

Electronic Supplementary Information

Amine-Boranes Bearing Borane-Incompatible Functionalities: Application to Selective Amine Protection and Surface Functionalization

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General Information:

^{11}B , ^1H , and ^{13}C NMR spectra were recorded at room temperature, on a Varian INOVA 300 MHz or Bruker 400 MHz NMR spectrophotometer. Chemical shifts (δ values) are reported in parts per million relative to $\text{BF}_3\cdot\text{Et}_2\text{O}$ for ^{11}B NMR respectively. Data are reported as: δ value, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, m = multiplet, br = broad) and integration. High resolution mass spectra (HRMS) were recorded on a Thermo Electron Corporation MAT 95XP-Trap spectrometer. Fourier transform infrared spectroscopy (FTIR) was performed using a Thermo Nicolet Nexus FTIR. Atomic force microscopy (AFM) topographic images were obtained on a Veeco Dimension 3100 AFM in tapping mode. Scanning Kelvin probe microscopy (SKPM) was performed using an Asylum Cypher ES atomic force microscope. Thin-layer chromatography was carried out on 0.20 mm silica plates (G/UV₂₅₄) using UV light or Iodine as visualizing agent. Flash chromatography was performed using silica gel 40-63 μm , 60 \AA and dichloromethane-methanol mixture as eluent.

All solvents for routine isolation of products and chromatography were reagent-grade. Tetrahydrofuran (THF, ACS grade containing 0.004% water and 0.025% BHT) was purchased from Fisher-Scientific. Sodium borohydride (powder, purity >99% by hydride estimation¹) was purchased in bulk from Dow Chemical Co. (Rohm and Haas). Sodium bicarbonate (ACS reagent, Macron), sodium carbonate (Anhydrous, Macron), sodium bisulfite (Purified, Mallinckrodt), sodium hydrogen sulfate (tech. grade, Sigma-Aldrich), potassium bicarbonate (ACS, Sigma-Aldrich), dipotassium hydrogen phosphate (Anhydrous, Fluka), and potassium dihydrogen phosphate (Assay >99.5%, Fluka) were purchased from the respective commercial sources and powdered prior to use. Amines used were purchased from commercial sources. Methyl 6-aminohexanoate² (**1y**), *N*-(3-aminopropyl)benzamide³ (**1z**), and 3-(pyridin-2-ylamino)propanol⁴ (**3**) was prepared in accordance with literature reports. 2-Diethylaminoethanethiol⁵ (**1w**) and 2-(4-nitrophenyl)ethylamine⁶ (**1ab**) were synthesized from their hydrochloride salts. Liquid amines were distilled while solid amines were used without any purification. Amine-boranes **2a-2o**, **2q**, and **2s** have been reported in prior literature.^{7,8,9,10,11} The 99.99% gold pellets purchased from R.D. Mathis Company were used as evaporation material for preparation of gold films. 6,13-Bis(triisopropylsilylethynyl)pentacene was purchased from Sigma-Aldrich and used without purification.

Table S1. Optimization of reaction conditions for the preparation of Et₃N-BH₃ from NaBH₄ and Et₃N^a

Entry	Salt	NaBH ₄ :Salt (equiv.)	Time (h)	Yield ^b (%)
1	NaHCO ₃	1:2	4	77
2	NaHCO ₃	1:1	24 ^c	65
3	Na ₂ CO ₃	1:2	48 ^c	20
4	NaHSO ₃	1:2	24 ^c	70
5	NaHSO ₄	1:2	24	Trace
6	KHCO ₃	1:2	24	49
7	K ₂ HPO ₄	1:2	24 ^c	14
8	KH ₂ PO ₄	1:1	24 ^c	47
9	KH ₂ PO ₄	1:2	24 ^c	30
10 ^d	NaHCO ₃	1:2	48 ^c	38
11 ^d	KHCO ₃	1:2	48 ^c	42
12	NaHCO₃	1:2	4^e	79
13	NaHCO ₃	1:2	4 ^f	78
14	NaHCO ₃	1:2	6 ^g	74

^aReactions were performed using 5 mmol each of NaBH₄ and Et₃N and the corresponding equivalents of salt in 2.5 mL of THF at rt open to air. Water was added as a 3.6% solution in THF (2.5 mL). ^bYields of isolated product. ^cNaBH₄ was present when reaction contents filtered (by ¹¹B NMR spectroscopy). ^dNaBH₄ replaced with KBH₄ (5 mmol) ^e2 M THF. ^f4 M THF. ^g4 M Diethyl ether.

Conclusion: On the basis of the above results (Table S1), 1:2:1 ratio of equivalents of sodium borohydride to sodium bicarbonate to amine in 2 M THF with respect to the amine (entry 12, highlighted in bold) was found to provide best yields of the product Et₃N-BH₃ (**2a**).

Table S2. Effect of equivalents of water on the preparation of Et₃N-BH₃^a

Entry	Salt	Water (equiv.)	Time (h)	Yield ^b (%)
1	NaHCO ₃	None	48	Trace
2	NaHCO ₃	0.5	24	81
3	NaHCO ₃	1	4	79
4	NaHCO₃	2	1	82
5	NaHCO ₃	4	0.5	66
6	NaHCO ₃	1:1 (THF:H ₂ O)	1	NP ^c

^aReactions were performed using 5 mmol each of NaBH₄ and Et₃N and 10 mmol of NaHCO₃ in 2 M THF at rt open to air. Water was added dropwise as a 14.4% v/v solution in THF. ^bYields of isolated product. ^cNP = No Product.

Conclusion: On the basis of the above results (Table S2), addition of 2 equivalents of water as a 14.4% v/v solution in THF was found to provide best results (entry 4, highlighted in bold).

Table S3. Effect of NaBH₄ stoichiometry on reaction conversion^a

Entry	NaBH ₄ :DMAP (equiv.)	Time (h)	Yield ^b (%)	1b:2b ^c
1	1:1	8	99	20:80
2	1.25:1	4	99	7:93
3	1.5:1	4	99	0:100
4	2:1	4	99	0:100

^aReactions were performed using 5 mmol of NaBH₄ and 10 mmol of NaHCO₃ in 2 M THF at rt open to air while varying the DMAP equivalents as necessary. Water was added dropwise as a 14.4% solution in THF. ^bYields of isolated product. ^cBy ¹H NMR spectroscopy.

Conclusion: On the basis of the above results (Table S3), 1.5:3:1 ratio of the equivalents of sodium borohydride to sodium bicarbonate to amine was found to yield optimal results (entry 3, highlighted in bold).

General procedure for the preparation of amine-boranes (2b-2o, 2q, 2x, and 2aa):

Sodium borohydride (0.28 g, 7.5 mmol) and powdered sodium bicarbonate (1.26 g, 15 mmol) were transferred to a 50 mL dry round bottom flask, charged with a magnetic stir-bar. The corresponding amine (**1b-1l**, **1n-1o**, **1q**, **1x**, **1aa**, 5 mmol) or diamine (**1m**, 2.5 mmol) was charged into the reaction flask followed by addition of reagent-grade tetrahydrofuran (1.9 mL for liquid amines / 5.7 mL for solid amines) at rt. Under vigorous stirring, 1.9 mL of 14.4% v/v solution water in THF was added drop-wise to prevent excessive frothing. Reaction progress was monitored by ^{11}B NMR spectroscopy (Note: A drop of anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment). Upon completion of the reaction (4-8 h, as determined by ^{11}B NMR), the reaction contents were filtered through sodium sulfate and celite and the solid residue washed with THF. Removal of the solvent *in vacuo* from the filtrate yielded the corresponding amine-borane in 86-99% yields.

General procedure for the preparation of functionalized amine-boranes (2a, 2p, 2r-2w, 2y-2z, 2ab-2ac, and 4):

Sodium borohydride (0.38 g, 10 mmol) and powdered sodium bicarbonate (1.68 g, 20 mmol) were transferred to a 50 mL dry round bottom flask, charged with a magnetic stir-bar. The corresponding amine (**1a**, **1p**, **1r-1w**, **1y-1z**, **1ab-1ac**, and **3**, 5 mmol) was charged into the reaction flask followed by addition of reagent-grade tetrahydrofuran (2.5 mL for liquid amines / 7.5 mL for solid amines) at rt. Under vigorous stirring, 2.5 mL of 14.4% v/v solution water in THF was added drop-wise to prevent excessive frothing. Reaction progress was monitored by ^{11}B NMR spectroscopy (Note: A drop of anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment). Upon completion of the reaction (4-48 h, as determined by ^{11}B NMR), the reaction contents were filtered through sodium sulfate and celite and the solid residue washed with THF. Removal of the solvent *in vacuo* from the filtrate yielded the corresponding crude amine-borane. Amine-boranes **2a** and **2p** did not need any further purification. The rest were purified by column chromatography using dichloromethane/methanol mixture as eluent.

General procedure for hydride analysis of amine-boranes (Hydrolysis reaction):

An aqueous solution of amine-borane (2 mmol in 1 mL H₂O) was transferred to a round bottom flask with a septum inlet fitted with a connecting tube. The connecting tube was attached to an analytical gas burette filled with CuSO₄ solution. A solution of RuCl₃ (4.2 mg, 1 mol% in 2 mL H₂O) was syringed into the vial, all at once. The hydrogen generated was measured using the analytical gas burette. The temperature of the reaction was maintained at 25°C.

Gold surface functionalization - Procedure and Characterization:

30 nm gold film was thermally evaporated on a SiO₂/Si substrate. The gold film was then immersed into the solution of **2w** in ethanol (10 mmol/L) for 3 hours, followed by sonication in ethanol. Atomic force microscopy (AFM) images of all samples showed typical gold film surface with no significant difference for samples with and without treatment with solution of **2w**. Scanning Kelvin probe microscopy (SKPM) was conducted to measure the surface potential of the gold film. A Si cantilever tip coated with Pt-Ir (SCM-PIT-V2, Bruker Co.) was used in the tapping mode. The sample surface topography and contact potential difference (CPD) map between the tip and sample were measured at the same time and shown in Figure S1. Topographic image of bare gold (Figure S1a) shows typical thermal evaporated gold film surface with roughness R_q around 0.67 nm. Figure S1b exhibits different topography from bare gold film with R_q around 0.78 nm, and that difference must be raised by amine-borane modification. The very smooth CPD maps (Figures S1c and S1d) show that the surface potential is uniform. The following equation is used to calculate the work function of the sample:

$$V_{\text{CPD}} = \frac{\Phi_{\text{tip}} - \Phi_{\text{sample}}}{e}$$

Where Φ_{tip} is the work function of the Pt-Ir coated conducting AFM tips (5.2 eV) and Φ_{sample} is the work function of the sample. The calculated work function of bare gold and thiol bearing amine-borane modified gold film is 5.02 eV and the 4.73 eV, respectively. This result shows that after thiol bearing amine-borane modification, the work function of gold film decreased by 0.29 eV.

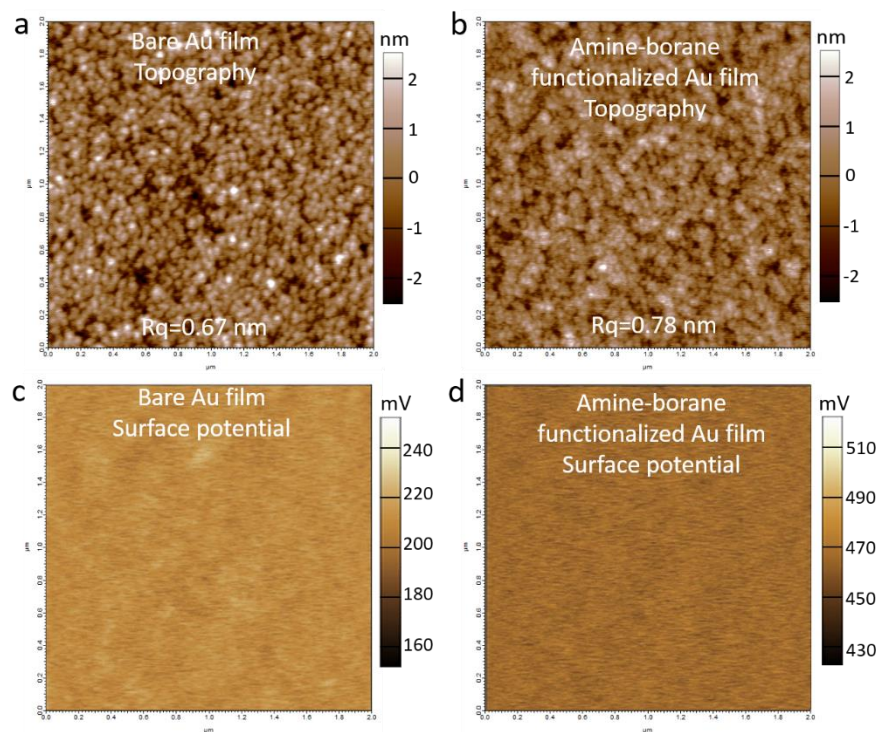


Figure S1. (a) and (b) represent topographic AFM images of bare Au film and amine-borane functionalized Au film, respectively. (c) and (d) are contact potential difference (CPD) map of bare Au film and amine-borane functionalized Au film, respectively.

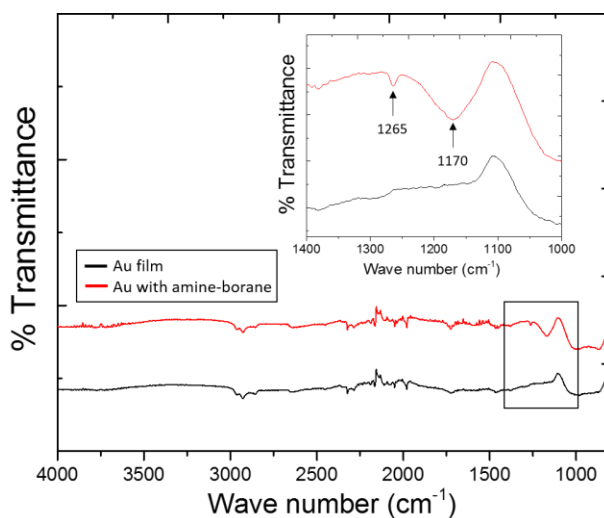


Figure S2. FTIR results of pure gold film and amine-borane modified gold film.

Silica surface modification - Procedure and Characterization:

Before APTES-borane-modification, the silica substrate was carefully cleaned by piranha solution to remove all organic residues and result in a highly hydroxylated SiO₂ surface.¹² After successive sonication in water and ethanol followed by drying in nitrogen, the silica substrate was immersed into the solution of **2ab** in ethanol (10 mmol/L) for 3 hours, followed by sonication in ethanol.

AFM measurements (Figure S3) show a smooth surface with root mean square roughness Rq around 0.140 nm, similar with the bare SiO₂ surface (0.122 nm).

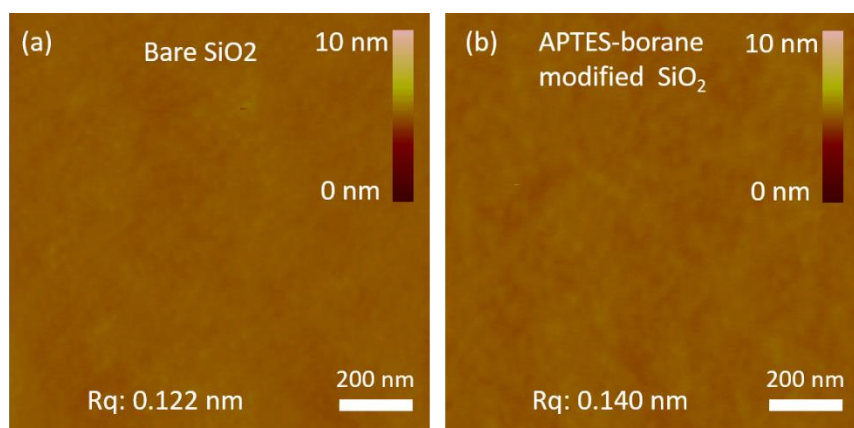


Figure S3. AFM images of (a) bare SiO₂ and (b) APTES-borane modified SiO₂ surface.

OFET fabrication:

Bottom gate bottom contact OFETs with Bis(triisopropylsilylethynyl) pentacene as semiconductor and gold as electrodes were fabricated to verify the APTES-borane modification on SiO₂ surface. A heavily n-doped Si wafer with a 300 nm SiO₂ surface layer (capacitance of 11 nF/cm²) was employed as the substrate with Si wafer serving as the gate electrode and SiO₂ as the dielectric. The gold source and drain electrodes were sputtered and patterned by photolithography technique. The device channel width was 1000 μm and the channel length was 60 μm for all of the OFETs. 30 nm Tips-Pentacene layer was then thermally evaporated onto both the bare and APTES-borane modified SiO₂/Si substrates. The OFETs devices were then measured using Keithley 4200 in ambient air. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_T is the threshold voltage.

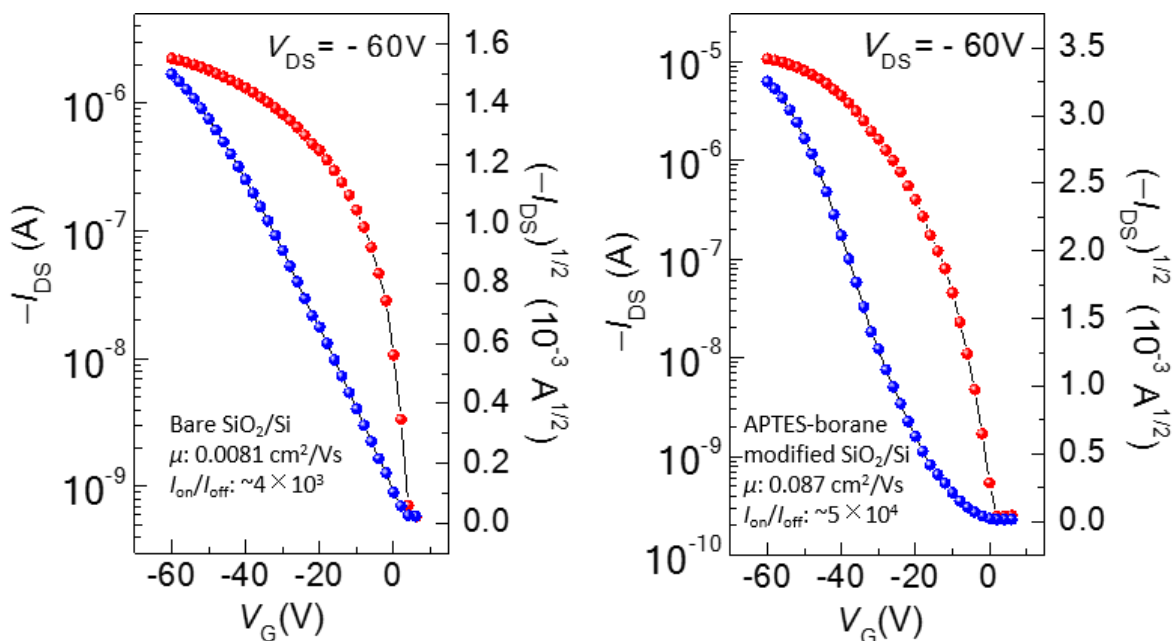


Figure S4. Transfer characteristics of OFETs using (a) bare SiO₂/Si and (b) APTES-borane modified SiO₂/Si as substrate.

Characterization of amine-boranes:

Triethylamine-borane (Et₃N-BH₃, 2a):

Colorless liquid.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 2.79 (q, *J* = 7.3 Hz, 6H), 1.19 (t, *J* = 7.3 Hz, 9H), 2.10 – 0.9 (br q, BH₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 52.5, 8.9.; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -13.96 (q, *J* = 97.0 Hz).

4-Dimethylaminopyridine-borane (DMAP-BH₃, 2b):

White solid.

¹H NMR (300 MHz, CDCl₃) 8.00-7.93 (m, 2H), 6.50-6.44 (m, 2H), 3.09 (s, 6H), 3.00-1.80 (br q, BH₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 154.3, 146.3, 106.3, 39.7; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -14.33 (q, *J* = 95 Hz).

1-Propanamine-borane (2c):

White Solid.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.83 (s, 2H), 2.78 (p, *J* = 7.3 Hz, 2H), 1.65 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.75-2.00 (br q, BH₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 50.7, 22.7, 11.4; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -20.01 (q, *J* = 95.0 Hz).

Cyclohexylamine-borane (2d):

White Solid.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.59 (s, 2H), 2.72 (tdt, *J* = 10.4, 7.7, 3.0 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.86 – 1.57 (m, 3H), 1.42 – 1.06 (m, 5H), 0.90 - 2.05 (br q, BH₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 57.3, 32.7, 25.6, 24.9; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -20.91 (q, *J* = 96.3 Hz).

tert-Butylamine-borane (2e):

White solid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 3.88 (s, 2H), 1.30 (s, 9H), 2.1 – 0.7 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 53.2, 28.2; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -23.31 (q, $J = 95.3$ Hz).

Benzylamine-borane (2f)

White solid.

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 7.48-7.17 (m, 5H), 5.71 (s, 2H), 3.79-3.58 (m, 2H), 2.3-0.9 (br q, BH_3); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ (ppm): 137.3, 128.5, 128.2, 127.4, 51.7; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -18.83 (q, $J = 96.1$ Hz).

***N,N*-Diethylamine-borane (2g)**

Colorless liquid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 3.42 (s, 1H), 2.98-2.72 (m, 4H), 1.27 (td, $J = 7.3, 0.9$ Hz, 6H), 2.10-0.90 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 49.0, 11.9; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -17.23 (q, $J = 96.1$ Hz).

Pyrrolidine-borane (2h)

Colorless liquid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.34 (s, 1H), 3.27 (dq, $J = 10.9, 5.5$ Hz, 2H), 2.84-2.58 (m, 2H), 2.06-1.78 (m, 4H), 2.00-0.80 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 54.4, 24.9; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -17.11 (q, $J = 95.1$ Hz).

Piperidine-borane (2i)

White solid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 3.81 (s, 1H), 3.35-3.18 (m, 2H), 2.63-2.39 (m, 2H), 1.87-1.71 (m, 2H), 1.66-1.24 (m, 4H), 2.10-0.80 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 53.5, 25.6, 22.8; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -15.49 (q, $J = 95.0$ Hz).

Morpholine-borane (2j)

White solid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.41 (s, 1H), 4.02-3.89 (m, 2H), 3.59 (dt, $J = 12.7, 2.3$ Hz, 2H), 3.15-3.05 (m, 2H), 2.91-2.70 (m, 2H), 2.10-0.80 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 65.9, 52.2; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -15.46 (q, $J = 97.5$ Hz).

***N*-Methylpyrrolidine-borane (2k)**

Colorless liquid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 3.24-3.13 (m, 2H), 2.85-2.69 (m, 2H), 2.66 (s, 3H), 2.22-2.04 (m, 2H), 2.04-1.89 (m, 2H), 2.20-1.10 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 63.0, 51.4, 23.3; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -11.06 (q, $J = 96.7$ Hz).

***N*-Ethylpiperidine-borane (2l)**

Colorless liquid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 3.00-2.79 (m, 4H), 2.79-2.63 (m, 2H), 1.93-1.76 (m, 2H), 1.68-1.47 (m, 4H), 1.26 (dtd, $J = 7.2, 4.4, 2.2$ Hz, 3H), 2.10-0.95 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 57.6, 54.8, 22.9, 20.5, 9.0; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -13.02 (q, $J = 96.8$ Hz).

***N,N*-dimethylpiperazine-bisborane (2m)**

White solid. Single diastereomer (as analyzed by ^{11}B NMR spectroscopy).

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 3.17-3.00 (m, 4H), 3.00-2.83 (m, 4H), 2.59 (s, 6H), 2.10-0.90 (br q, 2BH_3); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm): 53.7; ^{11}B NMR (96 MHz, $\text{DMSO}-d_6$) δ (ppm): -10.99 (br).

Pyridine-borane (2n)

Colorless liquid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.57 (dt, $J = 4.1, 2.2$ Hz, 2H), 7.96 (t, $J = 7.7$, 1H), 7.60-7.48 (m, 2H), 3.20-1.96 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 147.1, 139.1, 125.3; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -12.57 (q, $J = 97.6$ Hz).

2-Picoline-borane (2o)

White solid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.68 (d, $J = 6$ Hz, 1H), 7.91 – 7.80 (m, 1H), 7.47-7.37 (m, 1H), 7.33 (ddd, $J = 7.7, 6.0, 1.8$ Hz, 1H), 2.73 (s, 3H), 3.20-1.80 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 156.9, 148.0, 139.3, 126.5, 122.2, 22.4; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -14.22 (q, $J = 98.3$ Hz).

1-Methylimidazole-borane (2p)

Colorless liquid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.72 (s, 1H), 6.99-6.91 (m, 2H), 3.76 (s, 3H), 2.90-1.50 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 136.5, 126.9, 121.0, 34.9; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -19.79 (q, $J = 95$ Hz). **HRMS** (CI) calcd for $\text{C}_4\text{H}_8\text{BN}_2$ (M-H) $^+$: m/z , 95.0775, found 95.0777.

Allylamine-borane (2q)

Colorless oil.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 5.95 (ddt, $J = 16.7, 10.3, 6.3$ Hz, 1H), 5.39-5.18 (m, 2H), 4.29-3.95 (m, 2H), 3.46-3.27 (m, 2H), 2.10-0.90 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 132.3, 119.3, 51.0; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -19.81 (q, $J = 97.7$ Hz). **HRMS** (CI) calcd for $\text{C}_3\text{H}_9\text{BN}$ (M-H) $^+$: m/z , 70.0823, found 70.0826.

1,2,3,6-tetrahydropyridine-borane (2r)

White solid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 6.10 (s, 1H), 5.84-5.70 (m, 1H), 5.69-5.53 (m, 1H), 3.35-3.14 (m, 1H), 3.11-2.79 (m, 2H), 2.52-2.36 (m, 1H), 2.30-2.16 (m, 1H), 2.10-1.90 (m, 1H), 1.80-0.80 (br q, BH_3); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ (ppm): 124.9, 123.6, 50.1, 48.3, 23.3; ^{11}B NMR (96 MHz, $\text{DMSO}-d_6$) δ (ppm): -14.48 (br q, $J = 95.0$ Hz). **HRMS** (CI) calcd for $\text{C}_5\text{H}_{11}\text{BN}$ (M-H) $^+$: m/z , 96.0979, found 96.0976.

Propargylamine-borane (2s)

White solid.

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ (ppm): δ 5.71 (s, 2H), 3.50-2.97 (m, 3H), 1.90-0.50 (br q, BH_3); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ (ppm): 79.6, 75.5, 36.2; ^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) δ (ppm): -18.69 (br q). **HRMS** (CI) calcd for $\text{C}_3\text{H}_7\text{BN}$ (M-H) $^+$: m/z , 68.0666, found 68.0669.

2-(Hydroxymethyl)pyridine-borane (2t)

White solid.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.65 (d, $J = 5.8$ Hz, 1H), 8.02-7.91 (m, 1H), 7.85-7.75 (m, 1H), 7.44-7.32 (m, 1H), 5.03 (s, 2H), 3.17 (s, 1H), 3.00-1.75 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 158.6, 148.8, 140.0, 123.5, 123.4, 62.5; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -15.23 (q, $J = 98$ Hz). **HRMS** (CI) calcd for $\text{C}_6\text{H}_9\text{BNO}$ (M-H) $^+$: m/z , 122.0772, found 122.0772.

3-Aminopropan-1-ol-borane (2u)

Colorless oil.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 5.09 (s, 2H), 4.49 (t, $J = 5.0$ Hz, 1H), 3.40 (q, $J = 5.9$ Hz, 2H), 2.58-2.35 (m, 2H), 1.61 (p, $J = 6.5$ Hz, 2H), 1.70-0.80 (br q, BH_3); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ (ppm): 59.6, 46.3, 32.1; ^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) δ (ppm): -19.59 (q, $J = 93.5$ Hz). **HRMS** (CI) calcd for $\text{C}_3\text{H}_{11}\text{BNO}$ (M-H) $^+$: m/z , 88.0928, found 88.0926.

(S)-(+)-2-(Hydroxymethyl)pyrrolidine-borane (2v)

Colorless oil. Diastereomeric ratio = 92:8 (as analyzed by ^{11}B NMR spectroscopy).

Major diastereomer: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 4.48 (s, 1H), 4.09 (dd, $J = 11.6, 3.1$ Hz, 1H), 3.78-3.58 (m, 1H), 3.37 (dt, $J = 10.3, 6.5$ Hz, 1H), 3.06 (dtd, $J = 10.6, 7.6, 3.5$ Hz, 1H), 2.98-2.68 (m, 2H), 2.11-1.72 (m, 4H), 2.10-0.80 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 66.9, 60.2, 55.3, 27.4, 23.8; ^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) δ (ppm): -16.43 (q, $J = 96.0$ Hz). **HRMS** (CI) calcd for $\text{C}_5\text{H}_{13}\text{BNO}$ (M-H) $^+$: m/z , 114.1085, found 114.1087.

2-diethylaminoethanethiol-borane (2w)

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 2.98-2.69 (m, 8H), 1.19 (t, $J = 7.3$ Hz, 6H), 1.95-0.95 (br q, BH_3); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 61.9, 53.0, 18.7, 8.7; ^{11}B NMR (96 MHz,

CDCl₃) δ (ppm): -13.45 (q, $J = 99.1, 93.3$ Hz). **HRMS** (ESI) calcd for C₆H₁₇BNS (M-H)⁺: m/z , 146.1175, found 146.1176.

2,2-Dimethoxy-*N,N*-dimethylethylamine-borane (2x)

Colorless liquid.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 4.94-4.88 (m, 1H), 3.44-3.37 (m, 6H), 2.90-2.83 (m, 2H), 2.64 (m, 6H), 2.20-1.10 (br q, BH₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 101.3, 65.2, 54.5, 53.0; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -9.85 (q, $J = 99.0$ Hz). **HRMS** (CI) calcd for C₆H₁₇BNO₂ (M-H)⁺: m/z , 146.1347, found 146.1345.

Methyl 6-aminohexanoate-borane (2y)

White solid.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.87 (s, 2H), 3.68 (s, 3H), 2.81 (p, $J = 7.2$ Hz, 2H), 2.34 (t, $J = 7.3$ Hz, 2H), 1.75-1.56 (m, 4H), 1.44-1.31 (m, 2H), 2.10-0.80 (br q, BH₃); ¹³C NMR (101 MHz, CDCl₃) δ (ppm): 174.2, 51.8, 48.6, 33.8, 28.7, 26.1, 24.4; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -15.61 (q, $J = 98.0$ Hz). **HRMS** (CI) calcd for C₇H₁₇BNO₂ (M-H)⁺: m/z , 158.1347, found 158.1349.

***N*-(3-aminopropyl)benzamide-borane (2z)**

White solid.

¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 8.53 (t, $J = 5.9$ Hz, 1H), 7.89-7.76 (m, 2H), 7.58-7.38 (m, 3H), 5.19 (s, 2H), 3.26 (q, $J = 6.5$ Hz, 2H), 2.56-2.36 (m, 2H), 1.74 (p, $J = 7.1$ Hz, 2H), 1.75-0.80 (br q, BH₃); ¹³C NMR (101 MHz, DMSO-*d*₆) δ (ppm): 166.4, 134.4, 131.1, 128.3, 127.1, 45.4, 36.7, 28.3; ¹¹B NMR (96 MHz, DMSO-*d*₆) δ (ppm): -19.26 (br, BH₃). **HRMS** (CI) calcd for C₁₀H₁₆BN₂O (M-H)⁺: m/z , 191.1350, found 191.1348.

3-(dimethylamino)propanenitrile-borane (2aa)

Colorless liquid.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.11-2.88 (m, 4H), 2.66 (s, 6H), 2.19-0.94 (br q, BH₃); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 117.4, 59.5, 52.5, 14.2; ¹¹B NMR (96 MHz, CDCl₃) δ (ppm): -10.96 (q, $J = 98.6$ Hz). **HRMS** (CI) calcd for C₅H₁₂BN₂ (M-H)⁺: m/z , 111.1088, found 111.1087.

2-(4-nitrophenyl)ethylamine-borane (2ab)

White solid.

^1H NMR (400 MHz, DMSO- d_6) δ (ppm): 8.10 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 5.32 (s, 2H), 2.93 (dd, $J = 9.5, 6.4$ Hz, 2H), 2.76–2.58 (m, 2H), 1.85–0.80 (br q, BH_3); ^{13}C NMR (101 MHz, DMSO- d_6) δ 147.1, 146.2, 129.9, 123.6, 48.3, 33.9; ^{11}B NMR (96 MHz, DMSO- d_6) δ (ppm): -19.58 (q, $J = 101.7, 95.1$ Hz). **HRMS** (ESI) calcd for $\text{C}_8\text{H}_{12}\text{BN}_2\text{O}_2$ (M-H) $^+$: m/z , 179.0992, found 179.0992.

(3-aminopropyl)triethoxysilane-borane (2ac)

Colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 3.99–3.88 (m, 2H), 3.84 (qd, $J = 7.0, 2.9$ Hz, 6H), 2.82 (ddt, $J = 10.6, 6.9, 4.1$ Hz, 2H), 1.76 (pd, $J = 7.1, 3.0$ Hz, 2H), 1.24 (td, $J = 7.0, 2.9$ Hz, 9H), 0.66 (td, $J = 7.8, 3.0$ Hz, 2H), 2.10–1.10 (br q, BH_3); ^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 58.8, 50.9, 22.6, 18.4, 7.7; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -19.95 (q, $J = 100.5$ Hz). **HRMS** (ESI) calcd for $\text{C}_9\text{H}_{26}\text{BNO}_3\text{SiNa}$ (M+Na) $^+$: m/z , 257.1709, found 257.1711.

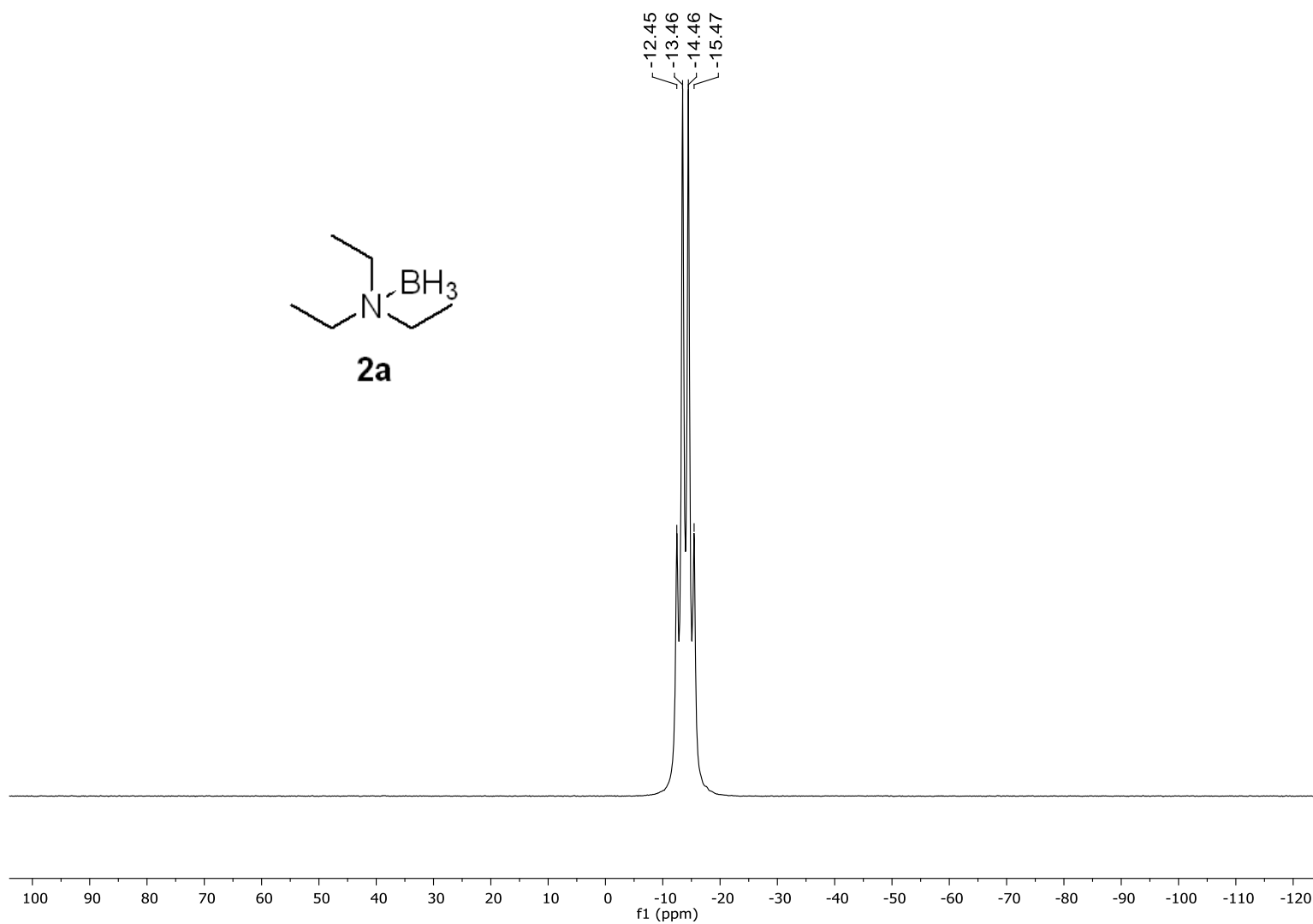
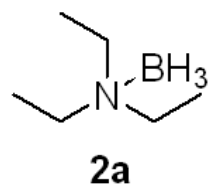
3-(pyridin-2-ylamino)propan-1-ol-borane (4)

Colorless oil.

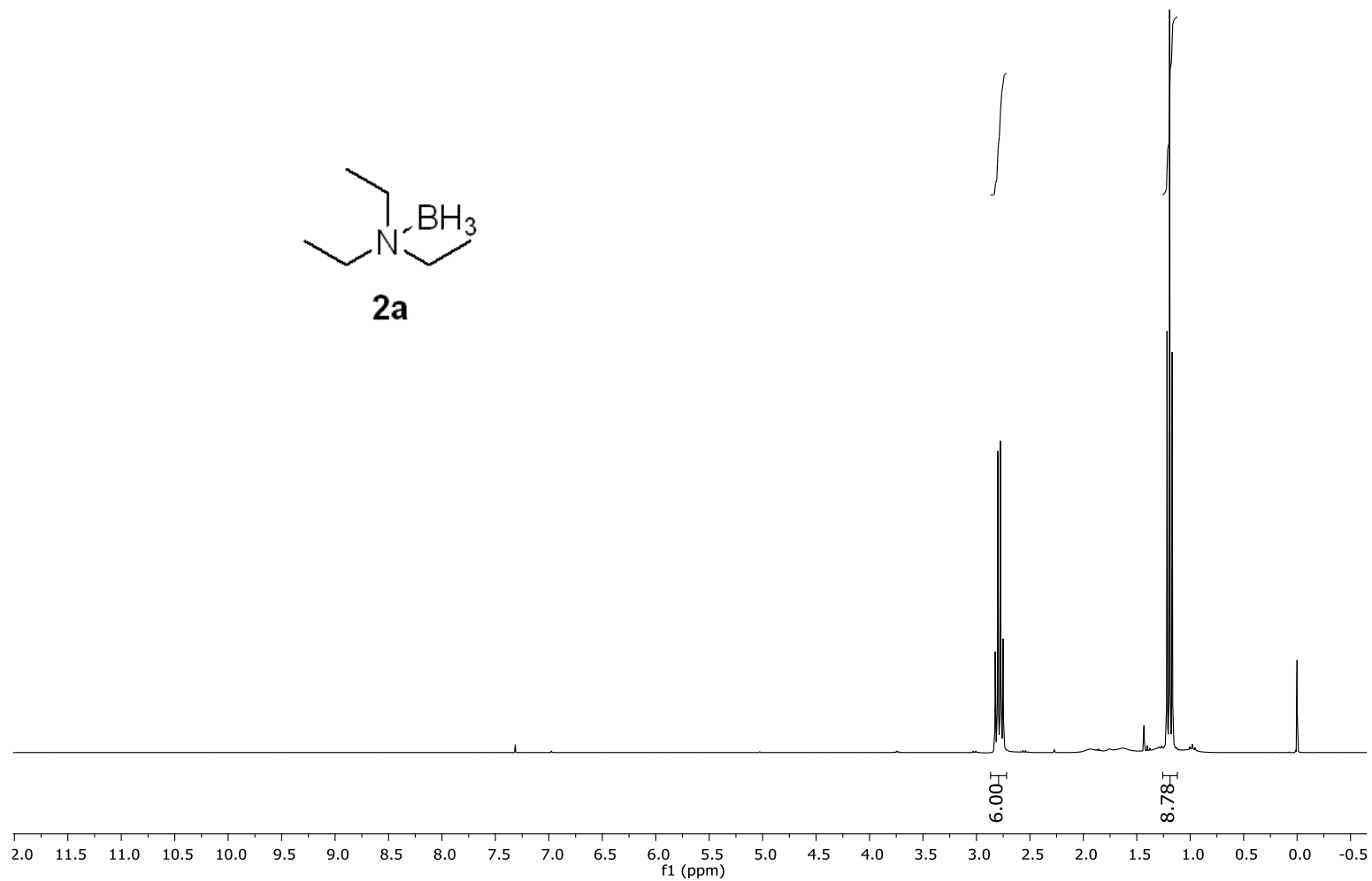
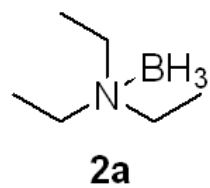
^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.09 (d, $J = 6.2$ Hz, 1H), 7.57 (t, $J = 9.0$ Hz, 1H), 6.64 (d, $J = 8.8$ Hz, 1H), 6.54 (t, $J = 6.6$ Hz, 1H), 6.41 (s, 1H), 3.79 (t, $J = 5.9$ Hz, 2H), 3.42 (q, $J = 6$ Hz, 2H), 2.55 (s, 1H), 1.92 (p, $J = 6$ Hz, 2H), 2.80–1.50 (br q, BH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 154.6, 145.9, 139.8, 111.2, 107.2, 59.9, 39.9, 31.5; ^{11}B NMR (96 MHz, CDCl_3) δ (ppm): -17.92 (q, $J = 97.5, 91.7$ Hz). **HRMS** (CI) calcd for $\text{C}_8\text{H}_{14}\text{BN}_2\text{O}$ (M-H) $^+$: m/z , 165.1194, found 165.1189.

