Supporting Information

One-pot Synthesis of Ammonia-Borane and Trialkylamine-Boranes from Trimethyl Borate

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General Information

Unless otherwise noted, all manipulations were carried out under inert atmosphere in flame-dried glassware cooled under nitrogen. All solvents for routine isolation of products and chromatography were reagent grade. Flash chromatography was performed using silica gel (100−200 mesh) with indicated solvents. Thin-layer chromatography carried out on 0.25 mm silica plates (60F-254) using UV light as visualizing agent. ^{11}B, ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded either on 400 MHz or on 300 MHz NMR spectrometer. Chemical shifts, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz (Hz) and number of protons. Flash chromatography was performed using silica gel 40-63 um, 60 Å and hexane-ethyl acetate mixture as eluent. Anhydrous THF was prepared by distillation over sodium benzophenone ketyl. Sodium borohydride and all of the ammonium salts were purchased from commercial sources and used as such. Trimethyl borate and all liquid amines were freshly distilled before the use.

Preparation of AB from $B(OMe)_3$ using LiH:

Trimethyl borate (0.5 g, 0.0048 moles) was added, under nitrogen atmosphere, to a suspension of lithium hydride (0.170 g, 0.04 mol) and ammonium chloride (0.518 g, 0.0096 mol) in THF (12 mL). Under vigorous stirring, aluminum chloride (0.769 g, 0.0057 mol) in THF (12 mL) was added, dropwise, over a period of 10 min at RT. The

reaction mixture was stirred at the same temperature for 3 h and was monitored by ^{11}B NMR spectroscopy (change in chemical shift from δ (ppm): +19 (s) to -21.6 (q)). The solvent was distilled under reduced pressure at RT to obtain a powdery solid residue, which was suspended in cold diethylether at 0° C and stirred for 30 min. The cold ether layer was filtered and the solvent was removed *in vacuo* to obtain 0.10 g (68%) of AB as a white crystalline solid in >99% purity. ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -21.66 (d, J = 99.7 Hz), mp 112-114 °C.

Preparation of AB from $B(OMe)_3$ using $LiAlH_4$: Trimethyl borate (0.5 g, 0.0048 mol) was added under nitrogen atmosphere to a suspension of ammonium chloride (0.518 g, 0.0096 mol) in THF (24 mL) at 0° C. Under vigorous stirring, lithium aluminum hydride (0.23 g, 0.0057 mol) in THF (12 mL) was added, dropwise, over a period of 1 h at the same temperature. The reaction mixture was warmed to room temperature and stirred for 2 h. The ^{11}B NMR shows the formation of AB (δ (ppm): -21.6 (q)). The solvent was distilled under reduced pressure using cannula distillation at rt to obtain a powdery solid residue, which was suspended in cold diethylether at 0° C and stirred for 30 min. The cold ether layer was filtered and the solvent was removed *in vacuo* to obtain 0.133 g (90%) of ammonia-borane as a white crystalline solid in >99% purity.

Represantative procedure for the preparation of trialkylamine-boranes: Trimethyl borate (0.5 g, 0.0048 mol) was added, under nitrogen atmosphere at rt, to a suspension of lithium hydride (0.210 g, 0.0264 mol) and triethylamine (0.5 mL, 0.0036 mol) in THF (10 mL) contained in an oven-dried round bottom flask. The reaction mixture was stirred for 1 h and was monitored by ^{11}B NMR spectroscopy (change in chemical shift from d (ppm): +19 to +3). (**Note**: Depending on the vigour of stirring this may take up to 4 h.) Aluminum chloride (0.960 g, 0.0072 mol) dissolved in THF (10 mL) was then added, dropwise, over a period of 1 h at 0 °C, and the stirring was continued at rt until the reaction was judged complete by ^{11}B NMR spectroscopy (chemical shift δ (ppm): -13.3) (q)). The solvent was removed under reduced pressure and the residue was stirred with anhydrous pentane for 1 h, filtered through celite under nitrogen atmosphere and the solvent was removed carefully *in vacuo* to obtain triethylamine-borane complex.

Notes:

1. For the preparation of diazabicylco[2,2,2]octyl monoborane, 0.0048 mol of diazabicylco[2,2,2]octane was used.

2. All other amine-boranes except triethylamine-borane and *N*,*N*-diisopropylethylamine-borane were extracted using dichloromethane.

3. The purity of LiH and $AlCl_3$ is crucial for the optimal yield of the amine-borane.

4. As this is heterogeneous reaction, it is very important to stirr the reaction vigorously to to get the desired yields.

5. No residual aluminum was observed in amine-boranes as determined by ^{27}Al-NMR sectoscopy.

Triethylamine borane (Et_3N-BH_3):[1]

Colorless liquid, 289 mg, 70%.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.79 (q, *J* = 7.3 Hz, 6H), 0.75-2.00 (broad q, BH_3), 1.19 (t, *J* = 7.3 Hz, 9H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 52.1, 8.3.; ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -13.32 (q, *J* = 95.0 Hz).

***N,N,*-diisopropylethylamine borane (DIPEA-BH_3):**[2]

Colorless liquid, 375 mg, 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.44 (dt, *J* = 13.4, 6.7 Hz, 2H), 2.89 (q, *J* = 7.3 Hz, 2H), 1.90-1.05 (broad q, BH_3), 1.30 (d, *J* = 6.7 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.14 (t, *J* = 7.3 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 56.5, 47.4, 18.7, 18.3, 9.9.; ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -13.49 (q, *J* = 103.6 Hz).

4-Dimethylaminopyridine borane (DMAP-BH_3):[3]

White solid, 352 mg, 72%. mp 17 °C.

1. Matsumura S.; Tokura, N. *Tetrahedron Lett.* **1968**, 4703.
2. Brown, H. C.; Zaidlewicz, .; Dalvi, P. V.; Narasimhan, S.; Mukhopadhyay, A. *Organometallics* **1999,** *18,* 1305.
3. Lesley, M. J. G.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, Duncan W.; Kakkar, A. K. *Chem. Mater*. **1998**, *10*, 1355.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 7.3 Hz, 2H), 6.56 – 6.28 (m, 2H), 3.01 (s, 6H), 2.31 (broad q, BH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 154.3, 146.3, 106.1, 39.2; ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -13.74 (q, *J* = 103.3 Hz).

2,6-Lutidine-BH_3:[4]

White solid, 322 mg, 74%. mp 108-110 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.64 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 2.80 (s, 6H), 1.6-3.0 (broad q, BH_3).; ^{13}C NMR (75 MHz,) δ (ppm): 158.4, 138.0, 124.6, 25.1.; ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -17.99 (q, *J* = 95.7 Hz).

2,4,6-Collidine-BH_3:[4]

White solid, 398 mg, 82%. mp 99-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.02 (s, 2H), 2.72 (s, 6H), 2.34 (s, 3H). 2.90-1.75 (broad q, BH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 157.5, 149.9, 125.4, 24.8, 20.6.; ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -18.45 (q, *J* = 103.3 Hz).

Diazabicylco[2,2,2]octyl bisborane (DABCO-$(BH_3)_2$):[5]

White solid, 402 mg, 80%. mp 320-328 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.71 (d, 12H), 1.74 – 0.74 (q, BH_3).; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 50.1; ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm): -11.01 (q, *J* = 105.2 Hz).

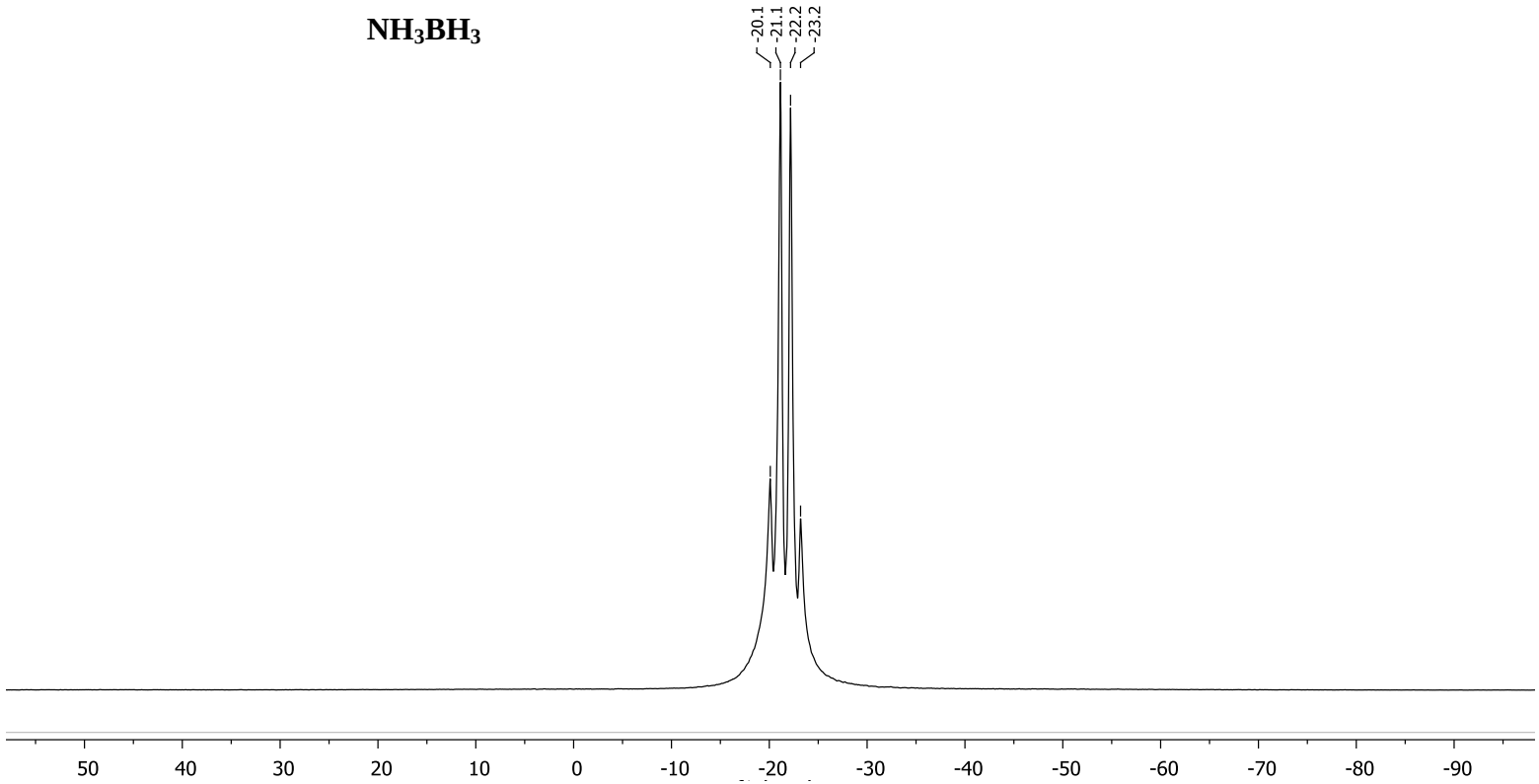
Procedure for large-scale preparation of 2,6-lutidine-borane

