5, C3), 59.7 (s, C2), 35.3 (d, *J* = 2.8, C4), 33.6 (s, C6), 29.0 (s, C5), 13.8 (d, *J* = 28.9, $PMe_3$). $^{31}$P NMR ($CDCl_3$): δ -8.34 ($J_{P\text{-}W}$ = 281 Hz). CV: $E_{p,a}$ = + 0.89 V. IR: $\nu_{BH}$ = 2492 cm$^{-1}$, $\nu_{CO}$ = 1593 cm$^{-1}$, $\nu_{NO}$ = 1562 cm$^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), diff. in ppm: 791.11305 (49.3), 791.11491 (45.8), 2.4; 792.11759 (48), 792.11712 (54.2), 0.6; 793.11539 (100), 793.11539 (100), 0; 794.11609 (75.5), 794.11759 (69.5), 1.9; 795.11838 (113), 795.11776 (100.1), 0.8. $[M + Na]^+$ obs'd (%), calc'd (%), ppm: 791.11305 (43.6), 791.11491 (45.8), -2.4; 792.11759 (42.4), 792.11712 (54.2), 0.6; 793.11539 (88.5), 793.11539 (99.9), 0; 794.11609 (66.8), 794.11759 (69.4), -1.9; 795.11838 (100), 795.11776

(100), 0.8. 796.12048 (32.6), 796.12064 (38.4), -0.2; 797.11798 (44.2), 797.11889 (46.9), -1.1.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(4-(1-methyl-1H-indol-3-yl)cyclohex-2-enone)) (15)**

To a 4-dram vial charged with a stir bar, in a fume hood, **4** (0.050 g, 0.084 mmol) and *N*-methylindole (0.054 g, 0.417 mmol) were added and dissolved in $CHCl_3$ (1mL). After 1 min, a 0.17 M TfOH/MeOH solution (0.05mL) was added to the reaction solution and stirred for 3 hrs. To the reaction solution 2 mL of 0.5M aq. $NaHCO_3$ was added and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5M aq. $NaHCO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug then the solvent was removed *in vacuo.* The residue was dissolved in $CHCl_3$ (1 mL) and added to a stirring solution of hexanes (50mL). A white precipitate was collected on a 15 mL fine-porosity fritted funnel under vacuum, and then rinsed with hexanes (3 x 5 mL), giving **15** (0.045 g, 0.0613 mmol, 73%).

$^1$H NMR ($CDCl_3$): δ 8.22 (d, 1H, *J* = 2.0, Pz3B), 7.90 (d, 1H, *J* = 2.0, Pz3A), 7.79 (d, 1H, *J* = 7.9, Ph4'), 7.77 (d, 1H, *J* = 2.0, Pz5B), 7.71 (d, 1H, *J* = 2.0, Pz5C), 7.58 (d, 1H, *J* = 2.0, Pz5A), 7.36 (d, 1H, *J* = 2.0, Pz3C), 7.34 (d, 1H, *J* = 8.2, Ph7' overlaps with Pz3C), 7.27 (m, 1H, Ph6' overlaps with chloroform), 7.19 (s, 1H, indole alkene H2'), 7.14 (t, 1H, *J* = 7.0, Ph5'), 6.37 (t, 1H, *J* = 2.0, Pz4B), 6.20 (t, 1H, *J* = 2.0, Pz4A), 6.19 (t, 1H, *J* = 2.0, Pz4C), 4.51 (br m, 1H, H4), 3.78 (s, 3H, NMe), 3.38 (ddd, 1H, *J* = 1.2, 9.8, 11.6, H3), 2.60-2.55 (m, 1H, H6), 2.55-2.49 (m, 1H, H5), 2.31 (d, 1H, *J* = 9.8, H2), 2.30-2.22 (m,

1H, H6), 2.08-2.01 (m, 1H, H5), 1.17 (d, 9H, *J* = 8.4, $PMe_3$). $^{13}C$ NMR ($CDCl_3$): δ 210.6 (s, C1), 143.7 (s, Pz3A), 143.7 (s, Pz3B), 140.3 (s, Pz3C), 137.4 (s, C7'a or C3a'), 136.8 (s, Pz5C), 136.5 (s, Pz5B), 135.7 (s, Pz5A), 127.1 (s, C7'a or C3a'), 127.0 (s, indole alkene C2'), 124.7 (s, indole alkene C3'), 121.6 (s, C6'), 119.2 (s, C4'), 118.7 (s, C5'), 109.5 (s, C7'), 107.0 (s, Pz4B), 106.1 (s, Pz4A or Pz4C), 106.0 (s, Pz4A or Pz4C), 68.2 (d, *J* = 13.1, C3), 59.7 (s, C2), 35.4 (d, *J* = 2.8 C4), 33.9 (s, C6), 32.8 (s, NMe), 29.8 (s, C5), 13.8 (d, *J* = 28.8, $PMe_3$). $^{31}P$ NMR ($CDCl_3$): δ -7.86 ($J_{P\text{-}W}$ = 283 Hz). CV: $E_{p,a}$ = + 1.00 V. IR: $\nu_{BH}$ = 2492 $cm^{-1}$, $\nu_{CO}$ = 1612 $cm^{-1}$, $\nu_{NO}$ = 1562 $cm^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), ppm: 727.21835 (89.6), 727.22008 (81.5), -2.4; 728.22153 (72.6), 728.2226 (81.3), -1.5; 729.22211 (100), 729.22256 (100), -0.6; 730.22491 (45.5), 730.22646 (46.8), -2.1; 731.22543 (73.3), 731.22577 (82.5), -0.5.

**[TpW(NO)(PMe3)(2,3-*η2*-*N*-(4-(1H-pyrrol-2-yl)cyclohex-2-enylidene)-*N*-methylmethanaminium)](OTf) (18).**

In a 4-dram vial, **7** (0.055 g, 0.071 mmol) and DPhAT (0.002 g, 0.0062 mmol) were dissolved in a solution of pyrrole (0.042 g, 0.62 mmol) in $CH_3CN$ (0.304 g) forming a homogeneous tan solution. The solution was allowed to react for 2 h. The reaction mixture was added to 50 mL of stirring $Et_2O$ to precipitate a light brown solid. The solid was dried *in vacuo* to give **18** (0.031 g, 0.0369 mmol, 52%). $^1H$ NMR ($CDCl_3$): δ 10.32 (s, 1H, N-H), 8.02 (d, 1H, *J* = 2.2, Tp), 7.82 (d, 1H, *J* = 2.2, Tp), 7.79 (d, 1H, *J* = 2.2, Tp), 7.77 (d, 1H, *J* = 2.2, Tp), 7.74 (d, 1H, *J* = 2.2, Tp), 7.05 (d, 1H, *J* = 2.2, Tp), 6.86 (dd, 1H, *J* = 2.6, 4.2, H5'), 6.4 (t, 1H, *J* = 2.2, Tp), 6.37 (t, 1H, *J* = 2.2, Tp), 6.31 (t, 1H, *J* = 2.2, Tp), 6.03 (dd, 1H, *J* = 2.8, 5.5, pyr-β), 5.95 (dd, 1H, *J* = 2.8, 4.8, pyr-β), 4.43 (m,

1H, H4), 3.97 (ddd, 1H, *J* = 3.3, 8.9, 15.0, H3), 3.46 (s, 3H, NMe'B), 2.76 (m, 2H, H6), 2.58 (d, 1H, *J* = 8.9, H2), 2.32 (s, 3H, NMe'A ), 2.19 (buried, 1H, H5b), 2.08 (m, 1H, H5a), 1.06 (d, 9H, *J* = 8.9, $PMe_3$). 13C NMR ($CDCl_3$): δ 186.8 (s, C1), 144.2(s, Tp), 143.1 (s, Tp), 142.4 (s, Tp), 137.7 (s, Tp), 137.6 (s, Tp), 137.5 (s, Tp), 137.4 (s, C2'), 118.7 (s, C5'), 107.8 (s, Tp), 107.0 (s, Tp), 106.4 (s, pyr-β), 106.4 (s, Tp), 105.4 (s, pyr-β), 69.6 (d, *J* = 14, C3), 56.9 (s, C2), 42.1 (s, NMe'B), 40.9 (s, NMe'A ), 37.2 (s, C4), 33.8 (s, C5), 27.2 (s, C6), 14.1 (d, *J* = 30, $PMe_3$). $^{31}P$ ($CD_3CN$): δ -8.06 ($J_{P\text{-}W}$ = 283 Hz). CV: $E_{p,a}$ = +1.29 V. IR: $\nu_{BH}$ = 2507 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1574 $cm^{-1}$. HRMS: ($M^+$) obs'd (%), calc'd (%), ppm: 690.2359 (82.6), 690.23602 (83.1), -0.2; 691.23784 (69.4), 691.23853 (80.9), -1; 692.23749 (100), 692.23844 (100), -1.4; 693.24245 (43.6), 693.24243 (44.9), 0; 694.24083 (79.4), 694.24168 (83.1), -1.2.

**[TpW(NO)($PMe_3$)N-methyl-N-(4-(5-methylfuran-2-yl)cyclohex-2-en-1-ylidene)methanaminium](OTf) (19)**

In a 4-dram vial charged with a stir bar, 2-methylfuran (1 mL, 13.38 mmol) was added, then mixed with MeCN (~0.2 mL). The resulting solution was treated with a solution of Triflic acid (TfOH) in DCM (10 mL, 0.0034 M) and allowed to stir for 1 min. To this mixture **7** (0.1200 g, 0.155 mmol) was added, giving a red and homogeneous solution. After 1 h, the reaction was quenched outside of the glovebox by the addition of 25 mL of a sat. aq. $NaHCO_3$ solution. The reaction mixture was extracted with DCM (3 x 30mL). The combined organic layers were dried over $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The residue was redissolved in DCM (4 mL), and $Et_2O$ (100 mL) was added slowly to

induce precipitation of an off-white solid. The solid was collected on a 15 mL fine porosity fritted funnel giving **19** (0.0965 g, 0.113 mmol, 73%).

$^{1}$H NMR ($CDCl_3$): δ 8.01 (d, *J* = 2.0, 1H, Pz3B), 7.89 (d, *J* = 2.0, 1H, Pz5C), 7.80 (d, *J* = 2.0, 1H, Pz5A or Pz5B), 7.79 (d, *J* = 2.0, 1H, Pz5A or Pz5B), 7.53 (d, 1H, *J* = 2.0, Pz3C), 7.12 (d, 1H, *J* = 2.0, Pz3A), 6.45 (t, *J* = 2.0, 1H, Pz4C), 6.37 (t, *J* = 2.0, 2H, Pz4A and Pz4B), 6.12 (d, 1H, *J* = 2.91, H5'), 5.95 (dd, *J* = 1.0, 2.91, 1H, H6'), 4.13 (m, 1H, H4), 3.6 (m, 1H, H3), 3.55 (s, 3H, NMe'B), 2.70 (m, 2H, H6), 2.35 (s, 3H, NMe'A), 2.30 (d, *J* = 1.0, 3H, Me-7'), 2.34 (buried, 1H, H5), 2.31 (buried, 1H, H2), 2.02 (m, 1H, H5), 1.21 (d, *J* = 8.93, 9H, $PMe_3$) $^{13}$C NMR ($CDCl_3$): δ 186.18 (s, C1), 159.64 (s, C4'), 151.16 (s, C7'), 144.43 (s, Pz3B), 143.44 (s, Pz3A), 140.94 (s, Pz3C), 138.33 (s, Pz5C), 138.27 (s, Pz5A or Pz5B), 138.07 (s, Pz5A or Pz5B), 108.02 (s, Pz4C), 107.82 (s, Pz4A or Pz4B), 107.52 (s, Pz4A or Pz4B), 106.68 (s, C6'), 106.32 (s, C5'), 68.08 (s, C3), 54.93 (s, C2), 42.49 (s, NMe'B), 41.18 (s, NMe'A), 37.01 (s, C4), 28.54 (s, C5), 26.63 (s, C6), 13.94 (s, Me-7') $^{31}$P ($CDCl_3$): δ -9.23 ($J_{P\text{-}W}$ = 281 Hz). CV (DMA): $E_{p,a}$ = +1.20 V. IR: $\nu_{BH}$ = 2507 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1568 $cm^{-1}$. HRMS ($M^+$) obs'd (%), calc'd (%), ppm: 705.23488 (56.7), 705.2357 (82.6), -1.2; 706.23708 (63), 706.23823 (80.9), -1.6; 707.23777 (100), 707.23815 (100), -0.5; 708.24074 (35.6), 708.24214 (45.5), -2; 709.24001 (75.6), 709.24137 (83), -1.9.

**[TpW(NO)($PMe_3$)*N*-(2',4'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1*H*)-ylidene)-*N*-methylmethanaminium](OTf) (20)**

In a 4-dram vial charged with a stir bar, 1,3-dimethoxybenzene (1.5 mL, 10.29 mmol) was added. To this a TfOH/DCM solution (10 mL, 0.0005 M) and MeCN (0.20 mL) were added. The mixture was stirred for 1 min. To this mixture **7** (0.3257 g, 0.42 mmol) was added. After 1 h, the reaction was quenched outside of the glovebox by the addition of 25 mL of a sat. aq. $NaHCO_3$ solution. The reaction was extracted with DCM (3 x 25 mL), and the combined organic layers dried over anhydrous $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The yellow residue was redissolved in MeCN (5 mL), and $Et_2O$ (150 mL) was slowly added to induce the precipitation of an off-white solid. The solid was collected on a 15 mL fine porosity fritted funnel giving **20** (0.2795 g, 0.3066 mmol, 73%).

$^1$H NMR ($CDCl_3$): δ 8.03 (d, *J* = 2.0, 1H, Pz3B), 7.85 (d, *J* = 2.0, 1H, Pz5C), 7.78 (t, *J* = 2.0, 2H, Pz5A and Pz5B), 7.55-7.52 (m, 2H, Pz3C and H6'), 7.12 (d, 1H, *J* = 2.0, Pz3A), 6.66 (dd, *J* = 2.4, 9.0, 1H, H5'), 6.48 (d, *J* = 2.4, 1H, H3'), 6.43 (t, *J* = 2.0, 1H, Pz4C), 6.37 (m, 2H, Pz4B and Pz4A), 4.75 (m, 1H, H1), 3.85 (s, 3H, H2'OMe or H4'OMe), 3.84 (s, 3H, H4'OMe or H2'OMe), 3.65 (m, 1H, H6), 3.54 (3H, s, NMe'B), 2.79 (m, 2H, H3), 2.47 (d, *J* = 9.38, 1H, H5), 2.39 (3H, s, NMe'A), 2.25 (m, 1H, H2), 1.75 (m, 1H, H2), 1.10 (d, *J* = 8.95, 9H, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 185.94 (s, C4), 159.54 (s, C2' or C4'), 157.08 (s, C2' or C4'), 144.15 (s, Pz3B), 143.42 (s, Pz3A), 140.98 (s, Pz3C), 138.08 (s, Pz5A), 137.88 (s, Pz5C), 137.73 (s, Pz5B), 129.61 (s, C1'), 129.21 (s, C6'), 107.90 (s, Pz4C), 107.51 (s, Pz4B), 107.07 (s, Pz4A), 105.37 (s, C5'), 98.77 (s, C3'), 71.23 (d, *J* = 13.5, C6), 56.49 (s, C5), 55.60 (s, H2'OMe or H4'OMe), 55.54 (s, H2'OMe or H4'OMe), 42.31 (s, NMe'B), 41.01 (s, NMe'A), 34.61 (s, C1), 32.65 (s, C2), 26.88 (s, C3), 14.16

(d, $J$ = 30.2, $PMe_3$). $^{31}P$ NMR ($CDCl_3$): δ -8.55 ($J_{P\text{-}W}$ = 286 Hz). CV (DMA): $E_{p,a}$ = 1.20 V. IR: $\nu_{BH}$ = 2503 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1567 $cm^{-1}$. HRMS ($M^+$) obs'd (%), calc'd (%), ppm: 761.26172 (100), 761.26196 (80.8), -0.3; 762.2634 (90.7), 762.26448 (81.3), -1.4; 763.26412 (100), 763.26446 (100), -0.4; 764.26713 (56.5), 764.26831 (47.6), -1.5; 765.268 (98.8), 765.26767 (82.4), 0.4.

**[TpW(NO)($PMe_3$)*N*-methyl-*N*-(2',4',6'-trimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1*H*) ylidene)methanaminium](OTf) (21)**

In a 4-dram vial charged with a stir bar, 1,3,5-trimethoxybenzene (1.021 g, 6.064 mmol) was added, then dissolved in MeCN (~0.2 mL) treated with a solution of TfOH in DCM (10 mL, 0.0034 M) and allowed to stir for 1 min. To this mixture **7** (0.2011 g, 0.26 mmol) was added. The mixture appeared red and homogeneous. After stirring for 1 h, the reaction was quenched outside of the glovebox by the addition of 30 mL of sat. aq. $NaHCO_3$ solution. The reaction mixture was extracted with DCM (3 x 30 mL). The organic layers were combined and dried over anhydrous $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The residue was redissolved in MeCN (6 mL), and $Et_2O$ (150 mL) was added slowly to induce precipitation of a white solid. The solid was collected on a 15 mL fine porosity fritted funnel giving **21** (0.1521 g, 3.759 mmol, 62%).

$^1H$ NMR ($CDCl_3$): δ 8.03 (d, $J$ = 2.0, 1H, Pz3B), 7.86 (d, $J$ = 2.0, 1H, Pz5C), 7.78 (d, $J$ = 2.0, 1H Pz5A), 7.77 (d, $J$ = 2.0, 1H, Pz5B), 7.38 (d, $J$ = 2.0, 1H, Pz3C), 7.02 (d, $J$ = 2.0, 1H, Pz3A), 6.44 (t, $J$ = 2.0, 1H, Pz4C), 6.37 (t, $J$ = 2.0, 2H, Pz4B and Pz4A), 6.21 (s, 2H,

H5' and H3'), 5.02 (ddd, 1H, *J* = 2.55, 6.15, 10.06, H1) 3.86 (s, 6H, H2'OMe and H6'OMe), 3.84 (s, 3H, H4'OMe), 3.84 (buried, 1H, H6), 3.57 (s, 3H, NMe'B), 2.85 (m, 2H, H3), 2.32 (s, 3H, NMe'A), 2.31 (buried, 1H, H5), 2.06 (m, 1H, H2), 1.97 (m, 1H, H2), 1.07 (d, *J* = 9.06, 9H, $PMe_3$). $^{13}C$ NMR ($CDCl_3$): δ 185.5 (s, Iminium), 160.2 (s, C2', C4', and C6'), 144.2 (s, Pz3B), 143.5 (s, Pz3A), 140.4 (s, Pz3C), 138.2 (s, Pz5A), 137.8 (s, Pz5C), 137.8 (s, Pz5B), 116.20 (s, C1'), 108.0 (s, Pz4C), 107.5 (s, Pz4B or Pz4A), 107.0 (s, Pz4B or Pz4A), 91.3 (s, C3' and C5'), 72 (d, *J* = 13.43, C6), 57.0 (s, C5), 55.9 (s, H2'OMe and H4'OMe or H6'OMe), 55.5 (s, H2'OMe and H4'OMe or H6'OMe), 42.3 (s, NMe'B), 40.8 (s, NMe'A), 32.0 (s, C1), 30.5 (s, C2) 27.4 (s, C3), 14.1 (d, *J* = 30.0, $PMe_3$). $^{31}P$ NMR ($CDCl_3$): δ -8.32 ($J_{P\text{-}W}$ = 290 Hz). CV (DMA): $E_{p,a}$ = 1.13 V. $\nu_{BH}$ = 2506 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1568 $cm^{-1}$. HRMS ($M^+$) obs'd (%), calc'd (%), ppm: 791.27138 (95), 791.27254 (80.1), -1.5; 792.27477 (82.1), 792.27506 (81.4), -0.4; 793.2743 (92.1), 793.27506 (100), -1; 794.27958 (54.4), 794.27887 (48.4), 0.9; 795.2786 (100), 795.27826 (82.2), 0.4.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(5-fluoro-4-(1H-indol-3-yl)cyclohex-2-enone)) (22)**

In a NMR tube, in a fume hood, **4** (0.021 g, 0.036 mmol) was added and dissolved in 0.5 mL DCM, giving a solution that was yellow and homogeneous. To this solution Selecfluor® (0.018 g, 0.050 mmol) dissolved in $CH_3CN$ (1 mL) was added, then $Na_2CO_3$ (0.011 g, 0.107 mmol) was added, resulting in a heterogeneous solution. The solutions were combined and stirred for 1 min, then indole (0.020 g, 0.175 mmol) was added to the reaction solution and it was stirred for 17 hrs. To the reaction solution 2 mL of sat. aq. $NaHCO_3$ was added and the two layers were

separated. The DCM layer was extracted two times with 1 mL of sat. aq. $NaHCO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug, then the solvent was removed *in vacuo*. The residue was dissolved in 1 mL $CHCl_3$ and added to 50 mL of stirring hexanes, which resulted in a yellow precipitate. The precipitate was collected on a 15 mL fine-porosity fritted disk under vacuum, then rinsed with hexanes (3 x 5 mL) and dried *in vacuo*, giving **22** (0.020 g, 0.0277 mmol, 77%).

$^1$H NMR ($d_6$-DMSO): δ 10.56 (br s, 1H, NH), 8.11 (d, 1H, *J* = 2.0, Pz3B), 7.83 (d, 1H, *J* = 2.0, Pz5B), 7.78 (d, 1H, *J* = 2.0, Pz5C), 7.70 (d, 1H, *J* = 2.0, Pz3A), 7.67 (d, 1H, *J* = 7.8, Ph4'), 7.63 (d, 1H, *J* = 2.0, Pz5A), 7.37 (d, 1H, *J* = 2.0, Pz3C), 7.36 (d, 1H, *J* = 2.3, indole alkene H2'), 7.34 (d, 1H, *J* = 7.8, Ph7'), 7.05 (t, 1H, *J* = 7.8, Ph6'), 6.98 (t, 1H, *J* = 7.8, Ph5'), 6.38 (t, 1H, *J* = 2.0, Pz4B), 6.22 (t, 1H, *J* = 2.0, Pz4C), 6.14 (t, 1H, *J* = 2.0, Pz4A), 5.16 (dddd, 1H, *J* = 4.0, 4.0, 6.0, 50.1, H5), 4.63 (dddd, 1H, *J* = 0.9, 2.5, 4.0, 23.9, H4), 3.29 (dddd, 1H, *J* = 2.5, 3.1, 9.5, 12.0, H3), 2.93 (ddd, 1H, *J* = 4.0, 16.3, 28.2, H6), 2.43 (dddd, 1H, *J* = 0.9, 6.0, 14.9, 16.3, H6), 2.11 (d, 1H, *J* = 9.5, H2), 0.98 (d, 9H, *J* = 8.6, $PMe_3$). $^{13}$C NMR ($d_6$-DMSO): δ 205.0 (s, C1), 143.2 (s, Pz3B), 142.4 (s, Pz3A), 139.9 (s, Pz3C), 136.6 (s, Pz5C), 136.3 (s, Pz5B), 136.0 (s, C7'a), 135.4 (s, Pz5A), 127.0 (s, C3'a), 123.3 (s, indole alkene C2'), 120.6 (s, C6'), 118.6 (s, C4'), 118.1 (s C5'), 118.0 (d, *J* = 3.3, C3'), 111.0 (s, C7'), 106.6 (s, Pz4B), 105.9 (s, Pz4C), 105.0 (s, Pz4CA), 93.3 (d, *J* = 172.3, C5), 62.1 (dd, *J* = 5.6, 12.8, C3), 58.1 (s, C2), 41.3 (d, *J* = 22.0, C6), 39.5 (s, overlaps with $d_6$-DMSO, C4), 12.9 (d, *J* = 29.0, $PMe_3$). $^{31}$P NMR ($CDCl_3$): δ -8.88 ($J_{P\text{-}W}$ = 280 Hz). CV: $E_{p,a}$ = + 0.93 V. IR: $\nu_{BH}$ = 2496 cm$^{-1}$, $\nu_{CO}$ = 1598 cm$^{-1}$, $\nu_{NO}$ = 1567 cm$^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), diff. in ppm: 731.19283 (84.1), 731.19499

(82.1), 3; 732.19579 (69.2), 732.19752 (81.1), 2.4; 733.19704 (100), 733.19746 (100), 0.6; 734.19874 (51.2), 734.2014 (46.1), 3.6; 735.20095 (91.1), 735.20067 (82.8), 0.4. $[M + Na]^+$ obs'd (%), calc'd (%), ppm: 731.19251 (68.8), 731.19499 (82.1), -3.4; 732.19627 (96), 732.19752 (81.1), -1.7; 733.19898 (100), 733.19746 (100), 2.1; 734.19747 (53.5), 734.2014 (46.1), -5.4; 735.19886 (93.3), 735.20067 (82.8), -2.5.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(5-fluoro-4-(1H-pyrrol-2-yl)cyclohex-2-enone)) (23)**

In a NMR tube, in a fume hood, **4** (0.053 g, 0.089 mmol) was added and dissolved in 0.5 mL DCM, giving a solution which was yellow and homogeneous. To this, Selecfluor® (0.039 g, 0.111 mmol) dissolved in 1 mL acetonitrile was added, then $Na_2CO_3$ (0.031 g, 0.294 mmol) was added resulting in a heterogeneous solution. The solution was stirred for 1 min, then pyrrole (0.244 g, 3.636 mmol) was added to the reaction solution and the mixture stirred for 4 hrs. To the reaction solution 2 mL of sat. aq. $NaHCO_3$ was added and the two layers separated. The DCM layer was extracted two times with 1 mL of sat. aq. $NaHCO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug then the solvent was removed *in vacuo*. The residue was dissolved in 1 mL $CHCl_3$ and added to 50 mL of stirring hexanes, which resulted in a yellow precipitate. The precipitate was collected on a 15 mL fine-porosity fritted disk under vacuum, then rinsed with hexanes (3 x 5 mL) and dried *in vacuo*. A yellow precipitate **23** was collected (0.034 g, 0.050 mmol, 56.1 % yield).

$^{1}$H NMR ($CDCl_3$): δ 9.11 (s, 1H, NH), 8.13 (d, 1H, *J* = 2.0, Pz3B), 7.75 (d, 1H, *J* = 2.0, Pz5B), 7.71 (d, 1H, *J* = 2.0, Pz3A), 7.69 (d, 1H, *J* = 2.0, Pz5C), 7.56 (d, 1H, *J* = 2.0, Pz5A), 7.34 (d, 1H, *J* = 2.0, Pz3C), 6.79 (ddd, 1H, *J* = 1.7, 2.3, 2.3, pyrrole H5'), 6.36 (t, 1H, *J* = 2.0, Pz4B), 6.20 (t, 1H, *J* = 2.0, Pz4C), 6.16 (t, 1H, *J* = 2.0, Pz4A), 6.12 (m, 2H, pyrrole H4' and H3'), 5.09 (dddd, 1H, *J* = 3.0, 3.0, 5.3, 50.4, H5), 4.47 (ddd, 1H, *J* = 2.7, 3.0, 35.0, H4), 3.20 (dddd, 1H, *J* = 1.5, 2.7, 9.4, 12.6, H3), 3.05 (ddd, 1H, *J* = 3.0, 16.4, 35.0, H6), 2.62 (dddd, 1H, *J* = 1.5, 5.3, 12.6, 16.4, H6), 2.28 (d, 1H, *J* = 9.4, H2), 0.98 (d, 9H, *J* = 8.6, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 206.5 (d, *J* = 4.5, C1), 143.9 (d, *J* = 1.9, Pz3B), 143.6 (s, Pz3A), 140.4 (s, Pz3C), 136.9 (s, Pz5C), 136.7 (s, Pz5B), 136.1 (s, Pz5A), 134.9 (d, *J* = 2.1, C2'), 118.0 (s, C5'), 107.4 (s, C3' or C4'), 107.2 (s, C3'/C4' or Pz4B), 107.2 (s, C3'/C4' or Pz4B), 106.4 (s, Pz4C), 105.9 (s, Pz4A), 96.2 (d, *J* = 172.5, C5), 60.6 (dd, *J* = 4.0, 13.2, C3), 59.1 (s, C2), 42.3 (dd, *J* = 2.4, 18.2, C4), 42.2 (d, *J* = 22.4, C6), 13.6 (d, *J* = 29.0, $PMe_3$). $^{31}$P NMR ($CDCl_3$): δ -9.68 ($J_{P\text{-}W}$ = 275 Hz). CV: $E_{p,a}$ = + 0.93 V. IR: $\nu_{BH}$ = 2493 $cm^{-1}$, $\nu_{CO}$ = 1614 $cm^{-1}$, $\nu_{NO}$ = 1557 $cm^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), ppm: 681.17903 (86.8), 681.17929 (84.2), -0.4; 682.18077 (82.5), 682.18183 (80.3), -1.6; 683.18074 (100), 683.18169 (100), -1.4; 684.1834 (45.7), 684.18581 (43.3), -3.5; 685.18549 (80.7), 685.18493 (83.8), 0.8.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(5-chloro-4-(1H-pyrrol-2-yl)cyclohex-2-enone)) (24)**

In a 4-dram vial with stir bar, in a fume hood, **4** (0.074 g, 0.124 mmol) was added and dissolved in 0.5 mL DCM. The yellow, homogeneous solution was placed in an ice bath. NCS (0.005 g, 0.039 mmol) was dissolved in 0.25 mL DCM, then placed in the ice bath. The two solutions were combined and stirred, still cold, for 30 sec,

resulting in the reaction solution turning a dark yellow color. After 30 sec, pyrrole (0.017 g, 0.255 mmol) was added to the reaction solution and stirred, still cold, for 4.5 hrs. To the reaction solution 2 mL of sat. aq. $Na_2CO_3$ was added and the two layers separated. The DCM layer was extracted two times with 1 mL of sat. aq. $Na_2CO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug then the solvent was removed *in vacuo*. The residue was dissolved in 1 mL $CHCl_3$ and added to 50 mL of hexanes, which resulted in a precipitate. The precipitate was collected on a 15 mL fine-porosity fritted disk under vacuum, then rinsed with $Et_2O$ (3 x 5 mL) and dried *in vacuo*. An off-white precipitate **24** was collected (0.060 g, 0.0868 mmol, 70%).

