Rational Ligand Design for the Arylation of Hindered Primary Amines Guided by Reaction Progress Kinetic Analysis

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I. General Information

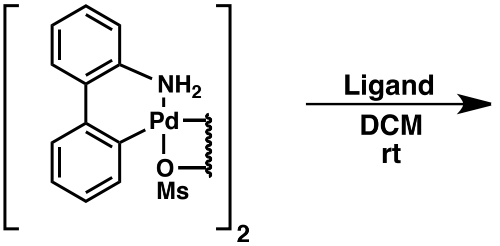
A) General Reagent Information:

THF was purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h, followed by passing it under argon pressure through two packed columns of neutral alumina. Anhydrous 1,4-dioxane was purchased from Aldrich Chemical Co. in Sure-Seal™ bottles and used as received. Sodium *tert*-butoxide was purchased from Aldrich Chemical Co. and stored in a nitrogen-filled glove box. Small quantities were stored on the bench in a desiccator for up to one week. Palladium acetate was purchased from Johnson Matthey. BrettPhos (**L1**) was purchased from Aldrich. Preparations of ligands PhBrettPhos (**L2**),[1] PhXPhos (**L3**),[2] PhCPhos (**L4**),[3] and CPhos (**L5**),[4] have been previously described. μ-OMs dimer **S1** and precatalysts **P1**, **P4** and **P5** were prepared following the literature procedure.[5] Biaryl bromide **S2**,[4] 5-chloro-1-(triisopropylsilyl)-1*H*-indole[6] and CODPd($CH_2TMS)_2$[7] were prepared according to literature procedures. All other reagents were purchased from Aldrich Chemical Co., Strem Chemicals, Acros Organics, Alfa Aesar, TCI America, Combi Blocks, Oakwood Chemical and Matrix Scientific and used as received. All liquid amines were filtered through a plug of oven-dried neutral alumina prior to use. Compounds were purified by flash chromatography using a Biotage Isolera 4 equipped with SNAP column cartridges packed with Silicycle SiliaFlash® F60 silica gel. Unless specified otherwise, reactions were carried out in oven-dried Fisher Scientific 16 × 125 mm screw-cap tubes (Cat. No. 1495925C) using Thermo Scientific PTFE/silicon F/15-425 10 septa (Cat. No. 03394A).

B) General Analytical Information: Compounds were characterized by ^{1}H NMR and ^{13}C NMR, as well as ^{19}F and ^{31}P NMR where applicable. Copies of the ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra can be found at the end of the Supporting Information. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer. Fluorine and phosphorus NMR spectra were recorded on a Varian 300 MHz spectrometer. All ^{1}H NMR experiments are reported in δ, parts per million (ppm), and were measured relative to the signals for residual $CDCl_3$ (δ 7.26 ppm) or CD_3OD (δ 3.31 ppm). All ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (δ 77.23 ppm) and were obtained with ^{1}H decoupling. All ^{19}F NMR spectra are reported in ppm relative to $CFCl_3$ (δ 0.00 ppm). All ^{31}P NMR spectra are reported in ppm relative to 85% aq. H_3PO_4 (δ 0.00 ppm). IR spectra were obtained on a Thermo Scientific iD5 ATR Nicolet iS5 FT-IR spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA. ESI-MS spectra were recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT- ICR-MS). Melting points were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic (GC) analyses were performed on an Agilent 7890A instrument (FID detector) using a J&W DB-1 column (10m, 0.1 mm I.D.). Reactions were monitored by GC and thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254)

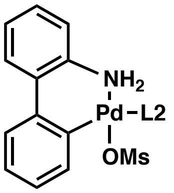
II. Experimental Procedures and Characterization Data

A) General Procedure for Preparing Precatalysts **P2** and **P3**



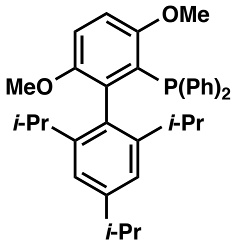
S1

General Procedure A: Preparation of Precatalysts P2 and P3: All precatalysts were synthesized according to a modified literature procedure.[5] A 20 mL scintillation vial equipped with a magnetic stir bar was charged with μ-OMs dimer **S1** (0.50 equiv) and ligand (**L2** or **L3**) (1.00 equiv). CH$_2$Cl$_2$ was added, the vial was capped, and the reaction mixture was stirred from 30 min to 3 h. Reaction progress was monitored via ^{31}P NMR, observing the disappearance of starting material and formation of a new peak at δ ~30-40 ppm. After completion, the solvent was removed in vacuo. The resulting solid was triturated with pentane and isolated by vacuum filtration.

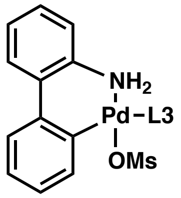


P2

L2: PhBrettPhos =

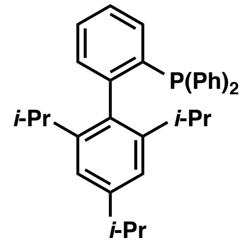


PhBrettPhos (L2) precatalyst (P2): Following General Procedure A, a mixture of **L2** (675 mg, 1.29 mmol, 1.00 equiv), **S1** (477 mg, 0.64 mmol, 0.5 equiv) and CH$_2$Cl$_2$ (10 mL) was stirred for 30 min at rt. The solvent was removed in vacuo and the resulting solid was washed with pentane to afford the desired product as an off-white solid. Yield: 1.146 g, 98%. **^{1}H NMR** (500 MHz, Methanol-d$_4$) δ 7.62 - 7.54 (m, 1H), 7.54 - 7.44 (m, 4H), 7.43 - 7.35 (m, 2H), 7.31 (d, J = 9.0 Hz, 1H), 7.26 (dd, J = 7.5, 1.6 Hz, 1H), 7.24 - 7.14 (m, 9H), 7.05 (t, J = 7.3 Hz, 1H), 6.90 - 6.82 (m, 1H), 6.56 - 6.47 (m, 1H), 6.18 (ddd, J = 7.8, 6.5, 1.0 Hz, 1H), 3.54 (s, 3H), 3.37 (dq, J = 13.8, 6.8 Hz, 1H), 3.32 - 3.31 (m, 3H), 3.02 (h, J = 6.6 Hz, 1H), 2.69 (s, 3H), 2.08 (p, J = 6.8 Hz, 1H), 1.83 (d, J = 6.9 Hz, 3H), 1.55 (d, J = 6.9 Hz, 3H), 1.50 (d, J = 6.9 Hz, 3H), 1.20 (d, J = 6.7 Hz, 3H), 0.74 (d, J = 6.8 Hz, 3H), 0.13 (d, J = 6.8 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, CDCl$_3$) δ 159.4, 159.1, 158.4, 157.7, 156.4, 156.3, 148.4, 144.1, 143.5, 141.1, 140.5, 139.1, 138.9, 138.5, 135.7, 135.1, 134.0, 132.9, 132.8, 132.5, 132.0, 131.8, 131.0, 130.9, 130.6, 130.2, 130.1, 129.9, 129.5, 128.6, 128.5, 127.3, 124.8, 124.2, 121.1, 118.8, 59.4, 59.0, 42.7, 38.8, 37.4, 36.1, 29.3, 28.9, 27.7, 27.4, 27.4, 26.6. ^{31}**P NMR** (121 MHz, Methanol-d_4) δ 31.91ppm



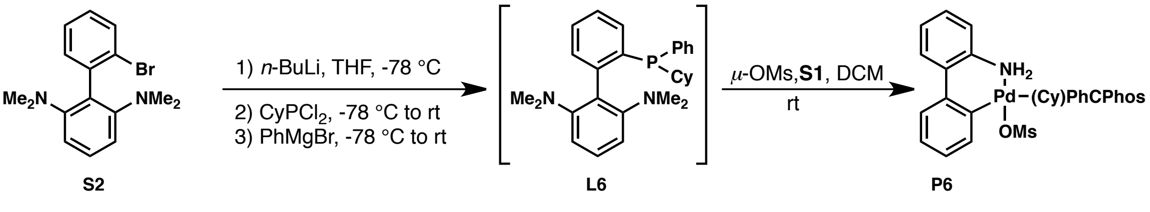
P3

L3: PhXPhos =



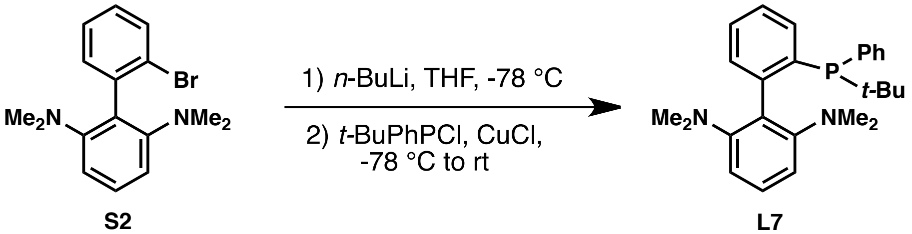
PhXPhos (L3) precatalyst (P3): Following General Procedure A, a mixture of **L3** (261 mg, 0.56 mmol, 1.00 equiv), μ-OMs dimer **S1** (208 mg, 0.28 mmol, 0.50 equiv) and CH_2Cl_2 (5 mL) was stirred for 30 min at rt. After removal of the solvent in vacuo, the crude product was triturated with pentane and filtered to afford **P3** as a light brown solid. Yield: 417 mg, 89%. ^{1}**H NMR** (500 MHz, Methanol-d_4) δ 7.72 - 7.59 (m, 5H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.55 - 7.48 (m, 3H), 7.48 - 7.42 (m, 1H), 7.38 - 7.21 (m, 7H), 7.16 - 7.09 (m, 2H), 7.08 - 7.01 (m, 2H), 6.92 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.52 (dddd, *J* = 8.0, 7.2, 1.7, 0.9 Hz, 1H), 6.21 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 3.40 (h, *J* = 6.9 Hz, 1H), 2.87 (p, *J* = 6.9 Hz, 1H), 2.69 (s, 3H), 1.87 (dd, *J* = 9.1, 7.1 Hz, 4H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.25 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 159.3, 157.5, 155.8, 149.2, 149.0, 146.9, 144.0, 143.4, 141.0, 140.8, 140.8, 140.6, 140.6, 140.5, 139.0, 138.7, 137.6, 137.2, 136.6, 136.5, 136.2, 133.8, 133.4, 133.3, 133.1, 132.9, 132.7, 132.3, 132.2, 132.2, 131.6, 131.3, 131.2, 131.1, 130.5, 130.3, 130.3, 129.0, 128.8, 128.0, 127.9, 124.9, 42.9, 38.9, 37.3, 36.2, 28.9, 28.5, 28.5, 28.0, 27.9, 27.8, 27.5, 26.5. ^{31}**P NMR** (121 MHz, Methanol-d_4) δ 36.02 ppm

B) Synthesis of **P6**



(Cy)PhCPhos (L6) precatalyst (P6): An oven dried two-neck 10 mL round bottom flask equipped with a magnetic stir bar and a rubber septum was charged with **S2** (95.7 mg, 0.30 mmol, 1.00 equiv). The reaction vessel was evacuated and backfilled with argon (this procedure was repeated a total of 3 times). Anhydrous THF (1.2 mL) was added via syringe and the solution was cooled to -78 °C in a dry ice/acetone bath. *n*-BuLi (2.5M in hexanes, 126 μL, 0.315 mmol, 1.05 equiv) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min. Cyclohexyldichlorophosphine (51.0 μL, 0.33 mmol, 1.10 equiv) was then added dropwise and the reaction mixture was warmed to rt and stirred for 4 h. The reaction was followed by ^{31}P NMR. After disappearance of the starting material and appearance of a peak at δ ~100 ppm, the reaction vessel was cooled to -78 °C and phenylmagnesium bromide (1M in THF, 900 μL, 0.90 mmol, 3.00 equiv) was added dropwise. The reaction mixture was warmed to rt and stirred overnight. After disappearance of the peak at ~100 ppm and appearance of a peak at -15 ppm, the reaction was diluted with EtOAc and washed with saturated aqueous NH_4Cl. The organic layer was separated and was additionally washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo. Several attempts of crystallization with a variety of organic solvents were unsuccessful, so the corresponding precatalyst **P6**, was made *in situ*. μ-OMs dimer **S1** (111 mg, 0.15 mmol, 0.50 equiv) and CH_2Cl_2 (5 mL), were added to the reaction vessel and the reaction mixture was stirred at rt for 1 h. The reaction was followed by ^{31}P-NMR. After completion the reaction mixture was filtered through a cotton plug to remove traces of Pd black. The solvent was removed in vacuo. The residue was triturated with pentane and isolated via vacuum filtration to afford the desired product as a light brown solid. Yield: 128 mg, 53%. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.70 (t, *J* = 8.1 Hz, 1H), 7.67 - 7.62 (m, 2H), 7.58 (qd, *J* = 7.8, 2.0 Hz, 3H), 7.50 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.48 - 7.36 (m, 5H), 7.35 - 7.24 (m, 5H), 7.23 - 7.16 (m, 3H), 7.12 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.3 Hz, 1H), 2.69 (s, 3H), 2.63 (s, 6H), 2.19 (s, 6H), 1.89 (s, 1H), 1.79 - 1.64 (m, 2H), 1.56 - 1.45 (m, 2H), 1.45 - 1.36 (m, 1H), 1.36 - 1.24 (m, 1H), 0.99 - 0.85 (m, 2H), 0.69 (qd, *J* = 12.7, 6.2 Hz, 1H), 0.47 (dddd, *J* = 15.6, 12.2, 7.8, 3.4 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.1, 156.4, 153.2, 151.0, 150.9, 150.8, 144.2, 142.7, 141.6, 141.6, 139.7, 138.9, 138.5, 137.9, 137.8, 137.4, 137.0, 135.3, 132.7, 132.4, 132.1, 131.8, 131.8, 131.6, 131.5, 131.4, 130.8, 130.3, 129.8, 124.6, 117.8, 117.8, 117.5, 117.2, 48.0, 47.2, 44.9, 44.6, 42.7, 34.8, 34.8, 34.2, 32.9, 32.9, 31.8, 31.7, 31.6, 31.5, 30.1, 30.1. **^{31}P NMR** (121 MHz, Methanol-d_4) δ 37.22 ppm.

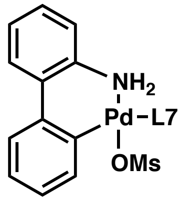
C) Synthesis of **L7** and **P7**



S2 **L7**

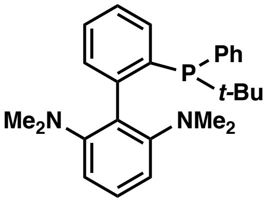
(*t*-Bu)PhCPhos (L7): An oven-dried two-neck 100 mL round-bottomed flask, equipped with a magnetic stir bar and a rubber septum was charged with **S2** (1.50 g, 4.70 mmol, 1.00 equiv). The reaction vessel was evacuated and backfilled with argon (this procedure was repeated a total of 3 times). Anhydrous THF (20 mL) was added via syringe and the solution was cooled to -78 °C. *n*-BuLi (2.5M in hexanes, 2.07 mL, 5.17 mmol, 1.10

equiv) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h. CuCl (465 mg, 4.70 mmol, 1.00 equiv) was added in one portion followed by dropwise addition of chloro(*tert*-butyl)phenylphosphine (1.30 mL, 7.05 mmol, 1.50 equiv). The reaction mixture was warmed to rt and stirred for an additional 6 h. The solution was then diluted with EtOAc and washed with aqueous NH_4OH until the aqueous phase was no longer blue. The organic phase was washed with brine, separated and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was triturated with MeOH. The residue was isolated via vacuum filtration. Yield: 1.52 g, 80% **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.50 - 7.35 (m, 5H), 7.26 - 7.17 (m, 4H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 6H), 1.72 - 1.62 (m, 6H), 1.05 (d, *J* = 11.7, 1.5 Hz, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.1, 153.0, 147.7, 147.5, 140.0, 139.8, 136.1, 136.0, 135.9, 135.7, 134.1, 134.0, 133.7, 133.5, 131.0, 129.5, 129.0, 127.9, 127.9, 127.4, 126.1, 114.1, 113.4, 44.8, 43.5, 32.6, 32.4, 30.7, 30.6. **^{31}P NMR** (121 MHz, Chloroform-d) δ 5.10 ppm.



P7

L7: (*t*-Bu)PhCPhos =

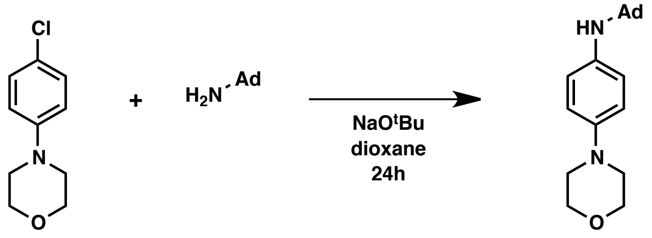


(*t*-Bu)PhCPhos (L7) precatalyst (P7): Following General Procedure A, a mixture of **S1** (915 mg, 1.24 mmol, 0.50 equiv), (*t*-Bu)PhCPhos, **L7** (1.00 g, 2.47 mmol, 1.00 equiv) and CH_2Cl_2 (15 mL) was stirred at rt for 3 h. After removal of the solvent in vacuo, the crude product was triturated with pentane and filtered to afford **P7** as a pale brown solid. Yield: 1.65 g, 86%. **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.87 (td, *J* = 7.7, 1.3 Hz, 1H), 7.71 - 7.61 (m, 3H), 7.61 - 7.53 (m, 4H), 7.53 - 7.45 (m, 2H), 7.36 - 7.30 (m, 2H), 7.30 - 7.14 (m, 5H), 7.11 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.3 Hz, 1H), 2.79 (s, 6H), 2.69 (s, 3H), 2.06 (s, 6H), 0.84 (d, *J* = 15.1 Hz, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.4, 160.0, 150.1, 149.9, 149.1, 144.5, 143.9, 141.6, 141.6, 140.0, 139.1, 139.1, 138.8, 138.6, 138.4, 137.3, 136.9, 135.1, 133.0, 132.7, 132.6, 132.6, 132.2, 131.6, 131.5, 131.3, 130.9, 129.8, 124.0, 117.6, 117.4, 117.3, 115.9, 58.1, 48.1, 47.9, 42.8, 42.0, 41.8, 33.2, 33.1. **^{31}P NMR** (121 MHz, Methanol-d_4) δ 45.33 ppm.

D) Arylation of α-trisubstituted amines using precatalyst **P7**

In the initial screening of the catalyst system based on **P7**, it was found that an additional equivalent of **L7** gave better results (Tables S1 and S2)

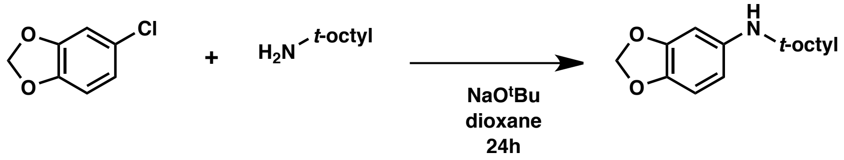
Table S1. Effect of the addition of an extra equivalent of **L7** on the reaction using **P7**[a]



P7	L7	T (°C)	SM[b]	Product[b]
0.5 %	-	80	27 %	72 %
0.5 %	0.5 %	70	-	100 %

[a] Reaction conditions: Aryl halide (0.5 mmol), amine (0.6 mmol), NaO*t*Bu (0.6 mmol), 1,4-dioxane (0.5 mL). [b] GC-yields

Table S2. Effect of the addition of an extra equivalent of **L7** on the reaction using **P7**[a]

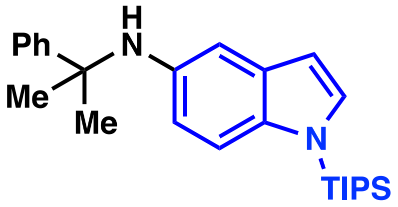


P7	L7	T (°C)	SM[b]	Product[b]
0.5 %	-	80	32 %	68 %
0.5 %	0.5 %	80	-	100 %
0.5 %	0.5 %	70	-	100 %

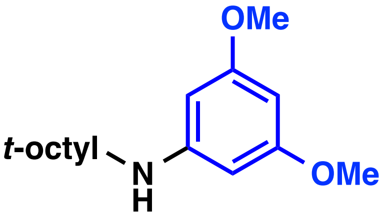
[a] Reaction conditions: Aryl halide (0.5 mmol), amine (0.6 mmol), NaO*t*Bu (0.6 mmol), 1,4-dioxane (0.5 mL). [b] GC-yields

General Procedure B: A 24 mL screw-top test tube equipped with a stir bar and Teflon septum was charged with aryl halide, if solid, (1.00 mmol, 1.00 equiv), amine, if solid, (1.20 mmol, 1.20 equiv), precatalyst **P7** (4.0-8.0 mg, 0.5-1.0 mol %), **L7** (2.0-4.0 mg, 0.5-1.0 mol %) and NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv). The tube was evacuated and backfilled with argon (this procedure was repeated a total of 3 times), after which aryl halide and/or amine, if liquid, were added via syringe. Lastly, 1,4-dioxane (1 mL) was added and the Teflon septum was replaced with a new unpunctured septum under positive pressure of argon. The reaction was placed in a preheated oil bath at 80-

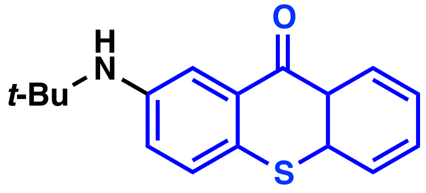
100 °C and stirred for 3-24 h. After completion the reaction was cooled to rt and diluted with EtOAc. The solution was filtered through Celite and concentrated in vacuo. The desired compound was purified by flash column chromatography in most cases, or triturated and filtered.



***N*-(2-phenylpropan-2-yl)-1-(triisopropylsilyl)-1*H*-indol-5-amine (15):** Following General Procedure B, a mixture of 5-chloro-1-(triisopropylsilyl)-1*H*-indole (308 mg, 1.00 mmol, 1.00 equiv), cumylamine (172 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (4.0 mg, 0.5 mol %), **L7** (2.0 mg, 0.5 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was purified by flash column chromatography, gradient elution from 100% hexanes to 9:1 hexanes:EtOAc, to provide the title compound as an off-white solid. Yield: 329 mg, 82%. mp = 97-100 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.67 - 7.57 (d, 2H), 7.36 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.28 - 7.24 (m, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 3.2 Hz, 1H), 6.57 - 6.47 (m, 1H), 6.36 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.33 (dd, *J* = 3.2, 0.8 Hz, 1H), 1.67 - 1.59 (m, 3H), 1.65 (s, 6H), 1.12 (d, *J* = 7.6 Hz, 18H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 149.2, 140.3, 135.9, 132.8, 132.0, 129.3, 127.1, 126.8, 114.7, 114.6, 107.7, 105.1, 57.2, 31.6, 19.1, 13.7 ppm. IR (neat, cm^{-1}): 2863, 1470, 1228, 1134, 881, 771,156, 722, 702, 688, 656, 640. Anal. Calcd. for $C_{26}H_{38}N_2Si$: C,76.79; H, 9.42, Found: C, 76.59; H, 9.54

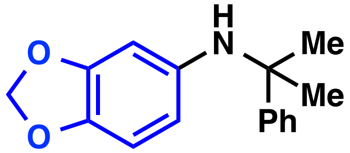


3,5-dimethoxy-*N*-(2,4,4-trimethylpentan-2-yl)aniline amine (16): Following General Procedure B, a mixture of 1-bromo-3,5-dimethoxybenzene (217 mg, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (4.0 mg, 0.50 mol %), **L7** (2.0 mg, 0.50 mol %) and dioxane (1 mL) was stirred at 80 °C for 6 h. The crude product was purified by flash column chromatography, gradient elution from 100% hexanes to 9:1 hexanes:EtOAc to provide the title compound as a pale yellow solid. Yield: 243 mg, 92%. mp = 54 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 5.87 (m, *J* = 1.6 Hz, 3H), 3.75 (s, 6H), 1.71 (s, 2H), 1.41 (s, 6H), 1.03 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 162.0, 149.3, 95.4, 89.9, 55.8, 55.7, 53.3, 32.5, 32.4, 31.3 ppm. IR (neat, cm^{-1}): 2961, 2933, 1613, 1584, 1475, 1201, 1170, 1151, 1072, 1062, 815, 801. Anal. Calcd. for $C_{16}H_{27}NO_2$: C, 72.41; H, 10.25, Found: C, 72.49; H, 10.28

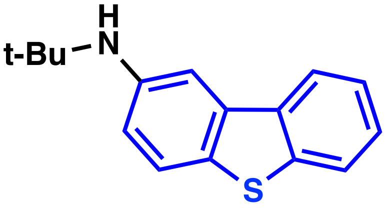


7-(*tert*-butylamino)-4a*H*-thioxanthen-9(9a*H*)-one (17): Following General Procedure B, a mixture of 7-chloro-4a*H*-thioxanthen-9(9a*H*)-one (246.7 mg, 1.00 mmol, 1.00 uiv.), *t*-butylamine (126 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %)

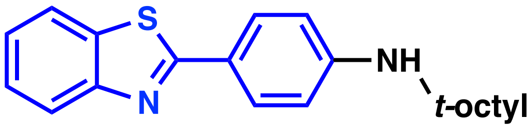
and dioxane (1 mL) was stirred at 80 °C for 12 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8.5:1.5 hexanes:EtOAc to provide the title compound as a white solid. Yield 264 mg, 93%. mp = 95 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.66 - 8.58 (m, 1H), 7.97 (d, *J* = 2.8 Hz, 1H), 7.62 - 7.54 (m, 2H), 7.45 (ddd, *J* = 8.2, 5.8, 2.4 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.07 (dd, *J* = 8.7, 2.8 Hz, 1H), 1.43 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 146.3, 138.4, 132.3, 130.5, 130.4, 129.4, 127.2, 126.6, 126.6, 126.3, 126.0, 123.9, 114.5, 52.3, 30.4 ppm. IR (neat, cm^{-1}): 3343, 2953, 1626, 1591, 1477, 1433, 1325, 1224, 808, 735, 630. Anal. Calcd. for $C_{17}H_{19}NOS$: C, 71.54; H, 6.71, Found: C, 71.99; H, 6.12



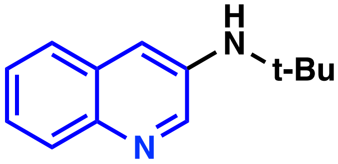
***N*-(2-phenylpropan-2-yl)benzo[*d*][1,3]dioxol-5-amine (18):** Following General Procedure B, a mixture of 5-chlorobenzo[*d*][1,3]dioxole (157 mg, 1.00 mmol, 1.00 equiv), cumylamine (172 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 80 °C for 6 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9:1 hexanes:EtOAc to provide the title compound as a yellow oil. Yield: 225 mg, 89%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.64 - 7.56 (m, 2H), 7.47 - 7.36 (m, 2H), 7.34 - 7.27 (m, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 6.03 (d, *J* = 2.3 Hz, 1H), 5.89 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.82 (s, 2H), 3.86 (s, 1H), 1.67 (s, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 148.5, 148.3, 142.2, 140.4, 129.4, 127.3, 126.5, 109.0, 108.8, 101.2, 99.5, 57.1, 31.3 ppm. IR (neat, cm^{-1}): 1500, 1485, 1196, 1036, 763, 699. Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71, Found: C, 75.28; H, 6.71



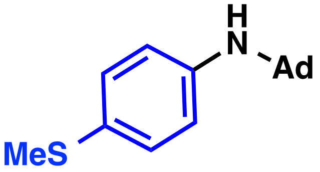
***N*-(*tert*-butyl)dibenzo[*b*,*d*]thiophen-2-amine (19):** Following General Procedure B, a mixture of 2-bromodibenzo[*b*,*d*]thiophene (263 mg, 1.00 mmol, 1.00 equiv), *t*-butylamine (126 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (4.0 mg, 1 mol %), **L7** (2.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8:2 hexanes:EtOAc to provide the title compound as a brown solid. Yield 212 mg, 83%. mp = 76-79 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.07 (ddd, *J* = 5.8, 3.3, 0.7 Hz, 1H), 7.86 - 7.76 (m, 1H), 7.62 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.59 - 7.54 (m, 1H), 7.47 - 7.36 (m, 2H), 6.97 (ddd, *J* = 8.5, 2.4, 0.7 Hz, 1H), 1.40 (d, *J* = 0.6 Hz, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 144.8, 141.0, 137.0, 136.2, 130.8, 127.1, 124.7, 123.6, 123.5, 122.1, 121.0, 111.4, 52.8, 30.9 ppm. IR (neat, cm^{-1}): 2958, 1429, 1359, 1207, 812, 776, 762, 736, 704, 625, 613. Anal. Calcd. for $C_{16}H_{17}NS$: C, 75.25; H, 6.71, Found: C, 75.20; H, 6.86



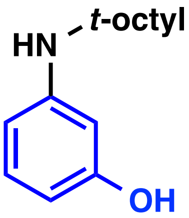
4-(benzo[*d*]thiazol-2-yl)-*N*-(2,4,4-trimethylpentan-2-yl)aniline (20): Following General Procedure B, a mixture of 2-(4-bromophenyl)benzo[*d*]thiazole (290 mg, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (4.0 mg, 0.50 mol %), **L7** (2.0 mg, 0.50 mol %) and dioxane (1 mL) was stirred at 80 °C for 3 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9:1 hexanes:EtOAc to provide the title compound as a yellow solid. Yield: 298 mg, 88%. mp = 108 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 - 7.79 (m, 3H), 7.43 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.30 (ddt, *J* = 8.3, 7.2, 1.2 Hz, 1H), 6.77 - 6.61 (m, 2H), 4.05 (s, 1H), 1.77 (d, *J* = 1.3 Hz, 3H), 1.47 (d, *J* = 1.3 Hz, 6H), 1.03 (d, *J* = 1.3 Hz, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 169.5, 155.1, 150.3, 135.2, 129.5, 126.7, 124.9, 123.0, 122.5, 122.1, 115.3, 55.9, 52.7, 32.5, 32.3, 31.2 ppm. IR (neat, cm^{-1}): 1603, 1467, 1435, 1338, 1312, 1219, 1179, 822, 756, 725, 693. Anal. Calcd. for $C_{21}H_{26}N_2S$: C, 74.51; H, 7.74, Found: C, 74.67; H, 7.69



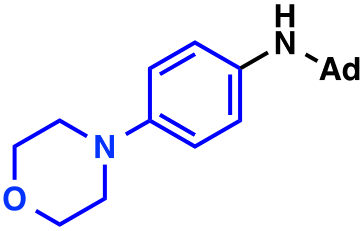
***N*-(*tert*-butyl)quinolin-3-amine (21)**: Following General Procedure B, a mixture of 3-bromoquinoline (208 mg, 1.00 mmol, 1.00 equiv), *t*-butylamine (126 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 100 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 6:4 hexanes:EtOAc to provide the title compound as a yellow oil. Yield 193 mg, 96%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.43 (d, *J* = 2.9 Hz, 1H), 8.04 - 7.86 (m, 1H), 7.75 - 7.55 (m, 1H), 7.45 - 7.38 (m, 2H), 7.30 - 7.27 (m, 1H), 4.17 (s, 1H), 1.44 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 146.0, 142.2, 140.6, 129.8, 129.3, 127.6, 126.8, 125.9, 114.9, 52.4, 30.1 ppm. IR (neat, cm^{-1}): 3274, 2973, 1602, 1543, 1388, 1364, 1351, 1214, 1187, 1141, 867, 843, 777, 746, 620. Anal. Calcd. for $C_{13}H_{16}N_2$: C,77.96; H, 8.05, Found: C, 77.40; H, 7.97



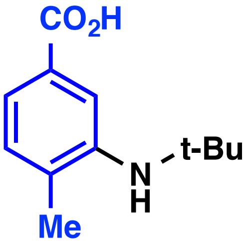
***N*-(4-(methylthio)phenyl)adamantan-1-amine (22):** Following General Procedure B, a mixture of 4-bromothioanisole (203 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (4.0 mg, 0.50 mol %), **L7** (2.0 mg, 0.50 mol %) and dioxane (1 mL) was stirred at 80 °C for 6 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8:2 hexanes:EtOAc to provide the title compound as a off-white solid. Yield: 257 mg, 94%. mp = 70 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.21 - 7.05 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 3.34 (s, 1H), 2.43 (s, 3H), 2.14 - 2.07 (m, 3H), 1.87 (d, *J* = 2.9 Hz, 6H), 1.73 - 1.60 (m, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 145.1, 130.7, 127.1, 120.3, 53.0, 44.0, 37.2, 30.4, 19.1 ppm. IR (neat, cm^{-1}): 2897, 1591, 1498, 1356, 1310, 1296, 817, 813, 805. Anal. Calcd. for $C_{17}H_{23}NS$: C, 74.67; H, 8.48, Found: C, 74.62; H, 8.44



3-((2,4,4-trimethylpentan-2-yl)amino)phenol amine (23): Following a modified General Procedure B, a mixture of 3-bromophenol (173 mg, 1.00 mmol, 1.00 equiv), *t*-octylamine (413 µl, 2.50 mmol, 2.50 equiv), NaO*t*-Bu (230 mg, 2.40 mmol, 2.40 equiv), **P7** (4.0 mg, 0.50 mol %), **L7** (2.0 mg, 0.50 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The reaction mixture was diluted in EtOAc and washed with a saturated aqueous solution of NH_4Cl. The two phases were separated and the aqueous phase was extracted with ~ 20 mL EtOAc (x2). The combined organic phases were dried over $MgSO_4$ and filtered through a plug of silica gel. The solvent was removed in vacuo and the resulting solid was triturated with pentane and filtered to afford the desired compound as a pale brown solid. Yield: 201 mg, 89%. mp = 99 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.97 (t, J = 8.0 Hz, 1H), 6.34 - 6.05 (m, 3H), 1.69 (s, 2H), 1.39 (s, 6H), 1.02 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 157.1, 148.1, 130.5, 111.1, 106.7, 105.7, 56.6, 53.8, 32.4, 32.4, 30.8 ppm. IR (neat, cm^{-1}): 2949, 1599, 1480, 1435, 1367, 1289, 1247, 1224, 1184, 1148, 861, 775, 695. Anal. Calcd. for $C_{14}H_{23}NO$: C, 75.97; H, 10.47, Found: C, 75.76; H, 10.36

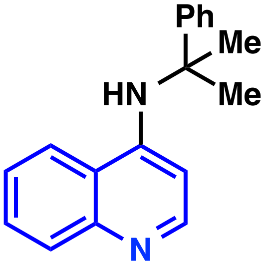


***N*-(4-morpholinophenyl)adamantan-1-amine (24):** Following General Procedure B, a mixture of 4-(4-chlorophenyl)morpholine (198 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (6.0 mg, 0.75 mol %), **L7** (3.0 mg, 0.75 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 9:1 hexanes:EtOAc to 1:1 hexanes:EtOAc to provide the title compound as a white solid. Yield: 274 mg, 88%. mp = 120 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.78 (q, J = 8.7 Hz, 4H), 3.97 - 3.73 (m, 4H), 3.05 (t, J = 4.6 Hz, 4H), 2.92 (s, 1H), 2.06 (t, J = 3.3 Hz, 3H), 1.75 (d, J = 2.9 Hz, 6H), 1.71 - 1.50 (m, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 146.72, 139.1, 124.1, 117.2, 67.7, 53.2, 51.0, 44.4, 37.1, 30.4 ppm. IR (neat, cm^{-1}): 2898, 1511, 1234, 1119, 925, 832. Anal. Calcd. for $C_{20}H_{28}N_2O$: C, 76.88; H, 9.03, Found: C, 77.07; H, 8.95

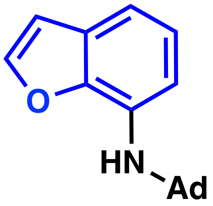


3-(*tert*-butylamino)-4-methylbenzoic acid (25): Following a modified General Procedure B, a mixture of 3-bromo-4-methylbenzoic acid (215 mg, 1.00 mmol, 1.00 equiv), *t*-butylamine (126 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (230 mg, 2.40 mmol, 2.40 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The reaction mixture was diluted in EtOAc and washed with a saturated aqueous NH_4Cl.

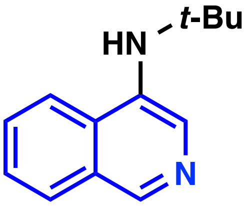
HCl (10% solution) was added until pH was neutral. The two phases were separated and the aqueous phase was extracted with ~20 mL EtOAc (x2). The organic phase was dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the resulting solid was triturated with pentane and filtered to afford the desired compound as an off-white solid. Yield: 152 mg, 74%. mp = 146-149 °C. ^{1}**H NMR** (500 MHz, Chloroform-d) δ 7.67 - 7.60 (m, 1H), 7.45 - 7.37 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 2.19 (s, 3H), 1.44 (s, 9H) ppm. ^{13}**C NMR** (126 MHz, Chloroform-d) δ 173.6, 145.0, 131.1, 130.7, 128.5, 120.0, 115.7, 52.4, 30.5, 19.1 ppm. IR (neat, cm^{-1}): 2978, 1679, 1430, 1296, 1267, 1227, 1209, 928, 875, 760. HRMS: Calcd. for $C_{12}H_{17}NO_2$, [M+H]: 208.1332, Found: [M+H]: 208.1327



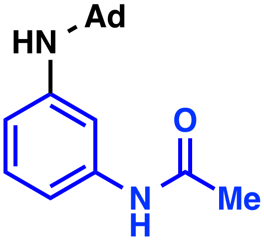
***N*-(2-phenylpropan-2-yl)quinolin-4-amine (26):** Following General Procedure B, a mixture of 4-chloroquinoline (164 mg, 1.00 mmol, 1.00 equiv), cumylamine (172 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 1:9 hexanes:EtOAc to provide the title compound as pale yellow solid. Yield: 182 mg, 69%. mp = 170 °C .^{1}**H NMR** (500 MHz, Chloroform-d) δ 8.25 (d, *J* = 5.4 Hz, 1H), 8.00 - 7.94 (m, 1H), 7.89 - 7.83 (m, 1H), 7.64 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.51 - 7.42 (m, 3H), 7.39 - 7.31 (m, 2H), 7.29 - 7.26 (m, 1H), 5.88 (d, *J* = 5.4 Hz, 1H), 5.43 (s, 1H), 1.82 (s, 6H) ppm. ^{13}**C NMR** (126 MHz, Chloroform-d) δ 150.5, 148.8, 147.8, 145.9, 130.6, 129.6, 129.5, 127.6, 125.9, 125.4, 119.9, 119.8, 103.5, 57.1, 31.0 ppm. IR (neat, cm^{-1}): 1571, 1538, 1393, 819, 765, 701. HRMS: Calcd. for $C_{18}H_{18}N_2$, [M+H]: 263.1543, Found: [M+H]: 263.1540



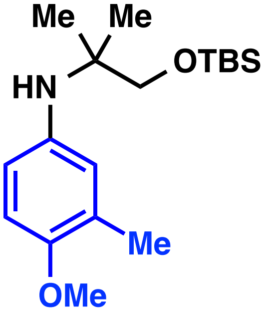
***N*-(adamantan-1-yl)benzofuran-7-amine (27):** Following General Procedure B, a mixture of 7-chlorobenzofuran (153 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was triturated with pentane and isolated via vacuum filtration to provide the title compound as a pale white solid. Yield 174 mg, 65%. mp = 150 °C. ^{1}**H NMR** (500 MHz, Chloroform-d) δ 7.56 (d, *J* = 2.1 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.73 (d, *J* = 2.1 Hz, 1H), 3.94 (s, 1H), 2.15 (q, *J* = 3.2 Hz, 3H), 2.01 (d, *J* = 2.9 Hz, 6H), 1.77 - 1.67 (m, 6H) ppm. ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 146.8, 144.5, 132.4, 127.9, 123.9, 112.6, 111.5, 108.0, 53.1, 43.9, 37.2, 30.4 ppm. IR (neat, cm^{-1}): 2958, 1466, 1429, 1359, 1207, 812, 776, 762, 736, 715, 704, 625, 613.



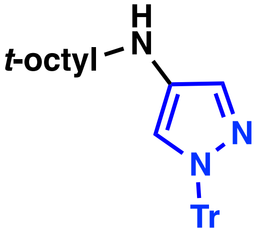
***N*-(*tert*-butyl)isoquinolin-4-amine (28):** Following General Procedure B, a mixture of 4-bromoisoquinoline (208 mg, 1.00 mmol, 1.00 equiv), *t*-butylamine (126 μl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (16.0 mg, 2 mol %), **L7** (8.0 mg, 2 mol %) and dioxane (1 mL) was stirred at 110 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 8:2 hexanes:EtOAc to 100% EtOAc to provide the title compound as a yellow solid. Yield: 152 mg, 75%. mp =118 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.69 (s, 1H), 8.18 (s, 1H), 7.90 (d, *J* = 16.6 Hz, 1H), 7.78 (dq, *J* = 8.5, 0.9 Hz, 1H), 7.62 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 4.07 (s, 1H), 1.48 (s, 9H) ppm**.** **^{13}C NMR** (126 MHz, Chloroform-d) δ 146.9, 145.4, 143.6, 134.6, 130.6, 130.5, 124.6, 121.9, 107.3, 52.1, 30.3 ppm. IR (neat, cm^{-1}): 2986, 1620, 1489, 1379, 1363, 1241, 1213, 825. Anal. Calcd. for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05, Found: C, 77.87; H, 7.8



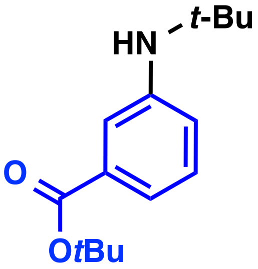
***N*-(3-((-adamantan-1-yl)amino)phenyl)acetamide (29):** Following a modified General Procedure B, a mixture of *N*-(3-chlorophenyl)acetamide (170 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (230 mg, 2.40 mmol, 2.40 equiv), **P7** (4.0 mg, 0.5 mol %), **L7** (2.0 mg, 0.5 mol %) and dioxane (1 mL) was stirred at 100 °C for 24 h. The reaction mixture was diluted with EtOAc and washed with a saturated aqueous solution of NH_4Cl. The two phases were separated and the aqueous phase was extracted with ~ 20 mL of EtOAc (x2). The organic phase was dried over $MgSO_4$ and filtered. The crude product was purified via Biotage SP4 (silica-packed 25 g snap cartridge; gradient from 5:5 hexanes:EtOAc to 100% EtOAc) to provide the title compound as an off-white solid. Yield: 220 mg, 78%. mp = 139 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.61 (s, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.76 - 6.67 (m, 1H), 6.51 (dd, *J* = 8.4, 2.3 Hz, 1H), 3.34 (s, 1H), 2.12 (s, 3H), 2.08 (d, *J* = 4.5 Hz, 3H), 1.87 (d, *J* = 2.9 Hz, 6H), 1.76 - 1.58 (m, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 169.0, 147.6, 139.2, 129.7, 114.7, 110.3, 110.1, 52.8, 43.9, 37.1, 30.4, 25.4 ppm. IR (neat, cm^{-1}): 2901, 1663, 1608, 1553, 1477, 1266, 762, 571. Anal. Calcd. for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51, Found: C, 76.02; H, 8.47



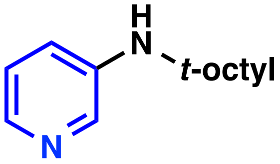
***N*-(1-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)-4-methoxy-3-methylaniline (30):** Following General Procedure B, a mixture of 4-bromo-1-methoxy-2-methylbenzene (201 mg, 1.00 mmol, 1.00 equiv), 1-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-2-amine (244 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 100 °C for 10 min. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8:2 hexanes:EtOAc to provide the title compound as a yellow oil. Yield: 247 mg, 77%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.75 - 6.70 (m, 2H), 6.67 (d, *J* = 9.4 Hz, 1H), 3.78 (s, 3H), 3.33 (s, 2H), 2.17 (t, *J* = 0.6 Hz, 3H), 1.13 (s, 6H), 0.95 (s, 9H), 0.07 (s, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 153.9, 138.9, 127.2, 126.9, 121.8, 110.9, 70.2, 56.5, 56.2, 26.6, 25.1, 19.0, 17.0, -4.7 ppm. IR (neat, cm^{-1}): 1498, 1223, 1090, 1038, 834, 806, 773. Anal. Calcd. for $C_{18}H_{22}NO_2Si$: C, 66.82; H, 10.28, Found: C, 66.52; H, 10.24



***N*-(2,4,4-trimethylpentan-2-yl)-1-trityl-1*H*-pyrazol-4-amine (31):** Following General Procedure B, a mixture of 4-bromo-1-trityl-1*H*-pyrazole (195 mg, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (12.0 mg, 3 mol %), **L7** (6.0 mg, 3 mol %) and dioxane (1 mL) was stirred at 100 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8.5:1.5 hexanes:EtOAc to provide the title compound as a pale yellow solid. Yield: 170 mg, 78%. mp = 130 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.34 (s, 1H), 7.30 (dd, *J* = 4.9, 2.2 Hz, 9H), 7.19 - 7.12 (m, 6H), 6.96 (s, 1H), 1.45 (s, 2H), 1.15 (s, 6H), 0.99 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 144.1, 136.4, 130.8, 128.3, 128.3, 127.7, 126.7, 79.0, 56.4, 54.3, 32.4, 32.2, 30.0 ppm. IR (neat, cm^{-1}): 2950, 1489, 1442, 1362, 1184, 762, 743, 696, 677, 658, 649, 640. Anal. Calcd. for $C_{30}H_{35}N_3$: C, 82.34; H, 8.06, Found: C, 81.88; H, 8.00

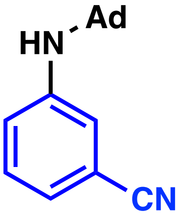


***tert*-butyl 3-(*tert*-butylamino)benzoate (32):** Following General Procedure B, a mixture of *tert*-butyl 3-bromobenzoate (192 µl, 1.00 mmol, 1.00 equiv), *t*-butylamine (126 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (4.0 mg, 0.5 mol %), **L7** (2.0 mg, 0.5 mol %) and dioxane (1 mL) was stirred at 80 °C for 4 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8:2 hexanes:EtOAc to provide the title compound as a white solid. Yield 197 mg, 82%. mp = 69-71 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.34 (s, 2H), 7.21 (d, *J* = 3.3 Hz, 1H), 6.92 - 6.86 (m, 1H), 1.58 (s, 9H), 1.36 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 166.8, 147.5, 133.3, 129.3, 121.4, 119.6, 118.2, 81.3, 52.2, 30.6, 28.9 ppm. IR (neat, cm^{-1}): 3390, 2972, 1693, 1297, 1282, 1223, 1175, 1153, 1109, 999, 753. Anal. Calcd. for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30, Found: C, 72.13; H, 9.27



***N*-(2,4,4-trimethylpentan-2-yl)pyridin-3-amine (33):** Following General Procedure B, a mixture of 3-chloropyridine (95.0 µl, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv),

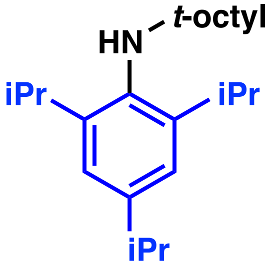
P7 (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 100 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 8:2 hexanes:EtOAc to 100% EtOAc to provide the title compound as a yellow solid. Yield: 149 mg, 73%. mp = 48 °C. ^{1}**H NMR** (500 MHz, Chloroform-d) δ 8.02 (d, *J* = 2.9 Hz, 1H), 7.93 - 7.85 (m, 1H), 7.00 (dd, *J* = 8.3, 4.5 Hz, 1H), 6.95 (ddd, *J* = 8.3, 2.9, 1.4 Hz, 1H), 3.64 (s, 1H), 1.66 (s, 2H), 1.37 (s, 6H), 0.98 (s, 9H) ppm. ^{13}**C NMR** (126 MHz, Chloroform-d) δ 143.7, 139.4, 139.0, 124.0, 122.2, 55.8, 53.2, 32.5, 32.2, 31.0 ppm. IR (neat, cm^{-1}): 2947, 1584, 1481, 1467, 1412, 1309, 1223, 1006, 793, 708. Anal. Calcd. for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75, Found: C, 75.56; H, 10.65



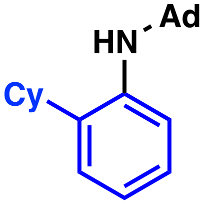
3-(adamantan-1-ylamino)benzonitrile (34): Following General Procedure B, a mixture of 3-bromobenzonitrile (183 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P7** (8.0 mg, 1 mol %), **L7** (4.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 100 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9:1 hexanes:EtOAc to provide the title compound as a white solid. Yield: 183 mg, 73%. mp = 99 °C. ^{1}**H NMR** (500 MHz, Chloroform-d) δ 7.18 (t, *J* = 7.9 Hz, 1H), 7.01 - 6.94 (m, 2H), 6.93 - 6.82 (m, 1H), 3.63 (s, 1H), 2.19 - 2.07 (m, 3H), 1.90 (d, *J* = 2.8 Hz, 6H), 1.75 - 1.60 (m, 6H) ppm. ^{13}**C NMR** (126 MHz, Chloroform-d) δ 147.3, 130.2, 122.1, 121.8, 120.2, 119.8, 113.2, 53.0, 43.5, 37.0, 30.2 ppm. IR (neat, cm^{-1}): 2906, 2227, 1593, 1475, 1356, 1266, 1258, 1120, 1094, 869, 791, 693, 649, 643. Anal. Calcd. for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99, Found: C, 80.64; H, 7.96

E) Arylation of α-trisubstituted amines using precatalyst **P4**

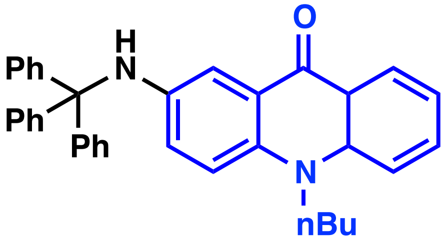
General Procedure C: A 24 mL screw-top test tube equipped with a stir bar and Teflon septum was charged with aryl halide, if solid, (1.00 mmol, 1.00 equiv), amine, if solid (1.20 mmol, 1.20 equiv), precatalyst **P4** (8.00-16.0 mg, 1-2 mol %) and NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv). The tube was evacuated and backfilled with argon (this procedure was repeated a total of 3 times), after which aryl halide and/or amine, if liquid, were added by syringe. Then, dioxane (1 mL) was added and the Teflon septum was replaced with a new unpunctured septum under a positive pressure of argon. The reaction was placed in a preheated oil bath at 80-120 °C and stirred for 6-24 h. After completion, the reaction was cooled to rt and diluted with EtOAc. The solution was filtered through Celite and concentrated in vacuo. The crude compound was purified by flash column chromatography.



