

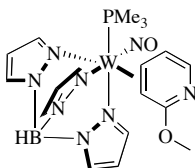
Supplementary Material

Selectfluor-Mediated Dialkoxylation of Tungsten η^2 -pyridinium ComplexesGeorge W. Kosturko,[†] Daniel P. Harrison,[†] Michal Sabat,[†] William H. Myers,[‡] W. Dean Harman[†][†]*Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904 and*[‡]*Department of Chemistry, University of Richmond, Richmond, Virginia 27173*

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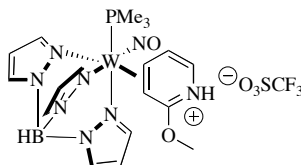
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General Methods All NMR spectra were obtained on either a 300 or 500 MHz Varian INOVA spectrometer. All chemical shifts are reported in ppm versus tetramethylsilane using residual shifts of the deuterated solvent as the internal standard. All ³¹P NMR data is reported versus an external standard in acetone (Triphenylphosphate, -16.58 ppm). Infrared spectra were obtained on a MIDAC Prospect Series spectrometer as a glaze on a Horizontal Attenuated Total Reflectance (HATR) cell from Pike Industries. Electrochemical measurements were taken under a nitrogen atmosphere using a BAS Epsilon EC-2000 potentiostat. Cyclic voltammetry data were obtained in a three-electrode cell from +1.7 to -1.7 V, with a glassy carbon working electrode, a platinum wire auxiliary electrode and a platinum wire reference electrode. All data were obtained using a 100 mV/s scan rate with tetrabutylammonium hexafluorophosphate (TBAH) as the electrolyte in *N,N*-dimethylacetamide (DMA) unless otherwise noted. All potentials were reported versus the Normal Hydrogen Electrode (NHE) using cobaltocinium hexafluorophosphate ($E_{1/2} = -0.78$ V) as an internal standard. For reversible waves the peak-to-peak separation was less than 100 mV. High Resolution Mass Spectrometry data (HRMS) was obtained from the University of Illinois Urbana-Champaign School of Chemical Sciences or the University of Richmond. The difference between calculated and observed peaks is reported in ppm. Thin layer chromatography was performed on a Uniplat silica gel GF from Analtech Inc. Methylene chloride and benzene were run down a column packed with activated alumina and purged with nitrogen prior to use. All other solvents and chemicals were used as received from Sigma-Aldrich, Acros Chemicals or Fischer Scientific. Compounds **5** and **5•HOTf** have been previously reported as diastereomeric mixtures.¹¹ 3-chloroperbenzoic acid (*m*CPBA) was recrystallized (CAUTION) by using a procedure from Bortolini *et al* (Bortolini, O.; Campestrini, S.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1987**, 52, 5093-5095).



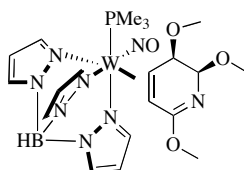
TpW(NO)(PMe₃)(3,4- η^2 -2-methoxypyridine) (5B)

A solution containing 0.469 g (7.776×10^{-4} mole) of **5A** and **5B** and 6 mL of MeOH was allowed to stir at ambient temperature for 24 h. After 24 h, the resulting heterogeneous solution was filtered over a 30 mL Fine fritted glass disc. The collected yellow precipitate was stored *in vacuo* as **5B** in an isolated yield of 32% (0.150 g, 2.452×10^{-4} mole). ¹H NMR (CDCl₃, 300 MHz, δ): 8.09 (1H, d, J =1.8 Hz, Tp), 7.95 (1H, d, J =2.3 Hz, Tp), 7.74 (1H, d, J =2.3 Hz, Tp), 7.72 (1H, d, J =1.8 Hz, Tp), 7.60 (1H, d, J =2.3 Hz, Tp), 7.14 (1H, d, J =2.1 Hz, Tp), 6.38 (1H, d, J =6.1 Hz, H6), 6.03 (1H, t, J =2.1, 4.4 Hz, Tp), 6.01 (2H, m, Tp), 5.99 (1H, dd, J =4.8, 6.1 Hz, H5), 3.85 (3H, s, H7), 3.79 (1H, m, H4) 3.44 (3H, s, MeOH), 2.25 (1H, d, J =1.7, 9.6 Hz, H3), 1.23 (9H, d, J =8.7 Hz, PMe₃). ¹³C NMR (CDCl₃, 75.4 MHz, δ): 173.4 (C2), 144.6 (Tp), 144.1 (Tp), 139.8 (Tp), 136.5 (Tp), 135.9 (Tp), 135.4 (Tp), 127.9 (C6), 115.8 (C5), 106.3 (Tp), 106.0 (Tp), 104.9 (Tp), 62.9 (d, J =9.2 Hz, C4), 55.9 (C9), 52.4 (C7), 51.6 (MeOH) 50.7 (C3), 13.2 (d, J =29.8 Hz, PMe₃). ³¹P NMR: -12.80 ppm, (satellite d (J = 298 Hz), PMe₃) IR: ν (NO) = 1571 cm⁻¹ (vs). CV: E_{p,a} = + 0.06 V.



TpW(NO)(PMe₃)(3,4- η^2 -2-methoxypyridinium triflate) (5•HOTf)

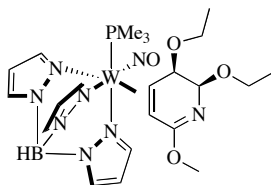
In a vial, 0.124 g (3.876×10^{-4} mole, 1.1 equiv) of diphenylammonium triflate (DPhAT) was solvated with 0.927 g of DME. The resulting stock solution was added to a vial containing 0.216 g of **5B** (3.524×10^{-4} mole, 1.0 equiv) and allowed to stir. Within 10 minutes, a fine yellow solid began to precipitate from the reaction solution. The precipitate was collected over a 15 mL Fine fritted glass disc and was washed with 10 mL of DME and then stored *in vacuo*, for an isolated yield of 91%. ¹H NMR (*d*₆-acetone, 300 MHz, δ): 10.66 (1H, s, NH) 8.15 (1H, d, J =2.3 Hz, Tp), 8.13 (1H, d, J =2.2 Hz, Tp), 8.11 (1H, d, J =2.3 Hz, Tp), 8.00 (1H, d, J =2.3 Hz, Tp), 7.79 (1H, d, J =2.1 Hz, Tp), 7.75 (1H, d, J =2.1 Hz, Tp), 6.54 (1H, dd, J = 4.8, 12.0 Hz, H5), 6.48 (2H, m, Tp), 6.40 (1H, t, J =2.3, 4.5 Hz, Tp), 5.98 (1H, dd J =4.8, 7.2 Hz, H6), 4.10 (1H, ddd, J = 4.8, 8.8, 13.6 Hz, H4), 3.97 (3H, s, H7), 3.45 (DME), 3.28 (DME) 2.14 (1H, d, J =8.8 Hz, H3), 1.35 (9H, d, J =8.9 Hz, PMe₃). ³¹P NMR: -13.20 ppm, (satellite d (J = 298 Hz), PMe₃). IR: ν (NO) = 1591 cm⁻¹ (vs). CV: E_{p,a} = + 0.74 V.



TpW(NO)(PMe₃)(3,4- η^2 -2,5,6-trimethoxy-5,6-dihydropyridine) (7)

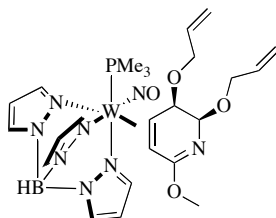
A solution containing 0.086 g of Selectfluor® (2.433×10^{-4} mole, 1.8 equiv) and 1.61 g of CH₃CN was stirred for 10 minutes until the solution was homogeneous. In a separate vial, 0.103 g

(1.351×10^{-4} mole, 1 equiv) of **5•HOTf** and 0.160 g of Na_2CO_3 was solvated with 4.003 g of MeOH and 0.500 mL of CH_2Cl_2 . The Selectfluor[®] solution was added slowly over 15 minutes to a stirring solution of **5•HOTf** and MeOH/ CH_2Cl_2 . The solution was allowed to react at ambient temperature for 1 h. After 1 h, the reaction solution was washed with saturated sodium bicarbonate (aq) and extracted with CH_2Cl_2 . The organic solution was dried over MgSO_4 and then concentrated to a residue. The concentrated solution was redissolved in THF and induced a precipitate by adding to 70 mL of a stirring Et_2O solution. A fine white precipitate **7** was collected over a 15 mL Fine Fritted glass disc and stored *in vacuo* for an isolated yield was 74% (0.065g, 9.997×10^{-5} mole). ^1H NMR (CD_3CN , 300 MHz, δ): 8.08 (1H, d, $J=1.8$ Hz, Tp), 7.91 (1H, d, $J=2.3$ Hz, Tp), 7.89 (1H, d, $J=2.3$ Hz, Tp), 7.81 (1H, d, $J=1.8$ Hz, Tp), 7.74 (1H, d, $J=2.3$ Hz, Tp), 7.59 (1H, d, $J=2.1$ Hz, Tp), 6.41 (1H, t, $J=2.1$, 4.4 Hz, Tp), 6.32 (1H, t, $J=2.3$, 4.4 Hz, Tp), 6.24 (1H, t, $J=2.3$, 4.1 Hz, Tp), 4.89 (1H, d, $J=3.4$ Hz, H6), 4.12 (1H, m, H5), 3.71 (3H, s, H7), 3.56 (3H, s, H8), 3.51 (3H, s, H9), 3.51 (1H, ddd, $J=1.7$, 9.7, 11.2 Hz, H4), 1.52 (1H, dd, $J=1.7$, 9.6 Hz, H3), 1.22 (9H, d, $J=8.7$ Hz, PMe_3). ^{13}C NMR (CD_3CN , 75.4 MHz, δ): 172.0 (C2), 145.7 (Tp), 144.5 (Tp), 141.9 (Tp), 138.5 (Tp), 137.9 (Tp), 136.9 (Tp), 107.8 (Tp), 107.3 (Tp), 106.7 (Tp), 89.7 (C6), 80.6 (C5), 57.4 (C8), 57.3 (d, $J=13.3$ Hz, C4), 55.9 (C9), 52.8 (C7), 43.8 (C3), 13.7 (d, $J=29.8$ Hz, PMe_3). ^{31}P NMR: -10.80 ppm (satellite d ($J=266$ Hz), PMe_3). IR: ν (NO) = 1570 cm^{-1} (vs), ν (imide) = 1641 cm^{-1} (s). CV: $E_{p,a} = +0.84$ V. HRMS (m/z , obs(I); calc(I); error (ppm)): 675.1965, 675.1965, 0.00 ppm.



