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Polarization of the Pyridine Ring: Highly Functionalized Piperidines from Tungsten−Pyridine Complex

Daniel P. Harrison,[†] Michal Sabat,[†] William H. Myers,[‡] and W. Dean Harman*[,†]

Departments of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States, and University of Richmond, Richmond, Virginia 27173, United States

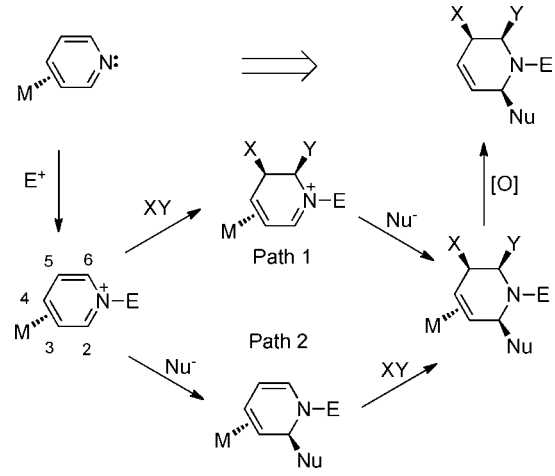
Received August 20, 2010; E-mail: wdh5z@virginia.edu

Abstract: The *N*-acetylpyridinium complex of {TpW(NO)(PMe_3)} undergoes regio- and stereoselective reactions with a broad range of common organic nucleophiles, providing a family of 1,2-dihydropyridine (DHP) complexes of the form TpW(NO)(PMe_3)(3,4-η^2-DHP). The present study explores the elaboration of these systems into novel piperidines. The addition of an acid to the DHP complexes generates highly asymmetric π-allyl complexes that in turn react with a second nucleophile at either C3 or C5. The subsequent oxidative decomplexation of these materials yields several piperidinamides with unconventional substitution patterns.

Introduction

Pyridines most commonly form complexes with transition metals via nitrogen coordination, but reports of η^6- and η^2-bound complexes have also emerged.[1−10] The latter types of complexes have shown potential as reagents for organic synthesis owing to the ability of the metal to modulate the reactivity of the pyridine ring through the π system.[11] For example, the complex TpW(NO)(PMe_3)(η^2-*N*-acetylpyridinium)[12,13] (**1**), prepared from pyridine−borane, acetic anhydride, and TpW(NO)(PMe_3)(η^2-benzene), smoothly undergoes 5,6-dialkoxylation (Scheme 1; X = Y = OR) when treated with Selectfluor reagent (Air Products and Chemicals, Inc.) in an alcoholic solvent,[14] without compromising the coordinating metal complex. Subsequent addition of a nucleophile followed by oxidative decomplexation has led to several novel Δ^3-piperidines (Scheme 1, path 1).[14] The goal of the present study is to explore the complementary reaction sequence (path 2), where nucleophilic addition at C2 provides an η^2-dihydropyridine[15] complex that is activated by the metal toward additional elaboration at the remaining exposed alkene (see Scheme 1).

Scheme 1. Two Pathways from a Pyridinium Complex to Δ^3-Piperidines



Results and Discussion

The acylpyridinium complex **1** has been shown to react with a broad range of nucleophilic reagents common to conventional organic synthesis (Scheme 2).[16] In every case examined, the nucleophile adds to C2 of the pyridine ring with complete stereocontrol, where the nucleophile adds anti to the metal

[†] University of Virginia.
[‡] University of Richmond.

(1) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Chem. Commun.* **1989**, 995–996.
(2) Fish, R. H.; Kim, H. S.; Fong, R. H. *Organometallics* **1989**, *8*, 1375–1377.
(3) Wucherer, E. J.; Muetterties, E. L. *Organometallics* **1987**, *6*, 1691–1695.
(4) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038–1040.
(5) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896–2900.
(6) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101–8102.
(7) Bonanno, J. B.; Viege, A. S.; Wolczanski, P. T.; Lobkovsky, E. B. *Inorg. Chim. Acta* **2003**, *345*, 173–184.
(8) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1997**, *119*, 247–248.
(9) Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2493–2508.
(10) Neithamer, D. R.; Parkanyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421–4423.
(11) Davies, S. G.; Edwards, A. J.; Shipton, M. R. *J. Chem. Soc., Perkin Trans.* **1991**, 1009–1017.
(12) Harrison, D. P.; Welch, K. D.; Nichols-Nielander, A. C.; Sabat, M.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 16844–16845.
(13) Welch, K. D.; Harrison, D. P.; Lis, E. C.; Liu, W.; Salomon, R. J.; Harman, W. D.; Myers, W. H. *Organometallics* **2007**, *26*, 2791–2794.
(14) Kosturko, G. W.; Harrison, D. P.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2009**, *28*, 387–389.
(15) The term "dihydropyridine" is a generic description of the 2-substituted 1-acetyl-1,2-dihydropyridine ligands found in Scheme 2.
(16) Harrison, D. P.; Zottig, V. E.; Kosturko, G. W.; Welch, K. D.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2009**, *28*, 5682–5690.

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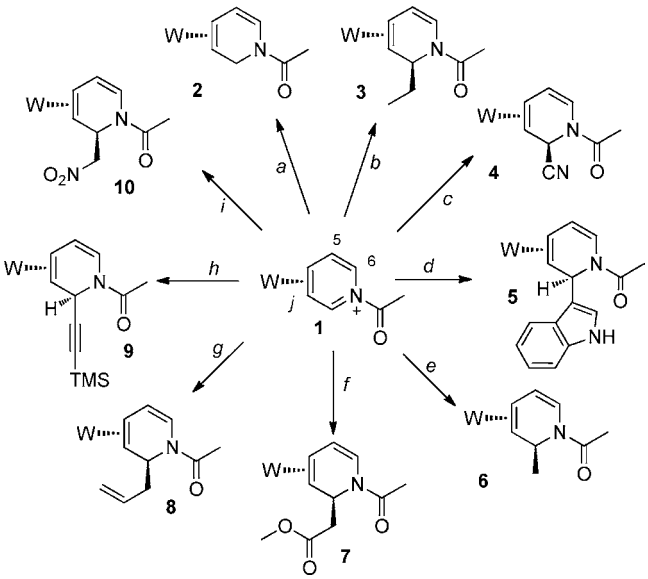
Scheme 2. Broad Scope of Nucleophilic Addition to Acetylpyridinium Complex **1**[a]



[a] Reagents and conditions: (a) $NaBH_4$, MeOH; (b) $ZnEt_2$; (c) TMSCN, DABCO; (d) indole, 2,6-lutidine; (e) MeMgBr; (f) Zn^0, methyl 2-bromoacetate; (g) Zn^0, allyl bromide; (h) MeLi, ethynyltrimethylsilane, $ZnBr_2$; (i) $MeNO_2$, NEt_3 or DABCO. In all cases W = {TpW(NO)(PMe_3)} with a coordination diastereomer ratio (cdr) > 10:1.

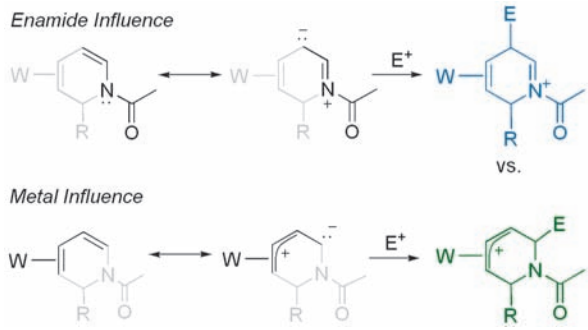


Figure 1

fragment. With a full range of η^2-1,2-dihydropyridine (DHP) complexes in hand (Scheme 2), we set out to functionalize the remaining double bond (C5−C6).

Enamides, like enamines, are polarized such that the β-carbon is nucleophilic.[17] In the case of the DHP complexes **2**−**10** (see Scheme 2), this implies that addition of an electrophile would occur at C5, as shown in Figure 1. However, previous studies of η^2-coordinated 1,3-diene complexes with π-basic metals indicate a clear regiochemical preference for electrophilic addition at the uncoordinated terminal alkene carbon.[18,19] By analogy, electrophiles would react with DHP complexes at C6. Thus, the conjugation of the C5−C6 bond to both the nitrogen and the tungsten presented the opportunity to determine which effect dominates.

To address this issue for the case in which the electrophile (E^+) is H^+ (Figure 1), the acid diphenylammonium triflate

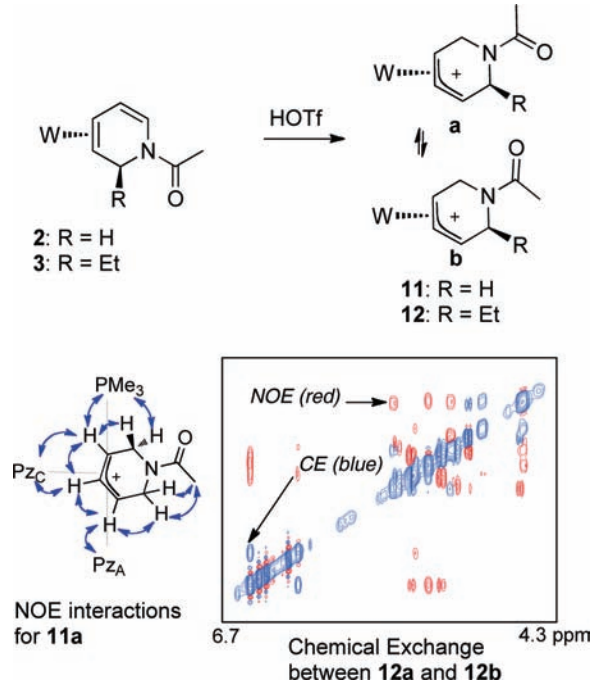


Figure 2

(DPhAT, 0.016 g, 0.050 mmol) was added to a solution of dihydropyridine complex **2** (0.026 g, 0.042 mmol) in MeCN (0.30 g). Monitoring the reaction via ^{31}P NMR revealed an immediate reaction (i.e., <3 min). The appearance of two new downfield ^{31}P resonances and an accompanying shift in the nitrosyl stretching frequency from 1558 (for **2**) to 1643 cm^{-1} indicated a significant reduction of the electron density on the metal.[13] Precipitation of complex **11** with diethyl ether was accomplished in 96% yield. A ^1H NMR spectrum indicated the presence of two complexes (**a**, **b**) in a 3:1 ratio, each signified by two diastereotopic methylene groups, and the absence of any deshielded resonance that could correspond to an acyl-iminium proton. COSY data supported the notion that both components (**11a**, **11b**) were allyl complexes; however, many of the resonances overlapped, making a complete ^1H NMR assignment difficult. Clarifying matters was a NOESY spectrum of **11**, which not only supported the structural features shown in Figure 2 but also revealed a chemical exchange (CE) between the two species, occurring on the time scale of proton relaxation. Taken together, these data are most consistent with **11a** and **11b** being C−N rotational isomers, distinguished by the orientation of the amide group (see Figure 2). Similar results were obtained when the ethyl analogue **3** was treated with triflic acid in MeCN (Figure 2), in this case forming allyl **12** (97% yield) as a 2.7:1 ratio of conformational isomers.

A crystal of **11** was grown suitable for X-ray analysis, which confirmed the expected structure (Figure 3). A comparison of bond lengths in allyl complex **11** reveals that the allyl ligand is highly asymmetric (i.e., $\sigma-\pi$ distortion), with C3 much farther from the tungsten atom (2.59 Å) than the other terminal allyl carbon C5 (2.28 Å; Δ = 0.31 Å). Pioneering work by Faller, Hoffmann, et al. demonstrated that asymmetry in a π allyl ligand can lead to highly selective nucleophilic additions to a terminal carbon,[20] a feature we hoped to utilize (*vide infra*). More

(17) Carbery, D. R. *Org. Biomol. Chem.* **2008**, *6*, 3455–3460.
(18) Lis, E. C.; Delafuente, D. A.; Lin, Y.; Mocella, C. J.; Todd, M. A.; Liu, W.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2006**, *25*, 5051–5058.
(19) Liu, W.; You, F.; Mocella, C. J.; Harman, W. D. *J. Am. Chem. Soc.* **2006**, *128*, 1426–1427.
(20) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592–598.

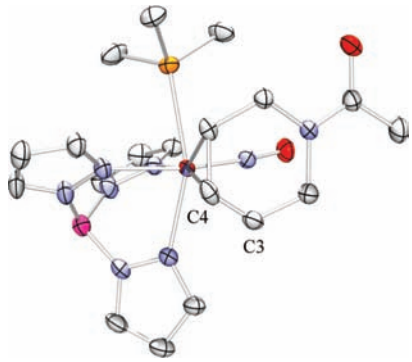
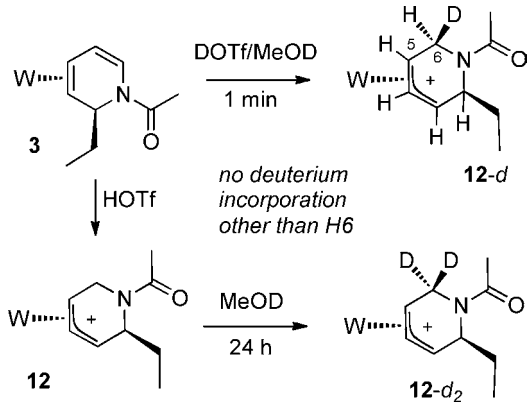


Figure 3. POV-ray diagram of allyl complex **11**. Bond distances: W−C3, 2.590 Å; W−C4, 2.289 Å; W−C5, 2.284 Å; C3−C4, 1.435 Å; C4−C5, 1.358 Å. Triflate anion omitted.

Scheme 3. Deuteration of Dihydropyridine Complex **3**

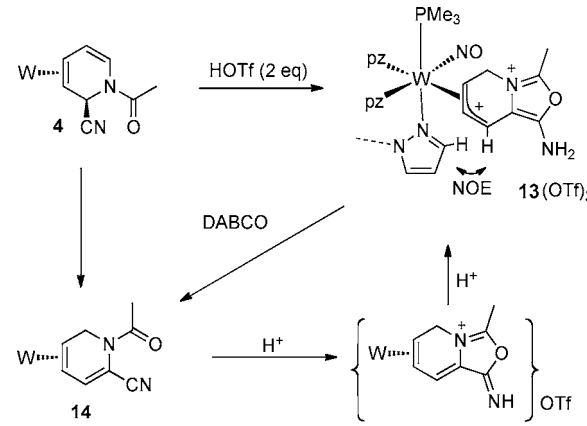


recently, Liebeskind[21] and Legzdins[22] have each reported asymmetrically bound allyl complexes for group VI metals (referred to by Liebeskind as "η^2-allyls"). This type of allylic distortion, which we attribute to the interaction of the allyl π^* orbital and the d orbital orthogonal to the NO, has also been observed by our group for a molybdenum system ($\Delta = 0.31$ Å).[23]

Deuterium studies were undertaken to probe the possibility that the kinetically controlled site of protonation might be the C5 pyridine carbon (see Figure 1). Addition of a DOTf/MeOD solution to the ethyldihydropyridine complex **3** resulted in >90% incorporation of deuterium at the exo position of the C6 methylene group (**12**-*d*) (Scheme 3). No incorporation was detected at any other ring hydrogen. Alternatively, the addition of MeOD to a CD_3CN solution of **12** resulted in nearly complete deuterium incorporation after 24 h at *both* of the C6 diastereotopic methylene protons. As before, no other ring protons suffered exchange. We note that while deuterium was not incorporated at C5, these experiments do not rule out this carbon from being transiently deuterated.[24]

Addition of HOTf to the cyano-substituted dihydropyridine complex **4** results in a deep red solution. Proton NMR

Scheme 4. Formation of the Reissert-like Allyl Complex **13**



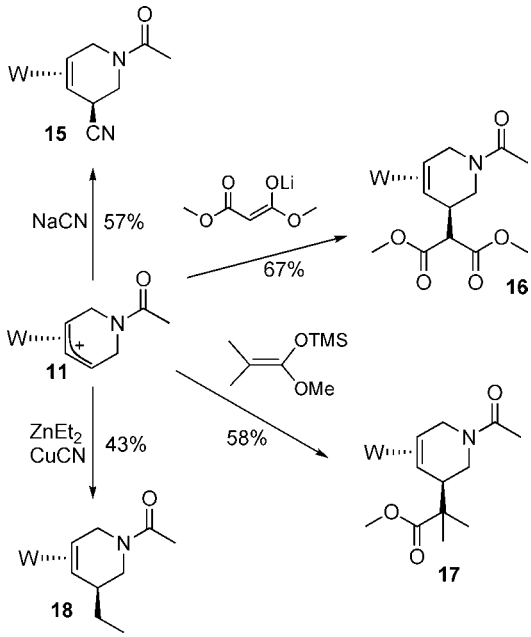
resonances of the resulting species **13** again suggest significant η^2-allyl character; the protons associated with the bound carbons C4 and C5 show nearly identical chemical shifts of 4.35 ppm (^{13}C: 61.2 and 78.9 ppm), while the chemical shift of H3 is 8.42 ppm (^{13}C: 147.9 ppm). Although a ^{1}H chemical shift of 8.42 ppm is not inconsistent with an iminium signal (resulting from C5 protonation), detailed COSY and NOESY analyses clearly indicate that **13** is a π-allyl complex, similar to its 2-ethyl and 2-hydrido cousins. The most deshielded signal (8.42 ppm) shows a coupling with one of the hydrogen atoms of the two bound carbons. Additionally, the 8.42 ppm signal shows a large nuclear Overhauser effect with the pyrazole trans to PMe_3 and no coupling with the geminal methylene group adjacent to piperidine nitrogen. Although these data are consistent with an allylic species similar to **11** and **12**, several spectroscopic features indicated that it was an entirely different class of compound. In the ^{1}H NMR spectrum, the amide methyl signal is no longer at 2.1 ppm as is typical of acetamides but rather at 2.77 ppm. Also present is a broad singlet with an integration of two protons at 8.1 ppm. The IR spectrum did not show any absorption consistent with a nitrile CN stretch, nor was any signal present in the ^{13}C NMR spectrum attributable to a nitrile ^{13}CN. Instead, three new chemical shifts at 103.1, 159.1, and 159.4 ppm were present. These data, combined with HSQC and HMBC studies, confirmed the formation of a dicationic allylic isoxazolium ring (Scheme 4), often referred to as a Reissert salt.[25−27] Addition of DABCO to **13** results in the isolation of compound **14**, a tautomer of **4**. Returning a sample of **14** to an acidic acetonitrile solution quantitatively regenerated allyl **13**.

