Supporting Information:

Intramolecular Hydroamination of Unbiased and Functionalized Primary Aminoalkenes Catalyzed by a Rhodium Aminophosphine Complex

Lisa D. Julian and John F. Hartwig

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General Experimental Information

General Procedures. All manipulations were conducted under an inert atmosphere using an argon-filled glovebox (Innovative Technologies, Newburyport, Massachusetts) equipped with an oxygen sensor (working oxygen level <20.0 ppm) and low-temperature refrigeration unit (–31 °C). All reactions were conducted in flame- or oven-dried round-bottomed flasks fitted with rubber septa under a positive pressure of argon or 1-dram vials fitted with a Teflon-lined screw cap (13-mm diameter, 425 GPI thread; supplied by Qorpak, Bridgeville, Pennsylvania) under an atmosphere of nitrogen, unless otherwise noted. Organic solutions were concentrated by rotary evaporation at 25–35 °C. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous potassium permanganate solution ($KMnO_4$), followed by brief heating.

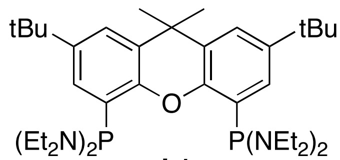
THF and diethyl ether were obtained as HPLC grade without inhibitors; benzene, toluene, dichloromethane, and acetonitrile were obtained as ACS reagent grade. THF, diethyl ether, benzene, toluene, and dichloromethane were degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column containing activated alumina. Anhydrous 1,4-dioxane was obtained from Aldrich and used without further purification. Anhydrous *t*BuOH was obtained from Aldrich and degassed with nitrogen prior to use. The rhodium catalyst $[Rh(CH_3CN)_2COD]BF_4$ and ligand **L1'** were obtained from Aldrich and used as received.

2,2-diphenylpent-4-en-1-amine (**1**),[1] N-benzyl-2,2-diphenylpent-4-en-1-amine,[1] 2-phenylpent-4-en-1-amine (**1b**),[2] 5-chloropenta-1,3-diene,[3] N-benzyl-pent-4-en-1-amine,[4] *t*Bu-Xantphos **L2**,[5] and Cy-xantphos **L3**,[6] were synthesized according to literature procedures.

Instrumentation. ^{1}H NMR spectra were obtained at 400 or 500 MHz and recorded relative to residual protio-solvent. ^{13}C NMR spectra were obtained at 100 or 125 MHz, and chemical shifts were recorded relative to the solvent resonance. ^{31}P NMR spectra were obtained 162 or 202 MHz, and chemical shifts are reported relative to external 85%

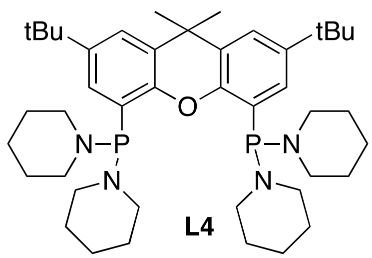
H_3PO_4. Analytical gas chromatography (GC) was performed using a Hewlett-Packard 6980 Gas Chromatograph fitted with a flame ionization detector.

Synthesis and Characterization of Ligands and Rh Complexes:



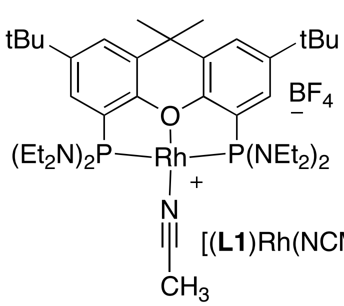
L1

4,5-(Bis[bis-diethylamido]phosphonito)-9,9-dimethylxanthene (L1). To a solution of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (1.11 g, 2.31 mmol) in THF (27 mL) at –78 °C was added *n*-BuLi (3.80 mL of a 1.2 M solution in hexanes, 4.62 mmol) dropwise. After stirring this mixture for 1 h at –78 °C, neat bis(diethylamino)-chlorophosphine (1.0 mL, 4.7 mmol) was added dropwise, and the reaction was slowly warmed to room temperature over a 1.5 h period. The reaction mixture was concentrated *in vacuo*, diluted with dry CH_2Cl_2, filtered through dry Celite, and concentrated again under reduced pressure. The residue was brought into the glovebox, diluted with pentane, and the resulting suspension was filtered. The filtrate was concentrated *in vacuo*. This material was diluted with a small amount of pentane and decanted (×2) to afford 350 mg of pure (>98%) ligand **L1** as a white solid. The decanted solution was placed in a –30 °C freezer and allowed to recrystallize. The crystals were collected and washed with cold pentane to give 300 mg of product. This recrystallization procedure was repeated an additional four times to give a total of 1.04 g of **L1** (67%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.70 (t, *J* = 2.5 Hz, 2H), 7.53 (s, 2H), 3.27 (m, 16H), 1.76 (s, 6H), 1.39 (s, 18H), 1.11 (t, *J* = 7.0 Hz, 24H). ^{13}C NMR (125 MHz, C_6D_6): δ 149.2 (t, *J* = 9.3 Hz), 144.4, 129.9 (d, *J* = 20.2 Hz), 129.0, 128.3, 122.9, 43.6 (t, *J* = 11.0 Hz), 34.8, 34.8, 33.7, 31.9, 14.9. ^{31}P NMR (202 MHz, C_6D_6): δ 93.5. Anal. Calcd for $C_{39}H_{68}N_4OP_2$: C, 69.82; H, 10.22; N, 8.35 Found: C, 69.54; H, 10.03; N, 8.10.



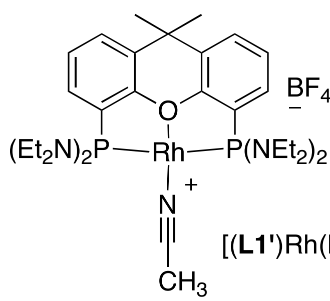
L4

4,5-(Bis[bis-dipiperidino]phosphonito)-9,9-dimethylxanthene (L4). To a solution of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (400 mg, 0.830 mmol) in THF (8 mL) at –78 °C was added *n*-BuLi (0.68 mL of a 2.5 M solution in hexane, 1.71 mmol) dropwise. After this mixture was stirred for 1 h at –78 °C, a solution of bis(dipiperidinyl)chlorophosphine[7] (401 mg, 1.71 mmol) in 0.5 mL of THF was added dropwise and then warmed to –35 °C over 15 min, at which point the cold bath was removed. The reaction mixture was concentrated *in vacuo*, diluted with dry CH_2Cl_2, filtered through dry Celite, and concentrated again under reduced pressure. The residue was brought into the glovebox, diluted with pentane, and filtered. The filtrate was concentrated *in vacuo*. This material was diluted with a small amount of pentane and decanted to obtain **L4** (120 mg, 20%) as a white powder. ^{1}H NMR (500 MHz, C_6D_6): δ 7.81 (s, 2H), 7.54 (s, 2H), 3.27 (m, 8H), 3.20 (m, 8H), 1.73 (s, 6H), 1.63 (m, 8H), 1.47 (m, 16H), 1.41 (s, 18H). ^{13}C NMR (125 MHz, C_6D_6): δ 149.8, (t, *J* = 8.3 Hz), 144.4, 129.2, 128.3, 128.1, 122.7, 50.8 (t, *J* = 10.1 Hz), 34.9, 34.8, 33.1, 31.9, 27.8 (t, *J* = 3.8 Hz), 25.5. ^{31}P NMR (202 MHz, C_6D_6): δ 92.3 (s). Anal. Calcd for $C_{43}H_{68}N_4OP_2$•0.8 C_5H_{12}: C, 72.68; H, 10.07; N, 7.21 Found: C, 72.26; H, 9.96; N, 6.85.



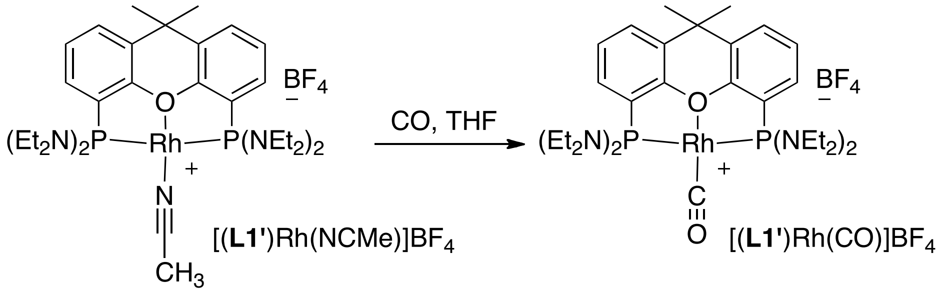
[(**L1**)Rh(NCMe)]BF_4

[(L1)Rh(NCMe)]BF_4. [Rh$(CH_3CN)_2$COD]BF_4 (200 mg, 0.526 mmol) and **L1** (360 mg, 0.537 mmol) were added to a vial and dissolved in 5 mL of THF. After being stirred for 10 min, the reaction mixture was filtered through a cotton plug and concentrated *in vacuo*. The residue was diluted with pentane, mixed thoroughly, and concentrated to give a yellow powder. The crude solid was suspended in pentane, decanted and washed with a 1:1 mixture of ether:pentane to afford 425 mg (89% yield) of the POP-pincer complex [(**L1**)Rh(NCMe)]BF_4 as a yellow solid This material was ~93% pure by ^{1}H NMR spectroscopy and was used without further purification for studies to determine the resting state of the catalyst. A small portion of this solid was recrystallized by dissolving the solid with a minimal amount of THF and diluting with pentane to afford an analytically pure sample. ^{1}H NMR (500 MHz, C_6D_6): δ 7.72 (s, 2H), 7.47 (s, 2H), 3.37 (m, 8H), 3.23 (m, 8H), 2.48 (s, 3H), 1.33 (s, 6H), 1.28 (s, 18H), 1.12 (t, *J* = 6.5 Hz, 24H). ^{13}C NMR (125 MHz, C_6D_6): δ 153.3 (t, *J* = 11.1 Hz), 148.4, 131.0, 129.1 (t, *J* = 14.8 Hz,), 128.4, 126.5, 125.8, 40.9 (*J* = 5.0 Hz). 34.7, 34.7, 32.3, 31.4, 14.3, 4.1. ^{31}P NMR (202 MHz, C_6D_6): δ 109.0 (d, *J* = 154 Hz). Anal. Calcd for $C_{41}H_{71}BF_4N_5OP_2Rh$: C, 54.61; H, 7.94; N, 7.77 Found: C, 54.93; H, 8.25; N, 7.72.



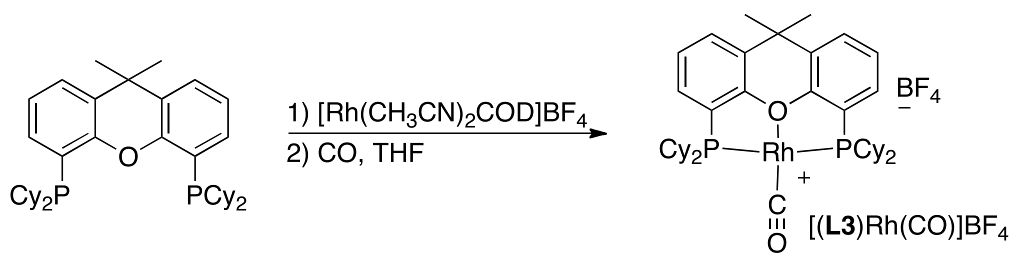
[(**L1'**)Rh(NCMe)]BF4

[(L1')Rh(NCMe)]BF_4. [Rh(CH_3CN)$_2$COD]BF_4 (49 mg, 0.13 mmol) and **L1'** (77 mg, 0.14 mmol) were added to a vial and dissolved in 1 mL of THF. After being stirred for 20 min, the reaction mixture was filtered through a cotton plug and concentrated *in vacuo*. The residue was diluted with benzene, filtered, and concentrated to give a yellow powder. The crude solid was suspended in ether, filtered, and washed repeatedly with ether to afford 68 mg (67% yield) of the POP-pincer complex [(**L1'**)Rh(NCMe)]BF_4 as a yellow solid in analytically pure form. ^{1}H NMR (500 MHz, THF-d_8): δ 7.75 (d, *J* = 8.0 Hz, 4H), 7.05 (t, *J* = 7.5 Hz, 2H), 3.32 (m, 16H), 2.52 (s, 3H), 1.62 (s, 6H), 1.16 (t, *J* = 7.0 Hz, 24H). ^{13}C NMR (125 MHz, THF-d_8): δ 155.8, (t, *J* = 10.7 Hz), 132.8, 132.7, 130.8, 130.0, 129.5, (t, *J* = 14.6 Hz), 126.6, 41.1, 35.1, 32.4, 14.2, 3.7. ^{31}P NMR (202 MHz, THF-d_8): δ 109.4 (d, *J* = 153 Hz). Anal. Calcd for $C_{33}H_{55}BF_4N_5OP_2Rh$: C, 50.20; H, 7.02; N, 8.87 Found: C, 50.22; H, 7.46; N, 8.46.



[(L1')Rh(CO)]BF$_4$. To a solution of [(**L1'**)Rh(NCMe)]BF$_4$ (40 mg, 0.05 mmol) in THF (1.5 mL) in a J. Young NMR tube was added CO (200 Torr) and mixed thoroughly. After 1 h, the solution was concentrated *in vacuo* to afford a light yellow solid (38 mg, 97%) in analytically pure form: ^{1}H NMR (500 MHz, THF-d$_8$): δ 7.99 (d, *J* = 8.0 Hz), 7.89 (m, 1H), 7.6 (t, *J* = 7.5 Hz), 3.29 (m, 16H), 1.72 (s, 6H), 1.14 (t, *J* = 7.0 Hz). ^{31}P NMR (202 MHz, THF-d$_8$): δ 114.3 (d, *J* = 138 Hz). Anal. Calcd for $C_{32}H_{52}BF_4N_4O_2P_2Rh$: C, 49.50; H, 6.75; N, 7.22. Found: C, 49.78; H, 6.80; N, 7.13. FT-IR (thin-film): ν(CO) = 1993.3 cm^{-1}.

[(L1')Rh(^{13}CO)]BF$_4$. The ^{13}C-labeled complex was synthesized according to the procedure described above, except 99% atom ^{13}CO was used to generate the ^{13}CO-enriched complex. ^{31}P NMR (162 MHz, THF-d$_8$): δ 114.2 (dd, $J_{(P\text{-}Rh)}$ = 138.0 Hz; $J_{(P\text{-}C)}$ = 14.7 Hz). ^{13}C NMR (125 MHz, THF-d$_8$): δ 191.3 (dt, $J_{(C\text{-}Rh)}$ = 91.8 Hz; $J_{(C\text{-}P)}$ = 14.7 Hz; ^{13}CO), 153.8 (t, *J* = 10.7 Hz), 133.3, 132.9, 131.2, 128.3, 126.8 (t, *J* = 19.5 Hz), 41.6 (t, *J* = 4.9 Hz), 35.3, 32.7, 14.0.



[(L3)Rh(CO)]BF$_4$. [Rh(CH$_3$CN)$_2$COD]BF$_4$ (30 mg, 0.079 mmol) and Cy-xantphos **L3** (50 mg, 0.083 mmol) were added to a vial and dissolved in 1 mL of THF. After 15 min, the reaction mixture was filtered through a cotton plug and concentrated *in vacuo*. The residue was first triturated from pentane and then triturated from benzene. The residual solid was washed again with pentane to give 40 mg (61%) a yellow powder: ^{1}H NMR (500 MHz, THF-d$_8$): δ 7.74 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 2.54 (s, 3H), 2.51 (m, 4H), 1.87 (app br d, J = 13.0 Hz, 4H), 1.68 (m, 20H), 1.63 (s, 6H), 1.34 (m, 16H). ^{31}P NMR (202 MHz, THF-d_8): δ 39.6 (d, J = 131 Hz).

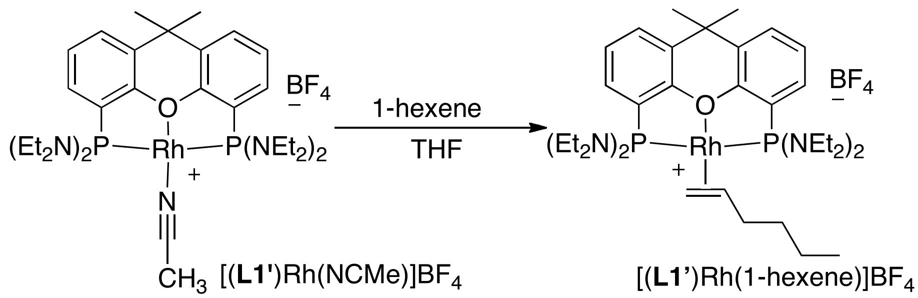
To a solution of the acetonitrile complex (22 mg, 0.026 mmol) in THF (0.6 mL) in a J. Young NMR tube was added CO (200 Torr) and mixed thoroughly. After 1 h, the solution was concentrated *in vacuo* to afford a light yellow powder (21 mg, 100%). The residue was first triturated from pentane and then triturated from benzene. The residual solid was washed again with pentane to give the CO complex [(**L3**)Rh(CO)]BF_4 in analytically pure form: ^{1}H NMR (500 MHz, THF-d_8): δ 7.99 (m, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 2H), 2.79 (m, 4H), 2.34 (app br d, J = 12.5 Hz, 4H), 1.84 (app br d, J = 13.0 Hz, 4H), 1.71 (m, 18H), 1.54 (qt, J = 13.0, 1.0 Hz, 4H), 1.32 (m, 16H). ^{31}P NMR (202 MHz, THF-d_8): δ 53.1 (d, J = 113.9 Hz). Anal. Calcd for $C_{40}H_{56}BF_4N_4O_2P_2Rh{\cdot}0.22C_6H_6$: C, 59.23; H, 6.90; N, 0.0. Found: C, 59.12; H, 6.85; N, 0.35. FT-IR (thin-film): ν(CO) = 1992.7 cm $^{-1}$.

[(L3)Rh(^{13}CO)]BF_4. The ^{13}C-labeled complex was synthesized according to the procedure described above, except 99% atom ^{13}CO was used to generate the ^{13}CO-enriched complex. ^{31}P NMR (202 MHz, THF-d_8): δ 56.5 (dd, $J_{(P\text{-}Rh)}$ = 113.5 Hz; $J_{(P\text{-}C)}$ = 14.8 Hz). ^{13}C NMR (125 MHz, THF-d_8): δ 191.3 (dt, $J_{(C\text{-}Rh)}$ = 86.5 Hz; $J_{(C\text{-}P)}$ = 13.8 Hz; ^{13}CO), 156.6 (t, J = 8.4 Hz), 134.4, 133.1, 132.4, 128.6, 118.4 (t, J = 14.6 Hz), 36.9 (t, J = 13.7 Hz), 34.9, 33.5, 31.5, 30.2, 27.2, 27.2, 26.9, 26.4, 25.8.

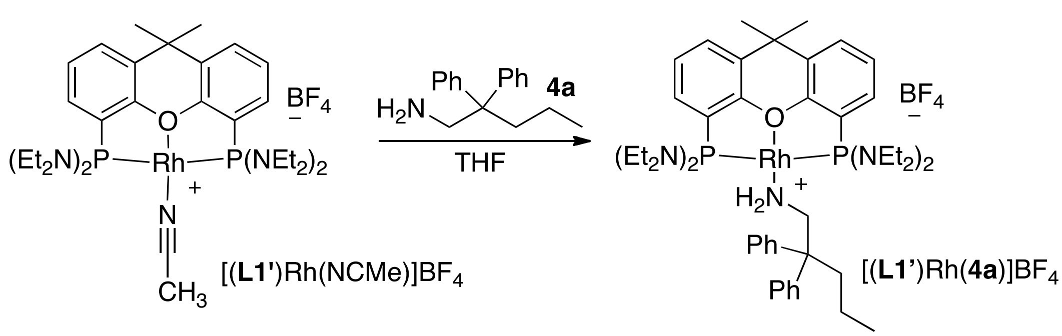
Procedures and Spectral Data for Determination of Catalyst Resting States:

Representative Procedure for Identification of the Catalyst Resting State in the Hydroamination of Aminoalkene 1b. A mixture of complex [(**L1**)Rh(NCMe)]BF_4 (13.2 mg, 0.0146 mmol), aminoalkene **1b** (40 mg, 0.25 mmol), and trimethoxybenzene (5.0 mg, 0.03 mmol) was dissolved in solvent (0.5 mL), transferred to an NMR tube, and monitored by ^{31}P{^{1}H} NMR spectroscopy. The initial spectrum was acquired at room temperature. The reaction was heated to 62 °C, and ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded during the course of the reaction until full conversion of the starting material was observed.

Independent Synthesis of Model Rh-intermediates:

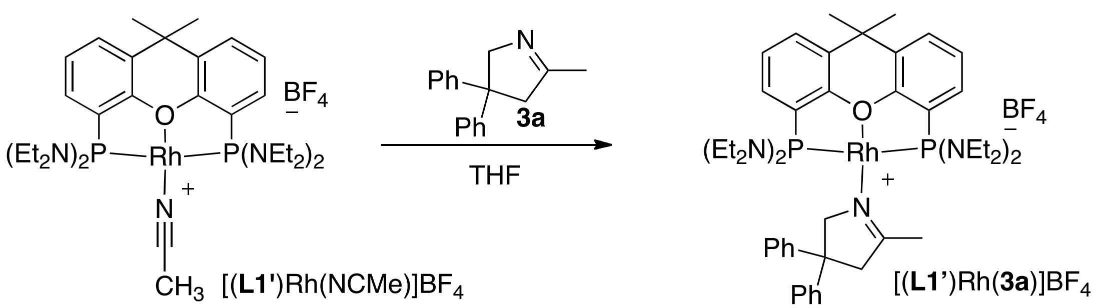


Synthesis of Model Olefin Complex: [(L1')Rh(1-hexene)]BF_4. The acetonitrile complex [(**L1'**)Rh(NCMe)]BF_4 (81.0 mg, 0.103 mmol) was dissolved in THF (0.14 mL) and 1-hexene (0.70 mL, 5.5 mmol). After being stirred for 21 h, the reaction mixture was concentrated and left under vacuum for 1 h. The residue was re-dissolved in THF (0.7 mL) and 1-hexene (0.70 mL, 5.5 mmol), stirred an additional 23 h, and concentrated *in vacuo*. The crude residue was washed with ether and pentane to afford [(**L1'**)Rh(1-hexene)]BF_4 (65 mg, 76%) as a yellow solid in analytically pure form. ^{1}H NMR (500 MHz, THF-d_8): δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.73 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 4.17 (br s, 1H), 3.53 (m, 4H), 3.41 (m, 1H), 3.32 (m, 4H), 3.23 (m, 4H), 3.06 (m, 4H), 2.47 (br, 1H), 2.37 (m, 1H), 1.66 (s, 6H), 1.43 (m, 5H), 1.13 (t, *J* = 7.0 Hz, 12H), 1.01 (t, *J* = 7.0 Hz, 12H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, THF-d_8): δ 155.0 (t, *J* = 12.8 Hz), 133.4, 131.3, 130.3, 128.1 (t, *J* = 14.7 Hz), 127.4, 68.0 (d, *J* = 14.6 Hz), 50.4 (d, *J* = 15.6 Hz), 41.7, 41.1, 40.3, 35.5, 35.3, 31.1, 23.3, 14.3, 14.3, 14.0. ^{31}P NMR (202 MHz, THF-d_8): δ 115.3 (d, *J* = 146 Hz); ^{31}P NMR (162 MHz, *t*BuOH, 60 °C): δ 112.0 (d, *J* = 147 Hz). Anal. Calcd for $C_{37}H_{64}BF_4N_4OP_2Rh$: C, 53.38; H, 7.75; N, 6.73 Found: C, 53.09; H, 7.80; N, 6.84.



Synthesis of Model Amine Complex: [(L1')Rh(4a)]BF_4. A solution of **4a** (37 mg, 0.16 mmol) in 0.8 mL of THF was added to complex [(**L1'**)Rh(NCMe)]BF_4 (53 mg, 0.067

mmol). After being stirred for 14 h at 50 °C, the reaction mixture was concentrated *in vacuo*. The crude residue was washed with a 3:1 mixture of pentane:ether (×3) to afford [(**L1'**)Rh(**4a**)]BF_4 (58 mg, 89%) as a yellow solid. A portion of this material (40 mg) was dissolved in a mixture of ether:THF and layered with pentane. The solvent was decanted, and the resulting solid was washed with pentane (×2) to afford 23 mg of [(**L1'**)Rh(**4a**)]BF_4 in analytically pure form. ^{1}H NMR (500 MHz, THF-d_8): δ 7.68 (m, 2H), 7.64 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 4H), 7.21 (overlapping m, 2H), 3.53 (m, 8H), 3.39 (m, 2H), 2.99 (m, 8H), 2.48 (br s, 1H), 2.44 (br s, 1H), 2.29 (br t, *J* = 6.9 Hz, 2H), 1.54 (s, 6H), 1.08 (t, *J* = 7.0 Hz, 24H), 1.00 (overlapping m, 2H), (0.91 (br s, 3H). ^{13}C NMR (125 MHz, THF-d_8): δ 156.2 (t, *J* = 9.8 Hz), 146.6, 132.9, 130.5 (t, *J* = 10.8 Hz), 129.8, 129.8, 129.4, 129.3, 129.2, 129.1, 127.2, 127.2, 125.9, 125.9, 53.8, 41.1, 41.1 37.9, 35.1, 31.4, 31.4, 19.0, 14.4, 14.3, 14.3. ^{31}P NMR (202 MHz, THF-d_8): δ 108.9 (d, *J* = 168 Hz); ^{31}P NMR (162 MHz, *t*BuOH, 60 °C): δ 105.9 (d, *J* = 166 Hz). Anal. Calcd for $C_{48}H_{73}BF_4N_5OP_2Rh$: C, 58.36; H, 7.45; N, 7.09 Found: C, 58.16; H, 7.80; N, 6.91.

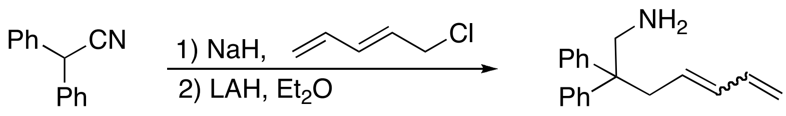


Independent Synthesis of Imine Complex: [(L1')Rh(3a)]BF_4. To a mixture of complex [(**L1'**)Rh(NCMe)]BF_4 (53.0 mg, 0.013 mmol) and imine **3a** (10 mg, 0.043 mmol) was added THF (0.5 mL). After being stirred for 1 h, the reaction mixture was diluted with Et_2O. The mixture was filtered through a glass frit and the yellow solid was washed repeatedly with Et_2O to afford the imine complex [(**L1'**)Rh(**3a**)]BF_4 (49 mg, 75% yield) in analytically pure form: ^{1}H NMR (500 MHz, THF-d_8): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.30 (m, 10H), 7.15 (t, *J* = 7.0 Hz, 4H), 4.65 (s, 2H), 3.59 (br, 4H), 3.59 (s, 2H), 3.05 (br, 12H), 2.85 (s, 3H), 1.41 (br, 6H), 0.99 (br, 24H). ^{31}P NMR (202 MHz, THF-d_8): δ 109.6 (d, *J* = 168 Hz). ^{31}P NMR (162 MHz, *t*BuOH, 60 °C): δ 105.5 (d, *J* = 168 Hz). ^{13}C NMR (125 MHz, THF-d_8): δ 184.9, 155.7 (t, *J* = 10.0 Hz), 147.4, 132.8 (br t, *J* = 2.9 Hz), 130.3, 130.0, 129.6 (t, J = 11.9 Hz), 129.4, 127.7, 127.2, 126.0, 78.7, 67.9, 56.3, 50.3, 43.8 (br), 40.6 (br), 35.0, 25.8, 16.4 (br), 13.1 (br) . Anal. Calcd for $C_{48}H_{69}BF_4N_5OP_2Rh$: C, 58.60; H, 7.07; N, 7.12 Found: C, 58.24; H, 7.20; N, 7.06.

Procedure for determination of relative binding affinities of amines and olefins for rhodium: A solution of [(**L1'**)Rh(1-hexene)]BF_4 (15.0 mg, 0.018 mmol) in THF (0.5 mL) was transferred to an NMR tube, and benzylamine (3.0 μL, 0.027 mmol) was added. After 13 min, the ratio of primary amine complex to olefin complex was measured to be 15:1, based on relative integrations of the two peaks in the ^{31}P NMR spectrum (δ 112.0, d, J = 147 Hz and δ 106.1, d, J = 168 Hz). The peaks were assigned by chemical shift and magnitude of the Rh-P coupling constant. These values were similar to those of the isolated primary amine complex [(**L1'**)Rh(**4a**)]BF_4. After 16 h, the reaction had reached equilibrium and the ratio of primary amine complex to olefin complex was measured to be 26:1.

A solution of [(**L1'**)Rh(1-hexene)]BF_4 (15.0 mg, 0.018 mmol) in THF (0.5 mL) was transferred to an NMR tube, and *N*-methylbenzylamine (3.5 μL, 0.027 mmol) was added. After 13 min, the ratio of secondary amine complex to olefin complex was measured to be 1:6.6 based on relative integrations of these two peaks in the ^{31}P NMR spectrum (δ 112.0, d, J = 147 Hz and δ 105.8, d, J = 175 Hz). The peaks were assigned by chemical shift and magnitude of the Rh-P coupling constant. We have not been able to isolate a stable complex of a secondary amine, but we assumed that the chemical shift and coupling constant would be similar to those of the primary amine complex [(**L1'**)Rh(**4a**)]BF_4. After 16 h, the reaction had reached equilibrium and the ratio of secondary amine complex to olefin complex was measured to be 1:2.5.

***Synthesis and Characterization of Aminoalkene Substrates*:**



SI-5 **10**

2,2-Diphenylhepta-4,6-dienyl-1-amine (10). To a suspension of NaH (60%dispersion in mineral oil, 1.25 g, 31.2 mmol) in DMF (30 mL) at room temperature was added a solution of diphenylacetonitrile **SI-5** (5.50 g, 28.4 mmol) in 6 mL of DMF. After being stirred for 20 min, the reaction mixture was cooled to 0 °C and 5-chloropenta-1,3-diene (3.06 g, 29.8 mmol) was added dropwise. The ice bath was removed and after being stirred for 12 h, the reaction mixture was poured into ice cold saturated aqueous NH_4Cl and diluted with EtOAc. The aqueous layer was extracted with EtOAc (×3) and the combined organic layers were washed with water (×2) and brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (5%→10% EtOAc/hexanes) to afford known 2,2-diphenylhepta-4,6-dienenitrile (4.49 g, 61%) as a 10:1 mixture of olefin isomers.[8]

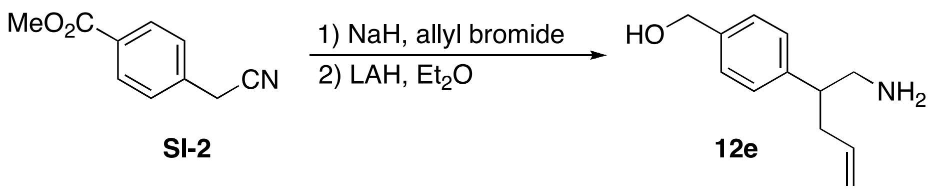
To a suspension of $LiAlH_4$ (1.31 g, 34.6 mmol) in Et_2O (25 mL) at 0 °C was slowly added a solution of diphenylhepta-4,6-dienenitrile (4.49 g, 17.3 mmol) in 5 mL of Et_2O. After addition of the substrate, the ice bath was removed. After being stirred for 18 h, the reaction mixture was cooled to 0 °C and quenched by slow, sequential addition of water (1.3 mL), 15% NaOH (1.3 mL) and water (3.9 mL). The mixture was warmed to room temperature, stirred for an additional 30 min, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (40%→100% EtOAc/hexanes) to afford 2,2-diphenylhepta-4,6-dienyl-1-amine **10** (4.4 g, 96%, 10:1 mixture of *E*:*Z* olefin isomers) as a colorless oil. Data reported for the major *E*-isomer: ^1H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.5 Hz, 4H), 7.20 (m, 6H), 6.67 (dt, *J* = 17.0, 10.0 Hz, 1H), 6.07 (dd, *J* = 15.0. 10.5 Hz, 1H), 5.23 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.06 (d, *J* = 17.0 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 3.32 (s, 2H), 2.97 (d, *J* = 7.5 Hz, 2H), 0.90 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.2, 137.0, 134.0, 130.7, 128.3, 128.2, 126.2, 115.6, 51.8, 48.7, 40.0. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.38; H, 8.18; N, 5.57.

2-(*tert*-Butyldiphenylsilyloxy)pent-4-en-1-amine (12a). To a solution of *tert*-butyl 2-oxoethylcarbamate **SI-1** (1.06 g, 6.67 mmol) in THF (60 mL) at 0 °C was added allylmagnesium bromide (13.7 mL of a 1 M solution in ether, 13.7 mmol) dropwise. After being stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated NH_4Cl, extracted with EtOAc, washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (10%→50% EtOAc/hexanes) to afford *tert*-Butyl-2-hydroxypent-4-enylcarbamate (480 mg, 36% yield) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.81 (m, 1H), 5.14 (d, overlapping, *J* = 17.5 Hz, 1H), 5.13 (d, overlapping, *J* = 10.5 Hz, 1H). 4.98 (br s, 1H), 3.75 (br s, 1H), 3.33 (m, 1H), 3.03 (m, 1H), 2.60 (br s, 1H), 2.23 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 134.1, 118.5, 79.8, 70.6, 46.1, 39.5, 28.5. Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52; N, 6.96 Found: C, 59.41; H, 9.70; N, 6.93.

TBDPSCl (0.64 mL, 2.4 mmol) was added to a solution of *tert*-Butyl 2-hydroxypent-4-enylcarbamate (450 mg, 2.23 mmol) and imidazole (167 mg, 2.45 mmol) and stirred at room temperature for 48 h. The reaction was quenched with water, extracted with EtOAc, washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (3%→6% EtOAc/hexanes) to afford *tert*-Butyl 2-(*tert*-butyldiphenylsilyloxy)pent-4-enylcarbamate (734 mg, 75%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (m, 4H), 7.44 (m, 2H). 7.38 (t, *J* = 7.5 HZ, 4H), 5.67 (m, 1H), 4.97 (d, *J* = 10.0 Hz, 1H), 4.93 (d, *J* = 17.0 Hz, 1H), 4.66 (br s, 1H), 3.83 (br s, 1H), 3.16 (m, 2H), 2.19 (m, 2H), 1.41 (s, 9H), 1.08 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 136.0, 135.9, 134.0, 133.9, 129.9, 129.9, 127.9, 127.8, 117.8, 79.1, 72.4, 45.4, 39.6, 28.5, 27.2, 19.5. Anal. Calcd for $C_{26}H_{37}NO_3Si$: C, 71.03; H, 8.48; N, 3.19. Found: C, 70.87; H, 8.33; N, 3.25.

The product carbamate (630 mg, 1.43 mmol) was dissolved in a 1:1 mixture (7 mL) of TFA:CH_2Cl_2. After being stirred for 50 min, the reaction mixture was quenched with 1

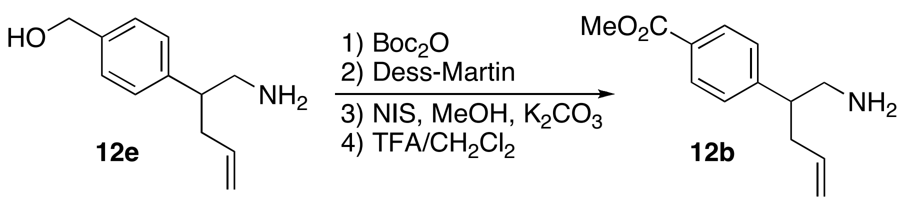
M NaOH and extracted with CH_2Cl_2. The organic layer was washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (50%→100% EtOAc/hexanes) to afford 2-(*tert*-butyldiphenylsilyloxy)pent-4-en-1-amine **12a** (374 mg, 77%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (m, 4H), 7.41 (m, 6H), 5.67 (dddd, *J* = 17.0, 10.0, 7.0, 7.0 Hz, 1H), 4.95 (m, 2H), 3.72 (m, 1H), 2.70 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.63 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.24 (m, 2H), 1.14 (br s, 2H)), 1.08 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.0, 135.9, 134.6, 134.3, 129.8, 127.8, 127.7, 117.2, 74.6, 46.9, 39.2, 27.2, 19.5. Anal. Calcd for $C_{21}H_{29}NOSi$: C, 74.28; H, 8.61; N, 4.13 Found: C, 74.21; H, 8.65; N, 4.15.



2-(4-Hydroxymethyl)phenylpent-4-en-1-amine (12e). To a suspension of NaH (60% dispersion in mineral oil, 503 mg, 12.6 mmol) in DMF (20 mL) at room temperature was added a solution of methyl 4-(cyanomethyl)benzoate **SI-2** (2.0 g, 11.4 mmol) in 5 mL of DMF. After being stirred for 15 min, the dark red mixture was cannulated into a separate flask containing a solution of allyl bromide (4.8 mL, 57.0 mmol) in DMF (20 mL) at 0 °C. After being stirred for 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and diluted with EtOAc. The aqueous layer was extracted with EtOAc (×3) and the combined organic layers were washed with water (×2) and brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (5% →10% →20% EtOAc/hexanes) to afford methyl 4-(1-cyanobut-3-enyl)benzoate (1.15 g, 47%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 5.78 (dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 5.19 (d, *J* = 9.5 Hz, 1H), 5.18 (dd, *J* = 17.0, 1.5 Hz, 1H), 3.94 (overlapping, 1H), 3.93 (s, 3H), 2.65 (m, 2H).