2,4,6-triisopropyl-*N*-(2,4,4-trimethylpentan-2-yl)aniline (35): Following General Procedure C, a mixture of 2-bromo-1,3,5-triisopropylbenzene (253 µl, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (16.0 mg, 2 mol %), and dioxane (1 mL) was stirred at 120 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 7:3 hexanes:EtOAc to provide the title compound as a yellow oil. Yield: 216 mg, 65%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.92 (s, 2H), 3.53 (hept, *J* = 6.9 Hz, 2H), 2.85 (hept, *J* = 6.9 Hz, 1H), 1.67 (s, 2H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 6.9 Hz, 12H), 1.11 (d, *J* = 2.8 Hz, 15H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 146.8, 144.7, 137.6, 121.5, 58.5, 58.4, 34.4, 32.7, 32.6, 30.1, 29.0, 25.0, 24.8 ppm. IR (neat, cm^{-1}): 2955, 1463, 1381, 1362, 1210, 874. Anal. Calcd. for $C_{23}H_{41}N$: C, 83.31; H, 12.46, Found: C, 82.85; H, 12.25

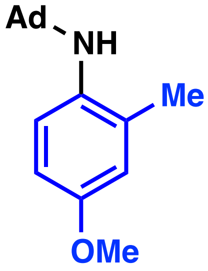


N-(2-cyclohexylphenyl)adamantan-1-amine (36): Following General Procedure C, a mixture of 1-bromo-2-cyclohexylbenzene (187 µl, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (8.0 mg, 1 mol %), and dioxane (1 mL) was stirred at 80 °C for 6 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9:1 hexanes:EtOAc to provide the title compound as a yellow solid. Yield: 294 mg, 95%. mp = 59-61 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.17 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.11 - 7.03 (m, 2H), 6.84 (ddd, *J* = 8.0, 6.8, 1.9 Hz, 1H), 3.49 (s, 1H), 2.54 (ddt, *J* = 11.3, 8.3, 3.2 Hz, 1H), 2.17 (t, *J* = 3.3 Hz, 3H), 1.97 (d, *J* = 2.9 Hz, 6H), 1.91 (ddt, *J* = 15.1, 8.0, 2.9 Hz, 4H), 1.87 - 1.80 (m, 1H), 1.79 - 1.70 (m, 6H), 1.46 (tt, *J* = 13.1, 9.9 Hz, 4H), 1.34 (tdd, *J* = 15.9, 8.3, 4.2 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 143.6, 135.6, 126.7, 126.5, 119.7, 119.4, 53.0, 44.5, 39.5, 37.4, 34.2, 30.7, 28.2, 27.2 ppm. IR (neat, cm^{-1}): 2896, 2848, 1447, 1258, 743. Anal. Calcd. for $C_{22}H_{31}N$: C, 85.38; H, 10.10, Found: C, 85.32; H, 10.05

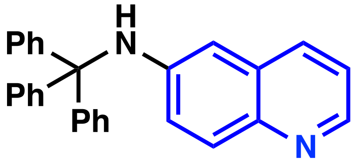


10-butyl-2-(tritylamino)-10,10a-dihydroacridin-9(8a*H*)-one (37): Following General Procedure C, a mixture of 10-butyl-2-chloro-10,10a-dihydroacridin-9(8a*H*)-one (286 mg, 1.00 mmol, 1.00 equiv), tritylamine (310 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (16.0 mg, 2 mol %), and dioxane (1 mL) was stirred at 120 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 7:3 hexanes:EtOAc to provide the title compound as a bright yellow solid. Yield: 490 mg, 96%. mp = 126-128 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.50 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.66 (d, *J* = 3.0 Hz, 1H), 7.62

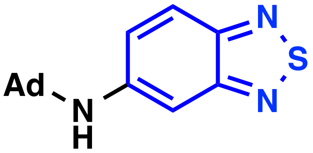
(ddd, *J* = 8.7, 6.9, 1.8 Hz, 1H), 7.45 - 7.40 (m, 6H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.33 - 7.27 (m, 6H), 7.24 - 7.15 (m, 4H), 7.06 (d, *J* = 9.3 Hz, 1H), 6.79 (dd, *J* = 9.3, 3.0 Hz, 1H), 5.24 (s, 1H), 4.24 - 4.11 (m, 2H), 1.88 - 1.74 (m, 2H), 1.50 (sextet, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 178.0, 145.9, 141.8, 141.7, 135.2, 133.9, 129.8, 128.7, 128.4, 127.6, 124.4, 123.6, 122.0, 120.8, 115.3, 114.8, 112.7, 72.3, 46.4, 29.9, 20.8, 14.5 ppm. IR (neat, cm^{-1}): 1591, 1500, 1488, 1464, 748, 699. HRMS: Calcd. for $C_{36}H_{34}N_2O$, [M+H]: 510.2700, Found: [M+H]: 510.2680



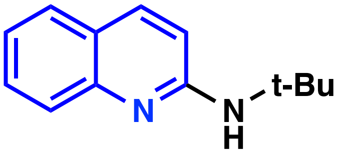
***N*-(4-methoxy-2-methylphenyl)adamantan-1-amine (38):** Following General Procedure C, a mixture of 1-bromo-4-methoxy-2-methylbenzene (201 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (16.0 mg, 2 mol %), and dioxane (1 mL) was stirred at 120 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9.5:0.5 hexanes:EtOAc) to provide the title compound as a yellow solid. Yield: 230 mg, 85%. mp = 60 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.94 (d, *J* = 8.7 Hz, 1H), 6.72 - 6.68 (m, 1H), 6.65 (ddd, *J* = 8.7, 3.1, 0.6 Hz, 1H), 3.75 (s, 3H), 2.21 (s, 3H), 2.09 (p, *J* = 3.2 Hz, 3H), 1.83 (d, *J* = 3.0 Hz, 6H), 1.74 - 1.57 (m, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 154.3, 137.8, 130.1, 123.2, 116.8, 111.9, 56.1, 53.8, 44.6, 37.2, 30.4, 19.6 ppm. IR (neat, cm^{-1}): 2885, 1495, 1214, 1049, 792, 721. Anal. Calcd. for $C_{18}H_{25}NO$: C, 79.66; H, 9.28, Found: C, 79.17; H, 9.21



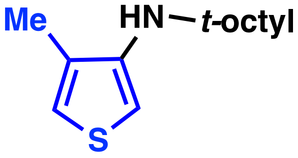
***N*-tritylquinolin-6-amine (39):** Following General Procedure C, a mixture of 6-chloroquinoline (164 mg, 1.00 mmol, 1.00 equiv), tritylamine (310 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (16.0 mg, 2 mol %), and dioxane (1 mL) was stirred at 100 °C for 24 h. The crude product was purified via flash chromatography, gradient of 8:2 hexanes:EtOAc to 1:1 hexanes:EtOAc to provide the title compound as a white solid. Yield: 451 mg, 91%. mp = 222 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.54 (dd, *J* = 4.3, 1.6 Hz, 1H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.57 - 7.50 (m, 1H), 7.44 - 7.37 (m, 6H), 7.33 - 7.27 (m, 6H), 7.26 - 7.20 (m, 3H), 7.11 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.06 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.30 (d, *J* = 2.6 Hz, 1H), 5.35 (s, 1H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 147.0, 145.5, 144.7, 143.5, 134.7, 130.1, 129.9, 129.8, 128.8, 127.7, 123.5, 121.7, 109.3, 72.3 ppm. IR (neat, cm^{-1}): 1619, 1511, 1489, 1379, 1235, 828, 757, 658, 689, 606. HRMS: Calcd. for $C_{28}H_{22}N_2$, [M+H]: 387.1856, Found: [M+H]: 387.1844



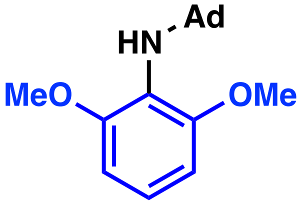
***N*-((3*s*,5*s*,7*s*)-adamantan-1-yl)benzo[*c*][1,2,5]thiadiazol-5-amine (40):** Following General Procedure C, a mixture of 5-chlorobenzo[*c*][1,2,5]thiadiazole (171 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (181 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (16.0 mg, 2 mol %), and dioxane (1 mL) was stirred at 120 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9.5:0.5 hexanes:EtOAc to provide the title compound as a bright yellow solid. Yield: 205 mg, 72%. mp = 155 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.66 (d, *J* = 9.3 Hz, 1H), 7.05 (s, 1H), 6.95 - 6.88 (m, 1H), 4.01 (s, 1H), 2.22 - 2.13 (m, 3H), 2.06 (d, *J* = 3.0 Hz, 6H), 1.74 (d, *J* = 2.9 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 157.5, 150.6, 146.8, 128.2, 121.8, 98.1, 53.2, 42.5, 37.0, 30.2 ppm. IR (neat, cm^{-1}): 2893, 1610, 1493, 1292, 1249, 1212, 813, 803, 666, 644. Anal. Calcd. for $C_{16}H_{19}N_3$: C, 67.33; H, 6.71, Found: C, 67.05; H, 6.70



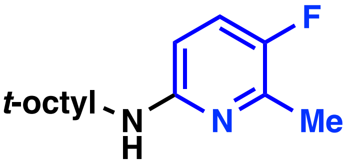
***N*-(*tert*-butyl)quinolin-2-amine (41):** Following General Procedure C, a mixture of 2-chloroquinoline (164 mg, 1.00 mmol, 1.00 equiv), *t*-butylamine (126 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (8.0 mg, 1 mol %) and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 6:4 hexanes:EtOAc) to provide the title compound as a yellow oil. Yield: 135 mg, 68%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.76 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.72 (ddt, *J* = 8.4, 1.3, 0.7 Hz, 1H), 7.60 - 7.56 (m, 1H), 7.54 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.21 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 6.60 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 1.57 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 157.2, 148.7, 137.2, 129.9, 128.0, 127.2, 123.6, 122.5, 113.7, 52.1, 30.2 ppm. IR (neat, cm^{-1}): 2959, 1616, 1518, 1397, 1222, 813, 778, 752, 622. Anal. Calcd. for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05, Found: C, 78.00; H, 7.94



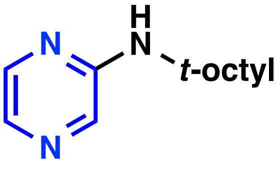
4-methyl-*N*-(2,4,4-trimethylpentan-2-yl)thiophen-3-amine (42): Following General Procedure C, a mixture of 3-bromo-4-methylthiophene (111 µl, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (8.0 mg, 1 mol %), and dioxane (1 mL) was stirred at 100 °C for 12 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 9:1 hexanes:EtOAc to provide the title compound as a brown oil. Yield: 176 mg, 78%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.91 - 6.66 (m, 1H), 5.99 (d, *J* = 3.1 Hz, 1H), 2.08 - 1.98 (m, 3H), 1.70 (s, 2H), 1.40 (s, 6H), 1.02 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 143.8, 130.3, 119.9, 97.0, 55.8, 53.1, 32.5, 32.3, 30.1, 14.6 ppm. IR (neat, cm^{-1}): 2951, 1500, 1472, 1364, 1223, 862, 760. HRMS: Calcd. for $C_{13}H_{23}NS$, [M+H]: 226.1624, Found: [M+H]: 226.1



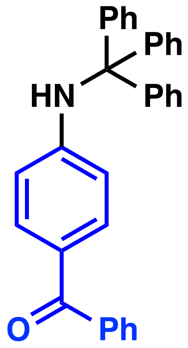
***N*-(2,6-dimethoxyphenyl)adamantan-1-amine (43):** Following General Procedure C, a mixture of 2-bromo-1,3-dimethoxybenzene (217 mg, 1.00 mmol, 1.00 equiv), 1-adamantylamine (182 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (8.0 mg, 1 mol %), and dioxane (1 mL) was stirred at 120 °C for 24 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 7:3 hexanes:EtOAc to provide the title compound as a white solid. Yield: 245 mg, 85%. mp = 127 °C. **^{1}H NMR** (500 MHz, Chloroform-d) δ 6.96 (t, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 6H), 2.02 (q, *J* = 3.0 Hz, 3H), 1.76 (d, *J* = 3.0 Hz, 6H), 1.65 - 1.52 (m, 6H)ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 156.2, 123.8, 104.4, 56.1, 55.5, 44.0, 37.2, 30.7 ppm. IR (neat, cm^{-1}): 2896, 1461, 1430, 1240, 1120,1108, 1101, 1090, 724. Anal. Calcd. for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77, Found: C, 75.37; H, 8.71



5-fluoro-6-methyl-*N*-(2,4,4-trimethylpentan-2-yl)pyridin-2-amine (44): Following General Procedure C, a mixture of 6-bromo-3-fluoro-2-methylpyridine (190 mg, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (8.0 mg, 1 mol %), and dioxane (1 mL) was stirred at 80 °C for 12 h. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8:2 hexanes:EtOAc to provide the title compound as an orange oil. Yield: 202 mg, 85%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.06 (t, *J* = 8.9 Hz, 1H), 6.20 (dd, *J* = 8.9, 2.7 Hz, 1H), 4.35 (s, 1H), 2.33 (d, *J* = 3.0 Hz, 3H), 1.77 (s, 2H), 1.43 (s, 6H), 0.99 (s, 9H) ppm. **^{13}C NMR** (126 MHz, Chloroform-d) δ 154.8 (d, *J* = 1.9 Hz), 151.6 (d, *J* = 240.1 Hz), 143.6 (d, *J* = 17.0 Hz), 124.7 (d, *J* = 21.5 Hz), 106.8 (d, *J* = 3.1 Hz), 55.2, 52.2, 32.4, 32.2, 30.9, 18.4 (d, *J* = 2.2 Hz) ppm. **^{19}F NMR** (282 MHz, Chloroform-d) δ – 143.20 (d, *J* = 8.7 Hz) ppm. IR (neat, cm^{-1}): 2995, 1499, 1462, 1234, 1212, 1113, 804. Anal. Calcd. for $C_{14}H_{23}N_2F$: C, 70.55; H, 9.73, Found: C, 70.63; H, 9.74



***N*-(2,4,4-trimethylpentan-2-yl)pyrazin-2-amine (45):** Following a modified General Procedure C, a mixture of 2-chloropyrazine (90.0 µl, 1.00 mmol, 1.00 equiv), *t*-octylamine (199 µl, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (16.0 mg, 2 mol %), and dioxane (1 mL) was stirred at 120 °C for 12 h. The reaction mixture was diluted with EtOAc and filtered through a cotton plug. The crude product was purified by flash column chromatography, gradient from 100% hexanes to 8:2 hexanes:EtOAc to provide the title compound as a white solid. Yield: 104 mg, 50%. mp = 82-84 °C. ^{1}**H NMR** (500 MHz, Chloroform-d) δ 7.94 (dd, *J* = 2.8, 1.5 Hz, 1H), 7.82 (d, *J* = 1.5 Hz, 1H), 7.71 (d, *J* = 2.8 Hz, 1H), 1.85 (s, 2H), 1.49 (s, 6H), 0.99 (s, 9H) ppm. ^{13}**C NMR** (126 MHz, Chloroform-d) δ 155.2, 142.1, 134.0, 132.1, 55.9, 51.8, 32.5, 32.2, 30.4 ppm. IR (neat, cm^{-1}): 2949, 1595, 1519, 1392, 1362, 1347, 1288, 1225, 1124, 1062, 999, 818. Anal. Calcd. for $C_{12}H_{21}N_3$: C, 69.52; H, 10.21, Found: C, 69.31; H, 10.17



Phenyl(4-(tritylamino)phenyl)methanone (46): Following General Procedure C, a mixture of (4-bromophenyl)(phenyl)methanone (261 mg, 1.00 mmol, 1.00 equiv), tritylamine (310 mg, 1.20 mmol, 1.20 equiv), NaO*t*-Bu (116 mg, 1.20 mmol, 1.20 equiv), **P4** (8.0 mg, 1 mol %), and dioxane (1 mL) was stirred at 80 °C for 24 h. The crude product was purified via flash column chromatography eluting with 10% EtOAc in hexanes to provide the title compound as a light-yellow solid. Yield: 433 mg, 98%. mp = 193 °C. ^{1}**H NMR** (500 MHz, Chloroform-d) δ 7.70 - 7.62 (m, 2H), 7.49 (dd, *J* = 14.3, 8.0 Hz, 3H), 7.40 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.36 - 7.21 (m, 14H), 6.38 (d, *J* = 8.6 Hz, 2H), 5.56 (s, 1H) ppm. ^{13}**C NMR** (126 MHz, Chloroform-d) δ 195.9, 151.3, 145.3, 139.6, 132.6, 131.9, 130.1, 129.8, 128.9, 128.7, 127.9, 127.0, 115.6, 72.2 ppm. IR (neat, cm^{-1}): 1590, 1574, 1513, 1314, 1148, 696, 636. Anal. Calcd. for $C_{32}H_{25}NO$: C, 87.44; H, 5.73, Found: C, 87.08; H, 5.77

F) Kinetic Studies: Calorimetry Data

F.1) General Procedure D: Calorimetric Studies using L4 as the supporting ligand. An oven-dried 16 mL vial equipped with a magnetic stir bar was charged with aryl halide and precatalyst **P4** and taken into a nitrogen-filled glovebox. The vial was charged with NaO*t*-Bu and 1,4-dioxane, fitted with a screw-cap Teflon septum, and taken out of the glovebox. The reaction mixture was placed in an Omnical CRC reaction calorimeter along with a syringe containing amine **3**. The calorimeter was set to 70 °C and allowed to thermally equilibrate. After equilibration, **3** was injected and the reaction was stirred until the heat flow on the calorimeter returned to the baseline level. A tau correction was then applied to the raw data due to the delay between heat release and detection. After each run, an equimolar amount of biphenyl (internal standard) was added to each vial and the total reaction conversion was determined by GC analysis. The corrected heat flow curve was then converted to rate by using eq 1 where q is the heat flow, ΔH_{rxn} is the heat of reaction, V is the reaction volume, and r is the reaction rate. The heat of reaction was found by integrating the heat flow *vs*. time curves.

$$q = \mathbf{\Delta} H_{rxn} V r \qquad (1)$$

The corrected heat flow curve was then converted to fractional conversion by dividing the area under the curve to any point by the total area under the curve (eq 2). The corresponding concentration was calculated through the conversion using eq 3.

$$fractional\ conversion = \frac{\int_0^t q\,dt}{\int_0^{t_f} q\,dt} \qquad (2)$$

$$[ArX] = (1 - fractional\ conversion)[ArX]_0 \qquad (3)$$

Different excess experiment with 1-chloro-3,5-dimethoxybenzene and L4 as supporting ligand: Following General Procedure D, two oven-dried 16 mL vials were charged with 1-chloro-3,5-dimethoxybenzene (**6**) (see Table S3), **P4** (32.0 mg, 0.04 mmol) NaO*t*-Bu (230 mg, 2.4 mmol) and 1,4-dioxane (2 mL). After equilibration, **3** (258 mg, 2.00 mmol) was injected. The heat of reaction was found to be 165.34 KJ/mol on average.

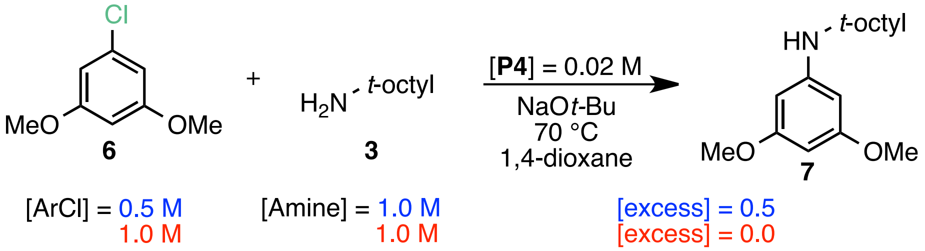
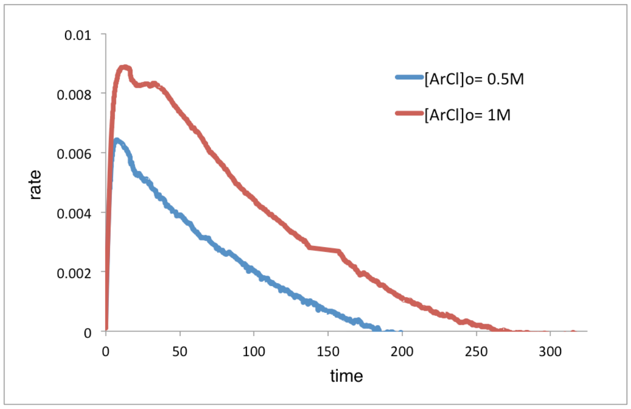


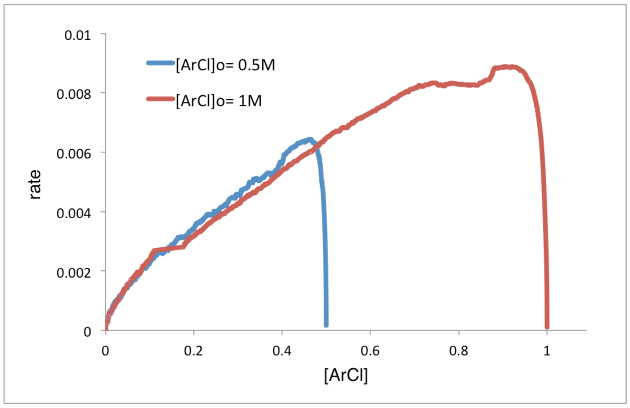
Table S3: Different excess experiment with 1-chloro-3,5-dimethoxybenzene, **6** using a precatalyst based on **L4**, **P4**

Reagent	Amount	mmol	Concentration	Excess
ArCl	173 mg	1.00	0.50 M	0.5 M
t-octylamine	258 mg	2.00	1.00 M	
ArCl	346 mg	2.00	1.00 M	0 M
t-octylamine	258 mg	2.00	1.00 M	
NaO^{t}Bu	230 mg	2.40	1.20 M	-
P4, Ph$_2$CPhosOMs	32.0 mg	0.04	0.02 M	-
1,4-dioxane	2 mL	-	-	-

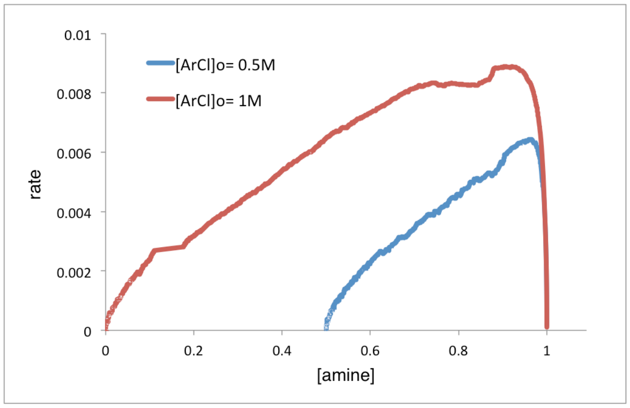
Plot of rate *vs.* time



Plot of rate *vs.* [ArCl]



Plot of rate *vs.* [amine]



Different excess experiment with 1-bromo-3,5-dimethoxybenzene and L4 as supporting ligand: Following General Procedure D, two oven-dried 16 mL vials were charged with 1-bromo-3,5-dimethoxybenzene (**12**) (see Table S4), **P4** (32.0 mg, 0.04 mmol) NaO*t*-Bu (230 mg, 2.4 mmol) and 1,4-dioxane (2 mL). After equilibration, **3** (258 mg, 2.00 mmol) was injected. The heat of reaction was found to be 190.35 KJ/mol on average.

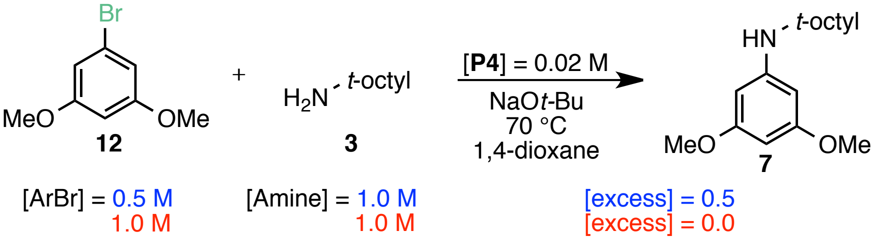
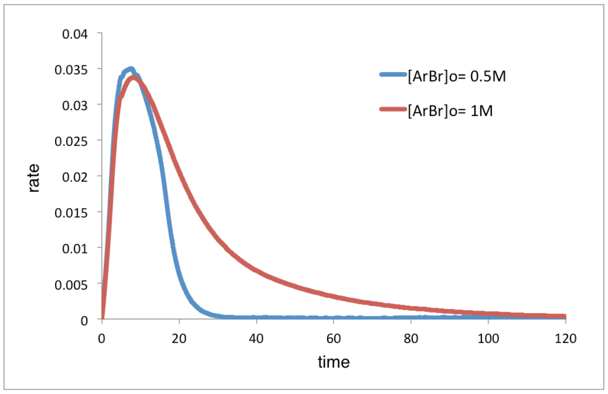


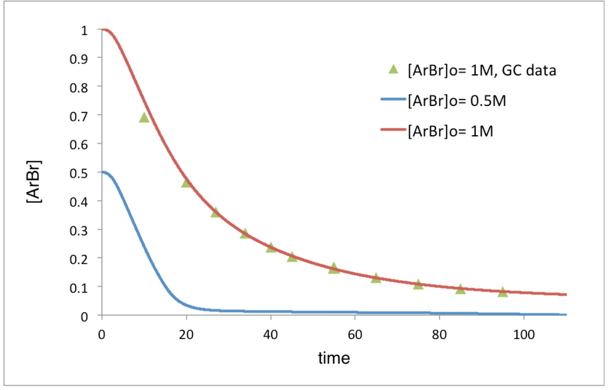
Table S4: Different excess experiment with 1-bromo-3,5-dimethoxybenzene, **7** using a precatalyst based on **L4**, **P4**

Reagent	Amount	mmol	Concentration	Excess
ArBr	217 mg	1.00	0.50 M	0.5 M
t-octylamine	258 mg	2.00	1.00 M	
ArBr	434 mg	2.00	1.00 M	0 M
t-octylamine	258 mg	2.00	1.00 M	
NaO^{t}Bu	230 mg	2.40	1.20 M	-
P4, Ph$_2$CPhosOMs	32.0 mg	0.04	0.02 M	-
1,4-dioxane	2 mL	-	-	-

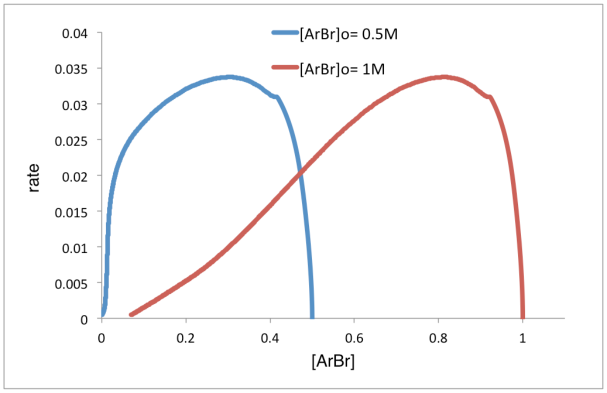
Plot of rate *vs.* time



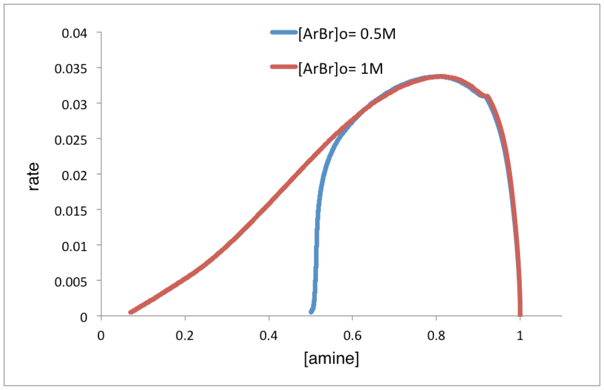
Plot of [ArBr] *vs.* time



Plot of rate *vs.* [ArBr]



Plot of rate *vs* [amine]



In order to confirm the calorimetry data, the $[ArBr]_0$= 1.00 M reaction was additionally monitored with GC-analysis. The data is plotted as aryl halide conversion *vs*. time and shows a good overlap with the conversion obtained in the experiment run in the calorimeter, proving that calorimetry is a reliable method to investigate the kinetics of the reaction.

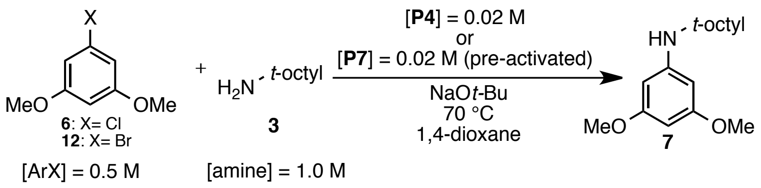
F.2) Calorimetric Studies using L7 as supporting ligand:

Ligand comparison

* **Note**: It was found that **P7** effects C-O cross-coupling between the aryl halide and NaO*t*-Bu during the equilibration time in the calorimeter. Therefore, the reaction setup was modified so the catalyst was added last through the injection. Several attempts of injecting a **P7** solution in 1,4-dioxane were unsuccessful due to solubility issues. For the initial comparison with the system based on **L4**, **P7** was activated with base previous to its injection in the calorimeter.

Procedure involving P7 preactivation: Two oven-dried 16 mL vials were equipped with a magnetic stir bar, charged with aryl halide (ArCl (**6**): 173 mg, 1.00 mmol/ ArBr (**12**): 217 mg, 1.00 mmol) and taken into the glovebox. Once in the glovebox, the vials were charged with amine **3** (258 mg, 2.00 mmol), NaO*t*-Bu (230 mg, 2.4 mmol) and 1,4-dioxane (1.60 mL). The vials were fitted with a screw-cap Teflon septum, and taken out of the glovebox. The reaction mixtures were placed in an Omnical CRC reaction calorimeter. The calorimeter was set to 70 °C and allowed to thermally equilibrate. Another vial was charged with **P7** (62.0 mg, 0.08 mmol), **L7** (32.0 mg, 0.08 mmol), 1-bromo-3,5-dimethoxybenzene (**12**) (17.3 mg, 0.08 mmol) and taken into the glovebox. Once in the glove box the vial was charged with NaO*t*-Bu (8.0 mg, 0.08 mmol) and 1,4-dioxane (0.8 mL). The mixture was stirred at rt for 10 min. After equilibration, the resulting solution was injected (0.4 mL to each vial) and the reaction was stirred until the heat flow on the calorimeter returned to the baseline level. A correction was then applied to the raw data due to the delay between heat release and detection. After each run, an equimolar amount of biphenyl (internal standard) was added to each vial and the total reaction conversion was determined by GC analysis.

The reaction with **P7** was run under the same conditions as the previous reaction with **P4** with both aryl halides (**6** and **12)**. It was immediately apparent that the hybrid-ligand **L7** dramatically accelerated the reaction compared to **L4**, as the reaction took less than 15 min to reach full conversion for both the chloride and bromide (Figure 1). The difference in reaction time for aryl chloride **6** was considerable (~155 min), and the reaction times for the aryl chloride and bromide (**6** and **12**) were very similar with precatalyst **P7**.



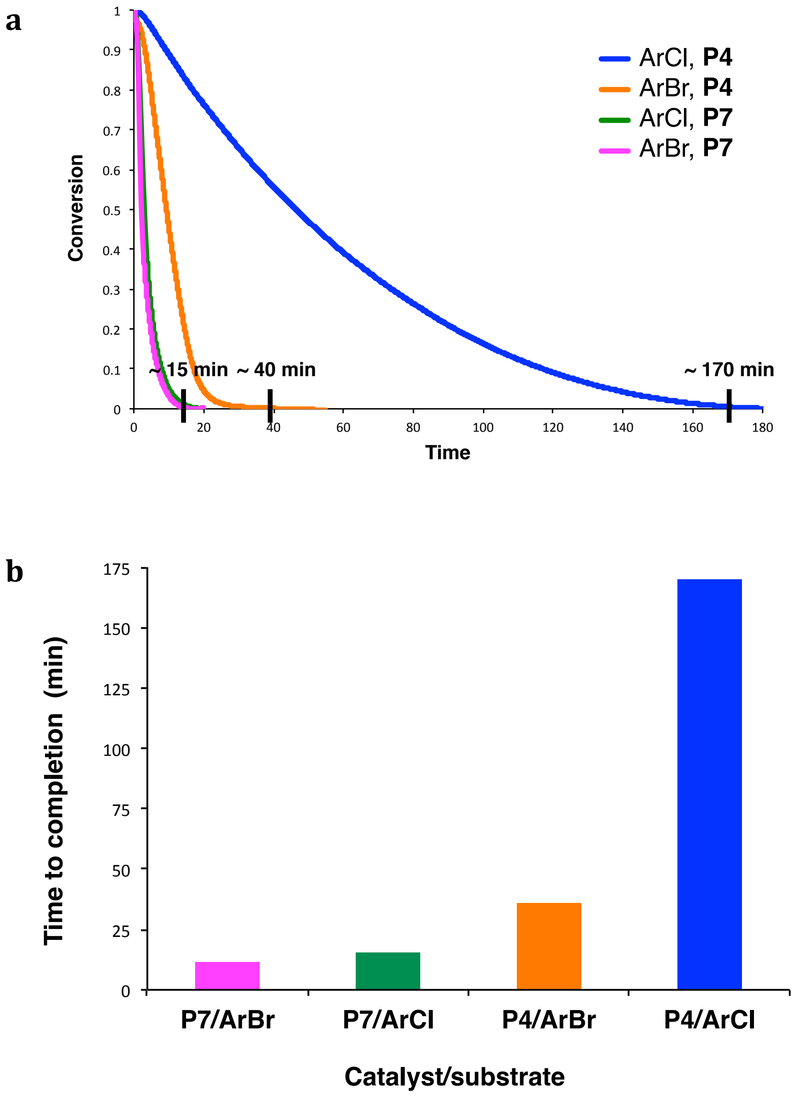
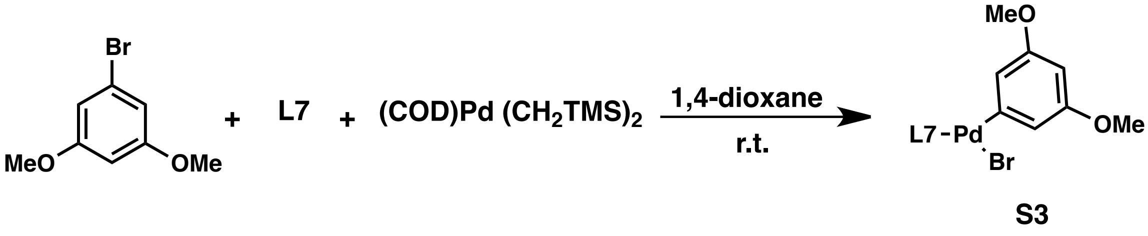


Figure 1. Ligand comparison under the same reaction conditions (2% precatalyst, 70 °C, [ArX]= 0.5 M, [Amine] = 1M, [NaO*t*Bu]= 1.2M). a) Conversion *vs*. time b) Reaction times for each aryl halide with each precatalyst.

General Procedure E: Calorimetric Studies using L7 as supporting ligand: ***Note:*** The reaction between 1-chloro-3,5-dimethoxybenzene (**6**) and 1-bromo-3,5-dimethoxybenzene (**12**) and *t*-octyl amine (**3**) using **L7** as supporting ligand under the same conditions as the reaction with **P4** (70 °C and [**P7**] = 0.02) was too fast to obtain accurate kinetic data (the reaction time should be longer than 15 min). The catalyst concentration was reduced to 0.005M for both aryl chloride **6** and aryl bromide **12** and the temperature was lowered to 60 °C for **12**

Note The reactions to investigate the kinetics of the reaction with **L7** were performed by forming an oxidative addition complex of aryl bromide **12** bearing **L7** *in situ* (**S3**) as palladium source.



An oven-dried 16 mL vial equipped with a magnetic stir bar, was charged with aryl halide and taken into a nitrogen-filled glovebox. The vial was charged with amine (**3**), NaO*t*-Bu and 1,4-dioxane. The vial was fitted with a screw-cap Teflon septum, and taken out of the glovebox. The reaction mixture was placed in an Omnical CRC reaction calorimeter. The calorimeter was set to 60 or 70 °C and allowed to thermally equilibrate. After equilibration, a solution of **S3** and extra ligand **L7** in 1,4-dioxane was injected and the reaction was stirred until the heat flow on the calorimeter returned to the baseline level. A correction was then applied to the raw data due to the delay between heat release and detection. After each run, an equimolar amount of biphenyl (internal standard) was added to each vial and the total reaction conversion was determined by GC analysis.

Different excess experiment with 1-chloro-3,5-dimethoxybenzene and L7 as supporting ligand: Following General Procedure E, two oven-dried 16 mL vials were charged with 1-chloro-3,5-dimethoxybenzene (**6**) (see Table S5), NaO*t*-Bu (230 mg, 2.4 mmol), amine (258 mg, 2.00 mmol) and 1,4-dioxane (1.6 mL). After equilibration, the solution of **S3** and extra **L7** in 1,4-dioxane (400 µL, 0.005 M) was injected. The heat of reaction was found to be 175.25 KJ/mol on average.

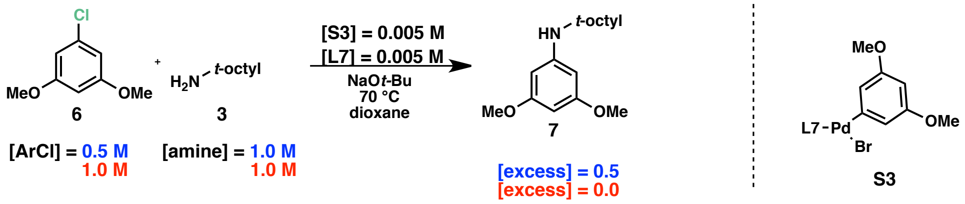
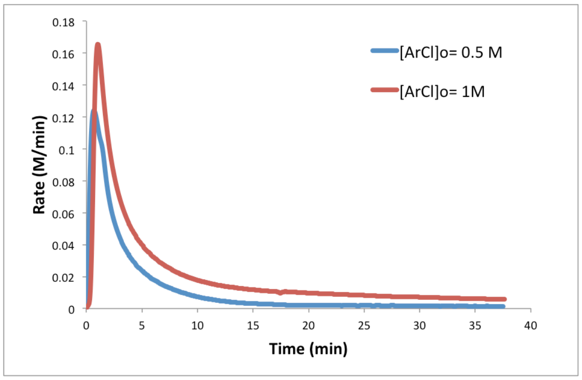


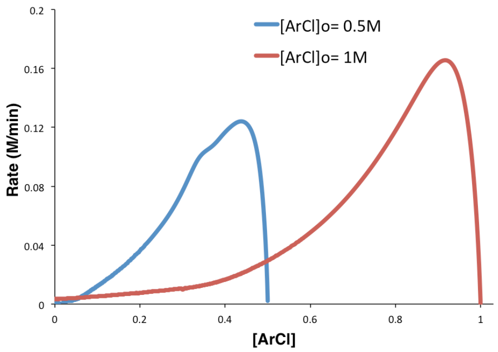
Table S5: Different excess experiment with 1-chloro-3,5-dimethoxybenzene, **6** using a catalyst based on **L7**

Reagent	Amount	mmol	Concentration	Excess
ArCl	173 mg	1.00	0.50 M	0.5 M
t-octylamine	258 mg	2.00	1.00 M	
ArCl	346 mg	2.00	1.00 M	0 M
t-octylamine	258 mg	2.00	1.00 M	
NaO^{t}Bu	230 mg	2.40	1.20 M	-
S3 solution (0.005M)	400 µL	0.01	0.005 M	-
1,4-dioxane	1.6 mL	-	-	-

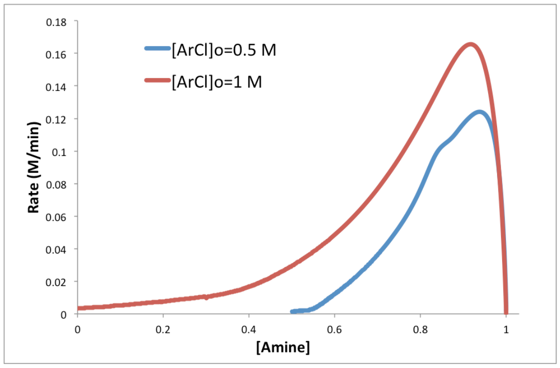
Plot of rate *vs.* time



Plot of rate *vs.* [ArCl]



Plot of rate *vs* [amine]



Different excess experiment with 1-bromo-3,5-dimethoxybenzene using L7 as supporting ligand: Following General Procedure E, two oven-dried 16 mL vials were charged with 1-bromo-3,5-dimethoxybenzene (**12**) (see Table S6), NaO*t*-Bu (230 mg, 2.40 mmol), amine (258 mg, 2.00 mmol) and 1,4-dioxane (1.6 mL). After equilibration, the solution of **S3** and extra **L7** in 1,4-dioxane (400 µL, 0.005 M) was injected. The heat of reaction was found to be 191.50 KJ/mol on average.

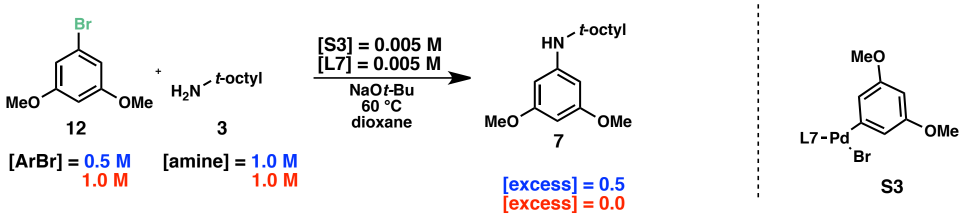
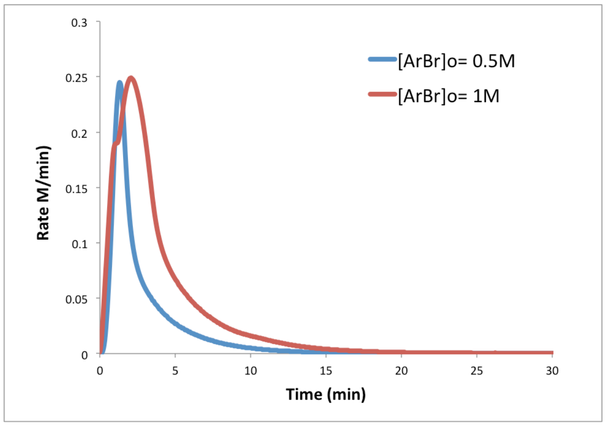


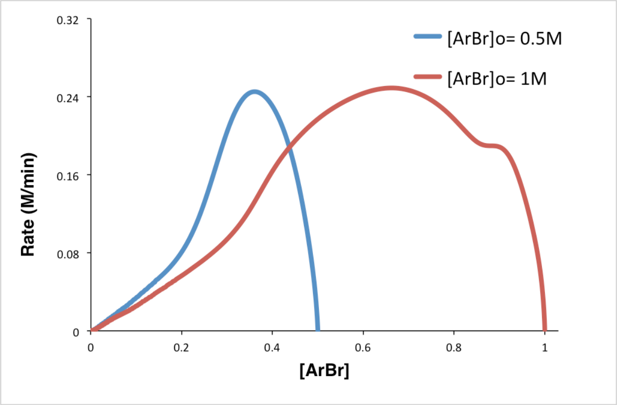
Table S6: Different excess experiment with 1-bromo-3,5-dimethoxybenzene, **7** using a catalyst based on **L7**

Reagent	Amount	mmol	Concentration	Excess
ArBr	217 mg	1.00	0.50 M	0.5 M
t-octylamine	258 mg	2.00	1.00 M	
ArBr	434 mg	2.00	1.00 M	0 M
t-octylamine	258 mg	2.00	1.00 M	
NaO^{t}Bu	230 mg	2.40	1.20 M	-
S3 solution (0.005M)	400 µL	0.01	0.005 M	-
1,4-dioxane	1.6 mL	-	-	-

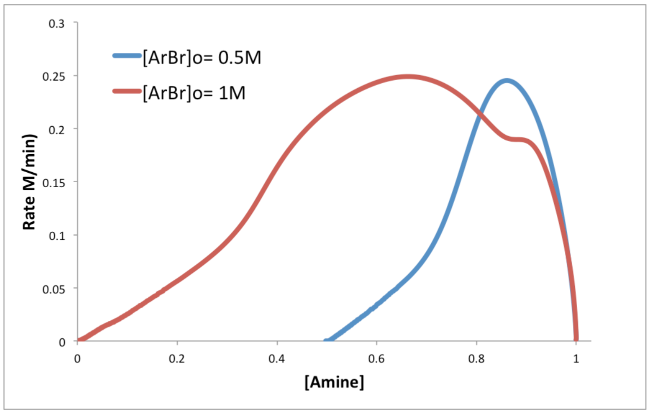
Plot of rate *vs.* time



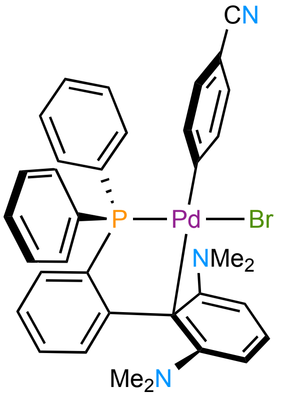
Plot of rate *vs.* [ArBr]



Plot of rate *vs* [amine]

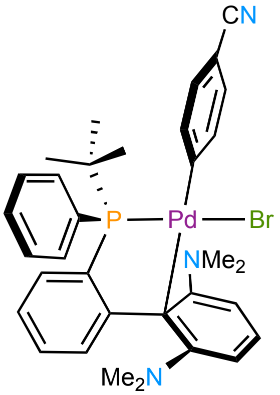


G) Oxidative Addition Complex Synthesis: **General Procedure F:** Ligand (1.0 equiv) and aryl halide (3 equiv) were added to an oven-dried vial in a nitrogen-filled glovebox. Cyclohexane was added dropwise with stirring until all of the ligand dissolved. (1,5- cyclooctadiene)Pd(CH_2SiMe_3)$_2$ (1.0 equiv) was added in one portion, and the reaction mixture was allowed to stir overnight at rt, during which time a precipitate formed. Pentane was added, and the reaction mixture was filtered through a fritted funnel. The resulting solid was washed with pentane, providing the oxidative addition complex without any further purification.



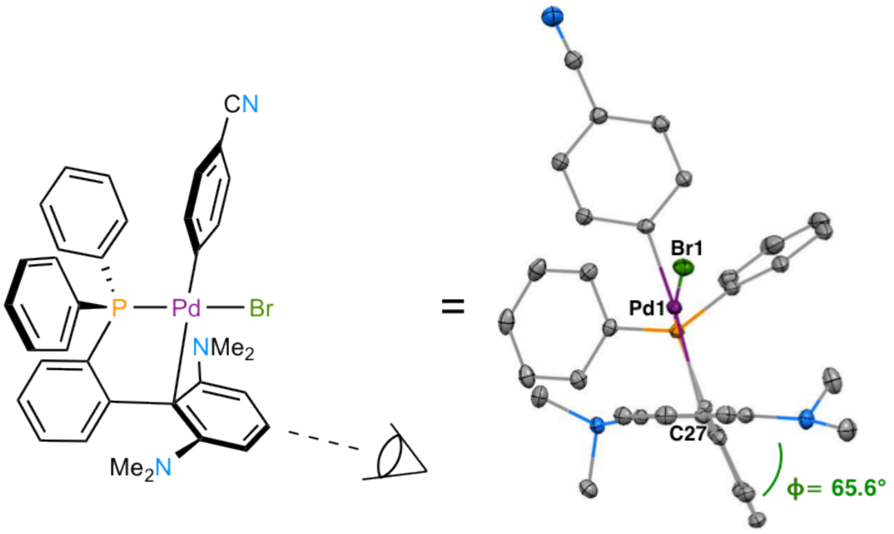
[(**PhCphos)**ArPdBr], **13**: Following General Procedure F, 4-bromobenzonitrile (129 mg, 0.71 mmol, 3.00 equiv) and **L4 (**100 mg, 0.23 mmol, 1.00 equiv) were added to an oven-dried vial together with the minimum amount of cyclohexane required for dissolution. (1,5- cyclooctadiene)Pd(CH_2SiMe_3)$_2$ (92 mg, 0.23 mmol, 1.00 equiv) was added in one portion and the reaction mixture turned bright yellow. The reaction mixture was stirred at rt overnight and was filtered through a sintered glass frit washing with pentane. Complex **13** was obtained as a bright yellow solid.

Yield: 151 mg, 85%. Crystals suitable for X-ray analysis were obtained by dissolving **13** in CH_2Cl_2 inside a small vial, which was then placed in a larger vial containing pentane, (vapor diffusion). ^{1}**H NMR** (500 MHz, Methylene Chloride-d2) δ 7.54 (dt, *J* = 14.4, 8.3 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 3H), 7.38 -7.32 (m, 5H), 7.31 - 7.27 (m, 1H), 7.27 - 7.15 (m, 4H), 7.00 - 6.83 (m, 5H), 2.46 (s, 12H). ^{13}**C NMR** (126 MHz, Methylene Chloride-d2) δ 249.1, 156.5, 151.7, 151.6, 147.1, 146.9, 137.9, 137.9, 136.3, 135.9, 135.5, 134.9, 134.2, 133.6, 133.6, 133.6, 133.2, 132.5, 132.5, 131.5, 131.1, 131.0, 129.2, 129.2, 129.1, 129.0, 127.5, 127.4, 120.2, 115.1, 106.8, 44.9 (observed complexity is due to C-P coupling). ^{31}**P NMR** (121 MHz, Methylene Chloride-d2) δ 23.32 ppm.



[(**(*t*Bu)PhCphos)**ArPdBr], **14**: Following General Procedure F, 4-bromobenzonitrile (135 mg, 0.74 mmol, 3.00 equiv) and **L7** (100mg, 0.25 mmol, 1.00 equiv) were added to an oven-dried vial together with the minimum amount of cyclohexane required for dissolution. (1,5- cyclooctadiene)Pd(CH_2SiMe_3)$_2$ (96.0 mg, 0.25 mmol, 1.00 equiv) was added in one portion and the reaction mixture turned bright yellow. The reaction mixture was stirred at rt overnight and was filtered through a sintered glass frit washing with pentane. Complex **14** was obtained as a bright yellow solid. Yield: 149 mg, 87%. Crystals suitable for X-ray analysis were obtained by dissolving **14** in CH_2Cl_2 inside a small vial, which was then placed in a larger vial containing pentane, (vapor diffusion). ^{1}**H NMR** (500 MHz, Methylene Chloride-d2) δ 7.97 (t, *J* = 7.5 Hz, 1H), 7.62 - 7.22 (m, 9H), 7.13 (d, *J* = 7.5 Hz, 4H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 2.94 (s, 6H), 1.83 (s, 6H), 1.11 (d, *J* = 14.8 Hz, 9H). ^{13}**C NMR** (126 MHz, Cd_2Cl_2) δ 158.5, 157.6, 150.6, 147.7, 136.2, 135.8, 134.6, 134.5, 134.4, 134.2, 134.0, 133.8, 133.7, 133.2, 132.1, 132.1, 131.1, 130.8, 130.3, 130.3, 129.5, 128.4, 128.3, 128.3, 126.7, 126.6, 120.3, 116.8, 115.1, 106.9, 45.5, 44.8, 38.6, 38.4, 30.1, 30.1 (observed complexity is due to C-P coupling). ^{31}**P NMR** (121 MHz, Methylene Chloride-d2) δ 36.26 ppm

It was found that the X-ray structures of complexes **13** and **14** reveal a torsion angle (ϕ)[8] of ~66°. This value deviates from the nearly 90° observed in other reported complexes of dialkylbiaryl phosphine ligands.[9] The origin of this conformation is unknown, but it appears to be a feature unique to CPhos-type ligands, and to be independent of the substitution pattern on the phosphorous atom.



