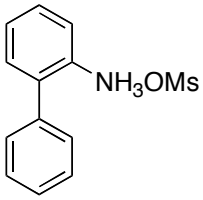
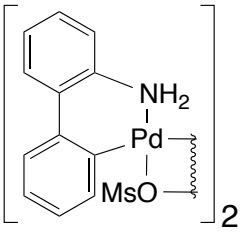
General: Reagent Information. THF, Et_2O, CH_2Cl_2 and toluene were purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF and Et_2O) or through neutral alumina and copper (II) oxide (for toluene and CH_2Cl_2). All reagents and solvents were purchased and used as received unless otherwise noted. The 0.5 M K_3PO_4 solution was prepared by dissolving K_3PO_4 (10.6 g, 50 mmol) in deionized water (100 mL) and degassed by performing several evacuation/argon refill cycles under sonication prior to use. 2-Aminobiphenyl (97%) was purchased from Aldrich Chemical Co (The MSDS for this compound should be read carefully prior to its use). Methanesulfonic acid (98%) was purchased from Fluka Chemicals. 2-Furanylboronic acid and 3-thienylboronic acid were purchased from Aldrich Chemical Co. Palladium acetate was received a gift from BASF and Strem. XPhos was received as a gift from Saltigo. *t*-ButylXPhos was received as a gift from Strem. *(±)*-BINAP was received as a gift from Rhodia. RuPhos, SPhos and XantPhos were purchased from Aldrich Chemical Co. BrettPhos was received as a gift from Aldrich Chemical Co. Aryl halides, amines, and arylboronic acids were purchased from Aldrich Chemical Co, Alfa Aesar, Acros Organics, Frontier Scientific, or TCI America and used as received. Anhydrous cesium carbonate was purchased from Strem. Sodium *t*-butoxide was purchased from Aldrich Chemical Company. The bases were stored in a nitrogen-filled glovebox and were taken out in small quantities and stored in a desiccator on the bench top for up to two weeks. Flash chromatography was performed with SiliCycle *SiliaFlash® F60* silica gel.

General Analytical Information: Compounds were characterized by ^1H NMR, ^{13}C NMR, and ^{31}P NMR (where applicable). Copies of the ^1H, ^{13}C, and ^{31}P NMR spectra can be found at the end of the Supporting Information. Proton and carbon Nuclear Magnetic Resonance spectra were recorded on a Varian 500 MHz instrument. Phosphorus Nuclear Magnetic Resonance spectra were recorded on a Varian 300 MHz instrument. All 1H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), methanol (3.31 ppm), or acetonitrile (1.94 ppm) in the deuterated solvent. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), methanol (49.00 ppm) or acetonitrile (118.26 ppm) and all were obtained with ^1H decoupling. All 31P NMR spectra are reported in ppm relative to 85% aq. phosphoric acid (0.00 ppm). All GC analyses were performed on an Agilent 6890 gas chromatograph with an FID detector using a J & W DB-1 column.

General Procedural Information



2-Ammoniumbiphenyl mesylate: A 300 mL round-bottomed flask equipped with a magnetic stir bar was charged with a stir bar, 2-aminobiphenyl (5.07 g, 30.0 mmol, 1.0 eq) and diethyl ether (100 mL). A solution of methanesulfonic acid (1.94 mL, 30.0 mmol, 1.0 eq) in diethyl ether (15 mL) was added slowly and the mixture was stirred for 30 min. The reaction mixture was then filtered, washed with diethyl ether (3x15 mL) and dried under vacuum to provide the title compound as a white solid. Yield: 7.81 g, 97%. ^{1}H NMR (300 MHz, CD_3OD) ∂ 7.64 - 7.40 (m, 9H), 4.93 (s, 2H), 2.68 (s, 3H) ppm. ^{13}C NMR (126 MHz, CD_3OD) ∂ 137.35, 136.48, 131.80, 129.46, 129.18, 129.14, 129.02, 128.70, 127.88, 123.91, 38.36 ppm. IR (neat, cm^{-1}): 3033, 1482, 1229, 1126, 774, 763, 701.

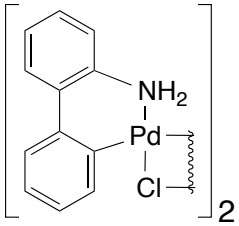


***μ*-OMs Dimer 5:** A 300 mL round-bottomed flask equipped with a magnetic stir bar and fitted with a rubber septum was charged with 2-ammoniumbiphenyl mesylate (7.89 g, 30.0 mmol, 1.00 eq) and palladium acetate (6.72 g, 30.0 mmol, 1.00 eq). The flask was evacuated and backfilled with argon (this sequence was repeated three times), after which 120 mL anhydrous toluene was added. The mixture was stirred at 50° C for 45 min or until it became milky and off-white in appearance. After cooling to room temperature the suspension was filtered, washed with toluene (25 mL) and diethyl ether (3x25 mL), and dried under vacuum for 24 hours to provide the title compound as an off-white to tan solid. Yield: 10.2 g, 92%. ^{1}H NMR (500 MHz, CD_3CN) ∂ 7.63 - 7.59 (m, 1H), 7.47 (dd, J = 7.6, 1.6 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.32 - 7.25 (m, 2H), 7.22 (dd, J = 7.8, 1.1 Hz, 1H), 7.17 (td, J = 7.4, 1.2 Hz, 1H), 7.08 (td, J = 7.5,

1.6 Hz, 1H), 6.49 (bs, 2H), 2.56 (s, 3H) ppm. ^{13}C NMR (126 MHz, CD_3CN) ∂ 139.53, 139.09, 137.08, 136.70, 135.94, 128.13, 128.09, 127.39, 126.49, 126.32, 125.44, 120.83, 39.33 ppm. IR (neat, cm^{-1}): 3259, 3210, 1571, 1497, 1425, 1233, 1104, 1023, 760, 739, 590. Anal. Calcd. for $C_{26}H_{26}NO_3PdS$: C, 42.23; H, 3.54. Found: C, 42.51; H, 3.63.

Procedure for large-scale preparation of *μ*-OMs dimer – 2-Ammoniumbiphenyl mesylate: To a 3-necked round-bottomed flask fitted with a mechanical stirrer, nitrogen inlet and addition funnel was added isopropyl acetate (2.5 L) and 2-aminobiphenyl (500 g, 3 mol). The reaction was aged for 30 minutes until the 2-aminobiphenyl was almost completely dissolved. The reaction was then cooled to 10 ºC and methanesulfonic acid added (192 mL, 3 mol) over 30 minutes. The reaction was aged for 2 h after which time the resultant white solid was collected by filtration and washed with isopropyl acetate (2 x 150 mL). The solid was dried by pulling N_2 through the cake for 24 h with intermittent agitation of the solid. Yield: 779 g, 99%. ^{1}H NMR (500 MHz, CD_3CN) ∂ 7.62 - 7.56 (1H, m), 7.45 (1H, dd, J = 7.5, 1.6), 7.38-7.36 (1H, m), 7.30-7.25 (2H, m), 7.20-7.15 (2H, m), 7.07 (1H, td, J = 7.5, 1.6), 6.1 (2H, br s), 2.53 (3H, s).

***μ*-OMs Dimer 5:** To a nitrogen flushed 3-necked round-bottomed flask fitted with a thermocouple and mechanical stirrer was added toluene (2.1 L). The toluene was sparged with N_2 for 30 minutes before adding 2-ammoniumbiphenyl mesylate (315 g, 1.186 mol, 1.01 eq) and palladium acetate (264 g, 1.175 mol, 1.00 eq) under a gentle flow of N_2. The dark orange slurry was heated to 65 ºC for 1.75 h after which time the slurry changed from brown to light yellow in color. The reaction was cooled to 18 ºC and treated with methyl *t*-butyl ether (0.5 L). The resultant solid was collected via filtration and the cake washed with 500 mL of 1:1 toluene / methyl *t*-butyl ether. The solid was dried by pulling N_2 through the cake for 24 h with intermittent agitation of the solid . Yield: 417 g, 96%. ^{1}H NMR (500 MHz, CD_2Cl_2 / d^5-pyr) ∂ 7.62 (1H, dd, J = 7.6, 1.3), 7.46 (1H, dd, J = 7.6, 1.5), 7.34 (1H, dd, J = 7.6, 1.3), 7.27 (1H, td, J = 7.5, 1.3), 7.21 (1H, td, J = 7.5, 1.3), 7.11 (1H, td, J = 7.5, 1.2), 6.87 (1H, td, J = 7.6, 1.5), 6.51 (1H, td, J = 7.6, 1.2), 6.28 (2H, br. s), 2.58 (3H, s).



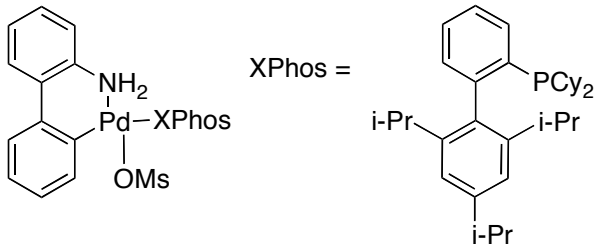
***μ*-Cl Dimer 7:** A 24 mL test tube equipped with a magnetic stir bar and fitted with a Teflon septum was charged with 2-ammoniumbiphenyl chloride (205 mg, 1.00 mmol, 1.00 eq) and palladium acetate (224 mg, 1.00 mmol, 1.00 eq). The tube was evacuated and backfilled with argon. This sequence was repeated three times, after which anhydrous acetonitrile (5 mL) was added. The mixture was stirred at 40° C overnight, until becoming a milky suspension. After cooling to room temperature the reaction mixture was diluted with diethyl ether (20 mL) and pentane (10 mL), filtered and washed with diethyl ether (2x10 mL). It was then dried under vacuum for 24 hours to provide the title compound as an off-white solid. Yield: 272 mg, 88%. ^{1}H NMR (500 MHz, DMSO) *∂* 7.55 (dd, *J* = 13.9, 9.9 Hz, 1H), 7.49 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.46 - 7.35 (m, 2H), 7.22 - 7.08 (m, 4H), 6.37 (s, 1H) ppm. ^{13}C NMR (126 MHz, DMSO) *∂* 148.71, 141.33, 139.70, 138.16, 137.30, 136.17, 128.17, 128.11, 126.38, 125.81, 125.57, 121.59 ppm. IR (neat, cm^{-1}): 3255, 3115, 1568, 1495, 1416, 1113, 1029, 940, 776, 698.

Procedure for large-scale preparation of *m*-Cl dimer – 2-Ammoniumbiphenyl chloride: Isopropyl acetate (600 mL) was charged to a 1 L 3-necked, round-bottomed flask fitted with a mechanical stirrer, N_2 inlet and thermocouple. To this was added methanol (35.9 mL, 0.866 mol) followed by trimethylsilyl chloride (85 mL, 0.665 mol). The solution was aged at 22 ºC for 1 h before adding 2-aminobiphenyl (75 g, 0.443 mol). The 2-aminobiphenyl hydrochloride formed a thick slurry which was stirred continuously for 3 h. The solid was collected by filtration, washed with IPAc (3 x 100 mL) and dried via pulling N_2 through the cake for 24 h. Yield: 90 g, 99%. ^{1}H NMR (500 MHz, CD_3CN) *∂* 7.59 - 7.54 (1H, m), 7.46-7.37 (1H, m), 7.32-7.20 (4H, m), 7.15-7.02 (2H, m), 5.55-5.39 (2H, br d).

***μ*-Cl Dimer 7:** To a 3-necked round-bottomed flask fitted with an overhead stirrer, N_2 inlet and thermocouple was added 2-aminobiphenyl hydrochloride (99.9 g, 0.486 mol) and THF (1000 mL). The

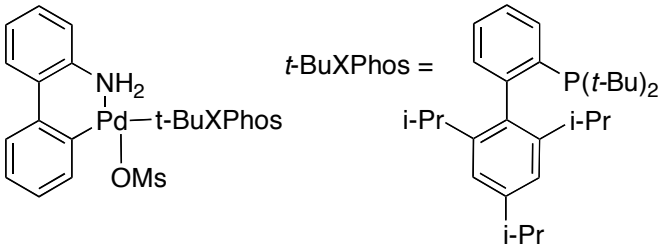
solution was sparged with N_2 for 10 minutes before adding palladium acetate (109 g, 0.486 mol). The slurry was heated to 60 ºC for 75 minutes before cooling to 20 ºC at which point a thick precipitate formed. Heptane (500 mL) was added over 5 minutes and the slurry aged for 15 minutes. The solid was collected by filtration and washed with 2:1 THF / heptane (2 x 500 mL) then MeOH (500 mL). The pale yellow solid was then dried for 24 h by pulling N_2 through the cake. Yield: 149 g, 94%. ^{1}H NMR (500 MHz, CD_2Cl_2 / d^5-pyr) ∂ 7.64 (1H, dd, J = 7.6, 1.4), 7.50 (1H, dd, J = 7.7, 1.5), 7.30 (2H, m), 7.23 (1H, td, J = 7.5, 1.6), 7.13 (1H, td, J = 7.4, 1.2), 6.86 (1H, td, J = 7.7, 1.6), 6.53 (1H, dd, J = 7.6, 1.2), 5.57 (2H, br. s).

General Procedure for Preparing Precatalysts 6a – 6n; **General Procedure A:** A test tube, equipped with a magnetic stir bar and fitted with a Teflon screw-cap, was charged with μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq) and ligand (1.00 mmol, 1.00 eq). The tube was sealed and evacuated and backfilled with argon (this was repeated two times), after which THF or DCM (5 mL) was added and the reaction was stirred for 15 min to 1 h. The reaction progress was monitored by ^{31}P NMR, observing the disappearance of free ligand signal and appearance of the precatalyst signal downfield. After completion, the reaction mixture was transferred to a scintillation vial and the solvent was removed under vacuum at room temperature until ~10% remained. The residue was then triturated with pentane. The resulting solid was isolated via filtration and further dried under vacuum.

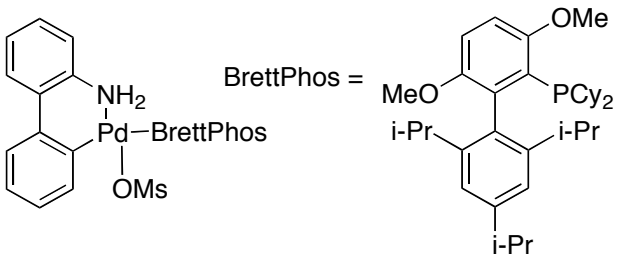


Precatalyst 6a: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), XPhos (477 mg, 1.00 mmol, 1.00 eq) and THF (10 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford

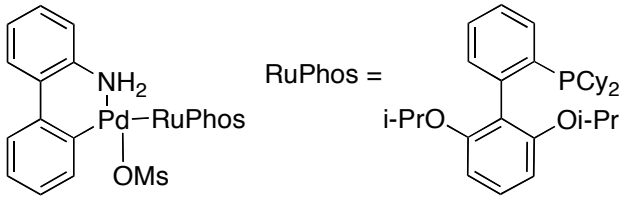
6a as an off-white solid. Yield: 740 mg (88%). ^{1}H NMR (500 MHz, CD_3OD) ∂ 7.97 (ddt, *J* = 8.0, 6.9, 3.2 Hz, 1H), 7.65 - 7.49 (m, 5H), 7.32 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.29 - 7.19 (m, 4H), 7.17 - 7.08 (m, 1H), 7.04 - 6.91 (m, 2H), 3.37 (h, *J* = 6.9 Hz, 1H), 2.93 (hept, *J* = 6.7 Hz, 1H), 2.69 (s, 3H), 2.55 (tdt, *J* = 12.3, 7.1, 2.4 Hz, 1H), 2.33 (ddt, *J* = 23.8, 20.8, 10.3 Hz, 2H), 2.20 - 2.06 (m, 1H), 2.06 - 1.75 (m, 9H), 1.71 - 1.49 (m, 7H), 1.49 - 0.98 (m, 11H), 0.97 - 0.72 (m, 7H), 0.17 (qdd, *J* = 13.7, 6.1, 4.1 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CD_3OD) - 156.26, 155.25, 150.83, 144.91, 140.63, 139.91, 139.51, 135.18, 133.96, 133.19, 133.10, 132.88, 131.76, 128.57, 128.54, 128.15, 127.30, 127.21, 127.10, 125.98, 124.79, 123.60, 121.19, 67.69, 38.40, 35.83, 35.59, 34.48, 34.17, 32.77, 31.99, 31.80, 31.41, 29.97, 29.62, 27.81, 27.53, 27.45, 26.25, 26.13, 26.03, 25.67, 25.35, 24.86, 24.53, 24.34, 23.33, 23.15, 22.95, 22.26, 13.29 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 65.21, 35.86 ppm. IR (neat, cm^{-1}): 2958, 2932, 2852, 1461, 1239, 1138, 1030, 1002, 877, 748, 736.



Precatalyst 6b: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), *t*-BuXPhos (424 mg, 1.00 mmol, 1.00 eq) and DCM (10 mL) was stirred at room temperature for 1 hour. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6b** as a yellow solid. Yield: 780 mg (94%) ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) ∂ 7.96 (dd, *J* = 9.3, 6.4 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.51 ∂ 7.42 (m, 3H), 7.40 ∂ 7.32 (m, 2H), 7.16 ∂ 7.00 (m, 5H), 6.88 (dt, *J* = 5.1, 3.5 Hz, 1H), 6.79 ∂ 6.67 (m, 2H), 3.39 (dt, *J* = 13.7, 7.0 Hz, 1H), 2.95 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.32 (d, *J* = 17.3 Hz, 3H), 2.05 ∂ 1.80 (m, 4H), 1.61 ∂ 1.40 (m, 15H), 1.34 ∂ 1.02 (m, 12H), 1.02 ∂ 0.77 (m, 10H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 158.13, 156.41, 152.01, 140.58, 139.24, 139.17, 137.39, 136.60, 135.43, 134.13, 131.00, 128.19, 127.96, 127.38, 127.17, 127.05, 126.78, 125.93, 125.42, 123.79, 120.73, 39.31, 39.16, 39.02, 38.88, 38.76, 34.38, 33.32, 32.10, 32.07, 31.36, 30.77, 30.73, 26.70, 25.99, 24.80, 24.47, 24.44, 24.10 ppm. ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 57.17 ppm. IR (neat, cm^{-1}):

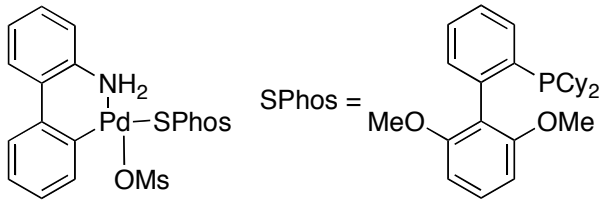


Precatalyst 6c: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), BrettPhos (537 mg, 1.00 mmol, 1.00 eq) and DCM (10 mL) was stirred at room temperature for 1 hour. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6c** as a yellow solid. Yield: 838 mg (94%) ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.47 - 7.34 (m, 2H), 7.25 (d, J = 1.8 Hz, 1H), 7.20 - 6.89 (m, 8H), 6.83 - 6.74 (m, 1H), 5.74 - 5.61 (m, 1H), 3.83 (s, 3H), 3.79 (s, 0H), 3.40 (s, 3H), 3.30 (hept, J = 7.8, 7.4 Hz, 1H), 2.82 (h, J = 6.7 Hz, 1H), 2.76 - 2.61 (m, 2H), 2.05 (d, J = 10.4 Hz, 1H), 1.66 - 1.54 (m, 1H), 1.54 - 1.09 (m, 11H), 1.10 - 0.60 (m, 12H), 0.28 (qdd, J = 12.8, 6.4, 3.4 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 156.33, 155.52, 155.00, 154.63, 151.84, 143.68, 140.41, 139.85, 136.40, 135.33, 134.80, 128.72, 128.25, 126.95, 126.73, 125.97, 124.44, 123.26, 120.89, 118.64, 115.30, 112.47, 55.58, 54.94, 39.37, 34.36, 34.19, 33.96, 33.02, 32.86, 30.89, 29.86, 29.49, 28.31, 27.96, 27.08, 26.78, 26.30, 25.93, 24.89, 24.84, 24.69, 24.46 ppm (Observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 43.33 ppm. IR (neat, cm^{-1}): 2922, 2852, 1577, 1462, 1443, 1254, 1224, 1183, 1034, 1008, 892, 926, 768, 724.

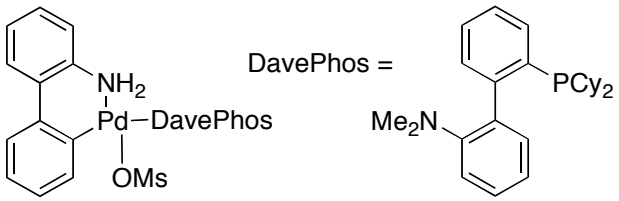


Precatalyst 6d: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), RuPhos (466 mg, 1.00 mmol, 1.00 eq) and THF (4 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6d** as a pale yellow solid. Yield: 780 mg (91%). ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.40 (t, J = 8.4 Hz, 1H),

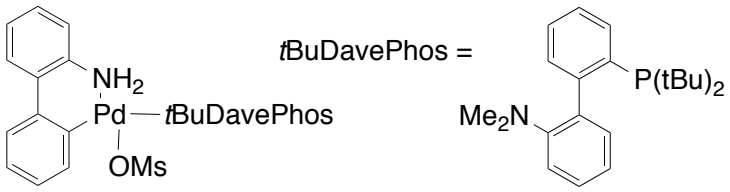
7.57 - 7.49 (m, 1H), 7.46 - 7.30 (m, 5H), 7.23 - 6.97 (m, 7H), 6.96 - 6.87 (m, 2H), 6.76 - 6.70 (m, 1H), 5.08 (d, J = 10.6 Hz, 1H), 4.77 (hept, J = 6.1 Hz, 1H), 4.43 (hept, J = 6.0 Hz, 1H), 3.73 (dddd, J = 7.0, 4.8, 2.4, 1.2 Hz, 1H), 3.35 (d, J = 11.1 Hz, 1H), 2.68 (s, 3H), 2.36 - 2.23 (m, 2H), 1.98 - 1.74 (m, 4H), 1.63 - 1.40 (m, 7H), 1.38 - 1.25 (m, 2H), 1.27 - 0.75 (m, 12H), 0.67 (d, J = 6.0 Hz, 3H), -0.10 (d, J = 11.3 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 162.51, 161.59, 145.11, 142.35, 140.34, 138.55, 137.77, 136.09, 132.22, 131.58, 128.96, 128.69, 127.71, 127.32, 127.17, 125.65, 121.57, 107.54, 106.12, 100.50, 72.56, 71.99, 40.18, 36.02, 35.78, 31.09, 29.93, 28.06, 27.79, 27.67, 27.33, 26.78, 26.40, 26.02, 22.73, 22.47, 22.40, 21.74, 21.64 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 41.57 ppm. IR (neat, cm^{-1}): 2926, 1569, 1455, 1215, 1184, 1106, 1032, 779, 761, 613.



Precatalyst 6e: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), SPhos (410 mg, 1.00 mmol, 1.00 eq) and THF (4 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6e** as an off-white solid. Yield: 712 mg (92%) ^{1}H NMR (500 MHz, CD_3OD) ∂ 8.08 (t, 1H), 7.81 (t, 1H), 7.57 (dd, 1H), 7.55 - 7.44 (m, 2H), 7.34 (dd, 1H), 7.32 - 7.22 (m, 4H), 7.13 (d, 1H), 7.08 (dd, 1H), 6.97 (d, 1H), 3.95 (s, 3H), 3.42 (s, 3H), 2.69 (s, 3H), 2.47 (m, 1H), 2.31 - 2.11 (m, 2H), 2.10 - 1.47 (m, 8H), 1.46 - 0.78 (m, 12H), -0.07 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 167.35, 166.00, 146.89, 146.74, 145.46, 144.05, 143.93, 140.95, 139.50, 139.45, 139.30, 139.24, 136.01, 135.28, 135.19, 132.18, 131.17, 130.87, 130.75, 129.53, 124.35, 109.97, 109.09, 108.61, 59.58, 59.07, 42.25, 39.27, 39.02, 34.58, 34.37, 33.03, 32.99, 31.53, 31.50, 31.47, 31.38, 31.21, 31.14, 30.25, 30.22, 30.12, 30.05, 29.67, 29.50 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 43.18 ppm. IR (neat, cm^{-1}): 2929, 1586, 1470, 1427, 1243, 1139, 1108, 1034, 1002, 768, 749, 728.

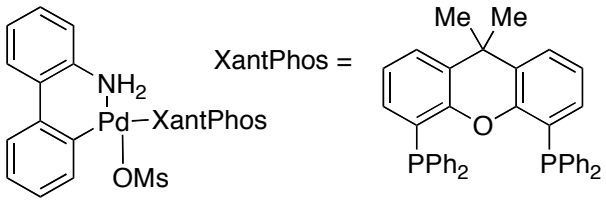


Precatalyst 6f: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), DavePhos (394 mg, 1.00 mmol, 1.00 eq) and THF (4 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6f** as a bright yellow solid. Yield: 735 mg (97%) ^{1}H NMR (500 MHz, CD_3OD) ∂ 7.86 (td, J = 7.7, 1.4 Hz, 1H), 7.72 (ddd, J = 8.1, 7.4, 1.7 Hz, 1H), 7.53 - 7.40 (m, 4H), 7.36 (dd, J = 7.4, 1.6 Hz, 1H), 7.30 (dt, J = 7.1, 1.4 Hz, 1H), 7.28 - 7.14 (m, 5H), 7.11 (td, J = 7.3, 0.9 Hz, 1H), 6.93 (dd, J = 7.8, 1.2 Hz, 1H), 2.83 - 2.71 (m, 1H), 2.69 (s, 3H), 2.59 (s, 7H), 2.32 (dddd, J = 25.1, 12.8, 9.1, 2.1 Hz, 1H), 2.24 - 2.09 (m, 2H), 2.01 - 1.90 (m, 1H), 1.90 - 1.79 (m, 1H), 1.77 - 1.42 (m, 5H), 1.42 - 1.23 (m, 2H), 1.11 - 0.65 (m, 5H), -0.12 - -0.25 (m, 1H) ppm. ^{13}C NMR (126 MHz, CD_3OD) ∂ 156.57, 143.89, 140.24, 139.87, 136.42, 134.15, 133.48, 131.99, 130.84, 128.26, 127.85, 127.82, 127.57, 127.22, 126.92, 125.37, 121.08, 120.36, 118.43, 115.72, 42.34, 38.32, 36.12, 32.88, 32.48, 28.49, 27.92, 27.66, 27.03, 26.48, 26.14, 25.97, 25.52 ppm (Observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 38.99 ppm. 2927, 2854, 1578, 1493, 1420, 1213, 1187, 1028, 1020, 748, 740, 615. IR (neat, cm^{-1}):

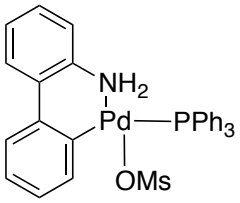


Precatalyst 6g: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), *t*BuDavePhos (341 mg, 1.00 mmol, 1.00 eq) and THF (4 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6g** as a bright yellow solid. Yield: 690 mg (97%) ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.04 (ddd, J = 8.3, 7.4, 1.7 Hz, 1H), 7.84 (ddd, J = 7.9, 6.4, 1.3 Hz, 1H), 7.52 (ddd, J = 7.5, 3.8, 1.3 Hz, 1H), 7.49 (dd, J = 8.3,

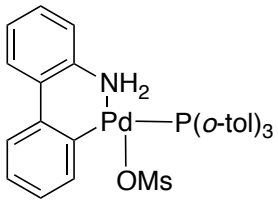
1.0 Hz, 1H), 7.40 - 7.33 (m, 1H), 7.33 - 7.25 (m, 2H), 7.23 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.19 - 7.10 (m, 4H), 7.10 - 7.01 (m, 4H), 5.23 - 5.15 (m, 1H), 3.03 (d, *J* = 11.1 Hz, 1H), 2.65 (s, 6H), 2.59 (s, 3H), 1.69 (d, *J* = 14.2 Hz, 9H), 0.84 (d, *J* = 14.8 Hz, 9H) ppm. ^{13}C NMR (126 MHz, CD_3OD) ∂ 156.85, 144.47, 139.41, 137.83, 136.98, 134.41, 131.70, 131.29, 131.22, 129.95, 128.19, 127.47, 127.27, 126.78, 126.47, 126.42, 125.51, 121.94, 120.18, 118.28, 115.49, 114.42, 67.69, 42.38, 39.31, 39.17, 39.02, 38.91, 38.35, 32.04, 32.00, 29.36, 29.32, 25.34 ppm (Observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 58.60 ppm.



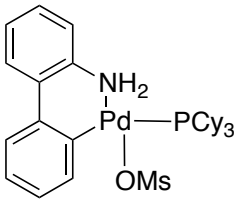
Precatalyst 6h: Following General Procedure A, a mixture of *μ*-OMs dimer **5** (370 mg, 0.500 mmol, 0.50 eq), XantPhos (578 mg, 1.00 mmol, 1.00 eq) and DCM (5 mL) was stirred at room temperature for 1 hour. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6h** as a yellow solid. Yield: 820 mg (87%) ^{1}H NMR (500 MHz, CD_3OD) ∂ 7.88 (d, *J* = 6.9 Hz, 2H), 7.58 - 7.49 (m, 3H), 7.44 (dd, *J* = 18.0, 8.1 Hz, 4H), 7.38 - 7.11 (m, 13H), 7.10 - 6.92 (m, 7H), 6.82 (t, *J* = 7.1 Hz, 2H), 6.69 (dt, *J* = 19.3, 8.3 Hz, 4H), 6.16 (d, *J* = 7.7 Hz, 1H), 2.68 (s, 3H), 1.76 (d, *J* = 5.3 Hz, 6H) ppm. ^{13}C NMR: A suitable spectrum could not be obtained. ^{31}^{31}P NMR (121 MHz, CD_2Cl_2) ∂ 41.38 , 23.49 , 16.31 (d, *J* = 28.9 Hz), 2.23 (d, *J* = 24.7 Hz) ppm. IR (neat, cm^{-1}): 2927, 1570, 1481, 1435, 1408, 1183, 1094, 1036, 1000, 739, 707, 616.



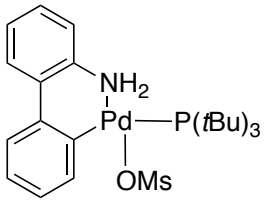
Precatalyst 6i: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), triphenylphosphine (262 mg, 1.00 mmol, 1.00 eq) and THF (5 mL) was stirred at rt for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated with pentane, filtered and dried under vacuum for 24 hours to provide **6i** as a white solid. Yield 562 mg, 88%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.58 - 7.52 (m, 1H), 7.50 - 7.38 (m, 10H), 7.34 - 7.23 (m, 10H), 6.95 - 6.88 (m, 1H), 6.46 (dddd, J = 7.8, 7.0, 1.6, 0.8 Hz, 1H), 6.42 (ddd, J = 7.7, 5.9, 1.3 Hz, 1H), 4.54 (s, 1H), 2.36 (s, 3H), ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 139.96, 138.34, 138.31, 134.95, 134.86, 130.94, 130.92, 129.67, 129.28, 128.62, 128.53, 128.51, 127.79, 127.44, 126.50, 125.84, 125.64, 121.16, 77.54, 77.28, 77.03, 39.27 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 34.40. IR (neat, cm-1): 3270, 1571, 1491, 1481, 1435, 1249, 1136, 1098, 1033, 1001, 744, 727, 707, 691.



Precatalyst 6j: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), tri(*o*-tolyl)phosphine (304 mg, 1.00 mmol, 1.00 eq) and THF (5 mL) was stirred at rt for 30 min. After removal of 90% of the solvent under vacuum the crude product was triturated with pentane, filtered and dried under vacuum for 24 hours to provide **6j** as a white solid. Yield: 552 mg, 84%. Complex NMR spectra likely due to rapid exchange in solution. IR (neat, cm^{-1}): 3047, 1590, 1495, 1448, 1223, 1134, 1045, 1019, 1002, 804, 717, 676.

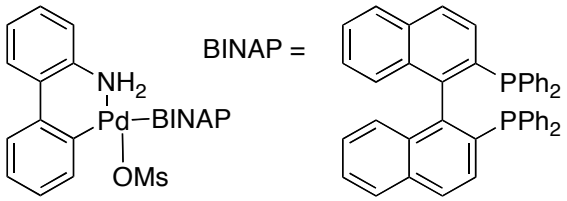


Precatalyst 6k: Following General Procedure A, in a nitrogen glove box, a mixture of μ-OMs dimer **5** (370 mg, 0.500 mmol, 0.500 eq), tricyclohexylphosphine (280 mg, 1.00 mmol, 1.00 eq) and THF (5 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum, the crude product was triturated from pentane and dried under vacuum for 24 h to afford **6k** as a white solid. Yield: 620 mg, 95%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.42 - 7.35 (m, 2H), 7.30 - 7.25 (m, 1H), 7.25 - 7.13 (m, 4H), 7.07 (td, J = 7.3, 1.2 Hz, 1H), 7.00 (td, J = 7.4, 1.6 Hz, 1H), 4.23 - 4.12 (m, 1H), 2.79 (s, 3H), 1.97 - 0.81 (m, 33H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 140.28, 140.10, 137.59, 137.54, 136.59, 128.40, 127.67, 127.31, 125.93, 125.60, 125.13, 120.60, 40.01, 32.84, 32.67, 30.14, 29.12, 27.94, 27.85, 27.79, 27.71, 26.51 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 38.60 ppm. IR (neat, cm^{-1}): 3137, 2925, 2850, 1613, 1491, 1440, 1236, 1152, 1070, 1032, 1002, 889, 850, 798, 735.

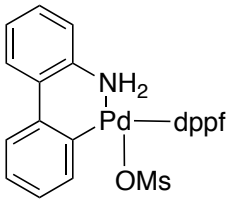


Precatalyst 6l: Following General Procedure A, in a nitrogen glove-box a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), P(tBu)$_3$ (1.00 mL, 1 M in PhMe, 1.00 mmol, 1.00 eq) and THF (5 mL) was stirred at room temperature for 30 min. After removal of 90% of the solvent under vacuum, the crude product was triturated with pentane and dried under vacuum for 24 h to afford **6l** as a brown solid. Yield: 498 mg, 87% ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.48 (d, J = 6.3 Hz, 1H), 7.40 (m, J = 7.7, 3.4, 1.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.23 (td, J = 7.6, 1.4 Hz, 1H), 7.16 (qd, J = 7.4, 1.3 Hz, 2H), 7.04 (td, J = 7.3, 0.9 Hz, 1H), 6.96 (td, J = 7.5, 1.6 Hz, 1H), 4.01 - 3.94 (m, 1H), 2.81 (s, 3H), 1.28 (d, J = 12.5 Hz, 27H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 145.83, 139.11, 138.48, 138.44, 128.64, 127.02, 126.38, 126.07, 125.66,

124.78, 119.68, 77.53, 40.41, 40.07, 40.01, 32.49, 32.47 ppm (Observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 72.00 ppm. IR (neat, cm^{-1}): 3105, 1594, 1488, 1418, 1392, 1369, 1243, 1137, 1011, 1000, 935, 773.

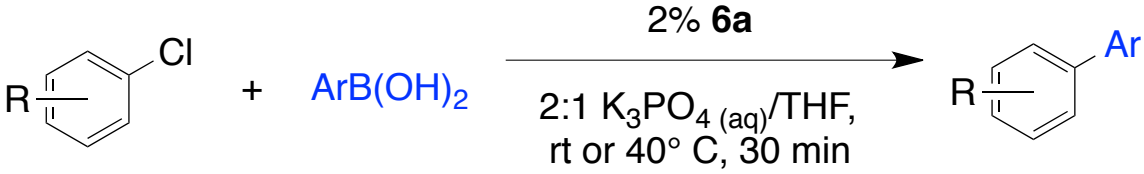


Precatalyst 6m: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), *(±)*-BINAP (622 mg, 1.00 mmol, 1.00 eq) and THF (5 mL) was stirred at room temperature for 1 hour. After removal of 90% of the solvent under vacuum the crude product was triturated from pentane to afford **6m** as a beige solid Yield: 936 mg (95%) ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.97 - 7.89 (m, 3H), 7.84 - 7.77 (m, 2H), 7.66 - 7.51 (m, 4H), 7.47 - 7.33 (m, 4H), 7.32 - 6.92 (m, 16H), 6.91 - 6.76 (m, 3H), 6.74 - 6.66 (m, 2H), 6.58 - 6.46 (m, 4H), 6.29 (tt, J = 7.4, 1.8 Hz, 1H), 6.21 (d, J = 7.6 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 140.34, 140.32, 139.49, 139.46, 139.40, 139.39, 139.36, 139.27, 139.22, 139.19, 139.18, 139.15, 139.12, 137.85, 136.64, 136.62, 135.86, 135.77, 134.89, 134.77, 134.48, 134.46, 134.33, 134.32, 133.99, 133.92, 132.78, 131.32, 131.24, 131.10, 130.79, 130.04, 129.98, 129.59, 129.51, 129.10, 129.06, 128.92, 128.79, 128.75, 128.68, 128.49, 128.41, 128.37, 128.33, 128.16, 128.13, 128.04, 127.93, 127.83, 127.64, 127.56, 127.34, 127.26, 127.14, 127.05, 126.85, 126.48, 126.31, 126.24, 126.19, 124.64, 124.30, 122.80, 122.38, 120.47, 39.64 ppm (Observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, $CDCl_3$) ∂ 36.37 (d, J = 42.2 Hz), 15.68 (d, J = 42.3 Hz) ppm. IR (neat, cm^{-1}): 3048, 1571, 1493, 1435, 1309, 1183, 1096, 1035, 816, 737, 721, 606.



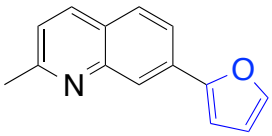
Precatalyst 6n: Following General Procedure A, a mixture of μ-OMs dimer **5** (370 mg, 0.50 mmol, 0.50 eq), 1, 1'-Bwas(diphenylphosphino)ferrocene (554 mg, 1.00 mmol, 1.00 eq) and THF (10 mL) was stirred at room temperature for 1 h. After removal of 90% of the solvent under vacuum, the crude product was triturated with pentane and dried under vacuum for 24 h to afford **6n** as an orange powder. Yield: 822 mg, 89%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.05 - 7.97 (m, 2H), 7.61 - 7.42 (m, 12H), 7.34 - 7.21 (m, 7H), 7.13 (t, J = 7.5 Hz, 1H), 7.04 (dt, J = 18.9, 5.6 Hz, 2H), 7.01 - 6.92 (m, 2H), 6.72 (dt, J = 13.9, 7.5 Hz, 2H), 6.47 (t, J = 7.3 Hz, 1H), 5.70 (d, J = 7.7 Hz, 1H), 4.37 (t, J = 13.3 Hz, 4H), 4.26 (d, J = 18.1 Hz, 2H), 3.96 (s, 1H), 3.84 (s, 1H), 2.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 140.09, 137.70, 136.09, 135.98, 135.09, 134.99, 133.71, 133.61, 133.08, 132.98, 132.35, 131.90, 131.57, 131.21, 130.89, 130.31, 130.25, 129.96, 129.89, 128.83, 128.75, 128.28, 128.19, 127.64, 127.45, 125.91, 125.49, 120.27, 76.43, 75.84, 74.52, 74.04, 73.49, 73.15, 71.13, 68.20, 39.34, 25.84 ppm (Observed complexity due to P-C splitting). ^{31}P NMR (121 MHz, CD_3OD) ∂ 32.37 (d, J = 33.7 Hz), 11.22 (d, J = 33.7 Hz) ppm. IR (neat, cm^{-1}): 3041, 1569, 1482, 1435, 1307, 1223, 1179, 1096, 1035, 825, 748, 733, 701, 629, 565.

General Procedure for the Suzuki-Miyura Coupling of Unstable Boronic Acids with Aryl Chlorides

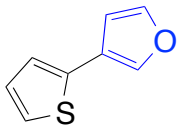


General Procedure B: A resealable tube equipped with a magnetic stir bar and Teflon septum was charged with precatalyst **6a** (2 mol%), the aryl halide (1 mmol) (if a solid), and the boronic acid (1.5 mmol). The tube was then evacuated and backfilled with argon. This process was repeated three times. Then the aryl halide (if a liquid) was added followed by THF (2 mL) and degassed 0.5 M K_3PO_4 solution (4 mL). The

reaction was then stirred at rt or 40° for 30 min. The reaction mixture was diluted with water (10 mL) and diethyl ether (10 mL) and the layers are separated. The aqueous layer was extracted with diethyl ether three times. The combined organic phases are dried over magnesium sulfate, concentrated under vacuum and purified via flash chromatography.

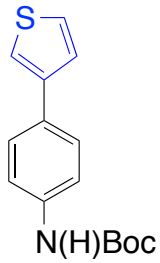


7-(furan-2-yl)-2-methylquinoline: Following general procedure B, a mixture of 7-chloro-2-methylquinoline (177 mg, 1.00 mmol, 1.00 eq), 2-furylboronic acid (168 mg, 1.50 mmol, 1.50 eq), **6a** (18.4 mg, 0.02 mmol, 2%), THF (2 mL) and 0.5 M aqueous K_3PO_4 was stirred at rt for 0.5 h. The crude product was purified by flash chromatography, eluting with with 30% ethyl acetate in hexanes, to provide the title compound as an orange solid. Yield: 198 mg, 95%. mp = 40 – 42° C. ^{1}H NMR (500 MHz, CD_3OD) ∂ 8.09 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.73 (s, 2H), 7.62 (d, J = 1.1 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 3.4 Hz, 1H), 6.55 (dd, J = 3.3, 1.7 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (126 MHz, CD_3OD) - 159.82, 153.18, 147.38, 143.29, 136.86, 132.19, 128.22, 125.95, 122.12, 121.91, 120.49, 111.94, 107.08, 23.48 ppm. IR (neat, cm^{-1}): 1623, 1512, 1219, 1156, 1011, 885, 842, 735, 594. Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.26; H, 5.30. Found: C, 79.86; H, 5.41.

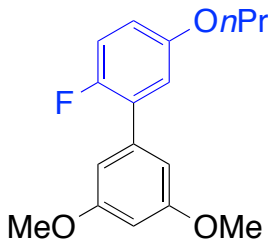


3-(thiophen-2-yl)furan: Following general procedure B, a mixture of 2-chlorothiophene (92 μL, 1.00 mmol, 1.00 eq), 3-furylboronic acid (168 mg, 1.50 mmol, 1.50 eq), **6a** (18.4 mg, 0.02 mmol, 2%), THF (2 mL) and 0.5 M aqueous K_3PO_4 was stirred at 40 °C for 30 min. The crude product was purified by flash chromatography, eluting with 10% ethyl acetate in hexanes, to provide the title compound as a light brown

oil. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.75 (dd, *J* = 1.5, 0.9 Hz, 1H), 7.50 (t, *J* = 1.7 Hz, 1H), 7.28 - 7.23 (m, 1H), 7.17 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.69 (dd, *J* = 1.9, 0.9 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 143.85, 138.46, 135.15, 127.87, 123.89, 123.67, 120.90, 109.72 ppm. IR (neat, cm^{-1}): 2924, 2851, 1602, 1451, 1327, 1260, 1238, 999, 800, 747, 721.



