Supplementary Data for:

Reactions of Iodine-Nitrene Reagents with Boranes†

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Synthesis of $(C_6F_5)_2BN(Ts)(C_6F_5)$ 1: A 50 mL Schlenk flask was charged with TsN=IPh (88.6 mg, 0.237 mmol) in pentane (10 mL) to form a white slurry. A solution of $B(C_6F_5)_3$ (121.5 mg, 0.237 mmol) in pentane (10 mL) was added to the flask. After stirring overnight, a white insoluble powder was collected via filtration. The crude product was dissolved in a small volume of CH_2Cl_2 (2 mL) and filtered through a plug of celite. The filtrate was collected and stored at – 35 °C to allow for the formation of small clear, colourless crystals. Yield 120 mg (74 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.35 (d, $^3J_{H-H}$ = 8 Hz, 2H, CH tol), 6.49 (d, $^3J_{H-H}$ = 8 Hz, 2H, CH tol), 1.75 (s, 3H, tol CH_3). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, 25 °C): δ 43.6 (br). ^{19}F (376 MHz, C_6D_6, 25 °C): δ – 128.60 (m, 2F, o-F (C_6F_5)), – 131.35 (m, 2F, o-F (C_6F_5)), – 142.19 (m, 2F, o-F N(C_6F_5)), – 146.68 (t, $^3J_{F-F}$ = 21 Hz, 1F, p-F (C_6F_5)), – 148.69 (t, $^3J_{F-F}$ = 22 Hz, 1F, p-F N(C_6F_5)), – 150.02 (t, $^3J_{F-F}$ = 19 Hz, 1F, p-F (C_6F_5)), – 159.04 (m, 2F, m-F (C_6F_5)), – 160.27 (m, 2F, m-F N(C_6F_5)), – 161.06 (m, 2F, m-F (C_6F_5)). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{25}H_7BF_{15}NO_2S$ 681.0085, Found 681.0068.

Synthesis of $(C_6F_5)_2BN(Ts)(C_6F_5) \cdot OPEt_3$ 2: A 4 dram scintillation vial was charged with **1** (53.3 mg, 0.0782 mmol) in toluene (1 mL). To the solution, $OPEt_3$ (10.5 mg, 0.0783 mmol) was added. The solution was left at room temperature overnight to afford large rectangular crystals, suitable for x-ray diffraction. Yield 56.1 mg (88 %). ^{1}H NMR (400 MHz, tol-d_8, 25 °C): δ 7.64 (d, $^3J_{H-H}$ = 8 Hz, 2H, tol CH), 6.66 (d, $^3J_{H-H}$ = 8 Hz, 2H, tol CH), 1.88 (m, 6H, CH_2 Et CH_2), 1.84 (s, 3H, tol CH_3), 0.68 (dt, $^3J_{P-H}$ = 18 Hz, $^3J_{H-H}$ = 8 Hz, 9H, Et CH_3). ^{11}B{^{1}H} NMR (128 MHz, tol-d_8, 25 °C): δ 1.41 (s). ^{19}F (376 MHz, tol-d_8, 25 °C): δ – 133.44 (br, 4F, *o*-F B(C_6F_5)), – 137.99 (s, 2F, *o*-F N(C_6F_5)), – 154.59 (s, 1F, *p*-F N(C_6F_5)), – 156.70 (br, 2F, *p*-F B(C_6F_5)), – 163.86 (br, 4F, *m*-F B(C_6F_5)), – 164.10 (s, 2F, *m*-F N(C_6F_5)). ^{31}P{^{1}H} NMR (162MHz, tol-d_8, 25 °C): δ 78.50 (s).

Synthesis of $(C_6F_5)_2BN(Ph)Ts$ 3: A 50 mL Schlenk flask was charged with TsN=IPh (17.4 mg, 0.0466 mmol) in pentane (10 mL). To the flask, a solution of $PhB(C_6F_5)_2$ (19.7 mg, 0.0467 mmol) in pentane (10 mL) was added. The reaction mixture was allowed to stir overnight. A white solid was collected via filtration. The solid was redissolved in CH_2Cl_2 and cooled to – 35 °C to afford clear colourless crystals. Yield 20.9 mg (76 %). ^{1}H NMR (400 MHz, tol-d_8, 25 °C): δ 7.36 (d, $^3J_{H-H}$ = 8 Hz, 2H, CH tol), 6.94 (d, $^3J_{H-H}$ = 7 Hz, 2H, CH Ph), 6.63 (m, 3H, CH Ph), 6.54 (d, $^3J_{H-H}$ = 8 Hz, 2H, CH tol), 1.81 (s, 3H, CH_3 tol). ^{11}B{^{1}H} NMR (128 MHz, tol-d_8, 25 °C): δ 42.00. ^{19}F (376 MHz, tol-d_8, 25 °C): δ –131.42 (br, 4F, *o*-F (C_6F_5)), –131.62 (br, 4F, *o*-F (C_6F_5)), –150.95 (t, $^3J_{F-F}$ = 18 Hz, 2F, *p*-F (C_6F_5)), –151.59 (t, $^3J_{F-F}$ = 18 Hz, 2F, *p*-F (C_6F_5)), –161.06 (br, 4F, *m*-F (C_6F_5)), –131.42 (br, 4F, *m*-F (C_6F_5)). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{25}H_{12}BF_{10}NO_2S$ 591.0522, Found 591.0529.

Aminoboranes of the general formula $(C_6F_5)_2BNH(R)$, where R = Ts, Ms, Cls, Ns, can be generated by reacting equimolar amounts of the appropriate ylide with either $(C_6F_5)_2BCl$ or $(C_6F_5)_2BH$. A sample preparation is provided below.

Synthesis of $(C_6F_5)_2BNH(Ts)$ 2a: A 50 mL schlenk was charged with TsN=IPh (16.6 mg, 0.044 mmol) in pentane (10 mL) to form a white slurry. A solution of $(C_6F_5)_2BCl$ (16.9 mg, 0.044 mmol) was added to the schlenk flask. The resulting slurry was stirred overnight and the white insoluble solid was subsequently collected by filtration. The powder was then dissolved in CH_2Cl_2 and stored at – 35 °C to allow for the formation of clear, colourless crystals. Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution for compounds 2a, b, d. $(C_6F_5)_2BNH(Ts)$

4: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.88 (s, 1H, NH), 7.74 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, tol CH), 6.67 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, tol CH), 1.84 (s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 25 °C): δ 34.4 (s). ^{19}F (376 MHz, C_6D_6, 25 °C): δ – 136.07 (br, 2F, *o*-F (C_6F_5)), – 136.43 (br, 2F, *o*-F (C_6F_5)), – 151.24 (br, 1F, *p*-F (C_6F_5)), – 156.19 (br, 1F, *p*-F (C_6F_5)), – 165.07 (br, 2F, *m*-F (C_6F_5)), – 165.35 (br, 2F, *m*-F (C_6F_5)). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_8BF_{10}NO_2S$ 515.0209, Found 515.0225. $(C_6F_5)_2BNH(Cls)$

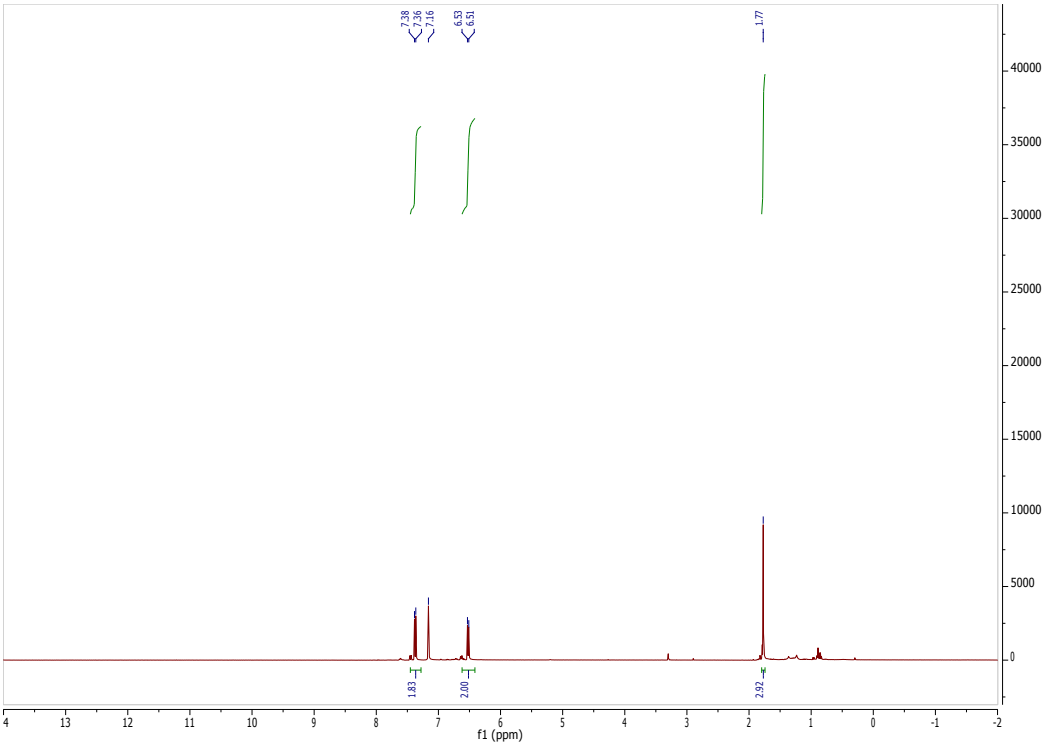
5: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.46 (s, 1H, NH), 7.20 (d, $^3J_{H\text{-}H}$ = 9 Hz, 2H, CH Ph), 6.73 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, CH Ph). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 25 °C): δ 39.30 (br). ^{19}F (376 MHz, C_6D_6, 25 °C): δ – 131.32 (s, 4F, *o*-F (C_6F_5)), – 145.84 (br, 2F, *p*-F (C_6F_5)), – 149.90 (br, 2F, *p*-F (C_6F_5)), – 160.73 (br, 4F, *m*-F (C_6F_5)). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_5BF_{10}NO_2S$ 534.9663, Found 534.9659. $(C_6F_5)_2BNH(Ms)$

