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Supplementary Information

A Modular and Concise Approach to MIDA Acylboronates via Chemoselective Oxidation of Unsymmetrical Geminal Diborylalkanes: Unlocking Access to a Novel Class of Acylborons

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General Information

Materials

All reagents were purchased from Sigma-Aldrich, Acros Organics or TCI America. Anhydrous solvents (sure seal bottles) were purchased from Sigma-Aldrich. The cationic ruthenium(II) complex [CpRu(P–N)(MeCN)]PF_6 (P–N: 2-P*i*Pr_2-4-*t*Bu-1-Me-imidazole) was purchased from Strem Chemicals. Reaction progress was monitored via thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 TLC plates. The TLC plates were visualized under a UV lamp and/or by treatment with $KMnO_4$. Flash column chromatography was performed using a Teledyne-Isco CombiFlash Rf purification system employing Silica gel 60 Å (230-400 or 400-632 mesh size). Chromatographic solvent systems are given as volume:volume ratios. Organic solutions were concentrated via rotary evaporation under reduced pressure with a bath temperature of 40 ºC unless otherwise mentioned. All reactions were performed in oven-dried glassware under an atmosphere of dry nitrogen/argon unless otherwise mentioned.

Apparatus

^{1}H and ^{13}C NMR spectra were recorded on a Varian-400 (400 MHz, ^{1}H; 100 MHz, ^{13}C) spectrometer. ^{11}B and ^{19}F NMR were recorded on a Bruker Avance III 400 spectrometer (128 MHz, ^{11}B; 376 MHz, ^{19}F) The ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) and referenced to residual chloroform, acetonitrile, dimethyl sulfoxide or methanol signal as applicable. ^{11}B chemical shifts are referenced to an external standard of $BF_3{\cdot}Et_2O$ (δ = 0 ppm). ^{19}F chemical shifts are referenced to an external standard of 0.05% $C_6H_5CF_3$ in $CDCl_3$. The following abbreviations are used to designate chemical shift multiplicities: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, q = quartet. All ^{13}C NMR spectra are proton decoupled. *The carbon atoms connected to boron atom (C-B) were not detected in ^{13}C NMR (due to quadrupolar relaxation)*. NMR spectra were processed using MestReNova software. High resolution mass spectra (HRMS) were obtained at the Center for Mass Spectrometry at Stevens Institute of Technology using a Micromass Q-Tof. Melting points were measured on a IA9000 series Digital Melting Point Apparatus and are uncorrected.

Single crystal X-ray diffraction

Data for all compounds was collected on an Agilent SuperNova diffractometer at Columbia University using mirror-monochromated Cu Kα radiation. Data collection, integration, scaling (ABSPACK) and absorption correction (face-indexed Gaussian integration[1]) were performed in CrysAlisPro.[2] Structure solution was performed using ShelXT.[3] Subsequent refinement was performed by full-matrix least-squares on F^2 in ShelXL.[4] Olex2[5] was used for viewing and to prepare CIF files. ORTEP graphics were prepared in CrystalMaker.[6] Thermal ellipsoids are rendered at the 50% probability level.

Experimental Section

1. Procedure for the synthesis of symmetrical geminal diborylalkanes (2)

General procedure A

A mixture of CuCl (0.05 equiv), KO*t*Bu (0.1 equiv), and Xantphos (0.06 equiv) in anhydrous toluene (2 mL) was stirred for 15 min in a round bottom flask.[7] Thereafter, pinacolborane (2.4 equiv) was added and the reaction mixture was stirred for 10 min at 23 ºC. The alkyne substrate (1.6 mmol) was added and the reaction mixture stirred at 23 ºC. After 15 h, the reaction mixture was filtered through a pad of Celite and concentrated. The resulting residue was subjected to flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 5:95) to obtain the pure product.

General procedure B

A mixture of CuCl (0.05 equiv), K*Ot*Bu (0.1 equiv), and Xantphos (0.06 equiv) in anhydrous toluene (2 mL) was stirred for 15 min in a round bottom flask under a nitrogen atmosphere.[7] Pinacolborane (1.2 eq) was added to the reaction, and the mixture was stirred for 10 min at 23 ºC. Thereafter, vinyl boronic acid pinacol ester (2.0 mmol) was added and the reaction mixture stirred at 23 ºC. After 15 h, the reaction mixture was filtered through a pad of Celite and concentrated. The resulting residue was subjected to flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 5:95) to obtain the pure product.

Synthesis of 2p and 2q

Synthesis of 6-iodohex-1-yne (6): To an oven dried round bottom flask, 6-chlorohex-1-yne (10 mmol), sodium iodide (2 equiv) and 2-butanone (10 mL) were added. The flask was capped with rubber septum, evacuated and filled back with nitrogen (three cycles). Reaction was allowed to stirred at 85 ºC for 15 h, then concentrated. The resulting crude was diluted with DCM and washed with water, then dried over Na_2SO_4 and evaporated to dryness. The crude product was used as such without further purification in the following step.

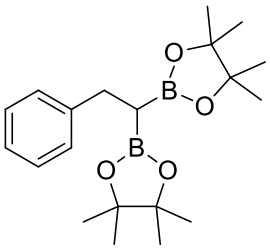
To a reaction vial equipped with a stir bar, diborylmethane (1 equiv) and THF (3 mL) were added. The vessel was evacuated and filled with nitrogen (three cycles).[8] LDA (1.1 equiv) was added via syringe at 0 ºC. The mixture was stirred for 5 min, then alkenyl or alkynyl halide (3.0 mmol) was added. The reaction mixture was allowed to reach room temperature (23 ºC) while stirring for 2 h, then diluted with EtOAc and washed with NH_4Cl. The organic layer was dried over Na_2SO_4, filtered and concentrated on vacuo, further purified by column chromatography (silica gel; EtOAc/hexanes, 0:10 to 5:95).

Synthesis of 2t

A 25 mL 3-neck flask was charged with B_2Pin_2 (2.5 equiv) and K_2CO_3 (0.6 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et_2O (3 mL), alkyne (1 mmol) and CH_3OH (5

equiv) were added. The reaction was allowed to stir at 50 °C for 15 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.[9]

2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2a)[10]



Following general procedure B; White solid; 65% yield.

R_f (EtOAc/Hexane, 1:9) = 0.50.

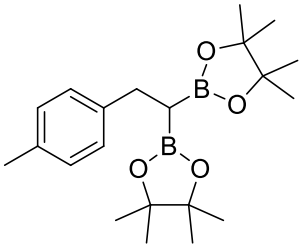
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 4H), 7.12 – 7.08 (m, 1H), 2.88 (d, *J* = 8.3 Hz, 2H), 1.18 – 1.16 (m, 25H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 128.5, 128.1, 125.5, 83.2, 31.4, 24.9, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.52.

Melting point: 44 – 45 ºC.

2,2'-(2-(p-tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b)[10]



Following general procedure A; White solid; 67% yield.

R_f (EtOAc/Hexane, 1:9) = 0.50.

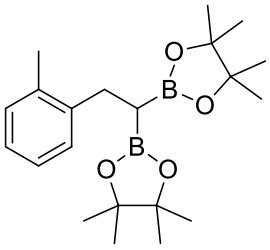
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 2H), 2.84 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H), 1.21 – 1.15 (m, 25H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 134.6, 128.7, 128.2, 83.1, 30.9, 24.9, 24.6, 21.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.85.

Melting point: 47 – 49 ºC.

2,2'-(2-(o-tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c)[10]



Following general procedure A; Sticky solid; 60% yield.

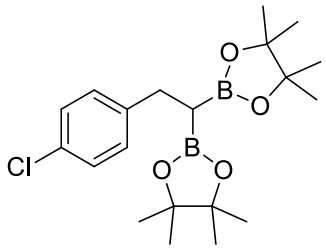
R_f (EtOAc/Hexane, 1:9) = 0.50.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.9 Hz, 1H), 7.05 – 6.95 (m, 3H), 3.07 (s, 2H), 2.33 (s, 3H), 1.16 (br s, 25H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.0, 129.2, 127.7, 124.9, 124.7, 83.0, 30.1, 24.7, 20.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.35.

2,2'-(2-(4-chlorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2d)[11]



Following general procedure B; white solid; 77% yield.

R_f (EtOAc/Hexane, 1:9) = 0.50.

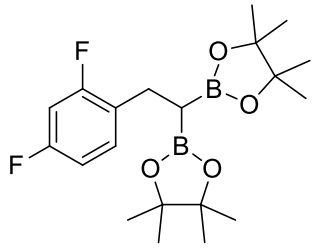
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 4H), 2.83 (d, *J* = 8.4 Hz, 2H), 1.18 (br s, 12H), 1.17 (br s, 13H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 131.1, 129.9, 128.1, 83.3, 30.8, 24.9, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.68.

Melting point: 63 – 65 ºC.

2,2'-(2-(2,4-difluorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2e)



Following general procedure B; White solid; 75% yield.

R_f (EtOAc/Hexane, 1:9) = 0.55.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 1H), 6.75 – 6.67 (m, 2H), 2.84 (d, *J* = 8.3 Hz, 2H), 1.62 (s, 1H), 1.18 (br s, 9H), 1.17 (br s, 15H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.4, 160.0, 131.1, 127.2, 110.5, 110.3, 103.4, 83.3, 25.0, 24.6, 24.2.

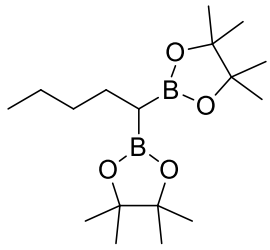
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.66.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.63, -114.83.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{20}H_{30}B_2F_2O_4Na$, calculated 417.2191; observed 417.2195.

Melting point: 72 – 73 ºC.

2,2'-(pentane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2f)



Following general procedure B; White solid; 88% yield.

R_f (EtOAc/Hexane, 1:9) = 0.68.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (q, *J* = 7.5 Hz, 2H), 1.25 – 1.22 (m, 4H), 1.20 (s, 12H), 1.20 (s, 12H), 0.84 (t, *J* = 6.8 Hz, 3H), 0.68 (t, *J* = 7.9 Hz, 1H).

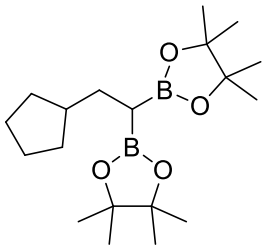
^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 35.0, 25.5, 25.0, 24.6, 22.8, 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.04.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{17}H_{34}B_2O_4Na$, calculated 347.2536; observed 347.2536.

Melting point: 57 – 58 ºC.

2,2'-(2-cyclopentylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2g)



Following general procedure A; White solid; 79% yield.

R_f (EtOAc/Hexane, 1:9) = 0.68.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 – 1.65 (m, 3H), 1.58 – 1.50 (m, 4H), 1.47 – 1.40 (m, 2H), 1.20 (s, 24H), 1.07 – 0.99 (m, 2H), 0.7 – 0.94 (m, 1H).

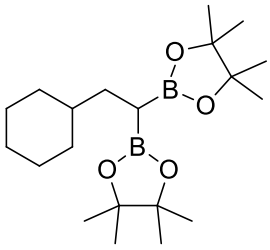
^{13}C NMR (100 MHz, $CDCl_3$) δ 82.9, 42.7, 32.5, 31.7, 25.2, 24.8, 24.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.86.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{19}H_{36}B_2O_4Na$, calculated 373.2692; observed 373.2694.

Melting point: 43 – 44 ºC.

2,2'-(2-cyclohexylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2h)[12]



Following general procedure A; Colorless oil; 74% yield.

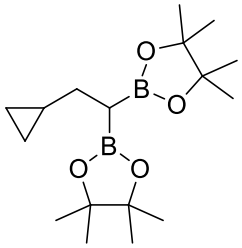
R_f (EtOAc/Hexane, 1:9) = 0.68.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 – 1.57 (m, 5H), 1.46 – 1.41 (m, 2H), 1.21 (m, 24H), 1.15 – 1.09 (m, 4H), 0.84 – 0.75 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 82.9, 39.9, 33.2, 33.0, 26.9, 26.6, 24.9, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.67.

2,2'-(2-cyclopropylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2i)



Following general procedure B; White solid; 83% yield.

R_f (EtOAc/Hexane, 1:9) = 0.68.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, *J* = 7.3 Hz, 2H), 1.20 (br s, 24H), 0.85 (t, *J* = 7.5 Hz, 1H), 0.70 – 0.62 (m, 1H), 0.34 – 0.29 (m, 2H), 0.02 (d, *J* = 4.5 Hz, 2H).

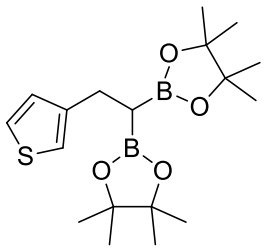
^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 31.0, 24.9, 24.7, 13.6, 4.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.85.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{17}H_{33}B_2O_4$, calculated 323.2560; observed 323.2565.

Melting point: 32 – 34 ºC.

2,2'-(2-(thiophen-3-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2j)[12]



Following general procedure B; Yellow liquid; 78% yield.

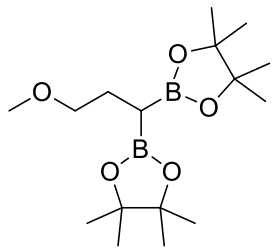
R_f (EtOAc/Hexane, 1:9) = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 6.97 – 6.93 (m, 2H), 2.88 (d, *J* = 8.3 Hz, 2H), 1.62 (s, 1H), 1.19 (s, 12H), 1.17 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 128.6, 124.8, 119.8, 83.3, 26.1, 24.9, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.85.

2,2'-(3-methoxypropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2k)[7]



Following general procedure B; Colorless oil; 77% yield.

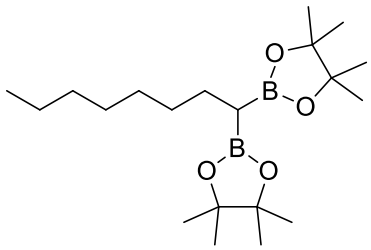
R_f (EtOAc/Hexane, 1:9) = 0.60.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 – 3.26 (m, 5H), 1.79 (q, *J* = 6.8 Hz, 2H), 1.20 (br s, 24H), 0.70 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 83.1, 74.7, 58.4, 25.7, 24.9, 24.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.67.

2,2'-(octane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2l)



Following general procedure B; Colorless oil; 88% yield.

R_f (EtOAc/Hexane, 1:9) = 0.68.

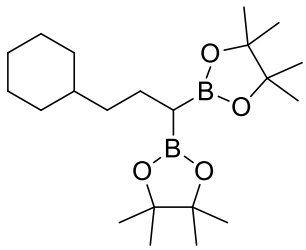
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 2H), 1.24 (br s, 10H), 1.22 (s, 12H), 1.21 (s, 12H), 0.85 (t, *J* = 6.6 Hz, 3H), 0.70 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 32.7, 32.0, 29.7, 29.4, 25.8, 25.0, 24.7, 22.8, 14.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.03.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{20}H_{40}B_2O_4Na$, calculated 389.3005; observed 389.3010.

2,2'-(3-cyclohexylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2m)[7]



Following general procedure A; White solid; 43% yield.

R_f (EtOAc/Hexane, 1:9) = 0.68.

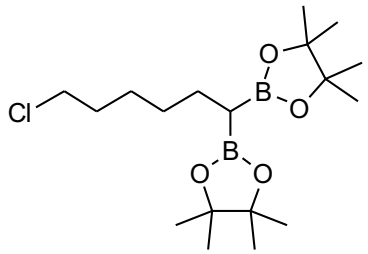
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 – 1.51 (m, 8H), 1.22 (s, 12H), 1.21 (s, 12H), 1.18 – 1.13 (m, 5H), 0.89 – 0.80 (m, 2H), 0.66 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 40.7, 37.9, 33.6, 26.9, 26.5, 25.0, 24.7, 23.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.95.

Melting point: 54 – 55 ºC.

2,2'-(6-chlorohexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 2n



Following general procedure A; colorless oil; 87% yield.

R_f (EtOAc/Hexane, 1:9) = 0.62.

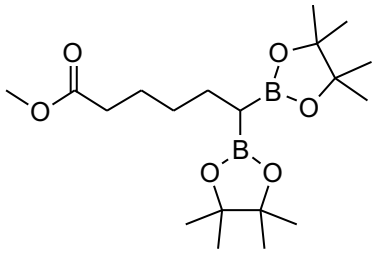
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (t, *J* = 6.9 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.58 – 1.51 (m, 2H), 1.45 – 1.36 (m, 2H), 1.34 – 1.28 (m, 2H), 1.22 (d, *J* = 3.7 Hz, 24H), 0.70 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 82.6, 44.7, 32.2, 31.3, 26.6, 25.2, 24.7, 24.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.67.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{18}H_{36}B_2ClO_4$, calculated 373.2483; observed 373.2485.

Methyl 6,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate 2o



Following general procedure A; colorless oil; 53% yield.

R_f (EtOAc/Hexane, 1:9) = 0.58.

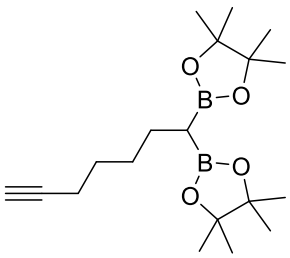
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.48 (m, 4H), 1.33 – 1.24 (m, 2H), 1.19 (d, *J* = 4.0 Hz, 24H), 0.67 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 83.0, 51.4, 34.2, 32.1, 25.3, 25.1, 24.9, 24.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.66.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{19}H_{37}B_2O_6$, calculated 383.2771; observed 383.2779.

2,2'-(hept-6-yne-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2p)



Following general procedure C; Colorless oil; 63% yield.

R_f (EtOAc/Hexane, 2:8) = 0.6.

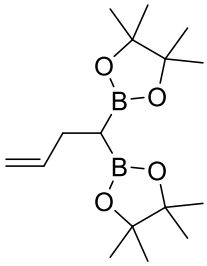
^{1}H NMR (400 MHz, CDCl3) δ 2.15 – 2.10 (m, 2H), 1.86 (t, *J* = 2.5 Hz, 1H), 1.57 – 1.44 (m, 4H), 1.40 – 1.32 (m, 2H), 1.20 (s, 12H), 1.19 (s, 12H), 0.68 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl3) δ 84.9, 83.0, 68.0, 31.7, 28.6, 25.2, 24.6, 18.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.05.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{19}H_{34}B_2O_4Na$, calculated 371.2536; observed 371.2543.

2,2'-(but-3-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2q)[8]



Following general procedure C; Colorless oil; 65% yield.

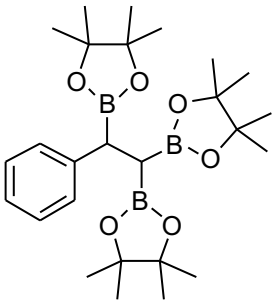
R_f (EtOAc/Hexane, 2:8) = 0.6.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.78 (m, 1H), 4.96 (d, *J* = 17.1 Hz, 1H), 4.83 (d, *J* = 10.0 Hz, 1H), 2.29 – 2.23 (m, 2H), 1.20 (s, 12H), 1.19 (s, 12H), 0.81 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 113.2, 83.1, 29.7, 24.9, 24.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.88.

2,2',2''-(2-phenylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 2t [9]



sticky liquid; 70% yield.

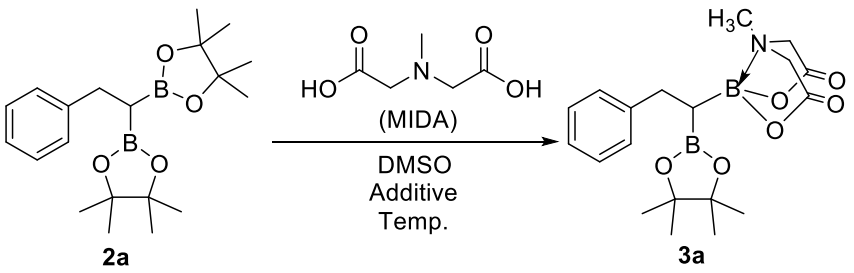
R_f (EtOAc/Hexane, 1:9) = 0.41.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 4H), 7.05 – 6.99 (m, 1H), 2.66 (d, *J* = 12.7 Hz, 1H), 1.44 (d, *J* = 12.8 Hz, 1H), 1.23 (d, *J* = 4.7 Hz, 12H), 1.13 (d, *J* = 8.3 Hz, 12H), 0.93 (d, *J* = 7.8 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 128.5, 127.8, 124.6, 24.9, 24.9, 24.7, 24.4, 24.4, 24.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.46.

Table S1. Optimization of reaction conditions for synthesis of unsymmetrical germinal boronate **(3)**



2a **3a**

Entry	MIDA (equiv)	Additive	Time (h)	Temp. (ºC)	Yield (%)[a]
1	1	-	15	130	<5
2	1	-	15	155	<5
3	1	-	15	160	<5
4	6	-	15	130	26
5	6	-	36	130	28
6	6	$HC(OEt)_3$ (4 equiv)	15	130	38
7	6	$HC(OEt)_3$ (4 equiv)	36	130	40

[a] Isolated yield.

2. Synthesis of unsymmetrical geminal diboryl compounds

2.1 General procedure for the synthesis of unsymmetrical geminal diboryl compounds 3

2 (2 mmol) and methyliminodiacetic acid (MIDA, 6 equiv) were placed in a thick wall high-pressure reaction tube equipped with a stir bar. DMSO (3 mL) and $HC(OEt)_3$ (4 equiv)[13] were added to the tube and purged with nitrogen, the resulting mixture was stirred at 130 ºC for 16 h. The reaction mixture was then cooled to room temperature and diluted with 15 mL H_2O. The mixture was extracted with EtOAc (3 x 200 mL). The combined organic phases were washed with brine, and then dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 10:0) to obtain **3**. The unreacted symmetrical diborylalkanes (**2**) were recovered and used again.

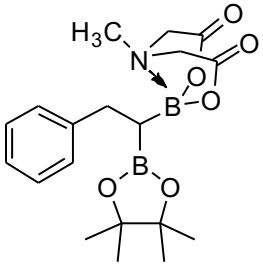
2.2 Synthesis of 3n and 3o

To a solution of **2n or 2o** (2 mmol) in a 2:1 mixture (12 mL) of acetone and water, ammonium acetate (3.1 eq.) and sodium periodate (3.1 eq.) were added. The resulting suspension was stirred at 80 °C (reflux) for 2 h. The mixture was then cooled down to room temperature and treated with 5 mL of saturated thiosulfate solution and 5 mL of water. The mixture was extracted with EtOAc(3 x 150 mL) The combined organic extracts were washed with brine, dried with Na_2SO_4, filtered and concentrated to afford the corresponding boronic acids.[14]

The crude residue and methyliminodiacetic acid (MIDA, 6 equiv) were placed in a thick wall high-

pressure reaction tube equipped with a stir bar. DMSO (3 mL) and $HC(OEt)_3$ (4 equiv)[13] were added to the tube and purged with nitrogen, the resulting mixture was stirred at 115 ºC for 16 h. The reaction mixture was then cooled to room temperature and diluted with 15 mL H_2O. The mixture was extracted with EtOAc (3 x 200 mL). The combined organic phases were washed with brine, and then dried over Na_2SO_4, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 10:0) to obtain **3n or 3o**.

6-methyl-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1,3,6,2-dioxazaborocane-4,8-dione (3a)



Sticky solid; 38% yield.

R_f (EtOAc) = 0.33.

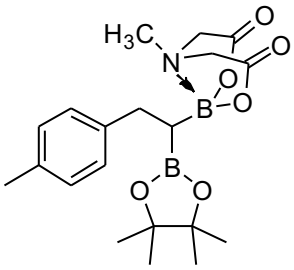
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 4H), 7.15 – 7.10 (m, 1H), 3.85 – 3.79 (m, 3H), 3.72 – 3.66 (m, 1H), 2.98 (s, 3H), 2.92 – 2.88 (m, 2H), 1.10 (d, *J* = 3.4 Hz, 12H), 0.89 – 0.83 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.9, 144.6, 128.8, 128.2, 125.6, 83.5, 63.1, 62.6, 46.2, 32.0, 25.1, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.27, 34.80.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{19}H_{27}B_2NO_6Na$, calculated 410.1923; observed 410.1917.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)ethyl)-1,3,6,2-dioxazaborocane-4,8-dione (3b)



White solid; 31% yield.

R_f (EtOAc) = 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 2H), 3.82 – 3.73 (m, 3H), 3.68 – 3.64 (m, 1H), 2.96 (s, 3H), 2.86 (d, *J* = 7.7 Hz, 2H), 2.28 (s, 3H), 1.12 (s, 12H), 0.82 (t, *J* = 7.5 Hz, 1H).

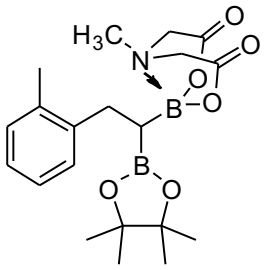
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.9, 141.5, 135.0, 128.8, 128.6, 83.4, 63.1, 62.7, 46.3, 31.6, 25.1, 24.9, 21.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.06, 34.78.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{20}H_{29}B_2NO_6Na$, calculated 424.2072; observed 424.2074.

Melting point: 207 – 210 ºC.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(o-tolyl)ethyl)-1,3,6,2-dioxazaborocane-4,8-dione (3c)



Sticky liquid; 30% yield.

R_f (EtOAc) = 0.33.

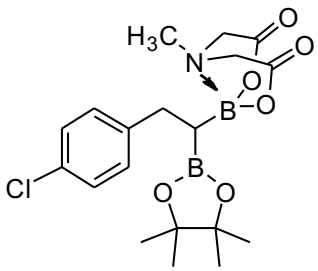
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 1H), 7.07 (q, *J* = 8.1, 7.4 Hz, 3H), 3.91 – 3.68 (m, 4H), 3.03 (s, 3H), 2.94 – 2.81 (m, 2H), 2.33 (s, 3H), 1.11 (d, *J* = 5.1 Hz, 12H), 0.90 – 0.77 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.8, 142.7, 136.3, 130.1, 128.8, 125.7, 125.6, 83.5, 63.1, 62.6, 46.3, 29.0, 25.2, 24.9, 19.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.61, 34.92.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{20}H_{29}B_2NO_6Na$, calculated 424.2073; observed 424.2080.

2-(2-(4-chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3d)



White solid; 60% yield.

R_f (EtOAc) = 0.33.

^{1}H NMR (400 MHz, CD_3CN) δ 7.24 (s, 4H), 4.30 – 3.63 (m, 4H), 3.00 (s, 3H), 2.88 – 2.53 (m, 2H), 1.06 (d, *J* = 4.7 Hz, 12H), 0.88 – 0.76 (m, 1H).

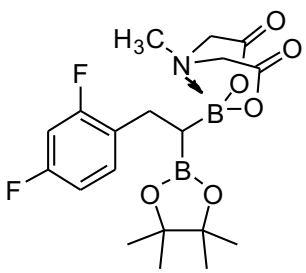
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.6, 143.3, 131.2, 130.2, 128.1, 83.6, 63.2, 62.6, 46.3, 31.5, 25.2, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.24, 34.98.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{19}H_{26}B_2ClNO_6Na$, calculated 444.1531; observed 444.1527.

Melting point: 223 – 224 ºC.

2-(2-(2,4-difluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3e)



Sticky solid; 42% yield.

R_f (EtOAc) = 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 6.77 – 6.67 (m, 2H), 3.93 – 3.75 (m, 4H), 3.07 (s, 3H), 2.85 – 2.82 (m, 2H), 1.11 (s, 12H), 0.86 (m, 1H).

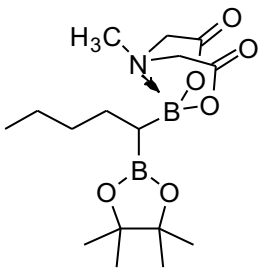
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.7, 162.5 (dd, J_{C-F} = 10.8, 22.2 Hz), 160.0 (dd, J_{C-F} = 10.7, 23.0 Hz), 131.9, 131.8, 131.8, 127.0 (d, *J* = 11.8 Hz), 110.5 (dd, *J* = 20.5, 3.7 Hz), 103.4 (t, *J* = 25.9 Hz), 83.6, 63.1, 62.7, 46.3, 31.1, 25.3, 25.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.07, 34.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.01, -114.43.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{19}H_{26}B_2F_2NO_6$, calculated 424.1909; observed 424.1914.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)-1,3,6,2-dioxazaborocane-4,8-dione (3f)



White solid; 40% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 – 3.74 (m, 4H), 3.01 (s, 3H), 1.67 – 1.54 (m, 1H), 1.52 – 1.44 (m, 1H), 1.43 – 1.36 (m, 1H), 1.33 – 1.25 (m, 3H), 1.22 (s, 12H), 0.87 (t, *J* = 6.5 Hz, 3H), 0.42 (m, 1H).

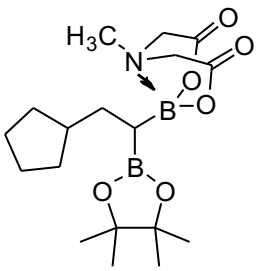
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.5, 83.2, 63.1, 62.8, 46.3, 34.5, 26.2, 25.1, 25.0, 23.1, 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.59, 34.90.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{16}H_{29}B_2NO_6Na$, calculated 376.2074; observed 376.2077.

Melting point: 48 – 50 ºC.

2-(2-cyclopentyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3g)



White solid; 38% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 – 3.74 (m, 4H), 3.01 (s, 3H), 1.89 – 1.80 (m, 1H), 1.77 – 1.68 (m, 3H), 1.60 – 1.55 (m, 2H), 1.51 – 1.45 (m, 2H), 1.38 – 1.31 (m, 1H), 1.22 (s, 12H), 1.10 – 1.00 (m, 2H), 1.12 – 0.98 (m, 1H).

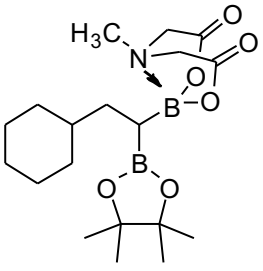
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.5, 83.2, 63.0, 62.7, 46.3, 42.2, 33.4, 32.6, 32.2, 25.3, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.77, 35.48.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{18}H_{32}B_2NO_6$, calculated 380.2411; observed 380.2422.

Melting point: 245 – 248 ºC.

2-(2-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3h)



White solid; 43% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 – 3.74 (m, 4H), 3.01 (s, 3H), 1.82 – 1.53 (m, 8H), 1.22 (s, 12H), 1.16 – 1.07 (m, 3H), 0.91 – 0.81 (m, 1H), 0.80 – 0.69 (m, 1H), 0.56 (d, *J* = 9.8 Hz, 1H).

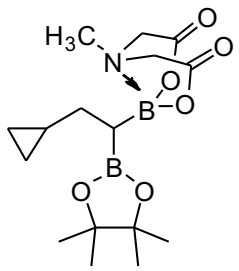
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.4, 83.2, 63.0, 62.7, 46.2, 39.5, 34.4, 33.9, 32.5, 26.9, 26.6, 26.5, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.62, 35.48.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{19}H_{33}B_2NO_6Na$, calculated 416.2386; observed 416.2389.

Melting point: 242 – 244 ºC.

2-(2-cyclopropyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3i)



Sticky solid; 83% yield.

R_f (EtOAc) = 0.5.

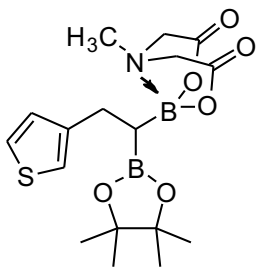
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 – 3.73 (m, 4H), 3.02 (s, 3H), 1.71 – 1.61 (m, 2H), 1.23 (s, 12H), 0.88 – 0.81 (m, 1H), 0.62 – 0.55 (m, 1H), 0.43 – 0.32 (m, 2H), 0.14 – 0.07 (m, 1H), 0.02 – -0.05 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.3, 83.3, 63.2, 62.8, 46.4, 31.7, 25.2, 25.0, 13.4, 5.7, 4.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.83, 35.48.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{16}H_{28}B_2NO_6$, calculated 352.2098; observed 352.2099.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-3-yl)ethyl)-1,3,6,2-dioxazaborocane-4,8-dione (3j)



Pale yellowish solid; 35% yield.

R_f (EtOAc) = 0.45.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 1H), 7.02 – 6.97 (m, 2H), 3.88 – 3.75 (m, 3H), 3.69 (d, *J* = 16.7 Hz, 1H), 2.97 (s, 3H), 2.93 – 2.86 (m, 2H), 1.14 (s, 12H), 0.84 (dd, *J* = 10.2, 4.6 Hz, 1H).

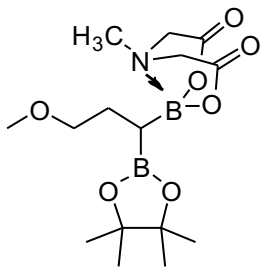
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.8, 145.1, 128.9, 124.9, 120.4, 83.5, 63.1, 62.7, 46.2, 26.6, 25.1, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.44, 34.97.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{17}H_{25}B_2NO_6SNa$, calculated 416.1481; observed 416.1483.

Melting point: 210 – 213 ºC.

2-(3-methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3k)



White solid; 72% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (d, *J* = 16.5 Hz, 1H), 3.79 (d, *J* = 14.2 Hz, 3H), 3.48 – 3.38 (m, 2H), 3.30 (s, 3H), 3.03 (s, 3H), 1.86 – 1.78 (m, 2H), 1.21 (s, 12H), 0.55 – 0.49 (m, 1H).

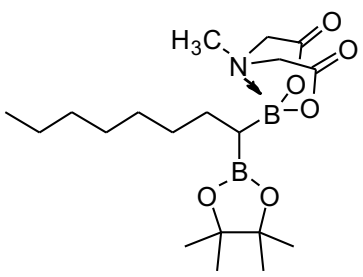
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.5, 83.4, 74.2, 63.3, 62.9, 58.4, 46.4, 26.3, 25.1, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.64, 35.86.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{15}H_{27}B_2NO_7Na$, calculated 378.1866; observed 378.1873.

Melting point: 178 – 179 ºC.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)-1,3,6,2-dioxazaborocane-4,8-dione (3l)



White solid; 51% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (d, *J* = 16.1 Hz, 1H), 3.81 – 3.74 (m, 3H), 3.01 (s, 3H), 1.55 – 1.38 (m, 2H), 1.28 – 1.25 (m, 7H), 1.22 (s, 15H), 0.87 (t, *J* = 6.5 Hz, 3H), 0.42 (d, *J* = 11.9 Hz, 1H).

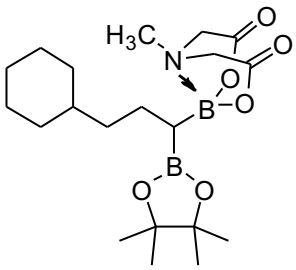
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 167.0, 83.3, 63.2, 62.8, 46.2, 32.3, 32.0, 30.0, 29.4, 26.6, 25.1, 25.0, 22.8, 14.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.62, 35.35.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{19}H_{35}B_2NO_6Na$, calculated 418.2543; observed 418.2551.

Melting point: 185 – 186 ºC.

2-(3-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3m)



White solid; 66% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 – 3.88 (m, 1H), 3.82 – 3.67 (m, 3H), 3.00 (s, 3H), 1.73 – 1.58 (m, 7H), 1.31 (m, 1H), 1.23 (s, 12H), 1.20 – 1.13 (m, 5H), 0.92 – 0.82 (m, 2H), 0.39 (d, *J* = 9.2 Hz, 1H).

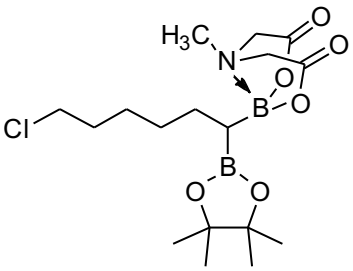
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.1, 83.3, 63.2, 62.8, 46.3, 40.2, 38.2, 33.8, 33.3, 26.9, 26.6, 26.5, 25.1, 25.0, 23.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 14.69, 35.34.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{20}H_{35}B_2NO_6Na$, calculated 430.2544; observed 430.2556.