$^1$H NMR ($CDCl_3$): δ 8.81 (br s, 1H, NH), 8.34 (d, 1H, *J* = 2.0, Pz3B), 7.77 (d, 1H, *J* = 2.0, Pz3A overlaps with Pz5B), 7.76 (d, 1H, *J* = 2.0, Pz5B overlaps with Pz3A), 7.71 (d, 1H, *J* = 2.0, Pz5C), 7.58 (d, 1H, *J* = 2.0, Pz5A), 7.35 (d, 1H, *J* = 2.0, Pz3C), 6.81 (ddd, 1H, *J* = 1.6, 2.6, 2.6, pyrrole H5'), 6.37 (t, 1H, *J* = 2.0, Pz4B), 6.23 (ddd, 1H, *J* = 1.6, 2.6, 2.6, pyrrole H3'), 6.21 (t, 1H, *J* = 2.0, Pz4C), 6.18 (m, 1H, pyrrole H4' overlaps with Pz4A), 6.18 (t, 1H, *J* = 2.0, Pz4A overlaps with pyrrole H4'), 4.81 (ddd, 1H, *J* = 3.6, 4.0, 6.5, H5), 4.54 (br s, 1H, H4), 3.17 (m, 1H, H3 overlaps with H6), 3.15 (dd, 1H, *J* = 4.0, 16.4, H6 overlaps with H3), 2.64 (ddd, 1H, *J* = 1.2, 6.5, 16.4, H6), 2.22 (d, 1H, *J* = 9.4, H2), 1.00 (d, 9H, *J* = 8.6, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 205.6 (s, C1), 143.9 (s, Pz3A or Pz3B), 143.8 (s, Pz3A or Pz3B), 140.4 (s, Pz3C), 137.0 (s, Pz5C), 136.8 (s, Pz5B), 136.0 (s, Pz5A), 135.0 (s, C2'), 117.6 (s, C5'), 108.3 (s, C3'), 108.0 (s, C4'), 107.2 (s, Pz4B), 106.4 (s, Pz4C), 106.0 (s, Pz4A), 65.3 (s, C5), 62.2 (d, *J* = 13.2, C3), 57.9 (s, C2),

45.3 (s, C6), 44.6 (d, $J$ = 2.4, C4), 13.6 (d, $J$ = 29.0, $PMe_3$). $^{31}P$ NMR ($CDCl_3$): δ -9.77 ($J_{P\text{-}W}$ = 277 Hz). CV: $E_{p,a}$ = + 1.01 V. IR: $\nu_{BH}$ = 2493 $cm^{-1}$, $\nu_{CO}$ = 1604 $cm^{-1}$, $\nu_{NO}$ = 1564 $cm^{-1}$. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), ppm: 681.17903 (86.8), 681.17929 (84.2), -0.4; 682.18077 (82.5), 682.18183 (80.3), -1.6; 683.18074 (100), 683.18169 (100), -1.4; 684.1834 (45.7), 684.18581 (43.3), -3.5; 685.18549 (80.7), 685.18493 (83.8), 0.8.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(5-chloro-4-(1H-indol-3-yl)cyclohex-2-enone)) (25)**

In a 4-dram vial charged with a stir bar, in a fume hood, **4** (0.050 g, 0.084 mmol) was added and dissolved in 0.5 mL $CHCl_3$. The yellow, homogeneous solution was placed in an ice bath. A separate solution was prepared of *N*-chlorosuccinimide (NCS) (0.015 g, 0.116 mmol) dissolved in MeCN (0.25 mL), and placed in the ice bath. The solutions were combined and stirred, still cold, for 2 min, resulting in the reaction solution turning a dark yellow color. After 2 min, indole (0.048 g, 0.416 mmol) was added to the reaction solution, still cold, and it was stirred for 25 min. To the reaction solution 2 mL of sat. aq. $Na_2CO_3$ was added and the two layers separated. The $CHCl_3$ layer was extracted two times with 1 mL of sat aq. $Na_2CO_3$ then dried over $MgSO_4$. The organic layer was filtered through a celite plug, then the solvent was removed *in vacuo*. The residue was dissolved in 1 mL $CHCl_3$ and added to stirring hexanes (50 mL), which resulted in a precipitate. The precipitate was collected on a 15 mL fine-porosity fritted funnel under vacuum, washed with hexanes (3 x 5 mL) and dried *in vacuo*. An off-white precipitate **25** was collected (0.038 g, 0.0512 mmol, 61%).

$^{1}$H NMR ($CDCl_3$): δ 8.48 (br s, 1H, NH), 8.17 (d, 1H, *J* = 2.0, Pz3B), 7.84 (d, 1H, *J* = 2.0, Pz3A), 7.83 (d, 1H, *J* = 7.8, Ph4') 7.77 (d, 1H, *J* = 2.0, Pz5B), 7.71 (d, 1H, *J* = 2.0, Pz5C), 7.59 (d, 1H, *J* = 2.0, Pz5A), 7.43 (d, 1H, *J* = 2.3, indole alkene H2'), 7.39 (t, 1H, *J* = 7.8, Ph7'), 7.31 (d, 1H, *J* = 2.0, Pz3C), 7.20 (t, 1H, *J* = 7.8, Ph6' overlaps with Ph5'), 7.16 (t, 1H, *J* = 7.8, Ph5' overlaps with Ph6'), 6.37 (t, 1H, *J* = 2.0, Pz4B), 6.20 (t, 1H, *J* = 2.0, Pz4A), 6.17 (t, 1H, *J* = 2.0, Pz4C), 5.00 (ddd, 1H, *J* = 4.7, 7.7, 8.6, H5), 4.81 (br m, 1H, H4), 3.31 (ddd, 1H, *J* = 2.8, 9.6, 12.2, H3), 3.23 (dd, 1H, *J* = 4.7, 17.0, H6), 2.77 (ddd, 1H, *J* = 0.9, 7.7, 17.0, H6), 2.30 (d, 1H, *J* = 9.6, H2), 1.08 (d, 9H, *J* = 8.5, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 206.6 (s, C1), 143.9 (s, Pz3A or Pz3B), 143.9 (s, Pz3A or Pz3B), 140.4 (s, Pz3C), 137.0 (s, Pz5C), 136.7 (s, Pz5B), 136.0 (s, C7'a), 136.0 (s, Pz5A), 128.0 (s, C3'a), 123.7 (s, indole alkene C2'), 122.0 (s, C6'), 120.7 (s, C3'), 119.6 (s, C5'), 119.4 (s C4'), 111.5 (s, C7'), 107.2 (s, Pz4B), 106.3 (s, Pz4CA or Pz4C), 106.0 (s, Pz4CA or Pz4C), 65.5 (d, *J* = 15.5, C3), 62.9 (s, C5), 58.1 (s, C2), 44.9 (s, C6), 42.1 (s, C4), 13.9 (d, *J* = 28.9, $PMe_3$). $^{31}$P NMR ($CDCl_3$): δ -8.90 ($J_{P\text{-}W}$ = 280 Hz). CV: $E_{p,a}$ = + 1.07 V. IR: $\nu_{BH}$ = 2494 $cm^{-1}$, $\nu_{CO}$ = 1602 $cm^{-1}$, $\nu_{NO}$ = 1557 $cm^{-1}$. HRMS: $[M + Na]^+$ obs'd (%), calc'd (%), ppm: 769.14892 (64.4), 769.14738 (65.1), 2.0; 770.14914 (69.3), 770.14973 (68.5), -0.8; 771.14728 (100), 771.14873 (100), -1.9; 772.14971 (57.6), 772.15133 (57.1), -2.1; 773.15087 (94.8), 773.15135 (90.9), -0.6.

**TpW(NO)($PMe_3$)(2,3-$\eta^2$-(5-hydroxy-4-(1H-indol-3-yl)cyclohex-2-enone)) (27)**

In a NMR tube, in a fume hood, **26** (0.014 g, 0.021 mmol) was added and dissolved in 0.5 mL $CHCl_3$, followed by the addition of indole (0.028 g, 0.246 mmol). The solution

was yellow and homogeneous. After 1 min, 0.02 mL of 0.17M TfOH/EtOH solution was added to the reaction solution and the mixture was stirred for 48 hrs. The solution became heterogeneous and the resulting solid was collected on a 15 mL fine-porosity fritted disk under vacuum, then rinsed with 5 mL of hexane and dried *in vacuo*. A yellow precipitate was obtained (0.009 g, 0.0126 mmol, 60%).

$^{1}$H NMR ($d_6$-DMSO): δ 10.88 (br s, 1H, NH), 8.19 (d, 1H, *J* = 2.0, Pz3B), 8.09 (d, 1H, *J* = 2.0, Pz5B), 8.06 (d, 1H, *J* = 2.0, Pz5C), 7.88 (d, 1H, *J* = 2.0, Pz3A), 7.76 (d, 1H, *J* = 2.0, Pz5A), 7.68 (d, 1H, *J* = 8.0, Ph4' or Ph7'), 7.61 (d, 1H, *J* = 2.0, Pz3C), 7.41 (d, 1H, *J* = 2.1, indole alkene H2'), 7.36 (d, 1H, *J* = 8.0, Ph4' or Ph7'), 7.06 (t, 1H, *J* = 8.0, Ph5' or Ph6'), 6.98 (t, 1H, *J* = 8.0, Ph5' or Ph6'), 6.49 (t, 1H, *J* = 2.0, Pz4B), 6.33 (t, 1H, *J* = 2.0, Pz4C), 6.27 (t, 1H, *J* = 2.0, Pz4A), 3.93 (s, 1H, OH) 4.49 (br m, 1H, H4), 4.29 (ddd, 1H, *J* = 4.5, 4.5, 6.8, H5), 3.23 (ddd, 1H, *J* = 2.5, 9.5, 12.2, H3), 2.65 (dd, 1H, *J* = 4.5, 16.0, H6), 2.09 (dd, 1H, *J* = 6.8, 16.0, H6'), 1.91 (d, 1H, *J* = 9.5, H2), 1.01 (d, 9H, *J* = 8.8, $PMe_3$). $^{13}$C NMR ($d_6$-DMSO): δ 207.4 (s, C1), 143.9 (s, Pz3B), 142.7 (s, Pz5A), 141.1 (s, Pz3C), 137.4 (s, Pz5C), 136.9 (s, Pz5B), 136.1 (s, C7'a), 136.1 (s, Pz3A), 127.9 (s, C3'a), 123.8 (s, indole alkene C2'), 120.5 (s, C5' or C6'), 119.8 (s, C3'), 118.9 (s, C4' or C7'), 117.9 (s C5' or C6'), 111.2 (s, C4' or C7'), 107.1 (s, Pz4B), 106.4 (s, Pz4C), 105.3 (s, Pz4A), 69.5 (s, C5), 64.3 (d, *J* = 13.6, C3), 58.4 (s, C2), 43.8 (s, C6), 41.1 (s, C4), 12.8 (d, *J* = 28.9, $PMe_3$). $^{31}$P NMR ($d_6$-DMSO): δ -6.45 ($J_{P\text{-}W}$ = 283 Hz). CV (DMA/DMSO): $E_{p,a}$ = + 0.84 V. IR: $\nu_{BH}$ = 2486 cm$^{-1}$, $\nu_{CO}$ = 1600 cm$^{-1}$, $\nu_{NO}$ = 1569 cm$^{-1}$. HRMS: $[M + Na]^+$ obs'd (%), calc'd (%), ppm: 751.17891 (78.3), 751.18127 (81.9), -3.1; 752.18242 (87.4), 752.1838 (81), -1.8; 753.18044 (100), 753.18374 (100), -4.4;

754.18811 (37.6), 754.18768 (46.2), 0.6; 755.18565 (79.0), 755.18696 (82.8), -1.7.

**[TpW(NO)($PMe_3$)*N*-2-fluoro-2',4'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1*H*)-ylidene)-*N*-methylmethanaminium] ](OTf) (30)**

In a 4-dram vial charged with a stir bar, 1,3-dimethoxybenzene (0.30 mL, 2.06 mmol) was added. To this a TfOH/DCM solution (1 mL, 0.0034 M) and MeCN (0.20 mL) was added. The homogeneous solution was stirred for 1 min. To this mixture **28** (0.0550 g, 0.066 mmol) was added, creating a light brown homogeneous solution. After 1.5 h, the reaction was quenched, outside of the glovebox, by the addition of 25 mL of sat. aq. $NaHCO_3$ solution. The reaction was extracted with DCM (3 x 25 mL), dried over $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The residue was redissolved in MeCN (3 mL), and $Et_2O$ (150 mL) was slowly added to induce the precipitation of a light brown solid. The solid was collected on a 15 mL fine porosity fritted funnel giving **30** (0.0290 g, 0.031 mmol, 47%).

$^1$H NMR (300 MHz, $CDCl_3$): 7.99 (d, *J* = 2.0, 1H, Pz3B), 7.87 (d, *J* = 2.0, 1H, Pz5C), 7.78 (d, *J* = 2.0, 2H, Pz5B and Pz5B), 7.57 (dd, *J* = 2.29, 8.61,1H, H6'), 7.52 (d, *J* = 2.0, 1H, Pz3C), 7.08 (d, *J* = 2.0, 1H, Pz3a), 6.64 (dd, *J* = 2.42, 8.91, 1H, H8'), 6.50 (d, *J* = 2.42, 1H, H9'), 6.44 (t, *J* = 2.0, 1H, Pz4C), 6.40 (t, *J* = 2.0, 1H, Pz4a), 6.36 (t, *J* = 2.0, 1H, Pz4B), 5.07 (m, 1H, H4), 4.87 (m, 1H, H5), 3.83 (s, 6H, H5'OMe and Hz'OMe), 3.59 (Burried, 1H, H3), 3.53 (s, 3H, NMe'B), 3.29 (m, 1H, H6), 3.09 (dd, *J* = 16.02, 42.14, 1H, H6), 2.49 (d, *J* = 11.43, 1H, H2), 2.30 (s, 1H, NMe'A), 0.99 (d, *J* = 9.09, 9H, $PMe_3$), $^{13}$C NMR ($CDCl_3$): 181.27 (s, C1), 160.32 (s, C7'), 157.41 (s, C5'), 144.68 (s, Pz3B), 143.63 (s, Pz3A), 140.82 (s, Pz3C), 138.52 (s, Pz5a or Pz5b orPz5c), 138.25 (s, Pz5a

or Pz5b or Pz5c), 138.22 (s, Pz5a or Pz5B or Pz5C), 131.60 (s, C9'), 122.67 (d, *J* = 2.96, C4'), 108. 11 (s, Pz4C), 107.91 (s, Pz4B), 107.65 (s, Pz4A), 105.56 (s, C8'), 98.48 (s, C6'), 92.22 (d, *J* = 178.47, C5), 65.84 (d, C3), 57.04 (s, C2), 55.73 (s, C5'OMe/C7'OMe), 42.89 (s, NMeB'), 41.22 (s, NMeA'), 38.62 (d, *J* = 17.98, C4), 33.42 (d, *J* = 23.03, C6), 14.39 (d, *J* = 30.11, $PMe_3$) $^{31}P$ NMR ($CDCl_3$): δ -9.08 ($J_{P\text{-}W}$ = 283 Hz). CV (DMA): $E_{p,a}$ = 1.27 V. IR: $\nu_{BH}$ = 2514 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1571 $cm^{-1}$. HRMS ($M^+$) obs'd (%), calc'd (%), ppm: 779.25124 (80.7), 779.25253 (80.8), -1.7; 780.25368 (74.3), 780.25506 (81.3), -1.8; 781.25432 (100), 781.25504 (100), -0.9; 782.2577 (49.9), 782.25889 (47.6), -1.5; 783.25644 (80.1), 783.25824 (82.4), -2.3.

**[TpW(NO)($PMe_3$)*N*-(2-fluoro-2',4',6'-trimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1*H*)-ylidene)-*N*-methylmethanaminium](OTf) (31)**

In a 4-dram vial charged with a stir bar, 1,3,5-trimethoxybenzene (0.3056 g, 1.81 mmol) was added. To this a TfOH/$CH_2Cl_2$ solution (1 mL, 0.0034 M) and MeCN (0.20 mL) was added and the mixture was stirred for 1 min. To this mixture **28** (0.1029 g, 0.1248 mmol) was added. After 1.5 h, the reaction was quenched, outside of the glovebox, by the addition of 25 mL of sat. aq. $NaHCO_3$. The reaction mixture was extracted with DCM (3 x 25 mL), dried over $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The residue was redissolved in MeCN (3 mL), and $Et_2O$ (150 mL) was slowly added to induce the precipitation of an off-white solid. The solid was collected on a 15 mL fine porosity fritted funnel giving **31** (0.0631 g, 0.066 mmol, 53%).

$^{1}$H NMR (500 MHz, $CDCl_3$): δ 8.0 (d, *J* = 2.0, 1H, Pz3B), 7.89 (d, *J* = 2.0, 1H, Pz5A or Pz5B or Pz5C), 7.79 (d, *J* = 2.0, 2H, Pz5A or Pz5B or Pz5C), 7.43 (d, *J* = 2.0, 1H, Pz3C), 7.09 (d, *J* = 2.0, 1H, Pz3A), 6.47 (t, *J* = 2.0, 1H, Pz4C), 6.41 (t, *J* = 2.0, 1H, Pz4A or PZ4B), 6.37 (t, *J* = 2.0, 1H, Pz4A or Pz4B), 6.25 (d, *J* = 2.3, 1H, H5' or H3'), 6.21 (d, *J* = 2.3, 1H, H5' or H3'), 5.27 (m, 1H, H1), 5.06 (m, 1H, H2), 4.06 (m, 1H, H6), 3.86 (s, 3H, H2'OMe or H4'OMe or H6'OMe), 3.85 (s, 3H, H2'OMe or H4'OMe or H6'OMe), 3.84 (s, 3H, H2'OMe or H4'OMe or H6'OMe), 3.60 (s, 3H, NMe'B), 3.15 (m, 2H, H3), 2.45 (d, J = 9.2, 1H, H5), 2.40 (s, 3H, NMe'A), 1.09 (d, *J* = 8.88, 9H, $PMe_3$). $^{13}$C NMR ($CDCl_3$): δ 183.0 (d, *J* = 3.04, C4), 161.18 (s, C2' or C4' or C6'), 160.76 (s, C2' or C4' or C6'), 158.16 (s, C2' or C4' or C6'), 144.37 (s, Pz3B), 143.22 (s, Pz3A), 140.27 (s, Pz3C), 138.27 (s, Pz5A or Pz5B or Pz5C), 138.11 (s, Pz5A or Pz5B or Pz5C), 137.93 (s, Pz5A or Pz5B or Pz5C), 110.23 (d, *J* = 3.75, C1'), 108.0 (s, Pz4C), 107.67 (s, Pz4A or Pz4B), 107.38 (s, Pz4A or Pz4B) 92.4 (s, C3' or C5'), 91.8 (d, *J* = 152.88, C2), 91.05 (s, C3' or C5'), 65.66 (d, *J* =12.86, C6), 56.24 (s, C5), 55.98 (s, 2'OMe or 4'OMe or 6'OMe), 55.51 (s, H2'OMe or H4'OMe or H6'OMe), 55.42 (s, H2'OMe or H4'OMe or H6'OMe), 42.43 (s, NMe'B), 41.22 (s, NMe'A), 37.3 (dd, *J* = 2.7, 19.3, C1), 33.94 (d, *J* = 25.0, C3) 13.89 (d, *J* = 30.2, $PMe_3$). $^{31}$P NMR ($CDCl_3$): δ -8.33 ($J_{P\text{-}W}$ = 284 Hz). CV(DMA): $E_{p,a}$ = 1.27 V. IR: $\nu_{BH}$ = 2507 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1587 $cm^{-1}$. HRMS ($M^+$) obs'd (%), calc'd (%), ppm: 809.26166 (96.1), 809.26311 (80.1), -1.8; 810.2647 (100), 810.26563 (81.4), -1.1; 811.26362 (99.7), 811.26564 (100), -2.5; 812.26717 (36.3), 812.26945 (48.4), -2.8; 813.26699 (86.7), 813.26884 (82.2), -2.3.

**TpW(NO)($PMe_3$)*N*-3-chloro-4-(2,4,6-trimethoxyphenyl)cyclohexylidene)-*N*-methylmethanaminium] (OTf) (32)**

In a 4-dram vial charged with a stir bar, 1,3,5-trimethoxybenzene (0.302 g, 1.79 mmol) was added. To this a TfOH/DCM solution (1 mL, 0.0034 M) and MeCN (0.20 mL) was added. This was stirred for 1 min. To this mixture **29** (0.0915 g, 0.1089 mmol) was added. After 1 h the reaction was quenched, outside of the glovebox, by the addition of 50 mL of sat. aq. $NaHCO_3$. The reaction mixture was extracted with DCM (3 x 50 mL), dried over $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The residue was redissolved in MeCN (3 mL), and $Et_2O$ (150 mL) was slowly added to induce the precipitation of a light yellow solid. The solid was collected on a 15 mL fine porosity glass fritted funnel giving **32** (0.0809 g, 0.082 mmol, 76%).

$^1$H NMR ($CDCl_3$): 8.11 (d, *J* = 2.0, 1H, Pz3B), 8.00 (d, *J* = 2.0, 1H, Pz5C), 7.95 (d, *J* =2.0, 1H, Pz5b), 7.93 (d, *J* = 2.0, 1H, Pz5a), 7.56 (d, *J* = 2.0, 1H, Pz3c), 7.37 (d, *J* = 2.0, 1H, Pz3a), 6.46 (d, *J* = 2.0, 1H, Pz4B), 6.44 (d, *J* = 2.0, 1H, Pz4C), 6.41 (d, *J* = 2.0, 1H, Pz4A), 6.33 (d, *J* = 2.32, 1H, H6'), 6.31 (d, *J* = 2.32, 1H, H6'), 5.37 (dt, *J* = 1.35, 6.99, 1H, H4), 5.13 (m, 1H, H5), 3.89 (s, 3H, H5'OMe), 3.86 (s, 3H, H7'OMe), 3.79 (m, 1H, H), 3.72 (s, 3H, H5'OMe), 3.51 (s, 3H, NMe'B), 3.31 (dd, *J* = 6.35, 18.19, 1H, H6 (syn)), 3.07 (dd, *J* = 7.48, 18.19, 1H, H6), 2.39 (d, *J* = 9.89, 1H, H2), 2.33 (s, 3H, NMe'A) 1.20 (d, *J* = 9.14, 9H, $PMe_3$), $^{13}$C NMR ($CDCl_3$): 161.37 (s, H5' or H7'), 161.15 (s, H5' or H7'), 159.67 (s, H5' or H7'), 145.1 (s, Pz3B), 144.46 (s, Pz3A), 142.1 (s, Pz3C), 138.78

(s, Pz5C or Pz5B or Pz5A), 113.45 (s, C4'), 108.25 (s, Pz4A or Pz4B or Pz4C), 108.11 (s, Pz4A or Pz4B or Pz4C), 108.10 (s, Pz4A or Pz4B or Pz4C), 92.48 (s, C6'), 91.74 (s, C6'), 67.22 (s, C3), 58.902 (s, C3), 56.75 (s, C5' OMe), 56.09 (s, C7'OMe or C5'OMe), 55.97 (s, C7'OMe or C5'OMe), 55.74 (s, C2), 42.53 (s, NMe'B), 41.39 (s, NMe'A), 39.13 (s, C4), 38.33 (s, C6), 13.37 (d, $J$ = 30.64, $PMe_3$) $^{31}P$ NMR ($CDCl_3$): δ -8.41 ($J_{P\text{-}W}$ = 283 Hz). CV (DMA): $E_{p,a}$ = 1.30 V. $\nu_{BH}$ = 2512 $cm^{-1}$, $\nu_{NO}$ + $\nu_{Iminium}$ = 1566 $cm^{-1}$. HRMS ($M^+$) obs'd (%), calc'd (%), ppm: 825.23306 (86.5), 825.23356 (70.2), -0.6; 826.23529 (84.4), 826.23591 (75.9), -0.8; 827.2343 (113.6), 827.23497 (110), -0.8; 828.23614 (54.1), 828.23753 (65.2), -1.7; 829.2377 (100), 829.23757 (100), 0.2. 830.2404 (38.1), 830.24004 (36.8), 0.4; 831.23777 (28.6), 831.23763 (27.4), 0.2.

**4-(1H-indol-3-yl)cyclohex-2-enone (33)**

In a 4-dram vial charged with a stir-bar, in a fume hood, **12** (0.104 g, 0.145 mmol) was added to and dissolved in 5 mL acetone. The solution was colorless and homogeneous. Finely ground CAN (0.089 g, 0.163 mmol) was added to the vial, forming a green slurry. After stirring for 25 min, the reaction solution was added to 200 mL of hexanes resulted in a heterogeneous suspension, which gradually formed an oily residue when allowed to settle. The suspension was filtered on a 60 mL medium-porosity fritted disk containing a celite pad. The filtrate was concentrated *in vacuo* leaving a yellow residue. A 0.5 inch silica plug in 60 mL medium-porosity fritted disk was activated with 2 minutes of microware irradiation. Once the silica plug cooled to room temperature, $Et_2O$ (50 mL) was added to make a slurry, then 1 inch of sand was added to the top of the slurry. The residue from the filtrate was dissolved in 100 mL of ether and passed through the silica plug, then eluted with

350 mL $Et_2O$. The solvent from the elutant was removed under vacuum leaving a yellow residue. That residue was dissolved in 1 mL of DCM, loaded onto a radial silica chromatotron and eluted with a 9:1 hexanes:EtOAc solution to give **33** as a colorless residue (0.018 g, 0.088 mmol, 61%).

$^1$H NMR ($CDCl_3$): δ 8.25 (br s, 1H, NH), 7.64 (d, 1H, *J* = 7.9, H4'), 7.41 (d, 1H, *J* = 8.1, H7'), 7.25 (ddd, 1H, *J* = 0.9, 7.2, 8.1, H6'), 7.16 (ddd, 1H, *J* = 0.9, 7.2, 7.9, H5' overlaps with H3), 7.13 (dd, 1H, *J* = 3.4, 10.0, H3 overlaps with H5'), 7.01 (d, 1H, *J* = 2.2, H2'), 6.16 (dd, 1H, *J* = 2.2, 10.0, H2), 4.06 (br m, 1H, H4), 2.59-2.49 (m, 2H, H6), 2.44-2.29 (m, 2H, H5). $^{13}$C NMR ($CDCl_3$): 199.9 (s, C1), 153.3 (s, C3), 136.8 (s, C7a'), 129.5 (s, C2), 126.4 (s, C3a'), 122.6 (s, C6), 121.6 (s, C2'), 119.9 (s, C5'), 118.8 (s, C4'), 116.6 (s, C3), 111.6 (s, C7'), 36.7 (s, C6), 33.7 (s, C4), 30.0 (s, C5). IR: $\nu_{CO}$ = 1673 cm$^{-1}$, $\nu_{CC}$ = 1658 cm$^{-1}$. HRMS: $[M + Na]^+$ obs'd (%), calc'd (%), diff.: 234.08967 (100), 234.08894 (100), 3.1

**4-(1H-indol-3-yl)phenol (34)**

In a fume hood, **12** (0.026 g, 0.036 mmol) was added and dissolved in 0.5 mL acetone. The solution was yellow and homogeneous. Finely ground CAN (0.022 g, 0.040 mmol) was added along with 0.5 mL MeCN and the solution became green and heterogeneous. After monitoring for 5 days, the reaction solution was added to 100 mL of $Et_2O$ resulting in a heterogeneous suspension, which gradually formed an oily residue when allowed to settle. The suspension was filtered onto a 60 mL medium-porosity fritted disk rinsed with 10 mL $Et_2O$. Solvent was removed from the filtrate

under vacuum leaving a green residue. A 0.5 inch neutral alumina plug with 1 inch of sand on top of the alumina was placed in a 60 mL medium-porosity fritted disk. The residue from the filtrate was dissolved in 20 mL of $Et_2O$ and passed through the Alumina plug then eluted with 400 mL ether for fraction 1. The column was then eluted with 40 mL MeOH for fraction 2. Fraction 1 was discarded and the solvent was removed from fraction 2 *in vacuo* leaving a green residue, **34**. No yield for an isolated product was obtained. $^1$H NMR ($d_6$-acetone): δ 10.3 (br s, 1H, NH), 7.84 (dt, 1H, *J* = 1.0, 8.0, H7'), 7.52 (d, 2H, *J* = 8.6, H3), 7.46 (s, 1H, H2' overlaps with H4'), 7.45 (m, 1H, H4' overlaps with H2'), 7.14 (ddd, 1H, *J* = 1.0, 7.0, 8.0, H5'), 7.08 (ddd, 1H, *J* = 1.0, 7.0, 8.0, H6'), 6.93 (d, 1H, *J* = 8.6, H2). $^{13}$C NMR ($d_6$-acetone): δ 156.4 (s, C1), 138.1 (s, C7a'), 129.1 (s, C3), 128.4 (s, C4), 126.8 (s, C3a'), 122.4 (s, C2' or C5'), 122.3 (s, C2' or C5'), 120.2 (s, C6'), 120.1 (s, C7'), 117.9 (s, C3'), 116.4 (s, C2), 112.5 (s, C4'). LRMS: observed mass 209.

**2',4'-dimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (35)**

In a fume hood, **20** (0.1031 g, 0.11 mmol), CAN (0.1265 g, 0.23 mmol), and acetone (5 mL) were combined in a test tube. The slurry was sonicated for 15 min. The light red solution was added to a round bottom flask containing 20 mL of sat. aq. $NaHCO_3$ and stirred. After 30 min, the reaction mixture was extracted with $Et_2O$ (3 x 50 mL). The $Et_2O$ layers were combined, dried over $MgSO_4$, filtered with a celite plug, and concentrated *in vacuo*. The solid was redissolved in small portions of DCM (3 x 0.3 mL) and loaded onto a 500 μm silica preparatory plate. The plate was eluted with 200 mL of 70:30 hexanes: EtOAc. A band $R_f$ = 0.46 - 0.53 was scraped off the plate and placed in a test tube. To the test tube EtOAc (20 mL) was added and the

mixture was sonicated for ~20 min. The silica was filtered over a 60 mL medium porosity fritted funnel and washed with EtOAc (100 mL). The filtrate was concentrated to a yellow oil, **35** (0.0096 g, 0.0418 mmol, 38%).

$^{1}$H NMR ($CDCl_3$): δ 6.99 (d, *J* = 8.91, 1H, H6'), 6.94 (ddd, *J* = 1.15, 3.11, 10.02, 1H, H3), 6.49 (d, *J* = 2.36, 1H, H9'), 6.46 (dd, *J* = 2.36, 8.91, 1H, H8'), 6.13 (dd, *J* = 2.50, 10.02, 1H, H2), 4.06 (m, 1H, H4) 3.83 (s, 3H, H5'OMe), 3.81 (s, 3H, H7'OMe), 2.48 (m, 2H, H6), 2.28 (m, 1H, H5), 2.01 (m, 1H, H5) $^{13}$C NMR ($CDCl_3$): δ 200.30 (s, C1), 160.30 (s, C5'/C7'), 158.12 (s, C5'/C7')', 154.63 (s, C3), 130.02 (s, C2), 128.79 (s, C6'), 123.39 (s, C4'), 104.47 (s, C9'), 99.21 (s, C8'), 55.75 (s, H5'OMe/H7'OMe), 55.73 (s, H5'OMe/H7'OMe), 37.42 (s, C6), 35.86 (s, C4), 30.62 (s, C5) $\nu_{CO}$ = 1674 $cm^{-1}$. HRMS: $(M+Na)^+$ obs'd (%), calc'd (%), ppm: 255.09902 (100), 255.09917 (100), -0.6; 256.10325 (18.1), 256.10256 (15.5), 2.7.