6: ^{1}H NMR (400 MHz, tol-d_8, 25 °C): δ 7.32 (s, 1H, NH), 2.26 (s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (128 MHz, tol-d_8, 25 °C): δ 39.74 (br). ^{19}F (376 MHz, tol-d_8, 25 °C): δ – 131.54 (br, 2F, *o*-F (C_6F_5)), – 132.19 (br, 2F, *o*-F (C_6F_5)), – 146.09 (br, 1F, *p*-F (C_6F_5)), – 150.01 (br, 1F, *p*-F (C_6F_5)), – 160.30 (br, 2F, *m*-F (C_6F_5)), – 161.38 (br, 2F, *m*-F (C_6F_5)). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_4BF_{10}NO_2S$ 438.9896, Found 438.9897. $(C_6F_5)_2BNH(Ns)$

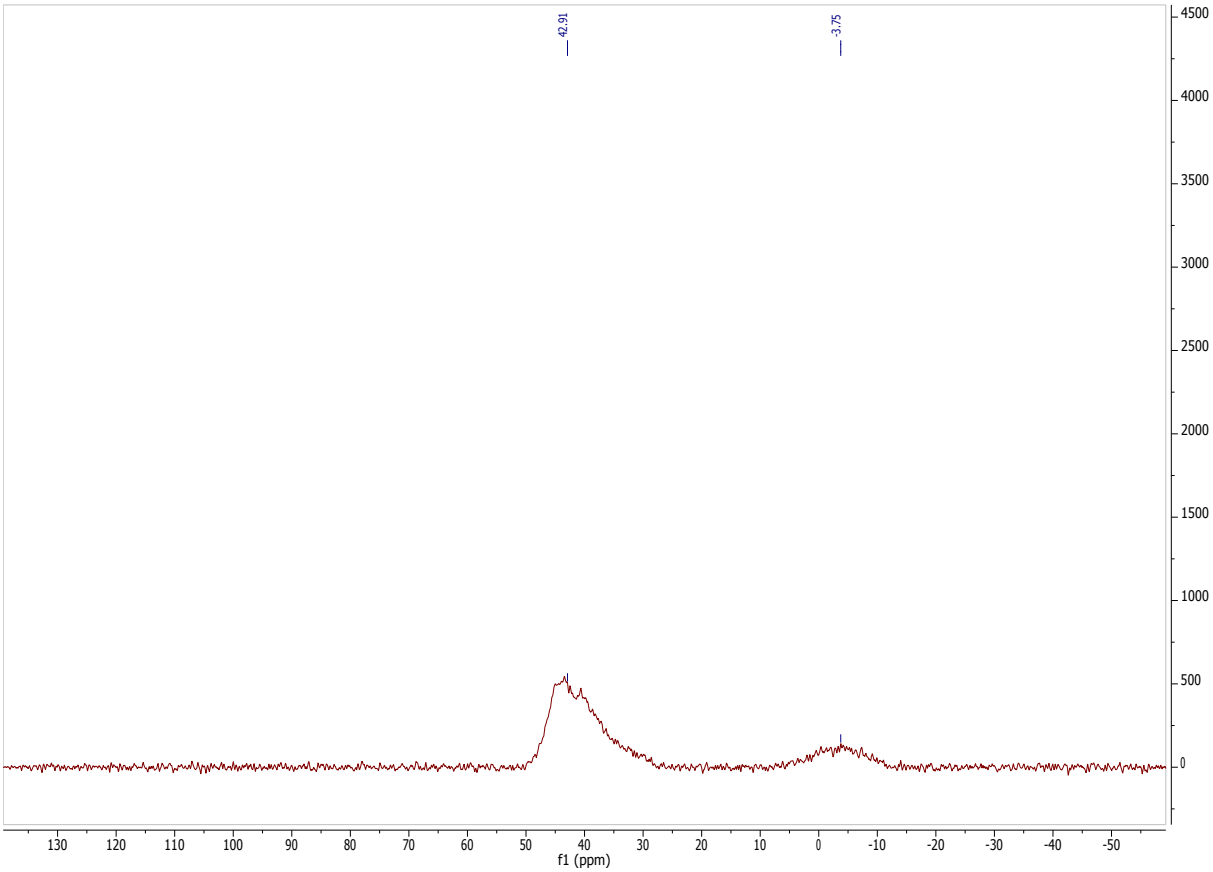
7: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.35 (d, $^3J_{H\text{-}H}$ = 9 Hz, 2H, CH Ph), 7.23 (s, 1H, NH), 7.09 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, CH Ph). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 25 °C): δ 39.55 (br). ^{19}F (376 MHz, C_6D_6, 25 °C): δ – 131.36 (s, 4F, *o*-F (C_6F_5)), – 144.69 (br, *p*-F (C_6F_5)), – 149.25 (br, *p*-F (C_6F_5)), – 160.31 (br, 4F, *m*-F (C_6F_5)). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_5BF_{10}N_2O_4S$ 545.9903, Found 545.9904.

Compound	^{31}P (ppm)	Δδ (ppm)
$(C_5F_5)_2BN(H)(Ms)$	79.79	28.32
$(C_5F_5)_2BN(H)(Ts)$	80.16	28.69
$(C_5F_5)_2BN(H)(C_6H_4Cl)$	80.52	29.05
$(C_5F_5)_2BN(H)(Ns)$	80.66	29.19