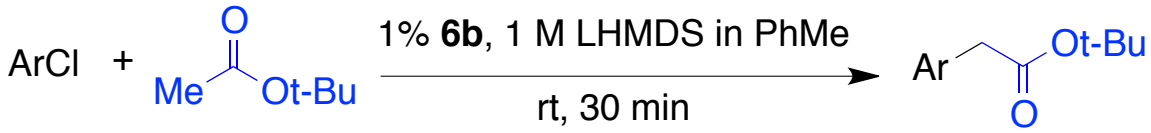
***t*-butyl 4-(4-(thiophen-3-yl)phenyl)piperazine-1-carboxylate:** Following general procedure B, a mixture of *t*-butyl (4-chlorophenyl)carbamate (228 mg, 1.00 mmol, 1.00 eq), 3-thiophenylboronic acid (192 mg, 1.50 mmol, 1.50 eq), **6a** (18.4 mg, 0.02 mmol, 2%), THF (2 mL) and 0.5 M aqueous K_3PO_4 was stirred at 40 °C for 0.5 h. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in hexanes, to provide the title compound as a white solid. Yield: 275 mg, 89%. mp = 151 – 153° C. ^{1}H NMR (500 MHz, Chloroform-d) ∂ 7.54 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.42 - 7.38 (m, 3H), 7.38 - 7.35 (m, 2H), 6.55 (s, 1H), 1.54 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 152.96, 142.08, 137.63, 131.01, 127.21, 126.41, 126.38, 119.64, 119.00, 28.60 ppm. IR (neat, cm^{-1}): 3372, 1704, 1512, 1235, 1165, 778



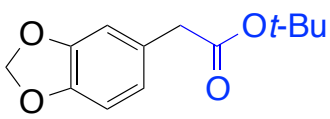
2-fluoro-5-isopropoxy-3',5'-dimethoxy-1,1'-biphenyl: Following general procedure B, a mixture of 3, 5-dimethoxychlorobenzene (172 mg, 1.00 mmol, 1.00 eq), 2-fluoro-5-isopropoxyboronic acid (297 mg, 1.50 mmol, 1.50 eq), **6a** (18.4 mg, 0.02 mmol, 2%), THF (2 mL) and 0.5 M aqueous K_3PO_4 was stirred at rt for 30 min. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in

hexanes, to provide the title compound as an orange solid. Yield: 261 mg, 90%. mp = 70 – 71° C. ^{1}H NMR (500 MHz, CD_2Cl_2) ∂ 7.12 - 7.06 (m, 1H), 6.99 (dd, *J* = 6.3, 3.1 Hz, 1H), 6.86 (dt, *J* = 8.9, 3.5 Hz, 1H), 6.73 - 6.70 (m, 2H), 6.52 (t, *J* = 2.3 Hz, 1H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 6H), 1.88 - 1.78 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) ∂ 160.98, 155.60, 155.59, 155.06, 153.15, 137.98, 129.65, 129.53, 116.77, 116.57, 116.24, 116.22, 114.83, 114.77, 107.33, 107.30, 99.90, 70.41, 55.59, 22.86, 10.48 ppm. IR (neat, cm^{-1}): 2960, 1593, 1456, 1406, 1251, 1212, 1193, 1148, 1057, 1019, 838, 809, 771, 690, 631.

General Procedure for the α-Arylation of *t*-Butyl Acetate

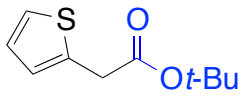


General Procedure C: An oven-dried, resealable tube was equipped with a stir bar and fitted with a Teflon screw-cap and charged with precatalyst **6b** (4 mg, 1%) and aryl halide, if solid (0.5 mmol). The flask was evacuated and backfilled with argon (this was repeated a total of three times). To this tube was then added *t*-butyl acetate (101 μL, 0.75 mmol), aryl halide, if liquid, and LHMDS (1.5 mL, 1M in toluene). The reaction was then stirred at room temperature for 30 min then shaken vigorously with 2 mL of saturated ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (5 mL) three times. The combined organic layers were concentrated by rotary evaporation and the crude products were purified by flash chromatography on silica gel, then dried under vacuum.

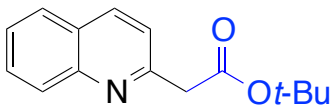


***t*-butyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate:** Following general procedure C, a mixture of 5-chloro benzo[*d*][1,3]dioxole (59 μL mg, 0.5 mmol), *t*-butyl acetate (110 μL, 0.75 mmol), precatalyst **6b** (4 mg,

0.005 mmol, 1 mol %) and LHMDS (1.5 mL, 1M in PhMe, 1.5 eq) was stirred at rt for 30 min. The crude product was purified by flash chromatography, eluting with 10% ethyl acetate in hexanes to provide the title compound as a light yellow oil. Yield: 108 mg, 91%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 6.80 - 6.74 (m, 2H), 6.73 - 6.69 (m, 1H), 5.94 (s, 2H), 3.44 (s, 2H), 1.45 (d, J = 4.2 Hz, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 171.29, 147.85, 146.71, 128.53, 122.56, 109.91, 108.44, 101.17, 81.08, 42.45, 28.28 ppm. IR (neat, cm^{-1}): 1713, 1634, 1434, 1317, 1286, 1269, 1193, 1149, 1052, 976, 758, 736.



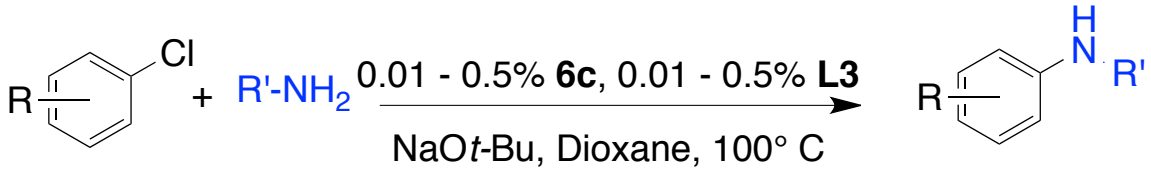
***t*-butyl 2-(thiophen-2-yl)acetate:** Following General Procedure C, a mixture of 2-chlorothiophene (46 μL, 0.5 mmol, 1.0 eq), *t*-butyl acetate (110 μL, 0.75 mmol, 1.5 eq), precatalyst **6b** (4 mg, 0.005 mmol, 1 mol %) and LHMDS (1.5 mL, 1M in PhMe, 1.5 eq) was stirred at rt for 30 min. The crude product was purified by column chromatography, eluting with 10% diethyl ether in hexanes, to provide the title compound as a brown-yellow oil. Yield: 93 mg, 95% ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.21 (d, J = 5.1 Hz, 1H), 6.98 - 6.94 (m, 1H), 6.93 (s, 1H), 3.76 (s, 2H), 1.49 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 169.95, 136.10, 126.88, 126.72, 125.08, 81.62, 37.08, 28.25 ppm. IR (neat, cm^{-1}): 1732, 1684, 1662, 1593, 1522, 1514, 1436, 1412, 1208, 1032, 834, 803, 753, 609.



***t*-butyl 2-(quinolin-2-yl)acetate:** Following General Proceure C, a mixture 2-methylquinoline (82 mg, 0.5 mmol, 1.0 eq), *t*-butyl acetate (110 μL, 0.75 mmol, 1.5 eq), precatalyst **6b** (4 mg, 0.005 mmol, 1 mol %), and LHMDS (1.5 mL, 1M in PhMe 1.5 eq) was stirred at rt for 30 min. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in hexanes, to provide the title compound as a fluorescent orange-yellow oil. Yield: 117 mg, 97%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.05 (dd, J = 13.6, 8.5 Hz, 2H), 7.74 (dd, J = 8.1, 1.3 Hz, 1H), 7.65 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.46 (ddd, J = 8.1, 6.9, 1.2 Hz,

1H), 7.39 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 2H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 169.70, 155.30, 147.75, 136.32, 129.40, 128.96, 127.44, 126.90, 126.18, 121.74, 81.24, 45.93, 28.00 ppm. IR (neat, cm^{-1}): 1723, 1597, 1366, 1268, 1257, 1128, 1116, 952, 839, 807, 782, 761, 602.

General Procedure for the C-N Cross Coupling Reaction of Primary Amines

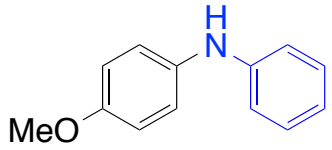


General Procedure D: An oven-dried, resealable tube equipped with a magnetic stir bar and Teflon septum was charged with precatalyst **6c** (0.01 – 1 mol%), NaO*t*-Bu (115 mg, 1.20 mmol, 1.20 eq), aryl halide (1.00 mmol, 1.00 eq) and amine (1.20 mmol, 1.20 eq) if they are solids. The tube was evacuated and backfilled with argon. This process was repeated three times. Then the aryl halide and amine are added if they are liquid, followed by 1 mL of dioxane. The reaction was heated at 100 °C and monitored by thin-layer chromatography or gas chromatography, observing the disappearance of aryl halide. After completion the reaction was cooled to room temperature, diluted with ethyl acetate, and filtered through a plug of Celite. The crude product was then purified by flash chromatography

General Procedure E: An oven-dried resealable tube equipped with a stir bar and Teflon septum was charged with precatalyst **6c** (0.01 – 1 mol%), NaO*t*-Bu (135 mg, 1.40 mmol, 1.40 eq), aryl iodide (1.00 mmol, 1.00 eq) and amine (1.40 mmol, 1.40 eq) if they are solids. The tube was evacuated and backfilled with argon. This was repeated three times. Then the aryl halide and amine are added if they are liquid, followed by 1 mL of toluene. The reaction was heated at 100 °C and monitored by thin-layer chromatography or gas chromatography, observing the dissappearance of aryl iodide. After completion the reaction was cooled to room temperature, diluted with ethyl acetate, and filtered through a plug of Celite. The crude product was then purified by column chromatography.

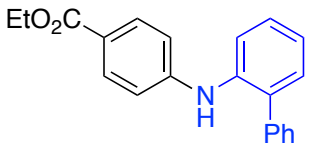
General Procedure F: An oven-dried resealable tube equipped with a stir bar and Teflon septum was charged with precatalyst **6c** (0.01 – 1 mol%), Cs_2CO_3 (391 mg, 1.20 mmol, 1.20 eq), aryl halide (1.00

mmol) and amine (1.20 mmol, 1.20 eq) if they are solids. The tube was evacuated and backfilled with argon. This was repeated three times. Then the aryl halide and amine are added if they are liquid followed by 1 mL of *t*BuOH. The reaction was heated at 100° C and monitored by thin-layer chromatography or gas chromatography, observing the disappearance of aryl halide. After completion the reaction was cooled to room temperature, diluted with ethyl acetate, and filtered through a plug of Celite. The crude product was then purified by flash chromatography.

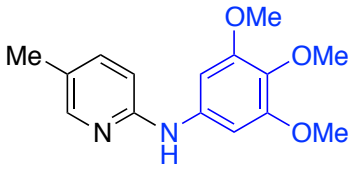


4-Methoxy-*N*-Phenylaniline: Following general procedure D, a mixture of 4-chloroanisole (123 μL, 1.00 mmol, 1.00 eq), aniline (110 μL, 1.20 mmol, 1.20 eq), NaO*t*-Bu (115 mg, 1.20 mmol, 1.20 eq), **6c** and **L3** (10 μL, 0.01 M in THF, 0.01 mol%) and dioxane (1 mL) was stirred at 100 °C for 24 h. The crude product was purified by flash chromatography, eluting with 10% ethyl acetate in hexanes, to provide the title compound as an off-white solid. Yield: 193 mg, 97%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.25 (dd, J = 15.2, 7.0 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.91 - 6.83 (m, 3H), 5.51 (s, 1H), 3.82 (s, 3H) ppm ^{13}C NMR (126 MHz, $CDCl_3$) - 155.49, 145.90, 145.39, 135.93, 129.56, 122.45, 119.80, 115.86, 114.90, 55.83 ppm. IR (neat, cm^{-1}): 2904, 1587, 1521, 1309, 1110, 808, 745.

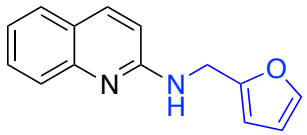
4-Methoxy-*N*-Phenylaniline: Following general procedure E, a mixture of 4-iodoanisole (234 mg, 1.00 mmol, 1.00 eq), aniline (110 μL, 1.20 mmol, 1.20 eq), NaO*t*-Bu (115 mg, 1.20 mmol, 1.20 eq), **6c** and **L3** (10 μL, 0.01 M in THF, 0.01 mol%) and THF (1 mL) was stirred at 100 °C for 5 min. The crude product was purified by flash chromatography, eluting with 10% ethyl acetate in hexanes, to provide the title compound as an off-white solid. Yield: 190 mg, 96%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.25 (dd, J = 15.2, 7.0 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.91 - 6.83 (m, 3H), 5.51 (s, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) - 155.49, 145.90, 145.39, 135.93, 129.56, 122.45, 119.80, 115.86, 114.90, 55.83 ppm.



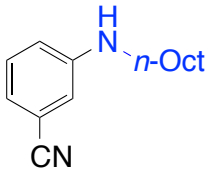
Ethyl 4-([1,1'-biphenyl]-2-ylamino)benzoate: Following general procedure F, a mixture of ethyl-4-chlorobenzoate (155 μL, 1.00 mmol, 1.00 eq), 2-aminobiphenyl (177 mg, 1.05 mmol, 1.05 eq) Cs_2CO_3 (391 mg, 1.2 mmol, 1.2 eq) **6c** (0.9 mg, 0.1 mol%) and *t*BuOH (1 mL) was stirred at 100 C° for 24 h. The crude product was purified by column chromatography, eluting with 20% ethyl acetate in hexanes, to provide the title compound as an off-white solid. Yield 288 mg, 88%. mp = 115 – 116° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.92 (d, J = 8.4 Hz, 2H), 7.51 - 7.32 (m, 7H), 7.16 (td, J = 7.5, 1.3 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 5.82 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 166.73, 148.57, 138.82, 138.14, 134.18, 131.67, 131.36, 129.45, 129.11, 128.54, 127.91, 123.67, 121.74, 121.18, 114.93, 60.69, 14.70 ppm. IR (neat, cm^{-1}): 1704, 1609, 1518, 1275, 1173, 1104, 745, 700.



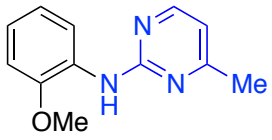
5-methyl-*N*-(3,4,5-trimethoxyphenyl)pyridin-2-amine: Following general procedure D, a mixture of 2-chloro-*5*-methylpyridine (135 μL, 1.00 mmol, 1.00 eq), 3, 4, 5-trimethoxyaniline (220 mg, 1.20 mmol, 1.20 eq), NaO*t*-Bu (115 mg, 1.20 mmol, 1.20 eq), **6c** (0.9 mg, 0.1%) and dioxane (1 mL) was stirred at 100 °C for 12 h. The crude product was purified by flash chromatography, eluting with ethyl acetate, to provide the title compound as a white solid. Yield: 245 mg, 89%. mp = 132 – 134° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.02 (d, J = 2.4 Hz, 1H), 7.31 (dd, J = 8.4, 2.4 Hz, 1H), 6.83 (s, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.57 (s, 2H), 3.82 (s, 6H), 2.21 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) - 154.62, 153.82, 148.15, 138.87, 137.45, 133.71, 124.03, 108.51, 98.21, 61.23, 56.27, 17.76 ppm. IR (neat, cm^{-1}): 1602, 1496, 1414, 1296, 1228, 1127, 1010, 818. Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.68; H, 6.61. Found: C, 65.95; H, 6.56.



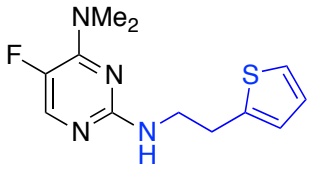
***N*-(furan-2-ylmethyl)quinolin-2-amine:** Following general procedure D, a mixture of 2-chloroquinoline (166 mg, 1.00 mmol, 1.00 eq), furfurylamine (96 μL, 1.2 mmol, 1.2 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq) **6c** (0.9 mg, 0.1 mol%) and dioxane (1 mL) was stirred at 100 C° for 20 h. The crude product was purified by column chromatography, eluting with 50% ethyl acetate in hexanes, to provide the title compound as a light yellow solid. Yield: 217 mg, 97%. mp = 152 – 153° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.81 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.53 (m, 2H), 7.39 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.28 - 7.21 (m, 1H), 6.65 (d, *J* = 8.9 Hz, 1H), 6.32 (ddd, *J* = 16.4, 3.2, 1.3 Hz, 2H), 5.12 (s, 1H), 4.75 (d, *J* = 5.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 156.52, 152.85, 148.09, 142.20, 137.60, 129.82, 127.71, 126.56, 123.86, 122.56, 111.88, 110.70, 107.49, 39.05 ppm. IR (neat, cm^{-1}): 3251, 1620, 1538, 1403, 1185, 1145, 1014, 911, 815, 755, 738. Anal. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39. Found: C,7 75.14; H, 5.55.



3-Cyano-*N*-(*n*-octly)aniline: Following general procedure F, a mixture of 3-chlorobenzonitrile (137 mg, 1.00 mmol, 1.00 eq), *n*-octylamine (202 μL, 1.20 mmol, 1.20 eq), Cs_2CO_3 (391 mg, 1.10 mmol, 1.20 eq), **6c** (0.25 mg, 0.025 mol%), and *t*BuOH (1 mL) was stirred at 100 °C for 24 h. The crude product was purified by column chromatography, eluting with 10% ethyl acetate in hexanes, to provide the title compound as a yellow oil. Yield: 213 mg, 93%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.23 - 7.17 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.80 - 6.72 (m, 2H), 3.94 (s, 1H), 3.08 (dd, *J* = 12.0, 7.0 Hz, 2H), 1.68 - 1.56 (m, 2H), 1.45 - 1.21 (m, 10H), 0.90 (dt, *J* = 13.9, 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 148.95, 130.05, 120.39, 119.90, 117.32, 114.79, 112.99, 43.81, 32.06, 29.61, 29.49, 29.42, 27.33, 22.91, 14.37 ppm. IR (neat, cm^{-1}): 2924, 2187, 1602, 1581, 1334, 843, 777, 680.

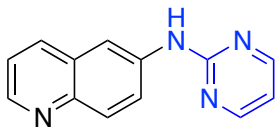


N-(2-methoxyphenyl)-4-methylpyrimidin-2-amine: Following general procedure D, a mixture of 2-chloroanisole (123 μL, 1.00 mmol, 1.00 eq), 2-amino-4-methylpyrimidine (131 mg, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **6c** (0.9 mg, 0.1 mol%) and *t*BuOH (1 mL) was stirred at 100 C° for 12 hours. The crude product was purified by flash chromatography, eluting with 50% ethyl acetate in hexanes, to provide the title compound as an off-white solid. Yield: 200 mg, 93%. mp = 61 – 62° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.61 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.27 (d, *J* = 5.0 Hz, 1H), 7.77 (s, 1H), 7.01 (td, *J* = 7.7, 1.5 Hz, 1H), 6.96 (td, *J* = 7.7, 1.7 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.54 (d, *J* = 5.0 Hz, 1H), 3.85 (s, 3H), 2.40 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 168.15, 160.10, 157.61, 147.97, 129.67, 121.69, 121.09, 118.55, 112.28, 110.07, 55.83, 24.41 ppm. IR (neat, cm^{-1}): 3423, 1528, 1446, 1238, 1117, 1023, 787, 749, 618. Anal. Calcd. for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09. Found: C, 66.98; H, 6.20.



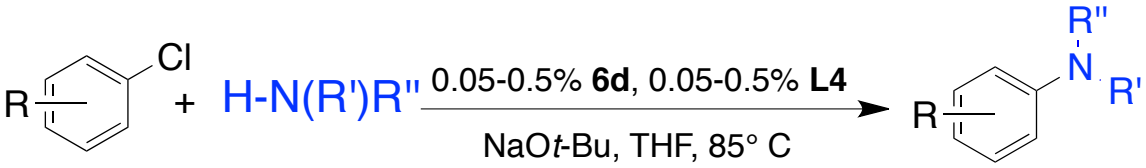
5-fluoro-*N*^{4},*N*^{4}-dimethyl-*N*^{2}-(2-(thiophen-2-yl)ethyl)pyrimidine-2,4-diamine: Following general procedure D, a mixture of 2-chloro-5-fluoro-*N*,*N*-dimethylpyrimidin-4-amine (175 mg, 1.00 mmol, 1.00 eq), 2-thiopheneethylamine (140 μL, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq) **6c** (0.9 mg, 0.1 mol%) and dioxane (1 mL) was stirred at 100 C° for 20 h. The crude product was purified by flash chromatography, eluting with 50% ethyl acetate in hexanes, to provide the title compound as a light yellow, crystalline solid. Yield: 242 mg, 91%. mp = 73° C. ^{1}H NMR (500 MHz, $CDCl_3$) - 7.67 (d, *J* = 6.9 Hz, 1H), 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.85 - 6.81 (m, 1H), 5.13 (s, 1H), 3.59 (q, *J* = 6.8 Hz, 2H), 3.15 (d, *J* = 2.2 Hz, 6H), 3.09 (t, *J* = 6.9 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 158.11, 158.09, 152.74, 152.69, 142.63, 142.42, 142.36, 140.75, 127.14, 125.32, 123.83, 77.62, 77.37, 77.11, 43.84, 38.94, 38.88, 30.44 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) ∂ -162.97 ppm. IR (neat, cm^{-1}): 3242, 1599,

1540, 1446, 1420, 1401, 1216, 1112, 770, 692. Anal. Calcd. for $C_{12}H_{15}FN_4S$: C, 54.11; H, 5.68. Found: C, 54.20; H, 5.64.



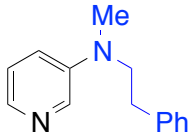
***N*-(pyrimidin-2-yl)quinolin-6-amine:** Following general procedure D, a mixture of 6-chloroquinoline (166 mg, 1.00 mmol, 1.00 eq), 2-aminopyrimidine (115 mg, 1.20 mmol, 1.20 eq), NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq) **6c** (0.9 mg, 0.1 mol%) and dioxane (1 mL) was stirred at 100 C° for 24 hours. The crude product was purified by column chromatography, eluting with 50% ethyl acetate in hexanes, to provide the title compound as a light yellow solid. Yield: 200 mg, 90%. mp = 149 – 150° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.78 (dd, J = 4.2, 1.7 Hz, 1H), 8.49 (d, J = 4.8 Hz, 2H), 8.43 - 8.35 (m, 2H), 8.13 - 8.07 (m, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.72 (dd, J = 9.1, 2.5 Hz, 1H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 6.77 (t, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 160.30, 158.25, 148.77, 145.11, 137.83, 135.70, 130.18, 129.34, 124.10, 121.67, 114.48, 113.27 ppm. IR (neat, cm^{-1}): 1566, 1534, 1450, 1024, 787, 751, 620.

General Procedure for the C-N Cross Coupling Reaction of Primary Amines

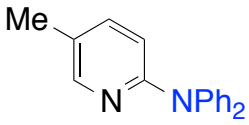


General Procedure G: An oven-dried resealable tube equipped with a stir bar and Teflon septum was charged with precatalyst **6d** (0.01 – 1 mol%), NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), aryl halide (1.00 mmol) and amine (1.20 mmol, 1.20 eq) if they are solids. The tube was evacuated and backfilled with argon. This was repeated three times. Then the aryl halide and amine are added if they are liquid followed

by 1 mL of THF. The reaction was heated at 85° C and monitored by thin-layer chromatography or gas chromatography, observing the disappearance of aryl halide. After completion the reaction was cooled to room temperature, diluted with ethyl acetate, and filtered through a plug of Celite. The crude product was then purified by flash chromatography.

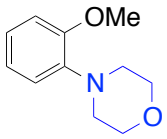


***N*-methyl-*N*-phenethylpyridin-3-amine**: Following general procedure G, a mixture of 3-chloropyridine (96 μL, 1.00 mmol, 1.00 eq), N-methylphenethyl amine (174 μL, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L4** (2.3 mg, 0.5 mol %), **6d** (4.1 mg, 0.5 mol %) and THF (1 mL) was stirred at 85 °C for 24 h. The crude product was purified by flash chromatography, eluting with 30% ethyl acetate in hexanes, to provide the title compound as a yellow oil. Yield: 170 mg, 80% ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.16 (t, J = 5.8 Hz, 1H), 7.97 (dd, J = 4.6, 1.2 Hz, 1H), 7.35 - 7.28 (m, 2H), 7.25 - 7.17 (m, 3H), 7.17 - 7.11 (m, 1H), 6.96 (ddd, J = 8.5, 3.1, 1.3 Hz, 1H), 3.62 - 3.56 (m, 2H), 2.90 (s, 3H), 2.89 - 2.83 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 144.77, 139.43, 137.56, 134.80, 129.03, 128.86, 126.64, 123.84, 118.50, 54.50, 39.83, 38.43, 33.08 ppm. IR (neat, cm^{-1}): 1581, 1492, 1356, 1182, 791, 745.

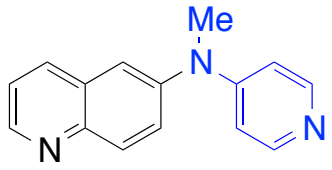


5-methyl-*N*,*N*-diphenylpyridin-2-amine: Following general procedure G, a mixture of 2-chloro-5-methylpyridine (110 μL, 1.00 mmol, 1.00 eq), diphenylamine (203 mg, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L4** (0.5 mg, 0.1 mol %), **6d** (0.8 mg, 0.1 mol %) and THF (1 mL) was stirred at 85 °C for 24 h. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in hexanes, to provide the title compound as an off-white solid. Yield: 228 mg, 88%. mp = 82 – 83° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.15 (d, J = 2.4 Hz, 1H), 7.38 - 7.29 (m, 5H), 7.24 - 7.16 (m, 4H), 7.13 (tt, J =

7.3, 1.3 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 2.28 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) - 157.42, 148.53, 146.74, 138.56, 129.59, 126.05, 125.97, 124.28, 114.83, 17.97 ppm. IR (neat, cm^{-1}): 1588, 1475, 1381, 1316, 1263, 1022, 820, 760, 692, 623. Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19. Found: C, 82.75; H, 6.36.

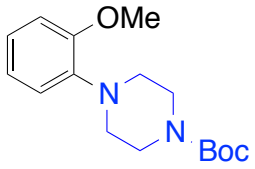


4-(2-methoxyphenyl)morpholine: Following general procedure G, a mixture of 2-chloroanisole (122 μL, 1.00 mmol, 1.00 eq), morpholine (104 μL, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L4** and **6d** (50 μL, 0.01 M in THF, 0.05 mol %) and THF (1 mL) was stirred at 85 °C for 24 h. The crude product was purified by flash chromatography, eluting with 10% ethyl acetate in hexanes, to provide the title compound as a light yellow oil. Yield: 185 mg, 96% IR (neat, cm-1): ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.03 (tt, *J* = 8.5, 4.2 Hz, 1H), 6.95 (d, *J* = 4.1 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.93 - 3.89 (m, 5H), 3.88 (s, 3H), 3.11 - 3.06 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) - 152.45, 141.30, 123.40, 121.26, 118.22, 111.46, 67.45, 55.59, 51.40 ppm. IR (neat, cm^{-1}): 1581, 1493, 1356, 1113, 791, 745.

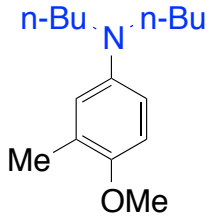


***N*-methyl-*N*-(pyridin-4-yl)quinolin-6-amine:** Following general procedure G, a mixture of 6-chloroquinoline (164 mg, 1.00 mmol, 1.00 eq), N-methyl-4-aminopyridine (130 mg, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L1** (4.7 mg, 1.00 mol %), **6a** (9.2 mg, 1.00 mol %) and THF (1 mL) was stirred at 85 °C for 4 h. The crude product was purified by flash chromatography, eluting with a 95:5:1 mixture of dichlormethane/methanol/triethylamine, to provide the title compound as a viscous yellow oil. Yield: 209 mg, 89%. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 8.94 - 8.88 (m, 1H), 8.26 (d, *J* = 6.1 Hz,

2H), 8.13 (dd, *J* = 19.8, 8.6 Hz, 2H), 7.64 (s, 1H), 7.59 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.66 (d, *J* = 6.1 Hz, 2H), 3.44 (d, *J* = 5.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) ∂ 153.73, 150.57, 150.21, 146.66, 144.35, 135.75, 131.55, 129.31, 128.85, 123.53, 121.90, 109.22, 77.74, 77.31, 76.89 ppm. IR (neat, cm^{-1}): 1593, 1544, 1496, 1379, 1355, 1335, 1224, 1118, 1071, 996, 922, 845, 803, 624.

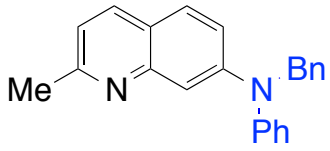


***t*-butyl 4-(2-methoxyphenyl)piperazine-1-carboxylate:** Following general procedure G, a mixture of 2-chloroanisole (122 μL, 1.00 mmol, 1.00 eq), *t*-butyl piperazine-1-carboxylate (223 mg, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L4** (0.9 mg, 0.2 mol %), **6d** (1.7 mg, 0.2 mol %) and THF (1 mL) was stirred at 85 °C for 4 h. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in hexanes, to provide the title compound as a light yellow solid. Yield: 268 mg, 92%. mp = 69 – 70° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.05 - 6.99 (m, 1H), 6.94 - 6.90 (m, 2H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 3.67 - 3.55 (m, 4H), 3.01 (d, *J* = 4.1 Hz, 4H), 1.49 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 155.04, 152.45, 141.31, 123.54, 121.22, 118.57, 111.42, 79.91, 55.62, 50.93, 28.70 ppm. IR (neat, cm^{-1}): 2975, 1697, 1502, 1421, 1242, 1173, 1122, 1030, 923, 747.



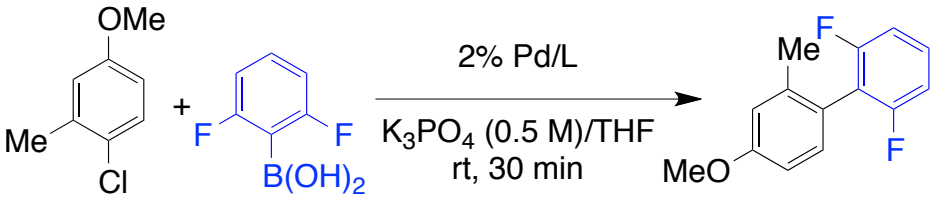
***N*,*N*-dibutyl-4-methoxy-3-methylaniline:** Following general procedure G, a mixture of 4-bromo-2-methylanisole (201 mg, 1.00 mmol, 1.00 eq), di-*n*-butylamine (202 μL, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L4** (2.3 mg, 0.5 mol %), **6d** (4.1 mg, 0.5 mol %) and THF (1 mL) was stirred at 85 °C for 24 h. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in

hexanes, to provide the title compound as a light yellow oil. Yield: 234 mg, 94% ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 6.84 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 3.0 Hz, 1H), 6.61 (dd, *J* = 8.8, 3.1 Hz, 1H), 3.86 (s, 3H), 3.33 - 3.23 (m, 5H), 2.33 (s, 3H), 1.70 - 1.58 (m, 4H), 1.45 (dq, *J* = 14.7, 7.4 Hz, 5H), 1.05 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 149.82, 143.36, 127.59, 117.02, 111.98, 111.59, 56.31, 52.00, 29.87, 20.78, 17.05, 14.38 ppm. IR (neat, cm^{-1}): 2957, 2872, 1615, 1510, 1465, 1369, 1246, 1187, 1040, 842, 790, 754, 692. Anal. Calcd. for $C_{16}H_{27}NO$: C, 77.06; H, 10.91. Found: C, 76.89; H, 10.67.



***N*-benzyl-2-methyl-*N*-phenylquinolin-7-amine:** Following general procedure G, a mixture of 7-chloro-2-methylquinoline (177 mg, 1.00 mmol, 1.00 eq), N-benzylaniline (220 mg, 1.20 mmol, 1.20 eq) NaO*t*Bu (115 mg, 1.20 mmol, 1.20 eq), **L4** (0.5 mg, 0.1 mol %), **6d** (0.8 mg, 0.1 mol %) and THF (1 mL) was stirred at 85 °C for 24 h. The crude product was purified by flash chromatography, eluting with 20% ethyl acetate in hexanes, to provide the title compound as a vibrant yellow solid. Yield: 288 mg, 89%. mp = 111 – 112° C. ^{1}H NMR (500 MHz, $CDCl_3$) ∂ 7.84 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.45 (s, 1H), 7.41 - 7.26 (m, 8H), 7.25 - 7.18 (m, 2H), 7.11 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.15 (s, 2H), 2.65 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) ∂ 159.41, 149.78, 149.34, 147.60, 138.69, 135.86, 129.95, 128.88, 128.14, 127.16, 126.82, 124.57, 124.31, 121.22, 119.47, 119.41, 112.49, 56.66, 25.62 ppm. IR (neat, cm^{-1}): 1618, 1594, 1492, 1384, 1350, 1327, 1223, 1153, 1060, 1029, 942, 833, 772, 272, 709, 667.

General Procedure for Screening of Ligands and Pd Sources for *in-situ* Generation of Precatalysts



Precatalyst Solution: A 7 mL scintillation vial equipped with a Teflon septum was charged with palladium source (0.01 mmol, 1.00 eq) and ligand (0.01 mmol, 1.00 eq). The vial was evacuated and refilled with argon. This was repeated twice. THF (1 mL) was then added and the solution was allowed to age for ten minutes, with occasional swirling, before use in a coupling reaction.

Suzuki-Miyaura Coupling of 4-Chloro-3-Methylanisole with 2, 6-Difluorophenylboronic Acid: An oven-dried, resealable tube equipped with a magnetic stir bar and Teflon septum was charged with 2, 6-difluorophenylboronic acid (119 mg, 0.75 mmol, 1.50 eq). It was then evacuated and refilled with argon. This was repeated three times. Then 4-chloro-3-methylanisole (70 μL, 0.50 mmol, 1.00 eq) was added by syringe, followed by the aged precatalyst solution in THF (1 mL, 2 mol % Pd) and aqueous K_3PO_4 (0.5 M, 2.00 mL, 1.00 mmol, 2.00 eq). The reaction was stirred at room temperature for half an hour, after which it was opened to air, diluted with diethyl ether and 1, 3, 5-trimethoxybenzene (250 μL, 1 M in diethyl ether) was added as an internal standard. The solvent was removed under vacuum and the yield was determined by ^{1}H NMR.

X-Ray Structure Determination

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for the structure of compound **6a** and on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo Kα radiation (λ = 0.71073 Å) from an IμS micro-source for the structure of compounds **2•L1**, **6b**, **6c, 6n** and **2•L13**. All structures were solved by direct methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[2] using established refinement techniques.[3] All non-hydrogen atoms were refined

anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters unless otherwise noted below.

Compound **6a** crystallizes in the triclinic space group *P-1* with one molecule in the asymmetric unit.

Compound **2•L1** crystallizes in the triclinic space group *P-1* with one molecule in the asymmetric unit. There is evidence of slight disorder of the C41,C41,C42 iPr group (namely elongated thermal ellipsoids of those atoms and residual electron density around them), however all attempts to parameterize this disorder failed (ratio refined to 95:5, thermal ellipsoids of minor component were poor, etc.).

Compound **6b** crystallizes in the triclinic space group *P-1* with one molecule in the asymmetric unit. Coordinates for the nitrogen bound hydrogen atoms were taken from the difference Fourier Synthesis. The hydrogen atoms in question were subsequently refined semi-freely with the help of distance restraints while constraining their U_{iso} to 1.2 times the value of the U_{eq} of the nitrogen atom to which they bind.

Compound **6c** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Coordinates for the nitrogen bound hydrogen atoms were taken from the difference Fourier Synthesis. The hydrogen atoms in question were subsequently refined semi-freely with the help of distance restraints while constraining their U_{iso} to 1.2 times the value of the U_{eq} of the nitrogen atom to which they bind.

Compound **6n** crystallizes in the triclinic space group *P-1* with two molecules in the asymmetric unit. There is a fairly complex solvent disorder (all CH_2Cl_2), which was refined with the help of extensive restraints and some equal-ADP constraints. The asymmetric unit contains two C_{56} H_{42} N P_2 Pd target molecules with two CH_3SO_4 counter ions as well as seven CH_2Cl_2 solvent molecules. Six of those solvent molecules are fully occupied, the seventh one is located in the asymmetric unit in form of two half occupied molecules, located near crystallographic inversion centers. Three of the solvent molecules are not

disordered, three are disordered over two positions. The two half occupied solvent molecules are highly disordered, one over four (two independent) and the other one over six (three independent) positions.

Compound **2•L13** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit.

Table 1. Crystal data and structure refinement for 6a

Identification code	12044	
Empirical formula	C50 H72 N O4 P Pd S	
Formula weight	920.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.3071(10) Å	a= 102.4550(10)°.
	b = 13.5653(11) Å	b= 94.4810(10)°.
	c = 14.7831(12) Å	g = 98.6540(10)°.
Volume	2366.8(3) $Å^3$	
Z	2	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.513 mm^{-1}	
F(000)	976	
Crystal size	0.33 x 0.30 x 0.14 mm^3	
Theta range for data collection	1.42 to 30.51°.	
Index ranges	-17<=h<=17, -19<=k<=19, -21<=l<=21	
Reflections collected	68495	
Independent reflections	14378 [R(int) = 0.0449]	
Completeness to theta = 30.51°	99.5 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9316 and 0.8489
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14378 / 269 / 599
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0757
R indices (all data)	R1 = 0.0370, wR2 = 0.0795
Largest diff. peak and hole	1.102 and -0.488 e.Å^{-3}

Table 2. Crystal data and structure refinement for 2•L1.

Identification code	x12053	
Empirical formula	C45 H59 Cl N P Pd	
Formula weight	786.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1656(13) Å	a= 97.346(3)°.
	b = 13.4105(18) Å	b= 101.171(3)°.
	c = 15.503(2) Å	g = 101.772(3)°.
Volume	1998.7(5) Å^3	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.603 mm^{-1}	
F(000)	828	
Crystal size	0.20 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.36 to 30.51°.	

Index ranges	-14<=h<=14, -19<=k<=19, -22<=l<=22
Reflections collected	126595
Independent reflections	12138 [R(int) = 0.0293]
Completeness to theta = 30.51°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9821 and 0.8890
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12138 / 2 / 454
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0533
R indices (all data)	R1 = 0.0217, wR2 = 0.0544
Largest diff. peak and hole	0.850 and -0.386 e.Å^{-3}

Table 3. Crystal data and structure refinement for 6b.

Identification code	x12064	
Empirical formula	C44 H62 Cl4 N O3 P Pd S	
Formula weight	964.18	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8288(9) Å	a= 110.420(2)°.
	b = 13.3096(11) Å	b= 93.341(2)°.
	c = 17.3470(15) Å	g = 103.421(2)°.
Volume	2252.3(3) Å^3	
Z	2	
Density (calculated)	1.422 Mg/m^3	

Absorption coefficient	0.770 mm^{-1}
F(000)	1004
Crystal size	0.25 x 0.24 x 0.23 mm^3
Theta range for data collection	1.27 to 31.30°.
Index ranges	-15<=h<=15, -19<=k<=19, -25<=l<=25
Reflections collected	221977
Independent reflections	14723 [R(int) = 0.0322]
Completeness to theta = 31.30°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8427 and 0.8307
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14723 / 15 / 515
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0603
R indices (all data)	R1 = 0.0253, wR2 = 0.0612
Largest diff. peak and hole	0.903 and -0.883 e.$Å^{-3}$

Table 4. Crystal data and structure refinement for 6c.

Identification code	x12062	
Empirical formula	C48 H66 N O5 P Pd S	
Formula weight	906.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 15.5569(6) Å	a= 90°.
	b = 17.0797(7) Å	b= 94.2220(10)°.

	c = 16.7243(6) Å g = 90°.
Volume	4431.7(3) $Å^3$
Z	4
Density (calculated)	1.359 Mg/m^3
Absorption coefficient	0.549 mm^{-1}
F(000)	1912
Crystal size	0.30 x 0.20 x 0.13 mm^3
Theta range for data collection	1.71 to 31.00°.
Index ranges	-22<=h<=22, -24<=k<=24, -21<=l<=24
Reflections collected	211874
Independent reflections	14118 [R(int) = 0.0474]
Completeness to theta = 31.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9321 and 0.8527
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14118 / 2 / 529
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0595
R indices (all data)	R1 = 0.0323, wR2 = 0.0637
Largest diff. peak and hole	0.567 and -0.363 $e.Å^{-3}$

Table 5. Crystal data and structure refinement for 6n.

Identification code	x12061
Empirical formula	C60.50 H52 Cl7 N O3 P2 Pd S
Formula weight	1289.58
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.9763(14) Å	a= 75.424(2)°.
	b = 20.426(2) Å	b= 85.472(2)°.
	c = 21.290(2) Å	g = 76.307(2)°.
Volume	5713.9(10) $Å^3$	
Z	4	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	0.791 mm^{-1}	
F(000)	2628	
Crystal size	0.30 x 0.25 x 0.05 mm^3	
Theta range for data collection	1.06 to 31.00°.	
Index ranges	-20<=h<=20, -29<=k<=29, -30<=l<=30	
Reflections collected	370048	
Independent reflections	36383 [R(int) = 0.0485]	
Completeness to theta = 31.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9615 and 0.7972	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	36383 / 828 / 1552	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1032	
R indices (all data)	R1 = 0.0536, wR2 = 0.1108	
Largest diff. peak and hole	1.593 and -1.092 e.$Å^{-3}$	

Table 6. Crystal data and structure refinement for 2•L13.