The asymmetric nature identified in the crystal structure of allyl **11** suggests that the pyridine ring carbon C3 may be considerably more electrophilic than C5, and ^{13}C NMR data for these two carbons further support this hypothesis, showing a dramatic contrast (64.6 vs 130.5 ppm, CD_2Cl_2) in the two terminal allyl resonances. True to expectation, when a series of nucleophilic reagents was introduced to the allyl complex **11**, addition occurred exclusively at the C3 position, thereby desymmetrizing the heterocyclic ring.

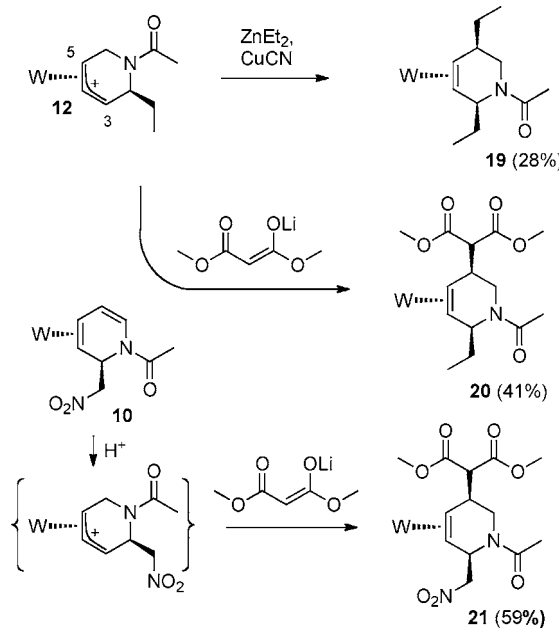
Although deprotonation sometimes pre-empted addition, the reaction of many nucleophiles with the parent allylic piperidine **11** produced Δ^3-piperidinamides (**15**−**18**). Following these

(21) Villanueva, L. A.; Ward, Y. D.; Lachicotte, R.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4190–4200.
(22) Tsang, J. Y. K.; Buschhaus, M. S. A.; Fujita-Takayama, C.; Patrick, B. O.; Legzdins, P. *Organometallics* **2008**, *27*, 1634–1644.
(23) Mocella, C. J.; Delafuente, D. A.; Keane, J. M.; Warner, G. R.; Friedman, L. A.; Sabat, M.; Harman, W. D. *Organometallics* **2004**, *23*, 3772–3779.
(24) Due to the diastereotopic nature of the purported resulting methylene group, deprotonation of such a species likely would also be *exo*-stereoselective, thus preventing net deuterium incorporation.
(25) McEwen, W. E.; Calabro, M. A.; Mineo, I. C.; Wang, I. C. *J. Am. Chem. Soc.* **1973**, *95*, 2392–2393.
(26) McEwen, W. E.; Cobb, R. L. *Chem. Rev.* **1955**, *55*, 511–549.
(27) Perrin, S.; Monnier, K.; Laude, B.; Kubicki, M.; Blacque, O. *Eur. J. Org. Chem.* **1999**, 297–303.

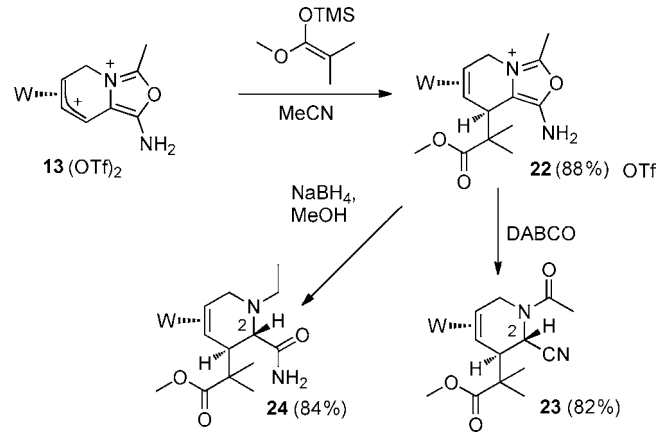
Scheme 5. Stereoselective Nucleophilic Addition to C3



Scheme 6. Stereoselective Nucleophilic Addition to C5



Scheme 7. Elaboration of the Reissert-like Allyl Complex **13**



reactions via ^{31}P NMR often revealed two major isomers (>90%) with a small amount of deprotonation of the homoallylic protons (<10%). NOESY analysis of isolated samples of **15**−**17** all displayed chemical exchange, signifying amide conformational isomers (*vide supra*). Of note, the two isomers (4:1 ratio) of **18** failed to display chemical exchange in $CDCl_3$. However, dissolution of a sample in acetone-d_6 resulted in a ratio of nearly 1:1 for the two isomers, and chemical exchange was observed via NOESY. Evaporation of the NMR solvent and redissolving the residue of the sample in $CDCl_3$ returned the equilibrium ratio to 4:1, providing good support that the two isomers of **18** are also amide conformational isomers (Scheme 5).

Addition of nucleophiles to the ethyl derivative **12** often resulted in deprotonation of a homoallylic proton, regenerating **3** (Scheme 6). However, under optimized reaction conditions, nucleophilic addition was effected. For example, when $ZnEt_2$ was combined with **12** in the presence of CuCN, nucleophilic addition resulted in complex **19** along with varying amounts of the dihydropyridine **3** (1.9:1 at −30 °C). In a similar vein, treatment of **12** with lithium dimethyl malonate mostly resulted in the dihydropyridine precursor at ambient temperature, but repeating this reaction at 0 °C provided a nucleophilic addition product, **20** (Scheme 6). A full NMR analysis (COSY, NOESY, HSQC, HMBC) indicated that these nucleophiles did not add to the pyridine ring C3 but rather at the other allylic position, C5 (Scheme 6). Presumably, the vicinal addition of two nucleophiles creates a steric interaction that overcomes the electronic bias for C3 addition described in earlier reactions (Scheme 5).

Given that the isoxazolium portion of **13** is presumably coplanar with the allylic portion of the complex, it is likely to be less sterically demanding than an ethyl or nitro group. Addition of (1-methoxy-2-methyl-1-propenyloxy)trimethylsilane (MMTP) to a solution of **13** produces a single new compound, **22**. ^{1}H, ^{13}C, ^{19}F, HSQC, HMBC, NOESY, and COSY NMR data confirm that MMTP added to the carbon adjacent to the still-intact isoxazolium ring (Scheme 7). Attempts to add other nucleophiles (e.g., LiDMM, $ZnEt_2$, NaCN) that successfully added to the hydrido- or ethylallyl complexes **11** and **12** resulted in deprotonation of the complex to generate the diene **14** (see Scheme 4). Addition of DABCO to **22** resulted in a 2-cyanopiperidine complex (Scheme 7). Alternatively, reduction of **22** with $NaBH_4$ in MeOH resulted in the 2-substituted primary amide, **24**. For both **23** and **24**, a H2−H3 coupling of <3 Hz indicates a similar stereochemistry for these protons. Full 2D NMR analysis (COSY, NOESY, HSQC, and HMBC) confirms the structural assignments of **23** and **24** provided in Scheme 7, where protonation at C2 late in the reaction sequence forces the cyano or amide group syn to the metal. X-ray analysis of a suitable crystal of **23** provides confirmation of its structure (Figure 4).

Δ^3-Piperidine Demetalation

With the Δ^3-piperidine complexes **15**−**24** in hand, our focus turned to the decomplexation and isolation of the organic Δ^3-piperidines. The strategy most commonly utilized for removal of the {TpW(NO)(PMe_3)} fragment involves oxidation of the metal, which curtails the metal−ligand back-bonding.[13,28] Treatment of various Δ^3-piperidine complexes with 1 equiv of

(28) Keane, J. M.; Harman, W. D. *Organometallics* **2005**, *24*, 1786–1798.

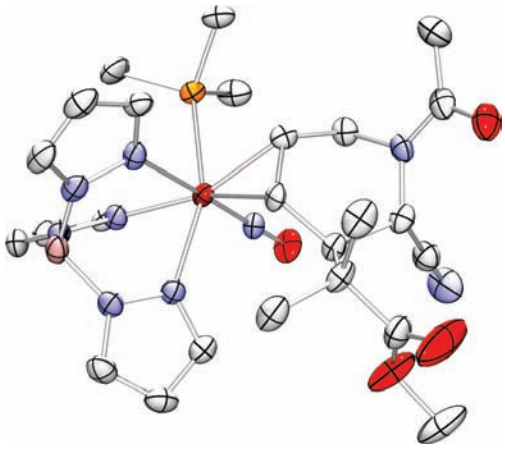


Figure 4. POV-ray diagram of tetrahydropyridine complex **23**.

ceric ammonium nitrate (CAN) successfully liberated the ligand (Scheme 8). Additionally, I_2 and dichlorodicyanoquinone (DDQ) could be used as effective oxidants (Scheme 8), the former being implemented only in the case of **27**, where other methods failed. We also explored the ability of molecular oxygen as a decomplexing agent. The highest recovery of organic compound by this method was obtained by stirring MeCN or EtOAc solutions of the complex and silica[29] overnight in a flask under 1 atm of $O_{2(g)}$. Analysis revealed that complexes with anodic peak potentials ($E_{p,a}$) of more than ~0.5 V (vs NHE) were resistant to oxidation with $O_{2(g)}$. In these cases, CAN could still be utilized to liberate the piperidines (*vide supra*). Likewise, when the decomplexation study was expanded to include selected dihydropyridine complexes, those with anodic peak potentials of greater than 0.5 V were found to be resistant to oxidation with $O_{2(g)}$, while those with anodic peak potentials less than 0.5 V reacted with O_2 to give only ill-defined paramagnetic complexes. In no case were 2-substituted pyridines recovered from these oxidative decomplexation procedures. Isolating the tetrahydropyridine (THP) complexes by their precipitation was often inefficient (see **29** in Scheme 8), so we settled on a procedure where the THP complexes were generated *in situ*. Several examples of DHP elaboration into organic piperidinamides (**25**−**27**, **29**−**36**) are summarized in Scheme 8.

The reactions described above constitute a procedure to generate piperidinamides with a diverse range of substituents, all from pyridine−borane in overall yields of 21−28% for a five-step process (>75%/step). Although examples of nucleophilic additions to C3 or C5 of the pyridine ring are possible using palladium coupling techniques,[30−32] we have found no examples where aromaticity of the pyridine is not regained. Intramolecular radical cyclizations of open-chain enamides have been used to generate 3-substituted piperidines.[33,34] Other examples use 3-substituted piperidines, synthesized via ring-closing metathesis,[35−37] to generate asymmetric palladium piperidine−allyl species via displacement of a leaving group. Addition of nucleophiles such as malonates and amines, generate 3-substituted piperidines in good yield and enantiomeric excess. While catalytic palladium has been utilized to generate allylic species similar to the tungsten allyl complexes (which are generated by addition of an electrophile rather than displacement of a nucleophile), we have found no examples where this has occurred with a second substituent on the piperidine ring, as is the case with dihydropyridine precursor complexes presented in this report.

Conclusions

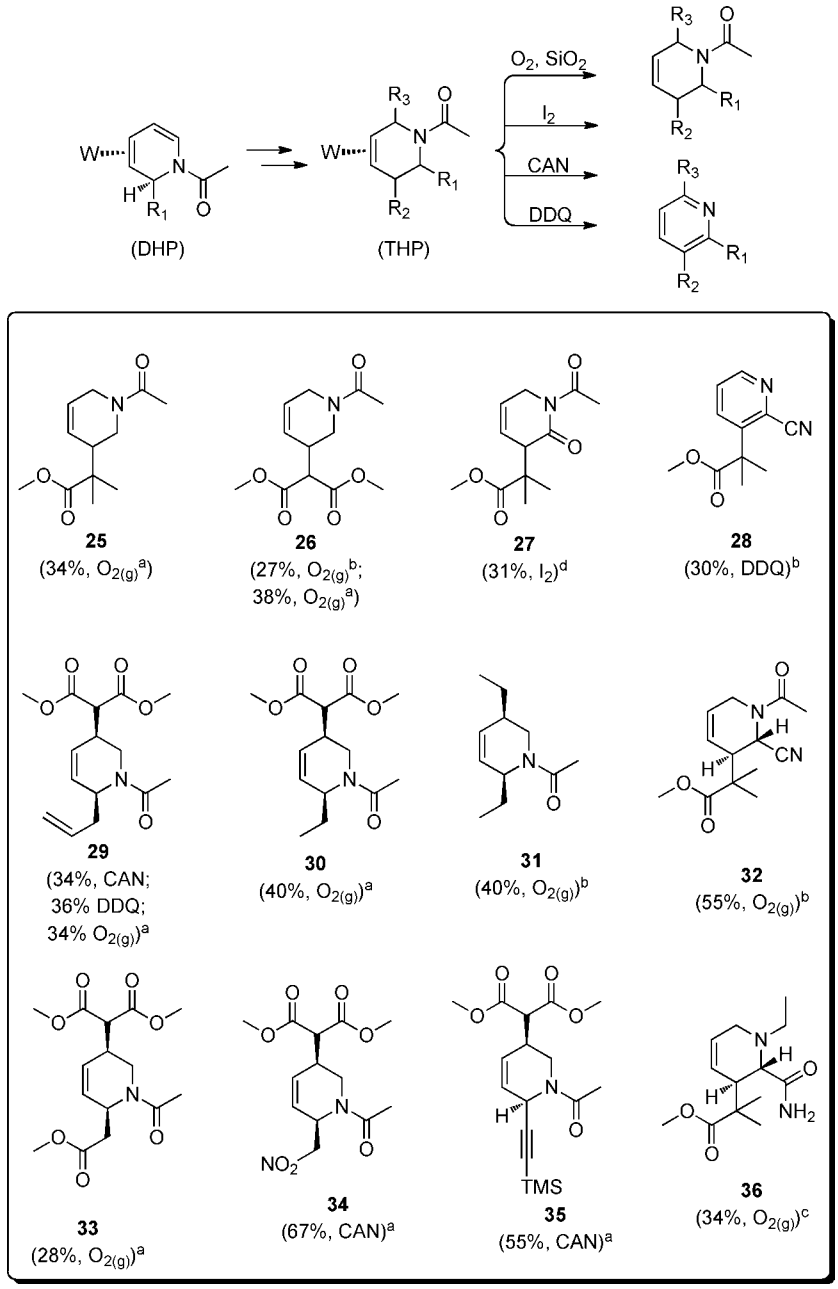
In previous work, the π base {TpW(NO)(PMe_3)} was used to generate a wide range of *N*-acetylated 2-substituted dihydropyridine complexes.[16] In this study, the potential synthetic value of these DHP complexes is demonstrated. Tungsten coordination directs protonation to C6 of the DHP ring, forming asymmetric π-allyl complexes. In this regard, the tungsten fragment can be thought of as an electron-donating group; the tungsten system is more effective at polarizing the C5−C6 bond than is the conjugated acetamide. Additionally, the metal fragment stereoselectively directs a subsequent nucleophilic addition anti to the metal, while the high electronic asymmetry influences the regiochemistry of the addition. Oxidative demetalation yields a diverse array of new Δ^3-piperidines with unusual substitution patterns, the formation of which signifies a reversal (i.e., umpolung) of the typical chemical reactivity associated with the C5−C6 segment of a pyridine ring.