**2',4',6'-trimethoxy-2,3-dihydro-[1,1'-biphenyl]-4(1H)-one (36)**

In a fume hood, **21** (0.1000 g, 0.106 mmol), CAN (0.1200 g, 0.218 mmol), and acetone (10 mL) were combined in a test tube. The slurry was sonicated for 15 min. The light red slurry was added to a round bottom flask containing 20 mL of sat. aq. $NaHCO_3$ solution. After 25 min, the reaction mixture was extracted with $Et_2O$ (3 x 50 mL). The $Et_2O$ layers were combined and washed with brine (50 mL), dried over $MgSO_4$, filtered through a celite plug, and concentrated *in vacuo*. The resulting solid was redissolved in small portions of DCM (3 x 0.3 mL) and loaded onto a 500 μm silica preparatory plate. The plate was eluted with 200 mL of 70:30 hexanes: EtOAc. A band $R_f$ = 0.60-0.70 was scraped off the plate, and placed in a test tube. To the test

tube EtOAc (20 mL) was added and the mixture was sonicated for ~20 min. The silica was filtered on a 60 mL medium porosity fritted funnel and washed with EtOAc (100 mL). The filtrate was concentrated to a yellow oil, **36** (0.0134 g, 0.0508 mmol, 48%). $^{1}$H NMR ($CDCl_3$): δ 6.97 (dt, *J* = 1.90, 10.20, 1H, H2), 6.13 (s, 2H, H3' and H5'), 5.98 (ddd, *J* = 1.0, 3.0, 10.20, 1H, H3), 4.23 (dddd, *J* = 1.90, 3.0, 4.90, 11.30, 1H, H1), 3.82 (s, 3H, C4' OMe), 3.77 (s, 6H, C2'OMe and C6'OMe), 2.53 (m, 2H, C5), 2.37 (m, 1H, C6), 1.97 (m, 1H, C6). $^{13}$C NMR ($CDCl_3$): δ 200.5 (s, C4), 169.14 (s, C2', C6'), 160.55 (s, C4'), 158.82 (C2), 127.11 (s, C3), 112.07 (s, C1'), 91.22 (s, C3', C5'), 55.69 (s, 2'OMe, 4'OMe or 6'OMe), 55.51 (s, 2'OMe, 4'OMe or 6'OMe), 39.09 (s, C5), 33.50 (s, C1), 29.32 (s, C6) $\nu_{CO}$= 1667 $cm^{-1}$. HRMS $(M+Na)^+$ obs'd (%), calc'd (%), ppm: 285.11043 (100), 285.10973 (100), 2.5; 286.11306 (19.7), 286.11313 (16.6), -0.2

**3-(1,2-dihydronaphthalen-2-yl)-1*H*-indole (37)**

In a fume hood, **9** (60 mg, 0.080 mmol) was mixed with acetone (1.986 g). A solution of ceric ammonium nitrate (CAN) (44 mg, 0.080 mmol) in water (1.496 g) was added to give a heterogeneous solution, which was stirred rapidly for 1.5 hours. The slurry was diluted with 20 mL of $Et_2O$ and washed with water (3 x 10 mL). The water layers were combined and back-extracted with $Et_2O$ (2 x 10 mL). The $Et_2O$ layers were combined and dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered on a 30 mL medium-porosity fritted funnel and the $Et_2O$ filtrate was concentrated *in vacuo* to yield an orange solid. The solid was redissolved in small portions of dichloromethane (DCM) (2 x 0.3 mL) and loaded onto a 250 μm silica preparatory plate. The plate was eluted with 100 mL of 70:30 hexanes: ethyl acetate (EtOAc). A

large band with $R_f$ = 0.8 was scraped into a test tube, to which 20 mL of EtOAc was added. The test tube was sonicated for 20 minutes and the slurry was filtered on a 60 mL medium-porosity fritted funnel and washed with 39 mL EtOAc. The filtrate was concentrated *in vacuo* to give **37** (12 mg, 0.048 mmol, 61%) as an oil.

$^1$H NMR ($CDCl_3$): δ 7.88 (s, NH), 7.70 (d, 1H, *J* = 8.0, H17), 7.36 (d, 1H, *J* = 8.1, H14), 7.23 (m, 1H, H15), 7.20 (m, 1H, H6 or H7), 7.16 (m, 1H, H6 or H7), 7.16 (m, 1H, H16), 7.13 (m, 1H, H5), 7.09 (d, 1H, *J* = 7.3, H8), 6.97 (d, 1H, *J* = 2.2, H12), 6.64 (dd, 1H, *J* = 2.1, 9.5, H4), 6.25 (dd, 1H, *J* = 3.8, 9.6, H3), 4.09 (ddd, 1H, *J* = 3.1, 6.8, 10.1, H2), 3.22 (dd, 1H, *J* = 7.2, 15.5, H1), 3.19 (dd, 1H, *J* = 10.3, 15.5, H1). $^{13}$C NMR ($CDCl_3$): δ 136.8 (s, C18), 135.2 (s, C10), 133.9 (s, C9), 132.8 (s, C3), 128.2 (s, C8), 127.7 (s, C4), 127.3 (s, C6 or C7), 126.8 (s, C6 or C7), 126.8 (s, C13), 126.2 (s, C5), 122.3 (s, C16), 121.5 (s, C12), 119.5 (s, C15), 119.4 (s, C17), 118.8 (s, C11), 111.5 (s, C14), 35.6 (s, C1), 31.9 (s, C2).

**2-(1,2-dihydronaphthalen-2-yl)-1*H*-pyrrole (38)**

In a fume hood, CAN (101 mg, 0.184 mmol) was weighed into a vial and dissolved in water (2.02 g). **10** (120 mg, 0.172 mmol) was added to a vial and dissolved in $CHCl_3$ (2.79 g). The two solutions were combined and the mixture was vigorously stirred for 5 hours. The mixture was diluted with $Et_2O$ (40 mL) and extracted with water (2 x 15 mL). The water layers were combined and extracted with four 20 mL portions of $Et_2O$ and the combined organic layers were dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered on a 60 mL medium-porosity fritted funnel and rinsed with $Et_2O$

(60 mL). The $Et_2O$ solution was concentrated *in vacuo* giving a brown oil, which was redissolved in minimal DCM and precipitated by addition to 70 mL stirring hexanes. The precipitate was filtered over a 60 mL fine-porosity fritted funnel, washed with 30 mL hexanes, and discarded. The filtrate was concentrated *in vacuo* to give an orange solid. The solid was dissolved in small portions of DCM (2 x .3 mL) and loaded onto a 500 μm silica preparatory plate. The plate was eluted with 100 mL 3:1 hexanes: EtOAc. A fluorescent band at $R_f$ = 0.7 was scraped off the plate and added into a test tube with 20 mL EtOAc. The test tube was sonicated for 20 minutes and the silica was filtered over a 60 mL medium-porosity fritted funnel and washed with 25 mL and 10 mL portions of EtOAc. The EtOAc was concentrated *in vacuo* to give **38** (9 mg, 0.108 mmol, 28%) as a light green oil.

$^1$H NMR ($CDCl_3$): δ 7.93 (s, 1H, NH), 7.20 (m, 1H, *J* = 7.1, H6), 7.16 (m, 1H, *J* = 7.5, H7), 7.12 (m, 1H, H8), 7.10 (m, 1H, H5), 6.61 (m, 1H, H14), 6.60 (d, 1H, *J* = 9.5, H4), 6.13 (m, 1H, H12), 6.10 (dd, 1H, *J* = 4.4, 9.4, H3), 6.01 (m, 1H, H13), 3.81 (m, 1H, H2), 3.19 (dd, 1H, *J* = 8.2, 15.5, H1), 3.00 (dd, 1H, *J* = 15.5,7.2, H1'). $^{13}$C NMR ($CDCl_3$): δ 134.1 (s, C11), 134.0 (s, C9), 133.4 (s, C10), 130.7 (s, C3), 128.2 (s, C8), 128.0 (s, C4), 127.7 (s, C7), 127.0 (s, C6), 126.3 (s, C5), 116.9 (s, C14), 108.3 (s, C12), 105.0 (s, C13), 35.5 (s, C1), 33.5 (s C2).

**5-(1,2-dihydronaphthalen-2-yl)-2,3-dimethylfuran (39)**

In a fume hood, CAN (47 mg, 0.086 mmol) was added to a vial and dissolved in water (1.416 g). **11** (62 mg, 0.085 mmol) was added to a second vial and dissolved

in acetone (1.511 g). The two solutions were combined and the mixture stirred for 30 minutes before being diluted with $Et_2O$ (30 mL) and extracted with water (2 x 15 mL). The water layers were combined and extracted with $Et_2O$ (4 x 10 mL). The $Et_2O$ layers were combined and dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered on a 60 mL medium-porosity fritted funnel and the filtrate was concentrated *in vacuo* to give a light orange solid. The solid was dissolved in DCM and precipitated over 30 mL of stirring hexanes. The resulting solid was filtered on 30 mL fine-porosity fritted funnel and discarded. The filtrate was concentrated *in vacuo* and dissolved in small portions of DCM (2 x 0.3 mL) and loaded onto a 250 μm silica preparatory plate. The preparatory plate was eluted with 100 mL of 3:1 hexanes: EtOAc. A large band at $R_f$ = 0.8-0.9 was scraped off the plate into a test tube. EtOAc (20 mL) was added to the test tube and the slurry was sonicated for 25 minutes. The silica was filtered on 60 mL medium-porosity fritted funnel and washed with 20 mL of EtOAc. The EtOAc was concentrated *in vacuo* to give **39** as an oil (9 mg, 0.0399 mmol, 47%) with a small amount of substituted naphthalene as an impurity.

$^1$H NMR ($CDCl_3$): δ 7.13-7.17 (m, 3H, H6, H7, and H8), 7.09 (d, 1H, *J* = 7.3, H5), 6.58 (dd, 1H, *J* = 2.2, 9.6, H4), 6.07 (dd, 1H, *J* = 3.8, 9.5, H3), 5.84 (s, 1H, H12), 3.69 (ddd, 1H, *J* = 3.0, 6.5, 10.2 H2), 3.07 (dd, 1H, *J* = 7.0, 15.4, 1H), 2.97 (dd, 1H, *J* = 10.4, 15.4 H1'), 2.13 (s, 1H, H15), 1.85 (s, 1H, H16). $^{13}$C NMR ($CDCl_3$): δ 155.0 (s, C11), 146.6 (s, C14), 135.1 (s, C9), 134.3 (s, C10), 130.1 (s, C3), 129.0 (s, C6, C7, or C8), 128.7 (s,

C4), 128.3 (s, C6, C7, or C8), 127.7 (s, C6, C7, or C8), 127.1 (s, C5), 115.2 (s, C13), 109.0 (s, C12), 34.8 (s, C2), 33.9 (s, C1), 11.4 (s, C15), 10.0 (s, C16).

**Supporting Information Available**: Full experimental procedures for all previously unpublished compounds and descriptions of their spectroscopic analysis. CIF files for **9**, **12**, **13**, and **32**; $^{1}H$ and $^{13}C$ NMR spectra of selected compounds. This information is available free of charge via the internet at http://pubs.acs.org.

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# Chapter 3

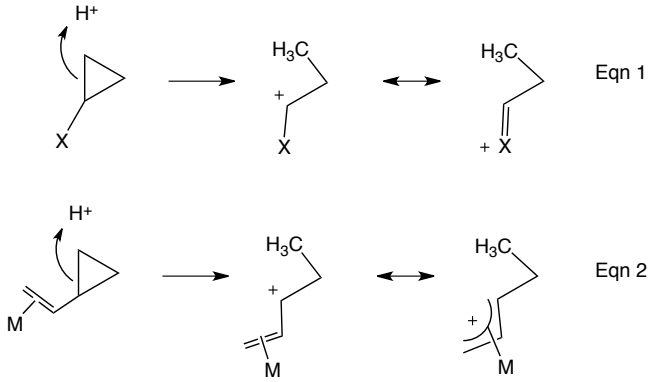
## Tungsten-Mediated Selective Ring Opening of Vinylcyclopropanes

**Abstract:**[1] The complexes TpW(NO)($PMe_3$)(L), where L = 2*H*-phenol, 2*H*-*p*-cresol, 2*H*-5,6,7,8-tetrahydro-2-naphthol, and 2*H*-*N*,*N*-dimethylanilinium were cyclopropanated using Simmons-Smith conditions. Cyclopropanated derivatives of *2H-N,N*-dimethylanilinium were selectively ring-opened with HOTf/MeCN to form allylic species, which could be coupled with various nucleophiles. The nucleophilic addition occurs *anti* to the metal fragment, as determined by X-ray crystallography. Moreover, the cyclopropane ring-opening occurs regioselectively, owing to the stabilization of the allylic cation by the metal fragment. The resulting ligands can, in some cases, be removed from the metal by oxidative decomplexation using ceric ammonium nitrate (CAN).

**Introduction:**

Cyclopropane rings are key structural features of a variety of natural products, pharmaceutical compounds, and commodity chemicals.[2,3] Due to their inherent ring-strain,[4] cycloproane rings exhibit unusual reactivity with well-defined stereochemistry, and chemists have utilized them as versatile building blocks of more complex structures.[5] Predictably, when the cyclopropane ring contains donor or acceptor groups, cleavage is greatly facilitated.[6] For example, protonolysis of the ring is readily carried out when the ring bears a donor group (X in Eqn 1) such as an alcohol or alkoxy group that can stabilize the resulting carbocation.[7] A vinyl group conjugated to the ring also influences ring-opening, as vinylcyclopropanes are well-known precursors to cyclopentenes.[8] We explored whether an electron-rich transition metal, bound to a vinylcyclopropane, could promote protonolysis by

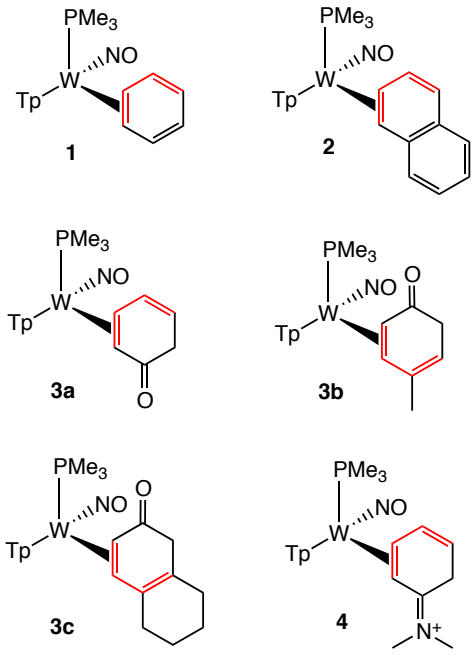
serving as a π-donor. During the cyclopropane ring-opening, an empty p orbital develops that can interact with the adjacent metal-alkene complex, ultimately providing a π-allyl species that could be used in subsequent reactions (Eqn 2). Although there is extensive research involving cyclopropane ring-opening,[9] there have been only a few examples of reactions involving cyclopropanes on organometallic scaffolds.[10-14] In part this is due to the propensity of cyclopropane rings to react directly with a metal center.[15,16]




In order to avoid direct interaction of the metal with the cyclopropane during complexation, we envisioned a strategy in which the cyclopropane unit was formed from a 1,3-diene in which two carbons were already coordinated by a metal.

**Results and Discussion.** Dihapto-coordinated diene complexes are common derivatives from $\eta^2$-arene precursors, but many have $d^5/d^6$ reduction potentials that are incompatible with the electrophilic conditions inherent to cyclopropanation (*vide infra*). For example, attempts to cyclopropanate the cyclohexadiene complex TpW(NO)($PMe_3$)(1,3-cyclohexadiene), or the benzene (**1**) or naphthalene (**2**)

derivatives using Simmons-Smith conditions were unsuccessful, with $^{31}$P-NMR spectra revealing the formation of a complex mixture of products. However, the 2H-phenol complex (**3a**), is more resistant to oxidation (the $d^5/d^6$ reduction potential is > 0.7 V, NHE) than typical diene complexes of TpW(NO)($PMe_3$) (~ 0.4 V NHE),[17] and in earlier work it was found that **3a** could be converted into a cyclopropanated cyclohexenone complex in good yield.[17] With the ready availability of other phenolic derivatives **(3b**, **3c)**[18] as well as the analogous dihapto-coordinated aniline derivative **(4)**,[19] other cyclopropane derivatives were envisioned that could be used as part of a more general study. These complexes included the tetrahydronaphthol analog **(3c)**, which is of interest as a simple analog for the binding of steroids such as β-estradiol. The molecular structure for **3c** in the solid state is included in Figure 1.



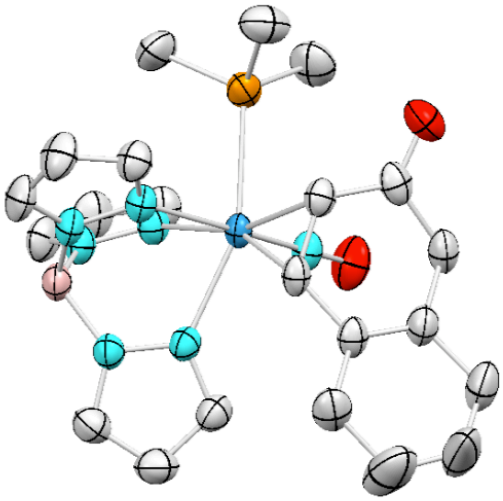


Figure 1: Arene-derived Complexes **1**-**4** and the Crystal Structure of **3c**.

Under reaction conditions similar to those used for the phenol complex **3a**,[17] complexes **3b**, **3c**, and the anilinium complex **4** were successfully cyclopropanated using $CH_2I_2$ and $ZnEt_2$ to generate analogs **5**-**8** (Figure 2). These materials were fully characterized using 2D-NMR, HRMS, CV, and IR data.[20] A common feature of all of these compounds is a set of highly shielded $^1$H-NMR resonances corresponding to the diastereotopic methylene protons of the cyclopropane ring.

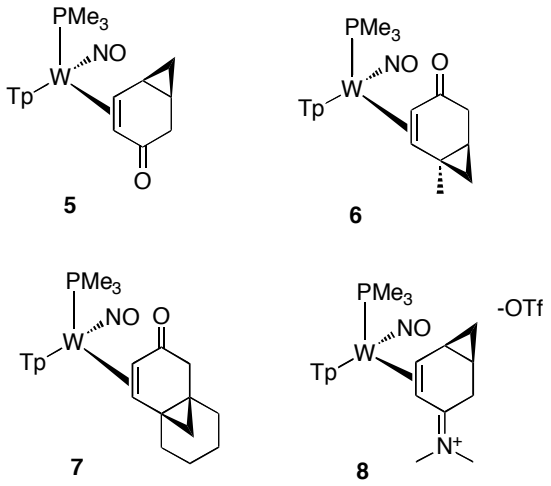
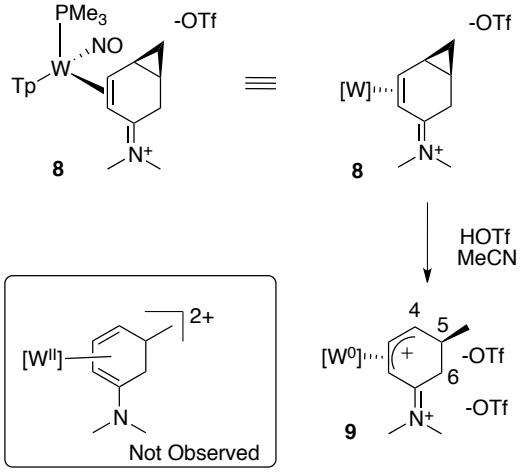



Figure 2: Cyclopropanated $\eta^2$–Vinylcyclopropanes Derived from $\eta^2$-Arene Complexes.

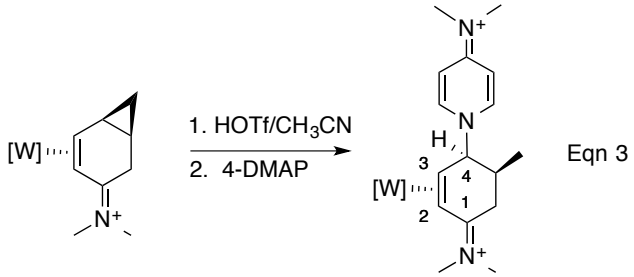
The reactivity of vinylcyclopropane complexes **5**-**8** was explored with several electrophiles. Exposing complexes **5**-**7** to various weak Brønsted acids (e.g., diphenylammonium triflate and pyridinium triflate) resulted in the formation of a complex mixture of products as shown by $^{31}$P-NMR. However, treating an acetonitrile solution of the anilinium derivative **8** with HOTf showed the formation of a single new species (**9**). This complex showed a resonance in the $^{31}$P-NMR spectrum with a $^{183}$W-$^{31}$P coupling of 250 Hz, a value similar to the *dicationic* π-allylic species generated from the protonation of the anilinium complex **4**.[19] Complex **9** was stable enough in acetonitrile-$d_3$ to allow for its full characterization by 2D-NMR techniques (Scheme 1). Three downfield resonances, which were not associated with the Tp ligand, corresponded to the allylic protons. Furthermore, the lack of resonances upfield of the $PMe_3$ doublet indicated the disappearance of the geminal cyclopropane protons, and the appearance of a doublet integrating to three

protons supported the formation of a methyl group. A carbon resonance at 181.4 ppm for **C1** is similar to the corresponding value for its precursor **8**, indicating that the metal is not directly coordinated to the iminium group. In other words, NMR data are inconsistent with an $\eta^4$-diene complex of W(II) (see Scheme 1). It has been previously reported that the parent dihapto-coordinated 2H-phenol complex **3a** can be protonated at the carbonyl under acidic conditions, leading to its eventual decomposition.[18] Whereas compounds **5-7** contain a carbonyl oxygen that likewise can be protonated, complex **8** does not contain any Lewis-basic lone pairs on the coordinated ligand that could compete with protonation of the cyclopropyl ring or level the external acid.

Scheme 1: Tungsten-mediated Cyclopropane Ring-opening with HOTf/MeCN.

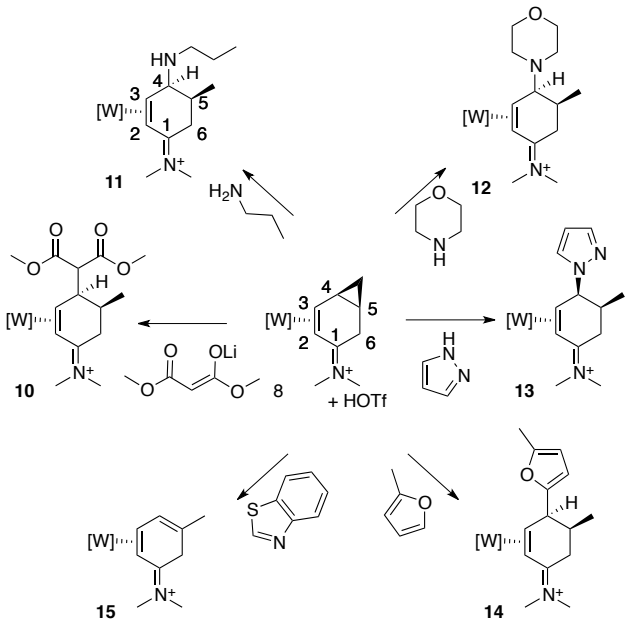


Using the allylic species **9** generated *in situ*, we next explored its reactivity. The dication **9** reacted with wide range of nucleophiles, including a lithiated enolate (giving **10**), both primary and secondary amines (giving **11** and **12**), and aromatic molecules (giving **13** and **14**). Parallel to the formation of **14**, pyrrole and indole were found to react with the newly formed allylic species in a Friedel-Crafts reaction, but we settled on the furan adduct **14** to carry out a full characterization.[21] Although amine nucleophiles can act as bases, amine addition to complex **9** was favored over deprotonation at C5 in all but one case. The reaction of the allyl complex **9** with benzothiazole led to its clean deprotonation to form the 3-methylated 2H-anilinium, **15**. Interestingly, more typical *N*-heterocyclic bases (e.g., pyridine and 4-DMAP) failed to cleanly deprotonate the allylic species. In the case of 4-DMAP, a new product formed upon the addition of the base to **9**. NOESY correlations between H2 of 4-DMAP and proton H4 on the bound complex revealed that the 4-DMAP had added to C4 of the anilinium carbocycle at the heterocyclic nitrogen. $^{1}$H-NMR resonances of the iminium methyl groups at 3.45 and 2.29 ppm, along with COSY data, showed that the 4-DMAP product (Eqn 3) resembled compounds **10-14**.




Eqn 3

Scheme 2: Coupling Allylic Species with Various Nucleophiles.




The stereochemistry for each of the complexes **10**-**14** was determined by a combination of X-ray diffraction and NMR data (NOESY). A crystal structure of the phenol-derived cyclopropane **5** confirmed that the newly formed methylene group added in a stereospecific fashion, *anti* to the metal. NOESY data suggested a similar structure in the anilinium derivative **8**, showing correlations between H4 and the $PMe_3$ ligand, and correlations between H4 and H5. Crystal structures of the dimethylmalonate derivative **10**, a protonated version of the propylamine analog **11**, and pyrazole adduct **13,** combined with NOE interactions in solution between H4 and the $PMe_3$ ligand, in each of these complexes, confirm that the nucleophile has added to the ring-face opposite to metal coordination (Scheme 2). Furthermore, the crystal structures of **10, 11,** and **13** all show the C4 substituent in an axial position.

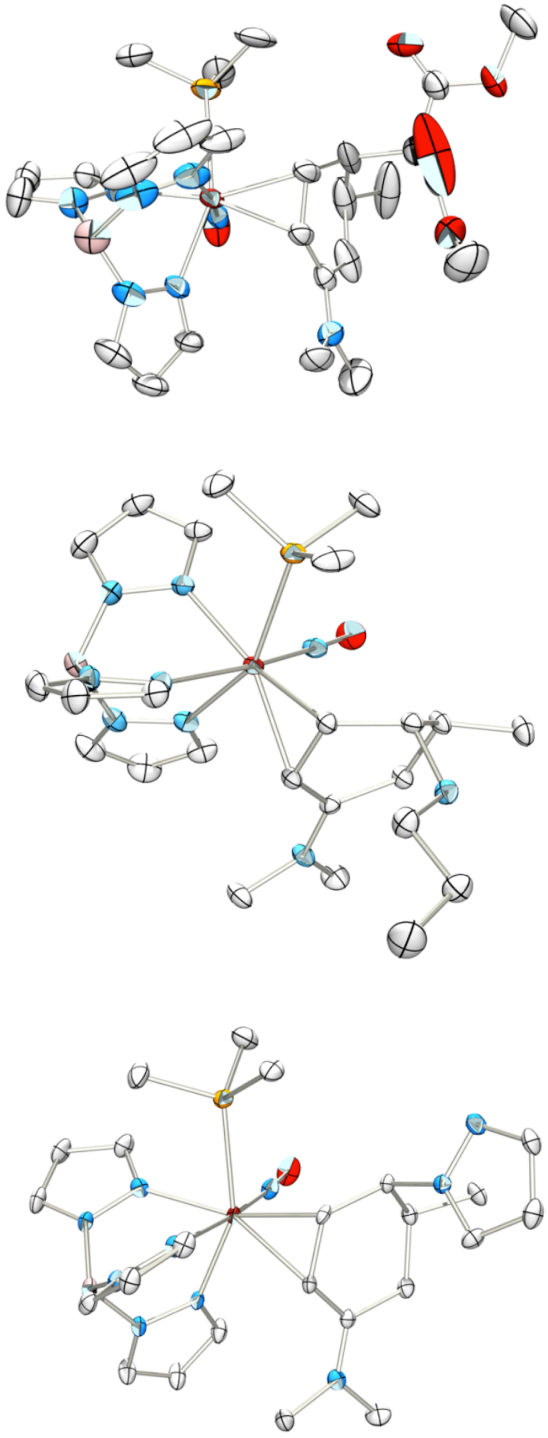


Figure 3: Crystal Structures of Compounds **10** (top), Protonated **11** (middle), and **13** (bottom). Triflate Counterions Omitted.

To better understand the selectivity of these additions, geometry optimizations and molecular orbital calculations were performed on complex **9** using DFT methods. Using B3LYP with a "hybrid" basis set (LANL2DZ pseudopotential and basis set on W and 6-31G(d) on all other atoms), we were able to compare compound **9** to other {TpW(NO)($PMe_3$)} allylic species.[18] Similar to that observed for the previously reported dication TpW(NO)($PMe_3$)($(Me)_2NPh$)•$2H^+$ (**4H**), compound **9** showed severe asymmetry in the π-allylic fragment. Whereas the calculated W-C2 and W-C3 bond lengths were very similar (2.34 Å and 2.32 Å, respectively), the W-C4 bond length was much longer (2.70 Å), suggesting the development of carbocation character at C4. This provides a convenient rationale for the explained regioselectivity of the addition products. Furthermore, the calculated LUMO of compound **9** shows a large orbital coefficient on **C4**, also supporting this selectivity of addition (Figure 4).

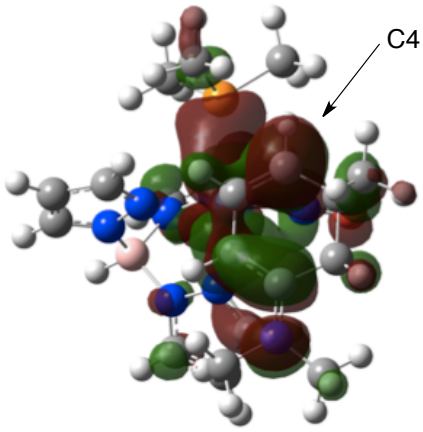
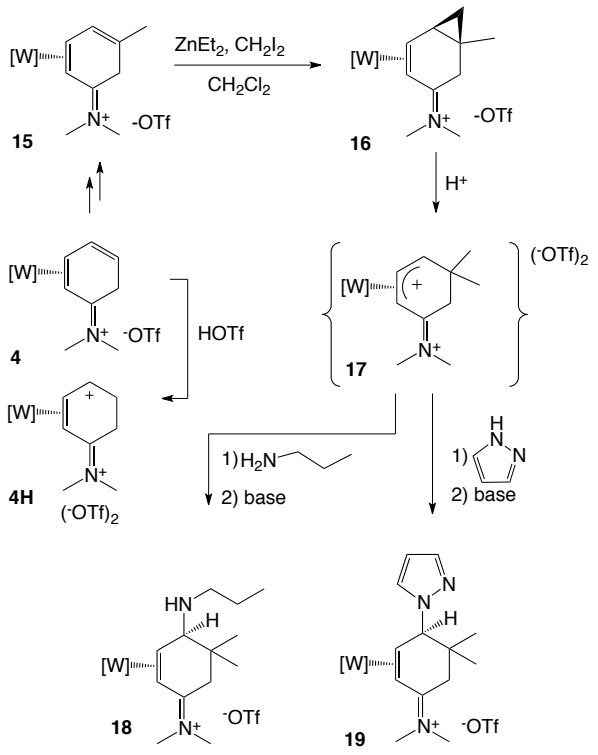



Figure 4: LUMO of Compound **9**. A Large Contribution to the LUMO can be seen on **C4**.

The *meta*-methylanilinium complex **15** was found to undergo reaction chemistry similar to that of its parent **(4)**. For example, cyclopropanation followed by ring opening and addition of propylamine or pyrazole nucleophiles generated *gem*-dimethyl derivatives (Scheme 3). The stereochemistry of the pyrazole derivative **19** was confirmed by the solid state molecular structure determination shown in Figure 5.