Identification code	x12094
Empirical formula	C57.50 H45 Cl4 N P2 Pd

Formula weight	1060.08	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 14.5500(18) Å	a= 90°.
	b = 13.7601(17) Å	b= 94.469(3)°.
	c = 23.806(3) Å	g = 90°.
Volume	4751.8(10) $Å^3$	
Z	4	
Density (calculated)	1.482 Mg/m^3	
Absorption coefficient	0.724 mm^{-1}	
F(000)	2164	
Crystal size	0.40 x 0.35 x 0.25 mm^3	
Theta range for data collection	1.59 to 32.03°.	
Index ranges	-21<=h<=21, -20<=k<=20, -35<=l<=35	
Reflections collected	420406	
Independent reflections	16548 [R(int) = 0.0491]	
Completeness to theta = 32.03°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8397 and 0.7605	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16548 / 1187 / 838	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0798	
R indices (all data)	R1 = 0.0382, wR2 = 0.0856	
Largest diff. peak and hole	0.944 and -0.843 $e.Å^{-3}$	

Computational Methods

All calculations were carried out with Q-Chem suite of computational programs[4]. Ground state geometry optimizations were evaluated using the B3LYP[5] density functional method. For C, H, N, P, S and Cl atoms, the 6-31G(d) basis set was used; while LANL2DZ effective core potentials of Hay and Wadt[6] with double-ζ basis sets were used for Pd atom. Frequency calculations were performed on all optimized structures to verify that they have no negative frequencies. Gibbs free energies were calculated at 298.18 K and 1 atm. All charges were evaluated using Natural Bond Orbital version 5.0 (NBO 5.0) population analysis as implemented in Q-Chem.[7]

Comparison of Natural Charges on Pd:

6a: 0.52891

2•L1: 0.47961

Net Positive Charge on **6a** Complex: 0.0493

Cartesian Coordinates for all Calculated Complexes:

6a

Pd 2.36008 -0.02901 0.37054

O 3.16060 1.94661 -0.25936

S 4.06845 2.64750 0.75821

O 3.36105 2.95328 2.01791

O 5.37242 1.93548 0.89665

C 4.44707 4.21274 -0.05186

H 5.12407 4.76918 0.59957

H 3.51951 4.76934 -0.19751

H 4.92658 4.00527 -1.01000

P 0.10401 0.49247 -0.17389

C -0.10200 2.08728 -1.16079

H -1.15625 2.09028 -1.46995

C 0.78134 2.07839 -2.43002

H 1.83172 2.01947 -2.12740

H 0.57157 1.19632 -3.04474

C 0.55921 3.34706 -3.27192

H 1.21679 3.32091 -4.15029

H -0.47302 3.36070 -3.65387

C 0.81232 4.61686 -2.44950

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H 0.61496 5.51117 -3.05452

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H 0.16884 5.51469 -0.57400

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H -0.52663 3.39697 0.53217

H 1.16730 3.34036 0.06699

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H -1.15224 -1.53561 -0.48349

C -1.84660 -0.37857 -2.17114

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H -1.43112 0.31930 -2.90941

C -2.47973 -1.55923 -2.93013

H -2.98555 -2.21965 -2.21307

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C -1.43342 -2.35711 -3.71766

H -1.01808 -1.72381 -4.51571

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H -0.68983 -3.54666 -2.07107

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H 0.82950 -0.97366 -2.75203

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C -2.14986 0.61489 1.80989

C -2.52976 0.94474 3.12688

H -3.56362 0.77466 3.41311

C -1.64445 1.48449 4.05514

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C -0.32508 1.71764 3.67671

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C 0.08458 1.37838 2.39050

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C -3.63674 -1.26098 0.95727

C -2.85005 -2.29914 1.75921

H -1.85751 -1.88524 1.96128

C -3.52511 -2.56166 3.12253

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H -2.95088 -3.29632 3.70029

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2•L1

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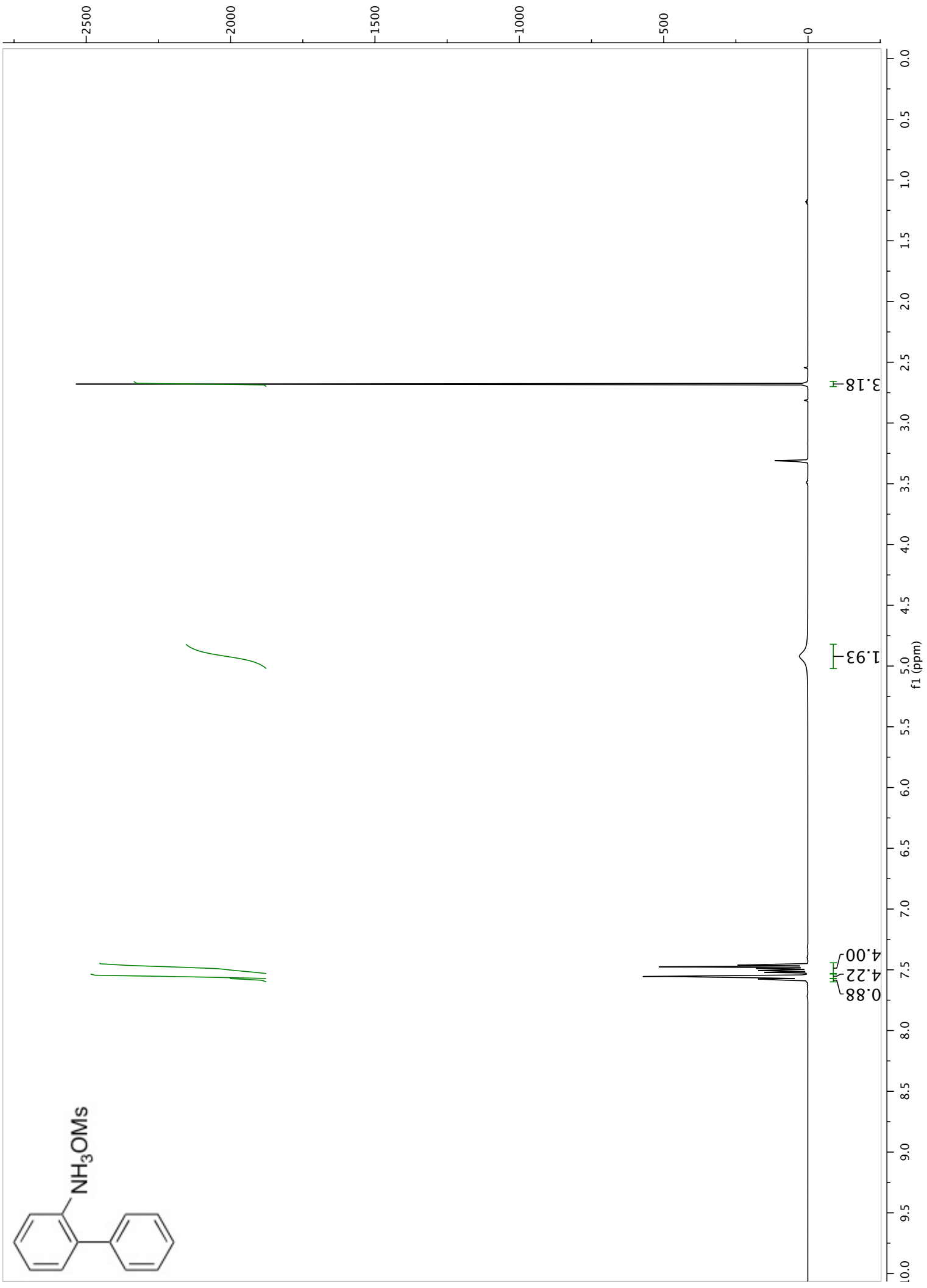

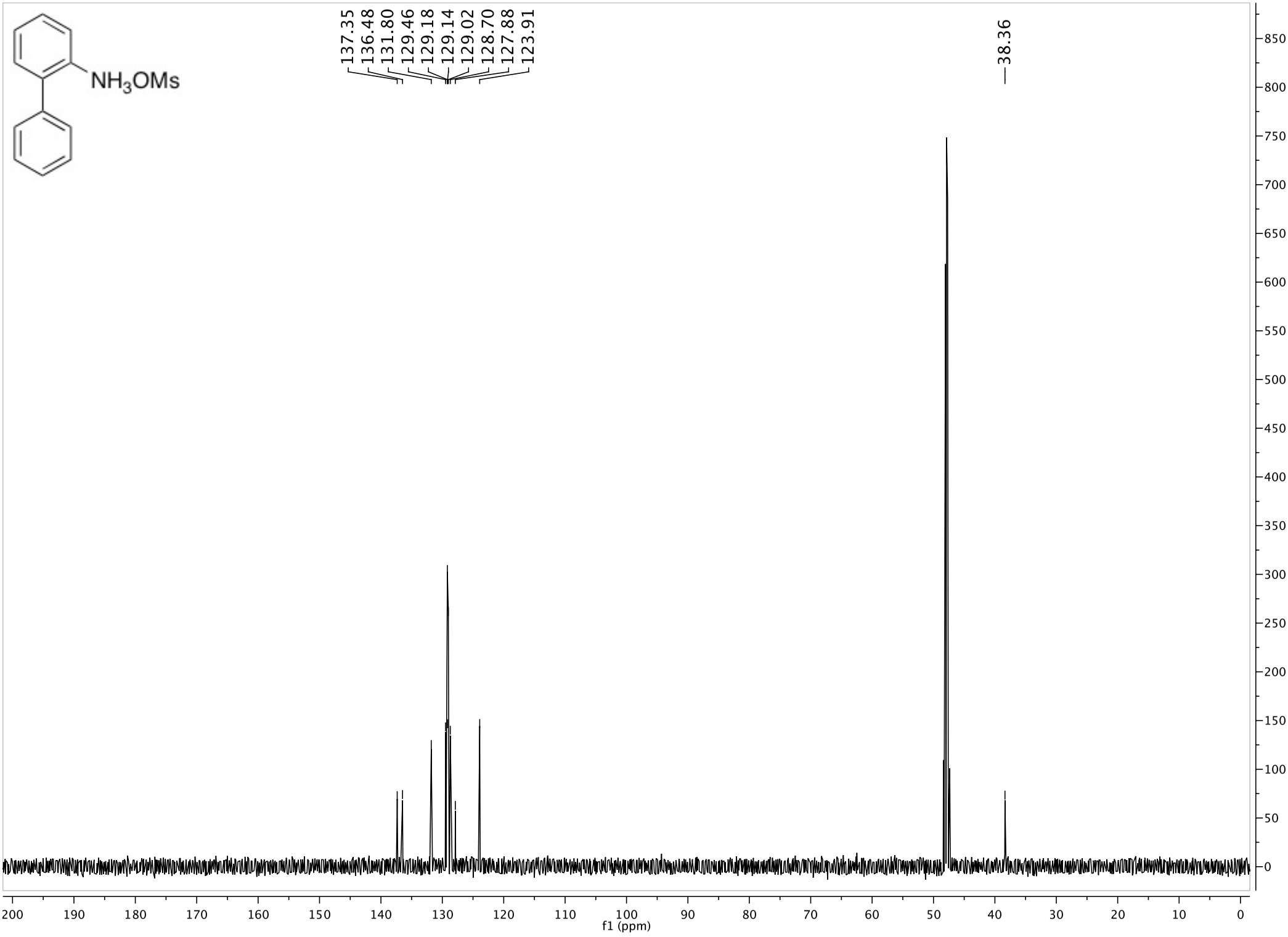

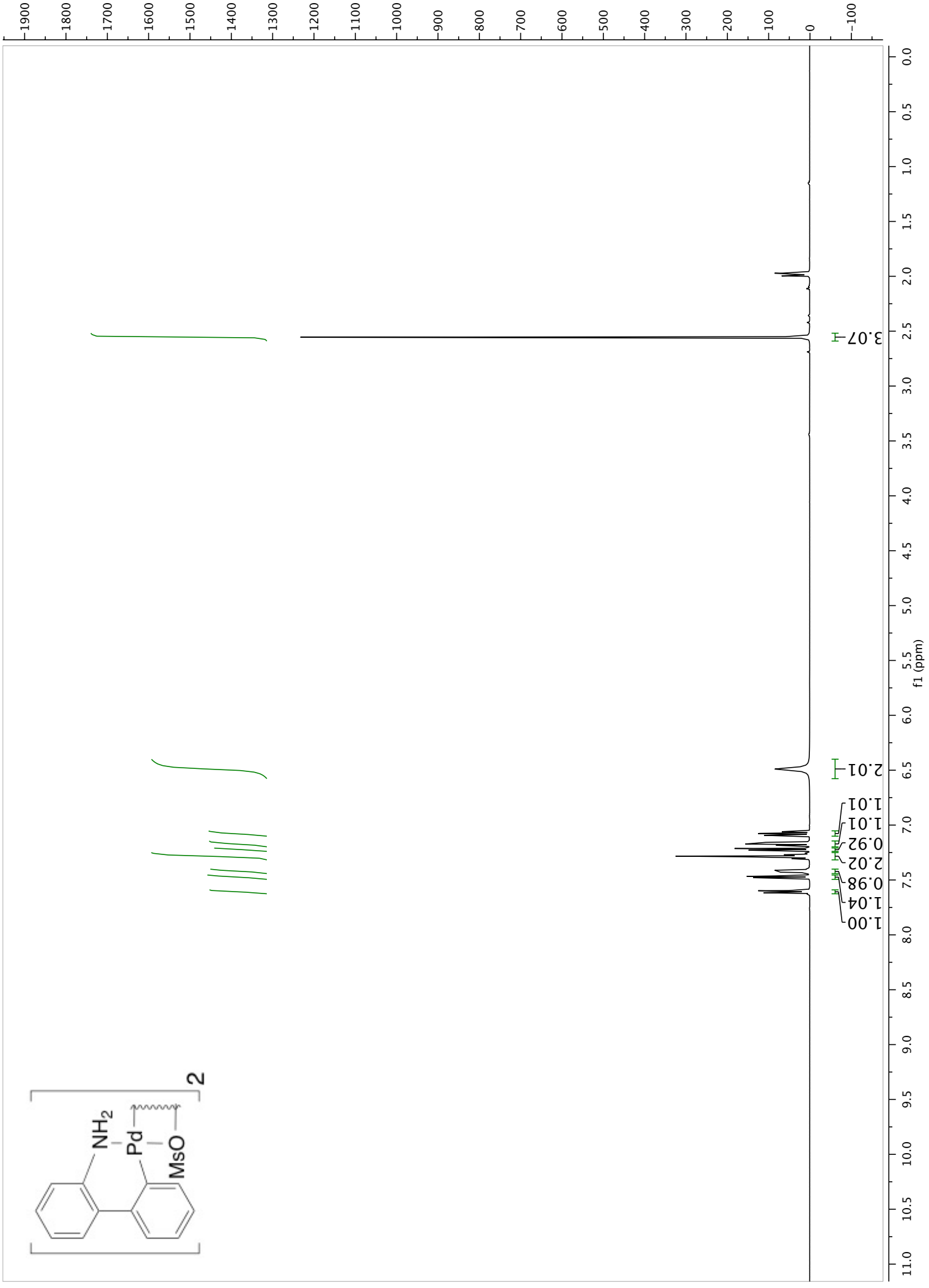
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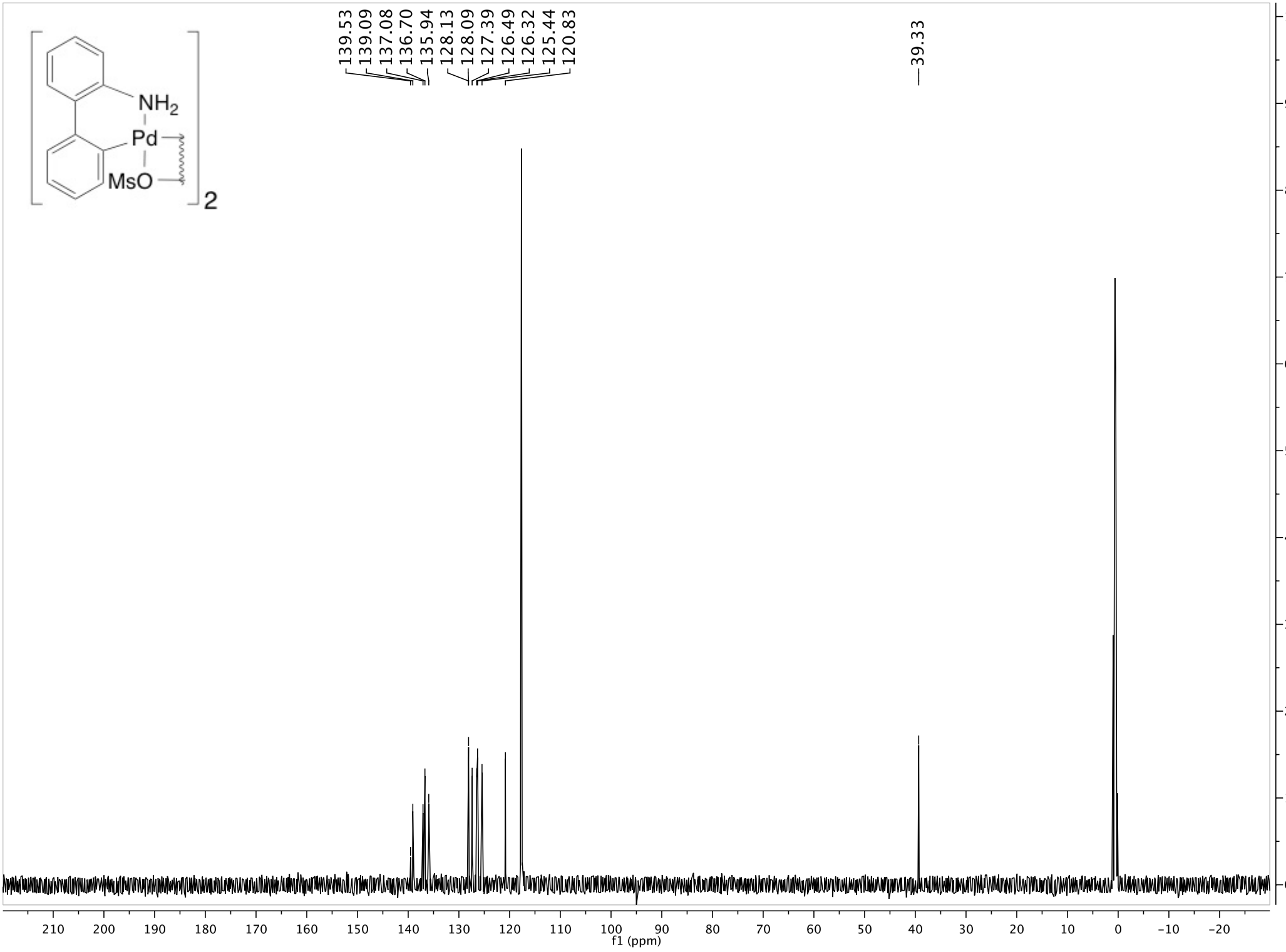

nmr500c h-1

u-mesylate in situ d5-pyridine c

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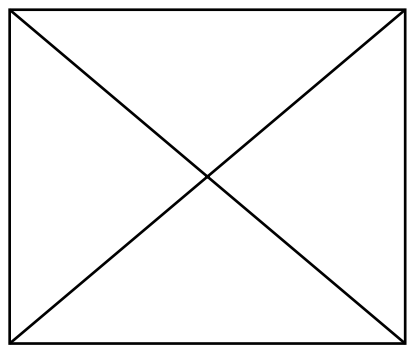
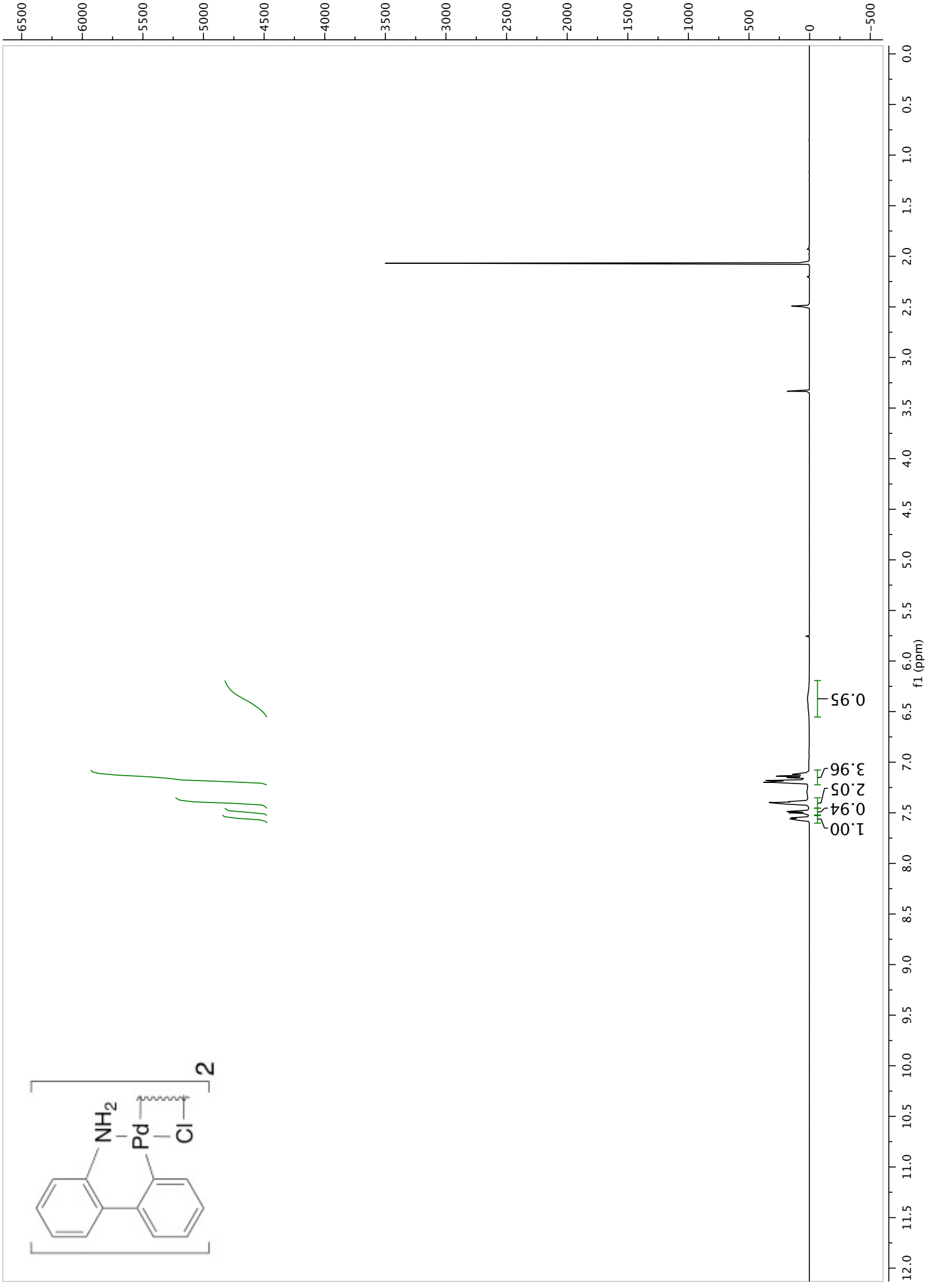
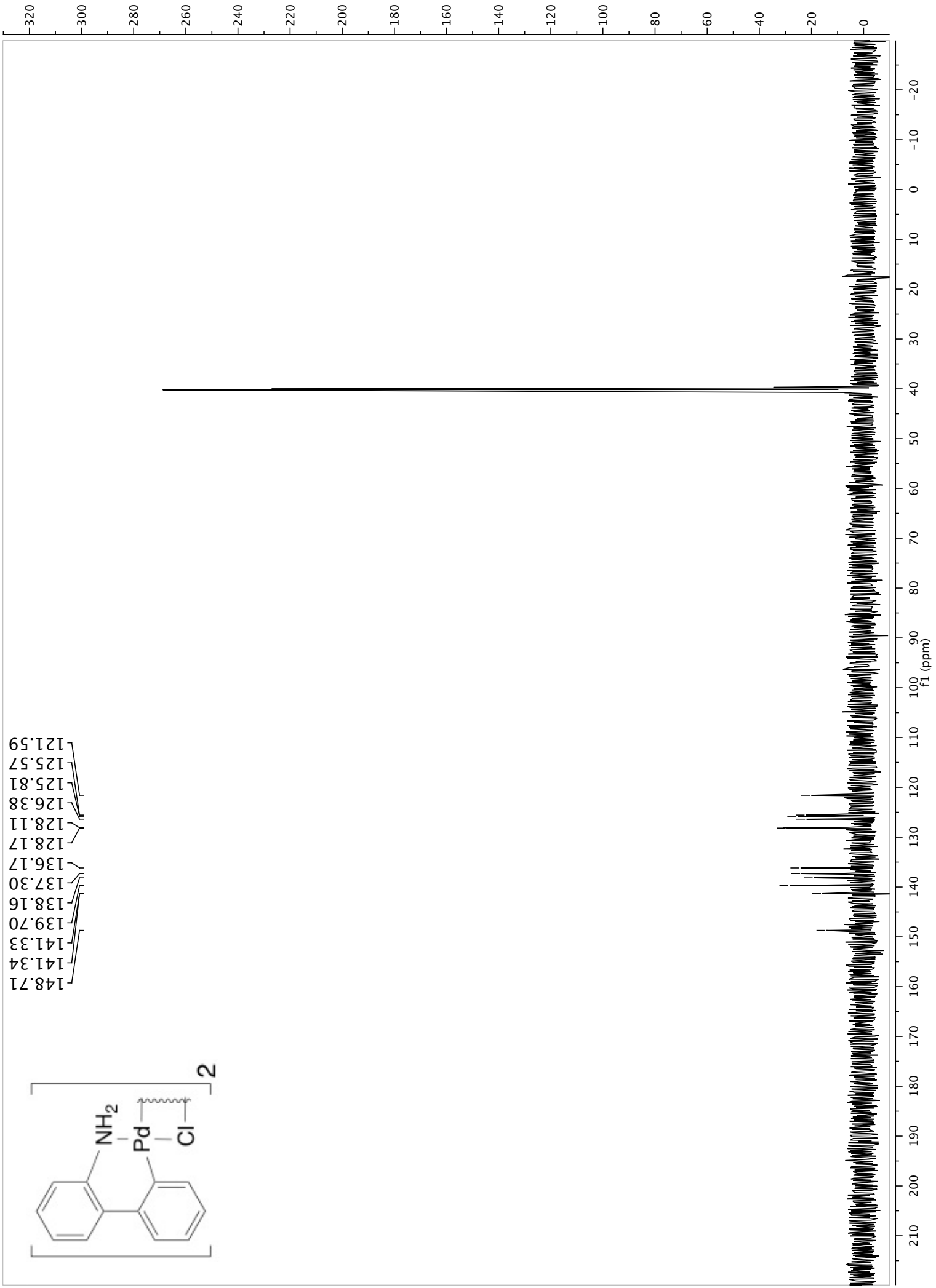
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	65536
SOLVENT	CD2C12
NS	8
DS	4
SWH	13020.833 Hz
FIDRES	0.198682 Hz
AQ	2.5166707 sec
RG	181
DW	38.400 usec
DE	6.50 usec
TE	300.0 K
D1	10.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	12.00 usec
PL1	-4.00 dB
SFO1	500.1330885 MHz
SI	32768
SF	500.1300203 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00







nmr500c h-1
u-Cl in situ d5-pyridine complex

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NAME        0316977_0005
EXPNO                  3
PROCNO                 1
Date_           20120321
Time               14.07
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT           CD2Cl2
NS                     8
DS                     4
SWH            13020.833 Hz
FIDRES          0.198682 Hz
AQ             2.5166707 sec
RG                   256
DW                38.400 usec
DE                 6.50 usec
TE                300.0 K
D1           10.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -4.00 dB
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300203 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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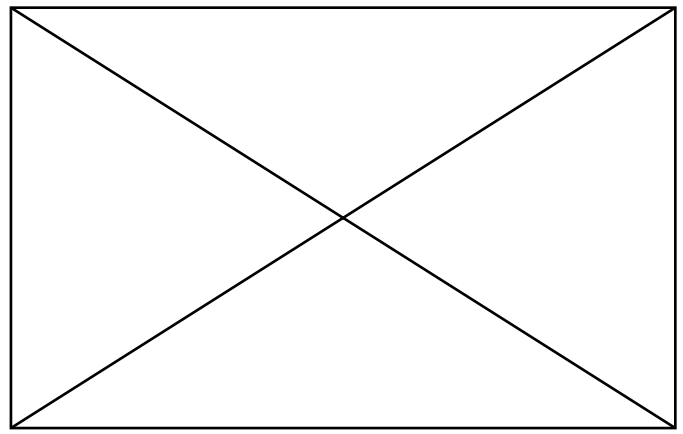
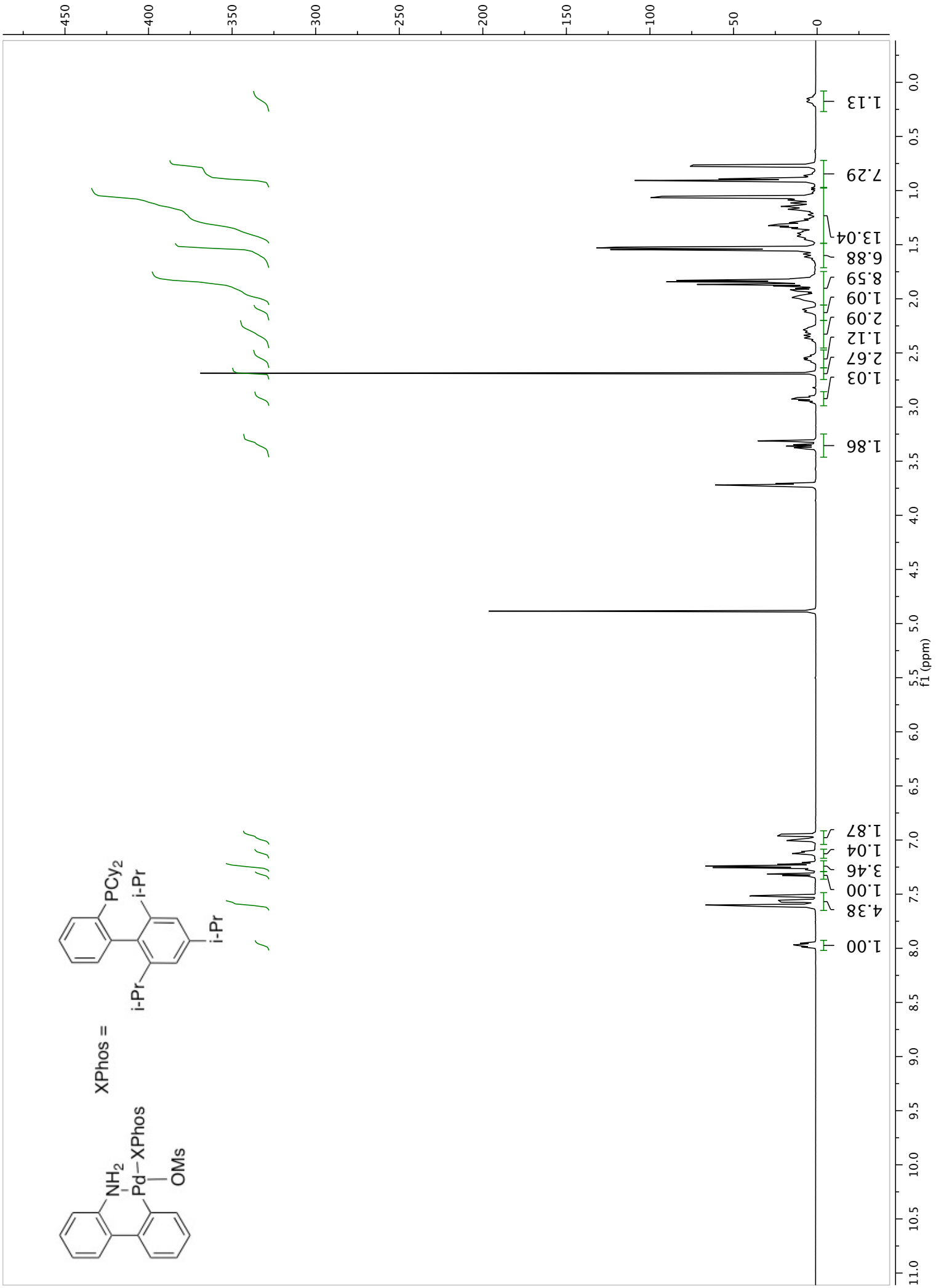
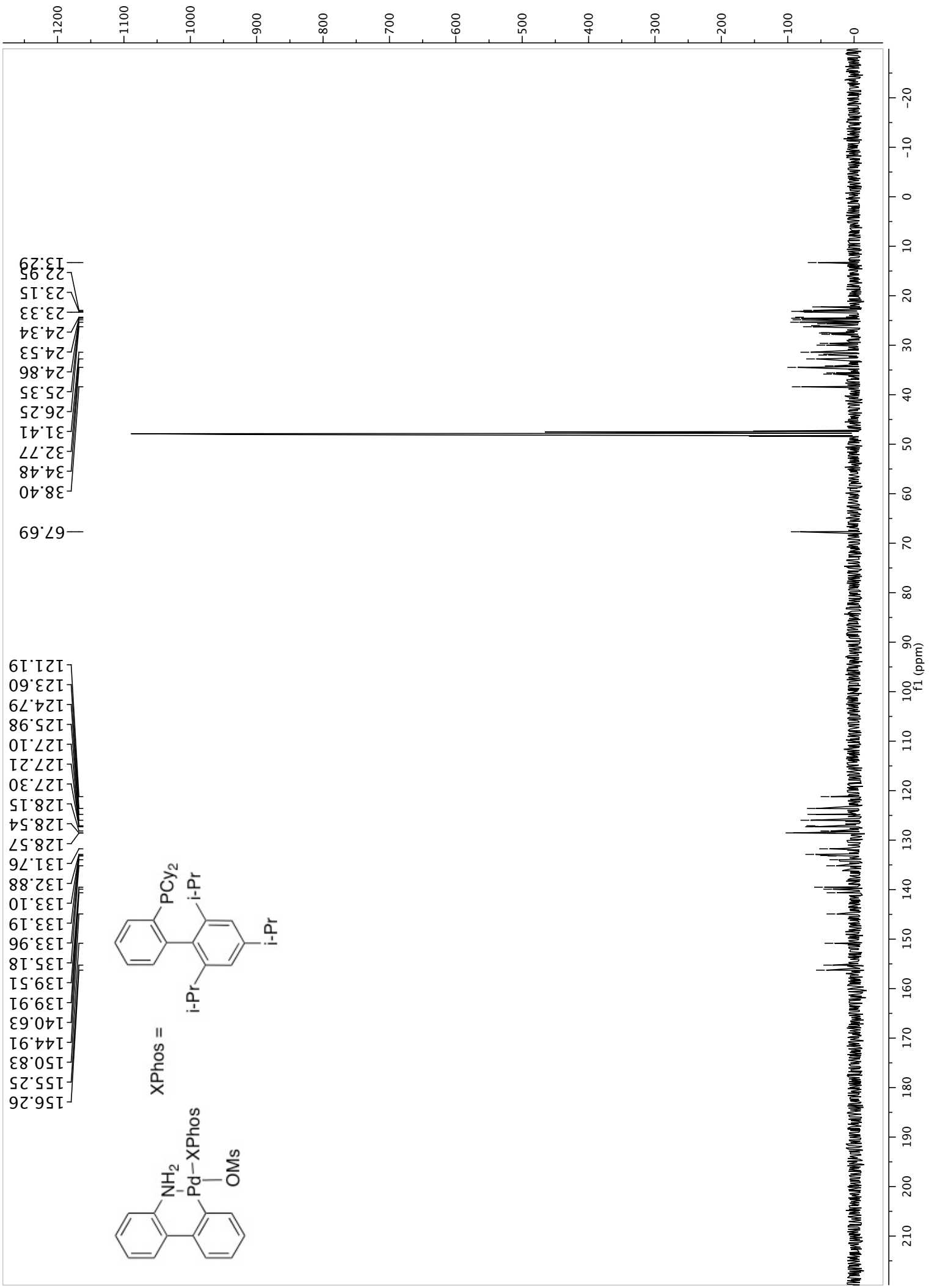
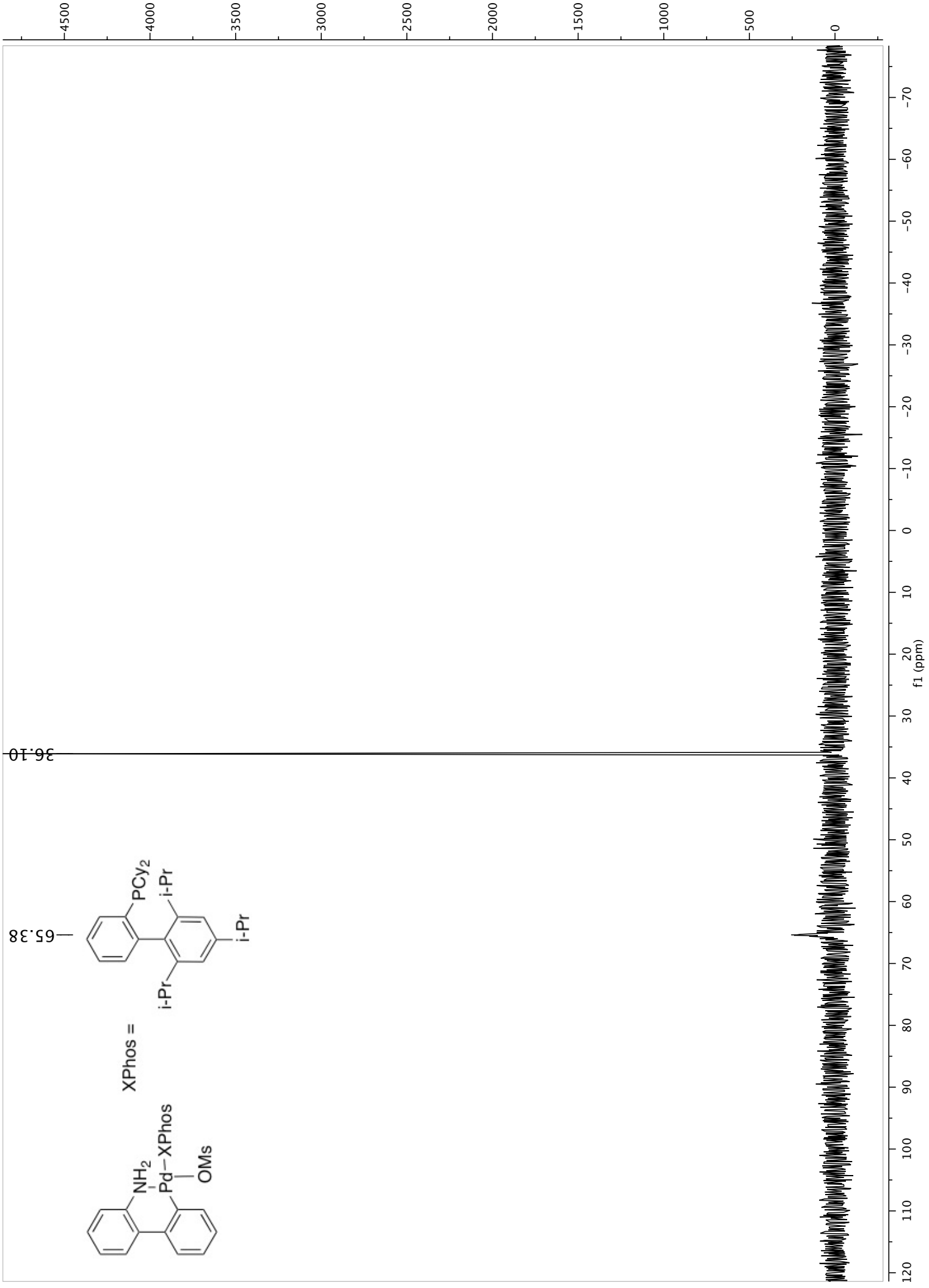
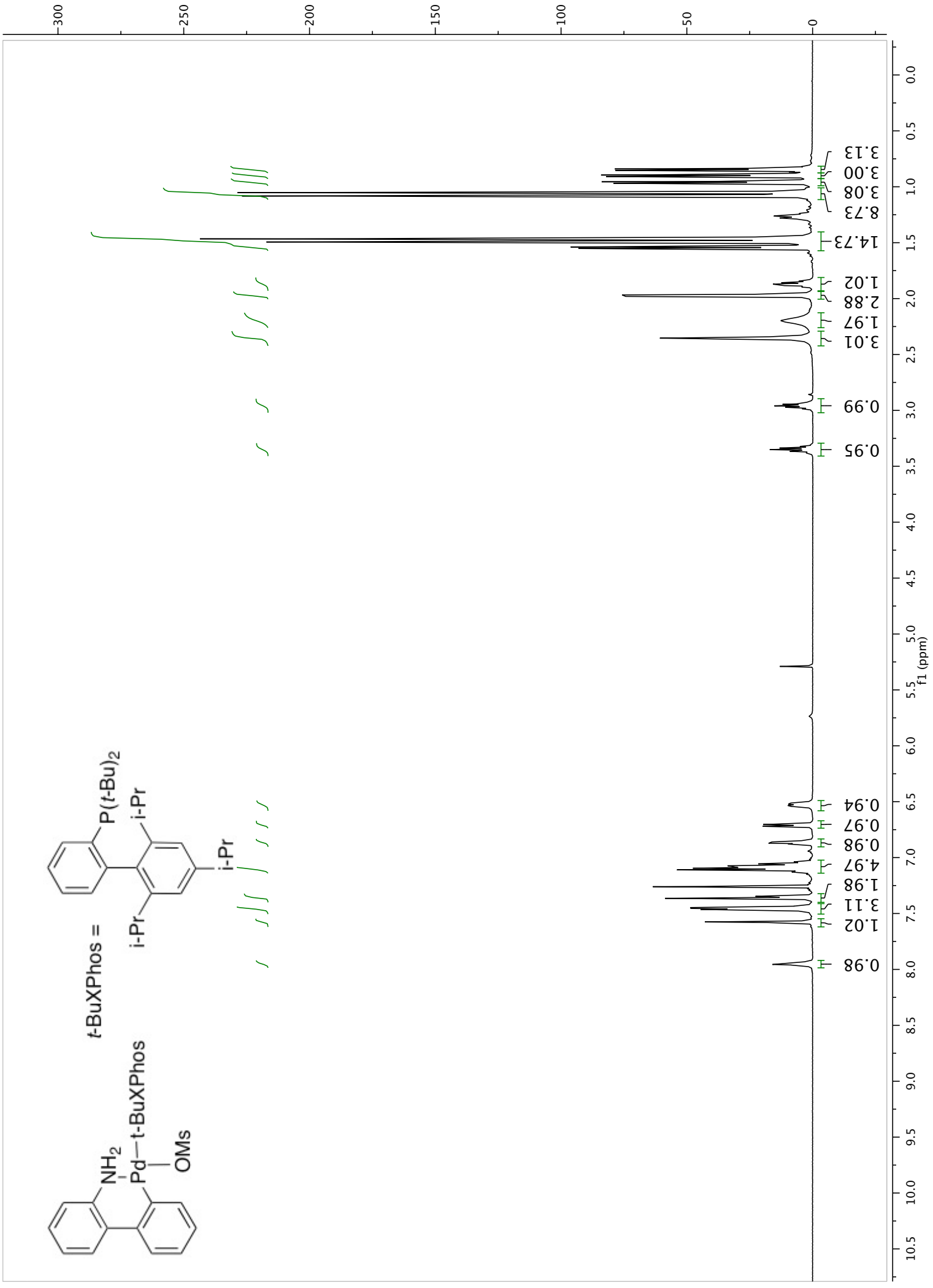
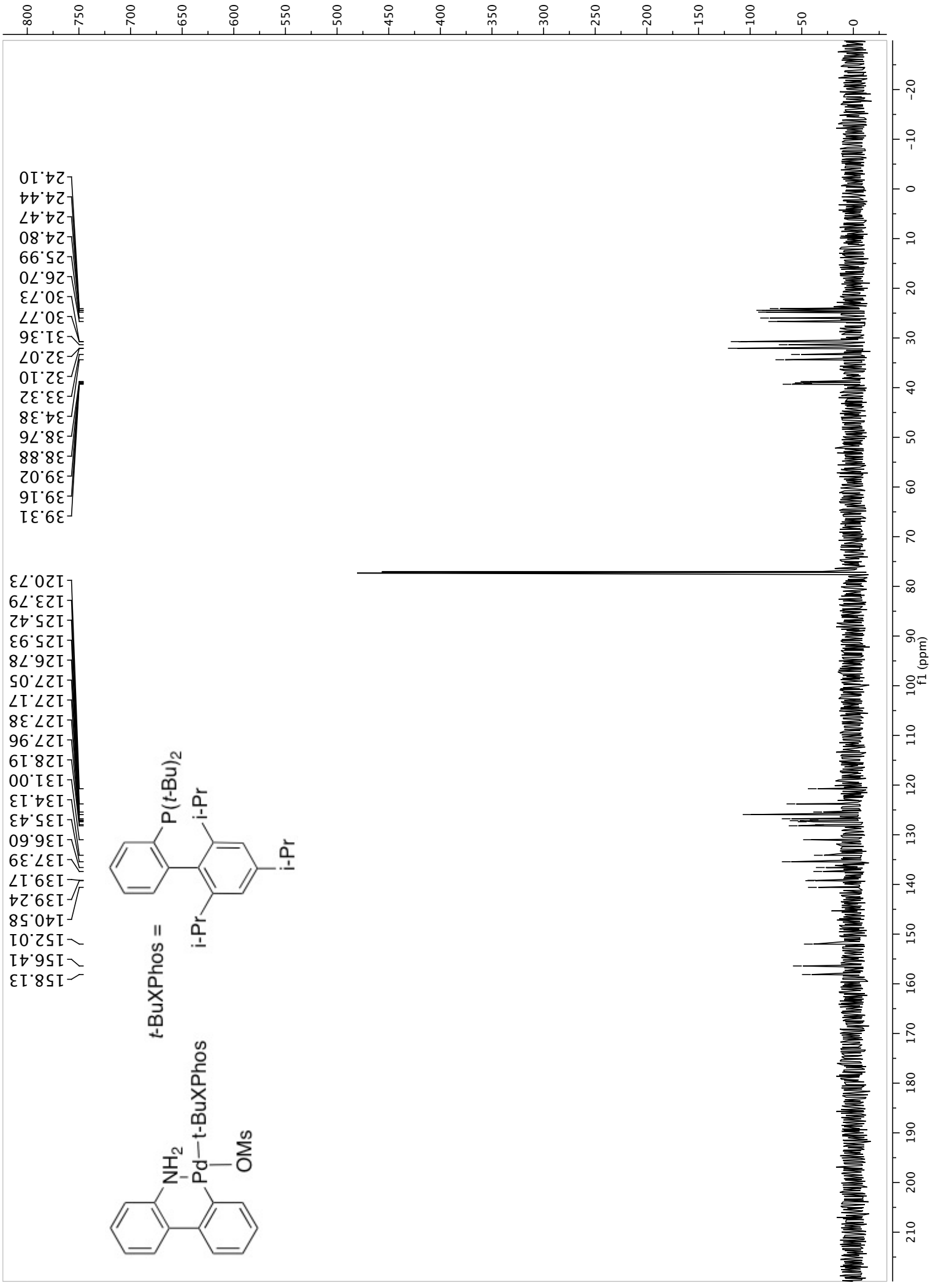