Experimental Section

General Methods. NMR spectra were obtained on 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 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 (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) or a Nicolet Avatar 320 FT-IR spectrometer with a diamond HATR attachment. 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 (25 °C) in a standard three-electrode cell with a glassy carbon working electrode using tetrabutylammonium hexafluorophosphate (TBAH) as an electrolyte (approximately 0.5 M in an appropriate solvent). All potentials are reported versus 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 from the University of Illinois at Urbana−Champaign Mass Spectrometry Laboratory or at the University of Richmond on a Bruker BioTOF-Q instrument running in ESI mode, the latter from samples dissolved in 1:3 water/acetonitrile solution containing trifluoroacetic acid and/or sodium trifluoroacetate (NaTFA), and using $[Na(NaTFA)_x]^+$ clusters as an

(29) Control reactions have deterimined that silica was not necessary for demetalation with $O_{2(g)}$ but that its inclusion significantly decreases the required reaction time (from 1 week to <15 h).
(30) Molander, G. A.; Jean-Gérard, L. *J. Org. Chem.* **2009**, *74*, 5446–5450.
(31) Schoeps, D.; Sashuk, V.; Ebert, K.; Plenio, H. *Organometallics* **2009**, *28*, 3922–3927.
(32) Fors, B. P.; Krattiger, P.; Strieter, E.; Buchwald, S. L. *Org. Lett.* **2008**, *10*, 3505–3508.
(33) Yuan, X.; Liu, K.; Li, C. *J. Org. Chem.* **2008**, *73*, 6166–6171.
(34) Taniguchi, T.; Yonei, D.; Sasaki, M.; Tamura, O.; Ishibashi, H. *Tetrahedron* **2008**, *64*, 2634–2641.
(35) Schleich, S.; Helmchen, G. N. *Eur. J. Org. Chem.* **1999**, 2515–2521.
(36) Evans, D. A.; Campos, K. R.; Tedrow, J. S.; Michael, F. E.; Gagné, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7905–7920.
(37) Miller, J. F.; Termin, A.; Koch, K.; Piscopio, A. D. *J. Org. Chem.* **1998**, *63*, 3158–3159.

Scheme 8. Organic Products Recovered from Tetrahydropyridine Complexes



[a] From DHP (three steps, one pot). [b] From THP (one step). [c] From **22** (two steps, one pot). [d] From **22** (one step).

internal standard. Unless otherwise noted, all synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere. DriSolve dichloromethane (DCM) and benzene were purified by passage through a column packed with activated alumina. DriSolve tetrahydrofuran (THF) was used as received. These and other solvents and liquid reagents were thoroughly purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes. MMTP and $ZnEt_2$ are commercially available and were used as received. Lithium dimethyl malonate was prepared by the addition of MeLi to a stirring solution of dimethyl malonate in Et_2O, precipitating a white solid that was filtered and used without further purification. Triflate salts were synthesized by slow addition of Et_2O to an ice-cooled vial containing triflic acid, followed by addition of this solution to an appropriate conjugate base dissolved in Et_2O. General proton assignments were made in accordance with Figure S1 (see Supporting Information). Pyrazole (Pz) protons of the (tris-pyrazolyl)borate (Tp) ligand were uniquely assigned using a combination of two-dimensional NMR experiments and phosphorus−proton coupling (Figure S2, Supporting Information). When unambiguous assignments were not possible, Pz protons were labeled as Tp protons. Coordination diastereomers are described by the defining feature's (i.e., heteroatom's) proximity to the PMe_3 ligand relative to the W−PMe_3 bond (e.g., fewer bonds from the PMe_3 passing through the upper portion of the coordinated ring system to the defining feature dictates the proximal (P) ligand).

Crystallography. The molecular structures of compounds **11** and **23** were solved by direct methods in SHELXTL. For compound **11**, difference Fourier maps revealed the presence of two triflate moieties. One of the moieties occupied general positions, and its atoms were refined with anisotropic thermal displacement parameters and occupancies of 1.0. However, the other triflate anion was found on an inversion center located halfway between the S and C atoms. The disorder was modeled by using half of the triflate moiety, in which the atomic scattering factors were (0.5O + 0.5F) for the overlapping F and O atoms and (0.5S + 0.5C) for the overlapping S and C atoms. The final refinement supported this

model, resulting in reasonable thermal and metric parameters. In addition, a careful inspection of the difference Fourier maps revealed the presence of a H atom bound to the amide O atom. This H atom is involved in a strong H bonding between the O atoms of the amide groups (O···H···O distance is 2.41 Å) from two complex molecules related by an inversion center. The observed arrangement of the H atom imposes a disorder, which was modeled by refining the H atom with an isotropic thermal displacement parameter and a population parameter of 0.5. The final refinement gave reasonable values of the thermal factors and the metric parameters describing the H bond system.

General Procedure 1: *In Situ* Generated Tetrahydropyridine Complexes. A solution of HOTf in MeCN was added to an oven-dried test tube containing the appropriate dihydropyridine complex precursor and was then placed into a 0 °C cold bath next to a separate oven-dried test tube containing a solution of LiDMM in MeCN. The solutions were allowed to cool for 10 min. The LiDMM solution was then quickly added to the tungsten allyl solution and allowed to stir at 0 °C for 30 min. The solution was then removed from the cold bath and taken out of the glovebox to stir at room temperature. After 15 min, the solution was diluted with 20 mL of DCM, extracted with 3 × 10 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 10 mL of DCM, the combined organic layers were dried over $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed *in vacuo* to leave a residue.

General Procedure 2: Demetalation−Oxidation with $O_{2(g)}$. Outside of the glovebox, the residue from general procedure 1 was transferred to a 250 or 500 mL round-bottom flask containing a side arm attached to a balloon. The flask was charged with a Teflon stirbar, SiO_2 (∼10 g), and 100 mL of EtOAc. The balloon was filled with $O_{2(g)}$, vented, and then refilled with $O_{2(g)}$. The heterogeneous solution was stirred rapidly overnight, after which time the reaction solution was filtered through a 150 mL medium porosity fritted funnel and washed with 250 mL of EtOAc. The solvent was removed *in vacuo*, the residue was transferred to a 4 dram vial, and the solvent was removed *in vacuo* once more. The organic compound was isolated according to general procedure 5.

General Procedure 3: Demetalation−Oxidation with CAN. Outside of the glovebox, CAN was added to the flask containing the residue from general procedure 1, followed by acetone. The solution was allowed to stir as the color changed from brown-orange to yellow over the course of 1 h. After this 1 h, the reaction solution was transferred to a separatory funnel containing 50 mL of $NaHCO_3$ (saturated, aqueous) and washed with 2 × 1 mL portions of acetone, and a white material precipitated. The water layer was extracted with 5 × 25 mL of DCM, the combined organic layers were dried over $MgSO_4$ and filtered through a 150 mL coarse porosity fritted funnel, and the solvent was removed in vacuo to yield a residue. The residue was transferred to a 4 dram vial with DCM, and the solvent was removed *in vacuo* once more. The organic compound was isolated according to general procedure 5.

General Procedure 4: Demetalation−Oxidation with DDQ. The residue from general procedure 1 was diluted with a solution of DDQ in acetone and allowed to react for 1−2 h. The reaction solution was then removed from the glovebox, diluted with 20 mL of DCM, extracted with 3 × 10 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 3 × 10 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 30 mL medium porosity fritted funnel, and the solvent was removed by rotary evaporation. The residue was transferred to a 4 dram vial with DCM, and the solvent was removed once more. The organic compound was isolated according to general procedure 5.

General Procedure 5: Isolation of Liberated Alkene. Outside of the glovebox, the residue was loaded onto a 20 cm × 20 cm × 500 μm SiO_2 preparatory TLC plate and a 20 cm × 2 cm (wide) × 500 μm SiO_2 preparatory TLC plate with 4 × 0.3 g of DCM and one or more 1 mL syringes. The preparatory TLC plates were eluted side-by-side with an appropriate solvent. Once elution was complete, the 2 cm wide plate was stained with $KMnO_4$ to help visualize the location of the liberated alkene. The band corresponding to the organic compound was scraped from the 20 cm wide plate, placed in a test tube with 15 mL of EtOAc, and sonicated for 10 min to break up the silica. The silica was collected on a 30 mL medium porosity fritted funnel and washed with 200 mL of EtOAc, and the solvent was removed from the filtrate. The residue was then transferred to a tared vial with DCM, the solvent was removed by rotary evaporation, and the product was dried *in vacuo* overnight.

TpW(NO)(PMe_3)(4,5-η^2-(1-acetylpiperidin-4-ylium))(OTf) (11). A solution of HOTf (0.269 g, 1.792 mmol) in DCM (2.1 g) was added to a dark yellow solution of **2** (1.000 g, 1.597 mmol) in DCM (4.1 g). After 2 min the reaction solution was diluted with DCM (6 g). It was then added to 300 mL of stirring Et_2O to form a tan precipitate. The slurry was allowed to stir for 0.5 h, and the precipitate was collected on a 15 mL medium porosity fritted funnel, washed with 2 × 15 mL of Et_2O, and placed under a vacuum (1.193 g, 1.537 mmol, 96% yield). ^{1}H NMR (CD_2Cl_2, δ): 8.34 (d, J = 2.0, 1H, PzB3), 8.23 (d, J = 2.0, 1H, PzA3), 8.10 (d, J = 2.0, 1H, PzC3), 7.99 (d, J = 2.0, 1H, PzC5), 7.91 (d, J = 2.0, 1H, PzB5), 7.75 (d, J = 2.0, 1H, PzA5), 6.67 (d(br), J = 7.2, 1H, H3), 6.61 (t, J = 2.0, 1H, PzC4), 6.54 (t, J = 2.0, 1H, PzB4), 6.36 (t, J = 2.0, 1H, PzA4), 5.27 (d, J = 19.5, 1H, H2), 5.13 (t, J = 7.8, 1H, H4), 4.99 (d, J = 19.5, 1H, H2′), 4.90 (d, J = 14.5, 1H, H6), 4.82 (d, J = 14.5, 1H, H6′), 4.34 (m, 1H, H5), 2.26 (s, 3H, Amide-Me), 1.26 (d, $^2J_{PH}$ = 9.6, 9H, PMe_3); selected minor isomer signals, 8.12 (d, J = 2.0, 1H, PzA3), 6.27 (m, 1H, H3), 5.40 (d, J = 18.6, 1H, H6), 5.24 (buried, 1H, H4), 4.70 (m, 1H, H5), 2.23 (s, 3H, Amide-Me), 1.27 (d, $^2J_{PH}$ = 9.6, 9H, PMe_3). ^{13}C NMR (CD_2Cl_2, δ): 173.3 (Amide-CO), 148.8 (PzA3), 145.0 (PzB3), 142.6 (PzC3), 139.3 (PzC5), 138.9 (PzA5/PzB5), 130.5 (C3), 109.2/109.1 (PzB4/PzC4), 108.0 (PzA4), 96.4 (C4), 64.6 (d, $^2J_{PC}$ = 15.4, C5), 46.9 (C2), 42.0 (C6), 21.8 (Amide-Me), 13.3 (d, $^1J_{PC}$ = 32.9, PMe_3); selected minor isomer signals, 122.8 (C3), 98.5 (C4), 67.6 (C5), 46.8 (C6), 13.4 (d, $^1J_{PC}$ = 32.7, PMe_3). ^{31}P NMR (CD_2Cl_2, δ): −6.73 (J_{WP} = 261), −7.80 (J_{WP} = 260). Isomer ratio: 3.1:1 (chemical exchange observed). IR: $\nu_{NO/amide}$ = 1643 cm^{-1}, ν_{BH} = 2515 cm^{-1}. CV (MeCN): $E_{p,a}$ = +2.05 V, $E_{p,c}$ = −0.81 V. ESI-MS obsd (%), calcd (%), ppm (M − OTf)$^+$: 625.1687 (98.5), 625.1736 (85.8), 7.8; 626.1747 (76.9), 626.1761 (79.6), 2.2; 627.1763 (100), 627.176 (100), 0.5; 628.1785 (50.9), 628.1802 (41.2), 2.7; 629.1817 (59.4), 629.1792 (84.6), 4.0. Anal. Calcd for $C_{20}H_{29}BF_3N_8O_5PSW\cdot CH_2Cl_2$: C, 29.29; H, 3.63; N, 13.01. Found: C, 29.50; H, 3.82; N, 12.95.

TpW(NO)(PMe_3)(4,5-η^2-(1-acetyl-2-ethylpiperidin-4-ylium))(OTf) (12). A solution of HOTf (0.241 g, 1.606 mmol) in MeCN (1.01 g) was added to a heterogeneous solution of **3** (1.007 g, 1.539 mmol) in MeCN (1.05 g) to make a homogeneous dark yellow solution. After 1 min, the reaction solution was added to 400 mL of stirring Et_2O to produce a tan precipitate. The precipitate was collected on a 30 mL medium porosity fritted funnel, washed with 2 × 10 mL of Et_2O, and placed under a vacuum (1.200 g, 1.492 mmol, 97% yield with <1:1 molar ratio of Et_2O to product via ^{1}H NMR). ^{1}H NMR (CD_3CN, δ): 8.38/8.34 (d, J = 2.0, 1H, PzB3), 8.27/8.17 (d, J = 2.0, 1H, PzA3), 8.06 (d, J = 2.0, 1H, PzC5), 8.02/8.00 (d, J = 2.0, 1H, PzC3), 7.98 (d, J = 2.0, 1H, PzB5), 7.86/7.84 (d, J = 2.0, 1H, PzA5), 6.59 (m, 1H, PzC4), 6.54 (m, 1H, PzB4), 6.39 (m, 1H, PzA4), 6.37/5.85 (m, 1H, H3), 5.57/5.53 (m, 1H, H2), 5.35/5.23 (t, J = 7.7, 1H, H4), 5.19/4.32 (d, J = 15.5, 2H, H6/H6′), 4.94/4.68 (d, J = 15.5, 2H, H6/H6′) 4.69/4.30 (m, 1H, H5), 2.24/2.21 (s, 3H, Amide-Me), 2.07/1.95 (m, 2H, H7/H7′), 1.21 (d, J = 10.0, 9H, PMe_3), 1.20 (d, $^2J_{PH}$ = 9.9, 9H, PMe_3(min)), 1.09/0.99 (t, J = 7.5, Ethyl-CH_3 (maj/min)). ^{13}C NMR (CD_3CN, δ): 172.9/172.6 (Amide-CO), 149.2/148.5 (PzA3), 145.4/145.1 (PzB3), 143.5/143.3 (PzC3), 139.9/139.7/139.5 (PzA5/PzB5/PzC5), 131.2/122.3 (C3(maj/min)), 109.5 (PzB4), 109.1/109.2 (PzC4), 108.2 (PzA4), 99.3/98.1 (C4(min/maj)), 72.7 (C5(min)), 66.2 (d, $^2J_{PC}$ = 15.0, C5(maj)), 57.1/54.6 (C2), 47.1/41.0 (C6), 31.2/

30.0 (C7), 22.0/21.9 (Amide-Me), 12.9 (d, $^1J_{PC}$ = 33.4, PMe_3), 9.4/9.1 (Ethyl-CH_3). ^{31}P NMR ($CDCl_3$, δ): −5.84 (J_{WP} = 262), −7.05 (J_{WP} = 259). Isomer ratio: 2.7:1 (chemical exchange observed). IR: ν_{BH} = 2511 cm^{-1}, $\nu_{NO/amide}$ = 1643 cm^{-1}. CV (MeCN): $E_{p,a}$ = +1.98 V, $E_{p,c}$ = −0.84 V. ESI-MS obsd (%), calcd (%), ppm (M − OTf)$^+$: 653.199 (97.5), 653.205 (84.7), 9.2; 654.2001 (96.7), 654.206 (80), 9; 655.2076 (100), 655.2073 (100), 0.5; 656.205 (60.3), 656.2115 (42.6), 9.9; 657.2084 (73.9), 657.2106 (84), 3.3.