Ligand	**CPhos (L5)**	**PhPhos (L4)**	**(*t*-Bu)PhCPhos (L8)**
Torsion angle, ϕ (°)	66.3	65.6	66.9

(1) Hicks, J. D.; Hyde, A. M.; Martinez Cuezva, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, 131*,* 16720

(2) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, 127, 4685

(3) DeBergh, J. R.; Niljianskul, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2013**, 135, 10638

(4) Han, C.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, 131*,* 7532

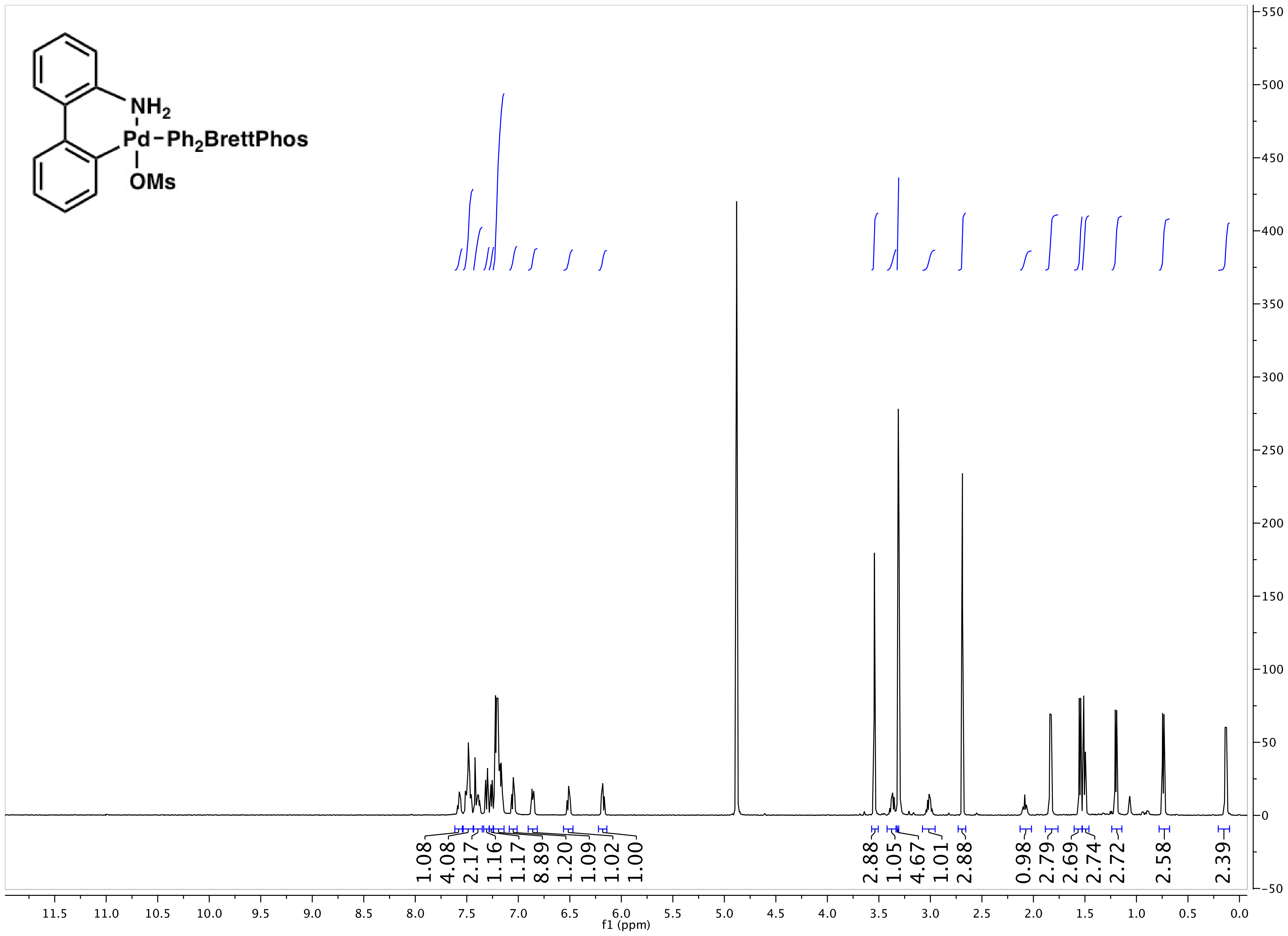
(5) Bruno, N. C.; Tudge, M. T.; Buchwald, S. L. *Chem. Sci*. **2013**, 4, 916

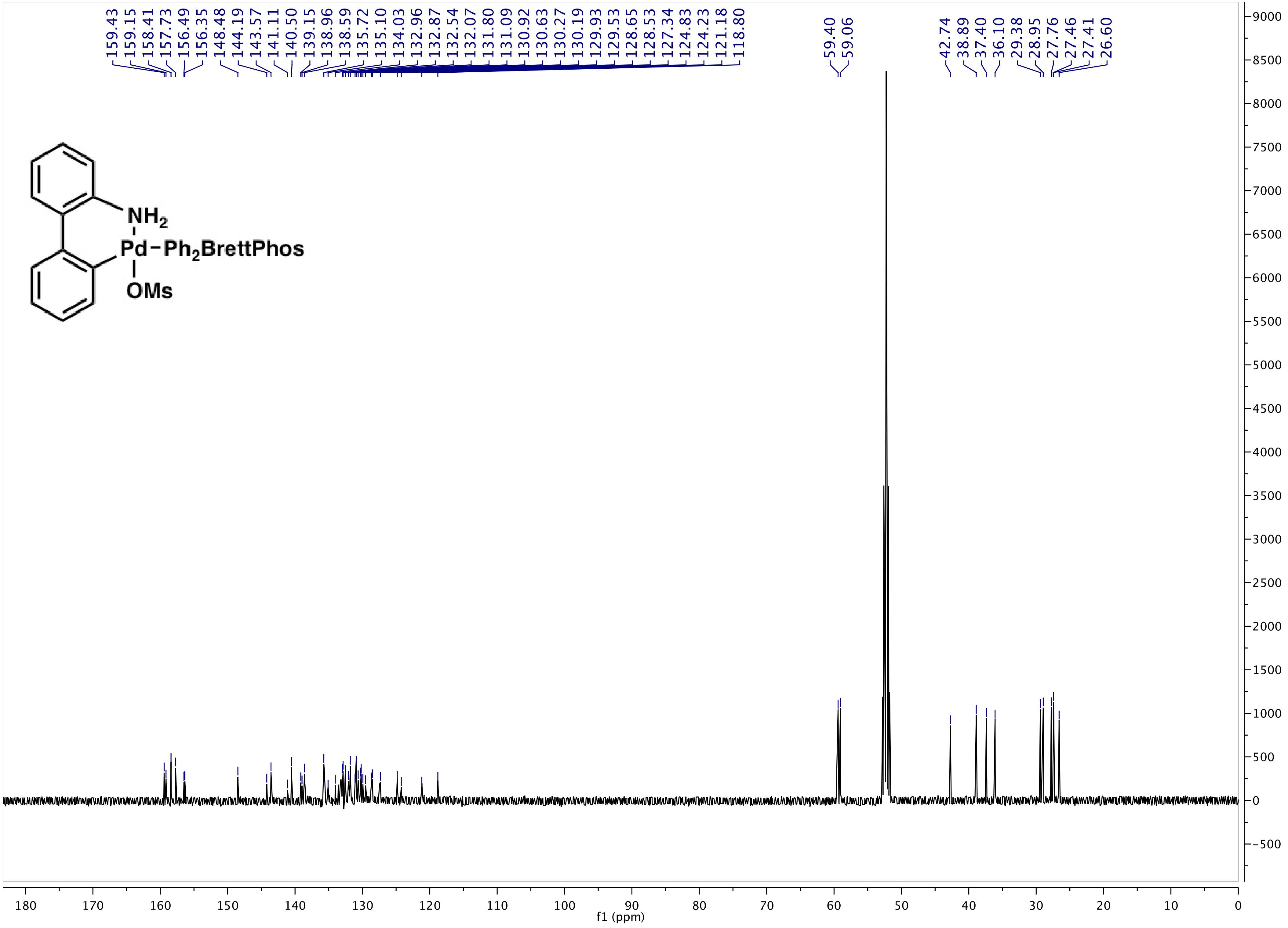
(6) Salvi, L.; Davis, N. R.; Ali, S. Z.; Buchwald, S. L. *Org. Lett*. **2012,** 14, 170

(7) Lee, H. G.; Milner, P. J.; Buchwald, S. L. *Org. Lett*. **2013**, 15, 21

(8) Angle between the planes containing the two arene rings

(9) Angles found: (a) SPhos: ϕ = 89.9 Duefert, A., Billingsley, K., Buchwald, S. L *J. Am. Chem. Soc*. **2013**, 135, 12877. (b) **L1**, BrettPhos: ϕ = 89.3, Fors, B. P.; Watson, D. A.; Biscoe M. R.; Buchwald S. L. *J. Am. Chem. Soc*. **2008**, 130, 13552. (c) *t*-BuBrettPhos: ϕ =85.7, Su, M.; Buchwald, S. L. *Angew. Chem. Int. Ed*. **2012**, 51, 4710. (d) *t*-BuXPhos: ϕ = 84.6 Milner, P. J.; Maimone, T. J.; Su, M.; Chen, J.; Muller, P.; Buchwald, S. L. *J. Am. Chem. Soc*. **2012**, 134, 19922


NH2
Pd−Ph2BrettPhos
OMs
1.08
4.08
2.17
1.16
1.17
8.89
1.20
1.09
1.02
1.00
2.88
1.05
4.67
1.01
2.88
0.98
2.79
2.69
2.74
2.72
2.58
2.39
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
−50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159.15
158.41
157.73
156.49
156.35
148.48
144.19
143.57
141.11
140.50
139.15
138.96
138.59
135.72
135.10
134.03
132.96
132.87
132.54
132.07
131.80
131.09
130.92
130.63
130.27
130.19
129.93
129.53
128.65
128.53
127.34
124.83
124.23
121.18
118.80
59.40
59.06
42.74
38.89
37.40
36.10
29.38
28.95
27.76
27.46
27.41
26.60
NH2
Pd–Ph2BrettPhos
OMs
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
–500
180
170
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150
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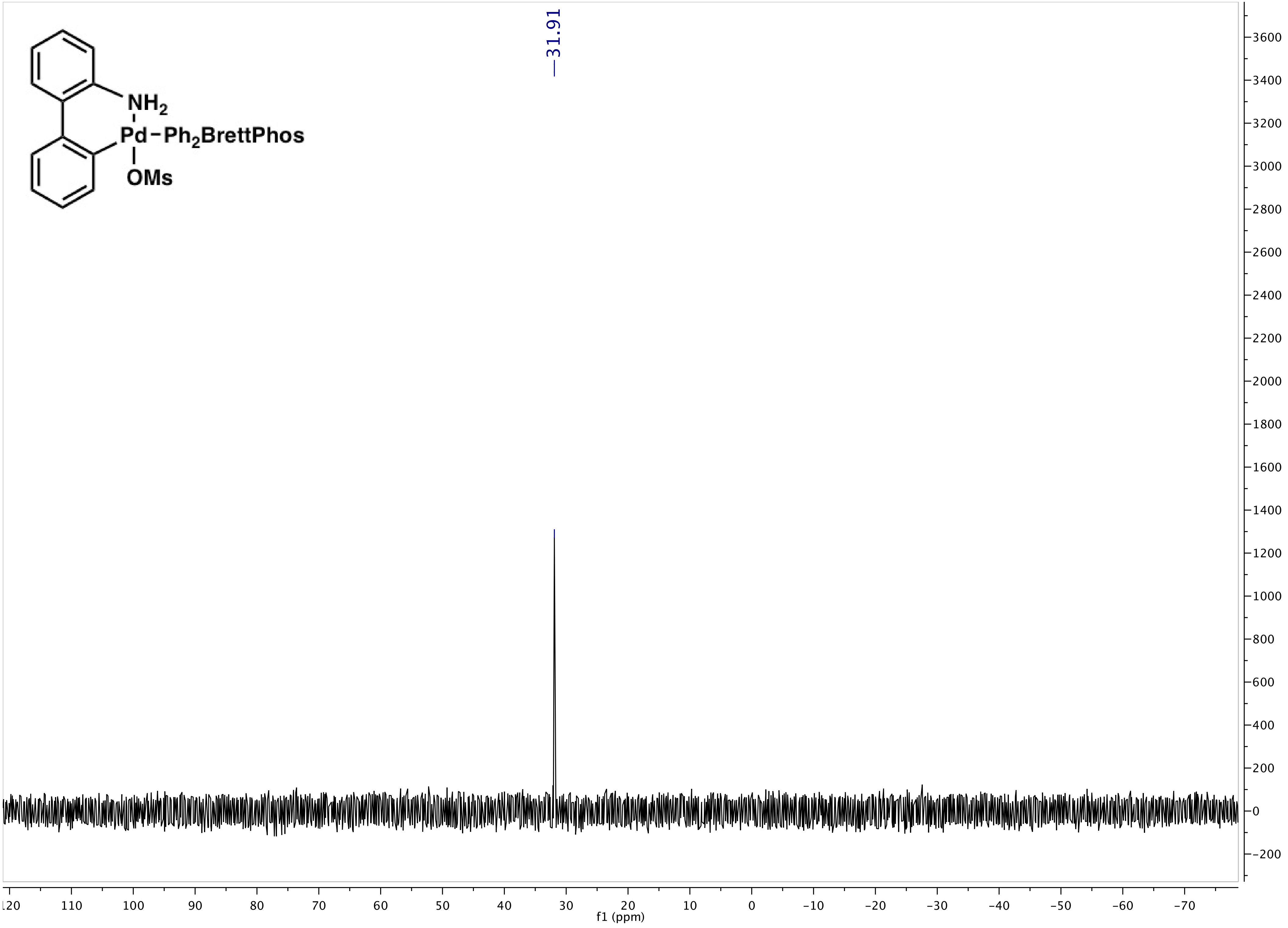
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Pd–Ph2BrettPhos
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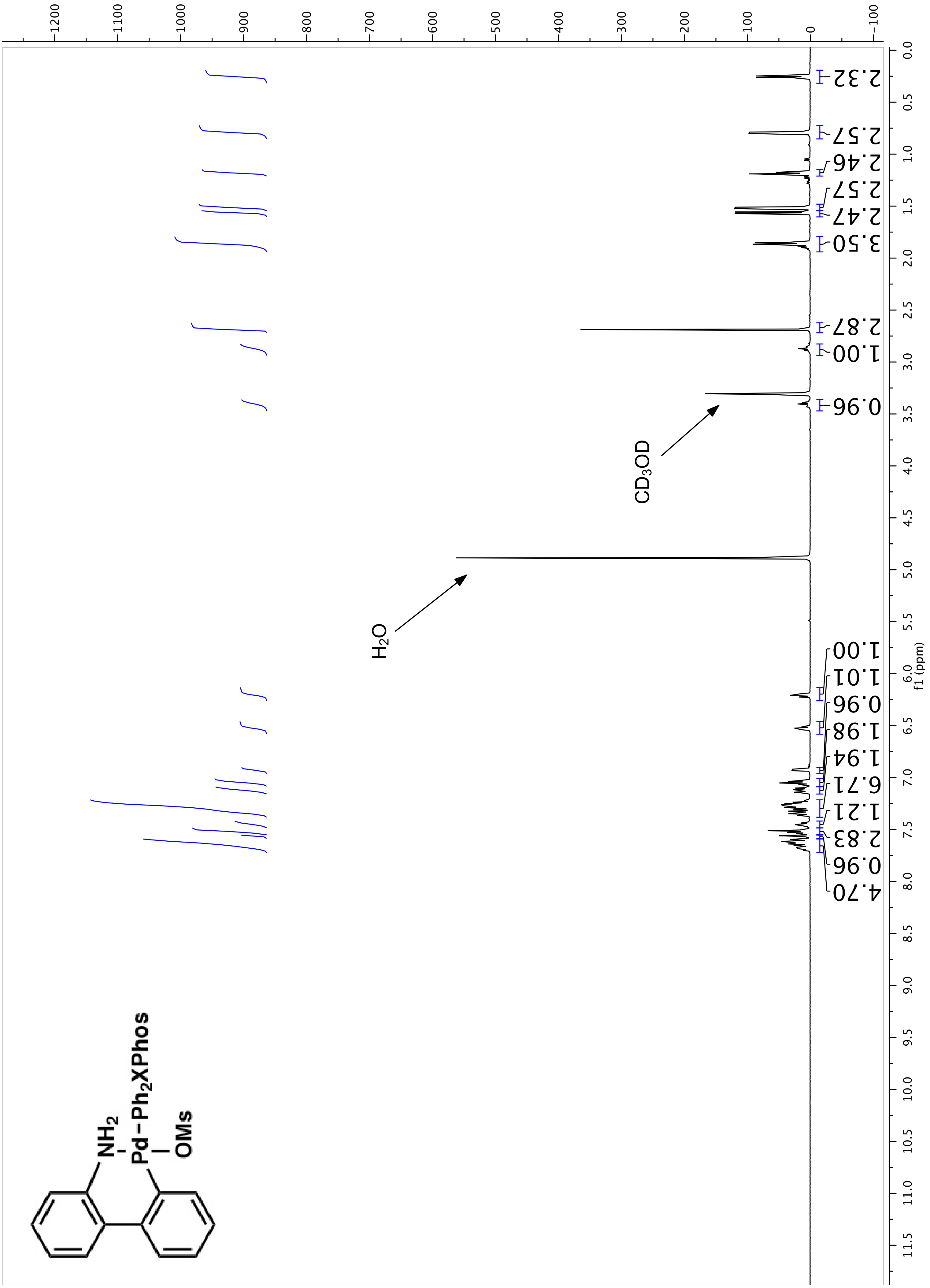
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)



NH$_2$
Pd-Ph$_2$XPhos
OMs
H$_2$O
CD$_3$OD
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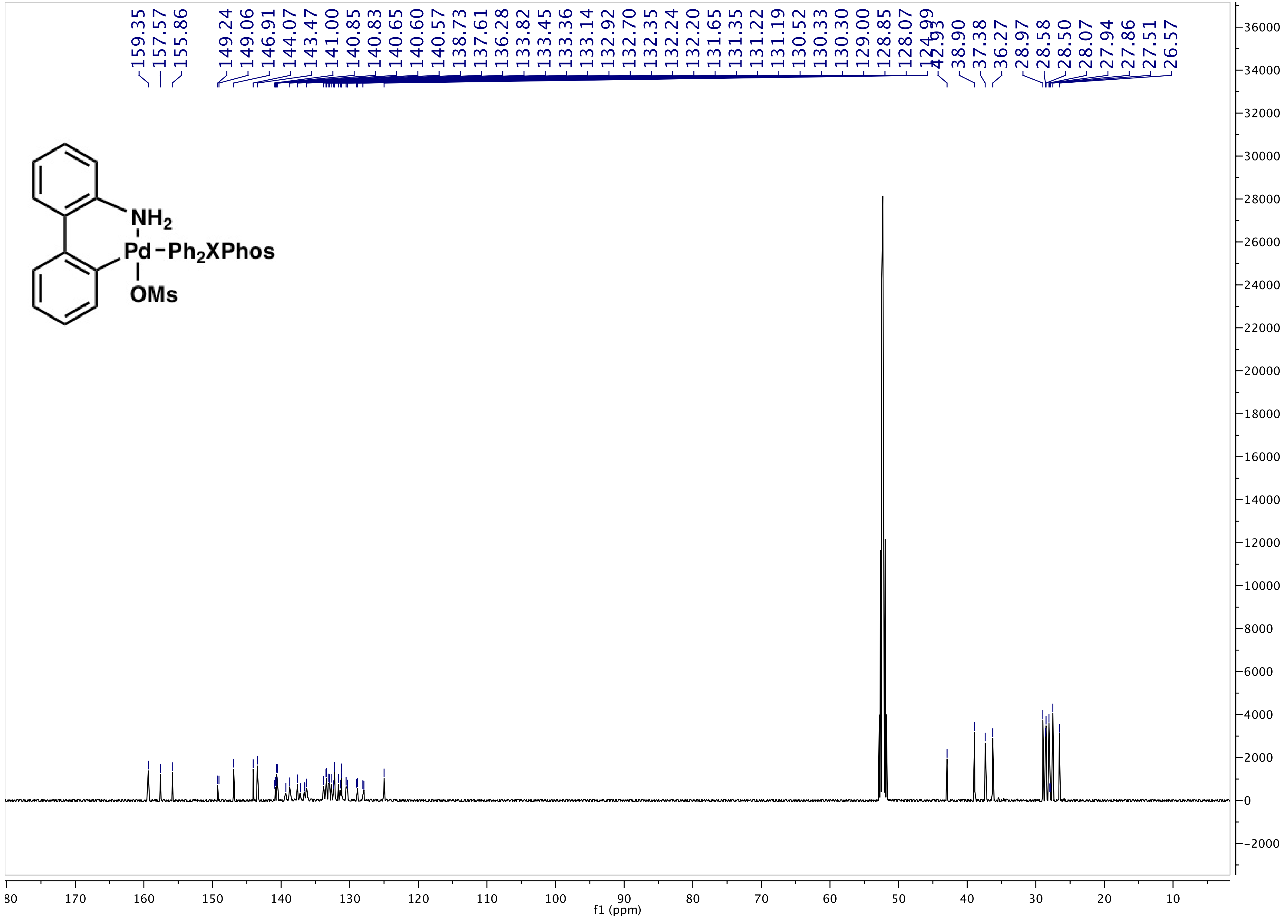
2.57
2.46
2.57
2.47
3.50
2.87
1.00
0.96
1.00
1.01
0.96
1.98
1.94
6.71
1.21
2.83
0.96
4.70
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

159.35
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155.86
149.24
149.06
146.91
144.07
143.47
141.00
140.85
140.83
140.65
140.60
140.57
138.73
137.61
136.28
133.82
133.45
133.36
133.14
132.92
132.70
132.35
132.24
132.20
131.65
131.35
131.22
131.19
130.52
130.33
130.30
129.00
128.85
128.07
124.99
42.93
38.90
37.38
36.27
28.97
28.58
28.50
28.07
27.94
27.86
27.51
26.57
NH2
Pd-Ph2XPhos
OMs
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
180
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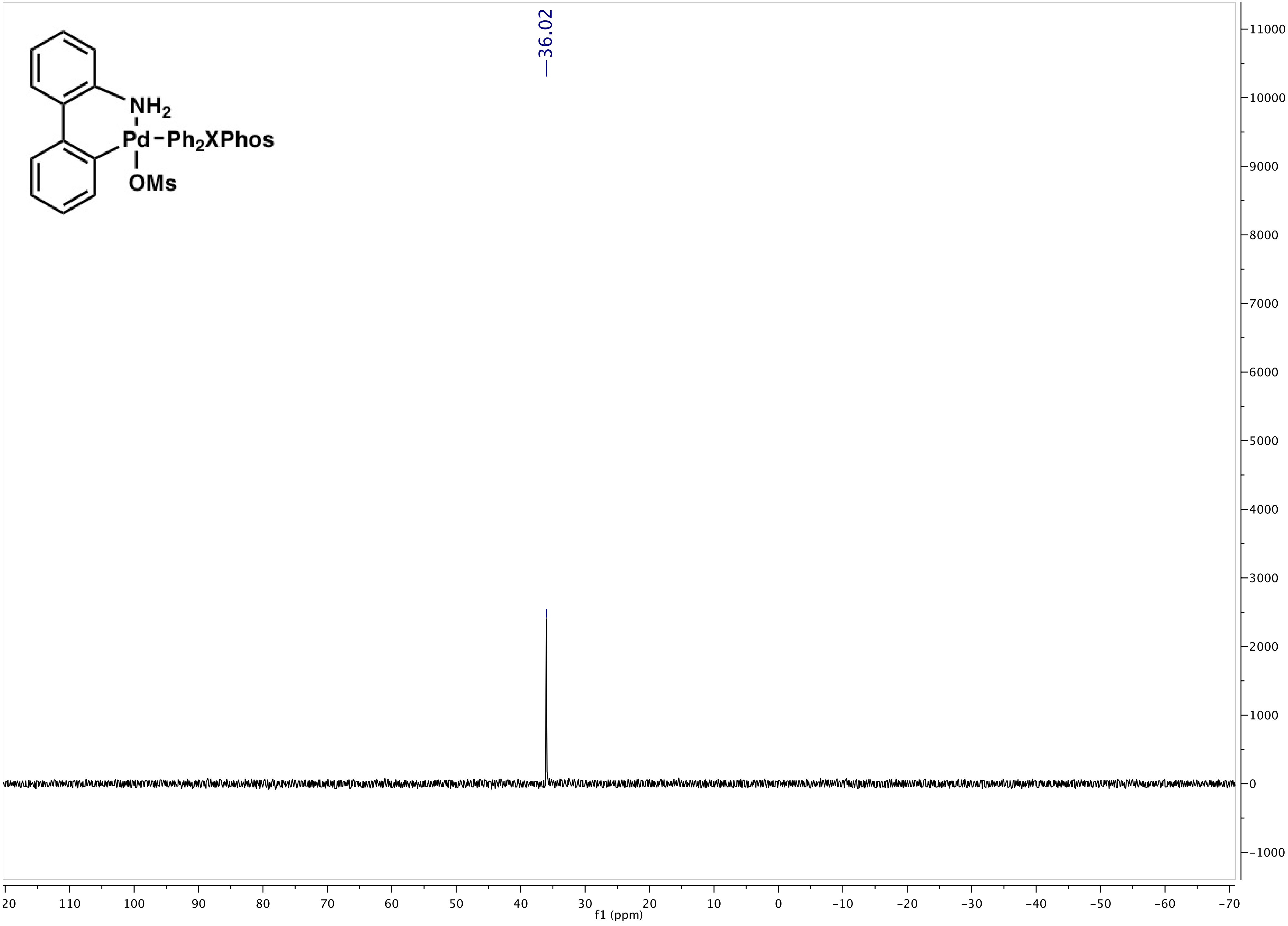
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


36.02
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Pd-Ph2XPhos
OMs
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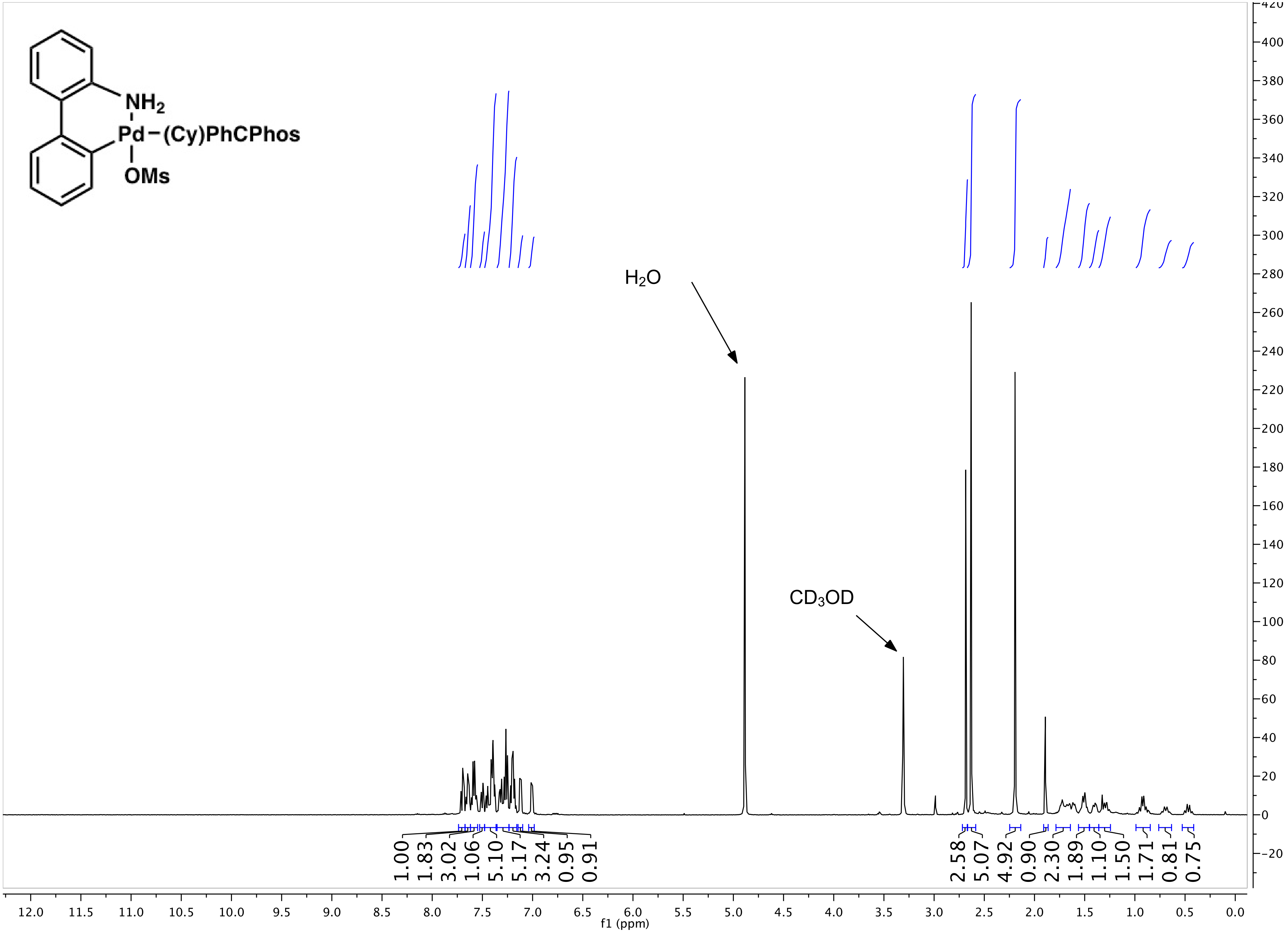
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)


NH2
Pd−(Cy)PhCPhos
OMs
H2O
CD3OD
1.00
1.83
3.02
1.06
5.10
5.17
3.24
0.95
0.91
2.58
5.07
4.92
0.90
2.30
1.89
1.10
1.50
1.71
0.81
0.75
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
420
400
380
360
340
320
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280
260
240
220
200
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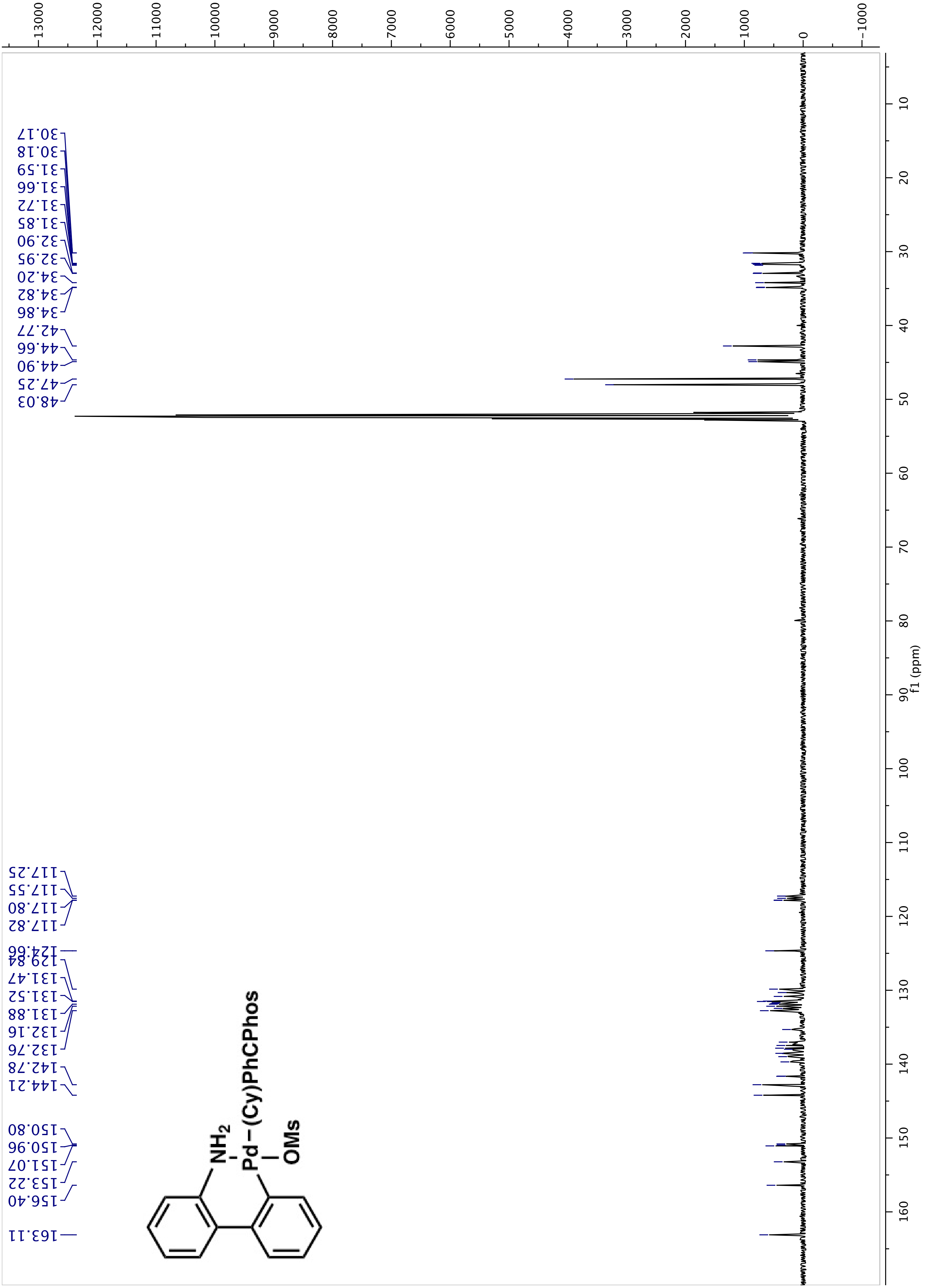
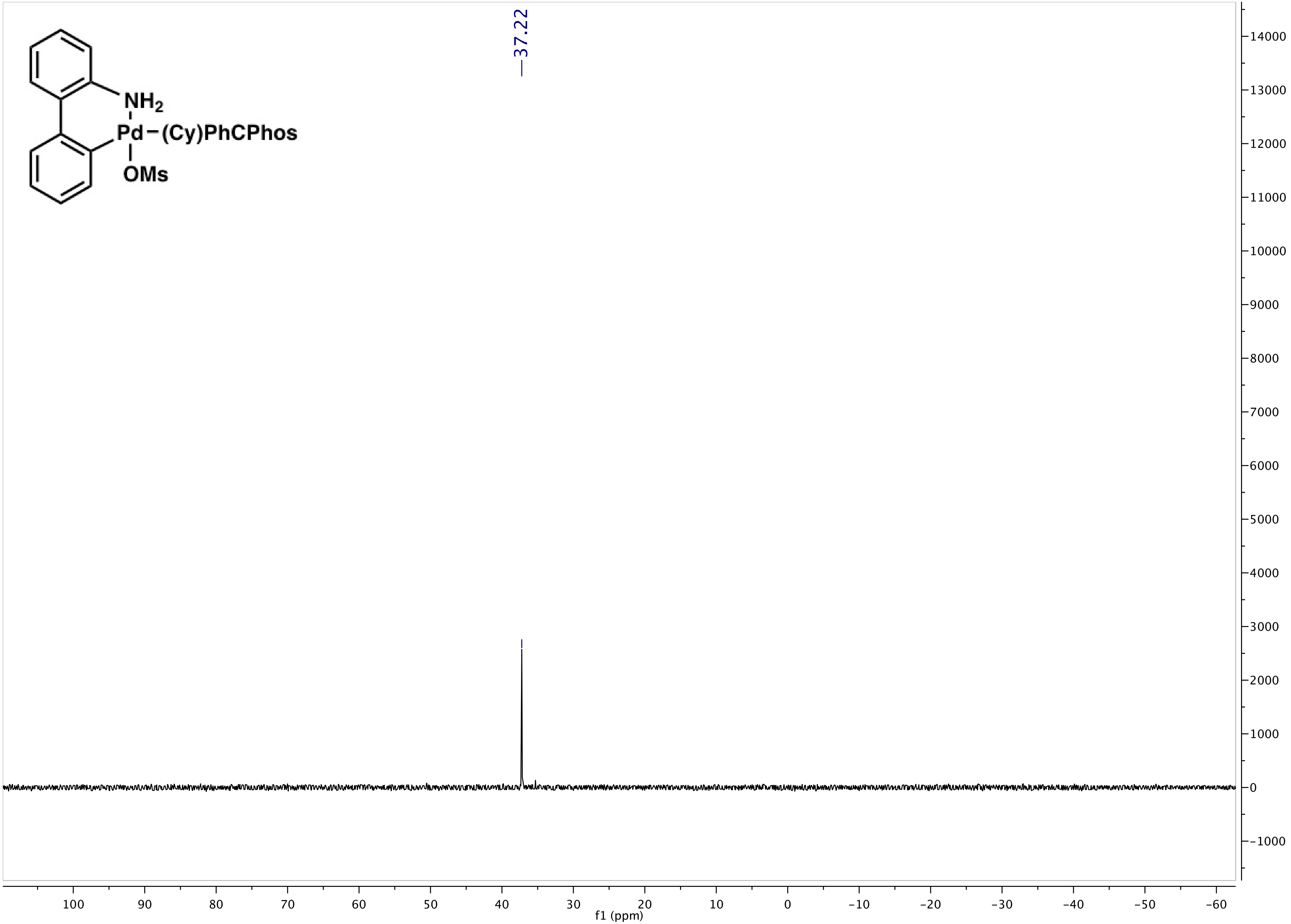
120
100
80
60
40
20
0
−20

163.11
156.40
153.22
151.07
150.96
150.80
144.21
142.78
132.76
132.16
131.88
131.52
131.47
129.84
124.66
117.82
117.80
117.55
117.25
48.03
47.25
44.90
44.66
42.77
34.86
34.82
34.20
32.95
32.90
31.85
31.72
31.66
31.59
30.18
30.17
NH2
Pd–(Cy)PhCPhos
OMs
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
–1000
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)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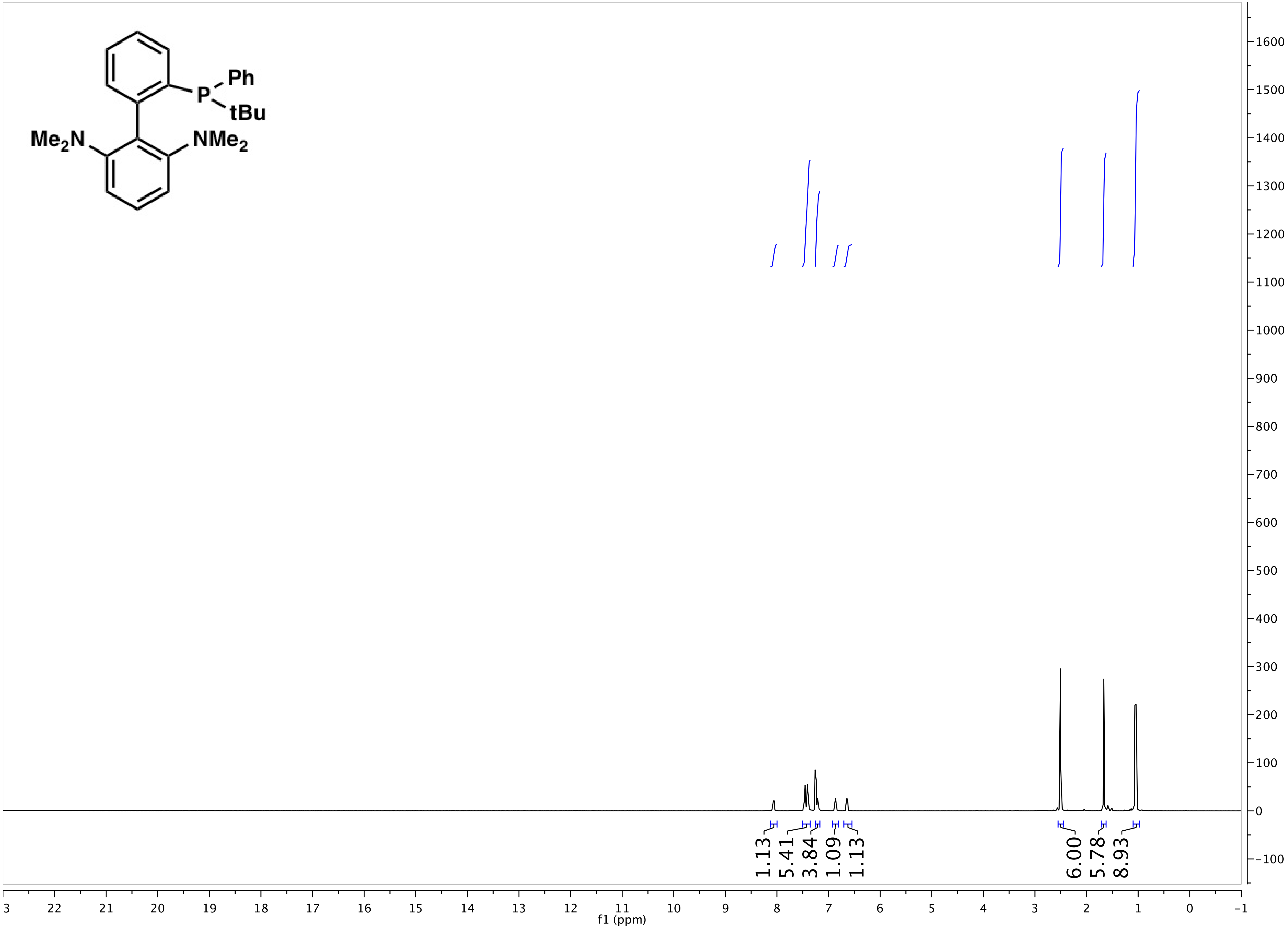
Pd−(Cy)PhCPhos
OMs
37.22
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
f1 (ppm)


Me$_2$N
NMe$_2$
P
Ph
tBu
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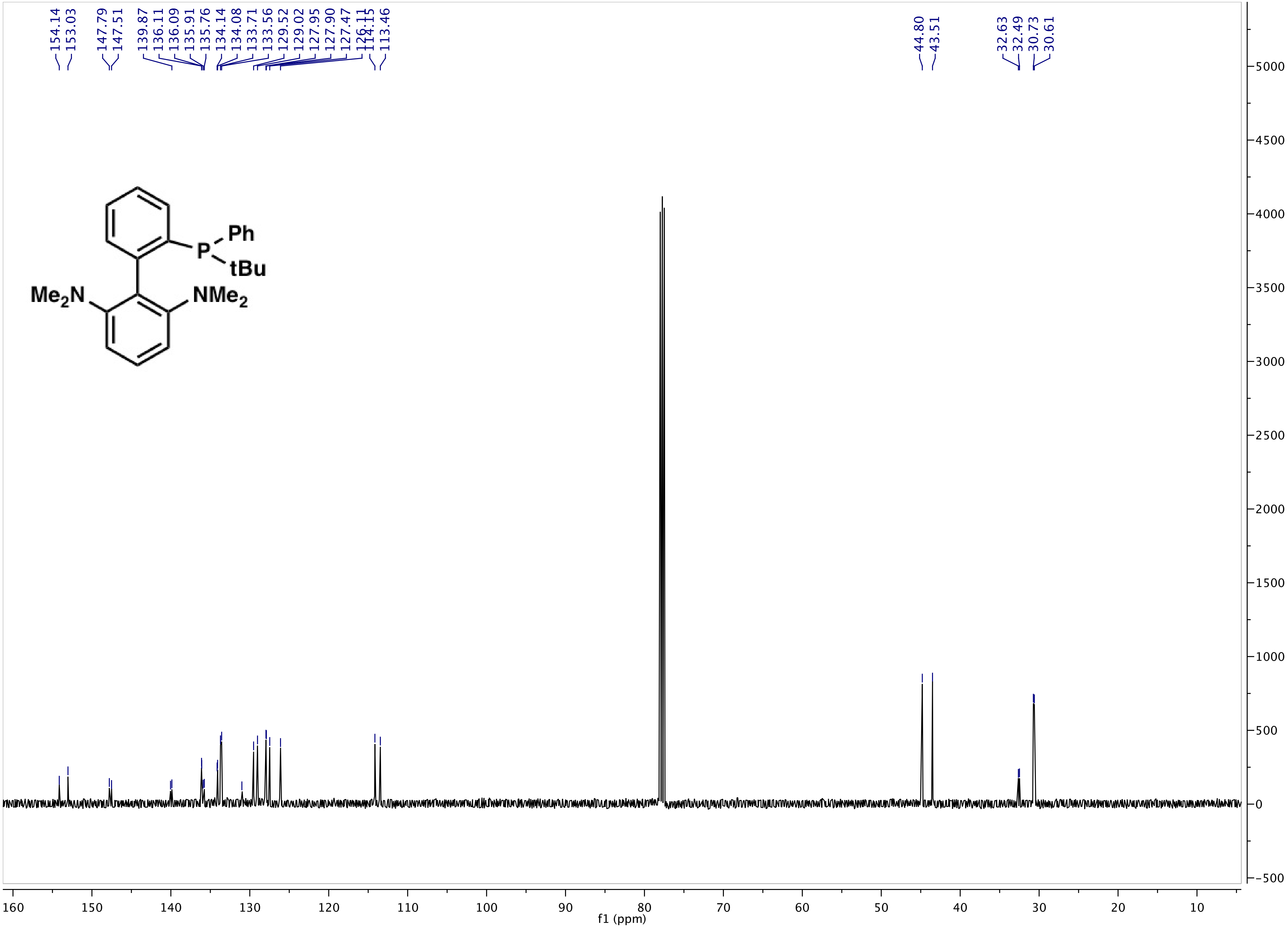
5.41
3.84
1.09
1.13
6.00
5.78
8.93
3
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


154.14
153.03
147.79
147.51
139.87
136.11
136.09
135.91
135.76
134.14
134.08
133.71
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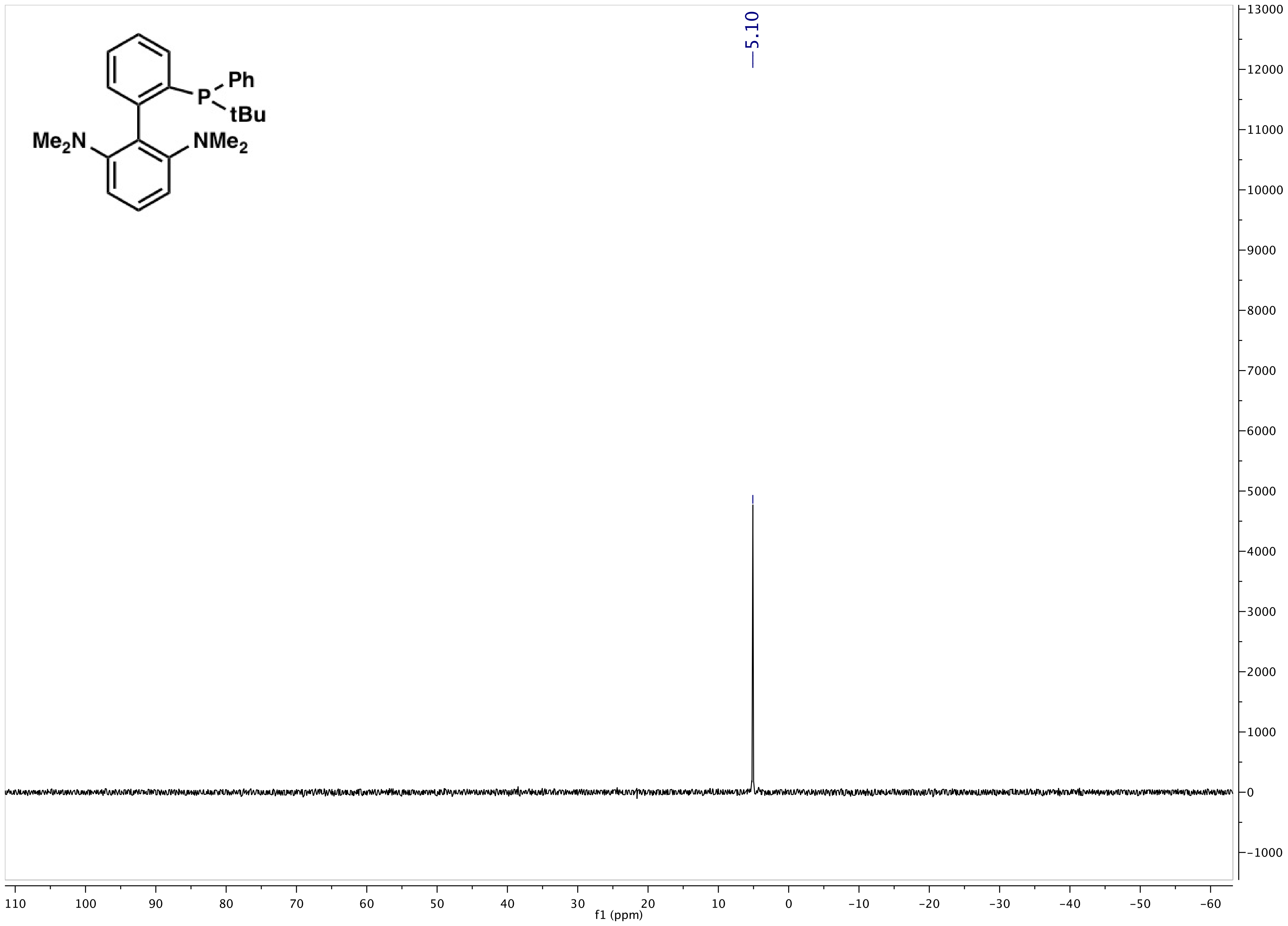
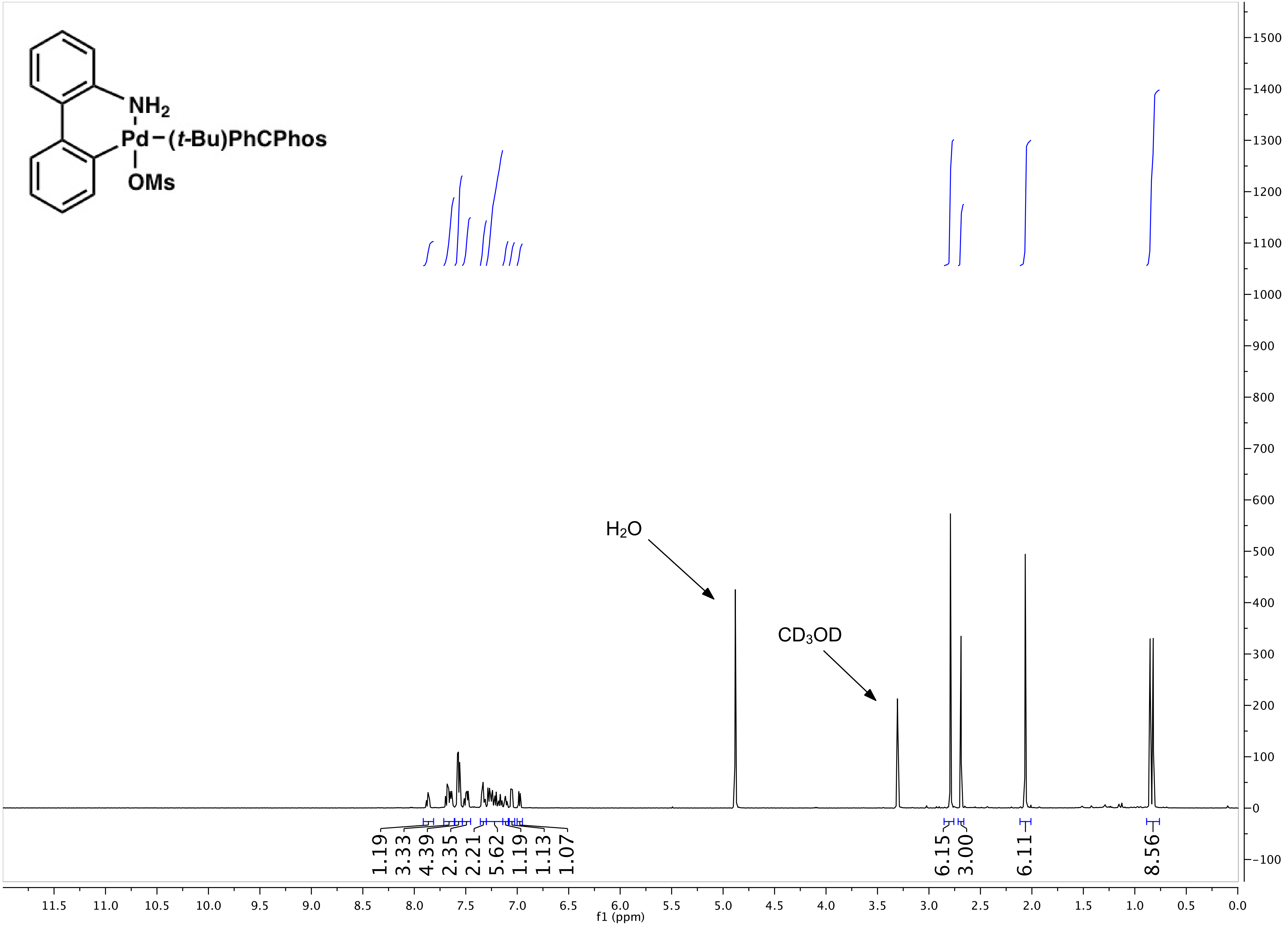
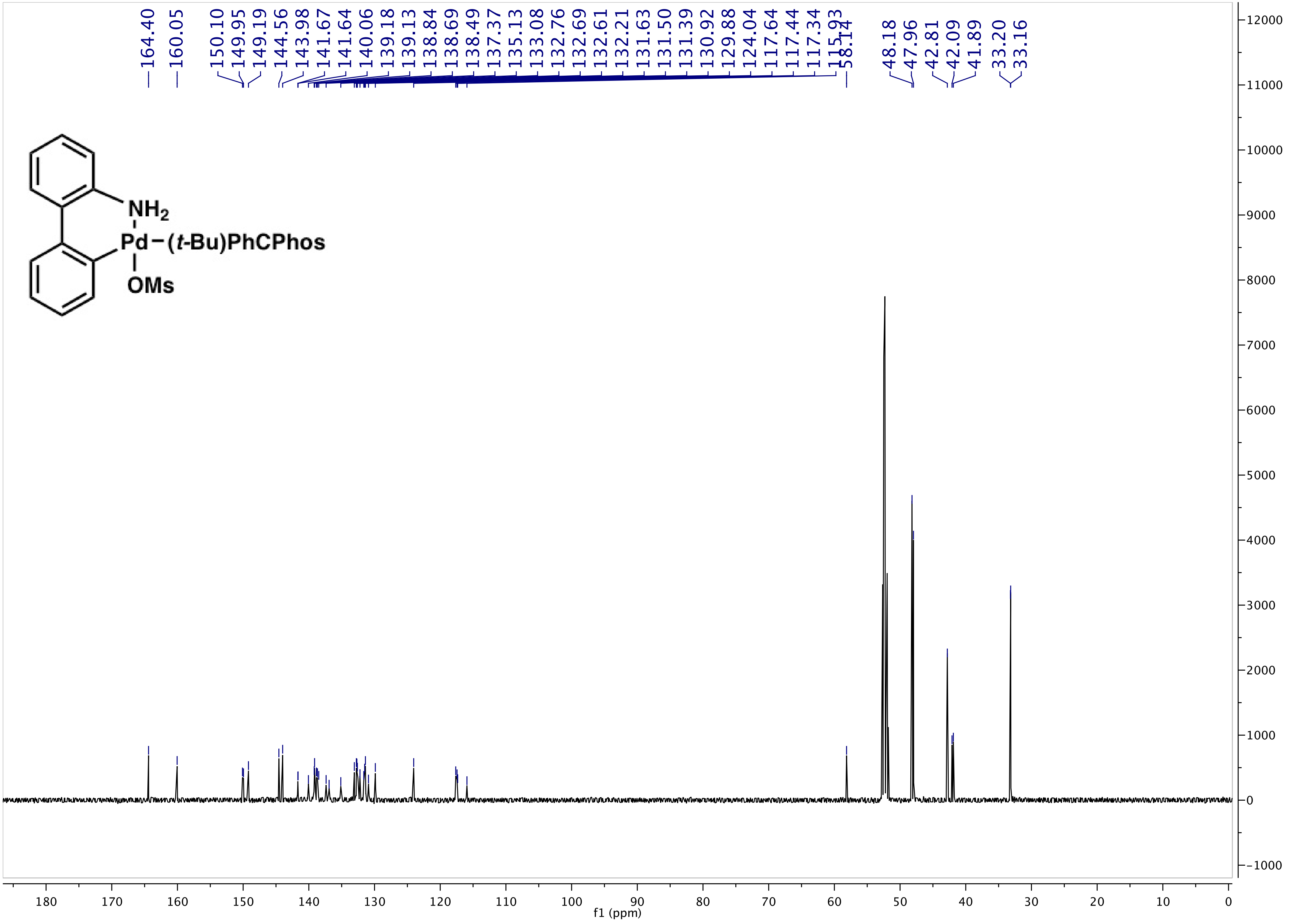
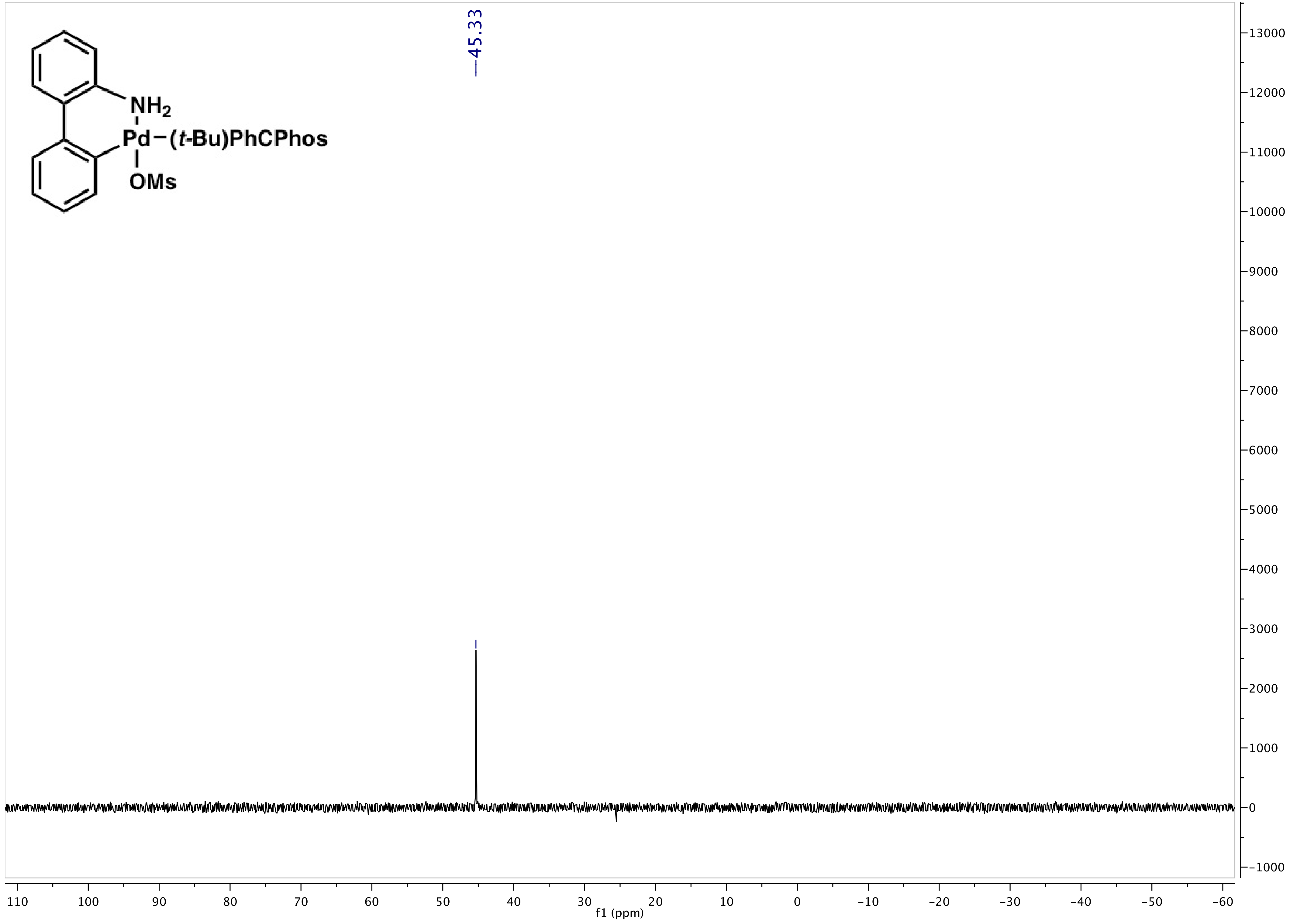
129.52
129.02
127.95
127.90
127.47
126.11
114.15
113.46
44.80
43.51
32.63
32.49
30.73
30.61
Ph
P
tBu
Me2N
NMe2
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

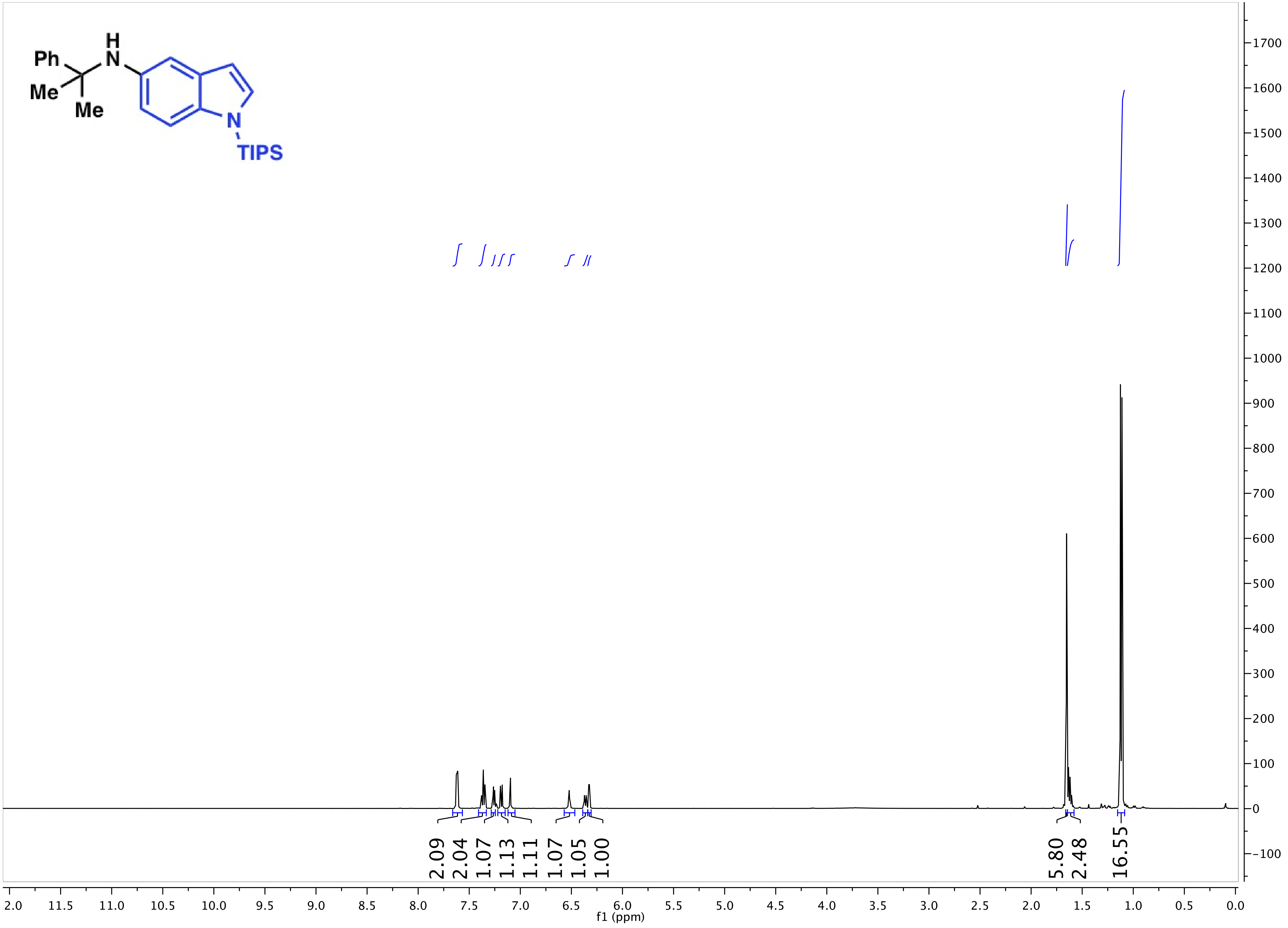

Me$_2$N
NMe$_2$
P
Ph
tBu
5.10
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
f1 (ppm)