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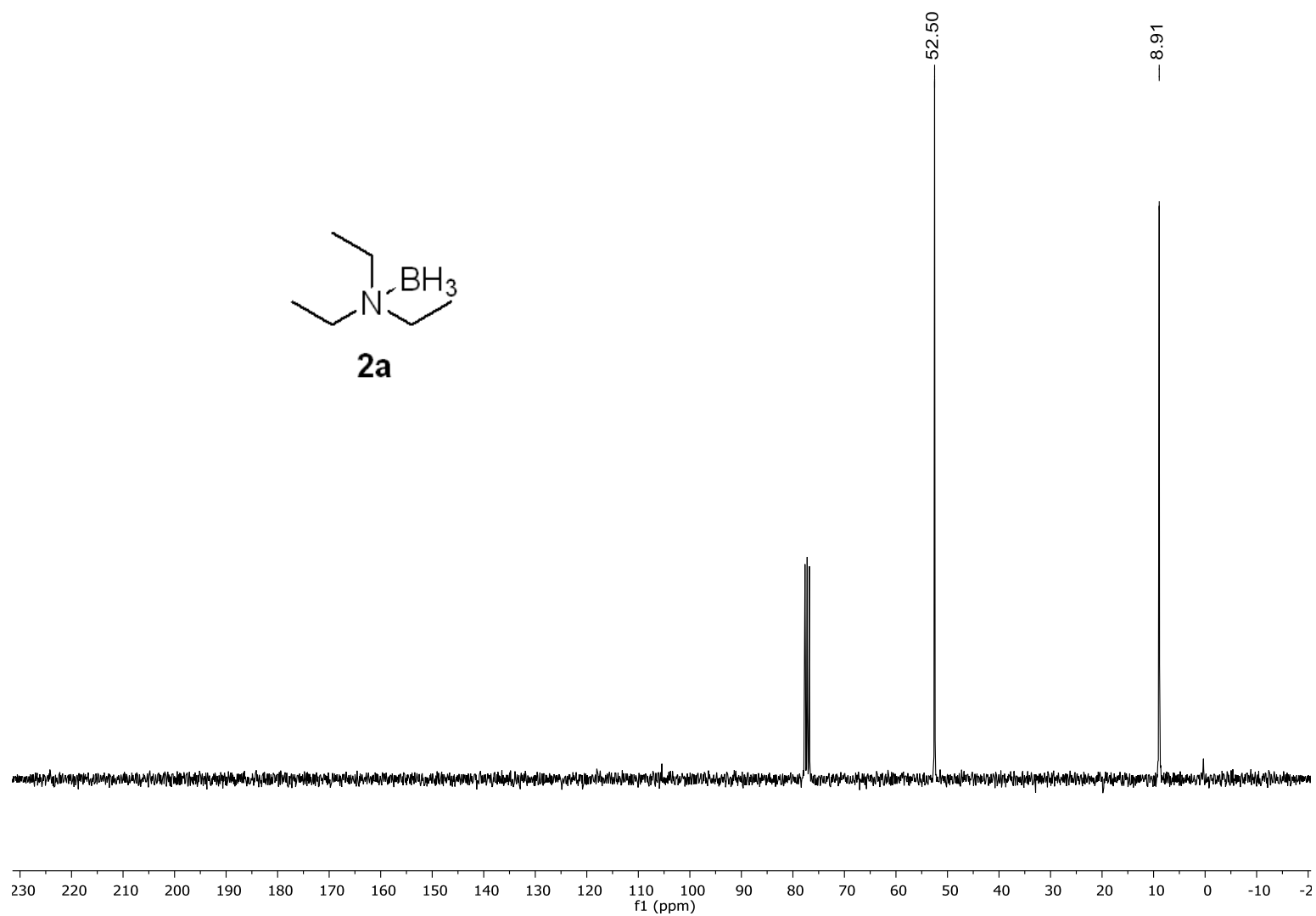
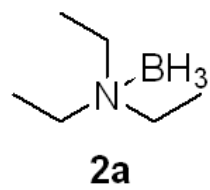
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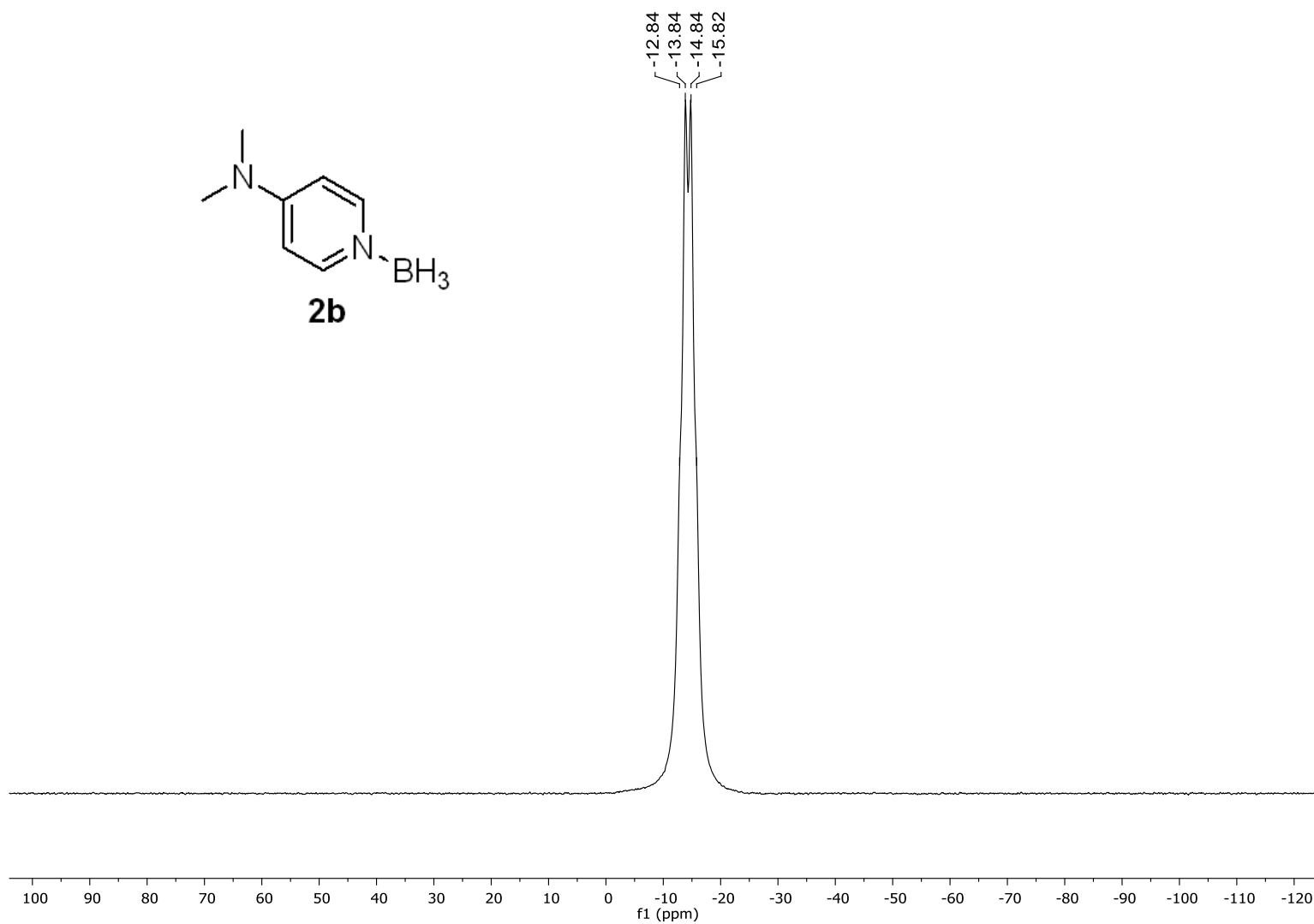
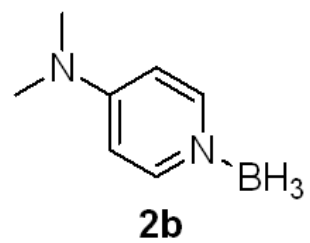
^{11}B NMR (96 MHz, CDCl_3) Triethylamine-borane ($\text{Et}_3\text{N-BH}_3$, **2a**)



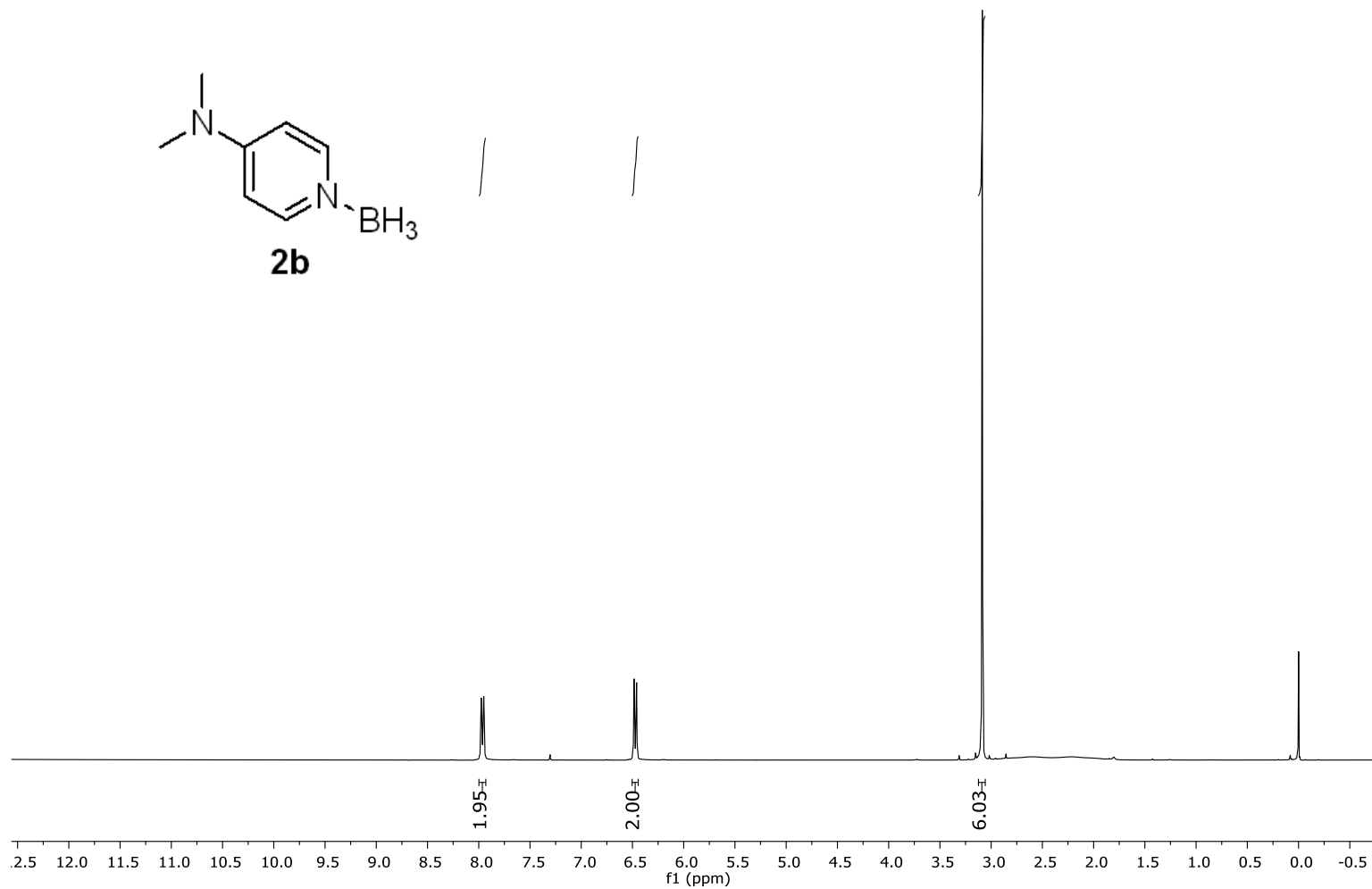
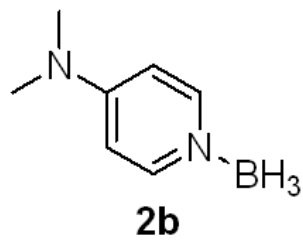
¹H NMR (300 MHz, CDCl₃) Triethylamine-borane (Et₃N-BH₃, **2a**)



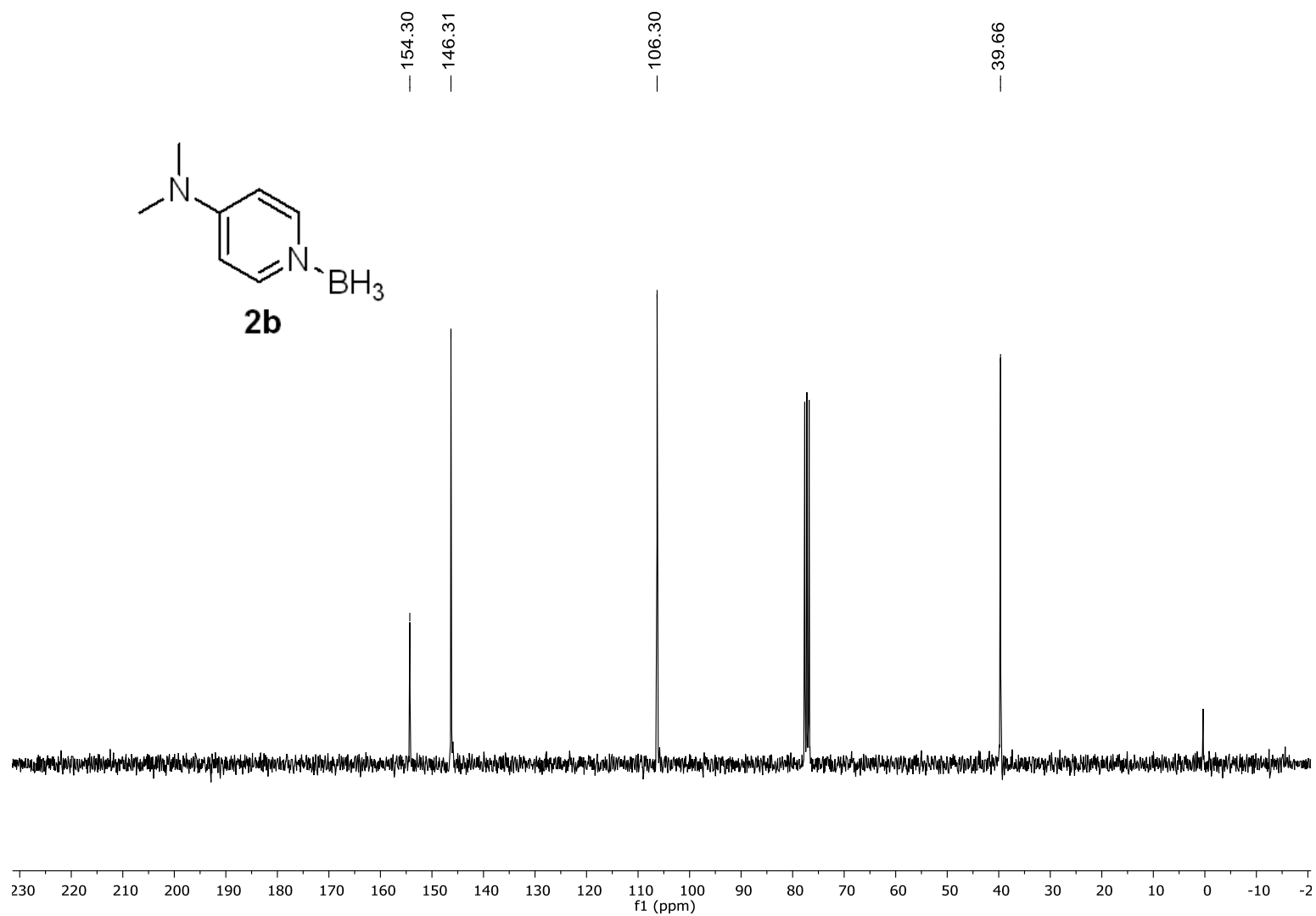
^{13}C NMR (75 MHz, CDCl_3) Triethylamine-borane ($\text{Et}_3\text{N-BH}_3$, **2a**)



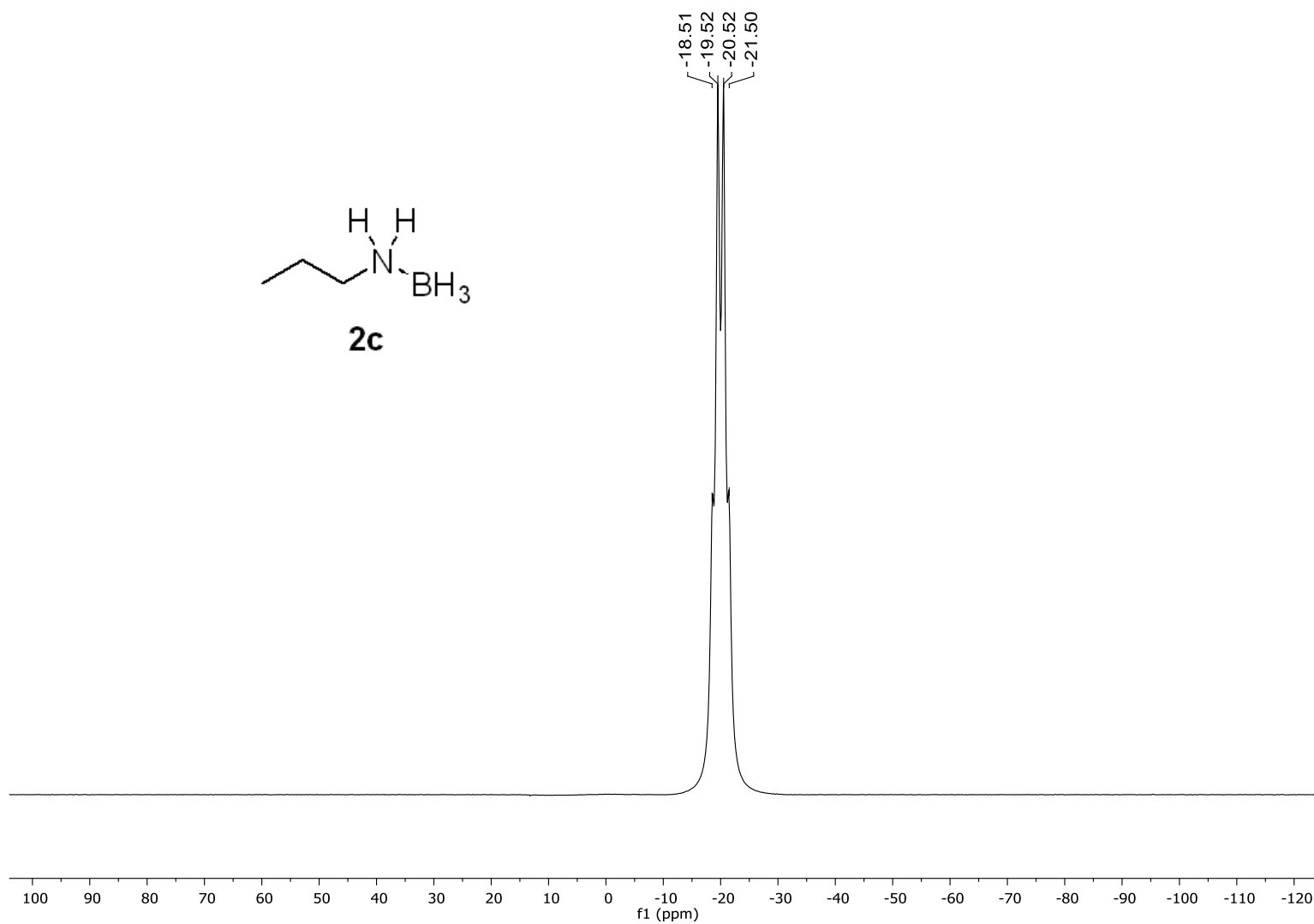
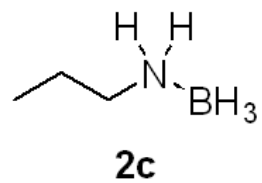
^{11}B NMR (96 MHz, CDCl_3) 4-Dimethylaminopyridine-borane (DMAP-BH_3 , **2b**)



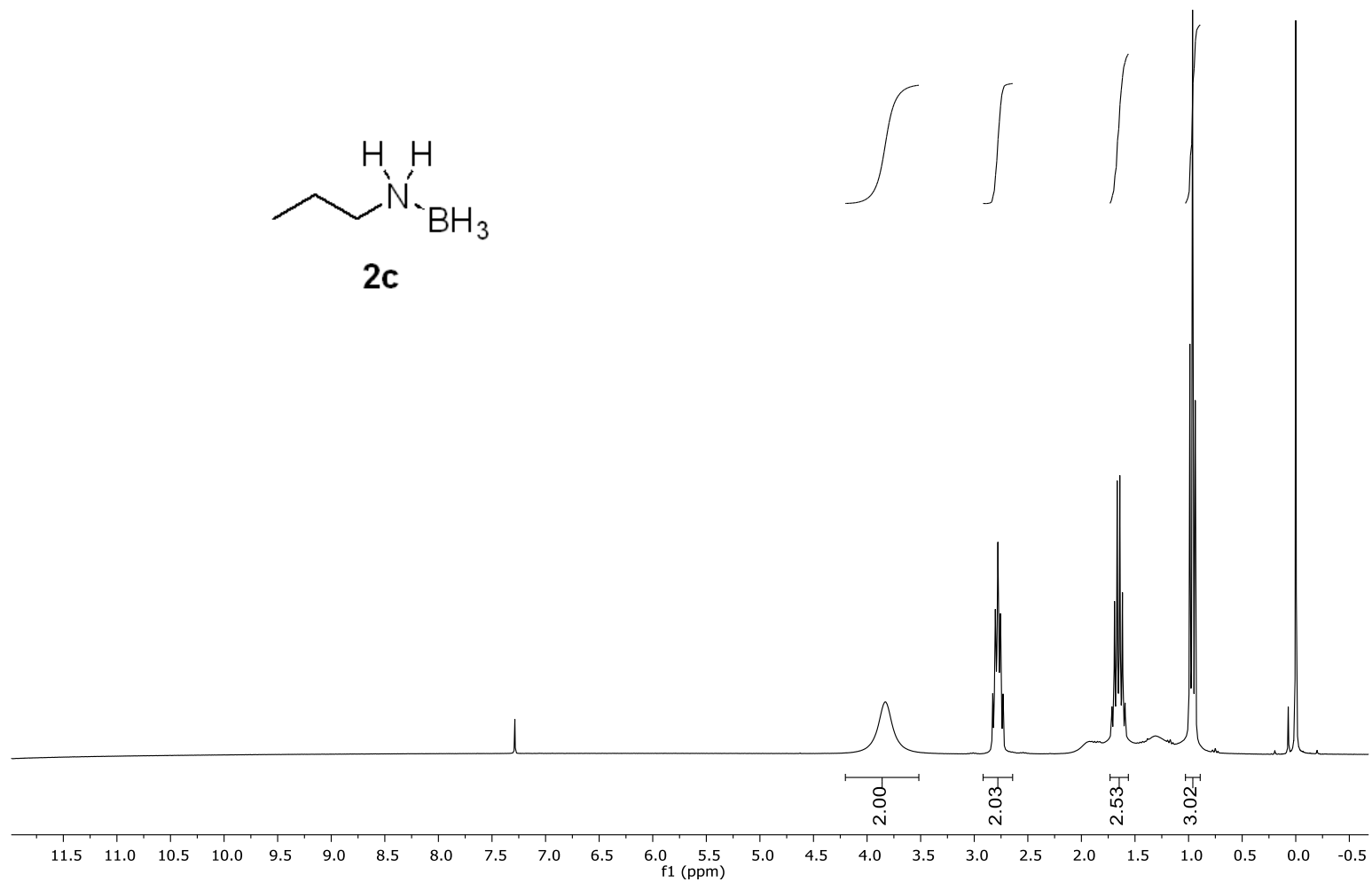
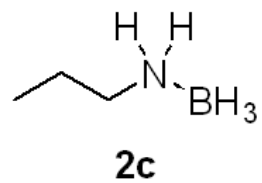
¹H NMR (300 MHz, CDCl₃) 4-Dimethylaminopyridine-borane (DMAP-BH₃, **2b**)



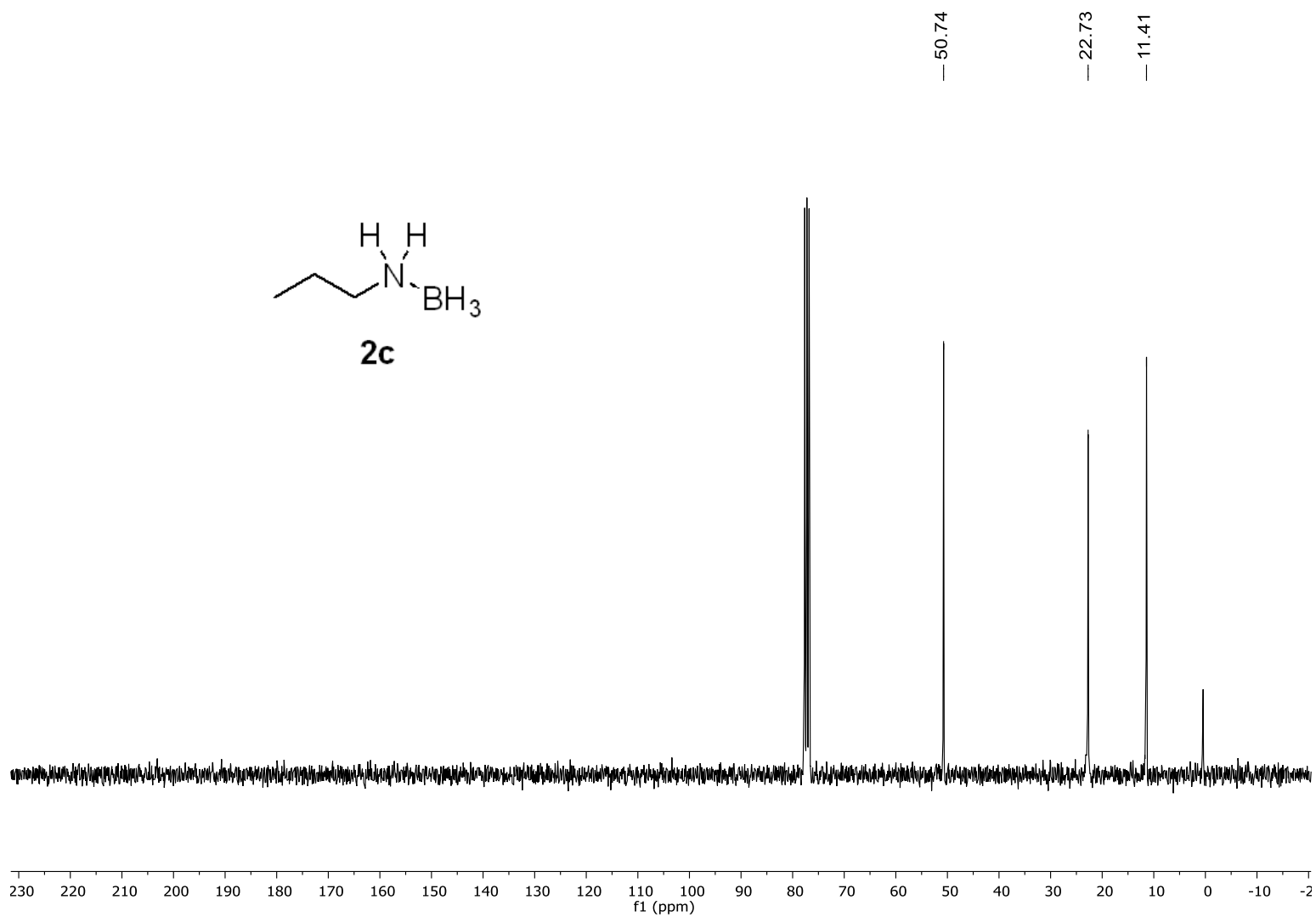
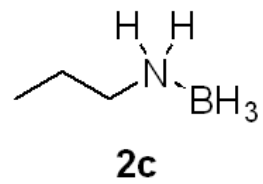
¹³C NMR (75 MHz, CDCl₃) 4-Dimethylaminopyridine-borane (DMAP-BH₃, **2b**)



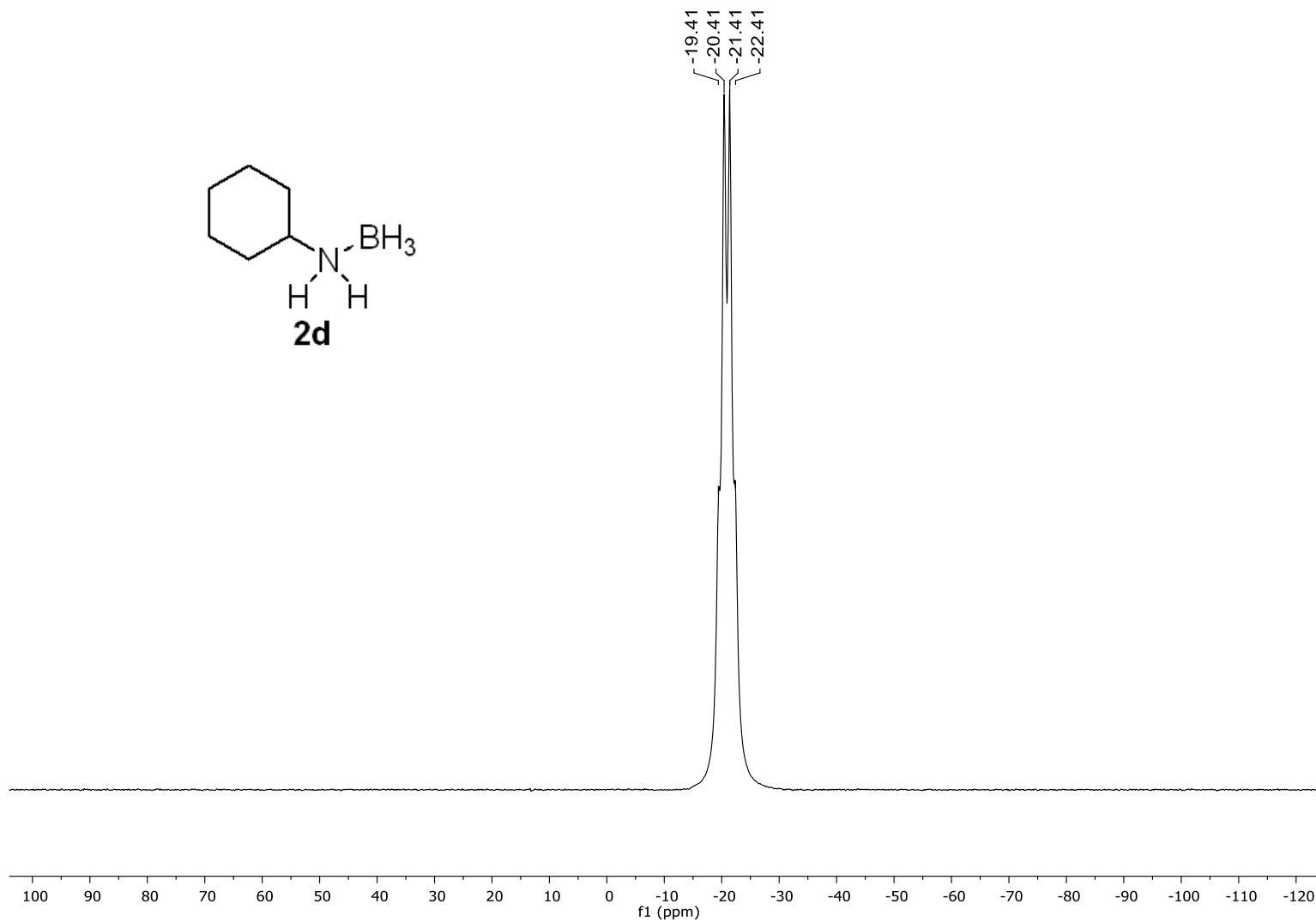
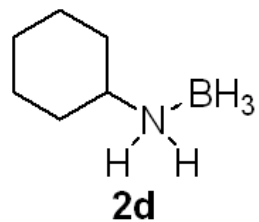
^{11}B NMR (96 MHz, CDCl_3) 1-Propanamine-borane (**2c**)



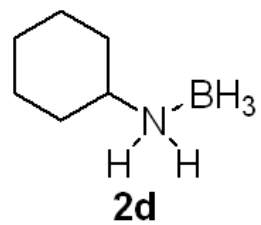
^1H NMR (300 MHz, CDCl_3) 1-Propanamine-borane (**2c**)



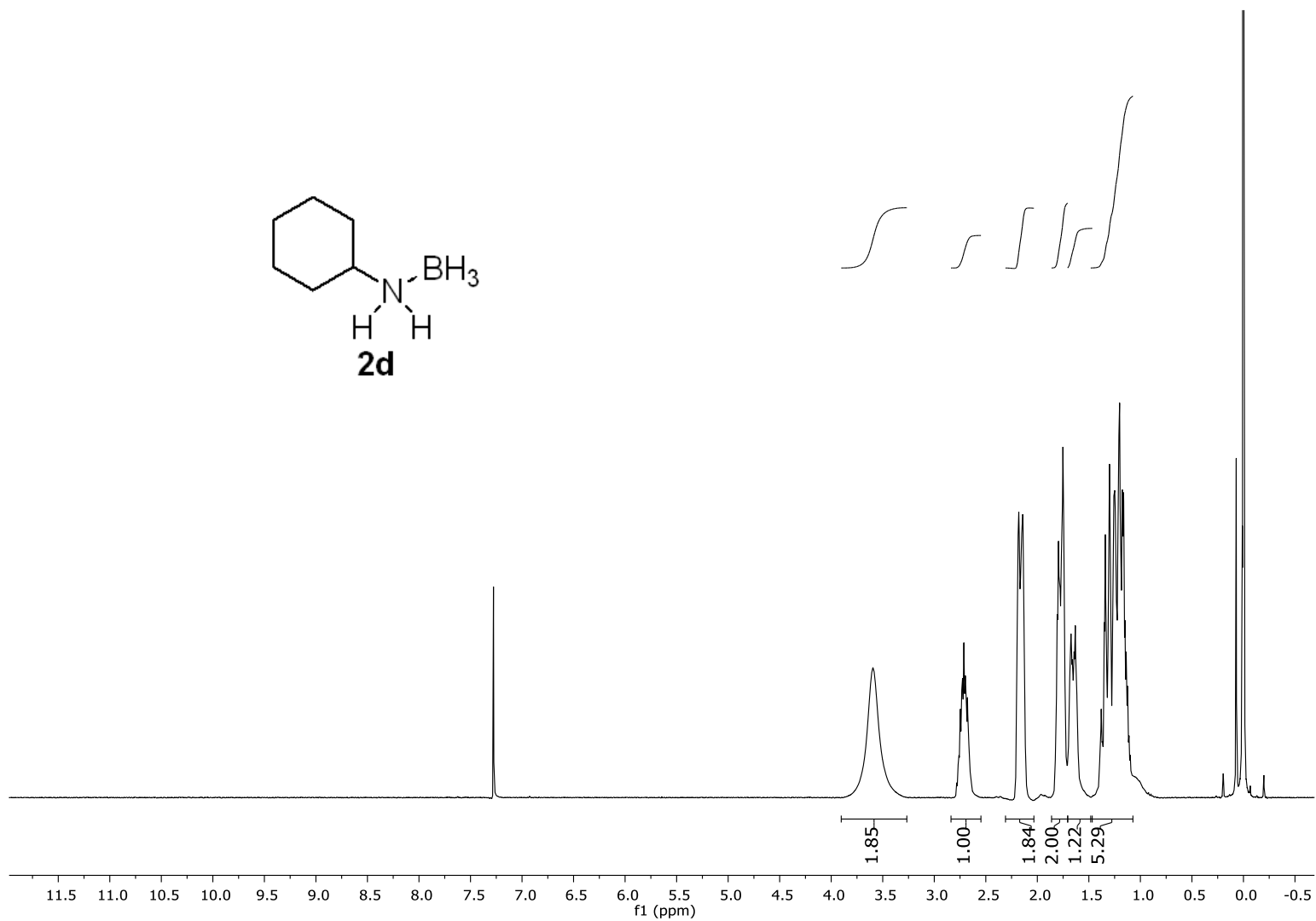
^{13}C NMR (75 MHz, CDCl_3) 1-Propanamine-borane (**2c**)



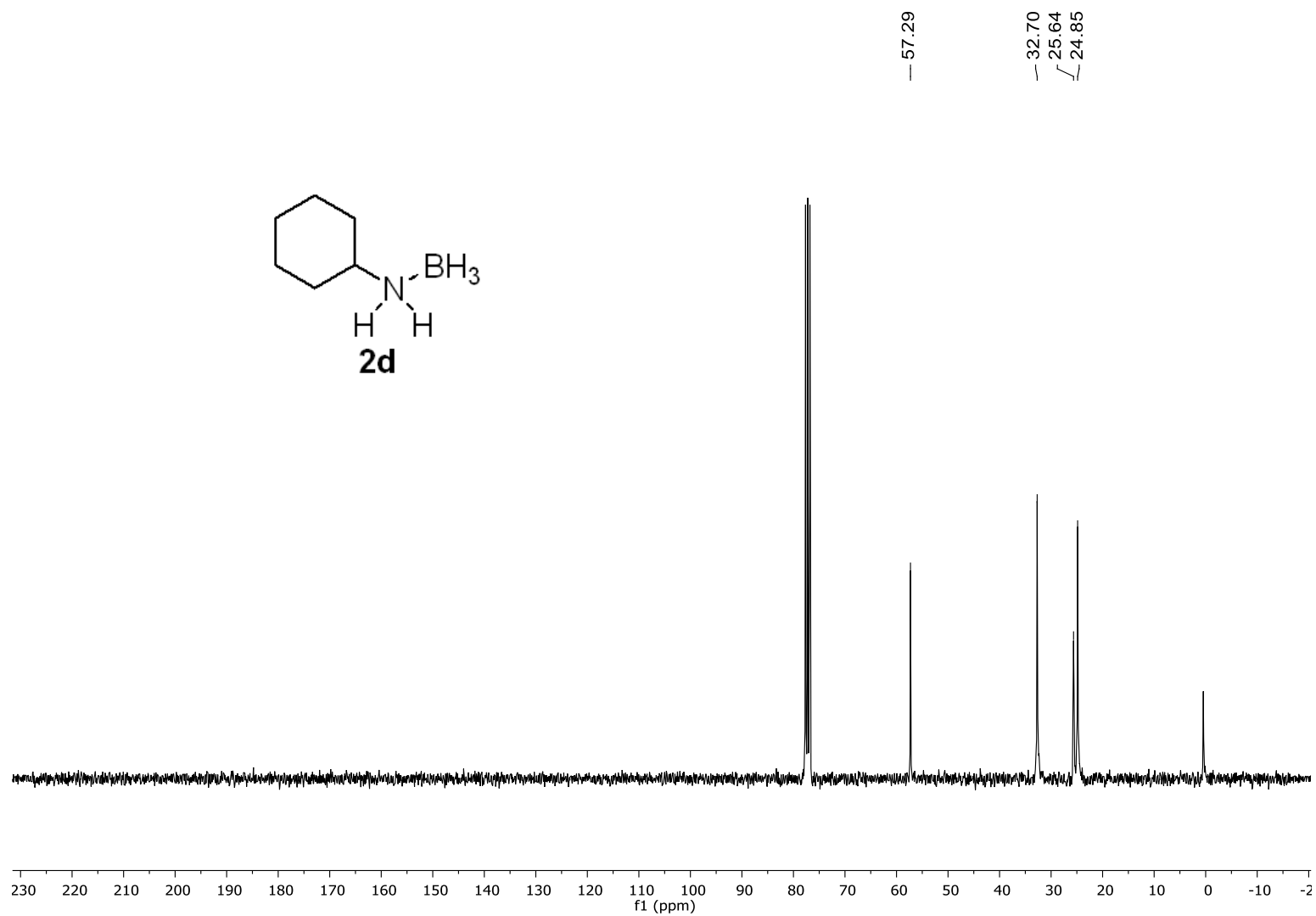
^{11}B NMR (96 MHz, CDCl_3) Cyclohexylamine-borane (**2d**)



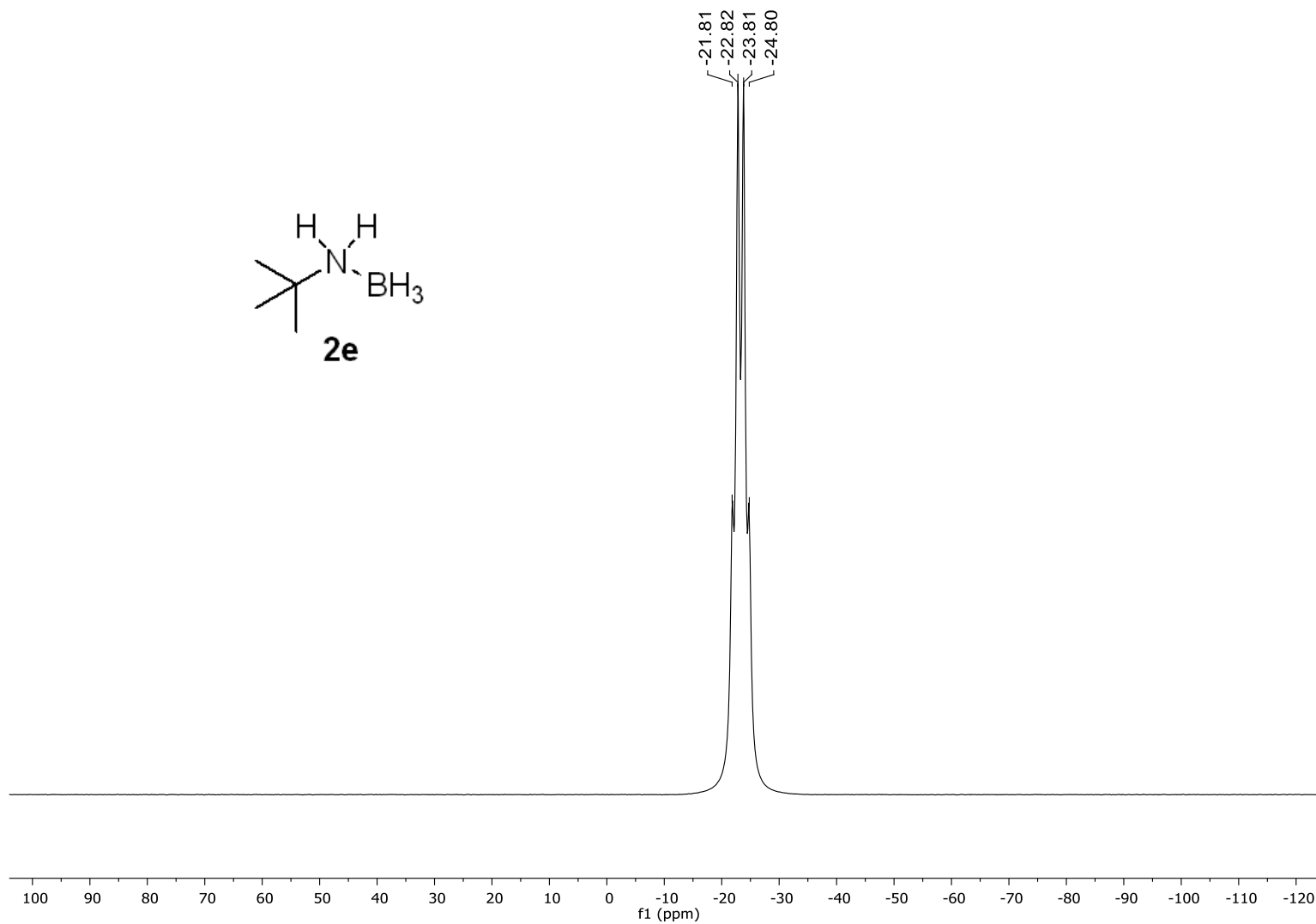
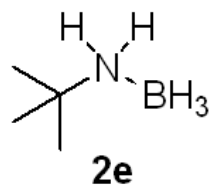
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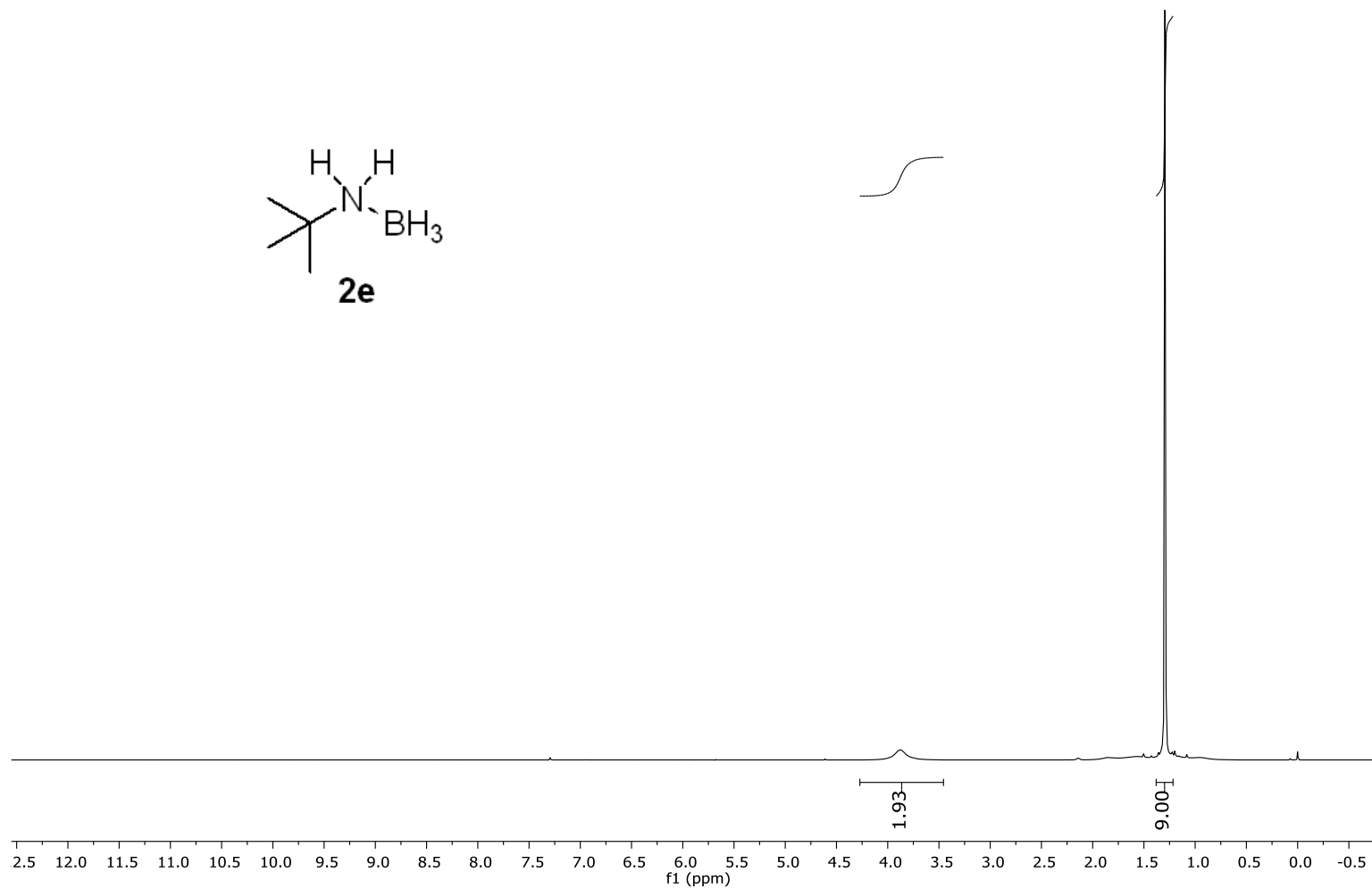
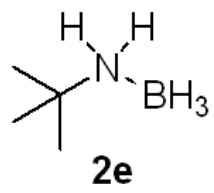
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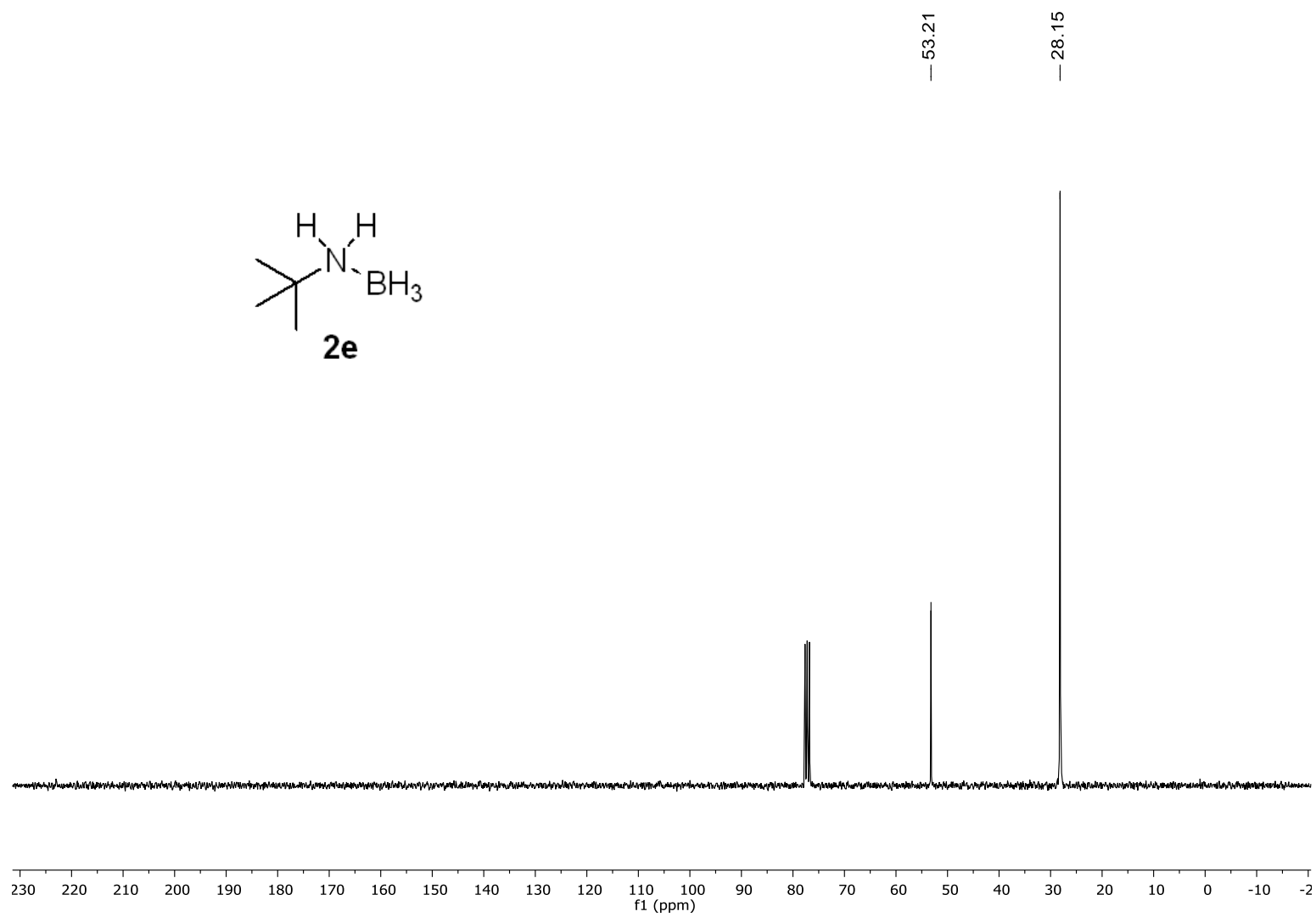
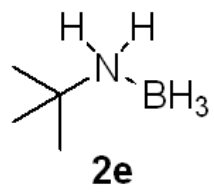
^{13}C NMR (75 MHz, CDCl_3) Cyclohexylamine-borane (**2d**)



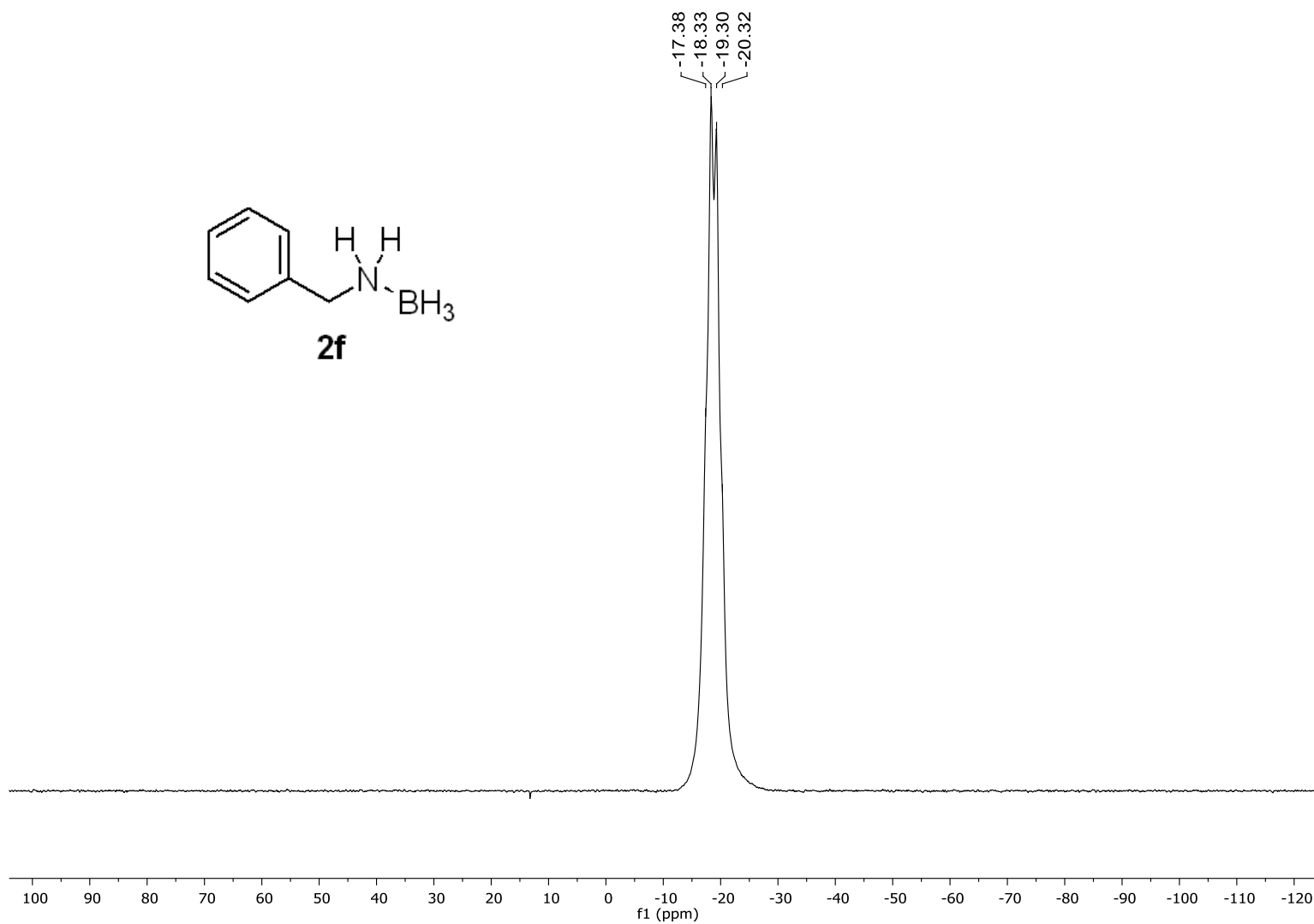
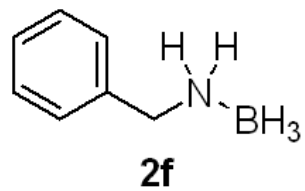
^{11}B NMR (96 MHz, CDCl_3) *tert*-Butylamine-borane (**2e**)