To a suspension of $LiAlH_4$ (790 mg, 20.8 mmol) in Et_2O (15 mL) at 0 °C was slowly added a solution of the nitrile (1.12 g, 5.2 mmol) in 5 mL of Et_2O. After addition of the substrate, the ice bath was removed. After being stirred for 1.5 h, the reaction mixture was cooled to 0 °C and quenched by slow, sequential addition of water (0.79

mL), 15% NaOH (0.79 mL) and water (1.6 mL). The mixture was warmed to room temperature, stirred for an additional 30 min, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (100:0→100:2 EtOAcEt$_3$N→100:5:2 CH_2Cl_2:MeOH:Et$_3$N) to afford the 2-(4-hydroxymethyl)phenylpent-4-en-1-amine (**12e**) (562 mg, 57%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.63 (dddd, J = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 4.98 (dd, J = 17.0, 1.5 Hz, 1H), 4.91 (dd, J = 10.0, 1.5 Hz, 1H), 4.56 (s, 2H), 2.88 (dd, J = 12.5, 5.0 Hz, 1H), 2.74 (dd, J = 12.5, 9.0 Hz, 1H), 2.64 (m, 1H), 2.33 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.6, 140.0, 136.3, 127.9, 127.2, 116.3, 64.2, 48.7, 47.0, 38.4. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32 Found: C, 75.13; H, 9.09; N, 7.11. HRMS (ES+) *m/z* Calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1388, found 192.1380.

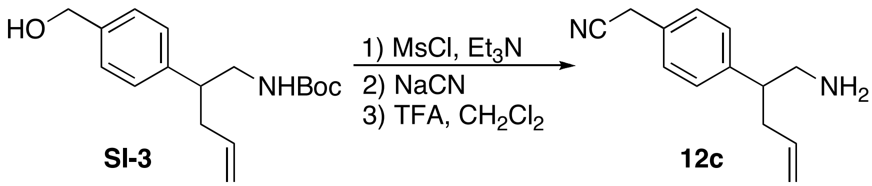


2-(4-Methylcarboxy)phenylpent-4-en-1-amine (12b). To a solution of 2-(4-hydroxymethyl)phenylpent-4-en-1-amine **12e** (crude material from the previous step) (1.02 g, 5.35 mmol) in EtOH (20 mL) was added $NaHCO_3$ (909 mg, 10.7 mmol) and Boc$_2$O (1.28 mg, 5.87 mmol). After being stirred for 19 h, the reaction mixture was concentrated to approximately half the volume and diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (×3) and the combined organic layers were washed with water (×2) and brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (20%→35% EtOAc/hexanes) to afford the product (802 mg, 52% over 2 steps) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.67 (dddd, J = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 5.00 (d, J = 16.5 Hz, 1H), 4.95 (d, J = 10.5 Hz, 1H), 4.68 (s, 2H), 4.37 (br s, 1H), 3.55 (ddd, J = 13.5, 6.5, 6.5 Hz, 1H), 3.14 (ddd, J = 14.0, 9.0, 4.5 Hz, 1H), 2.86 (m, 1H), 2.38 (m, 2H), 1.70 (br s, 1H), 1.40 (s, 9H).

To a mixture of the primary alcohol (1.65 g, 5.67 mmol) and $NaHCO_3$ (964 mg, 11.3 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added Dess-Martin periodinane (2.58 g, 6.08 mmol). After being stirred for 2 h at 0 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and excess solid $Na_2S_2O_3 \cdot 5H_2O$. After stirring vigorously for 30 min, the mixture was extracted with CH_2Cl_2 (×2), washed with brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (10%→30% EtOAc/hexanes) to afford the aldehyde (1.38 g, 84%) as a white waxy solid. ^1H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.65 (dddd, *J* = 17.5, 10.5, 7.0, 7.0 Hz, 1H), 5.00 (d, *J* = 17.5 Hz, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.40 (br s, 1H), 3.55 (m, 1H), 3.22 (ddd, *J* = 14.0, 9.0, 5.5 Hz, 1H), 2.99 (m, 1H), 2.42 (m, 2H), 1.39 (s, 9H).

To a mixture of the aldehyde (1.35 g, 4.67 mmol), and K_2CO_3 (1.61 g, 11.7 mmol) in MeOH (46 mL) was added *N*-iodosuccinimide (2.63 g 11.7 mmol). The flask was wrapped in foil and allowed to stir for 19 h at room temperature. The reaction mixture was quenched by addition of water and $Na_2S_2O_3 \cdot 5\ H_2O$ (4.5 g, 18.1 mmol). After being stirred for 5 min, the mixture was extracted with EtOAc (×2) and the combined organic layers were washed with brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (12%→16% EtOAc/hexanes) to afford the methyl ester (1.39 g, 93%) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.64 (dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.37 (br s, 1H), 3.91 (s, 3H), 3.56 (ddd, *J* = 13.0, 6.5, 6.5 Hz, 1H), 3.19 (ddd, *J* = 13.5, 9.0, 5.0 Hz, 1H), 2.95 (m, 1H), 2.40 (m, 2H), 1.39 (s, 9H).

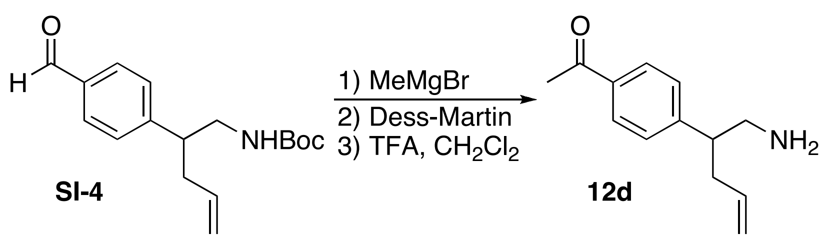
The methyl ester (1.33 g, 4.17 mmol) was dissolved in CH_2Cl_2 (12 mL) and TFA (6 mL). After being stirred at room temperature for 2.5 h, the reaction mixture was cooled to 0 °C and quenched by addition of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (×2), washed with brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (50%→100% EtOAc/hexanes%→100:2 EtOAc:Et_3N) to afford 2-(4-methylcarboxy)phenylpent-4-en-1-amine **(12b)** (717 mg, 79%) as a light yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.66 (dddd, *J* = 17.0, 10.0, 7.0, 7.0 Hz, 1H), 4.98 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.94 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.91 (s, 3H), 3.00 (dd, J = 13.0, 5.5 Hz, 1H), 2.89 (dd, J = 13.0, 8.5 Hz, 1H), 2.77 (ddd, J = 14.5, 8.5, 6.0 Hz, 2.45 (m, 1H), 2.36 (m, 1H), 1.04 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1, 148.8, 136.1, 130.0, 128.6, 128.1, 116.7, 52.1, 49.6, 47.4, 38.2. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.99; H, 7.59; N, 6.69.



2-(4-Cyano)phenylpent-4-en-1-amine (12c). To a solution of **SI-3** (see above, 380 mg, 1.31 mmol) in THF (13 mL) was added Et_3N (0.274 mL, 1.96 mmol), followed by MsCl (0.112 mL, 1.44 mmol). After being stirred for 20 min at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc (×1) and the combined organic layers were washed with brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material (477 mg) was used without further purification in the following reaction. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.65 (dddd, J = 17.5, 10.0, 6.5, 6.5 Hz, 1H), 5.22 (s, 2H), 4.98 (d, J = 18.0 Hz, 1H), 1.95 (d, J = 10.5 Hz, 1H), 4.38 (br s, 1H), 3.54 (m, 1H), 3.17 (ddd, J = 14.0, 9.0, 4.5 Hz, 1H), 2.92 (s, 3H), 2.90 (m, 1H), 2.38 (m, 2H), 1.39 (s, 9H).

A mixture of the mesylate (1.31 mmol), NaCN (128 mg, 2.62 mmol) and DMF (7.0 mL) was heated to 50 °C. After being stirred for 40 min, the reaction mixture was cooled to room temperature, quenched with saturated aqueous $NaHCO_3$, and diluted with EtOAc. The mixture was extracted with EtOAc (×1), washed with brine (×2), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (20%→30% EtOAc/hexanes) to afford the Boc-protected nitrile (311 mg, 79% over two steps) as a white waxy solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 5.65 (dddd, J = 17.0, 10.0, 7.0, 7.0 Hz, 1H), 4.99 (d, J = 17.0 Hz, 1H), 4.96 (d, J = 10.5 Hz, 1h), 4.37 (br s, 1H), 3.73 (s, 2H), 3.53 (m, 1H), 3.16 (ddd, J = 14.0, 9.0, 5.5 Hz, 1H), 2.88 (m, 1H), 2.38 (m, 2H), 1.40 (s, 9H).

To a solution of the Boc-protected nitrile (414 mg, 1.38 mmol) in dry CH_2Cl_2 (5 mL) was added TFA (2.5 mL). After being stirred for 2.5 h, the reaction was poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with 10% MeOH/CH_2Cl_2 (×3), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (100:0→100:2 EtOAcEt$_3$N) to afford 2-(4-cyano)phenylpent-4-en-1-amine **12c** (214 mg, 78%) as a colorless oil: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.66 (dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 4.98 (d, *J* = 17.5 Hz, 1H), 4.94 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.72 (s, 2H), 2.97 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.85 (dd, *J* = 13.0, 9.0 Hz, 1H), 2.70 (ddd, *J* = 14.0, 9.0, 6.0 Hz, 1H), 2.42 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 2.34 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 0.98 (br s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 143.3, 136.4, 128.8, 128.2, 128.1, 118.1, 116.5, 49.1, 47.5, 38.3, 23.4. HRMS (ES+) *m/z* Calcd for $C_{13}H_{16}N_2$ [M+H]$^+$ 200.1392, found 200.1390.

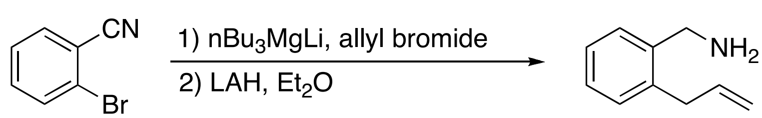


2-(4-Acetyl)phenylpent-4-en-1-amine (12d). To a solution of **SI-4** (see above, 599 mg, 2.07 mmol) in THF (40 mL) at 0 °C was added MeMgBr (1.7 mL of a 3M solution in Et$_2$O, 5.1 mmol). After being stirred for 1.5 h at 0 °C, the reaction mixture was quenched with saturated NH_4Cl, extracted with EtOAc (×3), washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (10%→30% EtOAc/hexanes) to afford the secondary alcohol (435 mg, 69% yield) as a colorless oil: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.66 (dddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.85 (q, *J* = 6.4 Hz, 1H), 4.44 (br s, 1H), 3.53 (m, 1H), 3.12 (ddd, *J* = 13.6, 8.8, 4.8 Hz, 1H), 2.83 (m, 1H), 2.37 (m, 2H), 2.16 (br s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H), 1.38 (s, 9H).

To a mixture of the secondary alcohol (408 mg, 1.34 mmol) and $NaHCO_3$ (228 mg, 2.68 mmol) in CH_2Cl_2 (13 mL) at 0 °C was added Dess-Martin periodinane (681 mg, 1.61

mmol). After being stirred for 1.25 h at 0 °C, the reaction mixture was warmed to room temperature, stirred an additional 30 min, then quenched with saturated aqueous $NaHCO_3$ and excess solid $Na_2S_2O_3 \cdot 5H_2O$. After stirring vigorously for 15 min, the mixture was extracted with CH_2Cl_2 (×2), washed with brine (×1), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (8%→15% EtOAc/hexanes) to afford the ketone (344 mg, 85%) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.64 (dddd, *J* = 17.0, 10.0, 7.0, 7.0 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 4.39 (br s, 1H), 3.55 (m, 1H), 3.19 (ddd, *J* = 14.0, 9.0, 5.5 Hz, 1H), 2.96 (m, 1H), 2.59 (s, 3H), 2.40 (m, 2H), 1.39 (s, 9H).

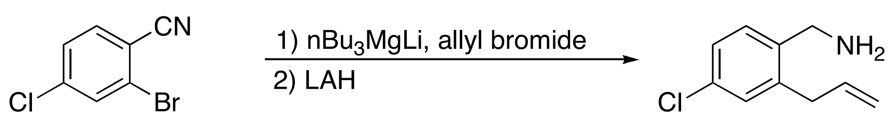
To a solution of the Boc-protected ketone (344 mg, 1.14 mmol) in dry CH_2Cl_2 (8 mL) at 0 °C was added TFA (4 mL). After being stirred for 1.75 h, the reaction was warmed to room temperature, stirred an additional 15 min, then poured into saturated aqueous $NaHCO_3$. The aqueous layer was further basified with 1 M NaOH, extracted with 10% $MeOH/CH_2Cl_2$ (×3), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (100:0→100:2 $EtOAc:Et_3N$→100:3:2 $CH_2Cl_2:MeOH:Et_3N$) to afford 2-(4-acetyl)phenylpent-4-en-1-amine **12d** (187 mg, 81%) as a waxy solid: ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.64 (dddd, *J* = 17.0, 10.0, 7.0, 7.0 Hz, 1H), 4.97 (d, *J* = 17.0 Hz, 1H), 4.93 (d, *J* = 10.5 Hz, 1H), 2.98 (dd, *J* = 13.0, 5.0 Hz, 1H), 2.88 (dd, *J* = 13.0, 9.0 Hz, 1H), 2.76 (m, 1H), 2.27 (m, 2H), 1.00 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9, 149.3, 136.1, 128.8, 128.5, 128.3, 116.7, 49.6, 47.4, 38.1, 26.6. HRMS (ES+) *m/z* Calcd for $C_{13}H_{17}NO$ $[M+H]^+$ 204.1388, found 204.1383.



SI-6 **14a**

2-Allylbenzylamine (14a). 2-allylbenzonitrile was prepared according to literature procedure.[9] Briefly, to a solution of *n*butylmagnesium bromide in THF (2.8 mL of a 1 M solution in THF, 2.8 mmol) at 0 °C was added *n*BuLi (4.60 mL of a 1.2 M solution in hexanes, 5.52 mmol). After being stirred for 10 min at 0 °C, the reaction mixture was cooled to –40 °C and 2-bromobenzonitrile (**SI-6**) (1.0 g, 5.52 mmol) was added slowly as a solution in 10 mL of THF. After being stirred an additional 30 min, a solution of CuCN·2LiCl (288 mg, 1.65 mmol) in 1.65 mL of THF was added, followed by allyl bromide (1.87 mL, 22.1 mmol). After 20 min, the reaction mixture was quenched with aqueous NH_4Cl and EtOAc, warmed to room temperature, and stirred vigorously for 30 min. The aqueous layer was extracted with EtOAc, washed with brine, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (10% EtOAc/hexanes) to afford 2-allylbenzonitrile[9] (655 mg, 83%) as a colorless oil.

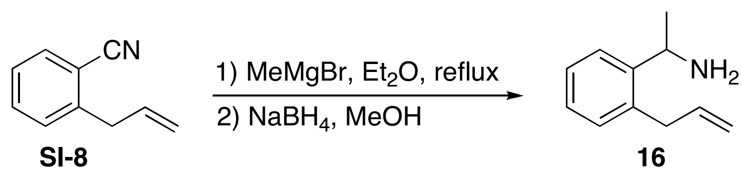
To a suspension of $LiAlH_4$ (556 mg, 14.7 mmol) in Et_2O (20 mL) at 0 °C was slowly added a solution of 2-bromobenzonitrile (655 mg, 4.58 mmol) in 2.5 mL of Et_2O. After being stirred for 1.25 h at 0 °C, the reaction mixture was quenched by slow, sequential addition of water (0.5 mL), 15% NaOH (0.5 mL) and water (1 mL). The mixture was warmed to room temperature, stirred for an additional 30 min, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (100% EtOAc→100:2 EtOAc:Et_3N) to afford 2-allylbenzylamine[10] **14a** (534 mg, 79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 1H), 7.21 (m, 3H), 5.99 (dddd, *J* = 17.2, 10.4, 6.4, 6.4 Hz, 1H), 5.03 (m, 2H), 3.90 (s, 2H), 3.45 (d, *J* = 6.4 Hz, 2H), 2.12 (br s, 2H).



SI-7 **14b**

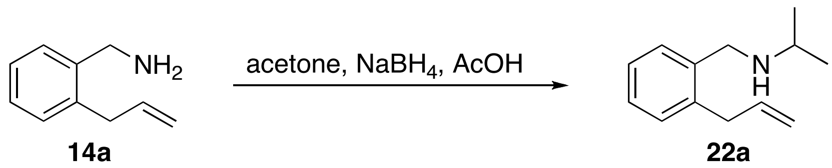
4-Chloro-2-allylbenzylamine (14b). 4-chloro-2-allylbenzonitrile was prepared using the procedure described above with the following modifications: After addition of 4-chloro-2-bromobenzonitrile **SI-7** (3.07 g, 14.2 mmol) to the reaction flask containing nBu$_3$MgLi at -50 °C, the mixture was stirred only 5 min prior to adding CuCN·2LiCl and allyl bromide. After being stirred 10 min, the reaction mixture was quenched with aqueous NH_4Cl and worked up as above. The crude product was purified by flash column chromatography (5%→10% EtOAc/hexanes) to afford 4-chloro-2-allylbenzonitrile (1.63 g, 65%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 1.5 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.92 (dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 5.16 (d, *J* = 17.0 Hz, 1H), 3.59 (d, *J* = 6.5 Hz, 2H).

4-chloro-2-allylbenzonitrile (554 mg, 3.10 mmol) was reduced using $LiAlH_4$ (354 mg, 9.30 mmol) following the exact procedure described above for the des-chloro compound. The crude material was purified by flash column chromatography (10% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N→100:7:2 CH_2Cl_2:MeOH:Et_3N) to afford 4-chloro-2-allylbenzylamine **14b** (421 mg, 75%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 5.95 (dddd, *J* = 17.0, 10.5, 6.5, 6.5 Hz, 1H), 5.10 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.01 (dd, *J* = 17.0, 1.5 Hz, 1H), 3.83 (s, 2H), 3.40 (d, *J* = 6.0 Hz, 2H), 1.35 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.7, 139.3, 136.4, 132.6, 129.7, 129.2, 126.8, 116.6, 43.2, 36.6. Anal. Calcd for $C_{10}H_{12}ClN$: C, 66.12; H, 6.66 N, 7.71 Found: C, 66.37; H, 6.94; N, 7.72

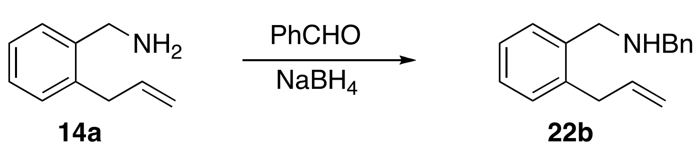


2-Allyl-(methylbenzyl)-amine (16). To a solution of 2-allylbenzonitrile **SI-8** (439 mg, 3.07 mmol) in Et_2O (3 mL) was added MeMgBr (5.11 mL of a 3 M solution in Et_2O, 15.3 mmol) and heated to reflux. After being stirred for 21 h, the reaction mixture was cooled to 0 °C, quenched with anhydrous MeOH (2 mL), diluted with Et_2O, filtered through a plug of celite and concentrated *in vacuo*. The crude imine was dissolved in anhydrous MeOH (8 mL) and $NaBH_4$ (190 mg, 5.07 mmol) was added in two portions. After being stirred for 1 h, the reaction mixture was quenched with saturated aqueous NaHCO3, extracted with EtOAc (×2), washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (50% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N) to afford the product **16** (224 mg, 45%) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.25 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.00 (dddd, *J* = 16.5, 10.0, 6.5, 6.5 Hz, 1H), 5.07 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.98 (dd, *J* = 16.0, 1.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 1H), 3.49 (dd, *J* = 16.0, 6.5 Hz, 1H), 3.44 (dd, *J* = 16.5, 6.0 Hz, 1H), 1.43 (br s, 2H), 1.36 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0, 137.8, 136.3, 130.0, 127.1, 126.8, 125.0, 115.8, 46.4, 37.0, 25.2. Anal. Calcd for

$C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 80.85; H, 9.25; N, 8.61. HRMS (ES+) *m/z* Calcd for $C_{11}H_{15}N$ $[M+H]^+$ 162.1283, found 162.1280.



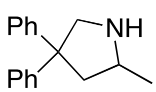
N-Isopropyl-2-allylbenzylamine (22a). To a solution of 2-allylbenzylamine **14a** (298 mg, 2.03 mmol) in AcOH (4 mL) was added acetone (0.47 mL, 8.11 mmol). After being stirred at room temperature for 1 h, $NaBH_4$ (131 mg, 3.45 mmol) was added in two portions. After being stirred for 45 min, an additional 0.23 mL of acetone was added followed by 38 mg of $NaBH_4$. After being stirred 30 min, the reaction mixture was cooled to 0 °C and quenched with 15% aqueous NaOH. Solid NaOH pellets were added until the mixture was strongly basic. The mixture was extracted with CH_2Cl_2 (×2), washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (0%→10% MeOH/CH_2Cl_2) to afford the product **22a** (326 mg, 85%) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (m, 1H), 7.19 (m, 3H), 6.00 (dddd, *J* = 16.5, 10.5, 6.5, 6.0 Hz, 1H), 5.06 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.00 (dd, *J* = 17.0, 2.0 Hz, 1H), 3.75 (s, 2H), 3.47 (d, *J* = 6.0 Hz, 2 H), 2.86 (septet, *J* = 6.0 Hz, 1H), 1.11 (br s, overlapping, 1H), 1.10 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 138.1, 137.8, 130.0, 129.3, 127.3, 126.6, 115.7, 49.2, 48.8, 37.0, 23.1. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.51; H, 9.98; N, 7.52.



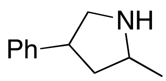
N-Benzyl-2-allylbenzylamine (22b). To a solution of 2-allylbenzylamine **14a** (150 mg, 1.02 mmol) in MeOH (2 mL) was added benzaldehyde (0.11 mL, 1.12 mmol). After being stirred for 1.5 h at room temperature, $NaBH_4$ (58.0 mg, 1.53 mmol) was added in two portions. After being stirred for an additional 20 min, the reaction mixture was quenched with 1 M NaOH. The aqueous layer was extracted with EtOAc (×2), washed with brine (×1), dried with $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (20%→50% EtOAc/hexanes) to afford the product **22b** (230 mg, 94%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 5H), 7.24 (m, 4H), 6.0 (m, 1H), 5.06 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.97 (dd, *J* = 17.5, 1.5 Hz, 1H), 3.87 (s, 2H), 3.82 (s, 2H), 3.48 (d, *J* = 5.5 Hz, 2H), 1.54 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 138.4, 138.3, 137.6, 126.5, 129.9, 128.5, 127.4, 127.0, 126.5, 115.7, 53.8, 50.8, 36.9. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.23; H, 8.33; N, 6.07.

General Hydroamination Procedure (0.5 mmol scale): To a vial containing $[Rh(CH_3CN)_2COD]BF_4$ (1.9 mg, 0.0050 mmol, 1 mol%) and ligand (4.0 mg, 0.0060 mmol, 1.2 mol%) was added the aminoalkene (0.5 mmol). Solvent (1 mL) was added to this mixture, and the vial was capped with a Teflon-lined screw cap. The vial was removed from the glovebox and was placed in a preheated oil bath at either 70 °C or 100 °C (or stirred at room temperature). After the time indicated, the reaction was removed from the oil bath and quenched with 1 M NaOH. The mixture was extracted with CH_2Cl_2 (×2) and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash column chromatography to afford the cyclized hydroamination product.

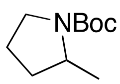
Tabulated Spectral Data for Products:



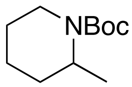
2-Methyl-4,4-diphenylpyrrolidine (2a). Reaction conducted on 0.5 mmol scale with 1 mol% [Rh] for 3 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (50% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N) and obtained in an 80% yield in *t*BuOH (94 mg) or 71% yield in THF (84 mg) as a colorless oil. Spectral data for this compound match literature values.[11] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (m, 8H), 7.19 (m, 2 H), 3.70 (dd, *J* = 11.0, 1.0 Hz, 1H), 3.49 (d, *J* = 11.0 Hz, 1H), 3.39 (ddq, *J* = 9.0, 6.5, 6.5 Hz, 1H), 2.76 (ddd, *J* = 13.0, 6.5, 1.0 Hz, 1H), 2.21 (br s, 1H), 2.06 (dd, *J* = 13.0, 9.0 Hz, 1H), 1.23 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.7, 147.0, 128.2, 128.2, 126.9, 126.9, 125.9, 125.8, 57.8, 57.2, 53.0, 47.0.



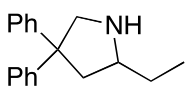
2-Methyl-4-phenylpyrrolidine (2b). Reaction conducted on 0.5 mmol scale in *t*BuOH with 3 mol% [Rh] for 15 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (66% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N→100:5:2 CH_2Cl_2:MeOH:Et_3N) and obtained in a 62% yield (50 mg, run 1) and 70% yield (run 2) as a light yellow oil. Spectral data match literature values. [12] ^{1}H NMR (500 MHz, $CDCl_3$, reported as a 2:1 mixture of diastereomers): δ ^{13}C NMR (125 MHz, $CDCl_3$): δ 7.26 (m, 7.5 H), 3.46 (m, 1H), 3.34 (m, 3H), 3.02 (m, 1H), 2.87 (dd, J = 11.0, 9.0 Hz, 0.5 H). 2.37 (m, 1H), 2.03 (m, 2H), 1.82 (dddd, J = 13.0, 9.5, 6.5, 6.5 Hz, 0.5H), 1.45 (m, 1H), 1.27 (d, J = 6 Hz, 3H), 1.25 (d, J = 6.5 Hz, 1.5 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 144.6, 128.5, 127.4, 127.2, 126.2, 126.2, 56.0, 55.4, 54.9, 54.6, 46.6, 45.5, 43.6, 42.1, 22.1, 21.6.



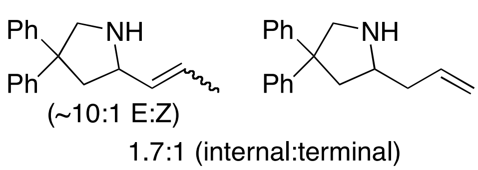
***N*-Boc-2-Methylpyrrolidine (7a-Boc).** Reaction conducted on 0.5 mmol scale in *t*BuOH with 4 mol% [Rh] for 7 h at 70 °C according to the general procedure with the following modifications: After cooling to room temperature, the reaction mixture was quenched directly with $NaHCO_3$ (84 mg, 0.99 mmol) and Boc_2O (131 mg, 0.60 mmol). After being stirred for 20 min, the mixture was quenched with brine and diluted with CH_2Cl_2. Trimethoxybenzene (9.7 mg, 0.058 mmol) was then added to this mixture. The aqueous layer was extracted with CH_2Cl_2 (×2) and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The indicated compound was obtained in a 76% NMR yield based on relative integrations to trimethoxybenzene as the internal standard. The crude material was purified by flash chromatography on silica gel (5%→10% EtOAc/hexanes) and obtained in a 67% yield as a 10:1:1 mixture of **7a-Boc**:*N*-Boc-3-amino-1-pentene:BocNEt_2 (62 mg) as a colorless oil. Spectral data for this compound match literature values.[13] ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 3.80 (br s, 1H), 3.27 (t, J = 8.5 Hz, 2H), 1.82 (m, 3H), 1.56 (m, 1H), 1.39 (s, 9H), 1.09 (d, J = 6.4 Hz, 3H).



***N*-Boc-2-Methylpiperidine (7b-Boc).** Reaction conducted on 0.5 mmol scale in *t*BuOH with 4 mol% [Rh] for 8 h at 70 °C according to the general procedure with the following modification: After cooling to room-temperature, the reaction mixture was quenched directly with $NaHCO_3$ (86 mg, 1.01 mmol) and Boc_2O (133 mg, 0.61 mmol). After being stirred for 20 min, the mixture was quenched with brine, extracted with CH_2Cl_2 (×2) and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (5%→10% EtOAc/hexanes) and obtained in a 77% yield (75 mg) as a colorless oil. Spectral data for this compound match literature values.[13] ^1H NMR (500 MHz, C_6D_6): δ 4.32 (br t, *J* = 5.5 Hz, 1H), 3.87 (dd, *J* = 13.5, 2.5 Hz, 1H), 2.76 (dt, *J* = 13.5, 3.0 Hz, 1H), 1.55 (m, 4H), 1.44 (m, 1H), 1.41 (s, 9H), 1.32 (m, 1H), 1.07 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 79.1, 46.2, 38.8, 30.2, 28.6, 25.8, 18.8, 15.8.

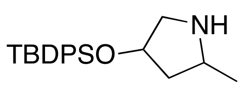


2-Ethyl-4,4-diphenylpyrrolidine (9). Reaction conducted on 0.5 mmol scale in dioxane with 18 mol% [Rh] for 15 h at 100 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (20%→66% EtOAc/hexanes→66% EtOAc/hexanes (with 2% Et_3N)→100:2 EtOAc:Et_3N) and obtained in a 48% yield (61 mg, run 1), 35% yield (44 mg, run 2), and 39% yield (49 mg, run 3) as a light yellow oil. Spectral data for this compound match literature values.[14] ^1H NMR (500 MHz, $CDCl_3$): δ 7.28 (m, 8H), 7.17 (dt, *J* = 7.0, 1.5 Hz, 2H), 3.70 (dd, *J* = 11.5, 1.5 Hz, 1H), 3.41, (d, *J* = 11.5 Hz, 1H), 3.14 (dddd, *J* = 13.5, 7.0, 6.5, 6.5 Hz, 1H), 2.77 (dd, 13.0, 6.5 Hz, 1H), 2.03 (dd, *J* = 13.0, 9.5 Hz, 1H), 1.87 (br s, 1H), 1.51 (m, 2H), 0.94, (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.9, 147.1, 128.5, 128.4, 127.2, 126.1, 59.5, 57.8, 56.9, 45.1, 30.1, 11.8.

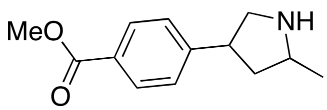


4,4-Diphenyl-2-(prop-1-enyl)pyrrolidine and 2-allyl-4,4-diphenylpyrrolidine (11).

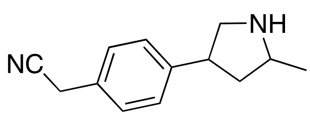
Reaction conducted on 0.5 mmol scale in dioxane with 3 mol% [Rh] for 14 h at 100 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (20% EtOAc/hexanes→60% EtOAc→100:2 EtOAc:Et_3N) and obtained in a 64% yield (84 mg) as a colorless oil (as the mixture indicated). ^1H NMR (500 MHz, $CDCl_3$) data for (*E*)-4,4-diphenyl-2-(prop-1-enyl)pyrrolidine: δ 7.27 (m, 10H), 5.51 (m, 2H), 4.13 (q, *J* = 8.5). ^1H NMR data for 2-allyl-4,4-diphenylpyrrolidine: (500 MHz, $CDCl_3$): δ 7.27 (m, 10H), 5.84 (dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 3.72 (d, *J* = 11.5 Hz, 1H), 3.45 (d, *J* = 11.5 Hz, 1H), 3.34 (m, 1H), 2.78 (m, 1H), 2.29 (m, 2H), 2.11 (dd, *J* = 13.0, 9.0 Hz, 1H), 1.93 (br s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) (reported as the mixture): δ 147.7, 147.6, 147.0, 146.9, 136.2, 134.3, 134.1, 128.5, 128.4, 128.4, 127.1, 127.0, 127.0, 126.1, 125.1, 116.6, 59.6, 58.0, 57.8, 57.7, 57.2, 56.8, 56.8, 53.9, 45.8, 45.6, 44.8, 41.7, 17.8, 13.3. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.72; H, 7.93; N, 5.31.



4-(*tert*-butyldiphenylsilyloxy)-2-methylpyrrolidine (13a). Reaction conducted on 0.25 mmol scale in *t*BuOH with 3 mol% [Rh] for 18 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (33% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N) and obtained in a 71% yield (60 mg, dr = 1.6:1) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$, reported as a 1.2:1 mixture of diastereomers): δ 7.66 (m, 8H), 7.40 (m, 10H), 4.38 (m, 0.8H), 4.35 (m, 1H), 3.46 (m, 0.8H), 3.02 (m, 1.8H), 2.96 (d, *J* = 12.0 Hz, 1H), 2.85 (dd, *J* = 12.0, 2.5 Hz, 0.8H), 2.66 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.01 (m, 1H), 1.90 (dd, *J* = 12.5, 5.5 Hz, 0.8H), 1.81 (br s, 1.8H), 1.37 (m, 1H), 1.26 (d, *J* = 6.5 HZ, 3H), 1.23 (m, overlapping, 0.8 H, 1.01 (d, *J* = 7.0 Hz, 2.4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.9, 135.8, 135.8, 134.4, 134.4, 134.3, 75.5, 75.0, 56.7, 56.2, 54.3, 53.0, 44.5, 44.3, 27.0, 21.9, 21.5, 19.2, 19.2. Anal. Calcd for $C_{21}H_{28}NOSi$: C, 74.28; H, 8.61; N, 4.13 Found: C, 74.58; H, 8.84; N, 4.17. HRMS (ES+) *m/z* Calcd for $C_{21}H_{30}NOSi$ $[M+H]^+$ 340.2097, found 340.2094.

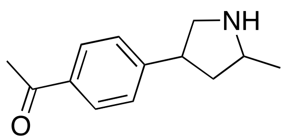


2-Methyl-4-(4-methylcarboxyphenyl)pyrrolidine (13b). Reaction conducted on 0.5 mmol scale in *t*BuOH with 3 mol% [Rh] for 21 h at 70 °C according to the general procedure except the reaction mixture was quenched with saturated aqueous $NaHCO_3$ instead of 1 M NaOH. The indicated compound was purified by flash chromatography on silica gel (60% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N) and obtained in a 64% yield (70 mg, dr = 1.6:1) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, reported as a 1.7:1 mixture of diastereomers): δ 7.94 (d, *J* = 8.0 Hz, 3.2H), 7.29 (d, *J* = 8.0 Hz, 3.2H), 3.87 (s, 4.7H), 3.44 (m, 1.2H), 3.33 (m, 2.6H), 2.99 (ddd, *J* = 11.5, 6.5, 6.5 Hz, 1H), 2.83 (dd, *J* = 11.0, 8.5 Hz, 0.6H), 2.35 (m, 1H), 2.00 (app dt, *J* = 13.0, 7.0 Hz, 0.6H), 2.36 (br s, 1.6H), 1.80 (dddd, *J* = 13.0, 9.5, 7.0, 7.0 Hz, 0.6H), 1.39 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.5 Hz, 1.8H). ^{13}C NMR (125 MHz, $CDCl_3$, reported as a 1.7:1 mixture of diastereomers): δ 167.1, 150.3, 150.3, 129.8, 128.1, 127.3, 127.2, 55.8, 55.4, 54.9, 54.4, 52.0, 46.5, 45.5, 43.5, 42.0, 21.9, 21.4. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.06; H, 8.02; N, 6.69.

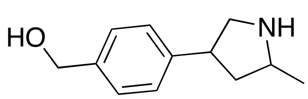


2-Methyl-4-(4-cyanomethylphenyl)pyrrolidine (13c). Reaction conducted on 0.5 mmol scale in *t*BuOH with 5 mol% [Rh] for 12.5 h at 70 °C according to the general procedure except the reaction mixture was quenched with saturated aqueous $NaHCO_3$ instead of 1 M NaOH. The indicated compound was purified by flash chromatography on silica gel (100% EtOAc→100:2 EtOAc:Et_3N→100:3:2 CH_2Cl_2:MeOH:Et_3N) and obtained in a 79% yield (80 mg, dr = 1.5:1) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, reported as a 1:1 mixture of diastereomers): δ 7.26 (m, 8 H), 4.26 (br s, 2H), 3.72 (s, 4H), 3.47 (m, 6H), 3.10 (dd, *J* = 10.5, 8.0 Hz, 1H), 2.92 (dd, *J* = 11.0, 9.0 Hz, 1H), 2.40 (ddd, *J* = 12.5, 6.5, 6.5 Hz, 1H), 2.05 (dt, *J* = 13.5, 8.0, 7.5 Hz, 1H), 1.89 (ddd, *J* = 13.0, 9.0, 6.5 Hz, 1H), 1.55 (app dt, *J* = 12.5, 10.5, 10.5 Hz, 1H), 1.38 (d, *J* = 6.0 Hz, 3H), 1.30 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 142.9, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 118.0, 118.0, 55.8, 55.0, 54.9, 53.1, 45.2, 44.4, 42.9, 41.7, 23.4, 21.3, 20.3. HRMS

(ES+) *m/z* Calcd for $C_{13}H_{16}N_2$ $[M+H]^+$ 200.1392, found 200.1389.