Trimethyl borate (20 g, 0.192 mol) was added, under nitrogen atmosphere at rt, to a suspension of lithium hydride (8.41 g, 1.058 mol) and 2,6-lutidine (15.46 g, 0.149 mol) in THF (400 mL) contained in an oven-dried round bottom flask equipped with overhead stirrer. The reaction mixture was stirred for 3 h and was monitored by ^{11}B NMR spectroscopy for the change in chemical shift from δ (ppm) 19 to 3. (**Note**: Depending on the vigour of stirrig this may need additional time). Aluminum chloride (35.5 g, 0.288

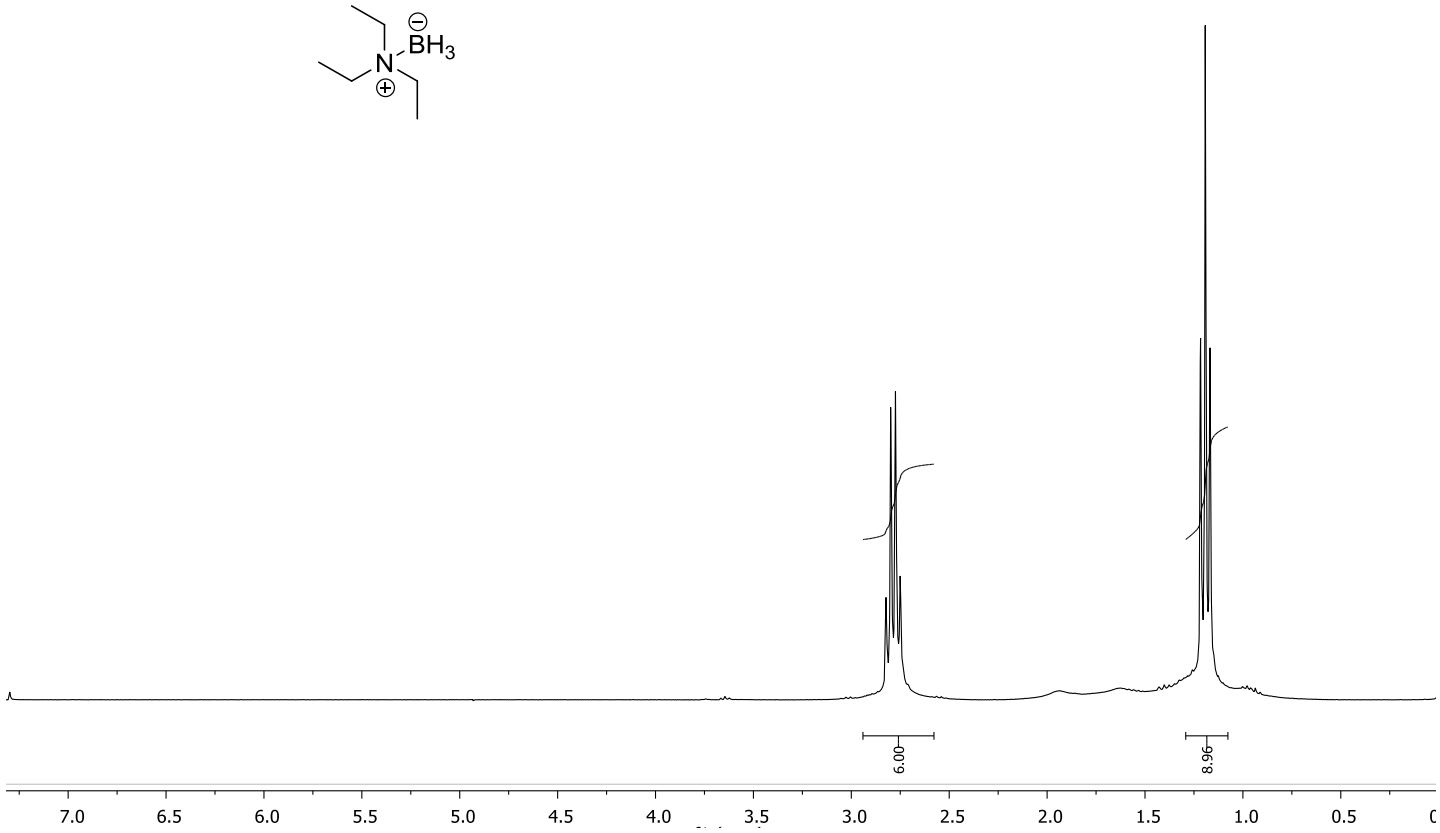
4. Ryschkewitsch, G. E.; Birnbaum, E. R. *Inorg. Chem*. **1965**, *4*, 575.

mol) dissolved in THF (400 mL) was then added, dropwise, over a period of 3 h at 0 °C, and the stirring was continued at rt until the reaction was complete, as determined by the change in ^{11}B NMR spectroscopic chemical shift to -13.3 (q). The solvent was removed under reduced pressure using cannula distillation and the obtained solid residue was stirred with anhydrous dichloromethane for 1 h, filtered through celite under nitrogen atmosphere and the solvent was removed *in vacuo* to obtain 2,6-lutidine-borane complex in 17.9 g (77% yield).

