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

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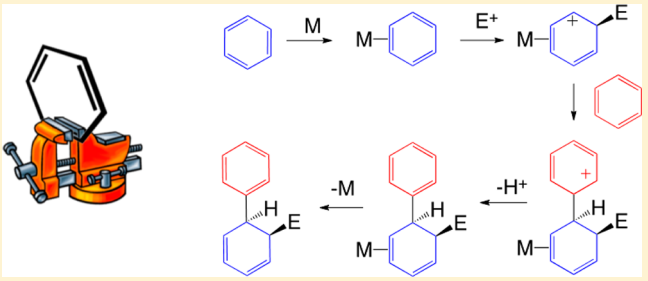
Supporting Information

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.



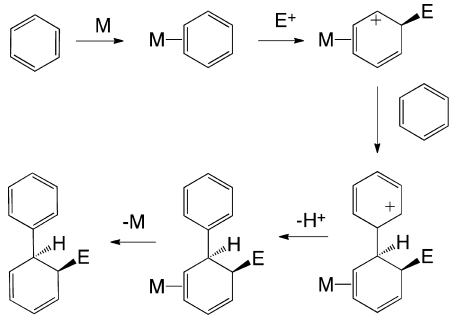
INTRODUCTION

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} bond are also known, but can be more difficult to perform,[11−13] 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.

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 η^2-coordinated arene complexes were considered as precursors

Scheme 1. Proposed Aromatic Coupling with η^2-Coordinated Arenes



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 nonaromatic 2*H*-tautomers.[16] Finally, 2*H*-arenium complexes derived from anisole (**6**) and *N*,*N*-dimethylaniline (**7**) were also included in the study, as these nonaromatic systems are structurally similar to the phenol analogues. The seven arene-derived tungsten complexes investigated are summarized in Figure 1.[17−22]

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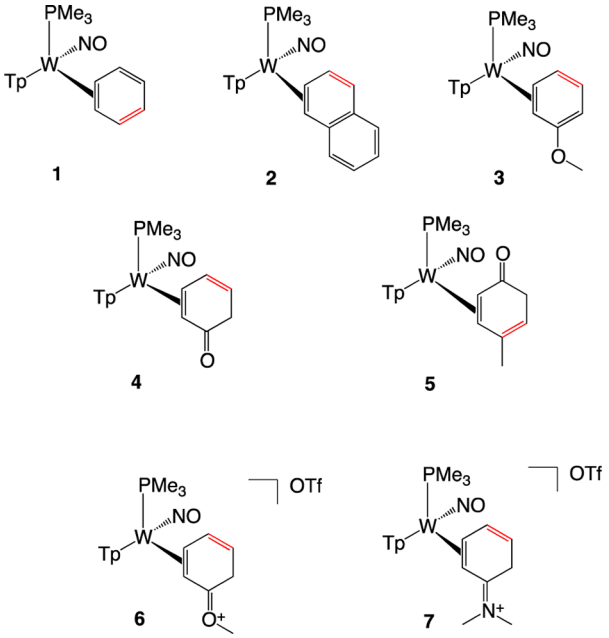


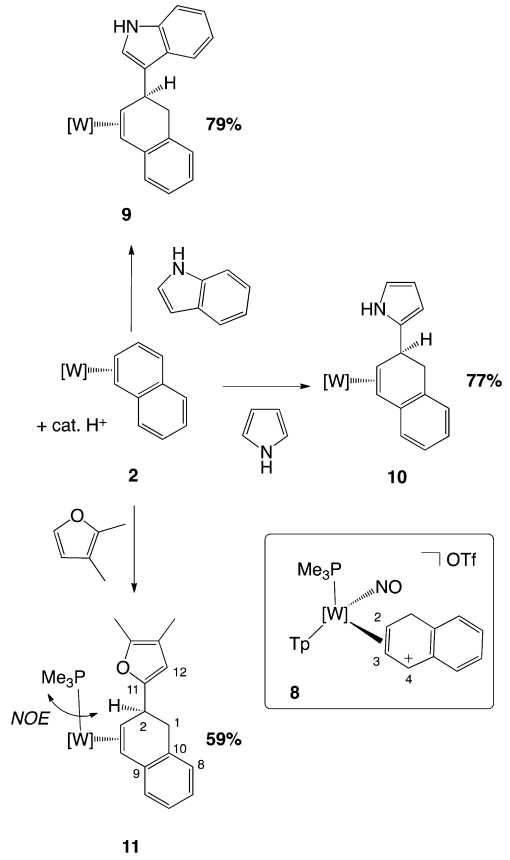
Figure 1. η^2-Arene-derived complexes for consideration as partners for Friedel–Crafts reactions.

