Supporting Information for

Ligand Effects and Kinetic Investigations of Sterically Accessible 2-Pyridonate Tantalum Complexes for Hydroaminoalkylation

*Jason W. Brandt, Eugene Chong, and Laurel L. Schafer**

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

Table of Contents

General Considerations:
All air and moisture sensitive reactions were performed using standard inert atmosphere techniques using a Schlenk double manifold with N_2 gas and high vacuum (10^{-2} mbar), or using a Mbraun LABmaster glovebox filled with a N_2 atmosphere. All pieces of glassware were dried for at least 4 hours in a 160 °C oven, or dried over a propane flame before being used on the Schlenk manifold or being transferred into the glovebox. Toluene and hexanes were dried by passing through columns of activated alumina under N_2 gas, collected into a Teflon sealed Strauss flask (or other appropriate teflon sealed bomb type Schenk flask), and sparged with N_2 gas for at least 30 minutes to remove dissolved O_2 gas. Diethyl ether was dried over Na/benzophenone under N_2 and distilled, once a deep purple colour was maintained, into a Teflon sealed Strauss flask. J. Young NMR tubes used for catalytic experiments had teflon screw-type caps and were 8" x 5 mm tubes. Thin layer chromatography (TLC) was performed on EMD silica gel 60 F254 plates. Visualization was achieved under a 254 nm UV light source and/or by staining with iodine or $KMnO_4$ solution. Flash chromatography was performed using Silicycle SiliaFlash F60 silica gel (230-400 mesh), glass columns, and ACS grade solvents.

Instrumentation:
^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 300 MHz, 400 MHz, or 600 MHz Avance spectrometer at ambient temperature, and chemical shifts are given relative to the corresponding residual protio solvent. Chemical shifts, δ, are reported in parts per million (ppm) and coupling constants *J* are given in Hertz (Hz). The following abbreviations are used to indicate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. For quantitative experiments, T_1 relaxation times for peaks of interest were estimated utilizing a spin-echo pulse sequence, and relaxation delays were appropriately extended when collecting ^{1}H NMR spectra. Mass spectra (MS) and elemental analyses (EA) were measured by the mass spectrometry and microanalysis service at the Department of Chemistry, University of British Columbia. Mass spectra were recorded on a Kratos MS-50 spectrometer using an electron impact (70 eV) source. Fragment signals are given in mass per charge number (*m/z*). Elemental analyses were performed using a Thermo Flash 2000 Elemental Analyzer. The content of the specified element is expressed in percent (%). UHPLC analysis was conducted on an Agilent 1290 Series UHPLC with a multi wavelength UV detector and 6150 Series Quadrapole ESI/MS, using an Agilent Poroshell 120 column (SB-C18, 2.7 μm, 2.1 x 50 mm) with a water:acetonitrile (0.1% TFA in acetonitrile) solvent system (gradient 80:20 to 0:100). Single crystal X-ray structure determinations were performed at the X-ray crystallography lab at the Department of Chemistry, University of British Columbia on either a Bruker X8 APEX or Bruker APEX DUO diffractometer by Damon Gilmour or Scott Ryken. Refinement of the structures was performed by the authors.

Materials:
All chemicals were purchased from commercial sources and used as received unless otherwise specified. Chemicals from commercial sources that were not dried and shipped under inert atmosphere, were appropriately dried and degassed of O_2 before being transferred to the glovebox or for use on the Schlenk manifold. All amines and alkenes were dried under N_2 atmosphere with CaH_2, distilled, and degassed by the freeze-pump-thaw method. 2-pyridones were sublimed under vacuum on a Schlenk maifold at 80 – 100 °C with water cooling, before being transferred into the glovebox. Compounds **1**,[1] $[Ta(NMe_2)_3Cl_2]_2$,[2] 3-phenyl-2-pyridone,[3] 3-mesityl-2-pyridone,[3] 6-phenyl-2-pyridone,[4] *N*-(methyl-d_3)aniline[5] were synthesized according to literature procedures.

Synthesis and Characterization of Compounds:

Synthesis of sodium-pyridonates. In a glovebox, equimolar amounts of pyridone (*ca.* 2.00 mmol) and NaHMDS (*ca.* 2.00 mmol) were slurried with ~ 6 mL toluene in a 20 mL scintillation vial, and stirred at ambient temperature for 12 hours. The volatiles were removed *in vacuo* to reveal a sticky white salt. ~2 mL of hexanes were added to form a slurry, and the volatiles were removed *in vacuo*. This was repeating one to two additional times and the resulting white to off-white powder was thoroughly dried *in vacuo*. These products were used without further purification or characterization.

General procedure for the synthesis of complexes 3 – 9. Based on the published procedure for the synthesis of **1**.[1] In a glovebox, a white suspension of the sodium pyridonate salt in toluene (~ 3 mL) was added to a stirring suspension of yellow $[Ta(NMe_2)_3Cl_2]_2$ in toluene (~ 3 mL) at ambient temperature. The resulting suspension was stirred for 12 hours at ambient temperature, and then filtered through a plug a Celite. The resulting clear yellow solution was concentrated *in vacuo*. The resulting sticky, pale yellow solid was dissolved in minimal warm toluene (~ 1.5 mL), and cooled first to ambient temperature, and then cooled for 10 minutes at -35 °C. This dark yellow solution was then layered with hexanes (~ 3 mL) and stored in the freezer at -35 °C to promote recrystallization. Products generally recrystallized within 24 hours. After thoroughly drying the crushed, recrystallized product *in vacuo*, samples were used for characterization.

Chlorotris(dimethylamido)(κ^2-*N,O*-3-(2,4,6-trimethylphenyl)-2-pyridonato)tantalum(V) (3). Using the general procedure described above, sodium 3-(2,4,6-trimethylphenyl)-2-pyridonate salt (0.045 g, 0.19 mmol) was added to $[Ta(NMe_2)_3Cl_2]_2$ (0.074 g, 0.01 mmol). A single recrystallization resulted in 0.090 g (84% yield) of yellow crystals.

^{1}H-NMR and ^{13}C-NMR spectra reveal fluctional behavior for the 2,6-dimethyl groups of the 2,4,6-trimethyphenyl group as exhibited by additional resonances in both spectrum (one sharp and one broad). The 4-methyl group of the same aryl ring also exhibits this behavior but results in a single broad resonance.
^{1}H-NMR (400 MHz, C_6H_6): δ 7.71 (dd, *J* = 5.4, 1.9 Hz, 1H), 7.11 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.82 (br. s, 2H), 6.38 (dd, *J* = 7.3, 5.4 Hz, 1H), 3.50 (br. s, 18H), 2.37 (br. s, 3H), 2.14/2.11 (s/br. s., 6H).
^{13}C-NMR (101 MHz, C_6H_6): δ 168.1, 141.4, 140.4, 138.2 (br. s), 137.2, 135.8 (br. s), 132.6, 129.0, 125.6, 113.0, 46.8, 21.2, 21.0 (br. s), 20.8 (br. s).
MS (EI): *m/z* 560 [M^+], 516 [M^+–NMe_2]
EA: Calc'd for $C_{20}H_{32}ClN_4OTa$: C 42.83, H 5.75, N 9.99; Found: C 43.12, H 5.80, N 9.80.

Chlorotris(dimethylamido)(κ^2-*N,O*-3-methyl-2-pyridonato)tantalum(V) (4). Using the general procedure described above, sodium 3-methyl-2-pyridonate salt (0.026 g, 0.20 mmol) was added to $[Ta(NMe_2)_3Cl_2]_2$ (0.076 g, 0.10 mmol). A single recrystallization resulted in 0.073 g (80% yield) of yellow crystals.

^{1}H-NMR (400 MHz, C_6H_6): δ 7.60-7.58 (m, 1H), 6.94-6.91 (m, 1H), 6.23 (dd, *J* = 7.2, 5.5 Hz, 1H), 3.55 (br. s, 18H), 2.02 (s, 3H).
^{13}C-NMR (101 MHz, C_6H_6): δ 169.5, 140.0, 138.7, 122.1, 112.8, 46.7, 14.6.

MS (EI): *m/z* 456 [M^+], 412 [M^+–NMe_2]
EA: Calc'd for $C_{12}H_{24}ClN_4OTa$: C 31.56, H 5.30, N 12.27; Found: C 31.64, H 5.58, N 12.24.

Chlorotris(dimethylamido)(κ^2-*N*,*O*-3-trifluoromethyl-2-pyridonato)tantalum(V) (5). Using the general procedure described above, sodium 3-trifluoromethyl-2-pyridonate salt (0.037 g, 0.19 mmol) was added to $[Ta(NMe_2)_3Cl_2]_2$ (0.076 g, 0.10 mmol). A single recrystallization resulted in 0.078 g (76% yield) of yellow crystals.

^{1}H-NMR (600 MHz, C_6H_6): δ 7.55-7.53 (m, 1H), 7.30-7.29 (m, 1H), 5.94-5.92 (m, 1H), 3.45 (br. s, 18H).
^{13}C-NMR (151 MHz, C_6H_6): δ 145.1, 133.0 (q, $^2J_{CF}$ = 4.5 Hz), 128.4, 111.5, 46.7. Could not locate *C*F_3 or *C*(O)N carbons.
^{19}F-NMR (282 MHz, C_6H_6): δ -62.93.
MS (EI): *m/z* 510 [M^+], 466 [M^+–NMe_2]
EA: Calc'd for $C_{12}H_{21}N_4ClF_3OTa$: C 28.22, H 4.14, N 10.97; Found: C 27.98, H 4.06, N 10.44.

Chlorotris(dimethylamido)(κ^2-*N*,*O*-2-pyridonato)tantalum(V) (6). Using the general procedure described above, sodium 2-pyridonate salt (0.025 g, 0.21 mmol) was added to $[Ta(NMe_2)_3Cl_2]_2$ (0.082 g, 0.11 mmol). A single recrystallization resulted in 0.080 g (84% yield) of yellow crystals.

^{1}H-NMR (400 MHz, C_6H_6): δ 7.63 (ddd, *J* = 5.5, 1.8, 0.9 Hz, 1H), 6.96 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 6.32 (ddd, *J* = 8.6, 0.9, 0.9 Hz, 1H), 6.18 (ddd, *J* = 7.1, 5.5, 0.9 Hz, 1H), 3.54 (br. s, 18H).
^{13}C-NMR (101 MHz, C_6H_6): δ 170.5, 141.4, 140.7, 112.7, 112.6, 46.6.
MS (EI): *m/z* 442 [M^+], 398 [M^+–NMe_2]
EA: Calc'd for $C_{11}H_{22}ClN_4OTa$: C 29.84, H 5.01, N 12.66; Found: C 29.72, H 5.03, N 12.25.