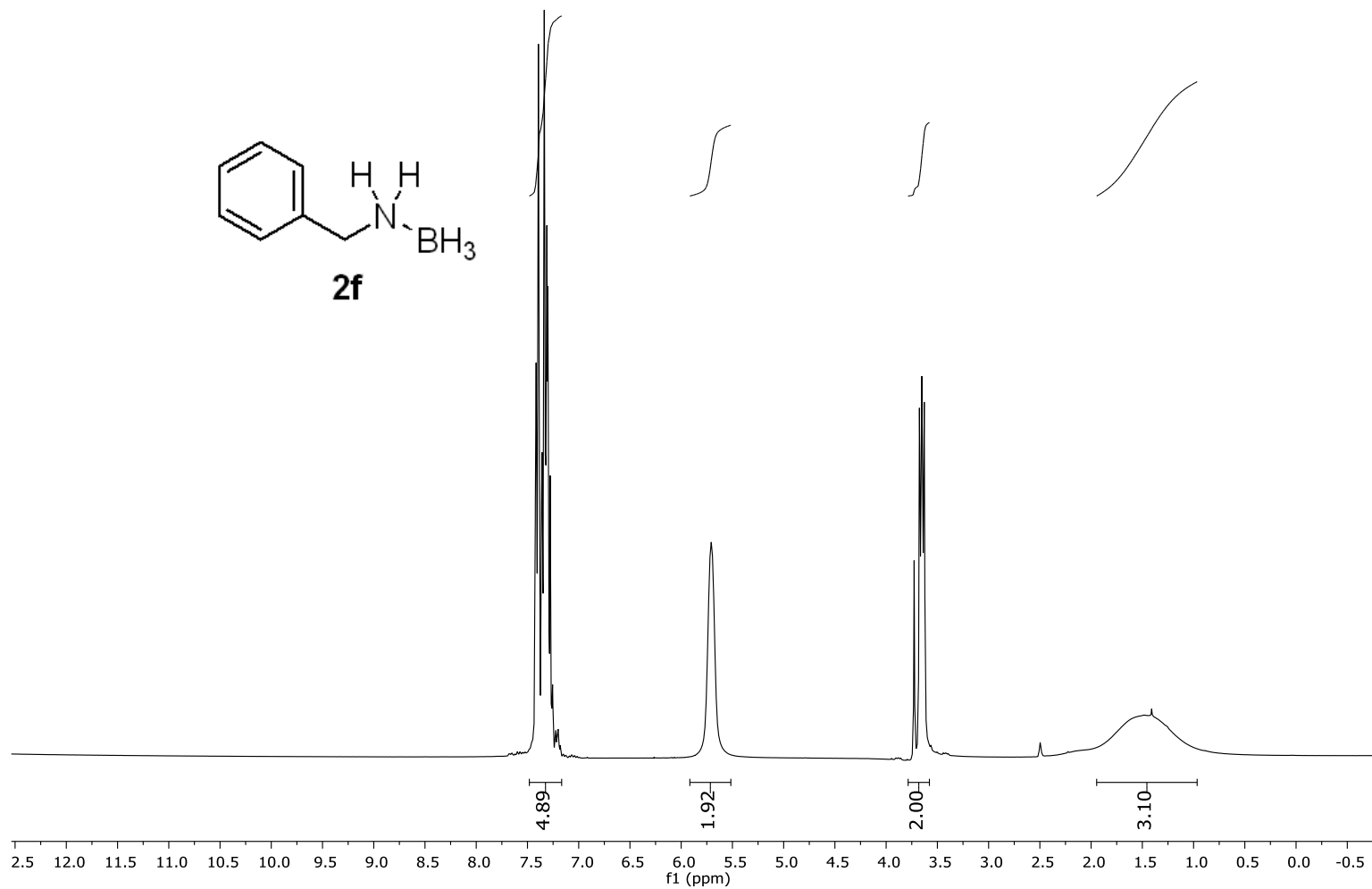
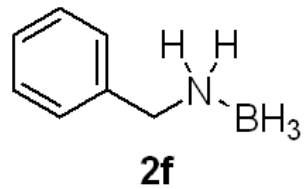
^1H NMR (300 MHz, CDCl_3) *tert*-Butylamine-borane (**2e**)



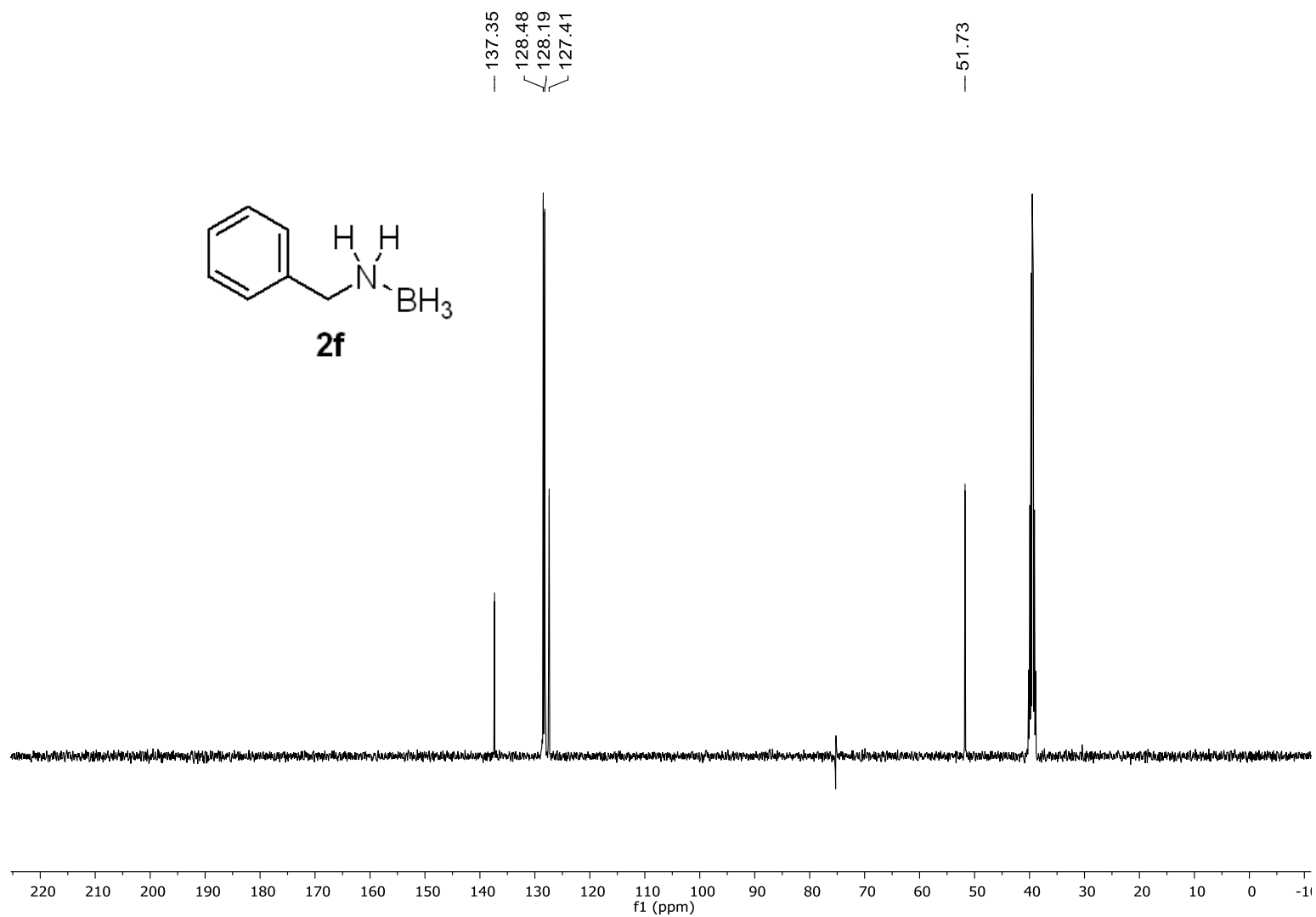
^{13}C NMR (75 MHz, CDCl_3) *tert*-Butylamine-borane (**2e**)



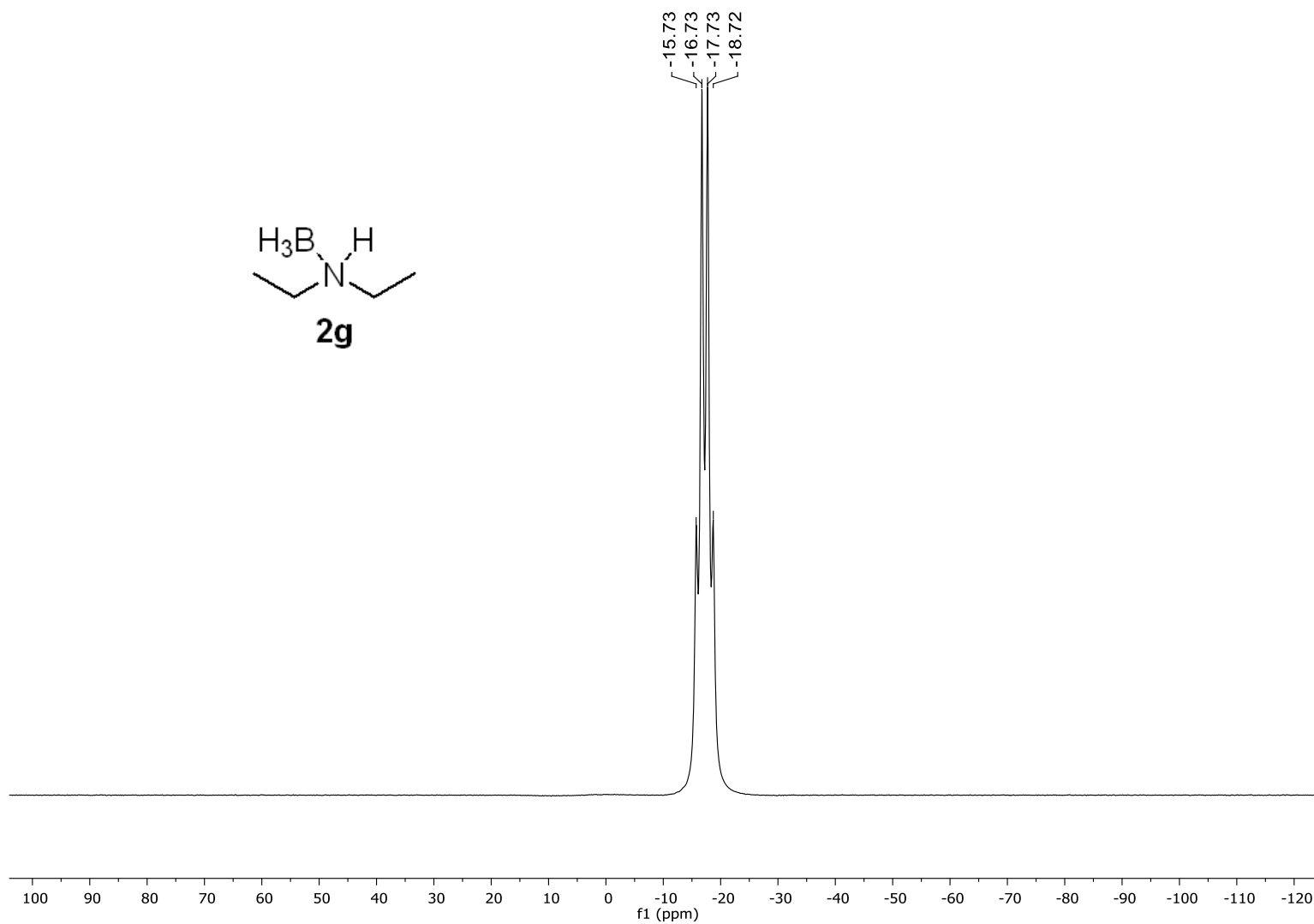
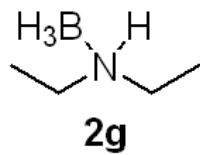
^{11}B NMR (96 MHz, CDCl_3) Benzylamine-borane (**2f**)



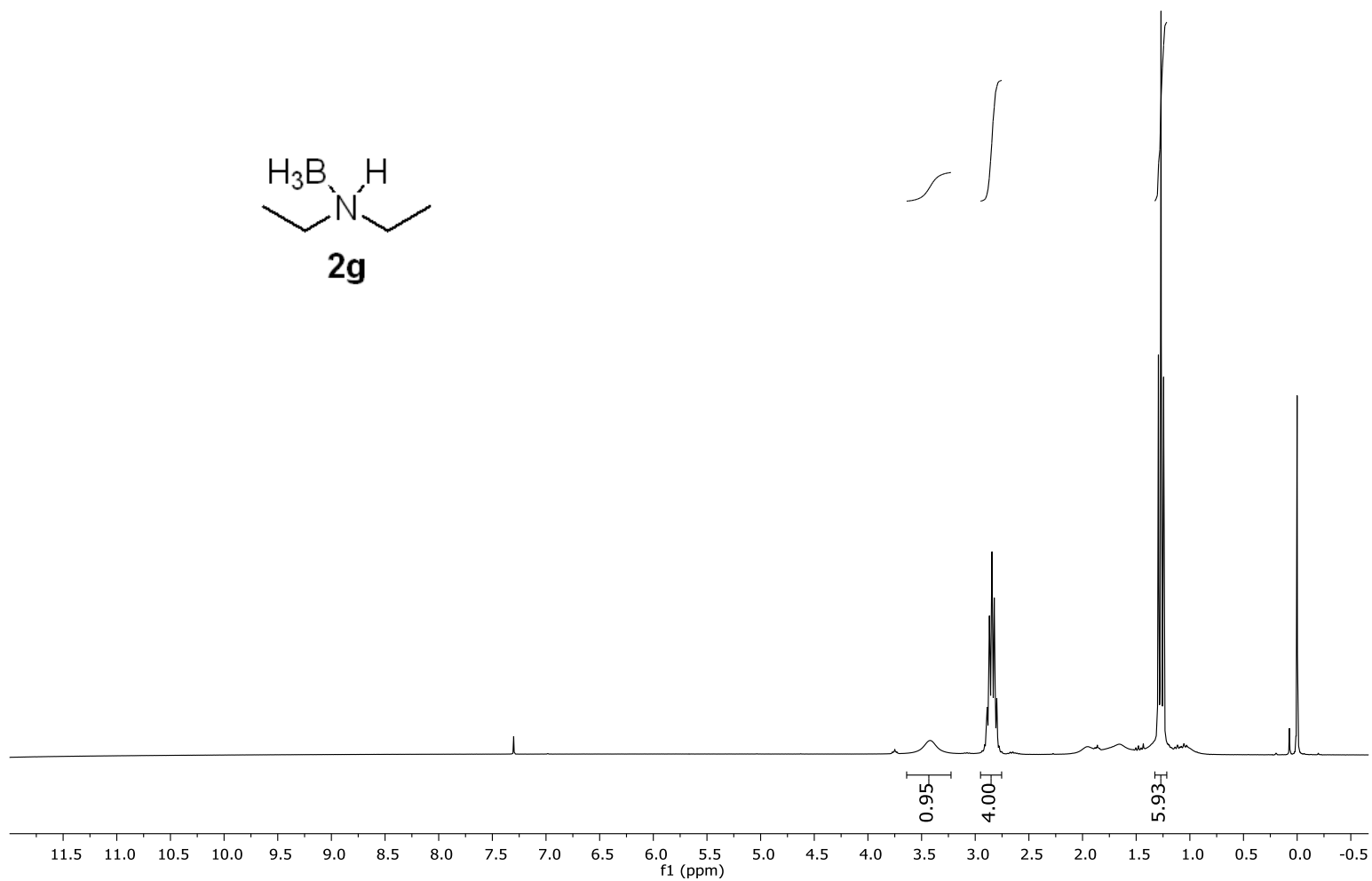
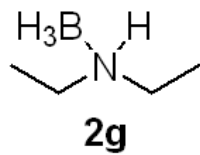
^1H NMR (300 MHz, $\text{DMSO-}d_6$) Benzylamine-borane (**2f**)



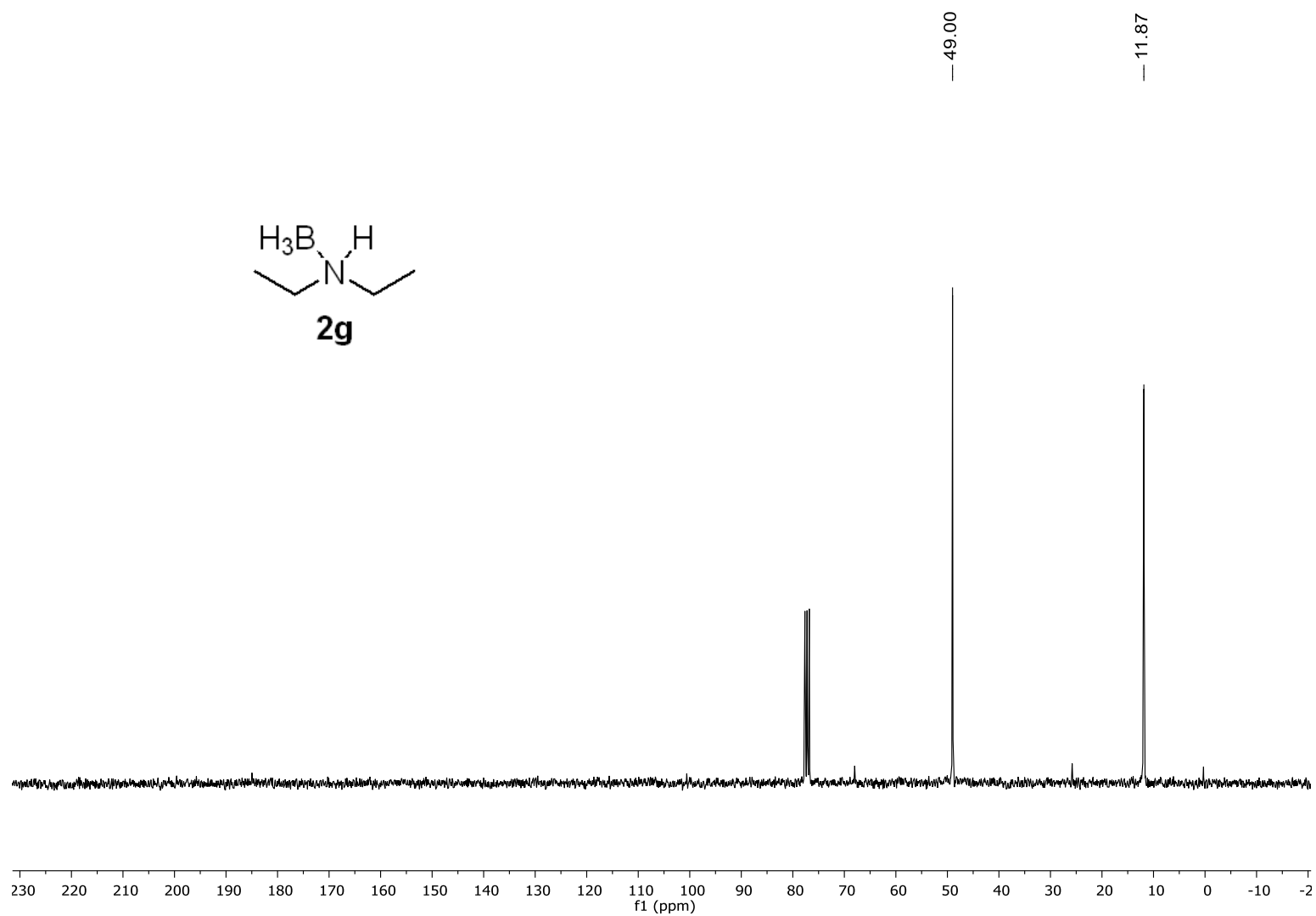
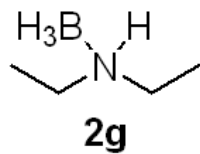
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) Benzylamine-borane (**2f**)



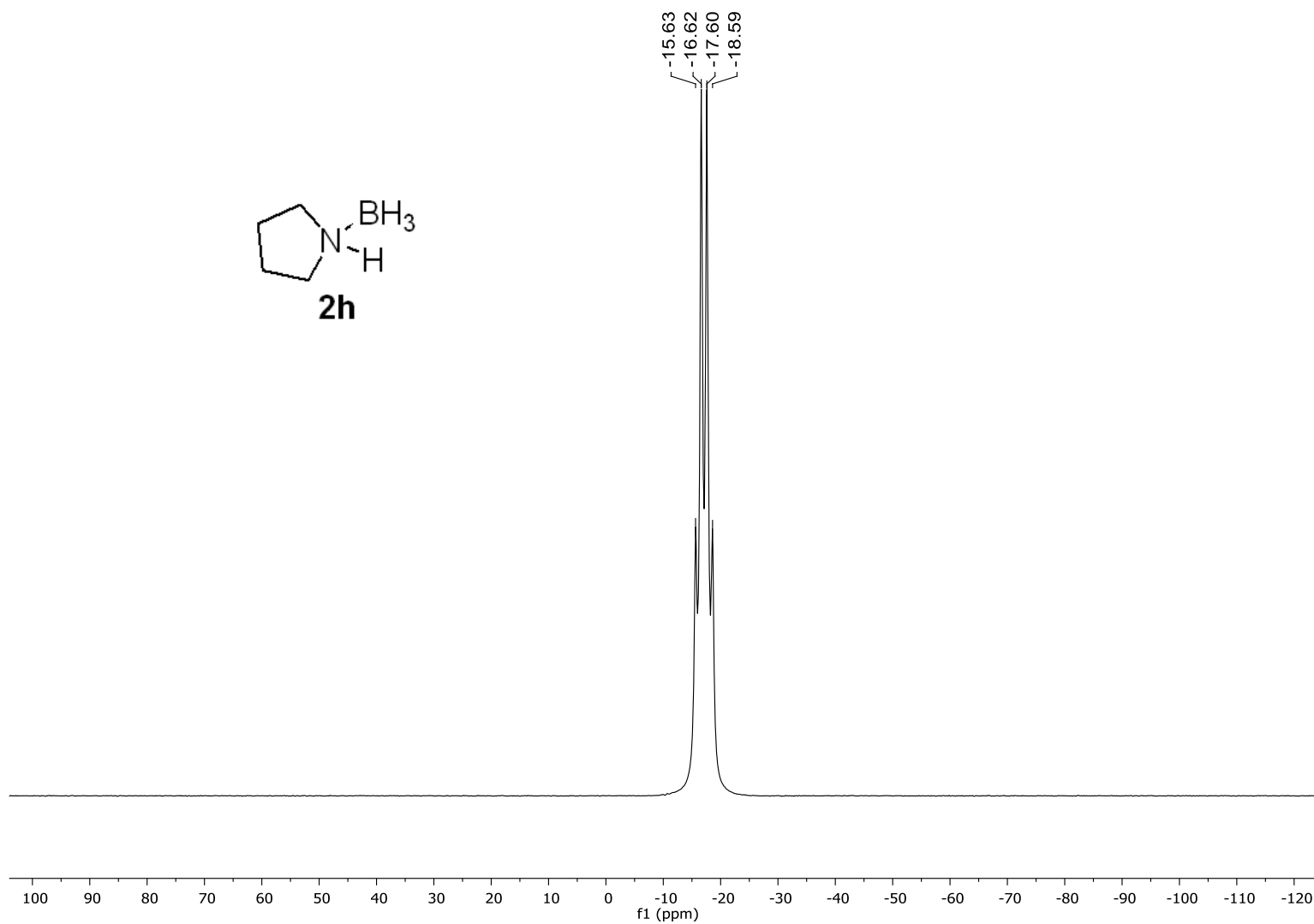
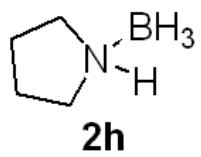
^{11}B NMR (96 MHz, CDCl_3) *N,N*-Diethylamine-borane (**2g**)



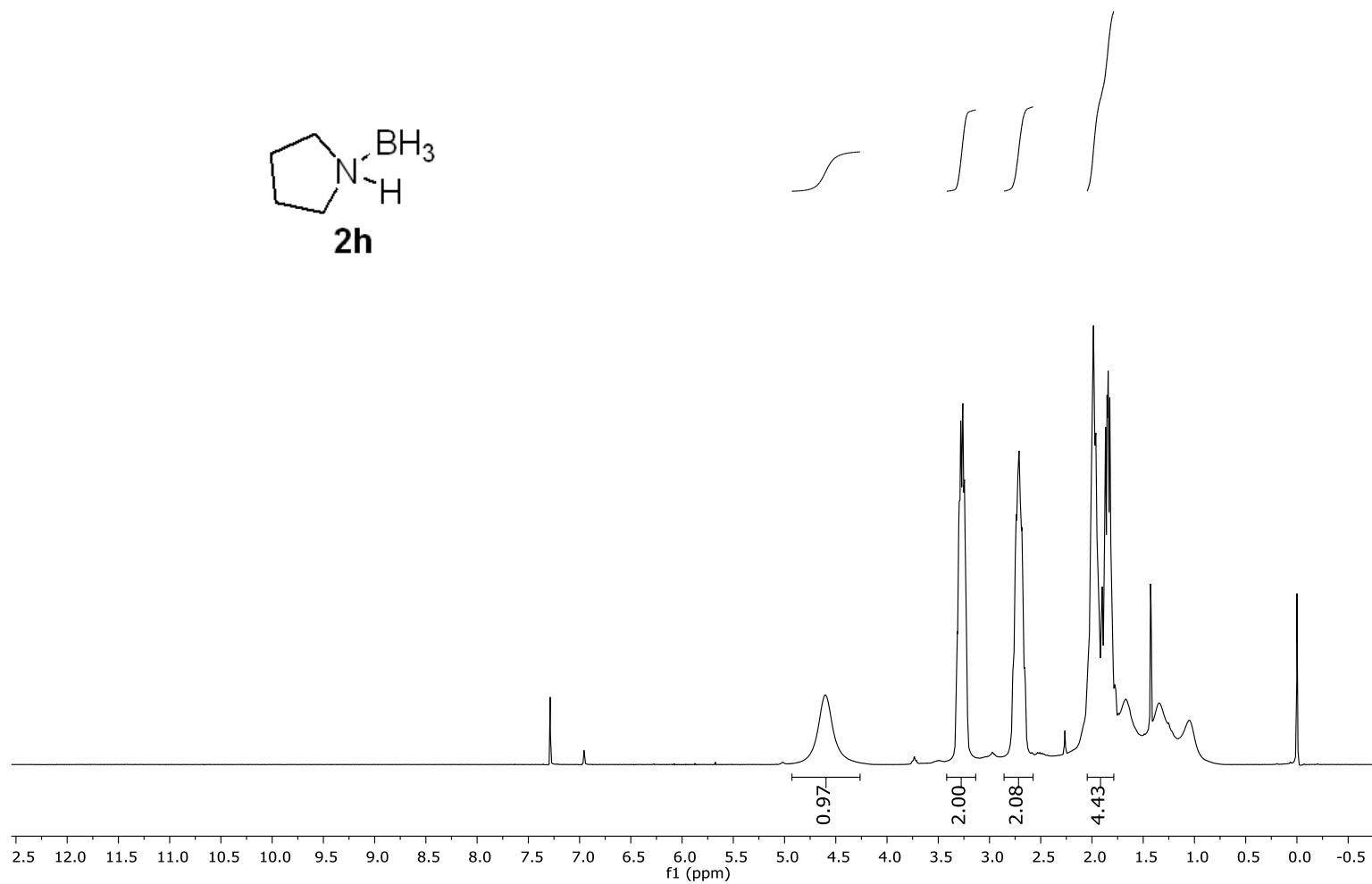
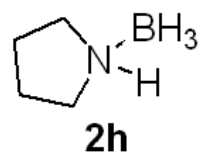
^1H NMR (300 MHz, CDCl_3) *N,N*-Diethylamine-borane (**2g**)

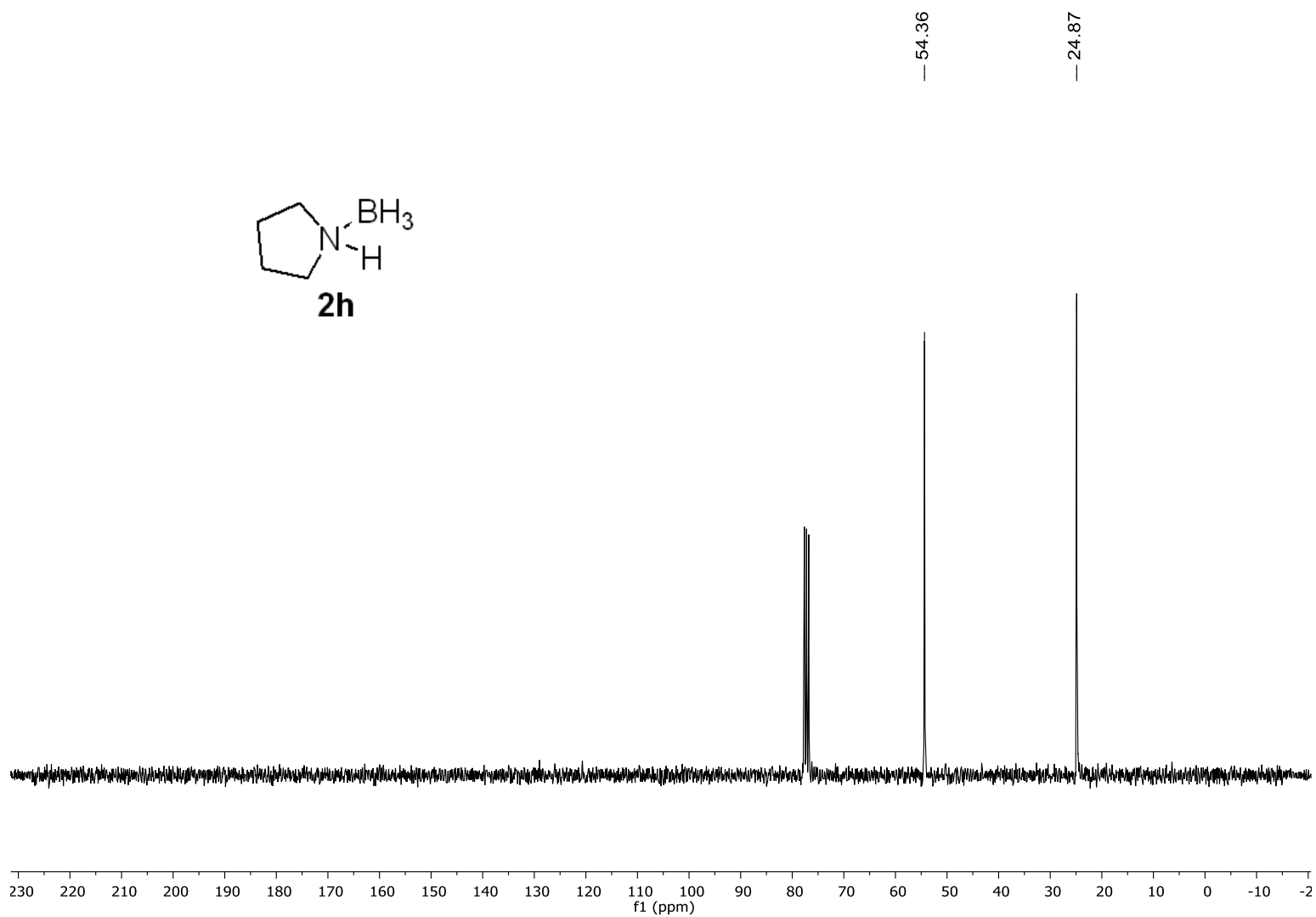
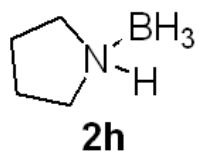


^{13}C NMR (75 MHz, CDCl_3) *N,N*-Diethylamine-borane (**2g**)

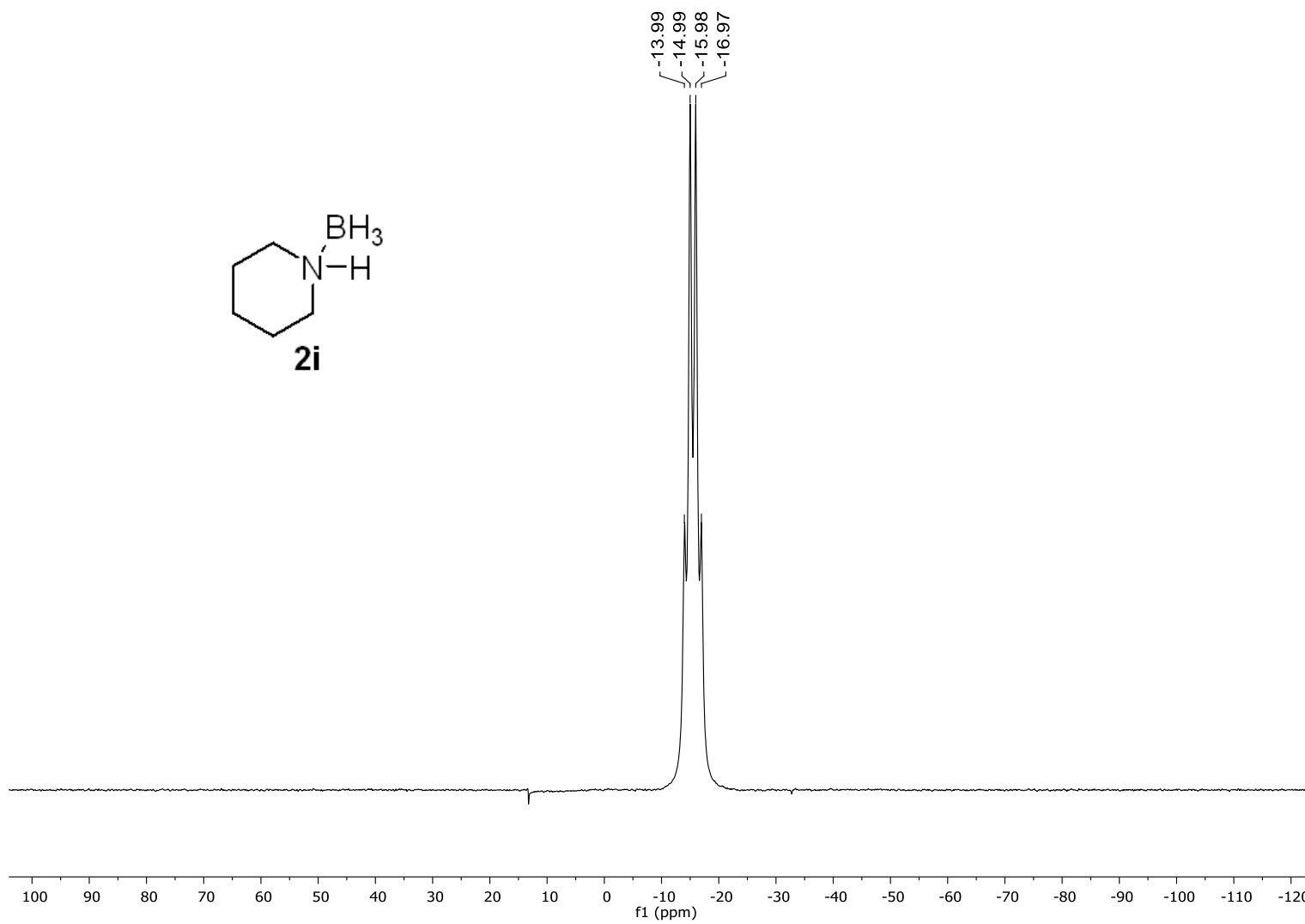
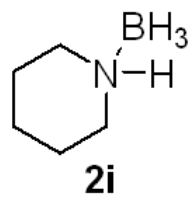


^{11}B NMR (96 MHz, CDCl_3) Pyrrolidine-borane (**2h**)

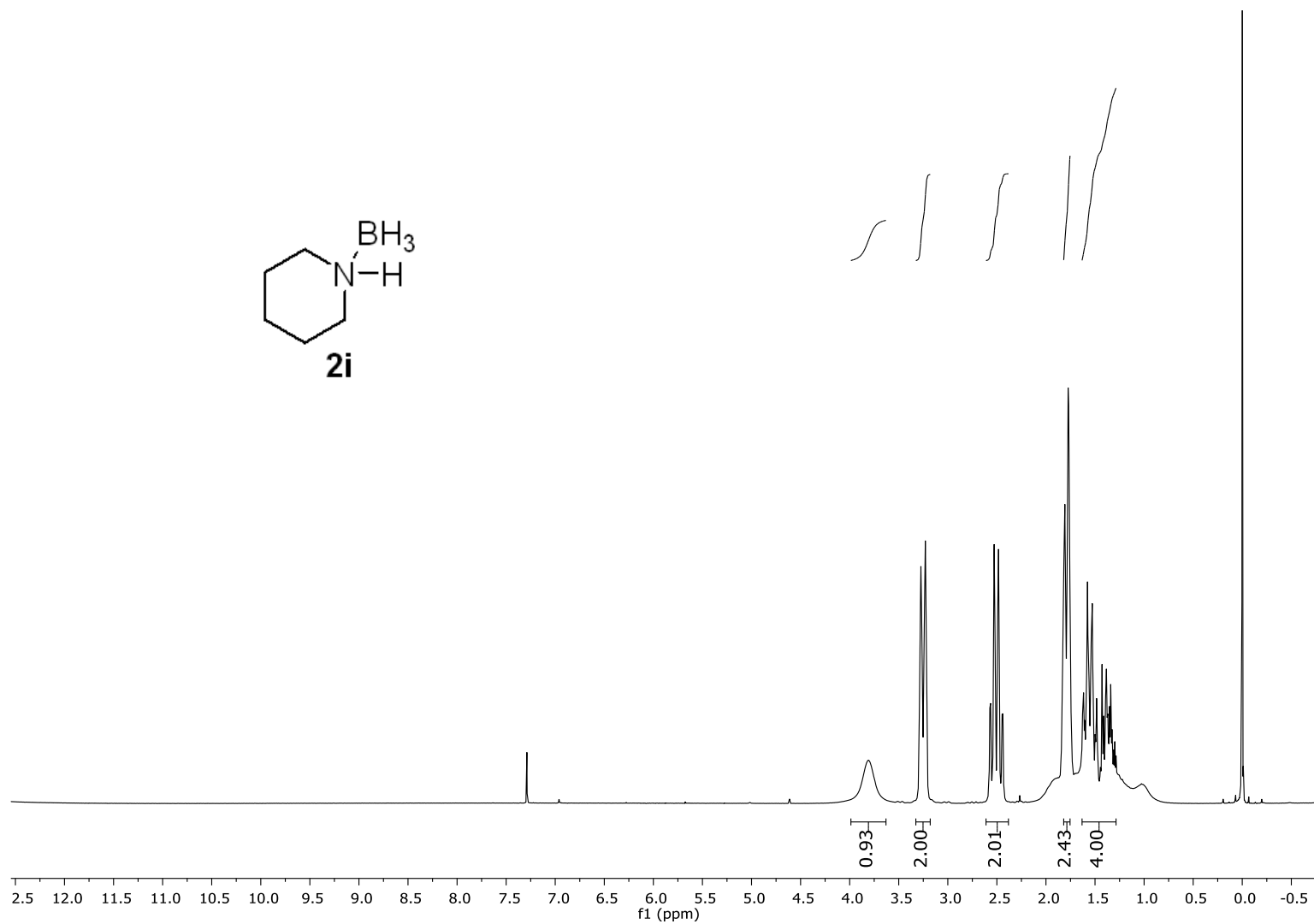


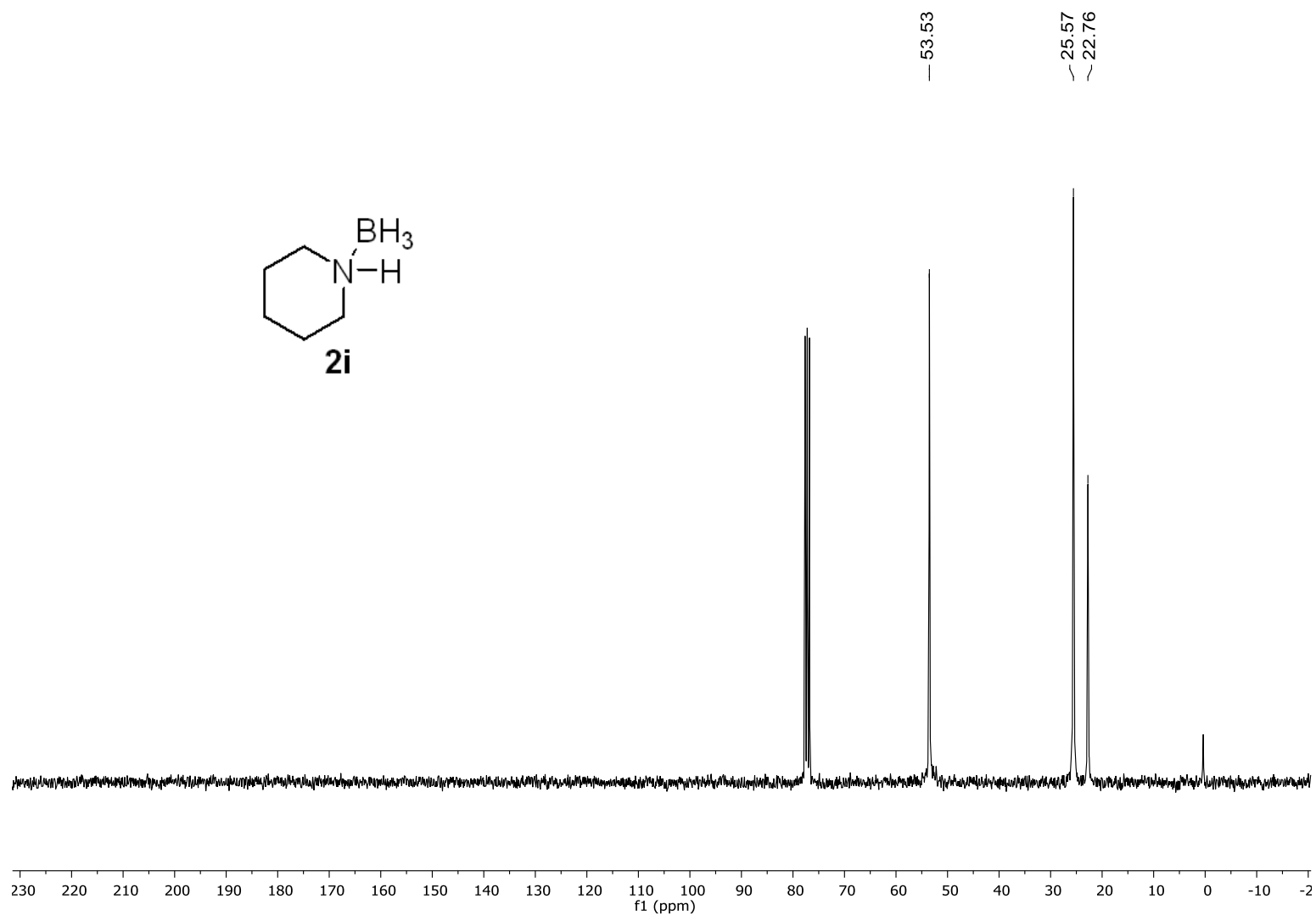
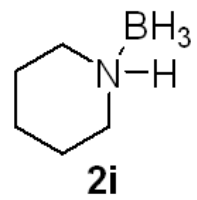


^{13}C NMR (75 MHz, CDCl_3) Pyrrolidine-borane (**2h**)

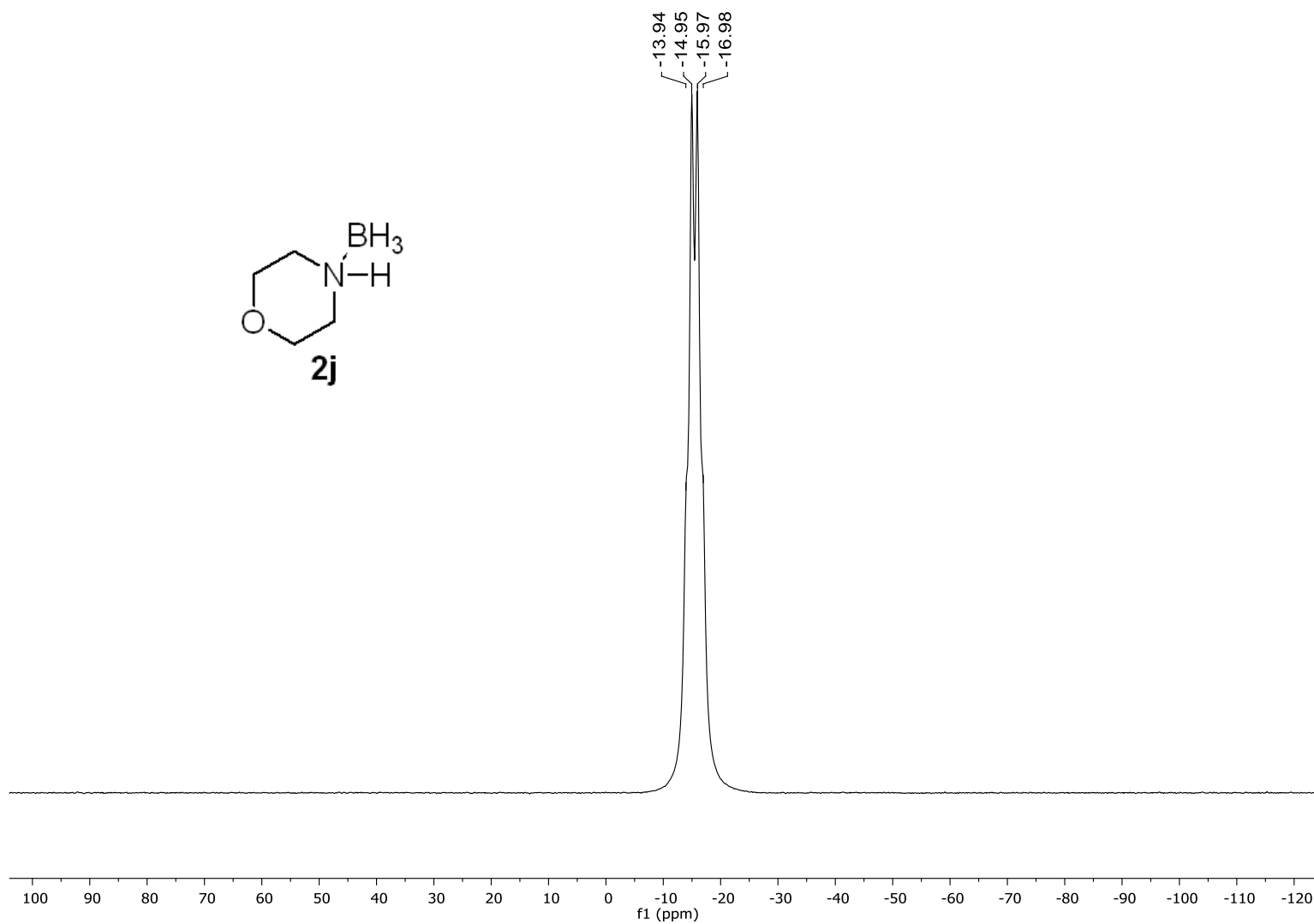
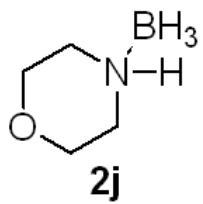


^{11}B NMR (96 MHz, CDCl_3) Piperidine-borane (**2i**)