Melting point: 54 – 55 ºC.

2-(6-chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3n)



White solid; 31% yield.

R_f (EtOAc) = 0.32.

^{1}H NMR (400 MHz, CD_3CN) δ 3.95 – 3.74 (m, 4H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.93 (s, 3H), 1.80 – 1.69 (m, 2H), 1.50 – 1.34 (m, 5H), 1.32 – 1.26 (m, 1H), 1.20 (s, 12H), 0.44 – 0.37 (m, 1H).

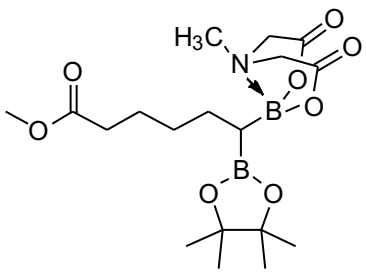
^{13}C NMR (100 MHz, CD_3CN) δ 169.2, 169.0, 83.8, 63.5, 63.4, 47.0, 46.2, 33.2, 32.0, 27.7, 27.1, 25.2, 25.2.

^{11}B NMR (128 MHz, CD_3CN) δ 13.22, 35.16.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{17}H_{30}B_2ClNO_6Na$, calculated 424.1840; observed 424.1847.

Melting point: 194 – 198 ºC.

Methyl 6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (3o)



White solid; 30% yield.

R_f (EtOAc) = 0.29.

^{1}H NMR (400 MHz, CD_3CN) δ 3.95 – 3.85 (m, 2H), 3.84 – 3.76 (m, 2H), 3.60 (s, 3H), 2.93 (s, 3H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.34 (m, 5H), 1.31 – 1.23 (m, 1H), 1.19 (s, 12H), 0.44 – 0.34 (m, 1H).

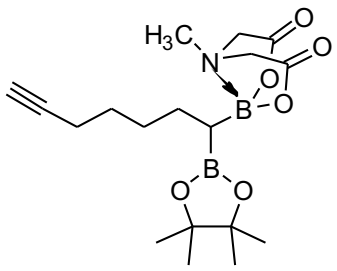
^{13}C NMR (100 MHz, CD_3CN) δ 174.7, 169.0, 63.0, 51.9, 47.4, 34.4, 25.3, 22.2.

^{11}B NMR (128 MHz, CD_3CN) δ 13.39, 35.26.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{18}H_{32}B_2NO_8$, calculated 412.2309; observed 412.2312.

Melting point: 189 – 195 ºC.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (3p)



Sticky solid; 67% yield.

R_f (EtOAc) = 0.42.

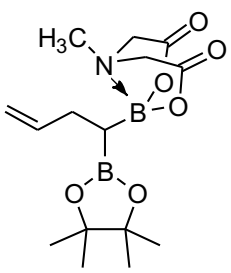
^{1}H NMR (400 MHz, CD_3CN) δ 3.95 – 3.75 (m, 4H), 2.93 (s, 3H), 2.18 – 2.10 (m, 3H), 1.54 – 1.32 (m, 6H), 1.20 (s, 12H), 0.40 (d, *J* = 9.4 Hz, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.2, 85.7, 83.8, 69.6, 63.5, 63.4, 46.9, 32.0, 29.6, 26.9, 25.2, 18.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 14.38, 36.23.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{18}H_{30}B_2NO_6$, calculated 378.2254; observed 378.2251.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (3q)



White solid; 70% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 – 5.90 (m, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 9.7 Hz, 1H), 3.97 – 3.73 (m, 4H), 3.03 (s, 3H), 2.39 – 2.27 (m, 2H), 1.21 (s, 12H), 0.54 – 0.49 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 167.1, 140.9, 113.7, 83.5, 63.2, 62.8, 46.4, 30.6, 25.2, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 13.63, 35.46.

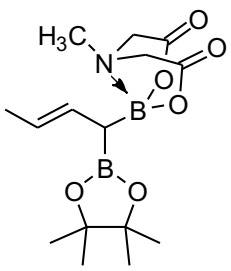
HRMS-ESI: *m/z* $[M+H]^+$ for $C_{15}H_{26}B_2NO_6$, calculated 338.1941; observed 338.1949.

Melting point: 175 – 178 ºC.

Isomerization of 3q

To a solution of **3q** (1.2 mmol) in DCM (4 mL), [CpRu(P-N)(MeCN)]PF_6 (0.02 eq) was added.[15] The reaction vial was evacuated and filled with nitrogen (three cycles) and stirred at 23 ºC. The reaction was monitored by NMR. Upon completion (after 15 h), the reaction mixture was filtered through a short plug of silica and rinsed with EtOAc. The filtrate was evaporated to afford the product as a yellowish solid which was found to be analytically pure.

6-methyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (3r)



White solid; 99% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 – 5.46 (m, 1H), 5.40 – 5.28 (m, 1H), 3.90 – 3.68 (m, 4H), 2.99 (s, 3H), 1.63 (d, *J* = 5.9 Hz, 3H), 1.54 (d, *J* = 8.7 Hz, 1H), 1.26 – 1.16 (m, 12H).

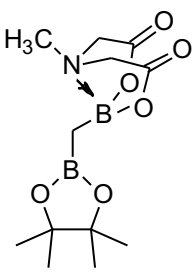
^{13}C NMR (100 MHz, CDCl3) δ 167.8, 167.5, 128.0, 125.2, 83.4, 62.9, 45.9, 24.9, 18.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.60, 34.24.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{15}H_{25}B_2NO_6Na$, calculated 360.1761; observed 360.1766.

Melting point: 83 – 85 ºC.

6-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,3,6,2-dioxazaborocane-4,8-dione (3s)



White solid; 40% yield.

R_f (EtOAc) = 0.25.

^{1}H NMR (400 MHz, CD_3CN) δ 3.96 – 3.77 (m, 4H), 2.90 (s, 3H), 1.20 (s, 12H), 0.08 (s, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 83.8, 63.0, 47.1, 25.1.

^{11}B NMR (128 MHz, CD_3CN) δ 13.43, 34.32.

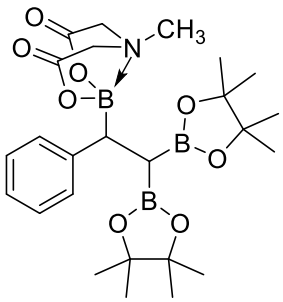
HRMS-ESI: *m/z* $[M+H]^+$ for $C_{12}H_{22}B_2NO_6$, calculated 298.1628; observed 298.1626.

Melting point: 174 – 181 ºC.

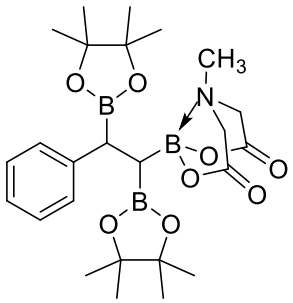
Attempted conversion of a 1,1,2-triBpin compound (2t) into unsymmetrical geminal diborylalkane

2t (0.8 mmol) and methyliminodiacetic acid (MIDA, 6 equiv) were placed in a thick wall high-pressure reaction tube equipped with a stir bar. DMSO (3 mL) and $HC(OEt)_3$ (4 equiv)[13] were added to the tube and purged with nitrogen, the resulting mixture was stirred at 130 ºC for 16 h. The reaction mixture was then cooled to room temperature and diluted with 15 mL H_2O. The mixture was extracted with EtOAc (3 x 200 mL). The combined organic phases were washed with brine,

and then dried over Na_2SO_4, filtered, and concentrated. The resulting residue was subjected to flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 10:0) to obtain **3t** and **3t'** as an inseparable mixture (1:1 ratio, NMR).

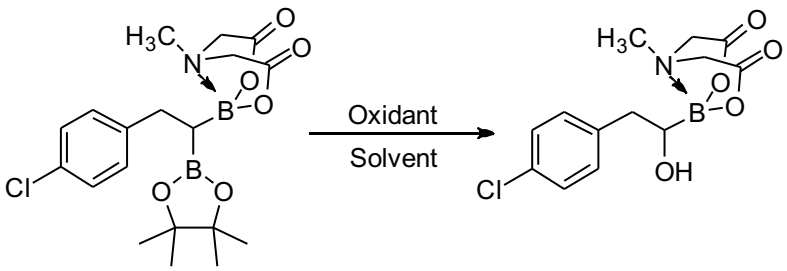


3t



3t'

Table S2. Optimization of reaction conditions for synthesis of α-hydroxy MIDA boronate



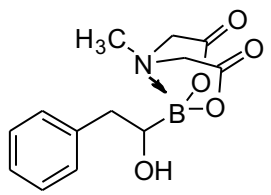
Entry	Oxidant	Solvent (v/v)	Temp. / Time (h)	Yield
1	$NaBO_3.H_2O$	ACN	23 ºC / 3 h	ND[a]
2	$NaBO_3.H_2O$	ACN	60 ºC / 3 h	ND
3	$NaBO_3.H_2O$	THF	23 ºC / 3 h	ND
4	$NaBO_3.H_2O$	THF / buffer (pH=7) (1:1)	23 ºC / 3 h	70%[b]
5	$NaBO_3.H_2O$	THF / H_2O (1:1)	23 ºC / 3 h	52%[b]
6	Oxone	THF / buffer (1:1)	23 ºC / 15 h	59%[c]

[a] Not Detected, [b] Isolated yield, [c] NMR yield.

3. General procedure for the synthesis of MIDA-hydroxyboronate (4)

To a stirred mixture of **3** (0.8 mmol) in THF (1.5 mL) and buffer (KH_2PO_4/NaOH, pH = 7, 1M, 1.5 mL) at 0 °C, $NaBO_3 \cdot H_2O$ (1.3 equiv) was added. The reaction mixture was allowed to reach room temperature (23 ºC) over 3 h. Thereafter, dry Na_2SO_4 was added, the reaction mixture was filtered and the residue washed with EtOAc. The filtrate was concentrated to give a residue which was subjected to flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 10:0) to obtain the pure product.

2-(1-hydroxy-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4a)[16]



Colorless oil; 73% yield.

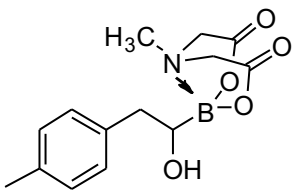
R_f (EtOAc) = 0.23.

^{1}H NMR (400 MHz, CD_3CN) δ 7.35 – 7.23 (m, 4H), 7.24 – 7.18 (m, 1H), 4.01 – 3.76 (m, 4H), 3.51 (m, 1H), 3.02 (s, 3H), 2.94 – 2.84 (m, 1H), 2.72 – 2.61 (m, 1H), 2.19 (m, 1H).

^{13}C NMR (100 MHz, CD_3OD) δ 171.3, 170.6, 142.1, 130.4, 129.2, 126.9, 63.6, 63.4, 46.1, 40.6.

^{11}B NMR (128 MHz, CD_3OD) δ 11.37.

2-(1-hydroxy-2-(p-tolyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4b)



Colorless oil; 73% yield.

R_f (EtOAc) = 0.23.

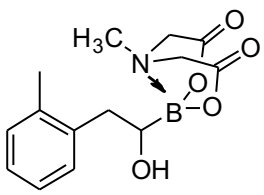
^{1}H NMR (400 MHz, CD_3OD) δ 7.18 – 7.05 (m, 4H), 4.23 – 4.04 (m, 2H), 4.01 – 3.87 (m, 2H), 3.56 – 3.41 (m, 1H), 3.08 (s, 3H), 2.91 – 2.81 (m, 1H), 2.73 – 2.61 (m, 1H), 2.29 (s, 3H). Exchangeable proton (OH) was not detected.

^{13}C NMR (100 MHz, CD_3CN) δ 170.0, 169.1, 138.3, 136.3, 130.2, 129.8, 63.3, 63.0, 46.3, 39.9, 21.1.

^{11}B NMR (128 MHz, CD_3CN) δ 10.99.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{14}H_{18}BNO_5Na$, calculated 314.1172; observed 314.1171.

2-(1-hydroxy-2-(o-tolyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4c)



Sticky liquid; 75% yield.

R_f (EtOAc) = 0.23.

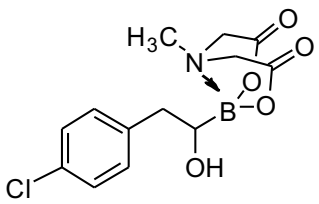
^{1}H NMR (400 MHz, CD_3CN) δ 7.20 – 7.14 (m, 2H), 7.13 – 7.09 (m, 2H), 4.00 – 3.87 (m, 2H), 3.85 – 3.79 (m, 2H), 3.49 (d, *J* = 11.5 Hz, 1H), 3.02 (s, 3H), 2.95 – 2.87 (m, 1H), 2.76 – 2.63 (m, 1H), 2.32 (s, 3H). Exchangeable proton (OH) was not detected.

^{13}C NMR (101 MHz, CD_3CN) δ 169.9, 169.1, 139.5, 137.6, 131.1, 127.0, 126.6, 63.3, 63.1, 46.2, 37.5, 19.8.

^{11}B NMR (128 MHz, CD_3CN) δ 10.97.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{14}H_{18}BNO_5Na$, calculated 314.1172; observed 314.1171.

2-(2-(4-chlorophenyl)-1-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4d)



Sticky solid; 70% yield.

R_f (EtOAc) = 0.23.

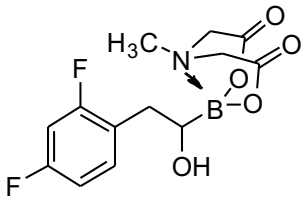
^{1}H NMR (400 MHz, CD_3CN) δ 7.34 – 7.21 (m, 4H), 4.03 – 3.76 (m, 4H), 3.52 – 3.42 (m, 1H), 3.01 (s, 3H), 2.89 – 2.82 (m, 1H), 2.76 – 2.62 (m, 1H), 2.37 – 2.27 (m, 1H).

^{13}C NMR (100 MHz, CD_3OD) δ 171.2, 170.5, 140.9, 132.6, 132.0, 129.2, 63.6, 63.4, 46.1, 40.0.

^{11}B NMR (128 MHz, CD_3CN) δ 11.16.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{15}BClNO_5Na$, calculated 334.0625; observed 334.0625.

2-(2-(2,4-difluorophenyl)-1-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4e)



Sticky liquid; 95% yield.

R_f (EtOAc) = 0.23.

^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (q, *J* = 8.3 Hz, 1H), 6.86 (t, *J* = 8.7 Hz, 2H), 4.23 – 4.07 (m, 2H), 4.01 – 3.87 (m, 2H), 3.51 (m, 1H), 3.09 (s, 3H), 2.99 – 2.93 (m, 1H), 2.79 – 2.69 (m, 1H). Exchangeable proton (OH) was not detected.

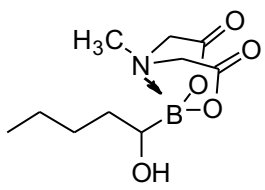
^{13}C NMR (100 MHz, CD_3OD) δ 171.2, 170.6, 164.05 (dd, J_{C-F} = 11.4, 22.2 Hz), 161.62 (dd, J_{C-F} = 11.4, 25.6 Hz), 133.85 (dd, J_{C-F} = 6.7, 9.4 Hz), 124.72, 124.68, 124.6, 124.5, 111.7, 111.6, 111.5, 111.4, 104.4, 104.1, 103.8, 63.6, 63.4, 46.1, 33.4.

^{11}B NMR (128 MHz, CD_3CN) δ 10.84.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.38, -115.68.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{14}BF_2NO_5Na$, calculated 336.0826; observed 336.0826.

2-(1-hydroxypentyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4f)[16]



Colorless oil; 87% yield.

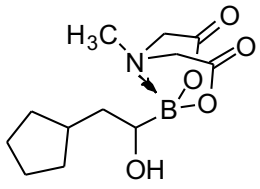
R_f (EtOAc) = 0.16.

^{1}H NMR (400 MHz, CD_3CN) δ 3.96 – 3.73 (m, 4H), 3.24 (s, 1H), 3.02 (s, 3H), 2.33 (s, 1H), 1.53 – 1.41 (m, 3H), 1.39 – 1.23 (m, 3H), 0.95 – 0.83 (m, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 170.0, 169.0, 63.3, 62.9, 46.2, 34.0, 29.4, 23.5, 14.4.

^{11}B NMR (128 MHz, CD_3CN) δ 16.44.

2-(2-cyclopentyl-1-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4g)



Sticky solid; 98% yield.

R_f (EtOAc) = 0.16.

^{1}H NMR (400 MHz, CD_3CN) δ 3.95 – 3.85 (m, 2H), 3.84 – 3.74 (m, 2H), 3.35 – 3.29 (m, 1H), 3.02 (s, 3H), 2.30 (d, *J* = 5.1 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.86 – 1.75 (m, 2H), 1.64 – 1.50 (m, 4H), 1.44 – 1.36 (m, 1H), 1.18 –

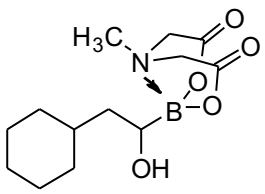
1.05 (m, 3H). Exchangeable proton (OH) was not detected.

^{13}C NMR (100 MHz, CD_3OD) δ 171.4, 170.7, 63.6, 63.3, 46.0, 40.7, 37.7, 34.5, 33.0, 26.2, 26.0.

^{11}B NMR (128 MHz, CD_3CN) δ 11.13.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{12}H_{20}BNO_5Na$, calculated 292.1327; observed 292.1328.

2-(2-cyclohexyl-1-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4h)



Colorless oil; 82% yield.

R_f (EtOAc) = 0.16.

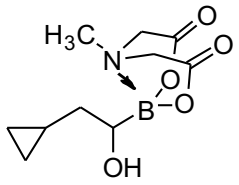
^{1}H NMR (400 MHz, CD_3CN) δ 3.96 – 3.85 (m, 2H), 3.85 – 3.73 (m, 2H), 3.44 – 3.36 (m, 1H), 3.02 (s, 3H), 2.25 (d, *J* = 5.2 Hz, 1H), 1.87 (d, *J* = 13.5 Hz, 1H), 1.73 – 1.62 (m, 4H), 1.50 – 1.39 (m, 2H), 1.31 – 1.17 (m, 4H), 1.04 – 0.92 (m, 1H), 0.86 – 0.74 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.9, 169.0, 63.3, 63.0, 46.2, 41.8, 35.5, 34.3, 33.0, 27.5, 27.4, 27.0.

^{11}B NMR (128 MHz, CD_3CN) δ 11.12.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{22}BNO_5Na$, calculated 306.1484; observed 306.1483.

2-(2-cyclopropyl-1-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4i)



Sticky liquid; 94% yield.

R_f (EtOAc) = 0.16.

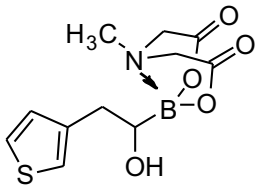
^{1}H NMR (400 MHz, CD_3CN) δ 3.94 – 3.86 (m, 2H), 3.84 – 3.75 (m, 2H), 3.41 – 3.33 (m, 1H), 3.03 (s, 3H), 2.44 (d, *J* = 4.0 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.33 – 1.24 (m, 1H), 0.88 – 0.79 (m, 1H), 0.52 – 0.43 (m, 1H), 0.41 – 0.34 (m, 1H), 0.14 – 0.08 (m, 1H), 0.03 – -0.03 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 170.0, 169.1, 63.3, 62.9, 46.2, 39.2, 9.2, 5.7, 4.1.

^{11}B NMR (128 MHz, CD_3CN) δ 13.46.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{10}H_{16}BNO_5Na$, calculated 264.1014; observed 264.1025.

2-(1-hydroxy-2-(thiophen-3-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4j)



Yellow sticky solid; 69% yield.

R_f (EtOAc) = 0.22.

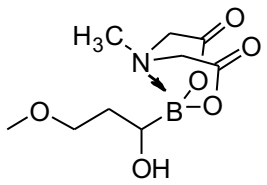
^{1}H NMR (400 MHz, CD_3CN) δ 7.34 (s, 1H), 7.07 (d, *J* = 29.4 Hz, 2H), 4.06 – 3.72 (m, 4H), 3.53 – 3.41 (m, 1H), 3.02 (s, 3H), 2.92 – 2.83 (m, 1H), 2.79 – 2.68 (m, 1H), 2.24 (s, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.9, 169.0, 141.8, 129.8, 126.4, 122.6, 63.3, 63.1, 46.3, 34.8.

^{11}B NMR (128 MHz, CD_3CN) δ 11.06.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{11}H_{14}BNO_5SNa$, calculated 306.0578; observed 306.0583.

2-(1-hydroxy-3-methoxypropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4k)



Sticky solid; 75% yield.

R_f (EtOAc) = 0.13.

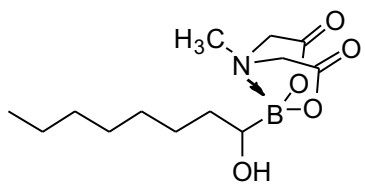
^{1}H NMR (400 MHz, CD_3CN) δ 3.98 – 3.86 (m, 2H), 3.85 – 3.76 (m, 2H), 3.62 – 3.56 (m, 1H), 3.55 – 3.48 (m, 1H), 3.48 – 3.40 (m, 1H), 3.30 (s, 3H), 3.03 (s, 3H), 1.72 (q, *J* = 5.9 Hz, 2H). Exchangeable proton (OH) was not detected.

^{13}C NMR (100 MHz, CD_3CN) δ 169.9, 169.0, 72.8, 63.3, 63.0, 58.9, 46.2, 33.4.

^{11}B NMR (128 MHz, CD_3CN) δ 10.92.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_9H_{16}BNO_6Na$, calculated 268.0963; observed 268.0964.

2-(1-hydroxyoctyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4l)



Colorless oil; 80% yield.

R_f (EtOAc) = 0.16.

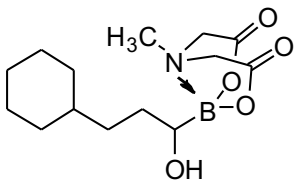
^{1}H NMR (400 MHz, CD_3CN) δ 3.96 – 3.85 (m, 2H), 3.84 – 3.75 (m, 2H), 3.28 – 3.22 (m, 1H), 3.02 (s, 3H), 2.35 (br s, 1H), 1.53 – 1.44 (m, 3H), 1.30 (br s, 9H), 0.89 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 170.1, 169.2, 63.3, 63.0, 46.2, 34.3, 32.7, 30.4, 30.1, 27.1, 23.4, 14.4.

^{11}B NMR (128 MHz, CD_3CN) δ 11.19.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{24}BNO_5Na$, calculated 308.1640; observed 308.1637.

2-(3-cyclohexyl-1-hydroxypropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4m)



Colorless oil; 68% yield.

R_f (EtOAc) = 0.16.

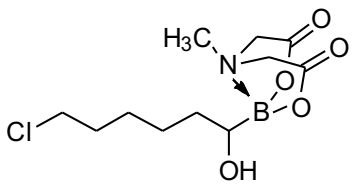
^{1}H NMR (400 MHz, CD_3OD) δ 4.19 – 4.02 (m, 2H), 3.97 – 3.87 (m, 2H), 3.26 – 3.20 (m, 1H), 3.09 (s, 3H), 1.80 – 1.58 (m, 6H), 1.55 – 1.41 (m, 2H), 1.30 – 1.09 (m, 5H), 1.00 – 0.85 (m, 2H). Exchangeable proton (OH) was not detected.

^{13}C NMR (100 MHz, CD_3OD) δ 171.5, 170.7, 63.6, 63.3, 46.1, 39.2, 35.4, 34.8, 34.5, 31.7, 27.9, 27.5.

^{11}B NMR (128 MHz, CD_3CN) δ 11.14.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{14}H_{24}BNO_5Na$, calculated 320.1640; observed 320.1642.

2-(6-chloro-1-hydroxyhexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4n)



Colorless oil; 80% yield.

R_f (EtOAc) = 0.25.

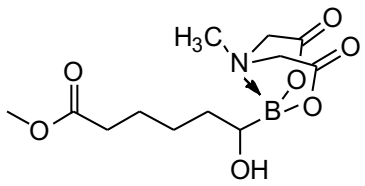
^{1}H NMR (400 MHz, CD_3CN) δ 3.95 – 3.85 (m, 2H), 3.84 – 3.74 (m, 2H), 3.59 (t, *J* = 6.7 Hz, 2H), 3.29 – 3.20 (m, 1H), 3.02 (s, 3H), 2.34 (d, *J* = 5.1 Hz, 1H), 1.83 – 1.70 (m, 2H), 1.57 – 1.29 (m, 6H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.9, 169.0, 63.2, 62.9, 46.3, 46.2, 34.1, 33.4, 27.6, 26.3.

^{11}B NMR (128 MHz, CD_3CN) δ 11.31.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{11}H_{19}BClNO_5Na$, calculated 314.0937; observed 314.0942.

Methyl 6-hydroxy-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hexanoate (4o)



Colorless oil; 60% yield.

R_f (EtOAc) = 0.20.

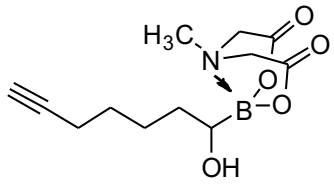
^{1}H NMR (400 MHz, CD_3CN) δ 3.94 – 3.85 (m, 2H), 3.84 – 3.74 (m, 2H), 3.61 (s, 3H), 3.24 (s, 1H), 3.01 (s, 3H), 2.40 – 2.35 (m, 1H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.67 – 1.42 (m, 5H), 1.38 – 1.27 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 174.9, 169.9, 169.0, 63.2, 62.9, 51.9, 46.2, 34.6, 33.9, 26.6, 25.7.

^{11}B NMR (128 MHz, CD_3CN) δ 11.01.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{12}H_{21}BNO_7$, calculated 302.1406; observed 302.1401.

2-(1-hydroxyhept-6-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4p)



Sticky solid; 67% yield.

R_f (EtOAc) = 0.21.

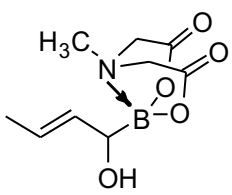
^{1}H NMR (400 MHz, CD_3CN) δ 3.96 – 3.86 (m, 2H), 3.85 – 3.76 (m, 2H), 3.30 – 3.18 (m, 1H), 3.02 (s, 3H), 2.43 – 2.34 (m, 1H), 2.19 (s, 2H), 2.15 (s, 1H), 1.60 – 1.37 (m, 6H).

^{13}C NMR (100 MHz, DMSO) δ 169.7, 168.5, 84.7, 71.0, 62.2, 61.8, 45.2, 32.8, 28.4, 25.3, 17.8.

^{11}B NMR (128 MHz, CD_3CN) δ 11.04.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{12}H_{19}BNO_5$, calculated 268.1351; observed 268.1349.

2-(1-hydroxybut-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4q)



White solid; 65% yield.

R_f (EtOAc) = 0.21.

^{1}H NMR (400 MHz, CD_3CN) δ 5.79 – 5.42 (m, 2H), 3.95 – 3.74 (m, 5H), 3.03 (s, 3H), 2.53 (s, 1H), 1.68 (s, 3H).

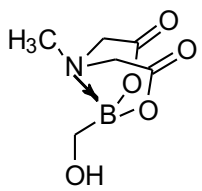
^{13}C NMR (100 MHz, CD_3CN) δ 169.8, 169.1, 133.7, 124.4, 63.1, 46.3, 18.1.

^{11}B NMR (128 MHz, CD_3CN) δ 10.44.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_9H_{15}BNO_5$, calculated 228.1038; observed 228.1041.

Melting point: 63 – 65 ºC.

2-(hydroxymethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4s)[17]



White solid; 44% yield.

R_f (Acetonitrile:EtOAc =2:8) = 0.28.

^{1}H NMR (400 MHz, CD_3CN) δ 4.01 – 3.76 (m, 4H), 3.23 (s, 2H), 3.03 (s, 3H), 2.33 (s, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.39, 63.11, 46.47.

^{11}B NMR (128 MHz, CD_3CN) δ 11.32.

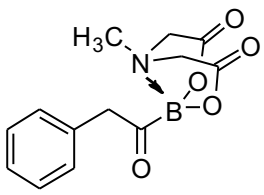
HRMS-ESI: *m/z* $[M+H]^+$ for $C_6H_{11}BNO_5$, calculated 188.0725; observed 188.0722.

Melting point: 132 – 135 ºC.

4. General procedure for the synthesis of MIDA-acylboronate 5

To a solution of α-hydroxyboronate **4** (0.5 mmol) in 2 mL of DCM, Dess-Martin periodinane (DMP, 1.1 equiv) was added.[16] The resulting mixture was stirred for 30 min and then washed sequentially with 10% $Na_2S_2O_3$ (2 ml), saturated aqueous $NaHCO_3$ (2 ml), followed by H_2O (2 ml) and brine (3 ml). The organic phase was dried over Na_2SO_4 and concentrated. The crude solid was further purified using flash column chromatography (EtOAc/hexanes 0:10 to 10:0) to afford the pure product (**5**).

6-methyl-2-(2-phenylacetyl)-1,3,6,2-dioxazaborocane-4,8-dione (5a)[16]



Sticky solid; 63% yield.

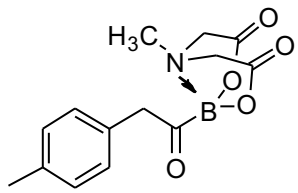
R_f (EtOAc) = 0.48.

^{1}H NMR (400 MHz, CD_3CN) δ 7.35 – 7.27 (m, 2H), 7.28 – 7.19 (m, 1H), 7.18 – 7.11 (m, 2H), 4.06 – 3.95 (m, 4H), 3.88 – 3.80 (m, 2H), 2.74 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 168.9, 135.1, 131.0, 129.3, 127.4, 63.0, 54.0, 47.5.

^{11}B NMR (128 MHz, CD_3CN) δ 4.51.

6-methyl-2-(2-(p-tolyl)acetyl)-1,3,6,2-dioxazaborocane-4,8-dione (5b)



Sticky solid; 55% yield.

R_f (EtOAc) = 0.48.

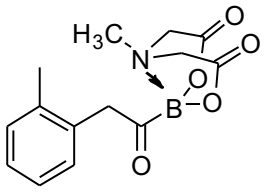
^{1}H NMR (400 MHz, CD_3CN) δ 7.12 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 4.01 (d, *J* = 17.0 Hz, 2H), 3.91 (s, 2H), 3.82 (d, *J* = 16.9 Hz, 2H), 2.73 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 137.1, 131.8, 130.9, 129.9, 63.0, 53.6, 47.5, 21.1.

^{11}B NMR (128 MHz, CD_3CN) δ 4.49.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{14}H_{16}BNO_5Na$, calculated 312.1014; observed 312.1014.

6-methyl-2-(2-(o-tolyl)acetyl)-1,3,6,2-dioxazaborocane-4,8-dione (5c)



Sticky solid; 73% yield.

R_f (EtOAc) = 0.48.

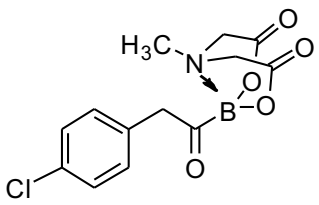
^{1}H NMR (400 MHz, CD_3CN) δ 7.18 – 7.09 (m, 3H), 7.04 (d, *J* = 7.5 Hz, 1H), 4.07 – 4.00 (m, 4H), 3.87 (d, *J* = 16.9 Hz, 2H), 2.81 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 138.3, 134.4, 131.7, 130.9, 127.8, 126.7, 63.1, 52.3, 47.5, 19.9.

^{11}B NMR (128 MHz, CD_3CN) δ 4.49.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{14}H_{16}BNO_5Na$, calculated 312.1014; observed 312.1014.

2-(2-(4-chlorophenyl)acetyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5d)



Sticky solid; 50% yield.

R_f (EtOAc) = 0.48.

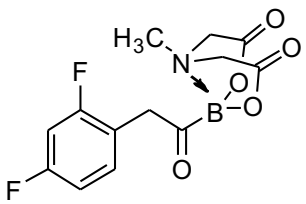
^{1}H NMR (400 MHz, CD_3CN) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.06 – 4.00 (m, 2H), 3.98 (s, 2H), 3.88 (d, *J* = 17.0 Hz, 2H), 2.78 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 168.9, 134.1, 132.8, 132.6, 129.1, 63.1, 53.0, 47.5.

^{11}B NMR (128 MHz, CD_3CN) δ 4.49.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{13}BClNO_5Na$, calculated 332.0465; observed 332.0468.

2-(2-(2,4-difluorophenyl)acetyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5e)



White solid; 53% yield.

R_f (EtOAc) = 0.48.

^{1}H NMR (400 MHz, CD_3CN) δ 7.16 (q, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 8.6 Hz, 2H), 4.08 (s, 1H), 4.04 (s, 1H), 4.03 (s, 2H), 3.91 (d, *J* = 17.0 Hz, 2H), 2.85 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 168.9, 134.1, 134.05, 133.98, 133.9, 111.91 (dd, J_{C-F} = 3.5, 21.0 Hz), 104.15 (t, J_{C-F} = 26.5 Hz). 63.1, 47.6, 47.3.

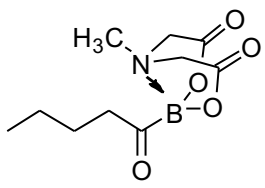
^{11}B NMR (128 MHz, CD_3CN) δ 7.00.

^{19}F NMR (376 MHz, CD_3CN) δ -113.85, -114.24.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{12}BF_2NO_5Na$, calculated 334.0669; observed 334.0664.

Melting point: > 250 ºC.

6-methyl-2-pentanoyl-1,3,6,2-dioxazaborocane-4,8-dione (5f)[16]



White solid; 70% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, CD_3CN) δ 4.03 (d, *J* = 16.9 Hz, 2H), 3.89 (d, *J* = 16.9 Hz, 2H), 2.81 (s, 3H), 2.65 – 2.60 (m, 2H), 1.51 – 1.43 (m, 2H), 1.33 – 1.22 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

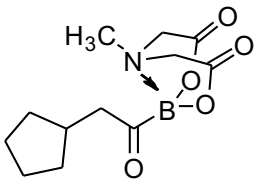
^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 63.0, 47.2, 24.9, 23.1, 14.3.

^{11}B NMR (128 MHz, CD_3CN) δ 4.27.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{10}H_{17}BNO_5$, calculated 242.1194; observed 242.1196.

Melting point: 112 – 114 ºC.

2-(2-cyclopentylacetyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5g)



White solid; 40% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, DMSO) δ 4.31 (d, *J* = 17.1 Hz, 2H), 4.04 (d, *J* = 17.1 Hz, 2H), 2.78 (s, 3H), 2.63 (d, *J* = 6.9 Hz, 2H), 2.22 – 2.13 (m, 1H), 1.76 – 1.67 (m, 2H), 1.58 – 1.52 (m, 2H), 1.50 – 1.43 (m, 2H), 1.06 – 0.95 (m, 2H).

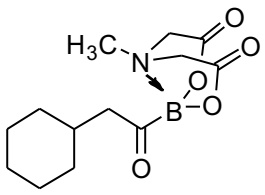
^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 63.0, 54.0, 47.4, 34.8, 33.3, 25.6.

^{11}B NMR (128 MHz, CD_3CN) δ 4.19.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{12}H_{18}BNO_5Na$, calculated 290.1171; observed 290.1173.

Melting point: 157 – 158 ºC.

2-(2-cyclohexylacetyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5h)



White solid; 48% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, CD_3CN) δ 4.01 (d, *J* = 16.9 Hz, 2H), 3.88 (d, *J* = 15.8 Hz, 2H), 2.80 (s, 3H), 2.50 (d, *J* = 7.8 Hz, 2H), 1.86 (s, 1H), 1.70 – 1.54 (m, 5H), 1.33 – 1.11 (m, 3H), 0.98 – 0.86 (m, 2H).