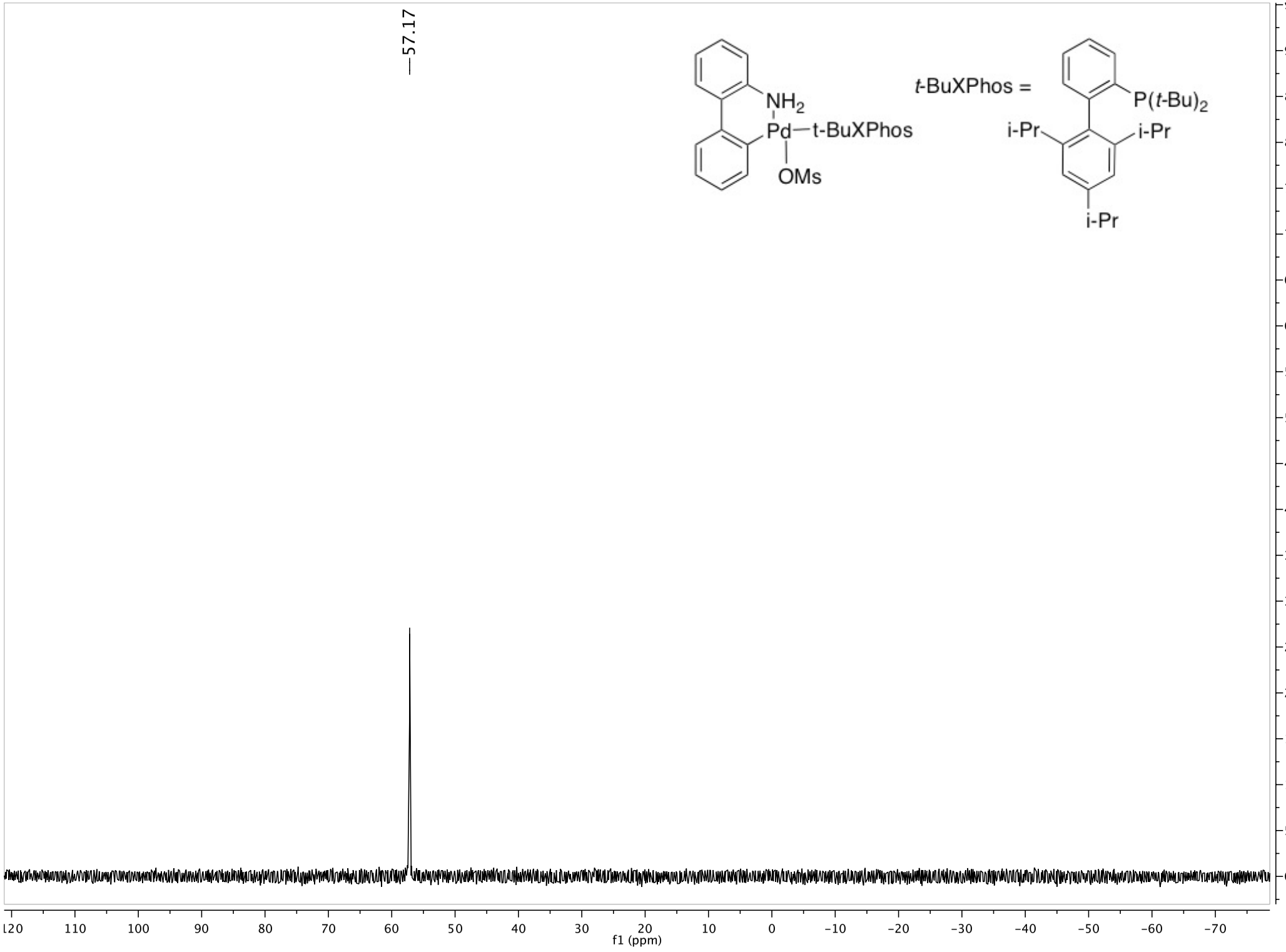


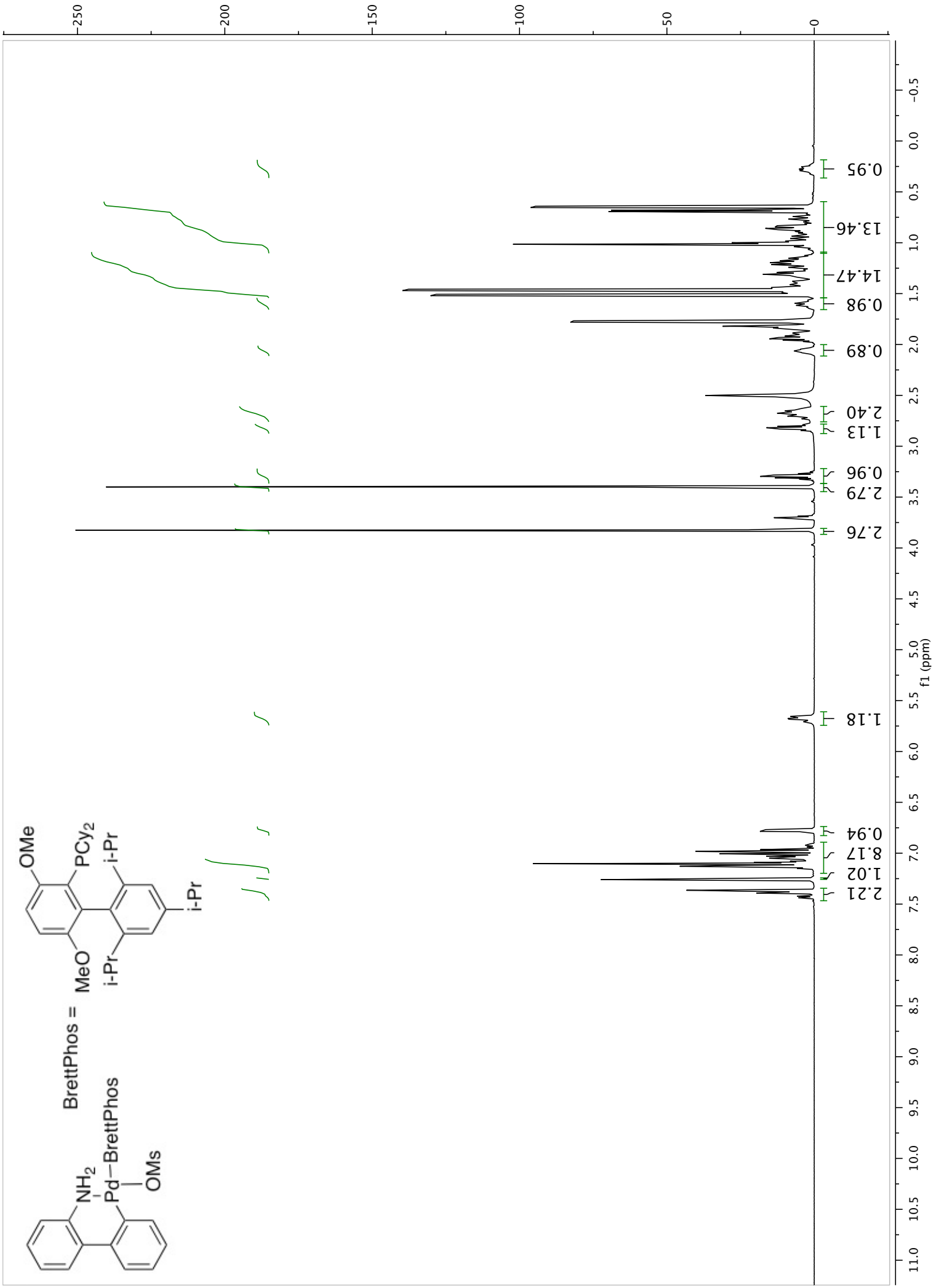


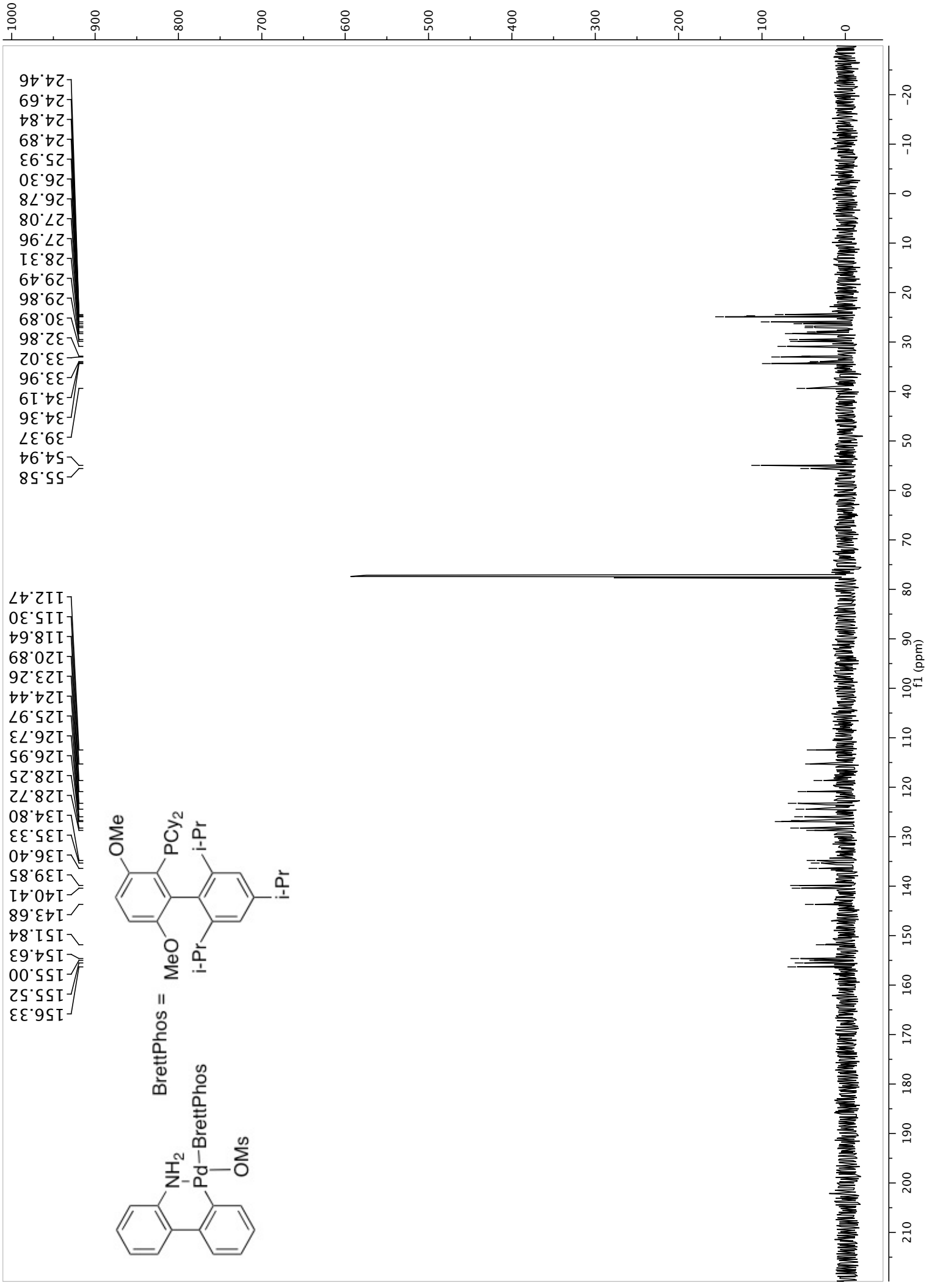

36.10
65.38
PCy2
i-Pr
i-Pr
i-Pr
XPhos =
NH2
Pd–XPhos
OMs
f1 (ppm)