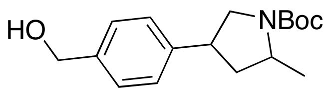


2-Methyl-4-(4-acetylphenyl)pyrrolidine (13d). Reaction conducted on 0.46 mmol scale in *t*BuOH with 5 mol% [Rh] for 16 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (100% EtOAc→100:2 EtOAc:Et_3N→100:3:2 CH_2Cl_2:MeOH:Et_3N) and obtained in a 61% yield (57 mg, dr = 1.5:1) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, reported as a 2:1 mixture of diastereomers): δ 7.89 (d, *J* = 8.0 Hz, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.31 (d, overlapping, *J* = 8.0 Hz, 1H), 3.47 (m, 1H), 3.37 (m, 3H), 3.02 (m, 1H), 2.87 (dd, *J* = 10.5, 8.5 Hz, 0.5H), 2.59 (s, 4.5H), 2.38 (m, 1H), 2.14 (br s, 1.5H), 2.04 (m, 0.5H), 1.83 (ddd, *J* = 13.0, 9.5, 7.0 Hz, 0.5H), 1.44 (m, 1.5H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.24 (d, *J* = 6.0 Hz, 1.5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9, 150.5, 135.4, 128.8, 127.6, 127.4, 55.8, 55.6, 55.0, 54.3, 46.4, 45.5, 43.5, 42.1, 26.7, 21.9, 21.4. HRMS (ES+) *m/z* Calcd for $C_{13}H_{16}NO$ $[M+H]^+$ 204.1388, found 204.1383.

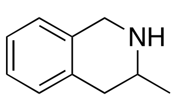


2-Methyl-4-(4-hydroxymethylphenyl)-pyrrolidine (13e). Reaction conducted on 0.5 mmol scale in *t*BuOH with 5 mol% [Rh] for 8 h at 70 °C according to the general procedure. After cooling to room temperature, trimethoxybenzene (11.1 mg, 0.066 mmol) was added to the reaction mixture and worked up according to the general procedure. An NMR yield of 62% was obtained on the crude reaction mixture using the trimethoxybenzene as an internal standard. The indicated compound was purified by flash chromatography on silica gel (100% EtOAc →100:2 EtOAc:Et_3N→100:2:2 CH_2Cl_2:MeOH:Et_3N →100:10:2 CH_2Cl_2:MeOH:Et_3N) and obtained in a 56% yield (53 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, reported as 1.4:1 mixture of diastereomers): δ 7.28 (d, *J* = 7.0 Hz, 3.4 H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1.4 H), 4.62 (s, 3.4H), 3.64 (br s, 3.4H), 3.41 (m, 0.7H), 3.35 (overlapping m, 0.7H), 3.33 (overlapping dd, *J* = 11.0, 8.0 Hz, 1H), 3.25 (m, 2.4H), 2.87 (ddd, *J* = 12.5, 8.5, 6.0

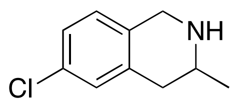
Hz, 1H), 2.68 (dd, J = 10.5, 8.5 Hz, 0.7H), 2.32 (m, 1H), 1.98 (m, 1H), 1.78 (ddd, J = 13.0, 9.5, 6.5 Hz, 0.7H), 1.43 (ddd, J = 12.5, 12.5, 10.0 Hz, 1H), 1.26 (d, J = 6.5 Hz, 3H), 1.22 (d, J = 6.0 Hz, 2.1H). This material contained 3% of an aldehyde byproduct and the desired amine product could not be isolated in analytically pure form. It was converted to the Boc carbamate **13e-Boc** and complete characterization data were obtained on this Boc-protected product (see below).



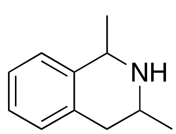
2-Methyl-4-(4-hydroxymethylphenyl)-*N*-Boc-pyrrolidine (13e-Boc). To a solution of 2-methyl-4-(4-hydroxymethylphenyl)-pyrrolidine **13e** (53 mg, 0.28 mmol) in EtOH (2.0 mL) was added $NaHCO_3$ (45 mg, 0.54 mmol) and Boc_2O (71 mg, 0.32 mmol). After being stirred for 4.25 h at room temperature, the reaction mixture was quenched with water (×1), extracted with EtOAc (×2), dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel (25%→40% EtOAc/hexanes) to afford the product **13e-Boc** (61 mg, 75%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, 55 °C, (reported as a 1.3:1 mixture of diastereomers): δ 7.31 (d, J = 8.0 Hz, 3.6H), 7.22 (d, J = 8.0 Hz, 3.6H), 4.66 (s, 3.6H), 4.06 (br s, 0.8H), 4.00 (br s, 0.8H), 3.92 (br s, 1H), 3.78 (dd, J = 10.0, 8.0 Hz, 0.8H), 3.48 (m, 0.8H), 3.34 (br s, 0.8H), 3.21 (m, 2H), 2.49 (ddd, J = 10.0, 6.0, 6.0 Hz, 1H), 2.15 (ddd, J = 11.5, 11.5, 8.0 Hz, 0.8H), 1.92 (m, 2H), 1.68 (m, 1H), 1.48 (s, 9H), 1.48 (s, 7.2H), 1.34 (d, J = 6.0 Hz, 3H), 1.27 (d, J = 6.0 Hz, 2.4H). ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C, (reported as a 1.3:1 mixture of diastereomers): δ 154.8, 154.6, 141.2, 140.5, 139.8, 139.8, 127.43, 127.41, 127.38, 79.4, 79.3, 65.1, 53.8, 53.2, 52.9 (br), 42.8, 42.5, 41.3 (br), 28.7, 21.3 (br), 20.9 (br). Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81 Found: C, 69.87; H, 8.90; N, 4.66. HRMS (ES+) m/z Calcd for $C_{17}H_{26}NO_3$ $[M+H]^+$ 292.1913, found 292.1906.



3-Methyl-1,2,3,4-tetrahydroisoquinoline (15a). Reaction conducted on 0.5 mmol scale in *t*BuOH with 1 mol% [Rh] for 5 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (50% EtOAc/hexanes→100% EtOAc→100:2 EtOAc:Et_3N) and obtained in an 87% yield (67 mg) as a light yellow oil. Spectral data for this compound match literature values.[15] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (m, 2H), 7.06 (m, 1H), 7.01 (m, 1H), 4.10 (d, *J* = 16.0 Hz, 1H), 4.03 (d, *J* = 16.0 Hz, 1H), 3.01 (ddq, *J* = 10.5, 6.0, 4.0 Hz, 1H), 2.77 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 2.50 (d, *J* = 16.0, 10.5 Hz, 1H), 2.12 (br s, 1H), 1.24 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.5, 135.1, 129.3, 126.3, 126.2, 126.0, 49.4, 48.7, 37.4, 22.7. (The reaction was also carried out at room temperature on 0.52 mmol scale using 10 mol % [Rh] for 24 h in THF to afford the product (59 mg) in 77% isolated yield).

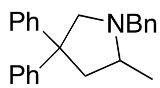


6-Chloro-3-methyl-tetrahydroisoquinoline (15b). Reaction conducted on 0.5 mmol scale in *t*BuOH with 2 mol% [Rh] for 6 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (20%→66% EtOAc/hexanes→100:2 EtOAc:Et_3N) and obtained in an 84% yield (76 mg) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.5 Hz, 1H), 7.05 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 4.04 (d, *J* = 16.0 Hz, 1H), 3.99 (d, *J* = 16.0 Hz, 1H), 2.98 (m, 1H), 2.73 (dd, *J* = 166.5, 3.5 Hz, 1H), 2.46 (dd, *J* = 16.5, 11.0 Hz, 1H), 1.51 br s, 1H), 1.23 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.0, 133.0, 131.5, 128.9, 127.4, 125.9, 49.0, 48.3, 37.1, 22.5. Anal. Calcd for $C_{10}H_{12}ClN$: C, 66.12; H, 6.66; N, 7.71 Found: C, 66.40; H, 6.80; N, 7.95.

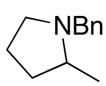


1,3-dimethyltetrahydroisoquinoline (17). Reaction conducted on 0.5 mmol scale in *t*BuOH with 1 mol% [Rh] for 7 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (60%→100% EtOAc/hexanes→100:2 EtOAc:Et_3N) and obtained in a 74% yield (59 mg, dr = 1.1:1) as a light yellow oil. Spectral data for this compound match literature values.[16] ^{1}H NMR (500 MHz, $CDCl_3$, reported as a 1.2:1 mixture of disatereomers): δ 7.13 (m, 8.4H), 4.24

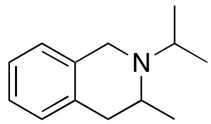
(q, J = 7.0 Hz, 1.2H), 4.16 (q, J = 6.0 Hz, 1H), 3.29 (ddq, J = 10.0, 6.5, 4.5 Hz, 1.2 H), 3.06 (ddq, J = 10.0, 6.5, 4.0 Hz, 1H), 3.16 (dd, J = 16.5, 4.5 Hz, 1.2H), 2.75 (dd, J = 16.0, 3.5 Hz, 1H), 2.57 (dd, J = 16.0, 11.0 Hz, 1H), 2.46 (dd, J = 16.0, 10.0 Hz, 1.2H), 1.54 (br s, 2.2 H), 1.48 (d, J = 6.5 Hz, 3H), 1.46 (d, J = 7.0 Hz, 3.6H), 1.25 (d, J = 6.5 Hz, 3H), 1.22 (d, J = 6.5 H, 3.6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.1, 140.0, 135.2, 134.5, 129.2, 129.0, 126.7, 126.0, 126.0, 125.9, 125.7, 125.2, 52.7, 50.9, 49.1, 42.8, 38.4, 37.6, 24.3, 22.7, 22.5, 22.4.



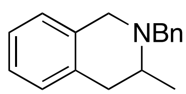
***N*-Benzyl-2-methyl-4,4-diphenylpyrrolidine (19).** Reaction conducted on 0.5 mmol scale in *t*BuOH with 1 mol% [Rh] according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (10% EtOAc/hexanes) and obtained in an 83% yield (107 mg) as a colorless oil. Spectral data for this compound match literature values.[11] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 3H), 7.22 (m, 10H), 7.12 (t, J = 7.0 Hz, 1H), 4.10 (d, J = 13.0 Hz, 1H), 3.64 (d, J = 10.0 Hz, 1H), 3.26 (d, J = 13.5 Hz, 1H), 2.93 (dd, J = 13.0, 7.5 Hz, 1H), 2.83 (m, 1H), 2.79 (d, J = 9.5 Hz, 1H), 2.21 (dd, J = 13.0, 7.5 Hz, 1H), 1.18 (d, J = 5.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 148.8, 140.2, 128.7, 128.3, 128.0, 127.6, 127.4, 126.9, 125.9, 125.5, 66.6, 59.8, 58.1, 52.6, 48.1, 19.6.



***N*-Benzyl-2-methylpyrrolidine (21).** Reaction conducted on 0.5 mmol scale in *t*BuOH with 3 mol% [Rh] according to the general procedure with the following modification: After cooling to room temperature, trimethoxybenzene (9.6 mg, 0.057 mmol) was added to the reaction mixture. The indicated compound was obtained in a 65% NMR yield based on relative integrations to trimethoxybenzene as the internal standard. Spectral data for this compound match literature values.[17] ^{1}H NMR (500 MHz, $CDCl_3$): δ ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (m, 5H), 4.04 (d, J = 12.5, Hz, 1H), 3.16 (d, J = 12.5 Hz, 1H), 2.93 (dt, J = 9.5, 2.5 Hz, 1H), 2.41 (m, 1H), 2.12 (q, J = 9.0 Hz, 1H), 1.96 (m, 1H), 1.69 (m, 2H), 1.52 (m, 1H), 1.20 (d, J = 6.0 Hz, 3H).



***N*-Isopropyl-3-methyl-tetrahydroisoquinoline (23a).** Reaction conducted on 0.5 mmol scale in *t*BuOH with 1 mol% [Rh] for 8 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (20% EtOAc/hexanes→100% EtOAc) and obtained in a 76% yield (73 mg, run 1) and 80% yield (75 mg, run 2) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (m, 2H), 7.05 (m, 2H), 3.76 (s, 2H), 3.15 (m, 2H), 2.95 (dd, *J* = 16.0, 4.5 Hz, 1H), 2.63 (dd, *J* = 16.0, 7.0 Hz, 1H), 1.22 (d, *J* = 6.5 Hz, 3H), 1.11 (d, *J* = 6.5 Hz, 3H), 1.05 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.3, 134.3, 128.7, 126.4, 126.0, 125.5, 49.8, 49.2, 46.7, 37.7, 21.8, 16.9, 16,4. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40 Found: C, 82.21; H, 10.00; N, 7.45.



***N*-Benzyl-3-methyl-tetrahydroisoquinoline (23b).** Reaction conducted on 0.5 mmol scale in *t*BuOH with 1 mol% [Rh] for 5 h at 70 °C according to the general procedure. The indicated compound was purified by flash chromatography on silica gel (10% →20% EtOAc/hexanes) and obtained in an 86% yield (101 mg) as a colorless oil. Spectral data for this compound match literature values.[18] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.19 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.91 (d, *J* = 13.5 Hz, 1H), 3.79 (d, *J* = 15.5 Hz, 1H), 3.70 (d, *J* = 16.0 Hz, 1H), 3.66 (d, *J* = 13.0 Hz, 1H), 3.20 (m, 1H), 3.10 (dd, *J* = 16.5, 5.0 Hz, 1H), 2.70 (dd, *J* = 16.5, 6.0 Hz, 1H), 1.23 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.6, 134.5, 134.1, 129.1, 129.0, 128.4, 127.0, 126.5, 126.1, 125.6, 57.4, 52.2, 51.7, 35.7, 15.2. (The reaction was also carried out at room temperature on 0.51 mmol scale using 10 mol% [Rh] for 24 h in THF to afford the product (89 mg) in 74% isolated yield).

Kinetic Data:

Representative Procedure for Conducting Kinetic Measurements:

$[Rh(CH_3CN)_2COD]BF_4$ (8.7 mg, 0.023 mmol, 5 mol %), **L1** (18.5 mg, 0.0276 mmol, 6 mol %), and trimethoxybenzene (11.7 mg 0.0696 mmol) were added to a 1 mL volumetric flask and diluted with ~0.2 mL of *t*-BuOH-d_9. In a separate vial, the substrate (75 mg, 0.46 mmol) was dissolved in ~0.5 mL of *t*-BuOH-d_9 and filtered through a cotton plug directly into the volumetric flask. The volumetric flask was filled to the line with solvent, mixed thoroughly, and a portion (~0.6 mL) of this solution was transferred to a screw-capped NMR tube. The tube was sealed with a teflon-lined screw cap and removed from the glovebox. Kinetic data were immediately recorded by ^{1}H NMR spectroscopy at 61 °C for at least 3 half-lives using an automated program.

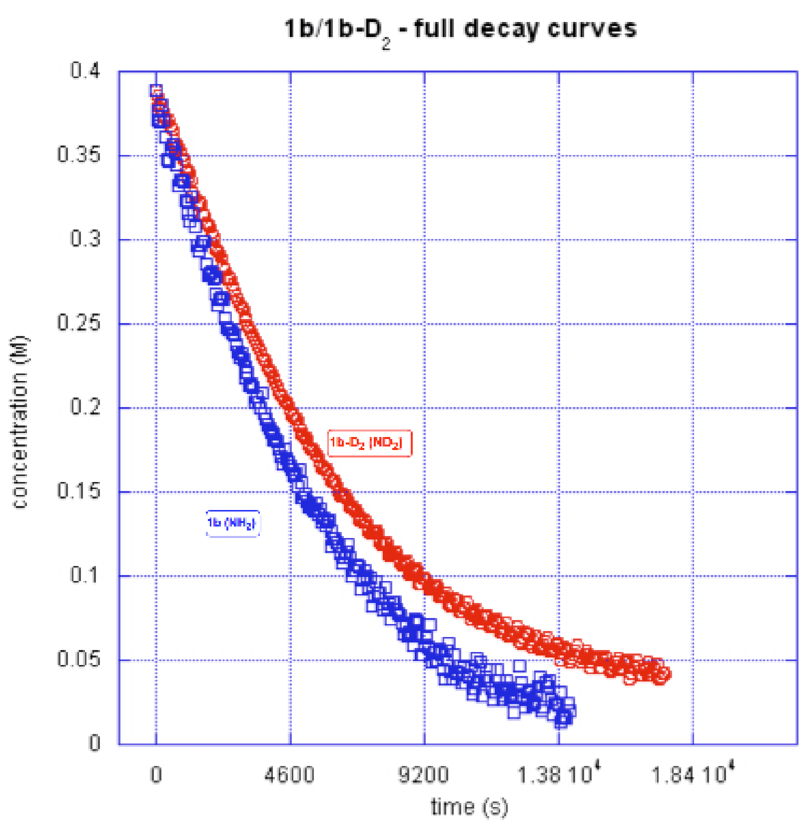


Figure SI-1. Overlay of full decay curves for primary amines **1b/1b-D$_2$** in BuOH-d_9/BuOH-d_{10}.

The full decay curves shown in Figure SI-1 deviate from the expected zero-order kinetic behavior due to formation of the imine complex [(**L1**)Rh(**3a**)]BF_4 as the hydroamination reaction proceeds toward complete conversion of aminoalkene. The reaction rate decreases as the concentration of the imine complex increases and this results in curvature of the full time course plots. Due to this complex kinetic behavior, the KIE for **1b/1b-D$_2$** was determined from initial rate data shown in Figure SI-2.

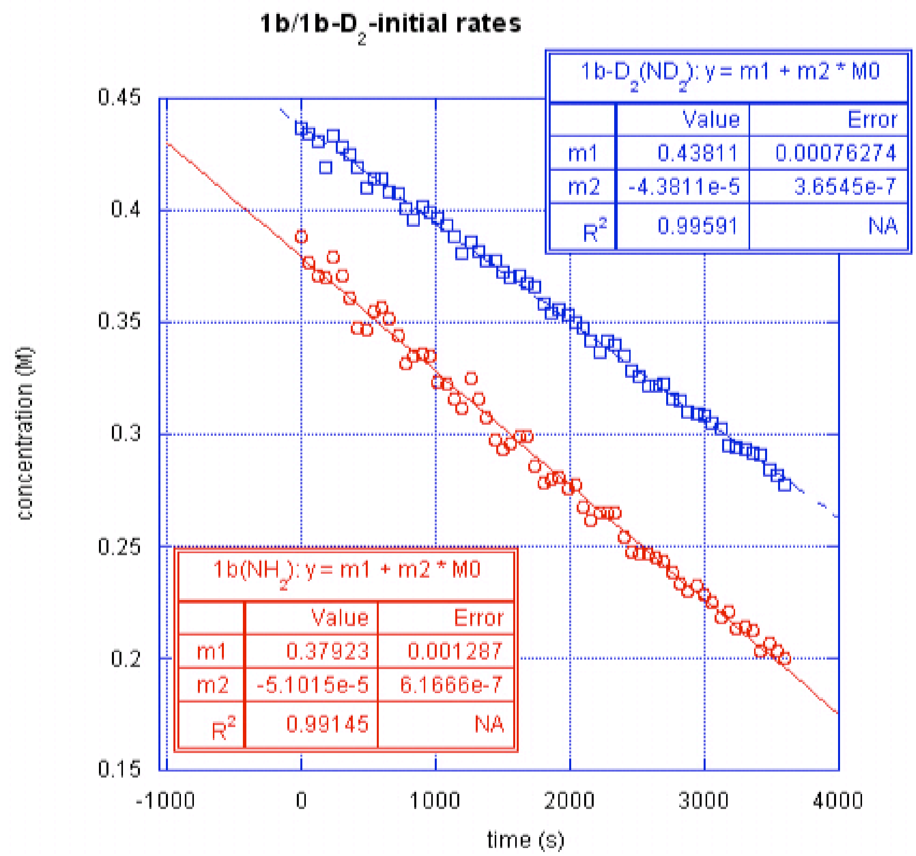


Figure SI-2. Initial rate data used to determine the KIE for **1b/1b-D$_2$** (KIE = 1.16 ± 0.10)

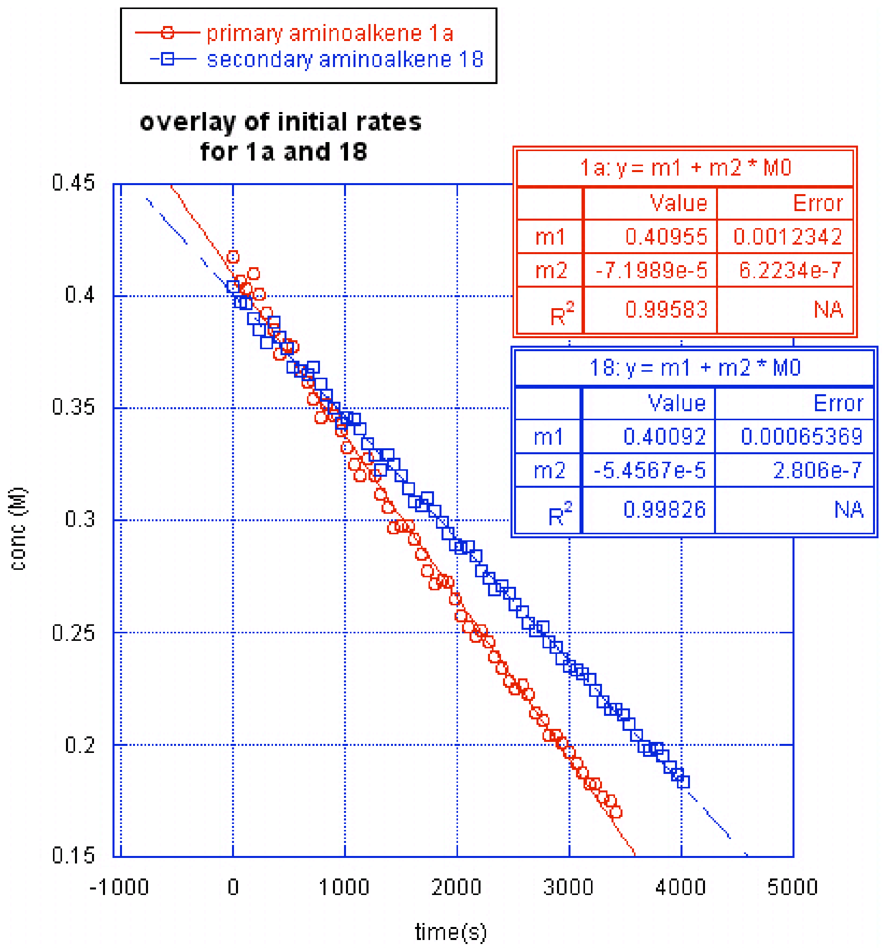


Figure SI-3. Initial rate data used to determine the relative rates of cyclization for primary amine **1a** and secondary amine **18** (k_{1a}/k_{18} = 1.3)

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Crystallographic data for [(L1')Rh-NCMe]BF$_4$

Table SI-1. Crystal data and structure refinement for [(**L1'**)Rh-NCMe]BF$_4$

Identification code	ba81da	
Empirical formula	C33 H55 B F4 N5 O P2 Rh	
Formula weight	789.48	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.3079(12) Å	a= 90°.
	b = 16.9887(11) Å	b= 104.227(5)°.
	c = 24.5185(17) Å	g = 90°.
Volume	7795.8(9) Å^3	
Z	8	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.571 mm^{-1}	
F(000)	3296	
Crystal size	0.11 x 0.08 x 0.04 mm^3	
Theta range for data collection	1.47 to 20.81°.	
Index ranges	-17<=h<=19, -16<=k<=16, -24<=l<=22	
Reflections collected	80549	
Independent reflections	8164 [R(int) = 0.2497]	
Completeness to theta = 20.81°	100.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.9794 and 0.9383	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8164 / 2622 / 1345	
Goodness-of-fit on F^2	0.989	
Final R indices [I>2sigma(I)]	R1 = 0.0762, wR2 = 0.1877	
R indices (all data)	R1 = 0.2036, wR2 = 0.2532	
Largest diff. peak and hole	0.608 and -0.556 e.Å^{-3}	

Table SI-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [(**L1'**)Rh-NCMe]BF$_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5639(5)	4338(8)	2251(4)	44(4)
C(2)	5528(6)	4126(8)	1702(5)	52(4)
C(3)	6051(6)	4337(9)	1400(5)	73(5)
C(4)	6671(6)	4714(9)	1681(6)	72(5)
C(5)	6766(6)	4905(8)	2237(5)	56(5)
C(6)	6281(6)	4734(8)	2539(5)	53(4)
C(7)	6404(5)	4969(8)	3141(5)	48(4)
C(8)	5799(5)	4728(8)	3408(5)	54(5)
C(9)	5815(6)	4901(9)	3962(5)	66(5)
C(10)	5272(7)	4696(10)	4207(5)	82(6)
C(11)	4655(7)	4329(9)	3886(5)	78(6)
C(12)	4618(6)	4154(8)	3320(5)	53(4)
C(13)	5191(6)	4362(8)	3102(5)	47(4)
C(14)	6505(8)	5859(9)	3195(7)	70(5)
C(15)	7085(8)	4534(12)	3497(7)	99(7)
N(1)	4366(6)	4185(5)	791(4)	75(3)
C(16)	3693(7)	3922(9)	394(5)	82(4)
C(17)	3617(12)	4250(16)	-194(5)	88(5)
C(18)	4442(8)	5054(6)	870(7)	83(4)
C(19)	3927(12)	5384(11)	1192(10)	91(5)
N(2)	4892(7)	2781(5)	1054(4)	78(3)
C(20)	5255(8)	2776(8)	590(5)	80(4)
C(21)	4950(12)	2160(11)	146(6)	81(5)
C(22)	4866(8)	2026(6)	1352(6)	82(3)
C(23)	5521(11)	1913(12)	1841(8)	88(4)
N(3)	3108(4)	4196(5)	2874(7)	90(3)
C(24)	2402(5)	3900(10)	2549(8)	98(5)
C(25)	1829(7)	4000(30)	2874(12)	103(5)
C(26)	3174(10)	5069(6)	2912(7)	95(4)
C(27)	3066(18)	5450(12)	2336(9)	97(5)
N(4)	3770(5)	2891(5)	3289(5)	98(3)
C(28)	4428(6)	2462(8)	3590(7)	105(4)
C(29)	4586(12)	1775(11)	3240(11)	106(4)

C(30)	3131(7)	2373(10)	3093(6)	102(4)
C(31)	2944(11)	1951(15)	3589(9)	104(5)
N(5)	3309(6)	3016(7)	1666(5)	56(4)
C(32)	2808(8)	2690(9)	1446(6)	50(5)
C(33)	2181(7)	2251(9)	1158(7)	84(6)
O(1)	5109(4)	4146(5)	2524(4)	48(3)
P(1)	4704(2)	3609(2)	1349(2)	55(1)
P(2)	3835(2)	3660(2)	2879(2)	54(1)
Rh(1)	4170(1)	3560(1)	2068(1)	53(1)
C(34)	9059(8)	1054(7)	4030(5)	71(6)
C(35)	9302(8)	1475(8)	3643(6)	82(6)
C(36)	9573(10)	1056(9)	3230(7)	129(9)
C(37)	9609(12)	242(9)	3247(8)	155(11)
C(38)	9384(11)	-154(8)	3658(8)	125(9)
C(39)	9072(9)	210(9)	4031(7)	104(8)
C(40)	8799(8)	-254(7)	4452(6)	98(7)
C(41)	8661(8)	254(8)	4931(6)	79(6)
C(42)	8498(10)	-72(8)	5399(6)	100(7)
C(43)	8348(12)	380(10)	5821(7)	134(9)
C(44)	8329(10)	1202(9)	5774(7)	111(8)
C(45)	8472(9)	1554(8)	5293(6)	81(6)
C(46)	8650(7)	1063(8)	4897(6)	68(6)
C(47)	8083(8)	-660(10)	4160(8)	94(7)
C(48)	9319(9)	-920(12)	4708(9)	123(8)
N(6)	8802(5)	2770(6)	3000(4)	133(3)
C(49)	8172(6)	2266(8)	2744(7)	139(4)
C(50)	7523(7)	2502(17)	2957(11)	146(5)
C(51)	8698(12)	3626(6)	2862(5)	137(4)
C(52)	8694(16)	3787(11)	2248(7)	138(4)
N(7)	10058(4)	2937(7)	3701(6)	104(3)
C(53)	10440(9)	3366(8)	4213(6)	107(4)
C(54)	10548(14)	4230(8)	4092(11)	108(6)
C(55)	10496(7)	2679(12)	3315(6)	110(4)
C(56)	11072(11)	2090(15)	3594(12)	115(6)
N(8)	7578(4)	2891(10)	5161(4)	95(3)
C(57)	7122(7)	3168(9)	4622(5)	99(3)

C(58)	6697(12)	2510(13)	4275(8)	105(5)
C(59)	7250(8)	2825(10)	5644(6)	102(4)
C(60)	6948(13)	3611(12)	5786(10)	108(5)
N(9)	8860(5)	2954(6)	5831(4)	97(3)
C(61)	9511(6)	2527(8)	6140(6)	103(4)
C(62)	10156(7)	2728(17)	5916(10)	101(4)
C(63)	8870(12)	3822(6)	5924(5)	99(4)
C(64)	8961(17)	4024(11)	6545(7)	102(5)
N(10)	8841(7)	3837(9)	4413(6)	74(5)
C(65)	8850(9)	4516(13)	4415(8)	70(6)
C(66)	8882(10)	5370(11)	4384(8)	111(7)
O(2)	8804(5)	1472(6)	4450(5)	68(3)
P(3)	9257(2)	2547(3)	3659(2)	78(2)
P(4)	8413(2)	2616(3)	5204(2)	69(2)
Rh(2)	8832(1)	2727(1)	4428(1)	66(1)
F(1)	1633(6)	756(8)	1970(5)	140(4)
F(2)	1587(7)	859(8)	2858(4)	148(5)
F(3)	576(5)	891(9)	2176(6)	156(5)
F(4)	1333(8)	1899(6)	2278(6)	143(5)
B(1)	1279(5)	1103(6)	2323(5)	138(4)
F(5)	3437(6)	810(12)	9828(7)	184(5)
F(6)	2633(9)	784(12)	10345(6)	194(4)
F(7)	2838(10)	1900(7)	9943(8)	211(4)
F(8)	2275(8)	915(13)	9417(6)	211(6)
B(2)	2798(6)	1102(8)	9882(5)	192(5)
N(11)	4316(7)	4057(8)	749(4)	77(3)
C(67)	4664(8)	4094(16)	276(5)	78(4)
C(68)	4135(15)	3980(30)	-291(5)	82(5)
C(69)	3728(8)	4625(8)	737(9)	82(3)
C(70)	3988(17)	5475(8)	745(19)	87(5)
N(12)	5021(7)	2787(6)	1121(6)	80(3)
C(71)	4512(8)	2239(10)	753(9)	80(4)
C(72)	4864(18)	1787(18)	356(13)	81(5)
C(73)	5666(8)	2406(8)	1488(12)	85(4)
C(74)	5511(18)	1562(13)	1634(18)	85(5)
N(13)	3147(5)	4221(8)	2920(5)	89(3)

C(75)	2932(6)	4345(13)	3452(5)	92(4)
C(76)	2150(8)	4140(20)	3397(10)	103(5)
C(77)	2861(7)	4791(10)	2460(7)	93(4)
C(78)	2063(8)	4693(18)	2218(11)	105(6)
N(14)	3690(7)	2815(6)	3175(6)	100(4)
C(79)	4000(7)	2069(7)	3031(9)	105(4)
C(80)	4812(8)	2091(18)	3170(20)	106(5)
C(81)	3443(9)	2817(13)	3702(6)	102(4)
C(82)	2690(11)	2480(30)	3613(12)	104(5)
N(15)	8809(7)	2905(9)	3034(5)	135(4)
C(83)	8046(7)	2671(15)	2828(6)	138(4)
C(84)	7819(13)	2620(30)	2191(7)	139(5)
C(85)	8970(11)	3735(10)	2905(10)	137(4)
C(86)	9501(17)	3770(20)	2536(15)	138(5)
N(16)	10073(8)	2870(20)	3657(16)	104(4)
C(87)	10583(11)	3100(20)	4159(18)	108(4)
C(88)	11040(20)	2410(20)	4332(15)	113(7)
C(89)	10228(16)	2860(30)	3051(15)	113(5)
C(90)	10690(20)	3540(20)	2996(15)	116(7)
N(17)	7565(4)	2889(6)	5160(9)	96(3)
C(91)	6974(7)	2366(10)	4857(9)	102(4)
C(92)	6721(14)	1817(14)	5259(14)	112(6)
C(93)	7400(8)	3749(7)	5096(12)	99(4)
C(94)	6811(15)	3985(13)	5378(18)	105(5)
N(18)	8867(6)	3098(11)	5773(5)	97(4)
C(95)	9658(6)	3150(15)	5877(8)	100(4)
C(96)	10029(12)	2590(20)	6345(13)	103(5)
C(97)	8582(11)	3106(12)	6284(6)	97(4)
C(98)	8589(19)	3929(15)	6533(12)	99(5)
F(9)	1796(7)	1399(11)	2173(9)	140(4)
F(10)	1638(11)	451(12)	2743(7)	145(7)
F(11)	742(7)	1285(13)	2386(10)	145(5)
F(12)	1077(13)	410(11)	1826(7)	152(6)
B(3)	1309(7)	883(9)	2284(6)	137(5)
F(13)	3290(8)	933(17)	9647(9)	191(5)
F(14)	2462(12)	447(11)	10030(11)	198(6)

F(15)	3086(14)	1511(14)	10409(8)	207(6)
F(16)	2292(11)	1609(15)	9583(11)	214(5)
B(4)	2779(8)	1126(11)	9921(7)	198(5)

Table SI-3. Bond lengths [Å] and angles [°] for [(**L1’**)Rh-NCMe]BF_4.