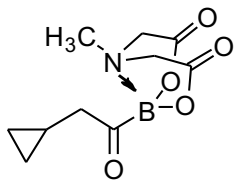
^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 63.0, 55.2, 47.4, 34.0, 33.0, 26.9.

^{11}B NMR (128 MHz, CD_3CN) δ 4.15.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{13}H_{20}BNO_5Na$, calculated 304.1327; observed 304.1322.

Melting point: > 250 ºC.

2-(2-cyclopropylacetyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5i)



Sticky liquid; 83% yield.

R_f (EtOAc) = 0.42.

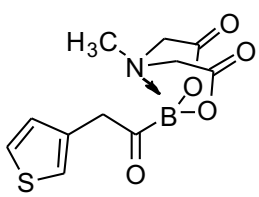
^{1}H NMR (400 MHz, CD_3CN) δ 4.08 – 4.01 (m, 2H), 3.94 – 3.87 (m, 2H), 2.82 (s, 3H), 2.52 (d, *J* = 6.6 Hz, 2H), 0.97 – 0.89 (m, 1H), 0.45 (d, *J* = 7.5 Hz, 2H), 0.05 (d, *J* = 4.4 Hz, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.4, 63.2, 52.7, 47.6, 5.6, 4.7.

^{11}B NMR (128 MHz, CD_3CN) δ 4.20.

HRMS-ESI: *m/z* $[M+Na]^+$ for $C_{10}H_{14}BNO_5Na$, calculated 262.0858; observed 262.0854.

6-methyl-2-(2-(thiophen-3-yl)acetyl)-1,3,6,2-dioxazaborocane-4,8-dione (5j)



Sticky solid; 50% yield.

R_f (EtOAc) = 0.46.

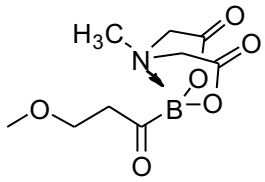
^{1}H NMR (400 MHz, CD_3CN) δ 7.40 – 7.30 (m, 1H), 7.11 (s, 1H), 6.98 – 6.91 (m, 1H), 4.10 – 3.95 (m, 4H), 3.87 (s, 1H), 3.83 (s, 1H), 2.75 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 134.8, 130.4, 126.3, 124.0, 63.0, 47.5.

^{11}B NMR (128 MHz, CD_3CN) δ 4.49.

HRMS-ESI: *m/z* [M+Na]$^+$ for $C_{11}H_{12}BNO_5SNa$, calculated 304.0422; observed 304.0421.

2-(3-methoxypropanoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5k)



Sticky solid; 40% yield.

R_f (EtOAc) = 0.40.

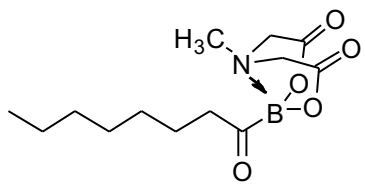
^{1}H NMR (400 MHz, CD_3CN) δ 4.02 (d, *J* = 17.0 Hz, 2H), 3.88 (d, *J* = 16.9 Hz, 2H), 3.62 (t, *J* = 6.1 Hz, 2H), 3.23 (s, 3H), 2.83 (d, *J* = 6.2 Hz, 2H), 2.80 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 67.6, 63.1, 58.7, 47.6, 47.2.

^{11}B NMR (128 MHz, CD_3CN) δ 6.65.

HRMS-ESI: *m/z* [M+Na]$^+$ for $C_9H_{14}BNO_6Na$, calculated 266.0807; observed 266.0805.

6-methyl-2-octanoyl-1,3,6,2-dioxazaborocane-4,8-dione (5l)



Sticky solid; 59% yield.

R_f (EtOAc) = 0.42.

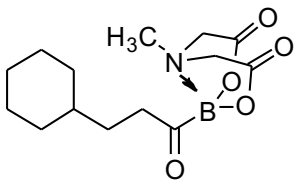
^{1}H NMR (400 MHz, CD_3CN) δ 4.02 (d, *J* = 16.9 Hz, 2H), 3.88 (d, *J* = 16.9 Hz, 2H), 2.80 (s, 3H), 2.62 (t, *J* = 7.2 Hz, 2H), 1.53 – 1.45 (m, 2H), 1.27 (br s, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 63.0, 47.4, 32.5, 30.0, 29.9, 23.3, 22.8, 14.4.

^{11}B NMR (128 MHz, CD_3CN) δ 4.29.

HRMS-ESI: *m/z* [M+Na]$^+$ for $C_{13}H_{22}BNO_5Na$, calculated 306.1484; observed 306.1489.

2-(3-cyclohexylpropanoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5m)



White solid; 55% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, CD_3CN) δ 4.45 (d, *J* = 17.0 Hz, 2H), 4.31 (d, *J* = 17.0 Hz, 2H), 3.23 (s, 3H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.15 – 2.02 (m, 5H), 1.80 (q, *J* = 7.1 Hz, 2H), 1.67 – 1.53 (m, 4H), 1.35 – 1.25 (m, 2H).

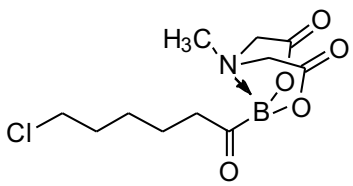
^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 63.0, 47.3, 45.0, 38.1, 33.9, 30.1, 27.3, 27.0.

^{11}B NMR (128 MHz, CD_3CN) δ 6.78.

HRMS-ESI: *m/z* [M+Na]$^+$ for $C_{14}H_{22}BNO_5Na$, calculated 318.1484; observed 318.1487.

Melting point: > 250 ºC.

2-(6-chlorohexanoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5n)



White solid; 58% yield.

R_f (EtOAc) = 0.42.

^{1}H NMR (400 MHz, CD_3CN) δ 4.07 – 3.82 (m, 4H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.80 (s, 3H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.56 – 1.46 (m, 2H), 1.43 – 1.33 (m, 2H).

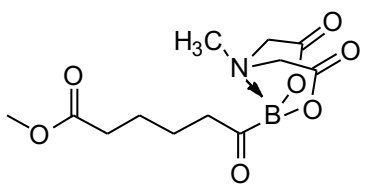
^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 63.0, 47.4, 46.1, 33.3, 27.2, 22.0.

^{11}B NMR (128 MHz, CD_3CN) δ 4.28.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{11}H_{18}BClNO_5$, calculated 290.0963; observed 290.0976.

Melting point: 140 – 148 ºC.

Methyl 6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-6-oxohexanoate (5o)



White solid; 50% yield.

R_f (EtOAc) = 0.45.

^{1}H NMR (400 MHz, CD_3CN) δ 4.08 – 3.73 (m, 4H), 3.60 (s, 3H), 2.80 (s, 3H), 2.65 (m, 2H), 2.29 (t, *J* = 6.8 Hz, 2H), 1.61 – 1.43 (m, 4H).

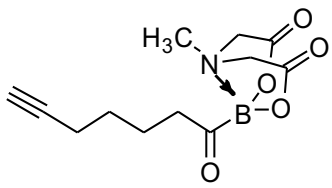
^{13}C NMR (100 MHz, CD_3CN) δ 174.7, 169.1, 63.0, 51.9, 47.4, 34.4, 25.3, 22.2.

^{11}B NMR (128 MHz, CD_3CN) δ 4.27.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{12}H_{19}BNO_7$, calculated 300.1249; observed 300.1245.

Melting point: 155 – 158 ºC.

2-(hept-6-ynoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5p)



White solid; 60% yield.

R_f (EtOAc) = 0.5.

^{1}H NMR (400 MHz, CD_3CN) δ 4.03 (d, *J* = 16.9 Hz, 2H), 3.89 (d, *J* = 16.9 Hz, 2H), 2.81 (s, 3H), 2.66 (t, *J* = 6.7 Hz, 2H), 2.20 – 2.12 (m, 3H), 1.62 – 1.54 (m, 2H), 1.51 – 1.42 (m, 2H).

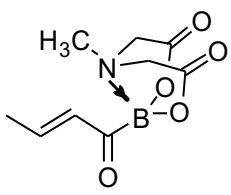
^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 85.3, 69.7, 63.0, 47.4, 46.8, 28.8, 21.9, 18.7.

^{11}B NMR (128 MHz, CD_3CN) δ 4.29.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_{12}H_{17}BNO_5$, calculated 266.1195; observed 266.1200.

Melting point: 146 – 148 ºC.

2-(but-2-enoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5q)



Yellow crystalline solid; 45% yield.

R_f (EtOAc) = 0.5.

^{1}H NMR (400 MHz, CD_3CN) δ 7.17 – 7.05 (m, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.00 (d, *J* = 16.7 Hz, 2H), 3.88 (d, *J* = 16.7 Hz, 2H), 2.80 (s, 3H), 1.88 (d, *J* = 6.7 Hz, 3H).

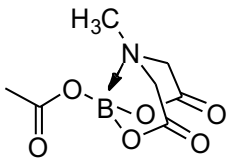
^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 146.5, 137.5, 62.8, 47.3, 19.0.

^{11}B NMR (128 MHz, CD_3CN) δ 4.91.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_9H_{13}BNO_5$, calculated 226.0882; observed 226.0883.

Melting point: 133 – 135 ºC.

6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl acetate (5s)[18]



White solid; 44% yield.

R_f (Acetonitrile: EtOAc = 2: 8) = 0.6.

^{1}H NMR (400 MHz, CD_3CN) δ 4.15 – 3.92 (m, 4H), 2.90 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 173.4, 168.2, 64.6, 46.8, 22.8.

^{11}B NMR (128 MHz, CD_3CN) δ 8.33.

HRMS-ESI: *m/z* $[M+H]^+$ for $C_7H_{11}BNO_6$, calculated 216.0675; observed 216.0679.

Melting point: 156 – 159 ºC.

5. X-ray Experiment

Molecular structure of 5m

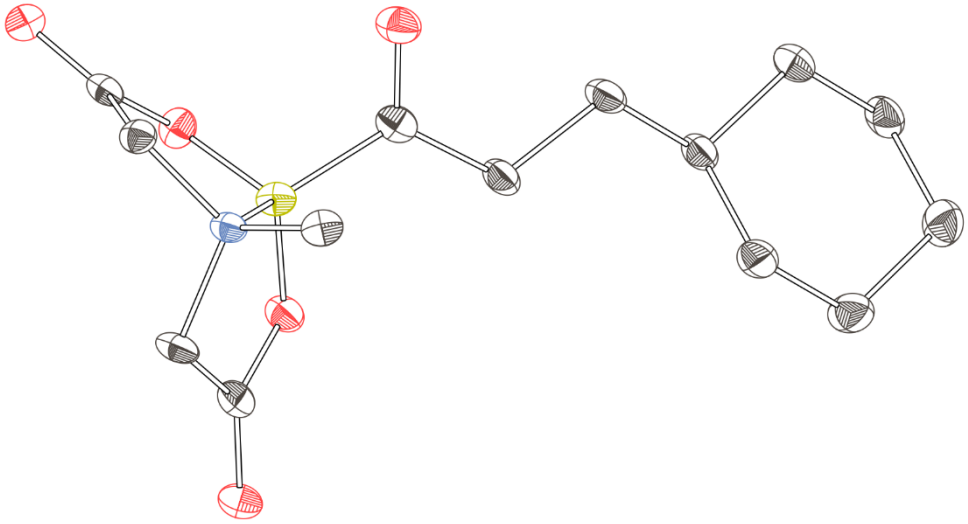


Figure S1. Molecular structure of **5m**.[19] One of the three independent molecules is shown.

An EtOAc solution of **5m** was diluted with Et_2O by vapor diffusion to afford a mass of colorless needles. Most of the crystals were hairlike and unsuitable for diffraction but a few (identified under a polarizing microscope) were slightly larger. A suitable fragment (.33 x .04 x .01 mm) was separated carefully, mounted on a glass fiber with Paratone oil, and cooled to 100 K on the diffractometer. The crystal system was tentatively assigned as monoclinic and complete data in 2/m were collected to 0.83 Å. 29418 reflections were collected (8883 unique, 5897 observed) with R(int) 7.5% and R(sigma) 8.0% after Gaussian absorption and beam profile correction (largest correction factor 1.4).

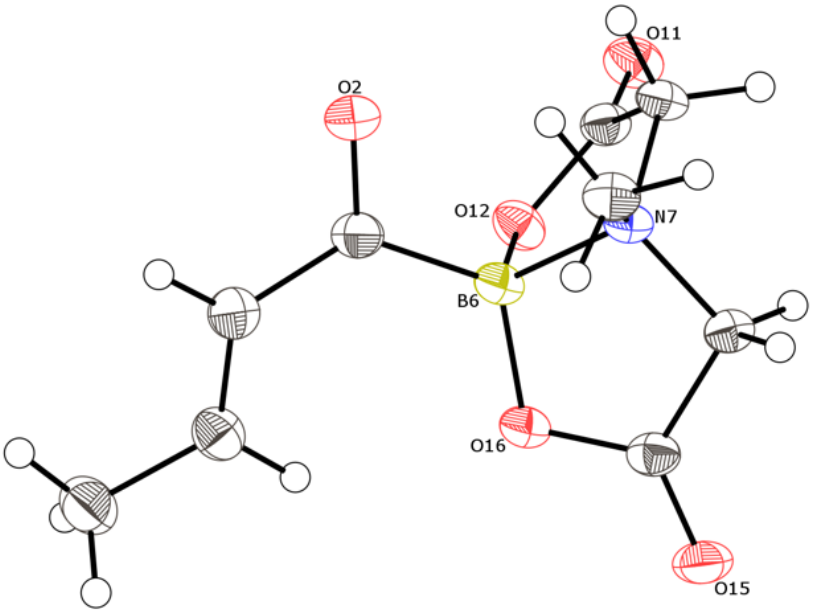
The space group was assigned as P21/c based on the systematic absences. The structure solved readily in ShelXT with 3 molecules in the asymmetric unit. All non-H atoms were located in Fourier maps and refined anisotropically with no restraints. C-H hydrogens were placed in calculated positions and refined with riding coordinates and ADPs.

The final refinement (8883 data, 0 restraints, 571 parameters) converged with R1 ($F_o > 4\sigma(F_o)$) = 5.1%, wR_2 = 12.0%, S = 1.03. The largest Fourier features were 0.26 and -0.29 $e^- A^{-3}$.

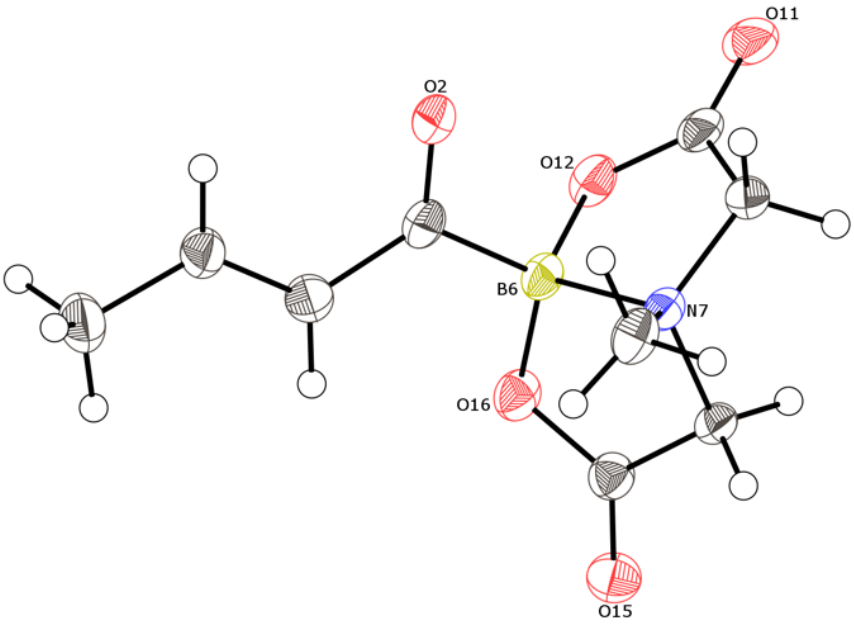
Crystal Data

Compound	5m
Formula	$C_{14}H_{22}BNO_5$
MW	295.13
Space group	$P2_1/c$
***a* (Å)**	24.3090(11)
***b* (Å)**	6.3645(2)
***c* (Å)**	31.2582(14)
***α* (°)**	90
***β* (°)**	110.597(5)
***γ* (°)**	90
V (Å^3)	4527.0(4)
Z	12
ρ_{calc} (g cm^{-3})	1.299
T (K)	100
λ (Å)	1.54184
$2\theta_{min}$, $2\theta_{max}$	8, 146
Nref	29418
R(int), R(σ)	.0748, .0796
μ(mm^{-1})	0.797
Size (mm)	.33 x .04 x .01
T_{max}/T_{min}	1.40
Data	8883
Restraints	0
Parameters	571
R_1(obs)	0.0510
wR_2(all)	0.1203
S	1.029
Peak, hole (e$^-$ Å^{-3})	0.26, -0.29

Molecular structure of 5q



(a)



(b)

Figure S2. Molecular structure of **5q**.[19] (a) *s-trans* isomer; (b) *s-cis* isomer (the 10% *s-trans* isomer

has been omitted for better clarity.

An EtOAc solution of **5q** was diluted with Et_2O by vapor diffusion to afford a mass of colorless needles. An irregular fragment (.30 x .18 x .16 mm) was separated, mounted with Paratone oil on a glass fiber, and cooled to 100 K on the diffractometer. Complete data were collected to 0.8 Å resolution. 11143 reflections were collected (4233 unique, 3853 observed) with R(int) 3.8% and R(sigma) 3.9% after Gaussian absorption and beam profile correction (largest correction factor 2.0).

The structure was triclinic and solved readily in P-1 using ShelXT with all non-H atoms located in the initial solution. There were two molecules in the asymmetric unit. The C(O)C3H5 moiety in one of the two independent molecules was disordered in a 9:1 ratio by rotation around the C(sp2)-C(sp2) bond, i.e. a 9:1 mixture of s-cis and s-trans isomers. The other independent molecule was exclusively s-trans. Except for the 10% occupied part of this disorder, all non-H atoms were freely refined with anisotropic ADPs. The minor part of the disordered group was refined with isotropic ADPs that were restrained by a short-range SIMU instruction. All H atoms were placed in calculated positions and refined with riding coordinates and ADPs.

The final refinement (4233 data, 43 restraints, 315 parameters) converged with R1 ($F_o > 4\sigma(F_o)$) = 4.2%, wR_2 = 11.9%, S = 1.03. The largest Fourier features were 0.34 and -0.24 $e^- A^{-3}$.

Compound	5q
Formula	$C_9H_{12}BNO_5$
MW	225.01
Space group	P-1
***a* (Å)**	10.3672(3)
***b* (Å)**	10.8231(3)
***c* (Å)**	10.9398(4)
***α* (°)**	78.441(3)
***β* (°)**	85.514(3)
***γ* (°)**	63.232(3)
V (Å^3)	1073.63(6)
Z	4
ρ_{calc} (g cm^{-3})	1.392
T (K)	100
λ (Å)	1.54184
$2\theta_{min}$, $2\theta_{max}$	8, 146
Nref	11143
R(int), R(σ)	.0379, .0390
μ(mm^{-1})	0.951
Size (mm)	.30 x .18 x .16
T_{max} / T_{min}	2.02
Data	4233
Restraints	43
Parameters	315
R_1(obs)	0.0423
wR_2(all)	0.1190
S	1.027
Peak, hole (e$^-$ Å^{-3})	0.34, -0.24

Molecular structure of 5s

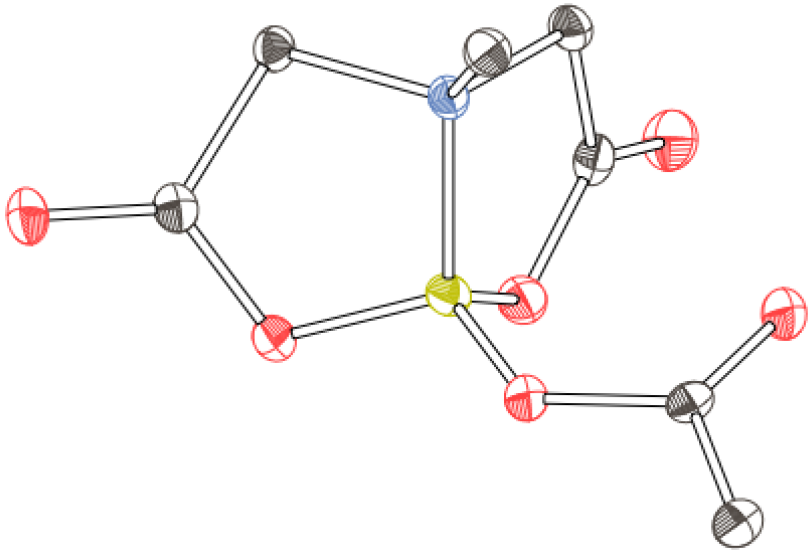


Figure S3. Molecular structure of **5s**.[19]

An EtOAc solution of **5s** was diluted with Et_2O by vapor diffusion to afford colorless, flat prisms. A small natural crystal (.40 x .06 x .03 mm) was separated carefully, mounted with STP oil treatment, and cooled to 100 K on the diffractometer. Complete data were collected to 0.815 Å. 10819 reflections were collected (3609 unique, 3155 observed) with R(int) 5.1% and R(sigma) 5.2% after Gaussian absorption and beam profile correction (maximum correction factor 1.43).

Using ShelXT, the structure solved readily in $P2_1/n$ with two molecules in the asymmetric unit. All non-H atoms were located in the initial solution and refined anisotropically with no restraints. C-H hydrogens were placed in calculated positions and refined with riding coordinates and ADPs.

The final refinement (3609 data, 0 restraints, 275 parameters) converged with R1 ($F_o > 4\sigma(F_o)$) = 4.4%, wR_2 = 11.7%, S = 1.04. The largest Fourier features were 0.30 and -0.34 $e^- A^{-3}$.

Compound	5s
Formula	$C_7H_{10}BNO_6$
MW	214.97
Space group	$P2_1/c$
***a* (Å)**	9.3307(3)
***b* (Å)**	21.4147(8)
***c* (Å)**	9.6557(4)
***α* (°)**	90
***β* (°)**	109.438(4)
***γ* (°)**	90
V (Å^3)	1819.38(12)
Z	8
ρ_{calc} (g cm^{-3})	1.57
T (K)	100
λ (Å)	1.54184
$2\theta_{min}$, $2\theta_{max}$	8, 146
Nref	10819
R(int), R(σ)	.0513, .0515
μ(mm^{-1})	1.176
Size (mm)	.40 x .06 x .03
T_{max} / T_{min}	1.43
Data	3609
Restraints	0
Parameters	275
R_1(obs)	0.0437
wR_2(all)	0.1168
S	1.035
Peak, hole (e$^-$ Å^{-3})	0.30, -0.34

6. References

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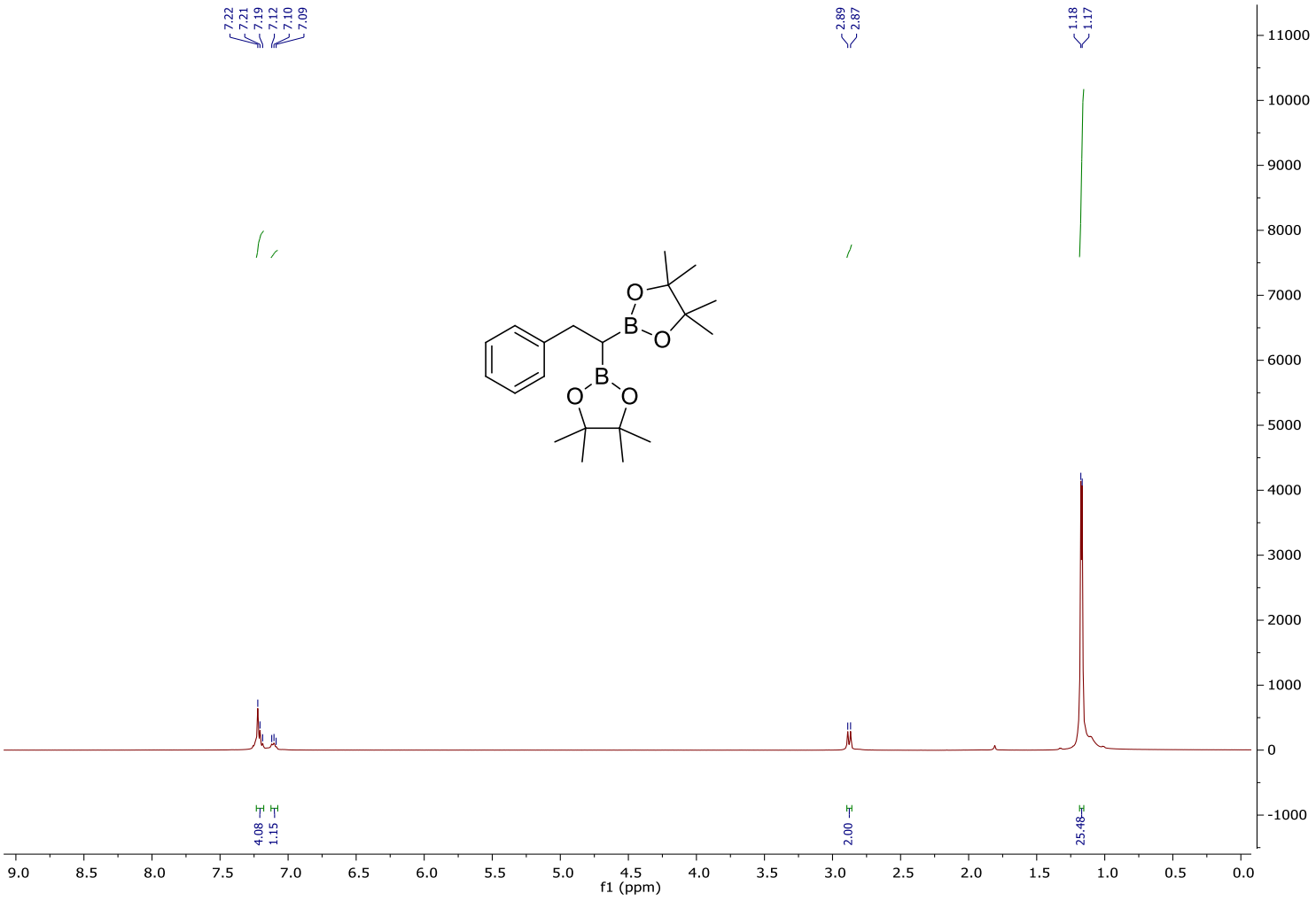
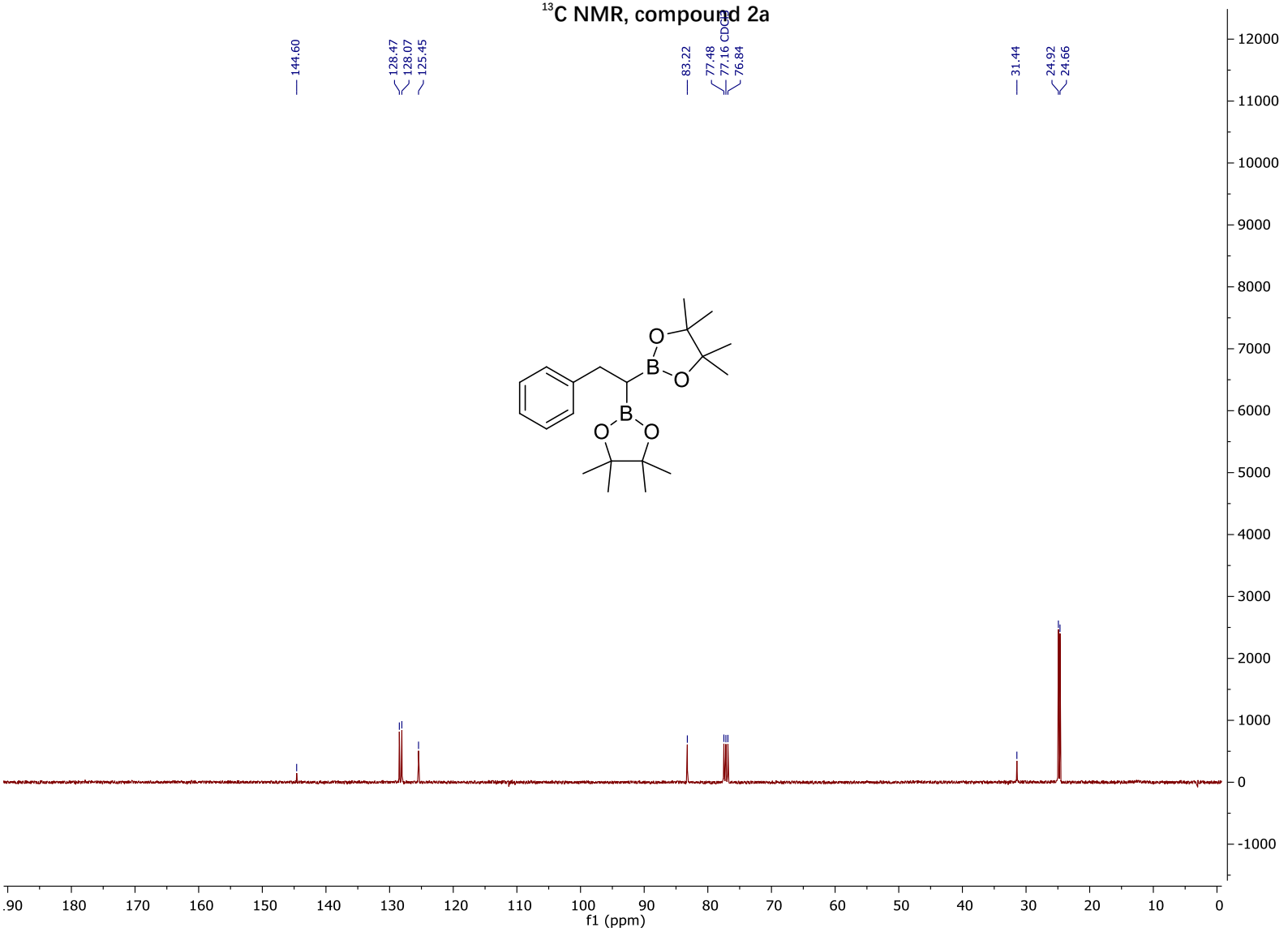
7. NMR spectra