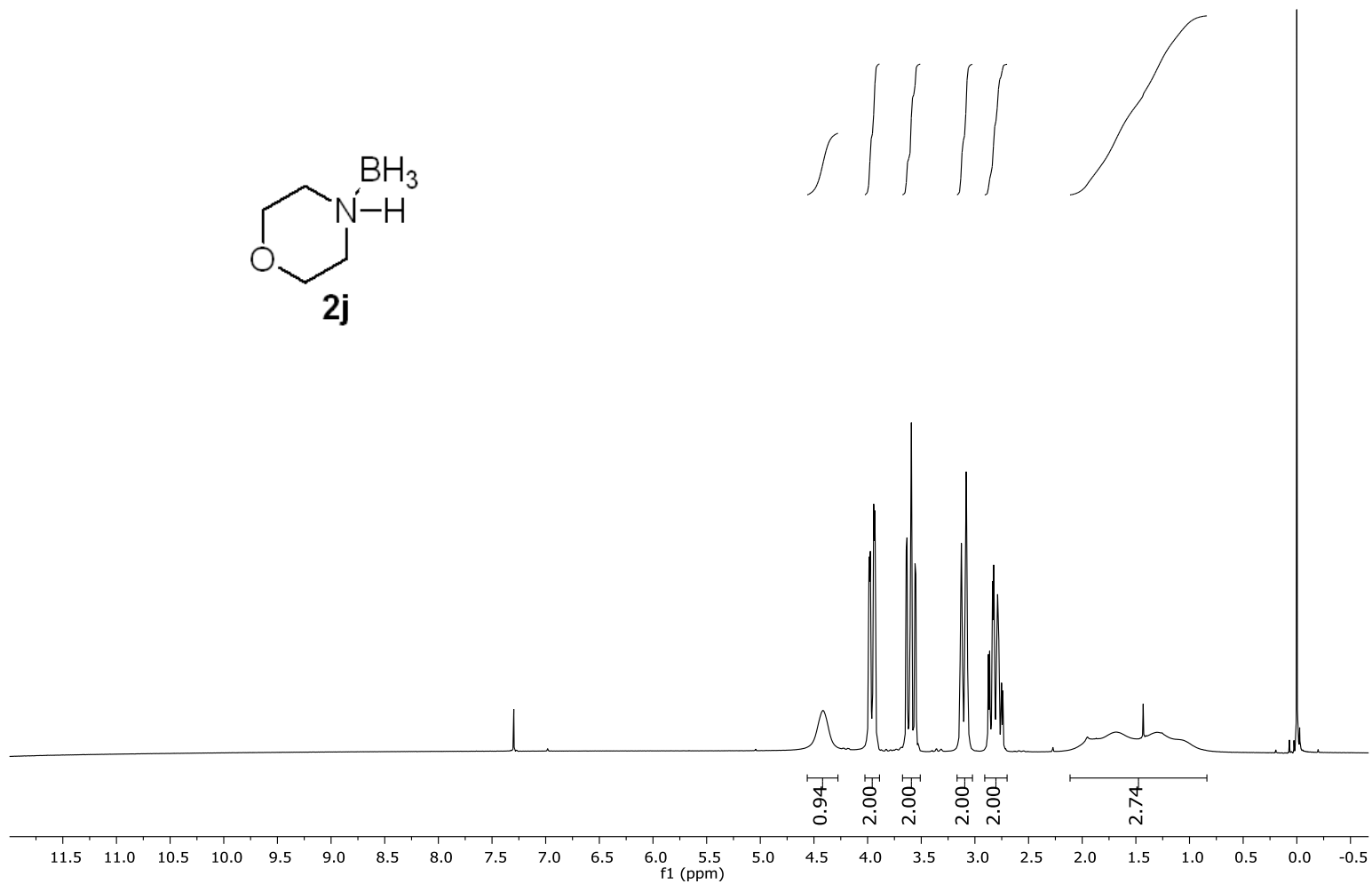
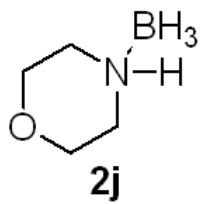


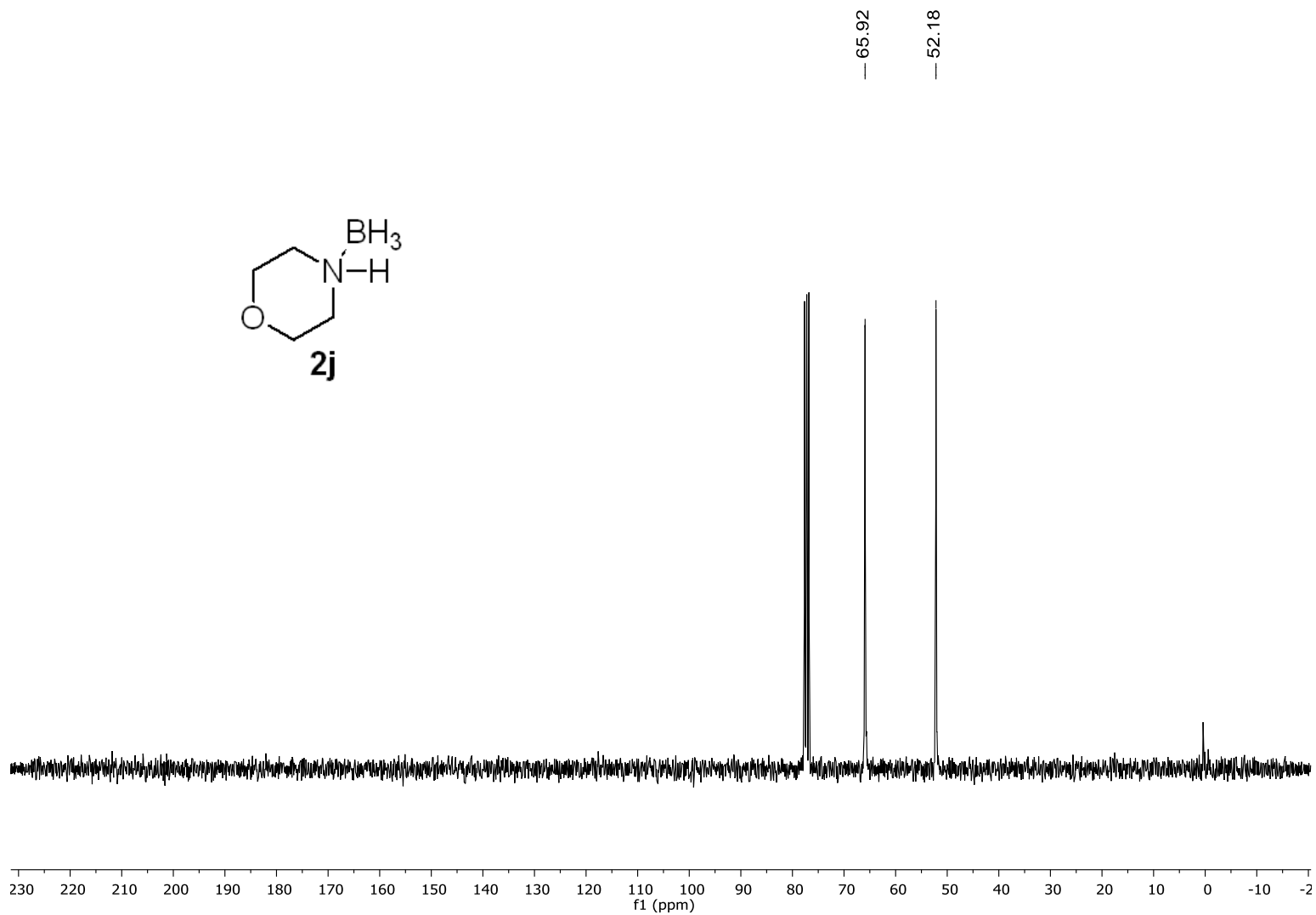
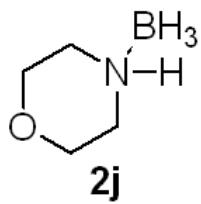


^{13}C NMR (75 MHz, CDCl_3) Piperidine-borane (**2i**)

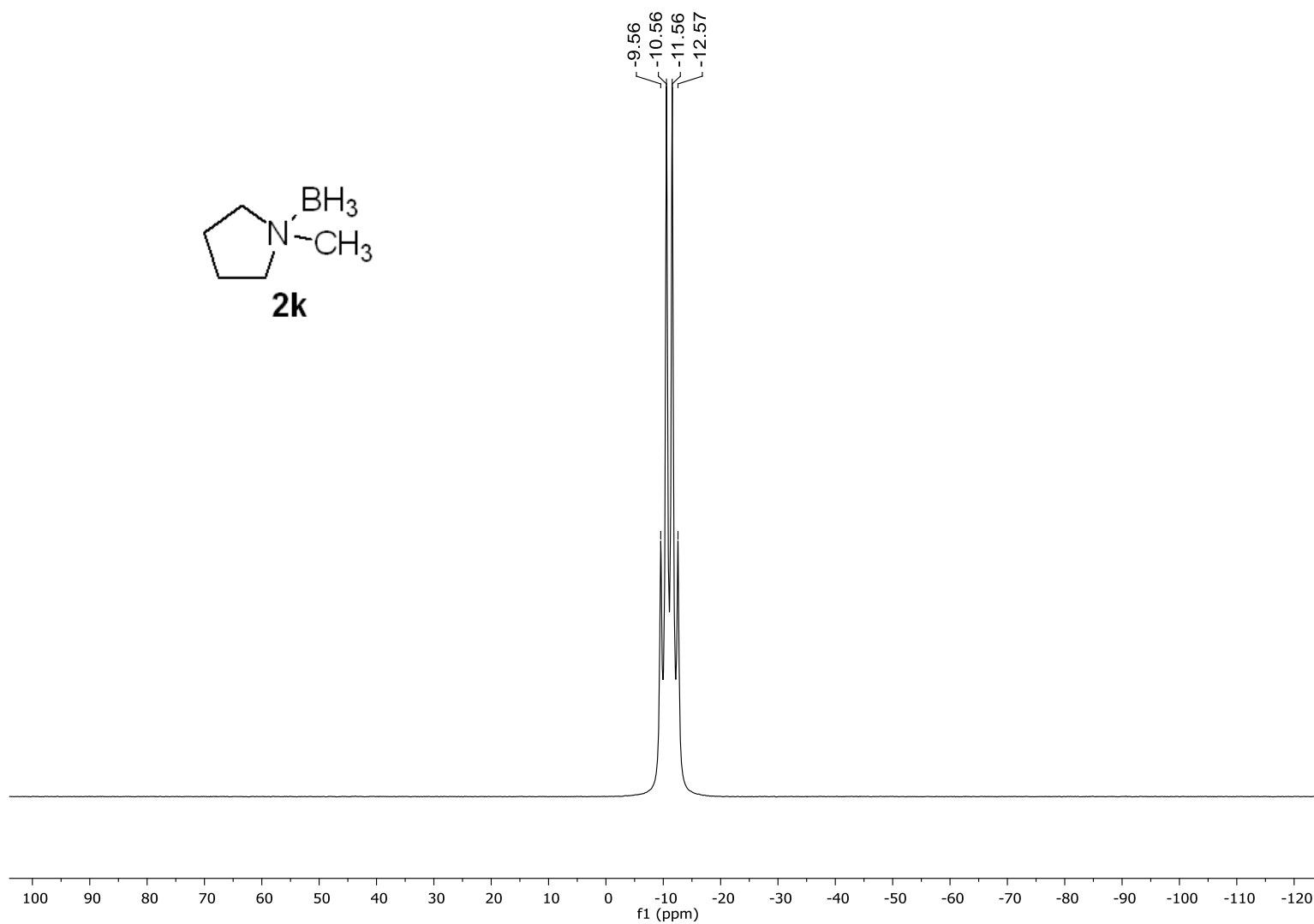
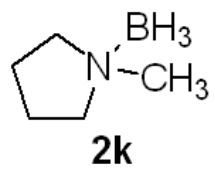


^{11}B NMR (96 MHz, CDCl_3) Morpholine-borane (**2j**)

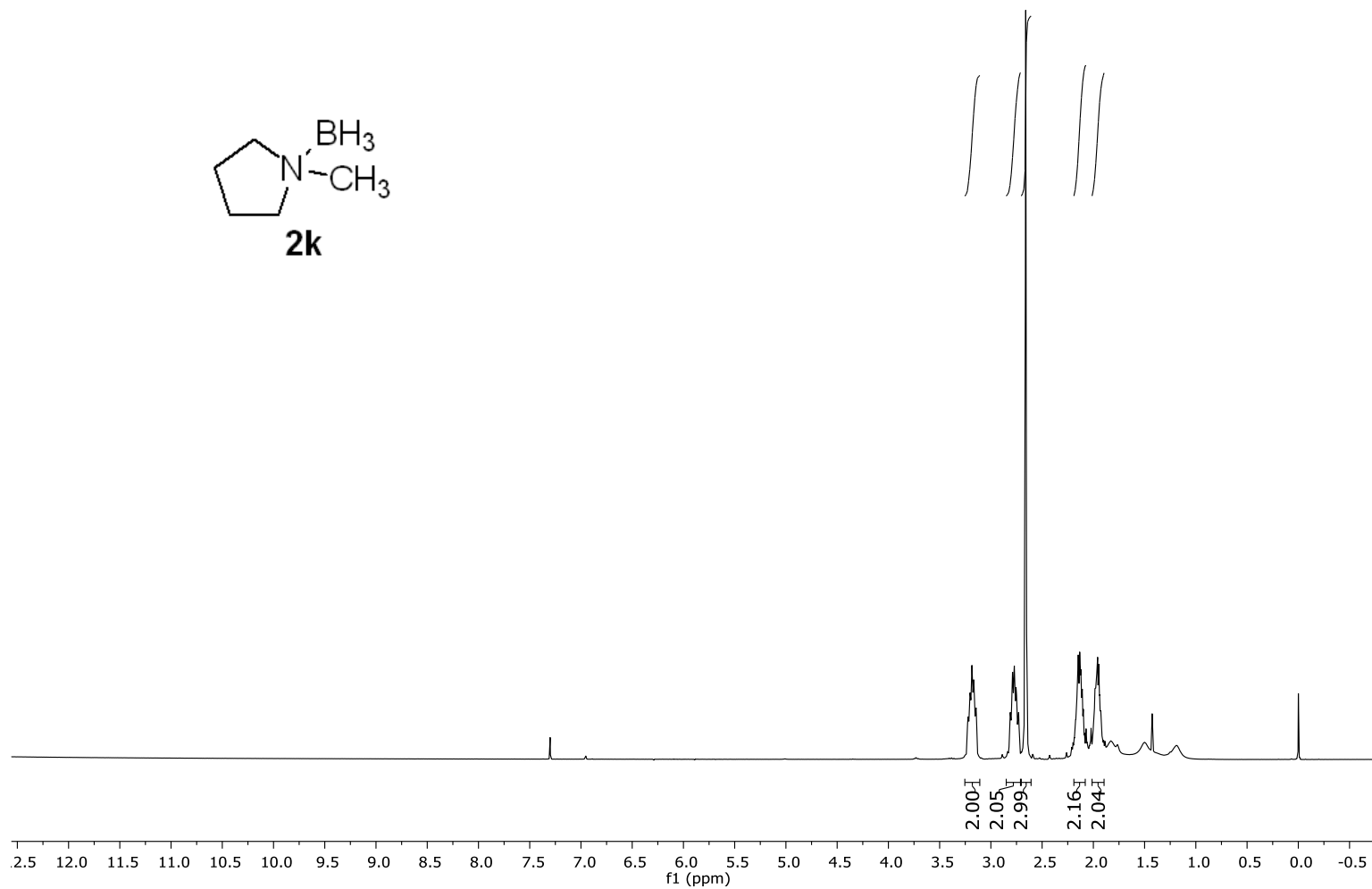
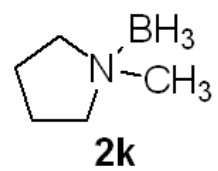




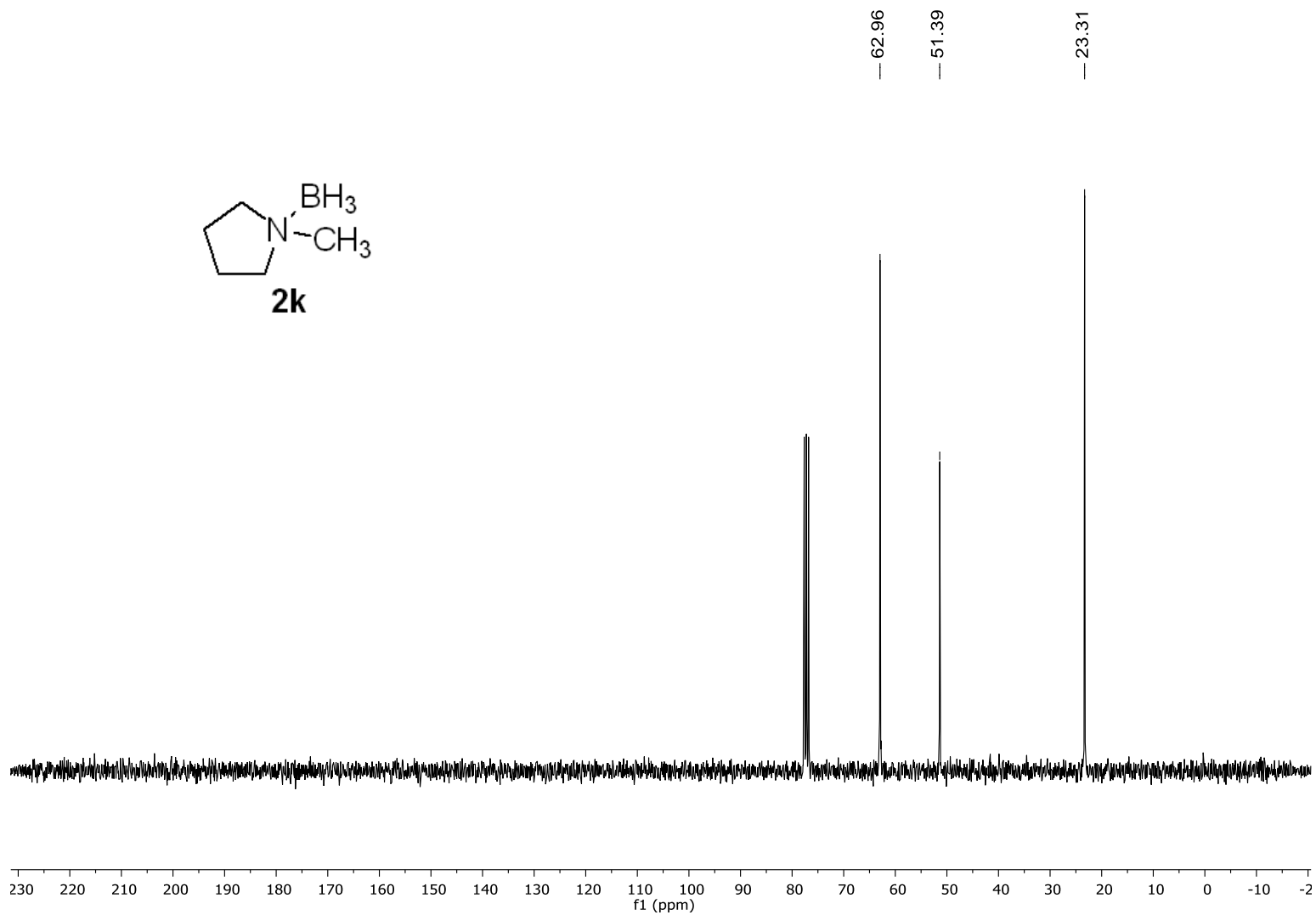
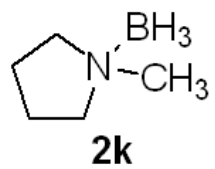
^{13}C NMR (75 MHz, CDCl₃) Morpholine-borane (**2j**)



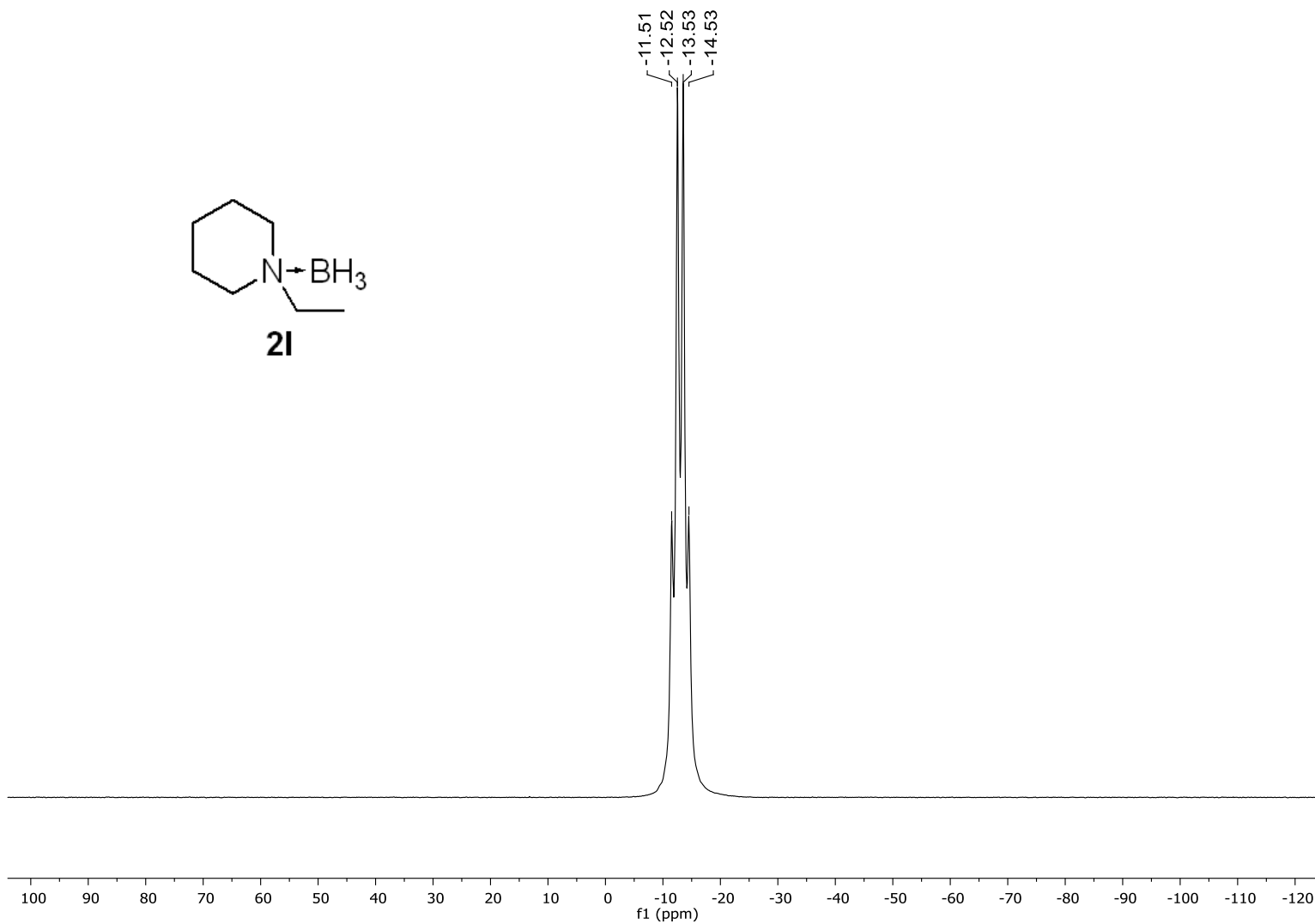
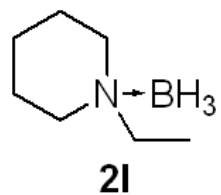
^{11}B NMR (96 MHz, CDCl_3) *N*-Methylpyrrolidine-borane (**2k**)



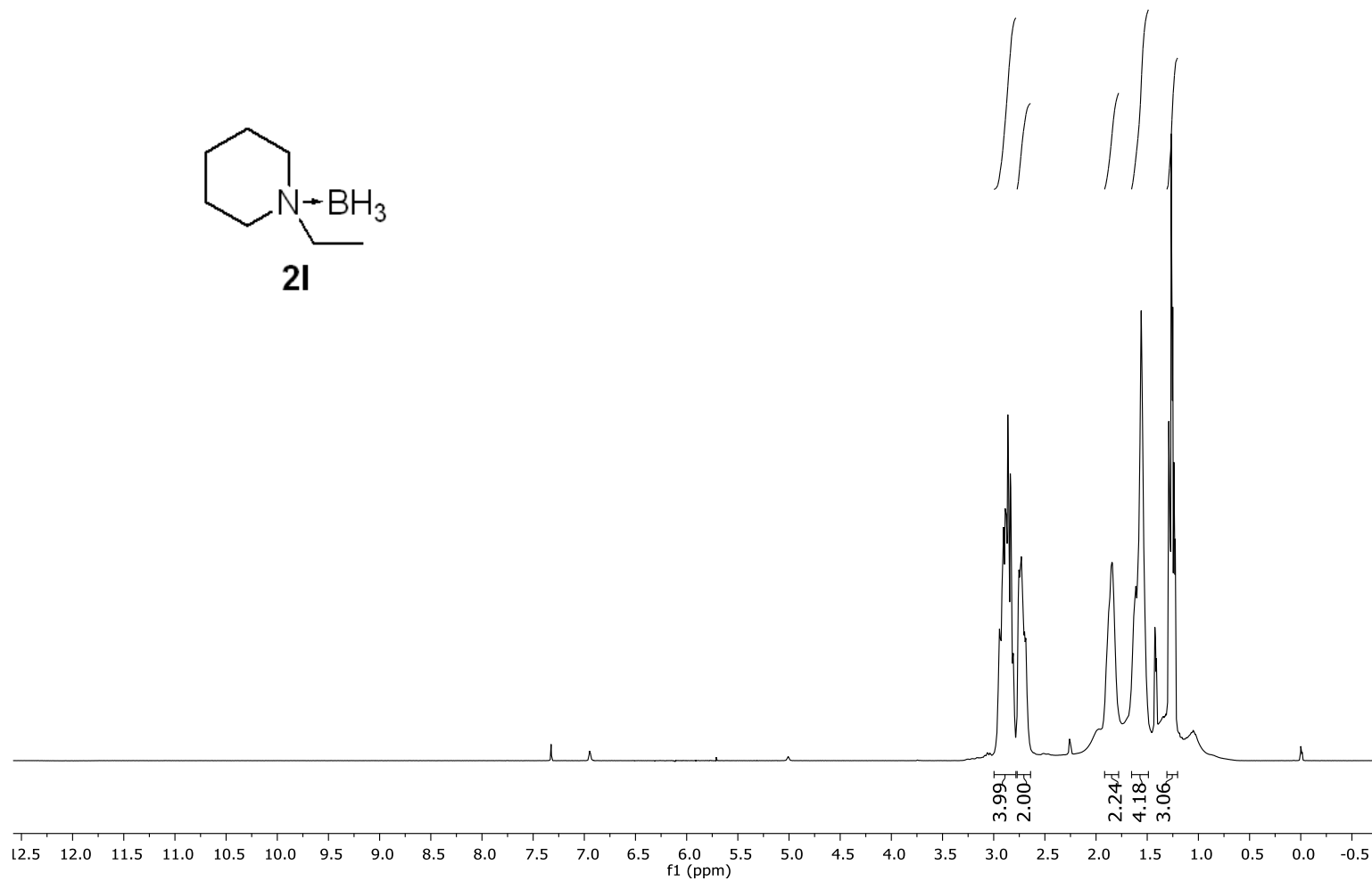
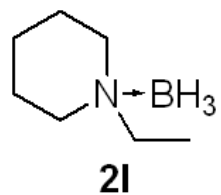
^1H NMR (300 MHz, CDCl_3) *N*-Methylpyrrolidine-borane (**2k**)

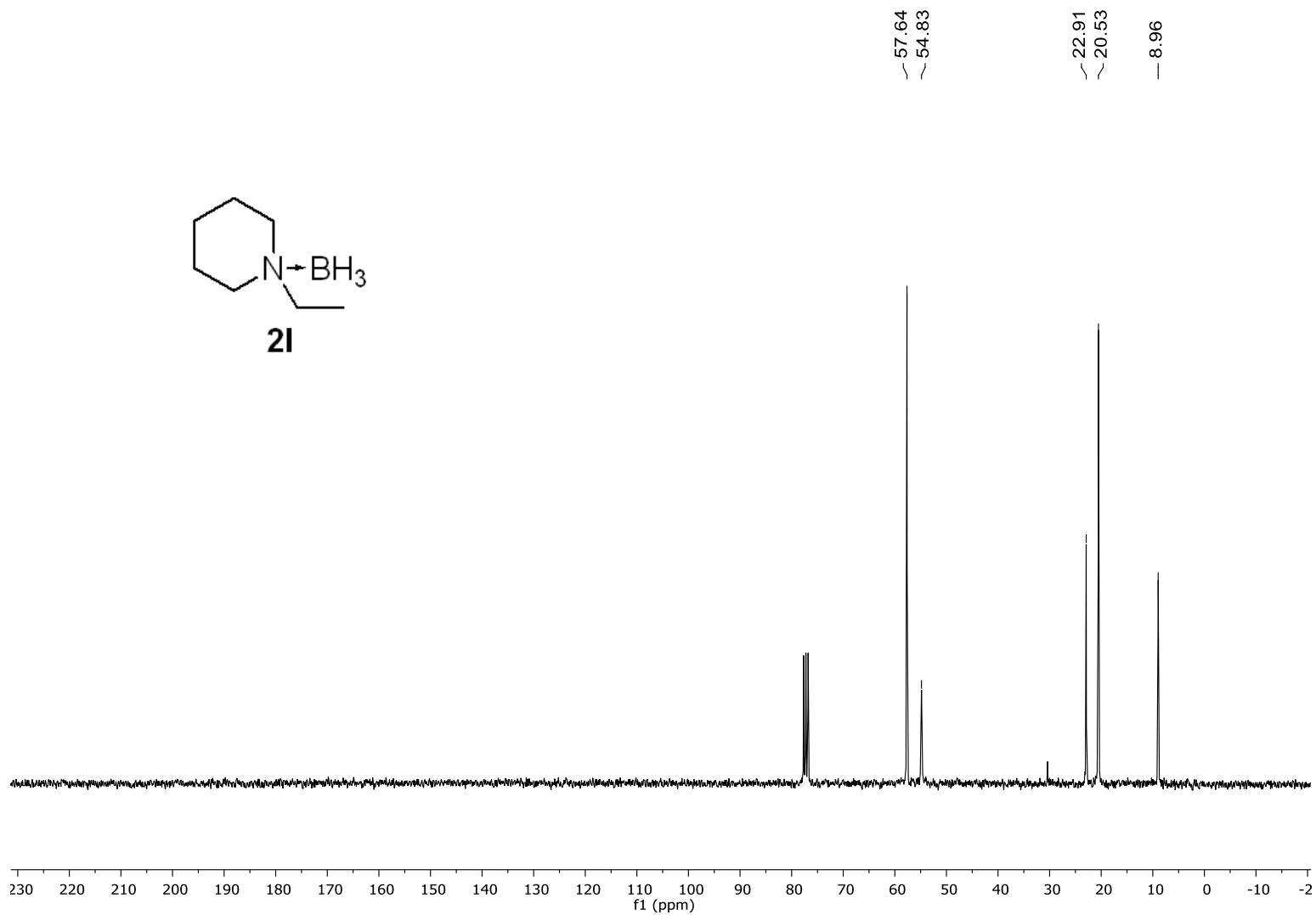
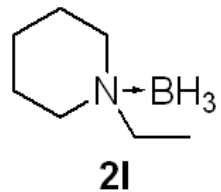


^{13}C NMR (75 MHz, CDCl_3) *N*-Methylpyrrolidine-borane (**2k**)

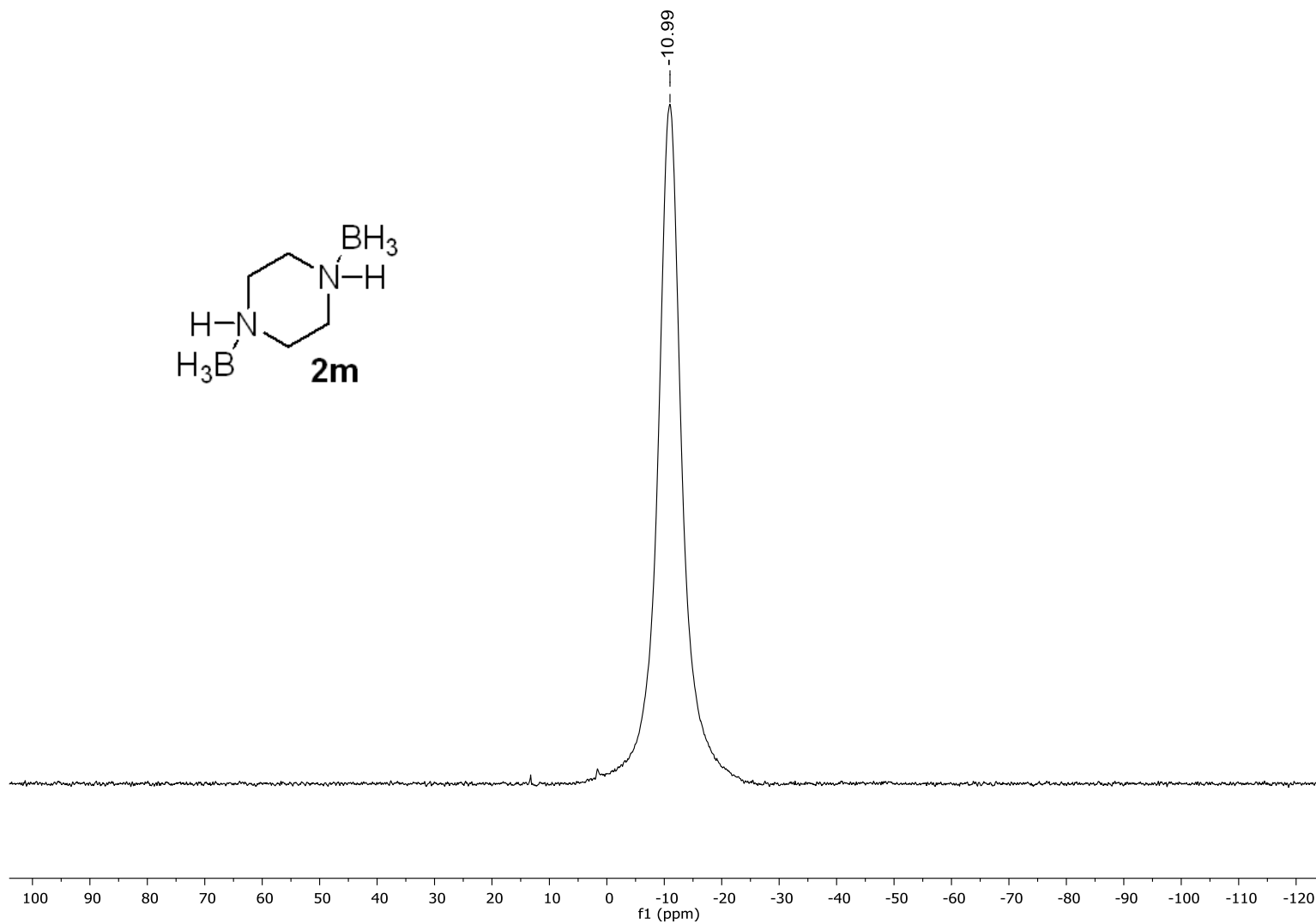
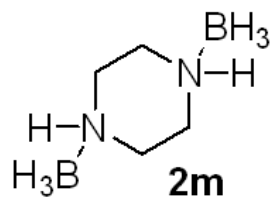


^{11}B NMR (96 MHz, CDCl_3) N-Ethylpiperidine-borane (**2I**)

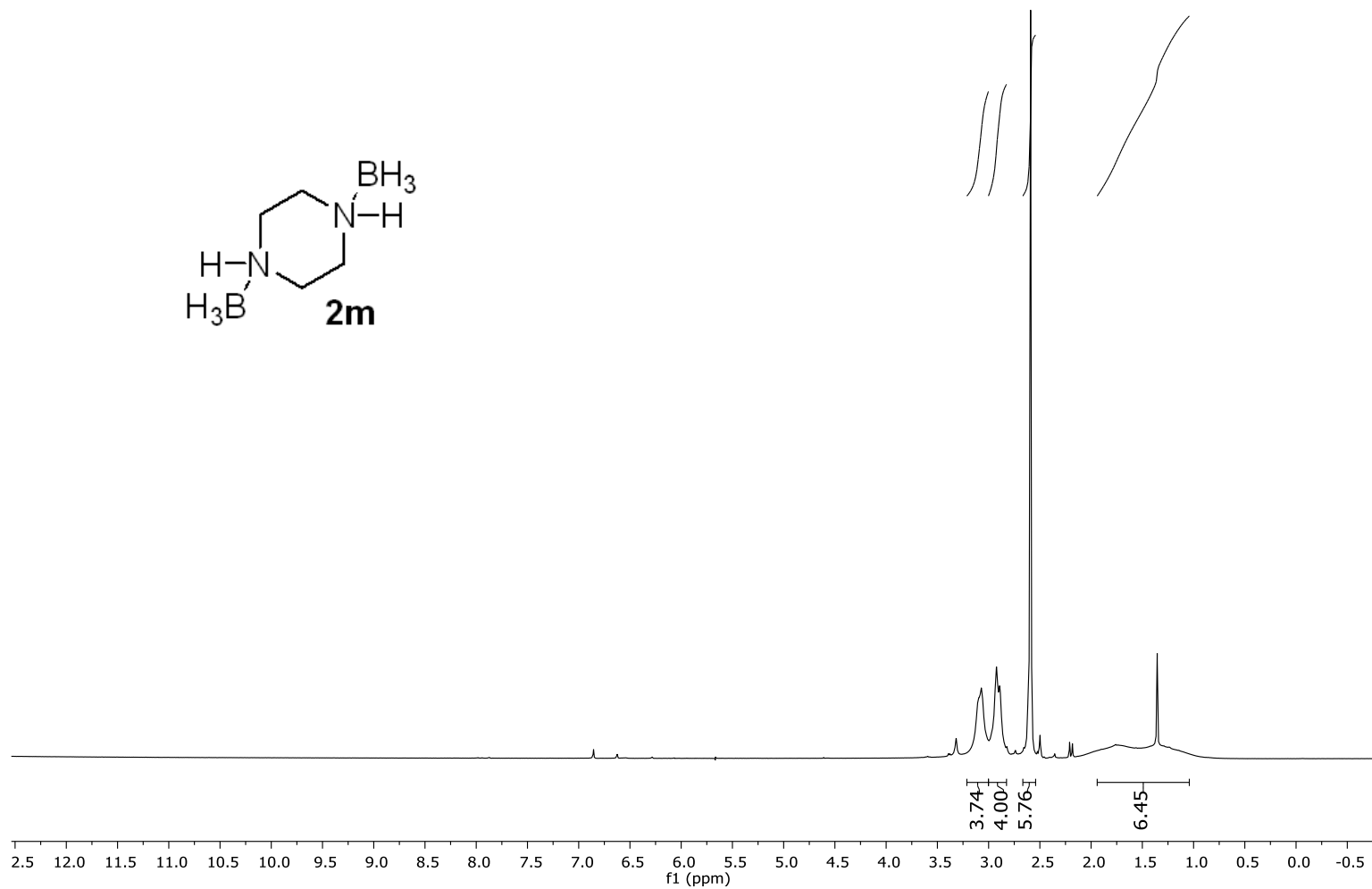
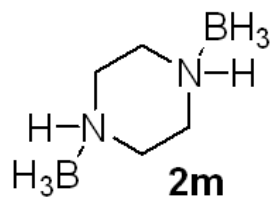


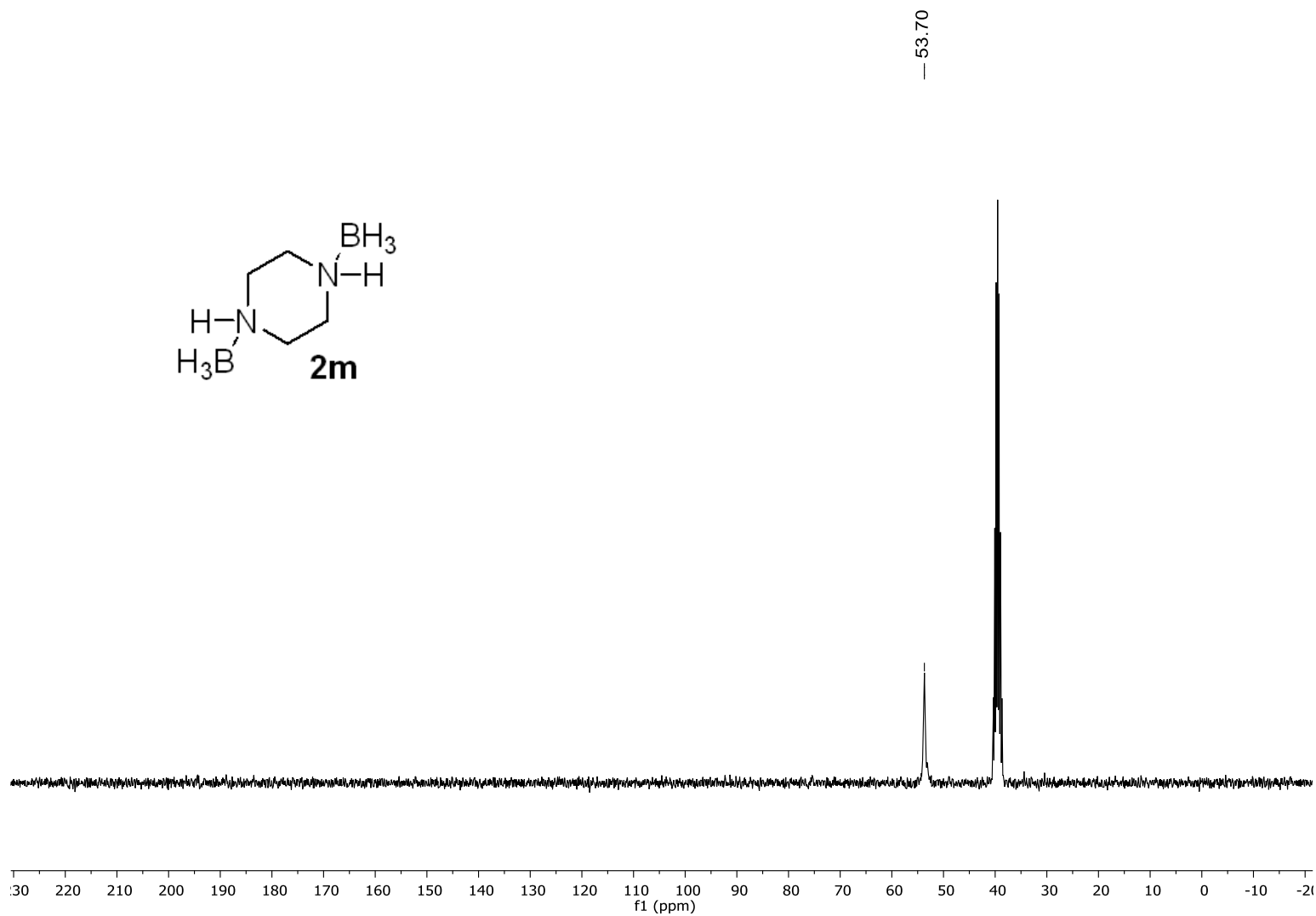
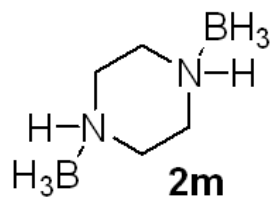


¹³C NMR (75 MHz, CDCl₃) *N*-Ethylpiperidine-borane (**2I**)

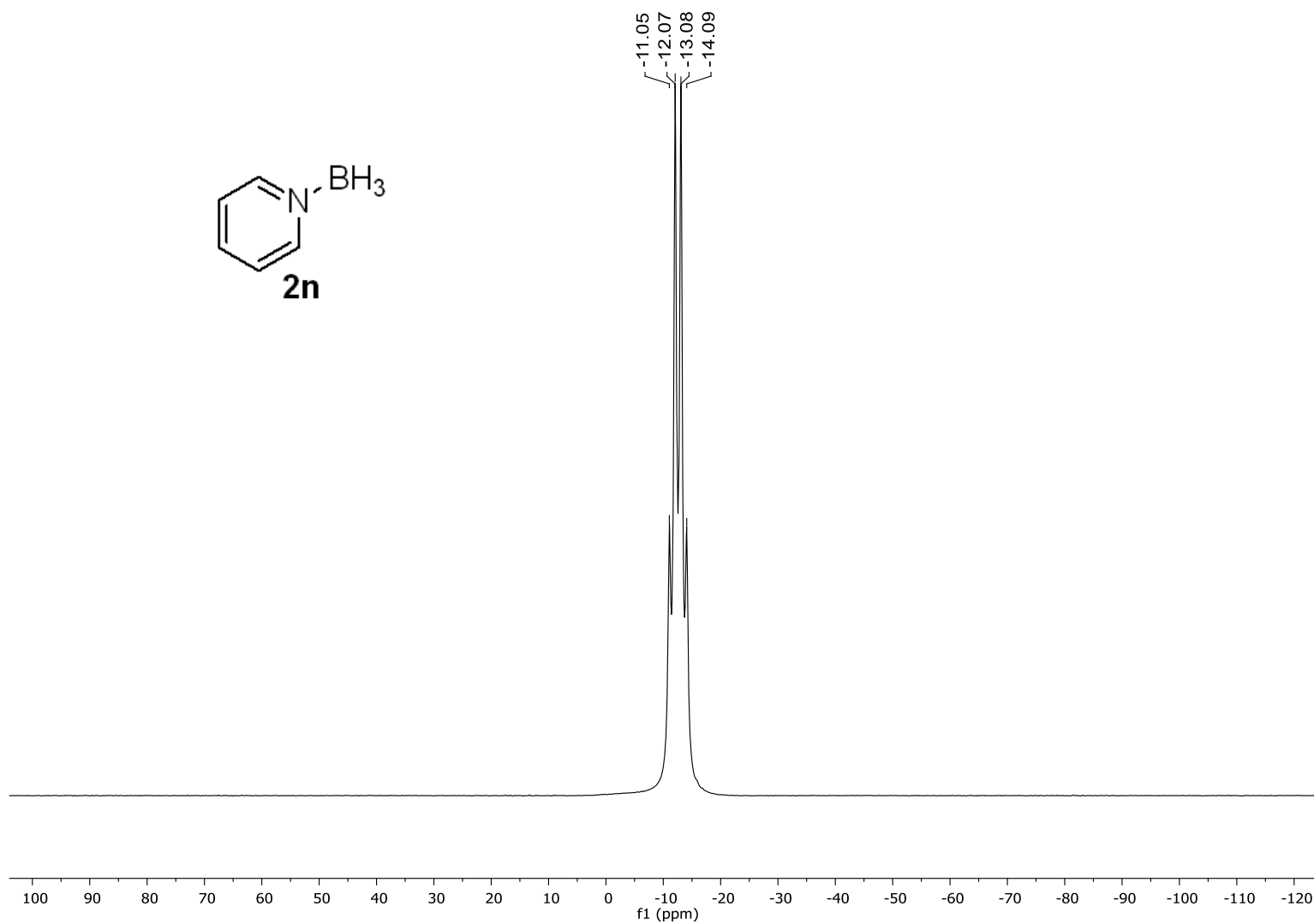
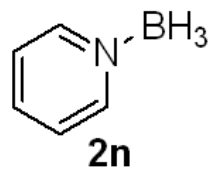


^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) N,N -Dimethylpiperazine-bisborane (**2m**)