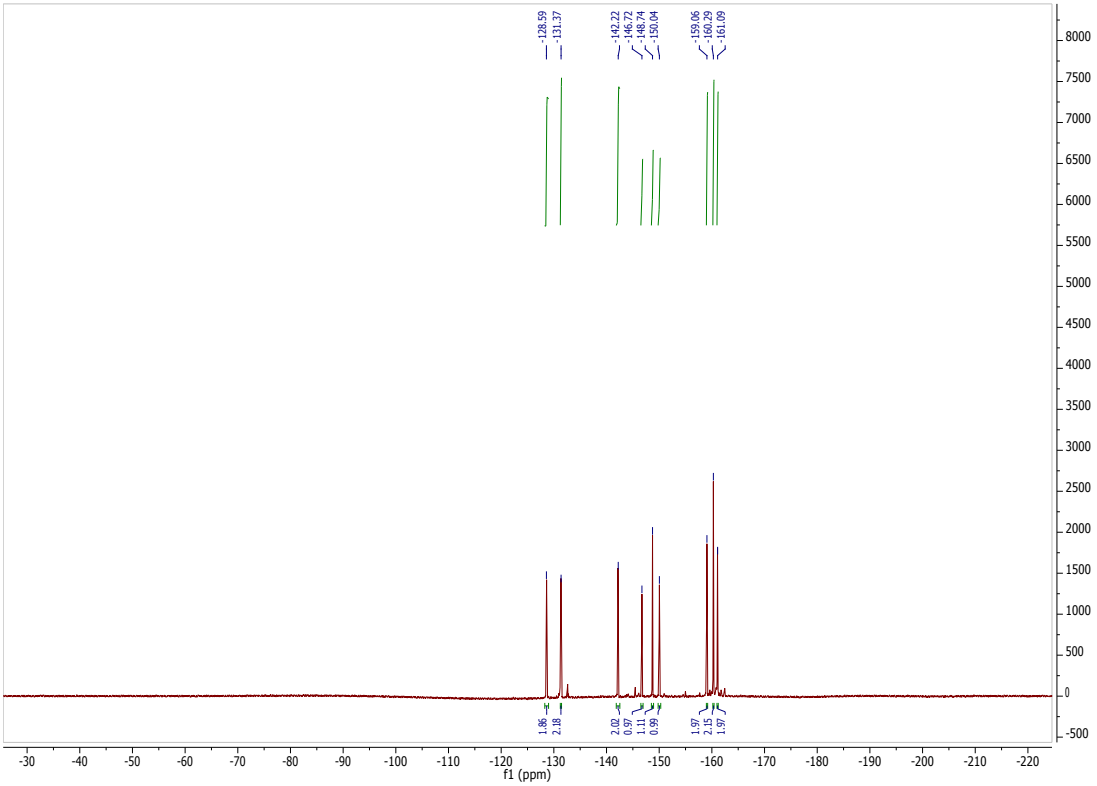
$(C_6F_5)_2BN(Ts)(C_6F_5)$ **1** ^{1}H



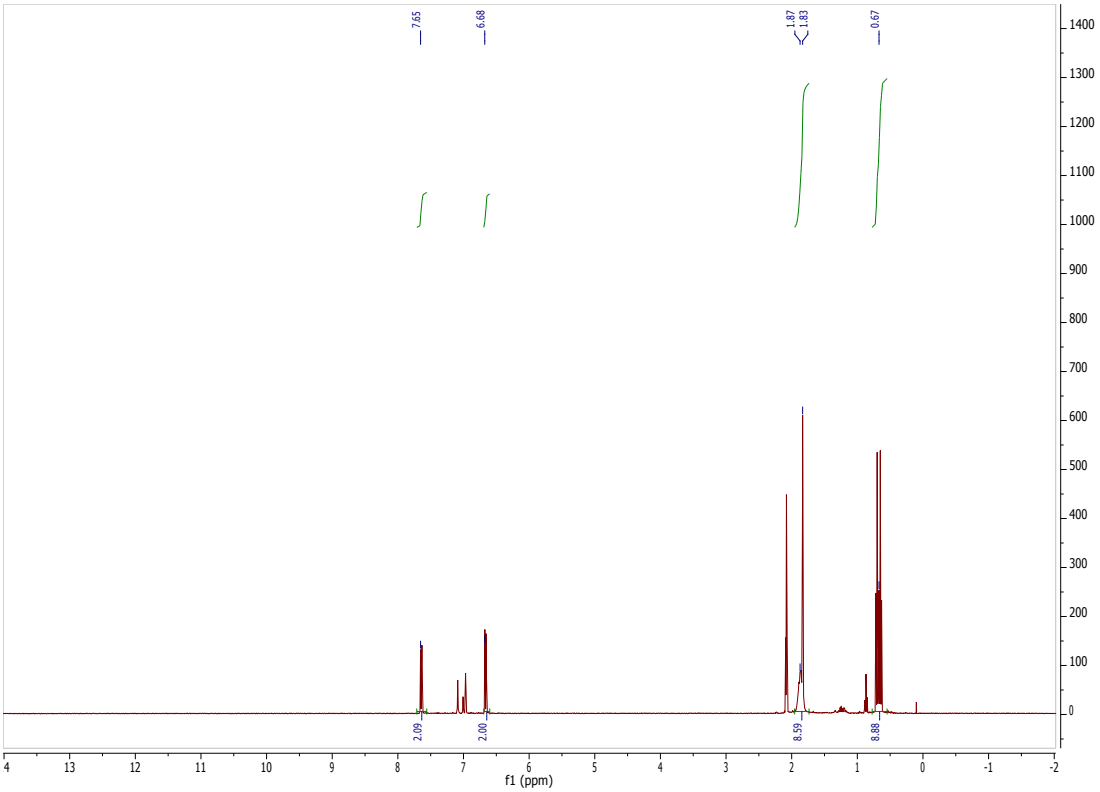
^{11}B



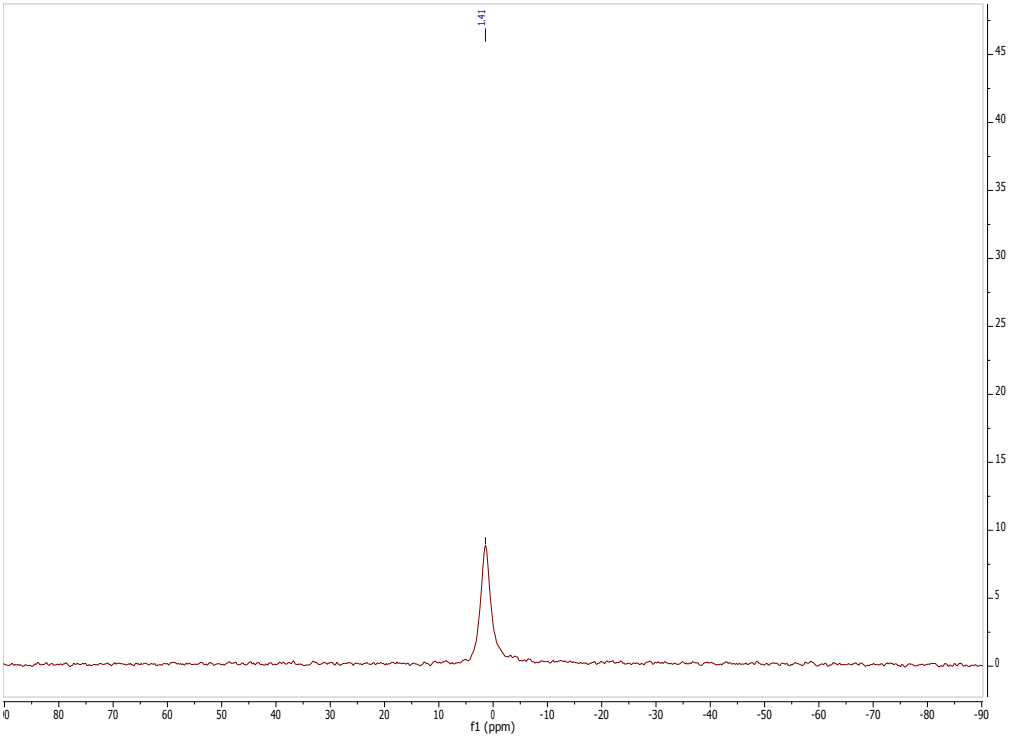
^{19}F



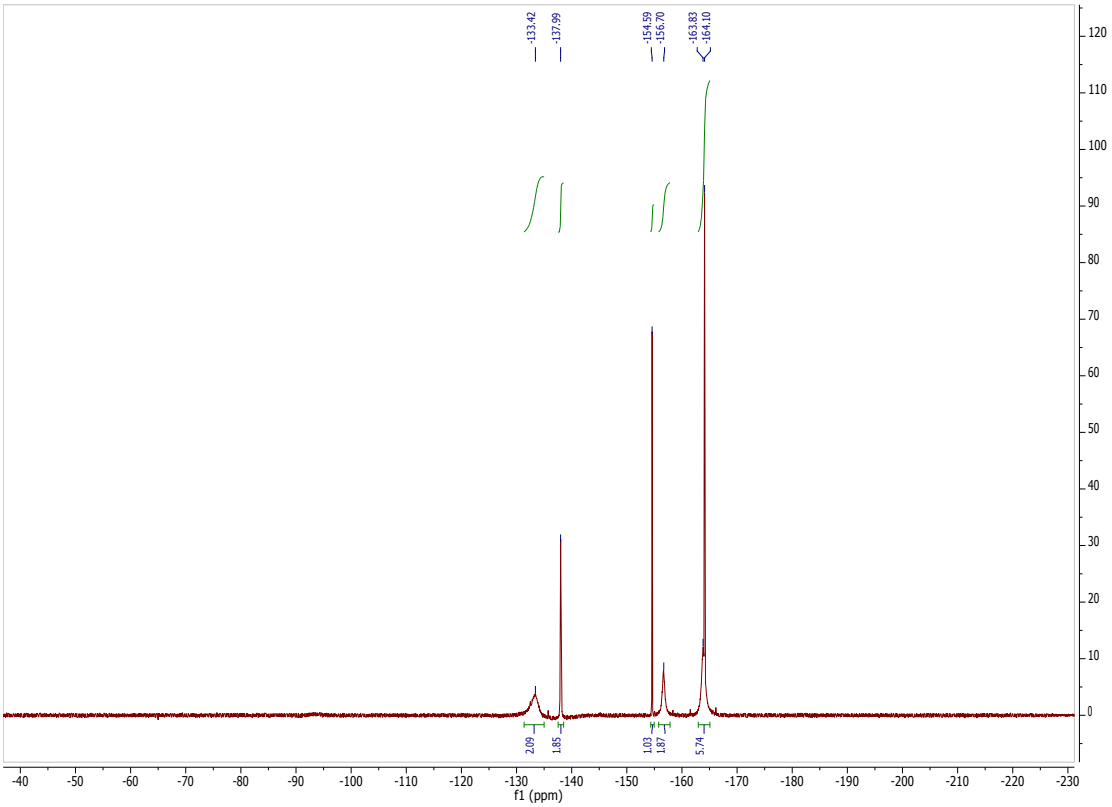
$(C_6F_5)_2BN(Ts)(C_6F_5) \cdot OPEt_3$ **2** ^1H