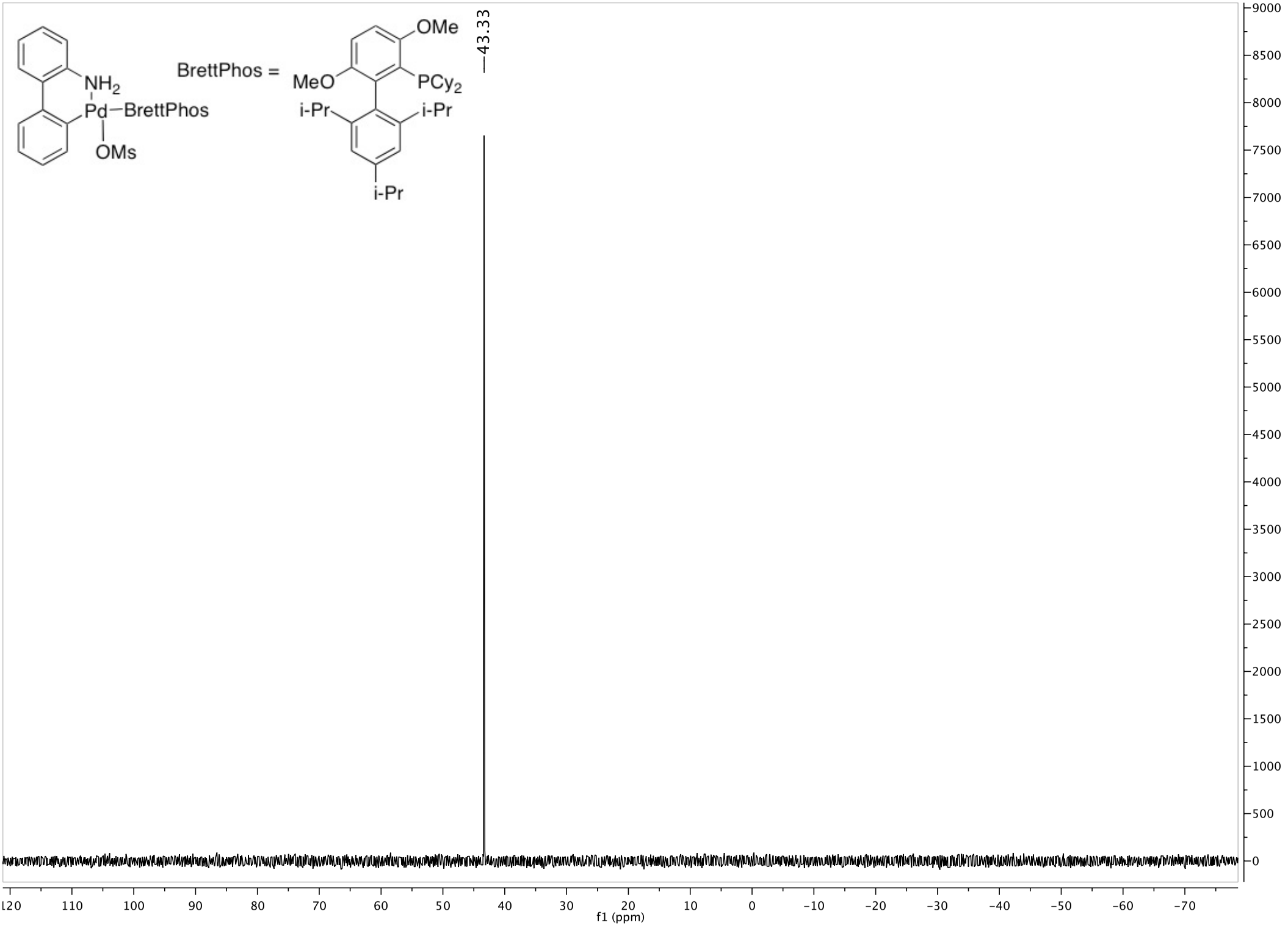


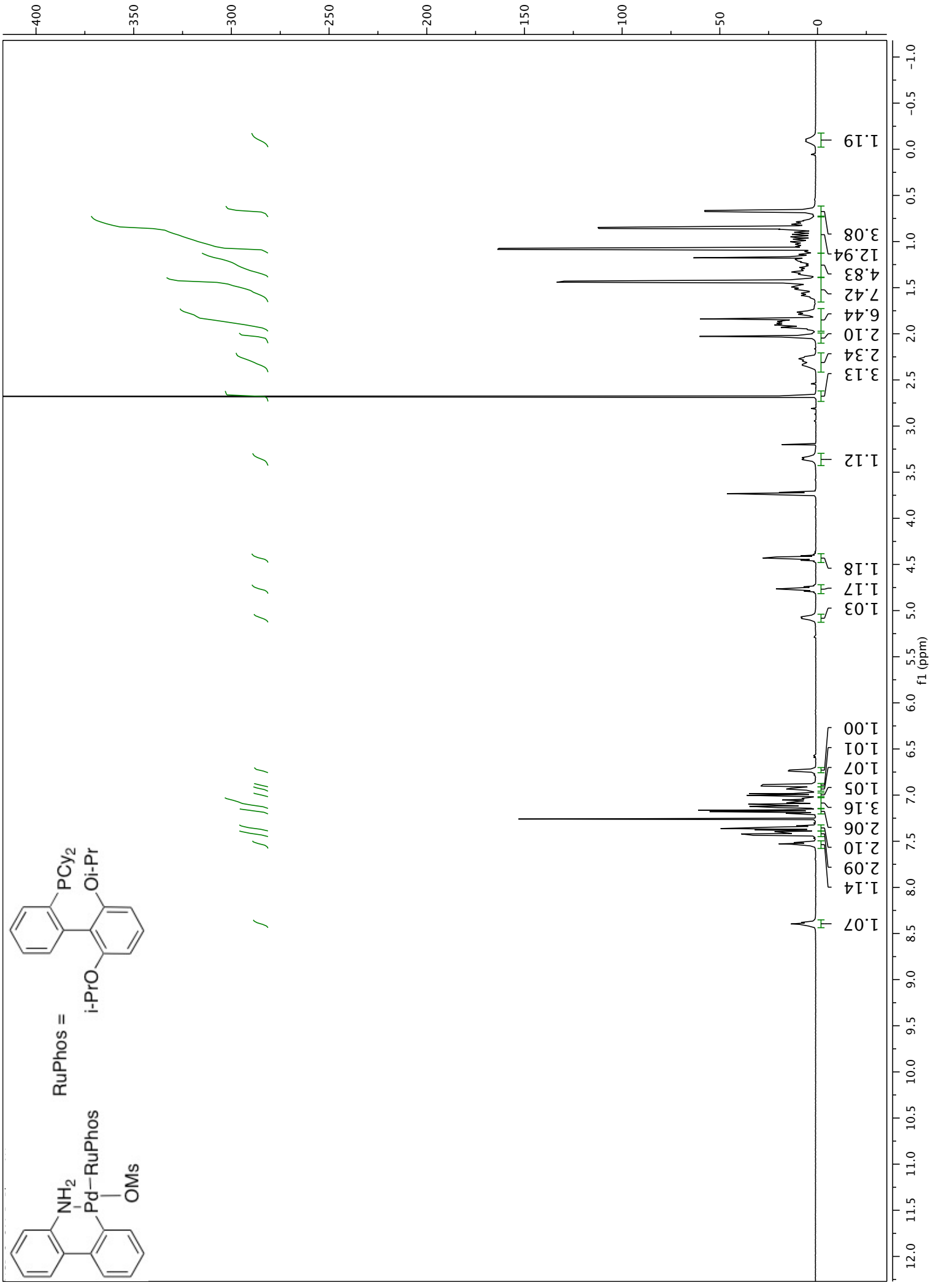


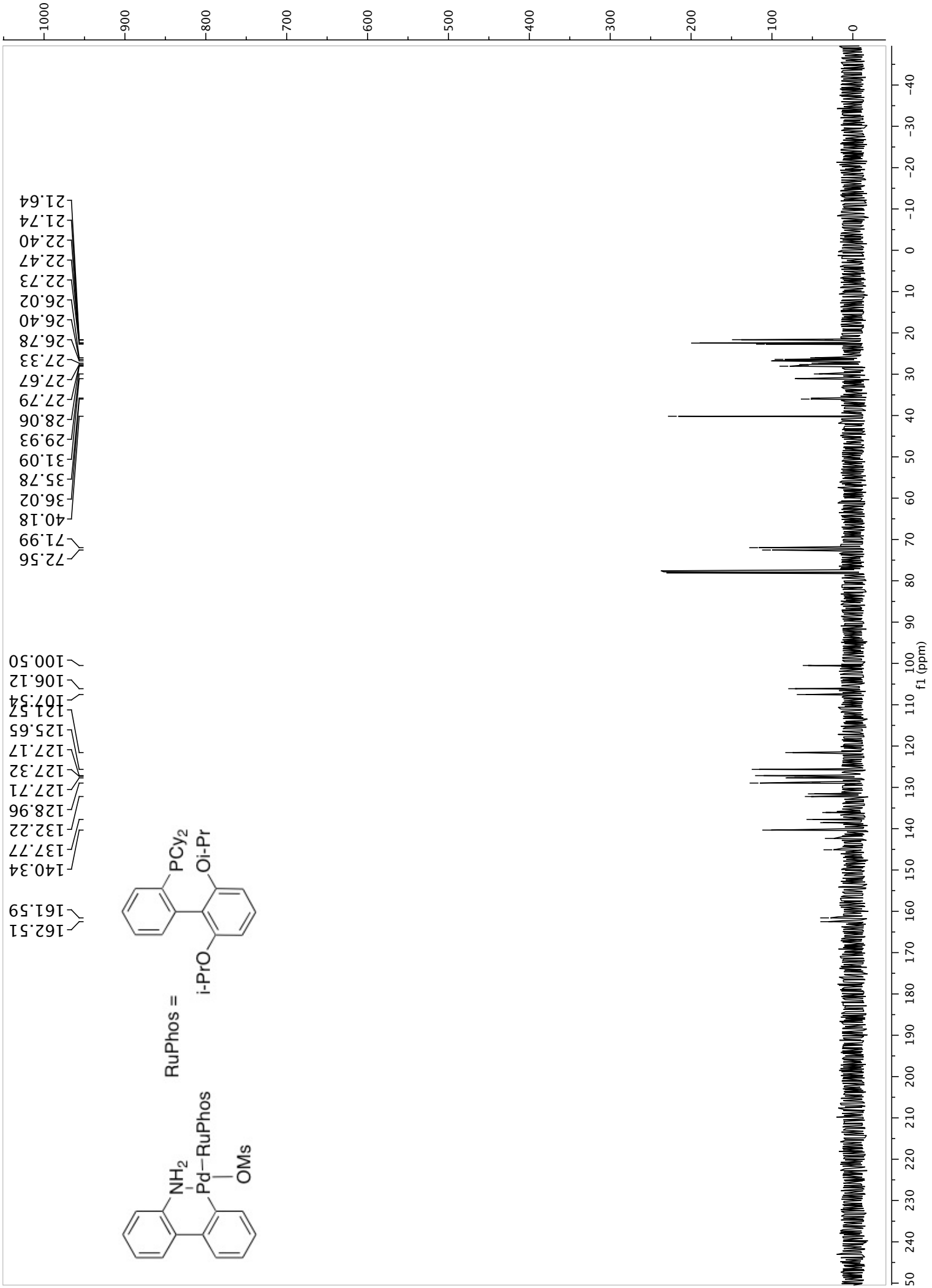


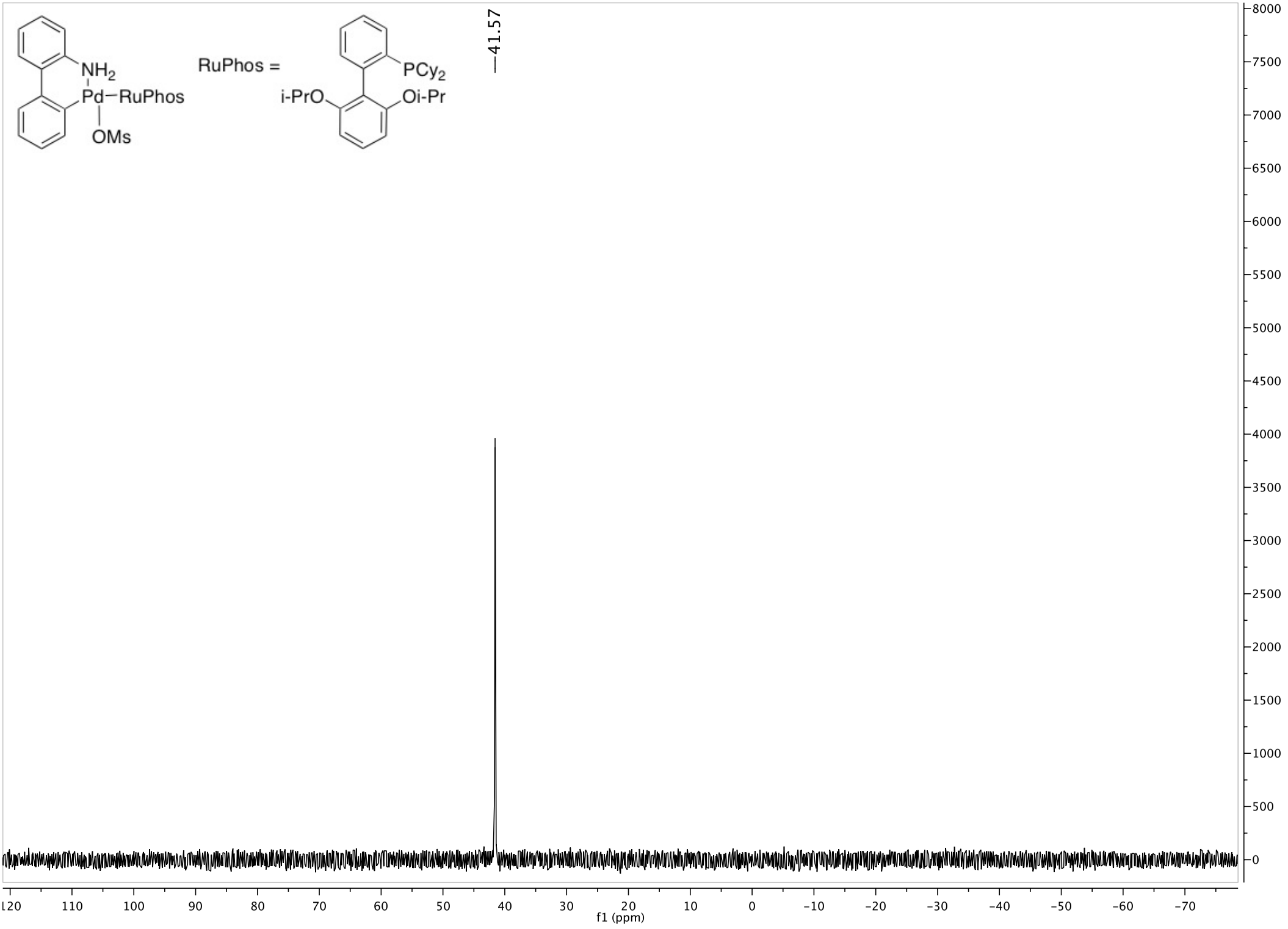


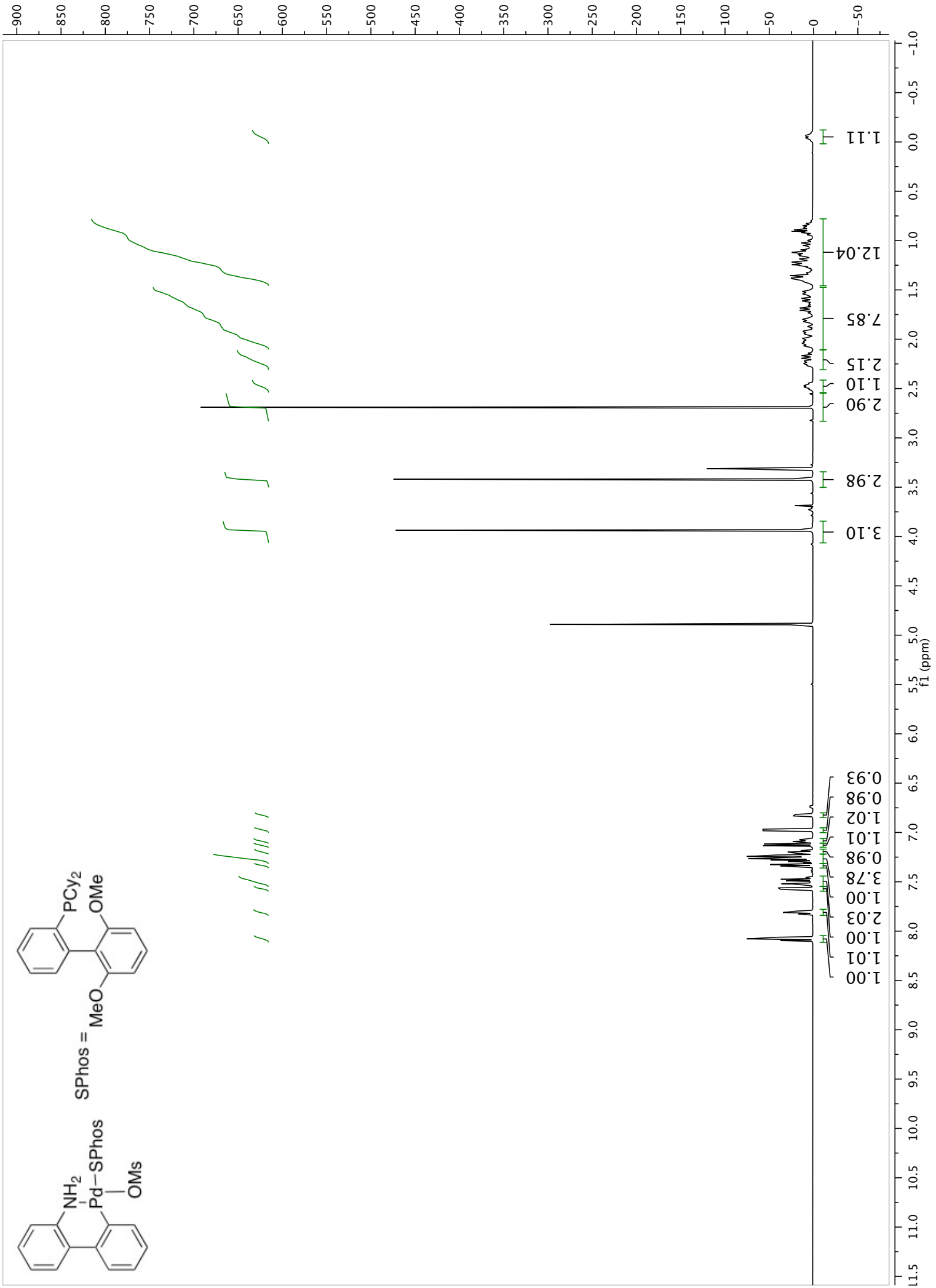


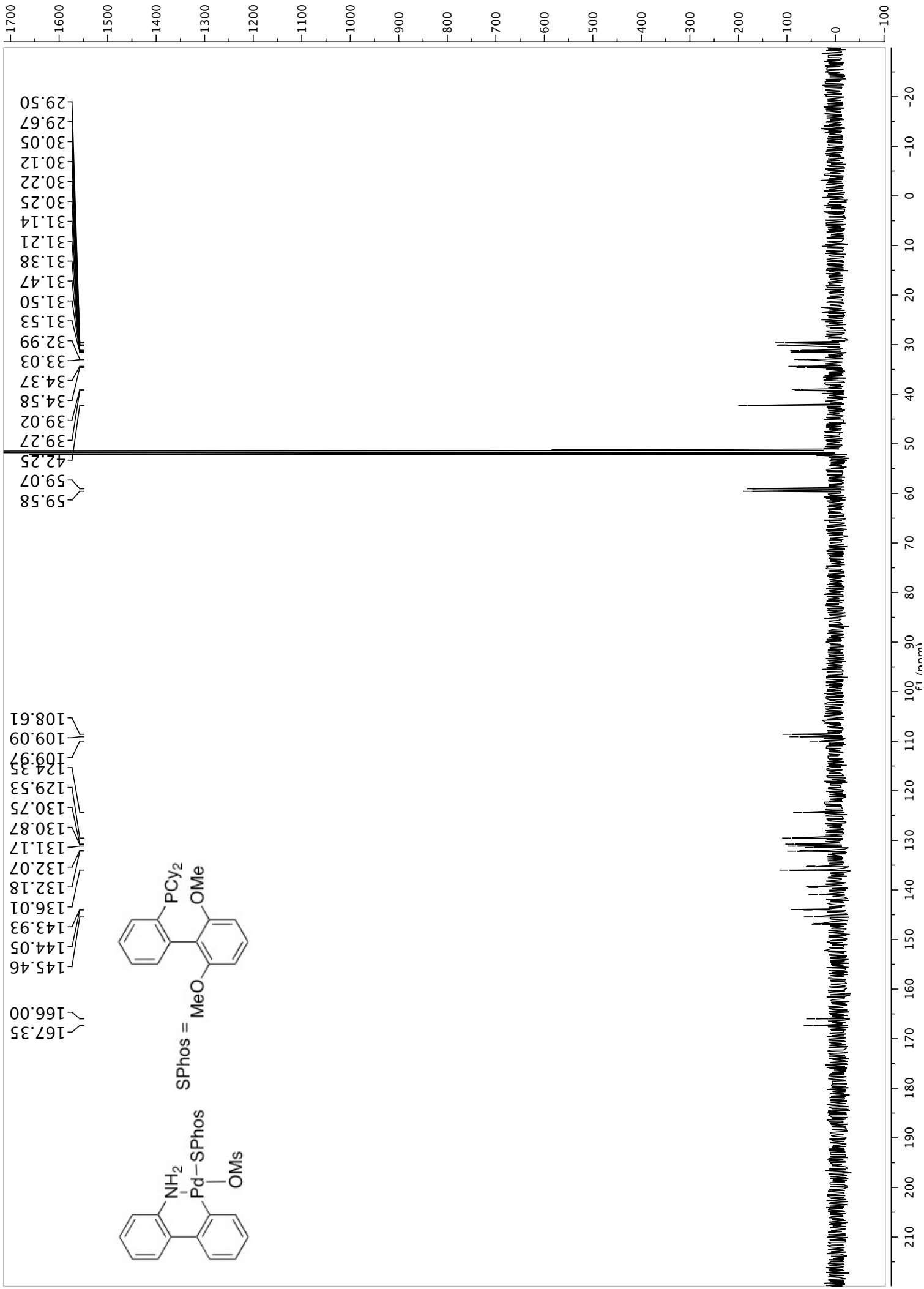


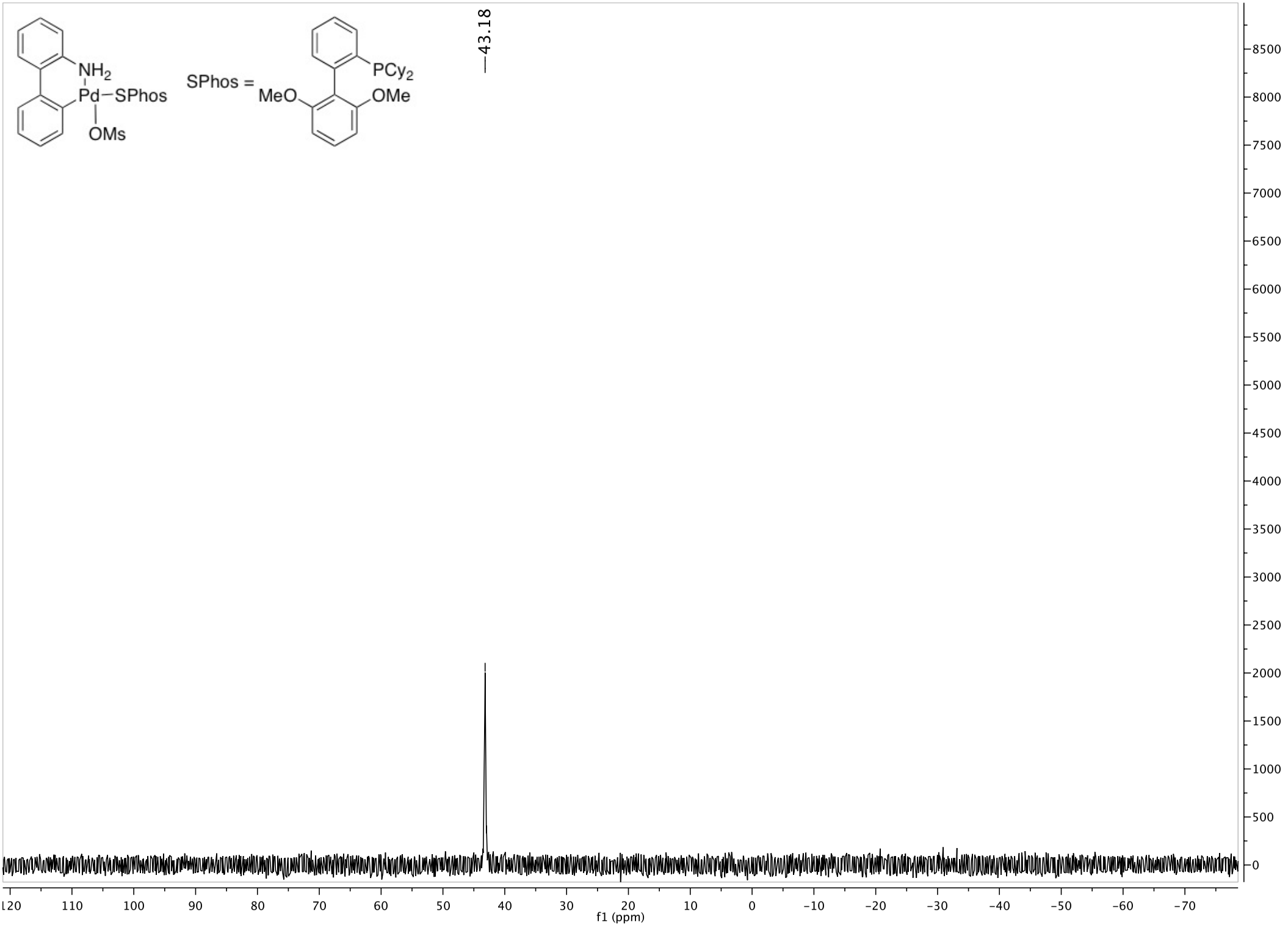


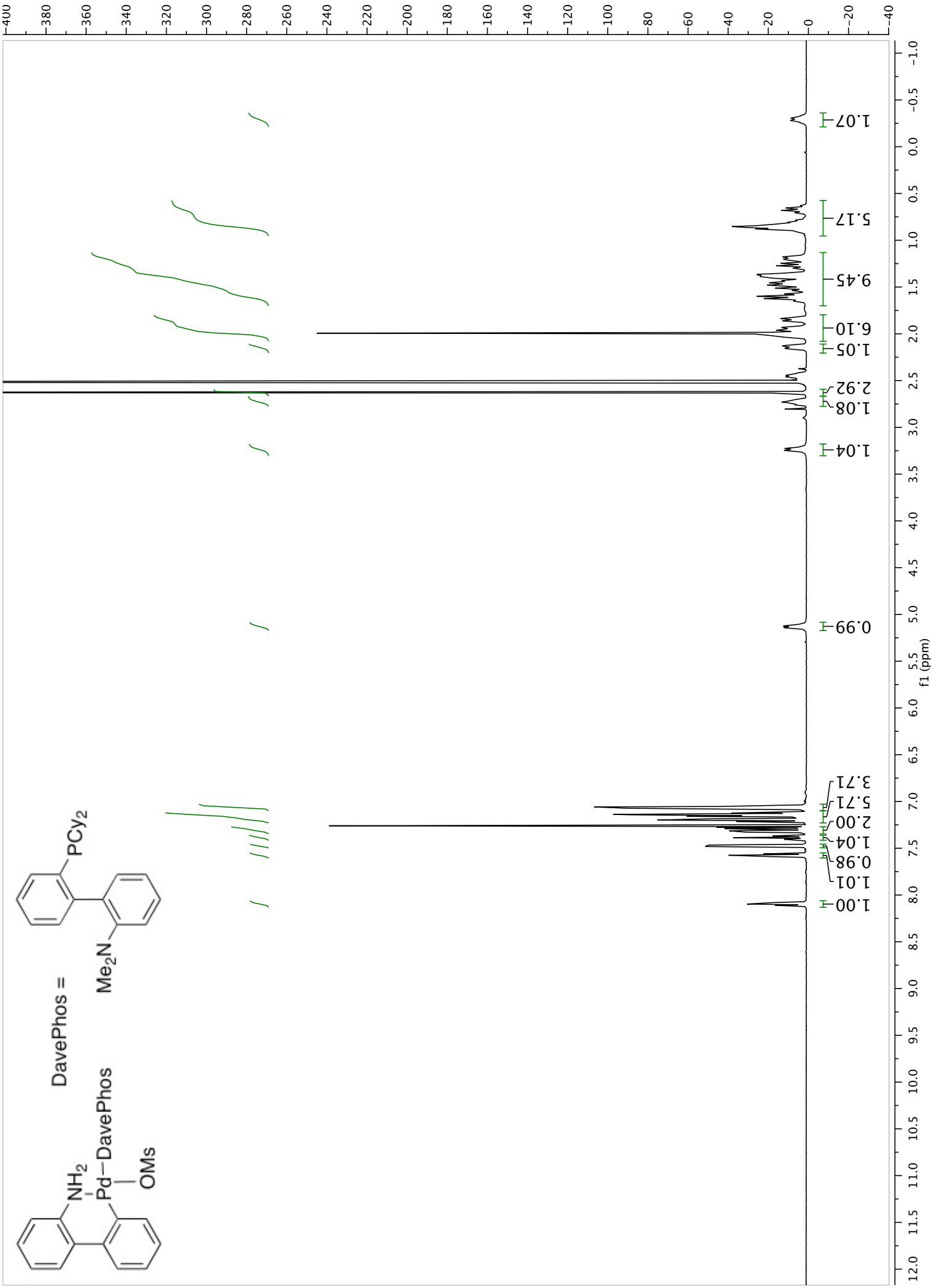


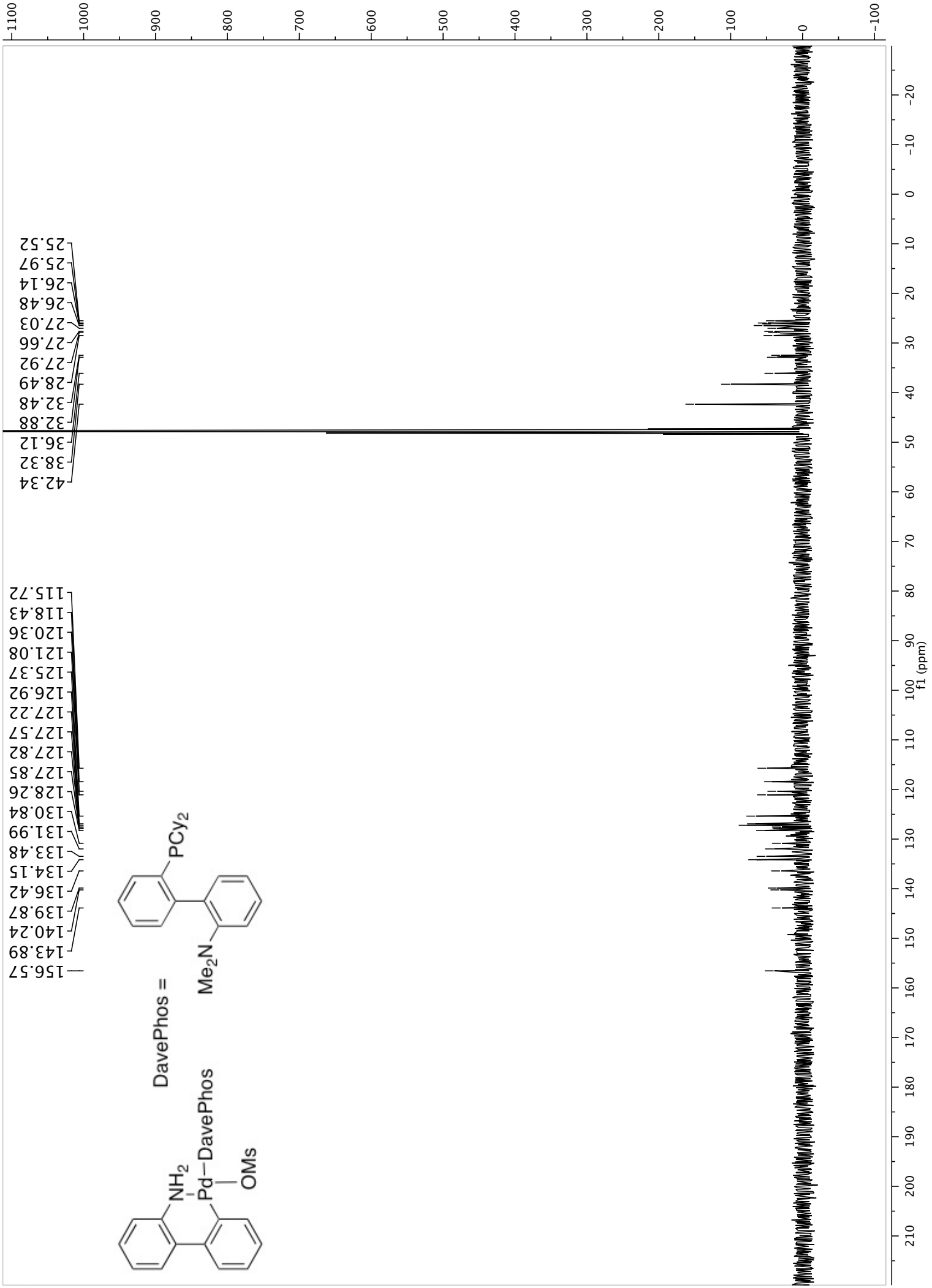


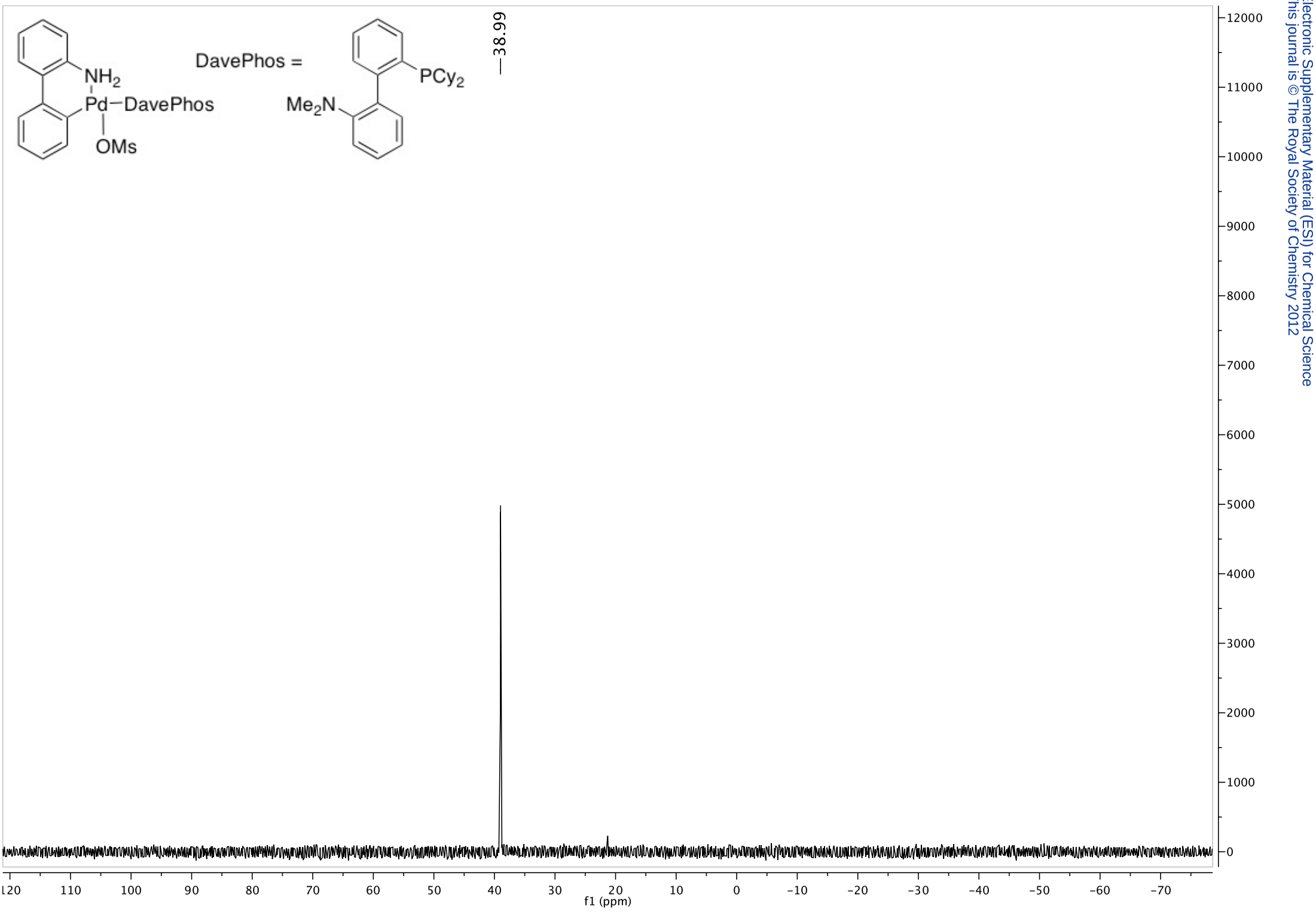

1.11
12.04
7.85
2.15
1.10
2.90
2.98
3.10
1.00
1.01
1.00
2.03
1.00
3.78
0.98
1.01
1.02
0.98
0.93
f1 (ppm)
SPhos =
PCy2
OMe
MeO
NH2
Pd
SPhos
OMs

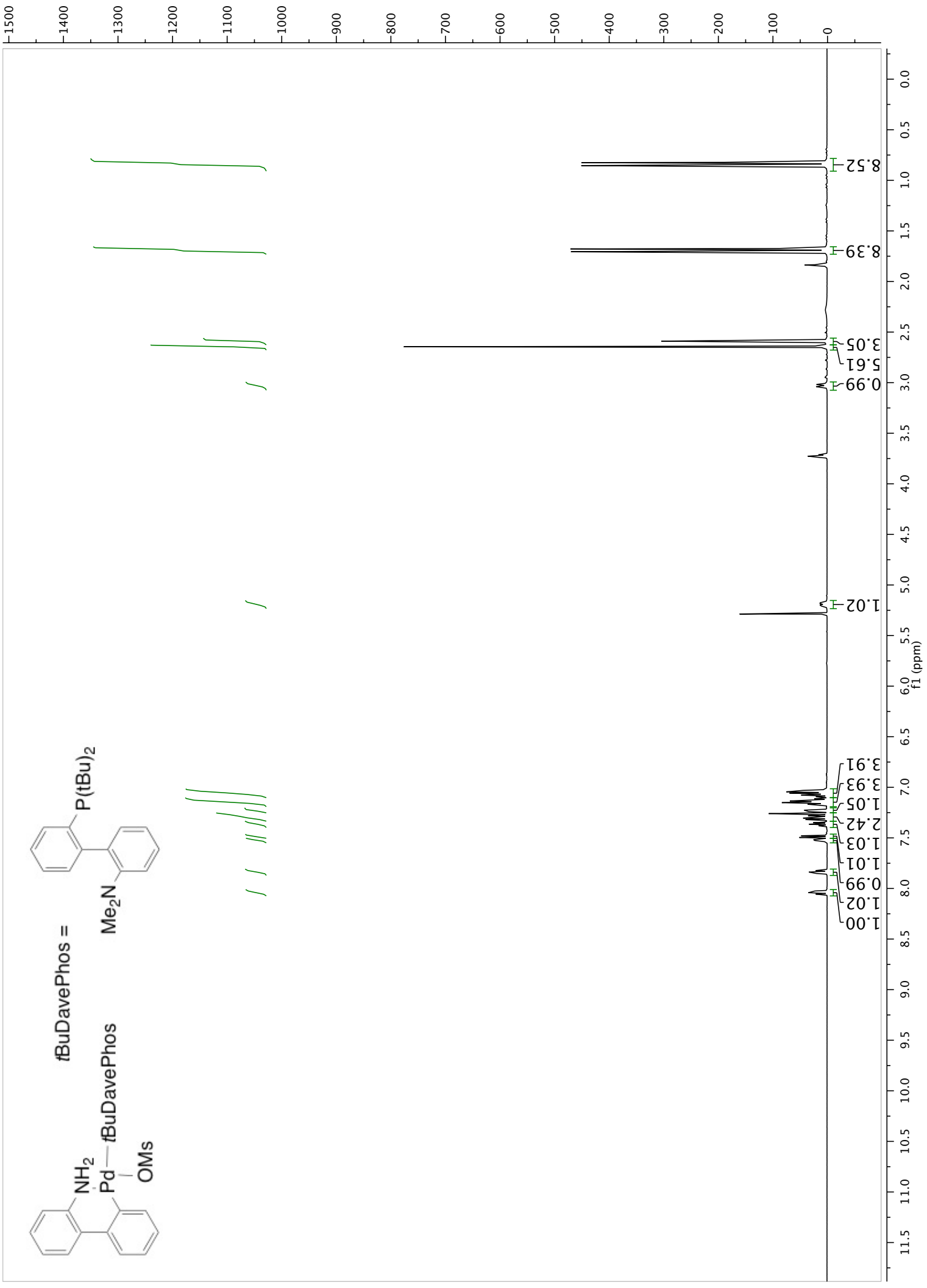


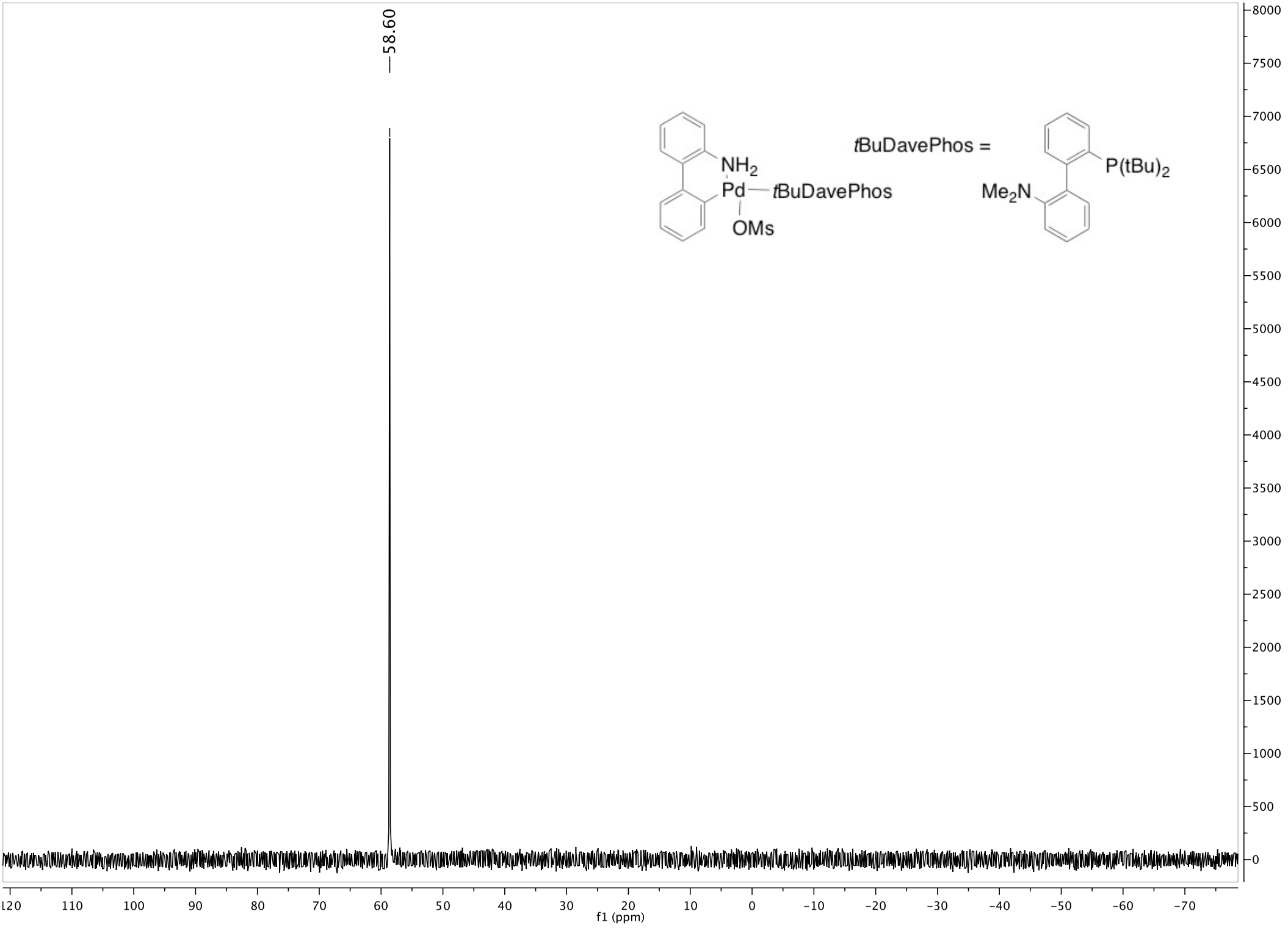


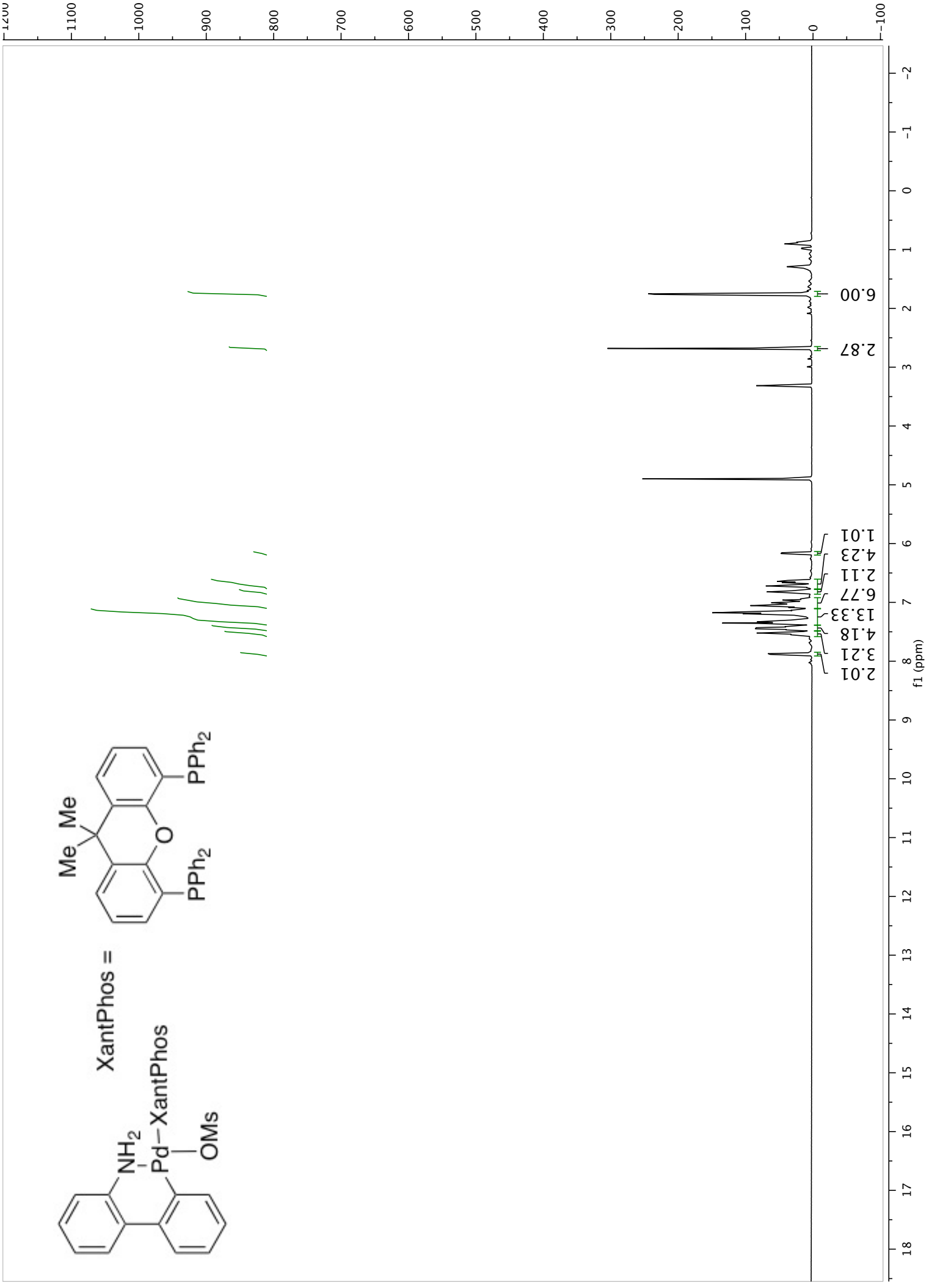


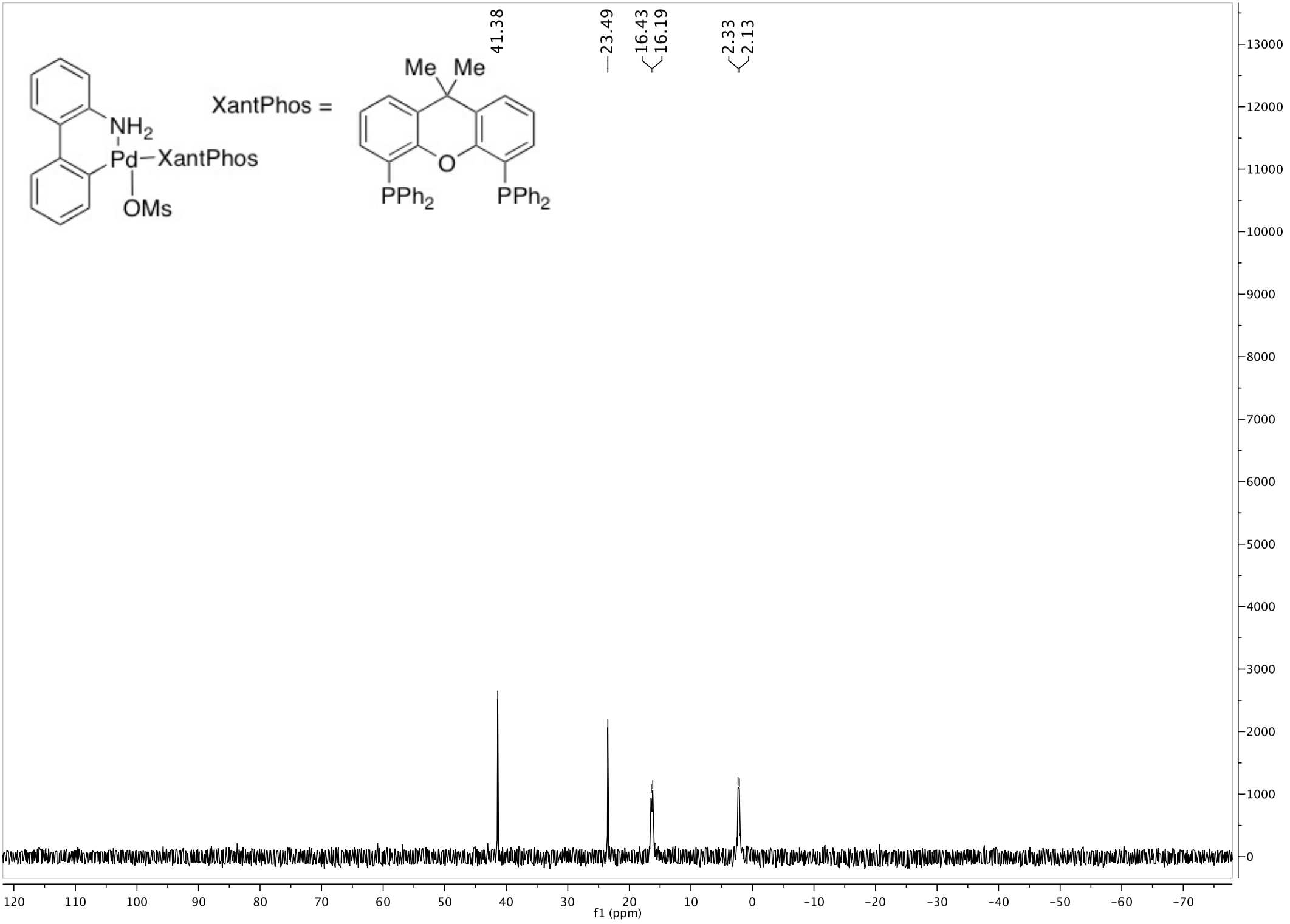


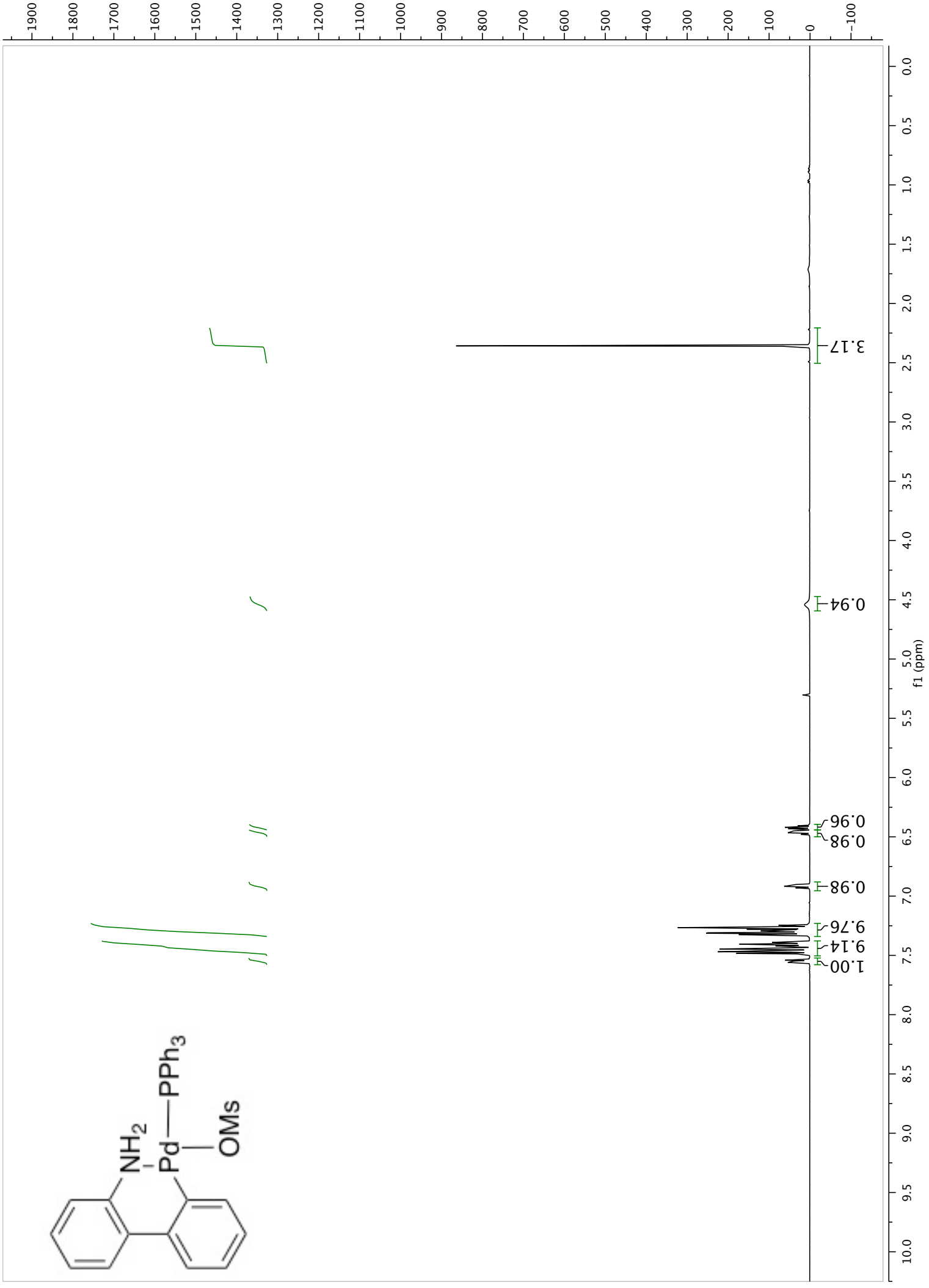


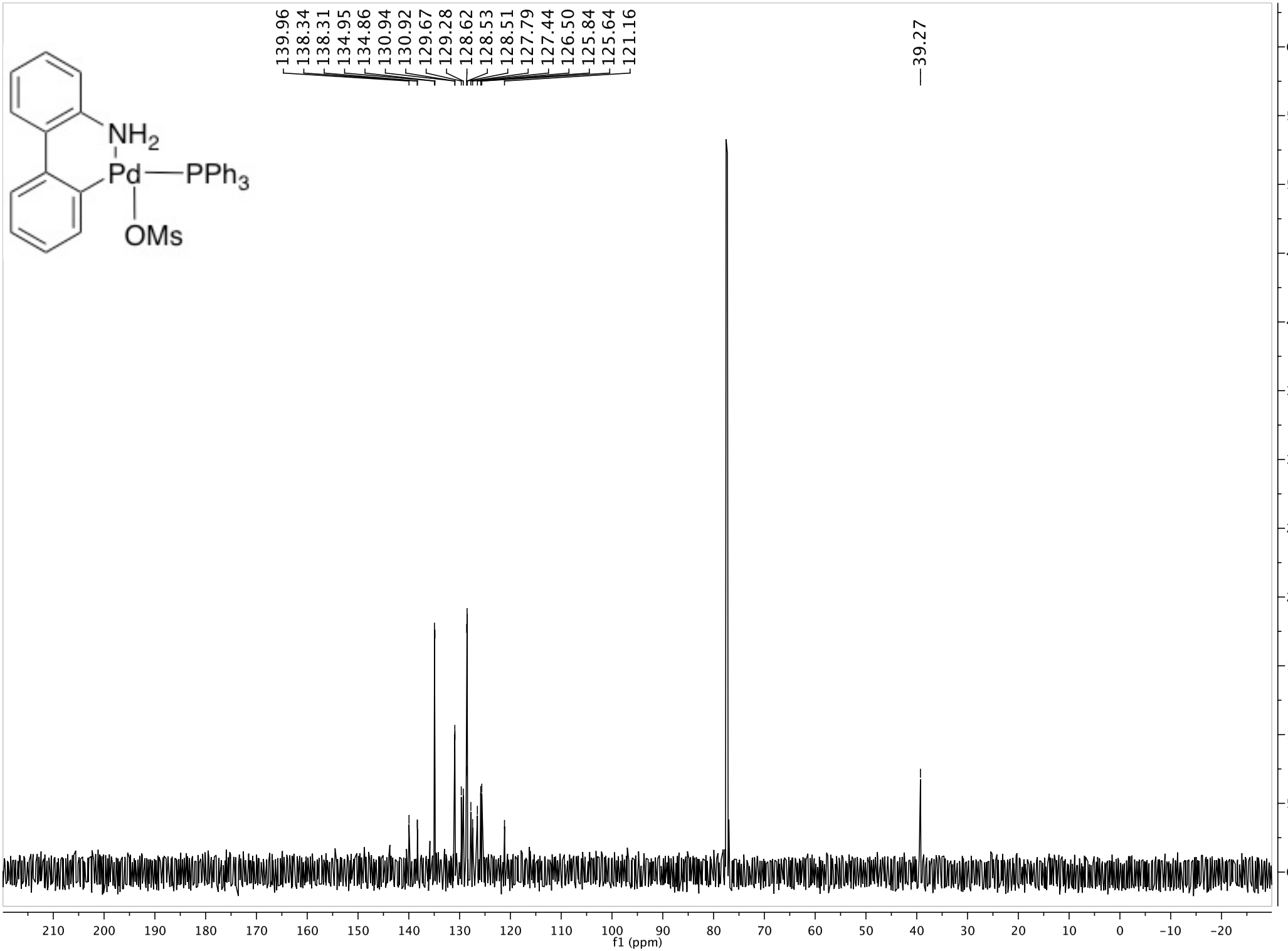


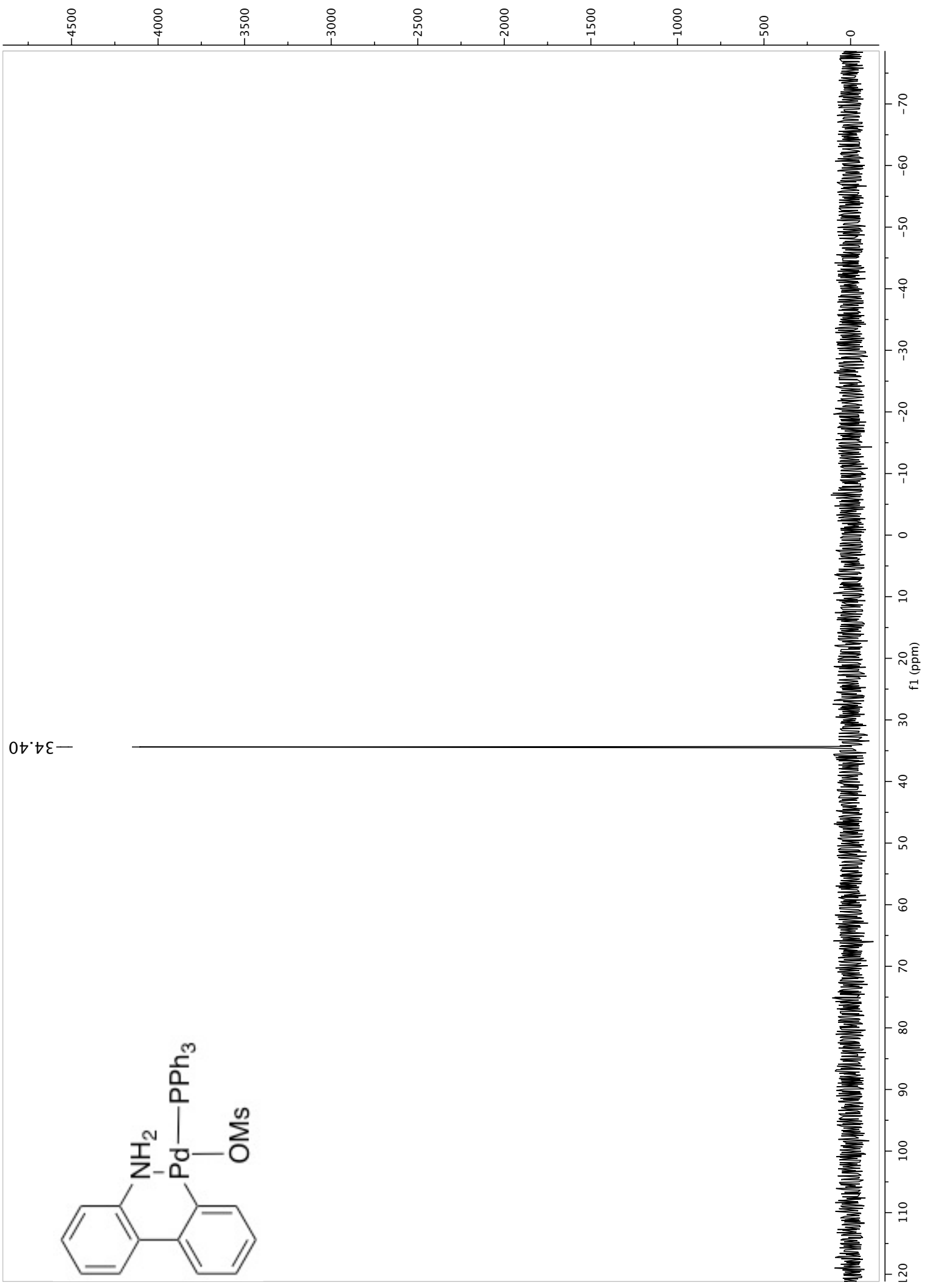


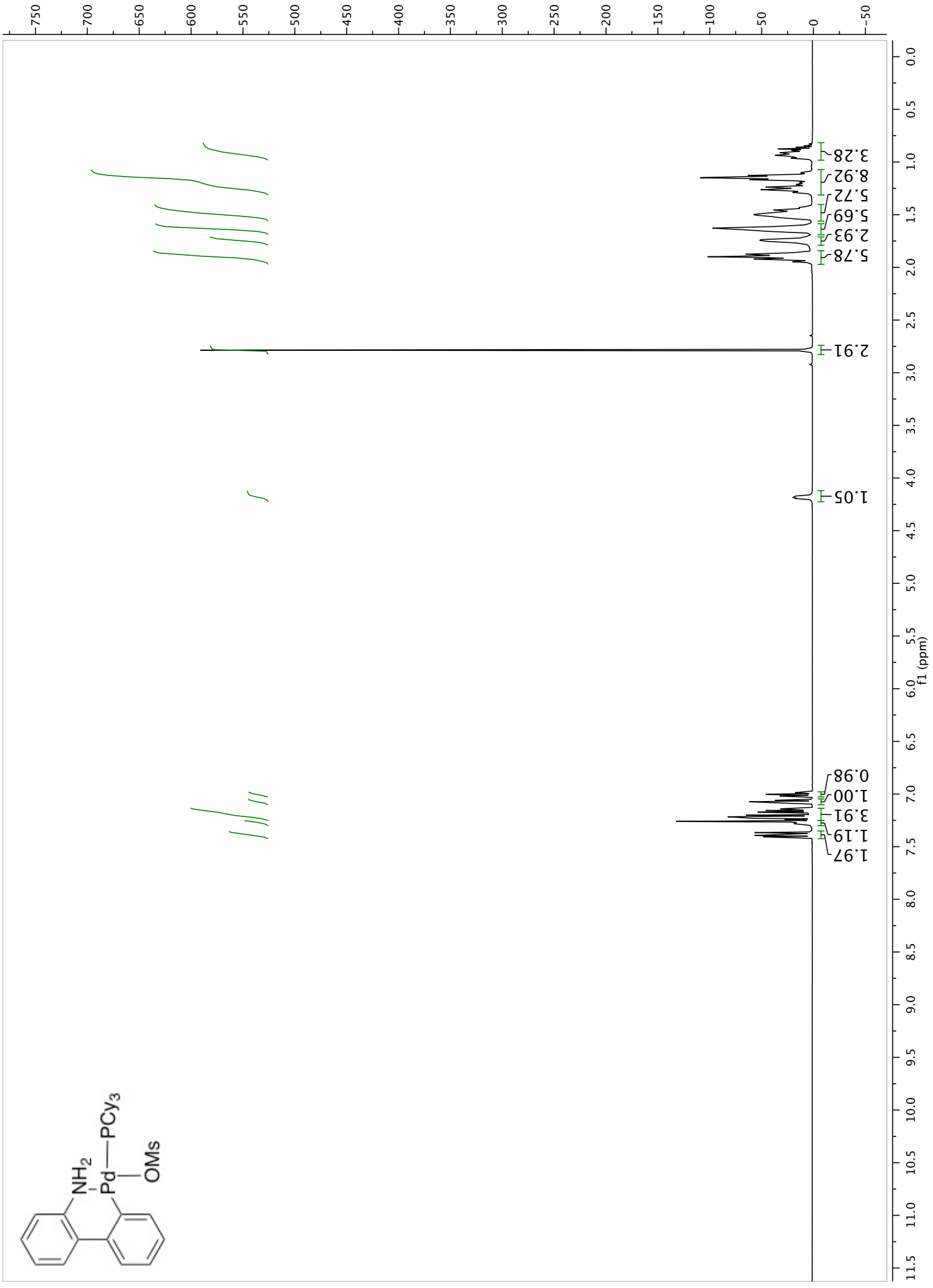

6.00
2.87
1.01
4.23
2.11
6.77
13.33
4.18
3.21
2.01
f1 (ppm)
XantPhos =
Me
Me
O
PPh2
PPh2
NH2
Pd
XantPhos
OMs