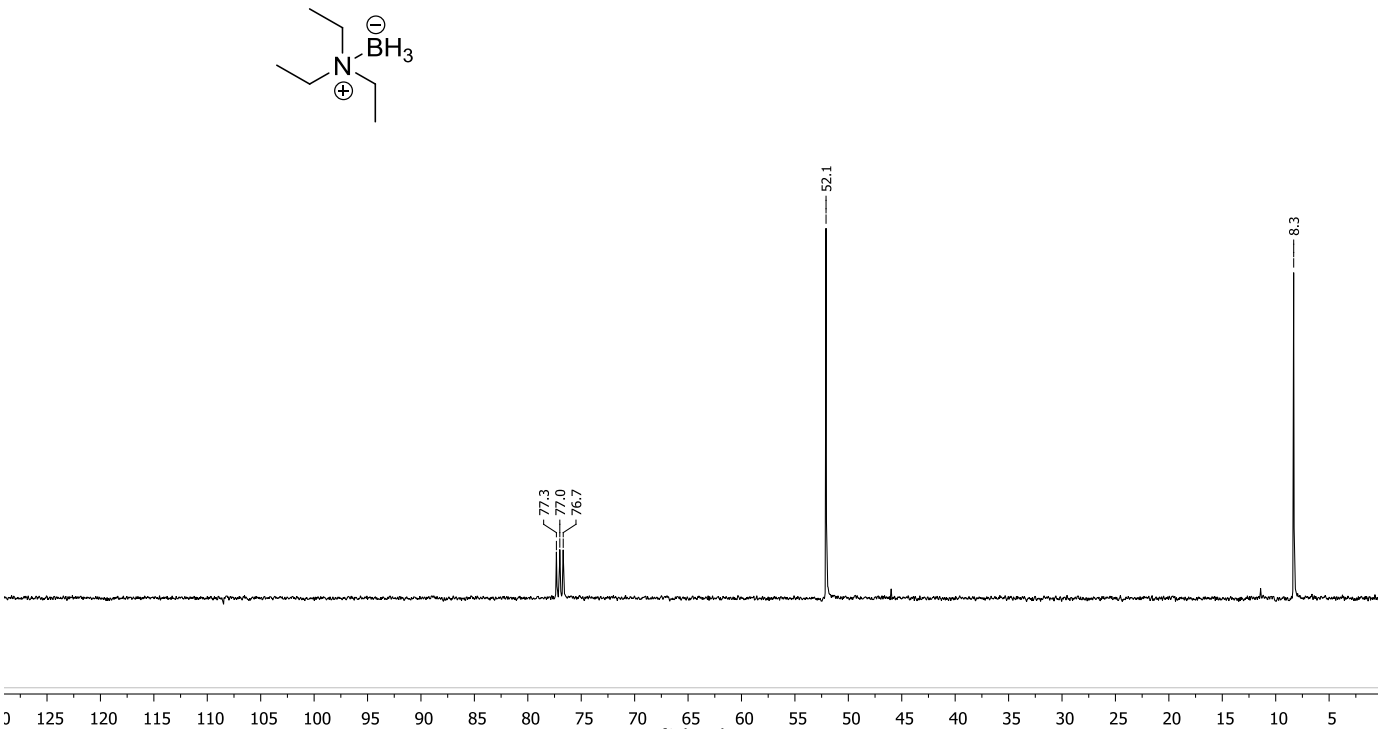
NMR Spectra



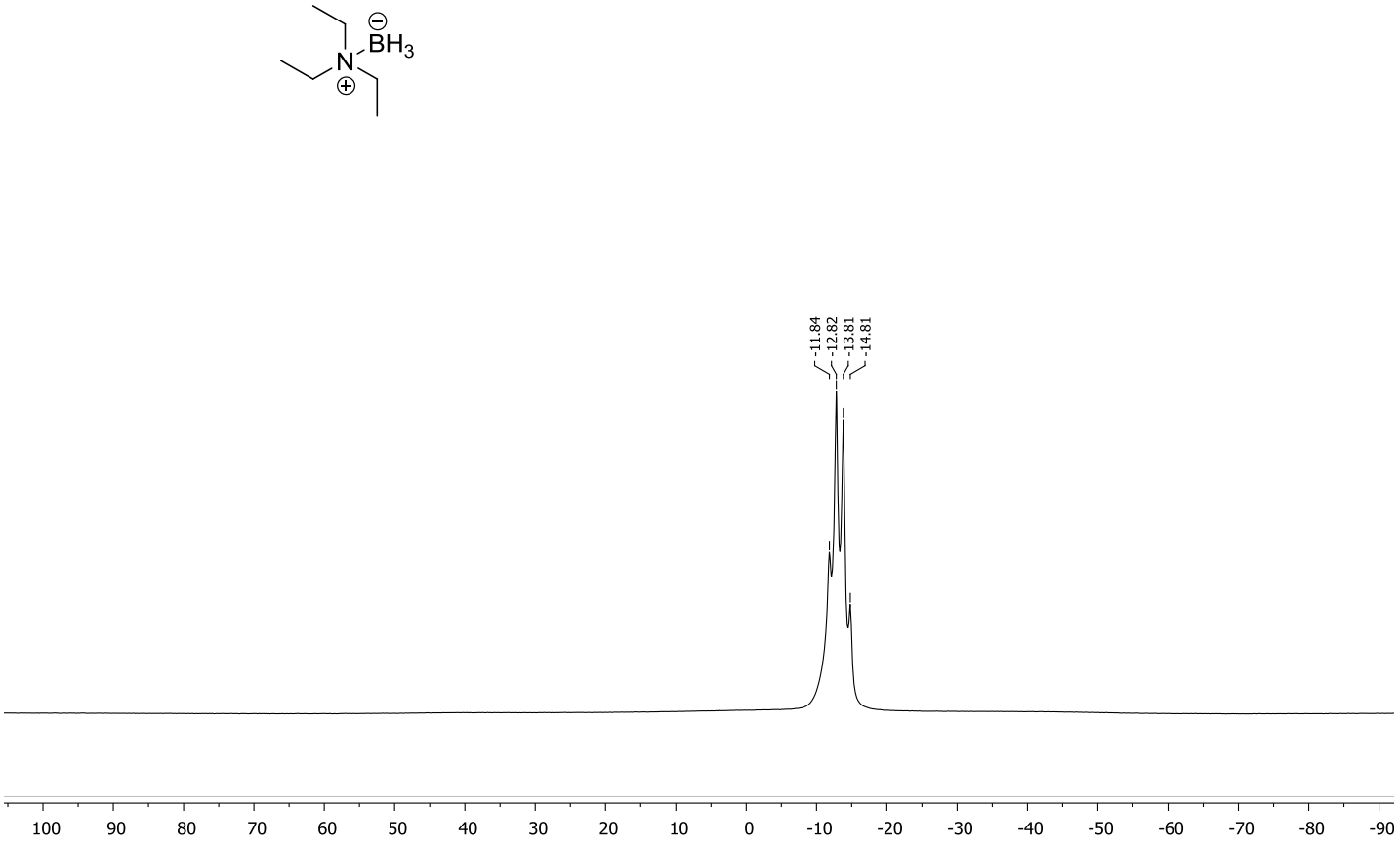
^{11}B NMR (96 MHz, $CDCl_3$) **NH_3-BH_3 (Table 2, Entry 1)**



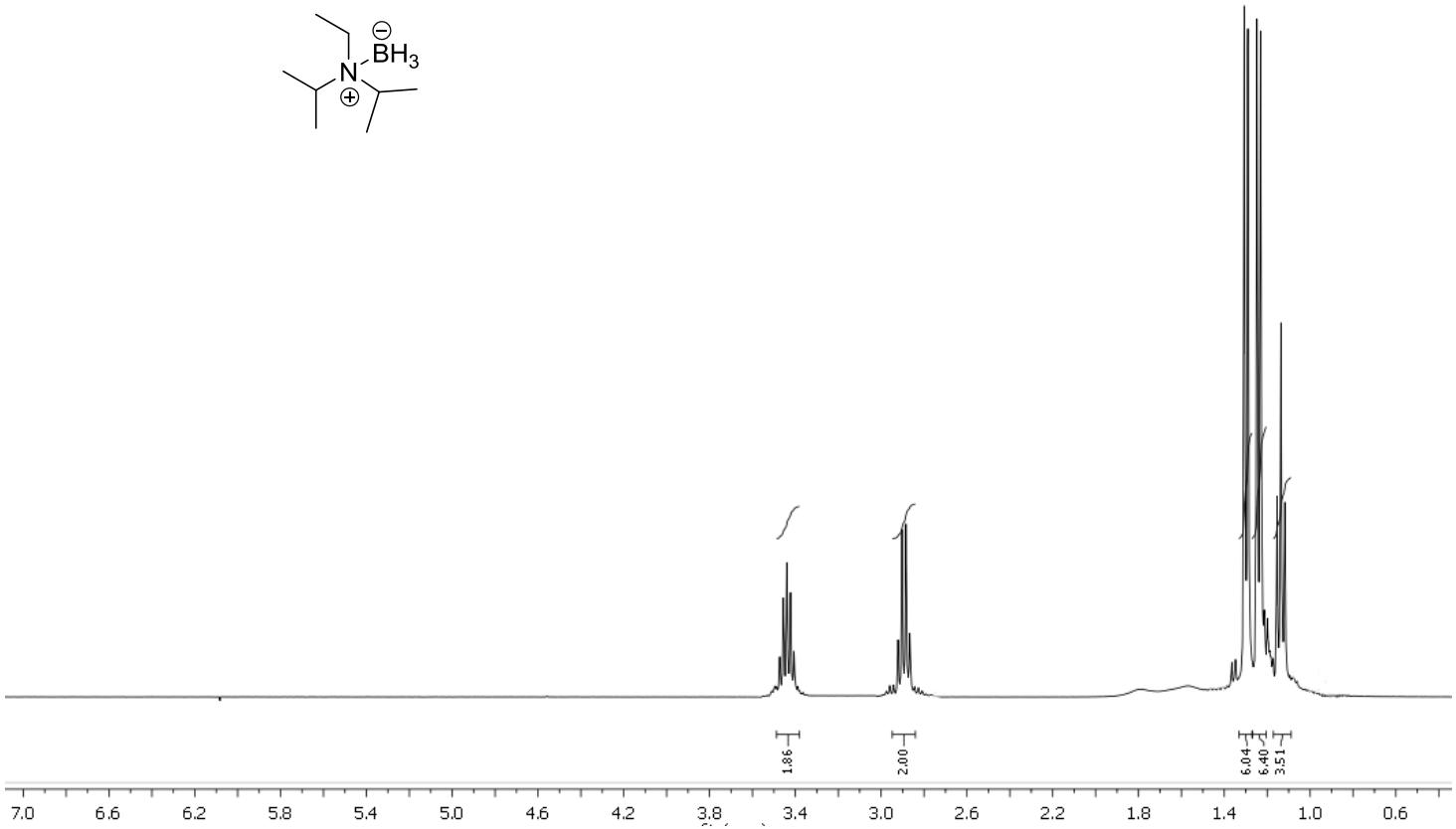
^{1}H NMR (300 MHz, $CDCl_3$) **Et_3N-BH_3 (Table 3, Entry 1)**



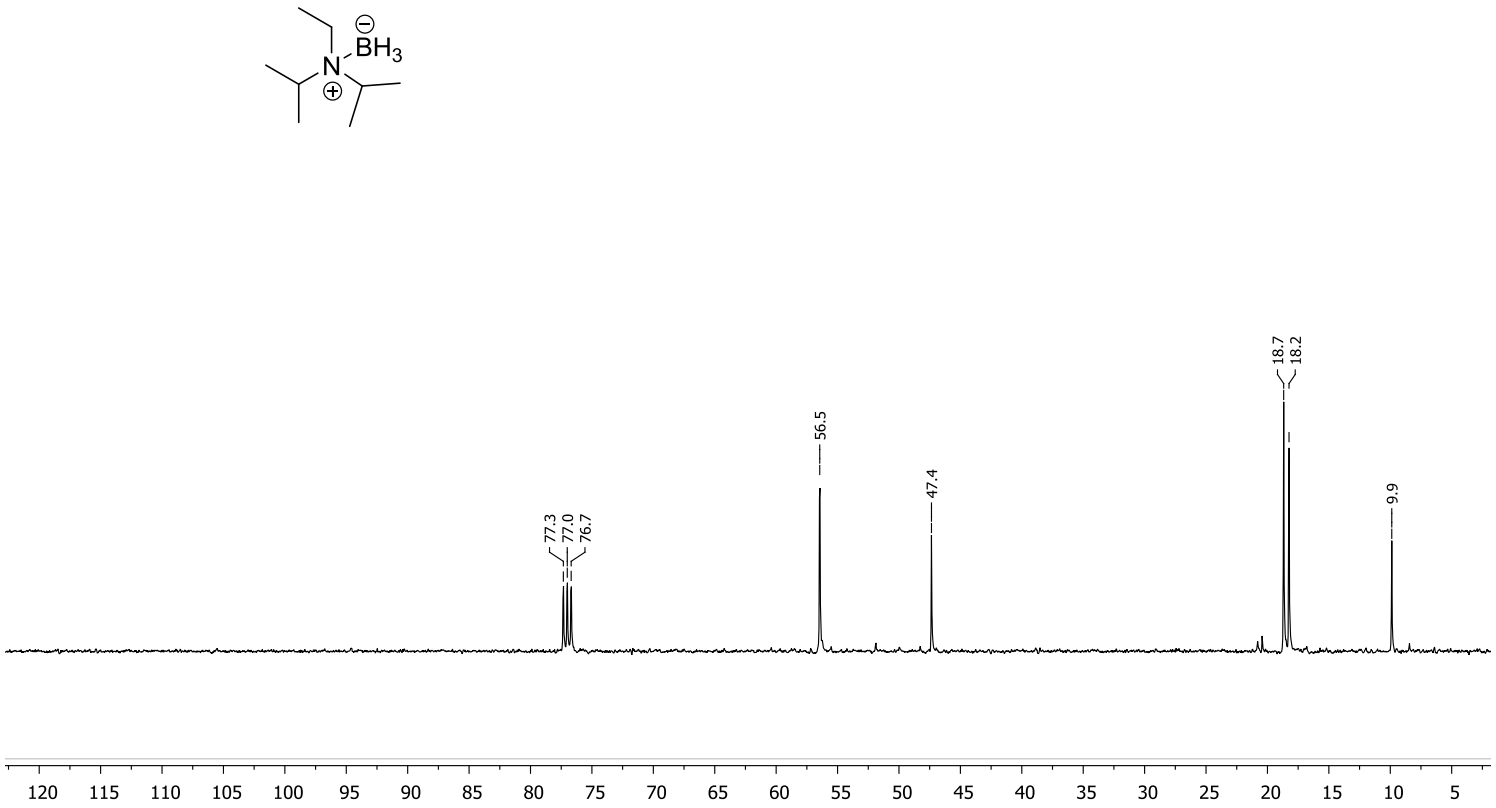
^{13}C NMR (101 MHz, $CDCl_3$) **Et_3N-BH_3 (Table 3, Entry 1)**



