Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION:

Activation of sodium borohydride via carbonyl reduction for the synthesis of amine- and phosphine-boranes

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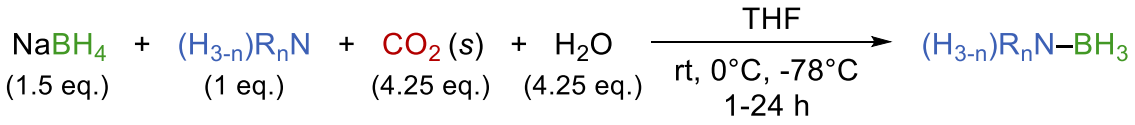
Contents:

General Information:

^{11}B, ^{1}H, and ^{13}C NMR spectra were recorded at room temperature on a Varian INOVA or MERCURY 300 MHz NMR instrument. For ^{11}B NMR, chemical shifts (δ values) are reported in parts per million relative to $BF_3 \bullet Et_2O$. Data are reported as: δ value, multiplicity, and integration. All solvents for preparation and isolation of products were reagent-grade. Tetrahydrofuran (THF, Optima®, meets ACS specifications, no preservatives, packaged under N_2, submicron filtered) and stabilized THF (Certified, contains about 0.025% butylated hydroxytoluene i.e., BHT, as a preservative, Safe-Cote®) were purchased from Fisher Chemical; after usage during initial optimization trials, stabilized THF was no longer implemented for further reactions due to the presence of BHT peaks in the ^{1}H and ^{13}C NMRs of purified products. Sodium borohydride (>95.0%) was purchased from Aldrich. Carbon dioxide gas (99%) was purchased from Indiana Oxygen. Deionized water was supplied from an in-house tap. Amines were purchased from commercial sources and used without further purification. Sodium sulfate (Anhydrous, granular, Certified ACS) was purchased from Fisher Chemical, and Celite® was purchased from Oakwood Products, Inc.

Optimization of reaction conditions:

Optimization of reaction using solid CO_2 (dry ice):



Scheme S1. Reaction equation for optimization using dry ice.

The amine (5.0 mmol, 1 eq.) and sodium borohydride (0.28 g, 7.5 mmol, 1.5 eq.) were transferred to an oven dried 25 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (5.0 mL, 1 M w.r.t. amine) at room temperature. The reaction mixture was left at room temperature, or brought to 0 °C with an ice/water bath, or brought to -78 °C with a dry ice/acetone bath. Once the reaction mixture had reached the desired temperature, dry ice (0.935 g, 21.25 mmol, 4.25 eq.) was quickly weighed and added to the reaction mixture portion wise to prevent excess sublimation causing the flask to overflow. Following complete addition of the dry ice, water (0.38 mL, 21.25 mmol, 4.25 eq.) was added dropwise via syringe with vigorous stirring of the reaction mixture. The reaction was continued with stirring for the prescribed time (1-24

hours). The completed reaction was analyzed by ^{1}H and ^{11}B NMR spectroscopy by dissolving an aliquot of the reaction mixture in $CDCl_3$ (Note: Anhydrous DMSO is added to the reaction aliquot before running the NMR experiments). Results of the initial optimization are summarized in **Table S1** below.

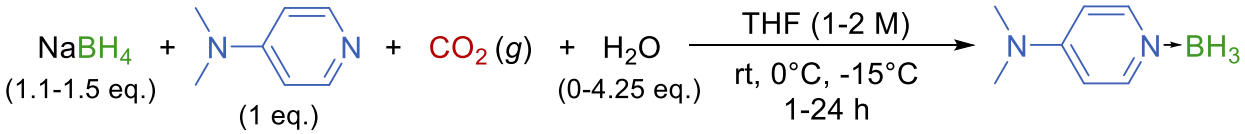
Entry	Equivalents (Amine:SBH:$CO_{2(s)}$:H_2O)	Amine	AB:Amine (^{1}H NMR)	AB:SBH:Other (^{11}B NMR)	Time (h)	Temp. (°C)
1	**1:1.5:~4.25:~4.25**	**DMAP**	**100:0**	**100:0:0**	**24**	**-78**
2	1:1.5:~4.25:~4.25	DMAP	---	97:1:2	24	None
3	1:1.5:~4.25:~4.25	DMAP	92:8	93:1:6	1	None
4	1:1.5:~4.25:~4.25	DMAP	100:0	88:0:12	1	0
5	1:1.5:~4.25:~4.25	DMAP	95:5	99:1:0	2.5	-78
6	1:1.1:~4.25:~4.25	DMAP	73:27	91:0:9	1	None
7	**1:1.5:~4.25:~4.25**	***i*Pr$_2$NH**	**---**	**100:0:0**	**24**	**0**
8	**1:1.5:~4.25:~4.25**	***i*Pr$_2$NH**	**---**	**100:0:0**	**1.5**	**-78**
9	**1:1.5:~4.25:~4.25**	**pyridine**	**---**	**100:0:0**	**24**	**-78**

Table S1. Optimization of reaction conditions for preparation of amine-boranes using dry ice

Note that $CO_{2(s)}$ was added to the reaction mixture before H_2O for all trials. AB = amine-borane; SBH = sodium borohydride ($NaBH_4$).

On the basis of the above results (**Table S1**), 1:1.5:~4.25:~4.25 equivalents of 4-DMAP to $NaBH_4$ to dry ice to water (with respect to the amine) in THF for 24 hours at -78°C resulted in the highest yield of 4-DMAP borane (**Table S1** entry 1, bolded). When the procedure was applied to diisopropylamine, full conversion to the respective borane was also observed in just 1.5 hours (**Table S1** entry 7, bolded). When applied to pyridine, full conversion to the amine-borane was similarly observed with full conversion after 24 hours (**Table S1** entry 9, bolded).

<u>Optimization of reaction using gaseous CO_2:</u>



Scheme S2. Reaction equation for optimization using gaseous CO_2.

The amine, 4-dimethylaminopyridine (0.61 g, 5.0 mmol, 1 eq.) and sodium borohydride (0.24-0.28 g, 6.25-7.5 mmol, 1.25-1.5 eq.) were weighed into an oven dried 25 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (5.0-10.0 mL, 1-2 M w.r.t. amine)

at room temperature. The flask was sealed with a rubber septum and the reaction mixture was left at room temperature. The order of addition of water (0-0.38 mL, 0-21.25 mmol, 0-4.25 eq.) and gaseous CO_2 was varied. CO_2 was introduced to the reaction mixture prior to water addition (**Table S2** entries 1-4), or water was added to the flask prior to CO_2 introduction (**Table S2** entries 5-12). No water was used for the reaction detailed in **Table S2** entry 13. The gaseous CO_2 was introduced to the reaction mixture via balloon for the early experiments (**Table S2** entries 1-9) by affixing a CO_2 filled balloon to a plastic syringe tube fitted with an 18 G needle and inserting the needle through the rubber septum. If multiple CO_2 filled balloons were used for a reaction, they were emptied into the reaction flask in either a consecutive (consec.) or time staggered (stag.) fashion. The later experiments introduced gaseous CO_2 via direct line with a flow rate of ~50 mL CO2(g)/min. (**Table S2** entries 10-13). The reaction was continued with stirring and reaction progress was monitored by ^{11}B NMR spectroscopy (Note: Anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment). The completed reactions were analyzed by ^{1}H and ^{11}B NMR spectroscopy by dissolving an aliquot of the reaction mixture in $CDCl_3$ (Note: Anhydrous DMSO is added to the reaction aliquot before running the NMR experiments). Results of the initial optimization are summarized in **Table S1** below.

Entry	Equivalents (Amine:SBH:CO_2:H_2O)	AB:Amine (^{1}H NMR)	AB:SBH:Other (^{11}B NMR)	Time (h)	Cooling (°C)
1	1:1.5:Balloon:4.25	---	96:0:4	24	None
2	1:1.25:Balloon:4.25	98:2	94:0:6	1	None
3	1:1.25:---:---	~100:0	~100:0:0	---	None
4	1:1.25:Balloon:2.00	~100:0	87:0:13	1	None
5	1:1.25:Balloon:2.00	69:31	98:2:0	1	None
6	1:1.25:Balloon:3.25	60:40	99:1:0	1	None
7	1:1.25:2 Balloons:4	54:46	99:1:0	1	None
8	1:1.25:1 Balloon (4 consec. 3 stag.):3	93:7	~100:0:0	1.33	None
9	1:1.25:1 Balloon (4 consec., 3 stag.):3 (2 M THF)	96:4	~100:0:0	0.75	None
10	1:1.25:Direct line:3	93:7	97:0:3	0.5	None
11	1:1.25:Direct line:4.25	92:8	98:0:2	0.5	None
12	1:1.5:Direct line:3	~100:0	~100:0:0	0.5	None
13	**1:1.5:Direct line:0**	**~100:0**	**~100:0:0**	**0.5**	**None**

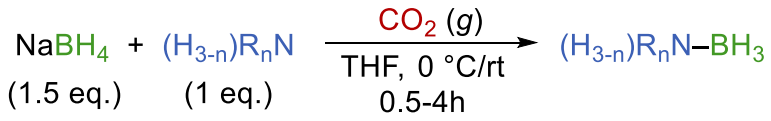
Table S2. Optimization of conditions for preparation of amine-boranes using gaseous CO_2

Note that CO_2 flow rate was measured using a gas burette and stopwatch. Optimal results are highlighted in bold. AB = amine-borane; SBH = sodium borohydride ($NaBH_4$).

On the basis of the above results (**Table S2**), 1:1.5 equivalents of 4-DMAP to $NaBH_4$ with a direct line of CO_2 at room temperature fully converts the amine to the amine-borane (**Table S2** entry 13, bolded).

Procedures for the preparation of amine- and phosphine-boranes:

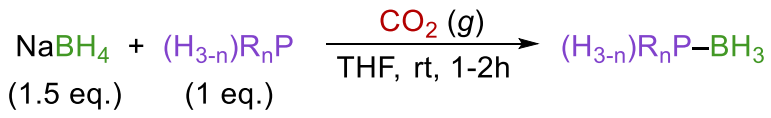
General procedure for the preparation of amine-boranes via $CO_{2(g)}$ **(2a-2af):**



Scheme S3. Reaction equation for the preparation of amine-boranes.

The amine (10.0 mmol) and sodium borohydride (0.57 g, 15.0 mmol) were weighed into an oven dried 25 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (10.0 mL, 1 M) at room temperature for the preparation of **2a-2c** and **2e-2af**, or 0 °C for **2d**. A direct $CO_{2(g)}$ line and venting outlet were added through the septum and CO_2 was passed over the stirred reaction mixture with a flow rate of ~50 mL $CO_{2(g)}$/min. at room temperature until completion (**2a-2c** and **2e-2af**). For amine-borane **2d**, the reaction continued until completion with equilibration to room temperature. Reaction progress can be monitored by ^{11}B NMR spectroscopy (Note: Anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment). Upon completion of the reaction, the reaction contents were quenched with deionized water (0.54 mL, 30.0 mmol) for 20 minutes then dried over sodium sulfate. The mixture was then filtered through Celite®, and the solid residue was washed with THF. Removal of the solvent in vacuo yielded the corresponding amine-borane (**2a-2af**).

Procedure for the preparation of phosphine-boranes via $CO_{2(g)}$ **(4a-4d):**



Scheme S4. Reaction equation for the preparation of phosphine-boranes.

The desired phosphine (2.623 g, 10.0 mmol) and sodium borohydride (0.57 g, 15.0 mmol) were weighed into an oven dried 50 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (10.0 mL, 1 M) at room temperature. A direct $CO_{2(g)}$ line and venting outlet were added through the septum and CO_2 was passed over the stirred reaction mixture with a flow rate of ~50 mL $CO_{2(g)}$/min. at room temperature until completion. Reaction progress was monitored by ^{11}B NMR spectroscopy (Note: Anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment). The reactions of phosphine-boranes could also be monitored by ^{31}P NMR, with completion being determined by conversion of the starting phosphine peak to the phosphine-borane. Upon completion of the reaction, the reaction contents were quenched with deionized water (0.54 mL, 30.0 mmol) for 20 minutes then dried over sodium sulfate. The mixture was then filtered through Celite®, and the solid residue was washed with THF. Removal of the solvent in vacuo yielded the corresponding phosphine-borane (**4a-4d**).

Mechanistic experiments:

^1H NMR study of reaction between $NaBH_4$ and CO_2 or formic acid:

Sodium borohydride (0.378 g, 10.0 mmol) was weighed into an oven dried 50 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (20.0 mL, 0.5 M) at room temperature. The reaction flask was sealed with a rubber septum. Depending on the desired conditions, the reaction flask was left at room temperature, or brought to -78 °C using a dry ice/acetone bath. A venting outlet was added through the septum. For the reactions utilizing CO_2, a direct $CO_{2(g)}$ line with a flow rate of ~50 mL $CO_{2(g)}$/min was inserted through the septum and bubbled through the vigorously stirred reaction mixture. For the reaction utilizing formic acid (0.38 mL, 10.0 mmol), it was added via syringe to the vigorously stirred reaction mixture. At the times described in the schemes below, reaction progress was monitored by ^{11}B NMR spectroscopy (Note: Anhydrous DMSO (3-4 drops) is added to the reaction aliquot before running the ^{11}B NMR experiment).

$$NaBH_4 + CO_2 \xrightarrow[-78\ ^oC\ 5\ min]{THF\ (0.5\ M)} Na[H_3B(OCHO)] + Na[H_2B(OCHO)_2] + Na[HB(OCHO)_3]$$

Scheme S5. Reaction of $NaBH_4$ and CO_2 at -78 °C for 5 minutes.

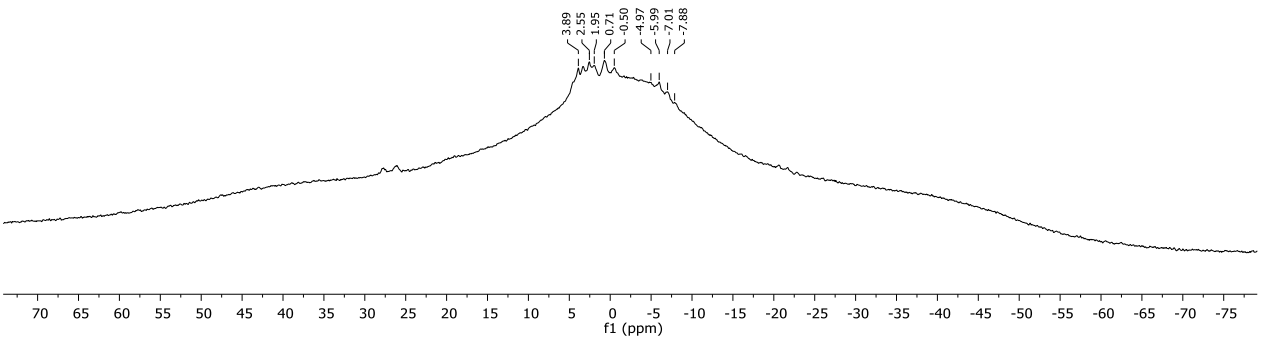


Figure S1.[11]B NMR (B-H coupled) spectrum of $NaBH_4$ and CO_2 at -78 °C for 5 minutes.

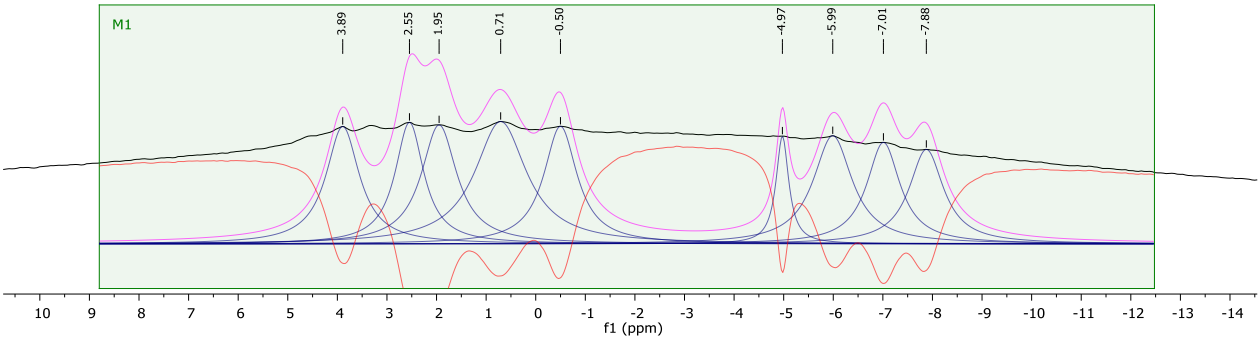


Figure S2.[11]B NMR (deconvoluted) spectrum of $NaBH_4$ and CO_2 at -78 °C for 5 minutes.

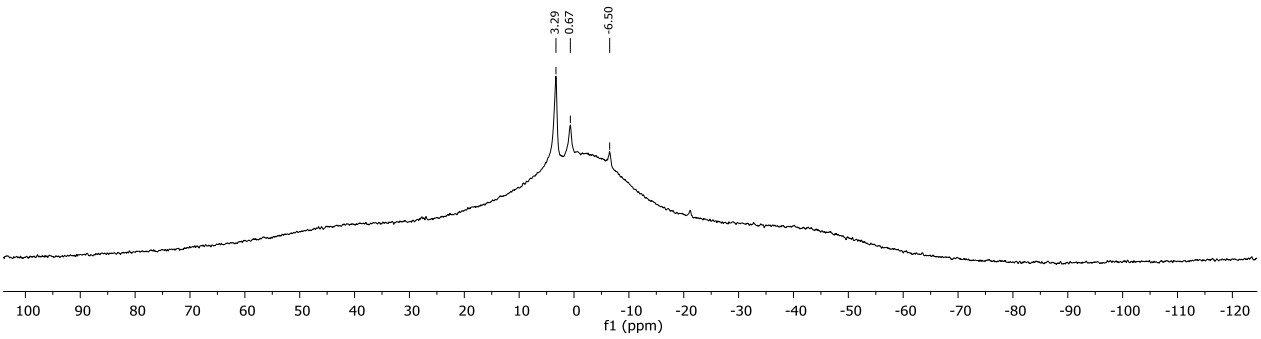
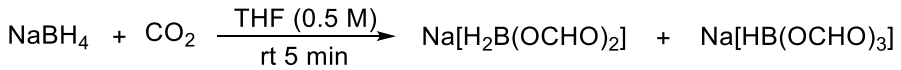


Figure S3.[11]B NMR (B-H decoupled) spectrum of $NaBH_4$ and CO_2 at -78 °C for 5 minutes.



Scheme S6. Reaction of $NaBH_4$ and CO_2 at rt for 5 minutes.

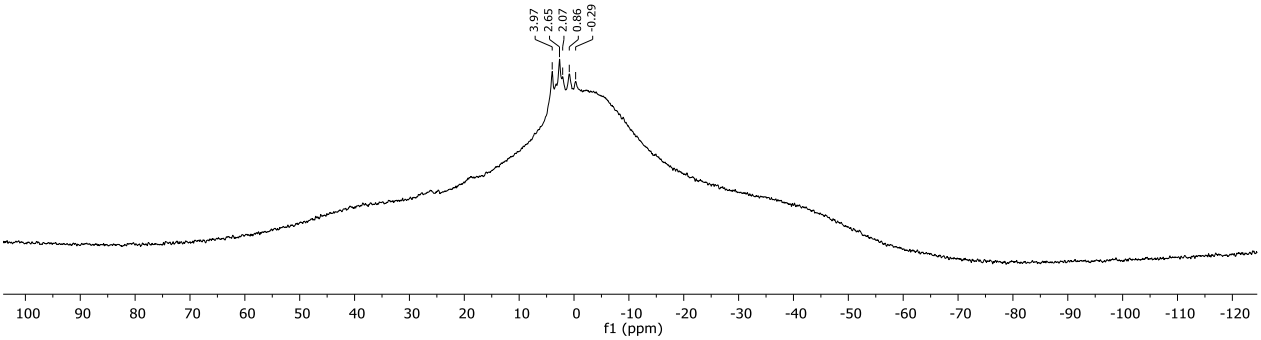


Figure S4.[11]B NMR (B-H coupled) spectrum of $NaBH_4$ and CO_2 at rt for 5 minutes.

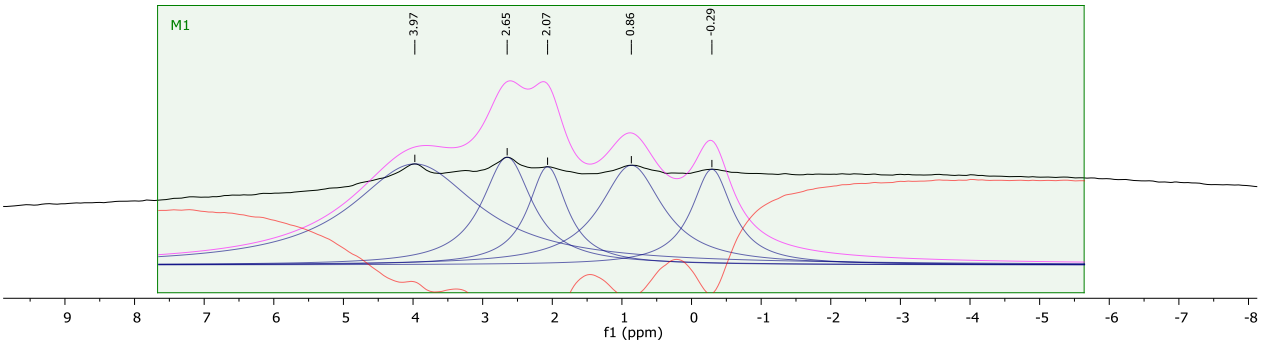


Figure S5.[11]B NMR (deconvoluted) spectrum of $NaBH_4$ and CO_2 at rt for 5 minutes.

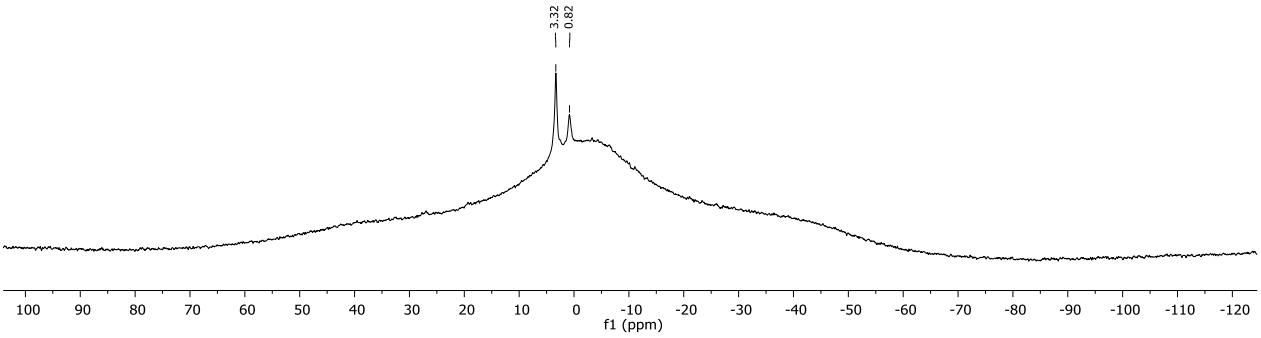
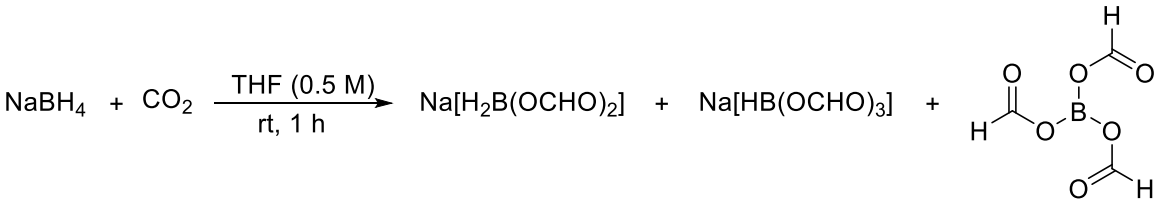


Figure S6.[11]B NMR (B-H decoupled) spectrum of $NaBH_4$ and CO_2 at rt for 5 minutes.



Scheme S7. Reaction of $NaBH_4$ and CO_2 at rt for 1 hour.

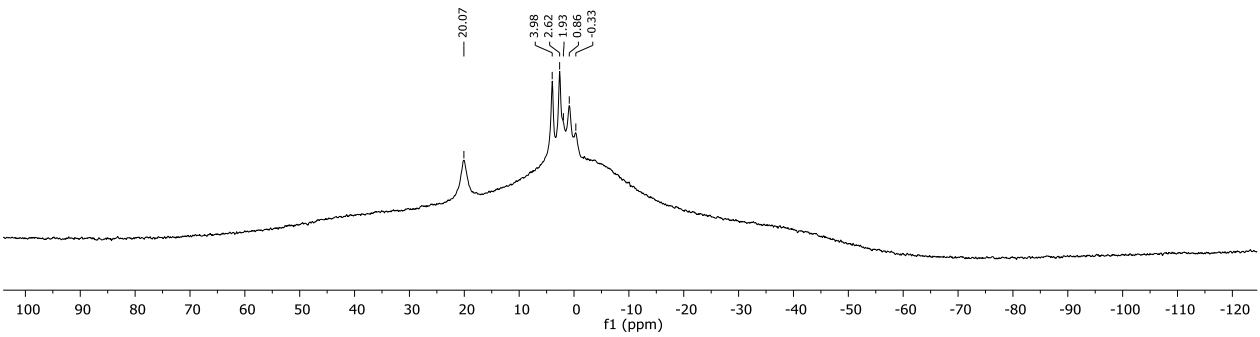


Figure S7.[11]B NMR (B-H coupled) spectrum of $NaBH_4$ and CO_2 at rt for 1 hour.

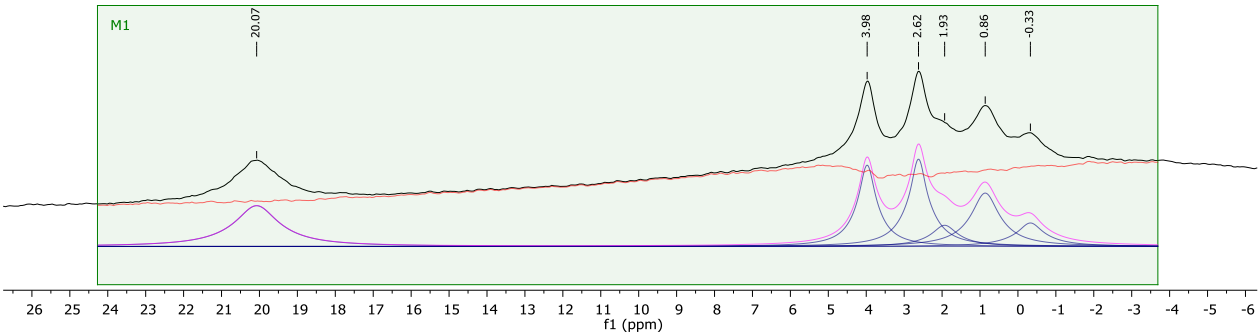


Figure S8.[11]B NMR (deconvoluted) spectrum of $NaBH_4$ and CO_2 at rt for 1 hour.

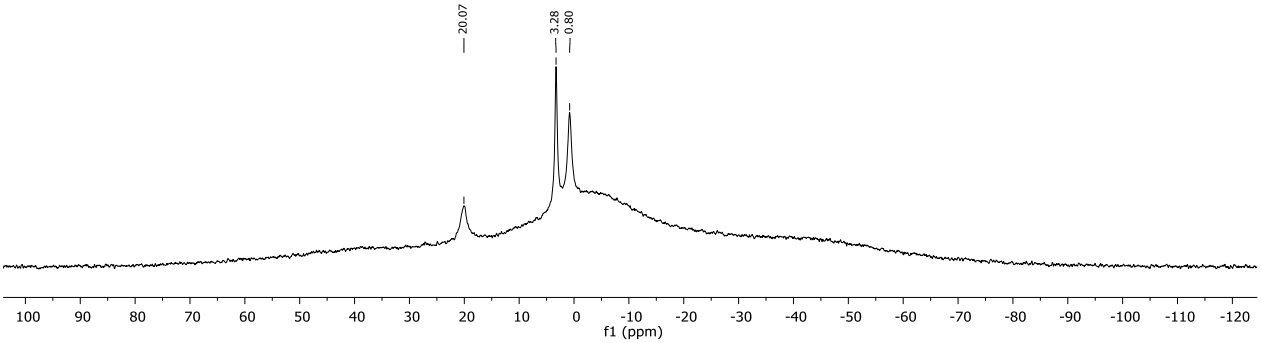
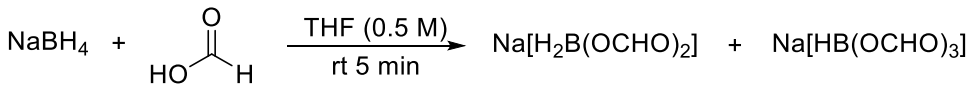


Figure S9.[11]B NMR (B-H decoupled) spectrum of $NaBH_4$ and CO_2 at rt for 1 hour.



Scheme S8. Reaction of $NaBH_4$ and formic acid at rt for 5 minutes.

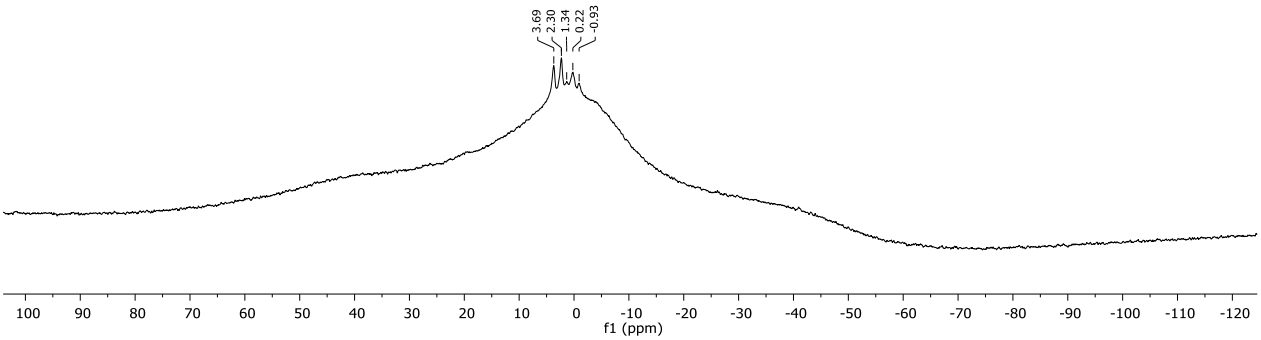


Figure S10.[11]B NMR (B-H coupled) spectrum of $NaBH_4$ and formic acid at rt for 5 minutes.

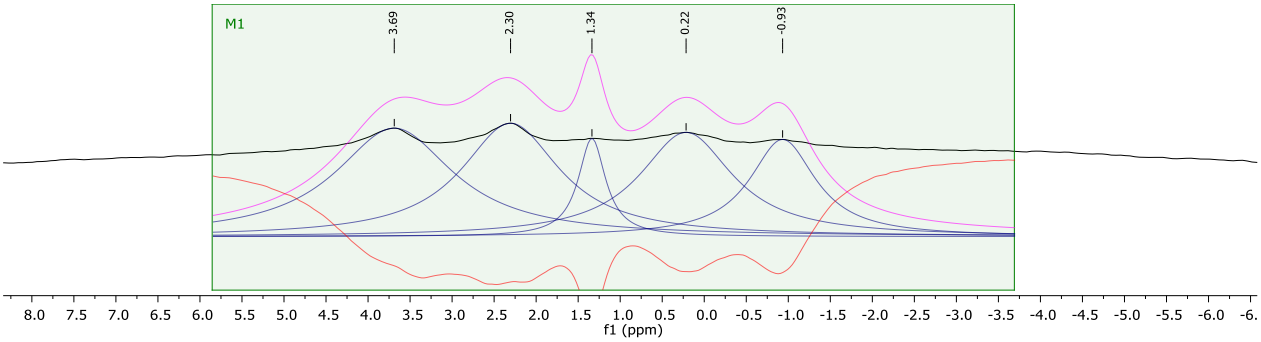


Figure S11.[11]B NMR (deconvoluted) spectrum of $NaBH_4$ and formic acid at rt for 5 minutes.

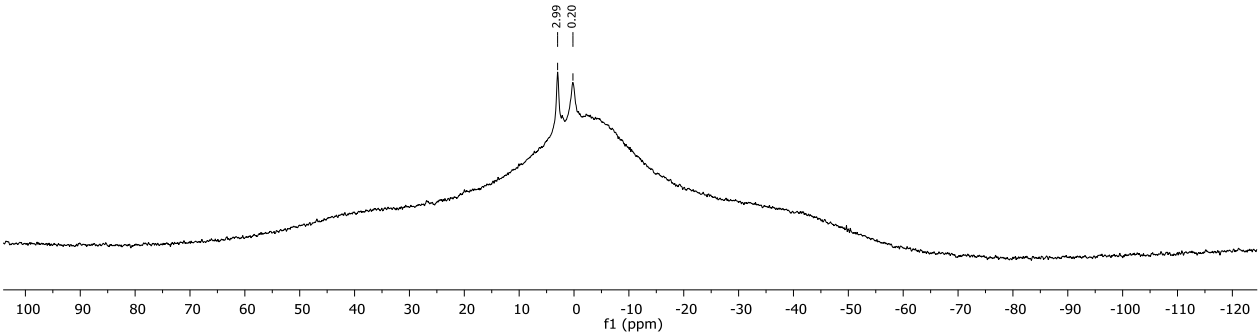
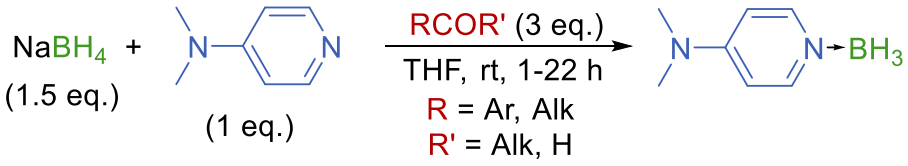


Figure S11.[11]B NMR (B-H decoupled) spectrum of $NaBH_4$ and formic acid at rt for 5 minutes.

<u>Examination of carbonyl-mediated synthesis of 4-dimethylaminopyridine-borane:</u>



Scheme S9. Reaction equation for the examination of carbonyl mediate amine-borane synthesis

4-Dimethylaminopyridine (0.244 g, 2.0 mmol) and sodium borohydride (0.113 g, 3.0 mmol) were weighed into an oven dried 25 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (5 mL, 0.4 M) at room temperature. The carbonyl being investigated (6 mmol) was added dropwise to the vigorously stirred reaction mixture at room temperature. Reaction progress was monitored by ^{1}H and ^{11}B NMR spectroscopy by dissolving an aliquot of the reaction mixture in $CDCl_3$ (Note: Anhydrous DMSO is added to the reaction aliquot before running the NMR experiments).

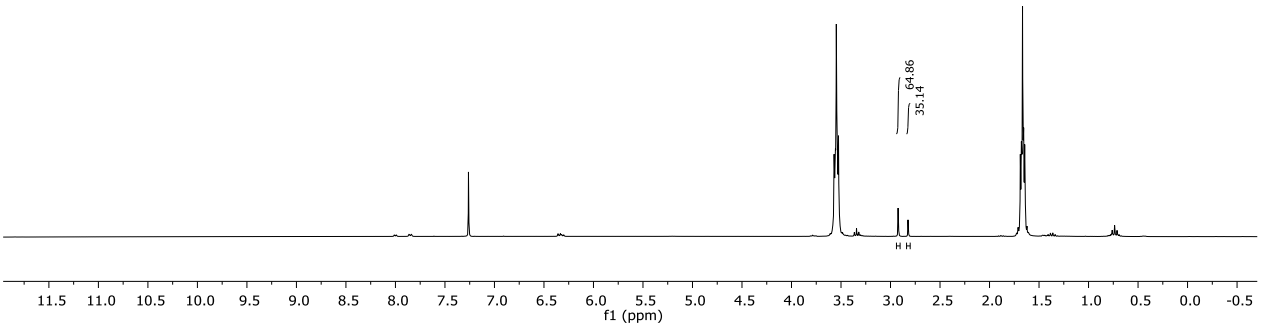


Figure S12.^{1}H NMR spectrum from the examination of propanal.

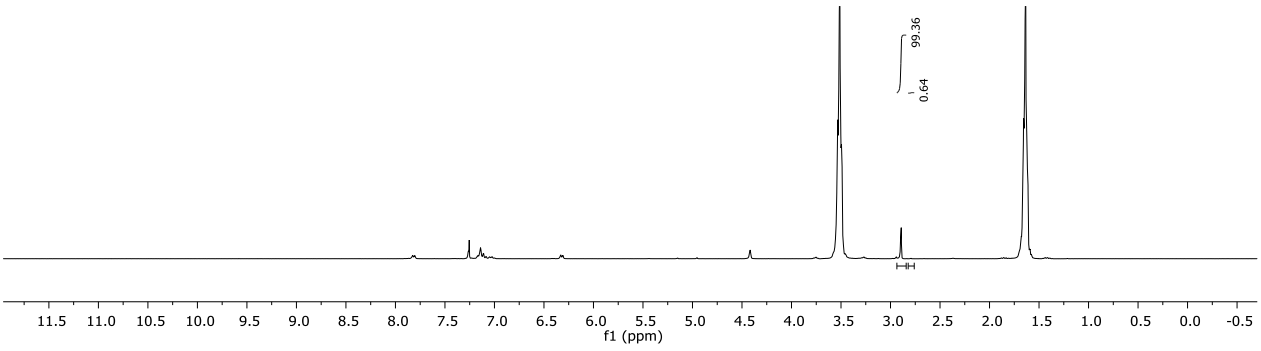


Figure S13.^{1}H NMR spectrum from the examination of benzaldehyde.

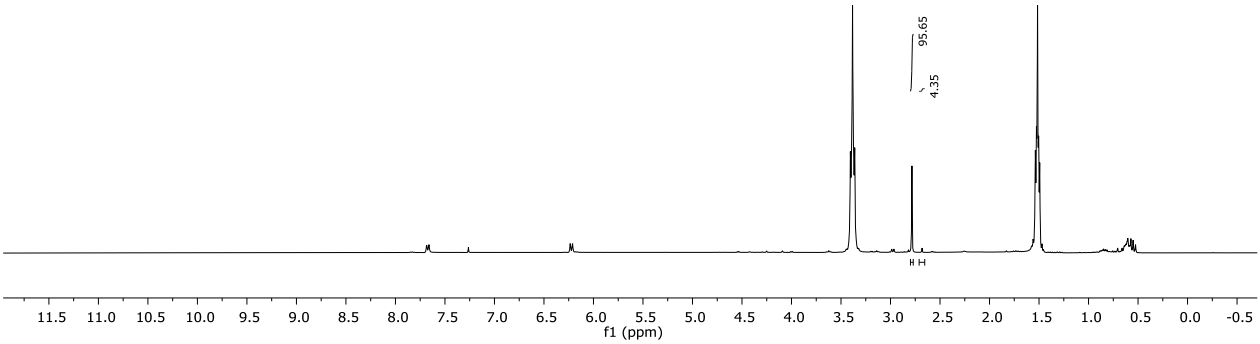


Figure S14.[1]H NMR spectrum from the examination of isobutyraldehyde.

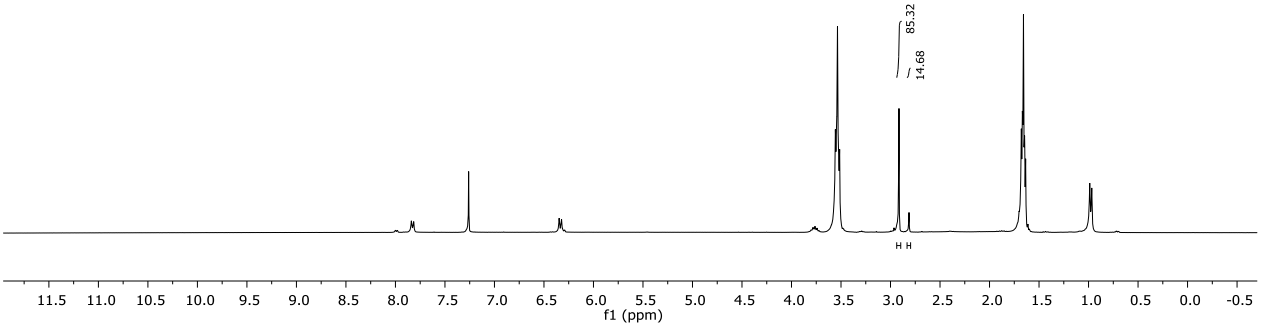


Figure S15.[1]H NMR spectrum from the examination of acetone.

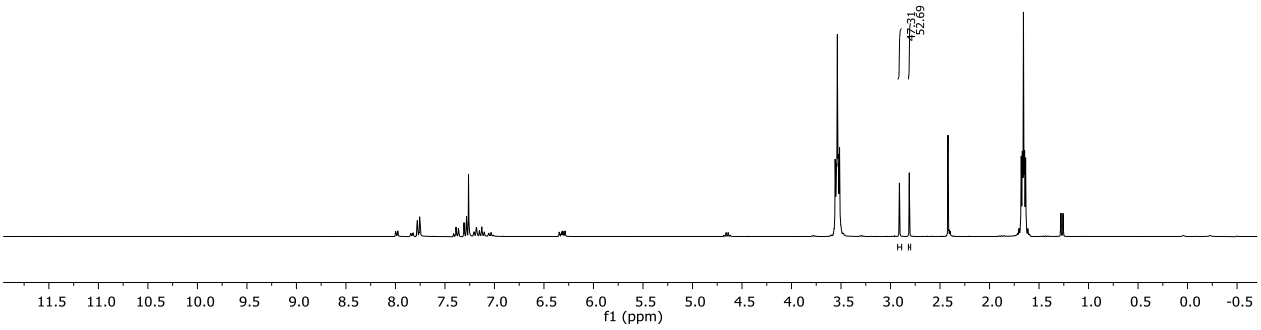
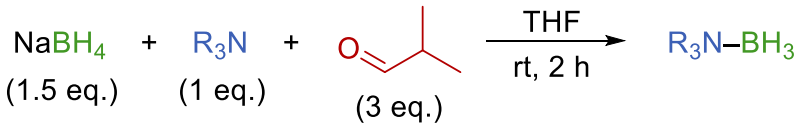


Figure S16.[1]H NMR spectrum from the examination of acetophenone.

Procedure for the preparation of amine-boranes via isobutyraldehyde (**2l**, **2s**, **2t**, **2x**, **2a**, **2y, 4c**):



Scheme S10. Reaction equation for the preparation of amine-boranes via isobutyraldehyde.

The amine (10.0 mmol) and sodium borohydride (0.57 g, 15.0 mmol) were weighed into an oven dried 25 mL round bottom flask containing a stir bar, followed by the addition of tetrahydrofuran (10.0 mL, 1 M) at room temperature. Then, at room temperature, the isobutyraldehyde (2.7 mL, 30.0 mmol) was added dropwise via syringe. The slow addition is critical to a avoid runaway reaction. After complete addition of the isobutyraldehyde, the reaction was stirred at room temperature for 2 hours. After completion, the reaction mixture was quenched slowly with methanol (20 mL). The volatile components were then removed via rotary evaporation. The crude mixture was dissolved using ethyl acetate (30 mL) and transferred into a separatory funnel. The organic layer was shaken with water (10 mL x 3), then brine (10 mL). The organic layer was then dried over sodium sulfate, filtered through cotton and condensed via rotary evaporation. The condensed mixture was transferred to a small preweighed vial, excess solvent evaporated, and to the resulting mixture was added hexanes (5 mL). Upon addition of hexanes, the solid amine-borane precipitated. The mixtures containing liquid amines were frozen using a dry ice/acetone bath, solidifying the amine-boranes, and leaving the byproduct isobutanol dissolved in hexanes. In the cases of solid and liquid amines the hexanes layer was removed by pipette. The hexanes wash was repeated as necessary to remove isobutanol. Removal of the residual solvent in vacuo yielded the corresponding amine-boranes and phosphine-borane (**2l**, **2s**, **2t**, **2x**, **2a**, **2y**, **4c**).

Characterization of amine-boranes:

4-Dimethylaminopyridine-borane (4-DMAP-BH_3, **2a**):

93% (1.265 g), white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.84 (m, 2H), 6.42 (dt, *J* = 5.9, 1.5 Hz, 2H), 3.03 (d, *J* = 1.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 146.4, 106.4, 39.6; ^{11}B NMR (96 MHz, $CDCl_3$) δ -12.59 (q, *J* = 97.4 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

n-Propylamine-borane (**2b**):

80% (583 mg), white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 2H), 2.80 – 2.56 (m, 2H), 1.58 (q, *J* = 7.4 Hz, 2H), 0.97 – 0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.5, 22.3, 11.2; ^{11}B NMR (96 MHz, $CDCl_3$) δ -19.94 (q, *J* = 94.8 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

sec-Butylamine-borane (**2c**):

78% (678 mg), colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (d, *J* = 57.2 Hz, 2H), 2.78 (dq, *J* = 10.2, 5.2, 3.7 Hz, 1H), 1.80 – 1.59 (m, 1H), 1.58 – 1.35 (m, 1H), 1.21 (dd, *J* = 6.6, 1.7 Hz, 3H), 0.90 (td, *J* = 7.5, 1.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 28.7, 18.3, 9.8; ^{11}B NMR (96 MHz, $CDCl_3$) δ -20.95 (q, *J* = 96.3, 95.9 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[2]

tert-Butylamine-borane (**2d**):

74% (643 mg), white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.3, 28.1; ^{11}B NMR (96 MHz, $CDCl_3$) δ -23.22 (q, *J* = 96.8, 96.2 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

Cyclohexylamine-borane (**2e**):

76% (859 mg), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.03 – 3.25 (m, 2H), 2.68 (ttt, *J* = 10.2, 6.4, 3.8 Hz, 1H), 2.12 (dt, *J* = 12.4, 3.7 Hz, 2H), 1.75 (dq, *J* = 12.3, 3.7, 3.2 Hz, 2H), 1.62 (dt, *J* = 12.3, 3.7 Hz, 1H), 1.37 – 1.10 (m, 5H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 57.0, 32.4, 25.4, 24.6. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -20.90 (q, *J* = 96.5, 95.8 Hz).
Characterization is in agreement with previous reports for this compound.[1]

1-Phenylethan-1-amine-borane (**2f**):
77% (1.039 g), white solid.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.25 (m, 5H), 4.39 – 3.97 (m, 2H), 3.94 (dt, *J* = 9.6, 3.2 Hz, 2H), 1.61 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.37, 129.11, 128.53, 126.20, 58.56, 19.92. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -20.02 (q, *J* = 101.0, 99.2 Hz).
Characterization is in agreement with previous reports for this compound.[4]

Diethylamine-borane (**2g**):
89% (774 mg), colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (m, 4H), 1.26 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.2, 12.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ -17.03 (q, *J* = 96.2 Hz, 3H).
Characterization is in agreement with previous reports for this compound.[1]

Diisopropylamine-borane (**2h**):
80% (920 mg), colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27 – 3.12 (m, 2H), 1.24 (ddd, *J* = 6.4, 4.1, 2.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.1, 21.1, 19.1; ^{11}B NMR (96 MHz, $CDCl_3$) δ -21.76 (q, *J* = 96.7 Hz, 3H).
Characterization is in agreement with previous reports for this compound.[2]

Piperidine-borane (**2i**):
73% (722 mg), white solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 1H), 3.17 (d, *J* = 13.4 Hz, 2H), 2.42 (q, *J* = 13.7, 12.5 Hz, 2H), 1.71 (d, *J* = 10.9 Hz, 3H), 1.60 – 1.18 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.3, 25.3, 22.6; ^{11}B NMR (96 MHz, $CDCl_3$) δ -14.64 (d, *J* = 95.9 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

2,2,6,6-Tetramethylpiperidine-borane (**2j**):

89% (1.380 g), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.83 (s, 1H), 1.80 – 1.66 (m, 4H), 1.53 (ddt, *J* = 11.2, 7.7, 3.8 Hz, 2H), 1.36 (d, *J* = 14.8 Hz, 12H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 58.59, 41.05, 34.01, 20.73, 16.70. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -22.40 (q, *J* = 96.6 Hz).

Characterization is in agreement with previous reports for this compound.[5]

N-Methylbenzylamine-borane (**2k**):

74% (999 mg), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 – 7.20 (m, 5H), 4.28 (dd, *J* = 13.9, 2.8 Hz, 2H), 3.58 – 3.43 (m, 1H), 2.40 (d, *J* = 5.8 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.03, 129.46, 128.95, 128.70, 60.83, 40.19. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -14.26 (q, *J* = 97.9 Hz).

Characterization is in agreement with previous reports for this compound.[6]

Triethylamine-borane (**2l**):

90% (1.035 g), colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.78 (q, *J* = 7.3 Hz, 6H), 1.19 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.4, 8.8; ^{11}B NMR (96 MHz, $CDCl_3$) δ -13.94 (q, *J* = 96.9 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

Tributylamine-borane (**2m**):

99% (1.972 g), pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.68 – 2.60 (m, 6H), 1.66 – 1.53 (m, 6H), 1.25 (h, *J* = 7.4 Hz, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 59.2, 25.1, 20.7, 14.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ -12.90 (d, *J* = 102.6 Hz, 3H).

Trioctylamine-borane (**2n**):

99% (3.638 g), pale yellow oil.

1H NMR (300 MHz, CDCl3) δ 2.70 – 2.61 (m, 6H), 1.63 (ddt, J = 14.7, 10.8, 5.5 Hz, 6H), 1.27 (s, 31H), 0.91 – 0.84 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 59.4, 31.9, 29.4, 29.3, 27.5, 23.1, 22.8, 14.2; ^{11}B NMR (96 MHz, $CDCl_3$) δ -13.07.

Tridodecylamine-borane (**2o**):

99% (5.305 g), pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64 (s, 6H), 1.25 (s, 60H), 0.90 – 0.83 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 59.4, 32.0, 29.7, 29.7, 29.5, 27.5, 23.0, 22.8, 14.3; ^{11}B NMR (96 MHz, $CDCl_3$) δ -12.58.

Diisopropylethylamine-borane (**2p**):

61% (872 mg), colorless liquid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.49 (p, *J* = 6.7 Hz, 2H), 2.94 (q, *J* = 7.3 Hz, 2H), 1.31 (dd, *J* = 18.4, 6.7 Hz, 12H), 1.18 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 56.71, 47.62, 19.03, 18.59, 10.23. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -14.12 (q, *J* = 97.5 Hz).

Characterization is in agreement with previous reports for this compound.[7]

Dimethylcyclohexylamine-borane (**2q**):

97% (1.368 g), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.54 (d, *J* = 7.1 Hz, 7H), 2.38 – 2.25 (m, 2H), 1.95 – 1.82 (m, 2H), 1.72 – 1.61 (m, 1H), 1.46 – 0.96 (m, 5H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 70.21, 48.89, 27.31, 26.02, 25.59. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -11.24 (q, *J* = 98.2 Hz).

Characterization is in agreement with previous reports for this compound.[8]

N-Methylpyrrolidine-borane (**2r**):

99% (980 mg), colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20 (p, *J* = 6.3 Hz, 2H), 2.76 (p, *J* = 5.9 Hz, 2H), 2.66 (s, 3H), 2.22 – 2.09 (m, 2H), 2.01 – 1.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.9, 51.3, 23.2; ^{11}B NMR (96 MHz, $CDCl_3$) δ -11.04 (q, *J* = 97.3, 96.7 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

N-Ethylpiperidine-borane (**2s**):

90% (1.143 g), colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (m, 4H), 2.75 – 2.63 (m, 2H), 1.82 (m, 2H), 1.55 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.7, 54.8, 22.9, 20.5, 8.9; ^{11}B NMR (96 MHz, $CDCl_3$) δ -12.99 (q, *J* = 96.8 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

Quinuclidine-borane (**2t**):

99% (1.237 g), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.14 – 2.89 (m, 6H), 2.00 (p, *J* = 3.2 Hz, 1H), 1.75 (ddd, *J* = 11.1, 6.8, 3.4 Hz, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 53.56, 25.18, 20.32. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -11.56 (q, *J* = 96.4 Hz).

Characterization is in agreement with previous reports for this compound.[9]

Dimethylbenzylamine-borane (**2u**):

99% (1.475 g), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 – 7.27 (m, 5H), 3.99 (s, 2H), 2.50 (s, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 132.11, 131.10, 129.03, 128.38, 67.53, 49.69. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -8.55 (q, *J* = 98.7, 98.3 Hz).

Characterization is in agreement with previous reports for this compound.[10]

Pyridine-borane (**2v**):

99% (920 mg), colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.7 Hz, 2H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 6.8 Hz, 2H), 3.14 – 1.96 (q, *J* = 93.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 139.3, 125.4; ^{11}B NMR (96 MHz, $CDCl_3$) δ -12.59 (q, *J* = 97.4 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

Quinoline-borane (**2w**):

88% (1.258 g), off-white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.16 (d, *J* = 5.4 Hz, 1H), 8.97 (d, *J* = 8.9 Hz, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 8.06 – 7.82 (m, 2H), 7.73 (td, *J* = 7.4, 1.1 Hz, 1H), 7.54 (dd, *J* = 8.3, 5.3 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.40, 142.78, 141.15, 132.08, 128.79, 128.22, 124.82, 120.61. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -13.80 (q, *J* = 98.4 Hz).
Characterization is in agreement with previous reports for this compound.[11]

2-Picoline-borane (**2x**):

92% (984 mg), white solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.9 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 6.7 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 148.5, 139.6, 126.8, 122.5, 22.6; ^{11}B NMR (96 MHz, $CDCl_3$) δ -14.26 (q, *J* = 97.5 Hz, 3H).
Characterization is in agreement with previous reports for this compound.[1]

1-Methylimidazole-borane (**2y**):

99% (950 mg), colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.05 (d, *J* = 1.5 Hz, 1H), 6.88 (t, *J* = 1.7 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 127.7, 121.0, 35.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ -19.83 (q, *J* = 94.9 Hz, 3H).
Characterization is in agreement with previous reports for this compound.[1]

Morpholine-borane (**2z**):

81% (818 mg), white solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.99 (dd, *J* = 12.6, 3.4 Hz, 2H), 3.57 (td, *J* = 12.4, 2.3 Hz, 2H), 3.21 – 3.05 (m, 2H), 2.96 – 2.75 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.0, 52.2; ^{11}B NMR (96 MHz, $CDCl_3$) δ -15.28 (q, *J* = 96.5 Hz, 3H).
Characterization is in agreement with previous reports for this compound.[1]

N-Ethylmorpholine-borane (**2aa**):

99% (1.277 g), colorless liquid.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.07 (ddd, *J* = 12.4, 9.6, 2.6 Hz, 2H), 3.61 (dt, *J* = 12.6, 3.7 Hz, 2H), 2.88 – 2.72 (m, 4H), 2.61 (ddd, *J* = 12.7, 9.6, 3.6 Hz, 2H), 1.21 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 61.86, 60.21, 57.26, 8.45. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -14.56 (q, *J* = 97.9 Hz).

(Dimethylamino)acetaldehyde dimethylacetal-borane (**2ab**):

98% (1.440 g), colorless liquid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.87 (t, *J* = 4.9 Hz, 1H), 3.36 (s, 6H), 2.81 (d, *J* = 4.9 Hz, 2H), 2.60 (s, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 101.26, 65.11, 54.38, 54.34, 52.89. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -9.86 (q, *J* = 97.9, 97.2 Hz).

Characterization is in agreement with previous reports for this compound.[1]

Allylamine-borane (**2ac**):

85% (602 mg), colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (q, *J* = 5.4 Hz, 1H), 5.46 – 5.18 (m, 2H), 3.97 (s, 2H), 3.39 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.3, 119.6, 51.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ -19.64 (q, *J* = 97.1, 96.7 Hz, 3H).

Characterization is in agreement with previous reports for this compound.[1]

Dimethylaminopropionitrile-borane (**2ad**):

86% (963 mg), colorless liquid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.05 – 2.96 (m, 2H), 2.94 – 2.85 (m, 2H), 2.62 (s, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 117.49, 59.30, 52.32, 14.00. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -10.95 (q, *J* = 98.4 Hz).

Characterization is in agreement with previous reports for this compound.[1]

(*S*)-Pyrrolidin-2-ylmethanol-borane (**2ae**):

83% (954 mg), colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.38 (s, 1H), 4.11 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.66 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.43 – 3.25 (m, 1H), 3.13 – 2.97 (m, 1H), 2.87 (dq, *J* = 11.8, 8.3 Hz, 1H), 2.48 (s, 1H), 2.05 – 1.77 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 66.69, 60.00, 55.20, 27.14, 23.53. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -17.55 (q, *J* = 96.5, 96.0 Hz).