Scheme 3: Double *meta*-Methylation Product **19** Derived from 2H-Anilinium Complex **4**.



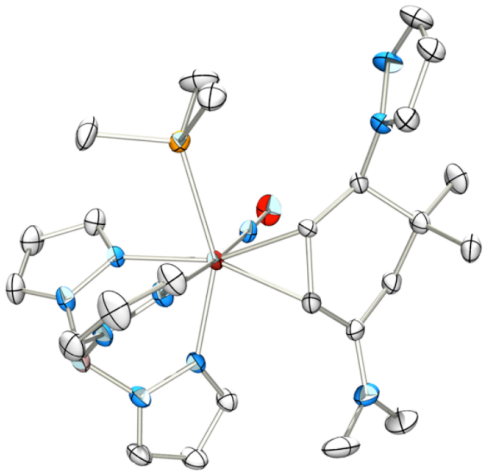


Figure 5: Crystal Structure of Compound **19**. Triflate Counterion Omitted.

As was the case with compound **8**, ring-opening of the cyclopropane is effected by treatment with triflic acid in acetonitrile, and the resulting dicationic allyl complex **17** readily reacts with amines and aromatic *N*-heterocycles. However, the carbon nucleophiles surveyed (silated enolates) failed to add to **17**.

Calculations of the dicationic complex **17** showed similar features to those obtained for compound **9** (*vide supra*). The W-C2 and W-C3 bond lengths were 2.34 Å and 2.33 Å, respectively, and the W-C4 bond length was 2.81 Å, showing an even higher degree of asymmetry. Note in Figure 6 the role of both methyl groups at C3 in stabilizing the dication through hyperconjugation with the p orbital of C4.

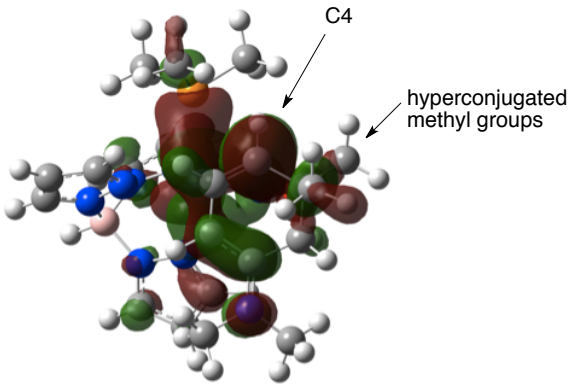
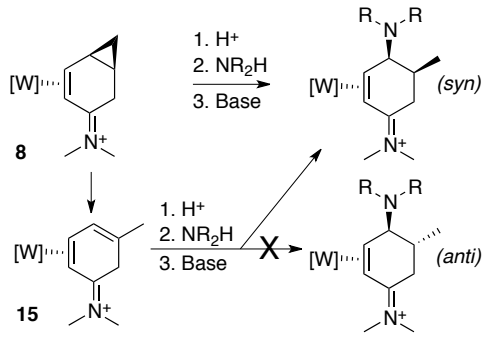



Figure 6: LUMO of Compound **17.** A Large Contribution to the LUMO can be seen on C4**.**

Access to the methylated anilinium complex **15** provided the possibility that hydroamination could deliver compounds similar to **10**-**14** but with complementary stereochemistry (Scheme 4).

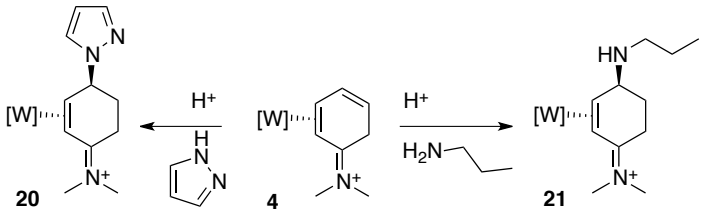
Scheme 4: Proposed (unrealized) Complementary Isomers of Methylation/Amination.




Unexpectedly, when a sample of the 3-methylated anilinium **15** was treated with acid followed by the addition of propylamine, the *syn* addition product **11** was

recovered. When this reaction was repeated without the addition of the amine, NMR data of the product matched that of compound **9**, in which the methyl group was oriented *anti* to metal coordination. This is likely a result of a steric interaction in the purported *anti* isomer between the methyl group and the tungsten complex, favoring proton addition to the *syn* face. In a related experiment, protonation of anilinium **4** with DOTF in acetonitrile-$d_3$ formed derivative **4H**-$d_2$, where both hydrogens at C5 have been replaced with deuterium. This isotopic scrambling indicates that protonation at the C5 carbon can occur *syn* to the metal, as was observed for protonation of **15),** as well as *anti*. Additionally, protonation of complex **4** in the presence of an amine nucleophile, also generates a hydroamination product. Complexes **20** and **21** were synthesized and partially characterized by NMR (Scheme 5).

Scheme 5: Reactions of $\eta^2$–*N,N*-dimethylanilinium with Acid and Amines.

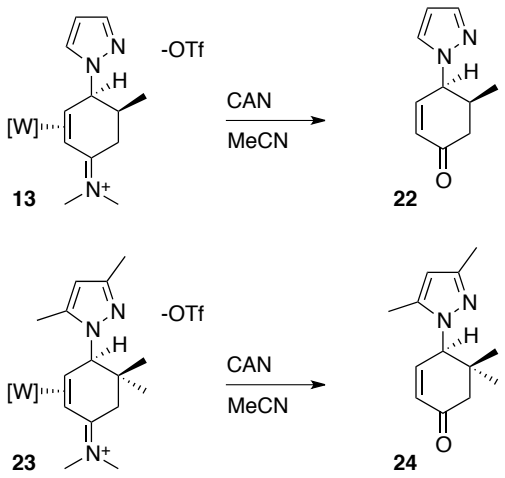



Attempts to open the cyclopropane ring of **8** with other electrophiles (e.g., isocyanates and peroxyacids) were ultimately unsuccessful. The addition of *N*-iodosuccinimide (NIS) and *N*-chlorosuccinimide (NCS) formed a single dominant species in each case, as indicated by $^{31}$P-NMR (NIS addition, $\delta$ = -9.43 $J_{WP}$ = 271, and

NCS addition, δ = -7.87 $J_{WP}$ = 285). However, attempts to either isolate these species cleanly or intercept them with nucleophiles (e.g., MeOH, EtOH, propylamine or pyrazole) failed.

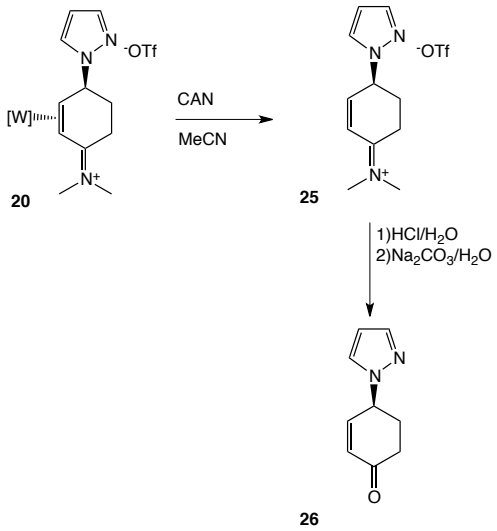
In order to liberate organic compounds, a one-electron oxidant was required with sufficient potential to oxidize the highly stabilized W(0)-eniminium systems ($d^5/d^6$ $E_{p,a}$ > 0.92 V). Ceric ammonium nitrate (CAN) in some cases proved to be suitable for this purpose. Similar to previously reported examples,[21] it was anticipated that upon oxidation, the iminium group could be hydrolyzed *in situ* to yield a cyclohexenone. While attempts to cleanly demetallate compounds **10-12** and **14** were unsuccessful (*vide infra*), pyrazole derivatives **(13** and **23)** were more accommodating **(**Scheme 6), as compounds **22** and **24** were isolated in moderate yield (30-46%). We note that *N*-substituted pyrazoles are found in a variety of pharmaceutical compounds (e.g., Celebrex).[22]

Scheme 6: Isolation of Cyclohexenones with Pyrazole Derivatives at the γ-Position.



In other cases compounds failed to undergo oxidation in the presence of CAN. For instance, when compound **10** was mixed with 1 eq of CAN in acetonitrile-$d_3$, no changes in the spectral characteristics of the species in solution were observed. Monitoring other reactions by $^1$H-NMR in deuterated solvents showed the presence of products with $^1$H-NMR resonances and coupling constants similar to the liberated enones **22** and **24**. For example, oxidation of **20** in acetonitrile-$d_3$ generated a derivative, which resembled an iminium salt (**25)**. This compound showed two singlets (3H) in the $^1$H-NMR spectrum, at 3.81 and 3.75 ppm, believed to correspond to diastereotopic methyl groups bound to the iminium nitrogen. Basic workup conditions (e.g., sat. aq. $Na_2CO_3$ or 1 M NaOH) failed to cleanly generate the cyclohexenone. However, clean hydrolysis of **25** was ultimately realized using an acid work up (1 M HCl), followed by a basic extraction to form **26**.

Scheme 7: Oxidation of Compound **20** and Elaboration to Enone **26**.



To our knowledge, none of the organic γ-substituted cyclohexenones reported in this paper has been previously synthesized. Additionally, the organic iminium salts represent an interesting class of novel compounds. It may be possible to further modify these salts via conjugate addition or electrocyclization reactions (e.g., Diels-Alder).[23-25]

The reactivity of organic α,β-unsaturated enones (*i.e.,* not coordinated by a metal), adjacent to a cyclopropyl group, has been previously studied. Treatment of these compounds with $(LiCu)Me_2$ opens the cyclopropyl ring. However, it is believed that this reaction initially involves conjugate addition to the double bond.[26] In contrast, the tungsten-vinylcyclopropane complexes react with electrophiles, providing a complementary reactivity pattern. With vinyl cylcopropanes, the protonation of the vinylic group is favored over ring-opening due to the charge-stabilizing ability of the cyclopropane moiety.[27] After protonation of the vinyl group, rearrangement can occur to open the cyclopropane ring. Protonation of the vinyl group is also operative in the polymerization of vinyl cyclopropane.[28,29]

In an elegant study by Liu et al., a spirocycle containing an iron-coordinated diene and a cyclopropyl ring was opened using an electrophile to generate a substituted cyclopentadienyl ligand.[14] Upon ring-opening, the diene was effectively converted to a cyclopentadiene ligand, changing the binding hapticity and oxidizing the metal center. That study bears some resemblance to the present work in that a transition metal was used to influence the ring-opening of a cyclopropyl group. However, in the Liu study, an electron-deficient metal fragment was utilized. In

contrast, the present work appears to be the first example of a π-basic (i.e., electron-rich) metal fragment selectively promoting the scission of a cyclopropyl ring.

**Conclusion:**

The {TpW(NO)($PMe_3$)} metal fragment can be used as synthetic tool for the stereoselective *meta*-methylation of aniline derivatives. The metal dihapto-coordinates the aniline, stabilize its protonation at C2, sets the stereochemistry of a cyclopropanation at C3-C4, promotes the regioselective ring-opening of the cyclopropane group, and determines the stereochemistry of nucleophilic addition at C4. Oxidation of the tungsten metal center liberates the aniline-derived ligands, producing several novel cyclohexenones. A similar sequence of reactions starting from other arenes (e.g., benzene or phenol) was not realized, owing either to oxidation of the metal during cyclopropanation or complications with opening of the cyclopropane ring.

**Experimental Section:**

General Methods: NMR spectra were obtained on a 300, 500, 600, or 800 MHz spectrometer (Varian INOVA or Bruker Avance). All chemical shifts are reported in ppm and proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual $^{1}H$ or $^{13}C$ signals of the deuterated solvents as an internal standard. Phosphorus NMR signals are referenced to 85% $H_3PO_4$ ($\delta = 0.00$) using a triphenylphosphate external standard ($\delta = -16.58$). Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a glaze on a MIDAC

Prospect Series (Model PRS) spectrometer fitted with a Horizontal Attenuated Total Reflectance (HATR) accessory (Pike Industries), or on a Nicolet Avatar 360 FT-IR spectrometer equipped with an ASI-DiComp diamond anvil ATR assembly. Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data was taken at ambient temperature (~25 °C) at 100 mV/s in a standard three-electrode cell with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMA) or acetonitrile (MeCN) solvent (unless otherwise specified), and tetrabutylammonium hexaflurophosphate (TBAH) electrolyte (approx. 0.5 M). All potentials are reported versus NHE (Normal Hydrogen Electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = -0.78 V), ferrocene ($E_{1/2}$ = +0.55 V), or decamethylferrocene ($E_{1/2}$ = +0.04 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. High resolution mass spectra were acquired in ESI mode, from samples dissolved in a 3:1 acetonitrile/water solution containing sodium trifluoroacetate (NaTFA). Mass spectra are reported as $M^+$ for monocationic complexes, or as $[M+H^+]$ or $[M+Na^+]$ for neutral complexes, using $[Na(NaTFA)_x]^+$ clusters as an internal standard. In all cases, observed isotopic envelopes were consistent with the molecular composition reported. For organic products, the monoisotopic ion is reported; for complexes, the major peaks in the isotopic envelope are reported. Spectra were collected either on a Bruker BioTOF-Q, a PerkinElmer Axion2 TOF, a Shimadzu IT-TOF, a Bruker MaXis Impact, an Agilent 6230 TOF, or a Waters Xevo G2Qtof.

Unless otherwise noted, all synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere. $CH_2Cl_2$ and benzene were purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were thoroughly purged with dry nitrogen prior to use. Triflate salts of amines were synthesized by addition of an $Et_2O$ solution of triflic acid to the appropriate conjugate base dissolved in $Et_2O$. Deuterated solvents were used as received from Cambridge Isotopes. Pyrazole (Pz) protons of the (trispyrazolyl) borate (Tp) ligand were uniquely assigned (eg., "PzB3") using a combination of 2-dimensional NMR data and phosphorous-proton NOE interactions (see Figure S1 in supplemental information). When unambiguous assignments were not possible, Tp protons were labeled as "Pz3/5 or Pz4".

**DFT Calculations**.

Initial structures were built in GAUSSVIEW (5.0.8) and optimized with the PM6 semiempirical method in GAUSSIAN 09. These structures were refined stepwise in Gaussian using B3LYP and a series of basis functions incorporating LANL2 pseudopotentials and associated basis functions provided in the GAUSSIAN package. The most demanding calculations reported here put the LANL2DZ pseudopotential and its basis only on the W atom and used the 6-31G(d) basis for all other atoms.

Syntheses of compounds **1, 2, 3a**, **3b**, **4**, and **5** have been previously reported.[17-19,30]

**Compound 3c**

Sodium dispersion (30–35% in wax, 3.290 g, 42.932 mmol) was added to a 2 L round-bottom flask containing a stir bar that was rinsed with hexanes followed by benzene. Fresh benzene (400 mL) was then added, followed by the addition of $TpW(NO)(PMe_3)Br$ (5.006 g, 8.588 mmol). After 24 h, the reaction mixture was filtered (2 cm of Celite in a 350 mL fritted funnel) and washed with 200 mL of benzene. The filtrate was placed in a 2 L filter flask along with 5,6,7,8-tetrahydro-2-naphthol (6.37 g, 0.042 mol). After 24 h of stirring, the reaction mixture was chromatographed on silica (3 cm, 350 mL fritted funnel), eluting first with toluene (100 mL), then $Et_2O$ (500 mL), and finally EtOAc (1 L). The EtOAc fraction was concentrated to an oil and dissolved in DCM (20 mL), and this solution was added to stirred hexanes (200 mL). A light brown precipitate was collected, giving **3c** (1.869 g, 2.870 mmol, 33%).

$^1$H NMR ($CDCl_3$, δ): 7.94 (d, *J* = 2, 1H, PzB3), 7.86 (d, *J* = 2, 1H, PzA3), 7.79 (d, *J* = 2, 1H, PzC5), 7.71 (d, *J* = 2, 1H, PzB5), 7.64 (d, *J* = 2, 1H, PzA5), 7.37 (d, *J* = 2, 1H, PzC3), 6.28 (t, *J* = 2, 1H, PzC4 overlaps with PzB4), 6.27 (t, *J* = 2, 1H, PzB4 over laps with PzC4), 6.17 (t, *J* = 2, 1H, PzA4), 3.63 (d, *J* = 21.9, 1H, H10), 3.41 (ddd, *J* = 2.4, 9.1, 11.9, 1H, H2), 2.83 (d, *J* = 21.9, 1H, H10), 2.60–2.67 (m, 2H, alkyl), 2.14 (m, 1H, alkyl), 1.84 (d, *J* = 9.1, 1H, H3), 1.60–1.65 (m, 5H, alkyl), 1.25 (d, *J* = 8.8, 9H, $PMe_3$). $^{13}$C NMR ($CDCl_3$, δ): 208.8 (C1), 144.0 (PzA3), 143.4 (PzB3), 140.3 (PzC3), 136.8 (PzC5), 136.2 (PzB5), 136.0 (PzA5), 133.0 (C4 or C9), 119.8 (C4 or C9), 106.5 (PzB4), 106.3 (PzC4), 105.4 (PzA4), 65.9 (C3), 57.7 (d, *J* = 6.7, C2), 45.2 (C10), 31.6 (C5 or C8), 28.9

(C5 or C8), 23.5 (C6 or C7), 23.1 (C6 or C7), 13.1 (d, $J$ = 28.2, $PMe_3$). $^{31}P$ NMR ($CDCl_3$, δ): −11.9 ($J_{wp}$ = 273.0). IR: $\nu_{BH}$ 2489 $cm^{-1}$, $\nu_{CO}$ 1614 $cm^{-1}$, and $\nu_{NO}$ 1567 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 0.61 V. HRMS: [M + $H^+$ = $C_{22}H_{31}BN_7O_2PW$ + $H^+$] (obsd (%), calcd (%), ppm) 650.1914 (88), 650.1935 (84), −3.2; 651.195 (78), 651.1960 (81), −1.5; 652.1947 (100), 652.1959 (100), −1.8; 653.1980 (39), 653.2000 (42), −3.1; 654.1996 (67), 654.1991 (83), 0.8.

**Compound 6**

$CH_2I_2$ (0.2396 g, 0.901 mmol) dissolved in DCM (10 mL) was added to a 50 mL round-bottom flask charged with a stir bar. A DCM (10 mL) solution of $ZnEt_2$ (0.0555 g, 0.451 mmol) was added dropwise into the flask with stirring. After 1 min, a cloudy white heterogeneous mixture was formed. To this was added a DCM (3 mL) solution of **3b** (0.1217 g, 0.199 mmol). The solution turned yellow, and after 1 h the reaction mixture was removed from the glovebox and treated with 5 mL of $NH_4Cl$ (saturated aqueous). The reaction mixture was then extracted with DCM (3 × 5 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to stirred hexanes (65 mL) to precipitate a light brown solid. This solid was collected on a 15 mL fine-porosity fritted funnel, yielding compound **6** (0.0490 g, 0.078 mmol, 39%).

$^1H$ NMR ($CDCl_3$, δ): 8.57 (d, $J$ = 2, 1H, PzA3), 8.26, (d, $J$ = 2, 1H, PzB3), 7.75 (d, $J$ = 2, 1H, PzB5), 7.72 (d, $J$ = 2, 1H, PzB5), 7.58 (d, $J$ = 2, 2H, PzC3 and PzA5), 6.33 (t, $J$ = 2,

1H, PzB4), 6.25 (t, *J* = 2, 1H, PzC4), 6.15 (t, *J* = 2, 1H, PzA4), 3.11 (td, *J* = 1.7, 8.4, 1H, H2), 3.0 (dd, *J* = 4.9, 1H, H6), 2.82 (td, *J* = 1.4, 10.1, 1H, H3), 2.52 (d, *J* = 16.1, 1H, H6), 1.46 (s, 3H, $CH_3$), 1.03 (d, *J* = 9.2, 9H, $PMe_3$), 0.72 (dd, *J* = 3.5, 8.5, 1H, H8), 0.43 (t, *J* = 4.9, 1H, H8). $^{13}C$ NMR ($CDCl_3$, δ): 211.7 (C1), 147.0 (PzA3), 143.9 (PzB3), 142.3 (PzC3 or PzA5), 137.3 (PzC5), 136.5 (PzB5), 136.1 (PzC3 or PzA5), 107.0 (PzB4), 106.0 (PzC4), 105.3 (PzA4), 71.8 (C3), 63.4 (C2), 38.0 (C6), 28.4 (C7), 27.8 (C8), 22.4 (C4 or C5), 21.7 (C4 or C5), 12.2 (d, *J* = 28.1, $PMe_3$). $^{31}P$ NMR ($CDCl_3$, δ): −13.04 ($J_{WP}$= 270). IR: $\nu_{BH}$ 2496 $cm^{-1}$, $\nu_{CO}$ 1616 $cm^{-1}$, and $\nu_{NO}$ 1568 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 0.64 V. HRMS: [M + $H^+$ = $C_{20}H_{29}BN_7O_2PW$ + $H^+$] (obsd (%), calcd (%), ppm) 624.17482 (85.5), 624.17778 (85.5), −4.7; 625.17768 (75.3), 625.18036 (79.7), −4.3; 626.17889 (100), 626.18016 (100), −2.0; 627.18158 (43.5), 627.18444 (41.7), −4.6; 628.18183 (73.8), 628.18341 (84.4), −2.5.

**Compound 7**

A solution of $CH_2I_2$ (0.3332 g, 1.25 mmol) dissolved in DCM (1 mL) was placed in a 25 mL round-bottom flask charged with a stir bar. $ZnEt_2$ (0.0812 g, 0.660 mmol), in DCM (1 mL) was added dropwise to the flask with stirring. A cloudy white heterogeneous mixture was formed. After 2 min of stirring, a DCM (3 mL) solution of **3c** (0.0507, 0.0779 mmol) was added dropwise, and the mixture was stirred for 80 min. The reaction mixture was removed from the glovebox and treated with 4 mL $NH_4Cl$ (saturated aqueous). The reaction mixture was extracted with DCM (3 × 5 mL), and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting brown oil was redissolved in a minimum amount of DCM and

then added to hexanes with stirring (40 mL). A dark brown precipitate formed and was discarded. The filtrate was then evaporated in vacuo, and a light tan precipitate formed and was collected, yielding **7** (0.0251 g, 0.0377 mmol, 47%).

$^{1}$H NMR ($CDCl_3$, δ): 8.26 (d, *J* = 2.2, 1H, PzA3), 8.06 (d, *J* = 1.9, 1H, PzB3), 7.79 (d, *J* = 2.2, 1H, PzC5), 7.67 (d, *J* = 2.4, 1H, PzB5), 7.62 (d, *J* = 2.4, 1H, PzA5), 7.46 (d, *J* = 2.1, 1H, PzC3), 6.28 (t, *J* = 2.2, 1H, PzC4), 6.26 (t, *J* = 2.1, 1H, PzB4), 6.13 (t, *J* = 2.3, 1H, Pz4A), 3.19 (m, 1H, H2), 2.98 (d, *J* = 16.1, 1H, alkyl), 2.54 (dd, *J* = 1.8, 10.4, 1H, H3), 2.50 (dd, *J* = 1.8, 16.5, 1H, alkyl), 2.06 (dt, *J* = 4.5, 14.6, 1H, alkyl), 1.78 (q, *J* = 4.6, 2H, alkyl), 1.56 (m, 1H, alkyl), 1.47 (m, 1H, alkyl), 1.40 (m, 1H, alkyl), 1.25 (m, 1H, alkyl), 1.12 (d, *J* = 8.9, 9H, $PMe_3$), 0.88 (m, 1H, alkyl), 0.66 (d, *J* = 3.6, 1H, H11), 0.51 (d, *J* = 3.6, 1H, H11). $^{13}$C NMR ($CDCl_3$, δ): 210.9 (C1), 146.4 (PzA3), 143.7 (PzB3), 141.2 (PzC3), 137.2 (PzC5), 137.0 (PzA5), 136.2 (PzB5), 106.5 (PzB4), 106.3 (PzC4), 105.3 (PzA4), 71.91 (C3), 60.2 (C2), 45.7 (alkyl), 32.9 (C11), 31.0 (alkyl), 30.3 (alkyl), 27.2 (C4 or C9), 24.0 (alkyl), 23.6 (alkyl), 21.1 (C4 or C9), 12.4 (d, *J* = 28.3, $PMe_3$). $^{31}$P NMR ($CDCl_3$, δ): −11.6 ($J_{WP}$ = 265). IR: $\nu_{BH}$ 2487 cm$^{-1}$, $\nu_{CO}$ 1614 cm$^{-1}$, and $\nu_{NO}$ 1565 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 0.67 V. HRMS: [M + H$^+$ = $C_{23}H_{33}BN_7O_2PW$ + H$^+$] (obsd (%), calcd (%), ppm) 664.20804 (88.9), 664.20912 (83.9), −1.6; 665.20926 (92), 665.21169 (80.4), −3.7; 666.21091 (100), 666.21155 (100), −1; 667.21307 (47.2), 667.21568 (43.8), −3.9; 668.21320 (73.8), 668.21478 (83.6), −2.4.

**Compound 8**

A solution of $CH_2I_2$ (17.1000 g, 63.844 mmol) in DCM (500 mL) was placed in a 1 L round-bottom flask charged with a stir bar. A DCM (10 mL) solution of $ZnEt_2$ (4.351 g, 35.23 mmol) was added dropwise to the flask with stirring. After 1 min, a cloudy white heterogeneous solution was formed. To this was added a DCM solution of **4** (3.0000 g, 3.875 mmol), and the solution turned yellow. After 1 h, the reaction mixture was removed from the glovebox and treated with 300 mL of $NH_4Cl$ (saturated aqueous). The reaction mixture was extracted with DCM (3 × 300 mL) and washed with deionized water (300 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (10 mL) and then added to $Et_2O$ with stirring (1000 mL) to induce precipitation of a light brown solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **8** (2.990 g, 3.794 mmol, 98%).

$^1$H NMR ($CDCl_3$, δ): 8.04 (d, *J* = 2, 1H, PzB3), 7.85 (d, *J* = 2, 1H, PzC5), 7.78 (d, *J* = 2, 1H, PzB5), 7.76 (d, *J* = 2, 1H PzA5), 7.63 (d, *J* = 2, 1H, PzC3), 7.00 (d, *J* = 2, 1H, PzA3), 6.46 (t, *J* = 2, 1H, PzC4), 6.37 (t, *J* = 2, 2H, Pz4A + Pz4B), 3.98 (dd, *J* = 8.9, 13.8, 1H, H3), 3.58 (s, 3H, NMeB), 3.12 (d, *J* = 18.4, 1H), 2.94 (dd, *J* = 8.9, 13.8, 1H), 2.38 (s, 3H, NMeA), 2.21 (d, *J* = 8.9, 1H, H2), 1.63 (m, 1H, H4), 1.42 (m, 1H, H5), 1.32 (d, *J* = 8.8, 9H, $PMe_3$), 0.93 (m, 1H, H7), 0.34 (m, 1H, H7). $^{13}$C NMR ($CDCl_3$, δ): 183.4 (C1), 144.6 (PzB3), 143.1 (PzA3), 141.4 (PzC3), 138.0 (PzB4 or PzC5), 138.0 (PzB5 or PzC5), 108.2 (Pz4C), 107.8 (PzB4), 107.3 (PzA4), 68.5 (d, *J* = 14.2, C3), 55.3 (C2), 43.0 (NMeB), 41.5 (NMeA), 28.4 (C6), 16.6 (C7), 16.2 (C4), 13.5 (d, *J* = 30.5, $PMe_3$), 11.1

(C5) $^{31}$P NMR ($CDCl_3$, δ): −9.04 ($J_{wp}$ = 285). IR: $\nu_{BH}$ 2512, $\nu_{NO}$ and $\nu_{iminium}$ 1566 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.07 V. HRMS: [$M^+ = C_{21}H_{33}BN_8OPW^+$] (obsd (%), calcd (%), ppm) 637.21131 (74.6), 637.20943 (84.9), 3.0; 638.21388 (70.1), 638.21198 (80.2), 3.0; 639.21429 (100), 639.21181 (100), 3.9; 640.21760 (36.4), 640.21599 (42.6), 2.5; 641.21706 (63), 641.21506 (84), 3.1. Anal. Calcd for $C_{22}H_{33}BF_3N_8O_4PSW \cdot 2H_2O$: C, 32.06; H, 4.52; N, 13.59. Found: C, 31.92; H, 4.39; N, 13.97.

**Compound 9**

In an NMR tube, compound **8** (0.020 g, 0.025 mmol) was dissolved in $CD_3CN$ (0.6 mL). To this was added a drop of HOTf, and after mixing the solution appeared dark yellow and homogeneous. The solution was analyzed by 2D-NMR and $^{31}$P NMR spectroscopy.

$^1$H NMR ($CD_3CN$, δ): 8.17 (d, *J* = 2, 1H, PzB3), 8.16 (d, *J* = 2, 1H, PzC5), 8.08 (d, *J* = 2, 1H, PzC3), 8.04 (dt, *J* = 0.7, 2.5, 1H, PzB5), 8.03 (dt, *J* = 0.7, 2.47, 1H, PzA5), 7.05 (d, *J* = 2, 1H, PzA3), 6.80 (m, 1H, H4), 6.62 (t, *J* = 2, 1H, PzC4), 6.54 (t, *J* = 2, 1H, PzB4), 6.43 (t, *J* = 2, 1H, PzA4), 5.77 (m, 1H, H3), 3.92 (d, *J* = 6.6, 1H, H2), 3.51 (s, 3H, NMeB), 3.32 (m, 1H, H5), 2.76 (dd, *J* = 9.7, 20.9, 1H), 2.67 (s, 3H, NMeA), 2.58 (d, *J* = 20.6, 1H), 1.61 (d, *J* = 7.3, 3H, 5-Me), 1.19 (d, *J* = 10.2, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 181.41 (C1), 145.4 (PzB3 or PzC3), 145.0 (PzB3 or PzC3), 142.5 (PzA3), 141.0 (Pz5), 140.9 (Pz5), 140.6 (Pz5), 132.8 (H4), 110.0 (PzB4), 109.6 (PzC4), 109.1 (PzA4), 93.8 (C3), 63.0 (C2), 43.9 (NMeA or NMeB), 43.8 (NMeA or NMeB), 32.61 (C6), 30.3 (C5), 25.2 (C5-Me), 10.2 (d, *J* = 33.5, $PMe_3$). $^{31}$P NMR (MeCN, δ): −3.68 ($J_{wp}$ = 249.8).

**Compound 10**

A solution of HOTf in MeCN (7 mL, 0.103 M) was placed in a 4 dram vial along with **8** (0.1105 g, 0.140 mmol), resulting in a brown homogeneous solution. This mixture was added to a 4 dram vial containing lithium dimethylmalonate (0.1798 g, 1.302 mmol). After 10 min, the reaction mixture was removed from the glovebox and treated with 10 mL of $NH_4Cl$ (saturated aqueous). The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (100 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **10** (0.0640 g, 0.071 mmol, 51%).