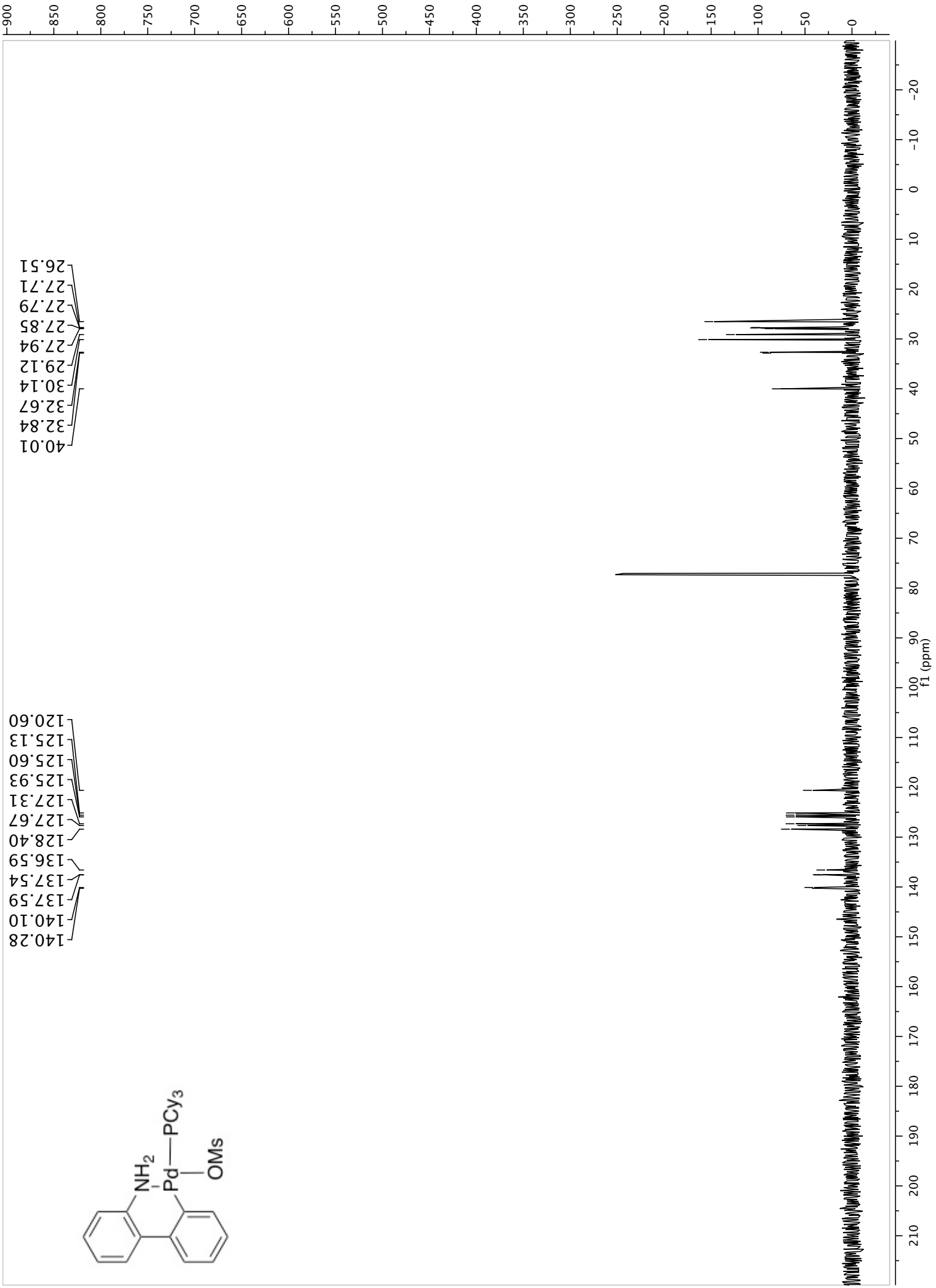


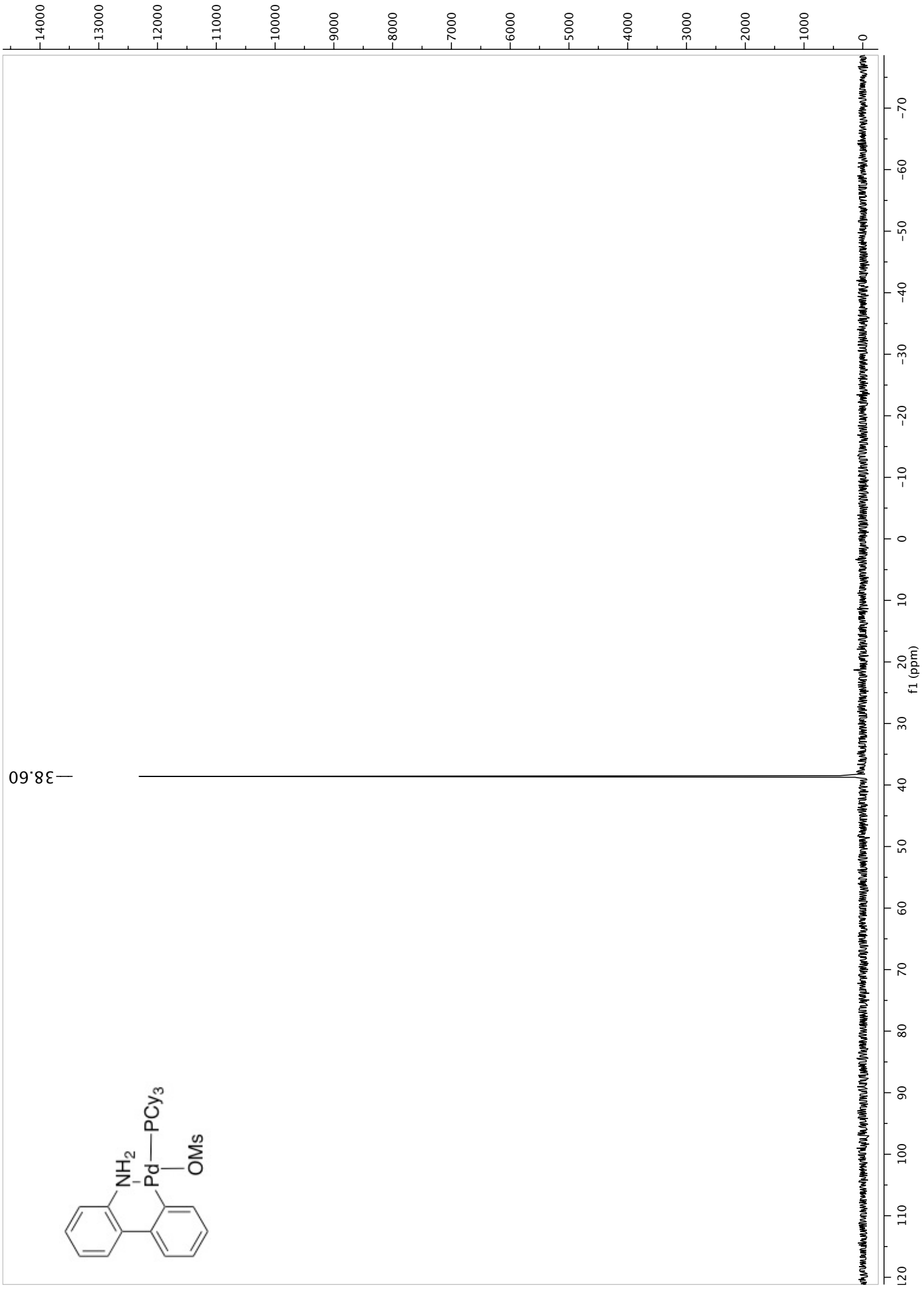


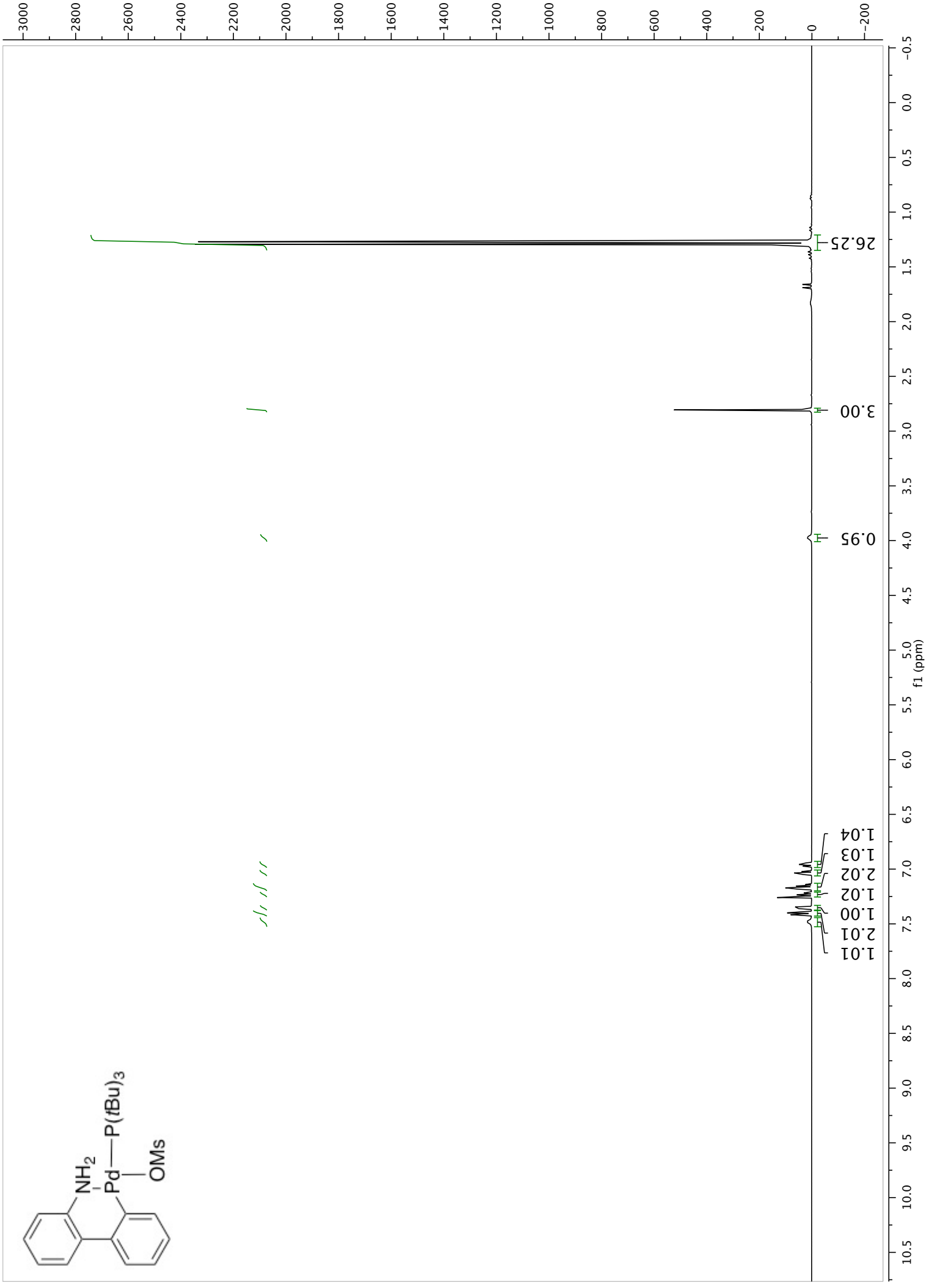


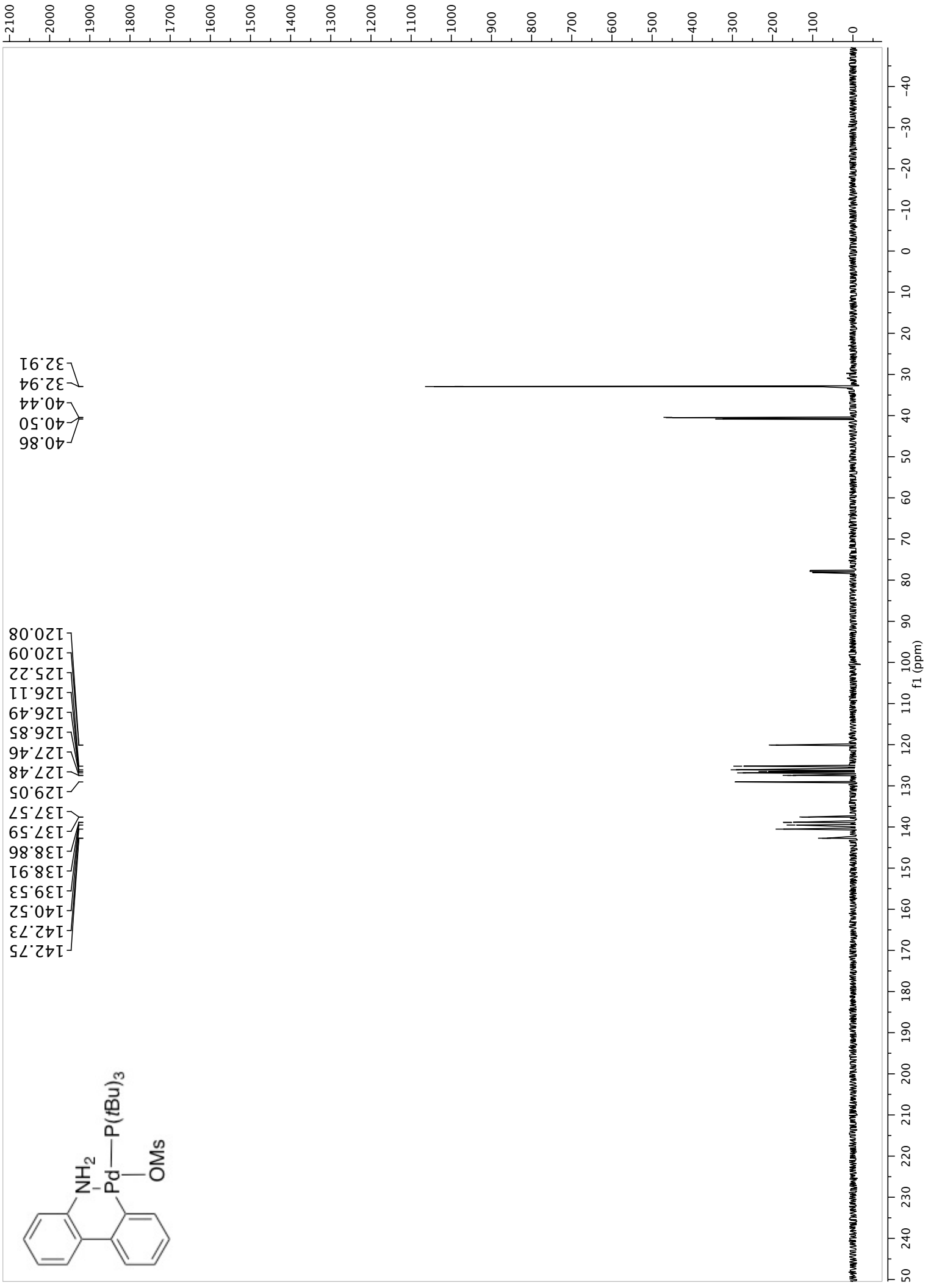


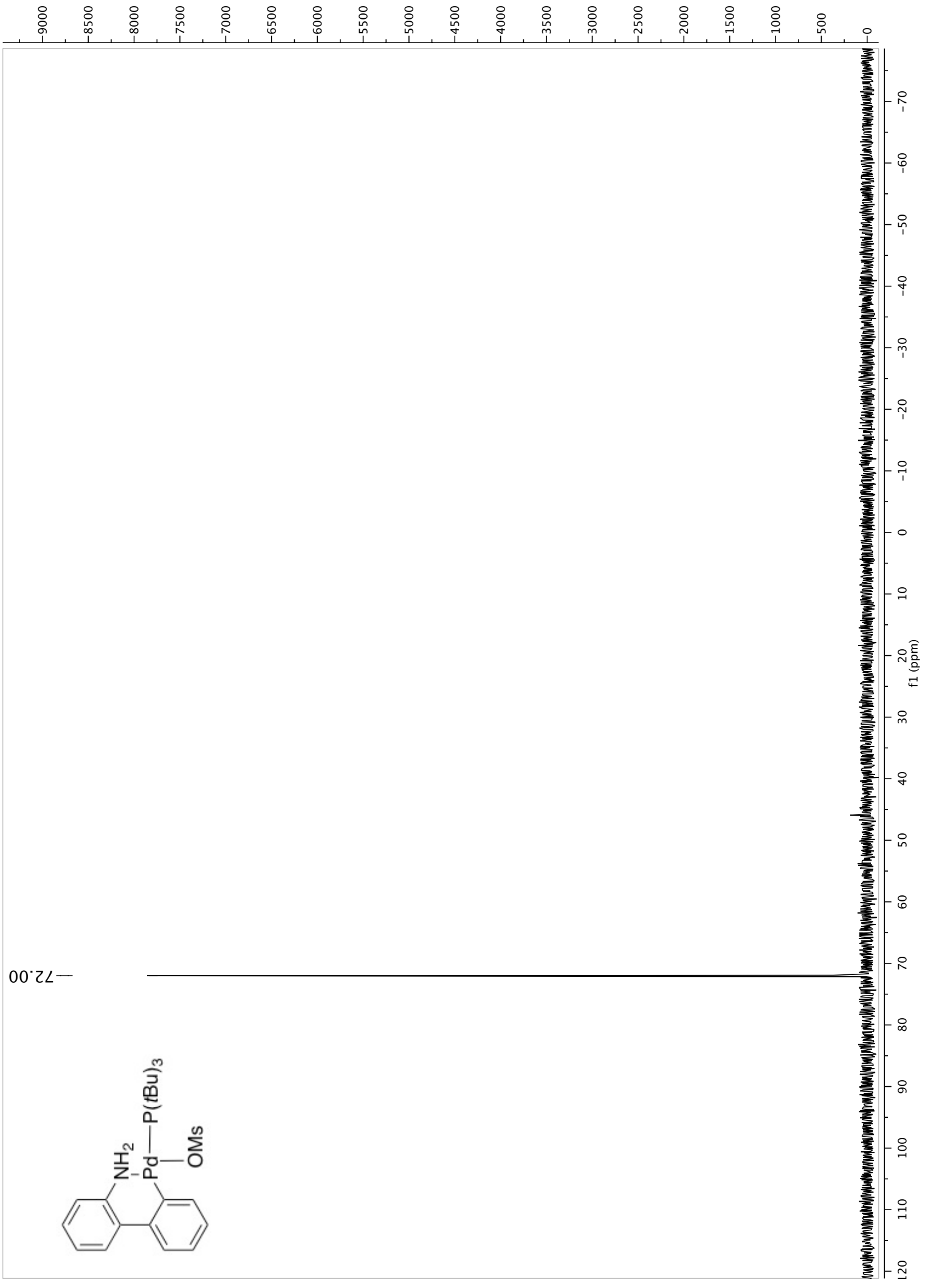


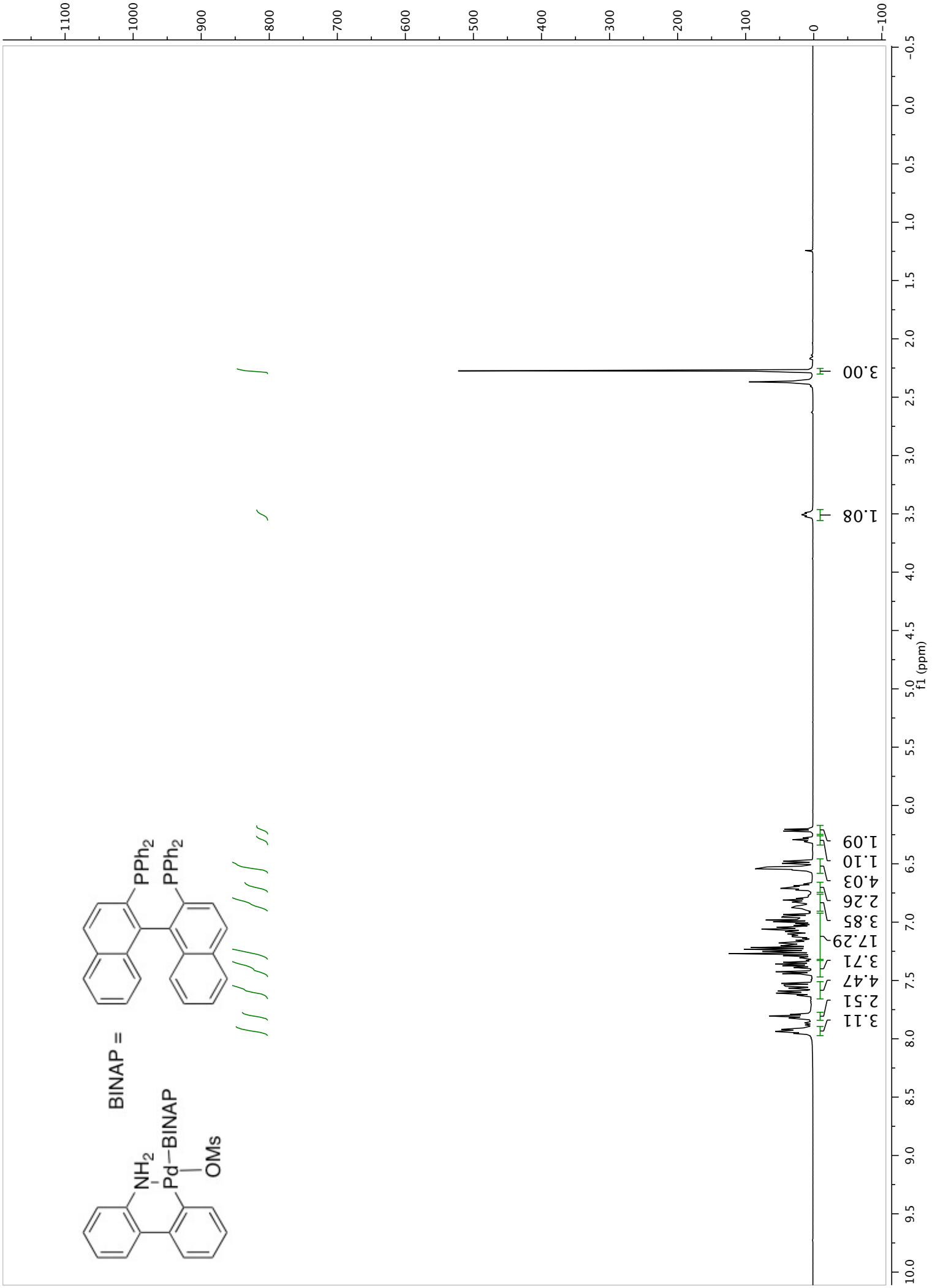


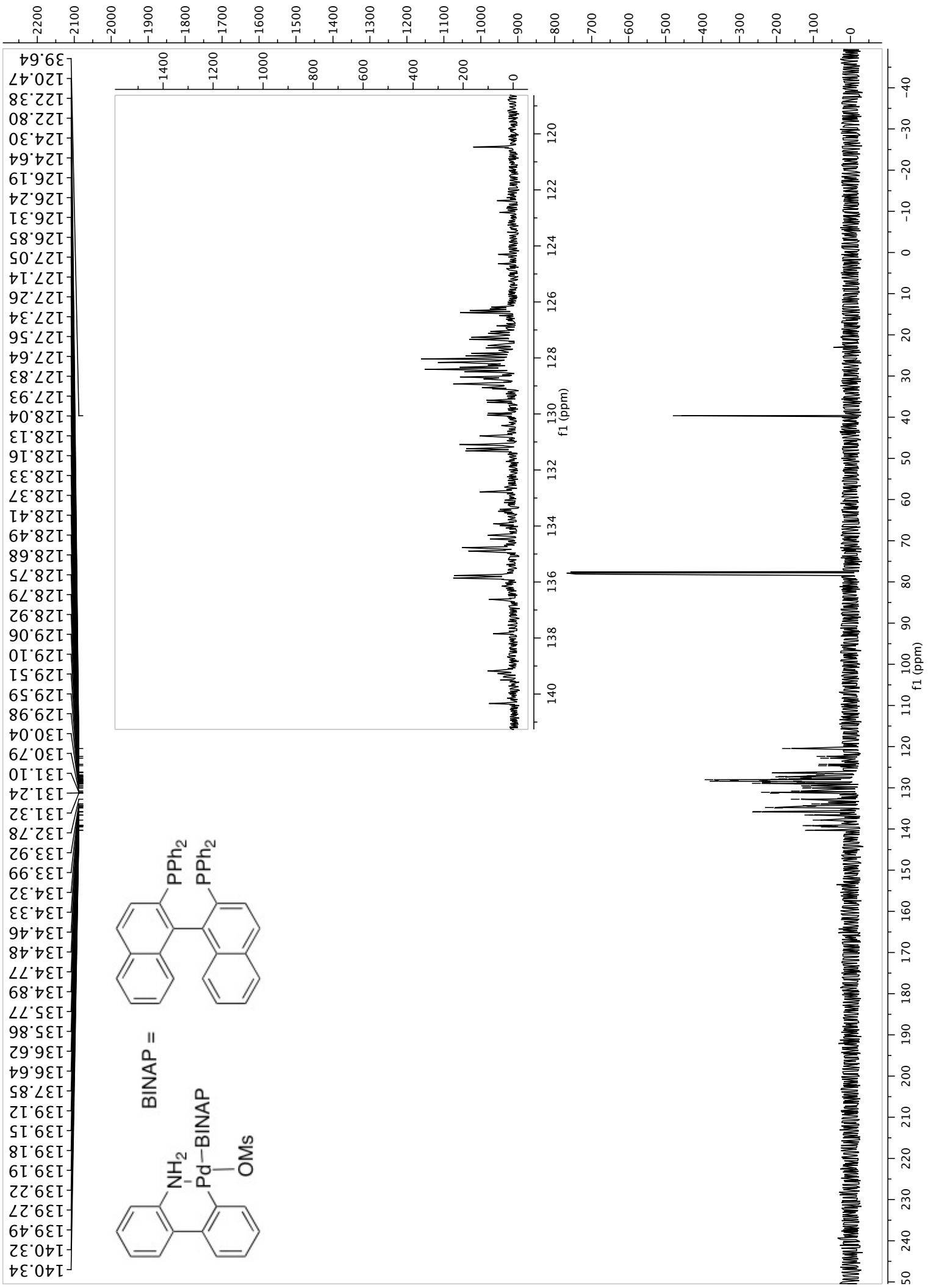

38.60
NH2
Pd
PCy3
OMs
f1 (ppm)

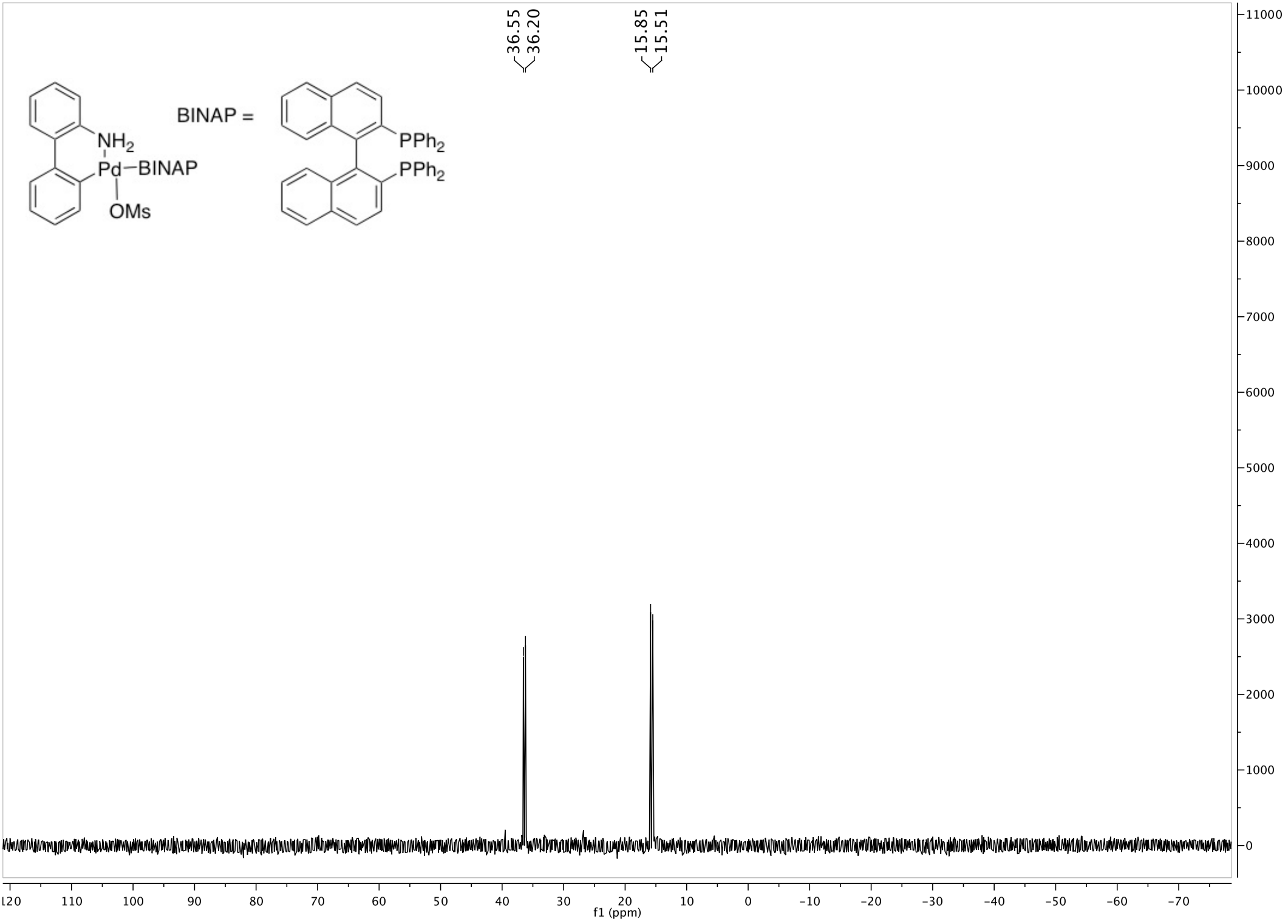


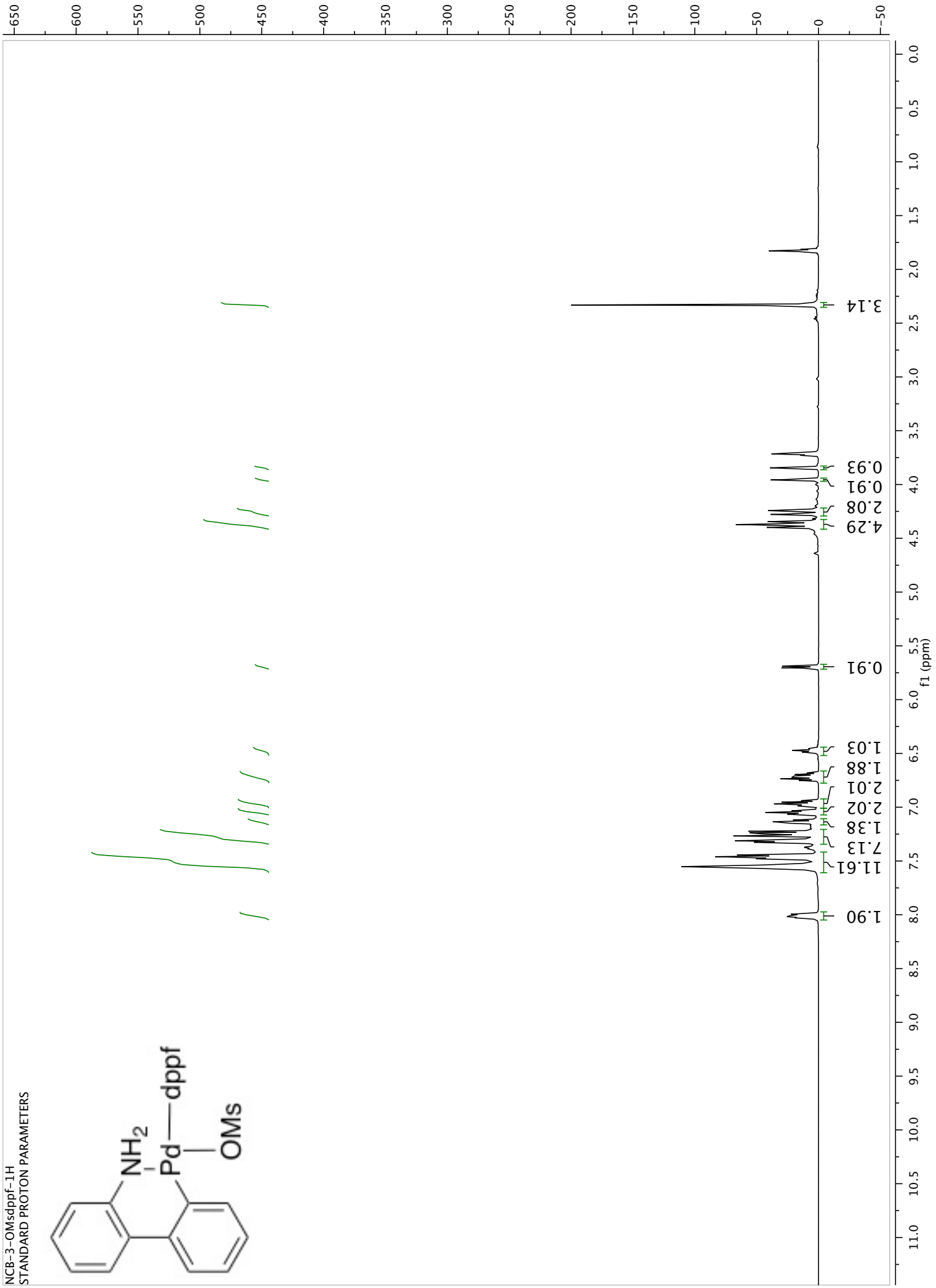

142.75
142.73
140.52
139.53
138.91
138.86
137.59
137.57
129.05
127.48
127.46
126.85
126.49
126.11
125.22
120.09
120.08
40.86
40.50
40.44
32.94
32.91
NH2
Pd
P(tBu)3
OMs
f1 (ppm)

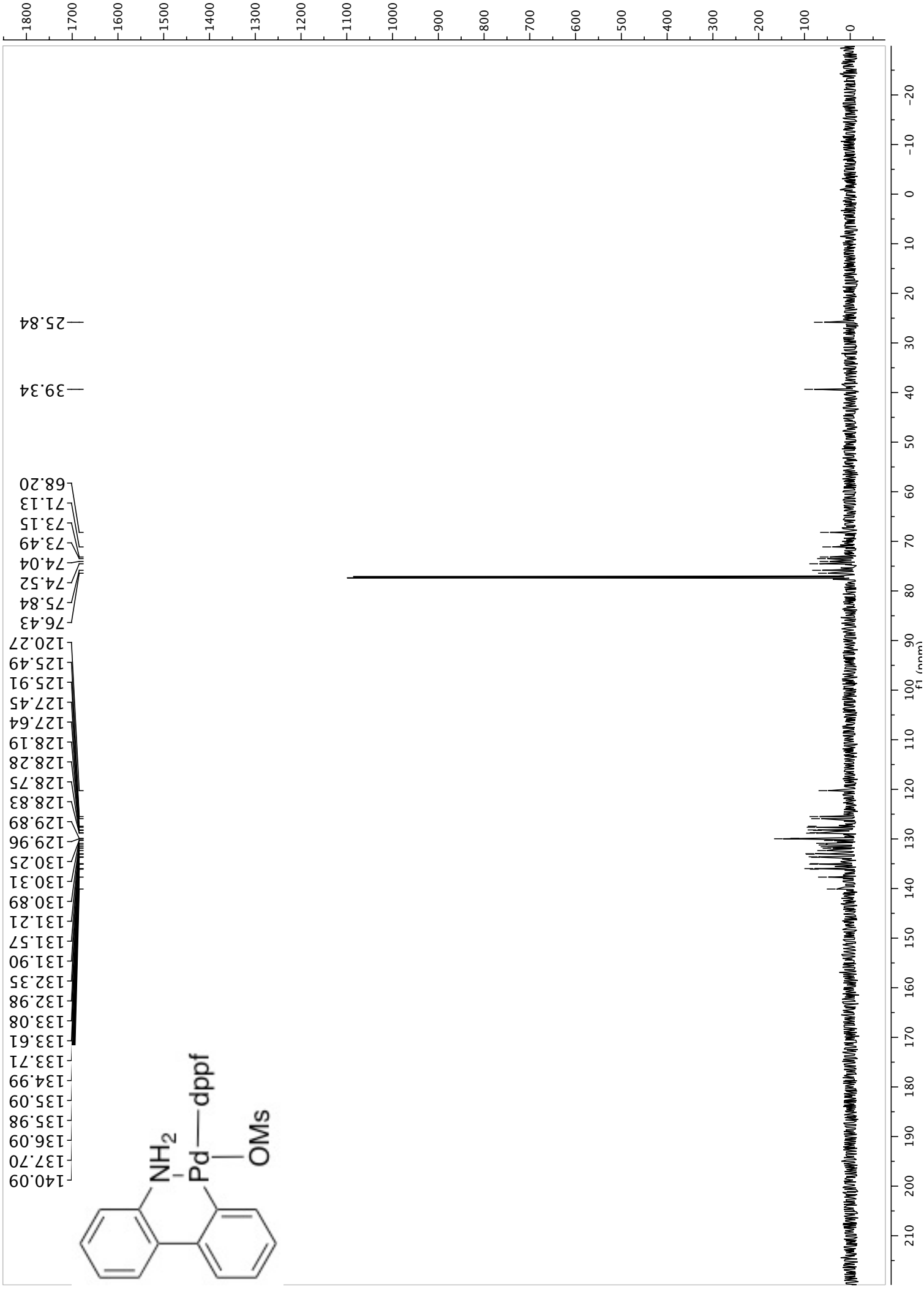

72.00
NH2
Pd
P(tBu)3
OMs
f1 (ppm)

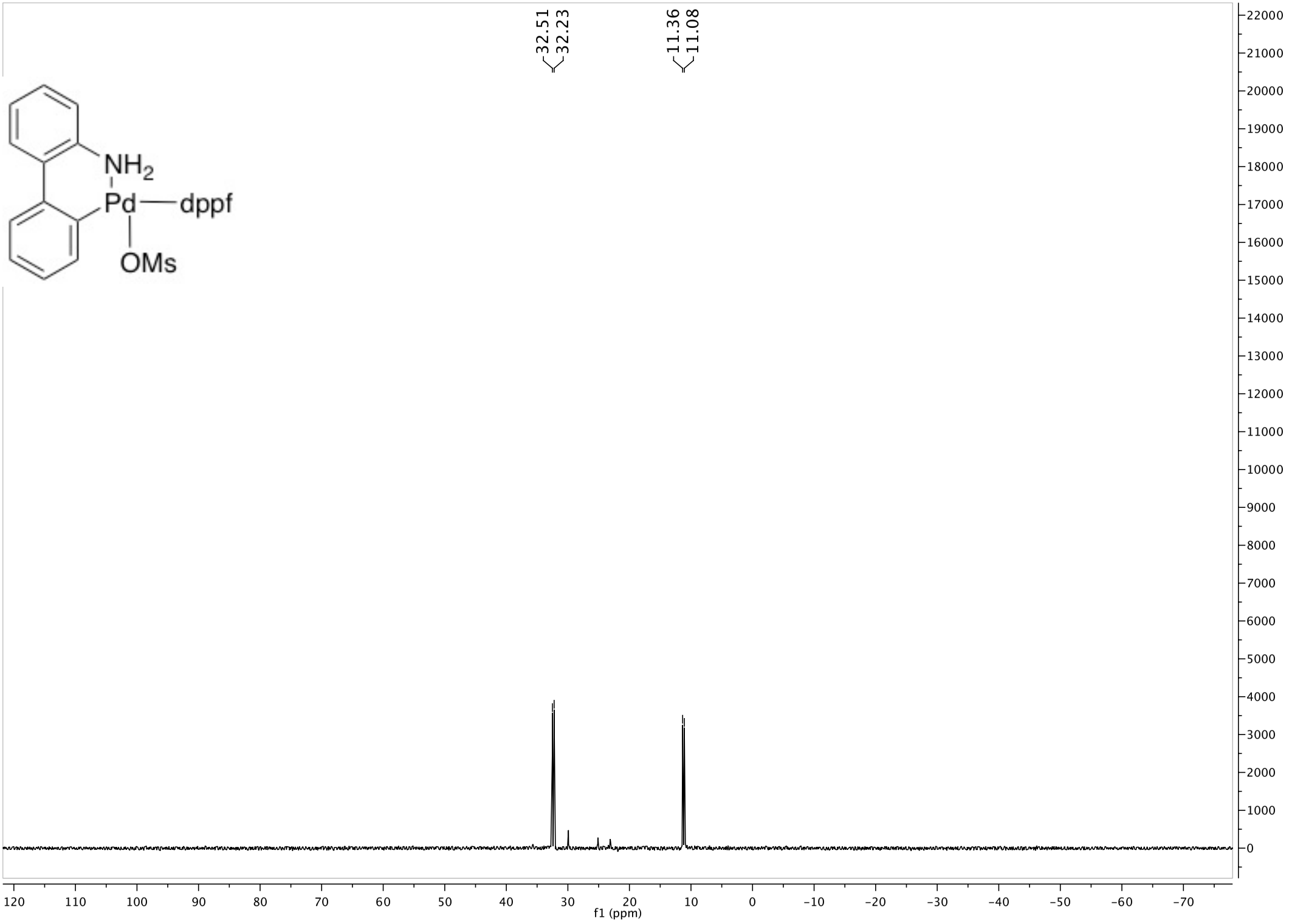

3.00
1.08
1.09
1.10
4.03
2.26
3.85
17.29
3.71
4.47
2.51
3.11
f1 (ppm)
BINAP =
PPh2
PPh2
NH2
Pd—BINAP
OMs