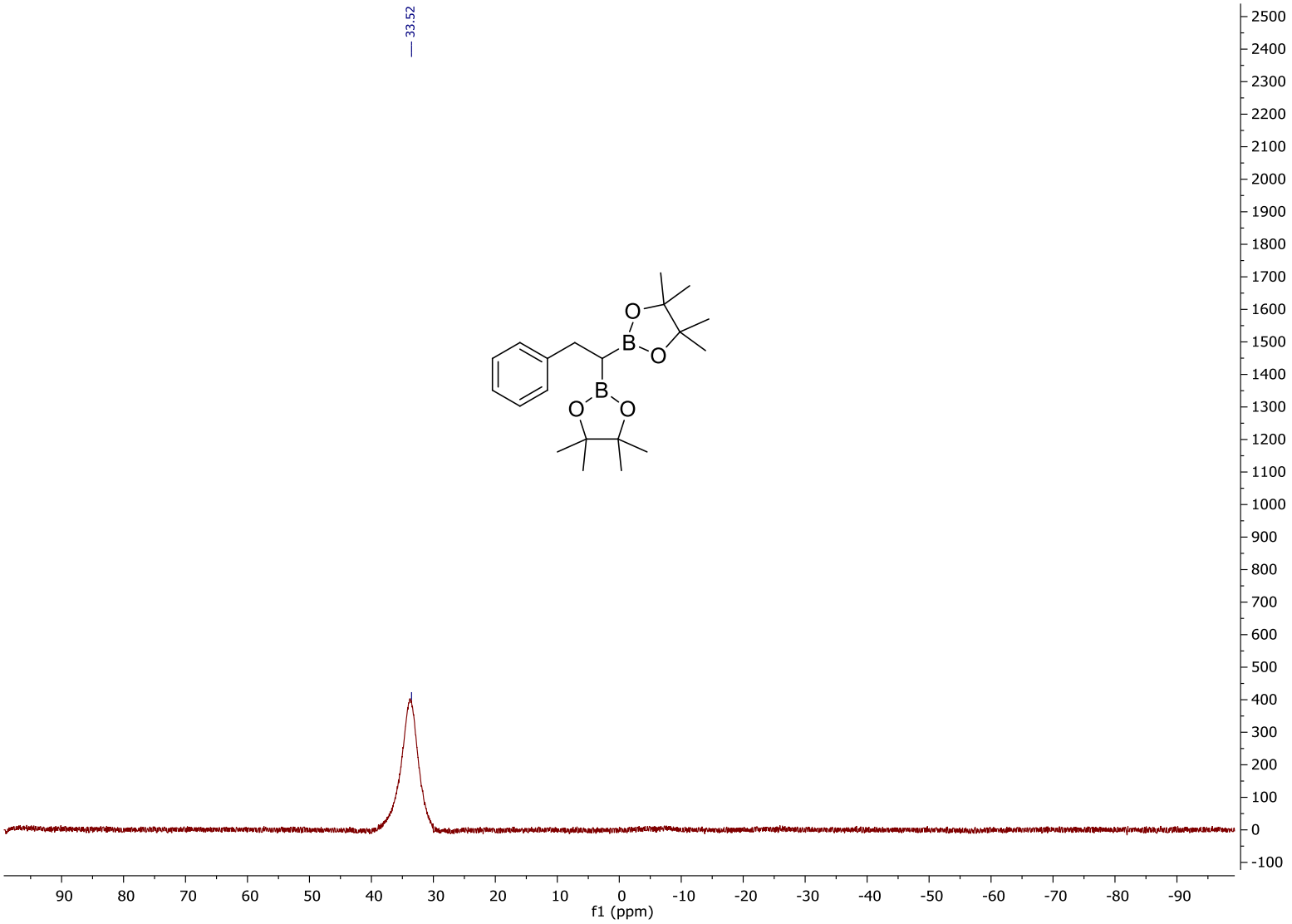
^{1}H NMR, compound 2a



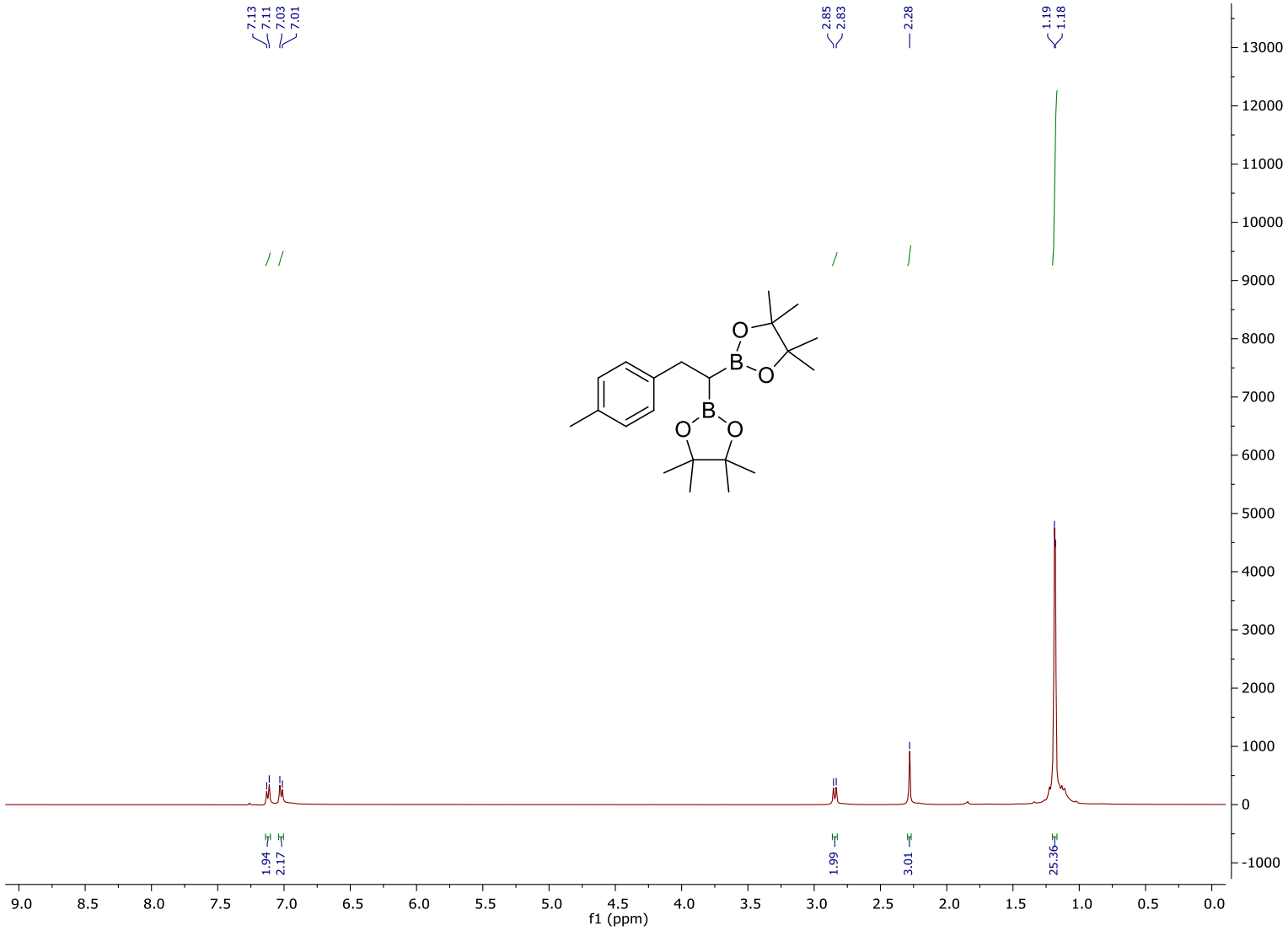
^{13}C NMR, compound 2a



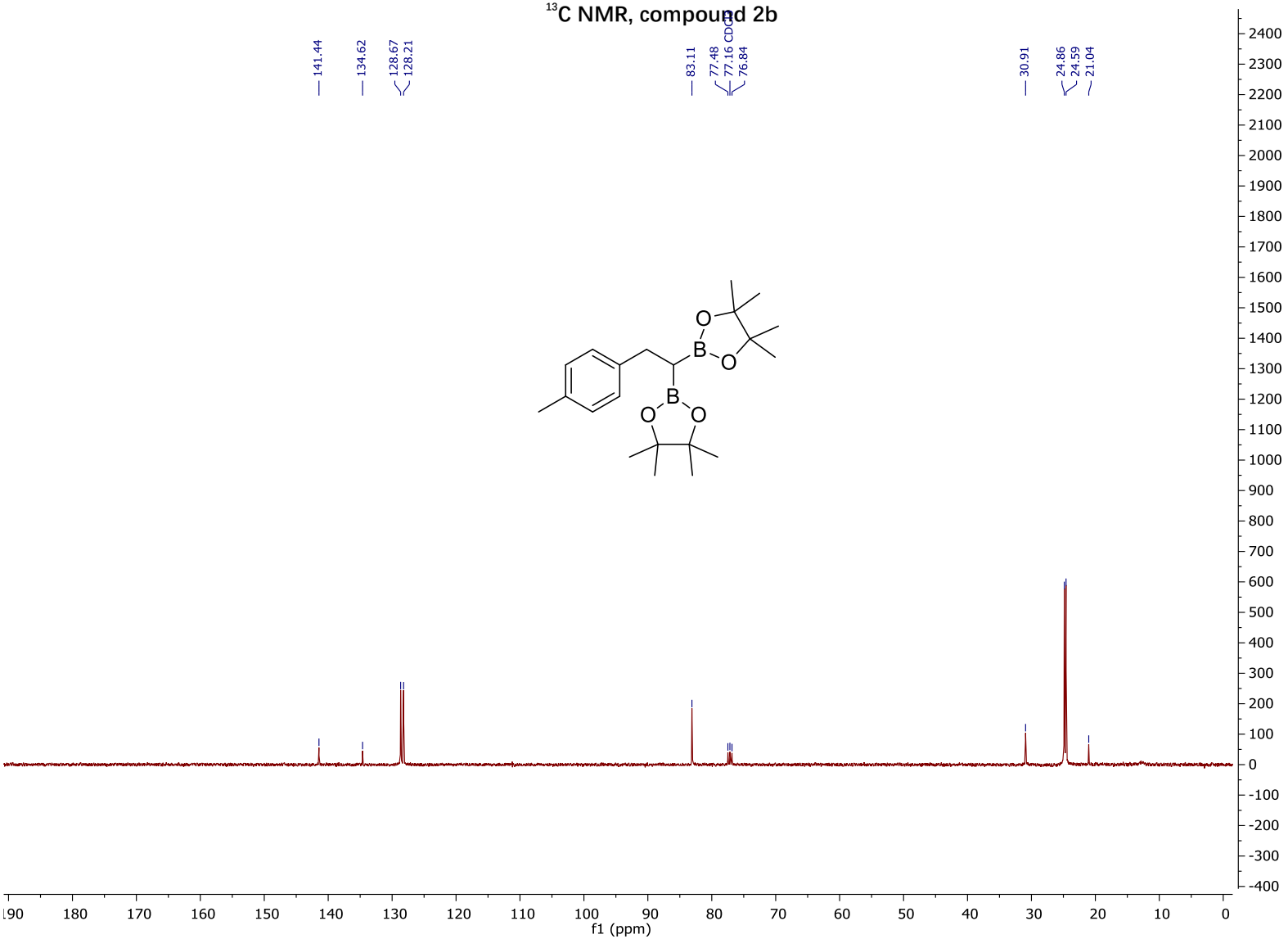
^{11}B NMR, compound 2a



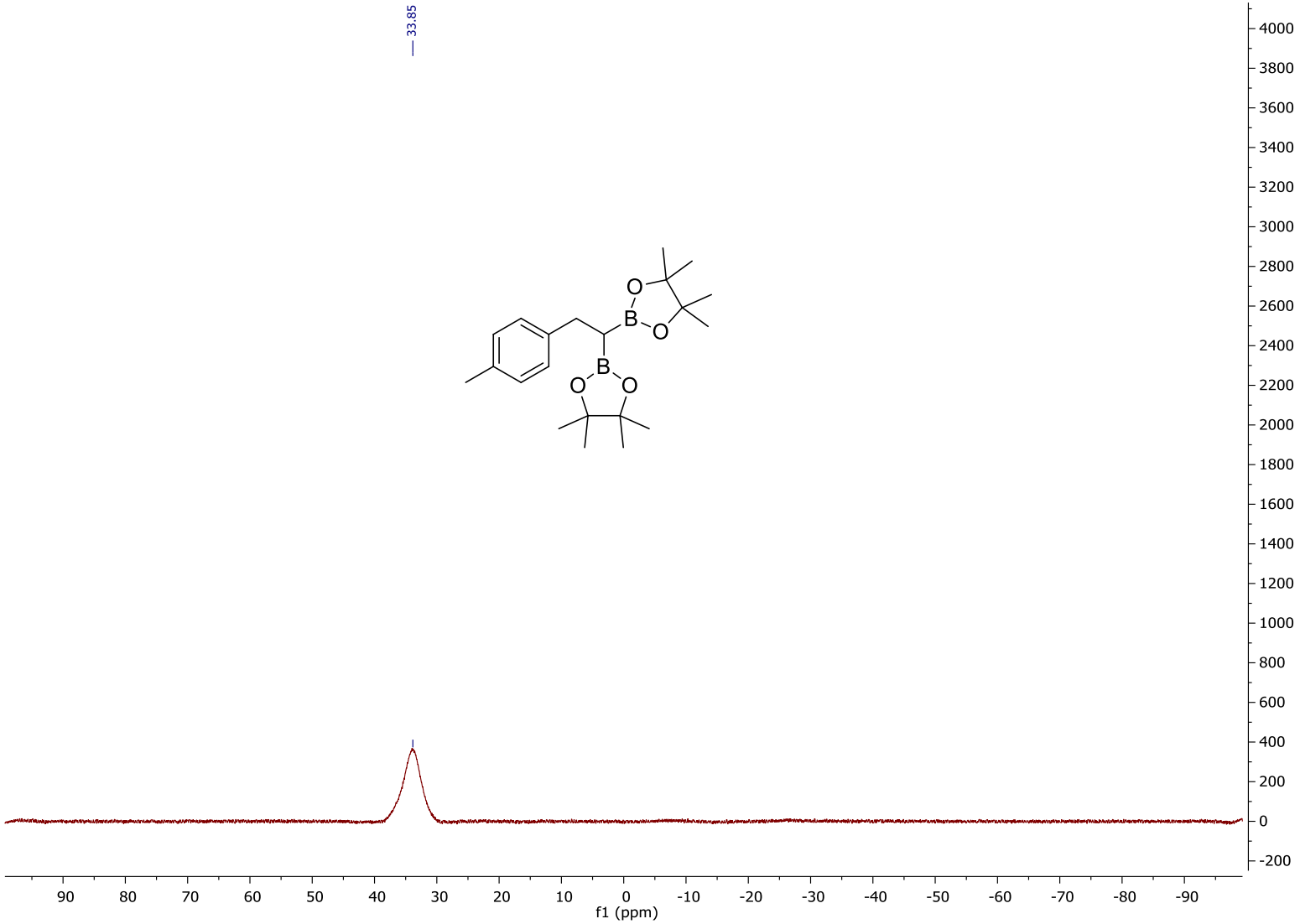
^{1}H NMR, compound 2b



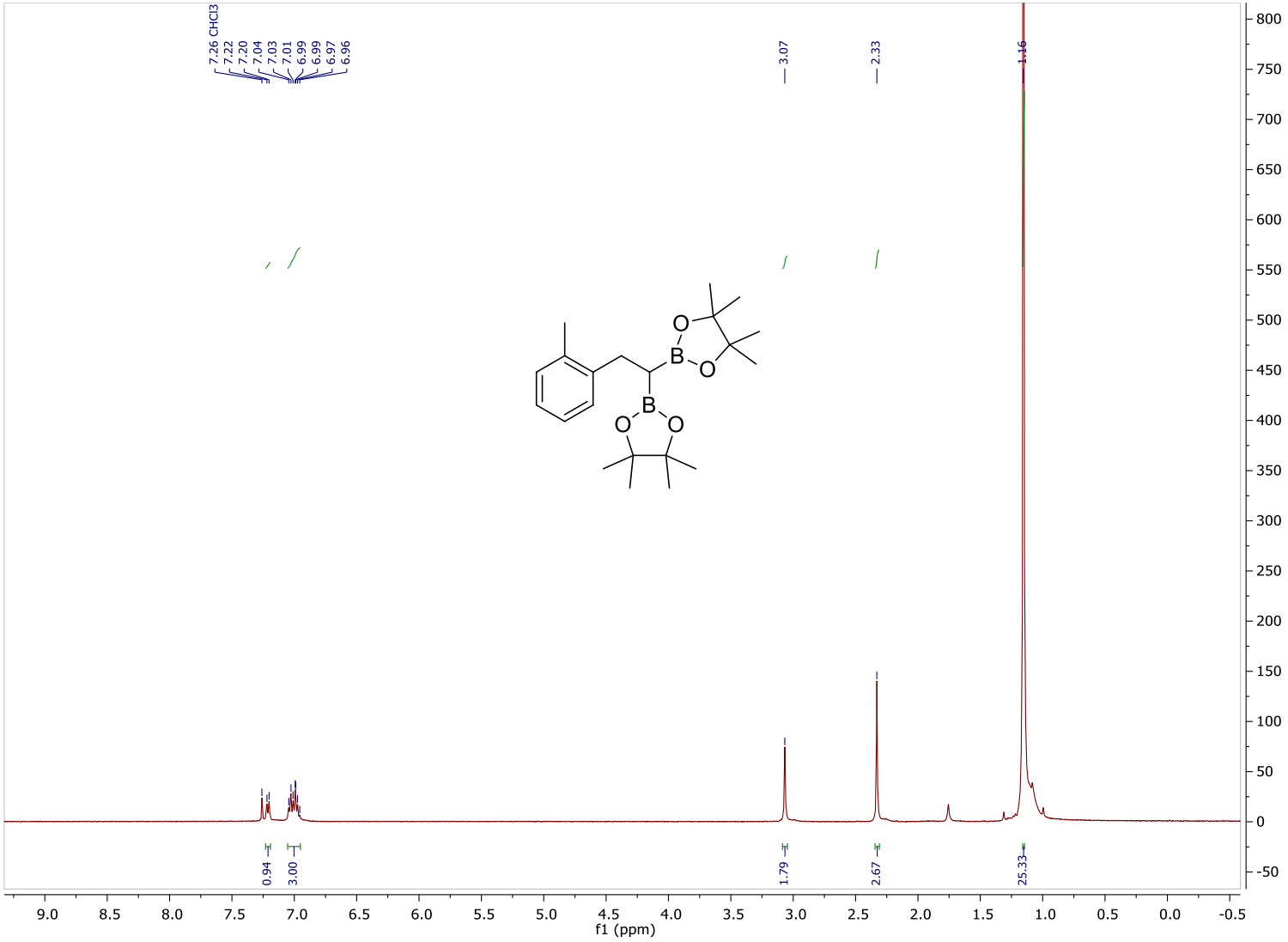
^{13}C NMR, compound 2b

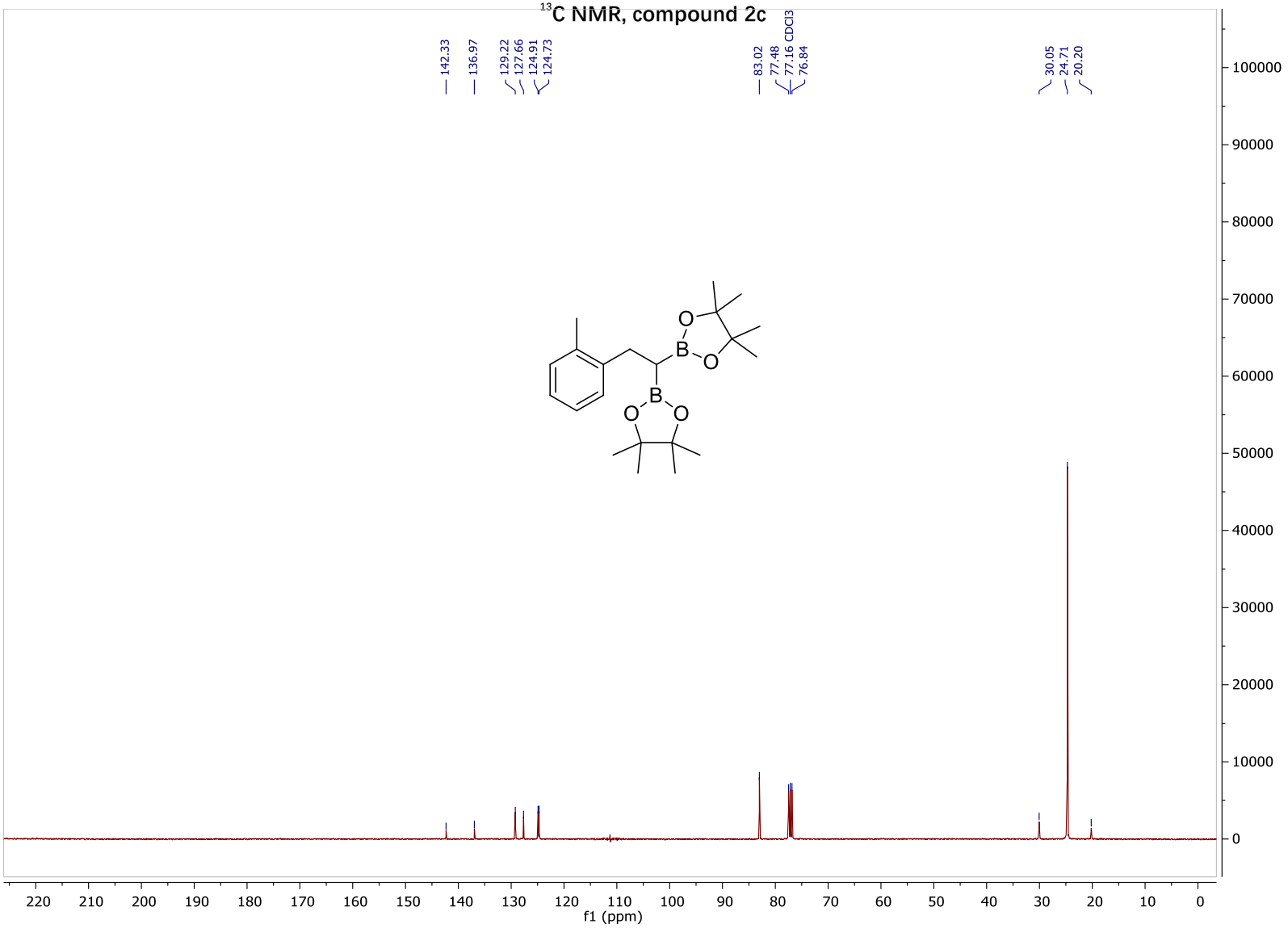


^{11}B NMR, compound 2b

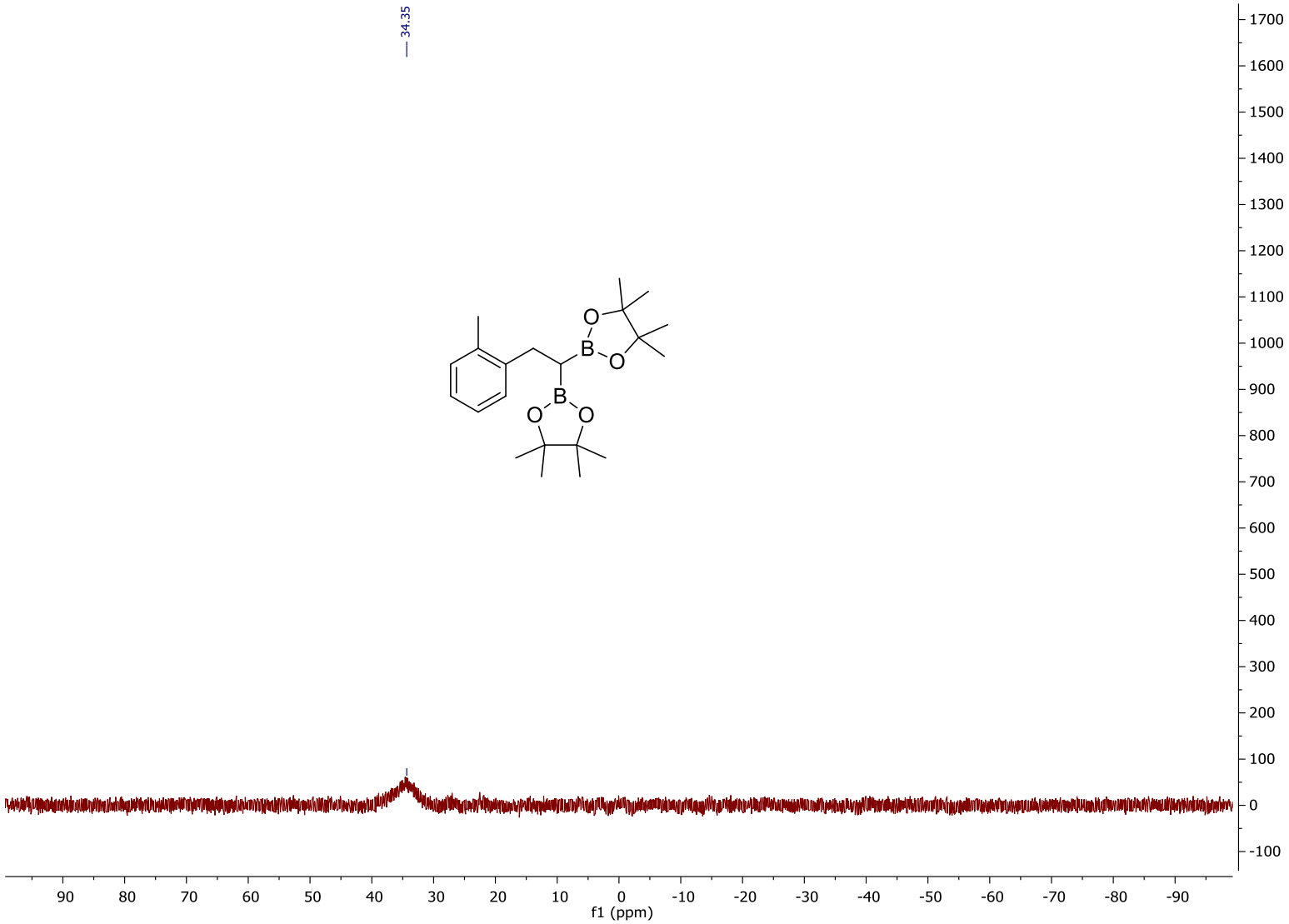


^{1}H NMR, compound 2c

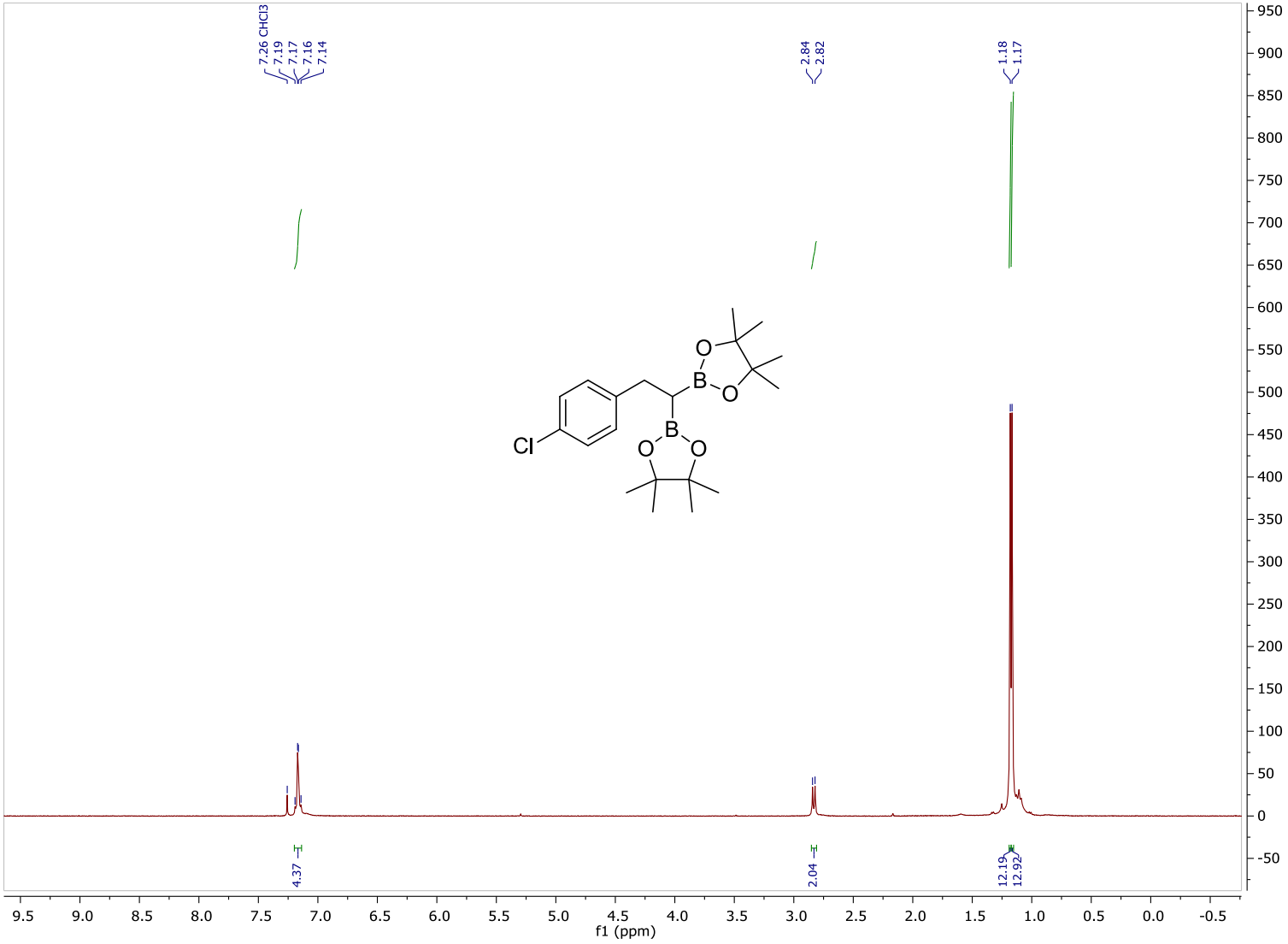


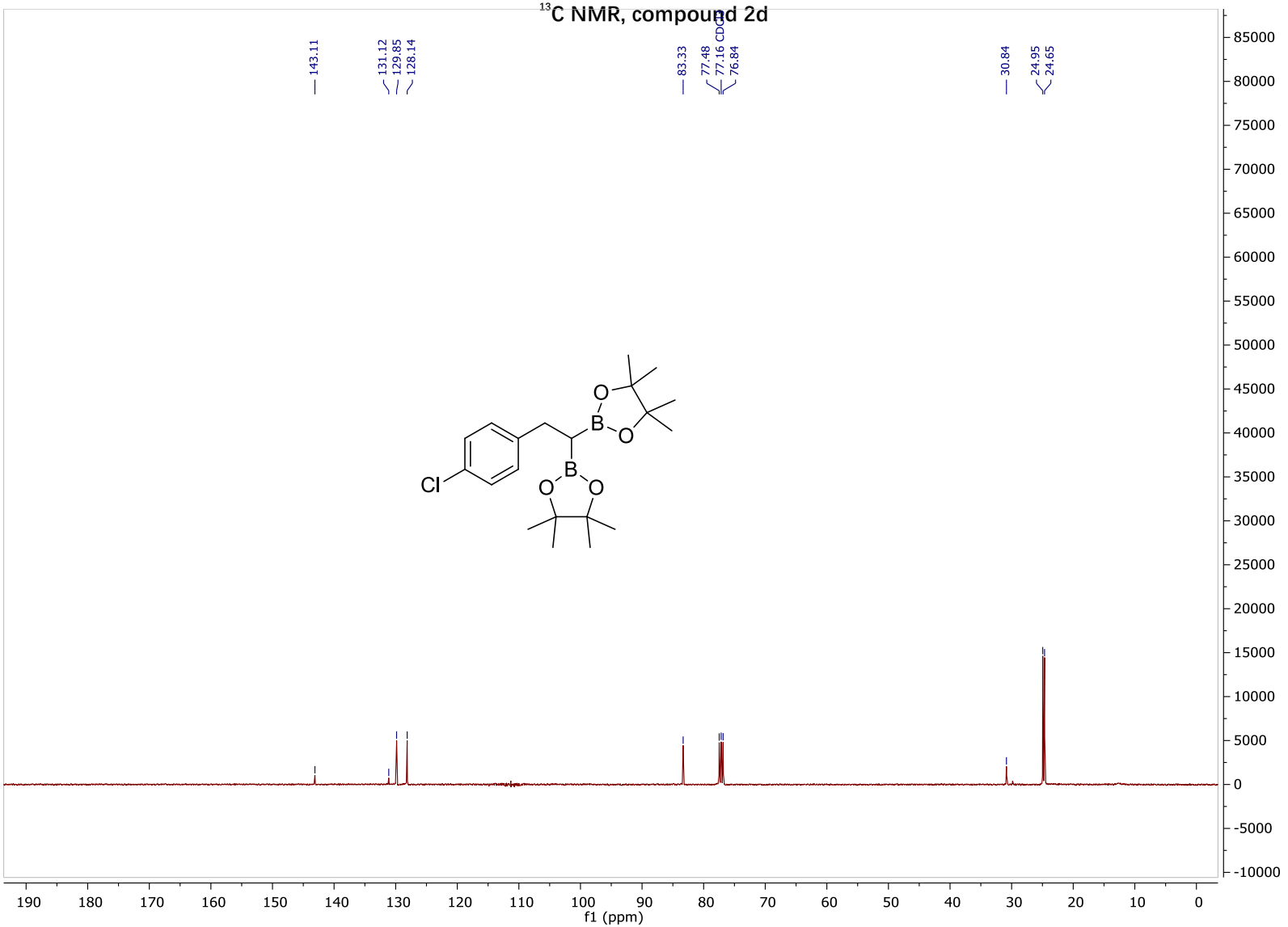

13C NMR, compound 2c
142.33
136.97
129.22
127.66
124.91
124.73
83.02
77.48
77.16 CDCl3
76.84
30.05
24.71
20.20
O
B
O
B
O
O
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{11}B NMR, compound 2c

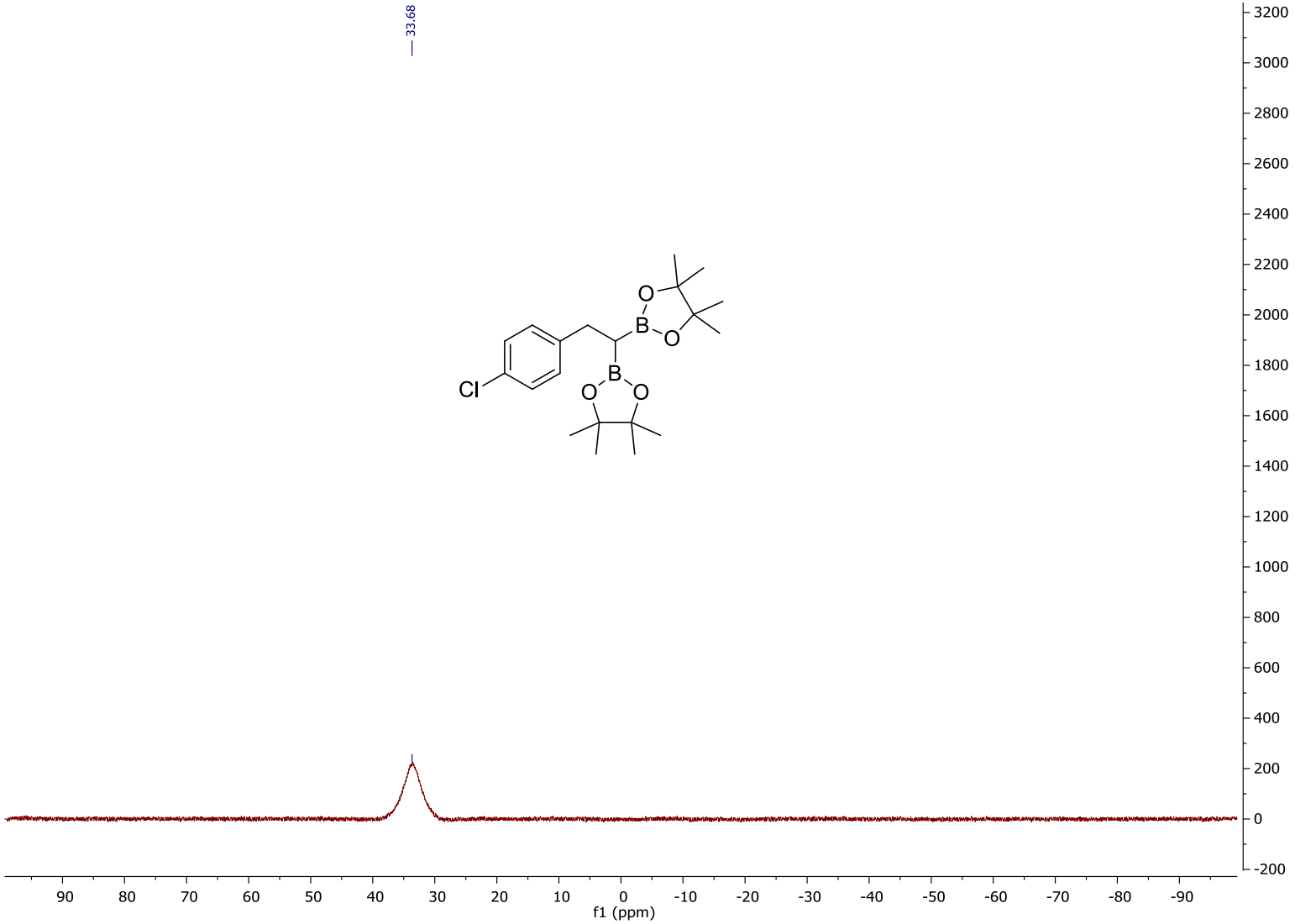


^{1}H NMR, compound 2d

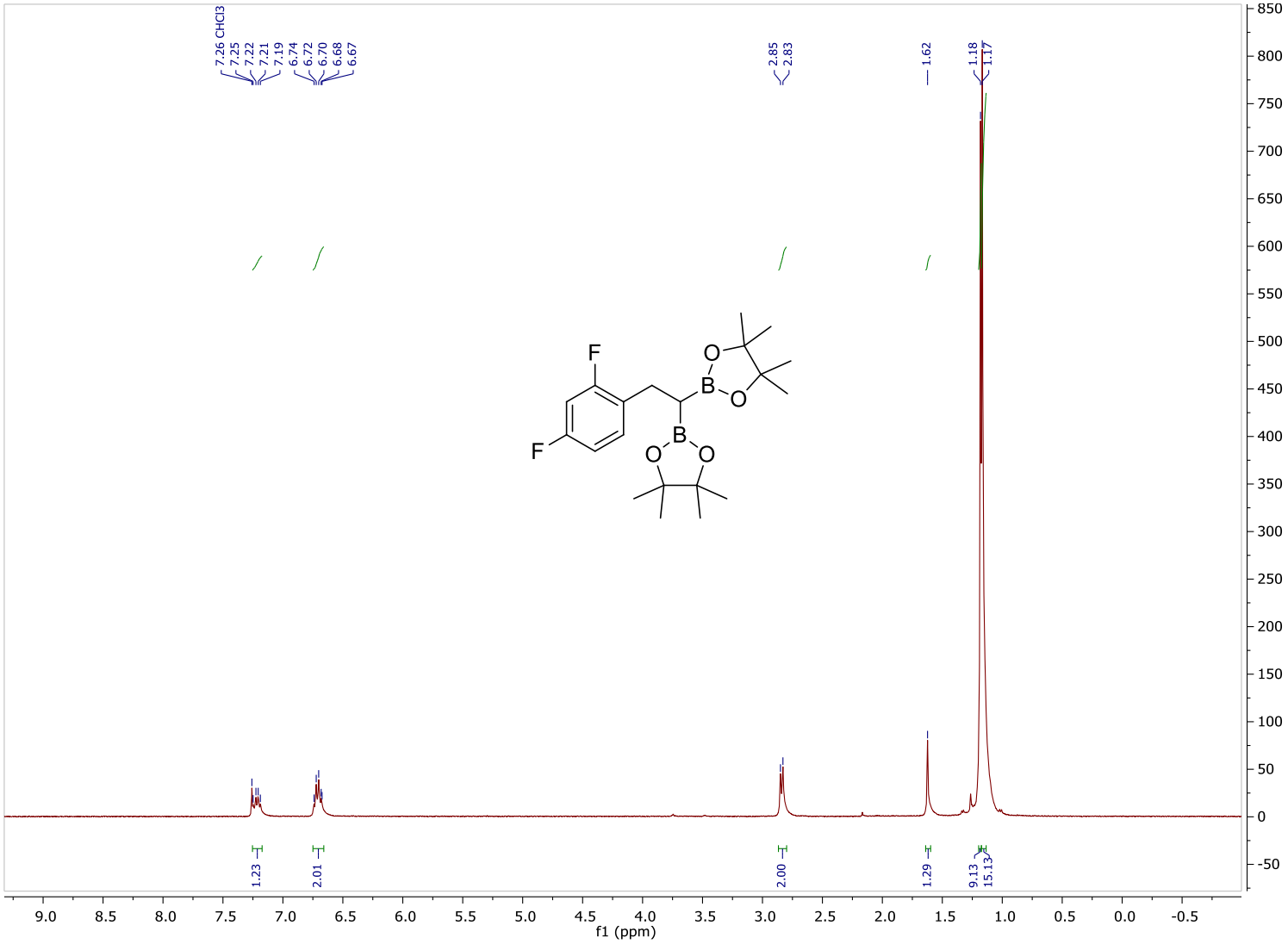


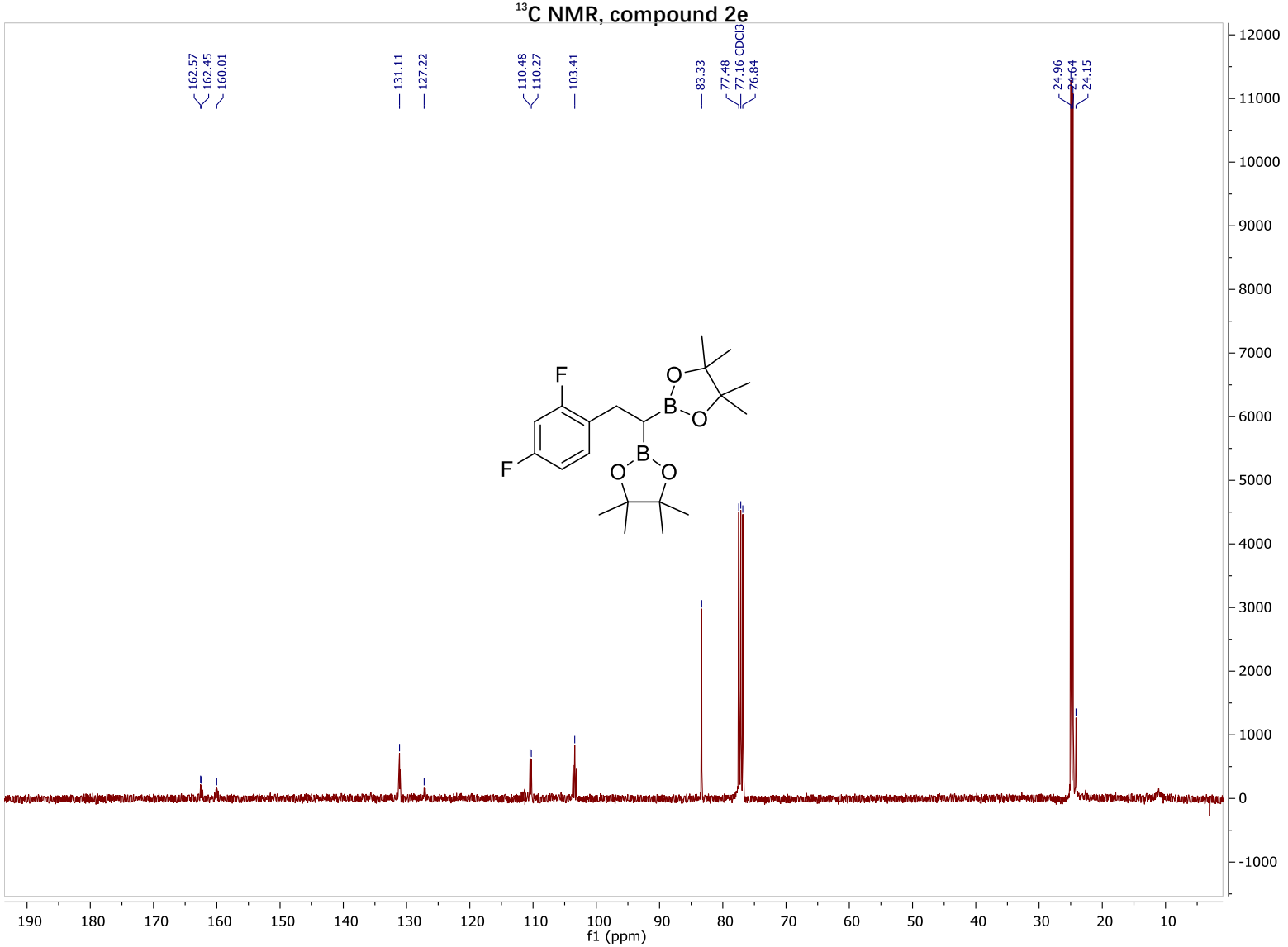

13C NMR, compound 2d
143.11
131.12
129.85
128.14
83.33
77.48
77.16 CDCl3
76.84
30.84
24.95
24.65
Cl
O
B
O
B
O
O
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{11}B NMR, compound 2d