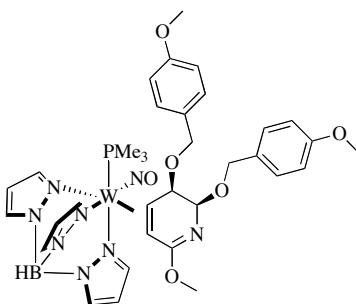
TpW(NO)(PMe₃)(3,4- η^2 -5,6-diethoxy-2-methoxy-5,6-dihydropyridine) (8**)**

A solution containing 0.060 g of Selectfluor[®] (1.694×10^{-4} mole, 1.8 equiv) and 1.78 g of CH_3CN was stirred for 10 minutes until the solution was homogeneous. In a separate vial, 0.072 g (1.351×10^{-4} mole, 1 equiv) of **5•HOTf** and 0.128 g of Na_2CO_3 was solvated with 4.003 g of ethanol and 0.500 mL of CH_2Cl_2 . The Selectfluor[®] solution was added slowly over 15 minutes to a stirring solution of **5•HOTf** and ethanol/ CH_2Cl_2 . The solution was allowed to react at ambient temperature for 1 h. After 1 h, the reaction solution was washed with a saturated sodium bicarbonate (aq) solution and extracted with CH_2Cl_2 . The organic solution was dried over MgSO_4 and then concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH_2Cl_2 and purified with silica chromatography (R_f : 0.22 in 30% CH_3CN : Et_2O) yielding a light-yellow oil with an isolated yield of 68% (0.045g, 9.186×10^{-4} mole). ^1H NMR (d_6 -acetone, 300 MHz, δ): 8.19 (1H, d, $J=2.0$ Hz, Tp), 8.09 (1H, d, $J=2.3$ Hz, Tp), 8.06 (1H, d, $J=2.4$ Hz, Tp), 7.92 (1H, d, $J=2.6$ Hz, Tp), 7.90 (1H, d, $J=2.6$ Hz, Tp), 7.78 (1H, d, $J=2.0$ Hz, Tp), 6.49 (1H, t, $J=2.3$, 4.4 Hz, Tp), 6.45 (1H, t, $J=2.1$, 4.4 Hz, Tp), 6.33 (1H, t, $J=2.3$, 4.6 Hz, Tp), 5.26 (1H, d, $J=3.1$ Hz, H6), 4.50 (1H, m, H5), 3.97 (2H, m, H10), 3.88 (3H, s, H7), 3.84 (2H, m, H8), 3.21 (1H, ddd, $J=2.1$, 9.5, 11.1 Hz, H4), 1.86 (1H, d, $J=9.5$ Hz, H3), 1.35 (9H, d, $J=9.0$ Hz, PMe_3), 1.23 (3H, t, $J=6.9$, 14.0 Hz, H9), 1.22 (3H, t, $J=7.0$, 13.9 Hz, H11). ^{13}C NMR (d_6 -acetone, 300 MHz, δ): 179.4 (C2), 144.7 (Tp), 144.4 (Tp), 141.7 (Tp), 138.6 (Tp), 137.9 (Tp), 137.2 (Tp), 107.7 (Tp), 107.3 (Tp), 106.7 (Tp), 86.1 (C6), 78.2 (C5), 66.4 (C10), 65.7 (C8), 60.8 (d, $J=14.7$ Hz, C4), 56.5 (C7), 40.2 (C3), 15.9 (C11), 15.1 (C9), 12.6 (d, $J=30.7$ Hz, PMe_3). ^{31}P NMR: -10.30 ppm (satellite d ($J=266$ Hz), PMe_3). IR: ν (NO) = 1571 cm^{-1} (vs), ν (imide) = 1644 cm^{-1} (s). CV: $E_{p,a} = +0.82$ V. HRMS (m/z , obs(I); calc(I); error (ppm)): 703.2256 (100%), 703.2278 (100%), 3.12 ppm.



TpW(NO)(PMe₃)(3,4- η^2 -5,6-bis(allyloxy)-2-methoxy-5,6-dihydropyridine) (9)

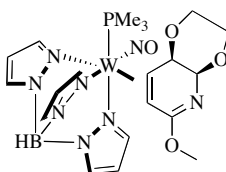
A solution containing 0.094 g of Selectfluor[®] (2.650×10^{-4} mole, 1.8 equiv) and 2.430 g of CH₃CN was stirred for 10 minutes until the solution was homogeneous. In a separate vial, 0.101 g (1.325×10^{-4} mole, 1 equiv) of **5•HOTf** and 0.190 g of Na₂CO₃ was solvated with 1.20 mL of allyl alcohol and 0.500 mL of CH₂Cl₂. The Selectfluor[®] solution was added slowly over 15 minutes to a stirring solution of **5•HOTf**. The solution was allowed to react at ambient temperature for 1 h. After 1 h, the reaction solution was washed with a saturated sodium bicarbonate (aq) solution and extracted with CH₂Cl₂. The organic solution was dried over MgSO₄ and then concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH₂Cl₂ and purified with silica chromatography, (R_f: 0.27 in 30% CH₃CN: Et₂O) yielding a light orange solution for an isolated yield of 52% (0.050 g, 6.890×10^{-5} mole) in a ratio of 3:1. ¹H NMR (*d*₆-acetone, 300 MHz, δ): 8.16 (1H, d, *J*=2.0 Hz, Tp), 8.02 (1H, d, *J*=2.1 Hz, Tp), 8.00 (1H, d, *J*=2.3 Hz, Tp), 7.95 (1H, d, *J*=2.0 Hz, Tp), 7.80 (2H, m, Tp major and minor), 7.71 (1H, d, *J*=2.1 Hz, Tp), 6.46 (1H, t, *J*=2.1, 4.3 Hz, Tp), 6.35 (1H, t, *J*=2.3, 4.5 Hz, Tp), 6.26 (1H, t, *J*=2.2, 4.2 Hz, Tp), 6.06 (4H, m, allyl), 5.37 (2H, ddd, *J*=2.1, 4.0, 6.1 Hz, allyl), 5.31 (2H, ddd, *J*=2.1, 4.0, 6.1 Hz, allyl), 5.17 (1H, d, *J*=3.3 Hz, H6), 4.63 (4H, m, allyl), 4.32 (1H, m, H5), 3.79 (3H, s, H7), 2.67 (1H, ddd, *J*=1.7, 9.9, 11.4 Hz, H4), 1.64 (1H, dd, *J*=1.7, 9.9 Hz, H3), 1.35 (9H, d, *J*=8.7 Hz, PMe₃). ¹³C NMR (*d*₆-acetone, 75.4 MHz, δ): 173.1 (C2), 146.9 (Tp), 145.4 (Tp), 142.8 (Tp), 139.6 (C9-allyl), 139.2 (Tp), 138.8 (C12-allyl), 138.5 (Tp), 137.5 (Tp), 116.4 (C10-allyl), 115.7 (C13-allyl), 108.6 (Tp), 108.1 (Tp), 107.2 (Tp), 89.6 (C6), 80.9 (C5), 73.2 (C8-allyl), 69.9 (C11-allyl), 59.9 (d, *J*=12.4 Hz, C4), 53.2 (C7), 45.4 (C3), 12.6 (d, *J*=29.2 Hz, PMe₃). ³¹P NMR: -10.20 ppm, (satellite d (*J*=266 Hz), PMe₃). IR: ν (NO) = 1573 cm⁻¹ (vs), ν (imide) = 1642 cm⁻¹ (s). CV: E_{p,a} = +0.94 V. HRMS (*m/z*, obs(I); calc(I); error (ppm)): 727.2286 (100%), 727.2278 (100%), 1.10 ppm.



TpW(NO)(PMe₃)(3,4- η^2 -2-methoxy-5,6-bis(4-methoxybenzyloxy)-5,6-dihydropyridine) (10)

A solution containing 0.071 g of Selectfluor[®] (2.007×10^{-4} mole, 1.8 equiv) and 1.960 g of CH₃CN was stirred for 10 minutes until homogeneous. In a separate vial, 0.085 g (1.115×10^{-4} mole, 1 equiv) of **5•HOTf** and 0.118 g of Na₂CO₃ was solvated with 1.20 mL of 4-methoxybenzyl alcohol and 0.500 mL of CH₂Cl₂. The Selectfluor[®] solution was added slowly over 15 minutes to a stirring