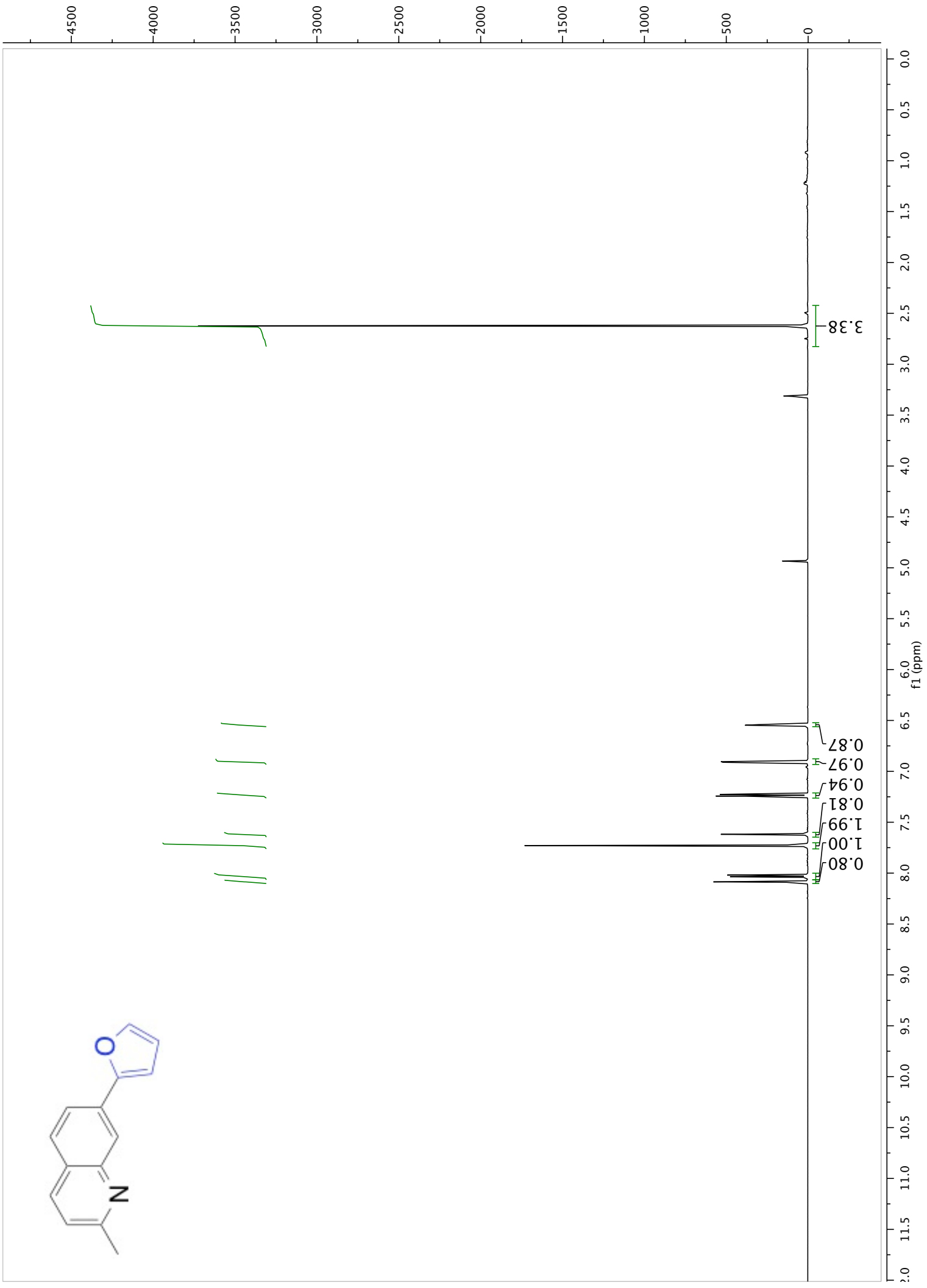


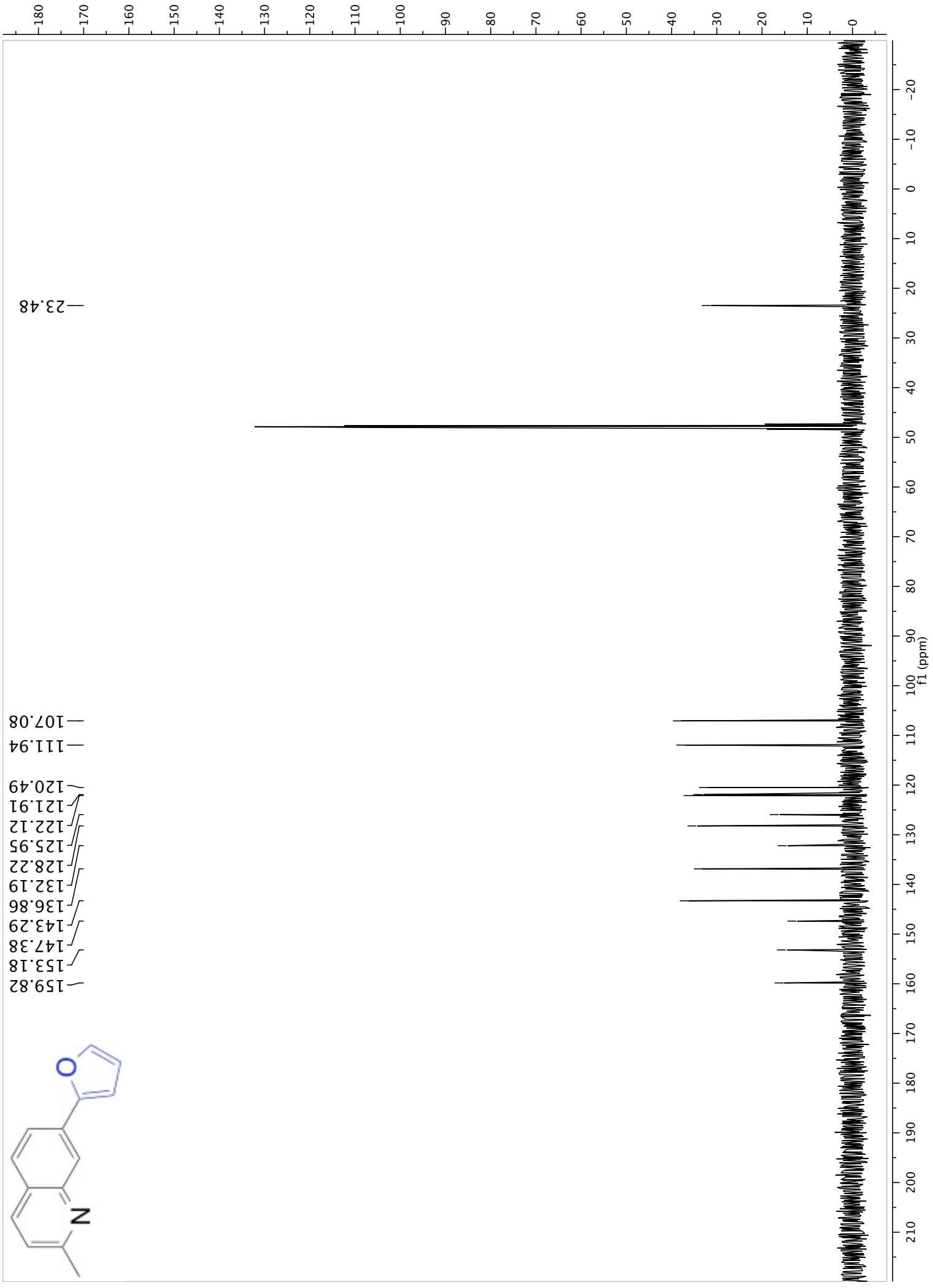


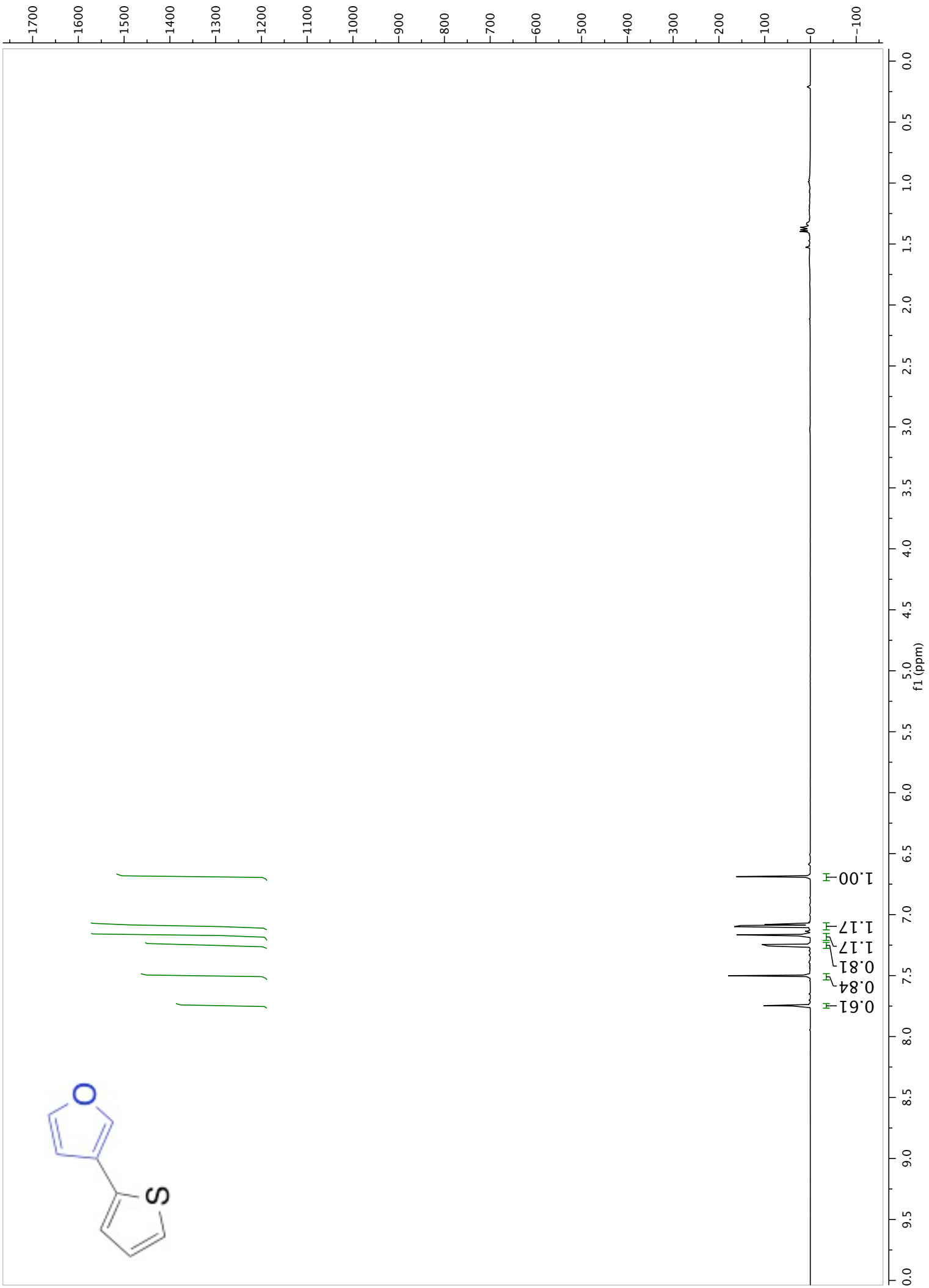


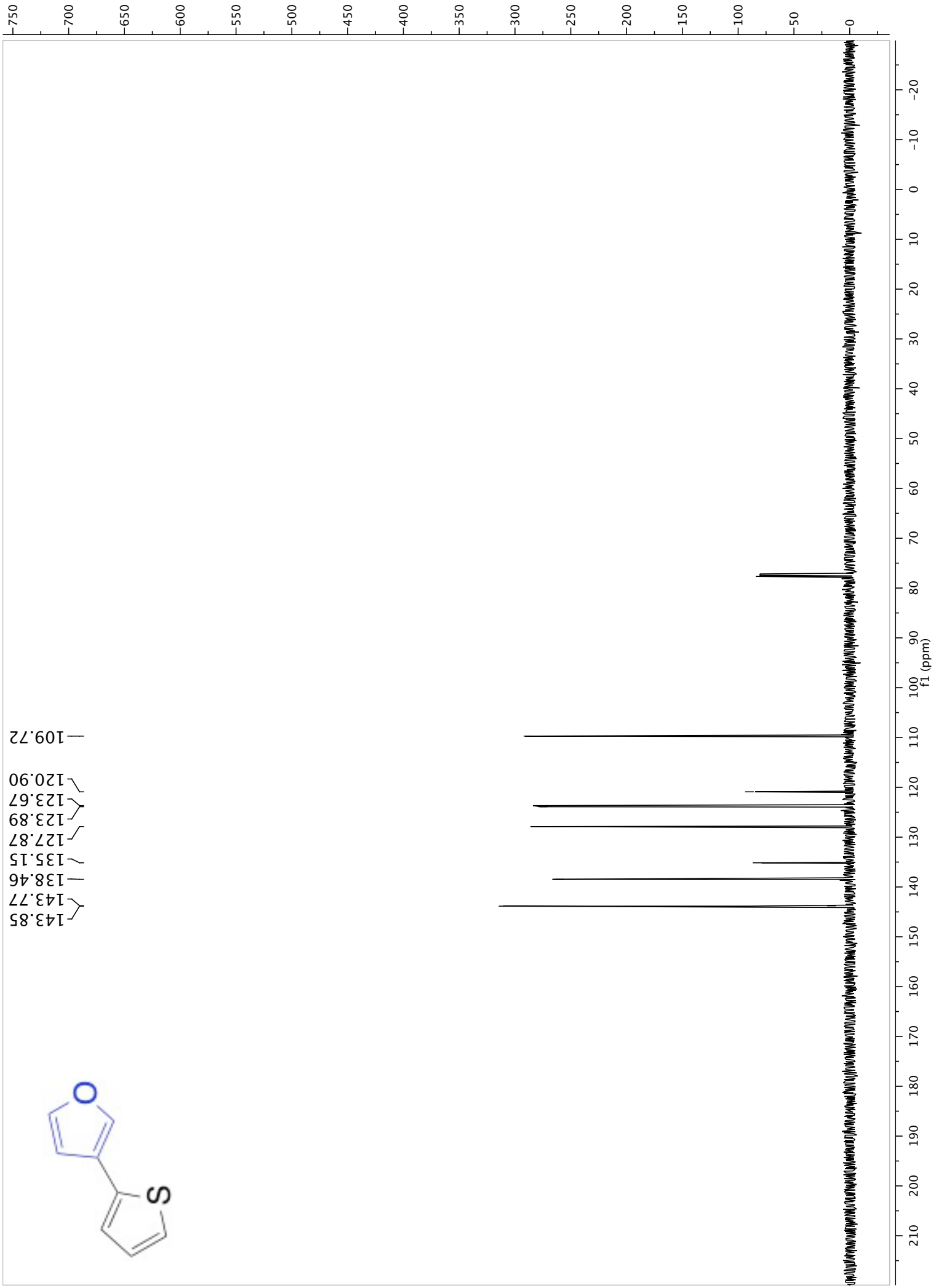


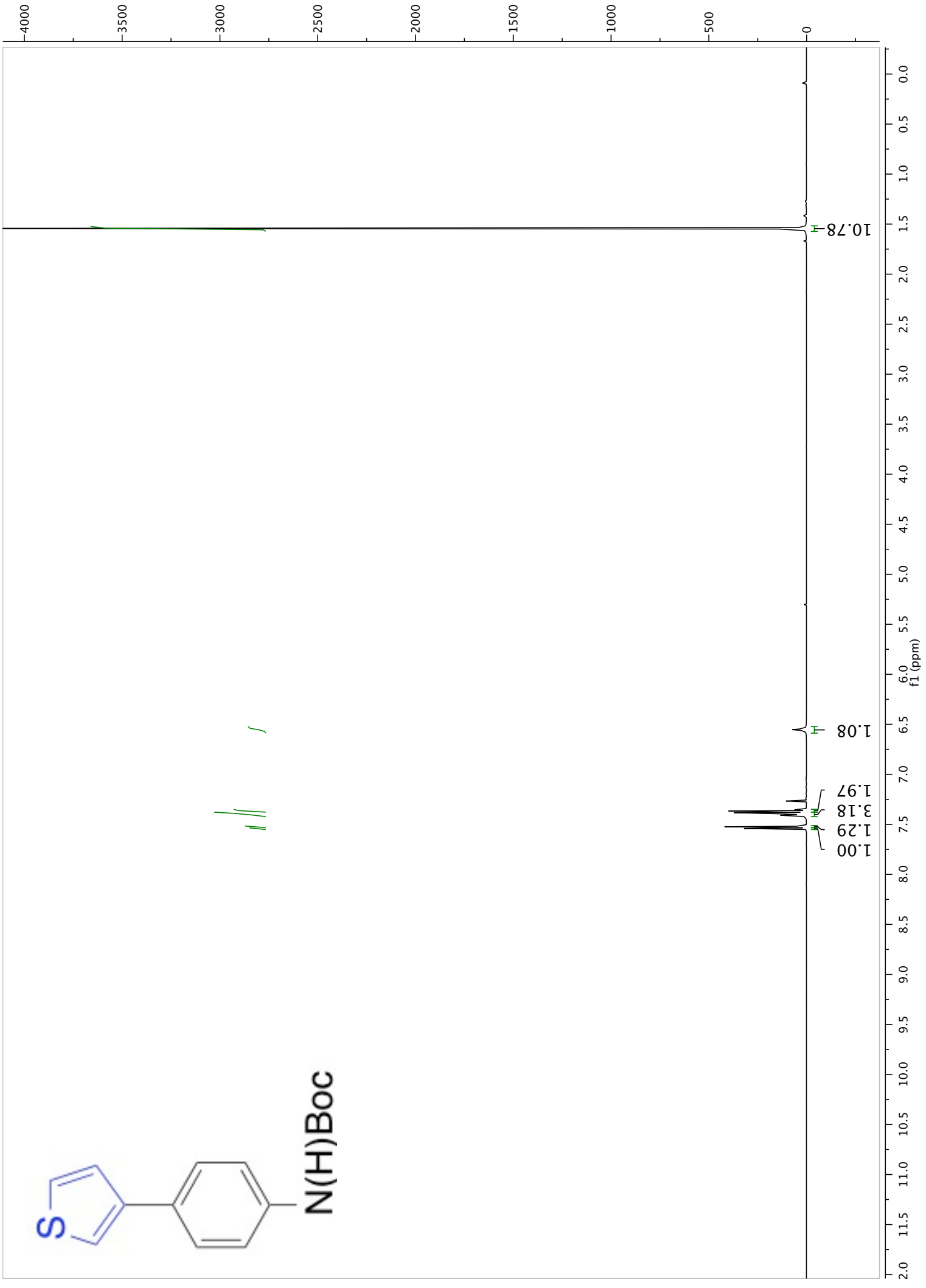


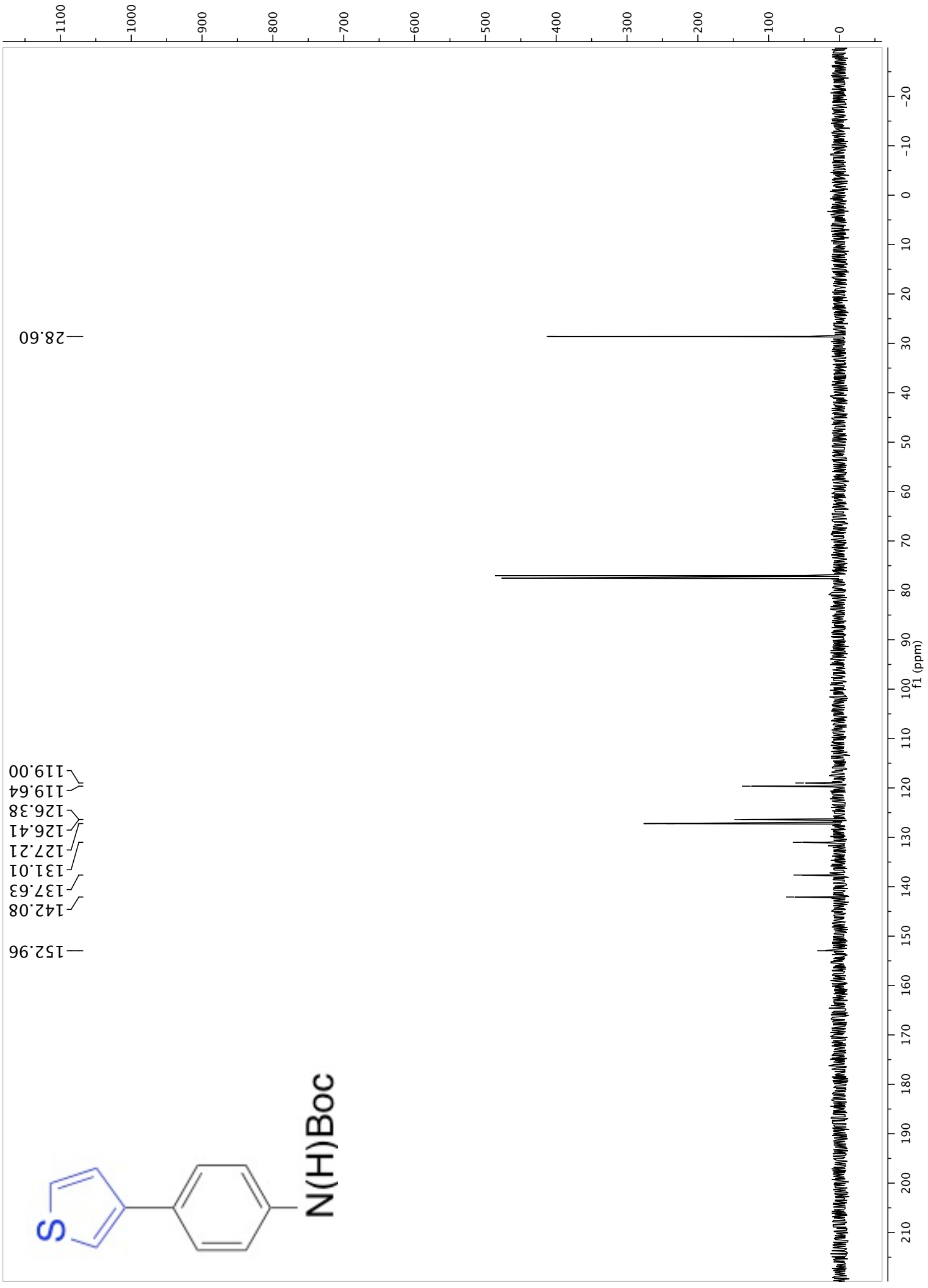


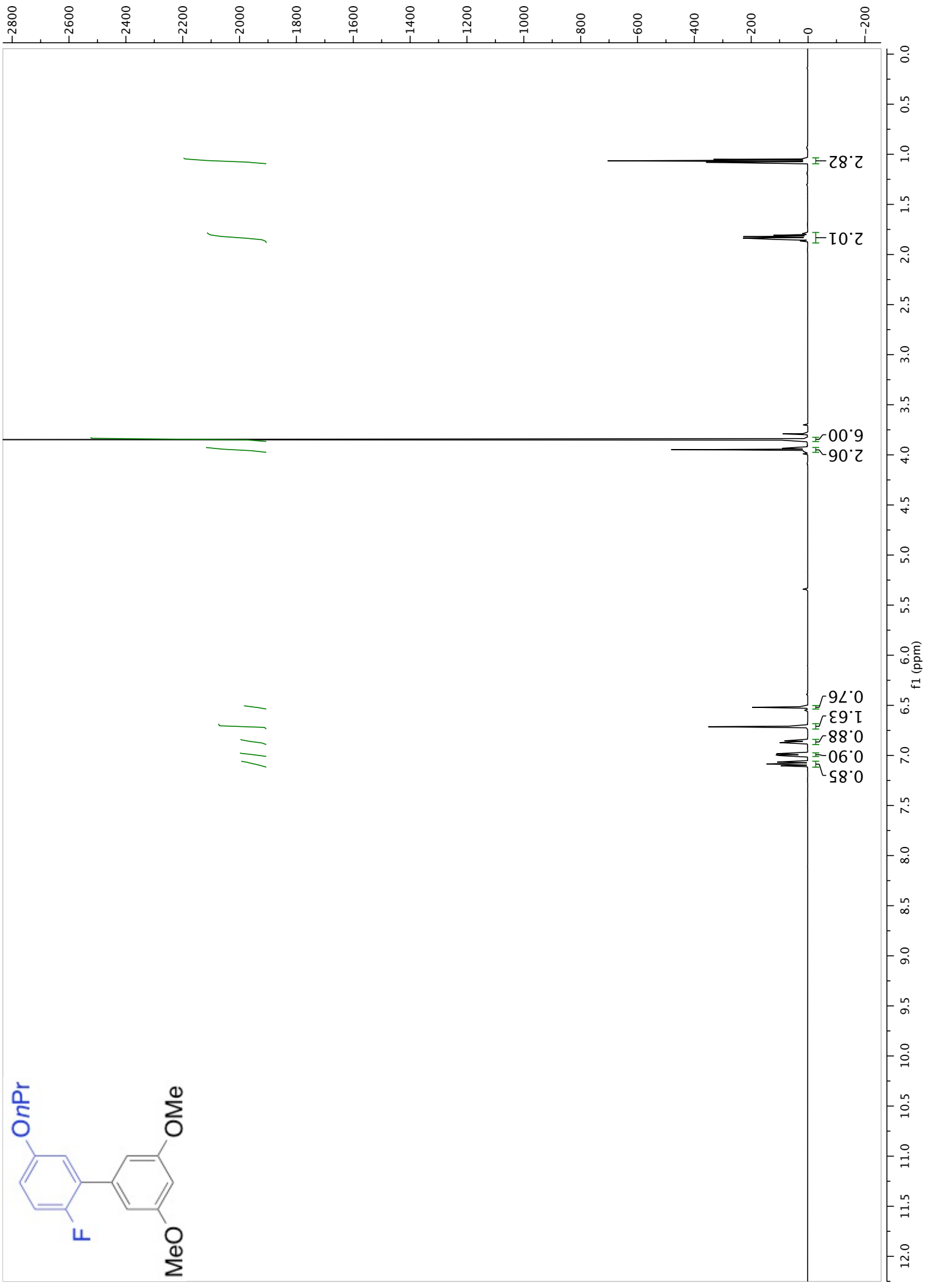


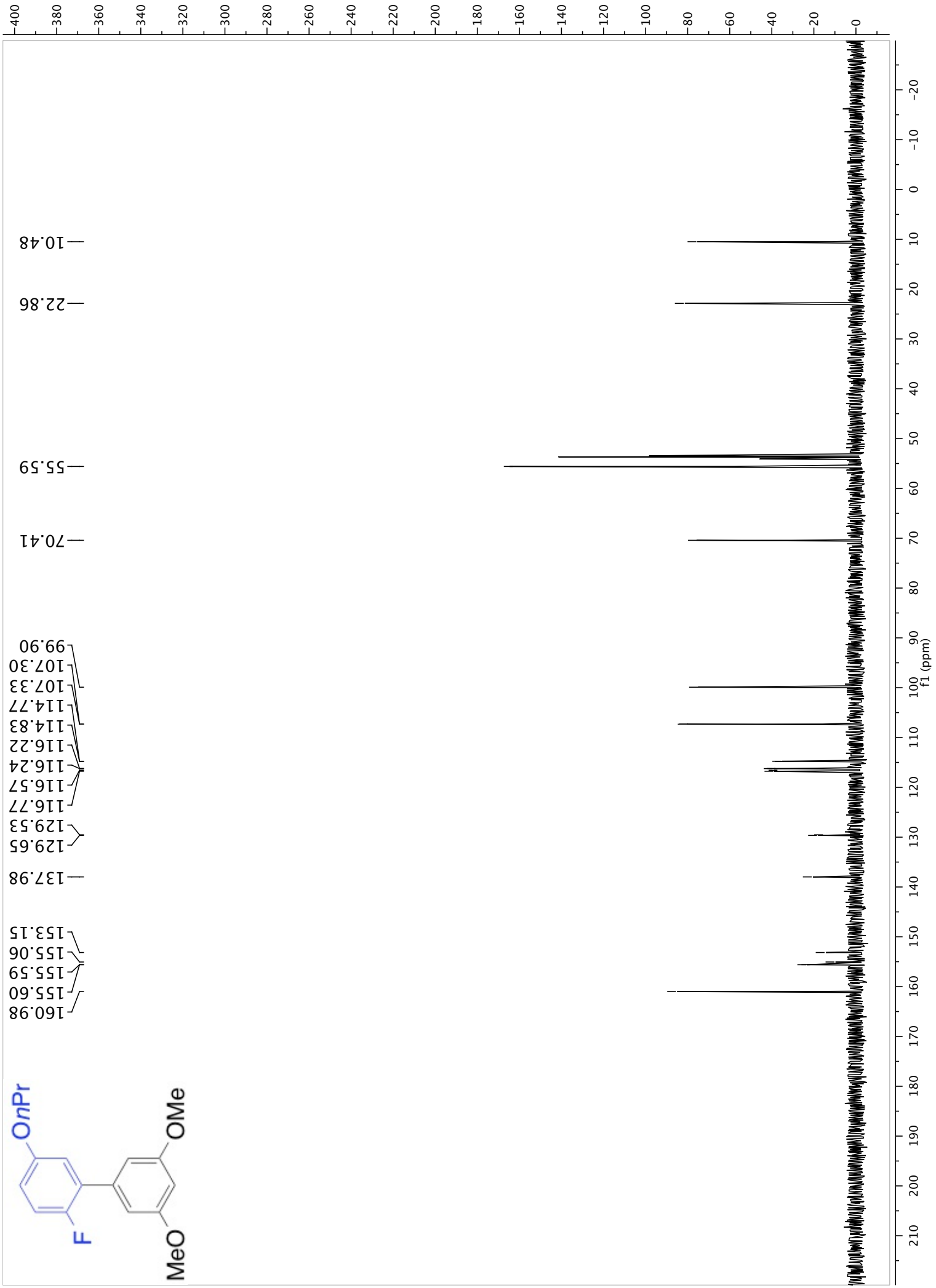


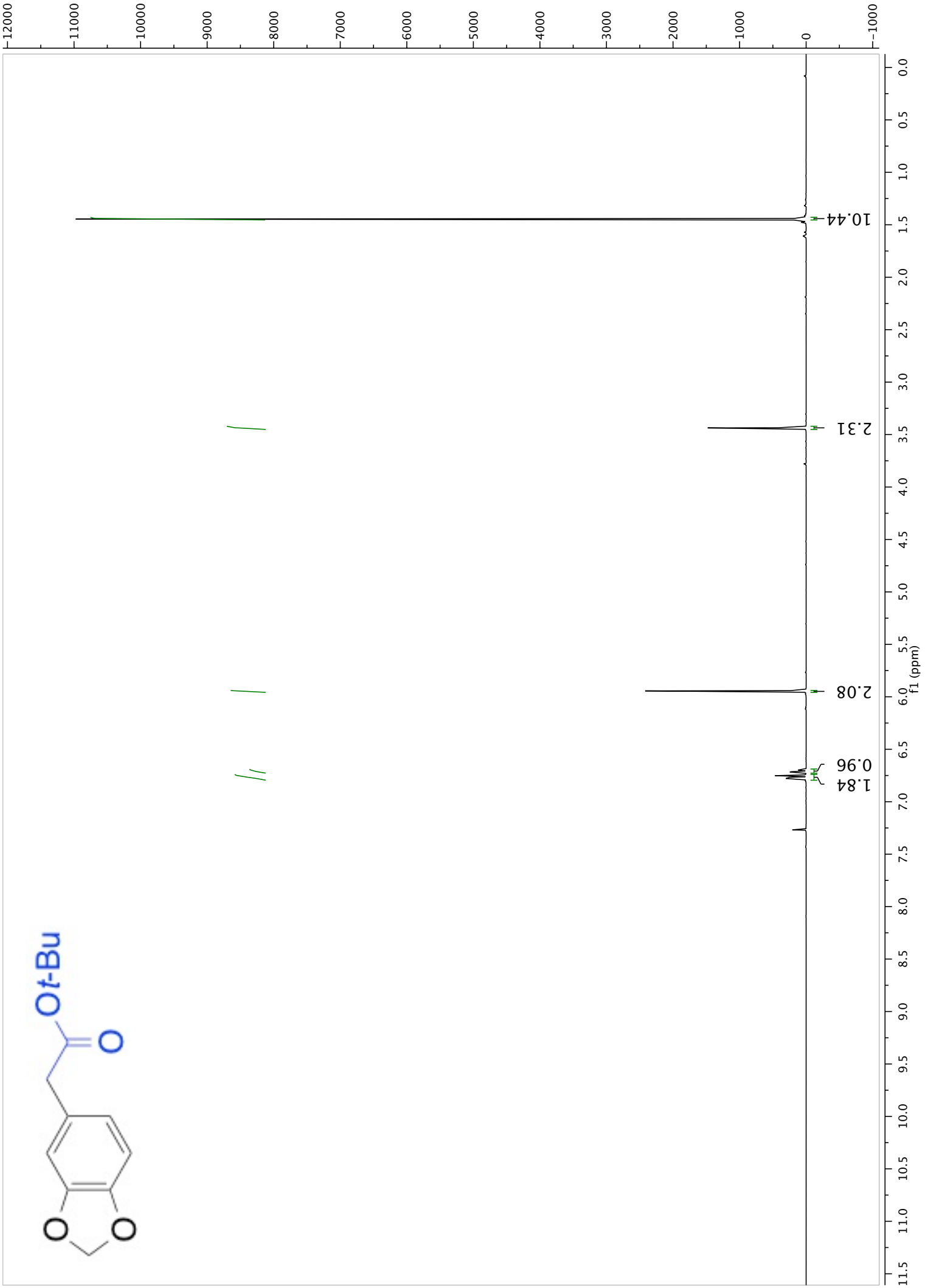


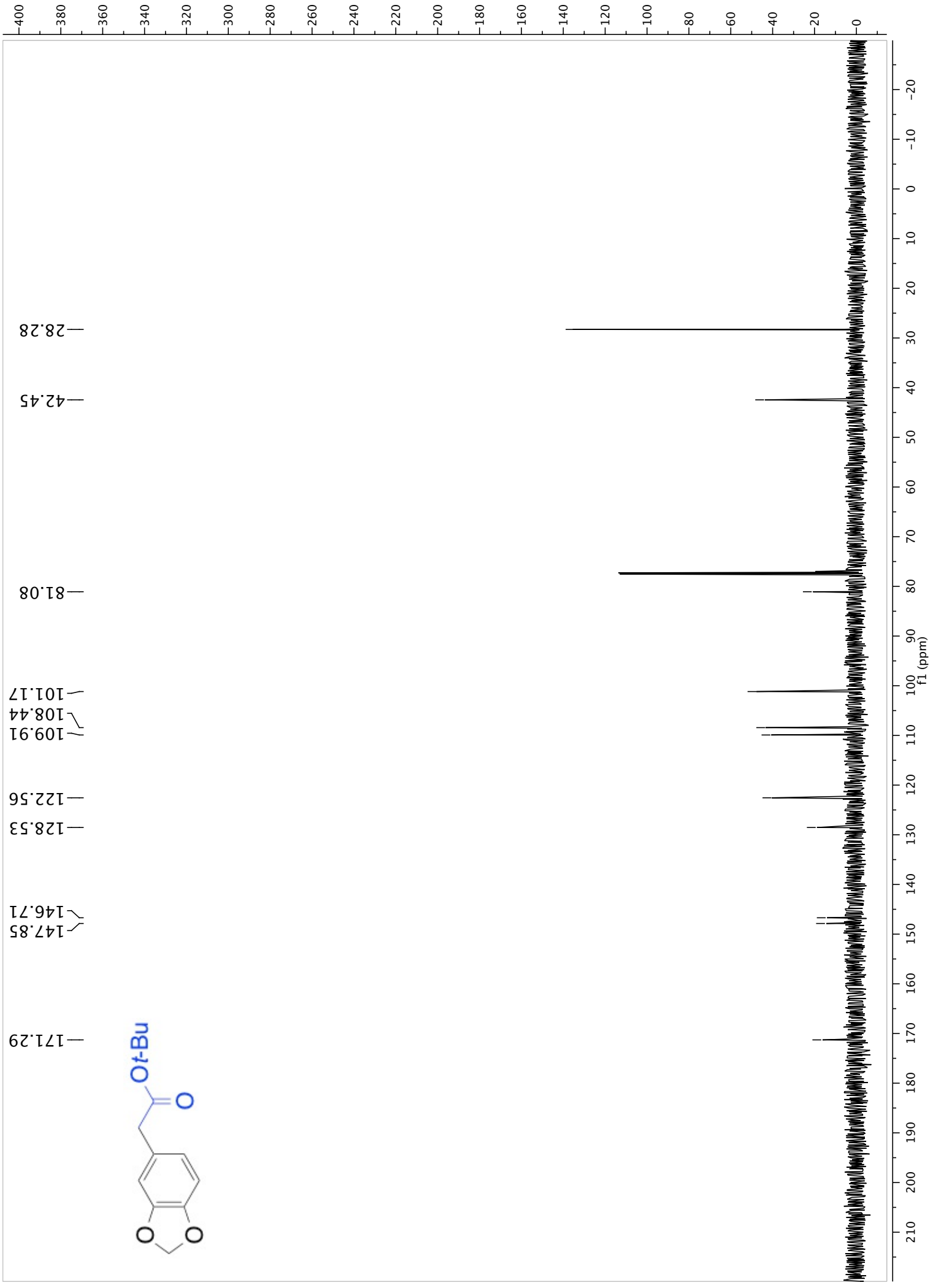


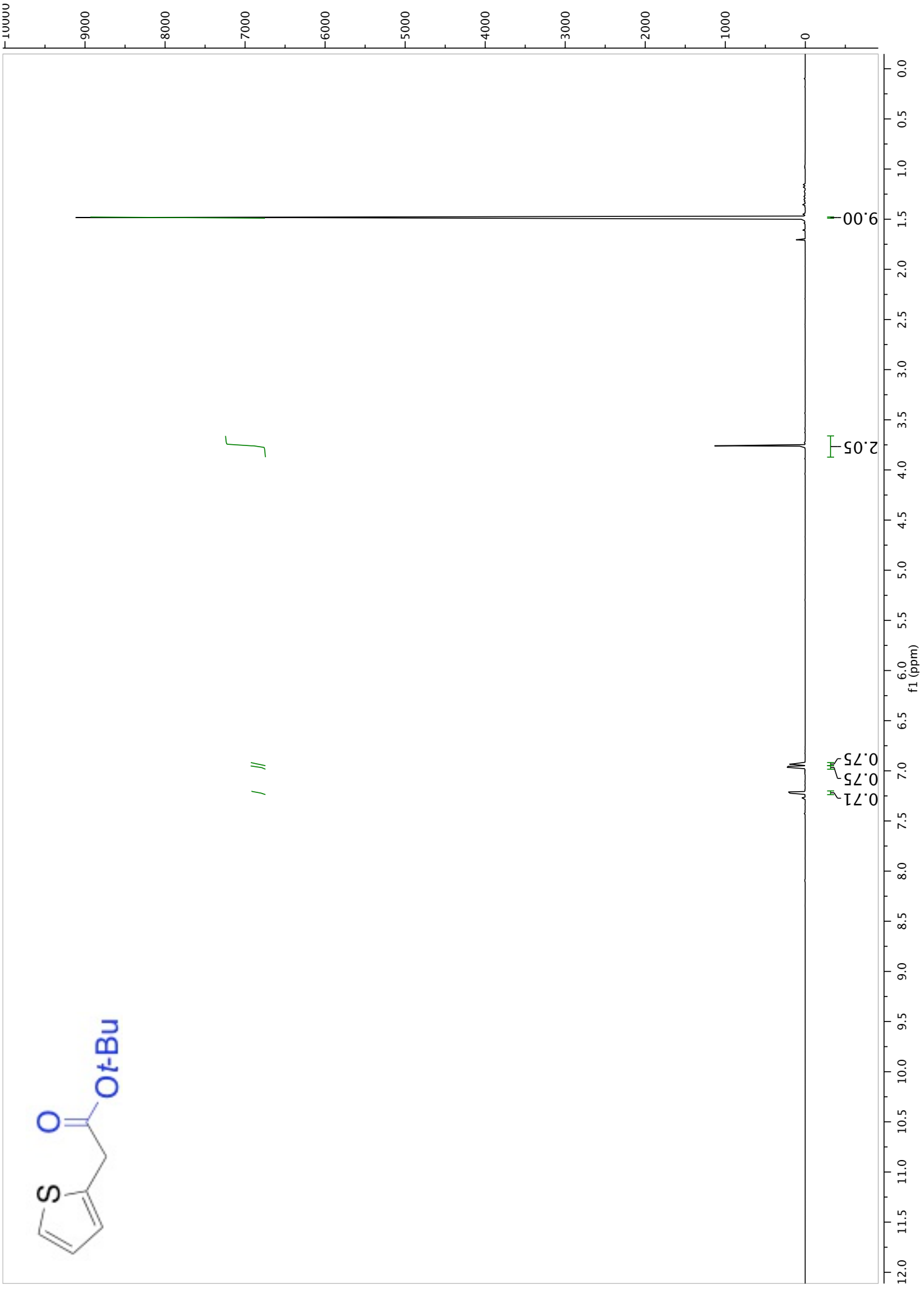


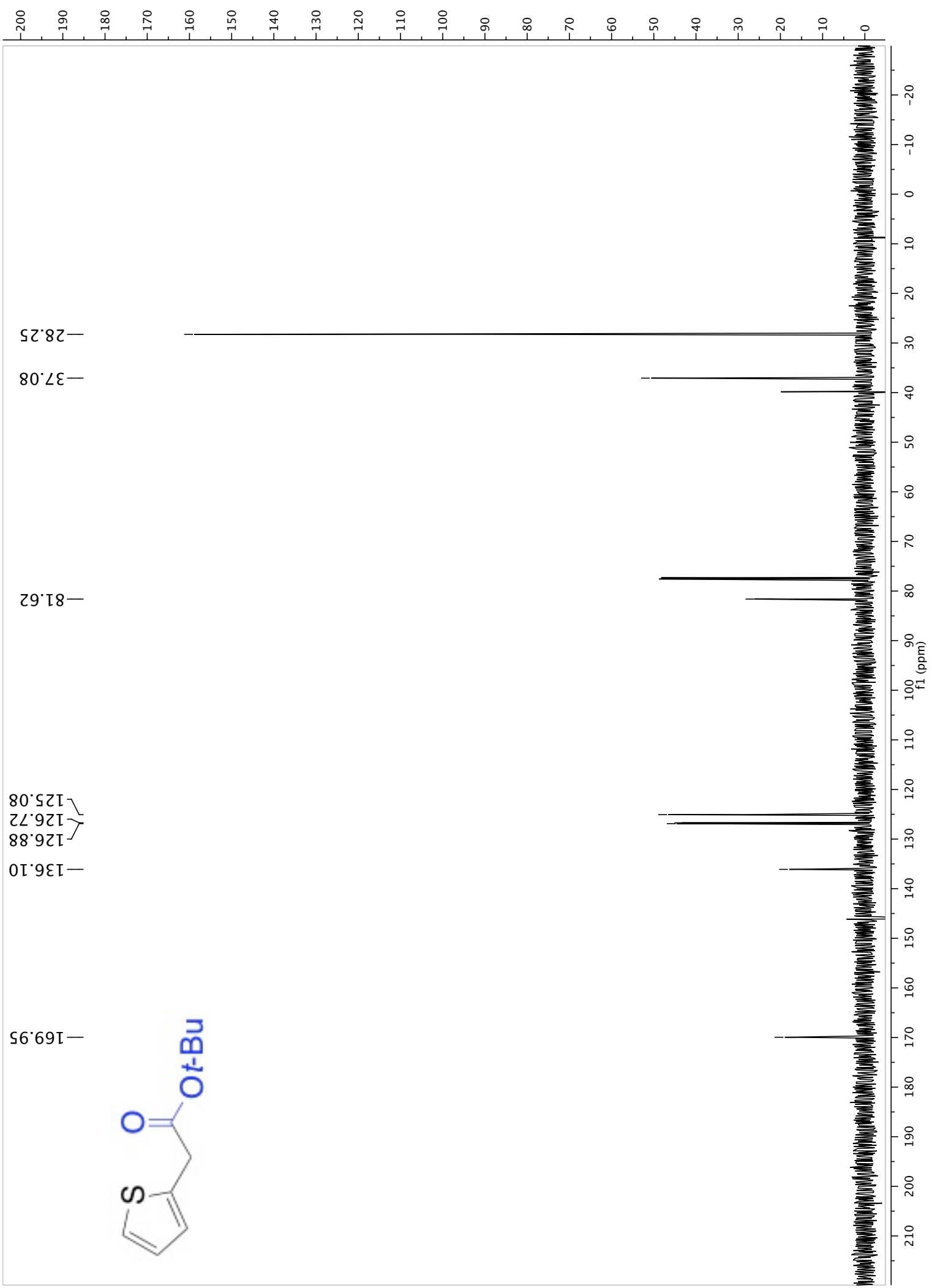


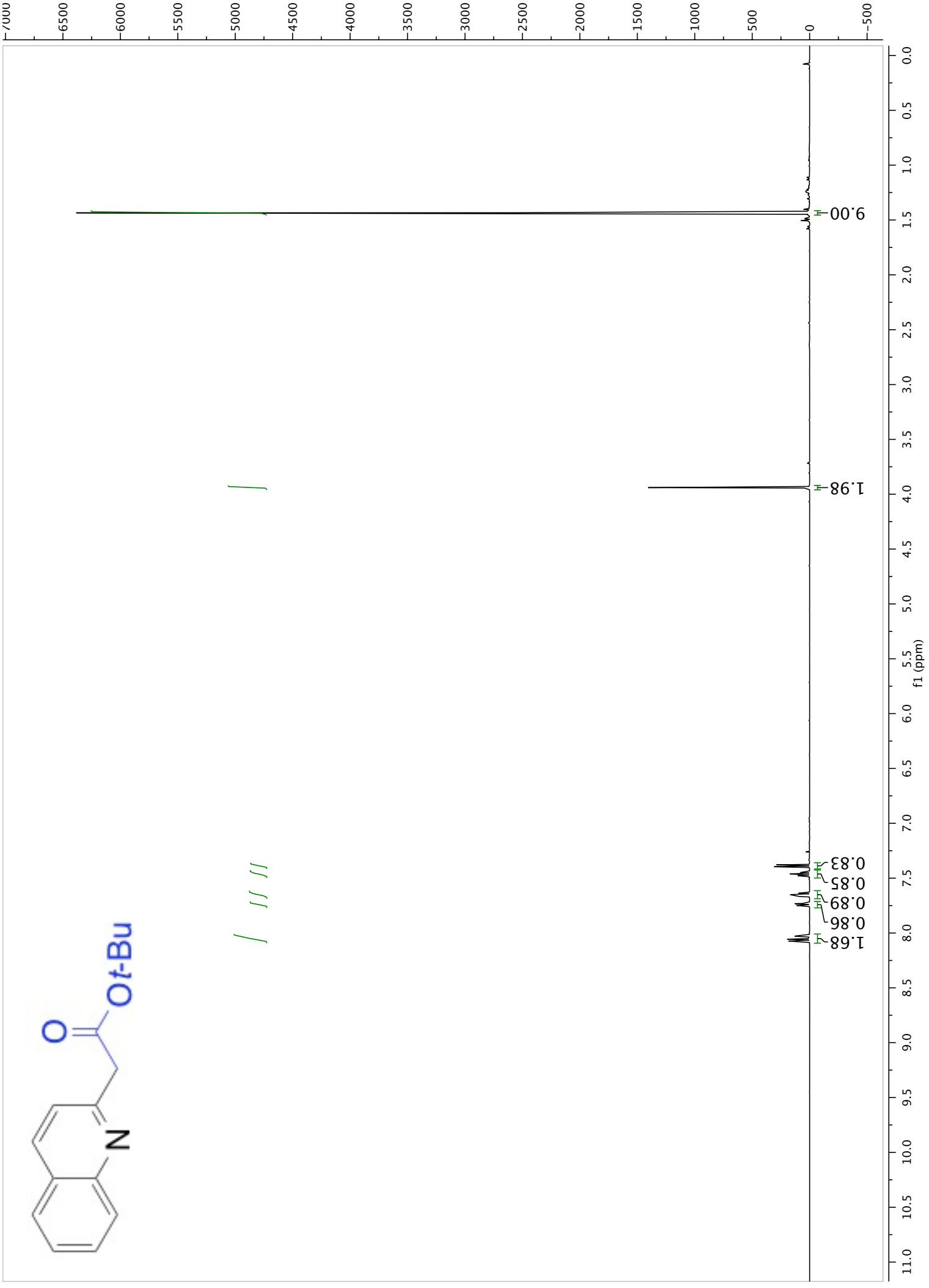


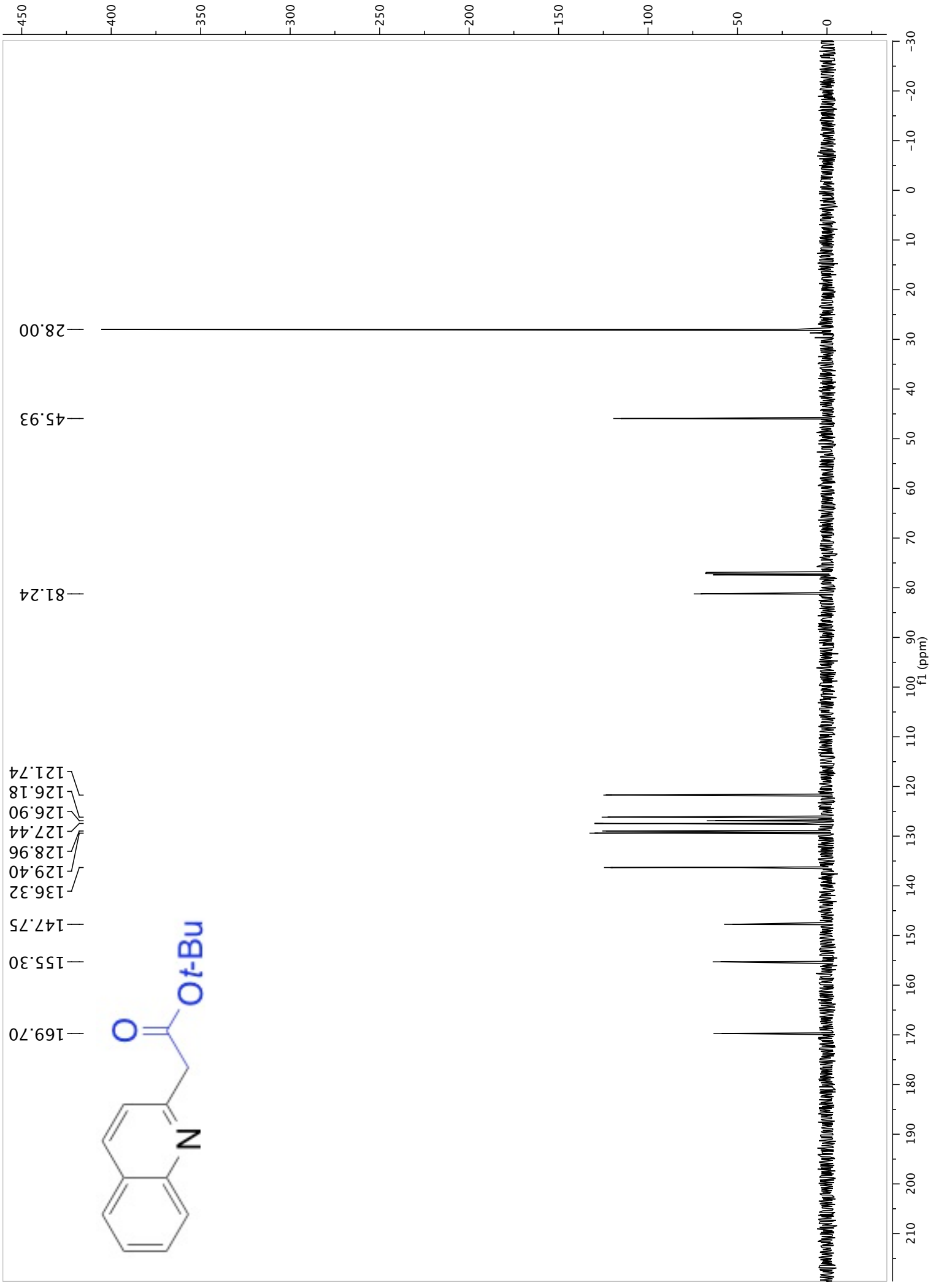


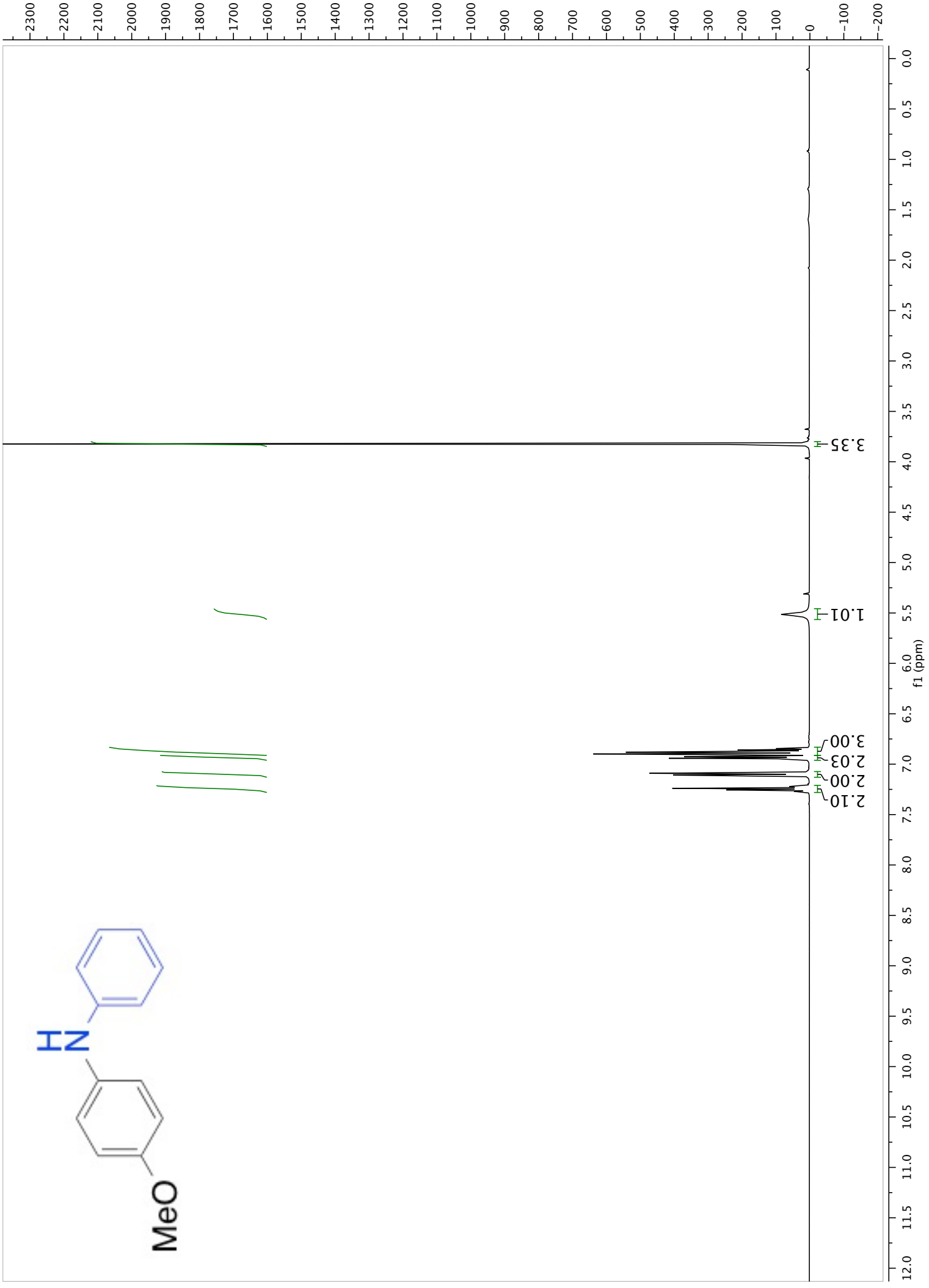