Characterization is in agreement with previous reports for this compound.[1]

N,*N*-Diethylaminethanethiol-borane (**2af**):

95% (1.397 g), colorless liquid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.71 (s, 4H), 2.49 (q, *J* = 7.2 Hz, 4H), 0.97 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 52.38, 47.10, 36.51, 11.97. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -13.46 (q, *J* = 101.4, 99.3 Hz).

Characterization is in agreement with previous reports for this compound.[1]

Diphenylphosphine-borane (**4a**):

95% (1.900 g), colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.63 (m, 4H), 7.55 – 7.48 (m, 2H), 7.45 (dddd, *J* = 8.5, 5.6, 2.4, 1.4 Hz, 4H), 6.32 (dq, *J* = 379.1, 7.0 Hz, 1H), 1.12 (dd, *J* = 197.8, 84.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.88 (d, *J* = 9.3 Hz), 131.61 (d, *J* = 2.5 Hz), 129.03 (d, *J* = 10.4 Hz), 126.13 (d, *J* = 57.3 Hz). ^{11}B NMR (96 MHz, Chloroform-*d*) δ -40.58 (qd, *J* = 99.2, 45.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 2.18 (d, *J* = 56.7 Hz).

Characterization is in agreement with previous reports for this compound.[12]

Trioctylphosphine-borane (**4b**):

99% (3.806 g), colorless liquid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.50 (qd, *J* = 9.9, 5.6 Hz, 12H), 1.36 – 1.20 (m, 30H), 0.87 (t, *J* = 6.5 Hz, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 31.89, 31.37 (d, *J* = 12.2 Hz), 29.20, 29.14, 23.14 (d, *J* = 34.2 Hz), 22.73, 14.21. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -36.76 – -45.83 (m). ^{31}P NMR (121 MHz, Chloroform-*d*) δ 15.26 (d, *J* = 83.1 Hz).

Characterization is in agreement with previous reports for this compound.[13]

Triphenylphosphine-borane (**4c**):

99% (2.734 g), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65 – 7.37 (m, 15H), 1.81 – 0.79 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 133.16, 133.03, 131.17, 129.44, 128.75, 128.62. ^{11}B NMR (96 MHz, Tetrahydrofuran) δ -22.38 (q, *J* = 95.3, 94.7 Hz, 3H). ^{31}P NMR (121 MHz, Chloroform-*d*) δ 21.48 (d, *J* = 77.5 Hz).

Characterization is in agreement with previous reports for this compound.[12]

Tri-p-tolylphosphine-borane (**4d**):

99% (3.150 g), white solid.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46 (ddd, *J* = 10.7, 8.1, 2.0 Hz, 6H), 7.26 – 7.19 (m, 6H), 2.39 (s, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.35, 132.98 (d, *J* = 9.9 Hz), 129.39 (d, *J* = 10.4 Hz), 126.09 (d, *J* = 59.8 Hz), 21.62. ^{11}B NMR (96 MHz, Chloroform-*d*) δ -33.71 – -42.77 (m). ^{31}P NMR (121 MHz, Chloroform-*d*) δ 19.28 (d, *J* = 64.7 Hz).

Characterization is in agreement with previous reports for this compound.[14]

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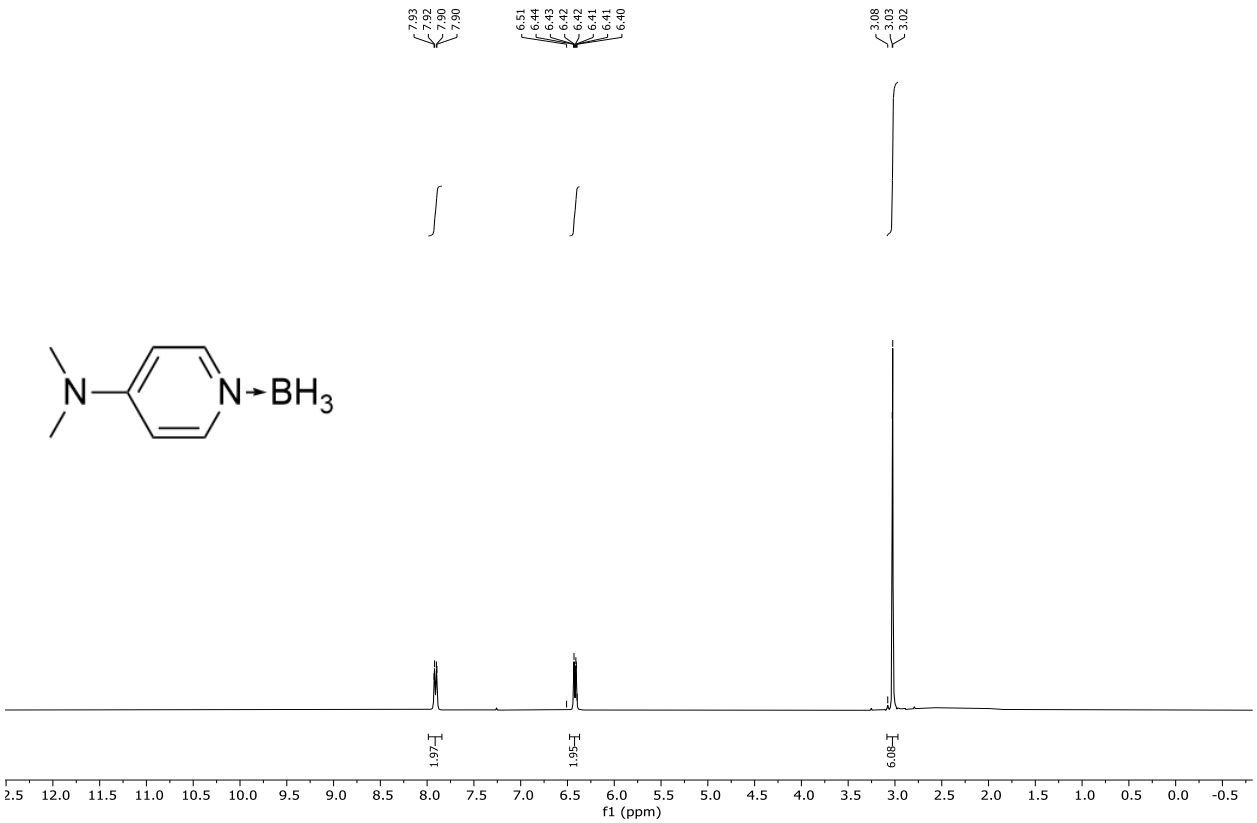
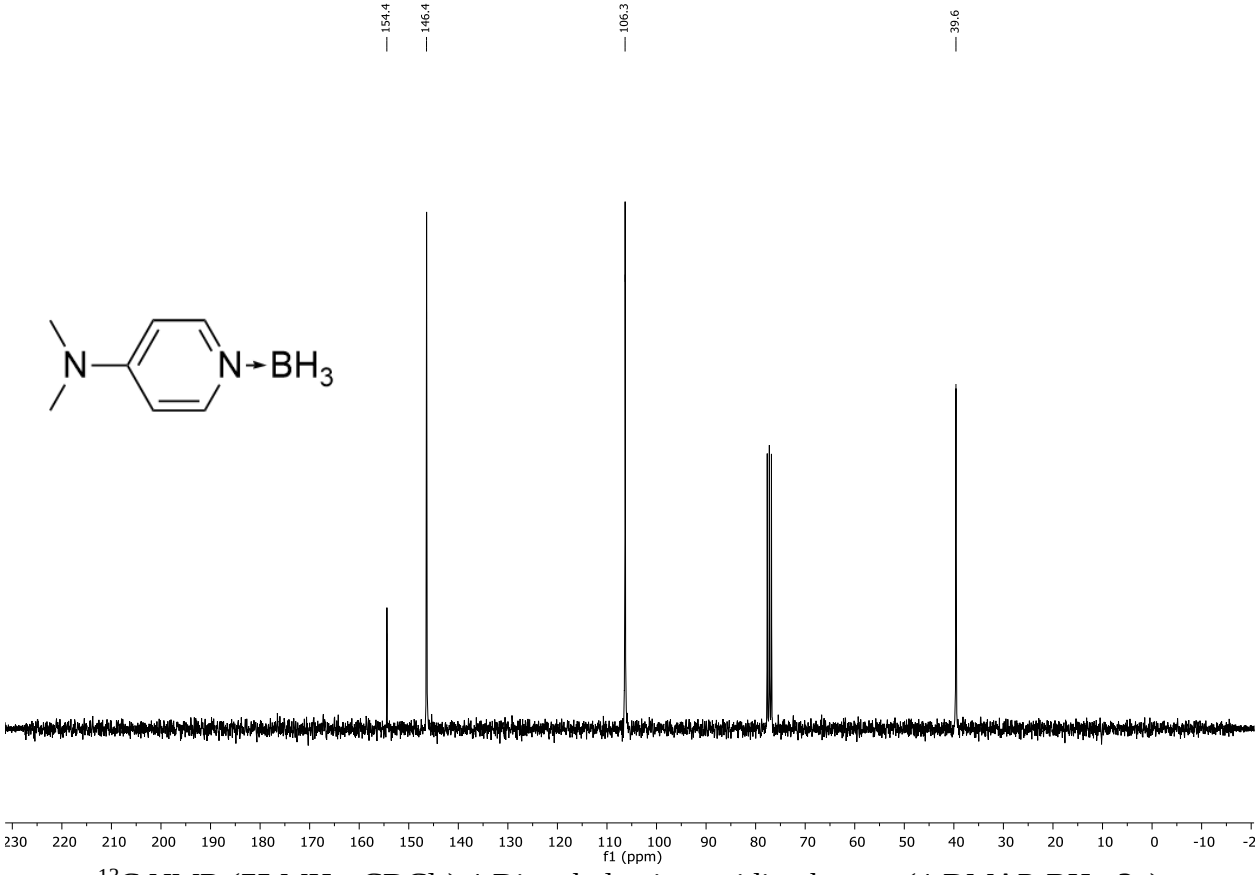
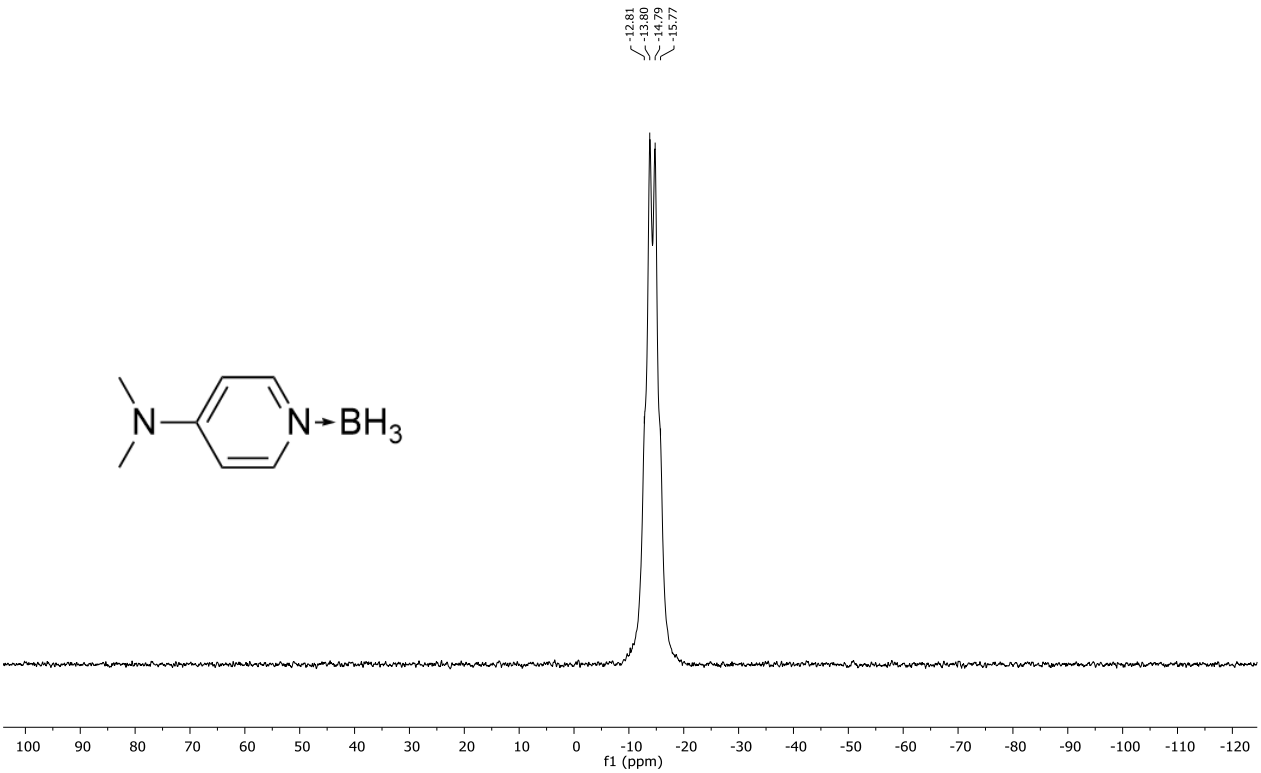
NMR spectra of amine- and phosphine-boranes:



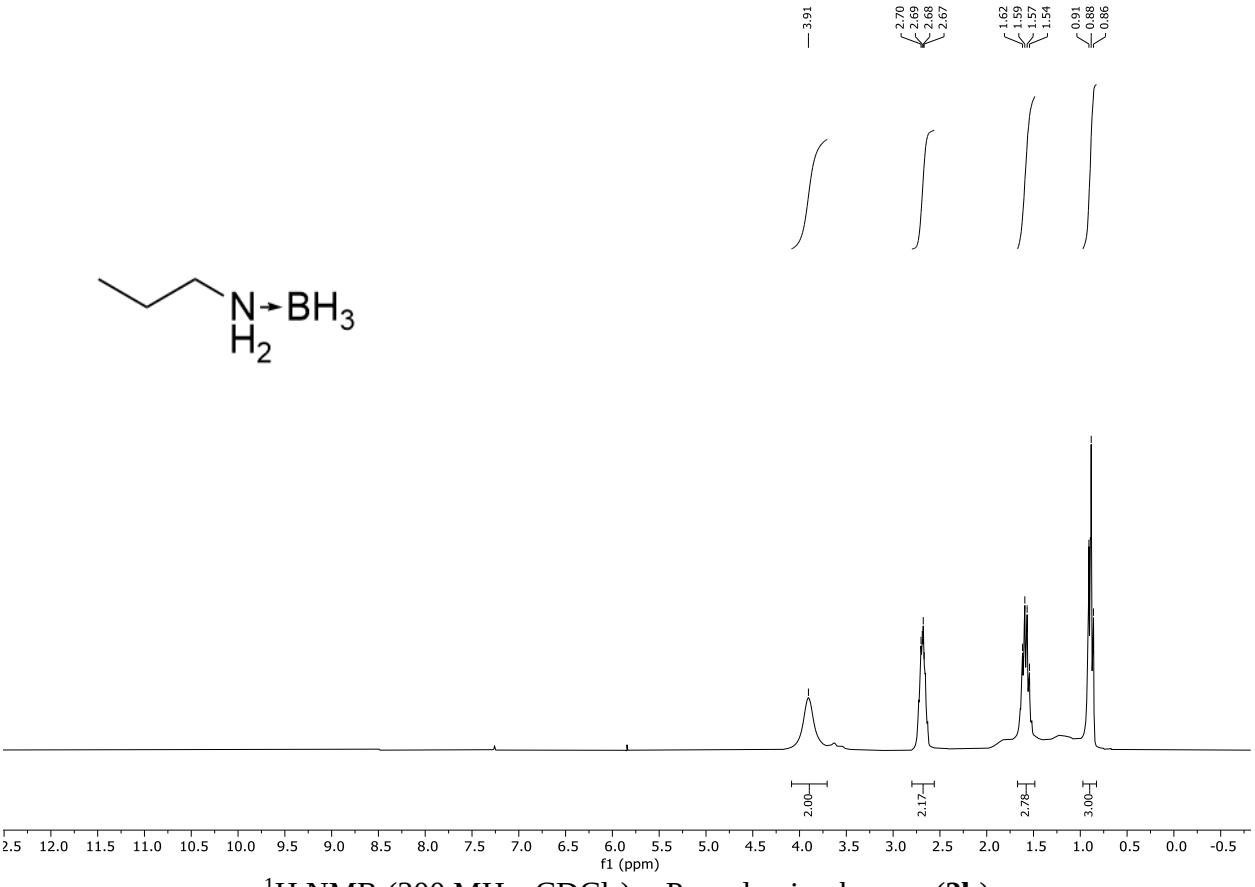
^{1}H NMR (300 MHz, $CDCl_3$) 4-Dimethylaminopyridine-borane (4-DMAP-BH_3, **2a**)



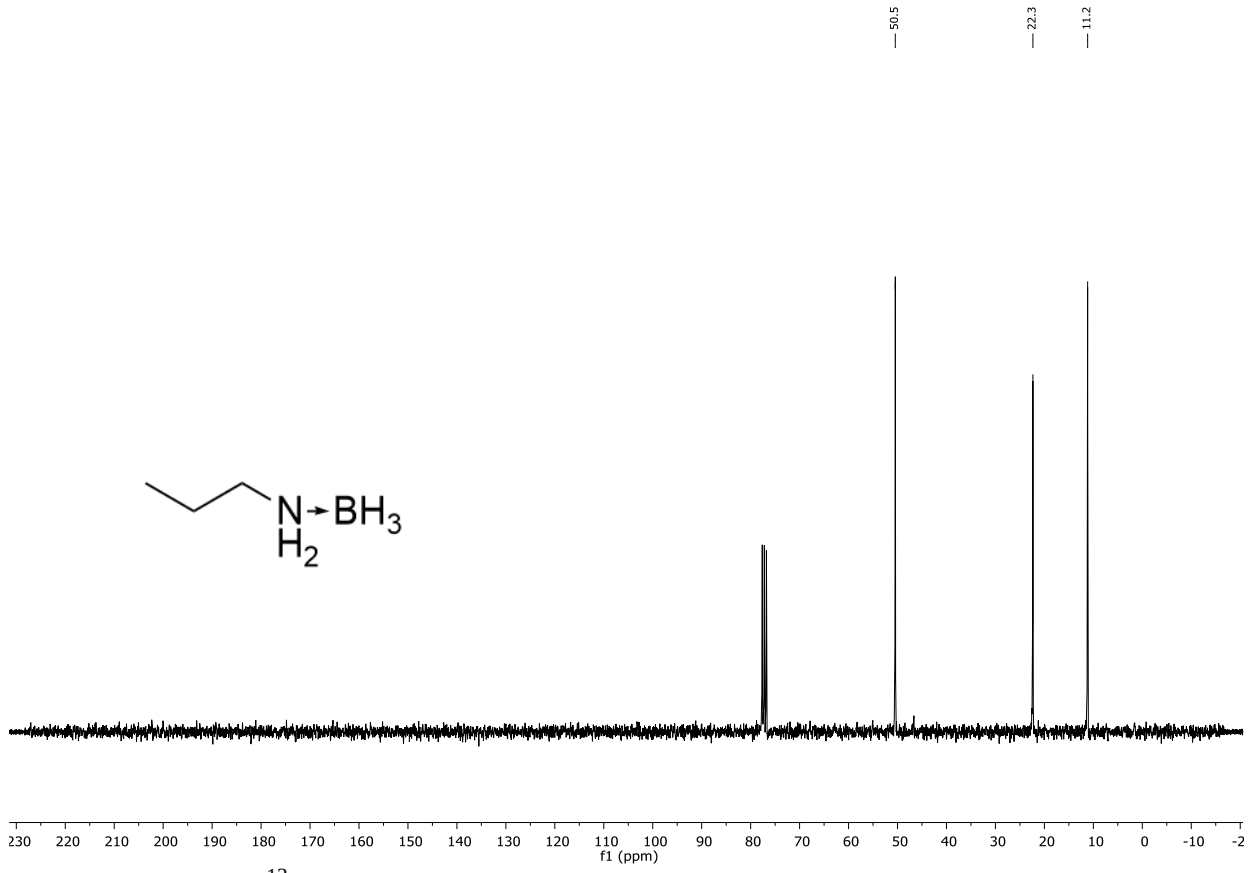
^{13}C NMR (75 MHz, $CDCl_3$) 4-Dimethylaminopyridine-borane (4-DMAP-BH_3, **2a**)



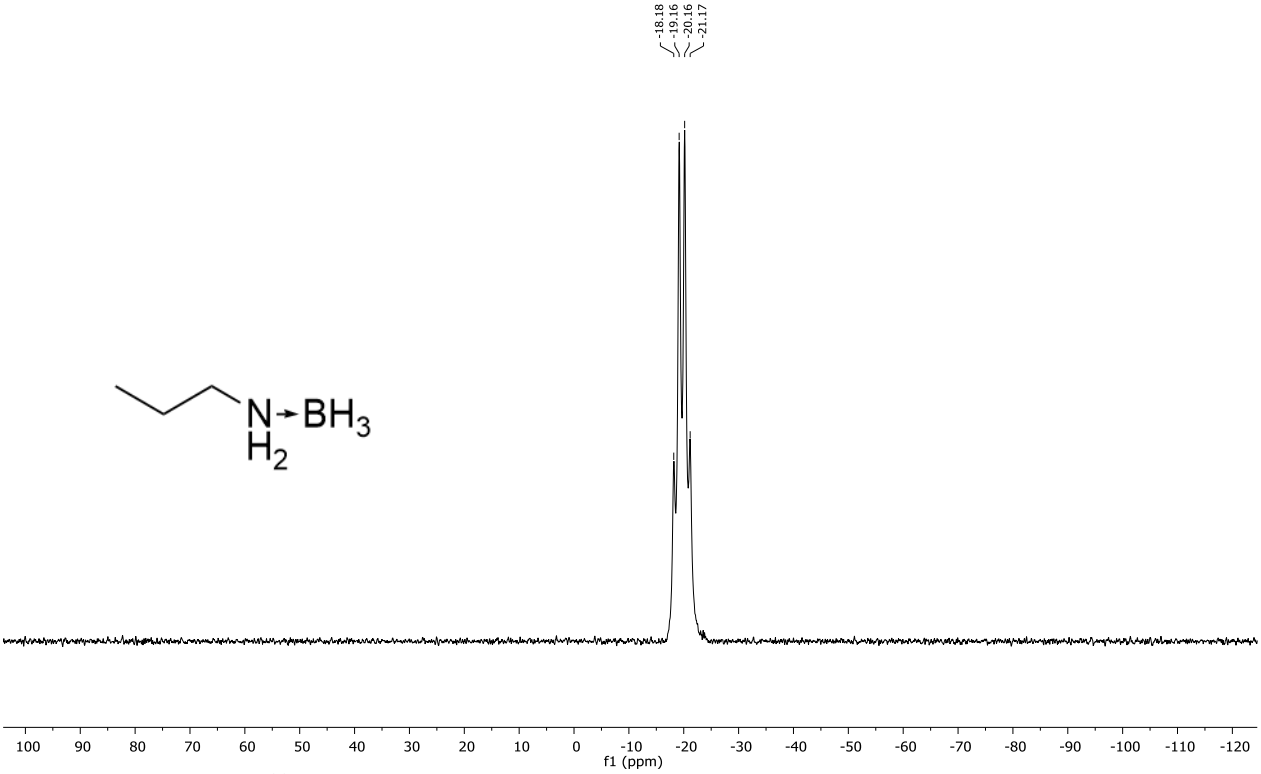
^{11}B NMR (96 MHz, $CDCl_3$) 4-Dimethylaminopyridine-borane (4-DMAP-BH_3, **2a**)



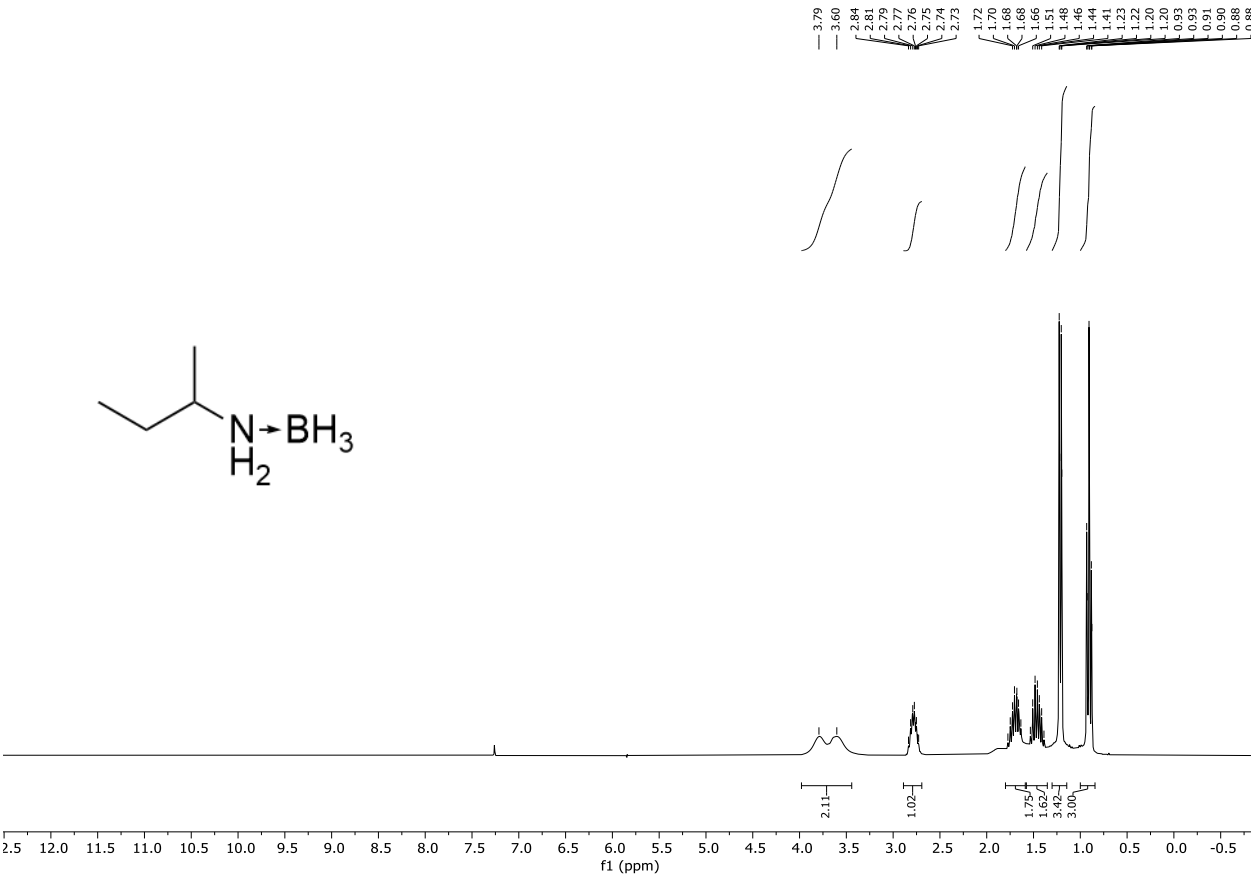
^{1}H NMR (300 MHz, $CDCl_3$) *n*-Propylamine-borane (**2b**)



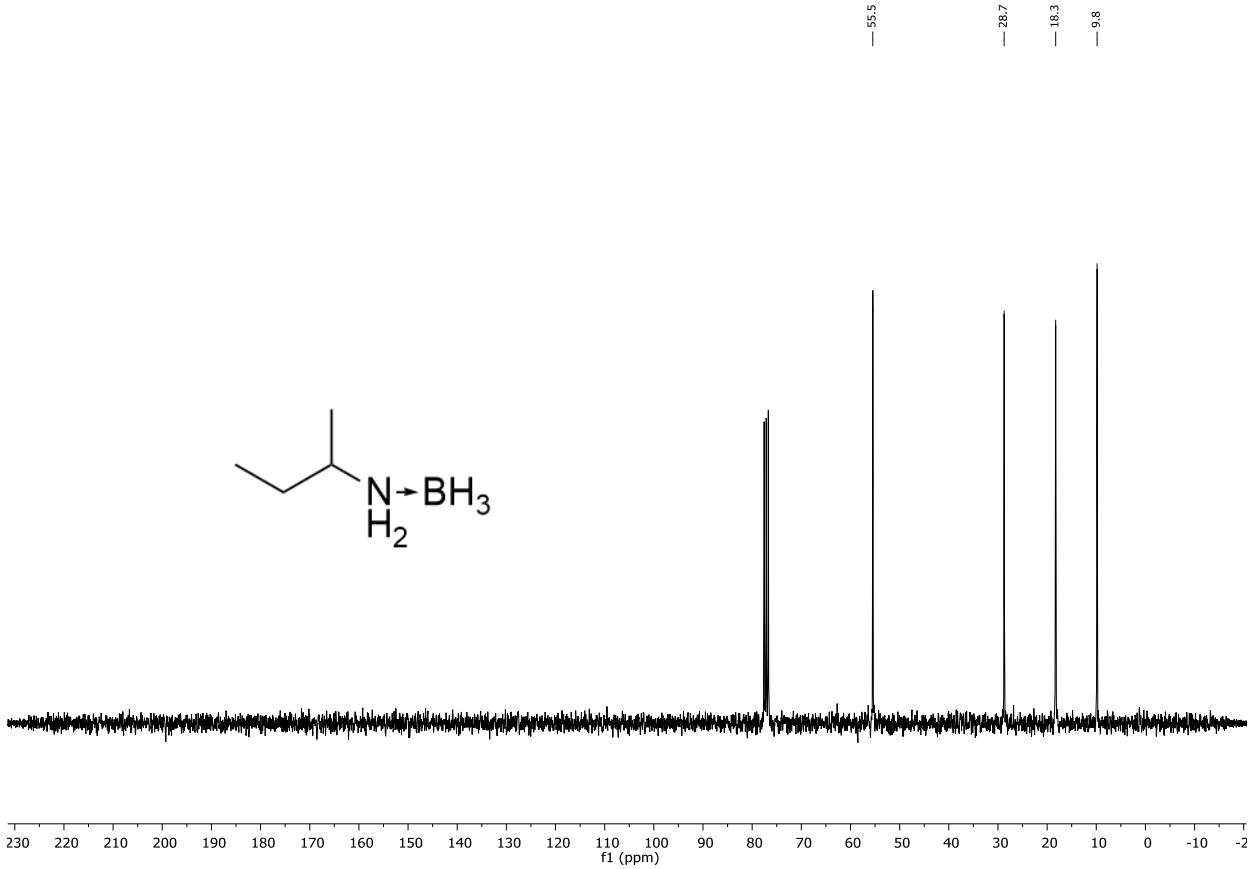
^{13}C NMR (75 MHz, $CDCl_3$) *n*-Propylamine-borane (**2b**)



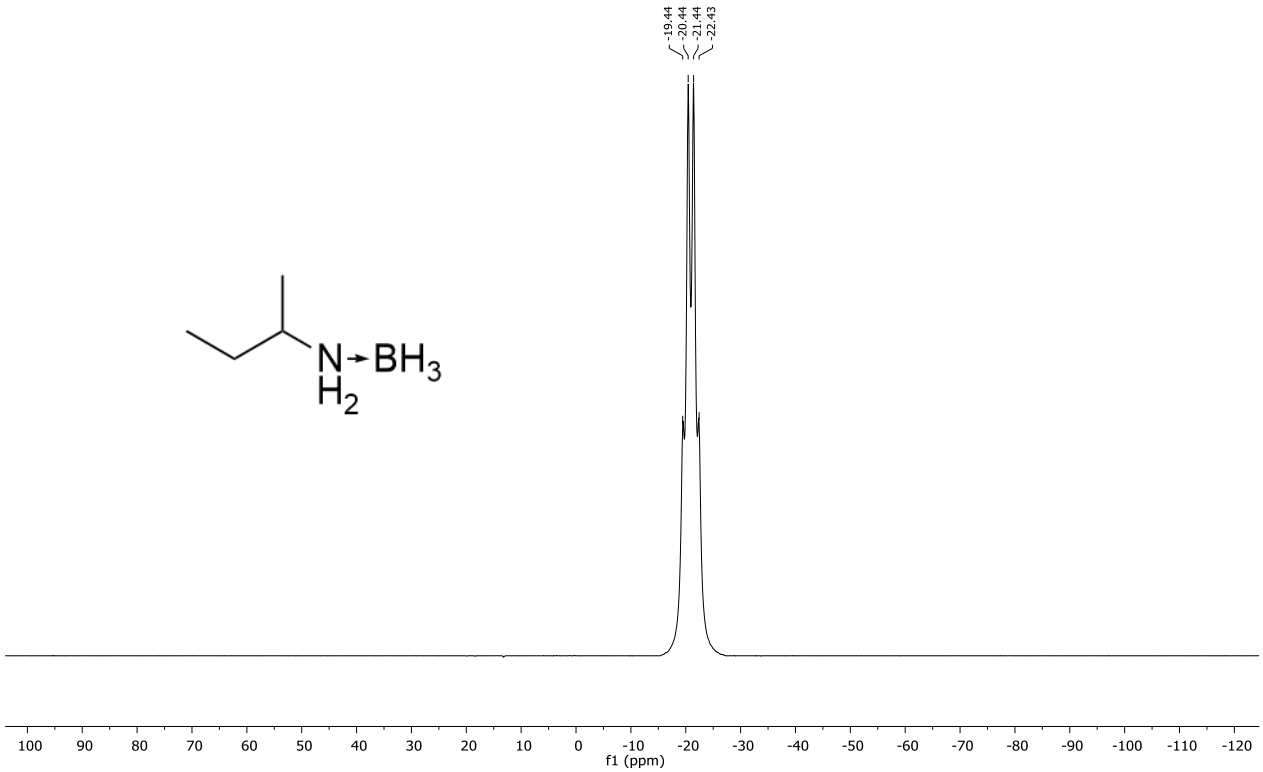
^{11}B NMR (96 MHz, $CDCl_3$) *n*-Propylamine-borane (**2b**)



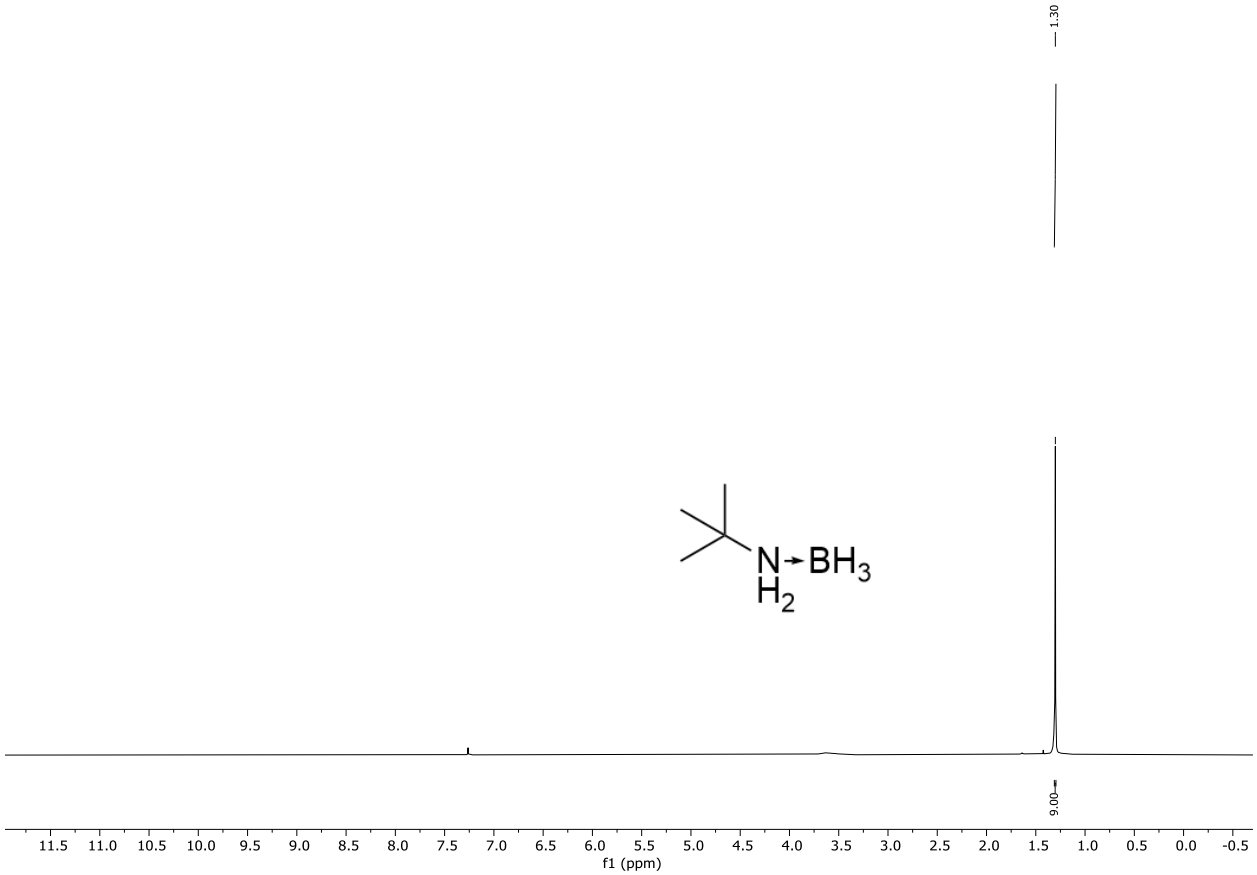
^{1}H NMR (300 MHz, $CDCl_3$) *sec*-Butylamine-borane (**2c**)



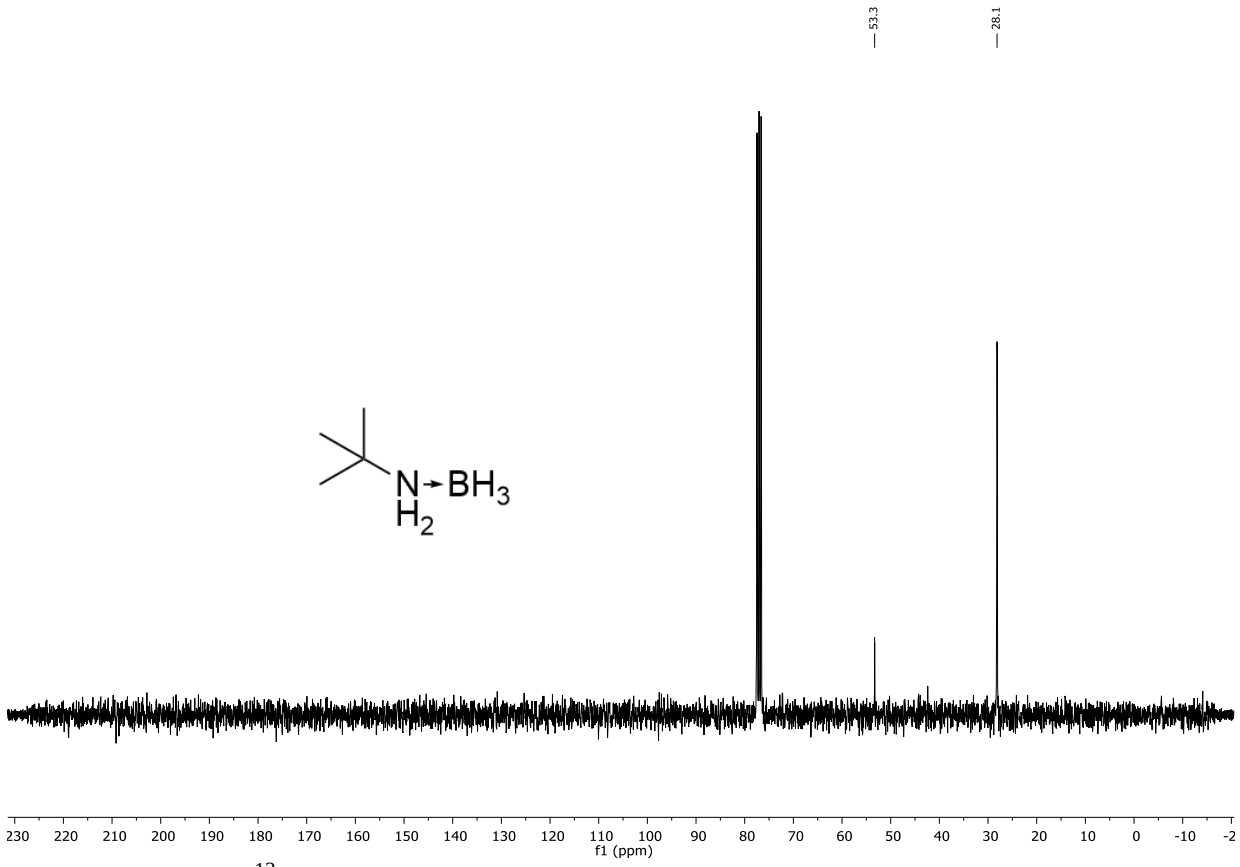
^{13}C NMR (75 MHz, $CDCl_3$) *sec*-Butylamine-borane (**2c**)



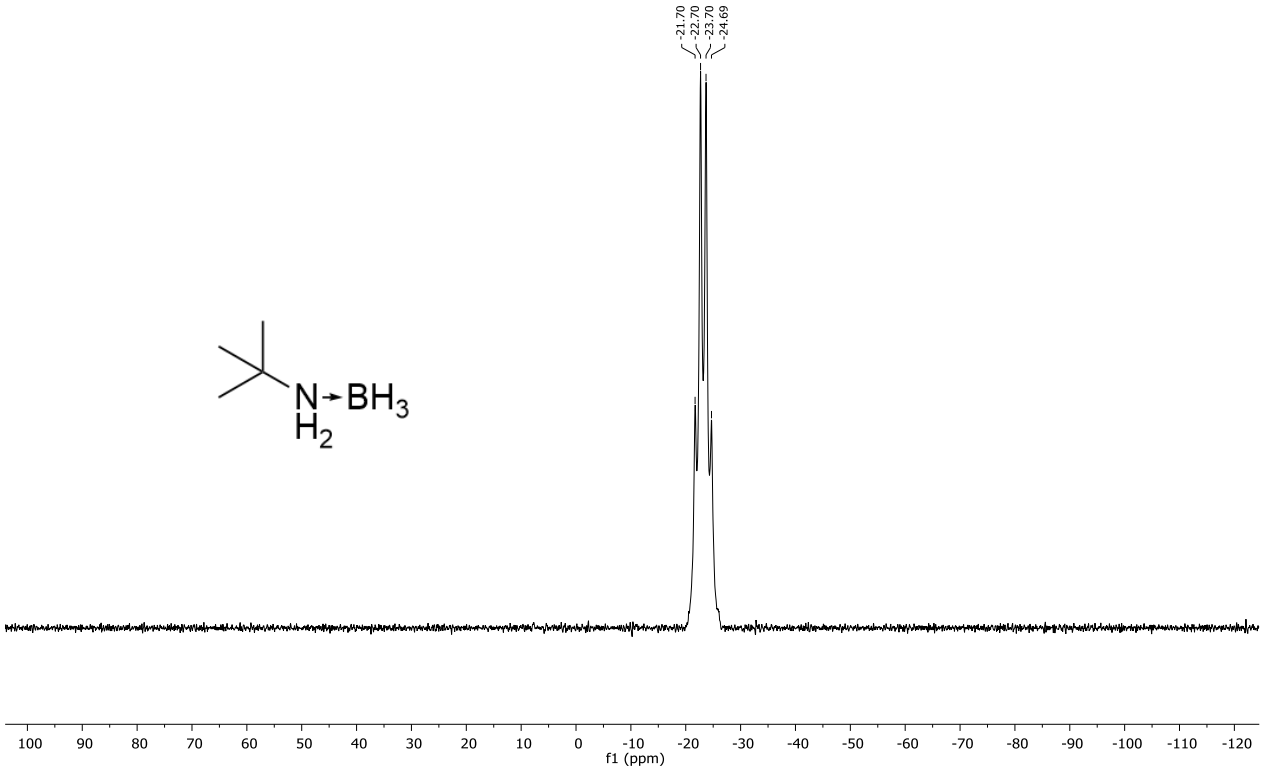
^{11}B NMR (96 MHz, $CDCl_3$) *sec*-Butylamine-borane (**2c**)



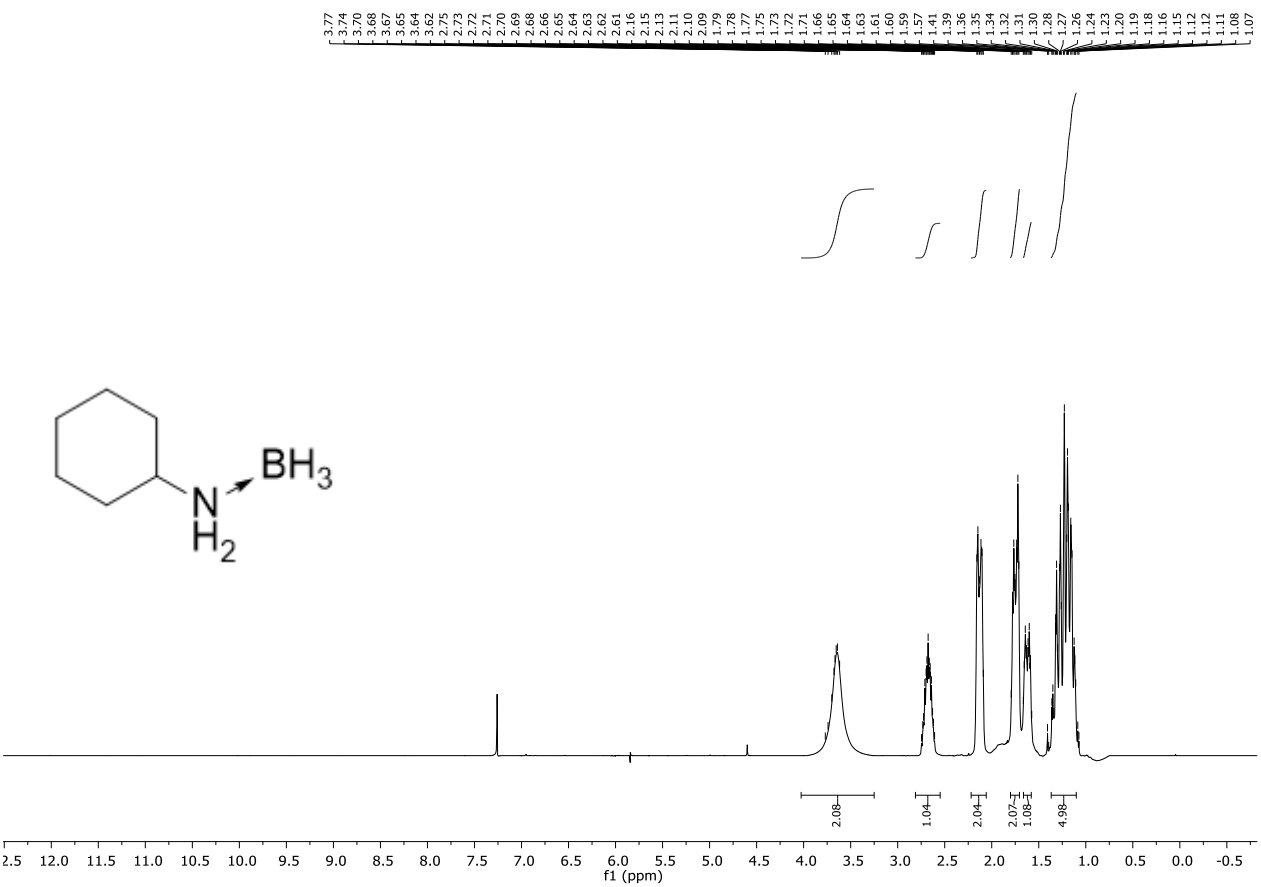
^{1}H NMR (300 MHz, $CDCl_3$) *tert*-Butylamine-borane (**2d**)



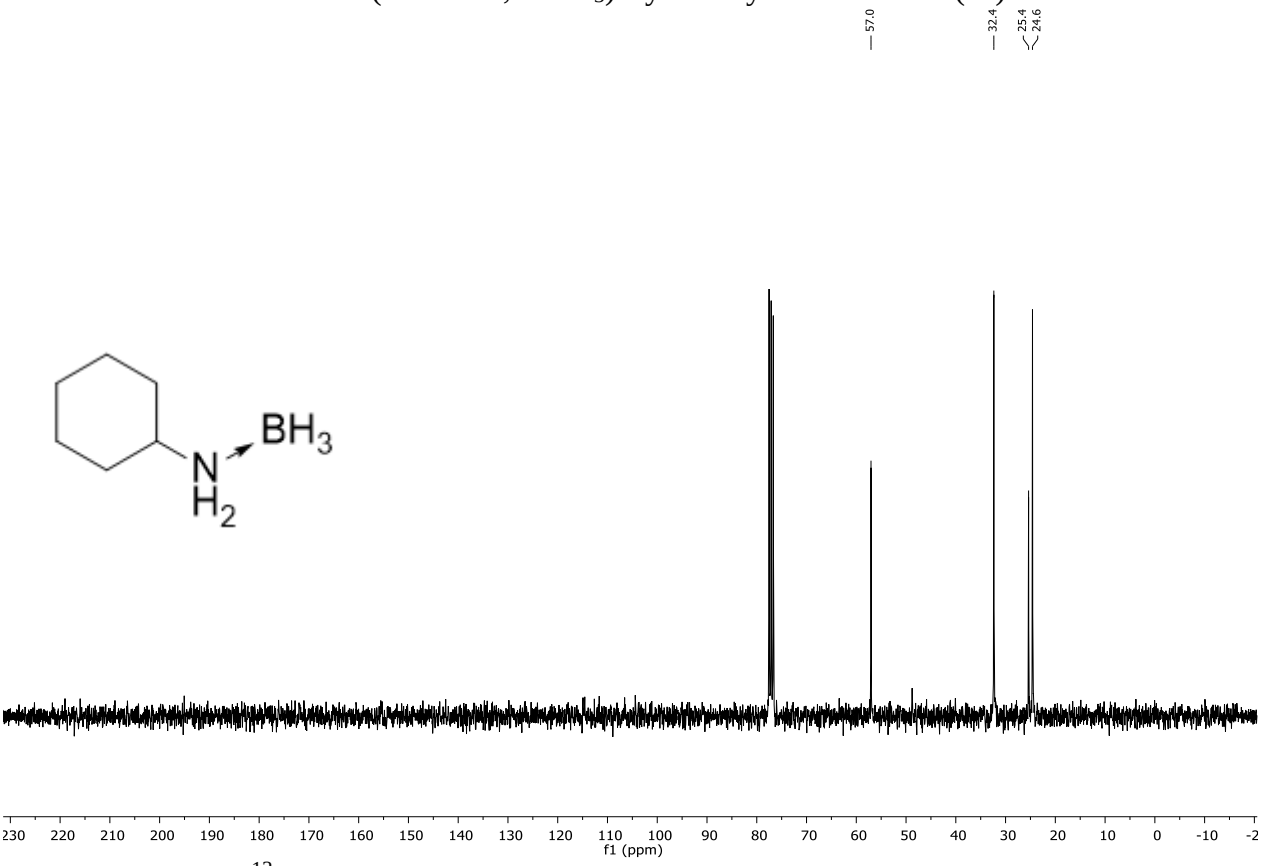
^{13}C NMR (75 MHz, $CDCl_3$) *tert*-Butylamine-borane (**2d**)



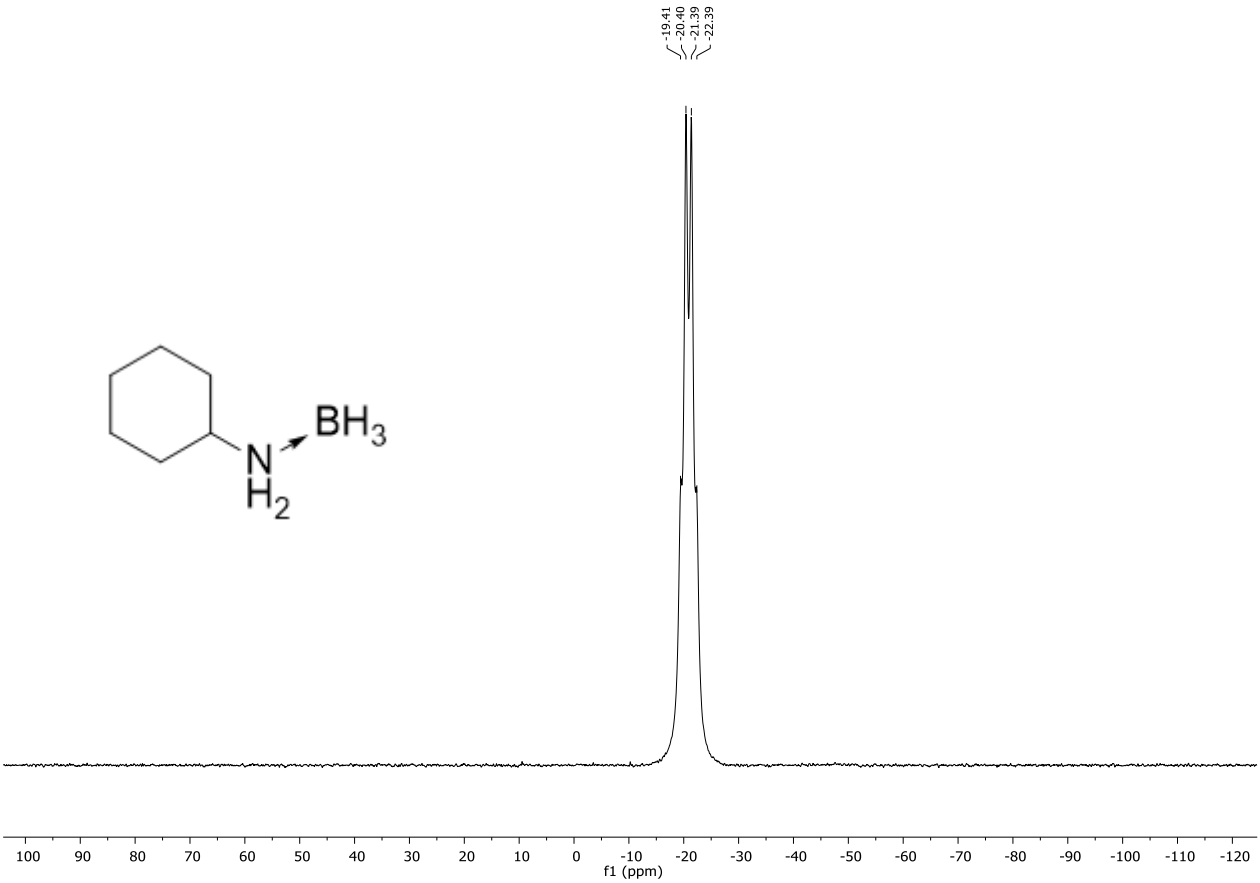
^{11}B NMR (96 MHz, $CDCl_3$) *tert*-Butylamine-borane (**2d**)