C(1)-C(2)	1.358(13)
C(1)-O(1)	1.393(13)
C(1)-C(6)	1.435(14)
C(2)-C(3)	1.438(14)
C(2)-P(1)	1.836(11)
C(3)-C(4)	1.383(15)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.370(15)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.360(14)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.491(14)
C(7)-C(8)	1.528(14)
C(7)-C(14)	1.526(18)
C(7)-C(15)	1.573(18)
C(8)-C(13)	1.376(13)
C(8)-C(9)	1.383(14)
C(9)-C(10)	1.374(15)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.402(15)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.403(14)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.389(14)
C(12)-P(2)	1.831(12)
C(13)-O(1)	1.433(13)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800

C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
N(1)-C(16)	1.489(9)
N(1)-C(18)	1.491(9)
N(1)-P(1)	1.678(7)
C(16)-C(17)	1.518(11)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.520(11)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
N(2)-C(20)	1.475(9)
N(2)-C(22)	1.484(9)
N(2)-P(1)	1.662(7)
C(20)-C(21)	1.521(10)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.528(11)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
N(3)-C(24)	1.487(9)
N(3)-C(26)	1.490(9)
N(3)-P(2)	1.671(7)
C(24)-C(25)	1.522(11)

C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.520(11)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
N(4)-C(28)	1.493(8)
N(4)-C(30)	1.497(9)
N(4)-P(2)	1.671(7)
C(28)-C(29)	1.523(11)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.528(11)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
N(5)-C(32)	1.130(16)
N(5)-Rh(1)	1.945(12)
C(32)-C(33)	1.45(2)
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
O(1)-Rh(1)	2.129(8)
P(1)-N(11)	1.661(7)
P(1)-N(12)	1.675(8)
P(1)-Rh(1)	2.254(4)

P(2)-N(13)	1.658(7)
P(2)-N(14)	1.663(7)
P(2)-Rh(1)	2.243(4)
C(34)-C(35)	1.360(14)
C(34)-O(2)	1.435(15)
C(34)-C(39)	1.434(15)
C(35)-C(36)	1.437(15)
C(35)-P(3)	1.825(14)
C(36)-C(37)	1.384(16)
C(36)-H(36A)	0.9500
C(37)-C(38)	1.369(16)
C(37)-H(37A)	0.9500
C(38)-C(39)	1.362(15)
C(38)-H(38A)	0.9500
C(39)-C(40)	1.495(15)
C(40)-C(48)	1.54(2)
C(40)-C(41)	1.532(14)
C(40)-C(47)	1.554(19)
C(41)-C(42)	1.379(15)
C(41)-C(46)	1.378(14)
C(42)-C(43)	1.374(16)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.401(15)
C(43)-H(43A)	0.9500
C(44)-C(45)	1.408(15)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.386(15)
C(45)-P(4)	1.817(14)
C(46)-O(2)	1.389(15)
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
N(6)-C(49)	1.494(9)

N(6)-C(51)	1.496(9)
N(6)-P(3)	1.681(7)
C(49)-C(50)	1.526(11)
C(49)-H(49A)	0.9900
C(49)-H(49B)	0.9900
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-C(52)	1.530(11)
C(51)-H(51A)	0.9900
C(51)-H(51B)	0.9900
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
N(7)-C(55)	1.483(9)
N(7)-C(53)	1.482(9)
N(7)-P(3)	1.662(7)
C(53)-C(54)	1.523(11)
C(53)-H(53A)	0.9900
C(53)-H(53B)	0.9900
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(55)-C(56)	1.527(11)
C(55)-H(55A)	0.9900
C(55)-H(55B)	0.9900
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
N(8)-C(57)	1.474(8)
N(8)-C(59)	1.476(9)
N(8)-P(4)	1.657(7)
C(57)-C(58)	1.518(11)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
C(58)-H(58A)	0.9800

C(58)-H(58B)	0.9800
C(58)-H(58C)	0.9800
C(59)-C(60)	1.530(11)
C(59)-H(59A)	0.9900
C(59)-H(59B)	0.9900
C(60)-H(60A)	0.9800
C(60)-H(60B)	0.9800
C(60)-H(60C)	0.9800
N(9)-C(61)	1.487(9)
N(9)-C(63)	1.491(9)
N(9)-P(4)	1.670(7)
C(61)-C(62)	1.520(11)
C(61)-H(61A)	0.9900
C(61)-H(61B)	0.9900
C(62)-H(62A)	0.9800
C(62)-H(62B)	0.9800
C(62)-H(62C)	0.9800
C(63)-C(64)	1.528(11)
C(63)-H(63A)	0.9900
C(63)-H(63B)	0.9900
C(64)-H(64A)	0.9800
C(64)-H(64B)	0.9800
C(64)-H(64C)	0.9800
N(10)-C(65)	1.15(2)
N(10)-Rh(2)	1.885(16)
C(65)-C(66)	1.45(2)
C(66)-H(66A)	0.9800
C(66)-H(66B)	0.9800
C(66)-H(66C)	0.9800
O(2)-Rh(2)	2.135(11)
P(3)-N(16)	1.668(9)
P(3)-N(15)	1.678(8)
P(3)-Rh(2)	2.253(5)
P(4)-N(18)	1.670(8)
P(4)-N(17)	1.681(7)
P(4)-Rh(2)	2.252(5)

F(1)-B(1)	1.362(8)
F(2)-B(1)	1.363(8)
F(3)-B(1)	1.363(8)
F(4)-B(1)	1.363(8)
F(5)-B(2)	1.365(8)
F(6)-B(2)	1.363(8)
F(7)-B(2)	1.365(8)
F(8)-B(2)	1.364(8)
N(11)-C(67)	1.476(9)
N(11)-C(69)	1.485(9)
C(67)-C(68)	1.522(11)
C(67)-H(67A)	0.9900
C(67)-H(67B)	0.9900
C(68)-H(68A)	0.9800
C(68)-H(68B)	0.9800
C(68)-H(68C)	0.9800
C(69)-C(70)	1.527(11)
C(69)-H(69A)	0.9900
C(69)-H(69B)	0.9900
C(70)-H(70A)	0.9800
C(70)-H(70B)	0.9800
C(70)-H(70C)	0.9800
N(12)-C(71)	1.487(9)
N(12)-C(73)	1.493(9)
C(71)-C(72)	1.523(11)
C(71)-H(71A)	0.9900
C(71)-H(71B)	0.9900
C(72)-H(72A)	0.9800
C(72)-H(72B)	0.9800
C(72)-H(72C)	0.9800
C(73)-C(74)	1.526(11)
C(73)-H(73A)	0.9900
C(73)-H(73B)	0.9900
C(74)-H(74A)	0.9800
C(74)-H(74B)	0.9800
C(74)-H(74C)	0.9800

N(13)-C(75)	1.477(9)
N(13)-C(77)	1.485(9)
C(75)-C(76)	1.525(11)
C(75)-H(75A)	0.9900
C(75)-H(75B)	0.9900
C(76)-H(76A)	0.9800
C(76)-H(76B)	0.9800
C(76)-H(76C)	0.9800
C(77)-C(78)	1.517(11)
C(77)-H(77A)	0.9900
C(77)-H(77B)	0.9900
C(78)-H(78A)	0.9800
C(78)-H(78B)	0.9800
C(78)-H(78C)	0.9800
N(14)-C(79)	1.480(9)
N(14)-C(81)	1.484(9)
C(79)-C(80)	1.522(11)
C(79)-H(79A)	0.9900
C(79)-H(79B)	0.9900
C(80)-H(80A)	0.9800
C(80)-H(80B)	0.9800
C(80)-H(80C)	0.9800
C(81)-C(82)	1.528(11)
C(81)-H(81A)	0.9900
C(81)-H(81B)	0.9900
C(82)-H(82A)	0.9800
C(82)-H(82B)	0.9800
C(82)-H(82C)	0.9800
N(15)-C(83)	1.488(9)
N(15)-C(85)	1.495(10)
C(83)-C(84)	1.518(11)
C(83)-H(83A)	0.9900
C(83)-H(83B)	0.9900
C(84)-H(84A)	0.9800
C(84)-H(84B)	0.9800
C(84)-H(84C)	0.9800

C(85)-C(86)	1.526(11)
C(85)-H(85A)	0.9900
C(85)-H(85B)	0.9900
C(86)-H(86A)	0.9800
C(86)-H(86B)	0.9800
C(86)-H(86C)	0.9800
N(16)-C(87)	1.43(4)
N(16)-C(89)	1.59(4)
C(87)-C(88)	1.48(3)
C(87)-H(87A)	0.9900
C(87)-H(87B)	0.9900
C(88)-H(88A)	0.9800
C(88)-H(88B)	0.9800
C(88)-H(88C)	0.9800
C(89)-C(90)	1.49(3)
C(89)-H(89A)	0.9900
C(89)-H(89B)	0.9900
C(90)-H(90A)	0.9800
C(90)-H(90B)	0.9800
C(90)-H(90C)	0.9800
N(17)-C(91)	1.492(9)
N(17)-C(93)	1.496(9)
C(91)-C(92)	1.522(11)
C(91)-H(91A)	0.9900
C(91)-H(91B)	0.9900
C(92)-H(92A)	0.9800
C(92)-H(92B)	0.9800
C(92)-H(92C)	0.9800
C(93)-C(94)	1.524(11)
C(93)-H(93A)	0.9900
C(93)-H(93B)	0.9900
C(94)-H(94A)	0.9800
C(94)-H(94B)	0.9800
C(94)-H(94C)	0.9800
N(18)-C(97)	1.487(9)
N(18)-C(95)	1.487(9)

C(95)-C(96)	1.526(11)
C(95)-H(95A)	0.9900
C(95)-H(95B)	0.9900
C(96)-H(96A)	0.9800
C(96)-H(96B)	0.9800
C(96)-H(96C)	0.9800
C(97)-C(98)	1.525(11)
C(97)-H(97A)	0.9900
C(97)-H(97B)	0.9900
C(98)-H(98A)	0.9800
C(98)-H(98B)	0.9800
C(98)-H(98C)	0.9800
F(9)-B(3)	1.362(8)
F(10)-B(3)	1.363(8)
F(11)-B(3)	1.364(8)
F(12)-B(3)	1.363(8)
F(13)-B(4)	1.364(8)
F(14)-B(4)	1.363(8)
F(15)-B(4)	1.363(8)
F(16)-B(4)	1.364(8)

C(2)-C(1)-O(1)	117.3(10)
C(2)-C(1)-C(6)	121.3(10)
O(1)-C(1)-C(6)	121.4(10)
C(1)-C(2)-C(3)	119.0(10)
C(1)-C(2)-P(1)	120.2(9)
C(3)-C(2)-P(1)	120.8(9)
C(4)-C(3)-C(2)	119.4(11)
C(4)-C(3)-H(3A)	120.3
C(2)-C(3)-H(3A)	120.3
C(3)-C(4)-C(5)	119.6(12)
C(3)-C(4)-H(4A)	120.2
C(5)-C(4)-H(4A)	120.2
C(6)-C(5)-C(4)	123.3(11)
C(6)-C(5)-H(5A)	118.3
C(4)-C(5)-H(5A)	118.4

C(5)-C(6)-C(1)	117.4(10)
C(5)-C(6)-C(7)	121.2(11)
C(1)-C(6)-C(7)	121.4(10)
C(6)-C(7)-C(8)	113.6(9)
C(6)-C(7)-C(14)	109.6(11)
C(8)-C(7)-C(14)	108.8(11)
C(6)-C(7)-C(15)	109.4(11)
C(8)-C(7)-C(15)	105.0(11)
C(14)-C(7)-C(15)	110.3(11)
C(13)-C(8)-C(9)	116.2(10)
C(13)-C(8)-C(7)	121.8(10)
C(9)-C(8)-C(7)	121.9(10)
C(10)-C(9)-C(8)	122.7(11)
C(10)-C(9)-H(9A)	118.6
C(8)-C(9)-H(9A)	118.6
C(9)-C(10)-C(11)	120.1(12)
C(9)-C(10)-H(10A)	120.0
C(11)-C(10)-H(10A)	120.0
C(12)-C(11)-C(10)	118.6(11)
C(12)-C(11)-H(11A)	120.7
C(10)-C(11)-H(11A)	120.7
C(11)-C(12)-C(13)	118.3(10)
C(11)-C(12)-P(2)	121.0(9)
C(13)-C(12)-P(2)	120.6(9)
C(8)-C(13)-C(12)	124.0(11)
C(8)-C(13)-O(1)	121.8(10)
C(12)-C(13)-O(1)	114.2(10)
C(7)-C(14)-H(14A)	109.5
C(7)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(7)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(7)-C(15)-H(15A)	109.5
C(7)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5

C(7)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(16)-N(1)-C(18)	115.1(7)
C(16)-N(1)-P(1)	117.4(8)
C(18)-N(1)-P(1)	117.7(7)
N(1)-C(16)-C(17)	112.0(8)
N(1)-C(16)-H(16A)	109.2
C(17)-C(16)-H(16A)	109.2
N(1)-C(16)-H(16B)	109.2
C(17)-C(16)-H(16B)	109.2
H(16A)-C(16)-H(16B)	107.9
N(1)-C(18)-C(19)	112.1(8)
N(1)-C(18)-H(18A)	109.2
C(19)-C(18)-H(18A)	109.2
N(1)-C(18)-H(18B)	109.2
C(19)-C(18)-H(18B)	109.2
H(18A)-C(18)-H(18B)	107.9
C(20)-N(2)-C(22)	117.1(7)
C(20)-N(2)-P(1)	122.4(7)
C(22)-N(2)-P(1)	118.7(7)
N(2)-C(20)-C(21)	112.4(8)
N(2)-C(20)-H(20A)	109.1
C(21)-C(20)-H(20A)	109.1
N(2)-C(20)-H(20B)	109.1
C(21)-C(20)-H(20B)	109.1
H(20A)-C(20)-H(20B)	107.8
N(2)-C(22)-C(23)	112.0(8)
N(2)-C(22)-H(22A)	109.2
C(23)-C(22)-H(22A)	109.2
N(2)-C(22)-H(22B)	109.2
C(23)-C(22)-H(22B)	109.2
H(22A)-C(22)-H(22B)	107.9
C(24)-N(3)-C(26)	115.0(8)
C(24)-N(3)-P(2)	118.6(8)
C(26)-N(3)-P(2)	118.9(9)

N(3)-C(24)-C(25)	111.9(9)
N(3)-C(24)-H(24A)	109.2
C(25)-C(24)-H(24A)	109.3
N(3)-C(24)-H(24B)	109.2
C(25)-C(24)-H(24B)	109.2
H(24A)-C(24)-H(24B)	107.9
N(3)-C(26)-C(27)	112.1(9)
N(3)-C(26)-H(26A)	109.2
C(27)-C(26)-H(26A)	109.2
N(3)-C(26)-H(26B)	109.2
C(27)-C(26)-H(26B)	109.2
H(26A)-C(26)-H(26B)	107.9
C(28)-N(4)-C(30)	113.9(7)
C(28)-N(4)-P(2)	119.9(8)
C(30)-N(4)-P(2)	116.4(8)
N(4)-C(28)-C(29)	111.1(8)
N(4)-C(28)-H(28A)	109.4
C(29)-C(28)-H(28A)	109.4
N(4)-C(28)-H(28B)	109.4
C(29)-C(28)-H(28B)	109.4
H(28A)-C(28)-H(28B)	108.0
N(4)-C(30)-C(31)	110.9(8)
N(4)-C(30)-H(30A)	109.4
C(31)-C(30)-H(30A)	109.4
N(4)-C(30)-H(30B)	109.5
C(31)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	108.0
C(32)-N(5)-Rh(1)	178.0(13)
N(5)-C(32)-C(33)	178.0(18)
C(32)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(1)-O(1)-C(13)	119.9(9)

C(1)-O(1)-Rh(1)	119.2(7)
C(13)-O(1)-Rh(1)	120.8(7)
N(11)-P(1)-N(12)	102.0(7)
N(2)-P(1)-N(1)	102.8(5)
N(11)-P(1)-C(2)	110.4(7)
N(2)-P(1)-C(2)	110.7(6)
N(12)-P(1)-C(2)	102.2(6)
N(1)-P(1)-C(2)	103.0(6)
N(11)-P(1)-Rh(1)	121.1(5)
N(2)-P(1)-Rh(1)	120.0(4)
N(12)-P(1)-Rh(1)	120.4(6)
N(1)-P(1)-Rh(1)	119.9(5)
C(2)-P(1)-Rh(1)	99.1(4)
N(13)-P(2)-N(14)	104.3(7)
N(3)-P(2)-N(4)	104.1(6)
N(13)-P(2)-C(12)	105.0(7)
N(14)-P(2)-C(12)	109.9(7)
N(3)-P(2)-C(12)	108.9(6)
N(4)-P(2)-C(12)	100.1(6)
N(13)-P(2)-Rh(1)	120.4(4)
N(14)-P(2)-Rh(1)	115.9(5)
N(3)-P(2)-Rh(1)	117.3(6)
N(4)-P(2)-Rh(1)	123.7(5)
C(12)-P(2)-Rh(1)	100.5(4)
N(5)-Rh(1)-O(1)	178.8(5)
N(5)-Rh(1)-P(2)	95.1(4)
O(1)-Rh(1)-P(2)	83.8(3)
N(5)-Rh(1)-P(1)	96.8(4)
O(1)-Rh(1)-P(1)	84.2(3)
P(2)-Rh(1)-P(1)	168.00(15)
C(35)-C(34)-O(2)	118.7(11)
C(35)-C(34)-C(39)	121.1(11)
O(2)-C(34)-C(39)	120.2(11)
C(34)-C(35)-C(36)	118.7(11)
C(34)-C(35)-P(3)	118.9(10)
C(36)-C(35)-P(3)	122.5(10)

C(37)-C(36)-C(35)	119.9(12)
C(37)-C(36)-H(36A)	120.1
C(35)-C(36)-H(36A)	120.1
C(38)-C(37)-C(36)	119.4(13)
C(38)-C(37)-H(37A)	120.3
C(36)-C(37)-H(37A)	120.3
C(37)-C(38)-C(39)	122.9(12)
C(37)-C(38)-H(38A)	118.6
C(39)-C(38)-H(38A)	118.5
C(38)-C(39)-C(34)	117.7(11)
C(38)-C(39)-C(40)	120.9(12)
C(34)-C(39)-C(40)	121.3(11)
C(39)-C(40)-C(48)	111.4(14)
C(39)-C(40)-C(41)	112.9(10)
C(48)-C(40)-C(41)	108.7(13)
C(39)-C(40)-C(47)	109.9(13)
C(48)-C(40)-C(47)	106.2(12)
C(41)-C(40)-C(47)	107.5(13)
C(42)-C(41)-C(46)	116.5(11)
C(42)-C(41)-C(40)	122.1(11)
C(46)-C(41)-C(40)	121.3(11)
C(43)-C(42)-C(41)	122.5(12)
C(43)-C(42)-H(42A)	118.8
C(41)-C(42)-H(42A)	118.8
C(42)-C(43)-C(44)	120.0(13)
C(42)-C(43)-H(43A)	120.0
C(44)-C(43)-H(43A)	120.0
C(43)-C(44)-C(45)	119.1(12)
C(43)-C(44)-H(44A)	120.5
C(45)-C(44)-H(44A)	120.4
C(46)-C(45)-C(44)	117.7(11)
C(46)-C(45)-P(4)	122.1(11)
C(44)-C(45)-P(4)	120.2(10)
C(45)-C(46)-C(41)	124.2(11)
C(45)-C(46)-O(2)	112.9(12)
C(41)-C(46)-O(2)	122.9(12)

C(40)-C(47)-H(47A)	109.5
C(40)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(40)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(40)-C(48)-H(48A)	109.5
C(40)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(40)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(49)-N(6)-C(51)	114.3(8)
C(49)-N(6)-P(3)	117.0(8)
C(51)-N(6)-P(3)	116.5(8)
N(6)-C(49)-C(50)	110.9(8)
N(6)-C(49)-H(49A)	109.5
C(50)-C(49)-H(49A)	109.4
N(6)-C(49)-H(49B)	109.5
C(50)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	108.0
N(6)-C(51)-C(52)	111.4(9)
N(6)-C(51)-H(51A)	109.4
C(52)-C(51)-H(51A)	109.4
N(6)-C(51)-H(51B)	109.3
C(52)-C(51)-H(51B)	109.4
H(51A)-C(51)-H(51B)	108.0
C(55)-N(7)-C(53)	116.3(8)
C(55)-N(7)-P(3)	120.8(8)
C(53)-N(7)-P(3)	120.7(9)
N(7)-C(53)-C(54)	111.9(9)
N(7)-C(53)-H(53A)	109.2
C(54)-C(53)-H(53A)	109.2
N(7)-C(53)-H(53B)	109.2
C(54)-C(53)-H(53B)	109.2
H(53A)-C(53)-H(53B)	107.9

N(7)-C(55)-C(56)	112.0(9)
N(7)-C(55)-H(55A)	109.2
C(56)-C(55)-H(55A)	109.2
N(7)-C(55)-H(55B)	109.2
C(56)-C(55)-H(55B)	109.2
H(55A)-C(55)-H(55B)	107.9
C(57)-N(8)-C(59)	117.6(7)
C(57)-N(8)-P(4)	120.3(8)
C(59)-N(8)-P(4)	122.0(8)
N(8)-C(57)-C(58)	112.9(9)
N(8)-C(57)-H(57A)	109.0
C(58)-C(57)-H(57A)	109.0
N(8)-C(57)-H(57B)	109.0
C(58)-C(57)-H(57B)	109.0
H(57A)-C(57)-H(57B)	107.8
N(8)-C(59)-C(60)	112.3(9)
N(8)-C(59)-H(59A)	109.2
C(60)-C(59)-H(59A)	109.1
N(8)-C(59)-H(59B)	109.2
C(60)-C(59)-H(59B)	109.2
H(59A)-C(59)-H(59B)	107.9
C(61)-N(9)-C(63)	115.3(8)
C(61)-N(9)-P(4)	118.7(8)
C(63)-N(9)-P(4)	117.8(8)
N(9)-C(61)-C(62)	111.9(8)
N(9)-C(61)-H(61A)	109.2
C(62)-C(61)-H(61A)	109.2
N(9)-C(61)-H(61B)	109.2
C(62)-C(61)-H(61B)	109.3
H(61A)-C(61)-H(61B)	107.9
N(9)-C(63)-C(64)	111.6(9)
N(9)-C(63)-H(63A)	109.3
C(64)-C(63)-H(63A)	109.3
N(9)-C(63)-H(63B)	109.3
C(64)-C(63)-H(63B)	109.3
H(63A)-C(63)-H(63B)	108.0

C(65)-N(10)-Rh(2)	178.7(16)
N(10)-C(65)-C(66)	176(2)
C(65)-C(66)-H(66A)	109.5
C(65)-C(66)-H(66B)	109.5
H(66A)-C(66)-H(66B)	109.5
C(65)-C(66)-H(66C)	109.5
H(66A)-C(66)-H(66C)	109.5
H(66B)-C(66)-H(66C)	109.5
C(46)-O(2)-C(34)	119.8(11)
C(46)-O(2)-Rh(2)	122.2(9)
C(34)-O(2)-Rh(2)	117.4(9)
N(16)-P(3)-N(15)	98.9(13)
N(7)-P(3)-N(6)	103.1(7)
N(7)-P(3)-C(35)	110.5(7)
N(16)-P(3)-C(35)	105.9(13)
N(15)-P(3)-C(35)	111.1(8)
N(6)-P(3)-C(35)	102.8(6)
N(7)-P(3)-Rh(2)	114.8(5)
N(16)-P(3)-Rh(2)	119.8(13)
N(15)-P(3)-Rh(2)	120.2(6)
N(6)-P(3)-Rh(2)	124.2(5)
C(35)-P(3)-Rh(2)	100.5(5)
N(8)-P(4)-N(9)	103.6(6)
N(18)-P(4)-N(17)	102.8(8)
N(8)-P(4)-C(45)	108.6(8)
N(9)-P(4)-C(45)	103.2(7)
N(18)-P(4)-C(45)	112.4(9)
N(17)-P(4)-C(45)	108.3(7)
N(8)-P(4)-Rh(2)	118.0(4)
N(9)-P(4)-Rh(2)	122.5(5)
N(18)-P(4)-Rh(2)	116.2(6)
N(17)-P(4)-Rh(2)	118.0(8)
C(45)-P(4)-Rh(2)	99.2(5)
N(10)-Rh(2)-O(2)	178.9(5)
N(10)-Rh(2)-P(4)	96.2(5)
O(2)-Rh(2)-P(4)	82.9(3)

N(10)-Rh(2)-P(3)	96.5(5)
O(2)-Rh(2)-P(3)	84.4(3)
P(4)-Rh(2)-P(3)	167.34(19)
F(1)-B(1)-F(3)	109.8(8)
F(1)-B(1)-F(4)	108.5(9)
F(3)-B(1)-F(4)	109.4(9)
F(1)-B(1)-F(2)	108.1(8)
F(3)-B(1)-F(2)	110.2(9)
F(4)-B(1)-F(2)	110.8(9)
F(6)-B(2)-F(8)	109.1(10)
F(6)-B(2)-F(5)	109.8(10)
F(8)-B(2)-F(5)	109.6(10)
F(6)-B(2)-F(7)	108.8(10)
F(8)-B(2)-F(7)	109.4(10)
F(5)-B(2)-F(7)	110.1(10)
C(67)-N(11)-C(69)	116.7(8)
C(67)-N(11)-P(1)	121.4(8)
C(69)-N(11)-P(1)	119.5(9)
N(11)-C(67)-C(68)	112.4(9)
N(11)-C(67)-H(67A)	109.1
C(68)-C(67)-H(67A)	109.1
N(11)-C(67)-H(67B)	109.1
C(68)-C(67)-H(67B)	109.1
H(67A)-C(67)-H(67B)	107.9
C(67)-C(68)-H(68A)	109.5
C(67)-C(68)-H(68B)	109.5
H(68A)-C(68)-H(68B)	109.5
C(67)-C(68)-H(68C)	109.5
H(68A)-C(68)-H(68C)	109.5
H(68B)-C(68)-H(68C)	109.5
N(11)-C(69)-C(70)	111.6(9)
N(11)-C(69)-H(69A)	109.3
C(70)-C(69)-H(69A)	109.3
N(11)-C(69)-H(69B)	109.3
C(70)-C(69)-H(69B)	109.3
H(69A)-C(69)-H(69B)	108.0

C(69)-C(70)-H(70A)	109.5
C(69)-C(70)-H(70B)	109.5
H(70A)-C(70)-H(70B)	109.5
C(69)-C(70)-H(70C)	109.5
H(70A)-C(70)-H(70C)	109.5
H(70B)-C(70)-H(70C)	109.5
C(71)-N(12)-C(73)	115.0(8)
C(71)-N(12)-P(1)	119.0(9)
C(73)-N(12)-P(1)	118.6(10)
N(12)-C(71)-C(72)	111.9(9)
N(12)-C(71)-H(71A)	109.3
C(72)-C(71)-H(71A)	109.3
N(12)-C(71)-H(71B)	109.2
C(72)-C(71)-H(71B)	109.2
H(71A)-C(71)-H(71B)	107.9
C(71)-C(72)-H(72A)	109.5
C(71)-C(72)-H(72B)	109.5
H(72A)-C(72)-H(72B)	109.5
C(71)-C(72)-H(72C)	109.5
H(72A)-C(72)-H(72C)	109.5
H(72B)-C(72)-H(72C)	109.5
N(12)-C(73)-C(74)	111.5(9)
N(12)-C(73)-H(73A)	109.3
C(74)-C(73)-H(73A)	109.3
N(12)-C(73)-H(73B)	109.3
C(74)-C(73)-H(73B)	109.3
H(73A)-C(73)-H(73B)	108.0
C(73)-C(74)-H(74A)	109.5
C(73)-C(74)-H(74B)	109.5
H(74A)-C(74)-H(74B)	109.5
C(73)-C(74)-H(74C)	109.5
H(74A)-C(74)-H(74C)	109.5
H(74B)-C(74)-H(74C)	109.5
C(75)-N(13)-C(77)	116.4(8)
C(75)-N(13)-P(2)	122.5(8)
C(77)-N(13)-P(2)	118.9(8)

N(13)-C(75)-C(76)	112.1(9)
N(13)-C(75)-H(75A)	109.2
C(76)-C(75)-H(75A)	109.2
N(13)-C(75)-H(75B)	109.2
C(76)-C(75)-H(75B)	109.2
H(75A)-C(75)-H(75B)	107.9
C(75)-C(76)-H(76A)	109.5
C(75)-C(76)-H(76B)	109.5
H(76A)-C(76)-H(76B)	109.5
C(75)-C(76)-H(76C)	109.5
H(76A)-C(76)-H(76C)	109.5
H(76B)-C(76)-H(76C)	109.5
N(13)-C(77)-C(78)	112.2(9)
N(13)-C(77)-H(77A)	109.2
C(78)-C(77)-H(77A)	109.1
N(13)-C(77)-H(77B)	109.2
C(78)-C(77)-H(77B)	109.2
H(77A)-C(77)-H(77B)	107.9
C(77)-C(78)-H(78A)	109.5
C(77)-C(78)-H(78B)	109.4
H(78A)-C(78)-H(78B)	109.5
C(77)-C(78)-H(78C)	109.5
H(78A)-C(78)-H(78C)	109.5
H(78B)-C(78)-H(78C)	109.5
C(79)-N(14)-C(81)	116.5(8)
C(79)-N(14)-P(2)	120.9(8)
C(81)-N(14)-P(2)	120.1(9)
N(14)-C(79)-C(80)	112.3(9)
N(14)-C(79)-H(79A)	109.1
C(80)-C(79)-H(79A)	109.2
N(14)-C(79)-H(79B)	109.1
C(80)-C(79)-H(79B)	109.2
H(79A)-C(79)-H(79B)	107.9
C(79)-C(80)-H(80A)	109.5
C(79)-C(80)-H(80B)	109.5
H(80A)-C(80)-H(80B)	109.5

C(79)-C(80)-H(80C)	109.5
H(80A)-C(80)-H(80C)	109.5
H(80B)-C(80)-H(80C)	109.5
N(14)-C(81)-C(82)	111.9(9)
N(14)-C(81)-H(81A)	109.2
C(82)-C(81)-H(81A)	109.2
N(14)-C(81)-H(81B)	109.2
C(82)-C(81)-H(81B)	109.3
H(81A)-C(81)-H(81B)	107.9
C(81)-C(82)-H(82A)	109.5
C(81)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5
C(81)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5
C(83)-N(15)-C(85)	114.8(8)
C(83)-N(15)-P(3)	117.3(8)
C(85)-N(15)-P(3)	116.7(10)
N(15)-C(83)-C(84)	112.2(9)
N(15)-C(83)-H(83A)	109.2
C(84)-C(83)-H(83A)	109.2
N(15)-C(83)-H(83B)	109.2
C(84)-C(83)-H(83B)	109.2
H(83A)-C(83)-H(83B)	107.9
C(83)-C(84)-H(84A)	109.5
C(83)-C(84)-H(84B)	109.5
H(84A)-C(84)-H(84B)	109.5
C(83)-C(84)-H(84C)	109.5
H(84A)-C(84)-H(84C)	109.5
H(84B)-C(84)-H(84C)	109.5
N(15)-C(85)-C(86)	111.5(9)
N(15)-C(85)-H(85A)	109.3
C(86)-C(85)-H(85A)	109.3
N(15)-C(85)-H(85B)	109.3
C(86)-C(85)-H(85B)	109.4
H(85A)-C(85)-H(85B)	108.0

C(85)-C(86)-H(86A)	109.4
C(85)-C(86)-H(86B)	109.5
H(86A)-C(86)-H(86B)	109.5
C(85)-C(86)-H(86C)	109.5
H(86A)-C(86)-H(86C)	109.5
H(86B)-C(86)-H(86C)	109.5
C(87)-N(16)-C(89)	124(2)
C(87)-N(16)-P(3)	123(3)
C(89)-N(16)-P(3)	113(2)
N(16)-C(87)-C(88)	105(3)
N(16)-C(87)-H(87A)	110.7
C(88)-C(87)-H(87A)	110.7
N(16)-C(87)-H(87B)	110.7
C(88)-C(87)-H(87B)	110.8
H(87A)-C(87)-H(87B)	108.8
C(87)-C(88)-H(88A)	109.5
C(87)-C(88)-H(88B)	109.5
H(88A)-C(88)-H(88B)	109.5
C(87)-C(88)-H(88C)	109.5
H(88A)-C(88)-H(88C)	109.5
H(88B)-C(88)-H(88C)	109.5
C(90)-C(89)-N(16)	110(3)
C(90)-C(89)-H(89A)	109.8
N(16)-C(89)-H(89A)	109.8
C(90)-C(89)-H(89B)	109.7
N(16)-C(89)-H(89B)	109.8
H(89A)-C(89)-H(89B)	108.2
C(89)-C(90)-H(90A)	109.5
C(89)-C(90)-H(90B)	109.5
H(90A)-C(90)-H(90B)	109.5
C(89)-C(90)-H(90C)	109.5
H(90A)-C(90)-H(90C)	109.5
H(90B)-C(90)-H(90C)	109.5
C(91)-N(17)-C(93)	114.4(8)
C(91)-N(17)-P(4)	118.7(10)
C(93)-N(17)-P(4)	117.1(8)

N(17)-C(91)-C(92)	111.8(9)
N(17)-C(91)-H(91A)	109.3
C(92)-C(91)-H(91A)	109.2
N(17)-C(91)-H(91B)	109.3
C(92)-C(91)-H(91B)	109.3
H(91A)-C(91)-H(91B)	107.9
C(91)-C(92)-H(92A)	109.5
C(91)-C(92)-H(92B)	109.4
H(92A)-C(92)-H(92B)	109.5
C(91)-C(92)-H(92C)	109.5
H(92A)-C(92)-H(92C)	109.5
H(92B)-C(92)-H(92C)	109.5
N(17)-C(93)-C(94)	111.9(9)
N(17)-C(93)-H(93A)	109.2
C(94)-C(93)-H(93A)	109.3
N(17)-C(93)-H(93B)	109.2
C(94)-C(93)-H(93B)	109.2
H(93A)-C(93)-H(93B)	107.9
C(93)-C(94)-H(94A)	109.5
C(93)-C(94)-H(94B)	109.5
H(94A)-C(94)-H(94B)	109.5
C(93)-C(94)-H(94C)	109.5
H(94A)-C(94)-H(94C)	109.5
H(94B)-C(94)-H(94C)	109.5
C(97)-N(18)-C(95)	115.6(8)
C(97)-N(18)-P(4)	118.8(9)
C(95)-N(18)-P(4)	118.6(9)
N(18)-C(95)-C(96)	111.5(9)
N(18)-C(95)-H(95A)	109.4
C(96)-C(95)-H(95A)	109.3
N(18)-C(95)-H(95B)	109.3
C(96)-C(95)-H(95B)	109.3
H(95A)-C(95)-H(95B)	108.0
C(95)-C(96)-H(96A)	109.5
C(95)-C(96)-H(96B)	109.5
H(96A)-C(96)-H(96B)	109.5

C(95)-C(96)-H(96C)	109.4
H(96A)-C(96)-H(96C)	109.5
H(96B)-C(96)-H(96C)	109.5
N(18)-C(97)-C(98)	112.1(9)
N(18)-C(97)-H(97A)	109.2
C(98)-C(97)-H(97A)	109.2
N(18)-C(97)-H(97B)	109.2
C(98)-C(97)-H(97B)	109.2
H(97A)-C(97)-H(97B)	107.9
C(97)-C(98)-H(98A)	109.5
C(97)-C(98)-H(98B)	109.5
H(98A)-C(98)-H(98B)	109.5
C(97)-C(98)-H(98C)	109.5
H(98A)-C(98)-H(98C)	109.5
H(98B)-C(98)-H(98C)	109.5
F(9)-B(3)-F(12)	108.5(10)
F(9)-B(3)-F(10)	107.8(10)
F(12)-B(3)-F(10)	110.8(10)
F(9)-B(3)-F(11)	109.9(10)
F(12)-B(3)-F(11)	109.3(11)
F(10)-B(3)-F(11)	110.5(10)
F(14)-B(4)-F(15)	110.8(11)
F(14)-B(4)-F(16)	110.7(11)
F(15)-B(4)-F(16)	109.4(11)
F(14)-B(4)-F(13)	107.8(10)
F(15)-B(4)-F(13)	109.6(10)
F(16)-B(4)-F(13)	108.5(10)

Table SI-4. Anisotropic displacement parameters ($Å^2$x 10^3) for [(**L1'**)Rh-NCMe]BF_4. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(9)	49(10)	56(11)	2(8)	13(8)	-7(8)

C(2)	48(10)	65(11)	47(11)	-14(9)	20(9)	-7(8)
C(3)	60(11)	117(16)	50(11)	-2(10)	25(9)	-2(11)
C(4)	37(10)	80(13)	100(15)	-8(11)	17(10)	-23(9)
C(5)	52(10)	68(12)	52(11)	-8(9)	22(9)	-20(9)
C(6)	54(11)	58(11)	46(11)	2(9)	10(9)	6(9)
C(7)	22(8)	59(12)	60(11)	-1(9)	5(8)	5(8)
C(8)	43(10)	62(11)	54(11)	-2(9)	8(9)	8(9)
C(9)	77(12)	63(12)	61(12)	-1(10)	21(10)	0(10)
C(10)	86(14)	99(15)	69(13)	-42(11)	33(11)	-22(12)
C(11)	82(13)	85(14)	73(13)	3(11)	33(11)	-38(11)
C(12)	76(11)	55(11)	38(10)	-10(8)	33(9)	-5(9)
C(13)	54(11)	52(11)	40(11)	-11(8)	22(9)	5(9)
C(14)	70(12)	62(13)	89(13)	-12(10)	37(10)	-16(10)
C(15)	61(12)	160(20)	67(13)	13(13)	3(10)	37(13)
N(1)	82(6)	75(5)	63(5)	10(5)	8(5)	3(5)
C(16)	88(6)	79(6)	71(6)	5(6)	3(6)	4(6)
C(17)	93(9)	83(9)	75(7)	0(8)	-3(8)	0(8)
C(18)	94(7)	78(6)	70(7)	6(6)	8(6)	11(6)
C(19)	105(9)	84(8)	78(9)	9(8)	13(8)	9(8)
N(2)	73(6)	59(6)	103(6)	-11(5)	25(5)	-6(6)
C(20)	74(7)	64(7)	103(7)	-10(6)	24(6)	-8(6)
C(21)	79(8)	70(9)	98(8)	-8(7)	27(8)	-9(8)
C(22)	75(6)	61(6)	109(6)	-6(5)	20(5)	-3(6)
C(23)	76(7)	66(7)	117(8)	-7(7)	15(7)	6(7)
N(3)	69(5)	125(6)	85(6)	-6(6)	34(5)	6(6)
C(24)	70(8)	137(9)	91(9)	-7(9)	28(7)	6(8)
C(25)	74(8)	146(10)	95(10)	-4(10)	31(8)	2(9)
C(26)	75(6)	125(6)	90(6)	-7(6)	30(6)	8(6)
C(27)	81(8)	121(8)	92(8)	-6(7)	29(8)	7(9)
N(4)	103(6)	75(6)	109(6)	37(6)	11(6)	-25(5)
C(28)	112(6)	77(7)	114(7)	40(6)	4(6)	-19(6)
C(29)	113(7)	74(8)	118(8)	42(7)	2(7)	-15(7)
C(30)	105(7)	84(7)	111(7)	36(7)	12(7)	-31(6)
C(31)	109(9)	87(9)	112(9)	37(8)	16(8)	-34(8)
N(5)	28(8)	72(10)	63(9)	9(7)	1(7)	3(7)
C(32)	37(10)	62(12)	54(11)	34(9)	16(9)	14(9)

C(33)	30(10)	67(12)	141(17)	14(12)	-6(10)	-13(9)
O(1)	27(6)	58(7)	62(7)	5(6)	15(5)	-10(5)
P(1)	43(2)	64(3)	63(3)	-10(3)	20(2)	-10(2)
P(2)	38(2)	66(3)	62(3)	4(2)	18(2)	-2(2)
Rh(1)	37(1)	62(1)	61(1)	-4(1)	15(1)	-5(1)
C(34)	50(11)	92(15)	66(13)	-30(12)	8(10)	-3(11)
C(35)	76(12)	98(16)	80(14)	-36(12)	38(11)	-29(12)
C(36)	120(16)	170(20)	121(17)	-101(16)	81(14)	-71(16)
C(37)	170(20)	62(16)	260(30)	-72(18)	110(20)	-32(16)
C(38)	160(20)	58(15)	190(20)	-32(15)	104(18)	-31(14)
C(39)	61(12)	119(19)	160(20)	-54(16)	74(13)	-37(13)
C(40)	44(12)	102(16)	140(19)	-56(15)	5(12)	3(12)
C(41)	53(11)	89(16)	100(16)	-32(13)	27(11)	-25(11)
C(42)	105(16)	88(17)	113(18)	-15(14)	41(14)	10(13)
C(43)	190(20)	100(20)	130(20)	15(16)	72(18)	-22(18)
C(44)	129(17)	77(16)	140(20)	-57(14)	62(15)	-26(13)
C(45)	86(13)	88(15)	87(14)	-24(12)	55(11)	-31(12)
C(46)	42(10)	83(15)	76(14)	-9(12)	7(10)	-29(10)
C(47)	51(11)	79(14)	131(17)	-18(12)	-19(11)	-19(10)
C(48)	63(13)	122(18)	170(20)	-34(16)	7(14)	13(13)
N(6)	139(6)	168(6)	93(6)	-31(6)	30(6)	34(6)
C(49)	137(7)	176(7)	104(7)	-36(7)	31(6)	34(6)
C(50)	138(7)	183(9)	116(9)	-38(9)	30(8)	31(8)
C(51)	144(7)	169(6)	99(6)	-29(7)	31(6)	39(6)
C(52)	149(8)	167(8)	99(7)	-26(7)	33(7)	41(8)
N(7)	91(6)	106(6)	138(6)	-25(6)	68(5)	-18(6)
C(53)	92(8)	108(8)	141(7)	-24(7)	64(7)	-19(7)
C(54)	93(11)	107(9)	144(12)	-25(10)	66(11)	-18(10)
C(55)	98(7)	112(7)	142(7)	-24(7)	70(6)	-16(6)
C(56)	99(10)	117(11)	149(12)	-32(10)	71(10)	-12(8)
N(8)	77(6)	84(6)	137(6)	0(5)	50(5)	1(5)
C(57)	81(6)	87(6)	140(6)	0(6)	45(5)	-2(6)
C(58)	81(8)	95(8)	146(8)	-3(8)	42(7)	-7(8)
C(59)	88(7)	90(7)	141(7)	1(7)	53(6)	6(7)
C(60)	95(9)	93(9)	147(9)	-1(8)	52(8)	7(8)
N(9)	99(5)	104(6)	84(6)	-41(5)	17(5)	6(6)

