Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Facile Synthesis of α-Aminoboronic Acids from Amines and Potassium Acyltrifluoroborates via Trifluoroborate-Iminiums (TIMs)

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Table of Contents

1 General information

Reactions with anhydrous solvents were carried out in oven-dried glassware under N_2 atmosphere using standard manifold techniques.

1.1 Materials

Compounds that are not described in the experimental part were synthesized according to literature procedures. Unless otherwise stated, chemicals were purchased from ABCR, Acros, Alfa Aesar, Apollo Scientific, Fluorochem, Maybridge, Merck, Sigma-Aldrich, Strem, or TCI, and were used without further purification. Common organic solvents were used as supplied (ACS or HPLC grade). Anhydrous CH_3CN, CH_2Cl_2, THF, and DMF (HPLC grade) were freshly dried by passage over activated alumina under an inert atmosphere of N_2. Anhydrous CH_3OH was purchased from Acros and supplied over 3 Å molecular sieves under an inert atmosphere.

1.2 Reaction monitoring and purification

Thin layer chromatography (TLC) was performed on aluminum-backed plates pre-coated with silica gel (*Merck*, Silica Gel 60 F254) and visualized by UV quenching, or by oxidative staining with basic $KMnO_4$ solution. Flash column chromatography was performed on silica gel (*Silicycle* SiliaFlash F60, 230–400 mesh) using a forced flow of eluent at 0.4–0.5 bar at room temperature. Organic solutions were concentrated under reduced pressure on a rotary evaporator.

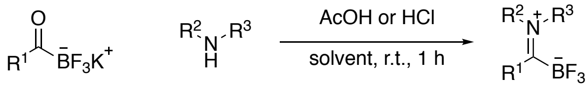
1.3 Characterization instruments

NMR spectra were recorded at 298 K in Acetone-d6 (DLM-9) supplied by Cambridge Isotope Laboratories, CD3OD (DLM-24) supplied by Cambridge Isotope Laboratories, D2O (DLM-4) supplied by Cambridge Isotope Laboratories, or CDCl3 supplied by Armar Isotopes. ^{1}H NMR spectra were recorded on a Bruker AV300 300 MHz spectrometer, on a Bruker AV400 400 MHz spectrometer, on a Bruker AV500 500 MHz spectrometer, or on a Bruker DRX500 500 MHz spectrometer, and are referenced to the solvent residual signal (Acetone-d6: 2.05 ppm, CDCl3: 7.26 ppm, CD3OD: 3.31 ppm). ^{13}C NMR spectra were recorded on a Bruker AV400 101 MHz spectrometer, on a Bruker AV500 126 MHz spectrometer, or on a Bruker AV600 151 MHz spectrometer with complete ^{1}H nuclei decoupling and are referenced to the solvent residual signal (Acetone-d6: 260.3 ppm, CDCl3: 77.16 ppm, CD3OD: 49.0 ppm). ^{19}F NMR spectra were recorded on a Bruker AV300 282 MHz spectrometer, on a Bruker AV400 376 MHz spectrometer, or on a Bruker DRX500 470 MHz spectrometer and are referenced to an external sample of trifluoroacetic acid. ^{11}B NMR spectra were recorded on a Bruker AV400 128 MHz spectrometer, or on a Bruker DRX500 160 MHz spectrometer and are referenced to an external sample of $BF_3 \cdot OEt_2$. All chemical shifts (δ) are reported in ppm. NMR coupling constants (*J*) are reported in Hz and splitting patterns are indicated as follows: s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Infrared (IR) data was obtained on a *JASCO* FT-IR-4100 spectrometer or on a Perkin Elmer Spectrum Two™ FT-IR spectrometer with only major peaks being reported. Melting points (m.p.) were measured on an *Electrothermal Mel-Temp* melting point apparatus and are uncorrected. High resolution mass spectra were measured by the Mass Spectrometry Service Facility of the Laboratorium für Organische Chemie at ETH Zürich on a Bruker maXis ESI-QTOF mass spectrometer or on a Bruker SolariX MALDI-FTICR mass spectrometer and the mass for the found ions are given in m/z units.

2 Preparation of trifluoroborate-iminiums (TIMs)

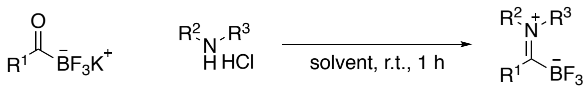
2.1 General procedures

General procedure A:



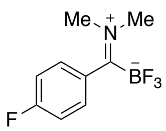
In a round-bottom flask, AcOH or 4.00 M HCl in dioxane (1.10 – 2.20 equiv) and the corresponding amine (1.10 – 2.20 equiv) were added to the corresponding potassium acyltrifluoroborate (1.00 equiv) in CH_3CN, CH_3CN / CH_3OH, or anhydrous DMF (0.10 – 0.40 M) and the mixture was stirred at r.t.. The reaction mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel or by washing with Et_2O to afford the corresponding TIM.

General Procedure B:

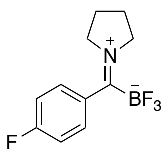


In a round-bottom flask, the corresponding amine·HCl salt (1.10 – 2.00 equiv) was added to the corresponding potassium acyltrifluoroborate (1.00 equiv) in CH_3CN (0.10 – 0.50 M) and the mixture was stirred at r.t.. The reaction mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel or by washing with Et_2O to afford the corresponding TIM.

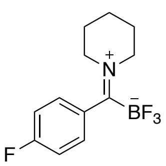
2.2 Synthesis of TIMs



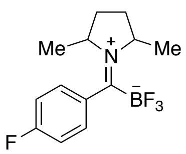
2 prepared according to general procedure A with potassium 4-fluorobenzoyl-trifluoroborate (50.0 mg, 0.22 mmol, 1.0 equiv), AcOH (14.3 µL, 0.24 mmol, 1.10 equiv), and dimethylamine (2.00 M solution in THF, 19.8 µL, 0.24 mmol, 1.10 equiv). Reaction in CH_3CN (0.50 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **2** as a white solid (44.3 mg, 93 %); **m.p.** 127 – 129 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.40 – 7.37 (m, 2 H), 7.32 – 7.28 (m, 2 H), 3.92 (s, 3 H) 3.51 (s, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 209.1 (m), 164.1 (d, *J* = 247.6 Hz), 134.4, 129.1 (d, *J* = 8.6 Hz), 116.2 (d, *J* = 22.2 Hz), 47.3, 46.7; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 112.7, – 141.4; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.40; **IR** (ν/cm^{-1}, thin film) ν = 1463, 1265, 1086, 1027, 1009; **HRMS (ESI)** calculated for $C_9H_{10}BF_4NNa$ $[M + Na]^+$: m/z = 242.0736, found: m/z = 242.0734; **EA** calculated for $C_9H_{10}BF_4N$: C, 49.36; H, 4.60; N, 6.40; F 34.70; Found: C, 49.38; H, 4.78: N, 6.34: F, 34.69.



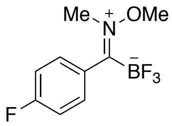
3 prepared according to general procedure A with potassium 4-fluorobenzoyl-trifluoroborate (50.0 mg, 0.22 mmol, 1.00 equiv), AcOH (14.3 μL, 0.24 mmol, 1.10 equiv) and pyrrolidine (19.8 μL, 0.24 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **3** as a white solid (51.2 mg, 96 %); **m.p.** 147 – 149 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.49 – 7.46 (m, 2 H), 7.32 – 7.27 (m, 2 H), 4.32 (t, *J* = 7.2 Hz, 2 H), 3.88 (t, *J* = 7.2 Hz, 2 H), 2.25 – 2.17 (m, 2 H), 2.12 – 2.07 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 204.5 (m), 164.1 (d, *J* = 247.6 Hz), 135.1, 129.1 (d, *J* = 8.6 Hz), 116.2 (d, *J* = 22.2 Hz), 56.6, 56.5, 25.0, 24.7; **^{19}F NMR** (282 MHz, Acetone-d6) δ [ppm] = – 108.5, – 144.4; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.36; **IR** (ν/cm^{-1}, thin film) ν = 3112, 3080, 2982, 2962, 2887, 1628, 1602, 1509, 1445, 1224, 1074, 1047, 1017; **HRMS (ESI)** calculated for $C_{11}H_{12}BF_4NNa$ $[M + Na]^+$: m/z = 268.0893, found: m/z = 268.0889.



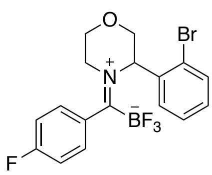
4 prepared according to general procedure A with potassium 4-fluorobenzoyl-trifluoroborate (50.0 mg, 0.22 mmol, 1.00 equiv), AcOH (14.3 μL, 0.24 mmol, 1.10 equiv) and piperidine (23.6 μL, 0.24 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **4** as a white solid (46.8 mg, 83 %); **m.p.** 175 – 176 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.35 – 7.28 (m, 4 H), 4.40 (t, *J* = 5.6 Hz, 2 H), 3.85 (t, *J* = 5.6 Hz, 2 H), 2.06 – 2.02 (m, 2 H), 1.89 – 1.86 (m, 4 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 207.0 (m), 163.9 (d, *J* = 247.6 Hz), 134.2, 128.5 (d, *J* = 7.6 Hz), 116.3 (d, *J* = 21.1 Hz), 58.0, 56.3, 28.52, 28.50, 23.9; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 113.1, – 140.9; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.37; **IR** (v/cm^{-1}, thin film) v = 2954, 2867, 1626, 1601, 1507, 1459, 1221, 1077, 1032; **HRMS (ESI)** calculated for $C_{12}H_{14}BF_4NNa$ [M + Na]$^+$: m/z = 282.1050, found: m/z = 282.1047.



5 prepared according to general procedure A with potassium 4-fluorobenzoyltrifluoroborate (30.0 mg, 0.13 mmol, 1.00 equiv), HCl (4.00 M in dioxane, 39.0 μL, 0.16 mmol, 1.20 equiv) and 2,5-dimethylpyrrolidine (15.5 mg, 0.16 mmol, 1.20 equiv). Reaction in CH_3CN (0.30 mL) for 5 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **5** as a white solid (18.5 mg, 52 %, two main stereoisomers 4:1); **m.p.** 100 – 101 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.48 – 7.44 (m, 0.4 H), 7.42 – 7.38 (m, 1.6 H), 7.31 – 7.27 (m, 2 H), 5.23 – 5.15 (m, 0.2 H), 5.12 – 5.07 (m, 0.8 H), 4.85 – 4.80 (m, 0.2 H), 4.57 – 4.48 (m, 0.8 H), 2.55 – 2.20 (m, 2 H), 2.05 – 1.90 (m, 2 H), 1.61 (d, *J* = 6.8 Hz, 2.4 H), 1.55 (d, *J* = 6.8 Hz, 0.6 H), 1.13 (d, *J* = 6.8 Hz, 2.4 H), 0.97 (d, *J* = 6.8 Hz, 0.6 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 207.4 (m), 164.0 (d, *J* = 247.6 Hz, minor), 163.6 (d, *J* = 246.1 Hz, major), 135.8 (minor), 135.3 (major), 128.7 (d, *J* = 7.6 Hz, minor), 127.6 (d, *J* = 7.6 Hz, major), 116.3 (d, *J* = 21.1 Hz, minor), 116.2 (d, *J* = 21.1 Hz, major), 64.3 (major), 63.9 (minor), 63.2 (major), 62.6 (minor), 30.8, 30.6, 22.6 (minor), 22.4 (major), 21.4 (major), 19.6 (minor); **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 113.2 (minor), – 113.9 (major), – 142.1 (major), – 142.0 (minor); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.31; **IR** (v/cm^{-1}, thin film) v = 2983, 1604, 1509, 1457, 1386, 1233, 1161, 1076, 1047, 1002; **HRMS (ESI)** calculated for $C_{13}H_{16}BF_4NNa$ [M + Na]$^+$: m/z = 296.1207, found: m/z = 296.1209.

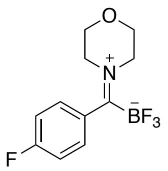


6 prepared according to general procedure B with potassium 4-fluorobenzoyl-trifluoroborate (40.0 mg, 0.17 mmol, 1.00 equiv), and N,O-dimethylhydroxyl-amine·HCl salt (18.7 mg, 0.19 mmol, 1.10 equiv). Reaction in DMF (0.30 mL) for 8 h. The product was extracted from the crude material with acetone, evaporated under reduced pressure, and washed with Et_2O to give **6** as a white solid (38.0 mg, 93 %); **m.p.** 102 – 104 °C; **^{1}H NMR** (500 MHz, Acetone-d6) δ [ppm] = 7.67 – 7.64 (m, 2 H), 7.32 – 7.29 (m, 2 H), 4.14 (s, 3 H), 3.82 (s, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 194.5 (m), 164.9 (d, *J* = 250.7 Hz), 131.8 (d, *J* = 9.1 Hz), 129.4, 115.9 (d, *J* = 22.7 Hz), 62.5, 44.0; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 110.1, – 141.7; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.30; **IR** (v/cm^{-1}, thin film) v = 3083, 3013, 2957, 1600, 1507, 1454, 1240, 1086, 1059; **HRMS (ESI)** calculated for $C_9H_{10}BF_4NNaO$ $[M + Na]^+$: m/z = 258.0685, found: m/z = 258.0688.

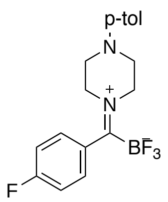


7 prepared according to general procedure B with potassium 4-fluoro-benzoyltrifluoroborate (200 mg, 0.87 mmol, 1.00 equiv), and 2-(3-bromo-phenyl)-morpholine hydrochloride (384 mg, 1.30 mmol, 1.50 equiv). Reaction in CH_3CN (3.00 mL) in the presence of MS 4 Å for 8 h. The crude material was purified by flash column chromatography on silica gel (hexanes / EtOAc = 1 : 1) to give **7** as a white amorphous solid (251 mg, 69 %, E:Z 1:1); **m.p.** 142 – 144 °C; **^{1}H NMR** (500 MHz, CDCl3) δ [ppm] = 8.02 (s, 0.5 H), 7.79 – 7.78 (m, 0.5 H), 7.59 – 7.58 (m, 0.5 H), 7.57 – 7.55 (m, 0.5 H), 7.52 – 7.51 (m, 0.5 H), 7.36 (t, *J* = 8.0 Hz, 0.5 H), 7.33 – 7.30 (m, 1.5 H), 7.25 – 7.17 (m, 3 H), 6.28 (s, 0.5 H), 5.35 (s, 0.5 H), 4.96 (d, *J* = 11.5 Hz, 0.5 H), 4.75 (d, *J* = 13.5 Hz, 0.5 H), 4.62 (d, *J* = 13.0 Hz, 0.5 H), 4.31 – 4.27 (m, 1 H), 4.09 – 3.94 (m, 2.5 H), 3.82 – 3.78 (m, 0.5 H), 3.75 – 3.70 (m, 0.5 H), 3.64 – 3.57 (m, 0.5 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 211.0, 163.8 (d, *J* = 252.2 Hz), 163.7 (d, *J* = 252.2 Hz), 136.4, 135.4, 132.7, 132.6, 131.8, 131.3, 131.2, 131.1, 130.9, 130.7, 127.5, 127.2, 126.0, 123.7, 123.4, 116.71, 116.6 (d, *J* = 22.7 Hz), 116.3 (d, *J* = 21.1 Hz), 69.4, 69.1, 68.7, 68.1, 65.1, 63.3, 52.5, 50.7; **^{19}F**

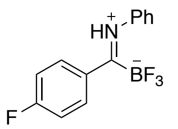
NMR (470 MHz, CDCl3) δ [ppm] = – 108.0, – 108.2, – 139.7, – 141.0; **^{11}B NMR** (160 MHz, CDCl3) δ [ppm] = – 0.28; **IR** (v/cm^{-1}, thin film) v = 3071, 2979, 2865, 1731, 1601, 1507, 1476, 1231, 1162, 1077, 1059, 996; **HRMS (ESI)** calculated for $C_{17}H_{14}BBrF_4NO$ [M - H]$^-$: m/z = 414.0297, found: m/z = 414.0303.



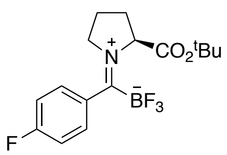
8 prepared according to general procedure A with potassium 4-fluorobenzoyl-trifluoroborate (321 mg, 1.23 mmol, 1.00 equiv), AcOH (84.6 μL, 1.48 mmol, 1.20 equiv) and morpholine (128 μL, 1.48 mmol, 1.20 equiv). Reaction in CH_3CN (6.00 mL) for 2 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **8** as a white solid (321 mg, 82 %); **m.p.** 163 °C; **^{1}H NMR** (500 MHz, Acetone-d6) δ [ppm] = 7.42 – 7.35 (m, 2 H), 7.33 – 7.26 (m, 2 H), 4.49 – 4.45 (m, 2 H), 4.07 – 4.04 (m, 2 H), 4.00 – 3.97 (m, 2 H), 3.95 – 3.91 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 208.7 (m), 164.3 (d, *J* = 248.2 Hz), 133.4, 129.4 (d, *J* = 8.7 Hz), 116.5 (d, *J* = 22.3 Hz) 68.4, 68.1, 57.7, 56.1; **^{19}F NMR** (471 MHz, Acetone-d6) δ [ppm] = – 112.4 (ddd, *J* = 14.2, 8.9, 5.3 Hz), – 140.6 (dd, *J* = 76.8, 38.2 Hz); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.39 (q, *J* = 38.4 Hz); **IR** (v/cm^{-1}, neat) v = 2988, 2969, 2901, 2871, 1605, 1509, 1460, 1168, 1066, 1042, 1006, 994, 929, 872, 814. **HRMS** (ESI pos.) calculated for $C_{11}H_{12}BF_4NNaO$ [M + Na]$^+$: 284.0842, found: 284.0838.



9 prepared according to general procedure A with potassium 4-fluorobenzoyl-trifluoroborate (250 mg, 1.09 mmol, 1.00 equiv), AcOH (74.6 μL, 1.30 mmol, 1.20 equiv) and N-(p-tolyl)piperazine (230 mg, 1.30 mmol, 1.20 equiv). Reaction in CH_3CN (6.00 mL) for 2 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **9** as a white solid (321 mg, 82 %); **m.p.** 191 °C; **^{1}H NMR** (500 MHz, Acetone-d6) δ [ppm] = 7.44 – 7.39 (m, 2 H), 7.35 – 7.28 (m, 2 H), 7.13 – 7.07 (m, 2 H), 6.97 – 6.92 (m, 2 H), 4.61 – 4.56 (m, 2 H), 4.11 – 4.07 (m, 2 H), 3.62 – 3.57 (m, 2 H), 3.48 – 3.44 (m, 2 H), 2.24 (s, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 208.8 (m), 164.3 (d, *J* = 248.1 Hz), 148.8, 133.8 (d, *J* = 3.4 Hz), 130.8, 130.7, 129.4 (d, *J* = 8.6 Hz), 117.8, 116.5 (d, *J* = 22.3 Hz), 56.6, 55.1, 51.5, 51.4, 20.6; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 112.5 (tt, *J* = 9.1, 5.3 Hz), – 140.4 (dd, *J* = 76.8, 38.1 Hz); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.35 (q, *J* = 38.5 Hz); **IR** (v/cm^{-1}, neat) v = 2972, 2901, 2812, 1507, 1231, 1084, 1057, 1035, 1001, 956, 884, 811, 547; **HRMS** (MALDI pos.) calculated for $C_{18}H_{19}BF_4N_2Na$ [M + Na]$^+$: 373.1470, found: 373.1469.

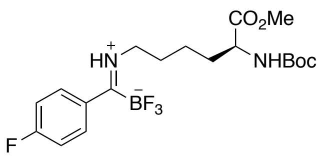


10 prepared according to general procedure A with 4-fluorobenzoyl-trifluoroborate (100 mg, 0.44 mmol, 1.00 equiv), HCl (4.00 M in dioxane, 120 μL, 0.48 mmol, 1.10 equiv) and aniline (44.5 ml, 0.48 mmol, 1.10 equiv). Reaction in CH_3CN (0.60 mL) in the presence of MS 4 Å for 5 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **10** as a white solid (105 mg, 90 %); **m.p.** 182 – 184 °C; **^{1}H NMR** (500 MHz, CDCl3) δ [ppm] = 11.2 (s, 1 H), 7.67 – 7.64 (m, 2 H), 7.47 – 7.45 (m, 3 H), 7.25 – 7.23 (m, 2 H), 7.06 – 7.02 (m, 2 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 204.8, 165.7 (d, *J* = 259.7 Hz), 136.3, 133.8 (d, *J* = 10.6 Hz), 130.4, 129.2, 127.3, 124.4, 116.4 (d, *J* = 21.1 Hz); **^{19}F NMR** (471 MHz, CDCl3) δ [ppm] = – 101.7, – 148.2; **^{11}B NMR** (160 MHz, CDCl3) δ [ppm] = 0.05; **IR** (v/cm^{-1}, thin film) v = 3253, 1617, 1594, 1510, 1493, 1463, 1241, 1194, 1165, 1050, 1027; **HRMS (ESI)** calculated for $C_{13}H_{11}BF_4N$ [M - H]$^-$: m/z = 268.0929, found: m/z = 268.0931.

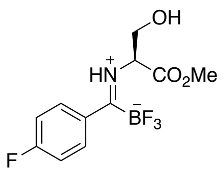


11 prepared according to general procedure B with potassium 4-fluoro-benzoyltrifluoroborate (50.0 mg, 0.22 mmol, 1.00 equiv), and L-proline ^{t}butyl ester hydrochloride (90.3 mg, 0.44 mmol, 2.00 equiv). Reaction in CH_3CN (0.40 mL) for 4 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **11** as a white amorphous solid (67.9 mg, 91 %, E:Z 2.3:1); **m.p.** 88 – 90 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.51 – 7.46 (m, 1.4 H), 7.41 – 7.27 (m, 2.6 H), 5.42 – 5.39 (m, 0.7 H), 5.03 – 5.00, (m, 0.3 H), 4.48 – 4.43

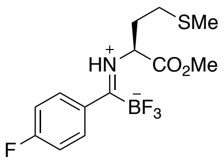
(m, 0.6 H), 4.07 – 4.00 (m, 0.7H), 3.89 – 3.82 (m, 0.7 H), 2.64 – 2.54 (m, 1 H), 2.39 – 2.13 (m, 2 H), 1.53 (s, 6.3 H), 1.34 (s, 2.7 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 208.9 (m), 169.0 (major), 168.3 (minor), 164.4 (d, *J* = 247.6 Hz, major), 164.2 (d, *J* = 247.6 Hz, minor), 134.9 (major), 129.0 (d, *J* = 7.6 Hz, major), 128.7 (d, *J* = 7.6 Hz, minor), 116.4 (d, *J* = 19.6 Hz, major), 116.2 (d, *J* = 19.6 Hz, minor), 84.1 (minor), 83.6 (major), 68.9 (major), 68.4 (minor), 57.5 (minor), 56.7 (major), 27.9 (major), 27.7 (minor), 23.7 (minor), 23.0 (major); **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 111.6 (major), – 112.3 (minor), – 142.4 (major), – 143.8 (minor); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.35; **IR** (v/cm^{-1}, thin film) v = 2981, 2937, 1737, 1603, 1508, 1603, 1508, 1456, 1371, 1350, 1291, 1230, 1155, 1099, 1054, 1013; **$[\alpha]_D^{25}$**: + 94.5 (*c* = 0.265, $CHCl_3$); **HRMS (ESI)** calculated for $C_{16}H_{20}BF_4NNaO_2$ $[M + Na]^+$: m/z = 368.1412, found: m/z = 368.1412.



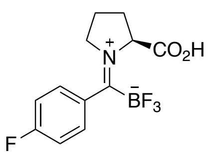
12 prepared according to general procedure A with potassium 4-fluorobenzoyltrifluoroborate (20.0 mg, 0.09 mmol, 1.00 equiv), AcOH (5.70 μL, 0.10 mmol, 1.10 equiv) and N$^{\alpha}$-Boc-L-Lysine methylester acetate salt (30.6 mg, 0.10 mmol, 1.10 equiv). Reaction in CH_3CN (0.20 mL) for 4 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **12** as a pale yellow oil (34.8 mg, 94 %, E:Z 3:2); **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 11.01 (br, 0.6 H), 7.88 – 7.90 (m, 1.2 H), 7.71 – 7.69 (m, 0.8 H), 7.38 – 7.35 (m, 0.8 H), 7.33 – 7.30 (m, 1.2 H), 6.25 (br, *J* = 9.0 Hz, 0.5 H), 6.18 (d, *J* = 9.0 Hz, 0.3 H), 4.17 – 4.12 (m, 2 H), 3.89 – 3.87 (m, 1 H), 3.68 (s, 1.8 H), 3.66 (s, 1.2 H), 1.98 – 1.82 (m, 3 H), 1.80 – 1.72 (m, 1 H), 1.70 – 1.55 (m, 2 H), 1.48 – 1.43 (m, 1 H), 1.39 (s, 5.4 H), 1.39 (s, 3.6 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 205.4 (m), 172.82, 172.80, 165.8 (d, *J* = 256.7 Hz, minor), 165.1 (d, *J* = 256.7 Hz, major), 156.1 (minor), 155.4 (major), 132.3 (minor), 131.2 (m, major and minor), 127.4 (minor), 116.5 (d, *J* = 21.1 Hz, major), 116.3 (d, *J* = 21.1 Hz, minor), 80.3 (minor), 80.2 (major), 52.7 (major), 52.6 (major), 52.5 (minor), 52.0 (minor), 50.2 (minor), 48.5 (major), 33.3 (minor), 32.3 (major), 28.2 (major), 27.96 (major), 27.94 (minor), 27.2 (minor), 22.34 (minor), 22.27 (major); **^{19}F NMR** (282 MHz, Acetone-d6) δ [ppm] = – 108.1 (major), – 109.8 (minor), – 139.1 (major), – 149.1 (minor); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.16 (major and minor); **IR** (v/cm^{-1}, thin film) v = 3660, 3072, 2977, 2866, 1732, 1600, 1507, 1231, 11162, 1077, 1059, 996; **$[\alpha]_D^{28}$**: + 30.2 (*c* = 0.1, $CHCl_3$); **HRMS (ESI)** calculated for $C_{19}H_{26}BF_4N_2O_4$ [M - H]$^-$: m/z = 433.1931, found: m/z = 433.1939.



13 prepared according to general procedure B with potassium 4-fluoro-benzoyltrifluoroborate (60.0 mg, 0.26 mmol, 1.00 equiv) and L-serine methyl ester hydrochloride (44.7 mg, 0.29 mmol, 1.10 equiv). Reaction in CH_3CN (0.50 mL) for 8 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **13** as a colorless oil (72.2 mg, 94 %, E:Z 2.3:1); **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 11.0 (br, 1 H), 7.99 – 7.95 (m, 1.4 H, major), 7.80 – 7.76 (m, 0.6 H, minor), 7.40 – 7.35 (m, 2 H, major and minor), 5.57 – 5.54 (m, 0.7 H, major), 5.18 – 5.16 (m, 0.3 H, minor), 4.97 (br, 0.2 H, minor), 4.76 (br, 0.4 H, major), 4.32 – 4.21 (m, 2 H, major and minor), 3.85 (s, 2.1 H, major), 3.82 (s, 0.9 H, minor); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 211.0 (m, minor), 208.0 (m, major), 169.0 (major), 167.9 (minor), 167.0 (d, *J* = 184.2 Hz, major), 165.9 (d, *J* = 181.2 Hz, minor), 133.6 (major), 132.9 (d, *J* = 9.1 Hz), 131.4 (d, *J* = 9.1 Hz, mixture), 129.9 (minor), 116.9 (d, *J* = 21.1 Hz, minor), 116.7 (d, *J* = 22.7 Hz, major), 65.2 (major), 63.1 (minor), 62.8 (major), 61.6 (minor), 53.7 (minor), 53.3 (major); **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 106.6 (major), – 108.8 (minor), – 138.9 (major), – 149.3 (minor); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 0.20 (major), – 0.26 (minor); **IR** (v/cm^{-1}, thin film) v = 3553, 3292, 3260, 2961, 1744, 1597, 1509, 1439, 1231, 1165, 1047; **$[\alpha]_D^{28}$**: + 14.7 (*c* = 0.05, $CHCl_3$); **HRMS (ESI)** calculated for $C_{11}H_{11}BF_4NO_3$ [M - H]$^-$: m/z = 292.0776, found: m/z = 292.0782.

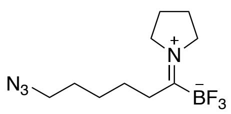


14 prepared according to general procedure B with potassium 4-fluorobenzoyltrifluoroborate (60.0 mg, 0.26 mmol, 1.00 equiv), and L-methionine methyl ester hydrochloride (44.7 mg, 0.29 mmol, 1.10 equiv). Reaction in CH_3CN (0.50 mL) for 8 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **14** as a colorless oil (72.2 mg, 94 %, E:Z 4:1); **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.98 – 7.94 (m, 1.6 H, major), 7.71 – 7.68 (m, 0.4 H, minor), 7.42 – 7.35 (m, 2 H), 5.61 – 5.56 (m, 0.8 H, major), 5.18 – 5.15 (m, 0.2 H, minor), 4.32 (q, *J* = 8.0 Hz, 0.4 H, minor), 4.31 (q, *J* = 8.0 Hz, 1.6 H, major), 2.79 – 2.66 (m, 2 H), 2.55 – 2.40 (m, 2 H), 2.13 (s, 2.4 H, major), 2.01 (s, 0.6 H, minor), 1.32 (t, *J* = 8.0 Hz, 3 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 203.5 (m), 169.7 (major), 167.6 (minor), 166.6 (d, *J* = 249.3 Hz, major), 165.4 (d, *J* = 256.9 Hz, minor), 132.0 (major), 131.7 (d, *J* = 9.5 Hz, major), 130.7 (d, *J* = 9.2 Hz, minor), 127.5 (minor), 116.9 (d, *J* = 22.2 Hz, major), 116.8 (d, *J* = 22.2 Hz, minor), 63.4 (minor), 63.2 (major), 61.1 (major), 59.0 (minor), 31.6 (major), 31.5 (minor), 29.4 (major), 29.3 (minor), 15.2 (minor), 15.1 (major), 14.1 (major), 14.0 (minor); **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 106.5 (major), – 108.9 (minor), – 138.8 (major), – 148.8 (minor); **^{11}B NMR** (160 MHz, CDCl3) δ [ppm] = – 0.02 (major and minor); **IR** (v/cm^{-1}, thin film) v = 3265, 2983, 2921, 1741, 1598, 1510, 1237, 1166, 1087, 1058; **$[\alpha]_D^{28}$**: – 1.8 (*c* = 0.05, $CHCl_3$); **HRMS (ESI)** calculated for $C_{14}H_{18}BF_4NNaO_2S$ [M + Na]$^+$: m/z = 374.0982, found: m/z = 374.0988.

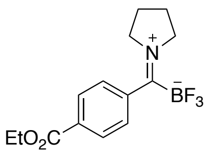


15 prepared according to general procedure A with potassium 4-fluorobenzoyltrifluoroborate (30.0 mg, 0.13 mmol, 1.00 equiv), HCl (4.00 M in dioxane, 71.5 μL, 0.29 mmol, 2.20 equiv) and L-proline (33.0 mg, 0.29 mmol, 2.20 equiv). Reaction in DMF (0.40 mL) for 2 h. The crude material was purified by flash column chromatography on silica gel (CH_2Cl_2 / CH_3OH = 5:1) to give **15** as a white solid (32.4 mg, 86 %, E:Z 3:2); **m.p.** 158 – 159 °C; **^{1}H NMR** (400 MHz, CD3OD) δ [ppm] = 8.22 – 8.18 (m, 0.3 H, minor), 7.50 – 7.46 (m, 1 H), 7.41 – 7.37 (m, 0.7 H, major), 7.29 –

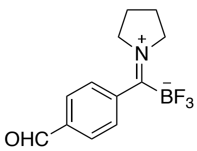
7.24 (m, 1 H), 7.22 – 7.17 (m, 1 H), 5.41 – 5.38 (m, 0.6 H), 4.51 – 4.40 (m, 1.0 H), 4.06 – 3.96 (m, 0.8 H), 3.66 – 3.58 (m, 0.6 H), 2.42 – 2.38 (m, 1 H), 2.28 – 1.97 (m, 3 H); **^{13}C NMR** (151 MHz, CD3OD) δ [ppm] = 205.0 (m), 176.8 (major), 175.5 (minor), 165.0 (d, *J* = 249.2 Hz, major), 164.7 (d, *J* = 249.2 Hz, minor), 135.4 (minor), 135.2 (major), 129.3 (d, *J* = 9.1 Hz, major), 129.0 (d, *J* = 9.1 Hz, minor), 116.6 (d, *J* = 22.7 Hz, major), 116.4 (d, *J* = 22.7 Hz, minor), 71.7 (minor), 71.2 (major), 56.8 (minor), 56.7 (major), 30.5 (minor), 30.4 (major), 23.6 (minor), 23.1 (major); **^{19}F NMR** (376 MHz, CD3OD) δ [ppm] = – 112.3 (major), – 113.0 (minor), – 143.1 (major), – 144.4 (minor); **^{11}B NMR** (160 MHz, CD3OD) δ [ppm] = – 0.29; **IR** (v/cm^{-1}, thin film) v = 3569, 1600, 1508, 1402, 1230, 1162, 1091, 1013; **$[\alpha]_D^{28}$**: – 23.1 (*c* = 0.05, CH_3OH); **HRMS (ESI)** calculated for $C_{12}H_{12}BF_4NNaO_2$ $[M + Na]^+$: m/z = 312.0792, found: m/z = 312.0792; **HRMS (ESI)** calculated for $C_{12}H_{11}BF_3NO_2$ $[M - H]^-$: m/z = 288.0827, found: m/z = 288.0831.



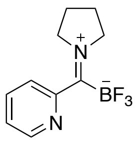
16 prepared according to general procedure A with potassium 6-azidohexoyltrifluoroborate (40.0 mg, 0.16 mmol, 1.00 equiv), AcOH (10.7 μL, 0.18 mmol, 1.10 equiv) and pyrrolidine (14.7 μL, 0.18 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **16** as a pale yellow oil (33.8 mg, 80 %); **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 4.11 – 4.08 (t, *J* = 14.0 Hz, 2 H), 4.04 – 4.00 (t, *J* = 14.0 Hz, 2 H), 3.39 – 3.35 (t, *J* = 13.2 Hz, 2 H), 2.67 – 2.63 (t, *J* = 16.0 Hz, 2 H), 2.18 – 2.08 (m, 4 H), 1.68 – 1.59 (m, 4 H), 1.56 – 1.50 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 210.0 (m), 56.3, 53.0, 51.8, 37.0, 29.2, 27.8, 25.2, 24.5; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 146.9; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.38; **IR** (v/cm^{-1}, thin film) v = 2943, 2871, 2098, 1633, 1454, 1277, 1064, 1041; **HRMS (ESI)** calculated for $C_{10}H_{18}BF_3N_4Na$ $[M + Na]^+$: m/z = 285.1471, found: m/z = 285.1474.



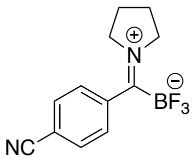
17 prepared according to general procedure A with potassium 4-ethoxy-carbonylbenzoyltrifluoroborate (50.0 mg, 0.17 mmol, 1.00 equiv), AcOH (11.6 μL, 0.19 mmol, 1.10 equiv) and pyrrolidine (16.0 μL, 0.19 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **17** as a white solid (44.2 mg, 84 %). **m.p.** 155 – 156 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 8.13 (t, *J* = 8.4 Hz, 2 H), 7.48 (t, *J* = 8.4 Hz, 2 H), 4.42 – 4.33 (m, 4 H), 3.83 (t, *J* = 7.2 Hz, 2 H), 2.27 – 2.20 (m, 2 H), 2.15 – 2.07 (m, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 205.5 (m), 166.1, 143.4, 132.2, 130.1, 125.9, 61.8, 56.7, 25.2, 24.7, 14.6; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 143.7; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.36; **IR** (v/cm^{-1}, thin film) v = 2982, 1717, 1609, 1446, 1368, 1278, 1182, 1104, 1049, 1011; **HRMS (ESI)** calculated for $C_{14}H_{17}BF_3NNaO_2$ $[M + Na]^+$: m/z = 322.1199, found: m/z = 322.1200.



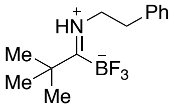
18 prepared according to general procedure A with potassium 4-formyl-phenyltrifluoroborate (40.0 mg, 0.17 mmol, 1.00 equiv), AcOH (10.0 μL, 0.18 mmol, 1.10 equiv) and pyrrolidine (13.8 μL, 0.18 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 1 : 1) to give **18** as a white solid (35.4 mg, 83 %); **m.p.** 182 – 183 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 10.12 (s, 1 H), 8.07 – 8.05 (m, 2 H), 7.58 – 7.56 (m, 2 H), 4.35 (t, *J* = 7.2 Hz, 2 H), 3.84 (t, *J* = 7.2 Hz, 2 H), 2.27 – 2.20 (t, *J* = 7.2 Hz, 2 H), 2.15 – 2.07 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 205.5 (m), 192.5, 144.6, 137.9, 130.2, 126.3, 56.7, 25.2, 24.7; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 143.6; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.36; **IR** (v/cm^{-1}, thin film) v = 3200, 2953, 2928, 2885, 2856, 1567, 1462, 1393, 1255, 1082, 1021; **HRMS (ESI)** calculated for $C_{12}H_{13}BF_3NNaO$ $[M + Na]^+$: m/z = 278.0937, found: m/z = 278.0938.



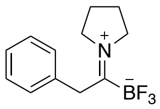
19 prepared by following general procedure A with potassium 2-isonicotinoyltrifluoroborate (30.0 mg, 0.14 mmol, 1.00 equiv), AcOH (16.1 μL, 0.28 mmol, 2.00 equiv) and pyrrolidine (12.8 μL, 0.16 mmol, 1.10 equiv) in CH_3CN / CH_3OH (0.40 / 0.10 mL) for 5 h. The crude material was purified by flash column chromatography on silica gel (EtOAc) to give **19** as a pale yellow solid (22.1 mg, 69 %); **m.p.** 114 – 115 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 8.71 – 8.70 (m, 1 H), 8.00 – 7.96 (m, 1 H), 7.58 – 7.56 (m, 1 H), 7.51 – 7.48 (m, 1 H), 4.37 (t, *J* = 7.2 Hz, 2 H), 3.90 (t, *J* = 7.2 Hz, 2 H), 2.25 – 2.18 (m, 2 H), 2.13 – 2.07 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 201.5 (m), 156.0, 149.9, 137.3, 125.6, 124.7, 56.9, 56.3, 24.9, 24.7; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 143.2; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.33; **IR** (ν/cm^{-1}, thin film) ν = 3297, 3246, 2964, 1623, 1582, 1449, 1431, 1295, 1042, 1021; **HRMS (ESI)** calculated for $C_{10}H_{12}BF_3N_2Na$ $[M + Na]^+$: m/z = 251.0940, found: m/z = 251.0946.



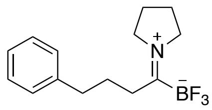
20 was according to general procedure A with potassium 4-cyanobenzoyltrifluoroborate (237 mg, 1.00 mmol, 1.00 equiv)), AcOH (68.7 μL, 1.20 mmol, 1.20 equiv) and pyrrolidine (100 μL, 1.20 mmol, 1.20 equiv). Reaction in CH_3CN (0.6 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **20** as a white solid (240 mg, 95 %). **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.95 – 7.89 (m, 2H), 7.57 – 7.52 (m, 2H), 4.33 (t, *J* = 7.3 Hz, 2H), 3.82 (t, *J* = 7.2 Hz, 2H), 2.25 – 2.18 (m, 2H), 2.13 – 2.06 (m, 2H); **^{13}C NMR** (100 MHz, Acetone-d6) δ [ppm] = 205.7 – 203.0 (m), 143.4, 133.1, 126.6, 118.8, 113.8, 56.8, 25.2, 24.6; **^{19}F NMR** (377 MHz, Acetone-d6) δ [ppm] = –143.0 – –144.4 (m); **^{11}B NMR** (400 MHz, Acetone-d6) δ [ppm] = –0.43 (q, *J* = 38.2 Hz); **IR** (ν/cm^{-1}, neat) ν = 2962, 2230, 1607, 1445, 1251, 1081, 1048, 888, 628, 555; **HRMS (ESI)** calculated for $C_{12}H_{12}BF_3N_2Na$ $[M + Na]^+$: m/z = 275.0940, found: m/z = 275.0935.



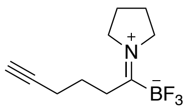
21 prepared according to general procedure A with potassium t-butoyltrifluoroborate (30.0 mg, 0.13 mmol, 1.00 equiv), HCl (4.00 M in dioxane, 58.5 μL, 0.23 mmol, 1.50 equiv) and phenylethylamine (35.5 μL, 0.23 mmol, 1.50 equiv). Reaction in CH_3CN (0.30 mL) for 5 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **21** as a white solid (26.1 mg, 65 %); **m.p**. 172–174 °C; ^{1}**H NMR** (400 MHz, Acetone-d6) δ [ppm] = 10.2 (br, 1 H), 7.37 – 7.26 (m, 5 H), 4.24 – 4.18 (m, 2 H), 3.13 – 2.86 (m, 2 H), 1.29 (s, 9 H); ^{13}**C NMR** (151 MHz, Acetone-d6) δ [ppm] = 219.6 (m), 138.5, 129.8, 129.5, 127.6, 51.9, 42.9, 36.2, 26.0; ^{19}**F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 138.5; ^{11}**B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.19; **IR** (ν/cm^{-1}, thin film) ν = 3296, 3246, 2968, 1641, 1476, 1454, 1364, 1061, 1046, 1024, 1007; **HRMS (ESI)** calculated for $C_{13}H_{18}BF_3N$ $[M - H]^-$: m/z = 256.1492, found: m/z = 256.1486.



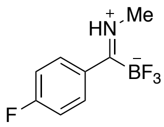
22 prepared according to general procedure A with potassium 2-phenylethanoyltrifluoroborate (50.0 mg, 0.22 mmol, 1.00 equiv), AcOH (14.6 μL, 0.24 mmol, 1.10 equiv) and pyrrolidine (20.1 μL, 0.24 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **22** as a white solid (48.0 mg, 90 %); **m.p.** 100 – 101 °C; ^{1}**H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.37 – 7.31 (m, 4 H), 7.29 – 7.25 (m, 1 H), 4.19 (t, *J* = 14.4 Hz, 2 H), 4.07 (br, 2 H), 3.96 (t, *J* = 13.6 Hz, 2 H), 2.16 –2.06 (m, 4 H); ^{13}**C NMR** (151 MHz, Acetone-d6) δ [ppm] = 208.5 (m), 134.7, 130.2, 129.6, 127.8, 56.8, 53.8, 41.4, 25.2, 24.6; ^{19}**F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 146.3; ^{11}**B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.33; **IR** (ν/cm^{-1}, thin film) ν = 3063, 3035, 2987, 2953, 2881, 1639, 1604, 1498, 1454, 1254, 1102, 1071, 1041; **HRMS (ESI)** calculated for $C_{12}H_{15}BF_3NNa$ $[M + Na]^+$: m/z = 264.1144, found: m/z = 264.1147.



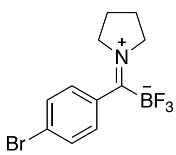
23 prepared according to general procedure A with potassium 3-phenyl-propanoyltrifluoroborate (55.9 mg, 0.22 mmol, 1.00 equiv), AcOH (14.6 μL, 0.24 mmol, 1.10 equiv) and pyrrolidine (20.1 μL, 0.24 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **23** as a white solid (48.0 mg, 90 %); **m.p.** 70 – 72 °C; **^{1}H NMR** (500 MHz, CDCl3) δ [ppm] = 7.30 – 7.27 (m, 2 H), 7.22 – 7.17 (m, 3 H), 4.15 (t, *J* = 6.5 Hz, 2 H), 3.50 (t, *J* = 6.5 Hz, 2 H), 2.75 (t, *J* = 7.5 Hz, 2 H), 2.60 (t, *J* = 8.0 Hz, 2 H), 2.05 – 2.01 (m, 4 H), 1.99 – 1.95 (m, 2 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 210.4 (m), 140.7, 128.5, 128.4, 126.3, 55.6, 51.8, 36.3, 35.8, 25.9, 24.5, 23.9; **^{19}F NMR** (470 MHz, CDCl3) δ [ppm] = – 147.7; **^{11}B NMR** (160 MHz, CDCl3) δ [ppm] = – 0.53; **IR** (v/cm^{-1}, thin film) v = 3027, 2954, 2881, 1632, 1496, 1454, 1236, 1071; **HRMS (ESI)** calculated for $C_{14}H_{19}BF_3NNa$ $[M + Na]^+$: m/z = 292.1457, found: m/z = 292.1448.



24 prepared according to general procedure A with potassium 5-hexynoyltrifluoroborate (50.0 mg, 0.25 mmol, 1.00 equiv), AcOH (16.3 μL, 0.27 mmol, 1.10 equiv) and pyrrolidine (22.5 μL, 0.27 mmol, 1.10 equiv). Reaction in CH_3CN (0.40 mL) for 8 h. The crude material was purified by flash column chromatography on silica gel twice (hexanes : acetone = 2 : 1 and hexanes : EtOAc = 1 : 1 to 0 : 1) to give **24** as a white amorphous solid (36.0 mg, 68 %); **m.p.** 91 – 93 °C **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 4.11 (t, *J* = 6.8 Hz, 2 H), 4.05 (t, *J* = 6.8 Hz, 2 H), 2.74 (br, 2H), 2.44 (t, *J* = 2.8 Hz, 1 H), 2.33 (dt, *J* = 2.8, 6.8 Hz, 2 H), 2.21 – 2.10 (m, 4 H), 1.86 – 1.79 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 209.5 (m), 83.9, 70.9, 56.4, 53.2, 36.4, 25.2, 24.5, 19.1; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 146.8; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.39; **IR** (v/cm^{-1}, thin film) v = 3282, 2958, 2115, 1638, 1469, 1440, 1239, 1077, 1034, 999, 980; **HRMS (ESI)** calculated for $C_{10}H_{15}BF_3NNa$ $[M + Na]^+$: m/z = 240.1144, found: m/z = 240.1146.

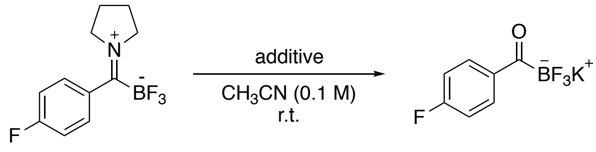


25 prepared according to general procedure B with potassium 4-fluorobenzoyltrifluoroborate (50.0 mg, 0.22 mmol, 1.00 equiv), and $MeNH_2 \cdot HCl$ salt (26.7 mg, 0.43 mmol, 2.00 equiv). Reaction in CH_3CN (0.43 mL) for 8 h. The crude material was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **25** as a white solid (40.5 mg, 91 %, E:Z 3:2); **m.p.** 144 – 145 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 11.14 – 10.99 (m, 1 H), 7.96 – 7.91 (m, 0.8 H), 7.84 – 7.79 (m, 1.2 H), 7.42 – 7.31 (m, 2 H), 3.72 (s, 1.2 H), 3.56 (s, 1.8 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 205.8 (m), 166.0 (d, *J* = 256.7 Hz, minor), 165.1 (d, *J* = 256.7 Hz, major), 132.4 (minor), 131.4 (d, *J* = 9.1 Hz, major), 131.3 (d, *J* = 9.1 Hz, minor), 127.3 (major), 116.6 (d, *J* = 21.1 Hz, minor), 116.5 (d, *J* = 21.1 Hz, major), 37.5 (minor), 35.7 (major); **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 108.0 (minor), – 109.1 (major), – 139.8 (minor), – 148.9 (major); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.24 (major and minor); **IR** (ν/cm^{-1}, thin film) ν = 3315, 3259, 1644, 1602, 1513, 1240, 1164, 1051; **HRMS (ESI)** calculated for $C_8H_8BF_4NNa$ $[M + Na]^+$: m/z = 228.0580, found: m/z = 228.0577; **EA:** calculated for $C_8H_8BF_4N$: C, 46.88; H, 3.93: N, 6.83. Found: C, 46.88; H, 3.96: N, 6.72.



26 prepared according to general procedure A with potassium 4-bromobenzoyltrifluoroborate (100 mg, 0.34 mmol, 1.00 equiv), AcOH (22.7 μL, 0.38 mmol, 1.10 equiv) and pyrrolidine (34.3 μL, 0.38 mmol, 1.10 equiv). Reaction in CH_3CN (0.6 mL) for 1 h. The crude material was purified by flash column chromatography on silica gel (hexanes : acetone = 2 : 1) to give **26** as a white solid (96.8 mg, 92 %); **m.p.** 151 – 153 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.73 – 7.70 (m, 2 H), 7.36 – 7.33 (m, 2 H), 4.32 (t, *J* = 7.2 Hz, 2 H), 3.87 (t, *J* = 7.2 Hz, 2 H), 2.25 – 2.18 (m, 2 H), 2.13 – 2.07 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 204.5 (m), 138.1, 132.3, 128.2, 124.2, 56.7, 56.6, 25.1, 24.7; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 143.6; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = – 0.36; **IR** (ν/cm^{-1}, thin film) ν = 3106, 2988, 2962, 2881, 1623, 1585, 1491, 1444, 1074, 1047, 1012; **HRMS (ESI)** calculated for $C_{11}H_{12}BBrF_3NNa$ [M + Na]$^+$: m/z = 328.0093, found: m/z = 328.0097.

2.3 Stability Tests for TIMs



Entry	Conditions	Conversion[a] 2 h	16 h	24 h
1	Et_3N (5.00 equiv)			0 %
2	Piperidine (20.0 equiv)			0 %
3	TFA (0.1 mL)[b]			0 %
4	aq. HCl (0.1 M, pH 1.2)			0 %
5	aq. citric acid (0.1 M, pH 2.0)			0 %
6	aq. citric acid / K_2HPO_4 buffer (0.1 M, pH 3.0)	0 %	2 %	
7	aq. citric acid / K_2HPO_4 buffer (0.1 M, pH 5.0)	2 %	5 %	
8	aq. KH_2PO_4 / K_2HPO_4 buffer (0.1 M, pH 7.0)	4 %	14 %	19 %

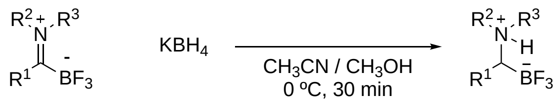
[a]Conversion determined using LC-MS and TLC. [b]CH_2Cl_2 used as solvent instead of CH_3CN.

Table 1 Stability tests for TIMs toward different reagents and in buffers at different pHs.

3 Synthesis of α-aminotrifluoroborates

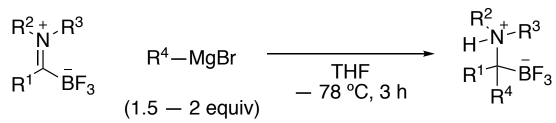
3.1 General procedures

General procedure A: reduction



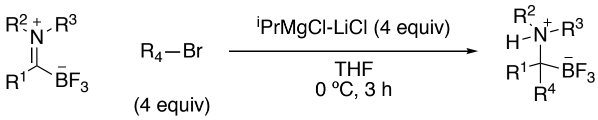
In a round-bottom flask, KBH_4 (0.50 equiv) was added to the corresponding TIM (1.00 equiv) in CH_3CN / CH_3OH (4:1, 0.10 M) at 0 ºC and the mixture was stirred for 0.5 h. The reaction mixture was quenched with aqueous KHF_2 solution (5.00 M, 5.00 equiv) at 0 ºC and concentrated under reduced pressure. The product was extracted from the residue with anhydrous acetone. Concentration under reduced pressure and washing with Et_2O afforded the corresponding α-monosubstituted α-aminotrifluoroborate.

General procedure B: 1,2-addition



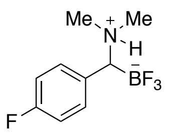
In a round-bottom flask, Grignard reagent (1.50 – 3.00 equiv) was added to the corresponding TIM (1.00 equiv) in anhydrous THF (0.20 – 0.50 M) at – 78 ºC and stirred for 0.5 h. The reaction mixture was quenched with EtOAc and aqueous KHF_2 solution (5.00 M, 5.00 equiv.), stirred at r.t. for 15 min, and concentrated under reduced pressure. The residue was filtered with acetone and the filtrate was concentrated under reduced pressure. The solid was washed with organic solvents or purified by flash column chromatography on silica gel to afford the corresponding α-disubstituted α-aminotrifluoroborate.

General procedure C: 1,2-addition using "Turbo-Grignard"

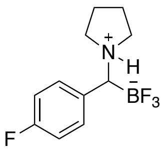


In a round-bottom flask, ^{i}PrMgCl·LiCl (1.30 M in THF, 4.00 equiv) was added to the aryl bromide (4.00 equiv) in anhydrous THF (4.00 M) at 0 ºC. The mixture was stirred for 2 h, added to the corresponding TIM (1.00 equiv) in anhydrous THF (1.00 M) at 0 ºC, and stirred for 1 h. The reaction mixture was quenched with EtOAc and aqueous KHF_2 solution (5.00 M, 5.00 equiv) at 0 ºC, stirred at r.t. for 15 min, and concentrated under reduced pressure. The residue was filtered with acetone or acetone / CH_3OH and the filtrate was concentrated under reduced pressure. The crude product was washed with Et_2O / CH_3OH or purified by flash column chromatography on silica gel to afford the corresponding α-disubstituted α-aminotrifluoroborate.

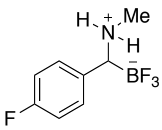
3.2 Synthesis of α-aminotrifluoroborates



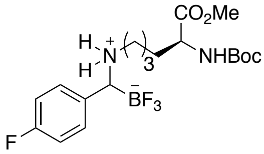
27 prepared according to general procedure A with TIM **2** (20.0 mg, 0.09 mmol, 1.00 equiv), KBH_4 (2.50 mg, 0.05 mmol, 0.50 equiv) in CH_3CN / CH_3OH (0.40 mL / 0.10 mL) to give **27** as a white solid (21.3 mg, 90 %); **m.p.** 145 – 146 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.71 (br, 0.8 H), 7.53 – 7.50 (m, 2H), 7.13 – 7.09 (m, 2 H), 3.36 (br, 1 H), 3.01 (s, 3 H), 2.75 (s, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 163.2 (d, *J* = 243.1 Hz), 134.0, 133.9 (d, *J* = 7.6 Hz), 115.7 (d, *J* = 21.4 Hz), 68.6, 44.5, 42.7; **^{19}F NMR** (282 MHz, Acetone-d6) δ [ppm] = – 116.8, – 143.2; **^{11}B NMR** (160 MHz, Acetone) δ [ppm] = 2.11; **IR** (ν/cm^{-1}, thin film) ν = 3674, 3173, 2987, 2901, 1606, 1513, 1483, 1428, 1220, 1147, 1058, 1004, 947; **HRMS (ESI)** calculated for $C_9H_{11}BF_4N$ $[M - H]^-$: m/z = 220.0928, found: m/z = 220.2925.



28 prepared according to general procedure A with TIM **3** (130 mg, 0.53 mmol, 1.00 equiv), KBH_4 (13.3 mg, 0.265 mmol, 0.5 equiv) in CH_3CN / CH_3OH (3.00 mL / 0.75 mL) to give **28** as a white solid (129 mg, 91 %); **m.p.** 171 – 173 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.92 (br, 1 H), 7.46 – 7.42 (m, 2H), 7.09 – 7.05 (m, 2H), 3.87 (br, 1H), 3.32 (br, 3H), 3.00 (br, 1H), 2.07 – 2.00 (m, 4H); **^{13}C NMR** (101 MHz, Acetone-d6) δ [ppm] = 161.8 (d, *J* = 243.4 Hz), 135.5 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 9.1 Hz), 114.7 (d, *J* = 21.2 Hz), 66.0, 54.3, 22.7, 22.0; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 117.7, – 144.0; **^{11}B NMR** (96 MHz, Acetone-d6) δ [ppm] = 2.15; **IR** (v/cm^{-1}, thin film) v = 3675, 3205, 2987, 2901, 1605, 1510, 1407, 1220, 1065, 1008, 964; **HRMS (ESI)** calculated for $C_9H_{11}BF_4N$ [M - H]$^-$: m/z = 246.1085, found: m/z = 246.1089.

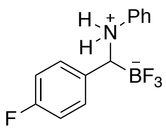


29 prepared according to general procedure A with TIM **25** (30.0 mg, 0.15 mmol, 1.00 equiv), KBH_4 (3.90 mg, 0.07 mmol, 0.50 equiv) in CH_3CN / CH_3OH (0.80 mL / 0.20 mL) to give **29** as a colorless oil (21.0 mg, 88 %, stereoisomers 3:2); **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.57 – 7.53 (m, 0.7 H), 7.46 – 7.42 (m, 1.3 H), 7.10 – 7.05 (m, 2 H), 4.79 (s, 0.3 H), 3.35 (s, 1 H), 3.27 (s, 0.7 H), 2.73 (s, 2 H), 2.71 – 2.64 (m, 1 H); **^{13}C NMR** (101 MHz, CD3OD) δ [ppm] = 162.0 (d, *J* = 244.4 Hz), 133.8, 130.2 (d, *J* = 8.1 Hz), 114.6 (d, *J* = 21.2 Hz), 59.3, 31.4; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 117.3 (minor), – 118.1 (major), – 143.7 (minor), – 148.4 (major); **^{11}B NMR** (96 MHz, Acetone-d6) δ [ppm] = 2.44; **IR** (v/cm^{-1}, thin film) v = 3659, 3226, 2987, 2901, 1606, 1512, 1464, 1409, 1225, 1131, 1065, 987; **HRMS (ESI)** calculated for $C_8H_9BF_4N$ [M - H]$^-$: m/z = 206.0771, found: m/z = 206.0765.

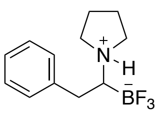


30 prepared according to general procedure A with TIM **12** (50.0 mg, 0.12 mmol, 1.00 equiv), KBH_4 (3.10 mg, 0.06 mmol, 0.50 equiv) in CH_3CN / CH_3OH (0.40 mL / 0.10 mL) to give **30** as a white amorphous solid (50.7 mg, 93 %); **m.p.** 71 – 73 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.45 –

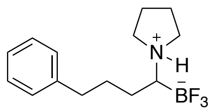
7.42 (m, 2 H), 7.08 – 7.04 (m, 2 H), 6.20 (d, *J* = 2.2 Hz, 1 H), 5.82 (br, 0.3 H), 4.15 – 4.09 (m, 1H), 4.00 (br, 0.3 H), 3.67 (s, 3 H), 3.35 (br, 1 H), 3.09 – 3.03 (m, 2 H), 1.92 – 1.66 (m, 4 H), 1.50 – 1.45 (m, 2 H), 1.40 (s, 9 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 173.7, 162.6 (d, *J* = 242.7 Hz), 156.5, 135.8, 131.5 (d, *J* = 7.6 Hz), 115.5 (d, *J* = 21.3 Hz), 79.3 59.2, 54.3, 52.2, 47.7, 32.0, 28.5, 26.3, 23.6; **^{19}F NMR** (471 MHz, Acetone-d6) δ [ppm] = – 118.2, – 147.1; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.16; **IR** (ν/ cm^{-1}, thin film) ν = 3660, 3384, 3203, 2978, 1694, 1606, 1512, 1367, 1223, 1162, 1050, 1015; **$[\alpha]_D^{28}$**: + 4.8 (*c* = 0.05, $CHCl_3$); **HRMS (ESI)** calculated for $C_{19}H_{28}BF_4N_2O_4$ [M - H]$^-$: m/z = 435.2087, found: m/z = 435.2090.



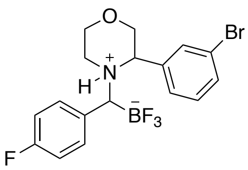
31 prepared according to general procedure A with TIM **10** (30.0 mg, 0.15 mmol, 1.00 equiv), KBH_4 (3.90 mg, 0.07 mmol, 0.50 equiv) in CH_3CN / CH_3OH (0.80 mL / 0.20 mL) to give **31** as a pale brown oil (21.0 mg, 88 %); **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.28 – 7.25 (m, 2 H), 6.96 – 6.92 (m, 2 H), 6.87 – 6.83 (m, 2 H), 6.51 – 6.48 (m, 2 H), 6.45 – 6.41 (m, 1 H), 3.50 (br, 1 H), 2.95 (br, 2 H); **^{13}C NMR** (101 MHz, Acetone-d6) δ [ppm] = 160.1 (d, *J* = 238.4 Hz), 150.0, 143.7, 128.4, 127.8 (d, *J* = 8.1 Hz), 115.1, 113.3 (d, *J* = 20.2 Hz), 113.1, 53.1; **^{19}F NMR** (377 MHz, Acetone-d6) δ [ppm] = – 123.0, – 149.0; **^{11}B NMR** (128 MHz, Acetone-d6) δ [ppm] = 3.13; **IR** (ν/cm^{-1}, thin film) ν = 3661, 3414, 2988, 2901, 1708, 1601, 1506, 1315, 1220, 1155, 1064, 1014; **HRMS (ESI)** calculated for $C_{13}H_{11}BF_4N$ [M - H]$^-$: m/z = 268.0929, found: m/z = 268.0931.



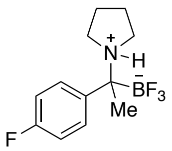
32 prepared according to general procedure A with TIM **22** (25.0 mg, 0.10 mmol, 1.00 equiv), KBH_4 (2.80 mg, 0.05 mmol, 0.50 equiv) in CH_3CN / CH_3OH (0.30 mL / 0.08 mL) to give **32** as a white solid (26.6 mg, 91 %); **m.p.** 146 – 148 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.37 – 7.35 (m, 2 H), 7.30 – 7.26 (m, 2 H), 7.22 – 7.17 (m, 1 H), 3.46 (br, 4 H), 3.15 (dd, *J* = 3.8, 1.3 Hz, 1 H), 2.85 (dd, *J* = 3.8, 2.2 Hz, 1 H), 2.72 (br, 1 H), 1.97 (br, 4 H); **^{13}C NMR** (101 MHz, Acetone-d6) δ [ppm] = 140.6, 129.0, 128.4, 126.1, 61.0, 52.6, 34.0, 23.2; **19F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 144.2; **11B NMR** (128 MHz, Acetone-d6) δ [ppm] = 1.83; **IR** (v/cm^{-1}, thin film) v = 3675, 3195, 2972, 2901, 1455, 1381, 1244, 1174, 1072, 1043, 1007, 996; **HRMS (ESI)** calculated for $C_{12}H_{16}BF_3N$ [M - H]$^-$: m/z = 242.1336, found: m/z = 242.1337.



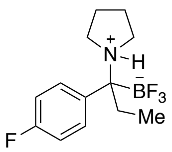
33 prepared by following general procedure with TIM **23** (100 mg, 0.37 mmol, 1.00 equiv), KBH_4 (10.0 mg, 0.19 mmol, 0.50 equiv) in CH_3CN / CH_3OH (1.8 ml / 0.2 ml) to give **33** as a white solid (81.3 mg, 71 %); **m.p.** 122 – 123 °C; **1H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.27 – 7.24 (m, 2 H), 7.21 – 7.19 (m, 2 H), 7.16 – 7.14 (m, 1 H), 3.54 – 3.28 (m, 4 H + 0.6 H), 2.64 – 2.58 (m, 2 H), 2.28 (br, 1 H), 2.07 – 2.03 (m, 4 H), 1.80 – 1.73 (m, 3 H), 1.63 – 1.61 (m, 1 H); **13C NMR** (151 MHz, Acetone-d6) δ [ppm] = 143.5, 129.2, 129.0, 126.4, 60.5, 53.2, 36.9, 29.3, 28.0, 24.0; **19F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 144.6; **11B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.26; **IR** (v/cm^{-1}, thin film) v = 3197, 3025, 2936, 2866, 2766, 1604, 1496, 1455, 1414, 1150, 1019; **HRMS (ESI)** calculated for $C_{14}H_{20}BF_3N$ [M - H]$^-$: m/z = 270.1649, found: m/z = 270.1651.



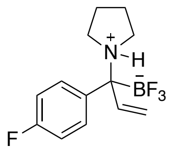
34 prepared by following general procedure with TIM **7** (50.0 mg, 0.12 mmol, 1.00 equiv), KBH_4 (3.20 mg, 0.06 mmol, 0.50 equiv) in CH_3CN / CH_3OH (0.40 mL / 0.10 mL) to give **34** as a white solid (50.2 mg, 90 %); **m.p.** 212 °C (decomp.); **1H NMR** (400 MHz, Acetone-d6) δ [ppm] = 8.06 (s, 1 H), 7.79 (d, *J* = 7.6 Hz, 1 H), 7.76 – 7.67 (m, 1 H + 0.4 H), 7.58 (t, *J* = 8.0 Hz, 1 H), 7.46 – 7.42 (m, 2 H), 7.17 – 7.12 (m, 2 H), 4.37 – 4.30 (m, 2 H), 4.20 – 4.12 (m, 2 H), 4.07 – 4.00 (m, 2 H), 3.55 (br, 1 H), 3.20 – 3.13 (m, 1 H); **13C NMR** (151 MHz, Acetone-d6) δ [ppm] = 163.7 (d, *J* = 246.0 Hz), 136.1 (d, *J* = 8.3 Hz), 135.8, 133.7, 132.3, 132.1, 130.0, 128.8, 123.9, 115.8 (d, *J* = 22.7 Hz), 70.2, 65.8, 64.2, 63.0, 50.6; **19F NMR** (377 MHz, Acetone-d6) δ [ppm] = – 115.3, – 143.7; **11B NMR** (128 MHz, Acetone-d6) δ [ppm] = 1.69; **IR** (v/cm^{-1}, thin film) v = 3661, 3153, 2967, 2901, 1608, 1569, 1513, 1434, 1232, 1136, 1095, 1067, 1036, 1003; **HRMS (ESI)** calculated for $C_{17}H_{16}BBrF_4NO$ [M - H]$^-$: m/z = 416.0453, found: m/z = 416.0452.



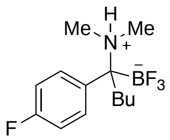
35 prepared according to general procedure B with TIM **3** (100 mg, 0.41 mmol, 1.00 equiv), MeMgBr (3.00 M in THF, 0.41 mL, 1.22 mmol, 3.00 equiv) in THF (2.0 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **35** as a white solid (67.2 mg, 63 %); **m.p.** 190 – 191 °C; **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.93 (br, 1 H), 7.68 – 7.66 (m, 2 H), 7.10 – 7.07 (m, 2 H), 3.62 – 3.52 (m, 2 H), 3.06 – 3.03 (m, 2 H), 2.05 – 2.00 (m, 2 H), 1.96 – 1.91 (m, 2 H), 1.53 (s, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 162.5 (d, *J* = 243.1 Hz), 139.6, 130.6 (d, *J* = 7.6 Hz), 115.3 (d, *J* = 21.1 Hz), 64.1 (br), 51.1, 49.6, 24.7, 24.1, 14.5; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 118.2, – 147.8; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.46; **IR** (v/cm^{-1}, thin film) v = 3662, 3184, 2987, 1604, 1515, 1460, 1410, 1389, 1227, 1169, 1045, 1010, 990; **HRMS (ESI)** calculated for $C_{12}H_{15}BF_4N$ [M - H]$^-$: m/z = 260.1241, found: m/z = 260.1243.



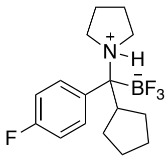
36 prepared according to general procedure B with TIM **3** (30.0 mg, 0.12 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.06 mL, 0.18 mmol, 1.50 equiv) in THF (0.40 mL). The residue was washed with Et_2O / CH_2Cl_2 (10 : 1) to give **36** as a white solid (30.2 mg, 90 %); **m.p.** 173 – 175 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.81 – 7.78 (m, 2 H + 1 H), 7.12 – 7.08 (m, 2 H), 3.61 – 3.52 (m, 1 H), 3.43 – 3.26 (m, 2 H), 3.05 – 2.98 (m, 1 H), 2.17 – 2.11 (m, 2 H), 2.00 – 1.88 (m, 4 H), 0.92 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 162.7 (d, *J* = 244.6 Hz), 137.0 (d, *J* = 3.0 Hz), 132.9 (d, *J* = 3.0 Hz), 115.3 (d *J* = 21.1 Hz), 67.9, 51.4, 50.0, 24.6, 24.2, 22.9, 10.0; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 117.2, – 139.9; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.69; **IR** (v/cm^{-1}, thin film) v = 3377, 3224, 2987, 2892, 1604, 1511, 1459, 1395, 1231, 1167, 1149, 1050, 1010, 983 **HRMS (ESI)** calculated for $C_{13}H_{17}BF_4N$ [M - H]$^-$: m/z = 274.1398, found: m/z = 274.1403.



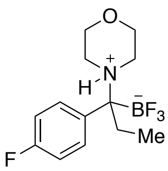
37 prepared according to general procedure B with TIM **3** (150 mg, 0.61 mmol, 1.00 equiv), vinylmagnesium bromide (1.00 M in THF, 0.92 mL, 0.92 mmol, 1.50 equiv) in THF (3.00 mL). The residue was washed with Et_2O / CH_2Cl_2 (10 : 1) to give **37** as a pale yellow oil (153 mg, 92 %); **^{1}H NMR** (300 MHz, Acetone-d6) δ [ppm] = 7.73 – 7.57 (m, 2 H), 7.11 – 7.01 (m, 2 H), 6.11 (dd, *J* = 17.1, 11.7 Hz, 1 H), 5.69 – 5.36 (m, 2 H), 3.40 (br, 4 H), 2.02 – 1.88 (m, 4 H); **^{13}C NMR** (126 MHz, Acetone-d6) δ [ppm] = 162.6 (d, *J* = 244.0 Hz), 137.8 (d, *J* = 3.3 Hz), 136.1, 132.1 (d, *J* = 7.6 Hz), 120.8, 115.2 (d, *J* = 21.1 Hz), 71.4, 51.9, 24.8; **^{19}F NMR** (282 MHz, Acetone-d6) δ [ppm] = – 117.9 (dd, *J* = 8.8, 5.4 Hz), – 142.6 – – 143.8 (m); **^{11}B NMR** (96 MHz, Acetone-d6) δ [ppm] = 2.25 (q, *J* = 50.1 Hz); **IR** (ν/cm^{-1}, neat) ν = 3542, 3207, 2974, 1604, 1511, 1459, 1403, 1229, 1167, 1006, 940, 916, 807; **HRMS (ESI)** calculated for $C_{13}H_{15}BF_4N$ $[M - H]^-$: m/z = 272.1242, found: m/z = 272.1245.



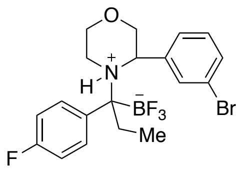
38 prepared according to general procedure B with TIM **2** (170 mg, 0.78 mmol, 1.00 equiv), ^{n}BuMgBr (0.83 M in THF, 1.90 mL, 1.56 mmol, 2.00 equiv) in THF (3.00 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 4 : 1 to 2 : 1) to give **38** as a white amorphous solid (190 mg, 88 %); **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.77 – 7.59 (m, 2 H), 7.43 – 7.06 (br, 1 H), 7.18 – 7.07 (m, 2 H), 3.06 – 2.94 (m, 3 H), 2.55 – 2.41 (m, 3 H), 2.12 – 2.02 (m, 1 H), 2.02 – 1.89 (m, 1 H), 1.70 – 1.53 (m, 1 H), 1.52 – 1.31 (m, 2 H), 1.26 – 1.13 (m, 1 H), 0.91 (t, J = 7.4 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 162.8 (d, *J* = 244.7 Hz), 137.0 (d, *J* = 3.3 Hz), 132.5, 115.5 (d, *J* = 20.9 Hz), 69.2 (br), 41.1, 38.5, 27.7, 27.1, 24.4, 14.4; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 116.9, – 140.4 (dd, J = 100.6, 46.1 Hz); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.59 (q, J = 53.2, Hz); **IR** (ν/cm^{-1}, thin film) ν = 3205, 2958, 2872, 1713, 1607, 1513, 1232, 1014, 909, 808; **HRMS (ESI)** calculated for $C_{13}H_{20}BF_4NNa$ $[M + Na]^+$: m/z = 300.1520, found: m/z = 300.1523.



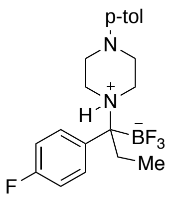
39 prepared according to general procedure B with TIM **3** (30.0 mg, 0.12 mmol, 1.00 equiv), ^{c}PenMgBr (2.00 M in THF, 0.09 mL, 0.18 mmol, 1.50 equiv) in THF (0.40 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **39** as a white solid (31.2 mg, 81 %); **m.p.** 186 – 188 °C; **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.89 – 7.87 (m, 2 H), 7.58 (br, 1 H), 7.10 – 7.07 (m, 2 H), 3.66 – 3.59 (m, 2 H), 3.58 – 3.54 (m, 1 H), 3.44 – 3.40 (m, 1 H), 2.70 – 2.67 (m, 1 H), 2.00 – 1.94 (m, 4 H), 1.91 – 1.87 (m, 1 H), 1.64 – 1.51 (m, 3 H), 1.50 – 1.39 (m, 4 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 162.5 (d, *J* = 244.6 Hz), 137.0 (d, *J* = 3.5 Hz), 133.0 (d, *J* = 5.0 Hz), 114.9 (d, *J* = 20.7 Hz), 71.1, 52.1, 51.8, 46.5, 29.0, 26.1, 25.1, 24.6, 24.2, 24.1; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 117.6, – 135.5; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.92; **IR** (v/cm^{-1}, thin film) v = 3675, 3218, 2960, 2396, 1611, 1519, 1454, 1406, 1247, 1177, 1046, 1018, 991; **HRMS (ESI)** calculated for $C_{16}H_{21}BF_4N$ $[M - H]^-$: m/z = 314.1712, found: m/z = 314.1716.



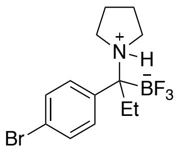
40 prepared according to general procedure B with TIM **8** (275 mg, 0.12 mmol, 1.00 equiv), EtMgBr (2.84 M in Et_2O, 0.56 mL, 1.58 mmol, 1.50 equiv) in THF (10.5 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **40** as a white solid (219 mg, 72 %); **m.p.**: 121 °C (decomp.); **^{1}H NMR** (500 MHz, Acetone-d6) δ [ppm] = 7.78 – 7.67 (m, 2 H), 7.17 – 7.07 (m, 2 H), 6.93 (br, 1 H), 4.04 – 3.97 (m, 1 H), 3.94 – 3.88 (m, 1 H), 3.85 – 3.77 (m, 2 H), 3.60 (d, *J* = 13.0 Hz, 1 H), 3.43 – 3.32 (m, 1 H), 3.27 – 3.15 (m, 1 H), 2.84 (d, *J* = 13.0 Hz, 1 H), 2.28 – 2.19 (m, 1 H), 2.18 – 2.08 (m, 1 H), 0.93 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR** (126 MHz, Acetone-d6) δ [ppm] = 163.0 (d, *J* = 245.2 Hz), 134.6 (d, *J* = 3.4 Hz), 133.8 (d, *J* = 7.8 Hz), 115.5 (d, *J* = 21.0 Hz), 72.5 (br), 65.1 (d, *J* = 16.6 Hz), 51.0 (d, *J* = 2.9 Hz), 47.7, 21.0, 10.3; **^{19}F NMR** (376 MHz, Acetone-d6) δ [ppm] = – 116.3 (tt, *J* = 8.8, 5.5 Hz), – 138.3 – – 138.8 (m); **^{11}B NMR** (128 MHz, Acetone-d6) δ [ppm] = 2.55 (q, *J* = 53.2 Hz); **IR** (v/cm^{-1}, neat) v = 3161, 2976, 2886, 1605, 1514, 1232, 1169, 1044, 1005, 890, 805, 631; **HRMS (ESI)** calculated for $C_{13}H_{17}BF_4NO$ $[M - H]^-$: 290.1347, found: 290.1346.



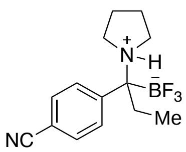
41 prepared according to general procedure B with TIM **7** (30.0 mg, 0.07 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.04 mL, 0.11 mmol, 1.50 equiv) in THF (0.50 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **41** as a white amorphous solid (32.1 mg, 82 %); **m.p.** 91 – 93 °C; **^{1}H NMR** (600 MHz, CDCl3) δ [ppm] = 7.60 – 7.59 (m, 1 H), 7.57 – 7.55 (m, 1 H), 7.33 – 7.32 (m, 1 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.16 – 7.14 (m, 2 H), 6.90 – 6.87 (m, 2 H), 6.62 (br, 0.8 H), 4.13 (dd, *J* = 10.2, 3.6 Hz, 1 H), 3.93 (dd, *J* = 12.6, 3.6 Hz, 1 H), 3.84 – 3.79 (m, 2 H), 3.76 – 3.71 (m, 1 H), 3.21 – 3.18 (m, 1 H), 3.08 – 3.03 (m, 1 H), 1.89 – 1.85 (m, 1 H), 1.80 – 1.77 (m, 1 H), 0.59 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 160.6 (d, *J* = 243.1 Hz), 143.5, 134.2, 133.2, 130.9 (d, *J* = 5.6 Hz), 126.6, 125.5, 123.2, 114.2 (d, *J* = 19.6 Hz), 75.5, 68.4, 63.3, 58.4, 44.4, 30.9, 30.3, 6.8; **^{19}F NMR** (282 MHz, Acetone-d6) δ [ppm] = – 115.8, – 116.1, – 117.4, – 134.6, – 138.1, – 140.4; **^{11}B NMR** (96 MHz, Acetone-d6) δ [ppm] = 2.55; **IR** (ν/cm^{-1}, thin film) ν = 3661, 2987, 2901, 1697, 1604, 1571, 1514, 1406, 1393, 1230, 1166, 1132, 1013; **HRMS (ESI)** calculated for $C_{19}H_{20}BBrF_4NO$ [M - H]$^-$: m/z = 444.0766, found: m/z = 444.0760.



42 was prepared according to general procedure B from TIM **9** (150 mg, 0.43 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.21 mL, 0.64 mmol, 1.50 equiv) in THF (4.3 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **42** as a white solid (116 mg, 72 %); **m.p.** 125 ºC (decomp.); **^{1}H NMR** (500 MHz, Acetone-d6) δ [ppm] = 7.79 – 7.74 (m, 2 H), 7.15 – 7.04 (m, 4 H), 6.92 – 6.81 (m, 2 H + 1 H), 3.91 – 3.65 (m, 3 H), 3.50 – 3.40 (m, 1 H), 3.35 – 3.26 (m, 1 H), 3.13 – 3.03 (m, 3 H), 2.31 – 2.14 (m, 5 H), 0.95 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 163.1 (d, *J* = 245.1 Hz), 149.0, 135.3, 135.2, 133.9 (d, *J* = 7.9 Hz), 130.6, 117.5, 115.6 (d, *J* = 20.9 Hz), 72.4, 50.7 (d, *J* = 15.3 Hz), 48.4 (d, *J* = 3.4 Hz), 48.2 (d, *J* = 3.2 Hz), 47.7 (d, *J* = 15.9 Hz), 21.3, 20.6, 10.5; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 116.5 (tt, *J* = 8.8, 5.5 Hz), – 138.8 (dd, *J* = 98.4, 42.5 Hz); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.59 (q, *J* = 53.6 Hz); **IR** (v/cm^{-1}, neat) v = 3169, 2987, 1604, 1514, 1458, 1394, 1235, 1168, 1004, 922, 877, 808; **HRMS (ESI)** calculated for $C_{20}H_{25}BF_4KN_2$ [M + K]$^+$: m/z = 419.1682, found: m/z = 419.1674.

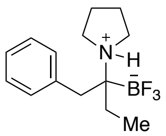


43 was prepared according to general procedure B from TIM **26** (360 mg, 1.18 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.59 mL, 1.77 mmol, 1.50 equiv) in THF (11.8 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **43** as a white solid (340 mg, 86 %); **m.p.** 198 ºC; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.74 – 7.57 (m, 2 H), 7.56 – 7.44 (m, 2 H), 3.71 – 3.48 (m, 1 H), 3.49 – 3.32 (m, 1 H), 3.32 – 3.19 (m, 1 H), 3.08 – 2.89 (m, 1 H), 2.14 – 2.06 (m, 2 H), 2.02 – 1.80 (m, 4 H), 1.03 – 0.83 (m, 3 H); **^{13}C NMR** (100 MHz, Acetone-d6) δ [ppm] = 140.3, 132.8, 131.8, 121.7, 67.5 (br), 51.4, 49.6, 24.6, 24.1, 21.8, 9.9; **^{19}F NMR** (377 MHz, Acetone-d6) δ [ppm] = – 136.3 – – 142.5 (m); **^{11}B NMR** (400 MHz, Acetone-d6) δ [ppm] = 2.58 (q, *J* = 53.1 Hz); **IR** (v/cm^{-1}, neat) v = 3198, 2988, 1739, 1587, 1494, 1399, 1152, 1007, 973, 514; **HRMS (ESI)** calculated for $C_{13}H_{18}BBrF_3NNa$ [M + Na]$^+$: m/z = 358.0562, found: m/z = 358.0564.

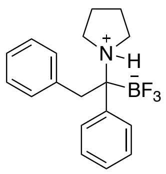


44 was prepared according to general procedure B from TIM **20** (252 mg, 1.00 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.43 mL, 1.30 mmol, 1.30 equiv) in THF (10 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 2 : 1) to give **44** as a white solid (260 mg, 93 %); **m.p.** 172 ºC; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 8.10 – 7.83 (m, 2 H), 7.83 – 7.63 (m, 2 H), 3.75 – 3.56 (m, 1 H), 3.57 – 3.39 (m, 1 H), 3.37 – 3.18 (m, 1 H), 3.06 – 2.89 (m, 1 H), 2.23 – 2.09 (m, 2 H), 2.03 – 1.82 (m, 4 H), 0.96 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR** (100 MHz, Acetone-d6) δ [ppm] = 146.8, 132.5, 131.3, 119.3, 111.6, 68.0 (br), 51.7, 49.8, 24.7, 24.2, 21.5, 9.8; **^{19}F NMR** (377 MHz, Acetone-d6) δ [ppm] = – 140.9 (dd, *J* = 99.9, 45.7 Hz); **^{11}B NMR** (400 MHz, Acetone-d6) δ [ppm] = 2.49 (q, *J* = 52.5 Hz); **IR** (v/cm^{-1}, neat): v =

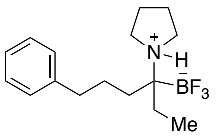
3161, 2980, 2232, 1739, 1606, 1037, 1005, 909, 750, 561; **HRMS (ESI)** calculated for $C_{14}H_{18}BF_3N_2Na$ $[M + Na]^+$: m/z = 305.1410, found: m/z = 305.1409.



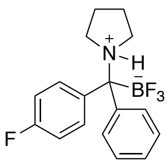
45 prepared by following general procedure with TIM **22** (50.0 mg, 0.21 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.10 ml, 0.31 mmol, 1.50 equiv) in THF (0.50 mL) and washed by Et_2O / CH_2Cl_2 (9 : 1) to give **45** as a white solid (54.2 mg, 96 %); **m.p.** 186 – 188 °C; **^{1}H NMR** (400 MHz, Acetone-d6) δ [ppm] = 7.46 – 7.43 (m, 2 H), 7.30 (br, 1 H), 7.24 – 7.21 (m, 2 H), 7.19 – 7.17 (m, 1 H), 3.63 – 3.54 (m, 2 H), 3.50 – 3.43 (m, 2 H), 3.05 (d, *J* = 13.2 Hz, 1 H), 2.88 (d, *J* = 13.2 Hz, 1 H), 2.04 – 1.99 (m, 4 H), 1.64 – 1.50 (m, 2 H), 1.02 (d, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 138.6, 132.2, 128.4, 126.9, 66.7, 50.3, 48.8, 37.8, 26.1, 25.1, 24.7, 9.4; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 142.1; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.47; **IR** (ν/cm^{-1}, thin film) ν = 3664, 3201, 2987, 2959, 1602, 1496, 1453, 1402, 1380, 1271, 1023; **HRMS (ESI)** calculated for $C_{14}H_{20}BF_3N$ $[M - H]^-$: m/z = 270.1649, found: m/z = 270.1643.



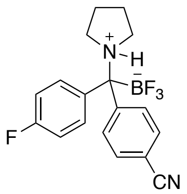
46 prepared by following general procedure with TIM **22** (20.0 mg, 0.08 mmol, 1.00 equiv), PhMgBr (1.00 M in THF, 0.12 mL, 0.12 mmol, 1.50 equiv) in THF (0.40 mL) and washed by Et_2O / CH_2Cl_2 (9 : 1) to give **46** as a white solid (20.6 mg, 78 %); **m.p.** 180 – 182 °C; **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.89 (br, 1 H), 7.77 – 7.75 (m, 2 H), 7.30 – 7.27 (m, 2 H), 7.24 – 7.21 (m, 1 H), 7.05 – 7.02 (m, 5 H), 3.93 – 3.88 (m, 1 H), 3.66 – 3.60 (m, 1 H), 3.55 (d, *J* = 9.6 Hz, 1 H), 3.50 – 3.45 (m, 2 H), 3.32 – 3.28 (m, 1 H), 2.10 – 2.03 (m, 2 H), 2.01 – 1.91 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 141.9, 138.3, 132.0, 130.6, 128.4, 128.1, 127.6, 126.6, 70.5, 53.0, 51.2, 40.2, 25.0, 24.7; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 137.6; **^{11}B NMR** (160 MHz, Acetone) δ [ppm] = 2.83; **IR** (ν/cm^{-1}, thin film) ν = 3663, 3184, 2987, 1497, 1456, 1394, 1251, 1048, 1024; **HRMS (ESI)** calculated for $C_{18}H_{20}BF_3N$ $[M - H]^-$: m/z = 318.1650, found: m/z = 318.1653.



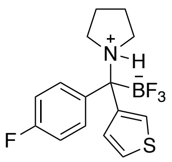
47 prepared by following general procedure with TIM **23** (50.0 mg, 0.19 mmol, 1.00 equiv), EtMgBr (3.00 M in THF, 0.19 mL, 0.56 mmol, 3.00 equiv) in THF (2.00 mL) and washed by Et_2O to give **47** as a colorless oil (43.5 mg, 78 %). **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.32 – 7.01 (m, 5 H + 1 H), 3.51 – 3.30 (m, 4 H), 2.64 – 2.57 (m, 2 H), 2.02 – 1.94 (m, 4 H),1.65 – 1.59 (m, 2 H),1.56 – 1.52 (m, 4 H), 0.94 (t, *J* = 9.4 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 143.7, 129.4, 129.2, 126.6, 66.1 (br), 49.4, 48.9, 37.7, 32.9, 27.2, 25.4, 24.9, 9.4; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 143.9 (dd, *J* = 104.8, 47.0 Hz); **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.35 (q, *J* = 55.2 Hz); **IR** (v/cm^{-1}, neat) v = 3197, 3025, 2966, 1454, 1404, 1008, 893, 750, 700; **HRMS (ESI)** calculated for $C_{16}H_{25}BF_3NNa$ $[M + Na]^+$: m/z = 322.1927, found: m/z = 322.1930.



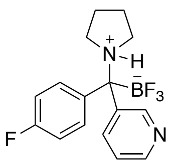
48 prepared according to general procedure B with TIM **3** (50.0 mg, 0.20 mmol, 1.00 equiv), PhMgBr (1.00 M in THF, 0.31 ml, 0.31 mmol, 1.50 equiv) in THF (0.50 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **48** as a white solid (51.5 mg, 78 %); **m.p.** 148 – 150 °C; **^{1}H NMR** (500 MHz, Acetone-d6) δ [ppm] = 8.64 (br, 1 H), 7.56 – 7.54 (m, 2 H), 7.48 – 7.46 (m, 2 H), 7.31 – 7.27 (m, 2 H), 7.25 – 7.22 (m, 1 H), 7.08 – 7.04 (m, 2 H), 3.67 – 3.62 (m, 2 H), 3.57 – 3.51 (m, 2 H), 2.02 – 1.97 (m, 2 H), 1.86 – 1.82 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 162.5 (d, *J* = 244.6 Hz), 143.0, 138.9, 133.7 (d, *J* = 5.1 Hz), 130.9, 128.3, 127.3 (d, *J* = 2.0 Hz), 114.9 (d, *J* = 6.1 Hz), 74.7 (br), 53.0, 52.90, 24.7, 24.6; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 117.7, – 140.5; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.56; **IR** (v/cm^{-1}, thin film) v = 3662, 3206, 2987, 2901, 1512, 1405, 1233, 1165, 1089, 1048, 1015; **HRMS (ESI)** calculated for $C_{17}H_{17}BF_4N$ $[M - H]^-$: m/z = 322.1399, found: m/z = 322.1394.



49 prepared according to general procedure C with ^{i}PrMgCl/LiCl (0.75 mL, 0.98 mmol, 4.00 equiv), 4-bromobenzonitrile (176 mg, 0.98 mmol, 4.00 equiv) in THF (0.25 mL), and TIM **3** (60.0 mg, 0.25 mmol, 1.00 equiv) in THF (0.25 mL). The residue was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **49** as a white solid (67.4 mg, 79 %); **m.p.** 180 – 181 °C; **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 8.63 (br, 1 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.66 – 7.64 (m, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.16 – 7.13 (m, 2 H), 3.79 – 3.73 (m, 2 H), 3.57 – 3.54 (m, 1 H), 3.47 – 3.43 (m, 1 H), 2.02 – 1.98 (m, 2 H), 1.92 – 1.89 (m, 1 H), 1.81 – 1.77 (m, 1 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 163.2 (d, *J* = 246.7 Hz), 149.6, 136.2 (d, *J* = 3.5 Hz), 135.3, 131.8, 130.5 (d, *J* = 2.0 Hz), 119.4, 115.6 (d, *J* = 21.0 Hz), 110.4, 74.7 (br), 53.4, 52.7, 24.5, 24.4; **^{19}F NMR** (470 MHz, Acetone-d6) δ [ppm] = – 115.5, – 141.6; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.29; **IR** (v/cm^{-1}, thin film) v = 3201, 3123, 2958, 2928, 1604, 1512, 1457, 1411, 1235, 1168, 1016; **HRMS (ESI)** calculated for $C_{18}H_{17}BF_4N_2Na$ [M + Na]$^{+}$: 371.1316, found: 371.1316.



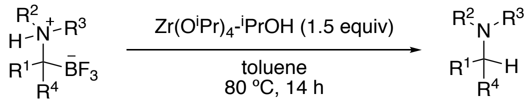
50 prepared according to general procedure C with ^{i}PrMgCl·LiCl (0.98 mmol, 0.75 mL, 4.00 equiv), 3-bromothiophene (0.98 mmol, 160 mg, 4.00 equiv) in THF (0.25 mL) and TIM **3** (60.0 mg, 0.25 mmol, 1.00 equiv) in THF (0.25 mL) and the residue was purified by flash column chromatography on silica gel (hexanes / acetone = 1 : 1) to give **50** as a pale yellow solid (66.9 mg, 83 %); **m.p.** 106 – 108 °C; **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 8.48 (s, 1 H), 7.75 – 7.74 (m, 1 H), 7.50 – 7.48 (m, 1 H), 7.35 – 7.32 (m, 2 H), 7.18 – 7.16 (m, 1 H), 7.06 – 7.02 (m, 2 H), 3.75 – 3.69 (m, 2 H), 3.56 – 3.52 (m, 1 H), 3.46 – 3.41 (m, 1 H), 2.04 – 1.95 (m, 2 H), 1.88 – 1.77 (m, 2 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ [ppm] = 162.1 (d, *J* = 243.1 Hz), 140.4, 139.6, 131.6 (d, *J* = 7.7 Hz), 131.2, 127.9, 125.5, 114.7 (d, *J* = 21.1 Hz), 71.5 (br), 53.1, 52.3, 24.8, 24.5; **^{19}F NMR** (377 MHz, Acetone-d6) δ [ppm] = – 118.8, – 143.7; **^{11}B NMR** (160 MHz, Acetone-d6) δ [ppm] = 2.36; **IR** (v/cm^{-1}, thin film) v = 3197, 2923, 2853, 2228, 1604, 1508, 1457, 1065, 1038; **HRMS (ESI)** calculated for $C_{15}H_{17}BF_4NS$ [M + H]$^+$: m/z = 330.1108, found: m/z = 330.1111.



51 prepared according to general procedure C with ^{i}PrMgCl/LiCl (0.98 mmol, 0.75 mL, 4.00 equiv) , 3-bromopyridine (0.98 mmol, 176 mg, 4.00 equiv) in THF (0.25 mL), TIM **3** (60.0 mg, 0.25 mmol, 1.00 equiv) in THF (0.25 mL) and the residue was washed by Et_2O : CH_3OH = 10 : 1 to give **51** as a pale yellow solid (54.0 mg, 68% two diastereomers 4:1); **m.p.** 136 – 138 °C; **^{1}H NMR** (600 MHz, CD3OD) δ [ppm] = 8.92 (s, 0.2 H), 8.88 (d, *J* = 5.4 Hz, 0.2 H), 8.73 (d, *J* = 5.4 Hz, 0.8 H), 8.52 (s, 0.8 H), 8.46 (d, *J* = 9.0 Hz, 0.8 H), 8.38 (d, *J* = 9.0 Hz, 0.2 H), 8.13 – 8.10 (m, 0.2 H), 8.05 – 8.03 (m, 0.8 H), 7.77 – 7.74 (m, 0.4 H), 7.72 – 7.70 (m, 1.6 H) , 7.27 – 7.24 (m, 0.4 H), 7.22 – 7.19 (m, 1.6 H), 3.76 – 3.72 (m, 1.0 H), 3.56 – 3.51 (m, 1.0 H), 3.46 – 3.36 (m, 2.0 H), 1.97 – 1.90 (m, 2.0 H), 1.84 – 1.80 (m, 1.0 H), 1.69 – 1.64 (m, 1.0 H); **^{13}C NMR** (151 MHz, CD3OD) δ [ppm] = 164.8 (d, *J* = 249.3 Hz, minor), 164.5 (d, *J* = 249.3 Hz, major), 146.2 (major), 145.9 (minor), 143.3 (minor), 142.6 (major), 140.2 (major), 138.7 (minor), 136.2 (d, *J* = 8.2 Hz, major), 134.0 (major), 132.5 (minor), 131.4 (d, *J* = 8.2 Hz, minor), 128.7 (major), 127.2 (major), 126.7 (minor), 117.9 (d, *J* = 8.2 Hz, minor), 116.8 (d, *J* = 21.6 Hz, major), 72.9 (br), 53.9, 52.5, 24.8, 24.6; **^{19}F NMR** (470 MHz, CD3OD) δ [ppm] = – 114.0, – 143.5; **^{11}B NMR** (160 MHz, CD3OD) δ [ppm] = 2.03; **IR** (v/cm^{-1}, thin film) v = 3197, 3058, 2981, 1509, 1457, 1396, 1234, 1168, 1039, 1017; **HRMS (ESI)** calculated for $C_{16}H_{17}BF_4N_2Na$ [M + Na]$^+$: m/z = 347.1316, found: m/z = 347.1321.

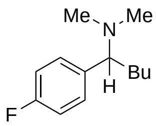
4 Protodeborylation of of α-aminotrifluoroborates

4.1 General procedure

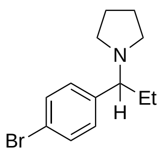


In a round-bottom flask, the α-aminotrifluoroborate (1.00 equiv) and Zr(O^{i}Pr)$_4$ (1.50 equiv) were dissolved in anhydrous toluene (0.50 M). The mixture was stirred for 14 h at 80 ºC and concentrated under reduced pressure. The residue was dissolved in EtOAc, extracted with aqueous saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

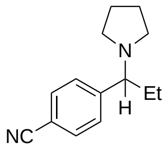
4.2 Protodeborylation of α-aminotrifluoroborates



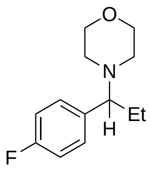
52 prepared according to the general procedure with **38** (55.4 mg, 0.20 mmol, 1.00 equiv) and obtained as a colorless oil (35 mg, 85 %); **^{1}H NMR** (600 MHz, CDCl3) δ [ppm] = 7.21 – 7.13 (m, 2 H), 7.05 – 6.94 (m, 2 H), 3.12 (dd, *J* = 9.6, 4.8 Hz, 1 H), 2.15 (s, 6 H), 1.93 – 1.80 (m, 1 H), 1.73 – 1.60 (m, 1 H), 1.36 – 1.16 (m, 2 H), 1.16 – 0.92 (m, 2 H), 0.82 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 162.0 (d, *J* = 244.5 Hz), 136.7 (d, *J* = 3.3 Hz), 130.0 (d, *J* = 7.8 Hz), 114.9 (d, *J* = 20.9 Hz), 70.3, 42.9, 33.2, 28.8, 22.9, 14.1; **^{19}F NMR** (470 MHz, CDCl3) δ [ppm] = – 116.2; **IR** (v/cm^{-1}, thin film) v = 2956, 2817, 1603, 1508, 1221, 1155, 1010, 830, 732, 563; **HRMS (ESI)** calculated for $C_{13}H_{21}FN$ [M + H]$^+$: m/z = 210.1653, found: m/z = 210.1653.



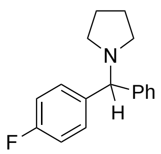
53 prepared according to the general procedure with **43** (83.8 mg, 0.25 mmol, 1.00 equiv) and obtained as a colorless oil (60 mg, 88 %); **^{1}H NMR** (600 MHz, CDCl3) δ [ppm] = 7.50 – 7.34 (m, 2 H), 7.25 – 7.00 (m, 2 H), 2.92 (dd, *J* = 9.9, 3.8 Hz, 1 H), 2.69 – 2.41 (m, 2 H), 2.40 – 2.23 (m, 2 H), 2.09 – 1.84 (m, 1 H), 1.85 – 1.50 (m, 5 H), 0.65 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (151 MHz, CDCl3) δ [ppm] = 142.3, 131.2, 130.0, 120.4, 72.2, 52.8, 28.5, 23.2, 10.3; **IR** (v/cm^{-1}, thin film) v = 2966, 2875, 2783, 1487, 1461, 1138, 1070, 1011, 843, 821; **HRMS (ESI)** calculated for $C_{13}H_{19}BrN$ [M + H]$^+$: m/z = 268.0695, found: m/z = 268.0702.



54 prepared according to the general procedure with **44** (70.5 mg, 0.25 mmol, 1.00 equiv) and obtained as a colorless oil (45.0 mg, 84 %); ^{1}**H NMR** (600 MHz, CDCl3) δ [ppm] = 7.69 – 7.51 (m, 2 H), 7.49 – 7.33 (m, 2 H), 3.03 (dd, *J* = 9.7, 3.8 Hz, 1H), 2.68 – 2.42 (m, 2 H), 2.42 – 2.20 (m, 2 H), 2.05 – 1.86 (m, 1 H), 1.84 – 1.56 (m, 5 H), 0.64 (t, *J* = .4 Hz, 3 H); ^{13}**C NMR** (151 MHz, CDCl3) δ [ppm] = 149.3, 132.1, 129.1, 119.2, 110.8, 72.5, 52.9, 28.6, 23.4, 10.2; **IR** (v/cm^{-1}, thin film) v = 2966, 2876, 2787, 2227, 1608, 1380, 1137, 832, 756, 564; **HRMS (ESI)** calculated for $C_{14}H_{19}N_2$ [M + Na]$^+$: m/z = 215.1543, found: m/z = 215.1546.



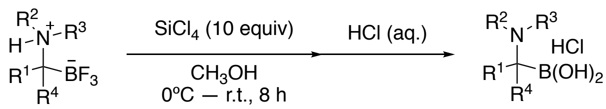
55 prepared according to the general procedure with **40** (0.47 mmol, 137 mg) and obtained as pale yellow oil (86.1 mg, 82 %); ^{1}**H NMR** (400 MHz, CDCl3) δ [ppm] = 7.22 – 7.15 (m, 2 H), 7.03 – 6.95 (m, 2 H), 3.66 (t, *J* = 4.7 Hz, 4 H), 3.08 (dd, *J* = 9.3, 4.6 Hz, 1 H), 2.49 – 2.27 (m, 4 H), 1.97 – 1.84 (m, 1 H), 1.70 – 1.54 (m, 1 H), 0.68 (t, *J* = 7.4 Hz, 3 H); ^{13}**C NMR** (101 MHz, CDCl3) δ [ppm] = 162.0 (d, *J* = 244.8 Hz), 136.6 (d, *J* = 3.2 Hz), 130.1 (d, *J* = 7.7 Hz), 115.0 (d, *J* = 21.0 Hz), 71.4, 67.3, 51.3, 25.5, 10.6; ^{19}**F NMR** (376 MHz, CDCl3) δ [ppm] = – 116.0 (tt, *J* = 8.7, 5.4 Hz); **IR** (v/cm^{-1}, neat) v = 2961, 2877, 2853, 2806, 1603, 1508, 1221, 1117, 1006, 839, 545; **HRMS (ESI)** calculated for $C_{13}H_{19}FNO$ [M + H]$^+$: m/z = 224.1445, found: m/z = 224.1442.



56 prepared according to the general procedure with **48** (0.25 mmol, 80 mg, 1.00 equiv) and obtained as a pale yellow oil (53.2 mg, 84 %); ^{1}**H NMR** (500 MHz, CDCl3) δ [ppm] = 7.47 – 7.40 (m, 4 H), 7.30 – 7.25 (m, 2 H), 7.22 – 7.14 (m, 1 H), 7.00 – 6.91 (m, 2 H), 4.16 (s, 1 H), 2.45 – 2.38 (m, 4 H), 1.84 – 1.72 (m, 4 H); ^{13}**C NMR** (126 MHz, CDCl3) δ [ppm] = 161.8 (d, *J* = 244.6 Hz), 144.3, 140.3, 129.0 (d, *J* = 7.8 Hz), 128.6, 127.5, 127.0, 115.3 (d, *J* = 21.2 Hz), 75.8, 53.8, 23.7; ^{19}**F NMR** (377 MHz, CDCl3) δ [ppm] = – 115.9 – – 116.1 (m); **IR** (v/cm^{-1}, neat) v = 2973, 2932, 2876, 2792, 1602, 1506, 1492, 1223, 1092, 817, 799, 695, 559, 519; **HRMS (ESI)** calculated for $C_{17}H_{19}FN$ [M + H]$^{+}$: m/z = 256.1496, found: m/z = 256.1494.

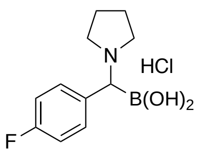
5 Synhesis of α-aminoboronic acids

5.1 General procedure

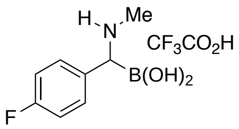


In a round-bottom flask, $SiCl_4$ (1.00 M in CH_2Cl_2, 5.00 equiv) was added to the corresponding α-aminotrifluoroborate (1.00 equiv) in anhydrous CH_3OH (0.20 M) at 0 ºC and the mixture was stirred at r.t. for 4 h. Again, $SiCl_4$ (1.00 M in CH_2Cl_2, 5.00 equiv) was added to the reaction mixture at 0 ºC and the mixture was stirred at r.t. for 4 h. After concentration under reduced pressure, aqueous HCl solution (1.00 M, 2.00 equiv) in CH_3OH (0.20 M) was added at 0 ºC, and the mixture was stirred at r.t. for 0.5 h. The reaction mixture was evaporated under reduced pressure and dried under high vacuum. The product was extracted with anhydrous CH_2Cl_2 / CH_3OH from the residue, the filtrate was concentrated under reduced pressure, and washed with Et_2O or purified by preparative HPLC.

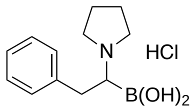
5.2 Synthesis of α-aminoboronic acids



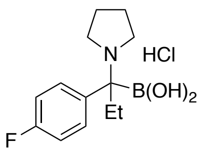
57 prepared according to the general procedure with α-aminotrifluoroborate **28** (30.0 mg, 0.12 mmol, 1.00 equiv), $SiCl_4$ (1.00 M in CH_2Cl_2, 1.22 mL, 1.22 mmol, 10.0 equiv) to give **57** as a colorless oil (25.4 mg, 81 %); **^{1}H NMR** (500 MHz, CD3OD) δ [ppm] = 7.56 – 7.51 (m, 2 H), 7.28 – 7.22 (m, 2 H), 4.21 (br, 1 H), 3.87 – 3.79 (m, 1 H), 3.20 – 3.13 (m, 1 H), 3.00 – 2.97 (m, 2 H), 2.19 – 2.05 (m, 3 H), 1.93 – 1.91 (m, 1 H); **^{13}C NMR** (151 MHz, CD3OD) δ [ppm] = 165.1 (d, J = 247.6 Hz), 133.8 (d, J = 8.6 Hz), 133.1, 117.3 (d, J = 22.0 Hz), 62.0 (br), 54.8, 23.8; **^{19}F NMR** (282 MHz, CD3OD) δ [ppm] = – 113.2; **^{11}B NMR** (96 MHz, CD3OD) δ [ppm] = 27.8; **IR** (ν/cm^{-1}, thin film) ν = 3391, 2960, 2673, 2556, 2481, 1611, 1513, 1456, 1427, 1227, 1167, 1064, 1016; **HRMS (ESI)** calculated for $C_{11}H_{16}BFNO_2$ $[M + H]^+$: m/z = 224.1255, found: m/z = 224.1256.



58 prepared according to the general procedure with α-aminotrifluoroborate **29** (30.0 mg, 0.15 mmol, 1.00 equiv), $SiCl_4$ (1.00 M in CH_2Cl_2, 1.45 mL, 1.45 mmol, 10.0 equiv). The residue was purified by preparative reverse-phase HPLC (YMC C18 column, gradient of 10–70% CH_3CN/H_2O + 0.1% TFA for 28 min, t_R = 12.5 min) to give **58** as a colorless oil (24.4 mg, 77 %); **^{1}H NMR** (600 MHz, CD3OD) δ [ppm] = 7.46 – 7.44 (m, 2 H), 7.22 – 7.19 (m, 2 H), 3.92 (s, 1 H), 2.50 (s, 3 H); **^{13}C NMR** (151 MHz, CD3OD) δ [ppm] = 164.6 (d, *J* = 247.8 Hz), 133.2 (d, *J* = 8.5 Hz), 130.3, 117.5 (d, *J* = 21.9 Hz), 54.5 (br), 32.4; **^{19}F NMR** (282 MHz, CD3OD) δ [ppm] = – 114.0; **^{11}B NMR** (96 MHz, CD3OD) δ [ppm] = 26.7; **IR** (ν/cm^{-1}, thin film) ν = 3355, 2964, 2772, 2199, 1655, 1605, 1512, 1406, 1317, 1298, 1271, 1223, 1162, 1098, 1017; **HRMS (ESI)** calculated for $C_8H_{12}BFNO_2$ $[M + H]^+$: m/z = 184.0941, found: m/z = 184.0942.