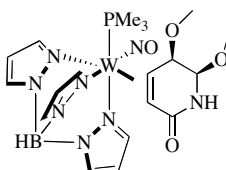
solution of **5•HOTf** and 4-methoxybenzyl alcohol/ CH_2Cl_2 . The solution was allowed to react at ambient temperature for 1 h. After 1 h, the reaction solution was washed with a saturated sodium bicarbonate (aq) solution and extracted with CH_2Cl_2 . The organic solution was dried over MgSO_4 and then concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH_2Cl_2 and purified with silica chromatography. (R_f : 0.32 in 30% CH_3CN : Et_2O). The resulting solution was concentrated to a residue and re-solvated in 0.500 mL of THF and added to 75 mL of a stirring hexanes solution. An off-white precipitate was generated and collected over a 15 mL Fine fritted glass disc and stored *in vacuo* for an isolated yield of 59% (0.058g, 6.578×10^{-5} mole). ^1H NMR (d_6 -acetone, 300 MHz, δ): 8.14 (1H, d, $J=2.0$ Hz, Tp), 8.00 (1H, d, $J=2.3$ Hz, Tp), 7.99 (2H, d, $J=2.1$ Hz, Tp), 7.79 (1H, d, $J=2.3$ Hz, Tp), 7.60 (1H, d, $J=2.0$ Hz, Tp), 7.43 (4H, dd, $J=8.5$, 17.0 Hz, Ar), 6.93 (4H, dd, $J=4.2$, 8.6 Hz, Ar), 6.44 (1H, t, $J=2.3$, 4.4 Hz, Tp), 6.34 (1H, t, $J=2.4$, 4.5 Hz, Tp), 6.26 (1H, t, $J=2.1$, 4.4 Hz, Tp), 5.27 (1H, d, $J=3.4$ Hz, H6), 5.18 (1H, d, $J=11.9$ Hz, benzylic), 4.94 (2H, q, $J=11.9$, 20.2 Hz, benzylic), 4.64 (1H, d, $J=11.9$ Hz, benzylic), 4.37 (1H, m, H5), 3.81 (3H, s, H7), 3.80 (3H, s, Ar-OMe), 3.79 (3H, s, Ar-OMe), 2.72 (1H, ddd, $J=1.8$, 9.9, 11.1 Hz, H4), 1.62 (1H, dd, $J=1.8$, 9.9 Hz, H3), 1.13 (9H, d, $J=8.4$ Hz, PMe_3). ^{13}C NMR (d_6 -acetone, 75.4 MHz, δ): 172.7 (C2), 159.9 (q-Ar), 159.7 (q-Ar), 146.0 (Tp), 144.6 (Tp), 141.8 (Tp), 138.2 (Tp), 137.5 (Tp), 136.5 (Tp), 133.7 (q-Ar), 130.5 (q-Ar and 2-Ar), 129.7 (2 Ar), 114.4 (4 Ar), 114.3 (2 Ar), 107.7 (Tp), 107.1 (Tp), 106.3 (Tp), 89.1 (C6), 79.2 (C5), 72.5 (benzylic), 71.1 (benzylic), 59.2 (d, $J=12.9$ Hz, C4), 55.6 (Ar-OMe), 55.2 (Ar-OMe), 52.3 (C7), 44.5 (C3), 13.2 (d, $J=29.3$ Hz, PMe_3). ^{31}P NMR: -11.60 ppm, (satellite d ($J=268$ Hz), PMe_3). IR: ν (NO) = 1569 cm^{-1} (vs), ν (imide) = 1644 cm^{-1} (s). CV: $E_{p,a} = +0.97\text{ V}$. HRMS (m/z , obs(I); calc(I); error (ppm)): 887.2791 (100%), 887.2813 (100%), 2.47 ppm.



TpW(NO)(PMe₃)(7,8- η^2 -6-methoxy-2,3,4a,8a-tetrahydro-[1,4]dioxino[5,6-*b*]pyridine) (11)

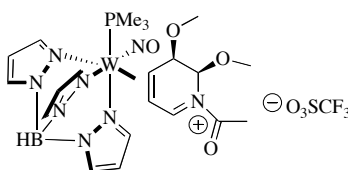
A solution of 0.060 g of Selectfluor® (1.694×10^{-4} mole, 1.8 equiv) and 1.842 g of CH_3CN was stirred for 10 min until the solution was homogeneous. In a separate vial, 0.071 g (9.317×10^{-5} mole, 1 equiv) of **5•HOTf** and 0.116 g of Na_2CO_3 was solvated with 2.213 g of ethylene glycol and 0.500 mL of CH_2Cl_2 . The Selectfluor® solution was added slowly over 15 minutes to a stirring solution of **5•HOTf** and ethylene glycol/ CH_2Cl_2 . The solution was allowed to react at ambient temperature for 1 h. After 1 h, the reaction solution was washed with a saturated sodium bicarbonate (aq) solution and extracted with CH_2Cl_2 . The organic solution was dried over MgSO_4 and then concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH_2Cl_2 and purified with silica chromatography. (R_f : 0.27 in 30% CH_3CN : Et_2O) with isolation of a light-yellow oil for an isolated yield of 66% (0.041g, 6.149×10^{-5} mole). ^1H NMR (d_6 -acetone, 300 MHz, δ): 8.16 (1H, d, $J=2.0$ Hz, Tp), 8.03 (1H, d, $J=2.3$ Hz, Tp), 8.02 (1H, d, $J=2.3$ Hz, Tp), 7.91 (1H, d, $J=2.1$ Hz, Tp), 7.83 (1H, d, $J=2.3$ Hz, Tp), 7.72 (1H, d, $J=2.1$ Hz, Tp), 6.46 (1H, t, $J=2.1$, 4.4 Hz, Tp), 6.38 (1H, t, $J=2.3$, 4.6 Hz, Tp), 6.27 (1H, t, $J=2.1$, 4.4 Hz, Tp), 5.25 (1H, d, $J=3.1$ Hz, H4a), 4.32 (1H, m, H8a), 4.07 (1H, ddd, $J=2.6$, 11.1, 11.3 Hz), 3.81 (1H, m), 3.80 (3H, s), 3.72 (1H, dd, $J=2.6$, 11.2 Hz), 3.39 (1H, dd, $J=1.8$, 11.3 Hz), 2.67 (1H, ddd, $J=1.6$, 9.7, 11.3 Hz, H8), 1.59 (1H, dd, $J=1.6$, 9.7 Hz, H7), 1.35 (9H, d, $J=8.7$ Hz, PMe_3). ^{13}C NMR (d_6 -acetone, 75.4 MHz, δ): 173.1 (C6), 145.1 (Tp), 143.8 (Tp), 141.1 (Tp), 137.7 (Tp), 137.1 (Tp), 136.1 (Tp), 107.1 (Tp), 106.7 (Tp), 105.8 (Tp), 80.9 (C4a), 76.3

(C8a), 66.7, 59.1, 58.7 (d, $J=13.7$ Hz, C8), 52.4, 42.9 (C7), 12.3 (d, $J=29.2$ Hz, PMe_3). ^{31}P NMR: -10.20 ppm, (satellite d ($J=266$ Hz), PMe_3). IR: $\nu(\text{NO}) = 1565\text{ cm}^{-1}$ (vs), $\nu(\text{imide}) = 1641\text{ cm}^{-1}$ (s). CV: $E_{\text{p,a}} = +0.97$ V. HRMS (m/z , obs(I); calc(I); error (ppm)): 673.1815 (100%), 673.1809 (100%), 0.89 ppm.



$\text{TpW}(\text{NO})(\text{PMe}_3)(3,4\text{-}\eta^2\text{-5,6-dimethoxy-5,6-dihydropyridin-2(1H)-one)$ (12)

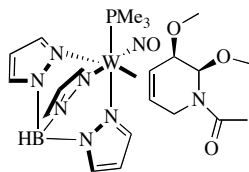
A solution was prepared containing 0.065 g (9.674×10^{-5} mole, 1.0 equiv) of **7** and 5 mL of CH_3CN . 1 mL of 1M HCl was added to the CH_3CN solution and allowed to react at ambient temperature for 16 h. The resulting reaction was quenched with 10 mL of a saturated sodium bicarbonate (aq) solution and extracted with CH_2Cl_2 . The organic solution was dried with MgSO_4 and filtered over a 15 mL M fritted glass disc and concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH_2Cl_2 and purified with silica chromatography, (R_f : 0.22 in 30% CH_3CN : Et_2O) with an isolation of a red-brown oil in 67% yield (0.042g, 6.481×10^{-5} mole). ^1H NMR (CD_3CN , 300 MHz, δ): 8.06 (1H, d, $J=1.8$ Hz, Tp), 7.91 (1H, d, $J=2.3$ Hz, Tp), 7.88 (1H, d, $J=2.3$ Hz, Tp), 7.83 (1H, d, $J=1.8$ Hz, Tp), 7.72 (1H, d, $J=2.4$ Hz, Tp), 7.55 (1H, d, $J=2.1$ Hz, Tp), 6.40 (1H, t, $J=2.1$, 4.4 Hz, Tp), 6.28 (1H, t, $J=2.3$, 4.6 Hz, Tp), 6.23 (1H, t, $J=2.3$, 4.6 Hz, Tp), 4.81 (1H, d, $J=3.4$ Hz, H6), 4.45 (1H, m, H5), 3.72 (3H, s, H7), 3.54 (3H, s, H8), 2.70 (1H, ddd, $J=1.7$, 9.8, 11.4 Hz, H4), 1.44 (1H, dd, $J=1.7$, 9.8 Hz, H3), 1.18 (9H, d, $J=8.9$ Hz, PMe_3). ^{13}C NMR (CD_3CN , 75.4 MHz, δ): 171.2 (C2), 145.8 (Tp), 144.3 (Tp), 141.8 (Tp), 138.3 (Tp), 137.7 (Tp), 136.8 (Tp), 107.8 (Tp), 107.2 (Tp), 106.5 (Tp), 89.1 (C6), 71.2 (C5), 60.1 (d, $J=13.7$ Hz, C4), 55.3 (C8), 52.8 (C7), 43.5 (C3), 12.9 (d, $J=29.8$ Hz, PMe_3). IR: $\nu(\text{NO}) = 1556\text{ cm}^{-1}$ (vs), $\nu(\text{amide}) = 1631\text{ cm}^{-1}$ (s). CV: $E_{\text{p,a}} = +0.97$ V. HRMS (m/z , obs(I); calc(I); error (ppm)): 661.1805 (100%), 661.1808 (100%), 0.45 ppm.