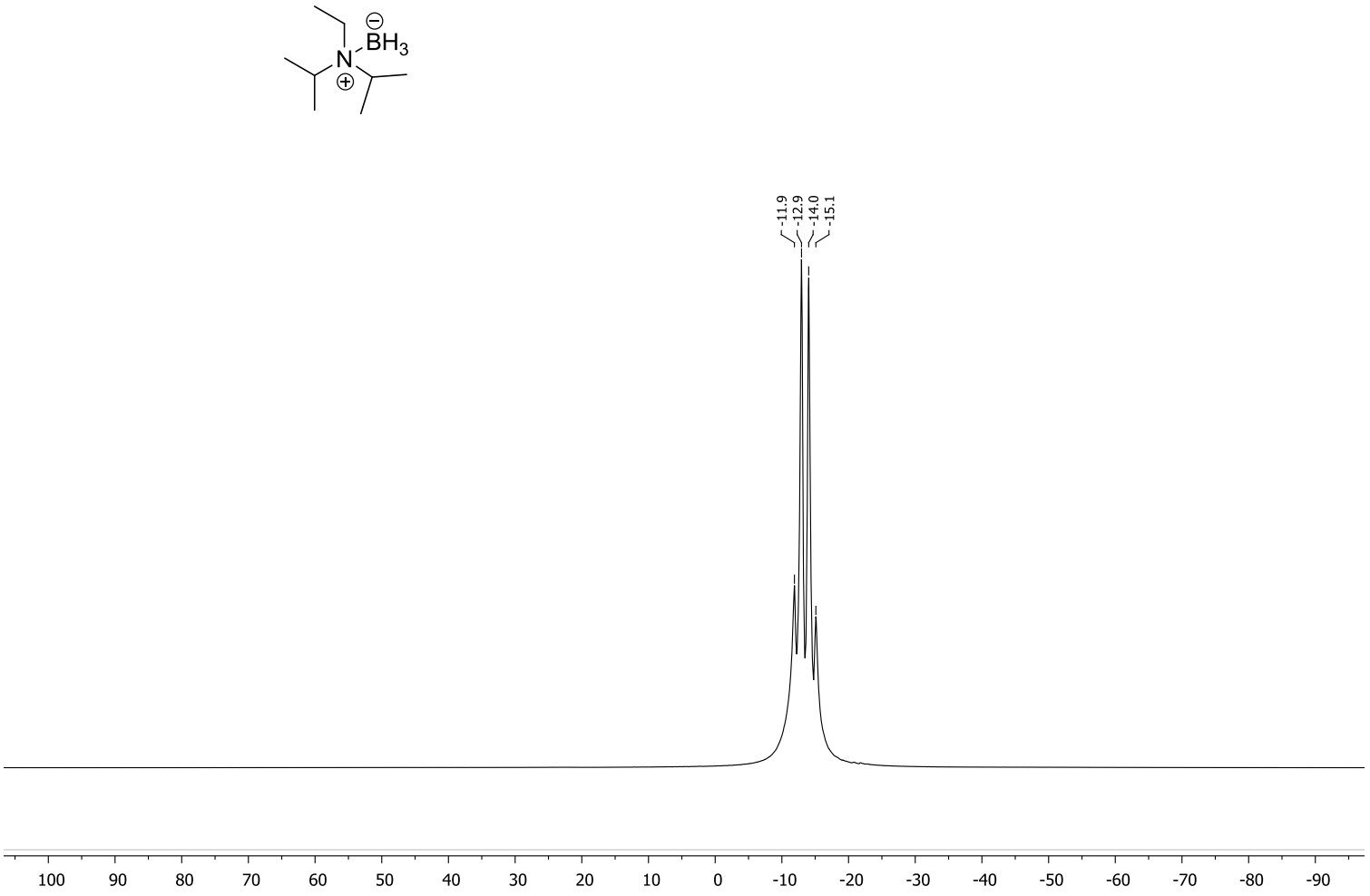
^{11}B NMR (96 MHz, $CDCl_3$) **Et_3N-BH_3 (Table 3, Entry 1)**



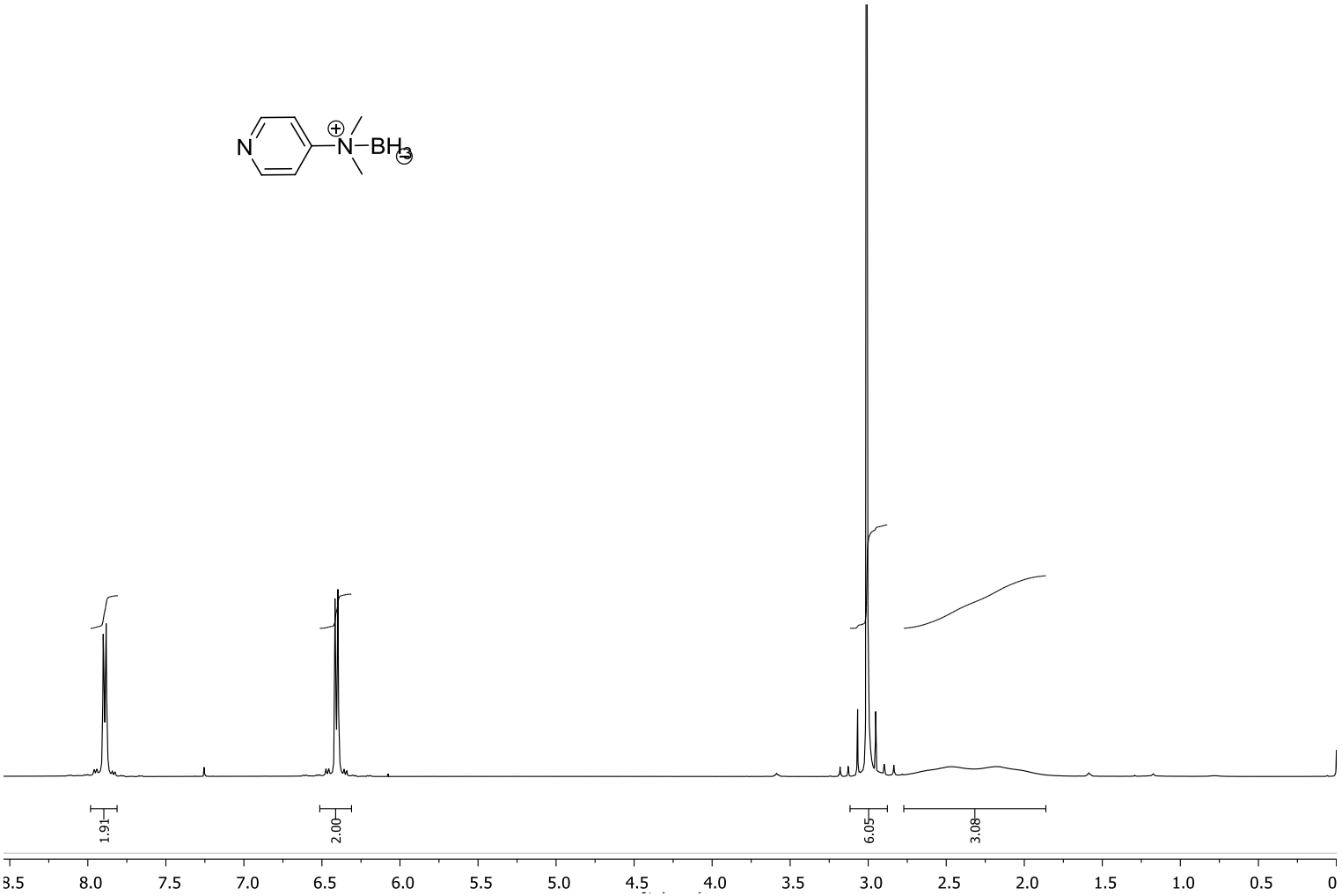
^{1}H NMR (400 MHz, $CDCl_3$) **DIPEA-BH_3 (Table 3, Entry 2)**



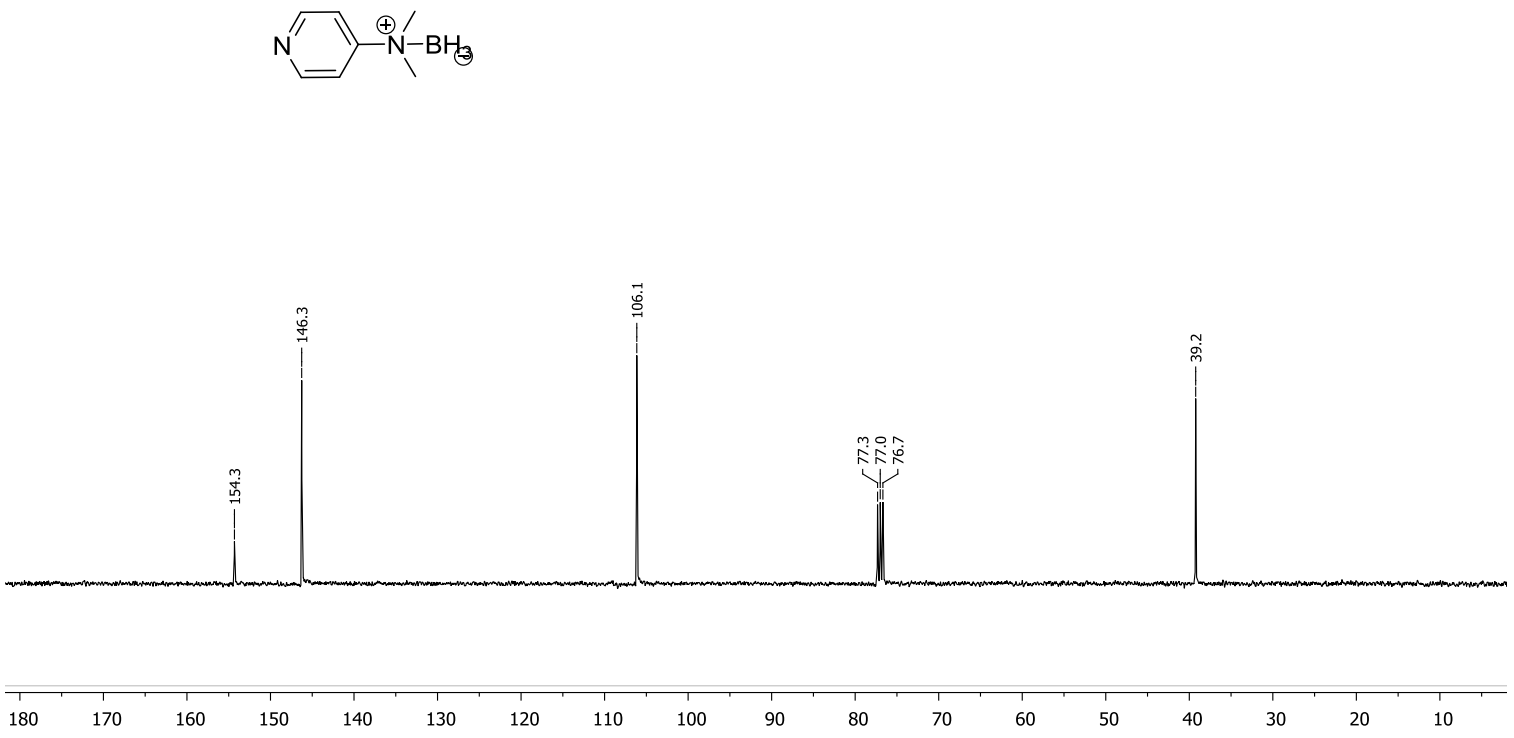
^{13}C NMR (101 MHz, $CDCl_3$) **DIPEA-BH_3 (Table 3, Entry 2)**