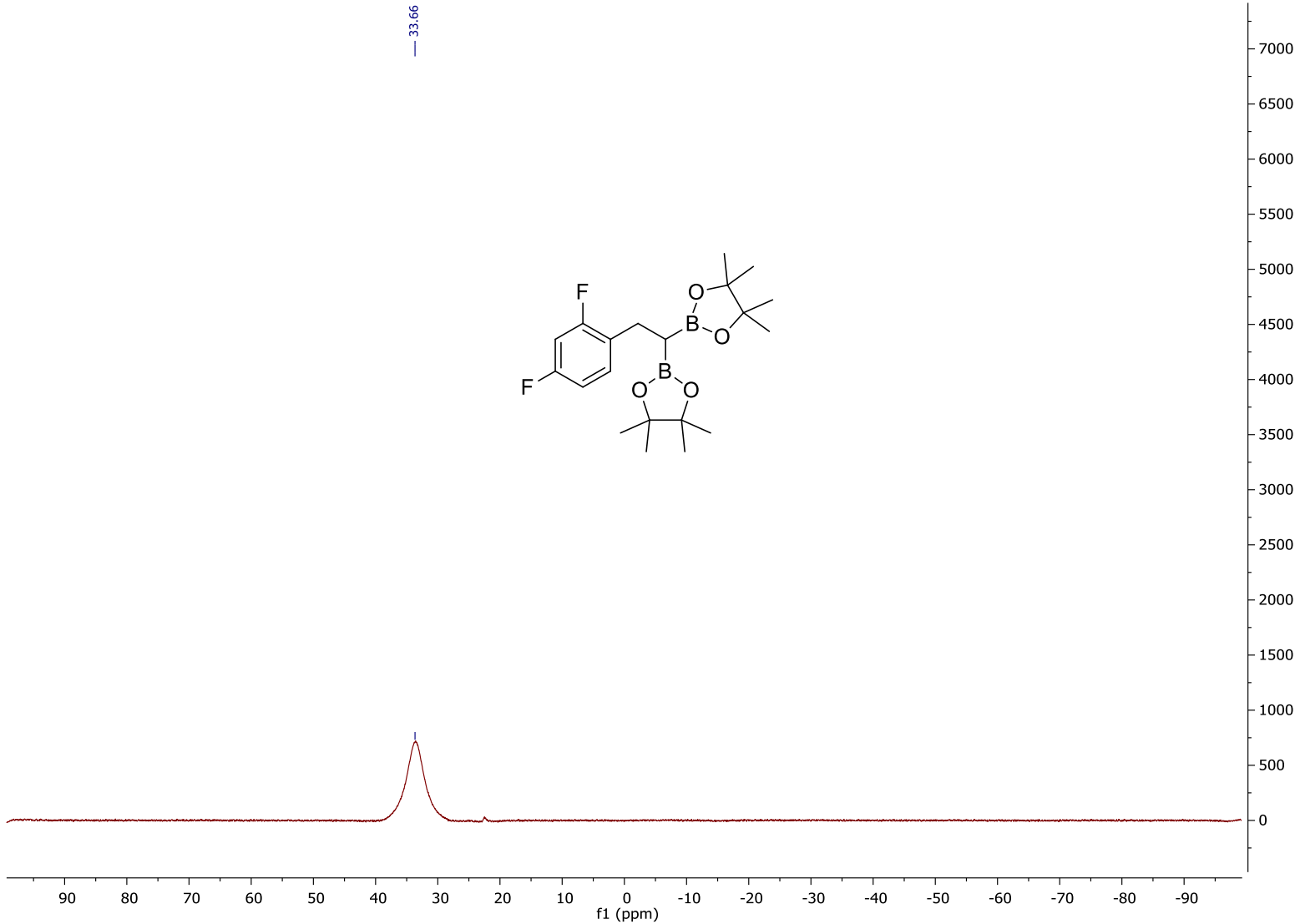


^{1}H NMR, compound 2e

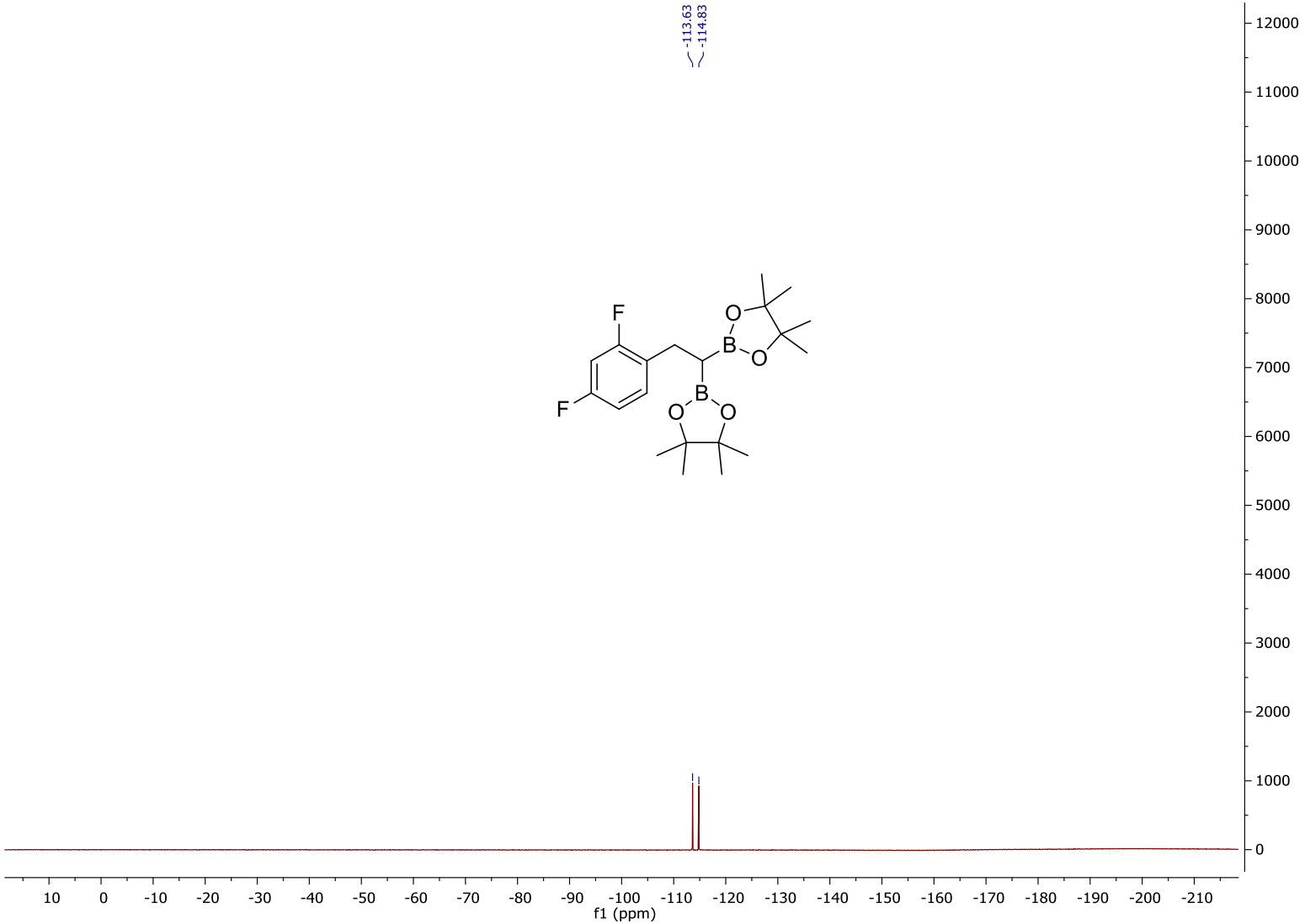



13C NMR, compound 2e
162.57
162.45
160.01
131.11
127.22
110.48
110.27
103.41
83.33
77.48
77.16 CDCl3
76.84
24.96
24.64
24.15
F
F
O
B
O
B
O
O
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

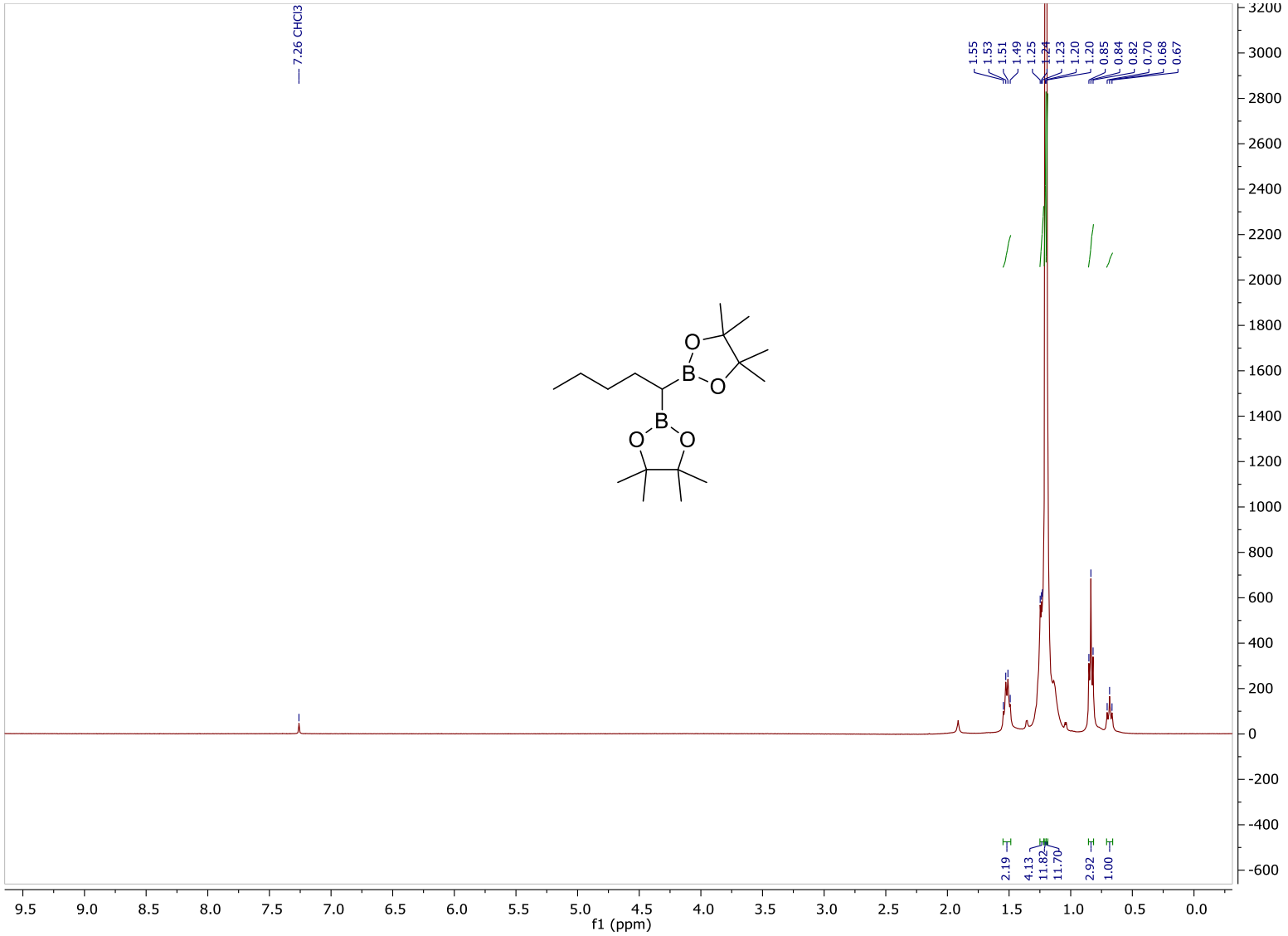
^{11}B NMR, compound 2e

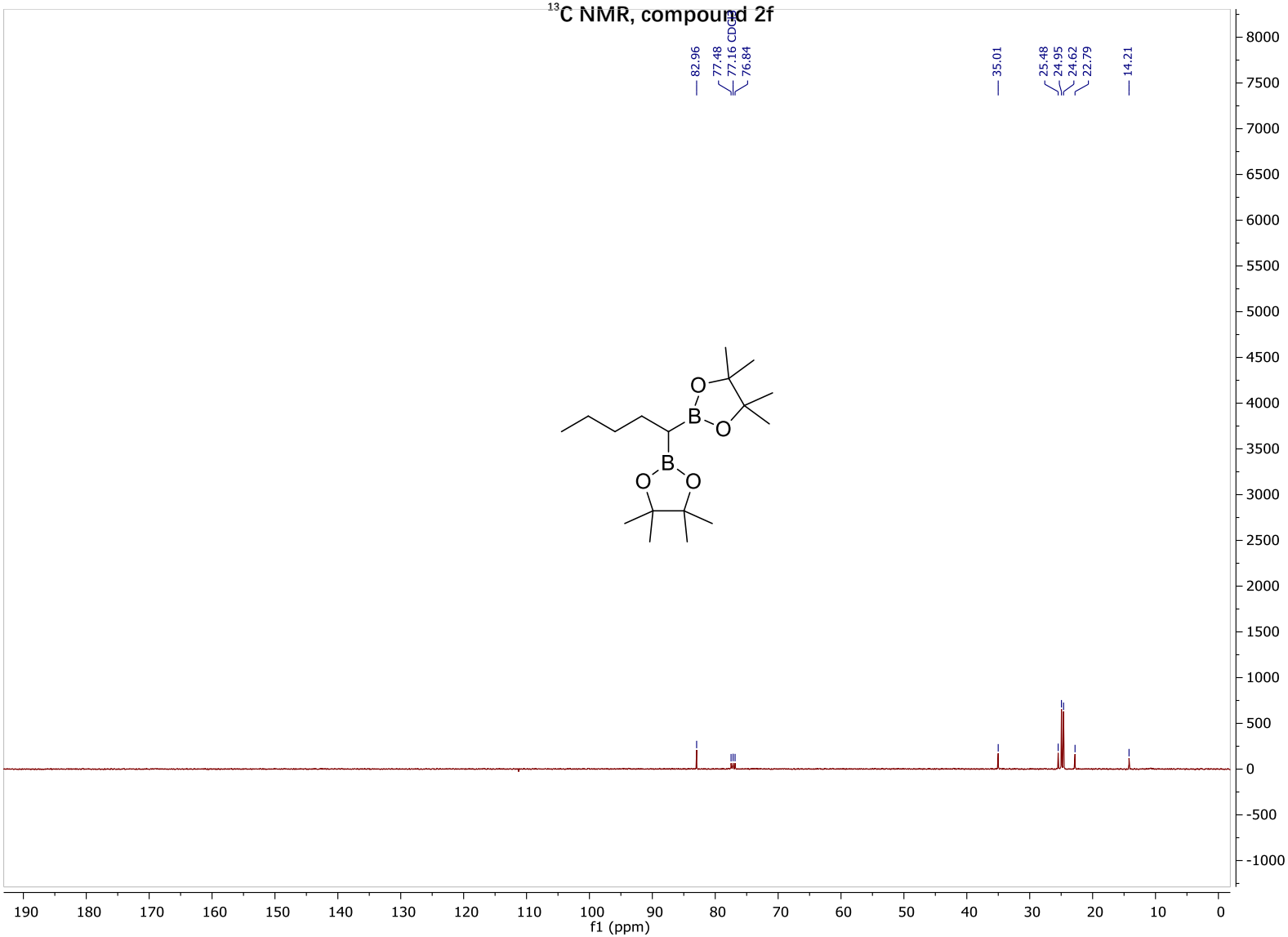


^{19}F NMR, compound 2e

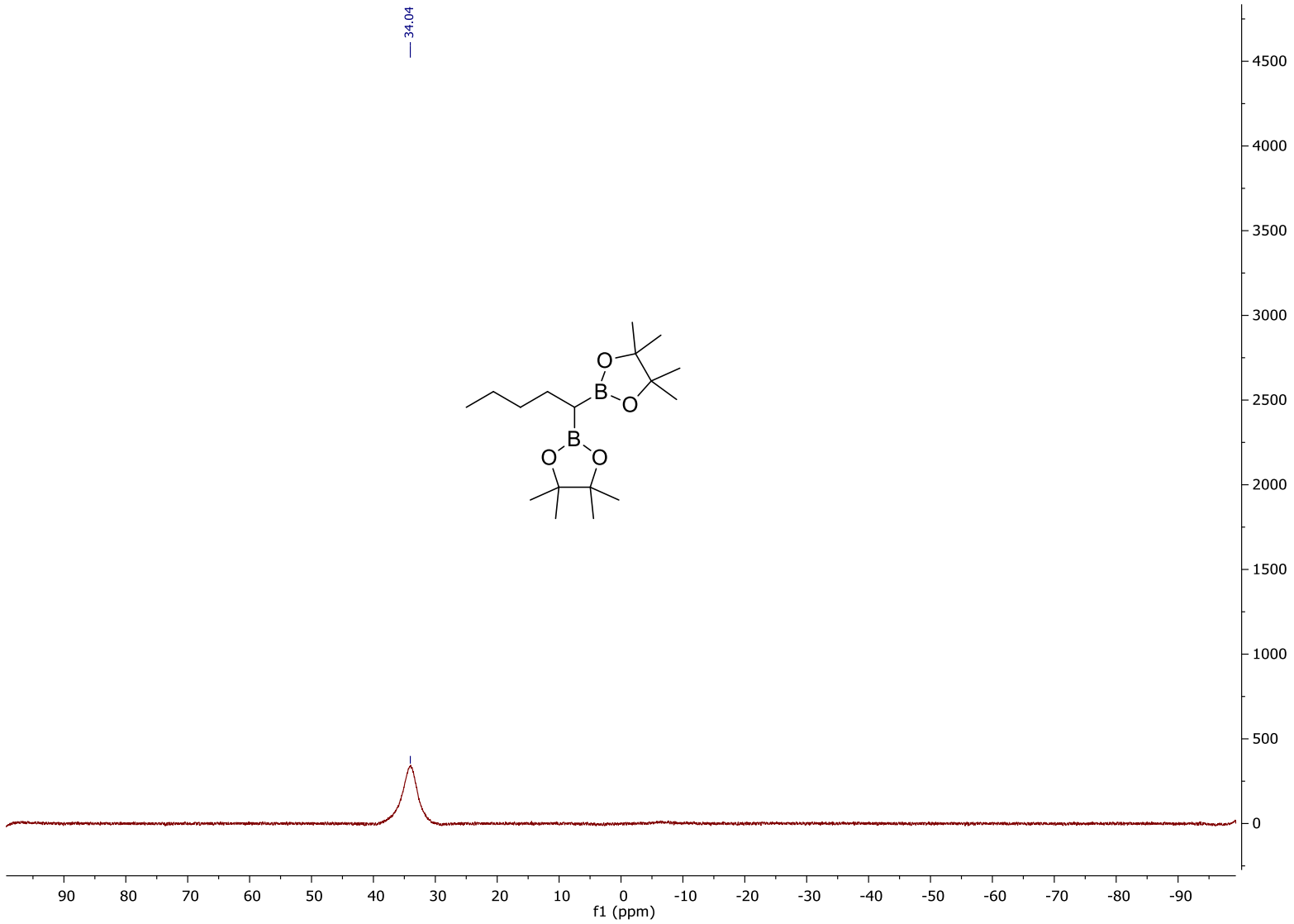


^{1}H NMR, compound 2f

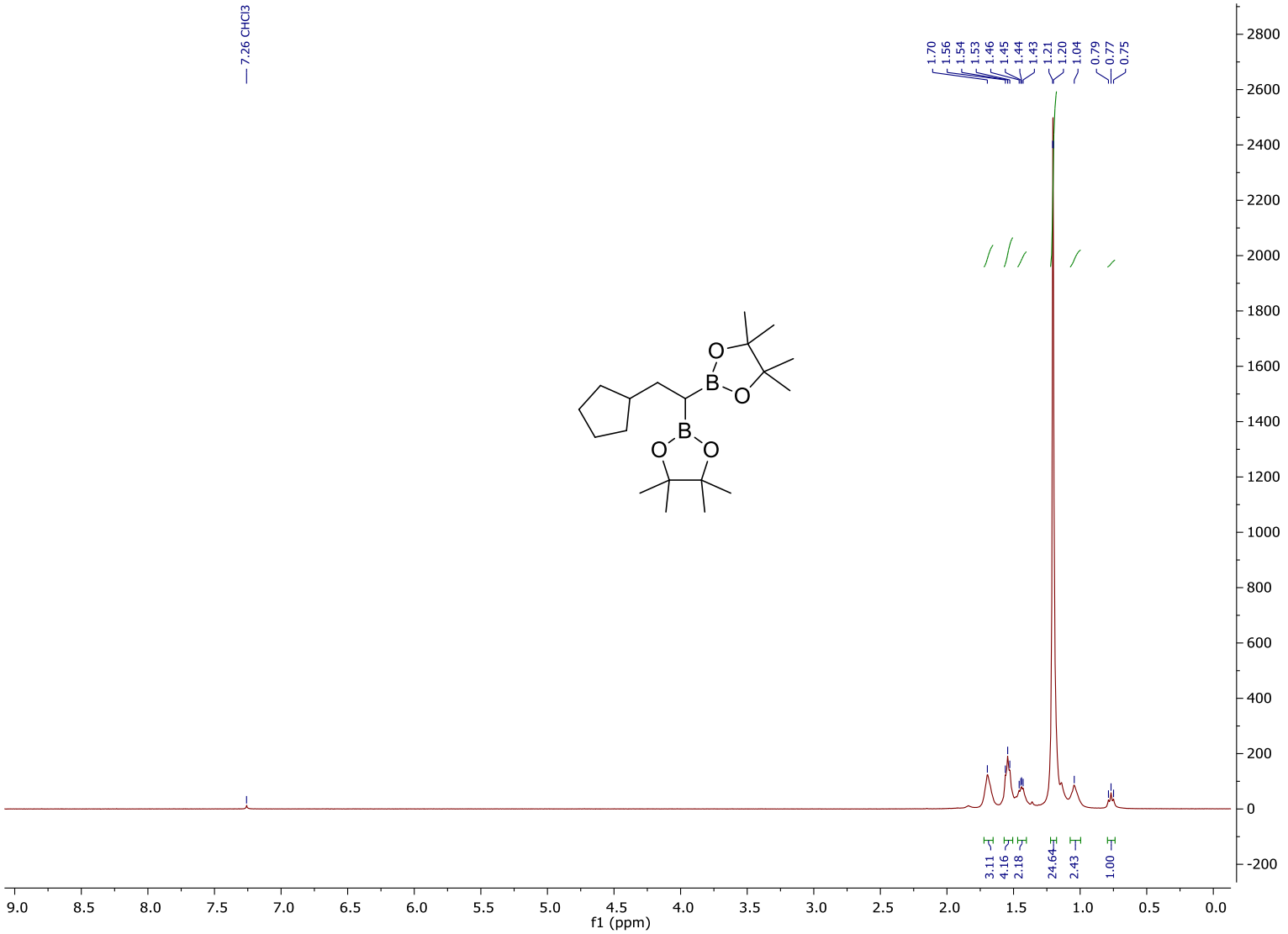


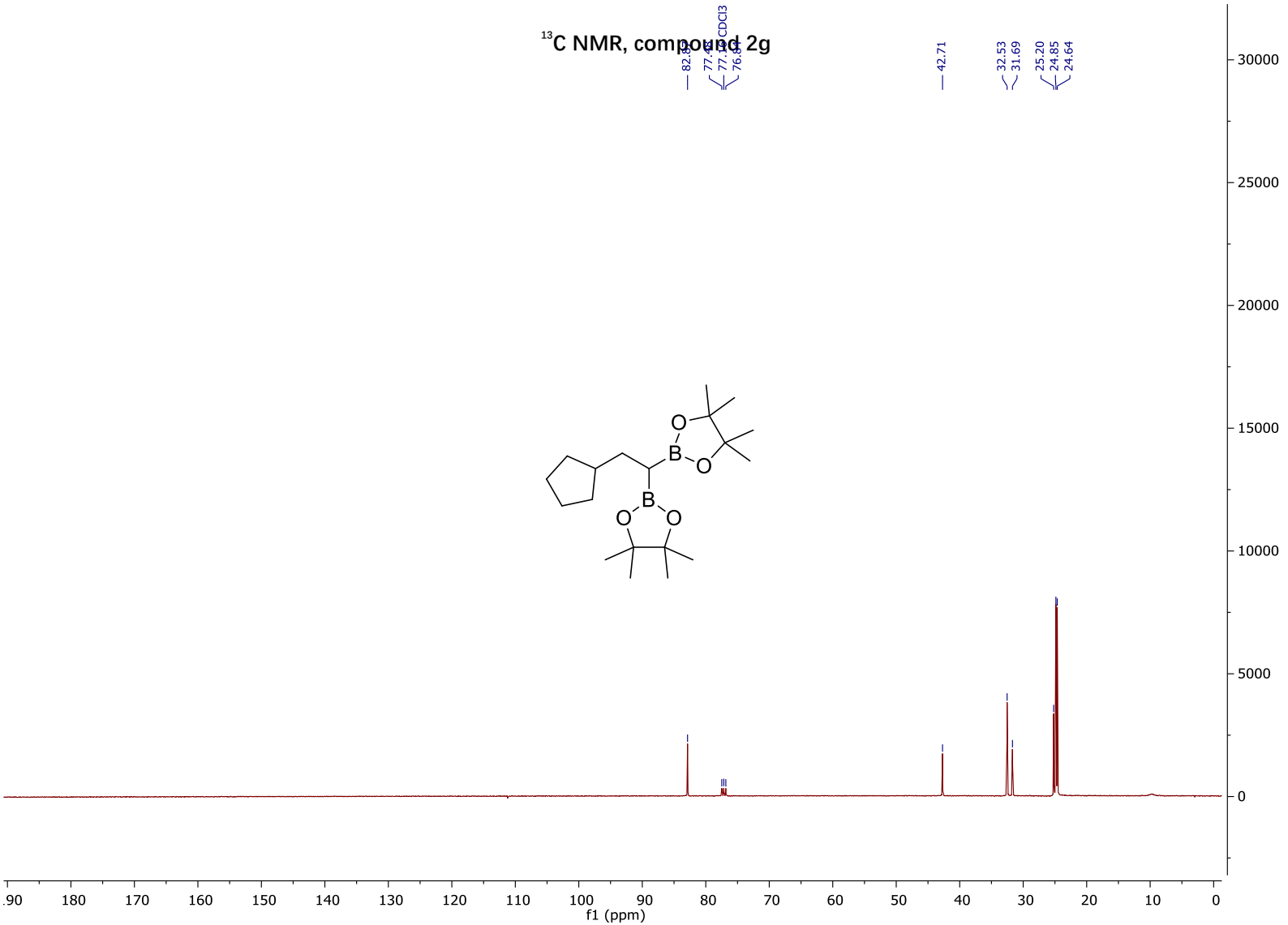

13C NMR, compound 2f
82.96
77.48
77.16 CDCl3
76.84
35.01
25.48
24.95
24.62
22.79
14.21
O
B
O
B
O
O
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{11}B NMR, compound 2f

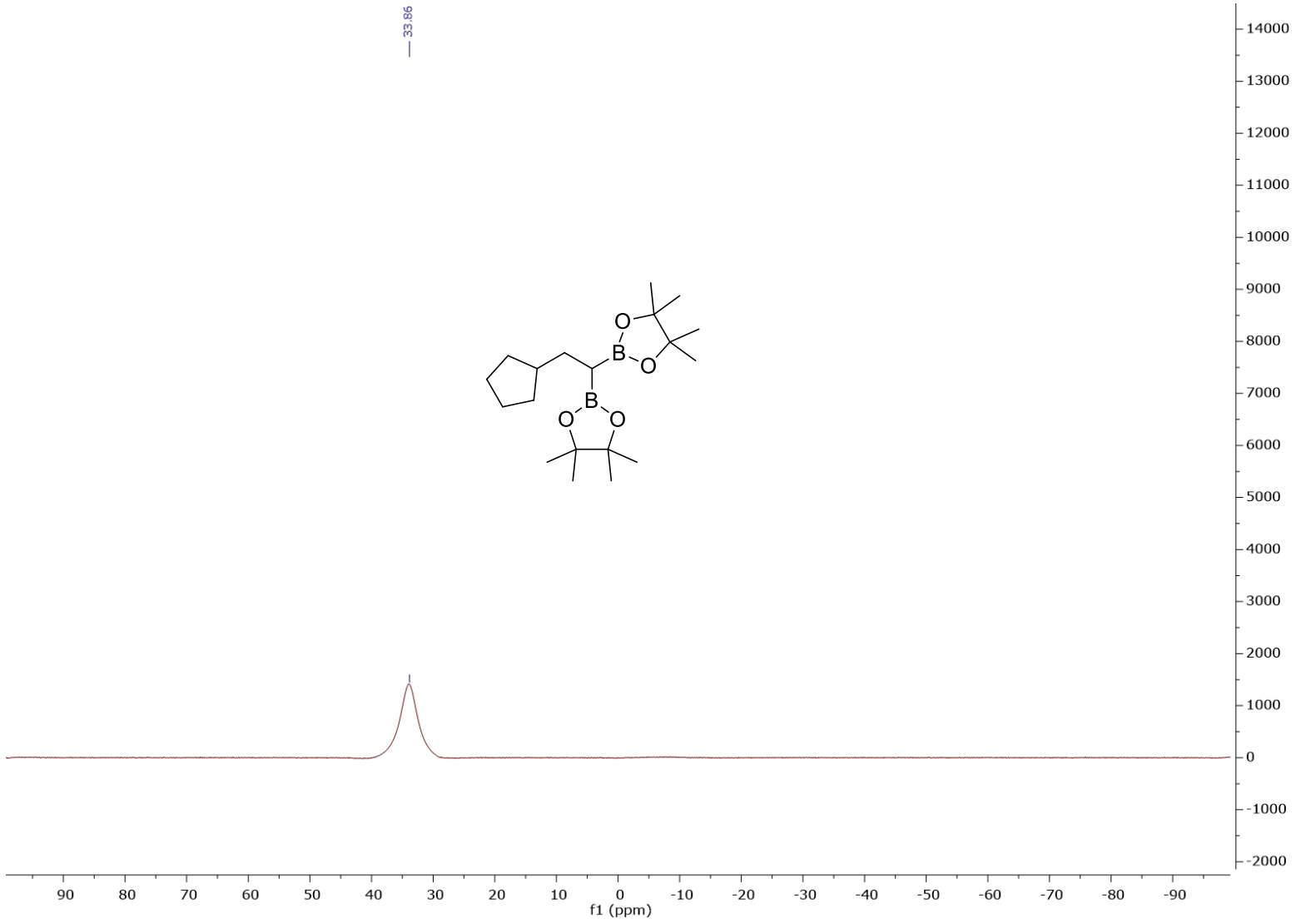


^{1}H NMR, compound 2g

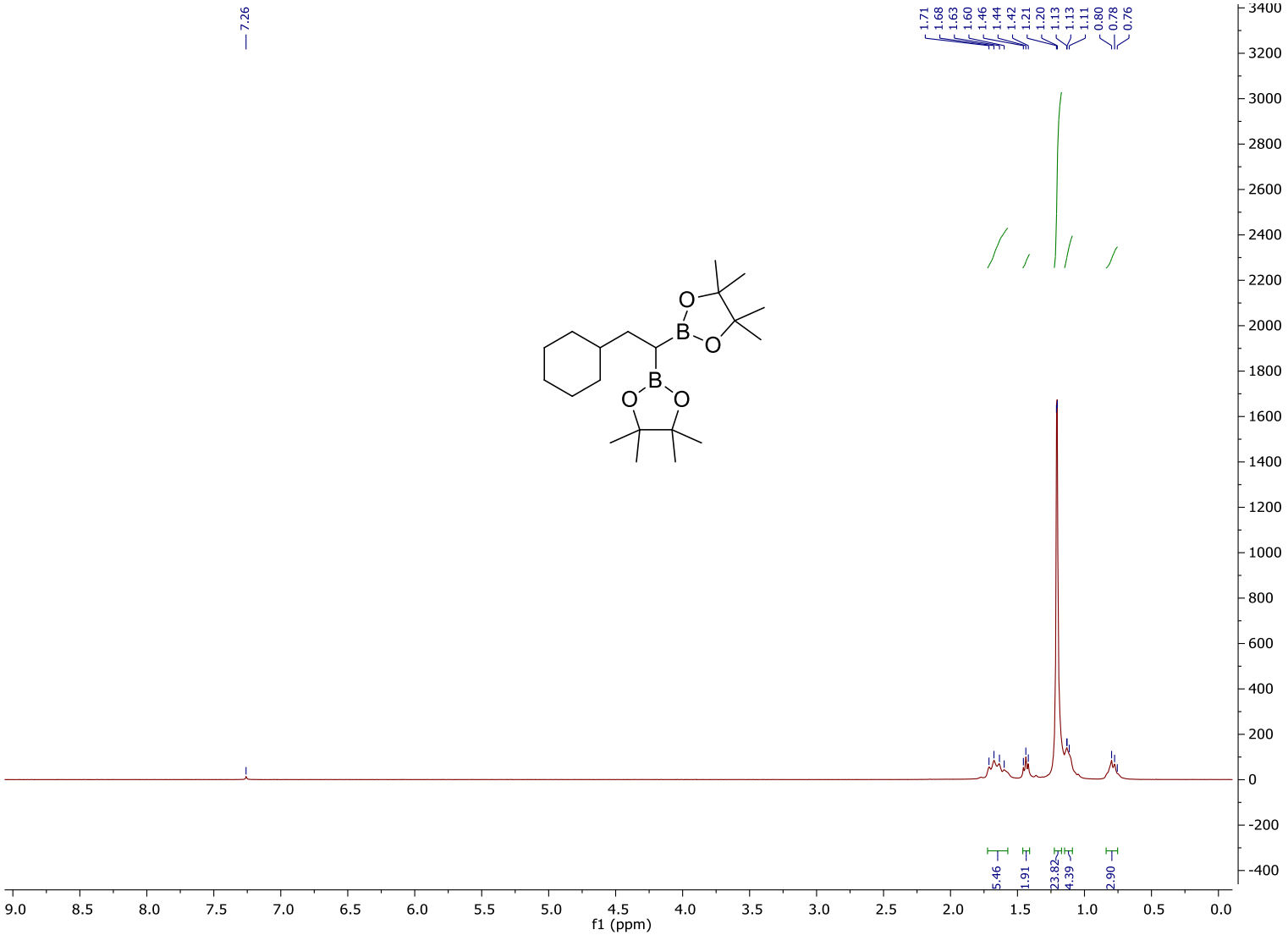



13C NMR, compound 2g
82.99
77.41
77.16 CDCl3
76.89
42.71
32.53
31.69
25.20
24.85
24.64
O
B
O
B
O
O
30000
25000
20000
15000
10000
5000
0
f1 (ppm)