C(61)	101(6)	108(6)	93(7)	-43(6)	12(6)	6(6)
C(62)	99(6)	109(8)	90(8)	-41(7)	13(7)	9(7)
C(63)	104(7)	104(6)	87(7)	-43(7)	20(7)	7(7)
C(64)	109(9)	105(8)	88(8)	-43(7)	16(9)	6(9)
N(10)	68(10)	94(13)	60(10)	-8(10)	12(8)	-5(10)
C(65)	44(11)	84(16)	83(14)	14(13)	19(9)	15(12)
C(66)	108(16)	83(17)	133(19)	-8(14)	12(14)	7(14)
O(2)	59(7)	71(8)	75(8)	-20(7)	16(6)	7(7)
P(3)	65(3)	100(4)	68(3)	-21(3)	15(3)	7(3)
P(4)	69(3)	75(4)	67(3)	-16(3)	26(3)	-14(3)
Rh(2)	58(1)	77(1)	66(1)	-13(1)	20(1)	-3(1)
F(1)	127(7)	168(8)	135(6)	-21(7)	53(6)	16(7)
F(2)	167(10)	141(13)	130(7)	-20(9)	25(8)	-2(10)
F(3)	110(7)	191(11)	171(11)	-12(10)	43(7)	10(8)
F(4)	153(10)	155(8)	131(9)	-19(7)	55(9)	14(8)
B(1)	122(7)	165(8)	134(7)	-20(7)	47(7)	9(7)
F(5)	115(7)	326(11)	114(10)	68(10)	33(7)	17(9)
F(6)	120(8)	335(9)	136(8)	48(8)	48(7)	20(9)
F(7)	144(8)	324(7)	152(8)	47(7)	12(7)	25(7)
F(8)	130(9)	334(12)	152(9)	37(10)	-2(9)	31(11)
B(2)	121(8)	326(9)	128(8)	58(9)	27(7)	21(9)
N(11)	83(6)	76(6)	64(6)	8(6)	7(6)	3(6)
C(67)	85(7)	77(7)	65(7)	6(7)	6(6)	1(7)
C(68)	88(9)	79(9)	69(7)	-1(9)	3(8)	-1(9)
C(69)	91(6)	80(6)	68(6)	7(6)	8(6)	8(6)
C(70)	101(8)	82(7)	71(8)	6(8)	10(8)	9(7)
N(12)	72(6)	61(6)	106(6)	-9(5)	22(5)	-4(5)
C(71)	75(6)	62(7)	104(7)	-9(6)	22(6)	-4(6)
C(72)	78(9)	66(9)	100(9)	-8(8)	25(8)	-6(9)
C(73)	73(7)	65(7)	113(8)	-9(7)	19(7)	3(7)
C(74)	75(8)	64(7)	113(8)	-9(7)	16(7)	4(7)
N(13)	68(6)	122(7)	84(6)	-6(6)	35(5)	5(6)
C(75)	69(7)	132(8)	86(6)	-3(7)	39(6)	6(7)
C(76)	77(8)	146(10)	95(9)	-4(9)	37(7)	2(9)
C(77)	73(6)	126(7)	86(6)	-2(6)	33(6)	5(7)
C(78)	82(9)	135(12)	98(11)	0(11)	25(9)	-1(11)

N(14)	106(6)	77(6)	111(6)	37(6)	12(6)	-24(6)
C(79)	113(7)	75(7)	115(7)	39(7)	4(7)	-17(6)
C(80)	113(7)	75(8)	117(8)	40(8)	3(8)	-15(7)
C(81)	108(7)	79(8)	110(7)	38(7)	12(7)	-30(7)
C(82)	111(8)	82(10)	111(9)	37(9)	14(8)	-35(9)
N(15)	141(6)	168(7)	96(6)	-29(6)	31(6)	35(6)
C(83)	139(6)	175(7)	102(6)	-34(7)	32(6)	34(6)
C(84)	138(9)	177(9)	102(8)	-35(9)	32(8)	34(9)
C(85)	145(7)	167(7)	100(7)	-27(7)	33(7)	37(7)
C(86)	149(9)	168(10)	101(9)	-25(9)	36(8)	37(9)
N(16)	91(7)	105(7)	137(7)	-27(7)	69(6)	-16(7)
C(87)	93(7)	109(7)	140(7)	-22(7)	65(6)	-17(7)
C(88)	99(11)	113(11)	143(12)	-14(11)	61(10)	-19(10)
C(89)	106(10)	117(10)	141(8)	-19(10)	75(8)	-7(9)
C(90)	111(13)	119(13)	142(12)	-16(12)	78(11)	-6(11)
N(17)	79(6)	86(6)	137(6)	0(6)	51(5)	0(5)
C(91)	82(6)	91(6)	142(7)	2(6)	46(6)	-5(6)
C(92)	90(11)	99(11)	152(11)	4(10)	42(11)	-16(9)
C(93)	83(6)	87(6)	138(7)	2(7)	48(6)	-1(6)
C(94)	90(9)	91(9)	144(9)	2(9)	49(8)	5(8)
N(18)	99(6)	105(7)	84(6)	-42(6)	17(6)	6(6)
C(95)	99(6)	109(6)	88(6)	-44(6)	17(6)	6(6)
C(96)	99(7)	109(8)	95(8)	-45(7)	12(7)	7(8)
C(97)	100(7)	104(7)	85(7)	-41(7)	18(6)	5(8)
C(98)	104(10)	103(9)	87(9)	-41(8)	19(9)	6(9)
F(9)	131(7)	167(8)	133(8)	-16(7)	54(7)	11(7)
F(10)	159(12)	136(15)	136(9)	-20(10)	28(10)	5(10)
F(11)	115(8)	178(10)	150(9)	-26(8)	46(8)	13(8)
F(12)	142(12)	182(11)	138(9)	-35(9)	43(10)	7(9)
B(3)	124(8)	164(9)	131(9)	-20(7)	47(8)	13(8)
F(13)	121(8)	329(10)	123(9)	63(9)	30(7)	14(8)
F(14)	123(11)	340(10)	139(12)	50(10)	50(10)	18(10)
F(15)	142(12)	324(11)	146(10)	43(10)	17(9)	40(11)
F(16)	136(9)	331(10)	159(9)	46(9)	3(8)	29(9)
B(4)	127(8)	327(8)	137(8)	52(8)	29(7)	24(7)

Table SI-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [(**L1’**)Rh-NCMe]BF_4.

	x	y	z	U(eq)
H(3A)	5971	4219	1011	88
H(4A)	7028	4839	1489	87
H(5A)	7192	5171	2421	67
H(9A)	6217	5173	4182	79
H(10A)	5316	4803	4594	99
H(11A)	4271	4201	4048	93
H(14A)	6072	6123	2980	106
H(14B)	6912	6015	3047	106
H(14C)	6595	6010	3591	106
H(15A)	7050	3970	3409	149
H(15B)	7116	4609	3899	149
H(15C)	7513	4751	3406	149
H(16A)	3280	4095	537	99
H(16B)	3685	3340	377	99
H(17A)	3499	3823	-469	132
H(17B)	4069	4495	-218	132
H(17C)	3236	4646	-274	132
H(18A)	4352	5312	497	99
H(18B)	4938	5178	1077	99
H(19A)	4093	5904	1343	136
H(19B)	3906	5029	1503	136
H(19C)	3450	5433	939	136
H(20A)	5770	2672	746	96
H(20B)	5208	3302	411	96
H(21A)	5173	2214	-170	122
H(21B)	4433	2234	13	122
H(21C)	5048	1633	310	122
H(22A)	4836	1585	1083	99
H(22B)	4430	2014	1496	99
H(23A)	5538	1367	1974	132
H(23B)	5491	2270	2149	132

H(23C)	5954	2030	1716	132
H(24A)	2445	3337	2460	117
H(24B)	2257	4192	2190	117
H(25A)	1957	3681	3220	155
H(25B)	1369	3815	2641	155
H(25C)	1792	4551	2971	155
H(26A)	3654	5209	3144	114
H(26B)	2815	5280	3100	114
H(27A)	3352	5932	2369	145
H(27B)	2560	5578	2189	145
H(27C)	3218	5084	2079	145
H(28A)	4364	2262	3954	126
H(28B)	4839	2829	3670	126
H(29A)	5054	1551	3420	159
H(29B)	4588	1961	2862	159
H(29C)	4217	1371	3212	159
H(30A)	3230	1978	2825	123
H(30B)	2718	2695	2894	123
H(31A)	3127	2256	3933	157
H(31B)	3161	1427	3632	157
H(31C)	2424	1901	3519	157
H(33A)	2309	1697	1130	126
H(33B)	1997	2467	780	126
H(33C)	1813	2291	1370	126
H(36A)	9727	1337	2946	155
H(37A)	9788	-38	2975	186
H(38A)	9449	-709	3684	150
H(42A)	8490	-628	5432	120
H(43A)	8257	135	6145	161
H(44A)	8221	1517	6062	133
H(47A)	8164	-1029	3874	141
H(47B)	7736	-260	3980	141
H(47C)	7898	-947	4441	141
H(48A)	9780	-694	4904	184
H(48B)	9386	-1271	4408	184
H(48C)	9121	-1220	4976	184

H(49A)	8291	1707	2839	166
H(49B)	8058	2319	2329	166
H(50A)	7369	2054	3150	219
H(50B)	7133	2661	2638	219
H(50C)	7650	2944	3220	219
H(51A)	9087	3932	3111	164
H(51B)	8239	3803	2933	164
H(52A)	8705	4356	2186	207
H(52B)	8261	3564	2002	207
H(52C)	9115	3543	2162	207
H(53A)	10911	3116	4366	129
H(53B)	10163	3326	4503	129
H(54A)	10829	4485	4434	163
H(54B)	10082	4490	3972	163
H(54C)	10801	4272	3793	163
H(55A)	10725	3144	3191	132
H(55B)	10181	2434	2977	132
H(56A)	11439	2064	3380	172
H(56B)	10856	1569	3600	172
H(56C)	11291	2260	3980	172
H(57A)	7427	3422	4401	119
H(57B)	6787	3571	4698	119
H(58A)	6277	2732	4011	157
H(58B)	6542	2136	4526	157
H(58C)	6997	2238	4065	157
H(59A)	7614	2636	5976	123
H(59B)	6861	2431	5555	123
H(60A)	6996	3642	6192	162
H(60B)	6443	3649	5588	162
H(60C)	7213	4045	5668	162
H(61A)	9422	1953	6104	123
H(61B)	9613	2664	6544	123
H(62A)	10583	2480	6154	151
H(62B)	10221	3300	5920	151
H(62C)	10081	2533	5530	151
H(63A)	8418	4053	5701	119

H(63B)	9268	4057	5791	119
H(64A)	8597	4408	6582	153
H(64B)	9437	4247	6697	153
H(64C)	8906	3545	6754	153
H(66A)	8587	5602	4616	167
H(66B)	8702	5539	3993	167
H(66C)	9378	5545	4523	167
H(67A)	5037	3682	327	94
H(67B)	4900	4611	280	94
H(68A)	4343	3625	-524	123
H(68B)	4030	4488	-480	123
H(68C)	3693	3747	-234	123
H(69A)	3528	4533	1066	98
H(69B)	3342	4537	393	98
H(70A)	3588	5834	736	130
H(70B)	4179	5570	415	130
H(70C)	4364	5567	1088	130
H(71A)	4102	2542	529	96
H(71B)	4328	1861	990	96
H(72A)	4506	1668	7	121
H(72B)	5066	1296	535	121
H(72C)	5245	2108	270	121
H(73A)	5826	2715	1839	102
H(73B)	6057	2406	1292	102
H(74A)	5894	1376	1948	128
H(74B)	5485	1223	1306	128
H(74C)	5055	1544	1741	128
H(75A)	3012	4903	3567	111
H(75B)	3236	4016	3750	111
H(76A)	2055	4121	3771	155
H(76B)	2048	3619	3218	155
H(76C)	1844	4534	3167	155
H(77A)	3111	4716	2156	111
H(77B)	2959	5333	2606	111
H(78A)	1890	5106	1939	157
H(78B)	1816	4735	2522	157

H(78C)	1968	4176	2039	157
H(79A)	3816	1965	2624	126
H(79B)	3844	1631	3239	126
H(80A)	4992	1607	3039	159
H(80B)	4998	2135	3581	159
H(80C)	4970	2546	2989	159
H(81A)	3448	3364	3843	122
H(81B)	3777	2503	3991	122
H(82A)	2505	2594	3942	155
H(82B)	2705	1908	3560	155
H(82C)	2377	2719	3278	155
H(83A)	7742	3060	2959	166
H(83B)	7973	2153	2990	166
H(84A)	8004	3076	2027	208
H(84B)	7296	2616	2068	208
H(84C)	8008	2136	2066	208
H(85A)	9169	4021	3261	165
H(85B)	8521	4002	2709	165
H(86A)	9246	3889	2147	208
H(86B)	9742	3260	2548	208
H(86C)	9855	4181	2675	208
H(87A)	10340	3253	4455	129
H(87B)	10868	3556	4083	129
H(88A)	11393	2519	4687	169
H(88B)	11294	2282	4040	169
H(88C)	10747	1957	4383	169
H(89A)	10468	2361	2995	136
H(89B)	9772	2893	2759	136
H(90A)	11103	3353	2863	174
H(90B)	10863	3793	3364	174
H(90C)	10419	3918	2727	174
H(91A)	7142	2049	4576	123
H(91B)	6568	2693	4654	123
H(92A)	6305	1518	5051	167
H(92B)	6588	2127	5555	167
H(92C)	7106	1452	5430	167

H(93A)	7250	3881	4691	119
H(93B)	7837	4054	5264	119
H(94A)	6484	4355	5135	157
H(94B)	7023	4237	5740	157
H(94C)	6545	3516	5440	157
H(95A)	9812	3696	5984	120
H(95B)	9801	3018	5527	120
H(96A)	10506	2794	6524	155
H(96B)	10074	2069	6184	155
H(96C)	9747	2547	6625	155
H(97A)	8873	2750	6571	116
H(97B)	8086	2903	6186	116
H(98A)	8603	3889	6934	148
H(98B)	8157	4213	6338	148
H(98C)	9012	4215	6486	148

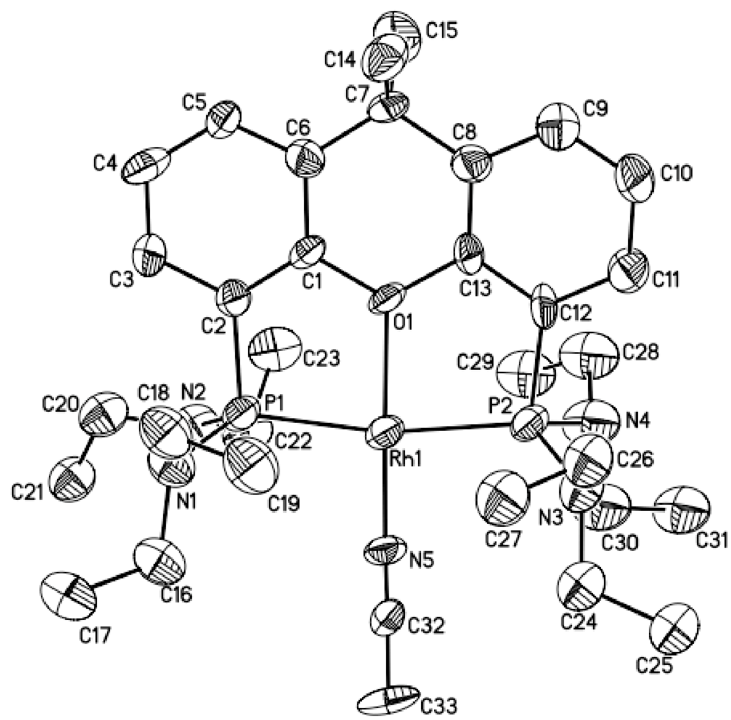
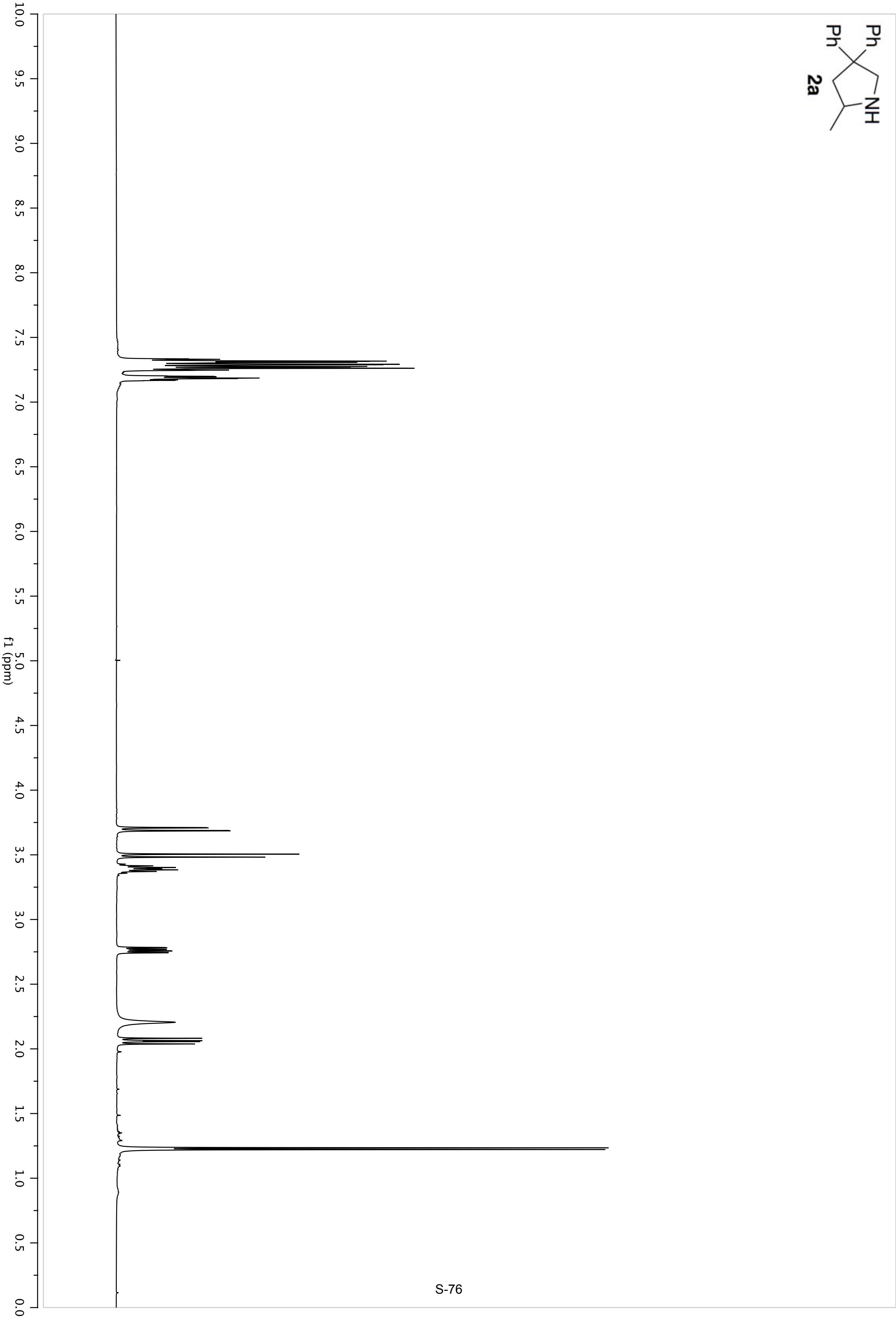
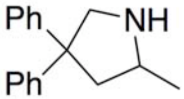
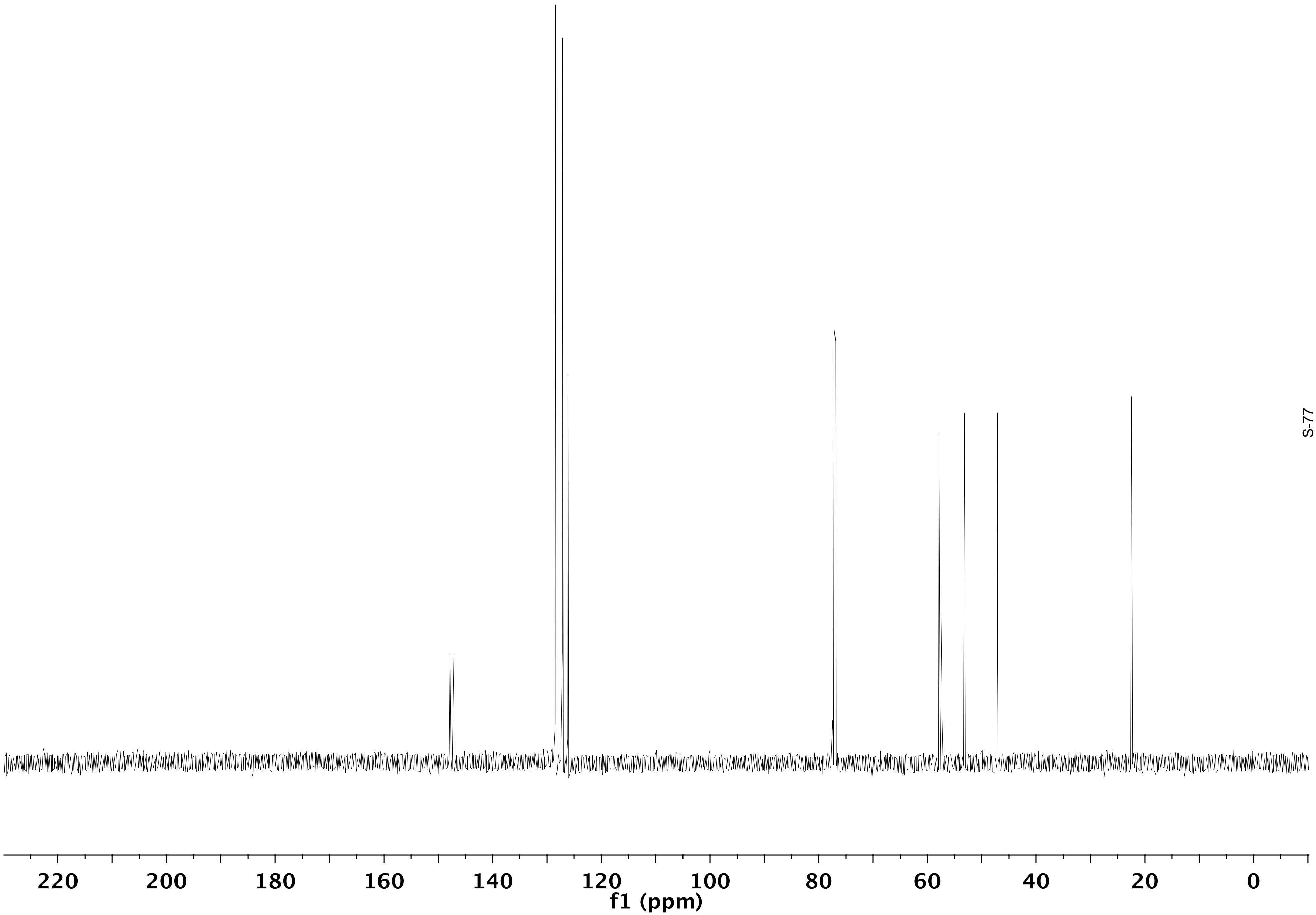


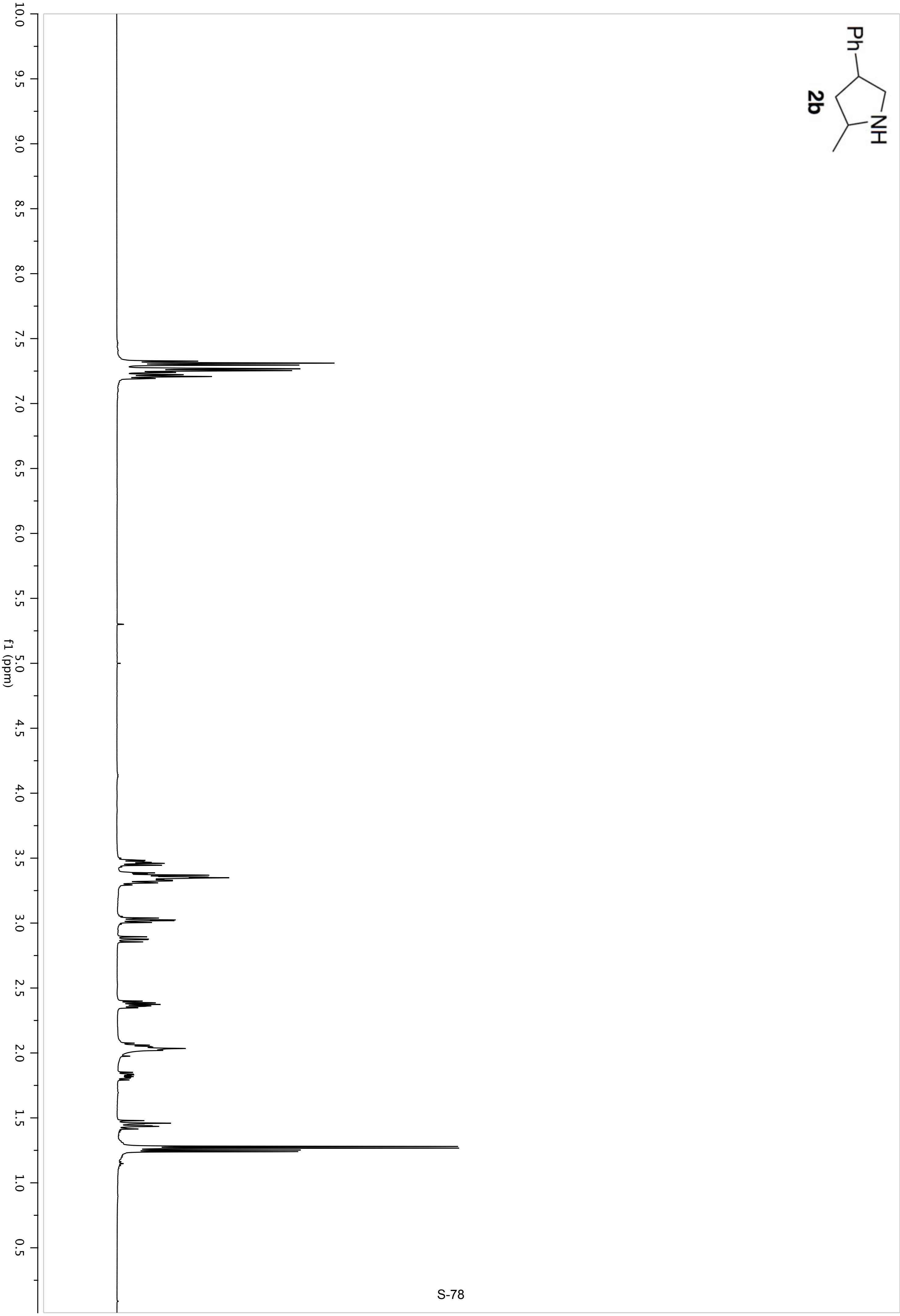
Figure SI-4. ORTEP diagram of [(**L1'**)Rh-NCMe]BF_4 (35% ellipsoids, hydrogens and BF_4 counterion omitted for clarity)