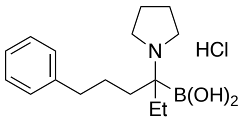


59 prepared according to the general procedure with α-aminotrifluoroborate **32** (20.0 mg, 0.08 mmol, 1.00 equiv), $SiCl_4$ (1.00 M in CH_2Cl_2, 0.82 mL, 0.82 mmol, 10.0 equiv) to give **59** as a colorless oil (15.2 mg, 82 %); **^{1}H NMR** (300 MHz, D_2O) δ [ppm] = 7.35 – 7.23 (m, 5 H), 3.67 – 3.62 (m, 2 H), 3.20 – 2.91 (m, 5 H), 2.07 – 2.02 (m, 2 H), 1.92 – 1.86 (m, 2 H); **^{13}C NMR** (101 MHz, D_2O) δ [ppm] = 136.4, 129.1, 129.0, 127.4, 57.9 (br), 54.7, 53.5, 34.3, 22.8, 22.6; **^{11}B NMR** (128 MHz, D_2O) δ [ppm] = 26.7; **IR** (ν/cm^{-1}, thin film) ν = 3316, 2971, 2709, 1603, 1454, 1417, 1224, 1066; **HRMS (ESI)** calculated for $C_{12}H_{19}BNO_2$ $[M + H]^+$: m/z = 220.1506, found: m/z = 220.1510.

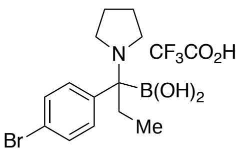


60 prepared according to the general procedure with α-aminotrifluoroborate **36** (30.0 mg, 0.11 mmol, 1.00 equiv), $SiCl_4$ (1.00 M in CH_2Cl_2, 1.05 mL, 1.05 mmol, 10.0 equiv) to give **60** as a colorless oil (19.8 mg, 88 %); **^{1}H NMR** (300 MHz, Acetone-d6) δ [ppm] = 8.65 (br, 1 H), 7.83 – 7.78 (m, 2 H), 7.27 – 7.21 (m, 2 H), 3.74 – 3.64 (m, 1 H), 3.46 – 3.38 (m, 1 H), 3.17 – 2.93 (m, 2 H), 2.62 – 2.48 (m, 2 H), 2.01 – 1.93 (m, 2 H), 1.81 – 1.73 (m, 2 H), 0.95 (t, *J* = 7.5 Hz, 3 H); **^{13}C NMR**

(151 MHz, CD3OD) δ [ppm] = 164.9 (d, *J* = 250.4 Hz, minor), 164.6 (d, *J* = 250.4 Hz, major), 134.8 (d, *J* = 8.3 Hz, major), 134.5 (d, *J* = 8.3 Hz, minor), 130.8 (major), 130.1 (minor), 117.4 (d, *J* = 21.1 Hz, minor), 116.8 (d, *J* = 21.1 Hz, minor), 68.0 (br), 54.0 (minor), 53.6 (major), 46.7, 27.9 (major), 25.1 (minor), 24.1 (major), 24.0 (minor), 23.7 (major), 23.5 (minor), 10.3 (minor), 10.2 (major); **^{19}F NMR** (282 MHz, Acetone-d6) δ [ppm] = – 114.6; **^{11}B NMR** (96 MHz, CD3OD) δ [ppm] = 27.4; **IR** (v/cm^{-1}, thin film) v = 3303, 2973, 2715, 1661, 1605, 1513, 1454, 1395, 1233, 1168, 1066, 1015; **HRMS (ESI)** calculated for $C_{13}H_{19}BFNNaO_2$ [M + Na]$^+$: m/z = 274.1398, found: m/z = 274.1400.



61 prepared according to the general procedure with α-aminotrifluoroborate **47** (20.0 mg, 0.07 mmol, 1.00 equiv), $SiCl_4$ (1.00 M in CH_2Cl_2, 0.74 mL, 0.74 mmol, 10.0 equiv) to give **61** as a colorless oil (19.3 mg, 84 %); **^{1}H NMR** (600 MHz, CD3OD) δ [ppm] = 7.28 – 7.24 (m, 2 H), 7.21 – 7.14 (m, 3 H), 3.39 – 3.35 (m, 2 H), 3.29 – 3.25 (m, 2 H), 2.67 – 2.60 (m, 2 H), 2.02 – 1.58 (m, 10 H), 0.95 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (151 MHz, CD3OD) δ [ppm] = 142.9, 129.6, 129.5, 127.1, 64.8 (br), 51.9, 51.8, 37.0, 32.8, 27.5, 26.3, 24.8, 9.39; **^{11}B NMR** (160 MHz, CD3OD) δ [ppm] = 28.2; **IR** (v/cm^{-1}, neat) v = 3025, 2948, 2881, 2395, 1453, 1395, 1263, 1395, 1263, 1074, 978, 749, 700; **HRMS (ESI)** calculated for $C_{16}H_{27}BNO_2$ [M + H]$^+$: m/z = 276.2132, found: m/z = 276.2132.



62 prepared according to the general procedure with α-aminotrifluoroborate **43** (57.0 mg, 0.17 mmol, 1.00 equiv), $SiCl_4$ (1.00 M in CH_2Cl_2, 1.70 mL, 1.70 mmol, 10.0 equiv). The residue was purified by preparative reverse-phase HPLC (YMC C18 column, gradient of 10–70% CH_3CN/H_2O + 0.1% TFA for 28 min, t_R = 17.2 min) to give **62** as a white solid (51.5 mg, 87 %); **^{1}H NMR** (600 MHz, Acetone-d6) δ [ppm] = 7.72 – 7.42 (m, 4 H), 3.86 – 3.76 (m, 1 H), 3.64 – 3.54 (m, 1 H), 3.35 – 2.98 (m, 2 H), 2.48 – 2.26 (m, 2 H), 2.02 – 1.76 (m, 4 H), 1.01 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (151 MHz, Acetone-d6) δ[ppm] = 134.2, 132.8, 132.6, 123.8, 67.6 (br), 53.5, 49.9, 24.0, 23.5, 10.3; **^{19}F NMR** (128 MHz, Acetone-d6) δ [ppm] = – 75.9 (CF_3CO_2H); **^{11}B NMR** (128 MHz, CD3OD) δ [ppm] = 28.9 (br); **IR** (v/cm^{-1}, neat) v = 2981, 1665, 1494, 1399, 1182, 1134, 1010, 831, 797, 721; **HRMS (ESI)** calculated for $C_{13}H_{20}BBrNO_2$ $[M + H]^+$: m/z = 312.0767, found: m/z = 312.0763.

6 X-ray crystallography data

6.1 X-ray crystallography data for TIM 25

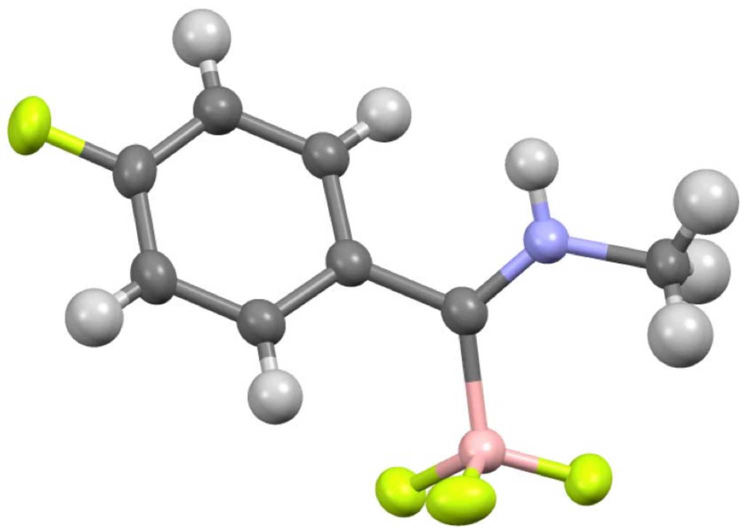


Figure 1 X-ray crystal structure for TIM 25

Experimental

A suitable crystal of $C_8H_8BF_4N$ (jb211116_1_1) was selected and measured on a XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2 [J. Appl. Cryst. 42, 339-341], the structure was solved with the XT [Acta Cryst. A71, 3-8] structure solution program using Intrinsic Phasing and refined with the XL [Acta Cryst. A64, 112-122] refinement package using Least Squares minimisation.

Table 1 Crystal data and structure refinement for jb211116_1_1.

Identification code	jb211116_1_1
Empirical formula	$C_8H_8BF_4N$
Formula weight	204.96
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.1042(2)
b/Å	37.0556(10)
c/Å	7.9394(2)
α/°	90
β/°	93.529(3)
γ/°	90
Volume/Å^3	1792.45(9)

Z	8
ρ_{calc}g/cm^3	1.519
μ/mm^{-1}	1.308
F(000)	832.0
Crystal size/mm^3	0.141 × 0.121 × 0.036
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.548 to 140.144
Index ranges	-7 ≤ h ≤ 5, -44 ≤ k ≤ 44, -9 ≤ l ≤ 9
Reflections collected	6644
Independent reflections	6644 [R_{int} = 0.0170, R_{sigma} = 0.0071]
Data/restraints/parameters	6644/89/290
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1939
Final R indexes [all data]	R_1 = 0.0692, wR_2 = 0.1980
Largest diff. peak/hole / e Å^{-3}	0.43/-0.26

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for jb211116_1_1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1A	11956(3)	6542.9(4)	2204(2)	41.0(4)
F2A	12179(3)	6787.6(5)	4810(2)	50.8(5)
F3A	10790(3)	7115.9(4)	2543(2)	49.7(5)
F4A	7432(3)	5127.4(4)	4680(3)	52.5(5)
N1A	6738(4)	6802.9(6)	3800(3)	35.1(5)
C1A	6532(5)	7195.2(7)	3717(4)	42.9(7)
C2A	8462(4)	6608.5(7)	3631(3)	33.2(6)
C3A	8195(4)	6215.3(7)	3834(3)	33.6(6)
C4A	9892(4)	6013.0(7)	4620(4)	37.8(6)
C5A	9640(5)	5647.6(8)	4911(4)	42.1(7)
C6A	7693(5)	5486.1(7)	4374(4)	40.8(6)
C7A	5997(5)	5672.1(8)	3559(4)	42.6(7)
C8A	6247(4)	6038.4(7)	3290(4)	37.8(6)
B1A	10914(5)	6778.5(8)	3268(4)	36.8(7)
F1B	7162(17)	6485(3)	10037(11)	39.6(13)
F2B	6779(11)	6656(3)	7302(6)	51.5(17)
F3B	5822(17)	7036.3(17)	9390(19)	56.4(18)
F4B	2715(3)	4999.5(4)	9102(3)	51.2(5)
N1B	1578(4)	6683.1(6)	8474(3)	35.3(5)
C1B	1341(5)	7076.4(7)	8352(4)	39.3(6)
C2B	3367(4)	6498.9(7)	8686(3)	33.3(6)
C3B	3145(4)	6103.3(7)	8794(3)	33.7(6)
C4B	4733(4)	5882.4(7)	8112(4)	36.5(6)
C5B	4576(5)	5509.6(7)	8192(4)	40.8(6)
C6B	2849(5)	5363.6(7)	8993(4)	41.0(6)
C7B	1261(5)	5568.9(8)	9690(4)	42.4(7)
C8B	1410(4)	5941.0(7)	9582(4)	37.6(6)
B1B	5837(5)	6689.0(8)	8863(4)	35.8(6)
F2C	6450(40)	6805(11)	7296(15)	59(5)

F1C	7300(50)	6455(6)	9610(40)	46(5)
F3C	5660(50)	7001(5)	9870(30)	45(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for jb211116_1_1. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1A	36.8(8)	40.1(9)	47.0(9)	-1.5(7)	10.9(7)	4.7(6)
F2A	42.5(10)	68.9(12)	41.4(10)	-5.3(8)	4.8(7)	-13.3(8)
F3A	44.7(9)	34.7(9)	71.6(12)	7.2(8)	19.6(8)	1.4(7)
F4A	54.4(11)	27.1(8)	76.4(13)	6.0(8)	8.7(9)	1.4(7)
N1A	32.8(12)	32.5(12)	40.8(12)	1.5(9)	8.5(9)	1.6(9)
C1A	38.9(15)	31.0(14)	59.5(18)	1.6(12)	10.1(13)	4.5(11)
C2A	34.1(13)	34.8(13)	30.8(12)	-1.2(10)	3(1)	3.3(10)
C3A	33.0(13)	34.1(13)	34.1(13)	0.1(10)	6.4(10)	3.2(10)
C4A	33.1(13)	37.1(14)	43.3(15)	-0.8(11)	2.7(11)	2.5(11)
C5A	40.9(15)	36.8(14)	48.5(16)	4.0(12)	2.4(12)	8.2(11)
C6A	46.1(16)	28.8(13)	48.3(16)	0.3(11)	10.2(12)	2.8(11)
C7A	36.0(14)	36.6(15)	55.7(17)	-2.1(12)	5.5(12)	0.2(11)
C8A	32.6(13)	35.4(14)	45.7(15)	-1.4(11)	4.7(11)	3.3(10)
B1A	33.8(15)	32.9(15)	44.7(17)	-1.2(12)	10.2(13)	0.4(11)
F1B	34.5(18)	40(2)	44(3)	0.7(19)	0.1(19)	0.6(14)
F2B	40(2)	71(4)	44.7(16)	5.6(17)	12.5(12)	-15(2)
F3B	38(2)	31.1(17)	99(5)	-2(2)	0(3)	-2.8(13)
F4B	55.1(11)	27.6(8)	71.4(12)	2.1(7)	9.0(9)	-3.9(7)
N1B	31.6(11)	31.3(11)	43.4(13)	0.2(9)	6.8(9)	-1.1(9)
C1B	37.3(14)	31.8(13)	49.3(16)	0.0(11)	6.1(12)	3.7(11)
C2B	33.6(13)	35.7(13)	31.0(12)	-0.2(10)	5.1(10)	1.1(10)
C3B	30.6(13)	34.5(13)	35.7(13)	-0.4(10)	0.8(10)	-0.9(10)
C4B	34.3(13)	33.3(13)	42.3(15)	0.2(11)	5.9(11)	-0.2(10)
C5B	39.6(15)	33.9(14)	49.2(16)	-2.1(11)	4.9(12)	1.8(11)
C6B	42.7(15)	31.1(14)	48.9(16)	-0.1(11)	0.9(12)	-2.7(11)
C7B	40.0(15)	37.8(15)	50.1(17)	2.2(12)	8.1(13)	-6.3(11)
C8B	33.3(13)	37.8(14)	42.0(15)	-1.9(11)	5.0(11)	-0.7(11)
B1B	32.3(14)	34.4(15)	40.8(16)	0.8(12)	3.4(12)	-2.9(11)
F2C	53(7)	83(12)	43(4)	7(5)	7(4)	-19(7)
F1C	34(5)	32(4)	73(11)	-3(7)	-4(8)	0(3)
F3C	49(7)	30(5)	55(7)	-11(4)	-4(5)	-7(4)

Table 4 Bond Lengths for jb211116_1_1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1A	B1A	1.395(3)	F3B	B1B	1.354(7)
F2A	B1A	1.407(4)	F4B	C6B	1.355(3)
F3A	B1A	1.377(4)	N1B	C1B	1.467(3)
F4A	C6A	1.362(3)	N1B	C2B	1.290(3)

N1A	C1A	1.460(3)	C2B	C3B	1.475(4)
N1A	C2A	1.289(3)	C2B	B1B	1.662(4)
C2A	C3A	1.476(4)	C3B	C4B	1.403(4)
C2A	B1A	1.665(4)	C3B	C8B	1.399(4)
C3A	C4A	1.394(4)	C4B	C5B	1.386(4)
C3A	C8A	1.402(4)	C5B	C6B	1.376(4)
C4A	C5A	1.384(4)	C6B	C7B	1.375(4)
C5A	C6A	1.375(4)	C7B	C8B	1.385(4)
C6A	C7A	1.372(4)	B1B	F2C	1.389(12)
C7A	C8A	1.384(4)	B1B	F1C	1.351(15)
F1B	B1B	1.415(6)	B1B	F3C	1.413(13)
F2B	B1B	1.403(5)			

Table 5 Bond Angles for jb211116_1_1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2A	N1A	C1A	128.3(2)	C3B	C2B	B1B	120.2(2)
N1A	C2A	C3A	116.3(2)	C4B	C3B	C2B	119.3(2)
N1A	C2A	B1A	123.7(2)	C8B	C3B	C2B	121.9(2)
C3A	C2A	B1A	119.9(2)	C8B	C3B	C4B	118.8(2)
C4A	C3A	C2A	119.7(2)	C5B	C4B	C3B	120.8(3)
C4A	C3A	C8A	118.6(2)	C6B	C5B	C4B	118.1(3)
C8A	C3A	C2A	121.7(2)	F4B	C6B	C5B	118.2(3)
C5A	C4A	C3A	120.9(3)	F4B	C6B	C7B	118.6(3)
C6A	C5A	C4A	118.5(3)	C7B	C6B	C5B	123.2(3)
F4A	C6A	C5A	118.6(3)	C6B	C7B	C8B	118.4(3)
F4A	C6A	C7A	118.7(3)	C7B	C8B	C3B	120.7(3)
C7A	C6A	C5A	122.7(3)	F1B	B1B	C2B	108.0(5)
C6A	C7A	C8A	118.6(3)	F2B	B1B	F1B	106.7(4)
C7A	C8A	C3A	120.7(3)	F2B	B1B	C2B	107.9(3)
F1A	B1A	F2A	107.2(2)	F3B	B1B	F1B	108.6(5)
F1A	B1A	C2A	108.4(2)	F3B	B1B	F2B	111.5(4)
F2A	B1A	C2A	108.0(2)	F3B	B1B	C2B	113.9(5)
F3A	B1A	F1A	109.3(2)	F2C	B1B	C2B	110.3(8)
F3A	B1A	F2A	110.8(2)	F2C	B1B	F3C	106.6(11)
F3A	B1A	C2A	112.9(2)	F1C	B1B	C2B	109.6(14)
C2B	N1B	C1B	127.8(2)	F1C	B1B	F2C	112.6(11)
N1B	C2B	C3B	116.9(2)	F1C	B1B	F3C	110.4(13)
N1B	C2B	B1B	122.9(2)	F3C	B1B	C2B	107.1(12)

Table 6 Torsion Angles for jb211116_1_1.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
F4A	C6A	C7A	C8A	178.3(3)	N1B	C2B	B1B	F1B	144.0(5)
N1A	C2A	C3A	C4A	-143.2(3)	N1B	C2B	B1B	F2B	-101.1(6)
N1A	C2A	C3A	C8A	35.3(4)	N1B	C2B	B1B	F3B	23.3(8)
N1A	C2A	B1A	F1A	-144.5(3)	N1B	C2B	B1B	F2C	-75.5(19)

N1A	C2A	B1A	F2A	99.6(3)	N1B	C2B	B1B	F1C	160.0(16)
N1A	C2A	B1A	F3A	-23.2(4)	N1B	C2B	B1B	F3C	40.2(12)
C1A	N1A	C2A	C3A	178.0(3)	C1B	N1B	C2B	C3B	179.1(2)
C1A	N1A	C2A	B1A	0.0(4)	C1B	N1B	C2B	B1B	0.0(4)
C2A	C3A	C4A	C5A	176.4(3)	C2B	C3B	C4B	C5B	179.9(2)
C2A	C3A	C8A	C7A	-177.2(3)	C2B	C3B	C8B	C7B	-178.9(3)
C3A	C2A	B1A	F1A	37.6(3)	C3B	C2B	B1B	F1B	-35.1(5)
C3A	C2A	B1A	F2A	-78.3(3)	C3B	C2B	B1B	F2B	79.9(6)
C3A	C2A	B1A	F3A	158.8(2)	C3B	C2B	B1B	F3B	-155.8(7)
C3A	C4A	C5A	C6A	1.4(4)	C3B	C2B	B1B	F2C	105.5(19)
C4A	C3A	C8A	C7A	1.3(4)	C3B	C2B	B1B	F1C	-19.1(16)
C4A	C5A	C6A	F4A	-179.1(3)	C3B	C2B	B1B	F3C	-138.9(12)
C4A	C5A	C6A	C7A	0.2(5)	C3B	C4B	C5B	C6B	-1.5(4)
C5A	C6A	C7A	C8A	-1.0(5)	C4B	C3B	C8B	C7B	0.1(4)
C6A	C7A	C8A	C3A	0.2(4)	C4B	C5B	C6B	F4B	-178.8(2)
C8A	C3A	C4A	C5A	-2.2(4)	C4B	C5B	C6B	C7B	1.0(5)
B1A	C2A	C3A	C4A	34.9(4)	C5B	C6B	C7B	C8B	-0.1(5)
B1A	C2A	C3A	C8A	-146.6(3)	C6B	C7B	C8B	C3B	-0.5(4)
F4B	C6B	C7B	C8B	179.7(3)	C8B	C3B	C4B	C5B	0.9(4)
N1B	C2B	C3B	C4B	145.0(3)	B1B	C2B	C3B	C4B	-35.9(4)
N1B	C2B	C3B	C8B	-36.1(4)	B1B	C2B	C3B	C8B	143.0(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for jb211116_1_1.

Atom	*x*	*y*	*z*	U(eq)
H1A	5430(40)	6695(8)	4010(40)	42
H1AA	6337	7271	2535	64
H1AB	7862	7307	4240	64
H1AC	5258	7271	4322	64
H4A	11240	6128	4960	45
H5A	10786	5511	5469	51
H7A	4680	5552	3188	51
H8A	5087	6171	2731	45
H1B	210(40)	6572(8)	8440(40)	42
H1BA	12	7135	7651	59
H1BB	2624	7179	7841	59
H1BC	1230	7178	9483	59
H4B	5931	5989	7588	44
H5B	5631	5359	7708	49
H7B	90	5458	10233	51
H8B	322	6088	10048	45

Table 8 Atomic Occupancy for jb211116_1_1.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F1B	0.73(4)	F2B	0.73(4)	F3B	0.73(4)

F2C	0.27(4)	F1C	0.27(4)	F3C	0.27(4)

6.2 X-ray crystallography data for TIM 26

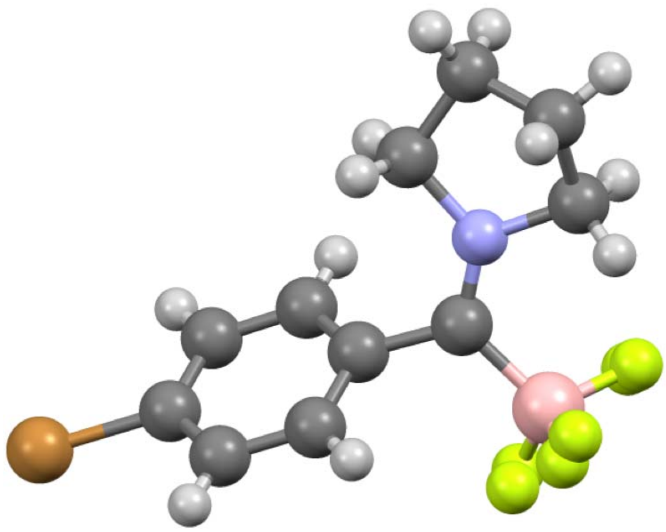


Figure 1 X-ray crystal structure for TIM 26

Experimental

A suitable crystal of $C_{11}H_{12}BBrF_3N$ (jb080616_1_1) was selected and measured on a 'Bruker/Nonius Kappa Apex2' diffractometer. The crystal was kept at 100.0(2) K during data collection. Using Olex2 [J. Appl. Cryst. 42, 339-341], the structure was solved with the XT [Acta Cryst. A71, 3-8] structure solution program using Intrinsic Phasing and refined with the XL [Acta Cryst. A64, 112-122] refinement package using Least Squares minimisation.

Table 1 Crystal data and structure refinement for jb080616_1_1.

Identification code	jb080616_1_1
Empirical formula	$C_{11}H_{12}BBrF_3N$
Formula weight	305.94
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.1247(8)
b/Å	11.1474(11)
c/Å	11.9275(12)
α/°	90
β/°	90.442(3)
γ/°	90
Volume/Å^3	1213.2(2)

Z	4
ρ_{calc}g/cm^3	1.675
μ/mm^{-1}	3.401
F(000)	608.0
Crystal size/mm^3	0.21 × 0.19 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.002 to 56.582
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	22040
Independent reflections	5908 [R_{int} = 0.0261, R_{sigma} = 0.0430]
Data/restraints/parameters	5908/136/335
Goodness-of-fit on F^2	0.908
Final R indexes [I>=2σ (I)]	R_1 = 0.0191, wR_2 = 0.0384
Final R indexes [all data]	R_1 = 0.0219, wR_2 = 0.0389
Largest diff. peak/hole / e Å^{-3}	0.34/-0.26
Flack parameter	0.017(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for jb080616_1_1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3497.5(3)	-406.9(2)	9132.8(2)	22.78(7)
Br2	1118.7(3)	4997.1(2)	912.5(2)	25.57(7)
F6	2114.4(15)	10414.7(12)	5205.2(12)	21.5(3)
F4	447.8(14)	9105.0(13)	4468.1(12)	23.0(3)
F5	1277.1(15)	8856.9(13)	6266.9(12)	20.1(3)
F3	3220(40)	6530(20)	6668(18)	24(3)
F2	4210(30)	6250(20)	8405(10)	36(3)
F1	4670(20)	4924(14)	6997(16)	32(3)
N2	4316(2)	8404.7(17)	5157.9(17)	14.7(4)
N1	866.1(19)	5234.9(17)	7823.8(16)	13.5(4)
C5	1916(2)	2607(2)	7493(2)	13.8(5)
C18	3020(2)	8361(2)	4725.3(19)	12.5(5)
C15	2711(2)	7498(2)	3808(2)	12.3(5)
C4	2463(2)	3554(2)	8135(2)	12.9(5)
C13	1264(2)	5817(2)	3159(2)	15.2(5)
C8	-486(2)	4541(2)	8115.9(19)	15.9(5)
C6	2242(2)	1425(2)	7791(2)	15.6(5)
C12	1804(2)	5999(2)	2091(2)	14.3(5)
C19	5584(2)	7623(2)	4848(2)	20.1(6)
C17	2817(2)	6889(2)	1861(2)	16.7(5)
C14	1701(2)	6582(2)	4013(2)	14.3(5)
C3	3351(2)	3314(2)	9067(2)	14.8(5)
C9	-1725(3)	5447(2)	7994(2)	23.4(6)
C22	4722(3)	9148(2)	6147(2)	20.3(6)
C7	2195(2)	4839(2)	7826.9(18)	14.9(5)
C16	3287(3)	7632(2)	2728(2)	15.9(5)

C2	3643(2)	2144(2)	9391(2)	15.0(5)
C20	6838(3)	8068(2)	5596(2)	24.2(6)
C11	461(3)	6517(2)	7609(2)	20.7(5)
C10	-992(3)	6643(2)	8214(2)	23.5(6)
C21	6038(3)	8506(2)	6644(2)	20.0(6)
C1	3089(2)	1216(2)	8737(2)	13.8(5)
B1	3607(3)	5701(3)	7508(3)	23.6(7)
B2	1657(3)	9221(3)	5187(2)	15.9(6)
F2A	3820(15)	6489(9)	8445(7)	33.5(16)
F3A	3300(20)	6357(14)	6557(9)	29(2)
F1A	4835(9)	5014(9)	7381(19)	46(2)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for jb080616_1_1. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	30.22(13)	15.21(13)	22.88(14)	3.45(11)	-2.02(10)	7.36(11)
Br2	30.09(13)	27.27(15)	19.29(14)	-10.45(11)	-2.84(10)	-1.63(11)
F6	25.9(8)	11.9(7)	26.7(9)	-0.6(6)	2.3(6)	2.6(6)
F4	17.1(7)	28.7(8)	23.1(8)	-7.8(7)	-4.1(6)	7.5(6)
F5	23.6(7)	19.0(8)	17.8(8)	2.6(6)	6.5(6)	7.1(6)
F3	17(4)	23(5)	33(5)	10(4)	3(4)	3(3)
F2	28(6)	49(6)	31(3)	5(3)	-7(3)	-21(4)
F1	20(4)	21(3)	56(6)	13(4)	15(4)	6(3)
N2	16.2(10)	11.1(10)	16.7(11)	-2.3(8)	2.5(8)	-0.7(8)
N1	13.3(9)	12.0(11)	15.1(10)	1.6(8)	-0.8(8)	-0.3(7)
C5	13.3(11)	15.0(12)	12.9(13)	1.5(10)	-1.0(9)	0.7(9)
C18	15.6(11)	8.9(11)	13.0(12)	2.6(9)	2.2(9)	-1.5(8)
C15	10.1(10)	11.2(12)	15.5(13)	-0.9(9)	1.1(9)	3.0(8)
C4	10.4(10)	12.6(12)	15.7(12)	0.1(10)	2.6(9)	0.4(9)
C13	12.3(11)	14.3(12)	19.0(13)	-0.1(10)	0.5(9)	-2.2(9)
C8	11.7(10)	20.3(12)	15.8(12)	1.0(11)	0.8(9)	-4.4(10)
C6	15.7(11)	15.6(12)	15.6(13)	-2.2(10)	0.9(10)	0.8(9)
C12	14.8(11)	14.3(12)	13.7(12)	-4.1(10)	-2.7(9)	5.0(9)
C19	12.4(11)	20.6(14)	27.3(16)	-7.5(12)	2.8(11)	2.5(10)
C17	16.8(11)	19.9(13)	13.6(13)	-0.8(10)	4.7(10)	3(1)
C14	12.8(10)	17.6(13)	12.5(12)	0.4(10)	2.3(9)	0.0(9)
C3	11.3(11)	15.7(13)	17.3(13)	-4.3(10)	0.8(10)	-0.8(9)
C9	15.5(12)	28.4(15)	26.3(15)	-1.1(12)	1.1(11)	4.2(11)
C22	21.5(12)	16.8(12)	22.6(14)	-7.4(11)	-5.6(11)	1.1(10)
C7	14.3(10)	16.6(14)	13.8(11)	-1.2(10)	-1.9(8)	1.7(9)
C16	15.7(11)	13.5(12)	18.7(14)	-0.6(10)	3.4(10)	-1.2(9)
C2	11.7(11)	20.1(13)	13.1(13)	1.2(10)	-0.9(9)	3.0(9)
C20	14.9(12)	22.7(15)	34.9(17)	-7.4(12)	-0.9(11)	-0.7(10)
C11	18.9(12)	15.2(12)	28.1(15)	4.9(11)	0.1(11)	3.1(10)
C10	21.9(13)	19.4(14)	29.3(16)	-1.2(12)	1.6(11)	7.0(11)
C21	18.0(12)	16.1(13)	25.7(15)	-3.9(11)	-4.6(11)	-1.3(10)

C1	16.1(11)	10.6(12)	14.6(13)	0.7(9)	3.9(9)	4.2(9)
B1	13.7(13)	16.4(15)	40.8(19)	10.2(13)	-1.6(12)	-2.7(11)
B2	16.9(13)	14.5(13)	16.4(15)	-2.1(11)	-0.1(11)	4.8(10)
F2A	24(4)	29(3)	48(2)	4.3(17)	-16(2)	-14(2)
F3A	22(3)	31(4)	35(3)	13(3)	6(2)	-4(3)
F1A	12.2(17)	24(2)	101(7)	20(4)	7(3)	-0.2(16)

Table 4 Bond Lengths for jb080616_1_1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.906(2)	C4	C3	1.397(3)
Br2	C12	1.898(2)	C4	C7	1.498(3)
F6	B2	1.395(3)	C13	C12	1.384(3)
F4	B2	1.398(3)	C13	C14	1.384(3)
F5	B2	1.396(3)	C8	C9	1.523(3)
F3	B1	1.409(14)	C6	C1	1.382(3)
F2	B1	1.348(11)	C12	C17	1.384(3)
F1	B1	1.439(10)	C19	C20	1.528(3)
N2	C18	1.287(3)	C17	C16	1.390(3)
N2	C19	1.497(3)	C3	C2	1.386(3)
N2	C22	1.486(3)	C9	C10	1.513(4)
N1	C8	1.500(3)	C22	C21	1.514(3)
N1	C7	1.291(3)	C7	B1	1.654(3)
N1	C11	1.498(3)	C2	C1	1.388(3)
C5	C4	1.394(3)	C20	C21	1.533(4)
C5	C6	1.397(3)	C11	C10	1.520(3)
C18	C15	1.483(3)	B1	F2A	1.434(8)
C18	B2	1.667(3)	B1	F3A	1.377(9)
C15	C14	1.398(3)	B1	F1A	1.367(8)
C15	C16	1.403(3)			

Table 5 Bond Angles for jb080616_1_1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C18	N2	C19	126.0(2)	N1	C7	B1	122.3(2)
C18	N2	C22	124.21(19)	C4	C7	B1	119.10(18)
C22	N2	C19	109.38(17)	C17	C16	C15	120.2(2)
C7	N1	C8	126.7(2)	C3	C2	C1	118.5(2)
C7	N1	C11	123.9(2)	C19	C20	C21	102.71(19)
C11	N1	C8	109.25(18)	N1	C11	C10	102.84(19)
C4	C5	C6	120.0(2)	C9	C10	C11	102.8(2)
N2	C18	C15	119.3(2)	C22	C21	C20	102.3(2)
N2	C18	B2	122.1(2)	C6	C1	Br1	117.97(18)
C15	C18	B2	118.60(19)	C6	C1	C2	122.2(2)
C14	C15	C18	117.8(2)	C2	C1	Br1	119.88(18)
C14	C15	C16	119.4(2)	F3	B1	F1	105.3(11)
C16	C15	C18	122.5(2)	F3	B1	C7	110.7(15)

C5	C4	C3	119.7(2)	F2	B1	F3	111.4(12)
C5	C4	C7	122.2(2)	F2	B1	F1	109.6(7)
C3	C4	C7	118.1(2)	F2	B1	C7	113.3(7)
C12	C13	C14	118.9(2)	F1	B1	C7	106.0(8)
N1	C8	C9	104.3(2)	F2A	B1	C7	106.1(5)
C1	C6	C5	118.9(2)	F3A	B1	C7	110.0(9)
C13	C12	Br2	118.54(18)	F3A	B1	F2A	110.0(7)
C17	C12	Br2	119.43(18)	F1A	B1	C7	109.9(5)
C17	C12	C13	122.0(2)	F1A	B1	F2A	108.9(5)
N2	C19	C20	104.10(19)	F1A	B1	F3A	111.7(9)
C12	C17	C16	118.8(2)	F6	B2	F4	109.4(2)
C13	C14	C15	120.5(2)	F6	B2	F5	109.8(2)
C2	C3	C4	120.7(2)	F6	B2	C18	109.24(19)
C10	C9	C8	103.96(19)	F4	B2	C18	109.4(2)
N2	C22	C21	103.85(19)	F5	B2	F4	109.8(2)
N1	C7	C4	118.6(2)	F5	B2	C18	109.2(2)

Table 6 Torsion Angles for jb080616_1_1.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Br2	C12	C17	C16	178.69(17)	C4	C7	B1	F3A	134.5(8)
N2	C18	C15	C14	115.6(2)	C4	C7	B1	F1A	11.1(10)
N2	C18	C15	C16	-70.2(3)	C13	C12	C17	C16	-1.0(3)
N2	C18	B2	F6	52.1(3)	C8	N1	C7	C4	0.8(3)
N2	C18	B2	F4	171.8(2)	C8	N1	C7	B1	-178.9(2)
N2	C18	B2	F5	-68.0(3)	C8	N1	C11	C10	21.3(3)
N2	C19	C20	C21	30.6(3)	C8	C9	C10	C11	40.5(3)
N2	C22	C21	C20	37.0(2)	C6	C5	C4	C3	0.8(3)
N1	C8	C9	C10	-27.1(2)	C6	C5	C4	C7	177.5(2)
N1	C7	B1	F3	-34.9(12)	C12	C13	C14	C15	-2.2(3)
N1	C7	B1	F2	91.1(14)	C12	C17	C16	C15	-1.6(3)
N1	C7	B1	F1	-148.6(9)	C19	N2	C18	C15	-2.1(3)
N1	C7	B1	F2A	73.3(6)	C19	N2	C18	B2	176.2(2)
N1	C7	B1	F3A	-45.7(8)	C19	N2	C22	C21	-18.3(3)
N1	C7	B1	F1A	-169.2(10)	C19	C20	C21	C22	-41.9(3)
N1	C11	C10	C9	-37.7(3)	C14	C15	C16	C17	2.3(3)
C5	C4	C3	C2	-2.9(3)	C14	C13	C12	Br2	-176.77(17)
C5	C4	C7	N1	63.7(3)	C14	C13	C12	C17	3.0(3)
C5	C4	C7	B1	-116.6(3)	C3	C4	C7	N1	-119.5(2)
C5	C6	C1	Br1	179.25(16)	C3	C4	C7	B1	60.2(3)
C5	C6	C1	C2	-0.9(3)	C3	C2	C1	Br1	178.70(16)
C18	N2	C19	C20	179.1(2)	C3	C2	C1	C6	-1.1(3)
C18	N2	C22	C21	154.9(2)	C22	N2	C18	C15	-174.1(2)
C18	C15	C14	C13	174.0(2)	C22	N2	C18	B2	4.2(3)
C18	C15	C16	C17	-171.7(2)	C22	N2	C19	C20	-7.9(3)
C15	C18	B2	F6	-129.5(2)	C7	N1	C8	C9	178.9(2)
C15	C18	B2	F4	-9.9(3)	C7	N1	C11	C10	-154.3(2)
C15	C18	B2	F5	110.3(2)	C7	C4	C3	C2	-179.8(2)

C4	C5	C6	C1	1.1(3)	C16	C15	C14	C13	-0.4(3)
C4	C3	C2	C1	3.0(3)	C11	N1	C8	C9	3.4(2)
C4	C7	B1	F3	145.3(12)	C11	N1	C7	C4	175.7(2)
C4	C7	B1	F2	-88.7(14)	C11	N1	C7	B1	-4.1(4)
C4	C7	B1	F1	31.6(10)	B2	C18	C15	C14	-62.7(3)
C4	C7	B1	F2A	-106.5(6)	B2	C18	C15	C16	111.4(2)

Table 7 Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for jb080616_1_1.

Atom	*x*	*y*	*z*	U(eq)
H5	1321	2766	6853	17
H13	604	5177	3304	18
H8A	-425	4231	8893	19
H8B	-629	3857	7596	19
H6	1889	775	7350	19
H19A	5827	7716	4045	24
H19B	5364	6769	4999	24
H17	3184	6989	1124	20
H14	1312	6484	4744	17
H3	3760	3961	9484	18
H9A	-2157	5421	7231	28
H9B	-2505	5292	8548	28
H22A	3909	9184	6691	24
H22B	4981	9975	5918	24
H16	4001	8234	2588	19
H2	4208	1980	10045	18
H20A	7381	8730	5233	29
H20B	7529	7411	5779	29
H11A	346	6675	6796	25
H11B	1206	7070	7924	25
H10A	-839	6777	9026	28
H10B	-1579	7312	7900	28
H21A	5734	7826	7123	24
H21B	6658	9060	7090	24

Table 8 Atomic Occupancy for jb080616_1_1.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F3	0.38(4)	F2	0.38(4)	F1	0.38(4)
F2A	0.62(4)	F3A	0.62(4)	F1A	0.62(4)

6.3 X-ray crystallography data for α-aminotrifluoroborate 28

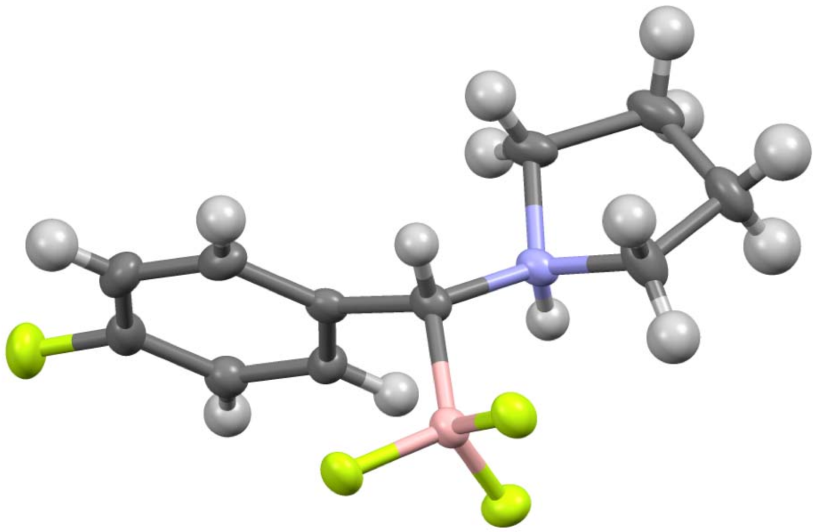


Figure 1 X-ray crystal structure for α-aminotrifluoroborate 28

Experimental

A suitable crystal of $C_{11}H_{14}BF_4N$ (jb120817_1_1) was selected and measured on a XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2 [J. Appl. Cryst. 42, 339-341], the structure was solved with the XT [Acta Cryst. A71, 3-8] structure solution program using Intrinsic Phasing and refined with the XL [Acta Cryst. A64, 112-122] refinement package using Least Squares minimisation.

Table 1 Crystal data and structure refinement for jb120817_1_1.

Identification code	jb120817_1_1
Empirical formula	$C_{11}H_{14}BF_4N$
Formula weight	247.04
Temperature/K	100.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.85970(10)
b/Å	11.13680(10)
c/Å	19.4080(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2347.25(4)
Z	8
ρ_{calc}g/cm^3	1.398

μ/mm^{-1}	1.092
F(000)	1024.0
Crystal size/mm^3	0.214 × 0.185 × 0.131
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.114 to 158.338
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections collected	89056
Independent reflections	5049 [R_{int} = 0.0532, R_{sigma} = 0.0171]
Data/restraints/parameters	5049/2/313
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0743
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0753
Largest diff. peak/hole / e Å^{-3}	0.31/-0.18
Flack parameter	-0.05(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for jb120817_1_1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1A	1487.6(16)	2368.8(13)	881.8(8)	51.3(4)
F2A	6082.9(12)	3083.8(12)	2625.2(6)	37.7(3)
F3A	5057.6(12)	3109.6(13)	3651.6(7)	40.6(3)
F4A	6552.7(12)	4467.3(13)	3442.3(8)	43.3(3)
N1A	3794.0(16)	5267.1(15)	3380.2(9)	25.8(3)
B1A	5586(2)	3824(2)	3129.2(12)	28.6(5)
C1A	4545.5(19)	4715.7(19)	2800.3(10)	26.3(4)
C2A	3706.5(19)	4091.7(18)	2293.7(10)	26.6(4)
C3A	3606(2)	4518(2)	1620.7(11)	32.6(5)
C4A	2870(2)	3938(2)	1140.7(11)	38.4(5)
C5A	2236(2)	2943(2)	1344.7(11)	35.4(5)
C6A	2291(2)	2491(2)	2002.7(11)	33.8(5)
C7A	3042(2)	3068.3(19)	2477(1)	29.6(4)
C8A	4499(2)	6180(2)	3807.3(11)	31.3(4)
C9A	3526(2)	7027(2)	4104.6(13)	40.4(5)
C10A	2288(2)	6550(2)	3844.4(13)	38.7(5)
C11A	2626.1(19)	5904.3(18)	3187.3(11)	30.6(4)
F1B	5477.7(13)	6171.0(12)	6782.1(7)	40.0(3)
F2B	6481.4(11)	1509.6(10)	4803.0(6)	30.3(3)
F3B	8329.4(11)	679.7(10)	5119.8(6)	28.2(3)
F4B	7104.5(11)	1509(1)	5931.7(6)	27.7(3)
N1B	8256.2(15)	3269.1(14)	4381.5(8)	22.8(3)
B1B	7497(2)	1630.1(19)	5242.5(11)	23.0(4)
C1B	8160.0(18)	2946.4(17)	5137.3(10)	23.2(4)
C2B	7488.0(18)	3912.4(17)	5529.5(10)	22.6(4)
C3B	7937(2)	4270.6(18)	6172.1(11)	28.9(4)
C4B	7274(2)	5030.1(19)	6594.5(11)	33.1(5)
C5B	6158(2)	5442.2(18)	6363.9(10)	29.2(4)

C6B	5690(2)	5153.5(18)	5727.4(10)	26.9(4)
C7B	6354.3(18)	4371.5(17)	5313.6(10)	24.1(4)
C8B	8943(2)	4422(2)	4238.8(11)	30.9(5)
C9B	9378(2)	4314(2)	3492.7(11)	36.2(5)
C10B	9214(2)	3002(2)	3293.0(12)	39.1(5)
C11B	8927(2)	2361(2)	3956.8(11)	34.5(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for jb120817_1_1. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1A	69.4(11)	42.9(8)	41.5(8)	-7.0(6)	-27.3(7)	-0.8(7)
F2A	35.1(7)	47.6(8)	30.5(6)	-3.1(5)	1.2(5)	13.8(6)
F3A	36.9(7)	52.6(8)	32.3(7)	17.9(6)	4.0(6)	11.5(6)
F4A	27.0(7)	50.4(8)	52.6(8)	-6.6(7)	-14.0(6)	6.9(6)
N1A	24.6(8)	26.7(8)	26.2(8)	5.0(7)	1.5(7)	2.0(7)
B1A	22.5(11)	38.9(12)	24.3(11)	0.3(9)	0.2(9)	4.4(9)
C1A	22.7(9)	32.5(10)	23.5(9)	4.8(8)	2.4(8)	-0.1(8)
C2A	23.6(10)	29.9(10)	26.2(9)	2.3(8)	-1.6(8)	4.1(8)
C3A	31.8(11)	36.2(11)	29.8(10)	9.1(9)	-0.7(9)	0.4(9)
C4A	46.1(14)	44.3(12)	24.7(10)	5.8(9)	-7.7(10)	5.9(11)
C5A	40.3(13)	35.7(11)	30.1(10)	-5.3(9)	-12.4(10)	4.1(10)
C6A	39.0(12)	29.7(10)	32.6(11)	-0.3(8)	-5.7(10)	-1.8(9)
C7A	34.6(11)	30.9(10)	23.4(9)	3.4(8)	-2.4(8)	1.6(9)
C8A	32.5(11)	31.9(10)	29.5(10)	1.0(8)	0.1(9)	-1.7(9)
C9A	49.9(15)	30.8(11)	40.5(12)	-1.5(10)	3.0(11)	4.2(10)
C10A	37.4(13)	27.6(10)	51.0(13)	7.7(10)	10.3(11)	9.0(9)
C11A	22.3(10)	29.4(10)	39.9(11)	10.2(9)	0.6(9)	2.9(8)
F1B	50.4(8)	37.4(7)	32.4(6)	-11.1(6)	8.0(6)	0.1(6)
F2B	27.8(6)	31.8(6)	31.2(6)	2.9(5)	-6.9(5)	-3.5(5)
F3B	29.7(6)	24.4(5)	30.5(6)	3.6(5)	3.9(5)	4.1(5)
F4B	33.5(6)	26.5(5)	23.1(5)	4.8(4)	5.3(5)	-2.8(5)
N1B	20.7(8)	24.9(8)	22.9(7)	5.7(6)	0.9(6)	-0.1(6)
B1B	23.2(10)	24.4(10)	21.4(10)	2.8(8)	1.0(8)	1.0(8)
C1B	21.8(9)	26.9(9)	20.8(9)	6.1(7)	-0.9(7)	-0.5(7)
C2B	23.1(9)	20.7(8)	24.1(9)	4.9(7)	1.4(8)	-4.3(7)
C3B	28(1)	29.2(10)	29.6(10)	3.9(8)	-7.3(8)	-5.9(8)
C4B	41.4(13)	32.6(10)	25.3(10)	-2.7(8)	-5.0(9)	-9.3(9)
C5B	37.7(11)	23.6(9)	26.3(10)	-3.0(8)	6.4(9)	-4.5(8)
C6B	27.1(10)	25.5(9)	28.2(10)	1.1(8)	1.1(8)	-1.1(8)
C7B	25.7(10)	25.1(9)	21.6(9)	-0.4(7)	-2.1(7)	-1.7(8)
C8B	25.3(10)	33.6(10)	33.8(11)	13.1(9)	-1.5(8)	-7.4(8)
C9B	25.4(10)	49.2(13)	33.9(11)	18.5(10)	1.8(9)	-3.4(10)
C10B	39.0(13)	48.6(13)	29.7(11)	8.8(10)	12.1(10)	5(1)
C11B	37.9(12)	34.3(11)	31.2(11)	8.4(9)	11.4(9)	12.6(10)

Table 4 Bond Lengths for jb120817_1_1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1A	C5A	1.370(2)	F1B	C5B	1.365(2)
F2A	B1A	1.389(3)	F2B	B1B	1.401(2)
F3A	B1A	1.411(3)	F3B	B1B	1.412(2)
F4A	B1A	1.408(3)	F4B	B1B	1.410(2)
N1A	C1A	1.520(3)	N1B	C1B	1.514(2)
N1A	C8A	1.519(3)	N1B	C8B	1.511(3)
N1A	C11A	1.501(2)	N1B	C11B	1.494(3)
B1A	C1A	1.634(3)	B1B	C1B	1.646(3)
C1A	C2A	1.510(3)	C1B	C2B	1.506(3)
C2A	C3A	1.394(3)	C2B	C3B	1.397(3)
C2A	C7A	1.395(3)	C2B	C7B	1.397(3)
C3A	C4A	1.387(3)	C3B	C4B	1.381(3)
C4A	C5A	1.364(3)	C4B	C5B	1.371(3)
C5A	C6A	1.374(3)	C5B	C6B	1.374(3)
C6A	C7A	1.388(3)	C6B	C7B	1.387(3)
C8A	C9A	1.529(3)	C8B	C9B	1.528(3)
C9A	C10A	1.532(4)	C9B	C10B	1.522(4)
C10A	C11A	1.509(3)	C10B	C11B	1.505(3)

Table 5 Bond Angles for jb120817_1_1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C8A	N1A	C1A	113.84(16)	C8B	N1B	C1B	114.42(15)
C11A	N1A	C1A	117.40(16)	C11B	N1B	C1B	114.05(15)
C11A	N1A	C8A	104.21(16)	C11B	N1B	C8B	103.47(16)
F2A	B1A	F3A	109.21(19)	F2B	B1B	F3B	109.24(16)
F2A	B1A	F4A	108.46(18)	F2B	B1B	F4B	109.30(16)
F2A	B1A	C1A	110.75(17)	F2B	B1B	C1B	110.74(15)
F3A	B1A	C1A	109.99(17)	F3B	B1B	C1B	111.51(16)
F4A	B1A	F3A	106.26(17)	F4B	B1B	F3B	106.37(15)
F4A	B1A	C1A	112.04(18)	F4B	B1B	C1B	109.58(16)
N1A	C1A	B1A	109.12(16)	N1B	C1B	B1B	111.21(15)
C2A	C1A	N1A	110.13(16)	C2B	C1B	N1B	110.70(15)
C2A	C1A	B1A	113.09(17)	C2B	C1B	B1B	111.19(15)
C3A	C2A	C1A	120.04(19)	C3B	C2B	C1B	119.06(18)
C3A	C2A	C7A	118.48(19)	C3B	C2B	C7B	118.08(19)
C7A	C2A	C1A	121.47(18)	C7B	C2B	C1B	122.45(17)
C4A	C3A	C2A	121.1(2)	C4B	C3B	C2B	121.51(19)
C5A	C4A	C3A	118.3(2)	C5B	C4B	C3B	118.19(19)
F1A	C5A	C6A	117.7(2)	F1B	C5B	C4B	118.90(19)
C4A	C5A	F1A	119.2(2)	F1B	C5B	C6B	118.3(2)
C4A	C5A	C6A	123.1(2)	C4B	C5B	C6B	122.8(2)
C5A	C6A	C7A	118.2(2)	C5B	C6B	C7B	118.4(2)
C6A	C7A	C2A	120.87(19)	C6B	C7B	C2B	120.95(18)
N1A	C8A	C9A	105.70(18)	N1B	C8B	C9B	105.02(18)
C8A	C9A	C10A	105.56(18)	C10B	C9B	C8B	106.32(17)

C11A	C10A	C9A	103.29(19)	C11B	C10B	C9B	105.14(19)
N1A	C11A	C10A	102.72(17)	N1B	C11B	C10B	104.62(17)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for jb120817_1_1.

Atom	*x*	*y*	*z*	U(eq)
H1A	3570(20)	4635(19)	3663(11)	31
H1AA	4971	5366	2557	32
H3A	4038	5203	1492	39
H4A	2811	4221	691	46
H6A	1837	1817	2127	41
H7A	3103	2769	2923	36
H8AA	5077	6619	3522	38
H8AB	4950	5785	4174	38
H9AA	3661	7842	3945	48
H9AB	3552	7020	4604	48
H10A	1921	6003	4175	46
H10B	1717	7201	3755	46
H11A	1990	5339	3053	37
H11B	2763	6467	2814	37
H1B	7469(18)	3380(20)	4213(11)	27
H1BA	8997	2893	5323	28
H3B	8700	3991	6319	35
H4B	7576	5256	7024	40
H6B	4946	5475	5578	32
H7B	6041	4149	4886	29
H8BA	9639	4507	4548	37
H8BB	8406	5111	4295	37
H9BA	8890	4827	3195	43
H9BB	10236	4547	3453	43
H10C	8544	2911	2967	47
H10D	9962	2687	3088	47
H11C	8416	1663	3873	41
H11D	9678	2107	4185	41

6.4 X-ray crystallography data for α-aminotrifluoroborate 36

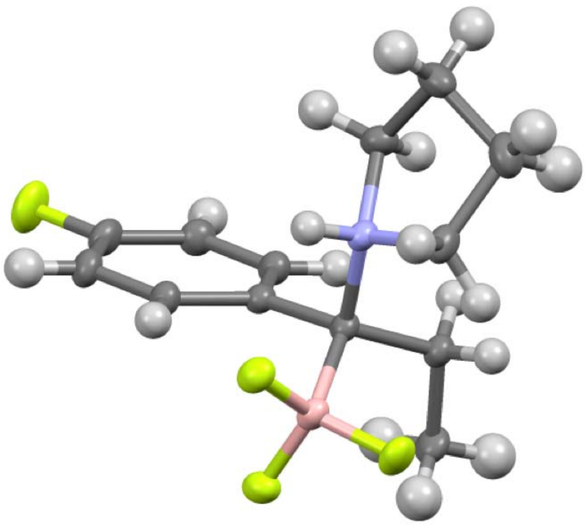


Figure 1 X-ray crystal structure for α-aminotrifluoroborate 36

Experimental

A suitable crystal of $C_{13}H_{18}BF_4N$ (jb190917_2_1) was selected and measured on a XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2 [J. Appl. Cryst. 42, 339-341], the structure was solved with the XT [Acta Cryst. A71, 3-8] structure solution program using Intrinsic Phasing and refined with the XL [Acta Cryst. A64, 112-122] refinement package using Least Squares minimisation.

Table 1 Crystal data and structure refinement for jb190917_2_1.

Identification code	jb190917_2_1
Empirical formula	$C_{13}H_{18}BF_4N$
Formula weight	275.09
Temperature/K	100.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.48310(10)
b/Å	8.79060(10)
c/Å	17.8568(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1331.61(3)
Z	4
ρ_{calc}g/cm^3	1.372

μ/mm^{-1}	1.017
F(000)	576.0
Crystal size/mm^3	0.163 × 0.094 × 0.039
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.906 to 159.426
Index ranges	-9 ≤ h ≤ 10, -11 ≤ k ≤ 10, -22 ≤ l ≤ 22
Reflections collected	27419
Independent reflections	2884 [R_{int} = 0.0396, R_{sigma} = 0.0160]
Data/restraints/parameters	2884/1/176
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0306, wR_2 = 0.0813
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0820
Largest diff. peak/hole / e Å^{-3}	0.30/-0.18
Flack parameter	-0.02(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for jb190917_2_1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	3443.8(12)	3721.4(12)	7386.3(6)	27.0(2)
F2	2216.0(12)	2280.3(12)	6489.9(6)	29.0(3)
F3	3877.5(14)	1164.3(12)	7325.6(6)	31.8(3)
F4	3747.3(16)	7208.9(13)	4098.8(7)	40.4(3)
N1	6388.2(17)	3607.7(16)	6798.8(8)	20.6(3)
C1	4713(2)	3927.3(18)	5696.3(9)	20.4(3)
C2	5353(2)	3841(2)	4975.5(9)	23.7(4)
C3	5839(2)	1295.2(19)	6018.9(10)	22.8(3)
C4	3703(2)	5152.2(19)	5850.6(10)	23.4(3)
C5	5128(2)	2787.4(18)	6316.5(9)	19.7(3)
C6	5032(2)	4937(2)	4436.1(10)	26.5(4)
C7	7008(2)	2732(2)	7477.4(10)	26.6(4)
C8	4056(2)	6129(2)	4621.6(10)	28.0(4)
C9	3375(2)	6261(2)	5318.3(10)	27.6(4)
C10	7820(2)	4213(2)	6391.3(11)	27.5(4)
C11	9088(2)	4277(2)	6981.9(13)	33.0(4)
C12	4648(2)	319(2)	5592.1(11)	28.3(4)
C13	8789(2)	2807(3)	7412.6(12)	36.9(5)
B1	3612(2)	2486(2)	6887.5(11)	22.7(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for jb190917_2_1. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	32.3(5)	23.1(5)	25.5(5)	-3.5(4)	5.9(4)	-1.5(4)
F2	23.8(5)	27.0(5)	36.3(6)	-3.4(5)	1.8(4)	-3.9(4)
F3	37.5(6)	22.3(5)	35.5(6)	9.6(4)	7.6(5)	0.0(4)

F4	58.9(8)	29.1(6)	33.1(6)	13.2(5)	-0.1(6)	9.4(6)
N1	23.6(7)	15.8(6)	22.3(6)	0.3(5)	-1.0(6)	-0.8(6)
C1	21.5(8)	17.1(8)	22.7(8)	-0.5(6)	-1.3(6)	-1.1(6)
C2	24.9(8)	20.3(8)	25.8(8)	-1.0(7)	0.7(6)	1.1(7)
C3	25.9(8)	16.6(7)	25.8(8)	-0.2(6)	-0.4(7)	1.1(7)
C4	26.4(8)	19.8(8)	24.1(8)	-1.0(6)	0.5(7)	2.4(7)
C5	22.0(8)	15.4(7)	21.8(7)	-1.5(6)	-2.5(6)	-0.4(6)
C6	29.9(9)	26.4(9)	23.2(8)	2.1(7)	1.0(7)	-0.3(8)
C7	36.2(10)	20.2(8)	23.2(8)	0.4(7)	-7.5(7)	1.7(7)
C8	35(1)	20.9(8)	28.1(9)	5.9(7)	-4.8(7)	-0.2(8)
C9	32.8(9)	18.5(7)	31.5(9)	-0.3(7)	-2.3(7)	4.4(7)
C10	24.8(9)	25.4(9)	32.2(9)	1.0(7)	1.3(7)	-5.1(7)
C11	21.7(9)	31.9(9)	45.3(11)	-10.5(8)	-2.1(8)	-0.6(7)
C12	34(1)	18.8(8)	32.3(9)	-6.4(7)	-3.0(8)	0.8(7)
C13	34.6(10)	35.5(11)	40.7(11)	-2.1(9)	-10.5(9)	8.9(8)
B1	25.7(9)	17.4(9)	25.0(9)	1.1(7)	3.5(7)	-0.8(7)

Table 4 Bond Lengths for jb190917_2_1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.412(2)	C2	C6	1.389(2)
F2	B1	1.392(2)	C3	C5	1.538(2)
F3	B1	1.419(2)	C3	C12	1.529(2)
F4	C8	1.357(2)	C4	C9	1.389(2)
N1	C5	1.551(2)	C5	B1	1.662(2)
N1	C7	1.529(2)	C6	C8	1.376(3)
N1	C10	1.512(2)	C7	C13	1.516(3)
C1	C2	1.399(2)	C8	C9	1.377(3)
C1	C4	1.403(2)	C10	C11	1.507(3)
C1	C5	1.535(2)	C11	C13	1.525(3)

Table 5 Bond Angles for jb190917_2_1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N1	C5	116.31(13)	C8	C6	C2	118.62(16)
C10	N1	C5	116.74(13)	C13	C7	N1	105.09(15)
C10	N1	C7	106.38(14)	F4	C8	C6	118.90(17)
C2	C1	C4	117.34(16)	F4	C8	C9	118.80(17)
C2	C1	C5	122.65(15)	C6	C8	C9	122.30(17)
C4	C1	C5	119.96(14)	C8	C9	C4	118.36(17)
C6	C2	C1	121.61(16)	C11	C10	N1	104.45(15)
C12	C3	C5	113.07(15)	C10	C11	C13	101.68(16)
C9	C4	C1	121.75(16)	C7	C13	C11	103.95(16)
N1	C5	B1	105.48(13)	F1	B1	F3	107.35(14)
C1	C5	N1	104.80(12)	F1	B1	C5	110.03(13)
C1	C5	C3	113.41(13)	F2	B1	F1	109.62(14)
C1	C5	B1	111.67(14)	F2	B1	F3	108.05(14)

C3	C5	N1	108.55(13)	F2	B1	C5	111.45(14)
C3	C5	B1	112.29(14)	F3	B1	C5	110.23(14)

Table 6 Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for jb190917_2_1.

Atom	*x*	*y*	*z*	U(eq)
H1	5890(20)	4420(20)	7012(12)	25
H2	6008.6	3029.53	4854.39	28
H3A	6713.8	1533.85	5689.62	27
H3B	6250.08	713.06	6436.91	27
H4	3241.86	5224.1	6321.65	28
H6	5468.86	4867.14	3959.61	32
H7A	6655.2	3201.56	7939.5	32
H7B	6647.64	1685.22	7466.95	32
H9	2711.24	7071.48	5429.9	33
H10A	8122.19	3537.77	5986.18	33
H10B	7614.8	5216.17	6187.63	33
H11A	8966.05	5161.94	7301.17	40
H11B	10131.18	4286.68	6759.86	40
H12A	4249.77	880.29	5171.62	43
H12B	3791.2	54.27	5918.56	43
H12C	5154.33	-591.85	5418.34	43
H13A	9195.13	1935.75	7141	44
H13B	9277.02	2842.24	7903.48	44

6.5 X-ray crystallography data for α-aminotrifluoroborate 48

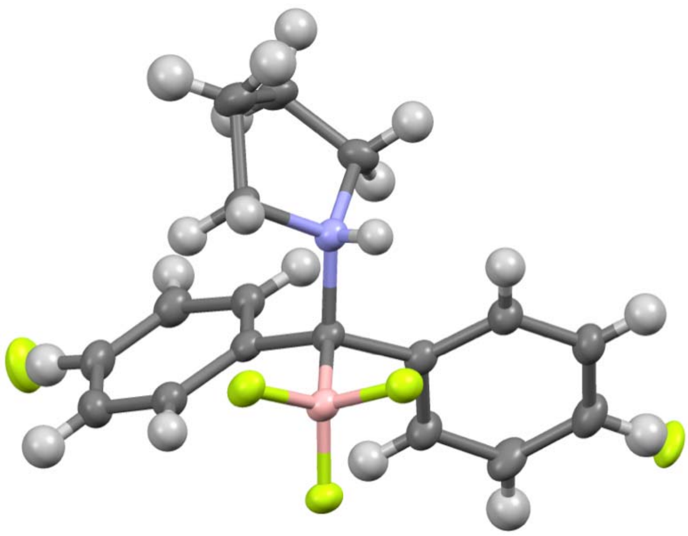


Figure 1 X-ray crystal structure for α-aminotrifluoroborate 48

Experimental

A suitable crystal of $C_{17}H_{18}BF_4N$ (jb110817_1_1) was selected and measured on a XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer. The crystal was kept at 100.0(1) K during data collection. Using Olex2 [J. Appl. Cryst. 42, 339-341], the structure was solved with the XT [Acta Cryst. A71, 3-8] structure solution program using Intrinsic Phasing and refined with the XL [Acta Cryst. A64, 112-122] refinement package using Least Squares minimisation.

Table 1 Crystal data and structure refinement for jb110817_1_1.

Identification code	jb110817_1_1
Empirical formula	$C_{35.5}H_{39}B_2F_8N_2O_{0.5}$
Formula weight	675.30
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.15540(10)
b/Å	14.81710(10)
c/Å	24.1310(2)
α/°	90
β/°	93.9310(10)
γ/°	90
Volume/Å^3	3265.82(5)
Z	4
ρ_{calc}g/cm^3	1.373
μ/mm^{-1}	0.953
F(000)	1408.0
Crystal size/mm^3	0.144 × 0.114 × 0.099
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.006 to 158.208
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -30 ≤ l ≤ 30
Reflections collected	7917
Independent reflections	7917 [R_{int} = ?, R_{sigma} = 0.0187]
Data/restraints/parameters	7917/154/515
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1196
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.1250
Largest diff. peak/hole / e Å^{-3}	0.29/-0.41

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for jb110817_1_1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F3A	6118.5(10)	6713.6(6)	6229.3(4)	28.3(2)
F4A	6332.6(10)	5934.7(6)	5427.4(4)	30.6(2)
F5A	7312(1)	7342.6(6)	5515.0(4)	29.9(2)
N1A	3329.9(14)	6653.2(8)	5599.3(5)	24.4(3)
C1A	1756.9(18)	7002.4(12)	5578.4(7)	31.4(4)
C3A	1643(2)	5488.3(13)	5264.9(9)	39.9(4)
C4A	3251.1(18)	5740.4(10)	5304.3(7)	28.7(3)
C5A	4559.5(17)	7286.4(10)	5417.6(6)	24.4(3)
C6A	4497.0(18)	8175.4(10)	5737.9(6)	25.5(3)
C7A	3961.9(19)	8249.5(11)	6264.3(7)	29.1(3)
C8A	4045(2)	9060.0(11)	6557.5(7)	32.3(4)
C9A	4684(2)	9802.6(11)	6330.6(7)	35.0(4)
C10A	5239(2)	9746.0(11)	5814.7(7)	36.2(4)
C11A	5148(2)	8939.5(11)	5521.2(7)	30.2(4)
C12A	4360.8(17)	7437.8(10)	4789.4(6)	24.9(3)
C13A	3189.8(18)	7944.0(11)	4554.1(6)	28.1(3)
C14A	2969(2)	8061.0(11)	3983.0(7)	31.9(4)
C15A	3968(2)	7695.8(12)	3647.9(7)	34.0(4)
C16A	5174(2)	7222.5(12)	3862.6(7)	33.8(4)
C17A	5357.4(19)	7087.5(11)	4432.9(7)	29.6(3)
B1A	6141(2)	6803.5(12)	5639.9(7)	25.5(4)
F1A	3752.5(19)	7783.0(11)	3102.7(5)	48.4(5)
C2A	896(3)	6434.3(16)	5174.2(10)	33.5(6)
F1B	4810(5)	10550(2)	6619.8(15)	36.6(11)
C2B	856(8)	6083(4)	5634(3)	41.8(17)
F3C	1983.6(10)	5255.1(7)	7290.0(4)	37.1(2)
F4C	3162.0(11)	4661.6(6)	6570.2(4)	35.3(2)
F5C	3243.1(10)	6167.2(6)	6721.2(4)	29.8(2)
N1C	6012.8(14)	5438.4(9)	7059.4(6)	26.4(3)
C1C	7496.8(18)	5687.7(13)	7346.4(8)	36.1(4)
C2C	8535(2)	4959.2(17)	7174.2(9)	49.0(5)
C3C	7936(2)	4732.4(15)	6586.4(8)	42.8(4)
C4C	6309.3(19)	4686.5(11)	6652.7(7)	32.1(4)
C5C	4714.6(17)	5253.8(10)	7423.4(6)	25.5(3)
C6C	4599.1(18)	6039.8(11)	7828.4(7)	29.4(3)
C7C	4935(2)	6930.2(12)	7690.9(8)	35.6(4)
C8C	4669(2)	7641.4(13)	8046.9(9)	44.4(5)
C9C	4072(2)	7476.0(14)	8539.3(9)	47.7(5)
C10C	3701(2)	6613.9(15)	8687.6(9)	47.8(5)
C11C	3967(2)	5900.6(13)	8330.5(8)	37.8(4)
C12C	4955.0(18)	4349.8(11)	7722.8(7)	27.6(3)
C13C	6074(2)	4236.0(12)	8142.2(7)	34.7(4)
C14C	6330(2)	3404.7(13)	8400.0(8)	41.0(4)
C15C	5431(2)	2688.3(12)	8250.1(8)	40.9(4)
C16C	4292(2)	2778.0(12)	7850.6(8)	38.5(4)
C17C	4064.6(19)	3611.1(11)	7586.1(7)	31.0(3)
B1C	3216(2)	5309.5(12)	6992.6(8)	27.3(4)
F1C	3906(2)	8162.8(14)	8902.0(9)	59.4(7)

F1D	5521(3)	1845.5(16)	8461.8(11)	37.8(8)
C1E	197(7)	9888(5)	5048(3)	66.5(14)
O1F	835(11)	9534(6)	5450(4)	47(3)
C2F	-1507(9)	9729(6)	4874(5)	28(2)
C3F	540(20)	10744(9)	4713(7)	44(4)
O1E	1216(7)	9382(4)	5109(4)	80(3)
C2E	-1317(9)	9671(5)	5197(5)	52(2)
C3E	325(9)	10894(5)	4855(4)	34.2(19)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for jb110817_1_1. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F3A	27.9(5)	29.7(5)	26.9(4)	3.6(3)	-1.4(4)	-1.8(4)
F4A	27.2(5)	25.1(4)	38.9(5)	-4.8(4)	-2.9(4)	1.9(4)
F5A	26.2(5)	32.5(5)	30.9(5)	-1.0(4)	0.4(4)	-7.3(4)
N1A	24.3(7)	21.8(6)	26.6(6)	-1.4(5)	-0.6(5)	-0.2(5)
C1A	23.5(8)	33.5(8)	37.4(8)	2.9(7)	3.5(7)	2.7(7)
C3A	27.7(9)	38.5(9)	53.3(11)	-10.3(8)	0.8(8)	-6.5(7)
C4A	27.3(8)	22.8(7)	35.7(8)	-6.2(6)	-0.2(6)	-3.7(6)
C5A	25.9(8)	21.5(7)	25.8(7)	-1.2(5)	0.5(6)	-3.2(6)
C6A	27.6(8)	22.4(7)	25.8(7)	-0.4(6)	-3.4(6)	0.6(6)
C7A	33.3(9)	24.5(7)	29.5(8)	-1.0(6)	0.7(6)	-1.2(6)
C8A	38.1(10)	29.7(8)	29.0(8)	-5.5(6)	0.6(7)	1.0(7)
C9A	43.9(11)	24.2(8)	35.6(9)	-6.1(6)	-6.7(8)	0.2(7)
C10A	49.5(11)	22.8(8)	34.9(9)	3.1(6)	-6.5(8)	-7.3(7)
C11A	38.4(10)	24.7(8)	26.9(7)	1.1(6)	-2.0(7)	-3.7(7)
C12A	27.0(8)	20.7(7)	26.7(7)	-1.8(5)	-1.1(6)	-4.7(6)
C13A	30.4(8)	25.0(7)	28.7(7)	-2.3(6)	1.3(6)	-0.4(6)
C14A	35.2(9)	28.2(8)	31.3(8)	1.0(6)	-5.5(7)	-0.7(7)
C15A	41.6(10)	34.8(9)	24.9(7)	-1.6(6)	-2.4(7)	-3.6(7)
C16A	34.8(10)	37.4(9)	29.6(8)	-4.5(7)	4.6(7)	-2.1(7)
C17A	28.9(9)	29.9(8)	29.6(8)	-2.4(6)	-0.4(6)	-0.7(6)
B1A	24.9(9)	23.8(8)	27.2(8)	-1.5(6)	-1.3(7)	-1.9(7)
F1A	59.9(11)	62.4(10)	22.4(7)	3.7(6)	-0.4(6)	12.5(8)
C2A	21.3(11)	34.8(12)	43.6(13)	-3.2(10)	-2.9(9)	-2.7(9)
F1B	56(3)	19.5(17)	34.0(19)	-10.3(14)	0.9(17)	-4.8(16)
C2B	33(3)	41(3)	51(4)	-2(3)	1(3)	-3(3)
F3C	20.8(5)	48.0(6)	42.5(5)	12.1(5)	1.5(4)	-2.7(4)
F4C	33.6(5)	31.4(5)	39.4(5)	-0.8(4)	-8.7(4)	-1.2(4)
F5C	26.4(5)	28.3(5)	34.3(5)	6.9(4)	-1.3(4)	2.2(4)
N1C	20.9(7)	27.2(6)	30.8(7)	5.5(5)	-1.2(5)	-0.9(5)
C1C	20.9(8)	48.6(10)	38.1(9)	7.6(8)	-3.3(7)	-6.0(7)
C2C	24.9(10)	78.1(15)	43.9(11)	9.1(10)	0.2(8)	10.0(9)
C3C	31.2(10)	56.9(12)	40.9(10)	8.0(9)	6.6(8)	12.5(9)
C4C	32.0(9)	30.2(8)	34.5(8)	3.5(7)	4.7(7)	3.7(7)
C5C	20.8(8)	25.1(7)	30.5(7)	4.1(6)	1.6(6)	-0.3(6)

C6C	21.7(8)	27.9(8)	37.6(9)	-0.8(6)	-4.0(6)	1.4(6)
C7C	36.1(10)	28.7(8)	40.6(9)	-0.3(7)	-8.0(7)	-0.8(7)
C8C	42.2(11)	29.6(9)	58.9(12)	-7.0(8)	-14.0(9)	1.2(8)
C9C	38.9(11)	43.4(11)	59.3(12)	-20.5(9)	-6.9(9)	8.2(9)
C10C	38.0(11)	54.0(12)	52.1(12)	-13.5(9)	7.7(9)	4.0(9)
C11C	31.5(9)	37.2(9)	45.1(10)	-3.9(8)	5.8(8)	0.9(7)
C12C	25.4(8)	27.6(8)	30.1(8)	3.6(6)	4.6(6)	2.9(6)
C13C	33.7(9)	36.4(9)	33.6(8)	7.7(7)	0.5(7)	3.8(7)
C14C	40.9(11)	45.2(10)	37.2(9)	13.4(8)	4.5(8)	14.2(8)
C15C	51.5(12)	30.1(9)	43.7(10)	14.4(7)	21.7(9)	14.2(8)
C16C	46.2(11)	26.3(8)	45.3(10)	5.3(7)	18.8(8)	1.1(7)
C17C	31.1(9)	27.5(8)	35.0(8)	3.0(6)	7.3(7)	0.8(7)
B1C	21.1(9)	26.7(8)	33.8(9)	4.4(7)	-1.2(7)	-0.8(7)
F1C	54.7(14)	51.3(12)	70.4(14)	-30.1(10)	-8.7(10)	13.9(10)
F1D	43.1(16)	26.8(13)	44.9(15)	14.8(10)	14.2(12)	11.4(11)
C1E	64(3)	74(3)	61(3)	9(2)	0(2)	12(2)
O1F	52(5)	40(4)	46(5)	1(3)	-8(4)	1(3)
C2F	32(4)	24(4)	29(5)	-10(4)	6(3)	3(3)
C3F	43(7)	60(6)	33(6)	5(5)	29(5)	11(5)
O1E	66(3)	67(3)	110(6)	10(3)	20(3)	42(3)
C2E	56(4)	37(3)	64(6)	5(3)	23(4)	-5(3)
C3E	24(3)	42(3)	39(4)	12(3)	17(3)	8(2)

Table 4 Bond Lengths for jb110817_1_1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F3A	B1A	1.4299(19)	N1C	C1C	1.527(2)
F4A	B1A	1.4013(19)	N1C	C4C	1.522(2)
F5A	B1A	1.387(2)	N1C	C5C	1.550(2)
N1A	C1A	1.528(2)	C1C	C2C	1.515(3)
N1A	C4A	1.5278(19)	C2C	C3C	1.523(3)
N1A	C5A	1.552(2)	C3C	C4C	1.510(3)
C1A	C2A	1.475(3)	C5C	C6C	1.529(2)
C1A	C2B	1.603(7)	C5C	C12C	1.531(2)
C3A	C4A	1.515(2)	C5C	B1C	1.665(2)
C3A	C2A	1.569(3)	C6C	C7C	1.400(2)
C3A	C2B	1.476(7)	C6C	C11C	1.394(3)
C5A	C6A	1.530(2)	C7C	C8C	1.392(3)
C5A	C12A	1.531(2)	C8C	C9C	1.364(3)
C5A	B1A	1.670(2)	C9C	C10C	1.375(3)
C6A	C7A	1.397(2)	C9C	F1C	1.357(3)
C6A	C11A	1.397(2)	C10C	C11C	1.395(3)
C7A	C8A	1.393(2)	C12C	C13C	1.400(2)
C8A	C9A	1.377(3)	C12C	C17C	1.391(2)
C9A	C10A	1.379(3)	C13C	C14C	1.392(2)
C9A	F1B	1.310(4)	C14C	C15C	1.376(3)
C10A	C11A	1.389(2)	C15C	C16C	1.377(3)
C12A	C13A	1.397(2)	C15C	F1D	1.350(3)

C12A	C17A	1.396(2)	C16C	C17C	1.399(2)
C13A	C14A	1.390(2)	C1E	C1E[1]	0.531(10)
C14A	C15A	1.372(3)	C1E	O1F	1.217(9)
C15A	C16A	1.379(3)	C1E	C2F	1.605(9)
C15A	F1A	1.323(2)	C1E	C3F	1.548(11)
C16A	C17A	1.390(2)	C1E	O1E	1.198(7)
F3C	B1C	1.381(2)	C1E	C2E	1.492(9)
F4C	B1C	1.399(2)	C1E	C3E	1.569(8)
F5C	B1C	1.4307(19)			

[1]-X,2-Y,1-Z

Table 5 Bond Angles for jb110817_1_1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1A	N1A	C5A	119.10(12)	C4C	C3C	C2C	101.91(15)
C4A	N1A	C1A	105.67(12)	C3C	C4C	N1C	104.84(14)
C4A	N1A	C5A	114.56(12)	N1C	C5C	B1C	105.57(12)
N1A	C1A	C2B	101.5(3)	C6C	C5C	N1C	108.50(12)
C2A	C1A	N1A	106.76(15)	C6C	C5C	C12C	112.26(13)
C4A	C3A	C2A	101.61(15)	C6C	C5C	B1C	105.73(13)
C2B	C3A	C4A	109.1(3)	C12C	C5C	N1C	109.33(12)
C3A	C4A	N1A	105.20(13)	C12C	C5C	B1C	115.06(13)
N1A	C5A	B1A	106.25(11)	C7C	C6C	C5C	122.71(15)
C6A	C5A	N1A	108.95(12)	C11C	C6C	C5C	119.62(15)
C6A	C5A	C12A	111.59(12)	C11C	C6C	C7C	117.19(16)
C6A	C5A	B1A	105.55(12)	C8C	C7C	C6C	121.10(18)
C12A	C5A	N1A	109.22(12)	C9C	C8C	C7C	119.96(19)
C12A	C5A	B1A	114.99(13)	C8C	C9C	C10C	120.96(18)
C7A	C6A	C5A	123.68(14)	F1C	C9C	C8C	119.7(2)
C7A	C6A	C11A	117.49(14)	F1C	C9C	C10C	119.2(2)
C11A	C6A	C5A	118.48(14)	C9C	C10C	C11C	119.1(2)
C8A	C7A	C6A	121.27(15)	C6C	C11C	C10C	121.68(18)
C9A	C8A	C7A	119.78(16)	C13C	C12C	C5C	121.41(15)
C8A	C9A	C10A	120.21(15)	C17C	C12C	C5C	120.91(14)
F1B	C9A	C8A	119.2(2)	C17C	C12C	C13C	117.68(15)
F1B	C9A	C10A	120.5(2)	C14C	C13C	C12C	121.46(18)
C9A	C10A	C11A	119.99(16)	C15C	C14C	C13C	119.06(18)
C10A	C11A	C6A	121.24(16)	C14C	C15C	C16C	121.32(16)
C13A	C12A	C5A	121.14(14)	F1D	C15C	C14C	126.5(2)
C17A	C12A	C5A	121.15(14)	F1D	C15C	C16C	112.2(2)
C17A	C12A	C13A	117.70(14)	C15C	C16C	C17C	119.12(18)
C14A	C13A	C12A	121.70(16)	C12C	C17C	C16C	121.31(17)
C15A	C14A	C13A	118.53(16)	F3C	B1C	F4C	110.44(14)
C14A	C15A	C16A	121.87(15)	F3C	B1C	F5C	109.27(13)
F1A	C15A	C14A	119.18(17)	F3C	B1C	C5C	109.90(13)
F1A	C15A	C16A	118.93(17)	F4C	B1C	F5C	106.09(13)
C15A	C16A	C17A	118.97(16)	F4C	B1C	C5C	114.04(14)

C16A	C17A	C12A	121.14(16)	F5C	B1C	C5C	106.88(13)
F3A	B1A	C5A	106.77(13)	C1E[1]	C1E	O1F	153(2)
F4A	B1A	F3A	106.80(12)	C1E[1]	C1E	C2F	50.2(15)
F4A	B1A	C5A	113.82(13)	C1E[1]	C1E	C3F	54.5(15)
F5A	B1A	F3A	109.50(12)	C1E[1]	C1E	O1E	161(2)
F5A	B1A	F4A	109.34(14)	C1E[1]	C1E	C2E	68.0(15)
F5A	B1A	C5A	110.46(13)	C1E[1]	C1E	C3E	48.6(15)
C1A	C2A	C3A	102.08(17)	O1F	C1E	C2F	123.4(8)
C3A	C2B	C1A	100.4(4)	O1F	C1E	C3F	131.6(10)
C1C	N1C	C5C	118.59(12)	C3F	C1E	C2F	102.4(8)
C4C	N1C	C1C	106.09(13)	O1E	C1E	C2E	124.3(7)
C4C	N1C	C5C	114.45(12)	O1E	C1E	C3E	123.9(7)
C2C	C1C	N1C	104.99(15)	C2E	C1E	C3E	111.5(5)
C1C	C2C	C3C	102.70(15)				

[1]-X,2-Y,1-Z

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for jb110817_1_1.

Atom	*x*	*y*	*z*	U(eq)
H1A	3600(20)	6526(13)	5962(6)	29
H1AA	1363	6957	5949	38
H1AB	1719	7642	5460	38
H1AC	1485	7312	5223	38
H1AD	1606	7419	5890	38
H3AA	1357	5200	5611	48
H3AB	1400	5080	4947	48
H3AC	1231	5556	4877	48
H3AD	1528	4851	5376	48
H4AA	3623	5789	4930	34
H4AB	3837	5283	5520	34
H7A	3533	7737	6426	35
H8A	3662	9100	6913	39
H9A	4743	10356	6530	42
H10A	5683	10259	5660	43
H11A	5535	8907	5166	36
H13A	2527	8215	4790	34
H14A	2146	8387	3828	38
H15A	3823	7771	3257	41
H16A	5869	6992	3624	41
H17A	6175	6751	4583	35
H2AA	973	6653	4790	40
H2AB	-149	6415	5256	40
H2BA	918	5857	6021	50
H2BB	-185	6156	5502	50
H1C	5740(20)	5925(12)	6833(7)	32
H1CA	7817	6289	7223	43

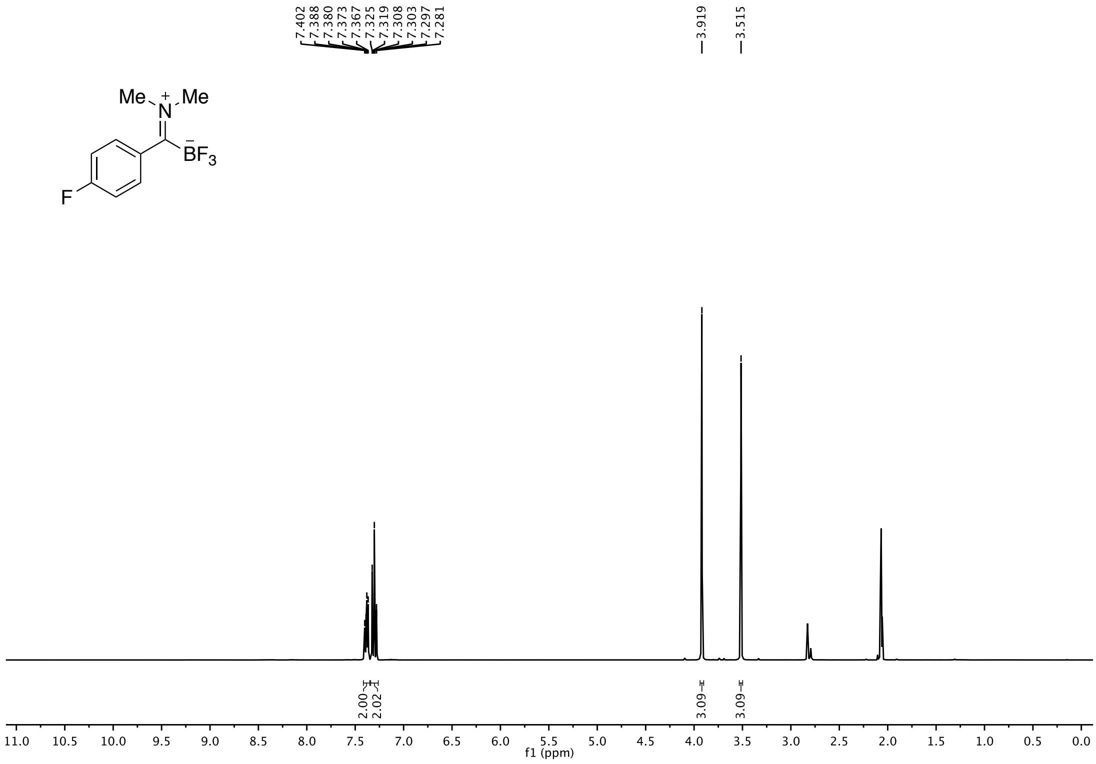
H1CB	7447	5696	7755	43
H2CA	8510	4426	7421	59
H2CB	9552	5187	7178	59
H3CA	8175	5210	6320	51
H3CB	8318	4147	6461	51
H4CA	6036	4093	6802	39
H4CB	5750	4785	6292	39
H7C	5352	7051	7349	43
H8C	4903	8242	7947	53
H9C	3910	7963	8783	57
H10C	3270	6505	9028	57
H11C	3710	5305	8432	45
H13C	6672	4737	8253	42
H14C	7113	3333	8676	49
H15C	5600	2120	8426	49
H16C	3670	2281	7756	46
H17C	3286	3674	7307	37
H2FA	-1780	9112	4971	42
H2FB	-2094	10160	5072	42
H2FC	-1688	9818	4473	42
H3FA	1607	10810	4704	67
H3FB	102	10688	4333	67
H3FC	142	11275	4891	67
H2EA	-1290	9148	5446	78
H2EB	-1727	10190	5384	78
H2EC	-1931	9532	4859	78
H3EA	1331	11106	4935	51
H3EB	70	10935	4454	51
H3EC	-346	11271	5054	51

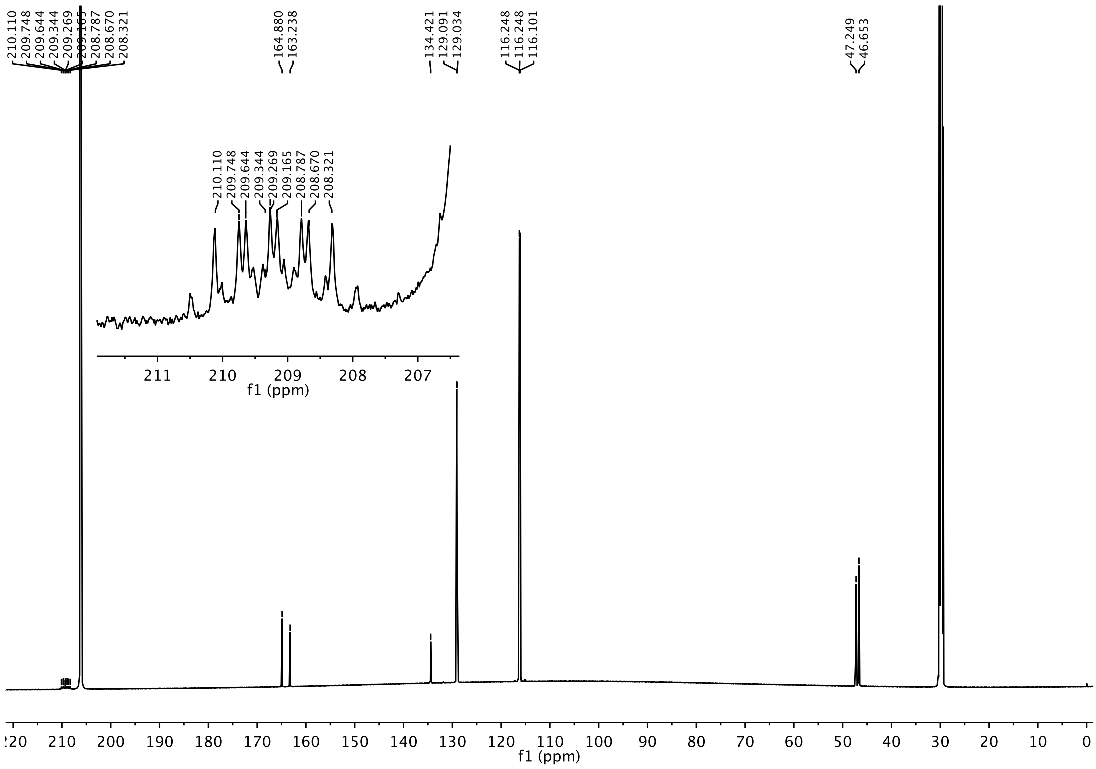
Table 7 Atomic Occupancy for jb110817_1_1.

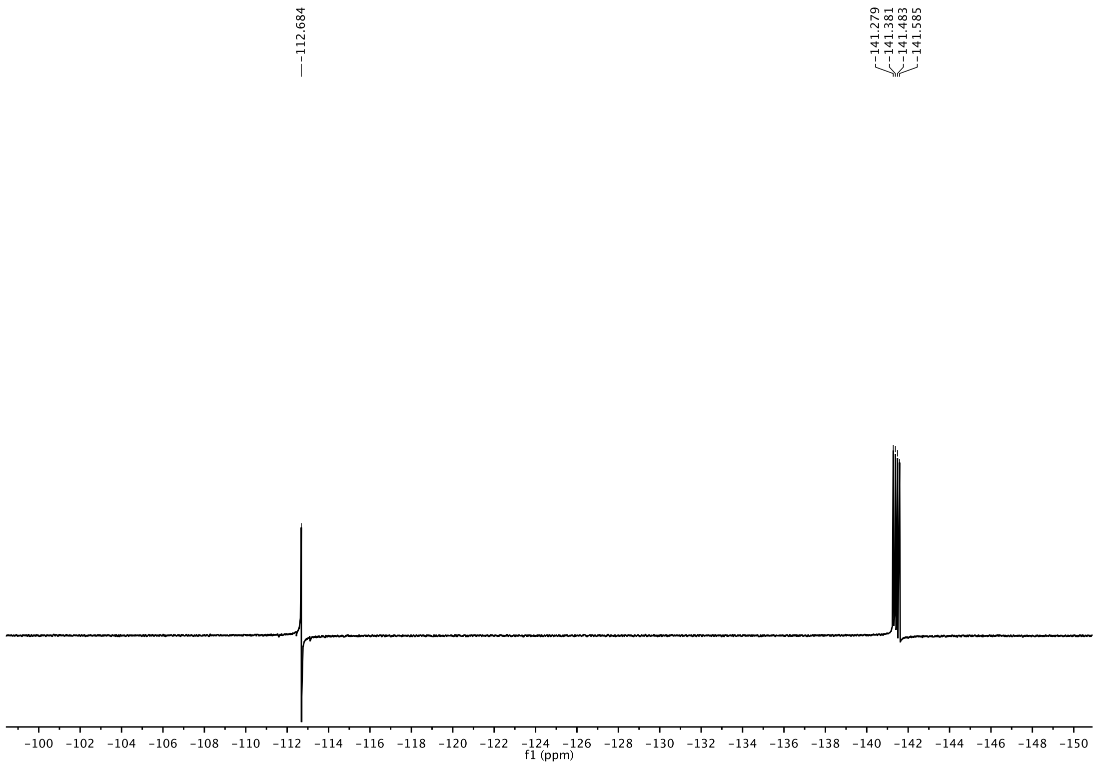
Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H1AA	0.733(3)	H1AB	0.733(3)	H1AC	0.267(3)
H1AD	0.267(3)	H3AA	0.733(3)	H3AB	0.733(3)
H3AC	0.267(3)	H3AD	0.267(3)	H9A	0.733(3)
H15A	0.267(3)	F1A	0.733(3)	C2A	0.733(3)
H2AA	0.733(3)	H2AB	0.733(3)	F1B	0.267(3)
C2B	0.267(3)	H2BA	0.267(3)	H2BB	0.267(3)
H9C	0.395(3)	H15C	0.605(3)	F1C	0.605(3)
F1D	0.395(3)	C1E	0.5	O1F	0.182(6)
C2F	0.182(6)	H2FA	0.182(6)	H2FB	0.182(6)
H2FC	0.182(6)	C3F	0.182(6)	H3FA	0.182(6)
H3FB	0.182(6)	H3FC	0.182(6)	O1E	0.318(6)
C2E	0.318(6)	H2EA	0.318(6)	H2EB	0.318(6)
H2EC	0.318(6)	C3E	0.318(6)	H3EA	0.318(6)
H3EB	0.318(6)	H3EC	0.318(6)		

7 NMR Spectra

7.1 Trifluoroborate-iminiums (TIMs)



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−141.585
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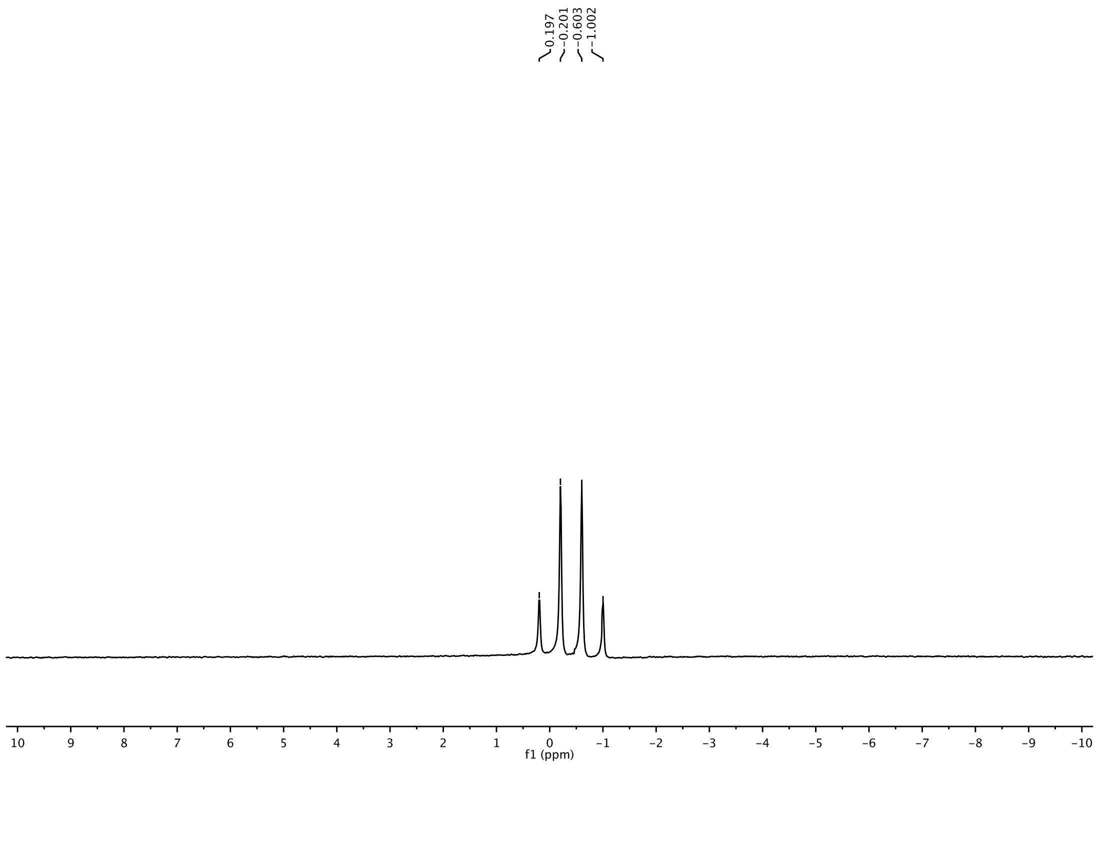
f1 (ppm)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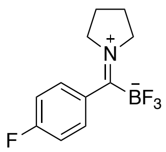
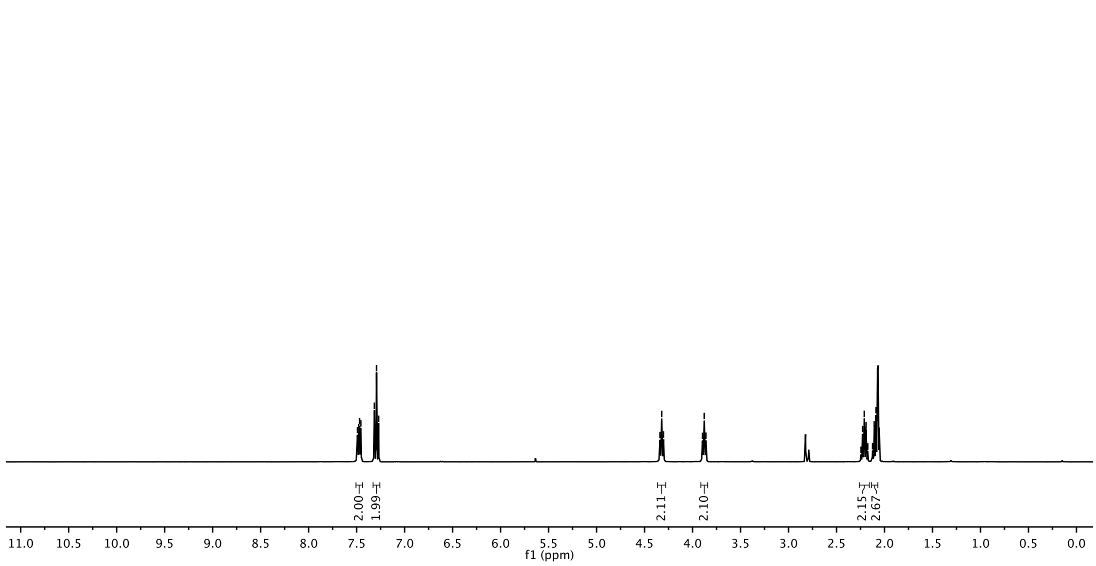