[TpW(NO)(PMe$_3$)(6,7-η^2-(1-amino-3-methyl-5,6,7,8-tetrahydrooxazolo[3,4-*a*]pyridin-4-ium-8-ylium))][(OTf)$_2$] (13). A solution of HOTf (0.659 g, 4.390 mmol) in MeCN (0.50 g) was quickly added to a vial containing a heterogeneous solution of **4** (1.303 g, 2.001 mmol) in MeCN (2.13 g) to make a deep red homogeneous solution upon manual mixing with a pipet. Once the solution was homogenenous, the solution was added to 500 mL of stirring Et_2O, and the resulting orange microcrystalline precipitate was collected on a 60 mL medium porosity fritted funnel, washed with 2 × 30 mL of Et_2O, and placed under a vacuum (2.010 g, with a 1:3 molar ratio of product:Et_2O; 1.573 g, 1.964 mmol, 98% estimated yield after adjustment for Et_2O). ^{1}H NMR (CD_3CN, δ): 8.42 (d, J = 7.4, 1H, H8), 8.18 (d, J = 2.0, 1H, PzB3), 8.08 (d+s(br), 4H, PzC3/PzC5/NH_2), 8.01 (d, J = 2.0, 1H, PzB5), 7.97 (d, J = 2.0, 1H, PzA3), 7.84 (d, J = 2.0, 1H, PzA5), 6.60 (t, J = 2.0, 1H, PzC4), 6.53 (t, J = 2.0, 1H, PzB4), 6.41 (t, J = 2.0, 1H, PzA4), 6.02 (dd, J = 15.2, 3.7, 1H, H5), 5.11 (d, J = 15.2, 1H, H5′), 4.35 (m, 2H, H6/H7), 2.77 (s, 3H, Amide-Me), 1.19 (d, $^2J_{PH}$ = 9.8, 9H, PMe_3). ^{13}C NMR (CD_3CN, δ): 159.4 (C3), 159.1 (C1), 150.6 (PzA3), 147.9 (C8), 146.7 (PzB4), 143.0 (PzC3), 140.0/139.8 (PzB5/PzC5), 139.0 (PzA5), 109.7 (PzC4), 109.0 (PzB4), 108.4 (PzA4), 103.1 (C2), 78.9 (C7), 61.2 (d, $^2J_{PC}$ = 14.7, C6), 49.5 (C5), 12.9 (d, $^1J_{PC}$ = 32.9, PMe_3), 12.3 (Amide-Me). ^{31}P NMR (CD_3CN, δ): −4.51 (J_{WP} = 267). IR: ν_{BH} = 2519 cm^{-1}, ν_{CN} = 2252 cm^{-1}, ν_{NO} = ν = 1685 cm^{-1}, ν = 1620 cm^{-1}, ν = 1540 cm^{-1}. CV (MeCN): $E_{p,a}$ = +2.04 V, $E_{p,c}$ = −0.52 V. ESI-MS obsd (%), calcd (%), ppm (M − OTf)$^+$: 650.1693 (85.0), 650.167 (85.1), 3.5; 651.1681 (82.0), 651.1713 (79.9), 4.9; 652.1679 (100), 652.171 (100), 4.8; 653.1736 (46.6), 653.1715 (42.1), 3.2; 654.1749 (84.6), 654.178 (84.2), 4.7. UV−vis (MeCN; λ, nm (ϵ, cm^{-1} M^{-1}): 229 (strong), 410 (weak). Anal. Calcd for $C_{22}H_{31}BF_6N_9O_8PS_2W\cdot 2H_2O$: C, 26.76; H, 3.37; N, 12.77. Found: C, 26.88; H, 3.42; N, 12.50.

TpW(NO)(PMe$_3$)(4,5-η^2-(1-acetyl-1,6-dihydropyridine-2-carbonitrile)) (14). DABCO (0.114 g, 1.016 mmol) was added to a dark red solution of **13** (0.808 g; 0.646 g estimated after correction for Et_2O in the sample, 0.806 mmol) in DCM (23 g) to make a dark yellow homogeneous solution. After several minutes, the solution was diluted with 25 mL of DCM, extracted with 3 × 25 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 20 mL of DCM, the combined organic layers were dried with Na_2SO_4 and filtered through a 30 mL fine porosity fritted funnel, and the solvent was removed *in vacuo*. MeCN (12 mL) was added to the residue, and a yellow solid precipitated. The precipitate was collected on a 30 mL medium porosity fritted funnel, washed with 2 × 1 mL of MeCN, and placed under a vacuum (0.201 g, 0.309 mmol, 37% yield). ^{1}H NMR ($CDCl_3$, δ): 8.04 (d, J = 2.0, 1H, PzA3), 8.00 (d, J = 2.0, 1H, PzB3), 7.75 (m, 2H, PzB5/PzC5), 7.58 (d, J = 2.0, 1H, PzA5), 7.42 (d, J = 7.1, 1H, H3), 7.37 (d, J = 2.0, 1H, PzC3), 6.32 (t, J = 2.0, 1H, PzB4), 6.25 (t, J = 2.0, 1H, PzC4), 6.22 (t, J = 2.0, 1H, PzA4), 5.57 (d, J = 13.0, 1H, H6 (syn-to-W)), 4.44 (d(br), J = 13.0, 1H, H6 (anti-to-W)), 3.20 (ddd, J = 13.0, 10.0, 3.0, 1H, H5), 2.40 (s, 3H, Acetyl-Me), 1.80 (dd, J = 10.0, 7.1, 1H, H4), 1.22 (d, J = 8.6, 9H, PMe_3). ^{13}C NMR ($CDCl_3$, δ): 170.3 (Amide-CO), 148.26 (C3), 145.6 (PzA3), 143.3 (PzB3), 140.1 (PzC3), 137.1/136.5 (PzB5/PzC5), 135.4 (PzA5), 118.1 (nitrile), 107.1 (PzB4), 106.3 (PzC4), 106.2 (PzA4), 101.8 (C2), 66.8 (C5, d, J = 14.1), 48.1 (C4), 44.8 (C6), 25.5 (Acetyl-Me), 13.4 (PMe_3, d, J = 28.8). ^{31}P NMR ($CDCl_3$, δ): −9.35 (J_{WP} = 276). IR: ν_{BH} = 2511 cm^{-1}, ν_{CN} = 2202 cm^{-1}, ν_{NO} = 1554 cm^{-1}, ν = 1635 cm^{-1}, ν = 1589 cm^{-1}. CV (DMA): $E_{p,a}$ = +0.77 V. ESI-MS obsd (%), calcd (%), ppm (M + H)$^+$: 650.1679 (85.7), 650.1689 (85.1), 1.5; 651.1699 (46.6), 651.1714 (79.9), 2.3; 652.1706 (100), 652.1712 (100), 0.9; 653.174 (21.6), 653.1754 (42.1), 2.2; 654.1741 (93.2), 654.1745 (84.2), 0.7. Anal. Calcd for $C_{20}H_{27}BN_9O_2PW$: C, 36.89; H, 4.18; N, 19.36. Found: C, 36.72; H, 4.14; N, 18.90.

TpW(NO)(PMe$_3$)(4,5-η^2-(1-acetyl-1,2,3,6-tetrahydropyridine-3-carbonitrile)) (15). In separate oven-dried test tubes, a solution of **11** (0.254 g, 0.327 mmol) in DCM (4.23 g) and a solution of NaCN (0.072 g, 1.469 mmol), DMSO (1.93 g), and DCM (1.91 g) were prepared and placed in a 0 °C cold bath. After 2 h, the solution of **11** was quickly added to the NaCN solution and allowed to stir for 1 h. The reaction solution was removed from the cold bath and glovebox. The reaction solution was extracted with 3 × 10 mL of NH_4Cl (saturated, aqueous) and back-extracted with 3 × 5 mL of DCM, the combined organic layers were dried with Na_2SO_4 and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed. The residue was dissolved in 1 mL of DCM and 1 mL of EtOAc was added, followed by the addition of hexanes (35 mL) to precipitate an off-white solid. The solution was cooled to 0 °C for 20 min, and the precipitate was collected on a 15 mL medium porosity fritted funnel. The filtrate was colorless. The remaining uncollected material on the flask was redissolved in 1 mL of DCM and 1 mL of EtOAc, followed by the addition of hexanes (35 mL) to precipitate an off-white solid that was collected on a separate 15 mL medium porosity fritted funnel and washed with 2 × 10 mL of hexanes (combined yield: 0.119 g, 0.182 mmol, 57% yield, with minor DMSO impurity). ^{1}H NMR ($CDCl_3$, δ): 8.02 (s, 2H, PzA3/PzB3), 7.73 (d, J = 2.0, 1H, Tp), 7.71 (d, J = 2.0, 1H, PzC5), 7.63 (d, J = 2.0, 1H, Tp), 7.21 (d, J = 2.0, 1H, PzC3), 6.32/6.26 (t, J = 2.0, 1H, PzA4/PzB4), 6.2 (t, J = 2.0, 1H, PzC4), 5.20 (dd, J = 13.9, 6.0, 1H, H6(anti)), 4.46 (dd, J = 13.3, 7.2, H, H6(anti,rotamer)), 4.16 (dd, J = 13.9, 6.0, 1H, H6(syn)), 3.92 (m, 2H, H3/H2), 3.66 (dd, J = 13.4, 8.4, 1H, H2′), 2.71 (m, 1H, H5), 1.21 (d, J = 8.3, 9H, PMe_3). ^{13}C NMR ($CDCl_3$, δ): 169.7 (Amide-CO), 143.6/143.3 (PzA3/PzB3), 140.2 (PzC), 136.9/136.4/136.0 (PzA5/PzB5/PzC5), 124.6 (CN), 106.8 (Tp), 106.3 (PzC4), 105.6 (Tp), 49.1 (C4), 48.9 (C5, d, J = 12.5), 43.2 (C6), 31.2 (C3), 22.3 (Amide-Me), 13.8 (PMe_3, d, J = 28.5). ^{31}P NMR ($CDCl_3$, δ): −11.43 (J_{WP} = 272), −12.25 (rotamer). Ratio of rotational isomers: 3.6:1 (chemical exchange observed). IR: ν_{BH} = 2488 cm^{-1}, $\nu_{nitrile}$ = 2225 cm^{-1}, ν_{amide} = 1624 cm^{-1}, ν_{NO} = 1550 cm^{-1}. CV (DMA): $E_{p,a}$ = +0.71 V. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 674.1642 (70.2), 674.1659 (85.1), 2.4; 675.1663 (100), 675.1684 (79.9), 3.1; 676.1684 (78.2), 676.1682 (100), 0.2; 677.1719 (37.3), 677.1724 (42.2), 0.8; 678.1707 (99.9), 678.1715 (84.2), 1.2.

TpW(NO)(PMe$_3$)(4,5-η^2-(dimethyl 2-(1-acetyl-1,2,3,6-tetrahydropyridin-3-yl)malonate)) (16). In separate flame-dried test tubes, a homogeneous solution of **11** (0.503 g, 0.648 mmol) and DCM (1.51 g) and a heterogeneous solution of LiDMM (0.191 g, 1.38 mmol) in DCM (1.52 g) were each placed in a 0 °C cold bath. After 15 min, the LiDMM solution was quickly added to the solution of **11**, and the mixture was allowed to stir. After 1 h 20 min, the reaction solution was removed from the cold bath and glovebox, diluted with 5 mL of DCM, extracted with 3 × 2 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 2 mL of DCM, the combined organic layers were dried with Na_2SO_4, filtered through a 30 mL coarse porosity fritted funnel, and washed with DCM, and the solvent was removed *in vacuo*. The residue was dissolved in 2.5 mL of DCM, followed by 2.5 mL of EtOAc, and then Et_2O (50 mL) was added to precipitate an off-white solid. The solution was cooled to 0 °C and stirred for 0.5 h, and the solid was collected on a 30 mL medium porosity fritted funnel and placed under a vacuum (0.331 g, 0.437 mmol, 67% yield). More material could be isolated by further precipitation of the filtrate residue with DCM, EtOAc, and hexanes in place of Et_2O. ^{1}H NMR ($CDCl_3$, δ): 8.07 (d, J = 2.0, 1H, PzB3), 8.06 (d, J = 2.0, 1H, PzA3), 7.71 (d, J = 2.0, 1H, PzB5), 7.69 (d, J = 2.0, 1H, PzC5), 7.61 (d, J = 2.0, 1H, PzA5), 7.20 (d, J = 2.0, 1H, PzC3), 6.31 (t, J = 2.0, 1H, PzB4), 6.24 (t, J = 2.0, 1H, PzA4), 6.18 (t, J = 2.0, 1H, PzC4), 5.16 (dd, J = 14.0, 6.3, 1H, H6), 4.58 (d, J = 14.0, 1H, H6′), 3.94

(dd, $J = 13.1, 4.5$, 1H, H2), 3.76 (d, $J = 9.5$, 1H, H7), 3.73 (s, 3H, Ester-Me), 3.66 (m (broad), 1H, H3), 3.51 (dd, $J = 13.1, 1.6$, 1H, H2′), 3.41 (s, 3H, Ester-Me′), 2.77 (dddd, $J = 13.9, 11.2, 6.6, 2.2$, 1H, H5), 2.03 (s, 3H, Amide-Me), 1.17 (d, 8.2, 9H, PMe_3), 0.92 (d, $J = 11.2$, 1H, H4); non-overlapping minor isomer signals, 4.73 (dd, $J = 13.2, 9.1$, 1H, H6), 4.32 (dd, $J = 13.2, 4.4$, 2H, H6′/H2′), 3.59 (d, $J = 9.8$, 1H, H7), 3.31 (dd, $J = 13.2, 4.0$, 1H, H2), 3.15 (s, 3H, Ester-Me′), 2.95 (m, 1H, H5), 2.16 (s, 3H, Amide-Me), 0.73 (d, $J = 11.2$, 1H, H4). ^{13}C NMR ($CDCl_3$, δ): 170.6 (Amide-CO), 169.7 (Ester-CO), 169.1 (Ester-CO′), 143 (PzA3/PzB3), 139.8 (PzC3), 136.5 (PzC5), 135.9 (PzB5), 135.7 (PzA5), 106.6 (PzB4), 106 (PzC4), 105.8 (PzA4), 59.6 (C7), 52.5 (Ester-Me), 52.1 (Ester-Me′), 50.9 (C4), 48.8 (C5, d, $J = 11.8$), 46.2 (C2), 43.5 (C6), 39.2 (C3), 22.0 (Amide-Me), 13.4 (PMe_3, d, $J = 28.1$). ^{31}P NMR ($CDCl_3$, δ): −10.31 ($J_{WP} = 279$), −11.08 (rotamer). Isomer ratio: 6.3:1 (chemical exchange observed). IR: $\nu_{BH} = 2488$ cm^{-1}, $\nu_{ester} = 1732$ cm^{-1}, $\nu_{amide} = 1624$ cm^{-1}, $\nu_{NO} = 1547$ cm^{-1}. CV (DMA): $E_{p,a} = +0.49$ V. ESI-MS obsd (%), calcd (%), ppm $(M + H)^+$: 757.2151 (86.9), 757.2159 (82.5), 1.1; 758.2173 (81.8), 758.2185 (80.3), 1.6; 759.2201 (100), 759.2184 (100), 2.2; 760.2237 (49.5), 760.2224 (45.2), 1.7; 761.2219 (80.5), 761.2216 (83.4), 0.4.

TpW(NO)(PMe_3)(4,5-η^2-(methyl 2-(1-acetyl-1,2,3,6-tetrahydropyridin-3-yl)-2-methylpropanoate)) (17). A solution of MMTP (0.250 g, 1.434 mmol) in DCM (7.96 g) was added in one portion to a 40 mL flame-dried beaker containing a rapidly stirring solution of **11** (0.501 g, 0.645 mmol) in DCM (8.1 g). After 10 min, the solution was diluted with 20 mL of DCM, extracted with 3 × 20 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 20 mL of DCM, the combined organic layers were dried with Na_2SO_4 and filtered through a 150 mL coarse porosity fritted funnel, and the solvent was removed. The residue was dissolved in 10 mL of DCM and then 10 mL of EtOAc, and a precipitate formed upon the addition of 100 mL of Et_2O. The tan precipitate was collected on a 15 mL medium porosity fritted funnel and washed with 2 × 10 mL of Et_2O. The filtrate solvent was removed *in vacuo*, the residue was dissolved in 5 mL of EtOAc, and 75 mL of hexanes was added to precipitate a tan-pink solid that was further precipitated with cooling in an ice bath for 0.5 h. The precipitate was collected on a 15 mL medium porosity fritted funnel, washed with 2 × 10 mL of hexanes, and placed under a vacuum (combined yield: 0.274 g, 0.376 mmol, 58% yield). ^{1}H NMR ($CDCl_3$, δ): 8.09 (d, $J = 2.0$, 1H, PzA3), 8.04 (d, $J = 2.0$, 1H, PzB3), 7.69 (m, 2H, PzB5/BzC3), 7.63 (d, $J = 2.0$, 1H, PzA5), 7.26 (d, $J = 2.0$, 1H, PzC3), 6.29 (t, $J = 2.0$, 1H, PzB4), 6.23 (t, $J = 2.0$, 1H, PzA4), 6.21 (t, $J = 2.0$, 1H, PzC4), 5.25 (dd, $J = 14.3, 7.7$, 1H, H6(anti)), 4.33 (d, $J = 14.3$, 1H, H6(syn)), 3.75 (dd, $J = 13.9, 5.7$, 1H, H2(syn)), 3.47 (s, 3H, Ester-Me), 3.45 (d, $J = 13.9$, 1H, H2(anti)), 3.34 (d, $J = 5.7$, 1H, H3), 2.9 (dddd, $J = 11.5, 7.5, 2.4$, $^3J_{PH} = 14.0$, 1H, H5), 2.1 (s, 3H, Amide-Me), 1.26 (s, 3H, Gem-Me), 1.17 (d, $J = 8.1$, 9H, PMe_3), 1.05 (s, 3H, Gem-Me′), 1.03 (d, $J = 11.5$, 1H, H4); non-overlapping minor isomer signals, 4.71 (dd, $J = 13.1, 9.0$, 1H, H6), 4.51 (d, $J = 14.3$, 1H, H2), 3.14 (dd, $J = 14.1, 5.3$, 1H, H2), 3.06 (dddd, $J = 11.3, 8.7, 3.7$, $^2J_{PH} = 15.2$, 1H, H5), 3.05 (s, 3H, Ester-Me), 2.09 (s, 3H, Amide-Me), 1.31 (s, 3H, Gem-Me), 1.19 (d, $J = 7.9$, 9H, PMe_3), 1.12 (s, 3H, Gem-Me), 0.80 (d, $J = 11.3$, 1H, H4). ^{13}C NMR ($CDCl_3$, δ): 179.0 (Ester-CO), 169.9 (Amide-CO), 168.3 (Amide-CO(rot)), 143.1 (PzA3), 142.5 (PzB3), 139.8 (PzC3), 136.2/136.1/136.0 (PzA5/PzB5/PzC5), 106.6 (PzB4), 106.2 (PzC4), 105.6 (PzA4), 51.6 (Ester-Me), 50.4 (C7), 49.8 (C4), 49.1 (d, $J = 11.3$, C5), 44.8 (C3), 44.6 (C2), 44.4 (C6), 24.5 (Gem-Me), 22.3 (Amide-Me), 22.1 (Gem-Me′), 13.7 (d, $J = 27.8$, PMe_3). ^{31}P NMR ($CDCl_3$, δ): −10.30 ($J_{WP} = 282$), −11.03 (rotamer). Isomer ratio: 5:1 (chemical exchange observed). IR: $\nu_{BH} = 2488$ cm^{-1}, $\nu_{ester} = 1724$ cm^{-1}, $\nu_{amide} = 1620$ cm^{-1}, $\nu_{NO} = 1543$ cm^{-1}. CV (DMA): $E_{p,a} = +0.45$ V. ESI-MS obsd (%), calcd (%), ppm, $(M + H)^+$: 726.2326 (76.7), 726.2333 (82.8), 1.1; 727.2353 (69.3), 727.2359 (80.5), 0.8; 728.2363 (100), 728.2358 (100), 0.7; 729.2401 (39.9), 729.2398 (45.0), 0.4; 730.2388 (76.5), 730.239 (83.3), 0.3. Anal. Calcd for $C_{24}H_{38}BN_8O_4PW \cdot H_2O$: C, 38.63; H, 5.40; N, 15.02. Found: C, 38.96, H, 5.31; N, 15.35.