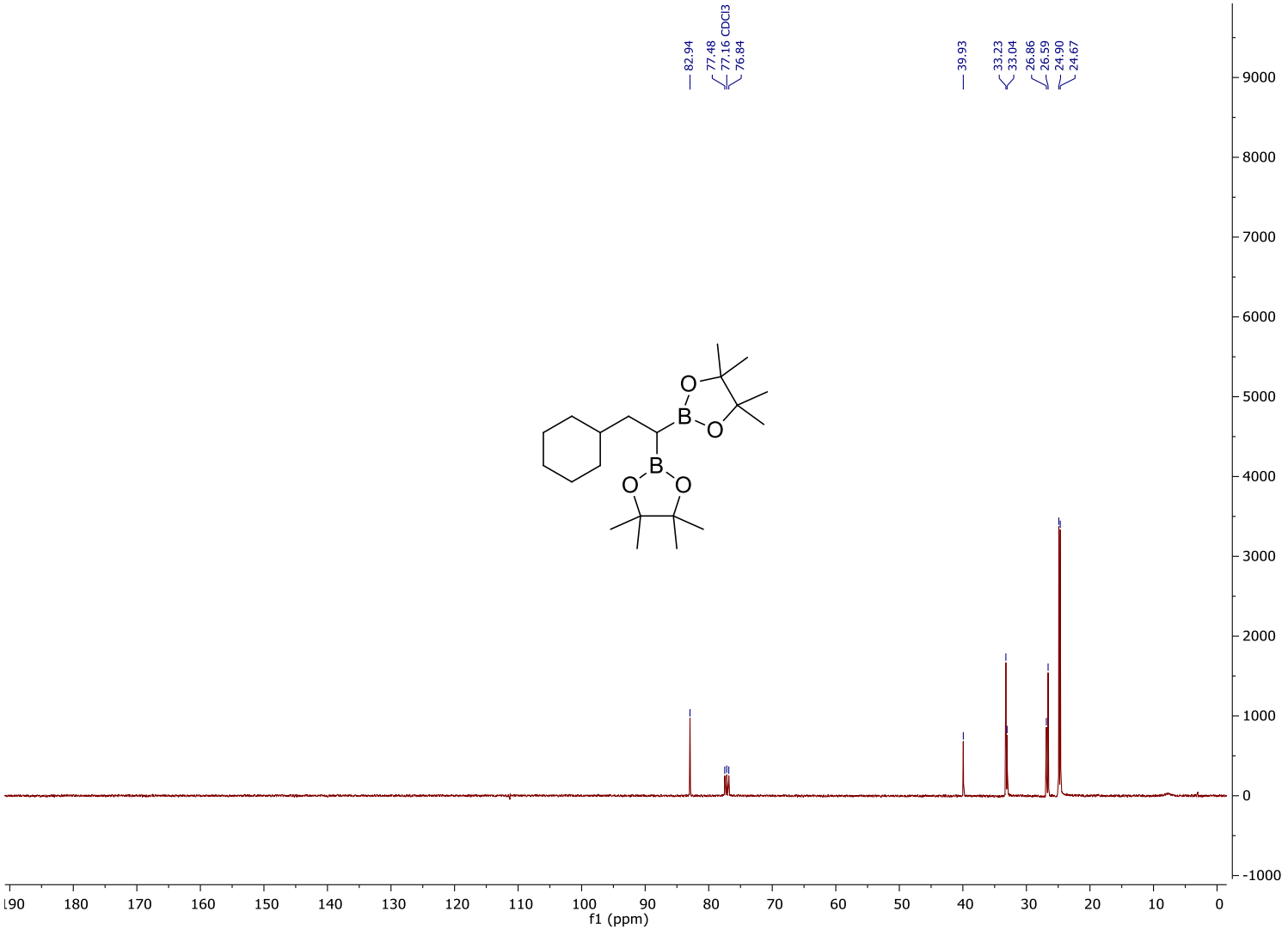
^{11}B NMR, compound 2g



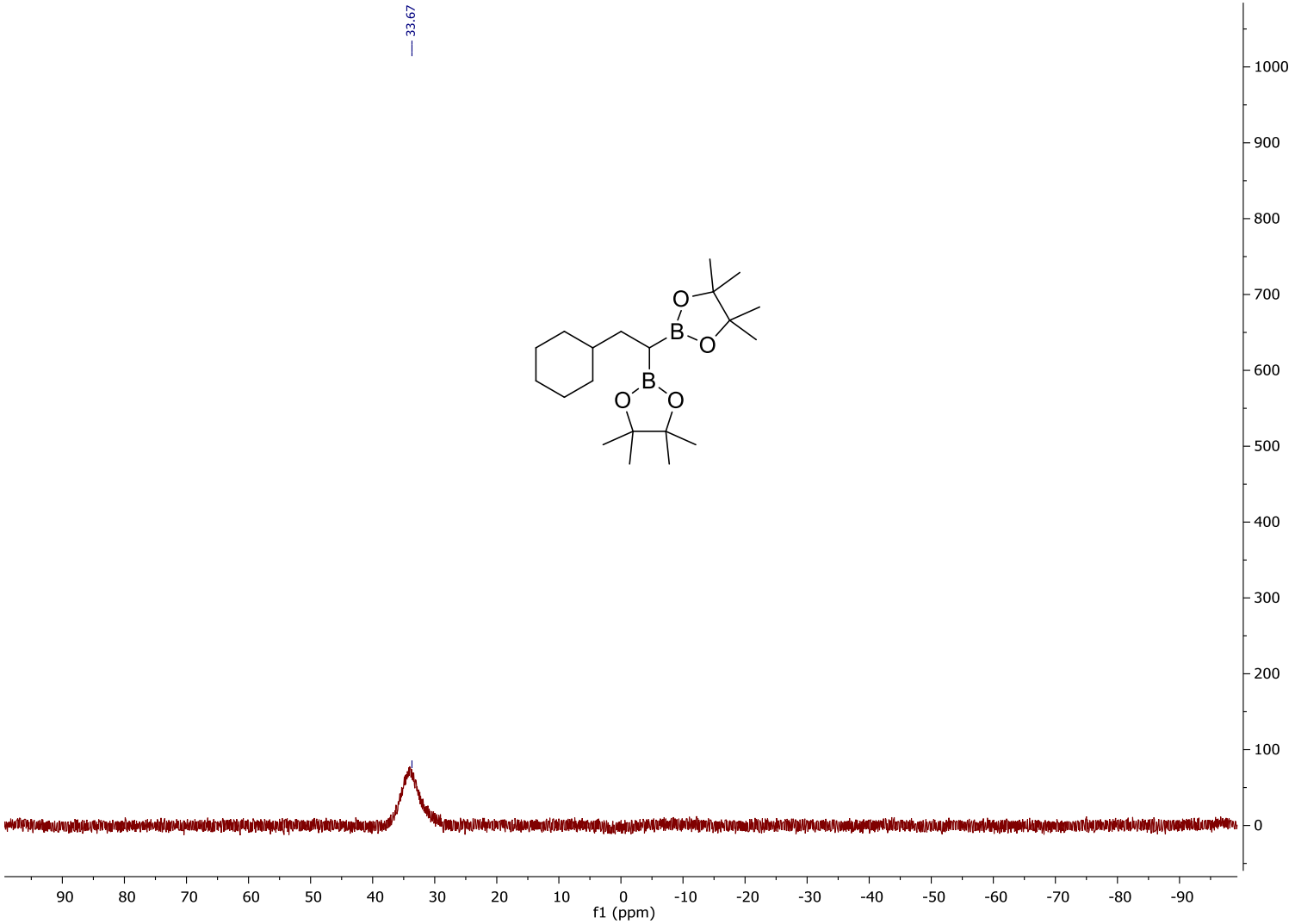
^{1}H NMR, compound 2h



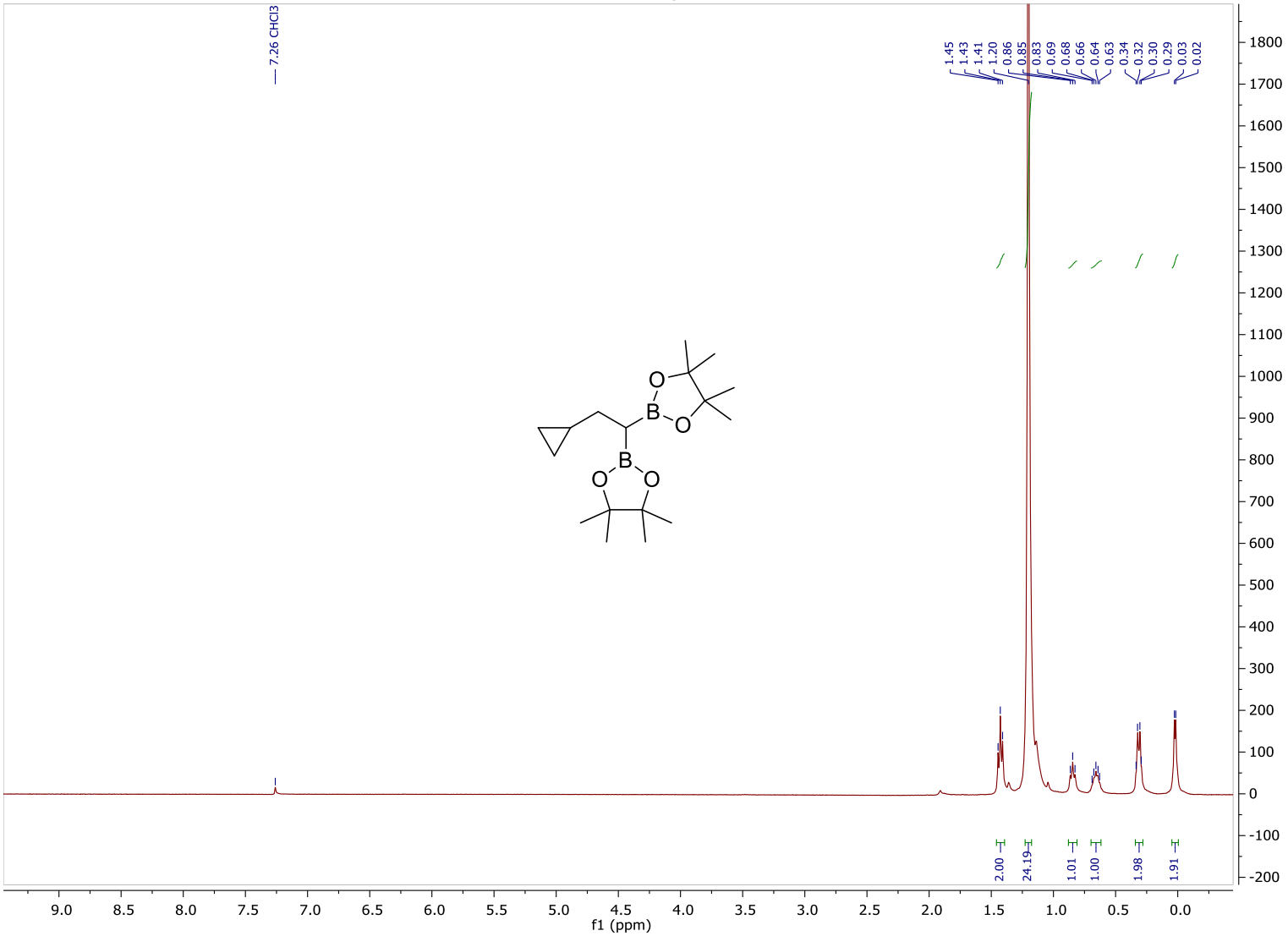
^{13}C NMR, compound 2h



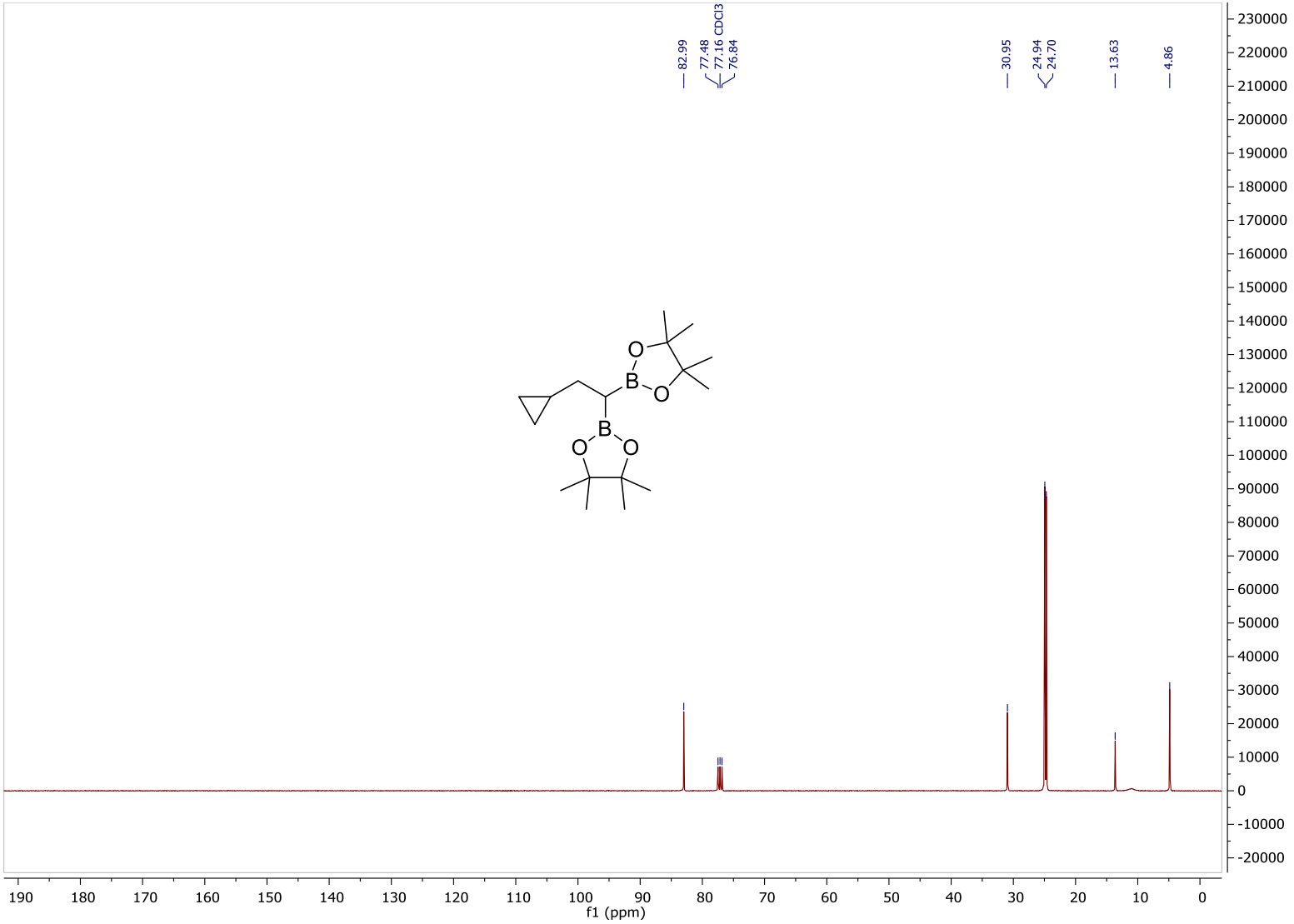
^{11}B NMR, compound 2h



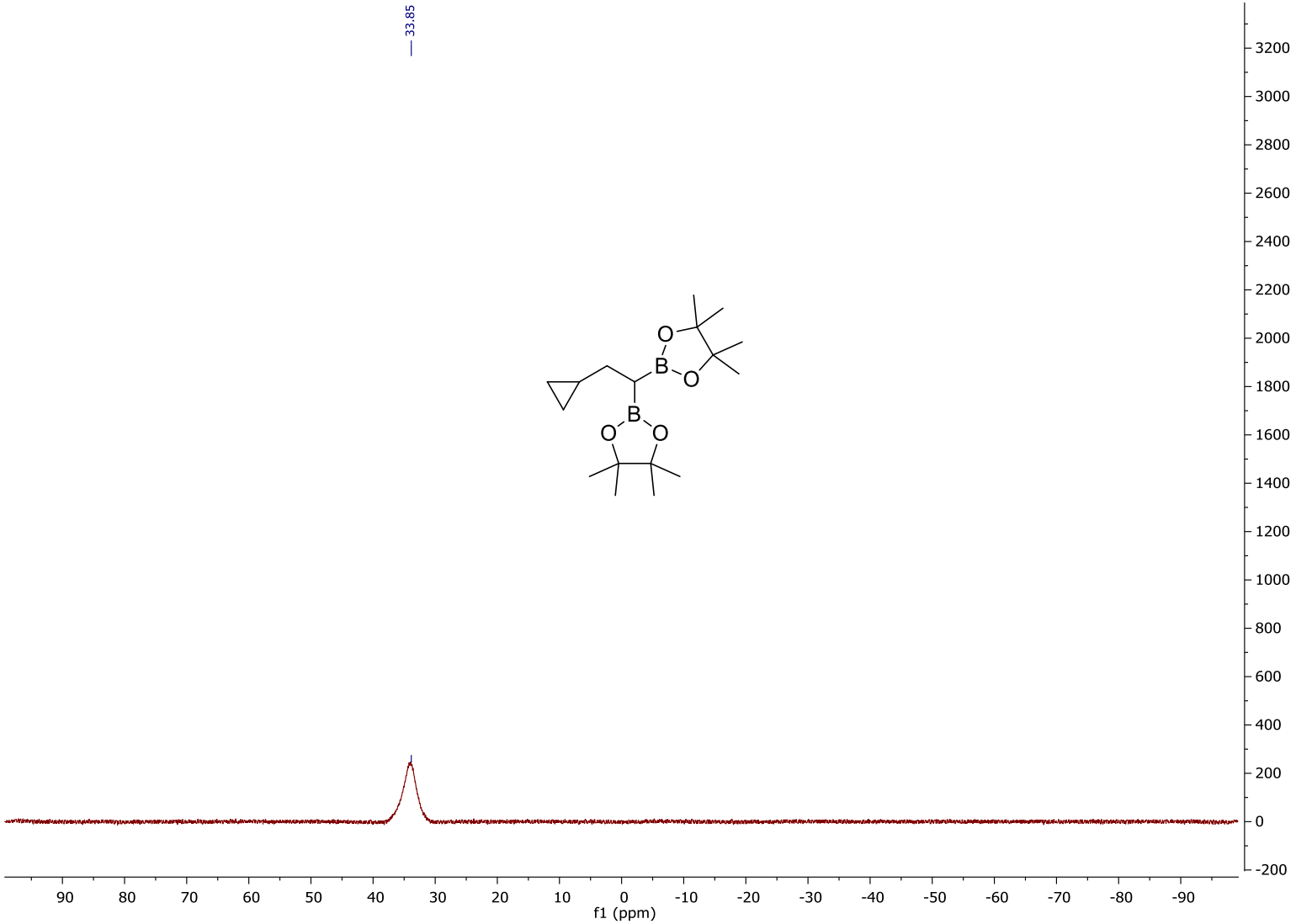
^{1}H NMR, compound 2i

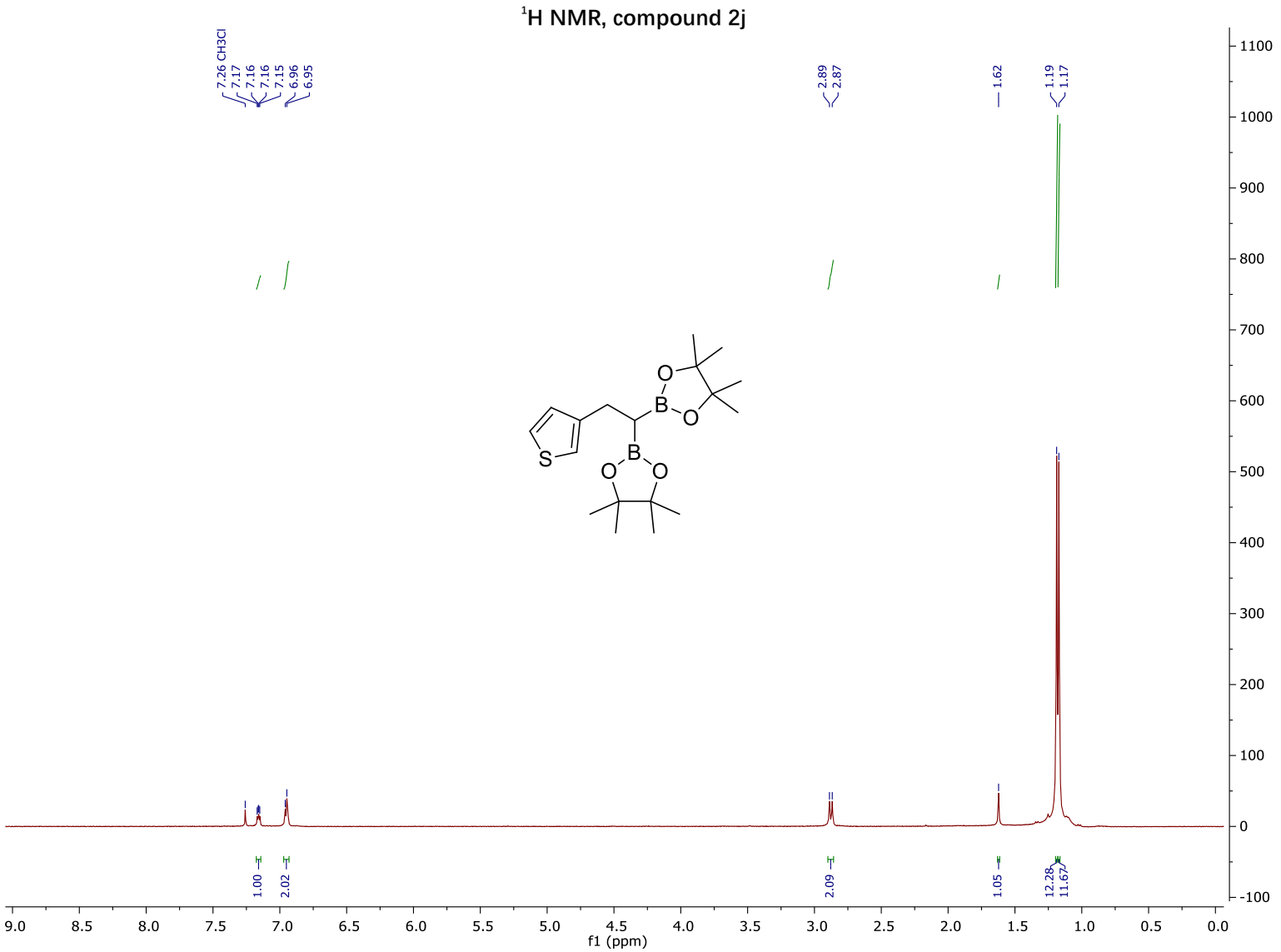


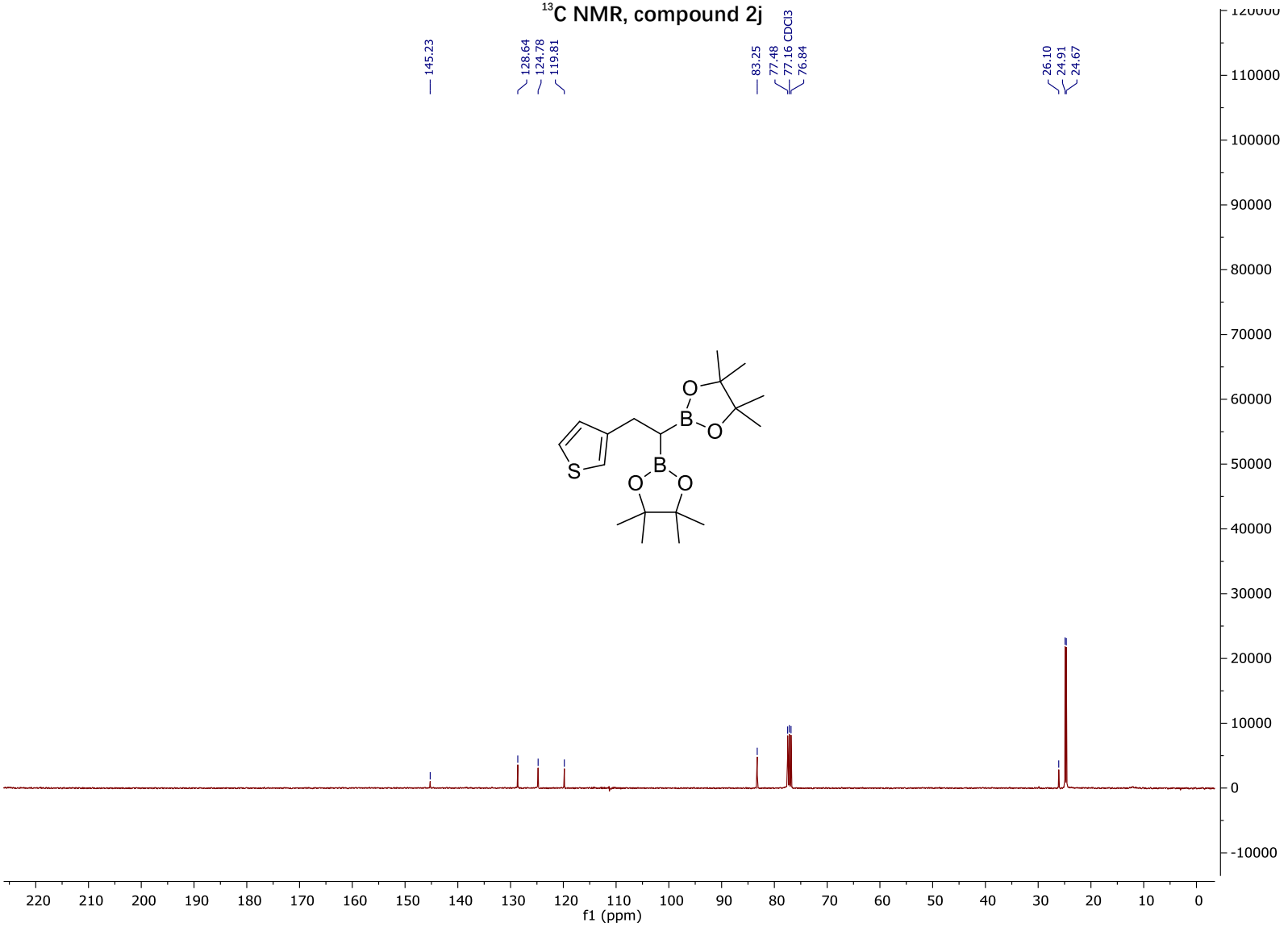
^{13}C NMR, compound 2i



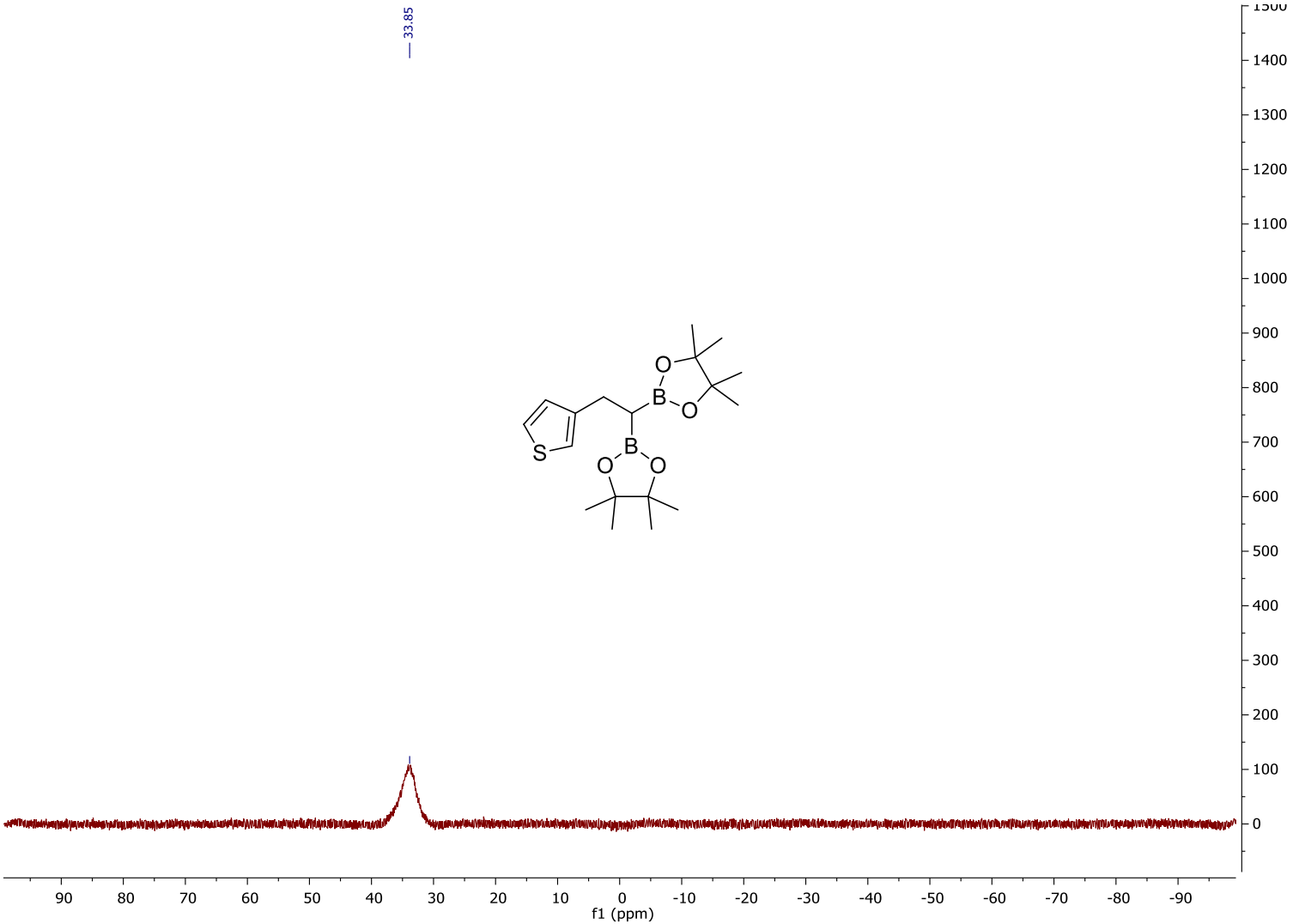
^{11}B NMR, compound 2i



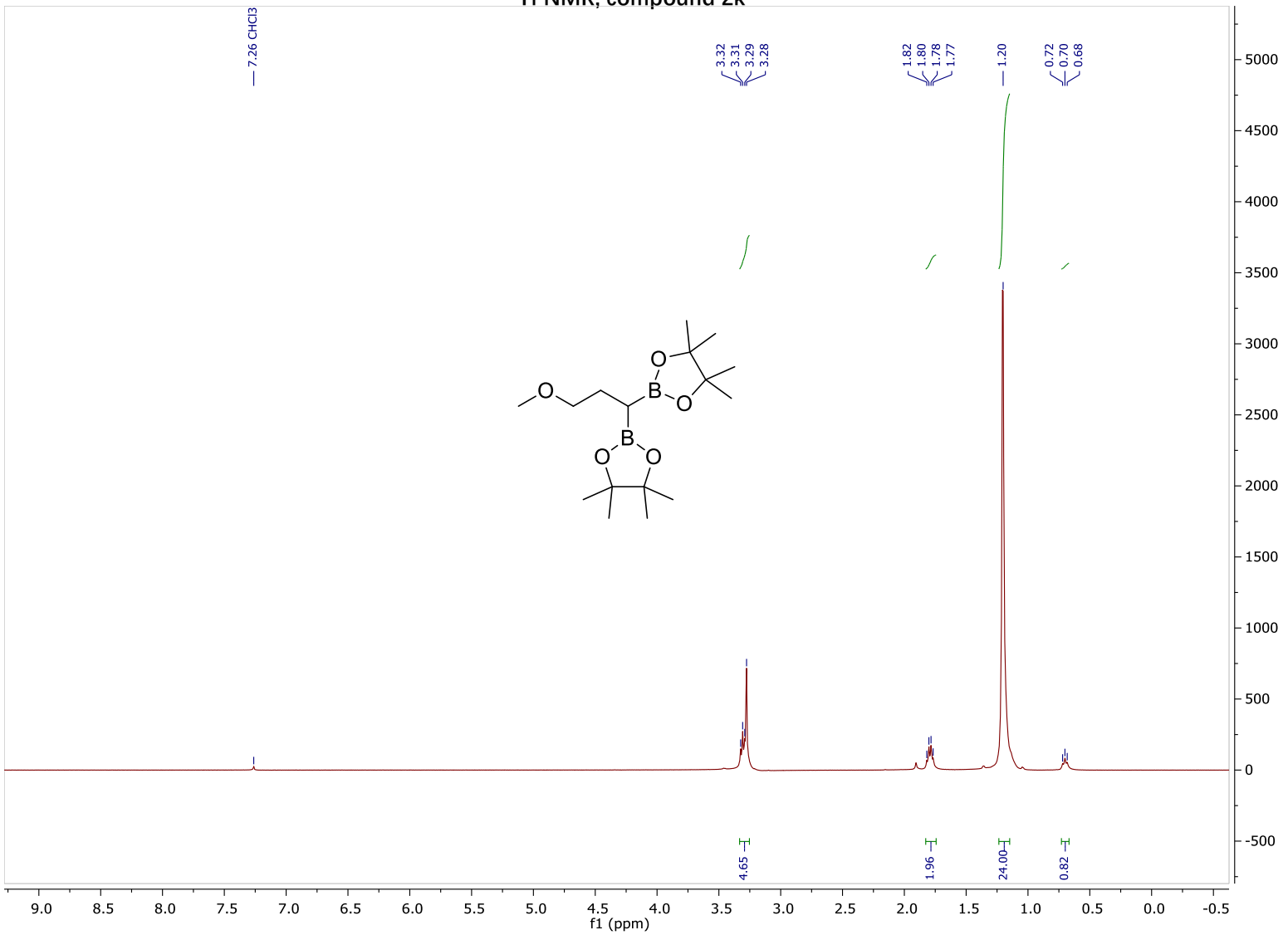

^{1}H NMR, compound 2j
7.26 CH3Cl
7.17
7.16
7.16
7.15
6.96
6.95
2.89
2.87
1.62
1.19
1.17
O
B
O
S
B
O
O
1.00
2.02
2.09
1.05
12.28
11.67
f1 (ppm)