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 the ^{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 led to either 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 analogue,[23] with the exception of H4, whose peak appears considerably more downfield for the W system owing to its "η^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. The 2,3-dimethylfuran-derived product **11** was chosen 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.

With regard to characterization of **9**–**11**, the H2 signal showed a strong NOE interaction with the PMe_3 ligand, which supports the assignment of nucleophilic addition anti to the metal fragment. Data from multidimensional 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 analogue **11**,

Scheme 2. Reactions with Naphthalene Complex 2 and Various Aromatic Nucleophiles[a]



[a][W] = TpW(NO)(PMe_3).

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 solid-state molecular structure determination for the indolyldihydronaphthalene **9** confirms that the addition of the indole occurs anti to the tungsten metal fragment (Figure 2).

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

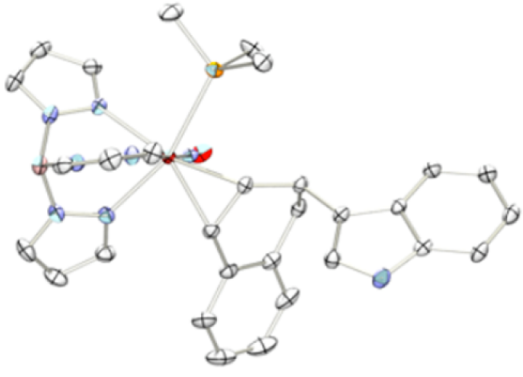


Figure 2. Solid-state molecular structure of the indolyldihydronaphthalene product **9**.

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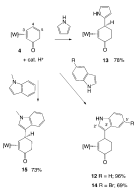
resulted in the decomposition of the starting material: the ^{31}P signal observed for **3** was replaced with a new signal that showed no $^{183}W-^{31}P$ coupling. Weaker acids failed to alter the starting material. However, for the dearomatized 2*H*-phenol complex (**4**), indole and pyrrole derivatives 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 biorelevant 5′-position was well tolerated (Scheme 3).

Scheme 3. Reactions of Phenol Complex 4 with Various Aromatic Nucleophiles[a]



[a][W] = TpW(NO)(PMe$_3$).

As shown in the solid-state molecular 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).

In contrast to the phenol complex (**4**), the *p*-cresol analogue **5** underwent quantitative protonation with DPhAT or $CH_3CN{\cdot}HOTf$ (Scheme 4). However, this allylic species failed to react with any aromatic nucleophiles. 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]

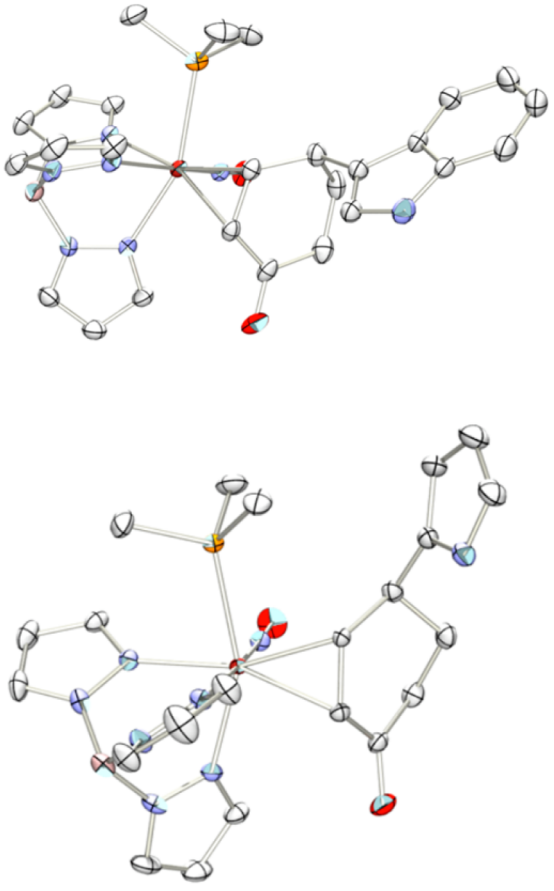
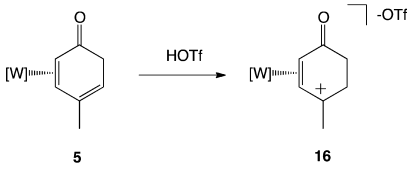


Figure 3. Solid-state molecular structure of indole (**12**; top) and pyrrole (**13**; bottom) addition products. Co-crystallized $CHCl_3$ is omitted for clarity from **12**.