$\text{TpW}(\text{NO})(\text{PMe}_3)(3,4\text{-}\eta^2\text{-1-acetyl-5,6-dimethoxy-5,6-dihydropyridinium triflate})$ (14)

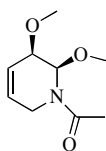
A solution containing 0.192 g (5.684×10^{-4} mole, 1.05 equiv) of Selectfluor[®] and 1.420 g of CH_3CN and 1.242 g of MeOH was allowed to stir at ambient temperature for 1 h. After 1h, the solution was added to a vial containing 0.400 g (5.167×10^{-4} mole, 1.00 equiv) of **13** and allowed to react for 2 h. After 2 h, the reaction solution was concentrated to a brown residue. The residue was re-dissolved with 20 mL of CH_2Cl_2 and filtered through a celite plug. The resulting filtrate was concentrated to a residue and then re-dissolved in 1 mL of CH_2Cl_2 and added to a 75 mL solution of Et_2O . The resulting light tan precipitate was isolated over a 30 mL Fine fritted glass disc. The precipitate was then dissolved in 2.28 g of THF and allowed to stir at ambient temperature for 16 h. After 16 h, the THF was filtered over a 15 mL fritted glass disc and washed with 5 mL of THF and then washed with 50 mL of hexanes. The light-yellow precipitate (**14**) was stored *in vacuo* overnight with an

isolated yield of 55% (0.235 g 2.811×10^{-4} mole). ^1H NMR (d_6 -acetone, 300 MHz, δ): 8.88 (1H, d, $J=2.2$ Hz, Tp), 8.39 (1H, d, $J=2.3$ Hz, Tp), 8.36 (1H, d, $J=3.6$ Hz, H2), 8.23 (1H, d, $J=2.3$ Hz, Tp), 8.17 (1H, d, $J=2.4$ Hz, Tp), 7.99 (1H, d, $J=2.3$ Hz, Tp), 7.59 (1H, d, $J=2.1$ Hz, Tp), 6.67 (1H, t, $J=2.3$, 4.7 Hz, Tp), 6.61 (1H, t, $J=2.3$, 4.7 Hz, Tp), 6.47 (1H, t, $J=2.3$, 4.7 Hz, Tp), 5.70 (1H, d, $J=4.3$ Hz, H6), 4.75 (1H, dd, $J=5.0$, 7.0 Hz, H4), 4.59 (1H, dd, $J=1.0$, 4.3 Hz, H5), 3.79 (1H, dd, $J=7.6$, 14.5 Hz, H3), 3.56 (3H, s, H9), 3.54 (3H, s, H10), 2.68 (3H, s, H8), 1.33 (9H, d, $J=9.9$ Hz, PMe_3). ^{13}C NMR (75.4 MHz, CD_3CN , δ): 171.8 (C7), 150.0 (Tp), 146.9 (Tp), 145.2 (C2), 143.0 (Tp), 139.6 (Tp), 139.4 (Tp), 109.5 (Tp), 108.8 (Tp), 108.4 (Tp), 82.4 (C3), 82.0 (C6), 80.1 (C5), 62.2 (d, $J=13.8$, C4), 56.9 (C9), 56.1 (C10), 22.5 (C8), 13.0 (d, $J=32.7$, PMe_3). ^{31}P NMR: -6.10 ppm, (satellite d ($J=266$ Hz), PMe_3). IR: ν (NO) = 1629 cm^{-1} (s) ν (amide) = 1697 cm^{-1} (m). HRMS(obs'd (%), calc'd (%), ppm): 687.1965 (100), 687.1978 (100), 1.9 ppm.



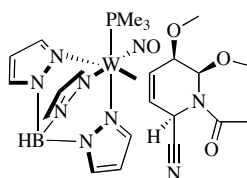
TpW(NO)(PMe₃)(3,4- η^2 -5,6-dimethoxy-5,6-dihydropyridin-1(2H)-yl)ethanone) (15)

In a test tube, 0.004 g of sodium borohydride (7.894×10^{-5} mole, 0.5 equiv) was solvated with 0.500 mL of THF and added to a cold bath at -20°C . In a separate test tube, 0.132 g (1.588×10^{-4} mole, 1.0 equiv) of **14** was solvated with 1 mL of MeOH and added to the cold bath at -20°C . After both test tubes were allowed to cool for 10 minutes, **14** was added to the NaBH_4 test tube and allowed to react at -20°C for 3 h. The reaction solution was concentrated to a residue and re-solvated in CH_2Cl_2 and filtered through a celite plug. The CH_2Cl_2 solution was concentrated to a residue and re-solvated in 0.5 mL of THF and added to a 75 mL stirring solution of hexanes, yielding a tan-white precipitate. The precipitate (**15**) was isolated over a 15 mL Fine Fritted glass disc and dried *in vacuo* for an isolated yield of 71% (0.077g, 5.605×10^{-5}). ^1H NMR (d_6 -acetone, 300 MHz, δ): (**Major rotational isomer**): 8.36 (1H, d, $J=1.8$ Hz, Tp), 8.07 (1H, d, $J=1.8$ Hz, Tp), 7.95 (1H, d, $J=2.3$ Hz, Tp), 7.91 (1H, d, $J=2.1$ Hz, Tp), 7.79 (1H, d, $J=2.4$ Hz, Tp), 7.41 (1H, d, $J=2.1$ Hz, Tp), 6.40 (1H, t, $J=2.1$, 4.3 Hz, Tp), 6.35 (2H, m, Tp), 5.16 (1H, d, $J=3.2$ Hz, H6), 4.70 (2H, dd, $J=12.5$, 20.0 Hz, H2A and H2B), 4.30 (1H, m, H5), 3.54 (3H, s, H9), 3.50 (3H, s, H10) 2.80 (1H, ddd, $J=5.3$, 11.6, 16.9 Hz, H4), 2.11 (3H, s, H8), 1.30 (9H, d, $J=8.9$ Hz, PMe_3) 1.20 (1H, buried, H3). (**Minor Rotational Isomer**): 8.13 (1H, d, $J=2.0$ Hz, Tp), 8.11 (1H, d, $J=1.8$ Hz, Tp), 7.97 (1H, d, $J=2.3$ Hz, Tp), 7.92 (1H, d, $J=2.3$ Hz, Tp), 7.81 (1H, d, $J=2.4$ Hz, Tp), 7.39 (1H, d, $J=1.8$ Hz, Tp), 6.43 (1H, t, $J=2.3$, 4.4 Hz, Tp), 6.35 (2H, m, Tp), 5.79 (1H, d, $J=2.4$ Hz, H6), 4.50 (2H, dd, $J=13.9$, 24.9 Hz, H2A and H2B), 4.00 (1H, m, H5), 3.48 (3H, s, H9), 3.46 (3H, s, H10) 2.80 (1H, ddd, $J=5.3$, 11.6, 16.9 Hz, H4), 2.14 (3H, s, H8), 1.50 (1H, buried, H3), 1.29 (9H, d, $J=9.0$ Hz, PMe_3). ^{13}C NMR (d_6 -acetone, 75.4 MHz, δ): 173.1 (C7), 145.6 (Tp), 143.9 (Tp), 142.7 (Tp), 138.8 (Tp), 138.6 (Tp), 138.5 (Tp), 125.3 (C7), 108.3 (Tp), 108.2 (Tp), 108.1 (Tp), 85.4 (C6), 81.3 (C5), 56.8 (C9), 56.3 (C10), 50.2 (C3), 48.7 (d, $J=11.9$ Hz, C4), 41.3 (C2), 24.1 (C8) 14.90 (d, $J=28.9$ Hz, PMe_3). ^{31}P NMR: -11.60 ppm, (satellite d ($J=268$ Hz), PMe_3). IR: ν (NO) = 1565 cm^{-1} (vs). CV: $E_{p,a} = +0.90$ V.



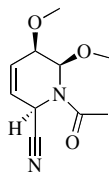
1-(5,6-dimethoxy-5,6-dihydropyridin-1(2H)-yl)ethanone (16)

In a vial, 0.087 g (2.653×10^{-4} mole, 2.0 equiv) of ceric ammonium nitrate was added to a vial containing 0.091 g (1.339×10^{-4} mole, 1.0 equiv) of **15**. The two reagents were solvated with 0.840 g of CDCl_3 . The resulting orange-brown heterogeneous mixture was allowed to stir at ambient temperature for 3 h. After 3h, the reaction solution was washed with a saturated sodium bicarbonate (aq) solution and extracted with CH_2Cl_2 . The organic solution was dried over MgSO_4 and then concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH_2Cl_2 and purified with silica chromatography. (R_f : 0.40 in 30% EtOAc: Et₂O). Compound **16** was isolated as a light yellow oil in a 40% yield (0.010g, 5.356×10^{-5} mole). ^1H NMR (d_6 -acetone, 500 MHz, δ): 6.03 (1H, dd, $J=1.4, 4.0$ Hz, H6) 5.70 (2H, m, H4 and H3), 4.45 (1H, $J=2.6, 3.8, 5.4, 6.2, 8.9$ Hz, H2A), 3.70 (1H, $J=2.4, 2.8, 4.0, 6.2$ Hz, H5), 3.42 (3H, s, H9), 3.40 (3H, s, H10) 3.21 (1H, buried, H2B) 2.10 (3H, s, H8). ^{13}C NMR (d_6 -acetone, 125 MHz, δ): 170.3 (C7), 125.1 (C4), 123.8 (C3), 82.2 (C6), 75.0 (C5), 55.5 (C9), 54.9 (C10), 38.1 (C2), 20.9 (C8). HRMS ($\text{C}_9\text{H}_{15}\text{N}_1\text{O}_3+\text{Na}$) (m/z , obs(I); calc(I); error (ppm)) 208.0950 (100%); 208.0958 (100%), 3.84 ppm.