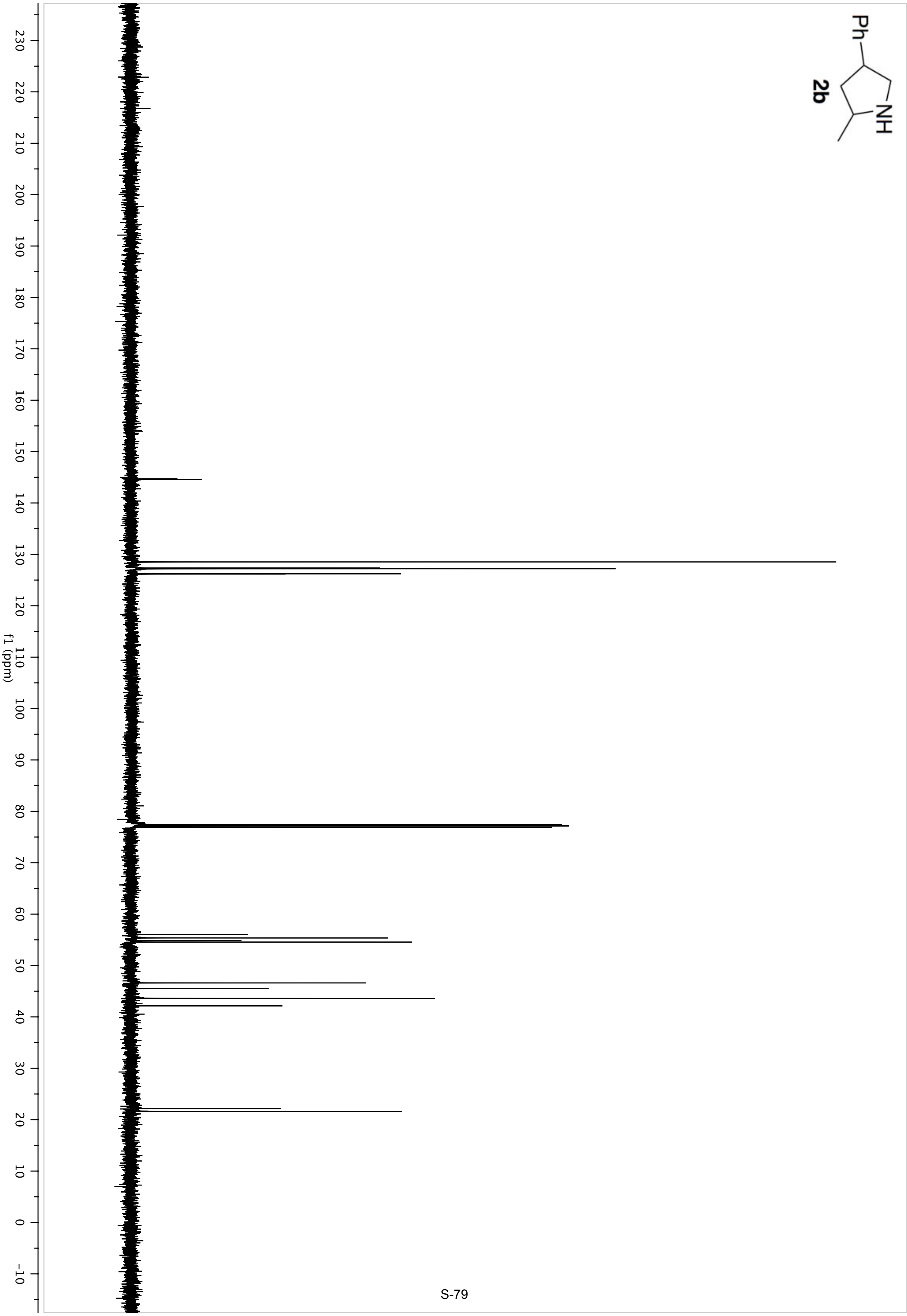

Ph
Ph
NH
2a
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

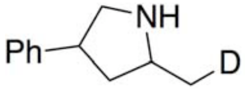


2a

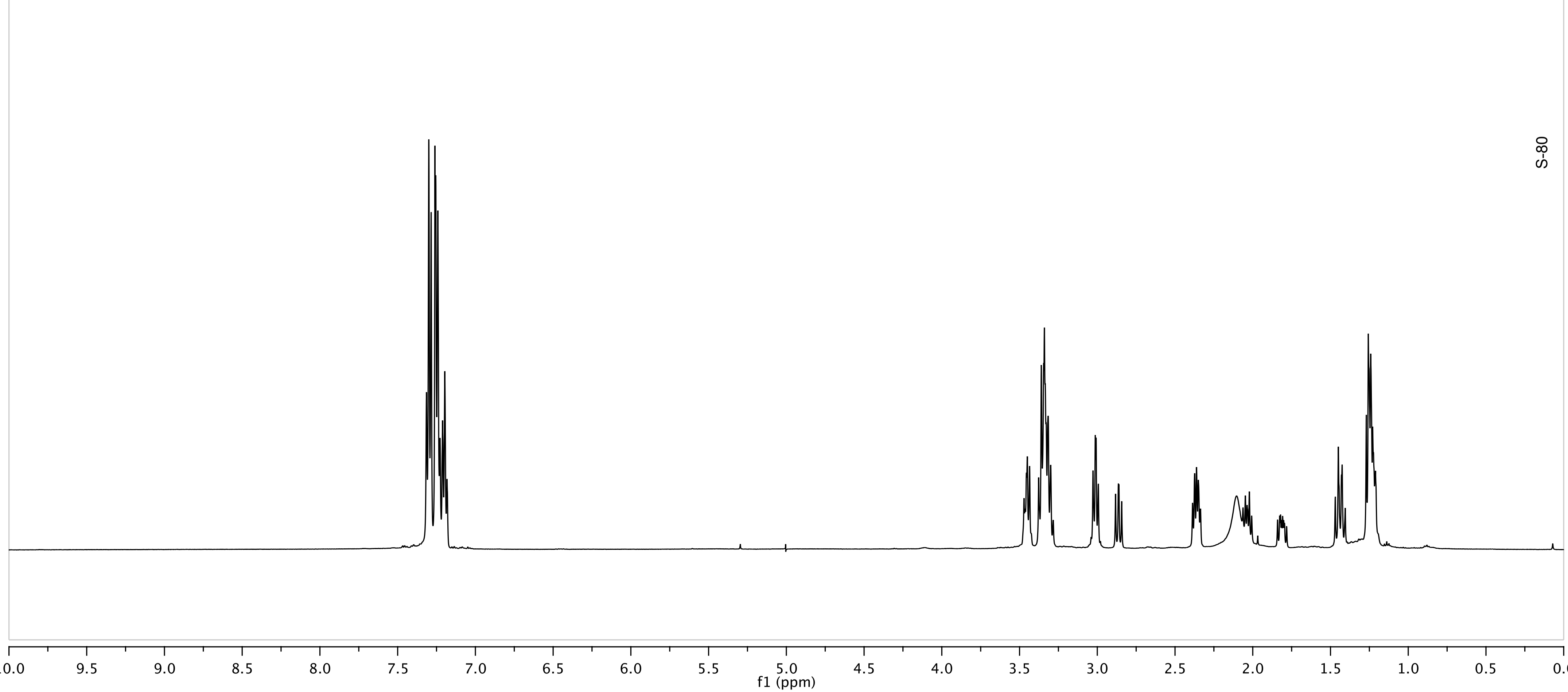


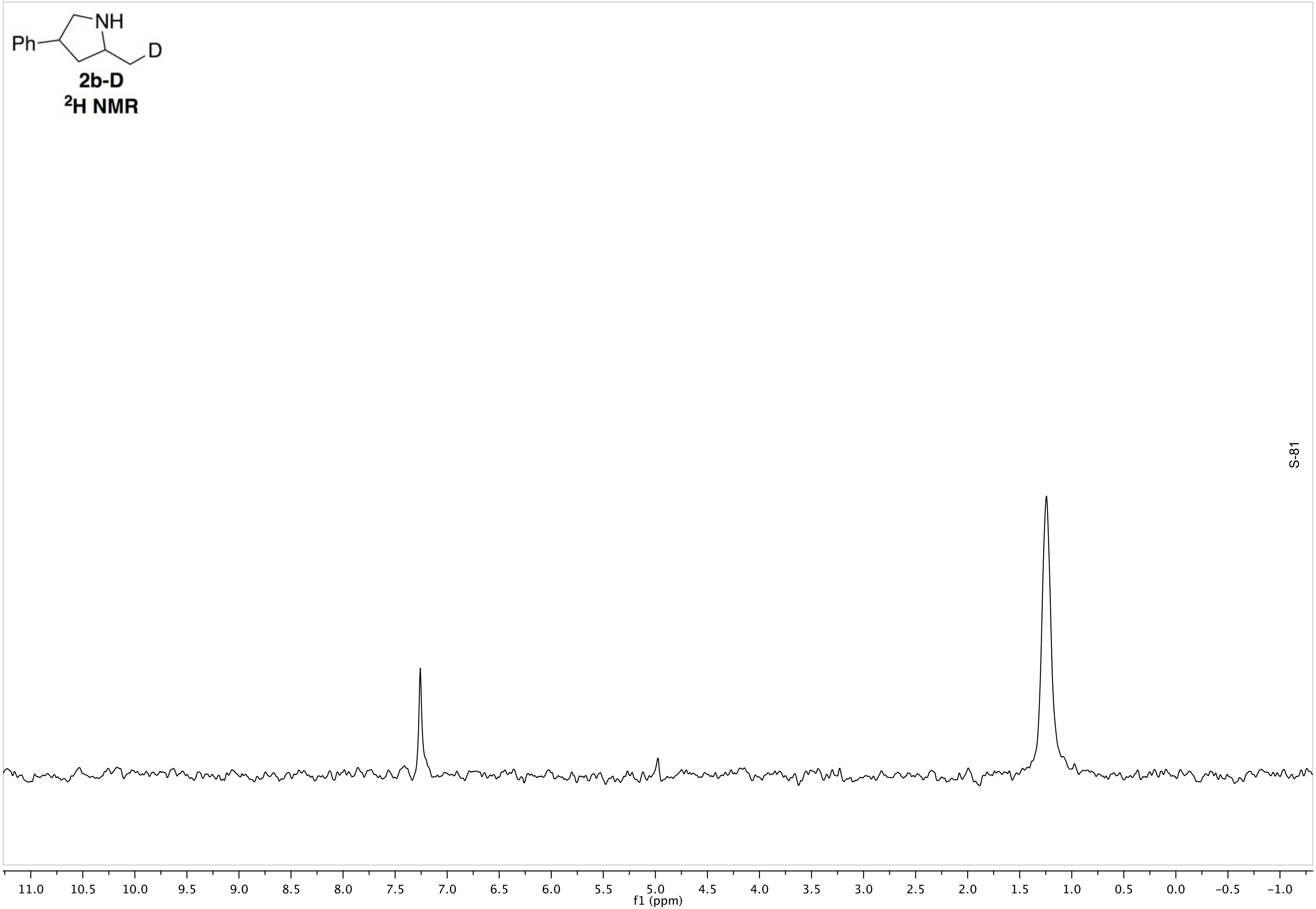

Ph
NH
2b
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

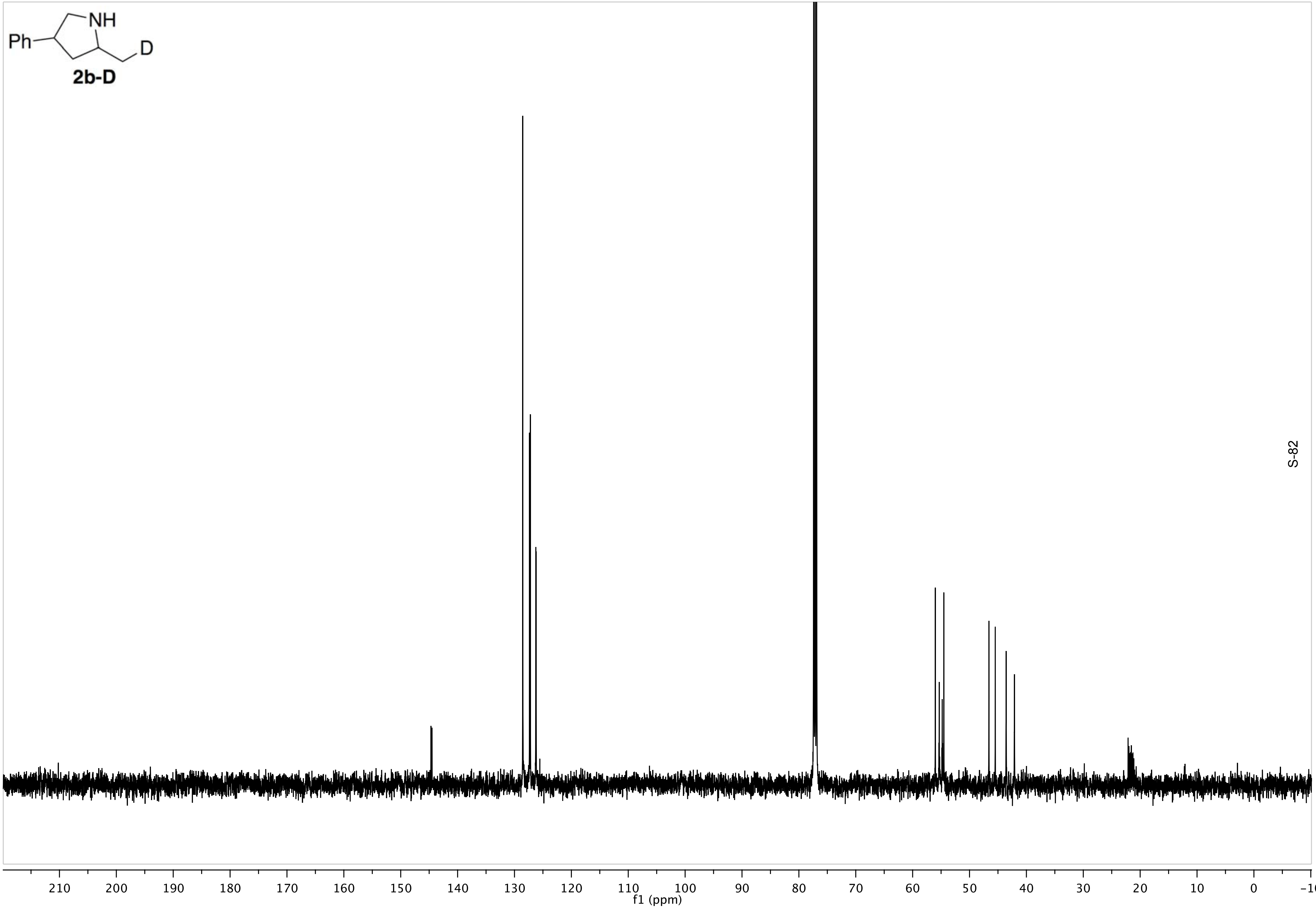

Ph
NH
2b
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

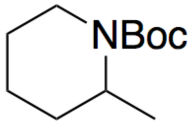


2b-D

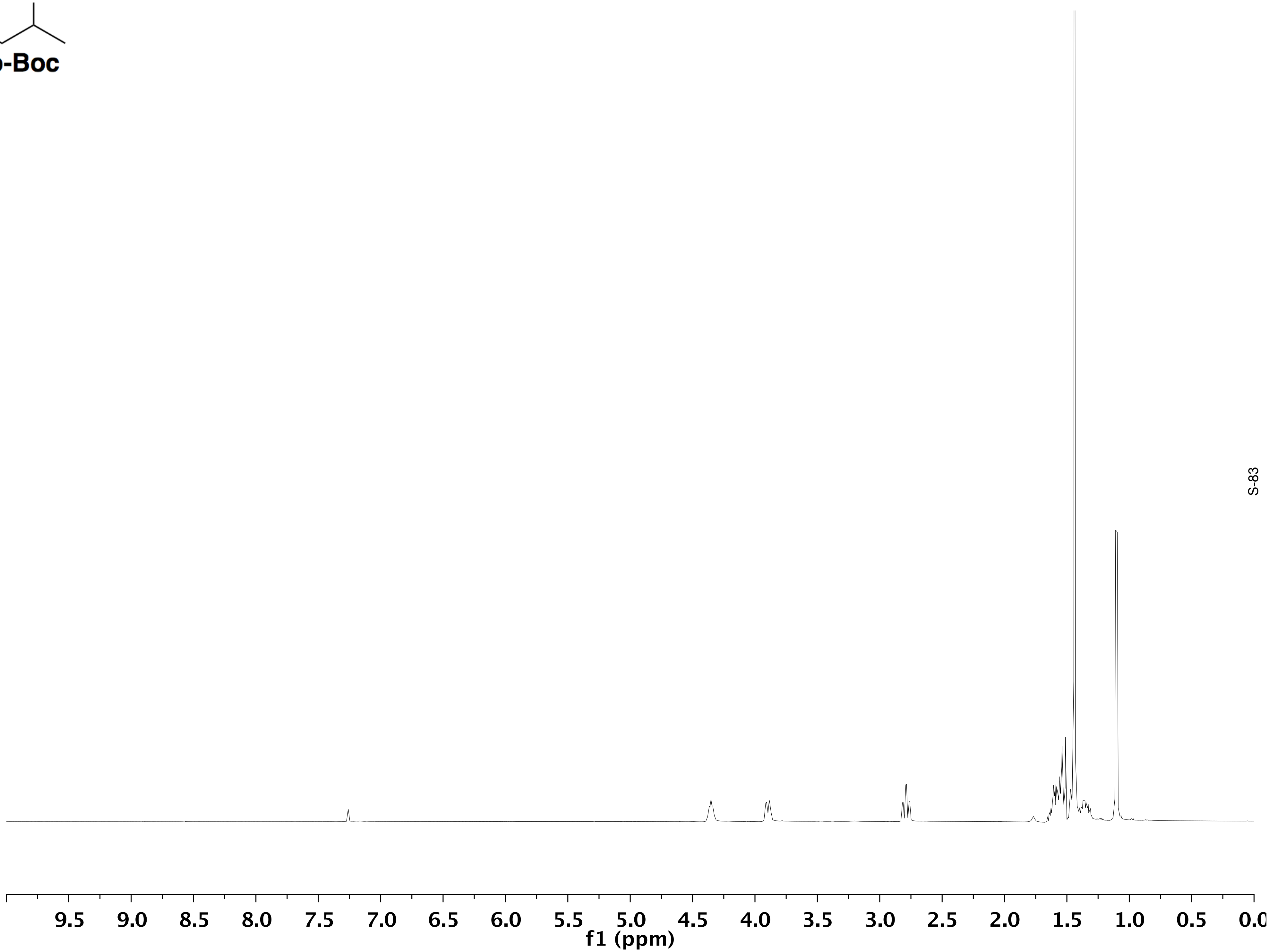


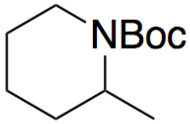

Ph
NH
D
2b-D
²H NMR
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0.5 –1.0
f1 (ppm)


NH
Ph
D
2b-D
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

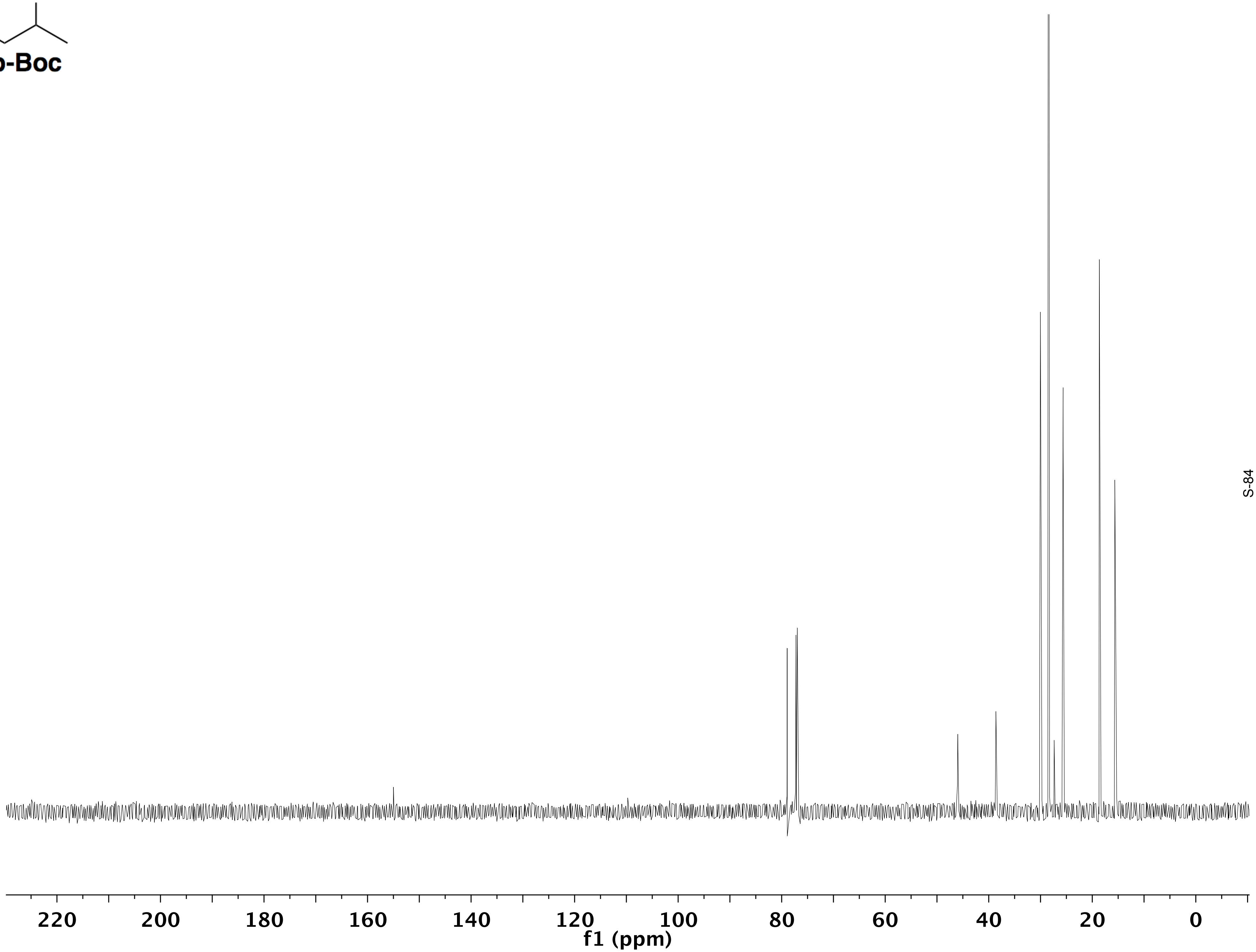


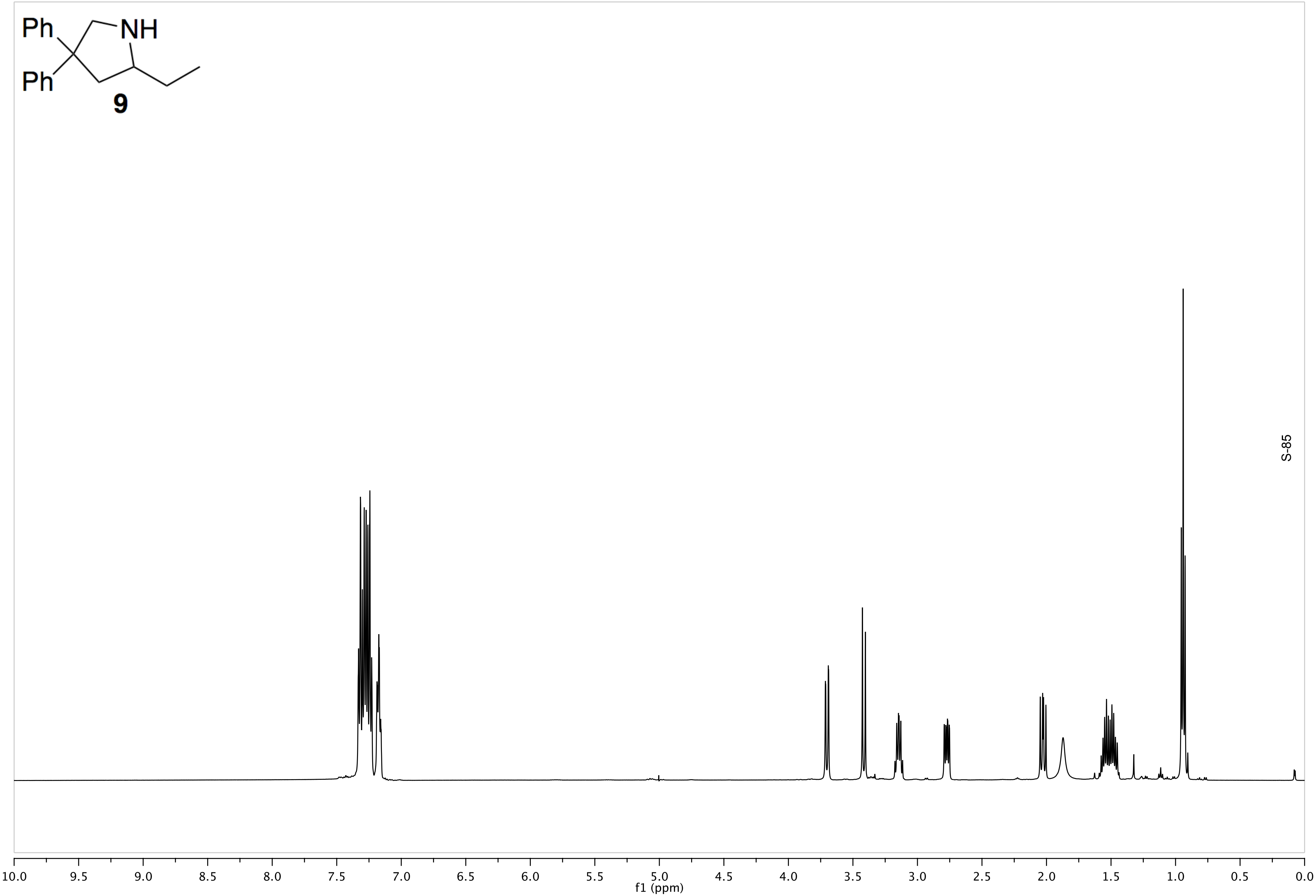
7b-Boc



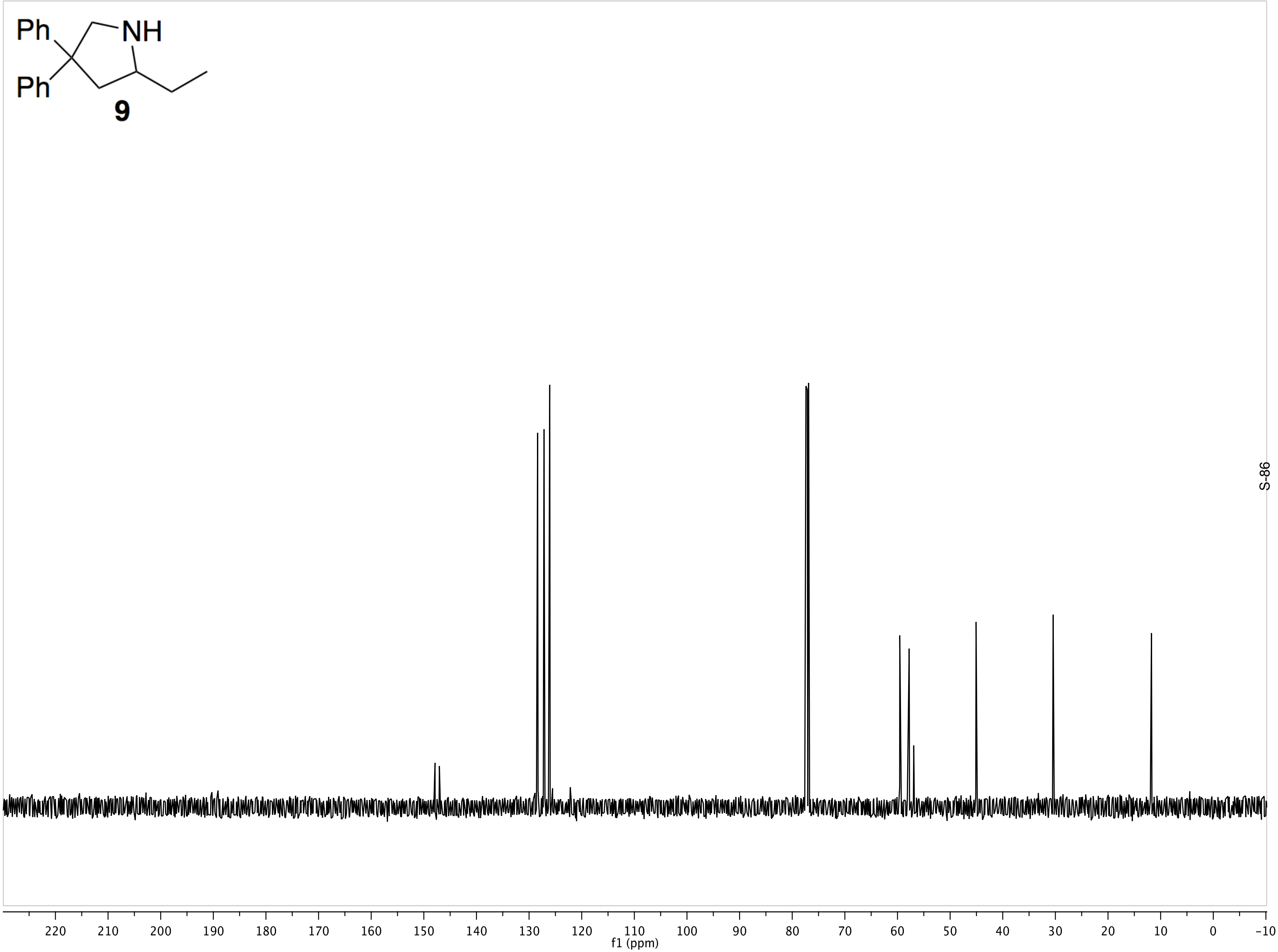


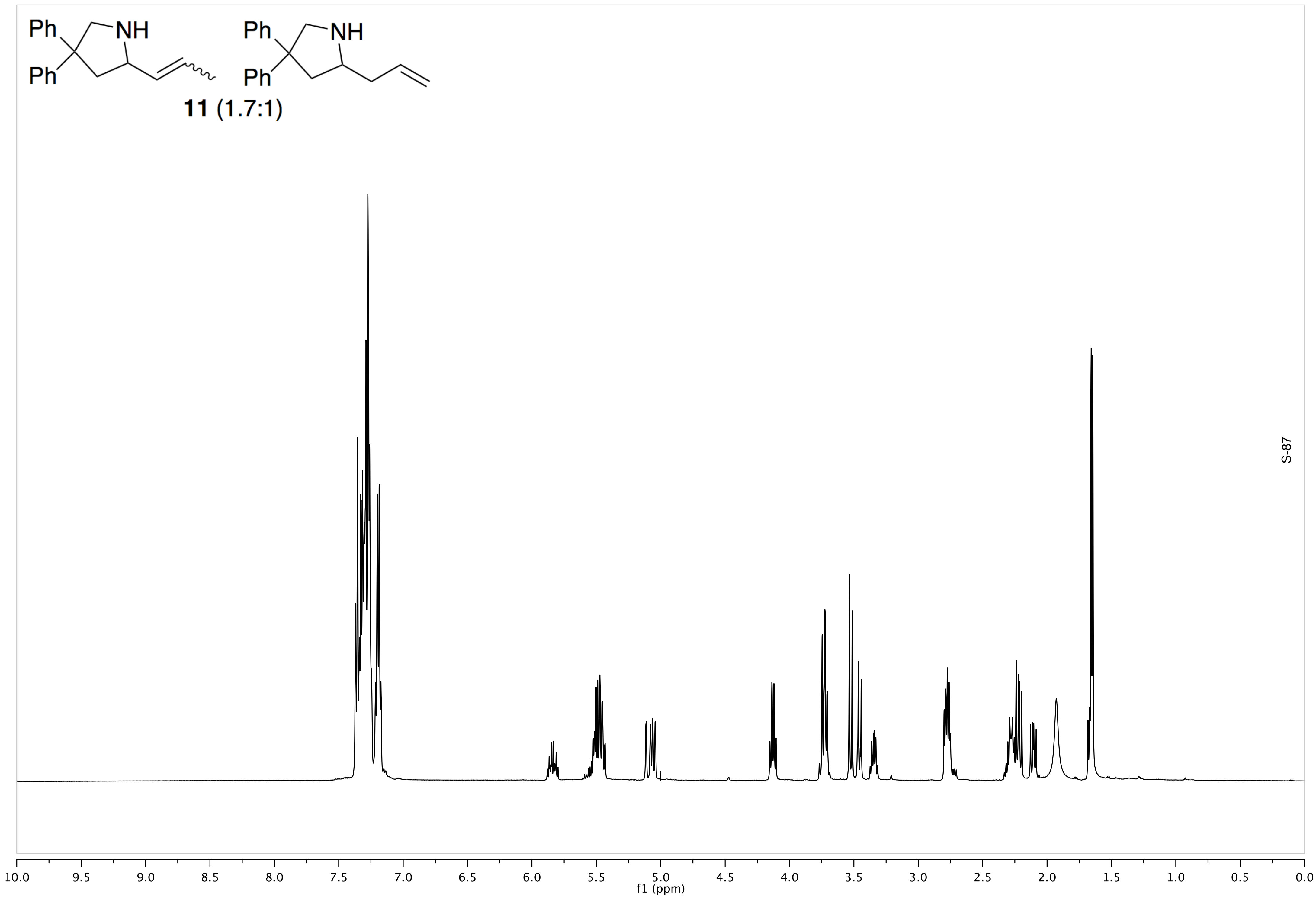
7b-Boc



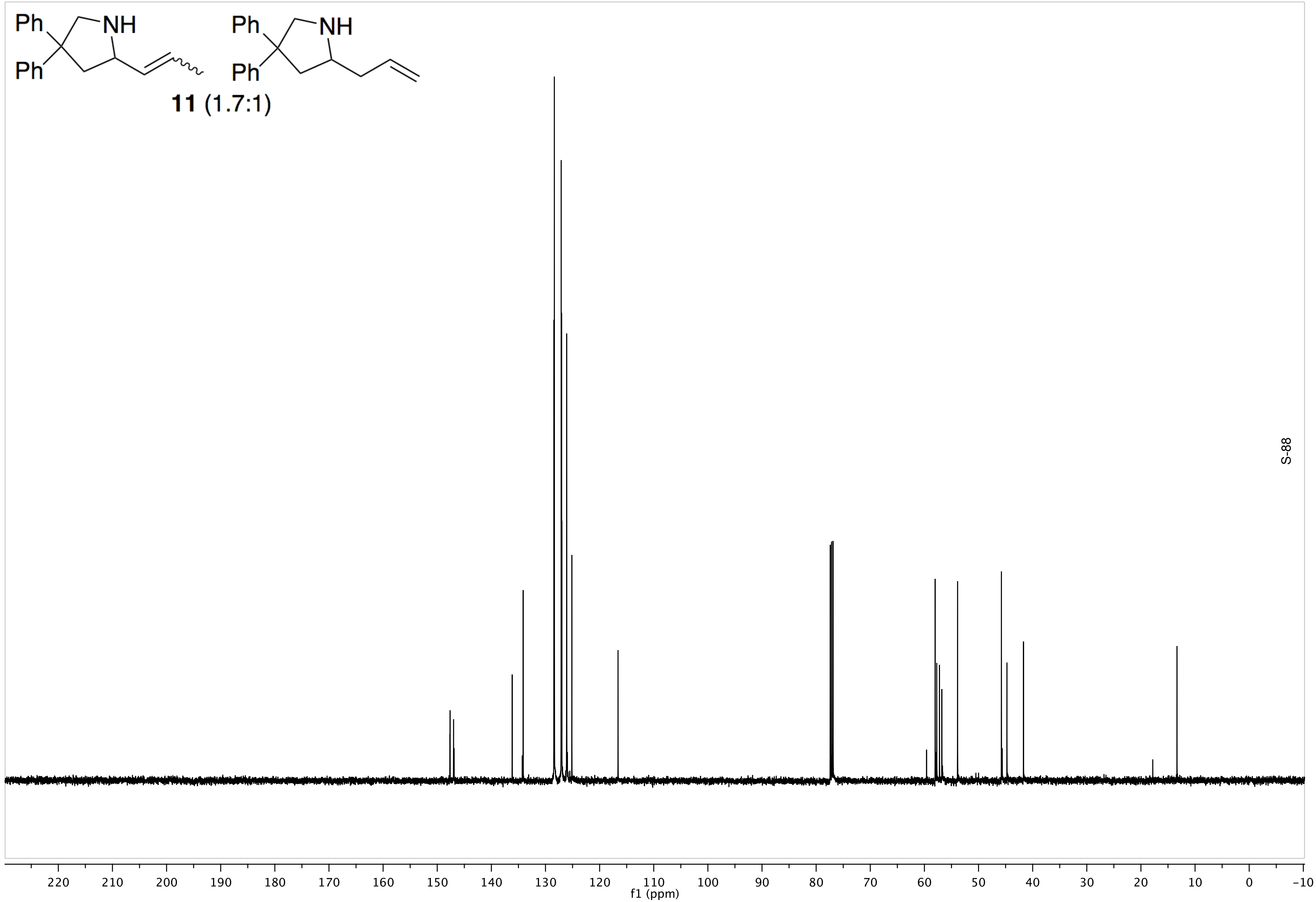


Ph
NH
Ph
9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

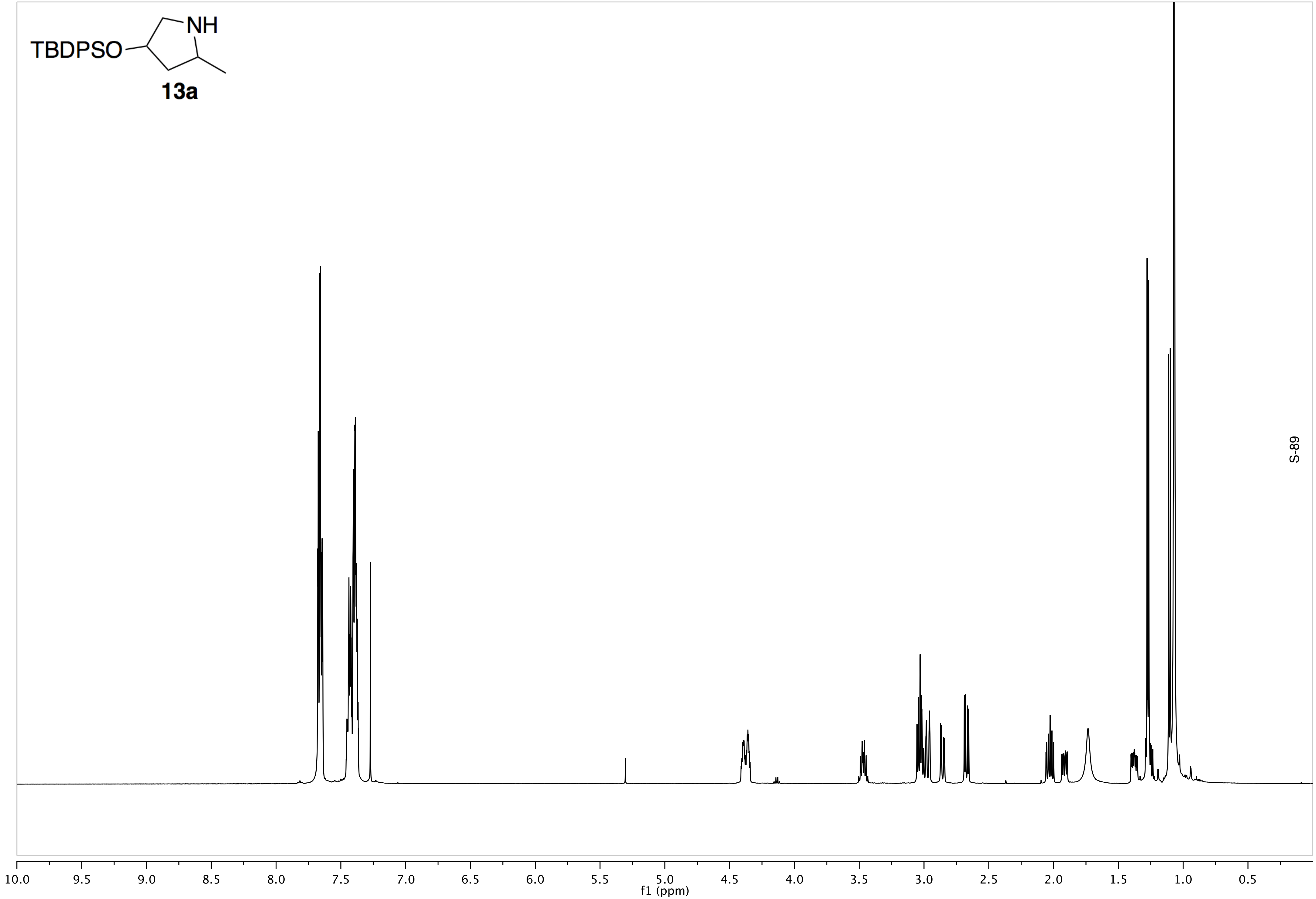

Ph
NH
Ph
9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

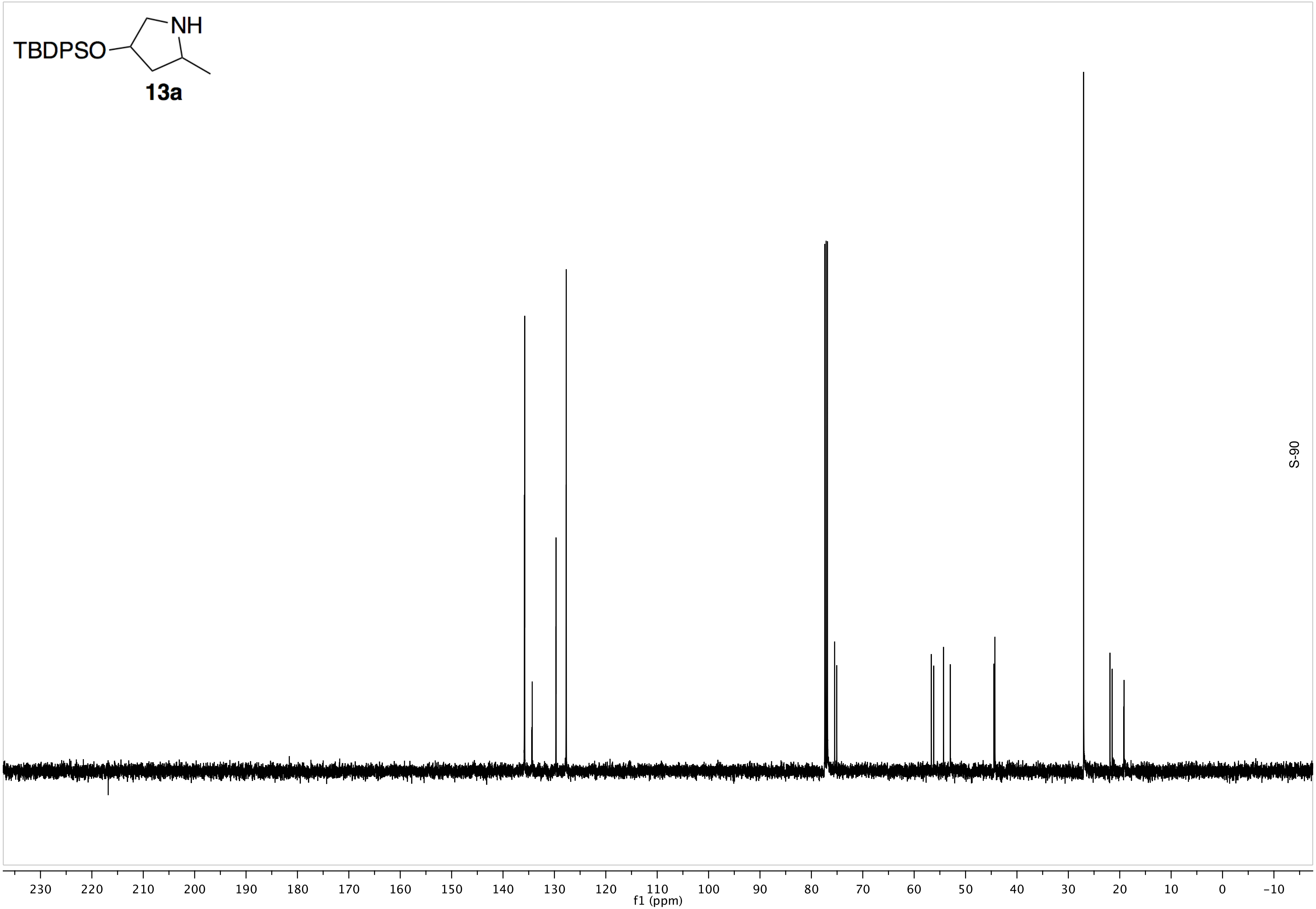


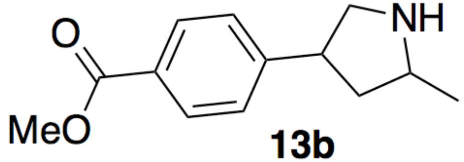
Ph
Ph
NH
11 (1.7:1)
Ph
Ph
NH
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