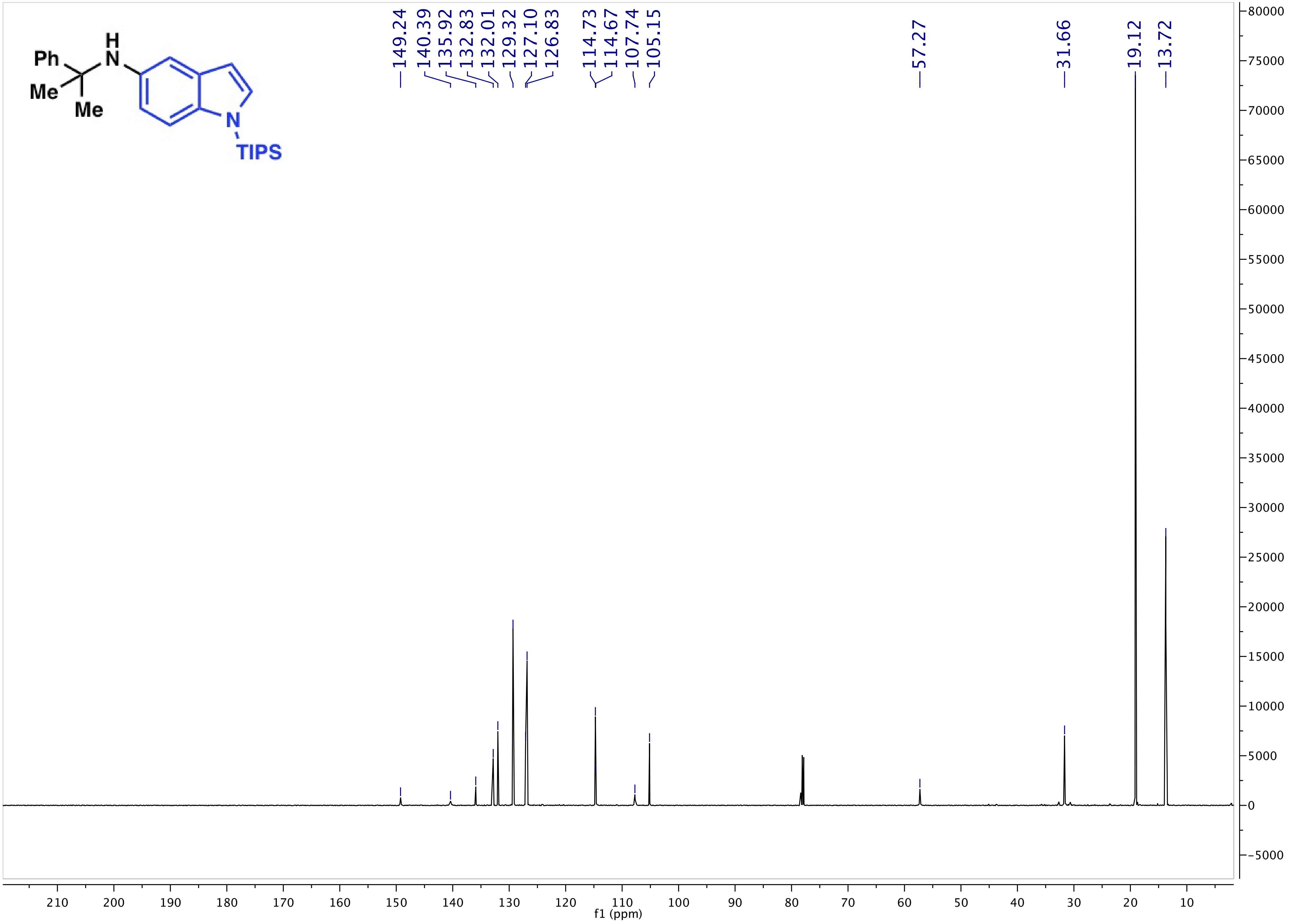

NH2
Pd−(t-Bu)PhCPhos
OMs
H2O
CD3OD
1.19
3.33
4.39
2.35
2.21
5.62
1.19
1.13
1.07
6.15
3.00
6.11
8.56
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100



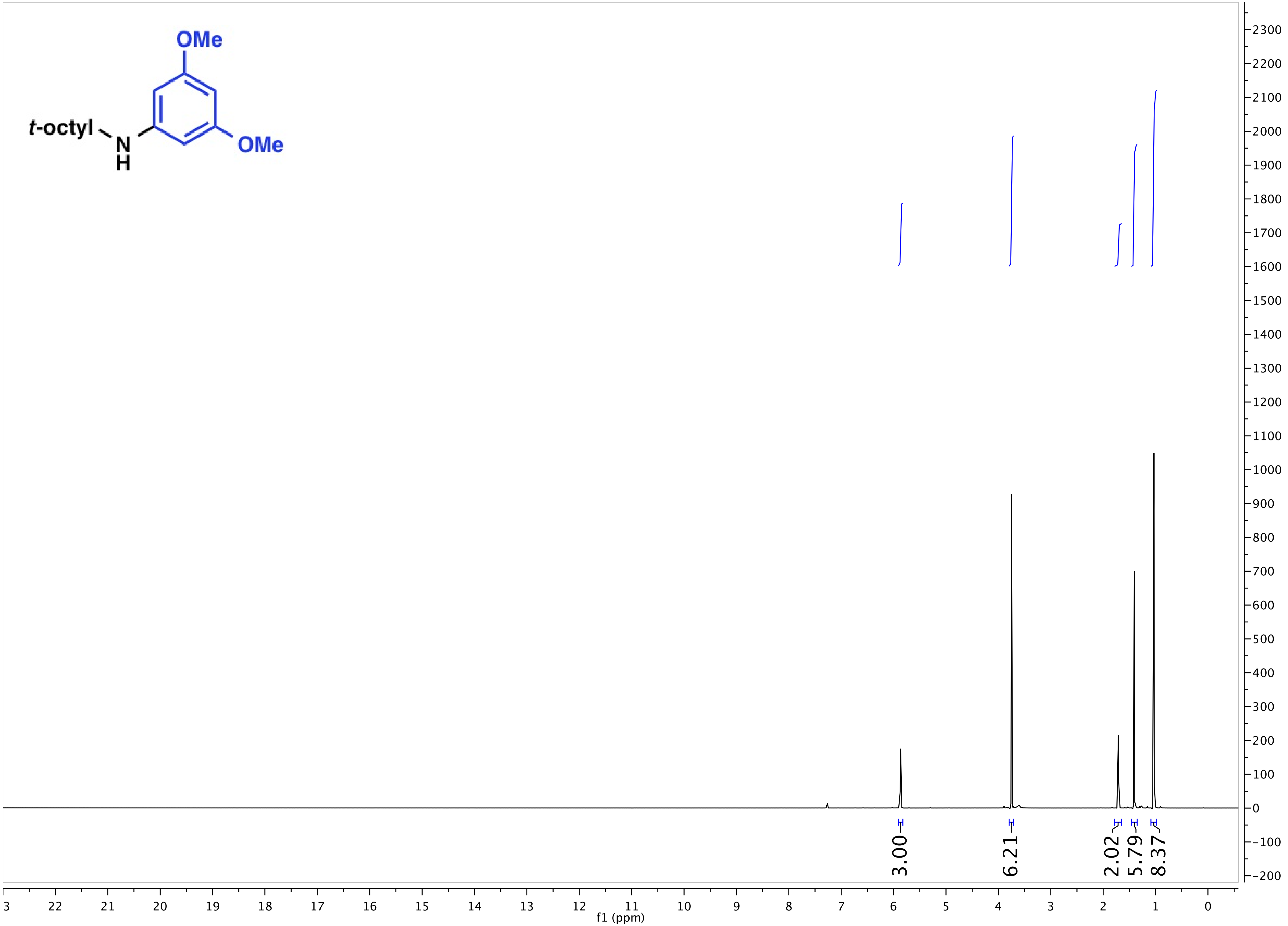
164.40
160.05
150.10
149.95
149.19
144.56
143.98
141.67
141.64
140.06
139.18
139.13
138.84
138.69
138.49
137.37
135.13
133.08
132.76
132.69
132.61
132.21
131.63
131.50
131.39
130.92
129.88
124.04
117.64
117.44
117.34
115.93
58.14
48.18
47.96
42.81
42.09
41.89
33.20
33.16
NH2
Pd−(t-Bu)PhCPhos
OMs
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

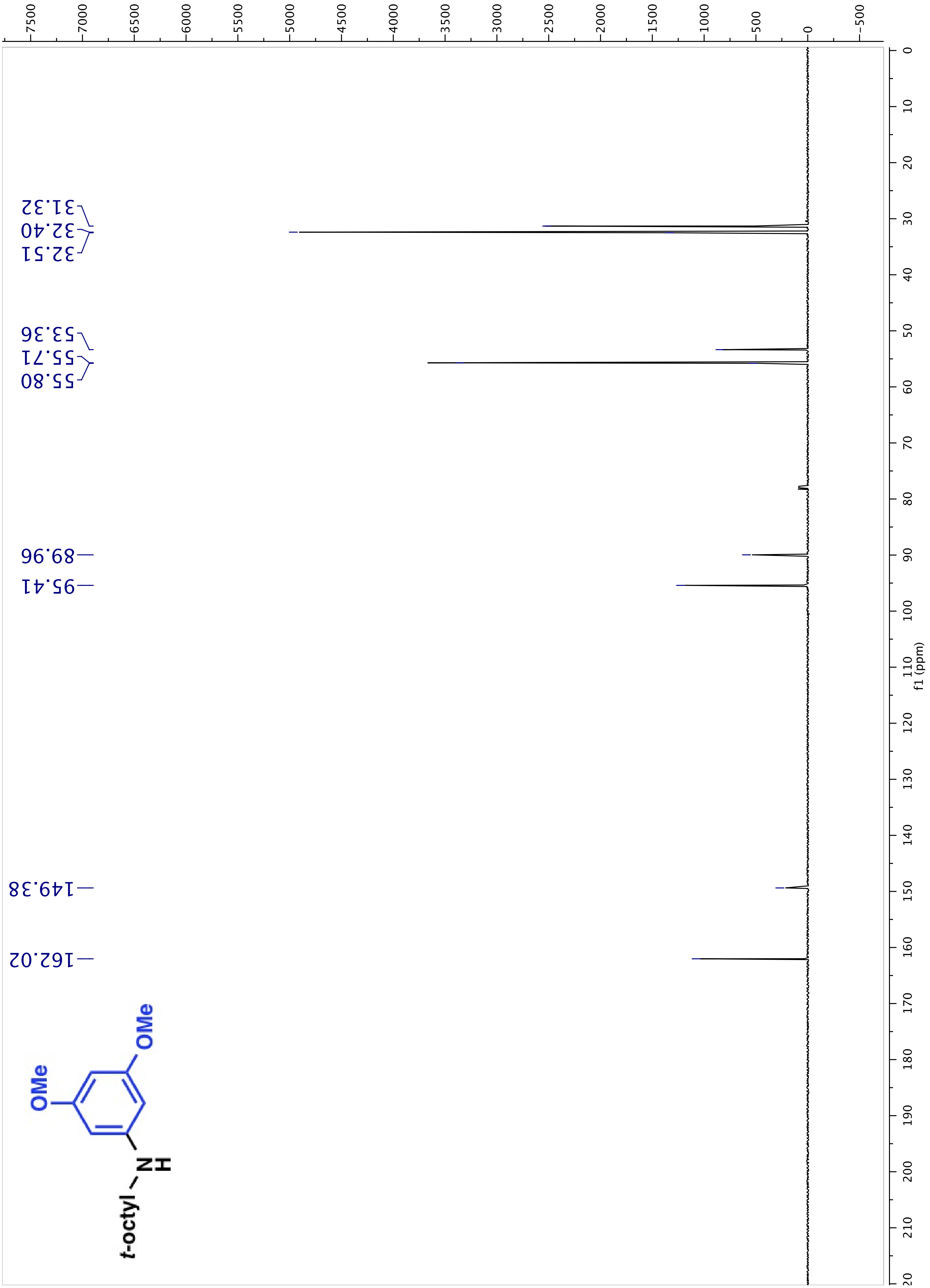

NH2
Pd−(t-Bu)PhCPhos
OMs
45.33
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
f1 (ppm)

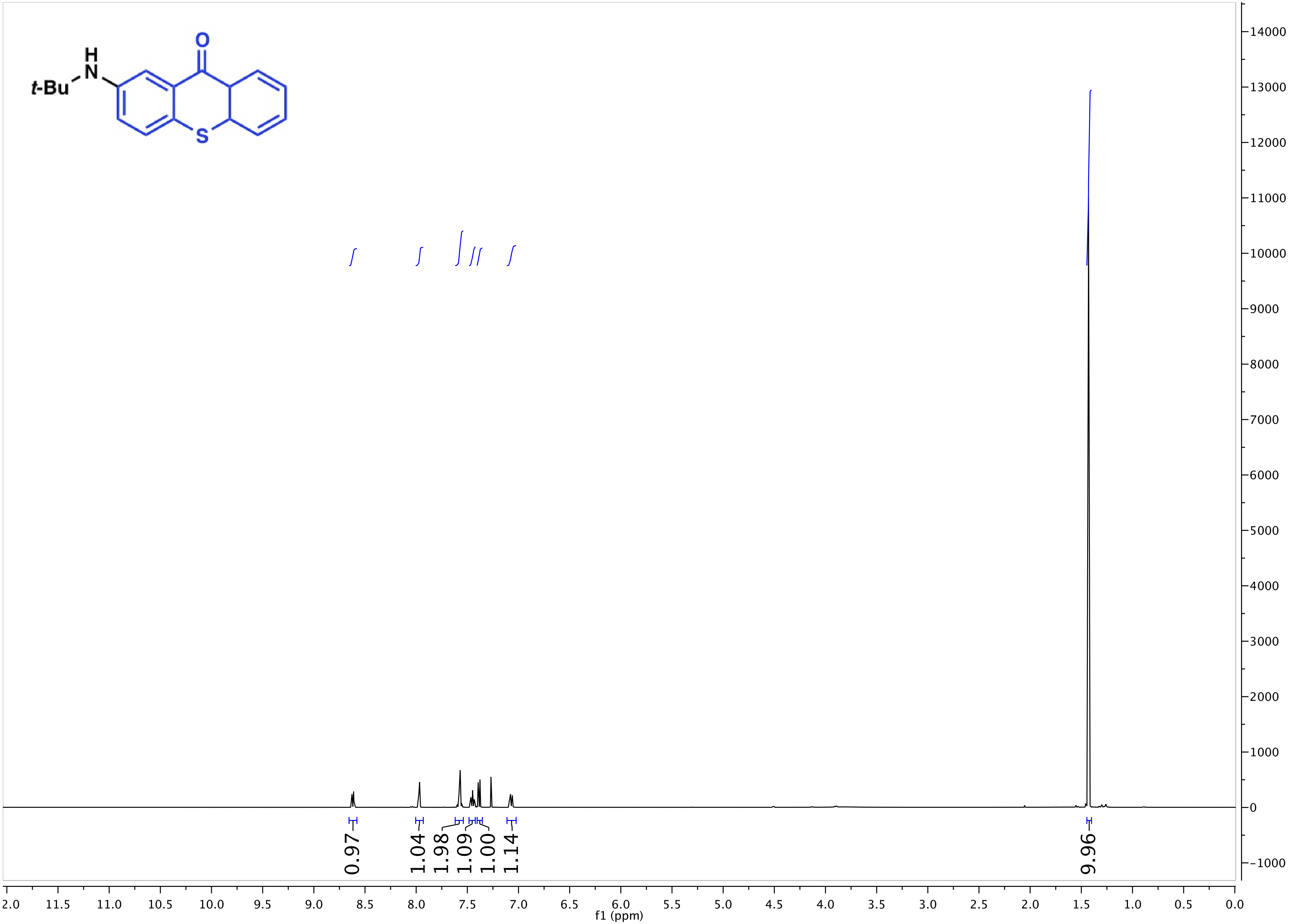

Ph
Me
Me
H
N
N
TIPS
2.09
2.04
1.07
1.13
1.11
1.07
1.05
1.00
5.80
2.48
16.55
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

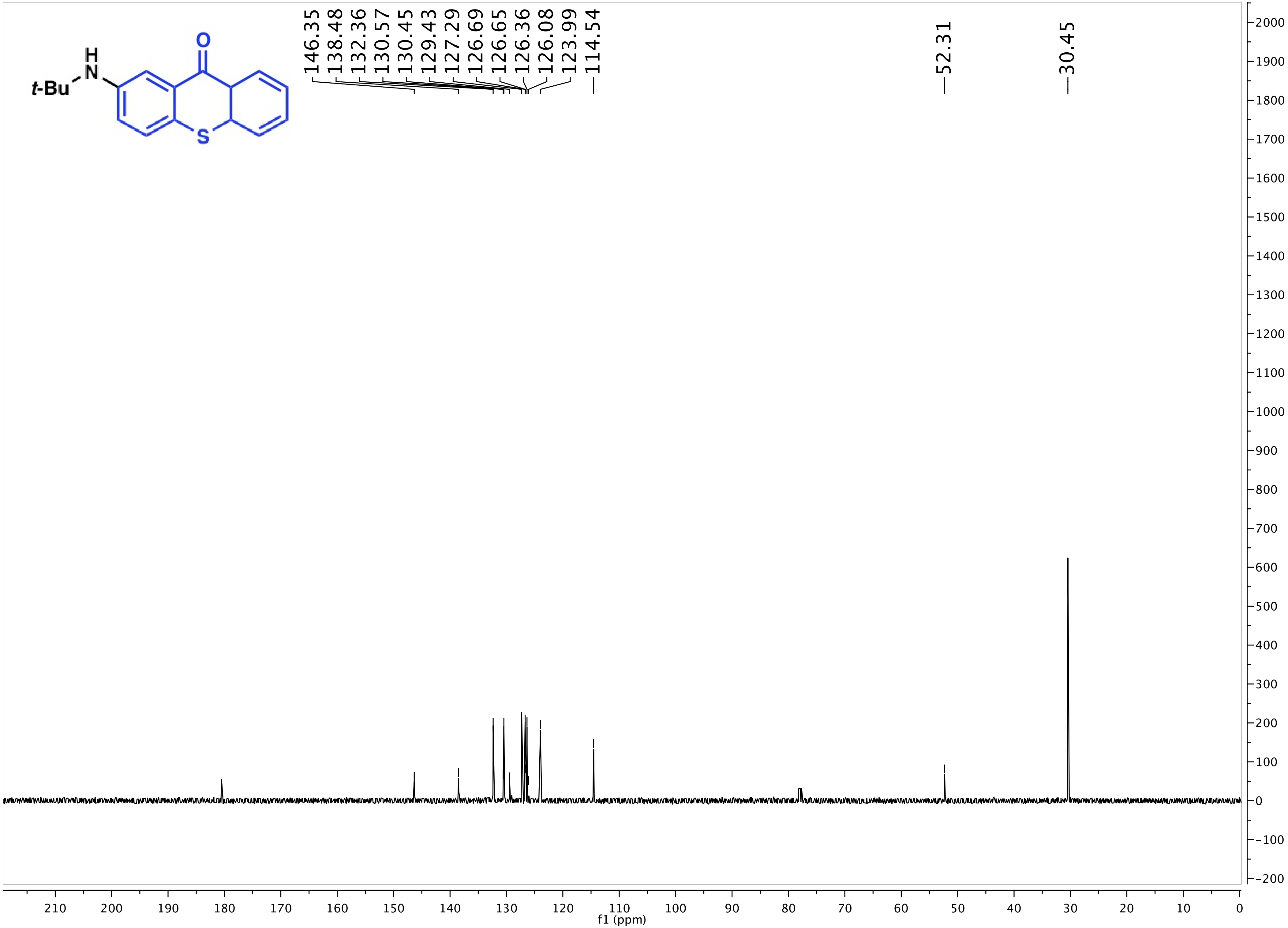


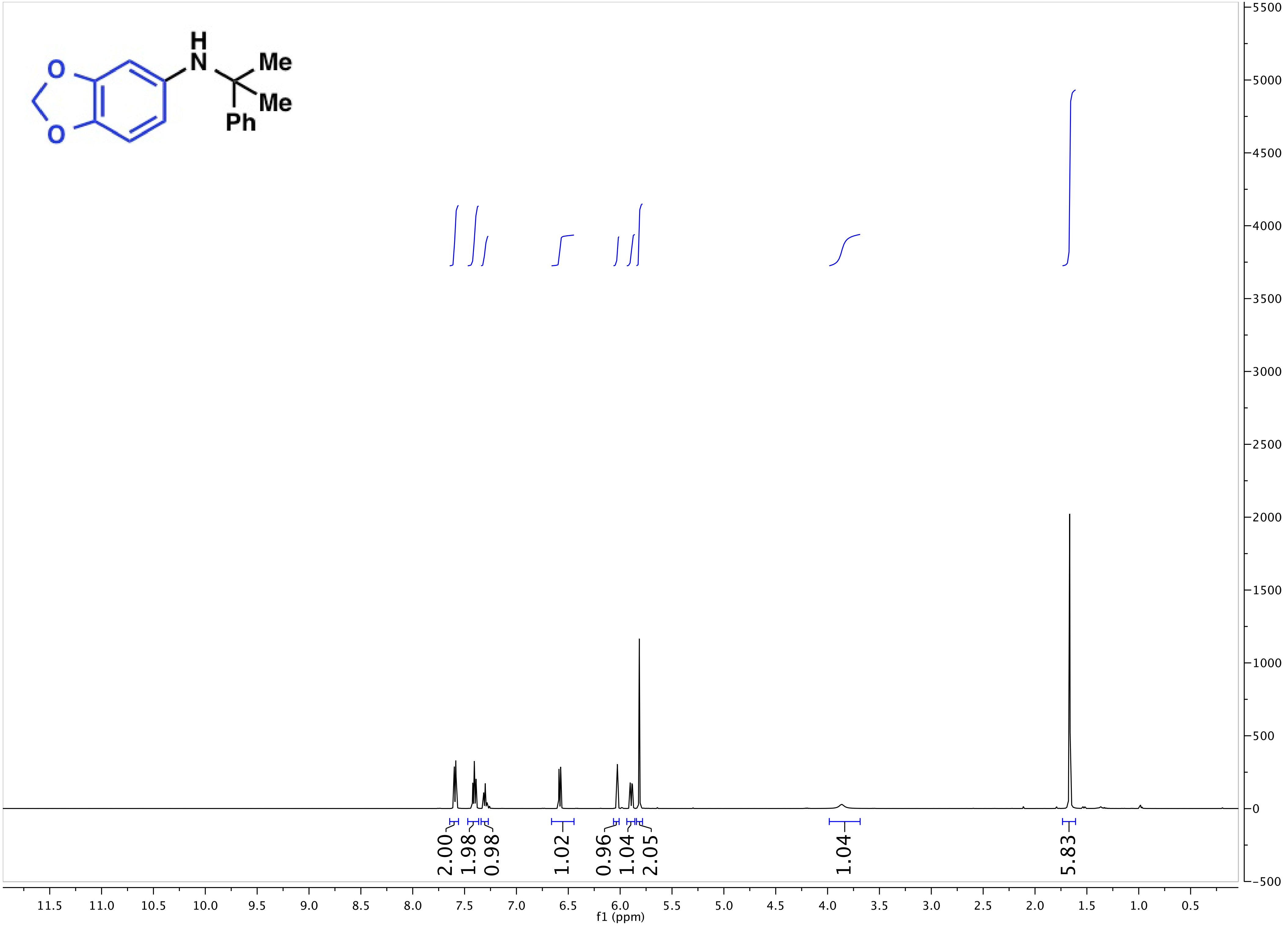
Ph
H
N
Me
Me
N
TIPS
149.24
140.39
135.92
132.83
132.01
129.32
127.10
126.83
114.73
114.67
107.74
105.15
57.27
31.66
19.12
13.72
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

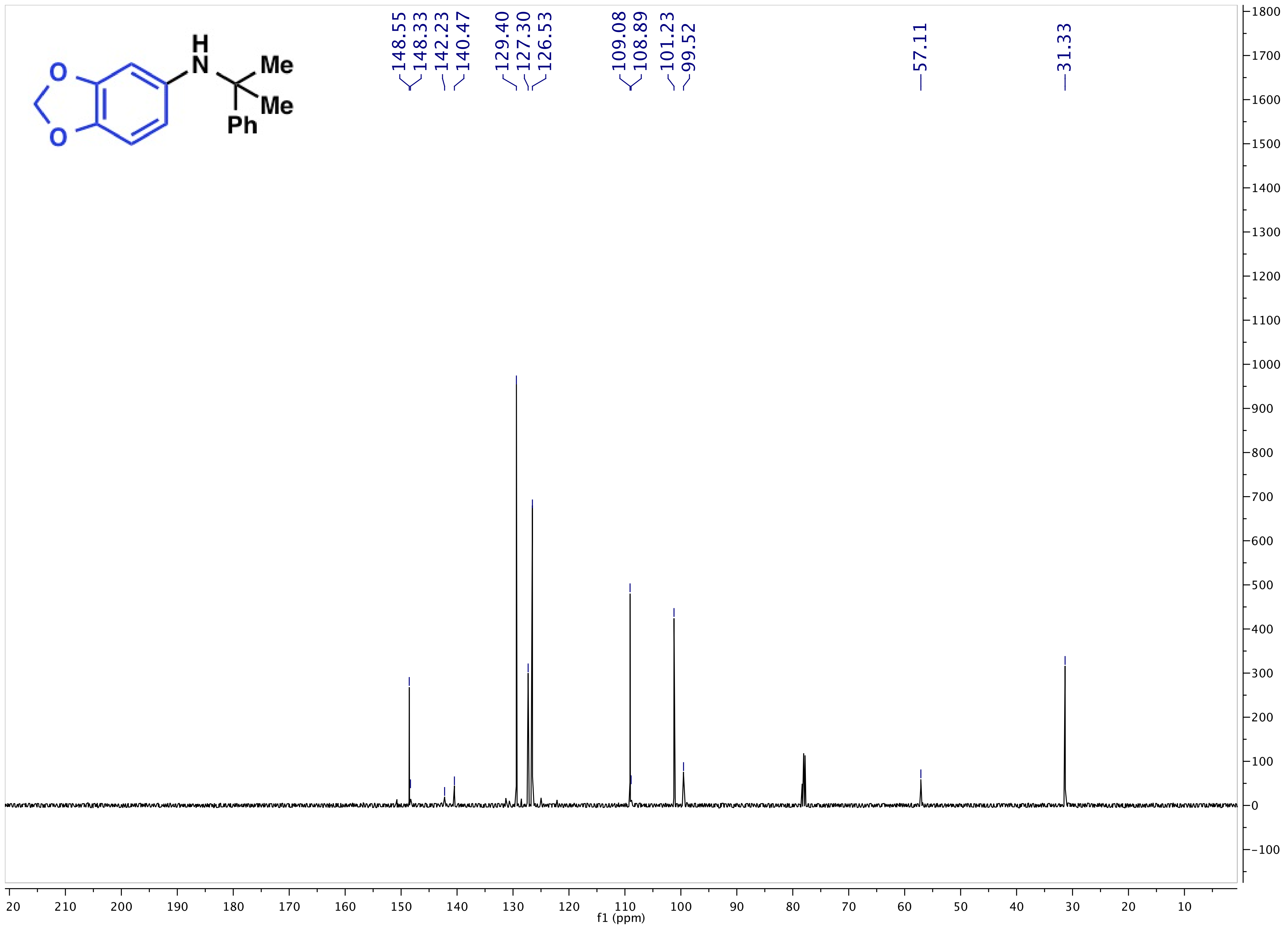

t-octyl
N
H
OMe
OMe
3.00
6.21
2.02
5.79
8.37
3
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200


31.32
32.40
32.51
53.36
55.71
55.80
89.96
95.41
149.38
162.02
OMe
OMe
t-octyl
N
H
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

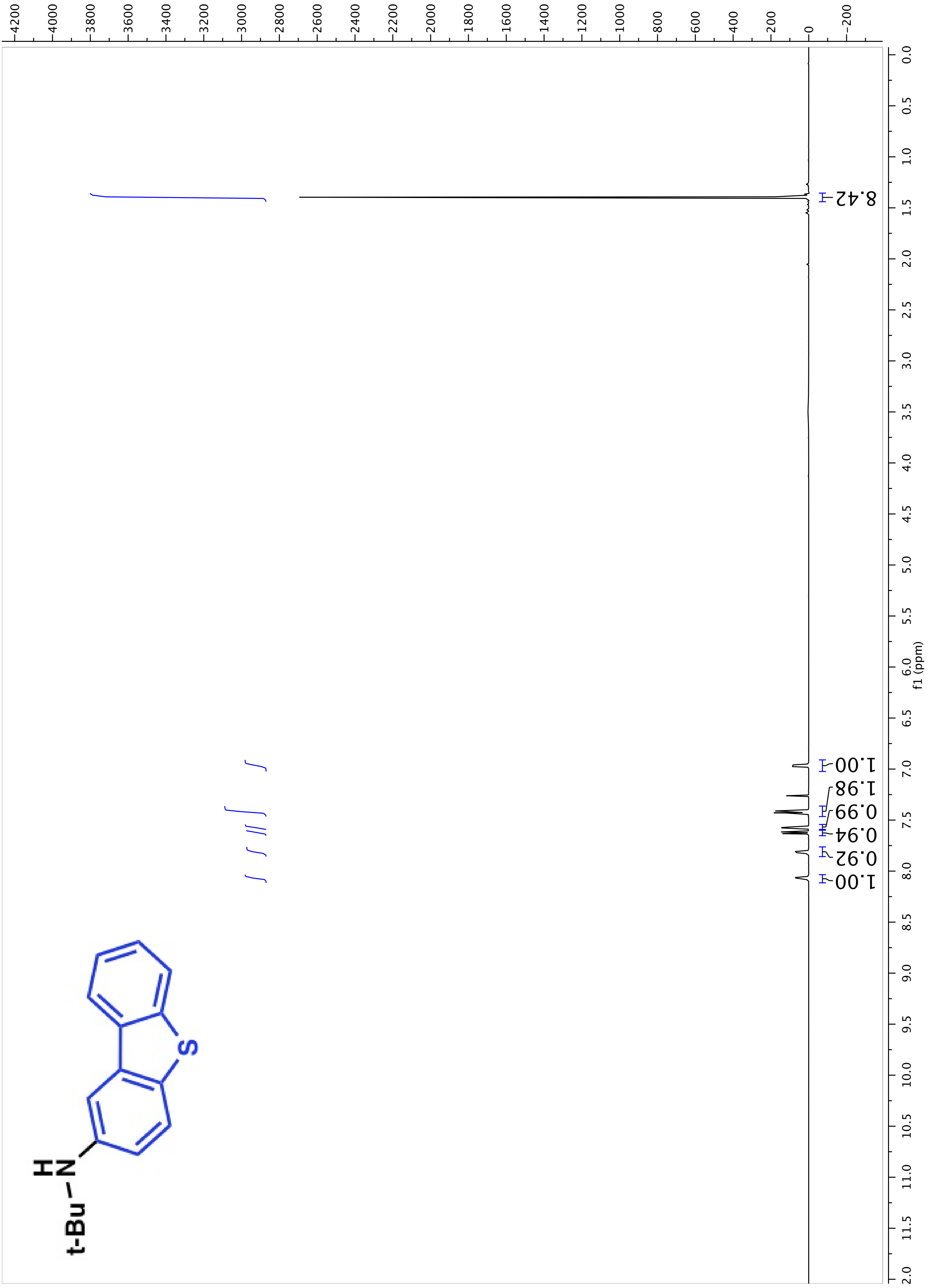

t-Bu
H
N
O
S
0.97
1.04
1.98
1.09
1.00
1.14
9.96
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000

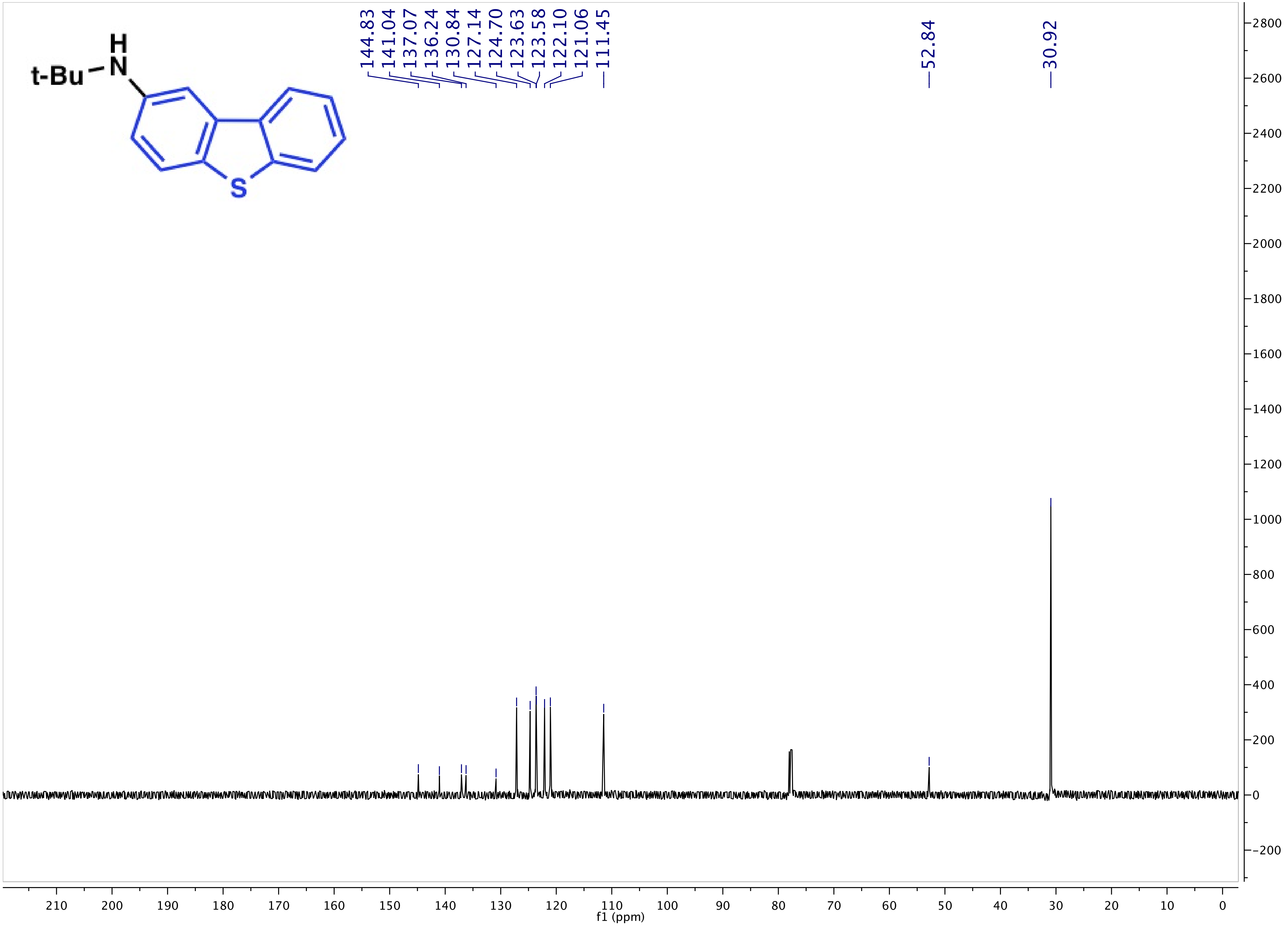

t-Bu
H
N
O
S
146.35
138.48
132.36
130.57
130.45
129.43
127.29
126.69
126.65
126.36
126.08
123.99
114.54
52.31
30.45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200

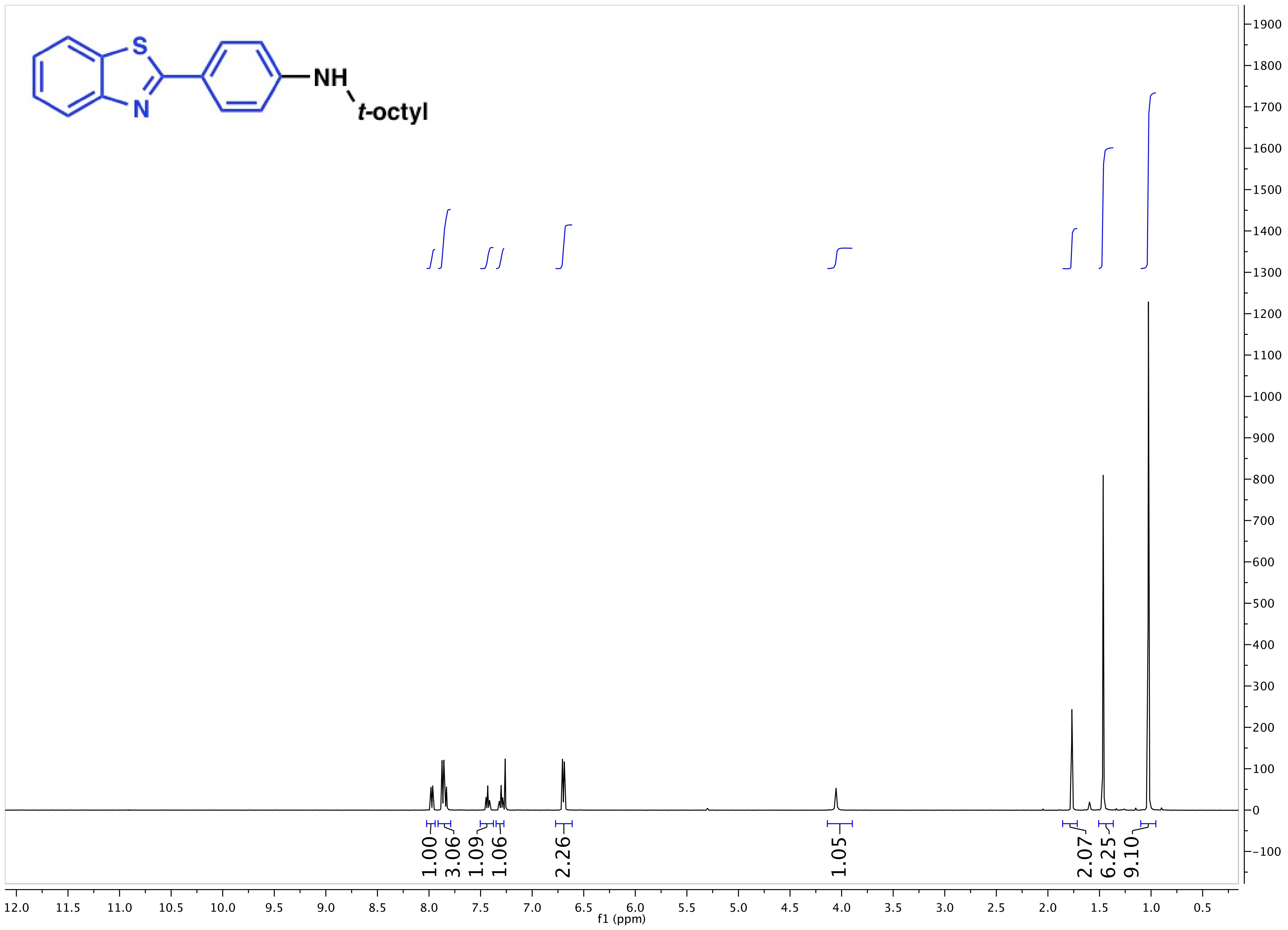

H
N
O
O
Me
Me
Ph
2.00
1.98
0.98
1.02
0.96
1.04
2.05
1.04
5.83
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500

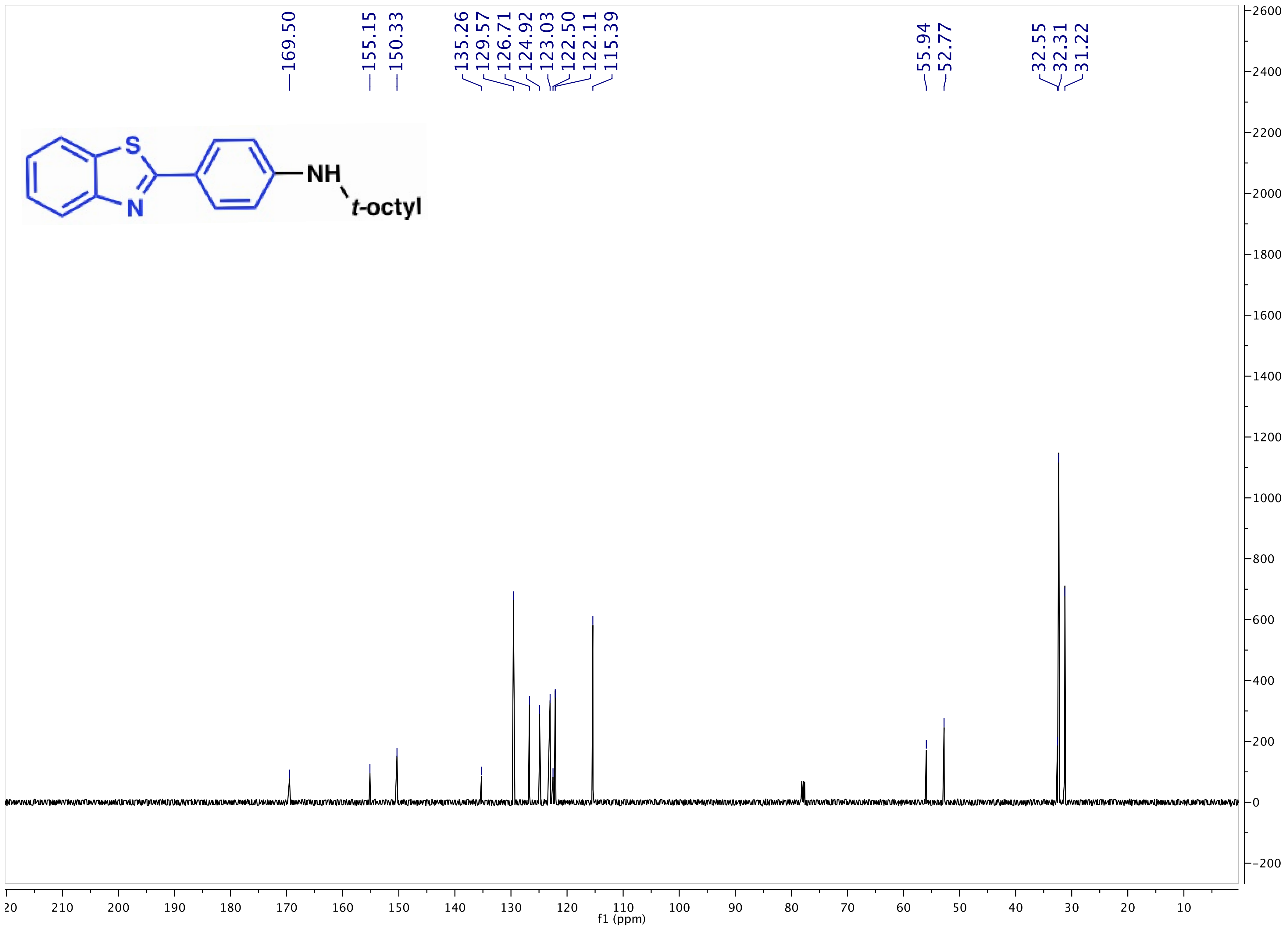


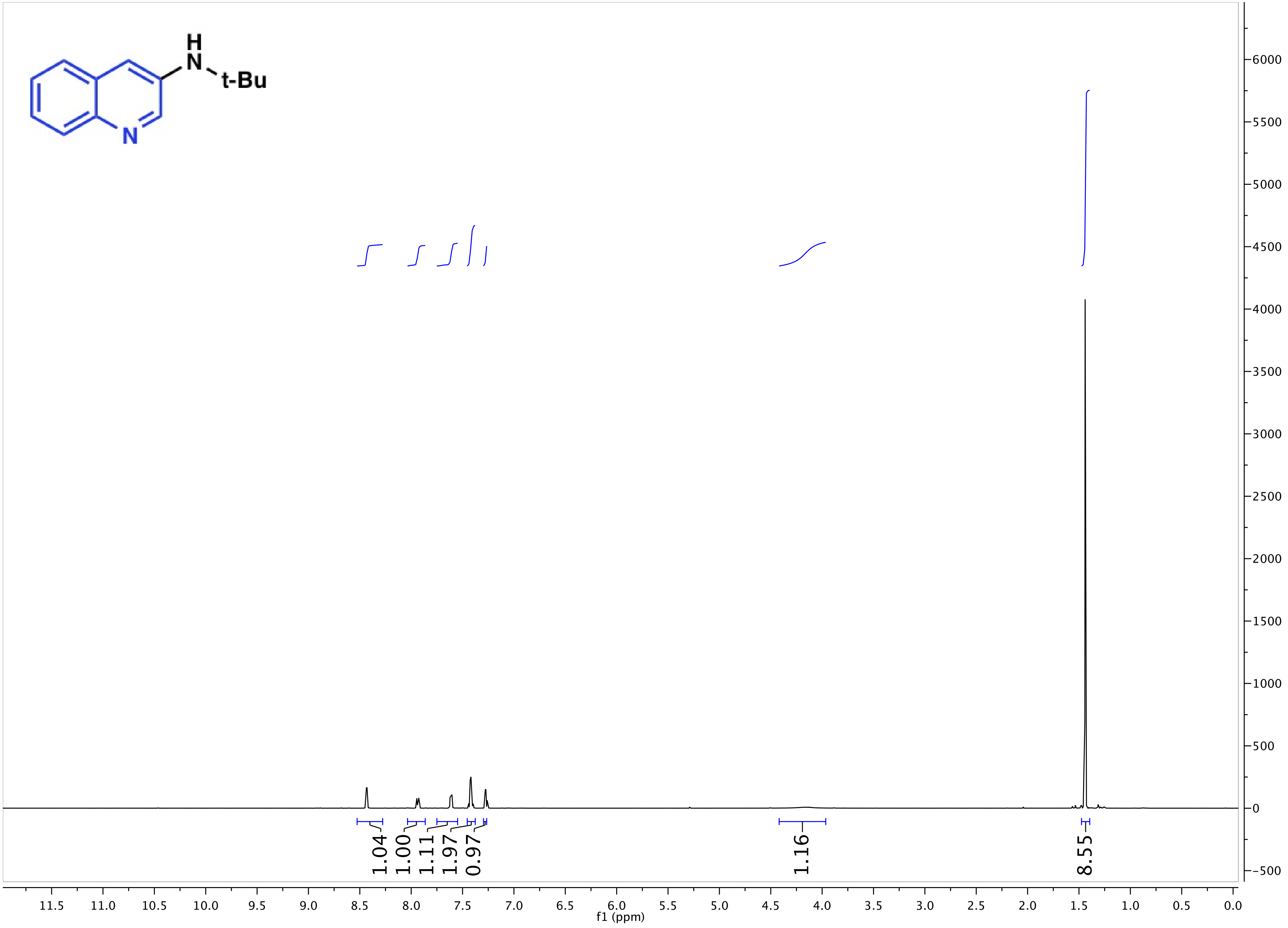
148.55
148.33
142.23
140.47
129.40
127.30
126.53
109.08
108.89
101.23
99.52
57.11
31.33
O
O
H
N
Me
Me
Ph
f1 (ppm)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100

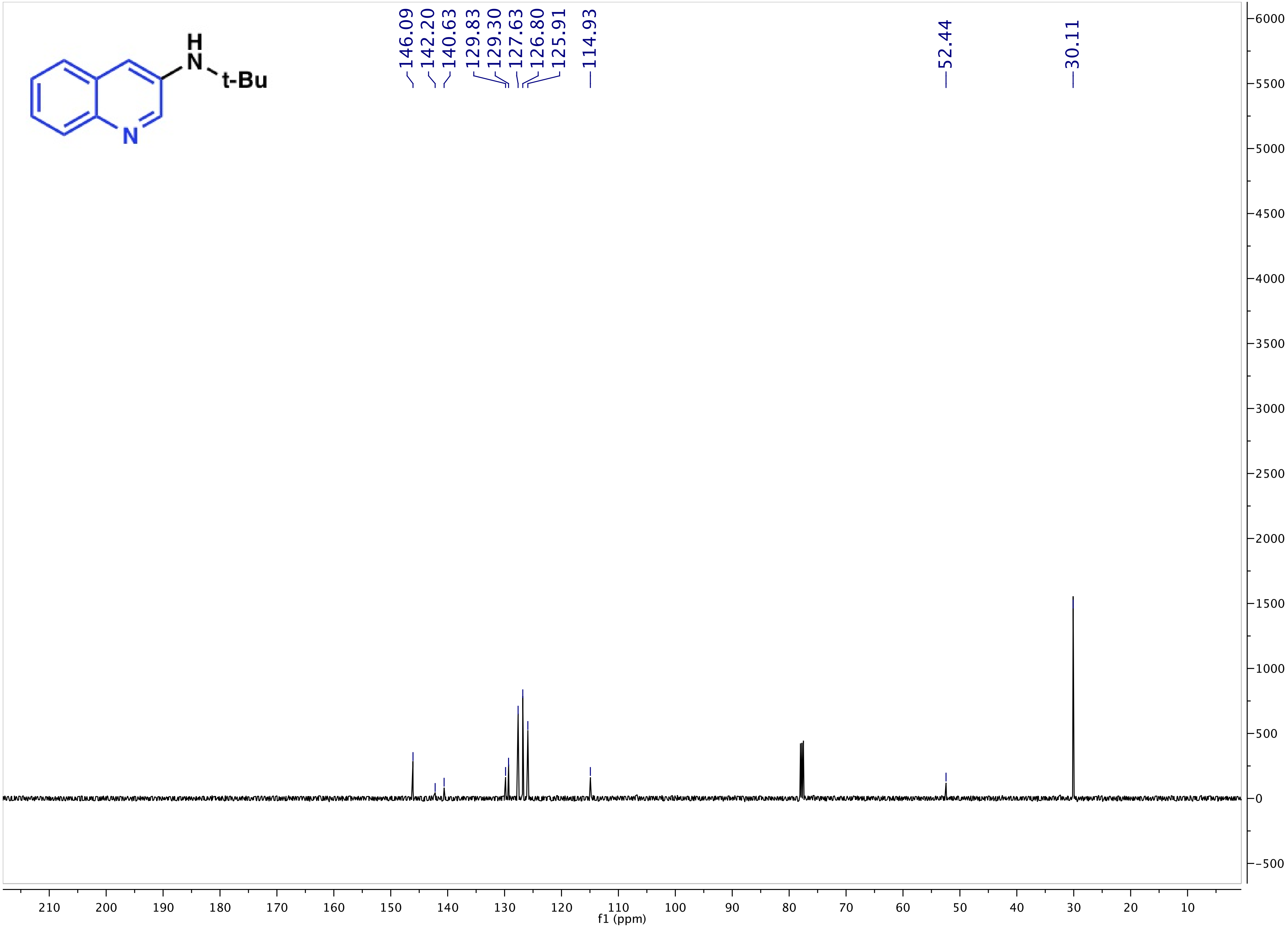

t-Bu
N
H
S
8.42
1.00
1.98
0.99
0.94
0.92
1.00
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

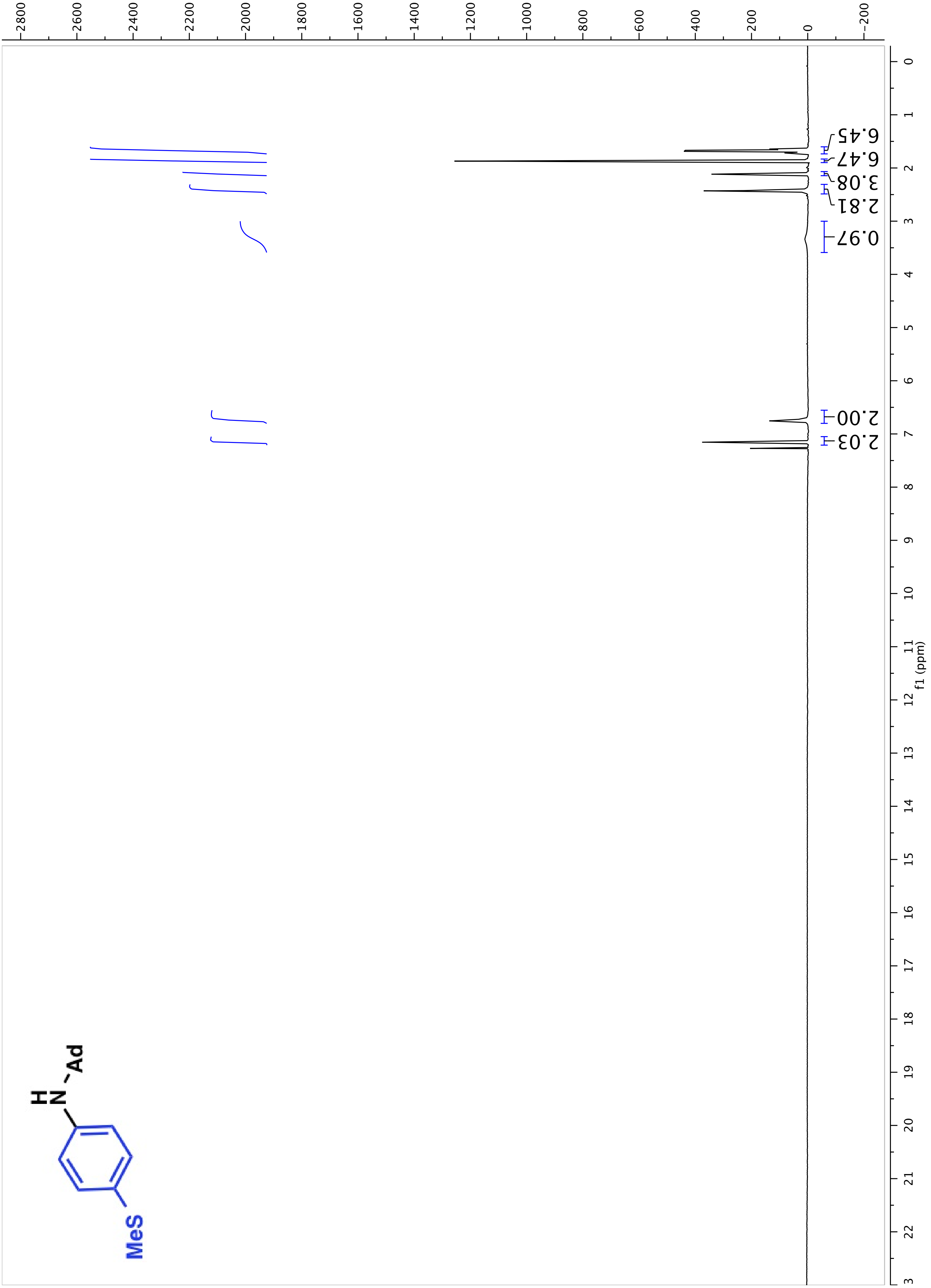

t-Bu
N
H
S
144.83
141.04
137.07
136.24
130.84
127.14
124.70
123.63
123.58
122.10
121.06
111.45
52.84
30.92
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S
N
NH
t-octyl
1.00
3.06
1.09
1.06
2.26
1.05
2.07
6.25
9.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100