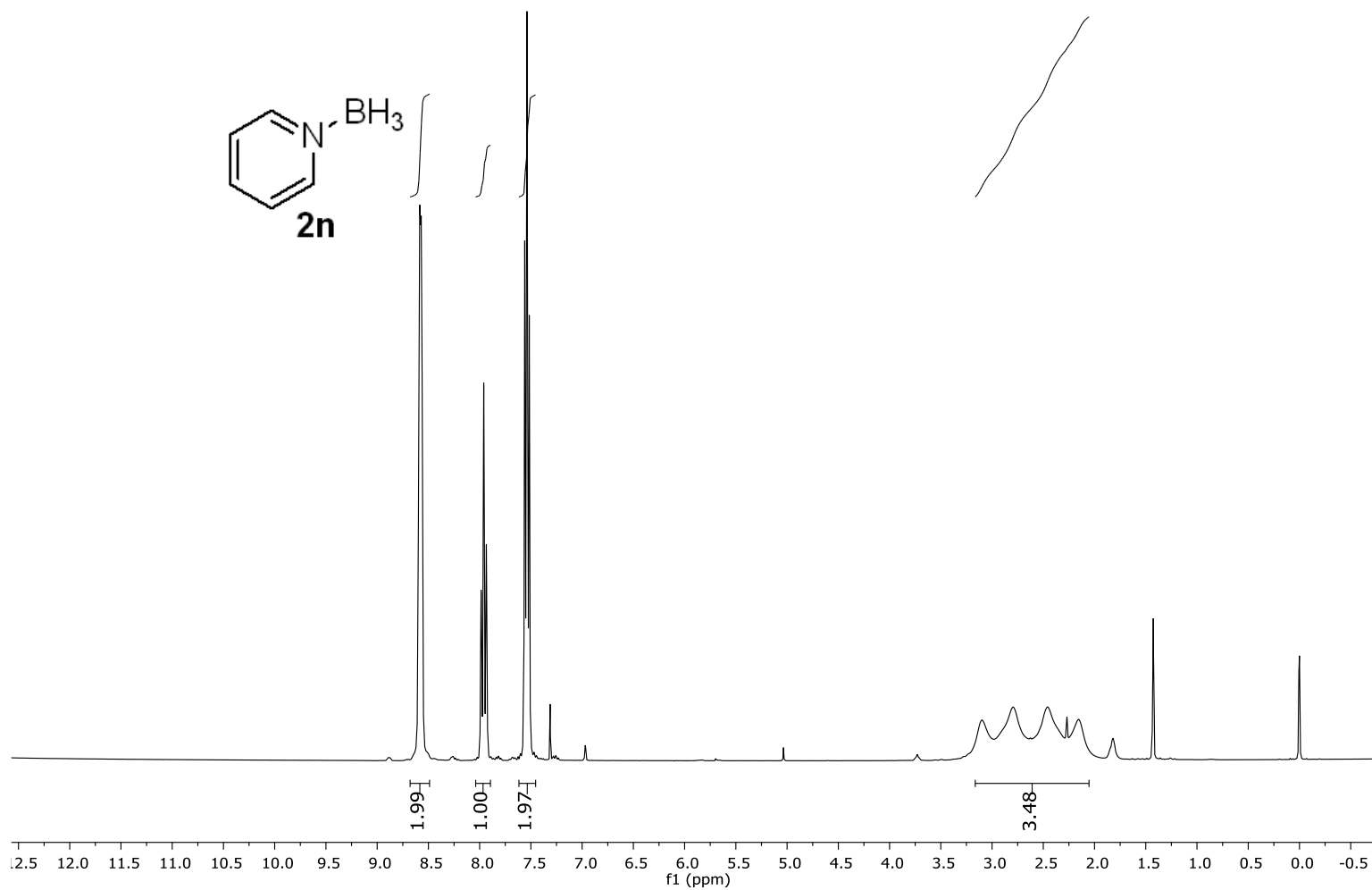




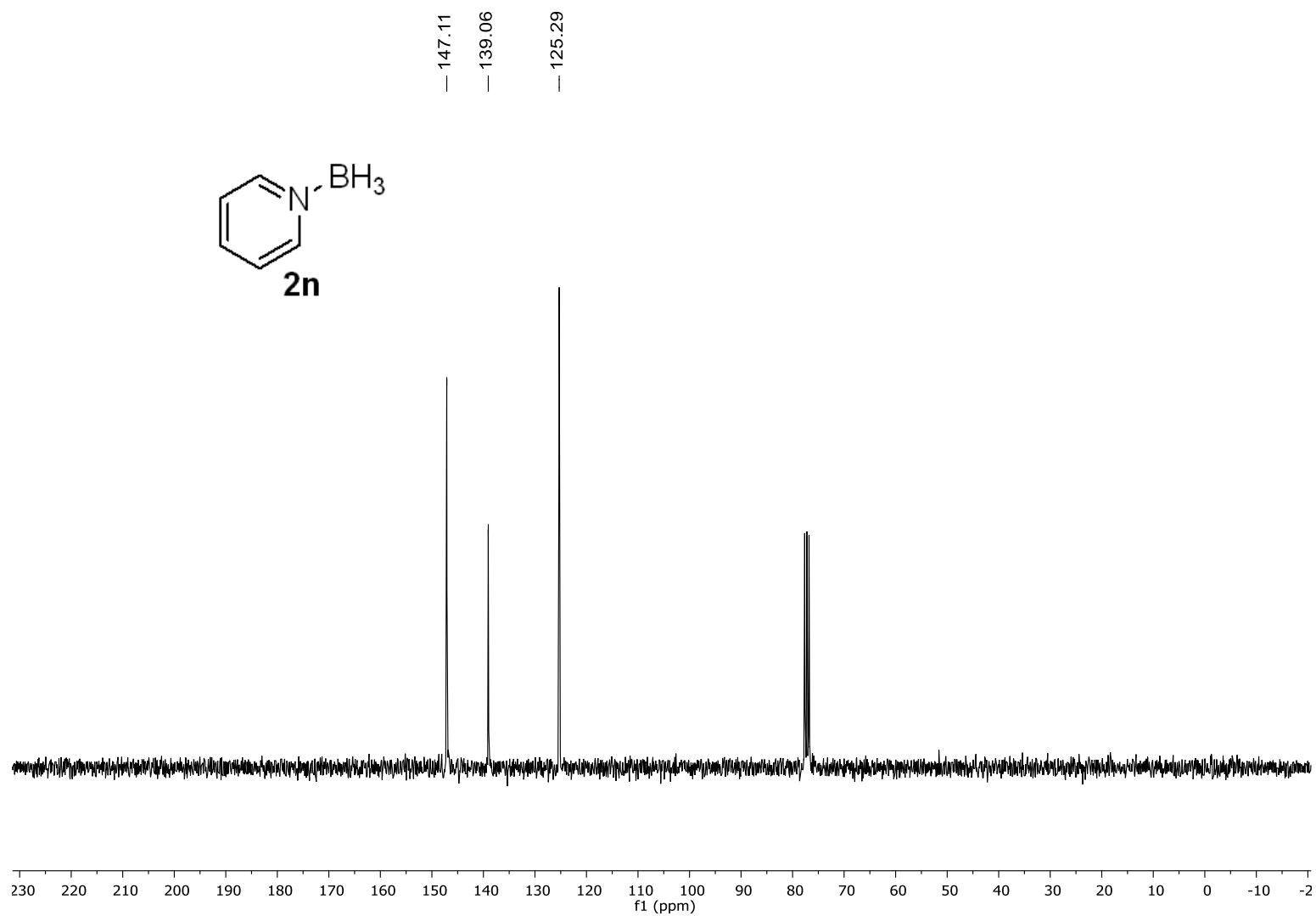
^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) *N,N*-Dimethylpiperazine-bisborane (**2m**)

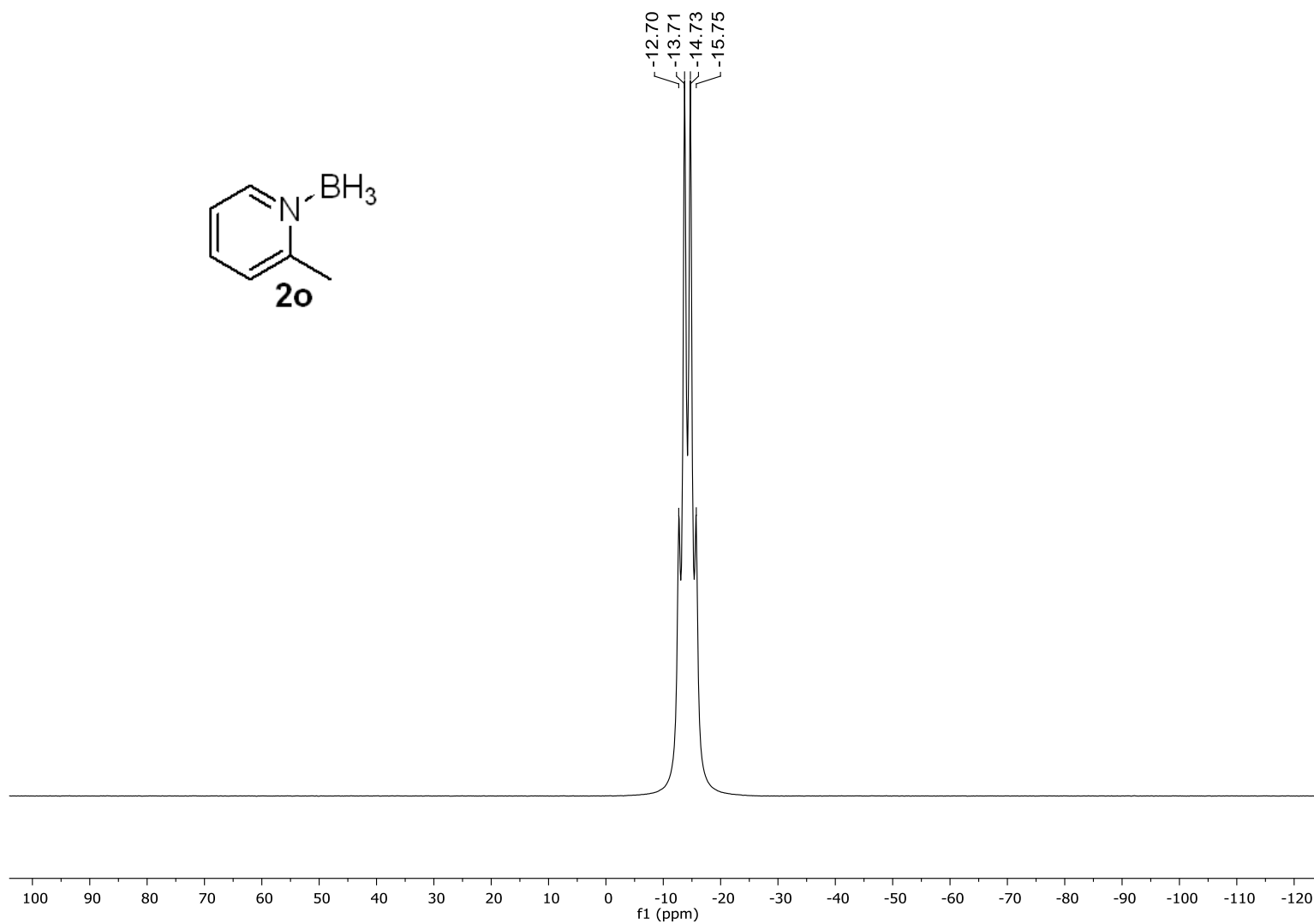


^{11}B NMR (96 MHz, CDCl_3) Pyridine-borane (**2n**)

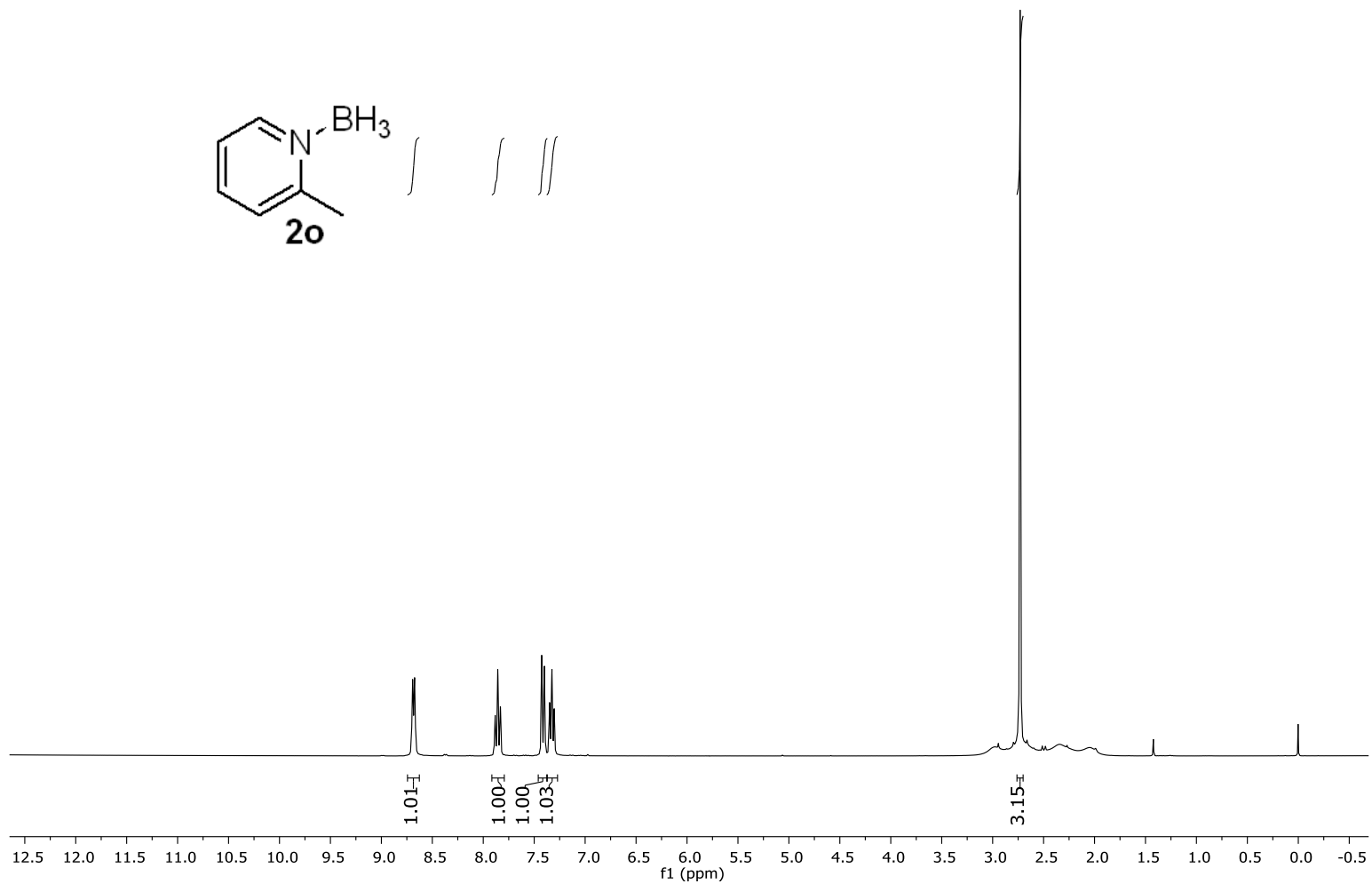
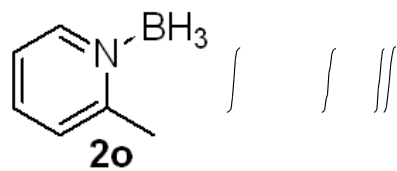


^1H NMR (300 MHz, CDCl_3) Pyridine-borane (**2n**)

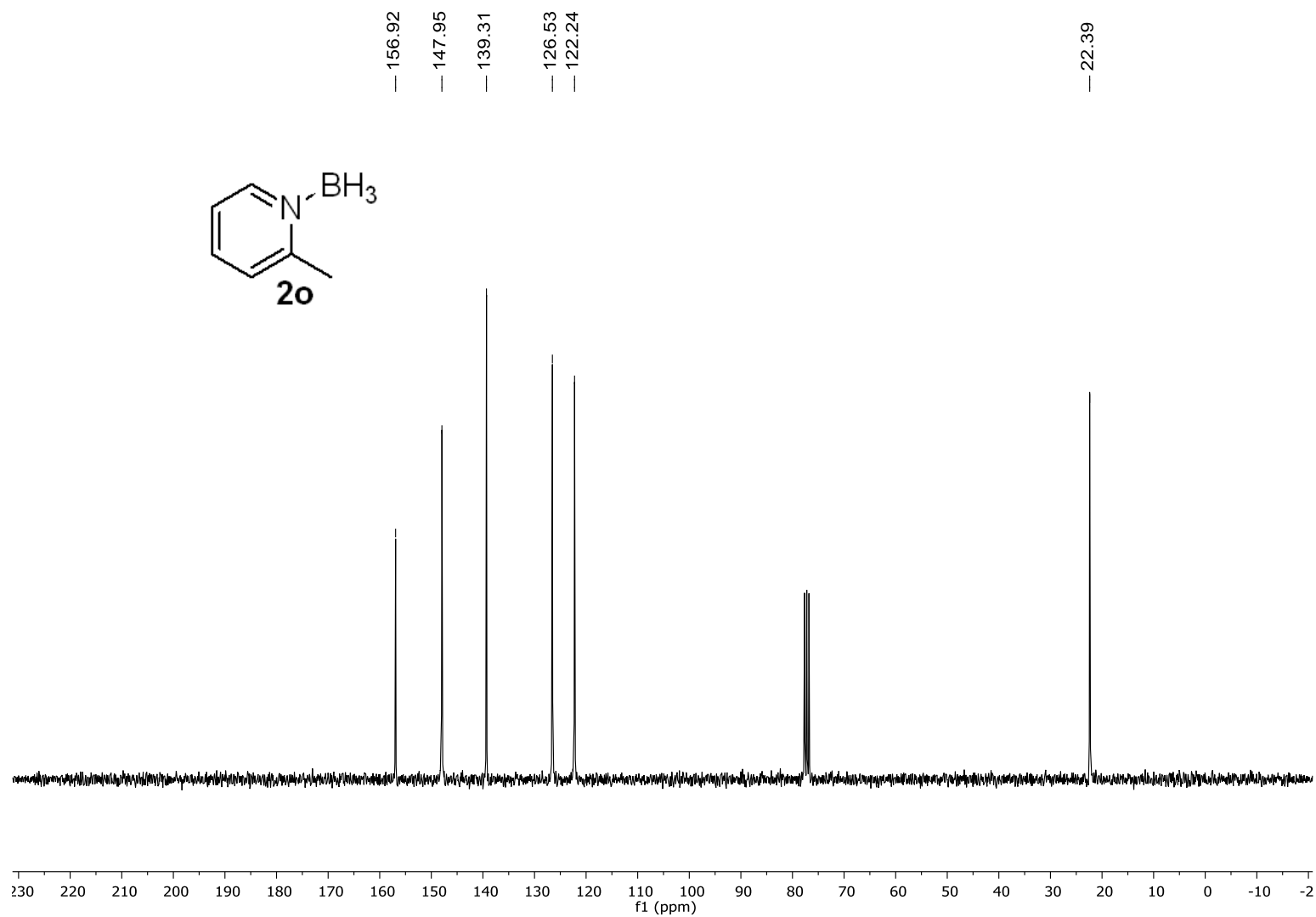


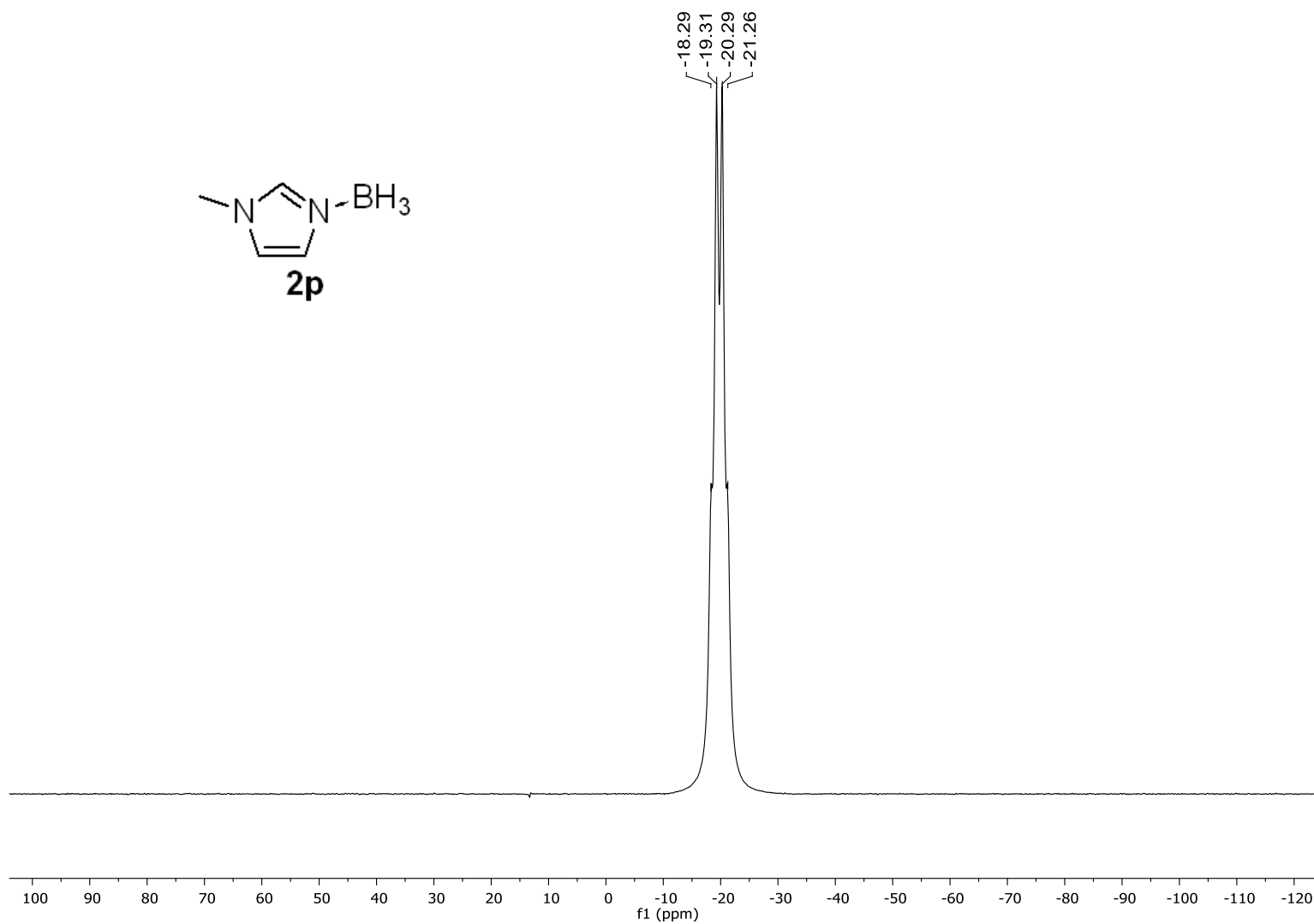
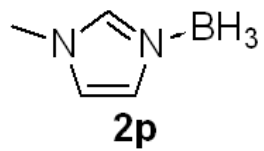


^{11}B NMR (96 MHz, CDCl_3) 2-Picoline-borane (**2o**)

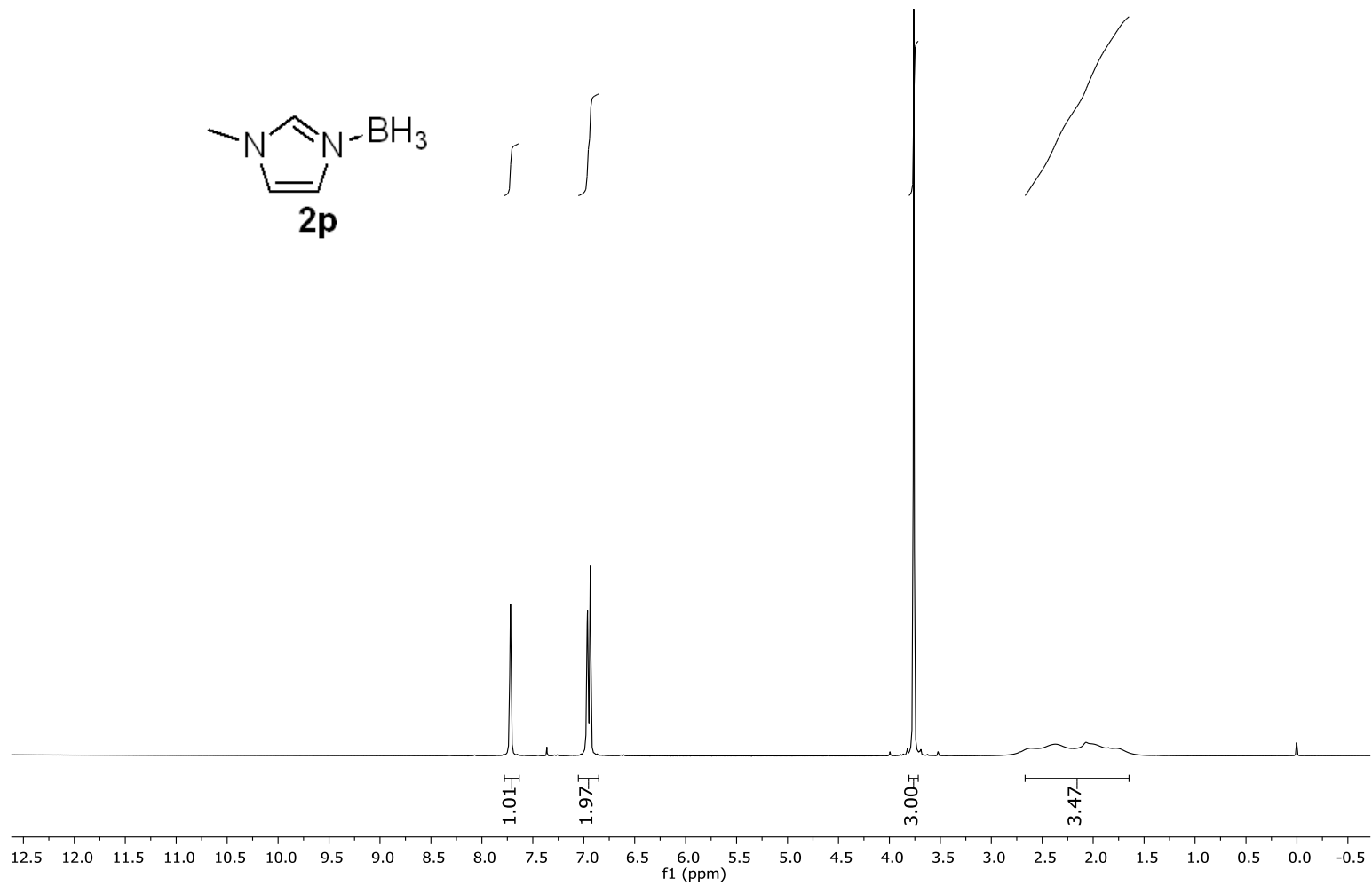
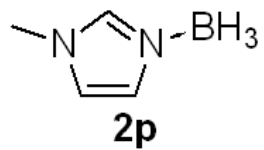


^1H NMR (300 MHz, CDCl_3) 2-Picoline-borane (**2o**)

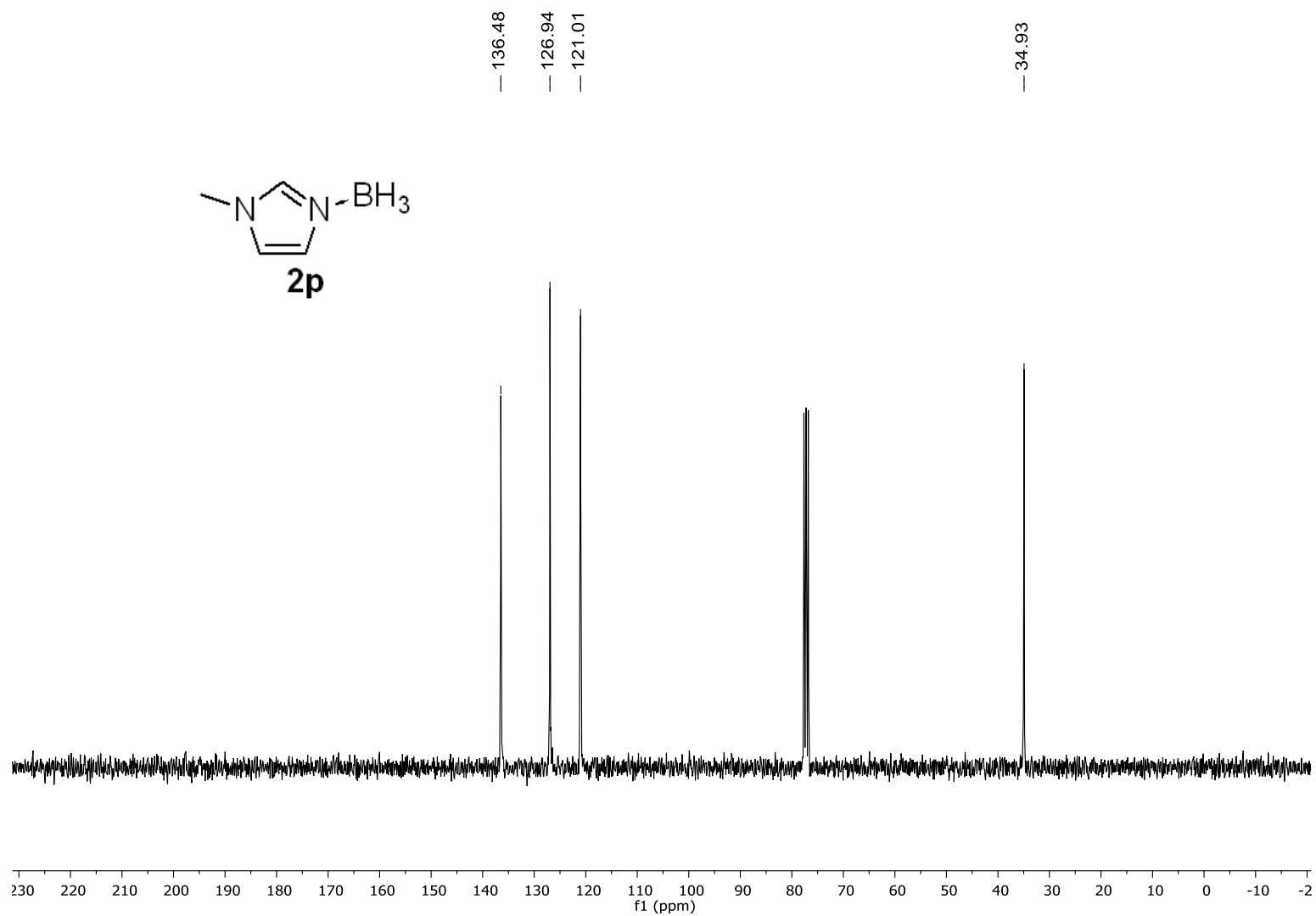


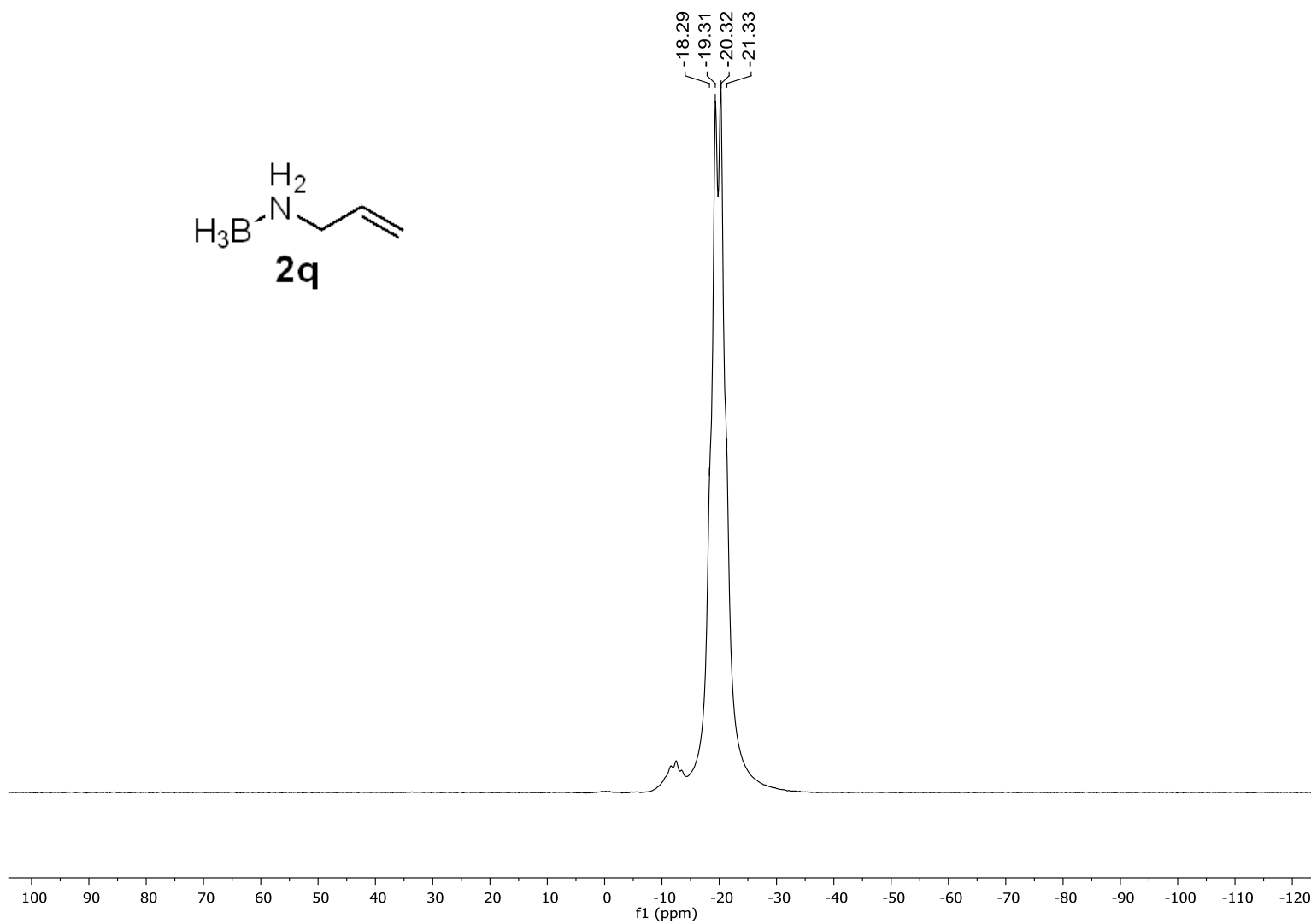
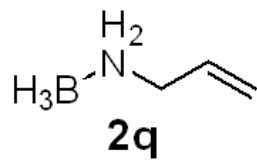


^{11}B NMR (96 MHz, CDCl_3) 1-Methylimidazole-borane (**2p**)

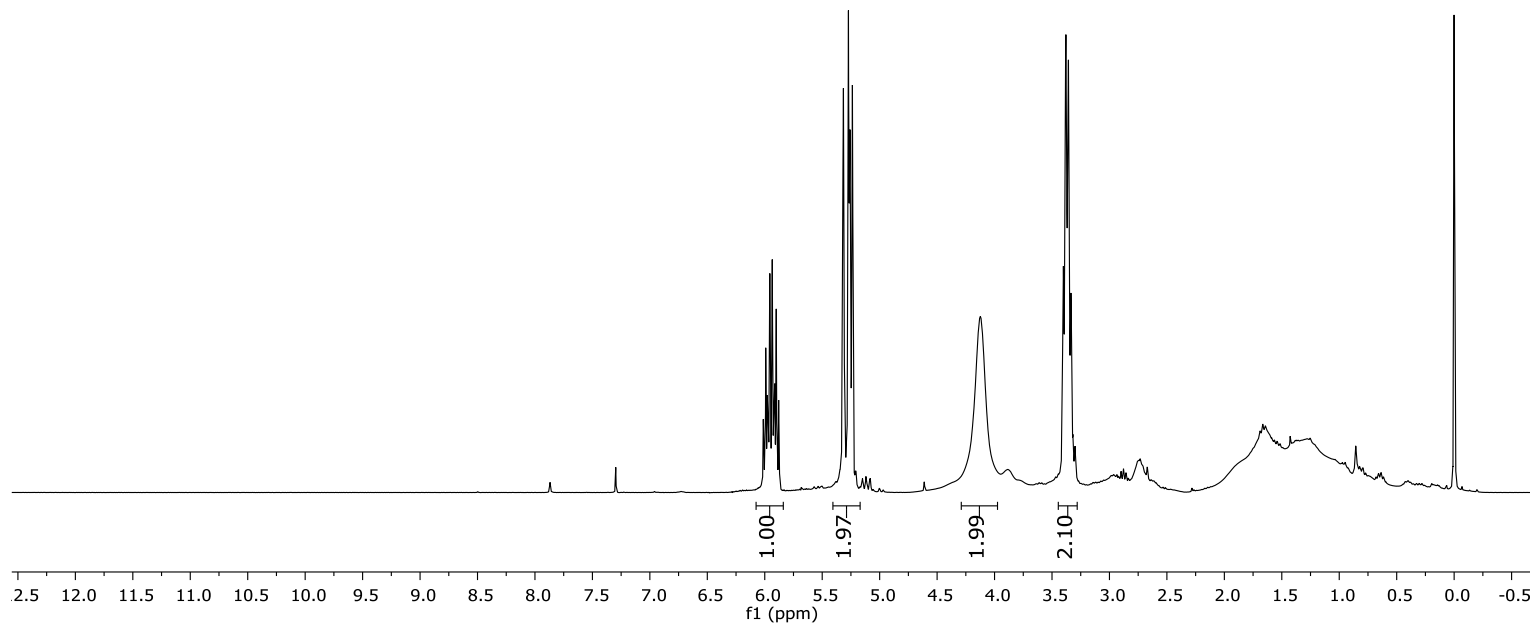
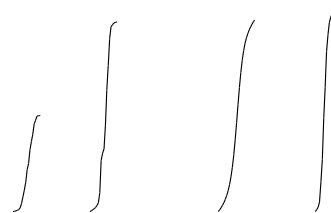
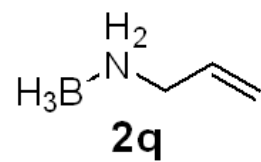


^1H NMR (300 MHz, CDCl_3) 1-Methylimidazole-borane (**2p**)

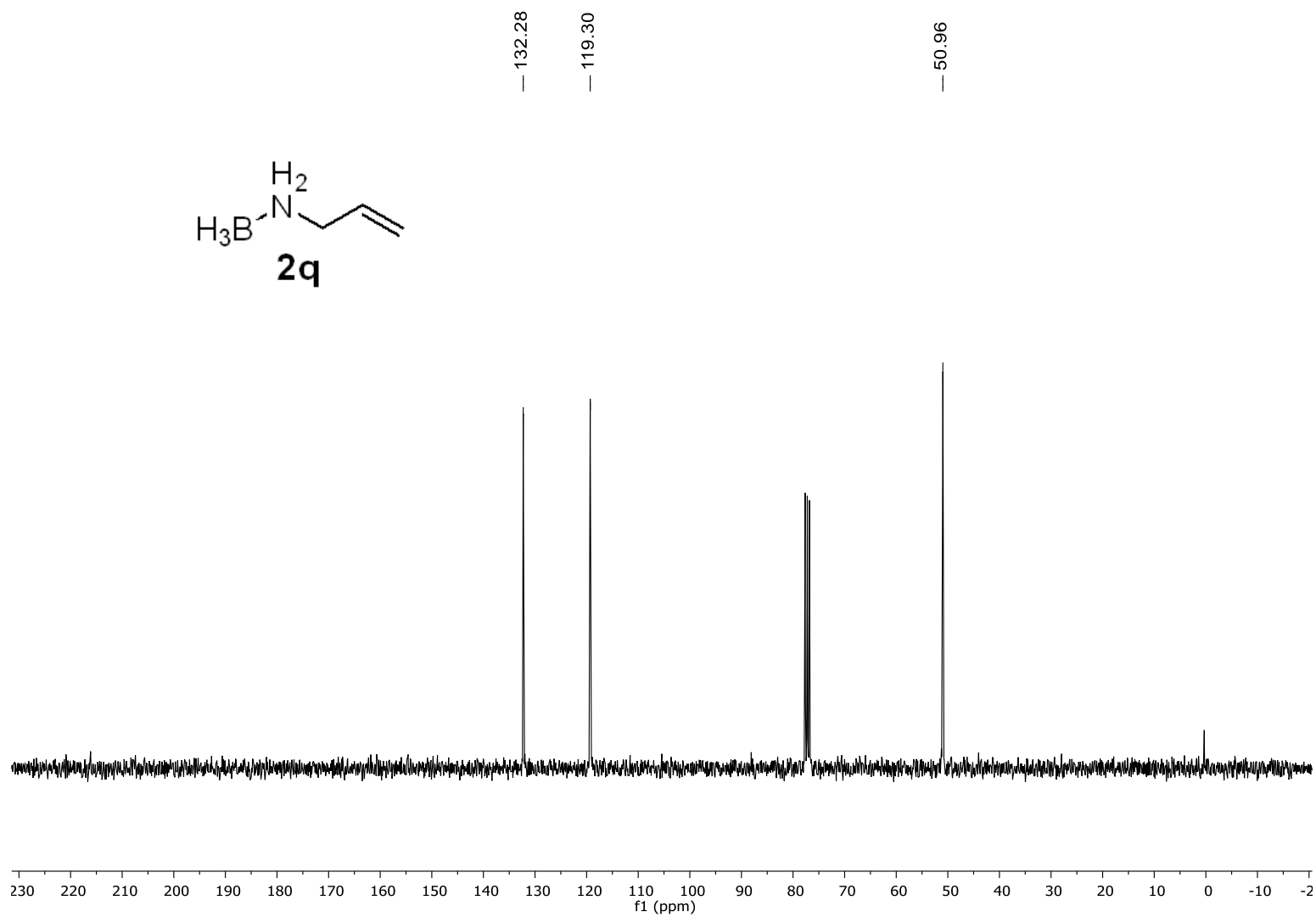
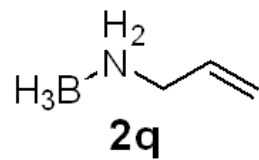




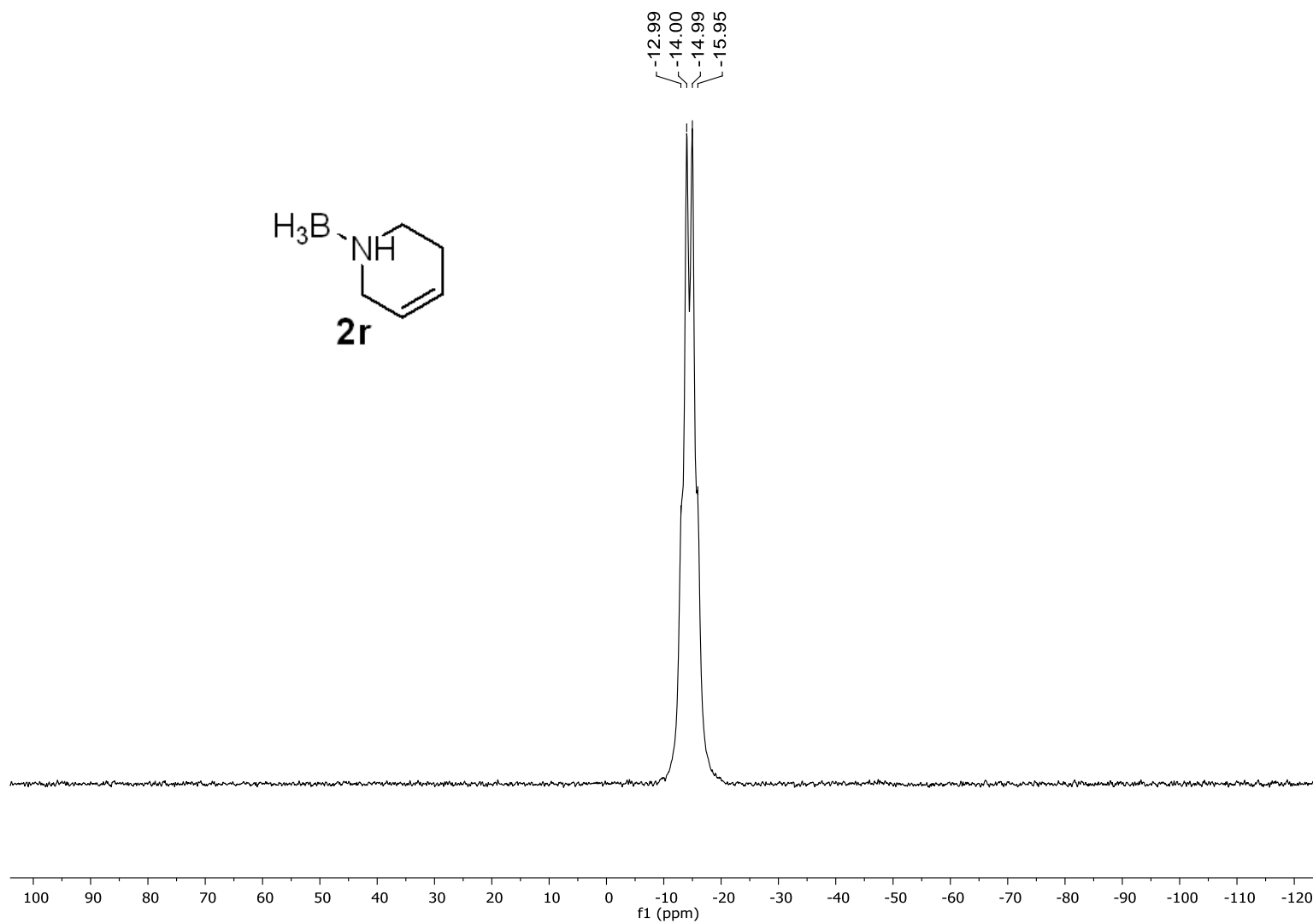
^{11}B NMR (96 MHz, CDCl_3) Allylamine-borane (**2q**)



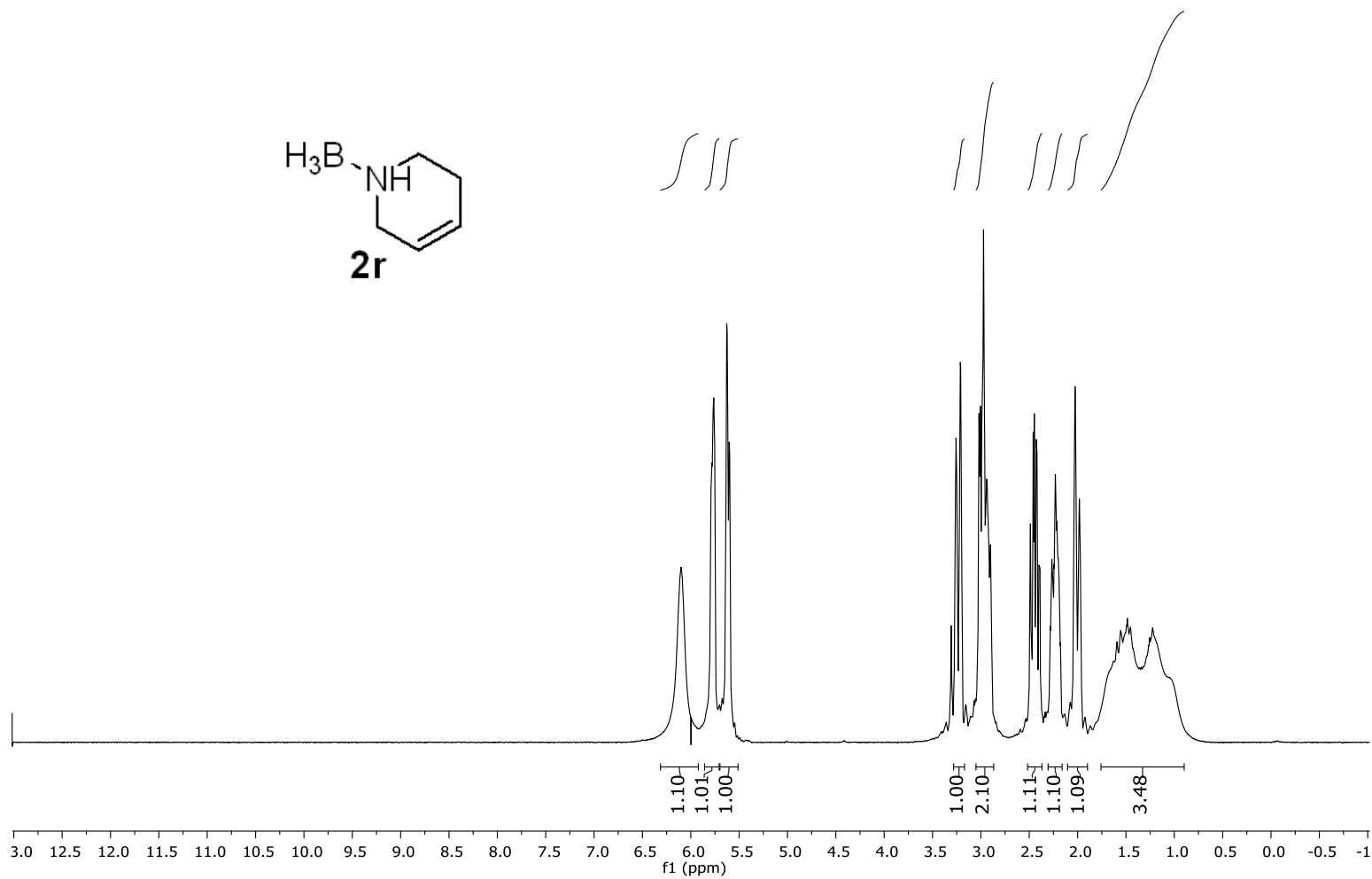
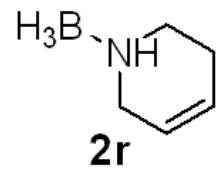
^1H NMR (300 MHz, CDCl_3) Allylamine-borane (**2q**)