Chlorotris(dimethylamido)(κ^2-*N*,*O*-6-phenyl-2-pyridonato)tantalum(V) (7). Using the general procedure described above, sodium 6-phenyl-2-pyridonate salt (0.035 g, 0.18 mmol) was added to $[Ta(NMe_2)_3Cl_2]_2$ (0.070 g, 0.09 mmol). A single recrystallization resulted in 0.062 g (66% yield) of yellow crystals.
^{1}H-NMR (300 MHz, C_6H_6): δ 7.89-7.85 (m, 2H), 7.24-7.18 (m, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 8.5, 7.4 Hz, 1H), 6.50 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.34 (dd, *J* = 8.5, 0.8 Hz, 1H), 3.51 (br. s, 18H).
^{13}C-NMR (75 MHz, C_6H_6): δ 170.8, 153.5, 140.9, 139.4, 128.9, 128.6, 128.5, 111.5, 111.4, 48.29.
MS (EI): *m/z* 474 [M^+–NMe_2]
Satisfactory elemental analysis could not be obtained for this product.
EA: Calc'd for $C_{17}H_{26}ClN_4OTa$: C 39.36, H 5.05, N 10.80; Found: C 38.70, H 5.23, N 10.35.

Chlorotris(dimethylamido)(κ^2-*N*,*O*-6-methyl-2-pyridonato)tantalum(V) (8). Using the general procedure described above, sodium 6-methyl-2-pyridonate salt (0.025 g, 0.19 mmol) was added to $[Ta(NMe_2)_3Cl_2]_2$ (0.073 g, 0.09 mmol). A single recrystallization resulted in 0.066 g (76% yield) of yellow crystals.
^{1}H-NMR (400 MHz, C_6H_6): δ 6.95 (dd, *J* = 8.5, 7.3 Hz, 1H), 6.20 (m, 1H), 6.08 (m, 1H), 3.60 (br. s, 18H), 2.10 (s, 3H).
^{13}C-NMR (101 MHz, C_6H_6): δ 170.9, 151.9, 141.1, 111.9, 109.7, 47.3, 21.8.

MS (EI): *m/z* 412 [M^+–NMe_2]
EA: Calc'd for $C_{12}H_{24}ClN_4OTa$: C 31.56, H 5.30, N 12.27; Found: C 31.91, H 5.37, N 12.47.

Tris(dimethylamido)triflato(κ^2-*N*,*O*-3-phenyl-2-pyridonato)tantalum(V) (8). In a glovebox, a 10 mL Schlenk tube was charged with **1** (0.071 g, 0.14 mmol) and AgOTf (0.035 g, 0.14 mmol). The flask was moved to the Schlenk line, charged with 3 mL dichloromethane to create a cloudy yellow solution, and stirred at ambient temperature for 12 h. Volatiles were removed *in vacuo* and the flask returned to the glovebox. The yellow white solid was extracted with 10 mL toluene and filtered through a celite plug. The resulting clear yellow solution was concentrated *in vacuo*. The resulting sticky, pale yellow solid was dissolved in minimal warm toluene (~ 1.5 mL), and cooled first to ambient temperature, and then cooled for 10 minutes at -35 °C. This dark yellow solution was then layered with hexanes (~ 3 mL) and stored in the freezer at -35 °C to promote recrystallization. Products generally recrystallized within 24 hours. After thoroughly drying the crushed, recrystallized product *in vacuo*, samples were used for characterization. A single recrystallization resulted in 0.053 g (61% yield) of yellow crystals.

^{1}H-NMR (300 MHz; C_6H_6): δ 7.86-7.82 (m, 2H), 7.64 (dd, *J* = 5.5, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.25-7.20 (m, 2H), 7.11-7.06 (m, 1H), 6.37 (dd, *J* = 7.5, 5.5 Hz, 1H), 3.43 (br. s, 18H).
^{13}C-NMR (101 MHz; C_6H_6): δ 169.0, 140.9, 140.8, 135.3, 128.9, 128.8, 128.1, 125.4, 122.2, 119.1, 114.5, 46.3.
^{19}F-NMR (282 MHz; C_6H_6): δ -78.2
MS (EI): *m/z* 632 [M^+], 588 [M^+–NMe_2], 483 [M^+–OTf]
EA: Calc'd for $C_{18}H_{26}F_3N_3O_4STa$: C 34.19, H 4.14, N 8.86; Found: C 33.88, H 4.05, N 8.50.

***N-deutero* aniline derivatives.** The requirement of dry substrates for these catalytic reactions does not allow for standard preparation of *N-deutero* substrates by exchange (with MeOD or DCl/D_2O), as drying with CaH_2 would be required. To avoid possible loss of deuteration during drying, this prcedure was developed to maintain dry substrate for catalysis.

***N-d-N*-methylaniline.** All manipulations were conducted in a glovebox or on a Schlenk manifold under N_2 with proper Schlenk technique. In a glovebox, a 50 mL pear-shaped Schlenk flask was charged with dried and degassed *N*-methylaniline (2.290 g, 27.2 mmol), 15 mL diethyl ether, and a stir bar. The mixture was stirred to ensure a homogenous mixture. The flask was attached to the schlenk line and cooled to 0 °C. With stirring, 17.2 mL of nBuLi solution (27.5 mmol, 1.6 M in hexanes) was added dropwise *via* syringe and stainless steel needle. The reaction was allowed to slowly warm to ambient temperature and stirred for 2 h. Separately, a small Schlenk flask was charged with D_2O, and sparged with N_2 for 30 min. After the 2 h stir period, 0.97 equivalents of D_2O (0.529 g, 0.48 mL, 26.4 mmol), was added dropwise *via* syringe and stainless steel needle. The reaction was allowed to stir for 2 h. After the 2 h stir period, a short-path distillation apparatus with a Teflon sealed Schlenk flask connected for collection of the product, was attached to the reaction flask. Vacuum was applied slowly, through the distillation apparatus, and the hexanes and diethyl ether were allowed to evaporate. Once complete, the product was distilled under dynamic vacuum (30 °C, 10^{-2} mbar), the receiving flask placed under N_2 gas, sealed, transferred into the glovebox, and the product transferred to a 20 mL scintillation vial. ^{1}H NMR spectrum revealed trace amounts of hexanes and diethyl ether, which can be removed *in vacuo* with stirring, inside

the glovebox, to yield 1.733 g (59% yield) of the product. ^{1}H NMR spectroscopy reveals >98% deuteration with no evidence for *N*-H protons. ^{2}D NMR spectroscopy confirms *N-deutero* incorporation.

^{1}H-NMR (400 MHz; C_6H_6): δ 7.21-7.16 (m, 2H), 6.78-6.74 (m, 1H), 6.42-6.39 (m, 2H), 2.30 (s, 3H).
^{2}H-NMR (61 MHz; C_6H_6): δ 2.84 (s, 1D)

***N-d-N*-(methyl-*d*$_3$)aniline.** All manipulations were conducted in a glovebox or on a Schlenk manifold under N_2 with proper Schlenk technique. In a glovebox, a 50 mL pear-shaped Schlenk flask was charged with dried and degassed *N*-(methyl-*d*$_3$)aniline (2.337 g, 21.2 mmol), 15 mL diethyl ether, and a stir bar. The mixture was stirred to ensure homogeneity. The flask was attached to the Schlenk line and cooled to 0 °C. With stirring, 13.5 mL of ^{n}BuLi solution (21.6 mmol, 1.6 M in hexanes) was added dropwise *via* syringe and stainless steel needle. The reaction was allowed to slowly warm to ambient temperature and stirred for 2 h. Separately, a small Schlenk flask was charged with ~ 1-2 mL of D_2O, and sparged with N_2 for 30 min. After the 2 h stir period, 0.98 equivalents of D_2O (0.416 g, 0.37 mL, 20.8 mmol), was added dropwise *via* syringe and stainless steel needle. The reaction was allowed to stir for 2 h. After the 2 h stir period, a short-path distillation apparatus with a Teflon sealed Schlenk flask connected for collection of the product, was attached to the reaction flask. Vacuum was applied slowly, through the distillation apparatus, and the hexanes and diethyl ether were allowed to evaporate. Once complete, the product was distilled under dynamic vacuum (30 °C, 10^{-2} mbar), the receiving flask placed under N_2 gas, sealed, transferred into the glovebox, and the product transferred to a 20 mL scintillation vial. ^{1}H NMR spectrum revealed trace amounts of hexanes and diethyl ether, which were removed *in vacuo* with stirring, inside the glovebox, to yield 2.012 g (87% yield) of the product. ^{1}H NMR spectroscopy indicates >98% deuteration with no evidence for *N*-H protons. ^{2}D NMR spectroscopy confirms *N-deutero* incorporation.

^{1}H-NMR (400 MHz; *d*$_8$-Tol): δ 7.14-7.09 (m, 2H), 6.71-6.67 (m, 1H), 6.35-6.32 (m, 2H)
^{2}H-NMR (61 MHz; Tol): δ 2.81 (s, 1D), 2.33 (s, 3D)

Reaction and Experimental Details:

Catalytic Screening Reactions (Scheme 3 and 4): In a glovebox, the pre-catalyst (0.025 mmol) was dissolved in *d*$_8$-toluene (500 μL, 0477 mg) in a 5 mL scintillation vial. *N*-methylaniline (0.50 mmol) and alkene (0.75 mmol) were weighed into a separate 5 mL scintillation vial. Using a glass disposable pipette, the solution of pre-catalyst was transferred between the two vials multiple times to ensure a complete dissolution and creation of a homogeneous mixture. The resulting solution was transferred to a J. Young NMR tube and the tube closed with a screw-type Teflon cap. The ^{1}H NMR spectrum was recorded, and the J. Young NMR tube was placed in a preheated oil bath at the specified temperature for the specified time. After the specified time, the tube was removed, allowed to cool to ambient temperature, and a ^{1}H NMR spectrum was recorded. Conversion was determined from this spectrum by integration of the *ortho*-proton signal of *N*-methylaniline centered at δ 6.33, and the appearance of product *ortho*-proton signals of product centered at δ 6.41.

Substrate Scope Investigations (Scheme 5): In a glovebox, the pre-catalyst (0.025 mmol) was dissolved in d_8-toluene (500 μL, 477 mg) in a 5 mL scintillation vial. Cp_2Fe (0.05-0.10 mmol) was weighed into a separate 5 mL scintillation vial and the mass recorded (used to calculated yield after the reaction was completed). *N*-methylaniline (0.50 mmol) and alkene (0.75 mmol) were weighed into the same 5 mL scintillation vial as the Cp_2Fe. Using a glass disposable pipette, the solution of pre-catalyst was transferred between the two vials multiple times to ensure a complete dissolution and creation of a homogeneous mixture. The resulting solution was transferred to a J. Young NMR tube and the tube closed with a screw-type Teflon cap. The ^{1}H NMR spectrum was recorded, and the J. Young NMR tube was placed in a preheated oil bath at the specified temperature for the specified time. After the specified time, the tube was removed, allowed to cool to ambient temperature, and a ^{1}H NMR spectrum was recorded. Yield was determined by ^{1}H NMR spectroscopy by calculating the moles of *N*-methylaniline (*ortho*-protons at δ 6.33) in the t = 0 h spectrum relative to the known moles of Cp_2Fe (singlet at δ 3.99) and by calculating the moles of product (*ortho*-protons at δ 6.41) at the end of the reaction relative to the known moles of Cp_2Fe.