Scheme 4. Protonation of the *p*-Cresol Complex 5[a]



5 **16**

[a][W] = TpW(NO)(PMe$_3$).

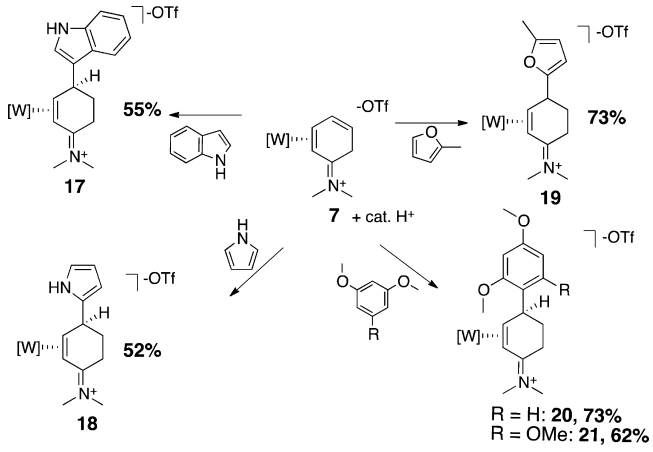
Quantitative protonation of anisole complex **3** forms **6**, an isolable, cationic species.[25] Under the conditions tested, compound **6** did not react cleanly with any aromatic nucleophiles. Monitoring reactions between **6** and an aromatic compound in different solvents showed in each case a substantial amount of decomposition.

Attempts to quantitatively protonate complex **6** with $CH_3CN{\cdot}HOTf$ 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 2*H*-anilinium ligand is formally a cation, strong back-bonding 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.

Electrophiles other than H^+ are capable of reacting with arene or arenium derivatives,[17,27] and Friedel−Crafts reactions

Scheme 5. Reactions with Anilinium Complex 7 and Various Aromatic Nucleophiles[a]



[a][W] = TpW(NO)(PMe$_3$).

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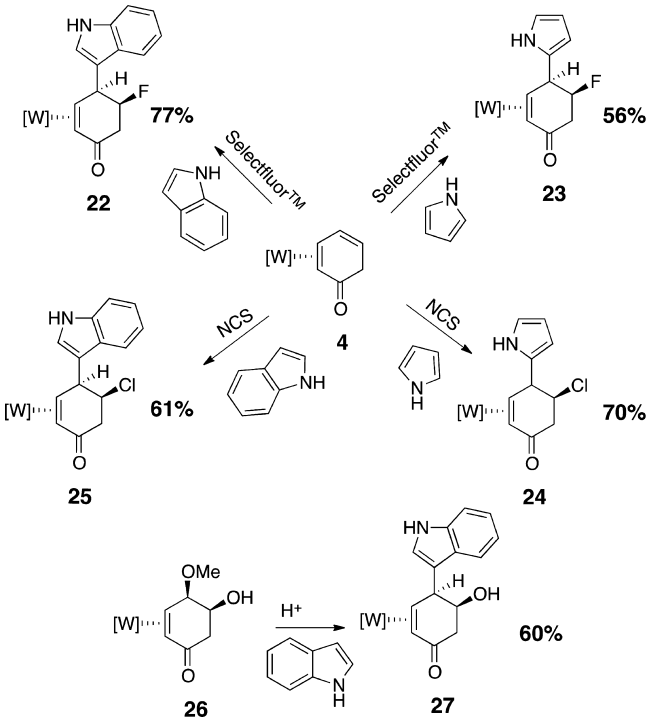
to form more functionalized ring-coupling products were also attempted.