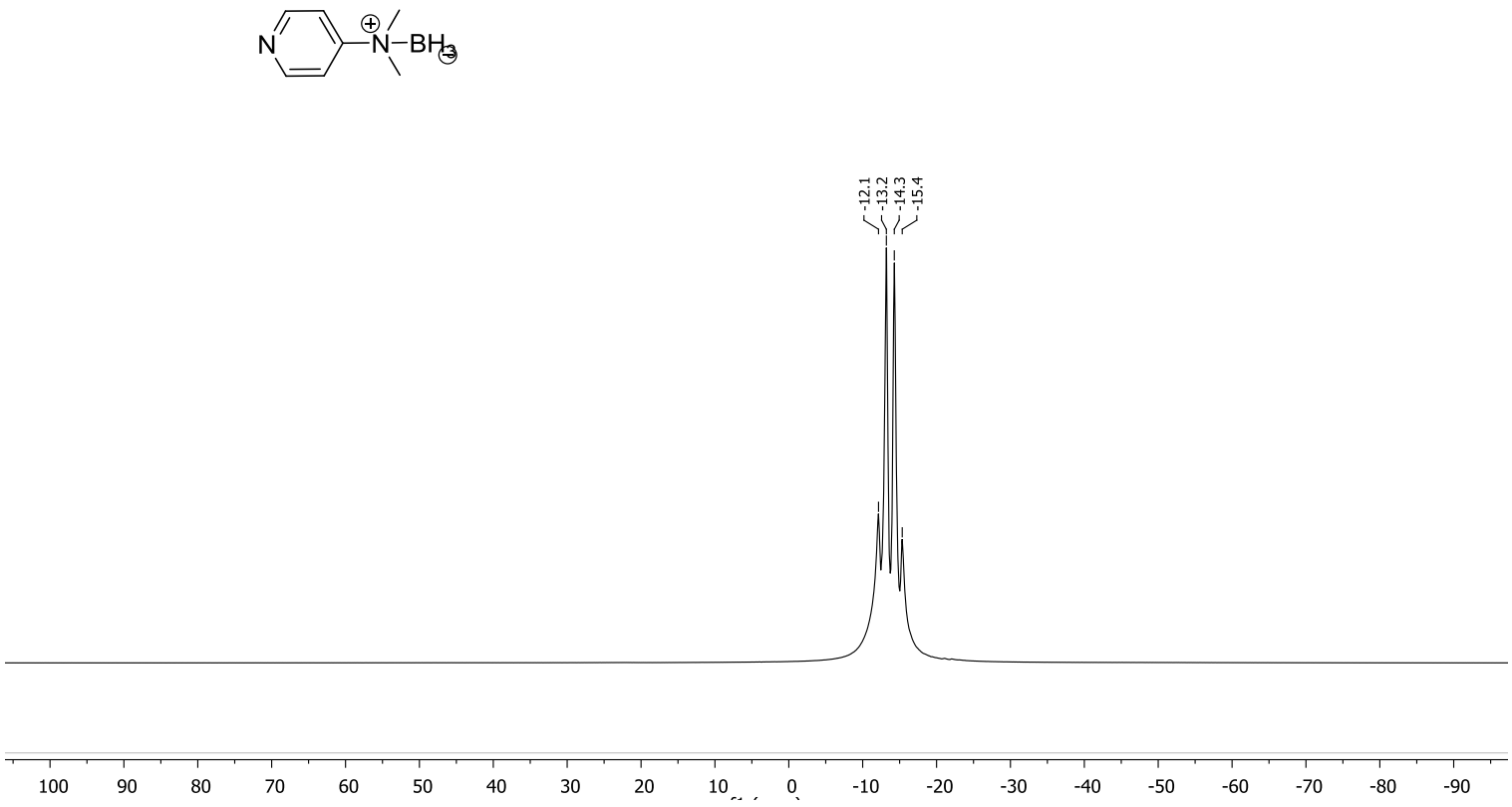
^{11}B NMR (96 MHz, $CDCl_3$) **DIPEA-BH_3 (Table 3, Entry 2)**



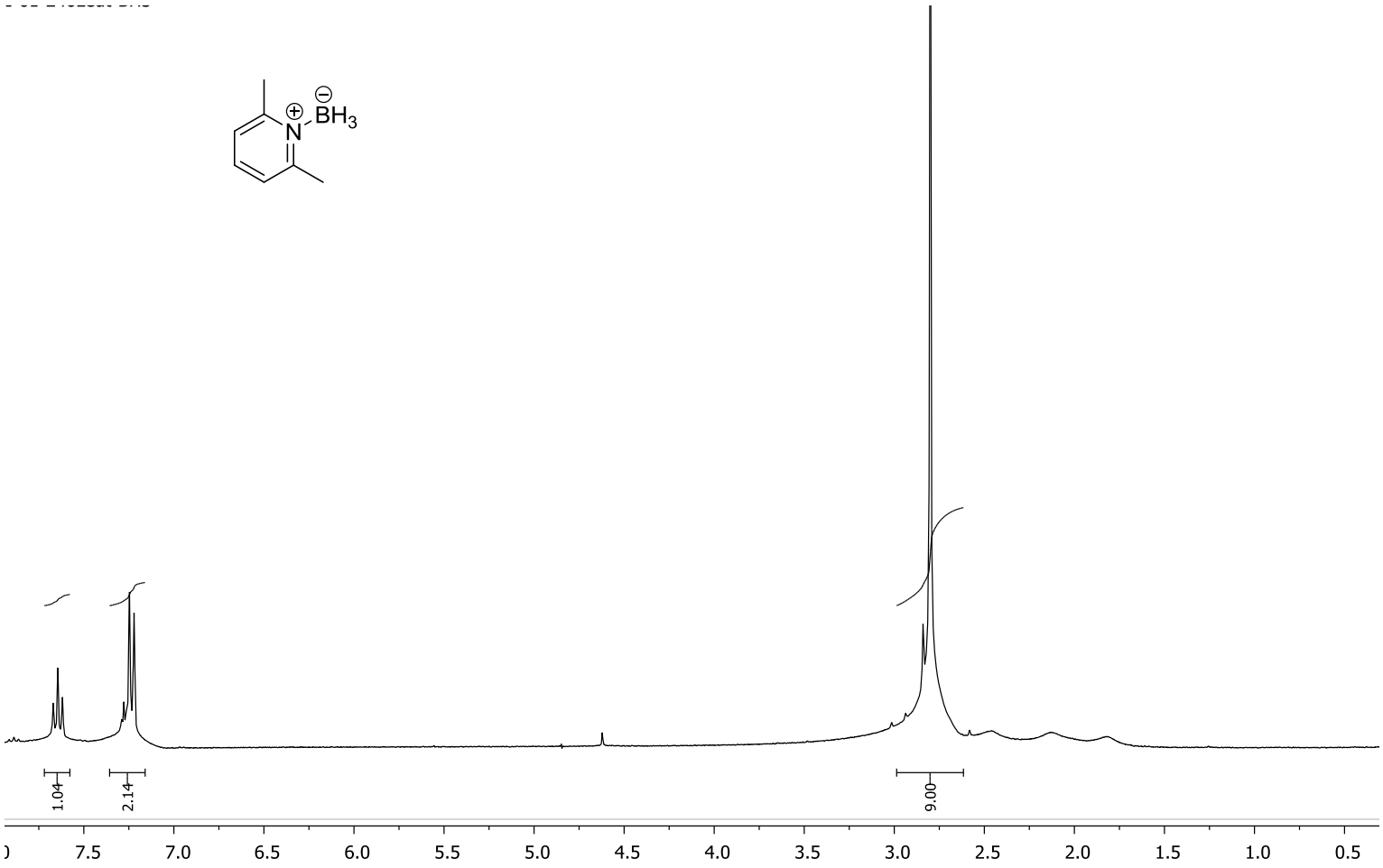
^{1}H NMR (400 MHz, $CDCl_3$) **DMAP-BH_3 (Table 3, Entry 3)**