TpW(NO)(PMe₃)(3,4- η^2 -1-acetyl-5,6-dimethoxy-1,2,5,6-tetrahydropyridine-2-carbonitrile) (17)

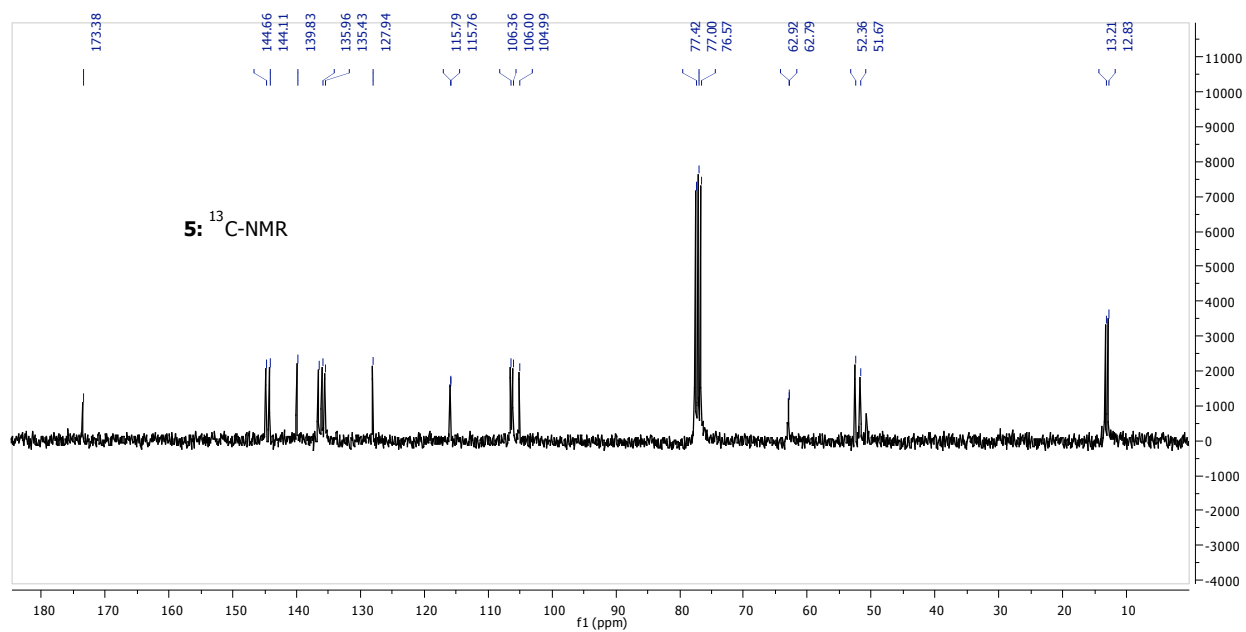
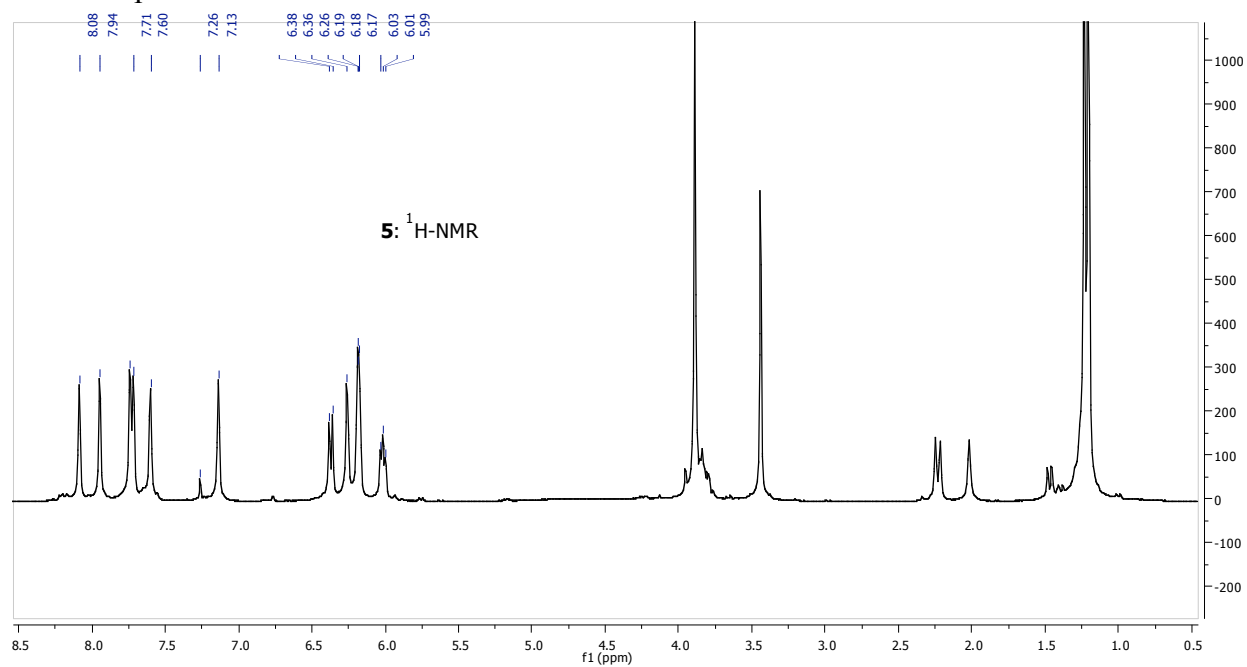
In a vial, 0.061 g of **14** (7.535×10^{-5} mole, 1 equiv) and 0.009 g sodium cyanide (1.507×10^{-4} mole, 2 equiv) was combined with 0.780 g of CH_3CN . The reaction was allowed to stir at ambient temperature for 1.5 h. The reaction solution was then concentrated to a residue. The residue was re-dissolved in 10 mL of CH_2Cl_2 and filtered through a celite plug. The resulting CH_2Cl_2 solution was concentrated to a residue and then re-dissolved in 0.284 g of THF and added to a 70 mL of a stirring hexanes solution, yielding a fine off-white precipitate. The precipitate (**17**) was isolated by filtering the hexanes solution over a 15 mL Fine fritted glass disc and stored *in vacuo* with an isolated yield of 72% (0.041g, 5.369×10^{-5} mole). ^1H NMR (d_6 -acetone, 300 MHz, δ): 8.20 (1H, d, $J=2.0$ Hz, Tp), 8.04 (1H, d, $J=1.8$ Hz, Tp), 7.96 (2H, m Tp), 7.88 (1H, d, $J=2.4$ Hz, Tp), 7.52 (1H, d, $J=2.0$ Hz, Tp), 6.57 (1H, s, H2), 6.38 (1H, t, $J=2.3, 4.4$ Hz, Tp), 6.35 (2H, m, Tp), 5.23 (1H, d, $J=4.1$ Hz, H6), 4.52 (1H, t, $J=3.0, 5.9$ Hz, H5), 3.54 (3H, s, H9), 3.52 (3H, s, H10) 2.75 (1H, ddd, $J=3.1, 12.8, 15.1$ Hz, H4), 2.17 (3H, s, H8), 1.29 (9H, d, $J=8.7$ Hz, PMe_3) 0.98 (1H, d, $J=12.8$ Hz, H3). ^{13}C NMR (d_6 -acetone, 300 MHz, δ): 173.1 (C7), 145.6 (Tp), 143.9 (Tp), 142.7 (Tp), 138.8 (Tp), 138.6 (Tp), 138.5 (Tp), 125.3 (C11-CN), 108.3 (Tp), 108.2 (Tp), 108.1 (Tp), 85.4 (C6), 81.3 (C5), 56.8 (C9), 56.3 (C10), 50.2 (C3), 48.7 (d, $J=11.9$ Hz, C4), 41.3 (C2), 24.1 (C8) 14.90 (d, $J=28.9$ Hz, PMe_3). ^{31}P NMR: -11.60 ppm, (satellite d ($J=268$ Hz), PMe_3). IR: ν (NO) = 1565 cm^{-1} (vs). CV: $E_{p,a} = +1.00$ V. HRMS (m/z , obs(I); calc(I); error (ppm)): 714.2065 (100%), 714.2081 (100%), 2.21 ppm.