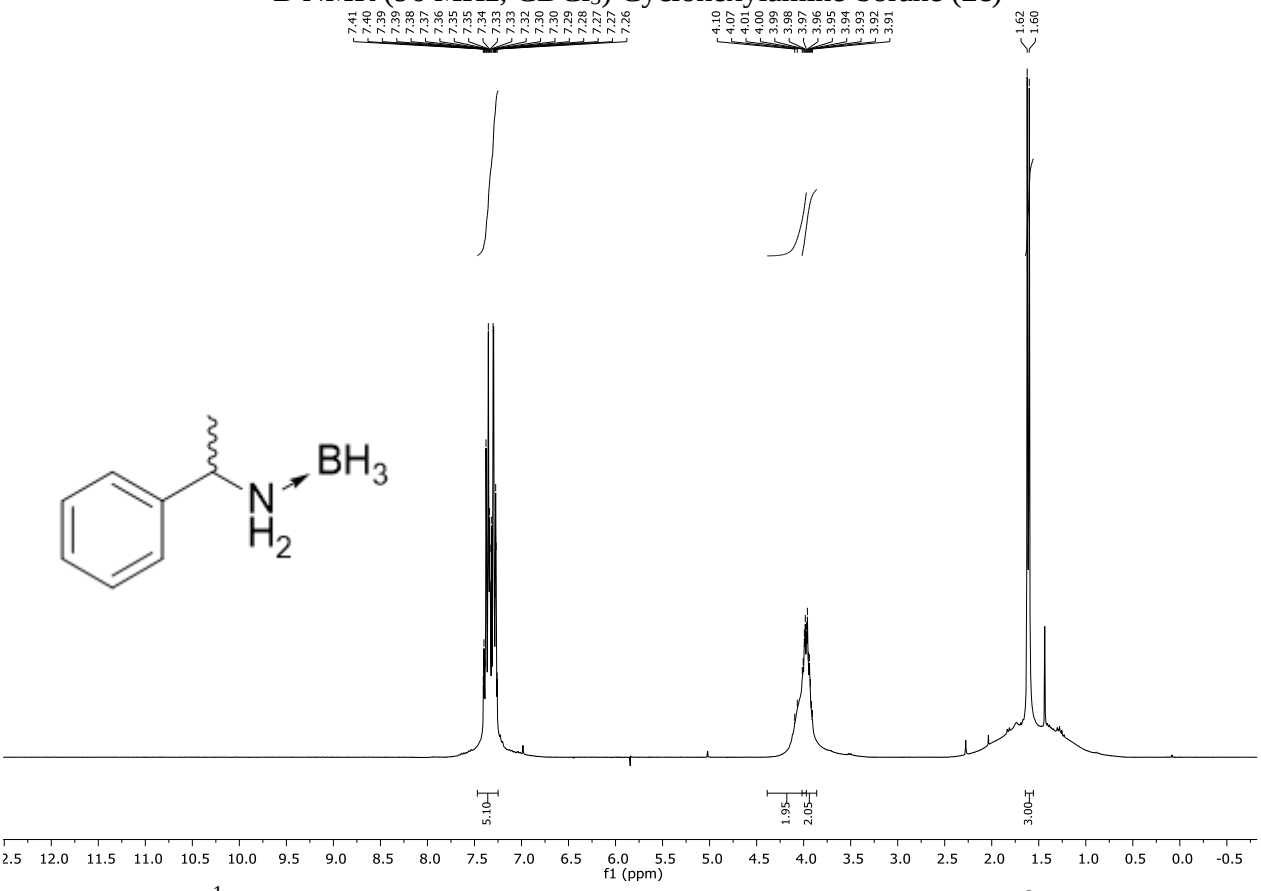
^{1}H NMR (300 MHz, $CDCl_3$) Cyclohexylamine-borane (**2e**)



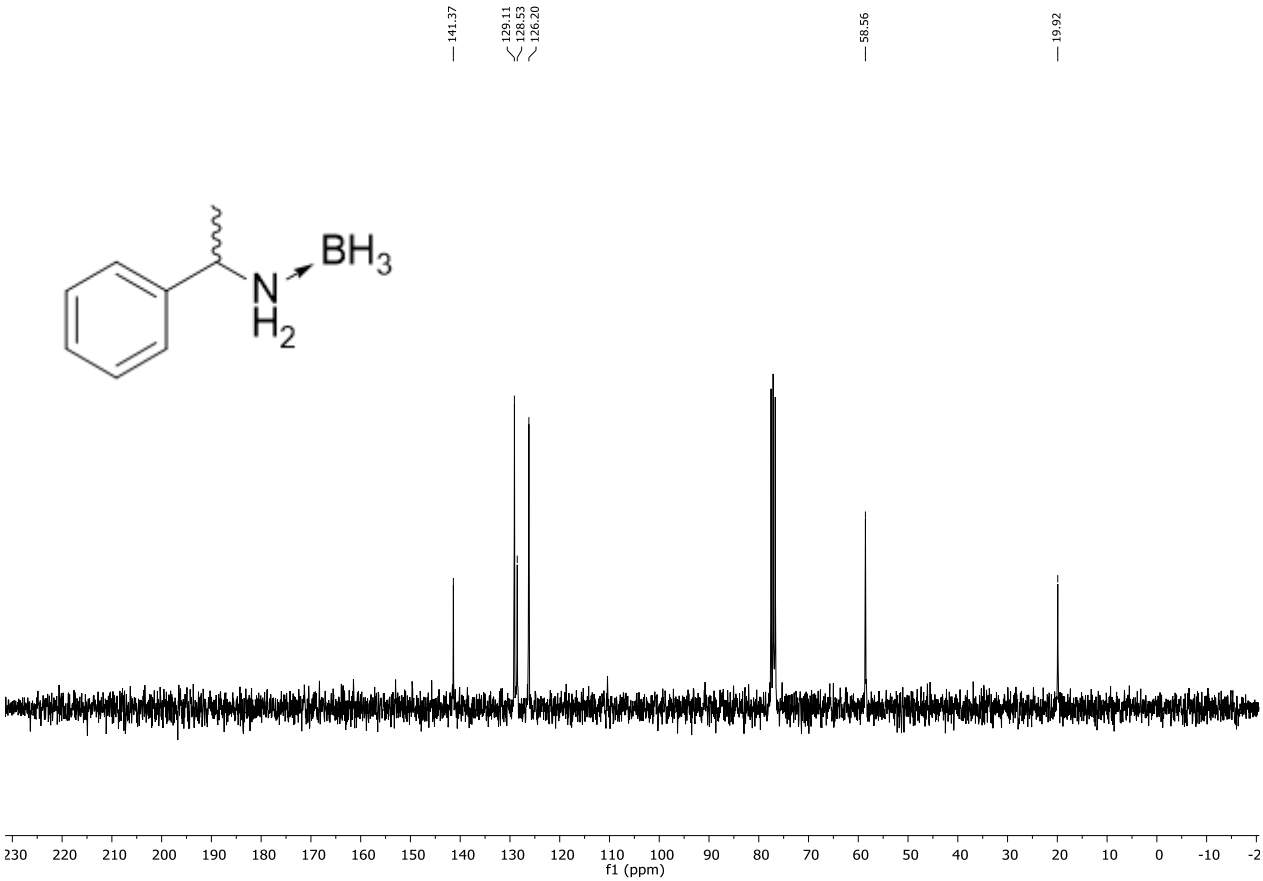
^{13}C NMR (75 MHz, $CDCl_3$) Cyclohexylamine-borane (**2e**)



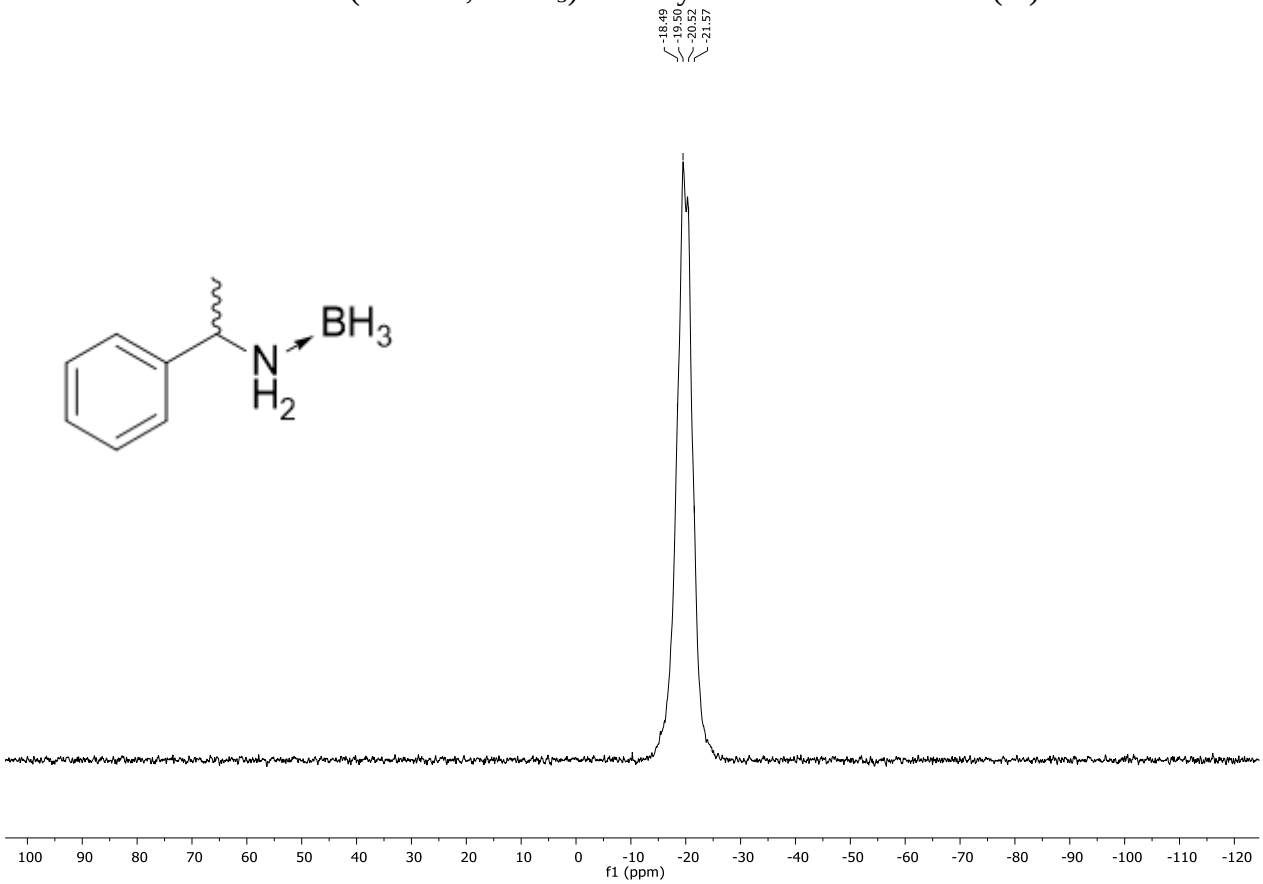
^{11}B NMR (96 MHz, $CDCl_3$) Cyclohexylamine-borane (**2e**)



^{1}H NMR (300 MHz, $CDCl_3$) 1-Phenylethan-1-amine-borane (**2f**)

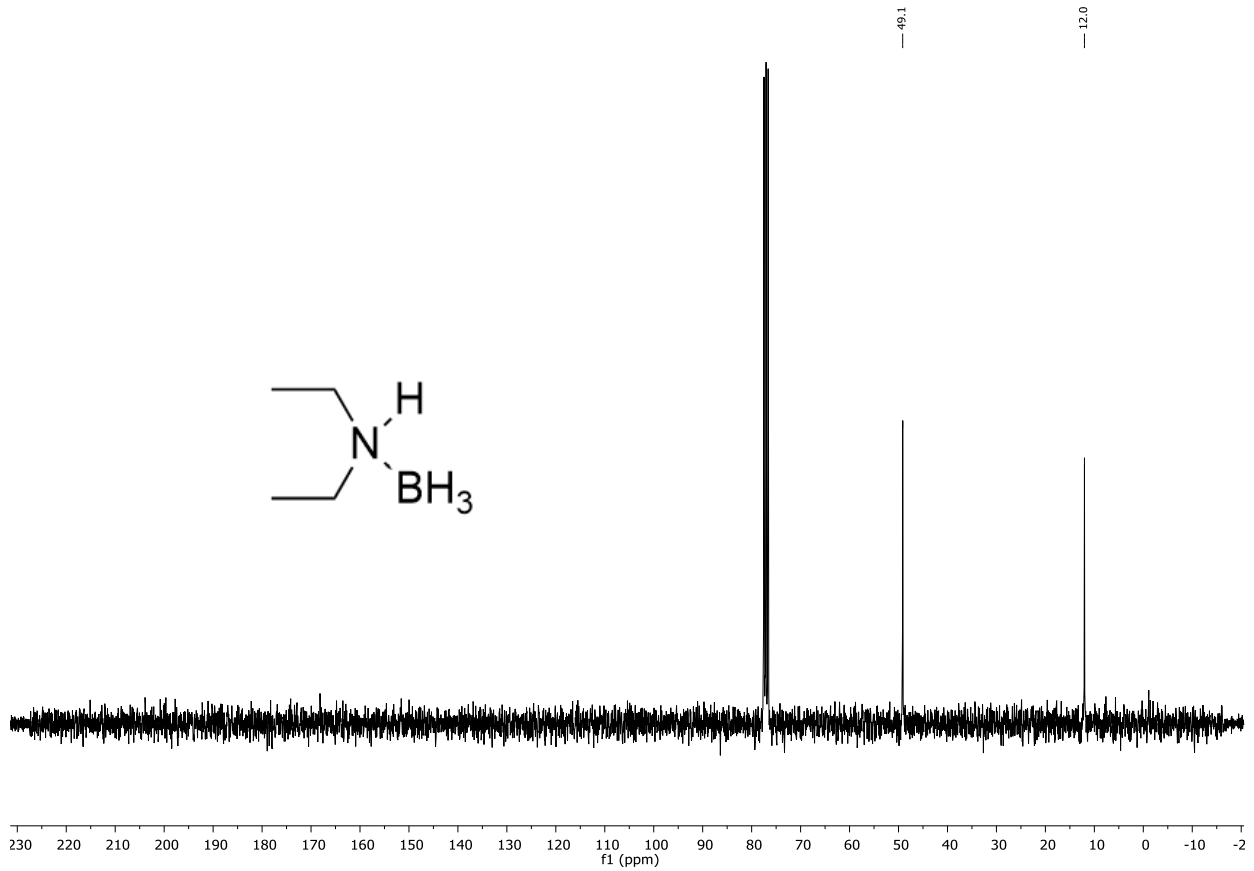


^{13}C NMR (75 MHz, $CDCl_3$) 1-Phenylethan-1-amine-borane (**2f**)

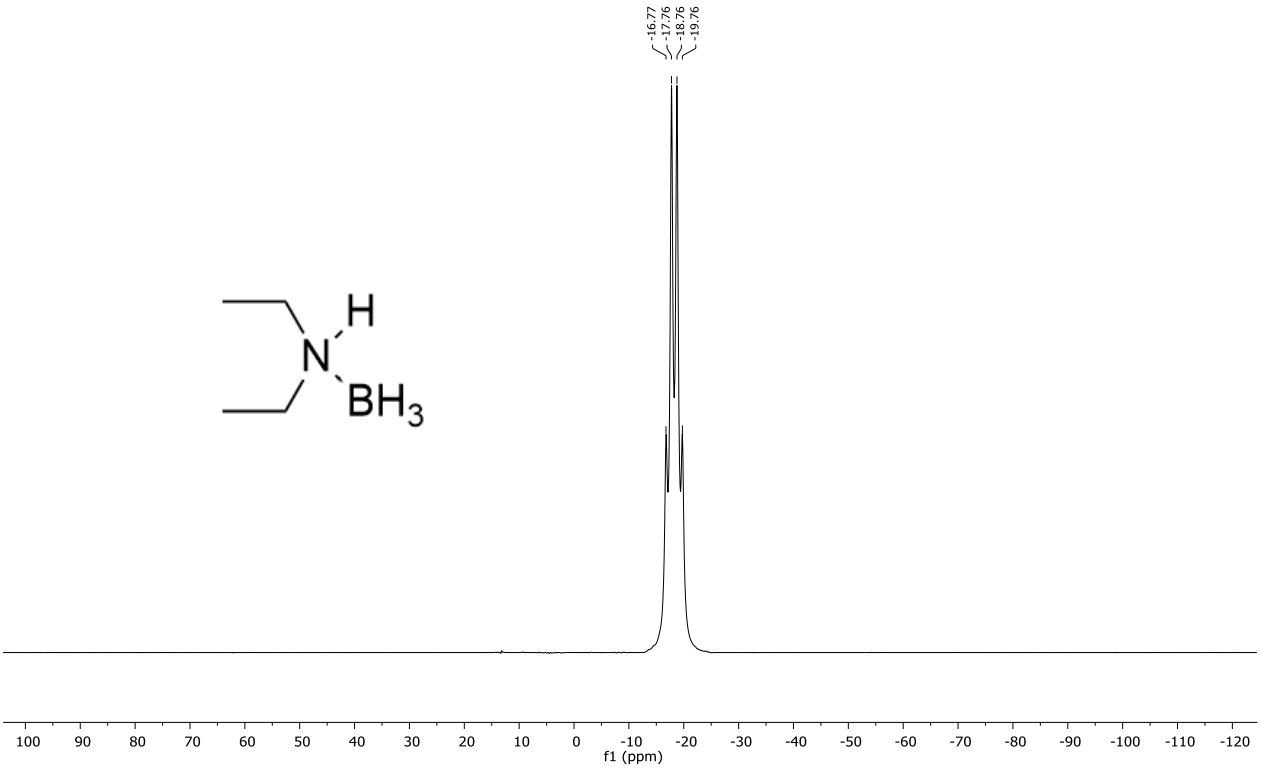


^{11}B NMR (96 MHz, $CDCl_3$) 1-Phenylethan-1-amine-borane (**2f**)

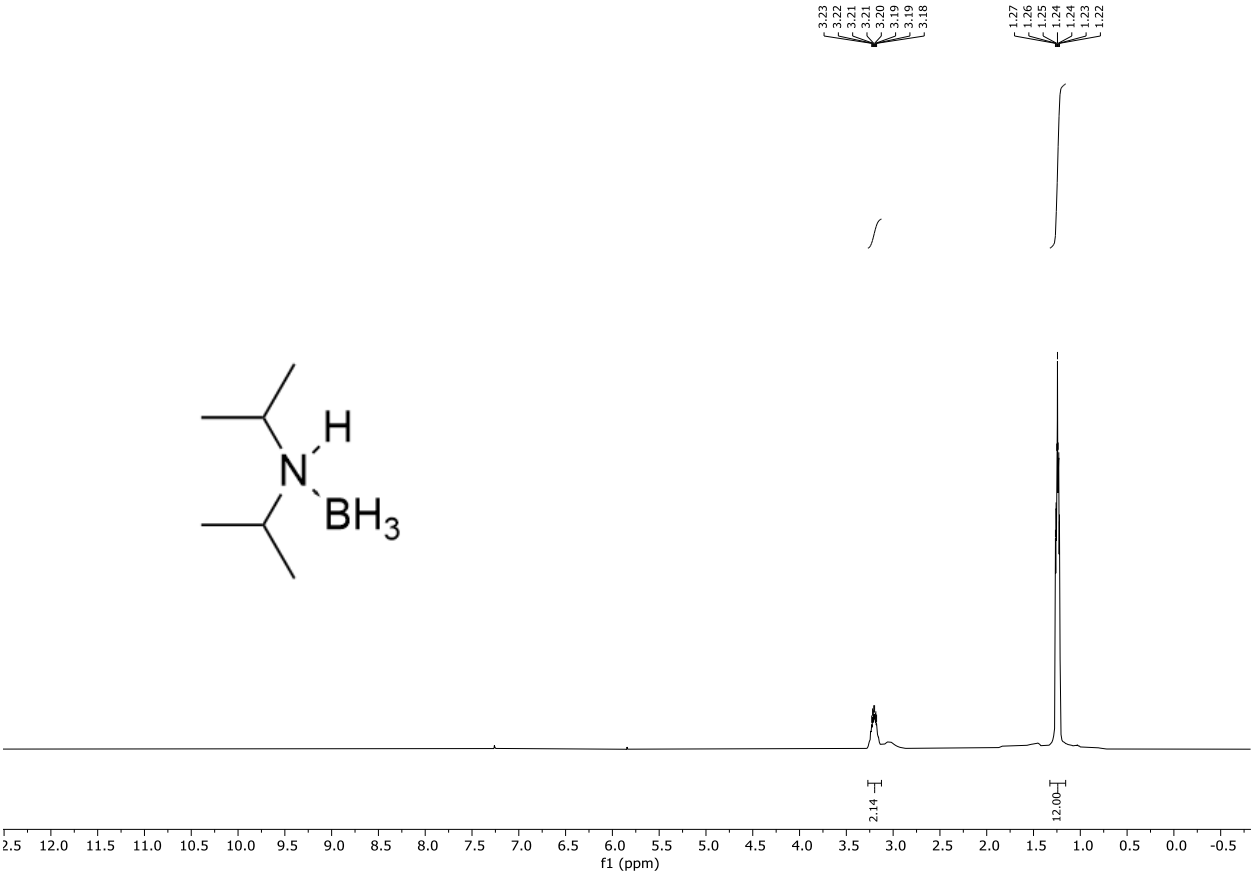
^{1}H NMR (300 MHz, $CDCl_3$) Diethylamine-borane (**2g**)



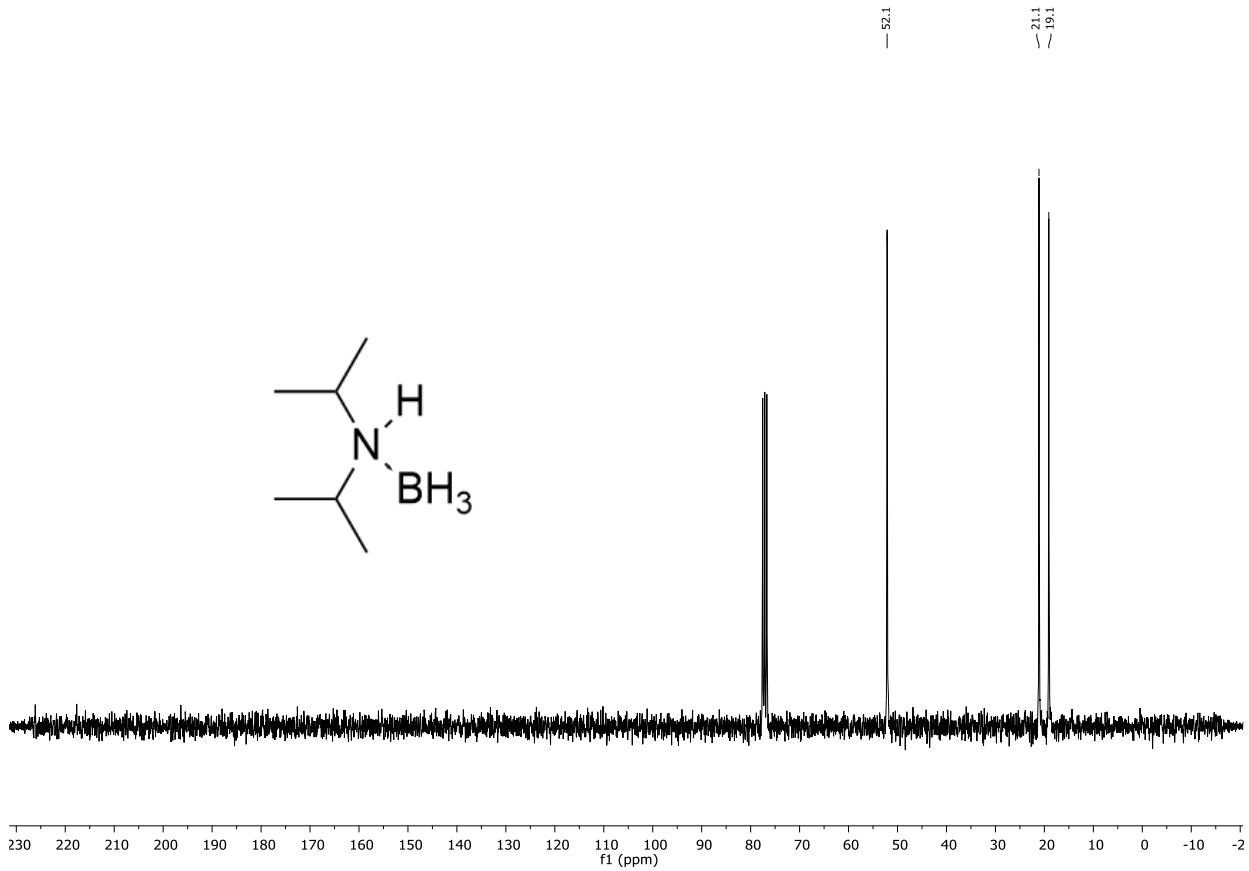
^{13}C NMR (75 MHz, $CDCl_3$) Diethylamine-borane (**2g**)



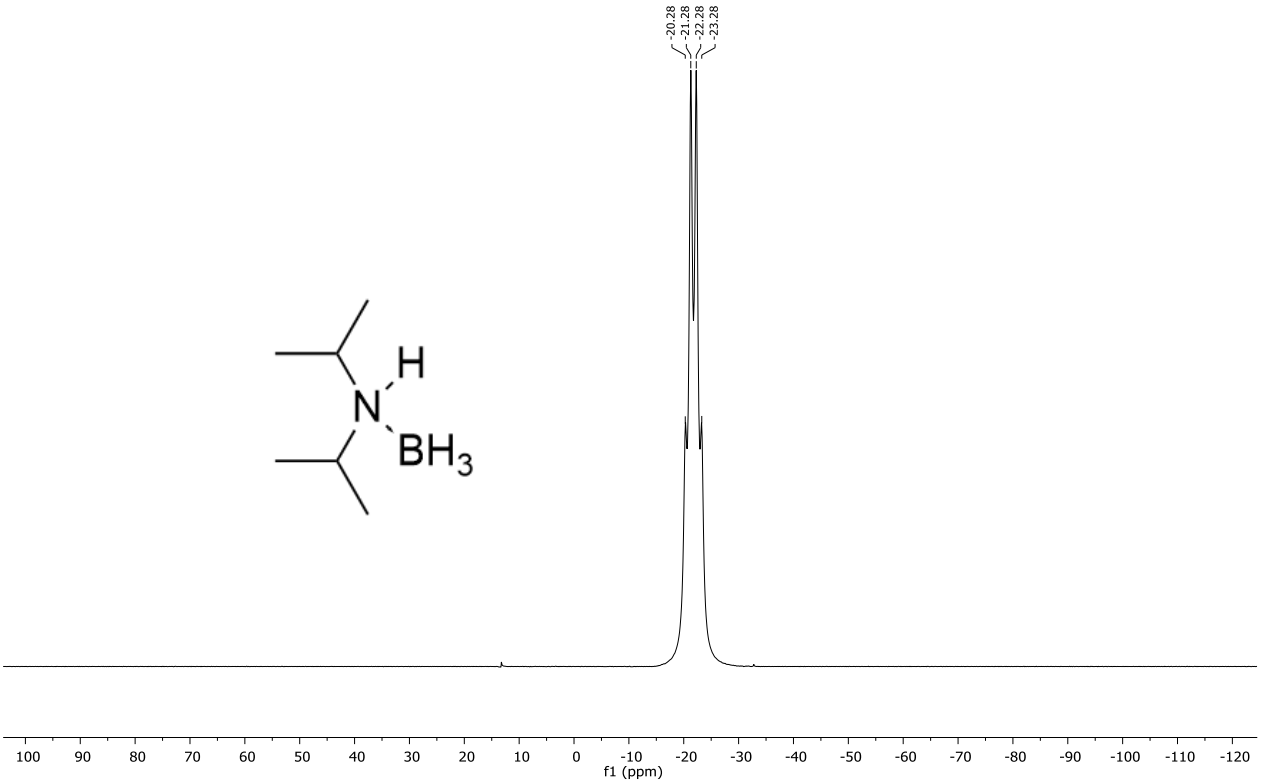
^{11}B NMR (96 MHz, $CDCl_3$) Diethylamine-borane (**2g**)



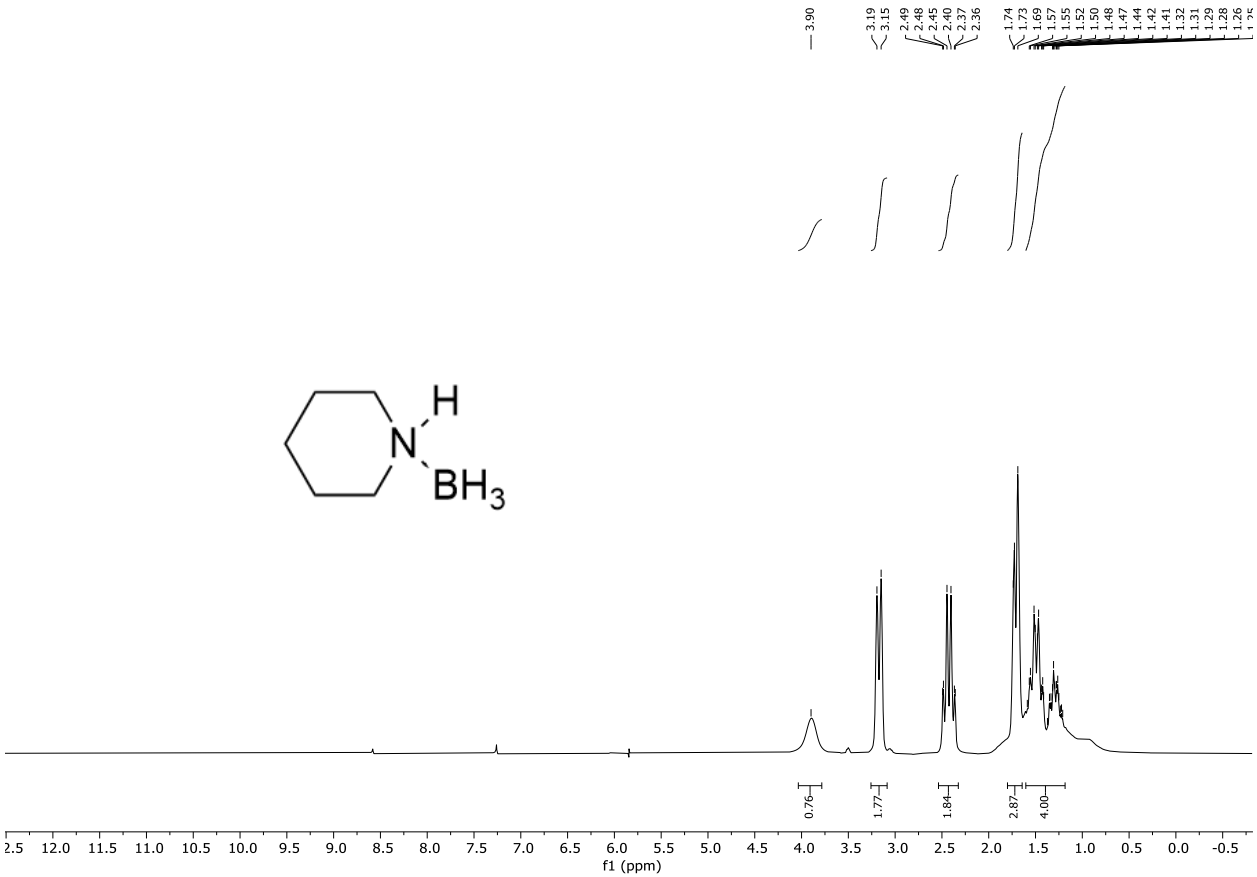
^{1}H NMR (300 MHz, $CDCl_3$) Diisopropylamine-borane (**2h**)



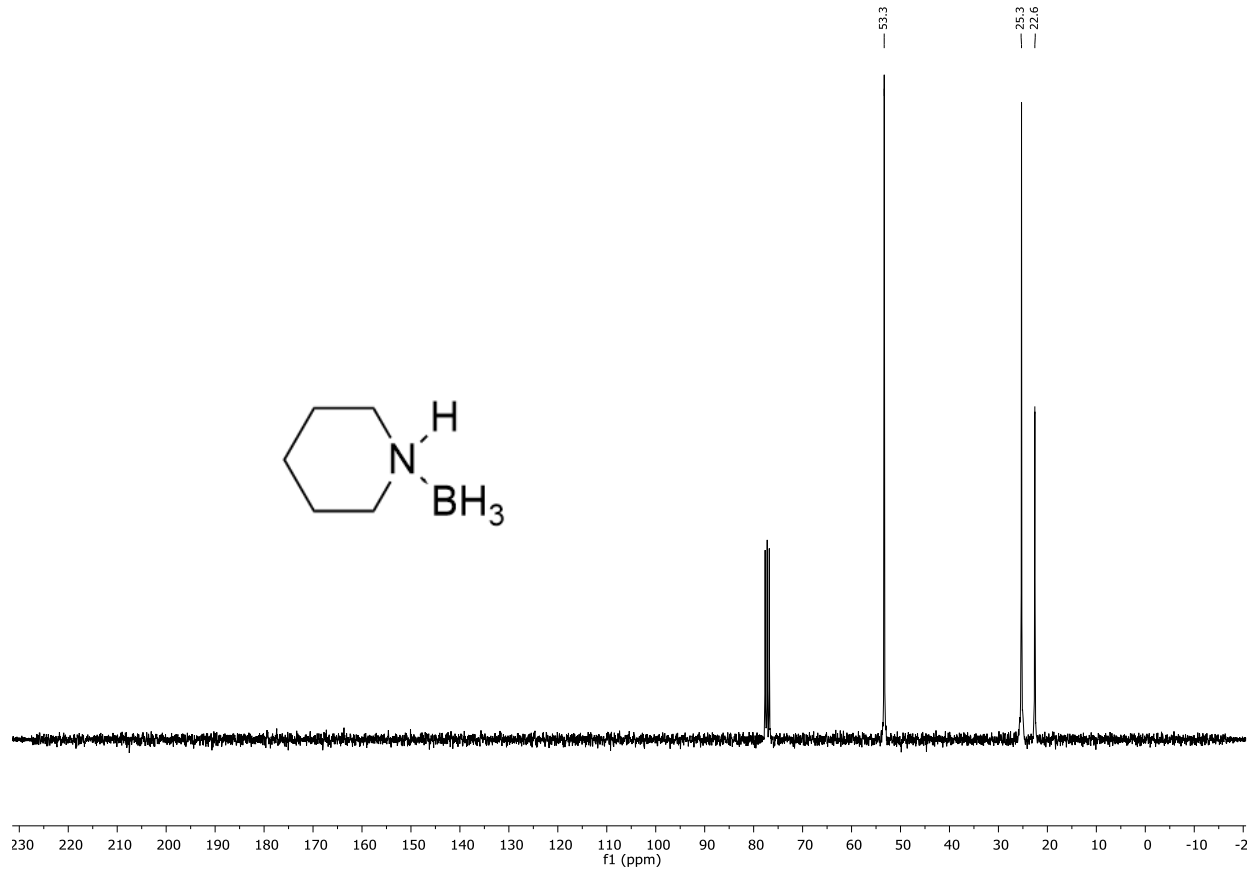
^{13}C NMR (75 MHz, $CDCl_3$) Diisopropylamine-borane (**2h**)



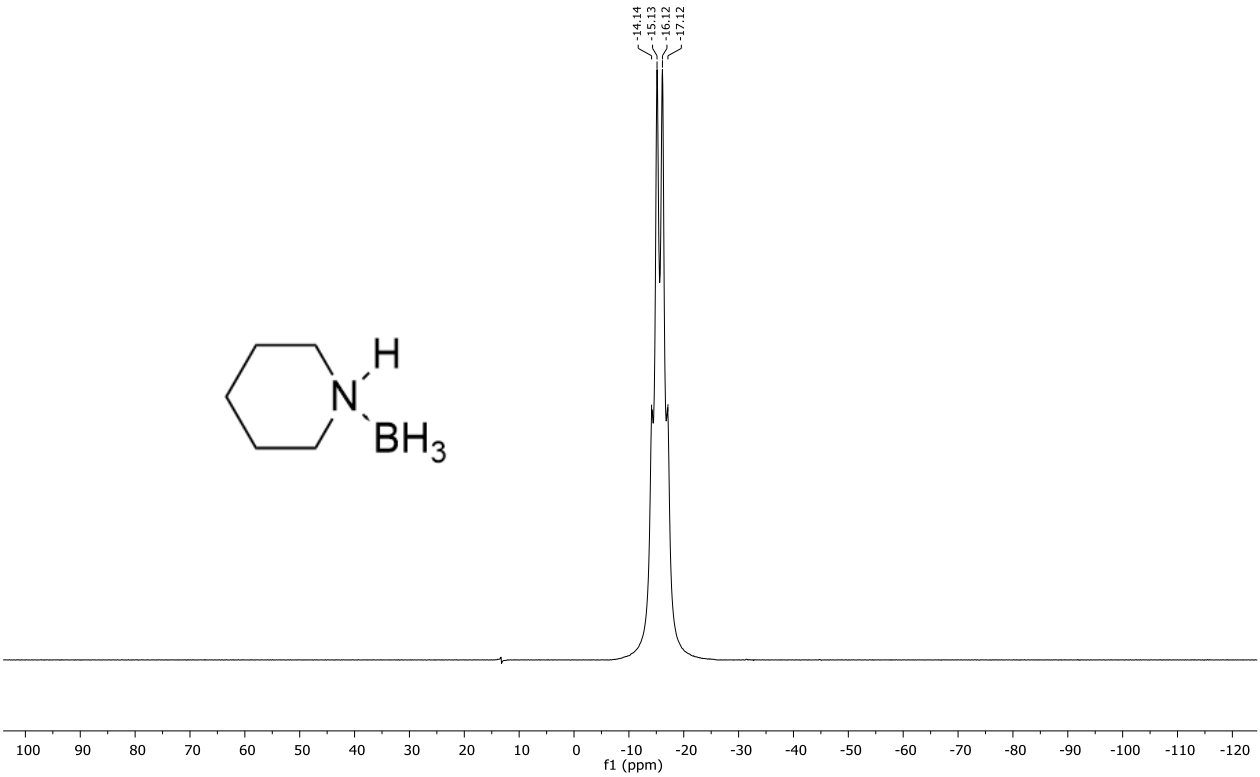
^{11}B NMR (96 MHz, $CDCl_3$) Diisopropylamine-borane (**2h**)



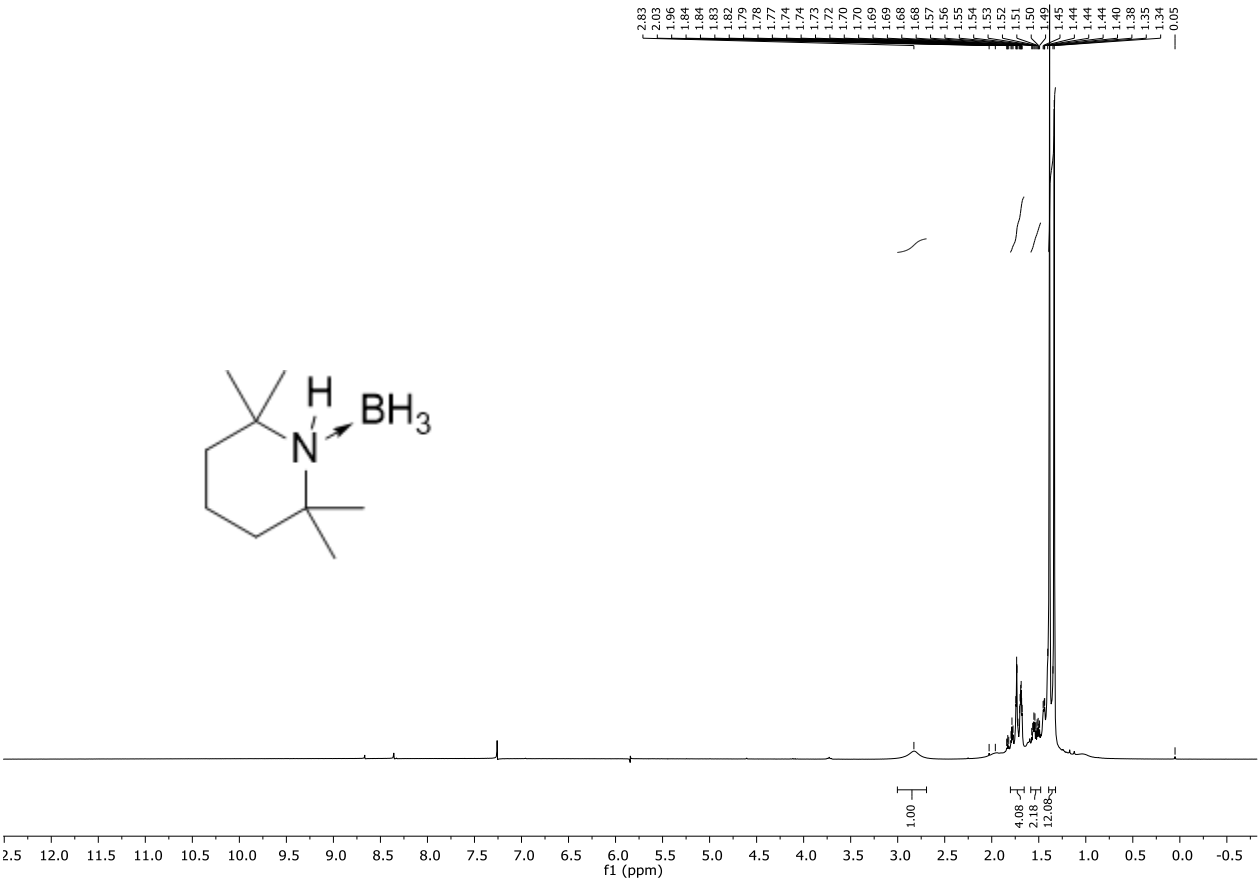
^{1}H NMR (300 MHz, $CDCl_3$) Piperidine-borane (**2i**)



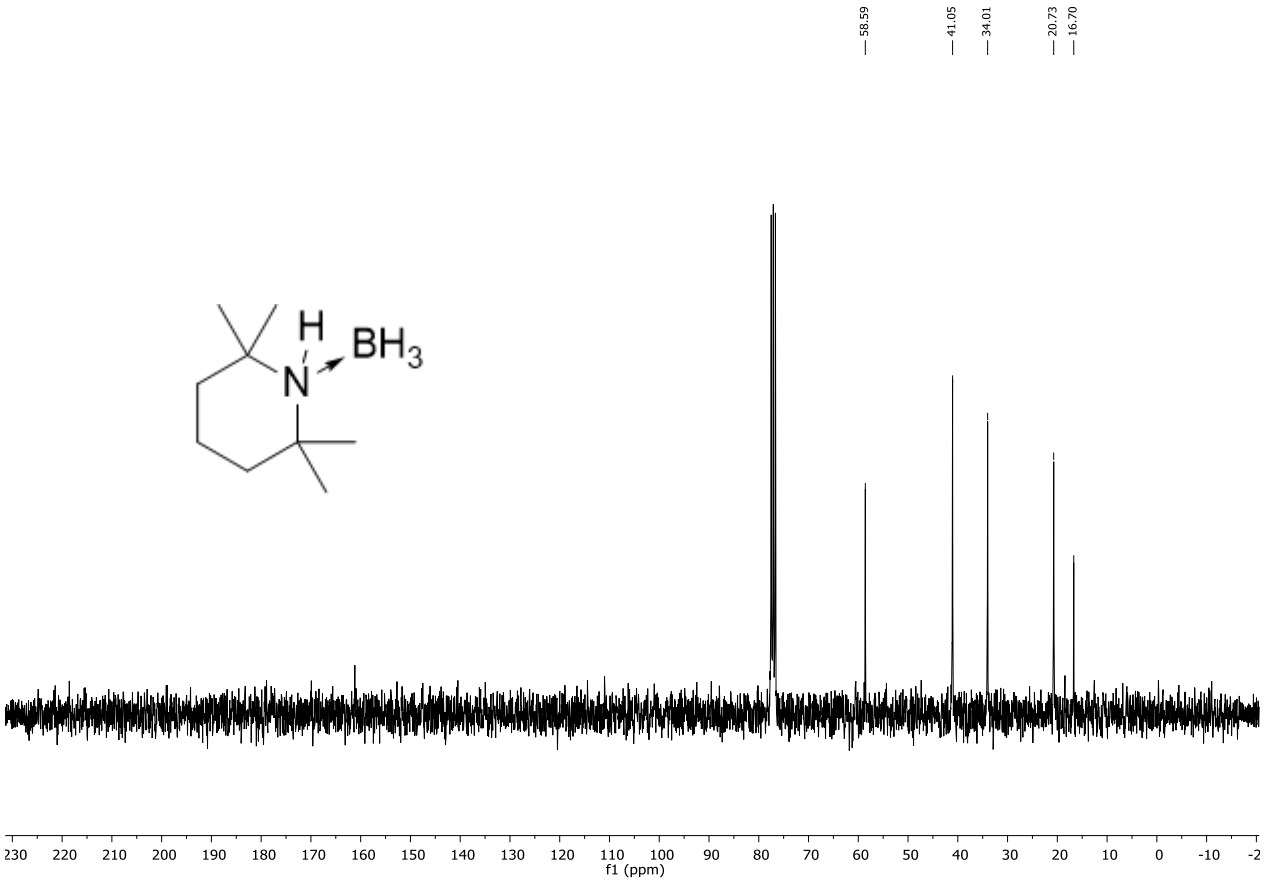
^{13}C NMR (75 MHz, $CDCl_3$) Piperidine-borane (**2i**)



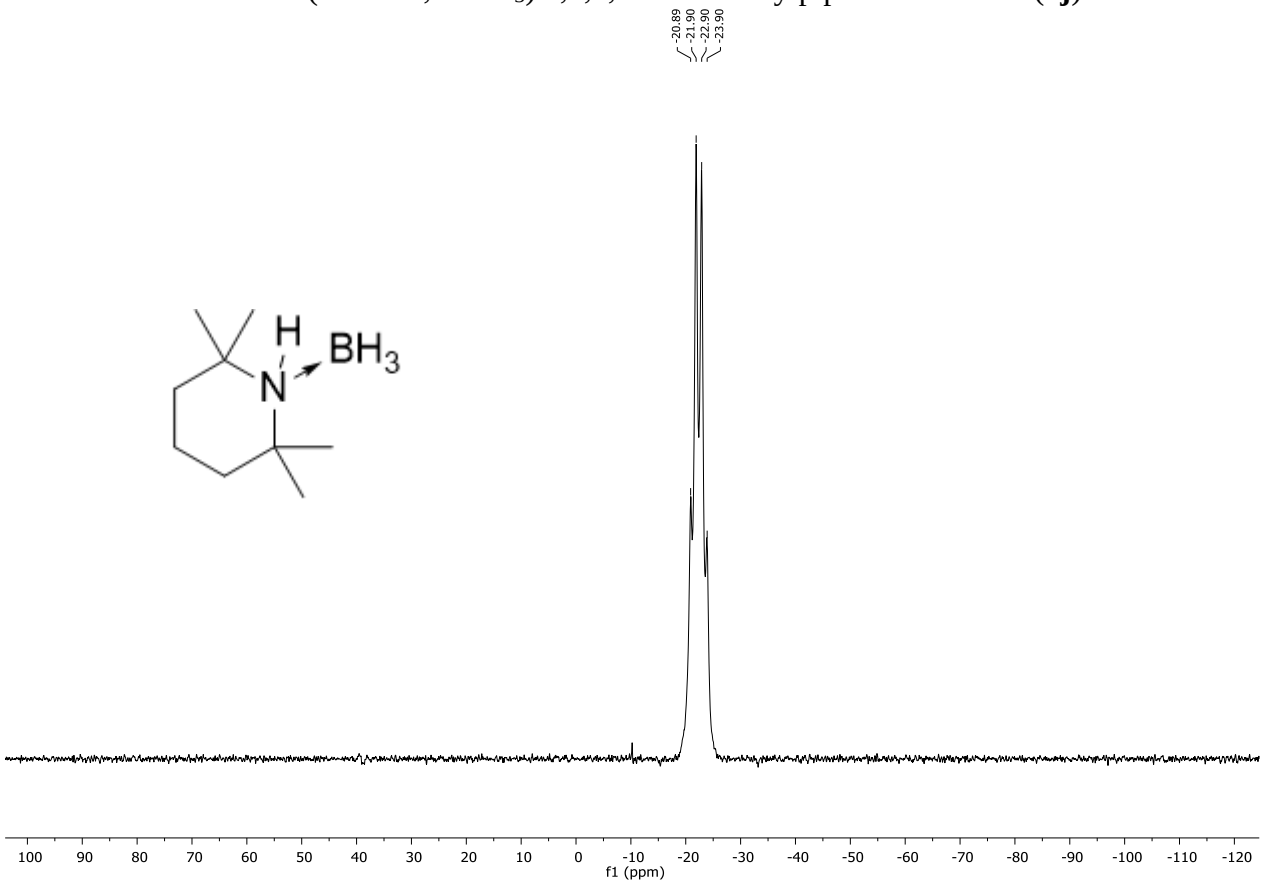
^{11}B NMR (96 MHz, $CDCl_3$) Piperidine-borane (**2i**)



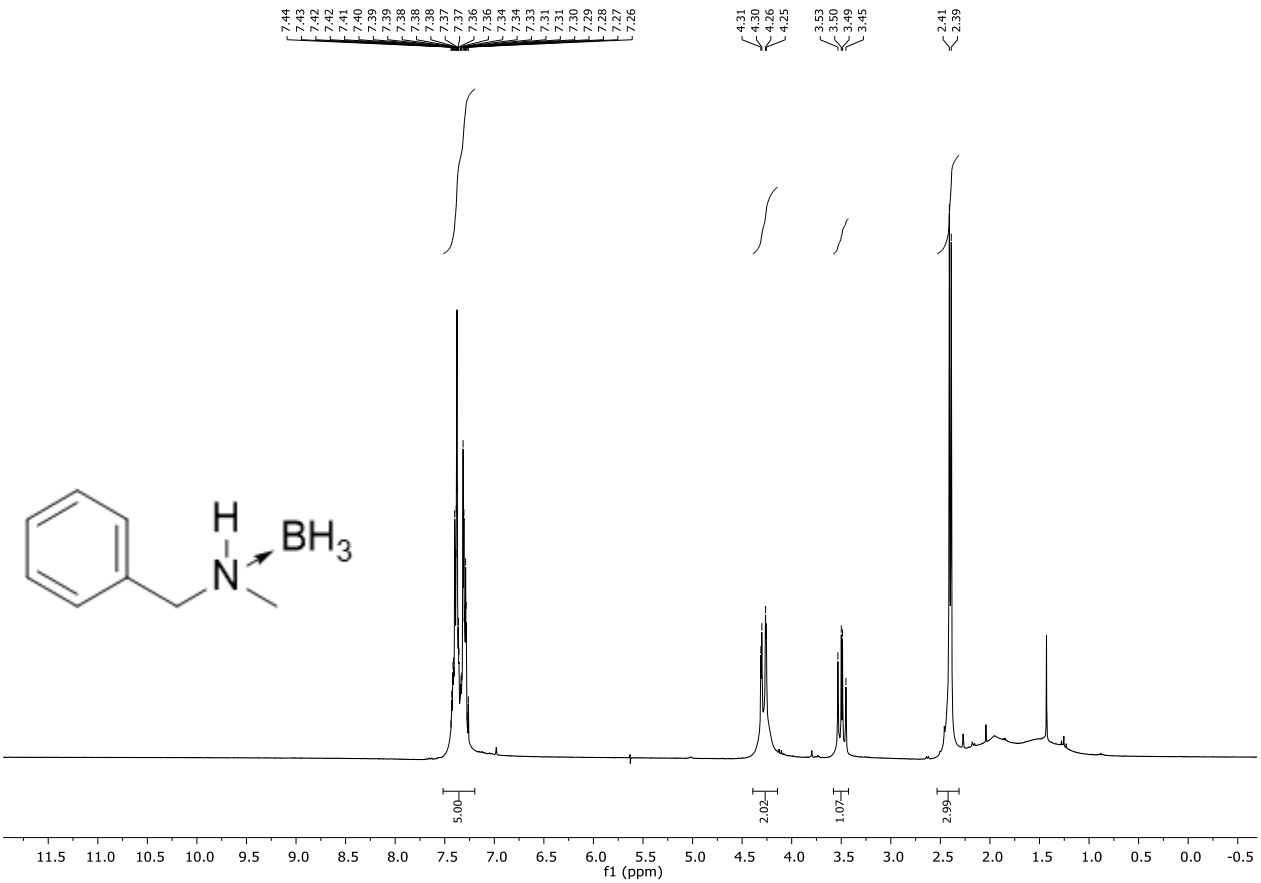
^{1}H NMR (300 MHz, $CDCl_3$) 2,2,6,6-Tetramethylpiperidine-borane (**2j**)



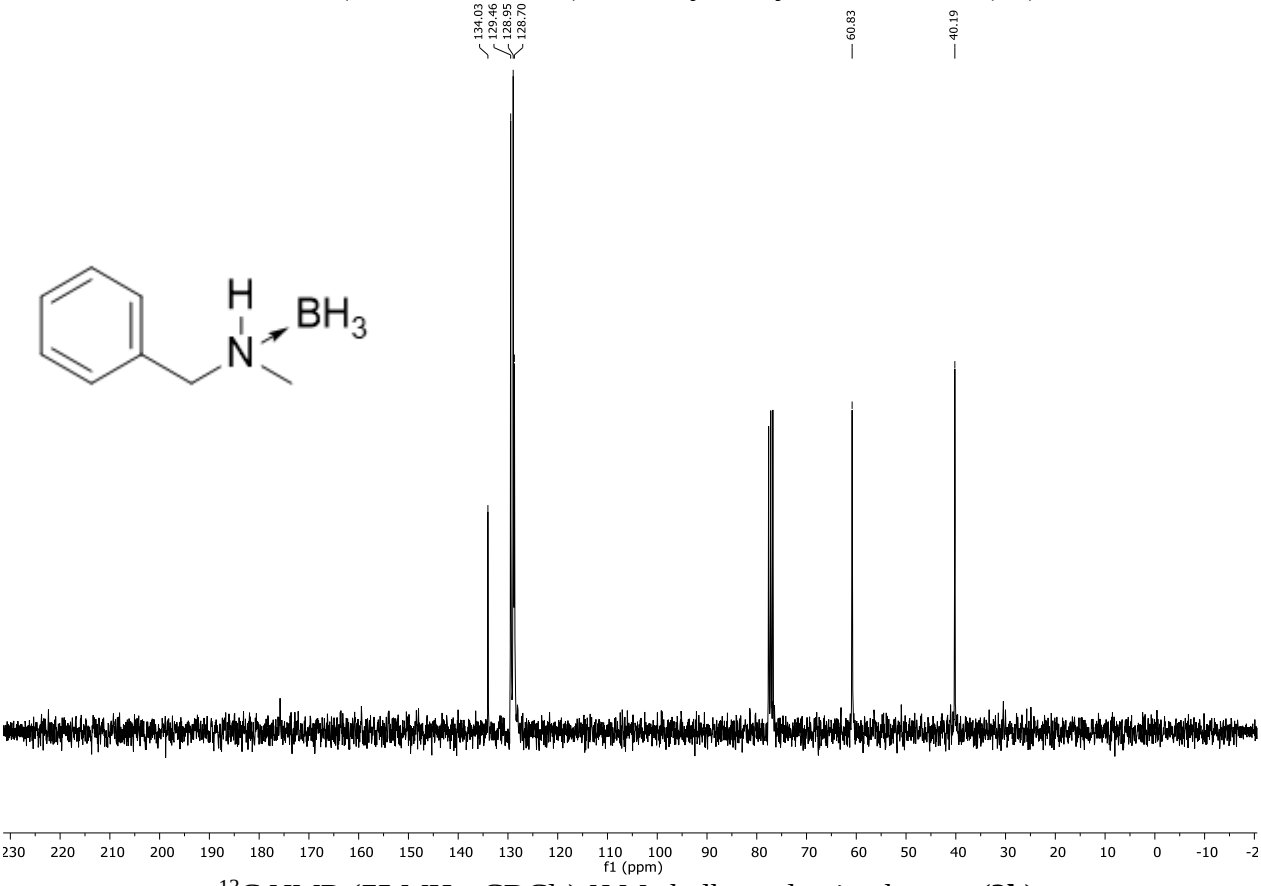
^{13}C NMR (75 MHz, $CDCl_3$) 2,2,6,6-Tetramethylpiperidine-borane (**2j**)