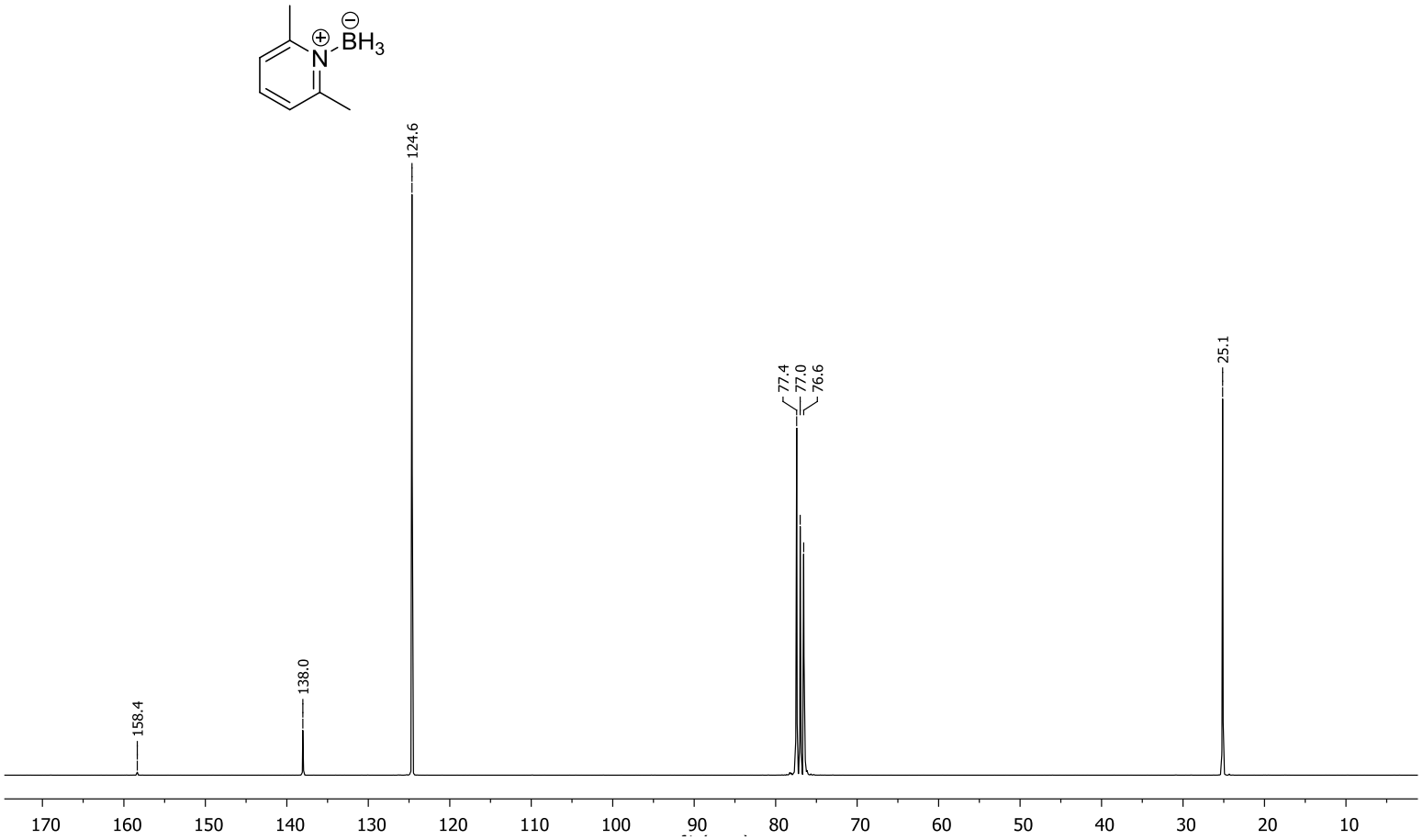
^{13}C NMR (101 MHz, $CDCl_3$) **DMAP-BH_3 (Table 3, Entry 3)**



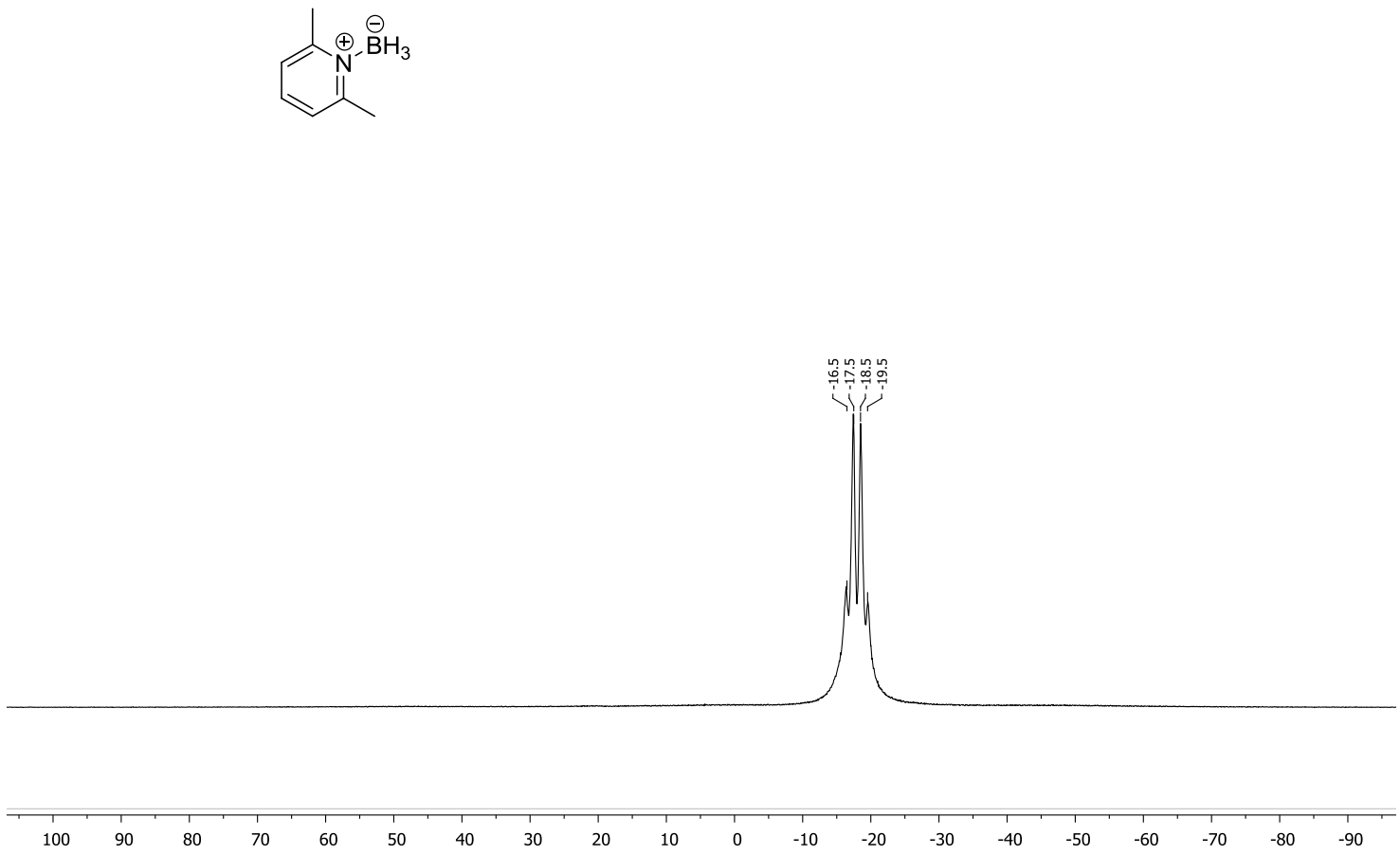
^{11}B NMR (96 MHz, $CDCl_3$) **DMAP-BH_3 (Table 3, Entry 3)**



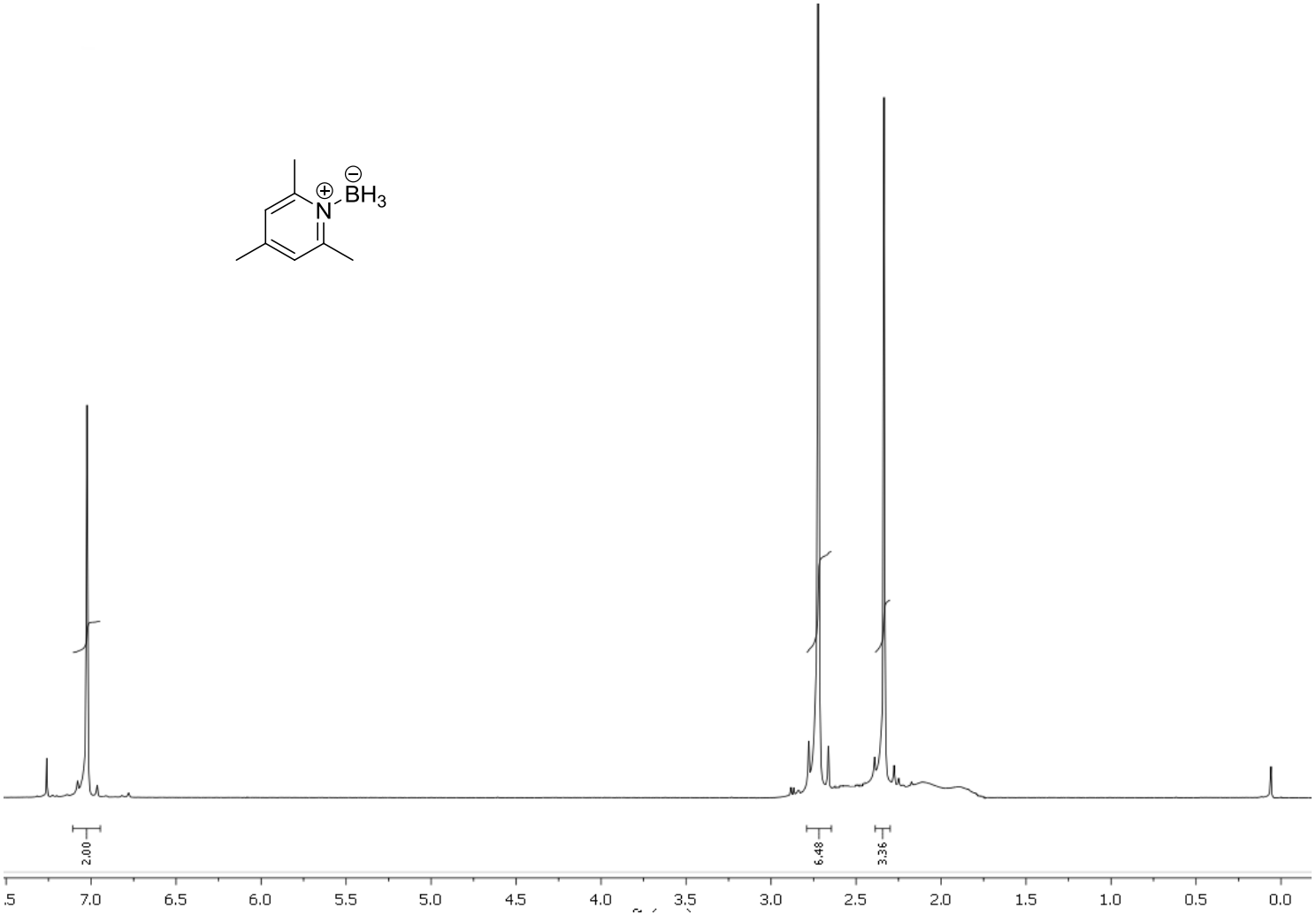
^{1}H NMR (300 MHz, $CDCl_3$) **2,6-lutidine-BH_3 (Table 3, Entry 4)**