N
+
BF3
F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7.292
7.287
7.286
7.276
7.270
4.339
4.321
4.303
3.896
3.878
3.860
2.246
2.228
2.211
2.195
2.192
2.177
2.174
2.125
2.122
2.107
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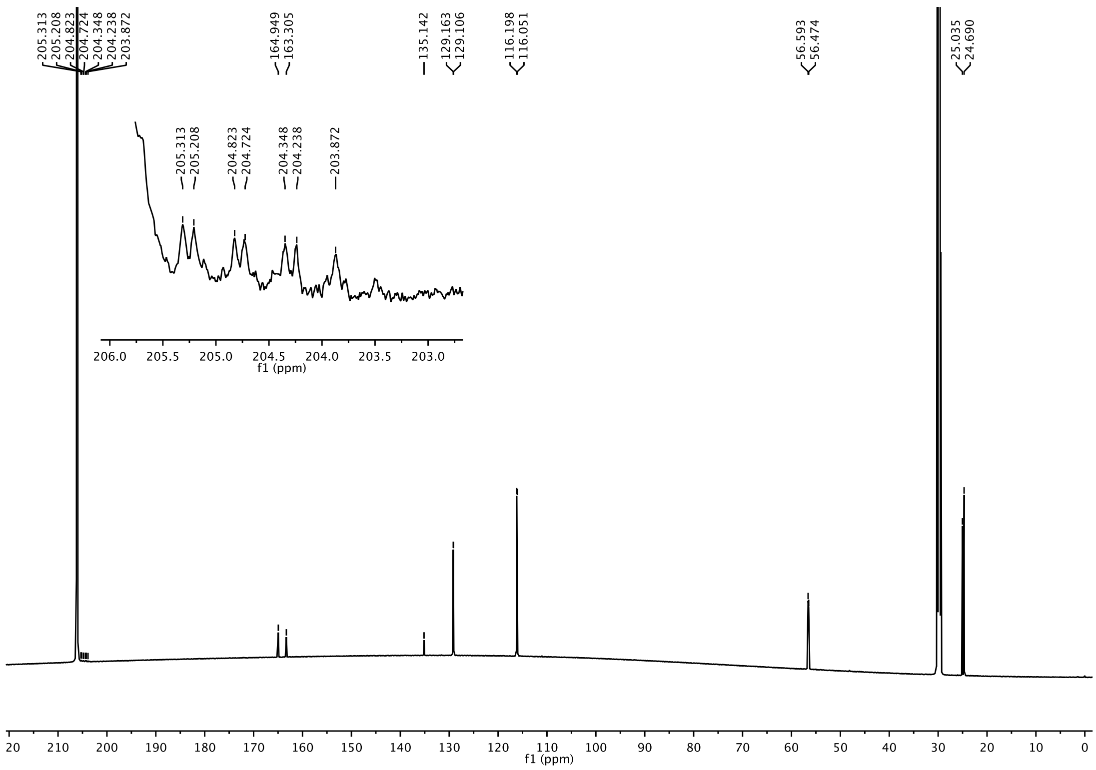
2.00
1.99
2.11
2.10
2.15
2.67
f1 (ppm)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24.690
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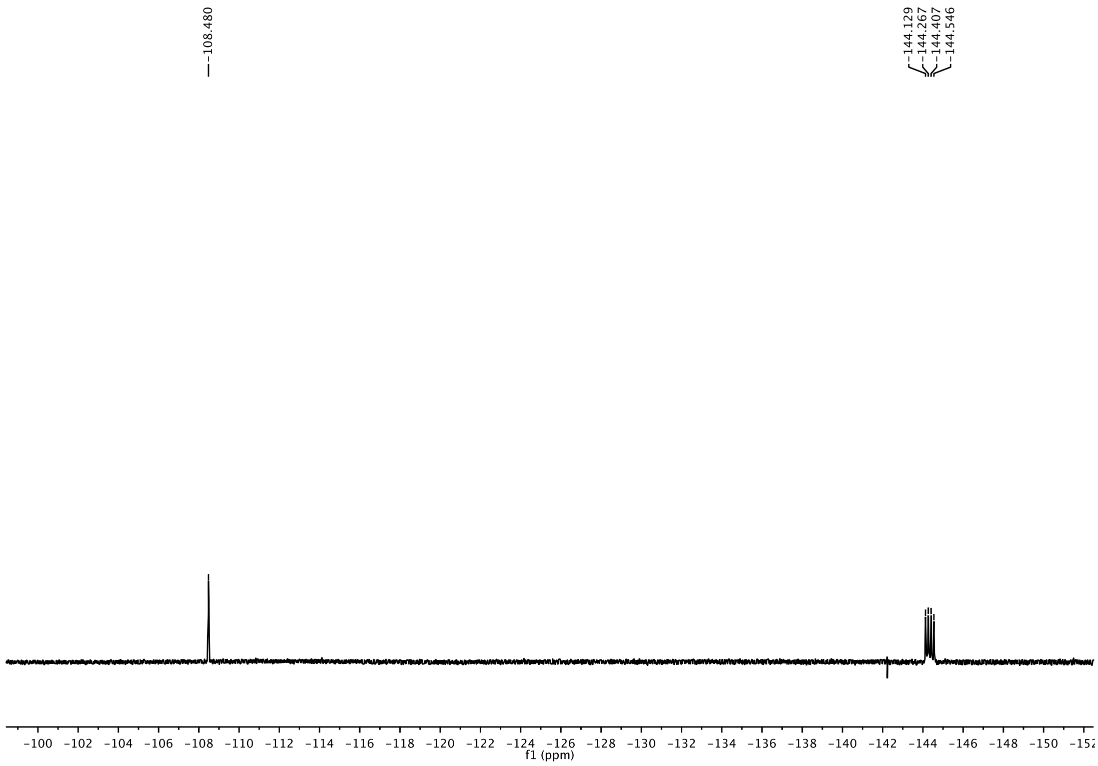
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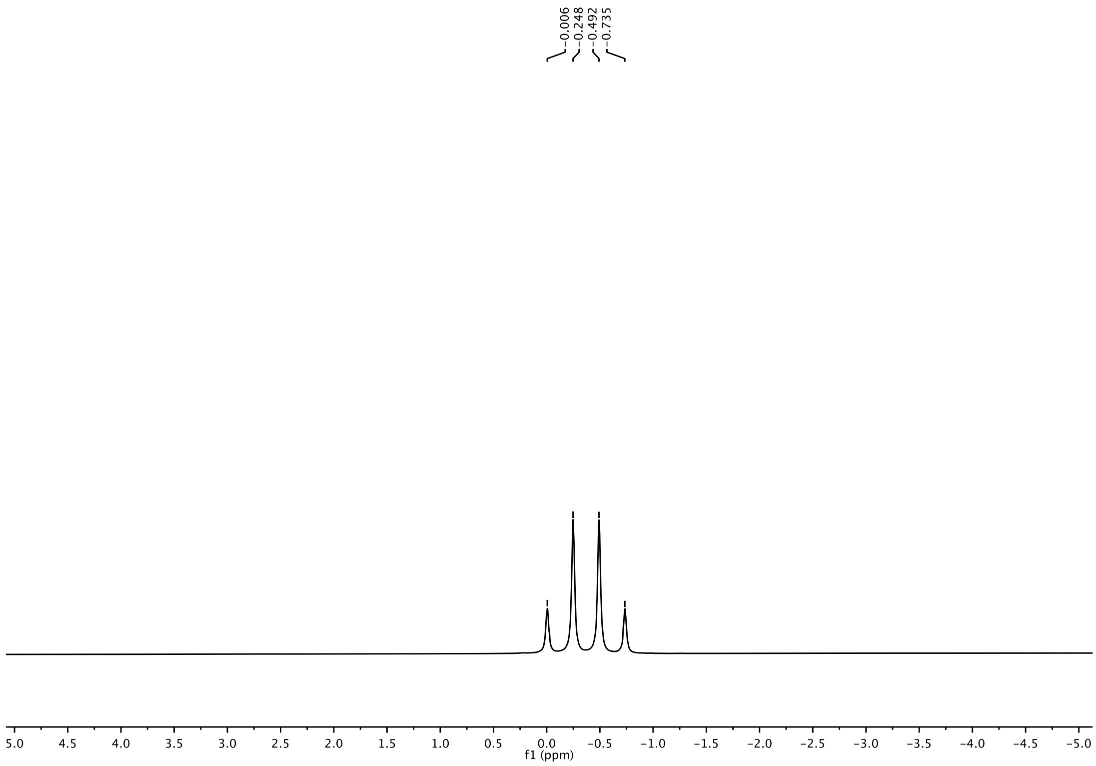
f1 (ppm)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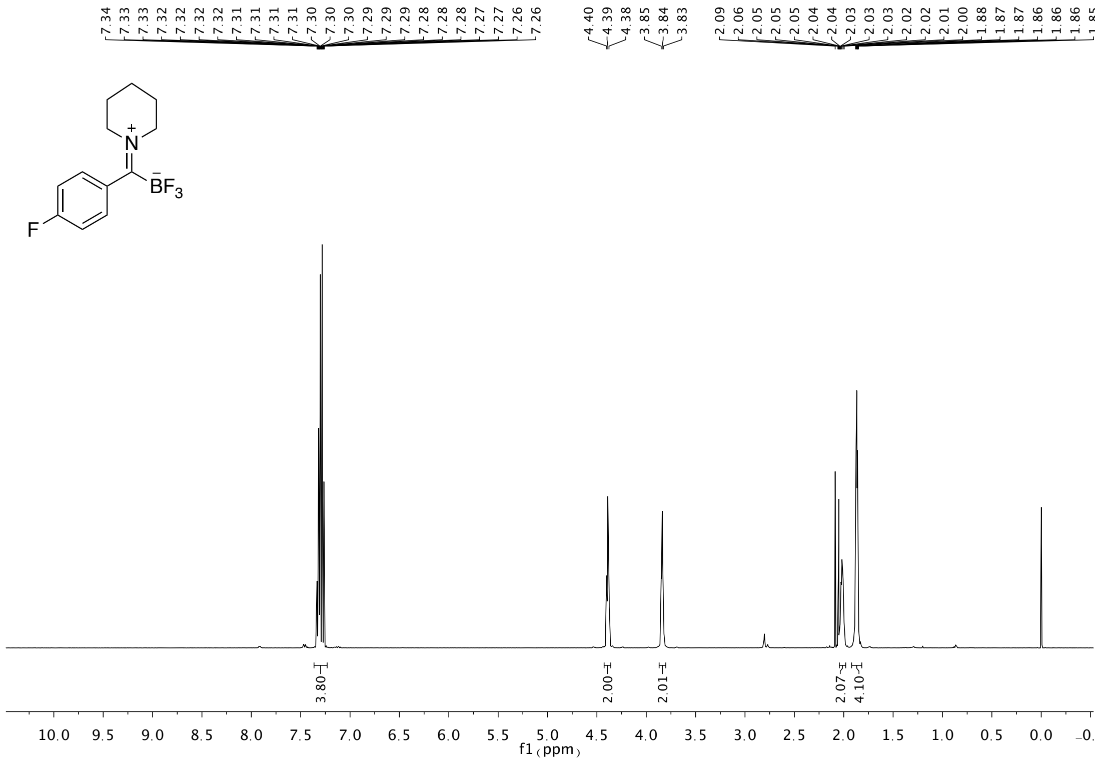
f1 (ppm)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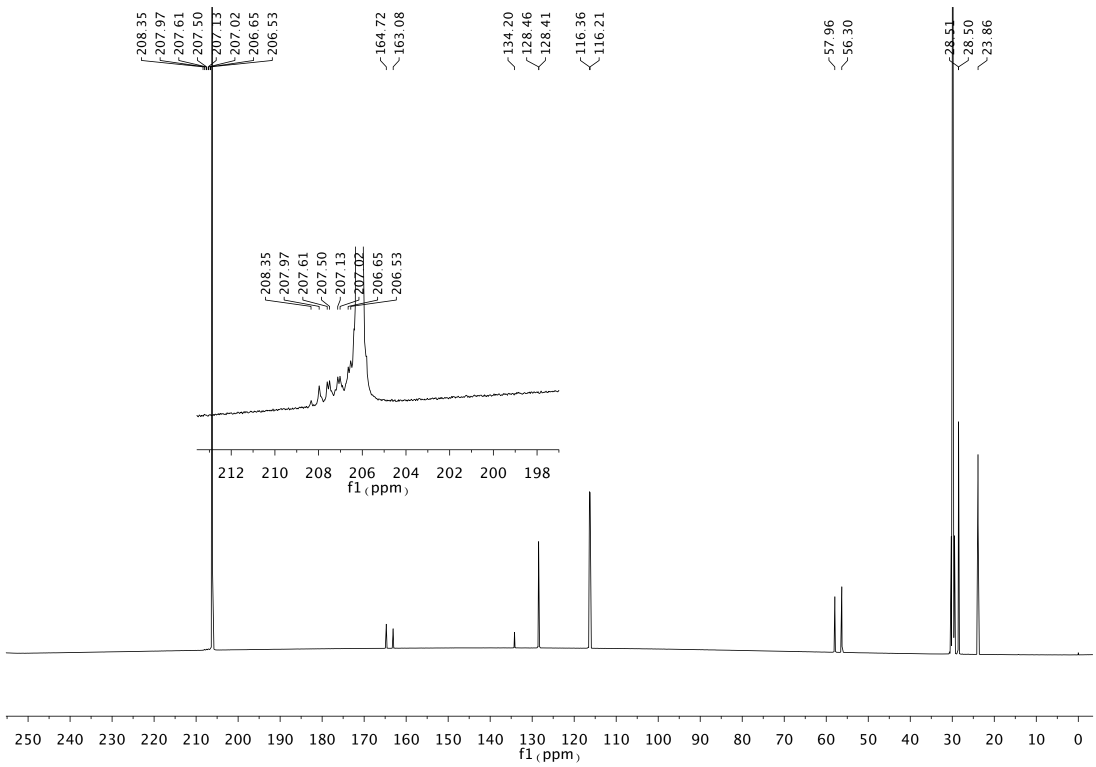
4.40 4.39 4.38 3.85 3.84 3.83
2.09 2.06 2.05 2.05 2.05 2.04 2.04 2.04 2.03 2.03 2.03 2.02 2.02 2.01 2.00 1.88 1.87 1.87 1.86 1.86
N
BF3
F
3.80
2.00
2.01
2.07
4.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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164.72 163.08
134.20 128.46 128.41
116.36 116.21
57.96 56.30
28.51 28.50 23.86
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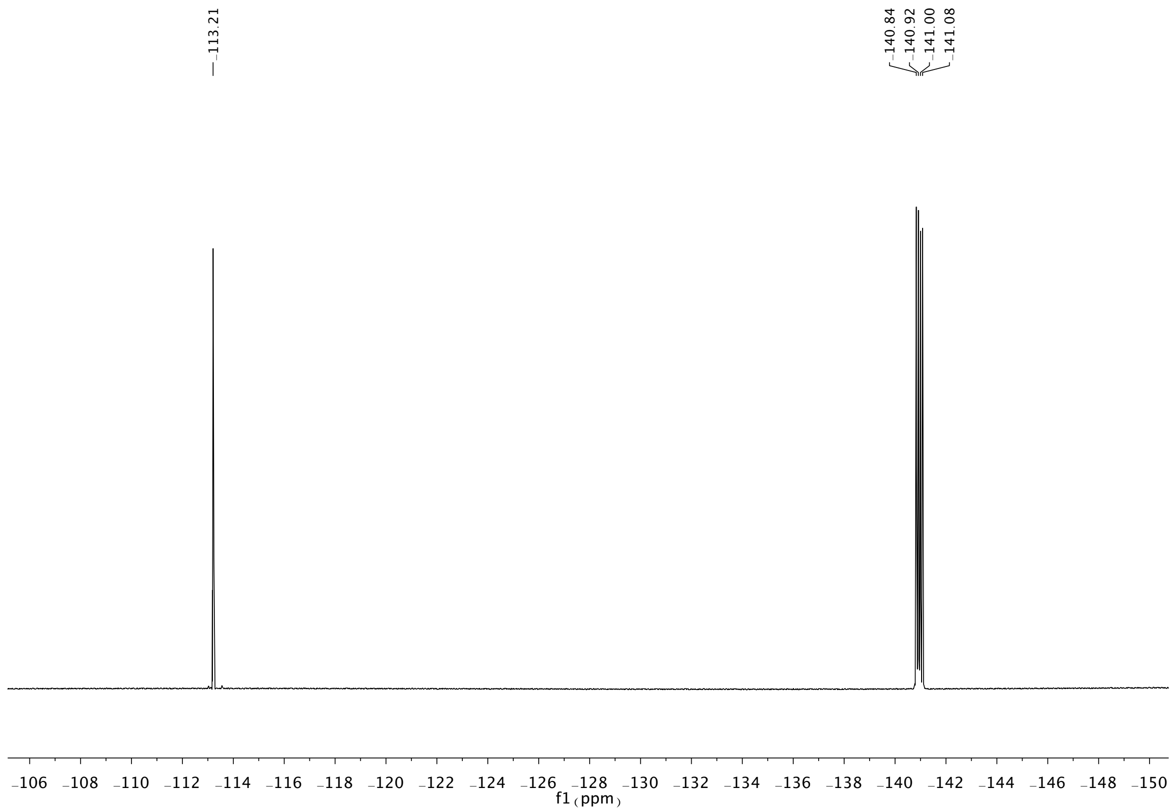
f1 (ppm)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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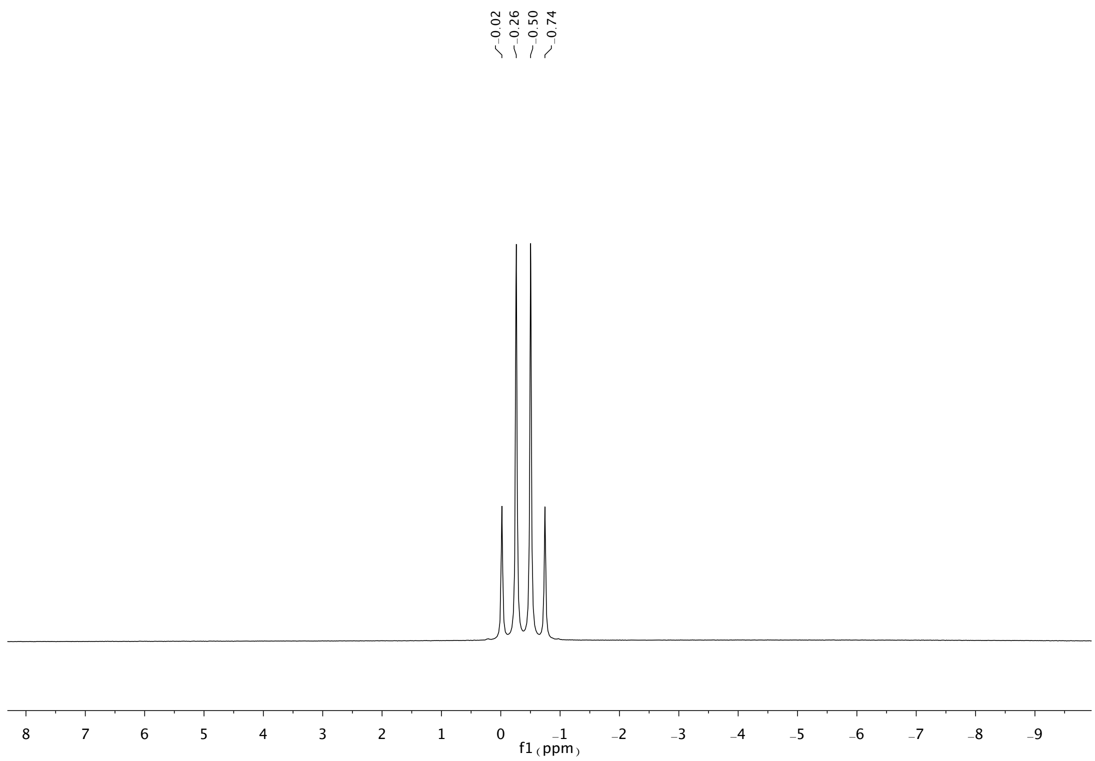
f1 (ppm)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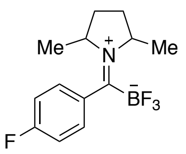
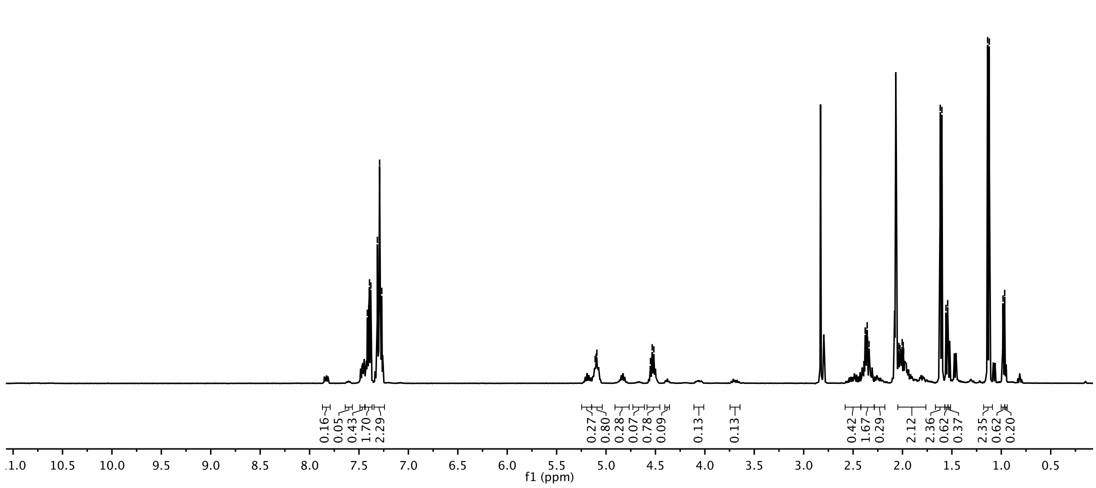

Me
Me
N
BF3
F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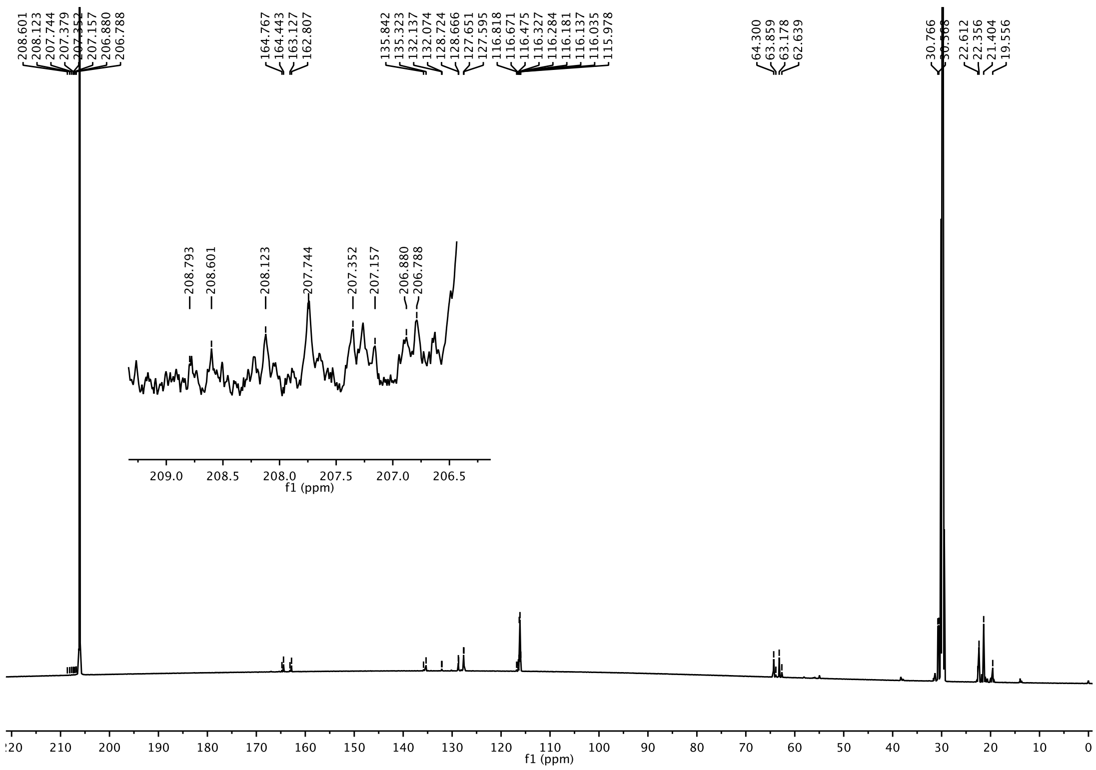
5.110 5.100 5.093
4.550 4.533 4.516
2.378 2.374 2.370 2.363 2.360 2.357 2.354 2.339 2.045 2.036 2.025 2.021 2.017 2.015 2.004 1.993 1.989
1.618 1.601 1.560 1.543 1.139 1.122 0.983 0.968 0.966
0.16 0.05 0.43 1.70 2.29
0.27 0.80 0.28 0.07 0.78 0.09 0.13 0.13
0.42 1.67 0.29 2.12 2.36 0.62 0.37 2.35 0.62 0.20
f1 (ppm)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164.767 164.443 163.127 162.807
135.842 135.323 132.137 132.074 128.724 128.666 127.651 127.595 116.818 116.671 116.475 116.327 116.284 116.181 116.137 116.035 115.978
64.300 63.859 63.178 62.639
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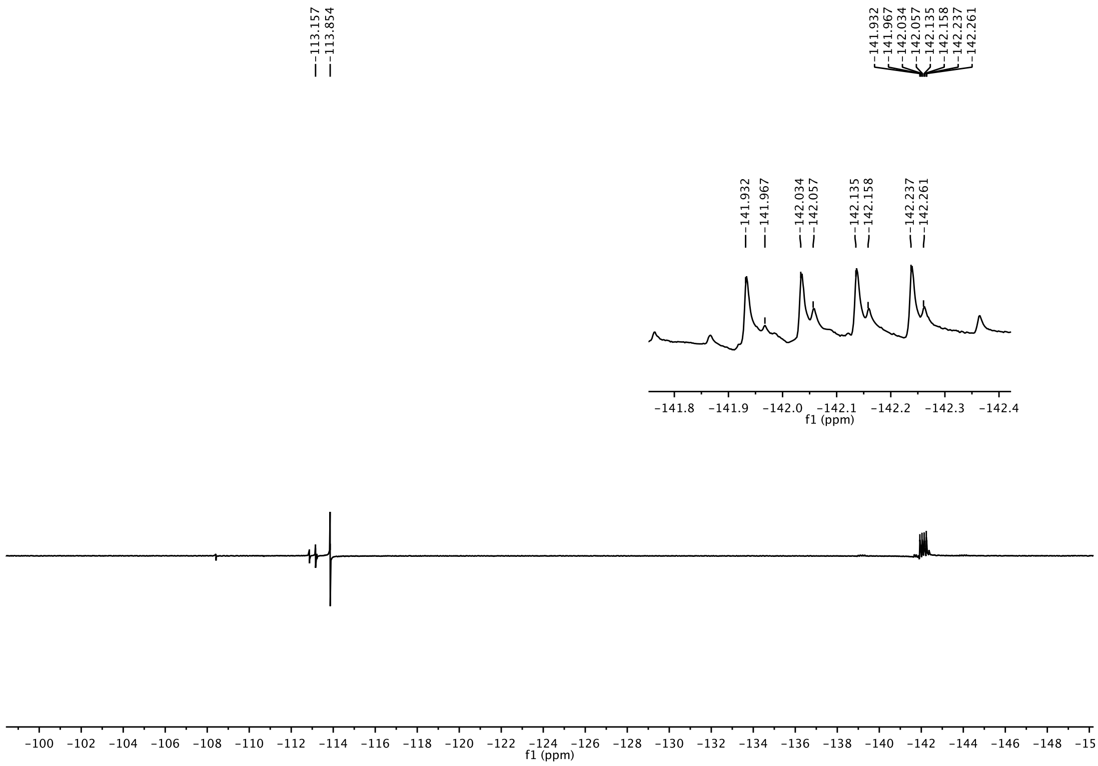
208.793 208.601 208.123 207.744 207.352 207.157 206.880 206.788
f1 (ppm)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-142.158
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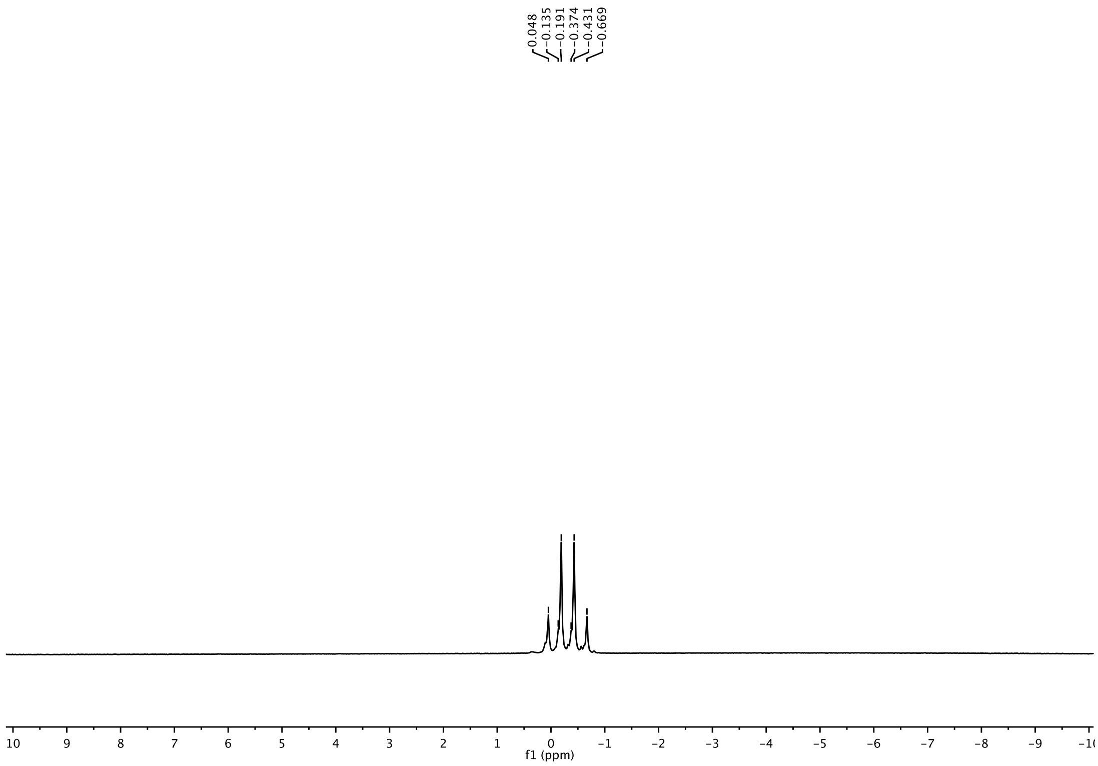
-142.261
f1 (ppm)
f1 (ppm)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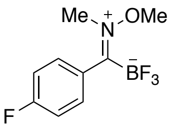
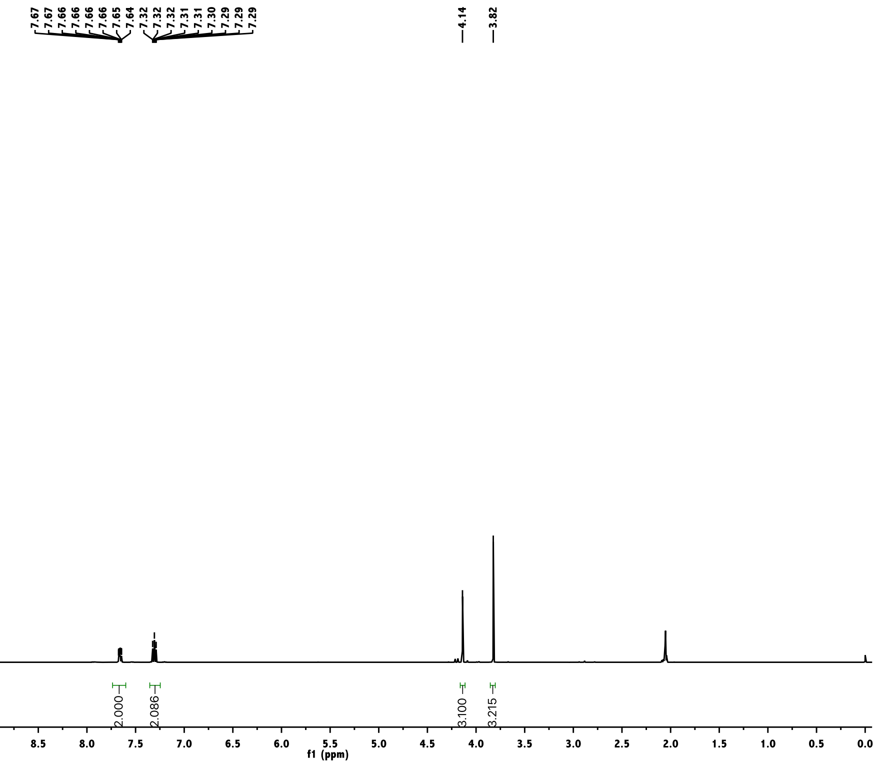

Me
OMe
N
BF3
F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7.67
7.66
7.66
7.66
7.66
7.65
7.64
7.32
7.32
7.32
7.32
7.31
7.31
7.30
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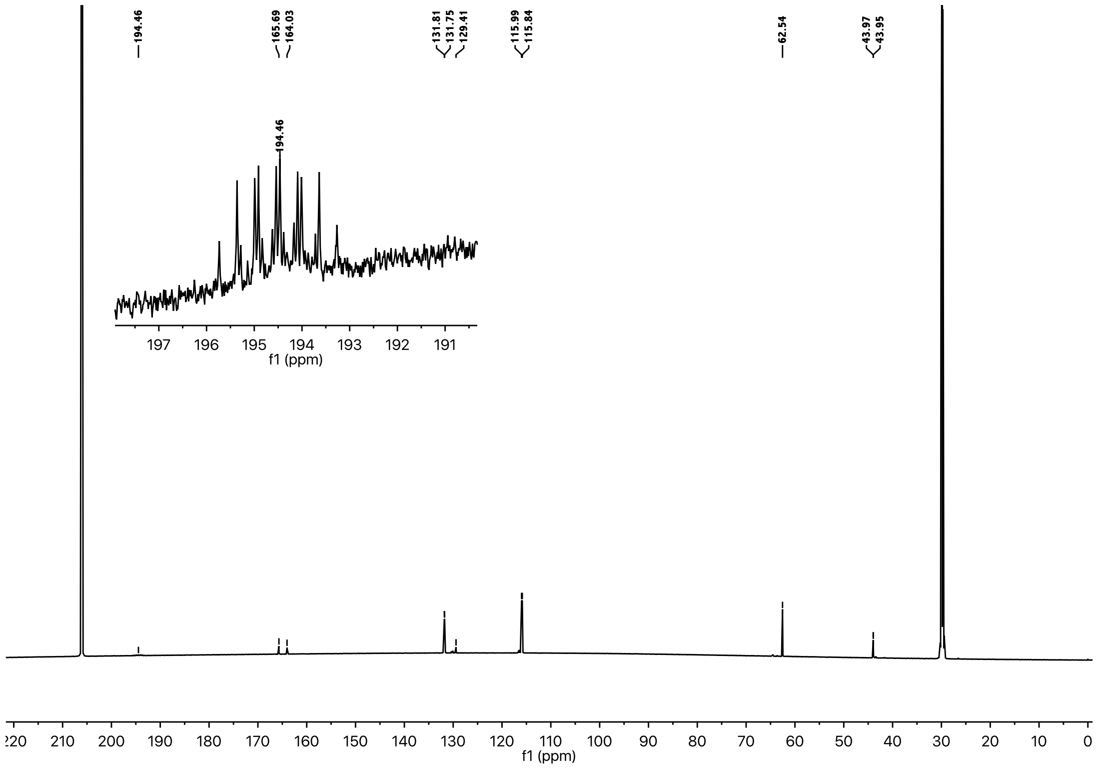
7.29
7.29
4.14
3.82
2.000
2.086
3.100
3.215
f1 (ppm)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165.69
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115.99
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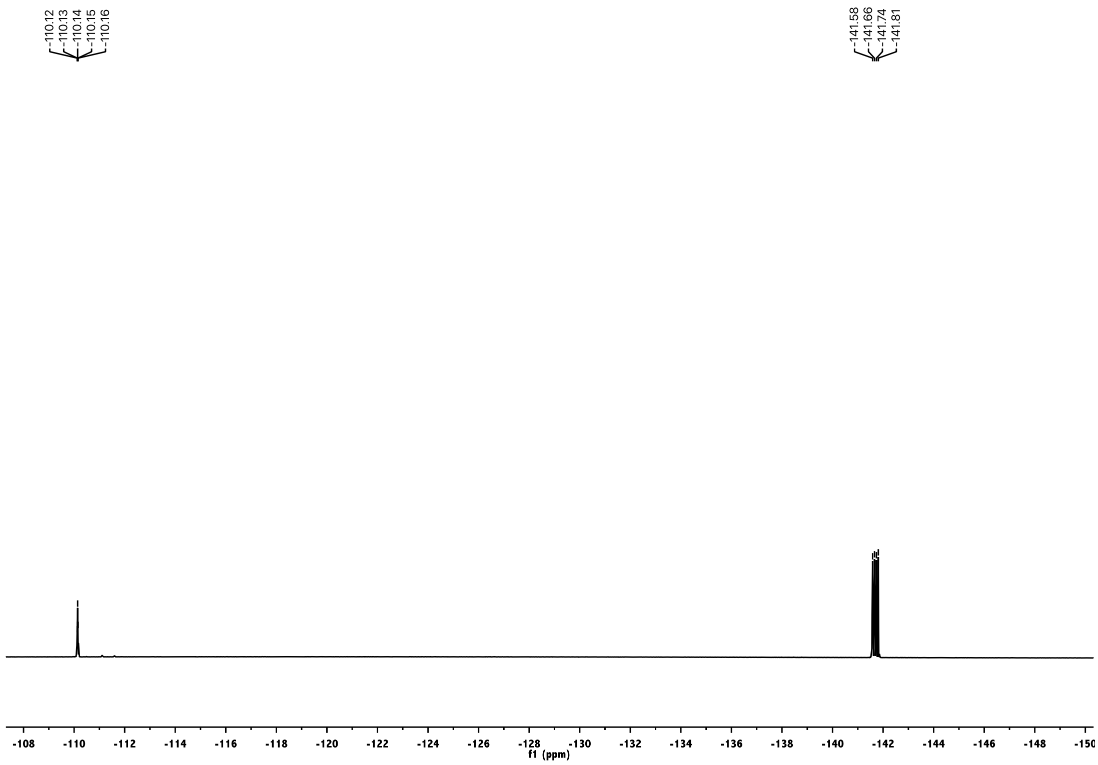
62.54
43.97
43.95
f1 (ppm)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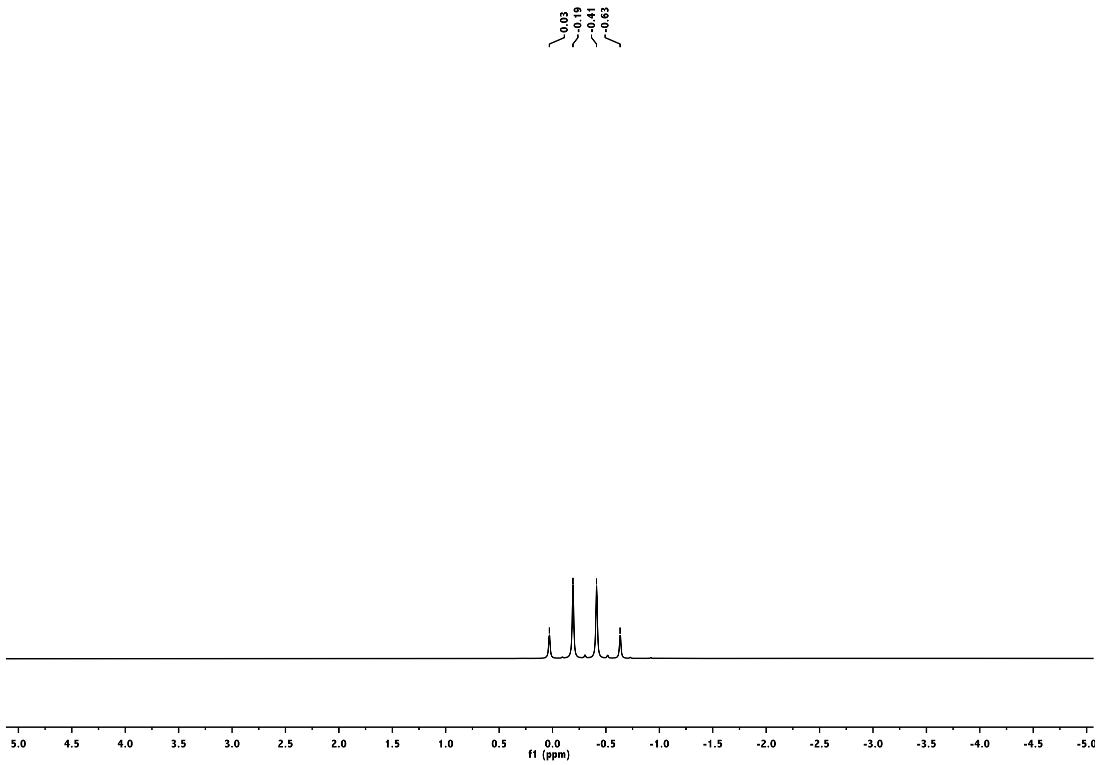
f1 (ppm)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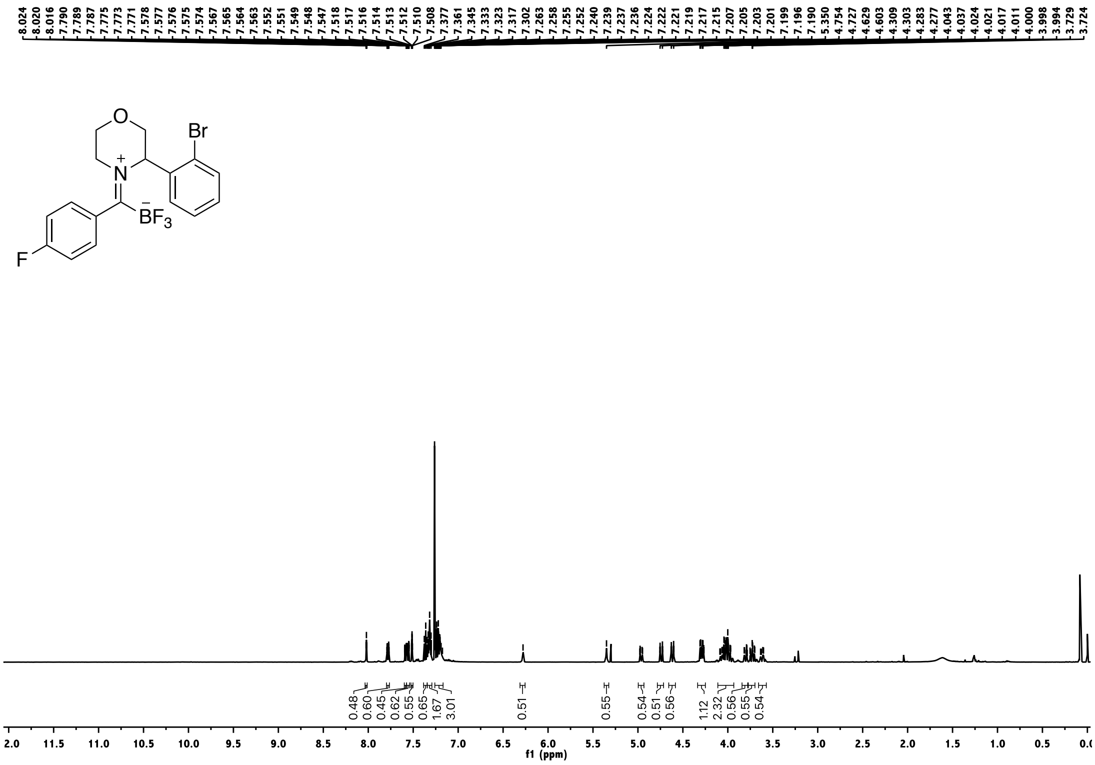
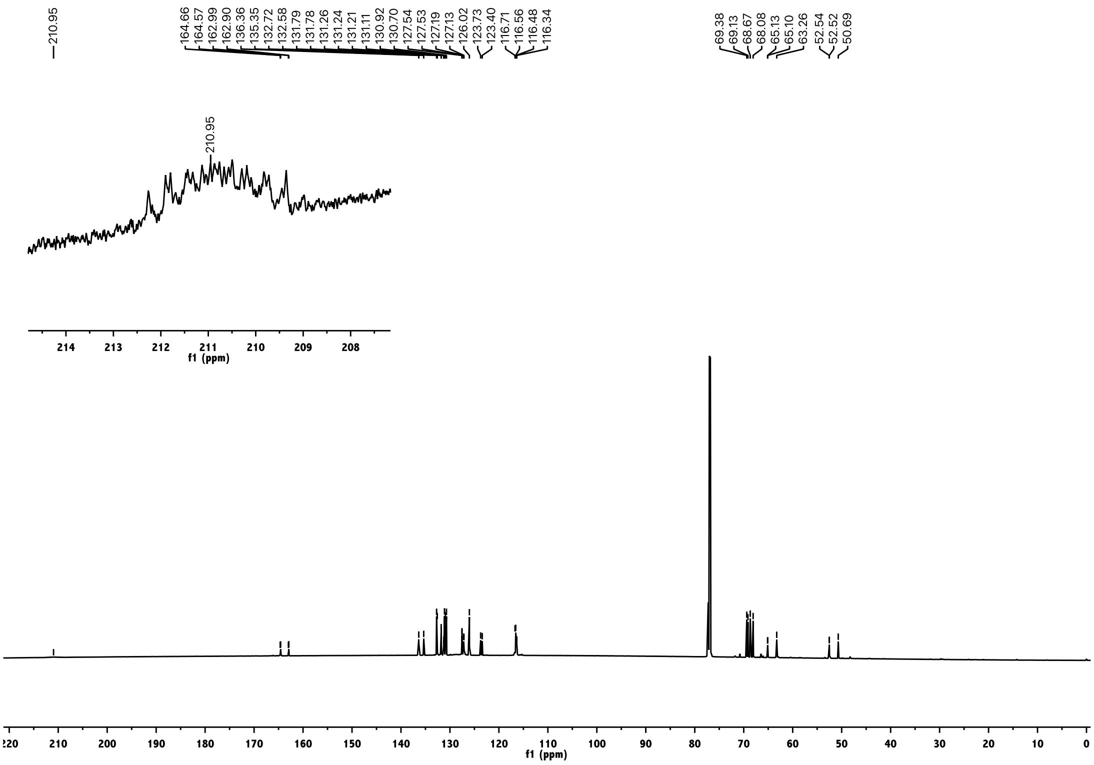

Br
N
BF3
F
O
f1 (ppm)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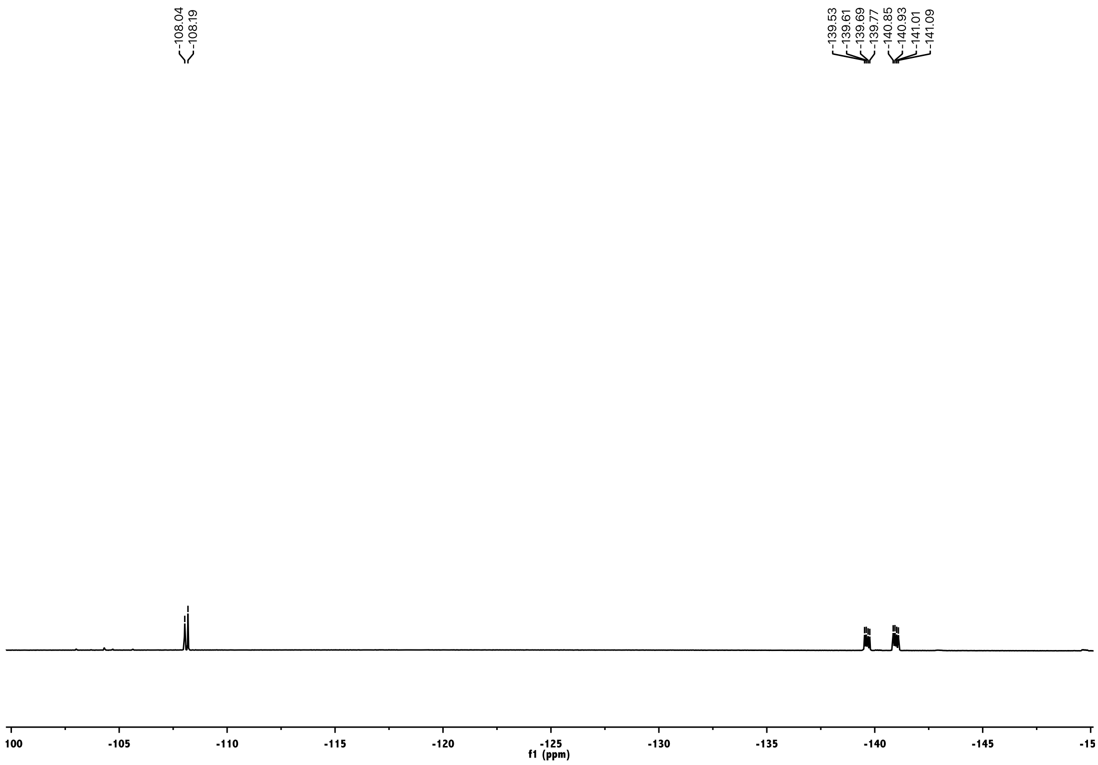
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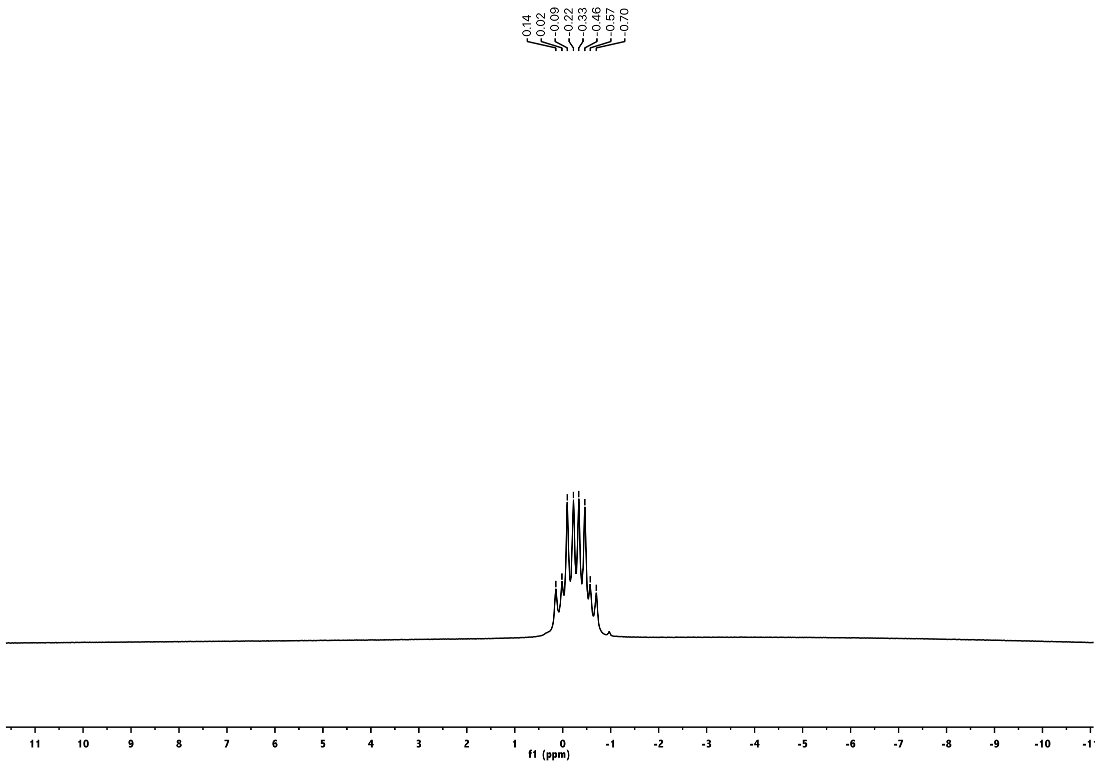
f1 (ppm)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-0.70
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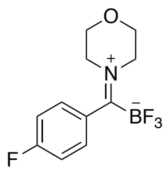
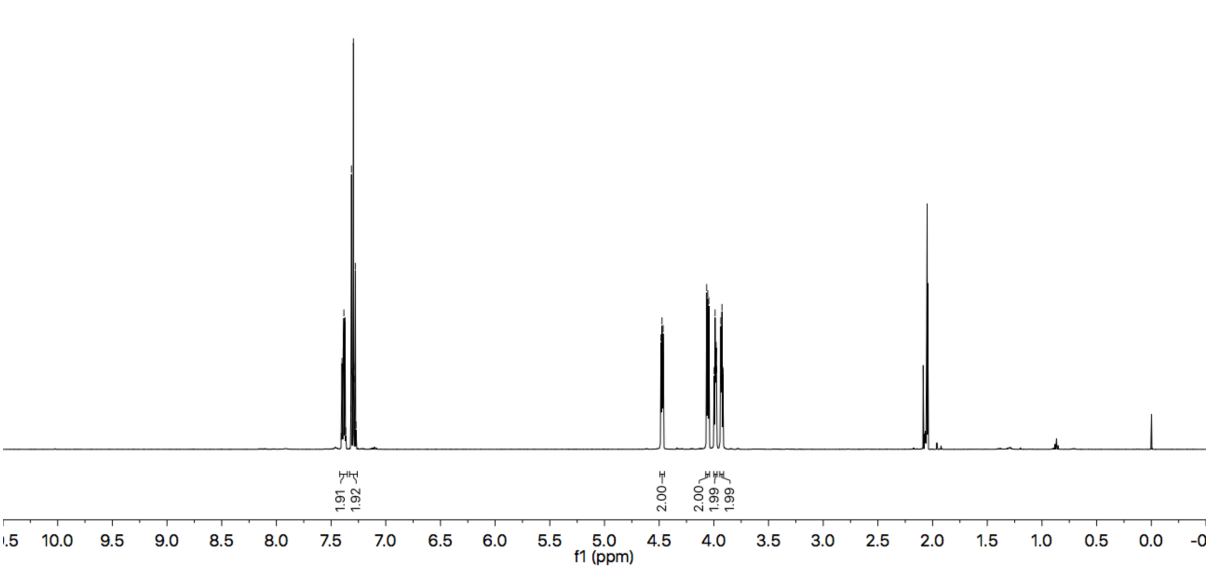

O
N
BF3
F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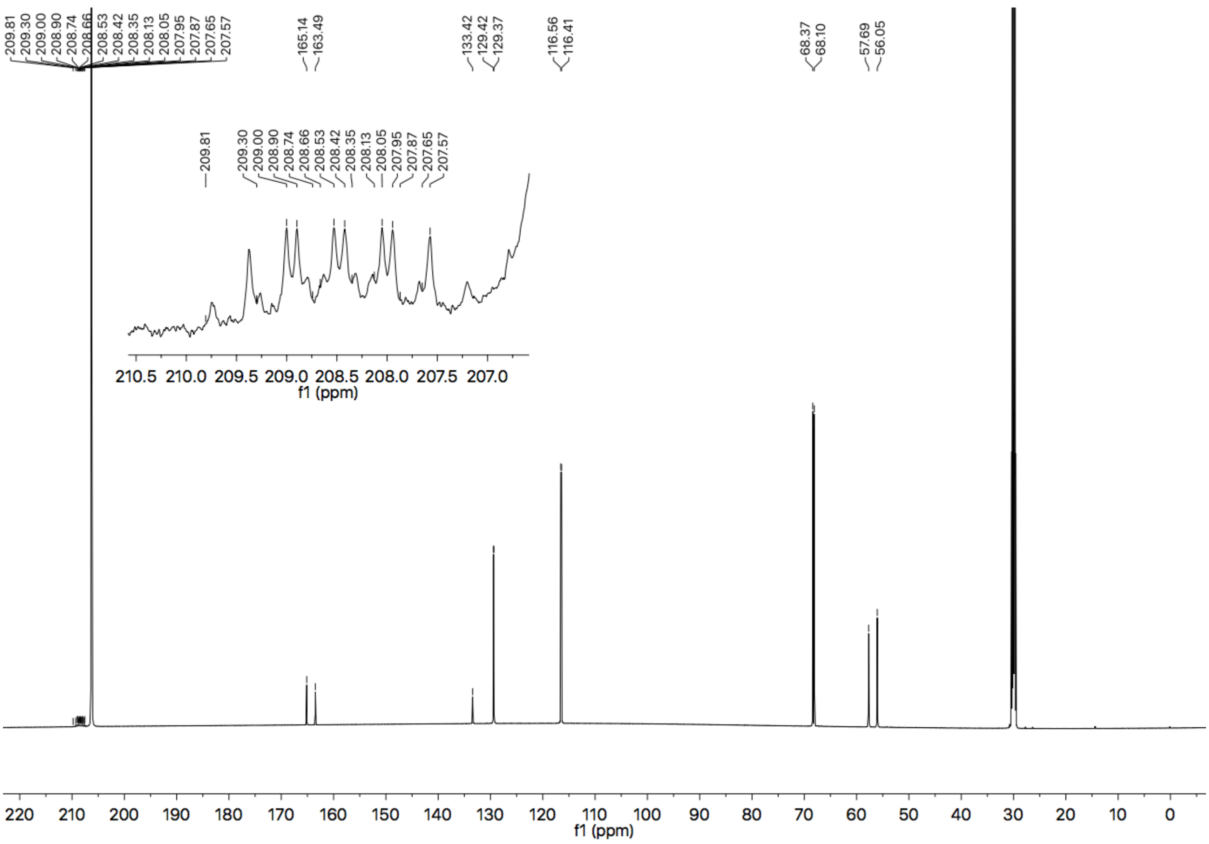
4.48 4.47 4.46 4.07 4.06 4.05 4.00 3.99 3.98 3.98 3.97 3.94 3.94 3.93 3.93 3.92 3.92
1.91 1.92 2.00 2.00 1.99 1.99
f1 (ppm)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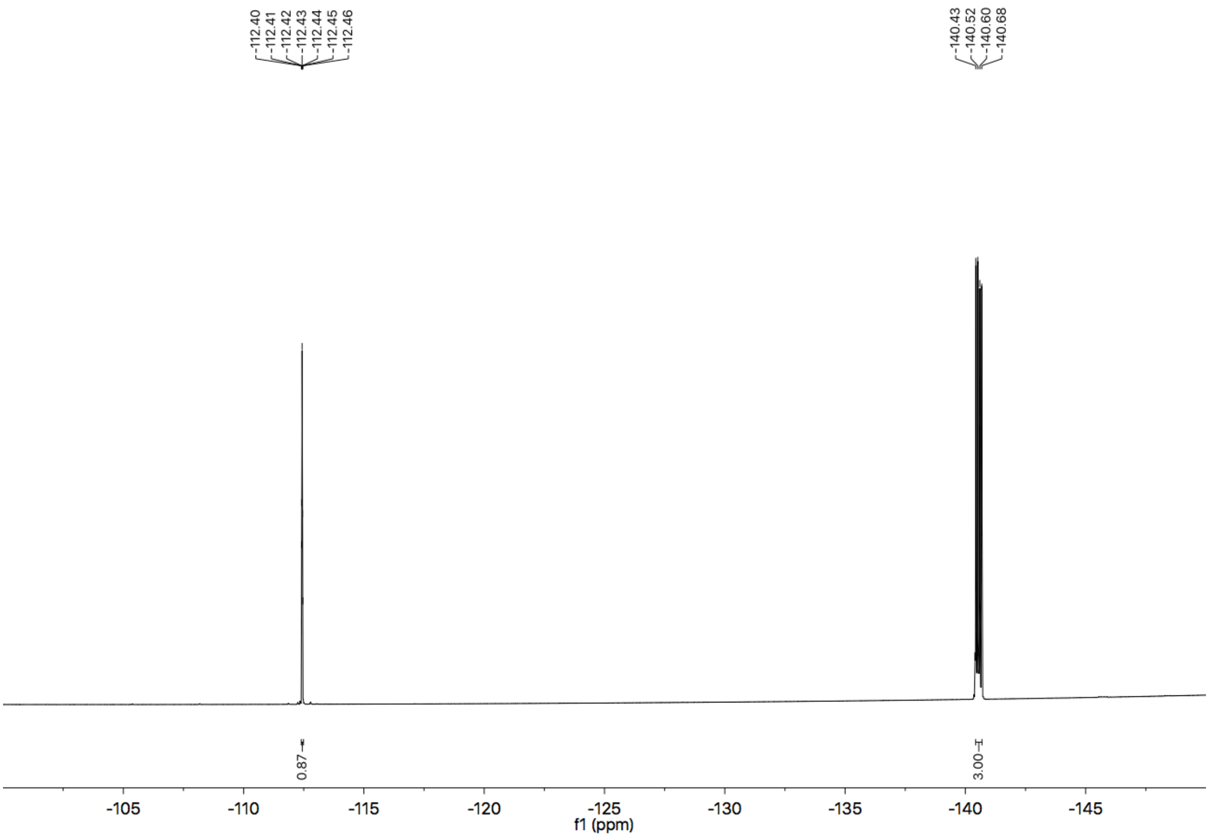
165.14 163.49
133.42 129.42 129.37
116.56 116.41
68.37 68.10
57.69 56.05
f1 (ppm)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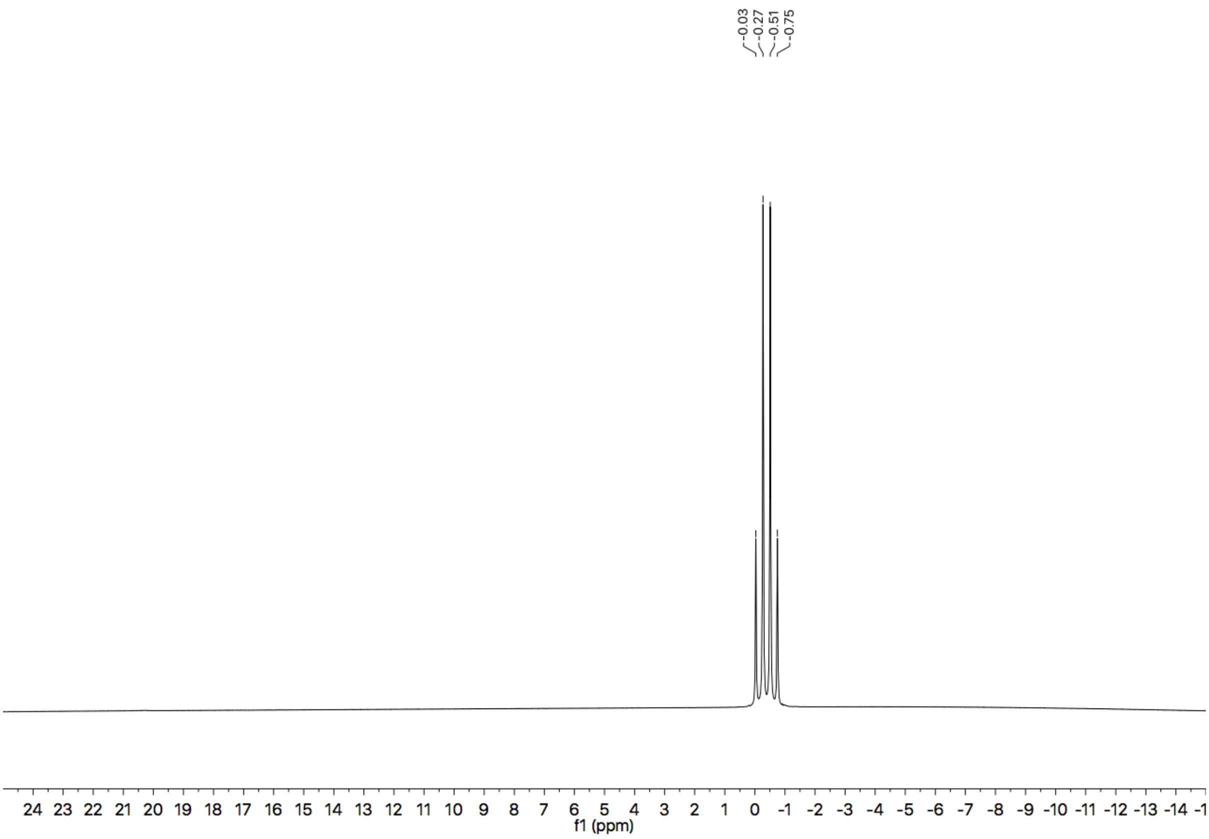
0.87
3.00
-105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)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-0.51
-0.75
24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -1
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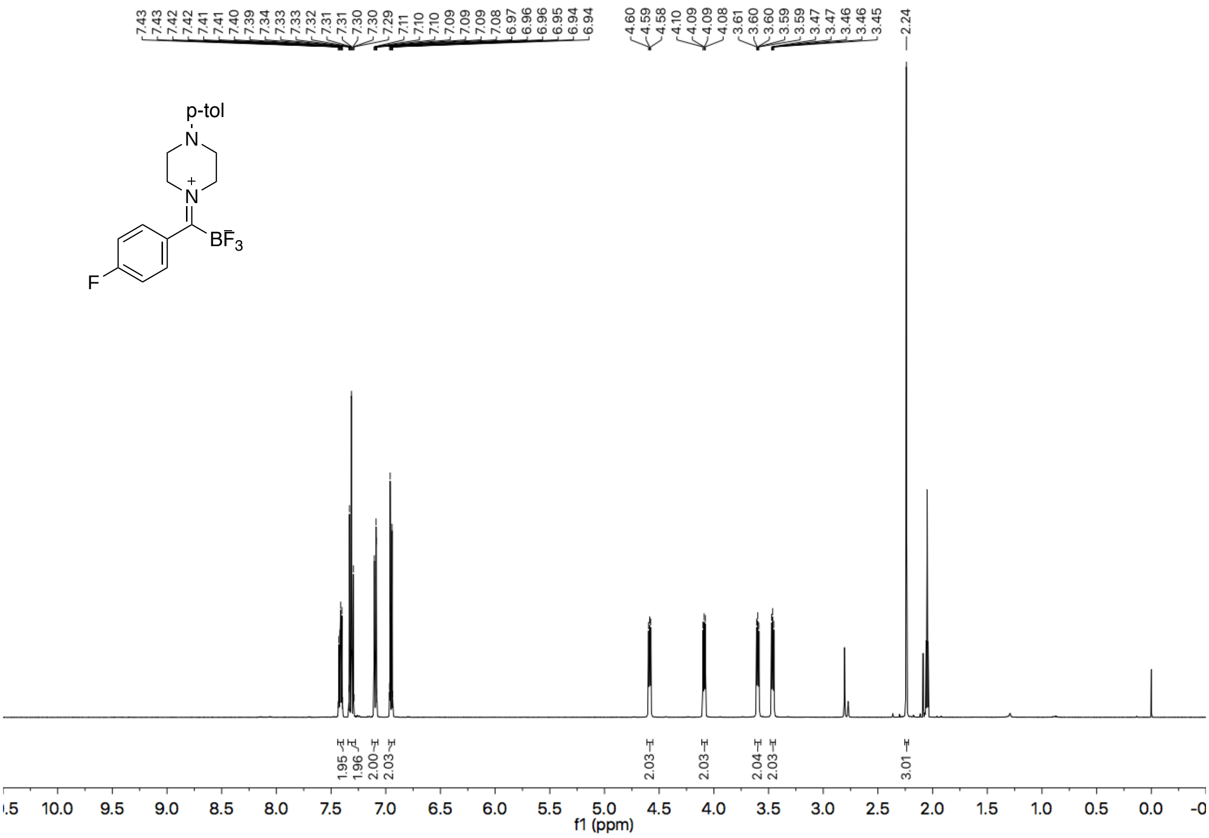
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F
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7.41
7.40
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7.33
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7.29
7.11
7.10
7.10
7.09
7.09
7.09
7.08
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3.59
3.59
3.47
3.46
3.46
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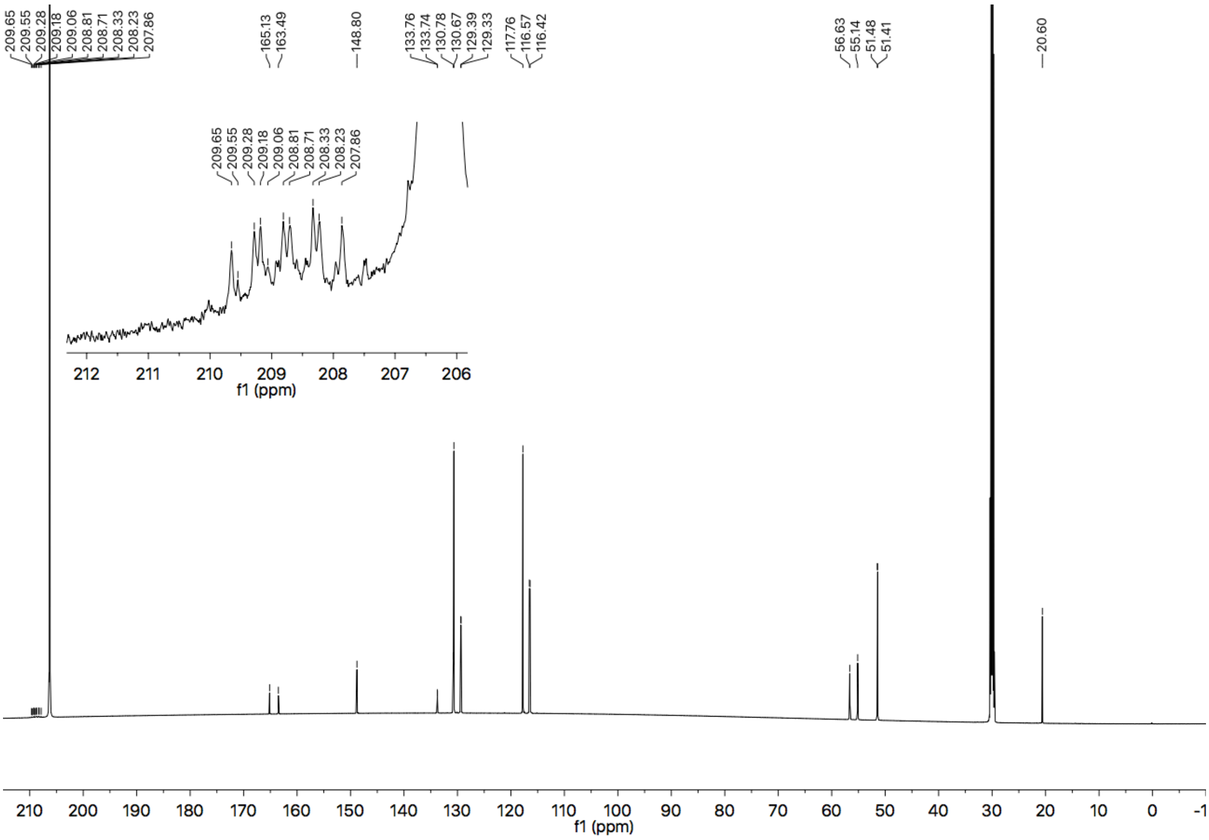
2.03
2.03
2.03
2.04
2.03
3.01
f1 (ppm)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163.49
148.80
133.76
133.74
130.78
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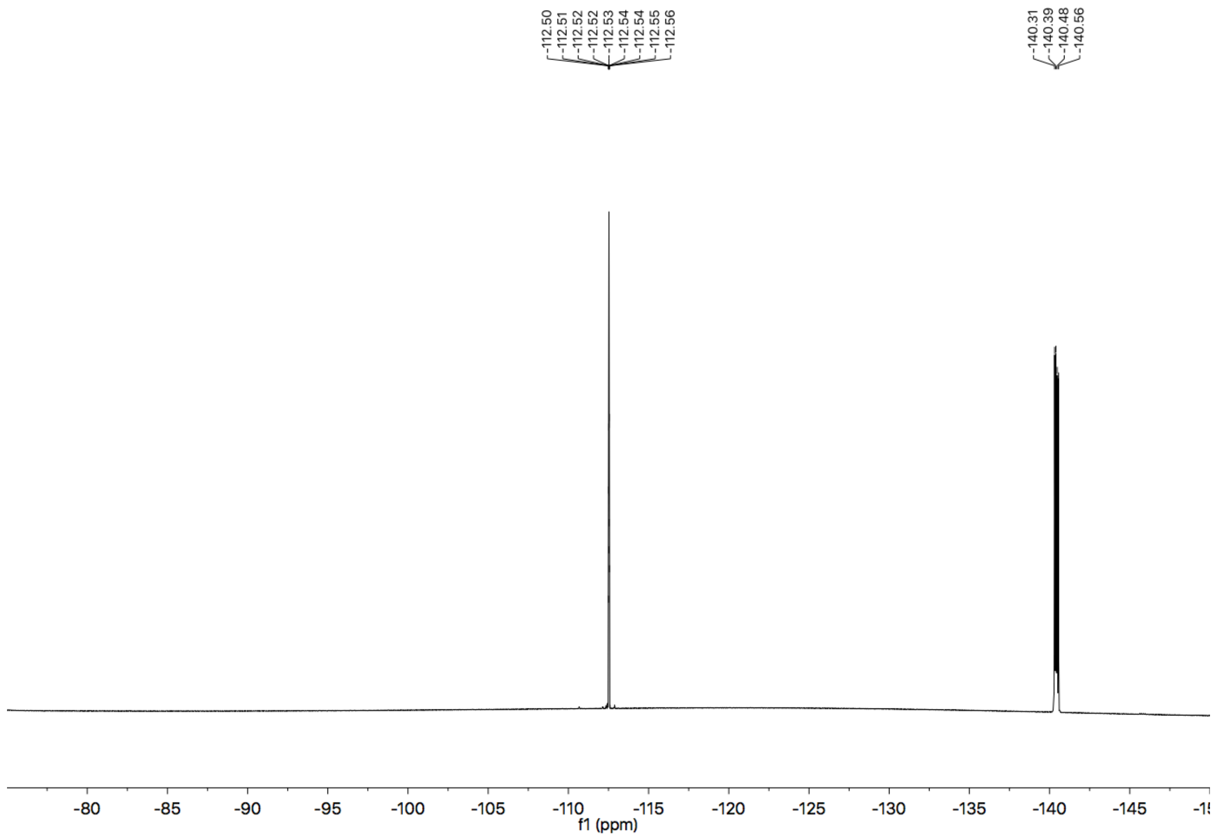
116.42
56.63
55.14
51.48
51.41
20.60
f1 (ppm)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-112.54
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-90
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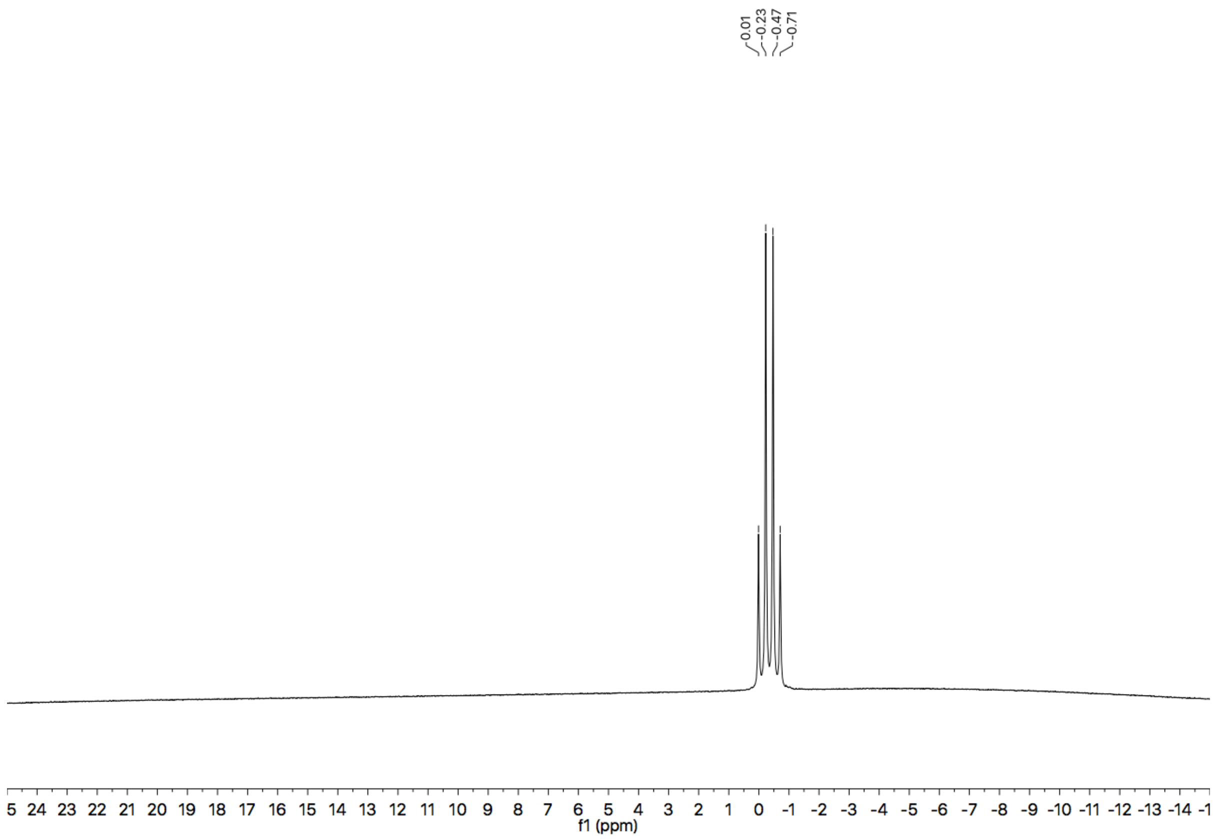
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)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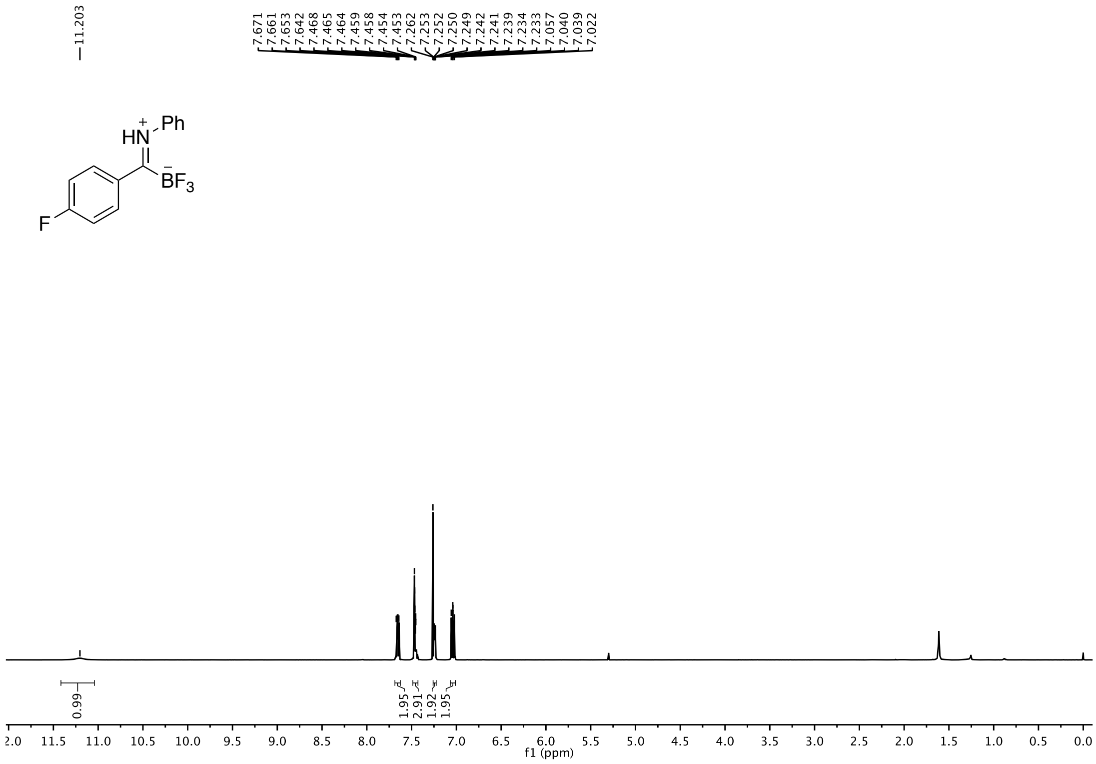
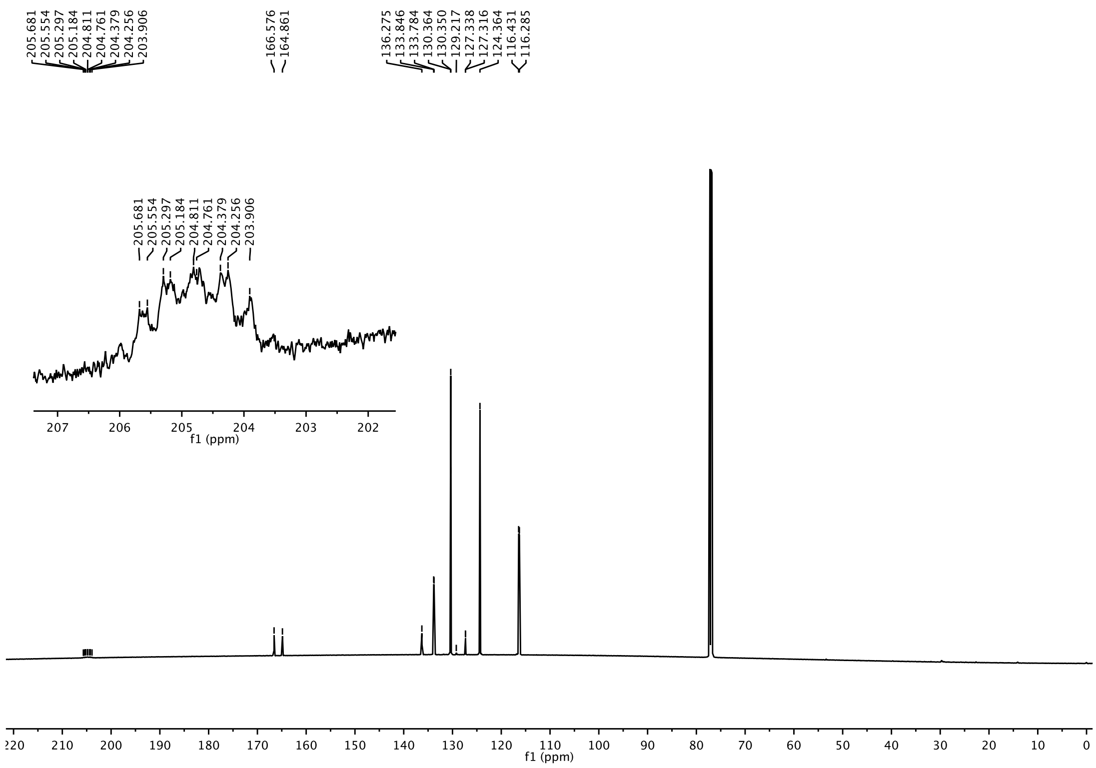
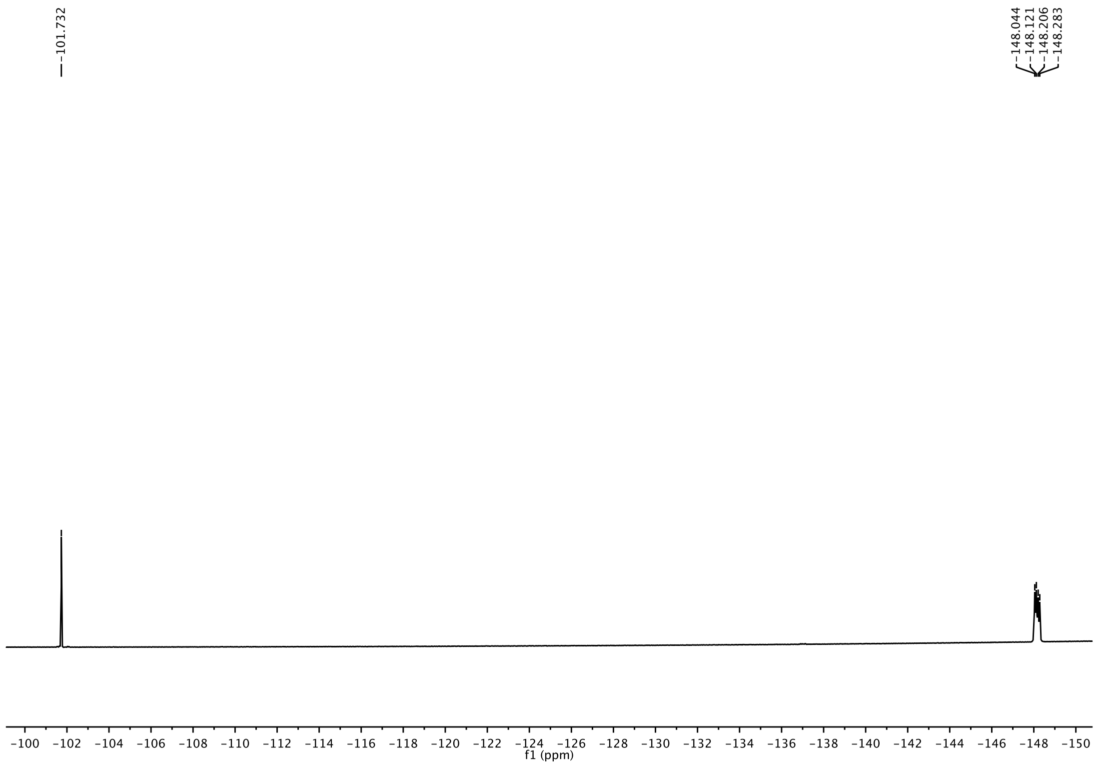
-0.23
-0.47
-0.71
24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14
f1 (ppm)



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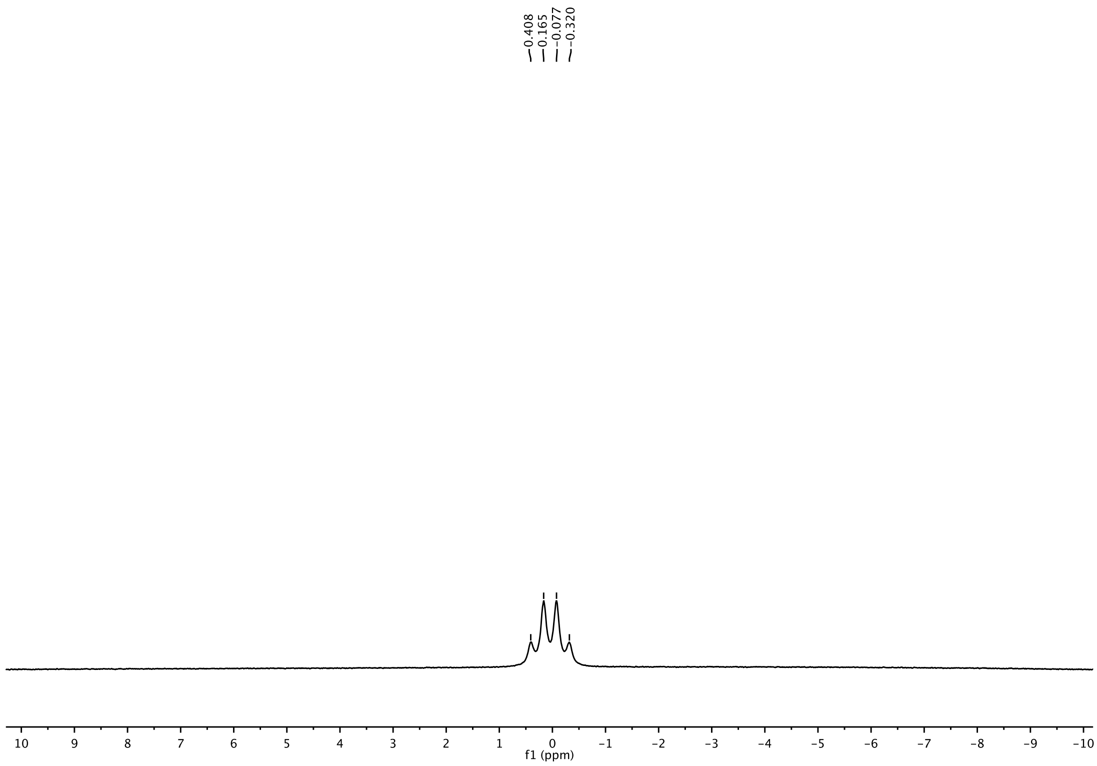
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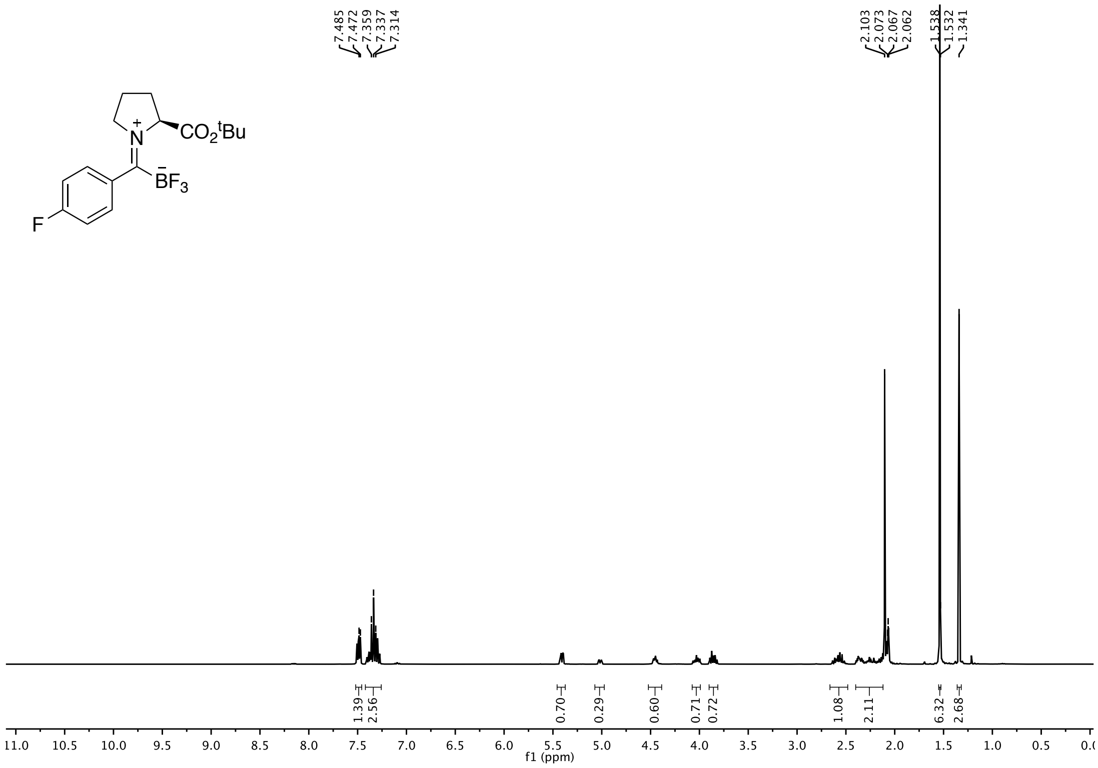
CO2tBu
BF3
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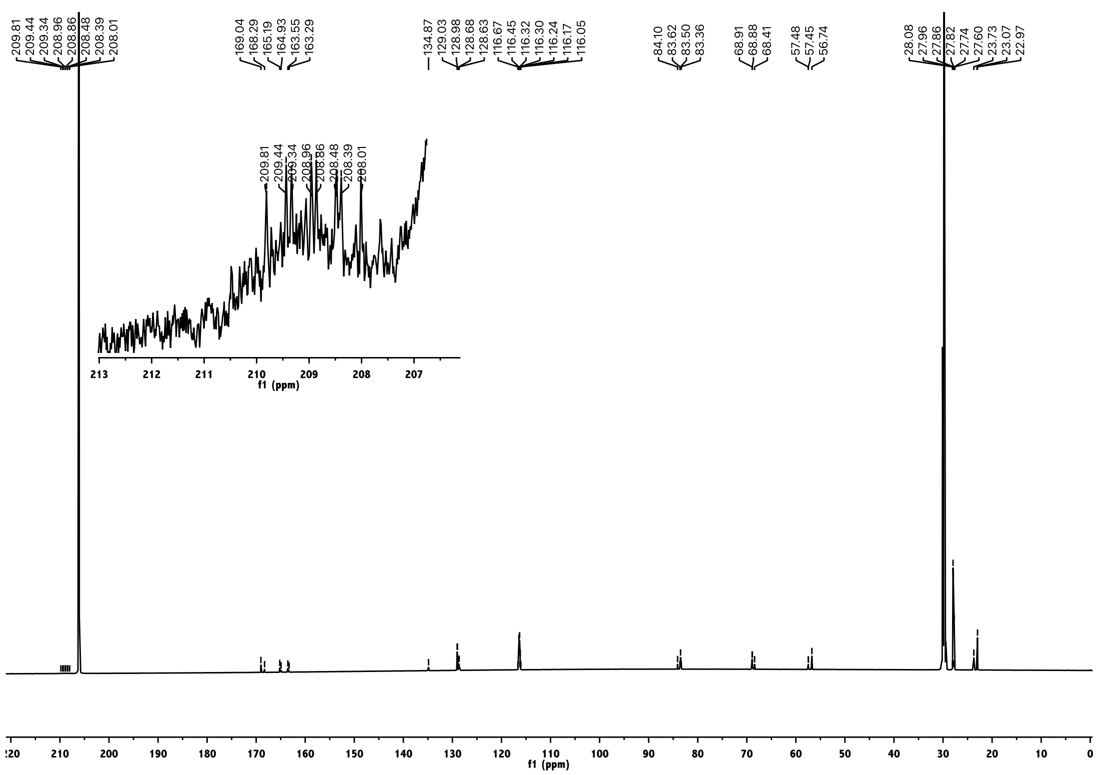
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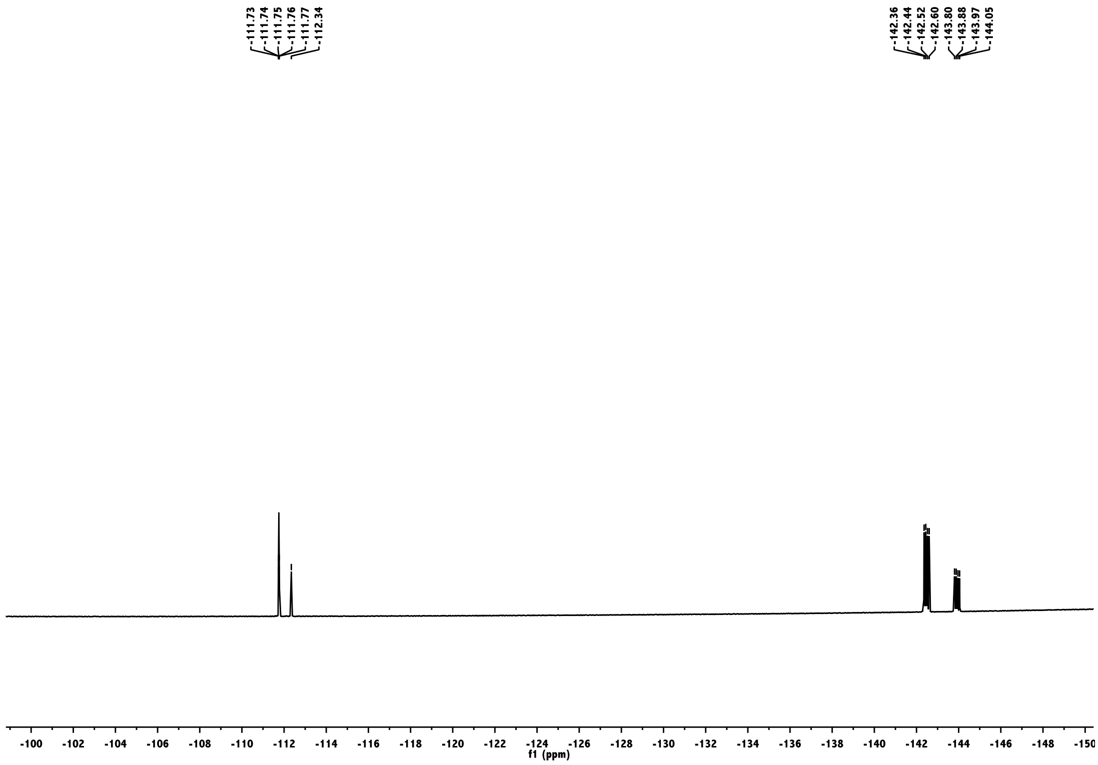

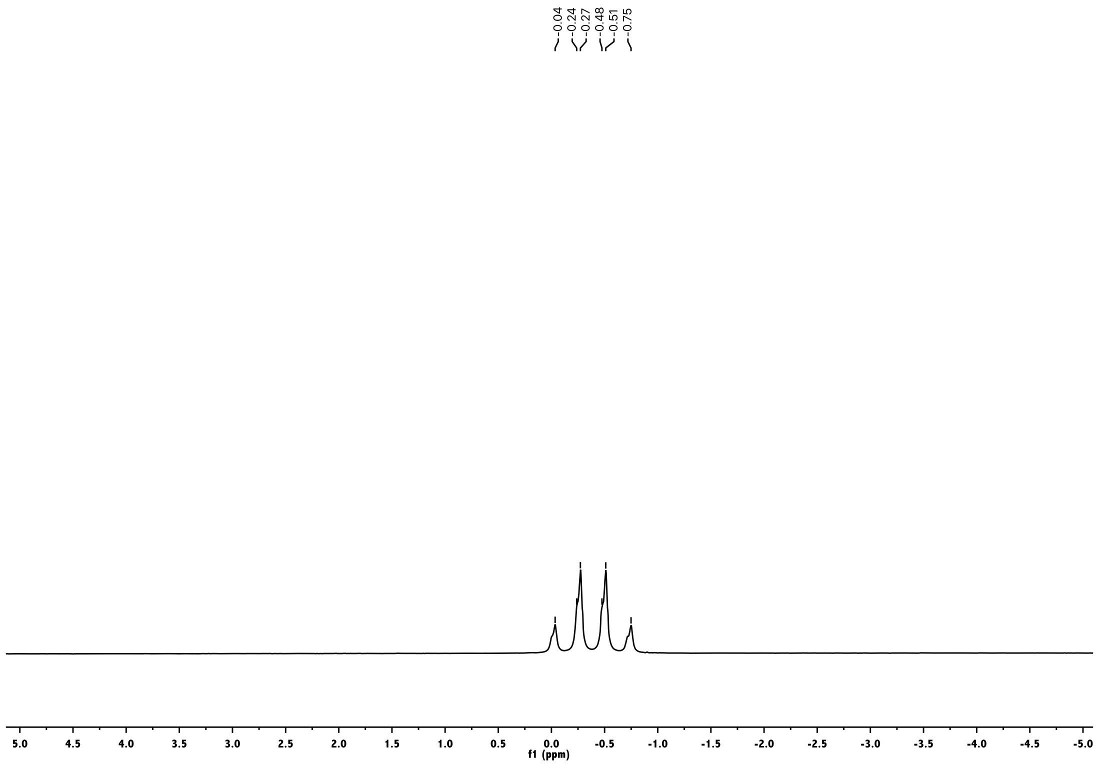

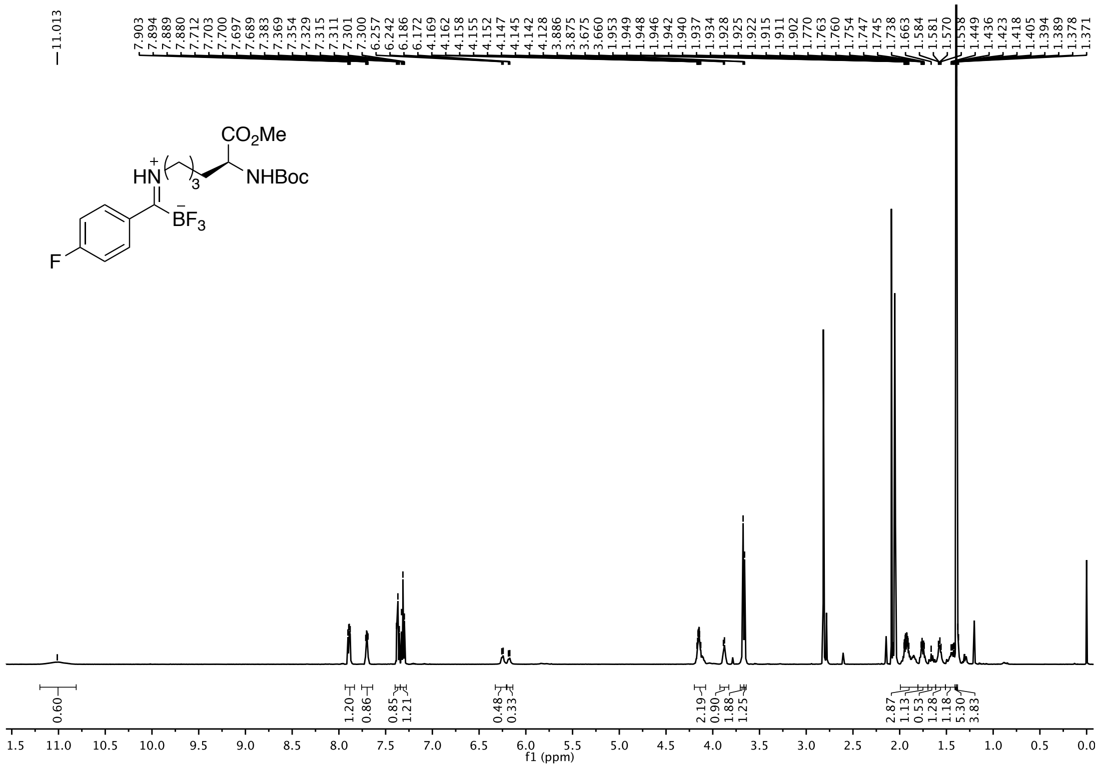

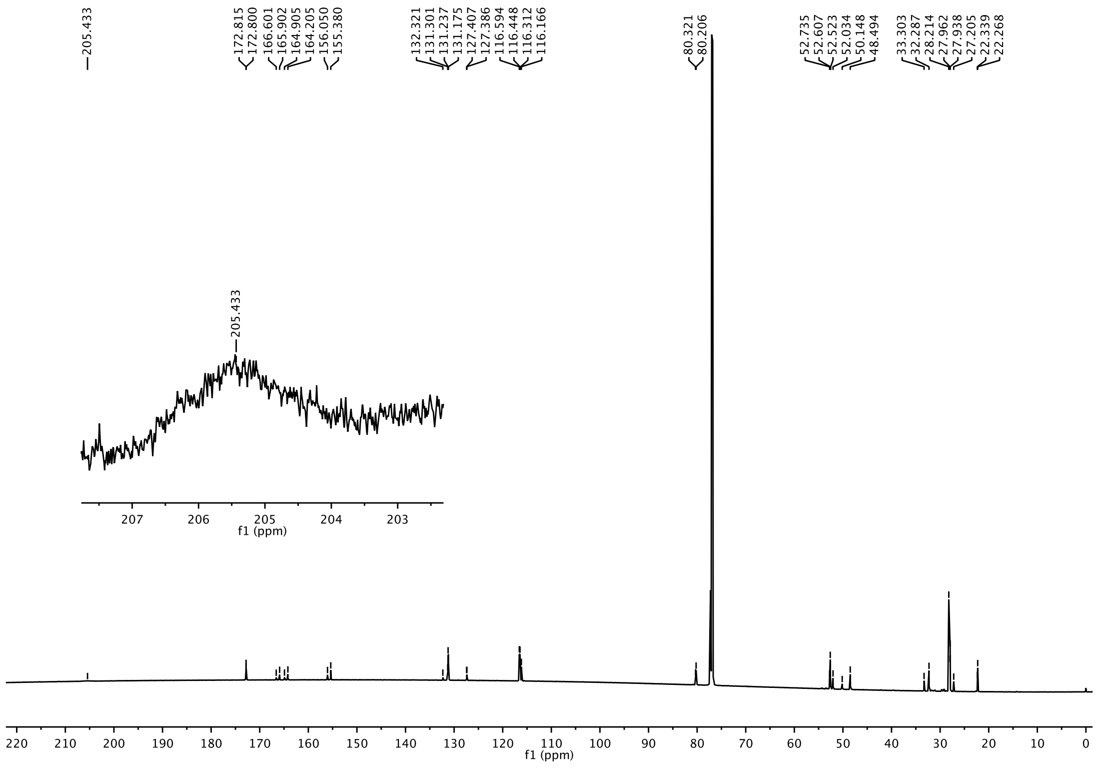

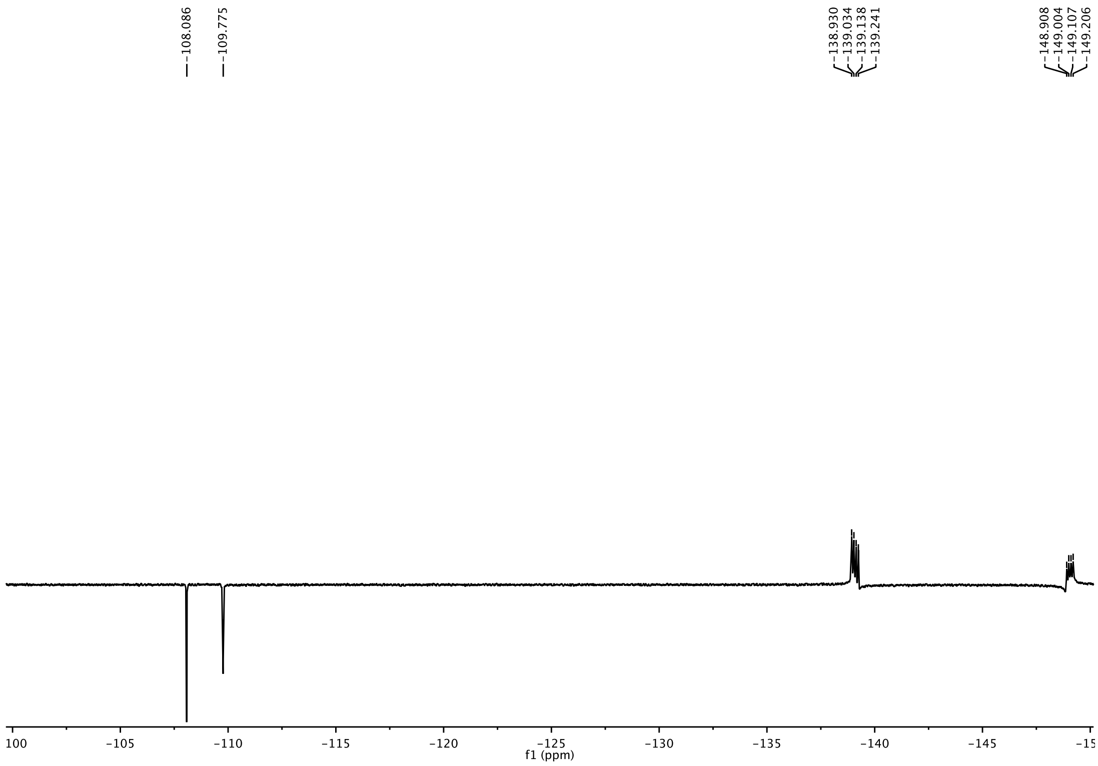
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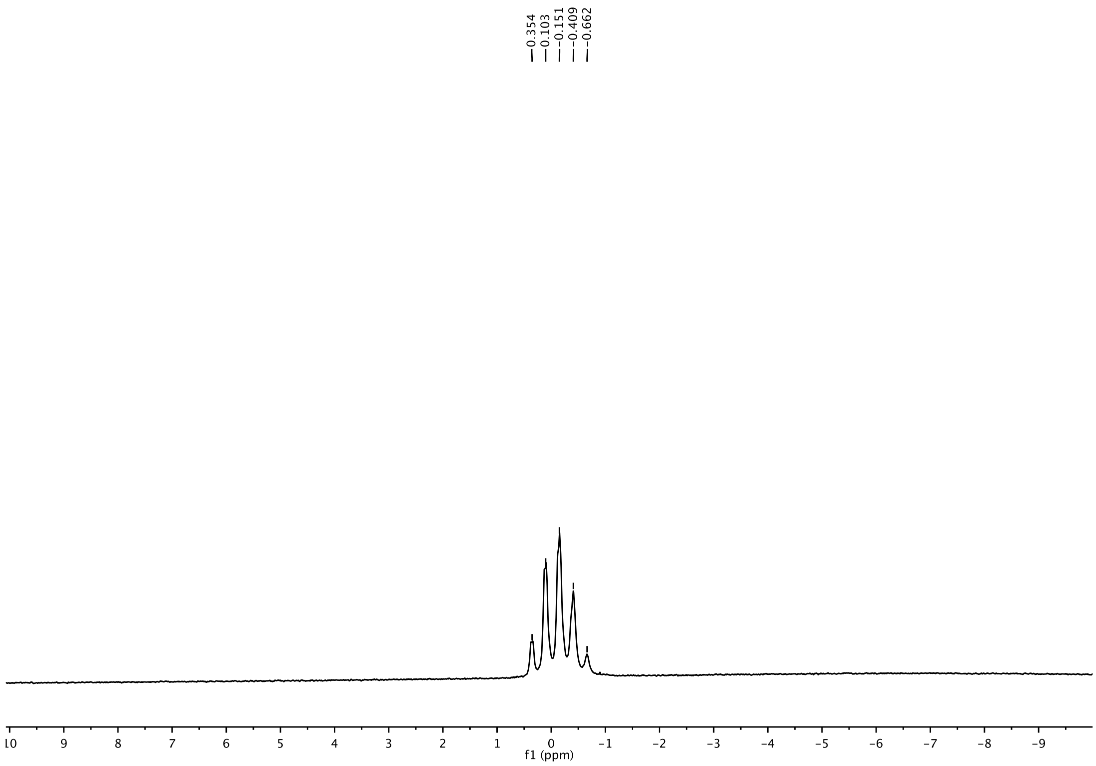
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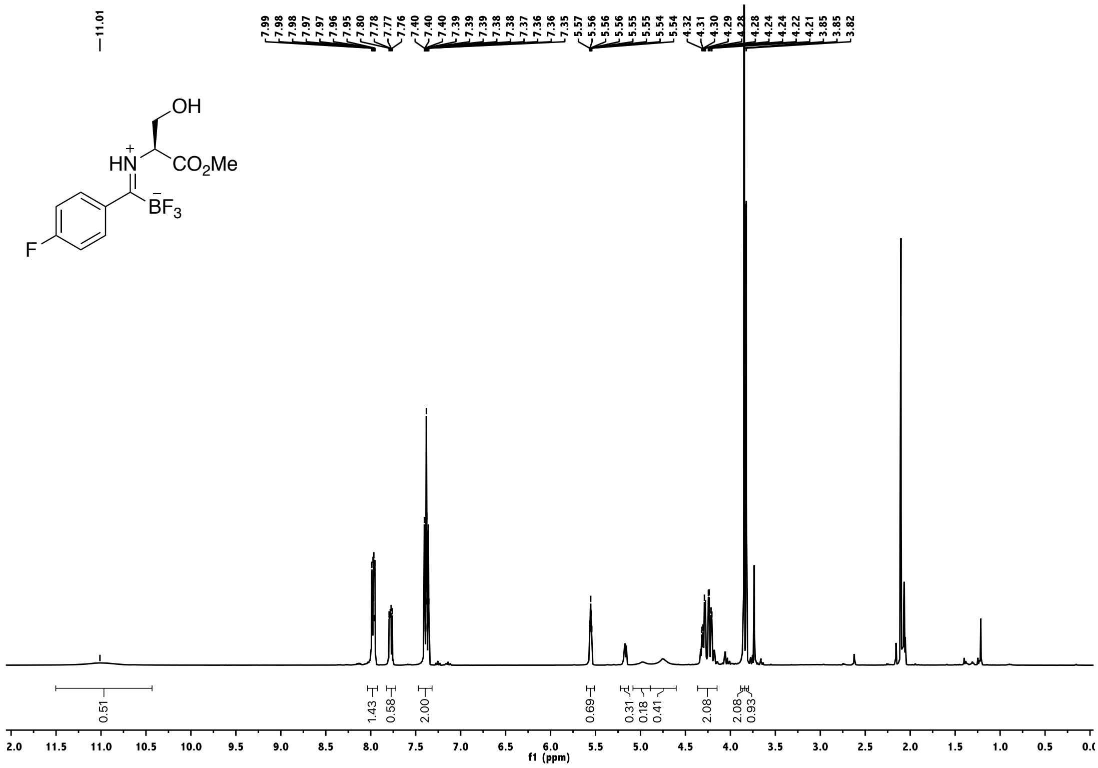
11.01
7.99 7.98 7.98 7.97 7.97 7.96 7.95 7.80 7.78 7.77 7.76 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.35 5.57 5.56 5.56 5.56 5.55 5.55 5.54 5.54 4.32 4.31 4.30 4.29 4.28 4.28 4.24 4.24 4.22 4.21 3.85 3.85 3.82
OH
HN
CO2Me
BF3
F
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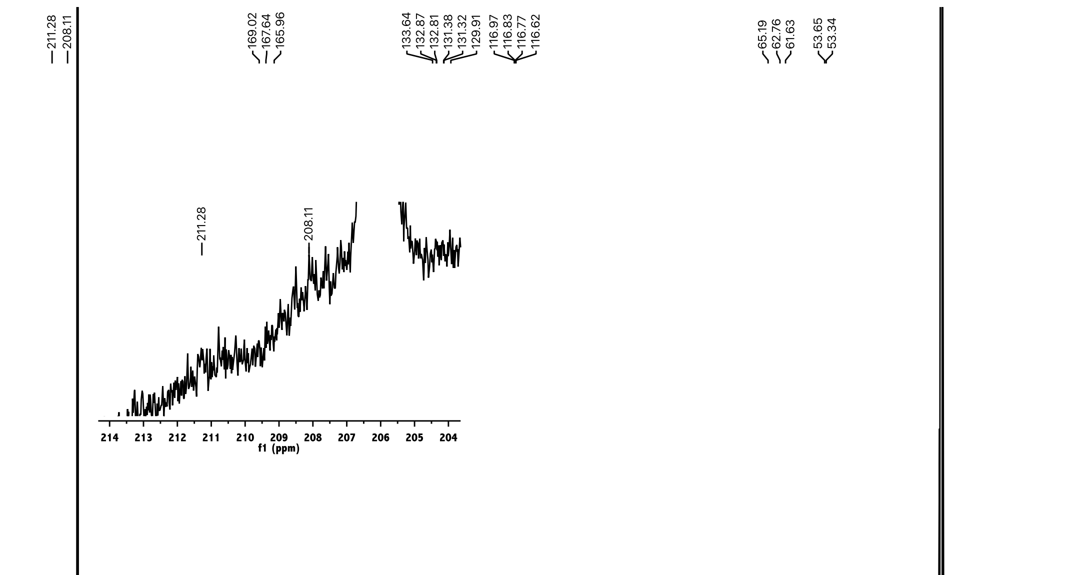
2.08
0.93
f1 (ppm)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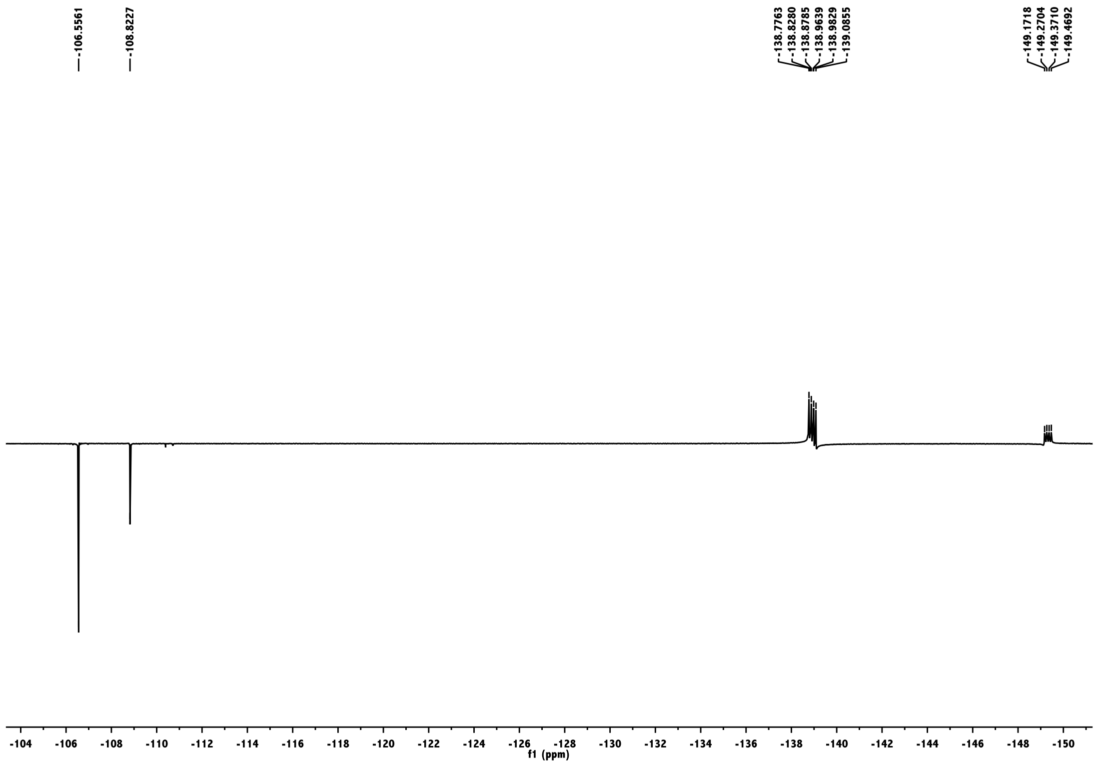
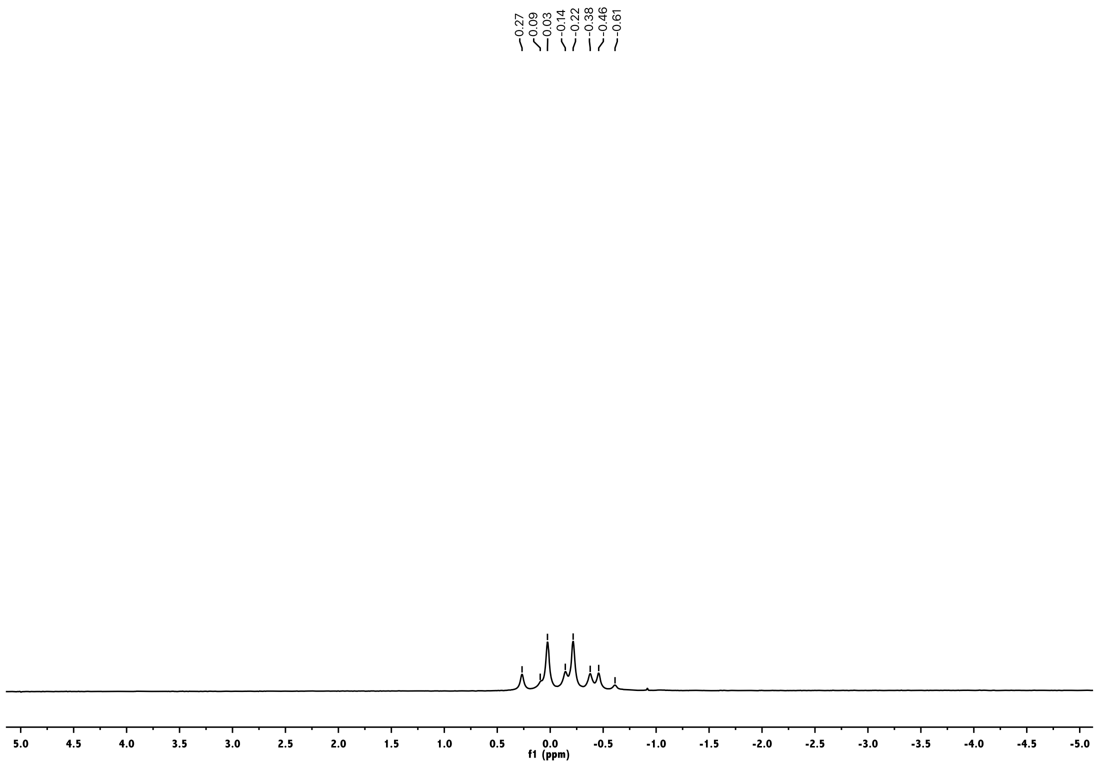
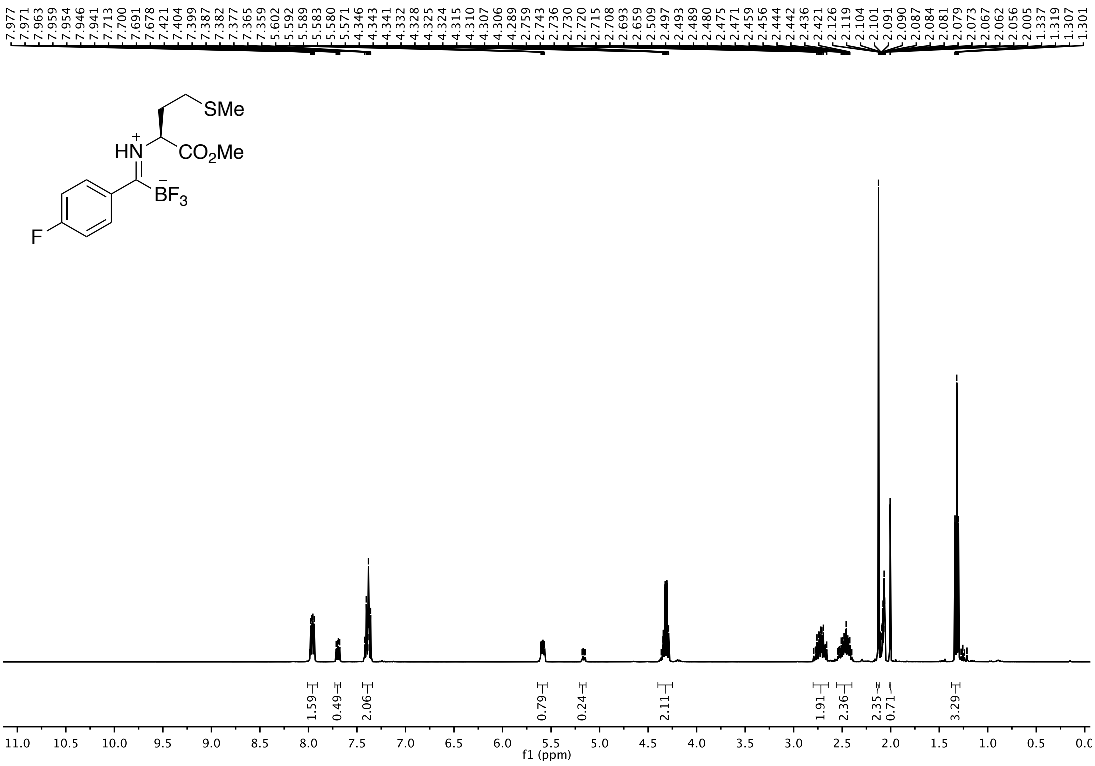
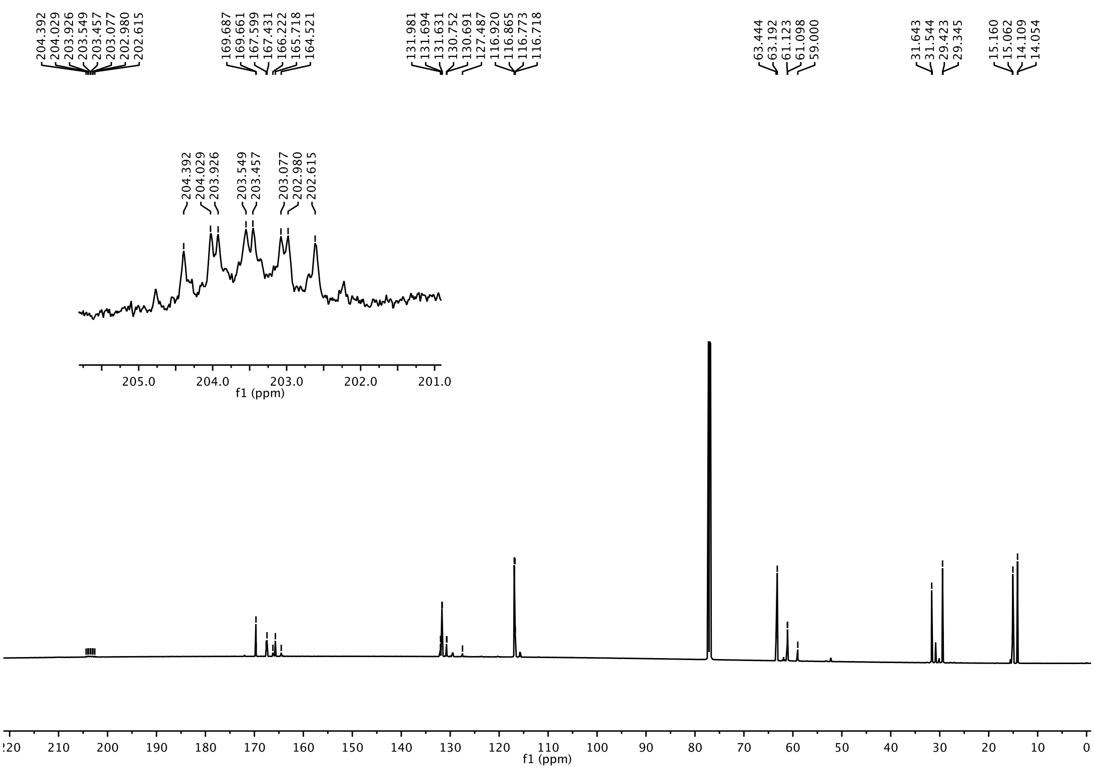
53.34
f1 (ppm)