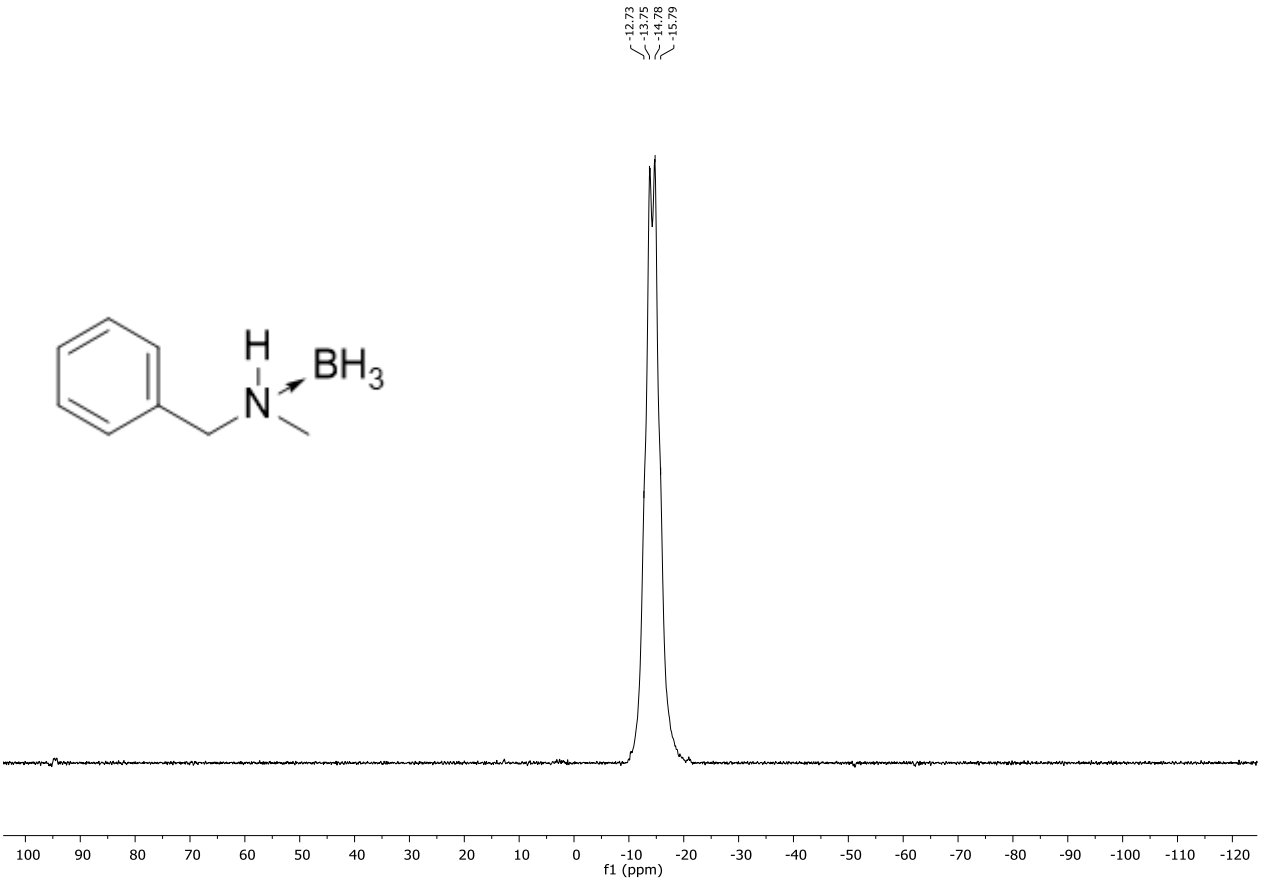
^{11}B NMR (96 MHz, $CDCl_3$) 2,2,6,6-Tetramethylpiperidine-borane (**2j**)



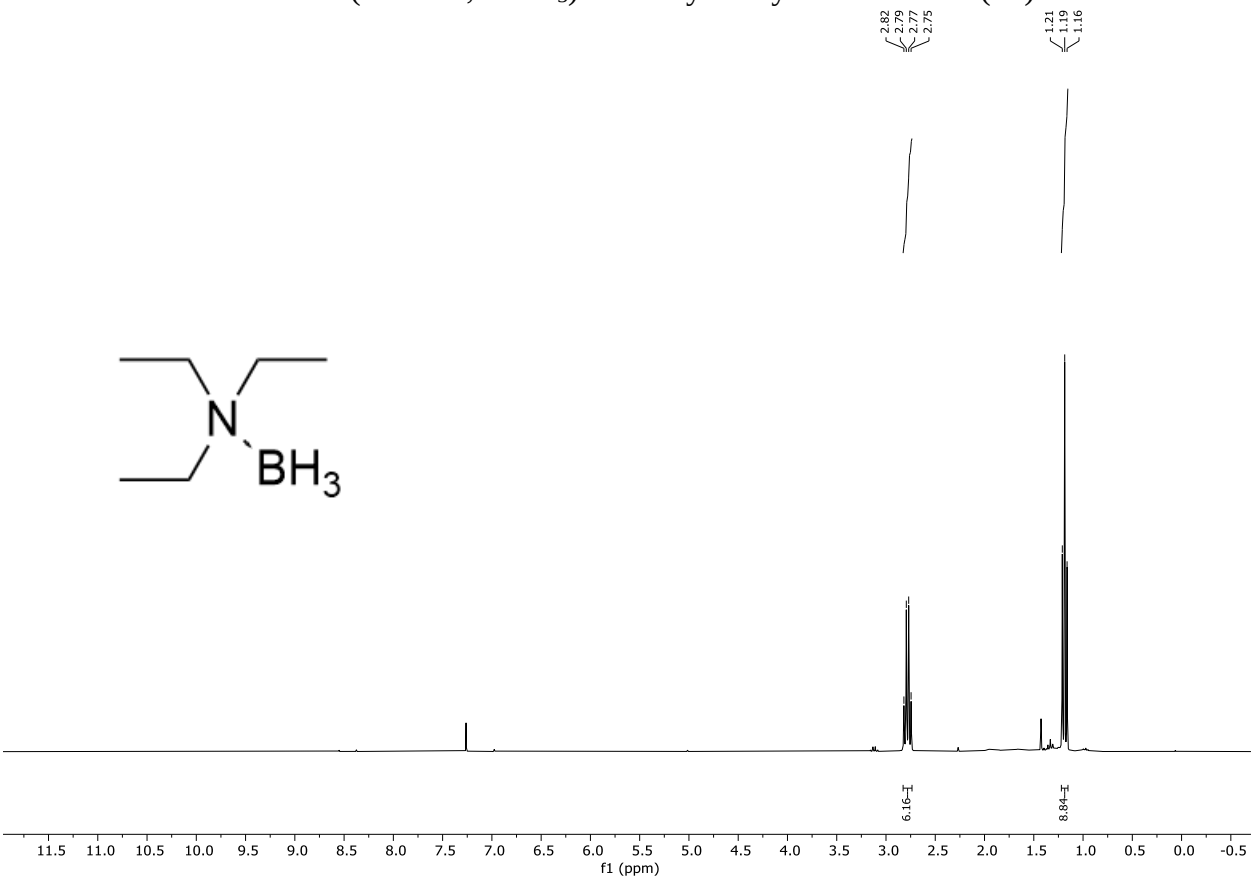
^{1}H NMR (300 MHz, $CDCl_3$) *N*-Methylbenzylamine-borane (**2k**)



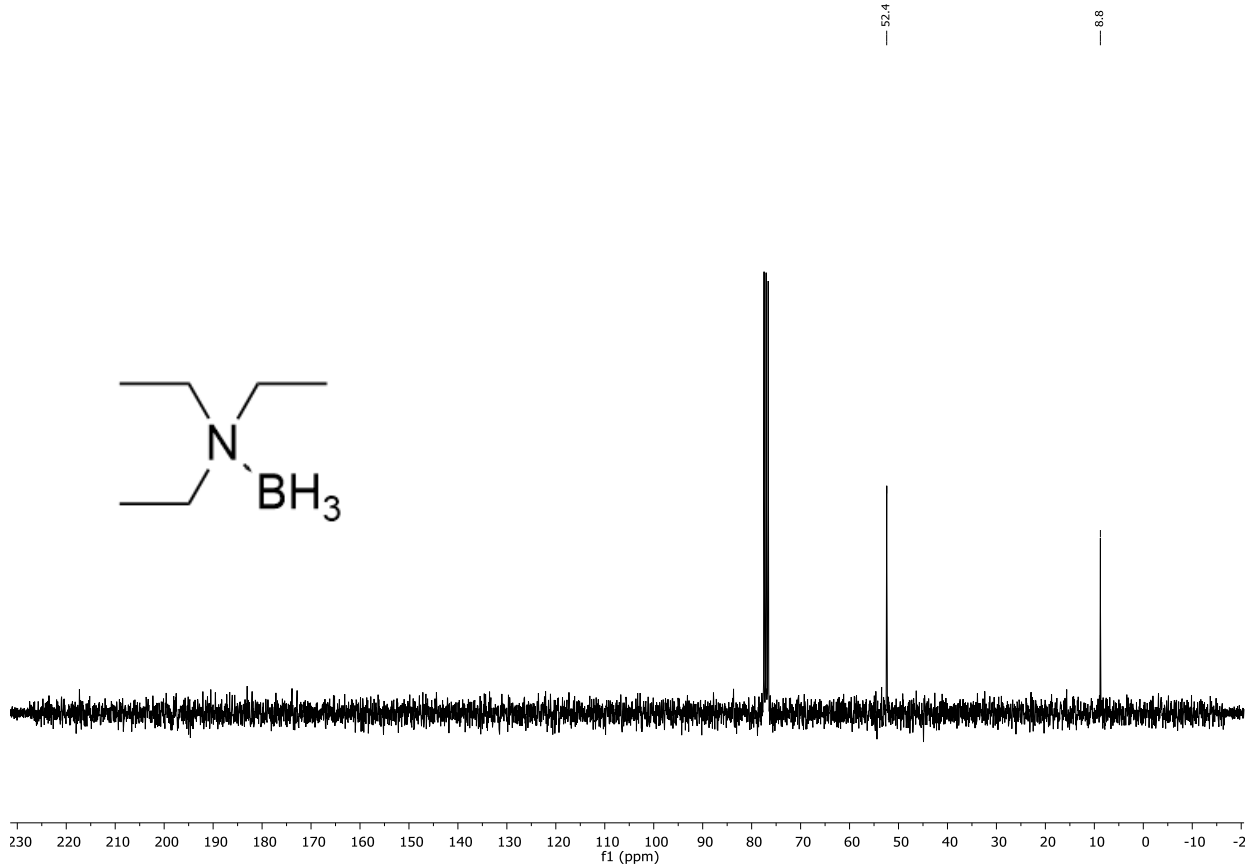
^{13}C NMR (75 MHz, $CDCl_3$) *N*-Methylbenzylamine-borane (**2k**)



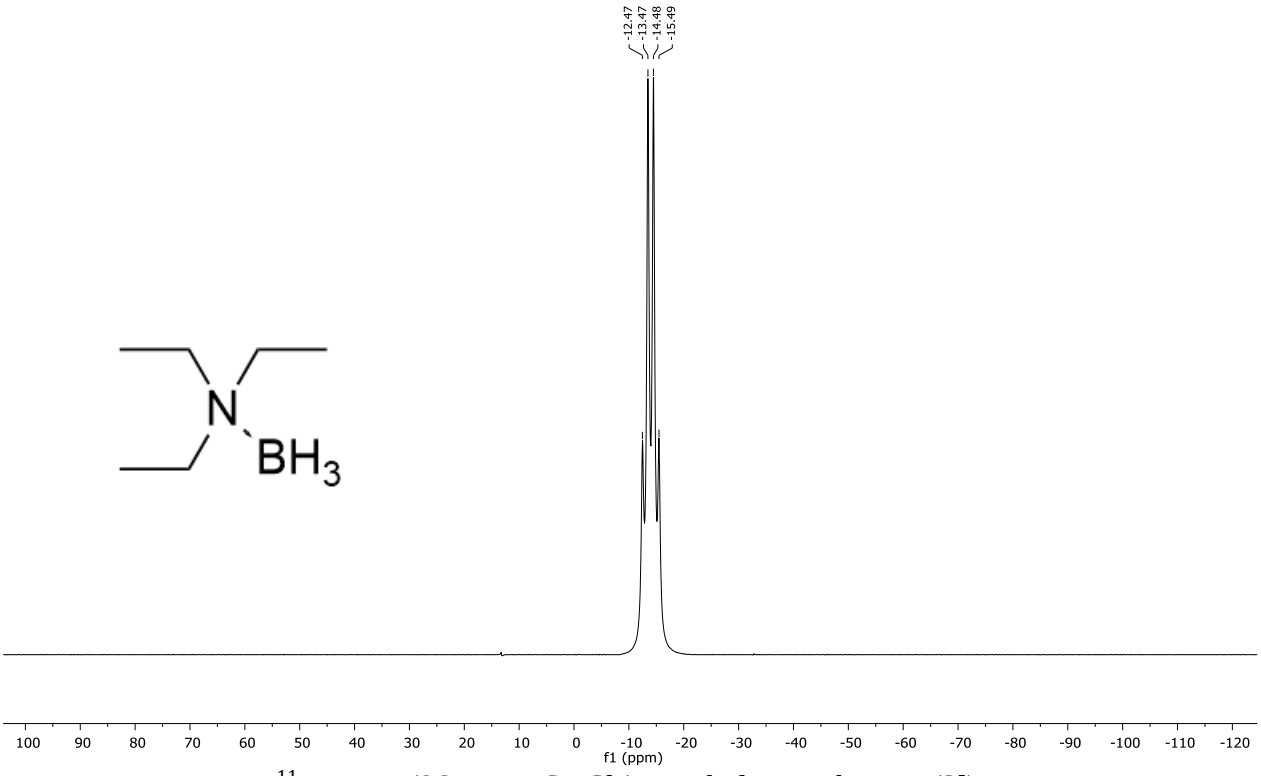
^{11}B NMR (96 MHz, $CDCl_3$) *N*-Methylbenzylamine-borane (**2k**)



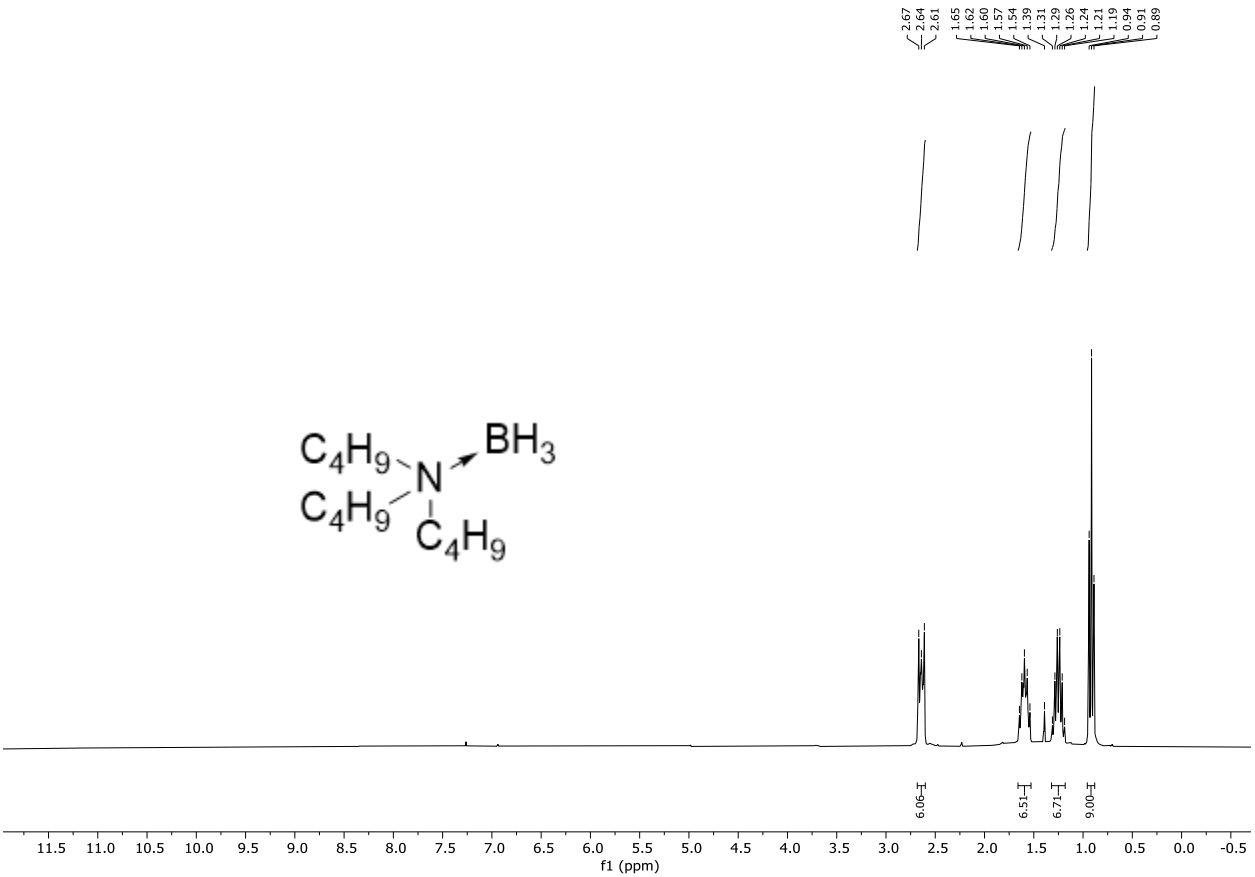
^{1}H NMR (300 MHz, $CDCl_3$) Triethylamine-borane (**2l**)



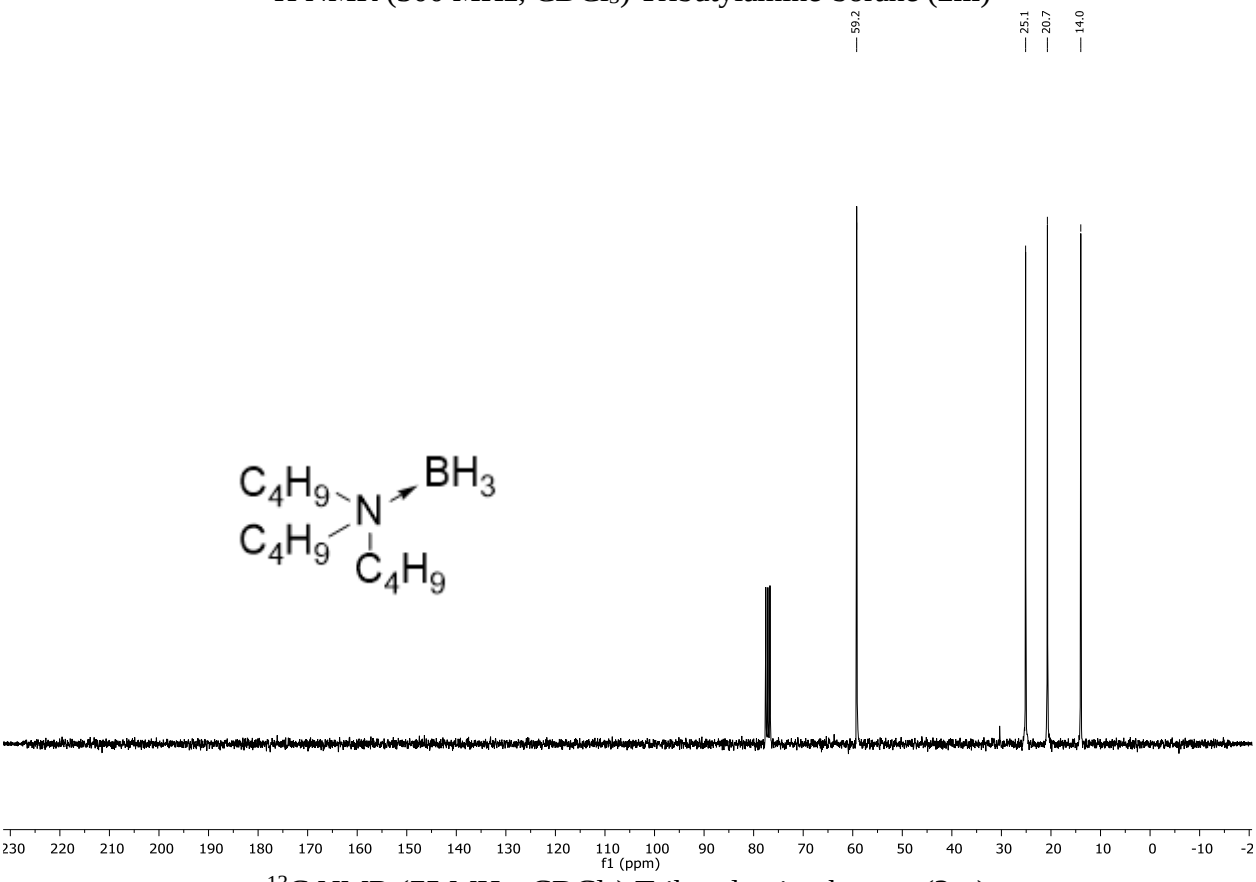
^{13}C NMR (75 MHz, $CDCl_3$) Triethylamine-borane (**2l**)



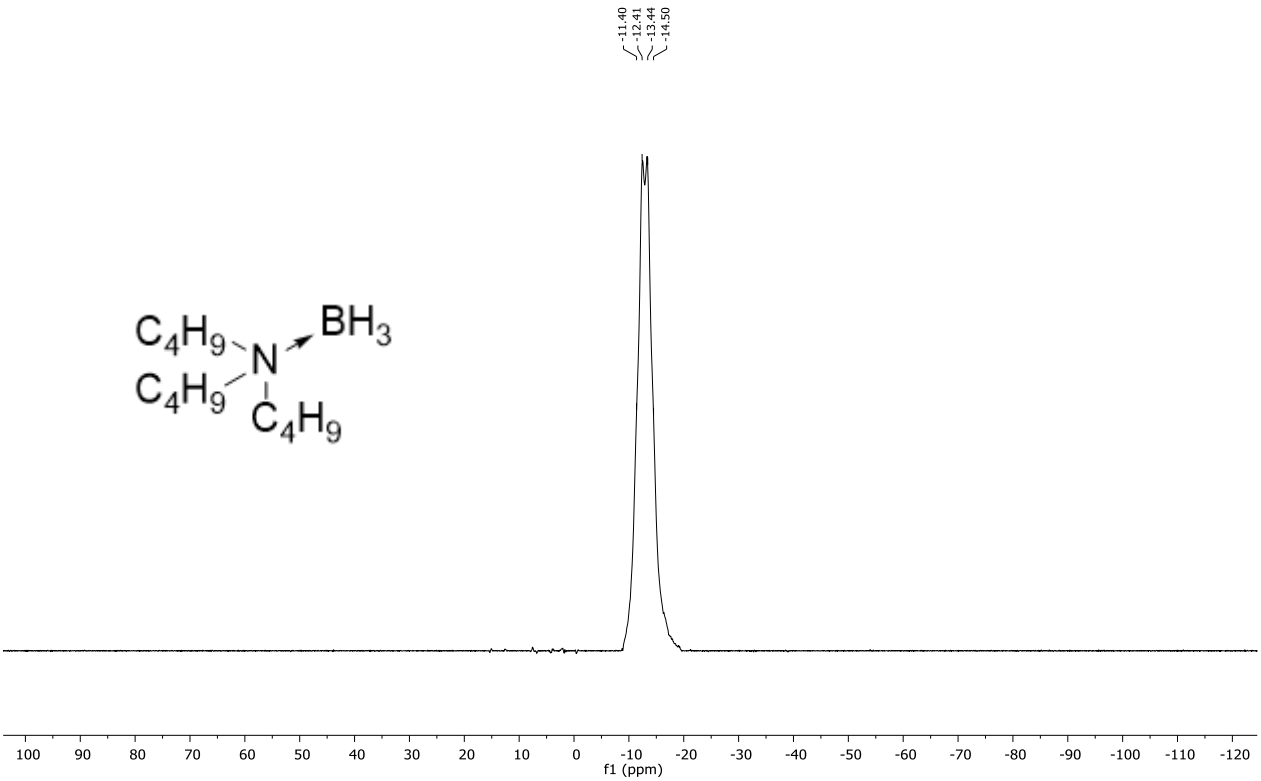
^{11}B NMR (96 MHz, $CDCl_3$) Triethylamine-borane (**2l**)



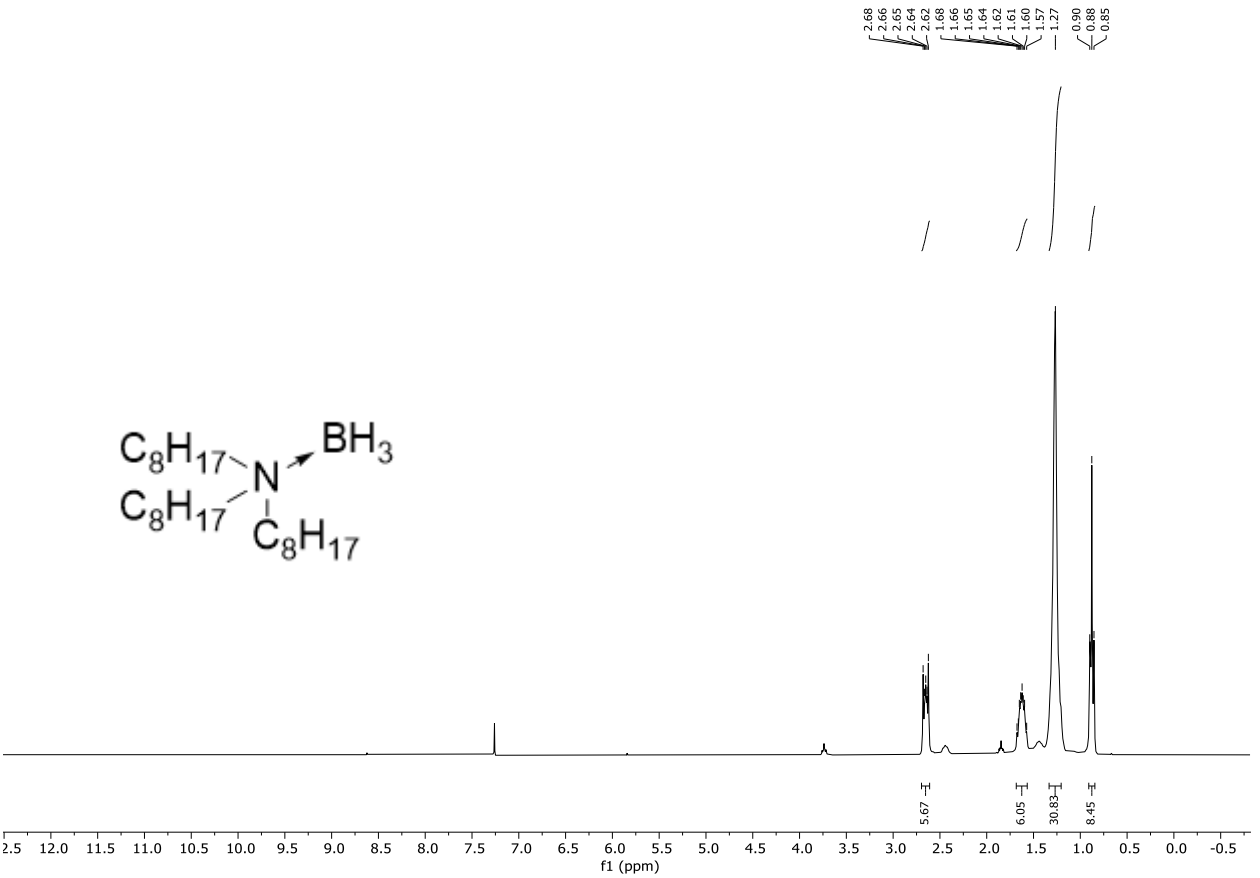
^{1}H NMR (300 MHz, $CDCl_3$) Tributylamine-borane (**2m**)



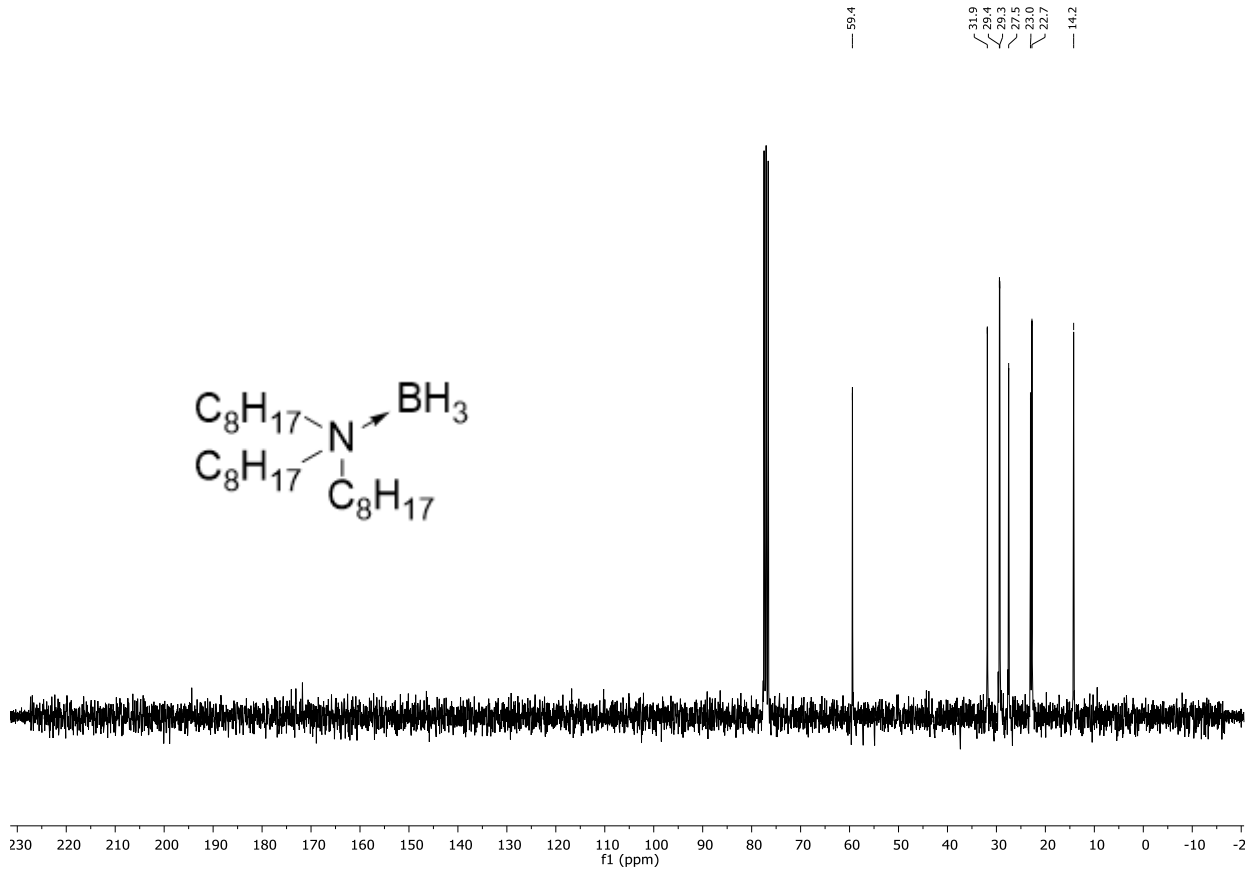
^{13}C NMR (75 MHz, $CDCl_3$) Tributylamine-borane (**2m**)



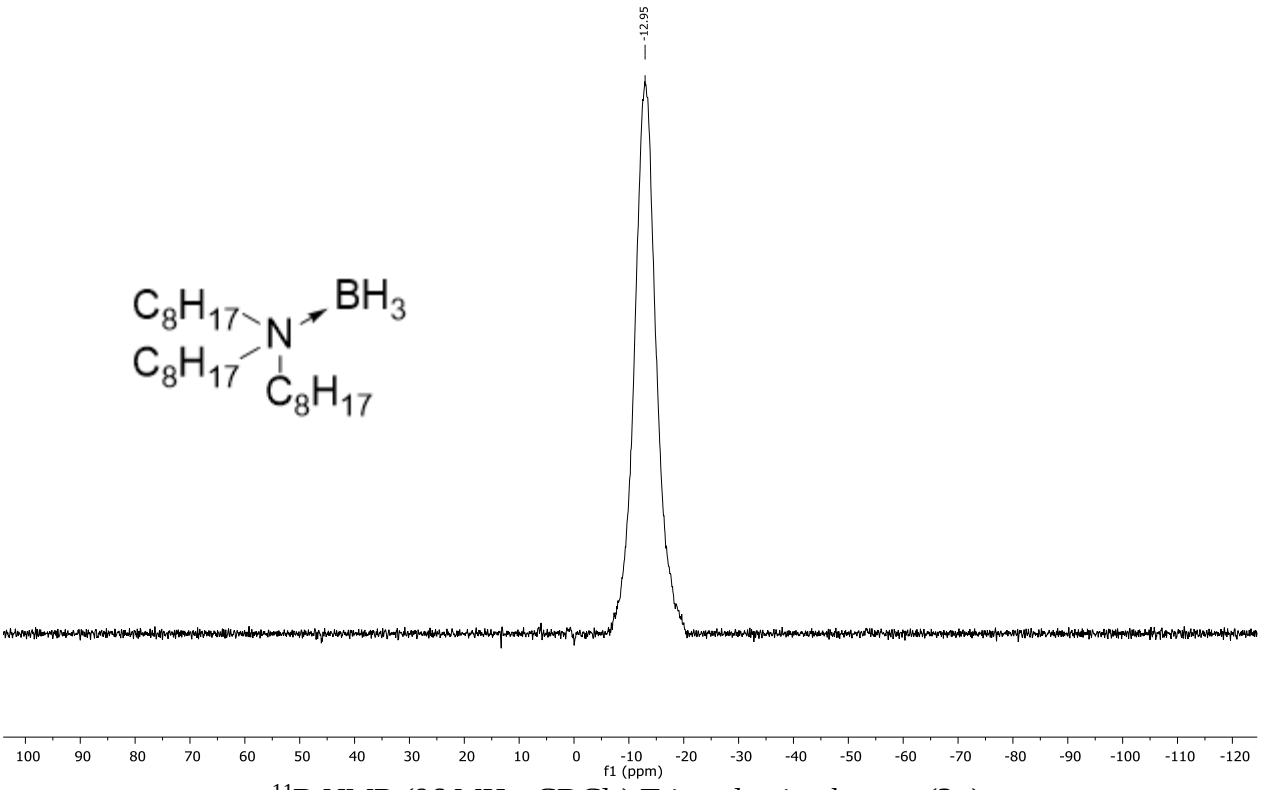
^{11}B NMR (96 MHz, $CDCl_3$) Tributylamine-borane (**2m**)



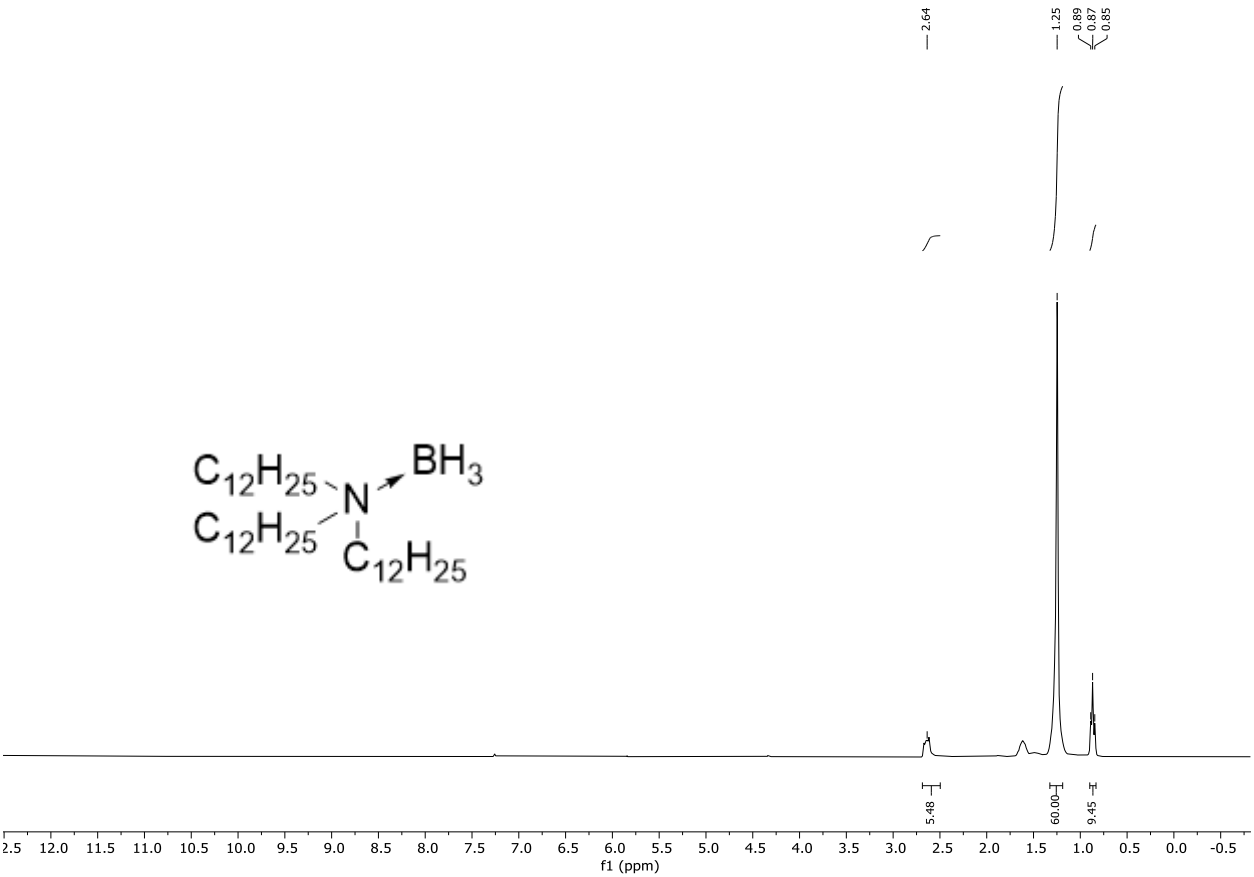
^{1}H NMR (300 MHz, $CDCl_3$) Trioctylamine-borane (**2n**)



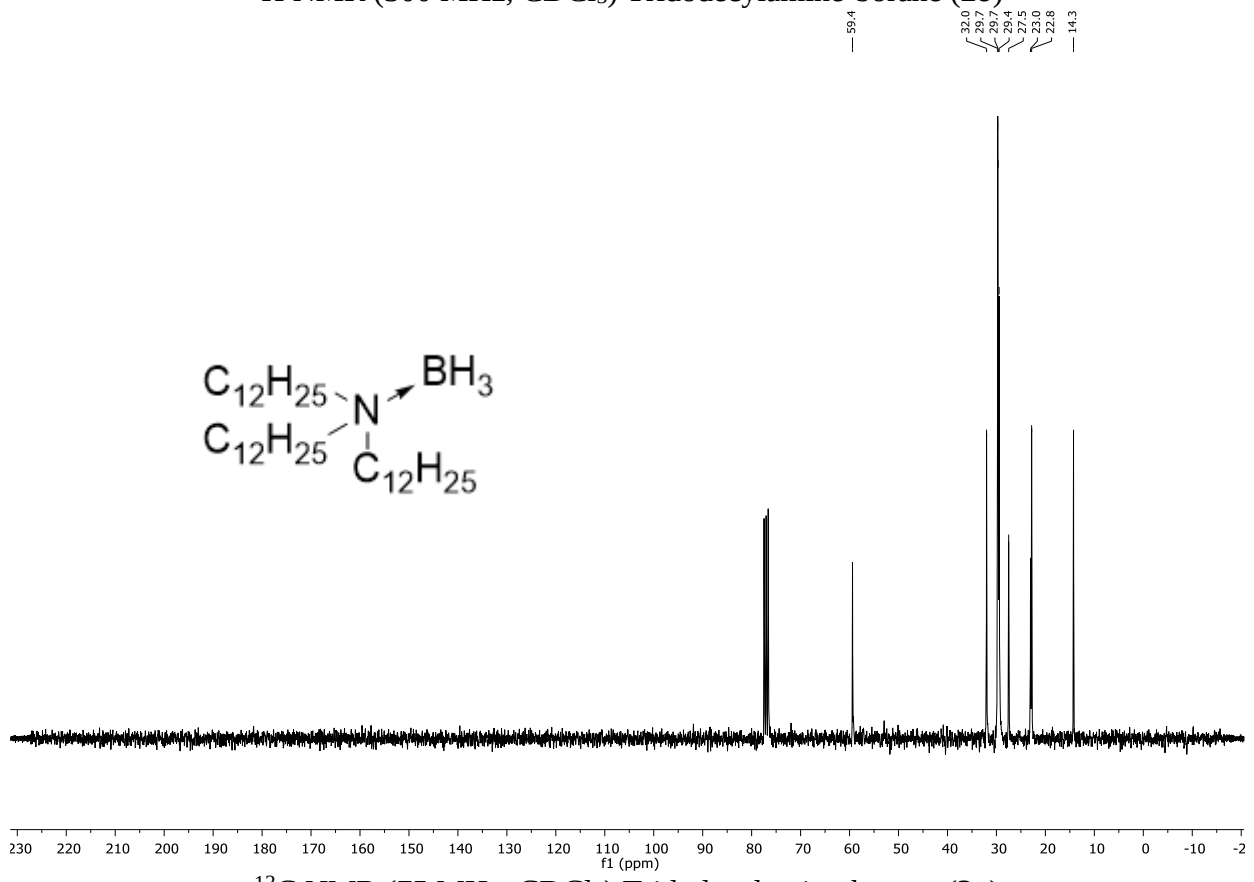
^{13}C NMR (75 MHz, $CDCl_3$) Trioctylamine-borane (**2n**)



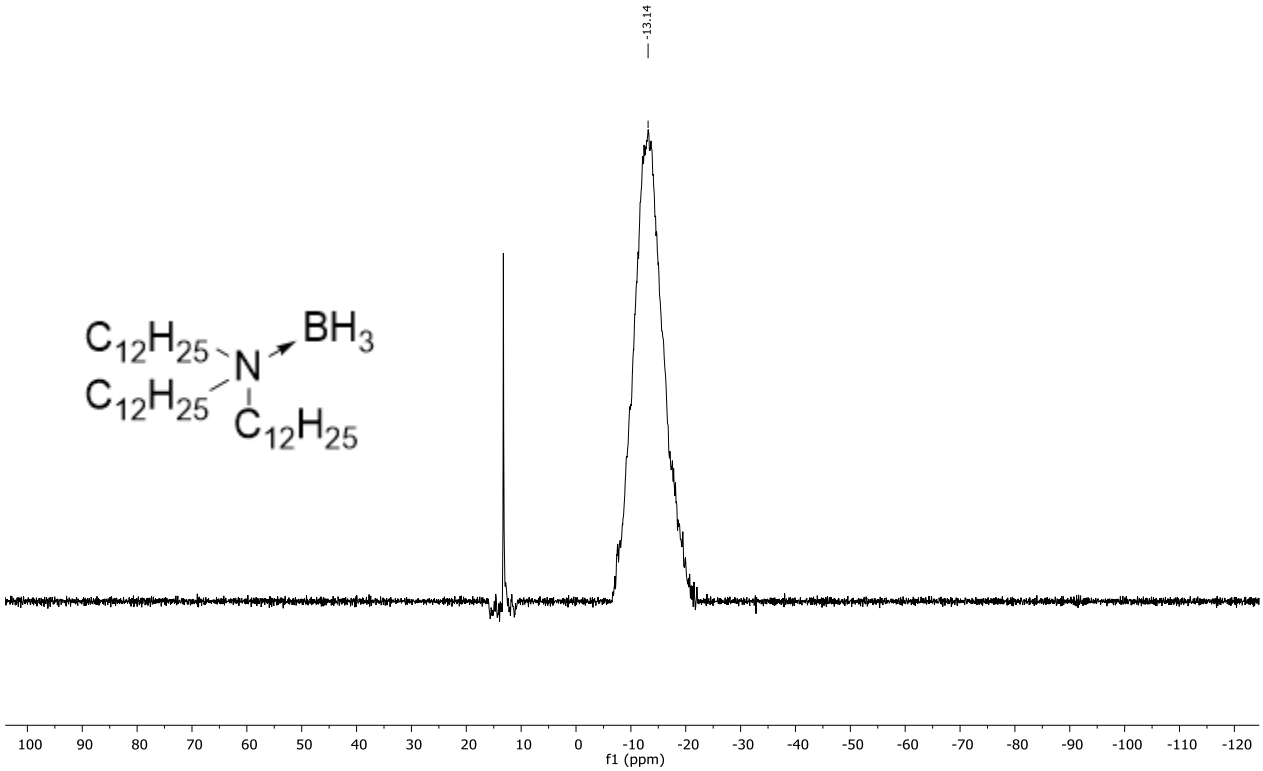
^{11}B NMR (96 MHz, $CDCl_3$) Trioctylamine-borane (**2n**)



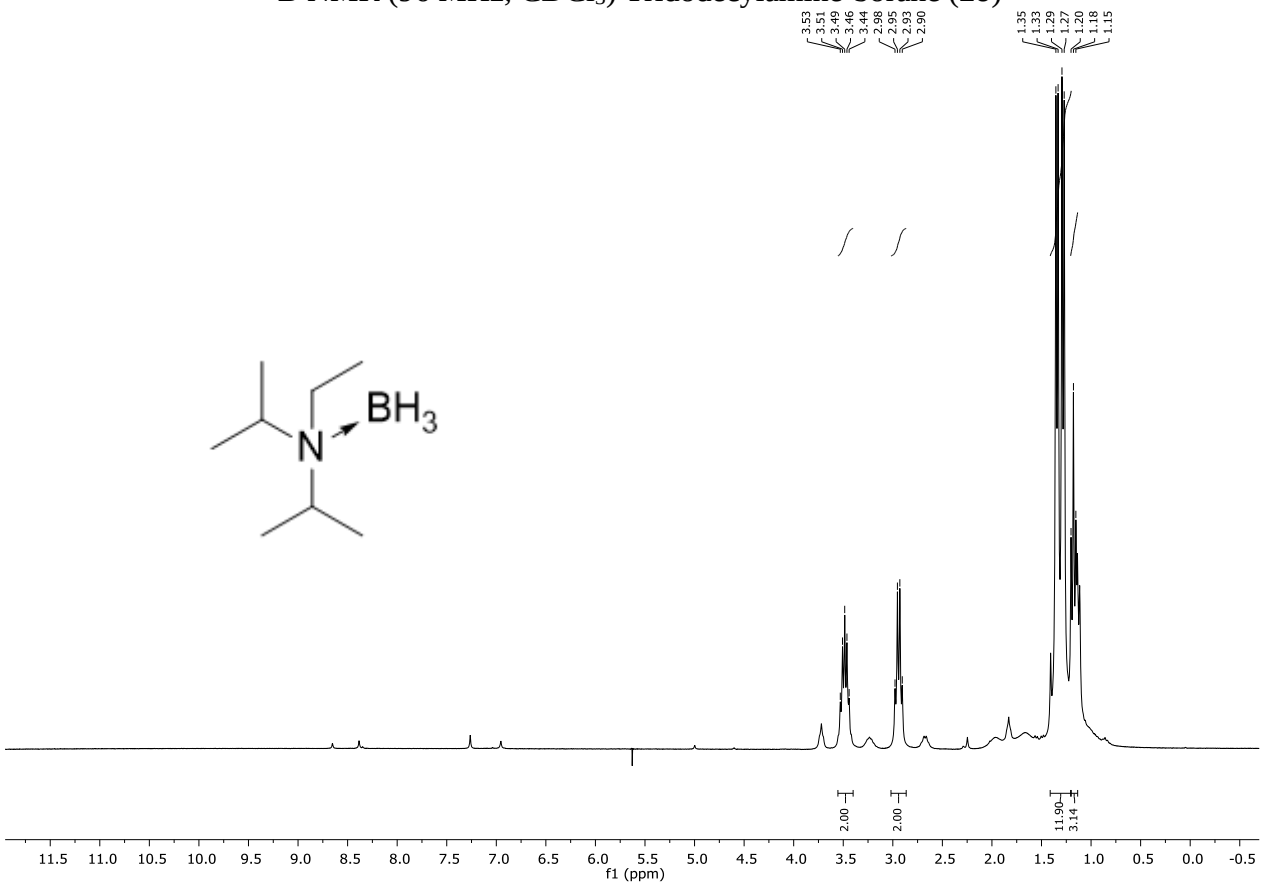
^{1}H NMR (300 MHz, $CDCl_3$) Tridodecylamine-borane (**2o**)



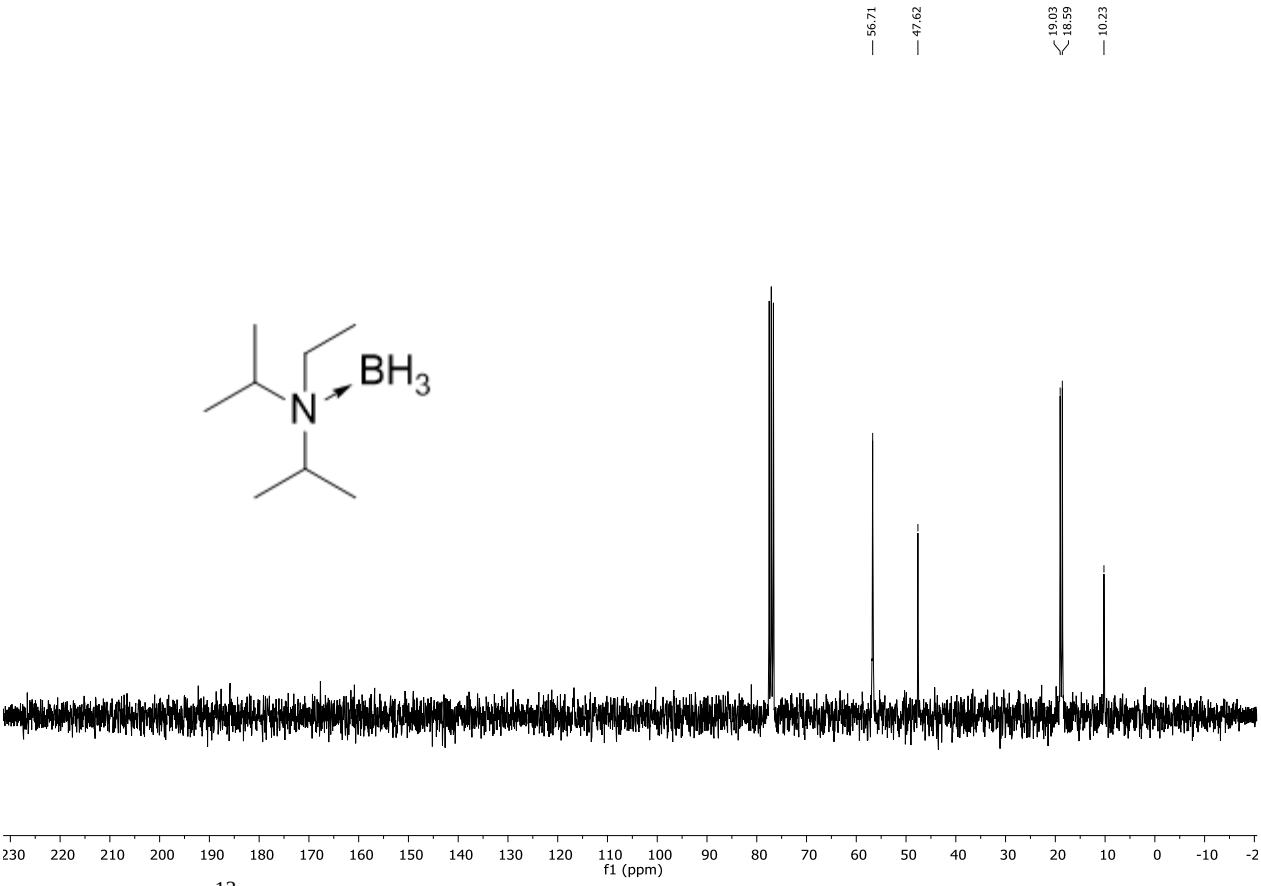
^{13}C NMR (75 MHz, $CDCl_3$) Tridodecylamine-borane (**2o**)



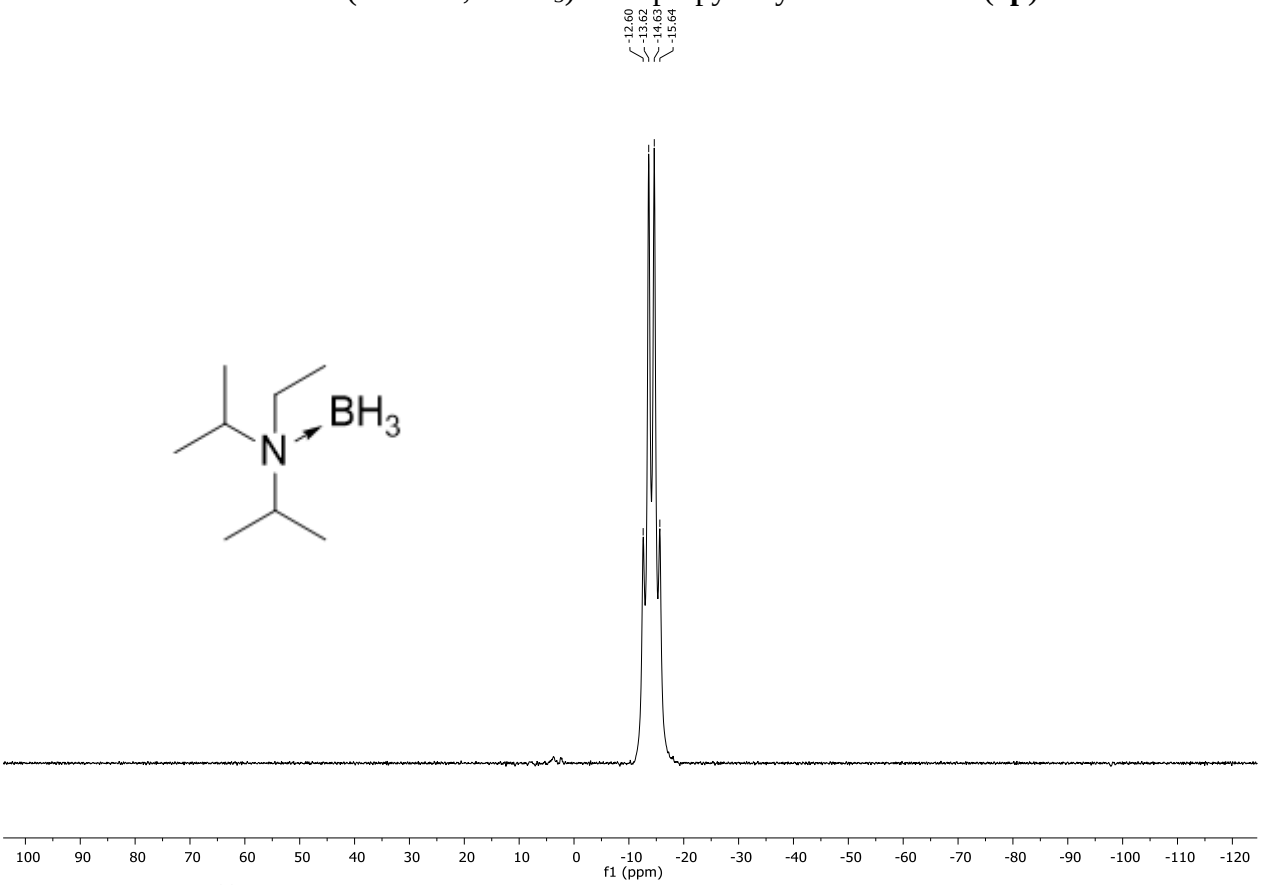
^{11}B NMR (96 MHz, $CDCl_3$) Tridodecylamine-borane (**2o**)



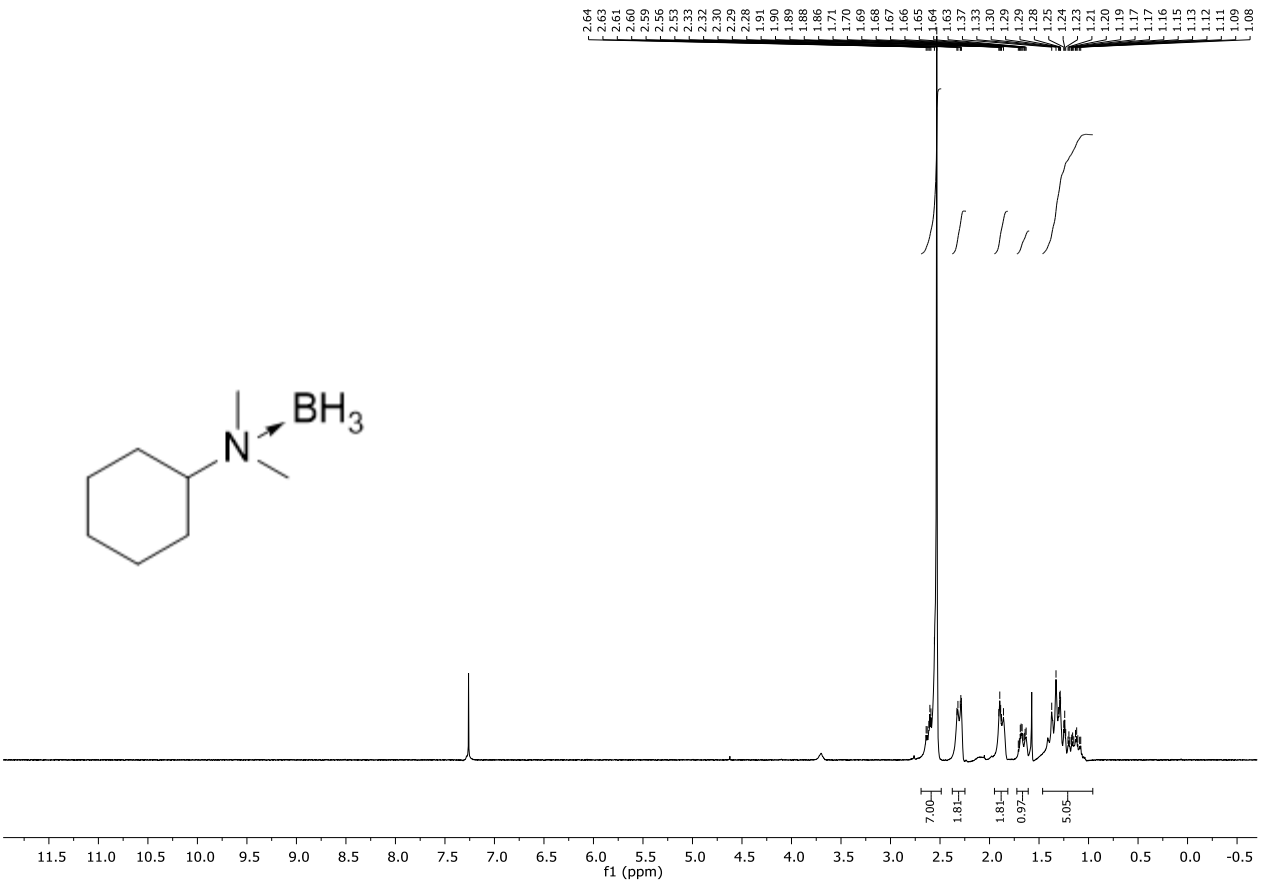
^{1}H NMR (300 MHz, $CDCl_3$) Diisopropylethylamine-borane (**2p**)