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 *N*-chlorosuccinimide did not seem to interfere with the Friedel–Crafts reaction step, 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[a]

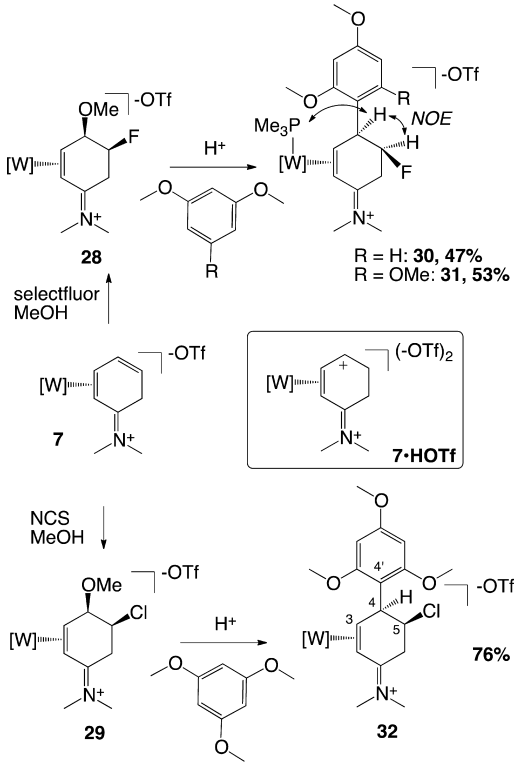


[a][W] = TpW(NO)(PMe$_3$).

Similar to the reaction with the hydroxylated enone **26**, by starting with the previously reported 5-halo-4-methoxy analogue 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.

A solid-state molecular structure of compound **32** confirms the relative stereochemistry of the hetereoatom electrophile and carbon nucleophile (Figure 4). Complexes **30** and **31** have NOE interactions between signals of H4 and H5, and the methine proton anti to the aromatic nucleophile (H4) has a strong NOE interaction with the PMe$_3$ ligand.

Scheme 7. Electrophilic Hetereoatom Addition Followed by Aromatic Nucleophilic Addition to Anilinium Complex 7[a]



[a][W] = TpW(NO)(PMe$_3$).

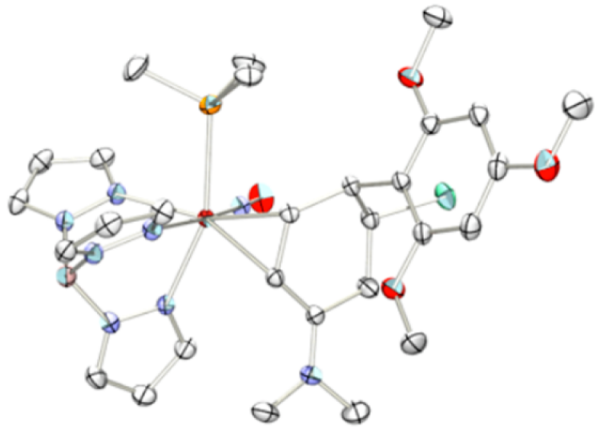


Figure 4. Solid-state molecular structure of the 5-chloro-4-arylated derivative **32**. Triflate counterion is omitted for clarity.

Interestingly, the methoxy groups in **32** are all nonequivalent, an observation suggesting slow rotation of the bulky aryl ring about the C4–C4′ axis on the NMR time scale.

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, either ceric ammonium nitrate (CAN) or 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) was sufficient, but for the iminium analogues, 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

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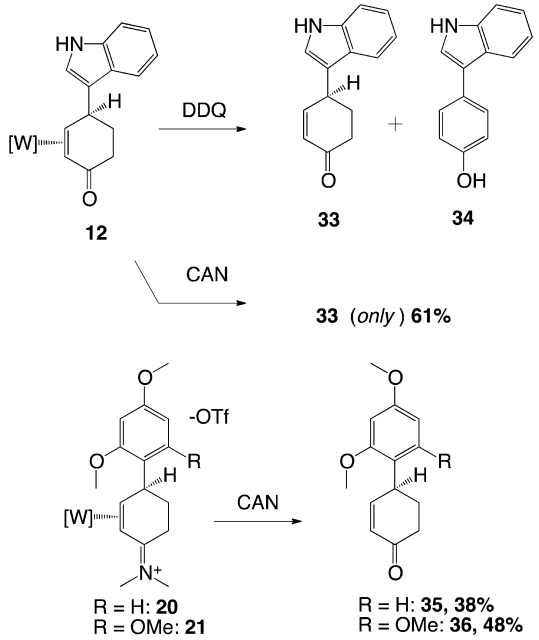
base to the reaction failed to prevent the formation of the *p*-indol-3-ylphenol impurity. In contrast, oxidation of **12** with CAN did not produce any of the aromatic side product. However, purification of **33** using basic alumina in the presence of O_2 effected its conversion to **34**. Rearomatization 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 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