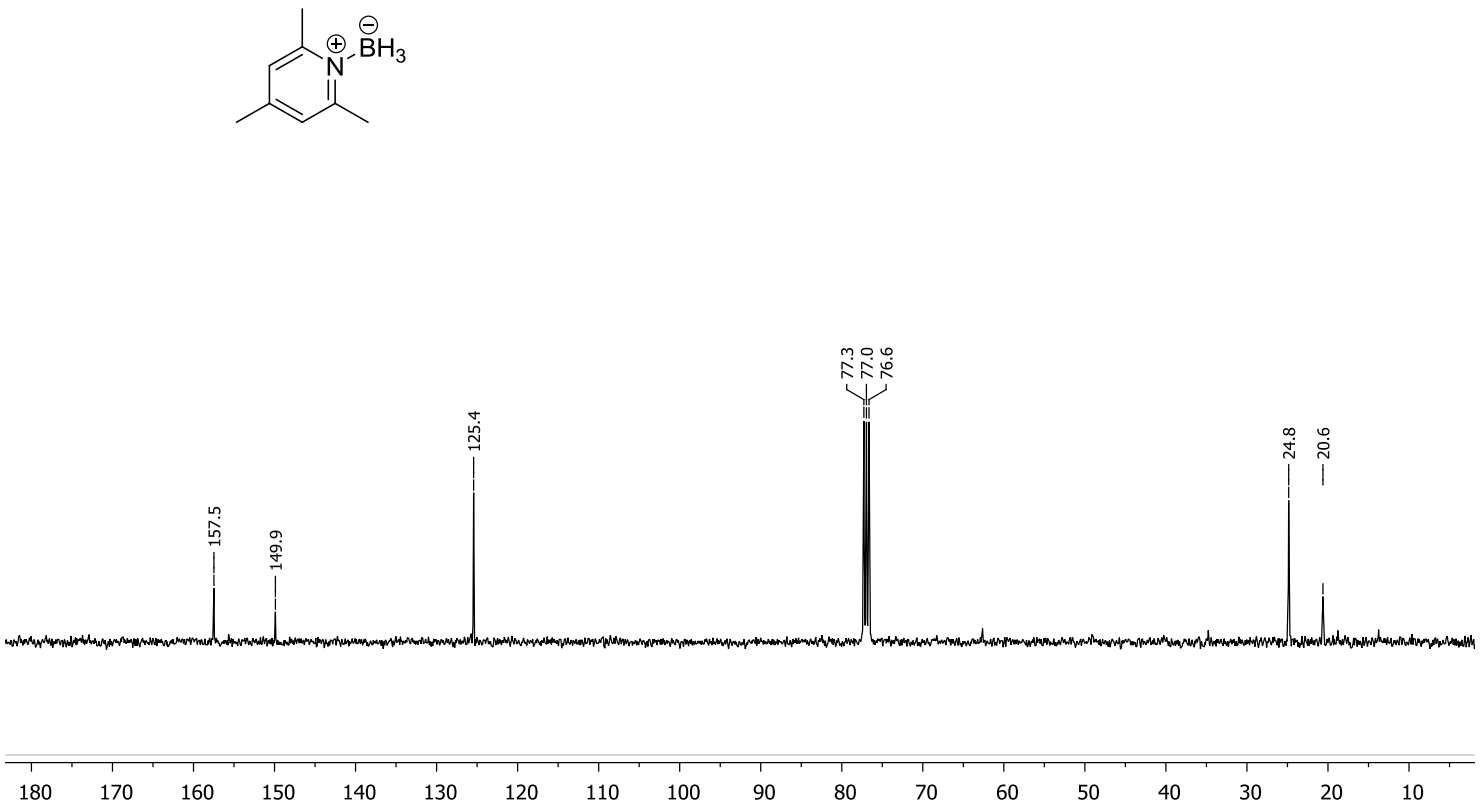
^{13}C NMR (101 MHz, $CDCl_3$) **2,6-lutidine-BH_3 (Table 3, Entry 4)**



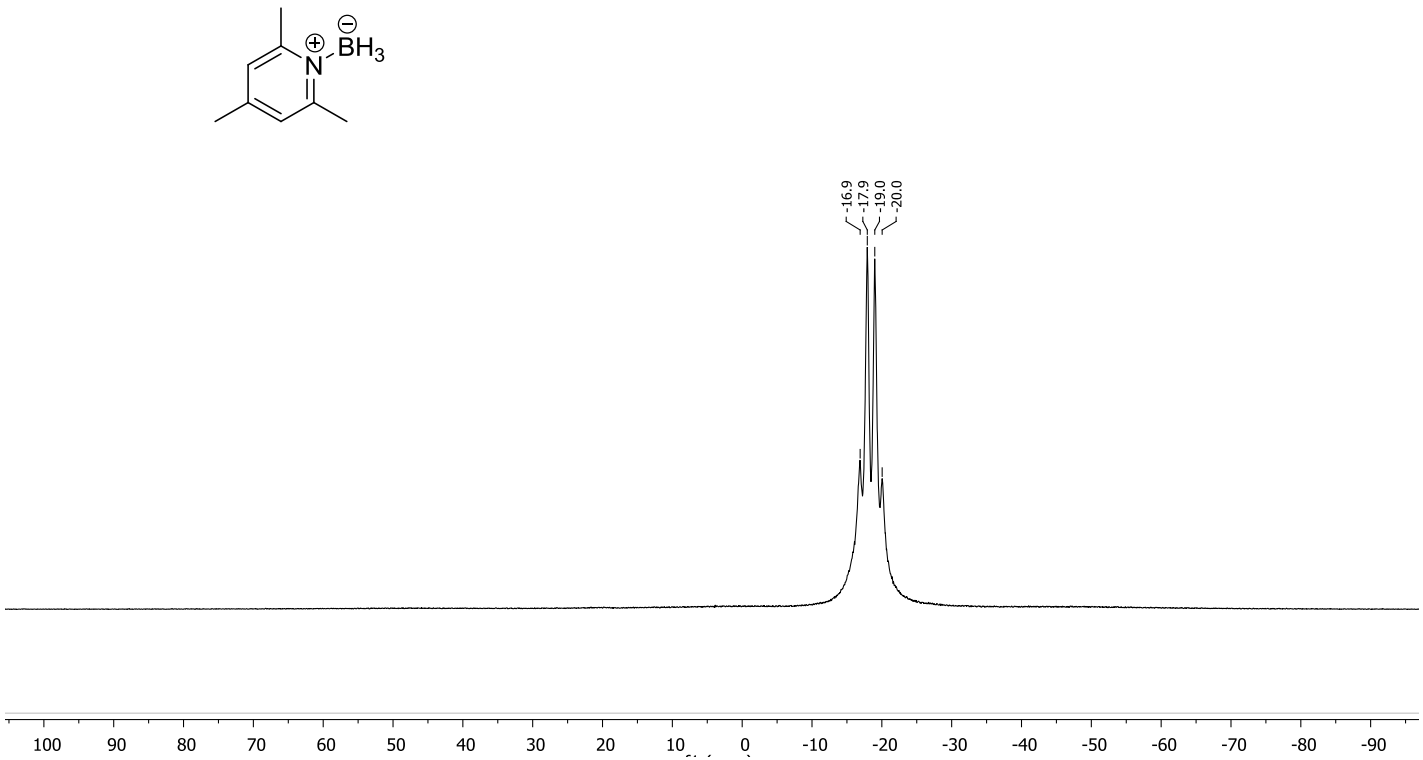
^{11}B NMR (96 MHz, $CDCl_3$) **2,6-lutidine-BH_3 (Table 3, Entry 4)**