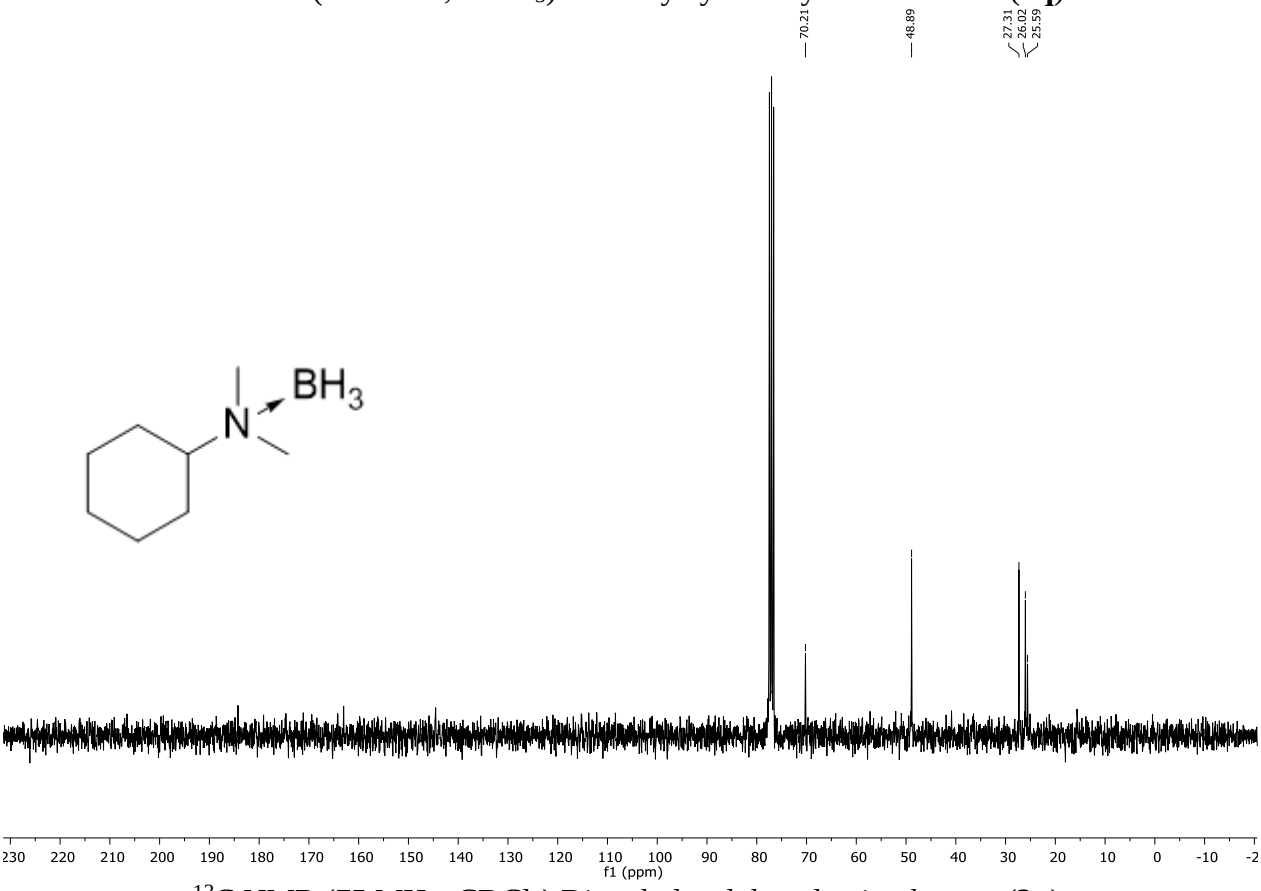
^{13}C NMR (75 MHz, $CDCl_3$) Diisopropylethylamine-borane (**2p**)



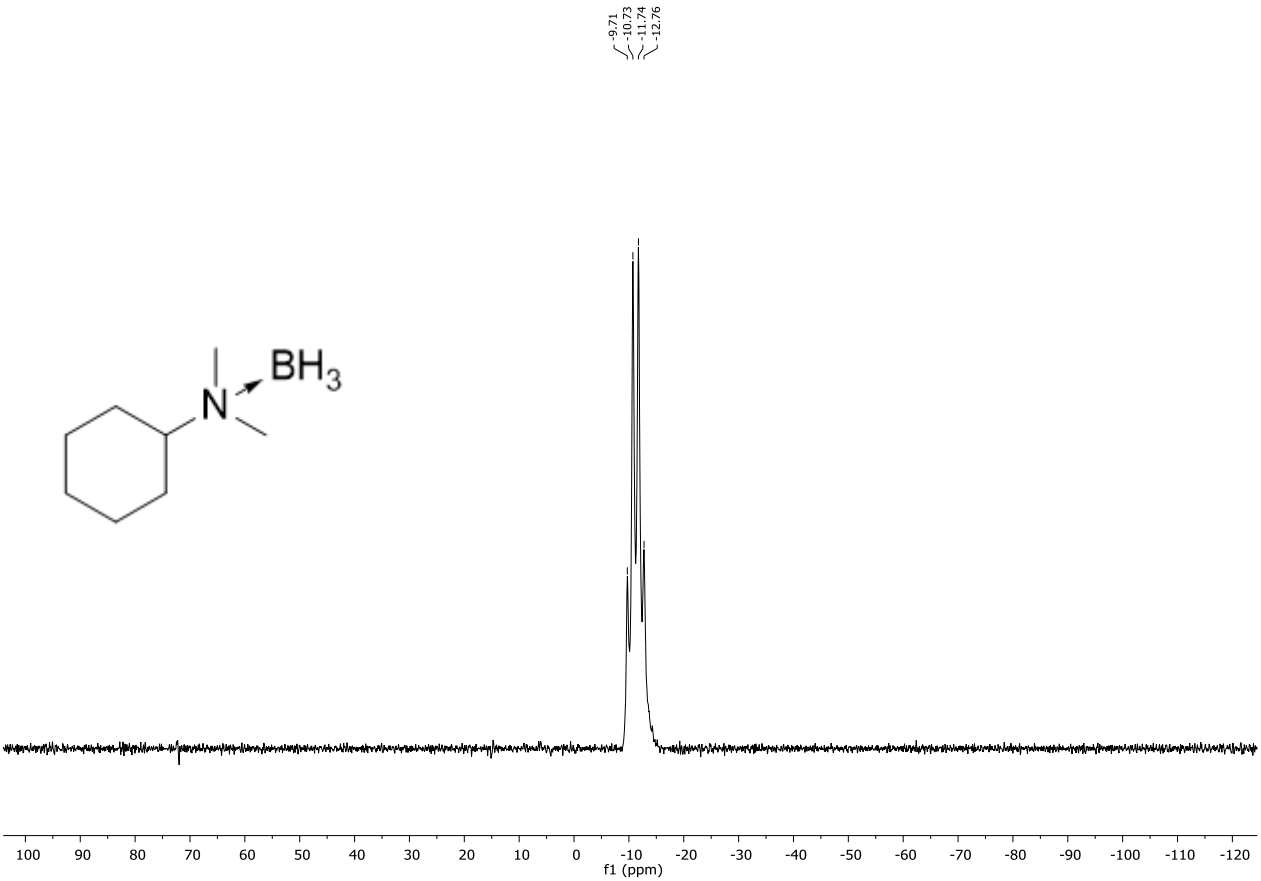
^{11}B NMR (96 MHz, $CDCl_3$) Diisopropylethylamine-borane (**2p**)



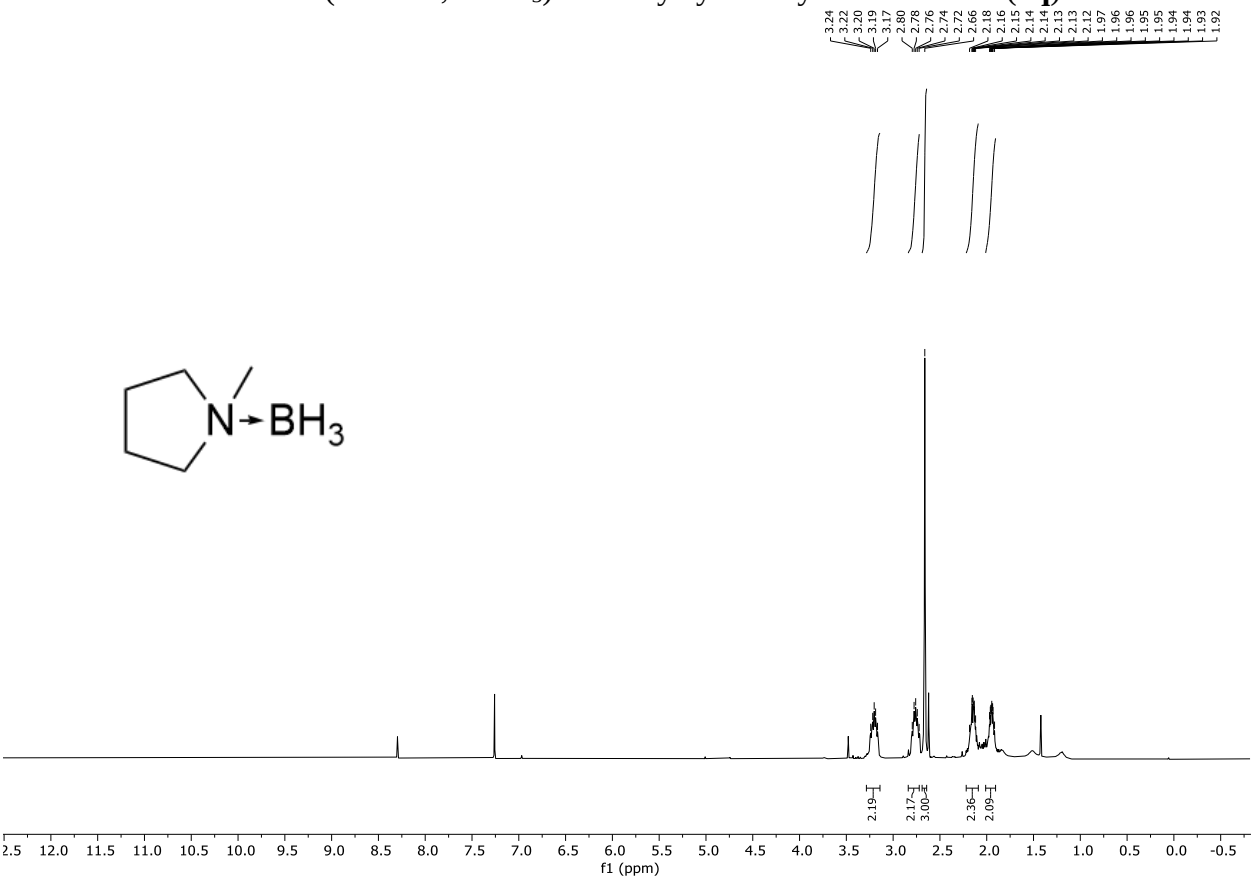
^{1}H NMR (300 MHz, $CDCl_3$) Dimethylcyclohexylamine-borane (**2q**)



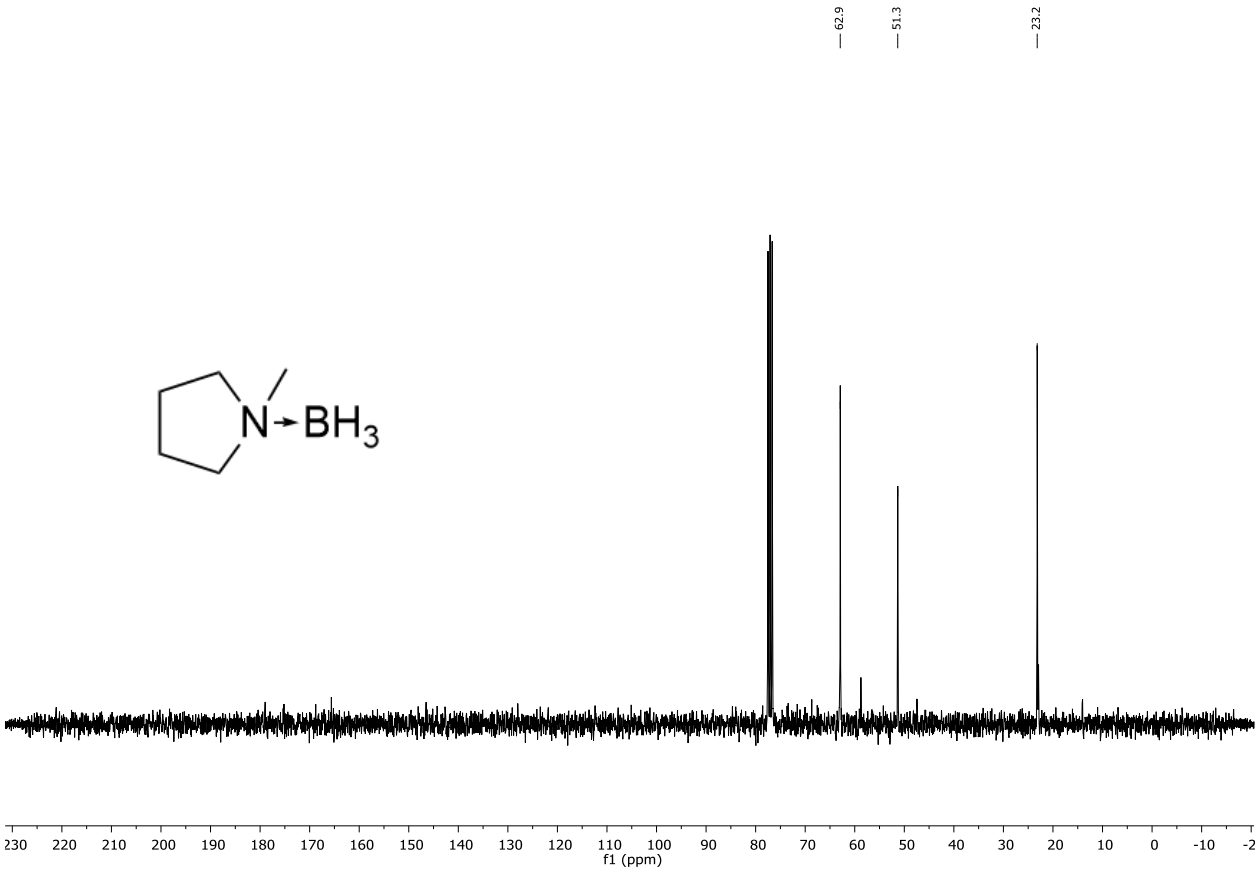
^{13}C NMR (75 MHz, $CDCl_3$) Dimethylcyclohexylamine-borane (**2q**)



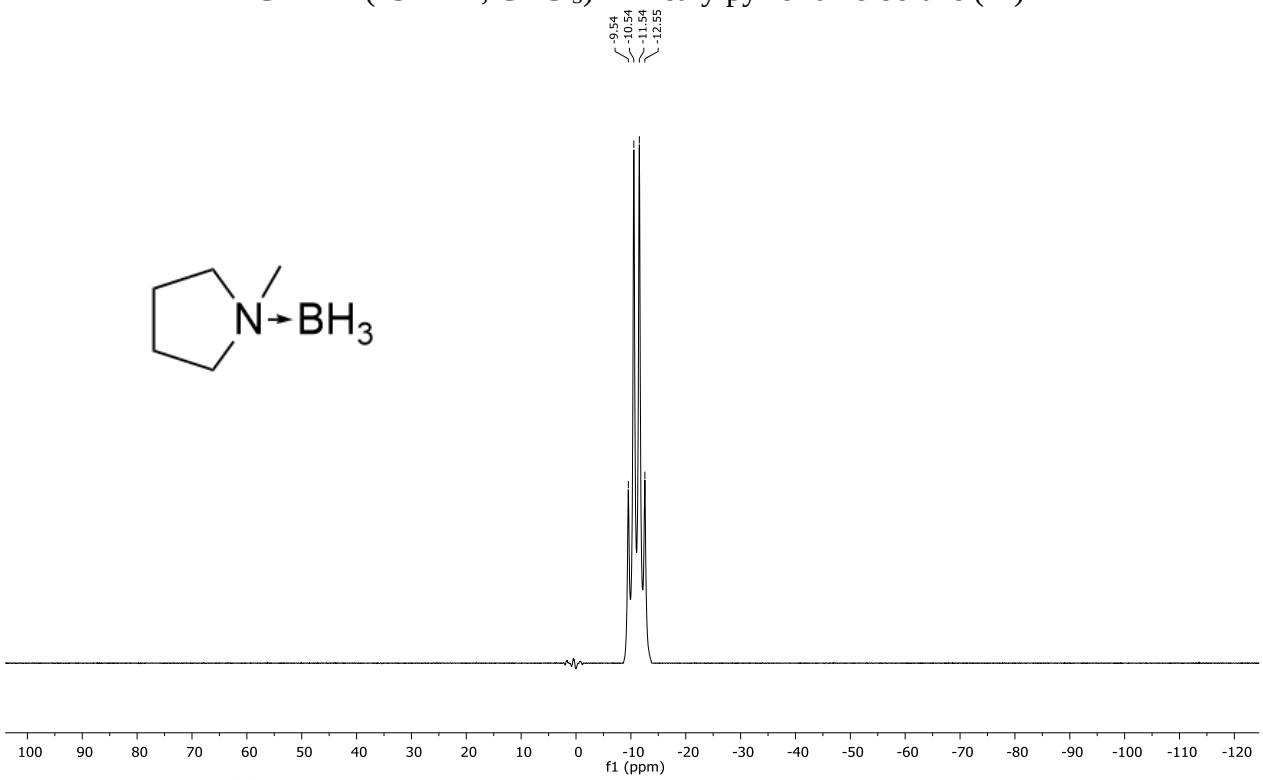
^{11}B NMR (96 MHz, $CDCl_3$) Dimethylcyclohexylamine-borane (**2q**)



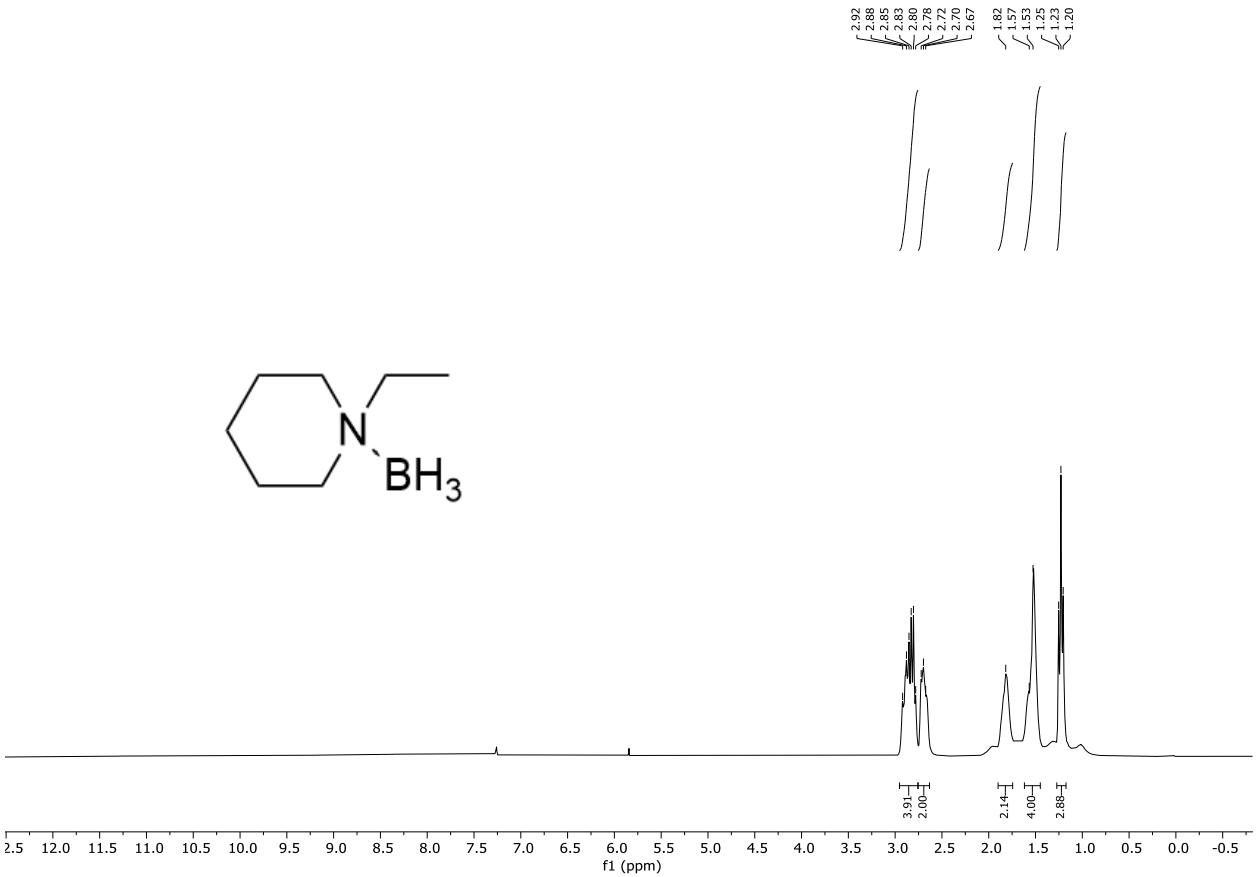
^{1}H NMR (300 MHz, $CDCl_3$) *N*-Methylpyrrolidine-borane (**2r**)



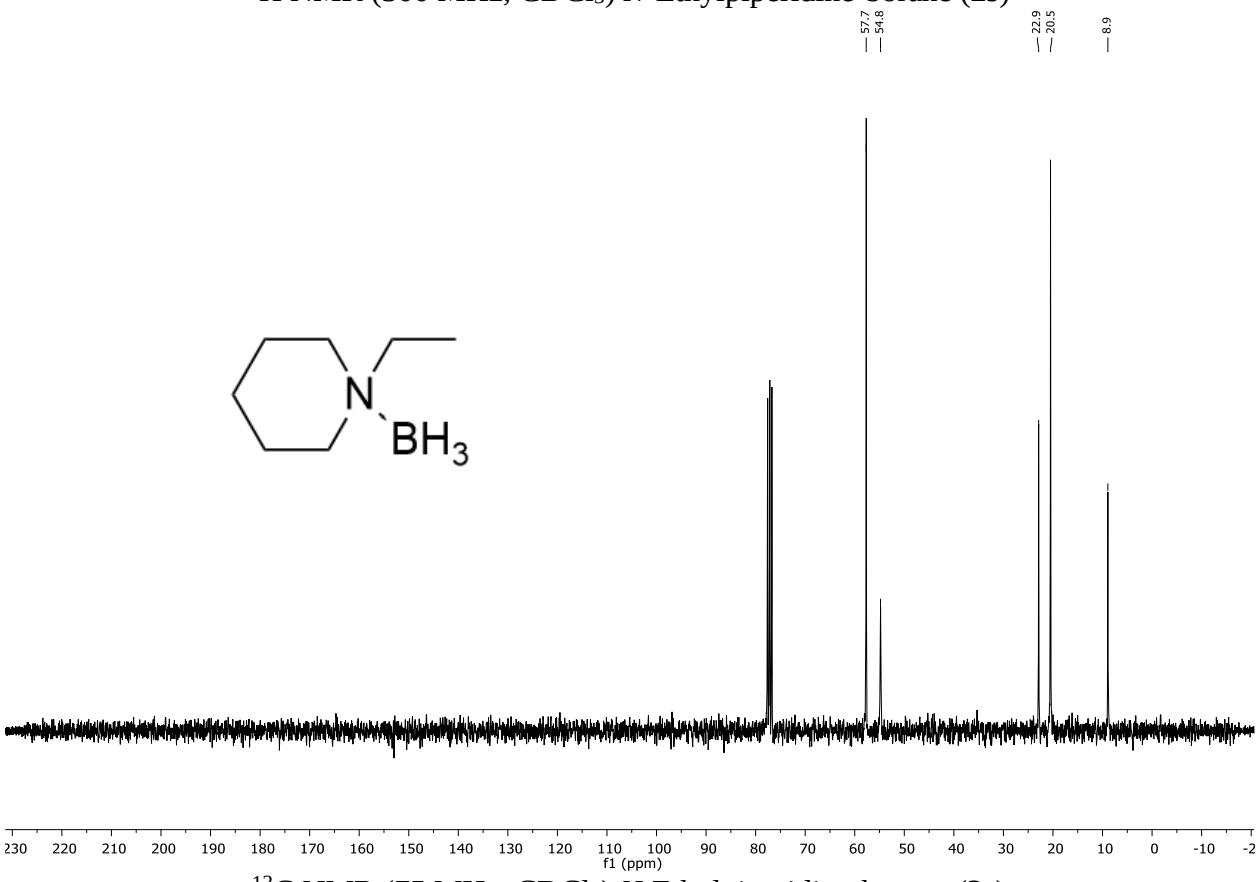
^{13}C NMR (75 MHz, $CDCl_3$) *N*-Methylpyrrolidine-borane (**2r**)



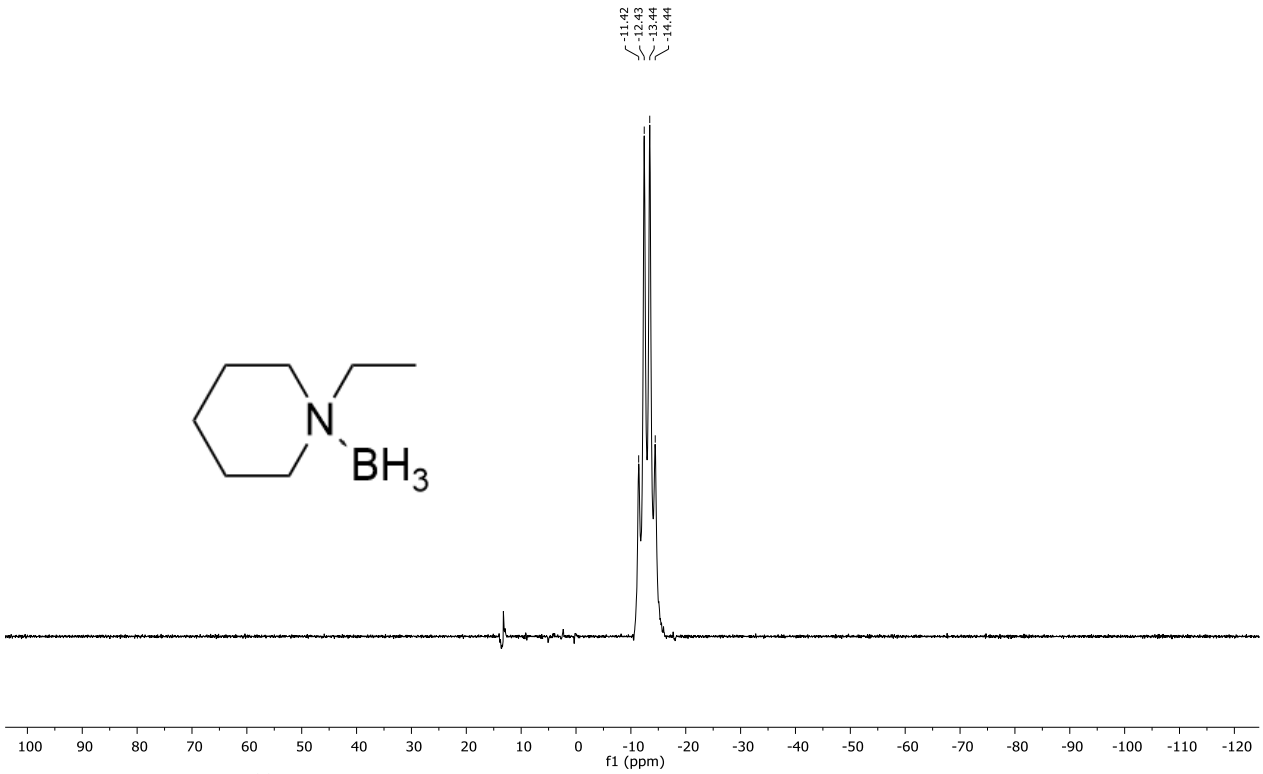
^{11}B NMR (96 MHz, $CDCl_3$) *N*-Methylpyrrolidine-borane (**2r**)



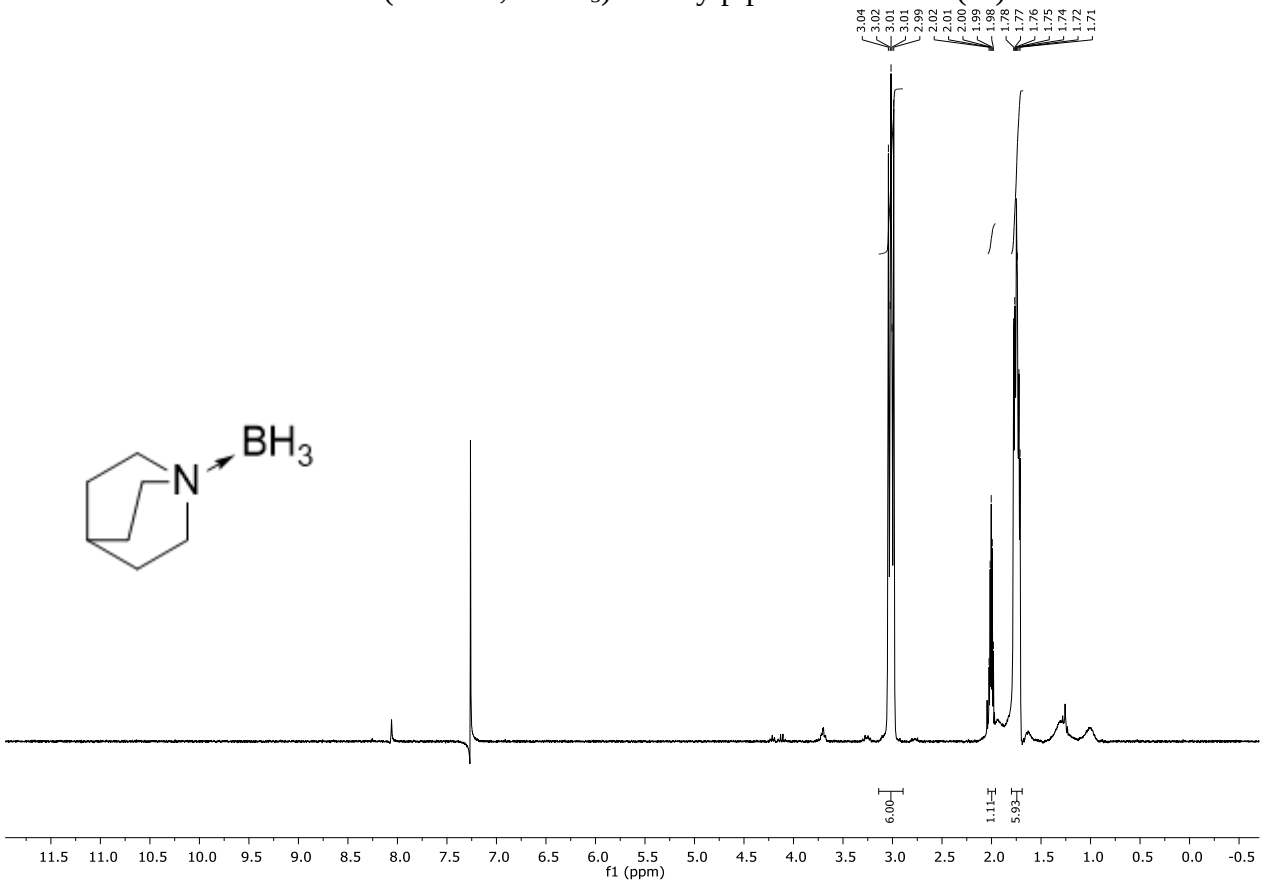
^{1}H NMR (300 MHz, $CDCl_3$) *N*-Ethylpiperidine-borane (**2s**)



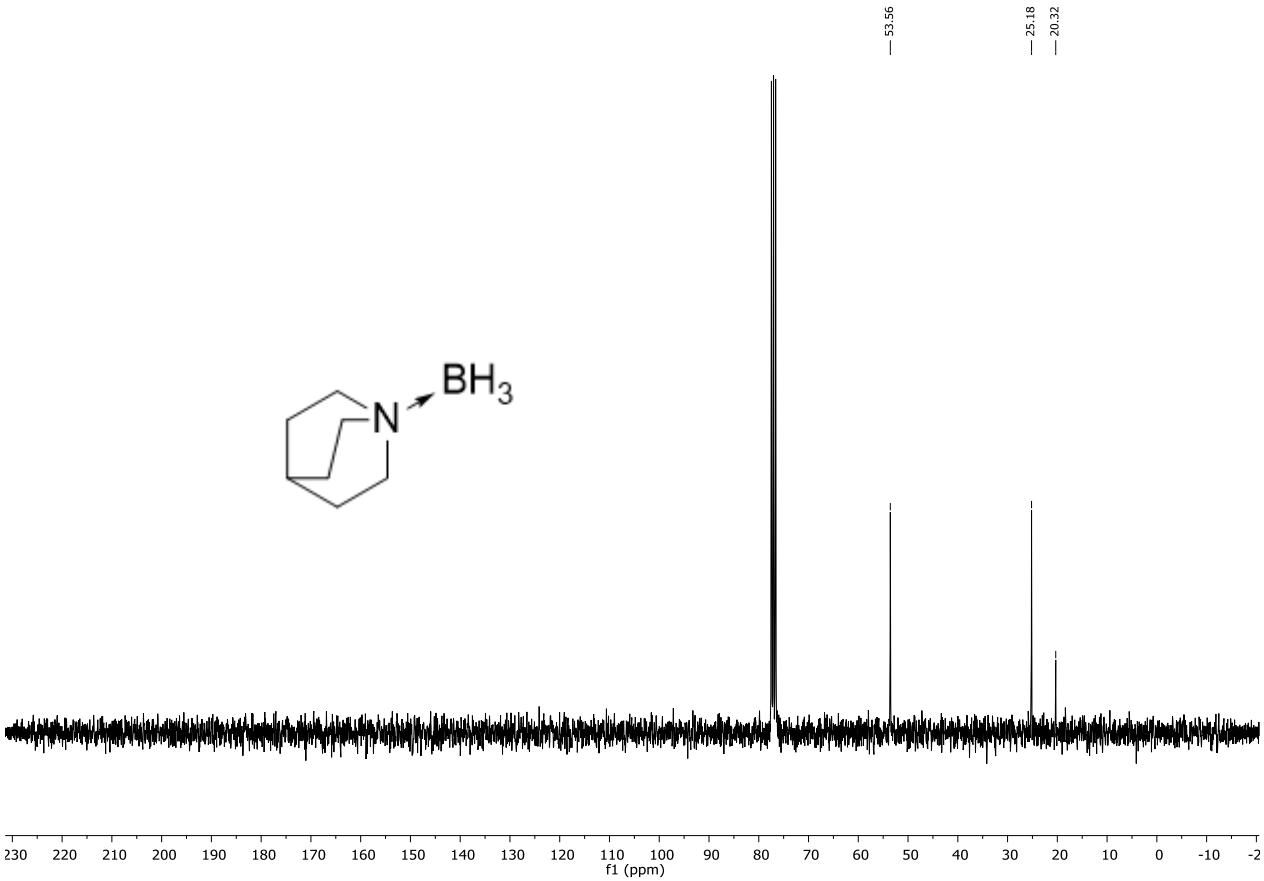
^{13}C NMR (75 MHz, $CDCl_3$) *N*-Ethylpiperidine-borane (**2s**)



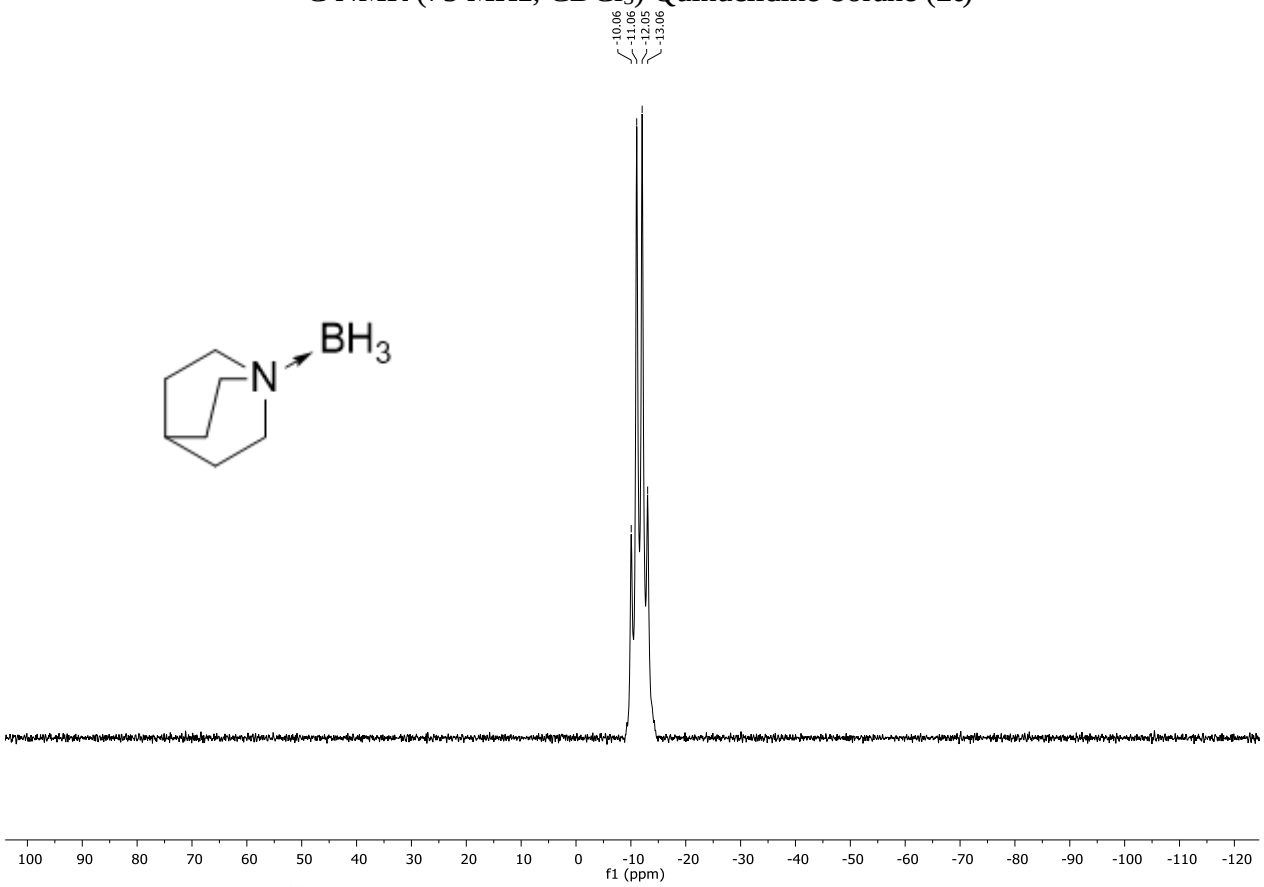
^{11}B NMR (96 MHz, $CDCl_3$) *N*-Ethylpiperidine-borane (**2s**)



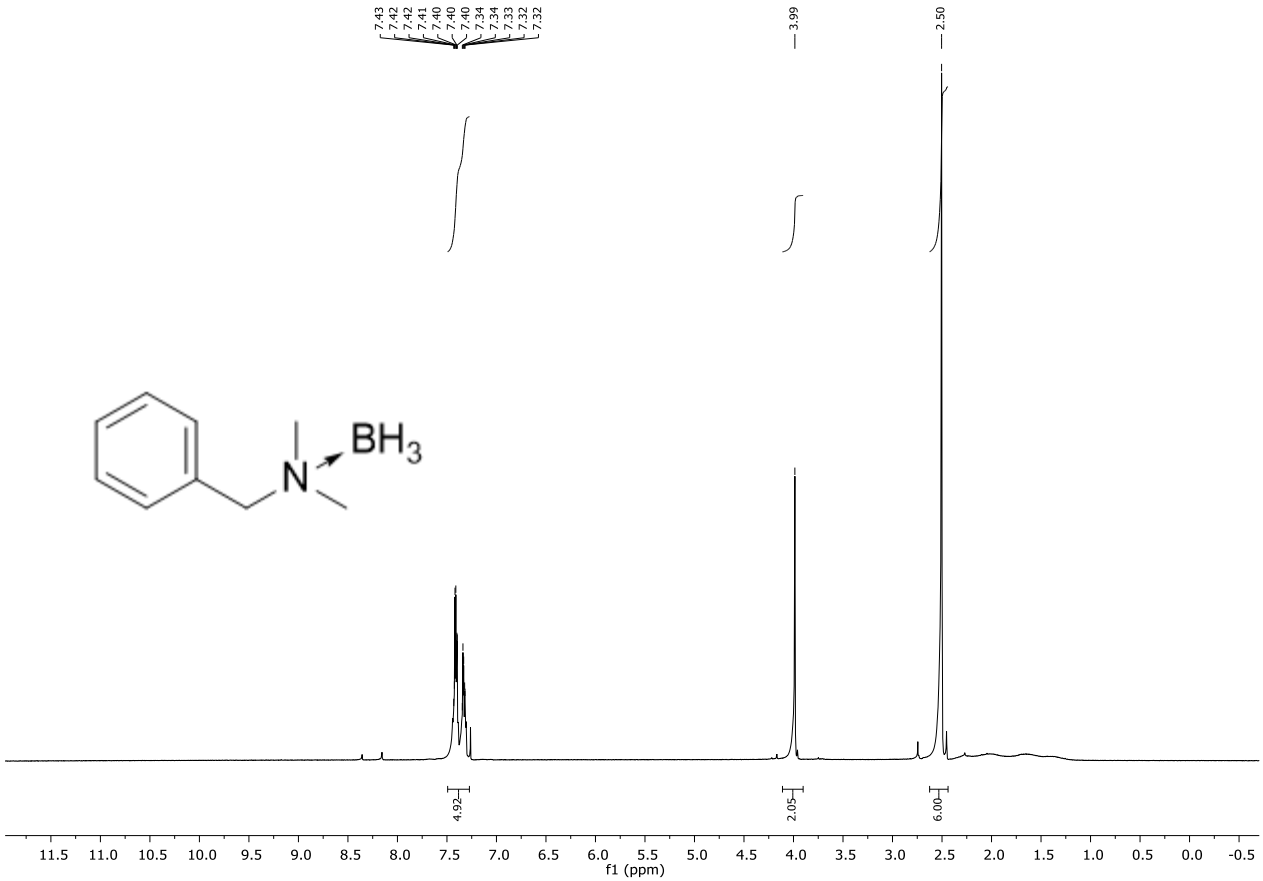
^{1}H NMR (300 MHz, $CDCl_3$) Quinuclidine-borane (**2t**)



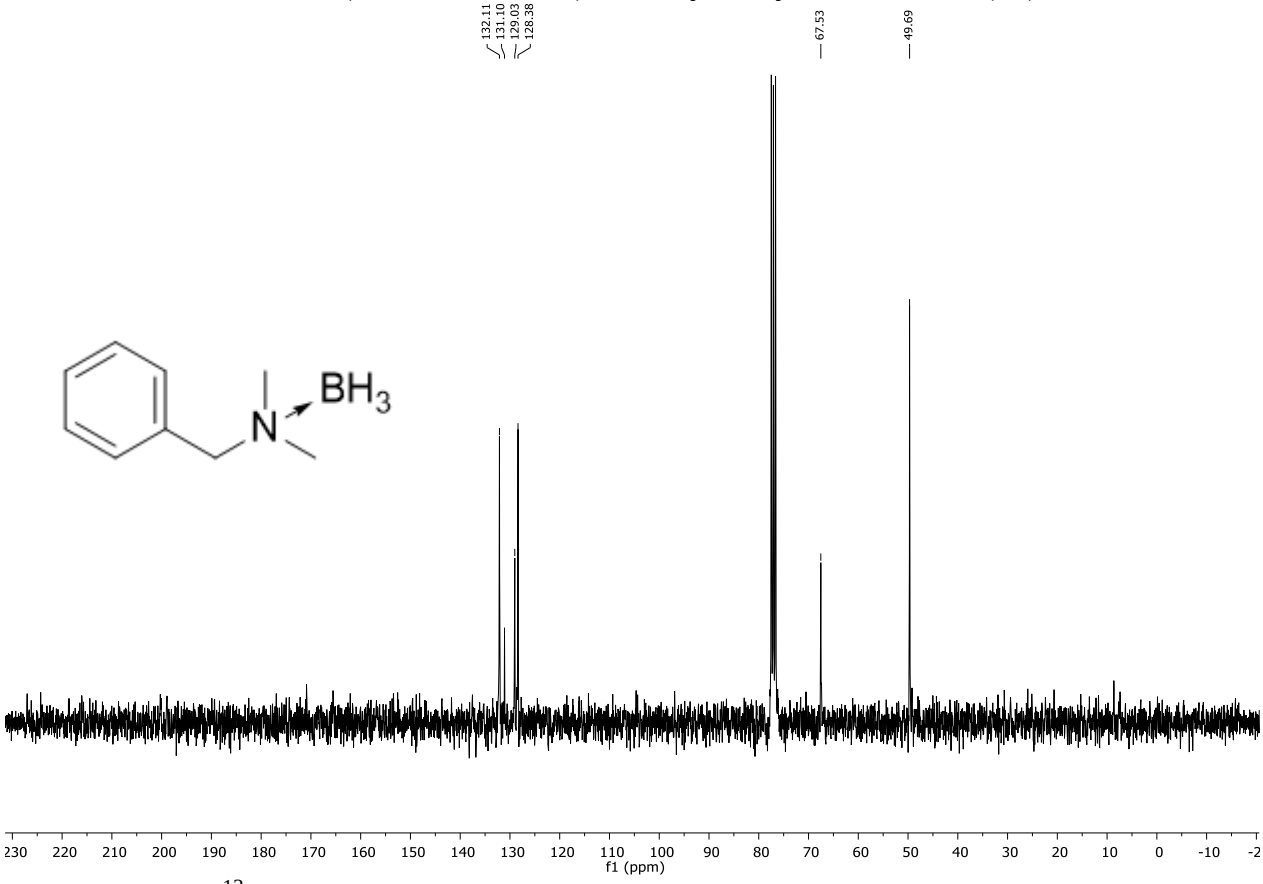
^{13}C NMR (75 MHz, $CDCl_3$) Quinuclidine-borane (**2t**)



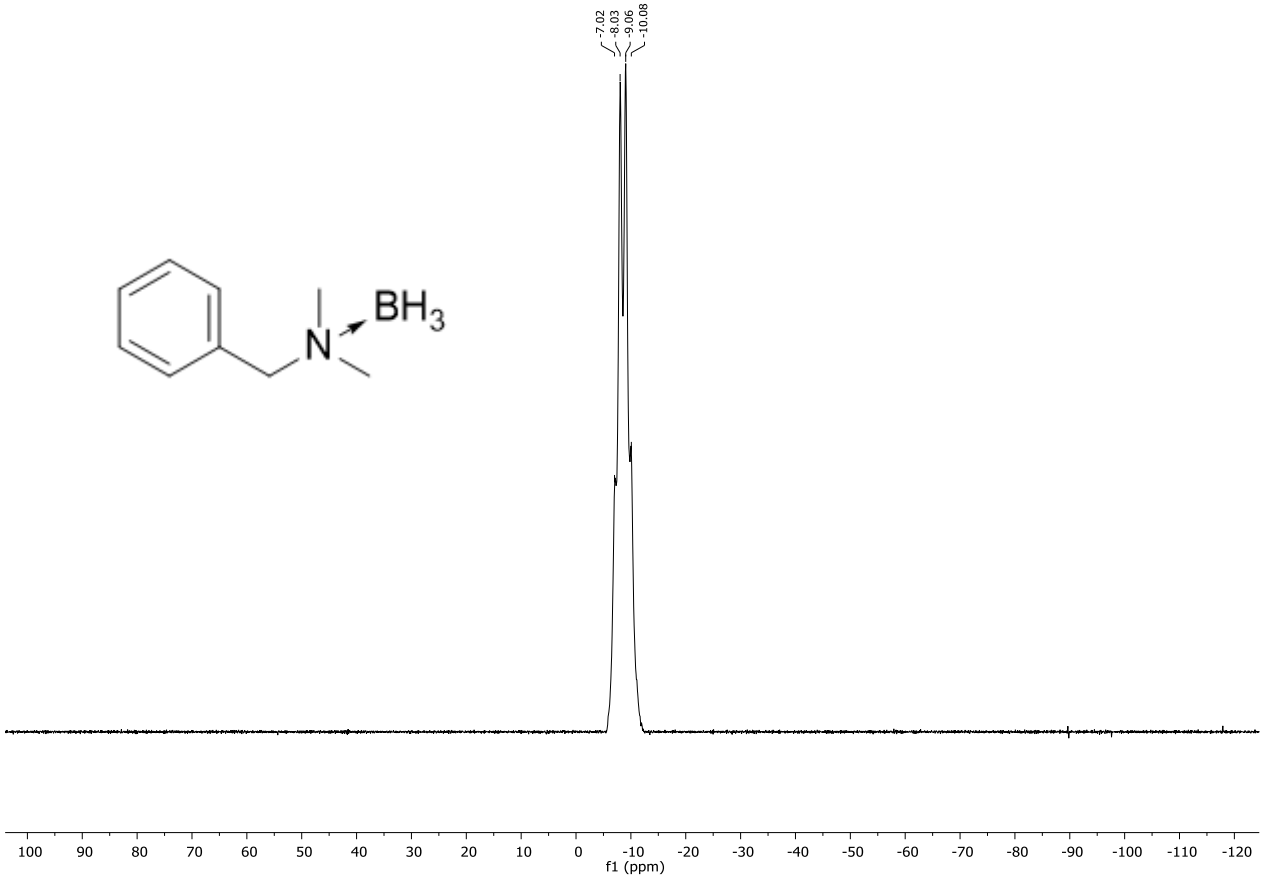
^{11}B NMR (96 MHz, $CDCl_3$) Quinuclidine-borane (**2t**)



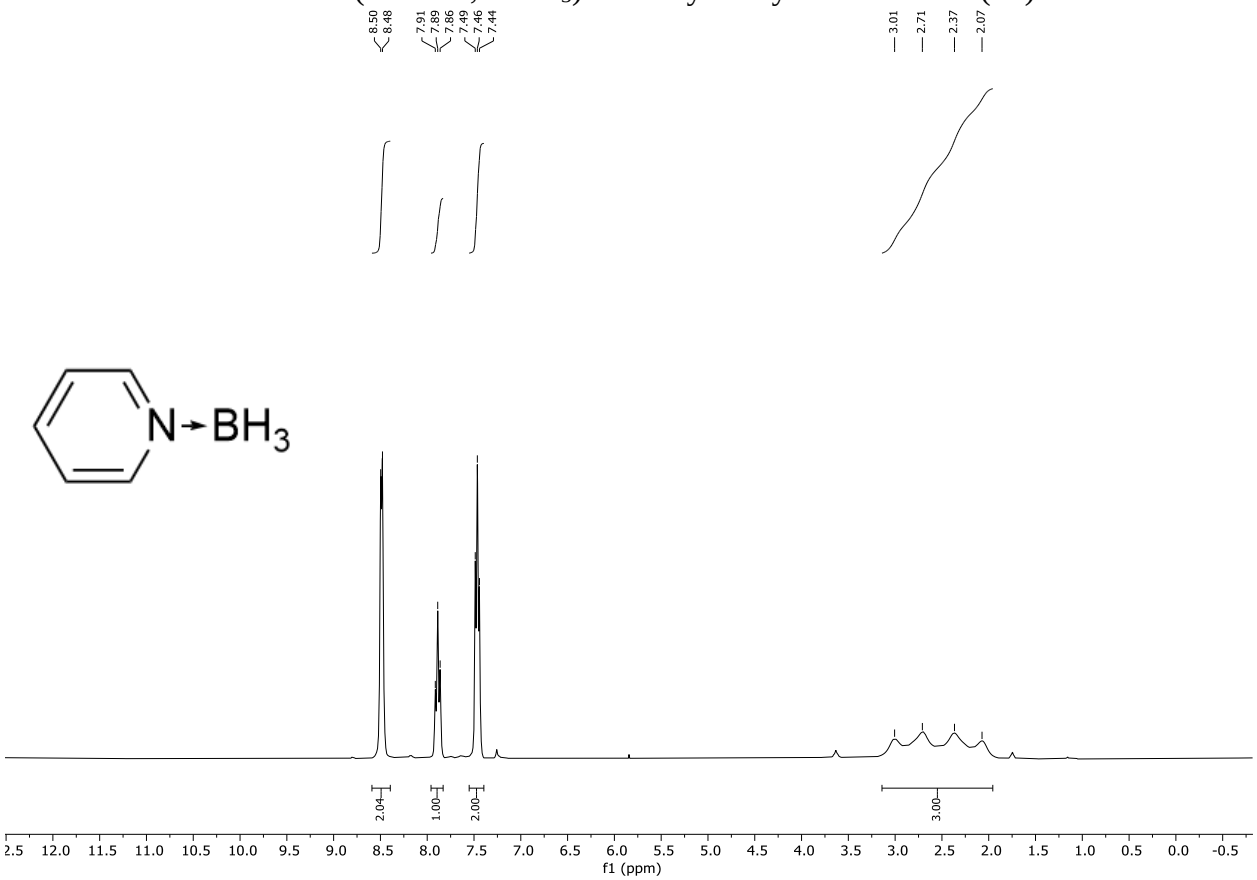
^{1}H NMR (300 MHz, $CDCl_3$) Dimethylbenzylamine-borane (**2u**)



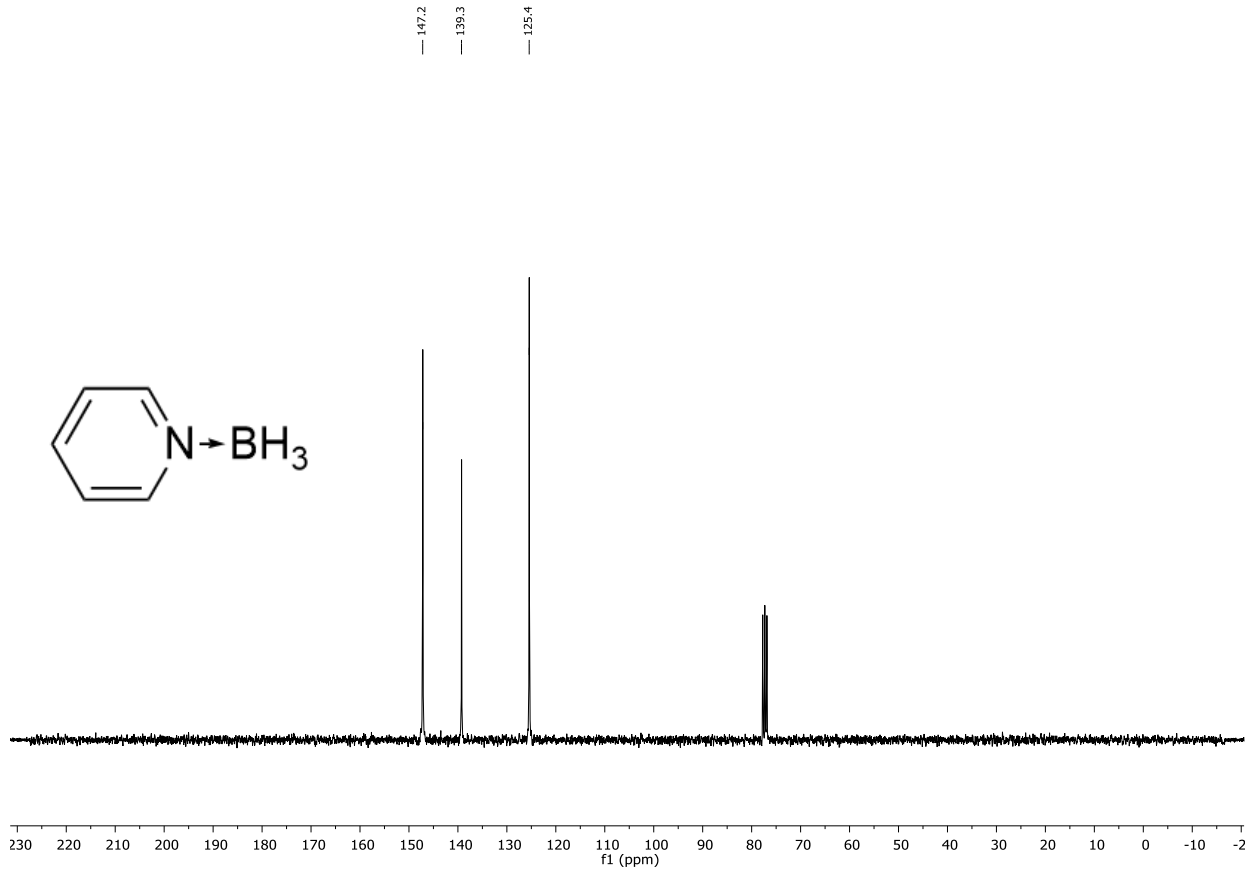
^{13}C NMR (75 MHz, $CDCl_3$) Dimethylbenzylamine-borane (**2u**)