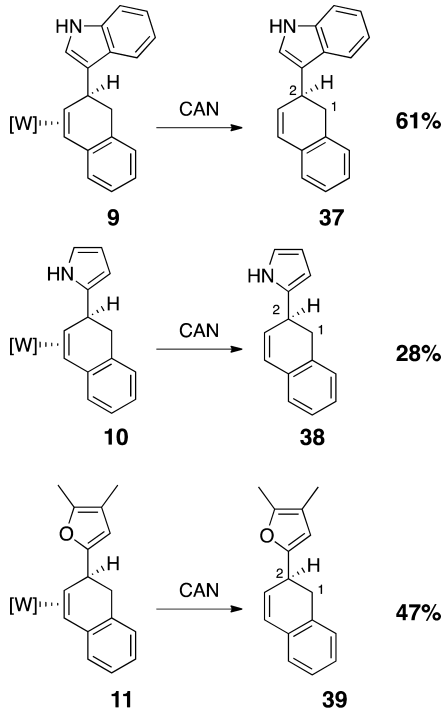
Unfortunately, the decomplexation conditions used for **33** did not work for the pyrrole analogue, and only phenol and pyrrole were recovered. Further, using these conditions with products containing halogens did not yield any clean organic compounds.

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 8). 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.

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

Scheme 9. Oxidative Decomplexation of Dihydronaphthalenes 9–11[a]



[a][W] = TpW(NO)(PMe$_3$).

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 have been previously synthesized. However, **33** closely resembles an advanced synthetic intermediate patented for use as an antidepressant.[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] η^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 the 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.

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CONCLUSION

A new method for coupling aromatic rings was explored in which the bicyclic product is partially dearomatized. The method utilizes a tungsten-activated arene prepared from the commercially available precursor $TpW(NO)Br_2$ (Sigma-Aldrich), which, 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.

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 ^1H 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 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 as an electrolyte [approximately 0.5 M in dimethylacetamide (DMA)] unless otherwise noted. All potentials are reported versus the 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 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 $[M + H]^+$ 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 were 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%).

^1H 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)-1H-indole)) (**9**).* Compound **2** (201 mg, 0.319 mmol), indole (178 mg, 1.521 mmol), and diphenylammonium triflate (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%).

^1H 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-W} = 281 Hz). CV (DMA): $E_{p,a}$ = +0.488 V. IR: ν_{NO} = 1550 cm^{-1}. HRMS $(M + Na)^+$ obsd (%), calcd (%), 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)-1H-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 for 2.5 h. The vial was removed from the glovebox, and the solution was diluted with 30 mL of dichloromethane (DCM) and extracted with 10 mL of saturated aqueous $NaHCO_3$ solution. The aqueous layer was back-extracted with 5 mL of 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 redissolved 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%).

^1H NMR ($CDCl_3$): δ 8.05 (d, 1H, J = 2.0, Pz3B), 7.87 (br 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-W} = 280 Hz). CV (DMA): $E_{p,a}$ = +0.533 V. IR: ν_{NO} = 1535 cm^{-1}. HRMS $(M + Na)^+$ obsd (%), calcd (%), 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;

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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-η^2-(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 h. The vial was removed from the glovebox, and the solution was diluted with DCM (20 mL) and extracted with 5 mL of a saturated aqueous $NaHCO_3$ solution. The aqueous layer was back-extracted with 5 mL of DCM. The DCM solution was extracted twice with 10 mL portions of water, each of which was back-extracted with DCM (5 mL). 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-W} = 280 Hz). CV (DMA): $E_{p,a}$ = +0.543 V. IR: ν_{NO} = 1552 cm^{-1}. HRMS $(M+Na)^+$ obsd (%), calcd (%), 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-η^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 a 0.17 M TfOH/MeOH solution was added to the reaction solution, and the resulting mixture was stirred for 3 h. To the reaction solution was added 2 mL of 0.5 M aqueous $NaHCO_3$, and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5 M 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 of $CHCl_3$ 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 × 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-W} = 284 Hz). CV: $E_{p,a}$ = +0.84 V. IR: ν_{BH} = 2484 cm^{-1}, ν_{CO} = 1601 cm^{-1}, ν_{NO} = 1562 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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-η^2-(4-(1H-pyrrol-2-yl)cyclohex-2-enone)) (**13**).* To a 4-dram vial charged with a stir bar were added **4** (0.050 g, 0.084 mmol) and pyrrole (0.079 g, 1.190 mmol), which were then 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, which was stirred for 3 h. To the reaction solution was added 2 mL of 0.5 M aqueous $NaHCO_3$, and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5 M aqueous $NaHCO_3$, 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 × 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-W} = 280 Hz). CV: $E_{p,a}$ = +0.82 V. IR: ν_{BH} = 2493 cm^{-1}, ν_{CO} = 1603 cm^{-1}, ν_{NO} = 1563 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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-η^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 were added **4** (0.050 g, 0.084 mmol) and 5-bromoindole (0.067 g, 0.346 mmol), which were 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, which was stirred for 3 h. To the reaction solution was added 2 mL of 0.5 M aqueous $NaHCO_3$, and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5 M aqueous $NaHCO_3$, 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 × 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