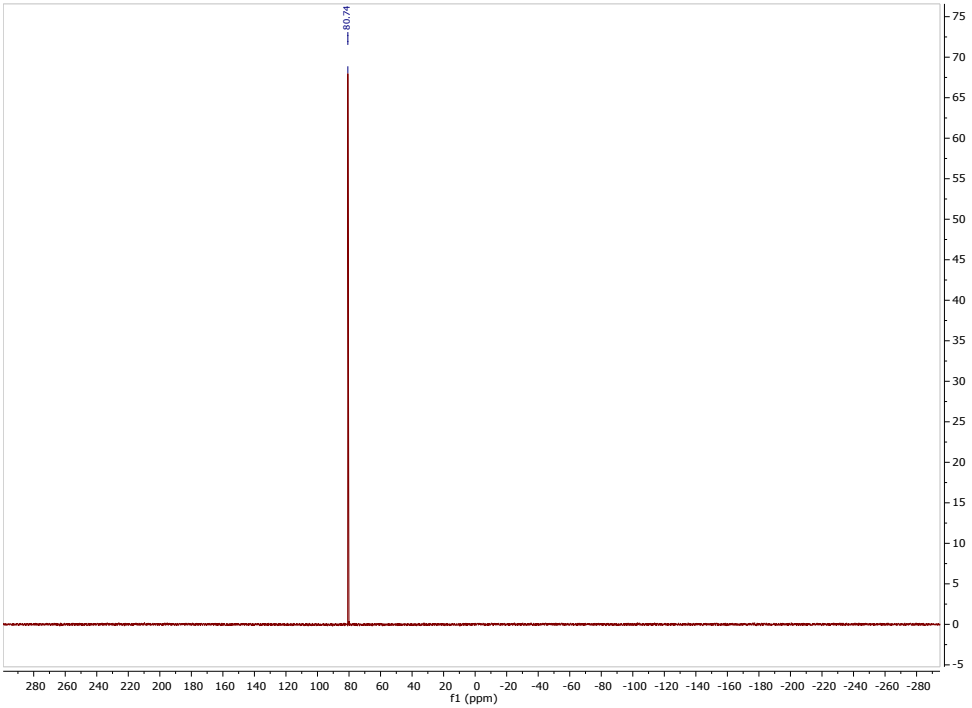
^{11}B


1.41
f1 (ppm)

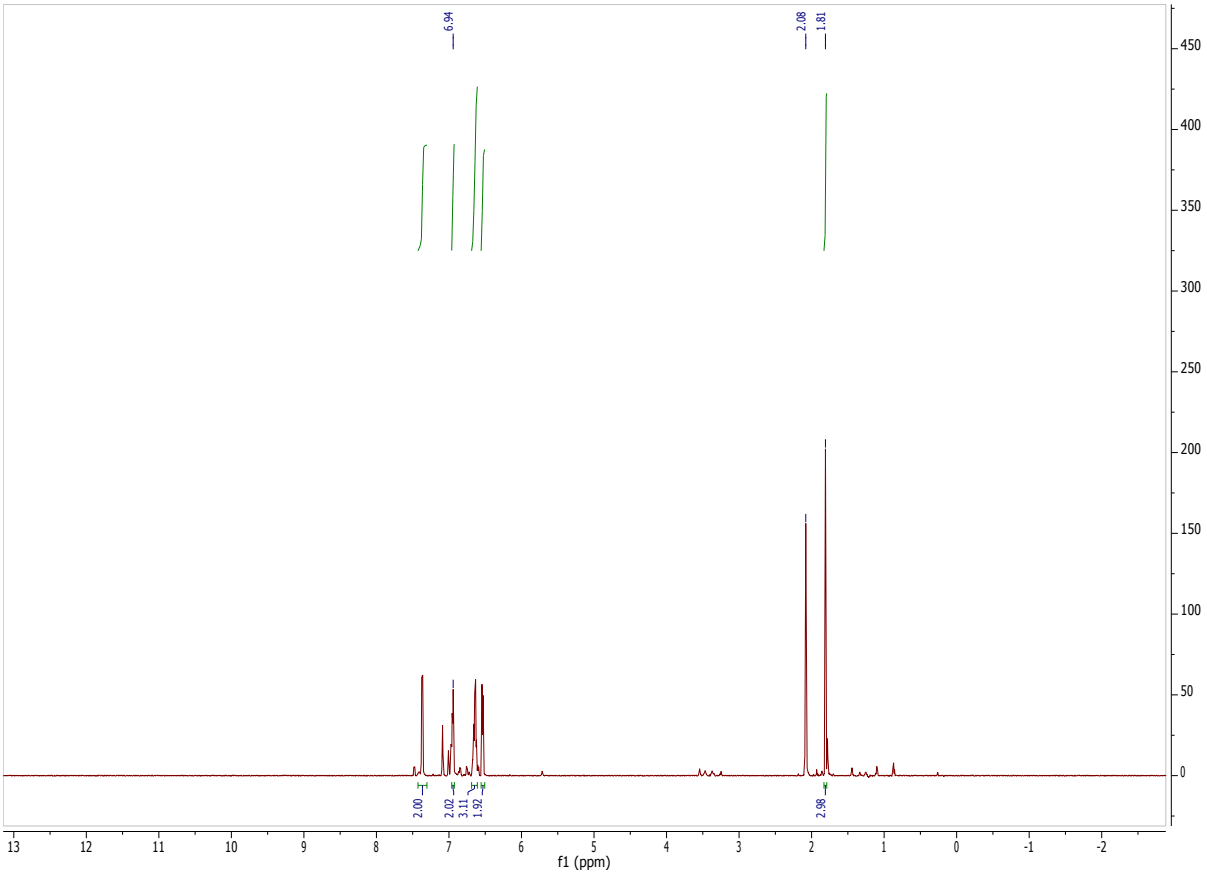
^{19}F


-133.42
-137.99
-154.59
-156.70
-163.83
-164.10
2.09
1.85
1.03
1.87
5.74
f1 (ppm)