13C NMR, compound 2j
145.23
128.64
124.78
119.81
83.25
77.48
77.16 CDCl3
76.84
26.10
24.91
24.67
O
B
O
S
B
O
O
f1 (ppm)

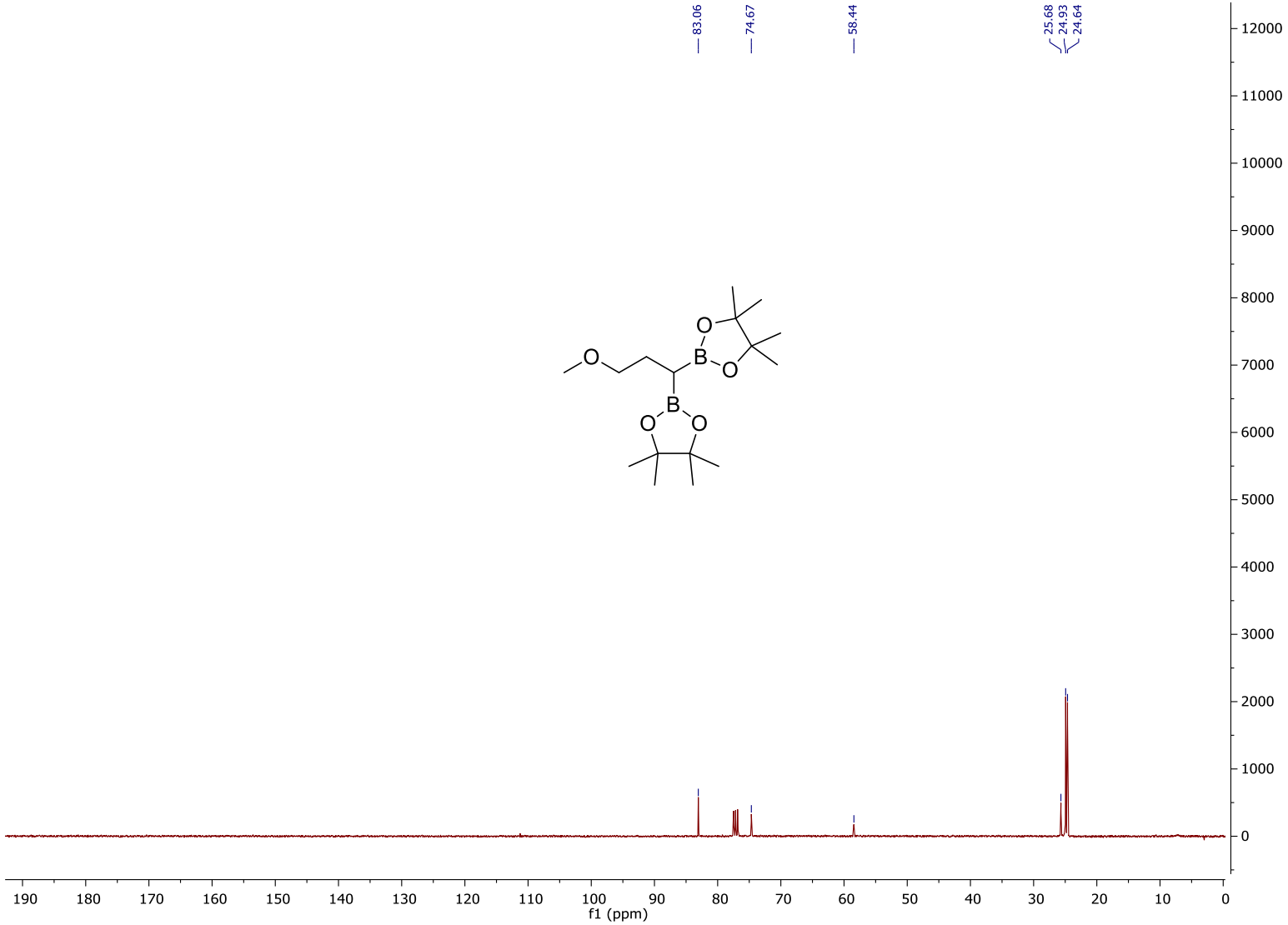
^{11}B NMR, compound 2j



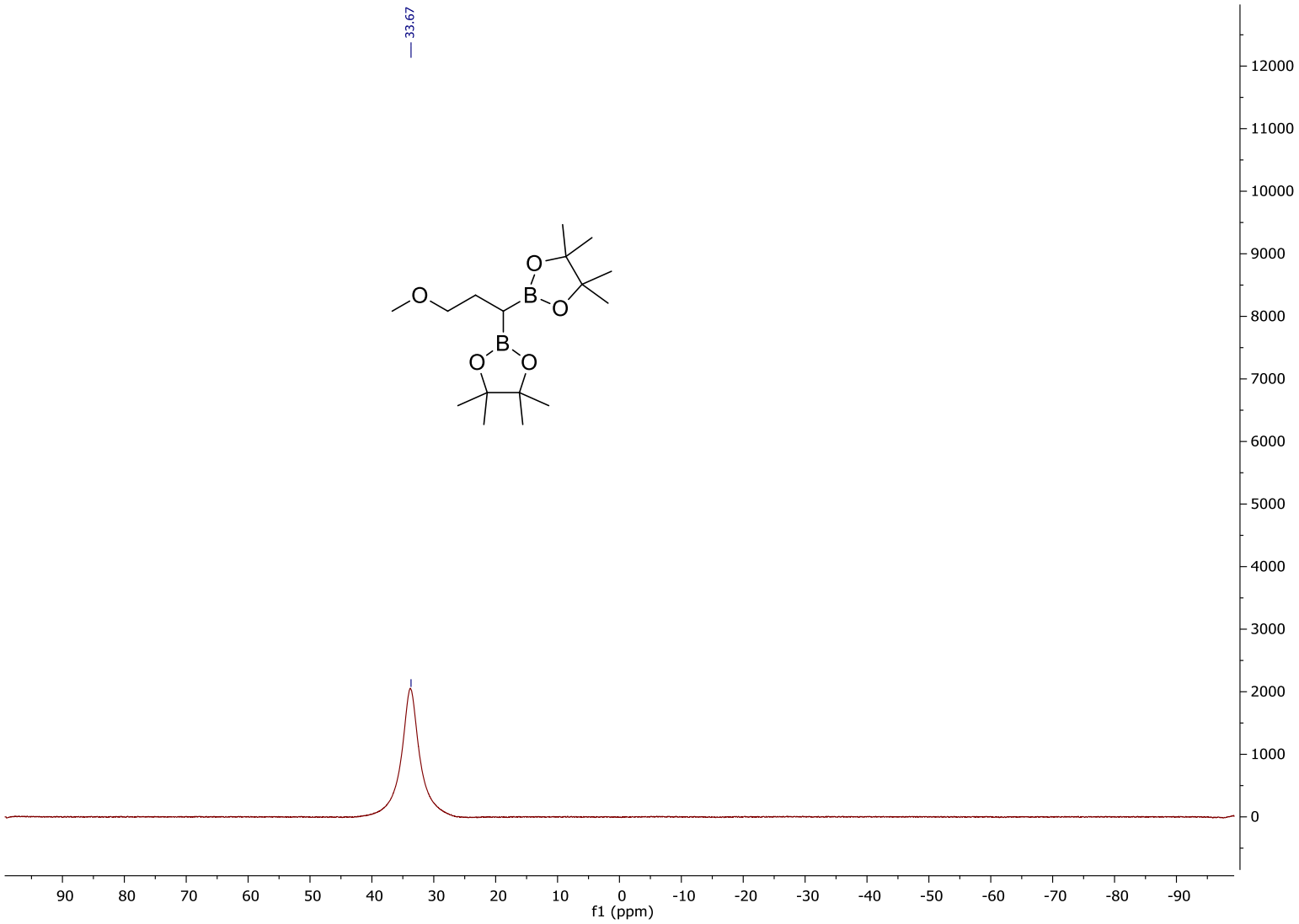
^{1}H NMR, compound 2k



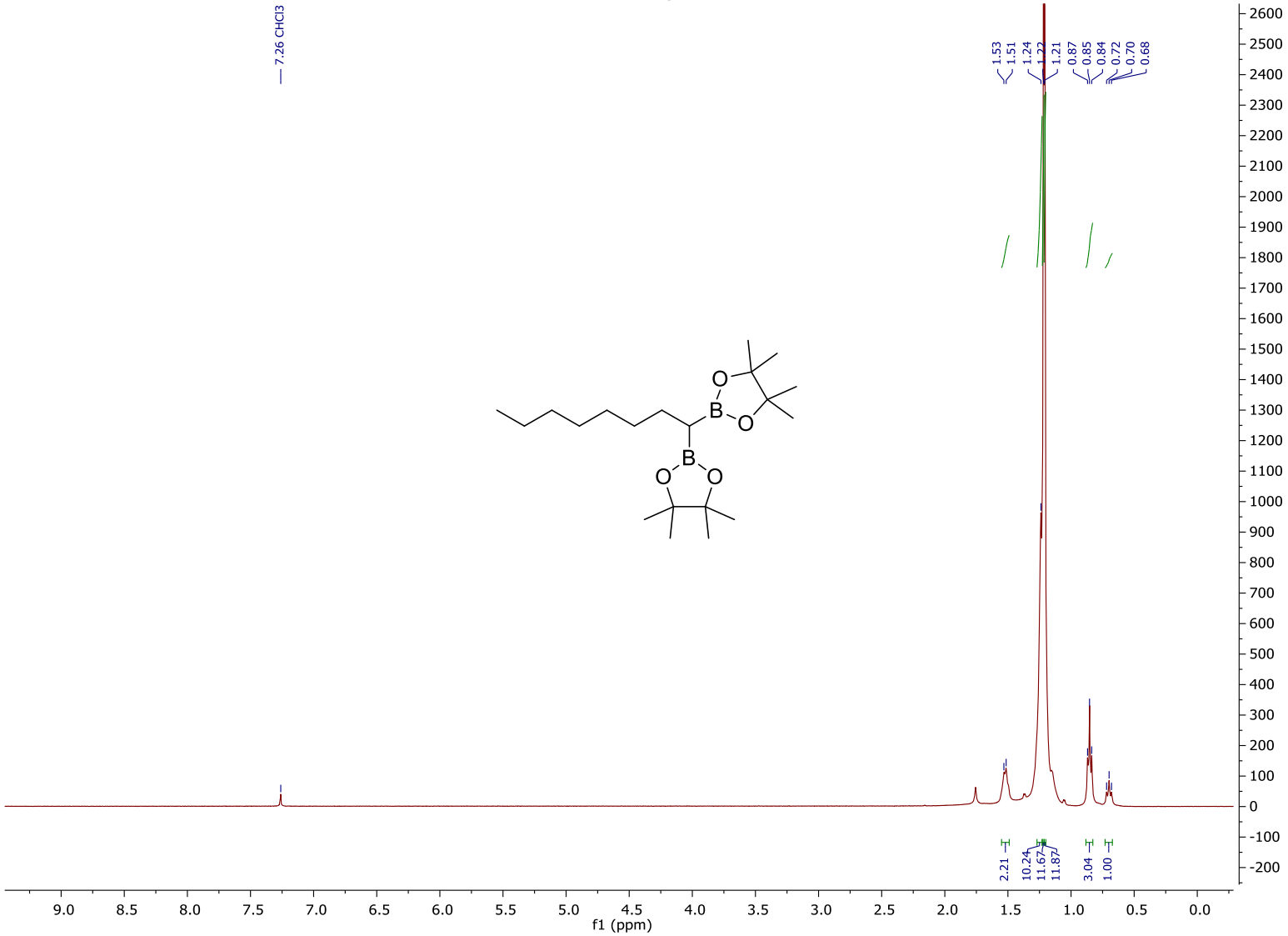
^{13}C NMR, compound 2k



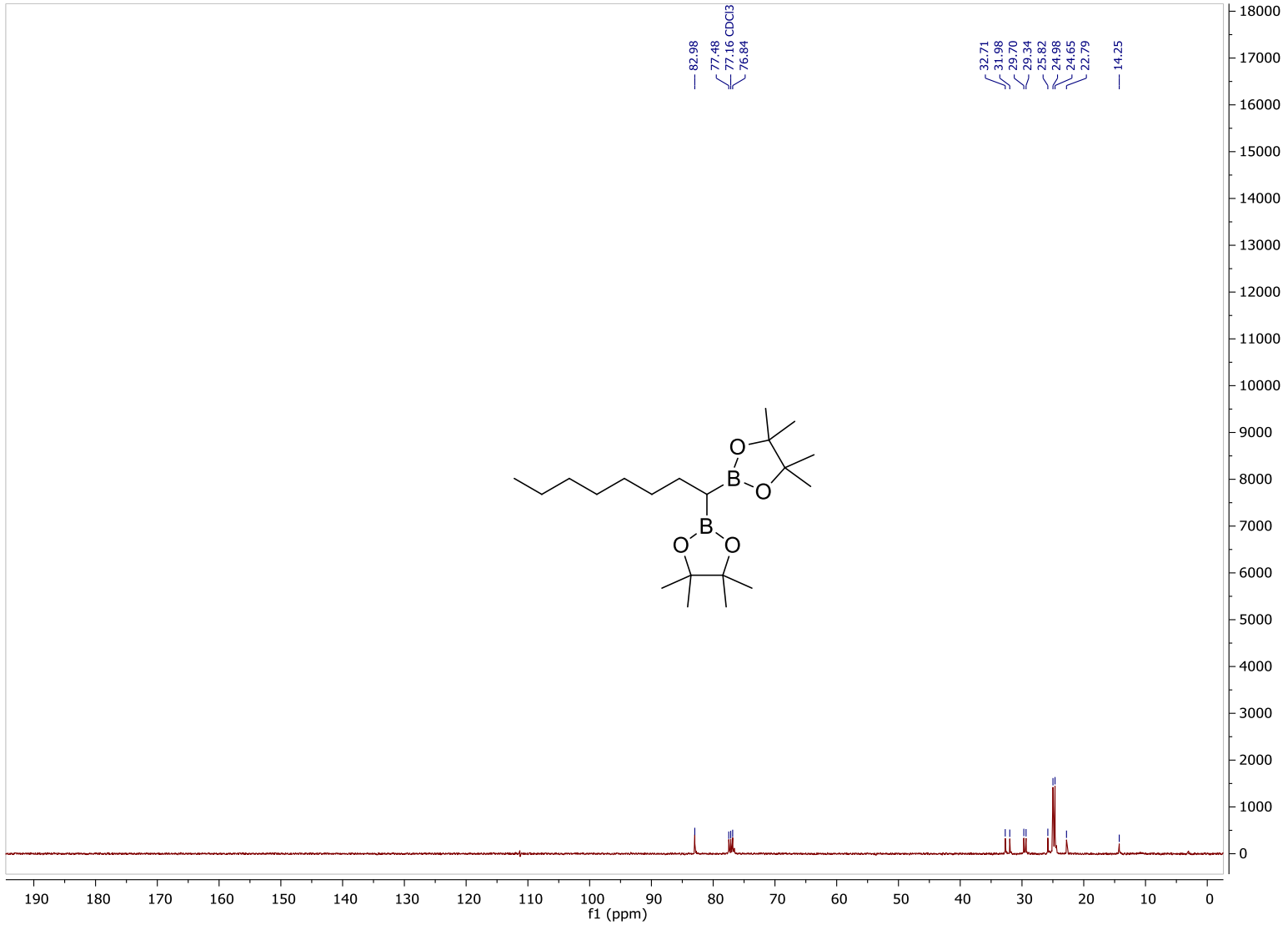
^{11}B NMR, compound 2k



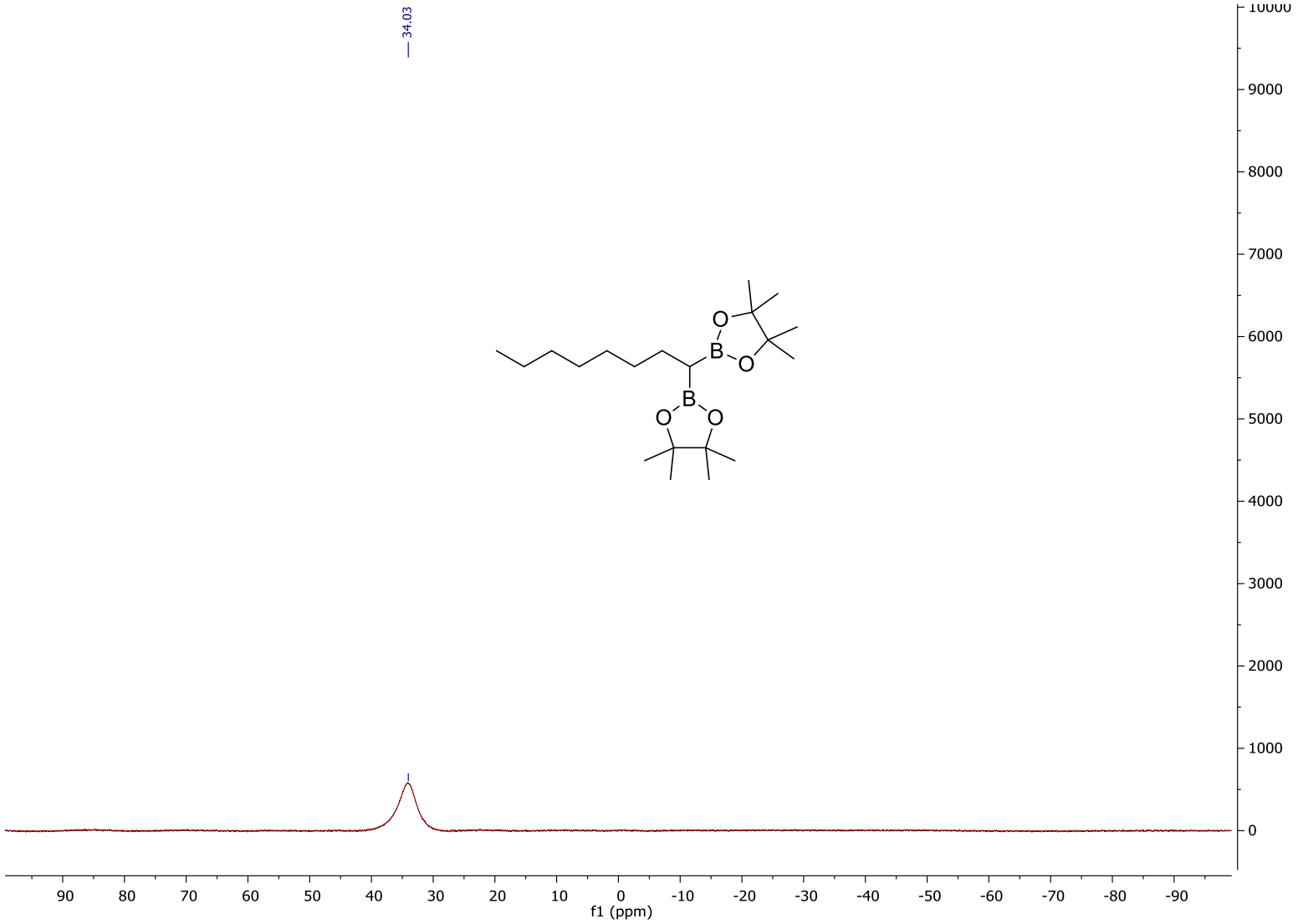
^{1}H NMR, compound 2l

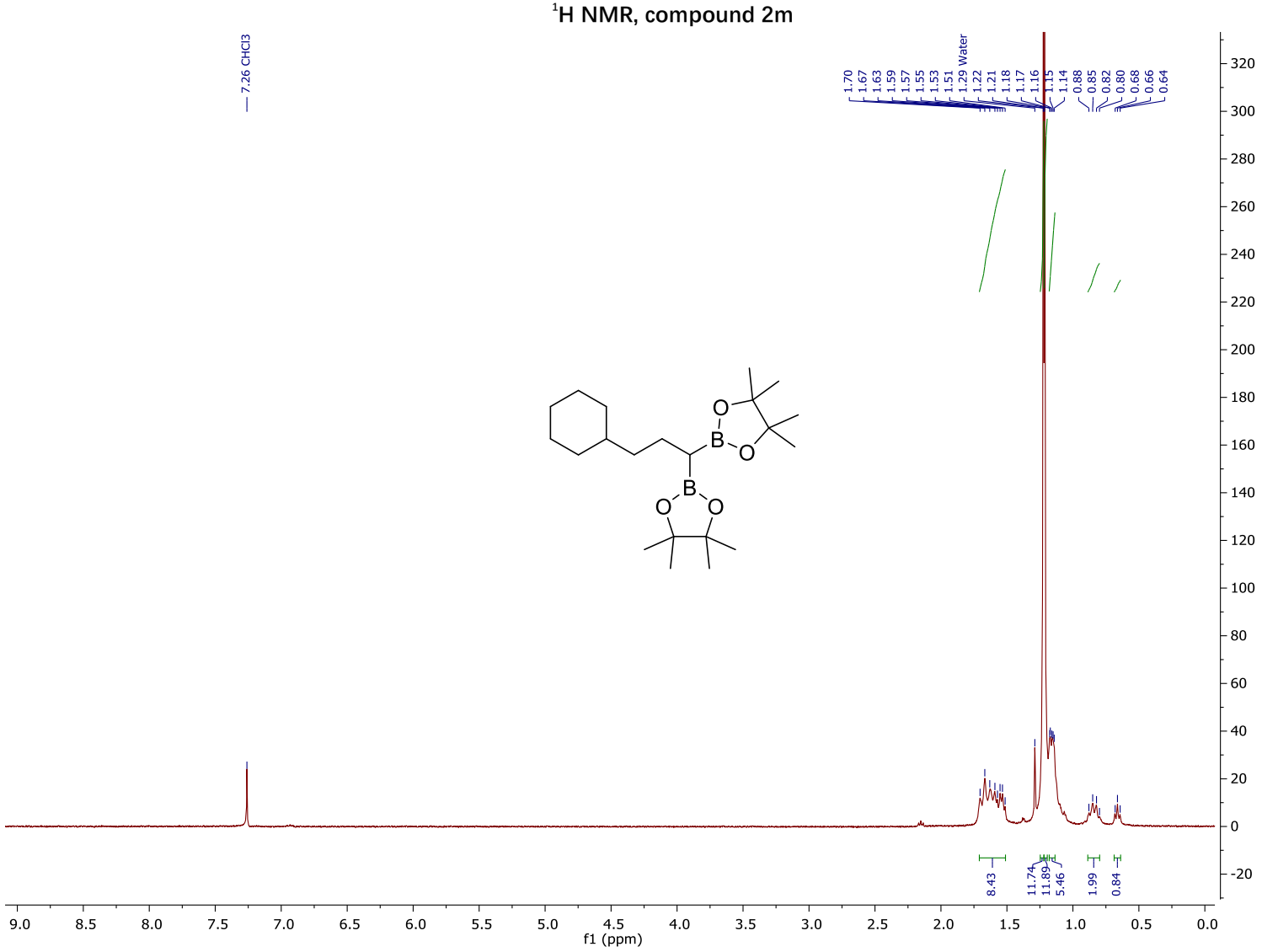


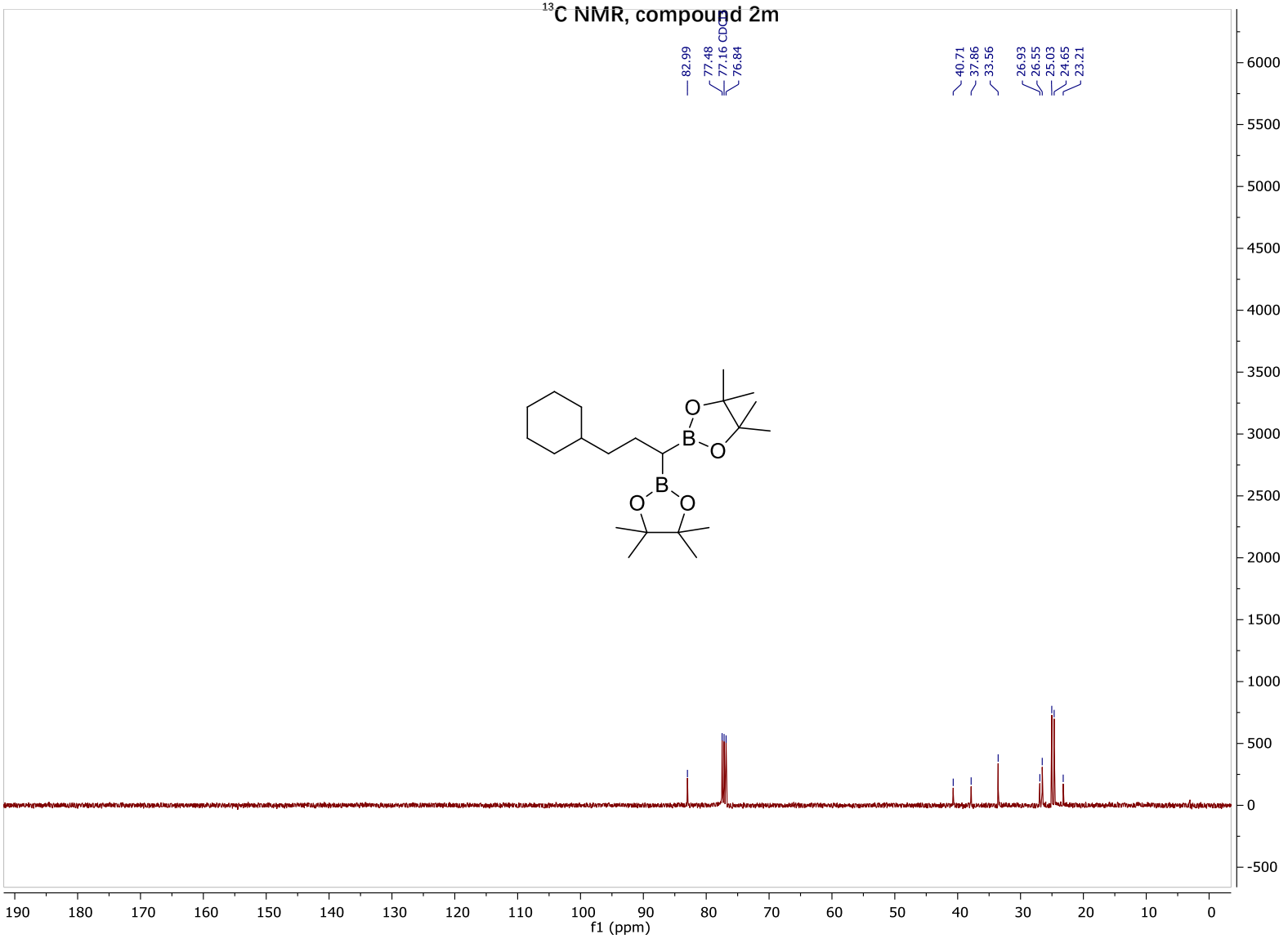
^{13}C NMR, compound 2l



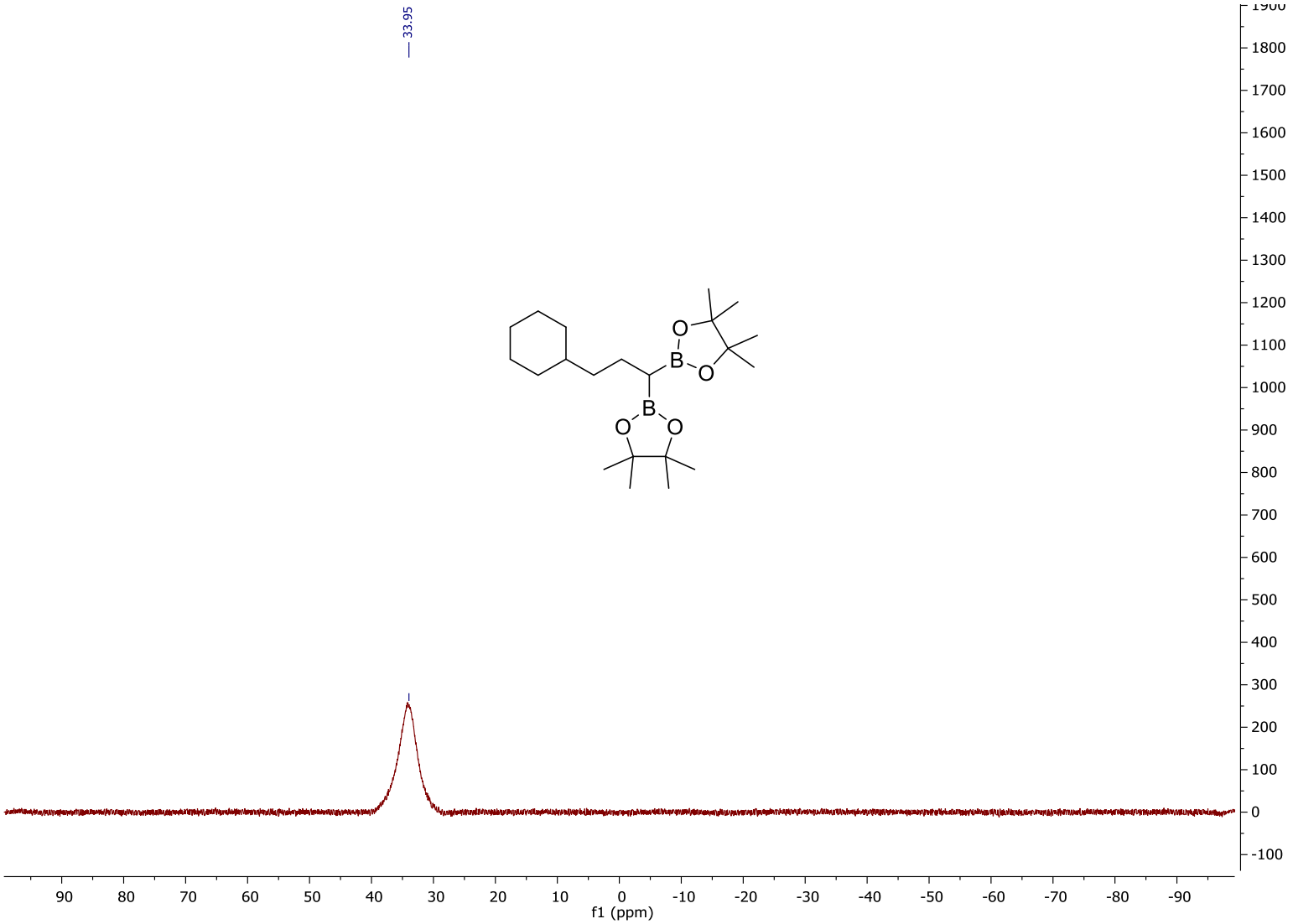
^{11}B NMR, compound 2l

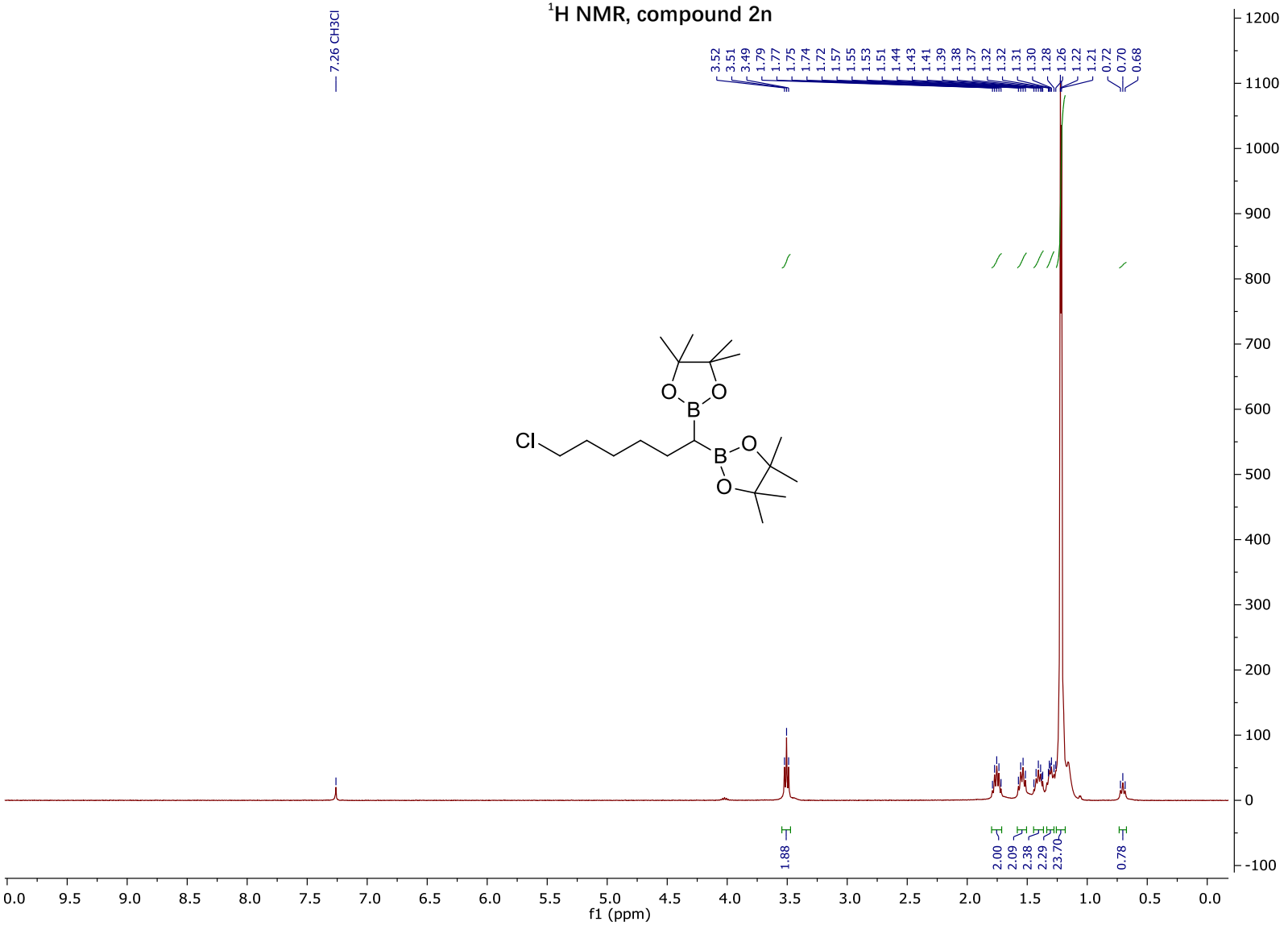



1H NMR, compound 2m
7.26 CHCl3
1.70
1.67
1.63
1.59
1.57
1.55
1.53
1.51
1.29 Water
1.22
1.21
1.18
1.17
1.16
1.15
1.14
0.88
0.85
0.82
0.80
0.68
0.66
0.64
O
B
O
B
O
O
8.43
11.74
11.89
5.46
1.99
0.84
f1 (ppm)