Deuterium Scrambling Experiments (Scheme 7): In a glovebox, **4** (15.0 mg, 0.033 mmol), *N*-methylaniline (or isotopically labelled variant) (0.033 mmol), and 1,3,5-trimethoxybenzene (5.5 mg, 0.033 mmol) were dissolved in d_8-toluene (500 μL, 477 mg) in a 5 mL scintillation vial. The homogenous solution was transferred into a J. Young NMR tube and sealed with a Teflon screw-type cap. The ^{1}H NMR spectrum was collected, and the tube place in a preheated 110 °C oil bath for 2 h. After the time, the tube was removed, cooled, and a ^{1}H NMR spectrum was collected. Experiments c) and d) were repeated in the same manner but in toluene, so that ^{2}H NMR spectra could be obtained.
In a), no change was observed in the integration of **4** or *N*-methylaniline relative to the 1,3,5-trimethoxybenzene internal standard.
In b), the experiment was set up as described but with 10 equivalents of *N*-methylaniline (35.2 mg, 0.328 mmol). Instead of being place into a pre-heated oil bath, the tube was placed into an NMR spectrometer, heated to 105 °C and allowed to stabilize for 15 minutes once the probe temperature was stable. A ^{1}H NMR spectrum was collected every 30 minutes for 2 h. As in a), no change was observed in the integration of **4** or *N*-methylaniline relative to the 1,3,5-trimethoxybenzene internal standard.
In c) and d), deuterium incorporation was determined by ^{1}H NMR spectroscopy. ^{2}H NMR spectra confirm the presence of deuterium in the dimethylamido ligands of **4** (deuterium signal at δ 3.51), the presence of an aniline *N-d* (deuterium signal at δ 2.82), and the presence of deuterium incorporated at methyl position of the aniline (deuterium signal at δ 2.30).

Stoichiometric Experiments with Variable Alkene Equivalents (Scheme 9): In a glovebox, **4** (12.5 mg, 0.027 mmol), *N*-methylaniline (2.9 mg, 0.027 mmol), variable amounts of either cyclohexene or 1-octene (~1–7 equivalents), and 1,3,5-trimethoxybeneze (1.5 mg, 0.009 mmol) were dissolved in d_8-toluene (500 μL, 477 mg) in a 5 mL scintillation vial. The homogeneous solution was transferred into a J. Young NMR tube and sealed with a Teflon screw-type cap. The ^{1}H NMR spectrum was collected, and the tube was placed in a preheated oil bath for 3 h (with cyclohexene at 145 °C; with 1-octene at 110 °C). After 3 h, the tube was removed and a ^{1}H NMR spectrum was collected. Initial alkene equivalents (proton signal at δ 5.66 for cyclohexene and at δ 5.76 ppm for 1-octene) were calculated from the t = 0 h spectrum relative to the known amount of 1,3,5-trimethoxybenzene internal standard (proton signal at δ 6.14). Product (*ortho*-protons

signal at δ 6.14) and remaining alkene were calculated from the t = 3 h spectrum relative to the known amount of 1,3,5-trimethoxybenzene. A convoluted alkyl region of ^{1}H NMR spectra prevents direct identification of the dimethylamine functionalized byproducts; they are calculated as such: functionalized byproducts = (alkene remaining) – (aniline product).

Reaction Monitoring (Scheme 10 and 12): In a glovebox, pre-catalyst **4** (5 mol%: 11.4 mg, 0.025 mmol; 8 mol%: 18.3 mg, 0.040 mmol; 12 mol%: 27.4 mg, 0.060 mmol) was dissolved in d_8-toluene (500 μL, 477 mg) in a 5 mL scintillation vial. 1,3,5-trimethoxybenzene (28.0 mg, 0.167 mmol) was weighed into a separate 5 mL scintillation vial (used to calculated yields after the reaction was completed). *N*-methylaniline, or isotopically labelled variant, (0.50 mmol) and 1-octene (84.2 mg, 0.75 mmol) were weighed into the same 5 mL scintillation vial as the 1,3,5-trimethoxybenzene. Using a glass disposable pipette, the solution of pre-catalyst was transferred between the two vials multiple times to ensure a complete dissolution and creation of a homogeneous mixture. These samples were consistently measured to have a volume of 0.55 mL by 1.0 mL syringe. The resulting solution was transferred to a J. Young NMR tube and the tube closed with a screw-type Teflon cap. The tube was then placed into the NMR spectrometer that was already pre-heated to 105 °C. This time point was taken to be t = 0 min. The sample was allowed ~ 10 minutes to reach equilibrium, followed by shimming of the magnet, and tuning and matching of the instrument. An ^{1}H NMR spectrum was collected every 17.6 minutes with the first ^{1}H NMR spectrum recorded at 17.4 minutes. Yield of *N*-methylaniline (*ortho*-protons at δ 6.33) and product (*ortho*-protons at δ 6.41) was determined by integration relative to the known amount of 1,3,5-trimethoxy benzene internal standard (aryl-protons at δ 6.04). Due to deuterium scrambling into the *ortho*-position of the product, only the yield of the starting material aniline is reported when using deuterated aniline substrates. Each kinetic monitoring experiment was repeated to confirm the reaction profile.

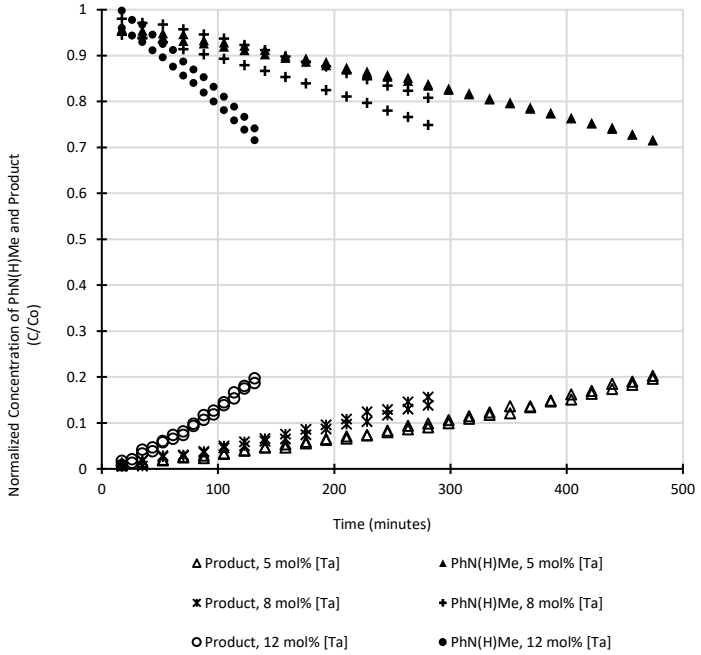


Chart S1: Plot of reaction monitoring experiments with 5, 8, and 12 mol% **4** as pre-catalyst. HAA reaction between *N*-methylaniline and 1-octene.

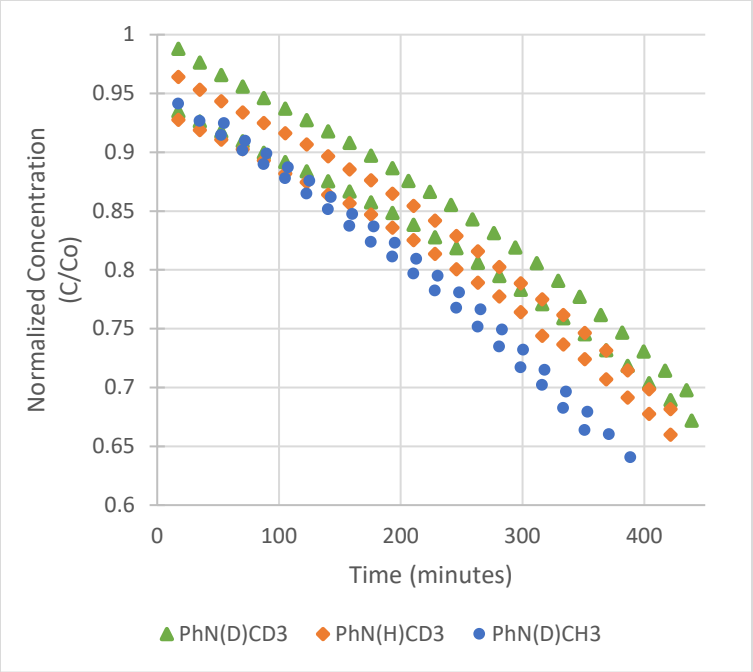


Chart S2: Plot of reaction monitoring experiments with 12 mol% **4** as pre-catalyst. HAA reaction between variably deuterated *N*-methylaniline and 1-octene.

Analysis of Deuterium Incorporation (Scheme 13): After collecting kinetic data, the reactions with the deuterated substrates were quenched with 2 mL methanol, transferred to 20 mL scintillation vial, and the solvents removed on a rotorary evaporator. The product aniline and the *N*-methylaniline starting material were isolated by column chromotography (10% EtOAc in hexanes, silica). Deuterium incorporation was determined by ^{1}H NMR spectroscopy and deuteration confirmed by ^{2}H NMR spectroscopy.

Solid State Molecular Structures and X-ray Data:

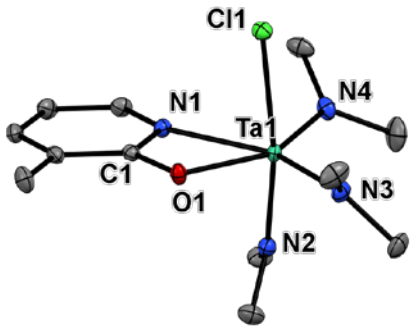


Figure S1: ORTEP representation of complex **4**, [(3-methyl-2-pyridonate)Ta(NMe_2)$_3$Cl]. Thermal ellipsoids are shown at 50% probability. H-atoms omitted.

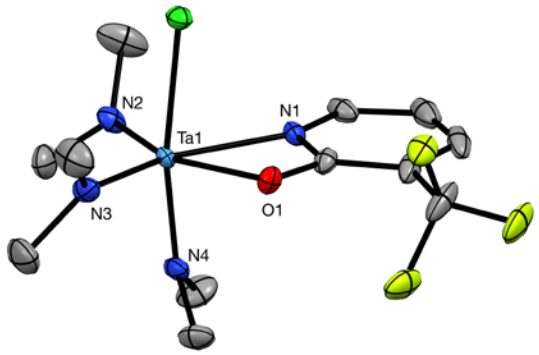


Figure S2: ORTEP representation of complex **5**, [(3-trifluoromethyl-2-pyridonate)Ta(NMe_2)$_3$Cl]. Thermal ellipsoids are shown at 50% probability. H-atoms omitted.