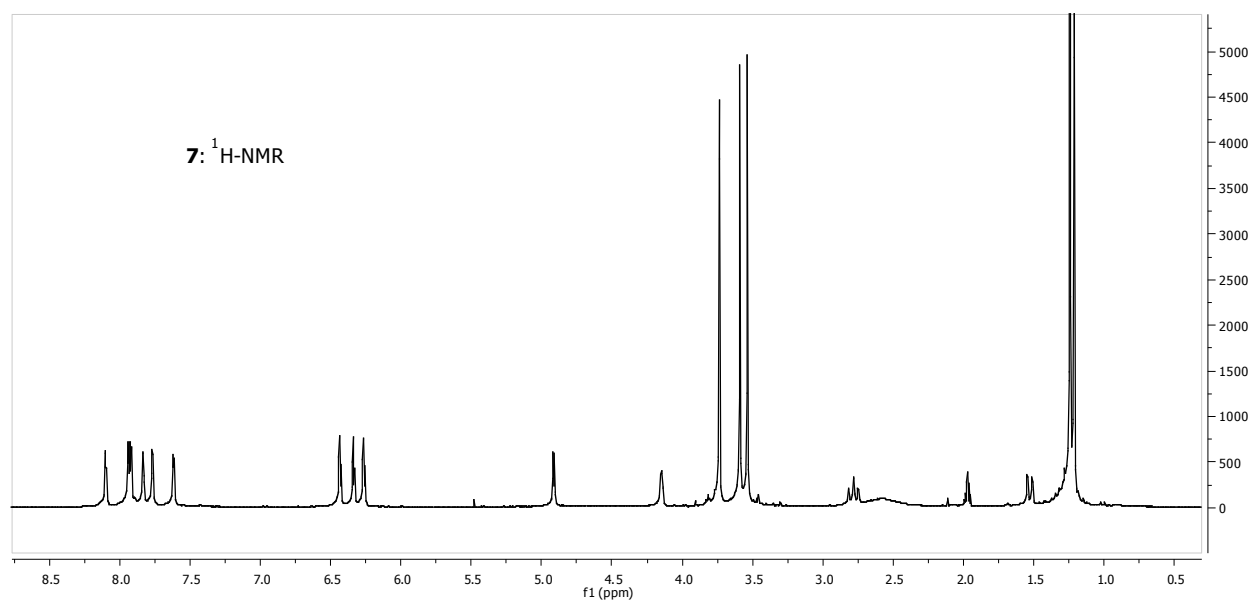
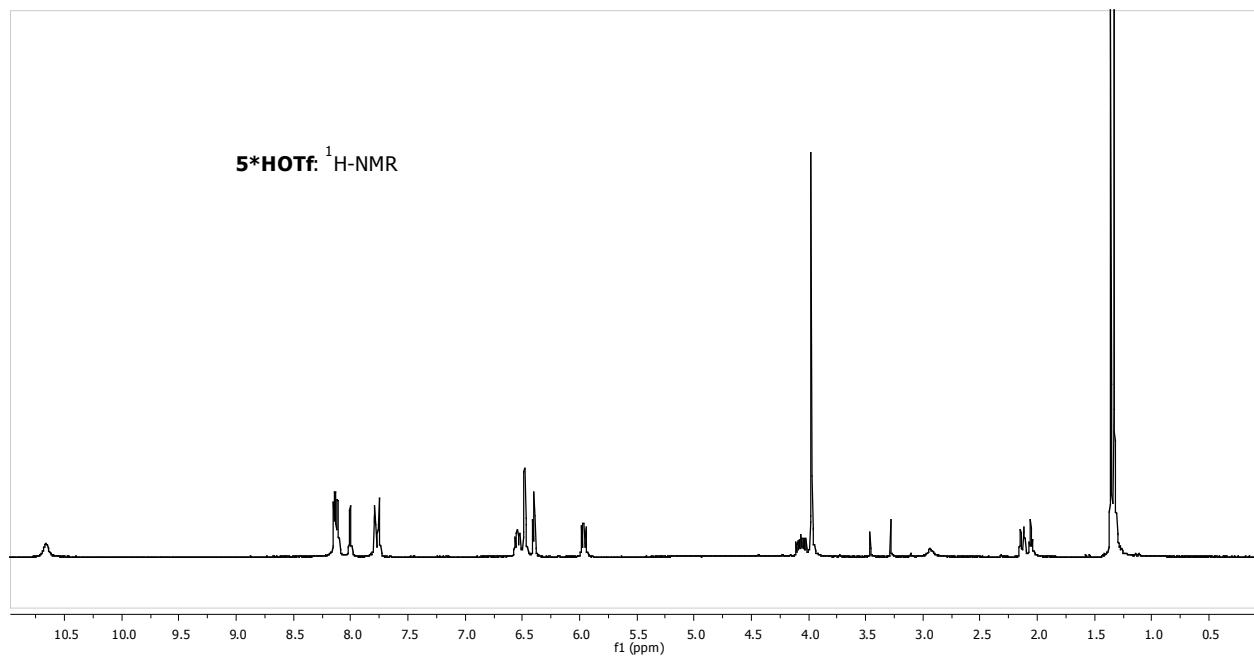


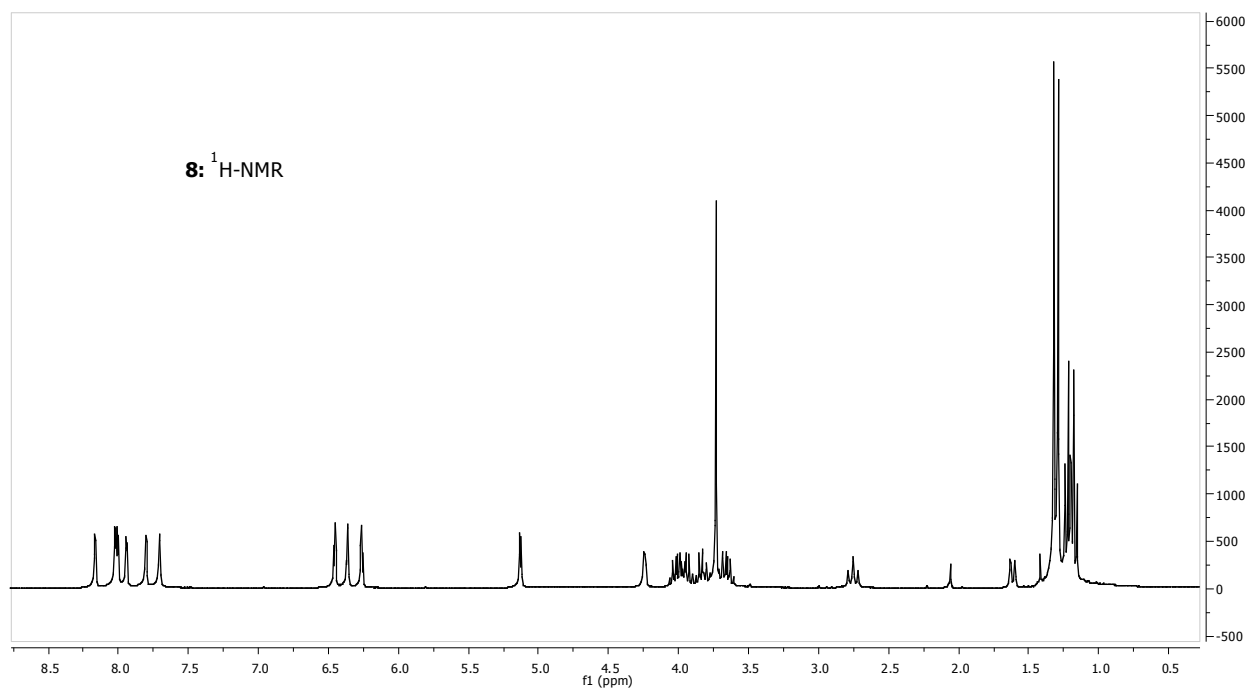
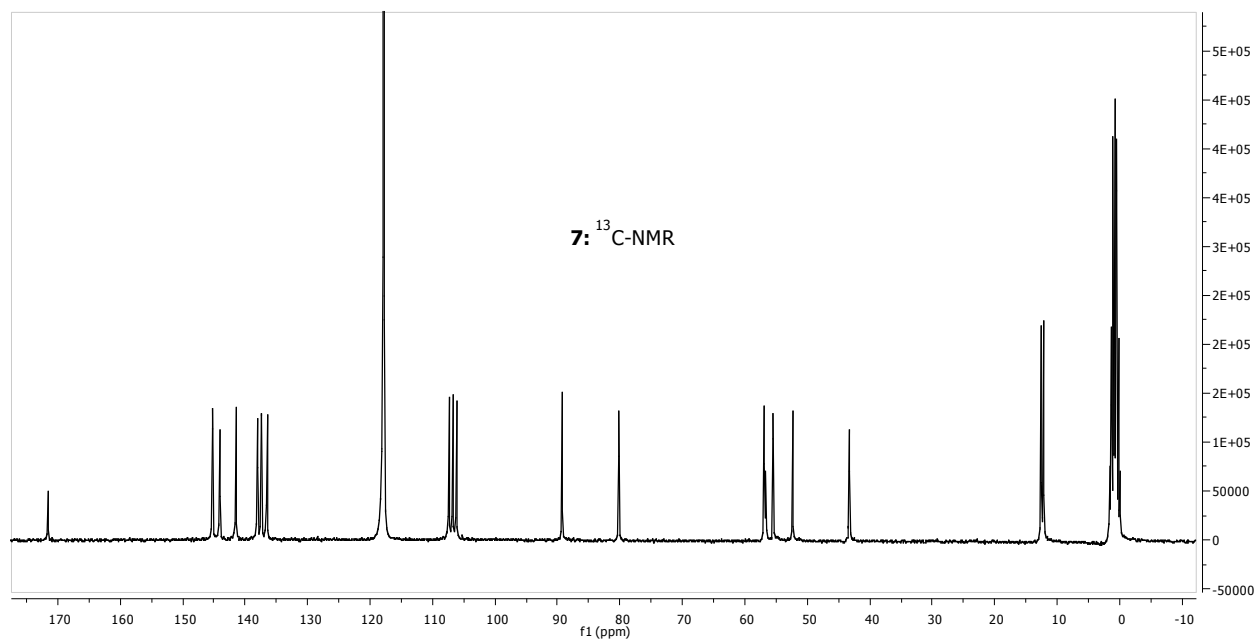
1-acetyl-5,6-dimethoxy-1,2,5,6-tetrahydropyridine-2-carbonitrile) (18)