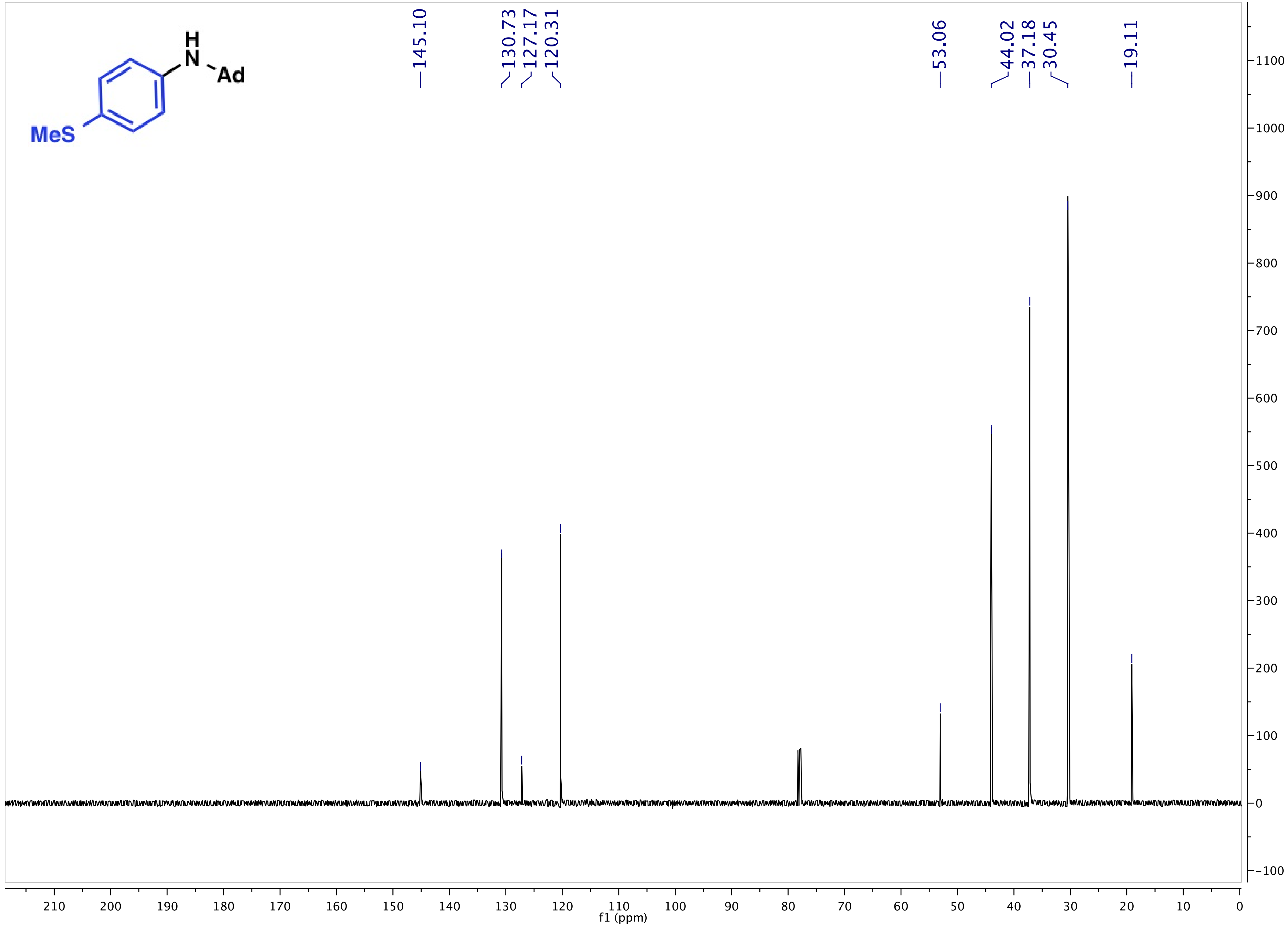

169.50
155.15
150.33
135.26
129.57
126.71
124.92
123.03
122.50
122.11
115.39
55.94
52.77
32.55
32.31
31.22
S
N
NH
t-octyl
f1 (ppm)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200

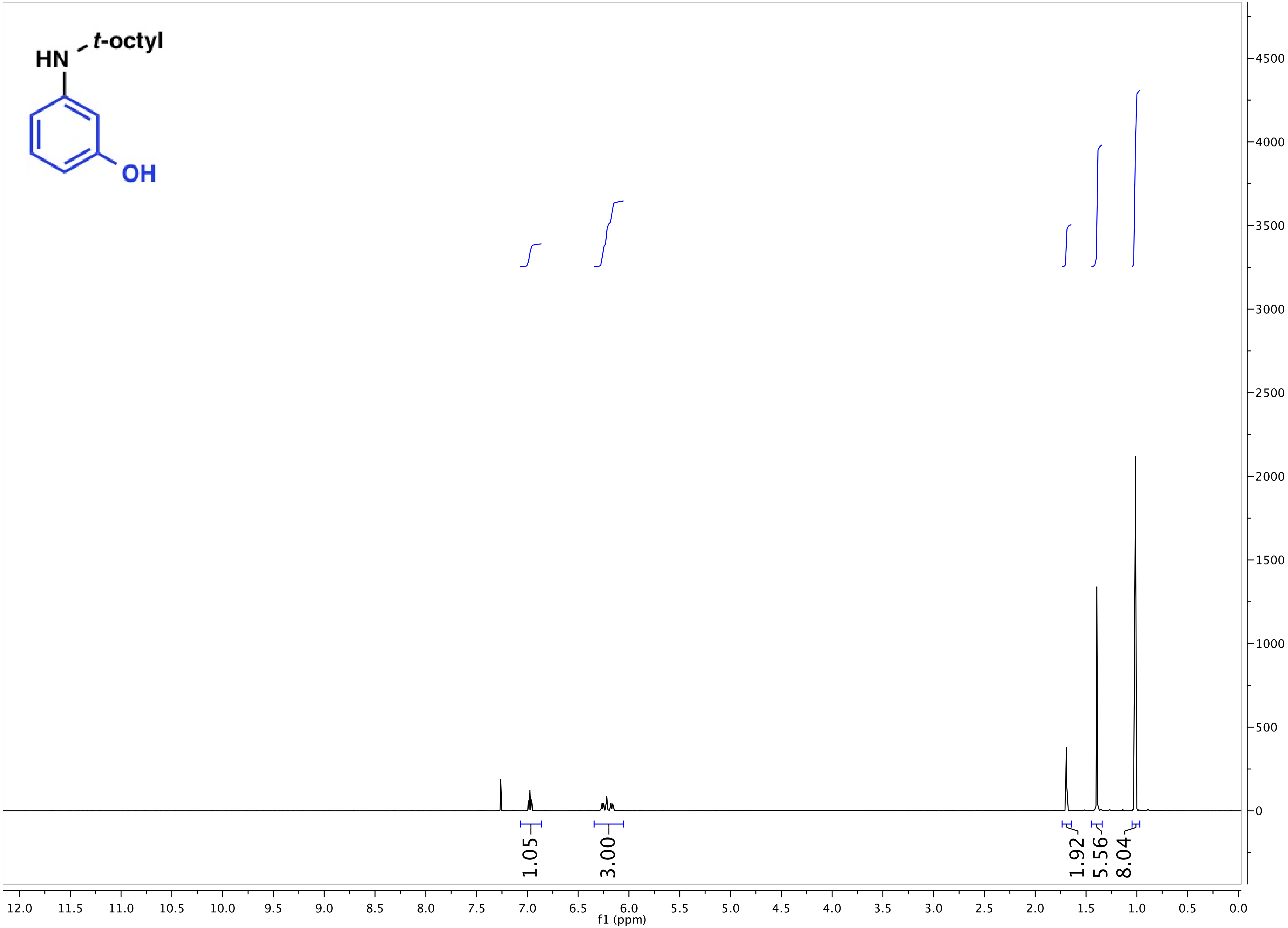

H
N
t-Bu
N
1.04
1.00
1.11
1.97
0.97
1.16
8.55
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

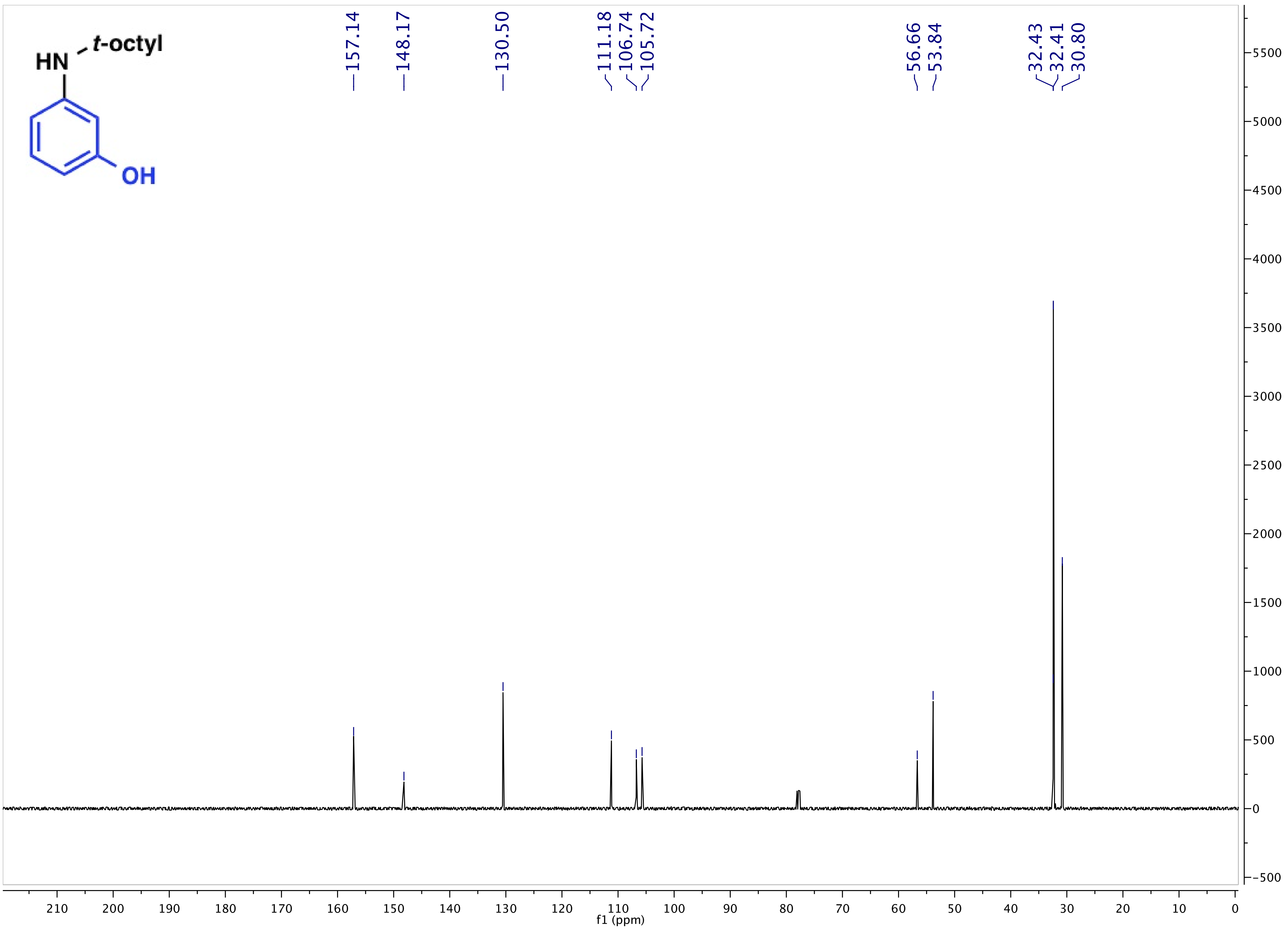

H
N
t-Bu
N
146.09
142.20
140.63
129.83
129.30
127.63
126.80
125.91
114.93
52.44
30.11
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

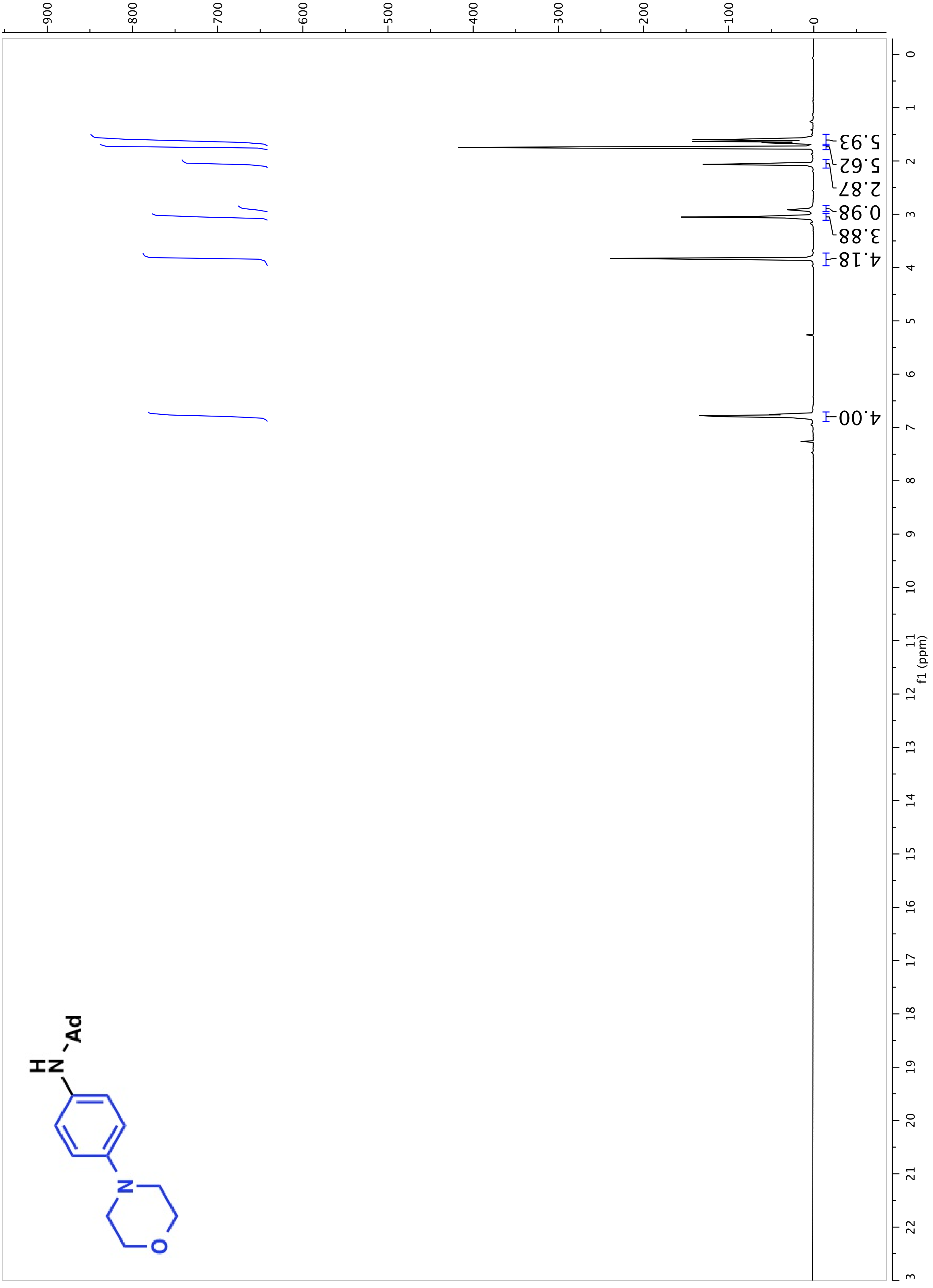


MeS
H
N
Ad
6.45
6.47
3.08
2.81
0.97
2.00
2.03
f1 (ppm)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

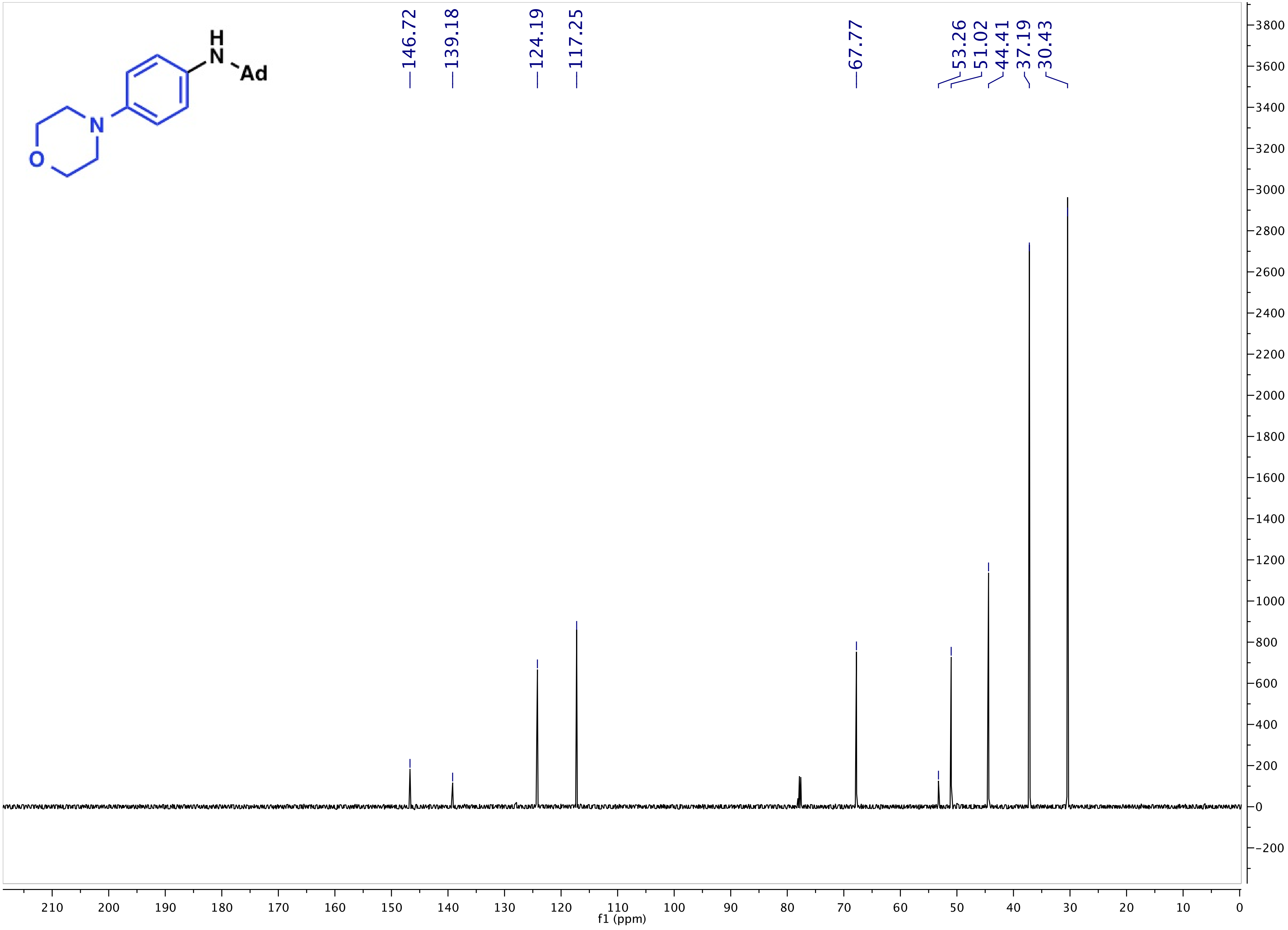

MeS
H
N
Ad
145.10
130.73
127.17
120.31
53.06
44.02
37.18
30.45
19.11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


HN
t-octyl
OH
1.05
3.00
1.92
5.56
8.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

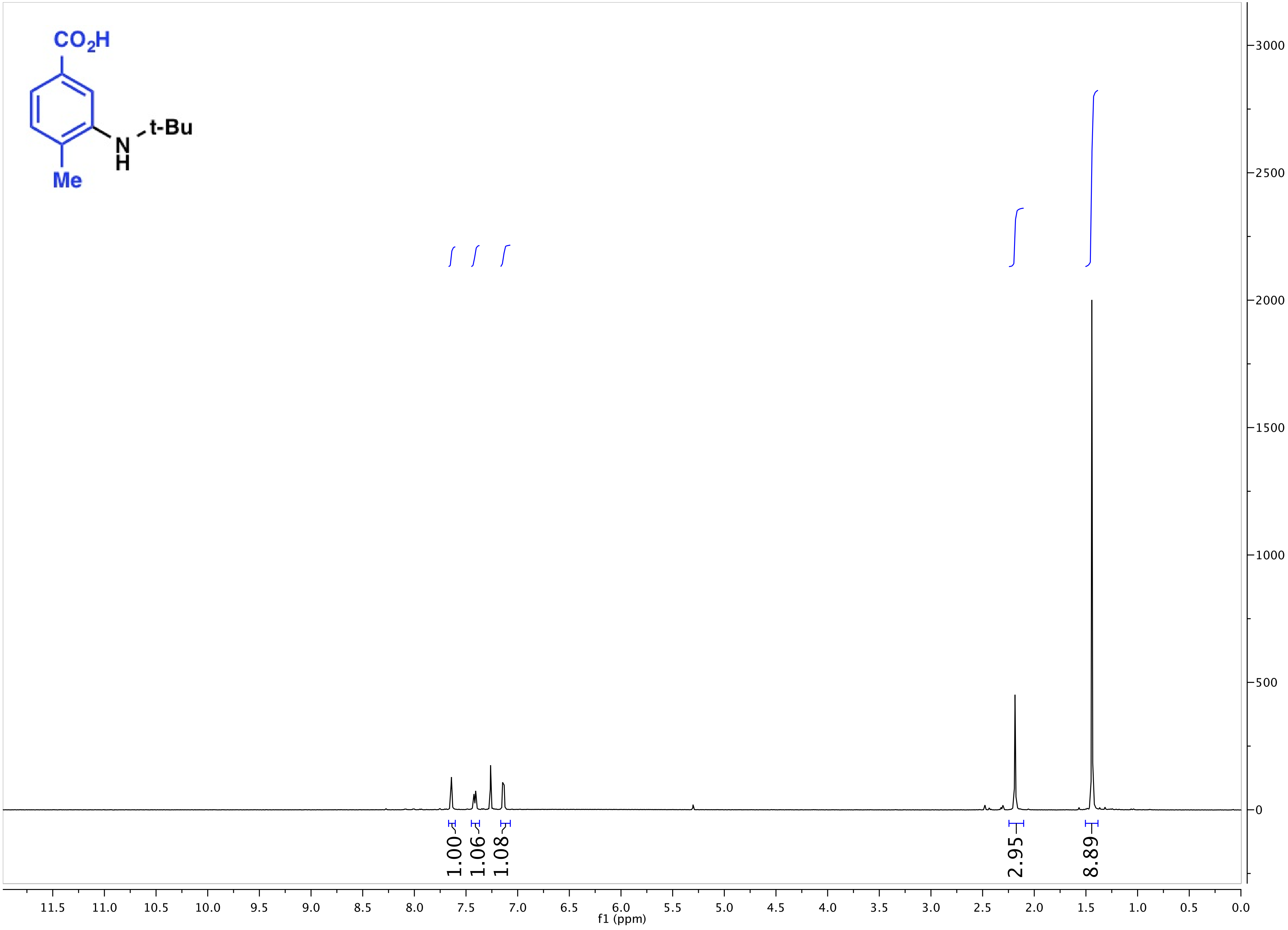

HN
t-octyl
OH
157.14
148.17
130.50
111.18
106.74
105.72
56.66
53.84
32.43
32.41
30.80
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

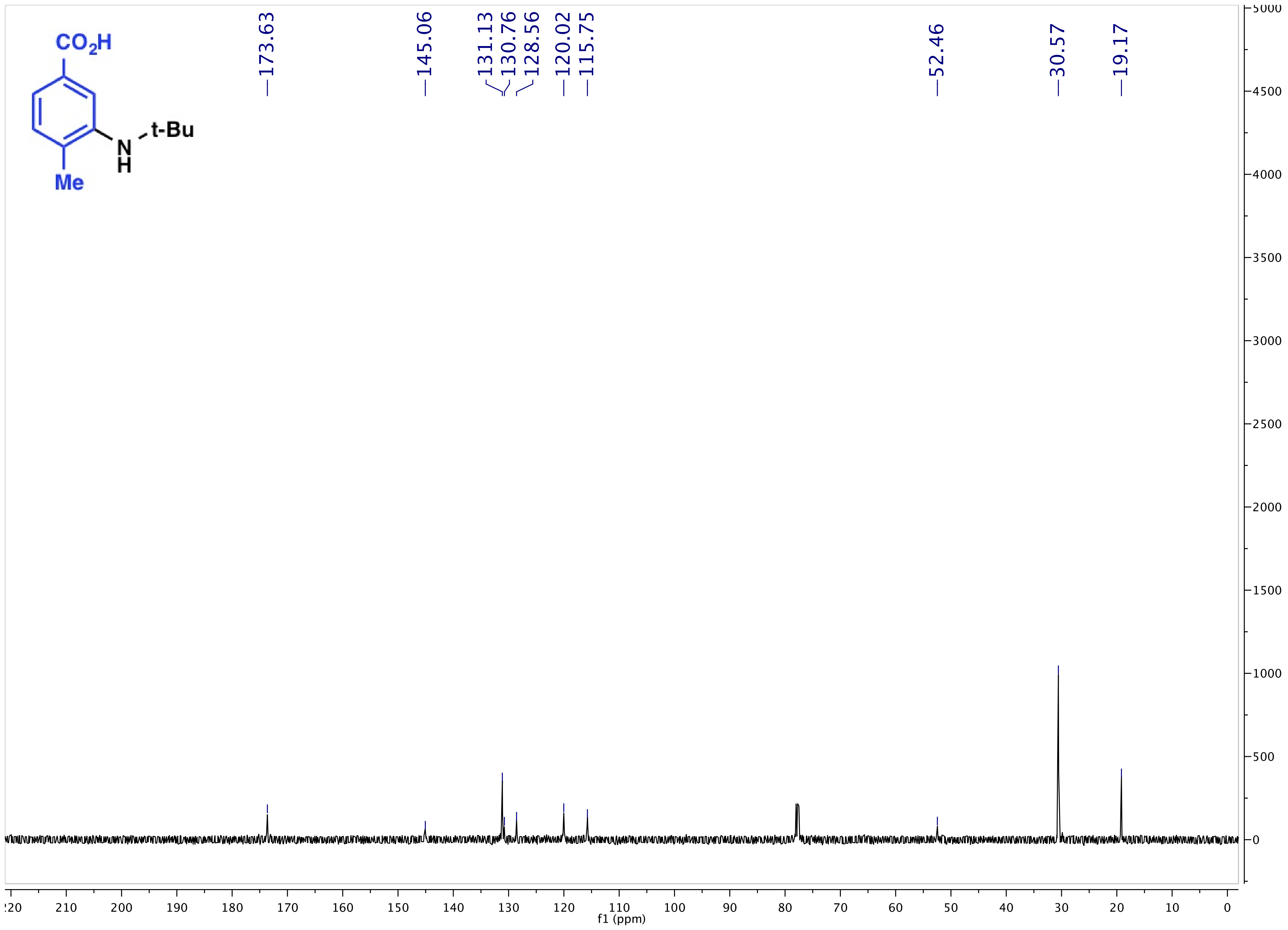


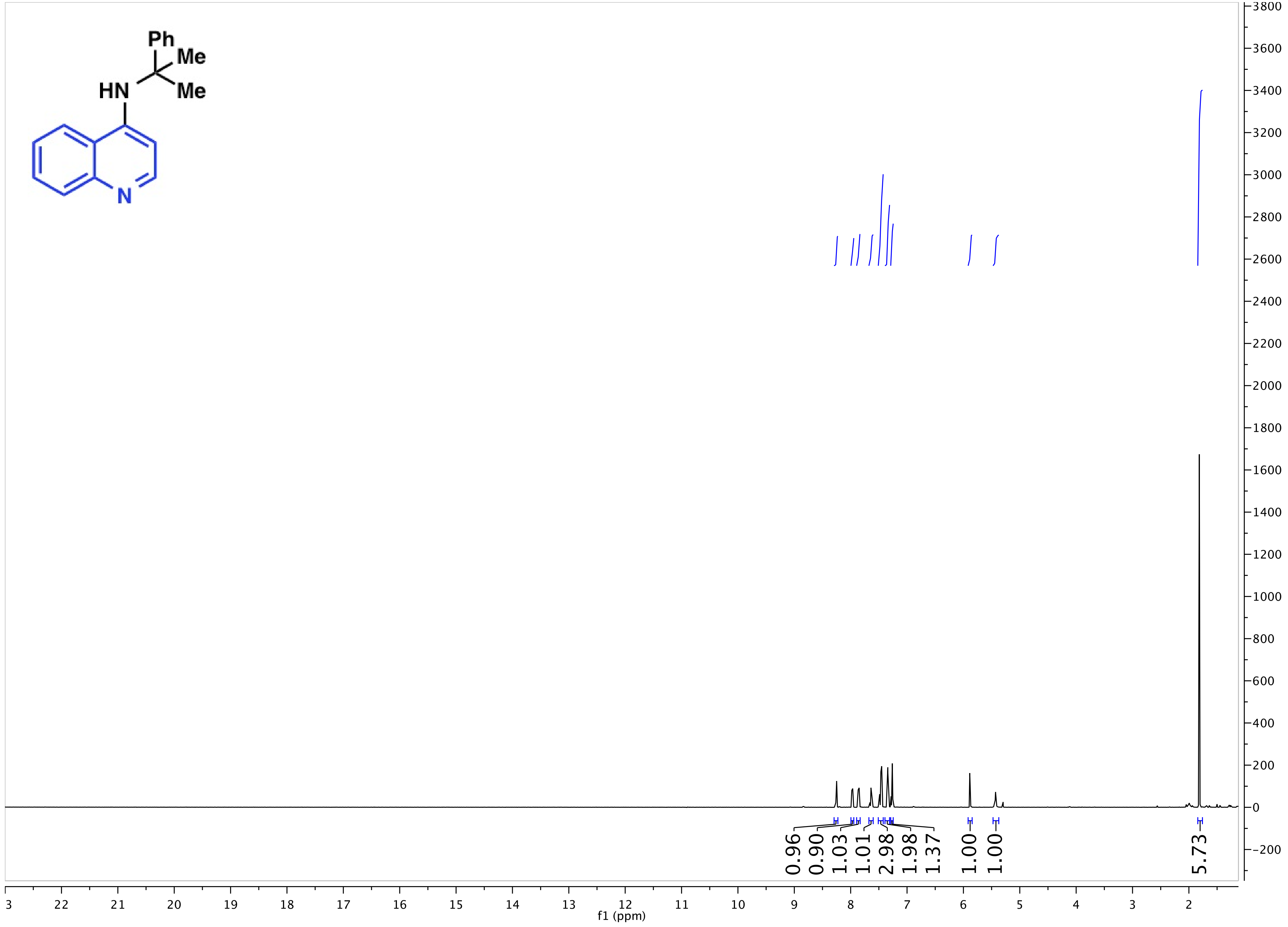
5.93
5.62
2.87
0.98
3.88
4.18
4.00
f1 (ppm)
H
N
Ad
N
O



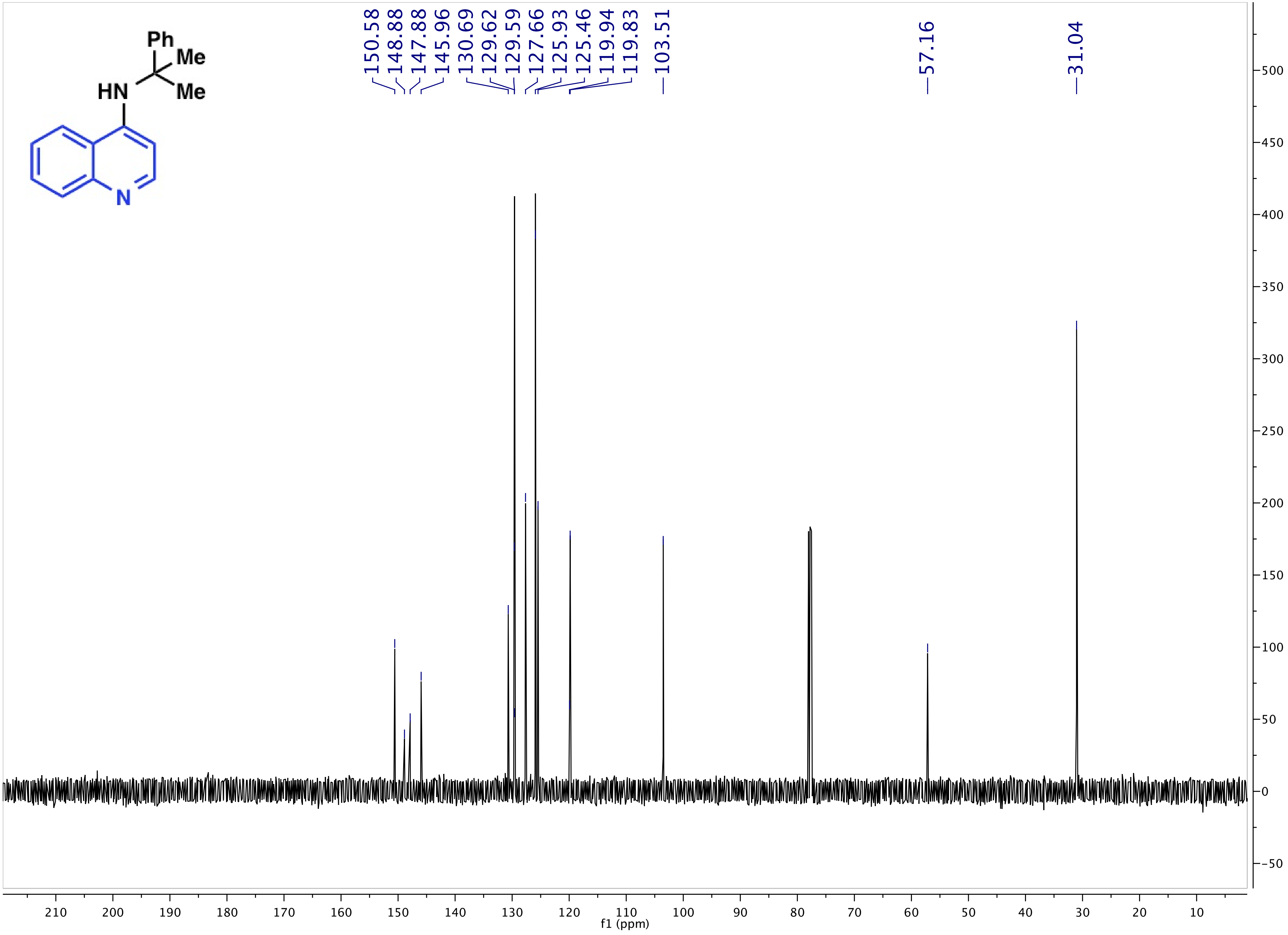
H
N
Ad
N
O
146.72
139.18
124.19
117.25
67.77
53.26
51.02
44.41
37.19
30.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

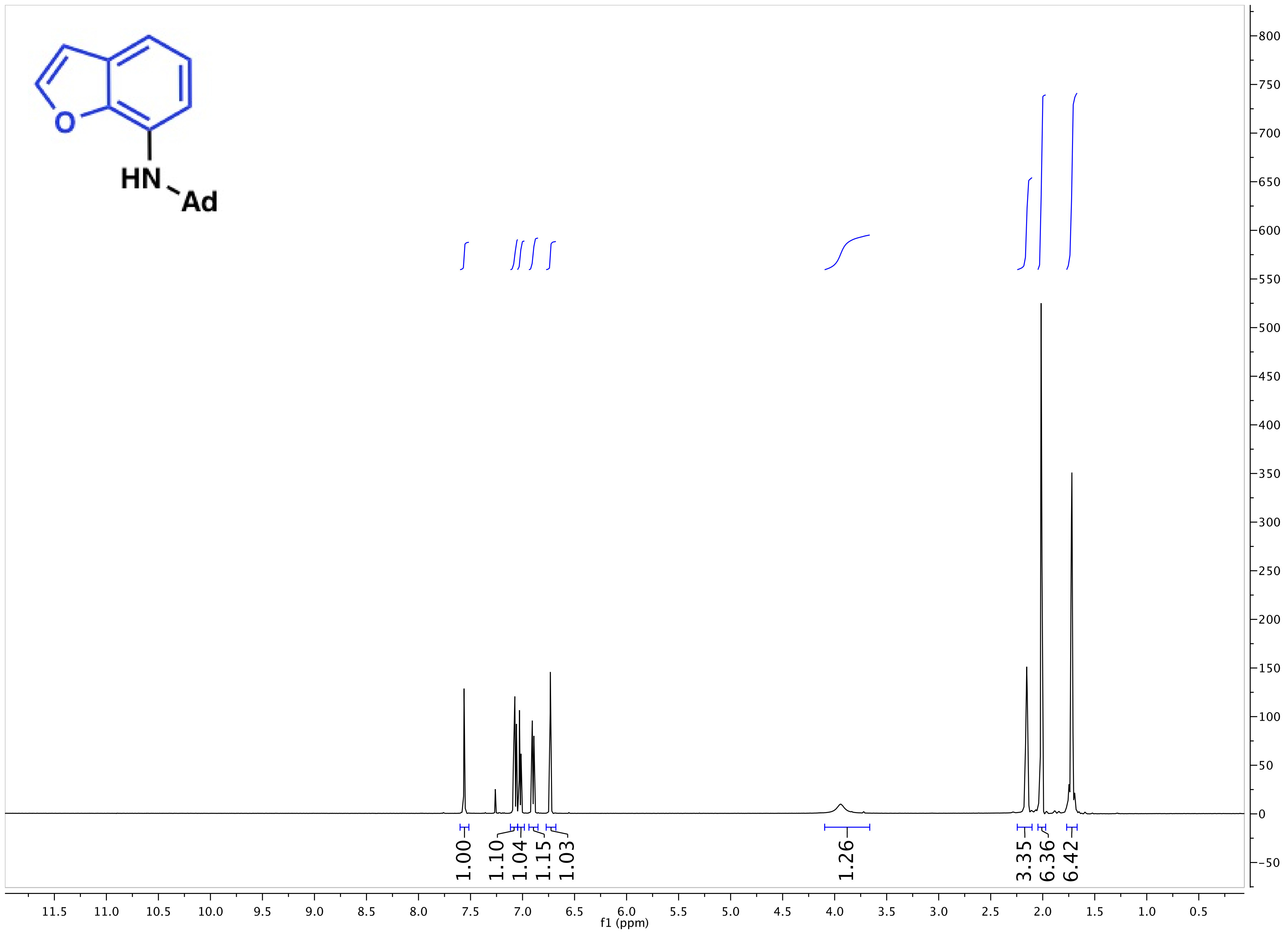

CO2H
N
H
t-Bu
Me
1.00
1.06
1.08
2.95
8.89
3000
2500
2000
1500
1000
500
0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

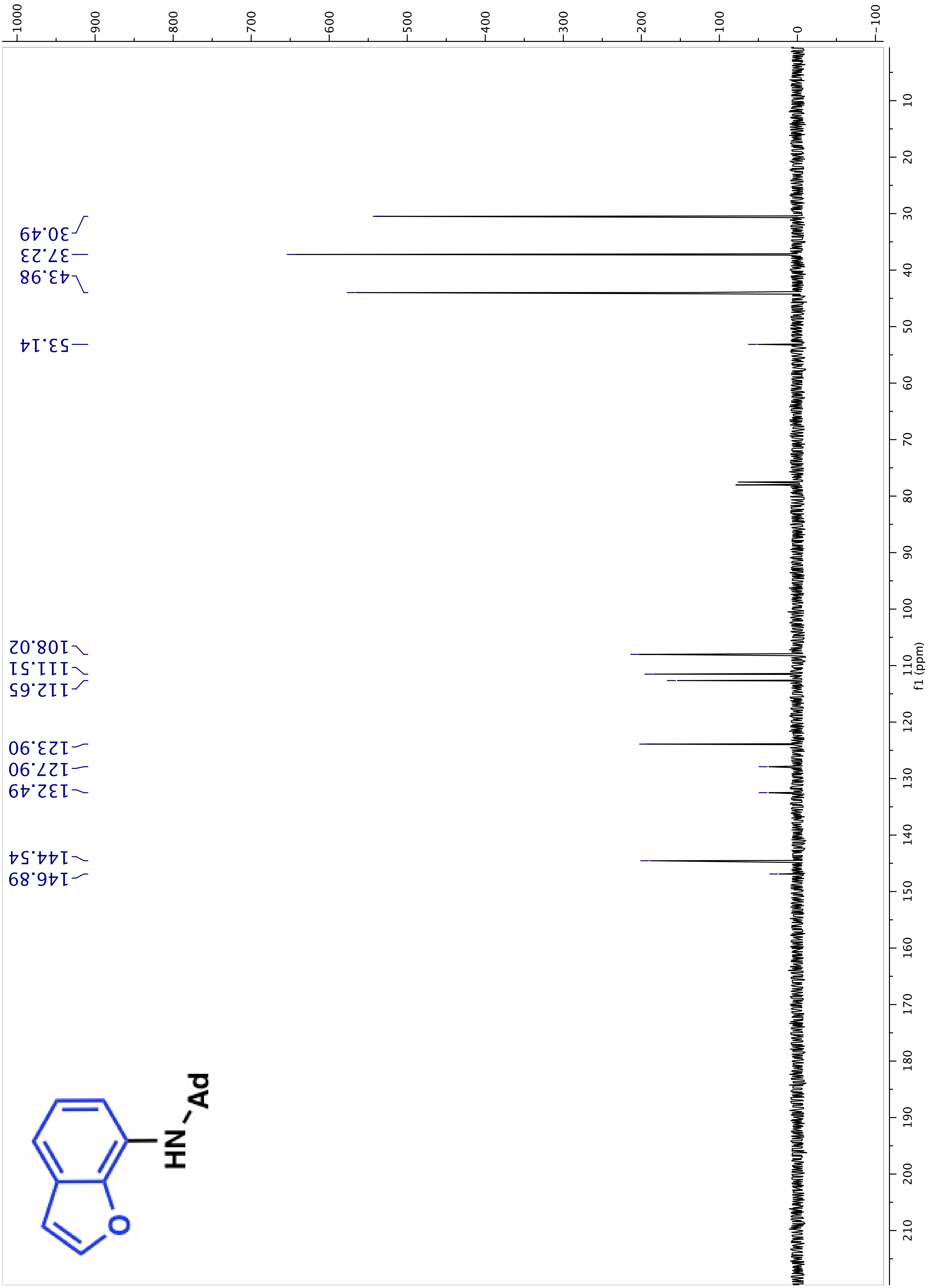

CO2H
N
H
t-Bu
Me
173.63
145.06
131.13
130.76
128.56
120.02
115.75
52.46
30.57
19.17
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0



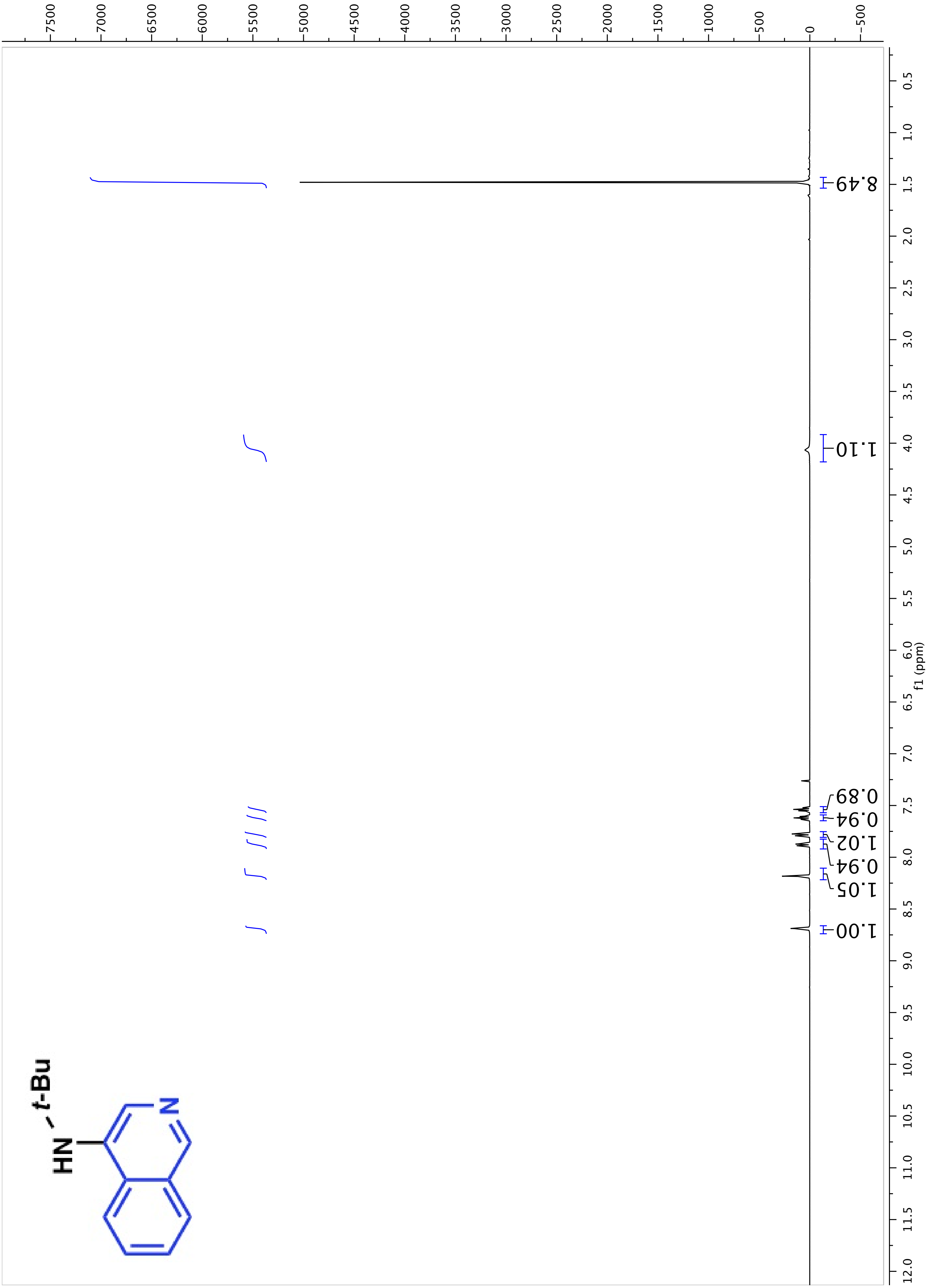
Ph
Me
HN
Me
N
0.96
0.90
1.03
1.01
2.98
1.98
1.37
1.00
1.00
5.73
3
22
21
20
19
18
17
16
15
14
13
12
f1 (ppm)
11
10
9
8
7
6
5
4
3
2
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

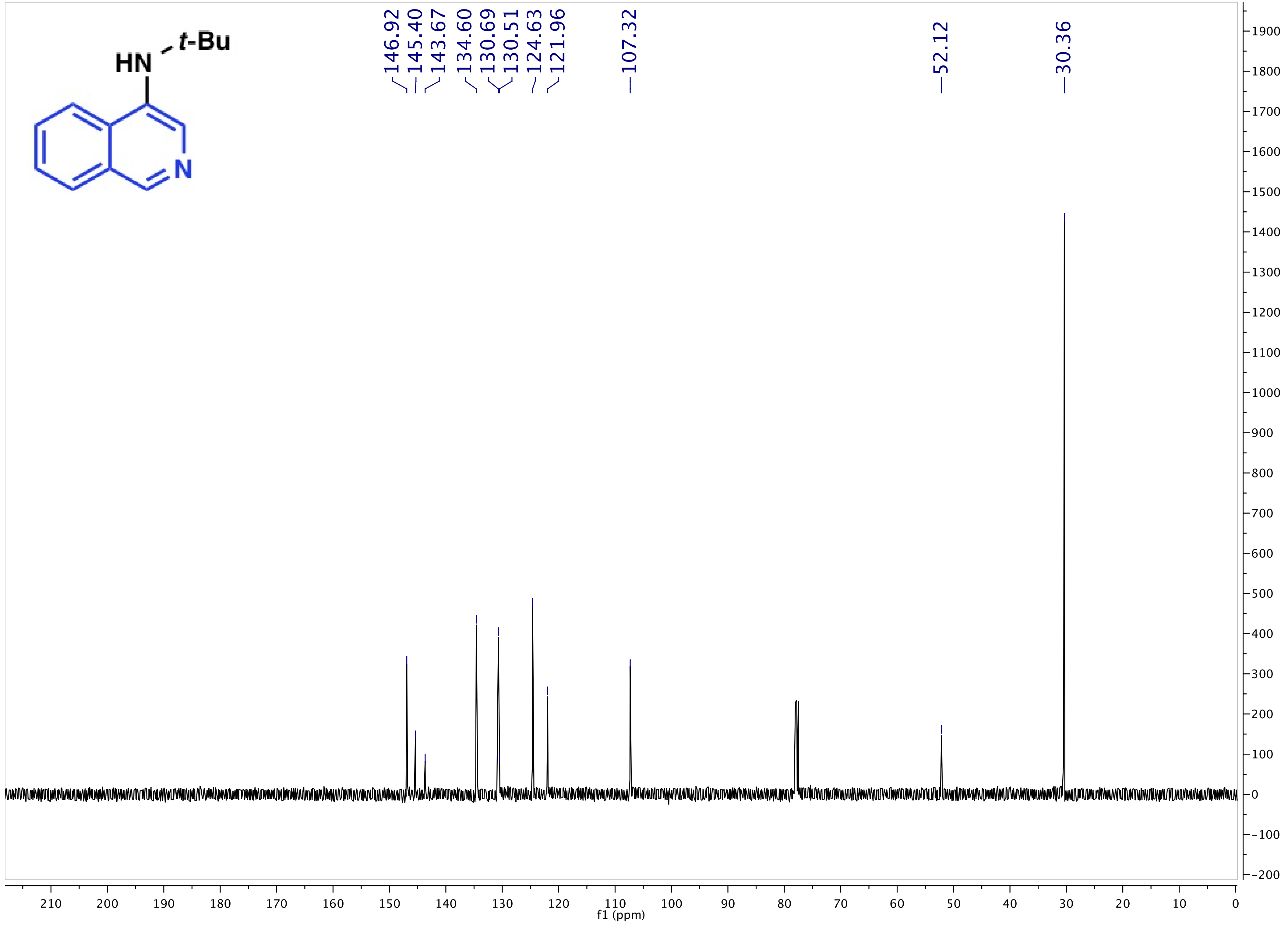

Ph
Me
Me
HN
N
150.58
148.88
147.88
145.96
130.69
129.62
129.59
127.66
125.93
125.46
119.94
119.83
103.51
57.16
31.04
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

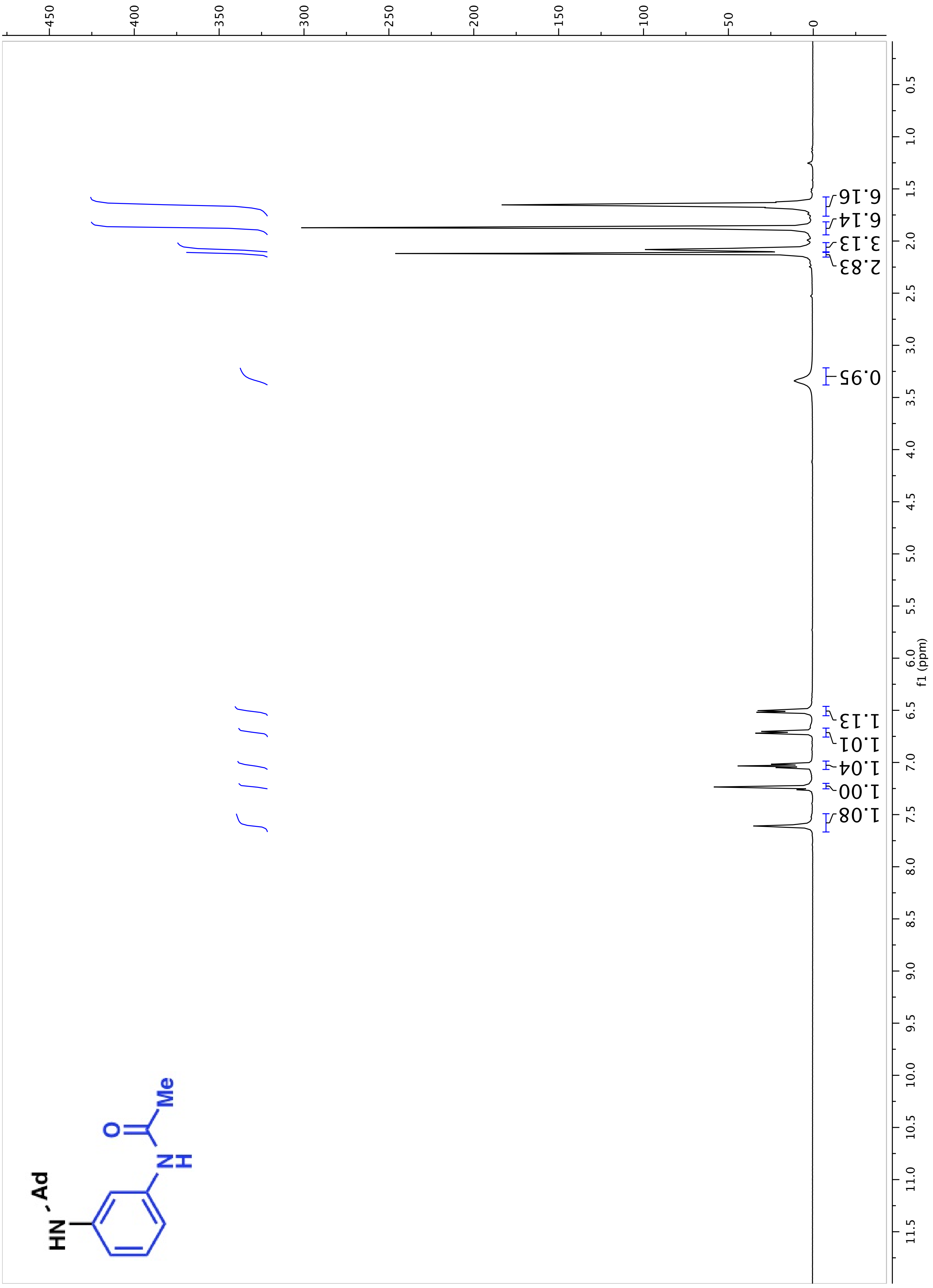

HN
Ad
1.00
1.10
1.04
1.15
1.03
1.26
3.35
6.36
6.42
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50