SMe
HN
CO2Me
BF3
F
f1 (ppm)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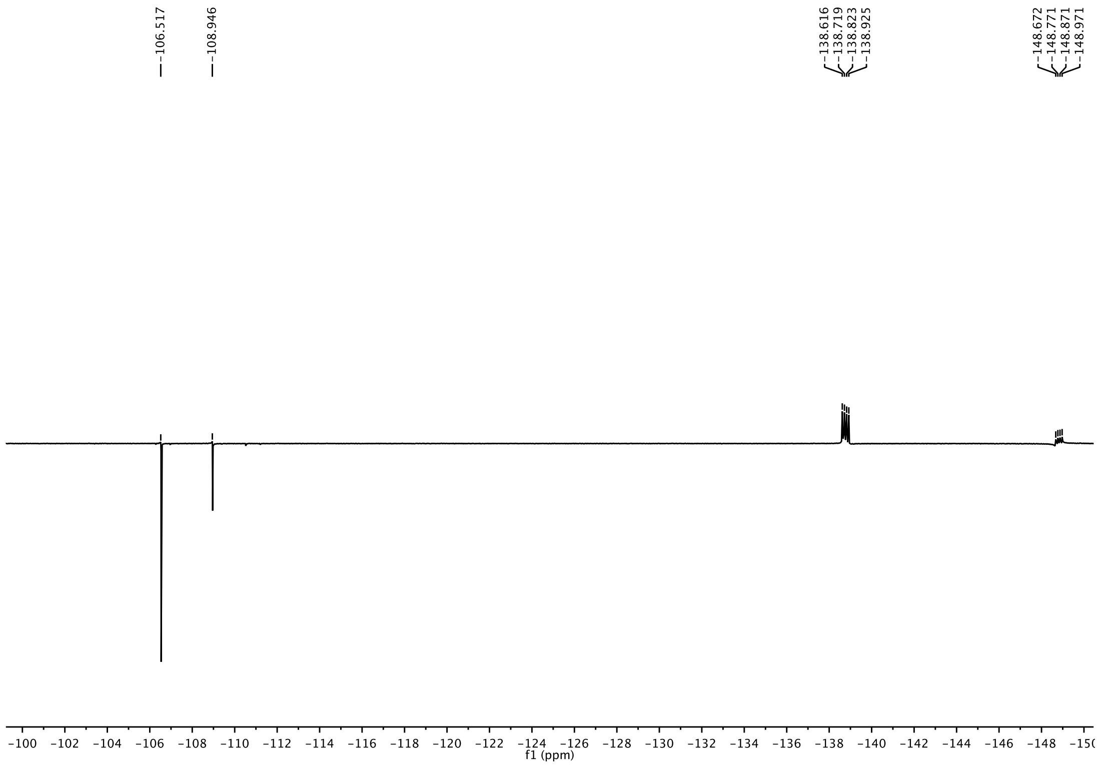
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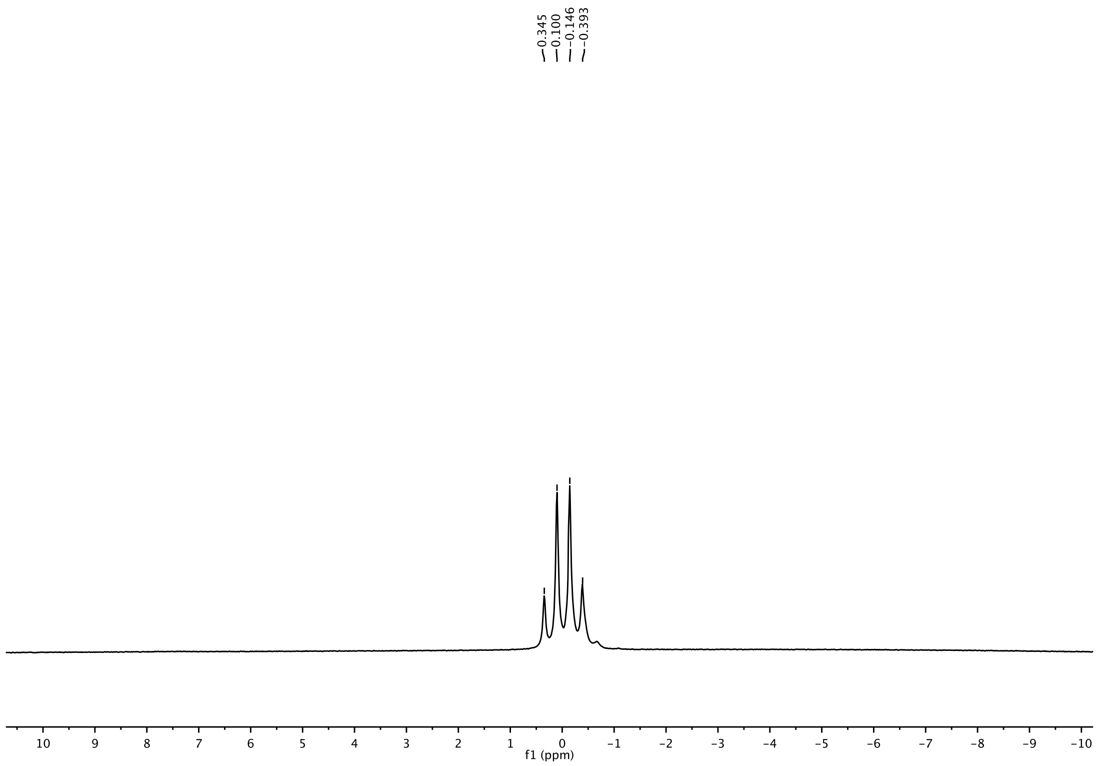
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)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-0.393
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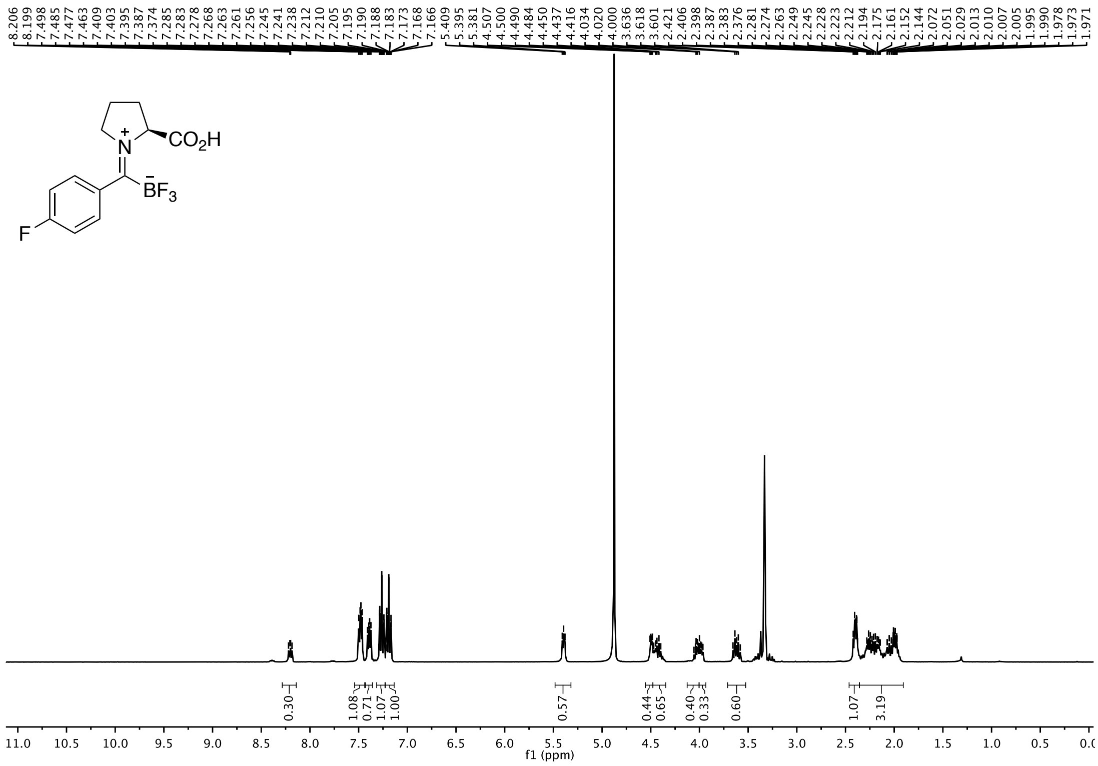
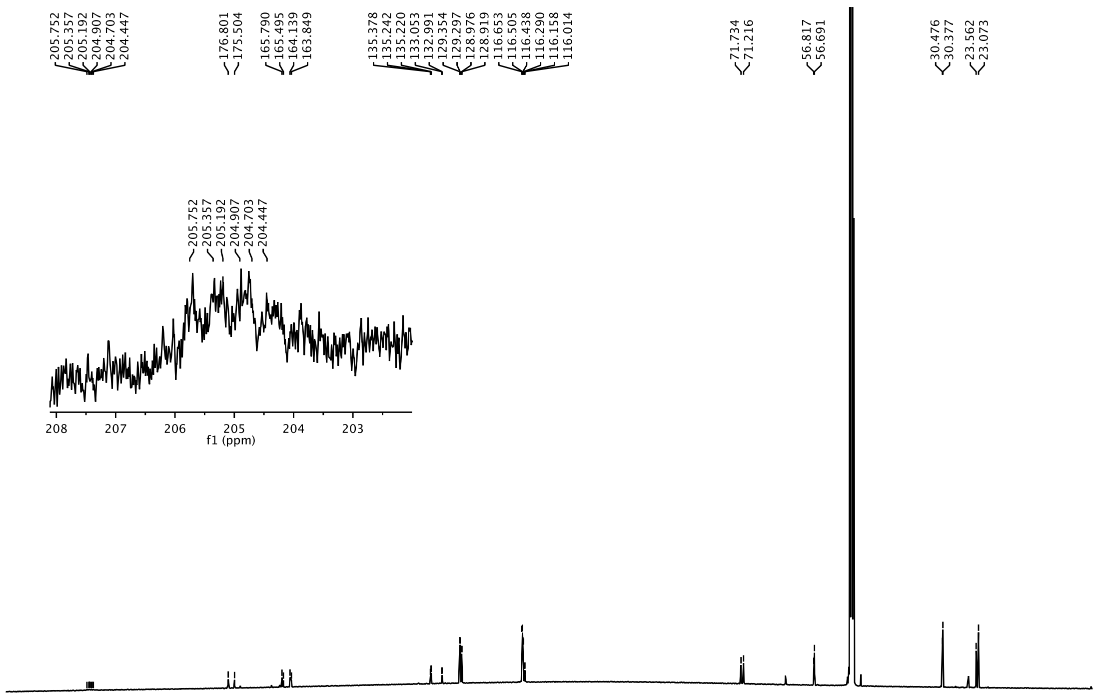
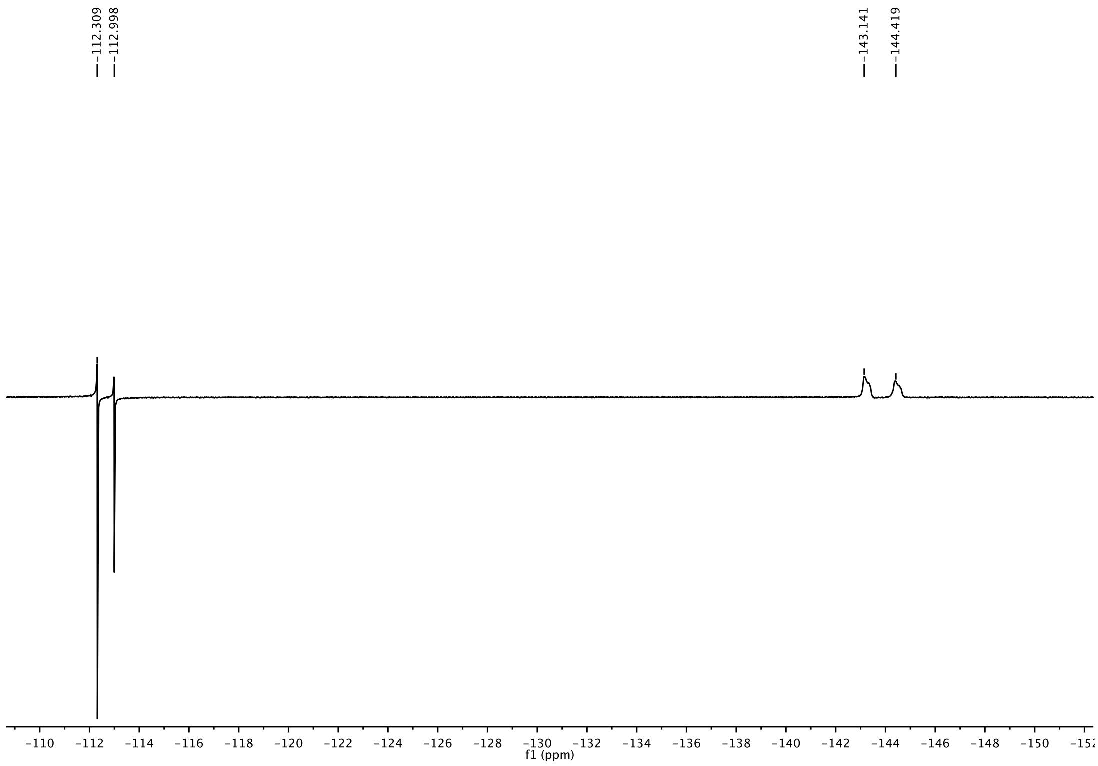
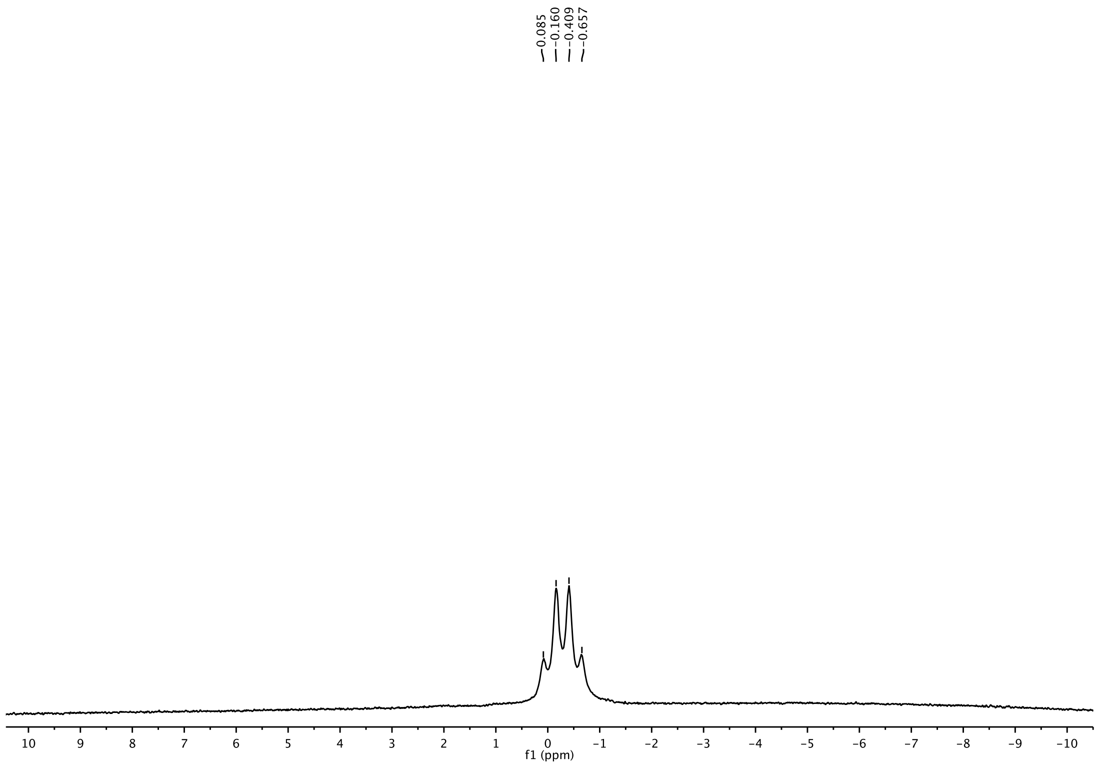
f1 (ppm)


8.206 8.199 7.498 7.485 7.477 7.463 7.409 7.403 7.395 7.387 7.374 7.285 7.283 7.278 7.268 7.263 7.261 7.256 7.245 7.241 7.238 7.212 7.210 7.205 7.195 7.190 7.188 7.183 7.173 7.168 7.166 5.409 5.395 5.381 4.507 4.500 4.490 4.484 4.450 4.437 4.416 4.034 4.020 4.000 3.636 3.618 3.601 2.421 2.406 2.398 2.387 2.383 2.376 2.281 2.274 2.263 2.249 2.245 2.228 2.223 2.212 2.194 2.175 2.161 2.152 2.144 2.072 2.051 2.029 2.013 2.010 2.007 2.005 1.995 1.990 1.978 1.973 1.971
N
+
CO_2H
$\bar{B}F_3$
F
0.30 1.08 0.71 1.07 1.00 0.57 0.44 0.65 0.40 0.33 0.60 1.07 3.19
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


205.752 205.357 205.192 204.907 204.703 204.447
176.801 175.504
165.790 165.495 164.139 163.849
135.378 135.242 133.220 133.053 132.991 129.354 129.297 128.976 128.919 116.653 116.505 116.438 116.290 116.158 116.014
71.734 71.216
56.817 56.691
30.476 30.377
23.562 23.073
205.752 205.357 205.192 204.907 204.703 204.447
208 207 206 205 204 203
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.309
-112.998
-143.141
-144.419
-110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


0.085
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-0.657
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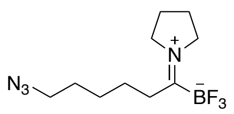
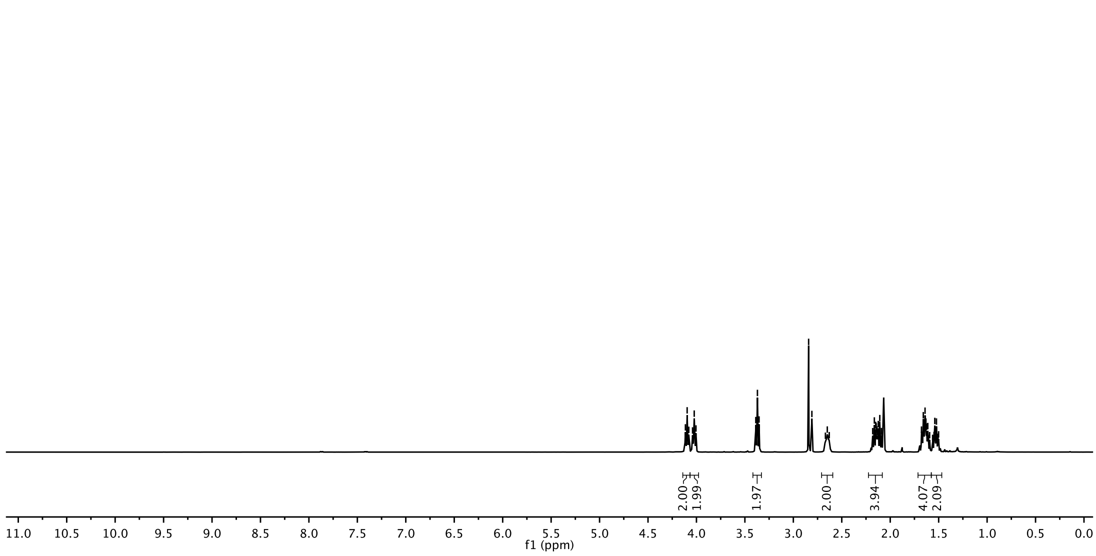
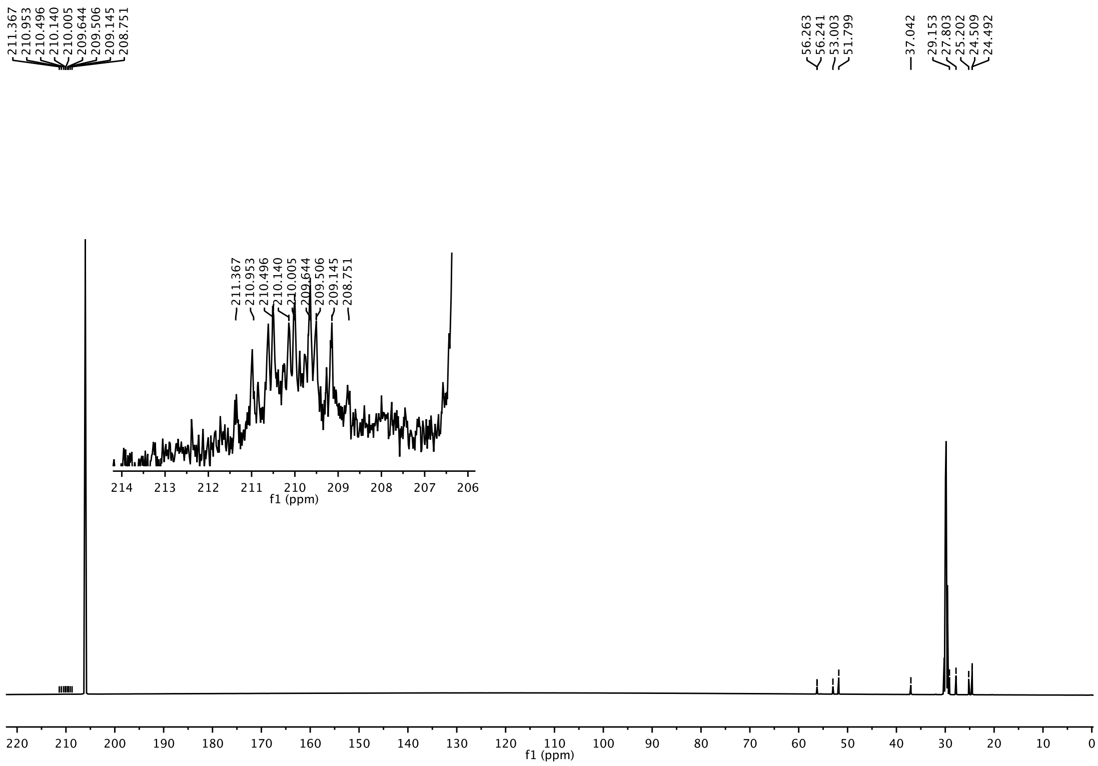
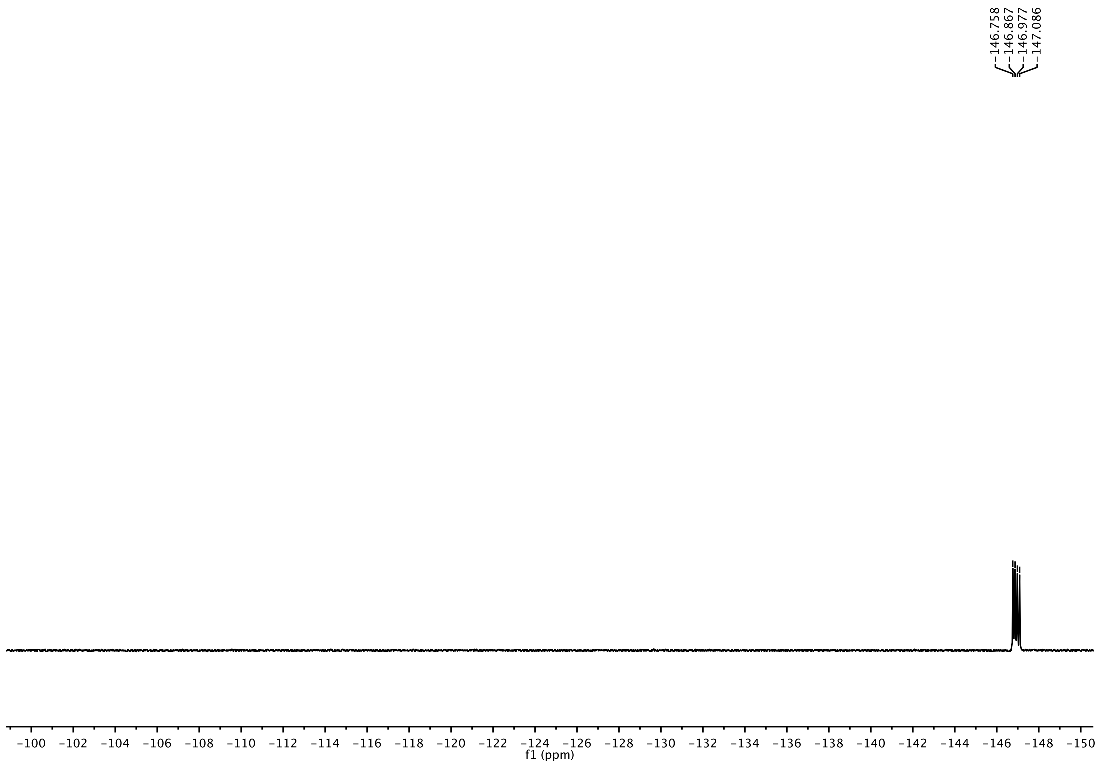
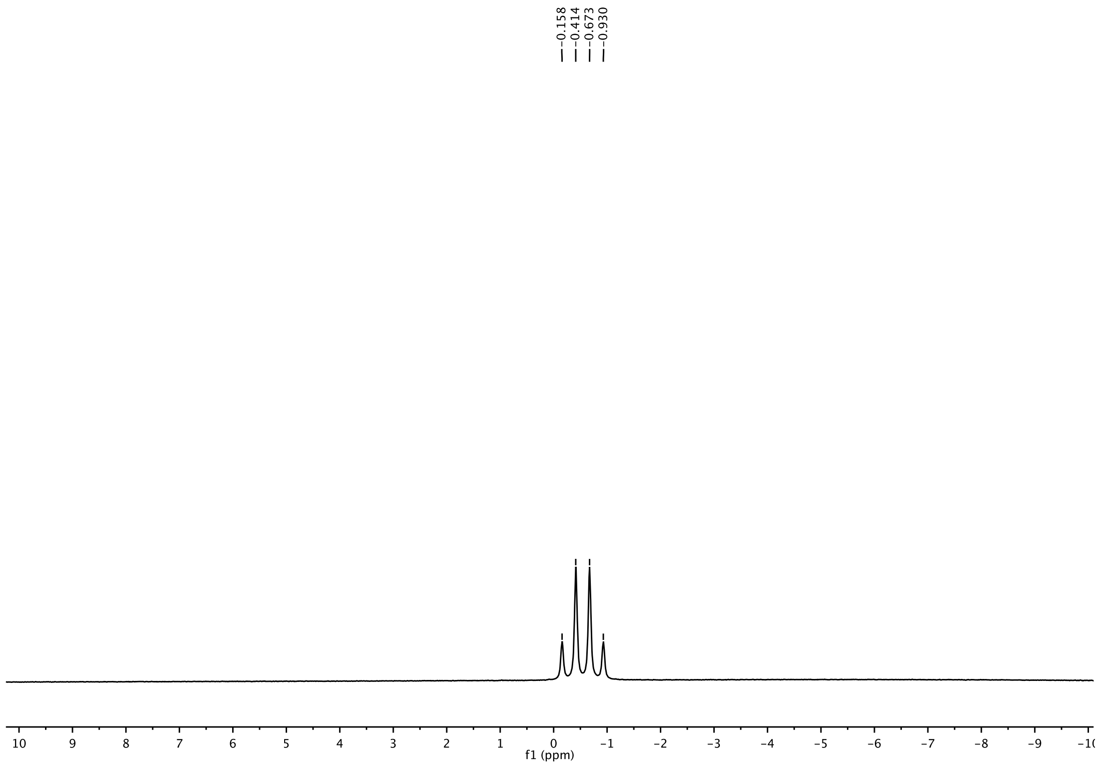
f1 (ppm)


N3
N
+
BF3


4.114 4.096 4.079 4.040 4.023 4.005 3.387 3.371 3.354 2.842 2.809 2.669 2.649 2.629 2.181 2.164 2.150 2.144 2.137 2.133 2.124 2.108 2.091 2.086 1.677 1.670 1.659 1.652 1.641 1.632 1.623 1.612 1.605 1.593 1.562 1.559 1.548 1.540 1.532 1.523 1.511 1.506 1.501
2.00
1.99
1.97
2.00
3.94
4.07
2.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


211.367 210.953 210.496 210.140 210.005 209.644 209.506 209.145 208.751
56.263 56.241 53.003 51.799
37.042
29.153 27.803 25.202 24.509 24.492
214 213 212 211 210 209 208 207 206
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-146.758
-146.867
-146.977
-147.086
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


-0.158
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-0.673
-0.930
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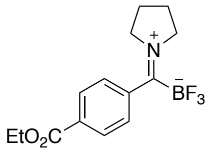
f1 (ppm)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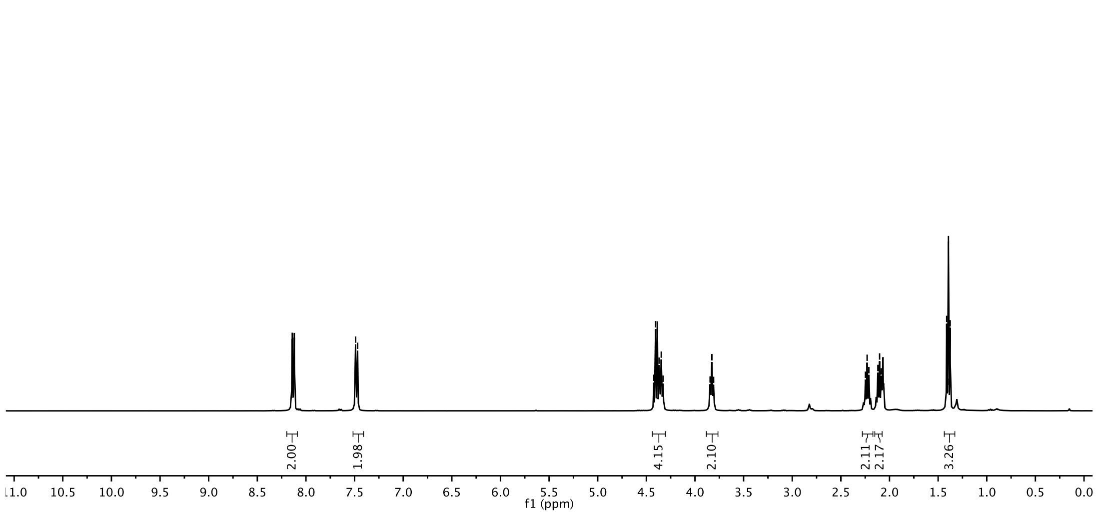
BF3
EtO2C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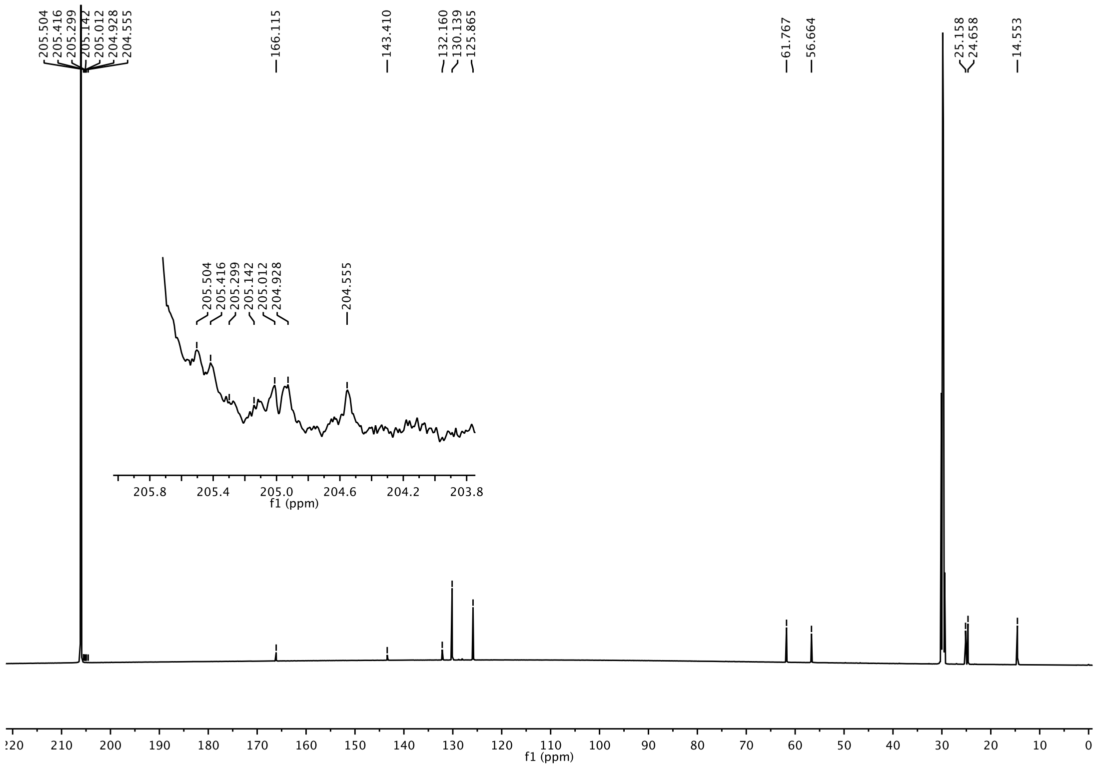
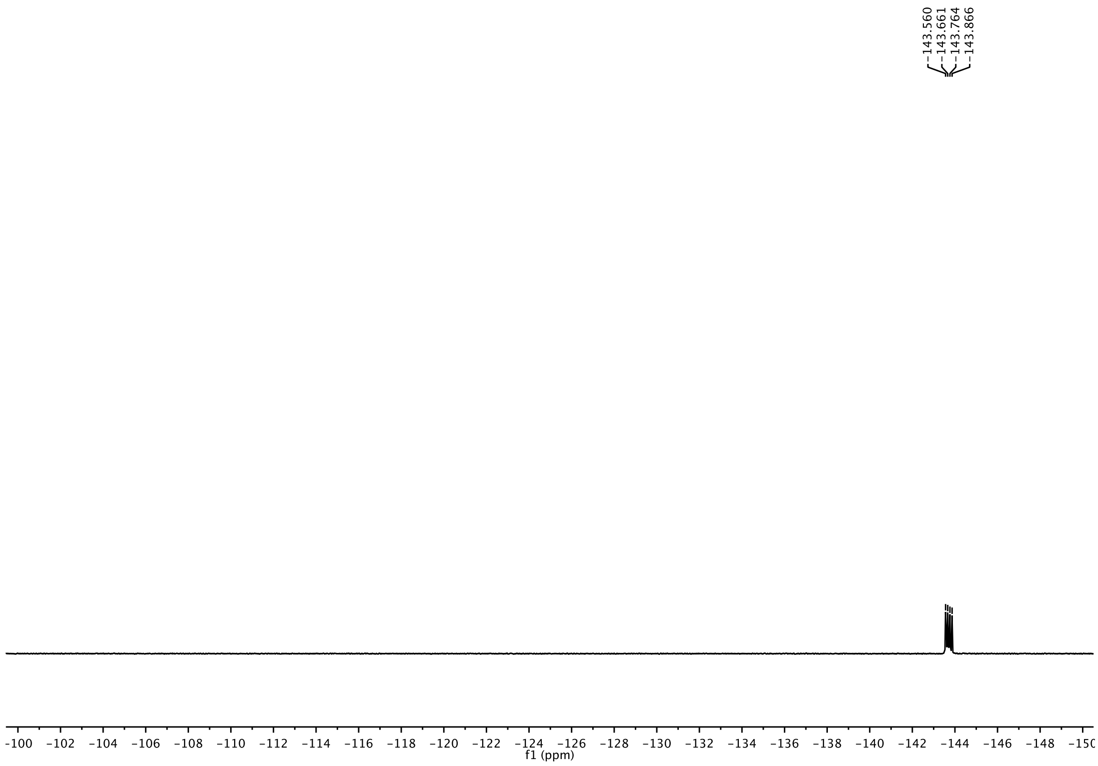
8.120
7.489
7.469
4.423
4.405
4.387
4.369
4.364
4.347
4.329
3.845
3.827
3.809
2.248
2.230
2.213
2.119
2.102
2.085
2.078
1.412
1.394
1.389
1.376
2.00
1.98
4.15
2.10
2.11
2.17
3.26
f1 (ppm)


205.504
205.416
205.299
205.142
205.012
204.928
204.555
166.115
143.410
132.160
130.139
125.865
61.767
56.664
25.158
24.658
14.553
f1 (ppm)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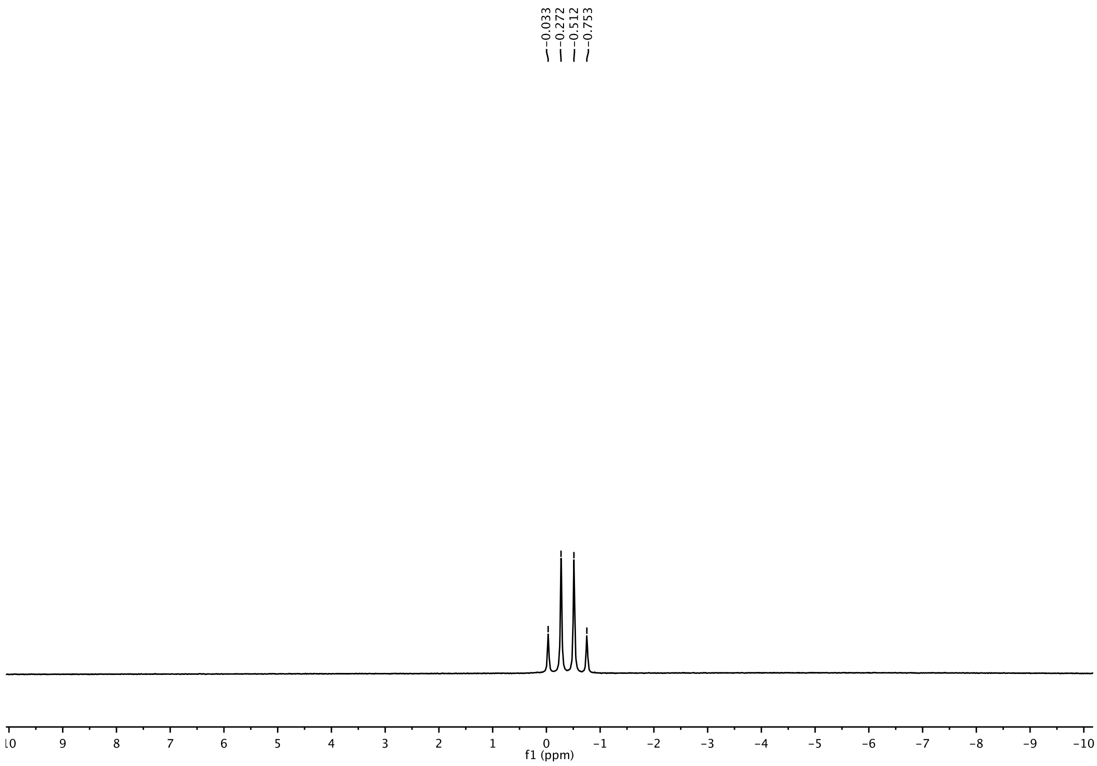
-143.661
-143.764
-143.866
f1 (ppm)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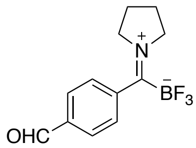
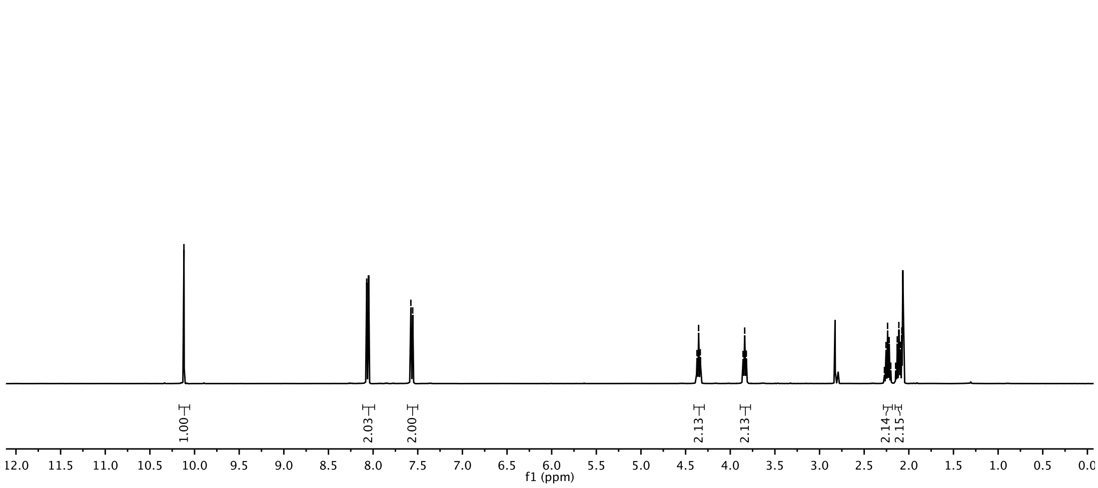
-0.272
-0.512
-0.753
f1 (ppm)


N
BF3
OHC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8.067
8.055
8.050
7.577
7.572
7.561
7.556
4.372
4.354
4.336
3.856
3.838
3.820
2.273
2.255
2.238
2.220
2.202
2.147
2.129
2.112
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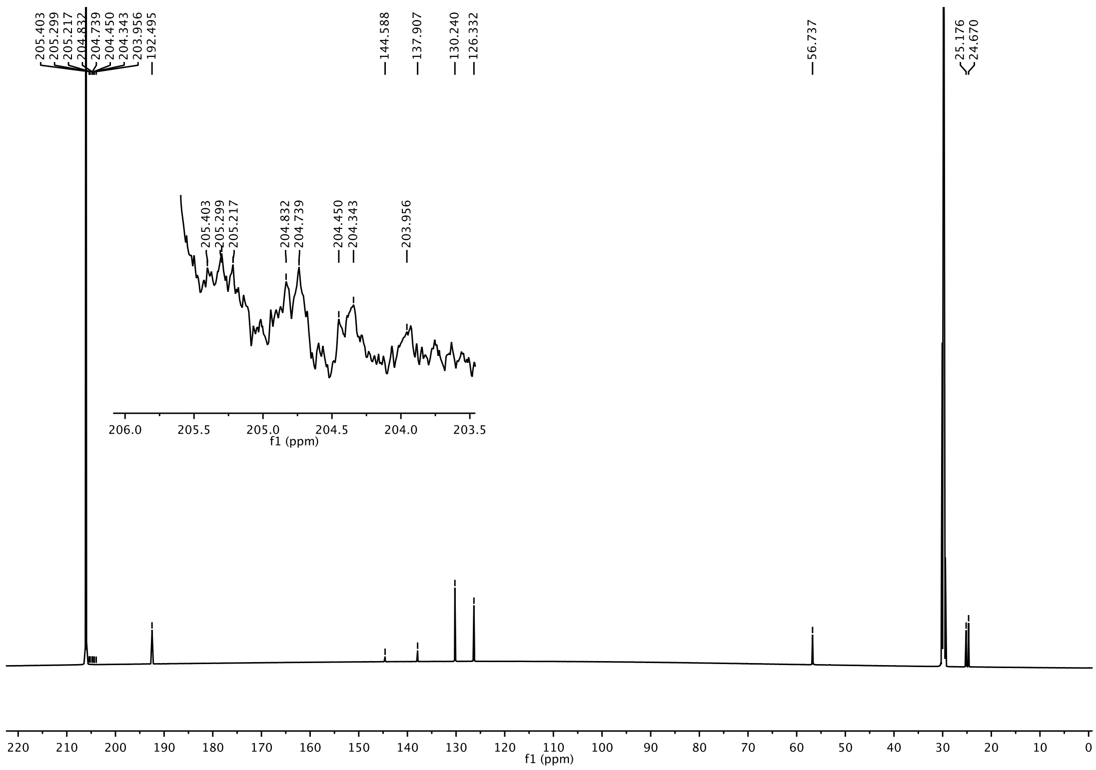
2.078
1.00
2.03
2.00
2.13
2.13
2.14
2.15
f1 (ppm)


205.403
205.299
205.217
204.832
204.739
204.450
204.343
203.956
192.495
144.588
137.907
130.240
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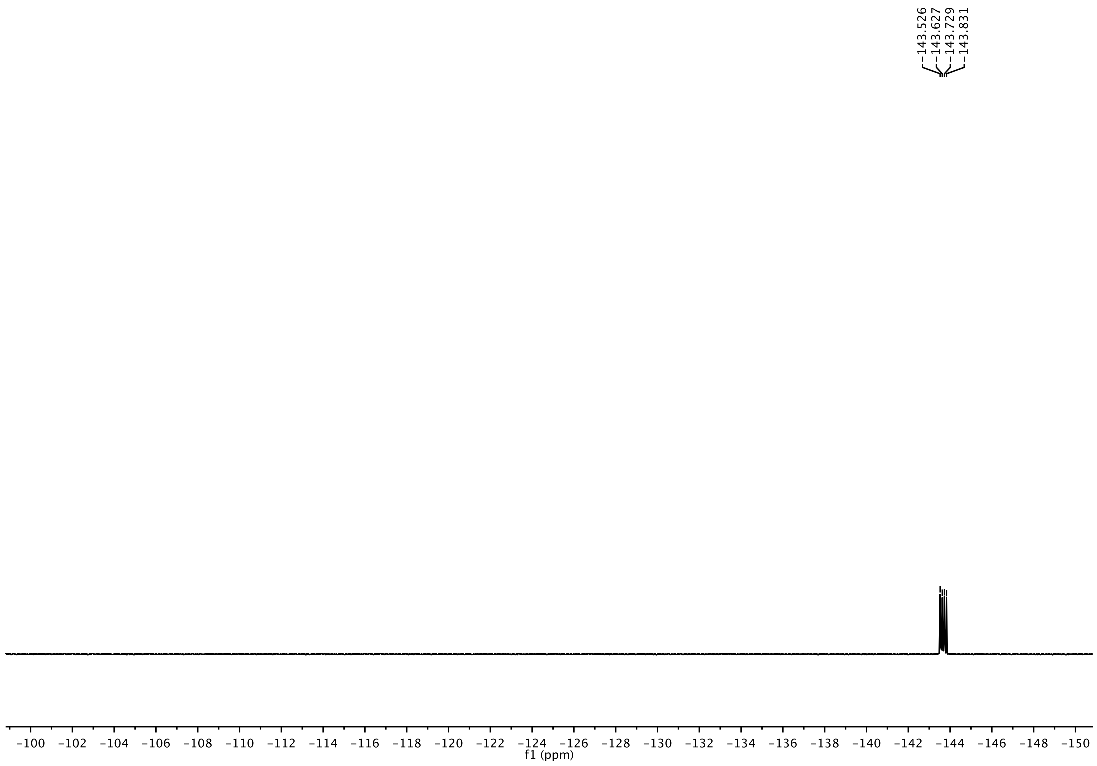
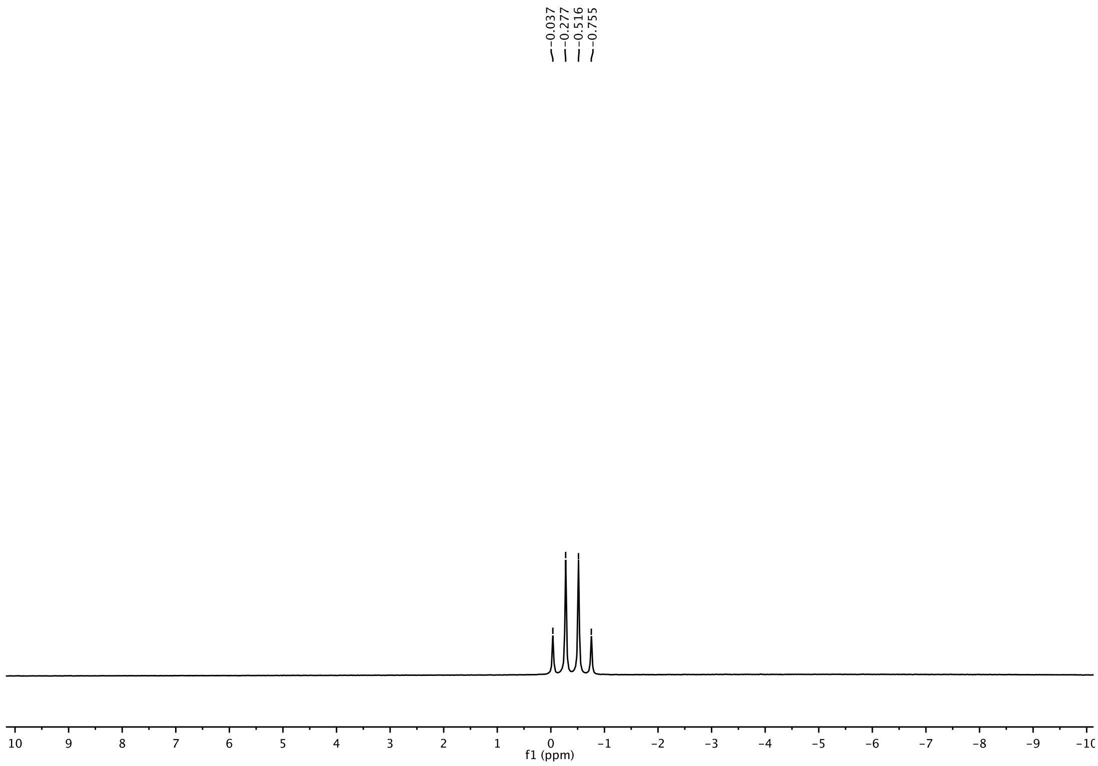
56.737
25.176
24.670
f1 (ppm)


-143.526
-143.627
-143.729
-143.831
−100 −102 −104 −106 −108 −110 −112 −114 −116 −118 −120 −122 −124 −126 −128 −130 −132 −134 −136 −138 −140 −142 −144 −146 −148 −150
f1 (ppm)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-0.277
-0.516
-0.755
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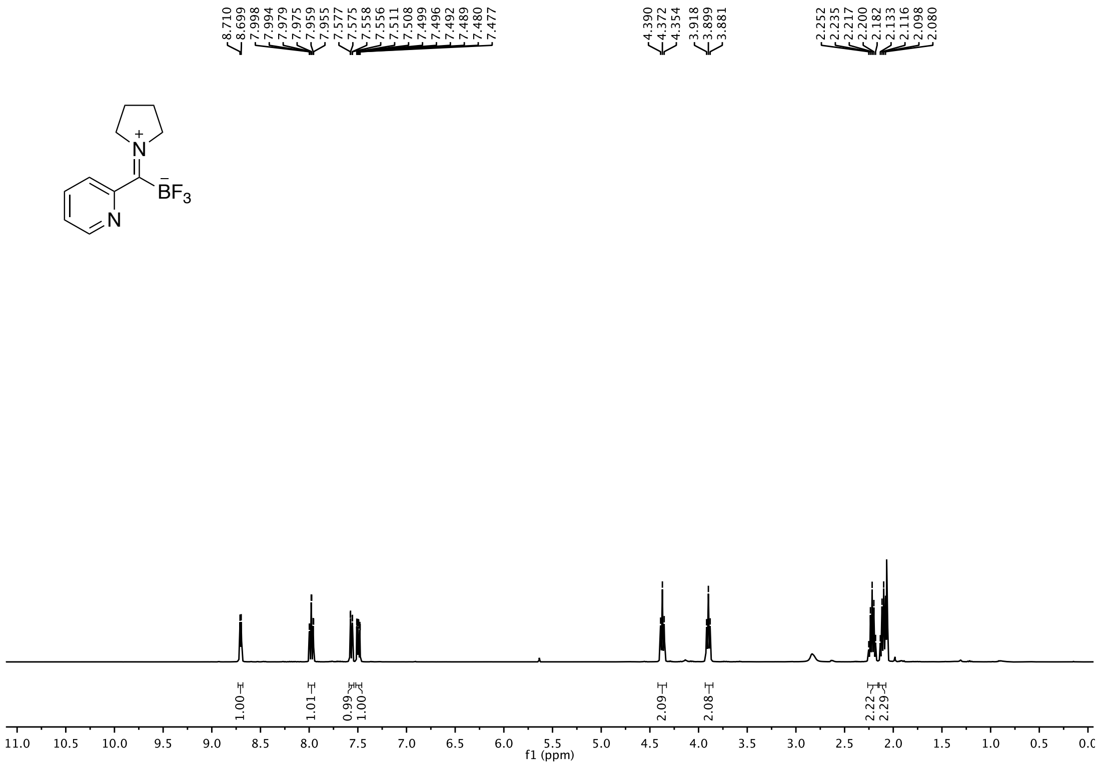
f1 (ppm)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BF3
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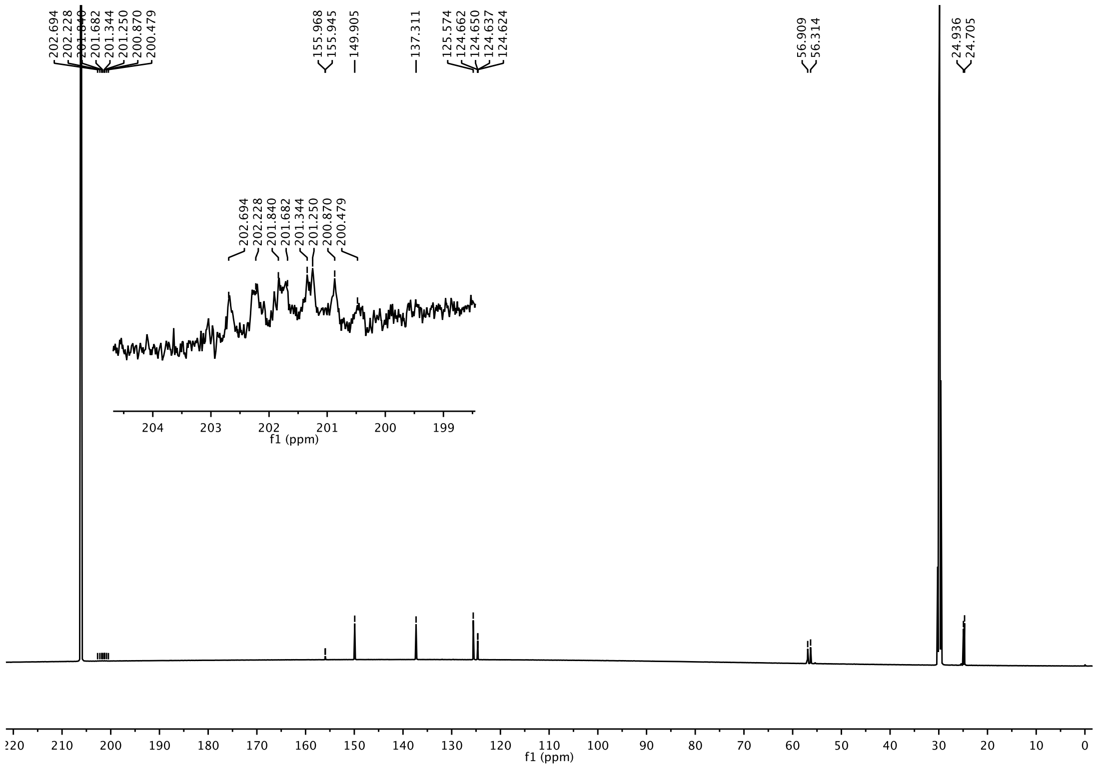
7.994
7.979
7.975
7.959
7.955
7.577
7.575
7.558
7.556
7.511
7.508
7.499
7.496
7.492
7.489
7.480
7.477
4.390
4.372
4.354
3.918
3.899
3.881
2.252
2.235
2.217
2.200
2.182
2.133
2.116
2.098
2.080
1.00
1.01
0.99
1.00
2.09
2.08
2.22
2.29
f1 (ppm)


202.694
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201.682
201.344
201.250
200.870
200.479
155.968
155.945
149.905
137.311
125.574
124.662
124.650
124.637
124.624
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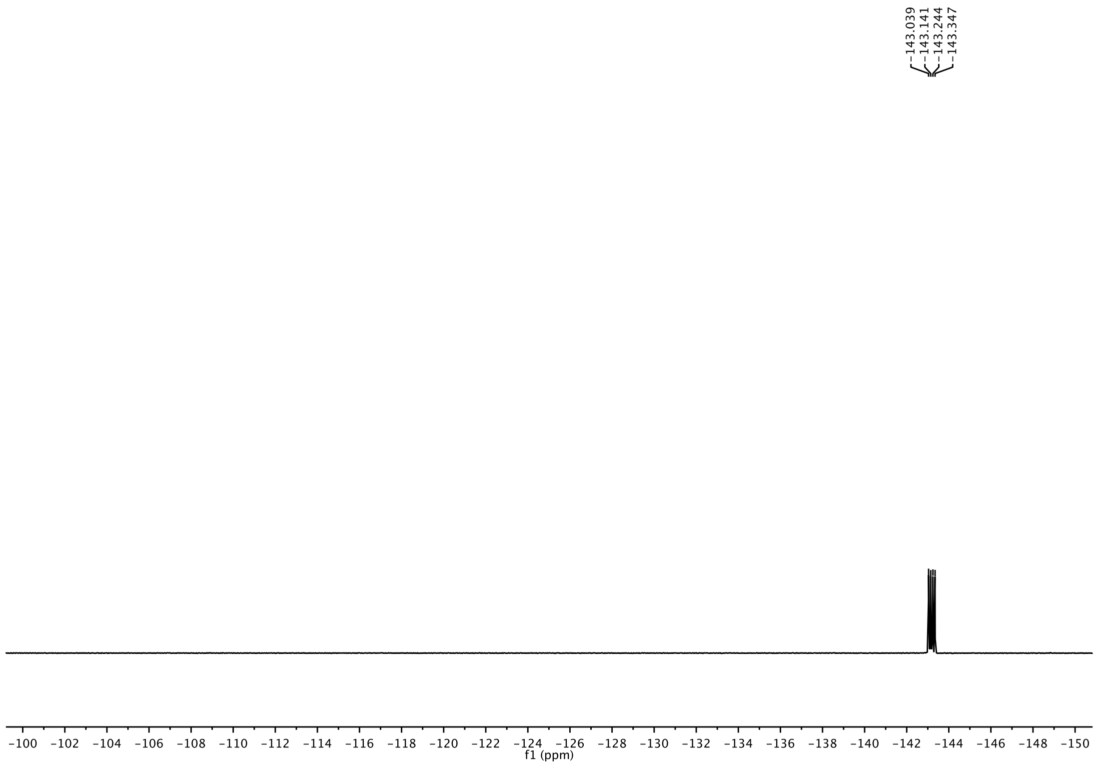
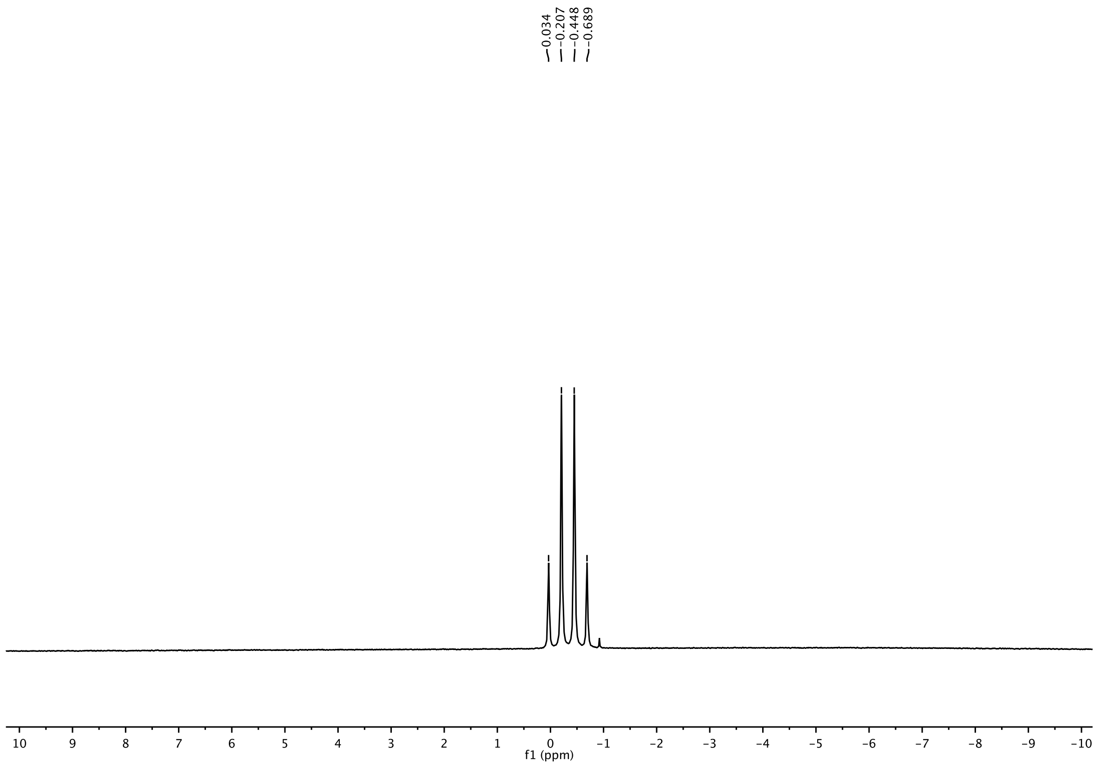
56.314
24.936
24.705
f1 (ppm)


-143.039
-143.141
-143.244
-143.347
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)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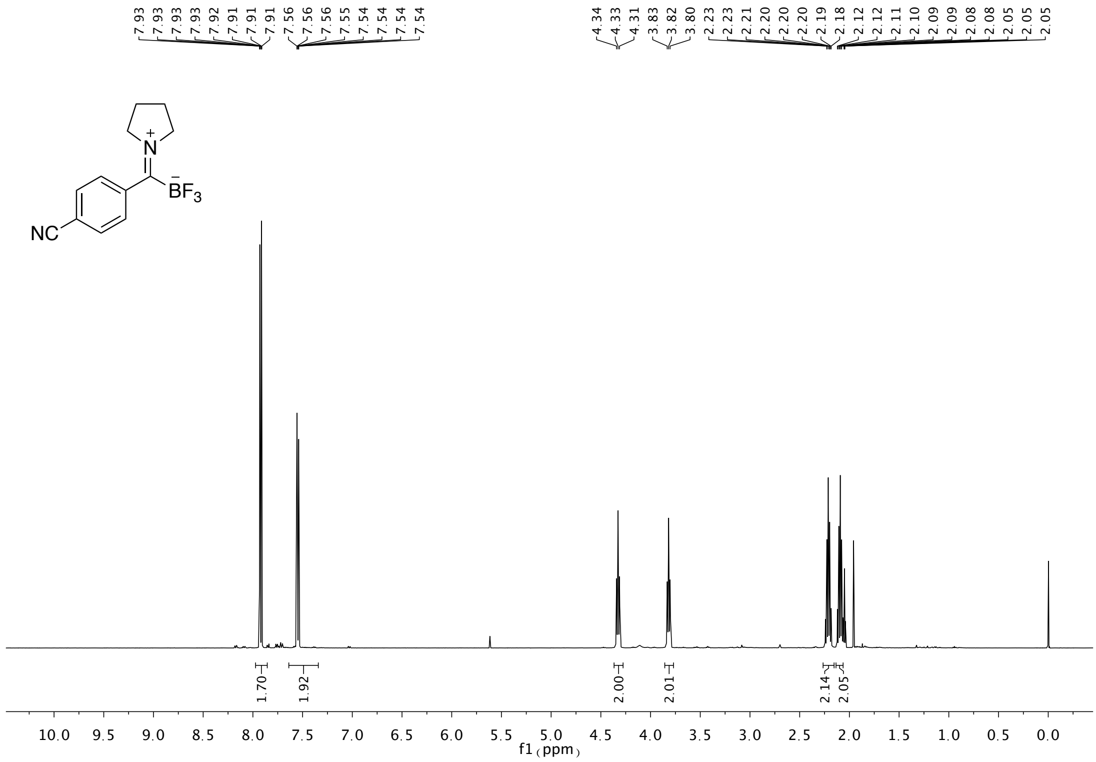
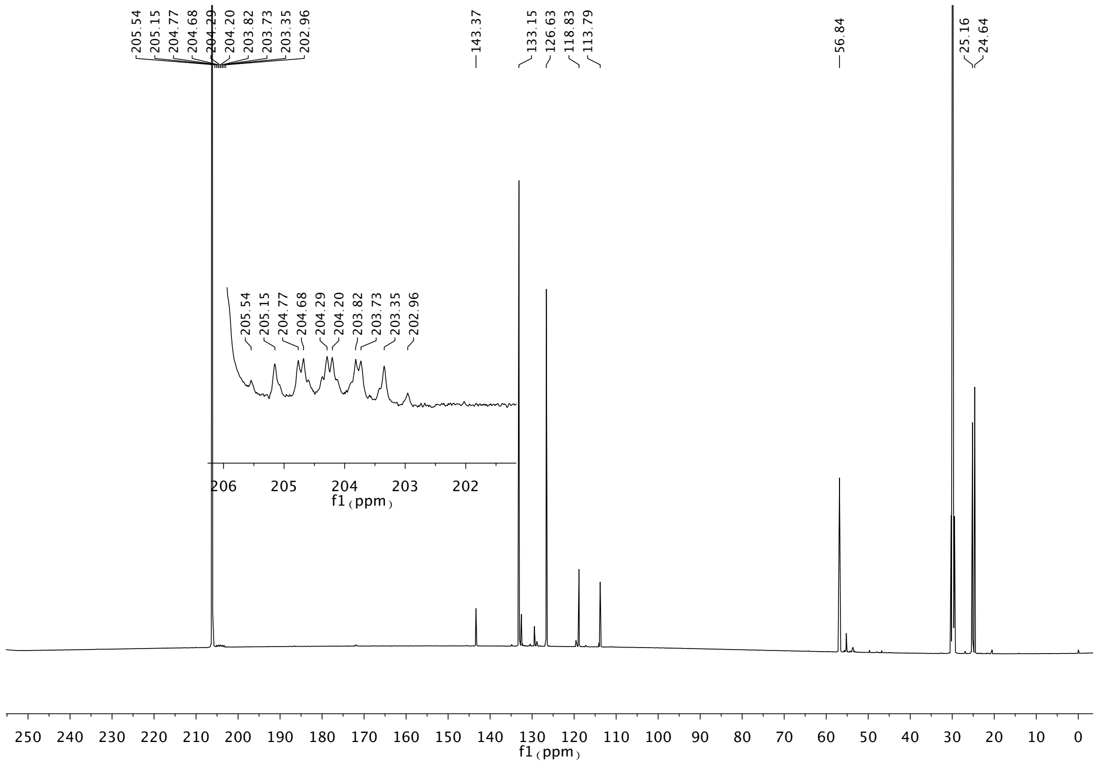
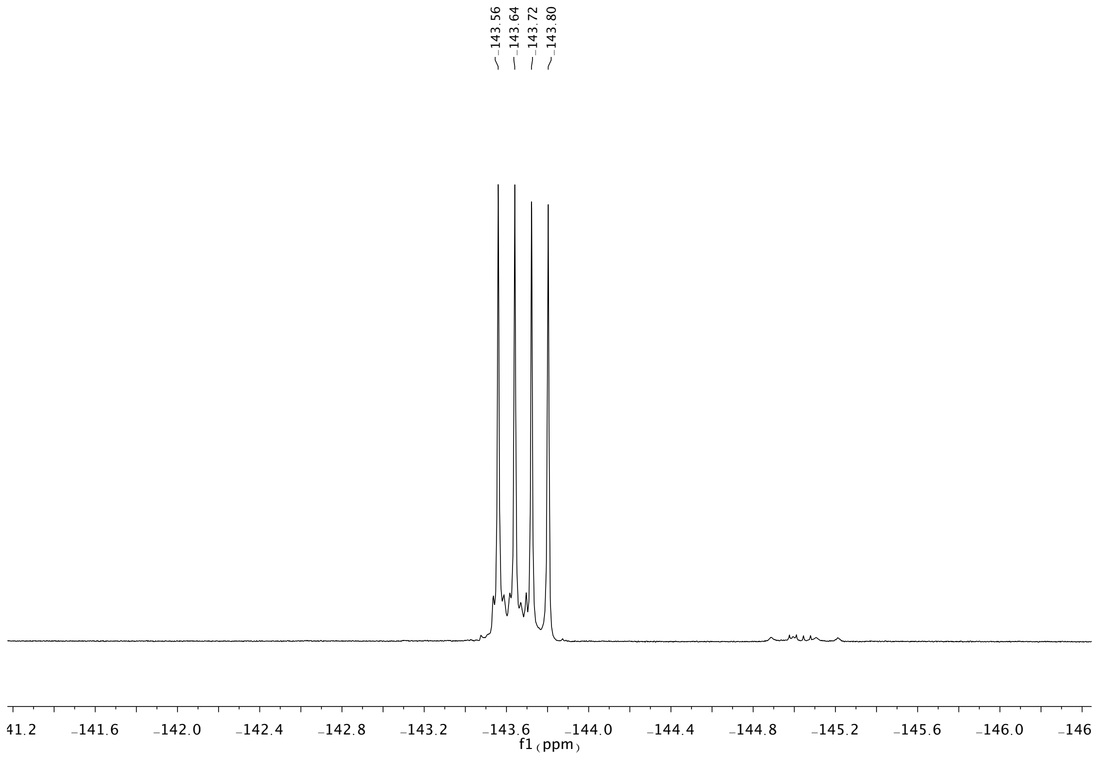
f1 (ppm)


7.93 7.93 7.93 7.93 7.92 7.91 7.91 7.91 7.56 7.56 7.56 7.55 7.54 7.54 7.54 7.54
4.34 4.33 4.31 3.83 3.82 3.80 2.23 2.23 2.21 2.20 2.20 2.20 2.19 2.18 2.12 2.12 2.11 2.10 2.09 2.09 2.08 2.08 2.05 2.05 2.05
NC
N
+
BF3
1.70
1.92
2.00
2.01
2.14
2.05
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)


205.54 205.15 204.77 204.68 204.29 204.20 203.82 203.73 203.35 202.96
143.37
133.15 126.63 118.83 113.79
56.84
25.16 24.64
206 205 204 203 202
f1 (ppm)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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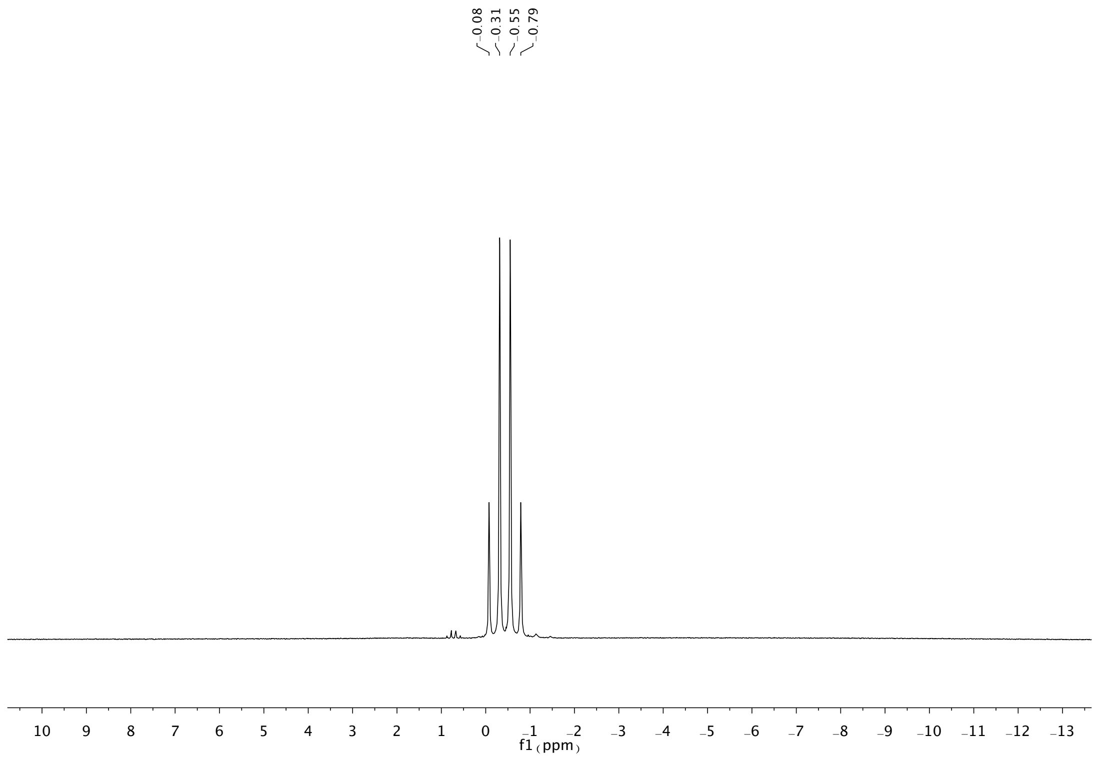
-143.64
-143.72
-143.80
41.2
-141.6
-142.0
-142.4
-142.8
-143.2
-143.6
-144.0
-144.4
-144.8
-145.2
-145.6
-146.0
-146
f1 (ppm)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-0.31
-0.55
-0.79
10
9
8
7
6
5
4
3
2
1
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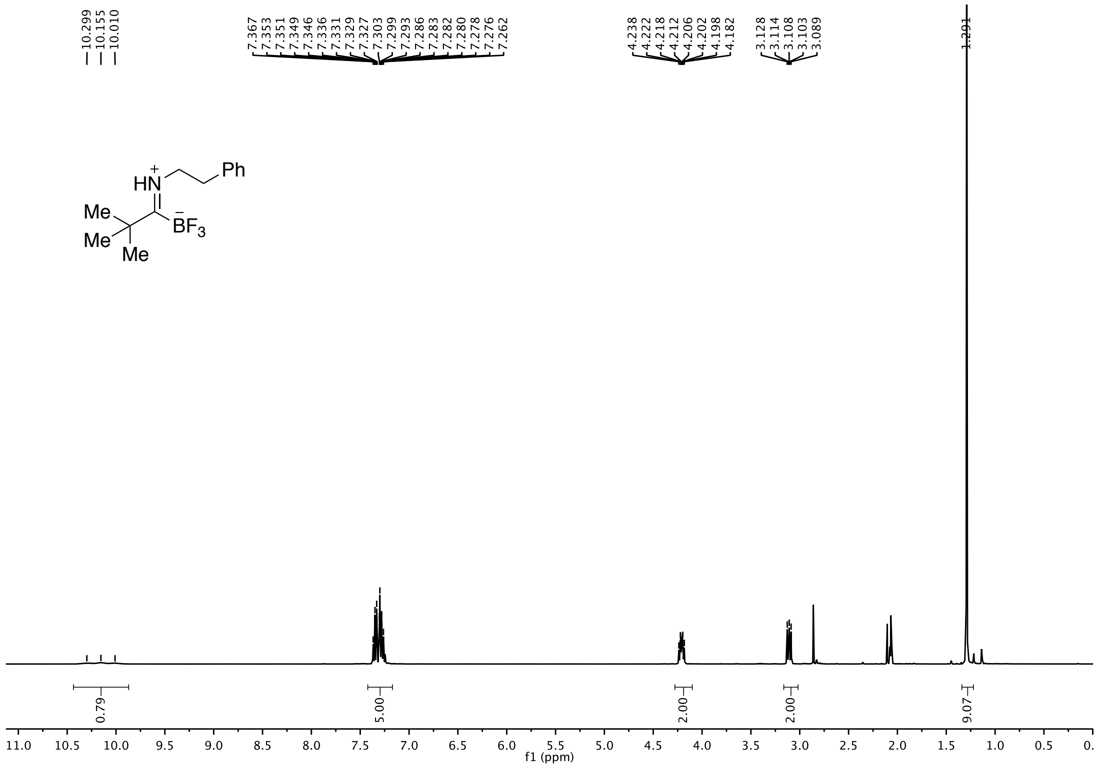
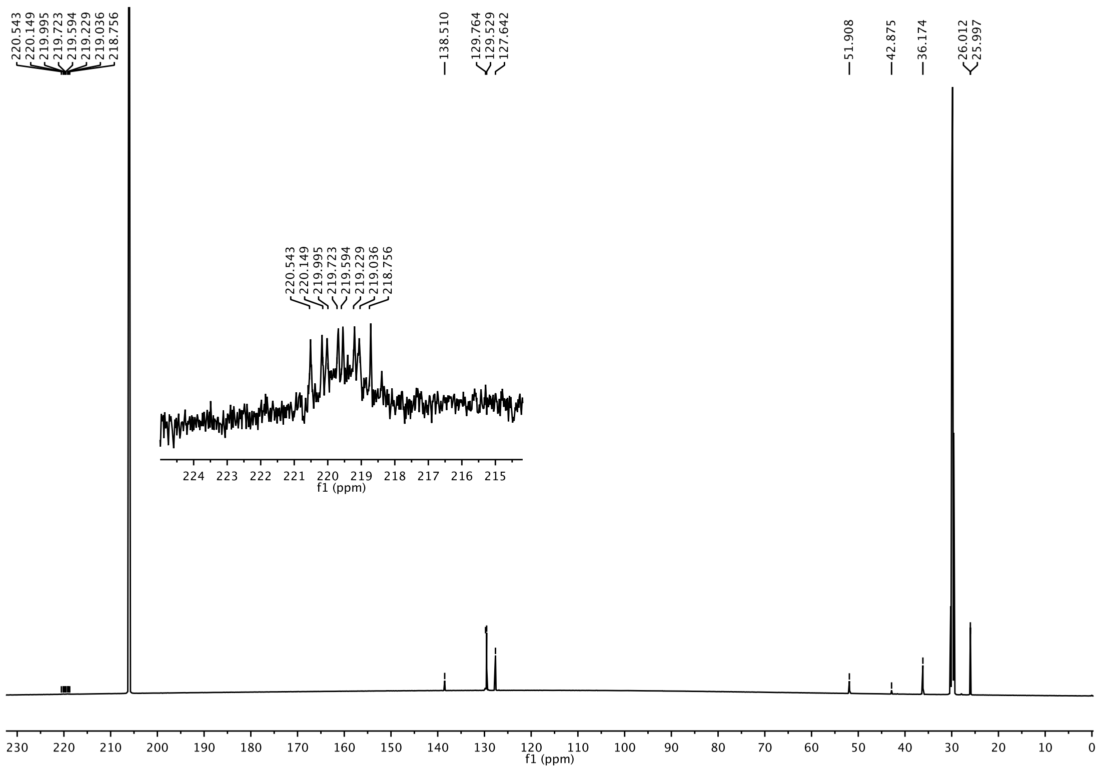
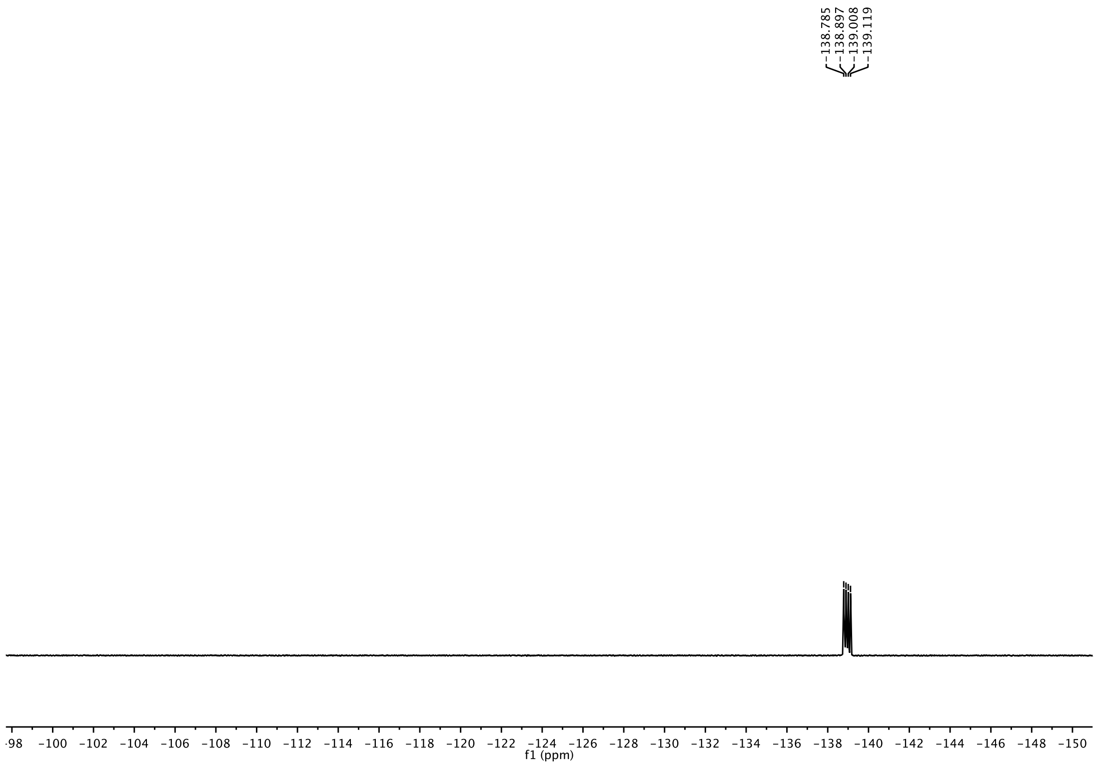
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
f1 (ppm)







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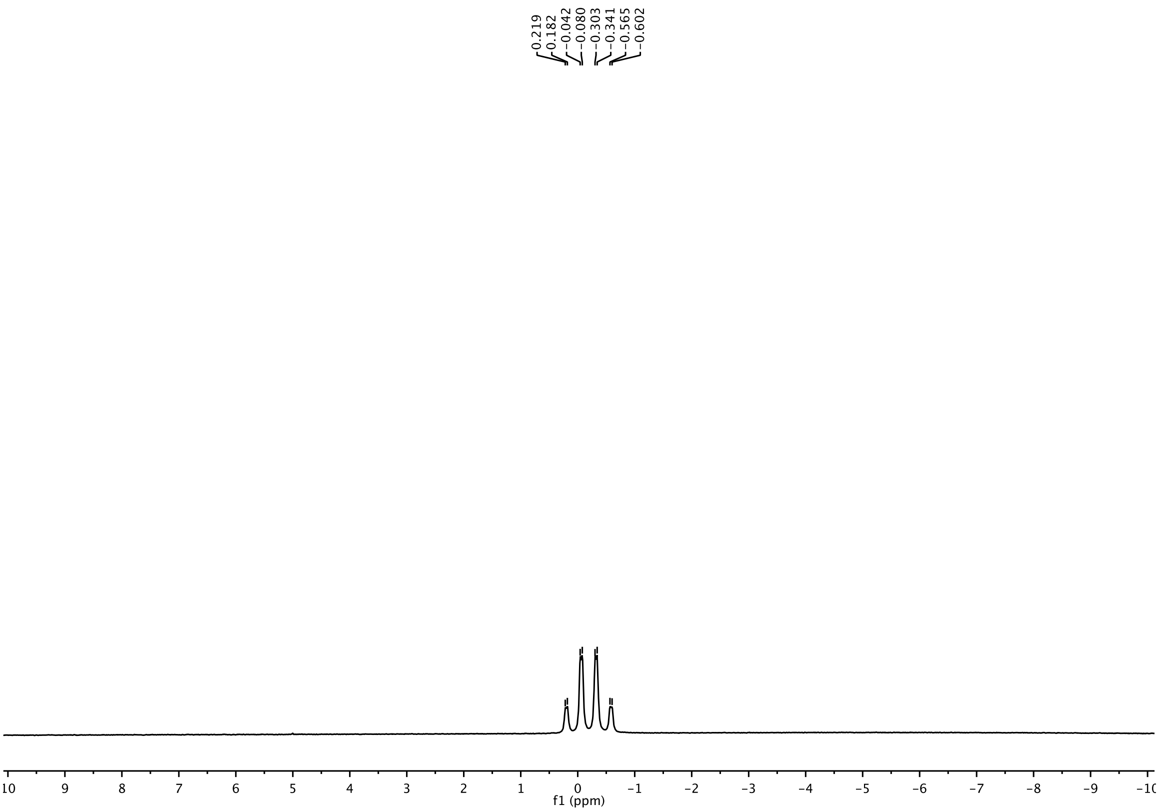
-139.119
f1 (ppm)



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-0.303
-0.341
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-0.602
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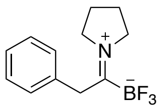
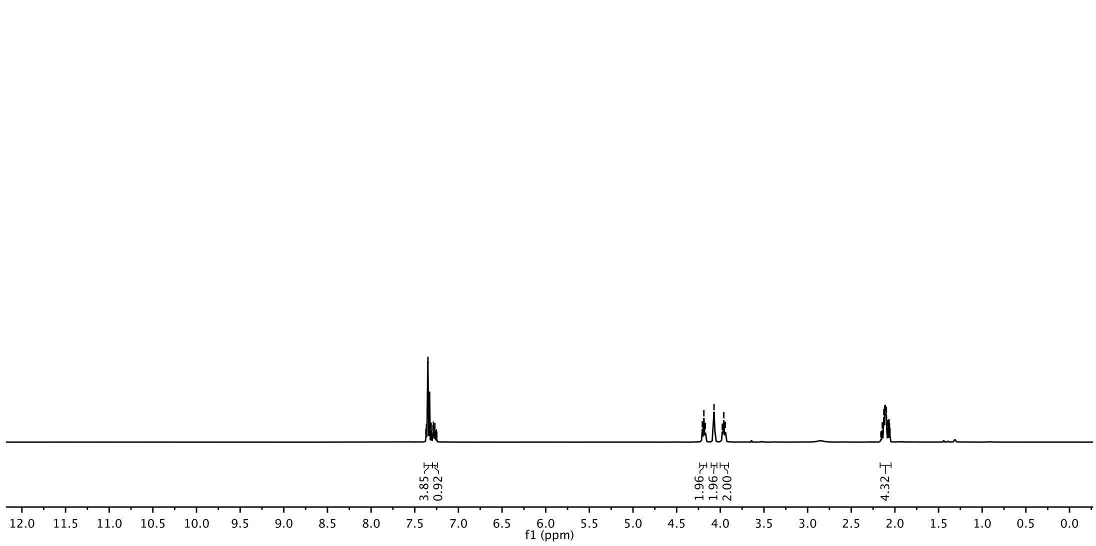

N
BF3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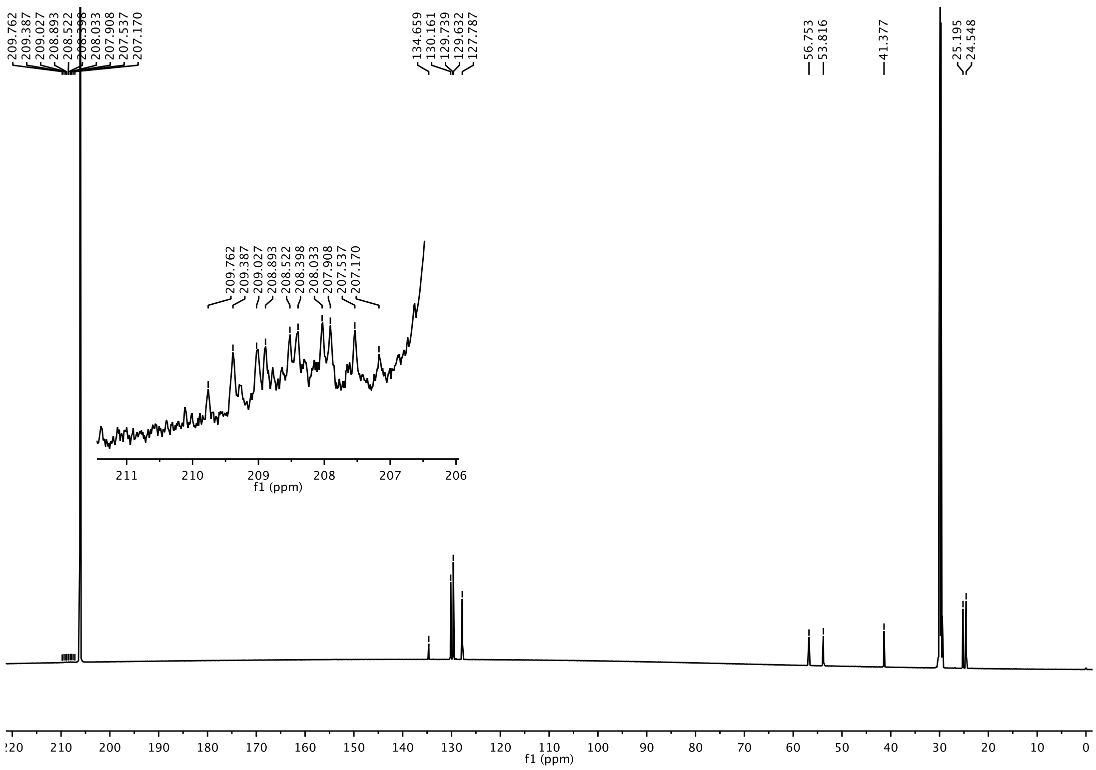
7.254
7.248
4.205
4.188
4.171
4.072
3.977
3.960
3.943
2.160
2.152
2.144
2.133
2.126
2.121
2.115
2.109
2.098
2.091
2.079
2.073
2.067
2.062
2.056
3.85
0.92
1.96
1.96
2.00
4.32
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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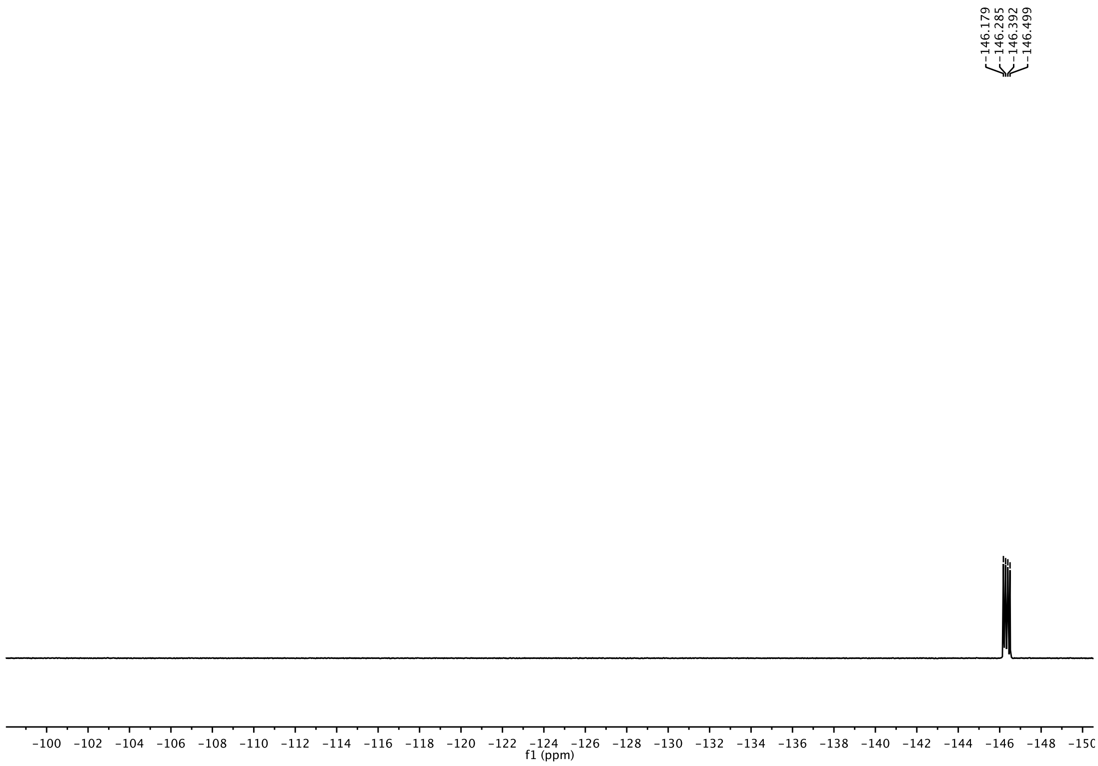
207.537
207.170
134.659
130.161
129.739
129.632
127.787
56.753
53.816
41.377
25.195
24.548
211 210 209 208 207 206
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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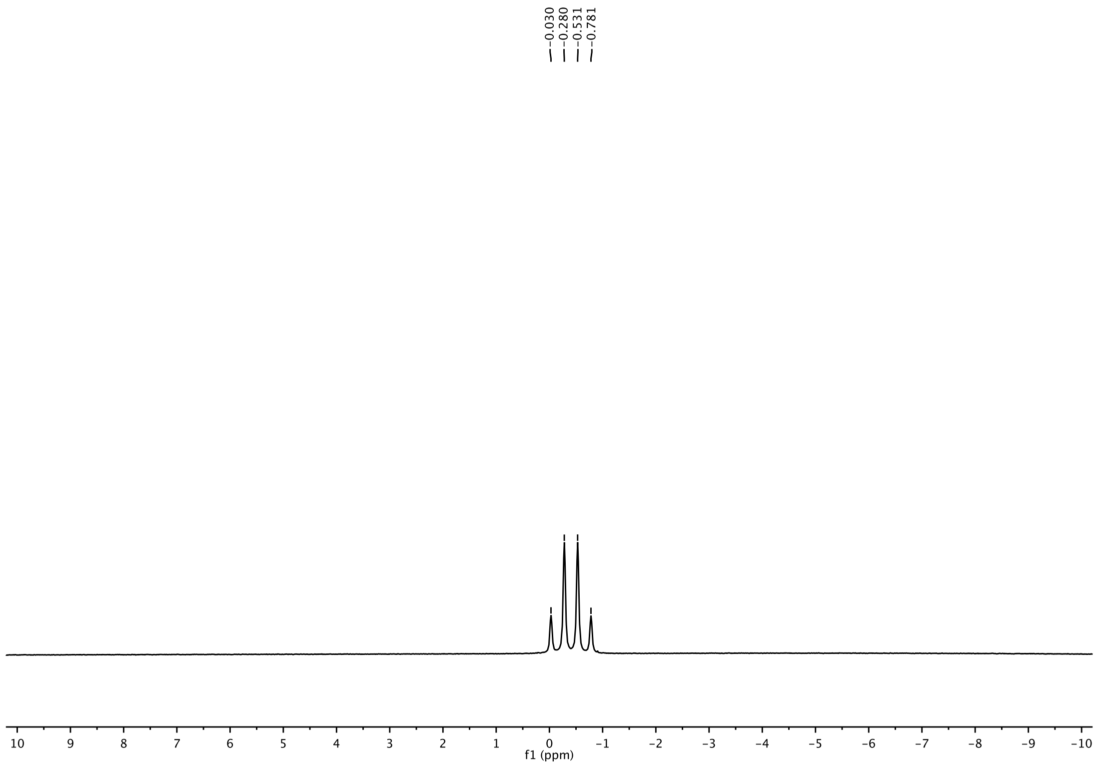
-146.285
-146.392
-146.499
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