TpW(NO)(PMe_3)(3,4-η^2-(1-(5-ethyl-5,6-dihydropyridin-1(2*H*)-yl)ethanone)) (18). In three separate oven-dried test tubes, a solution of **11** (0.225 g, 0.290 mmol) in DCM (5.16 g), CuCN (0.133 g, 1.485 mmol), and a solution of $ZnEt_2$ (0.118 g, 0.955 mmol), DCM (3.05 g), and THF (0.116 g) were added to a 0 °C cold bath. After 20 min, the **11** solution was quickly added to the CuCN-containing tube, and the suspension was quickly added to the $ZnEt_2$ solution and allowed to stir for 3 h. The solution was removed from the glovebox and neutralized under a stream of $N_{2(g)}$ with NH_4Cl (saturated, aqueous) solution. The solution was diluted with 5 mL of DCM, extracted with 5 × 10 mL of NH_4Cl (saturated, aqueous), and back-extracted with 2 × 4 mL of DCM. The combined organic layers were dried over Na_2SO_4 for 2 h and filtered through a 30 mL coarse porosity fritted funnel, and the solvent was removed. The residue was dissolved in 1 mL of DCM and then 1 mL of EtOAc, followed by the addition of Et_2O (35 mL) to precipitate a dark brown solid that was collected on a 15 mL medium porosity fritted funnel and discarded. The filtrate solvent was concentrated *in vacuo*, and the residue was dissolved in 1 mL of DCM and then 1 mL of EtOAc, followed by the addition of hexanes (35 mL) to precipitate an off-white solid. The solution was cooled to 0 °C for 30 min, and the precipitate was collected on a 15 mL medium porosity fritted funnel (0.082 g, 0.125 mmol, 43% yield). ^{1}H NMR ($CDCl_3$, δ): 8.08 (d, $J = 2.0$, 1H, PzA3), 8.04 (d, $J = 2.0$, 1H, PzB3), 7.70 (m, 2H, PzB5/PzC5), 7.62 (d, $J = 2.0$, 1H, PzA5), 7.23 (d, $J = 2.0$, 1H, PzC3), 6.29 (t, $J = 2.0$, 1H, PzB4), 6.20 (t, $J = 2.0$, 1H, PzA4), 6.19 (t, $J = 2.0$, 1H, PzC4), 5.08 (dd, $J = 13.7, 6.5$, 1H, H2), 4.48 (dd, $J = 13.7, 3.2$, 1H, H2′), 3.83 (dd, $J = 12.4, 5.0$, 1H, H6), 3.13 (dd, $J = 12.4, 6.1$, 1H, H6′), 2.90 (s (br), 1H, H5), 2.75 (m, 1H, H3), 2.11 (s, 3H, Amide-Me), 1.59 (m, 1H, H7), 1.49 (m, 1H, H7′), 1.21 (d, $J = 8.7$, 9H, PMe_3), 1.10 (d, $J = 11.4$, 1H, H4), 0.95 (t, $J = 7.5$, Ethyl-CH_3); non-overlapping minor isomer signals, 8.11 (d, $J = 2.0$, 1H, PzA3), 8.02 (d, $J = 2.0$, 1H, PzB3), 7.17 (d, $J = 2.0$, 1H, PzC3), 4.46 (m(buried), 1H, H2), 4.20 (dd, $J = 13.2, 6.5$, 1H, H2′), 3.91 (dd, $J = 12.5, 4.6$, 1H, H6), 3.16 (m(shoulder), 1H, H6′), 2.18 (s, 3H, Amide-Me), 1.24 (d, $J = 7.9$, 9H, PMe_3). ^{13}C NMR ($CDCl_3$, δ): 169.9 (Amide-CO), 143.3 (PzB3), 142.6 (PzA3), 140.1 (PzC3), 136.5/135.8 (PzA5/PzB5/PzC5), 106.5 (PzB4), 106.0/105.5 (PzA4/PzC4), 55.0 (C4), 50.6 (C3, d, $J = 11.7$), 49.9 (C6), 44.6 (C2), 40.7 (C5), 32.0 (C7), 22.4 (Amide-Me), 13.8 (PMe_3, d, $J = 27.9$), 12.6 (Ethyl-CH_3); non-overlapping minor isomer signals, 168.8 (Amide-CO), 143.4 (PzB3), 143.2 (PzA3), 140.0 (PzC3), 50.3 (C2), 47.8 (C6), 22.3 (Amide-Me), 14.2 (PMe_3, d, $J = 28.1$). ^{31}P NMR ($CDCl_3$, δ): −11.45 ($J_{WP} = 271$), −12.27 (rotamer). Isomer ratio: 4.3:1 (chemical exchange observed). IR: $\nu_{BH} = 2480$ cm^{-1}, $\nu_{amide} = 1620$ cm^{-1}, $\nu_{NO} = 1547$ cm^{-1}. CV (DMA): $E_{p,a} = +0.46$ V. ESI-MS obsd (%), calcd (%), ppm, $(M + H)^+$: 655.2182 (79.3), 655.22 (84.8), 2.7; 656.2195 (84.7), 656.2226 (80.1), 4.7; 657.2219 (100), 657.2224 (100), 0.7; 658.2263 (61.5), 658.2266 (42.7), 0.4; 659.2232 (74.9), 659.2256 (84), 3.7.

TpW(NO)(PMe_3)(3,4-η^2-(1-(2,5-diethyl-5,6-dihydropyridin-1(2*H*)-yl)ethanone)) (19). In three separate oven-dried test tubes, a dark yellow homogeneous solution of **12** (0.500 g, 0.622 mmol) in DCM (10.05 g), a solution of $ZnEt_2$ (0.232 g, 1.88 mmol) in DCM (10.05 g) and THF (0.242 g), and CuCN (0.232 g, 2.59 mmol) were all placed in a −35 °C cold bath. After 20 min, the solution of **12** was added to the tube containing CuCN, the suspension was transferred to the test tube containing the $ZnEt_2$ solution at −32 °C, and the mixture was allowed to stir. After 52 h, the mixture was removed from the now −30 °C cold bath and allowed to warm to room temperature outside the glovebox under a stream of $N_{2(g)}$ for 15 min. The solution was neutralized with NH_4Cl (saturated, aqueous) until effervescence stopped. The solution was then extracted with 5 × 20 mL of NH_4Cl (saturated, aqueous) and back-extracted with 2 × 20 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse

porosity fritted funnel, and the solvent was removed. The residue was dissolved in 2.5 mL of DCM and then 2.5 mL of EtOAc, and 50 mL of Et_2O was added to precipitate a brown solid. The solid was collected on a 30 mL medium porosity fritted funnel, washed with 2 × 15 mL of Et_2O, and discarded. The filtrate solvent was removed *in vacuo*, the residue was dissolved in 1 mL of DCM and then 1 mL of EtOAc, and 50 mL of hexanes was added to precipitate a tan-pink solid. The solution was cooled in an ice bath for 1 h, and the solid was collected on a 30 mL medium porosity fritted funnel, washed with 2 × 10 mL of hexanes, and placed under a vacuum (0.180 g of a 1.9:1 mixture of **19**:**3**; 0.118 g, 0.172 mmol, 28% yield of desired product). ^{1}H NMR ($CDCl_3$, δ): 8.90 (d, J = 2.0, 1H, PzA3), 7.97 (d, J = 2.0, 1H, PzB3), 7.69 (d, J = 2.0, 1H, Tp), 7.65 (d, J = 2.0, 1H, Tp), 7.57 (d, J = 2.0, 1H, Tp), 7.17 (d, J = 2.0, 1H, PzC3), 6.25−6.17 (m, 3H, Tp), 5.52 (t(br), J = 7.3, 1H, H2), 3.66 (dd, J = 12.8, 6.5, 1H, H6), 2.94 (q(br), J = 7.9, 1H, H5), 2.84 (dd, J = 12.8, 9.7, 1H, H6′), 2.49 (ddd, J = 11.4, 2.0, $^3J_{PH}$ = 13.7, 1H, H4), 2.14 (s, 3H, Amide-Me), 1.86 (m, 2H, Ethyl-CH_2), 1.53 (m, 2H, Ethyl-CH_2), 1.15 (d, $^2J_{PH}$ = 8.1, 9H, PMe_3), 1.04 (t, J = 7.5, 3H, Ethyl-CH_3), 0.96 (d, J = 11.4, 1H, H3), 0.79 (t, J = 7.3, 3H, Ethyl-CH_3). ^{1}H assignments were made using a combination of 2D experiments of the mixture (COSY, NOESY, HSQC, HMBC) and difference spectra with authentic **3** and the isolated mixture. IR: ν_{BH} = 2488 cm^{-1}, ν_{amide} = 1620 cm^{-1}, ν_{NO} = 1550 cm^{-1}. CV (DMA): $E_{p,a}$ = +0.35 V. ESI-MS obsd (%), calcd (%), ppm, $(M + H)^+$: 683.2474 (85.8), 683.2513 (83.7), 5.8; 684.2519 (95.5), 684.2539 (80.5), 2.8; 685.2538 (100), 685.2537 (100), 0.1; 686.255 (65.3), 686.2578 (44.1), 4.1; 687.2574 (100), 687.257 (83.5), 0.6.

TpW(NO)(PMe$_3$)(4,5-η^2-(dimethyl 2-(1-acetyl-6-ethyl-1,2,3,6-tetrahydropyridin-3-yl)malonate)) (20). In separate oven-dried test tubes, a solution of **12** (0.503 g, 0.648 mmol) in MeCN (4.22 g) and a solution of LiDMM (0.183 g, 1.326 mmol) in MeCN (4.21 g) were placed in a 0 °C cold bath. After 0.5 h, the **12** solution was quickly added to the LiDMM solution, and the mixture was allowed to stir for 2 h. The reaction solution was removed from the cold bath, diluted with 10 mL of DCM, extracted with 3 × 10 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 10 mL of DCM, the combined organic layers were dried with Na_2SO_4 and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed. The residue was dissolved in 2.5 mL of DCM and then 2.5 mL of EtOAc, followed by the addition of Et_2O (50 mL) to precipitate a brown solid that was discarded. The yellow filtrate solvent was removed, the residue was dissolved in 1 mL of DCM, and then 1 mL of EtOAc and hexanes (35 mL) was added to precipitate a tan solid. The solution was cooled to 0 °C for 30 min, and the precipitate was collected on a 15 mL medium porosity fritted funnel, washed with 2 × 5 mL of hexanes, and placed under a vacuum (0.211 g, 0.268 mmol, 41% yield). ^{1}H NMR ($CDCl_3$, δ): 8.53 (d, J = 2.0, 1H, PzA3), 8.01 (d, J = 2.0, 1H, PzB3), 7.71/7.58 (d, J = 2.0, 2H, PzA5/PzC5), 7.67 (d, J = 2.0, 1H, PzB5), 7.14 (d, J = 2.0, 1H, PzC3), 6.24 (t, J = 2.0, 1H, PzB4), 6.20 (t, J = 2.0, 2H, PzA4/PzC4), 5.32 (t(br), J = 6.8, 1H, H6), 4.10 (d, J = 8.0, 1H, H9), 3.85 (s, 3H, Ester-Me), 3.81 (s, 3H, Ester-Me′), 3.72 (dd, J = 12.9, 5.8, 1H, H2), 3.62 (q(br), J = 6.4, 1H, H3), 3.36 (dd, J = 12.9, 5.5, 1H, H2′), 2.34 (ddd, J = 11.7, 2.2, $^3J_{PH}$ = 11.7, 1H, H4), 2.08 (s, 3H, Acyl-Me), 2.02 (m, 1H, H7), 1.6 (m, 1H, H7′), 1.22 (d, J = 8.0, 9H, PMe_3), 1.16 (d(br), J = 11.7, 1H, H5), 0.82 (t, J = 7.5, 3H, Methyl). ^{13}C NMR ($CDCl_3$, δ): 171.5 (Amide-CO), 169.7 (Ester-CO/Ester-CO′), 144.2 (PzA3), 143.4 (PzB3), 140.1 (PzC3), 136.7/136.0/135.9 (PzA5/PzB5/PzC5), 106.3/106.1/105.9 (PzA4/PzB4/PzC4), 59.4 (C9), 55.4 (C5), 52.7 (Ester-Me), 52.6 (Ester-Me′), 51.9 (C6), 47.5 (d, J = 11.1, C4), 43.5 (C2), 38.1 (C3), 34.2 (C7), 23.3 (Amide-Me), 14.1 (d, J = 27.5, PMe_3), 11.9 (C8). ^{31}P NMR ($CDCl_3$, δ): −12.04 (J_{WP} = 279). IR: ν_{BH} = 2480 cm^{-1}, ν_{ester} = 1732 cm^{-1}, ν_{amide} = 1624 cm^{-1}, ν_{NO} = 1554 cm^{-1}. CV (DMA): $E_{p,a}$ = +0.41 V. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 807.2262 (75.6), 807.2286 (81.4), 3.1; 808.2306 (82), 808.2312 (80.7), 0.7; 809.2283 (100), 809.2311 (100), 3.4; 810.2332 (47), 810.235 (46.6), 2.3; 811.2333 (85), 811.2343 (83), 1.2. Anal. Calcd for $C_{26}H_{40}BN_8O_6PW$: C, 39.72; H, 5.13; B, 1.37; N, 14.25. Found: C, 39.38; H, 5.23; N, 14.28.

TpW(NO)(PMe$_3$)(3,4-η^2-(dimethyl 2-(1-acetyl-6-(nitromethyl)-1,2,3,6-tetrahydropyridin-3-yl)malonate)) (21). General procedure 1 was used to generate the THP complex precursor. Test tube 1: **10** (0.104 g, 0.152 mmol); HOTf (0.024 g, 0.159 mmol); MeCN (1.17 g). Test tube 2: LiDMM (0.061 g, 0.442 mmol); MeCN (0.73 g). Oxidation with $O_{2(g)}$ failed to liberate the organic compound following general procedure 2. SiO_2 (10.1 g); reaction time 16 h. The complex was isolated in a manner analogous to general procedure 5. Yellow-tan solid located between R_f = 0.18 and R_f = 0.38 when 5% hexanes in EtOAc was used as the eluent (0.073 g, 0.089 mmol, 59% yield). ^{1}H NMR ($CDCl_3$, δ): 8.32 (d, J = 2.0, 1H, PzA3), 8.01 (d, J = 2.0, 1H, PzB3), 7.71 (d, J = 2.0, 1H, PzC5), 7.69 (d, J = 2.0, 1H, PzB5), 7.58 (d, J = 2.0, 1H, PzA5), 7.12 (d, J = 2.0, 1H, PzC3), 6.27 (t, J = 2.0, 1H, PzB4), 6.24 (t, J = 2.0, 1H, PzA4), 6.20 (t, J = 2.0, 1H, PzC4), 6.15 (t(br), J = 6.9, 1H, H6), 5.05 (dd, J = 11.0, 6.0, 1H, H7), 4.61 (dd, J = 11.0, 8.0, 1H, H7′), 3.88 (d, J = 8.7, 1H, H8), 3.85 (dd, J = 13.0, 5.7, 1H, H2), 3.84 (s, 3H, Ester-Me), 3.83 (s, 3H, Ester-Me′), 3.64 (s(br), 1H, H3), 3.35 (dd, J = 13.0, 3.7, 1H, H2′), 2.22 (ddd, J = 11.3, 1.8, $^3J_{PH}$ = 11.3, 1H, H4), 2.07 (s, 3H, Amide-Me), 1.20 (d, J = 8.1, 9H, PMe_3), 1.07 (d, J = 11.3, 1H, H5). ^{13}C NMR ($CDCl_3$, δ): 172.6 (Amide-CO), 169.5 (Ester-CO), 169.4 (Ester-CO′), 143.6 (PzA3), 143.3 (PzB3), 140.1 (PzC3), 137.0 (PzC5), 136.3/136.2 (PzA5/PzB5), 106.6 (PzB4), 106.4 (PzA4), 106.2 (PzC4), 83.2 (C7), 60.0 (C8), 52.9 (Ester-Me), 52.7 (Ester-Me′), 50.4 (C6), 49.8 (C5), 48.0 (d, $^2J_{PC}$ = 12.2, C4), 44.6 (C2), 37.9 (C3), 23.2 (Amide-Me), 13.8 (d, $^1J_{PC}$ = 28.0, PMe_3). ^{31}P NMR ($CDCl_3$, δ): −11.86 (J_{WP} = 278). IR: ν_{BH} = 2488 cm^{-1}, ν_{ester} = 1732 cm^{-1}, ν_{amide} = 1643 cm^{-1}, ν_{NO} = 1547 cm^{-1}. CV (MeCN): $E_{p,a}$ = +0.66 V. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 838.1979 (89.2), 838.198 (81.5), 0.2; 839.1999 (84.3), 839.2006 (80.4), 0.8; 840.1996 (100), 840.2005 (100), 1.0; 841.2036 (44.1), 841.2044 (46.4), 1.0; 842.2028 (76.5), 842.2037 (83.3), 1.1.