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(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-W} = 281 Hz). CV: $E_{p,a}$ = +0.89 V. IR: ν_{BH} = 2492 cm^{-1}, ν_{CO} = 1593 cm^{-1}, ν_{NO} = 1562 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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. $[M + Na]^+$ obsd (%), calcd (%), 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-η^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 were added **4** (0.050 g, 0.084 mmol) and *N*-methylindole (0.054 g, 0.417 mmol), which were then 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 h. To the reaction solution was added 2 mL of 0.5 M aqueous $NaHCO_3$, and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of 0.5 M 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 $CHCl_3$ (1 mL) and added to a stirring solution of hexanes (50 mL). A white precipitate was collected on a 15 mL fine-porosity fritted funnel under vacuum and then rinsed with hexanes (3 × 5 mL), giving **15** (0.045 g, 0.0613 mmol, 73%).

^1H 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-W} = 283 Hz). CV: $E_{p,a}$ = +1.00 V. IR: ν_{BH} = 2492 cm^{-1}, ν_{CO} = 1612 cm^{-1}, ν_{NO} = 1562 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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-η^2-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). ^{13}C 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 NMR (CD_3CN): δ −8.06 (J_{P-W} = 283 Hz). CV: $E_{p,a}$ = +1.29 V. IR: ν_{BH} = 2507 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1574 cm^{-1}. HRMS: (M^+) obsd (%), calcd (%), 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 was added 2-methylfuran (1 mL, 13.38 mmol), which was 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 was added **7** (0.1200 g, 0.155 mmol), 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 saturated aqueous $NaHCO_3$ solution. The reaction mixture was extracted with DCM (3 × 30 mL). 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%).

^1H 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 NMR ($CDCl_3$): δ −9.23 (J_{P-W} = 281 Hz). CV (DMA): $E_{p,a}$ = +1.20 V. IR: ν_{BH} = 2507 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1568 cm^{-1}. HRMS (M^+) obsd (%), calcd (%), 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(1H)-ylidene)-N-methylmethanaminium](OTf) (**20**).* In a 4-dram vial charged with a stir bar was added 1,3-dimethoxybenzene (1.5 mL, 10.29 mmol). To this were added a TfOH/DCM solution (10 mL, 0.0005 M) and MeCN (0.20 mL). The mixture was stirred for 1 min. To this mixture was added **7** (0.3257 g, 0.42 mmol). After 1 h, the reaction was quenched outside of the glovebox by the addition of 25 mL of a saturated aqueous $NaHCO_3$ solution. The reaction was extracted with DCM (3 × 25 mL), and the combined organic layers were 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%).

^1H 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

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(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-W} = 286 Hz). CV (DMA): $E_{p,a}$ = 1.20 V. IR: ν_{BH} = 2503 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1567 cm^{-1}. HRMS (M^+) obsd (%), calcd (%), 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(1H)-ylidene)methanaminium](OTf) (**21**).* In a 4-dram vial charged with a stir bar was added 1,3,5-trimethoxybenzene (1.021 g, 6.064 mmol), which was 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 was added **7** (0.2011 g, 0.26 mmol). 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 saturated aqueous $NaHCO_3$ solution. The reaction mixture was extracted with DCM (3 × 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%).