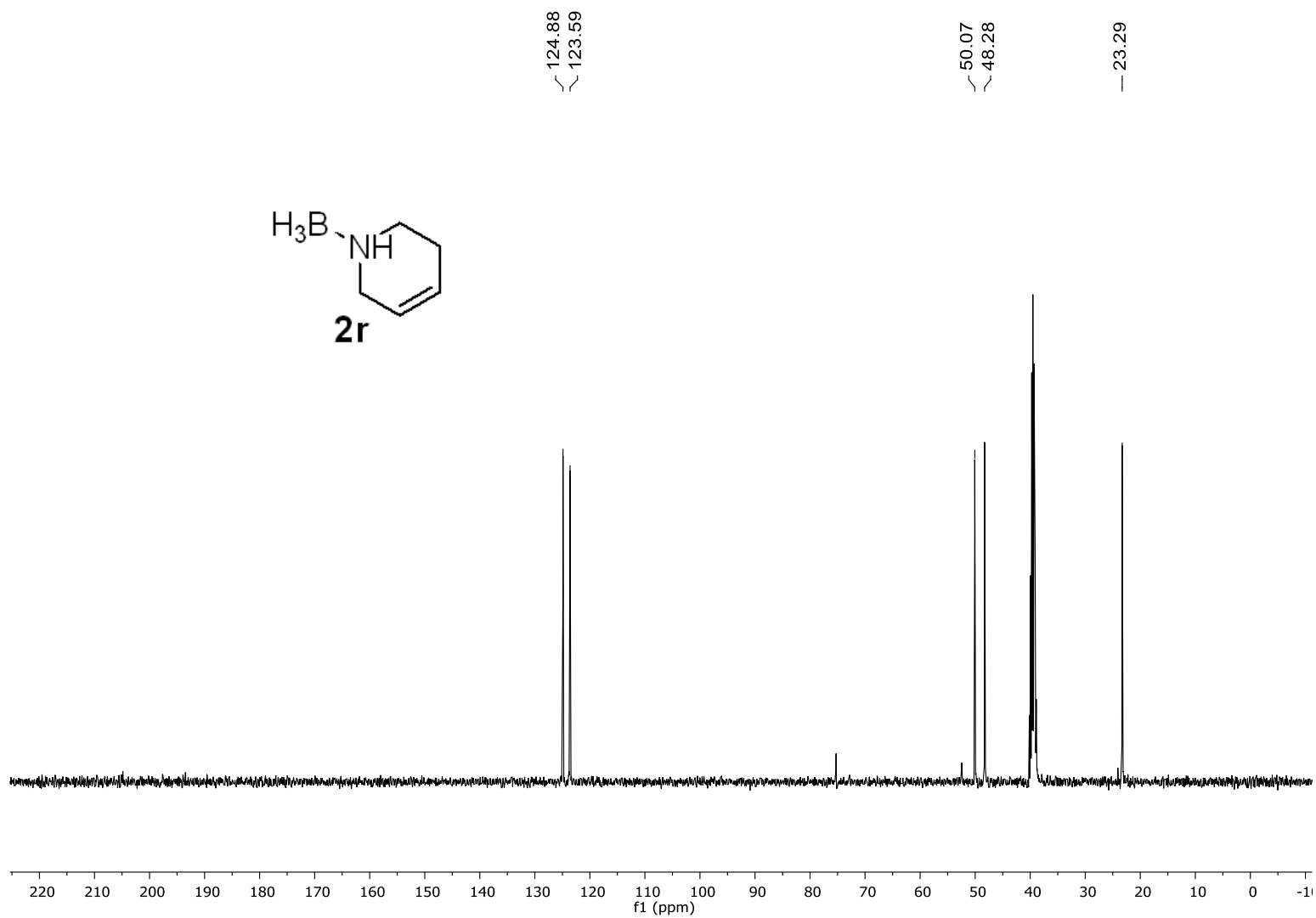
¹³C NMR (75 MHz, CDCl₃) Allylamine-borane (**2q**)



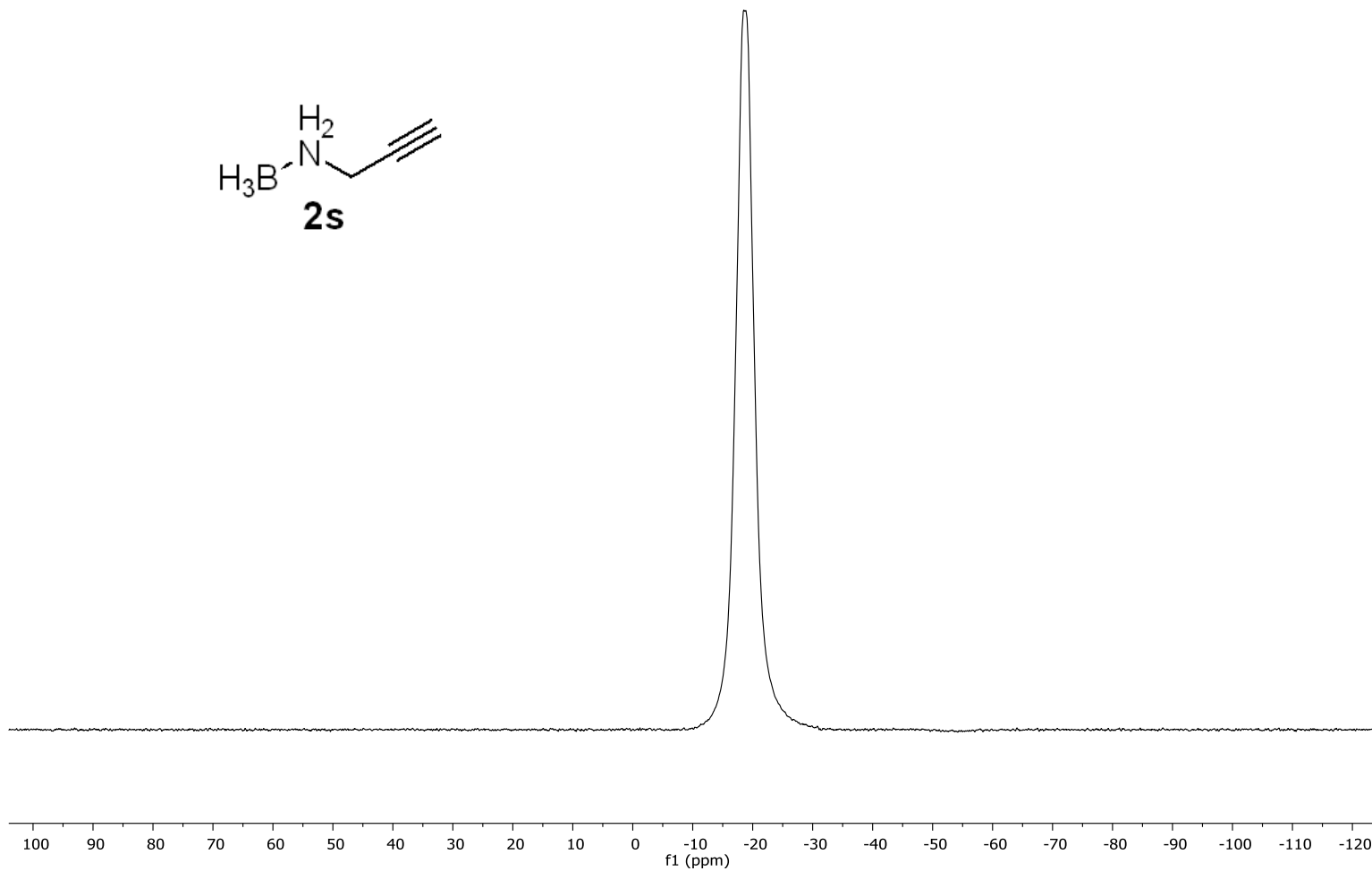
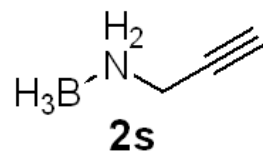
^{11}B NMR (96 MHz, $\text{DMSO}-d_6$) 1,2,3,6-tetrahydropyridine-borane (**2r**)



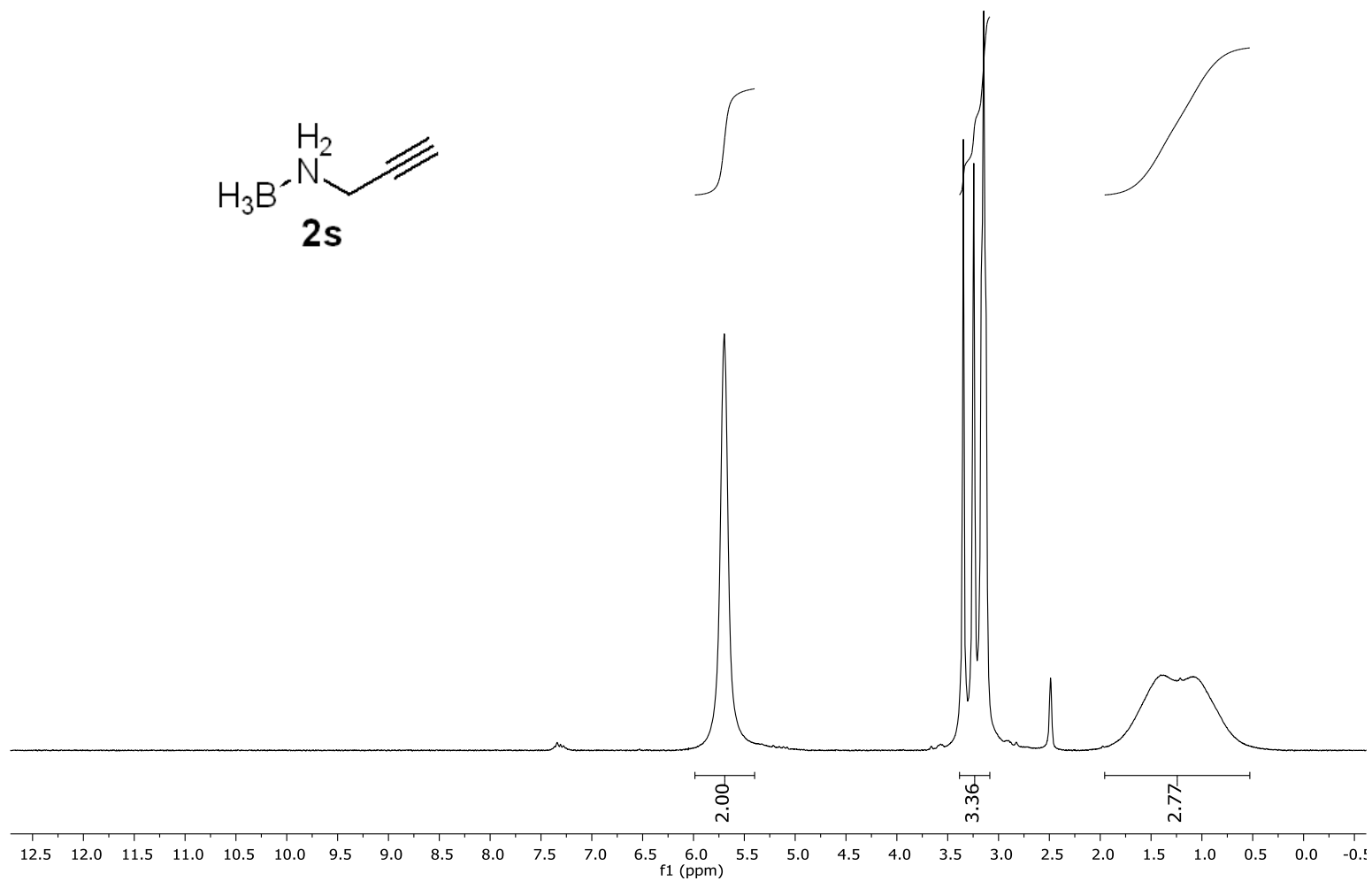
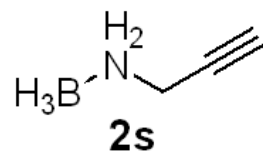
^1H NMR (400 MHz, $\text{DMSO-}d_6$) 1,2,3,6-tetrahydropyridine-borane (**2r**)



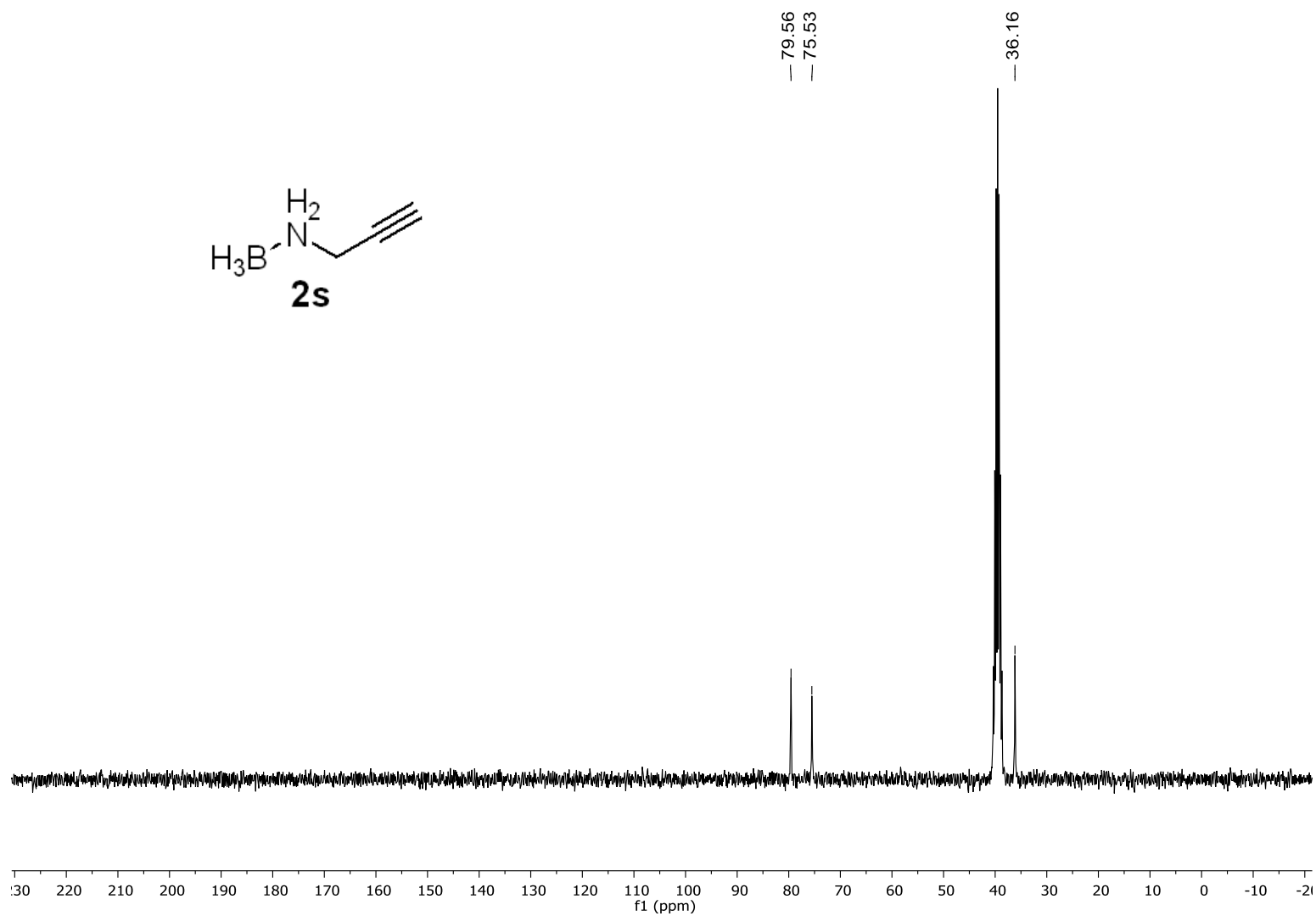
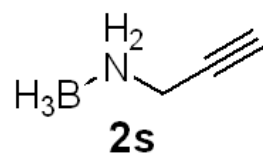
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) 1,2,3,6-tetrahydropyridine-borane (**2r**)



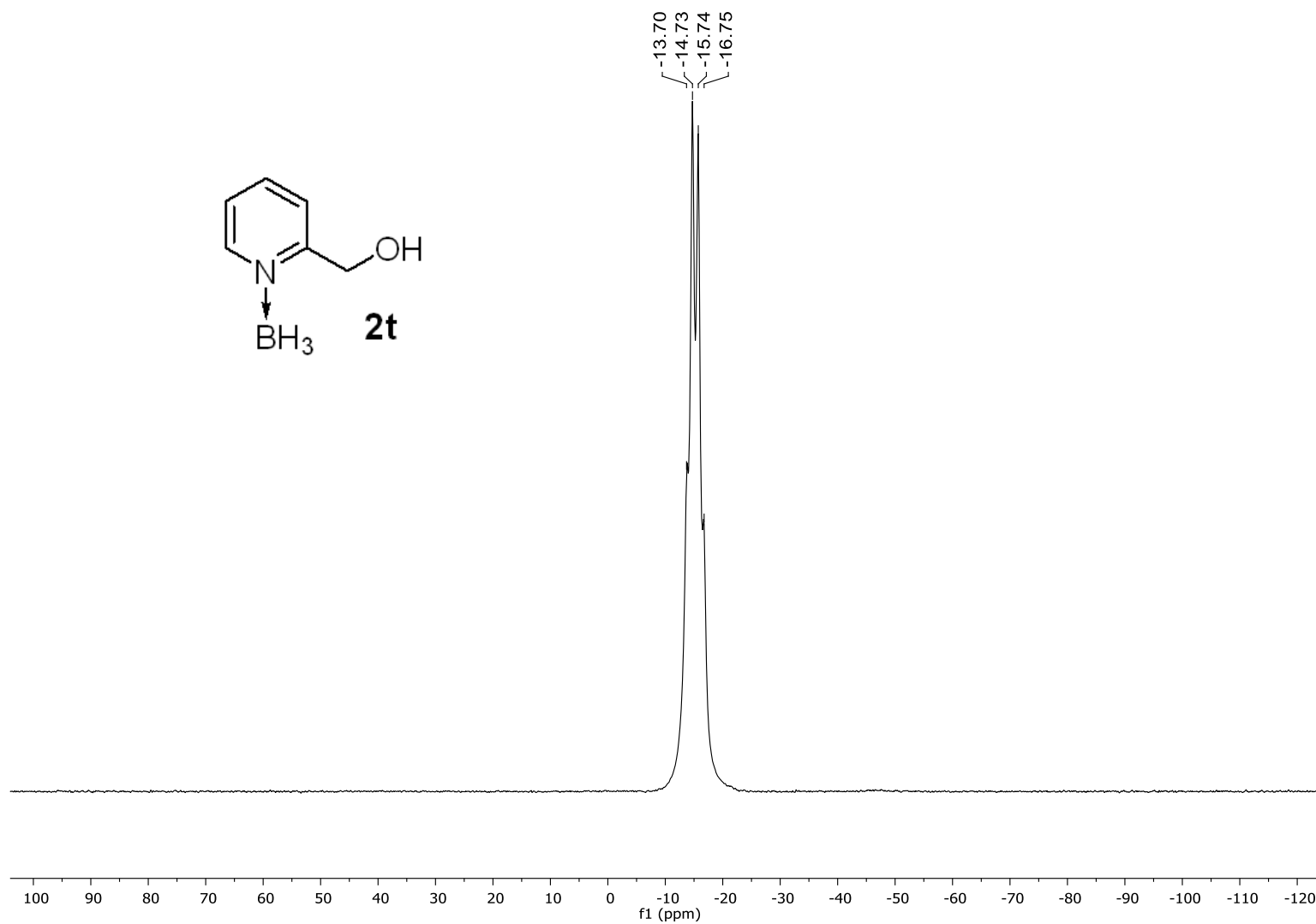
^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) Propargylamine-borane (**2s**)



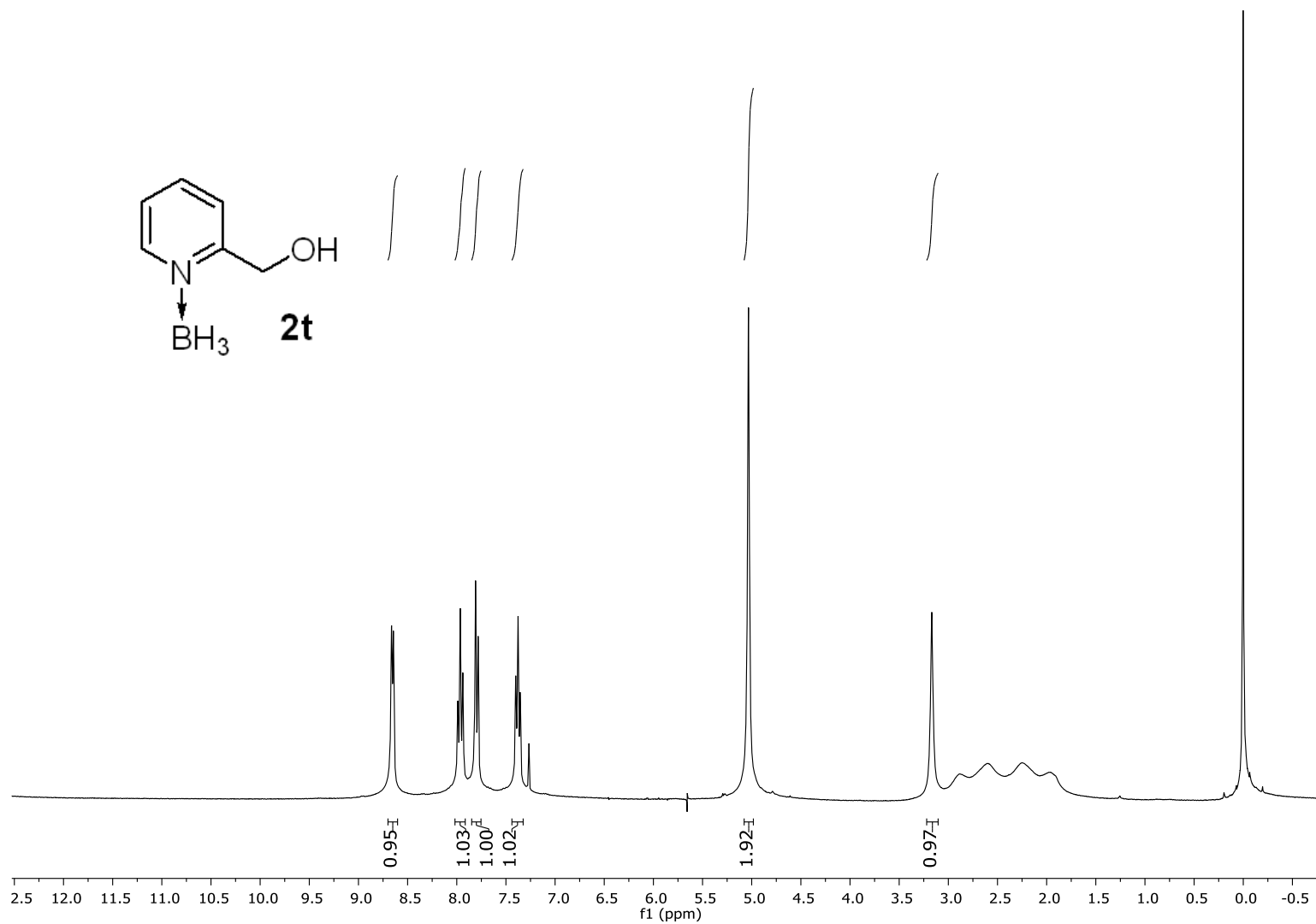
¹H NMR (300 MHz, DMSO-*d*₆) Propargylamine-borane (**2s**)



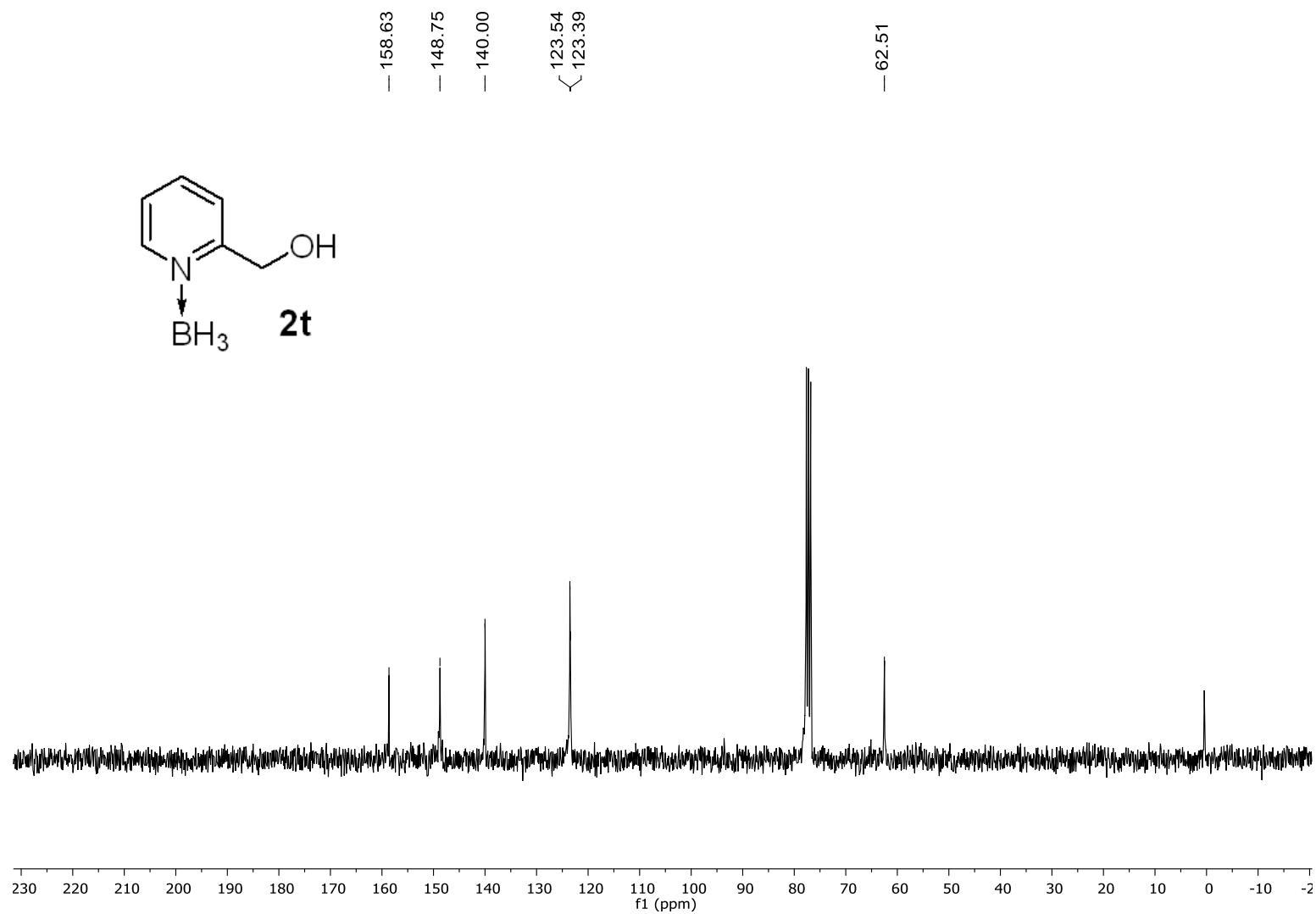
^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) Propargylamine-borane (**2s**)



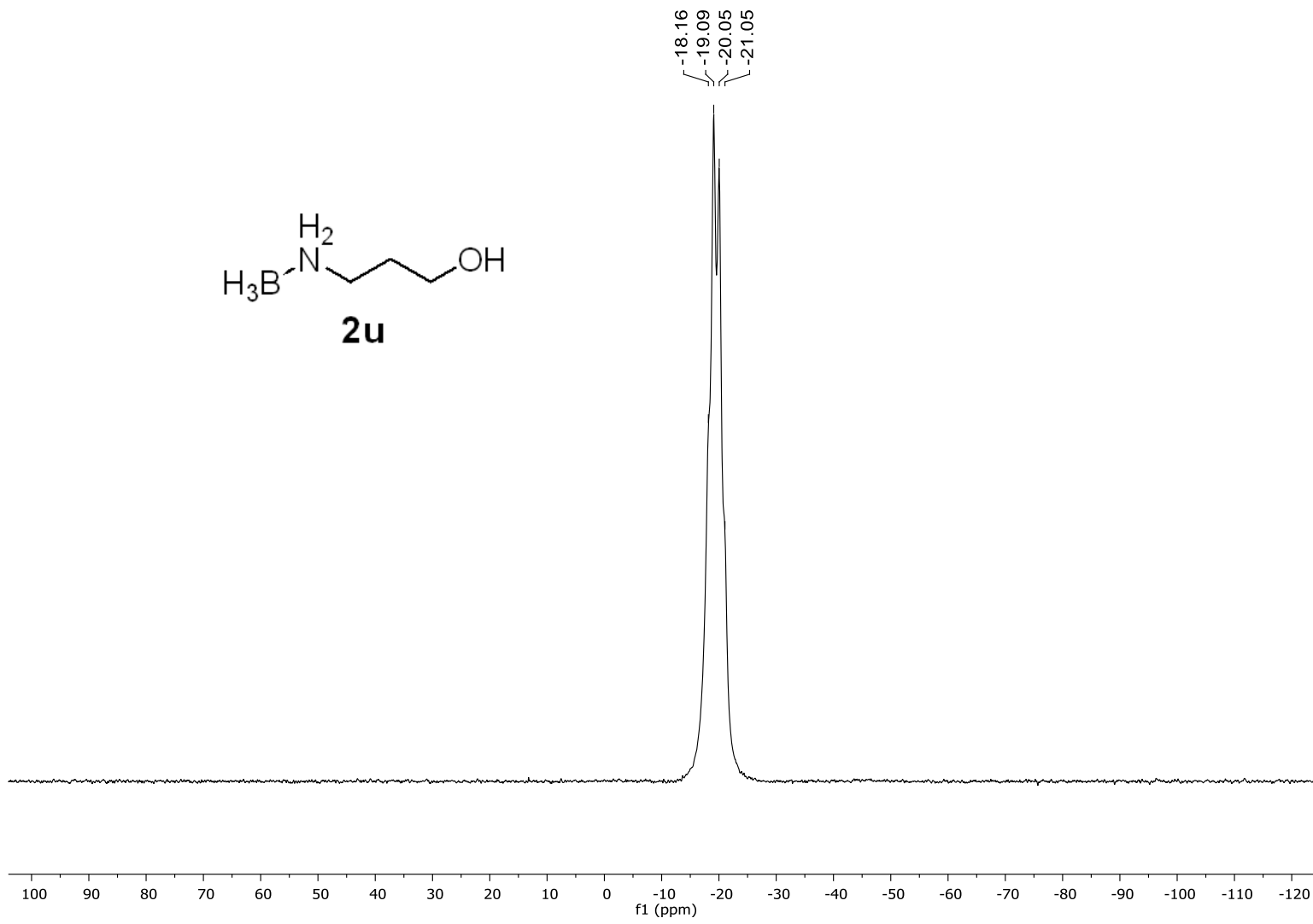
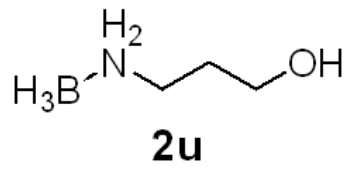
^{11}B NMR (96 MHz, CDCl_3) 2-(Hydroxymethyl)pyridine-borane (**2t**)



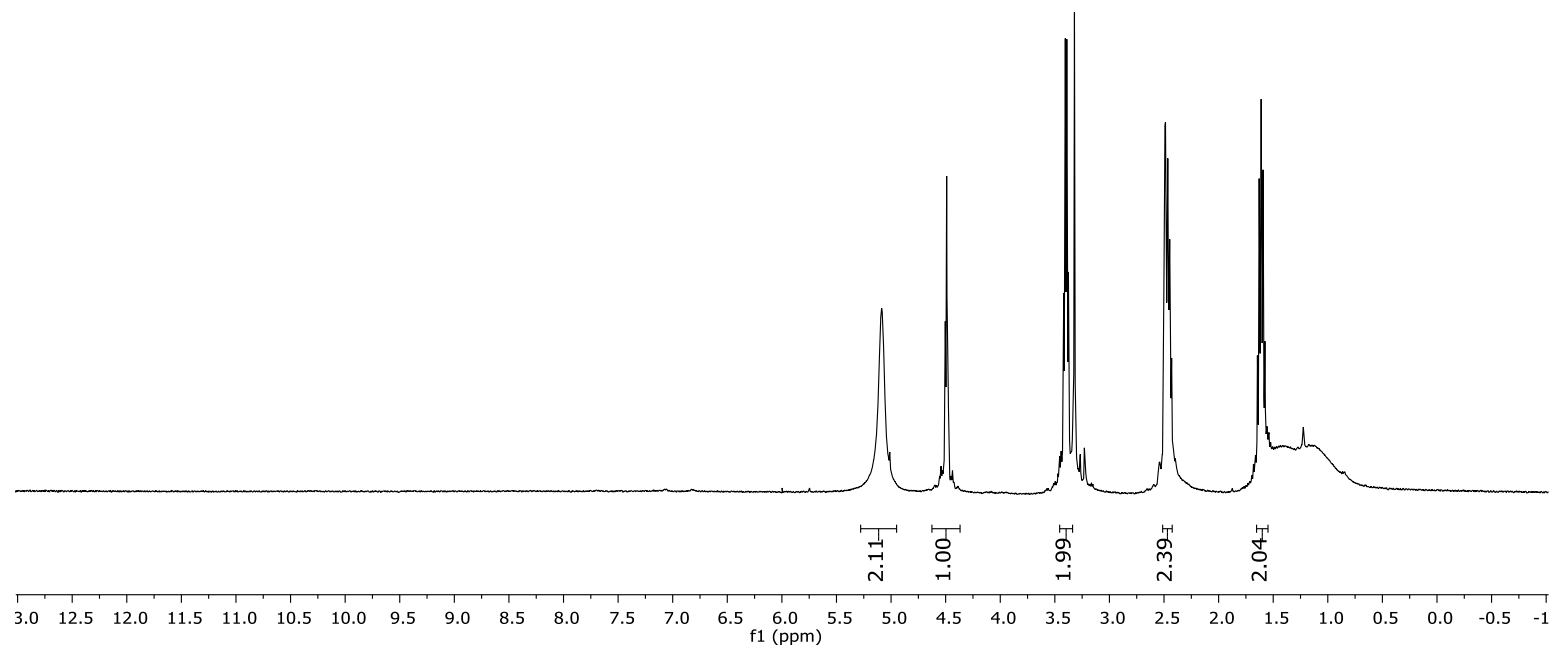
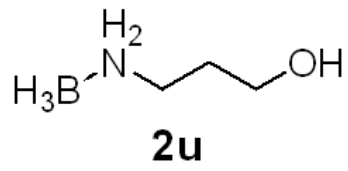
^1H NMR (300 MHz, CDCl_3) 2-(Hydroxymethyl)pyridine-borane (**2t**)



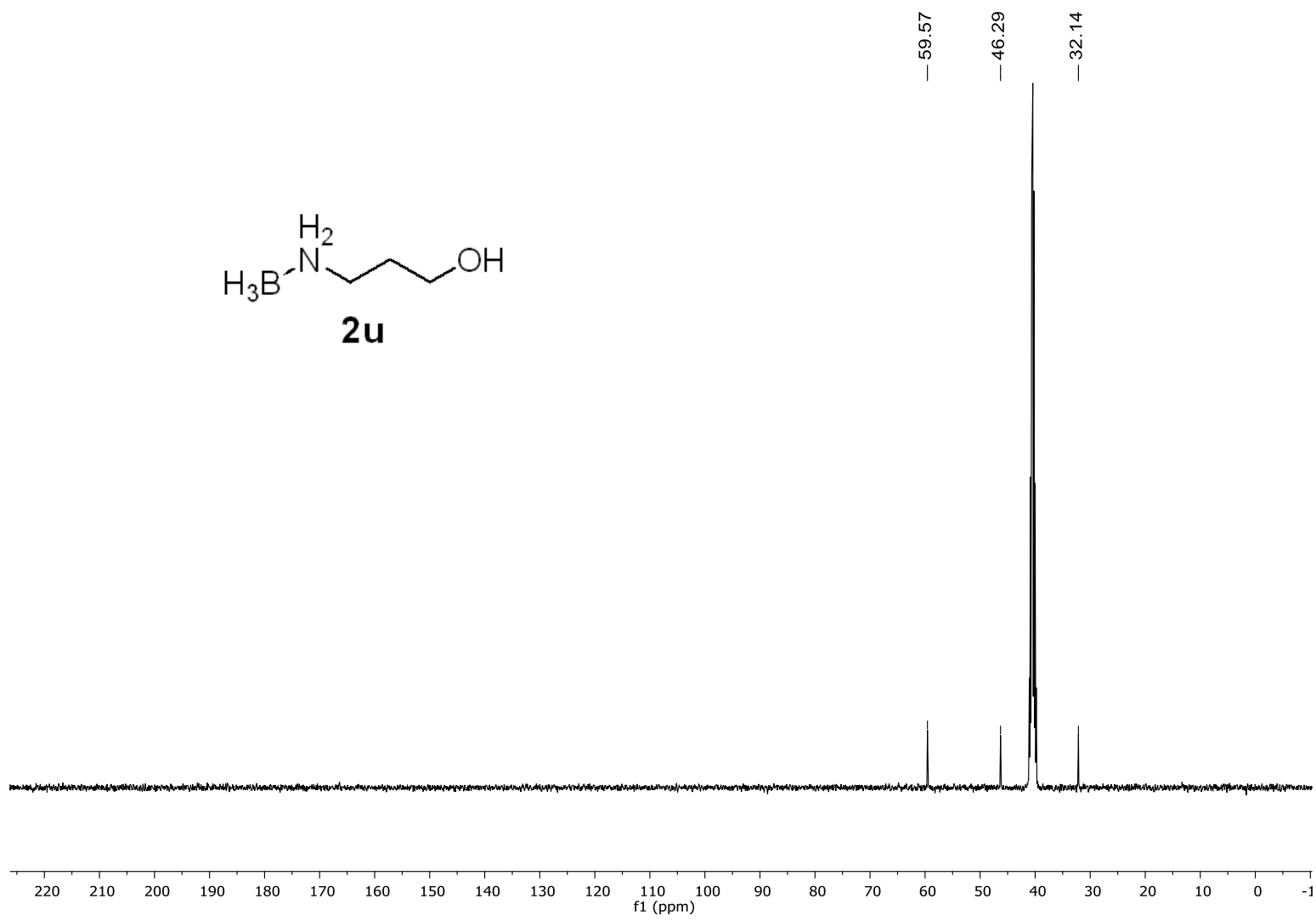
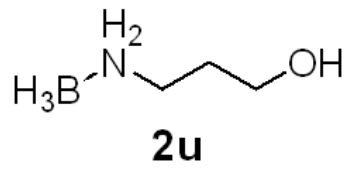
^{13}C NMR (75 MHz, CDCl_3) 2-(Hydroxymethyl)pyridine-borane (**2t**)



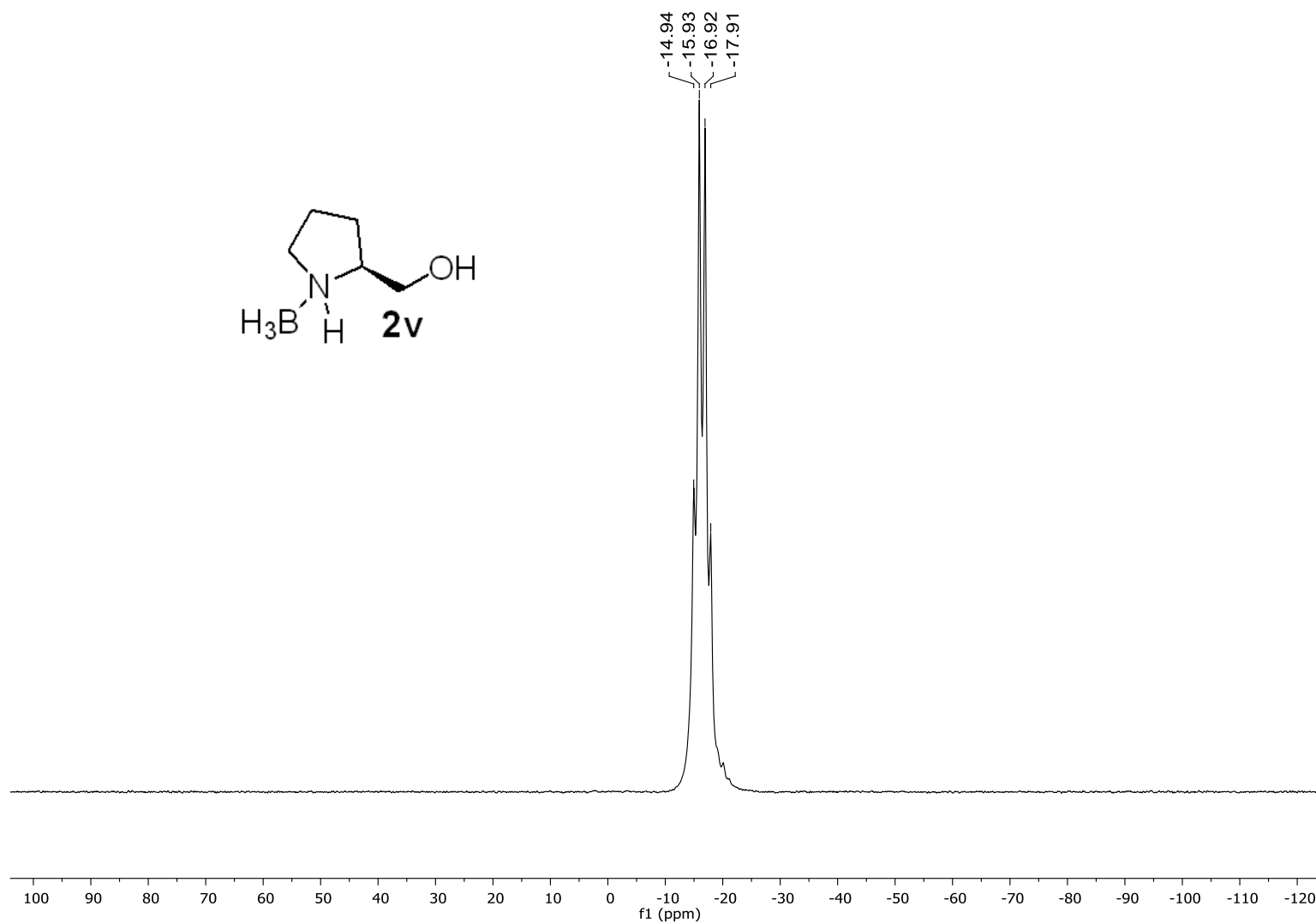
^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) 3-Aminopropan-1-ol-borane (**2u**)

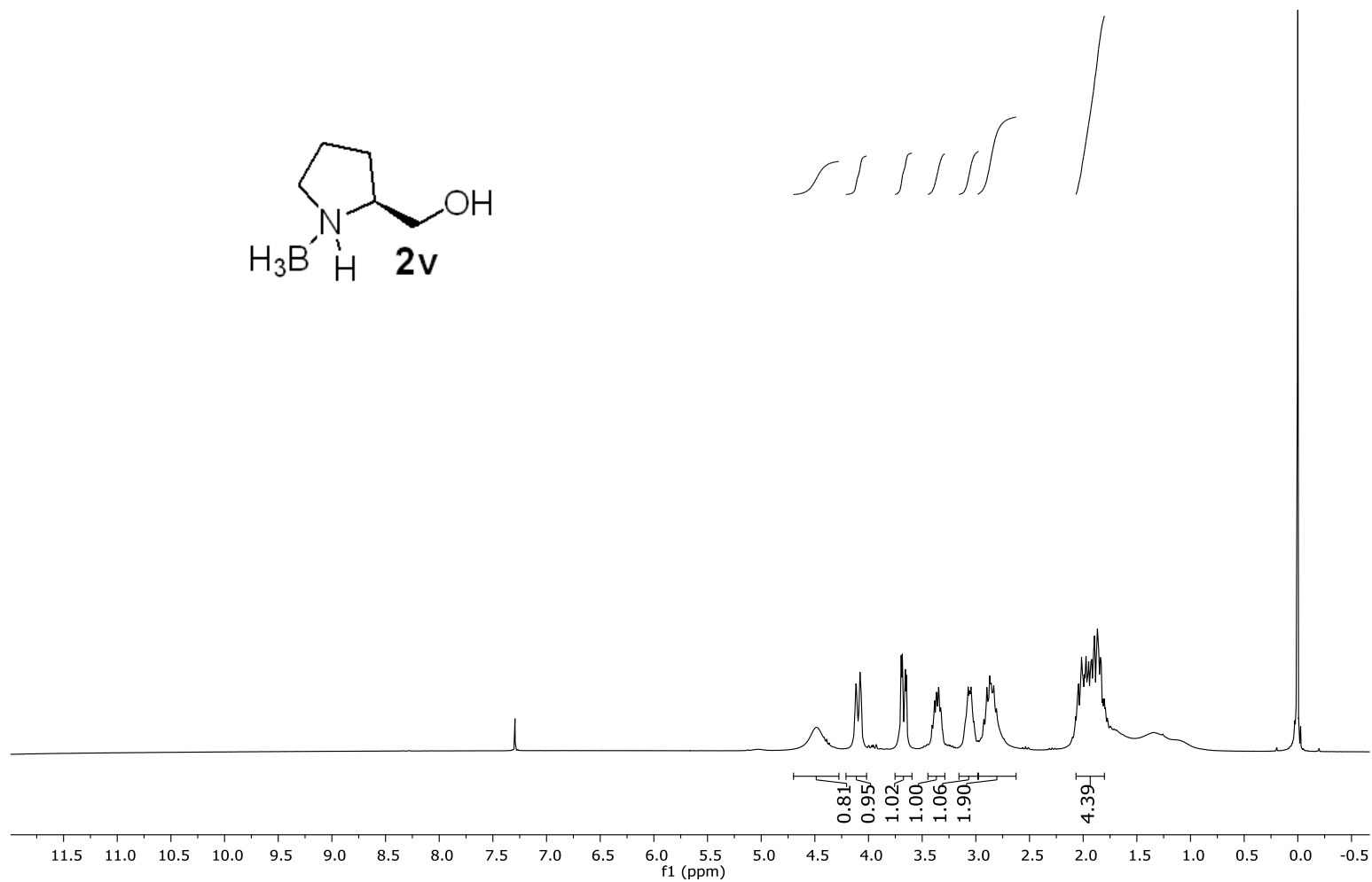
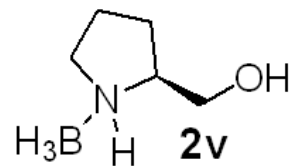