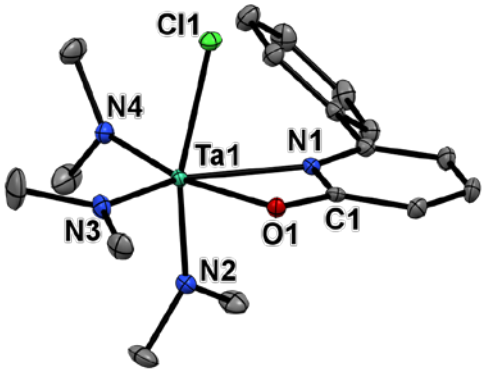


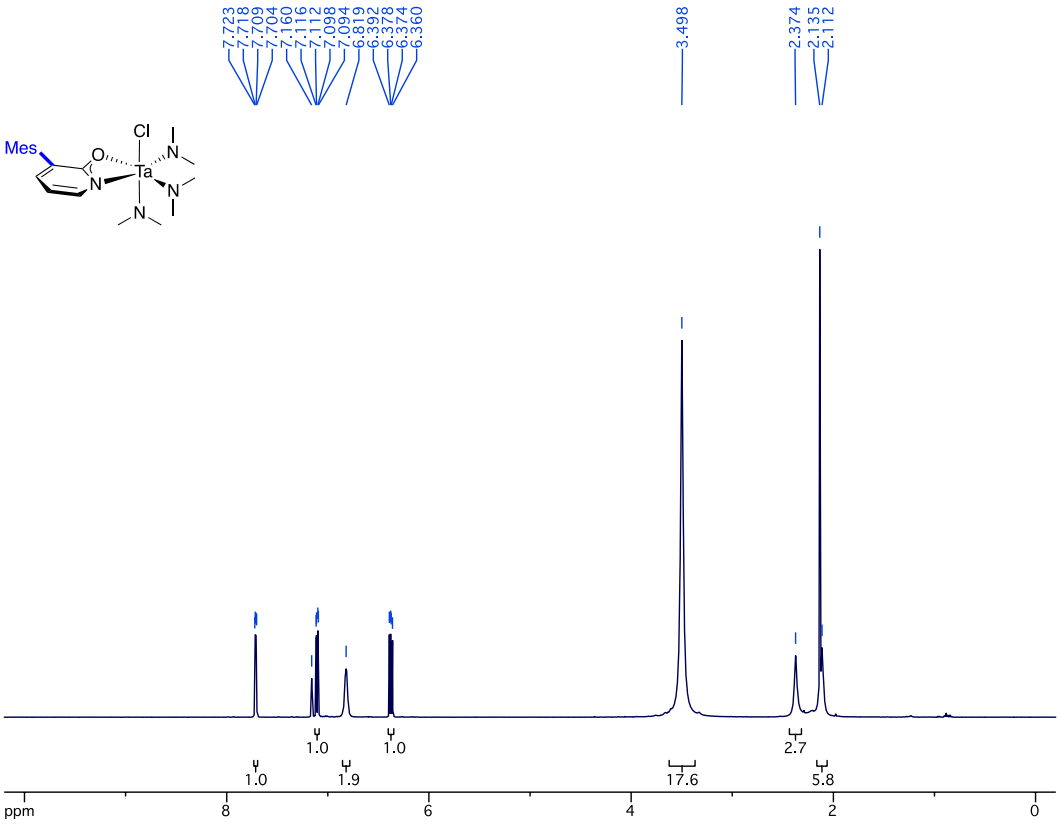
Figure S3: ORTEP representation of complex **7**, [(6-phenyl-2-pyridonate)Ta(NMe_2)$_3$Cl]. Thermal ellipsoids are shown at 50% probability. H-atoms omitted.

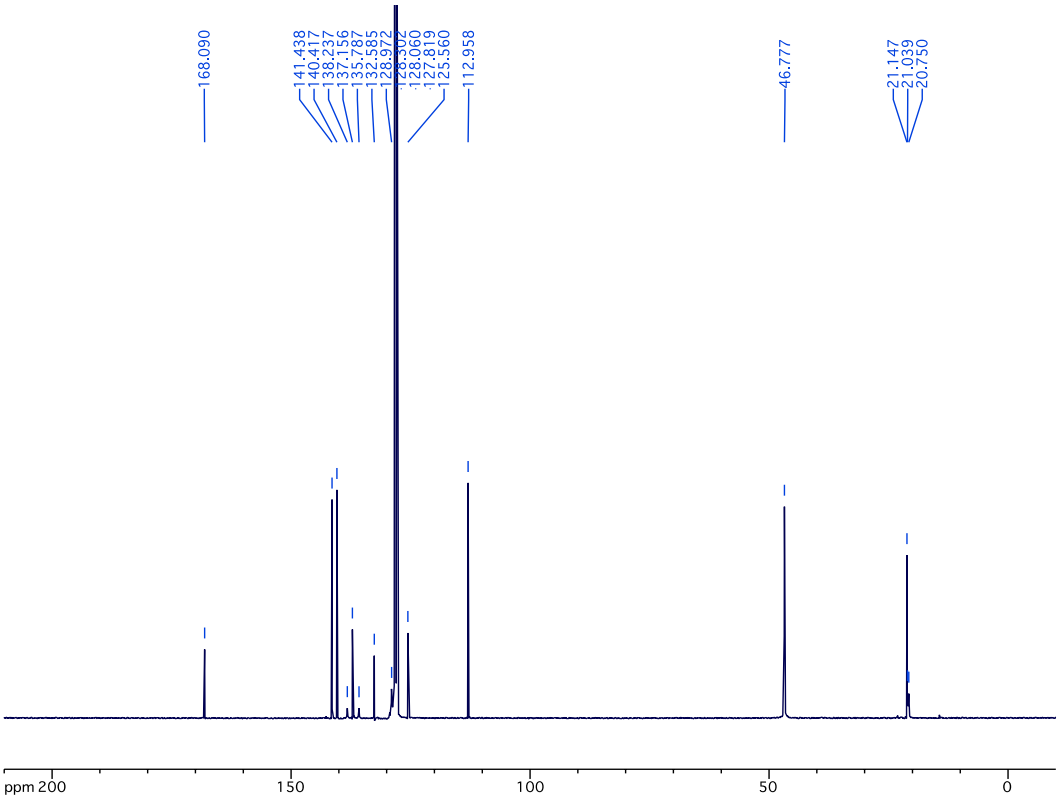
Table S1: Crystallographic parameter for **4**, **5**, and **7**.

	4	**5**	**7**
formula	$C_{12}H_{24}ClN_4OTa$	$C_{12}H_{21}ClF_3N_4OTa$	$C_{17}H_{26}ClN_4OTa$
F_w	456.75	510.73	518.82
crystal size (mm)	0.25 x 0.19 x 0.17	0.16 x 0.12 x 0.07	0.36 x 0.28 x 0.21
color, habit	yellow, plate	yellow, plate	yellow, prism
crystal system	Monoclinic	Triclinic	orthorhombic
space group	$P2_1/c$	P-1	Pbca
T (K)	100	100	90
a (Å)	8.6755(12)	7.9749(8)	9.6112(4)
b (Å)	12.7009(19)	8.4714(8)	14.3447(6)
c (Å)	15.100(2)	14.7644(15)	28.6697(12)
α (Å)	90	89.788	90
β (Å)	97.197(3)	86.448	90
γ (Å)	90	61.895	90
V (Å^3)	1650.7(4)	877.79(15)	3952.7(3)
Z	4	2	8

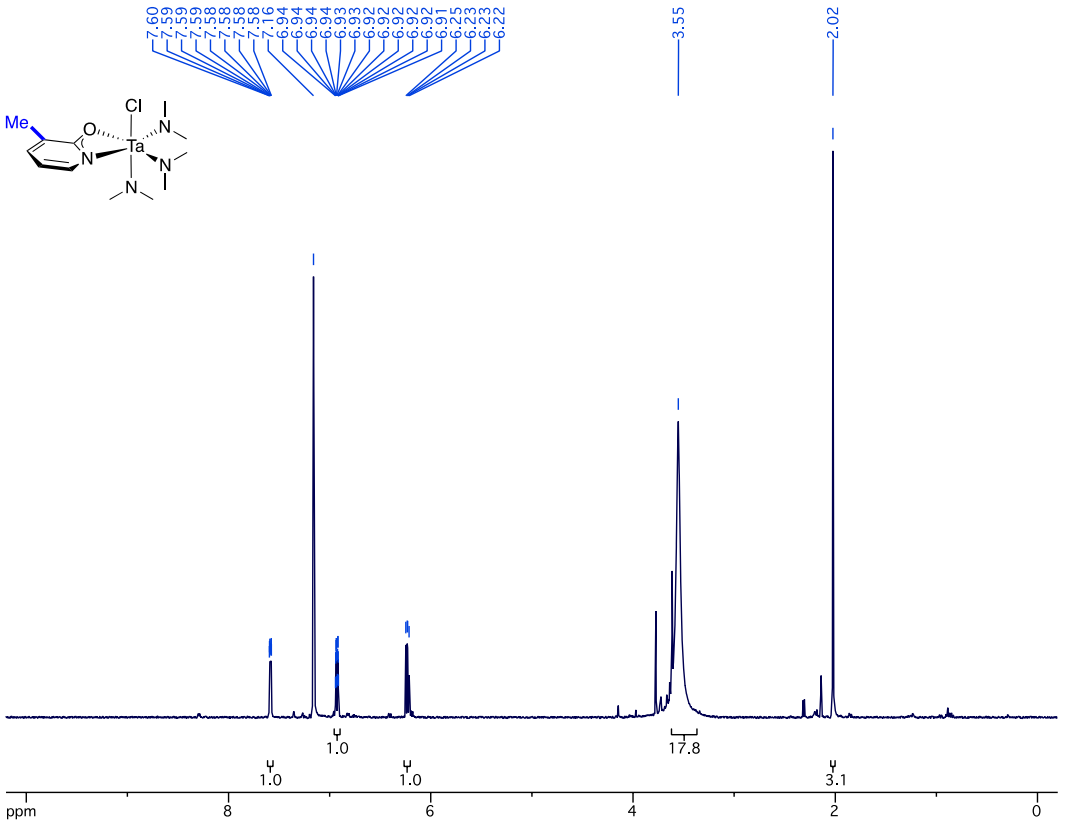
ρ_{calcd} (g cm^{-3})	1.838	1.932	1.744
F(000)	888.0	492.0	2032.0
μ (Mo$_{K\alpha}$) (mm^{-1})	6.819	6.447	5.708
$2\theta_{max}$ (°)	60.084	60.05	60.096
total no. of reflns	20011	5107	30947
no. of unique reflns	4839	5107	5797
R_1 (F^2, all data)	0.0152	0.0377	0.0230
wR_2 (F^2, all data)	0.0316	0.0559	0.0394
R_1 (F, $I > 2\sigma(I)$)	0.0132	0.0292	0.0194
wR_2 (F, $I > 2\sigma(I)$)	0.0310	0.0545	0.0384
goodness of fit	1.037	1.076	1.097