$^1$H NMR ($CD_3CN$, δ): 8.07 (d, *J* = 2, 1H, PzB3), 7.99 (d, *J* = 2, 1H, PzC5), 7.89 (d, *J* = 2, 1H, PzB5), 7.87 (d, *J* = 2, 1H, PzA5), 7.54 (d, *J* = 2, 1H, PzC3), 7.24 (d, *J* = 2, 1H, PzA3), 6.47 (t, *J* = 2, 1H, PzC4), 6.40 (t, *J* = 2, 1H, PzB4), 6.33 (t, *J* = 2, 1H, Pz4A), 3.74 (s, 3H, methoxy), 3.70 (d, *J* = 6.4, 1H, 4′), 3.68 (s, 3H, methoxy), 3.41 (s, 3H, NMeB), 3.38 (t, *J* = 5.3, 1H, H4), 3.27 (m, 1H, H3), 2.70 (m, 1H, H5), 2.62 (dd, *J* = 7.5, 18.9, 1H, H6), 2.39 (s, 3H, NMeA), 2.26 (d, *J* = 9.6, 1H, H2), 2.19 (dd, *J* = 10.0, 19.5, 1H, H6), 1.32 (d, *J* = 9.6, 9H, $PMe_3$), 1.04 (d, *J* = 6.7, 3H, 5-Me). $^{13}$C NMR ($CD_3CN$, δ): 186.3 (C1), 170.9 (ester C═O), 170.8 (ester C═O), 139.2/138.8/138.7 (Pz5), 142.0 (PzC3), 143.8 (PzA3), 108.3/108.1/107.9 (Pz4), 69.3 (d, *J* = 14.9, C3), 57.5 (C4′), 53.3 (C-methoxy),

53.3 (C-methoxy), 53.07 (C2), 42.4 (NMeB), 41.9 (H4 or NMeA), 41.8 (H4 or NMeA), 28.84 (C5), 34.7 (C6), 19.5 (C5-Me), 14.0 (d, $J$ = 30.8, $PMe_3$). $^{31}P$ NMR ($CD_3CN$, δ): −7.77 ($J_{wp}$ = 275.0). IR: $\nu_{BH}$ 2506 $cm^{-1}$, $\nu_{CO}$ 1728, $\nu_{NO}$ and $\nu_{iminium}$ 1593 and 1570 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.19 V. HRMS: [$M^+ = C_{26}H_{41}BN_8O_5PW^+$] (obsd (%), calcd (%), ppm) 769.2526 (78.4), 769.2518 (81.6), 1.0; 770.2550 (77.0), 770.2543 (80.8), 0.9; 771.2551 (100), 771.2542 (100), 1.2; 772.2587 (40.9), 772.2582 (46.5), 0.6; 773.2582 (78.4), 773.2575 (82.9), 0.9.

**Compound 11**

A solution of HOTf in MeCN (10 mL, 0.103 M) was added to **8** (0.1208 g, 0.153 mmol), resulting in a dark yellow, homogeneous solution. This solution was added to a 4 dram vial containing propylamine (1 mL, 23.5 mmol), resulting in a slightly lighter yellow homogeneous solution. After 30 min, the reaction mixture was removed from the glovebox and treated with 30 mL of $Na_2CO_3$ (saturated aqueous). The reaction mixture was extracted with DCM (3 × 50 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (100 mL) to induce precipitation of a yellow solid. The product was collected on a 30 mL fine-porosity fritted funnel, yielding **11** (0.1113 g, 0.131 mmol, 86%).

$^1H$ NMR ($CD_3CN$, δ): 8.05 (d, $J$ = 2, 1H, Pz3B), 7.97 (d, $J$ = 2, 1H, Pz5C), 7.90 (d, $J$ = 2, 1H, Pz5A), 7.87 (d, $J$ = 2, 1H, Pz5A), 7.68 (d, $J$ = 2, 1H, Pz3C), 7.21 (d, $J$ = 2, 1H, Pz3A),

6.44 (t, *J* = 2, 1H, Pz4C), 6.40 (t, *J* = 2, 1H, Pz4B), 6.34 (t, *J* = 2, 1H, Pz4A), 3.74 (bs, 1H, H4), 3.42 (s, 3H, NMeB), 3.42 (buried m, 1H, H3), 2.70 (t, *J* = 6.8, H7), 2.65 (dd, *J* = 4.8, 17.2, 1H, H6), 2.54 (m, 1H, H5), 2.48 (dd, *J* = 4.8, 17.2, 1H, H6), 2.23 (s, 3H, NMeA), 2.13 (d, *J* = 9.2, 1H, H2), 1.53 (m, 2H, H8), 1.33 (d, *J* = 9.3, 9H, $PMe_3$), 1.03 (d, *J* = 6.6, 3H, C5-Me), 0.98 (t, *J* = 7.3, 3H, H9). $^{13}C$ NMR ($CD_3CN$, δ): 187.3 (C1), 145.6 (Pz3B), 144.2 (Pz3B), 142.2 (Pz3C), 138.8 (Pz5), 138.7 (Pz5), 70.3 (C3 based on HSQC), 60.3 (C4), 54.3 (C2), 42.7 (NMeB), 41.4 (NMeA), 34.2 (C6), 32.0 (C5), 24.7 (C8), 14.0 (d, *J* = 30.4, $PMe_3$), 15.2 (C9 or C5-Methyl), 12.42 (C9 or C5-Me). $^{31}P$ NMR (MeCN, δ): −8.41 ($J_{wp}$ = 280.4). IR: $\nu_{BH}$ 2504 $cm^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1570 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.05 V. HRMS: [$M^+$ = $C_{24}H_{42}BN_9OPW^+$] (obsd (%), calcd (%), ppm) 696.2839 (72.2), 696.2830 (83), 1.3; 697.2871 (65.6), 697.2855 (82.5), 2.3; 698.2862 (100), 698.2854 (100), 1.1; 699.2901 (33.9), 699.2894 (47.5), 1.0; 700.2915 (73.3), 700.2886 (82), 4.1. Anal. Calcd for $C_{25}H_{42}BF_3N_9O_4PSW$: C, 35.44; H, 5.00; N, 14.88. Found: C, 35.14; H, 5.04; N, 14.86.

**Compound 12**

A solution of HOTf in MeCN (8 mL, 0.103 M) was placed in a 4 dram vial along with **8** (0.1108 g, 0.141 mmol), resulting in a light yellow, homogeneous solution. This solution was placed in a 4 dram vial containing morpholine (1 mL, 11.4 mmol). After 1 h, the reaction was quenched outside of the glovebox by the addition of 10 mL of a $Na_2CO_3$ (saturated aqueous) solution. The reaction mixture was extracted with DCM (3 × 50 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting

yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (100 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **12** (0.0798 g, 0.0911 mmol, 65%).

$^1$H NMR ($CD_3CN$, δ): 8.06 (d, *J* = 2, 1H, PzB3), 8.00 (d, *J* = 2, 1H, PzC5), 7.90 (d, *J* = 2, 1H, PzB5), 7.89 (d, *J* = 2, 1H, PzA5), 7.79 (d, *J* = 2, 1H, PzC3), 7.17 (d, *J* = 2, 1H, PzA3), 6.46 (t, *J* = 2, 1H, PzC4), 6.41 (t, *J* = 2, 1H, PzB4), 6.35 (t, *J* = 2, 1H, PzA4), 3.68 (bm, 4H, H3′), 3.53 (d, *J* = 5.7, 1H, H4), 3.39 (s, 3H, NMeB), 3.39 (buried m, 1H, H3), 2.74–2.65 (H2′ + H6), 2.57 (m, 1H, H5), 2.44 (d, *J* = 9.3, 1H, H2), 2.32 (s, 3H, NMeA), 2.22 (dd, *J* = 9.1, 19.6, 1H, H6), 1.27 (d, *J* = 9.1, 9H, $PMe_3$), 1.18 (d, *J* = 6.8, 3H, H5-Me). $^{13}$C NMR ($CD_3CN$, δ): 186.44 (C1), 145.3 (PzB3), 144.0 (PzC3), 142.7 (PzC3), 139.1 (Pz5), 139.0 (Pz5), 138.9 (Pz5), 108.3 (PzB4), 108.2 (PzC4), 108.0 (PzA4), 68.2 (C3′), 66.2 (C4), 63.89 (d, *J* = 13.9, C3), 55.9 (C2), 51.9 (2′), 42.4 (NMeB), 41.6 (NMeA), 36.1 (C6), 29.2 (C5), 19.6 (C5-Me), 13.73 (d, *J* = 31.0, $PMe_3$). $^{31}$P NMR ($CD_3CN$, δ): −9.83 ($J_{wp}$ = 282.0). IR: $\nu_{BH}$ 2511 cm$^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1590 and 1569 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.11 V. HRMS: [$M^+ = C_{25}H_{42}BN_9O_2PW^+$] (obsd (%), calcd (%), ppm) 724.2781 (87.5), 724.2780 (81), 0.3; 725.2797 (81.7), 725.2804 (81.5), −1.0; 726.2794 (100), 726.2804 (100), −1.3; 727.2835 (43.3), 727.2843 (47.5), −1.1; 728.2837 (79.2), 728.2836 (81), 0.2.

**Compound 13**

A solution of HOTf in MeCN (8 mL, 0.103 M) was placed in a 4 dram vial along with **8** (0.101 g, 0.128 mmol), resulting in a light-yellow, homogeneous solution. This solution was placed in a 4 dram vial containing pyrazole (0.1580 g, 2.332 mmol). After 1 h, the reaction mixture was quenched outside of the glovebox by the addition of 10 mL of a $Na_2CO_3$ (saturated aqueous) solution. The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (100 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **13** (0.0897 g, 0.105 mmol, 82%).

$^1$H NMR ($CD_3CN$, δ): 8.10 (d, *J* = 2, 1H, Pz3B, 7.97 (d, *J* = 2, 1H, Pz5), 7.29 (d, *J* = 2, 1H, Pz5), 7.90 (d, *J* = 2, 1H, Pz5), 7.73 (d, *J* = 2, 1H, H5′), 7.59 (d, *J* = 2, 1H, Pz3C), 7.48 (d, *J* = 2, 1H, H3′), 7.34 (d, *J* = 2, 1H, Pz3A), 6.43 (t, *J* = 2, 1H, Pz4), 6.38 (two overlapping t, 2H, Pz4), 6.31 (t, *J* = 2, 1H, H4′), 5.24 (dt, *J* = 1.5, 4.9, 1H, H4), 3.47 (s, 3H, NMeB), 3.38 (m, 1H, H3), 2.88 (m, 1H, H5), 2.82 (dd, *J* = 7.4, 18.7, 1H, H6), 2.41 (dd, *J* = 9.2, 18.8, 1H, H6), 2.38 (s, 3H, NMeA), 2.35 (d, *J* = 9.0, 1H, H2), 1.27 (d, *J* = 9.1, 1H, $PMe_3$), 0.71 (d, *J* = 6.6, 3H C5-Me). $^{13}$C NMR ($CD_3CN$, δ): 188.5 (C1), 145.0 (Pz3B), 144.2 (Pz3A), 142.3 (Pz3C), 139.5 (C3′), 139.0 (Pz5), 138.8 (Pz5), 130.2 (C5′), 108.3 (Pz4), 108.1 (Pz4), 108.0 (Pz4), 105.5 (C4′), 68.1 (d, *J* = 14.1, C3), 64.9 (C4), 53.8 (C2), 42.5 (NMeB), 41.7 (NMeA), 34.9 (C6), 29.9 (C5), 18.2 (C5-Me), 13.6 (d, *J* = 31.2, $PMe_3$). $^{31}$P

NMR ($CD_3CN$, δ): −8.54 ($J_{wp}$ = 274.1). IR: $\nu_{BH}$ 2501 $cm^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1572 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.24 V. HRMS: [$M^+ = C_{24}H_{37}BN_{10}OPW^+$] (obsd (%), calcd (%), ppm) 705.2463 (80), 705.2469 (82), −0.9; 706.2493 (79), 706.2491 (81), 0.3; 707.2491 (100), 707.2493 (100), −0.3; 708.2534 (43), 708.2533 (46), 0.2; 709.2528 (80), 709.2526 (80), 0.3.

**Compound 14**

A solution of HOTf in MeCN (10 mL, 0.103 M) was placed in a 4 dram vial with **8** (0.1005 g, 0.127 mmol), resulting in a red homogeneous solution. This solution was placed in a 4 dram vial containing 2-methylfuran (1 mL, 13.1 mmol). After 1 h, the reaction mixture was quenched outside of the glovebox by the addition of 30 mL of a $Na_2CO_3$ (saturated aqueous) solution. The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (100 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **14** (0.0899 g, 0.103 mmol, 81%).

$^1$H NMR ($CD_3CN$, δ): 8.08 (d, *J* = 2, 1H, PzB3), 7.97 (d, *J* = 2, 1H, PzC5), 7.91 (d, *J* = 2, 1H, PzB5), 7.89 (d, *J* = 2, 1H, PzA5), 7.63 (d, *J* = 2, 1H, PzC3), 7.31 (d, *J* = 2, 1H, PzA3), 6.41 (t, *J* = 2, 1H, PzB4), 6.40 (t, *J* = 2, 1H, PzC4), 6.36 (t, *J* = 2, 1H, PzA4), 6.11 (d, *J* = 3.0, 1H, H2′), 5.97 (m, 1H, H3′), 3.98 (m, 1H, H4), 3.46 (s, 3H, NMeB), 2.79 (dd, *J* = 6.4, 18.6, 1H, H6), 2.70 (m, 1H, H5), 2.36 (s, 3H, NMeA), 2.35–2.28 (m, 2H, H6 and

H2), 2.26 (s, 3H, 4′-Me), 1.23 (d, $J$ = 9.0, 9H, $PMe_3$), 0.89 (d, $J$ = 6.7, 3H, 5-Me). $^{13}C$ NMR ($CD_3CN$, δ): 188.7 (C1), 159.6 (C1′ or C4′), 151.9 (C1′ or C4′), 145.53 (PzB3), 144.5 (PzA3), 142.6 (PzC3), 139.2/139.0 (Pz5), 108.4/108.3/108.3/108.2 (Pz4 or H2′), 107.2 (C3′), 70.0 (d, $J$ = 14.9, C3), 54.5 (C2), 43.21 (C4), 42.9 (NMeB), 41.9 (NMeA), 35.7 (C6), 30.9 (C5), 19.49 (C5-Me), 14.0 (d, $J$ = 30.3, $PMe_3$), 13.91 (C4-Me). $^{31}P$ NMR (MeCN, δ): −7.47 ($J_{wp}$ = 281.0). IR: $\nu_{BH}$ 2504 $cm^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1570 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.19 V. HRMS: [$M^+$ = $C_{26}H_{39}BN_8O_2PW^+$] (obsd (%), calcd (%), ppm) 719.2492 (71.7), 719.2514 (82), −3.0; 720.2517 (74.9), 720.2539 (87), −3.0; 721.2525 (100), 721.2538 (100), −1.8; 722.2544 (49.2), 722.2578 (47.5), −4.7; 723.2538 (92.6), 723.2571 (82), −4.5. Anal. Calcd for $C_{27}H_{31}BF_3N_8O_5PSW$: C, 37.26; H, 4.52; N, 12.87. Found: C, 37.60; H, 4.58; N, 12.61.

**Compound 15**

A solution of HOTf in MeCN (15 mL, 0.103 M) was added to **8** (0.2973 g, 0.384 mmol), resulting in a dark yellow homogeneous solution. This solution was placed in a 4 dram vial containing benzothiazole (0.4220 g, 3.12 mmol), resulting in a slightly lighter yellow homogeneous solution. After 30 min, the reaction mixture was removed from the glovebox and treated with 40 mL of $Na_2CO_3$ (saturated aqueous). The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 2 mL) and then added to $Et_2O$ with stirring (300 mL) to induce precipitation of a yellow solid. The

product was collected on a 30 mL fine-porosity fritted funnel, yielding **15** (0.2453 g, 0.317 mmol, 83%).

$^{1}$H NMR ($CD_3CN$, δ): 8.04 (d, *J* = 2, 1H, PzB3), 7.96 (d, *J* = 2, 1H, PzC5), 7.89 (d, *J* = 2, 1H, PzA5 or PzB5), 7.88 (d, *J* = 2, 1H, PzA5 or PzB5), 7.70 (d, *J* = 2, 1H, PzC3), 7.22 (d, *J* = 2, 1H, PzA3), 6.44 (t, *J* = 2H, 1H, PzC4), 6.39 (t, *J* = 2, 1H, PzB4), 6.35 (t, *J* = 2, 1H, PzA4), 6.26 (bs, 1H, H4), 3.81 (m, 1H, H3), 3.47 (s, 3H, NMeB), 3.46 (d buried, *J* = 21.9, 1H, H6), 3.24 (d, *J* = 23.3, 1H, H6), 2.39 (dd, *J* = 2.4, 7.9, H2), 2.35 (s, 3H, NMeA), 2.17 (s, 3H, 5-Me), 1.28 (d, *J* = 9.06, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 184.46 (C1), 145.9 (PzB3), 142.6 (PzC3 or PzA3), 142.4 (PzC3 or PzA3), 139.0/138.7/138.6 (Pz5), 108.2/108.1/107.7 (Pz4), 124.4 (C4), 65.5 (d, *J* = 12.1, C3), 55.0 (C2), 42.8 (NMeB), 41.5 (NMeA), 35.9 (C6), 20.61 (C5-Me) 13.64 (d, *J* = 30.7, $PMe_3$). $^{31}$P NMR ($CDCl_3$, δ): −9.58 ($J_{wp}$ = 289.8). IR: $\nu_{BH}$ 2502 cm$^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1572 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 0.92 V. HRMS: [$M^+$ = $C_{21}H_{33}BN_8OPW^+$] (obsd (%), calcd (%), ppm) 637.2082 (77.7), 637.2094 (85), −1.9; 638.2125 (76.4), 638.2120 (81), 0.8; 639.2109 (100), 639.2118 (100), −1.4; 640.2155 (44.5), 640.2160 (42.5), −0.8; 641.2147 (90.1), 641.2151 (82), −0.6. Anal. Calcd for $C_{22}H_{33}BF_3N_8O_4PSW$: C, 33.52; H, 4.22; N, 14.22. Found: C, 33.12; H, 4.38; N, 14.02.

**Compound 16**

A solution of $CH_2I_2$ (0.2396 g, 0.901 mmol) in DCM (5 mL) was placed in a 50 mL round-bottom flask charged with a stir bar. A solution of $ZnEt_2$ (0.0555 g, 0.451 mmol) dissolved in DCM (5 mL) was added dropwise to the first solution. After 1

min, a cloudy white heterogeneous solution appeared. To this was added **14** (0.394 g, 0.0500 mmol), dissolved in DCM (5 mL), and the solution turned yellow. After 1 h, the reaction mixture was removed from the glovebox and treated with 30 mL of $NH_4Cl$ (saturated aqueous). The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 2 mL) and then added to $Et_2O$ with stirring (200 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **16** (0.0255 g, 0.0318 mmol, 64%).

$^1$H NMR ($CDCl_3$, δ): 8.02 (d, *J* = 2, 1H, PzB3), 7.86 (d, *J* = 2, 1H, PzC5), 7.78 (d, *J* = 2, 1H, PzB5), 7.76 (d, *J* = 2, 1H, PzA5), 7.66 (d, *J* = 2, 1H, PzA3), 6.46 (t, *J* = 2, 1H, PzC4), 6.38 (t, *J* = 2, 1H, PzB4), 6.36 (t, *J* = 2, 1H, Pz4A), 4.04 (dd, *J* = 9.0, 13.9, 1H, H3), 3.58 (s, 3H, NMeB), 3.03 (d, *J* = 18.2, 1H, H6 *anti*), 2.73 (d, *J* = 18.6, 1H, H6), 2.41 (s, 3H, NMeA), 2.18 (d, *J* = 8.9, 1H, H2), 1.42 (m, 1H, H4), 1.33 (d, *J* = 8.8, 9H, $PMe_3$), 1.27 (s, 3H, H5-Methyl), 0.79 (dd, *J* = 4.4, 7.44, 1H, H7), 0.52 (t, *J* = 4.8, 1H, H7) $^{13}$C NMR ($CDCl_3$, δ): 184.5 (C1), 144.3 (PzB3), 142.7 (PzA3), 141.3 (PzC3), 138.85/138.01/137.77 (Pz5), 108.0 (PzC4), 107.6 (PzB4), 107.0 (Pz4A), 70.2 (d, *J* = 14.21, C3), 54.4 (C2), 43.0 (NMeB), 41.9 (NMeA) 34.3 (C6), 25.8 (C4), 26.41 (C7), 24.68 (C5-Me), 17.4 (C5), 13.6 (d, *J* = 30.3, $PMe_3$). $^{31}$P NMR (MeCN, δ): −8.41 ($J_{wp}$ = 288.1). IR: $\nu_{BH}$ 2510 cm$^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1590 and 1569.7 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.16 V. HRMS: [$M^+$ = $C_{22}H_{35}BN_8OPW^+$] (obsd (%), calcd (%), ppm) 651.2253 (79.7), 651.2251 (84), 0.3; 652.2278 (78.4), 652.2276 (82.5), 0.2; 653.2276 (100), 653.2275 (100), 0.2; 654.2315 (40.7), 654.2316 (35), −0.2; 655.2310 (85.1),

655.23070 (83), 0.4. Anal. Calcd for $C_{23}H_{35}BF_3N_8O_4PSW \cdot H_2O$: C, 33.68; H, 4.55; N, 13.66. Found: C, 33.31; H, 4.61; N, 13.63.

**Compound 17**

In an NMR tube, compound 16 (0.020 g, 0.025 mmol) was dissolved in $CD_3CN$ (0.6 mL). A drop of HOTf was added, and after mixing the solution appeared dark yellow and homogeneous. The solution was analyzed by 2D-NMR and $^{31}P$ NMR spectroscopy.

$^1H$ NMR ($CD_3CN$, δ): 8.17 (d, *J* = 2, 1H, PzB3), 8.16 (d, *J* = 2, 1H, PzC5), 8.03 (d, *J* = 2, 1H, PzA5), 8.01 (d, *J* = 2, 1H, PzB5), 8.00 (d, *J* = 2, 1H, PzC3), 7.16 (t, *J* = 5.9, 1H, H4), 7.10 (d, *J* = 2, 1H, PzA3), 6.61 (t, *J* = 2, 1H, PzC4), 6.53 (t, *J* = 2, 1H, PzB4), 6.47 (t, *J* = 2, 1H, PzA4), 5.69 (m, 1H, H3), 4.03 (d, *J* = 6.6, 1H, H2), 3.64 (s, 3H, NMeB), 3.18 (d, *J* = 19.2, 1H, H6), 2.80 (d, *J* = 18.9, 1H, H6), 2.79 (s, 3H, NMeA), 1.59 (s, 3H, 5-Me), 1.57 (s, 3H, 5-Me), 1.27 (d, *J* = 10.0, 9H, $PMe_3$). $^{13}C$ NMR ($CD_3CN$, δ): 180.6 (C1), 145.0 (Pz3/5 or H4), 144.6 (Pz3/5 or H4), 144.1 (Pz3/5 or H4), 141.9 (Pz3/5 or H4), 141.2 (Pz3/5 or H4), 141.0 (Pz3/5 or H4), 140.5 (Pz3/5 or H4), 110.0 (PzB4), 109.6 (PzC4), 109.2 (PzA4), 97.6 (C3), 63.4 (NMeA and NMeB), 44.4 (C2), 39.5 (C6), 38.9 (C5-Me), 22.7 (C5-Me), 13.1 (d, *J* = 33.2, $PMe_3$). $^{31}P$ NMR (MeCN, δ): −4.69 ($J_{wp}$ = 250.1).

**Compound 18**

A solution of HOTf in MeCN (15 mL, 0.103 M) was placed in a 4 dram vial with **16** (0.2976 g, 0.301 mmol), resulting in a brown homogeneous solution. This solution was added dropwise into a 4 dram vial containing propylamine (2 mL, 47 mmol). After 1 h, the reaction mixture was quenched outside of the glovebox by the addition of 50 mL of a $Na_2CO_3$ (saturated aqueous) solution. The reaction was extracted with DCM (1 × 100 mL and then 2 × 50 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (200 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **18** (0.2219 g, 0.258 mmol, 86%).

$^1$H NMR ($CD_3CN$, δ): 8.07 (d, *J* = 2, 1H, PzB3), 7.95 (d, *J* = 2, 1H, PzC5), 7.90 (d, *J* = 2, 1H, PzB5), 7.87 (d, *J* = 2, 1H, PzA5), 7.56 (d, *J* = 2, 1H, PzC3), 7.11 (d, *J* = 2, 1H, PzA3), 6.42 (t, *J* = 2, 1H, PzC4), 6.41 (t, *J* = 2, 1H, PzB4), 6.34 (t, *J* = 2, 1H, PzA4), 4.07 (d, *J* = 2, 1H, H4), 3.44 (s, 3H, NMeB), 3.26 (m, 1H, H3), 3.08 (m, 1H, H7), 2.69 (d, *J* = 16.0, 1H, H6 *anti*), 2.62 (m, 1H, H7), 2.52 (dd, *J* = 2.3, 16.0, 1H, H6 *syn*), 2.14 (s, 3H, NMeA), 2.13 (1H buried, H2), 1.51 (m, 2H, H8), 1.36 (d, *J* = 9.5, 9H, $PMe_3$), 1.20 (s, 3H, 5-Me *anti*), 1.03 (s, 3H, 5-Me *syn*), 0.95 (t, *J* = 7.5, 3H, H9). $^{13}$C NMR ($CD_3CN$, δ): 186.6 (C1), 145.7 (PzB3), 144.4 (PzA3), 142.1 (PzC3), 140.4/140.1 (Pz5), 108.26/108.05/107.77 (Pz4), 71.1 (d, *J* = 13.3, C3), 67.3 (d, *J* = 2.3, C4), 57.73 (C2), 53.02 (H7), 43.9 (C5), 43.0 (NMeB), 41.7 (C6), 40.94 (NMeA), 29.45 (5-Me anti), 25.7 (C8), 19.76 (5-Me *syn*) 14.7 (*d*, *J* = 30.2, $PMe_3$), 12.1 (C9). $^{31}$P NMR (acetone, δ): −7.47

($J_{wp}$ = 288.1). IR: $\nu_{BH}$ 2506 $cm^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ = 1571 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.08 V. HRMS: [$M^+$ = $C_{25}H_{44}BN_9OPW^+$] (obsd (%), calcd (%), ppm) 710.2975 (91.7), 710.29864 (76), −1.6; 711.3001 (89.6), 711.30115 (75.5), −1.5; 712.3 (100), 712.30108 (100), −1.5; 713.304 (47.9), 713.30502 (45), −1.4; 714.3032 (89.6), 714.3043 (74), −1.5. Anal. Calcd for $C_{26}H_{44}BF_3N_9O_4PSW$: C, 36.25; H, 5.15; N, 14.64. Found: C, 36.11; H, 5.12; N, 14.61.

**Compound 19**

A solution of HOTf in MeCN (10 mL, 0.103 M) was placed in a 4 dram vial with **16** (0.1003 g, 0.125 mmol), resulting in a brown homogeneous solution. This solution was added dropwise into a 4 dram vial containing pyrazole (0.1085 g, 1.594 mmol). After 1 h, the reaction was removed from the glovebox and treated with 30 mL of $Na_2CO_3$ (saturated aqueous). The reaction was extracted with DCM (3 × 50 mL), and the combined organic layers were washed with deionized water (50 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (200 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **19** (0.0988 g, 0.114 mmol, 91%).

$^1$H NMR ($CD_3CN$, δ): 8.09 (d, *J* = 2, 1H, PzB3), 7.97 (d, *J* = 2, 1H, PzC5), 7.92 (two overlapping d, PzB5, H5′), 7.90 (d, *J* = 2, 1H, PzA5), 7.57 (d, *J* = 2, 1H, PzC3), 7.55 (d, *J* = 2, 1H, H3′), 7.20 (d, *J* = 2, 1H, PzA3), 6.43 (t, *J* = 2, 1H, PzC4), 6.42 (t, *J* = 2, 1H, PzB4), 5.80 (d, *J* = 2, 1H, H4), 3.88 (bs, 1H, H3), 3.51 (s, 3H, NMeB), 2.80 (s, 2H, H6), 2.39 (d, *J* = 8.9, 1H, H2), 2.22 (s, 3H, NMeB), 1.01 (s, 3H, C5-Me), 0.97 (s, 3H, C5-Me),

0.85 (d, $J$ = 9.1, 9H, $PMe_3$). $^{13}C$ NMR ($CD_3CN$, δ): 185.8 (C1), 145.6 (Pz3/5 or C3′/C5′), 144.5 (Pz3/5 or C3′/C5′), 142.3 (Pz3/5 or C3′/C5′), 139.2 (Pz3/5 or C3′/C5′), 139.1 (Pz3/5 or C3′/C5′), 139.0 (Pz3/5 or C3′/C5′), 138.8 (Pz3/5 or C3′/C5′), 108.5 (Pz4 or C4′), 108.2 (Pz4 or C4′), 108.0 (Pz4 or C4′), 106.7 (Pz4 or C4′), 71.1 (C4), 65.3 (d, $J$ = 13.0, C3), 56.7 (C2), 43.4 (NMeB), 42.8 (C5), 41.4 (NMeA), 40.6 (C6), 27.3 (C5-Me), 21.5 (C5-Me), 13.6 (d, $J$ = 30.7, $PMe_3$). $^{31}P$ NMR (acetone, δ): −8.38 ($J_{wp}$ = 284.6). IR: $\nu_{BH}$ 2507 $cm^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1572 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.24 V. HRMS: [$M^+$ = $C_{25}H_{39}BN_{10}OPW^+$] (obsd (%), calcd (%), ppm) 719.2633 (78.4), 719.2626 (82.4), 1.0; 720.2658 (75.8), 720.2651 (81.1), 1.0; 721.2659 (100), 721.265 (100), 1.2; 722.2694 (40.2), 722.2689 (45.8), 0.7; 723.2689 (77.9), 723.2682 (82.8), 1.0.

**Compound 20**

A solution of HOTf in MeCN (15 mL, 0.103 M) was placed in a 4 dram vial with **4** (0.2990, 0.386 mmol), resulting in a light yellow homogeneous solution. This solution was placed in a 4 dram vial containing pyrazole (1.0600 g, 15.570 mmol). After 1 h, the reaction mixture was removed from the glovebox and treated with 30 mL of $Na_2CO_3$ (saturated aqueous). The reaction mixture was extracted with DCM (1 × 50 mL and then 2 × 30 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (200 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **20** (0.2800 g, 0.333 mmol, 86%).