^{1}H 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-W} = 290 Hz). CV (DMA): $E_{p,a}$ = 1.13 V. ν_{BH} = 2506 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1568 cm^{-1}. HRMS (M^+) obsd (%), calcd (%), 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-η^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 of DCM, giving a solution that was yellow and homogeneous. To this solution was added Selectfluor (0.018 g, 0.050 mmol) dissolved in CH_3CN (1 mL); 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 h. To the reaction solution was added 2 mL of saturated aqueous $NaHCO_3$, and the two layers were separated. The DCM layer was extracted two times with 1 mL of saturated 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 of $CHCl_3$ 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 × 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-W} = 280 Hz). CV: $E_{p,a}$ = +0.93 V. IR: ν_{BH} = 2496 cm^{-1}, ν_{CO} = 1598 cm^{-1}, ν_{NO} = 1567 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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. $[M + Na]^+$ obsd (%), calcd (%), 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-η^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 of DCM, giving a solution that was yellow and homogeneous. To this was added Selectfluor (0.039 g, 0.111 mmol) dissolved in 1 mL of acetonitrile; 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 h. To the reaction solution was added 2 mL of saturated aqueous $NaHCO_3$, and the two layers were separated. The DCM layer was extracted two times with 1 mL of saturated 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 of $CHCl_3$ 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 × 5 mL) and dried *in vacuo*. 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-W} = 275 Hz). CV: $E_{p,a}$ = +0.93 V. IR: ν_{BH} = 2493 cm^{-1}, ν_{CO} = 1614 cm^{-1}, ν_{NO} = 1557 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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-η^2-(5-chloro-4-(1H-pyrrol-2-yl)cyclohex-2-enone)) (**24**).* In a 4-dram vial with a stir bar, in a fume hood, **4** (0.074 g, 0.124 mmol) was added and dissolved in 0.5 mL of DCM. The yellow, homogeneous solution was placed in an ice bath. *N*-Chlorosuccinimide (0.005 g, 0.039 mmol) was dissolved in 0.25 mL of DCM, then placed in the ice bath. The two solutions were combined and stirred, still cold, for 30 s, resulting in the reaction solution turning a dark yellow color. After 30 s, pyrrole (0.017 g, 0.255 mmol) was added to the reaction solution and stirred, still cold, for 4.5

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h. To the reaction solution was added 2 mL of saturated aqueous Na_2CO_3, and the two layers were separated. The DCM layer was extracted two times with 1 mL of saturated aqueous 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 of $CHCl_3$ 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 × 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-W} = 277 Hz). CV: $E_{p,a}$ = +1.01 V. IR: ν_{BH} = 2493 cm^{-1}, ν_{CO} = 1604 cm^{-1}, ν_{NO} = 1564 cm^{-1}. HRMS: $[M + H]^+$ obsd (%), calcd (%), 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-η^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 of $CHCl_3$. The yellow, homogeneous solution was placed in an ice bath. A separate solution was prepared of *N*-chlorosuccinimide (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 was added 2 mL of saturated aqueous Na_2CO_3, and the two layers were separated. The $CHCl_3$ layer was extracted two times with 1 mL of saturated aqueous 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 of $CHCl_3$ 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 × 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, Pz4A or Pz4C), 106.0 (s, Pz4A 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-W} = 280 Hz). CV: $E_{p,a}$ = +1.07 V. IR: ν_{BH} = 2494 cm^{-1}, ν_{CO} = 1602 cm^{-1}, ν_{NO} = 1557 cm^{-1}. HRMS: $[M + Na]^+$ obsd (%), calcd (%), 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-η^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 of $CHCl_3$, 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 a 0.17 M TfOH/EtOH solution was added to the reaction solution, and the mixture was stirred for 48 h. 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-W} = 283 Hz). CV (DMA/DMSO): $E_{p,a}$ = +0.84 V. IR: ν_{BH} = 2486 cm^{-1}, ν_{CO} = 1600 cm^{-1}, ν_{NO} = 1569 cm^{-1}. HRMS: $[M + Na]^+$ obsd (%), calcd (%), 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(1H)-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 were added a TfOH/DCM solution (1 mL, 0.0034 M) and MeCN (0.20 mL). The homogeneous solution was stirred for 1 min. To this mixture was added **28** (0.0550 g, 0.066 mmol), 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 saturated aqueous $NaHCO_3$ solution. The reaction was extracted with DCM (3 × 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, $CDCl_3$): δ 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-W} = 283 Hz). CV (DMA): $E_{p,a}$ = 1.27