-0.030
-0.280
-0.531
-0.781
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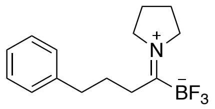
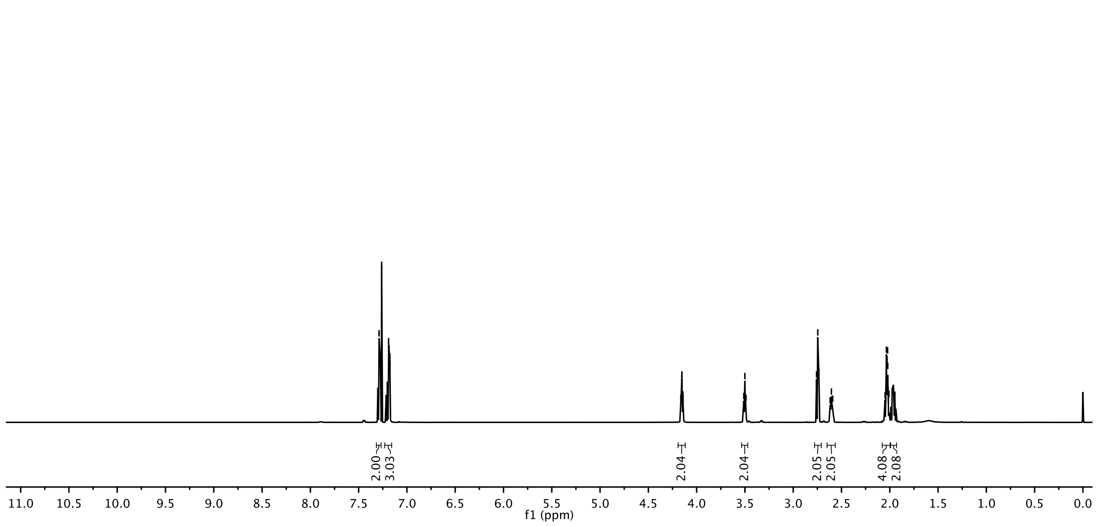
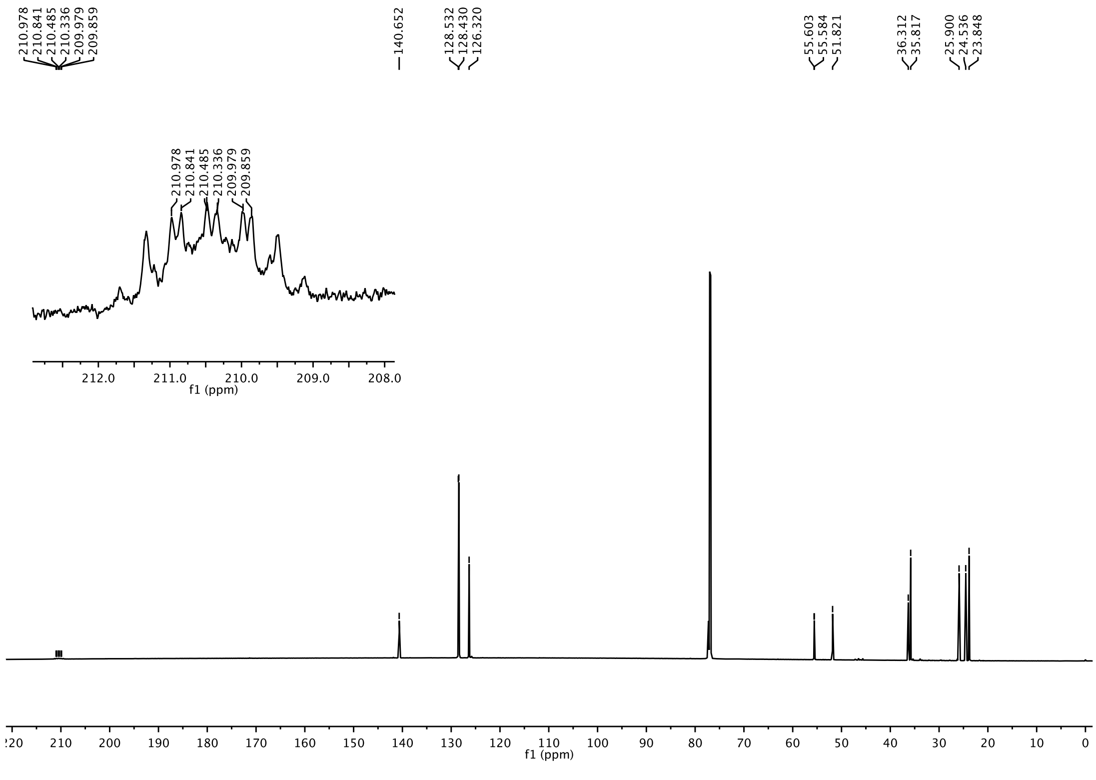
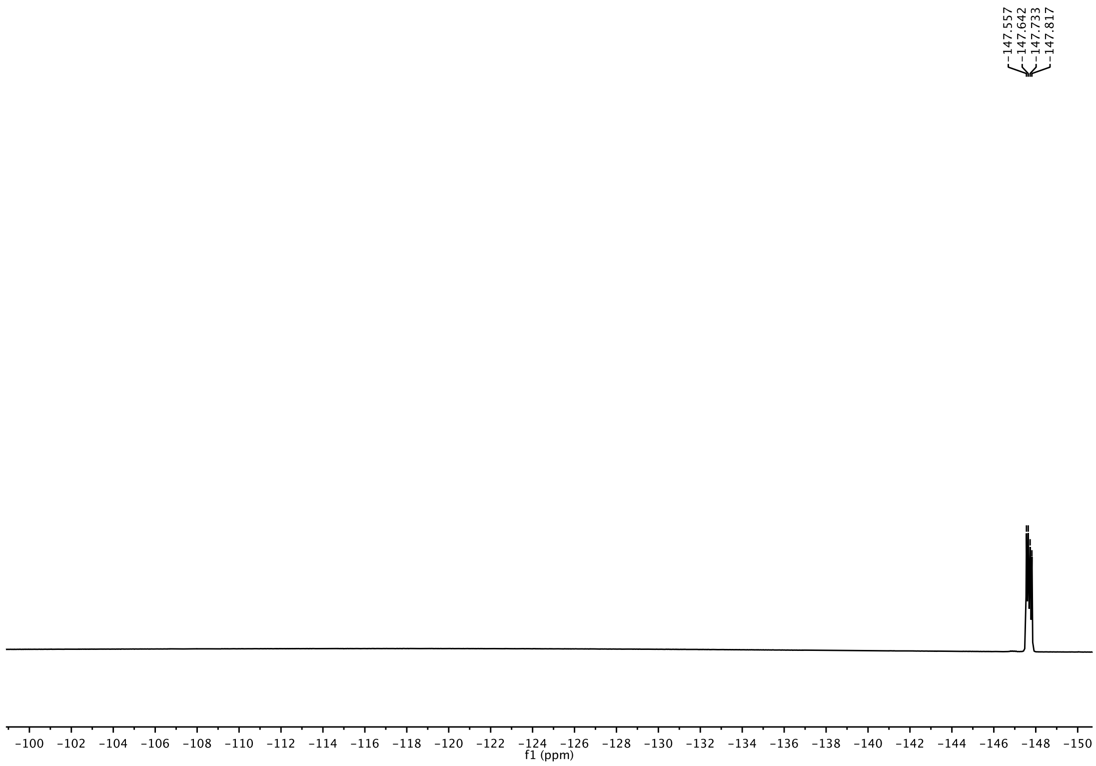
f1 (ppm)








-147.557
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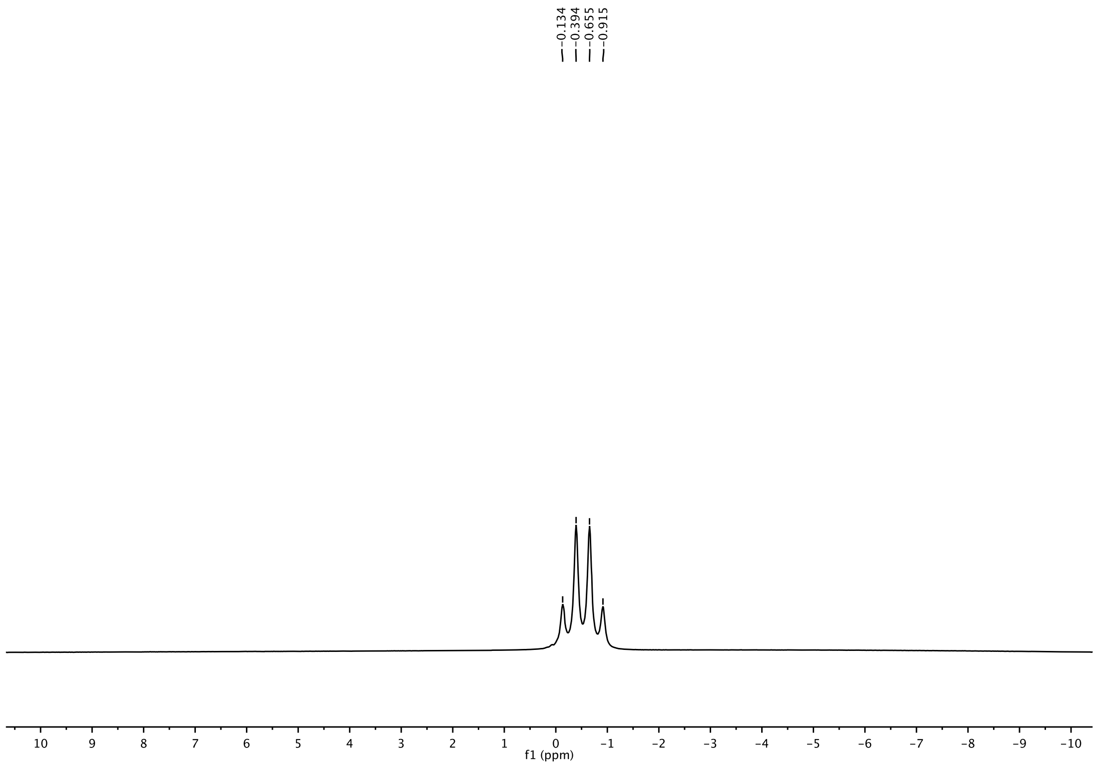
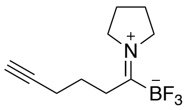
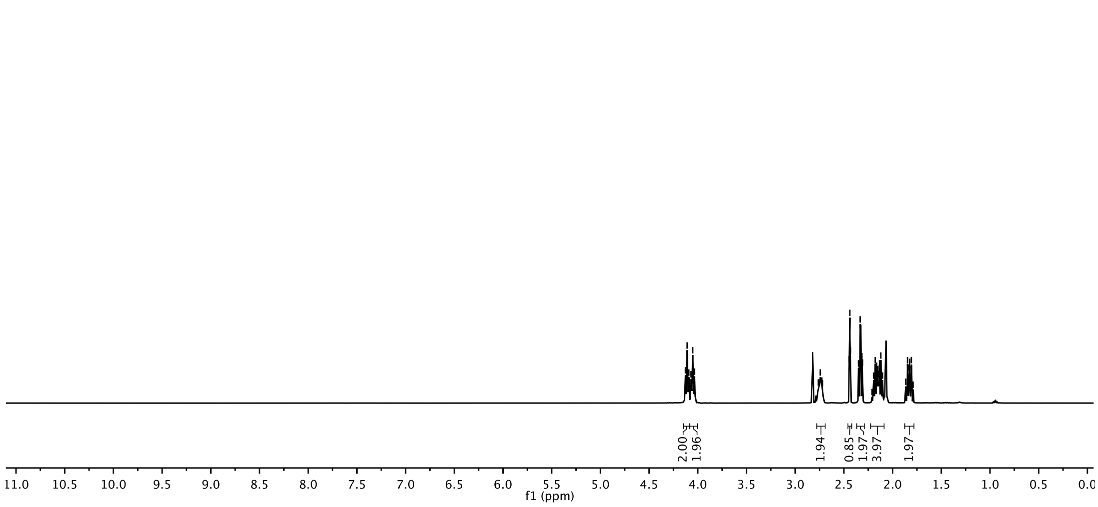
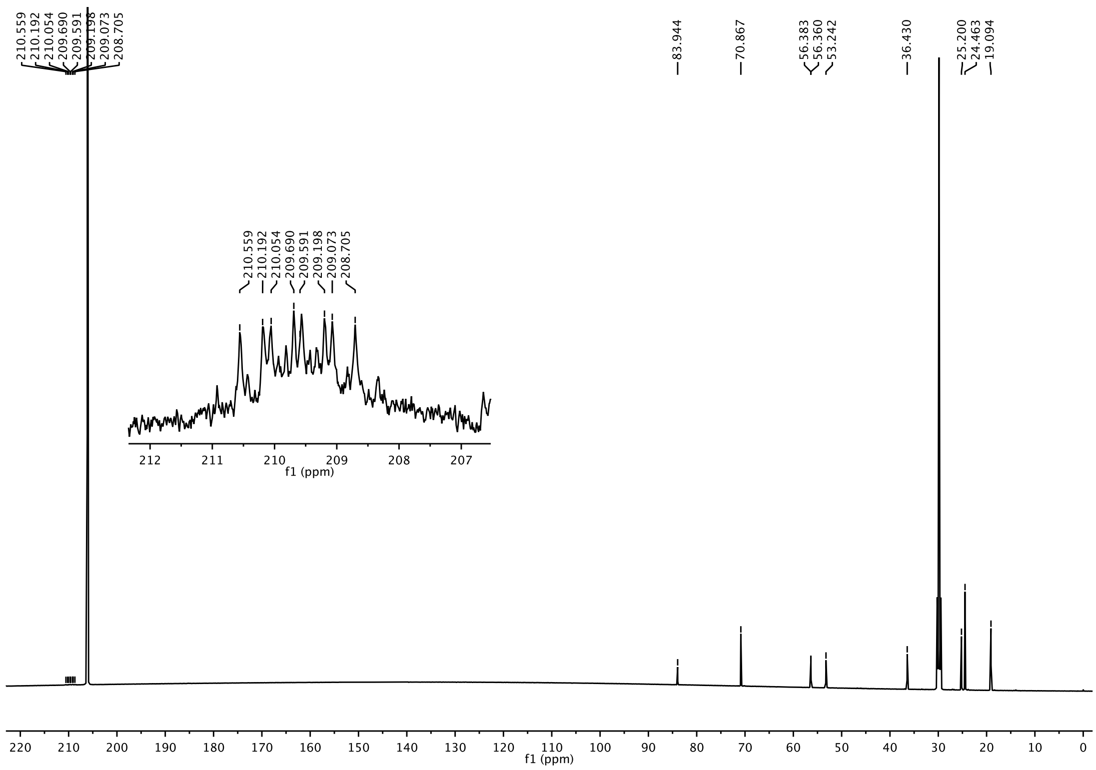
-147.733
-147.817
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


-0.134
-0.394
-0.655
-0.915
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10
f1 (ppm)


N
BF3


4.127
4.109
4.092
4.069
4.052
4.034
2.742
2.726
2.445
2.439
2.432
2.350
2.343
2.332
2.326
2.315
2.308
2.195
2.178
2.163
2.159
2.151
2.146
2.138
2.134
2.121
2.103
1.847
1.829
1.825
2.00
1.96
1.94
0.85
1.97
3.97
1.97
f1 (ppm)


210.559
210.192
210.054
209.690
209.591
209.198
209.073
208.705
83.944
70.867
56.383
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53.242
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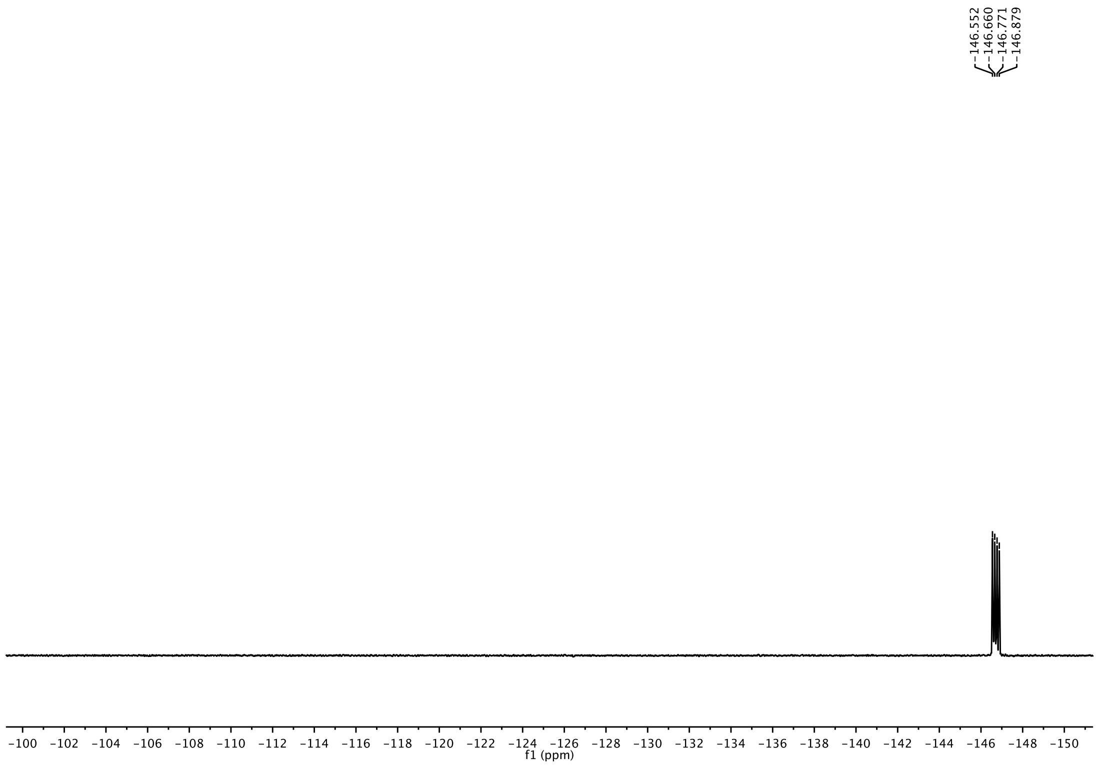
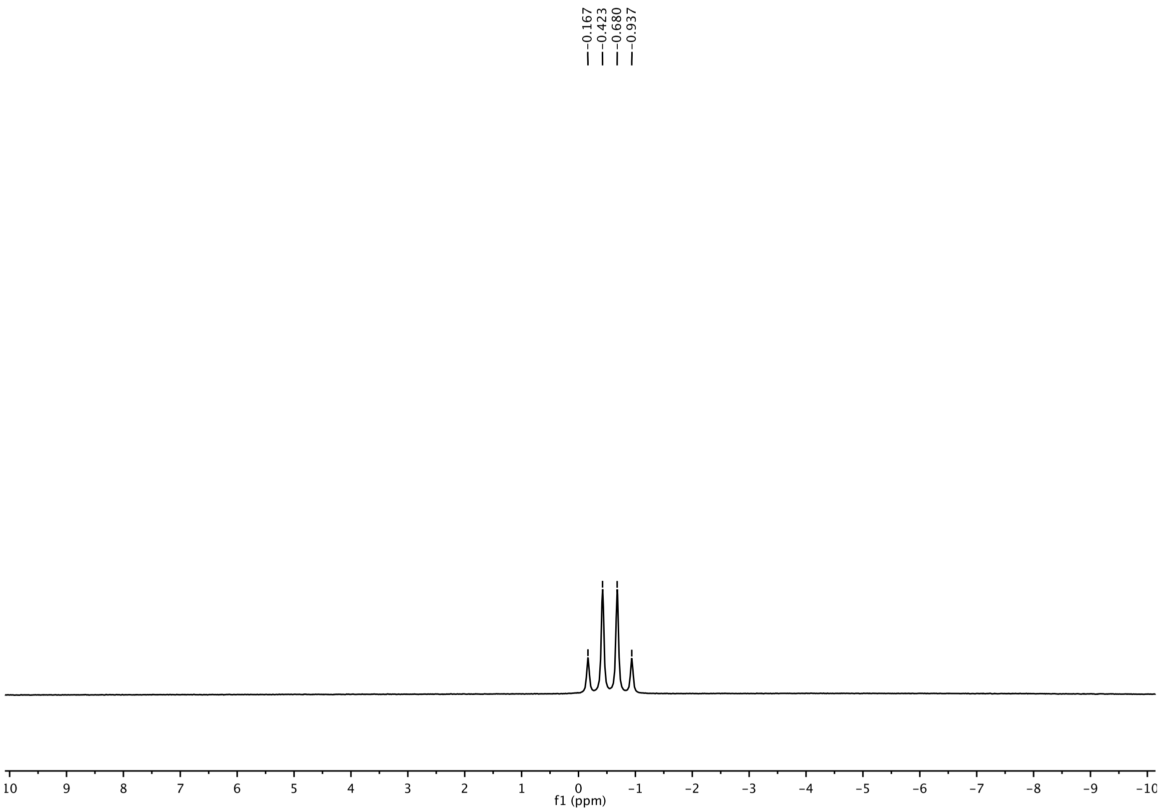
24.463
19.094
f1 (ppm)


-146.552
-146.660
-146.771
-146.879
–100 –102 –104 –106 –108 –110 –112 –114 –116 –118 –120 –122 –124 –126 –128 –130 –132 –134 –136 –138 –140 –142 –144 –146 –148 –150
f1 (ppm)


-0.167
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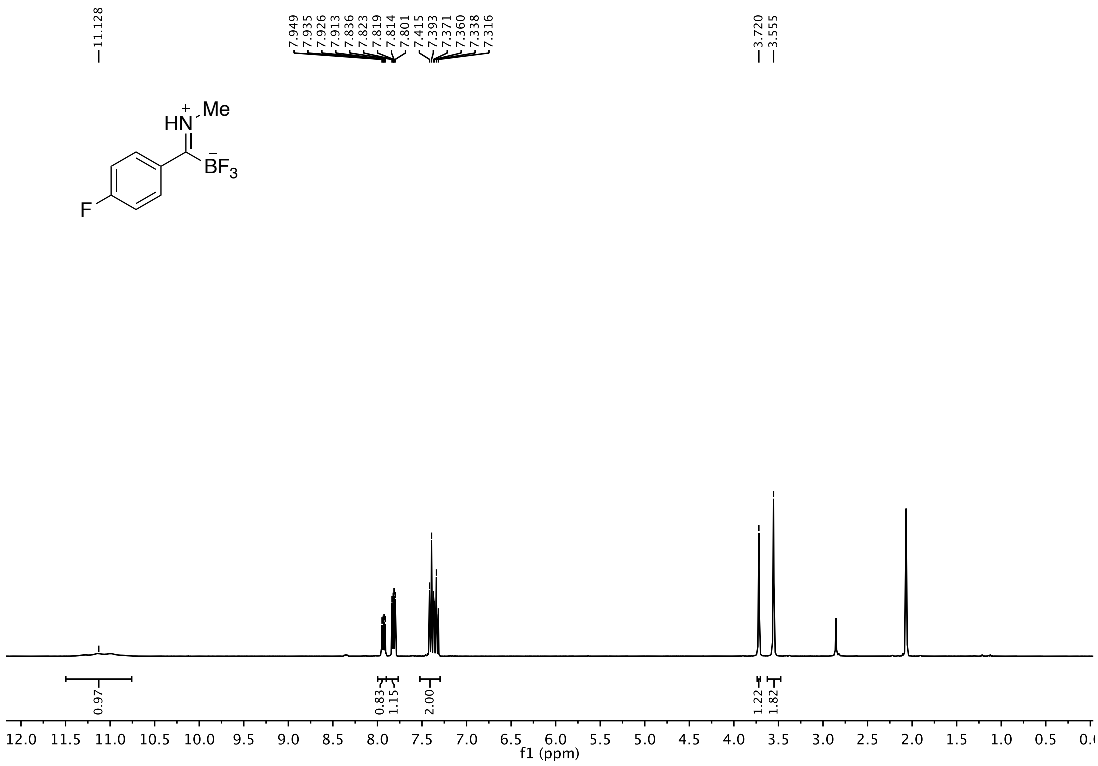
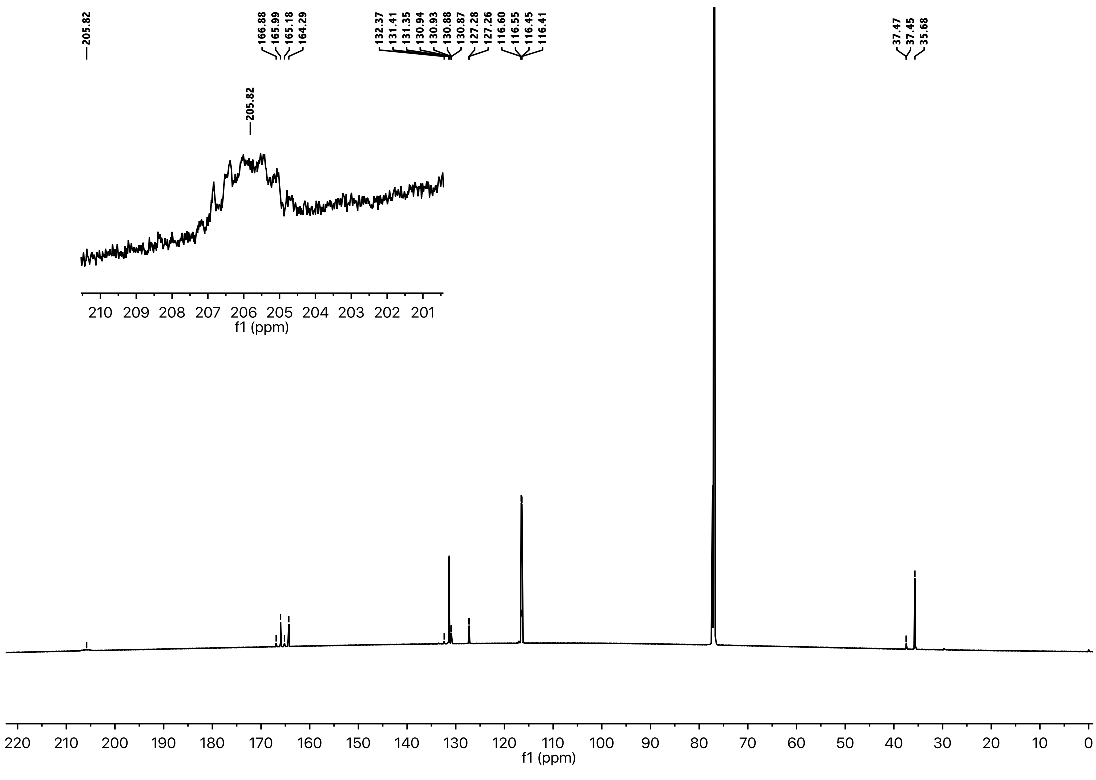
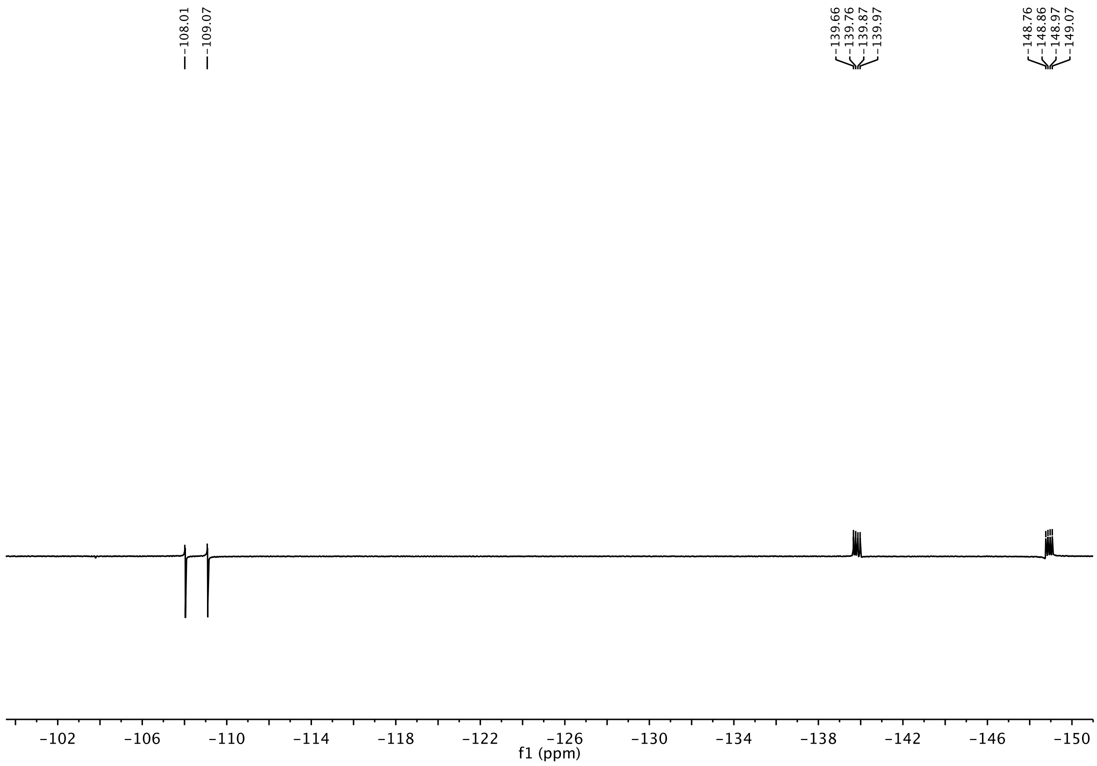
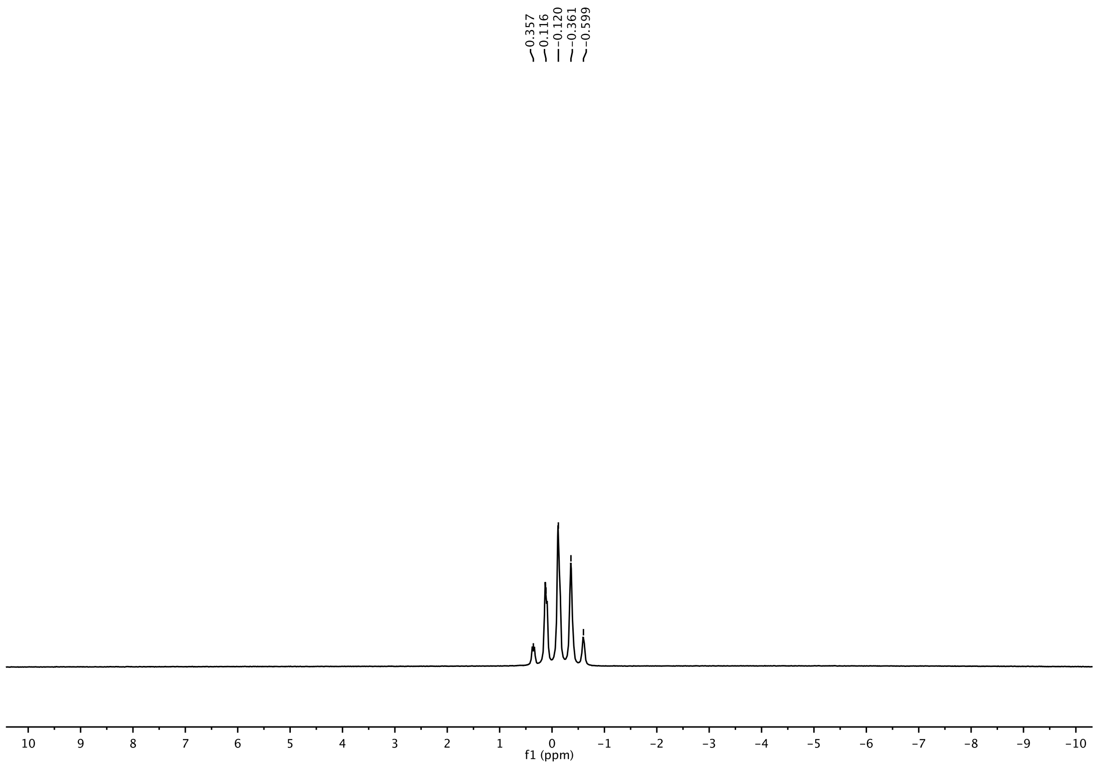
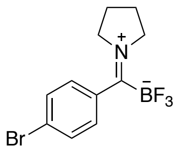
-0.937
10 9 8 7 6 5 4 3 2 1 0 –1 –2 –3 –4 –5 –6 –7 –8 –9 –10
f1 (ppm)

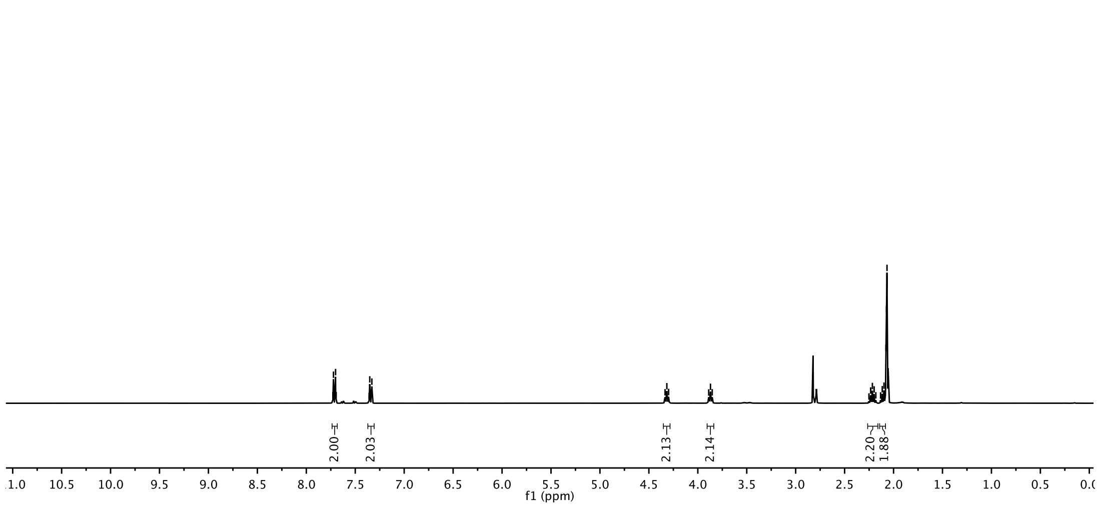


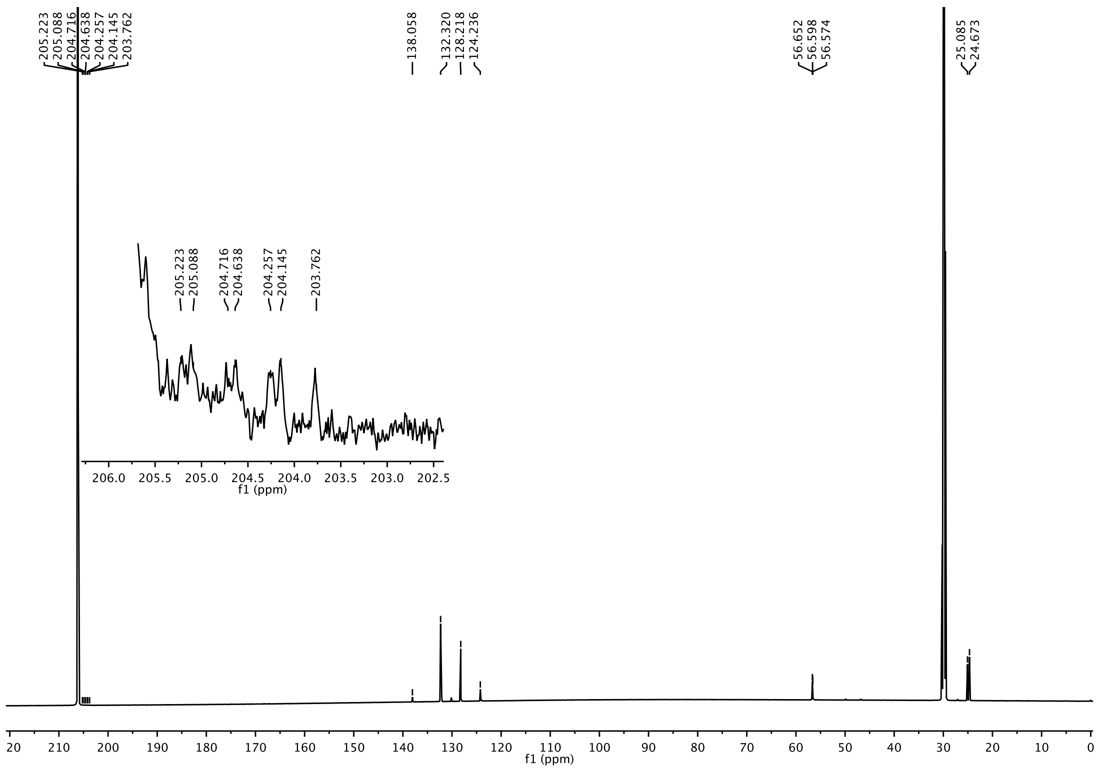


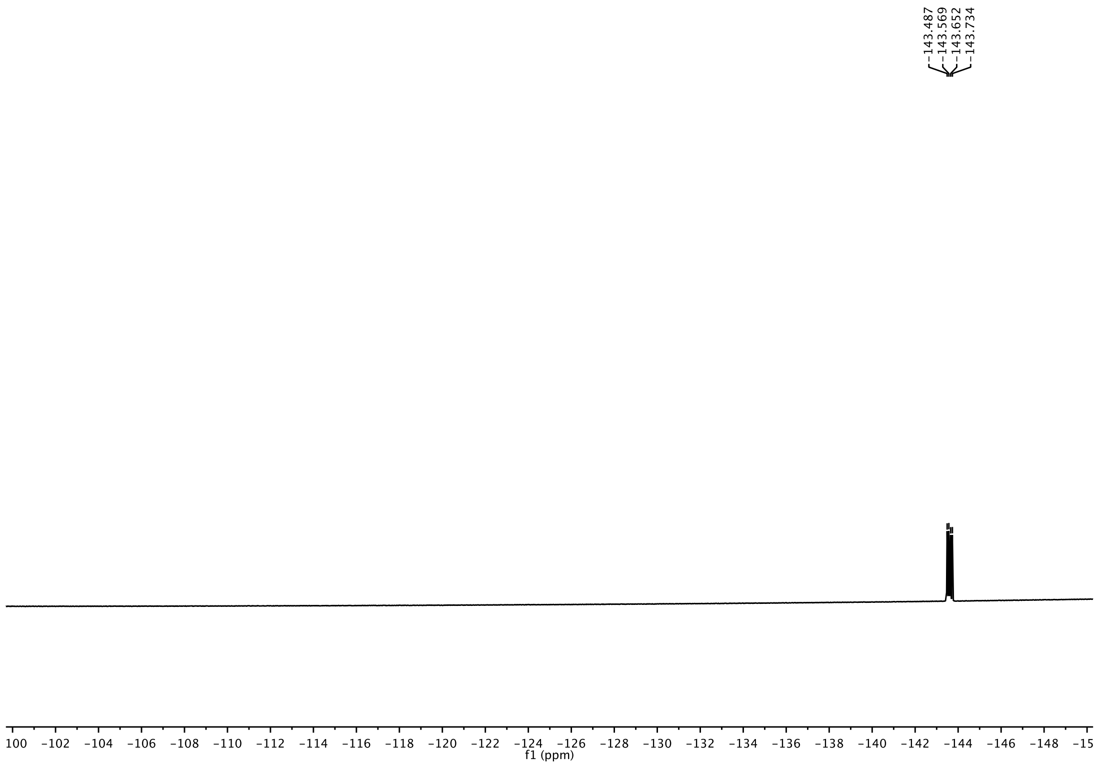

-108.01
-109.07
-139.66
-139.76
-139.87
-139.97
-148.76
-148.86
-148.97
-149.07
-102 -106 -110 -114 -118 -122 -126 -130 -134 -138 -142 -146 -150
f1 (ppm)

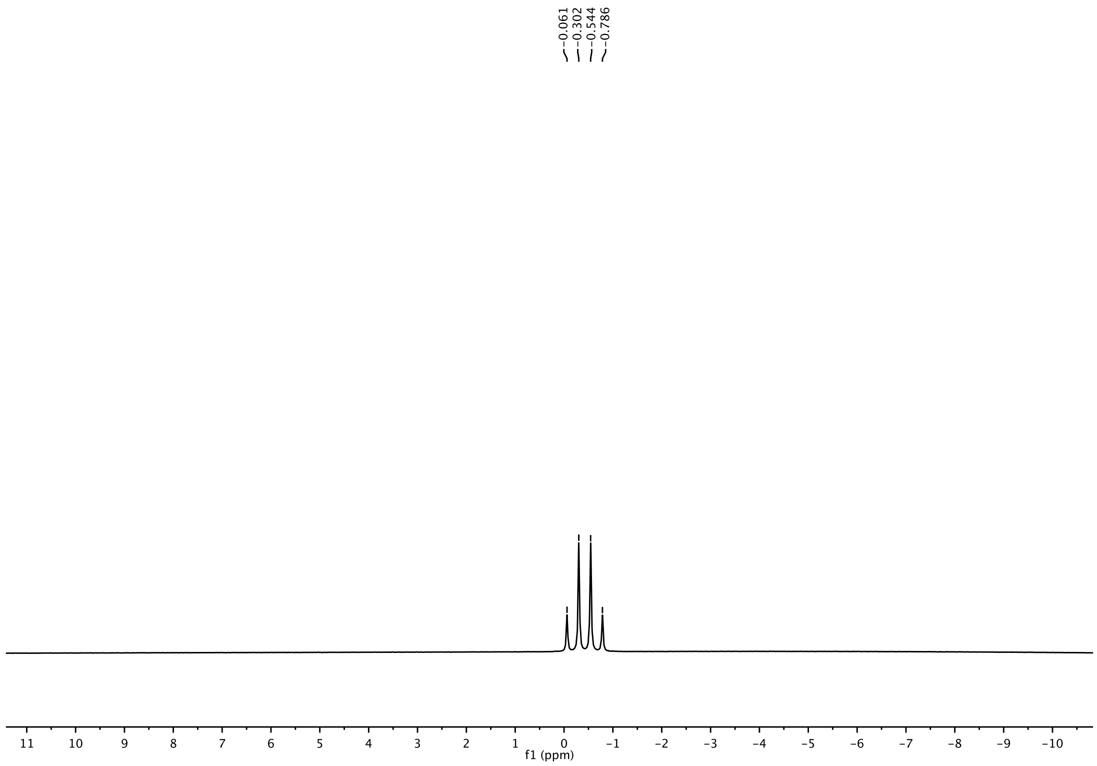

0.357
0.116
-0.120
-0.361
-0.599
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10
f1 (ppm)



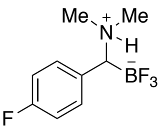


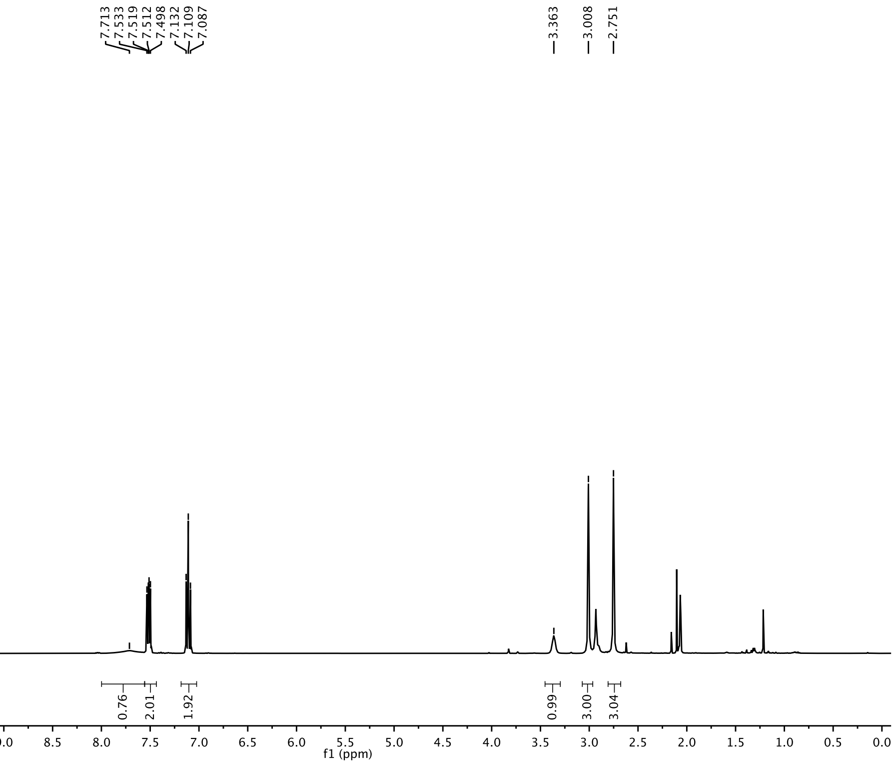


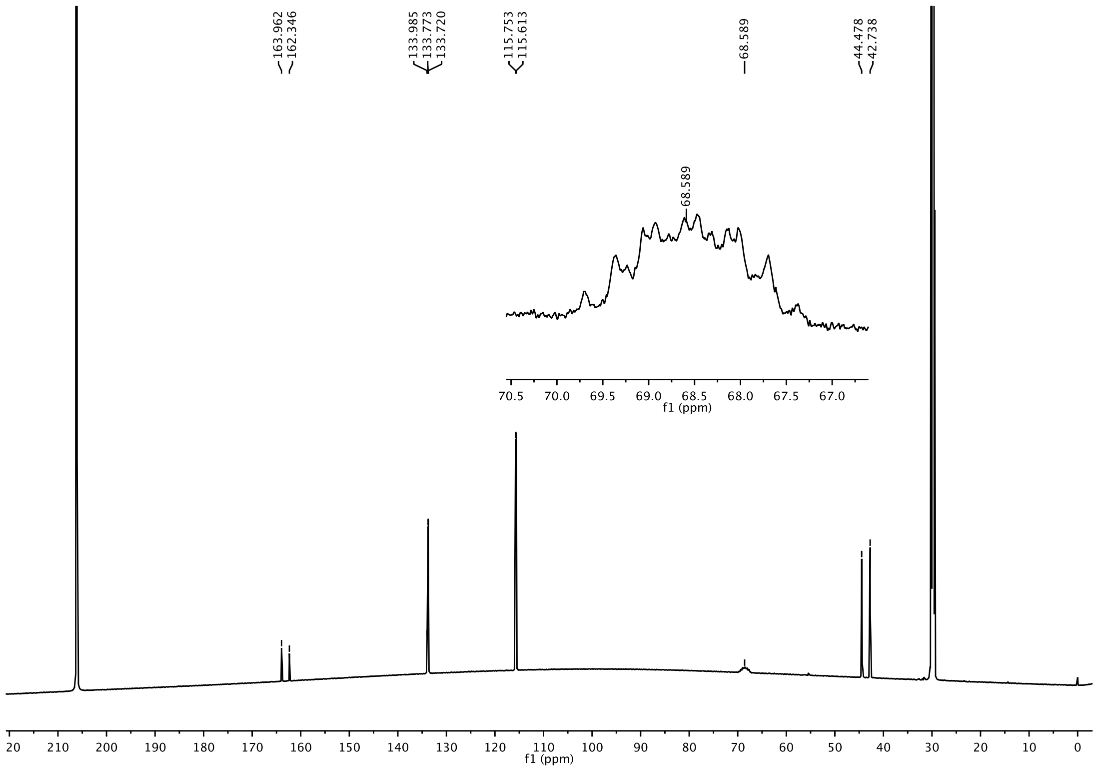

-143.487
-143.569
-143.652
-143.734
f1 (ppm)

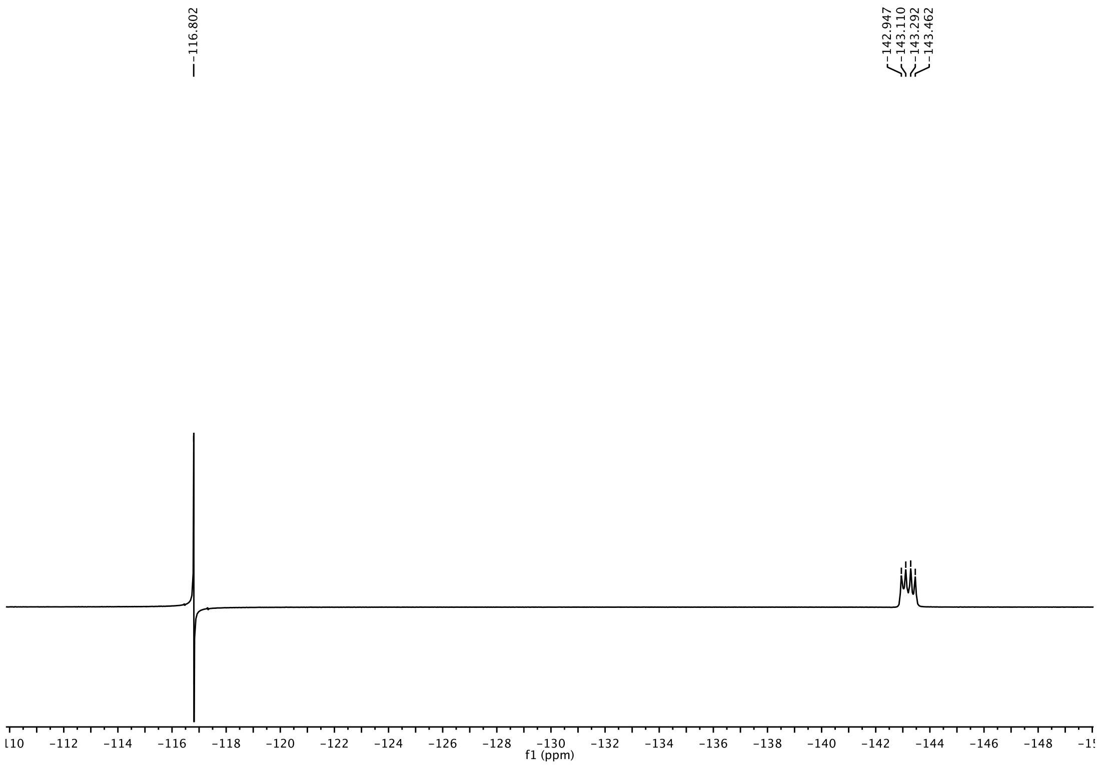

-0.061
-0.302
-0.544
-0.786
f1 (ppm)

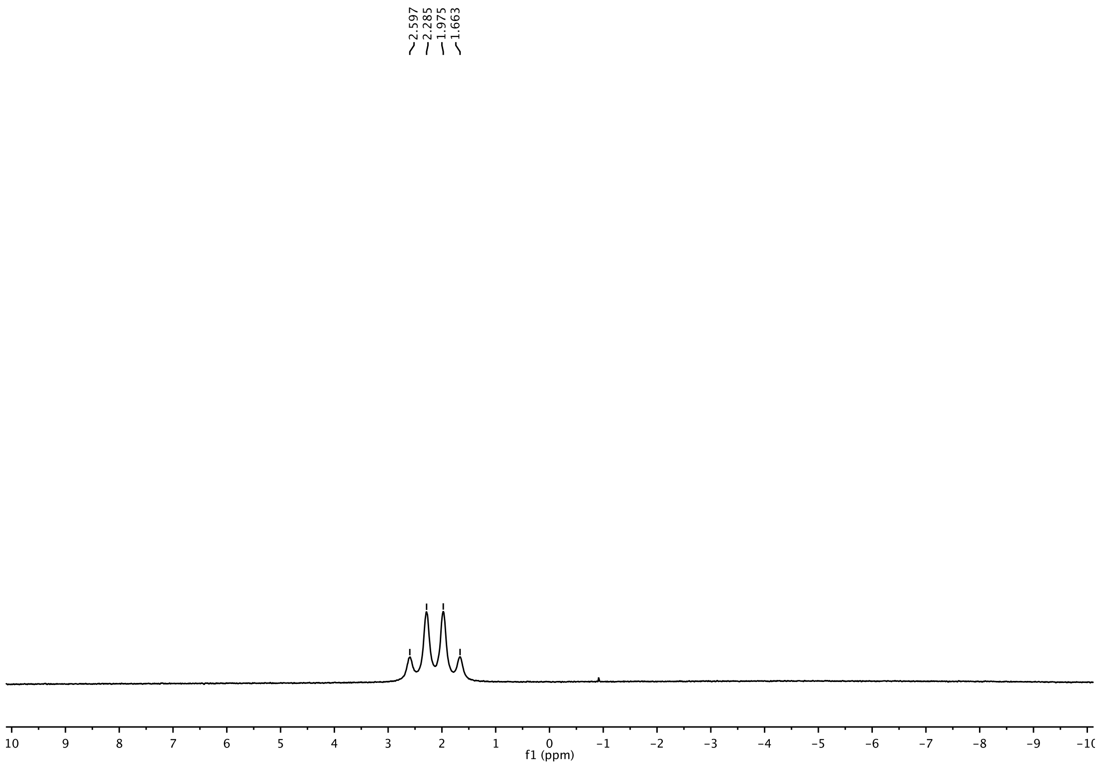
7.2 α-Aminotrifluoroborates

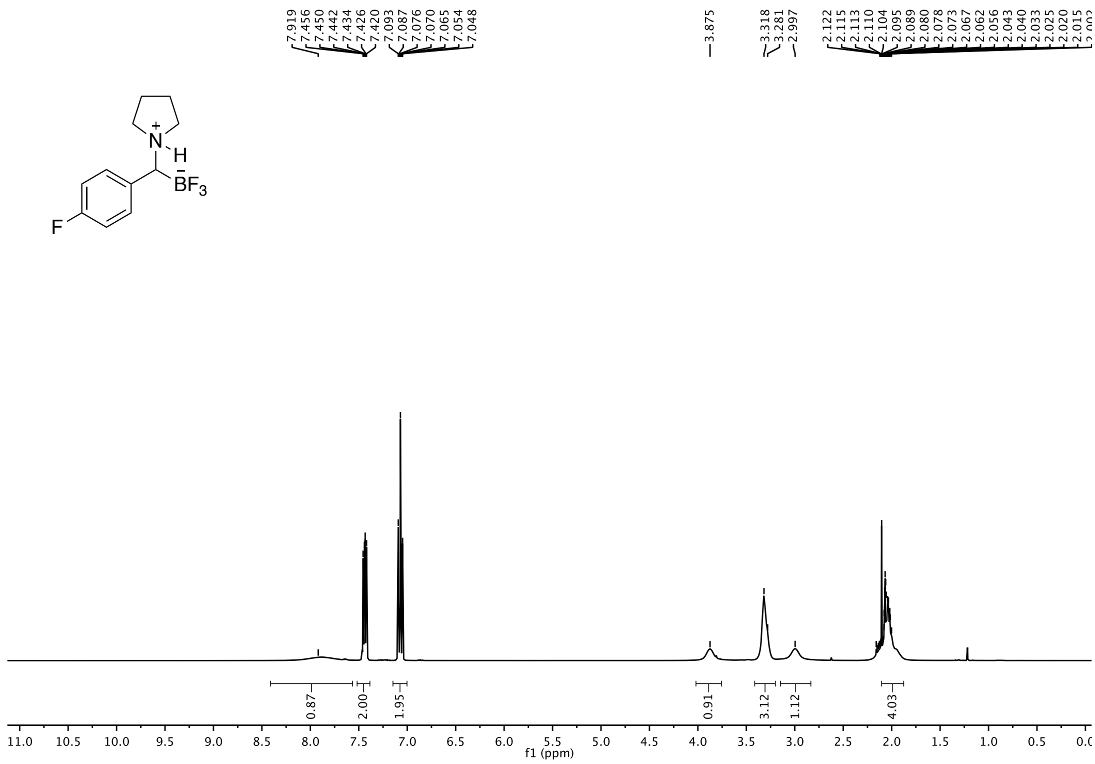


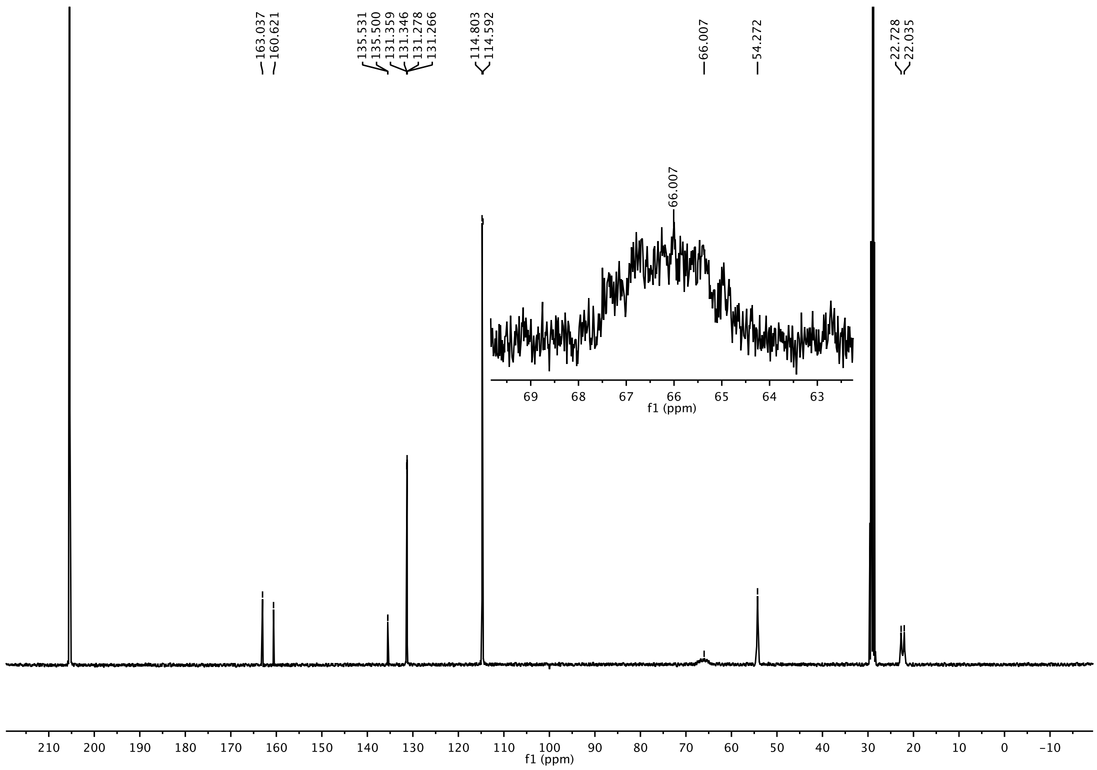


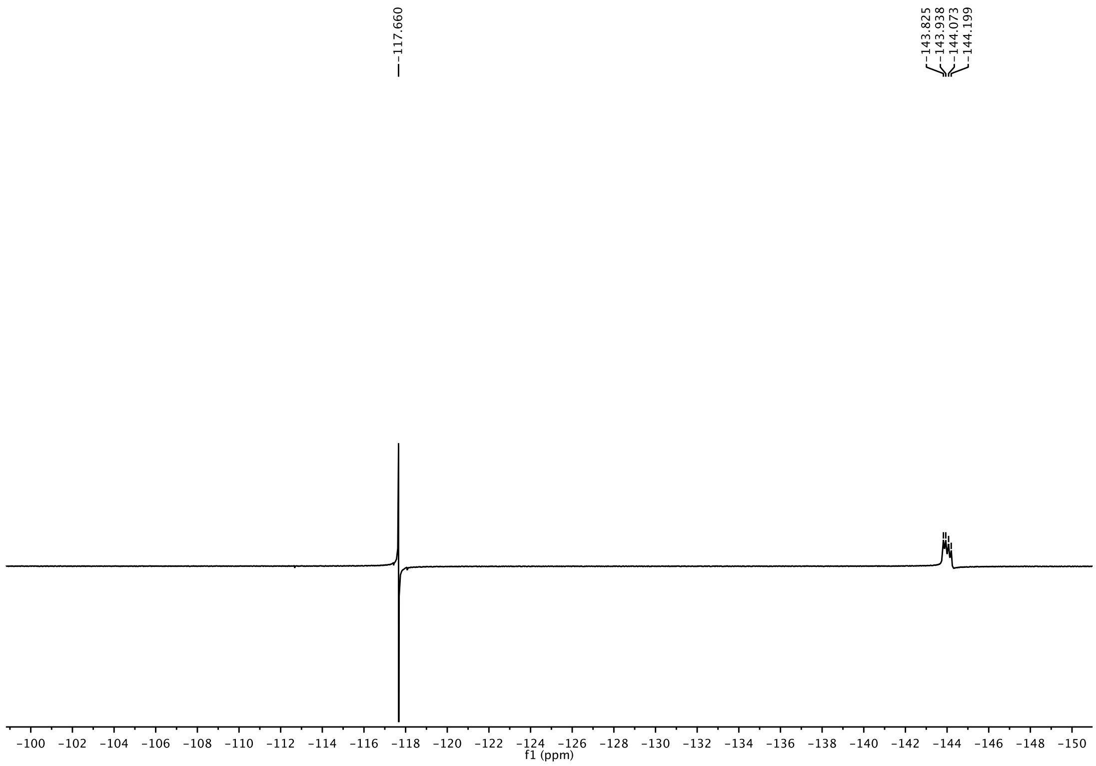


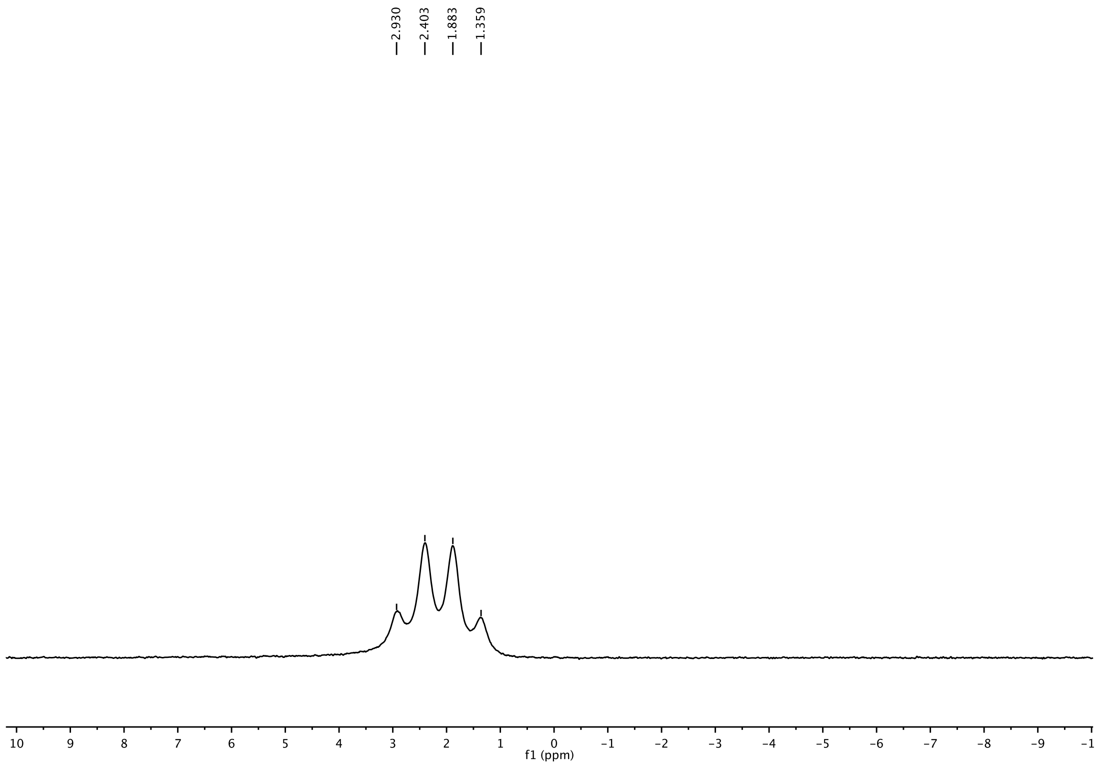

-116.802
-142.947
-143.110
-143.292
-143.462
f1 (ppm)

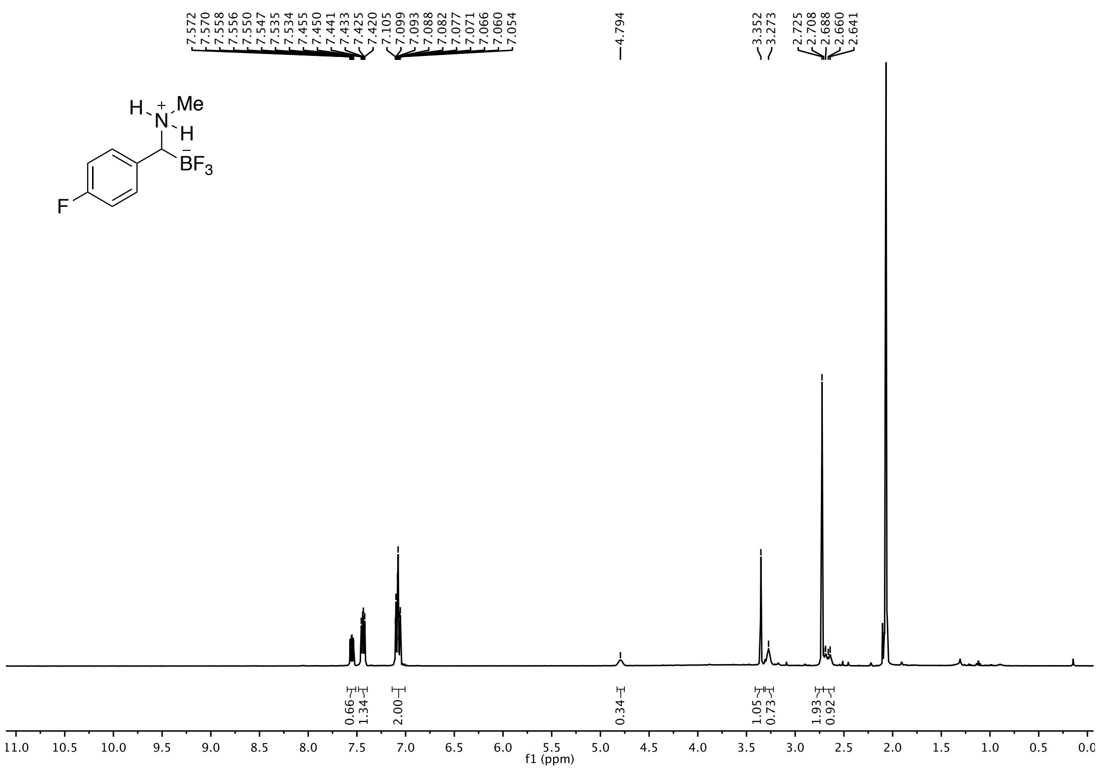

2.597
2.285
1.975
1.663
f1 (ppm)


7.919
7.456
7.450
7.442
7.434
7.426
7.420
7.093
7.087
7.076
7.070
7.065
7.054
7.048
3.875
3.318
3.281
2.997
2.122
2.115
2.113
2.110
2.104
2.095
2.089
2.080
2.078
2.073
2.067
2.062
2.056
2.043
2.040
2.033
2.025
2.020
2.015
N
H
BF3
F
0.87
2.00
1.95
0.91
3.12
1.12
4.03
f1 (ppm)

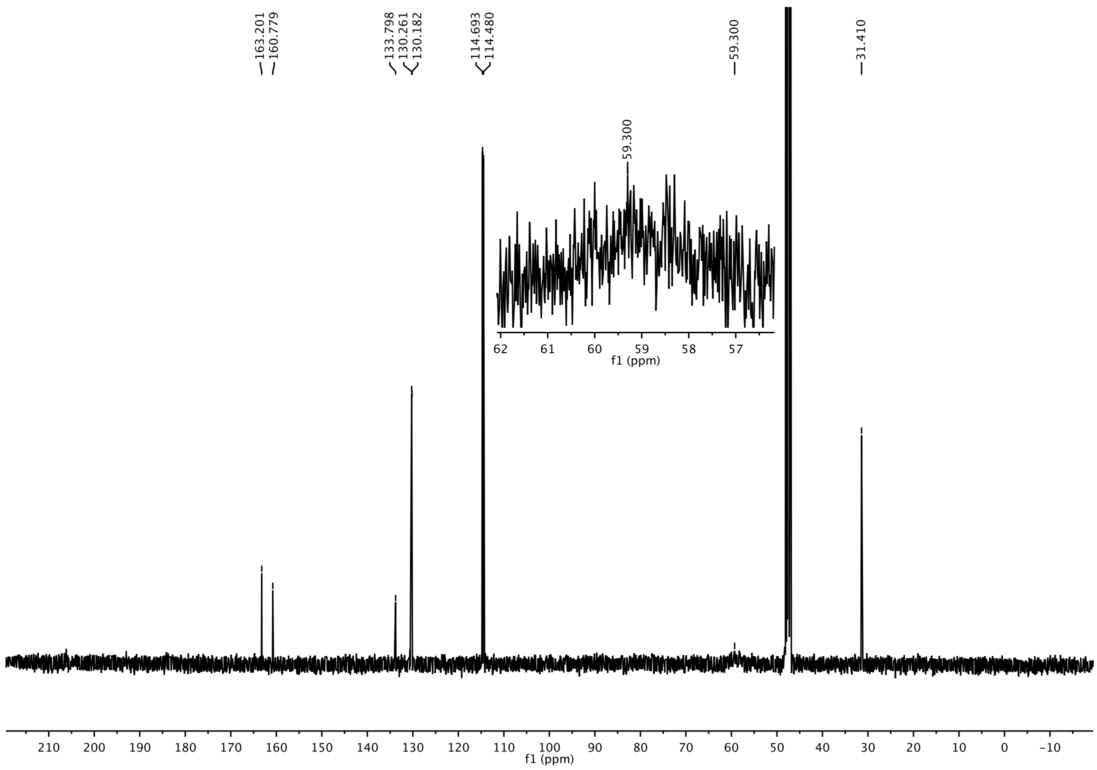

163.037
160.621
135.531
135.500
131.359
131.346
131.278
131.266
114.803
114.592
66.007
54.272
22.728
22.035
66.007
f1 (ppm)
f1 (ppm)


-117.660
-143.825
-143.938
-144.073
-144.199
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)

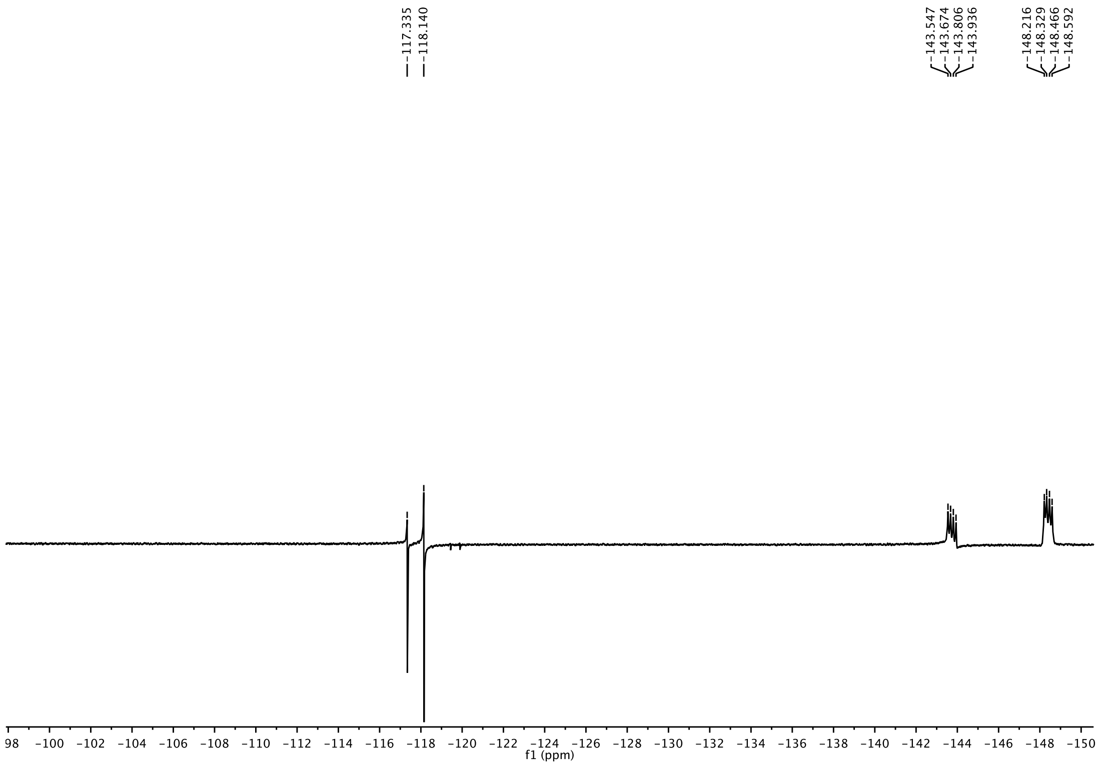

2.930
2.403
1.883
1.359
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -1
f1 (ppm)



H N Me H BF3 F
7.572 7.570 7.558 7.556 7.550 7.547 7.535 7.534 7.455 7.450 7.441 7.433 7.425 7.420 7.105 7.099 7.093 7.088 7.082 7.077 7.071 7.066 7.060 7.054
4.794
3.352 3.273
2.725 2.708 2.688 2.660 2.641
0.66 1.34 2.00 0.34 1.05 0.73 1.93 0.92
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



163.201 160.779
133.798 130.261 130.182
114.693 114.480
59.300
31.410
59.300
62 61 60 59 58 57
f1 (ppm)
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)


-117.335
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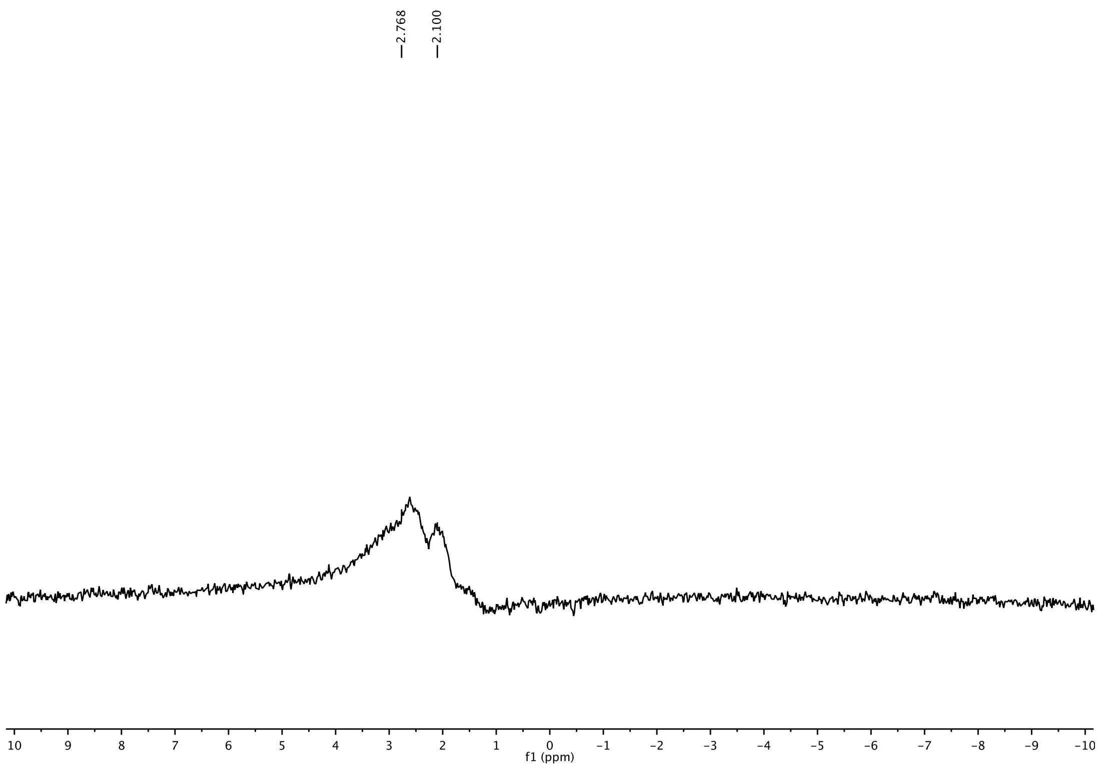
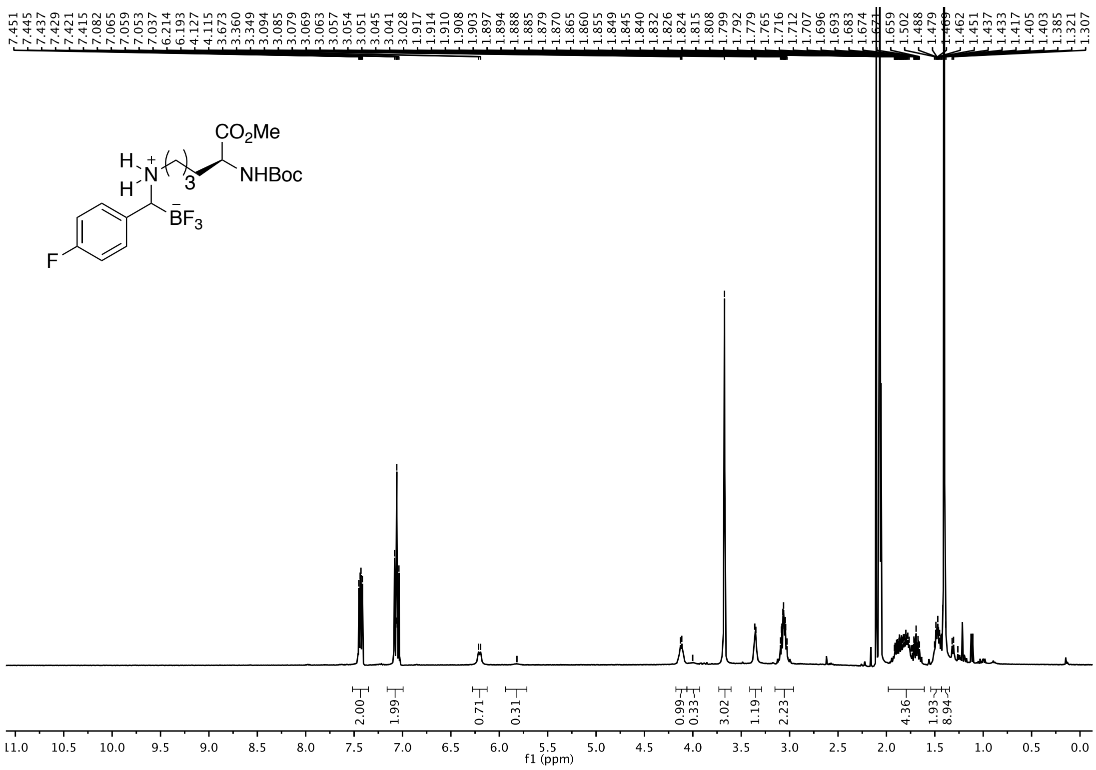
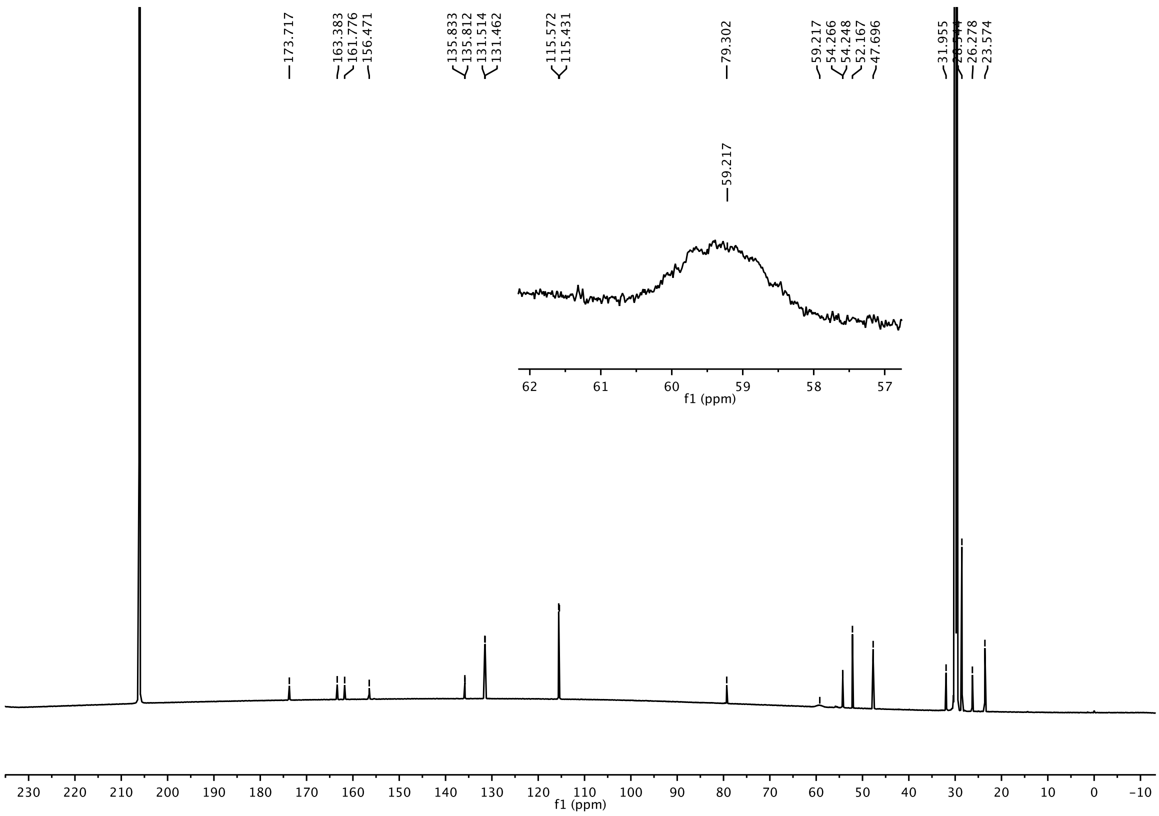
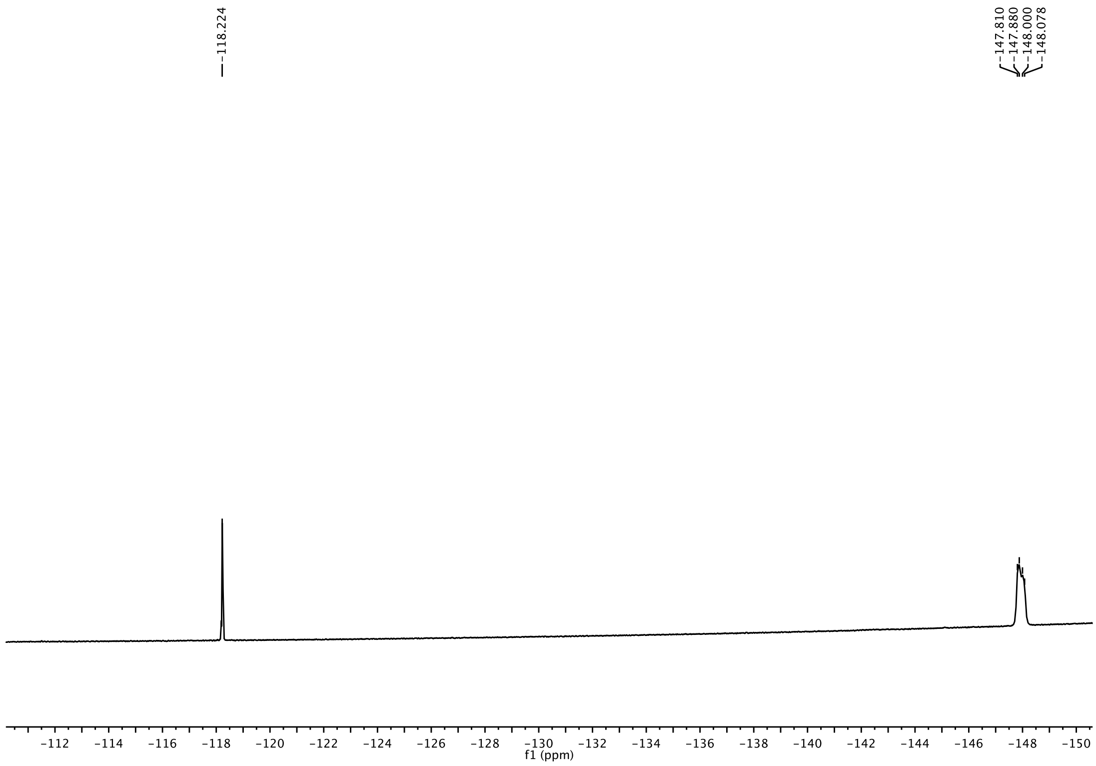
-143.547
-143.674
-143.806
-143.936
-148.216
-148.329
-148.466
-148.592
98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


2.768
2.100
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10
f1 (ppm)






-118.224
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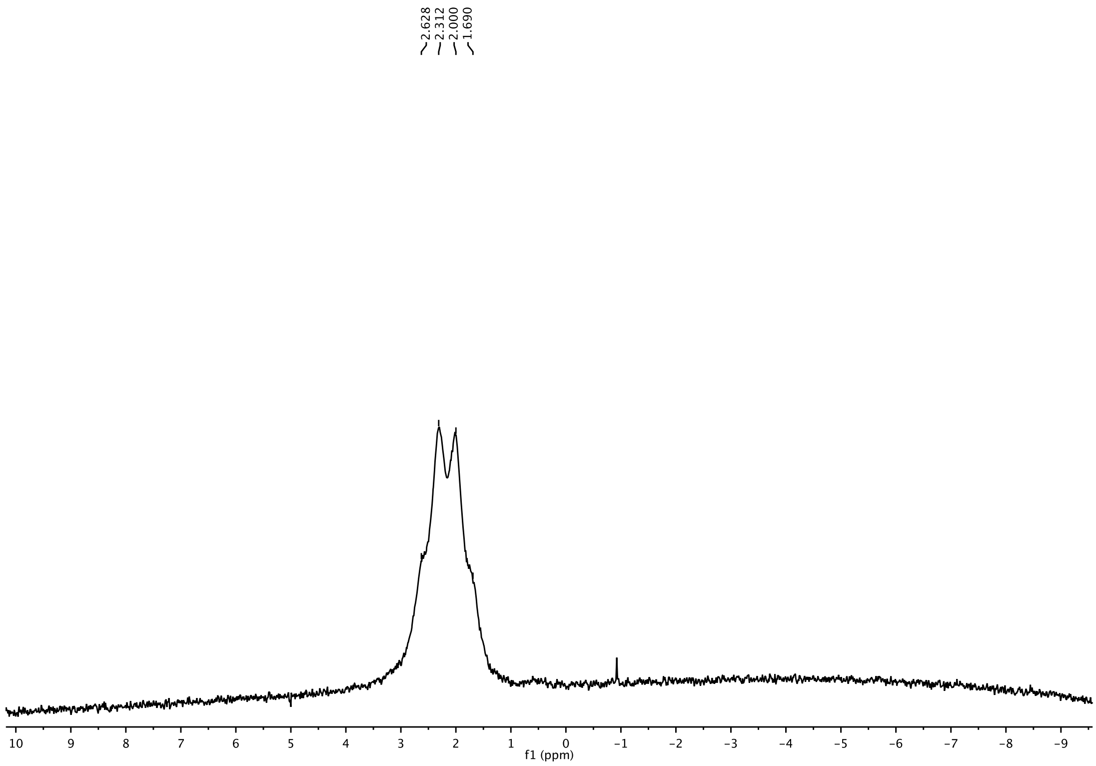
-148.078
-112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)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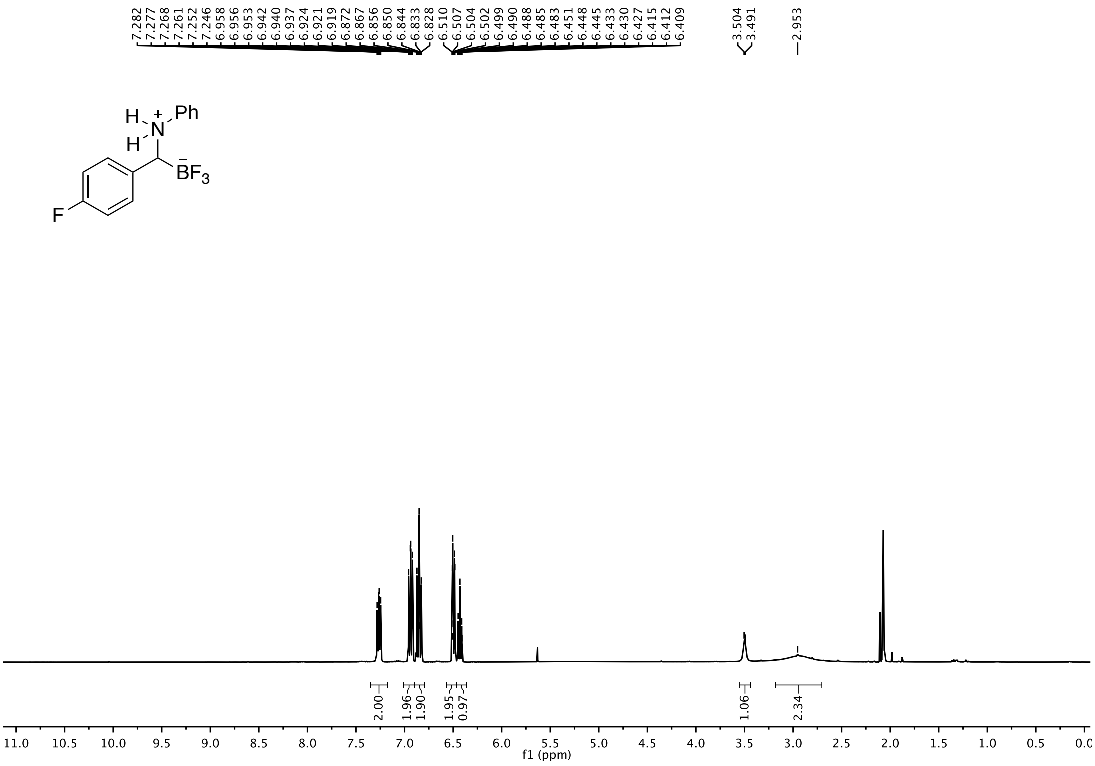
f1 (ppm)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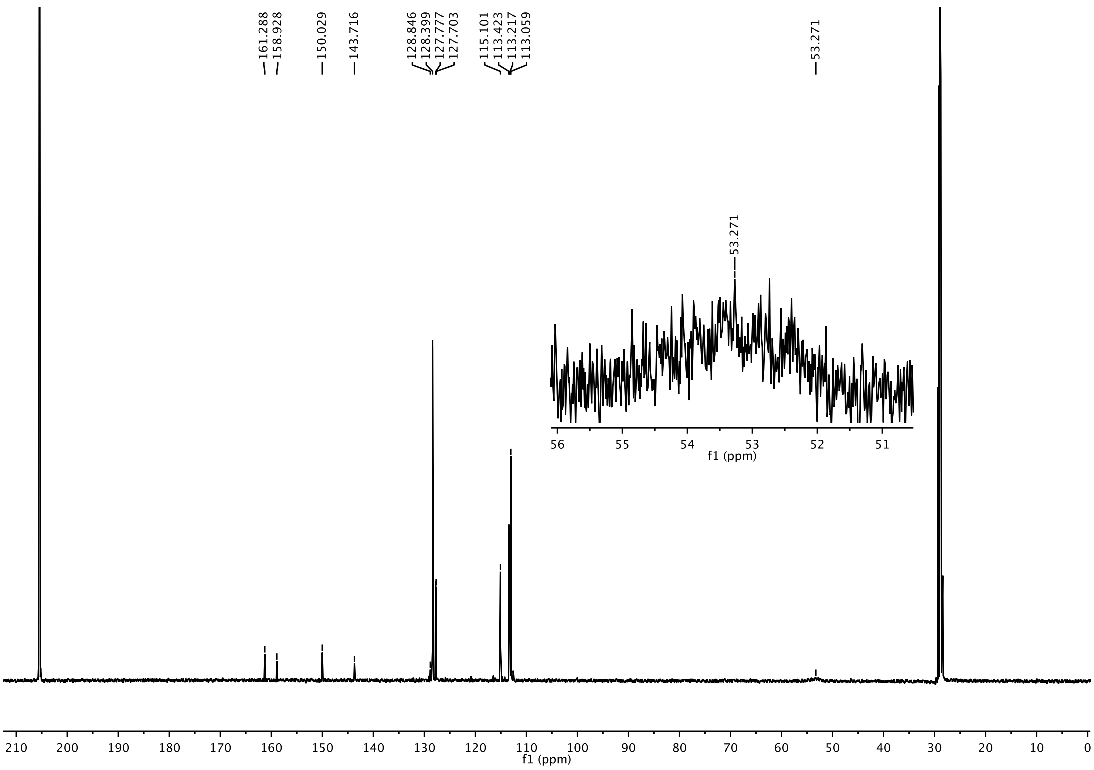
7.246
6.958
6.956
6.953
6.942
6.940
6.937
6.924
6.921
6.919
6.872
6.867
6.856
6.850
6.844
6.833
6.828
6.510
6.507
6.504
6.502
6.499
6.490
6.488
6.485
6.483
6.451
6.448
6.445
6.433
6.430
6.427
6.415
6.412
6.409
3.504
3.491
2.953
H
N
Ph
H
BF3
F
2.00
1.96
1.90
1.95
0.97
1.06
2.34
f1 (ppm)


161.288
158.928
150.029
143.716
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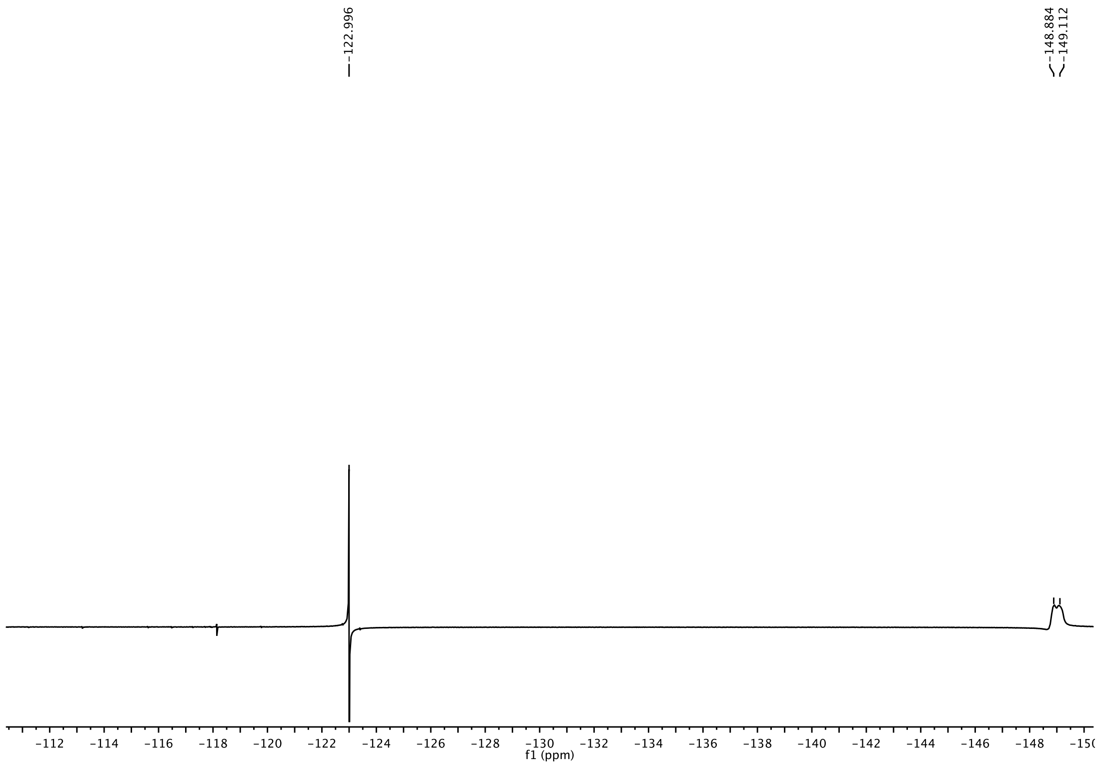
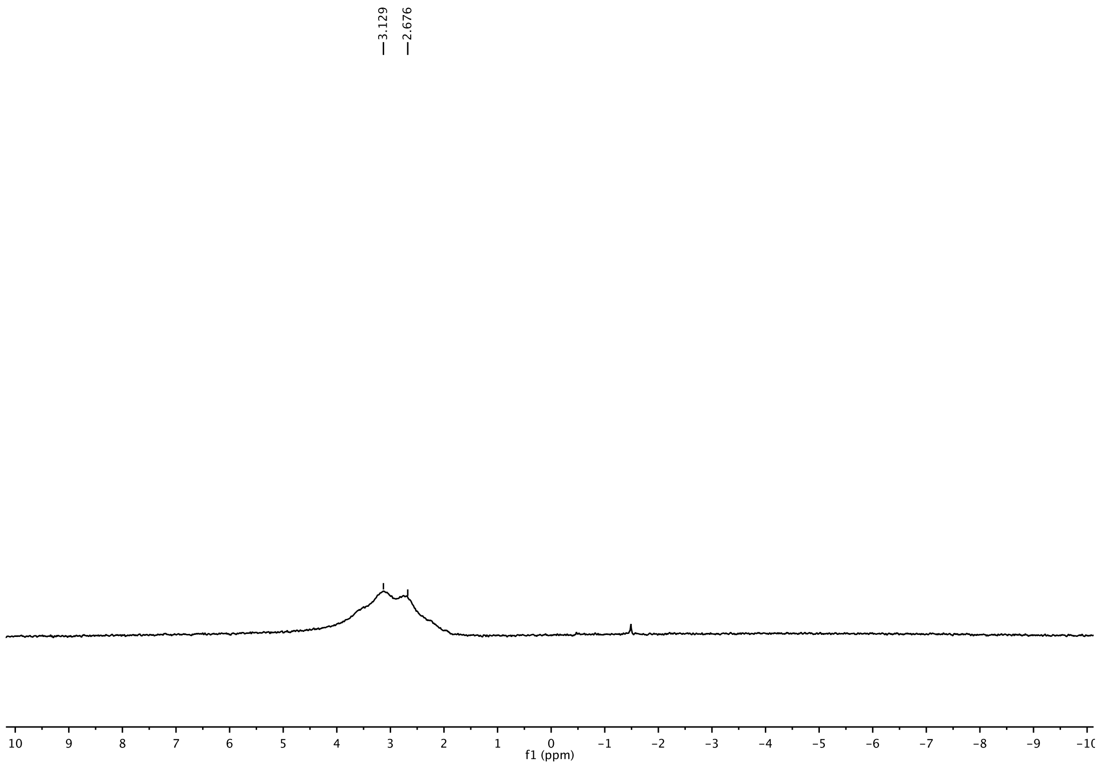
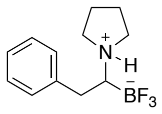
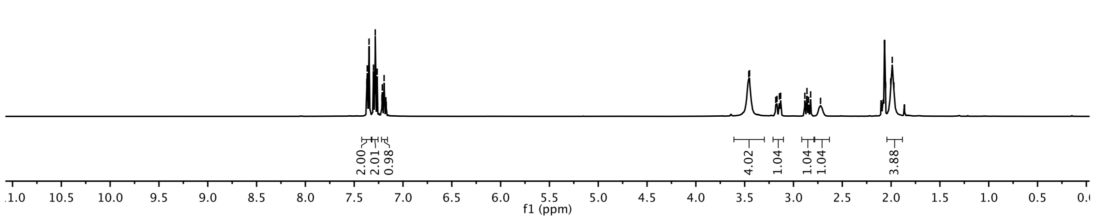
128.399
127.777
127.703
115.101
113.423
113.217
113.059
53.271
f1 (ppm)


-122.996
-148.884
-149.112
f1 (ppm)


3.129
2.676
f1 (ppm)


N
H
BF3


7.370
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7.361
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7.293
7.289
7.284
7.280
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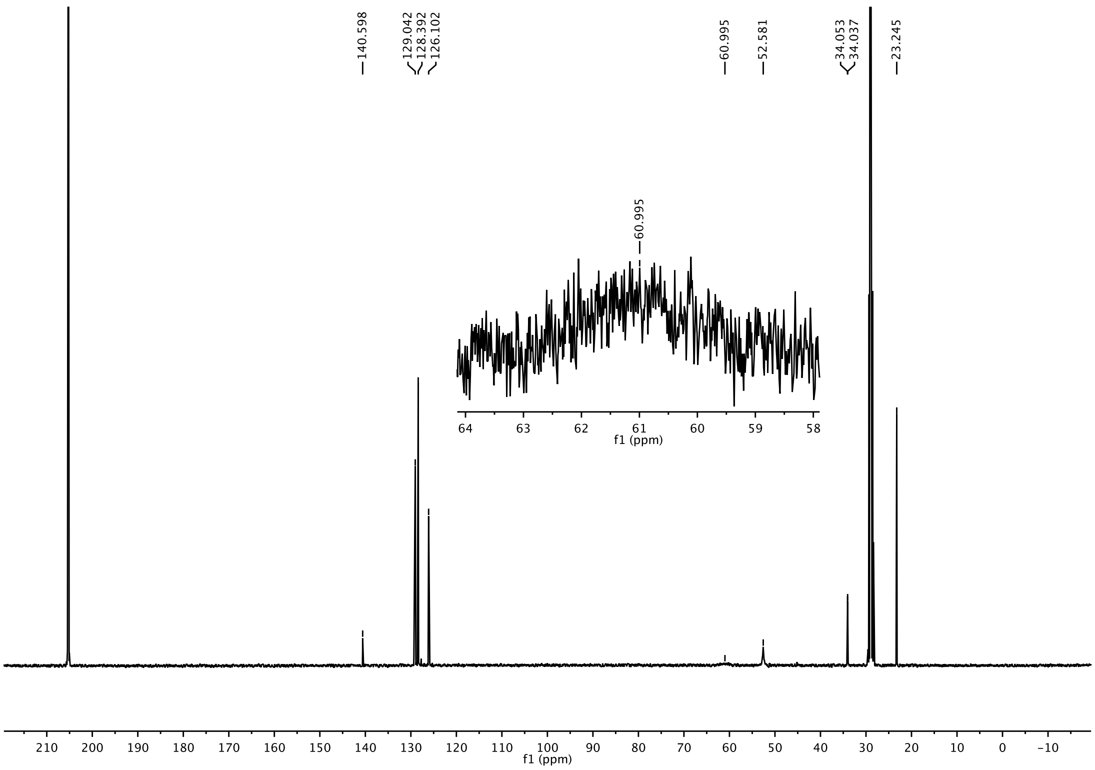
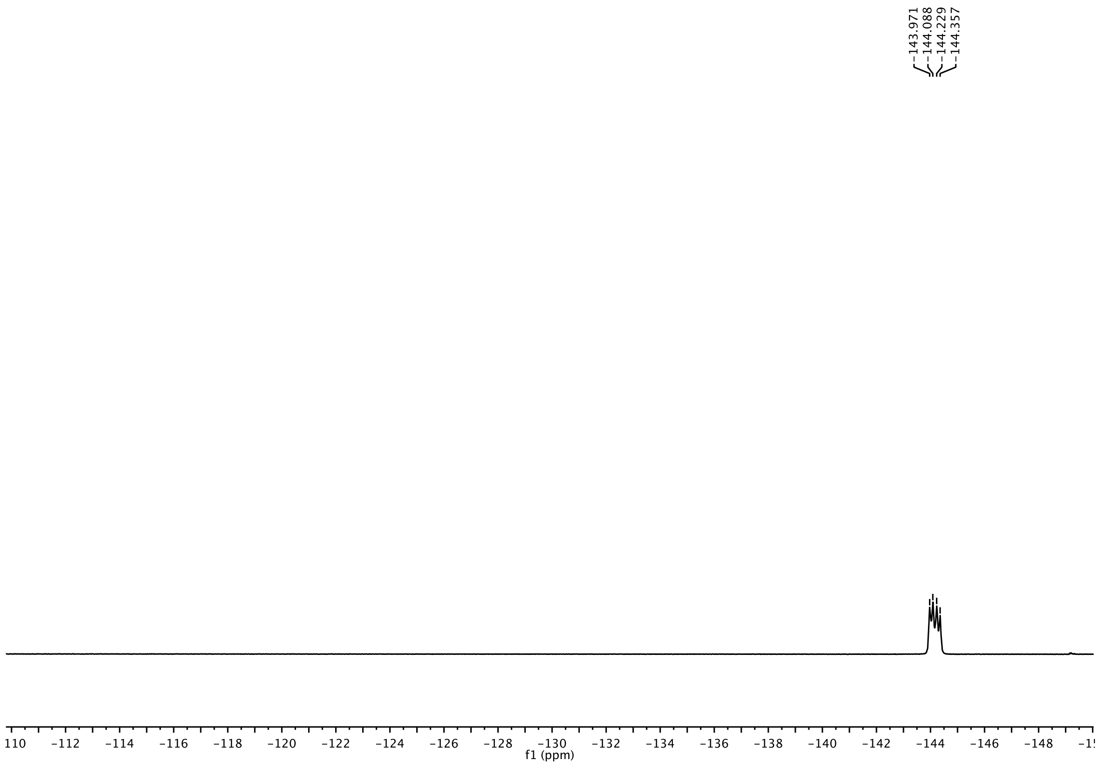
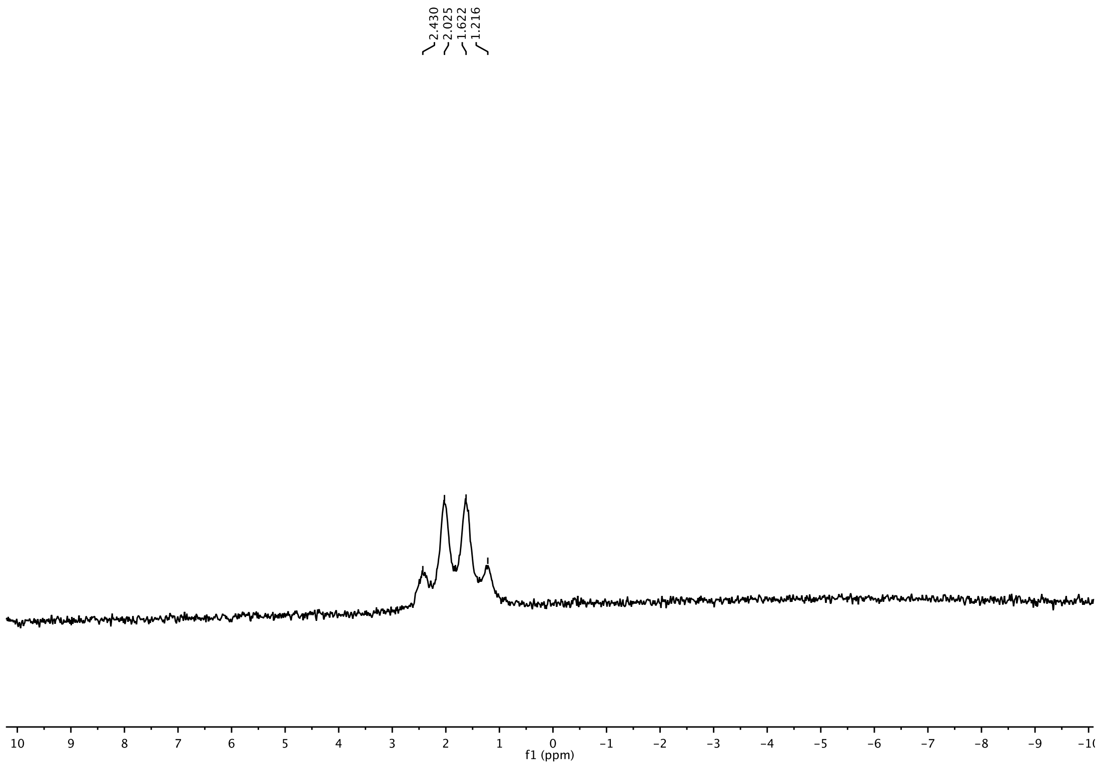
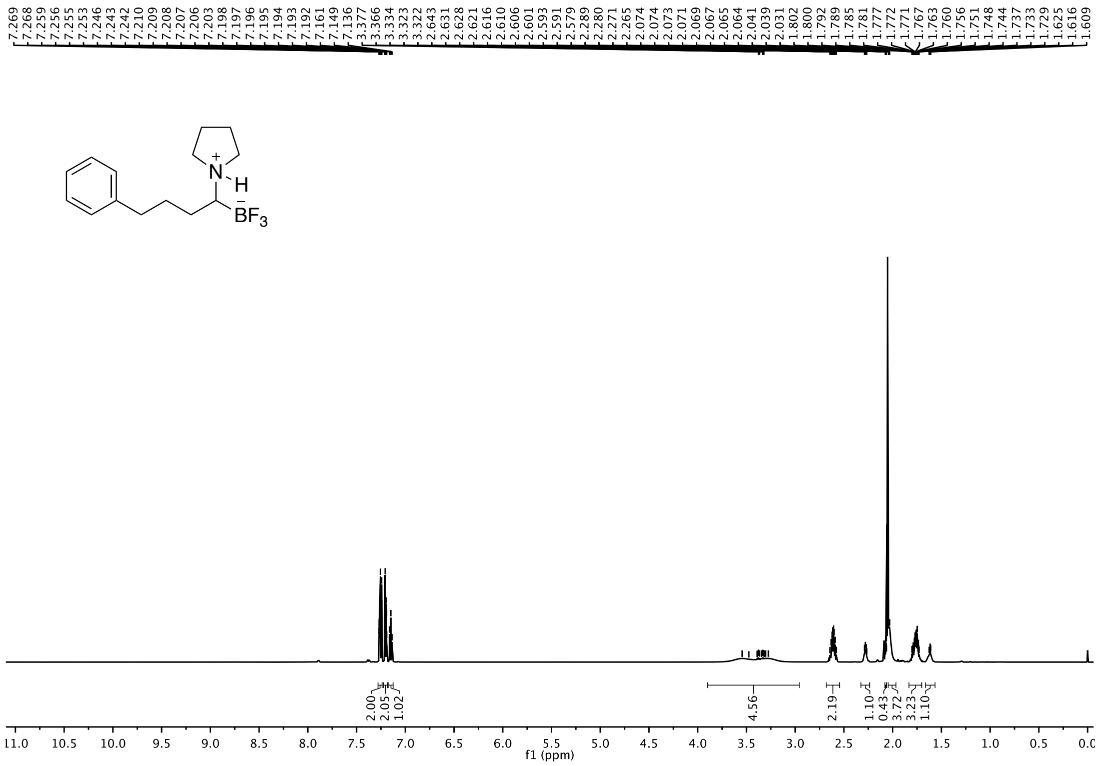
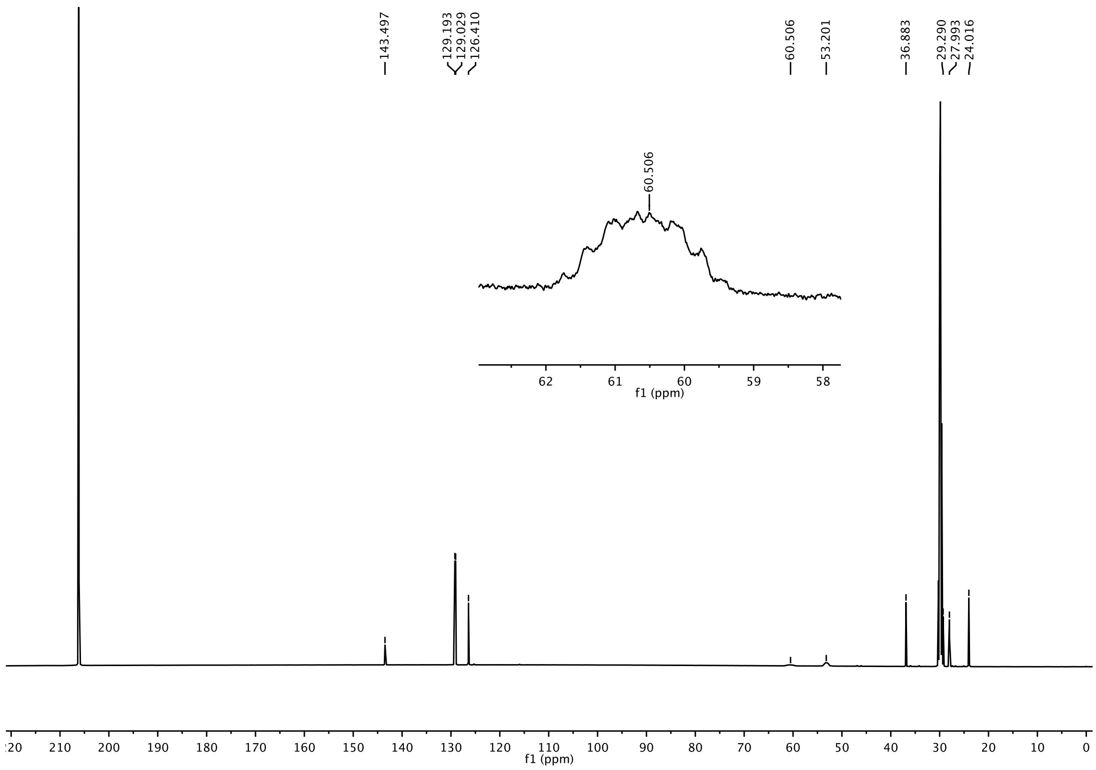
7.265
7.216
7.212
7.208
7.199
7.194
7.188
7.179
7.175
7.172
3.458
3.450
3.181
3.169
3.144
3.131
2.883
2.862
2.846
2.824
2.723
2.056
2.004
1.988
1.971
2.00
2.01
0.98
4.02
1.04
1.04
1.04
3.88
f1 (ppm)