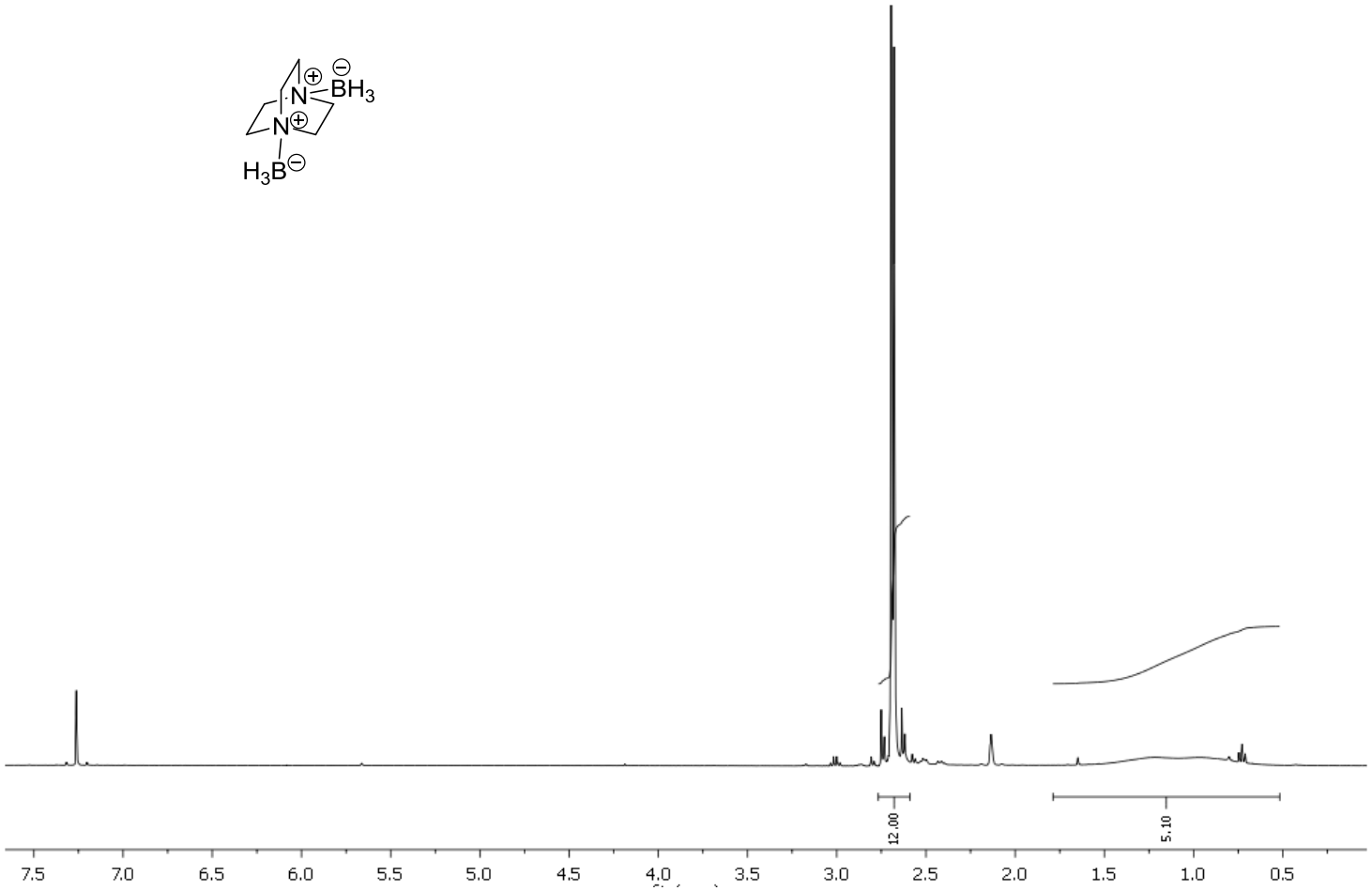
^{1}H NMR (400 MHz, $CDCl_3$) **2,4,6-Collidine-BH_3 (Table 3, Entry 6)**



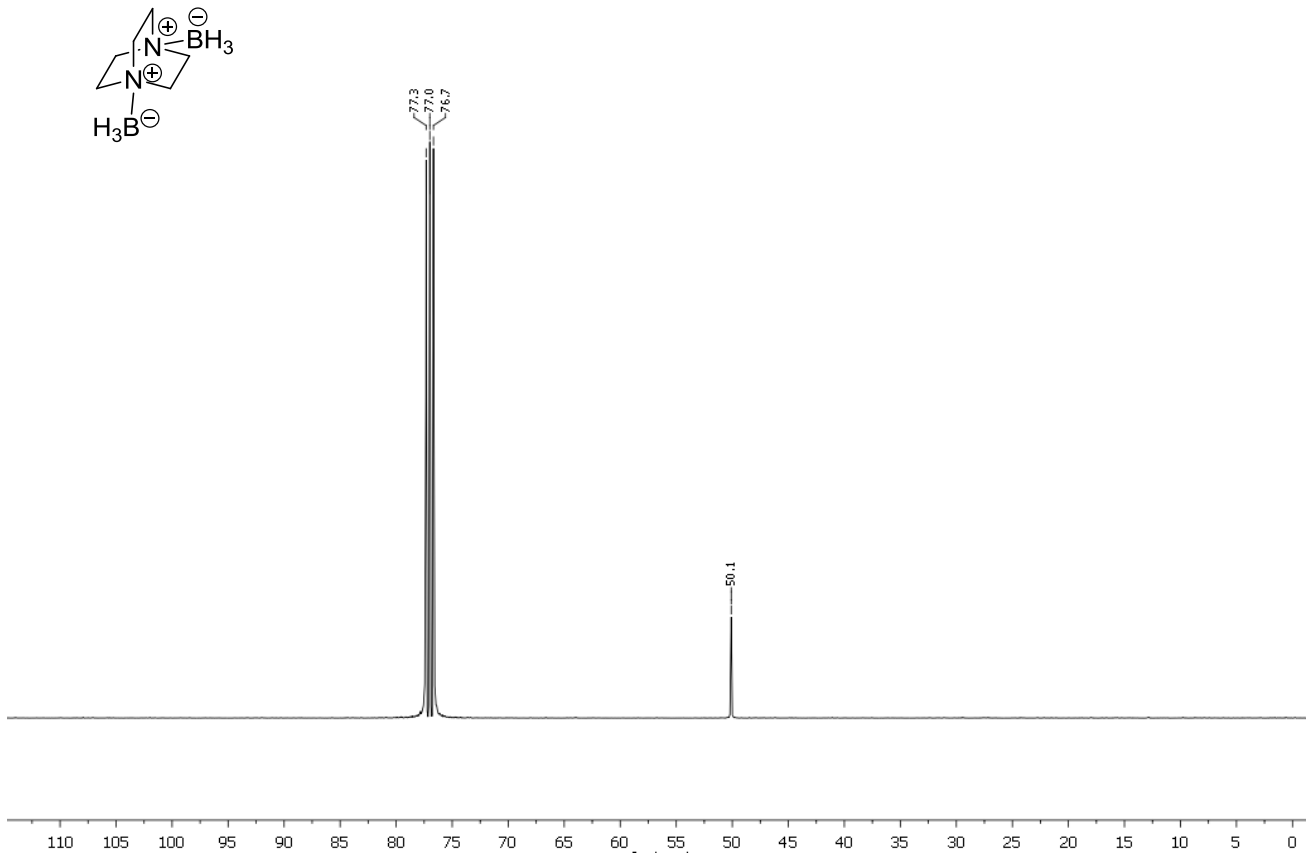
^{13}C NMR (101 MHz, $CDCl_3$) **2,4,6-Collidine-BH_3 (Table 3, Entry 6)**



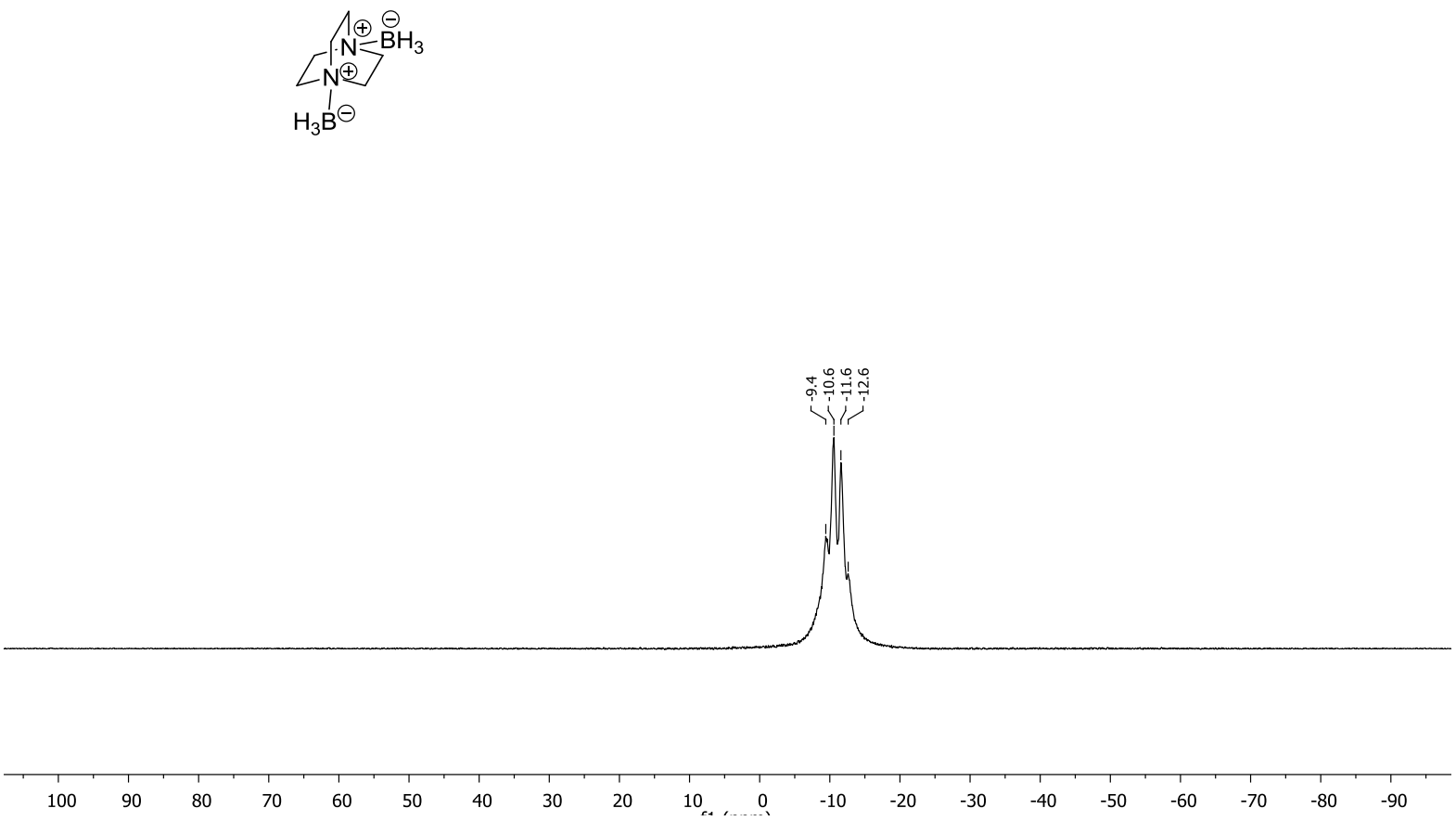
^{11}B NMR (96 MHz, $CDCl_3$) **2,4,6-Collidine-BH_3 (Table 3, Entry 6)**



^{1}H NMR (400 MHz, $CDCl_3$) **DABCO-$(BH_3)_2$ (Table 3, Entry 7)**



^{13}C NMR (101 MHz, $CDCl_3$) **DABCO-$(BH_3)_2$ (Table 3, Entry 7)**



^{11}B NMR (96 MHz, $CDCl_3$) **DABCO-$(BH_3)_2$ (Table 3, Entry 7)**