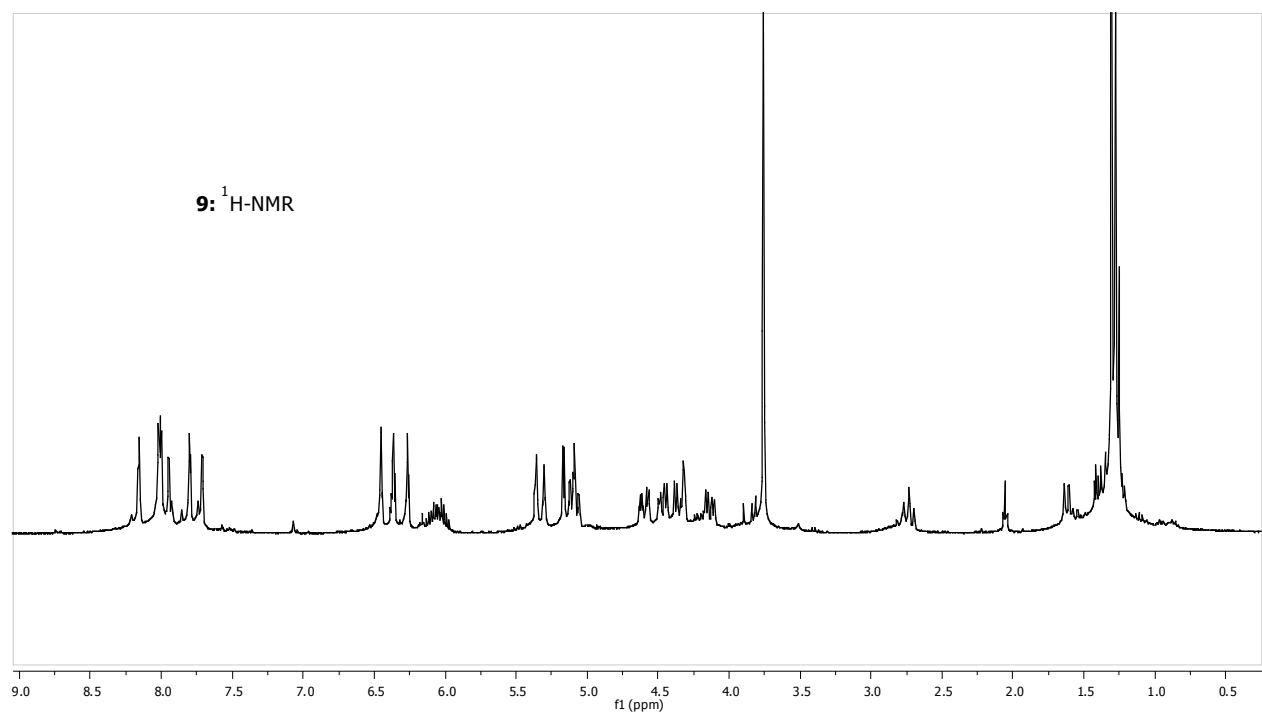
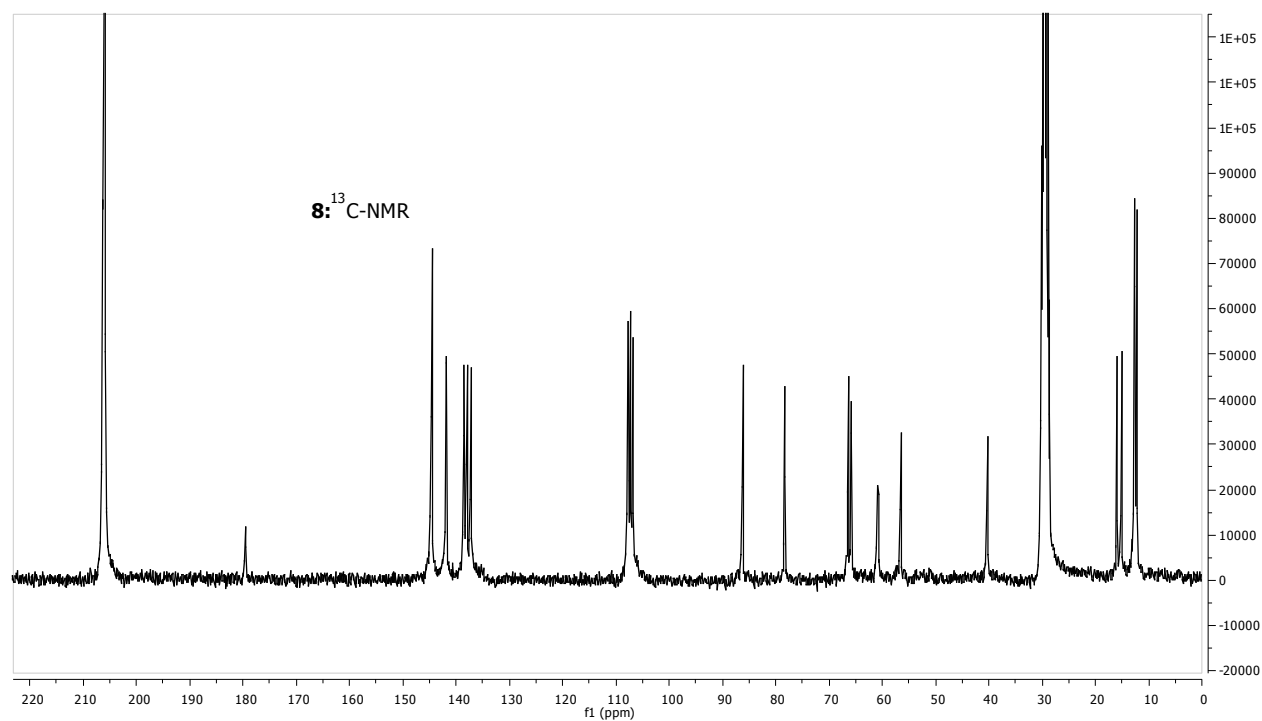
In a vial, 0.069 g (2.105×10^{-4} mole, 2.0 equiv) of ceric ammonium nitrate was added to 0.076 g (1.052×10^{-4} mole, 1 equiv) of **17**. The two reagents were solvated with 0.773 g of CDCl_3 . The resulting orange-brown heterogeneous mixture was allowed to stir at ambient temperature for 3 h. After 3h, the reaction solution was washed with a saturated sodium bicarbonate (aq) solution and extracted with CH_2Cl_2 . The organic solution was dried over MgSO_4 and then concentrated to a residue. The residue was re-dissolved in 0.500 mL of CH_2Cl_2 and purified with silica chromatography. (R_f : 0.35 in 30% EtOAc: Et_2O). Compound **18** was isolated as a light yellow oil in a 62% yield (0.014g, 6.524×10^{-5} mole). ^1H NMR (d_6 -acetone, 500 MHz, δ): **Major Rotational Isomer**: 5.90 (2H (major and minor rotational isomer), dddd, $J = 10.2, 2.4, 1.2, 3.6$ Hz, H3), 5.82 (1H, dddd, $J = 10.2, 3.5, 2.4$ Hz, H4), 5.58 (1H, ddd, $J = 2.4, 2.8, 3.4$ Hz, H2), 5.52 (1H, dd, $J = 1.2, 4.2$ Hz, H6), 4.15 (1H, dddd, $J = 2.4, 2.8, 3.6, 4.2$ Hz, H5), 3.45 (3H, s, H9), 3.42 (3H, s, H10) 2.31 (3H, s, H8). ^{13}C NMR (d_6 -acetone, 500 MHz, δ): **Major rotational isomer**: 171.6 (C7), 129.9 (C3), 120.9 (C4), 118.5 (C11-CN), 84.1 (C6), 76.1 (C5), 57.4 (C9), 56.7 (C10), 40.3 (C2), 22.7 (C8). **Minor rotational isomer**: 172.0 (C7), 130.8 (C3), 120.4 (C4), 118.6 (C11-CN), 78.0 (C6), 75.7 (C5), 57.4 (C9), 57.3 (C10), 44.3 (C2), 22.8 (C8). HRMS ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_3 + \text{Na}$) (m/z , obs(I); calc(I); error (ppm)) 233.0900 (100%); 233.0902 (100%), 0.85 ppm.

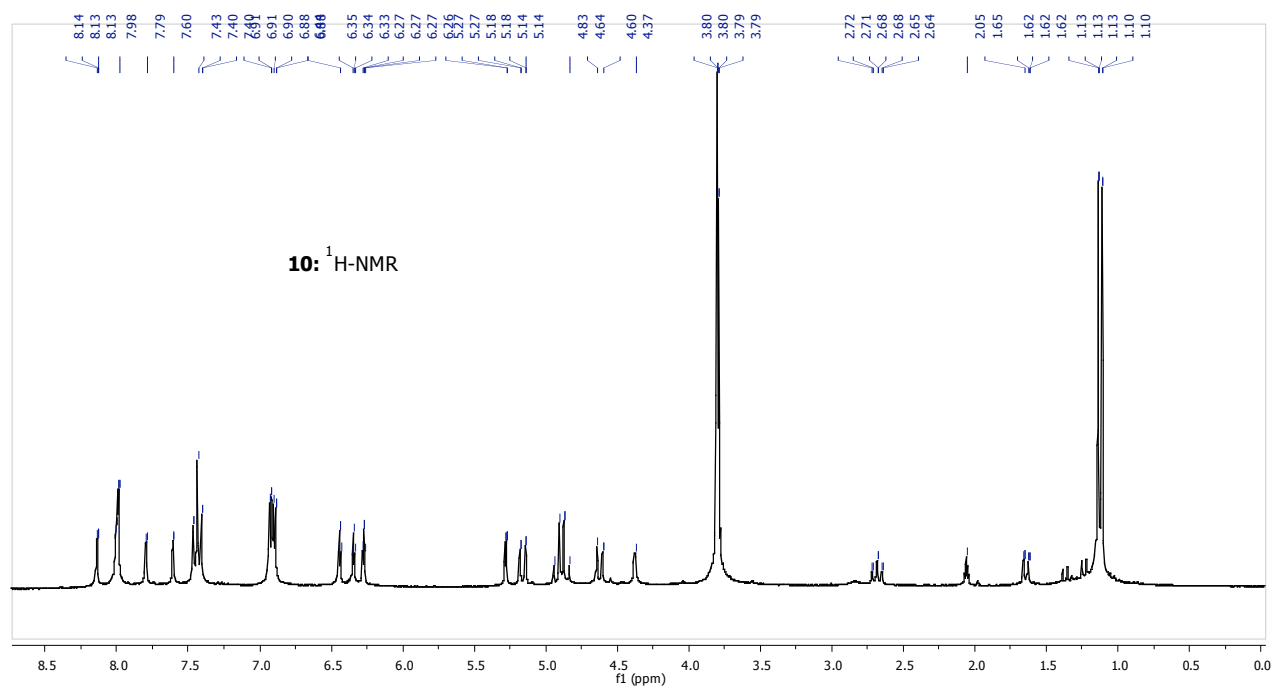
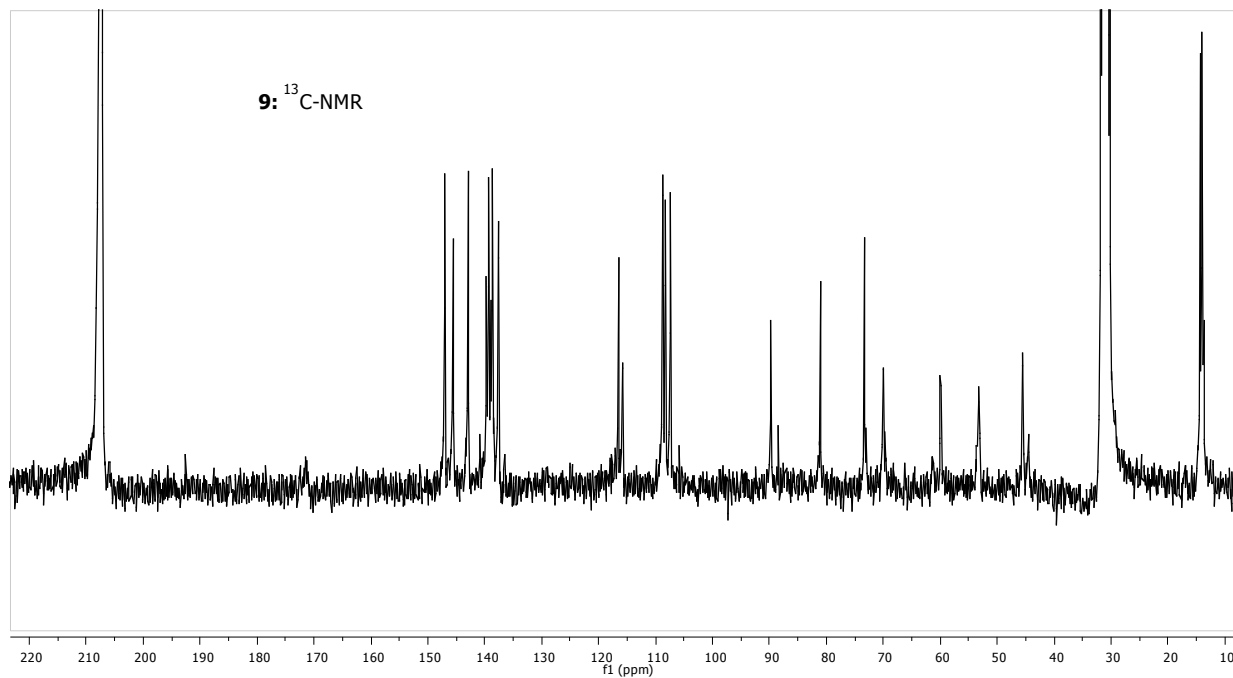
Selected Spectra:

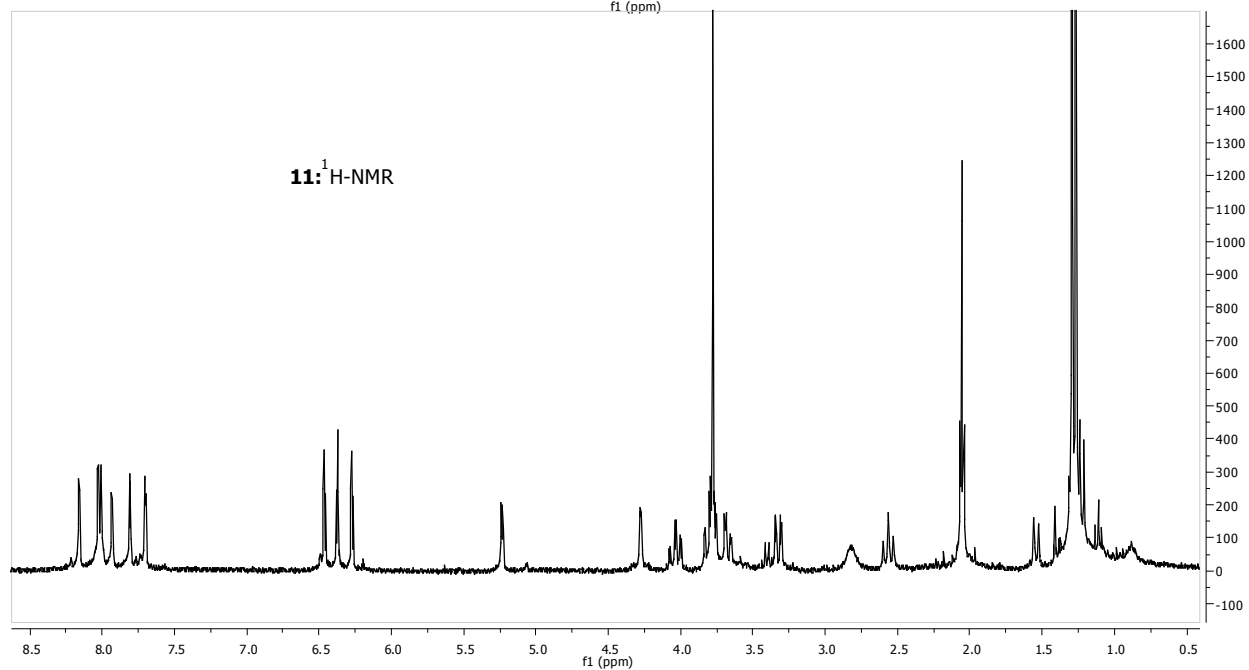
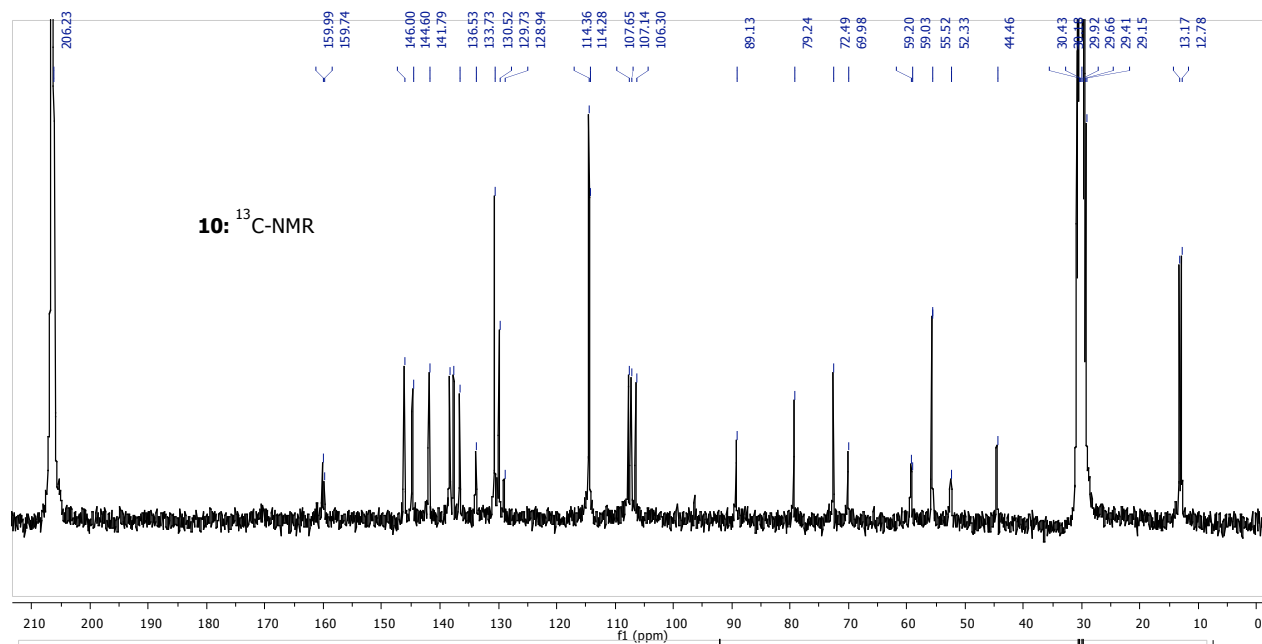




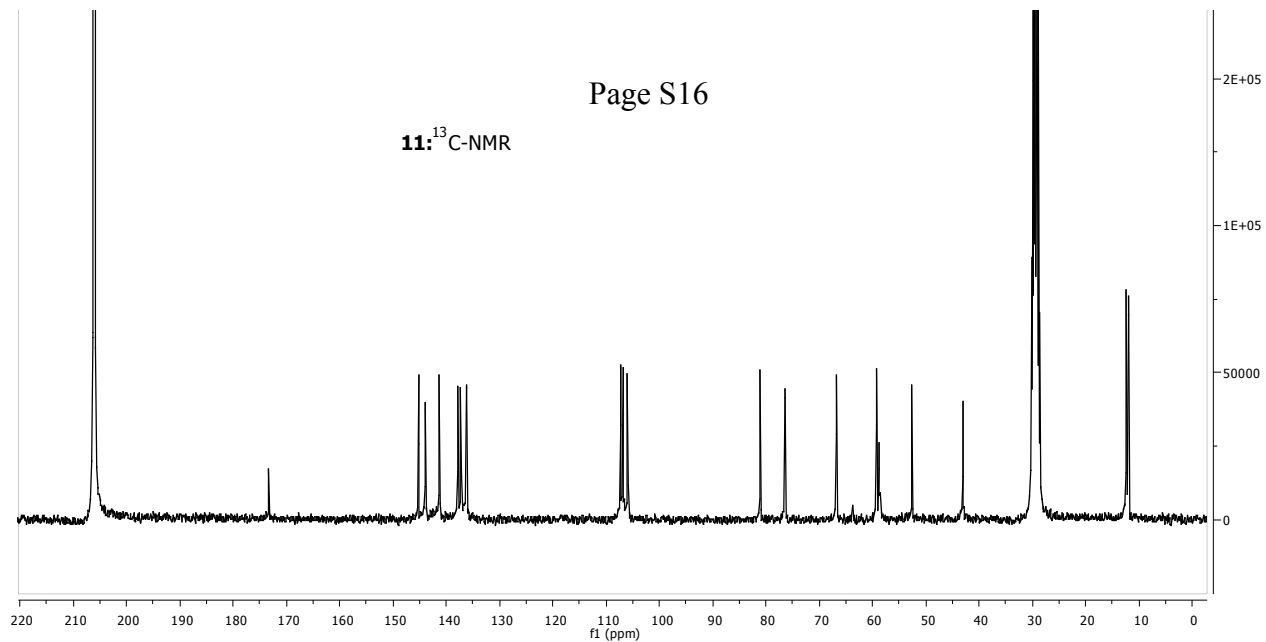








11: ^{13}C -NMR



12: ^1H -NMR