$^{1}$H NMR ($CD_3CN$, δ): 8.11 (d, *J* = 2, 1H, PzB3), 7.98 (d, *J* = 2, 1H, PzC5), 7.93 (d, *J* = 2, 1H, PzB5), 7.91 (d, *J* = 2, 1H, PzA5), 7.83 (d, *J* = 2, 1H, 5′), 7.63 (d, *J* = 2, 1H, PzC3), 7.51 (d, *J* = 2, 1H, 3′), 7.27 (d, *J* = 2, 1H, PzA3), 6.44 (t, *J* = 2, 1H, PzB4), 6.41 (t, *J* = 2, 1H, PzC4), 6.38 (t, *J* = 2, 1H, PzA4), 6.34 (t, *J* = 2, 1H, 4′), 5.52 (m, 1H, H4), 3.57 (m, 1H, H3), 3.45 (s, 3H, NMeB), 2.82 (m, 1H, H6), 2.72 (m, 1H, H6), 2.52 (m, 1H, H5), 2.33 (d, *J* = 9.1 Hz, 1H, H2), 2.29 (s, 3H, NMeA), 2.12 (m, 1H, H5), 1.20 (d, *J* = 9.2, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 186.6 (C1), 145.2 (PzB3), 144.3 (PzA3) 142.4 (PzC3), 139.5/139.0/138.9 (Pz5 or C3′), 128.7 (C5′), 108.4/108.2/108.0 (Pz4), 106.2 (C4′), 67.4 (d, *J* = 14.1, C3), 60.8 (C4), 54.2 (C2), 41.4 (NMeB), 42.7 (NMeB), 28.47 (C5), 26.1 (C6), 13.51 (d, *J* = 31.4, $PMe_3$). $^{31}$P NMR (*d*-acetone, δ): −8.58 ($J_{wp}$ = 281.0). IR: $\nu_{BH}$ 2507 cm$^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1571 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.27 V. Anal. Calcd for $C_{24}H_{35}BF_3N_{10}O_4PSW$: C, 34.22; H, 4.19; N, 16.63. Found: C, 34.43; H, 4.00; N, 16.80.

**Compound 21**

A solution of HOTf in MeCN (20 mL, 0.103 M) was placed in a 4 dram vial with **4** (0.3941, 0.509 mmol), resulting in a yellow homogeneous solution. This solution was placed in a 4 dram vial containing propylamine (1.2215 g, 20.665 mmol). After 30 min, the reaction was removed from the glovebox and treated with 30 mL of $Na_2CO_3$ (saturated aqueous). The reaction mixture was extracted with DCM (1 × 60 mL then 2 × 30 mL), and the combined organic layers were washed with deionized water (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$

with stirring (100 mL) to induce precipitation of a light yellow solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **21** (0.3449 g, 0.413 mmol, 81%).

$^{1}$H NMR ($CD_3CN$, δ): 8.08 (d, *J* = 2, 1H, Pz), 8.00 (d, *J* = 2, 1H, Pz), 7.93 (d, *J* = 2, 1H, Pz), 7.90 (d, *J* = 2, Pz), 7.73 (d, *J* = 2, 1H, Pz), 7.27 (d, *J* = 2, 1H, Pz), 6.46 (t, *J* = 2, 1H, Pz), 6.43 (t, *J* = 2, 1H, Pz), 6.37 (t, *J* = 2, 1H, Pz), 3.71 (bs, 1H, H4), 3.43 (s, 3H, NMeA), 3.40 (m, 1H), 2.81–2.51 (m, 4H), 2.29 (s, 3H, NMeB), 2.28 (m, 1H), 2.18 (d, *J* = 9.4, 1H), 1.78 (m, 1H), 1.55 (m, 2H), 1.31 (d, *J* = 8.8, 9H, $PMe_3$), 1.00 (t, *J* = 7.5, 3H). $^{31}$P NMR ($CD_3CN$, δ): −8.13 ($J_{wp}$ = 279.9). IR: $\nu_{BH}$ 2506 cm$^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1588 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.12 V. HRMS: [$M^+ = C_{23}H_{40}BN_9OPW^+$] (obsd (%), calcd (%), ppm) 682.2677 (84.3), 682.2673 (72.5), 0.6; 683.2703 (84.3), 683.2698 (81.3), 0.7; 684.2700 (100), 684.2697 (100), 0.4; 685.2737 (46.3), 685.2738 (35), −0.1; 686.2733 (80.6), 686.2730 (65), 0.5.

**Compound 22**

Outside of the glovebox, a solution was prepared of compound **13** (0.1373 g, 0.160 mmol), MeCN (5 mL), and ceric ammonium nitrate (0.0879 g, 0.168 mmol). The reaction mixture was sonicated for 20 min and then treated with 30 mL of $Na_2CO_3$ (saturated aqueous). The resulting mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow oil was loaded onto a preparative TLC plate and eluted with EtOAc/hexanes (1/4 v/v). The bands were visualized using a

$KMnO_4$ stain. A band in the $R_f$ range 0.88–0.94 was scraped off and sonicated in a test tube with EtOAc (50 mL). The resulting slurry was added to a 30 mL medium-porosity frit and further eluted with 50 mL of EtOAc. The resulting solution was concentrated in vacuo to give **23** as a yellow oil (8.5 mg, 0.048 mmol, 30%).

$^1$H NMR ($CDCl_3$, δ): 7.57 (d, *J* = 2, 1H, H3′ or H5′), 7.47 (d, *J* = 2, 1H, H3′ or H5′), 7.01 (dd, *J* = 4.3, 10.0, 1H, H3), 6.36 (t, *J* = 2, 1H, H4′), 6.30 (dd, *J* = 1.9, 10.1, 1H, H2), 5.22 (m, 1H, H4), 2.74 (m, 1H, H5), 2.68 (dd, *J* = 9.7, 16.4, 1H, H6), 2.55 (dd, *J* = 4.4, 16.5, 1H, H6), 0.78 (d, *J* = 7.1, 3H, H5-Me). $^{13}$C NMR ($CDCl_3$, δ): 198.4 (C1), 143.6 (C3), 139.9 (C3′ or C5′), 131.9 (C2), 129.3 (C3′ or C5′), 106.1 (C4′), 60.0 (C4), 42.4 (C6), 34.5 (C5), 15.8 (C5-Me). IR: $\nu_{CO}$ 1674 $cm^{-1}$. HRMS: [M + $Na^+$ = $C_{10}H_{12}N_2O$ + $Na^+$] (obsd, calcd, ppm) 199.0845, 199.0842, 1.6.

**Compound 23**

A solution of HOTf in MeCN (10 mL, 0.103 M) was placed in a 4 dram vial with **16** (0.1616, 0.201 mmol), resulting in a yellow homogeneous solution. This solution was placed in a 4 dram vial containing 3,5-dimethylpyrazole (0.2950 g, 3.069 mmol). After 1 h, the reaction mixture was quenched outside of the glovebox by the addition of 30 mL of a $Na_2CO_3$ (saturated aqueous) solution. The reaction mixture was extracted with DCM (3 × 50 mL), and the combined organic layers were washed with deionized water (50 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting yellow residue was redissolved in DCM (2 × 1 mL) and then added to $Et_2O$ with stirring (200 mL) to induce precipitation of a yellow solid. The

solid was collected on a 15 mL fine-porosity fritted funnel, yielding **23** (0.1317 g, 0.147 mmol, 73%).

$^{1}$H NMR ($CD_3CN$, δ): 8.08 (d, *J* = 2, 1H, PzB3), 7.97 (d, *J* = 2, 1H, Pz5), 7.93 (d, *J* = 2, 1H, Pz5), 7.91 (d, *J* = 2, 1H, Pz5), 7.50 (d, *J* = 2, 1H, PzC3), 7.20 (d, *J* = 2, 1H, PzA3), 6.44 (t, *J* = 2, 1H, PzA4), 6.43 (t, *J* = 2, 1H, PzB4), 6.39 (t, *J* = 2, 1H, PzC4), 5.94 (s, 1H, H4′), 5.69 (d, *J* = 4.2, 1H, H4), 4.33 (m, 1H, H3), 3.48 (s, 3H, NMeB), 2.73 (two overlapping d, *J* = 17.9, 2H, H6; *note*: almost looks like a singlet because of second-order coupling effects), 2.38 (s, 3H, NMeA), 2.38 (buried, 1H, H2), 2.21 (s, 3H, C3′-Me or C5′-Me), 2.13 (s, 3H, C3′-Me or C5′-Me), 1.07 (s, 3H, C5-Me), 0.97 (s, 3H, C5-Me), 0.79 (d, *J* = 9.1, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 186.5 (C1), 145.3 (PzB3), 144.6 (PzA3), 142.0 (PzC3), 139.1 (Pz5), 139.1 (Pz5), 138.7 (Pz5), 108.5 (Pz4), 108.4 (Pz4), 108.0 (Pz4), 106.3 (C4′), 65.7 (d, *J* = 13.6, C3), 65.2 (C4), 57.7 (C2), 44.6 (C5), 43.3 (NMeB), 41.0 (NMeA or C6), 40.9 (NMeA or C6), 27.7 (C5-Me), 21.5 (C5-Me), 13.8 (C3′-Me or C5′-Me), 13.7 (d, *J* = 31.2, $PMe_3$), 12.82 (C3′-Me or C5′-Me). $^{31}$P NMR (acetone, δ): −8.81 ($J_{wp}$ = 284.6). IR: $\nu_{BH}$ 2520 cm$^{-1}$, $\nu_{NO}$ and $\nu_{iminium}$ 1570 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.17 V.

**Compound 24**

Outside of the glovebox, a solution of compound **23** (0.0829 g, 0.092 mmol), MeCN (5 mL), and ceric ammonium nitrate (0.0506 g, 0.092 mmol) was prepared. The reaction mxiture was sonicated for 30 min and treated with 30 mL of a saturated aqueous $Na_2CO_3$ solution. The resulting mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and

concentrated in vacuo. The resulting yellow oil was loaded onto a preparative TLC plate and eluted with EtOAc/hexanes (3/7 v/v). The bands were visualized using a $KMnO_4$ stain. A band in the $R_f$ range 0.24–0.29 was scraped off and sonicated in a test tube with EtOAc (15 mL). The resulting slurry was placed on a 30 mL medium-porosity frit and further eluted with 50 mL of EtOAc. The resulting solution was concentrated to give **22**, as a yellow oil (9.2 mg, 0.042 mmol, 46%).

$^1$H NMR (*d*-acetone, δ): 6.81 (dd, *J* = 3.7, 10.0, 1H, H3), 6.03 (dd, *J* = 2.4, 10.3, 1H, H2), 5.84 (s, 1H, H4′), 4.93 (m, 1H, H4), 2.78 (d, *J* = 17.1, 1H, H6), 2.34 (s, 3H, C5′-Me), 2.32 (d, *J* = 15.9, 1H, C6), 2.10 (s, 3H, C3′-Me), 1.10 (s, 3H, C5-Me), 0.81 (s, 3H, C5-Me). $^{13}$C NMR (*d*-acetone, δ): 199.2 (C1), 148.4 (C3′ or C5′), 147.7 (C3), 141.5 (C3′ or C5′), 131.3 (C2), 106.1 (C4′), 61.9 (C4), 51.1 (C6), 40.4 (C5), 28.1 (C5-Me), 24.0 (C5-Me), 14.3 (C3′-Me), 12.0 (C5′-Me), IR: $\nu_{CO}$ 1679 cm$^{-1}$. HRMS: [M + Na$^+$ = $C_{13}H_{18}N_2O$ + Na$^+$] (obsd, calcd, ppm) 241.1311, 241.1311, −0.1.

**Compound 25**

An NMR tube was charged with compound **20** (0.0199 g, 0.024 mmol), $CD_3CN$ (0.6 mL), and ceric ammonium nitrate (0.0286 g, 0.052 mmol). The heterogeneous reaction solution was sonicated, outside of the glovebox, for 10 min and then centrifuged and analyzed using $^1$H NMR spectroscopy.

$^1$H NMR ($CD_3CN$, δ): 7.43 (d, *J* = 10.5, 1H, H3), 7.15 (d, *J* = 10.2, 1H, H2), 5.88 (d, *J* = 9.9, 1H, H4), 3.81 (s, 3H, NMe), 3.75 (s, 3H, NMe), 3.24 (m, 1H, H6), 3.29 (m, 1H, H6), 2.72 (m, 1H, H5), 2.48 (m, 1H, H5). *Note*: ring protons were correlated by COSY spectroscopy.

**Compound 26**

Outside of the glovebox, a solution was prepared of compound **20** (0.4060 g, 0.482 mmol), MeCN (5 mL), and ceric ammonium nitrate (0.2642 g, 0.482 mmol). The reaction mixture was stirred for 5 min and treated with 10 mL of 1 M HCl (aqueous). The resulting mixture was stirred for 5 min and extracted with DCM (3 × 30 mL). The organic layers were discarded, and the aqueous layer was added to 80 mL of $Na_2CO_3$ (saturated aqueous). The resulting mixture was extracted with DCM (3 × 30 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting yellow oil was loaded onto a preparative TLC plate and eluted with MeOH/DCM (1/19 v/v). The desired band was visualized using a $KMnO_4$ stain. A band in the $R_f$ range 0.44–0.55 was scraped off and sonicated in a test tube with EtOAc (15 mL). The resulting slurry was placed on a 30 mL medium-porosity frit and further eluted with 50 mL of EtOAc. The resulting solution was concentrated to give **25** as a yellow oil (33.7 mg, 0.208 mmol, 43%).

$^1$H NMR ($CD_3Cl$, δ): 7.58 (d, *J* = 2.0, 1H, H3′), 7.47 (d, *J* = 2.0, 1H, H5′), 7.00 (ddd, *J* = 1.4, 2.7, 10.4, 1H, H3), 6.33 (t, *J* = 2.0, 1H, H4′), 6.19 (ddd, *J* = 0.9, 2.4, 10.3, 1H, H2), 5.25 (m, 1H, H4), 2.67 (m, 1H, H5 or H6), 2.59–2.41 (m, 3H, H5 and H6). $^{13}$C NMR ($CD_3Cl$, δ): 197.5 (C1), 147.6 (C3), 140.1 (C3′ or C5′), 131.21 (C2), 127.81 (C5′ or C3′), 106.3 (C4′), 57.68 (C4), 36.0 (C5 or C6). IR: $\nu_{CO}$ 1679 cm$^{-1}$.

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**Supporting Information Available**: Full experimental procedures for all previously unpublished compounds and descriptions of their spectroscopic analysis. CIF files for structures of compounds **3c**, **10**, **11**, and **13**; $^{1}H$ and $^{13}C$ NMR spectra of selected compounds. This information is available free of charge via the internet at http://pubs.acs.org.

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# Chapter 4

## Double Electrophilic Additions to Pyridine and Pyrimidine Scaffolds Promoted by a Tungsten π-Base

**Abstract:**

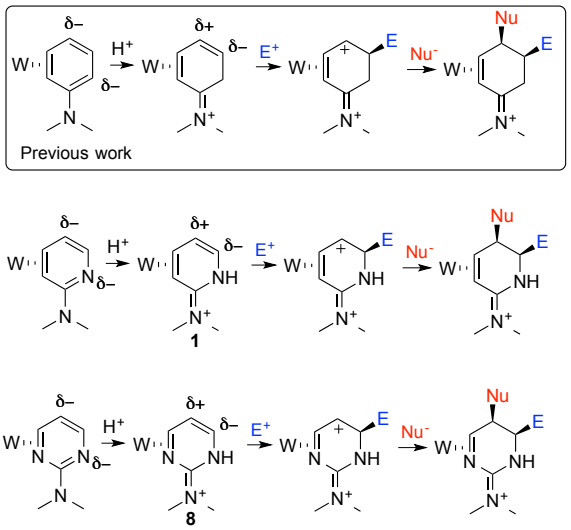
Pyridine and pyrimidine derivatives form $\eta^2$-bound complexes with the dearomatization agent [TpW(NO)($PMe_3$)] that can be stabilized and isolated as their conjugate acids. These species, although cationic, are able to undergo a second electrophilic addition. In the case of coordinated 2-dimethylaminopyridine (2-DMAP), the resulting dicationic allyl species reacts with nucleophiles to form new C-C and C-O bonds. Oxidation of an $\eta^2$- coordinated pyridine motif, using ceric ammonium nitrate, affords a novel amidine derivative.

**Introduction:**

Arenes dihapto-coordinated to a π-basic metal fragment display dramatic increases in their basicity.[1] The incorporation of an electron donor group (EDG) within the aromatic molecule further augments this reactivity.[2] Upon protonation, the resulting arenium ion can undergo nucleophilic addition reactions with various carbon nucleophiles (e.g., silyl ketene acetals, enol ethers, indoles, pyrroles, furans).[3] However, in rare cases, the combination of a highly π-basic metal complex, such as [TpW(NO)($PMe_3$)], combined with a strong EDG (e.g., -$NMe_2$) can result in a species capable of a second electrophilic addition.[4] These double electrophilic addition reactions are often highly regio- and stereospecific.[5] For example, the complex [TpW(NO)($PMe_3$)($\eta^2$-*N*,*N*-dimethylanilinium)] and its conjugate acid each exist primarily as one stereoisomer (coordination diastereomer ratio (cdr) > 20:1), owing to the asymmetric nature of the HOMO of the [TpW(NO)($PMe_3$)] fragment.[6] A strategy was envisioned to functionalize pyridines and pyrimidines using EDGs to

enhance the basicity of the aromatic system, so that a double electrophilic addition could be accessed. Our results are reported herein using a dimethylamino moiety as the EDG (Scheme 1).

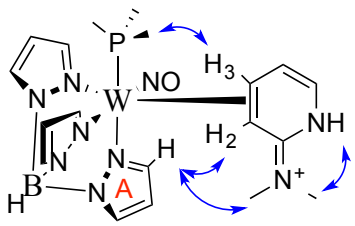
Scheme 1: Proposed Functionalization of Pyridines and Pyrimidines ($^{-}$OTf Anions Omitted)




Coordination of 2-DMAP to [TpW(NO)(PMe$_3$)] exploits the amidine character of this pyridine and produces a species that readily protonates at the pyridine nitrogen. Once protonated, the second electrophilic addition occurs adjacent to the endocyclic nitrogen, demonstrating a reversal in polarity with respect to the uncoordinated, organic ligand.[7] Although compound **1** has been previously isolated as its conjugate base, protonation of this compound increases its stability.[8,9] As expected, the anodic wave for compound **1** is more positive (0.58 V) than its

deprotonated precursor (-0.17 V), and this potential is sufficiently positive (> 0.5 V NHE) that it resists air oxidation.[10]

Compound **1** displays a carbon signal in the $^{13}C$ NMR spectrum at 164 ppm, consistent with the presence of an amidine species. NMR data also show that compound **1** has features similar to the previously reported [TpW(NO)($PMe_3$)($\eta^2$-*N*,*N*-dimethylanilinium)] complex. The protonated, bound 2-DMAP contains a doublet (~2 ppm) with a coupling constant (~9 Hz) representative of the hydrogen on the tungsten-bound carbon distal to the $PMe_3$ (H2). This distal proton shows an NOE interaction with a proton on the PzA ring (Figure 1). This PzA ring proton also shows an NOE correlation with a methyl group on the nitrogen. A signal near 4 ppm, which shows an NOE with the $PMe_3$ and correlates to H2 in a COSY spectrum, is consistent with the bound methine proximal to the $PMe_3$ (H3).



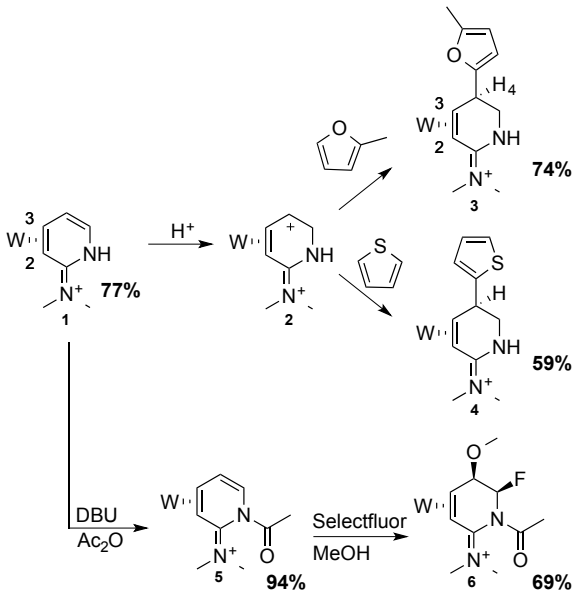

**Compound 1**

Figure 1: Relevant NOE Interactions (blue) for Compound **1** (triflate anion omitted)

Protonation of the pyridine derivative **(1)** with HOTf/$CD_3CN$ results in the formation of a new species. 2D NMR data indicate that protonation of the C4-C5 π bond occurs to form an allylic species (**2**), primarily as one isomer ((cdr) > 20:1).[11] Furthermore, because **2** exists as a dicationic species, relatively weak nucleophiles

can be added to the C3 position. Adding an excess of 2-methylfuran[12] or thiophene to complex **2** produces the Friedel-Crafts products **3** and **4**, respectively (Scheme 2). NOESY correlations between H4 and the $PMe_3$ ligand suggest that the nucleophile added *anti* to the metal center, as would be expected.[5] A solid-state structure of complex **3** confirms this stereochemistry (Figure 2).

Scheme 2: Reactivity Screening of Compound **1** (triflate anions omitted)



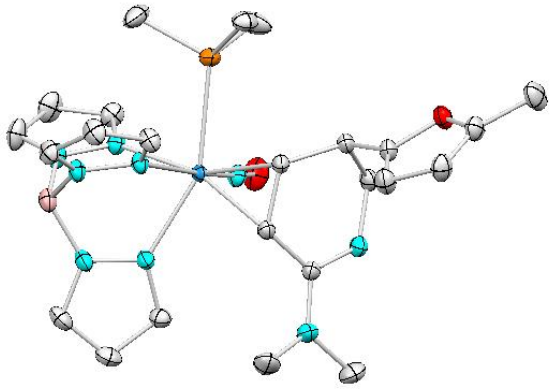
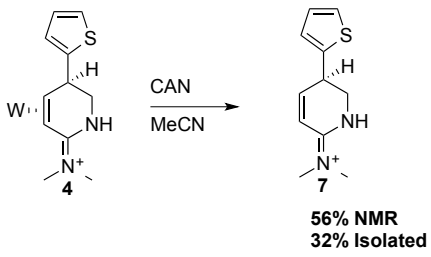


Figure 2: Solid-State Structure of Complex **3** (triflate anion omitted)

Prior to electrophilic addition, complex **1** can be modified by acetylation with DBU and acetic anhydride to give complex **5**. Following the acetylation, complex **5** is still able to undergo electrophilic additions, evidenced by the tandem addition of "$F^+$" and "$OMe^-$" to form **6**.[14] Moreover, all of these products prove to be air stable, as purification through extraction and precipitation, can be performed in air. Oxidation of compound **4** by ceric ammonium nitrate (CAN) produces the corresponding amidine (**7)** (Scheme 3).

Scheme 3: Oxidation of Compound **4** (triflate anion omitted)

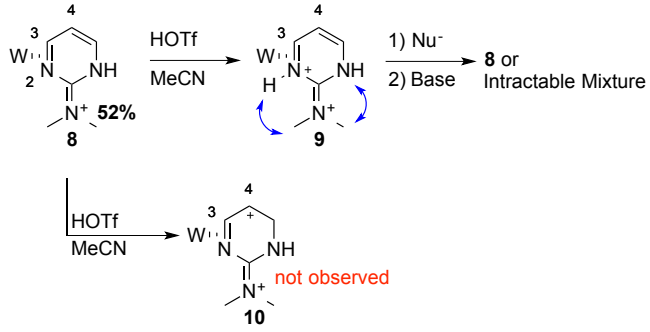


In contrast, electrophilic additions to free pyridine are challenging due to the already electron deficient nature of the ring system and the reactive lone pair that is not part of the aromatic π-system. In many cases, the lone pair of the nitrogen is exploited to generate pyridinium salts, which can be further modified through nucleophilic aromatic substitution.[15] Direct electrophilic aromatic substitution of pyridine can be promoted with harsh conditions (e.g., heating with $Cl_2$ and a Lewis acid in fuming sulfuric acid); however, these strategies typically result in low yields of products.[16] Moreover, electrophilic addition to 2-DMAP can occur at the dimethylamino moiety, generating an ammonium salt.[17] In order to modify the pyridine core of 2-DMAP, electrophilic additions can be promoted by first generating the *N*-oxide, followed by subsequent bromination at the C5 position.[18] Direct iodination of 2-DMAP can be realized through the use of a KI-$VO(acac)_2$ system to add "$I^+$" to the C5 position of 2-DMAP.[19] Whereas the use of these strategies results in an electrophilic addition at the C5 position, exploitation of a π-basic metal fragment results in nucleophilic addition at this position.

In an effort to expand this double-electrophilic addition reactivity pattern to other heterocycles, a 2-(*N*,*N*-dimethyl)pyrimidine derivative, **8**, was synthesized. Similar to the DMAP-derived complex **1**, compound **8** can be protonated with HOTf/MeCN (**Scheme 4**). Upon the addition of this acid, the $^{183}W$-$^{31}P$ coupling constant for compound **8** changes from 288 to 277 Hz, indicative of a chemical change. NMR experiments show that the new complex **9** contains two proton resonances that do not correlate to carbon peaks (Edited-HSQC), and therefore are thought to be N-H protons. These protons show NOE interactions with the methyl

groups on the guanidinium group; however, each one of these protons only correlates to one *N*-methyl group. These data, along with other NOE correlations, suggest that in **9** the tungsten-coordinated nitrogen is also protonated. When treated with various nucleophiles (e.g., amines or aromatic molecules) the reactions led either to starting material (**8**) or intractable mixtures of products.

Scheme 4: Protonation of Compound **8** to form **9** and Relevant NOE Interactions (blue)




To better understand the preferred protonation of compound **8**, a series of DFT calculations were performed. Using B3LYP with a "hybrid" basis set (LANL2DZ pseudopotential and basis set on W and 6-31G(d) on all other atoms), the dication **9** is estimated to be 3.8 kcal/mol more stable than its isomer (**10**) resulting from protonation of the **C4-C5** π bond. The electronic energy difference reflects an approximate acidity of compounds **9** and **10** showing the preferred protonation site is the nitrogen, as compound **9** is more basic.[20]

In summary, we have generated $\eta^2$-pyridine and $\eta^2$-pyrimidine derivatives that can undergo two sequential electrophilic addition reactions. Following the second electrophilic addition, the coordinated 2-DMAP (**1**) is able to react with

various nucleophiles, thereby generating a number of novel cyclic amidine complexes. In one case, the removal of the organic ligand was demonstrated.

**Experimental Section:**

General Methods: NMR spectra were obtained on a 300, 500, 600, or 800 MHz spectrometer (Varian INOVA or Bruker Avance). All chemical shifts are reported in ppm and proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual $^{1}H$ or $^{13}C$ signals of the deuterated solvents as an internal standard. Phosphorus NMR signals are referenced to 85% $H_3PO_4$ ($\delta$ = 0.00) using a triphenylphosphate external standard ($\delta$ = -16.58). Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a glaze on a MIDAC Prospect Series (Model PRS) spectrometer fitted with a Horizontal Attenuated Total Reflectance (HATR) accessory (Pike Industries), or on a Nicolet Avatar 360 FT-IR spectrometer equipped with an ASI-DiComp diamond anvil ATR assembly. Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data was taken at ambient temperature (~25 °C) at 100 mV/s in a standard three-electrode cell with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMA) or acetonitrile (MeCN) solvent (unless otherwise specified), and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (approx. 0.5 M). All potentials are reported versus NHE (Normal Hydrogen Electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = -0.78 V), ferrocene ($E_{1/2}$ = +0.55 V), or decamethylferrocene ($E_{1/2}$ = +0.04 V) as an internal standard. The peak-to-peak

separation was less than 100 mV for all reversible couples. High-resolution mass spectra were acquired in ESI mode, from samples dissolved in a 3:1 acetonitrile/water solution containing sodium trifluoroacetate (NaTFA). Mass spectra are reported as $M^+$ for monocationic complexes, or as $[M+H^+]$ or $[M+Na^+]$ for neutral complexes, using $[Na(NaTFA)_x]^+$ clusters as an internal standard. In all cases, observed isotopic envelopes were consistent with the molecular composition reported. For organic products, the monoisotopic ion is reported; for complexes, the major peaks in the isotopic envelope are reported. Spectra were collected either on a Bruker BioTOF-Q, a PerkinElmer Axion2 TOF, a Shimadzu IT-TOF, a Bruker MaXis Impact, an Agilent 6230 TOF, or a Waters Xevo G2Qtof.

Unless otherwise noted, all synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere. $CH_2Cl_2$ and benzene were purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were thoroughly purged with dry nitrogen prior to use. Triflate salts of amines were synthesized by addition of an $Et_2O$ solution of triflic acid to the appropriate conjugate base dissolved in $Et_2O$. Deuterated solvents were used as received from Cambridge Isotopes. Pyrazole (Pz) protons of the (trispyrazolyl) borate (Tp) ligand were uniquely assigned (eg., "PzB3") using a combination of 2-dimensional NMR data and phosphorus-proton NOE interactions (see Figure S1 in supplemental information). When unambiguous assignments were not possible, Tp protons were labeled as "Pz3/5 or Pz4". All *J* values for Pz protons are 2 (± 0.2) Hz. $[TpW(NO)(PMe_3)(\eta^2\text{-benzene})]$ was synthesized using a previously reported method.[21]

**DFT Calculations**.

Initial structures were built in GAUSSVIEW (5.0.8) and optimized with the PM6 semiempirical method in GAUSSIAN 09. These structures were refined stepwise in Gaussian using B3LYP and a series of basis functions incorporating LANL2 pseudopotentials and associated basis functions provided in the GAUSSIAN package. The most demanding calculations reported here put the LANL2DZ pseudopotential and its basis only on the W atom and used the 6-31G(d) basis for all other atoms.

**Compound 1**

[TpW(NO)($PMe_3$)($\eta^2$-benzene)] **(**2.988 g, 5.142 mmol) was combined with diisopropylammonium triflate (DiPAT) (1.462 g, 5.822 mmol). To this heterogeneous mixture, a DME (7 mL) solution of 2-DMAP (5.528 g, 5.818 mmol) was added. This light-brown and homogeneous solution was stirred overnight (~14 h), forming a precipitate. The reaction mixture was filtered through a 30 mL fine-porosity fritted funnel. The off-white solid was washed with DME (2x2 mL) and $Et_2O$ (2x50 mL), yielding **1** (2.290 g, 3.941 mmol, 77%).