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V. IR: ν_{BH} = 2514 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1571 cm^{-1}. HRMS (M^+) obsd (%), calcd (%), 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(1H)-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 were added a TfOH/CH_2Cl_2 solution (1 mL, 0.0034 M) and MeCN (0.20 mL), and the mixture was stirred for 1 min. To this mixture was added **28** (0.1029 g, 0.1248 mmol). After 1.5 h, the reaction was quenched, outside of the glovebox, by the addition of 25 mL of saturated aqueous $NaHCO_3$. The reaction mixture was extracted with DCM (3 × 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, C2′OMe or C4′OMe or C6′OMe), 55.51 (s, C2′OMe or C4′OMe or C6′OMe), 55.42 (s, C2′OMe or C4′OMe or C6′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-W} = 284 Hz). CV (DMA): $E_{p,a}$ = 1.27 V. IR: ν_{BH} = 2507 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1587 cm^{-1}. HRMS (M^+) obsd (%), calcd (%), 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 were added a TfOH/DCM solution (1 mL, 0.0034 M) and MeCN (0.20 mL). This was stirred for 1 min. To this mixture was added **29** (0.0915 g, 0.1089 mmol). After 1 h the reaction was quenched, outside of the glovebox, by the addition of 50 mL of saturated aqueous $NaHCO_3$. The reaction mixture was extracted with DCM (3 × 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 ($CDCl_3$): δ 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-W} = 283 Hz). CV (DMA): $E_{p,a}$ = 1.30 V. ν_{BH} = 2512 cm^{-1}, ν_{NO} + $\nu_{Iminium}$ = 1566 cm^{-1}. HRMS (M^+) obsd (%), calcd (%), 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 of 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, resulting 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 in. silica plug in a 60 mL medium-porosity fritted disk was activated with 2 min of microwave irradiation. Once the silica plug cooled to room temperature, Et_2O (50 mL) was added to make a slurry; then 1 in. 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 of 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 ($CDCl_3$): δ 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: ν_{CO} = 1673 cm^{-1}, ν_{CC} = 1658 cm^{-1}. HRMS: $[M + Na]^+$ obsd (%), calcd (%), 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 of acetone. The solution was yellow and homogeneous. Finely ground CAN (0.022 g, 0.040 mmol) was added along with 0.5 mL of 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 of Et_2O. Solvent was removed from the filtrate under vacuum, leaving a green residue. A 0.5 in. neutral alumina plug with 1 in. 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 of ether for fraction 1. The column was then eluted with 40 mL of 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.

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*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 saturated aqueous $NaHCO_3$ and stirred. After 30 min, the reaction mixture was extracted with Et_2O (3 × 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 × 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 at R_f = 0.46−0.53 was scraped off the plate and placed in a test tube. To the test tube was added EtOAc (20 mL), 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, C5′OMe/C7′OMe), 55.73 (s, C5′OMe/C7′OMe), 37.42 (s, C6), 35.86 (s, C4), 30.62 (s, C5) IR: ν_{CO} = 1674 cm^{-1}. HRMS: $(M + Na)^+$ obsd (%), calcd (%), 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 saturated aqueous $NaHCO_3$ solution. After 25 min, the reaction mixture was extracted with Et_2O (3 × 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 × 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 at R_f = 0.60−0.70 was scraped off the plate, and placed in a test tube. To the test tube was added EtOAc (20 mL), 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). IR: ν_{CO} = 1667 cm^{-1}. HRMS $(M + Na)^+$ obsd (%), calcd (%), 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)-1H-indole (**37**).* In a fume hood, **9** (60 mg, 0.080 mmol) was mixed with acetone (1.986 g). A solution of 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 h. The slurry was diluted with 20 mL of Et_2O and washed with water (3 × 10 mL). The water layers were combined and back-extracted with Et_2O (2 × 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 DCM (2 × 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 min, and the slurry was filtered on a 60 mL medium-porosity fritted funnel and washed with 39 mL of 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)-1H-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 h. The mixture was diluted with Et_2O (40 mL) and extracted with water (2 × 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 of stirring hexanes. The precipitate was filtered over a 60 mL fine-porosity fritted funnel, washed with 30 mL of hexanes, and discarded. The filtrate was concentrated *in vacuo* to give an orange solid. The solid was dissolved in small portions of DCM (2 × 0.3 mL) and loaded onto a 500 μm silica preparatory plate. The plate was eluted with 100 mL of 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 of EtOAc. The test tube was sonicated for 20 min, and the silica was filtered over a 60 mL medium-porosity fritted funnel and washed with 25 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 was stirred for 30 min before being diluted with Et_2O (30 mL) and extracted with water (2 × 15 mL). The water layers were combined and extracted with Et_2O (4 × 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 a 30 mL fine-porosity fritted funnel and discarded. The filtrate was concentrated *in vacuo*, dissolved in small portions of DCM (2 × 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 min. The silica was filtered on a 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

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(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).

■ ASSOCIATED CONTENT

Supporting Information

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.

■ AUTHOR INFORMATION

Author Contributions

$^{\perp}$These authors contributed equally.

Notes

The authors declare no competing financial interest.

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