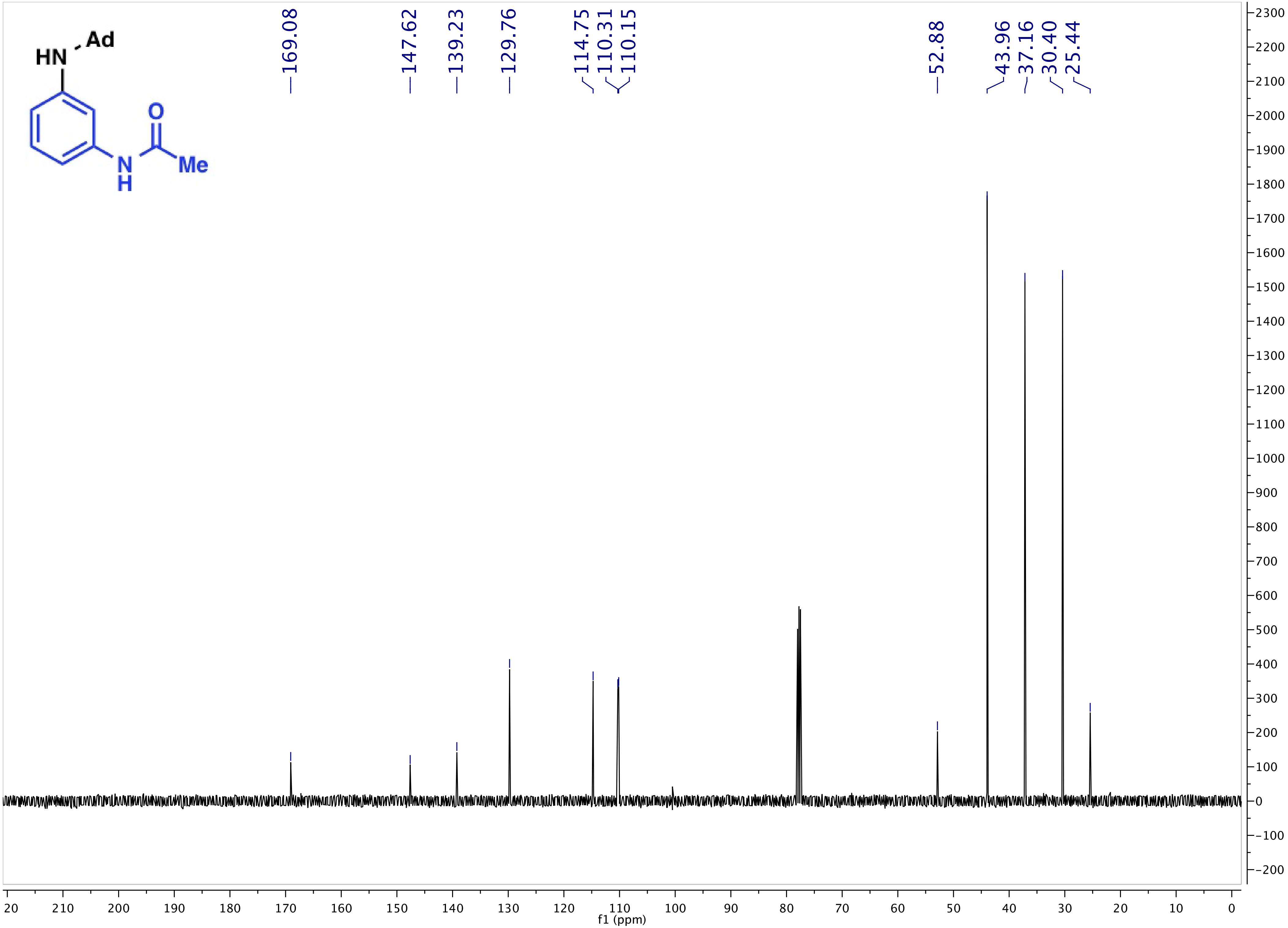
30.49
37.23
43.98
53.14
108.02
111.51
112.65
123.90
127.90
132.49
144.54
146.89
HN
Ad
O
f1 (ppm)
1000
900
800
700
600
500
400
300
200
100
0
−100
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

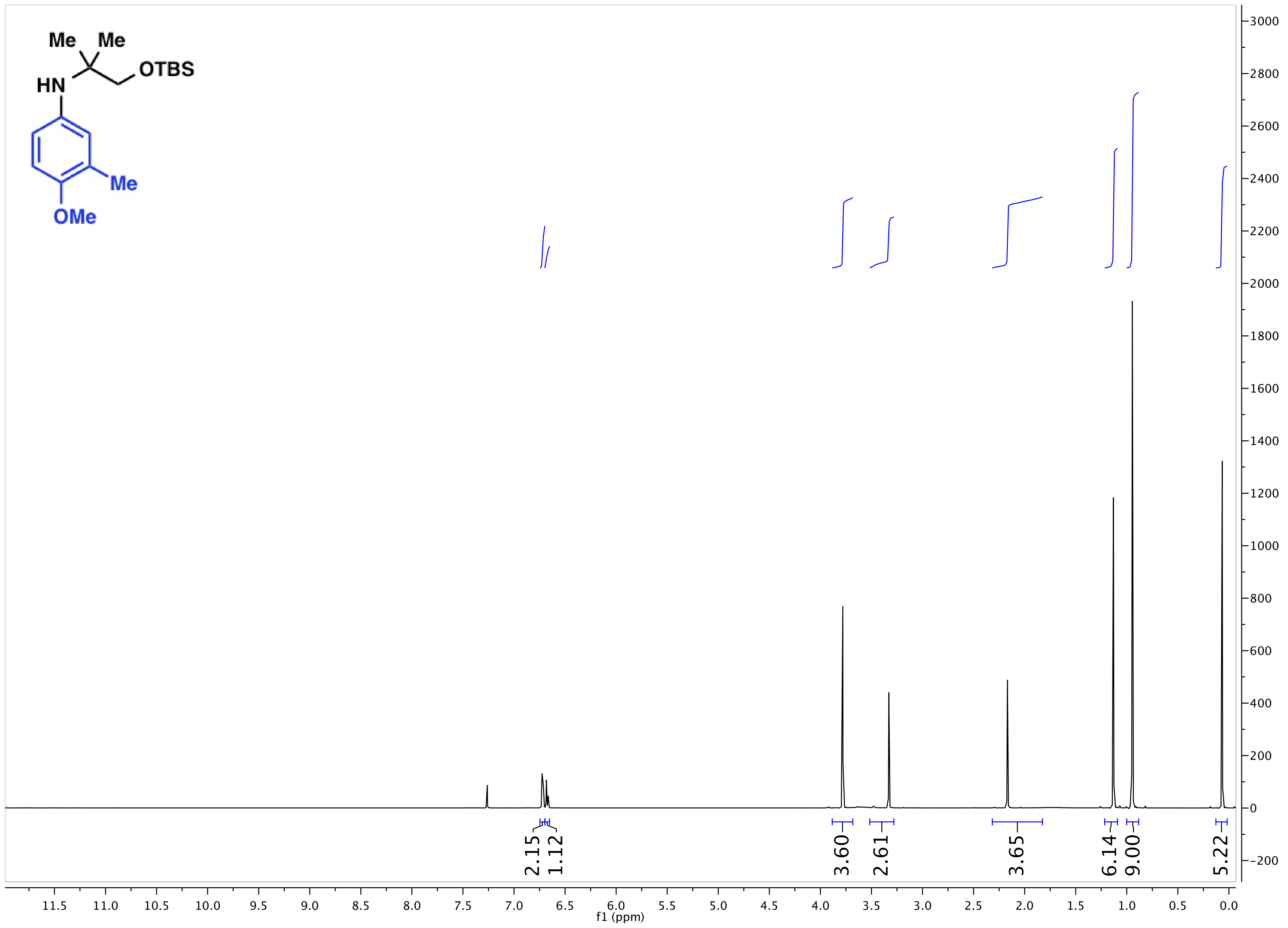
HN
t-Bu
N
8.49
1.10
0.89
0.94
1.02
0.94
1.05
1.00
f1 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

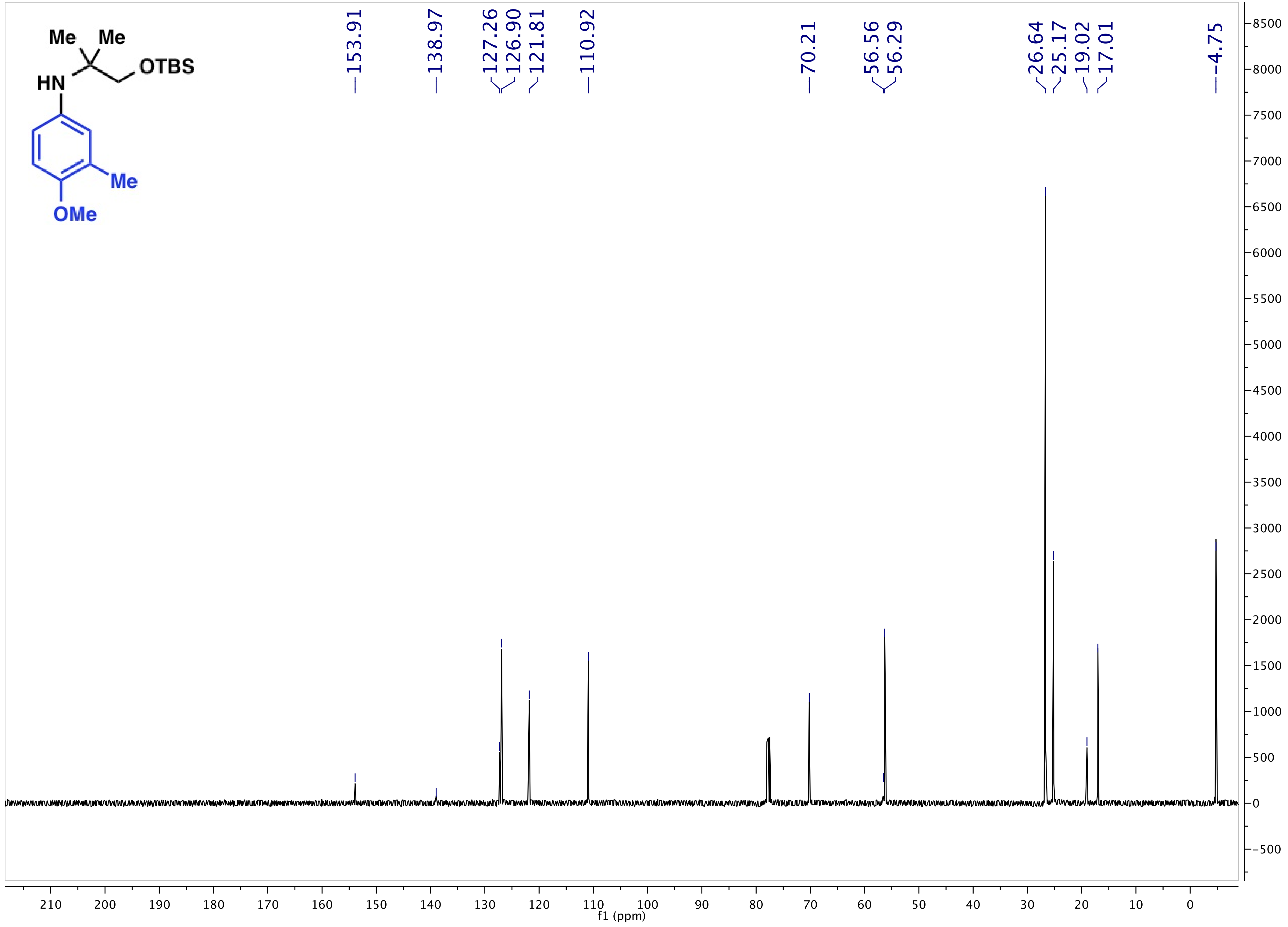

HN
t-Bu
N
146.92
145.40
143.67
134.60
130.69
130.51
124.63
121.96
107.32
52.12
30.36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200

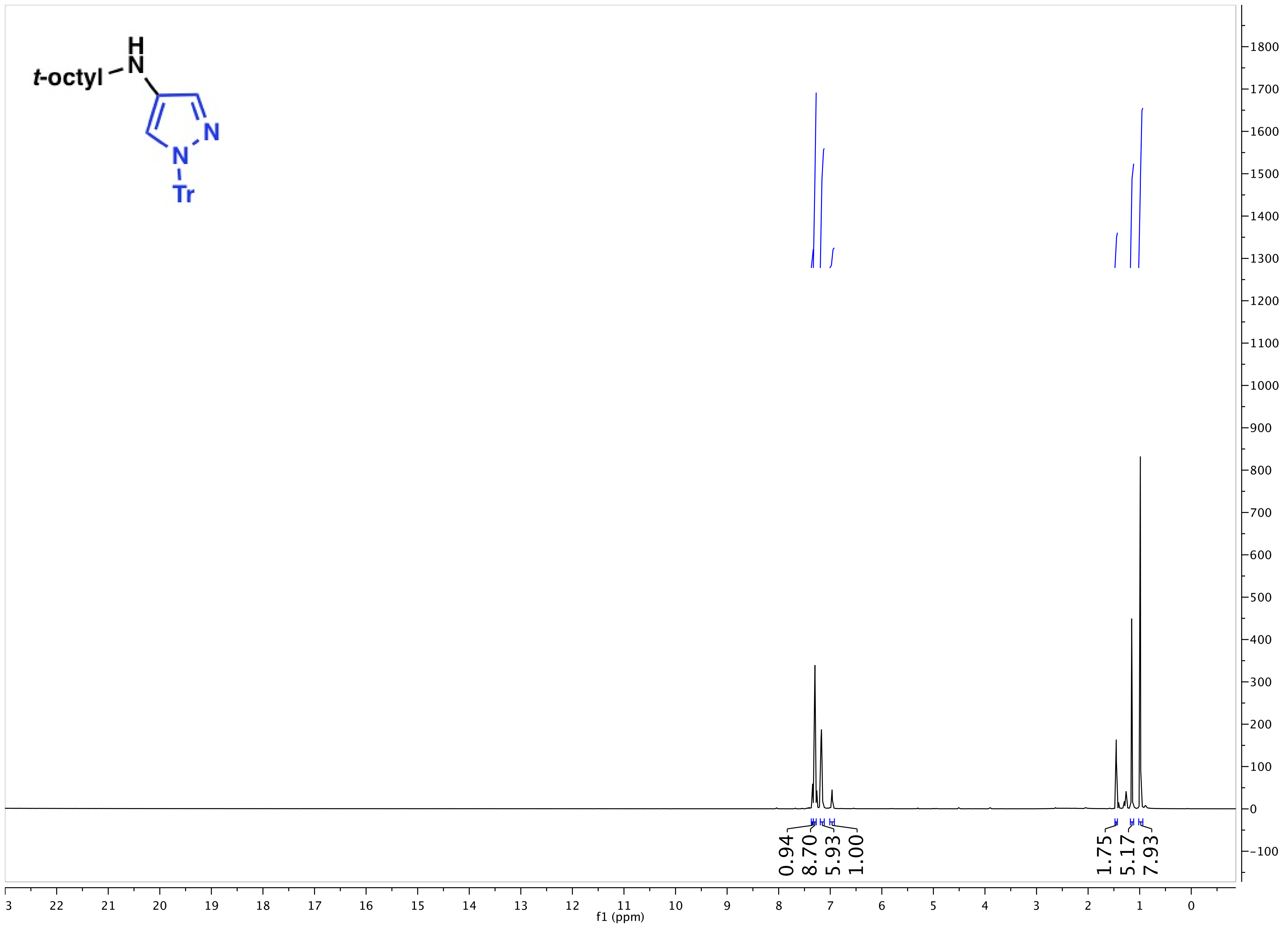


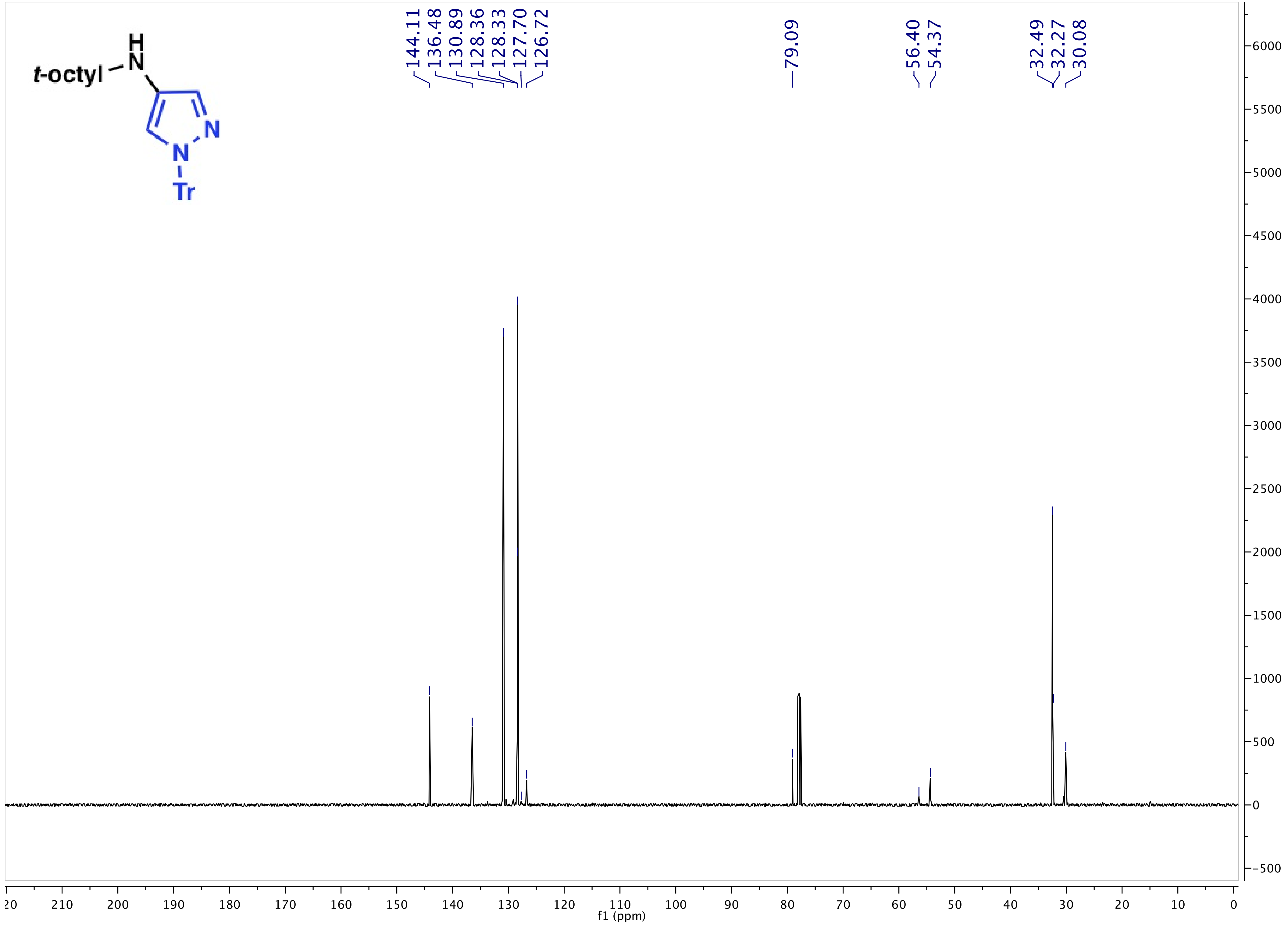
450
400
350
300
250
200
150
100
50
0
6.16
6.14
3.13
2.83
0.95
1.13
1.01
1.04
1.00
1.08
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
HN
Ad
N
H
O
Me

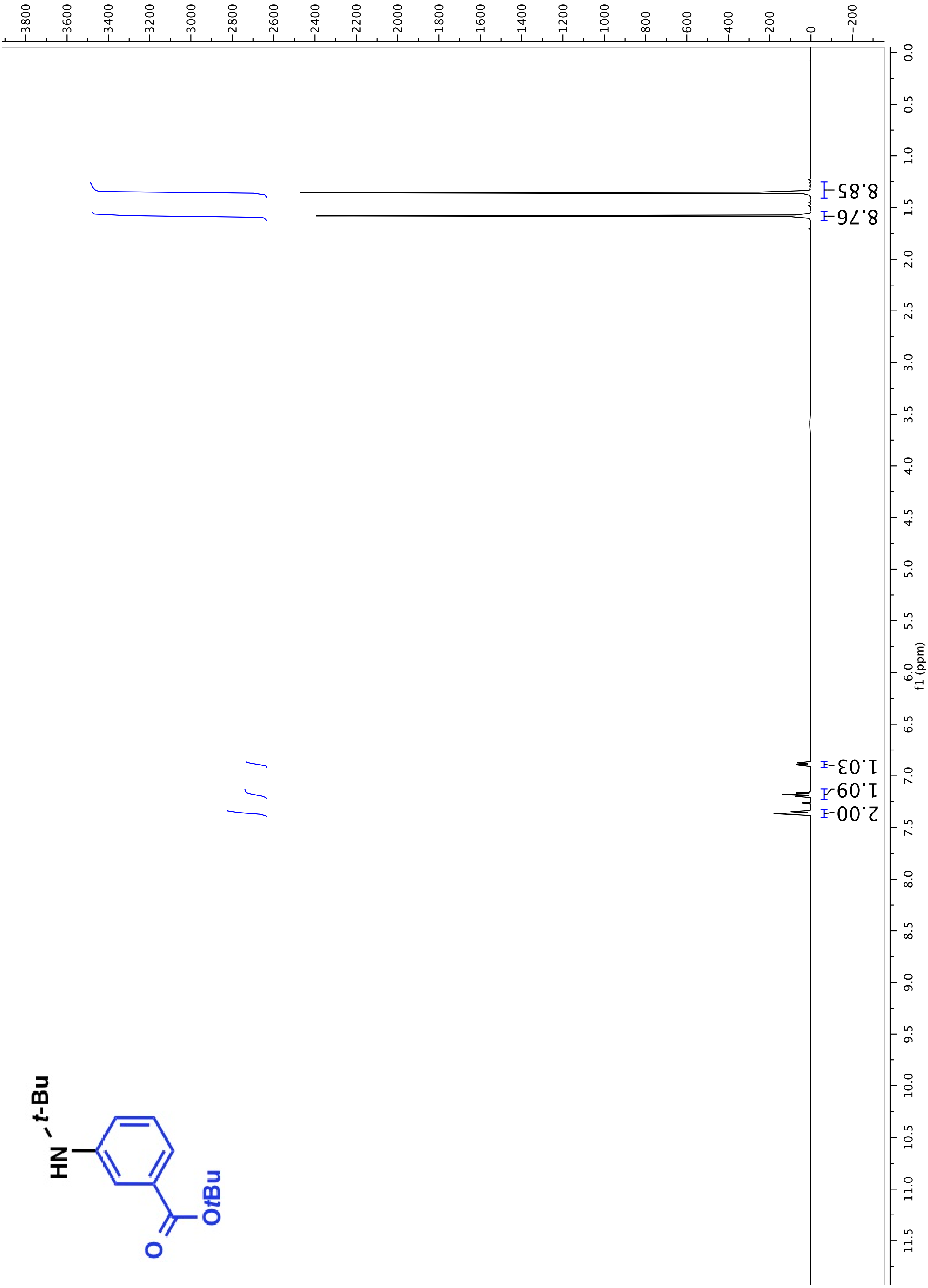

HN
Ad
N
H
O
Me
169.08
147.62
139.23
129.76
114.75
110.31
110.15
52.88
43.96
37.16
30.40
25.44
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
HN
OTBS
Me
OMe
2.15
1.12
3.60
2.61
3.65
6.14
9.00
5.22
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

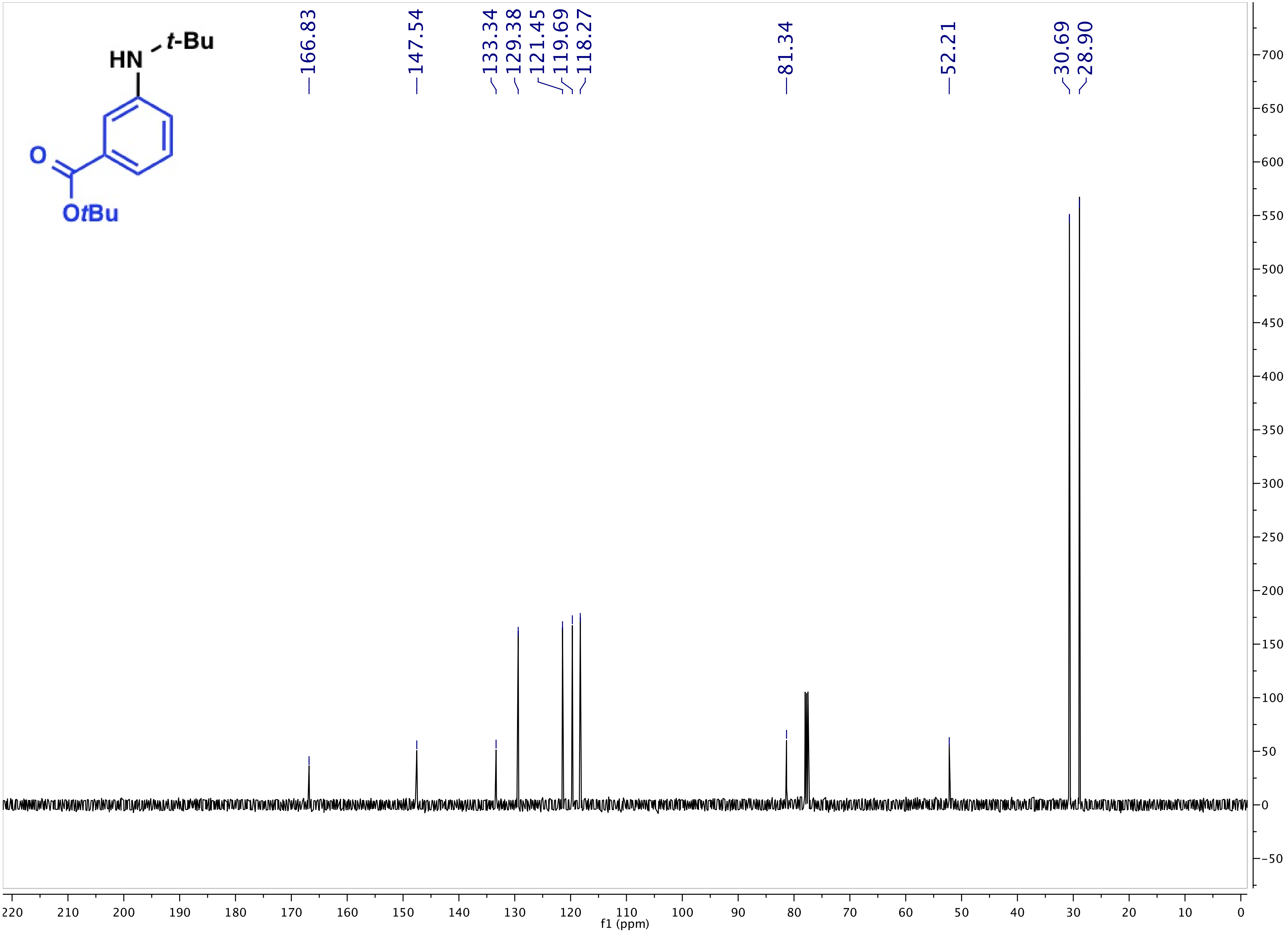

Me
Me
HN
OTBS
Me
OMe
153.91
138.97
127.26
126.90
121.81
110.92
70.21
56.56
56.29
26.64
25.17
19.02
17.01
-4.75
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

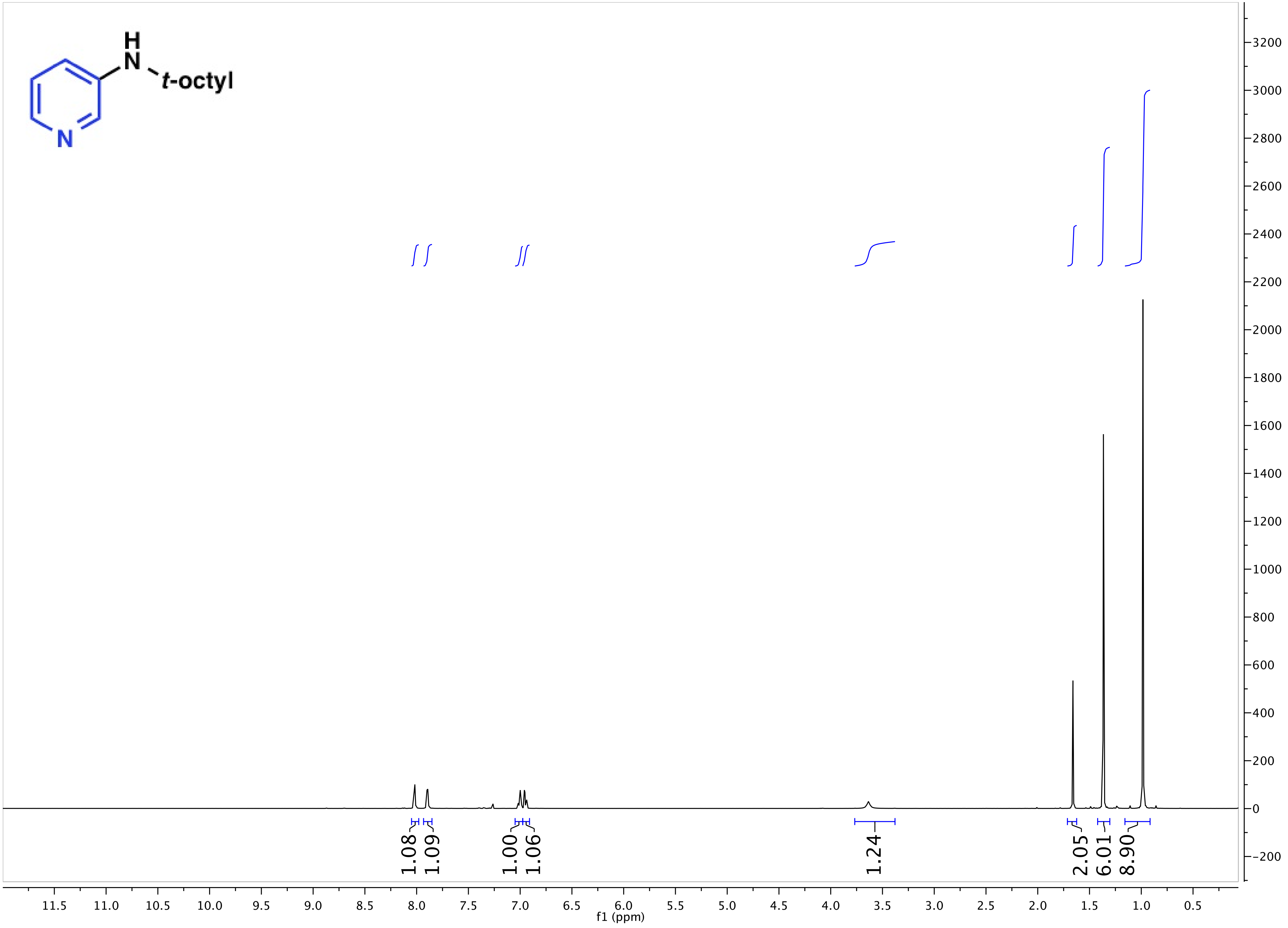

t-octyl
H
N
N
N
Tr
0.94
8.70
5.93
1.00
1.75
5.17
7.93
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
3
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

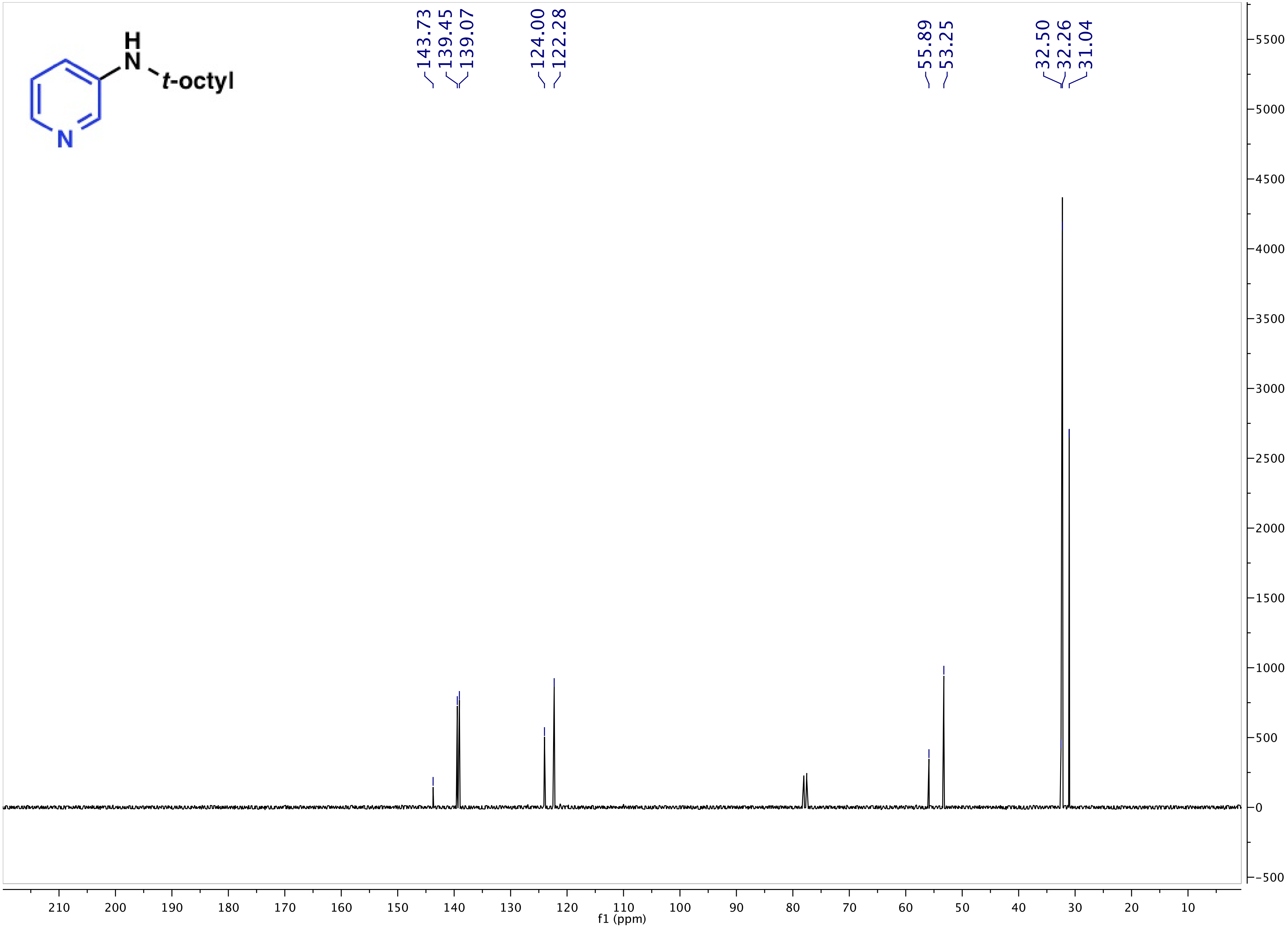

t-octyl
H
N
N
N
Tr
144.11
136.48
130.89
128.36
128.33
127.70
126.72
79.09
56.40
54.37
32.49
32.27
30.08
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

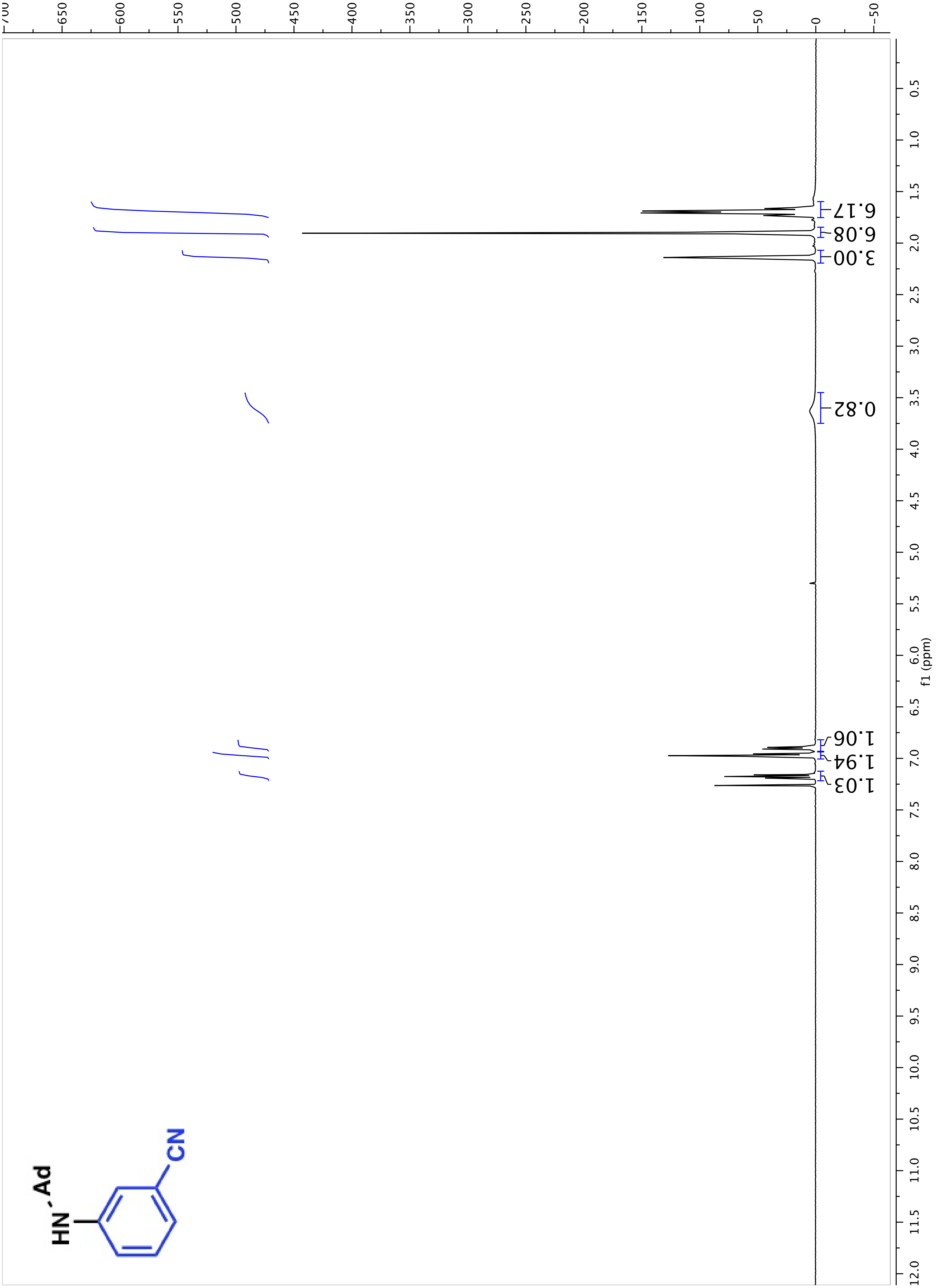


HN
t-Bu
O
OtBu
8.85
8.76
1.03
1.09
2.00
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

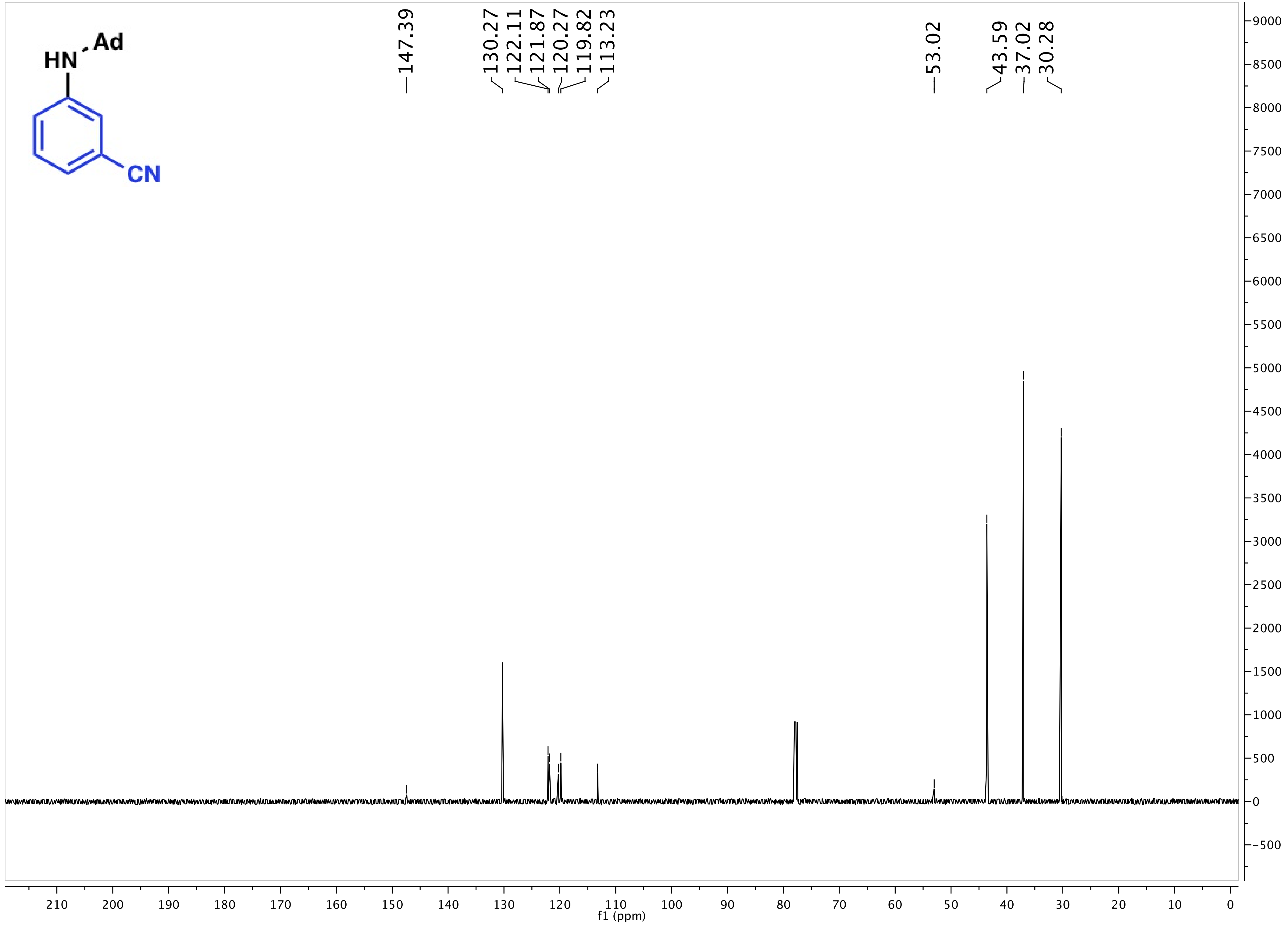

HN
t-Bu
O
OtBu
166.83
147.54
133.34
129.38
121.45
119.69
118.27
81.34
52.21
30.69
28.90
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

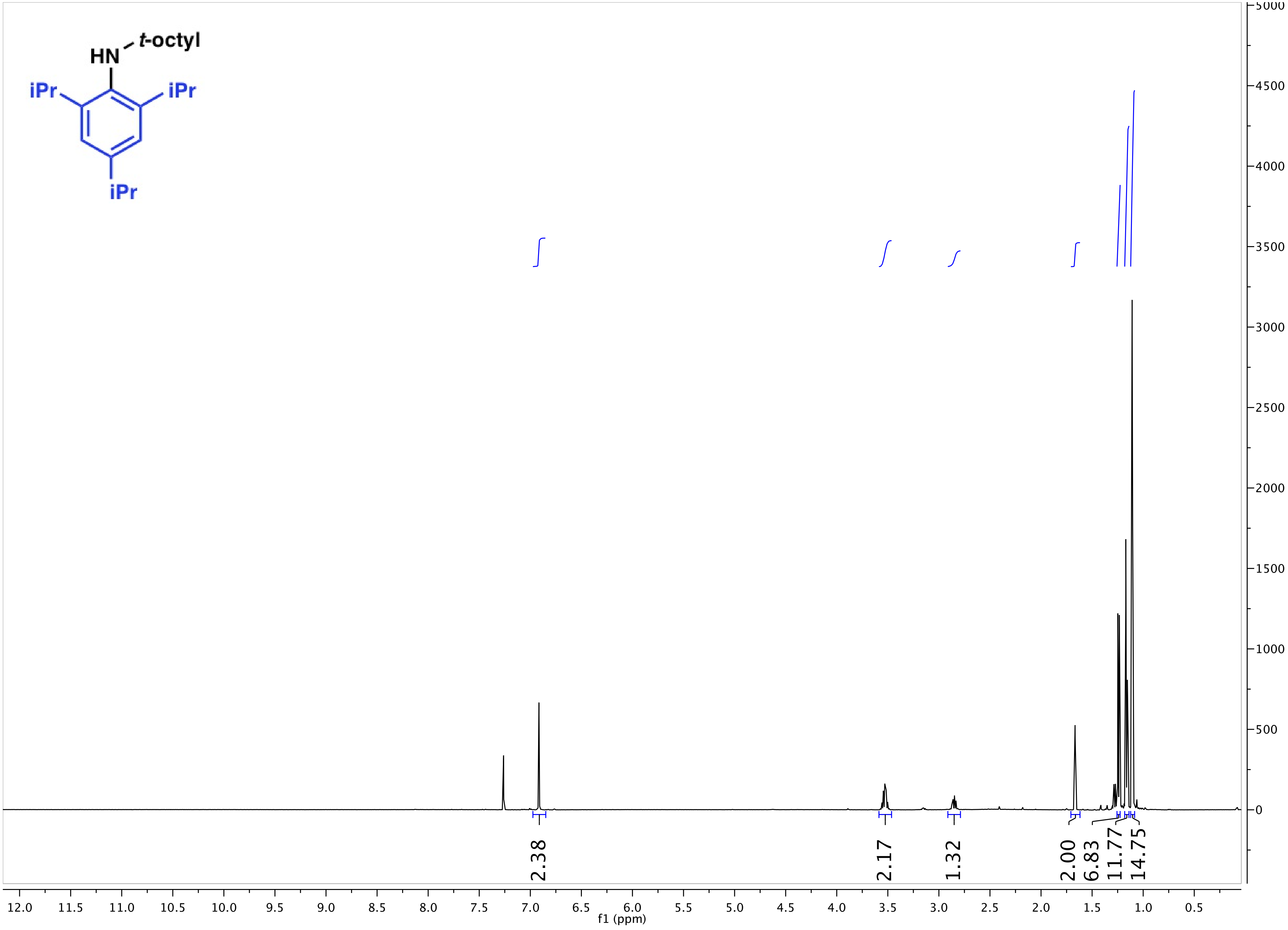

H
N
t-octyl
N
1.08
1.09
1.00
1.06
1.24
2.05
6.01
8.90
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

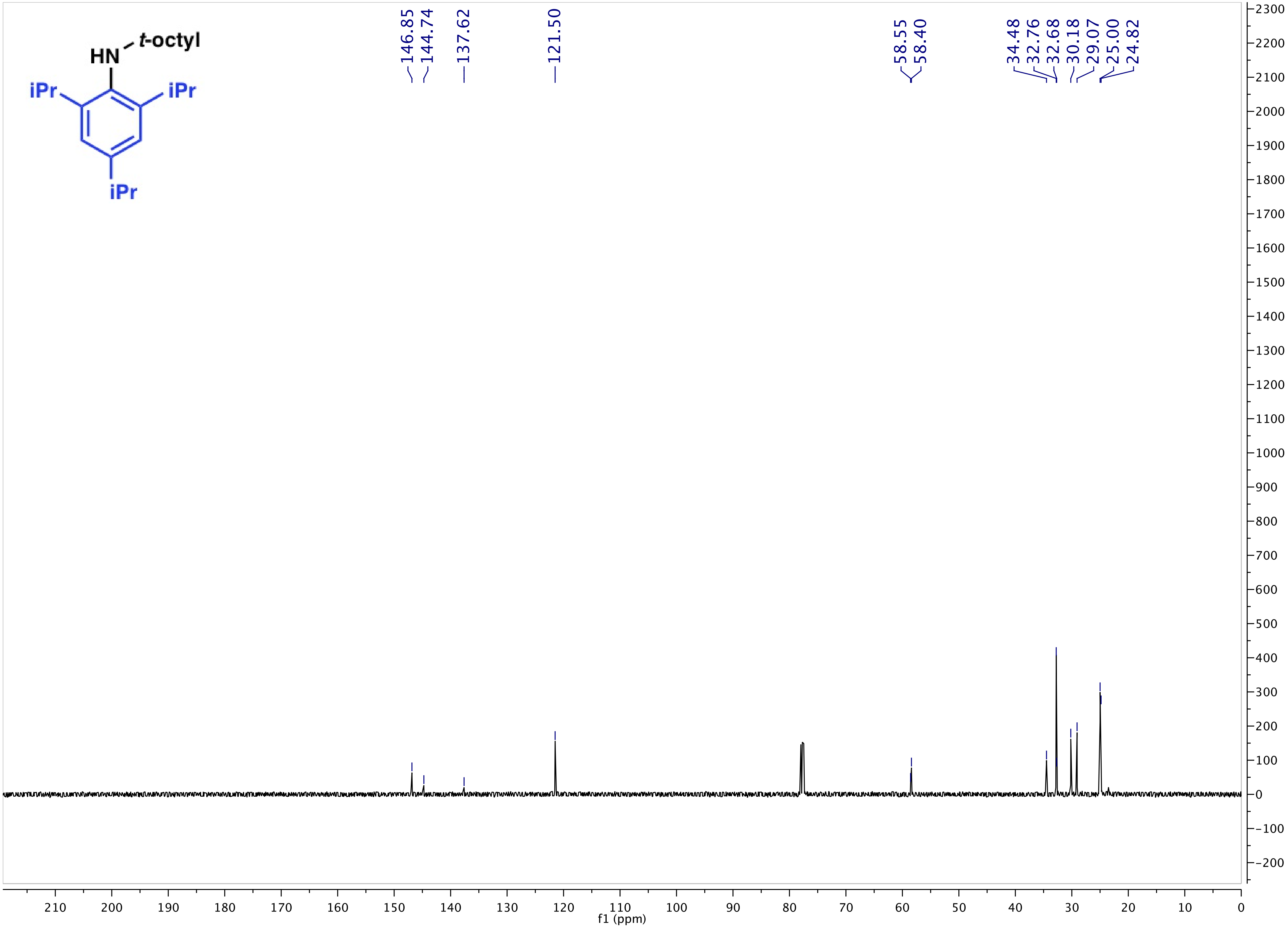

N
H
t-octyl
143.73
139.45
139.07
124.00
122.28
55.89
53.25
32.50
32.26
31.04
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

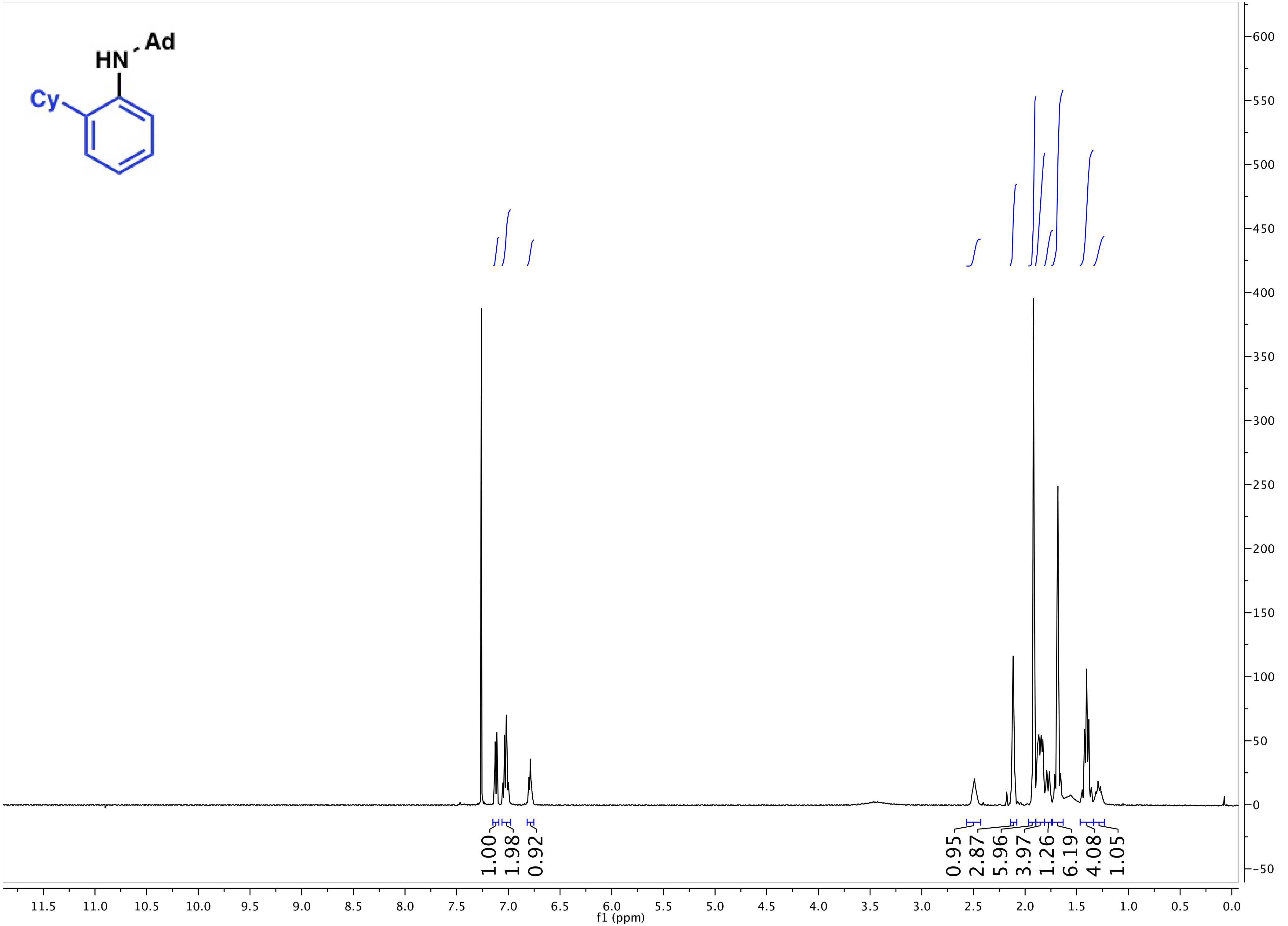


HN
Ad
CN
6.17
6.08
3.00
0.82
1.06
1.94
1.03
f1 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