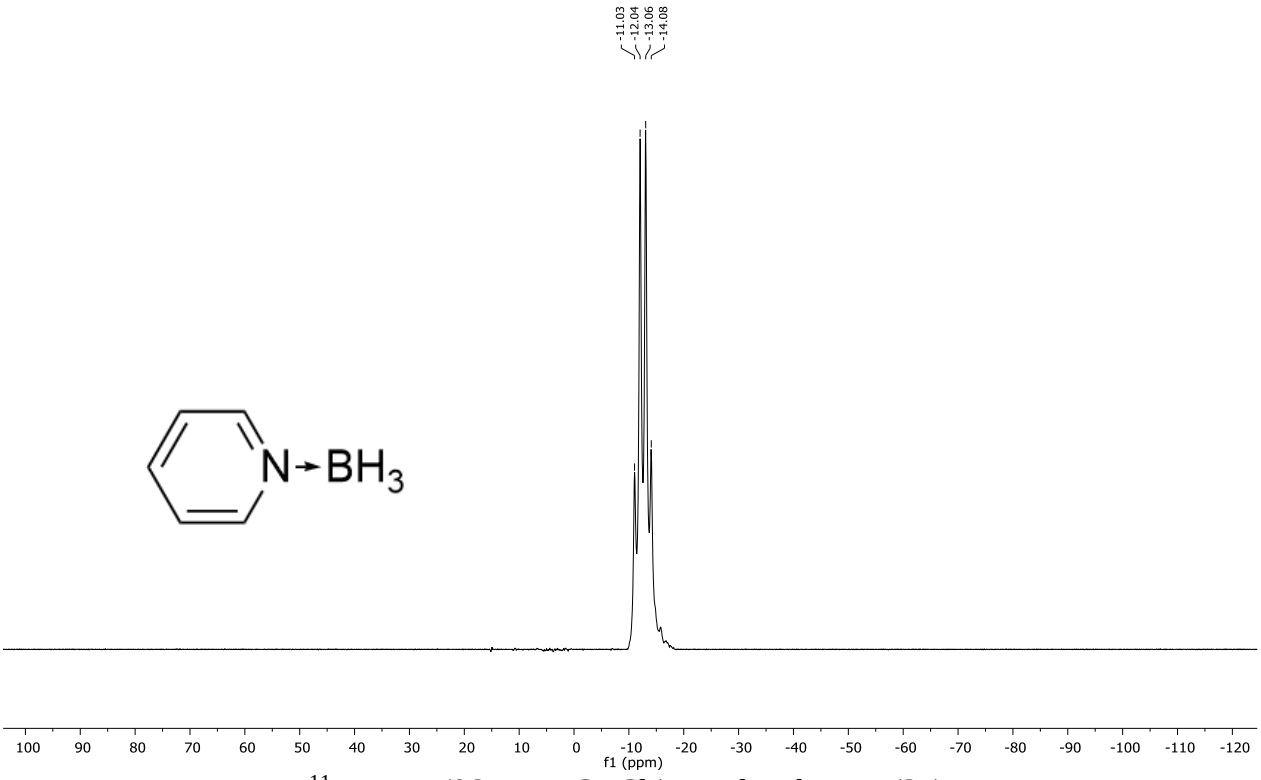
^{11}B NMR (96 MHz, $CDCl_3$) Dimethylbenzylamine-borane (**2u**)



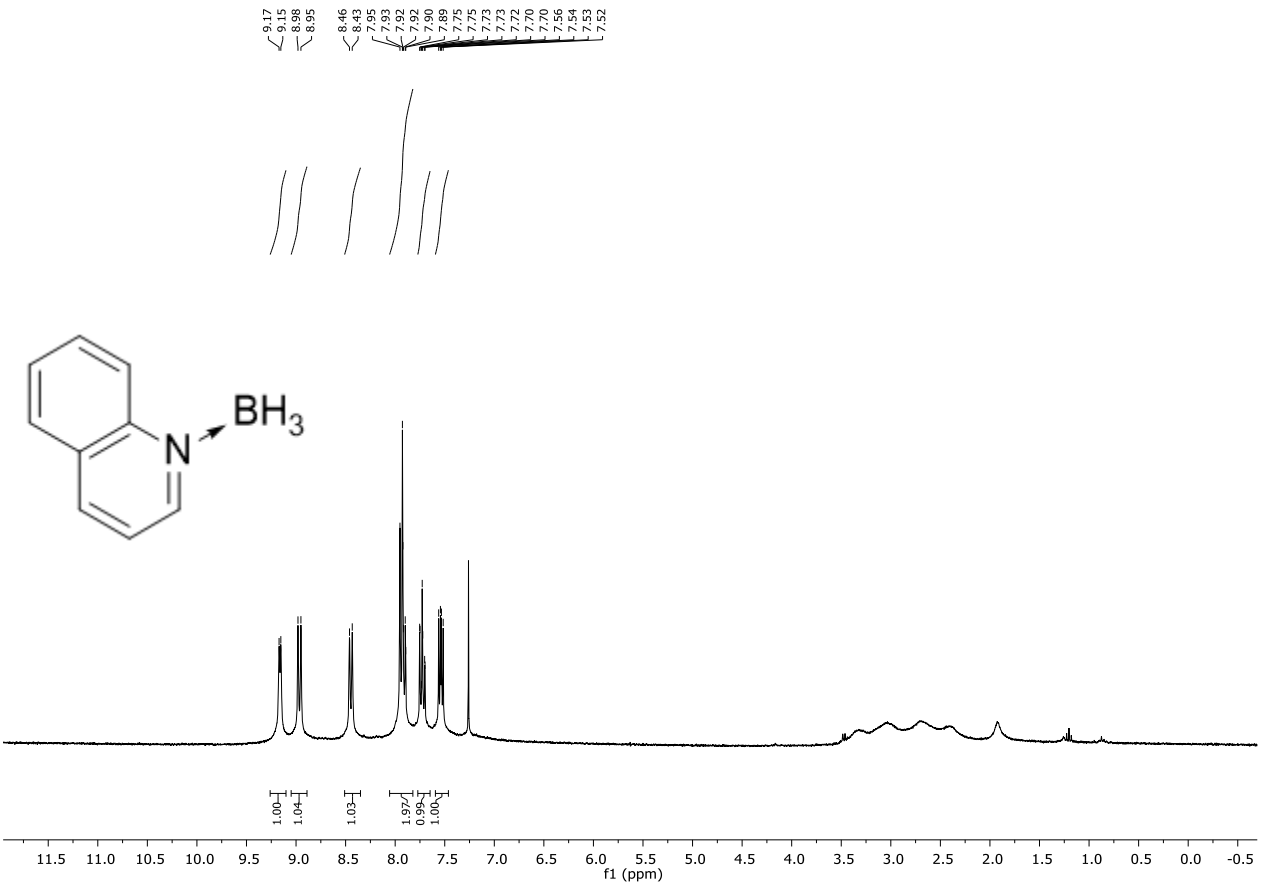
^{1}H NMR (300 MHz, $CDCl_3$) Pyridine-borane (**2v**)



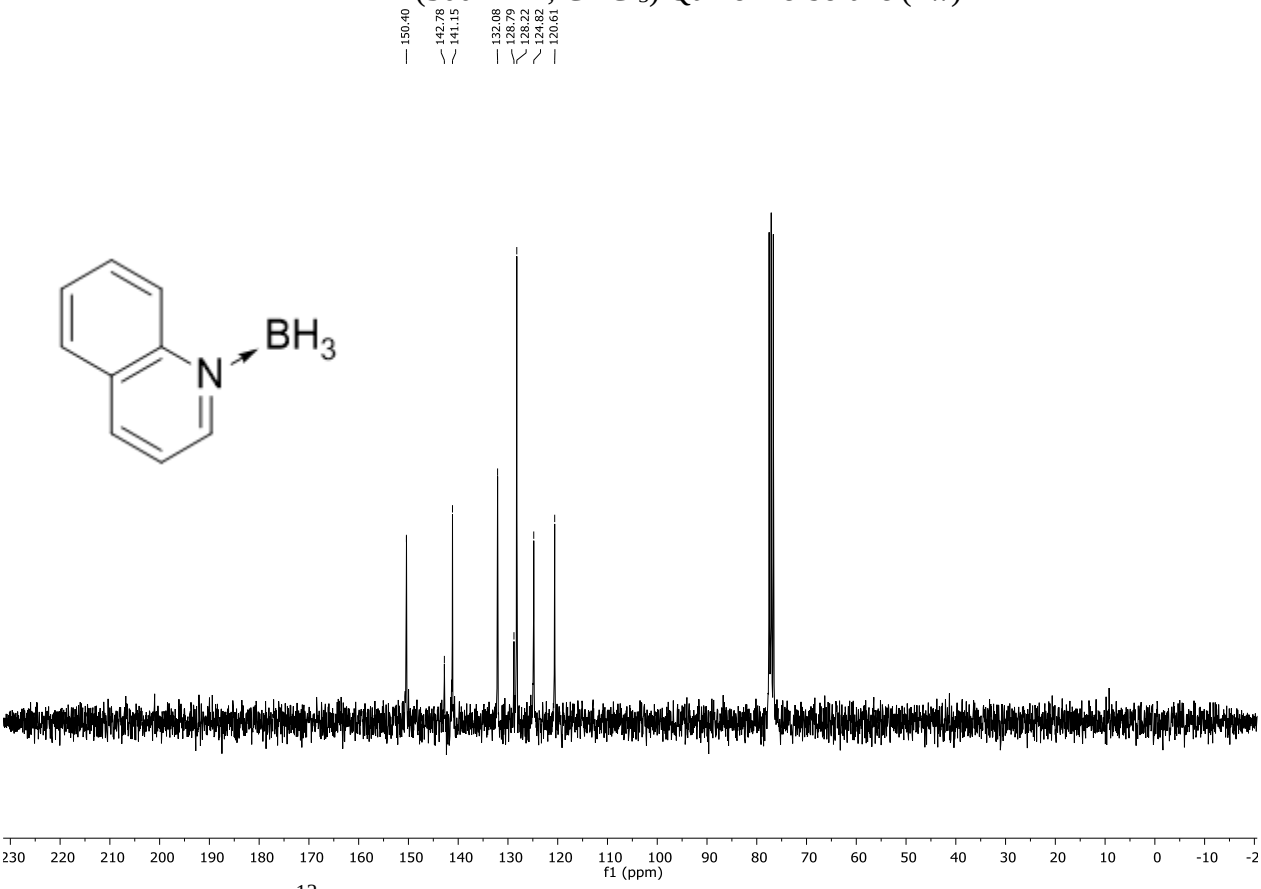
^{13}C NMR (75 MHz, $CDCl_3$) Pyridine-borane (**2v**)



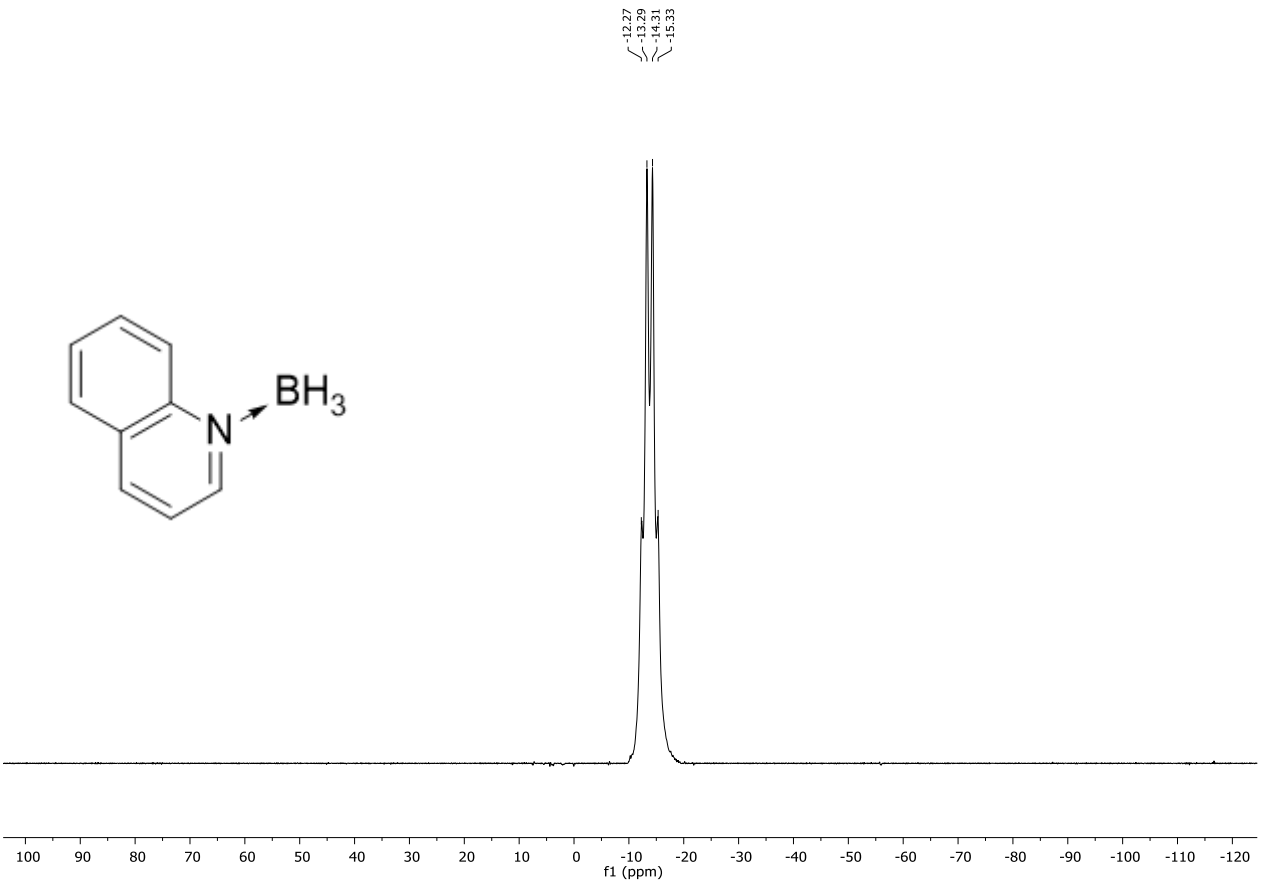
^{11}B NMR (96 MHz, $CDCl_3$) Pyridine-borane (**2v**)



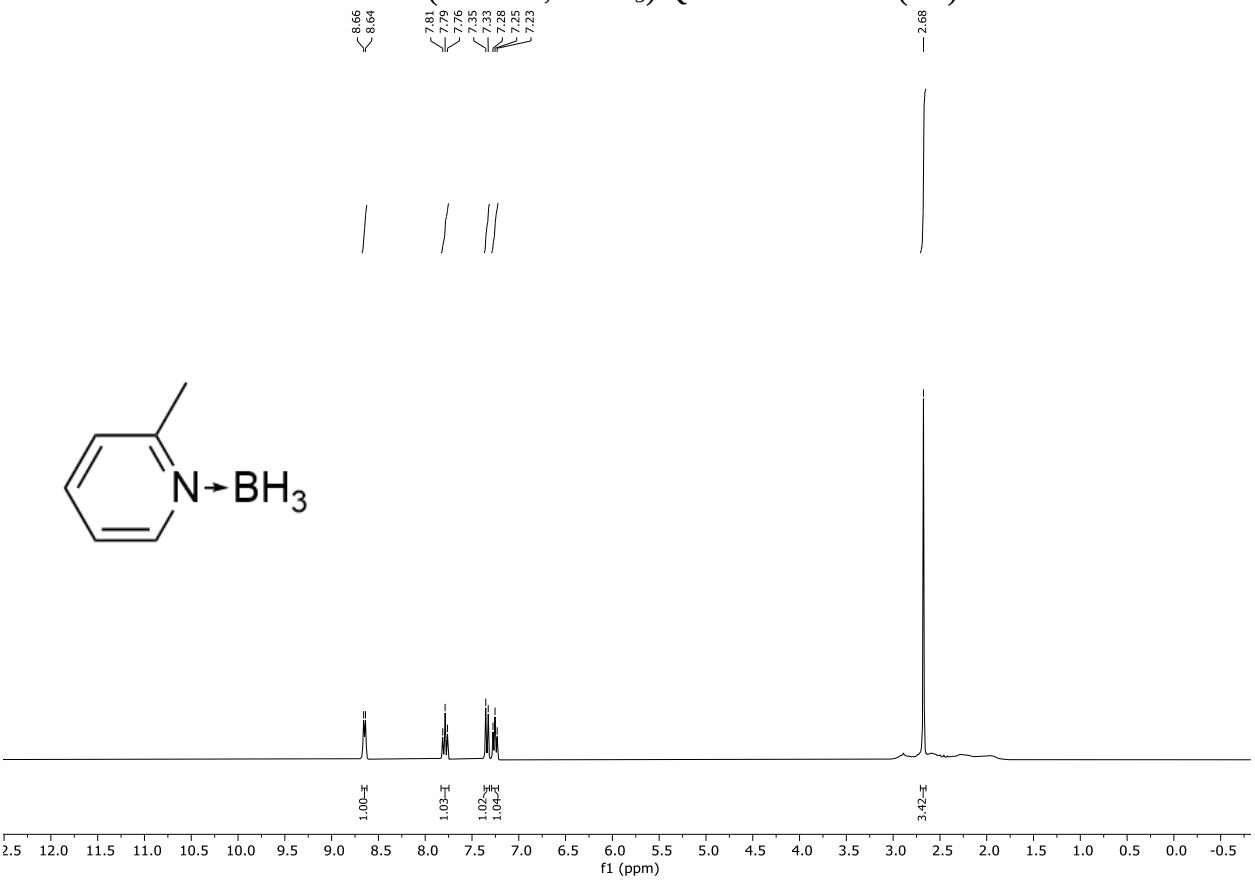
^{1}H NMR (300 MHz, $CDCl_3$) Quinoline-borane (**2w**)



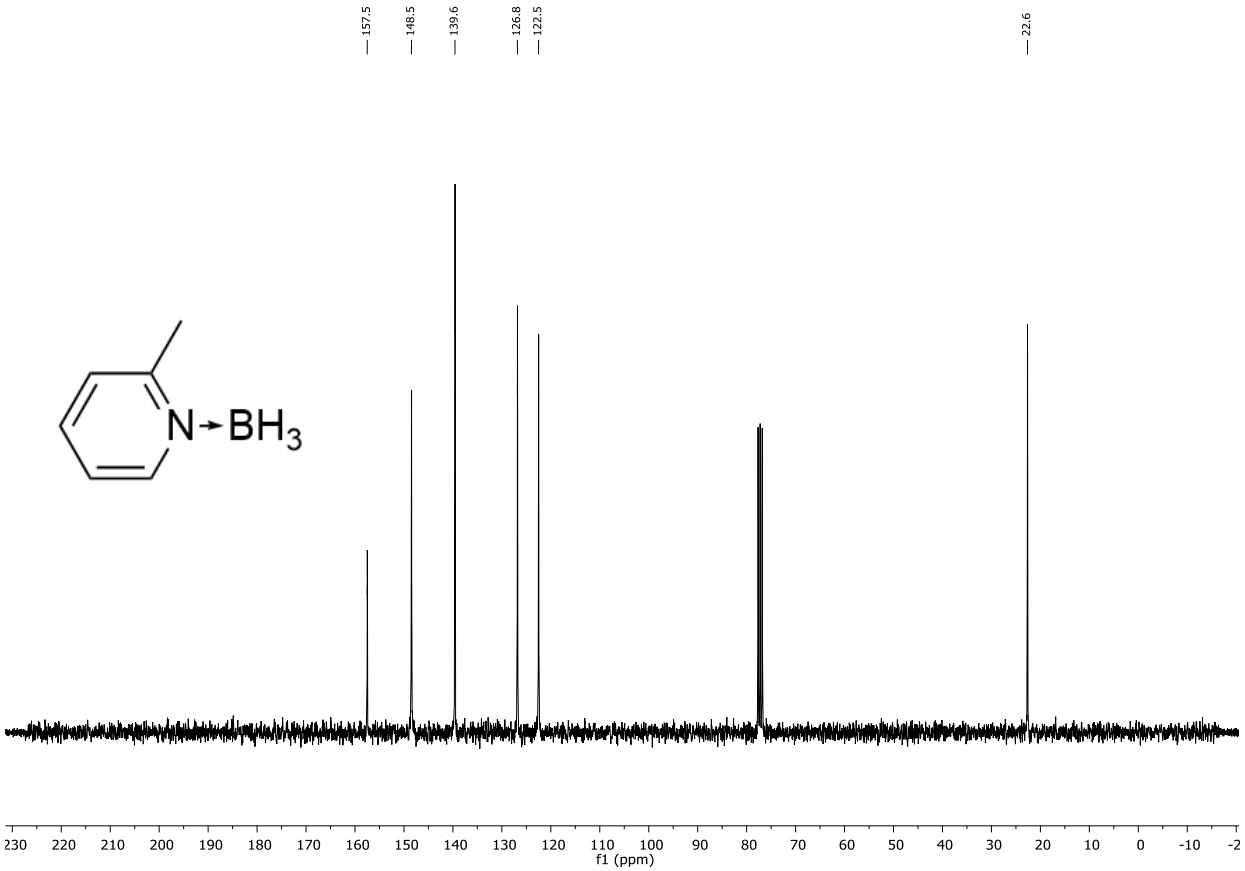
^{13}C NMR (75 MHz, $CDCl_3$) Quinoline-borane (**2w**)



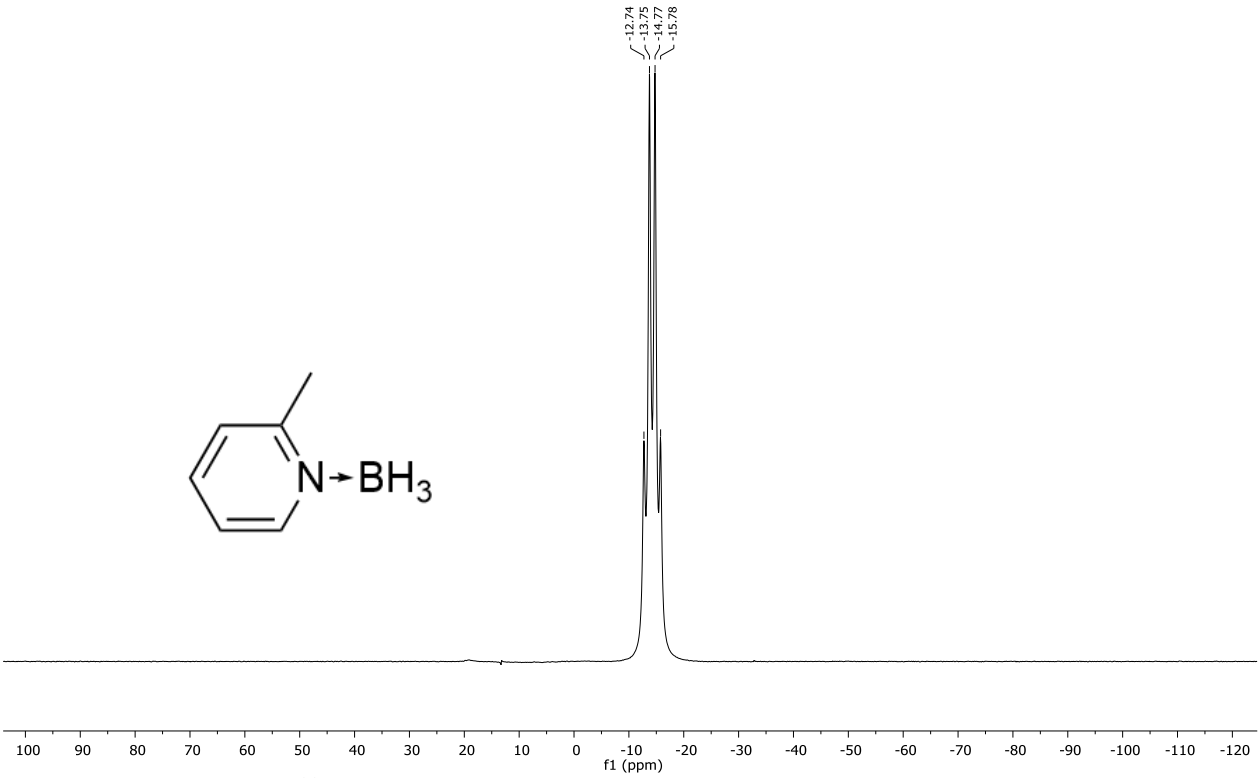
^{11}B NMR (96 MHz, $CDCl_3$) Quinoline-borane (**2w**)



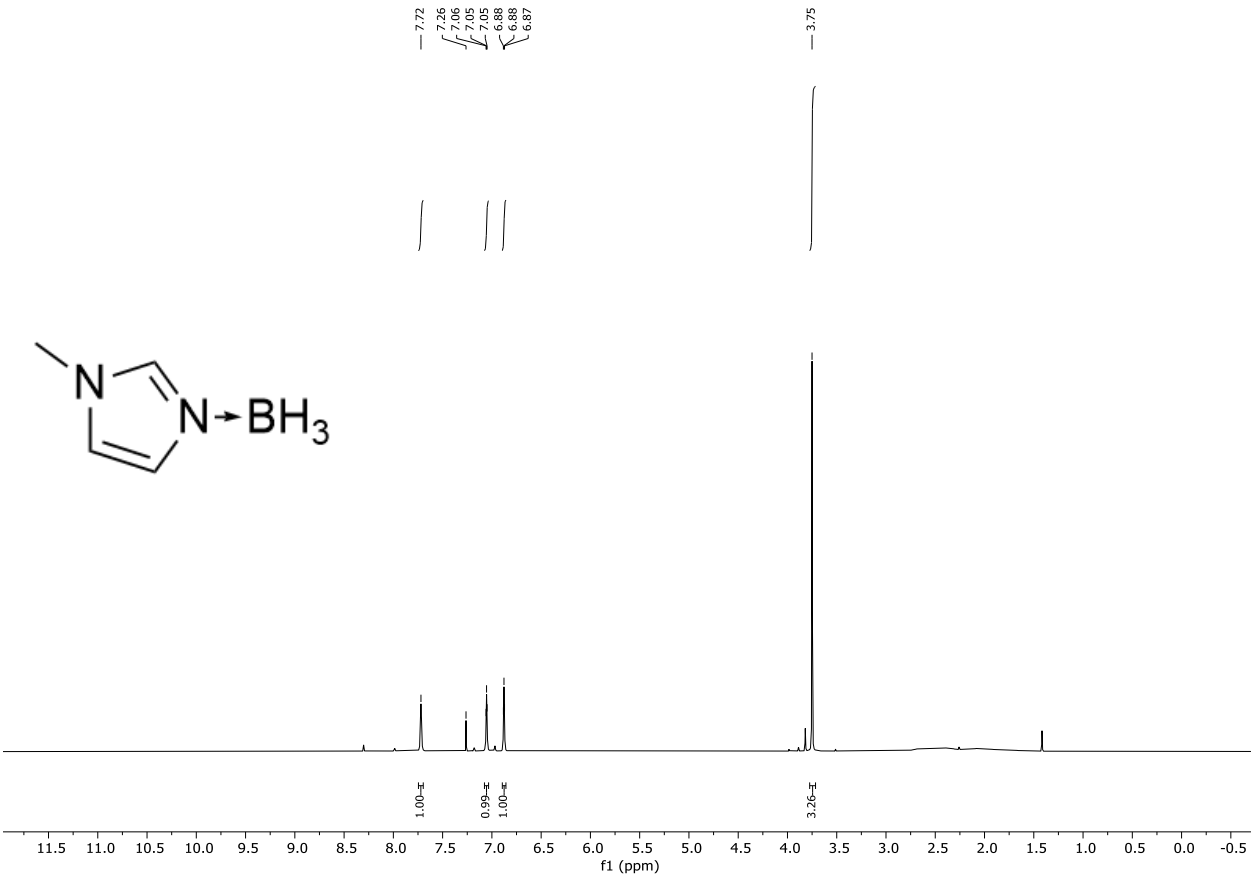
^{1}H NMR (300 MHz, $CDCl_3$) 2-Picoline-borane (**2x**)



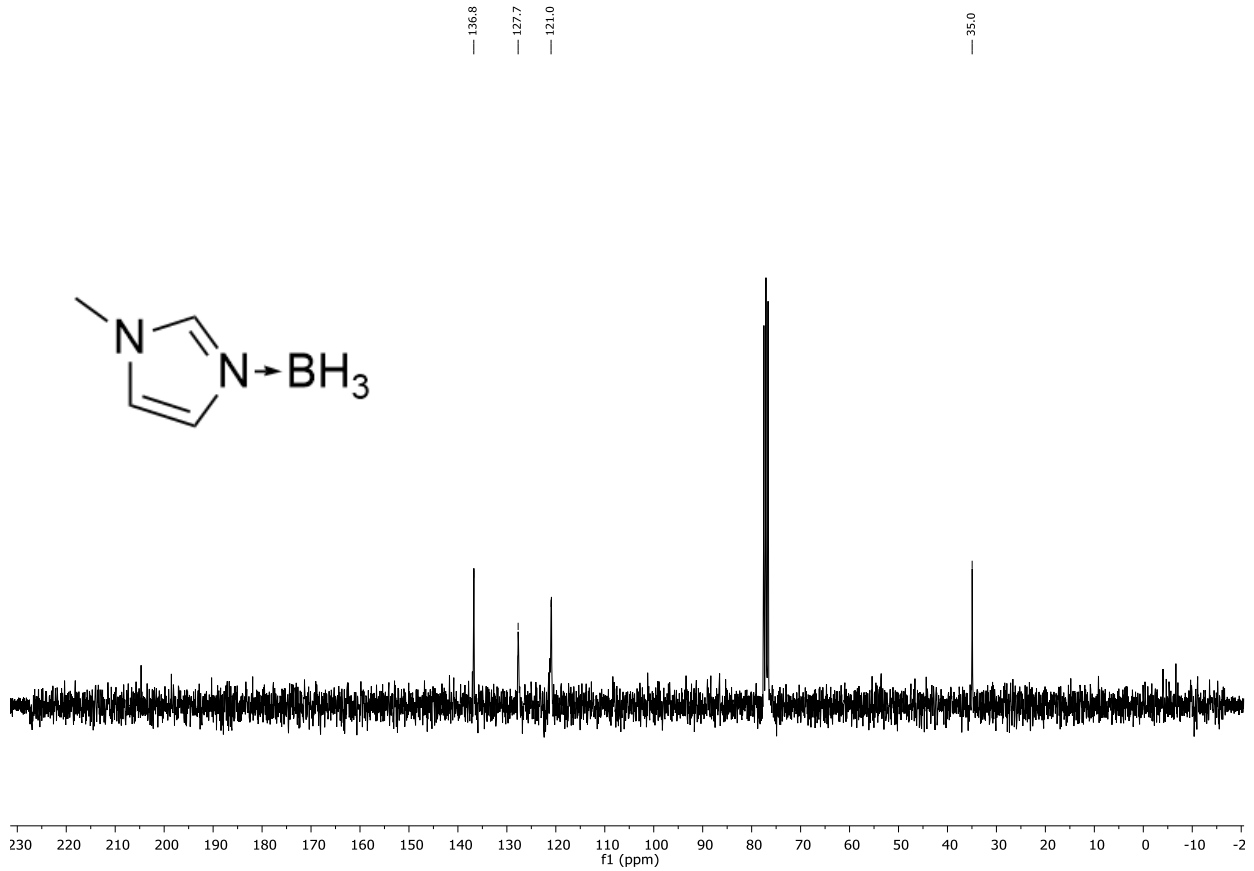
^{13}C NMR (75 MHz, $CDCl_3$) 2-Picoline-borane (**2x**)



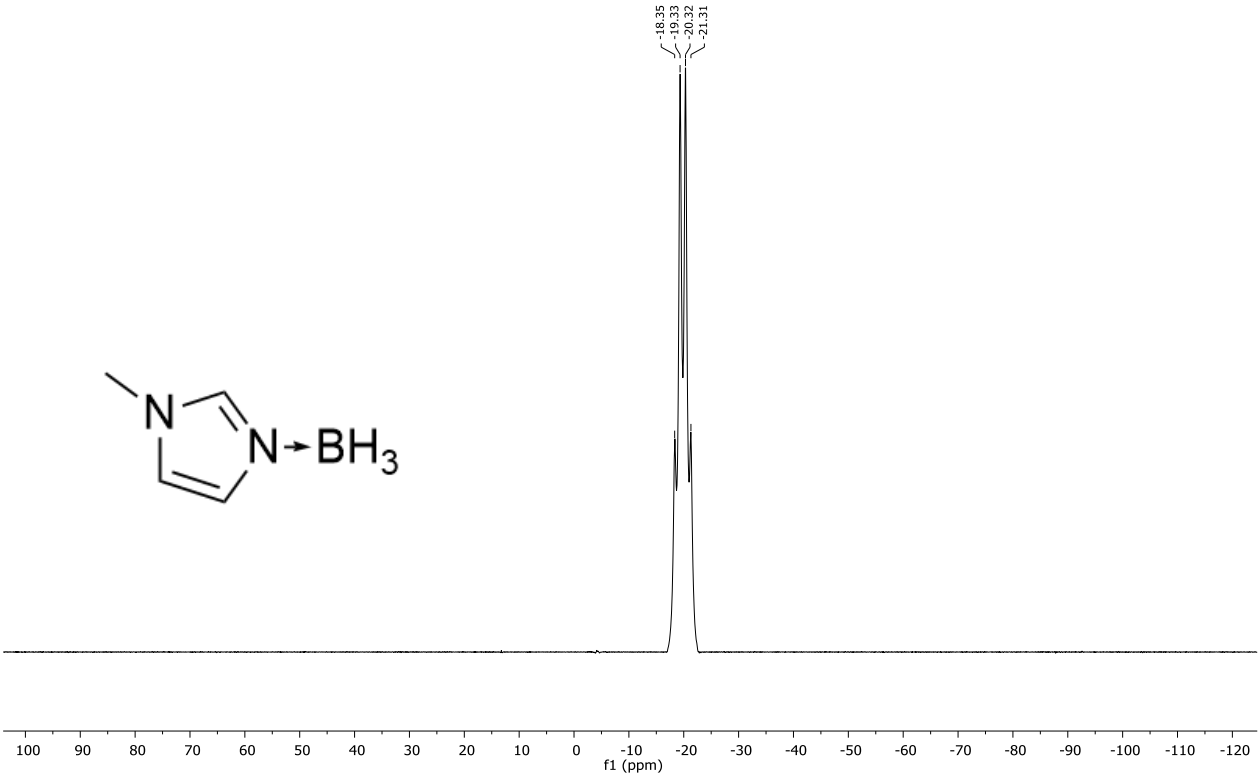
^{11}B NMR (96 MHz, $CDCl_3$) 2-Picoline-borane (**2x**)



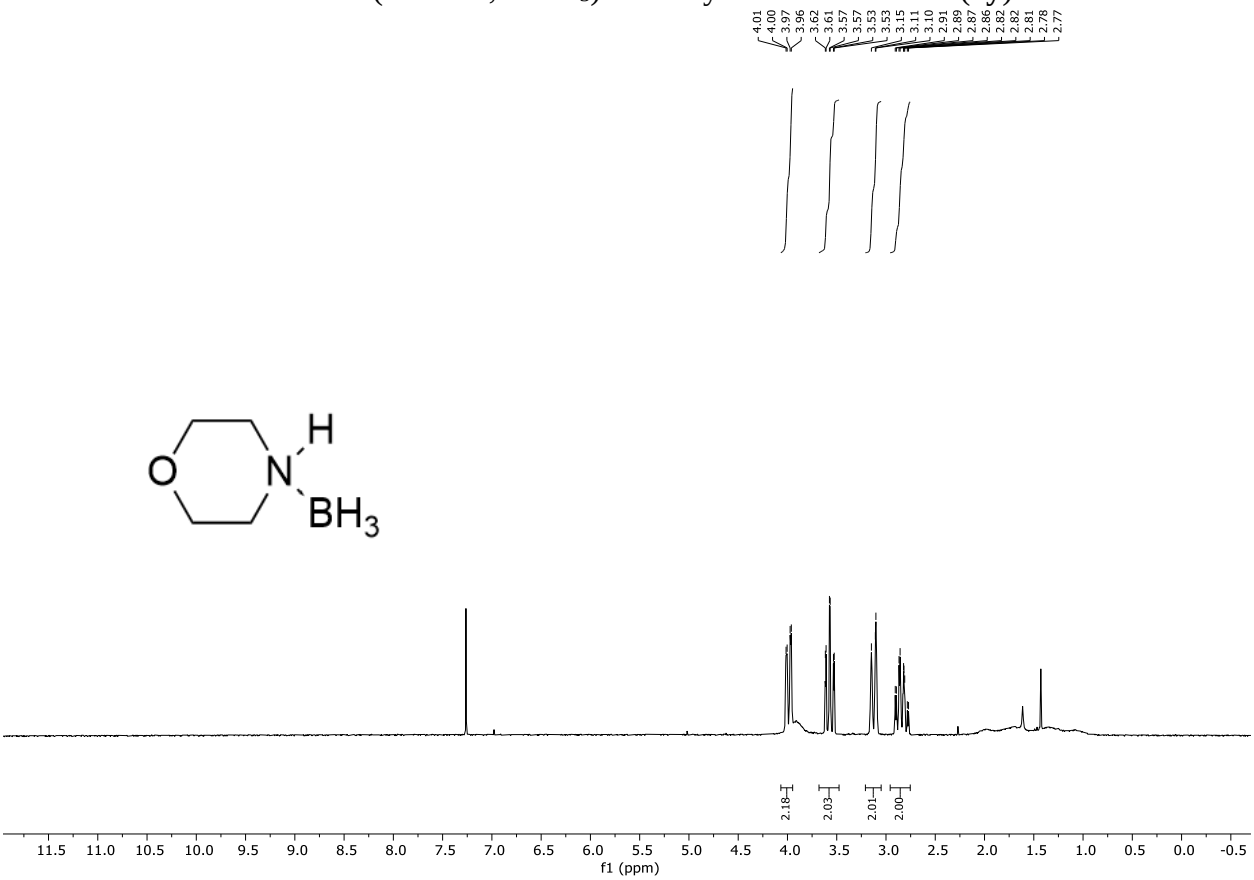
^{1}H NMR (300 MHz, $CDCl_3$) 1-Methylimidazole-borane (**2y**)



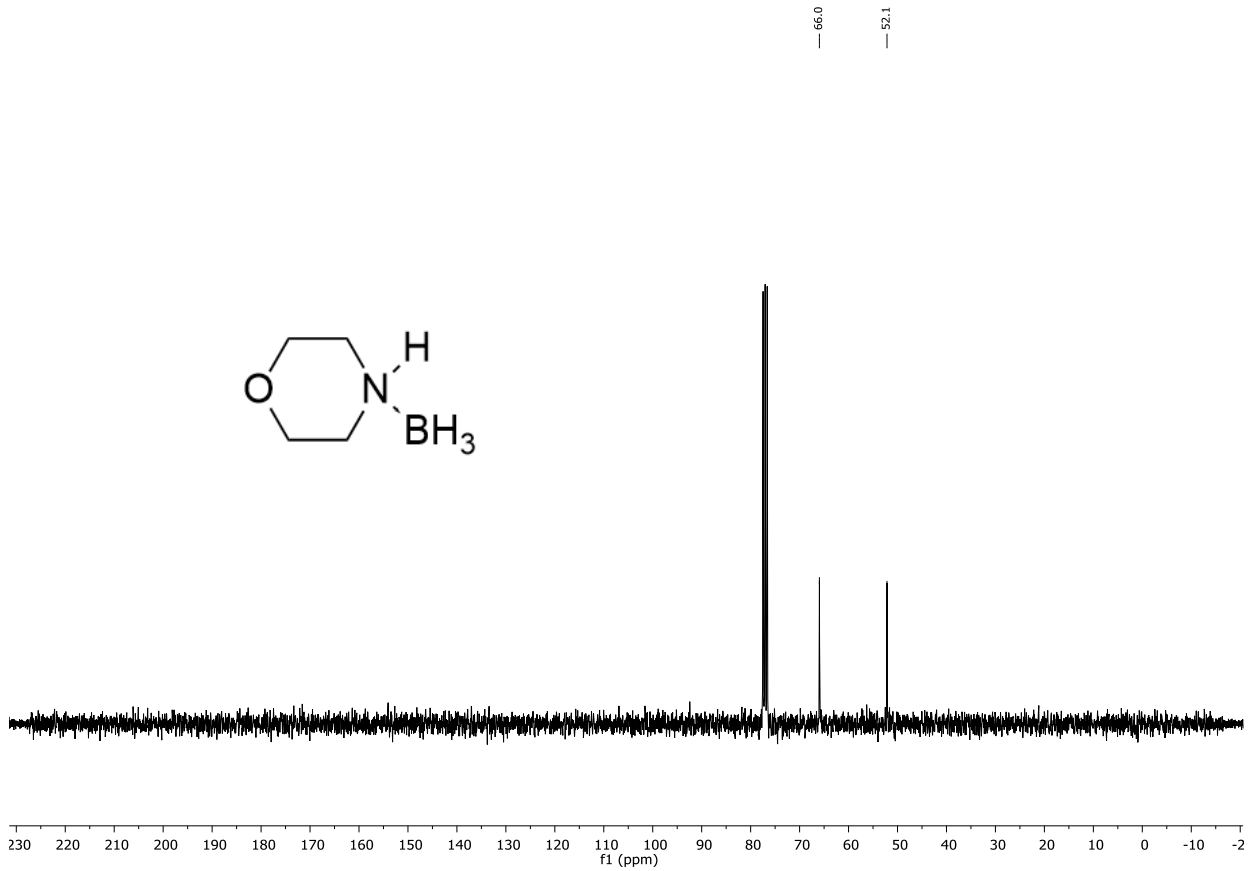
^{13}C NMR (75 MHz, $CDCl_3$) 1-Methylimidazole-borane (**2y**)



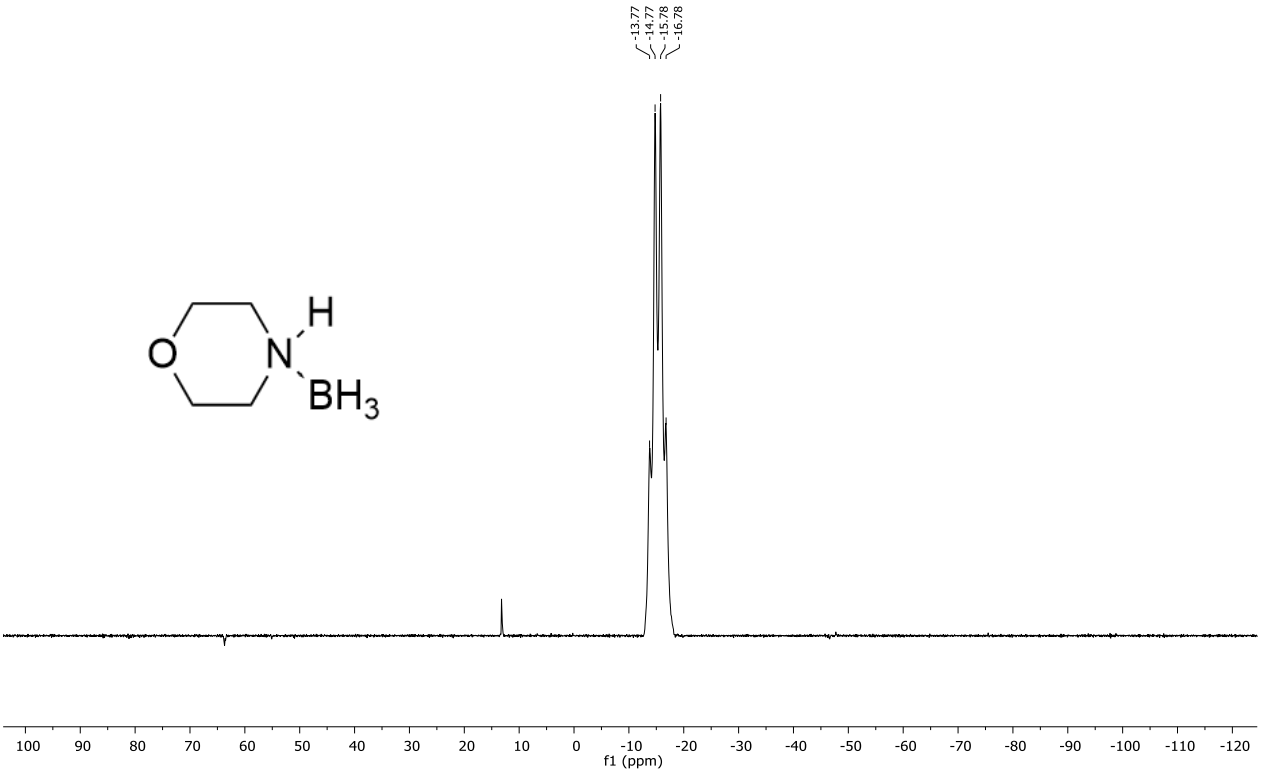
^{11}B NMR (96 MHz, $CDCl_3$) 1-Methylimidazole-borane (**2y**)



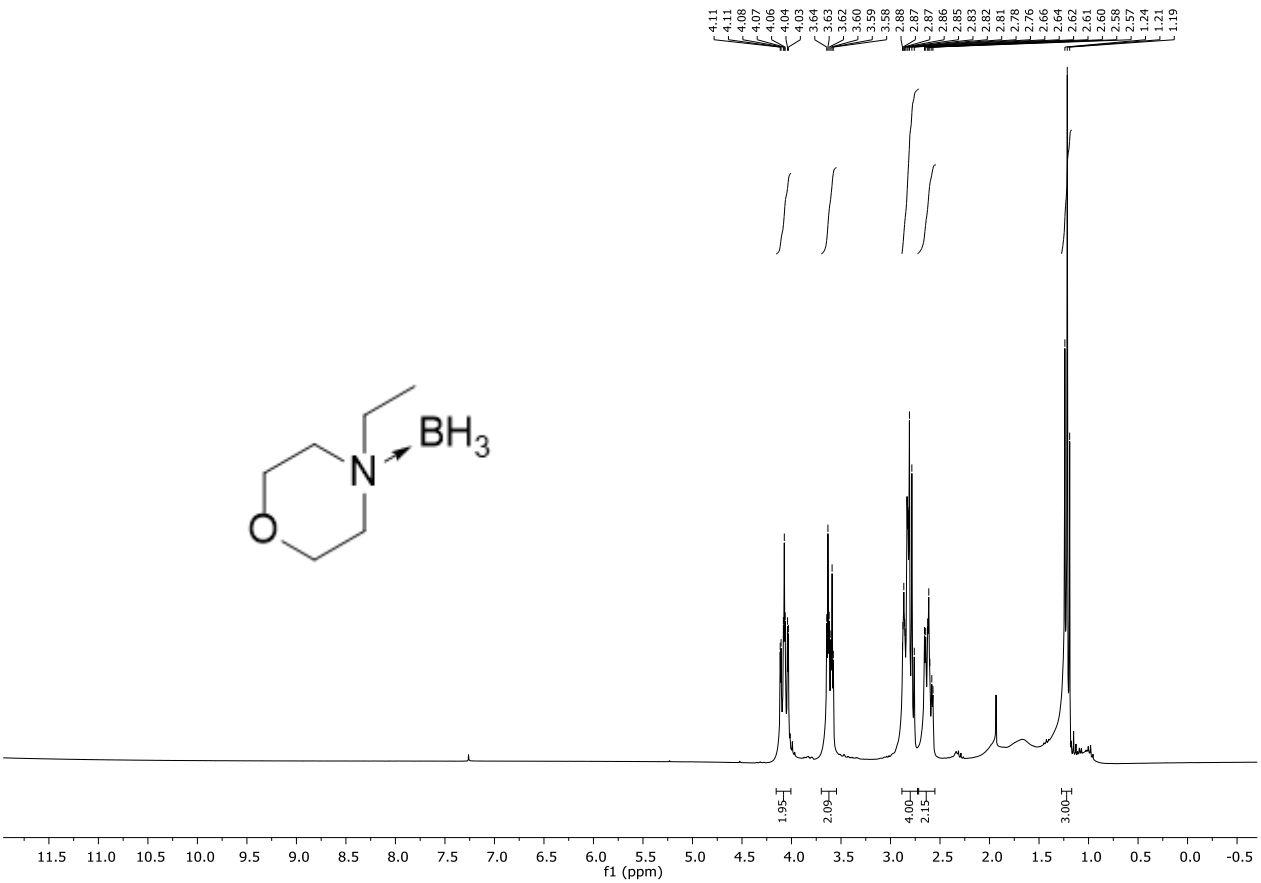
^{1}H NMR (300 MHz, $CDCl_3$) Morpholine-borane (**2z**)



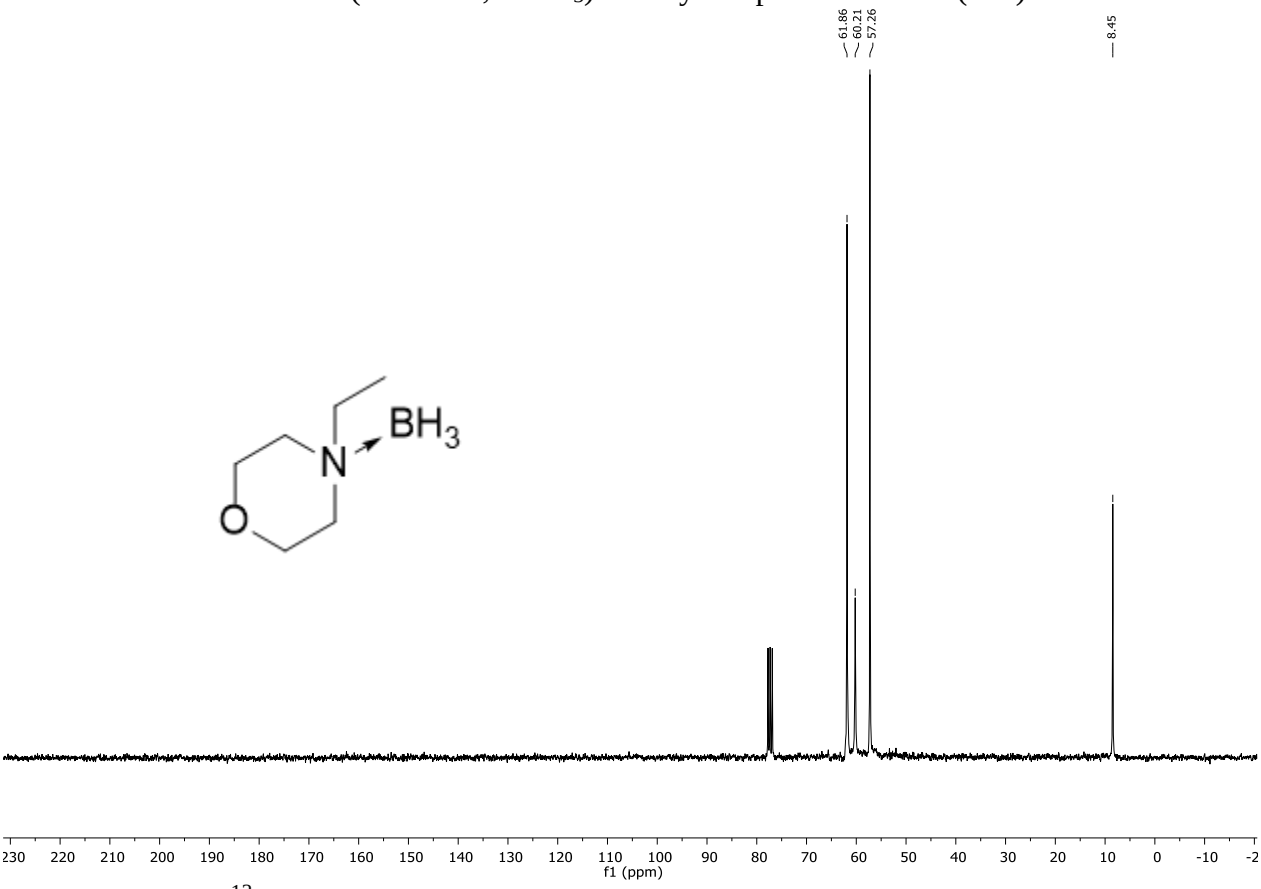
^{13}C NMR (75 MHz, $CDCl_3$) Morpholine-borane (**2z**)



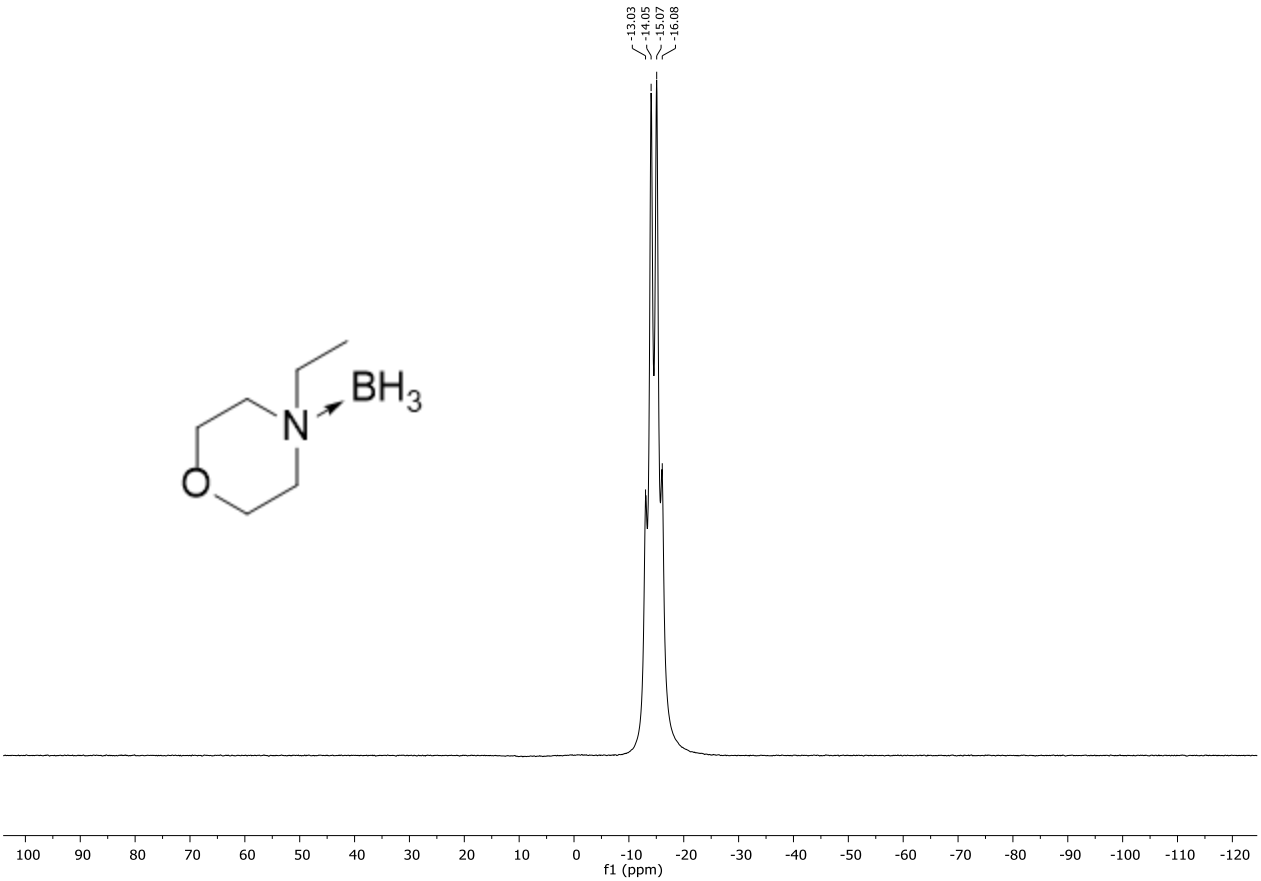
^{11}B NMR (96 MHz, $CDCl_3$) Morpholine-borane (**2z**)