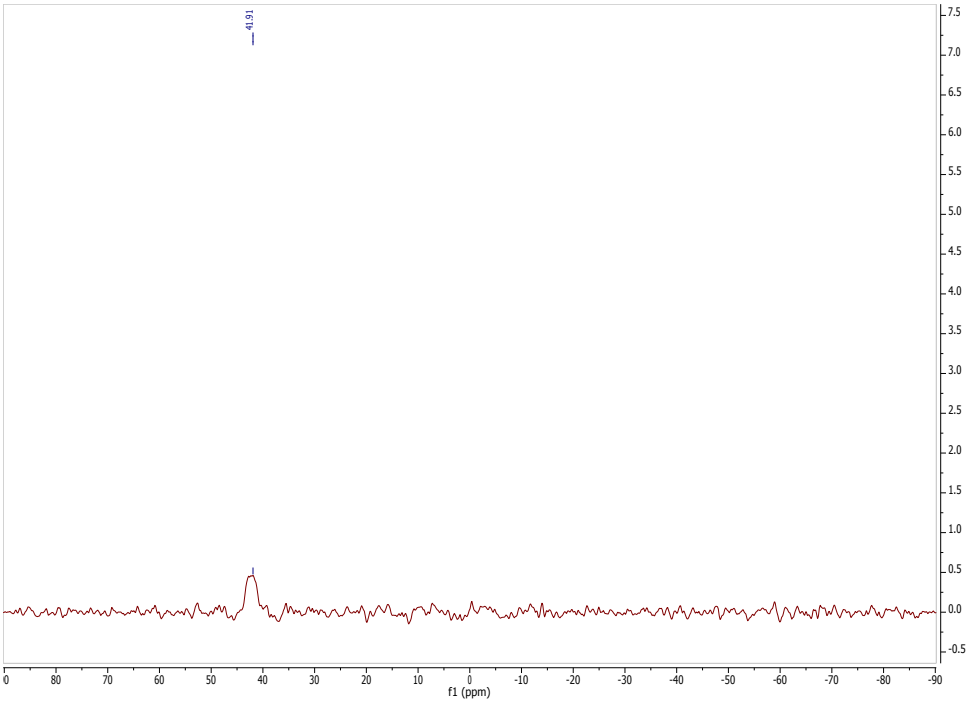
^{31}P



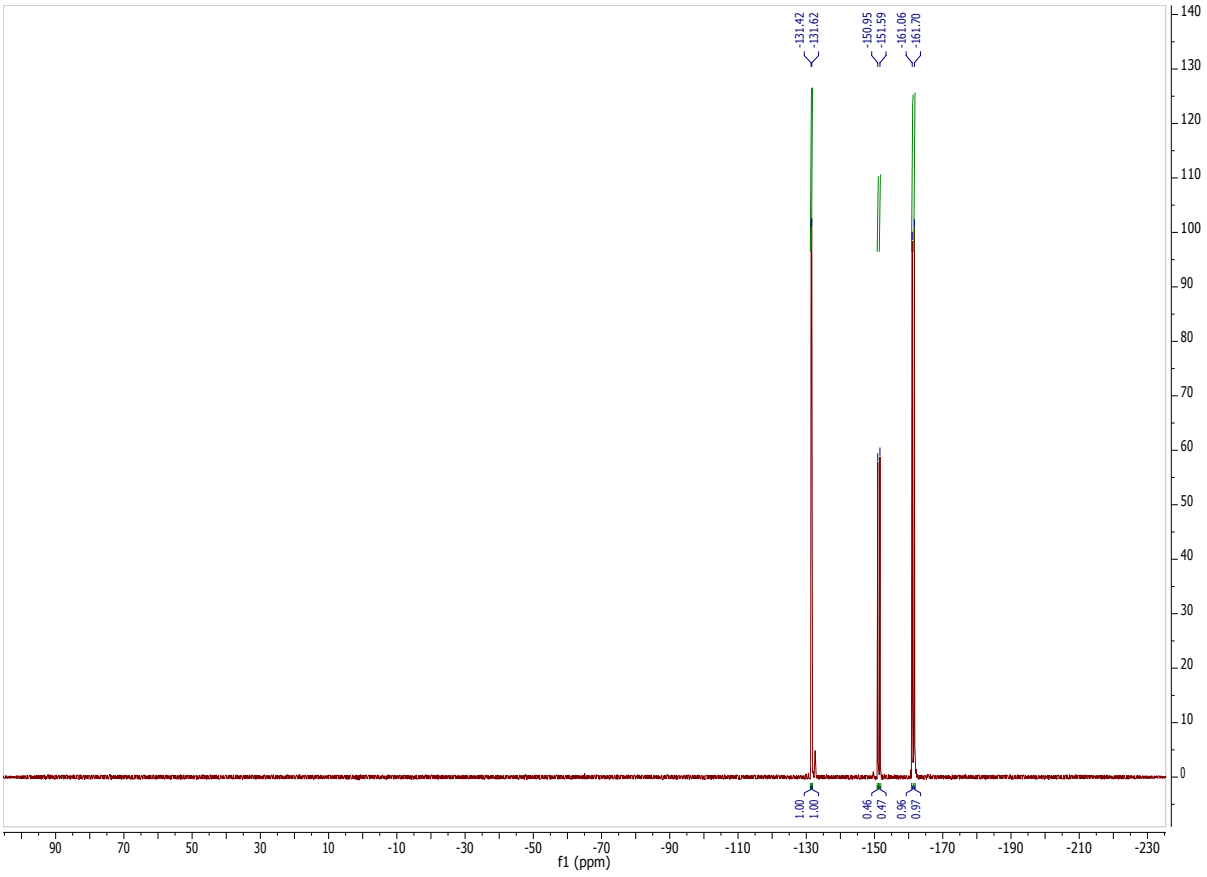
$(C_6F_5)_2BN(Ph)Ts$ **3** ^{1}H



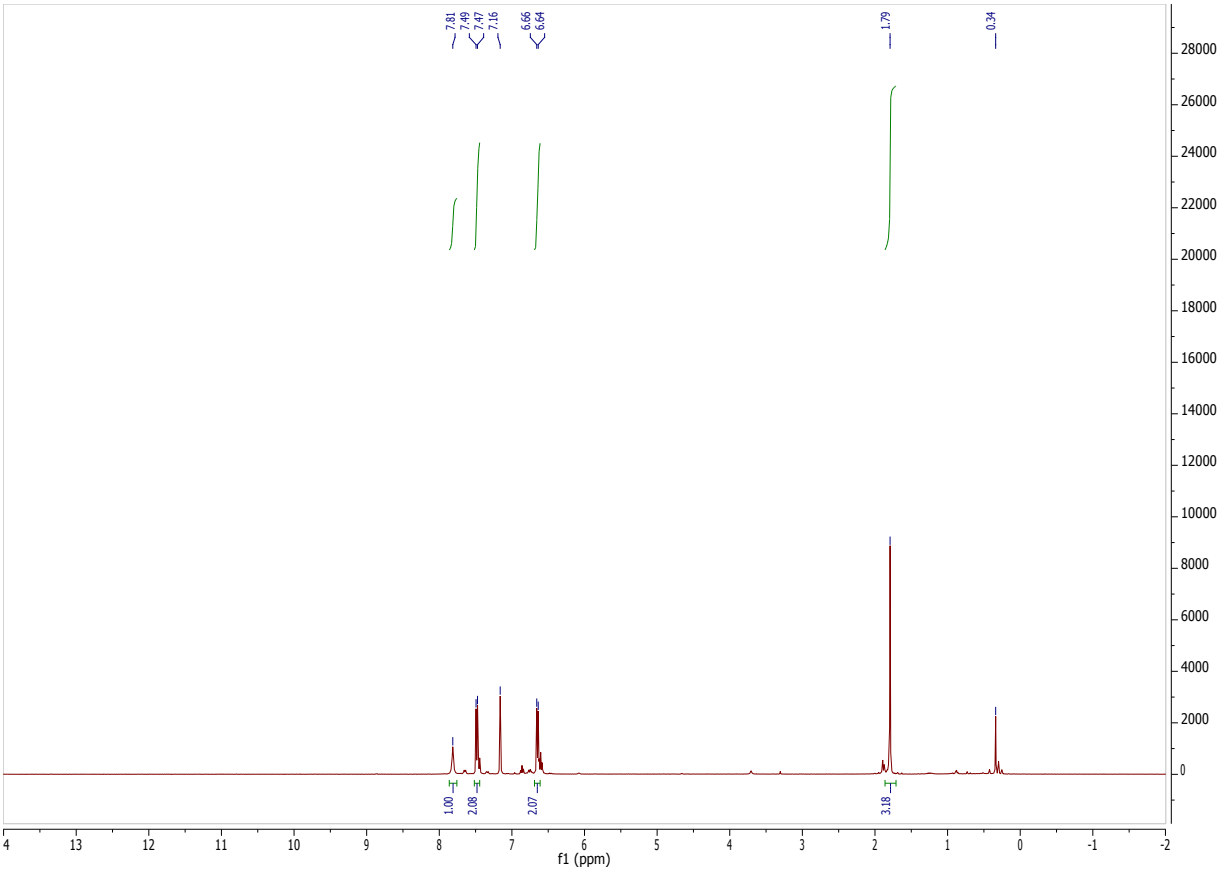
^{11}B


41.91
f1 (ppm)

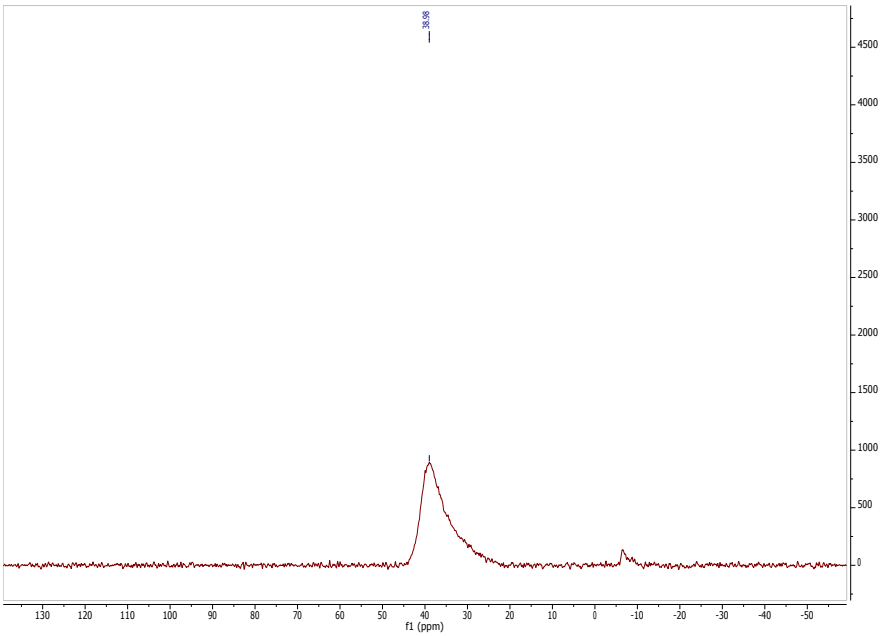
^{19}F


-131.42
-131.62
-150.95
-151.59
-161.06
-161.70
1.00
1.00
0.46
0.47
0.96
0.97
f1 (ppm)