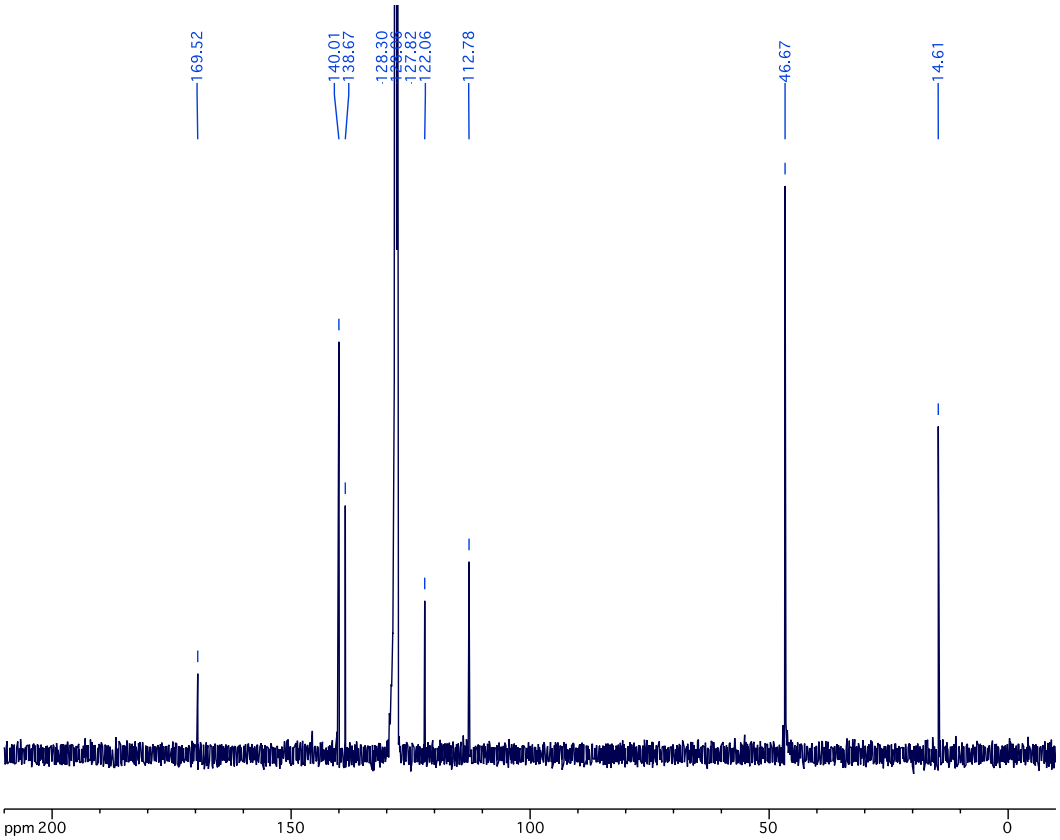
NMR Spectra:
Compound **3**



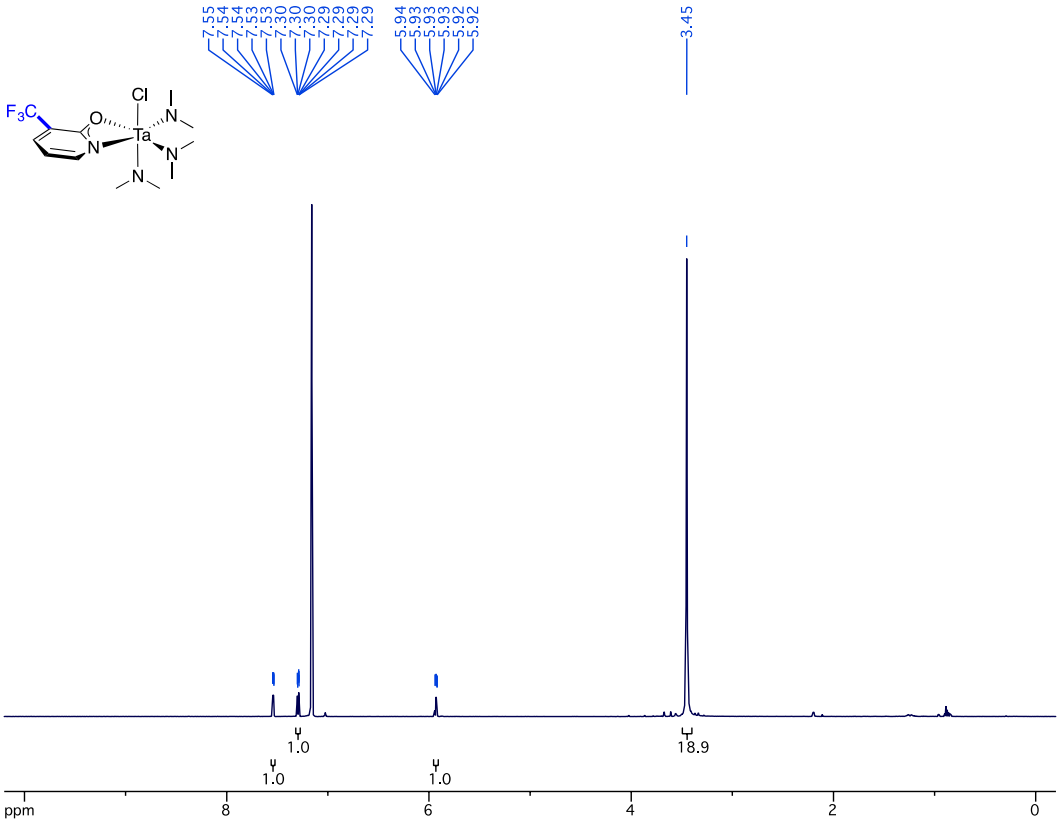


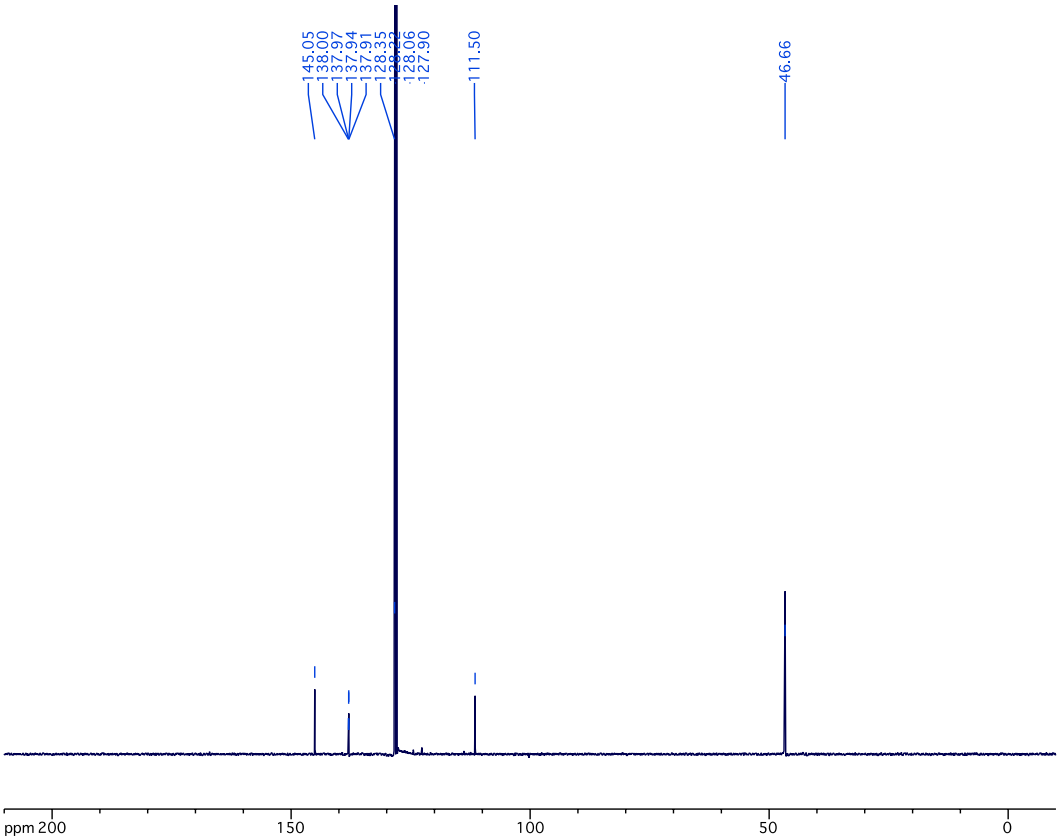
Compound **4**


7.60
7.59
7.59
7.59
7.58
7.58
7.58
7.58
7.16
6.94
6.94
6.94
6.94
6.93
6.93
6.92
6.92
6.92
6.92
6.92
6.91
6.25
6.23
6.23
6.22
3.55
2.02
Me
Cl
O
N
Ta
N
N
N
1.0
17.8
1.0
1.0
3.1
ppm
8
6
4
2
0