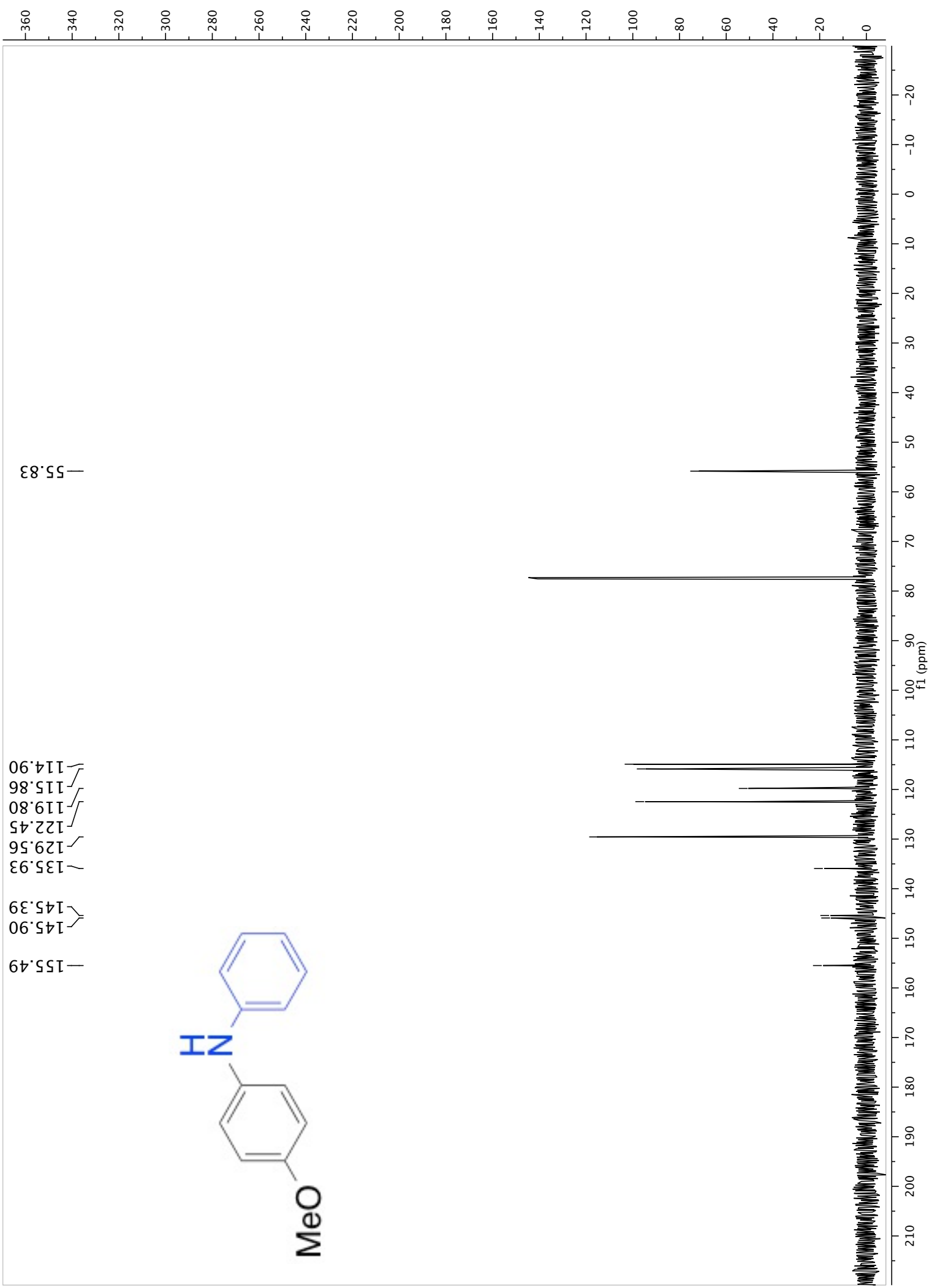


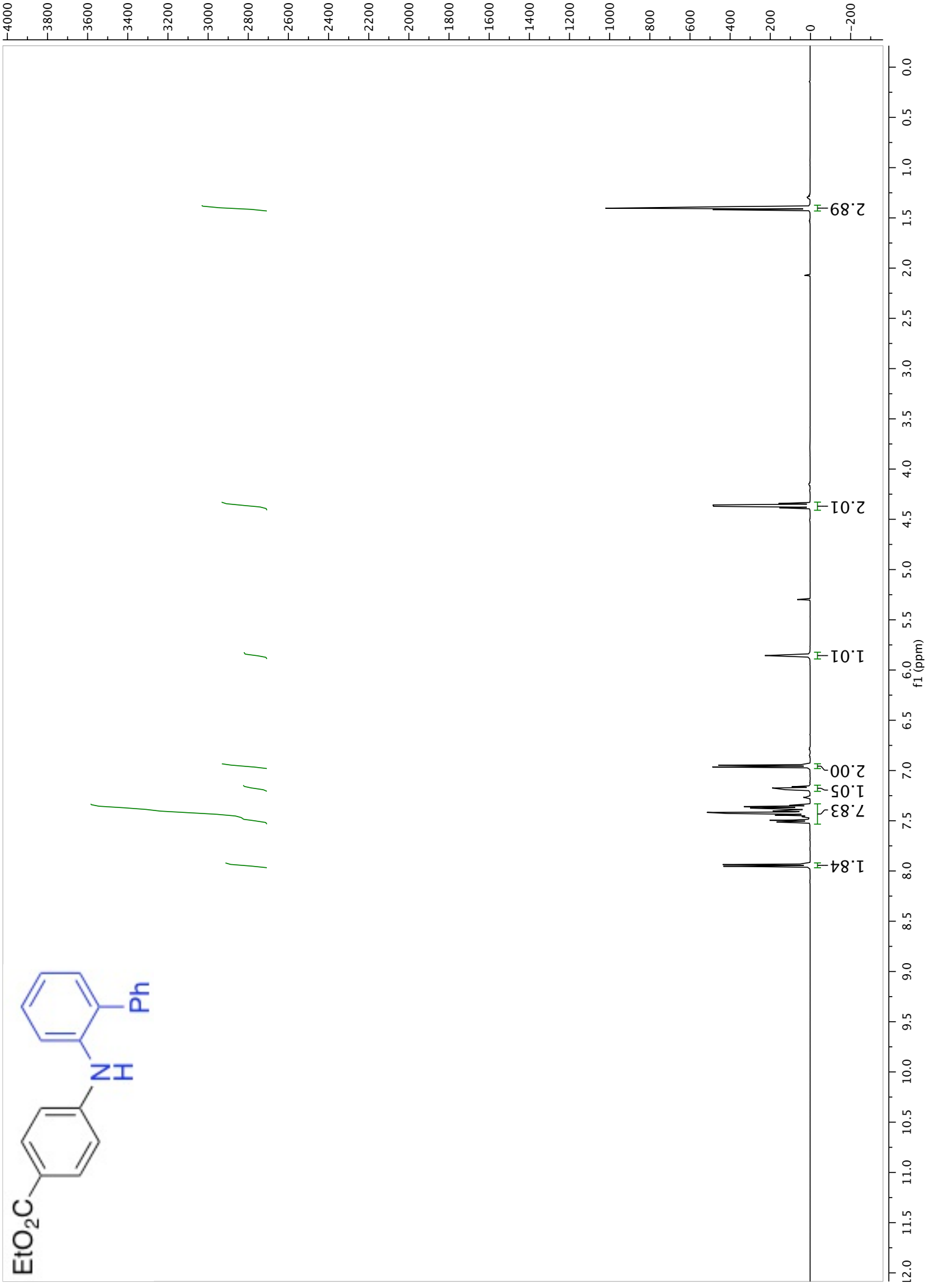


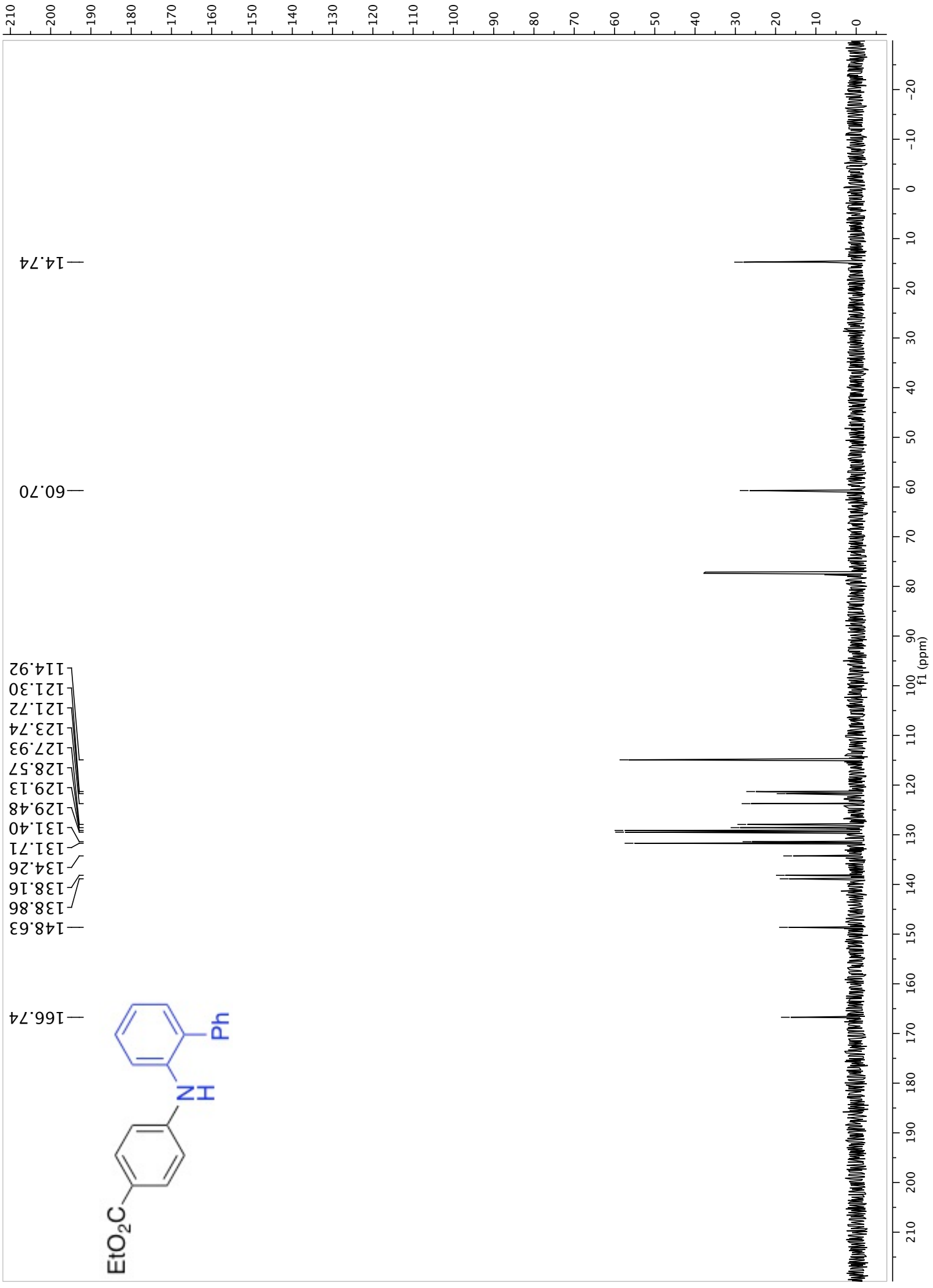


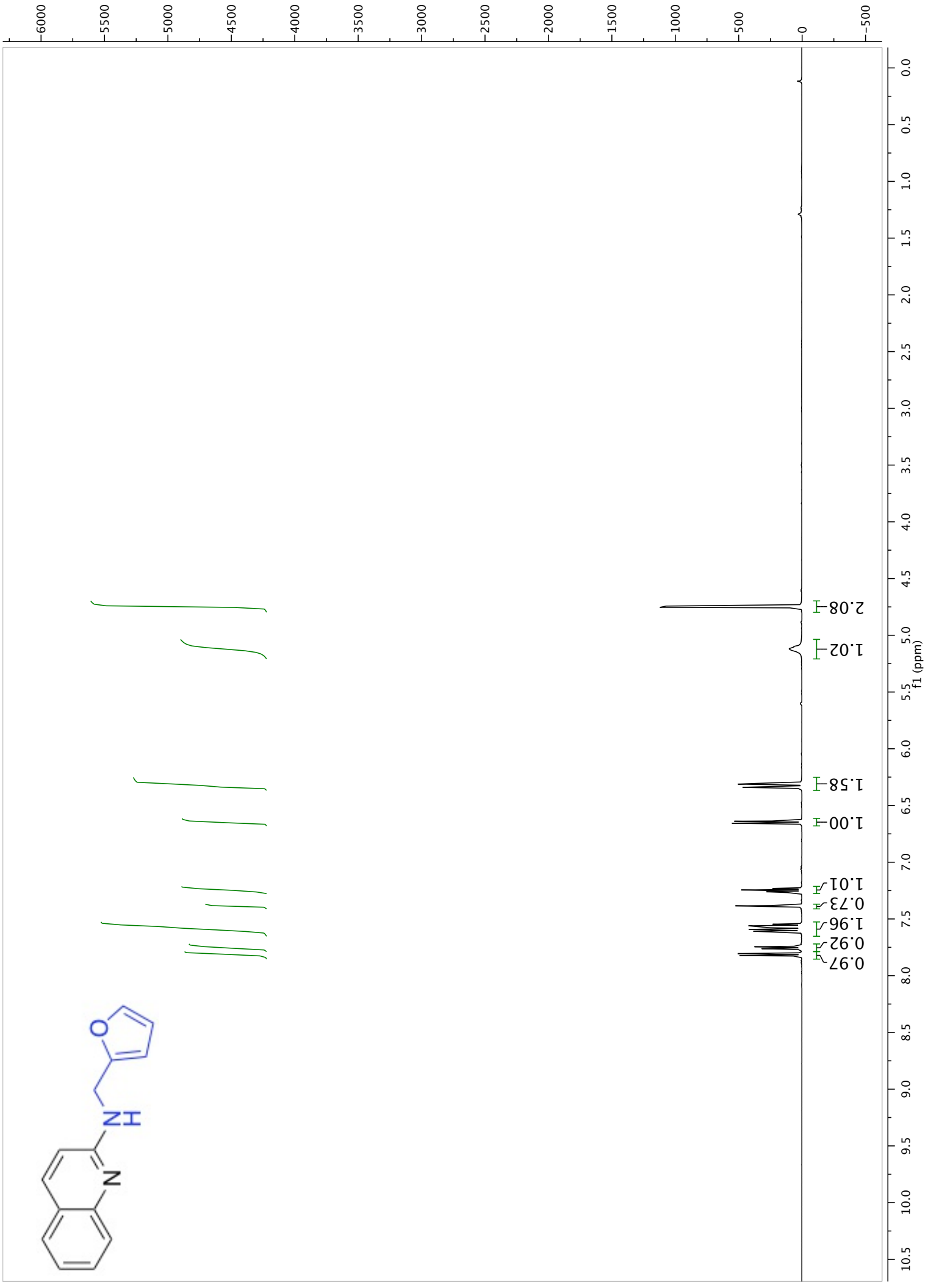


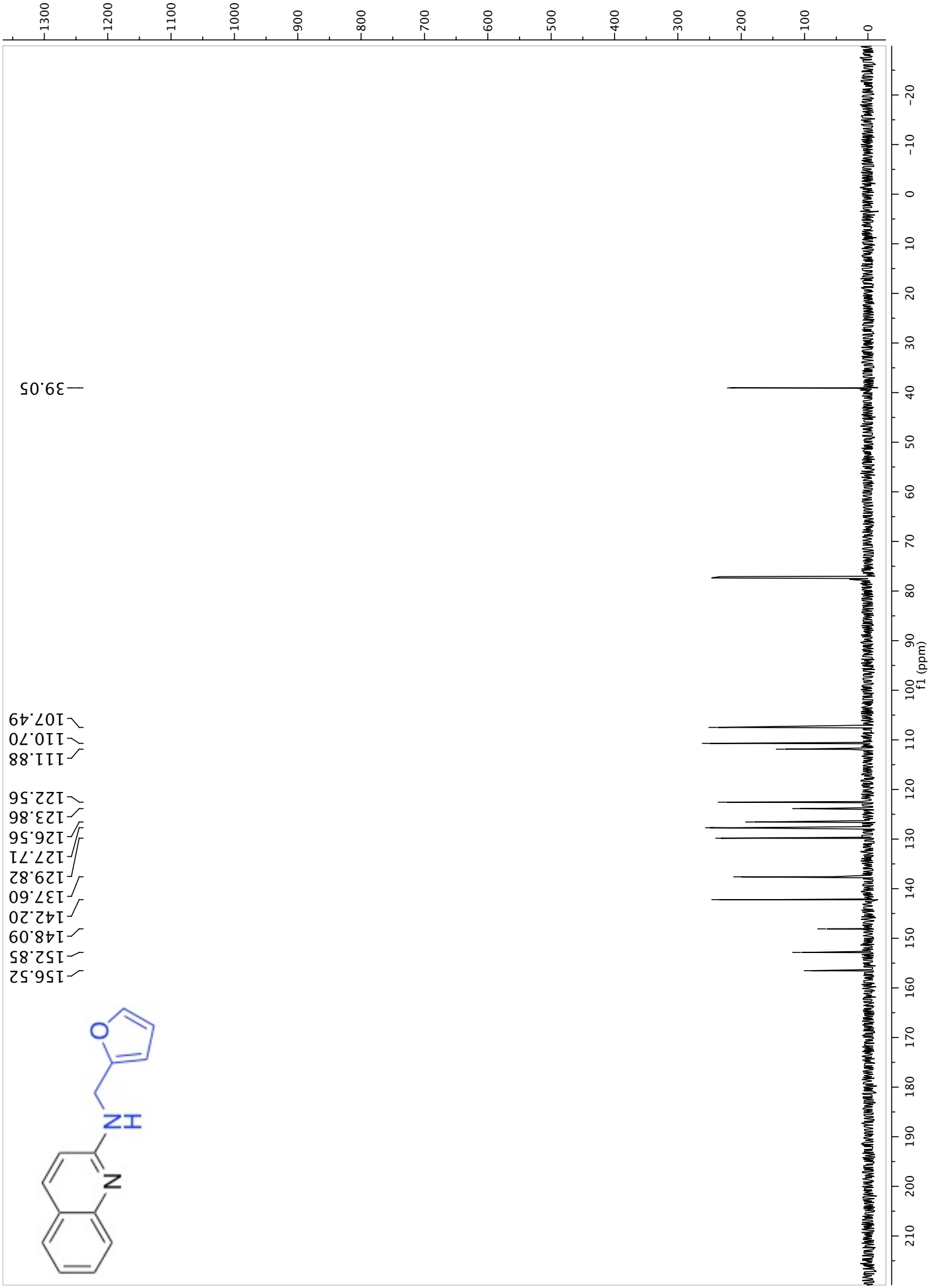


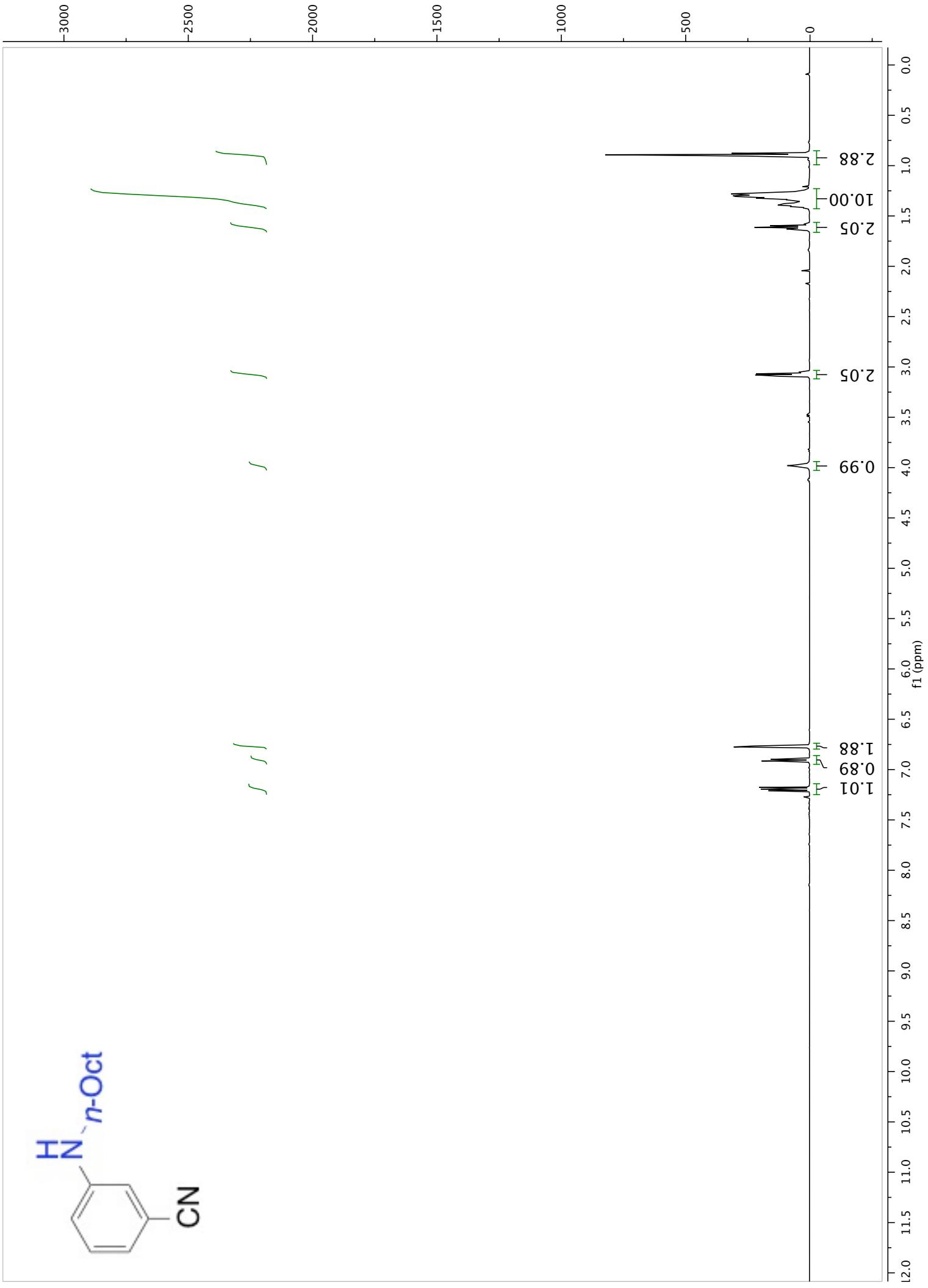


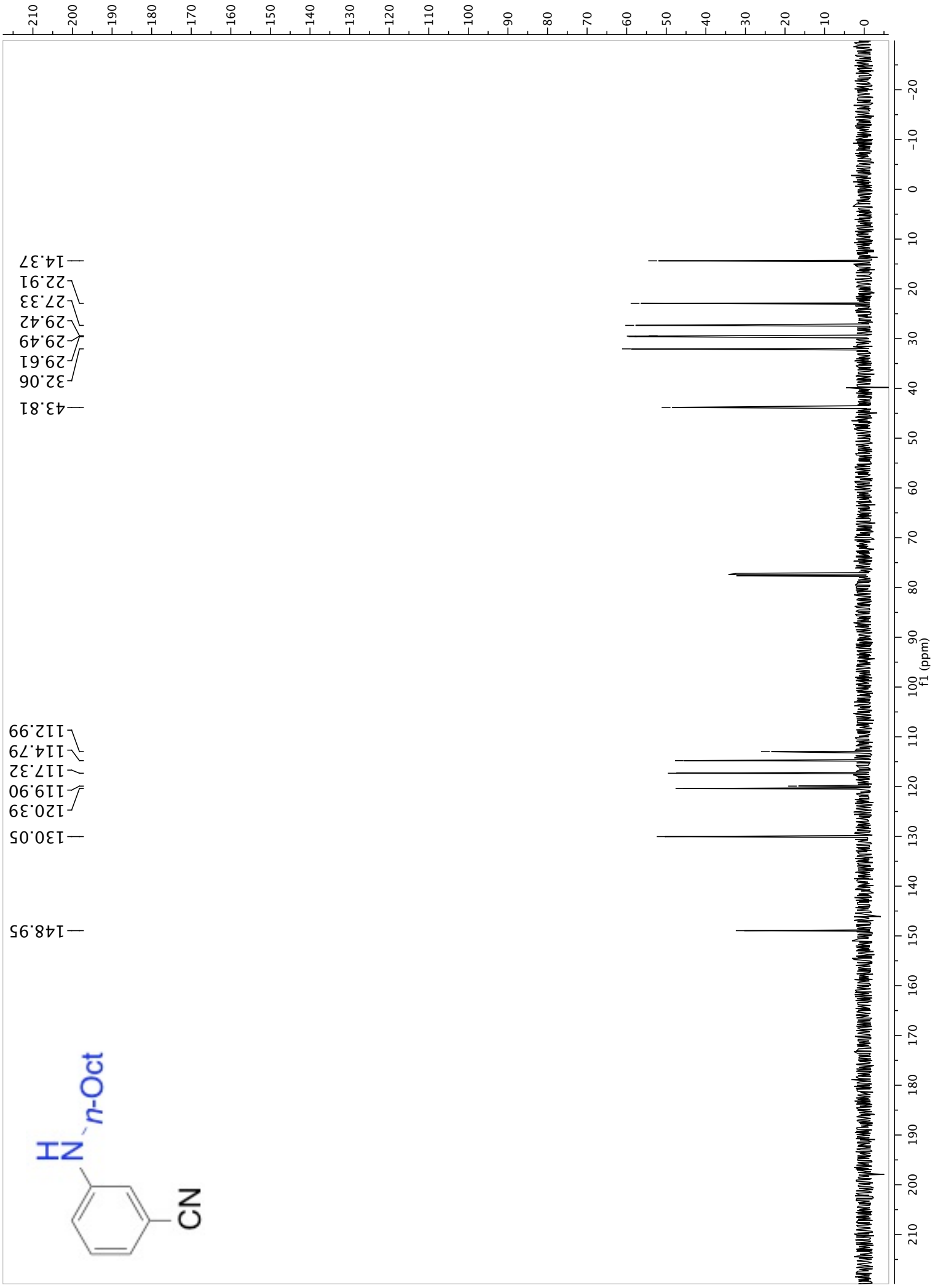








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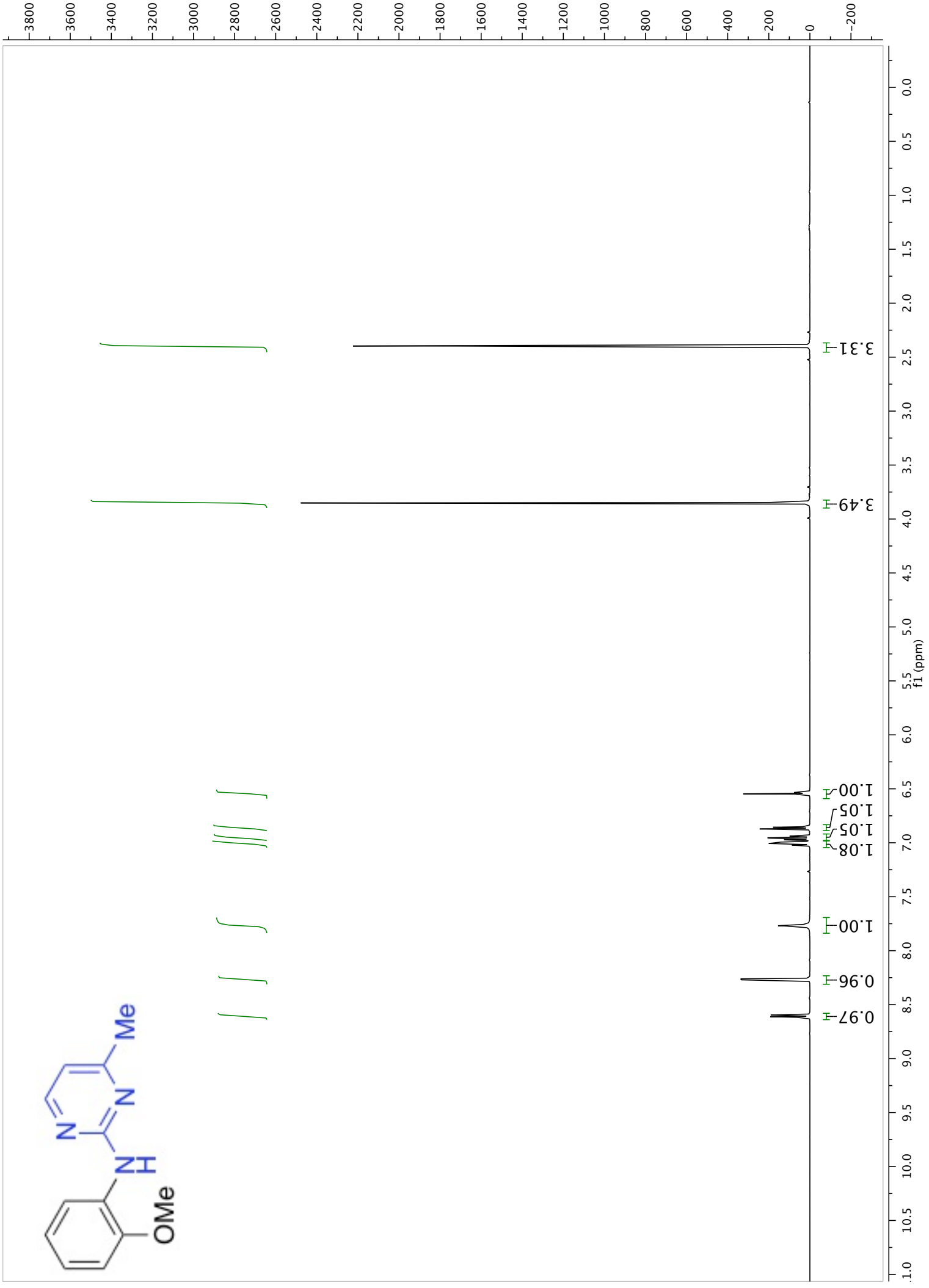
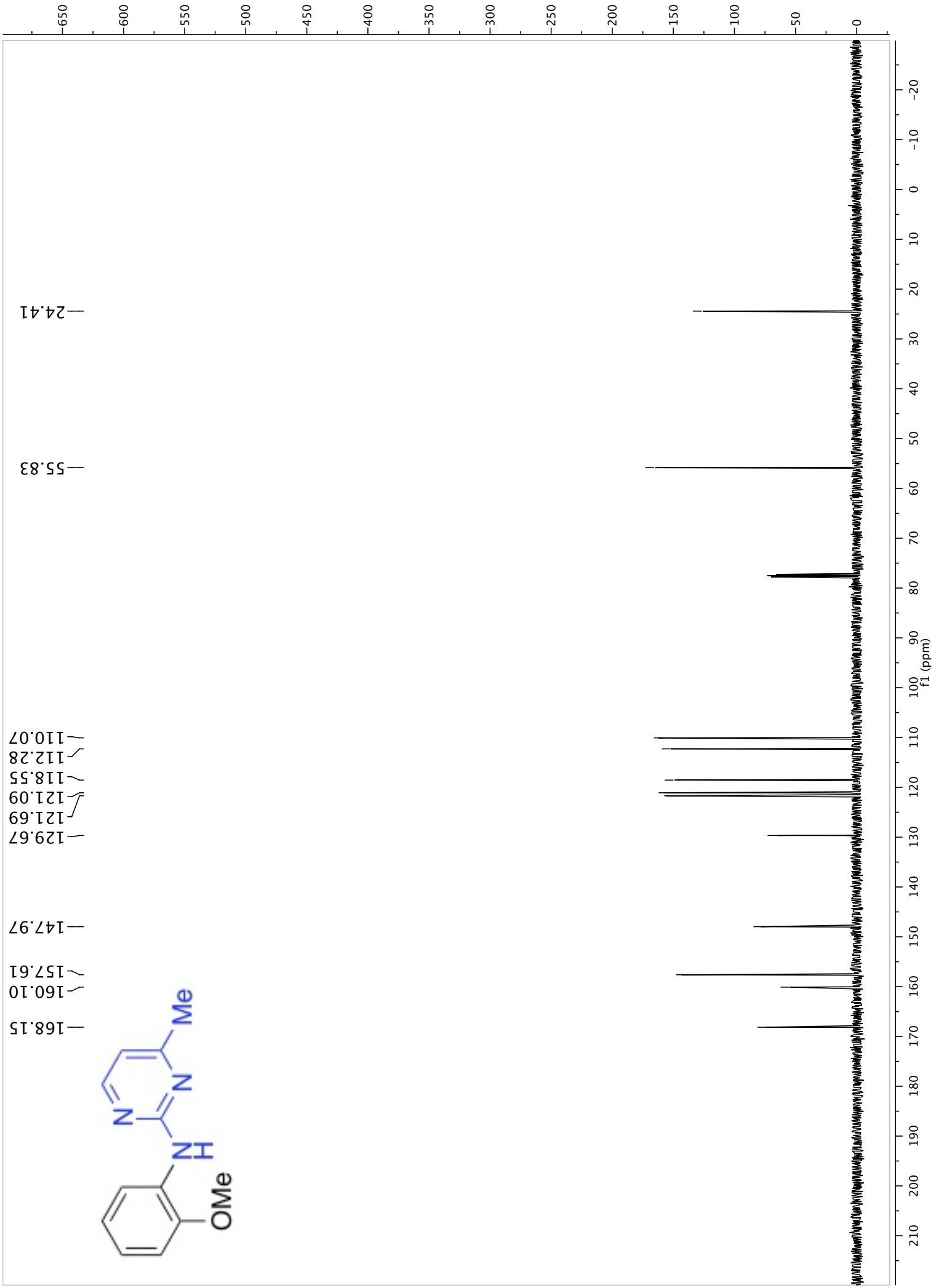
27.33
29.42
29.49
29.61
32.06
43.81
112.99
114.79
117.32
119.90
120.39
130.05
148.95
HN
n-Oct
CN
f1 (ppm)




24.41
55.83
110.07
112.28
118.55
121.09
121.69
129.67
147.97
157.61
160.10
168.15
Me
N
N
NH
OMe
f1 (ppm)