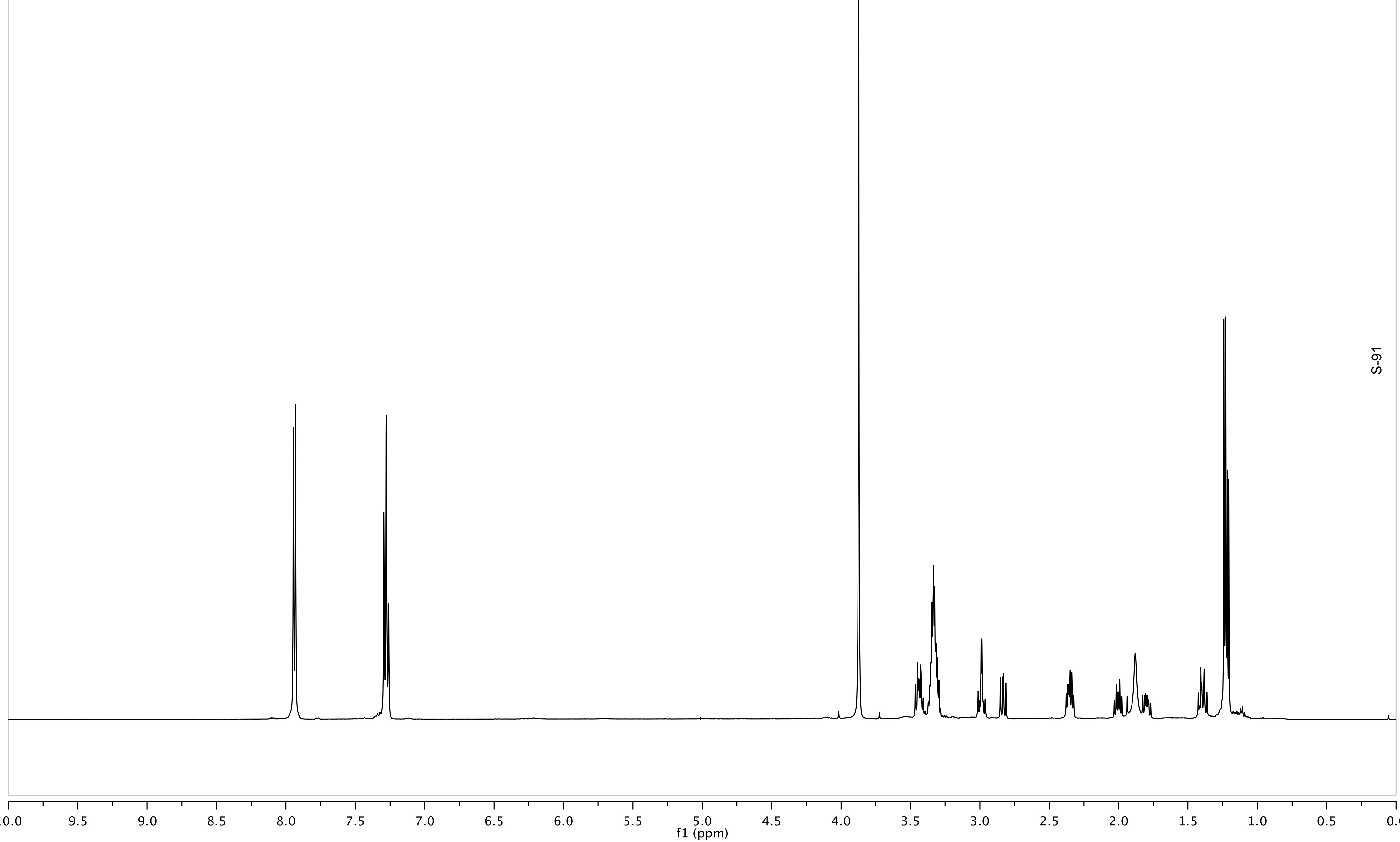
Ph
NH
Ph
11 (1.7:1)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