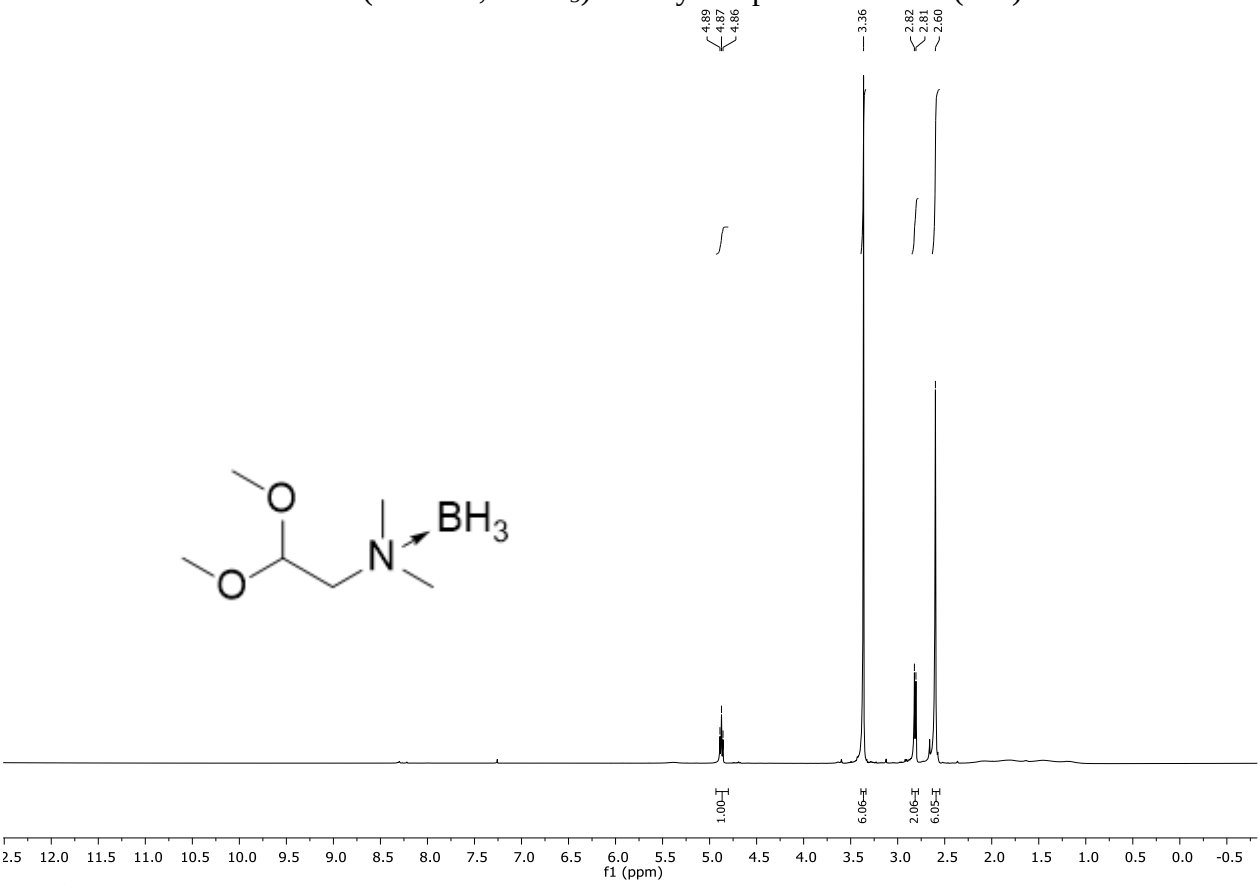
^{1}H NMR (300 MHz, $CDCl_3$) *N*-Ethylmorpholine-borane (**2aa**)



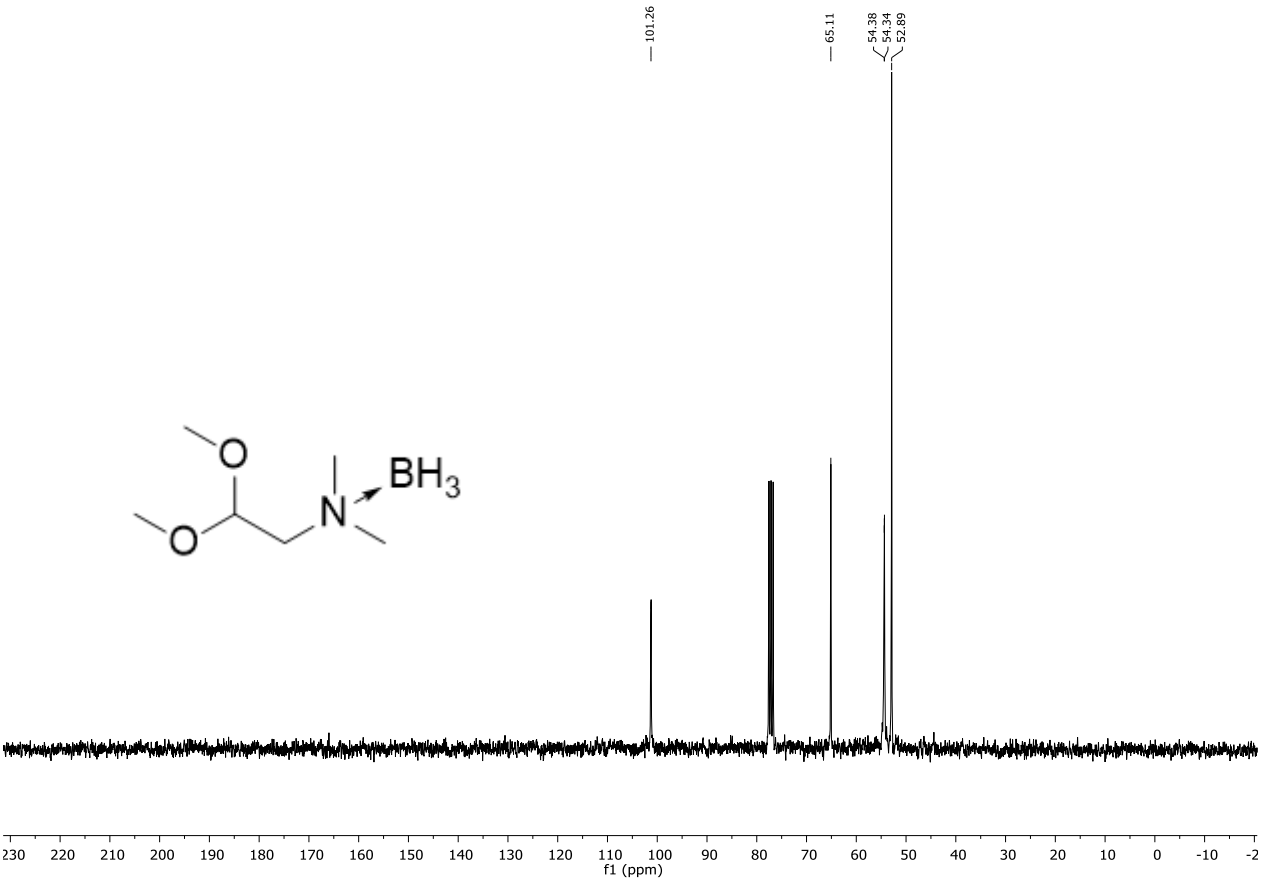
^{13}C NMR (75 MHz, $CDCl_3$) *N*-Ethylmorpholine-borane (**2aa**)



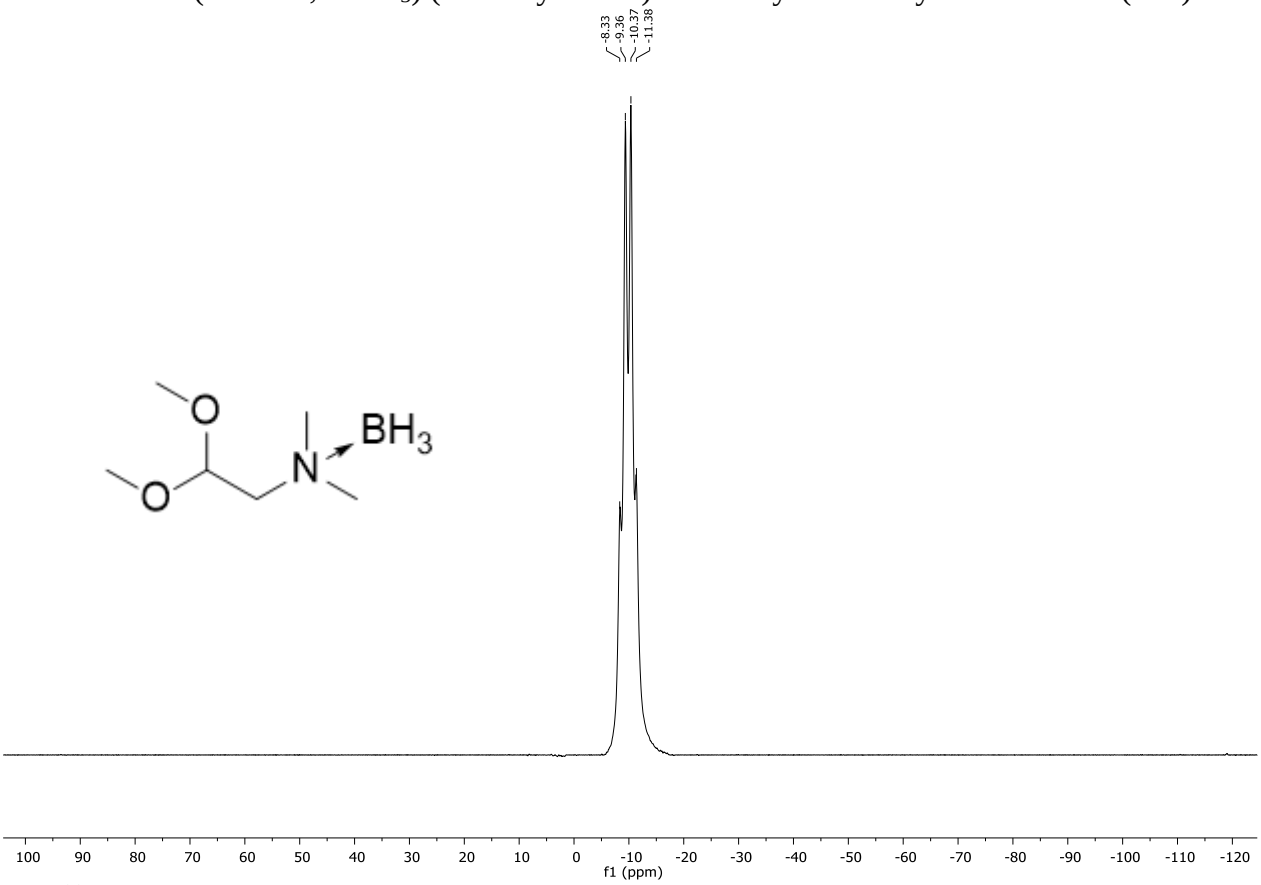
^{11}B NMR (96 MHz, $CDCl_3$) *N*-Ethylmorpholine-borane (**2aa**)



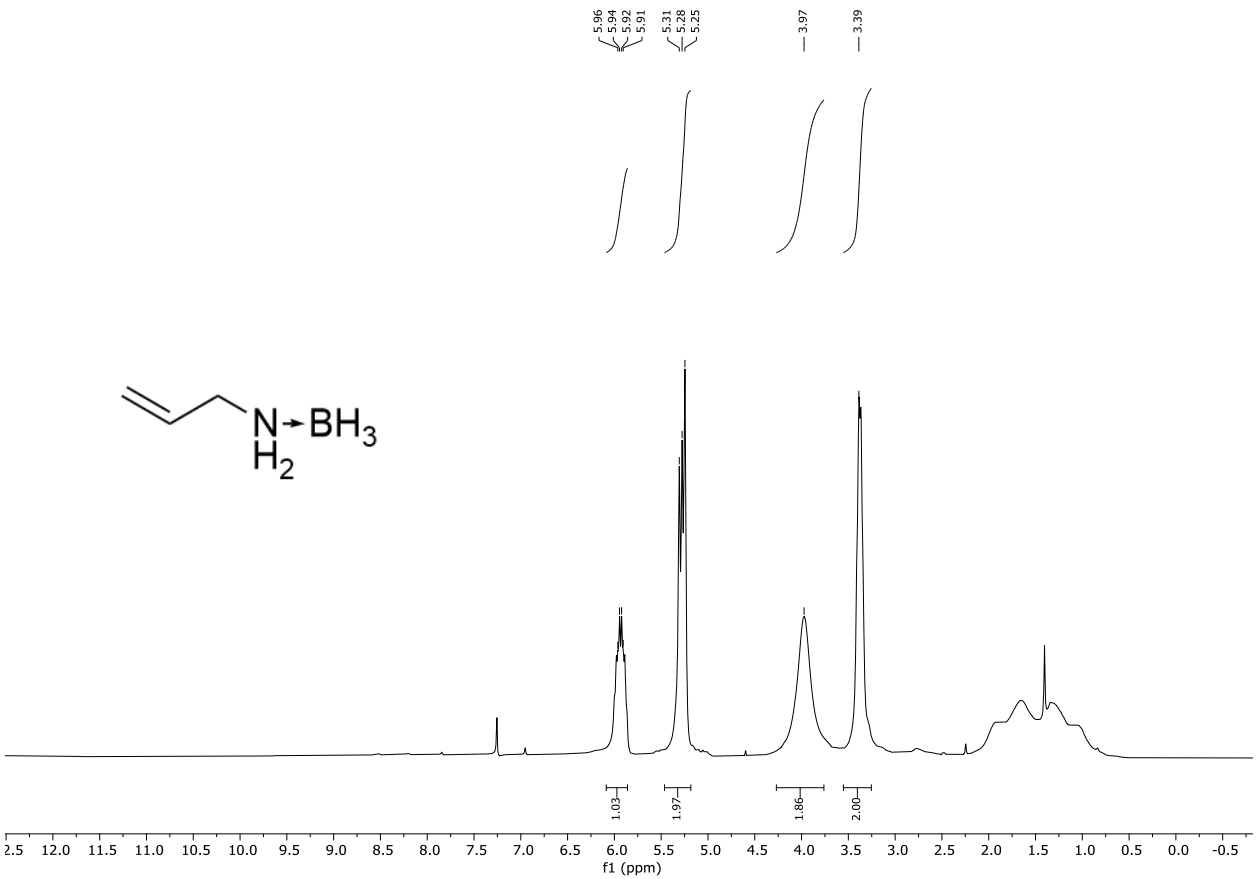
^{1}H NMR (300 MHz, $CDCl_3$) (Dimethylamino)acetaldehyde dimethylacetal-borane (**2ab**)



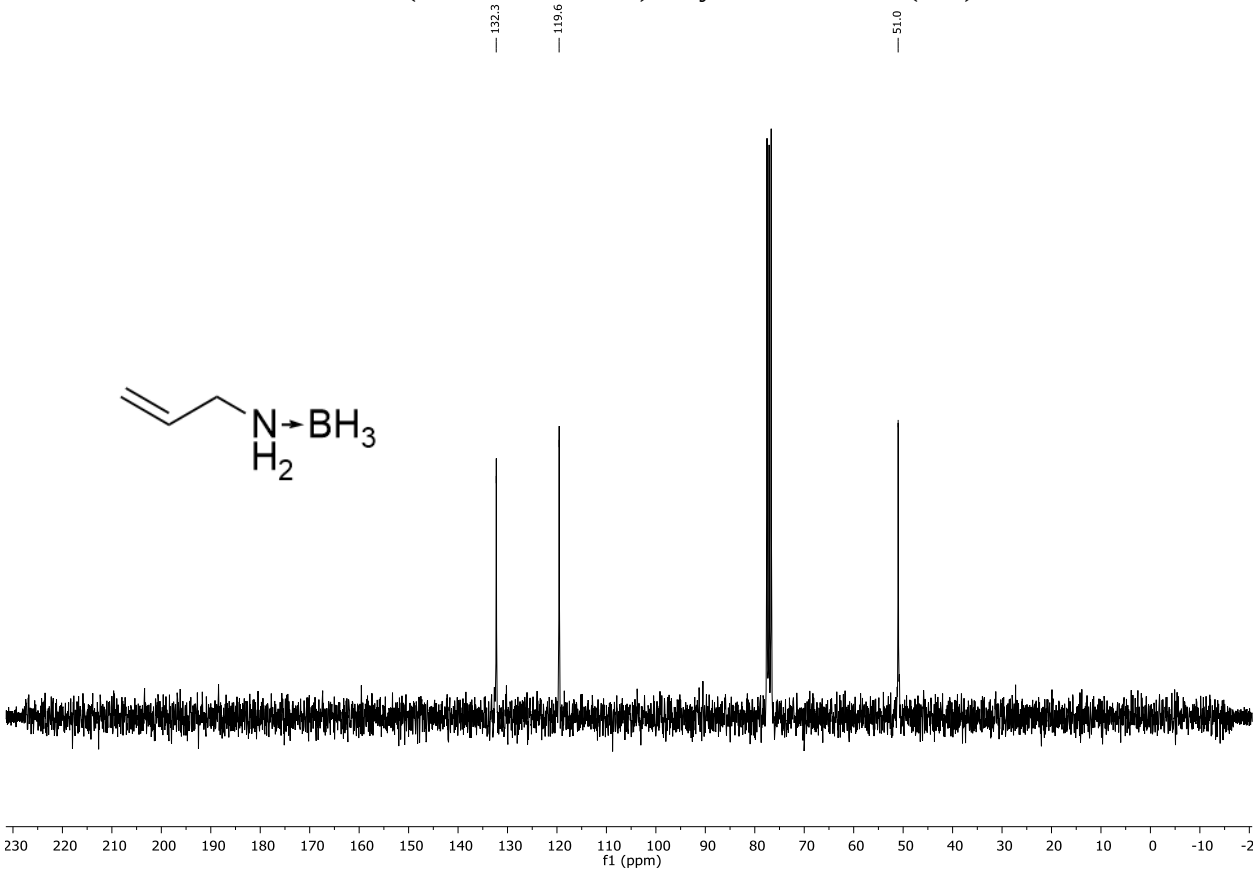
^{13}C NMR (75 MHz, $CDCl_3$) (Dimethylamino)acetaldehyde dimethylacetal-borane (**2ab**)



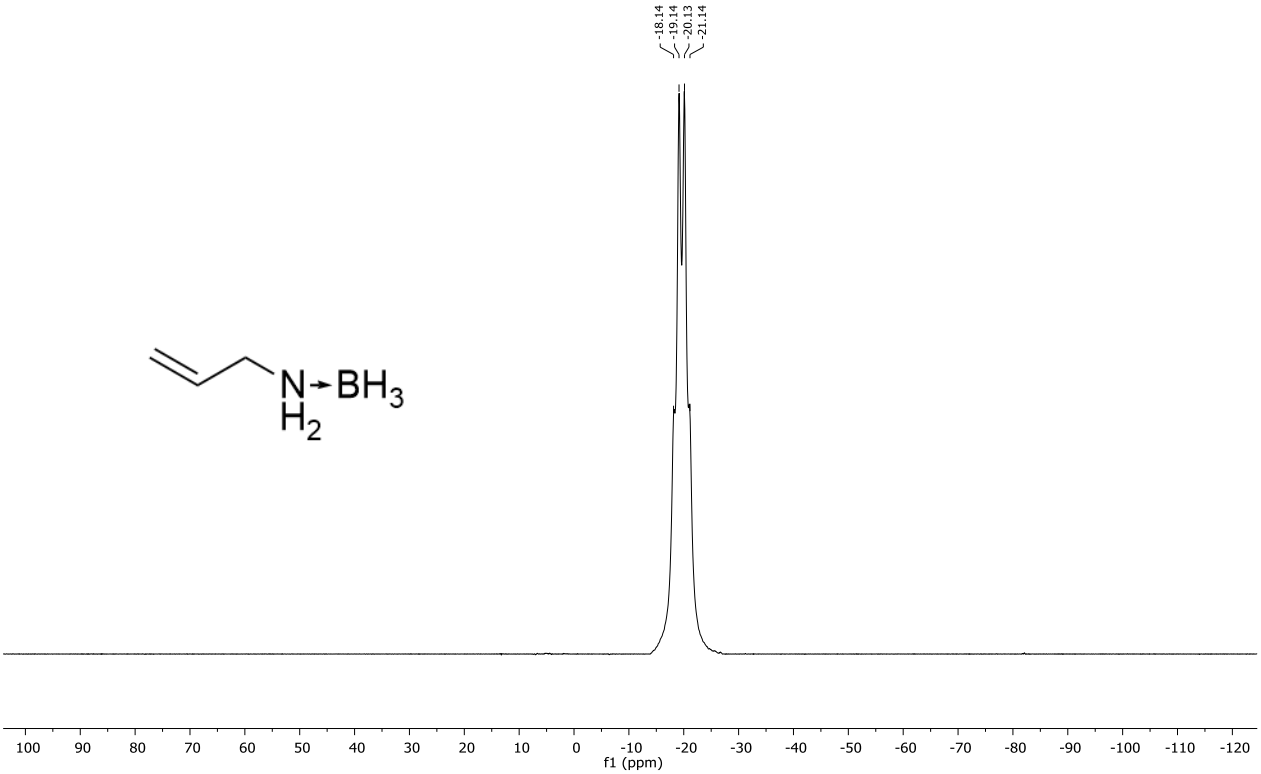
^{11}B NMR (96 MHz, $CDCl_3$) (Dimethylamino)acetaldehyde dimethylacetal-borane (**2ab**)



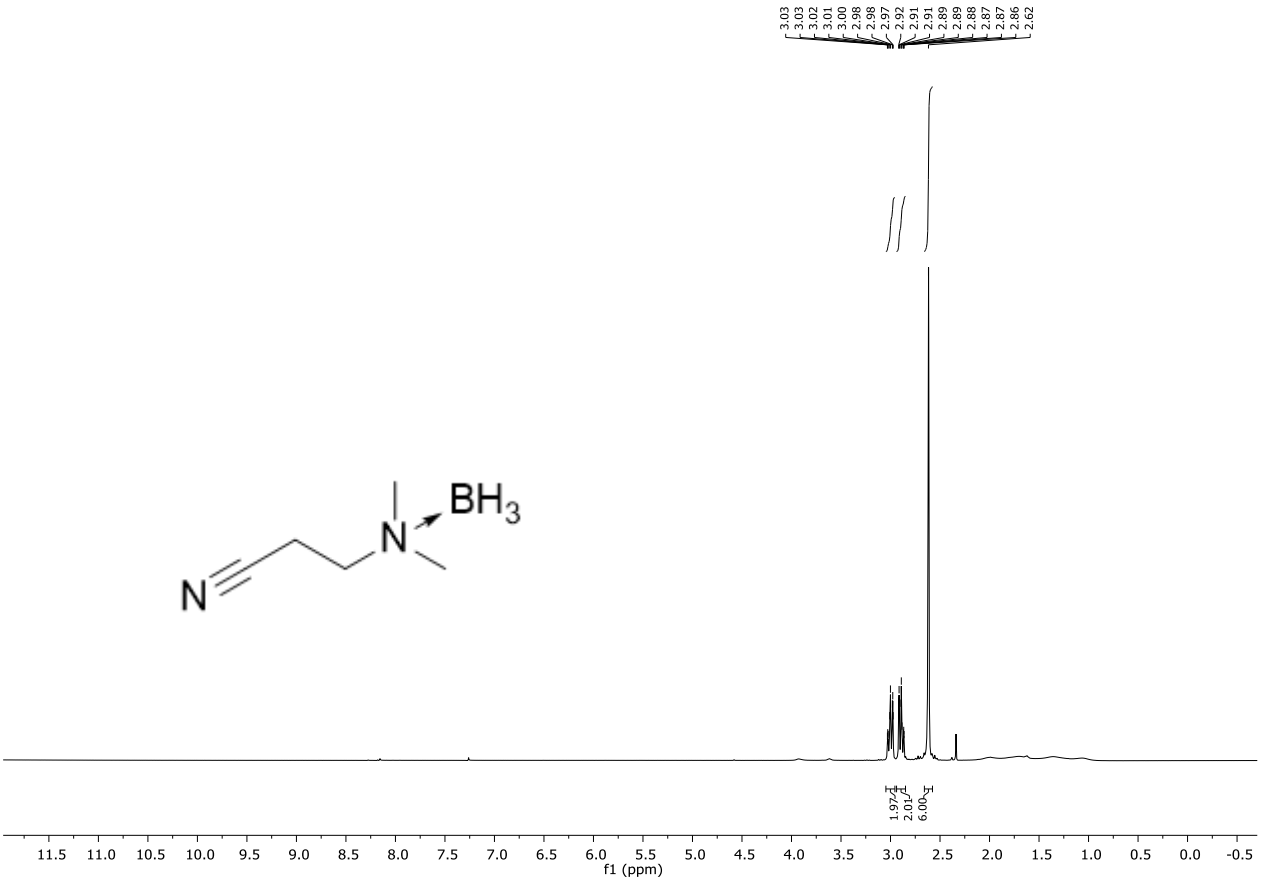
^{1}H NMR (300 MHz, $CDCl_3$) Allylamine-borane (**2ac**)



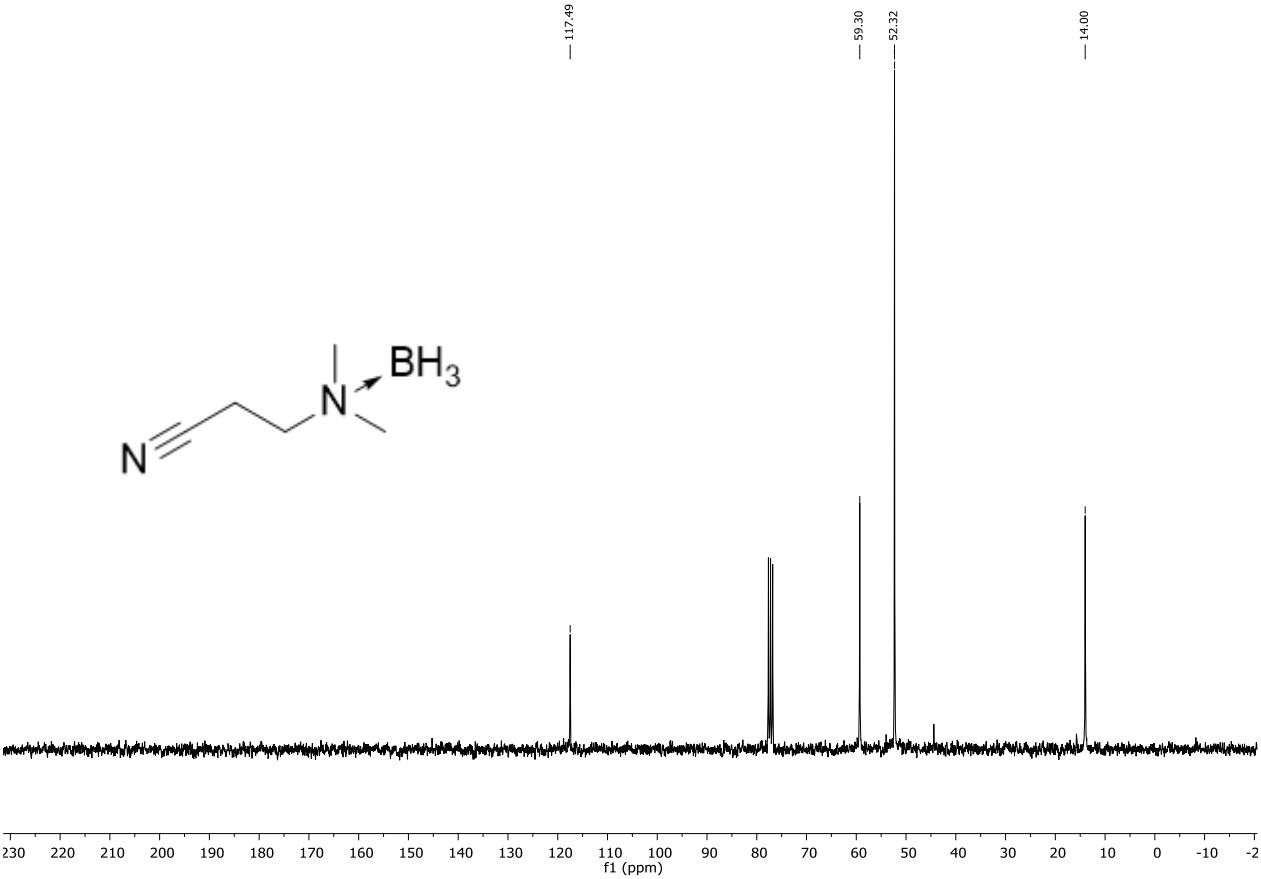
^{13}C NMR (75 MHz, $CDCl_3$) Allylamine-borane (**2ac**)



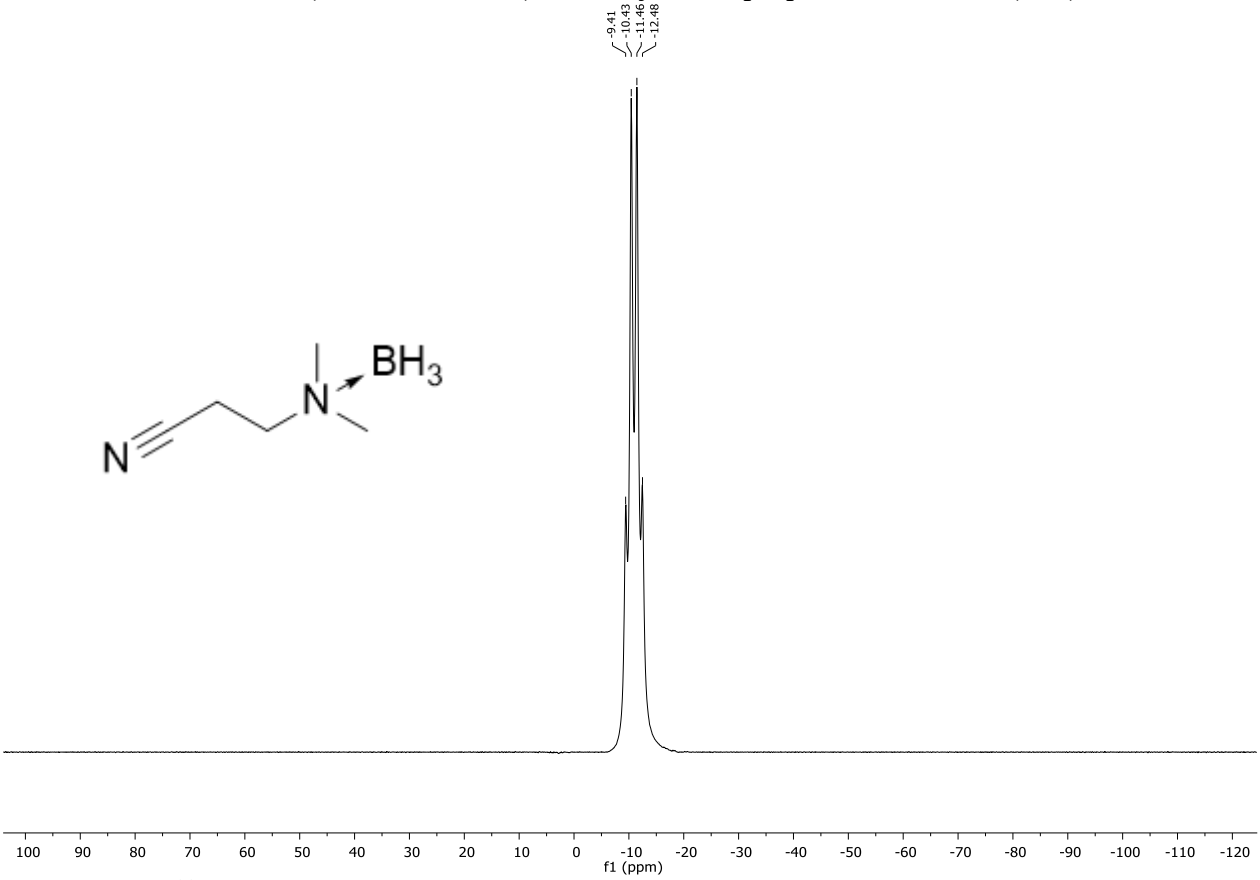
^{11}B NMR (96 MHz, $CDCl_3$) Allylamine-borane (**2ac**)



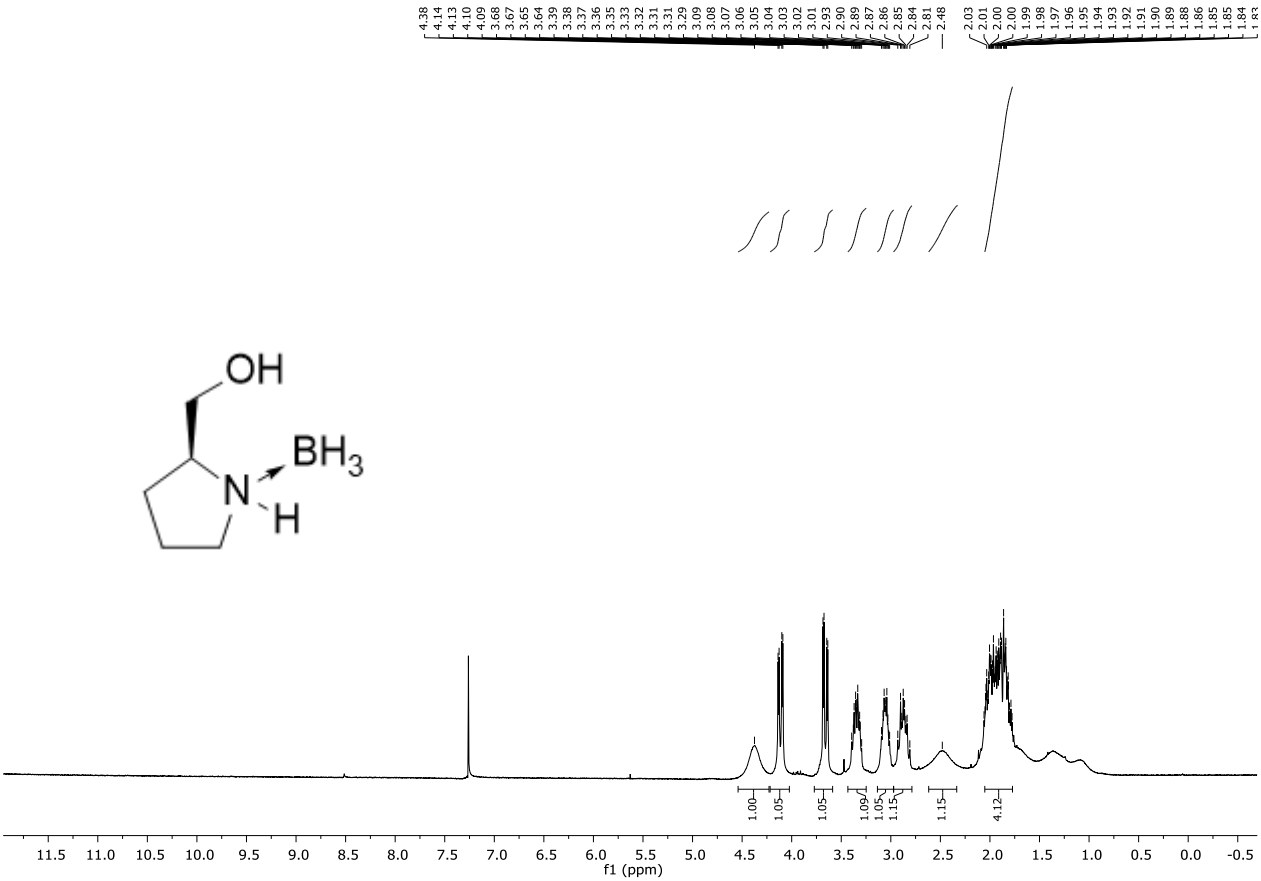
^{1}H NMR (300 MHz, $CDCl_3$) Dimethylaminopropionitrile-borane (**2ad**)



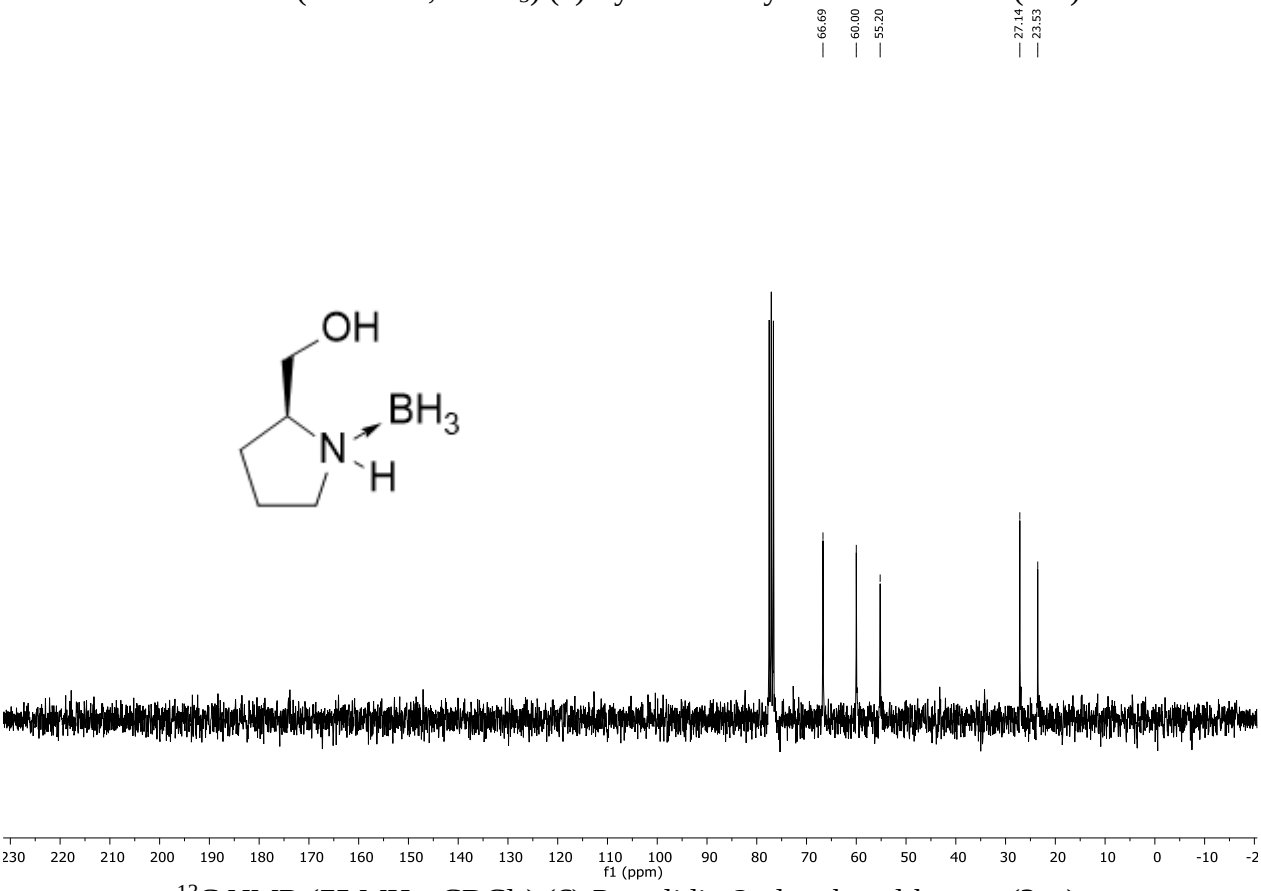
^{13}C NMR (75 MHz, $CDCl_3$) Dimethylaminopropionitrile-borane (**2ad**)



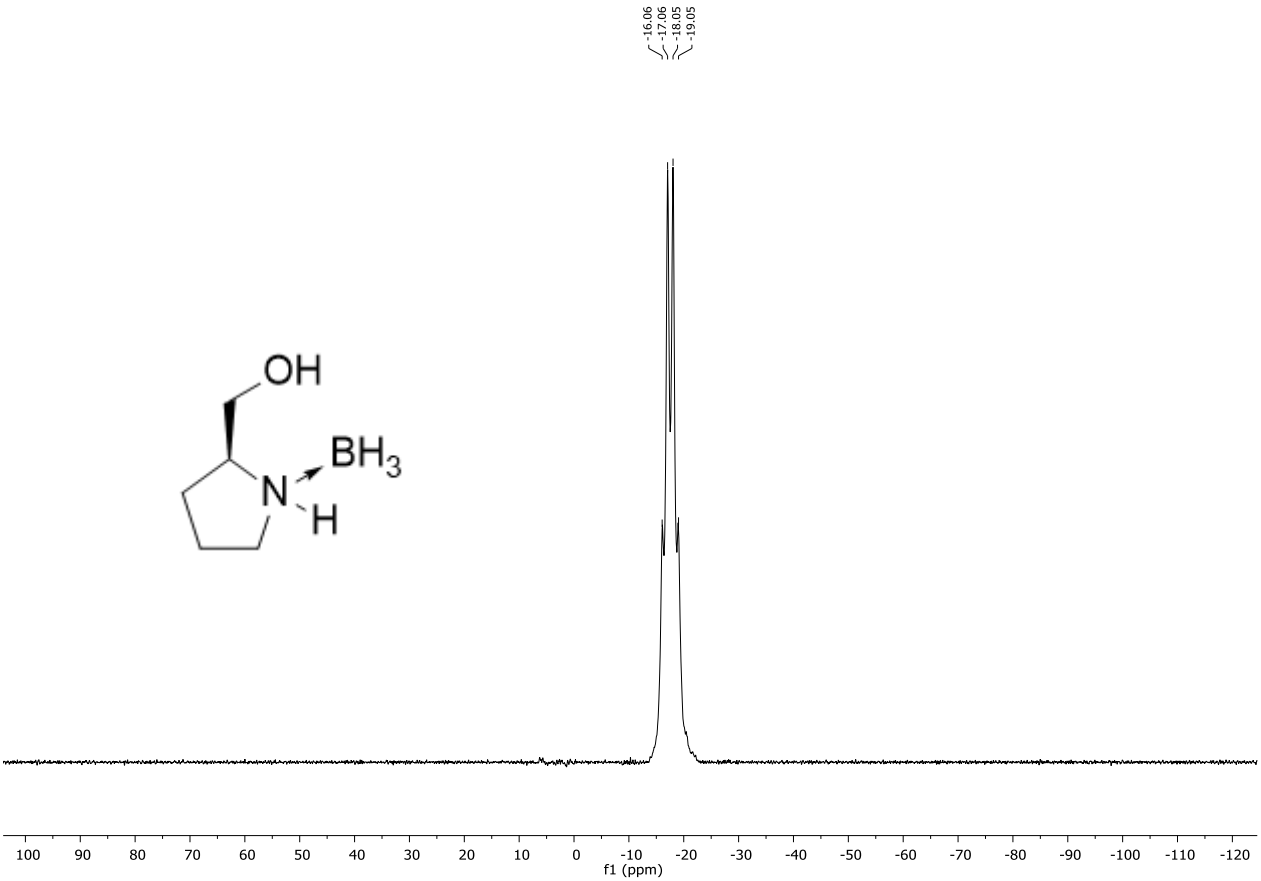
^{11}B NMR (96 MHz, $CDCl_3$) Dimethylaminopropionitrile-borane (**2ad**)



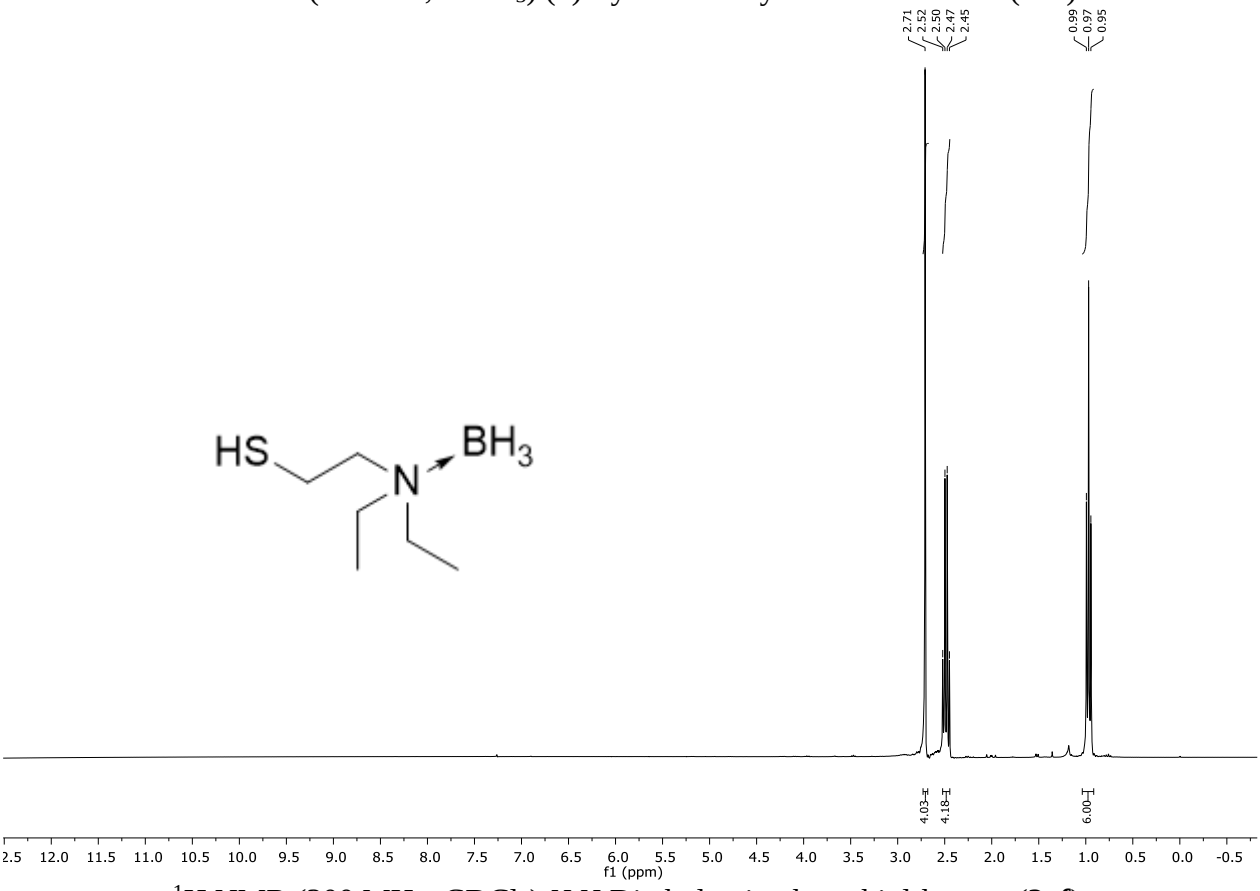
^{1}H NMR (300 MHz, $CDCl_3$) (*S*)-Pyrrolidin-2-ylmethanol-borane (**2ae**)



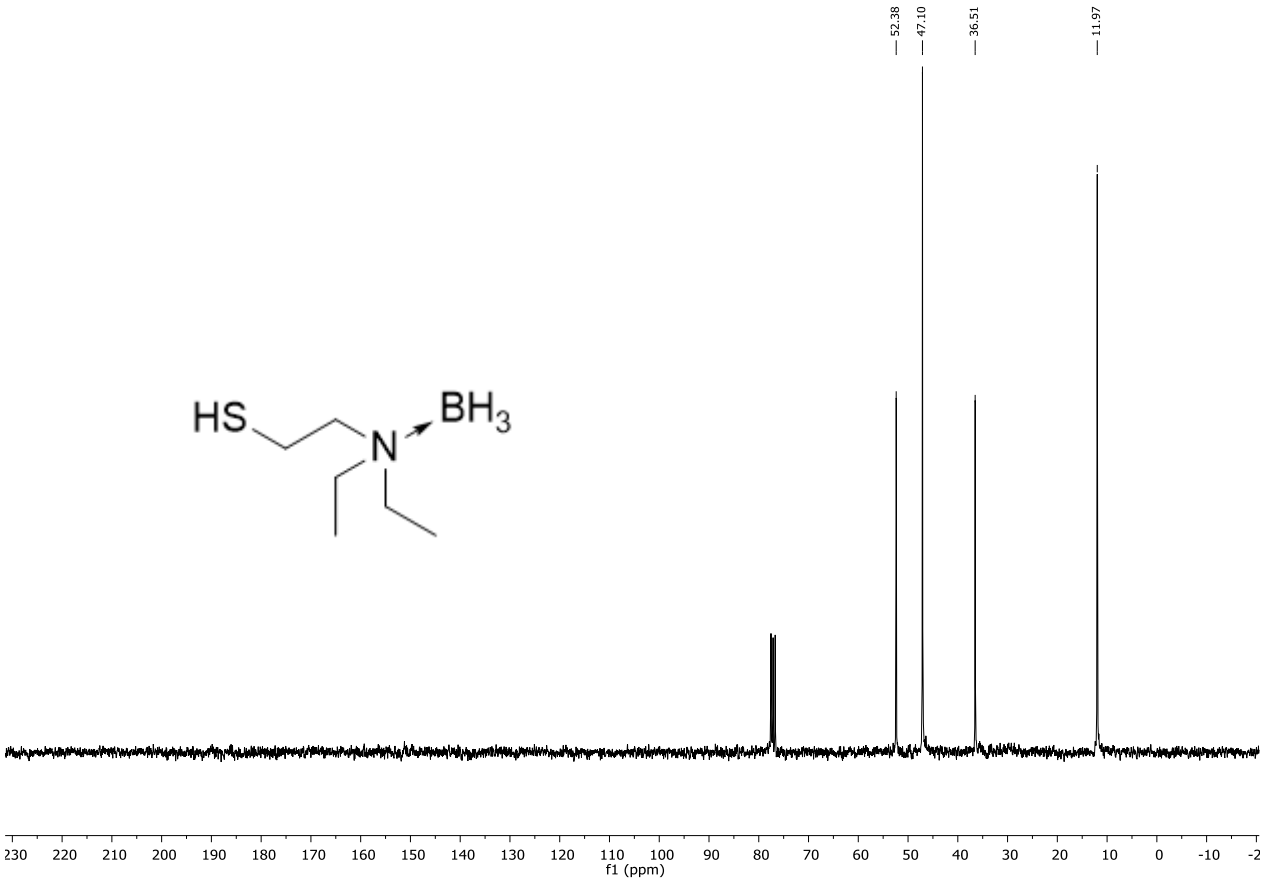
^{13}C NMR (75 MHz, $CDCl_3$) (*S*)-Pyrrolidin-2-ylmethanol-borane (**2ae**)



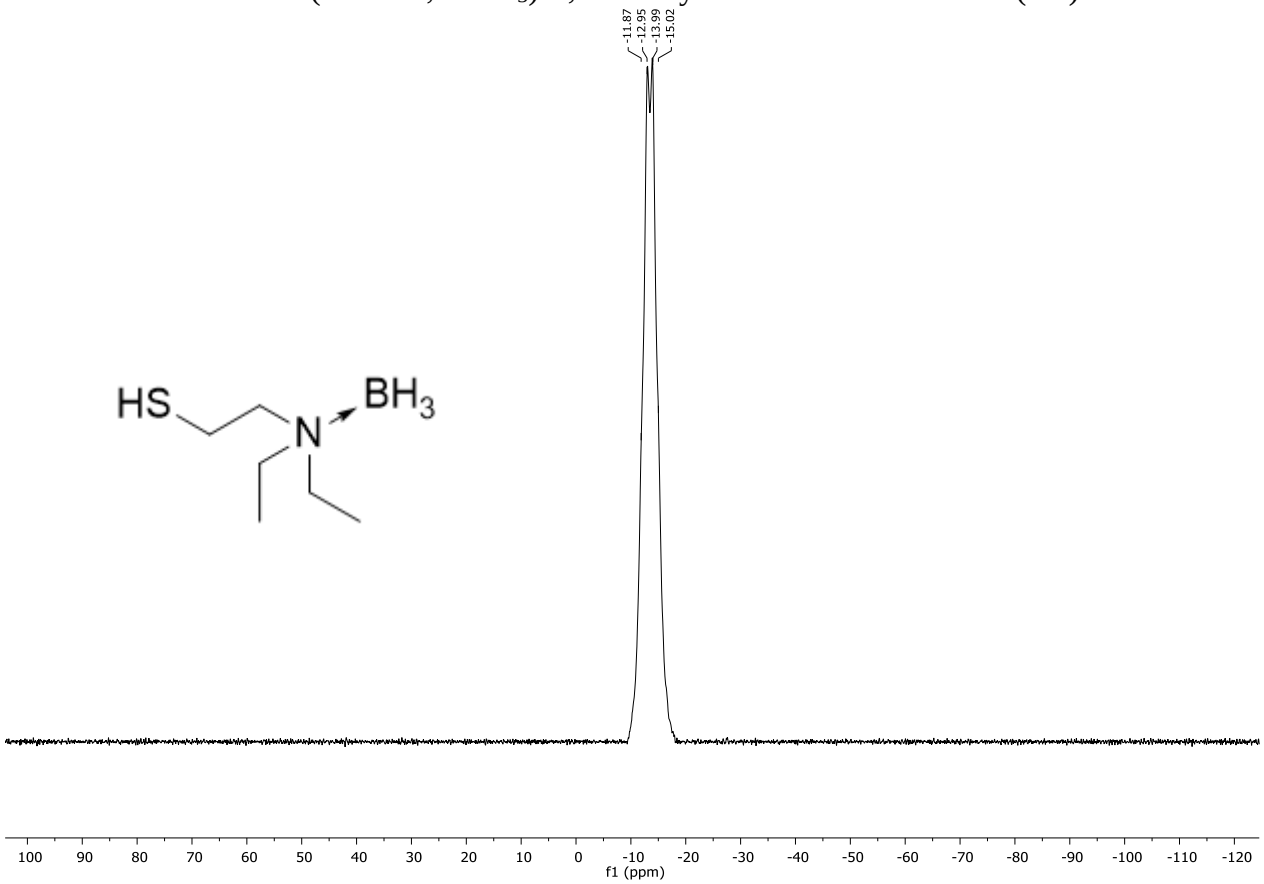
^{11}B NMR (96 MHz, $CDCl_3$) (*S*)-Pyrrolidin-2-ylmethanol-borane (**2ae**)