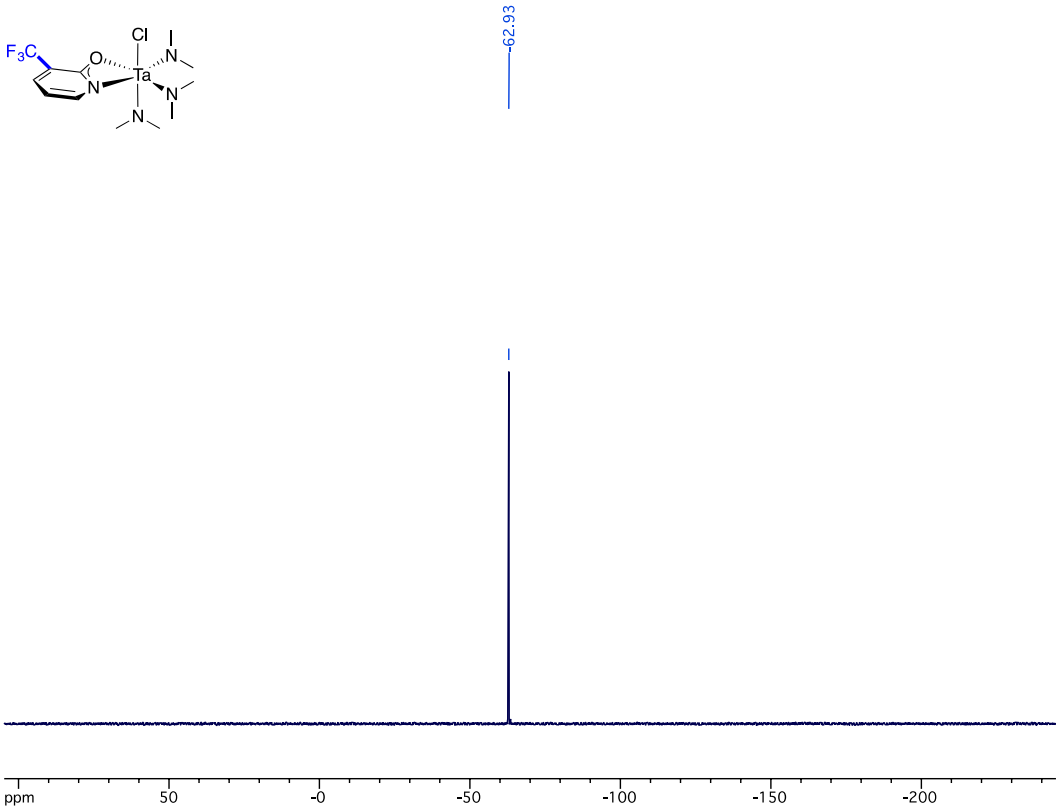

169.52
140.01
138.67
128.30
127.82
122.06
112.78
46.67
14.61
ppm 200
150
100
50
0

Compound **5**

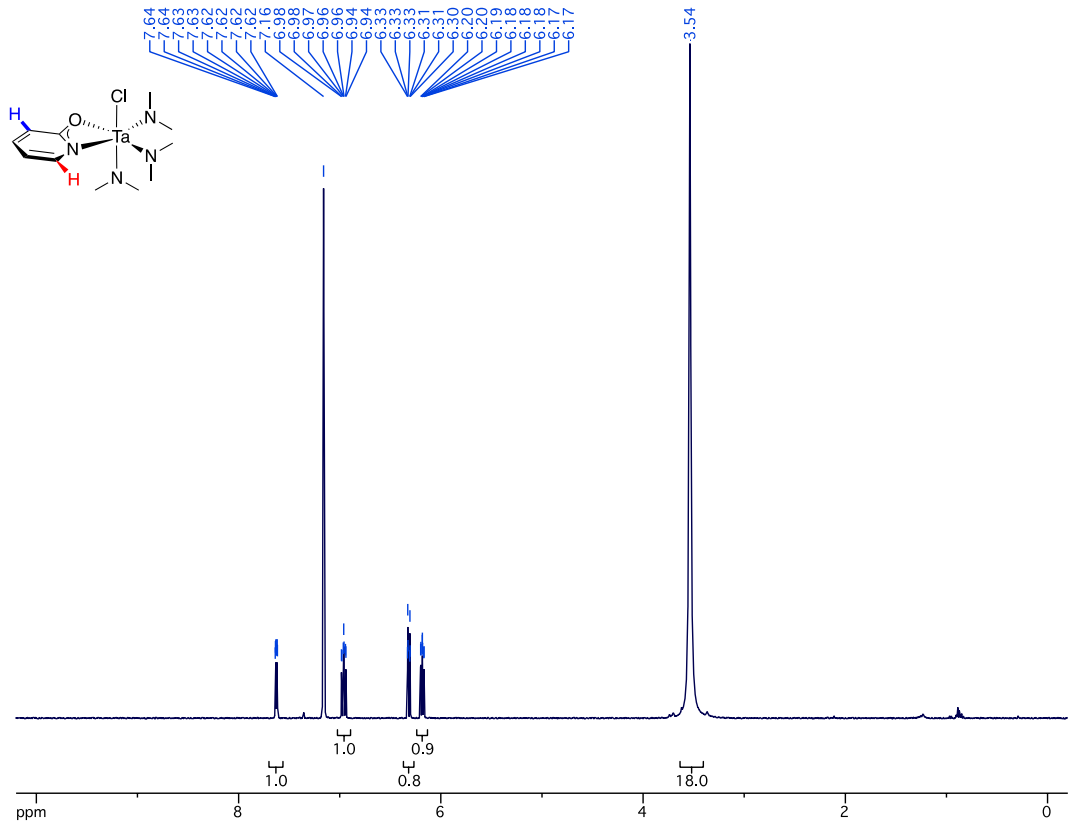

7.55
7.54
7.54
7.53
7.53
7.30
7.30
7.29
7.29
7.29
7.29
5.94
5.93
5.93
5.93
5.92
5.92
3.45
Cl
F3C
O
N
Ta
N
N
N
1.0
1.0
1.0
18.9
ppm
8
6
4
2
0

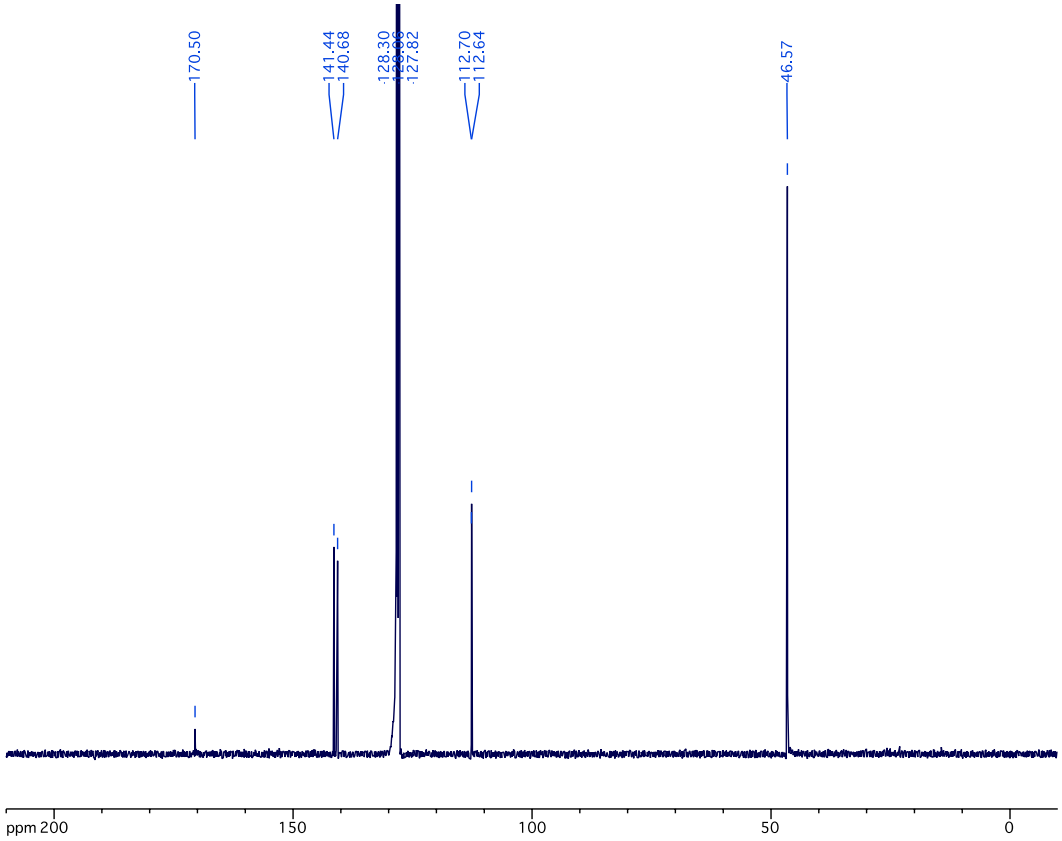

145.05
138.00
137.97
137.94
137.91
128.35
129.06
127.90
111.50
46.66
ppm 200
150
100
50
0

Compound **5**

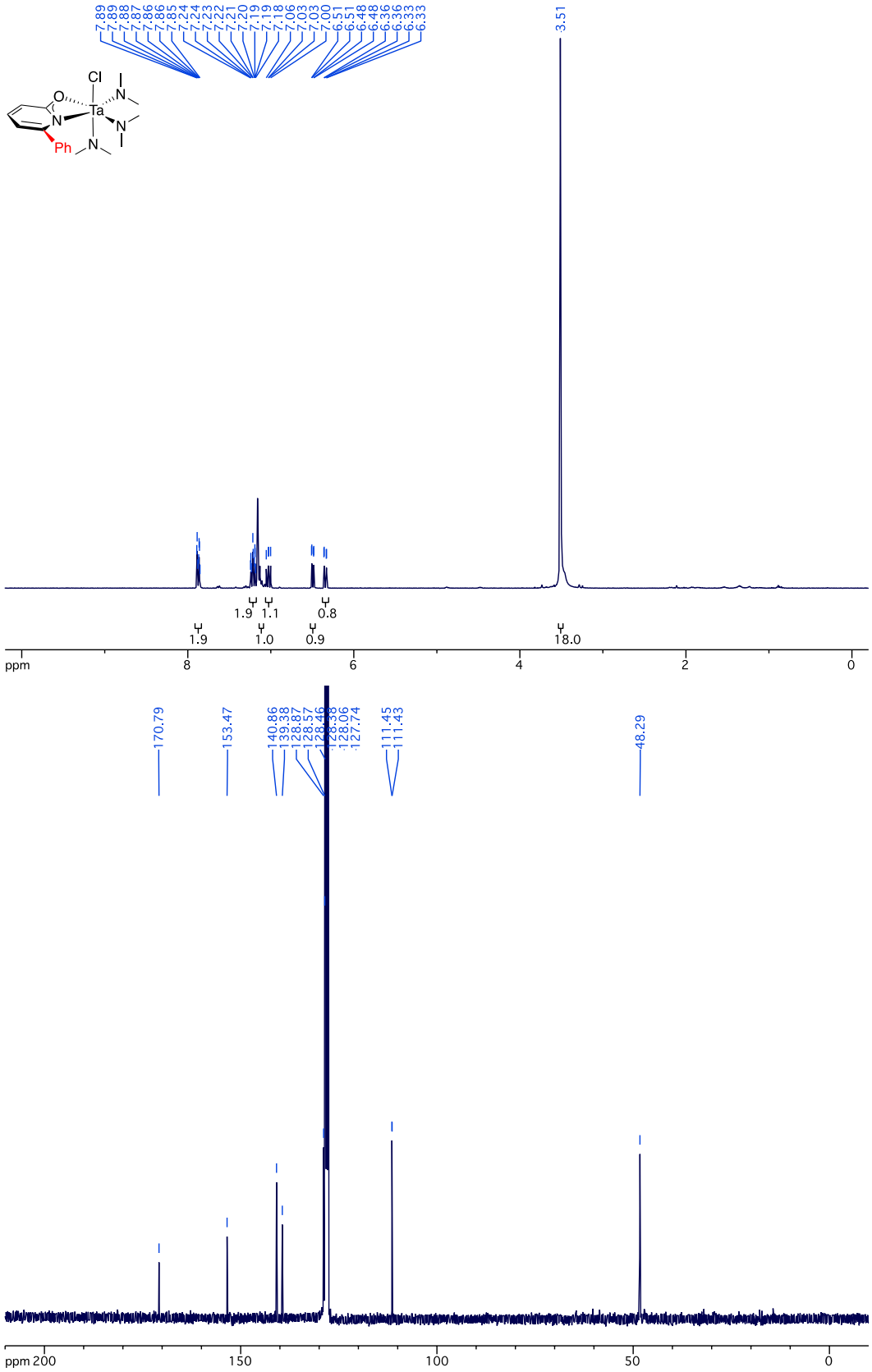


Compound **6**

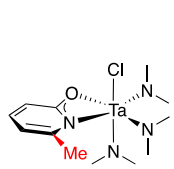

7.64
7.64
7.63
7.63
7.62
7.62
7.62
7.62
7.16
6.98
6.98
6.97
6.96
6.96
6.94
6.94
6.33
6.33
6.33
6.31
6.31
6.30
6.20
6.20
6.19
6.18
6.18
6.18
6.17
6.17
3.54
Cl
H
O
N
Ta
N
N
N
H
1.0
0.9
1.0
0.8
18.0
ppm
8
6
4
2
0