$^1$H NMR ($CD_3CN$, δ): 8.06 (bm, 1H, NH), 7.96 (d, *J* = 2, 1H, Pz5), 7.94 (d, *J* = 2, 1H, PzB3), 7.91 (d, *J* = 2, 1H, Pz5), 7.89 (d, *J* = 2, 1H, Pz5), 7.50 (d, *J* = 2, 1H, PzA3), 7.41 (d, *J* = 2, 1H, PzC3), 6.38 (d, *J* = 2, 1H, Pz4), 6.37 (d, *J* = 2, 1H, Pz4), 6.33 (d, *J* = 2, Pz4),

6.06 (dd, *J* = 4.6, 7.3, 1H, H4), 5.75 (d, *J* = 7.3, 1H, H5), 3.67 (m, 1H, H3), 3.15 (s, 3H, NMeB), 2.28 (s, 3H, NMeA), 1.81 (d, *J* = 9.2, 1H, H2), 1.26 (d, *J* = 8.8, 9H, $PMe_3$). $^{13}C$ NMR ($CD_3CN$, δ): 167.6 (C1), 145.4 (d, *J* = 1.9, Pz3), 143.2 (Pz3), 142.0 (Pz3), 138.6 (Pz5), 138.5 (Pz5), 138.4 (Pz5), 115.2 (C5), 113.6 (d, *J* = 3.1, C4), 107.9 (Pz4), 107.8 (Pz4), 60.0 (d, *J* = 11.6, C3), 47.6 (d, *J* = 1.7, C2), 39.8 (NMe), 39.3 (NMe), 13.31 (d, *J* = 29.8, $PMe_3$). $^{31}P$ NMR ($CD_3CN$, δ): -11.52 ($J_{wp}$ = 291). IR: $\upsilon_{BH}$ = 2503 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{amidine}$ = 1606 and 1545 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 0.58 V. HRMS: [$M^+$ = $C_{19}H_{30}N_9OBPW^+$] = obsd (%), calcd (%), ppm: 624.1889 (83), 624.1890 (86), -0.2; 625.1899 (94), 625.1915 (80), -2.6; 626.1924 (100), 626.1913 (100), 1.7; 627.1930 (70), 627.1956 (41), -4.1; 628.1953 (90), 628.1946 (84), 1.1. Anal. Calc'd for $C_{20}H_{30}BF_3N_9O_4PSW$: C, 30.99; H, 3.90; N, 16.26. Found: C, 31.26; H, 4.12; N, 16.10.

**Compound 2**

In an NMR tube, **Compound 1** (0.02 g, 0.03 mmol) was dissolved in $CD_3CN$ (0.6 mL). To this a drop of HOTf was added and, after mixing, the solution appeared dark yellow and homogeneous.

$^1H$ NMR ($CD_3CN$, δ): 8.13 (d, *J* = 2, 1H, Pz3/5), 8.11 (d, *J* = 2, 1H, Pz3/5), 8.03 (d, *J* = 2, 1H, Pz3/5), 7.99 (d, *J* = 2, 2H, Pz3/5), 7.31 (d, *J* = 2, 1H, Pz3/5), 7.00 (bs, 1H, H4), 6.77 (bs, 1H, NH), 6.58 (t, *J* = 2, 1H, Pz4), 6.53 (t, *J* = 2, 1H, Pz4), 6.41 (t, *J* = 2, 1H, Pz4), 5.73 (m, 1H, H3), 4.86 (m, 1H, H5a), 4.44 (m, 1H, H5b), 3.62 (m, 1H, H2), 1.20 (d, *J* = 9.8, $PMe_3$). $^{31}P$ NMR ($CD_3CN$, δ): -7.66 ($J_{wp}$ = 248).

**Compound 3**

A solution of HOTf in MeCN (50 mL, 0.103 M) was added to **1** (0.491 g, 0.633 mmol), resulting in a light-yellow, homogenous solution. To this, 2-methylfuran (5.0 mL, 56.5 mmol) was added. The bright-red homogeneous solution was stirred for 1 h. The mixture was removed from the glovebox and was treated with 50 mL of $Na_2CO_3$ (saturated, aq). The reaction mixture was extracted with DCM (1x250 mL followed by 2x100 mL), and the combined organic layers were washed with deionized water (100 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The yellow oil was redissolved in minimal DCM and added to a stirring solution of $Et_2O$ (200 mL) to induce precipitation of a light-white solid. The powder was collected on a 30 mL fine-porosity fritted funnel, and washed with $Et_2O$ (100 mL), yielding **3** (0.4033 g, 0.470 mmol, 74%).

$^1$H NMR (*d*-acetone, δ): 8.20 (d, *J* = 2, 1H, PzB3), 8.12 (d, *J* = 2, 1H, PzA5), 8.05 (d, *J* = 2, 1H, PzB5), 7.99 (d, *J* = 2, 1H, PzC5), 7.83 (d, *J* = 2, 1H, PzA3), 7.69 (d, *J* = 2, 1H, PzC3), 6.48 (t, *J* = 2, 1H, PzB4), 6.46 (t, *J* = 2, 1H, PzA4), 6.40 (t, *J* = 2, 1H, PzC4), 6.30 (d, *J* = 3, 1H, H5'), 5.97 (m, 1H, H6'), 4.10 (m, 2H, H4 + H5a), 3.61 (d, *J* = 13.0, 1H, H5b), 3.37 (m, 1H, H3), 3.30 (s, 3H, NMeB), 2.47 (s, 3H, NMeA), 2.28 (s, 3H, 7'Me), 1.88 (d, *J* = 10.0, 1H, H2), 1.40 (d, *J* = 8.9, 1H, $PMe_3$). $^{13}$C NMR (*d*-acetone, δ): 171.2 (C1), 160.5 (C4' or C7'), 151.2 (C4' or C7'), 144.7 (PzB3), 144.3 (PzA3), 142.1 (PzC3), 138.7 (Pz5), 138.7 (Pz5), 138.0 (Pz5), 107.9 (Pz4), 107.8 (Pz4), 107.6 (Pz4), 107.1

(C5' or C6'), 106.7 (C5' or C6'), 61.5 (d, $J$ = 15.0, 1H, C3), 43.7 (C5), 40.8 (C2), 39.7 (NMeA), 39.0 (NMeB), 38.1 (C4), 13.6 (7'Me), 13.10 (d, $J$ = 30.1, $PMe_3$). $^{31}P$ NMR ($CH_2Cl_2$, δ): -10.4 ($J_{wp}$ = 277). IR: $\upsilon_{BH}$ = 2505 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{amidine}$ = 1613 and 1577 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 0.61 V. HRMS: [$M^+ = C_{24}H_{36}N_9O_2BPW^+$ = obsd (%), calcd (%), ppm: 706.2311 (70), 706.2309 (83), 0.2; 707.2341 (75), 707.2334 (81), 0.9; 708.2337 (100), 708.2334 (100), 0.5; 709.2382 (48), 709.2373 (45), 1.2; 710.2372 (96), 710.2366 (83), 0.9.

**Compound 4**

A solution of HOTf in MeCN (26 mL, 0.103 M) was added to **6** (0.254 g, 0.328 mmol), resulting in a dark-yellow, homogenous solution. To this thiophene (2.0 mL, 25.0 mmol) was added. The resulting light-yellow homogeneous solution was stirred for 30 min. The mixture was removed from the glovebox and was treated with 50 mL $Na_2CO_3$ (saturated, aq). The reaction mixture was extracted with DCM (1x200 mL, followed by 1x50 mL), and the combined organic layers were washed with deionized water (50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The yellow oil was redissolved in DCM (6 mL) and to this $Et_2O$ (200 mL) was slowly added to induce a pale-yellow precipitate. The solid was collected on a 15 mL fine-porosity fritted funnel, and washed with $Et_2O$ (100 mL), yielding **4** (0.165 g, 0.192 mmol, 59%).

$^1H$ NMR (*d*-acetone, δ): 8.20 (d, $J$ = 2, 1H, PzB3), 8.12 (d, $J$ = 2, 1H, PzC5), 8.06 (d, $J$ = 2, 1H, PzB5), 8.01 (d, $J$ = 2, 1H, PzA5), 7.83 (d, $J$ = 2, 1H, PzC3), 7.72 (d, $J$ = 2, 1H,

PzA3), 7.59 (bs, 1H, NH), 7.33 (dd, *J* = 1.1, 5.1, 1H, H7'), 7.17 (m, 1H, H5'), 7.02 (dd, *J* = 3.4, 5.2, 1H, H6'), 6.49 (t, *J* = 2, 1H, PzB4), 6.45 (t, *J* = 2, 1H, PzC4), 6.41 (t, *J* = 2, 1H, PzA4), 4.54 (m, 1H, H4), 4.24 (m, 1H, H5a), 3.42 (m, 1H, H5b), 3.36 (s, 3H, NMeB), 3.33 (m, 1H, H3), 2.55 (s, 3H, NMeA), 1.94 (d, *J* = 9.9, 1H, H2), 1.41 (d, *J* = 9.0, 9H, $PMe_3$). $^{13}C$ NMR (*d*-acetone, δ): 171.6 (C1), 153.8 (C4'), 144.7 (Pz3), 144.3 (Pz3), 142.1 (Pz3), 138.8 (Pz5), 138.3 (Pz5), 138.1 (Pz5), 127.5 (C6'), 124.4 (C5' or C7'), 124.2 (C5' or C7'), 108.0 (Pz4), 107.9 (Pz4), 107.7 (Pz4), 66.0 (d, *J* = 15.3, C3), 47.2 (C5), 40.8 (C2), 39.9 (C4 and NMeA), 39.1 (NMeB), 13.3 (d, *J* = 30.5, $PMe_3$). $^{31}P$ NMR ($CH_2Cl_2$, δ): -10.1 ($J_{wp}$ = 274). IR: $\upsilon_{BH}$ = 2511 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{amidine}$ = 1612 and 1578 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.10 V. HRMS: [$M^+ = C_{23}H_{34}N_9OBPSW^+$] = obsd (%), calcd (%), ppm: 708.1946 (75), 708.1924 (80), 3.1; 709.1964 (75), 709.1949 (79), 2.1; 710.1968 (100), 710.1946 (100), 3.1; 711.2004 (48), 711.1982 (47), 3.1; 712.1990 (90), 712.1977 (84), 1.8.

**Compound 5**

**Compound 1** (1.001 g, 1.291 mmol), MeCN (20 mL), acetic anhydride (2.204 g, 21.59 mmol), and DBU (0.381 g, 2.50 mmol) were added to a 50 mL round bottom flask charged with a stir bar. The solution turned green and then bright-yellow. The yellow homogeneous solution was stirred overnight (~18 h). The solution was removed from the glovebox and was treated with 50 mL of $NH_4Cl$ (saturated, aq). This mixture was extracted with DCM (3x50 mL), and the combined organic layers were washed with deionized water (50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting yellow residue was redissolved in minimal

DCM and then added to stirring $Et_2O$ (500 mL) to induce precipitation of a bright-yellow solid. The solid was collected on a 30 mL fine-porosity fritted funnel, yielding **5** (0.988 g, 1.21 mmol, 94%).

$^1$H NMR ($CD_3CN$, δ): 8.15 (d, *J* = 2, 1H, PzA3), 7.98 (d, *J* = 2, 1H, PzC3 or PzB5), 7.87 (d, *J* = 2, 1H, PzC3 or PzB5), 7.93 (d, *J* = 2, 1H, PzC5), 7.82 (d, *J* = 2, 1H, PzA5), 7.62 (d, *J* = 2, 1H, PzB3), 6.42 (t, *J* = 2, 1H, PzB4), 6.40 (t, *J* = 2, PzC4), 6.35 (m, 1H, H4), 6.32 (t, *J* = 2, 1H, PzA4), 6.06 (d, *J* = 7.1, 1H, H5), 4.04 (m, 1H, H3), 3.20 (s, 3H, NMeB), 2.58 (d, *J* = 9.2, 1H, H2), 2.69 (s, 3H, NMeA), 2.39 (s, 3H, amide), 1.21 (d, 9H, *J* = 9.5, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 173.8 (amide or C1), 170.15 (amide or C1), 147.4 (Pz3), 145.4 (Pz3), 142.1 (Pz3), 138.8 (Pz5), 138.6 (Pz5), 138.0 (Pz5), 118.7 (d, *J* = 2.9, C4), 117.7 (C5), 108.2 (Pz4), 107.9 (Pz4), 107.79 (Pz4), 68.7 (d, *J* = 12.6, C3), 57.6 (d, *J* = 2.6, C2), 45.7 (NMeB), 42.8 (NMeA), 13.0 (d, *J* = 30.8, $PMe_3$). $^{31}$P NMR ($CH_2Cl_2$, δ): -12.6 ($J_{wp}$ = 292). IR: $\upsilon_{BH}$ = 2505 cm$^{-1}$, $\upsilon_{amide}$ = 1698 cm$^{-1}$, $\upsilon_{NO}$ and $\upsilon_{amidine}$ = 1593 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 0.61 V. HRMS: [$M^+ = C_{21}H_{32}N_9O_2BPW^+$] = obsd (%), calcd (%), ppm: 666.1994 (85), 666.1996 (85), -0.3; 667.2035 (78), 667.2021 (80), 2.1; 668.2026 (100), 668.2020 (100), 1.0; 669.2071 (35), 669.2061 (43), 1.5; 670.2061 (80), 670.2052 (84), 1.3.

**Compound 6**

To a solution of **Compound 5** (0.101 g, 0.124 mmol) in MeOH (2 mL) was added a solution of Selectfluor™ (0.090 g, 0.254 mmol) in MeCN (2 mL). The bright-yellow homogeneous solution was stirred for 15 min. The solution was removed from the

glovebox and was treated with 50 mL of $Na_2CO_3$ (saturated, aq). This mixture was extracted with DCM (3x50 mL), and the combined organic layers were washed with deionized water (100 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting yellow residue was redissolved in minimal DCM and then added to stirring $Et_2O$ (200 mL) to induce precipitation of a white solid. The solid was collected on a 15 mL fine-porosity fritted funnel, yielding **6** (0.075 g, 0.086 mmol, 69%).

$^1$H NMR ($CD_3CN$, δ): 8.27 (d, *J* = 2, 1H, PzA3), 8.03 (d, *J* = 2, 1H, PzB3), 7.97 (d, *J* = 2, 1H, Pz5), 7.93 (d, *J* = 2, 1H, Pz5), 7.84 (d, *J* = 2, 1H, Pz5), 7.71 (d, *J* = 2, 1H, PzC3), 6.43 (t, *J* = 2, 2H, Pz4), 6.42 (dd, *J* = 3.6, 48.3, 1H, H5), 6.34 (t, *J* = 2, 1H, Pz4), 4.93 (dt, *J* = 3.6, 21.6, 1H, H4), 3.61 (s, 3H, OMe), 3.52 (t, *J* = 10.4, 1H, H3), 3.25 (s, 3H, NMeB), 2.54 (s, 3H, NMeA), 2.44 (s, 3H, amide), 2.27 (d, *J* = 9.5, 1H, H2), 1.29 (d, *J* = 9.1, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 173.1 (amide or C1), 169.9 (amide or C1), 147.1 (Pz3), 145.3 (Pz3), 142.3 (Pz3), 139.0 (Pz5), 138.8 (Pz5), 138.6 (Pz5), 108.5 (Pz4), 108.1 (Pz4), 108.0 (Pz4), 96.2 (d, *J* = 213.4, C5), 78.7 (dd, *J* = 3.5, 22.7, C4), 66.6 (d, *J* = 16.2, C3), 57.9 (OMe), 50.8 (C2), 44.3 (NMeB), 41.9 (NMeA), 25.4 (amide), 13.19 (d, *J* = 30.4, $PMe_3$). $^{31}$P NMR ($CH_2Cl_2$, δ): -10.15 ($J_{wp}$ = 268). IR: $\upsilon_{BH}$ = 2512 cm$^{-1}$, $\upsilon_{amide}$ = 1709 cm$^{-1}$, $\upsilon_{NO}$ and $\upsilon_{amidine}$ = 1582 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.43 V. HRMS: [$M^+$ = $C_{22}H_{35}N_9O_3BFPW^+$] = obsd (%), calcd (%), ppm: 716.2158 (72), 716.2164 (84), -0.8; 717.2180 (72), 717.2189 (80), -1.3; 718.2184 (100), 718.2188 (100), -0.5; 719.2220 (45), 719.2229 (44), -1.2; 720.2206 (94), 720.2220 (84), -2.0.

**Compound 7**

CAN (.091 g, 0.166 mmol) was added to a stirring solution of **Compound 4** (0.130 g, 0.151 mmol) in acetonitrile (5 mL). After 10 min, the solution was added to added to a 4 cm silica plug in a 15 mL medium porosity fritted funnel. This was eluted with 50 mL of MeOH and the filtrate was concentrated to dryness. The residue was loaded onto a 20 cm x 20 cm x 500 $\mu$m $SiO_2$ preparatory TLC place with 2 x 0.3 mL DCM and 0.3 mL MeCN. The plate was developed using a 10% MeOH/DCM solution. A band, which stained positive with $KMnO_4$, was scraped and placed in a round bottom flask with 50 mL of a 10% MeOH/DCM solution. After sonicating for 10 min, the resulting slurry was added to a 15 mL fine porosity fritted funnel and was washed with 10 mL DCM. The filtrate was stripped to dryness and the residue was redissolved in minimal MeCN (1.5 mL). This was added to 50 mL of stirring $Et_2O$ to precipitate a light tan solid. The precipitate was collected on a 15 mL fine porosity fritted funnel yielding **7** (17.3 mg, 0.049 mmol, 32%)

$^1$H NMR ($CD_3CN$, $\delta$): 7.43 (bs, 1H, NH), 7.36 (dd, *J* = 5.1, 1.2, 1H, H7'), 7.11 (dd, *J* = 10.1, 4.7, 1H, H3), 7.02 (dd, *J* = 5.2, 3.5, 1H, H5'), 6.99 (m, 1H, H6'), 6.62 (m, 1H, H2), 4.21 (m, 1H, H4), 3.78 (m, 1H, H5a), 3.58 (m, 1H, H5b), 3.28 (s, 3H, NMeA), 3.10 (s, 3H, NMeB). $^{13}$C NMR ($CD_3CN$, $\delta$): 157.27 (C1), 149.43 (C3), 141.52 (C4'), 128.60 (C5' or C6'), 127.35 (C5' or C6'), 126.69 (C7'), 116.05 (C2), 46.77 (C5), 41.44 (NMeA), 40.05 (NMeB), 34.96 (C4).

**Compound 7 NMR Yield**

In an NMR tube, compound 4 (0.039 g, 0.046 mmol) was dissolved in $CD_3CN$ (1 mL). To this solution was added CAN (0.032 g, 0.058 mmol). The resulting heterogeneous mixture was sonicated for 5 min, centrifuged, and a $^1$H-NMR spectrum was taken. After initial $^1$H NMR data was obtained, DCM (0.1 mL) was added to the NMR tube. Yield was based on the known DCM standard.

**Compound 8**

[TpW(NO)($PMe_3$)($\eta^2$-benzene)] **(**0.602 g, 1.035 mmol) was combined with DiPAT (0.306 g, 1.217 mmol). To this heterogeneous mixture was added to *N*,*N*-dimethylpyrimidin-2-amine (1.002 g, 8.133 mmol) in DME (2 mL). The resulting dark-yellow, homogeneous solution was stirred overnight (~14 h), forming a precipitate. The solid was collected on a 30 mL fine-porosity fritted funnel. The white powder was washed with DME (2x2 mL), pentane (3x15 mL), and $Et_2O$ (3x15 mL), yielding **8** (0.416 g, 0.536 mmol, 52%).

$^1$H NMR ($CD_3CN$, δ): 8.01 (bs, 1H, NH), 7.99 (d, *J* = 2, 1H, PzB3), 7.96 (d, *J* = 2, 1H, PzB5), 7.93 (d, *J* = 2, 1H, PzC5), 7.89 (d, *J* = 2, 1H, PzA5), 7.56 (d, *J* = 2, 1H, PzA3), 7.34 (d, *J* = 2, 1H, PzC3), 6.41 (t, *J* = 2, 1H, PzB4), 6.36 (t, *J* = 2, 1H, PzA4), 6.35 (t, *J* = 2, 1H, PzC4), 6.02 (dd, *J* = 1.5, 7.7, 1H, H4), 5.90 (d, *J* = 7.7, 1H, H5), 4.10 (dd, *J* = 1.7, 15.0, 1H, H3), 2.92 (s, 3H, NMeB), 1.83 (s, 3H, NMeA), 1.30 (d, *J* = 9.6, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 164.2 (C1), 145.4 (PzB3), 143.79 (PzA3), 141.9 (PzC3), 139.2 (Pz5),

138.5 (Pz5), 137.8 (Pz5), 117.8 (C5), 111.6 (C4), 107.9 (Pz4), 107.8 (Pz4), 65.7 (d, *J* = 16.3, C3), 36.8 (NMeB), 36.7 (NMeA), 13.15 (d, *J* = 31.6, $PMe_3$). $^{31}P$ NMR ($CD_3CN$, δ): -9.04 ($J_{wp}$ = 288). IR: $\upsilon_{BH}$ = 2519 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{iminium}$ = 1541 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 0.59 V. HRMS: [$M^+$ = $C_{18}H_{29}N_{10}OBPW^+$] = obsd (%), calcd (%), ppm: 625.1834 (78), 625.1842 (86), -1.3; 626.1860 (85), 626.1867 (80), -1.2; 627.1870 (100), 627.1865 (100), 0.7; 628.1893 (56), 628.1908 (41), -2.3; 629.1898 (93), 629.1898 (85), 0.0. Anal. Calc'd for $C_{19}H_{29}BF_3N_{10}O_4PSW$: C, 29.40; H, 3.77; N, 18.05. Found: C, 29.67; H, 3.80; N, 17.82.

**Compound 9**

In an NMR tube, **Compound 8** (0.02 g, 0.03 mmol) was mixed with $CD_3CN$ (0.6mL). To this a drop of HOTf was added and, after mixing, the solution appeared dark yellow and homogeneous.

$^1H$ NMR ($CD_3CN$, δ): 9.06 (s, 1H, NH), 8.10 (d, *J* = 2, 1H, Pz3/5), 8.04 (d, *J* = 2, 1H, Pz3/5), 7.97 (d, *J* = 2, 1H, Pz3/5), 7.96 (d, *J* = 2, 1H, Pz3/5), 7.83 (d overlapping, *J* = 2, 2H, Pz3/5), 7.10 (d, *J* = 6.4, 1H, NH), 6.53 (t, *J* = 2, 1H, Pz4), 6.49 (t, *J* = 2, 1H, Pz4), 6.44 (t, *J* = 2, 1H, Pz4), 6.39 (dd, *J* = 3.0, 7.6, 1H, H4 ), 6.05 (dd, *J* = 5.2, 7.7, 1H, H5), 4.59 (m, 1H, H3), 3.28 (s, 3H, NMeA), 2.44 (s, 3H, NMeB), 1.29 (d, 9H, *J* = 9.9, $PMe_3$). $^{31}P$ NMR ($CD_3CN$, δ): -9.04 ($J_{wp}$ = 271).

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# Chapter 5

## Synthesis of Tetrahydroindoline Derivatives Promoted by a Tungsten π-Base

**Abstract:** Indoline and quinoline derivatives form $\eta^2$-bound complexes with the dearomatization agent [TpW(NO)($PMe_3$)] that can be stabilized as their conjugate acids and isolated. Surprisingly, nitrogen substitution affects the stereoisomer ratio present after the initial coordination. In the case of coordinated *N*-ethylindoline and *N*-isopropylindoline, the high stereoisomer ratio (>10:1) formed, after coordination and protonation, was exploited to form new C-C and C-N bonds. Oxidation of the W(0) system, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), yields a novel organic compound.

Indoline and tetrahydroquinoline derivatives are prevalent in a wide variety of natural products and pharmaceutical compounds.[1-10] As a consequence, a number of strategies for their synthesis have been reported. A variety of these synthetic methodologies utilize dearomatization reactions,[11] typically exploiting the pyrrole portion of an indole ring.[12-22] However, there have been few examples of indoline derivatization where the arene portion of indoline has been directly modified (Figure 1).[23,24]

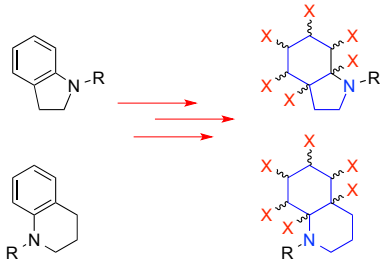



Figure 1: Dearomatization of Indoline and Tetrahydroquinoline

It was anticipated that by coordination of indoline or tetrahydroquinoline ring systems to a π-basic metal center, more elaborate octahydroindole or decahydroquinoline systems could be obtained. These compounds, like their indoline and tetrahydroquinoline precursors, are biologically active and are prevalent in a variety of natural products (Figure 2). Regarding the *cis*-fused ring systems, *Dysinosin A*[1] acts as a serine protease inhibitor; whereas, *Pumiliotoxin C* acts as a nicotinic antagonist.[25,26] *Cycloclavine*[2] and *Ergoline*,[3,27] which contain the *trans*-fused motifs, are ergot alkaloids.[28] Ergot alkaloids have been clinically used for vasoconstriction,[4] migraines,[29] and Parkinson's disease treatments.[30]

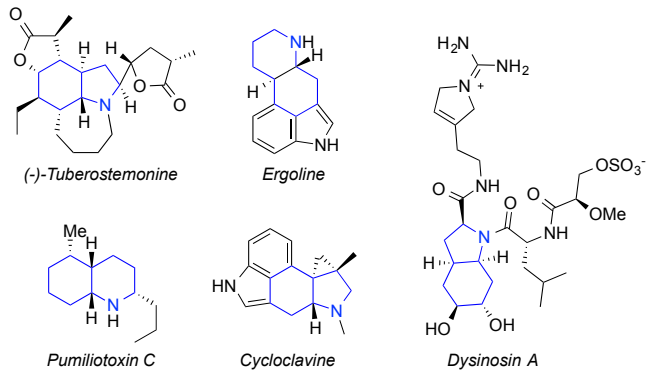



Figure 2: Natural Products Containing Octahydroindole or Decahydroquinoline Cores

Previous work has shown that *N*,*N*-dimethylaniline can be coordinated by the [TpW(NO)($PMe_3$)] metal fragment and trapped as its conjugate acid in the presence of diisopropylammonium triflate (DiPAT).[31] Various cyclohexene derivatives have been generated from synthetic modifications of the resulting metal-bound 2H-arene (Figure 3).[32,33]

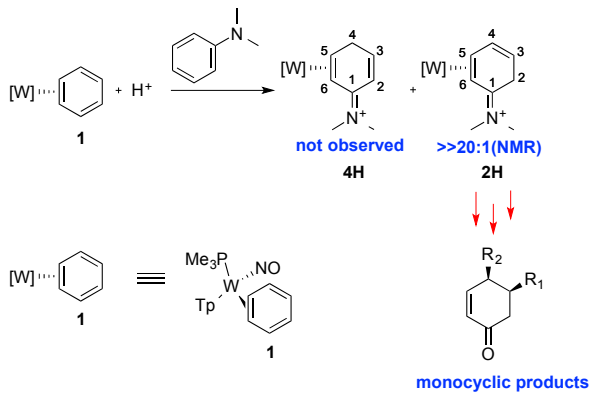
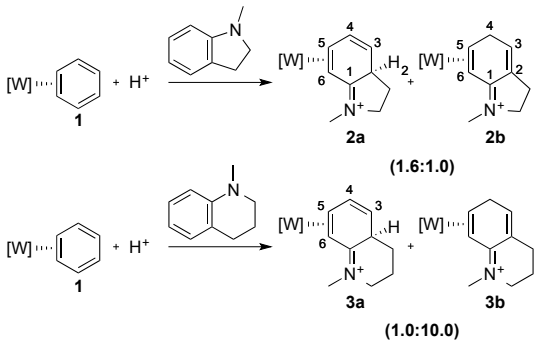



Figure 3: Synthetic Modifications of Coordinated *N,N*-dimethylaniline

Similar to the *N,N*-dimethylaniline ligand, *N*-methylindoline in the presence of DiPAT, DME, and [TpW(NO)($PMe_3$)($\eta^2$-benzene)], produces two new $\eta^2$-species that precipitate out of solution in >47% yields (Scheme 1). Analysis of the product mixture showed the formation of two isomers, **2a** and **2b**, in a ratio of (1.6:1). Although monitoring ligand exchange reactions with 1-methyl-1,2,3,4-tetrahydroquinoline, in the presence of DiPAT, showed the formation of the analogous cationic complex ($J_{183W\text{-}31P}$ = 286 Hz) this product failed to precipitate out of DME. However by performing a ligand exchange reaction as a heterogeneous mixture of [TpW(NO)($PMe_3$)($\eta^2$-benzene)], DiPAT, and 1-methyl-1,2,3,4-tetrahydroquinoline in hexanes the quinoline species was also isolated as two isomers, **3a** and **3b**, in a ratio of (1:10). By layering a DCM solution of (**3a** + **3b**), acetone, and isooctane, a crystal of **3b** was produced and analyzed by X-ray diffraction. An ORTEP diagram (Figure 4) confirms the assigned structure of **3b.**

Scheme 1: Dearomatization of Hetereocycles



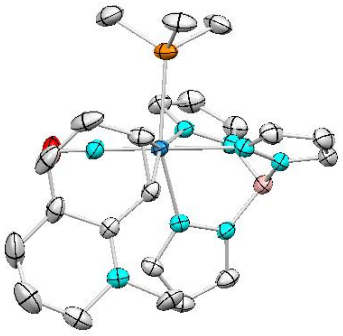



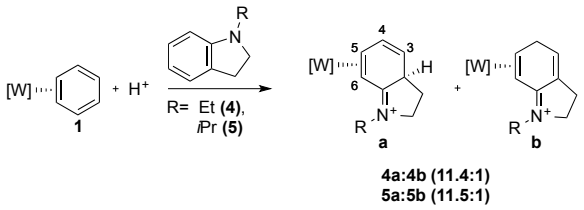
Figure 4: Crystal Structure of Compound **3b**

In both the coordinated indoline (**2a** + **2b**) and tetrahydroquinoline (**3a** + **3b**) mixtures, computational data[34] suggest that protonation at **C4**, as opposed to **C2**, produces the thermodynamic product. Of the two possible 2H stereoisomers, protonation *syn* to the metal fragment (**2a**) produces the thermodynamic isomer. *Anti* protonation at the **C2** position would cause an unfavorable steric interaction between the 5-membered ring of the indoline system and the Tp ligand.

The observations above imply that the synthesis of **2a** is under kinetic control, as protonation at the bridgehead carbon (**C2**) is slightly favored under the ligand exchange conditions. Unfortunately with the low stereoisomer ratio, the compound mixture (**2a** + **2b**) is not a viable synthetic precursor.

In hopes of kinetically favoring bridgehead-protonation to a greater extent, *N*-derivatized indoline molecules were synthesized and exchanged with [TpW(NO)($PMe_3$)($\eta^2$-benzene)] (**1**). It was found that increasing the steric bulk around the nitrogen dramatically favored bridgehead-protonation (**C2**) over protonation at (**C4**) after initial coordination (Scheme 2). Using this method, compound mixtures (**4a** + **4b**) and (**4a** + **4b**) were formed in the ratios of 11.4:1 and 11.5:1, respectively.

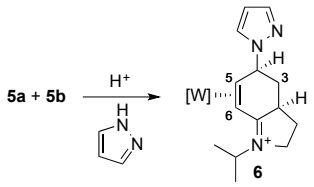
Scheme 2: Dearomatization of *N*-substituted Hetereocycles




In order to obtain a solid-state structure of a coordinated indoline molecule, further synthetic modifications were performed in hopes of producing a more pure sample. Preliminary reactivity studies ($^{31}$P-NMR) of (**5a** + **5b**) showed that, once protonated, **5a** could react with various amines and activated aromatic compounds. We settled on the characterization of a pyrazole addition (**6**) because of its ease of

crystallization (Scheme 3). A solid-state analysis of **6**, using X-ray diffraction, confirms this result (Figure 5).