[TpW(NO)(PMe$_3$)(6,7-η^2-(1-amino-8-(1-methoxy-2-methyl-1-oxopropan-2-yl)-3-methyl-5,8-dihydrooxazolo[3,4-*a*]pyridin-4-ium))][OTf] (22). A solution of MMTP (0.504 g, 2.89 mmol) in MeCN (0.502 g) was quickly added to a vial containing a deep red solution of **13** (1.247 g including Et_2O impurity; estimated 1.0 g with correction for Et_2O, 1.3 mmol) in MeCN (4.52 g) to give a dark-brown solution. After 10 min, the solution was removed from the glovebox, diluted with 20 mL of DCM, extracted with 3 × 10 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 3 × 20 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse fritted funnel, and the solvent was removed. The residue was dissolved in 5 mL of DCM and then diluted with 5 mL of EtOAc, followed by the addition of 100 mL of hexanes to precipitate an off-white solid that was collected on a 30 mL medium porosity fritted funnel. The remaining material on the precipitation glassware was redissolved in 2.5 mL of DCM, diluted with 2.5 mL of EtOAc, precipitated with 50 mL of hexanes, and collected on the same funnel. The combined precipitate was washed with 2 × 15 mL of hexanes and placed under a vacuum (0.860 g, 1.142 mmol, 88% yield). ^{1}H NMR (CD_3CN, δ): 7.94 (d, J = 2.0, 1H, PzB3), 7.87 (m, 4H, Tp), 7.43 (d, J = 2.0, 1H, PzC3), 6.38 (m, 3H, Tp), 5.73 (dd, J = 14.5, 3.7, 1H, H5), 4.92 (d+s, J = 14.5, 3H, H5′/NH2), 4.27 (s, 1H, H8), 3.33 (s, 3H, Ester-Me), 2.90 (ddd, J = 11.3, 3.7, $^3J_{PH}$ = 11.3, 1H, H6), 2.63 (s, 3H, Amide-Me), 1.34 (s, 3H, Gem-Me), 1.26 (s, 3H, Gem-Me), 1.16 (d, $^2J_{PH}$ = 8.4, 9H, PMe_3), 0.94 (d, J = 11.3, 1H, H7). ^{13}C NMR (CD_3CN, δ): 178.2 (Ester-CO), 155.2 (C3), 152.3 (C1), 144 (PzB3), 143.6 (PzA3), 141.6 (PzC3), 138.2/137.9 (PzA5/PzB5/PzC5), 107.8/107.7/107.1 (PzA4/PzB4/PzC4), 107.0 (C9), 53.3 (C10), 52.3 (Ester-Me), 50.7 (d, J = 2.5, C5), 48.4 (d, J = 1.5, C7), 44.1 (d, $^2J_{PC}$ = 12.1, C6), 42.6 (C8), 24.4 (Gem-Me), 21.5 (Gem-Me), 12.8 (d, $^1J_{PC}$ = 29.3, PMe_3), 12.5 (Amide-Me). ^{31}P NMR ($CDCl_3$, δ): −12.57 (J_{WP} = 268). IR: ν_{BH} = 2495 cm^{-1},

ν_{ester} = 1724 cm^{-1}, ν = 1689 cm^{-1}, ν = 1616 cm^{-1}, ν_{NO} = 1547 cm^{-1}. CV (DMA): $E_{p,a}$ = +0.80 V. ESI-MS obsd (%), calcd (%), ppm, (M − H)$^+$: 752.2367 (93.5), 752.2364 (84.8), 0.3; 753.2390 (93.8), 753.2390 (79.7), 0.0; 754.2391 (100), 754.2389 (100), 0.3; 755.2415 (56.4), 755.2428 (42.4), 1.8; 756.2401 (81.5), 756.2421 (84.3), 2.7. Anal. Calcd for $C_{26}H_{45}BF_3N_9O_7PSW\cdot H_2O$: C, 33.89; H, 4.38; N, 13.68; Found: C, 33.90; H, 4.30; N, 13.73.

[TpW(NO)(PMe$_3$)(4,5-η^2-(1-acetyl-2-cyanopiperidin-4-yliu-m))][OTf] (23). A solution of DABCO (0.061 g, 0.544 mmol) in MeCN (1.01 g) was added to a homogeneous tan solution of **22** (0.100 g, 0.111 mmol) in MeCN (1.91 g), and the solution was allowed to stir in a 58 °C oil bath. After 7.5 h, the reaction solution was removed from the oil bath and glovebox, diluted with 30 mL of DCM, extracted with 3 × 15 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 15 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed *in vacuo*. The residue was dissolved in 1 mL of DCM and then 1 mL of EtOAc, and the solution was diluted with 50 mL of hexanes to precipitate a tan solid. The solution was cooled to 0 °C for 1.5 h, and the solid was collected with a 15 mL fine porosity fritted funnel, rinsed with 30 mL of hexanes, and then placed under a vacuum (0.068 g, 0.090 mmol, 82% yield). ^{1}H NMR ($CDCl_3$, δ): 8.14 (m, 2H, PzA3/PzB3), 7.74 (d, J = 2.0, 1H, PzC5), 7.72/7.66 (d, J = 2.0, 2H, PzB5/PzC5), 7.13 (d, J = 2.0, 1H, PzC3), 6.31/6.29 (t, J = 2.0, 2H, PzA4/PzB4), 6.26 (t, J = 2.0, 1H, PzC4), 5.82 (s(br), 1H, H2), 4.31 (dd, J = 14.2, 8.2, 1H, H6), 4.25 (dd, J = 14.2, 7.5, 1H, H6′), 3.56 (s(br), 1H, H3), 3.11 (m, 4H, H5/Ester-Me), 2.21 (s, 3H, Amide-Me), 1.31 (d, $^2J_{PH}$ = 8.1, 9H, PMe$_3$), 1.19 (s, 3H, Gem-Me), 0.88 (s, 3H, Gem-Me′), 0.45 (d, J = 11.5, 1H, H4). ^{13}C NMR ($CDCl_3$, δ): 177.4 (Ester-CO), 168.1 (Amide-CO), 143.9/143.4 (PzA3/PzB3), 139.7 (PzC3), 136.2 (PzA5/PzB5/PzC5), 118.9 (CN), 106.6/106.5/106.4 (PzA4/PzB4/PzC4), 51.4 (Ester-Me), 51.2 (C7), 49.2 (C4), 47.6 (C6), 46.7 (C3), 46.4 (C5), 29.4 (C2), 22.3 (Gem-Me), 21.8 (Amide-Me), 20.9 (Gem-Me′), 14.1 (d, $^1J_{PC}$ = 27.9, PMe$_3$). ^{31}P ($CDCl_3$, δ): −12.51 (J_{WP} = 268 Hz), −12.34 (Amide confomer; 4.9:1, respectively). IR: ν_{BH} = 2488 cm^{-1}, $\nu_{nitrile}$ = 2233 cm^{-1}$_{(weak)}$, ν_{ester} = 1724 cm^{-1}, ν_{amide} = 1643 cm^{-1}, ν_{NO} = 1562 cm^{-1}. CV (MeCN): $E_{p,a}$ = +0.60 V. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 774.2184 (61), 774.2184 (82.1), 0.0; 775.2208 (61.2), 775.2209 (80.8), 0.1; 776.2209 (100), 776.2208 (100), 0.0; 777.2246 (47.7), 777.2248 (45.9), 0.3; 778.223 (65.1), 778.2241 (83), 1.3. Anal. Calcd for $C_{25}H_{37}BN_9O_4PW\cdot H_2O$: C, 39.39; H, 5.02; N, 16.54. Found: C, 39.36; H, 4.77; N, 16.19.

TpW(NO)(PMe$_3$)(4,5-η^2-(methyl2-carbamoyl-1-ethyl-1,2,3,6-tetrahydropyridin-3-yl)-2-methylpropanoate) (24). $NaBH_4$ (0.102 g, 2.70 mmol) was directly added to a flame-dried 40 mL beaker containing a stirring tan homogeneous solution of **22** (0.101 g, 0.112 mmol) in MeOH (4.70 g) to effervesce vigorously. After 10 min, once effervescence had settled, the sample was removed from the glovebox, diluted with 50 mL of DCM, extracted with 3 × 20 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 20 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed *in vacuo*. The residue was dissolved in 1 mL of DCM and then 1 mL of EtOAc, and 50 mL of hexanes added to precipitate a fine tan solid. The solution was cooled to 0 °C for ∼20 min, and the precipitate was collected on a 15 mL medium porosity fritted funnel, rinsed with ∼20 mL of hexanes, and placed under a vacuum (0.071 g, 0.094 mmol, 84% yield). ^{1}H NMR ($CDCl_3$, δ): 8.98 (s, 1H, NH), 8.19 (d, J = 2.0, 1H, PzA3), 8.06 (d, J = 2.0, 1H, PzB3), 7.70 (d, J = 2.0, 1H, PzB5), 7.67 (d, J = 2.0, 1H, PzC5), 7.61 (d, J = 2.0, 1H, PzA5), 7.20 (d, J = 2.0, 1H, PzC3), 6.29 (t, J = 2.0, 1H, PzB4), 6.25 (t, J = 2.0, 1H, PzA4), 6.20 (t, J = 2.0, 1H, PzC4), 5.10 (s, 1H, NH), 4.03 (dd, J = 11.6, 2.5, 1H, H6), 3.64 (d, J = 11.6, 1H, H6′), 3.43 (d, J = 2.5, 1H, H3), 2.95 (ddd, J = 11.8, 2.5, $^3J_{PH}$ = 11.8, 1H, H5), 2.86 (s, 3H, Ester-Me), 2.80 (d, J = 4.9, 1H, H2), 2.59 (m, 1H, H7), 2.18 (m, 1H, H7′), 1.30 (s, 3H, Gem-Me), 1.23 (d, $^2J_{PH}$ = 8.0, 9H, PMe$_3$), 1.20 (s, 3H, Gem-Me′), 1.13 (t, J = 7.1, 3H, Ethyl-CH$_3$), 0.43 (d, J = 11.8, 1H, H4). ^{13}C NMR ($CDCl_3$, δ): 180.9 (Ester-CO), 178.6 (Amide-CO), 144.0 (PzA3), 143.6 (PzB3), 139.6 (PzC3), 136.3 (PzC5), 135.9 (PzB5), 135.4 (PzA5), 106.6 (PzB4), 106.4 (PzC4), 106.2 (PzA4), 65.6 (C2), 52.5 (C9), 52.2 (d, $^2J_{PH}$ = 11.8, C5), 51.2 (C4), 51.1 (C6/C7), 50.8 (Ester-Me), 45.1 (C3), 24.7 (Gem-Me), 20.4 (Gem-Me′), 13.3 (d, $^1J_{PC}$ = 27.1, PMe$_3$), 12.8 (Ethyl-CH$_3$). ^{31}P ($CDCl_3$, δ): −10.26 (J_{WP} = 278 Hz). IR: ν_{BH} = 2484 cm^{-1}, ν_{ester} = 1724 cm^{-1}, ν_{amide} = 1682 cm^{-1}, ν_{NO} = 1539 cm^{-1}. CV (MeCN): $E_{p,a}$ = +0.41. ESI-MS obsd (%), calcd (%), ppm, (M + H)$^+$: 756.2666 (80.9), 756.2677 (82.1), 1.4; 757.2695 (71.7), 757.2703 (80.8), 1.0; 758.2694 (100), 758.2702 (100), 1.1; 759.2729 (39.7), 759.2741 (46), 1.6; 760.2726 (72.2), 760.2734 (83), 1.1.

Methyl 2-(1-Acetyl-1,2,3,6-tetrahydropyridin-3-yl)-2-methylpropanoate (25). $O_{2(g)}$ oxidation of **17** (0.095 g, 0.130 mmol) was performed in a manner analogous to general procedure 2. SiO_2 (10.5 g); reaction time: 16 h. The piperidine was isolated following general procedure 5. Pale yellow oil located between R_f = 0.21 and R_f = 0.36 when using 1:1 EtOAc:Et$_2$O as the eluent (0.010 g, 0.0448 mmol, 34% yield). ^{1}H NMR ($CDCl_3$, δ): major, 5.83 (ddd, J = 10.4, 5.3, 2.6, 1H, H5), 5.71 (ddd, J = 10.4, 4.8, 2.7, 1H, H4), 4.31 (ddd, J = 18.9, 5.3, 3.0, 1H, H6), 3.71 (s, 3H, Ester-Me), 3.68 (buried, 1H, H6′), 3.59 (dd, J = 13.3, 4.8, 1H, H2), 3.20 (dd, J = 13.3, 8.5, 1H, H2′), 2.62 (m, 1H, H3), 2.11 (s, 3H, Amide-Me), 1.22 (s, 3H, Gem-Me), 1.16 (s, 3H, Gem-Me′); minor, 5.75 (m, 2H, H4/H5), 4.05 (dd, J = 13.0, 5.4, 1H, H2), 3.93 (dd, J = 18.2, 3.5, 1H, H6), 3.85 (dd, J = 18.2, 2.5, 1H, H6′), 3.69 (s, 3H, Ester-Me), 3.18 (dd, J = 13.0, 8.7, 1H, H2′), 2.62 (m, 1H, H3), 2.08 (s, 1H, Amide-Me). ^{13}C NMR ($CDCl_3$, δ): major, 177.3 (Ester-CO), 169.7 (Amide-CO), 126.7 (C5), 125.4 (C4), 52.2 (Ester-Me), 45.1 (C2), 44.6 (C7), 42.8 (C3), 42.2 (C6), 23.4 (Gem-Me), 21.5 (Amide-Me), 21.4 (Gem-Me′); minor, 177.3 (Ester-CO), 169.6 (Amide-CO), 127.8/124.7 (C4/C5), 52.0 (Ester-Me), 45.6 (C6), 44.8 (C7), 41.8 (C3), 39.4 (C2), 23.0 (Gem-Me), 22.1 (Gem-Me′), 21.6 (Amide-Me). Isomer ratio: 1.1:1 (chemical exchange observed). IR: ν_{ester} = 1727 cm^{-1}, ν_{amide} = 1640 cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 248.1257 (100), 248.1253 (100), 1.7.