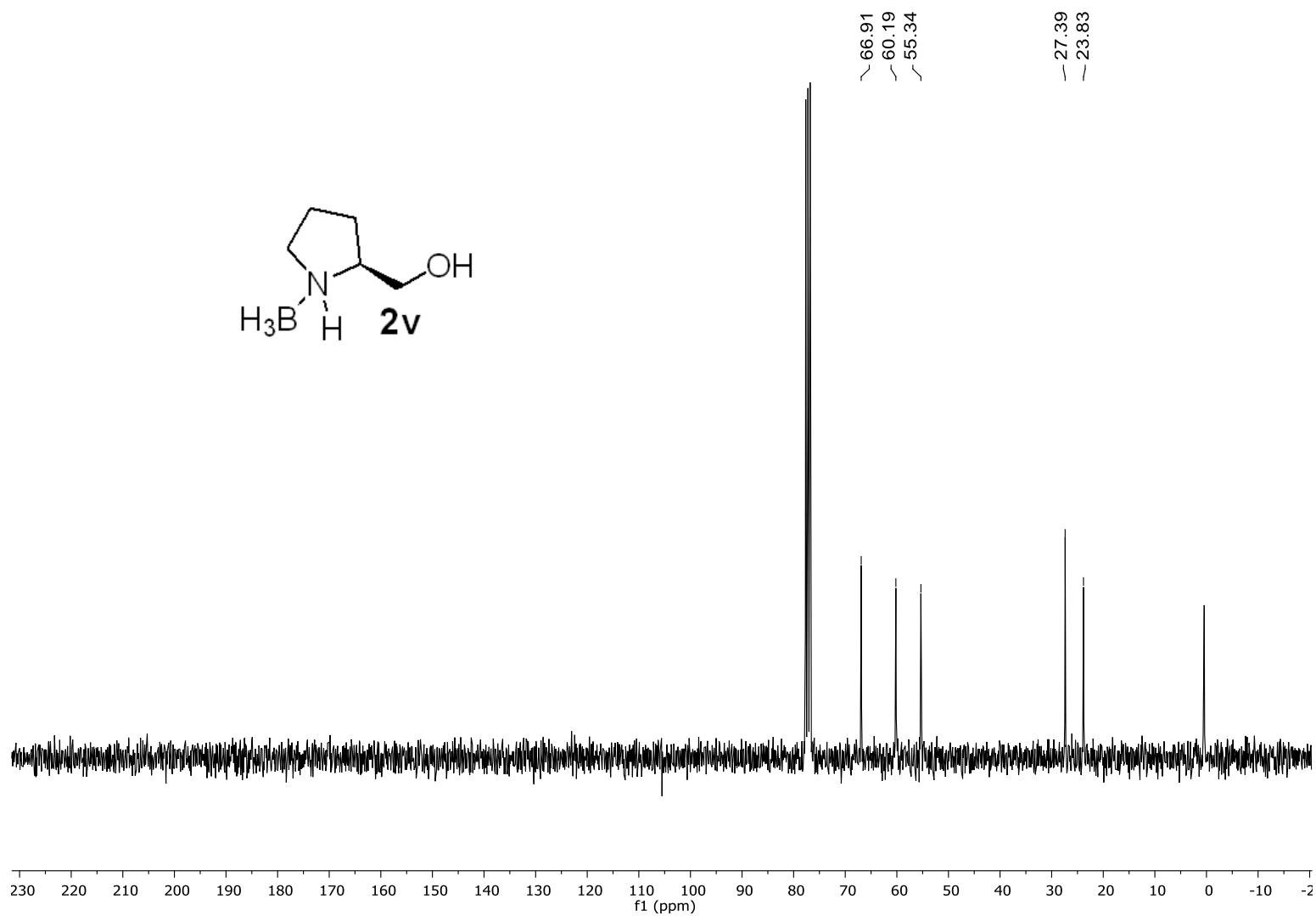
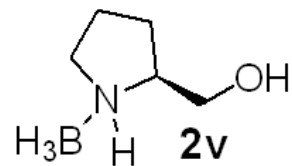
¹H NMR (400 MHz, DMSO-*d*₆) 3-Aminopropan-1-ol-borane (**2u**)

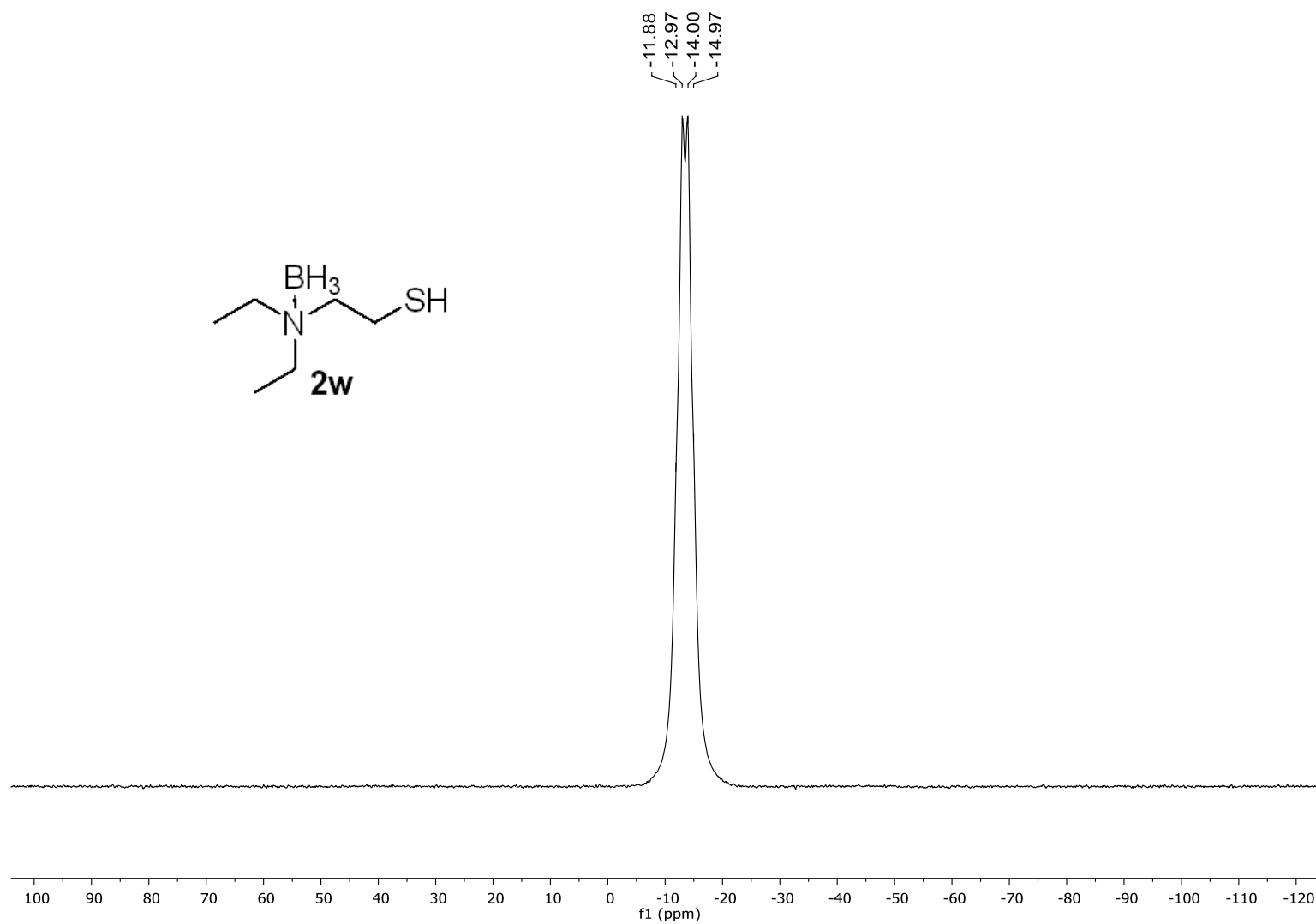


¹³C NMR (101 MHz, DMSO-*d*₆) 3-Aminopropan-1-ol-borane (**2u**)

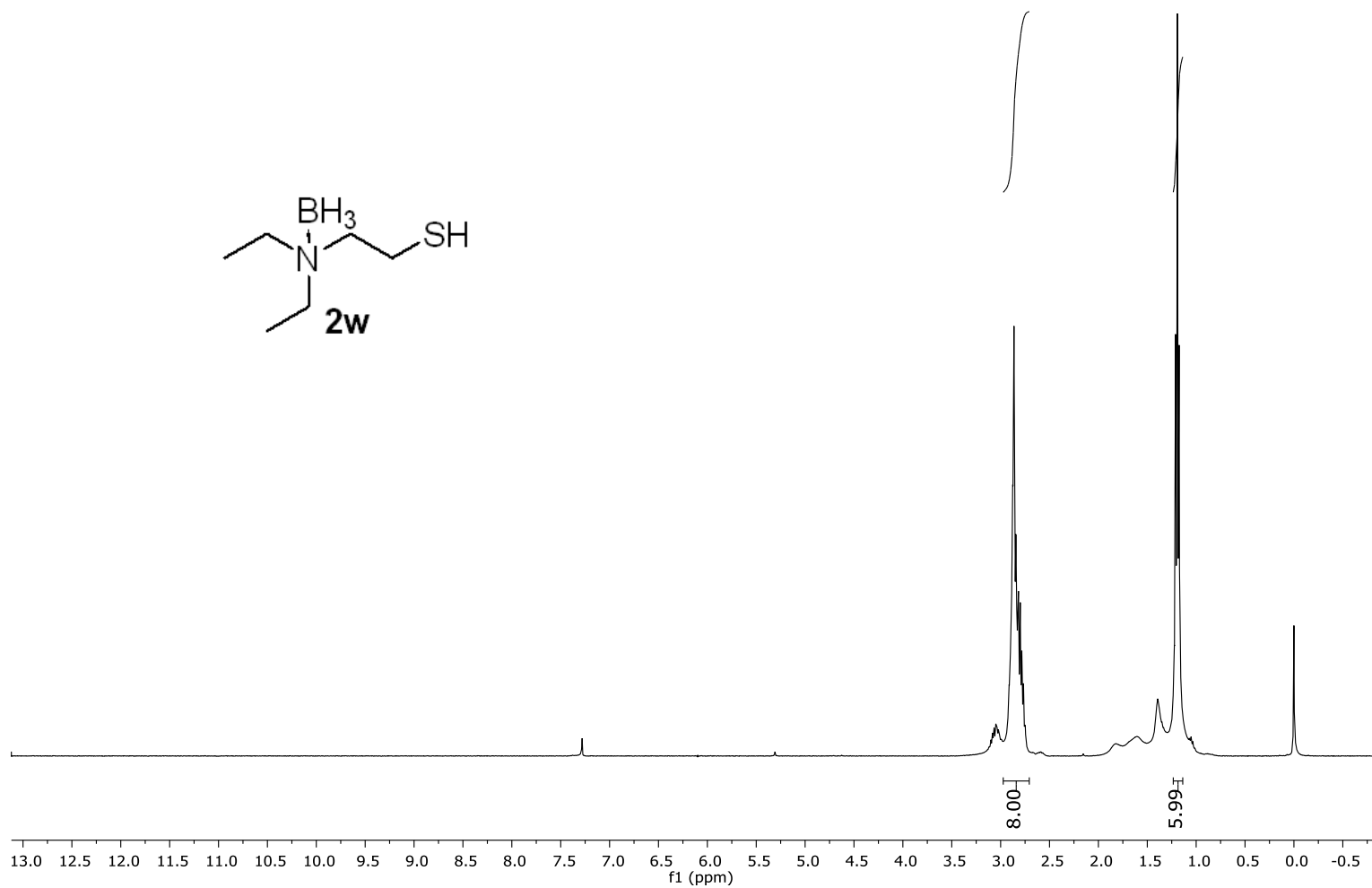
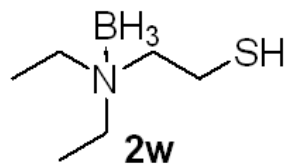




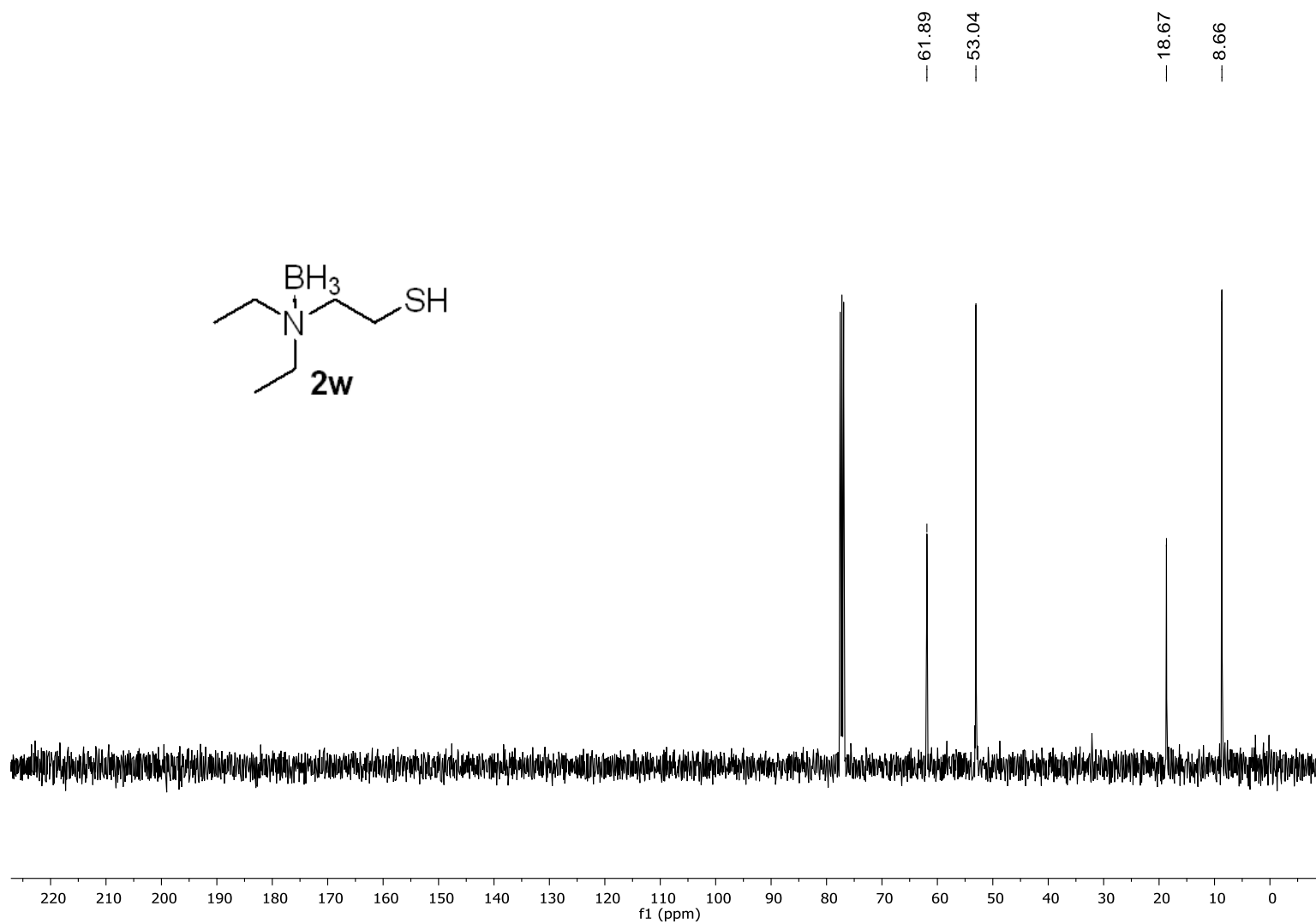


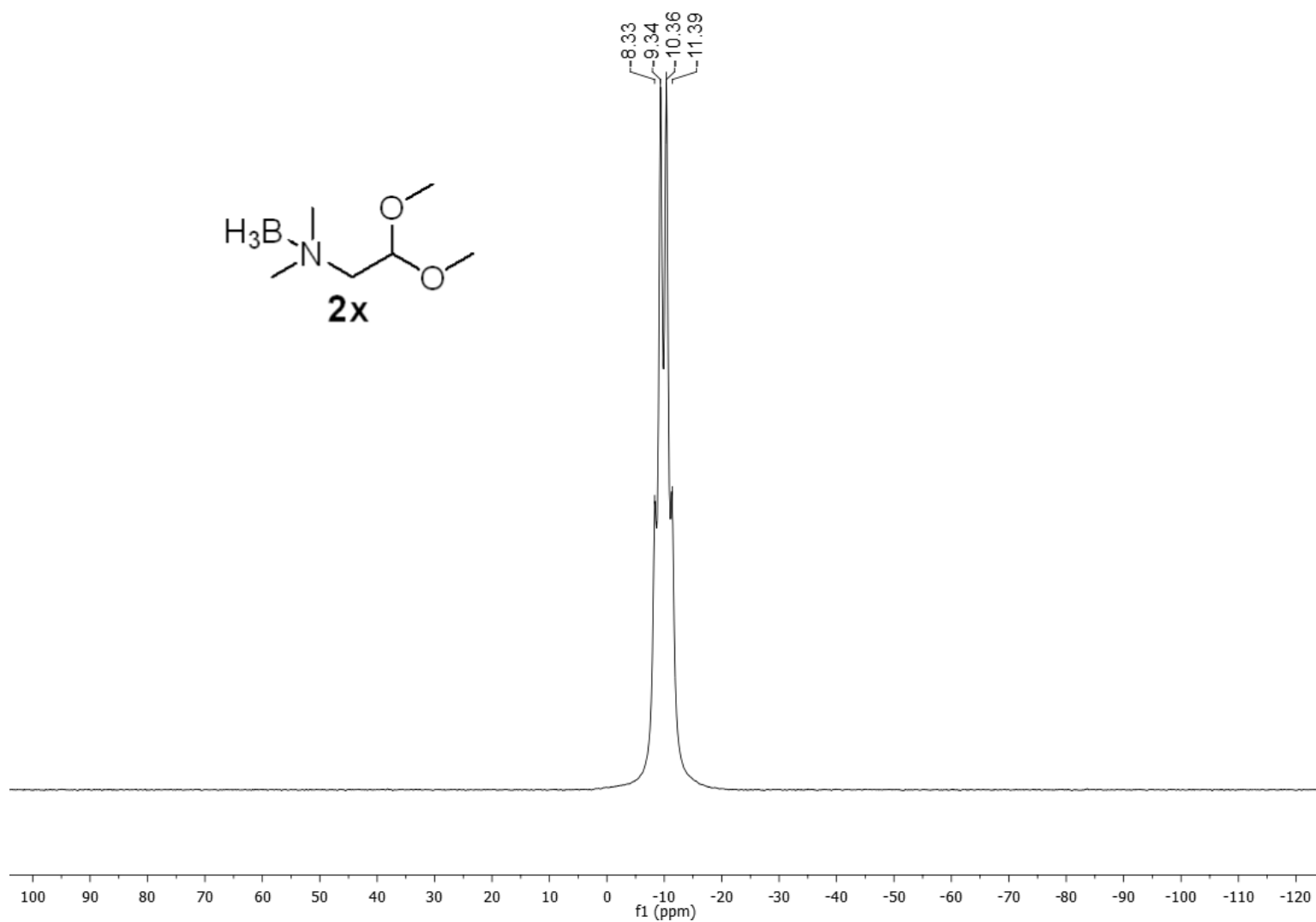


^{11}B NMR (96 MHz, CDCl_3) 2-diethylaminoethanethiol-borane (**2w**)

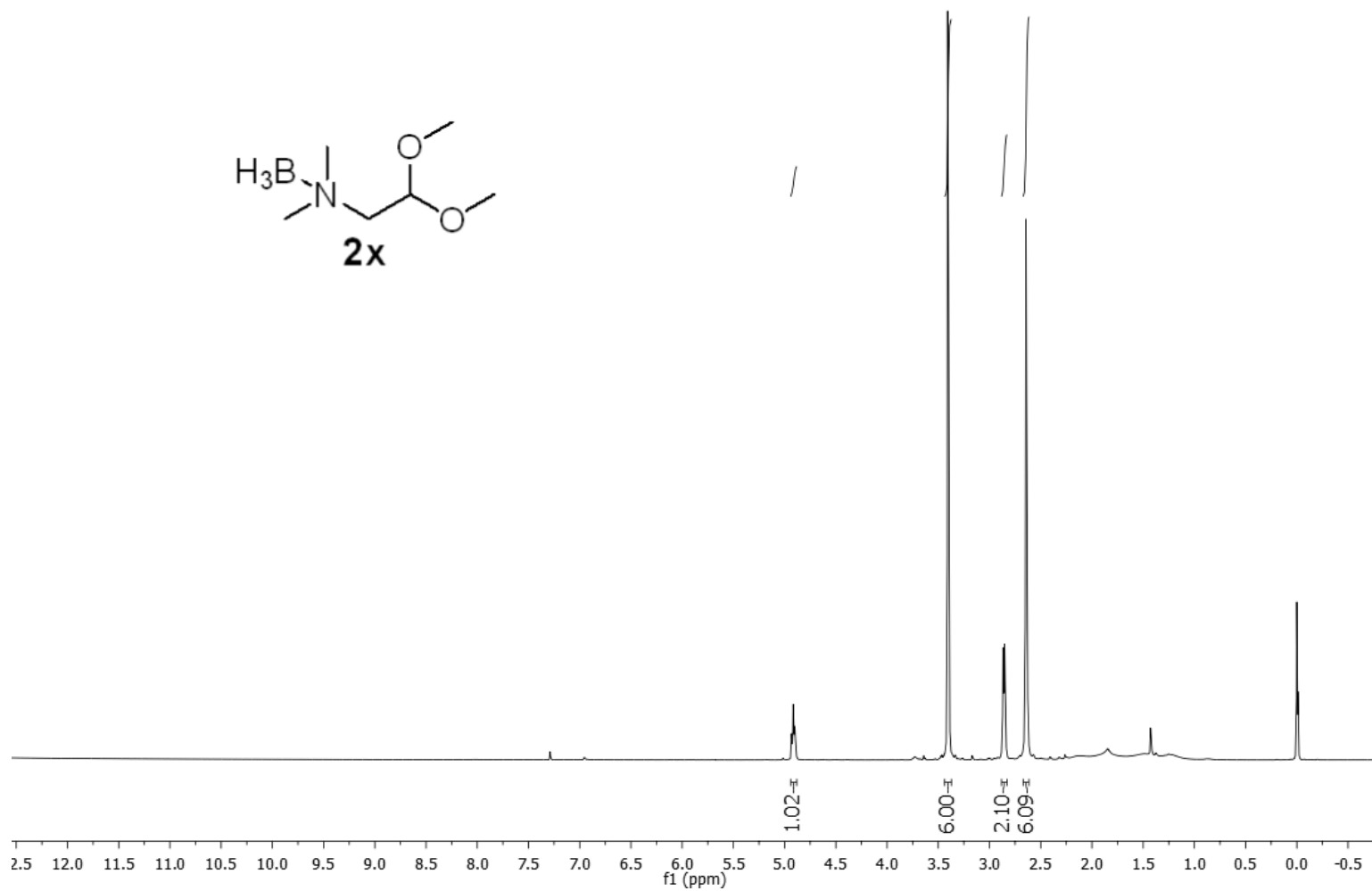
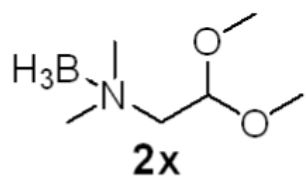


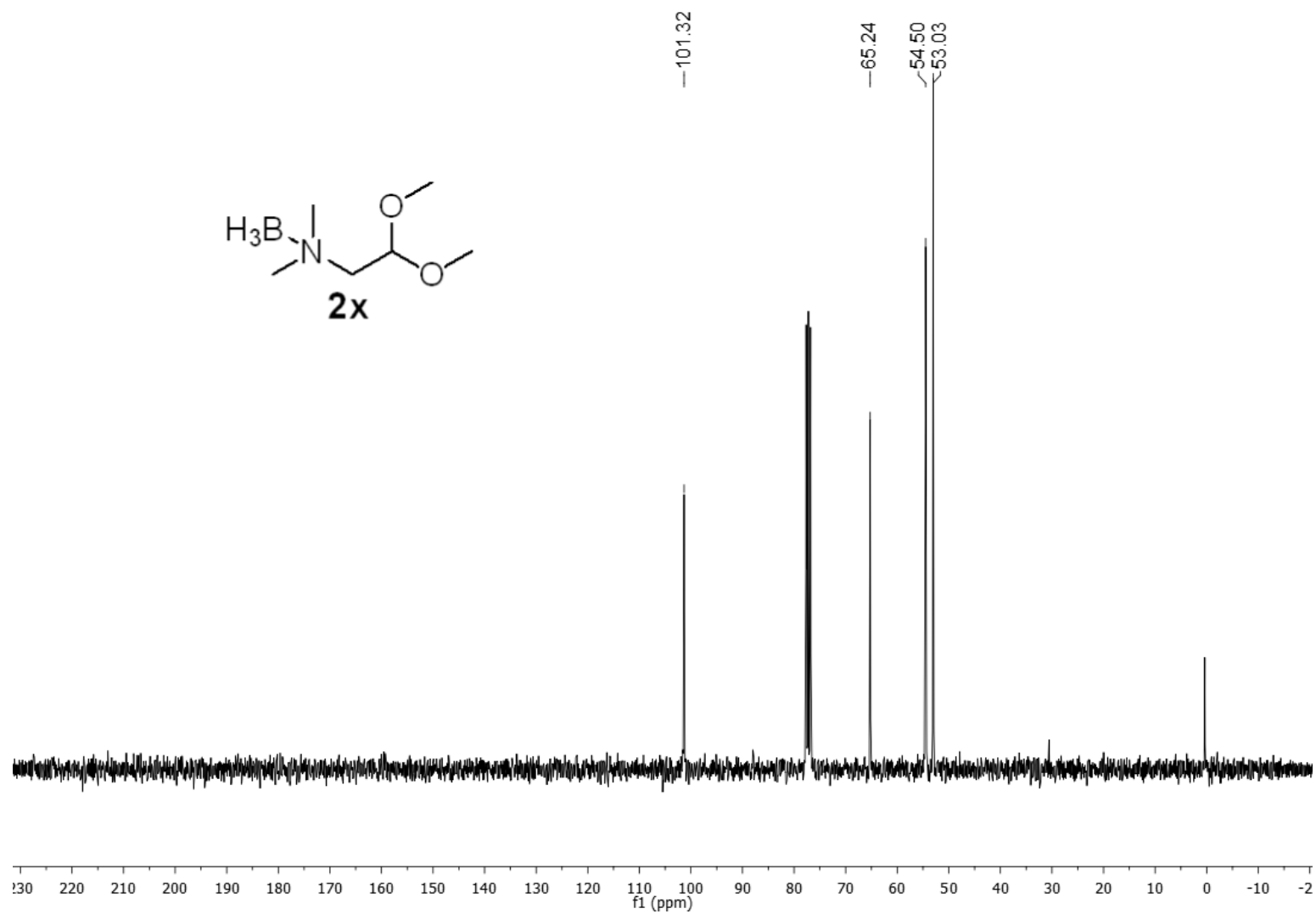
¹H NMR (400 MHz, CDCl₃) 2-diethylaminoethanethiol-borane (**2w**)



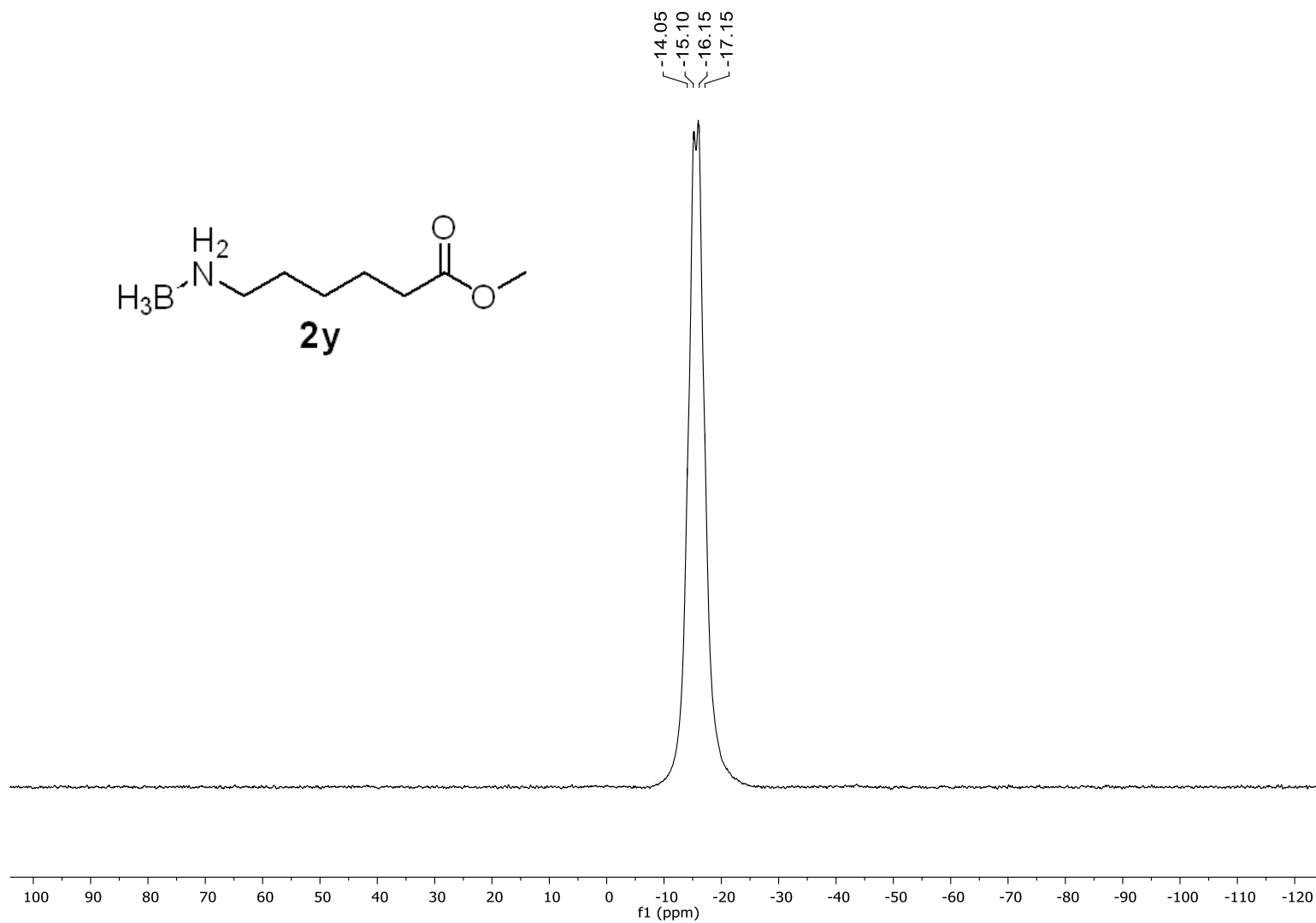


^{11}B NMR (96 MHz, CDCl_3) 2,2-Dimethoxy-*N,N*-dimethylethylamine-borane (**2x**)

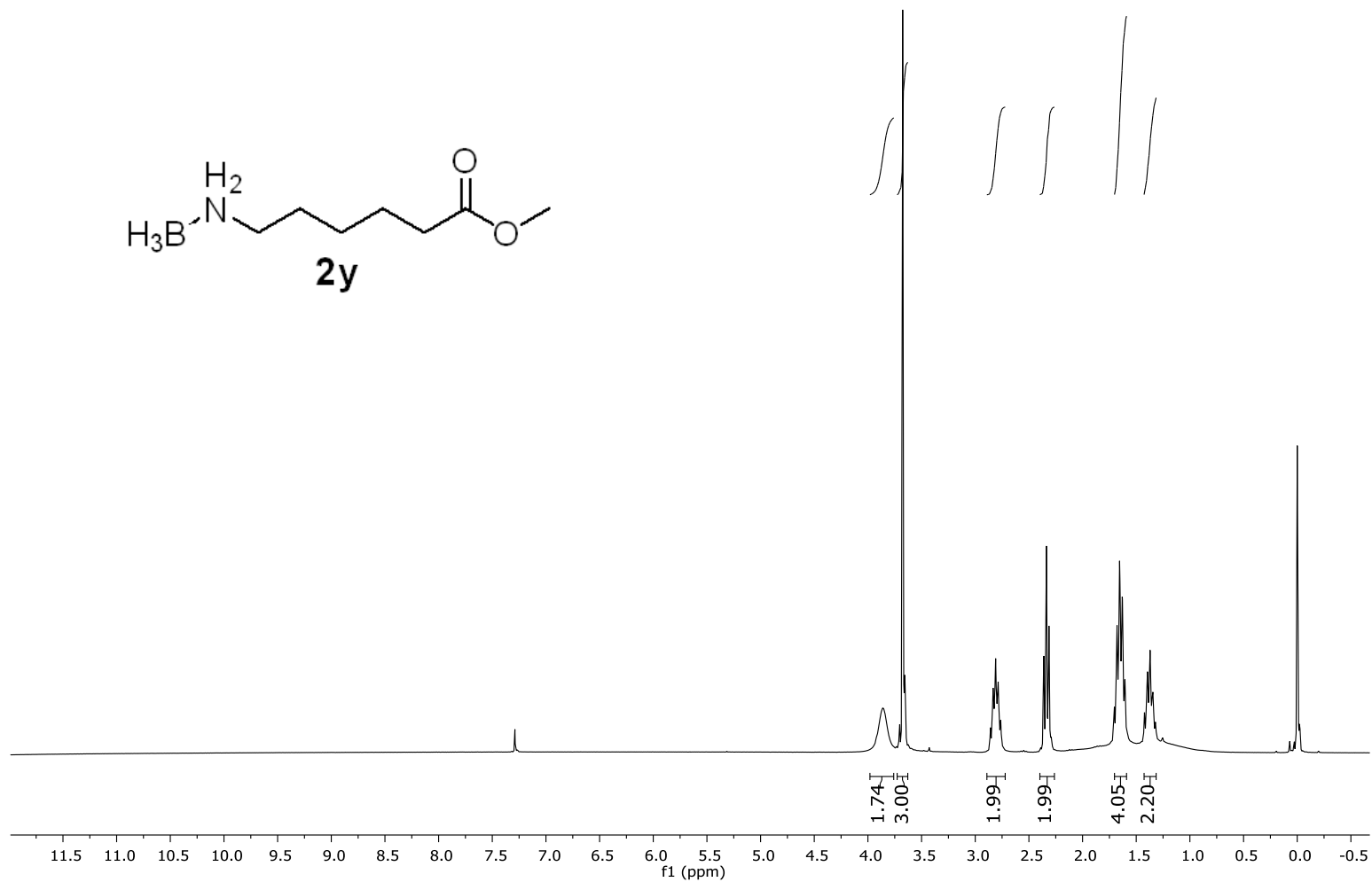
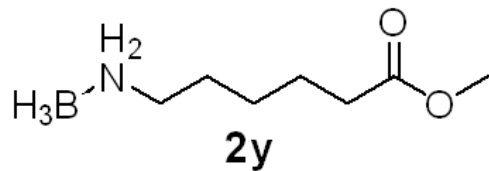


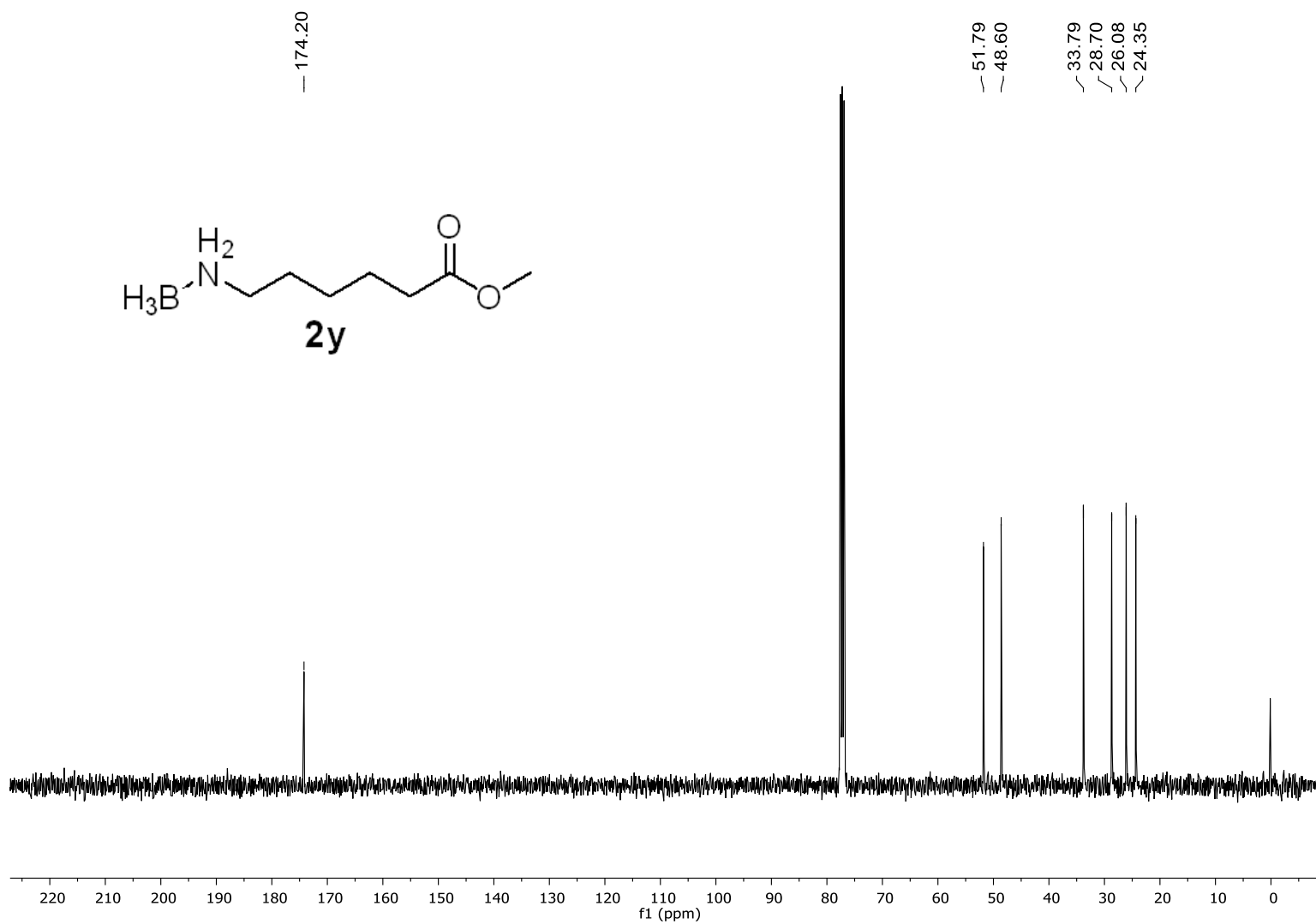


^{13}C NMR (75 MHz, CDCl_3) 2,2-Dimethoxy-*N,N*-dimethylethylamine-borane (2x)

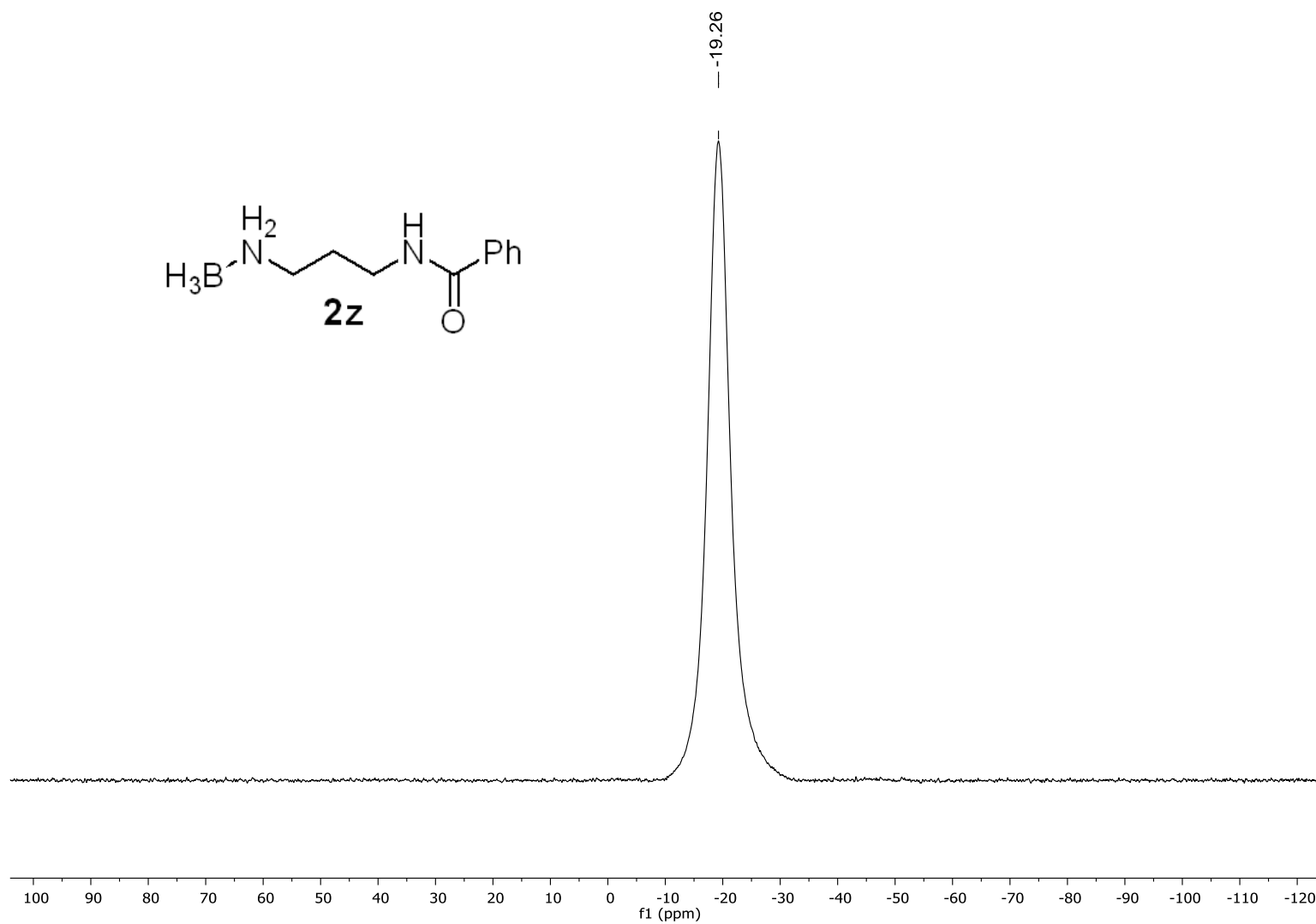


^{11}B NMR (96 MHz, CDCl_3) Methyl 6-aminohexanoate-borane (**2y**)

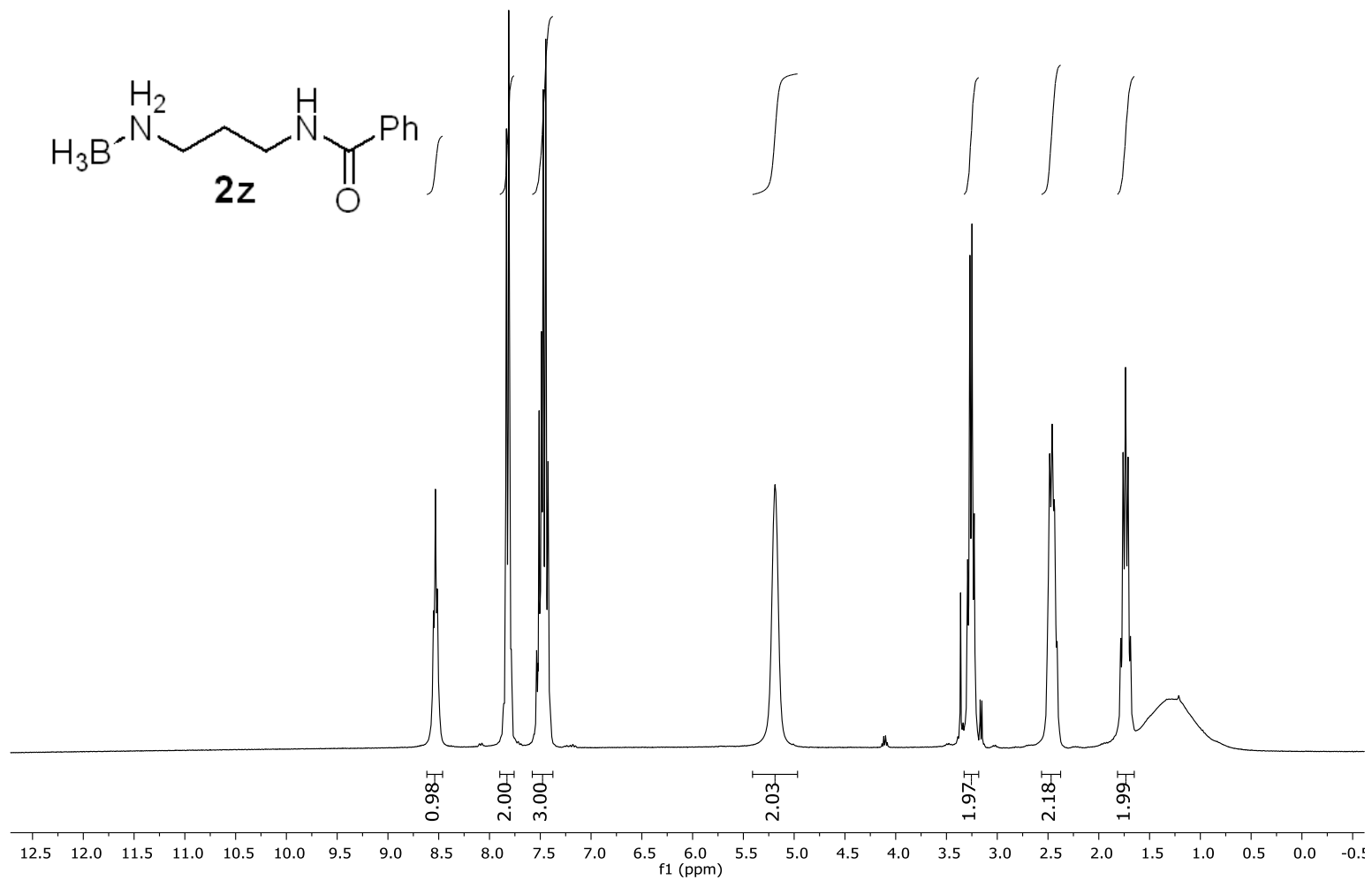




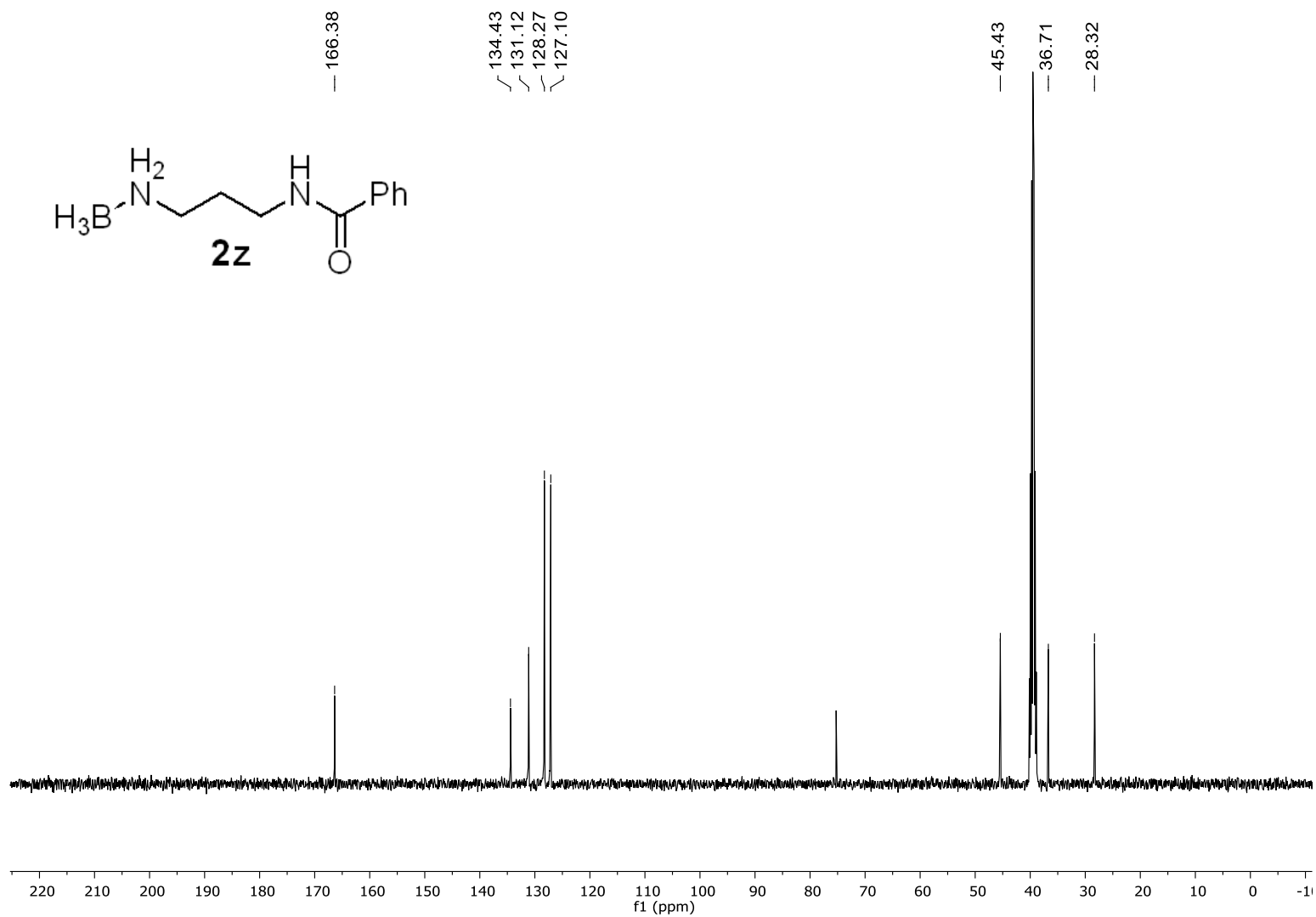
¹³C NMR (101 MHz, CDCl₃) Methyl 6-aminohexanoate-borane (**2y**)