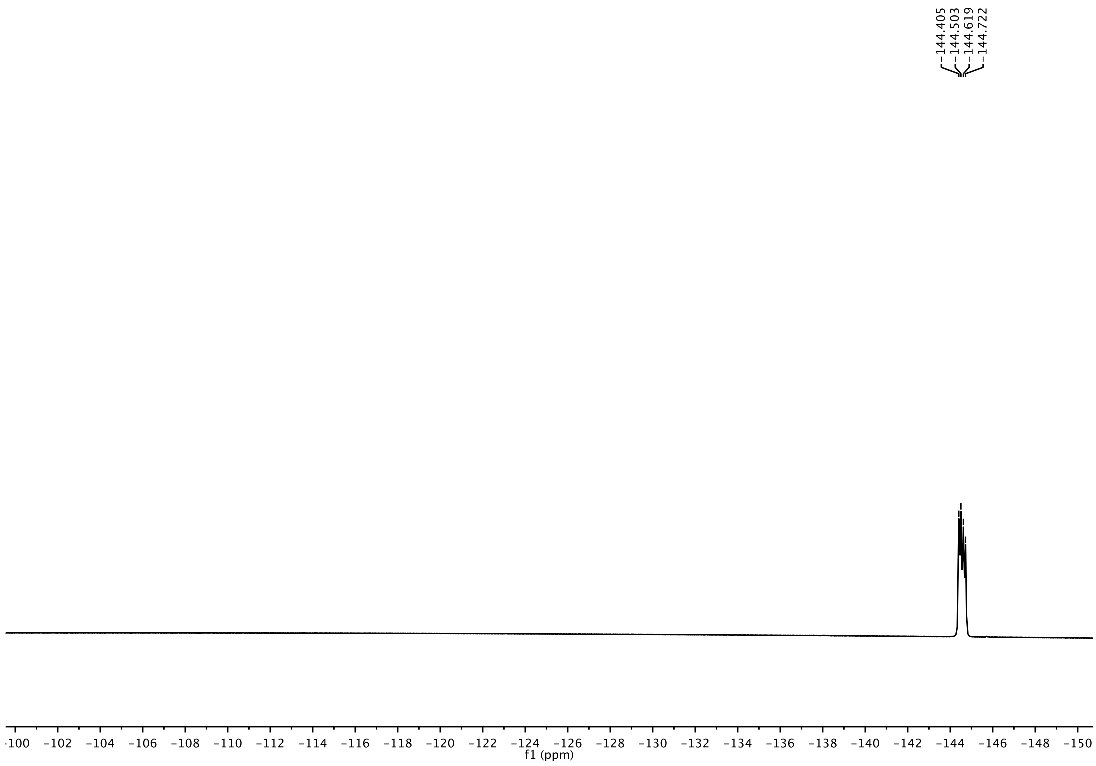

140.598
129.042
128.392
126.102
60.995
52.581
34.053
34.037
23.245
60.995
f1 (ppm)
f1 (ppm)

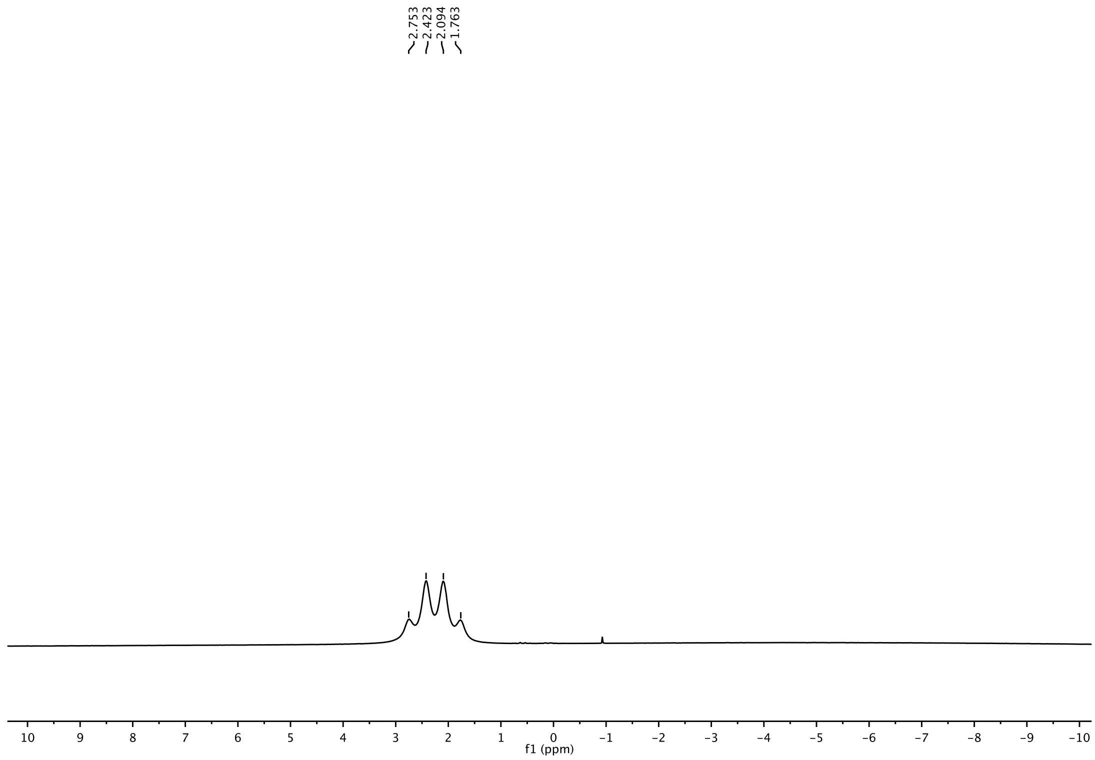

-143.971
-144.088
-144.229
-144.357
110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148
f1 (ppm)

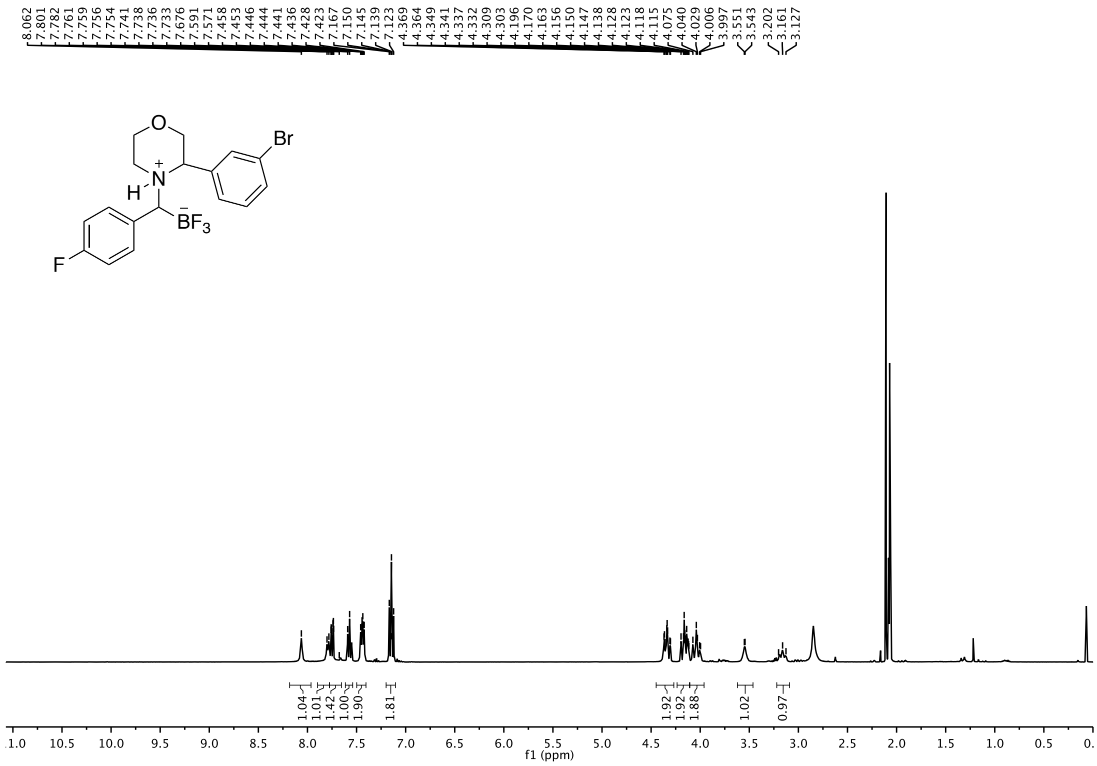

2.430
2.025
1.622
1.216
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9
f1 (ppm)

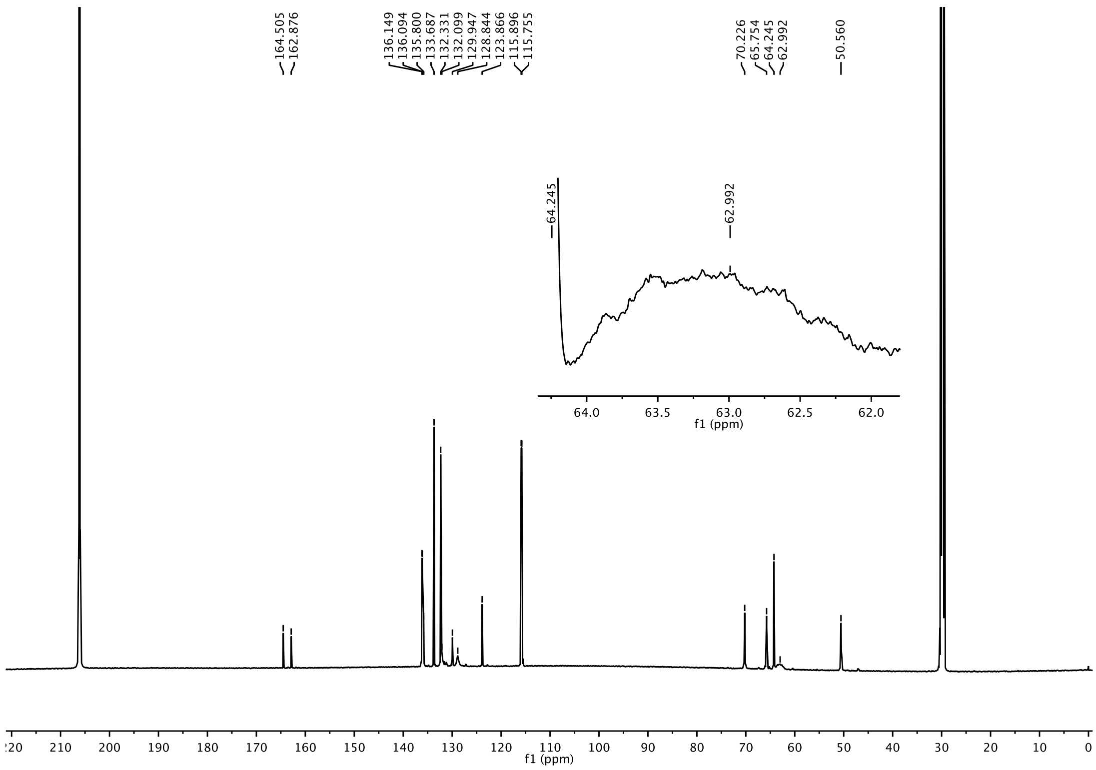


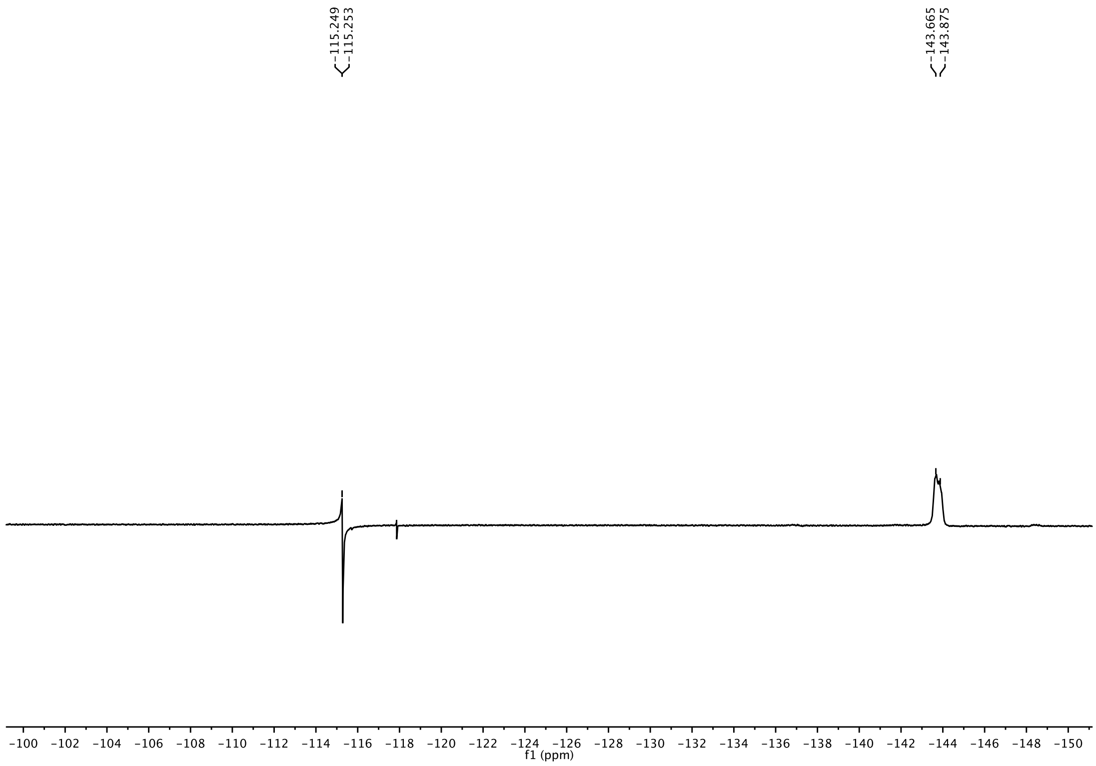


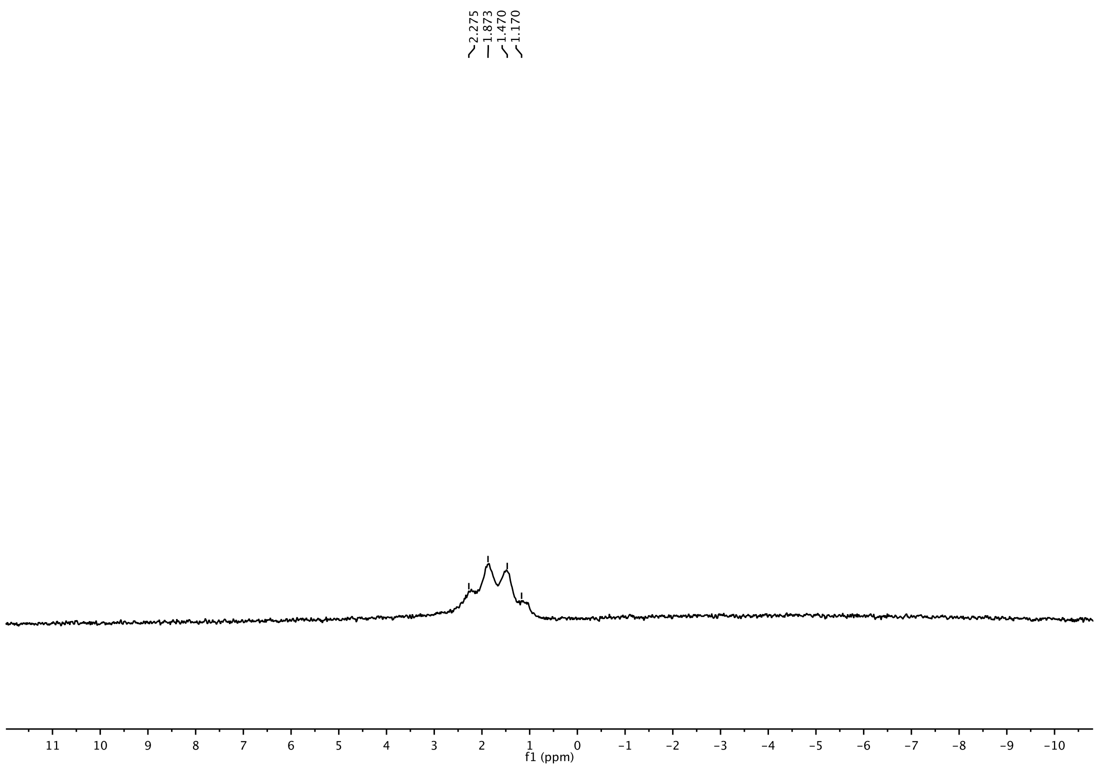

-144.405
-144.503
-144.619
-144.722
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)


2.753
2.423
2.094
1.763
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10
f1 (ppm)






-115.249
-115.253
-143.665
-143.875
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)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1.170
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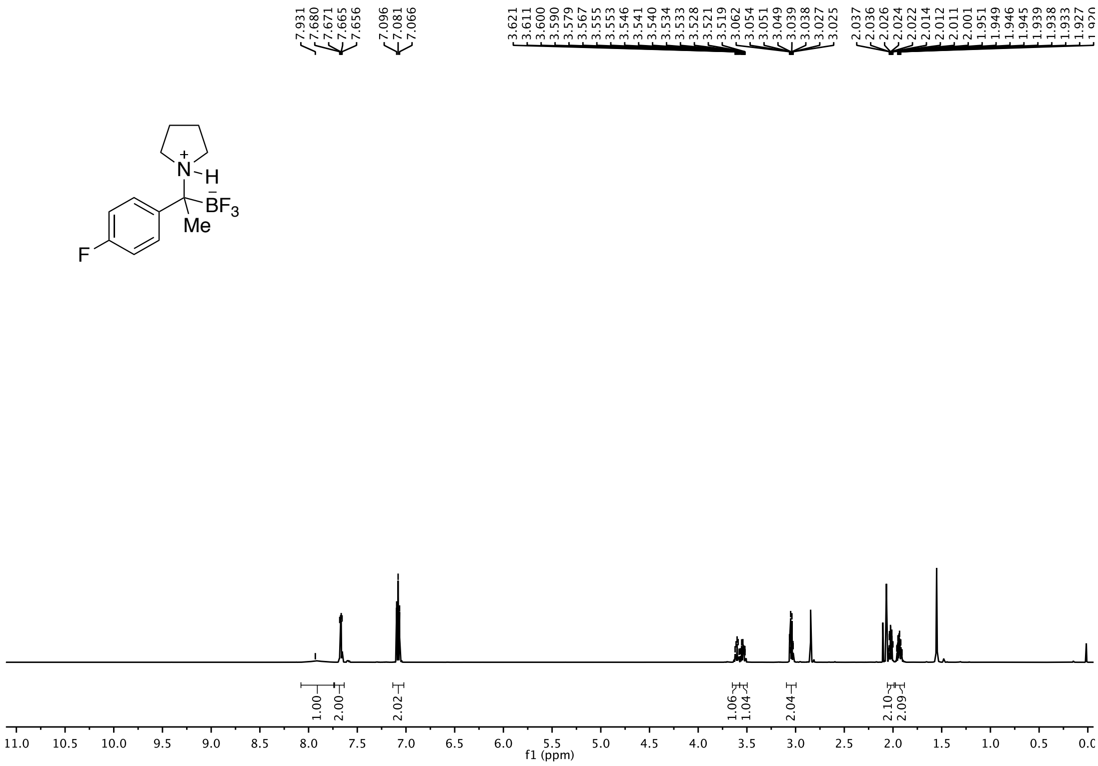
f1 (ppm)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Me
F
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7.656
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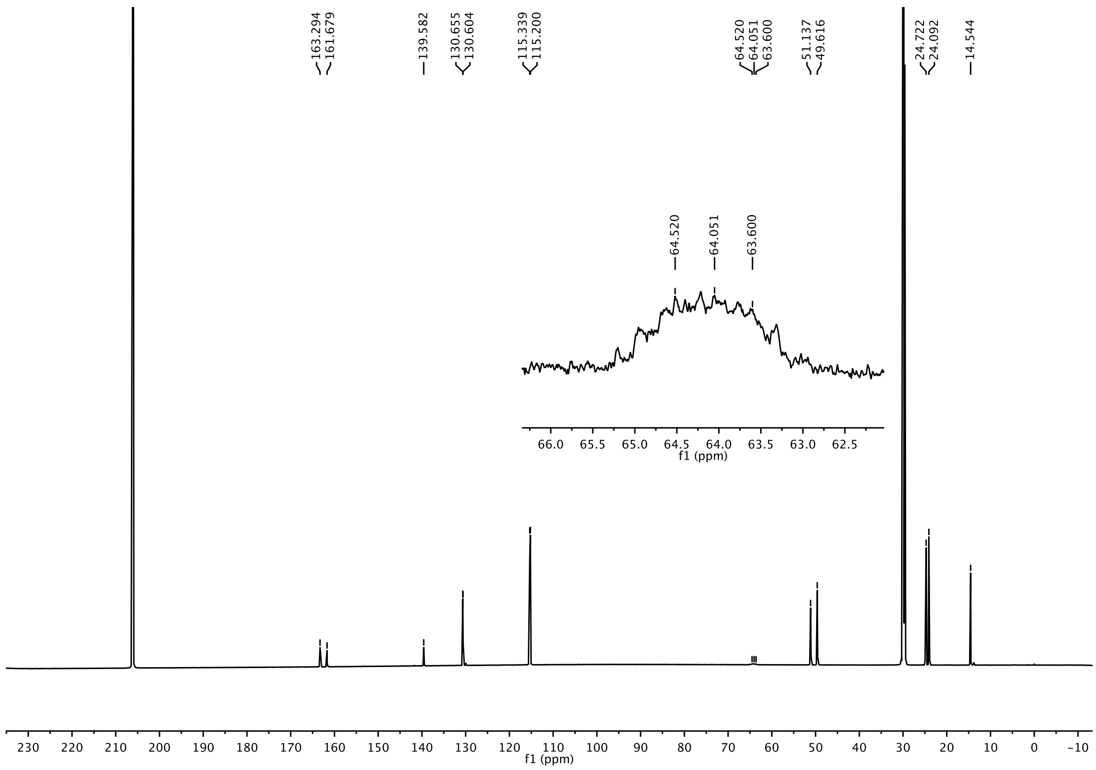
2.00
2.02
1.06
1.04
2.04
2.10
2.09
f1 (ppm)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63.600
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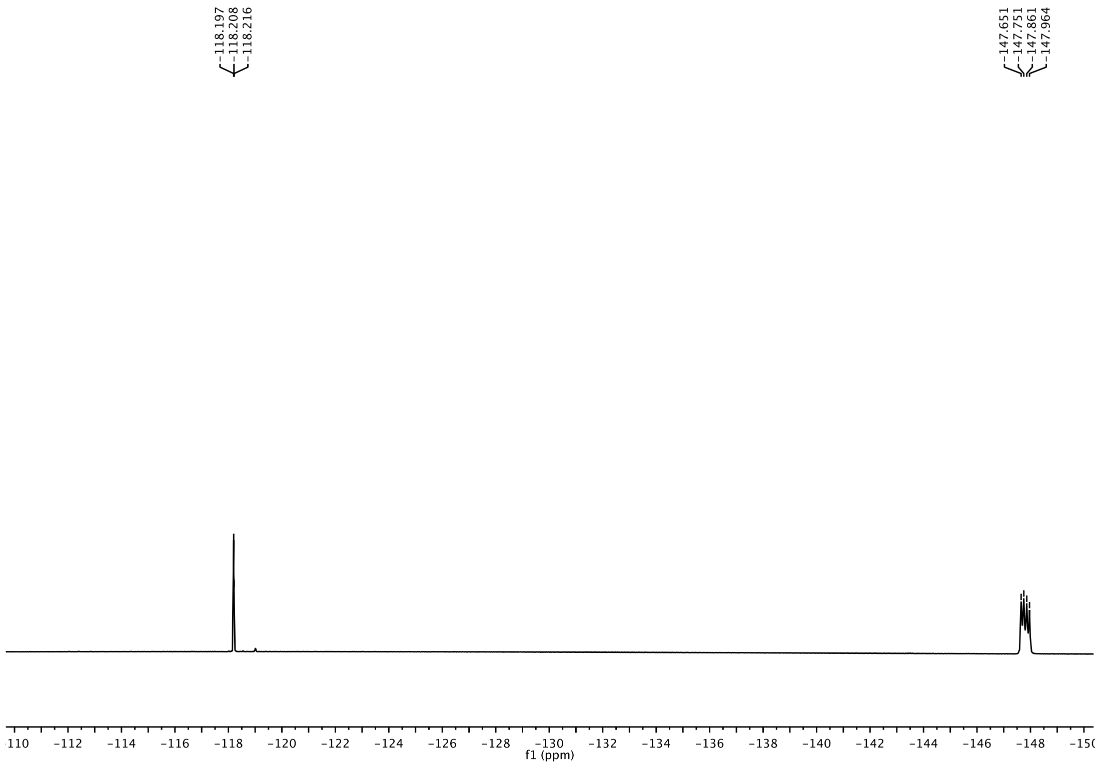
f1 (ppm)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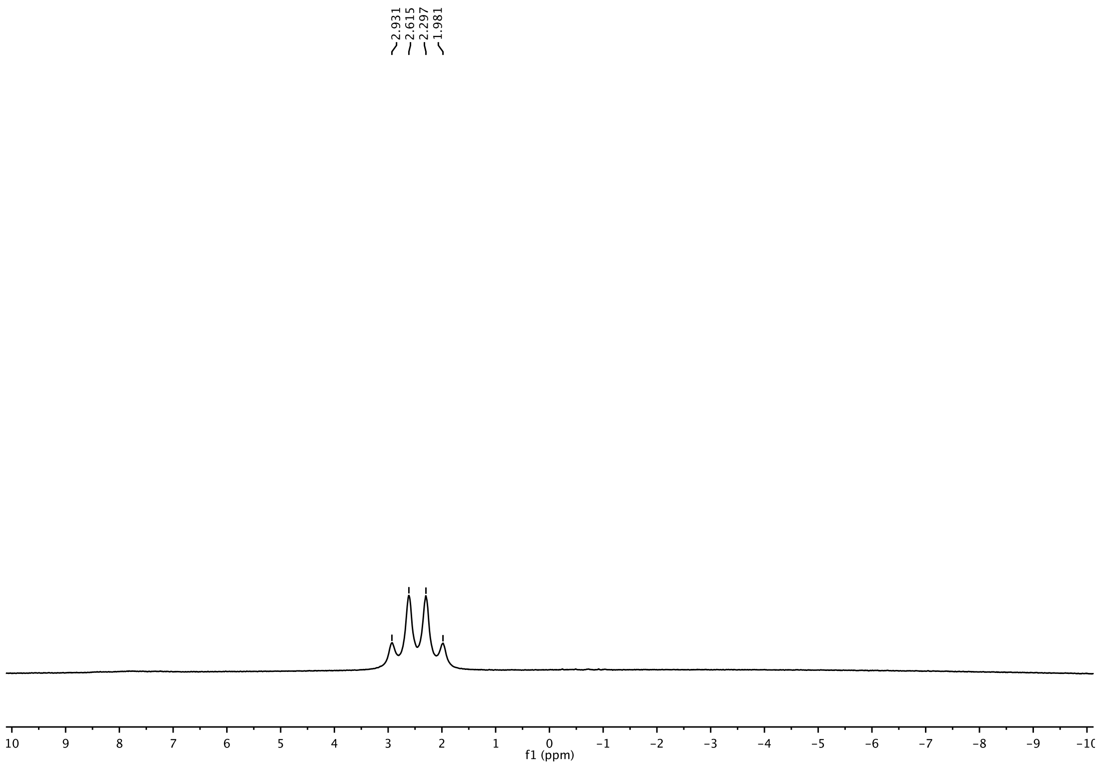
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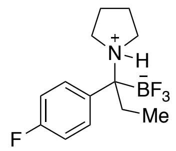
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BF3
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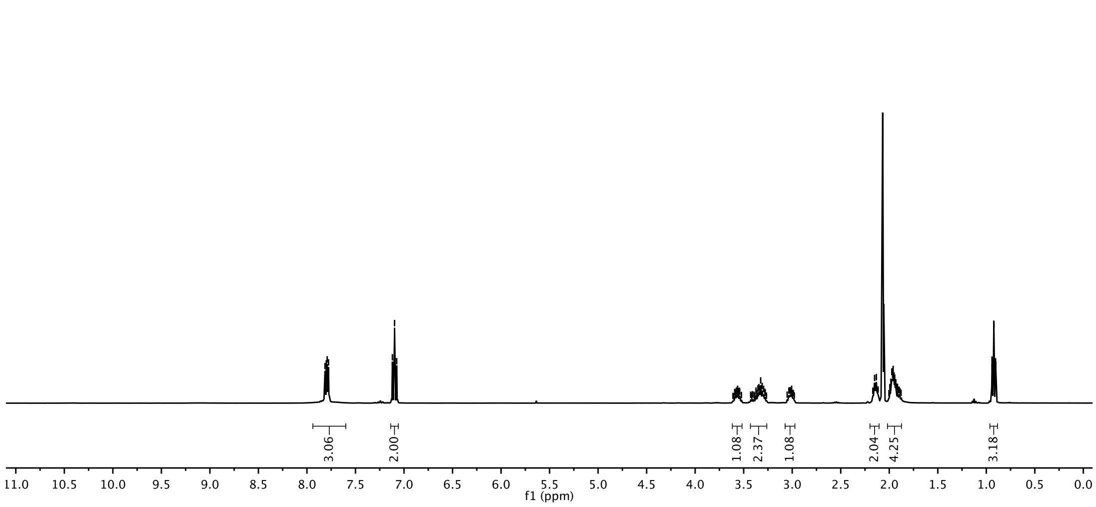
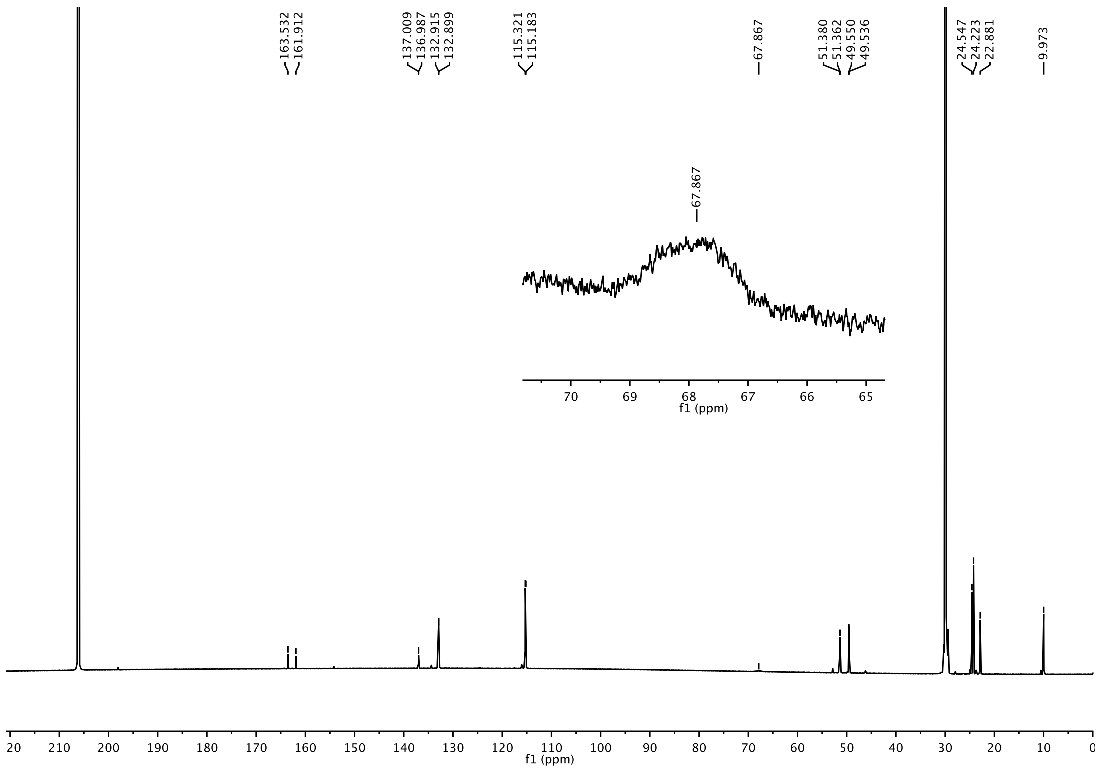
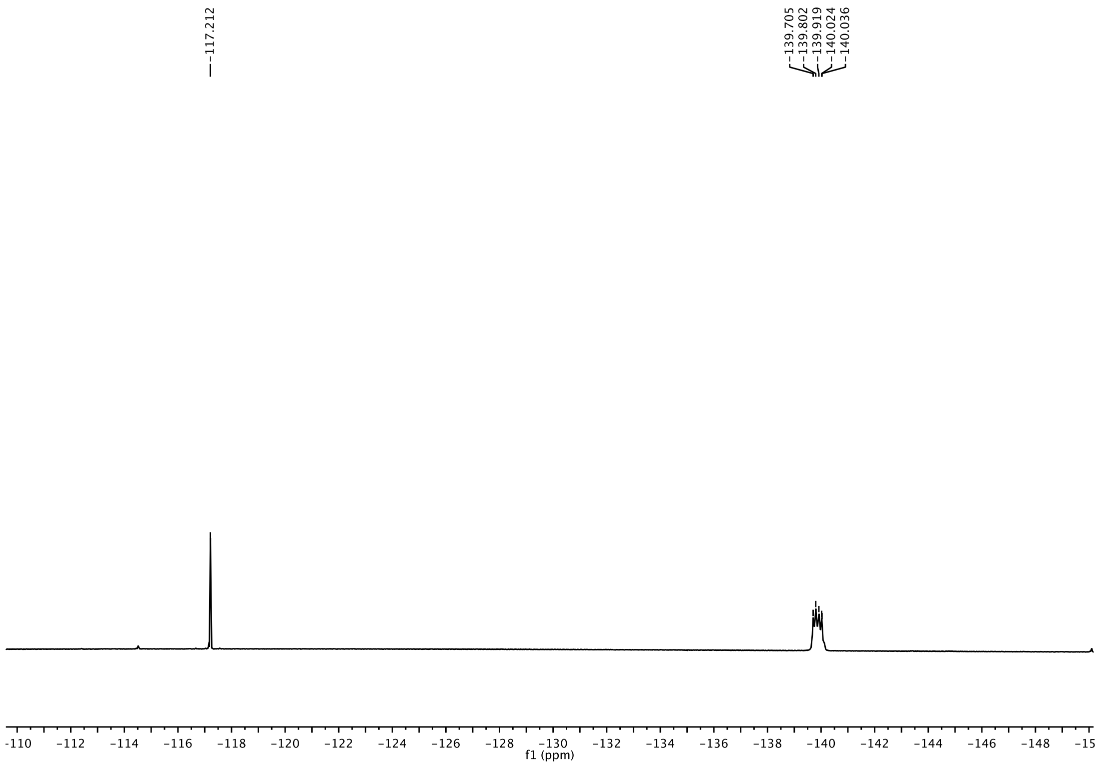
F



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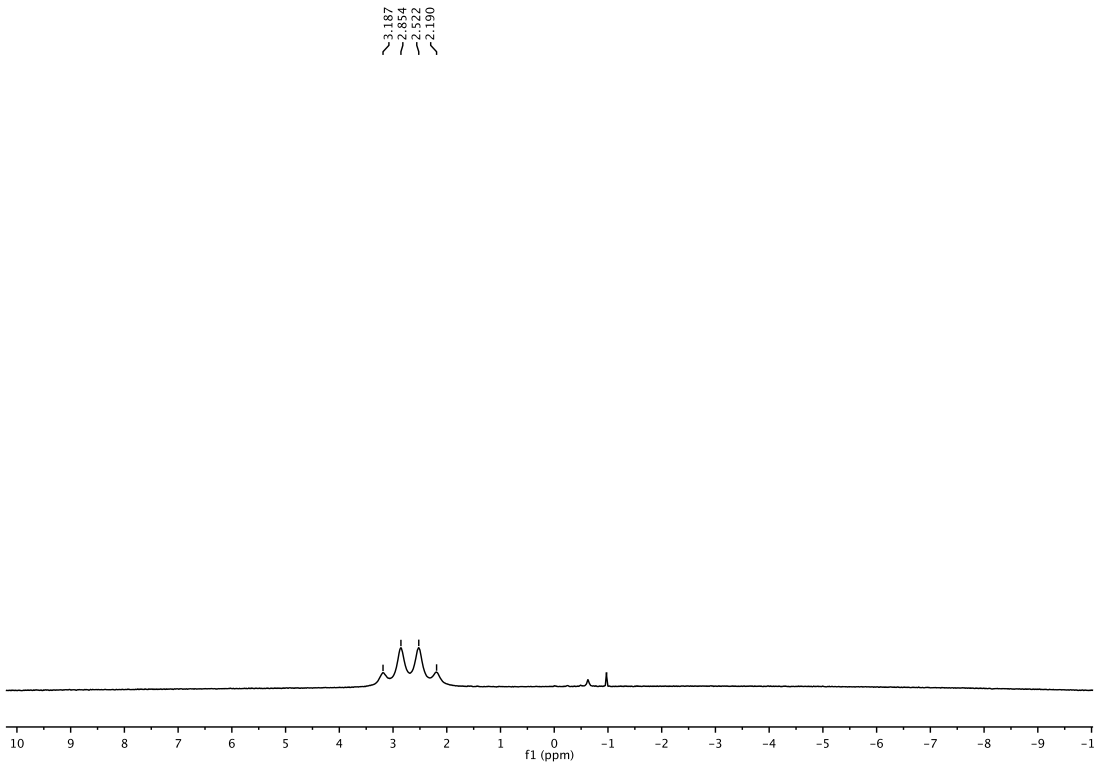
f1 (ppm)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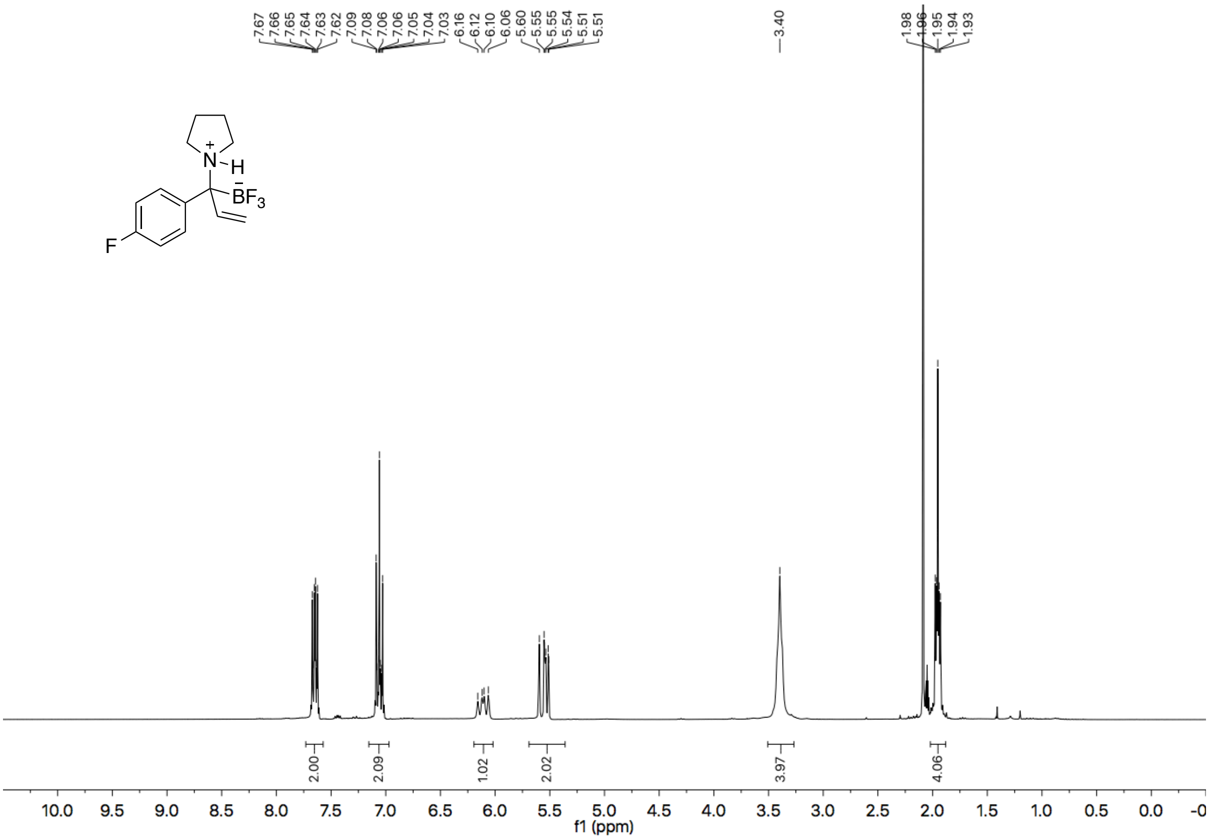
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7.08
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7.03
6.16
6.12
6.10
6.06
5.60
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5.55
5.54
5.51
5.51
3.40
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1.96
1.95
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H
BF3
F
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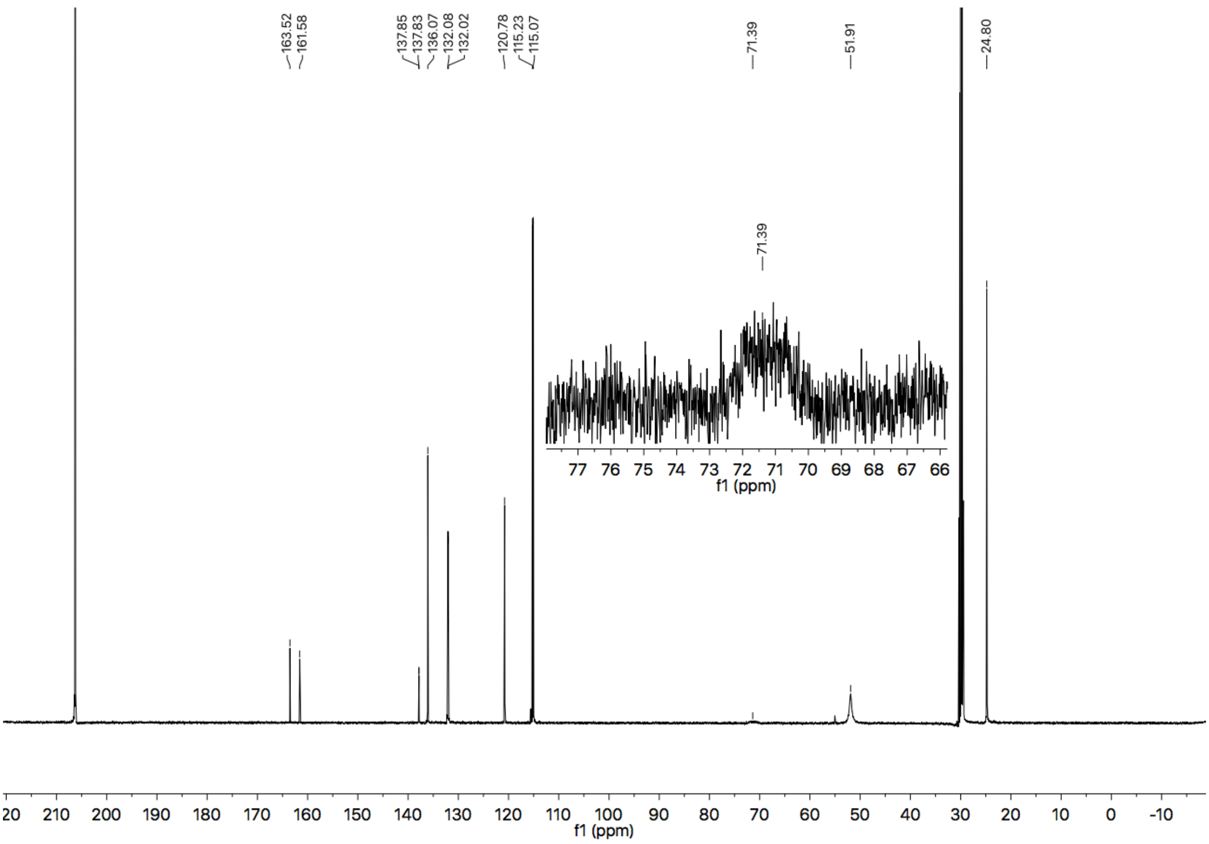
4.06
f1 (ppm)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136.07
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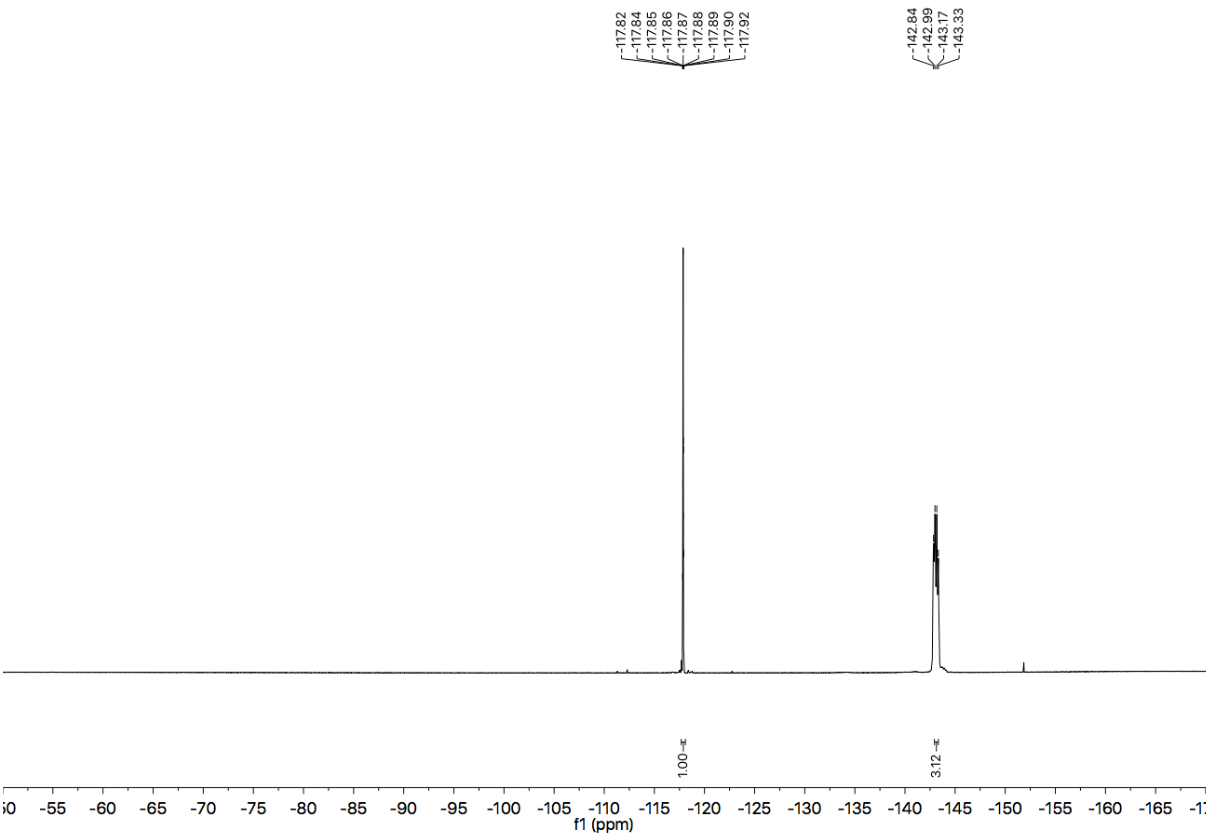
115.07
71.39
51.91
24.80
71.39
f1 (ppm)
f1 (ppm)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-117.88
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-143.33
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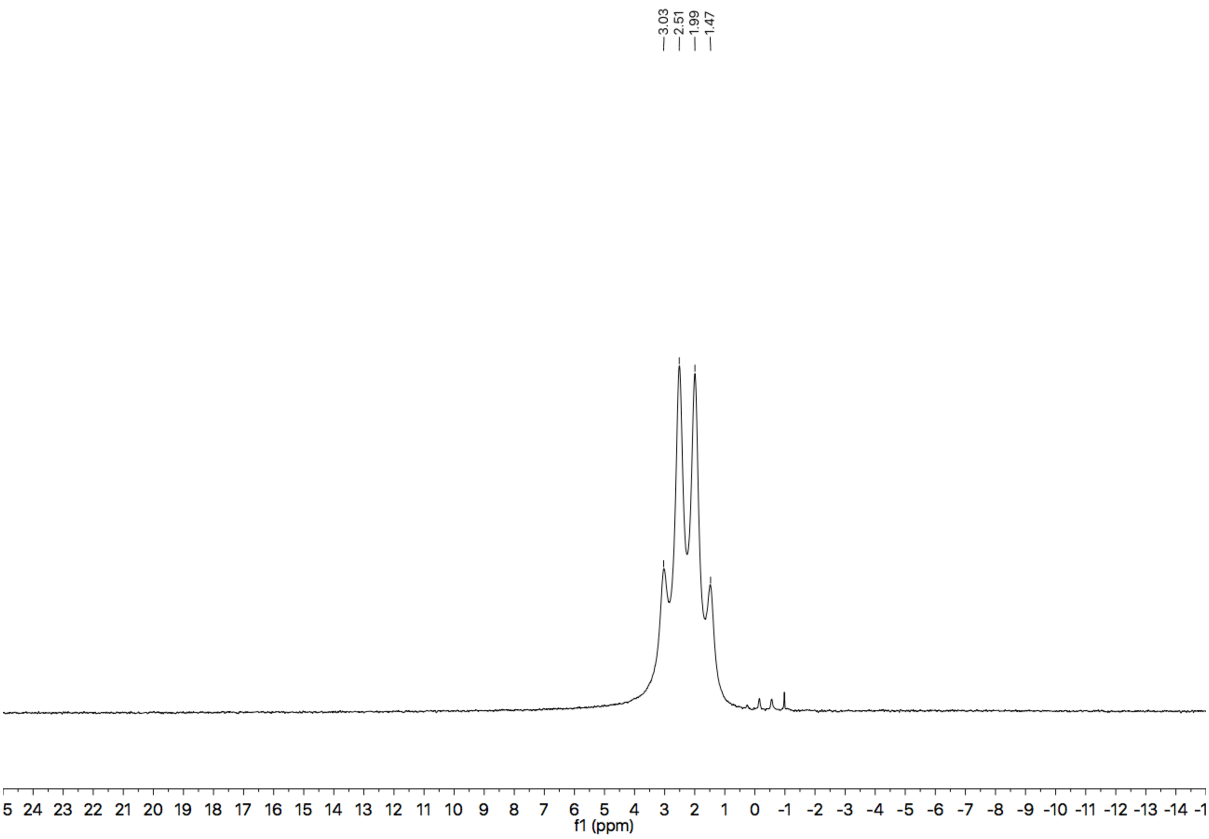
3.12
f1 (ppm)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1.99
1.47
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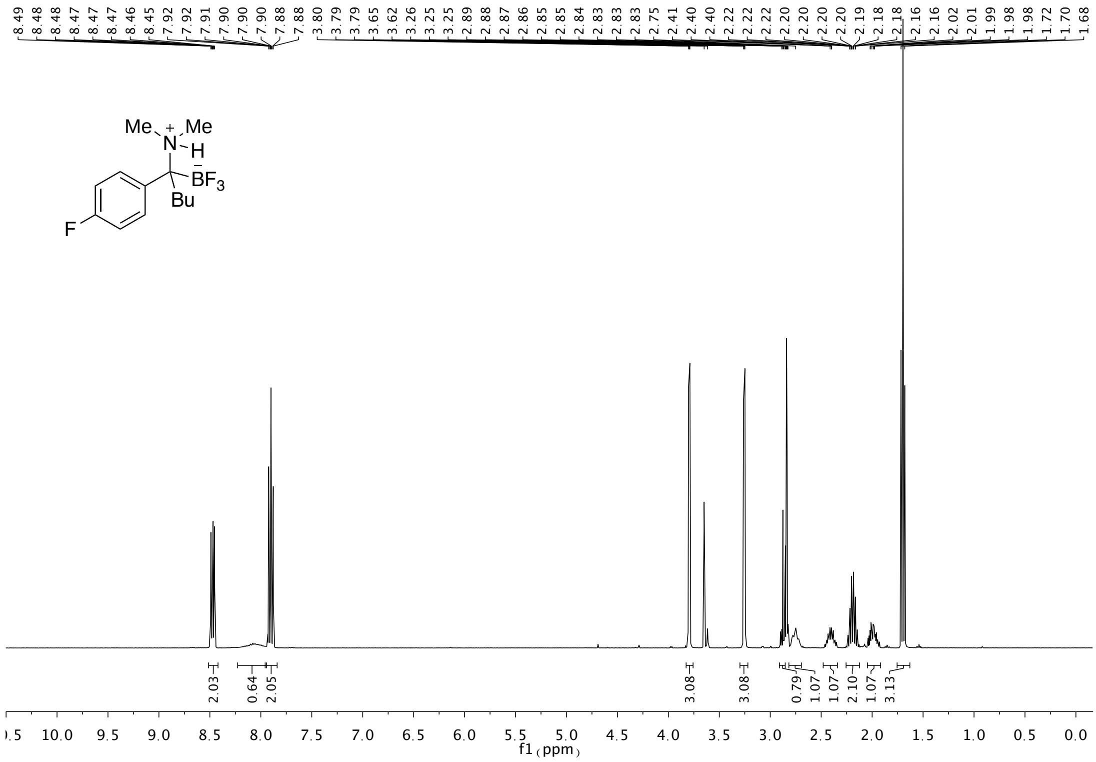

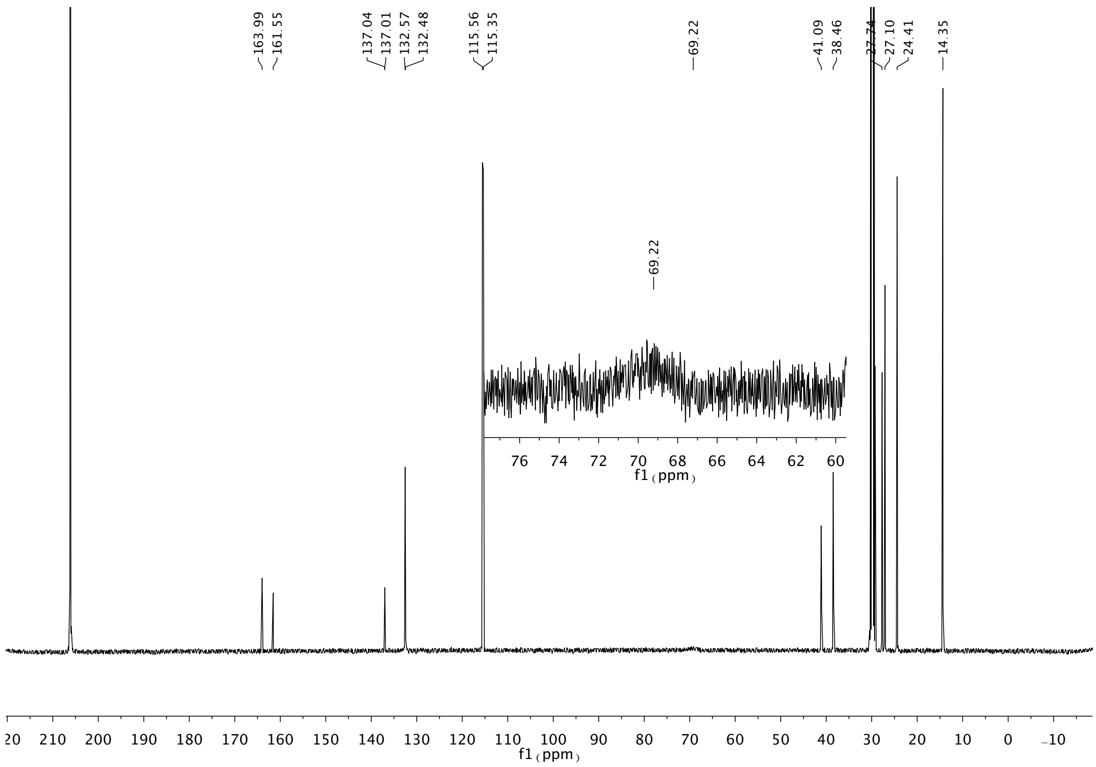

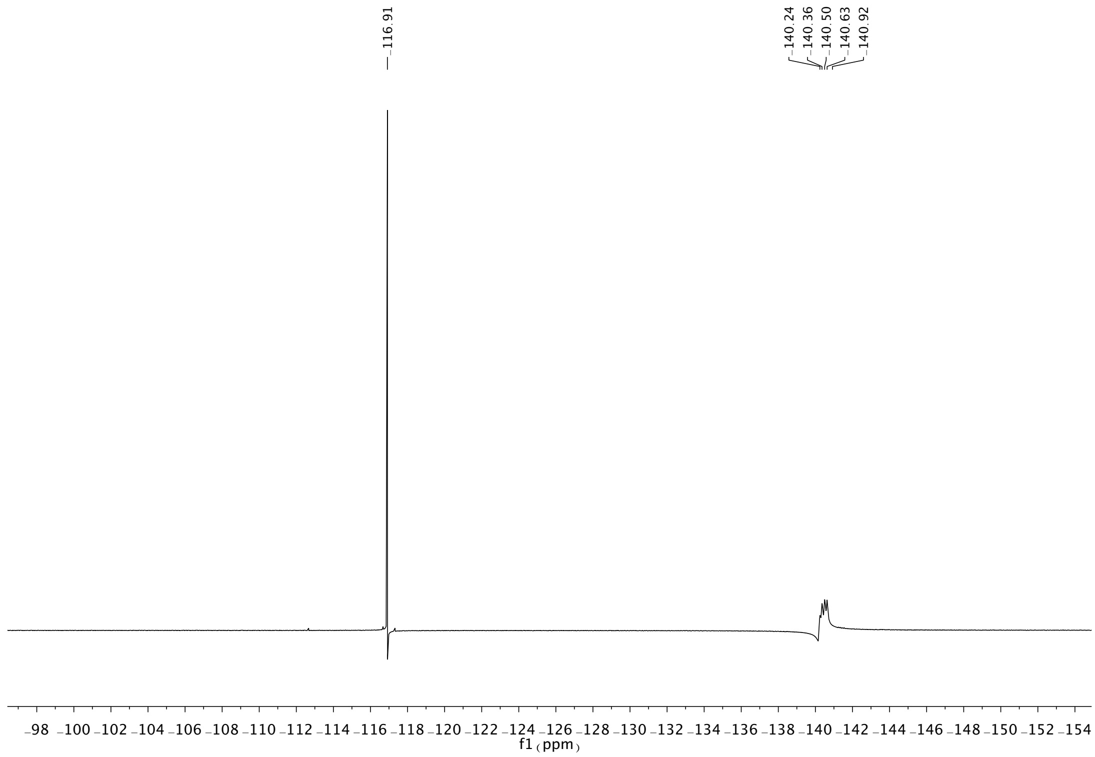
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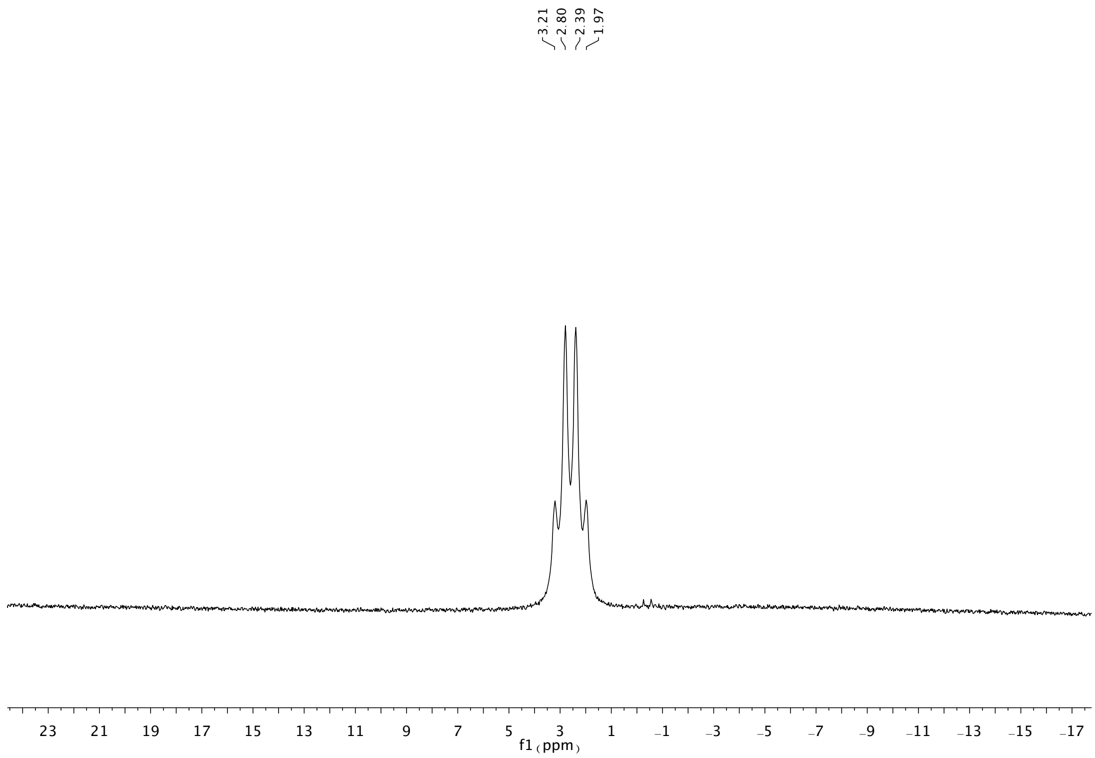
-98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154
f1 (ppm)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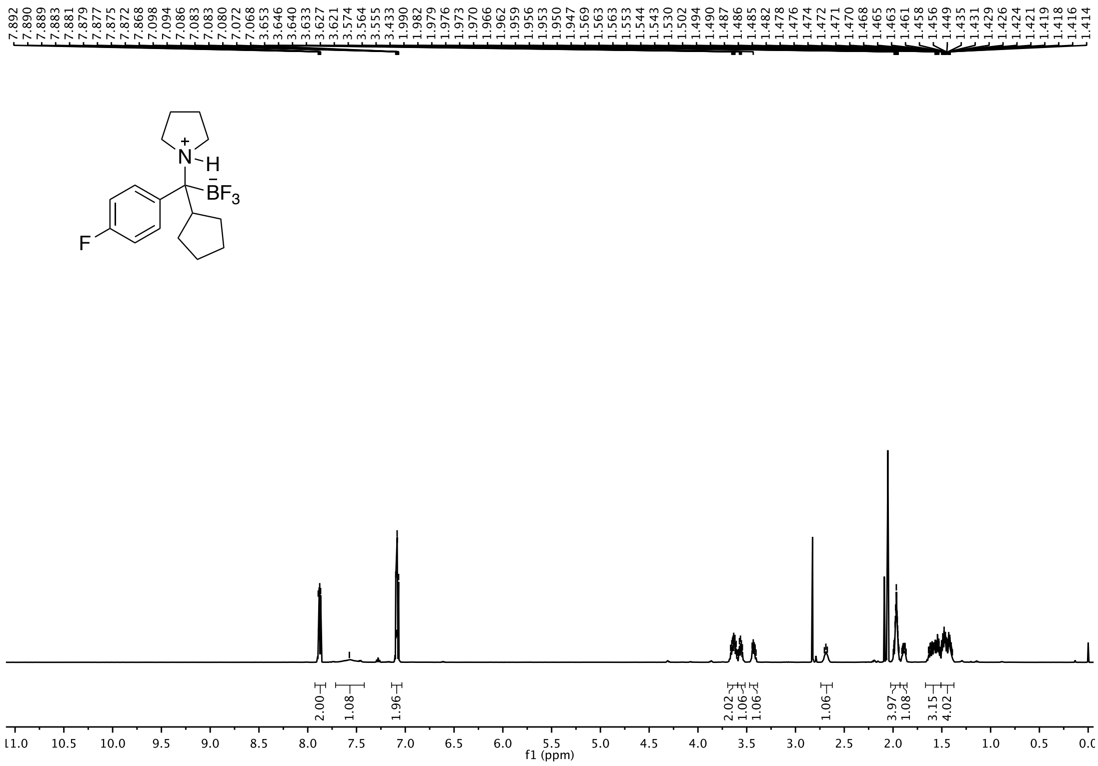
2.80
2.39
1.97
23 21 19 17 15 13 11 9 7 5 3 1 -1 -3 -5 -7 -9 -11 -13 -15 -17
f1 (ppm)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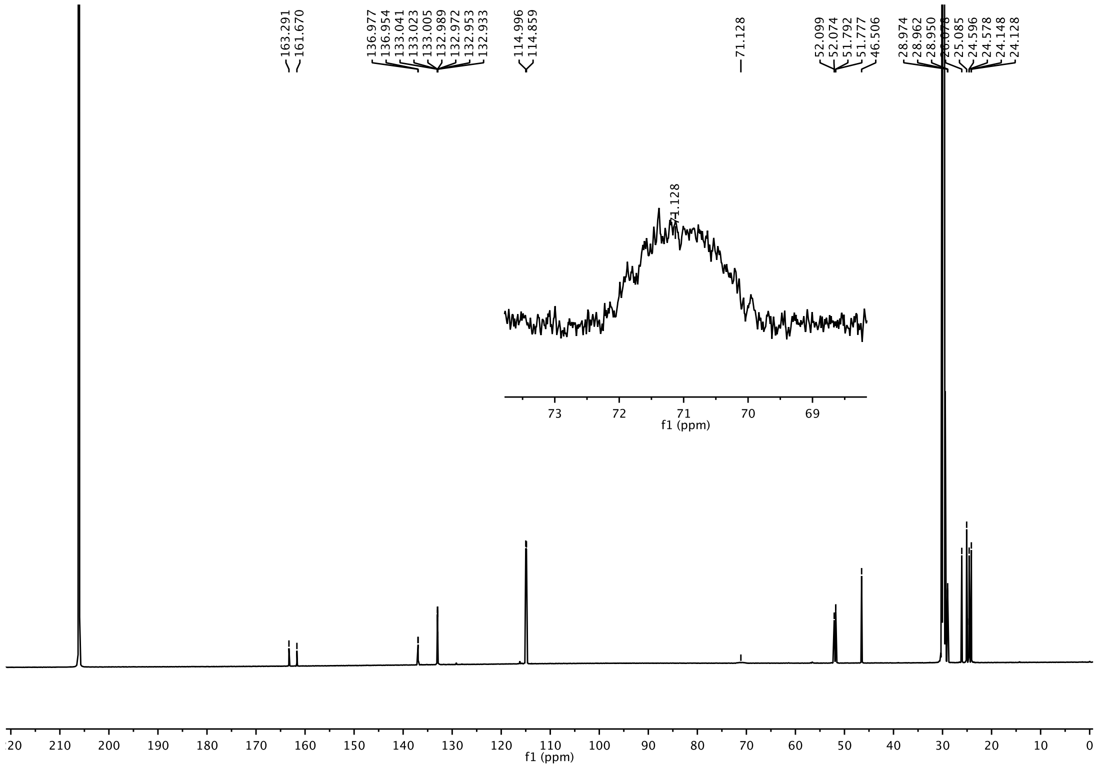
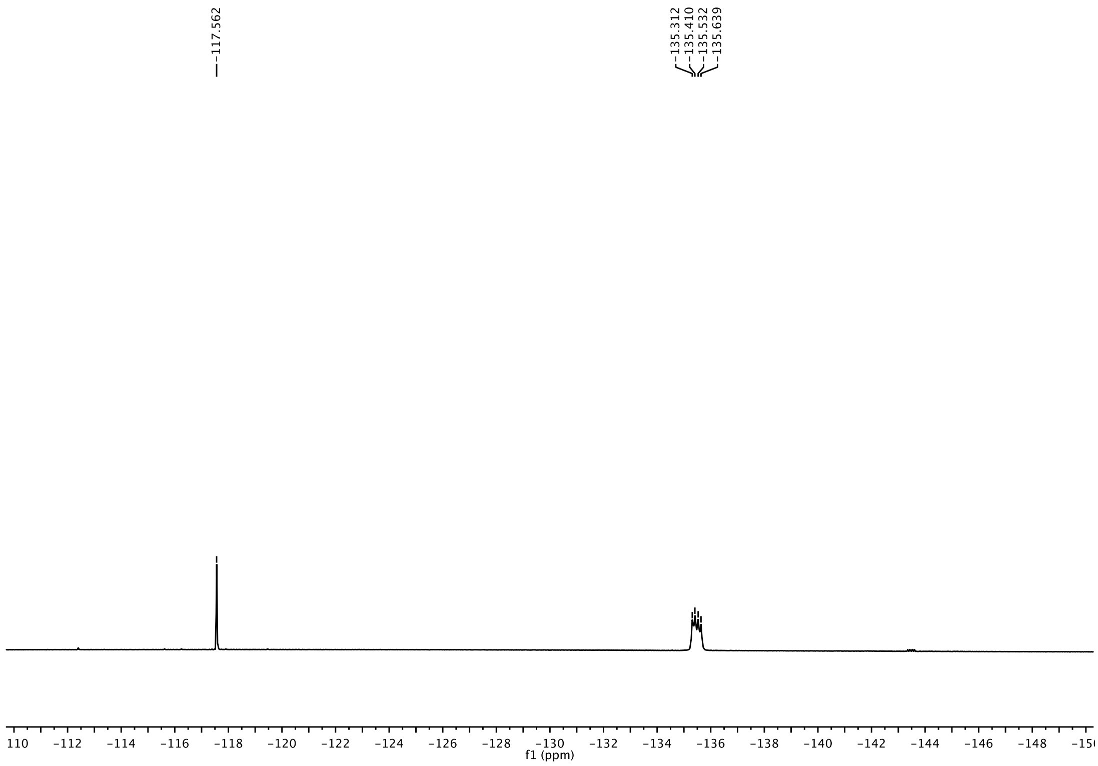
N H BF3 F
2.00 1.08 1.96 2.02 1.06 1.06 1.06 3.97 1.08 3.15 4.02
f1 (ppm)


163.291 161.670 136.977 136.954 133.041 133.023 133.005 132.989 132.972 132.953 132.933 114.996 114.859 71.128 52.099 52.074 51.792 51.777 46.506 28.974 28.962 28.950 25.085 24.596 24.578 24.148 24.128
71.128
f1 (ppm)
f1 (ppm)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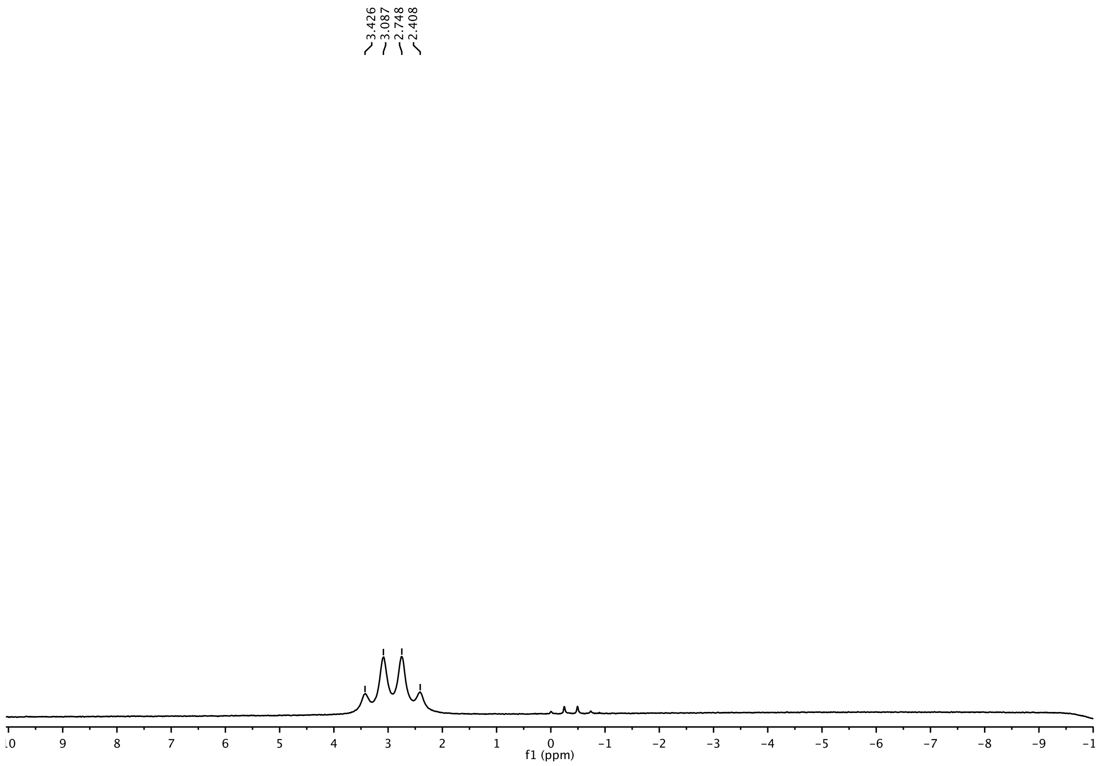
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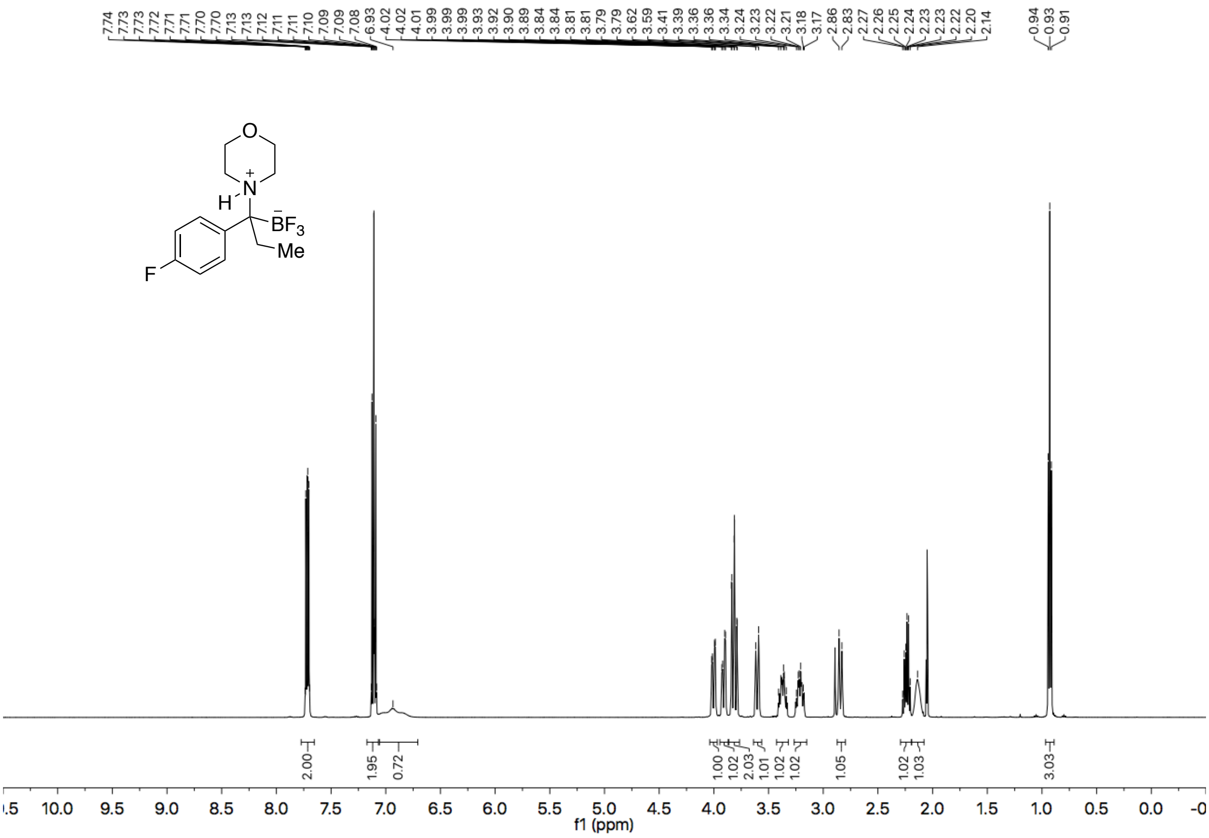

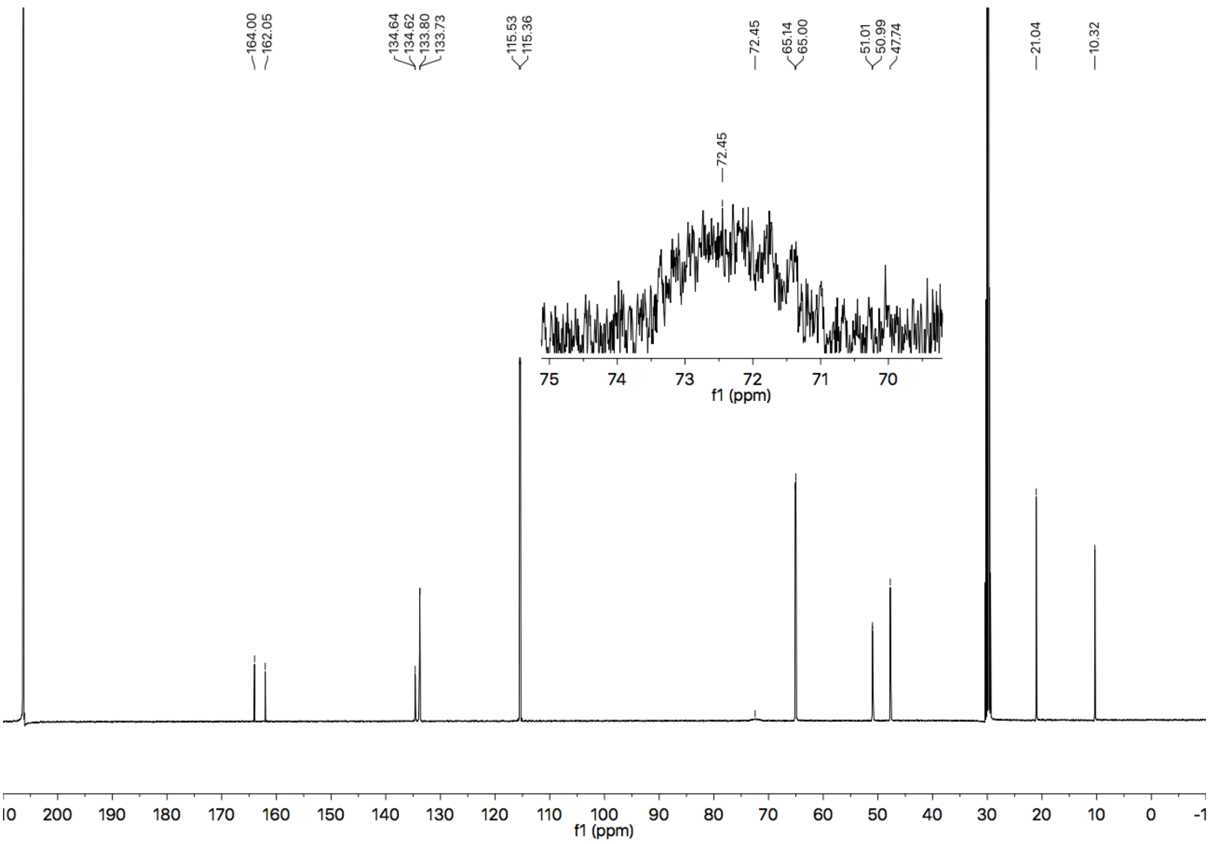

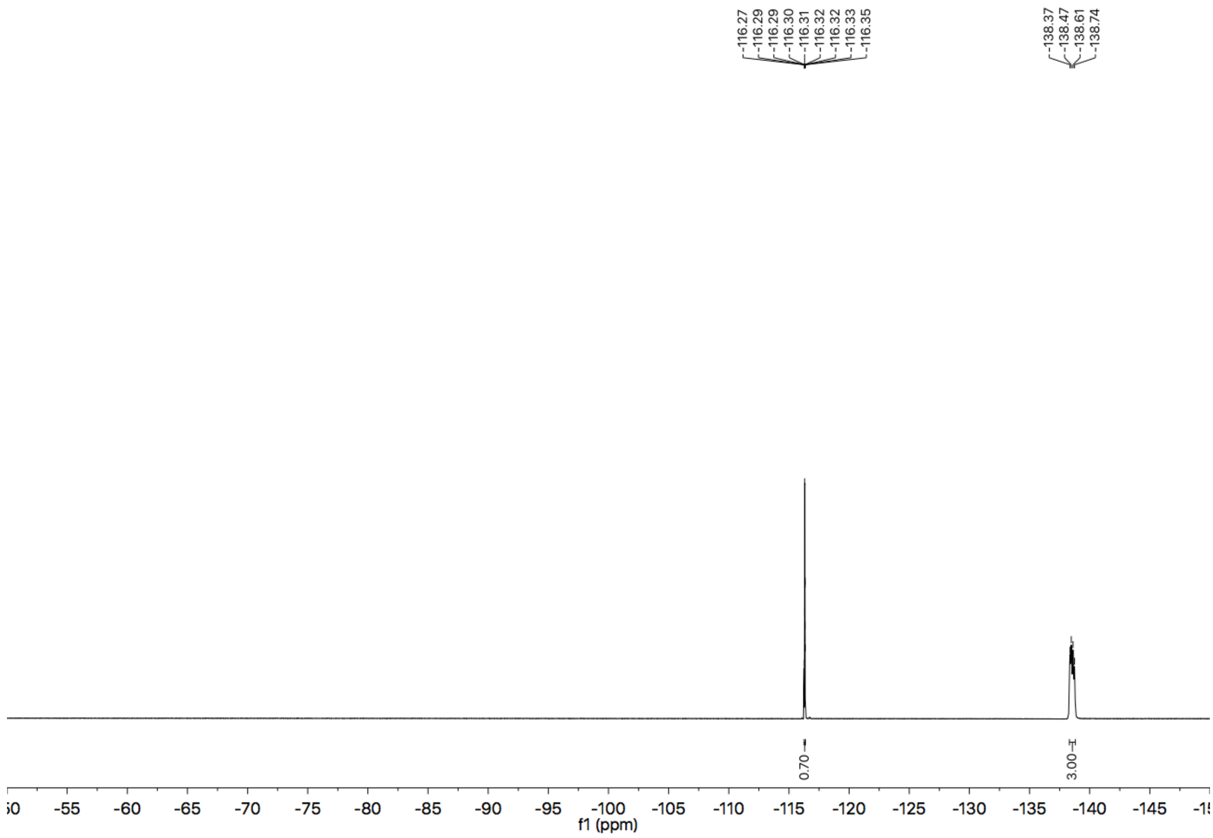
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-138.47
-138.61
-138.74
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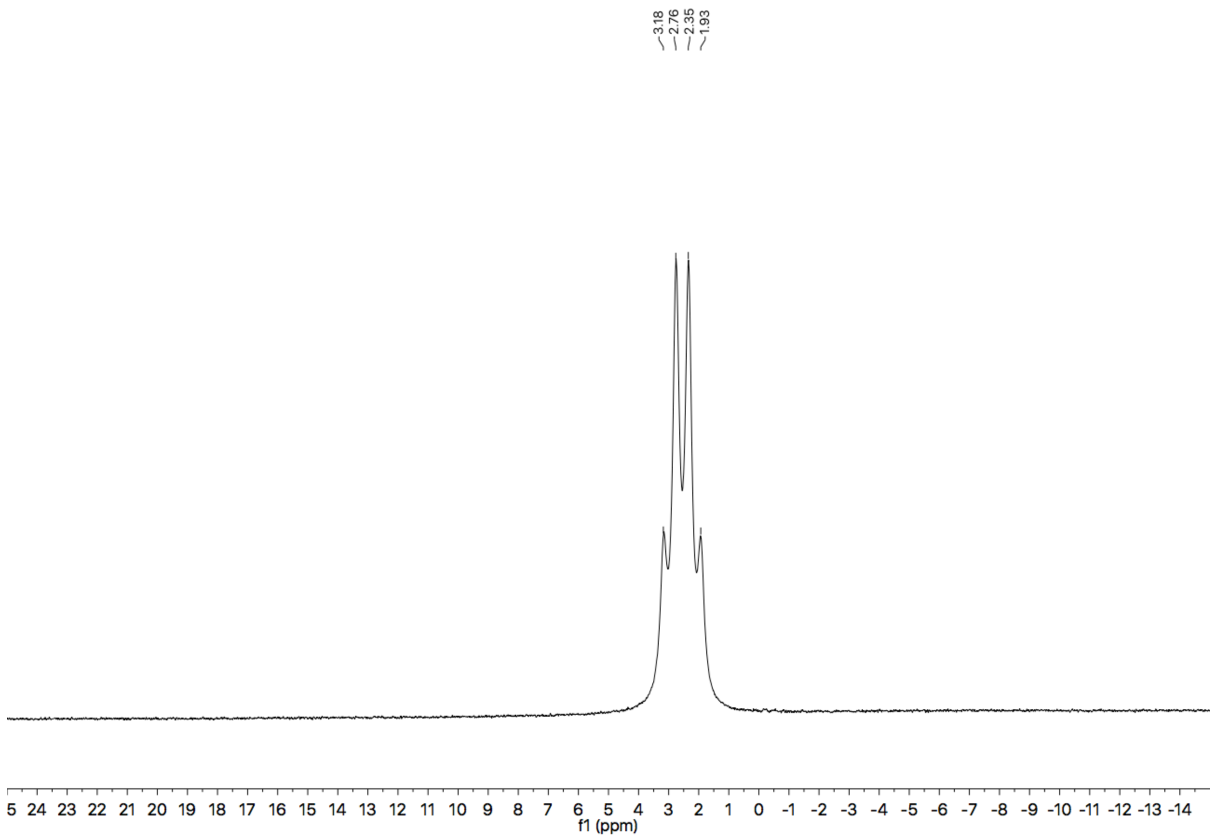
3.00
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)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2.35
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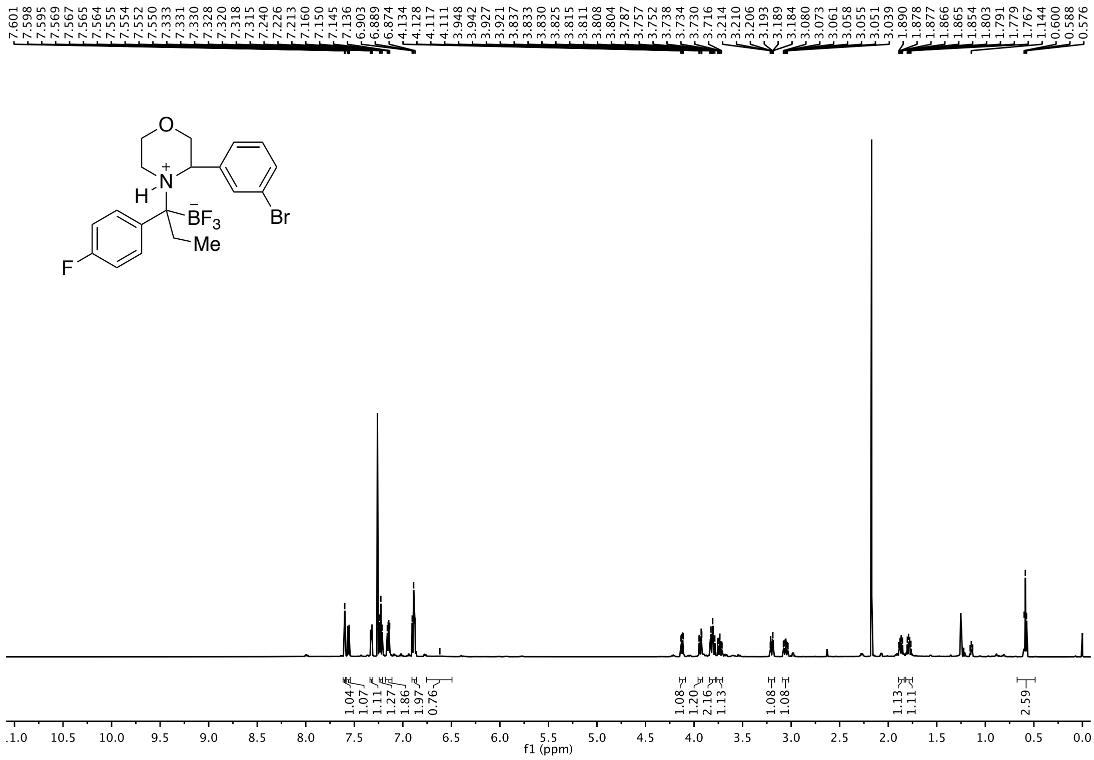
f1 (ppm)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7.145
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6.874
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4.128
4.117
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3.948
3.942
3.927
3.921
3.837
3.833
3.830
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3.808
3.804
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0.588
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O
H
N
+
B
F3
Br
Me
F
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1.08
1.20
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1.08
1.08
1.13
1.11
2.59
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10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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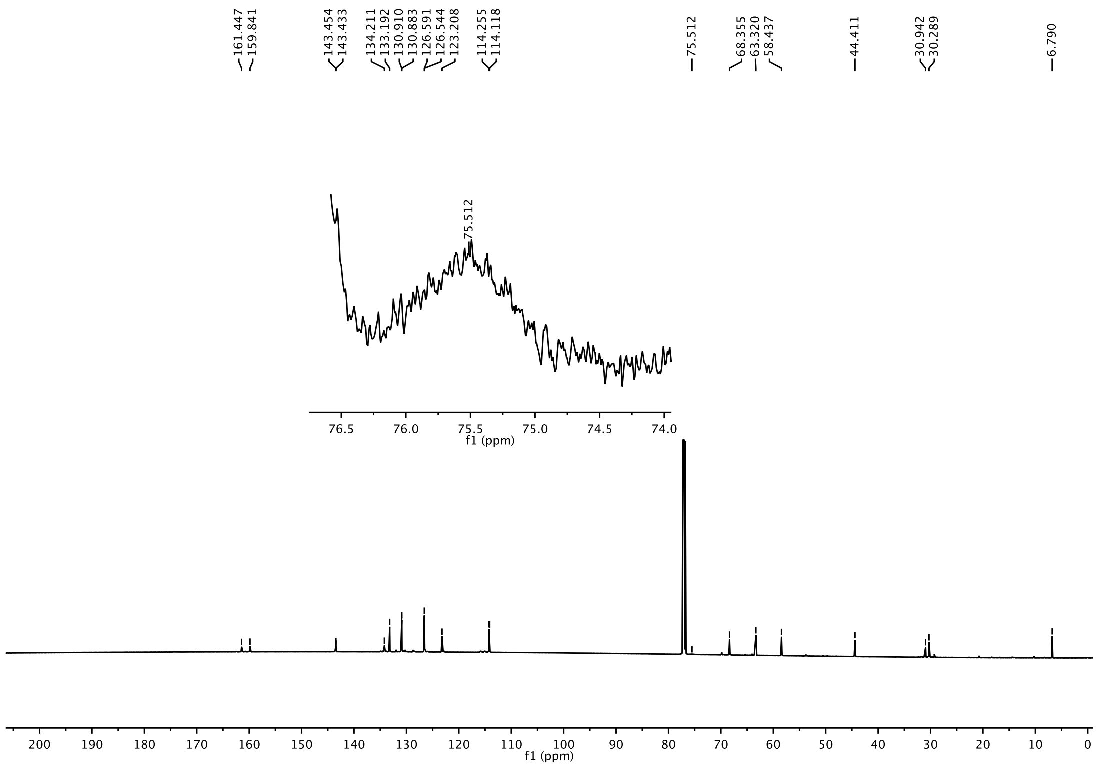
0.0
f1 (ppm)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68.355
63.320
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44.411
30.942
30.289
6.790
75.512
76.5
76.0
75.5
75.0
74.5
74.0
f1 (ppm)
200
190
180
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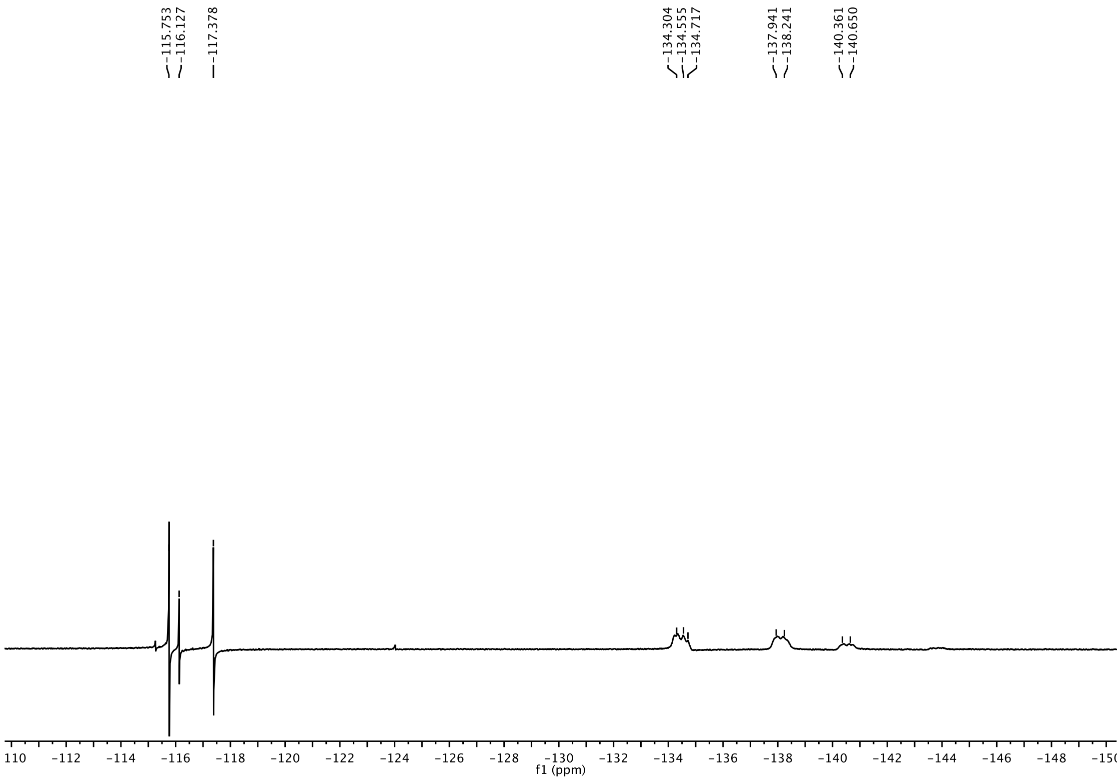
50
40
30
20
10
0
f1 (ppm)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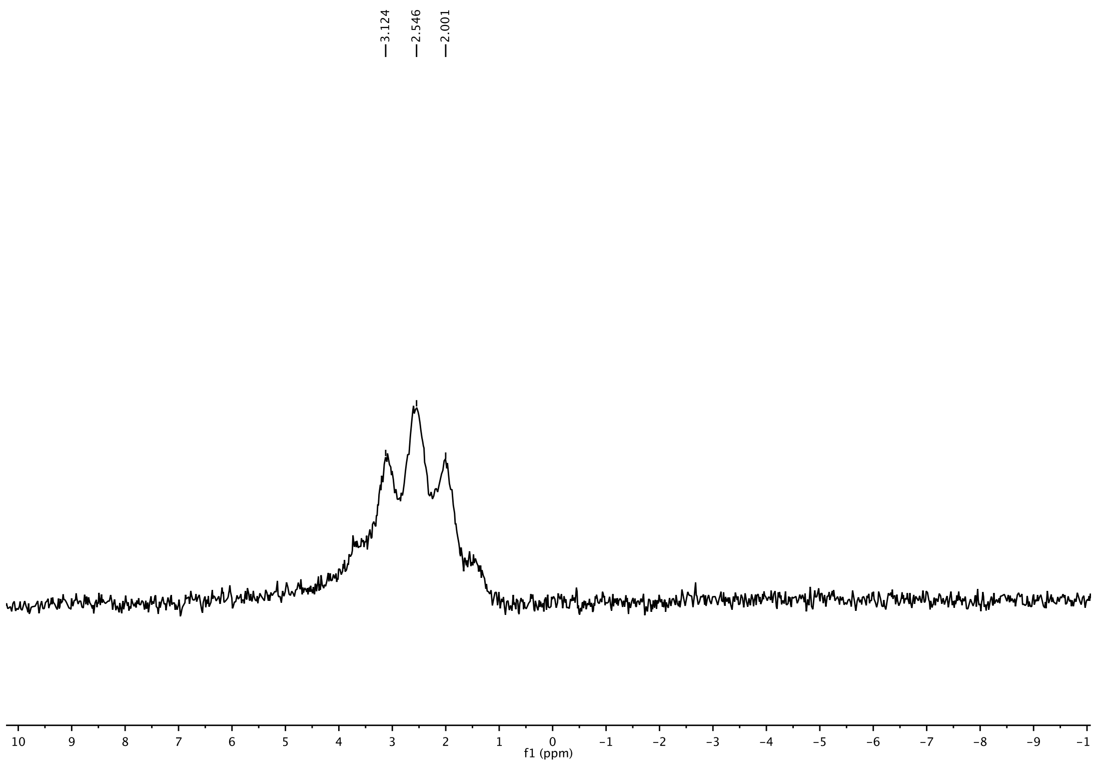
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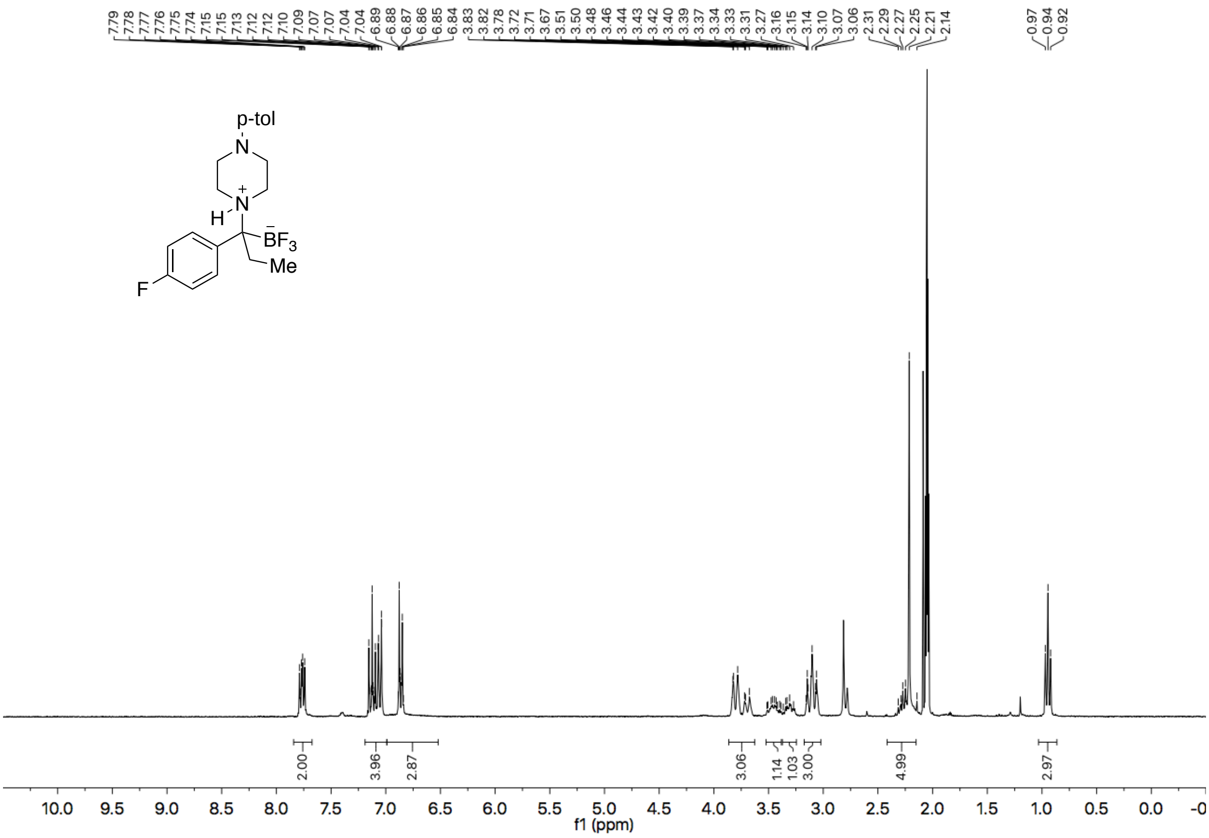
p-tol
Me
F
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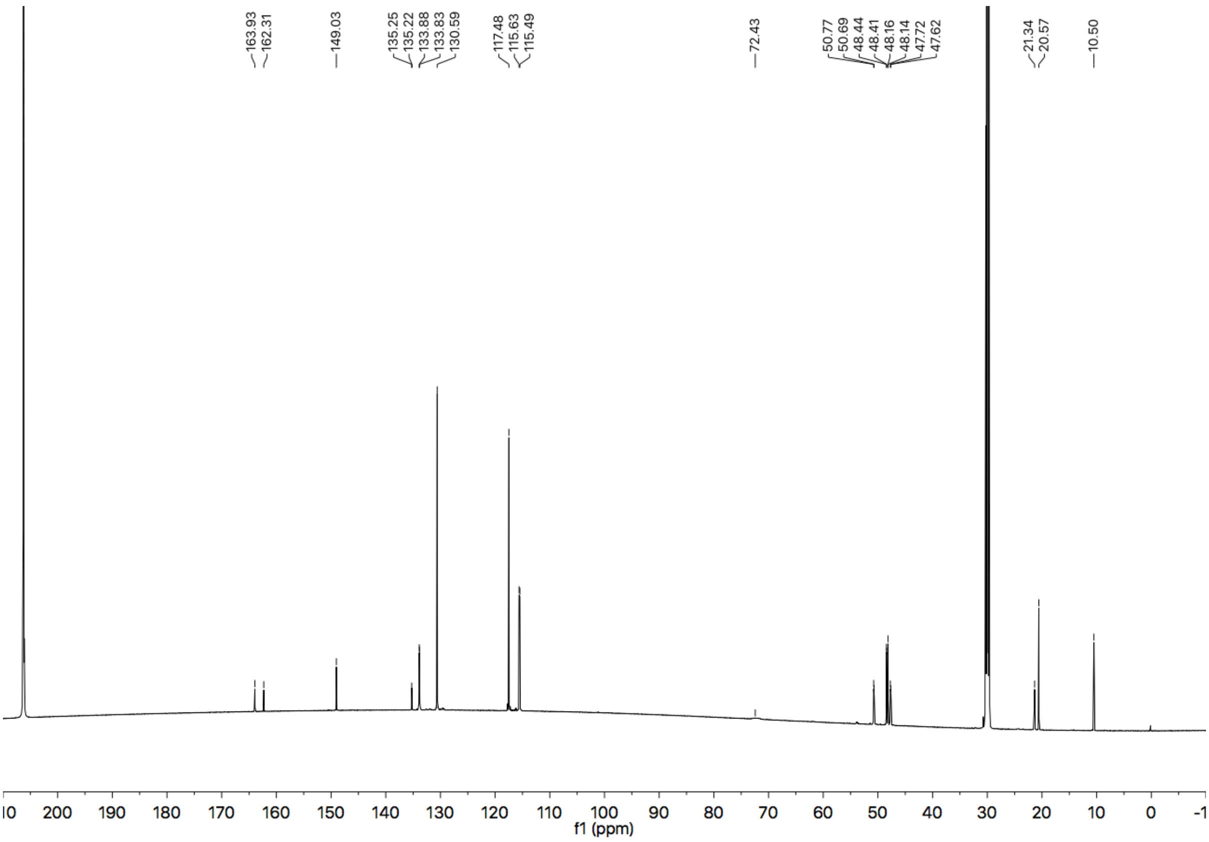
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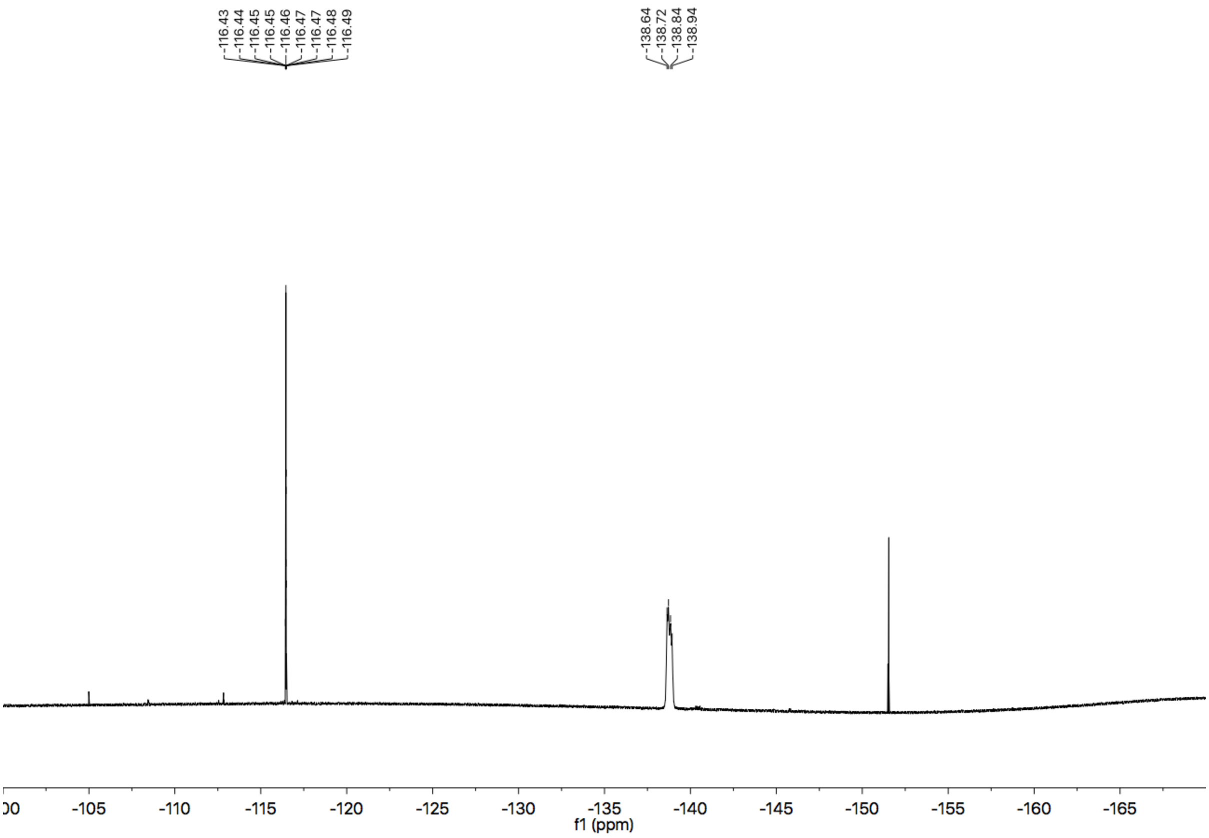
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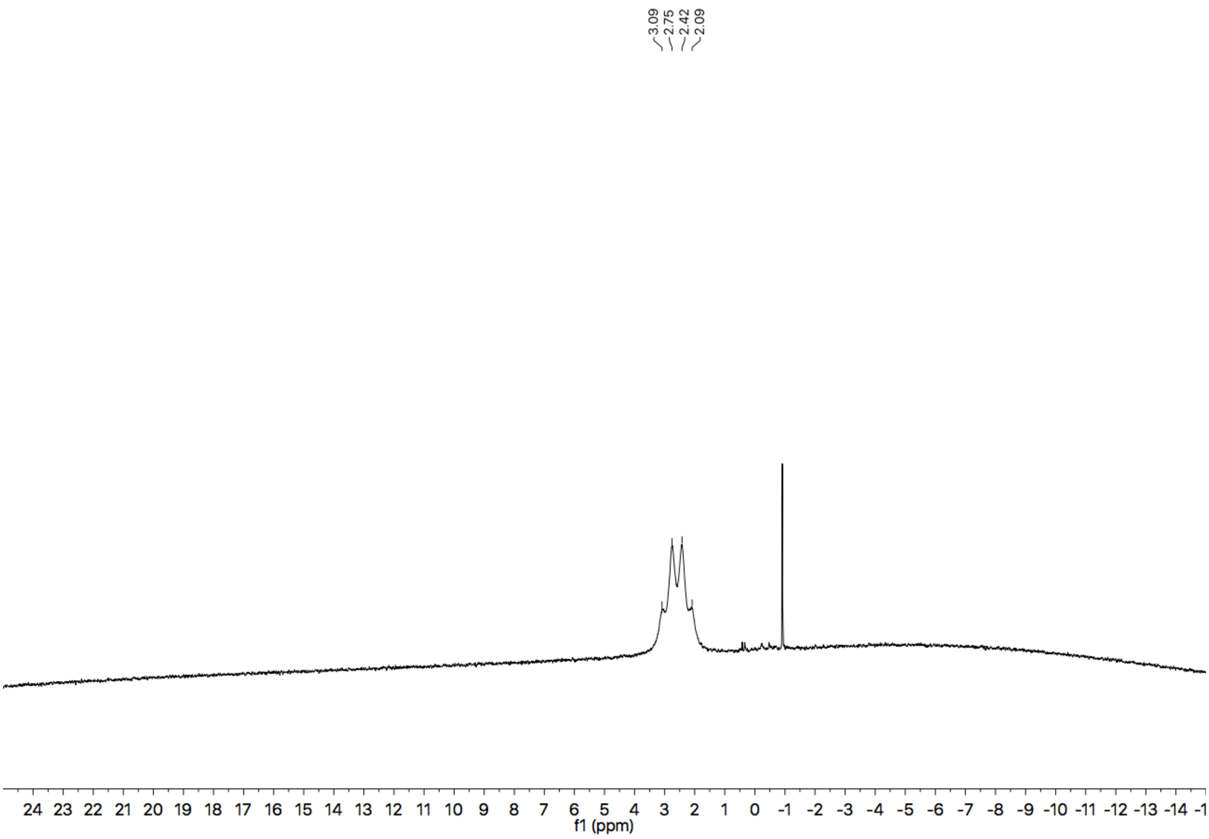
f1 (ppm)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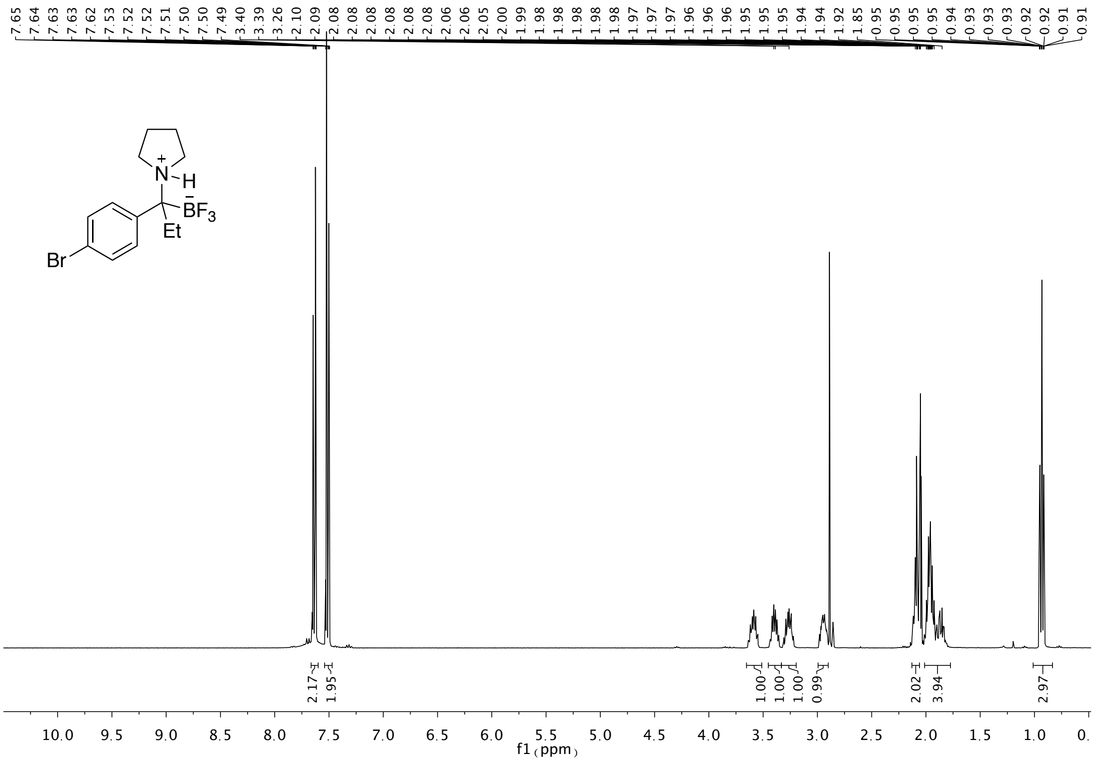