170.50
141.44
140.68
128.30
127.82
112.70
112.64
46.57
ppm 200
150
100
50
0

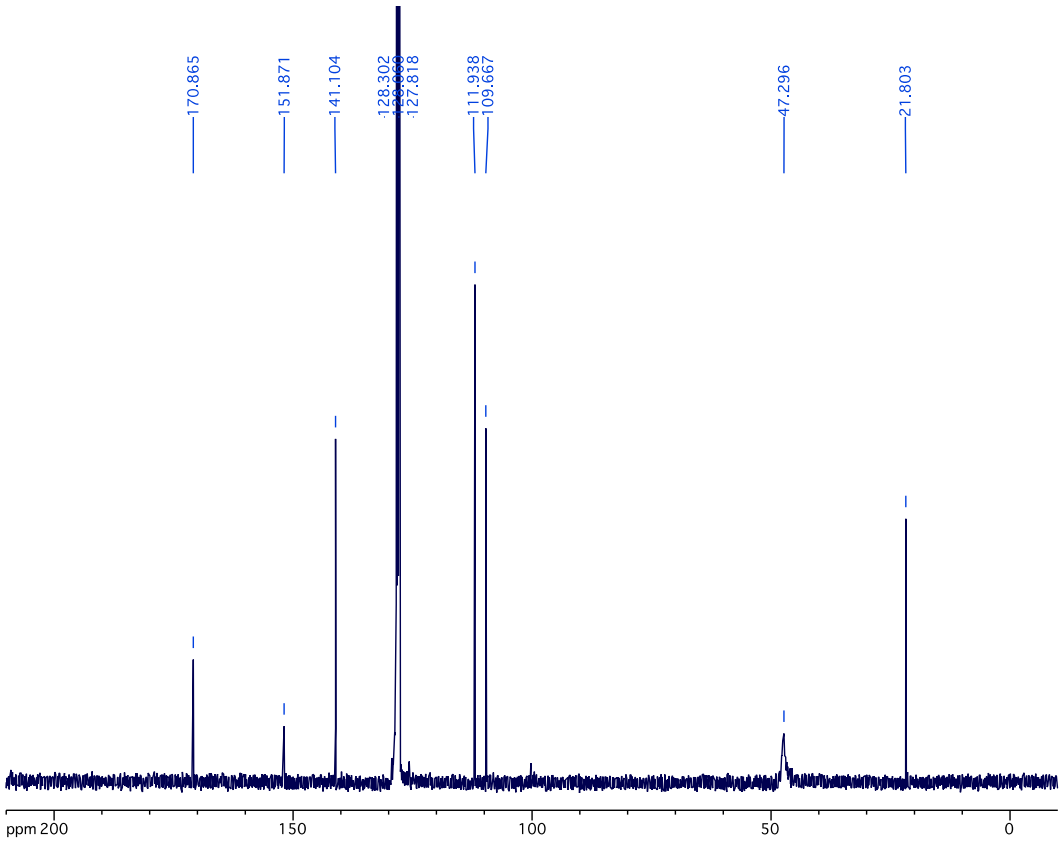
Compound **7**


7.89
7.89
7.88
7.87
7.86
7.86
7.85
7.24
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.06
7.03
7.03
7.00
6.51
6.51
6.48
6.48
6.36
6.36
6.33
6.33
3.51
Cl
O
N
Ta
N
N
N
Ph
1.9
1.1
0.8
1.9
1.0
0.9
18.0
ppm
8
6
4
2
0
170.79
153.47
140.86
139.38
128.87
128.57
128.46
128.38
128.06
127.74
111.45
111.43
48.29
ppm 200
150
100
50
0

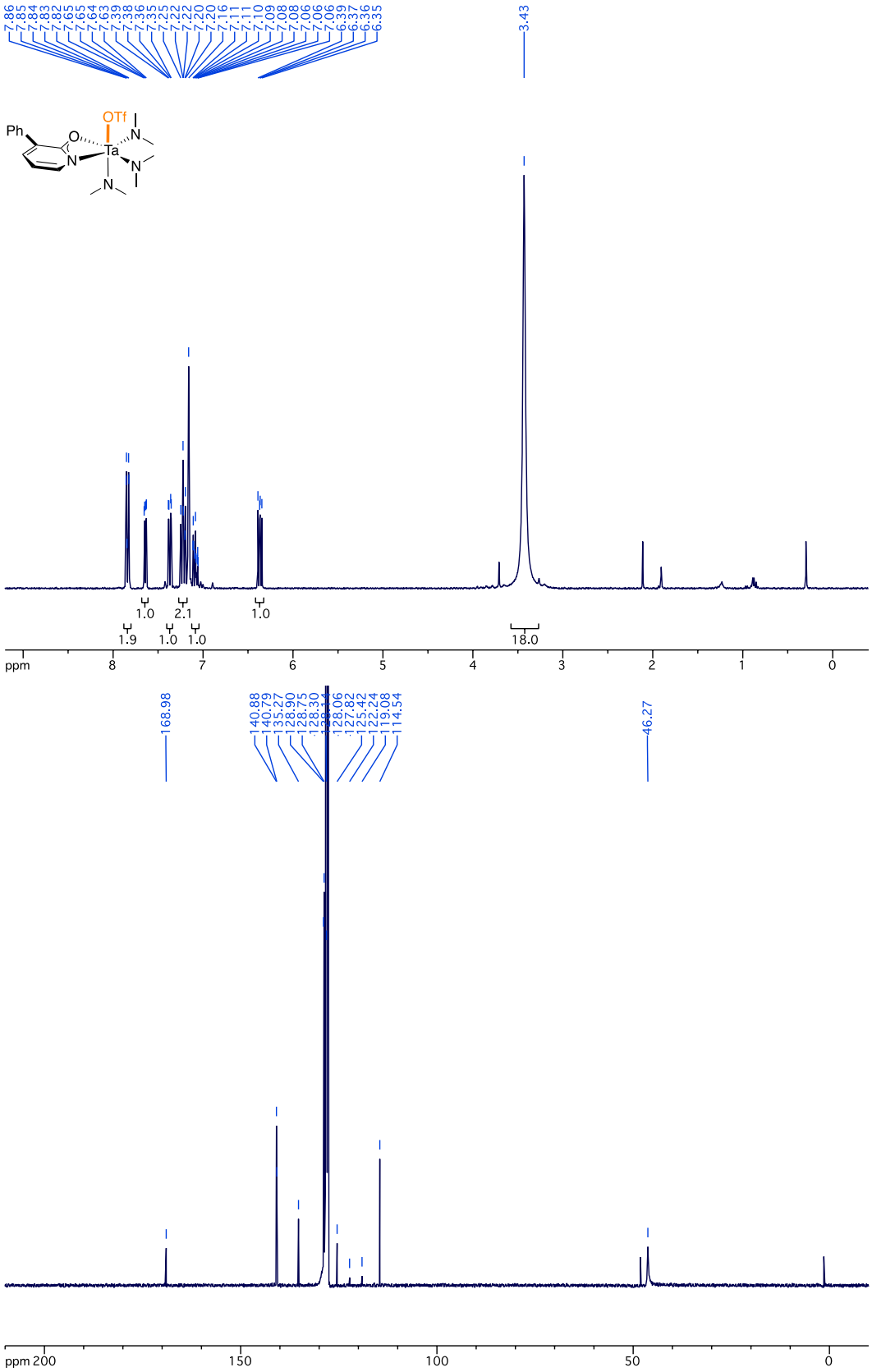
Compound **8**


Cl
O
N
Ta
N
N
N
Me

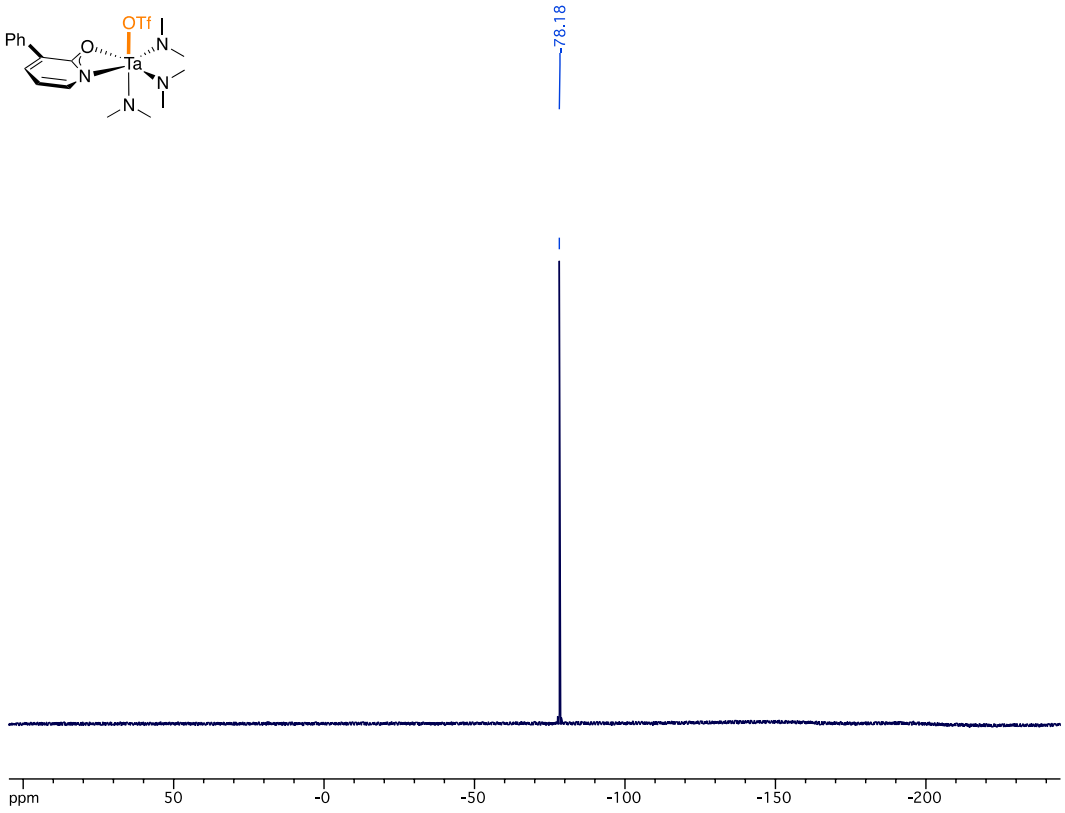
7.160
6.967
6.949
6.946
6.928
6.215
6.213
6.211
6.194
6.192
6.190
6.091
6.089
6.087
6.073
6.071
6.069
3.598
2.105
0.9
18.3
1.1
1.0
3.4
ppm
8
6
4
2
0