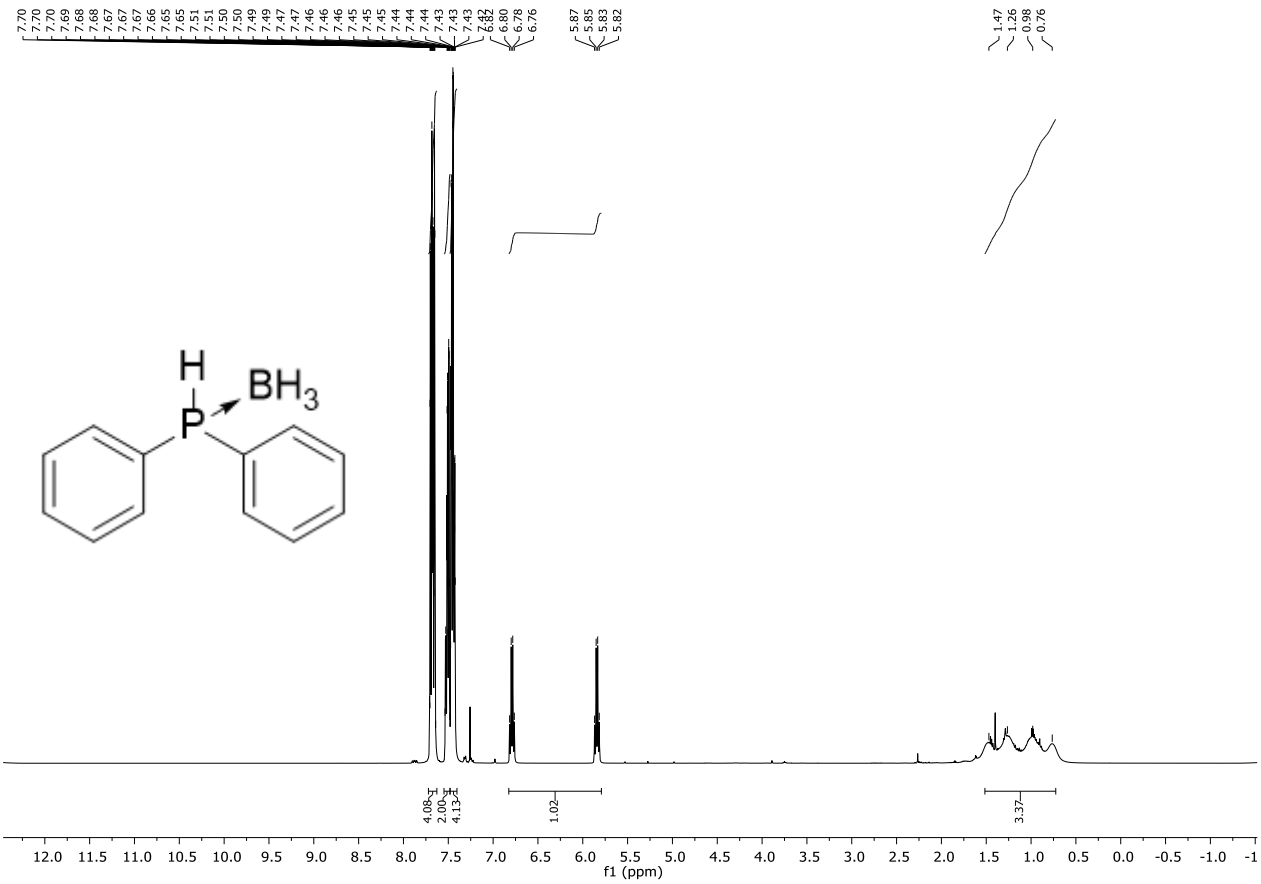
^{1}H NMR (300 MHz, $CDCl_3$) *N*,*N*-Diethylaminethanethiol-borane (**2af**)



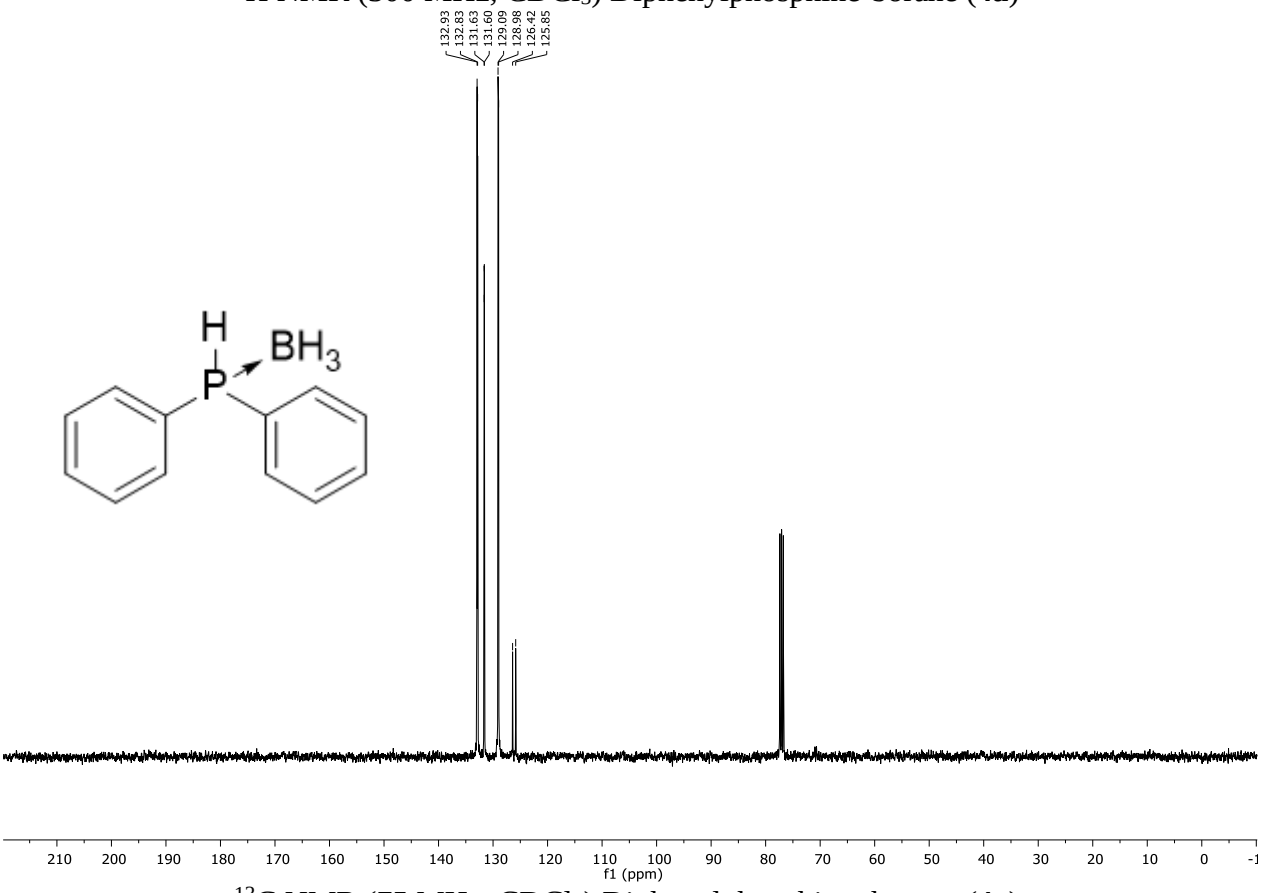
^{13}C NMR (75 MHz, $CDCl_3$) *N*,*N*-Diethylaminethanethiol-borane (**2af**)



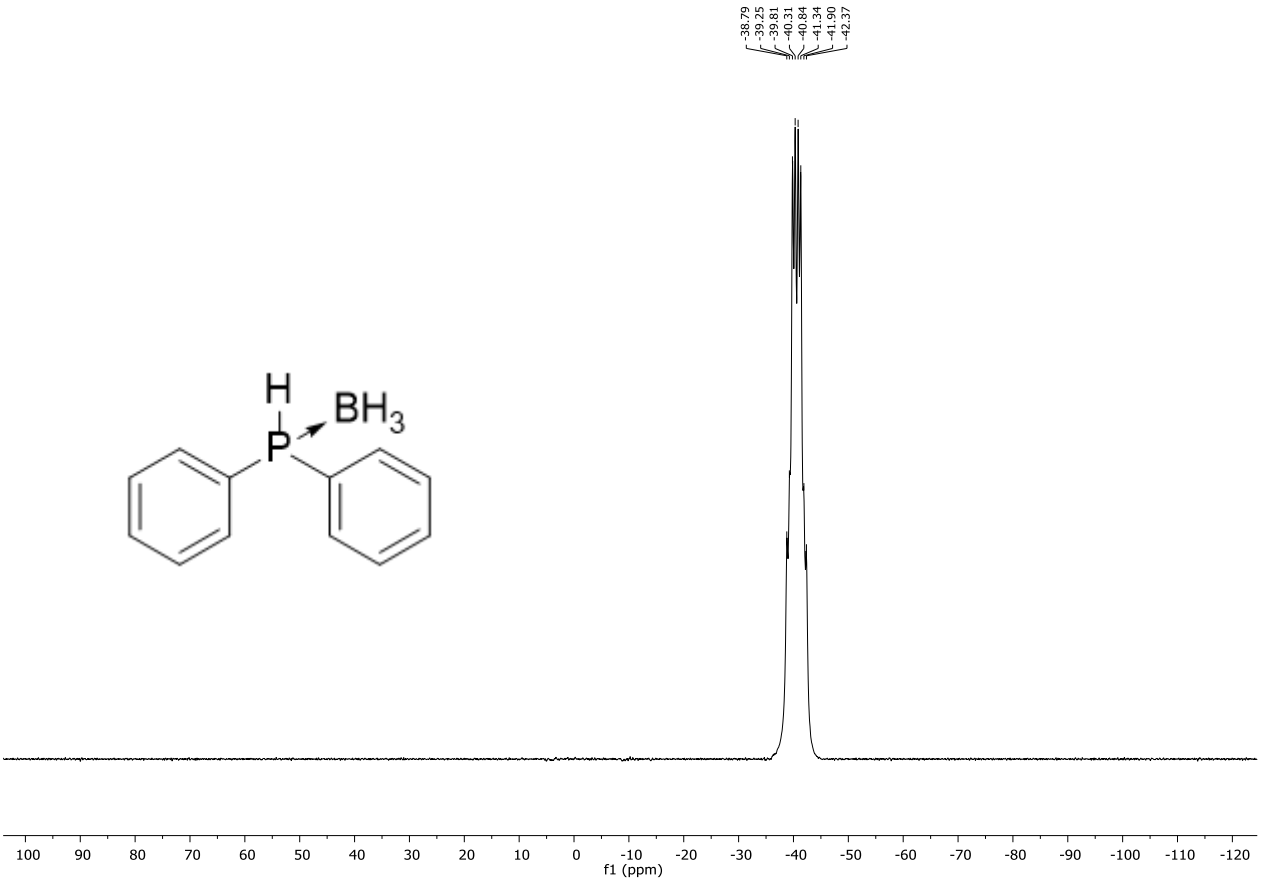
^{11}B NMR (96 MHz, $CDCl_3$) *N*,*N*-Diethylaminethanethiol-borane (**2af**)



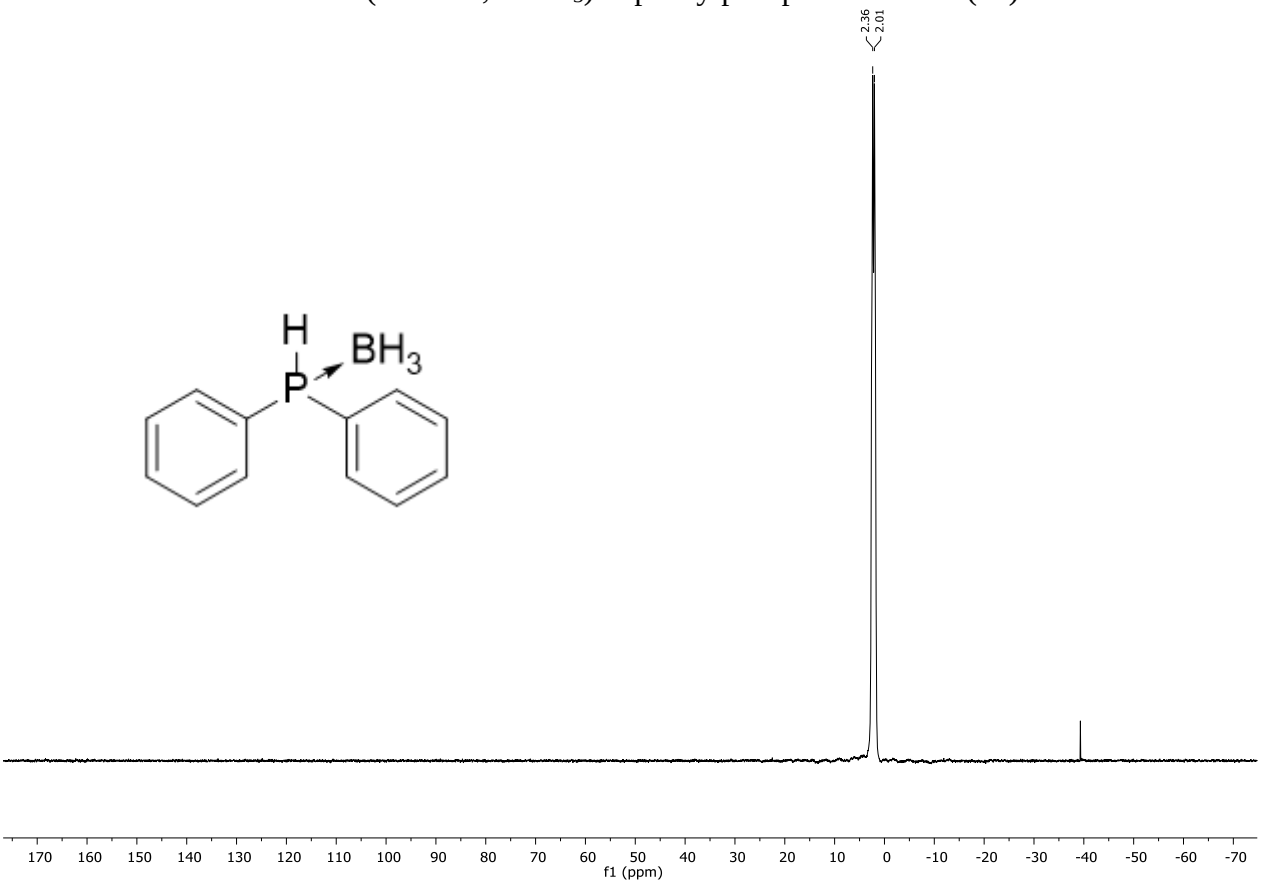
^{1}H NMR (300 MHz, $CDCl_3$) Diphenylphosphine-borane (**4a**)



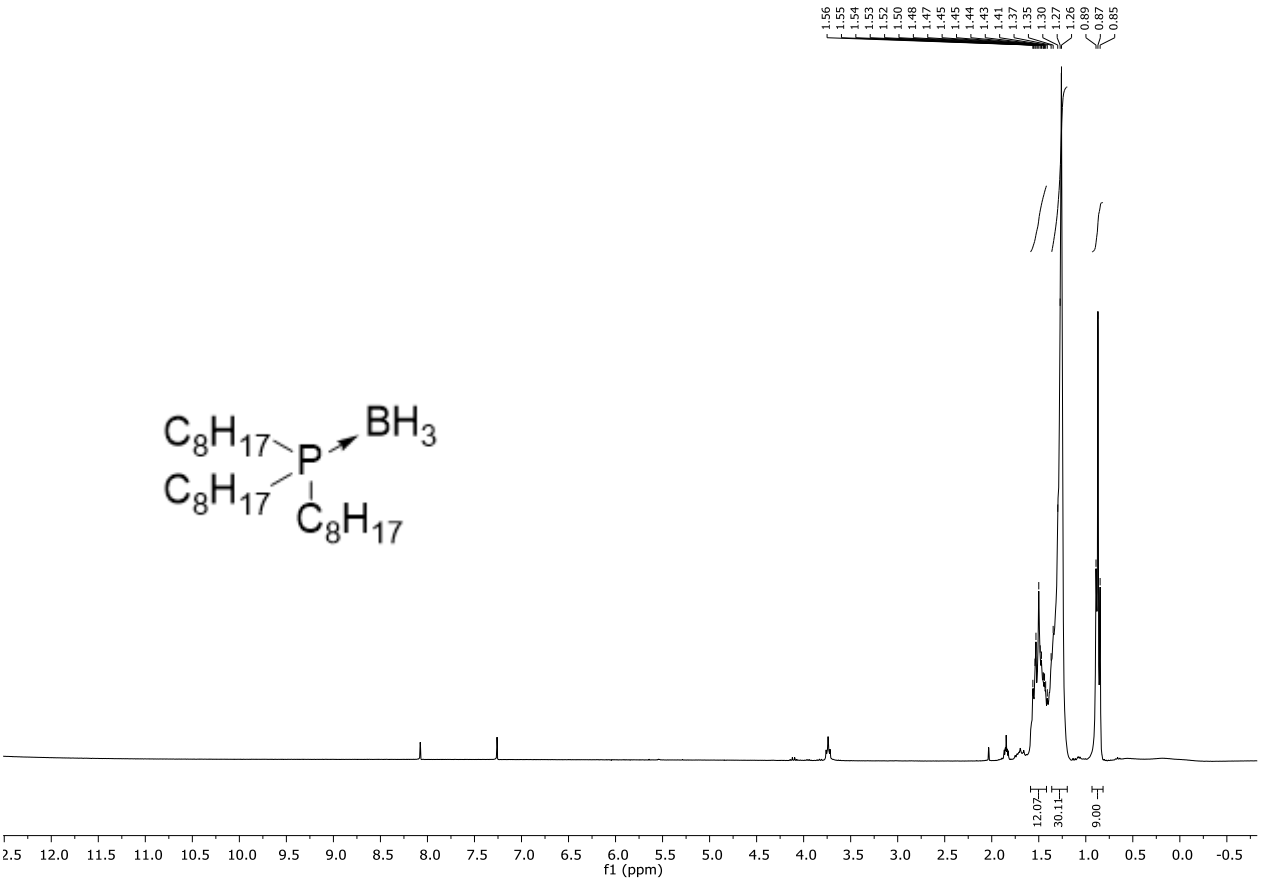
^{13}C NMR (75 MHz, $CDCl_3$) Diphenylphosphine -borane (**4a**)



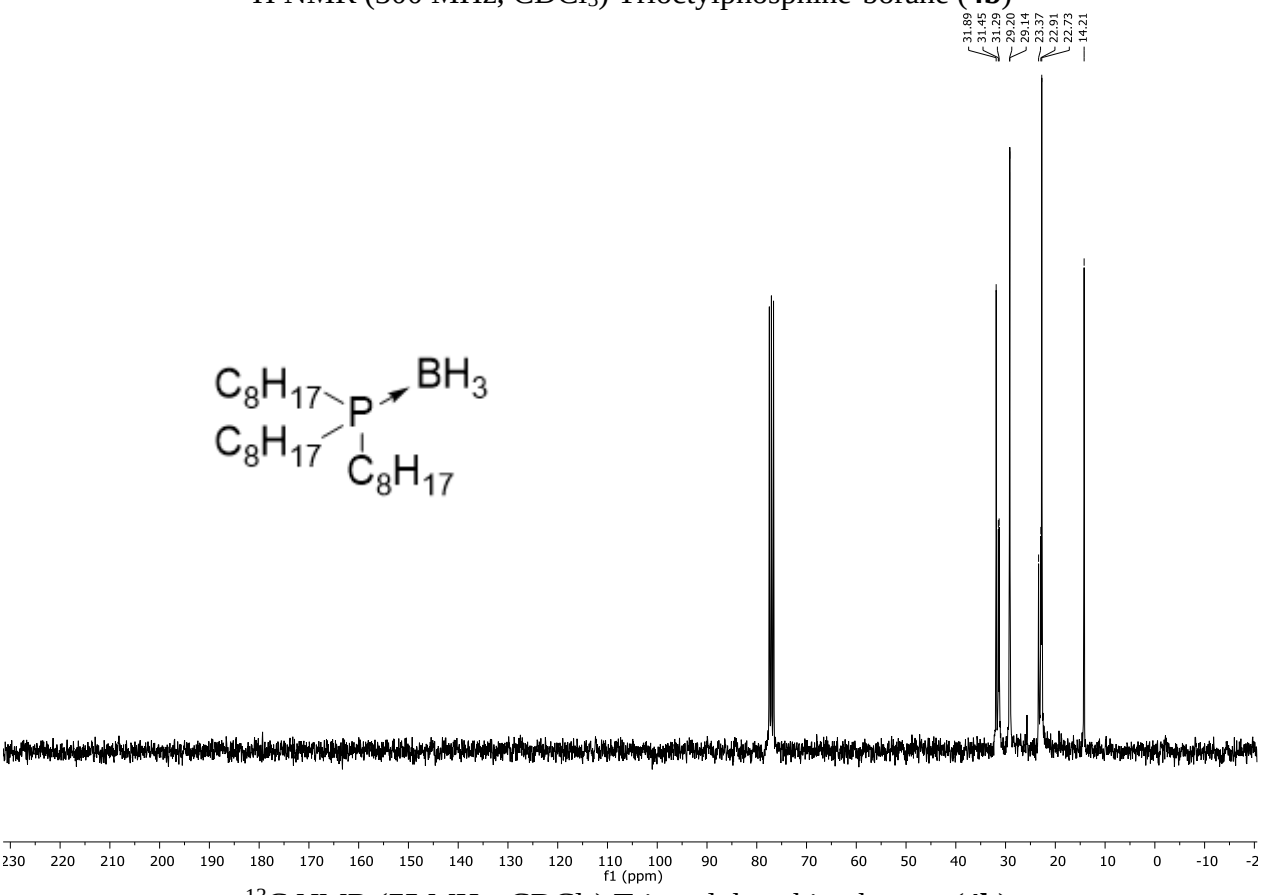
^{11}B NMR (96 MHz, $CDCl_3$) Diphenylphosphine -borane (**4a**)



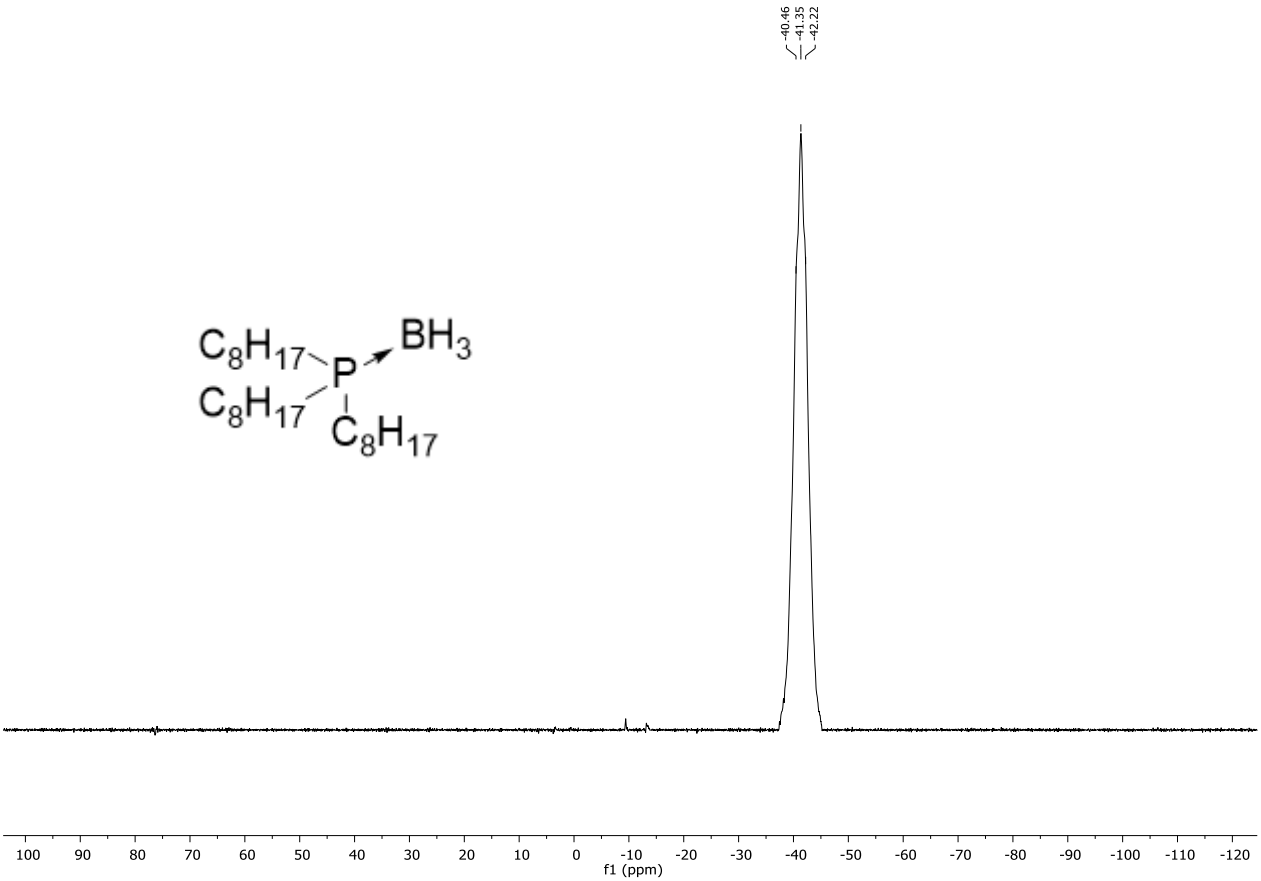
^{31}P NMR (121 MHz, $CDCl_3$) Diphenylphosphine -borane (**4a**)



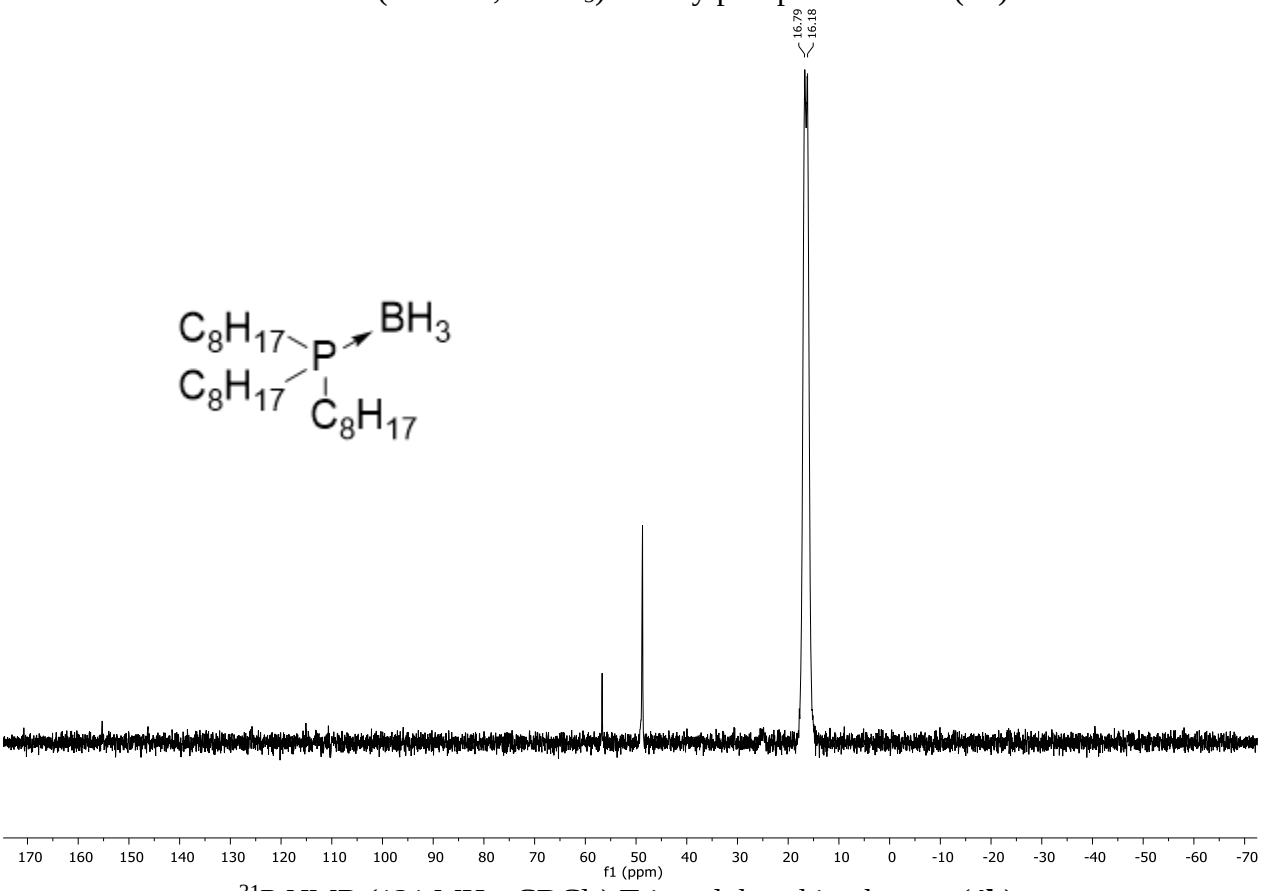
^{1}H NMR (300 MHz, $CDCl_3$) Trioctylphosphine-borane (**4b**)



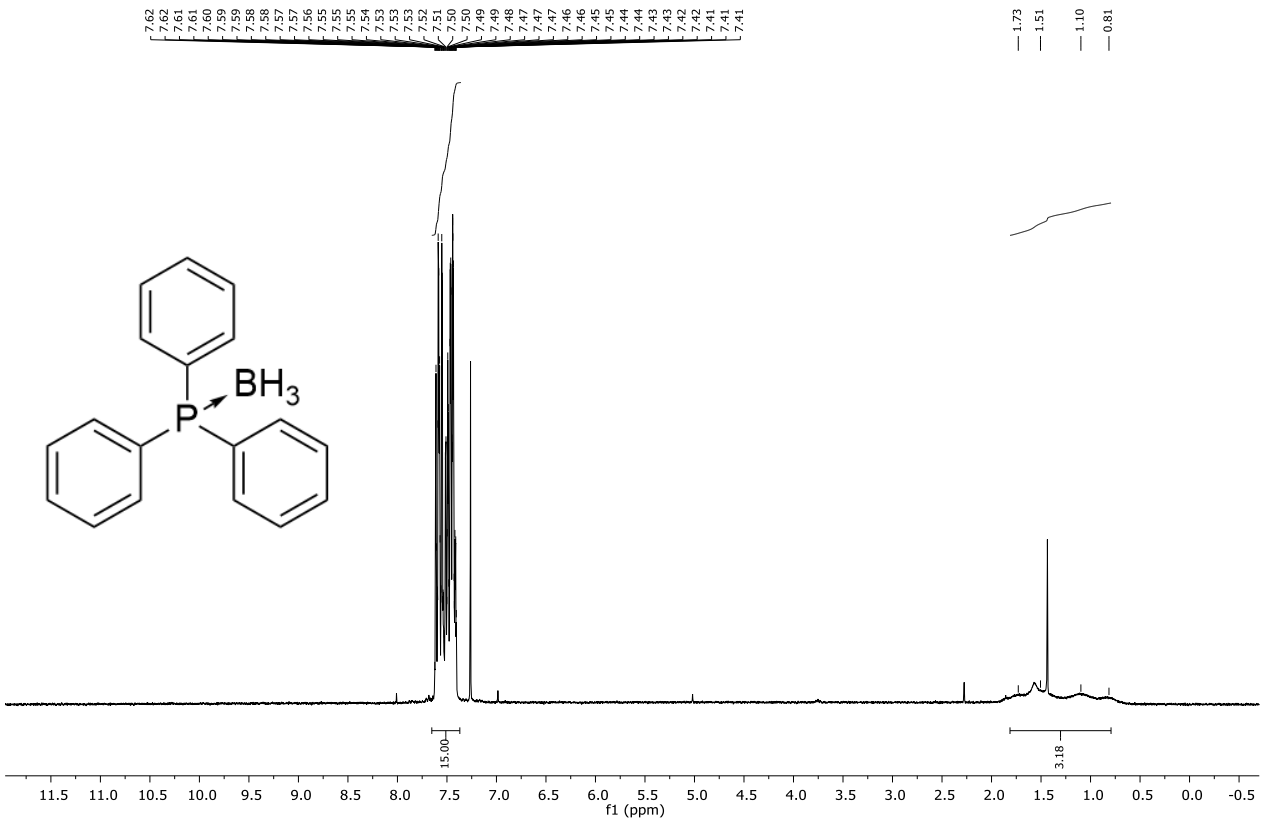
^{13}C NMR (75 MHz, $CDCl_3$) Trioctylphosphine-borane (**4b**)



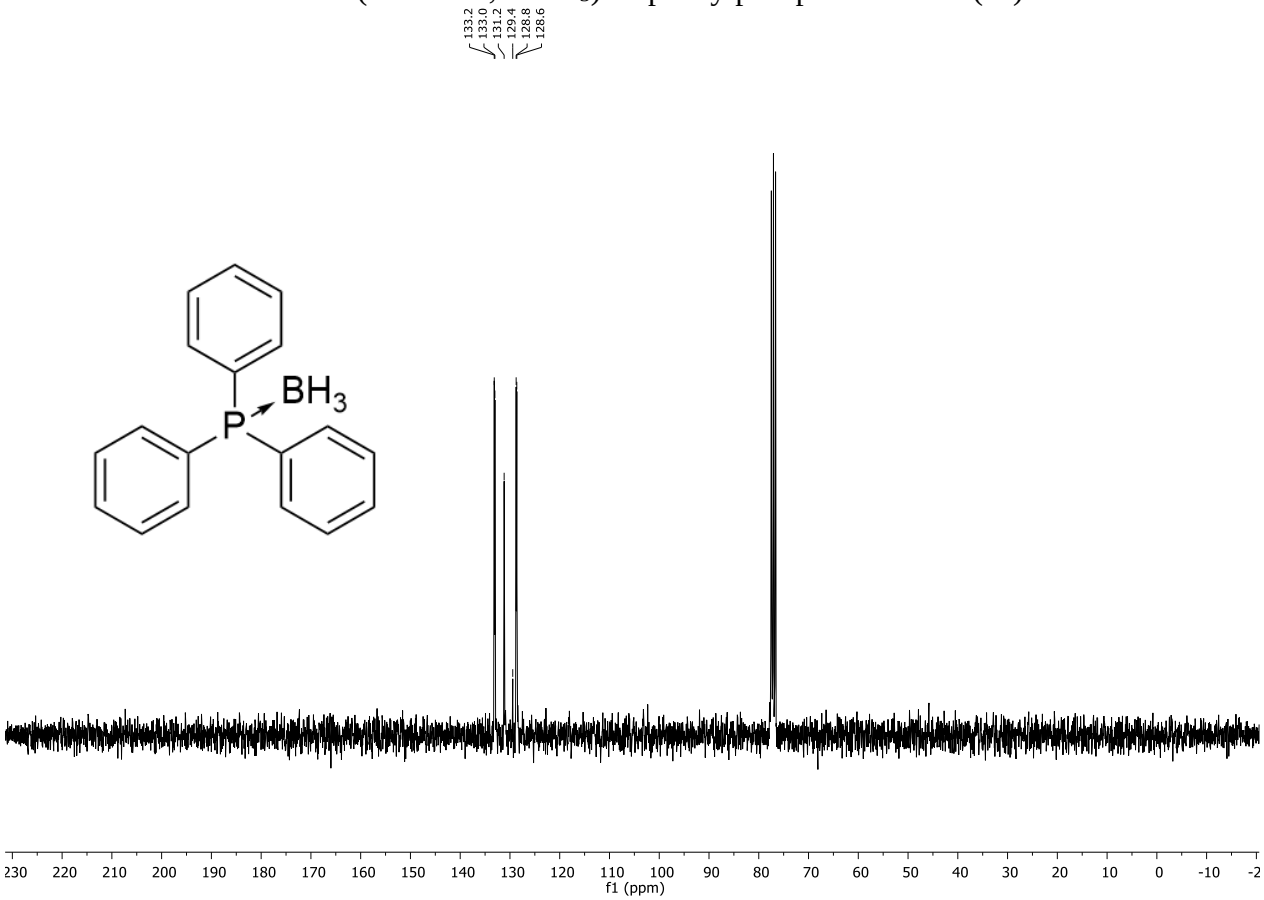
^{11}B NMR (96 MHz, $CDCl_3$) Trioctylphosphine-borane (**4b**)



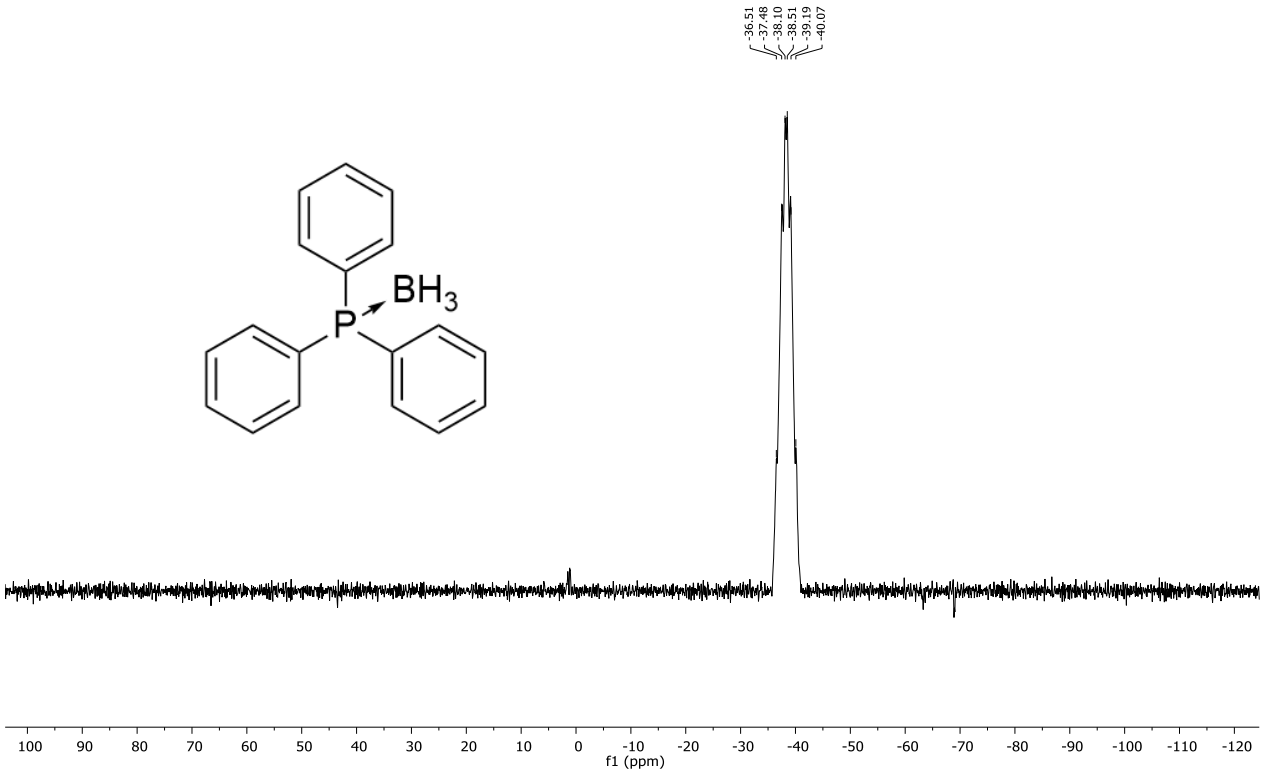
^{31}P NMR (121 MHz, $CDCl_3$) Trioctylphosphine-borane (**4b**)



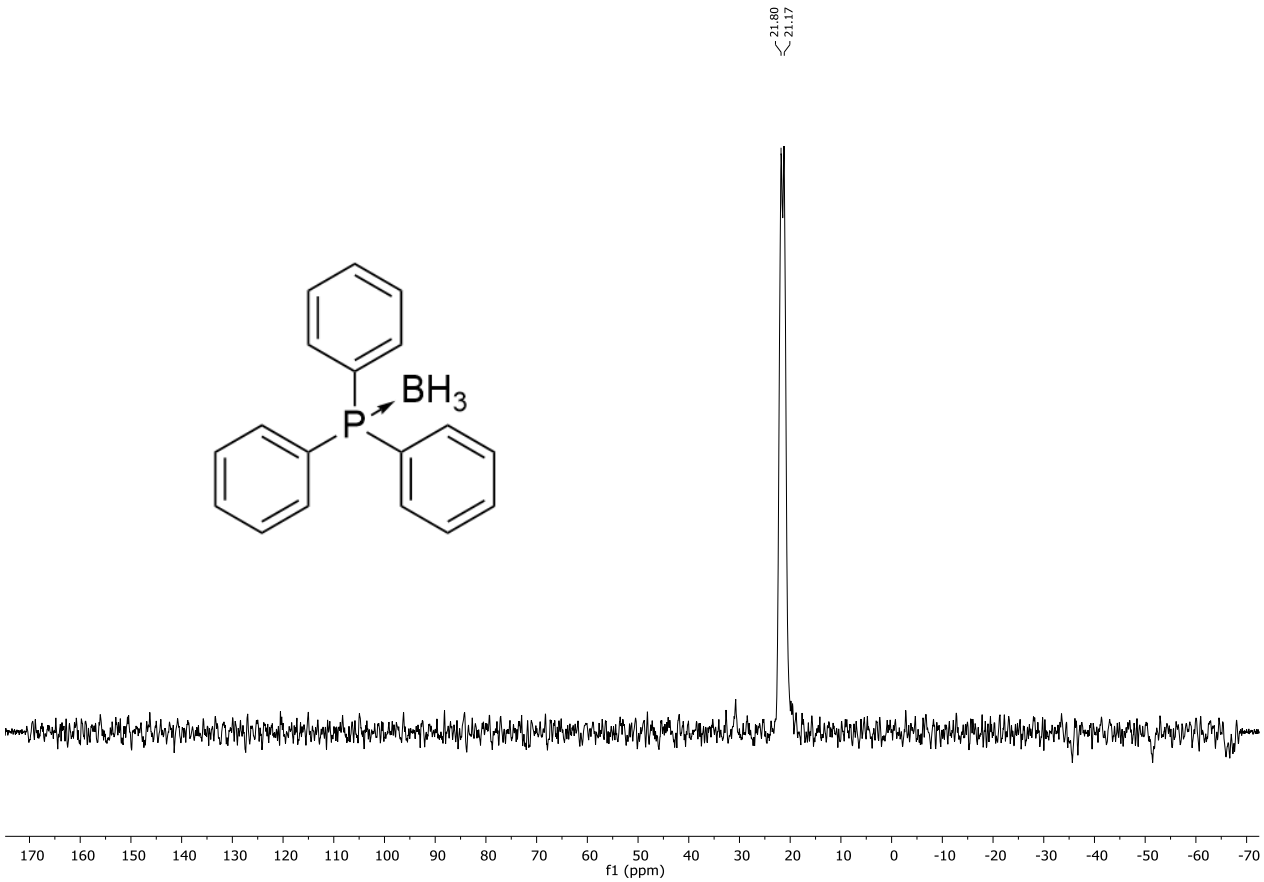
^{1}H NMR (300 MHz, $CDCl_3$) Triphenylphosphine-borane (**4c**)



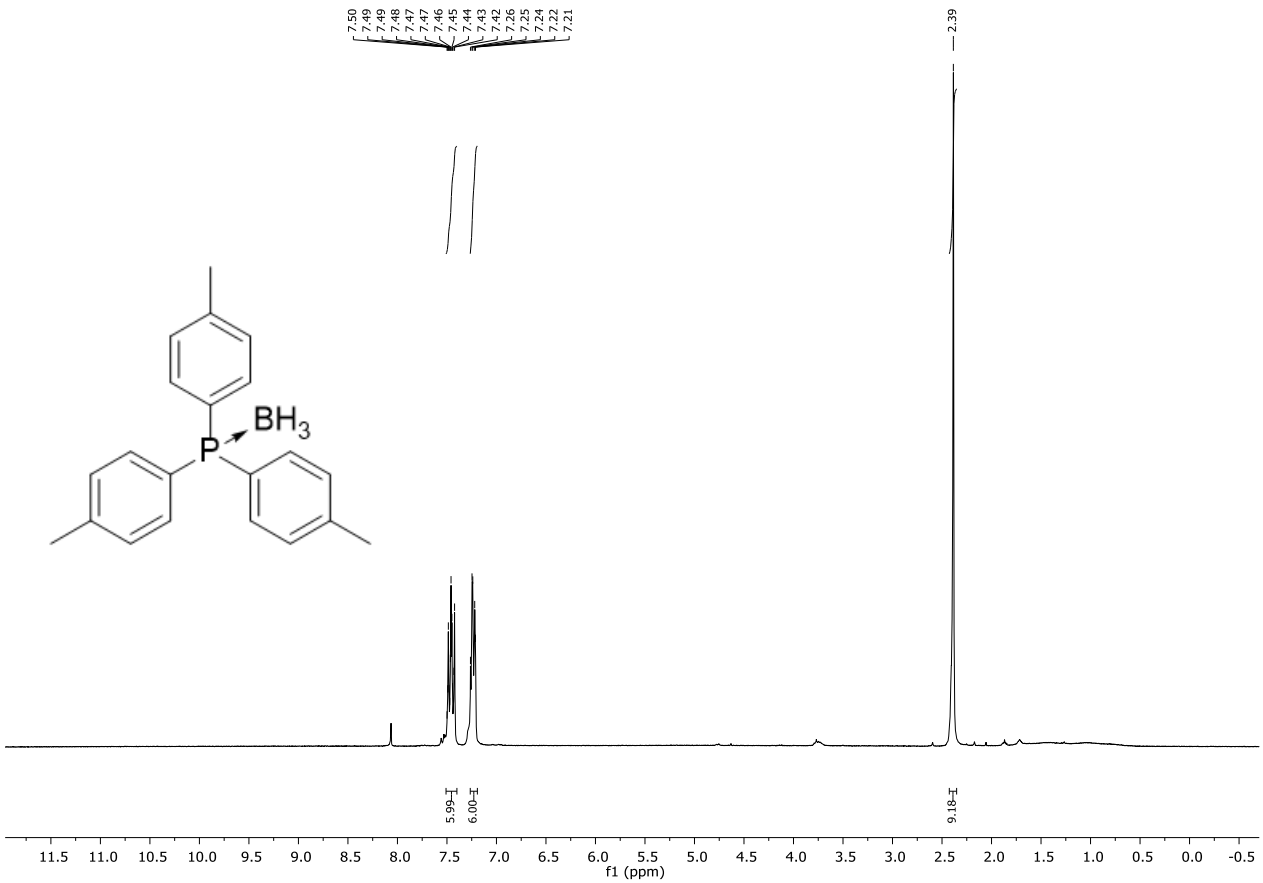
^{13}C NMR (75 MHz, $CDCl_3$) Triphenylphosphine -borane (**4c**)



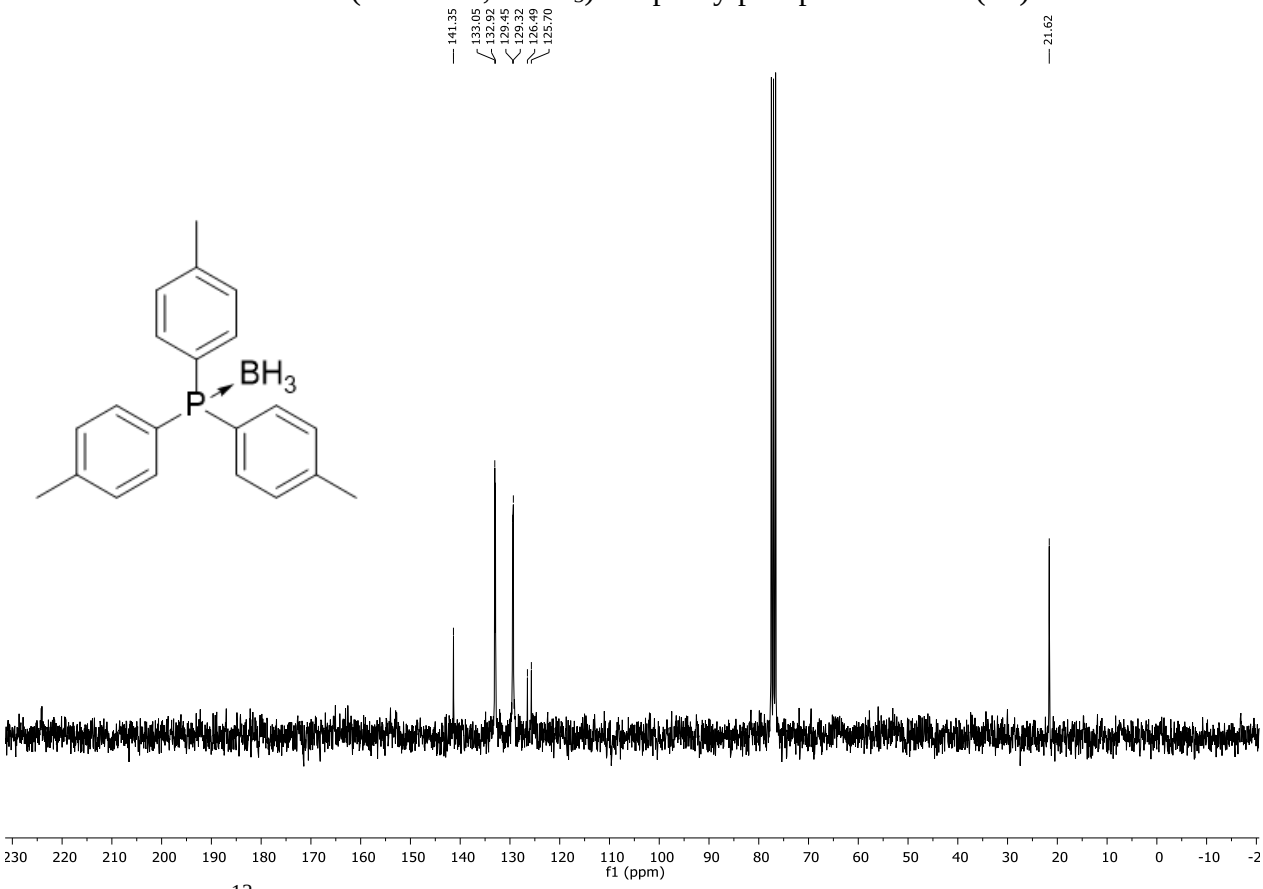
^{11}B NMR (96 MHz, $CDCl_3$) Triphenylphosphine -borane (**4c**)



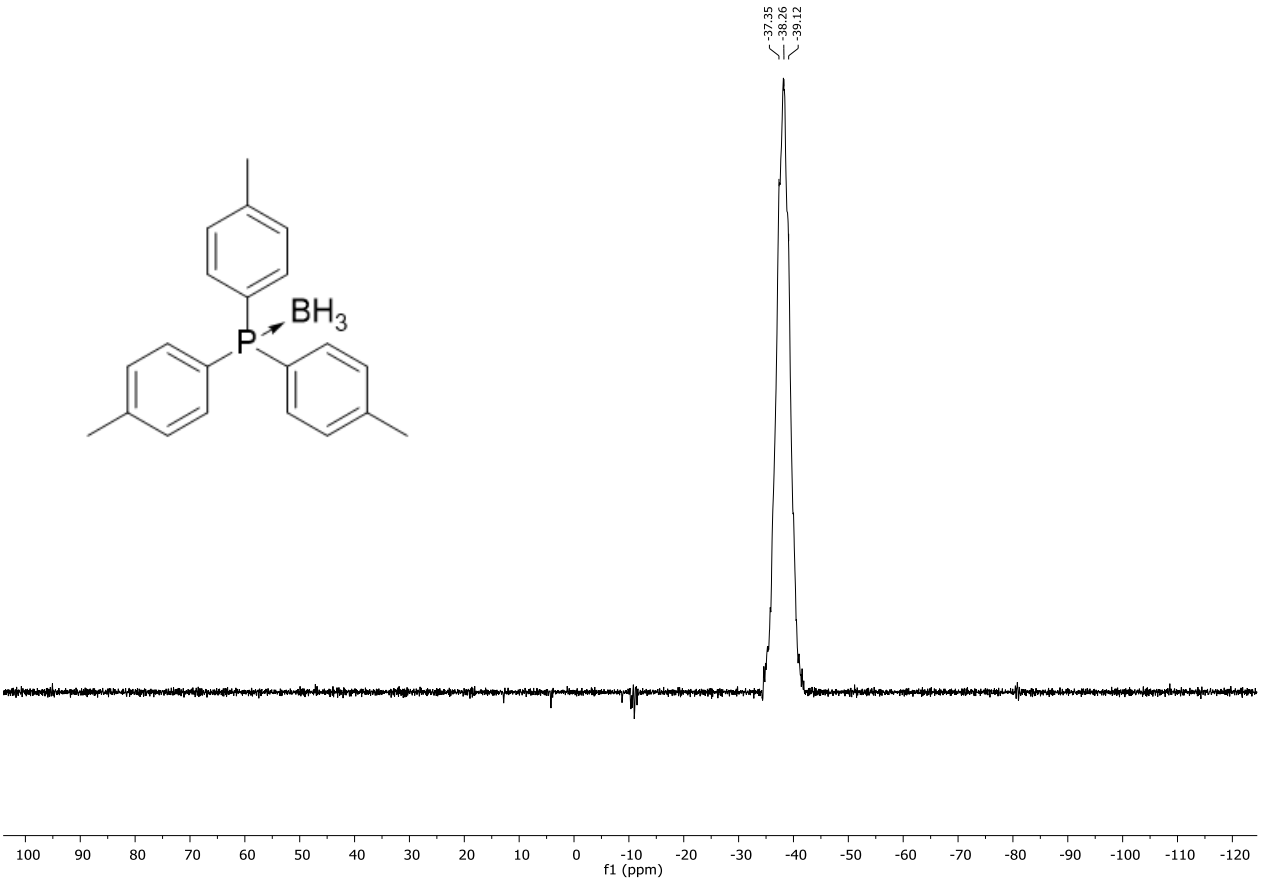
^{31}P NMR (121 MHz, $CDCl_3$) Triphenylphosphine -borane (**4c**)



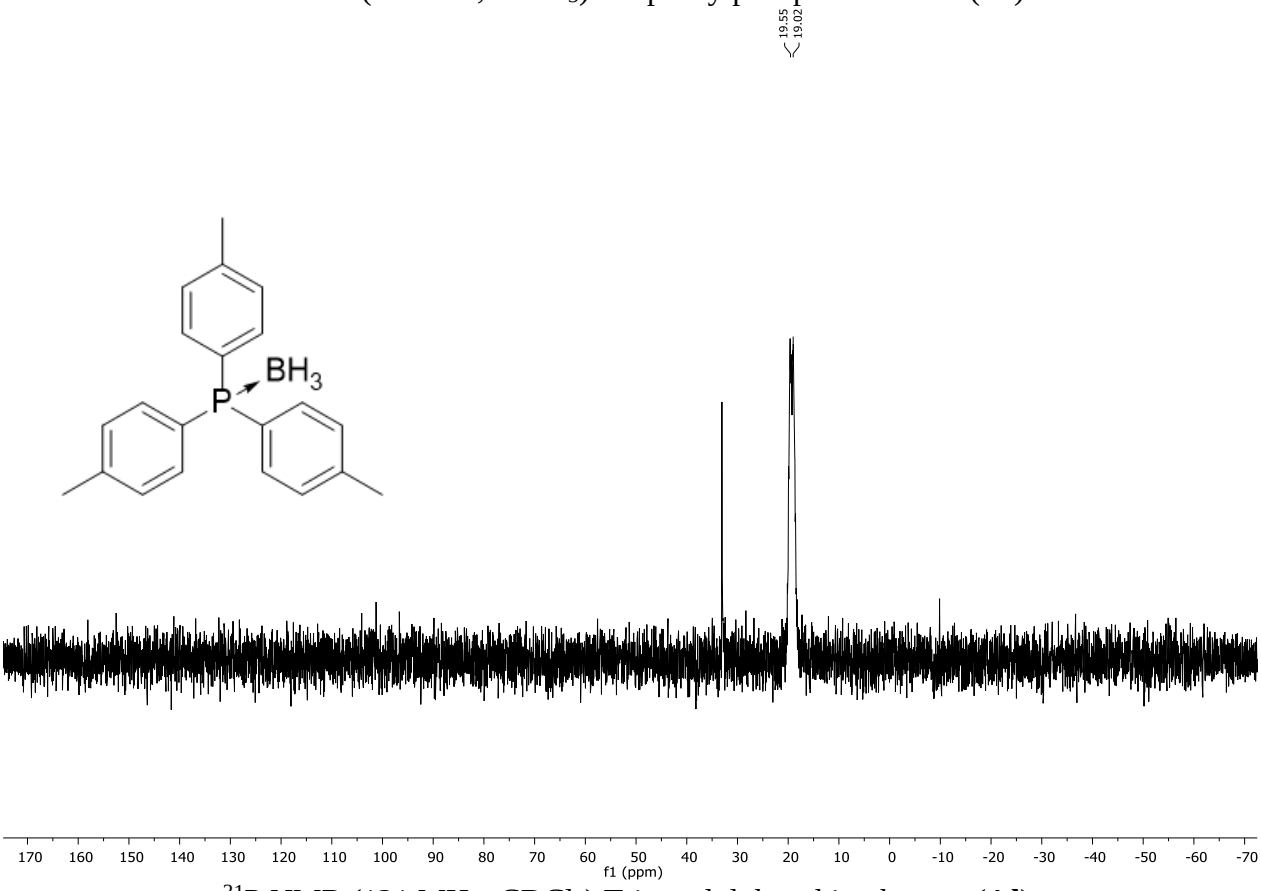
^{1}H NMR (300 MHz, $CDCl_3$) Tri-p-tolylphosphine-borane (**4d**)



^{13}C NMR (75 MHz, $CDCl_3$) Tri-p-tolylphosphine-borane (**4d**)



^{11}B NMR (96 MHz, $CDCl_3$) Tri-p-tolylphosphine-borane (**4d**)



^{31}P NMR (121 MHz, $CDCl_3$) Tri-p-tolylphosphine-borane (**4d**)