Dimethyl 2-(1-Acetyl-1,2,3,6-tetrahydropyridin-3-yl)malonate (26). Method 1: $O_{2(g)}$ oxidation of **16** (0.100 g, 0.132 mmol) was performed in a manner analogous to general procedure 2. SiO_2 (10.0 g); reaction time, 18 h. The piperidine was isolated following general procedure 5. Pale yellow oil located between R_f = 0.18 and R_f = 0.31 when using 1:1 EtOAc:Et$_2$O as an eluent (0.009 g, 0.0353 mmol, 27% yield). One-pot method: A solution of HOTf (0.025 g, 0.167 mmol) in DCM (2.08 g) was added to an oven-dried test tube containing **2** (0.085 g, 0.136 mmol) and was placed into a 0 °C cold bath next to a separate oven-dried test tube containing a solution of LiDMM (0.056 g, 0.406 mmol) and DCM (1.75 g). The solutions were allowed to cool for 10 min. The LiDMM solution was quickly added to the tungsten allyl solution and allowed to stir at 0 °C for 30 min. The solution was then removed from the cold bath and taken outside of the glovebox to stir at room temperature. After 15 min, the solution was diluted with 20 mL of DCM, extracted with 3 × 10 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 10 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed to leave a yellow-brown residue. Crude **16** was oxidized with $O_{2(g)}$ in a manner similar to general procedure 2. SiO_2 (10.0 g); reaction time, 20 h. General procedure 5 was followed to isolate the product. Pale yellow oil located between R_f = 0.17 and R_f = 0.32 when 1:1 EtOAc:Et$_2$O was used as the eluent (0.013 g, 0.0517 mmol, 38% yield). ^{1}H NMR ($CDCl_3$, δ): major, 5.69−5.86 (m, 2H, H4/H5), 4.09 (ddd, J = 19.3, 2.5, 2.4, 1H, H6), 3.97 (ddd, J = 19.3, 2.6, 2.4, 1H, H6′), 3.76 (s(shoulder), 3H, Ester-Me(maj,min)), 3.75 (s, 3H, Ester-Me′), 3.63 (dd, J = 13.8, 4.3, 1H, H2), 3.53 (dd, J = 13.8, 5.5, 1H, H2′), 3.40 (d, J = 9.4, 1H, H7), 3.03 (s(broad), 1H, H3), 2.09 (s, 3H, Amide-Me); minor, 5.69−5.86 (m(overlap with maj), 2H, H4/H5), 3.93 (m, 2H, H6/

H6′), 3.76 (s(shoulder of maj)), 3H, Ester-Me), 3.73 (s, 3H, Ester-Me′), 3.86 (dd, J = 13.4, 4.9, 1H, H2), 3.49 (dd, J = 13.4, 4.4, 1H, H2′), 3.34 (d, J = 9.5, 1H, H7), 3.03 (s(broad, overlap of maj), 1H, H3), 2.10 (s, 3H, Amide-Me). ^{13}C NMR ($CDCl_3$, δ): major, 170.2 (Amide-CO), 168.6 (Ester-CO), 168.3 (Ester-CO′), 127.4/125.4 (C4/C5), 53.9 (C7), 52.9 (Ester-Me), 52.8 (Ester-Me′), 46.0 (C2), 42.2 (C6), 35.6 (C3), 21.3 (Amide-Me); minor, 169.8 (Amide-CO), 168.3 (Ester-CO), 168.2 (Ester-CO′), 127.3/125.7 (C4/C5), 54.2 (C7), 52.9 (Ester-Me), 52.7 (Ester-Me′), 45.8 (C6), 41.1 (C2), 34.9 (C3), 21.9 (Amide-Me). Isomer ratio: 1.7:1 (chemical exchange observed). IR: ν_{ester} = 1732 cm^{-1}, ν_{amide} = 1639 cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 278.0987 (100), 278.0999 (100), 4.4.

Methyl 2-(1-Acetyl-2-oxo-1,2,3,6-tetrahydropyridin-3-yl)-2-methylpropanoate (27). Acetone (4.17 g) was added to a vial containing **22** (0.102 g, 0.135 mmol) and I_2 (0.207 g, 0.816 mmol), and the dark brown solution was allowed to stir. After 1 h the reaction solution was transferred to a separatory funnel containing 50 mL of $NaHCO_3$ (saturated, aqueous) to precipitate a brown solid, which dissolved in the following 5 × 25 mL of DCM extractions. The organic layer was dried with $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, the solvent was removed *in vacuo*, and the residue was transferred to a vial with DCM which was then removed *in vacuo*. The residue was transferred to a preparatory TLC plate with 4 × 0.3 g of DCM and two 1 mL syringes. The plate was eluted with 4:1 hexanes:Et_2O. The band between R_f = 0.15 and R_f = 0.27 was removed, placed in a test tube with 15 mL of EtOAc, and sonicated for 10 min. The silica for this band was collected on a 30 mL medium porosity fritted funnel, the product was washed off the silica with 200 mL of EtOAc, solvent was removed from the filtrate *in vacuo*, the residue was transferred to a tared vial with DCM, and the solvent was again removed *in vacuo*. The vial was placed under a vacuum overnight, yielding a colorless oil (0.010 g, 0.042 mmol, 31% yield). ^{1}H NMR ($CDCl_3$, δ): major, 6.01 (ddt, J = 10.1, 3.5, 1.6, 1H, H5), 5.80 (ddt, J = 10.1, 3.8, 1.9, 1H, H4), 4.23 (ddd, J = 3.5, 3.3, 1.9, 2H, H6/H6′), 3.74 (s, 3H, Ester-Me), 3.55 (ddd, J = 3.8, 3.3, 1.6, 1H, H3), 2.53 (s, 3H, Acyl-Me), 1.26 (s, 3H, Gem-Me), 1.19 (s, 3H, Gem-Me′); minor, 5.94/5.74 (m, 2H, H5/H4), 3.93 (m, 2H, H6/H6′), 3.73 (s, 3H, Ester-Me), 3.44 (ddd, J = 8.4, 4.2, 1.6, 1H, H3), 1.23 (s, 3H, Gem-Me), 1.2 (s, 3H, Gem-Me′). ^{13}C NMR ($CDCl_3$, δ): major, 176.8 (Ester-CO), 173.6 (Amide-CO), 171.7 (C2), 124.4 (C5), 122.9 (C4), 52.4 (Ester-Me), 51.7 (C2), 46.5 (C7), 45.6 (C6), 27.7 (Amide-Me), 24.0 (Gem-Me), 21.1 (Gem-Me′); minor, 123.7/123.5 (C4/C5), 52.2 (Ester-Me), 47.9 (C3), 46.2 (C7), 43.8 (C6), 23.3 (Gem-Me), 21.4 (Gem-Me′). Isomer ratio: 4.6:1. IR: ν_{ester} = 1733 cm^{-1}, ν_{imide} = 1698 cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 262.1050 (100), 262.1050 (100), 0.0.

Methyl 2-(2-Cyanopyridin-3-yl)-2-methylpropanoate (28). Acetone (4.01 g) was added to a vial containing **22** (0.100 g, 0.133 mmol) and DDQ (0.123 g, 0.542 mmol) to give a dark red homogeneous solution that was removed from the glovebox after several minutes and exposed to air for 0.5 h. The reaction was allowed to stir for 14 h and then diluted with 20 mL of DCM, extracted with 3 × 10 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 3 × 10 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed *in vacuo*. The residue was transferred to a 4 dram vial with DCM, and the solvent was removed once more *in vacuo*. The residue was loaded onto a 20 cm × 20 cm × 500 μm SiO_2 preparatory TLC plate with 4 × 0.3 g of DCM and a 1 mL syringe. The preparatory TLC plate was eluted with Et_2O, and the band that was UV-active between R_f = 0.55 and R_f = 0.69 was removed from the TLC plate, placed in a test tube with 15 mL of EtOAc, and sonicated for 10 min to break up the silica. The silica was collected on a 30 mL medium porosity fritted funnel and washed with 200 mL of EtOAc, and the solvent was removed from the filtrate *in vacuo*. The residue was then transferred to a tared vial with DCM, the solvent was removed, and the resulting material was placed under a vacuum overnight (colorless oil, 0.008 g, 0.039 mmol, 30% yield). ^{1}H NMR ($CDCl_3$, δ): 8.60 (dd, J = 4.8, 1.5, 1H, H6) 7.83 (dd, J = 8.2, 1.5, 1H, H4), 7.52 (dd, J = 8.2, 4.8, 1H, H5), 3.79 (s, 3H, Ester-Me), 1.71 (s, 6H, Gem-DiMe). ^{13}C NMR ($CDCl_3$, δ): 175.7 (Ester-CO) 148.8 (C6), 145.2 (C3), 134.2 (C4), 133.8 (C2), 126.8 (C5), 116.6 (CN), 53.1 (Ester-Me), 46.3 (C7), 26.6 (Gem-DiMe). IR: $\nu_{nitrile}$ = 2233 cm^{-1}, ν_{ester} = 1735 cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 227.0798 (100), 227.0791 (100), 2.9.

Dimethyl 2-(1-Acetyl-6-allyl-1,2,3,6-tetrahydropyridin-3-yl)malonate (29). One-pot method 1: General procedure 1 was used to generate the THP complex precursor. Test tube 1: **8** (0.105 g, 0.158 mmol); HOTf (0.025 g, 0.165 mmol); MeCN (1.26 g). Test tube 2: LiDMM (0.063 g, 0.456 mmol); MeCN (0.73 g). Oxidation of the complex was performed following general procedure 2. SiO_2 (10.1 g); reaction time, 15 h. General procedure 5 was followed to isolate the product. Pale yellow oil located between R_f = 0.21 and R_f = 0.33 when Et_2O was used as the eluent (0.016 g, 0.0535 mmol, 34% yield). One-pot method 2: General procedure 1 was used to generate the THP complex precursor. Test tube 1: **8** (0.100 g, 0.150 mmol); HOTf (0.024 g, 0.161 mmol); MeCN (1.19 g). Test tube 2: LiDMM (0.063 g, 0.456 mmol); MeCN (0.80 g). Oxidation of the complex was performed following general procedure 3. Acetone (4.04 g); CAN (0.083 g, 0.152 mmol); reaction time, 1 h. General procedure 5 was followed to isolate the product. Pale yellow oil located between R_f = 0.21 and R_f = 0.35 when Et_2O was used as the eluent (0.015 g, 0.0508 mmol, 34% yield). One-pot method 3: General procedure 1 was used to generate the THP complex precursor. Test tube 1: **8** (0.100 g, 0.150 mmol); HOTf (0.024 g, 0.158 mmol); MeCN (1.16 g). Test tube 2: LiDMM (0.064 g, 0.464 mmol); MeCN (0.74 g). Oxidation of the complex was performed following general procedure 4. Acetone (2.05 g); DDQ (0.069 g, 0.304 mmol); reaction time, 1.5 h. General procedure 5 was followed to isolate the product. Pale yellow oil located between R_f = 0.20 and R_f = 0.35 when Et_2O was used as the eluent (0.016 g, 0.0535 mmol, 36% yield). ^{1}H NMR ($CDCl_3$, δ): 5.84−5.73 (m, 2H, H4(maj,min)/H5(maj,min)/H8(min)) 5.61 (d, J = 10.3, 1H, H8(min)), 5.15−5.00 (m, 2H, H9(maj,min)/H9′(maj/min)), 4.92 (m, 1H, H6), 4.66 (dd, J = 12.5, 5.3, 1H, H2(min)), 4.15 (m, 1H, H6(min)), 3.89 (dd, J = 12.5, 3.1, 1H, H2), 3.77/3.76/3.74 (s, 6H, Ester-Me(maj,min)/Ester-Me′ (maj,min)), 3.37 (d, J = 7.1, 1H, H10(min)), 3.34 (d, J = 7.4, 1H, H10), 3.02 (dd, J = 12.5, 11.1, 1H, H2′), 2.97 (m, 1H, H3(maj,min)), 2.63 (dd, J = 12.5, 11.3, 1H, H2′(min)), 2.35 (t, J = 7.1, 1H, H7(min)/H7′(min)), 2.30 (t, J = 7.1, 1H, H7/H7′), 2.12 (s, 3H, Amide-Me), 2.09 (s, 3H, Amide-Me(min)). ^{13}C NMR ($CDCl_3$, δ): 169.3 (Amide-CO(maj,min)) 168.2 (Ester-CO(maj,min),Ester-CO′ (maj,min)), 134.4/130.7 (C4/C5), 133.6/128.8/127.9 (C4(min)/C5(min)/C8(min)), 126.1 (C8), 118.8 (C9(min)), 117.6 (C9), 54.6 (C6(min)), 53.8 (C10), 53.6 (C10(min)), 52.0/52.8/52.6 (Ester-Me(maj,min),Ester-Me′ (maj,min)), 49.9 (C6), 43.6 (C2), 39.0 (C7(min)) 38.0 (C7), 37.6 (C2(min)), 35.5 (C3), 34.6 (C3(min)), 21.9 (Amide-Me), 21.8 (Amide-Me(min)). Isomer ratio: 2.3:1 (chemical exchange observed). IR: ν_{ester} = 1734 cm^{-1}, ν_{amide} = 1639 cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, (M + Na)$^+$: 318.1319 (100), 318.1312 (100), 2.2.

Dimethyl 2-((3*S*,6*S*)-1-Acetyl-6-ethyl-1,2,3,6-tetrahydropyridin-3-yl)malonate (30). General procedure 1 was used to generate the THP complex precursor. Test tube 1: **3** (0.103 g, 0.157 mmol); HOTf (0.025 g, 0.168 mmol); MeCN (1.10 g). Test tube 2: LiDMM (0.070 g, 0.507 mmol); MeCN (0.74 g). Oxidation of the complex was performed following general procedure 2. SiO_2 (10.3 g); reaction time, 15 h. General procedure 5 was followed to isolate the product. Pale yellow oil from the band located between R_f = 0.28 and R_f = 0.43 using 9:1 Et_2O:EtOAc as the eluent (0.018 g, 0.063 mmol, 40% yield). ^{1}H NMR ($CDCl_3$, δ): major, 5.81 (ddd, J = 10.3, 3.7, 2.2, 1H, H5), 5.58 (dd, J = 10.3, 1.0, 1H, H4), 4.80 (m, 1H, H6), 3.90 (dd, J = 11.1, 1.8, 1H, H2), 3.77 (s, 3H, Ester-Me), 3.76 (s, 3H, Ester-Me′), 3.33 (d, J = 6.9, 1H, H9), 3.03 (d, J = 11.1, 1H, H2′), 3.00 (m, 1H, H3), 2.14 (s, 3H, Amide-Me), 1.55

(m, 2H, Ethyl-CH_2), 0.92 (t, $J = 7.7$, Ethyl-CH_3); minor, 5.78 (m, 2H, H4/H5), 4.66 (dd, $J = 12.5$, 5.4, 1H, H2), 4.00 (dd, $J = 6.8$, 6.6, 1H, H6), 3.76 (s(shoulder of major), 3H, Ester-Me), 3.74 (s, 3H, Ester-Me′), 3.36 (d, $J = 7.1$, 1H, H9), 3.00 (m(buried), 1H, H3), 2.61 (dd, $J = 12.5$, 12.5, 1H, H2′), 2.10 (s, 3H, Amide-Me), 1.66 (m, 2H, Ethyl-CH_2), 0.97 (t, $J = 7.4$, Ethyl-CH_3). ^{13}C NMR ($CDCl_3$, δ): major, 169.3 (Amide-CO), 168.2 (Ester-CO/Ester-CO′), 131.3 (C5), 125.6 (C4), 53.9 (C9), 52.9 (Ester-Me), 52.8 (Ester-Me′), 51.5 (C6), 43.3 (C2), 35.7 (C3), 26.6 (Ethyl-CH_2), 21.8 (Amide-Me), 10.6 (Ethyl-CH_3); minor, 169.3 (Amide-CO), 168.3 (Ester-CO/Ester-CO′), 129.1/127.6 (C4/C5), 56 (C6), 53.7 (C9), 52.8 (Ester-Me), 52.6 (Ester-Me′), 37.7 (C2), 34.7 (C3), 27.7 (Ethyl-CH_2), 21.7 (Amide-Me), 10.9 (Ethyl-CH_3). Isomer ratio: 1.9:1 (chemical exchange observed). IR: $\nu_{ester} = 1735$ cm^{-1}, $\nu_{amide} = 1632$ cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 306.1309 (100), 306.1312 (100), 0.9.

1-(2,5-Diethyl-5,6-dihydropyridin-1(2*H*)-yl)ethanone (31). Silica (11 g) was added to a 100 mL 14/20 pear-shaped round-bottom flask containing **19** (0.102 g; 0.066 g, 0.097 mmol, adjusted for **3** impurity) and 50 mL of MeCN. Parafilm was placed over the opening, and a small hole was poked in it. The solution was allowed to stir rapidly for 23 h. The solution was filtered through 1 cm Celite on top of 1 cm of sand and washed with 200 mL of EtOAc. The solvent was evaporated, and the residue was loaded onto a SiO_2 predatory TLC plate and eluted with EtOAc. The band between $R_f = 0.38$ and $R_f = 0.52$ was removed from the plate, loaded onto a 30 mL coarse porosity fritted funnel containing 2 cm Celite on top of 2 cm of sand, and covered with 1 cm of sand. The product was washed off with 300 mL of EtOAc, and the solvent was evaporated from the filtrate. The residue was transferred to a tared vial with DCM, the solvent was removed *in vacuo*, and the vial was placed under a vacuum (0.007 g, 0.0386 mmol, 40% yield). ^{1}H NMR ($CDCl_3$, δ): 5.78−5.61 (m, 2H, H3/H4(maj,min)) 4.78 (br s, 1H, H2), 4.65 (dd, $J = 12.4$, 5.1, 1H, H6(min)), 3.97 (br s, 1H, H2(min)), 3.67 (dd, $J = 13.5$, 5.3, 1H, H6), 2.79 (dd, $J = 13.5$, 11.2, 1H, H6′), 2.27 (dd, $J = 12.4$, 10.9, 1H, H6′(min)), 2.15 (br s, 1H, H5), 2.10 (s, 3H, Amide-Me), 2.09 (s, 3H, Amide-Me(min)), 1.75−1.48 (m, 2H, Et-CH_2), 1.41−1.19 (m, 2H, Et-CH_2), 1.03−0.87 (m, 6H, Et-CH_3). ^{13}C NMR ($CDCl_3$, δ): major, 168.9 (Amide-CO), 129.6/128.7 (C3/C4), 51.6 (C2), 45.9 (C6), 37.3 (C5), 26.8 (Et-CH_2), 25.9 (Et-CH_2′), 22.0 (Amide-Me); minor, 169.2 (Amide-CO), 131.6/127.0 (C3/C4), 56.1 (C2), 40.2 (C6), 36.3 (C5), 27.9 (Et-CH_2), 26.1 (Et-CH_2′), 21.7 (Amide-Me), 11.0/10.9/10.7 (Et-CH_3 (maj,min)). Isomer ratio: 1:1.3 (chemical exchange observed). IR: $\nu_{amide} = 1634$ cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 204.1371 (100), 204.1359 (100), 5.7.