170.865
151.871
141.104
128.302
127.818
111.938
109.667
47.296
21.803
ppm 200
150
100
50
0

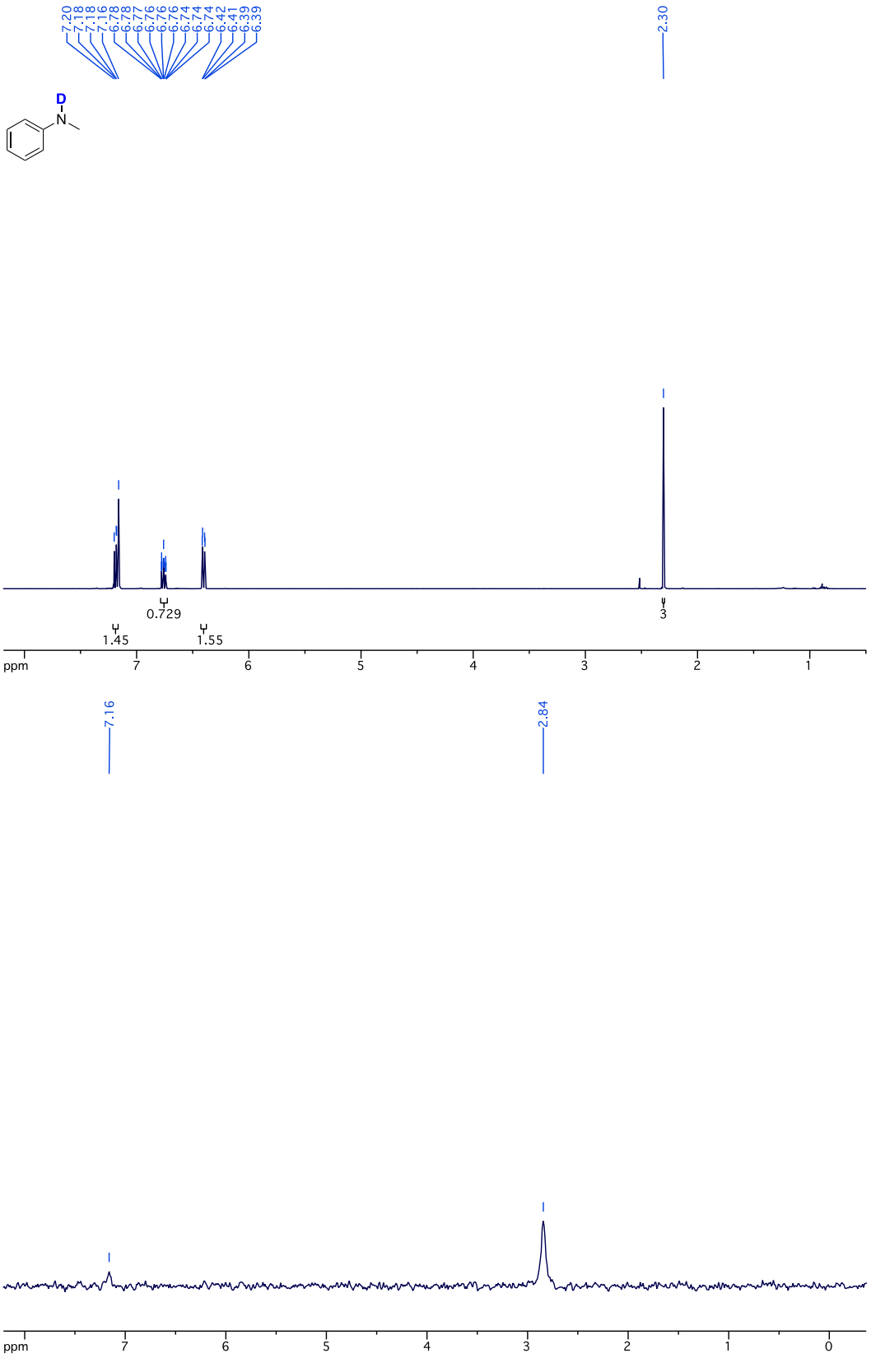
Compound **9**


7.86
7.85
7.84
7.83
7.82
7.65
7.64
7.63
7.39
7.38
7.36
7.35
7.25
7.22
7.22
7.20
7.20
7.16
7.11
7.11
7.10
7.09
7.08
7.08
7.06
7.06
7.06
6.39
6.37
6.36
6.35
3.43
OTf
Ph
O
N
Ta
N
N
N
1.0
2.1
1.0
1.9
1.0
1.0
18.0
ppm
8
7
6
5
4
3
2
1
0
168.98
140.88
140.79
135.27
128.90
128.75
128.30
128.06
127.82
125.42
122.24
119.08
114.54
46.27
ppm 200
150
100
50
0

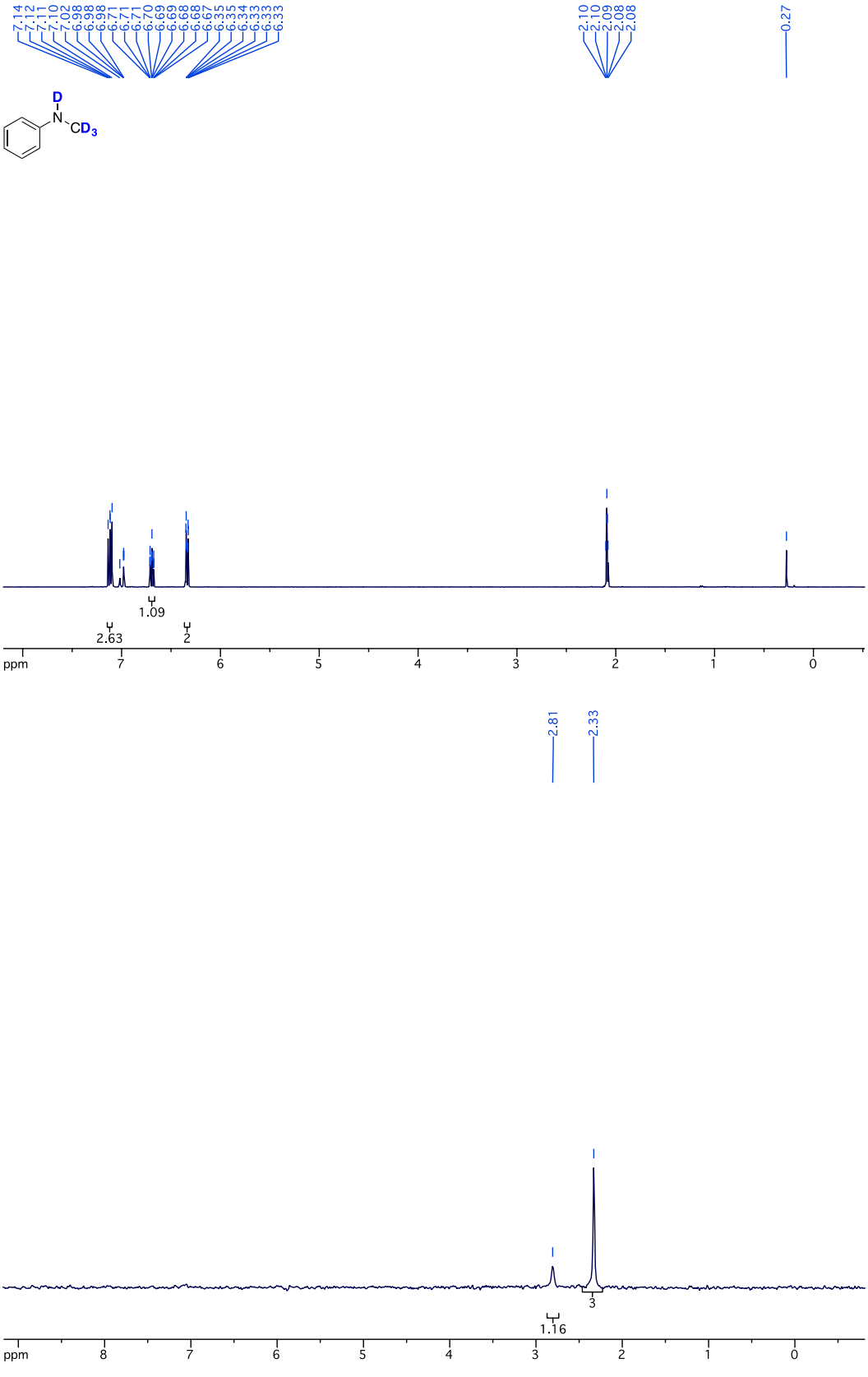
Compound **8**



N-d-N-methylaniline



N-*d*-*N*-(methyl-d_3)aniline:



References:

(1) Chong, E.; Brandt, J. W.; Schafer, L. L. *J. Am. Chem. Soc.* **2014**, *136*, 10898-10901.

(2) Chisholm, M. H.; Huffman, J. C.; Tan, L. S. *Inorg Chem* **1981**, *20*, 1859-1866.

(3) Chong, E.; Schafer, L. L. *Org. Lett.* **2013**, *15*, 6002-6005.

(4) Gallagher, T.; Smith, C.; Hirschhäuser, C.; Malcolm, G.; Nasrallah, D. *Synlett* **2014**, *25*, 1904-1908.

(5) Fusco, R.; Sannicolò, F. *J. Org. Chem.* **1984**, *49*, 4374-4378.