Scheme 3: Hydroamination of **5a**



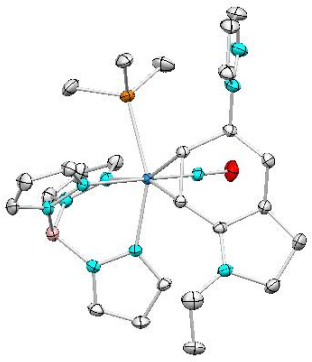
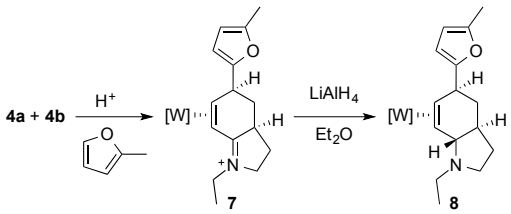



Figure 5: Crystal Structure of Compound **6**

In a similar fashion, the mixture of compounds (**4a** + **4b**) is able to react with acid and 2-methylfuran to produce the Friedel-Crafts product (**7**).[35,36] As a means of creating a *trans*-ring junction, compound **7** was reduced using $LiAlH_4$ in $Et_2O$ yielding **8** in 83 % yield (Scheme 4). A diffractable crystal was obtained by layering a DMSO solution of **8** and water. The X-ray structure (Figure 6) shows the additional hydrogen adding *anti* to the metal center and *trans* to the proton set during the initial complexation.

Scheme 4: Derivatizations of Compound **4a**



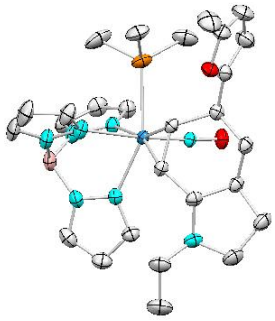
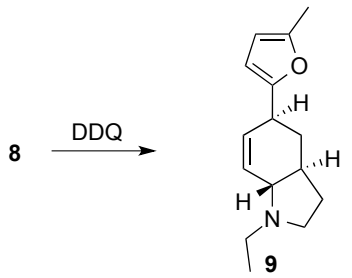



Figure 6: Crystal Structure of Compound **8**

Consistent with the decreased π-acidity of the ligand, the anodic wave (cyclic voltammetry) for compound **8** is less positive than its iminium precursor. This was reflected in the liberation of the final organic from the metal center. Although the coordinated iminium compound (**7**) fails to oxidize in the presence of DDQ at room temperature, the reduced species under similar conditions, is liberated from the metal center and can be isolated. 2D NMR data confirms that the three new stereocenters remain intact after oxidation (Scheme 5).

Scheme 5: Oxidation of Compound **8**




Regarding compound **9**, similar hydroindole ring systems have been synthesized directly through palladium mediated ring closure reactions with cyclic dienes.[37] However, the annulation process, which sets the stereocenters at the bridgehead positions, produces a *cis*-fused ring system, to which, our method serves as a complement.

In an elegant study by Wipf et al., *trans*-perhydroindoles were directly formed through a dearomatization reaction of L-Tyrosine with $PhI(OAc)_2$, followed by intramolecular nucleophilic addition of an NH to the resultant α,β-unsaturated enone. These scaffolds were further elaborated to biologically active natural products, (-)-tuberostemonine[38] and (-)-stenine.[39] These alkaloids have an unusually broad range of biological activity, serving as pulmonary tuberculosis and bronchitis medicine to glutamate antagonists.[40-42] These compounds are a subset of

the stemona group of alkaloids, in which, the majority of these natural products contain a *trans*-hydroindole ring system.[43]

To our knowledge, the reported hydroindole derivative (**9**) is unique. Moreover, based on the stability of the dearomatized precursor (**4a**) and its ability to react like previously reported tungsten systems, compound **4a** and similar species should serve as viable sources for the rapid generation of other complex hydroindole derivatives. Ongoing efforts continue to find conditions that favor bridgehead protonation of quinoline derivatives similar to **3a**. Moreover, the chemical nature of the 4H system (e.g., **2b** and **3b**) continues to be explored.

**Experimental Section:**

General Methods: NMR spectra were obtained on a 300, 500, 600, or 800 MHz spectrometer (Varian INOVA or Bruker Avance). All chemical shifts are reported in ppm and proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual $^{1}H$ or $^{13}C$ signals of the deuterated solvents as an internal standard. Phosphorus NMR signals are referenced to 85% $H_3PO_4$ ($\delta$ = 0.00) using a triphenylphosphate external standard ($\delta$ = -16.58). Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a glaze on a MIDAC Prospect Series (Model PRS) spectrometer fitted with a Horizontal Attenuated Total Reflectance (HATR) accessory (Pike Industries), or on a Nicolet Avatar 360 FT-IR spectrometer equipped with an ASI-DiComp diamond anvil ATR assembly. Electrochemical experiments were performed under a dinitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data was taken at ambient

temperature (~25 °C) at 100 mV/s in a standard three-electrode cell with a glassy carbon working electrode, *N*,*N*-dimethylacetamide (DMA) or acetonitrile (MeCN) solvent (unless otherwise specified), and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (approx. 0.5 M). All potentials are reported versus NHE (Normal Hydrogen Electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = -0.78 V), ferrocene ($E_{1/2}$ = +0.55 V), or decamethylferrocene ($E_{1/2}$ = +0.04 V) as an internal standard. The peak-to-peak separation was less than 100 mV for all reversible couples. High-resolution mass spectra were acquired in ESI mode, from samples dissolved in a 3:1 acetonitrile/water solution containing sodium trifluoroacetate (NaTFA). Mass spectra are reported as $M^+$ for monocationic complexes, or as $[M+H^+]$ or $[M+Na^+]$ for neutral complexes, using $[Na(NaTFA)_x]^+$ clusters as an internal standard. In all cases, observed isotopic envelopes were consistent with the molecular composition reported. For organic products, the monoisotopic ion is reported; for complexes, the major peaks in the isotopic envelope are reported. Spectra were collected either on a Bruker BioTOF-Q, a PerkinElmer Axion2 TOF, a Shimadzu IT-TOF, a Bruker MaXis Impact, an Agilent 6230 TOF, or a Waters Xevo G2Qtof.

Unless otherwise noted, all synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere. $CH_2Cl_2$ and benzene were purified by passage through a column packed with activated alumina. Other solvents and liquid reagents were thoroughly purged with dry nitrogen prior to use. Triflate salts of amines were synthesized by addition of an $Et_2O$ solution of triflic acid to the appropriate conjugate base dissolved in $Et_2O$. Deuterated solvents were used as received from

Cambridge Isotopes. Pyrazole (Pz) protons of the (trispyrazolyl) borate (Tp) ligand were uniquely assigned (eg., "PzB3") using a combination of 2-dimensional NMR data and phosphorus-proton NOE interactions (see Figure S1 in supplemental information). When unambiguous assignments were not possible, Tp protons were labeled as "Pz3/5 or Pz4". All *J* values for Pz protons are 2 (± 0.2) Hz. [TpW(NO)($PMe_3$)($\eta^2$-benzene)] was synthesized using a previously reported method.[44,45]

**DFT Calculations**.

Initial structures were built in GAUSSVIEW (5.0.8) and optimized with the PM6 semiempirical method in GAUSSIAN 09. These structures were refined stepwise in Gaussian using B3LYP and a series of basis functions incorporating LANL2 pseudopotentials and associated basis functions provided in the GAUSSIAN package. The most demanding calculations reported here put the LANL2DZ pseudopotential and its basis only on the W atom and used the 6-31G(d) basis for all other atoms.

**Compounds (2a + 2b)**

**Compound 1 (**1.79 g, 3.08 mmols) was combined with DiPAT (0.81 g, 3.22 mmols). To this heterogeneous mixture was added a DME (6 mL) solution of *N*-methylindoline (4.05 g, 30.41 mmols). This dark-yellow and homogeneous solution was stirred overnight (~14 h), forming a precipitate. The reaction mixture was filtered through a 30 mL fine-porosity fritted funnel. The collected yellow solid was

washed with DME (2x2 mL), and $Et_2O$ (2x50 mL), yielding a mixture of (**2a + 2b)** (1.14 g, 1.45 mmol, 47%).

Major Species $^1$H NMR ($CD_3CN$, δ): 8.09 (d, *J* = 2, 1H, Pz3/5), 7.98 (d, *J* = 2, 1H, Pz3/5), 7.93 (d, *J* = 2, 1H, Pz3/5), 7.84 (d, *J* = 2, 1H, Pz3/5), 7.73 (d, *J* = 2, 1H, Pz3/5), 7.39 (d, *J* = 2, 1H, Pz3/5), 6.57 (m, 1H, H4), 6.44 (overlapping triplets, *J* = 2, 2H, Pz4), 6.32 (t, *J* = 2, Pz4), 4.92 (dd, *J* = 1.9, 9.3, 1H, H3), 4.28 (m, 1H, H7a), 3.96 (m, 2H, H5 + H2), 3.79 (dd, *J* = 8.9, 10.5, H7b), 2.82 (s, 3H, NMe), 2.54 (m, 1H, H8a), 2.29 (d, *J* = 8.0, 1H, H6), 1.95 (m, 1H, H8b), 1.24 (d, *J* = 9.3, 1H, $PMe_3$). $^{13}$C NMR $^{31}$P NMR (*d*-acetone, δ): -9.03 ($J_{wp}$ = 285).

Minor Species $^1$H NMR ($CD_3CN$, δ): 8.00 (d, *J* = 2, 1H, Pz3/5), 7.97 (d, *J* = 2, 1H, Pz3/5), 7.91 (d, *J* = 2, 1H, Pz3/5), 7.89 (d, *J* = 2, 1H, Pz3/5), 7.63 (d, *J* = 2, 1H, Pz3/5), 7.38 (d, *J* = 2, 1H, Pz3/5), 6.43 (t, *J* = 2, 1H, Pz4), 6.39 (t, *J* = 2, 1H, Pz4), 6.35 (t, *J* = 2, 1H, Pz4), 6.30 (bs, 1H, H3), 4.28 (m buried, 1H, H4a), 4.04 (m, 1H, H7a), 3.82 (m, 1H, H7b), 3.57 (m, 1H, H5), 3.46 (d, *J* = 22.4, 1H, H4b), 2.90 (m, 2H, H8a/b), 2.60 (s, 3H, NMe), 2.01 (d, *J* = 8.8, 1H, H6), 1.19 (d, *J* = 8.9, 9H, $PMe_3$). $^{31}$P NMR (*d*-acetone, δ): -7.62 ($J_{wp}$ = 285).

Analysis of the Mixture

IR: $\upsilon_{BH}$ = 2505 cm$^{-1}$, $\upsilon_{C=C}$ = 1698, $\upsilon_{NO}$ and $\upsilon_{iminium}$ = 1585 and 1608 cm$^{-1}$. CV (DMA): $E_{p,a}$ = 1.11 V. HRMS: [M$^+$] = [$C_{21}H_{31}N_8OBPW^+$] obsd (%), calcd (%), ppm: 635.1936 (73), 635.1938 (85), -0.3; 636.1965 (74), 636.1963 (80), 0.3; 637.1961 (100), 637.1962 (100), -0.1; 638.2002 (44), 638.2003 (43), -0.2; 639.1994

(94), 639.1994 (84), 0.0. Anal. Calc'd for $C_{22}H_{31}BF_3N_8O_4PSW$: C, 33.61; H, 3.97; N, 14.33. Found: C, 33.57; H, 3.80; N, 14.33.

**Compounds (3a + 3b)**

**Compound 1 (**1.552 g, 2.670 mmols) was combined with DiPAT (0.803 g, 3.195 mmols). To this heterogeneous mixture was added a hexanes (24 mL) solution of 1-methyl-1,2,3,4-tetrahydroquinoline (3.622 g, 24.606 mmols). The pale-brown and hetereogeneous reaction mixture was stirred for 72 h. The reaction mixture was filtered through a 30 mL medium-porosity fritted funnel, yielding a dark-yellow solid. The solid was removed from the frit and triturated with DME (5 mL) for 5 min. This bright-yellow solid was collected on a 30 mL medium-porosity fritted funnel, washed with DME (5 mL), and hexanes (2x30 mL), yielding a mixture of **Compounds (3a + 3b)** (1.153 g, 1.441 mmol, 54%).

Major Species $^1$H NMR ($CD_3CN$, δ): 7.99 (d, *J* = 2, 1H, PzB3), 7.96 (d, *J* = 2, 1H, PzC3), 7.91 (d, *J* = 2, 1H, PzA5 or PzB5), 7.90 (d, *J* = 2, 1H, PzA5 or PzB5), 7.58 (d, *J* = 2, 1H, PzC3), 7.36 (d, *J* = 2, 1H, PzA3), 6.42 (t, *J* = 2, 1H, Pz4C), 6.39 (t, *J* = 2, 2H, PzA/B4), 6.35 (bs, 1H, H3), 4.33 (dd, *J* = 8.7, 22.7, 1H, H4a), 3.83 (m, 1H, H7a), 3.55 (m, 2H, H5 + H7b), 3.48 (dd, *J* = 4.7, 23.4, 1H, H4), 2.55 (m, 2H, H9a/b), 2.24 (s, 3H, NMe), 2.05 (m, 1H, H8a), 2.03 (d, *J* = 9.1, 1H, H6), 1.94 (m, 1H, H8b), 1.21 (d, *J* = 8.6, 9H, $PMe_3$). $^{31}$P NMR ($CD_3CN$, δ): -8.4 ($J_{wp}$ = 286).

Minor Species Key Features $^1$H NMR ($CD_3CN$, δ): 6.51 (m, 1H, H4), 4.72 (dd, *J* = 2.2, 9.3, 1H, H3), 1.27 (d, *J* = 9.3, 9H, $PMe_3$). $^{31}$P NMR ($CD_3CN$, δ): -9.3.

Analysis of the Mixture

IR: $\upsilon_{BH}$ = 2505 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{iminium}$ = 1590 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 0.95 V. HRMS: [$M^+$] = [$C_{22}H_{33}N_8OBPW^+$] obsd (%), calcd (%), ppm: 649.2087 (70), 649.2094 (84), -1.1; 650.2109 (69), 650.2120 (80), -1.7; 651.2136 (99), 651.2118 (100), 2.7; 652.2177 (44), 652.2160 (43), 2.7; 653.2168 (100), 653.2151 (84), 2.6. Anal. Calc'd for $C_{23}H_{33}BF_3N_8O_4PSW·H_2O$: C, 33.76; H, 4.31; N, 13.69. Found: C, 33.67; H, 3.97; N, 13.31.

**Compounds (4a + 4b)**

**Compound 1 (**0.3085 g, 0.532 mmols) was combined with DiPAT (0.152 g, 0.605 mmols). To this heterogeneous mixture was added a DME (1 mL) solution of 1-ethylindoline (0.580 g, 3.940 mmols). This light-brown and homogeneous solution was stirred overnight (~14 h), yielding a precipitate. The reaction mixture was filtered through a 15 mL fine-porosity fritted funnel. The collected yellow solid was washed with DME (1 mL), and hexanes (15 mL), yielding a mixture of **Compounds (4a + 4b)** (0.131 g, 0.164 mmol, 31%).

Major Species $^1$H NMR ($CD_3CN$, δ): 8.08 (d, *J* = 2, 1H, PzB3), 7.97 (d, *J* = 2, 1H, Pz5B or Pz5C), 7.93 (d, *J* = 2, 1H, Pz5B or Pz5C), 7.83 (d, *J* = 2, 1H, PzA5), 7.72 (d, *J* = 2, 1H, PzC3), 7.39 (d, *J* = 2, 1H, PzA3), 6.57 (m, 1H, H4), 6.43 (t, *J* = 2, 2H, PzB4 and PzC4), 6.28 (t, *J* = 2, 1H, PzA4), 4.92 (dd, *J* = 1.7, 9.5, 1H, H3), 4.15 (m, 1H, H7a), 4.00-3.87 (m, 3H, H5 and H2 and H7b), 3.08 (dd, *J* = 6.9, 14.2, 2H, N-Ethyl), 2.56 (m, 1H, H8a), 2.31 (d, *J* = 8.0, 1H, H6), 1.90 (m, 1H, H8b), 1.24 (d, *J* = 9.2, 9H, $PMe_3$), 1.90 (t, *J*

= 7.2, 3H, N-ethyl). $^{13}$C NMR ($CD_3CN$, δ): 191.0 (C1), 145.6 (PzB3), 143.4 (PzA3), 142.5 (PzC3), 138.8 (Pz5), 138.7 (Pz5), 138.2 (Pz5), 131.5 (d, *J* = 3.0, C4), 116.2 (C3), 108.4 (Pz4), 107.9 (Pz4), 107.4 (Pz4), 71.0 (d, *J* = 12.7, C5), 55.2 (C7), 49.9 (C6), 45.1 (C2), 43.6 (N-Etyl-$CH_2$), 29.3 (C8), 13.5 (d, *J* = 30.0, $PMe_3$), 12.1 (N-Ethyl-$CH_3$). $^{31}$P NMR (*d*-acetone, δ): -8.94 ($J_{wp}$ = 279).

Minor Species $^1$H NMR ($CD_3CN$, δ): 1.18 (d, *J* = 8.7, 9H, $PMe_3$), 1.02 (t, *J* = 7.0, 3H, N-Ethyl). HRMS: [$M^+$] = [$C_{22}H_{33}N_8OBPW^+$] obsd, calcd, ppm: 649.2084 (81), 649.2094 (84), -1.6; 650.2129 (80), 650.2120 (80), 1.4; 651.2126 (100), 651.2118 (100), 1.2; 652.2170 (39), 652.2160 (43), 1.6; 653.2146 (83), 653.2151 (84), -0.7.

Analysis of the Mixture

IR: $\upsilon_{BH}$ = 2507 $cm^{-1}$, $\upsilon_{C=C}$ = 1699 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{iminium}$ = 1581 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.07 V.

**Compounds (5a + 5b)**

**Complex 1 (**2.220 g, 3.820 mmols) was combined with DiPAT (1.156 g, 4.604 mmols). To this heterogeneous mixture was added 1-isopopylindoline (3.233 g, 21.963 mmols) dissolved in DME (6 mL). This light-brown and homogeneous solution was stirred overnight (~14 h), yielding a precipitate. The reaction mixture was filtered through a 60 mL medium-porosity fritted funnel. The collected light-yellow solid was washed with DME (3x3 mL), and $Et_2O$ (2x60 mL), yielding a mixture of **(5a + 5b)** (1.332 g, 1.636 mmol, 43%).

Major Species $^{1}$H NMR ($CD_3CN$, δ): 8.08 (d, *J* = 2, 1H, PzB3), 7.98 (d, *J* = 2, 1H, Pz5), 7.93 (d, *J* = 2, 1H, Pz5), 7.83 (d, *J* = 2, 1H, Pz5), 7.73 (d, *J* = 2, 1H, PzC3), 7.46 (d, *J* = 2, 1H, PzA3), 6.56 (m, 1H, H4), 6.43 (t, *J* = 2, 2H, Pz4), 6.30 (t, *J* = 2, 1H, Pz4), 4.90 (dd, *J* = 2.3, 9.5, H3), 4.08 (m, 1H, H7a), 4.00 (m, 1H, H5), 3.91 (dd, *J* = 9.3, 12.2, H7b), 3.89 (m, 1H, H2), 3.46 (m, 1H, *i*Pr), 2.57 (m, 1H, H8a), 2.33 (d, *J* = 8.2, 1H, H6), 1.84 (m, 1H, H8b), 1.23 (d, *J* = 9.2, 9H, $PMe_3$), 1.17 (d, *J* = 6.7, 3H, *i*Pr), 1.09 (d, *J* = 6.7, 1H, *i*Pr). $^{13}$C NMR ($CD_3CN$, δ): 191.0 (C1), 145.6 (PzB3), 143.3 (PzA3), 142.5 (PzC3), 138.8 (Pz5), 138.7 (Pz5), 138.1 (Pz5), 131.3 (d, *J* = 3.13, C4), 116.2 (C3), 108.4 (Pz4), 108.0 (Pz4), 107.5 (Pz4), 71.5 (d, *J* = 12.3, C5), 51.1 (C7), 50.1 (*i*Pr-methine), 50.0 (C6), 45.0 (C2), 29.3 (C8), 19.4 (*i*Pr-methyl), 19.1 (*i*Pr-methyl), 13.5 (d, *J* = 31.5, $PMe_3$). $^{31}$P NMR ($CH_2Cl_2$, δ): -10.26 ($J_{wp}$ = 281). IR: $\upsilon_{BH}$ = 2500 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{iminium}$ = 1595 and 1576 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.07 V. HRMS: [$M^+$] = [$C_{23}H_{35}N_8OBPW^+$] obsd (%), calcd (%), ppm: 663.2251 (75), 663.2251 (84), 0.0; 664.2276 (76), 664.2276 (81), -0.1; 665.2274 (100), 665.2275 (100), -0.2; 666.2321 (46), 666.2316 (44), 0.8; 667.2305 (92), 667.2308 (83), -0.4.

**Compound 6**

A solution of HOTf in MeCN (30 mL, 0.113 M) was added to **(5a + 5b)** (0.332 g, 0.408 mmol), resulting in a dark-yellow, homogenous solution. To this pyrazole (2.08 g, 24.2 mmol) was added. The resulting light-yellow homogeneous solution stirred for 30 min. The mixture was removed from the glovebox and was treated with 100 mL of $Na_2CO_3$ (saturated, aq). The reaction mixture was extracted with DCM (1x200 mL, followed by 2x50 mL), and the combined organic layers were

washed with deionized water (200 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The yellow oil was redissolved in minimal DCM and then added to stirring $Et_2O$ (400 mL) to induce precipitation of a white solid. The solid was collected on a 30 mL fine-porosity fritted funnel, washed with $Et_2O$ (2x50 mL), yielding **6** (0.250 g, 0.283 mmol, 69%).

$^1$H NMR ($CD_3CN$, δ): 8.13 (d, *J* = 2, 1H, PzB3), 7.96 (d, *J* = 2, 1H, PzC5), 7.95 (d, *J* = 2, 1H, PzB5), 7.86 (d, *J* = 2, 1H, H5'), 7.84 (d, *J* = 2, 1H, PzA5), 7.58 (d, *J* = 2, 1H, PzC3), 7.49 (d, *J* = 2, 1H, H3'), 7.40 (d, *J* = 2, 1H, PzA3), 6.46 (t, *J* = 2, 1H, PzB4), 6.39 (t, *J* = 2, 1H, PzC4), 6.35 (t, *J* = 2, 1H, H4'), 6.32 (t, *J* = 2, PzA4), 5.70 (m, 1H, H4), 4.06 (m, 1H, H7a), 3.89 (t, *J* = 11.4, H7b), 3.75 (m, 1H, H5), 3.45 (m, 1H, H2), 3.32 (sep, *J* = 6.3, 1H, *i*Pr), 2.56 (m, 1H, H3a), 2.44 (m, 1H, H8a), 2.31 (d, *J* = 9.4, 1H, H6), 1.90-1.80 (m, 2H, H4b + H8b), 1.15 (d, *J* = 6.3, 3H, *i*Pr), 1.12 (d, *J* = 6.3, 3H, *i*Pr), 1.06 (d, *J* = 9.2, 9H, $PMe_3$). $^{13}$C NMR ($CD_3CN$, δ): 191.3 (C1), 145.2 (PzB3), 144.5 (PzA3), 142.4 (PzC3), 139.4 (C3'), 138.9 (Pz5), 138.8 (Pz5), 138.3 (Pz5), 128.9 (C5'), 108.6 (PzB4), 108.0 (PzC4), 107.9 (PzA4), 106.6 (C4'), 72.8 (d, *J* = 14.0, C5), 63.0 (d, *J* = 2.4, C4), 50.5 (C7), 49.8 (*i*Pr methine), 49.7 (C6), 41.6 (C2), 39.9 (C3), 28.9 (C8), 19.5 (*i*Pr methyl), 19.2 (*i*Pr methyl), 13.33 (d, *J* = 30.8, $PMe_3$). $^{31}$P NMR ($CH_2Cl_2$, δ): -9.9 ($J_{wp}$ = 278). IR: $\upsilon_{BH}$ = 2502 $cm^{-1}$, $\upsilon_{NO}$ and $\upsilon_{iminium}$ = 1595 and 1575 $cm^{-1}$. CV (DMA): $E_{p,a}$ = 1.29 V. HRMS: [$M^+$] = [$C_{26}H_{39}N_{10}OBPW^+$] obsd (%), calcd (%), ppm: 731.2591 (68), 731.2626 (82), -4.8; 732.2642 (64), 732.2651 (81), -1.2; 733.2636 (100), 733.2650 (100), -2.0; 734.2674 (47), 734.2689 (47), -2.0; 735.2667 (84), 735.2683 (83), -2.1.

**Compound 7**

HOTf (1 mL) was added to a MeCN solution of **(5a + 5b)** (0.723 g, 0.903 mmol), resulting in a dark-yellow, homogenous solution. To this 2-methylfuran (3 mL, 34 mmol) was added. The resulting dark-red homogeneous solution stirred for 1 h. The mixture was removed from the glovebox and was treated with 100 mL of $Na_2CO_3$ (saturated, aq). The reaction mixture was extracted with DCM (3x100 mL), and the combined organic layers were washed with deionized water (200 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The yellow oil was redissolved in minimal DCM and then added to stirring $Et_2O$ (500 mL) to induce precipitation of a light-yellow solid. The solid was collected on a 30 mL fine-porosity fritted funnel, washed with $Et_2O$ (2x50 mL), yielding **7** (0.715 g, 0.809 mmol, 90%).

HRMS: $[M^+] = [C_{27}H_{39}N_8O_2BPW^+]$ obsd (%), calcd (%), ppm: 731.2521 (84), 731.2514 (82), 1.0; 732.2558 (80), 732.2539 (81), 2.6; 733.2550 (100), 733.2539 (100), 1.6; 734.2609 (45), 734.2578 (47), 4.3; 735.2580 (80), 735.2571 (83), 1.3.

**Compound 8**

$LiAlH_4$ (0.156 g, 4.110 mmol) was added to a stirring mixture of **7** (0.715 g, 0.809 mmol) in $Et_2O$ (100 mL). After 30 min, the grey, heterogeneous solution was filtered through a 60 mL M frit packed with 1 inch of celite. The frit was washed with an additional 50 mL of $Et_2O$ and the filtrate was concentrated *in vacuo*. The resulting clear oil was redissolved in DCM (50 mL) and washed with 50 mL of $Na_2CO_3$

(saturated, aq). The aqueous layer was back extracted with DCM (2 x 50 mL). The resulting organic fractions were combined, washed with deionized water (100 mL), and dried over anhydrous $MgSO_4$. Concentrating the solution *in vacuo* produced a yellow powder, compound **8** (0.525 g, 0.715 mmol, 83%)

HRMS: $[M+H]^+$ = $[C_{27}H_{40}BN_8O_2PW+H^+]$ obsd (%), calcd (%), ppm: 733.2657 (85), 733.2670 (82), -1.8; 734.2684 (81), 734.2696 (81), -1.6; 735.2685 (100), 735.2695 (100), -1.4; 736.2732 (47), 736.2734 (47), -0.3; 737.2726 (80), 737.2727 (83), -0.2.

**Compound 9**

Currently optimizing the procedure.

$^1$H NMR ($CDCl_3$, δ) 6.07 (1H, H7), 5.858 (1H, H4' or H3'), 5.839 (1H, H4' or H3'), 5.74 (1H, H6), 3.63 (1H, H5), 3.35 (1H, H2), 3.00 (1H, $H_{Et}$), 2.30 (1H, H2), 2.51 (1H, H7a), 2.12 (1H, $H_{Et}$), 2.00 (1H, H3a), 1.90 (1H, H3), 1.47 (1H, H3), 1.13 (3H, $H_{Et}$).

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# Chapter 6

## Concluding Remarks and Acknowledgments

As the indoline and quinoline project (**Chapter 5**) stays in the hands of two more graduate students, I do not believe it is fair to say that the work is truly done. I am glad that this project will continue when I am gone.

I would like to thank **everyone** who has helped me during my 5 years at the University of Virginia. It feels sad to leave the University of Virginia; however, I am excited for what the future has in store.

**Dr. Harman:** I could not have asked for a better mentor. Although Dr. Harman lacks croquet skills, he is an excellent teacher and he has helped me get through the difficult times in graduate school. Thank you for being patient with me. I hope we stay in touch. Good luck with the Tunngsten Chemistry!

**Dr. Myers:** Thank you for teaching me NMR spectroscopy. Some of my best memories in graduate school came from our time in the conference room. Eventually, I will buy you a Whittaker Smoother at a bar.

**Dr. Ellena:** Thank you for showing me how to use all of the NMR instruments (and showing me again, and again, and again, …..) Remember the time **Vlad** dropped the depth gauge in the Trition and the time **Sisi** got stuck to the Burger with a wrench?

**Dr. Snyder:** Thank you for showing me how to be an organic chemist! I learned so much working with you at Hamilton.

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**Laura:** Thanks for helping me with my fantasy baseball team and making me cupcakes!

**Ben:** We had some good times. Remember when you brought sodium outside of the box and you only told me about it? I promise I won't verbally tell anyone that story. I had so much fun with you when we ran the Charlottesville 10 miler together. Thanks for always smiling at work.

**Victor:** It was such a wonderful experience working with you. You are a funny guy and I am glad we continue to go out for hamburgers together. I really enjoyed when we would set up two-hour reactions on Sundays and then go for sandwiches.

**Vlad:** Thanks for making ice pops with me in lab. You are a great guy and I'm glad I finally gave you back your jacket.

**Anne:** Thank you for all of your help! I had a lot of fun working with you in lab. Good luck in medical school! ACETONITRILE!

**Andrew:** Good luck in graduate school! You are a very cool guy and when you're a famous chemist (or professional croquet player) please hire me.

**Phil:** Thank you for always pressuring **Andrew** to drink maple syrup. One day we will trick him. I WILL REALLY MISS YOUR SARCASM. Good luck with everything and don't lose your wallet.

**Jeff:** I really enjoyed doing Gaussian calculations with you. I really hope you'll be able to bind that Mo-phenol derivative. Thank you for always being supportive and helpful. I enjoyed running O'hill with you and playing catch after work on nice days. Thank you for teaching me how to make coffee.

**Bri:** It has been a pleasure working with you on the indoline and quinoline chemistry. I really hope that the project will be successful! I can't wait to come back and listen to your thesis defense.

**Katy:** Good luck! I have no doubt that you'll be successful in graduate school.

**Gunnoe Lab:** Maybe I'll return those chemicals I borrowed before I leave… Thanks **Sam** for helping me with inorganic chemistry!

**Ducks on a Pond:** I had a great time playing softball with you guys. Big shout out to Aaron and Kelly.

**Morganne:** Thank you for always being supportive of my decisions! Love you! I'm glad we got to go on vacation this summer (even though I had to write this document!).

**Steve**, **Jordan**, **Justin**, **Becca**, **Matt**, **Joe**, and **Ezra**: I'm so glad that we kept in touch after college/high school. I've had a lot of fun with you guys (beach trips, vineyards, breweries, etc.) I'm glad we still find time to see each other.