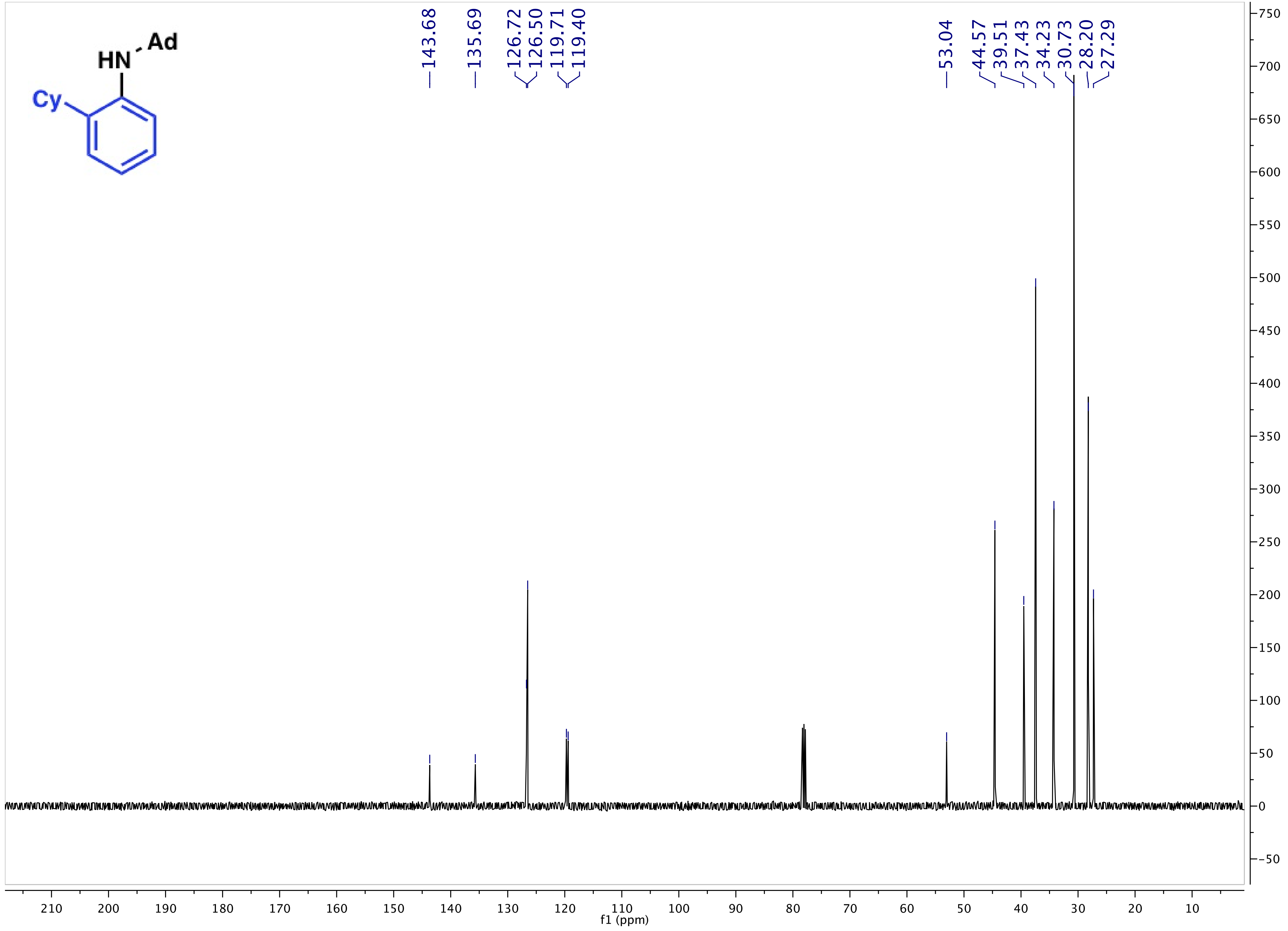

HN
Ad
CN
147.39
130.27
122.11
121.87
120.27
119.82
113.23
53.02
43.59
37.02
30.28
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
–500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HN
t-octyl
iPr
iPr
iPr
2.38
2.17
1.32
2.00
6.83
11.77
14.75
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

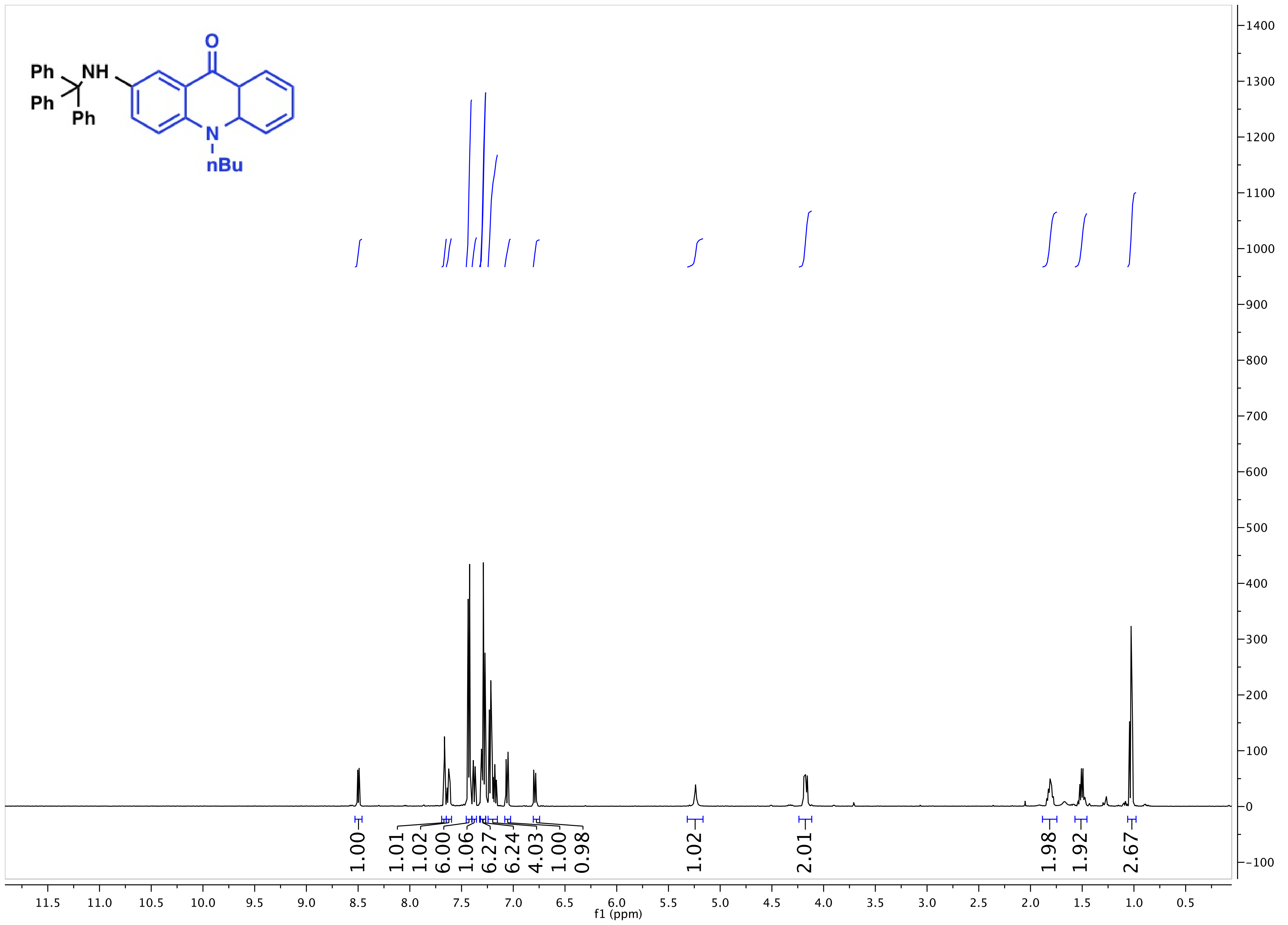

HN
t-octyl
iPr
iPr
iPr
146.85
144.74
137.62
121.50
58.55
58.40
34.48
32.76
32.68
30.18
29.07
25.00
24.82
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

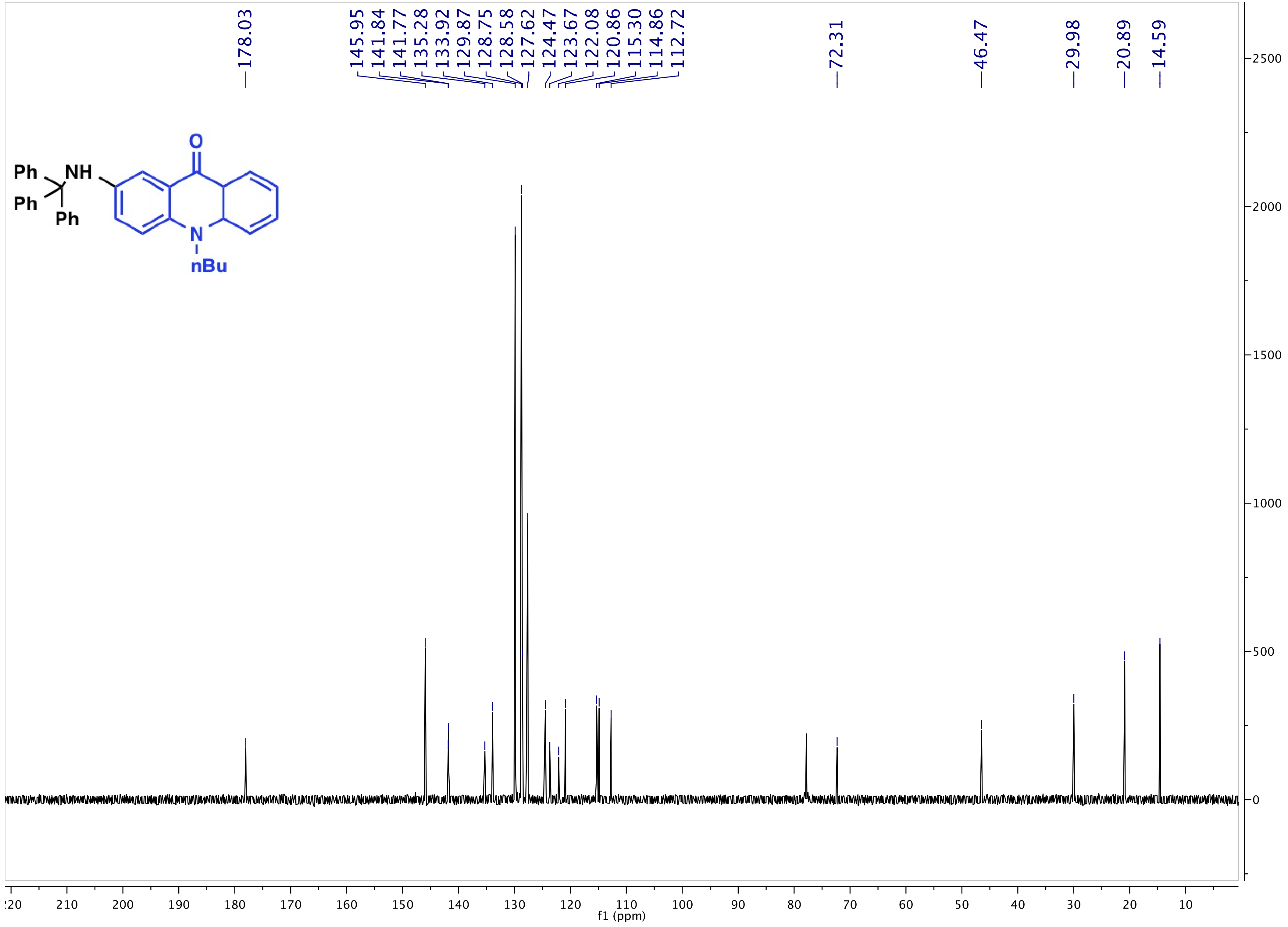


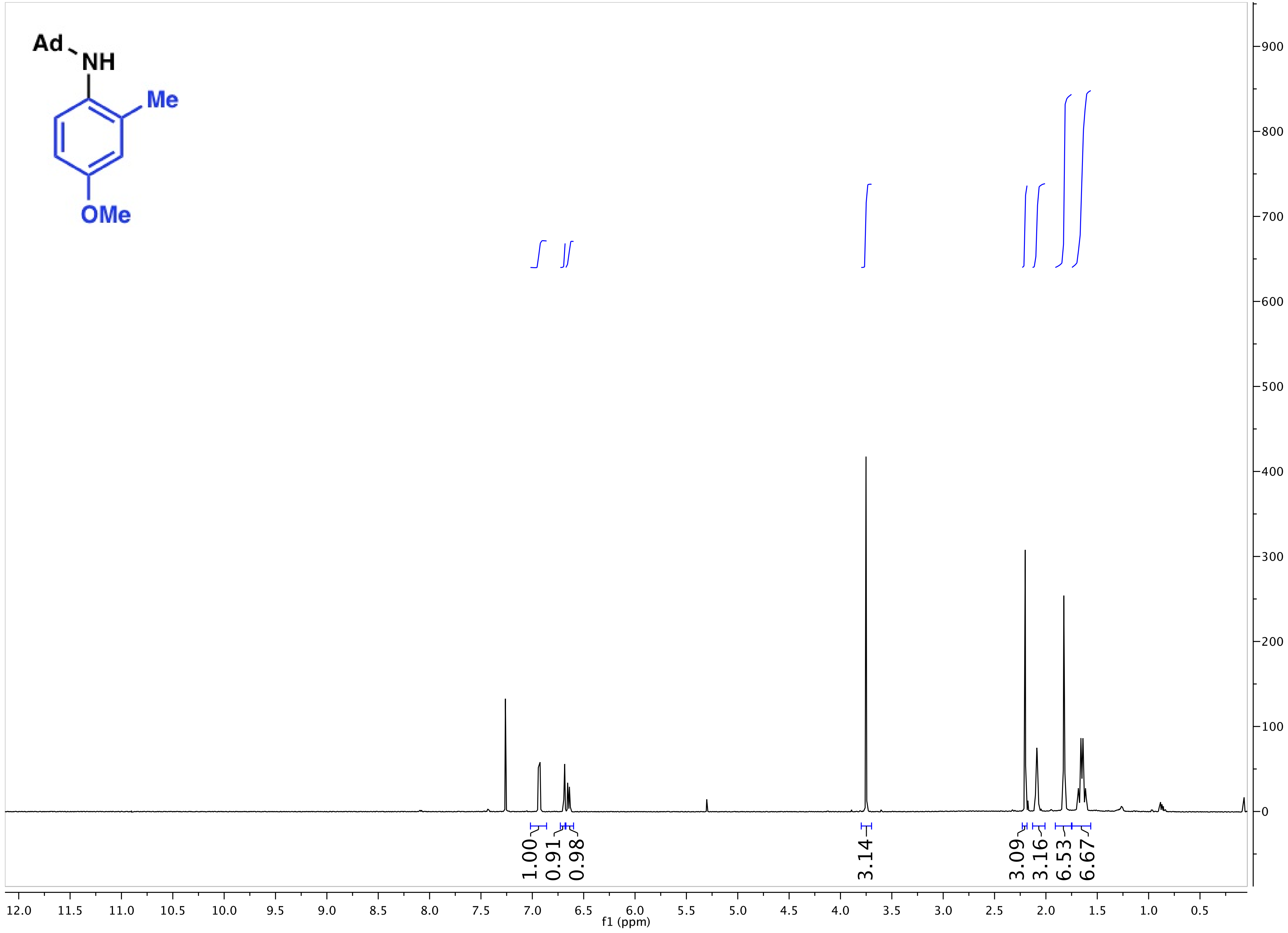
HN
Ad
Cy
1.00
1.98
0.92
0.95
2.87
5.96
3.97
1.26
6.19
4.08
1.05
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

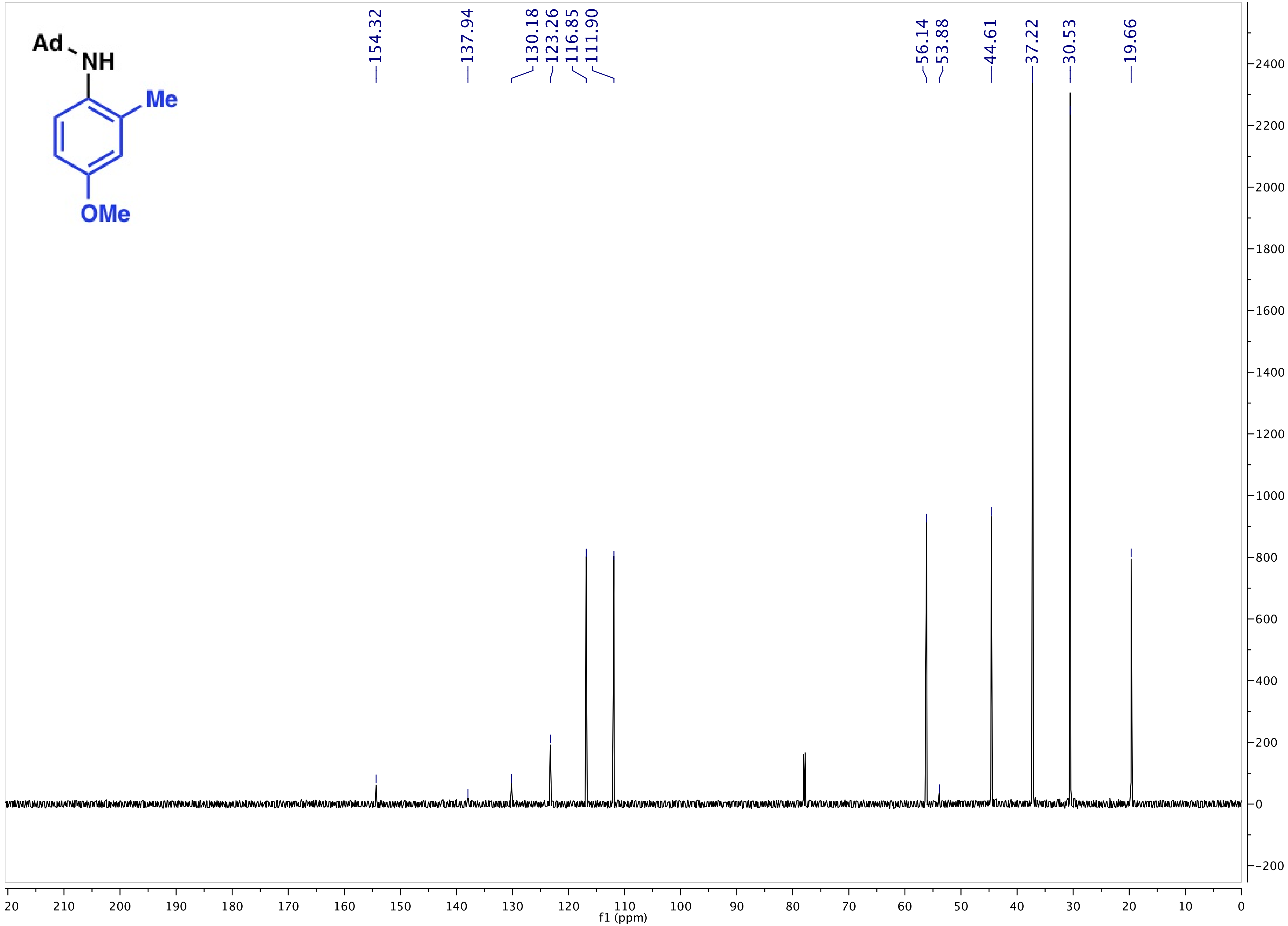


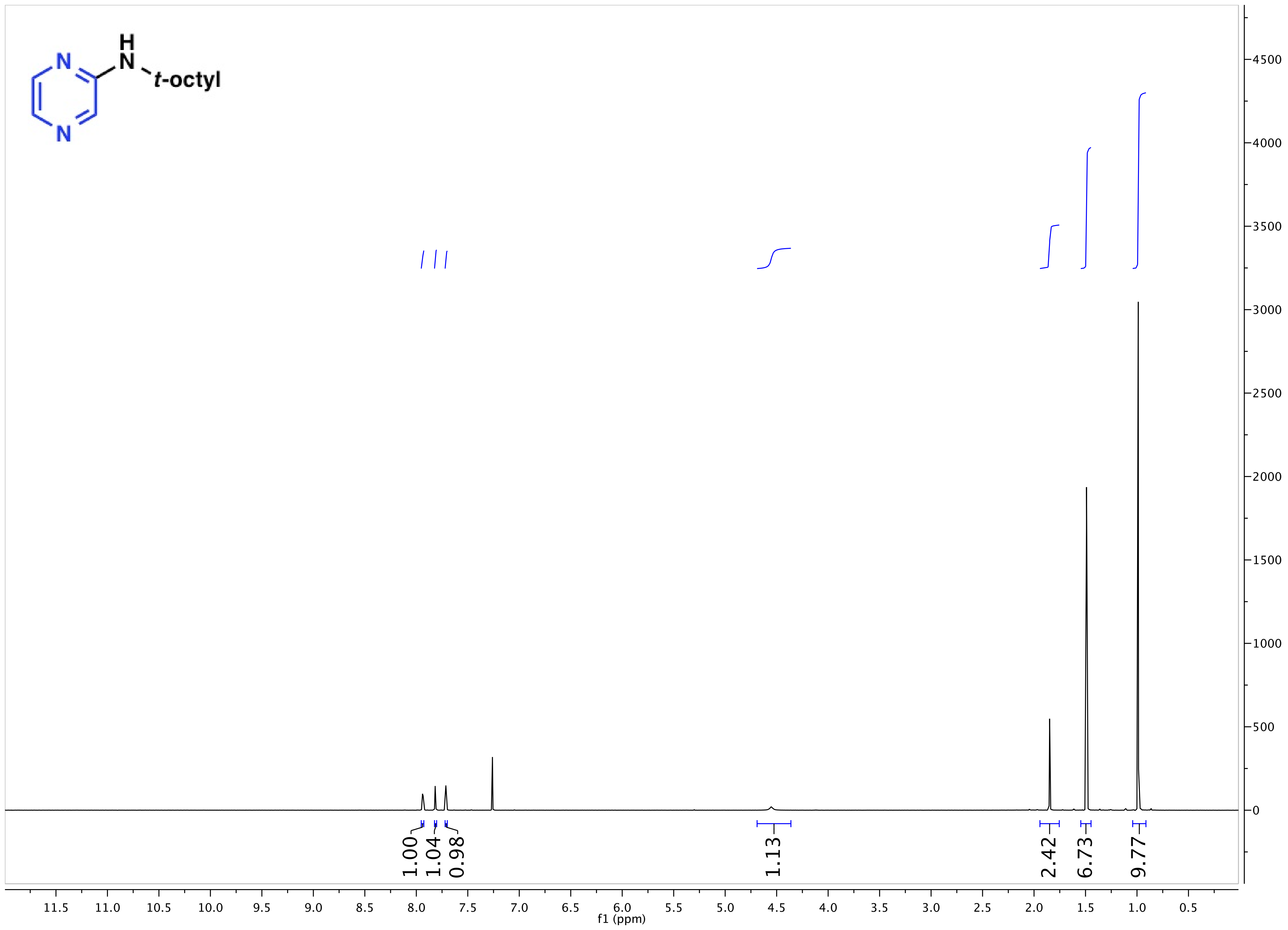
HN
Ad
Cy
143.68
135.69
126.72
126.50
119.71
119.40
53.04
44.57
39.51
37.43
34.23
30.73
28.20
27.29
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

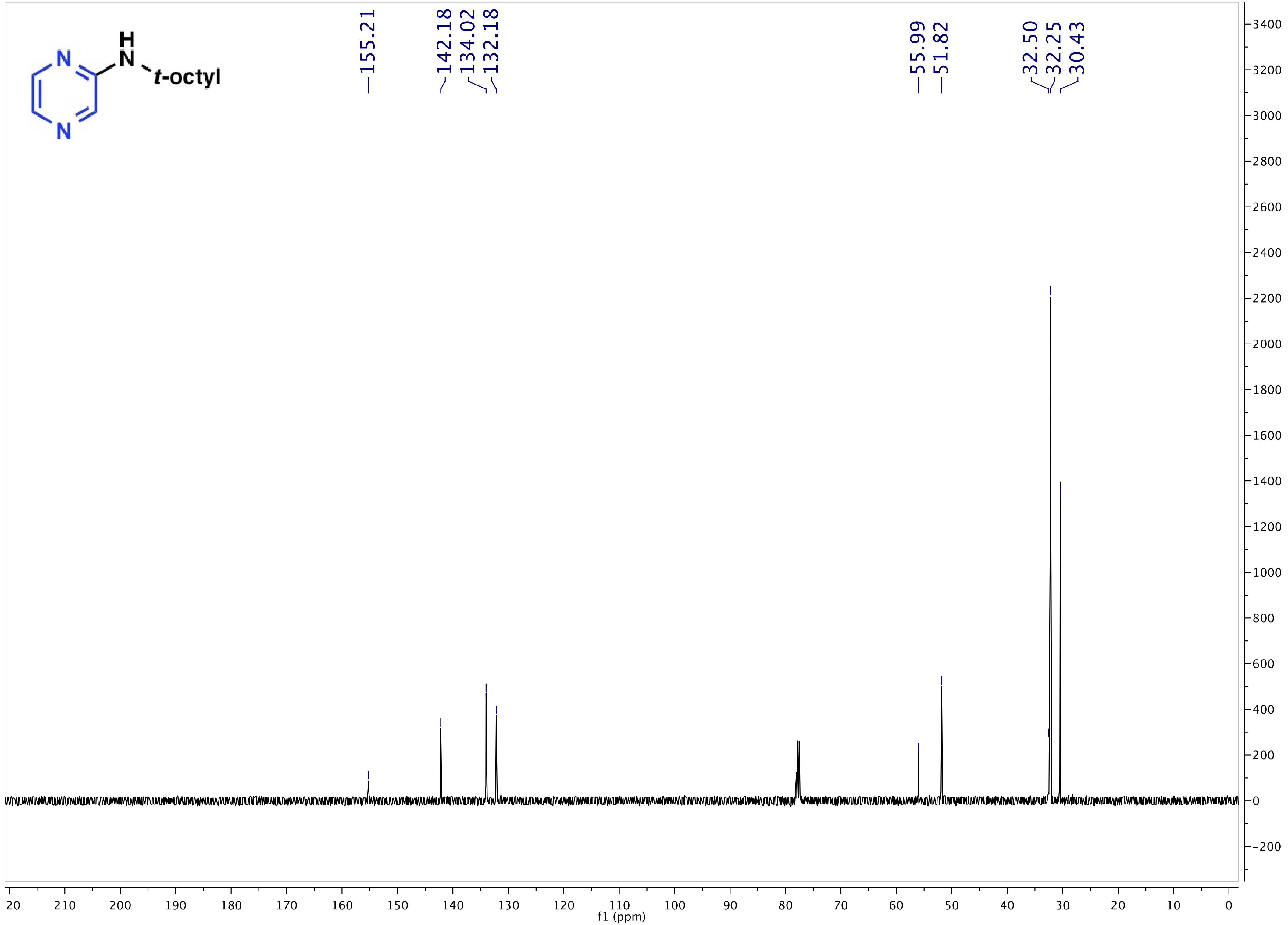

O
Ph
NH
Ph
Ph
N
nBu
1.00
1.01
1.02
6.00
1.06
6.27
6.24
4.03
1.00
0.98
1.02
2.01
1.98
1.92
2.67
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

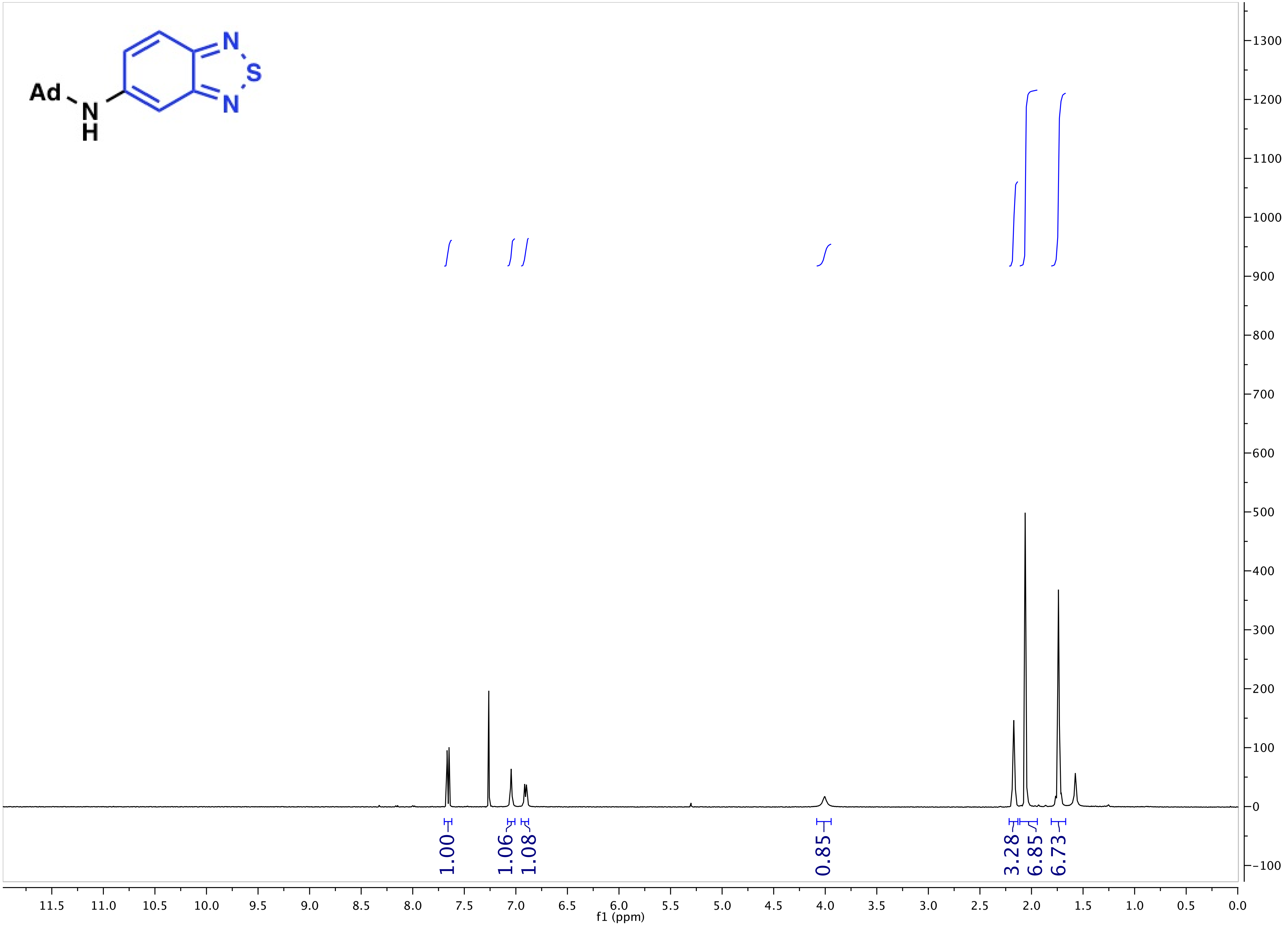

178.03
145.95
141.84
141.77
135.28
133.92
129.87
128.75
128.58
127.62
124.47
123.67
122.08
120.86
115.30
114.86
112.72
72.31
46.47
29.98
20.89
14.59
Ph
NH
Ph
Ph
O
N
nBu
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
2500
2000
1500
1000
500
0

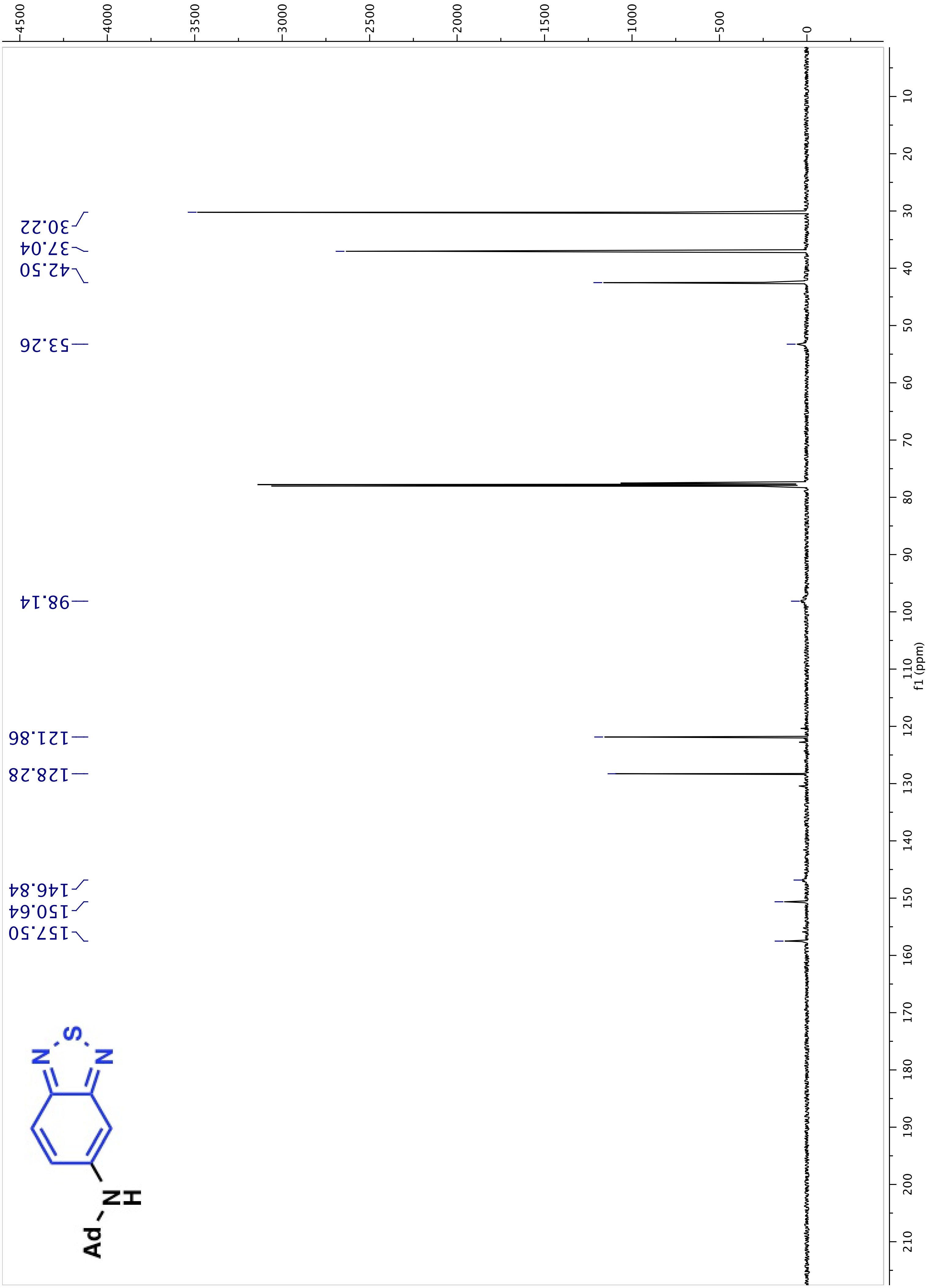

Ad
NH
Me
OMe
1.00
0.91
0.98
3.14
3.09
3.16
6.53
6.67
900
800
700
600
500
400
300
200
100
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

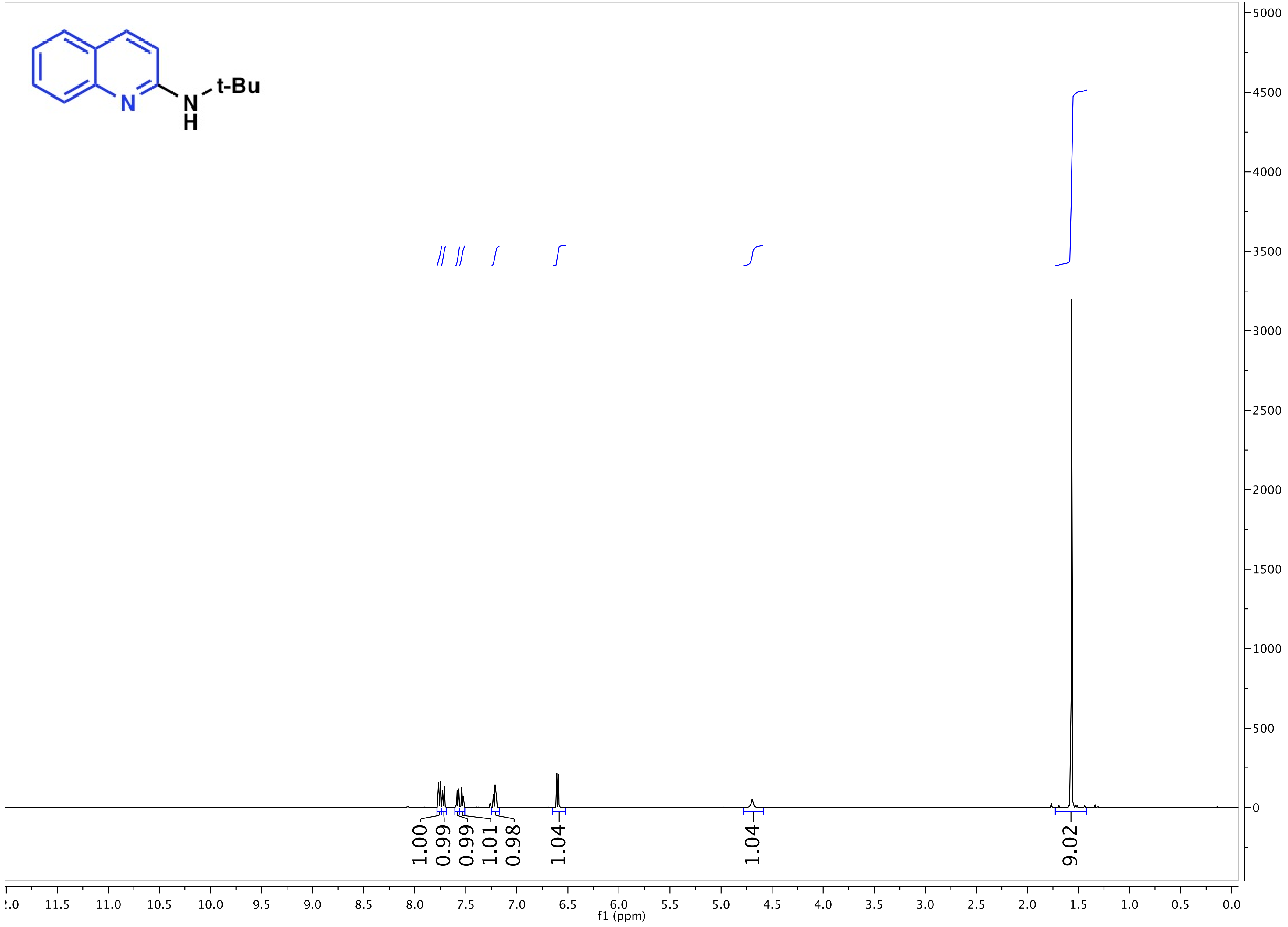

Ad
NH
Me
OMe
154.32
137.94
130.18
123.26
116.85
111.90
56.14
53.88
44.61
37.22
30.53
19.66
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

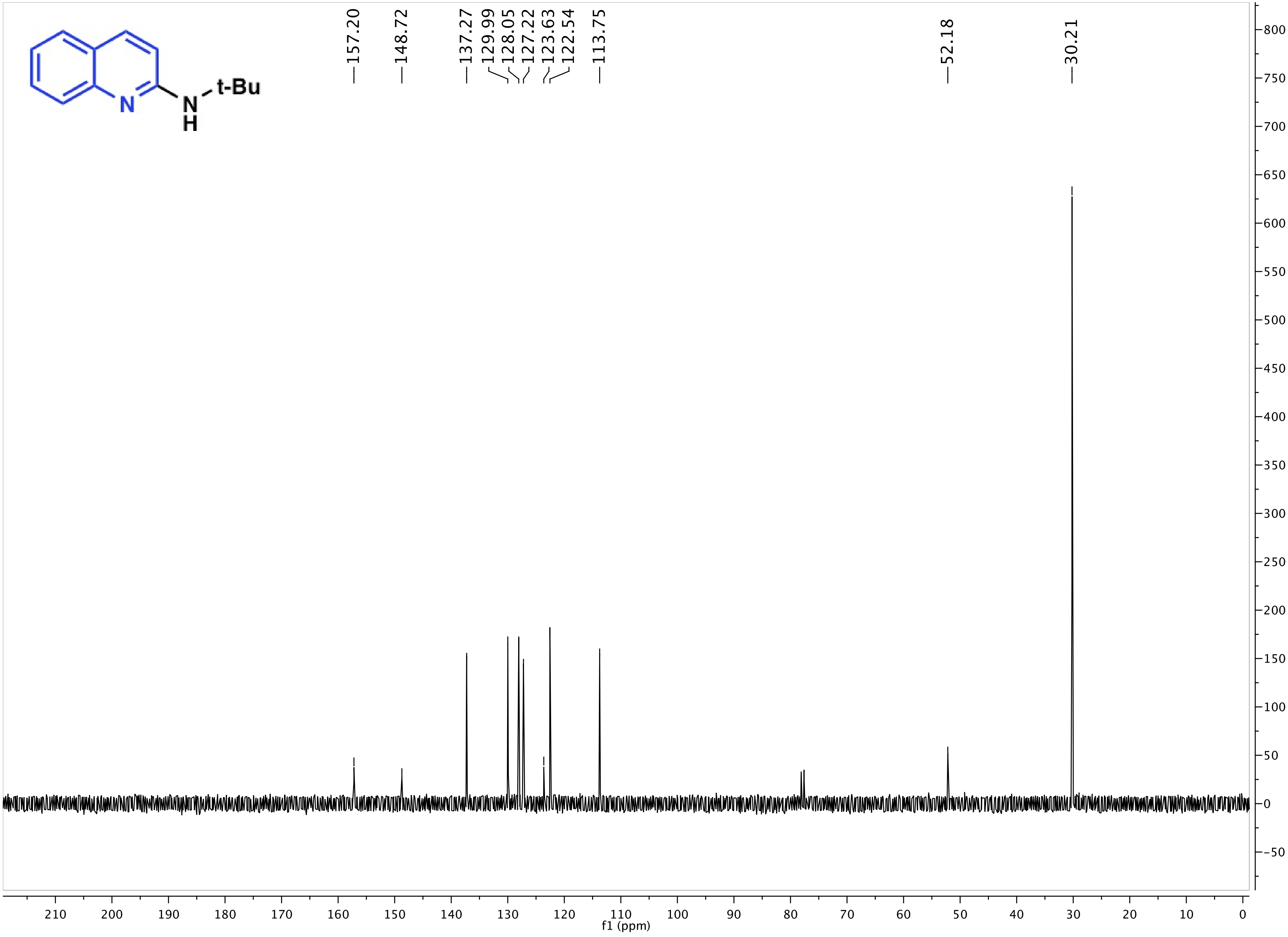

N
N
H
N
t-octyl
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.04
0.98
1.13
2.42
6.73
9.77
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

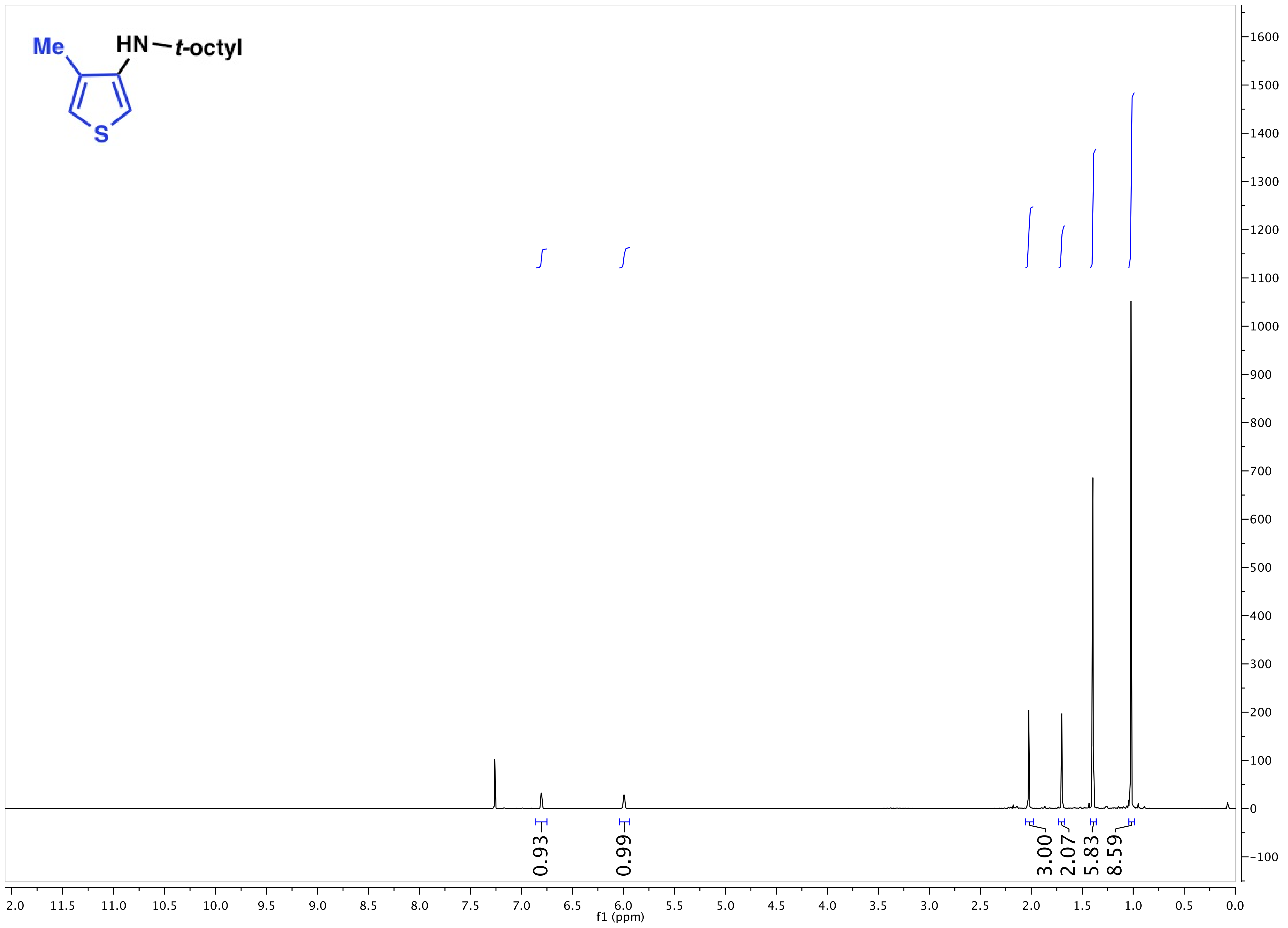

N
H
N
t-octyl
155.21
142.18
134.02
132.18
55.99
51.82
32.50
32.25
30.43
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

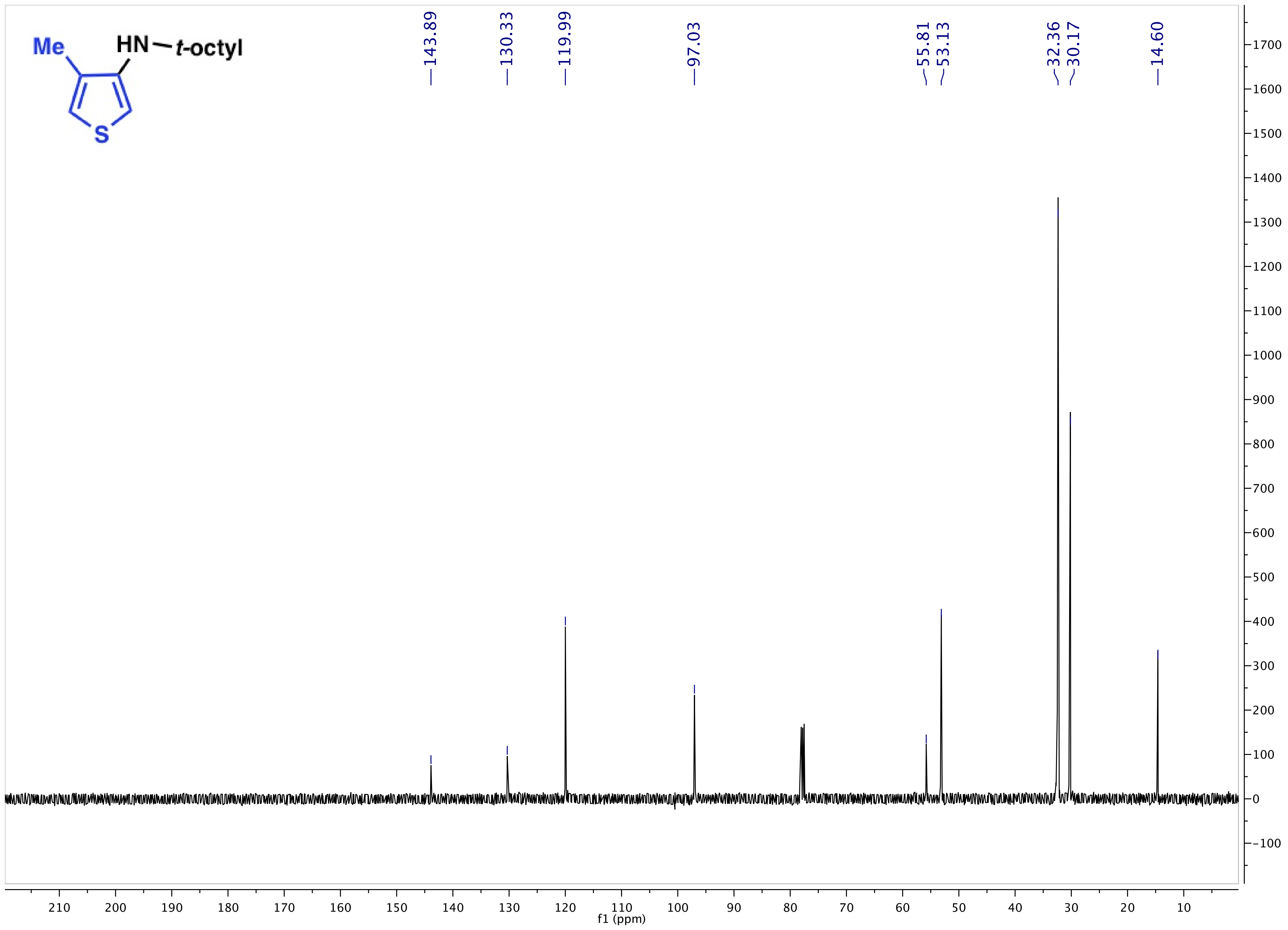

Ad
N
H
N
S
N
1.00
1.06
1.08
0.85
3.28
6.85
6.73
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100


30.22
37.04
42.50
53.26
98.14
121.86
128.28
146.84
150.64
157.50
Ad
N
H
N
S
N
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
4500
4000
3500
3000
2500
2000
1500
1000
500
0

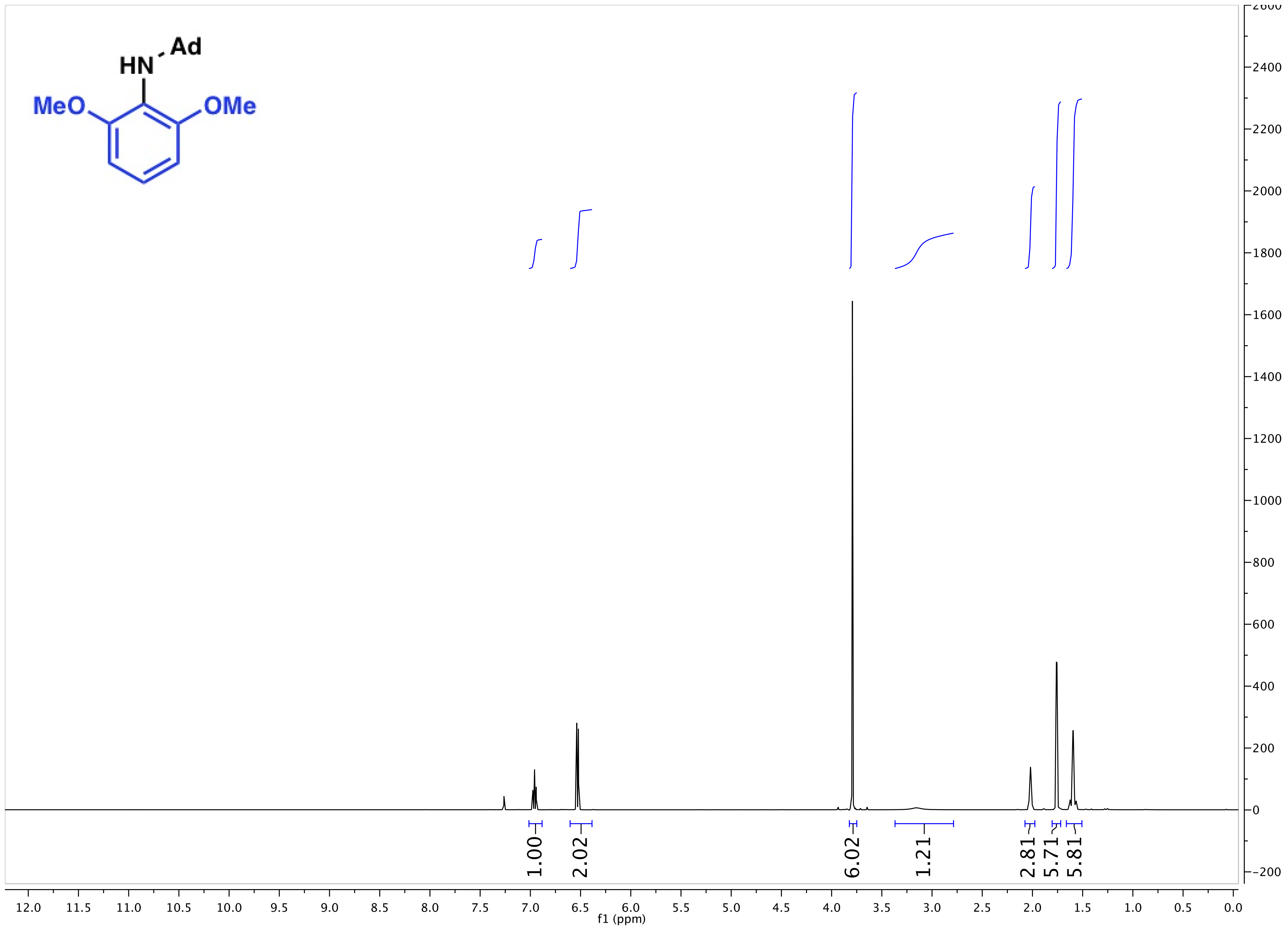

t-Bu
N
H
N
1.00
0.99
0.99
1.01
0.98
1.04
1.04
9.02
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