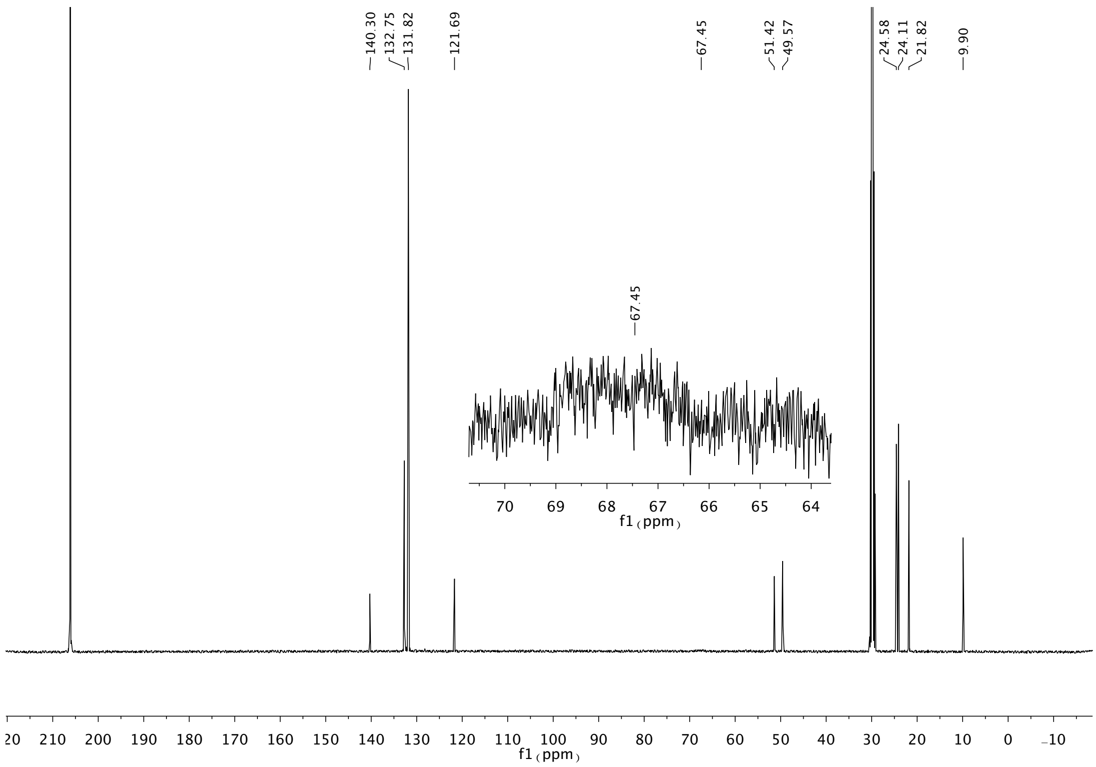

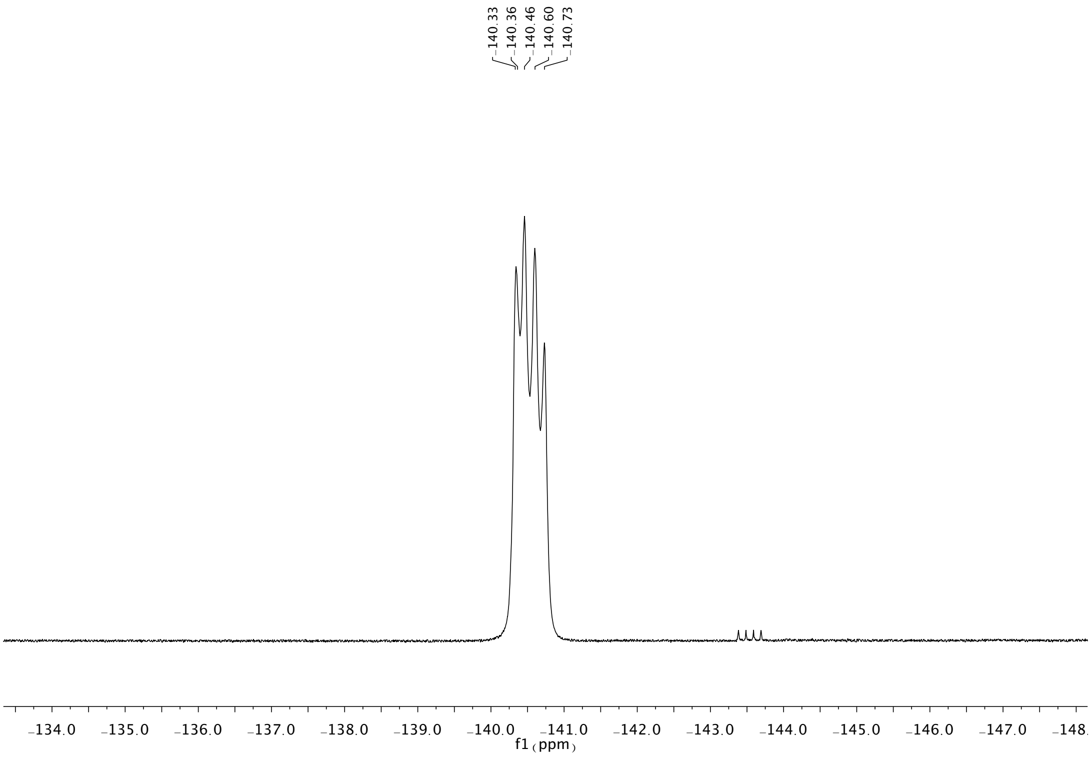
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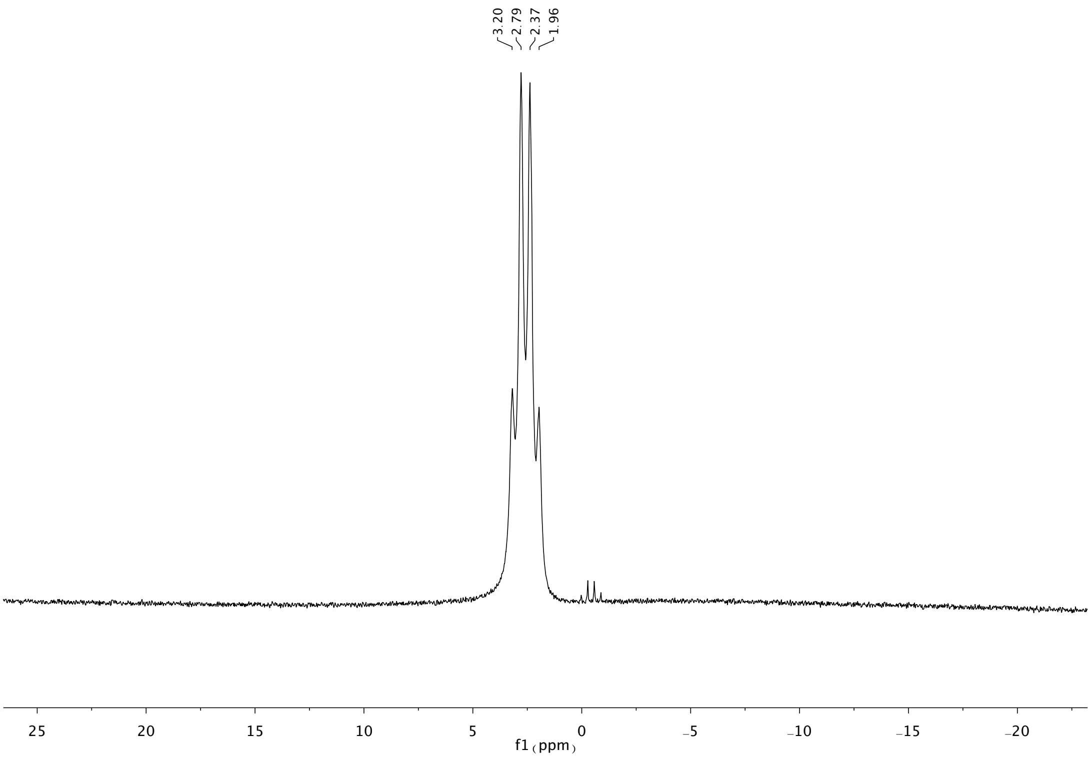
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-15
-20
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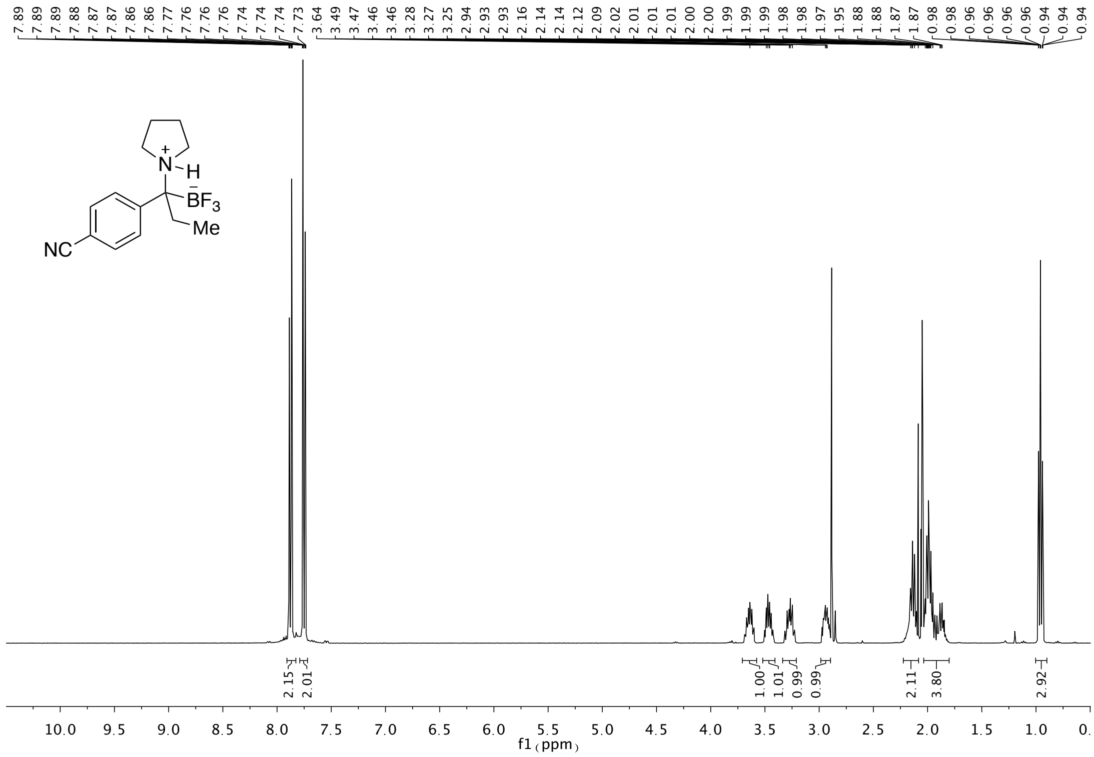
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7.73
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3.25
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BF3
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1.01
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2.92
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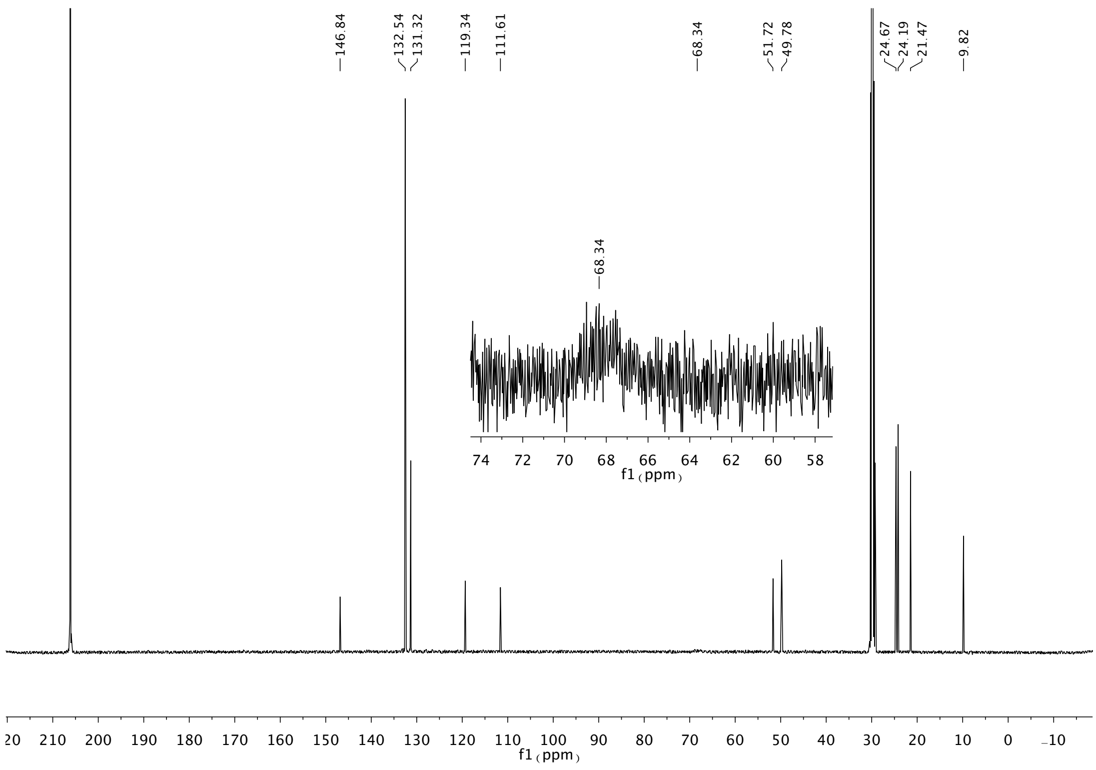
1.0
f1 (ppm)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74
72
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68
66
64
62
60
58
f1 (ppm)
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200
190
180
170
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30
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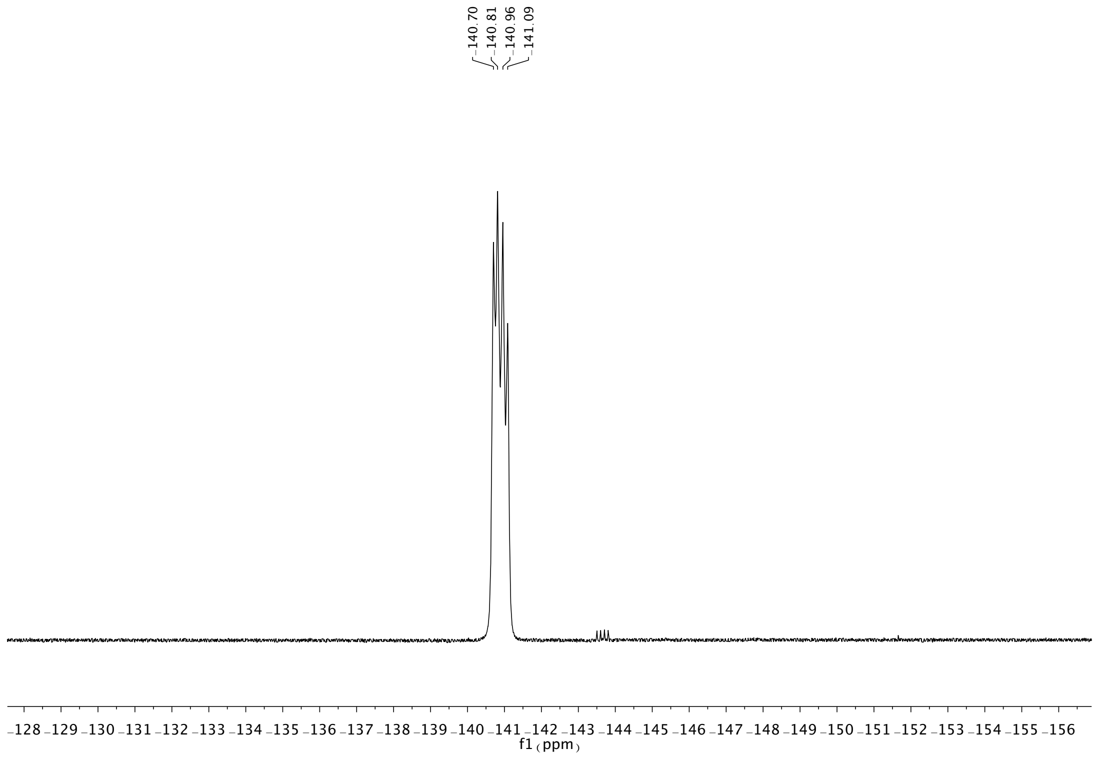
f1 (ppm)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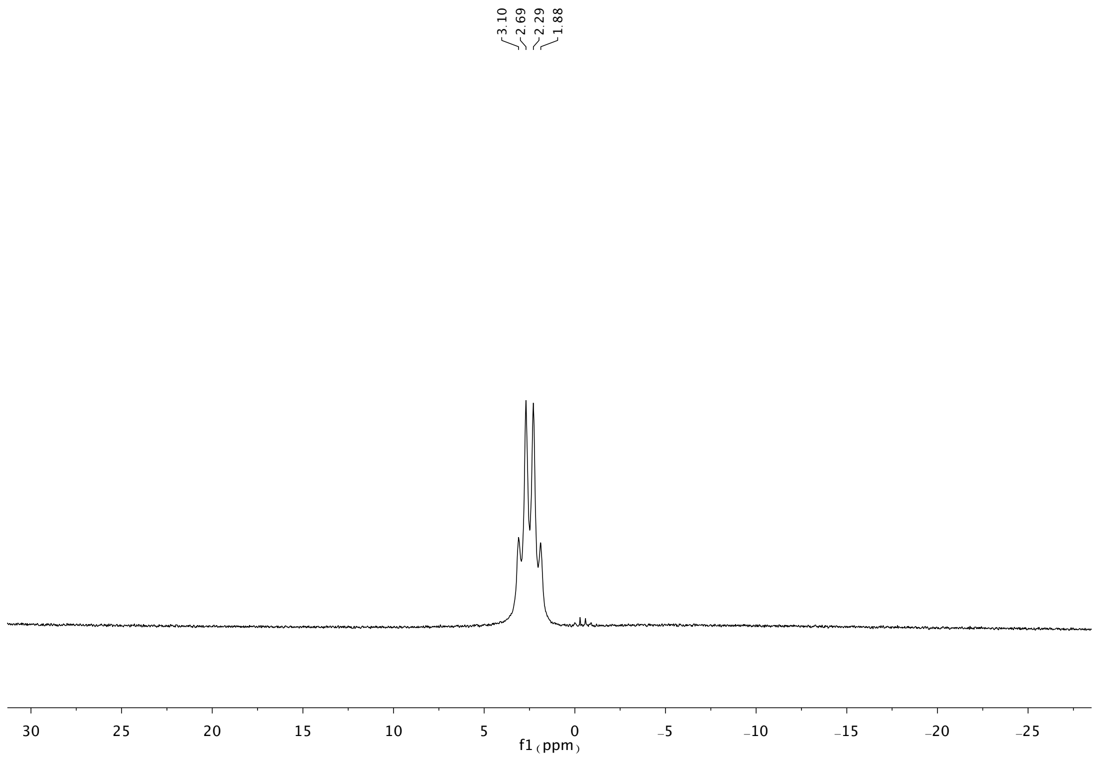
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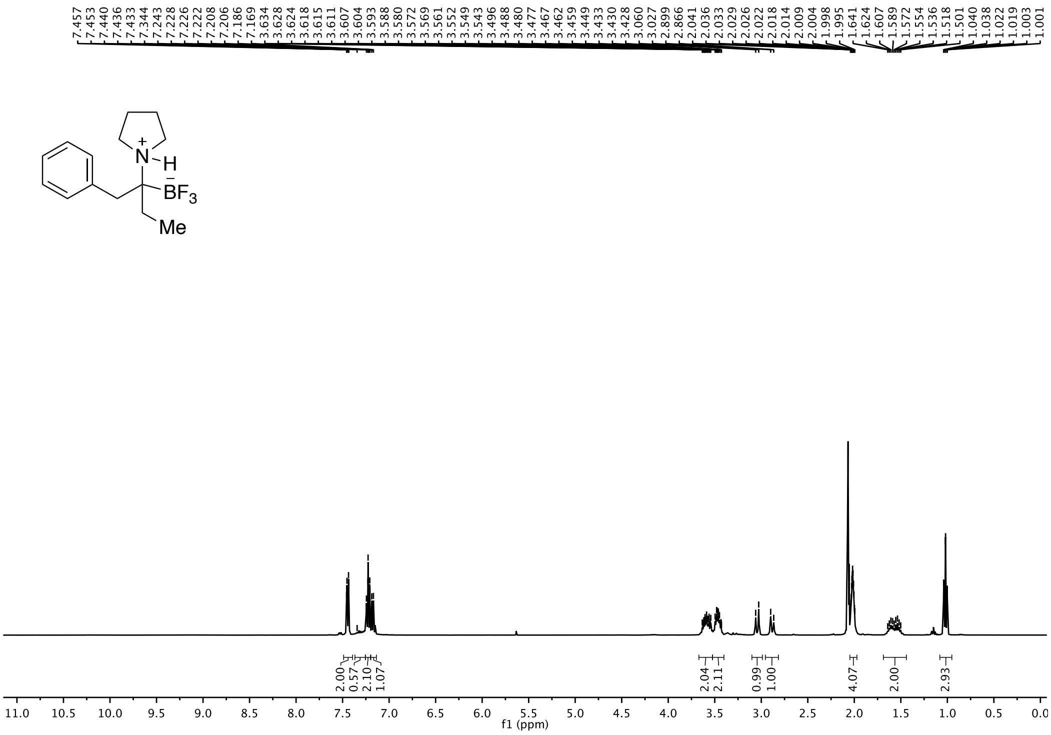
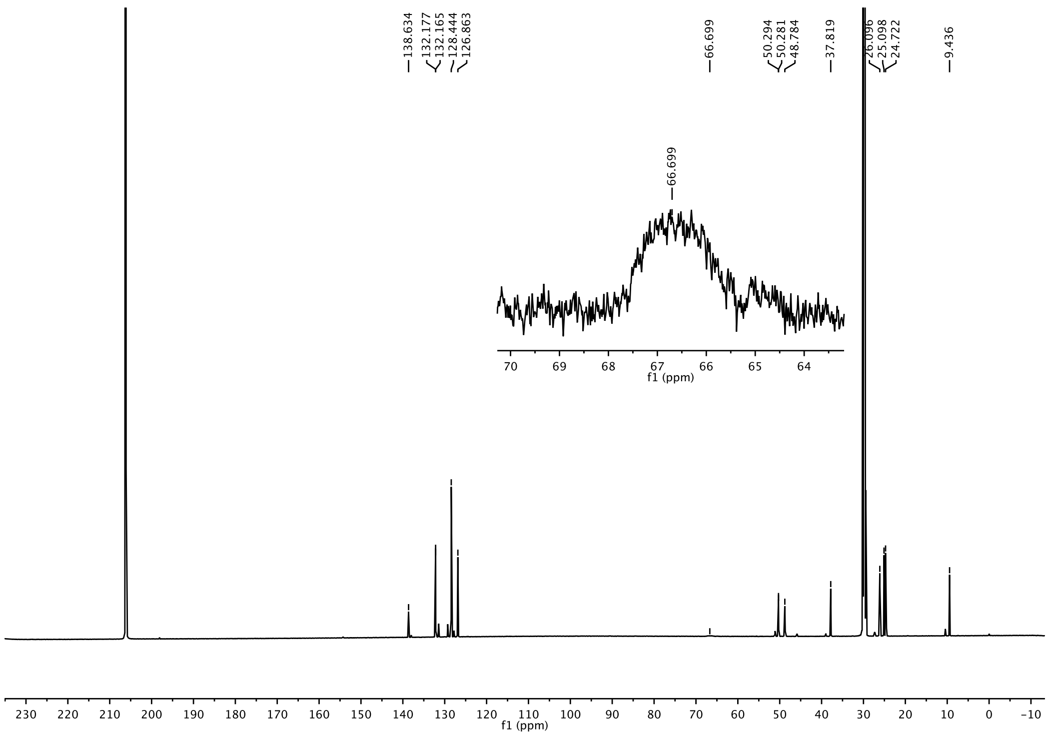
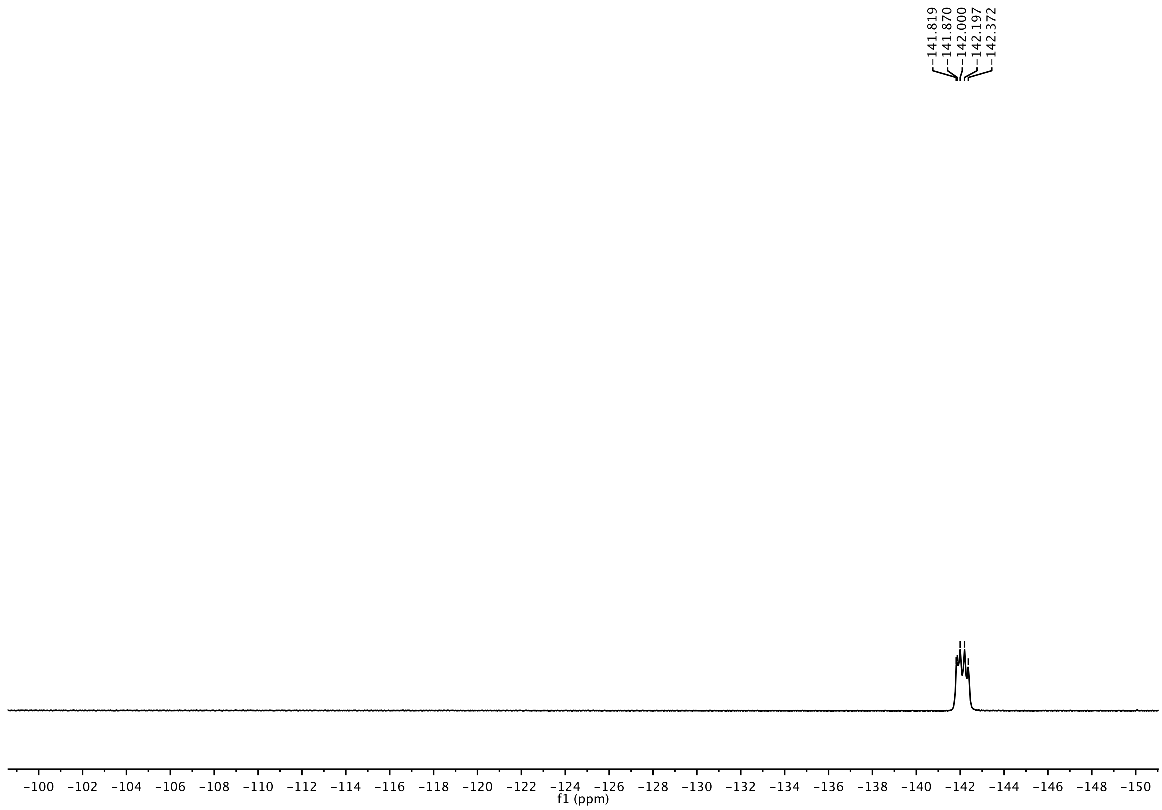
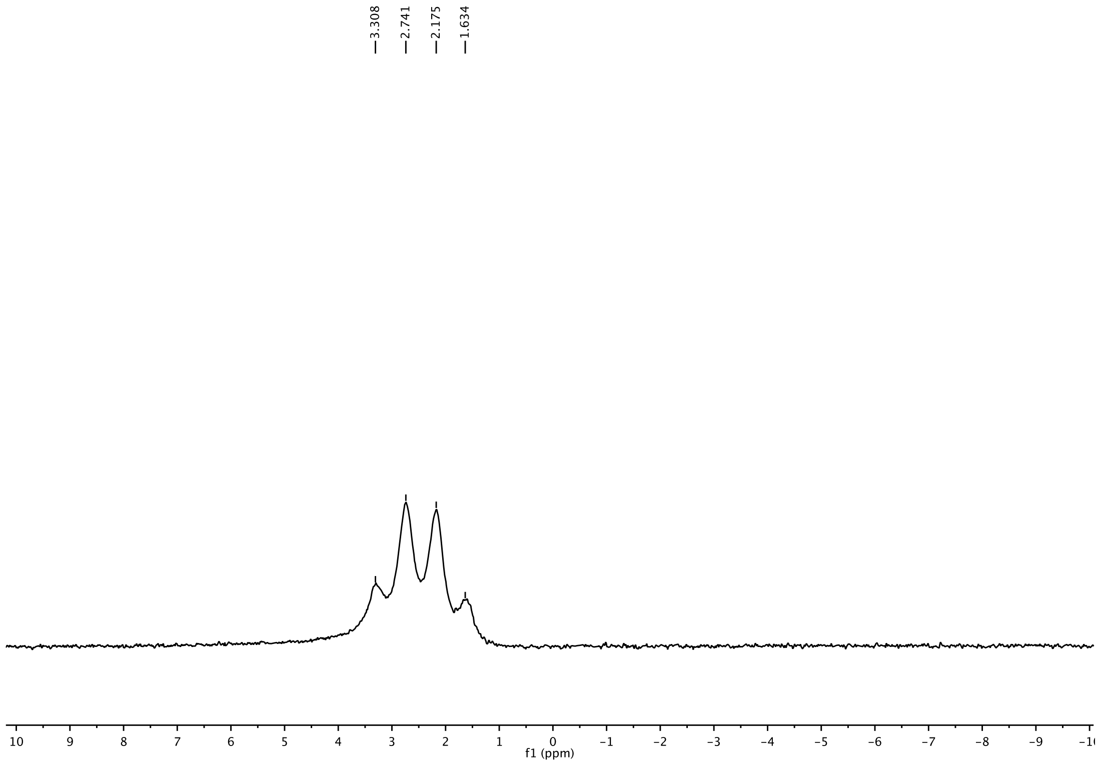
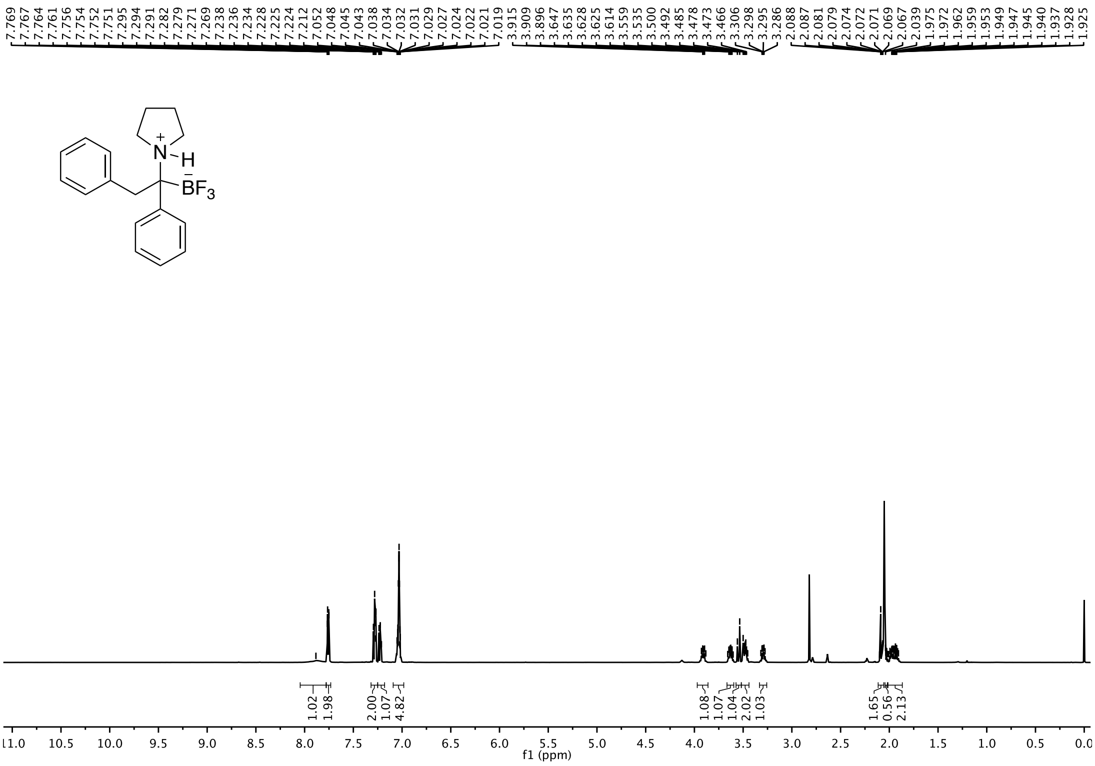
1.88
30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

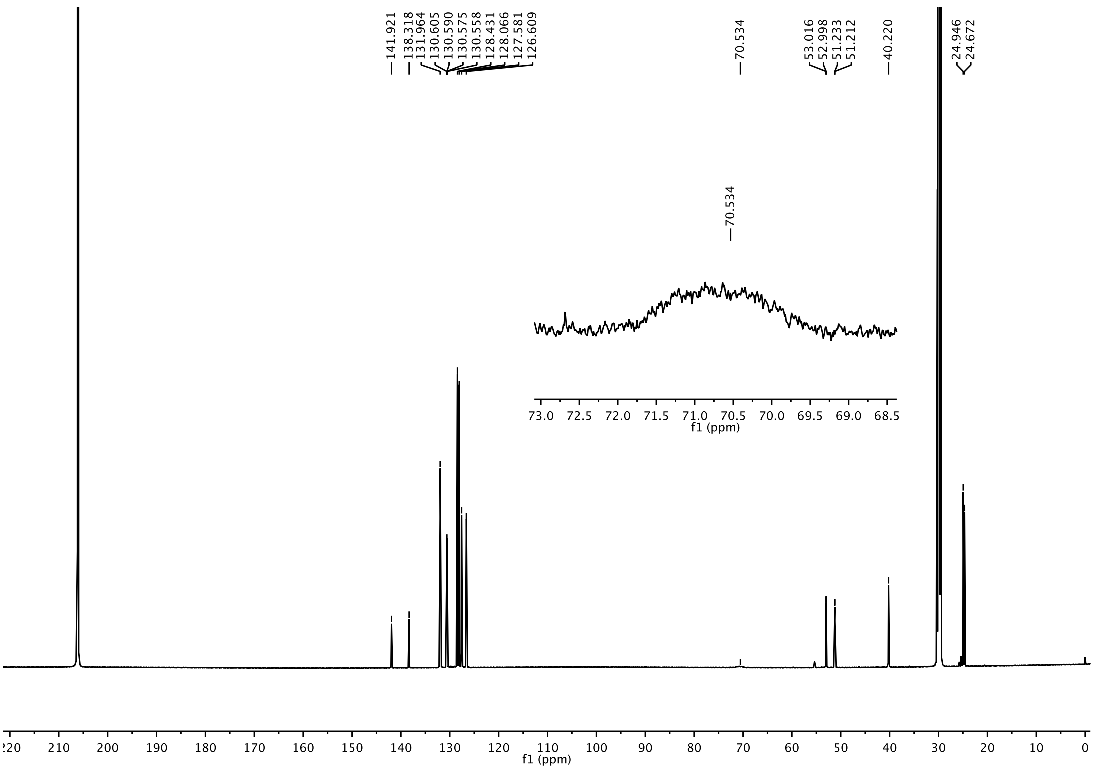

N
H
BF3
Me
f1 (ppm)

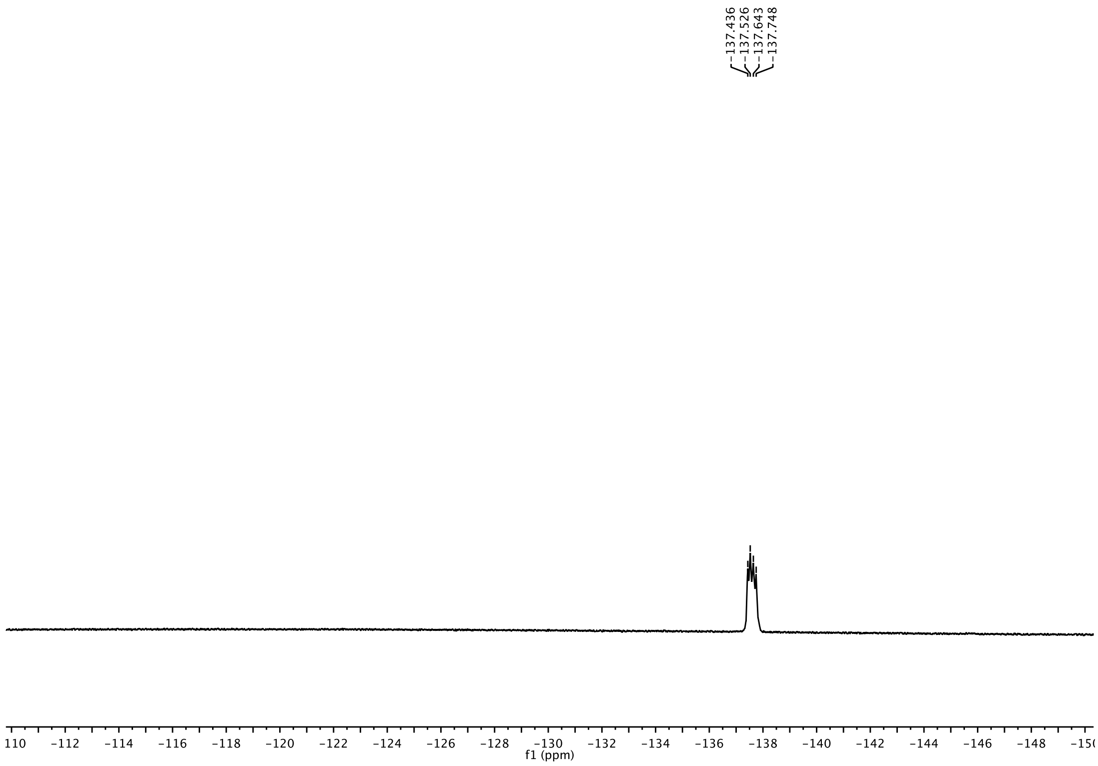

f1 (ppm)

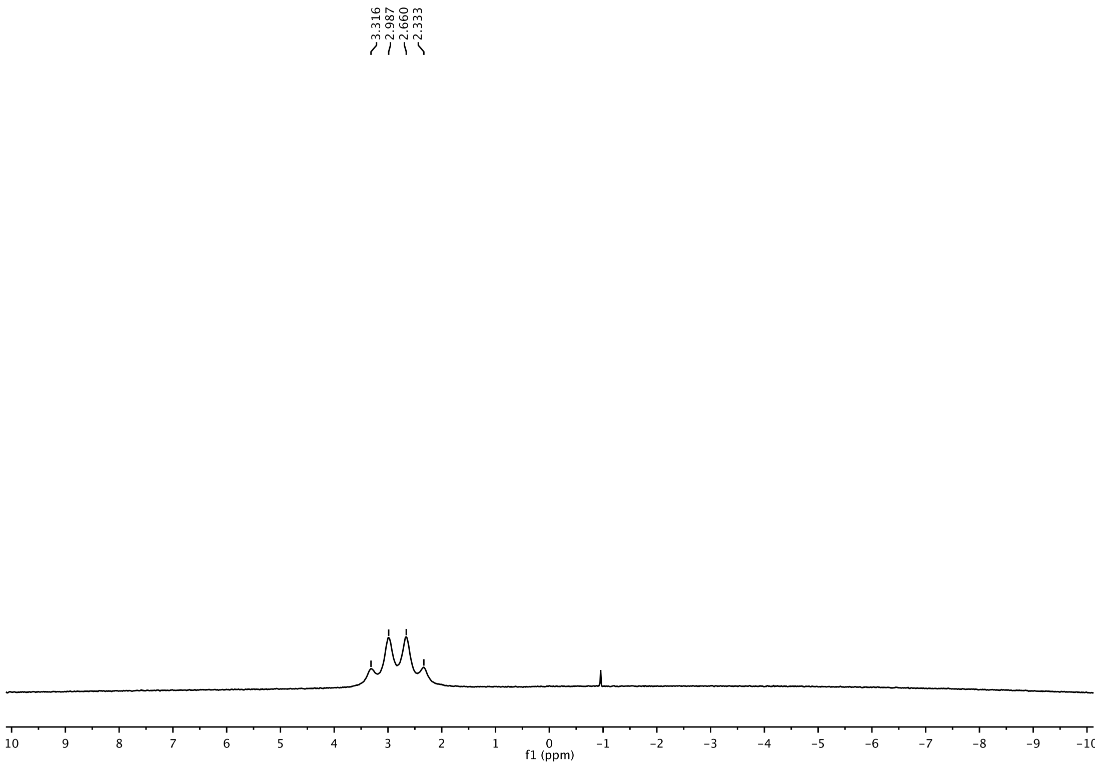

-141.819
-141.870
-142.000
-142.197
-142.372
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)

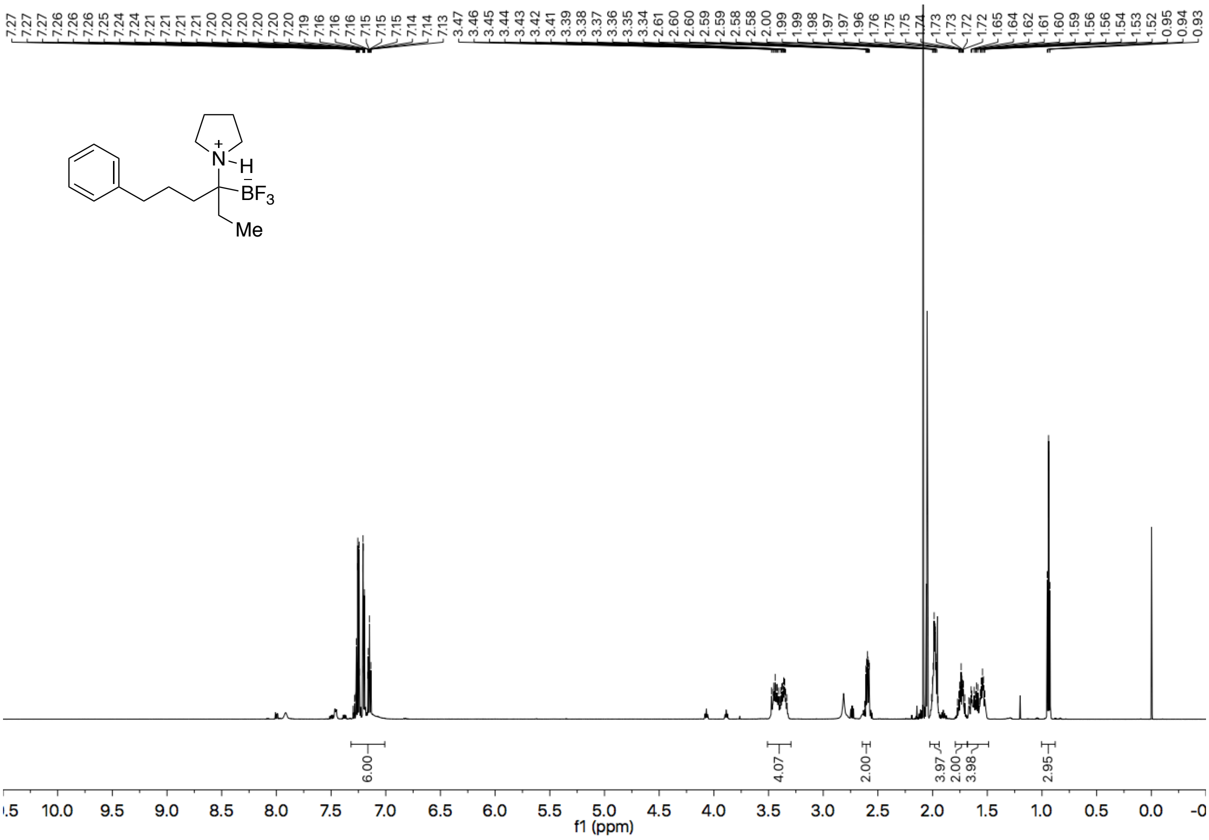

3.308
2.741
2.175
1.634
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10
f1 (ppm)

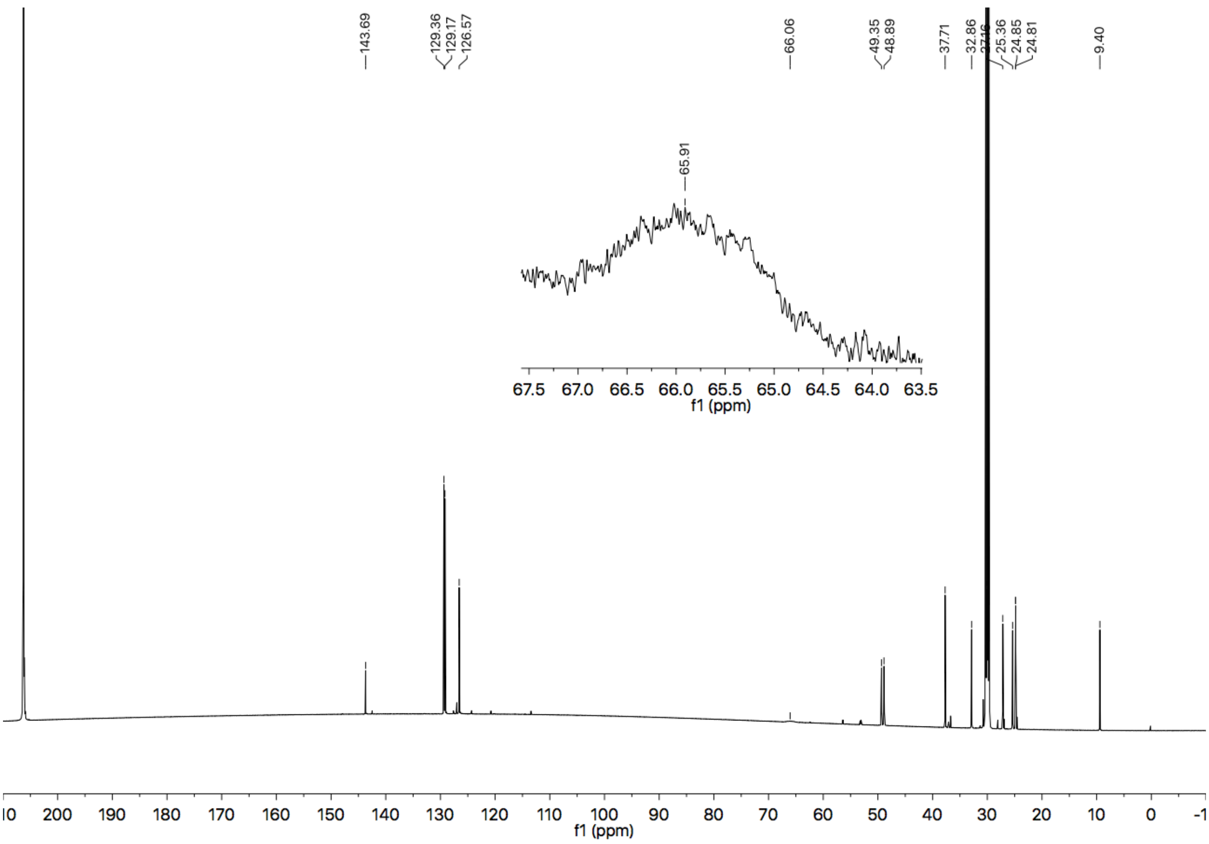

7.769
7.767
7.764
7.761
7.756
7.754
7.752
7.751
7.295
7.294
7.291
7.282
7.279
7.271
7.269
7.238
7.236
7.234
7.228
7.225
7.224
7.212
7.052
7.048
7.045
7.043
7.038
7.034
7.032
7.031
7.029
7.027
7.024
7.022
7.021
7.019
3.915
3.909
3.896
3.647
3.635
3.628
3.625
3.614
3.559
3.535
3.500
3.492
3.485
3.478
3.473
3.466
3.306
3.298
3.295
3.286
2.088
2.087
2.081
2.079
2.074
2.072
2.071
2.069
2.067
2.039
1.975
1.972
1.962
1.959
1.953
1.949
1.947
1.945
1.940
1.937
1.928
1.925
N
H
BF3
1.02
1.98
2.00
1.07
4.82
1.08
1.07
1.04
2.02
1.03
1.65
0.56
2.13
f1 (ppm)

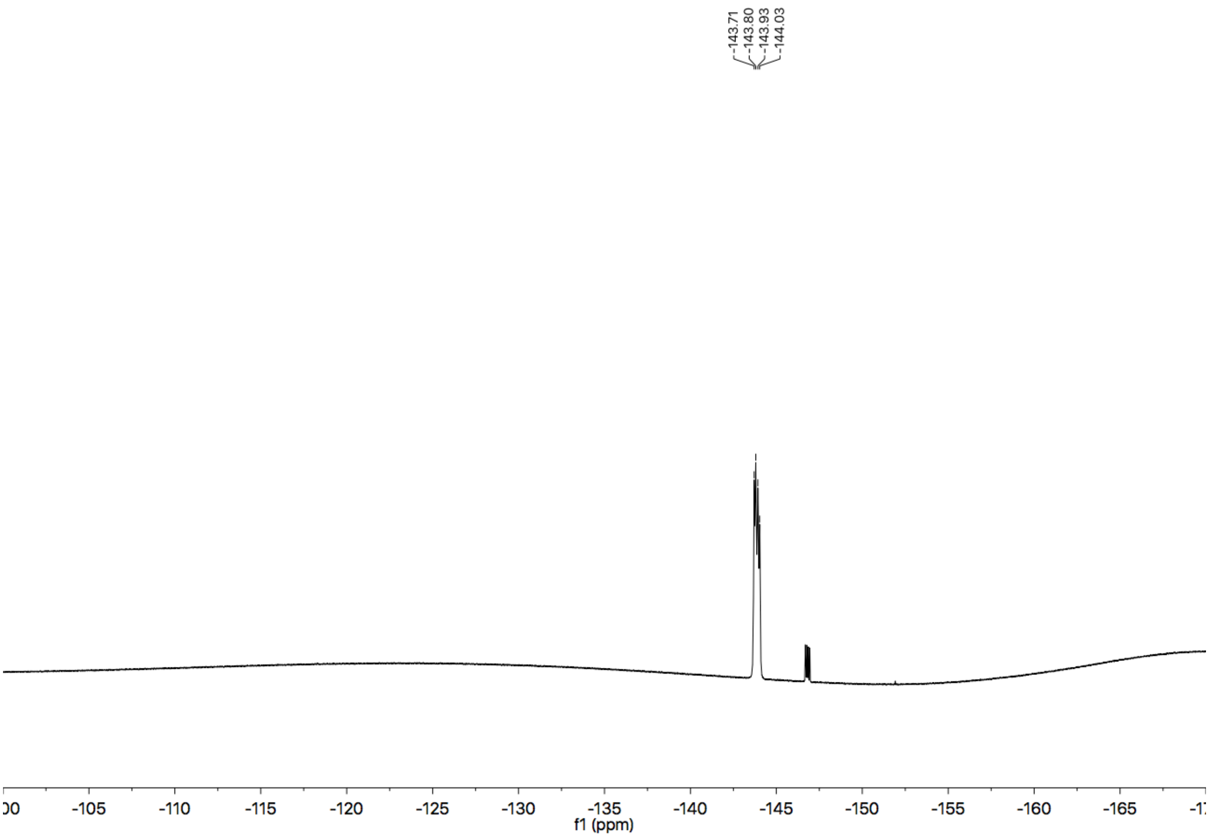

141.921
138.318
131.964
130.605
130.590
130.575
130.558
128.431
128.066
127.581
126.609
70.534
53.016
52.998
51.233
51.212
40.220
24.946
24.672
70.534
f1 (ppm)
f1 (ppm)

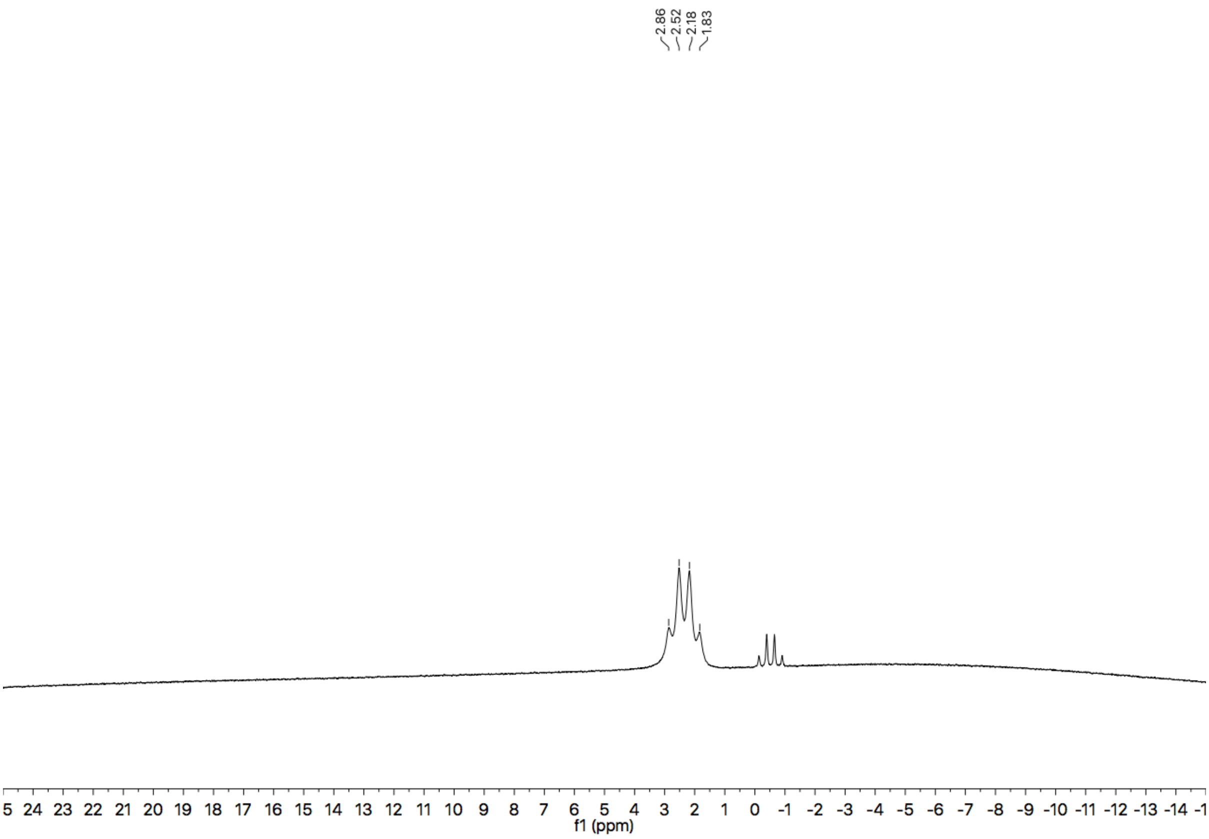

-137.436
-137.526
-137.643
-137.748
110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
f1 (ppm)

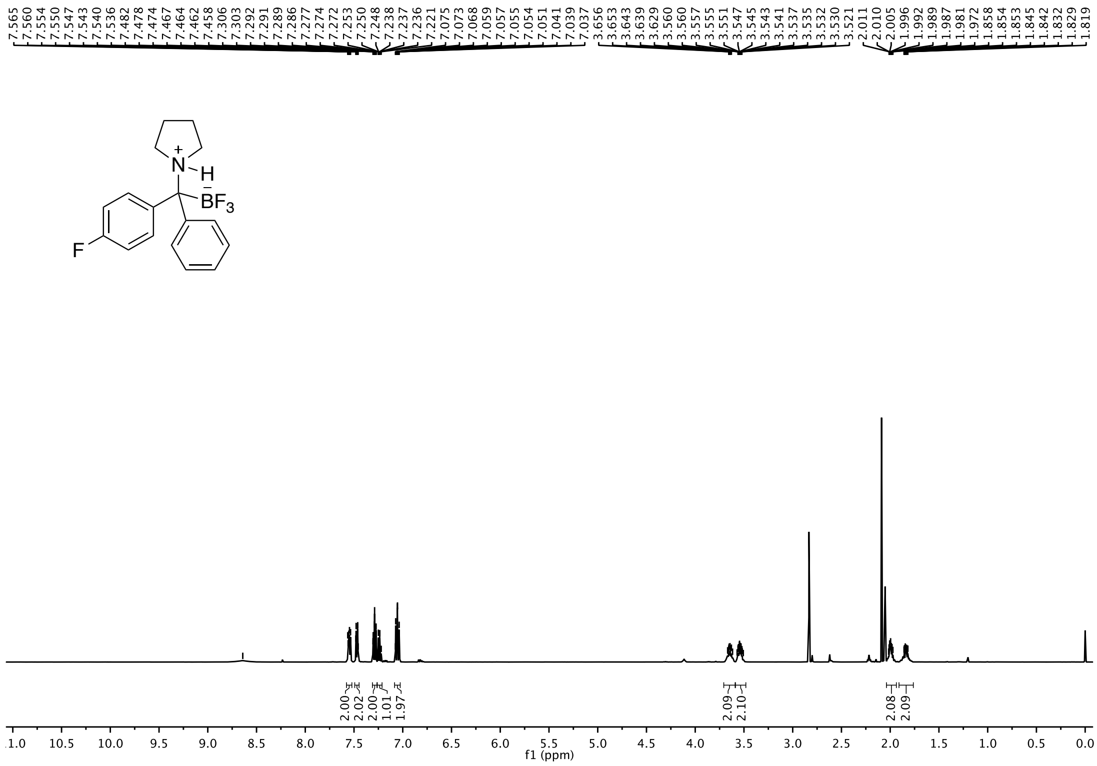

3.316
2.987
2.660
2.333
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
f1 (ppm)

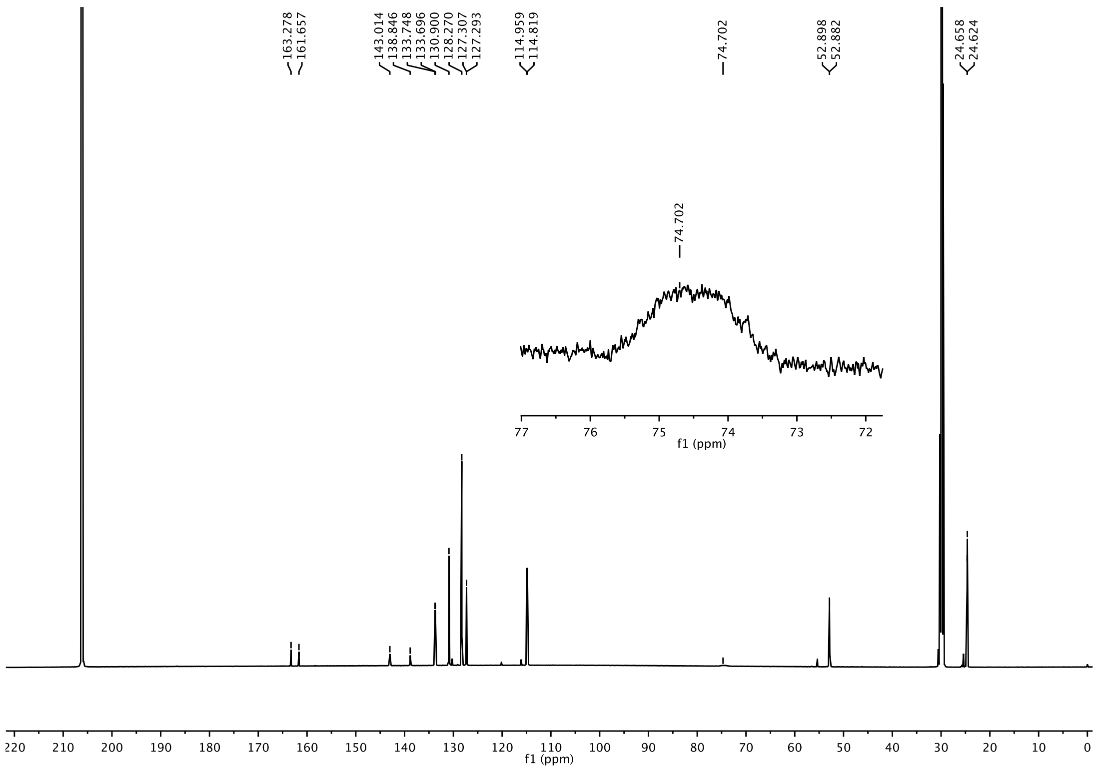

H
BF3
Me
f1 (ppm)

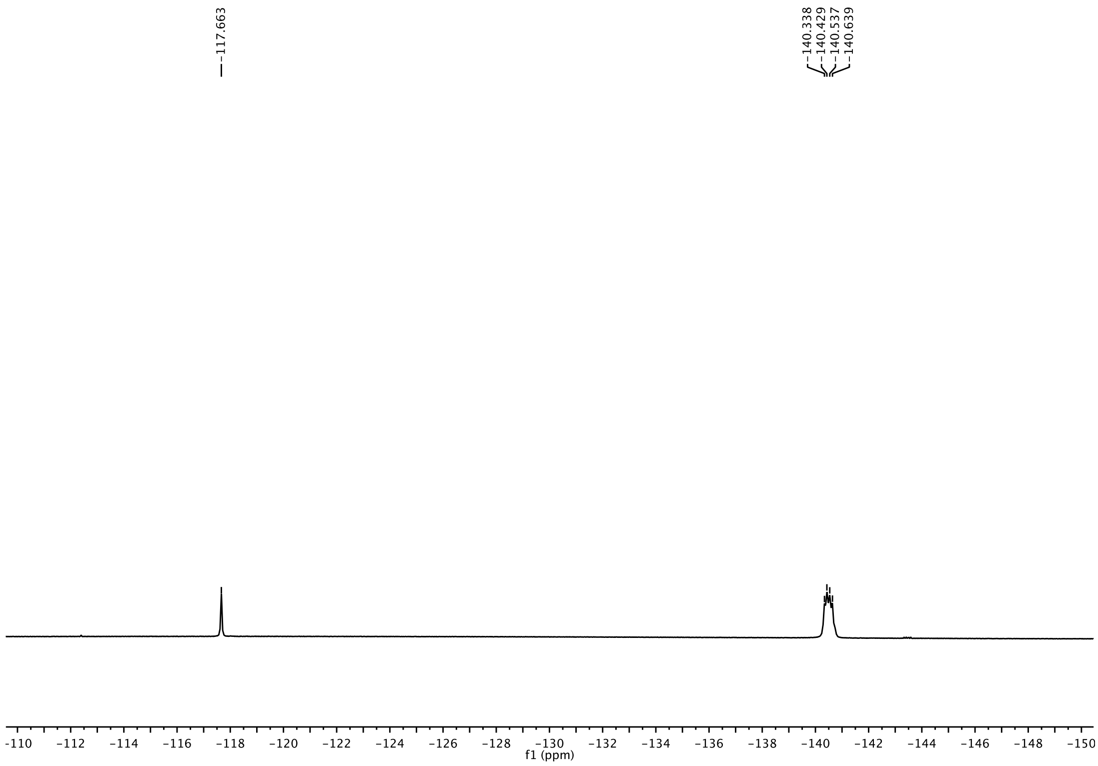

143.69
129.36
129.17
126.57
66.06
49.35
48.89
37.71
32.86
25.36
24.85
24.81
9.40
65.91
f1 (ppm)

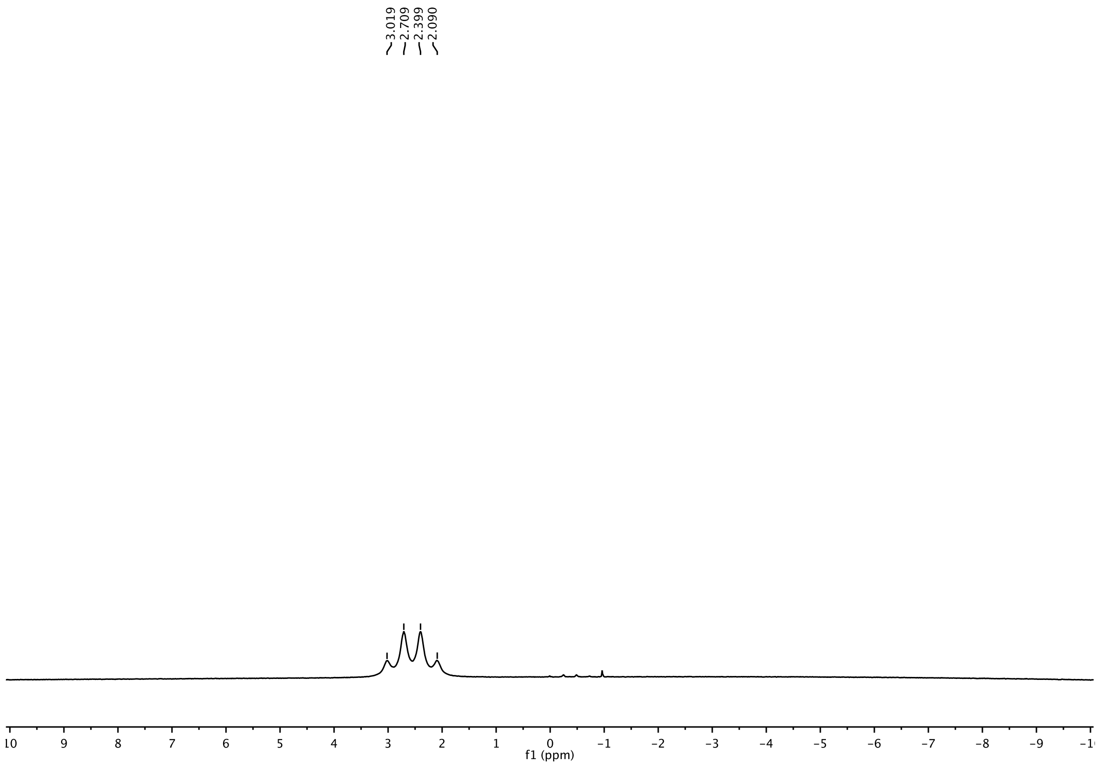

-143.71
-143.80
-143.93
-144.03
f1 (ppm)

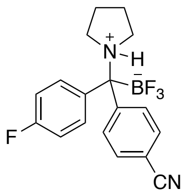

2.86
2.52
2.18
1.83
f1 (ppm)

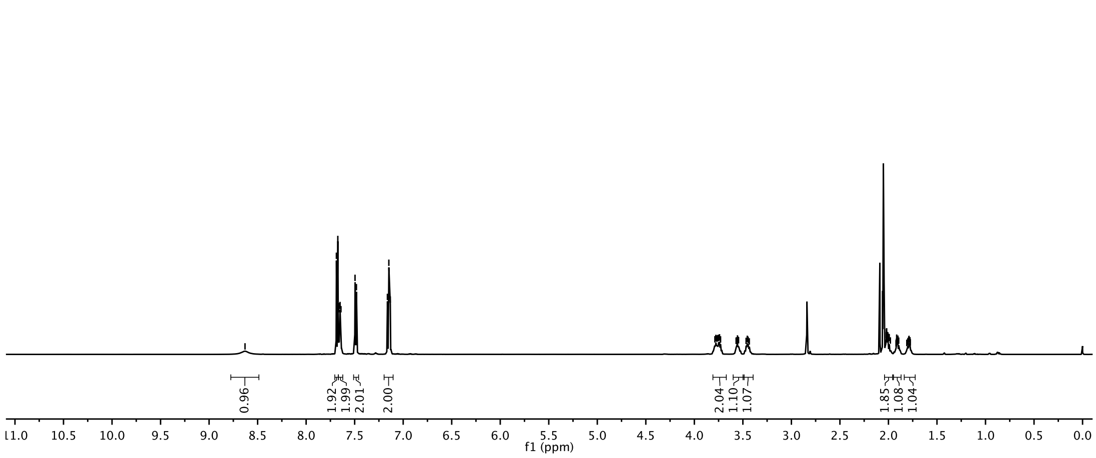

f1 (ppm)

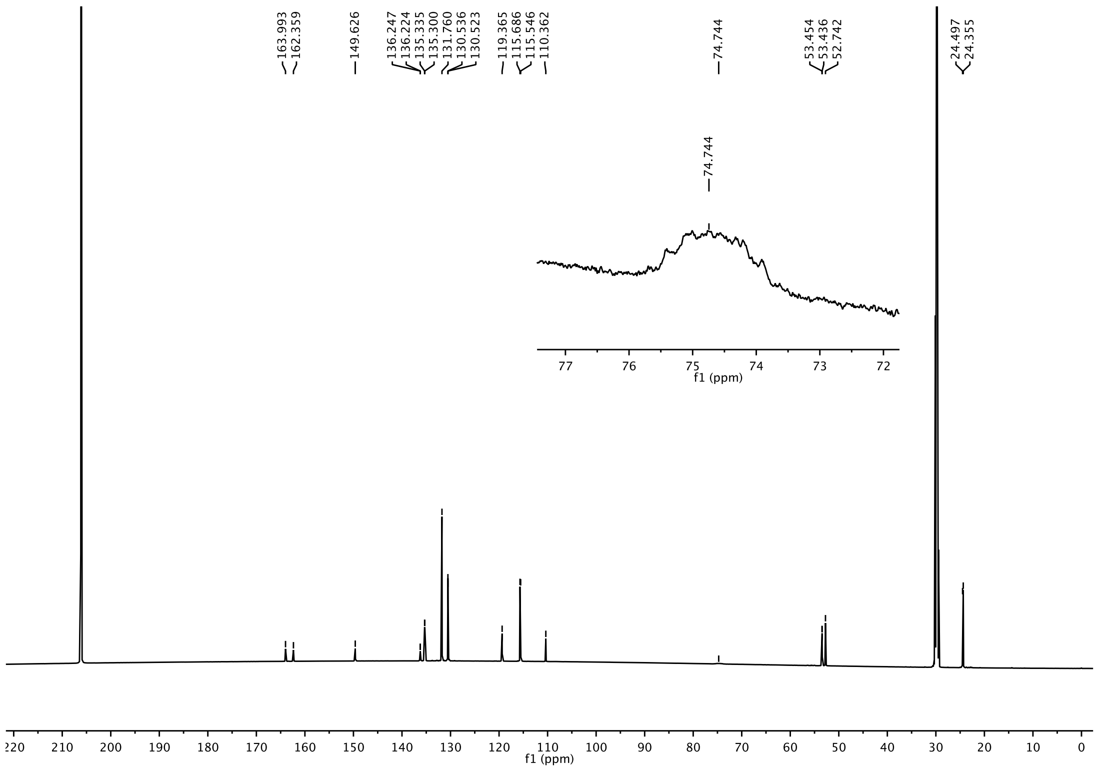

163.278
161.657
143.014
138.846
133.748
133.696
130.900
128.270
127.307
127.293
114.959
114.819
74.702
52.898
52.882
24.658
24.624
f1 (ppm)

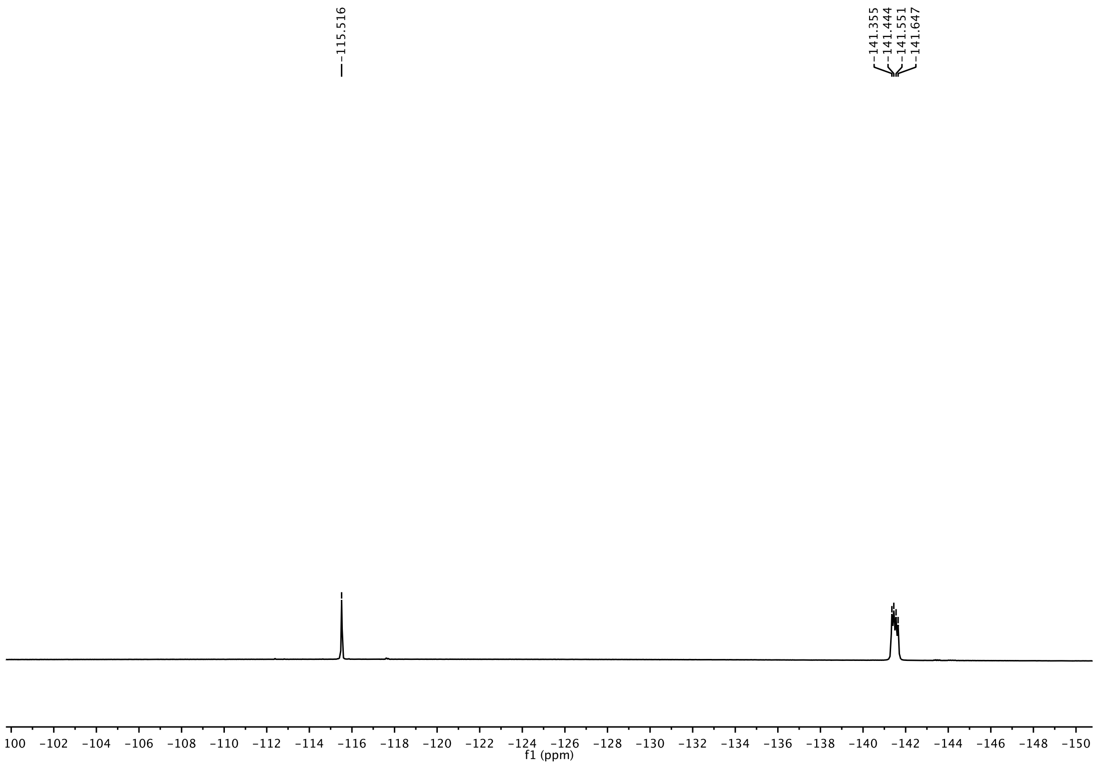

-117.663
-140.338
-140.429
-140.537
-140.639
-110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)

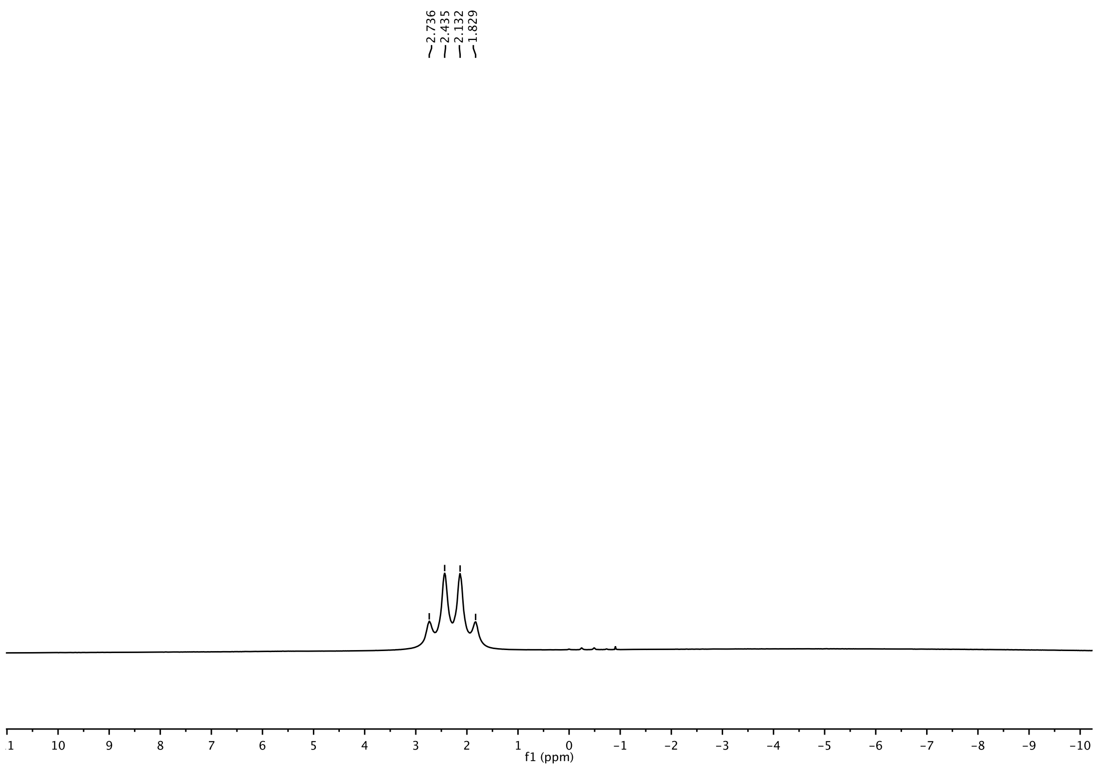

3.019
2.709
2.399
2.090
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9
f1 (ppm)

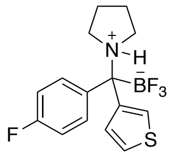

N
H
BF3
F
CN

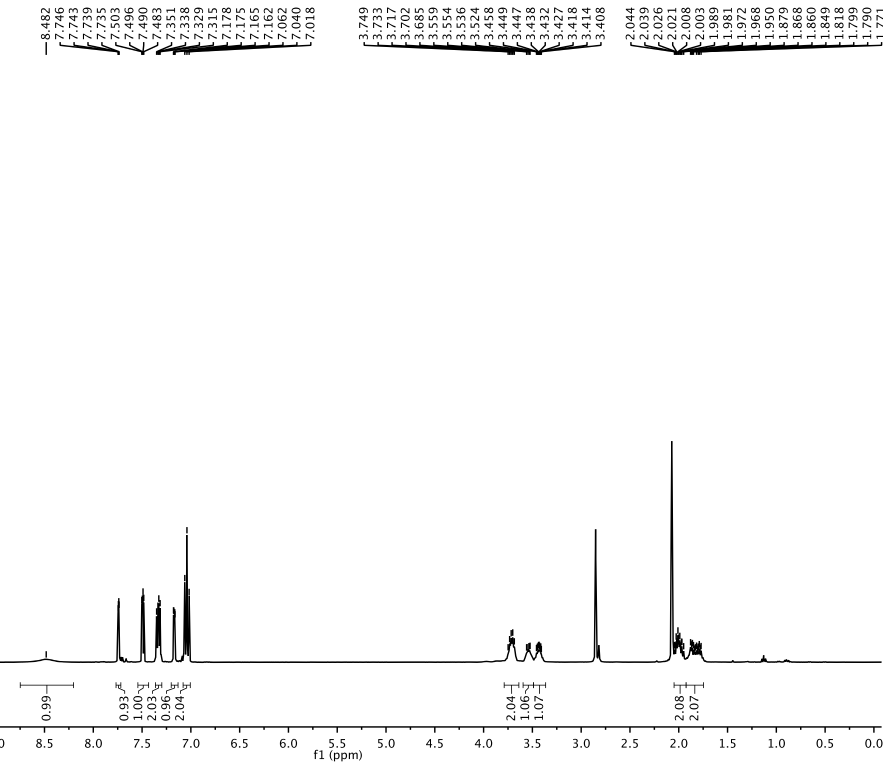

8.629
7.688
7.677
7.673
7.665
7.656
7.650
7.641
7.496
7.482
7.162
7.148
7.133
3.788
3.778
3.769
3.760
3.750
3.740
3.730
3.569
3.567
3.559
3.555
3.548
3.544
3.466
3.454
3.446
3.434
2.024
2.021
2.018
2.014
2.013
2.009
2.006
2.004
2.002
1.994
1.992
1.980
1.915
1.907
1.902
1.894
1.790
1.788
0.96
1.92
1.99
2.01
2.00
2.04
1.10
1.07
1.85
1.08
1.04
f1 (ppm)

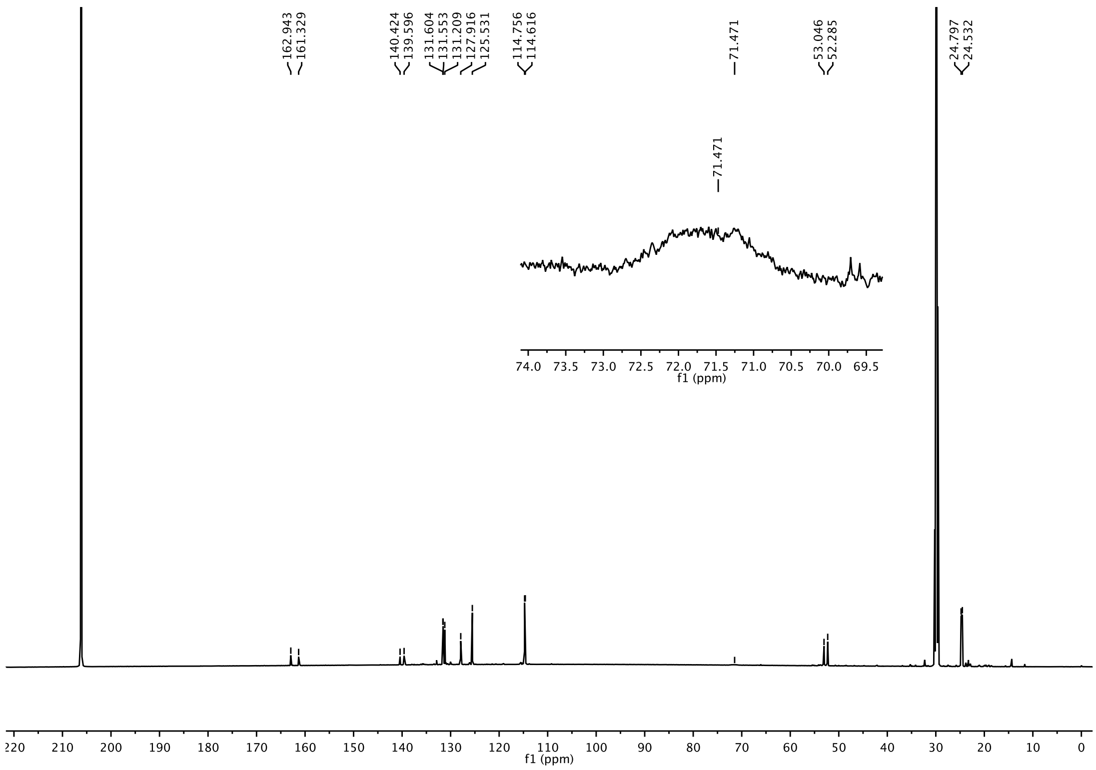

163.993
162.359
149.626
136.247
136.224
135.335
135.300
131.760
130.536
130.523
119.365
115.686
115.546
110.362
74.744
53.454
53.436
52.742
24.497
24.355
74.744
f1 (ppm)
f1 (ppm)

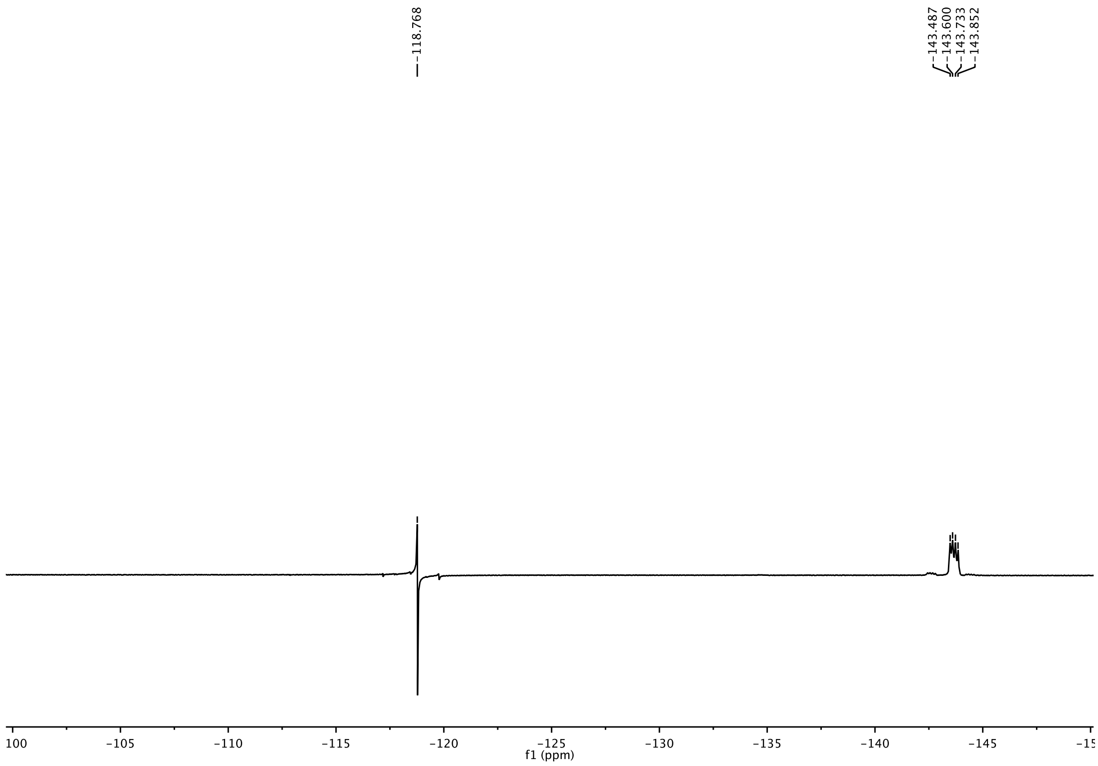

-115.516
-141.355
-141.444
-141.551
-141.647
f1 (ppm)

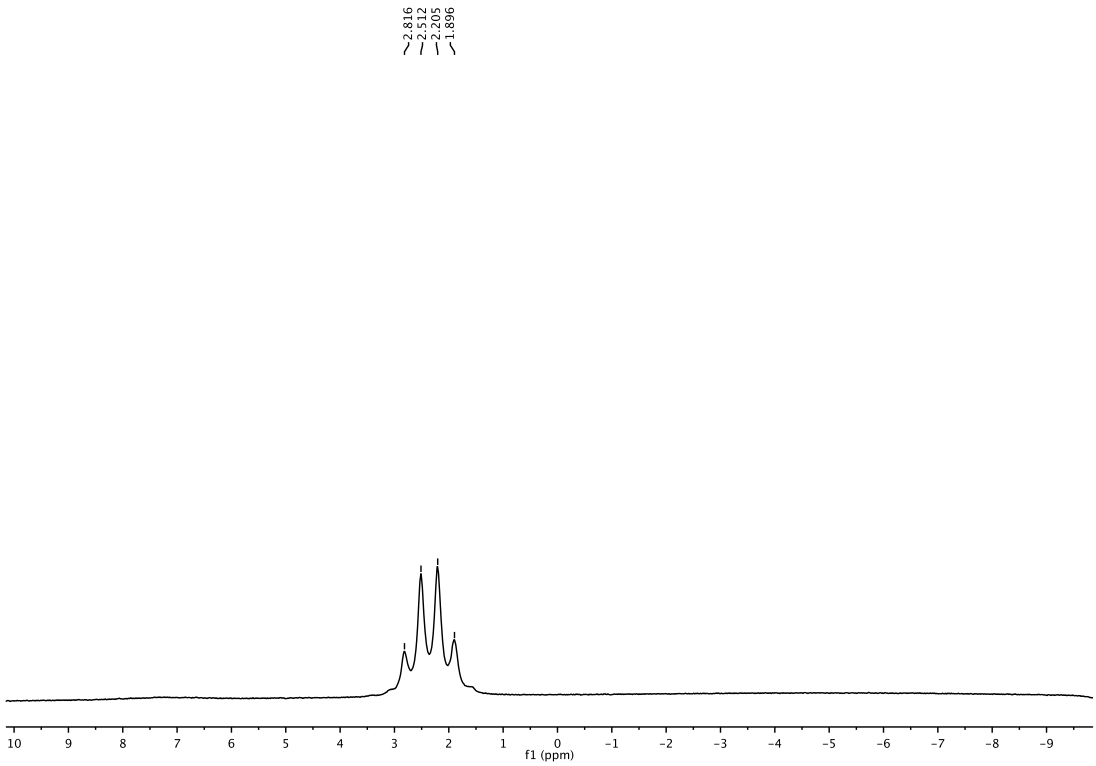

2.736
2.435
2.132
1.829
f1 (ppm)

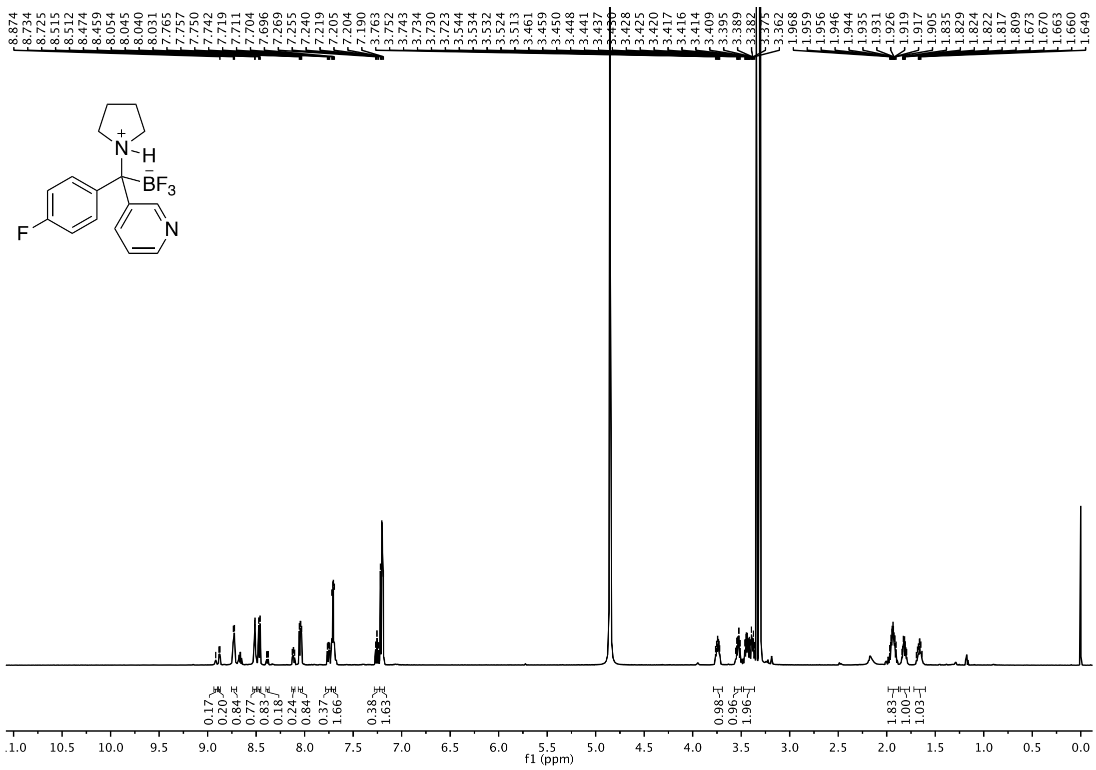

N
H
BF3
F
S

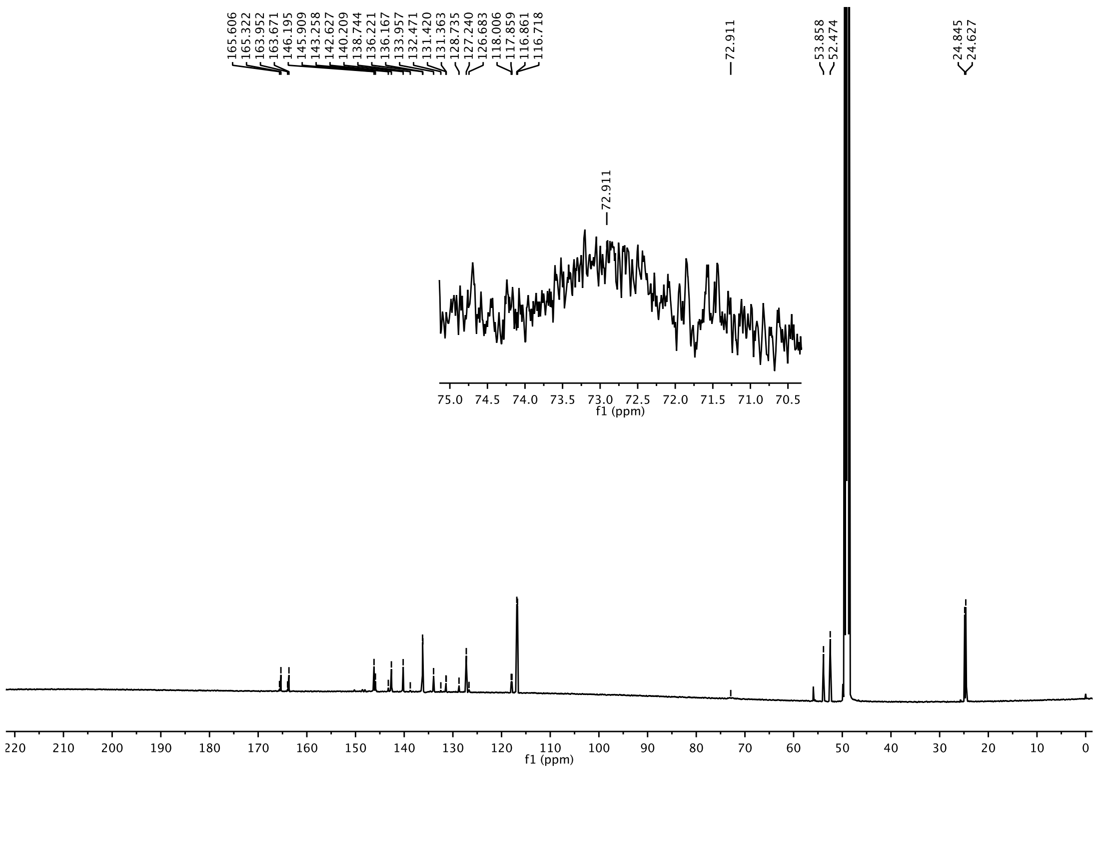

8.482
7.746
7.743
7.739
7.735
7.503
7.496
7.490
7.483
7.351
7.338
7.329
7.315
7.178
7.175
7.165
7.162
7.062
7.040
7.018
3.749
3.733
3.717
3.702
3.685
3.559
3.554
3.536
3.524
3.458
3.449
3.447
3.438
3.432
3.427
3.418
3.414
3.408
2.044
2.039
2.026
2.021
2.008
2.003
1.989
1.981
1.972
1.968
1.950
1.879
1.868
1.860
1.849
1.818
1.799
1.790
1.771
0.99
0.93
1.00
2.03
0.96
2.04
2.04
1.06
1.07
2.08
2.07
f1 (ppm)