Methyl 2-(1-Acetyl-2-cyano-1,2,3,6-tetrahydropyridin-3-yl)-2-methylpropanoate (32). A solution of DABCO (0.062 g, 0.553 mmol) in MeCN (1.0 g) was added to an oven-dried test tube containing a tan solution of **22** (0.105 g, 0.116 mmol) in MeCN (1.90 g), and the resulting mixture was allowed to stir in a 58 °C oil bath. After 7 h 45 min, the solution was removed from the glovebox, diluted with 30 mL of DCM, extracted with 3 × 15 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 15 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL coarse porosity fritted funnel, and the solvent was removed *in vacuo*. An oxidation was attempted with $O_{2(g)}$ in a manner similar to general procedure 2. SiO_2 (10.0 g); reaction time, 17 h. A crude NMR in $CDCl_3$ of the residue of evaporated solvent revealed that only starting material remained, indicating the oxidation had failed. Oxidation similar to general procedure 4 was performed with DDQ using MeCN as the solvent. The residue was dissolved in MeCN (3.7 g) and diluted with a solution of DDQ (0.060 g, 0.264 mmol) in MeCN (1.3 g) to make a purple solution that was allowed to stir. After 23 min, the reaction solution was removed from the glovebox and worked up according to general procedure 4. General procedure 5 was followed to isolate the product. Pale yellow oil from the band located between $R_f = 0.35$ and $R_f = 0.47$ when Et_2O was used as the eluent (0.016 g, 0.064 mmol, 55% yield). ^{1}H NMR ($CDCl_3$, δ): 6.08 (d, $J = 11.1$, 1H, H5(minor)), 5.98 (m, 1H, H5), 5.88 (s, 1H, H2), 5.82 (m, 1H, H4), 5.02 (s, 1H, H2(minor)), 4.43 (d, $J = 19.5$, 1H, H6(minor)), 4.08 (m, 1H, H6), 4.02 (ddd, $J = 17.7$, 4.9, 2.5, 1H, H6′), 3.71 (s, 3H, Ester-Me), 3.64 (d, $J = 19.5$, 1H, H6′(minor)), 3.02 (ddd, $J = 5.3$, 2.5, 1.1, 1H, H3), 2.88 (d(br), $J = 4.8$, 1H, H3(minor)), 2.22 (s, 3H, Amide-Me(minor)), 2.13 (s, 3H, Amide-Me), 1.29 (s, 3H, Gem-Me(minor)), 1.19 (s, 3H, Gem-Me), 1.14 (s, 3H, Gem-Me′ (minor)), 1.12 (s, 3H, Gem-Me′). ^{13}C NMR ($CDCl_3$, δ): 176.4 (Ester-CO), 170.0 (Amide-CO), 127.5 (C5(minor)), 125.5 (C5), 123.3 (C4), 120.7 (C4(minor)), 117.6 (Nitrile), 52.5 (Ester-Me), 46.0 (C7), 45.3 (C3), 42.9 (C6), 39.1 (C2), 22.5 (Gem-Me), 22.2 (Gem-Me′). Isomer ratio: 5.5:1 (chemical exchange observed). IR: $\nu = 2983$ cm^{-1}, $\nu = 2951$ cm^{-1}, $\nu = 2851$ cm^{-1}, $\nu_{nitrile} = 2236$ cm^{-1}, $\nu_{ester} = 1725$ cm^{-1}, $\nu_{amide} = 1659$ cm^{-1}, 1408 cm^{-1}, 1131 cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 273.12 (100), 273.121 (100), 3.7.

Dimethyl 2-(1-Acetyl-6-(2-methoxy-2-oxoethyl)-1,2,3,6-tetrahydropyridin-3-yl)malonate (33). One-pot method: General procedure 1 was used to generate the THP complex precursor. Test tube 1: **7** (0.100 g, 0.143 mmol); HOTf (0.023 g, 0.154 mmol); MeCN (1.16 g). Test tube 2: LiDMM (0.062 g, 0.449 mmol); MeCN (0.775 g). Oxidation of the complex was performed following general procedure 2. SiO_2 (10.3 g); reaction time, 15 h. General procedure 5 was followed to isolate the product. Pale yellow oil from the band located between $R_f = 0.30$ and $R_f = 0.45$ when 1:1 EtOAc:Et_2O was used as the eluent (0.013 g, 0.0406 mmol, 28% yield). ^{1}H NMR ($CDCl_3$, δ): major, 5.85 (ddd, $J = 10.5$, 3.6, 2.3, 1H, H3), 5.67 (ddd, $J = 10.5$, 1.9, 1.6, 1H, H4), 5.19 (m, 1H, H2), 3.94 (q, $J = 9.9$, 1H, H6), 3.77 (s, 3H, C8-Ester-Me), 3.76 (s, 3H, C8-Ester-Me′), 3.66 (s, 3H, C2-Ester-Me), 3.35 (d, $J = 7.3$, 1H, C8), 3.03 (m, 1H, H6′), 3.00 (m, 1H, H5), 2.53 (dq, $J = 14.5$, 7.0, 2H, H7/H7′), 2.13 (s, 3H, Amide-Me); minor, 6.83 (buried, 1H, H4), 5.78 (ddd, $J = 10.3$, 3.8, 2.5, 1H, H3), 4.64 (m, 2H, H2/H6), 3.76 (s, 3H, C8-Ester-Me), 3.75 (s, 3H, C8-Ester-Me′), 3.69 (s, 3H, C2-Ester-Me), 3.38 (d, $J = 6.5$, 1H, H8), 3.00 (buried, 1H, H5), 2.63 (m, 3H, H6/H7/H7′), 2.15 (s, 3H, Amide-Me). ^{13}C NMR ($CDCl_3$, δ): major, 171.2 (C2-Ester-CO) 169.3 (Amide-CO), 168.1 (C8-Ester-CO/C8-Ester-CO′), 129.8 (C3), 127.0 (C4), 53.6 (C8), 52.9 (C8-Ester-Me), 52.8 (C8-Ester-Me′), 51.9 (C2-Ester-Me), 47.4 (C2), 43.4 (C6), 37.8 (C7), 35.5 (C5), 21.8 (Amide-Me); minor, 171 (C2-Ester-CO), 169.5 (Amide-CO), 168.2 (C8-Ester-CO), 168.1 (C8-Ester-CO′), 128.9 (C4), 128.1 (C3), 53.4 (C8), 52.8 (C8-Ester-Me), 52.7 (C8-Ester-Me′), 52.1 (C2-Ester-Me), 51.4 (C2), 39.0 (C7), 37.6 (C6), 34.4 (C5), 21.5 (Amide-Me). Isomer ratio: 2.1:1 (chemical exchange observed). IR: $\nu_{ester} = 1732$ cm^{-1}, $\nu_{ester} = 1639$ cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 350.1231 (100), 350.1216 (100), 4.3.

Dimethyl 2-(1-Acetyl-6-(nitromethyl)-1,2,3,6-tetrahydropyridin-3-yl)malonate (34). One-pot method: General procedure 1 was used to generate the THP complex precursor. Test tube 1: **10** (0.101 g, 0.147 mmol); HOTf (0.023 g, 0.156 mmol); MeCN (1.15 g). Test tube 2: LiDMM (0.062 g, 0.449 mmol); MeCN (0.73 g). Oxidation of the complex was performed following general procedure 3. Acetone (4.1 g); CAN (0.083 g, 0.151 mmol); reaction time, 1 h 15 min. General procedure 5 was followed to isolate the product. Pale yellow oil from the band located between $R_f = 0.29$ and $R_f = 0.43$ when 3:1 EtOAc:Et_2O was used as the eluent (0.031 g, 0.0986 mmol, 67% yield). ^{1}H NMR ($CDCl_3$, δ): major, 5.89 (ddd, $J = 10.3$, 3.6, 1.9, 1H, H4), 5.81 (ddd, $J = 10.3$, 3.1, 2.3, 1H, H5), 5.38 (m, 1H, H6), 4.59 (dd, $J = 11.4$, 5.2, 1H, H7), 4.49 (dd, $J = 11.4$, 5.8, 1H, H7′), 4.00 (d(br), 1H, H2), 3.77 (s, 3H, Ester-Me), 3.76 (s, 3H, Ester-Me′), 3.38 (d, $J = 7.5$, 1H, H8), 2.99 (shoulder, 1H, H3), 2.97 (dd, $J = 11.4$, 10.8, 1H, H2′), 2.17 (s, 3H, Amide-Me); minor, 6.03 (d, $J = 10.5$, 1H, H4), 5.73 (ddd, $J = 10.5$, 4.0, 2.4, 1H, H5), 4.98 (m, 1H, H6), 4.68 (dd, $J = 13.3$, 5.7, 1H, H2), 3.76 (s, 3H, Ester-Me), 3.75 (s, 3H, Ester-Me′), 3.44 (d, $J = 5.9$, 1H, H8), 2.97 (buried, 1H, H3), 2.74 (dd, $J = 13.3$, 11.5, 1H, H2′), 2.11 (s, 3H, Amide-Me). ^{13}C NMR ($CDCl_3$, δ):

major, 170.2 (Amide-CO), 167.9 (Ester-CO/Ester-CO′), 130.2 (C4), 125.3 (C5), 76.5 (C7), 53.2 (C8), 53.0 (Ester-Me), 52.9 (Ester-Me′), 48.6 (C6), 43.6 (C2), 35.1 (C3), 21.8 (Amide-Me); minor, 169.7 (Amide-CO), 168.1 (Ester-CO), 167.9 (Ester-CO′), 132.4 (C4), 123.6 (C5), 76.1 (C7), 52.9/52.8/52.7 (Ester-Me/Ester-Me/C8/C6), 37.3 (C2), 34.2 (C3), 21.2 (Amide-Me). Isomer ratio: 5.5:1 (chemical exchange observed). IR: $\nu_{ester} = 1735$ cm^{-1}, $\nu_{ester} = 1641$ cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 337.1 (100), 337.1006 (100), 1.8.

Dimethyl 2-(1-Acetyl-6-((trimethylsilyl)ethynyl)-1,2,3,6-tetrahydropyridin-3-yl)malonate (35). One-pot method: General procedure 1 was used to generate the THP complex precursor. Test tube 1: **9** (0.100 g, 0.138 mmol); HOTf (0.022 g, 0.146 mmol); MeCN (1.09 g). Test tube 2: LiDMM (0.057 g, 0.413 mmol); MeCN (0.74 g). Oxidation of the complex was performed following general procedure 3. Acetone (4.1 g); CAN (0.077 g, 0.140 mmol); reaction time, 1 h. General procedure 5 was followed to isolate the product. Pale yellow oil from the band located between $R_f = 0.45$ and $R_f = 0.65$ when Et_2O was used as the eluent (0.027 g, 0.0768 mmol, 55% yield). ^{1}H NMR ($CDCl_3$, δ): 5.74−5.44 (m, 3H, H4(maj,min)/H5(maj,min)/H6(maj)) 4.70 (s, 1H, H6(min)), 4.50 (dd, $J = 12.7$, 4.2, 1H, H2(min)), 3.83 (dd, $J = 13.6$, 4.3, 1H, H2), 3.64 (s, 6H, Ester-Me/Ester-Me′), 3.64/3.62 (s, 6H, Ester-Me(min)/Ester-Me′(min)), 3.24 (d, $J = 8.1$, 1H, H9(maj,min)), 3.11 (dd, $J = 13.6$, 12.7, 1H, H2′), 2.88 (m, 1H, H3(maj,min)), 2.55 (dd, $J = 12.7$, 11.0, 1H, H2′(min)), 2.04 (s, 3H, Amide-Me(min)), 2.02 (s, 3H, Amide-Me), 0.00 (s, 9H, TMS). ^{13}C NMR ($CDCl_3$, δ): major, 168.7 (Amide-CO), 168.1 (Ester-CO/Ester-CO′), 128.2/126.4 (C4/C5), 102.1 (C7), 88.3 (C8), 53.7 (C9), 52.9 (Ester-Me/Ester-Me′), 43.8 (C2), 42.6 (C6), 35.5 (C3), 21.4 (Amide-Me), 0.04 (TMS); minor, 169.6 (Amide-CO), 168.1 (Ester-CO/Ester-CO′), 128.4/125.6 (C4/C5), 101.1 (C7), 89.7 (C8), 53.7 (C9), 52.9/52.7 (Ester-Me/Ester-Me′), 46.9 (C6), 38.5 (C2), 34.6 (C3), 21.7 (Amide-Me), 0.04 (TMS). Isomer ratio: 1.8:1 (chemical exchange observed). IR: $\nu_{alkyne} = 2170$ cm^{-1}, $\nu_{ester} = 1734$ cm^{-1}, $\nu = 1661$ cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + Na)^+$: 374.1381 (100), 374.1394 (100), 3.6.

Methyl 2-(Carbamoyl-1-ethyl-1,2,3,6-tetrahydropyridin-3-yl)-2-methylpropanoate (36). $NaBH_4$ (0.106 g, 2.80 mmol) was added directly to a 25 mL flame-dried Erlenmeyer flask containing a tan homogeneous solution of **22** (0.102 g, 0.113 mmol) in MeOH (4.65 g), giving vigorous effervescence. Ten minutes later, after effervescence had ceased, the solution was removed from the glovebox, diluted with 50 mL of DCM, extracted with 3 × 20 mL of $NaHCO_3$ (saturated, aqueous), and back-extracted with 2 × 20 mL of DCM, the combined organic layers were dried with $MgSO_4$ and filtered through a 60 mL medium porosity fritted funnel, and the solvent was removed *in vacuo*. General procedure 2 was followed to liberate the organic compound. SiO_2 (10.0 g); reaction time, 16 h. The residue of the evaporated material revealed that oxidation was incomplete, with a 3:1 ratio of **22**:**24**. The crude material was replaced in a 250 mL flask with the original SiO_2 and EtOAc, and general procedure 2 was resumed to enable complete liberation. Reaction time, 171 h. General procedure 5 was followed to isolate the piperidine. Pale yellow solid from the band located between $R_f = 0.21$ and $R_f = 0.29$ when Et_2O was used as the eluent (0.010 g, 0.038 mmol, 34% yield). Melting point: 64−68 °C. ^{1}H NMR ($CDCl_3$, δ): 6.10 (s(br), 1H, NH), 5.99 (dddd, $J = 10.2$, 4.0, 2.4, 1.8, 1H, H5), 5.65 (dddd, $J = 10.2$, 4.6, 2.6, 2.3, 1H, H4), 5.30 (s(br), 1H, NH), 3.71 (s, 3H, Ester-Me), 3.44 (dddd, $J = 17.5$, 2.8, 2.6, 2.4, 1H, H6), 3.31 (d, $J = 1.0$, 1H, H2), 3.24 (dddd, $J = 17.5$, 24.0, 2.3, 1.6, 1H, H6′), 2.75 (ddddd, $J = 4.6$, 2.8, 1.8, 1.6, 1.0, 1H, H3), 2.7 (dq, $J = 12.5$, 7.3, 1H, H7), 2.63 (dq, $J = 12.5$, 7.3, 1H, H7′), 1.24 (s, 3H, Gem-Me), 1.23 (s, 3H, Gem-Me′), 1.06 (t, $J = 7.3$, 3H, Ethyl-Me). ^{13}C NMR ($CDCl_3$, δ): 179.0 (Ester-CO), 175.7 (Amide-CO), 129.4 (C5), 121.6 (C4), 61.3 (C2), 52.2 (Ester-Me), 49.3 (C7), 47.3 (C8), 47.2 (C6), 45.0 (C3), 25.1 (Gem-Me), 21.6 (Gem-Me′), 13.2 (C8). IR: $\nu = 3438$ (br) cm^{-1}, $\nu = 3341$ (br) cm^{-1}, $\nu = 3194$ (br) cm^{-1}, $\nu = 2975$ cm^{-1}, $\nu = 2935$ cm^{-1}, $\nu_{ester} = 1723$ cm^{-1}, $\nu_{amide} = 1669$ cm^{-1}, $\nu = 1246$ cm^{-1}, $\nu = 1133$ cm^{-1}. ESI-MS obsd (%), calcd (%), ppm, $(M + H)^+$: 255.1709 (100), 255.1703 (100), 2.1.

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Supporting Information Available: CIF files for **11** and **23**; ^{1}H and ^{13}C NMR of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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