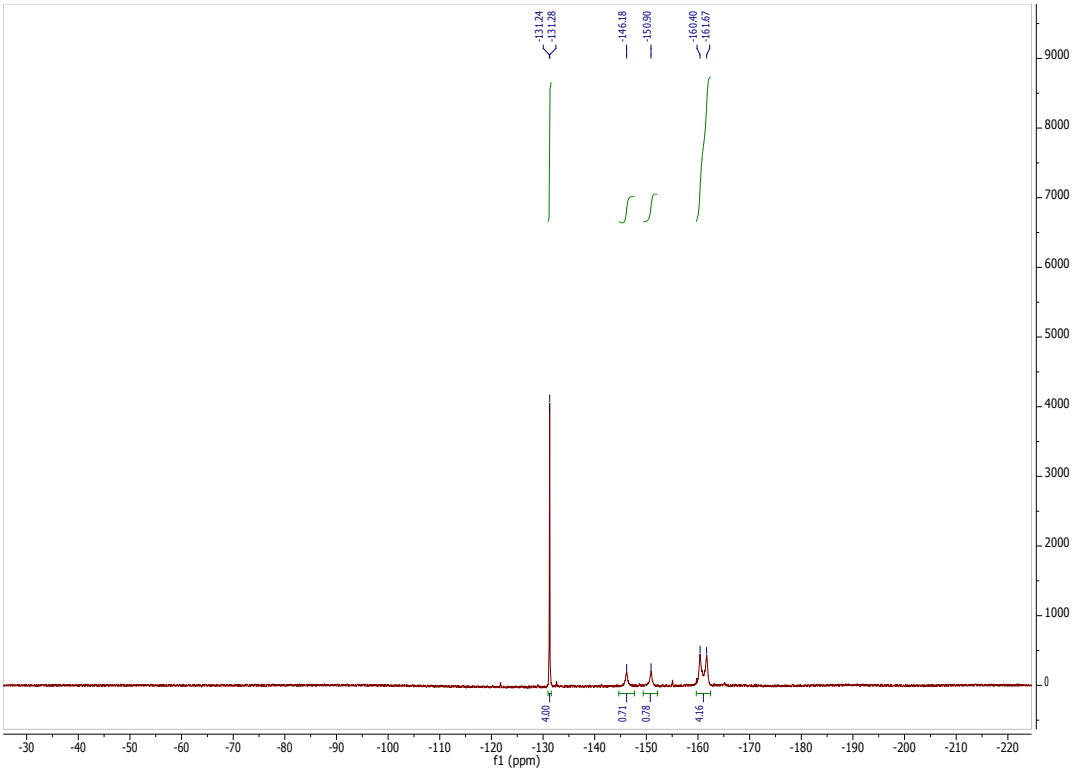
$(C_6F_5)_2BNH(Ts)$ **4** **^{1}H**



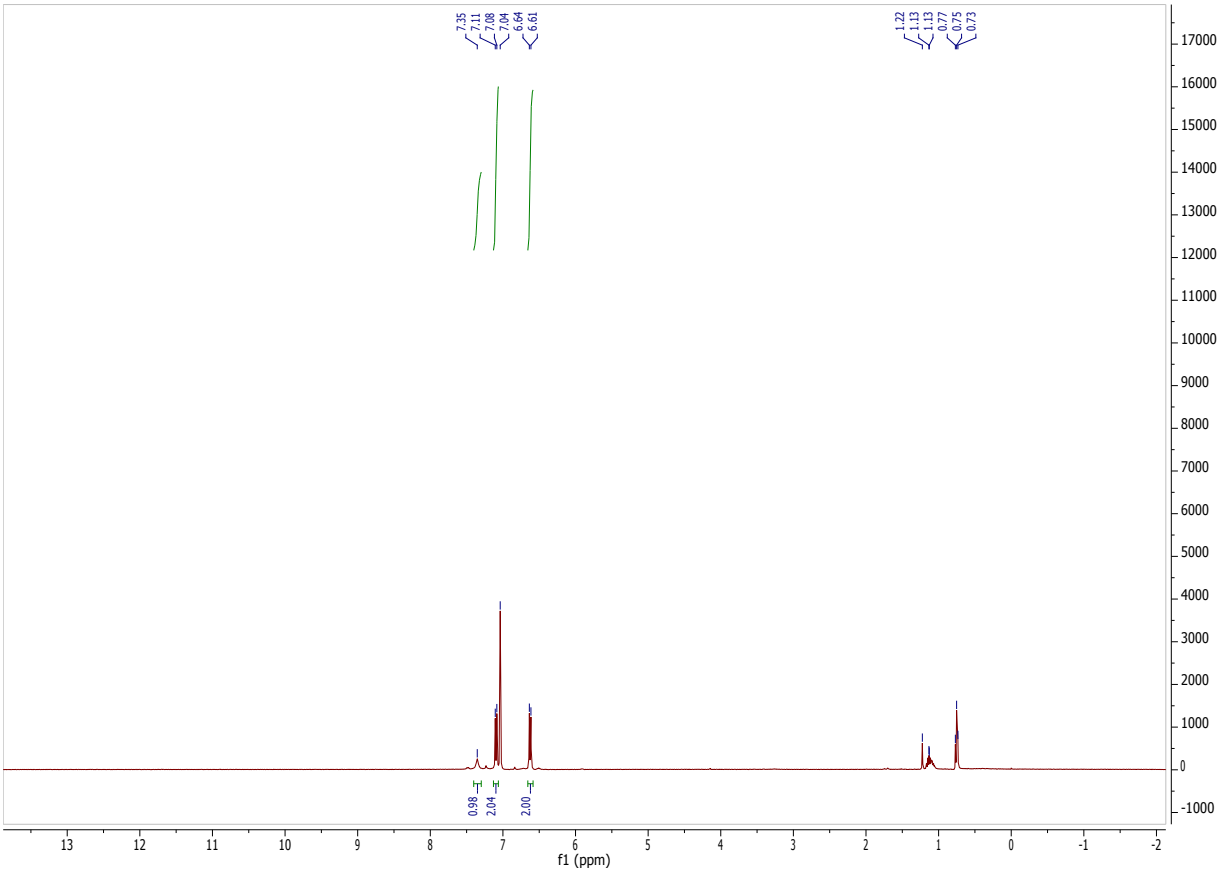
^{11}B



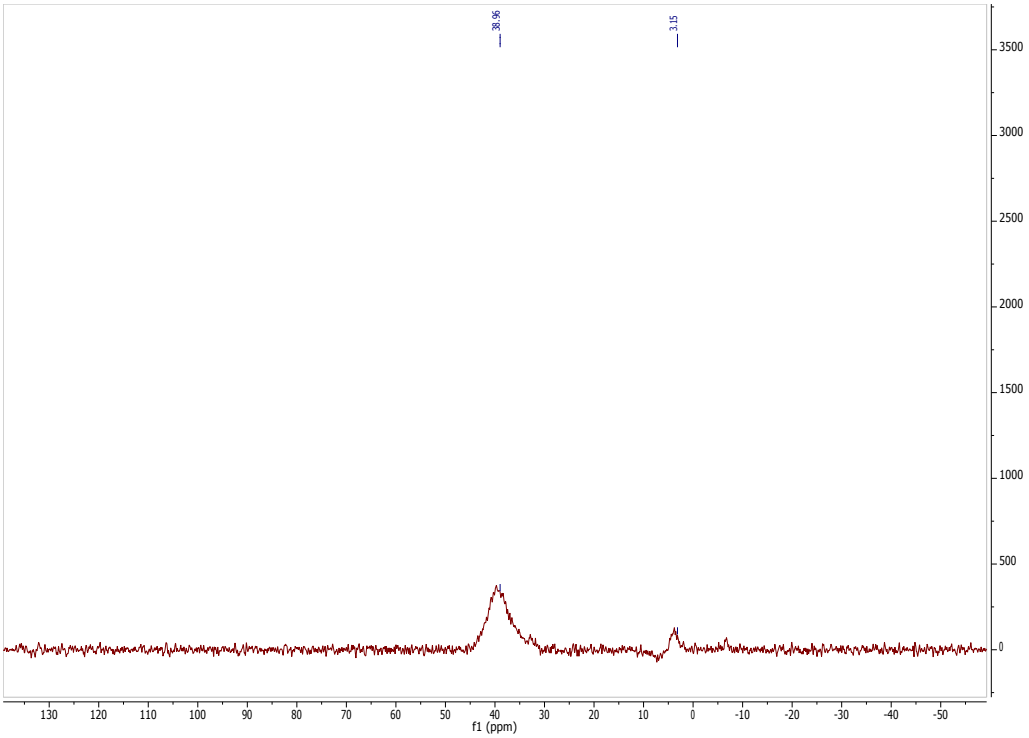
^{19}F



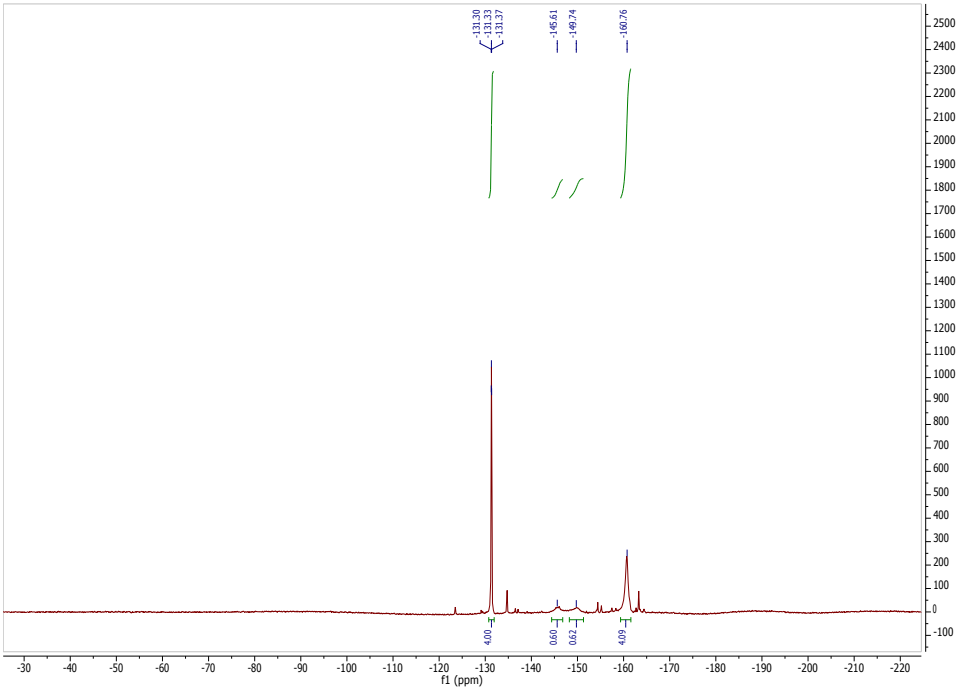
$(C_6F_5)_2BNH(Cls)$ **5** ^1H