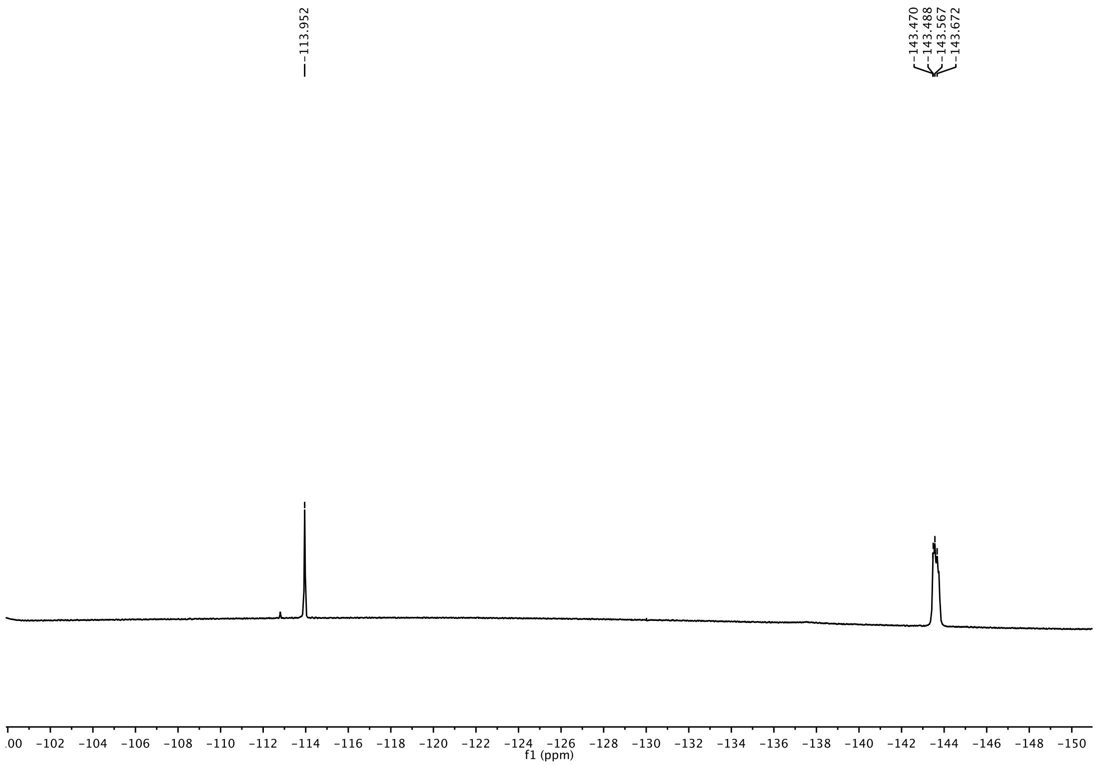

162.943
161.329
140.424
139.596
131.604
131.553
131.209
127.916
125.531
114.756
114.616
71.471
53.046
52.285
24.797
24.532
71.471
f1 (ppm)
f1 (ppm)

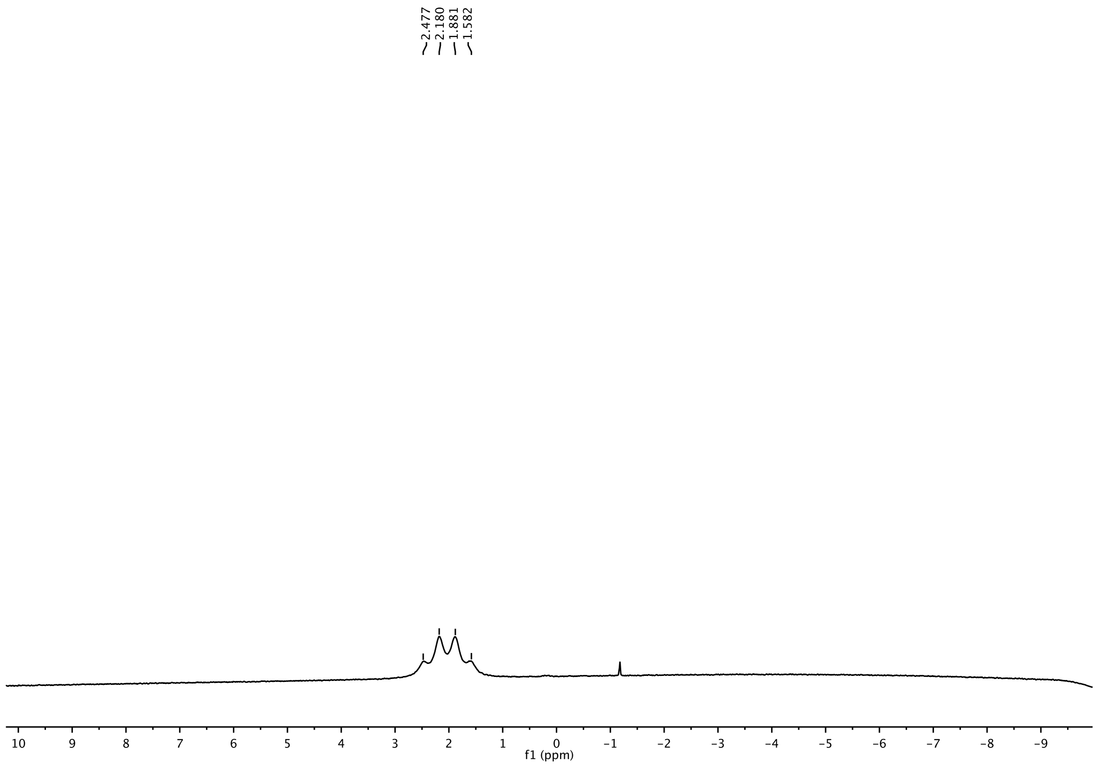

-118.768
-143.487
-143.600
-143.733
-143.852
100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)


2.816
2.512
2.205
1.896
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
f1 (ppm)

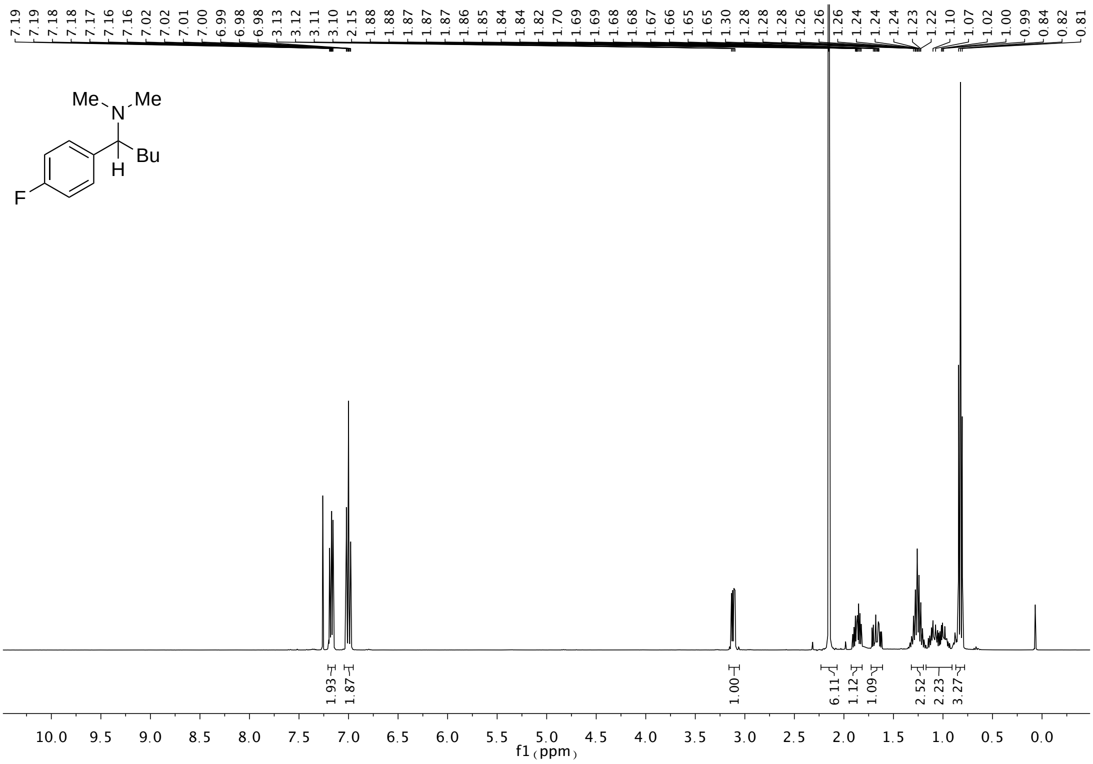

f1 (ppm)

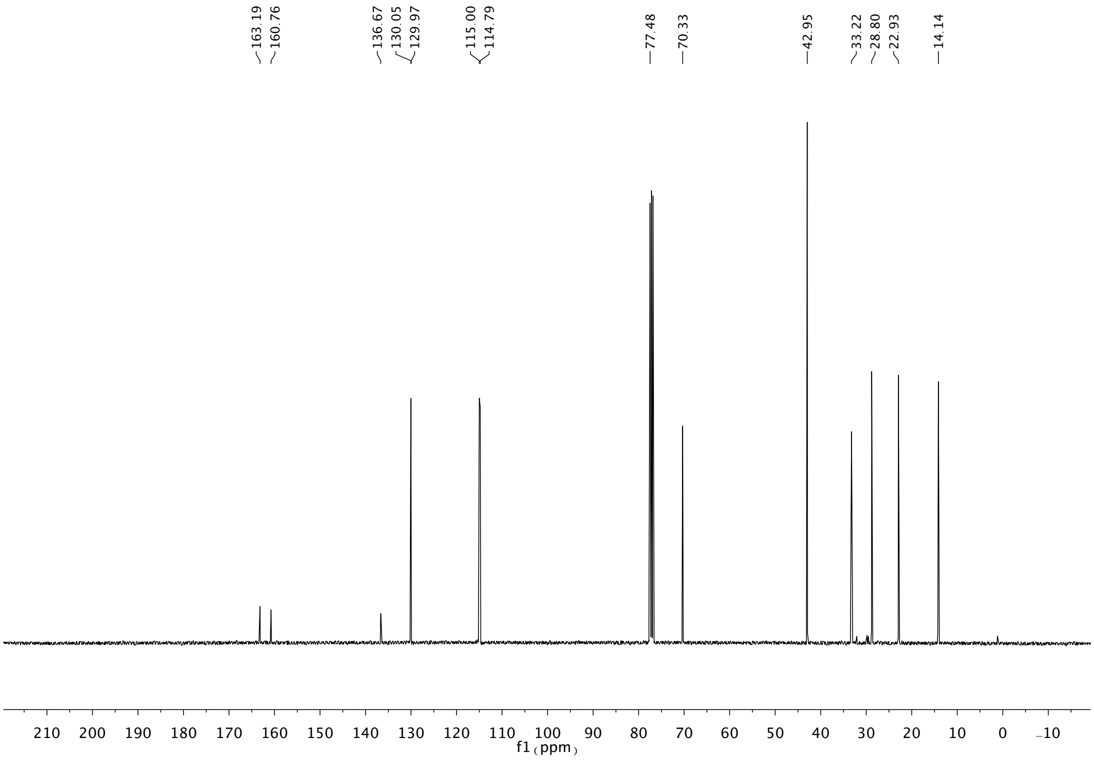

f1 (ppm)

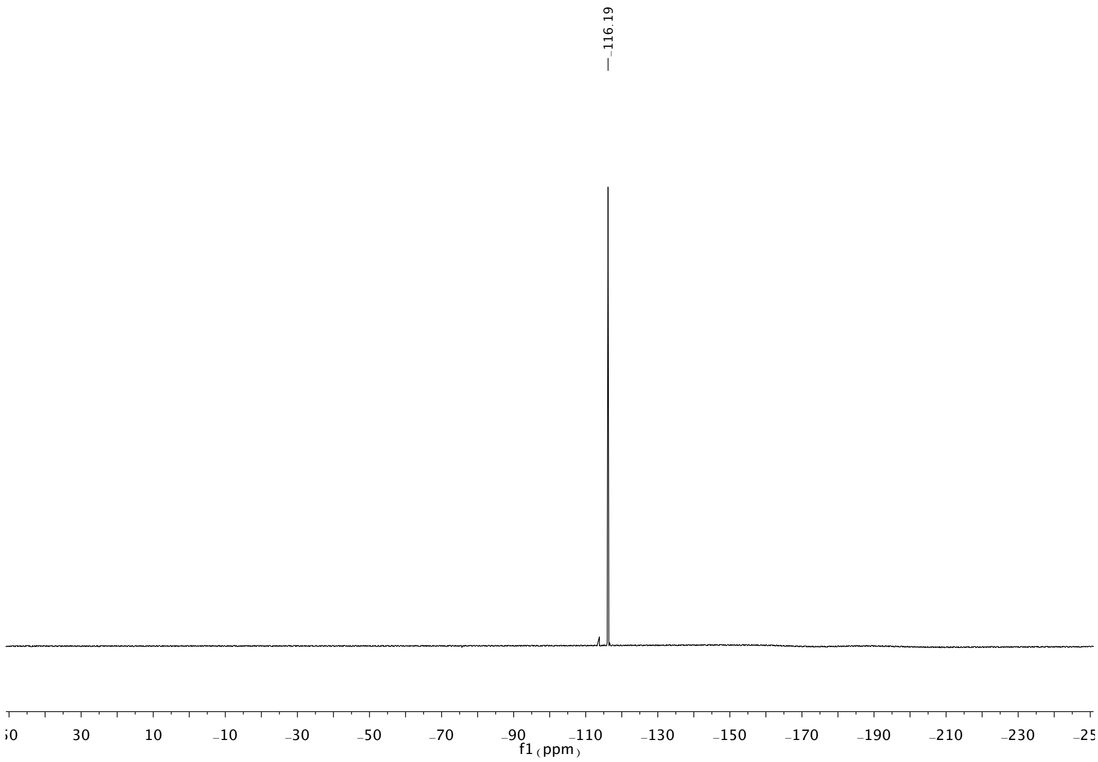

-113.952
-143.470
-143.488
-143.567
-143.672
.00 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)

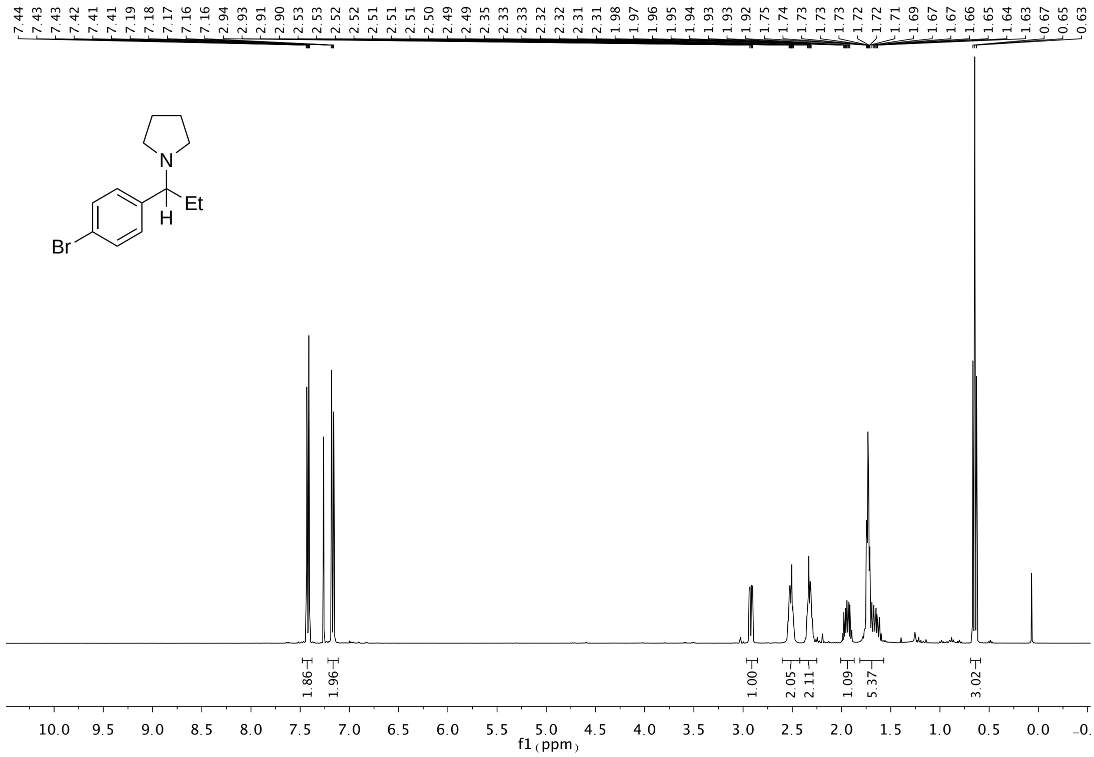

2.477
2.180
1.881
1.582
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9
f1 (ppm)

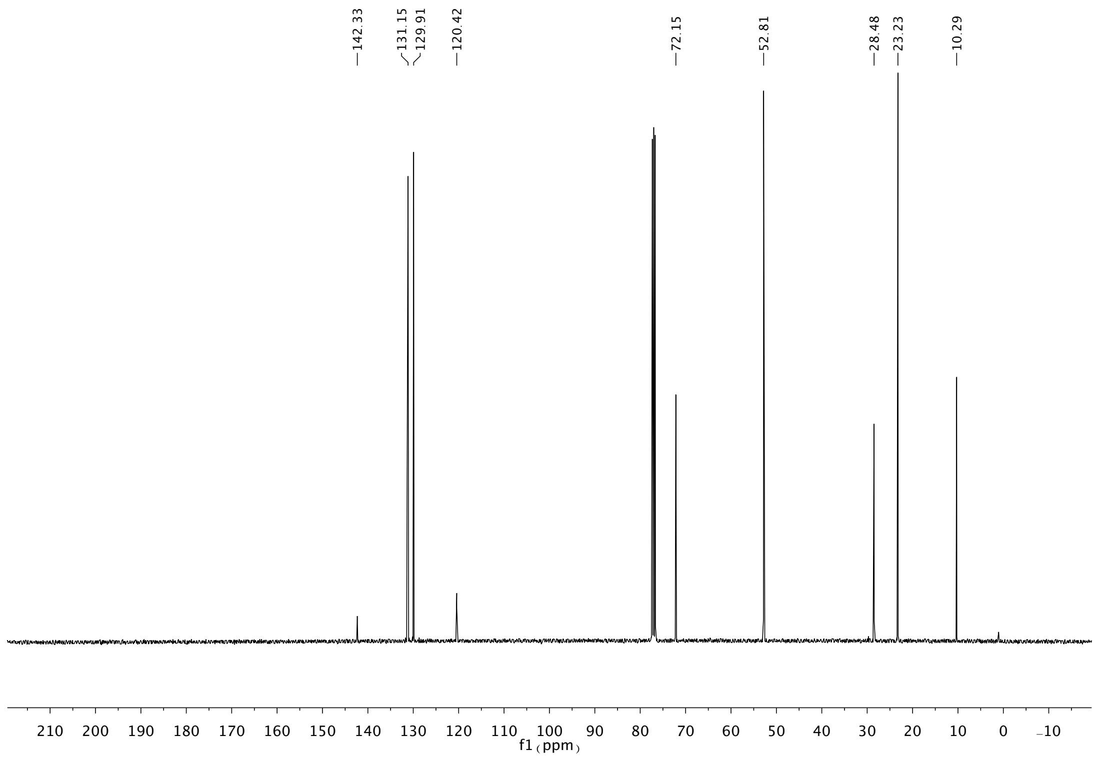
7.3 Protodeborylation of α-aminotrifluoroborates

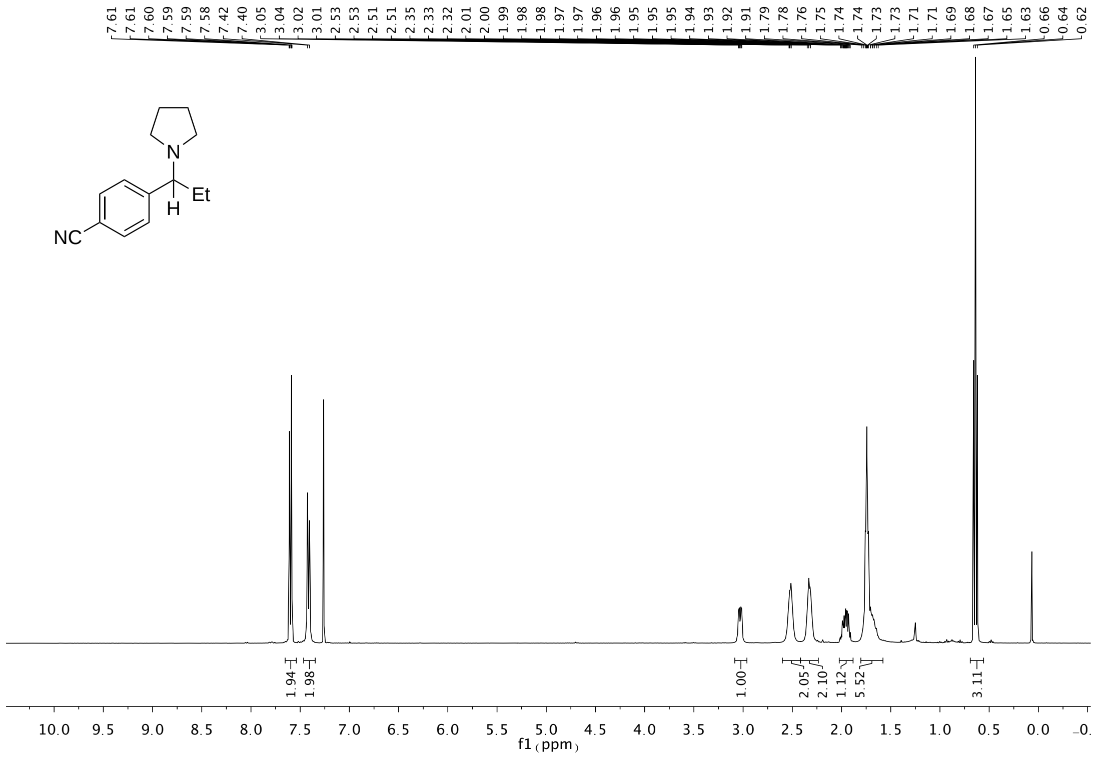


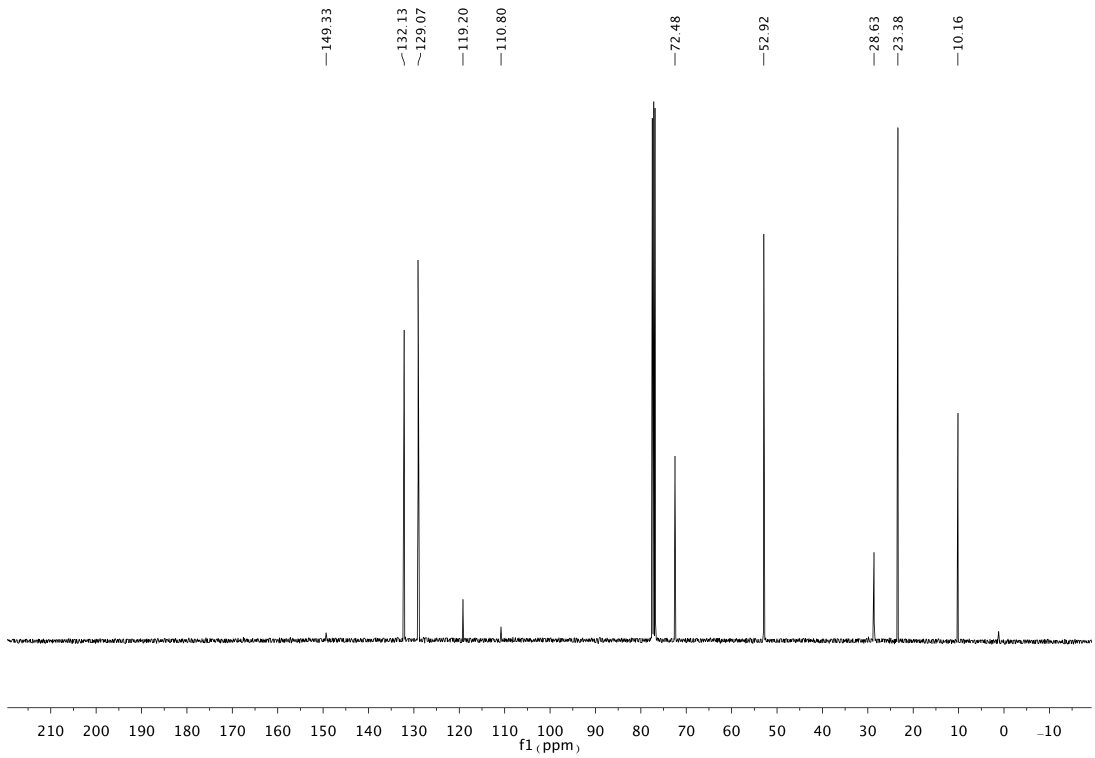


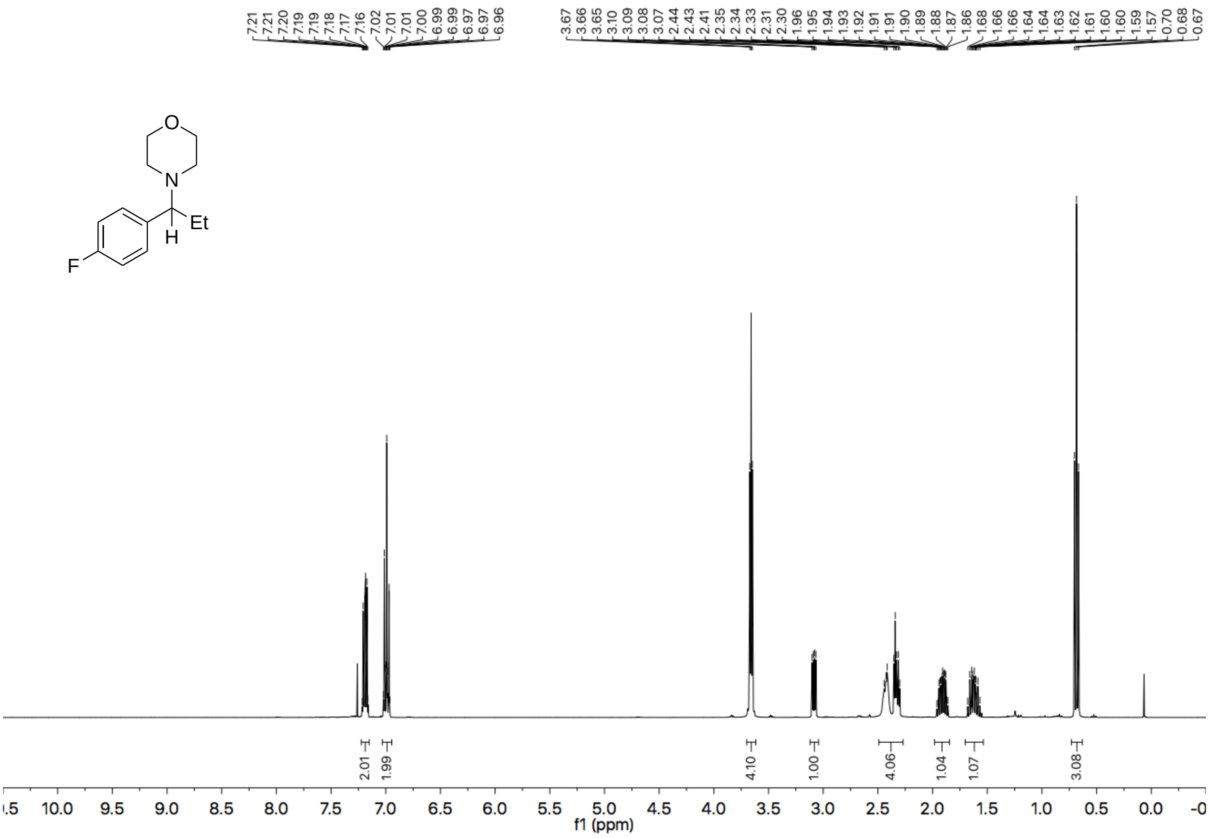

—116.19
f1 (ppm)

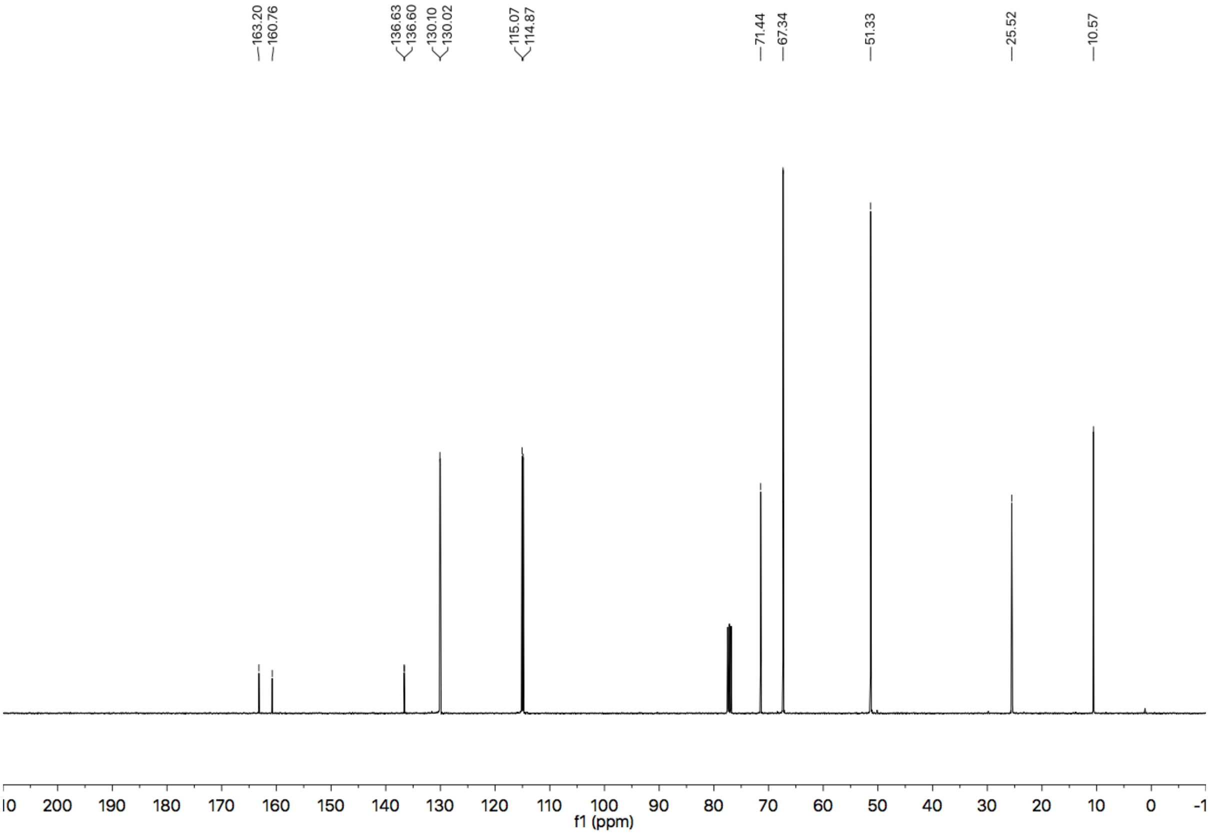


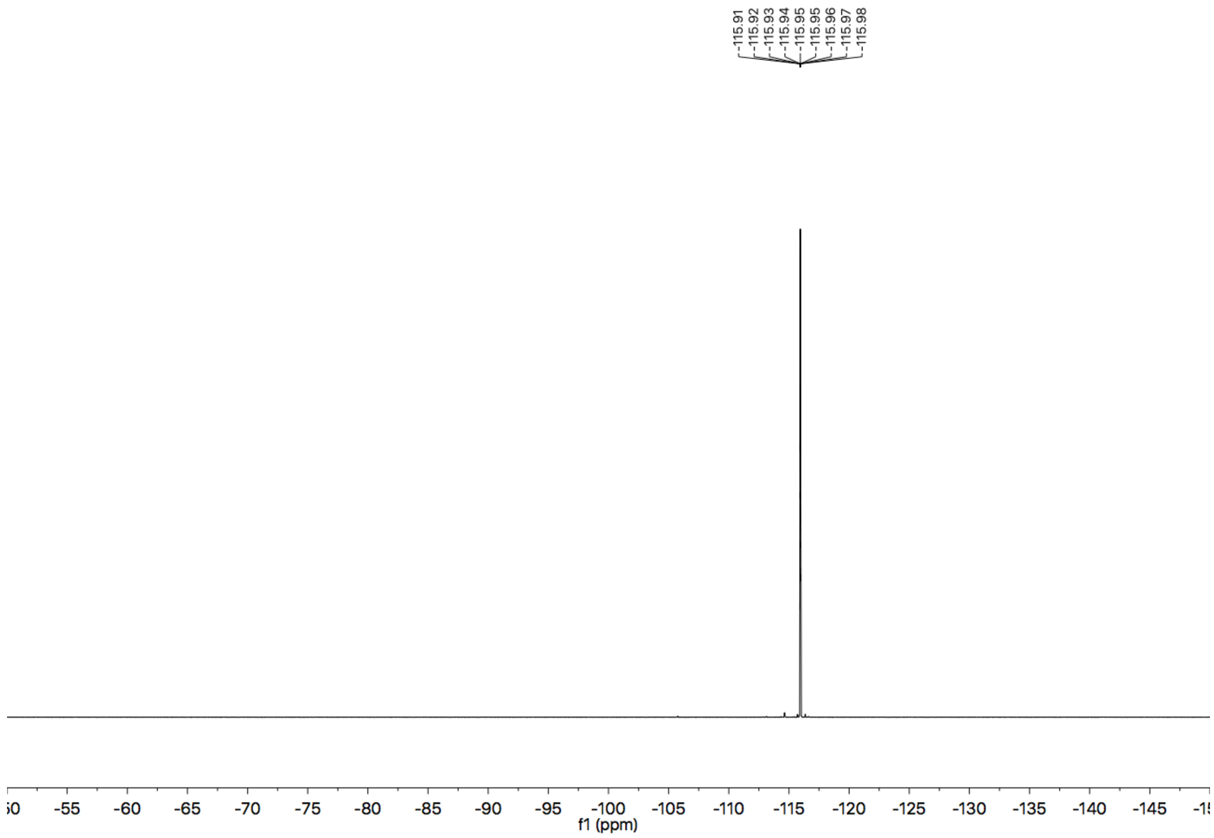


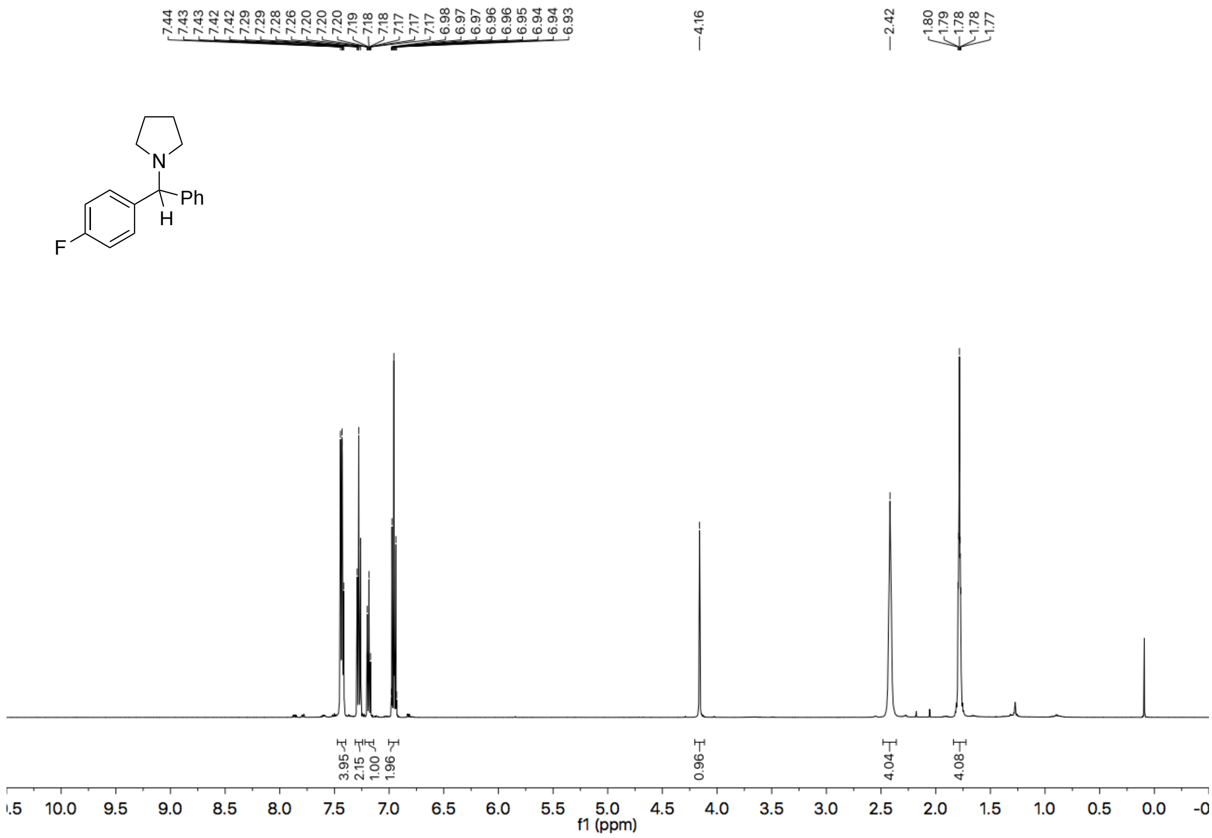


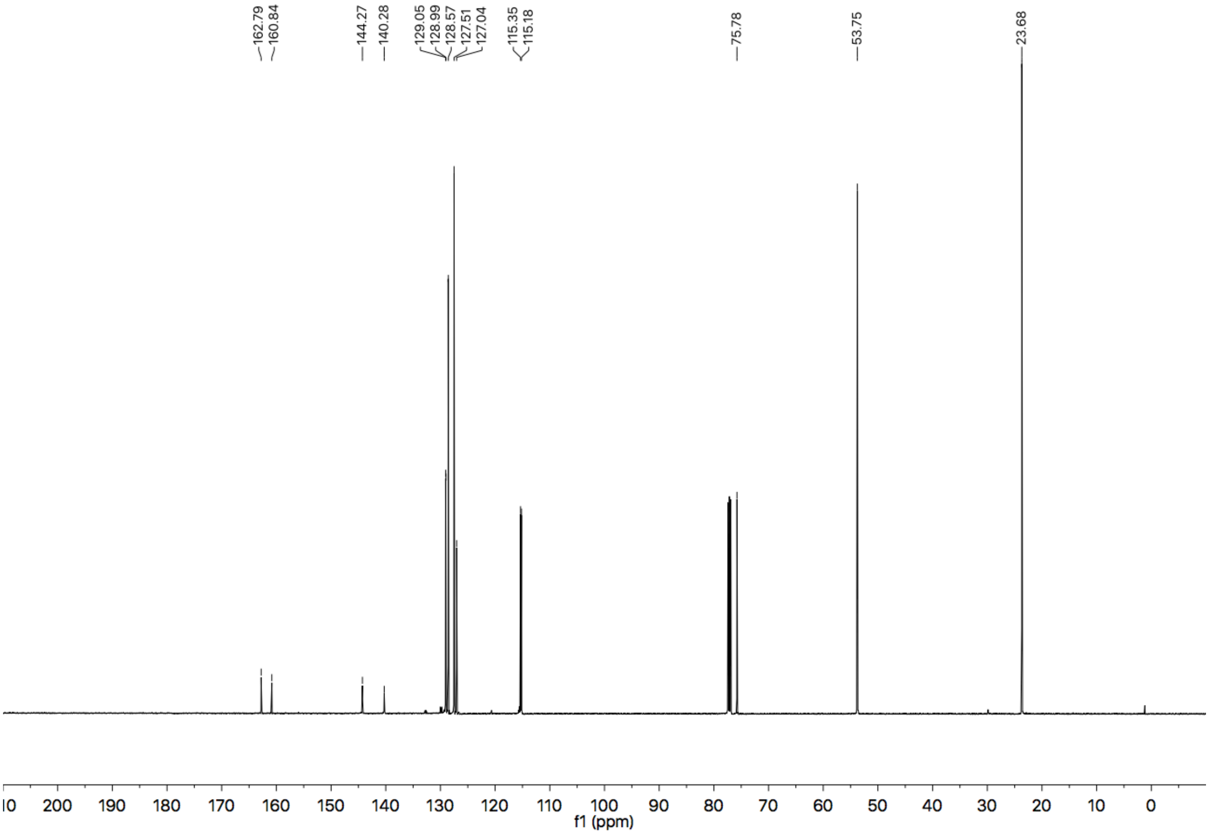


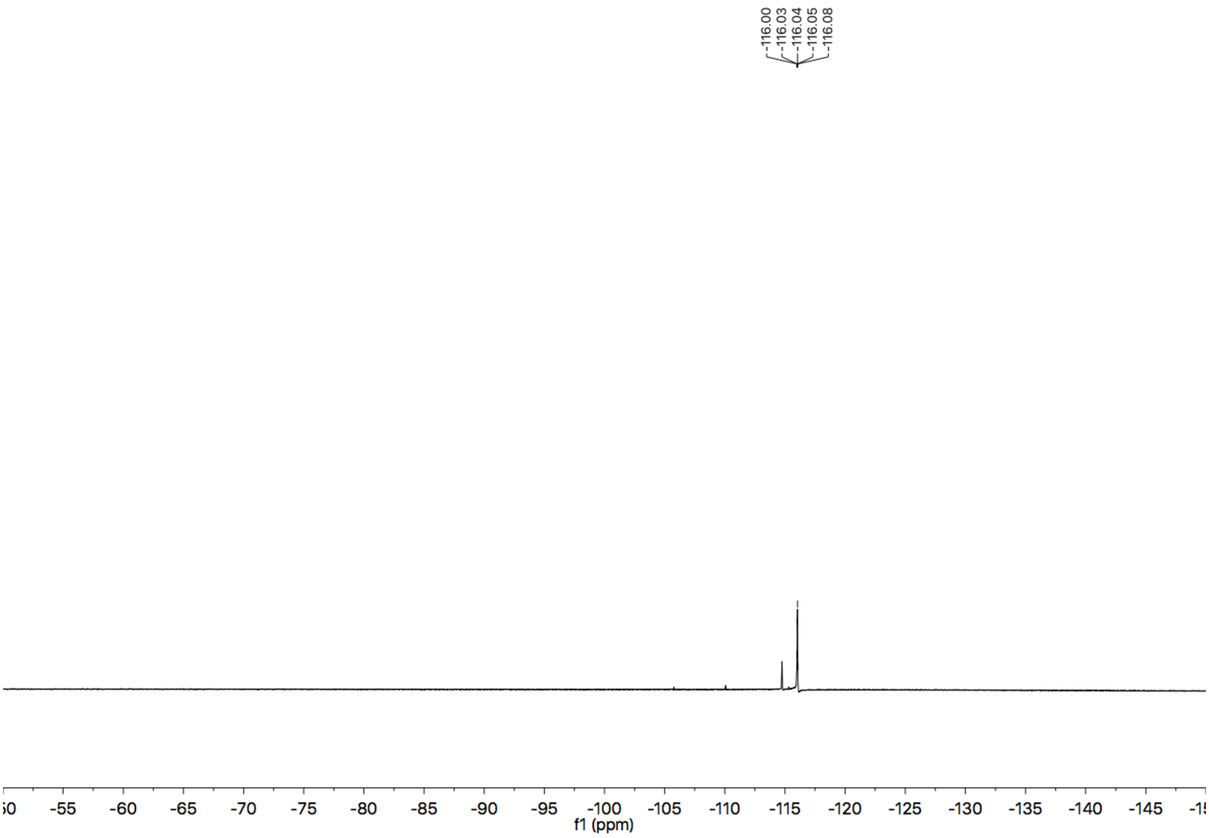




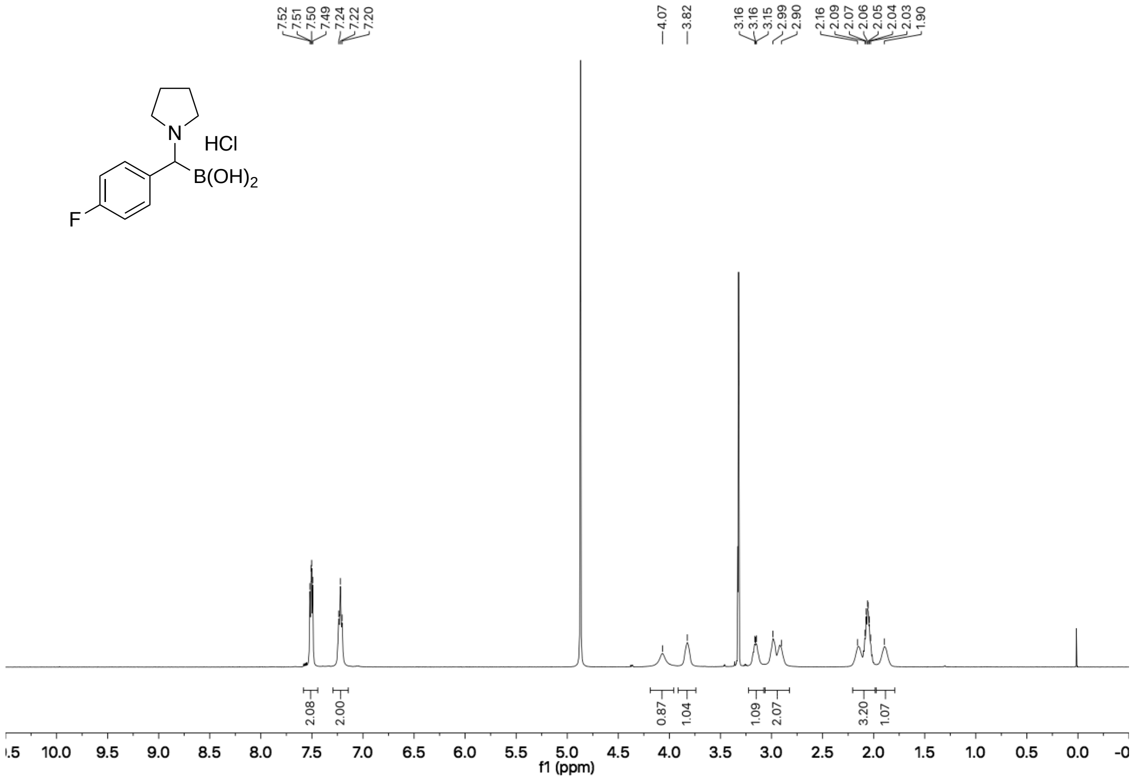

-115.91
-115.92
-115.93
-115.94
-115.95
-115.95
-115.96
-115.97
-115.98
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

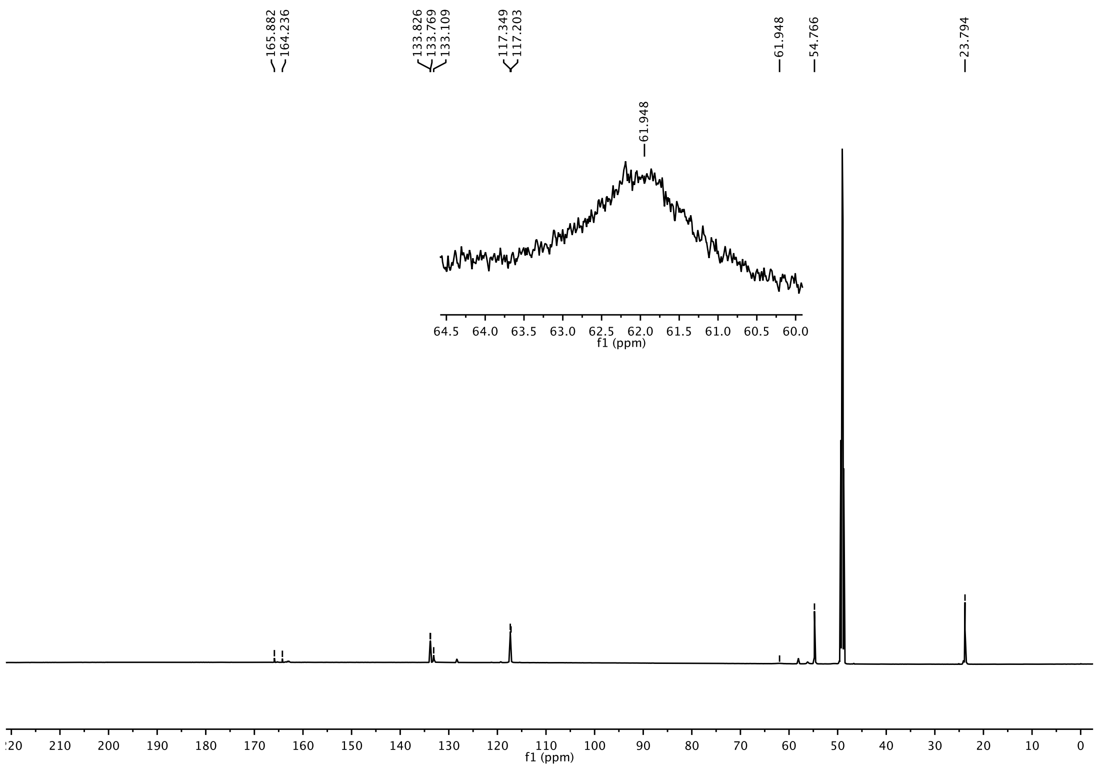

7.44 7.43 7.43 7.42 7.42 7.29 7.29 7.28 7.26 7.20 7.20 7.20 7.19 7.18 7.18 7.17 7.17 7.17 6.98 6.97 6.97 6.96 6.96 6.95 6.94 6.94 6.93
4.16
2.42
1.80 1.79 1.78 1.78 1.77
N
Ph
H
F
3.95 2.15 1.00 1.96
0.96
4.04
4.08
f1 (ppm)

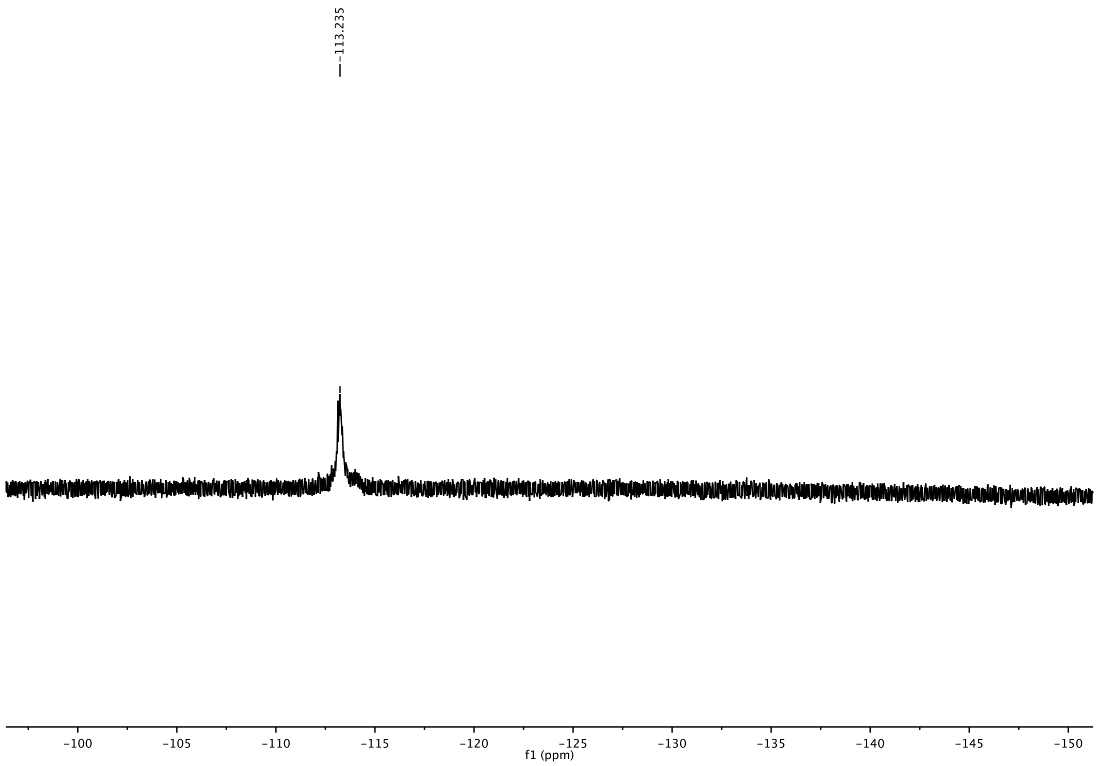

162.79 160.84
144.27
140.28
129.05 128.99 128.57 127.51 127.04
115.35 115.18
75.78
53.75
23.68
f1 (ppm)

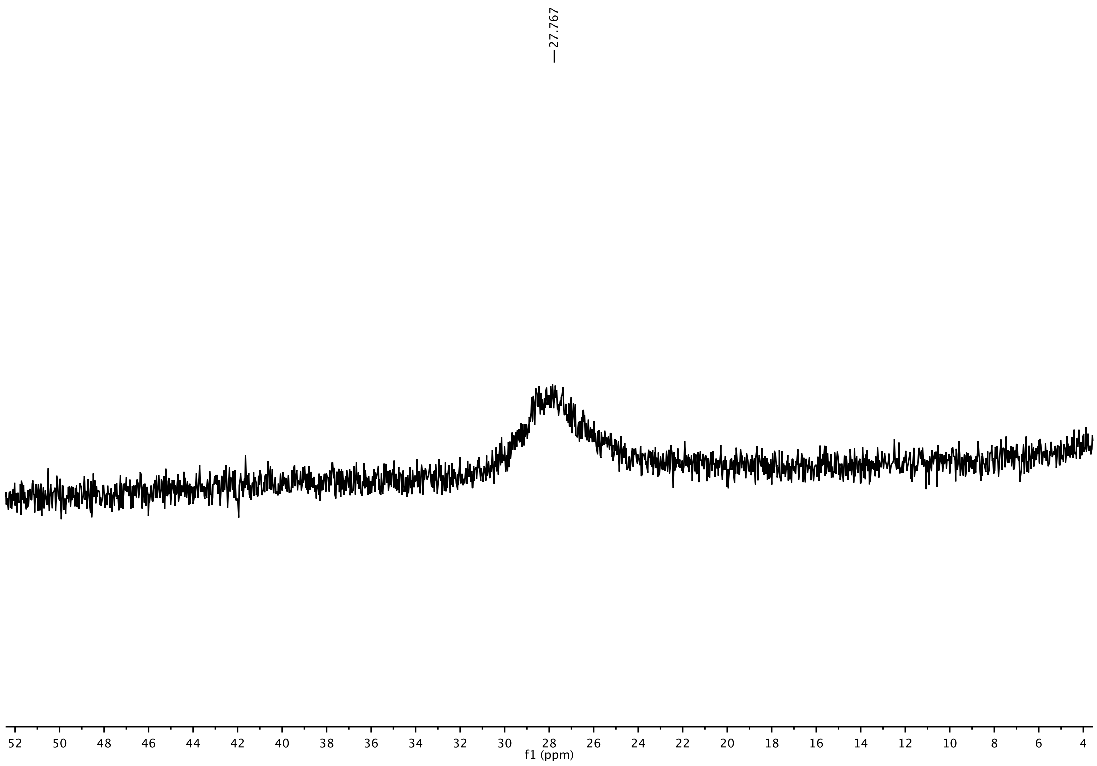

-116.00
-116.03
-116.04
-116.05
-116.08
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

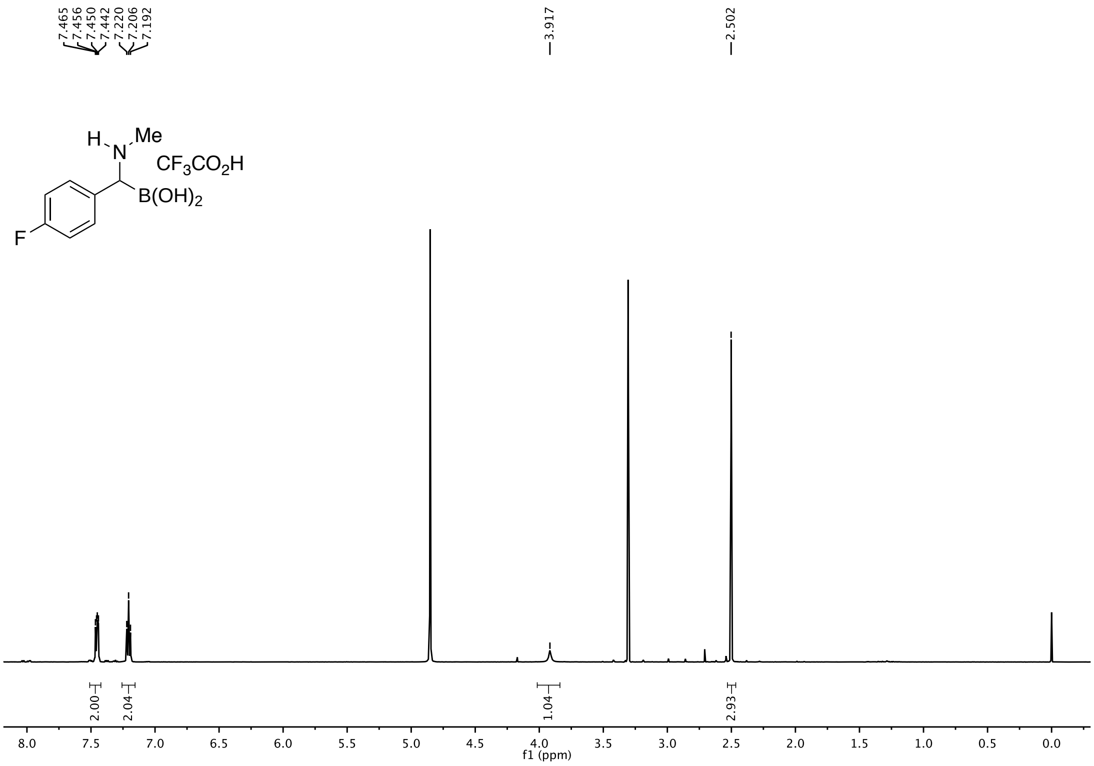
7.4 α-Aminoboronic acids

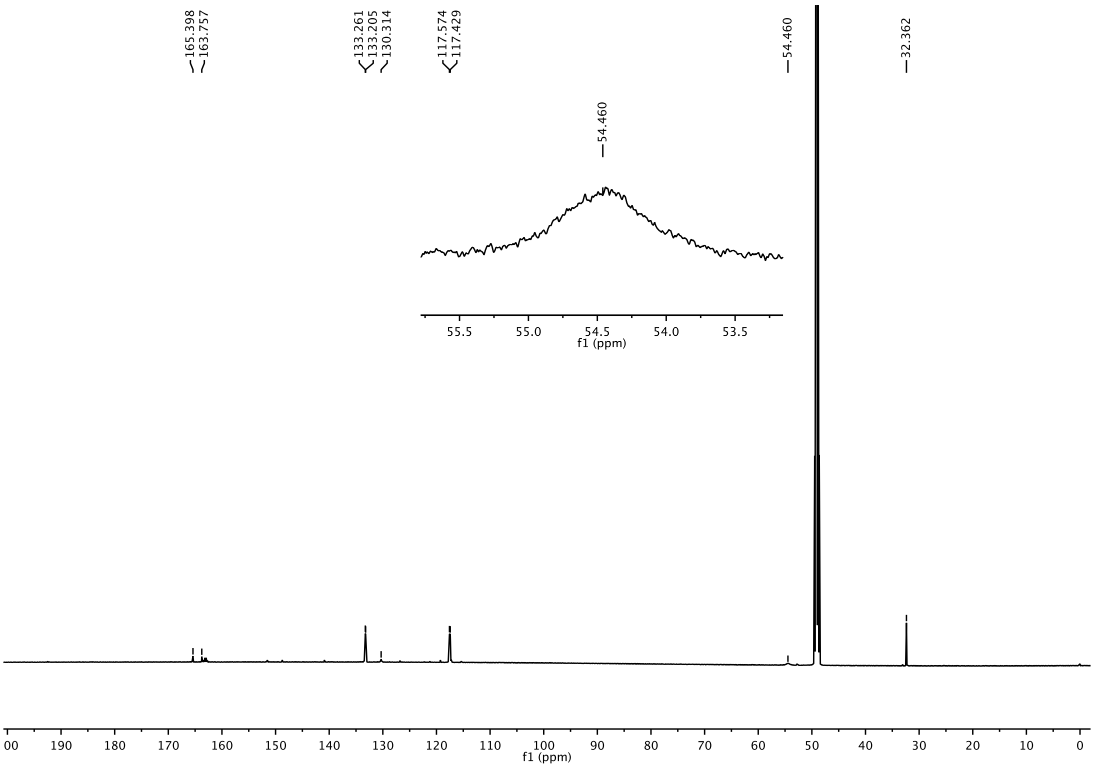


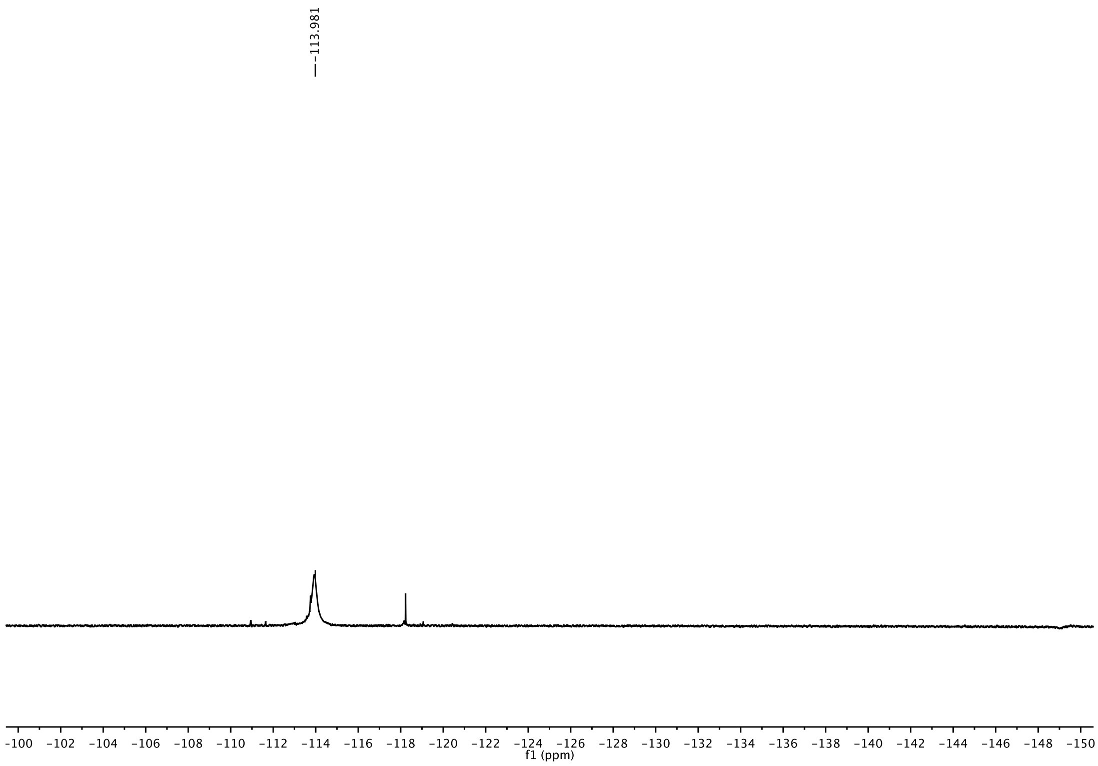


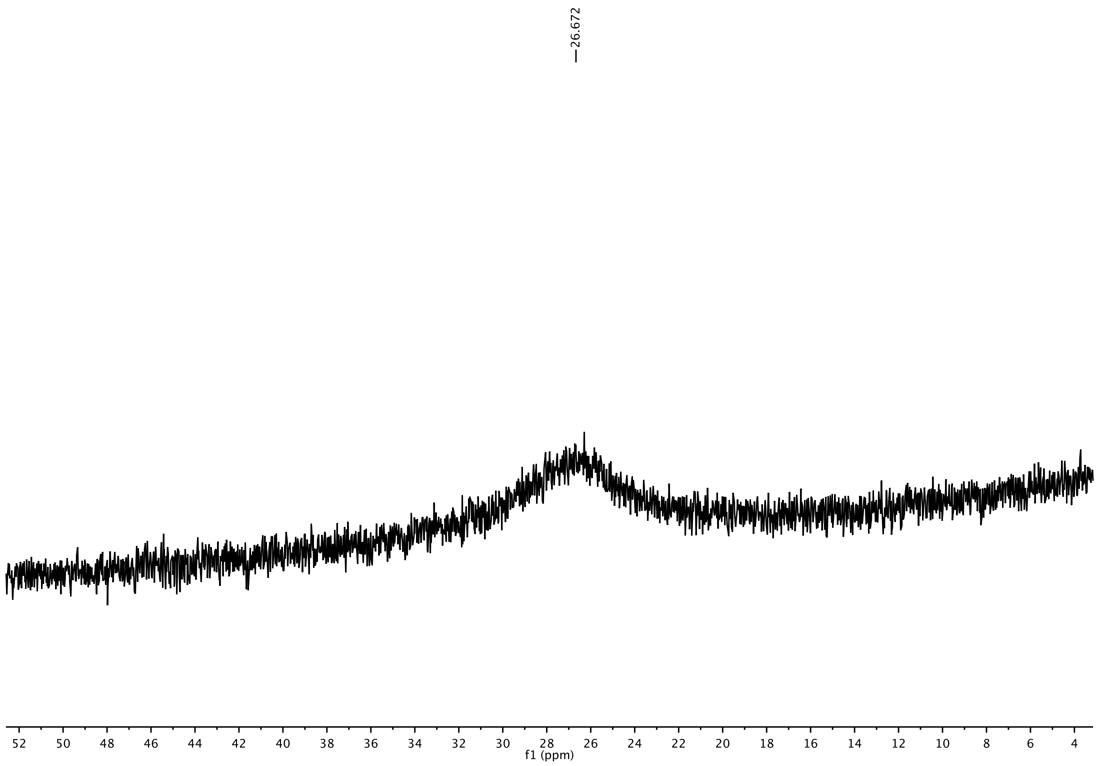

-113.235
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

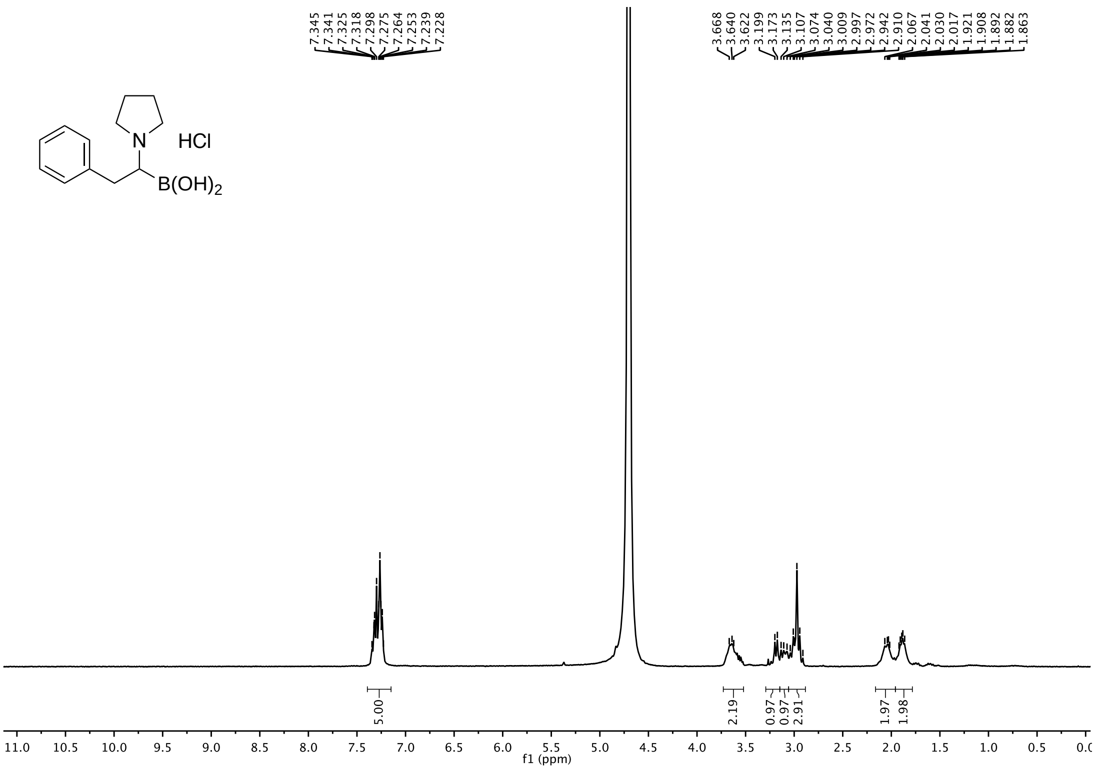

27.767
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
f1 (ppm)

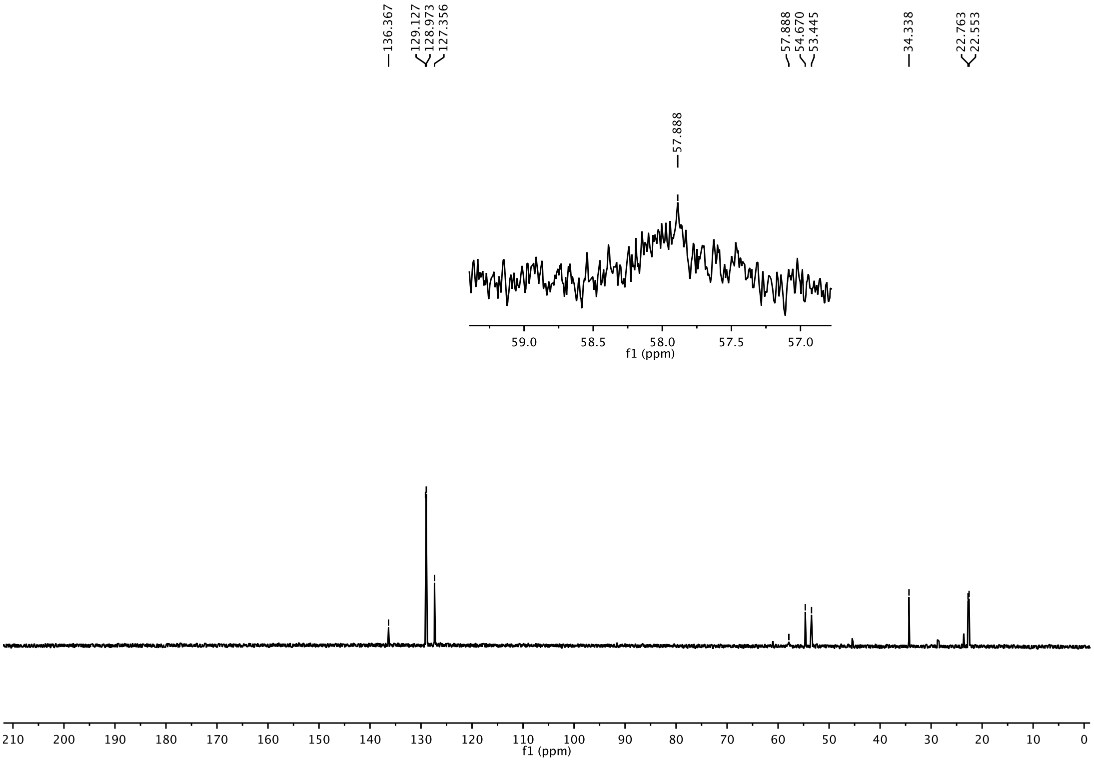

7.465
7.456
7.450
7.442
7.220
7.206
7.192
3.917
2.502
H
N
Me
CF3CO2H
B(OH)2
F
2.00
2.04
1.04
2.93
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

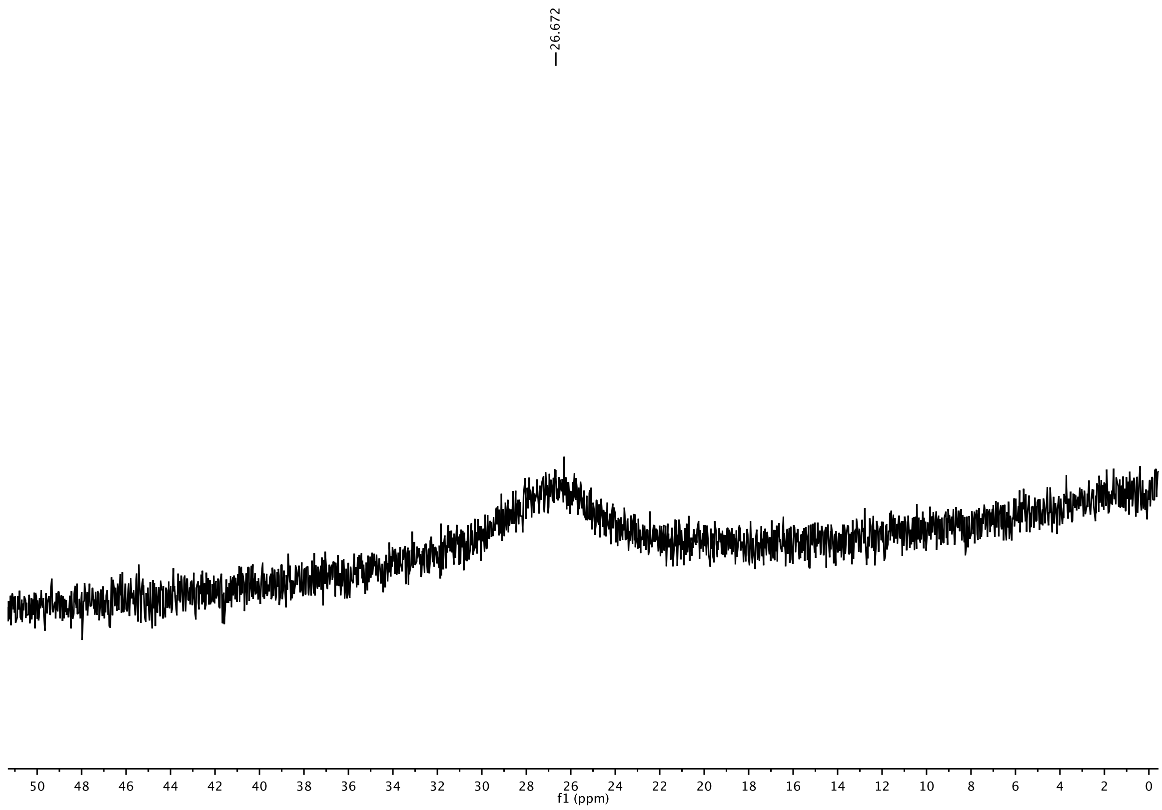

165.398
163.757
133.261
133.205
130.314
117.574
117.429
54.460
32.362
54.460
55.5 55.0 54.5 54.0 53.5
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

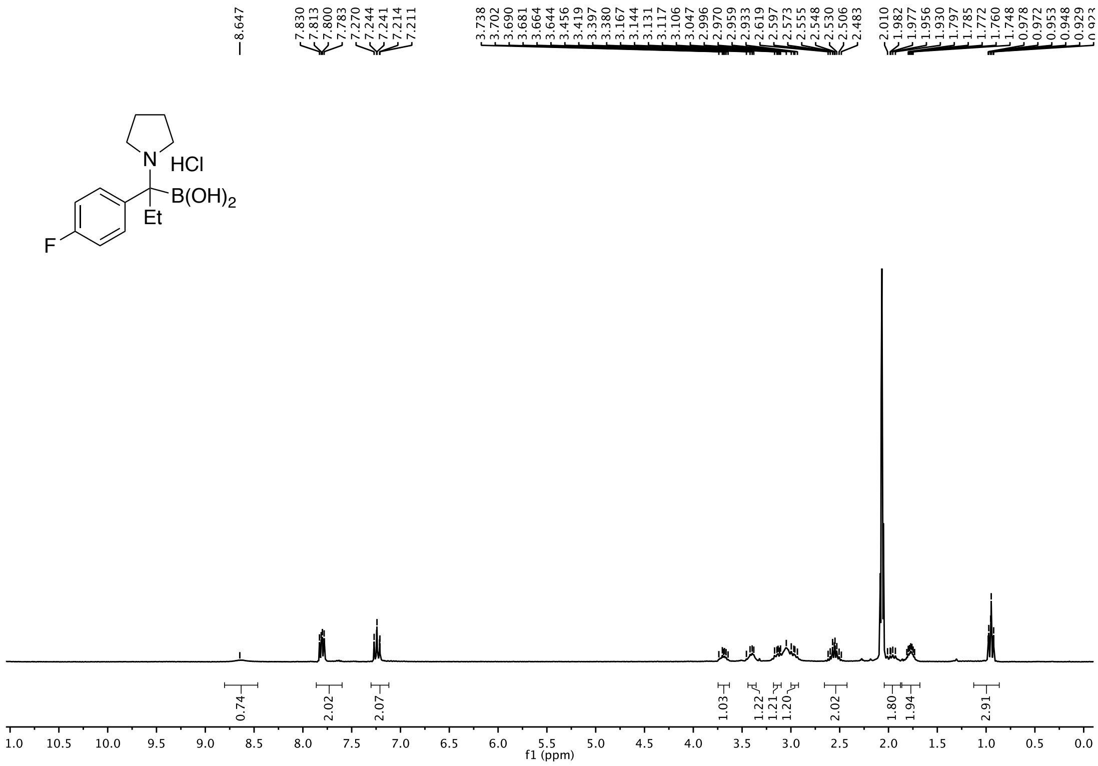

-113.981
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)

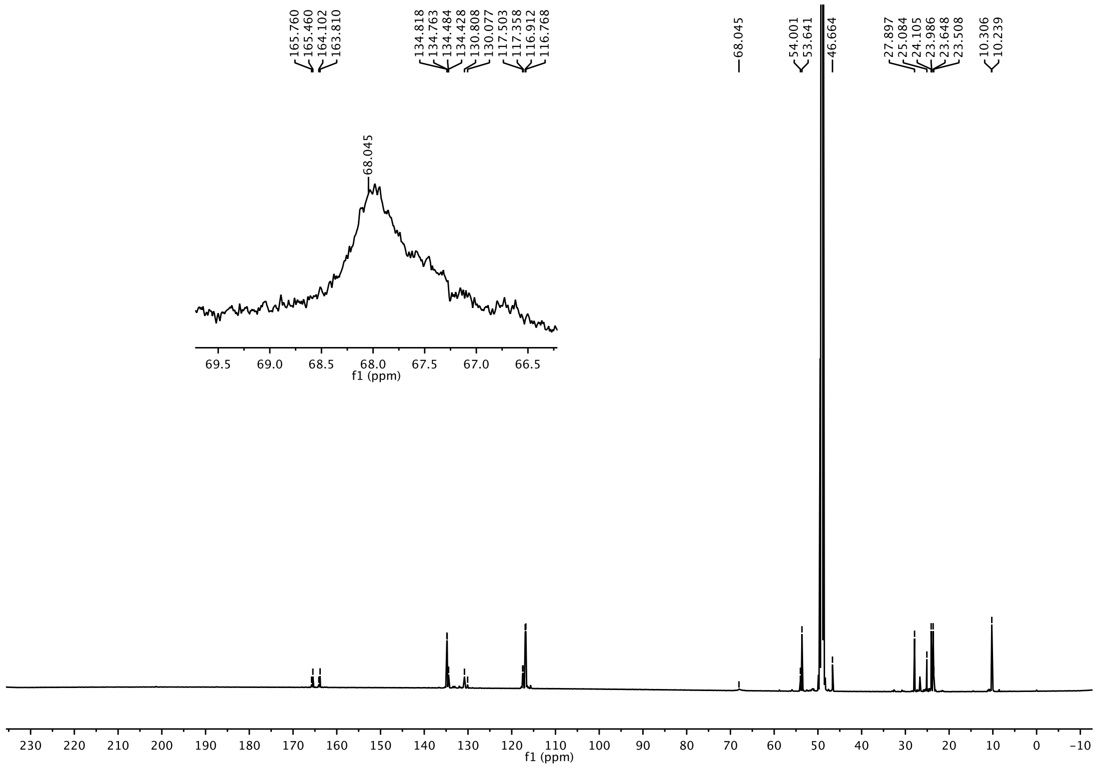

26.672
52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)

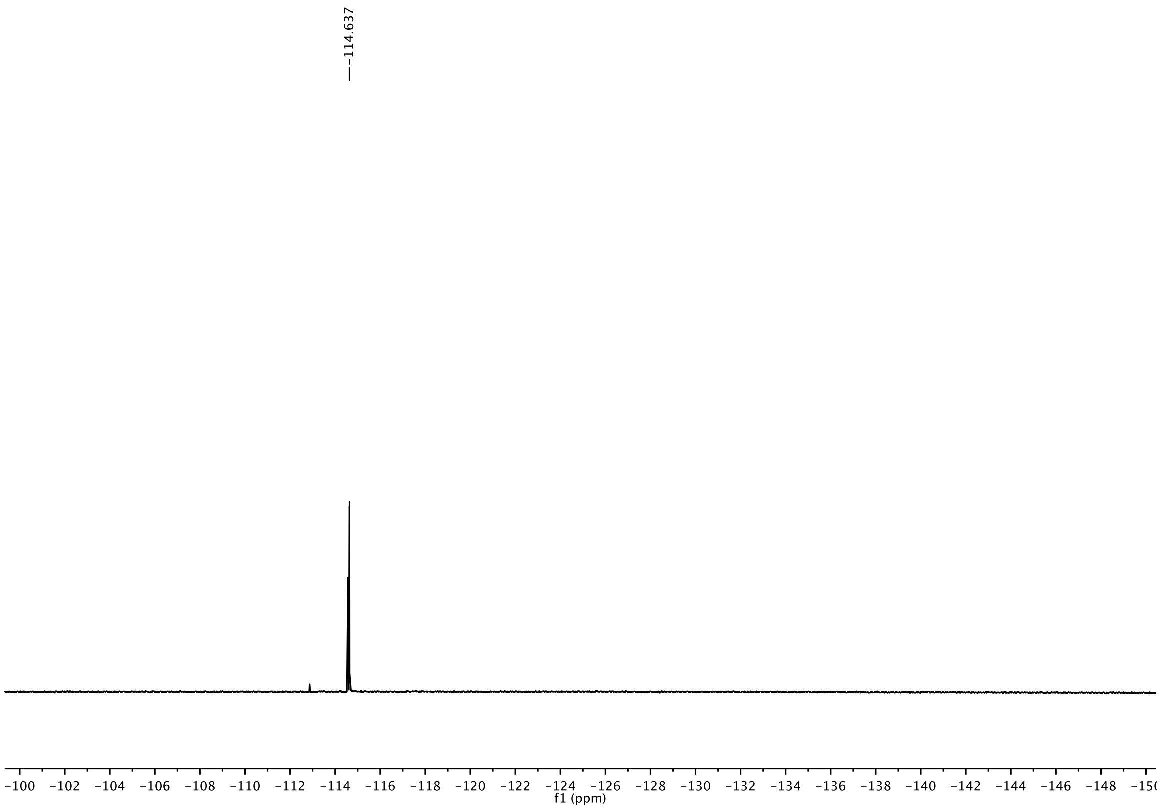

HCl
N
B(OH)2
7.345
7.341
7.325
7.318
7.298
7.275
7.264
7.253
7.239
7.228
3.668
3.640
3.622
3.199
3.173
3.135
3.107
3.074
3.040
3.009
2.997
2.972
2.942
2.910
2.067
2.041
2.030
2.017
1.921
1.908
1.892
1.882
1.863
5.00
2.19
0.97
0.97
2.91
1.97
1.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

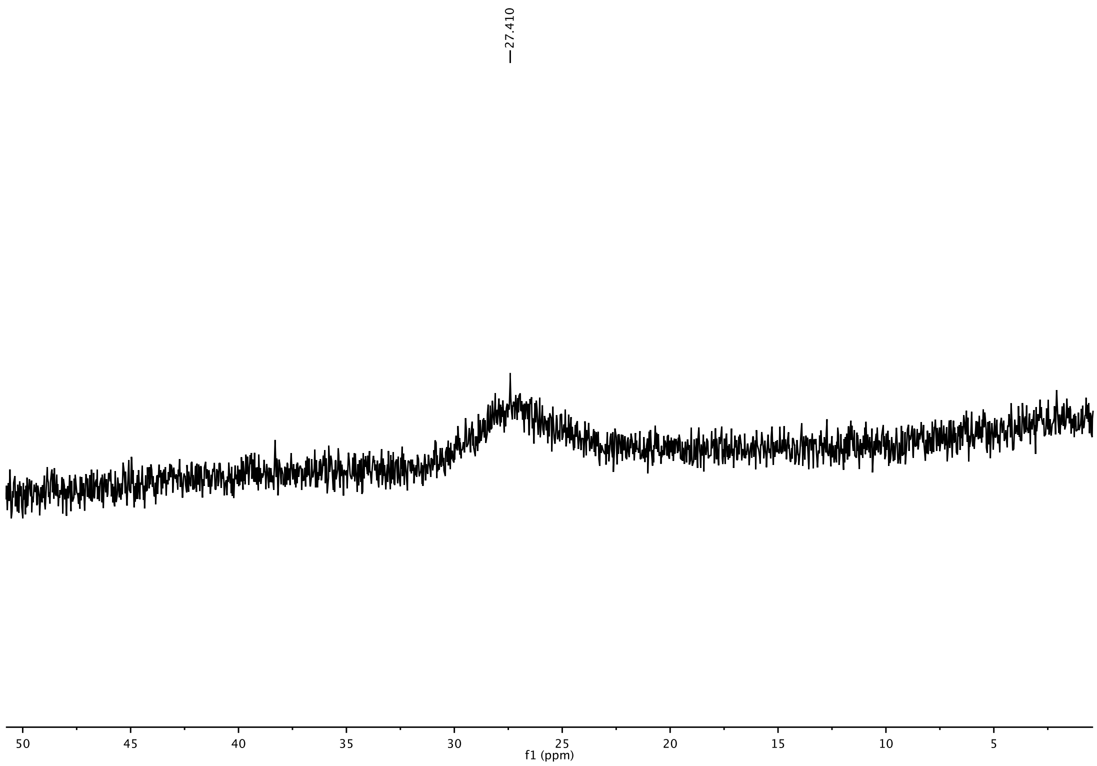

136.367
129.127
128.973
127.356
57.888
54.670
53.445
34.338
22.763
22.553
57.888
59.0 58.5 58.0 57.5 57.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

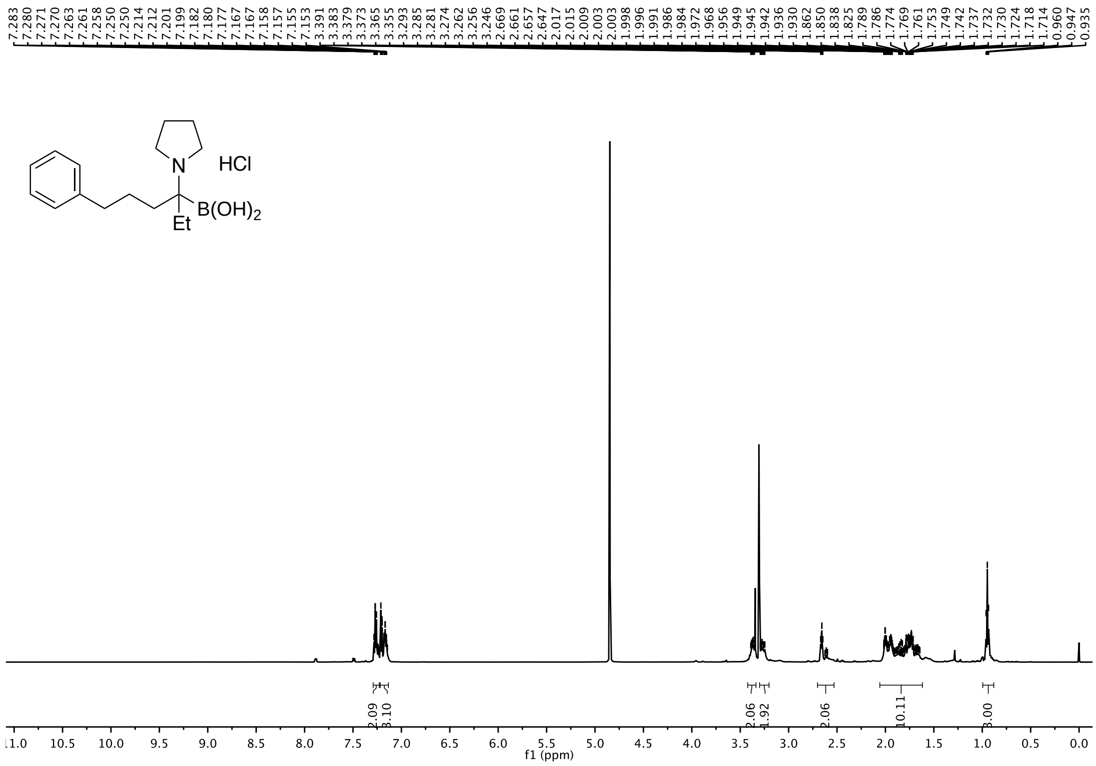

26.672
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)

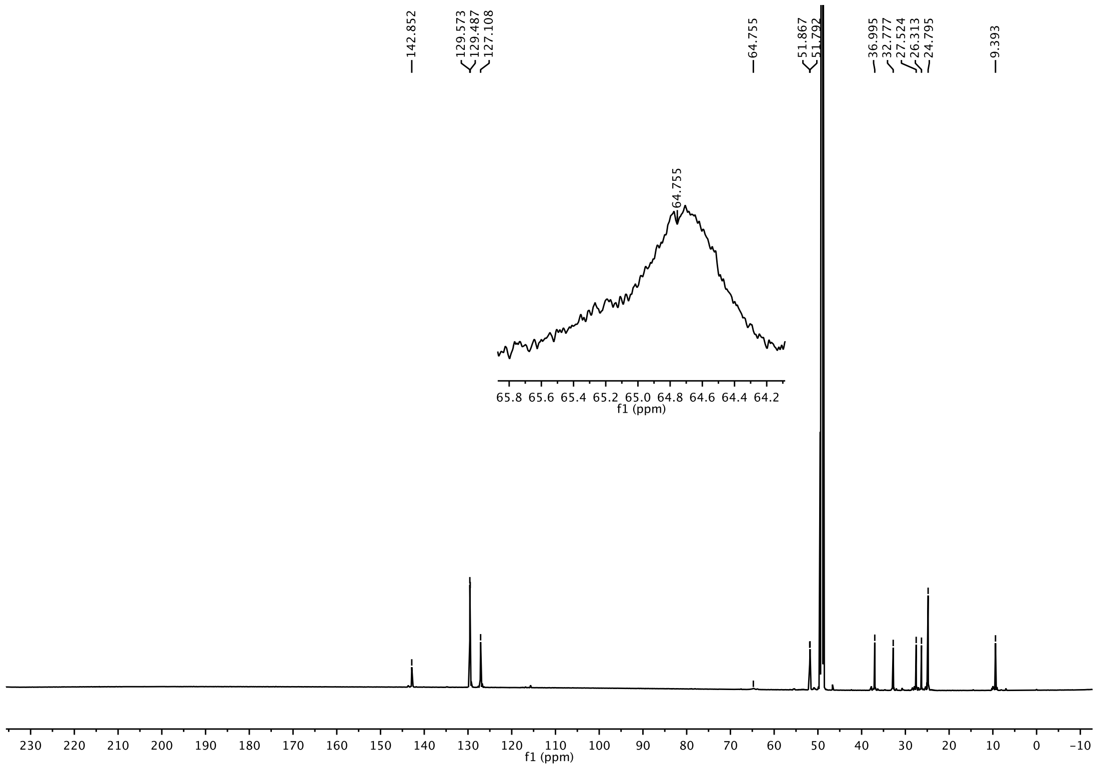


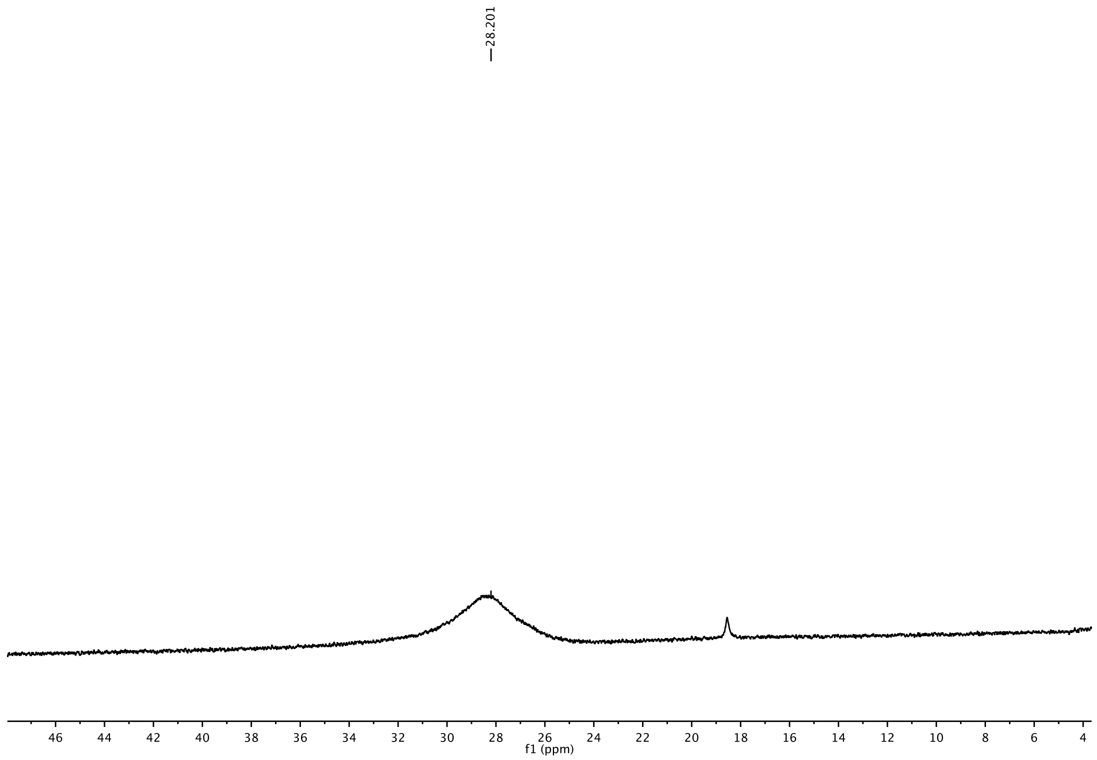


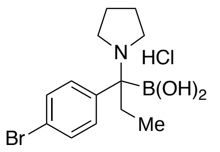

-114.637
-100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150
f1 (ppm)

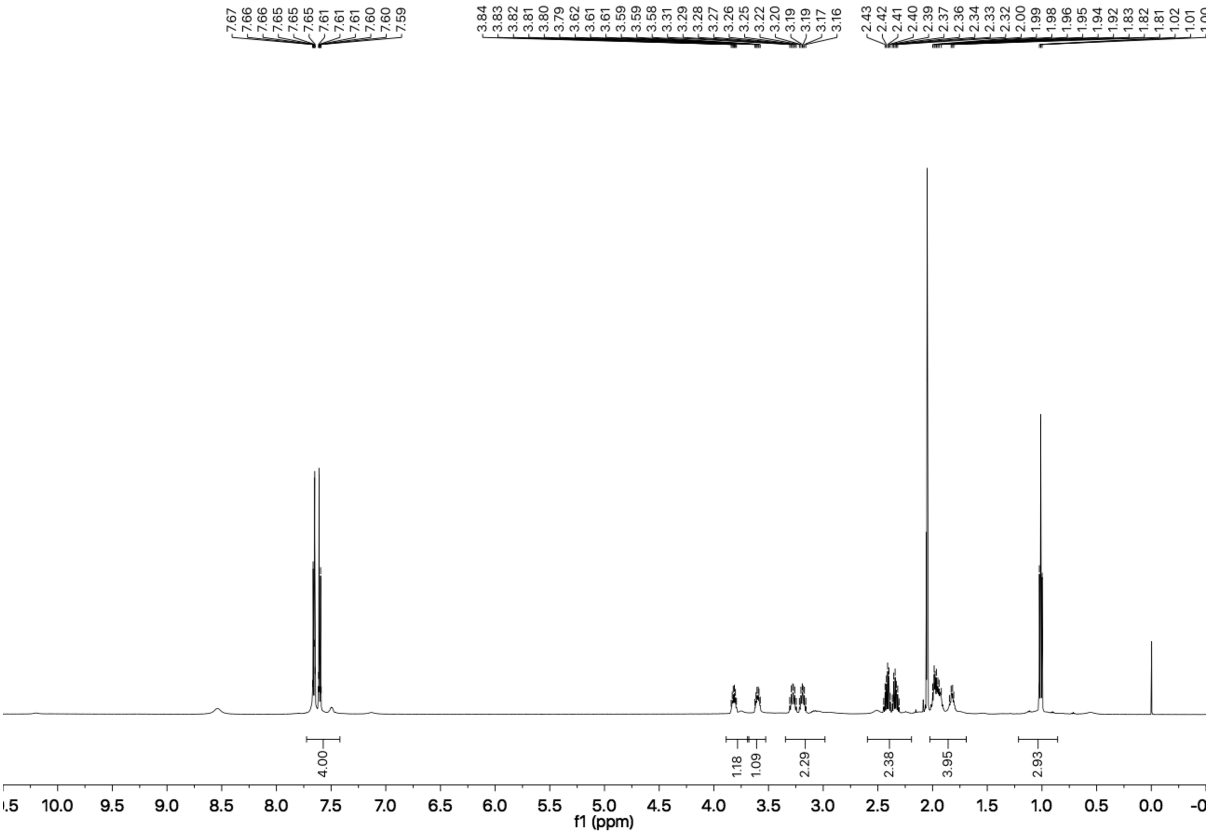

27.410
50 45 40 35 30 25 20 15 10 5
f1 (ppm)

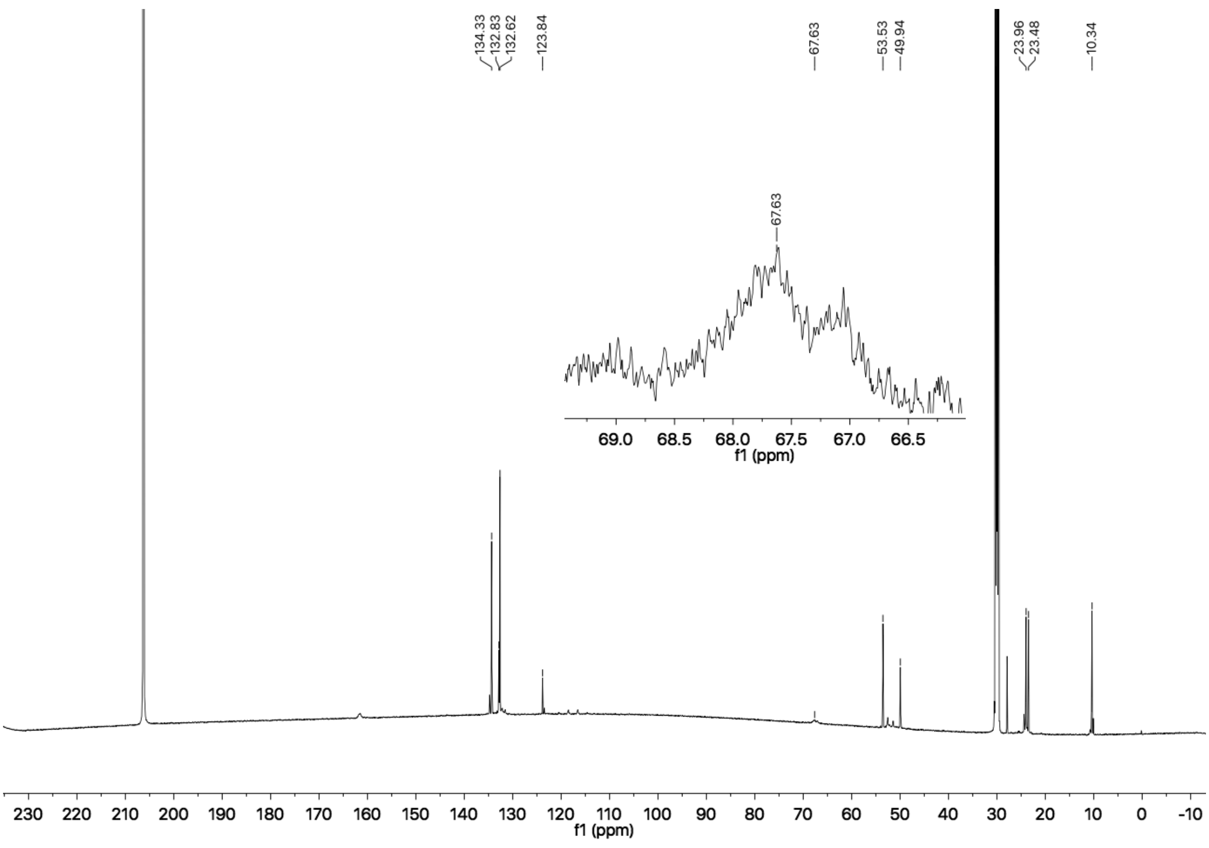

HCl
N
B(OH)2
Et
f1 (ppm)

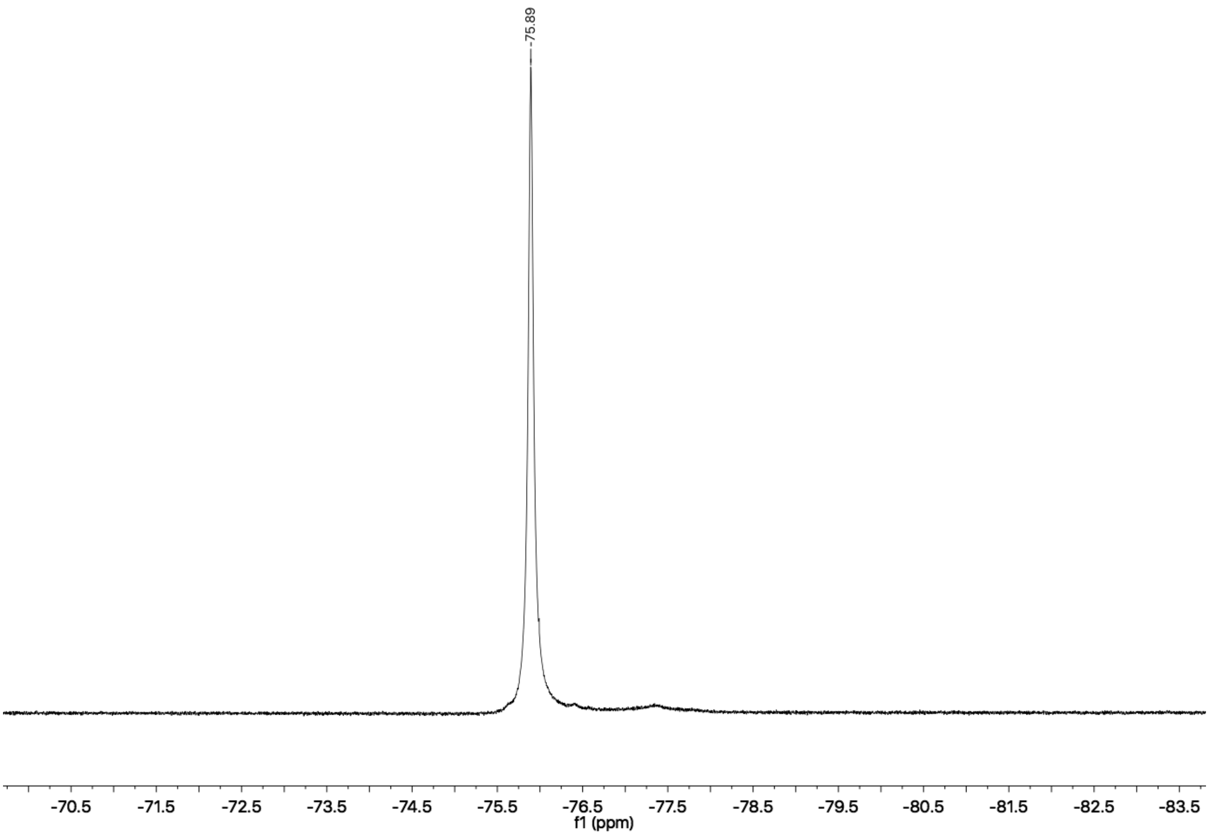

f1 (ppm)

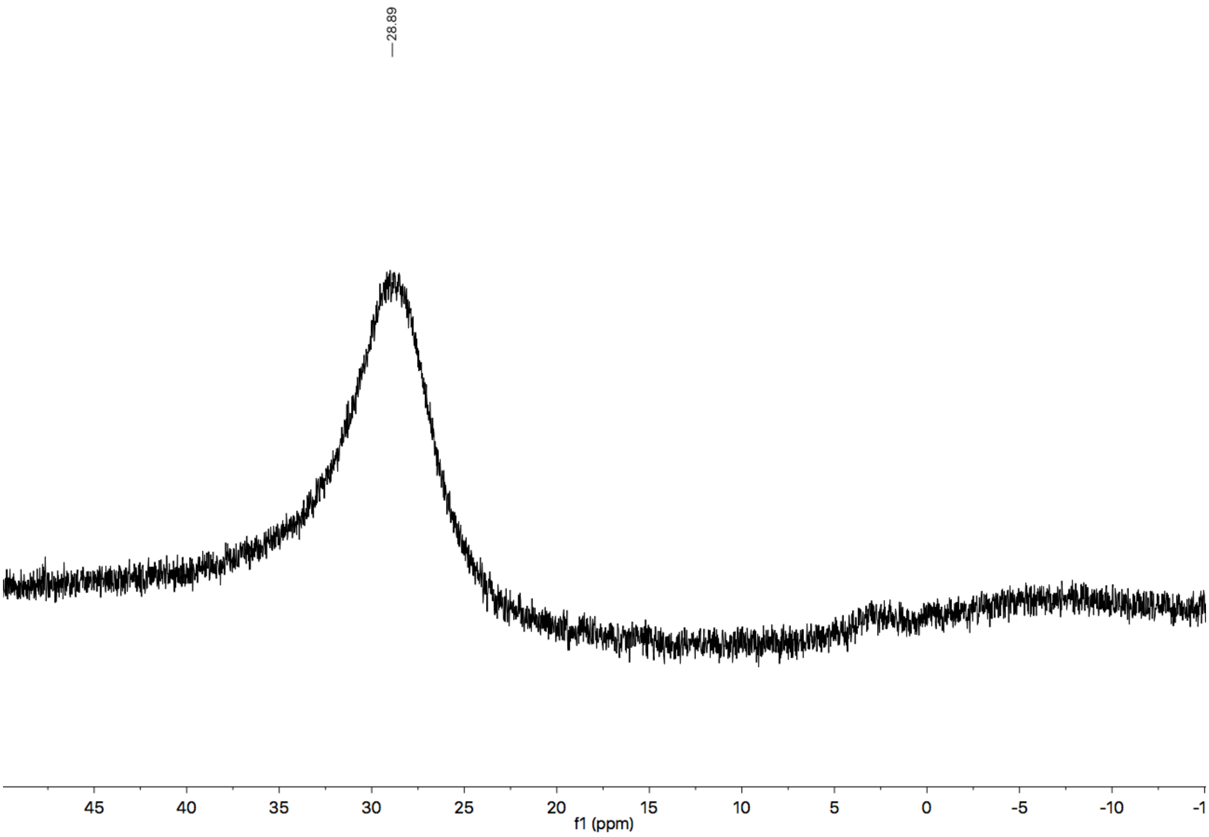

28.201
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
f1 (ppm)


HCl
B(OH)2
Me
Br


f1 (ppm)


f1 (ppm)


-75.89
-70.5
-71.5
-72.5
-73.5
-74.5
-75.5
-76.5
-77.5
-78.5
-79.5
-80.5
-81.5
-82.5
-83.5
f1 (ppm)


28.89
45
40
35
30
25
20
15
10
5
0
-5
-10
-1
f1 (ppm)