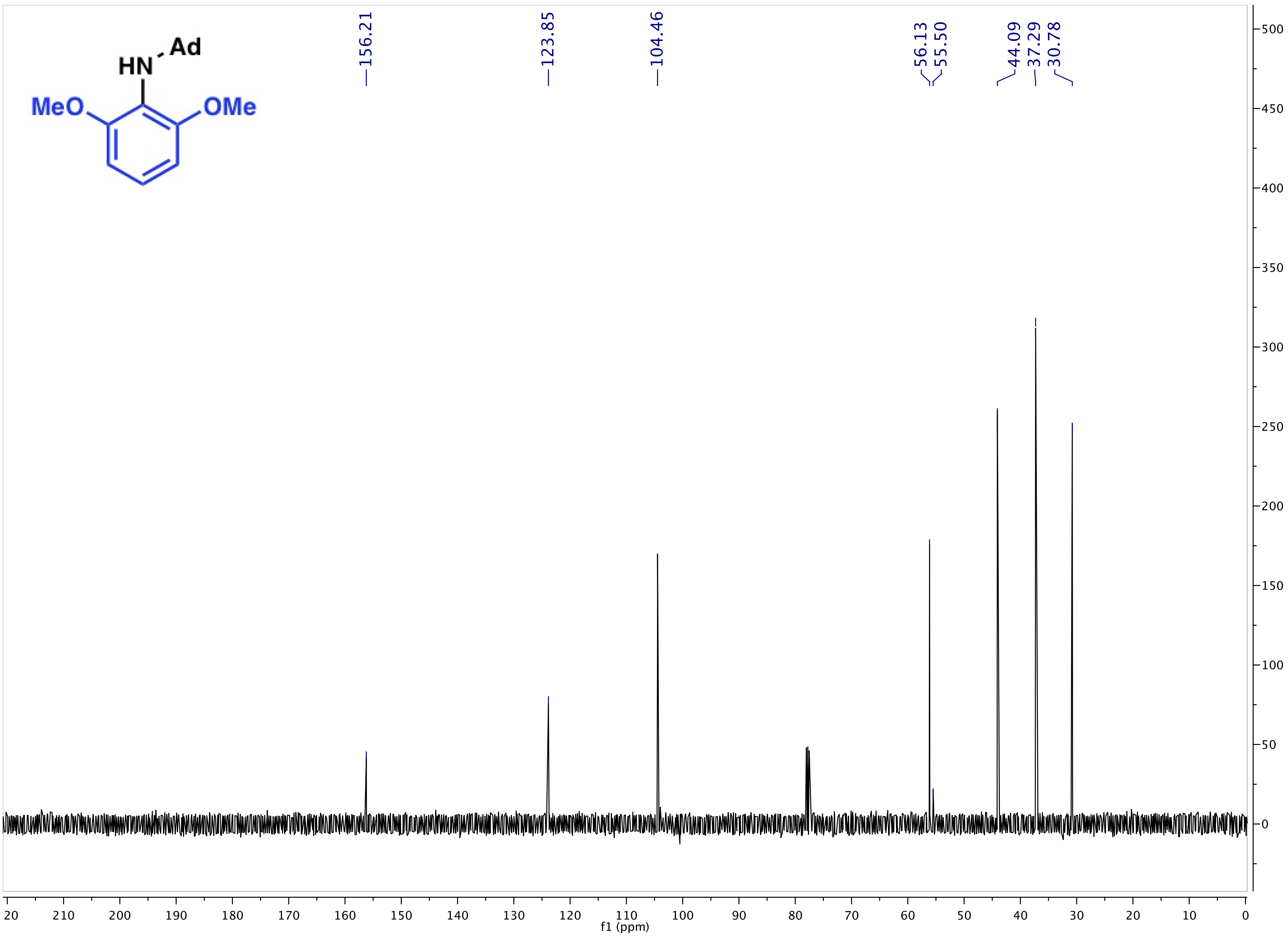

N
N
H
t-Bu
157.20
148.72
137.27
129.99
128.05
127.22
123.63
122.54
113.75
52.18
30.21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50

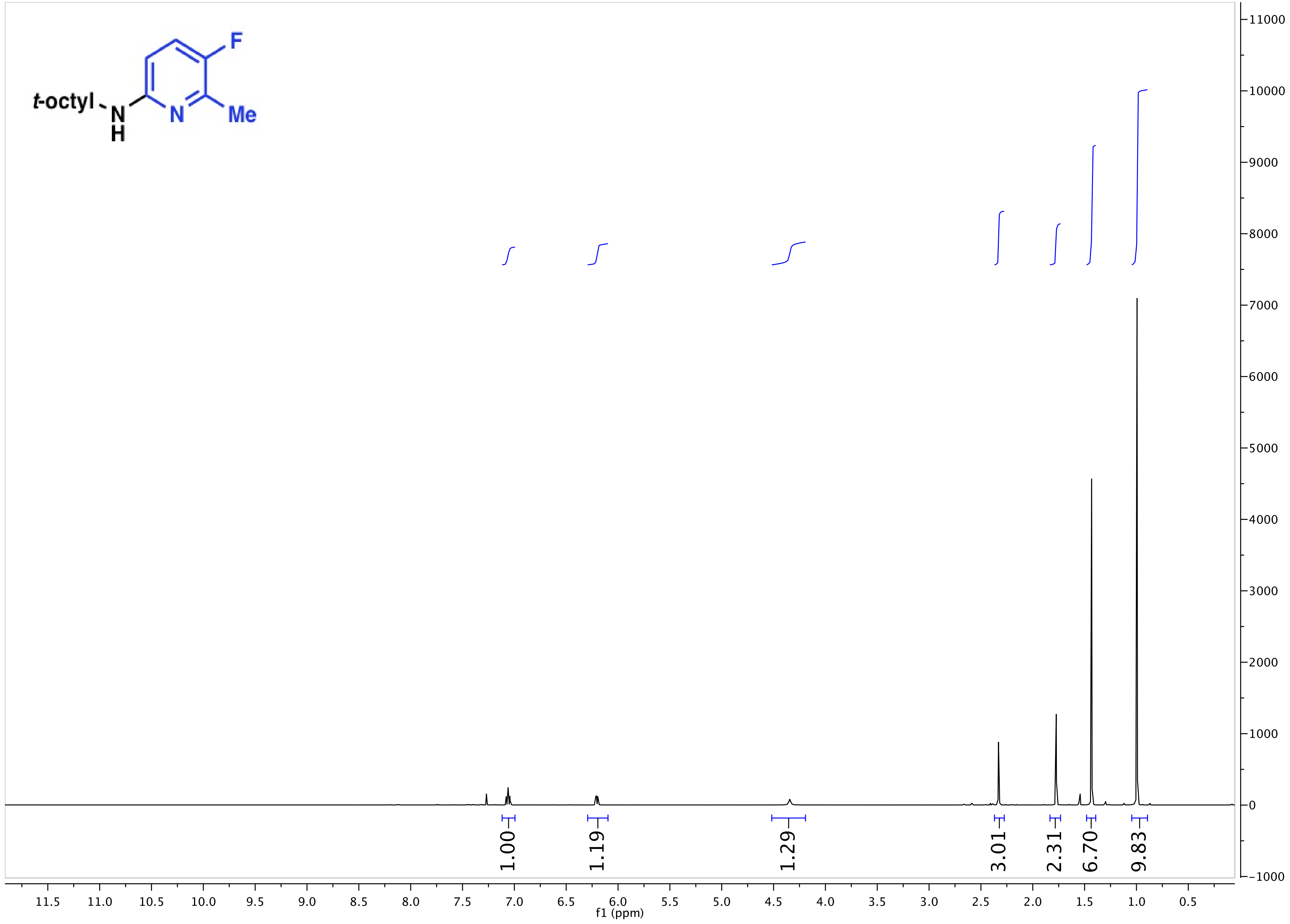

Me
HN
t-octyl
S
0.93
0.99
3.00
2.07
5.83
8.59
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

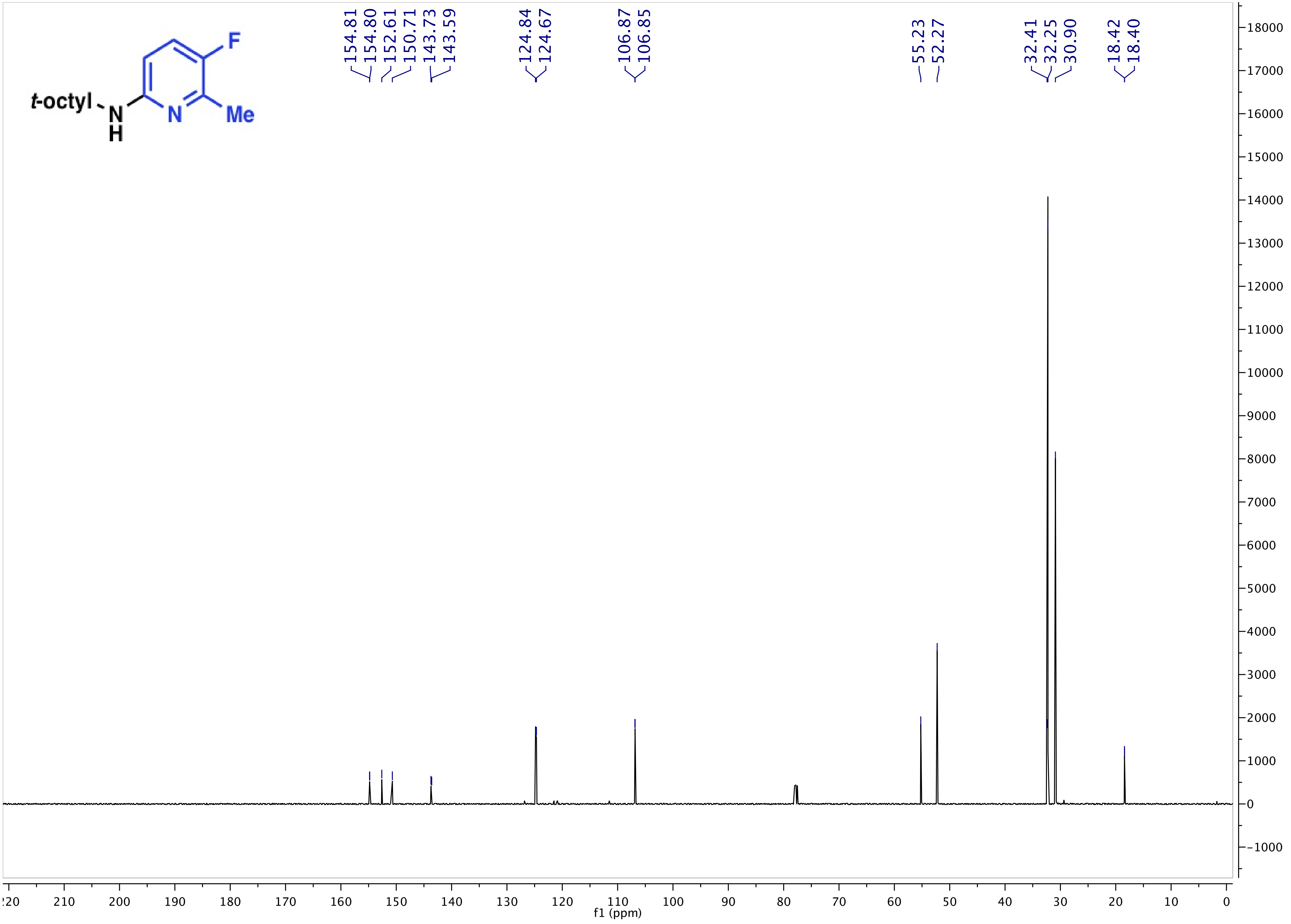


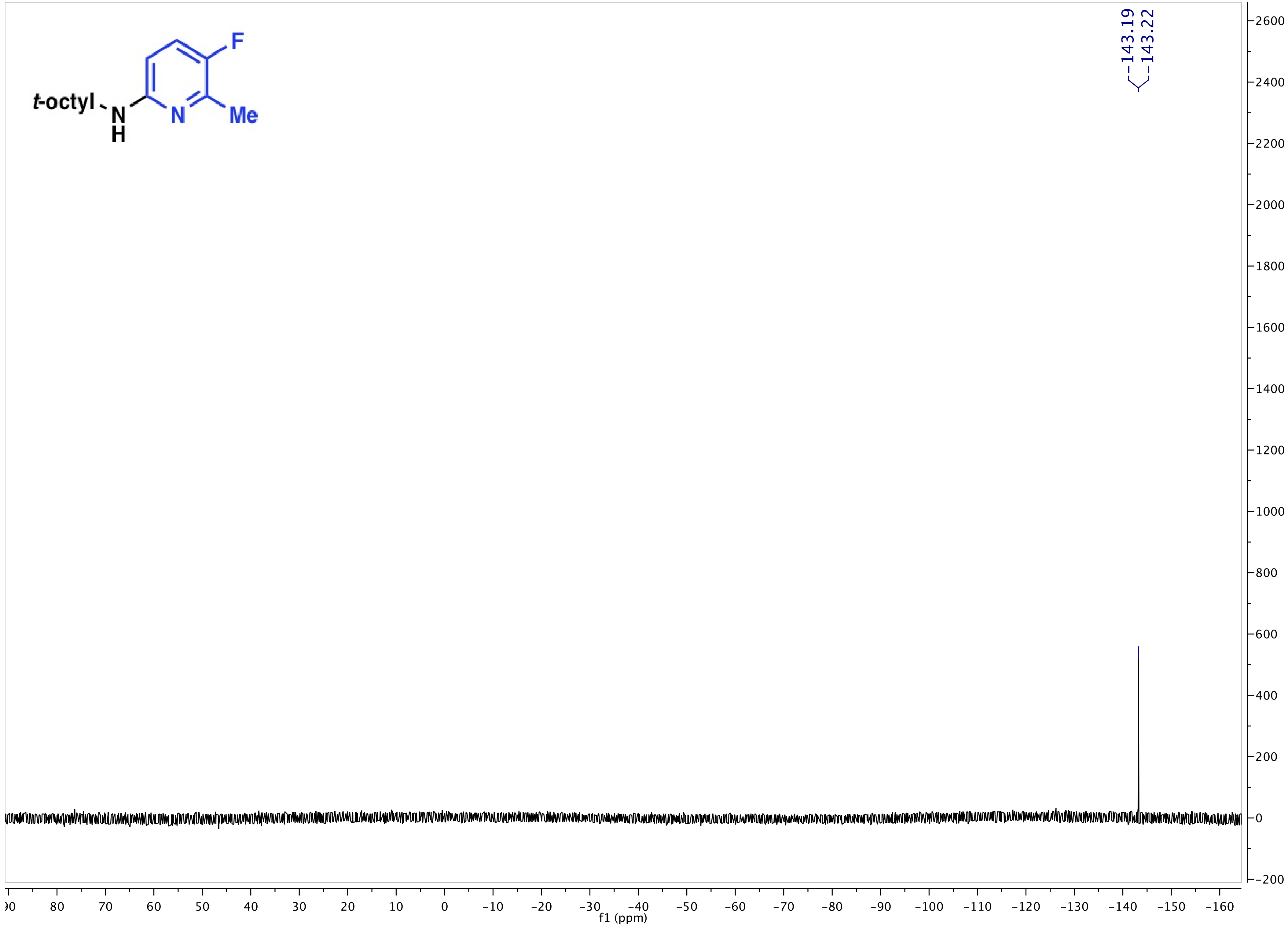
Me
HN—t-octyl
S
143.89
130.33
119.99
97.03
55.81
53.13
32.36
30.17
14.60
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100

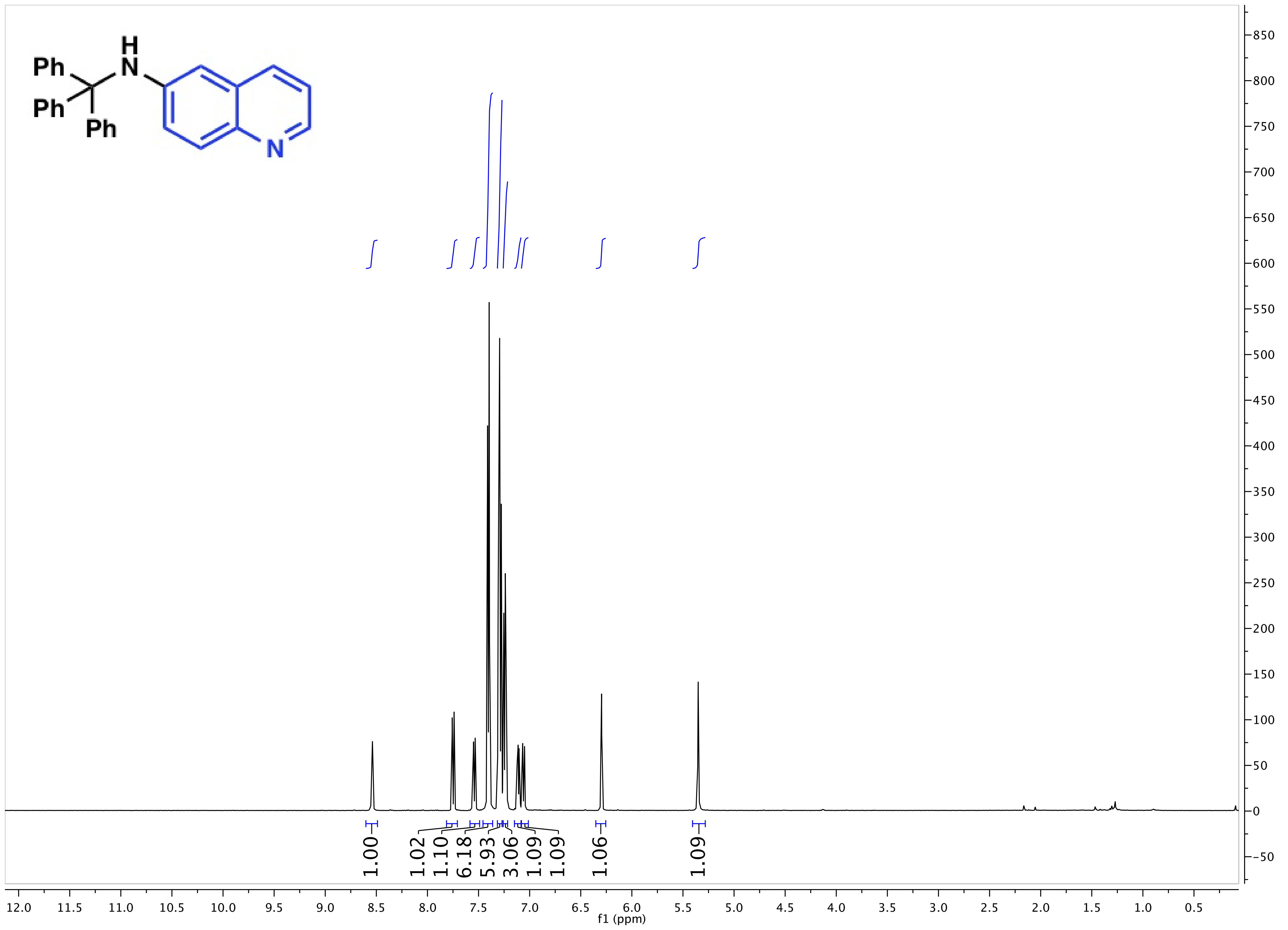

HN
Ad
MeO
OMe
1.00
2.02
6.02
1.21
2.81
5.71
5.81
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200

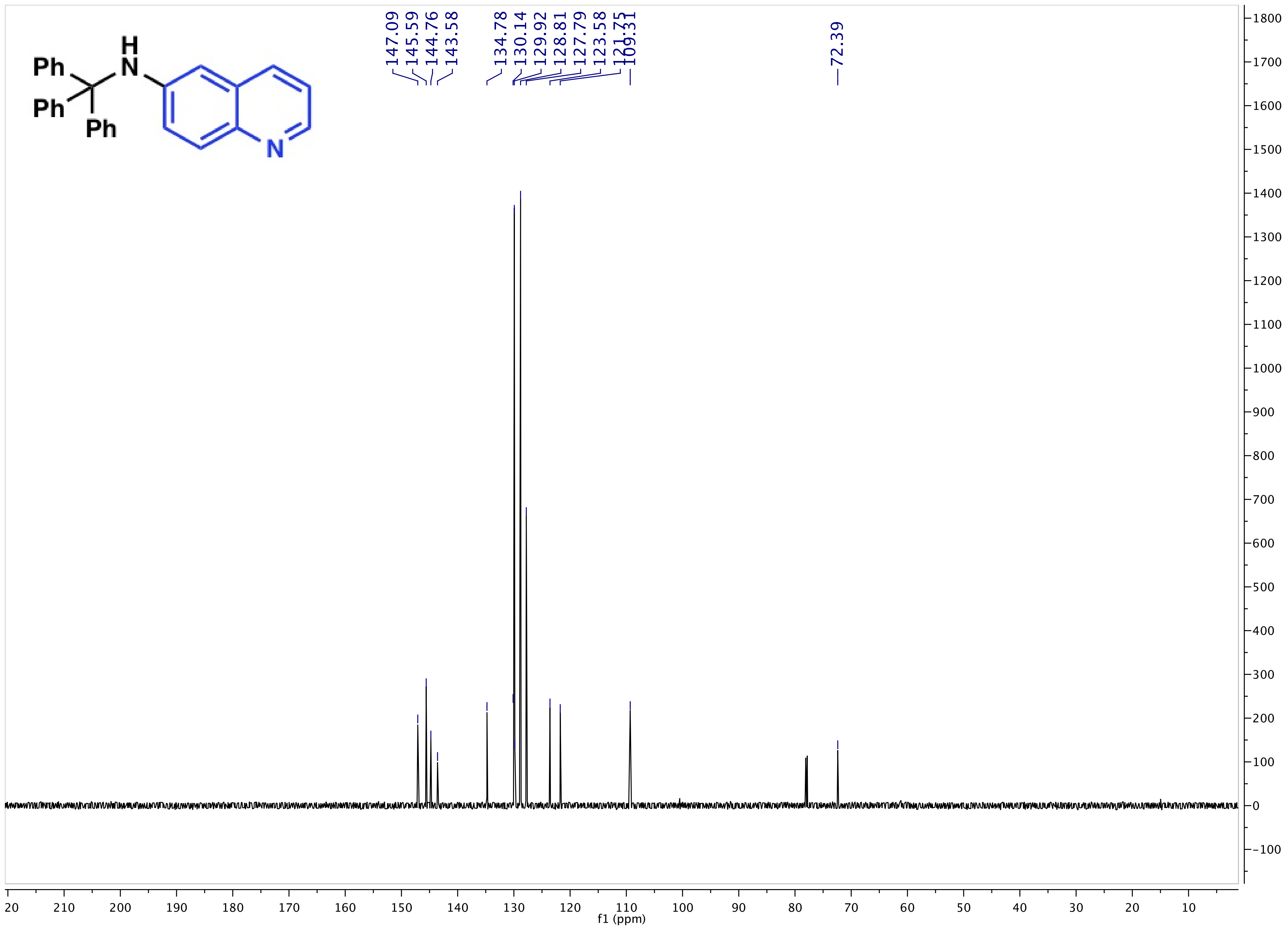

HN
Ad
MeO
OMe
156.21
123.85
104.46
56.13
55.50
44.09
37.29
30.78
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0

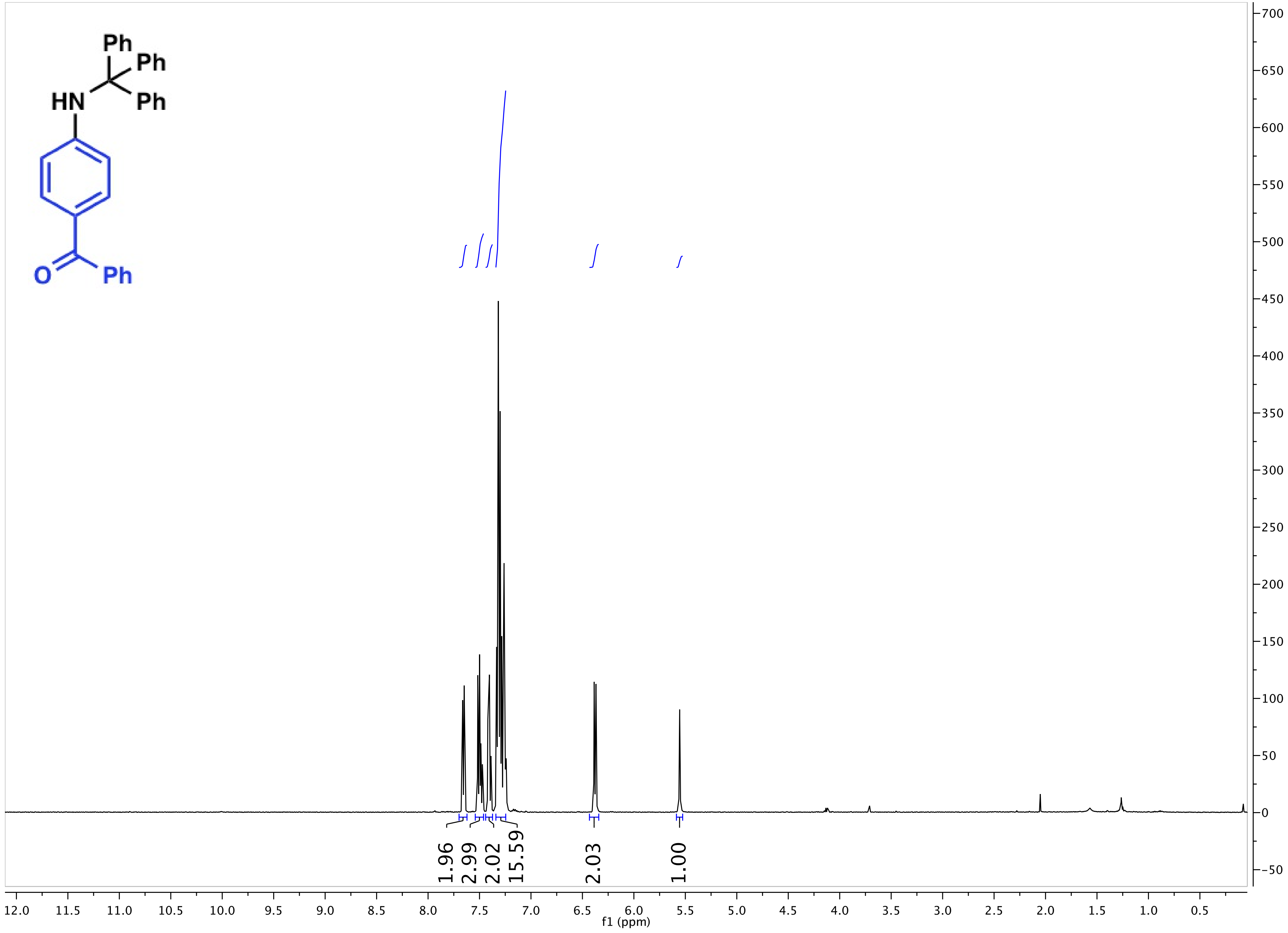

t-octyl
N
H
N
Me
F
1.00
1.19
1.29
3.01
2.31
6.70
9.83
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

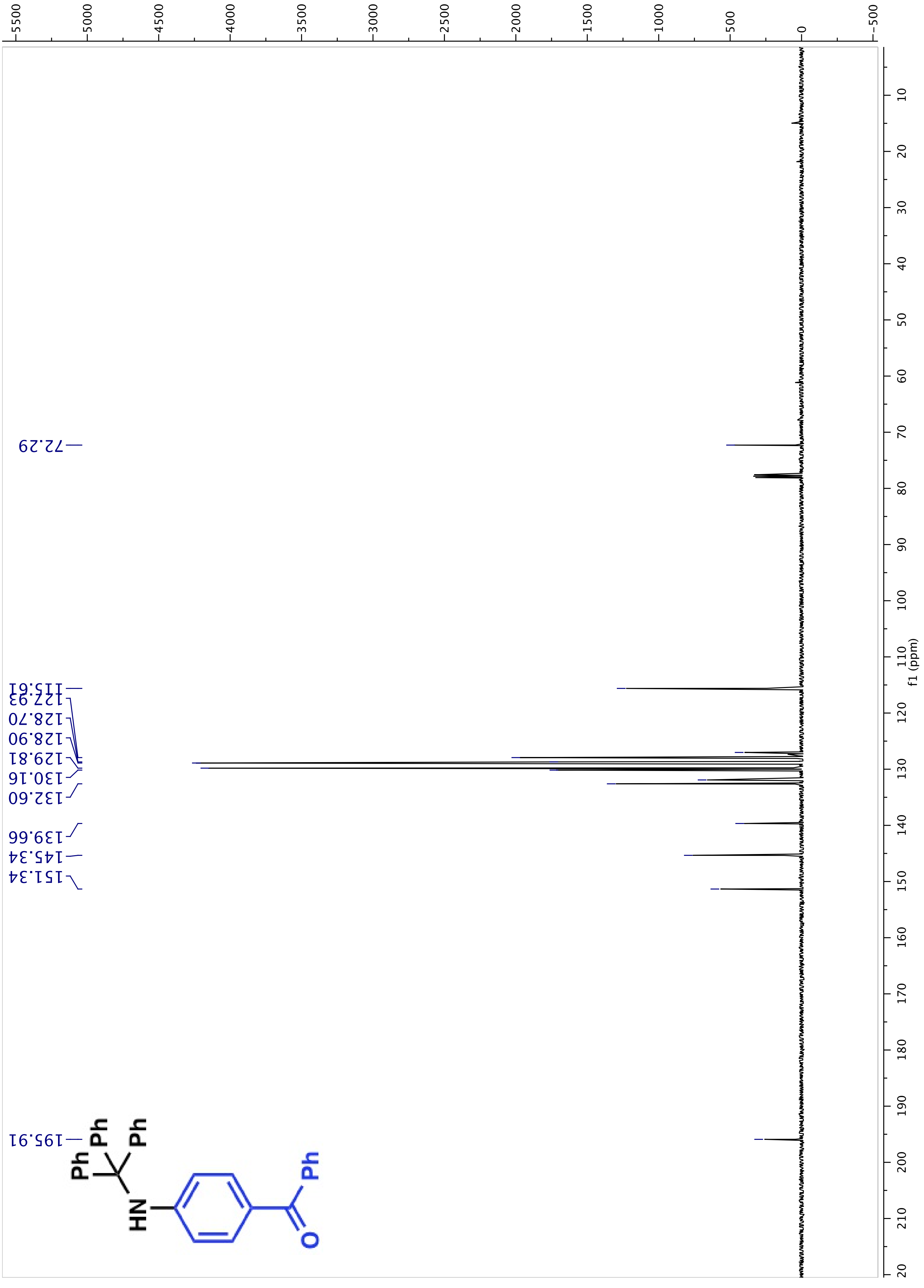

t-octyl
N
H
N
Me
F
154.81
154.80
152.61
150.71
143.73
143.59
124.84
124.67
106.87
106.85
55.23
52.27
32.41
32.25
30.90
18.42
18.40
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


t-octyl
N
H
N
Me
F
-143.19
-143.22
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

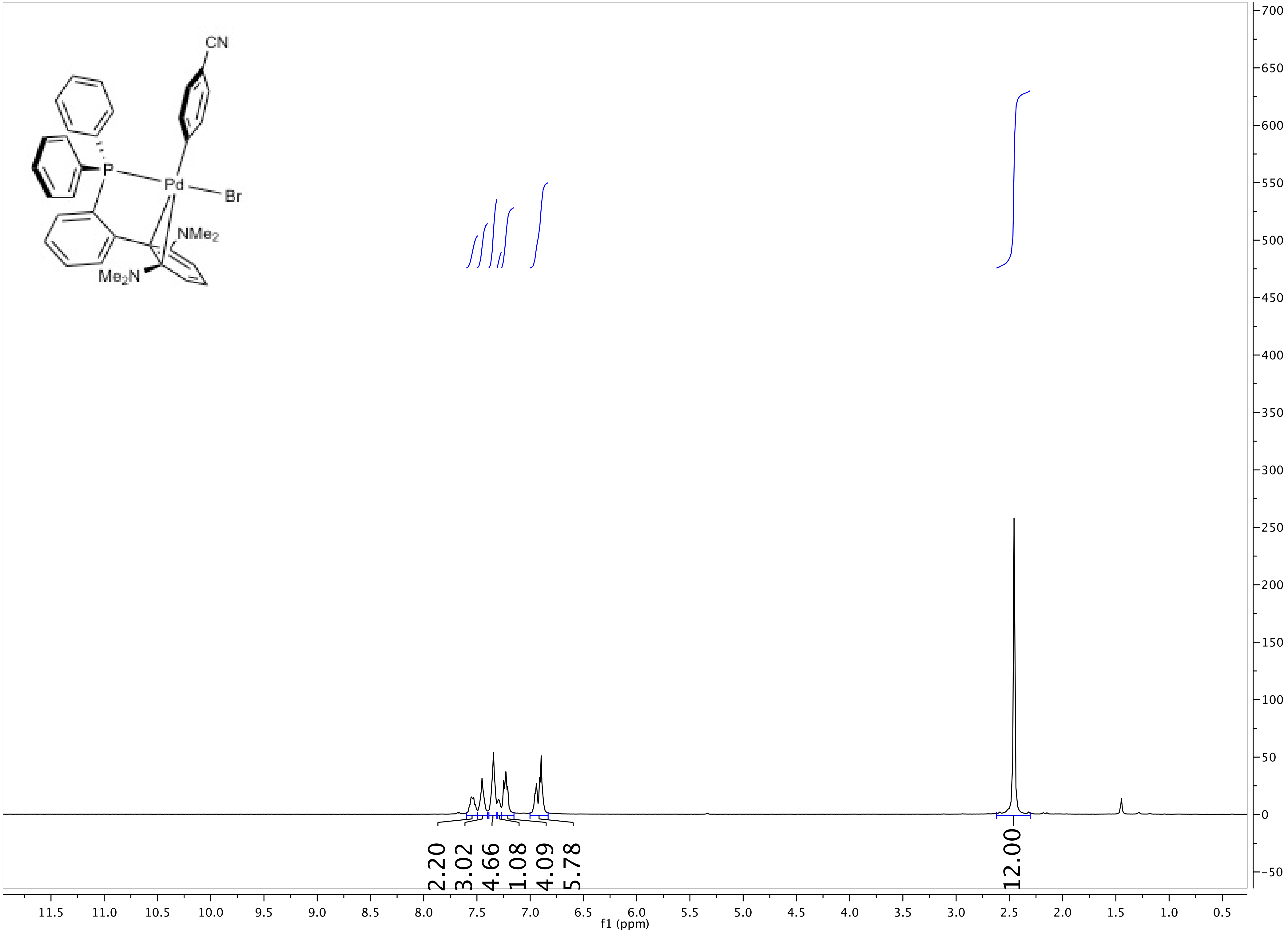

Ph
Ph
Ph
H
N
N
1.00
1.02
1.10
6.18
5.93
3.06
1.09
1.09
1.06
1.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50

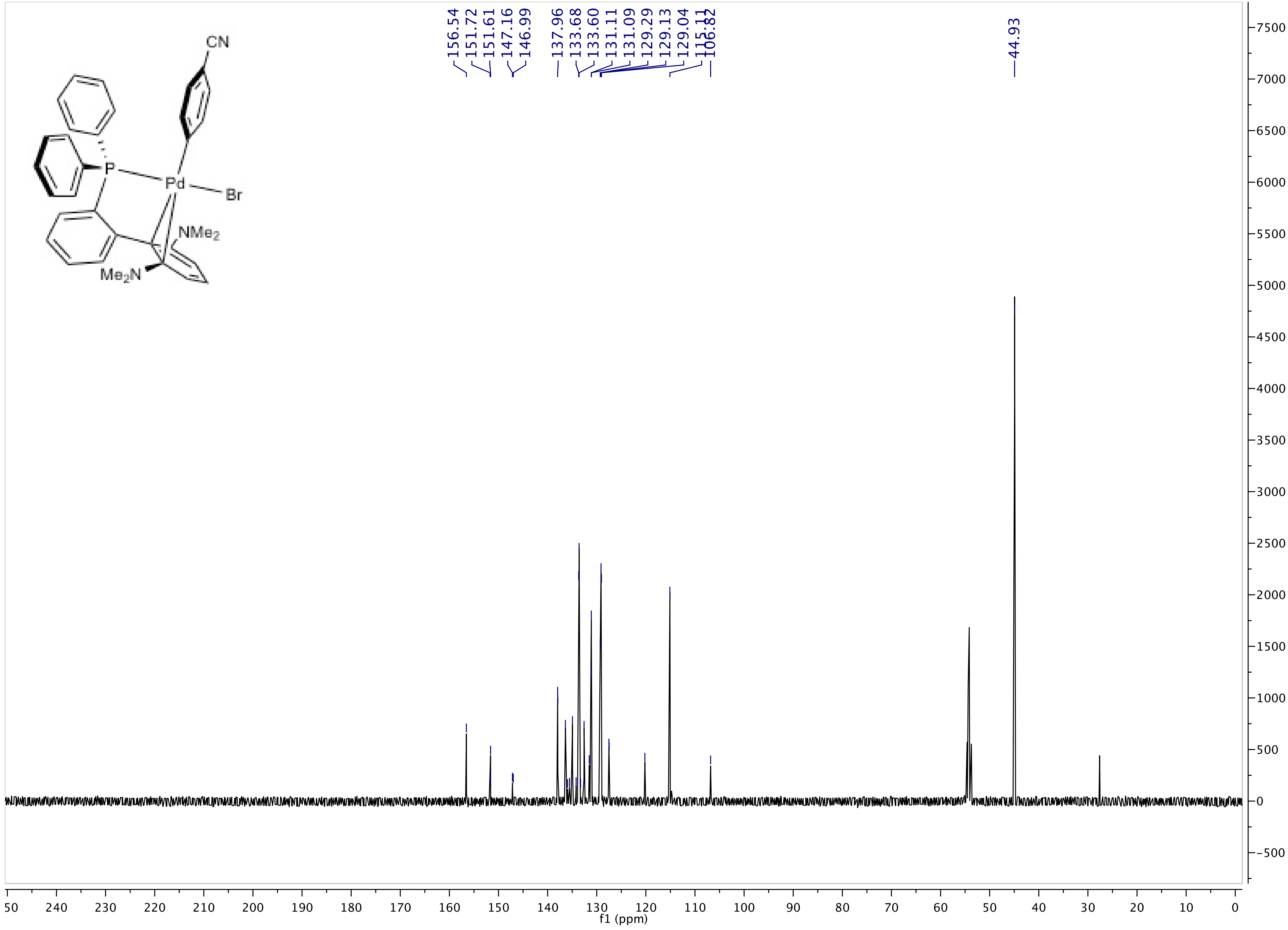

147.09
145.59
144.76
143.58
134.78
130.14
129.92
128.81
127.79
123.58
121.75
109.31
72.39
Ph
Ph
Ph
H
N
N
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100

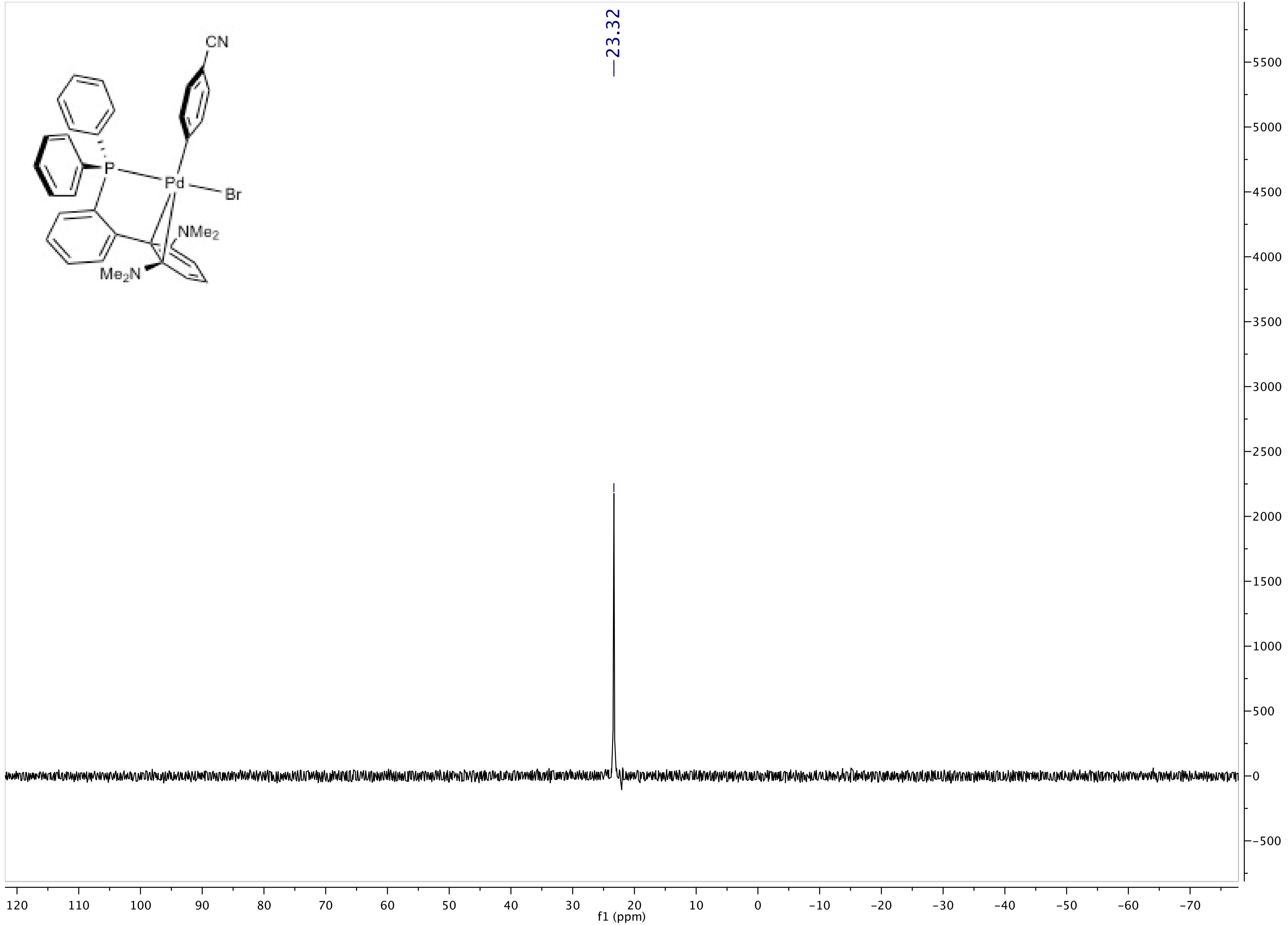

Ph
Ph
HN
Ph
O
Ph
1.96
2.99
2.02
15.59
2.03
1.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50



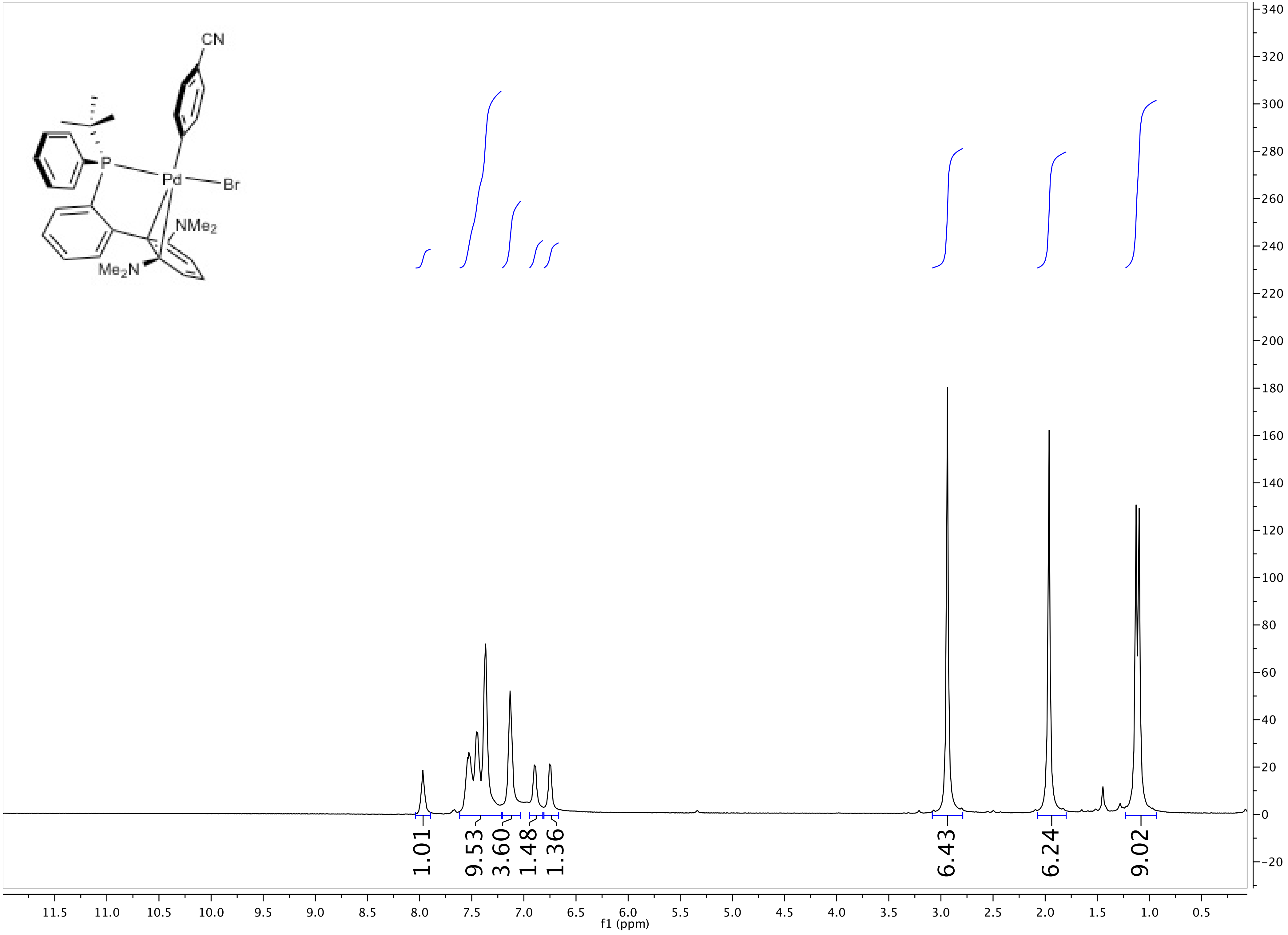
195.91
151.34
145.34
139.66
132.60
130.16
129.81
128.90
128.70
127.93
115.61
72.29
Ph
Ph
Ph
HN
Ph
O
f1 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

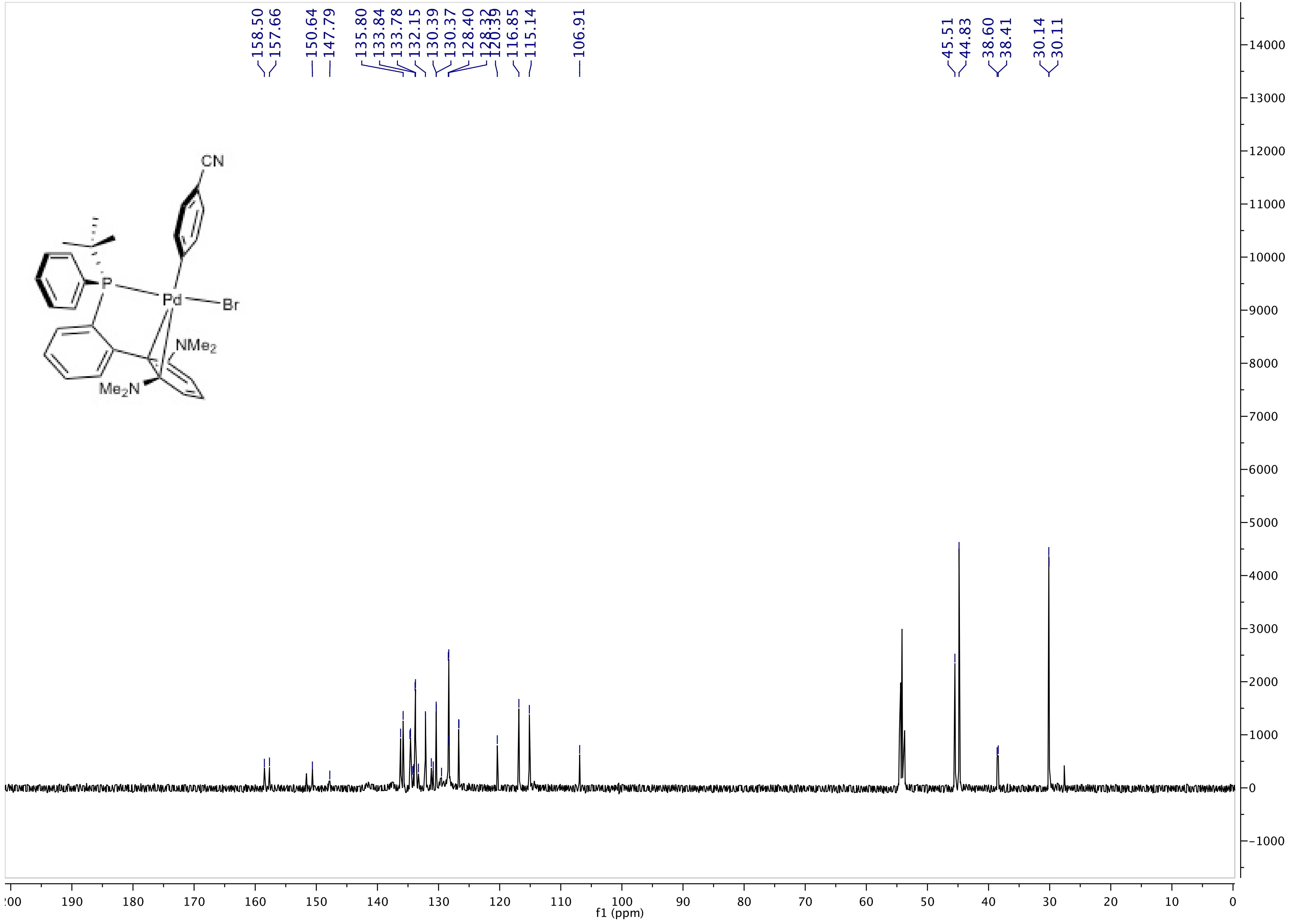

CN
P
Pd
Br
NMe2
Me2N
2.20
3.02
4.66
1.08
4.09
5.78
12.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50

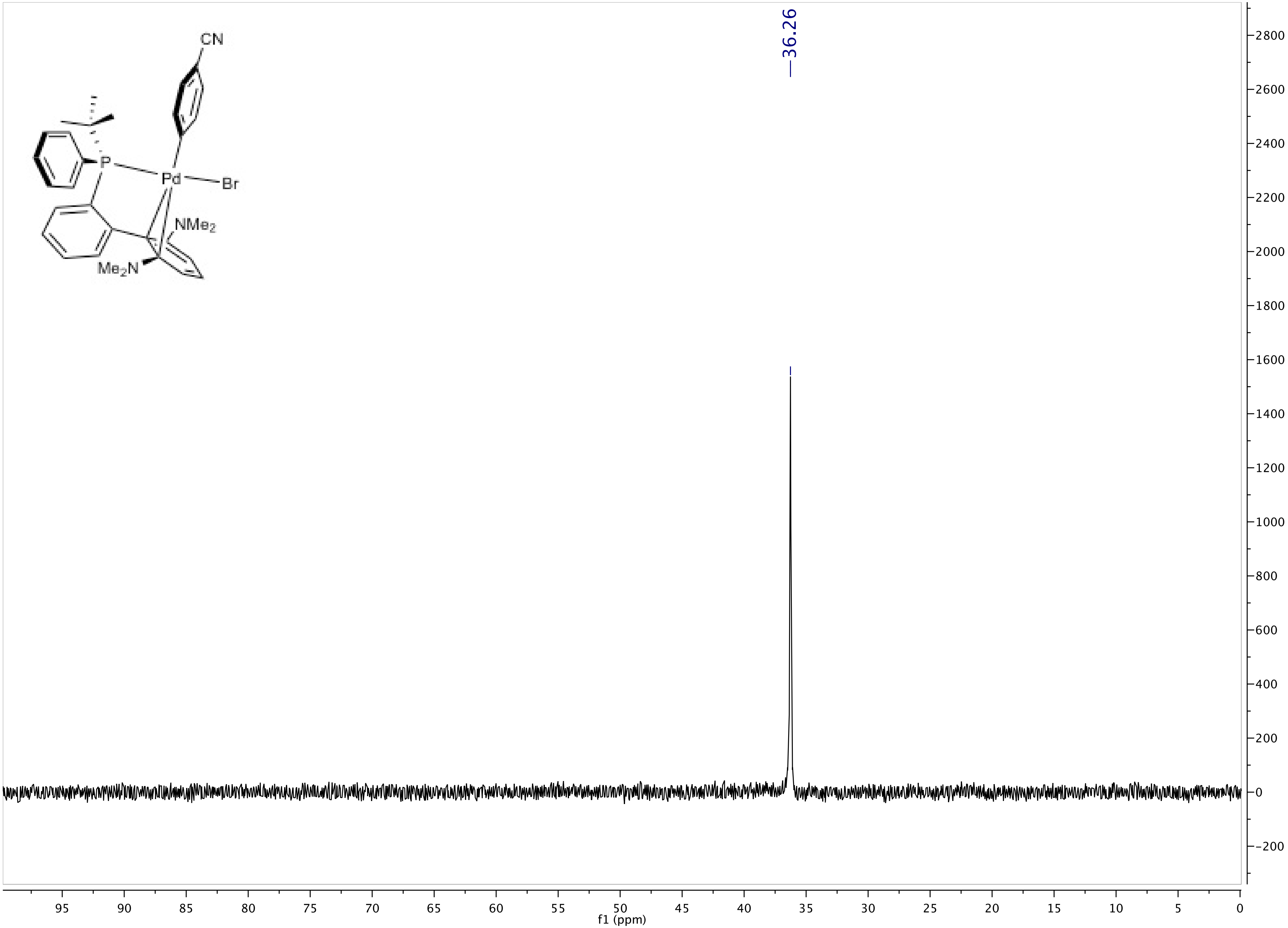

156.54
151.72
151.61
147.16
146.99
137.96
133.68
133.60
131.11
131.09
129.29
129.13
129.04
115.11
106.82
44.93
CN
P
Pd
Br
NMe2
Me2N
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



—23.32
CN
P
Pd
Br
NMe2
Me2N
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500


CN
P
Pd
Br
NMe2
Me2N
1.01
9.53
3.60
1.48
1.36
6.43
6.24
9.02
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20


158.50
157.66
150.64
147.79
135.80
133.84
133.78
132.15
130.39
130.37
128.40
128.32
120.39
116.85
115.14
106.91
45.51
44.83
38.60
38.41
30.14
30.11
CN
P
Pd
Br
NMe2
Me2N
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



36.26
CN
P
Pd
Br
NMe2
Me2N
f1 (ppm)
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200