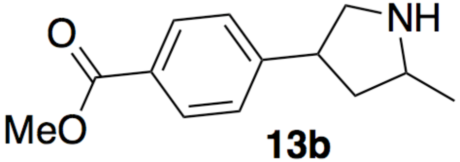

TBDPSO
NH
13a
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


TBDPSO
NH
13a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



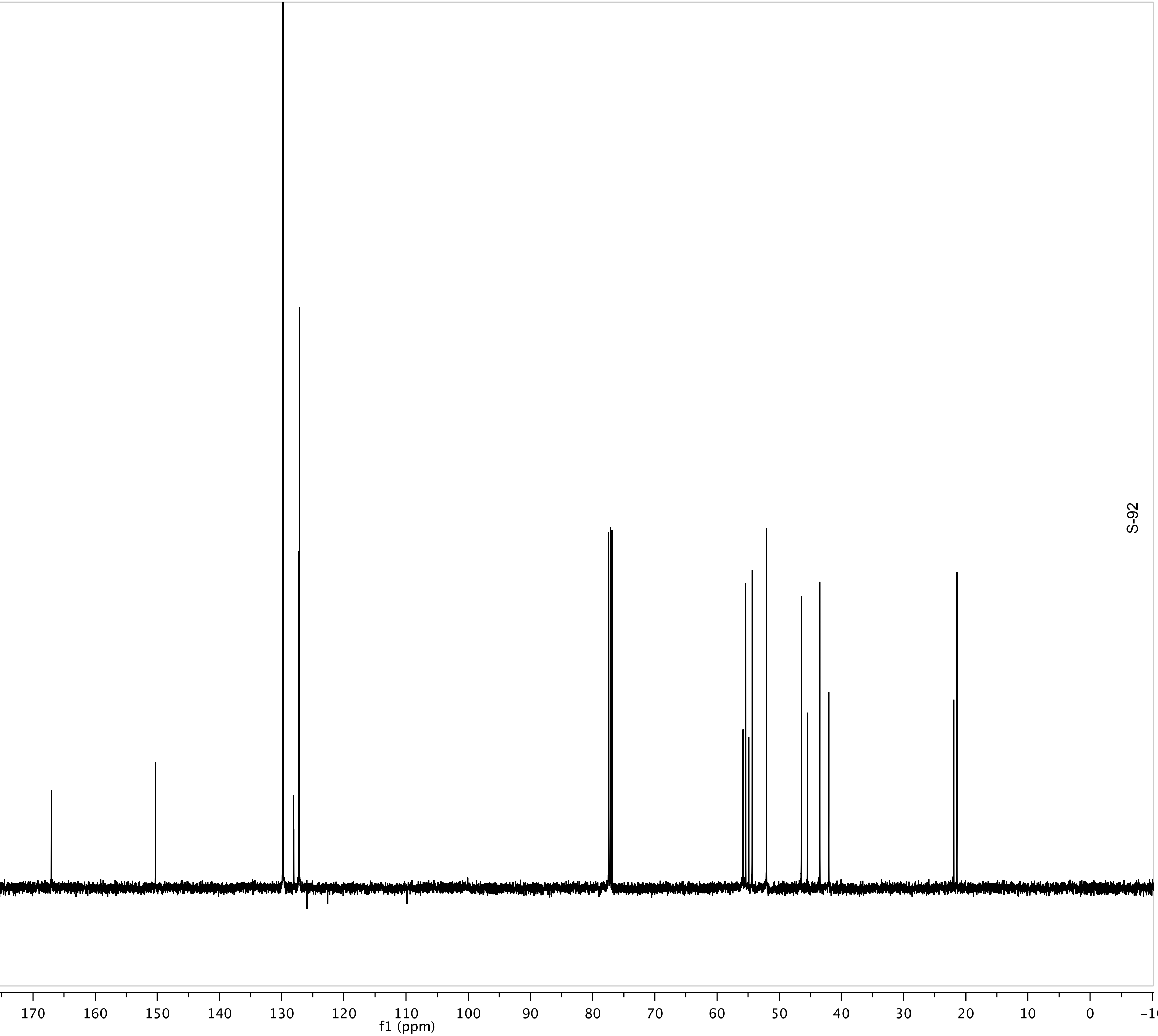
13b



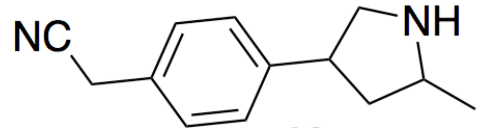


O
MeO
NH

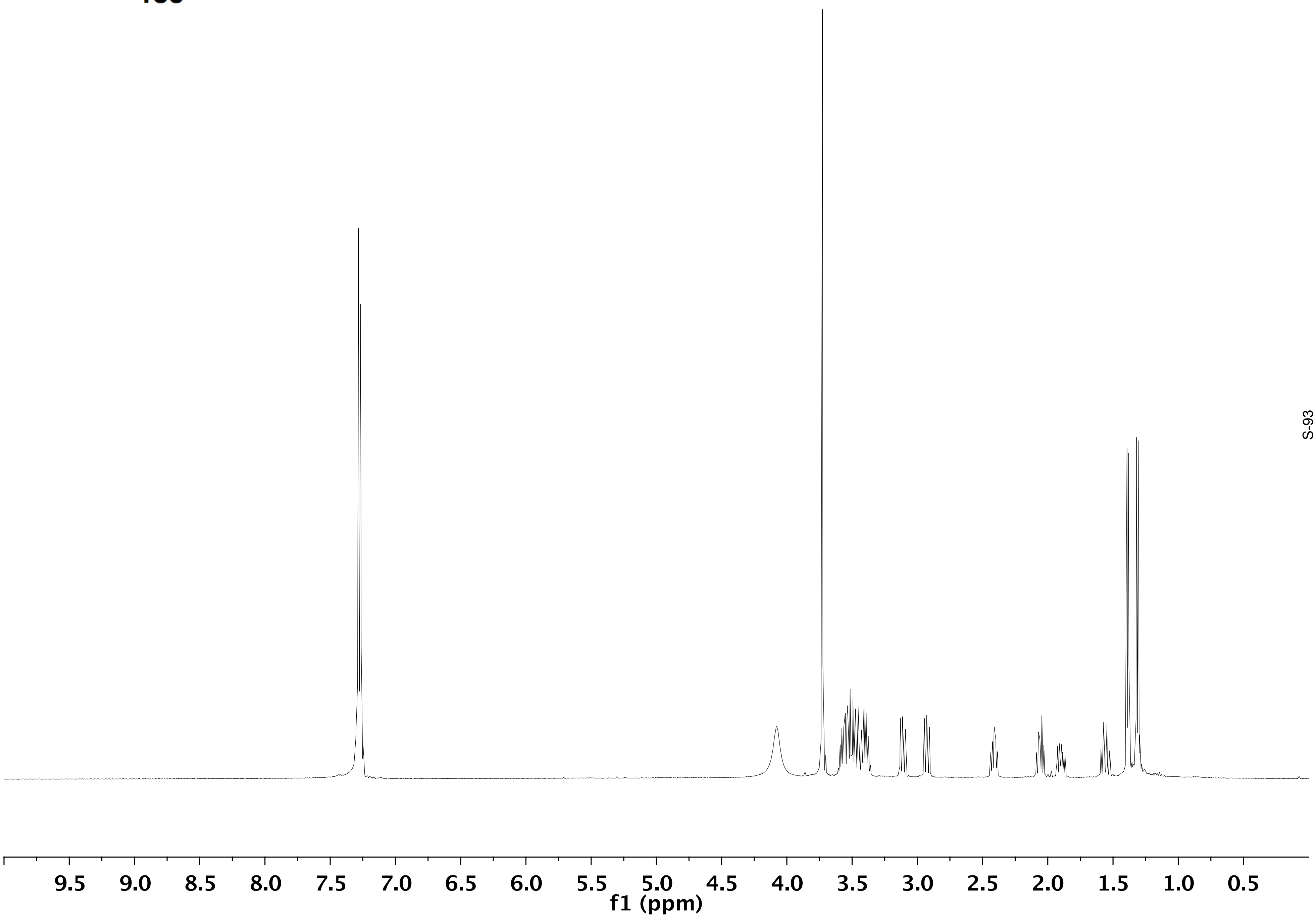
13b

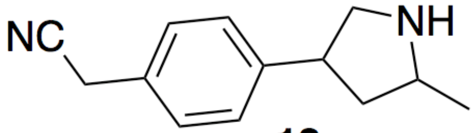


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

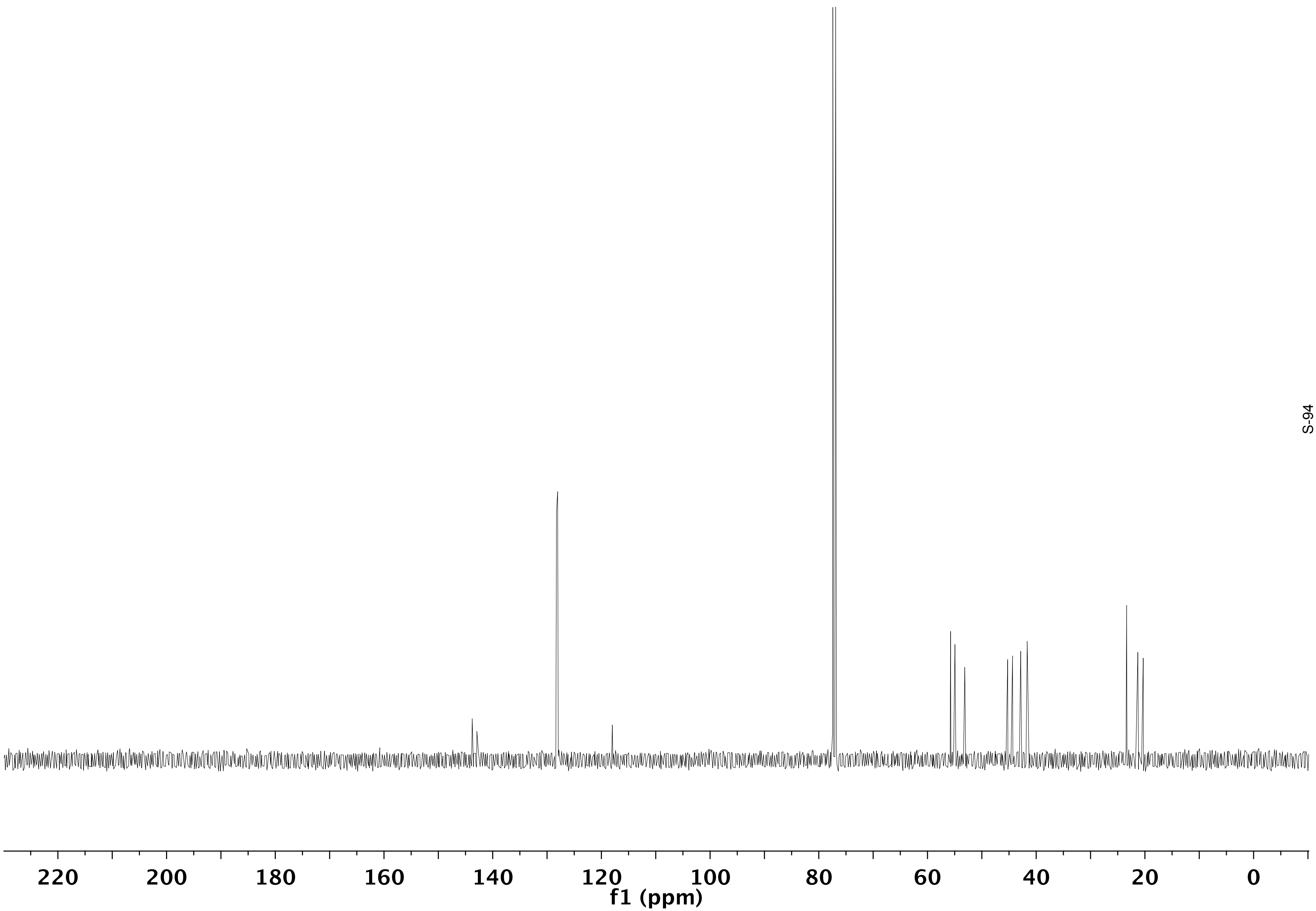


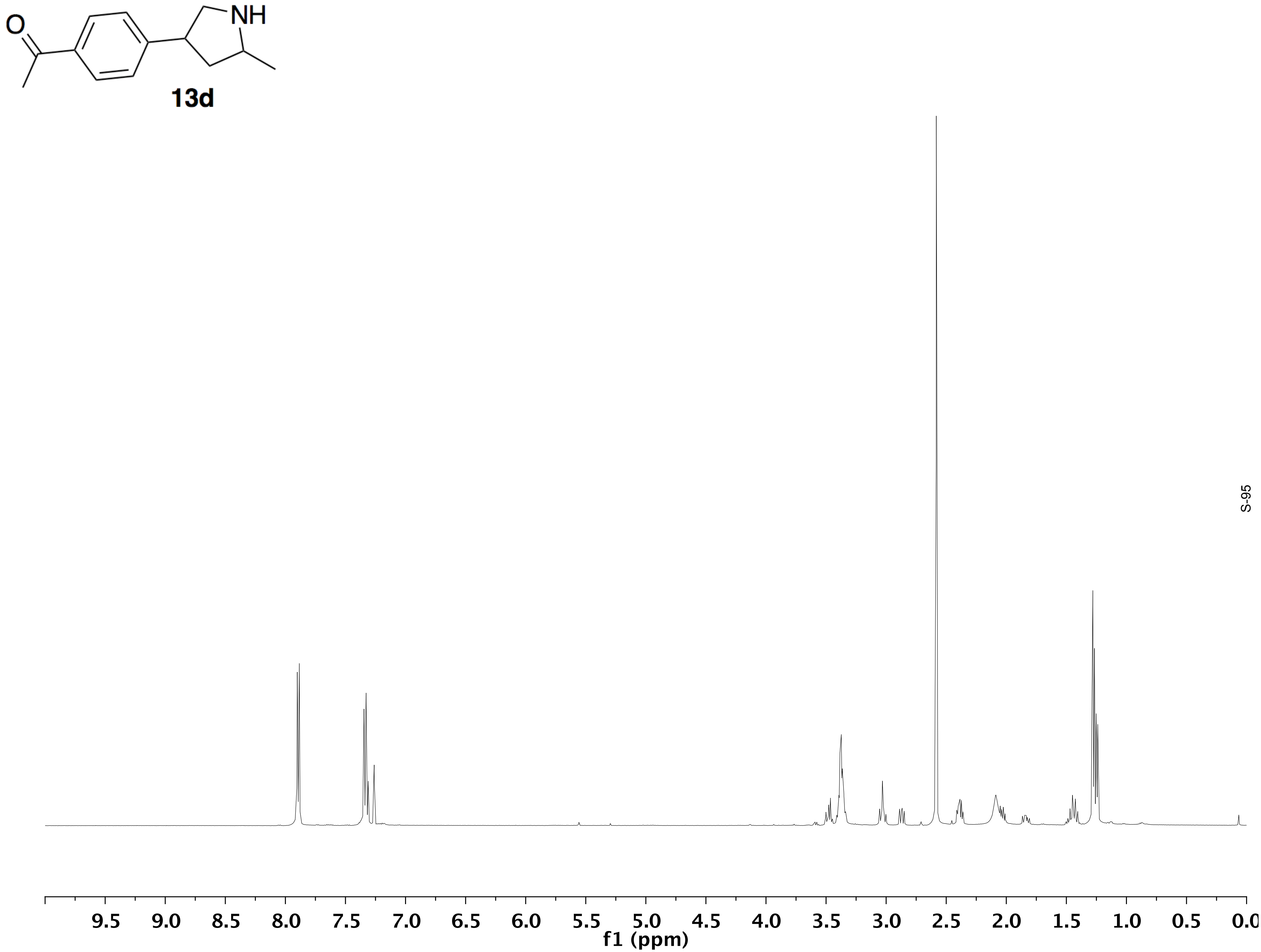
13c

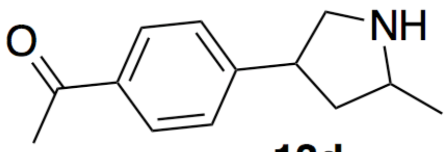


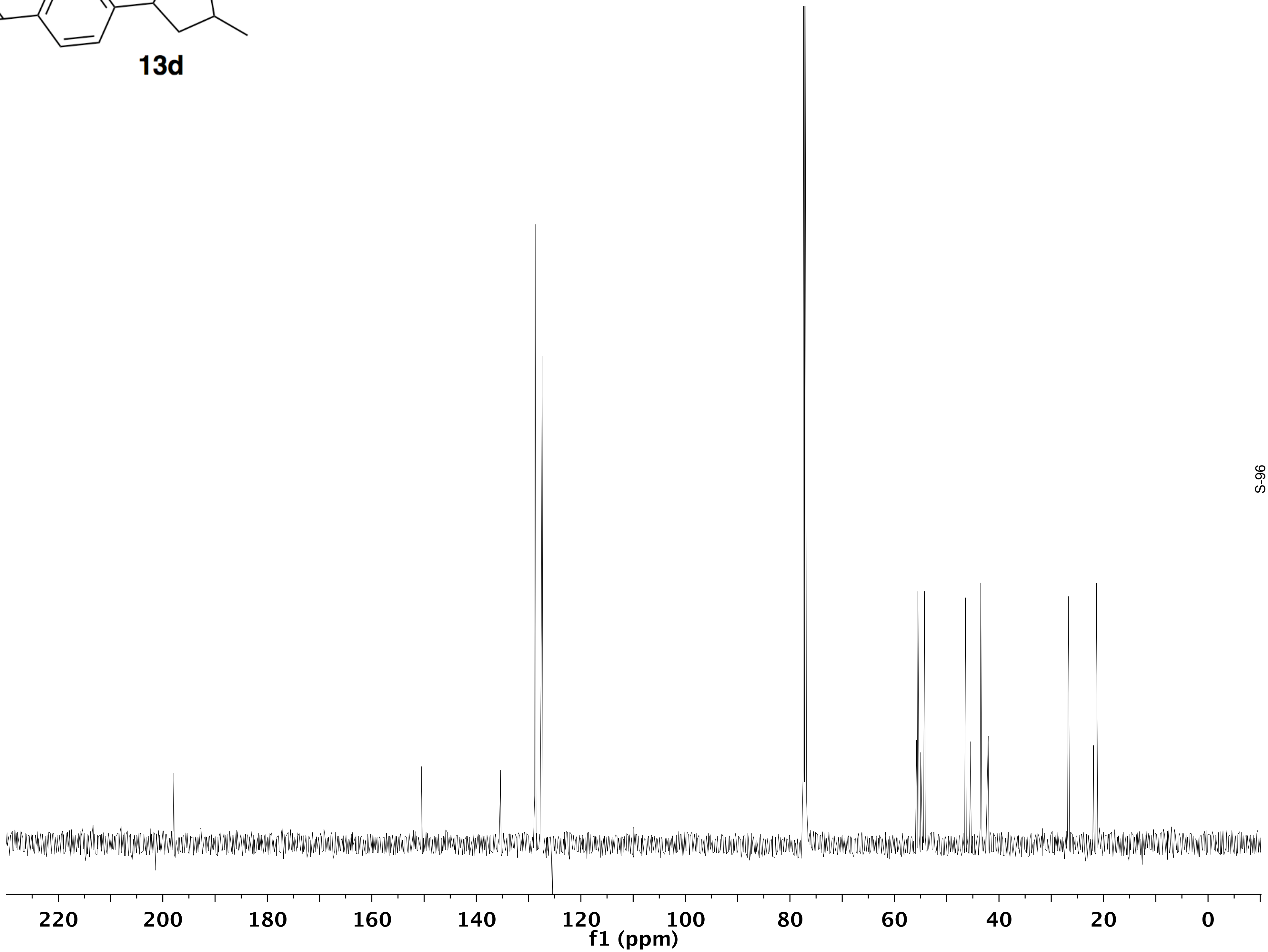


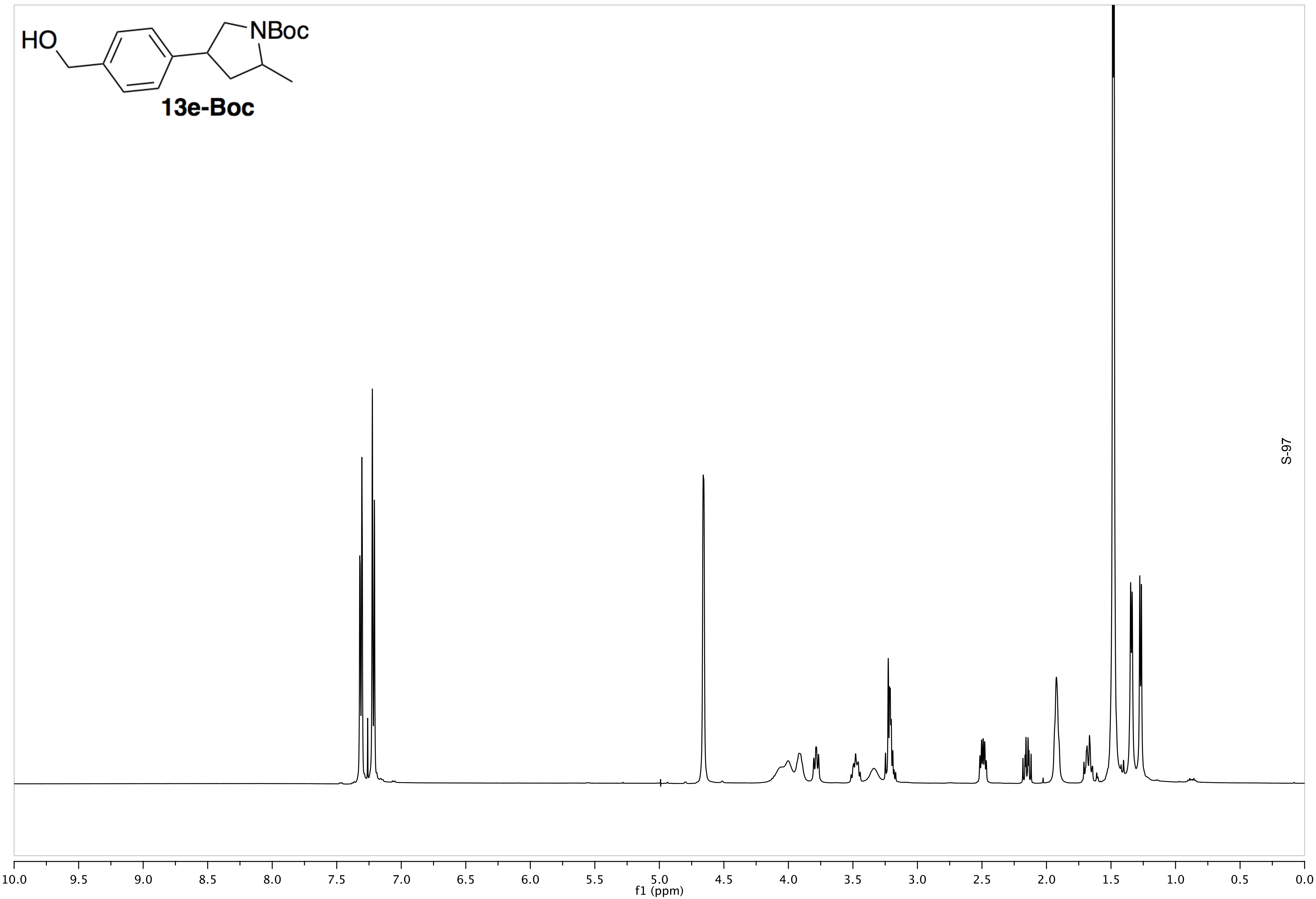
13c

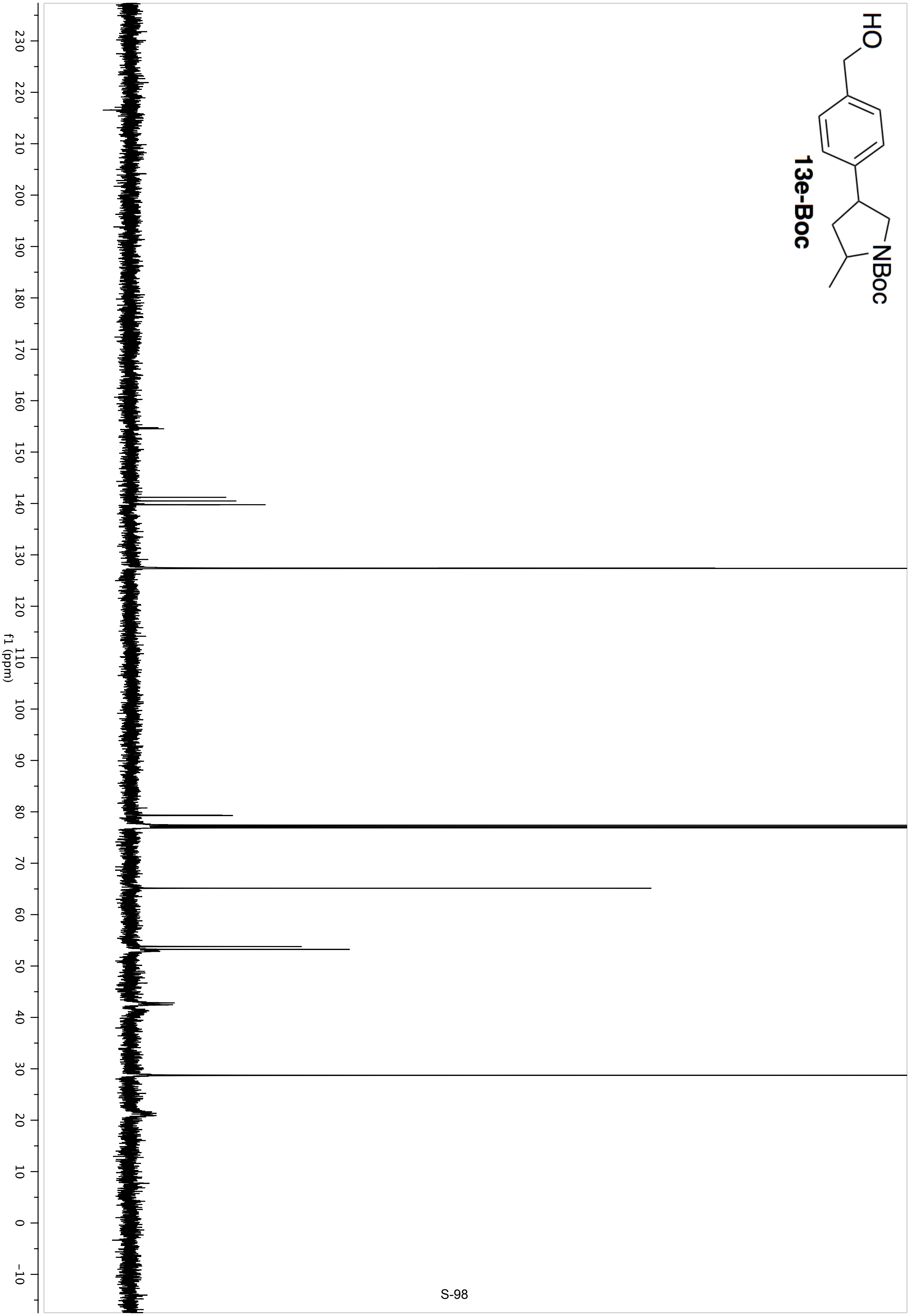


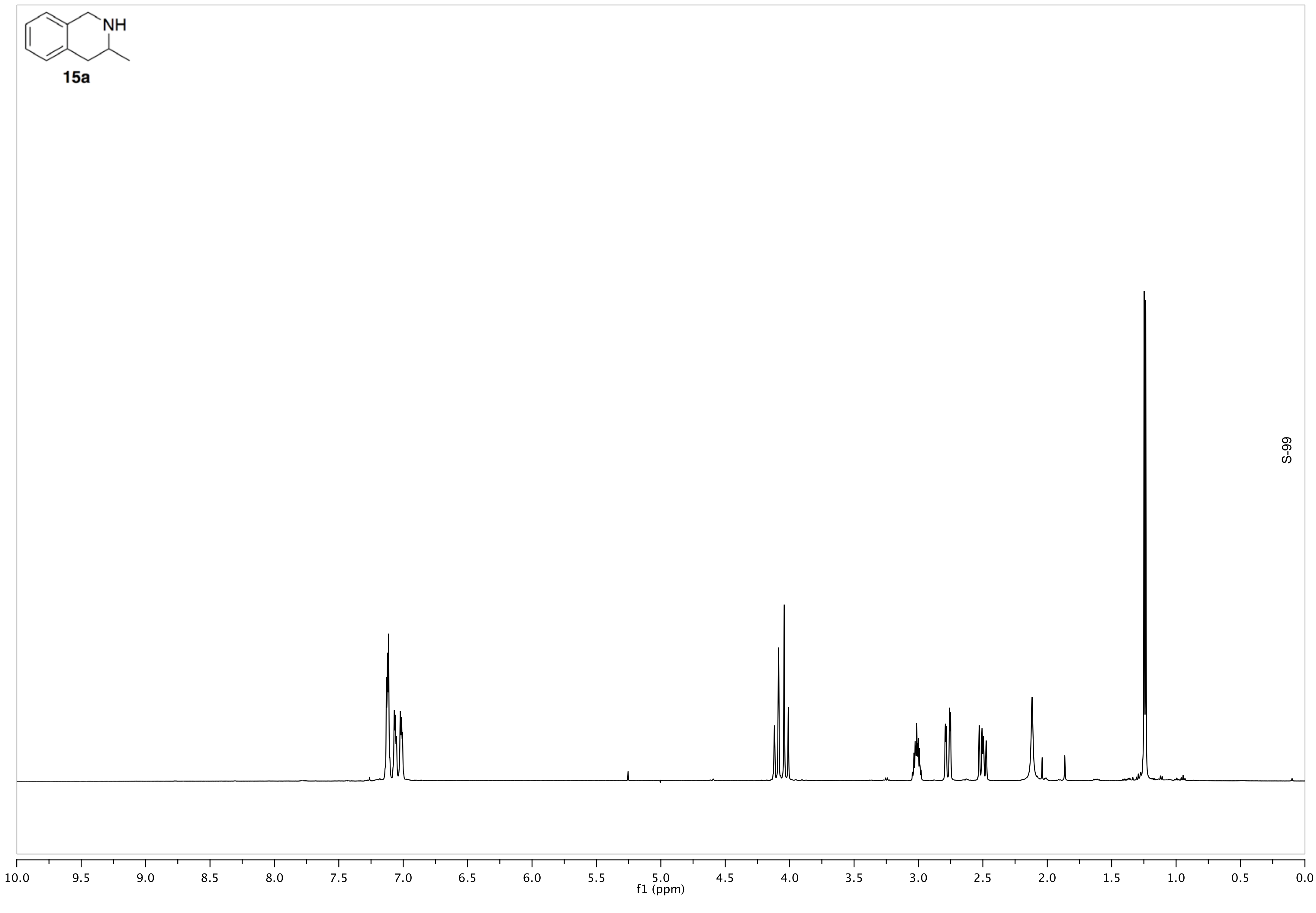

O
NH
13d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

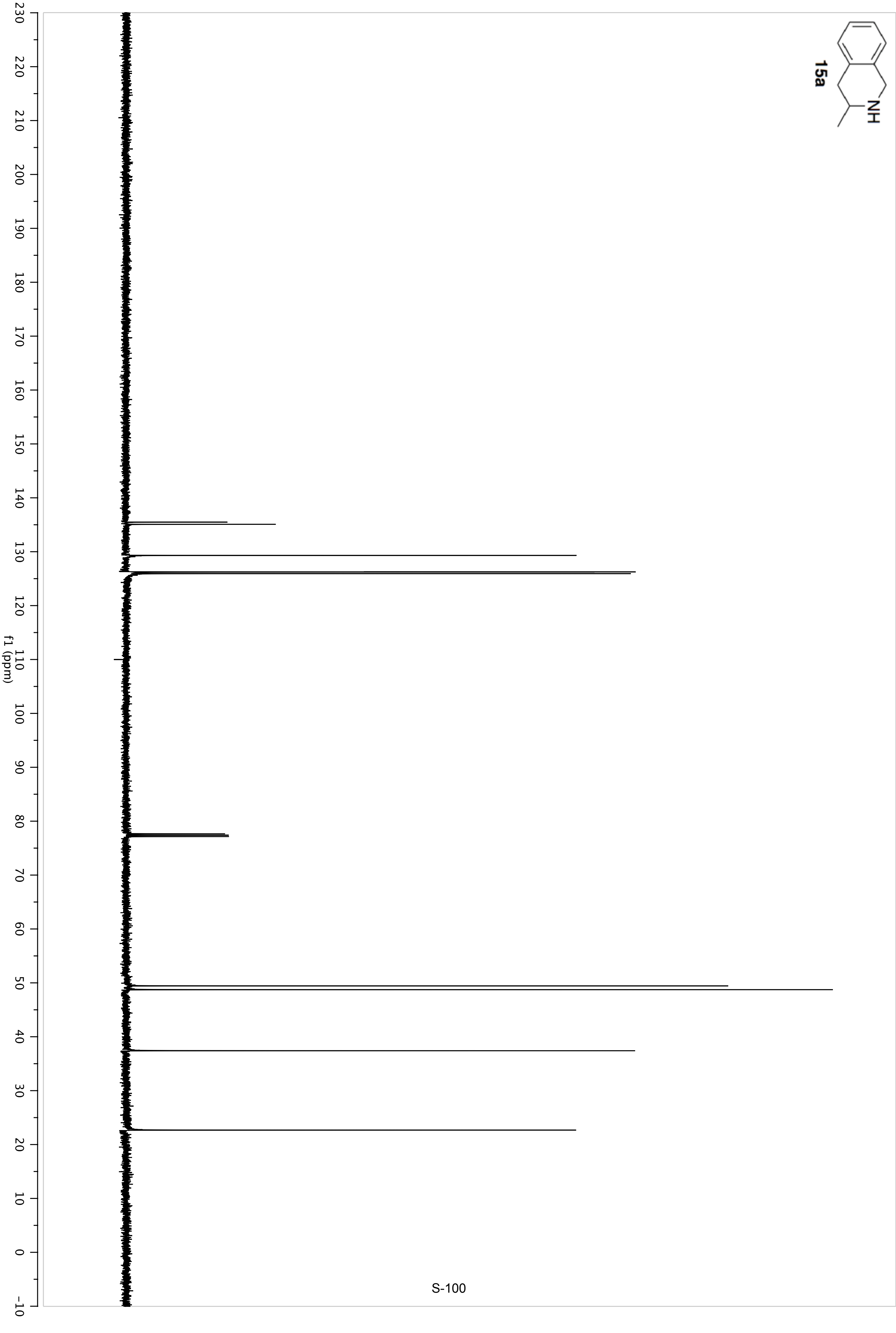

13d

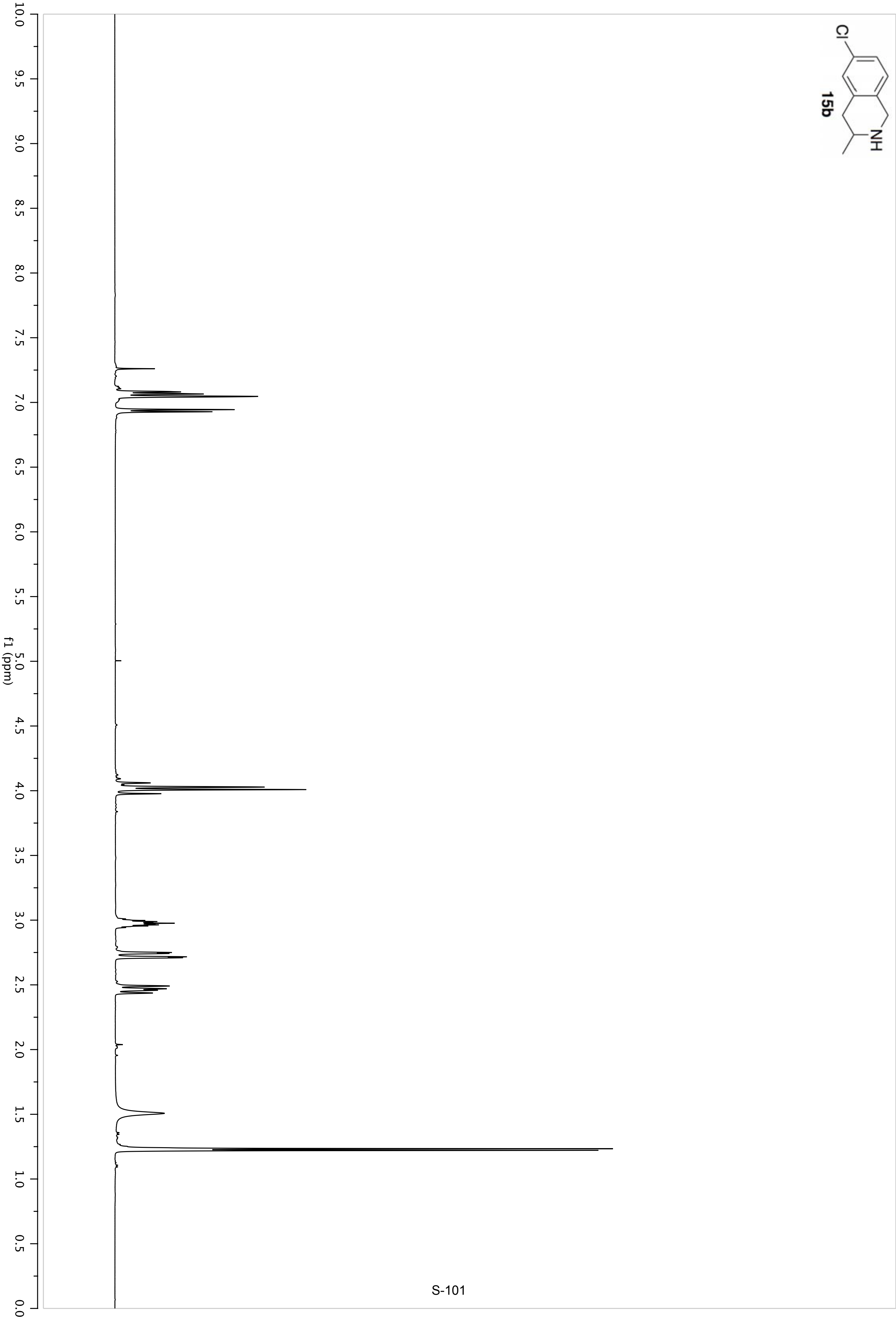


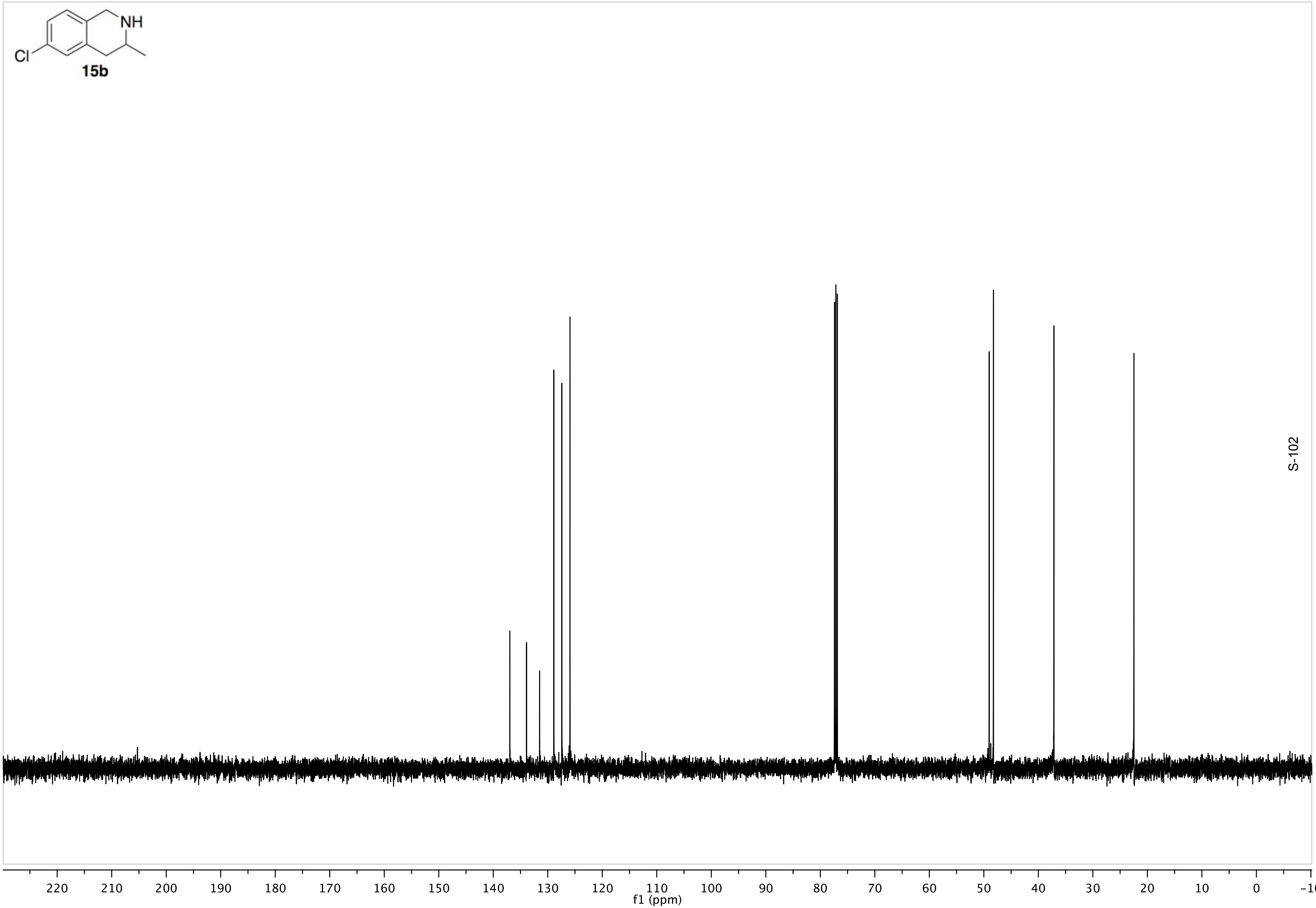

HO
NBoc
13e-Boc
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

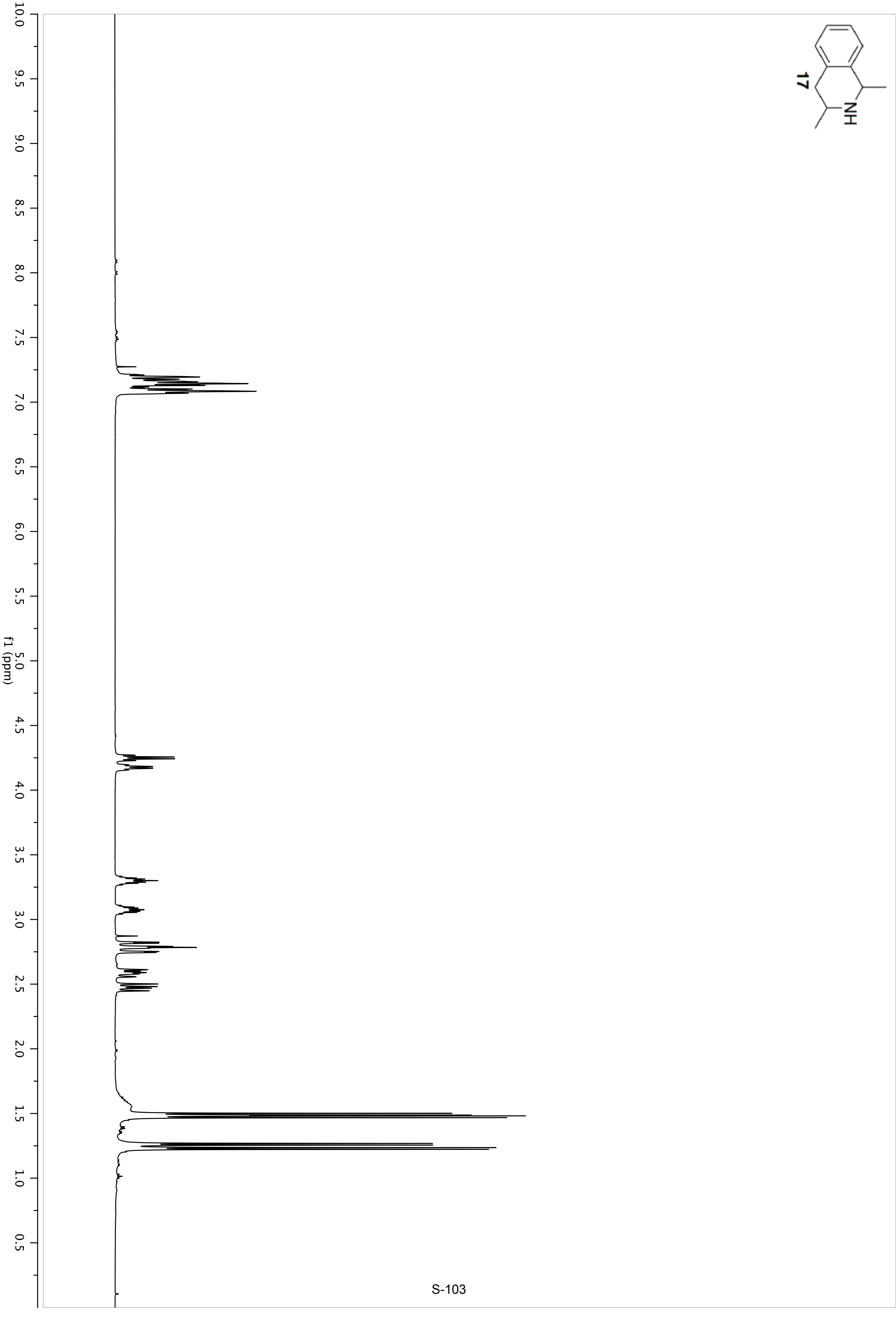

HO
NBoc
13e-Boc
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

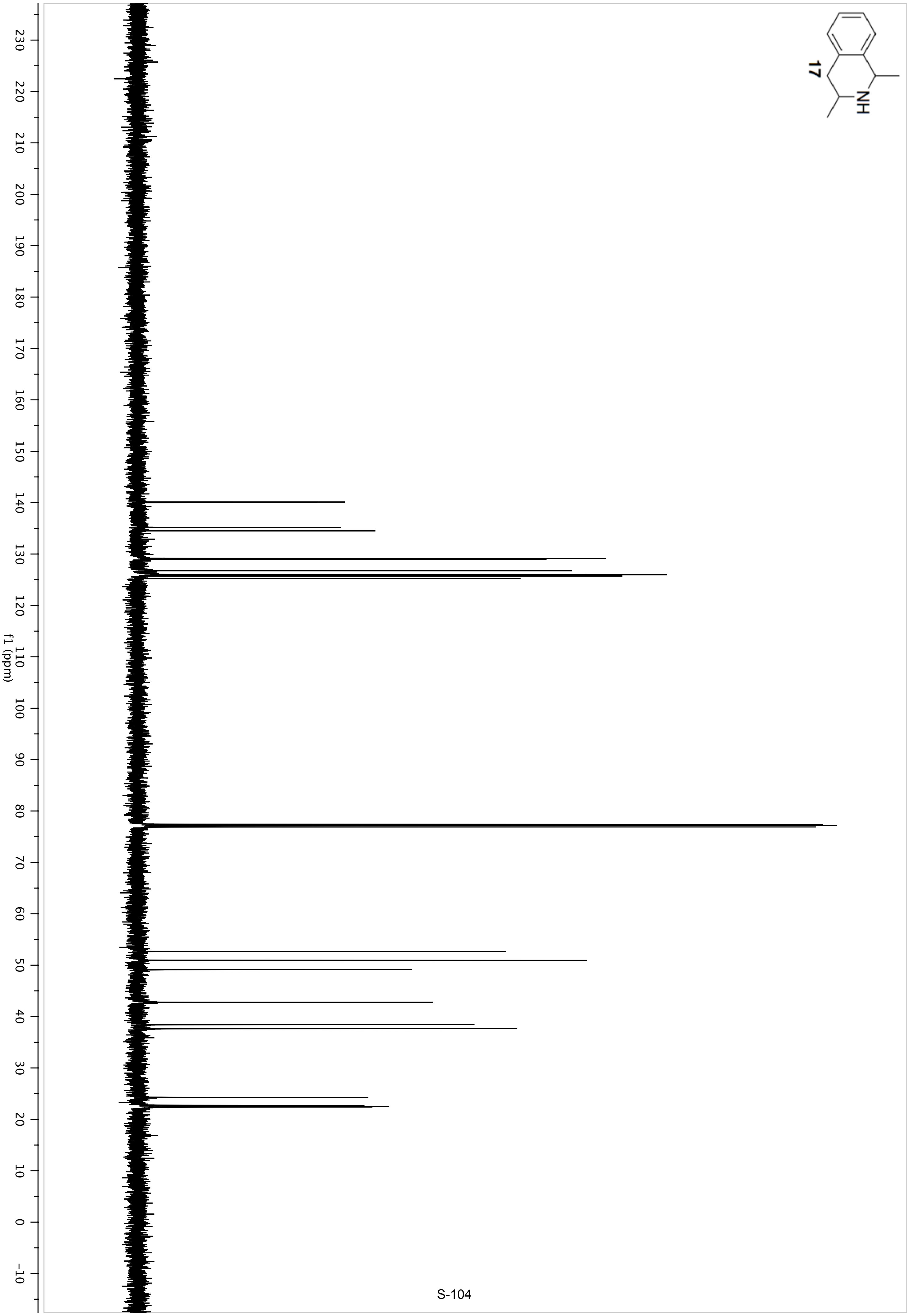

NH
15a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

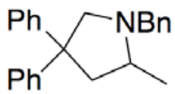

NH
15a
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10


Cl
NH
15b
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)

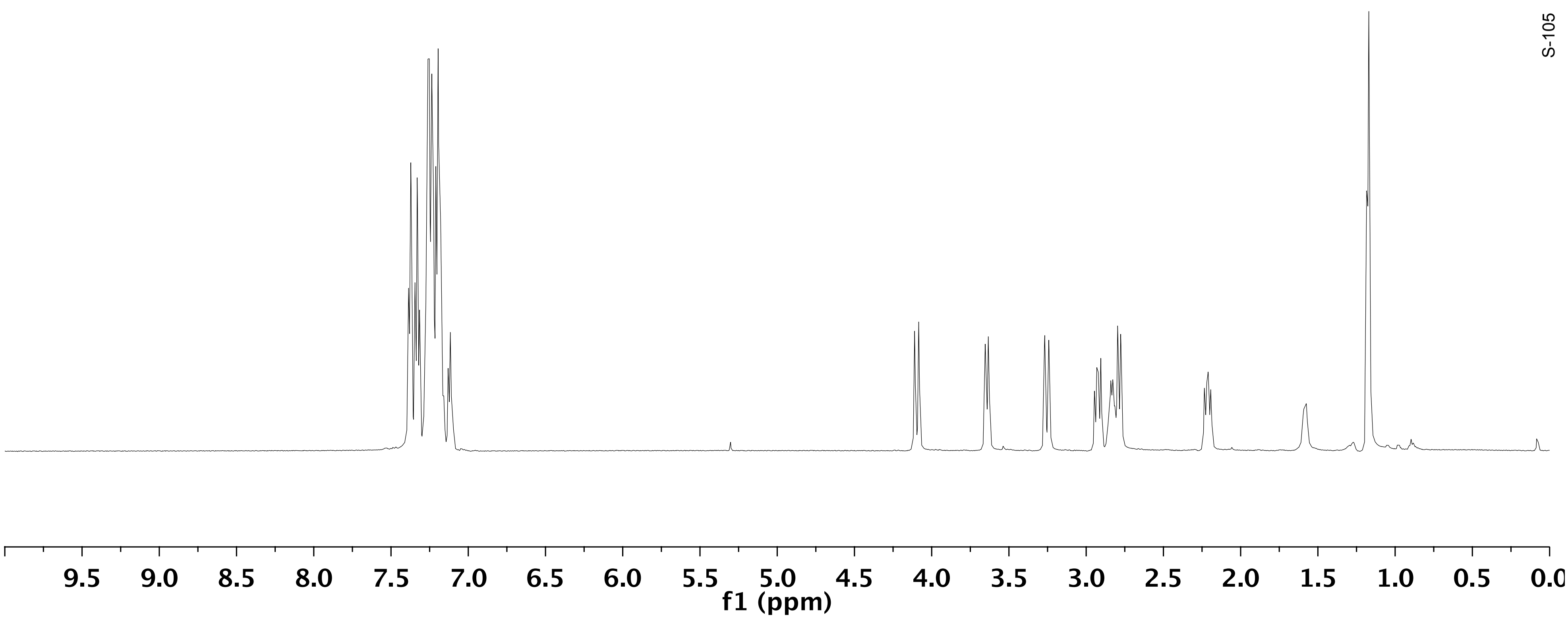

Cl
NH
15b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 –10
f1 (ppm)

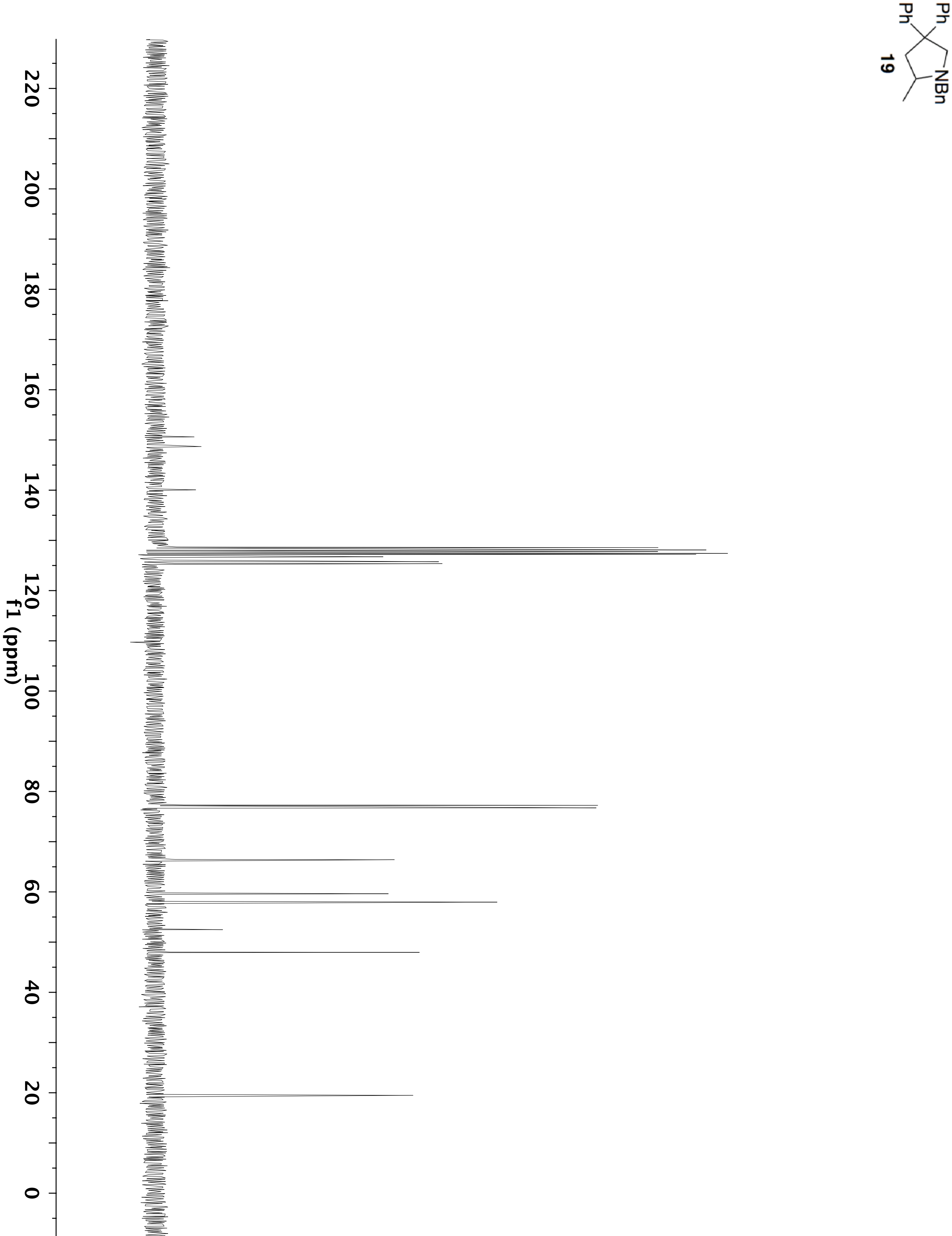

17
NH
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

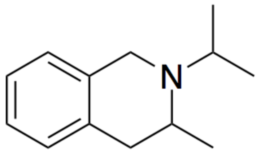

17
NH
f1 (ppm)


Ph
NBn
Ph

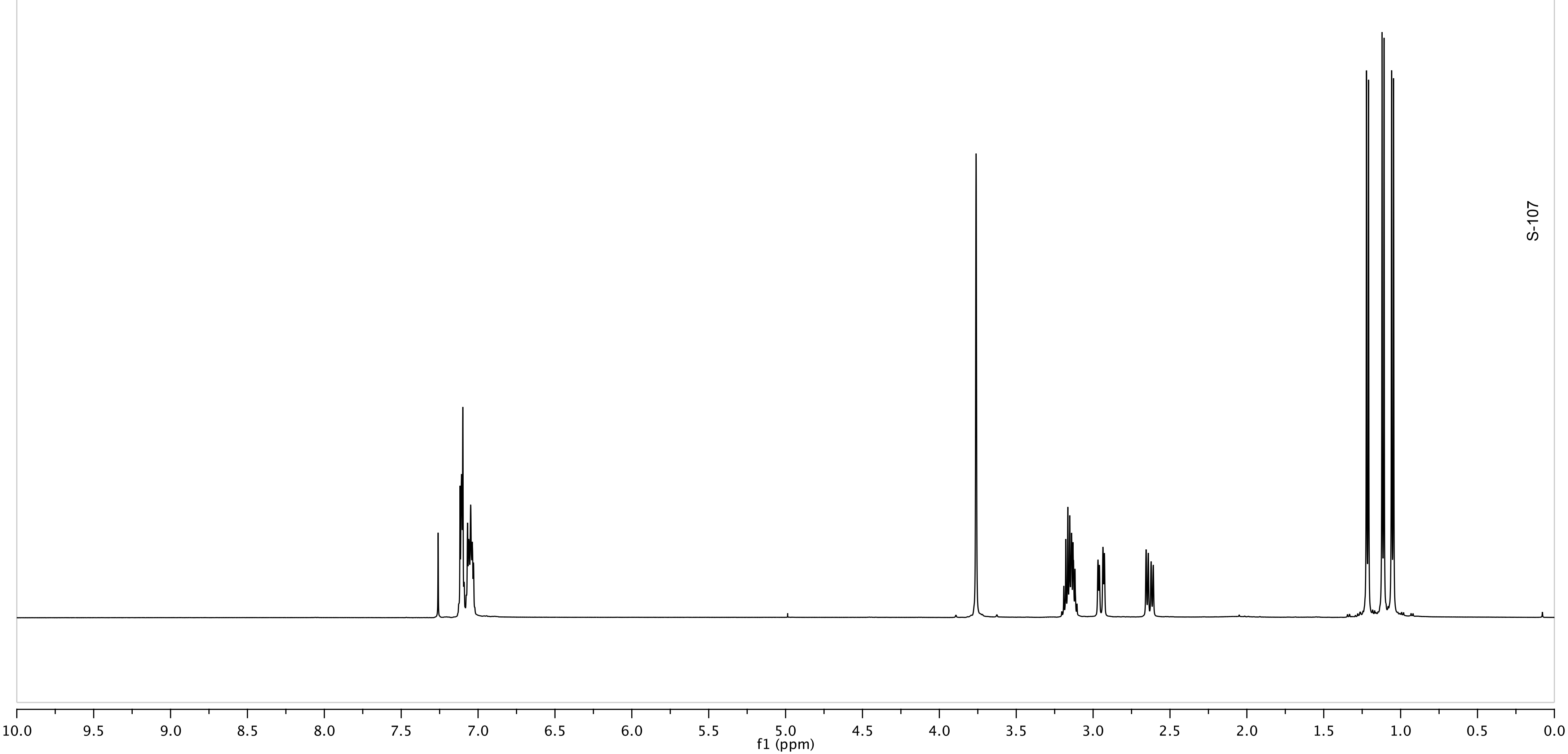
19

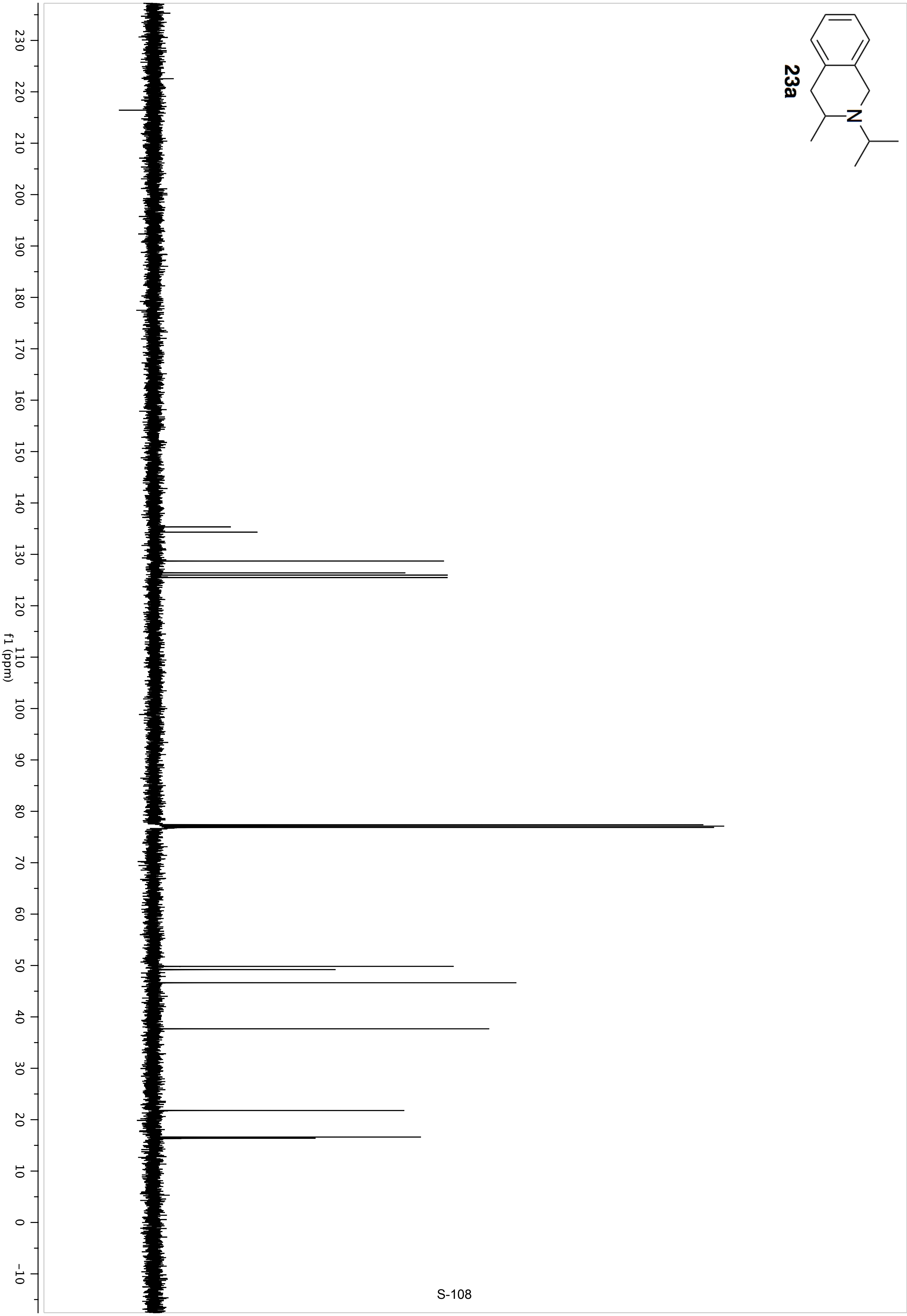

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

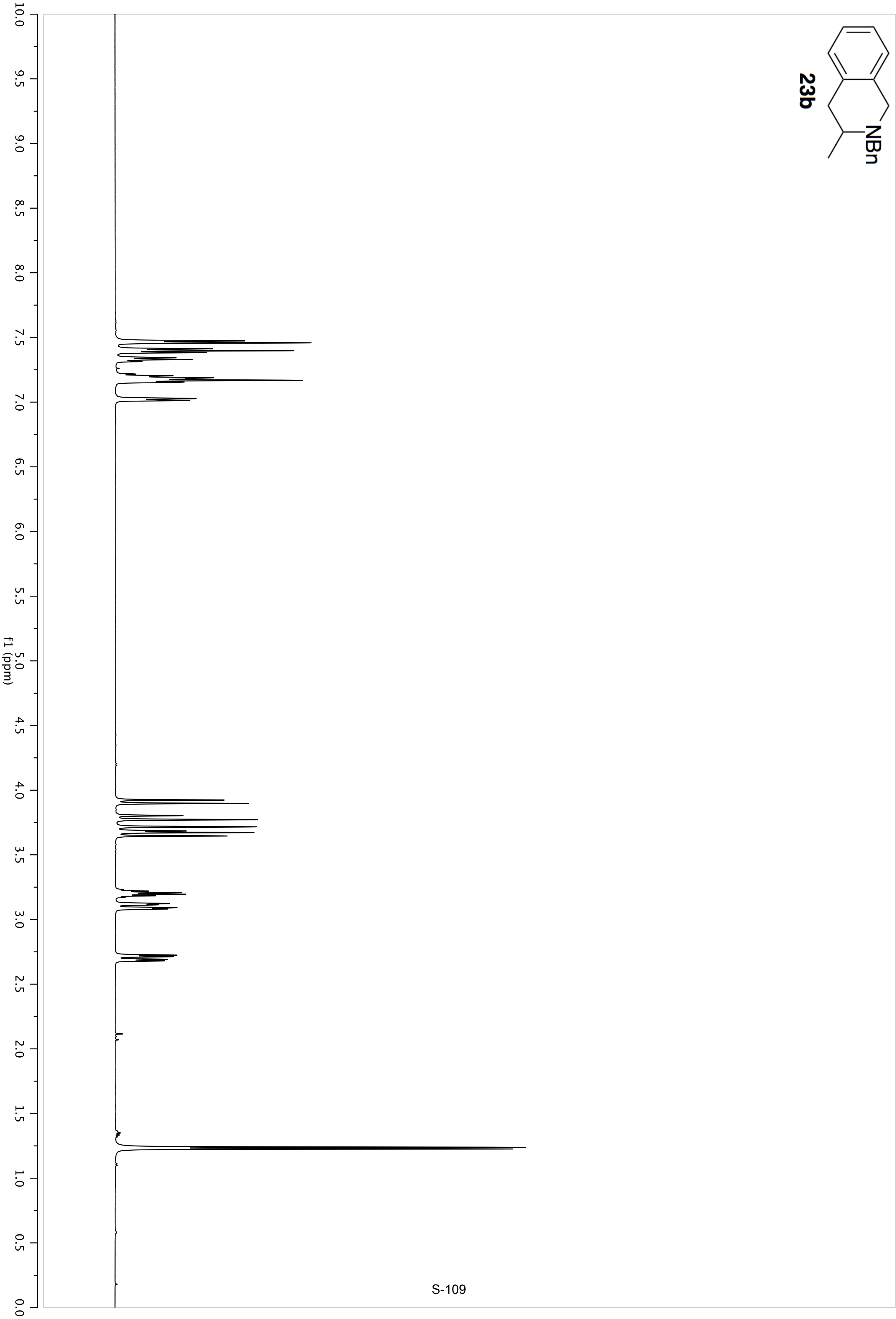

Ph
Ph
NBn
19
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0

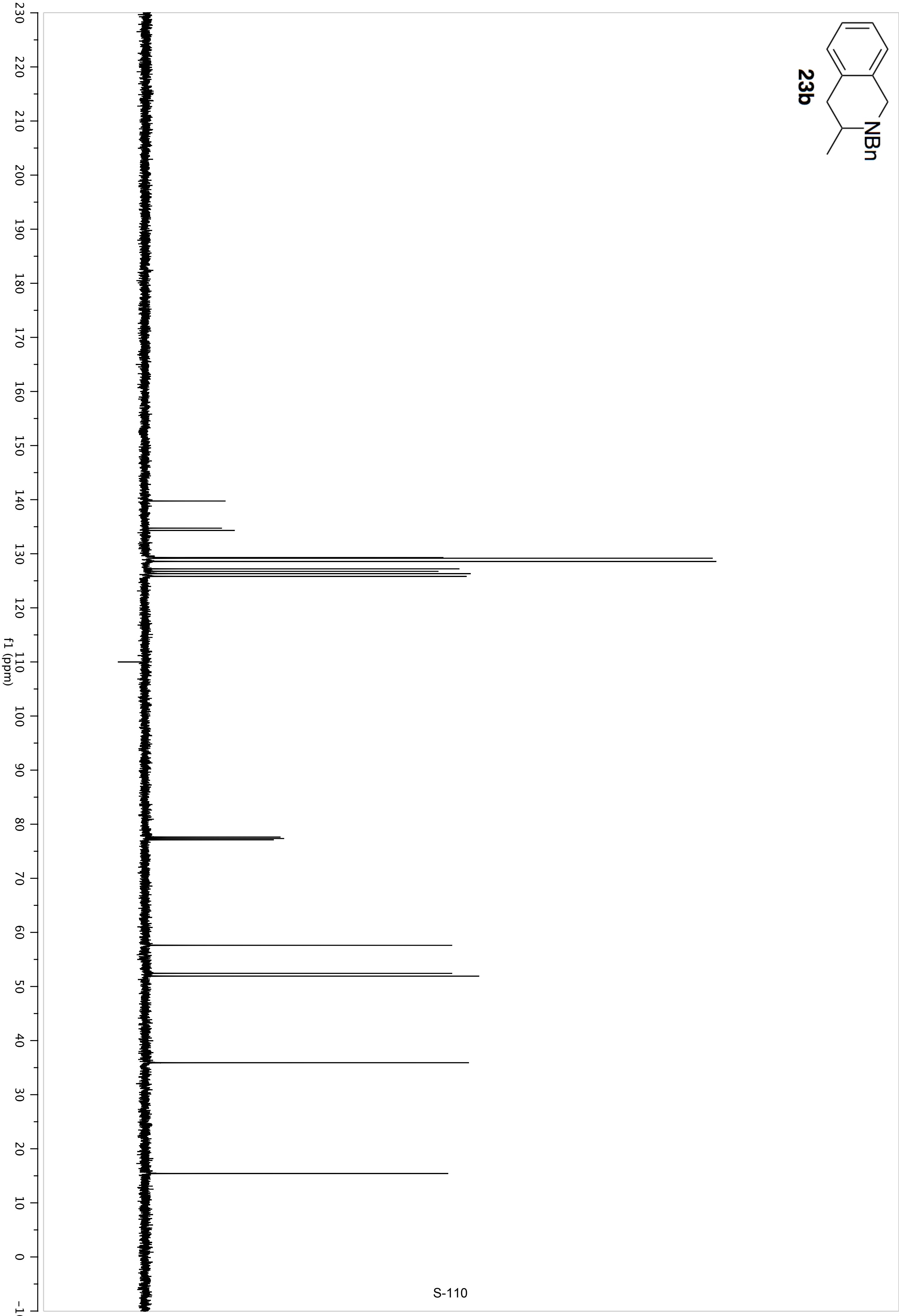


23a




23a
N
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


23b
NBn
f1 (ppm)
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



23b
NBn
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10