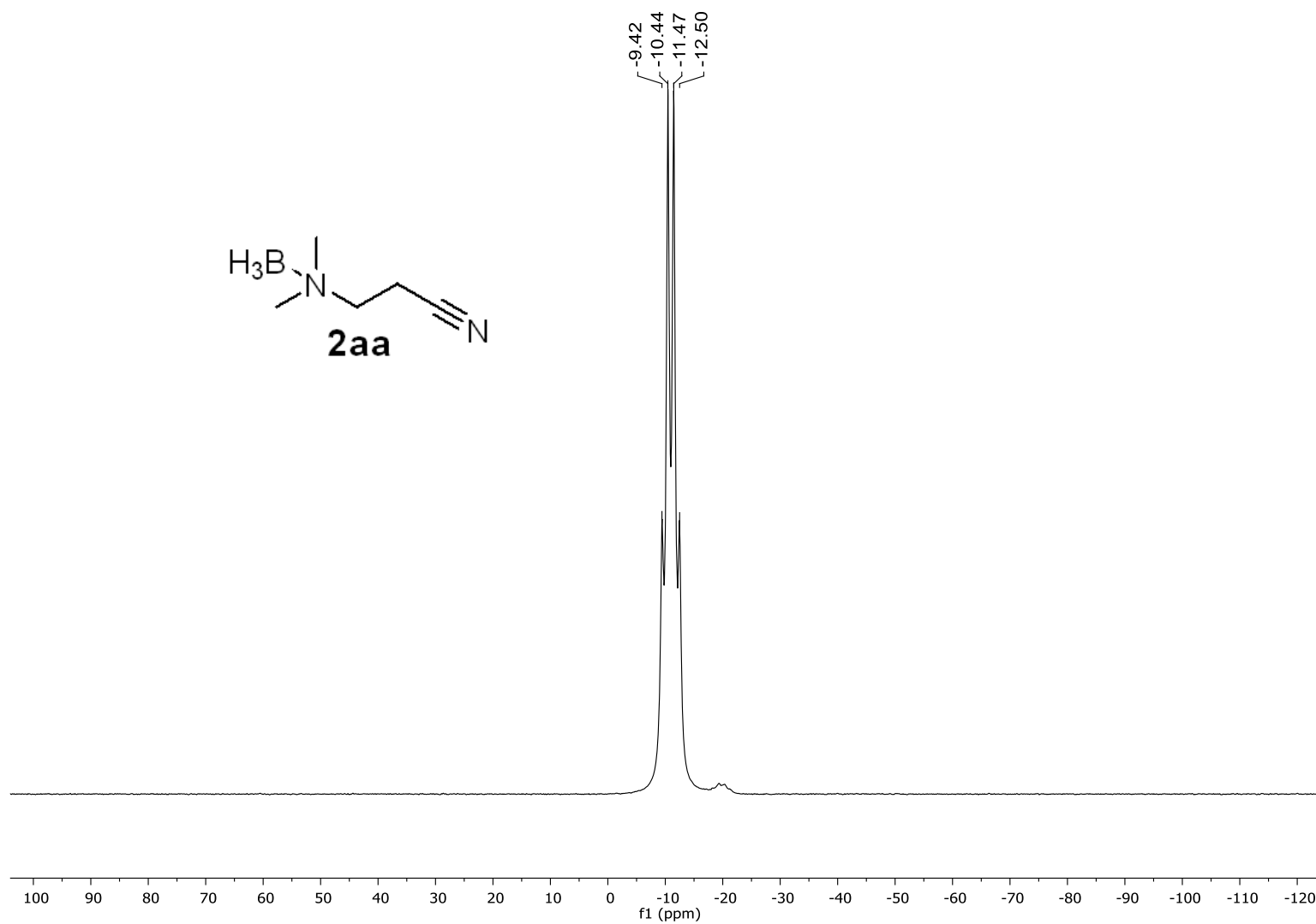
^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) *N*-(3-aminopropyl)benzamide-borane (**2z**)



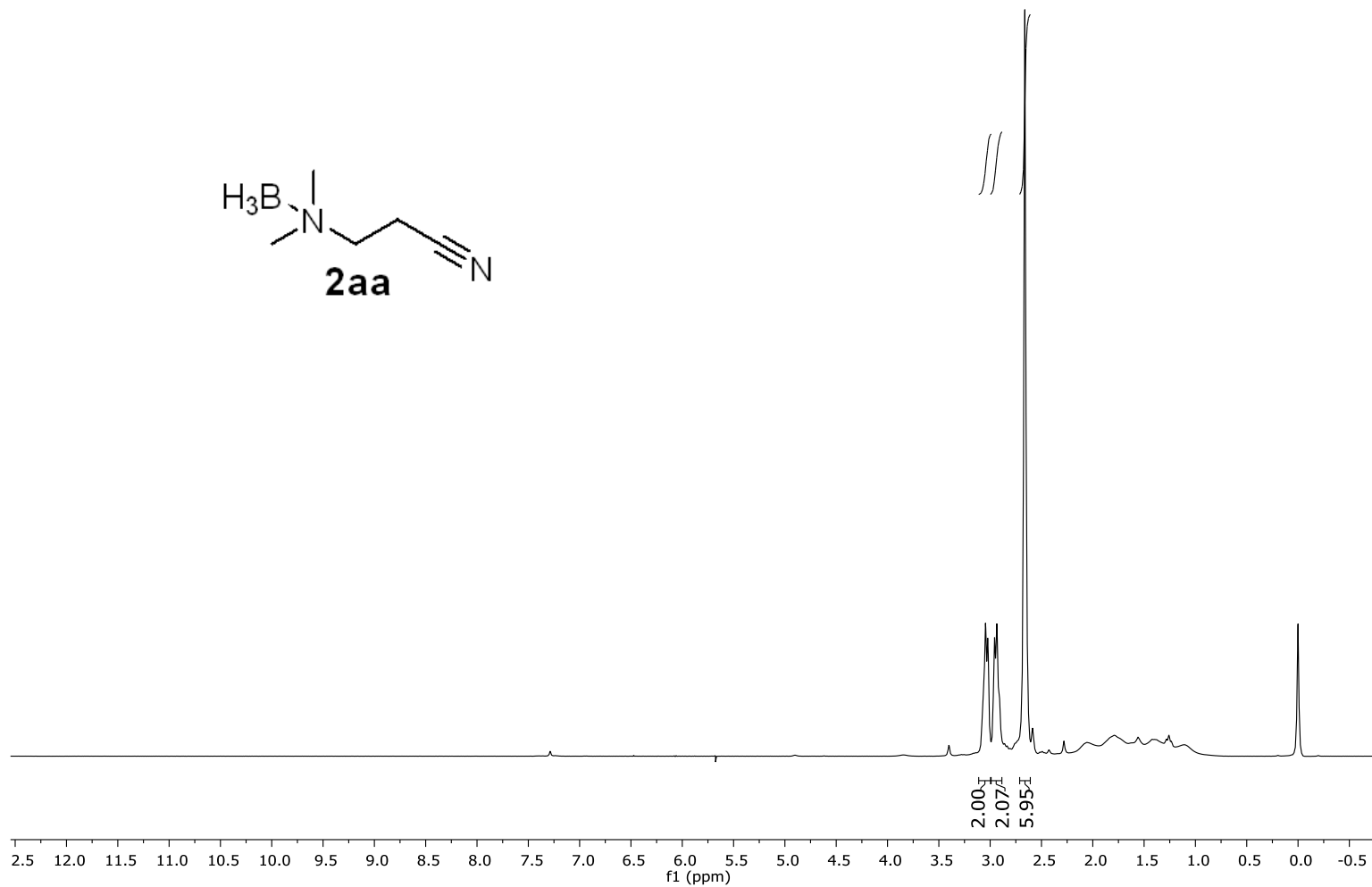
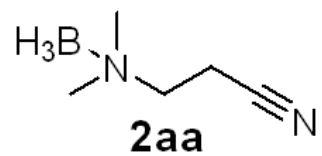
¹H NMR (300 MHz, DMSO-*d*₆) *N*-(3-aminopropyl)benzamide-borane (**2z**)



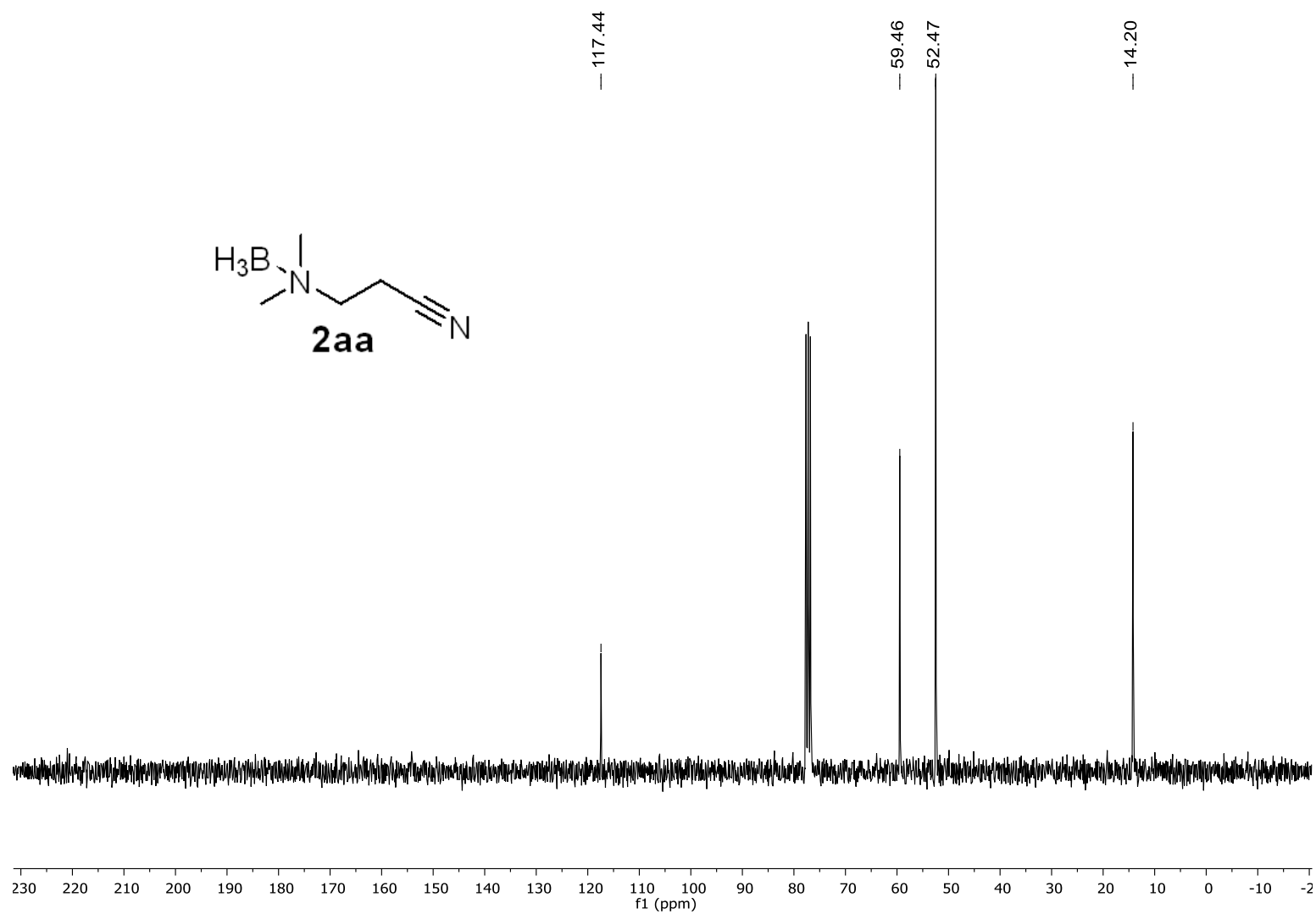
¹³C NMR (101 MHz, DMSO-*d*₆) *N*-(3-aminopropyl)benzamide-borane (**2z**)



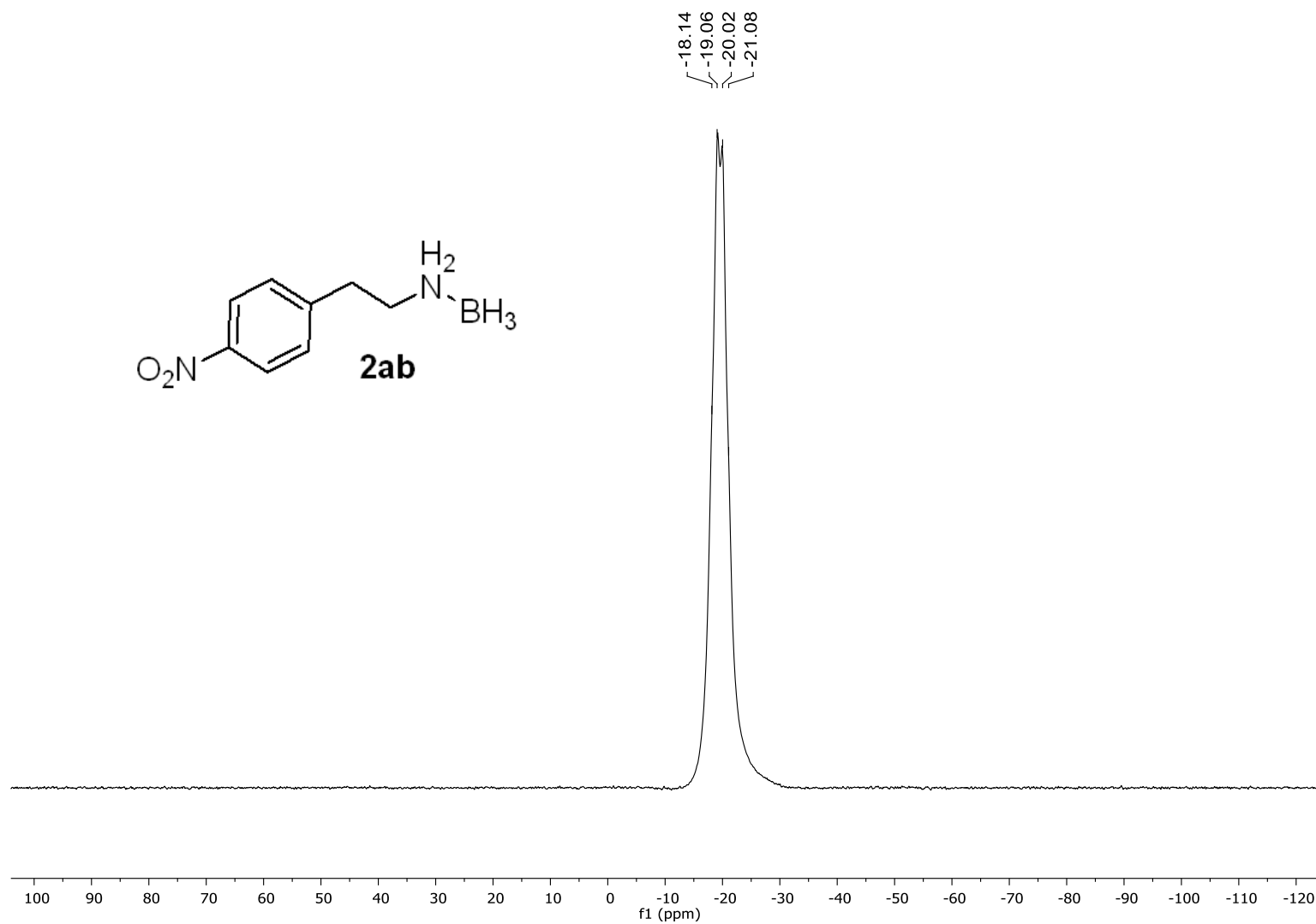
^{11}B NMR (96 MHz, CDCl_3) 3-(dimethylamino)propanenitrile-borane (**2aa**)



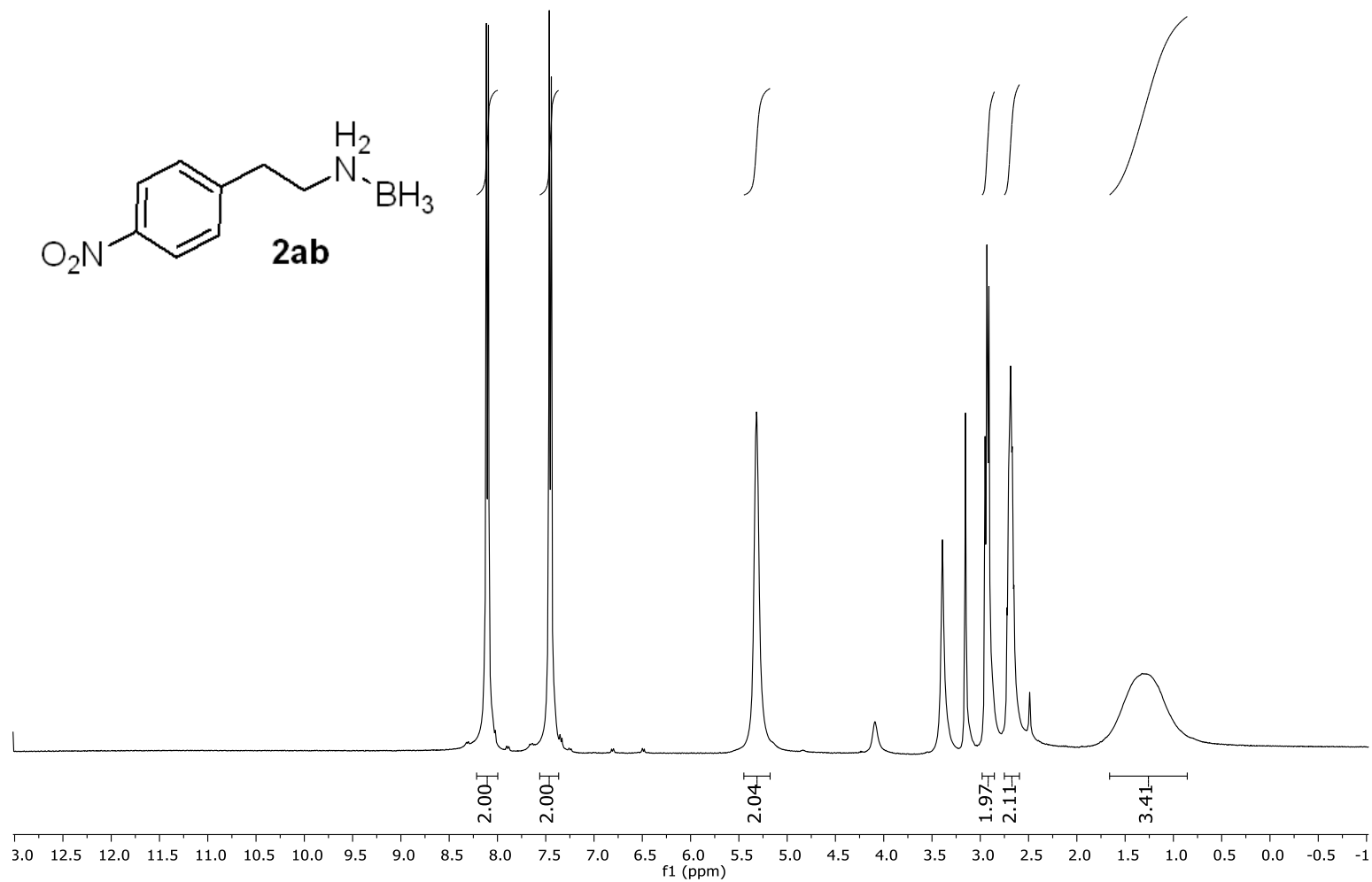
^1H NMR (300 MHz, CDCl_3) 3-(dimethylamino)propanenitrile-borane (**2aa**)



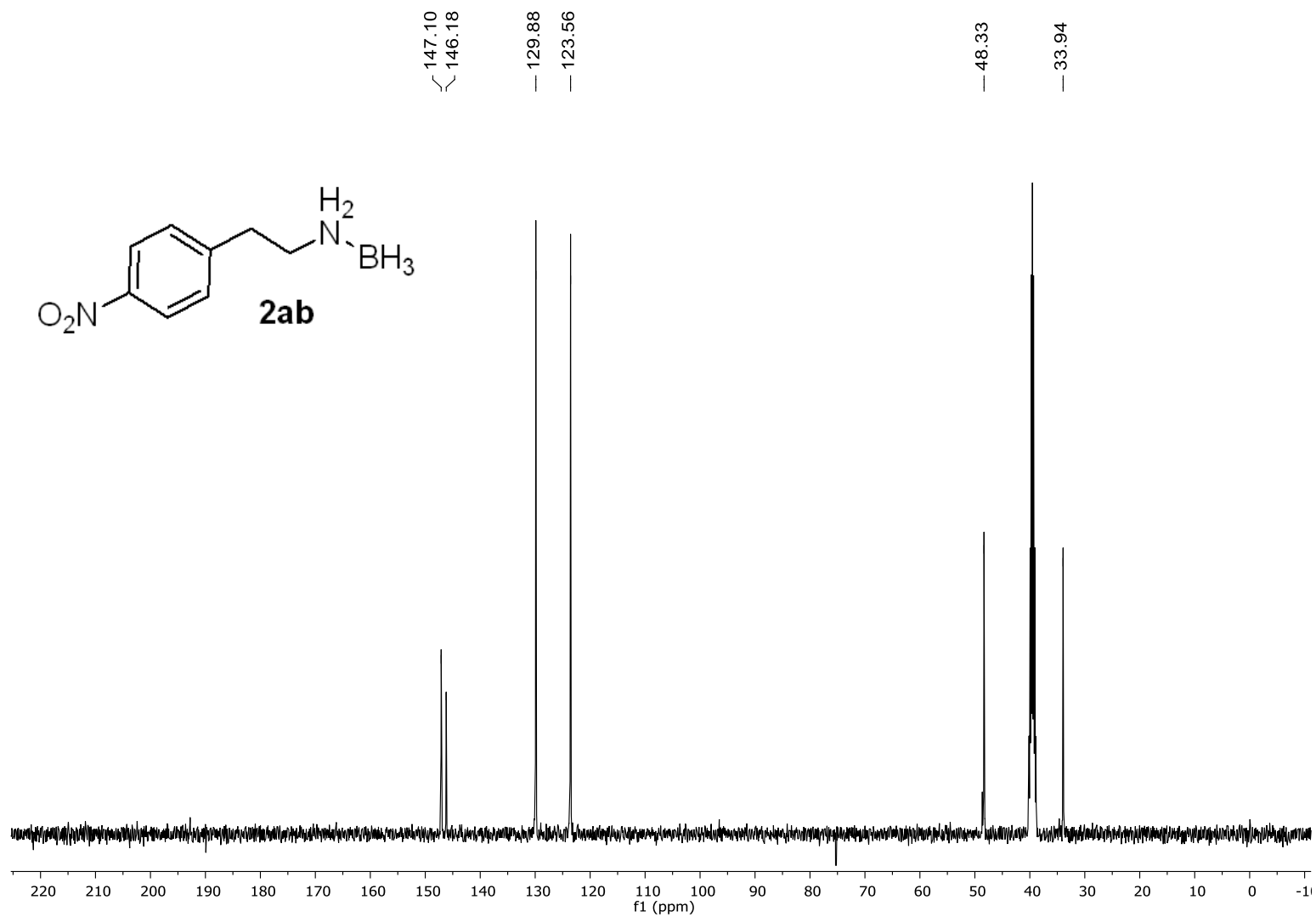
^{13}C NMR (101 MHz, CDCl_3) 3-(dimethylamino)propanenitrile-borane (**2aa**)



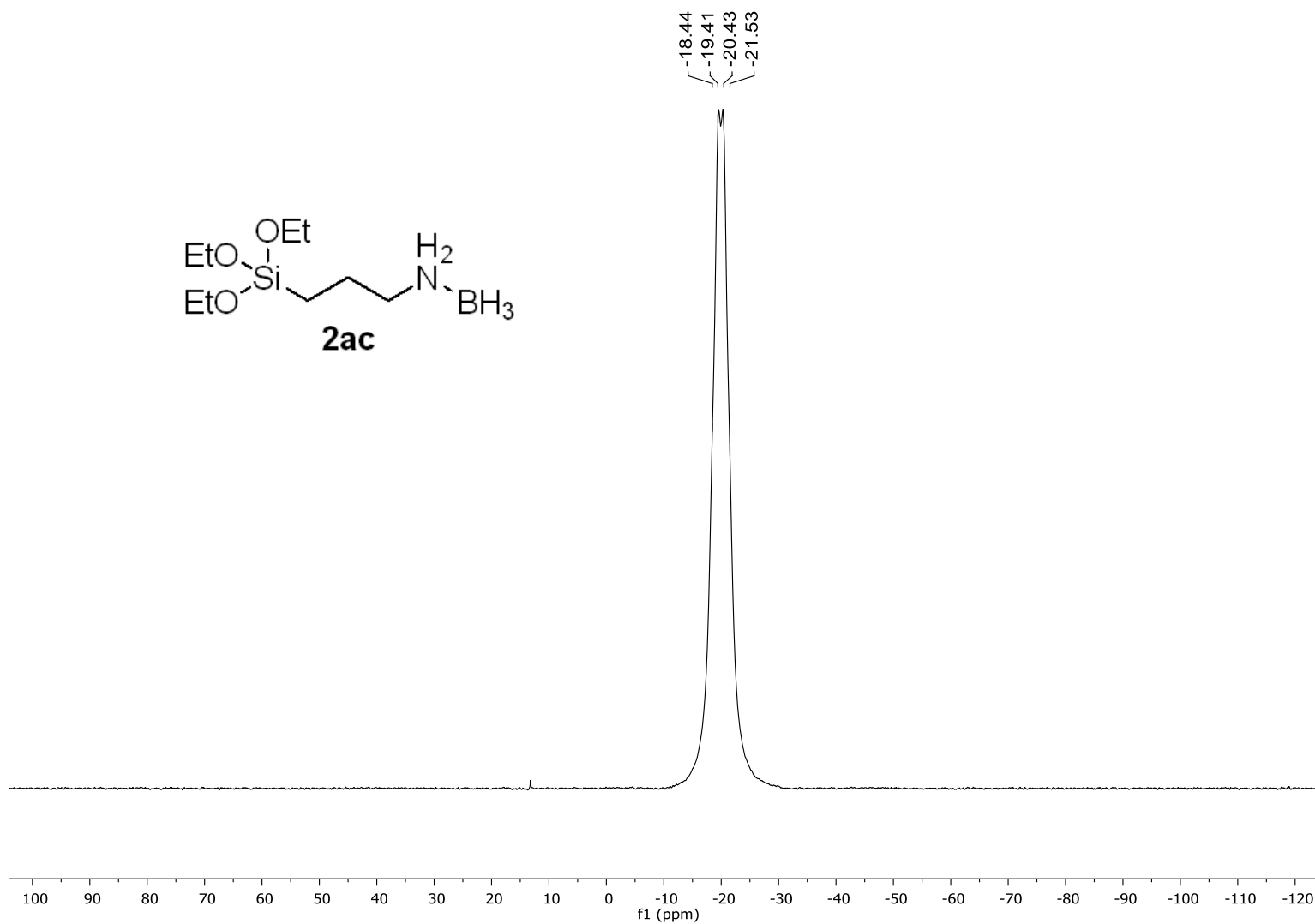
^{11}B NMR (96 MHz, $\text{DMSO-}d_6$) 2-(4-nitrophenyl)ethylamine-borane (**2ab**)



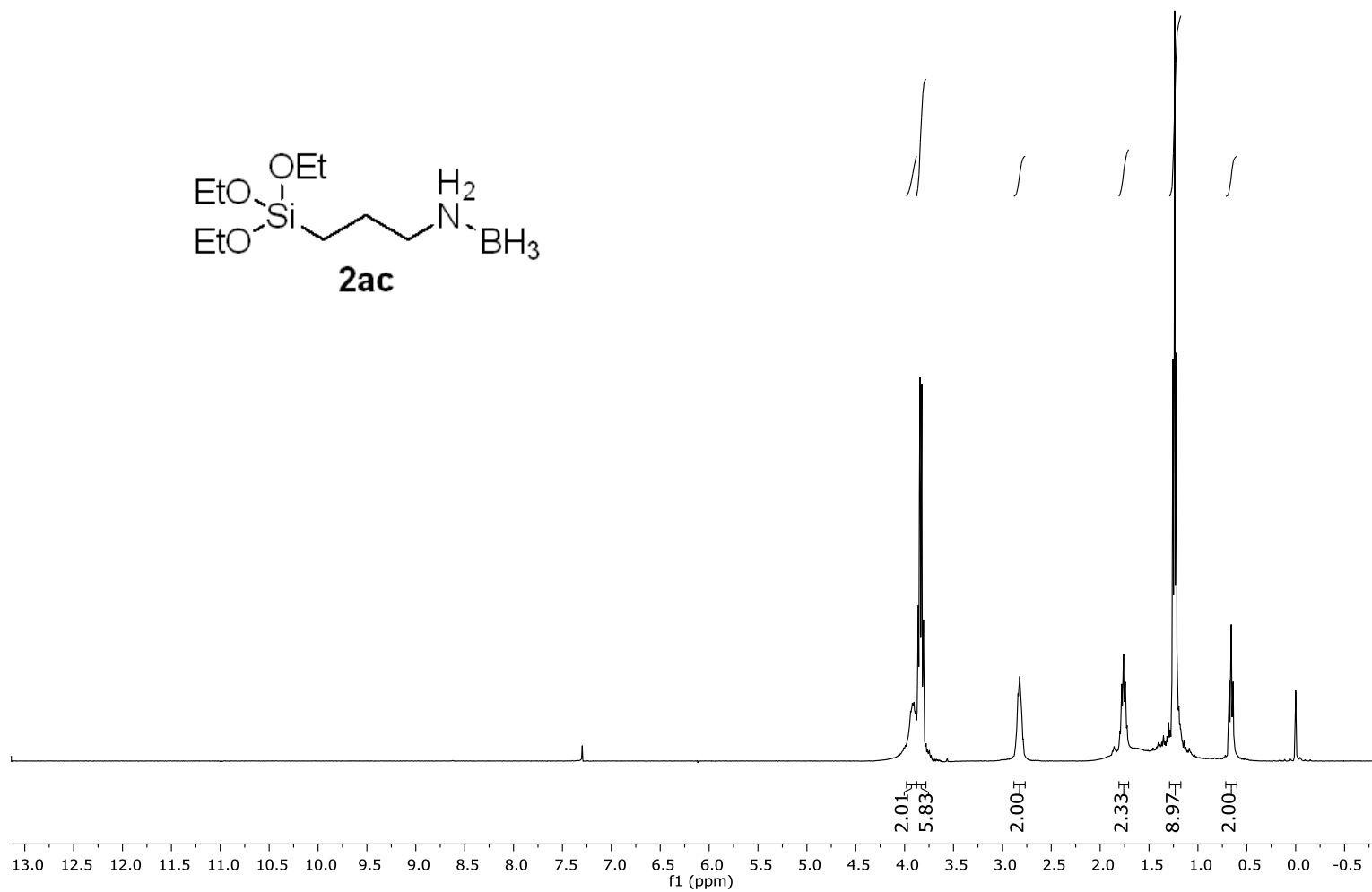
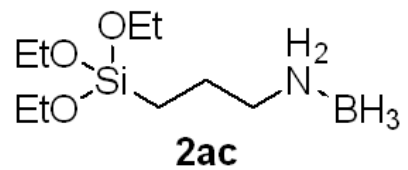
¹H NMR (400 MHz, DMSO-*d*₆) 2-(4-nitrophenyl)ethylamine-borane (**2ab**)



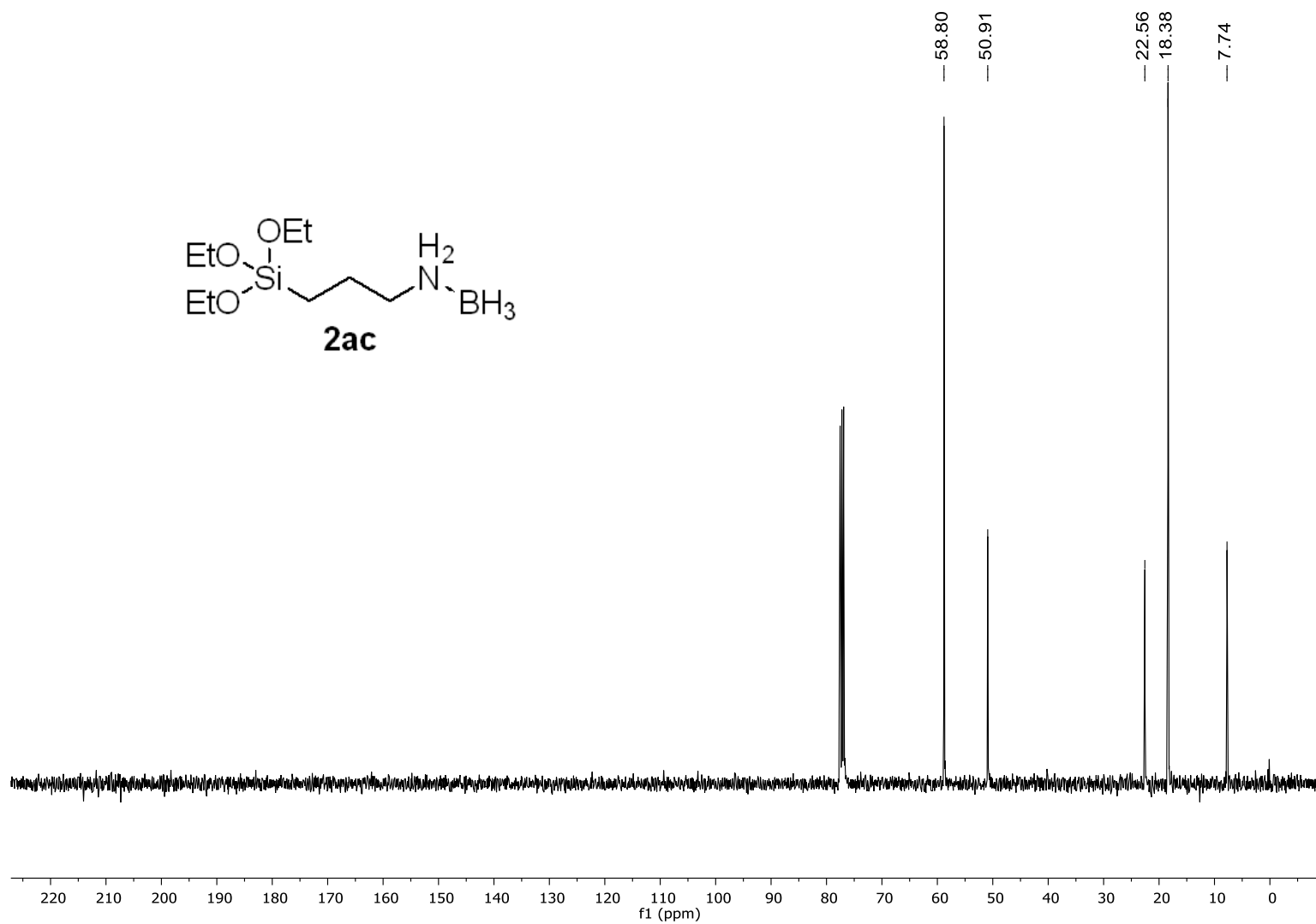
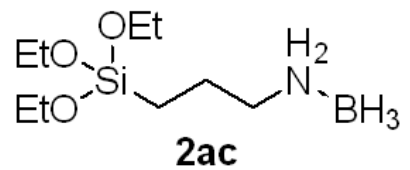
¹³C NMR (101 MHz, DMSO-*d*₆) 2-(4-nitrophenyl)ethylamine-borane (**2ab**)



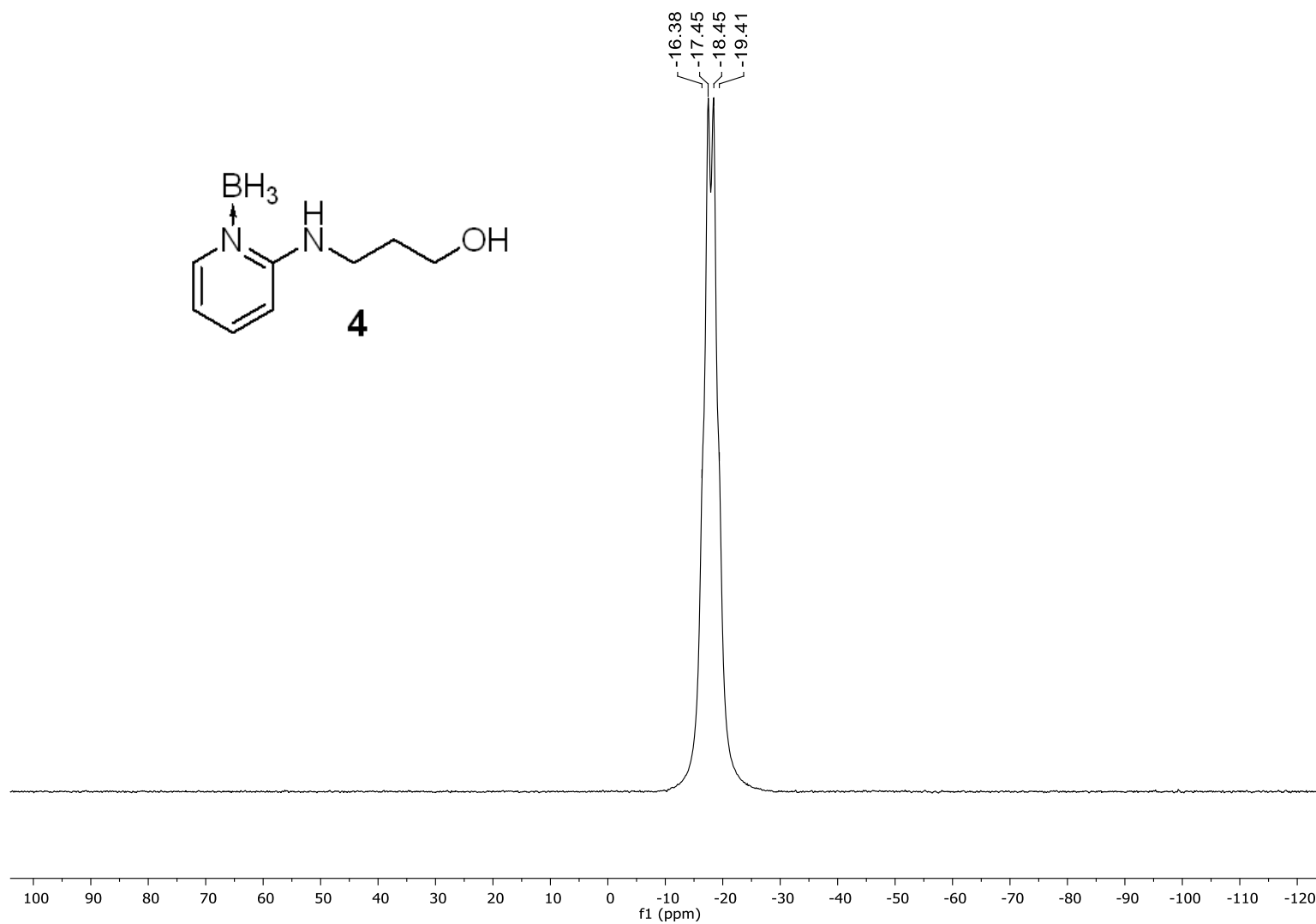
^{11}B NMR (96 MHz, CDCl_3) (3-aminopropyl)triethoxysilane-borane (**2ac**)



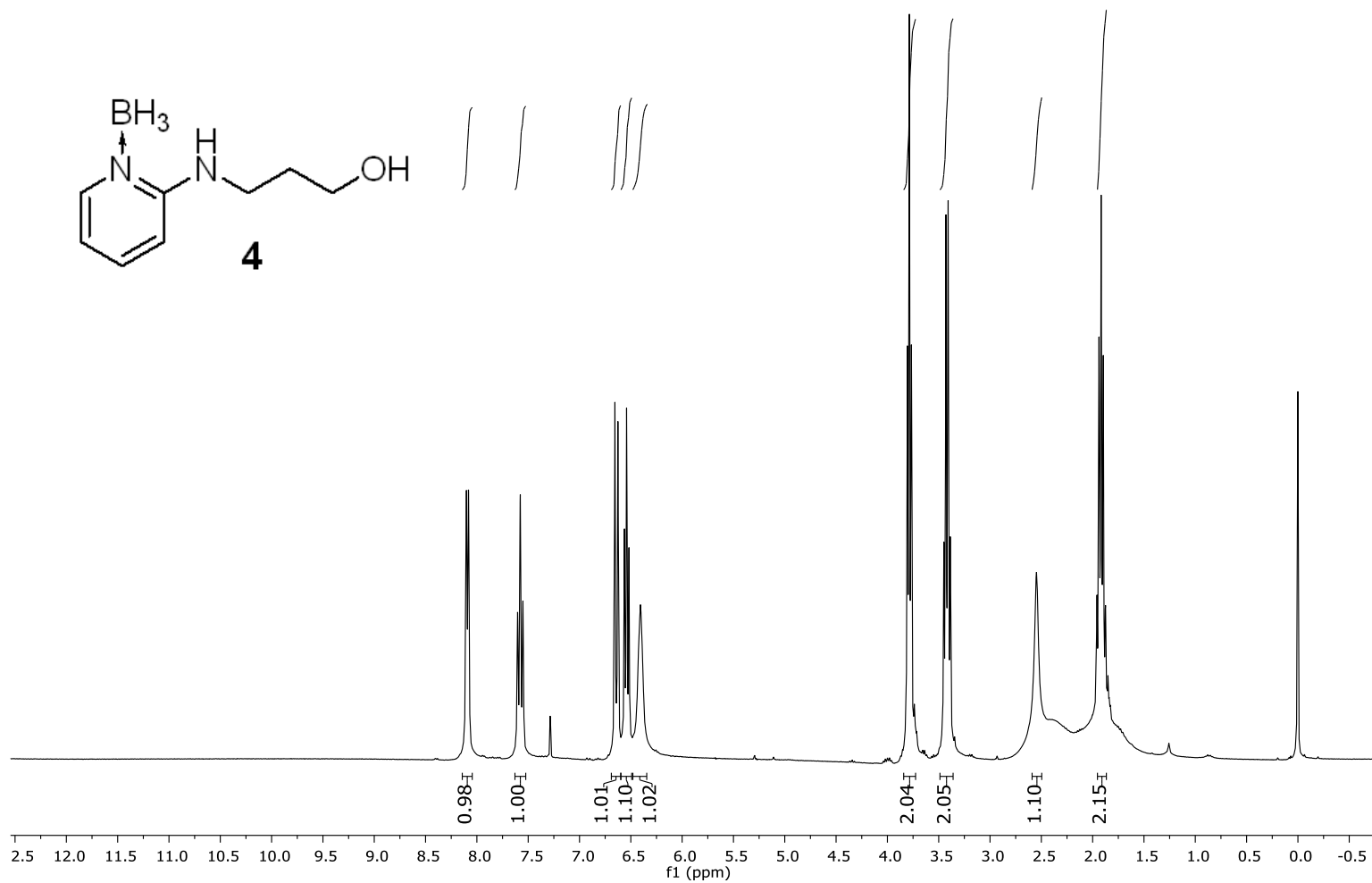
¹H NMR (400 MHz, CDCl₃) (3-aminopropyl)triethoxysilane-borane (**2ac**)



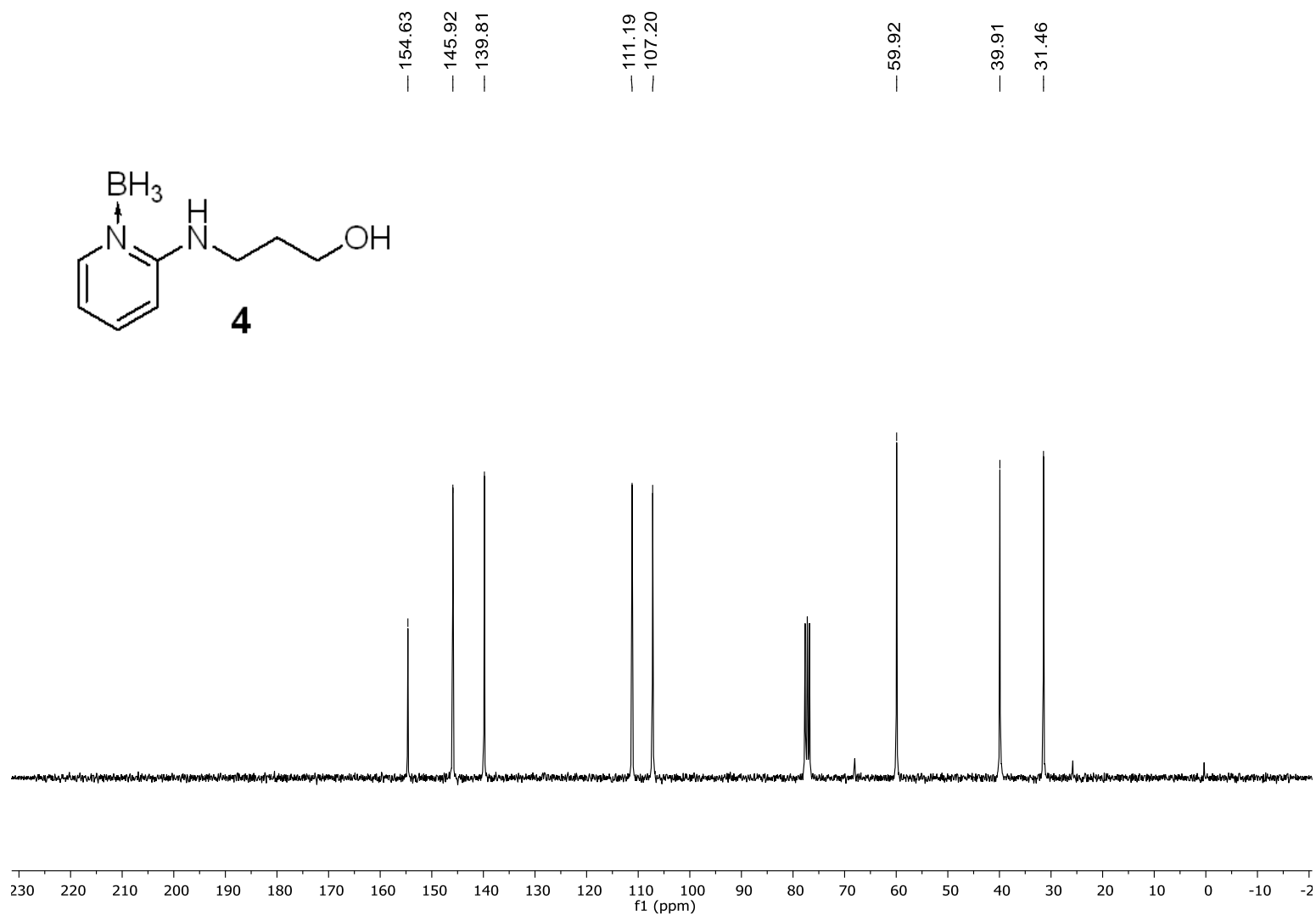
¹³C NMR (101 MHz, CDCl₃) (3-aminopropyl)triethoxysilane-borane (**2ac**)



^{11}B NMR (96 MHz, CDCl_3) 3-(pyridin-2-ylamino)propan-1-ol-borane (**4**)



¹H NMR (300 MHz, CDCl₃) 3-(pyridin-2-ylamino)propan-1-ol-borane (**4**)



^{13}C NMR (75 MHz, CDCl_3) 3-(pyridin-2-ylamino)propan-1-ol-borane (**4**)