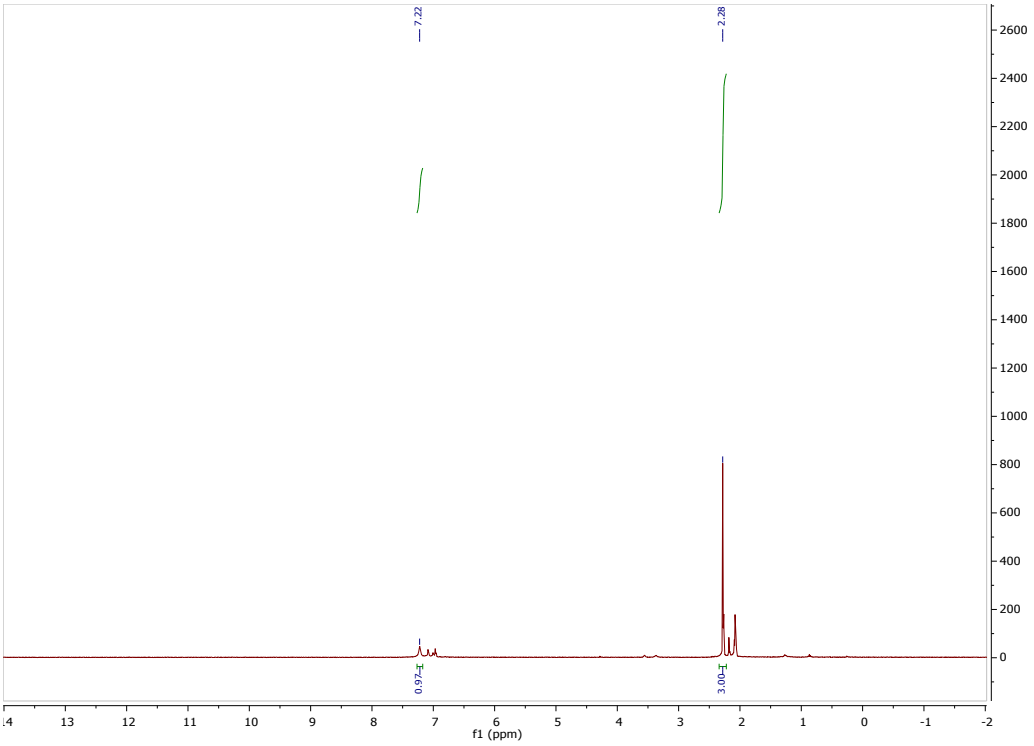
^{11}B


38.96
3.15
f1 (ppm)

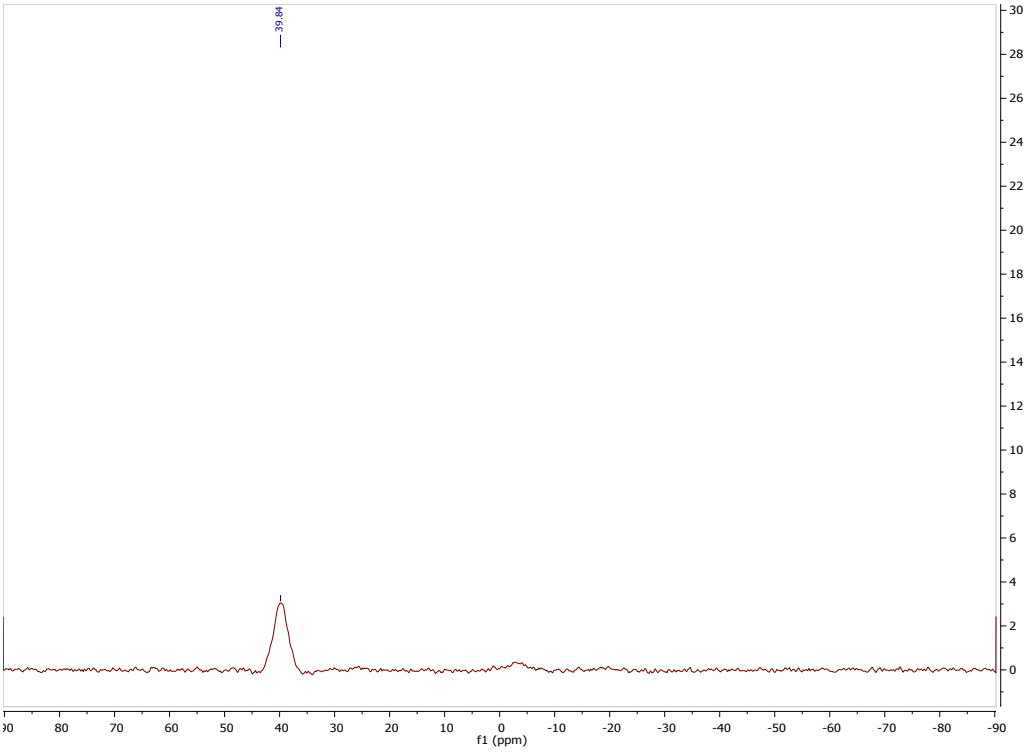
^{19}F

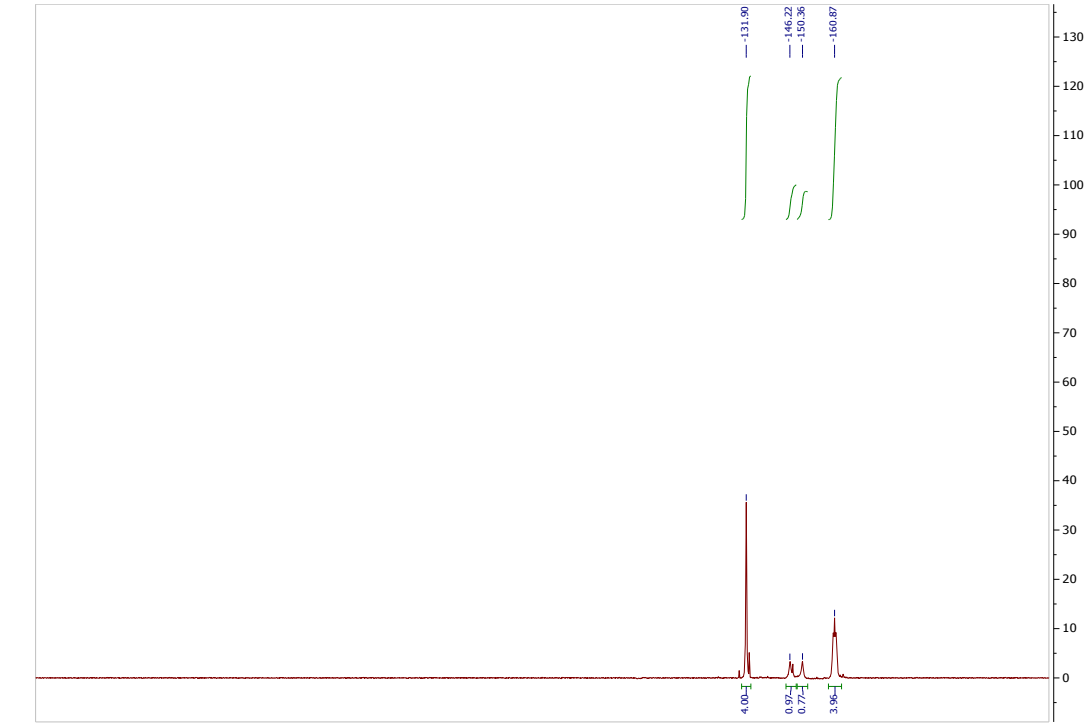

-131.30
-131.33
-131.37
-145.61
-149.74
-160.76
4.00
0.60
0.62
4.09
f1 (ppm)

$(C_6F_5)_2BNH(Ms)$ **6** ^1H



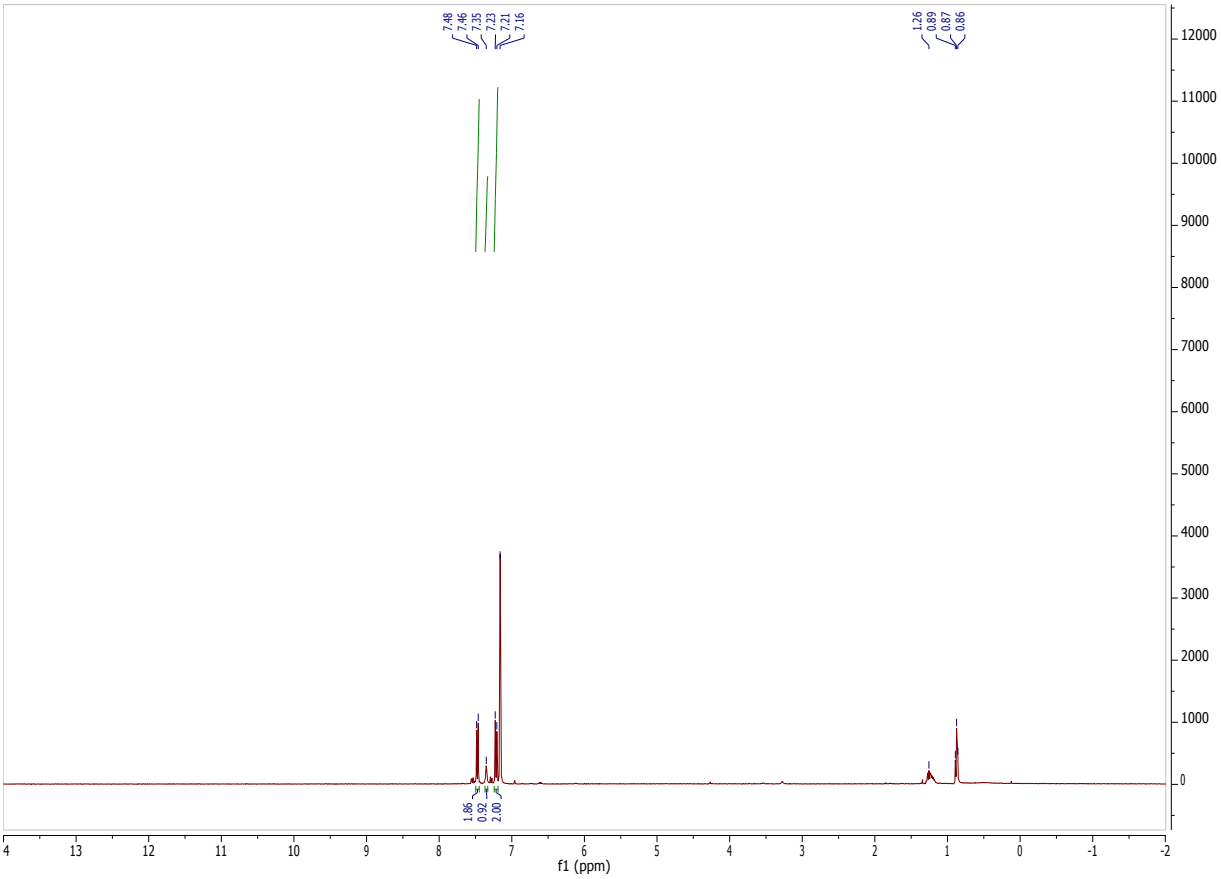
^{11}B



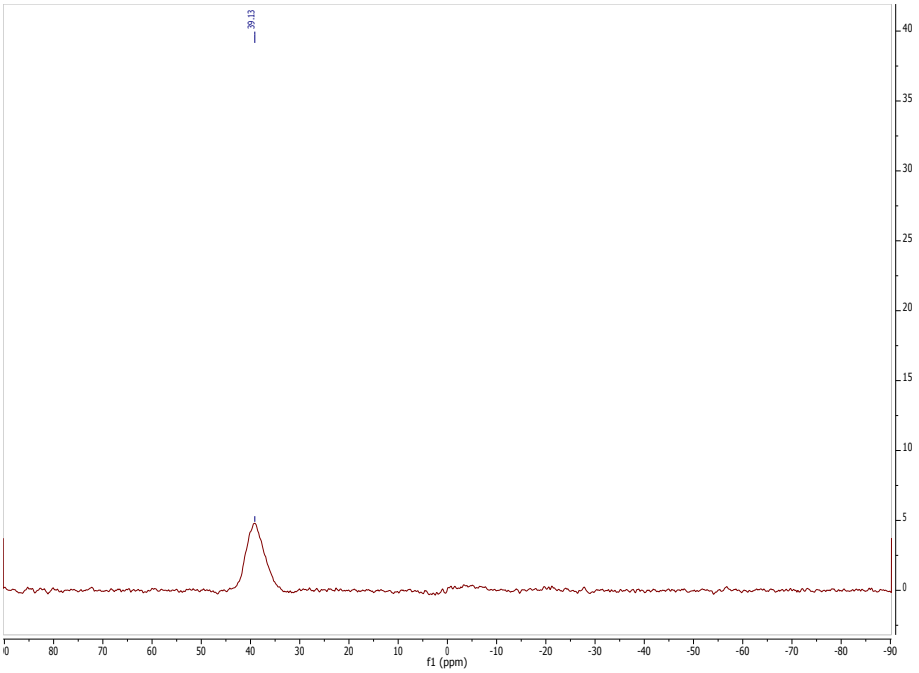


^{19}F

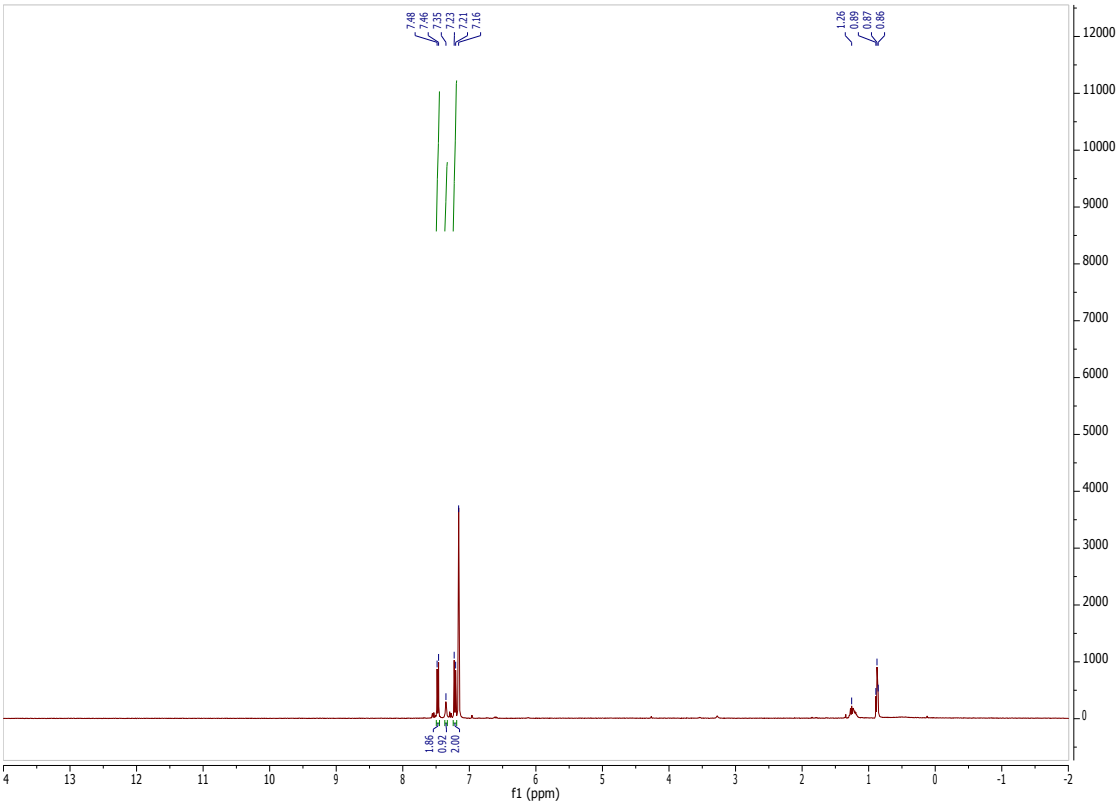
$(C_6F_5)_2BNH(Ns)$ **7** ^{1}H



^{11}B


39.13
f1 (ppm)

^{1}H


7.48
7.46
7.35
7.23
7.21
7.16
1.26
0.89
0.87
0.86
1.86
0.92
2.00
f1 (ppm)