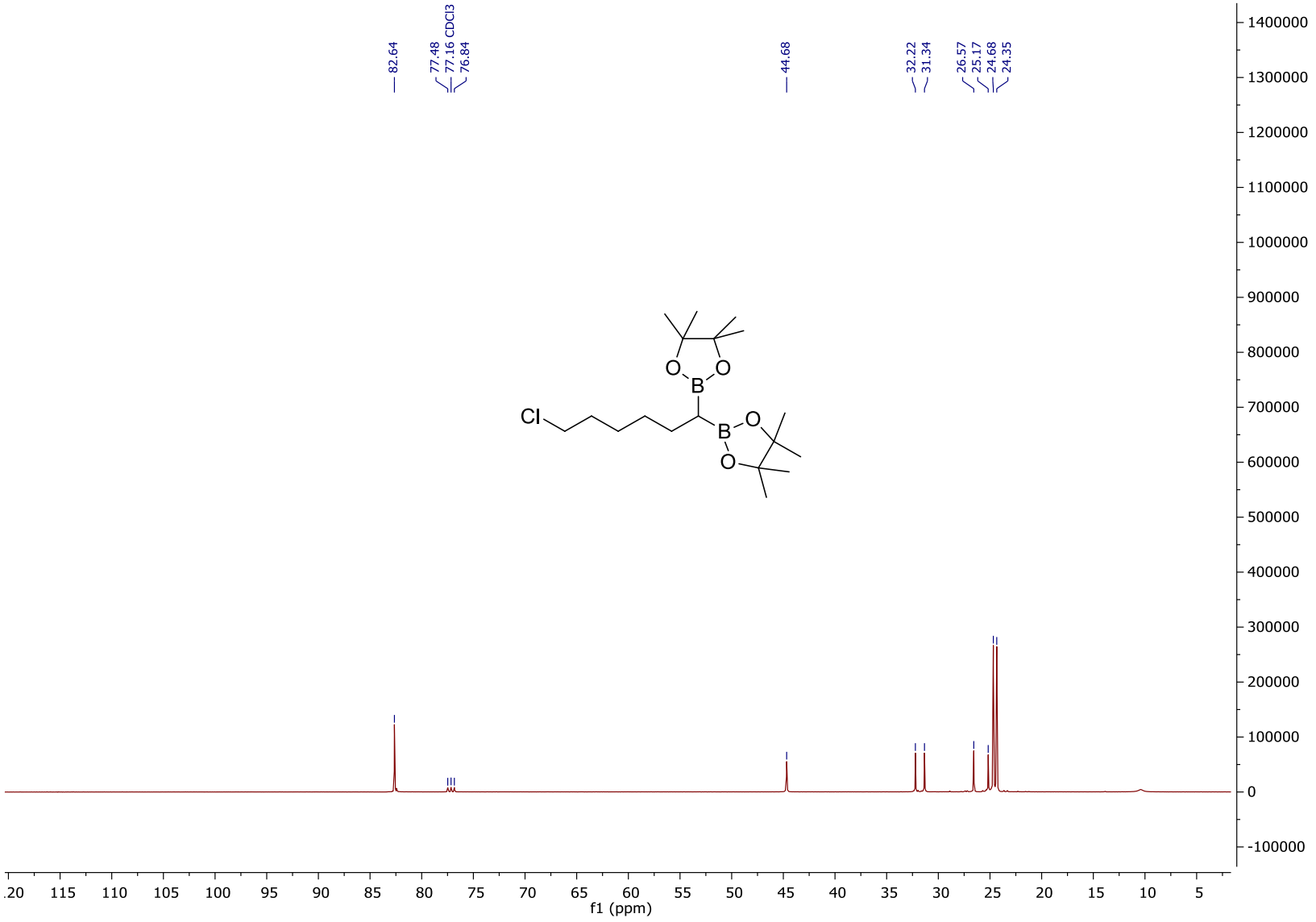

13C NMR, compound 2m
82.99
77.48
77.16 CDCl3
76.84
40.71
37.86
33.56
26.93
26.55
25.03
24.65
23.21
O
B
O
B
O
O
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{11}B NMR, compound 2m

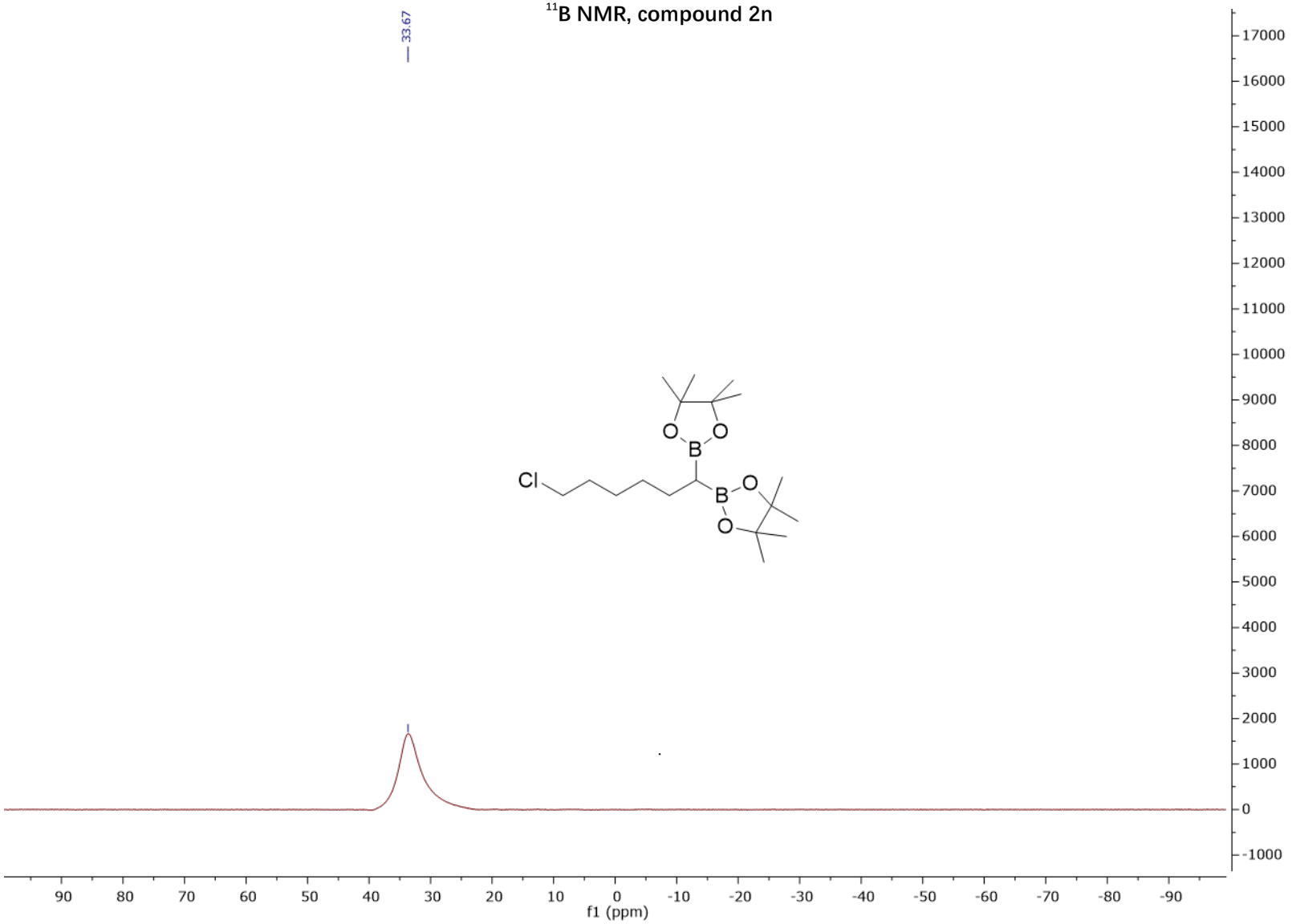



^{1}H NMR, compound 2n
7.26 CH3Cl
3.52
3.51
3.49
1.79
1.77
1.75
1.74
1.72
1.57
1.55
1.53
1.51
1.44
1.43
1.41
1.39
1.38
1.37
1.32
1.32
1.31
1.30
1.28
1.26
1.22
1.21
0.72
0.70
0.68
Cl
B
O
O
B
O
O
1.88
2.00
2.09
2.38
2.29
23.70
0.78
f1 (ppm)

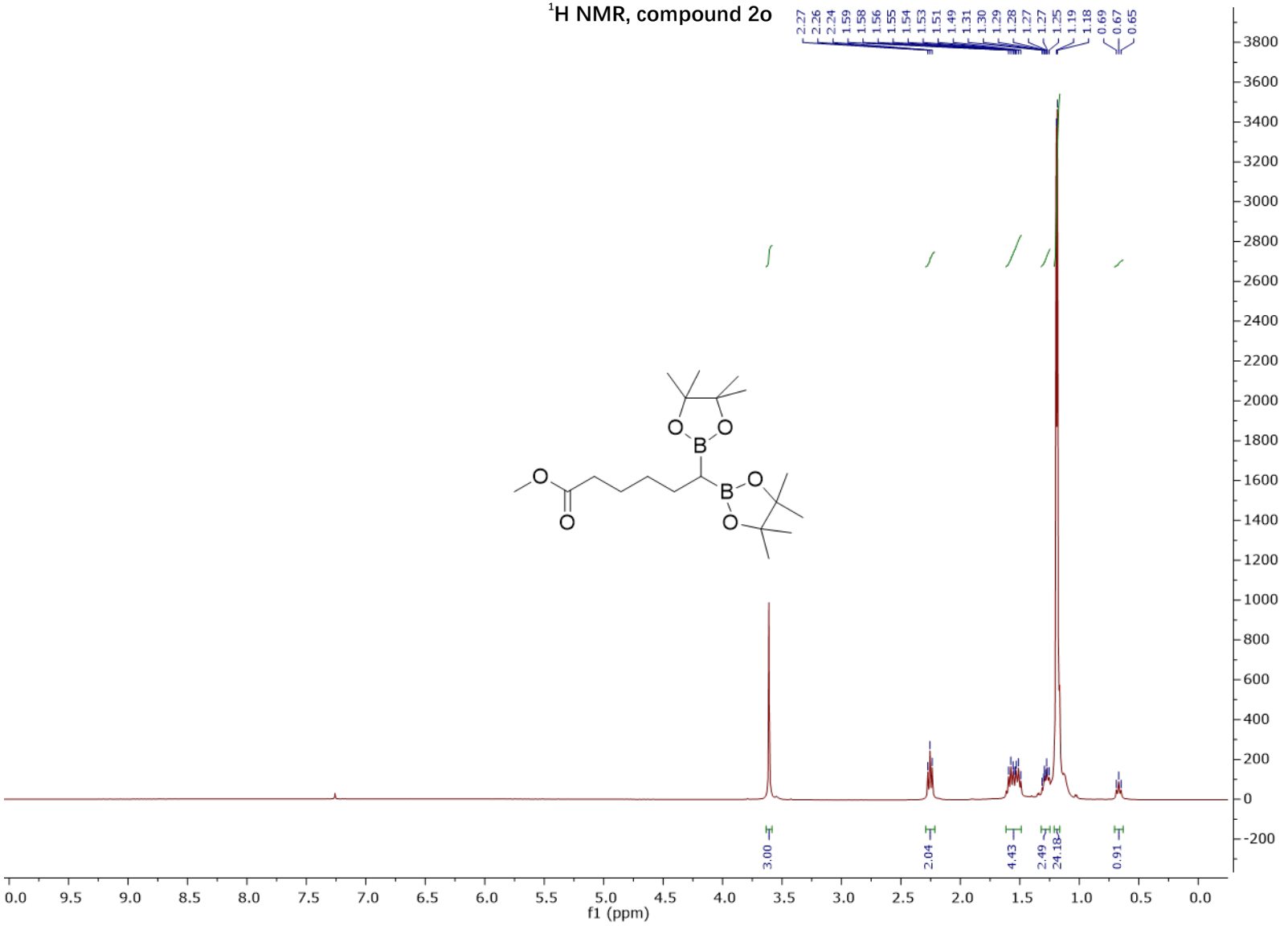
^{13}C NMR, compound 2n



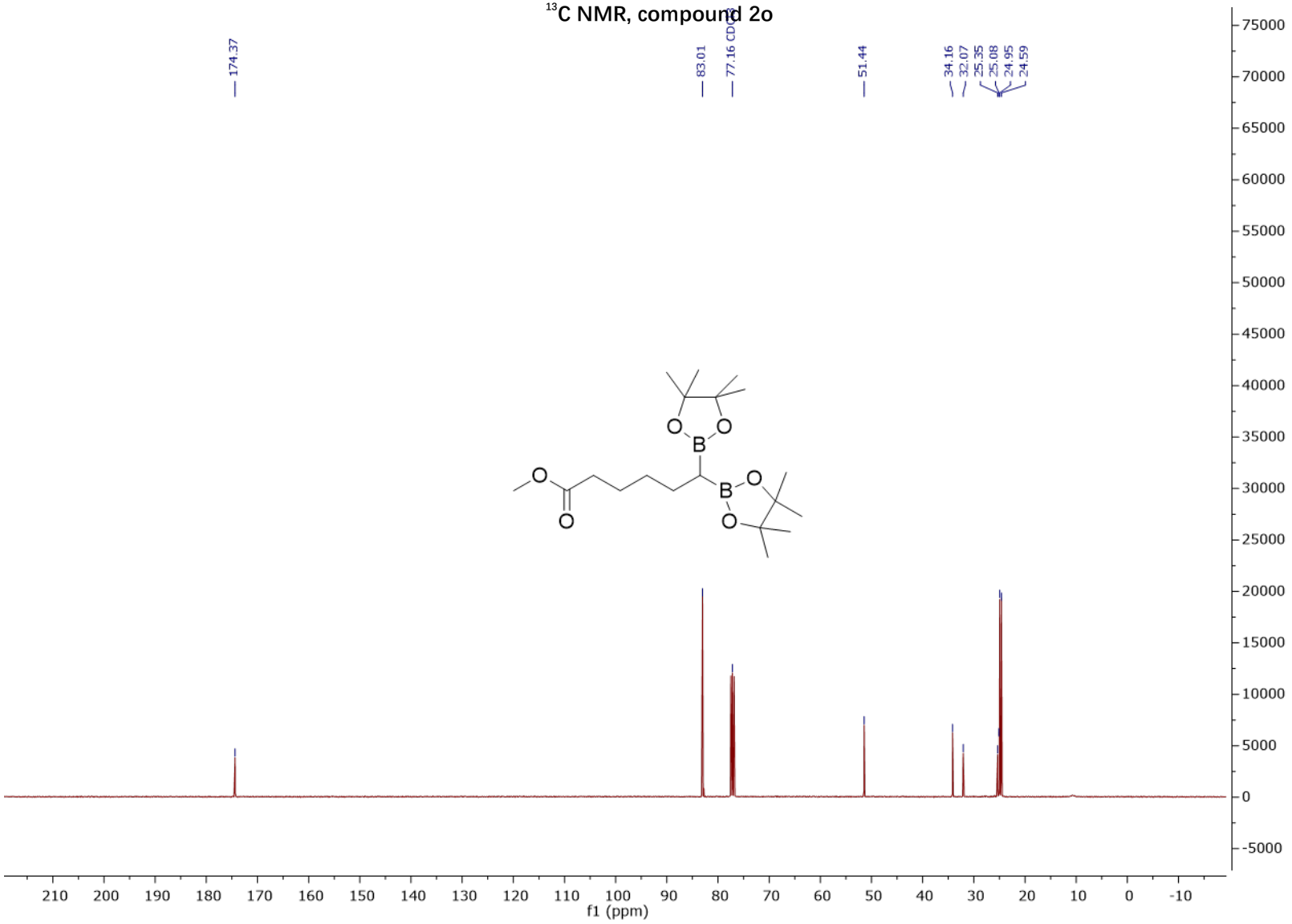
^{11}B NMR, compound 2n



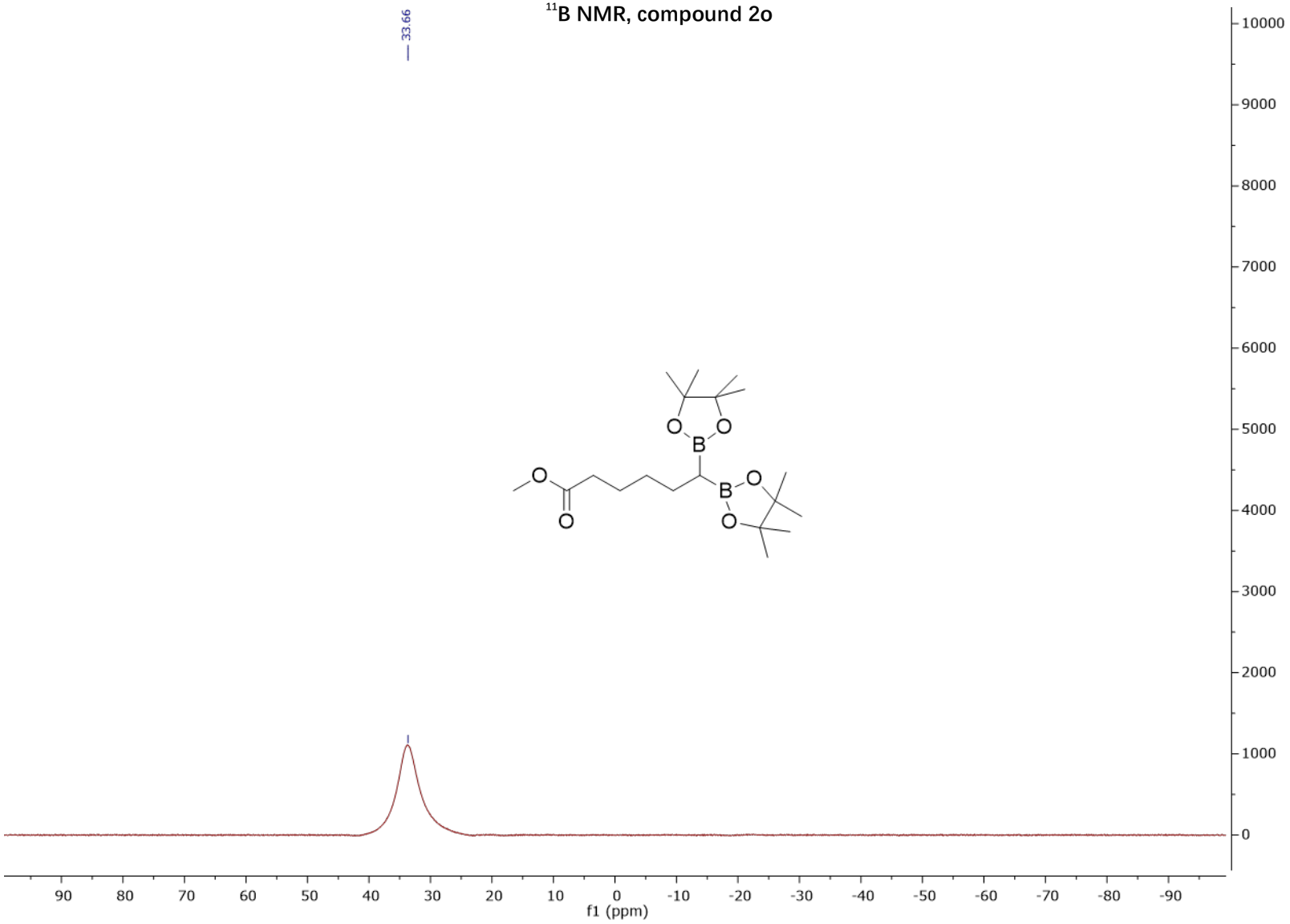
^{1}H NMR, compound 2o

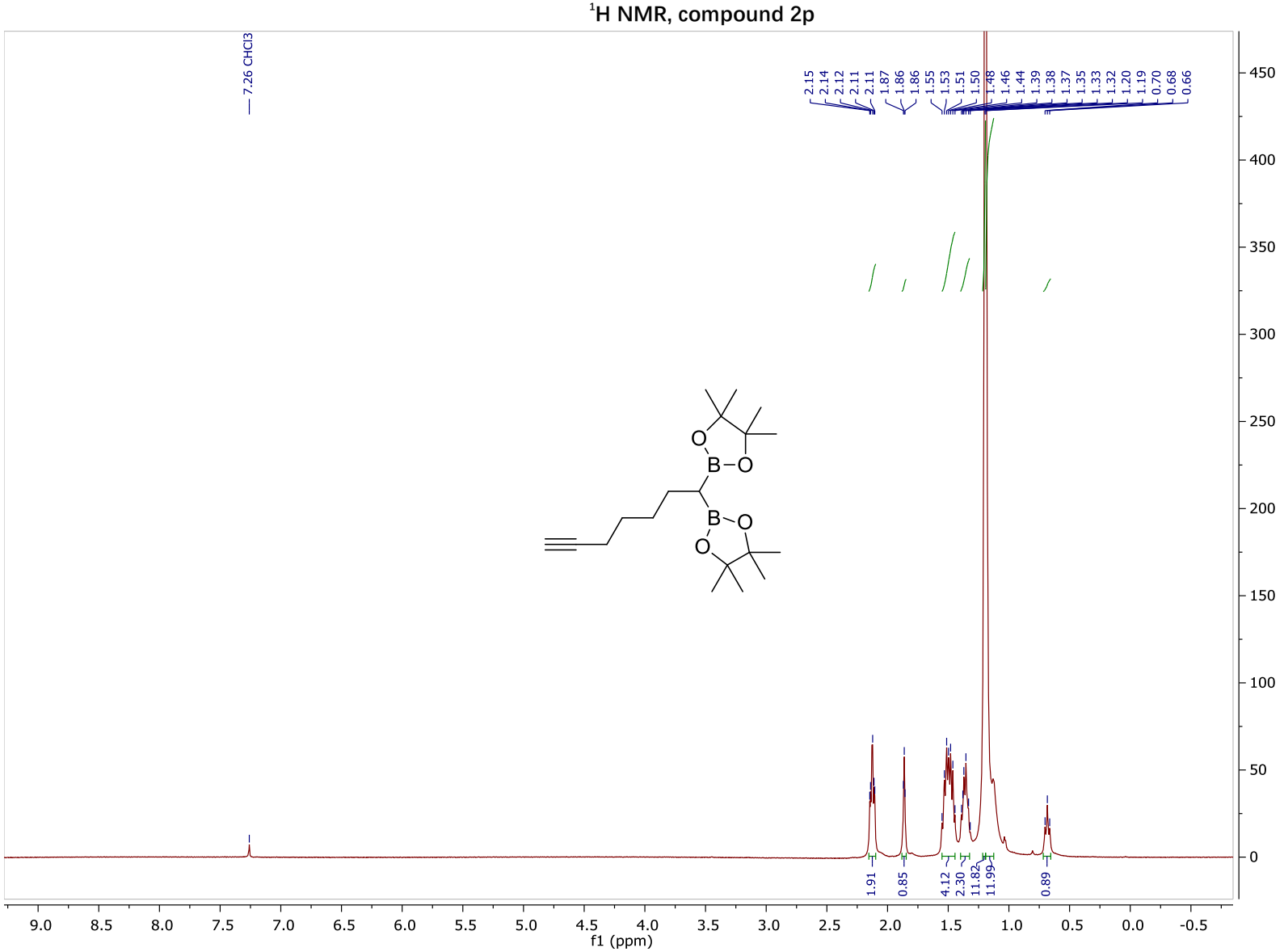


^{13}C NMR, compound 2o

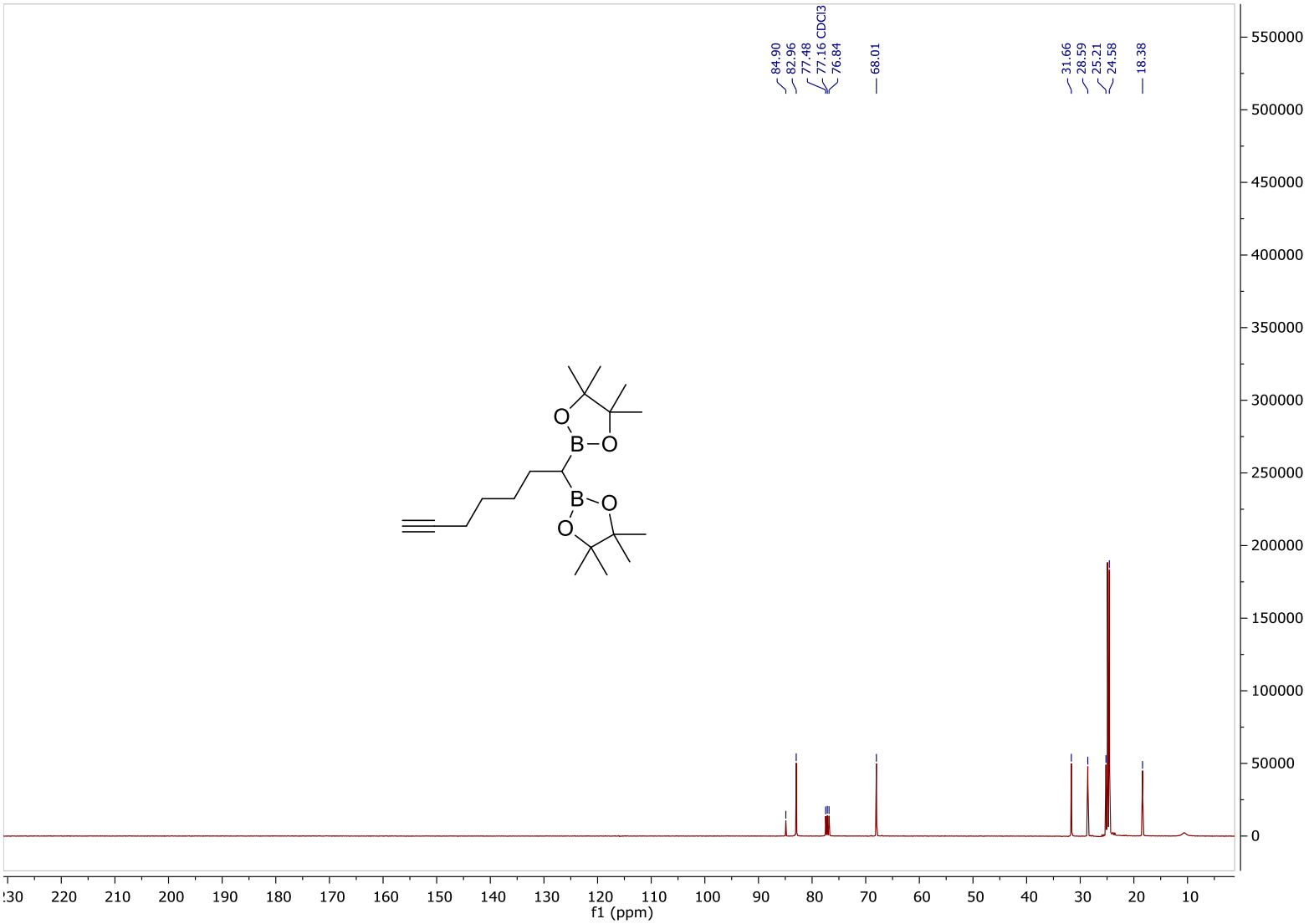


^{11}B NMR, compound 2o

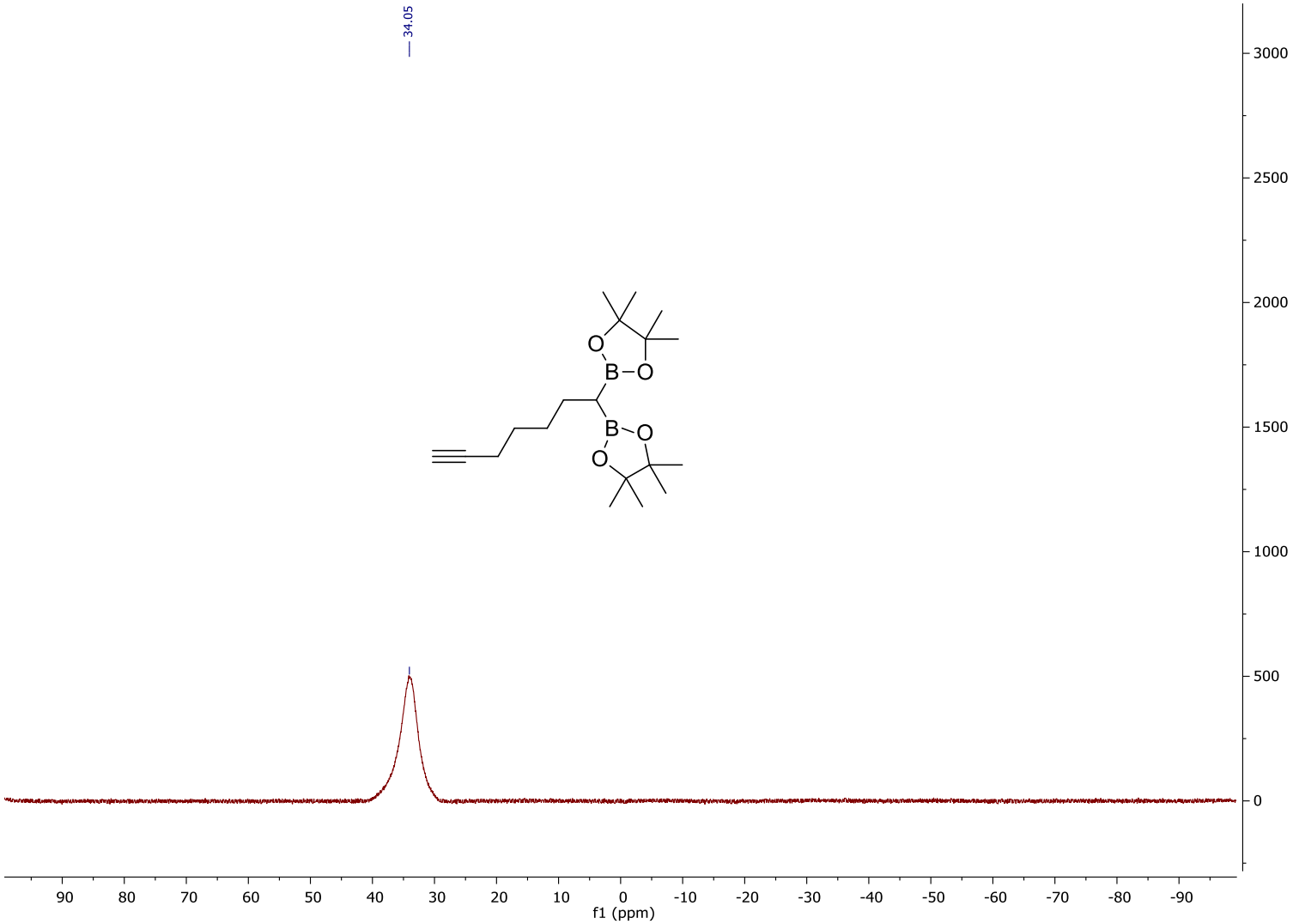



¹H NMR, compound 2p
7.26 CHCl3
2.15
2.14
2.12
2.11
2.11
1.87
1.86
1.86
1.55
1.53
1.51
1.50
1.48
1.46
1.44
1.39
1.38
1.37
1.35
1.33
1.32
1.20
1.19
0.70
0.68
0.66
O
B–O
B–O
O
1.91
0.85
4.12
2.30
11.82
11.99
0.89
f1 (ppm)

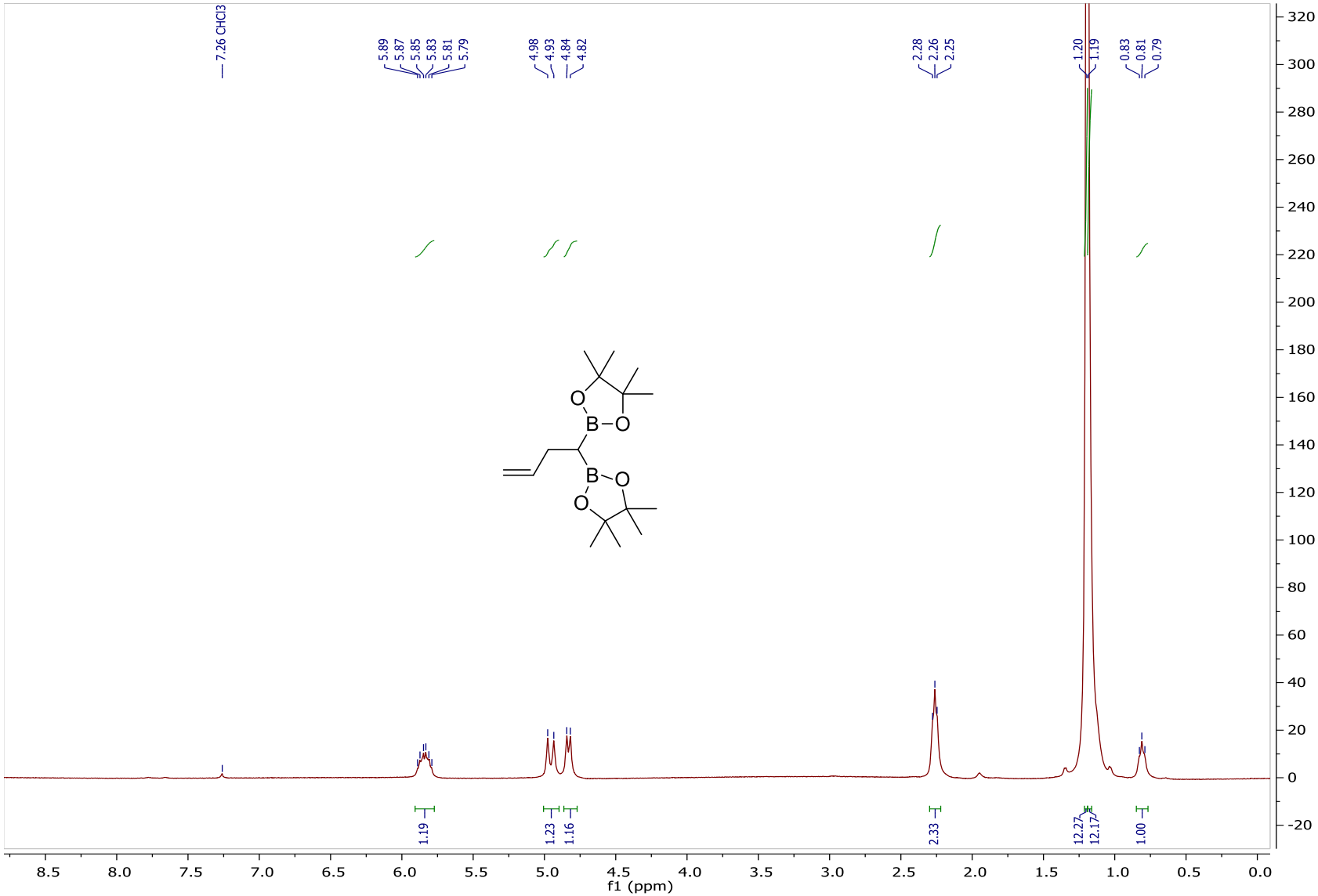
^{13}C NMR, compound 2p



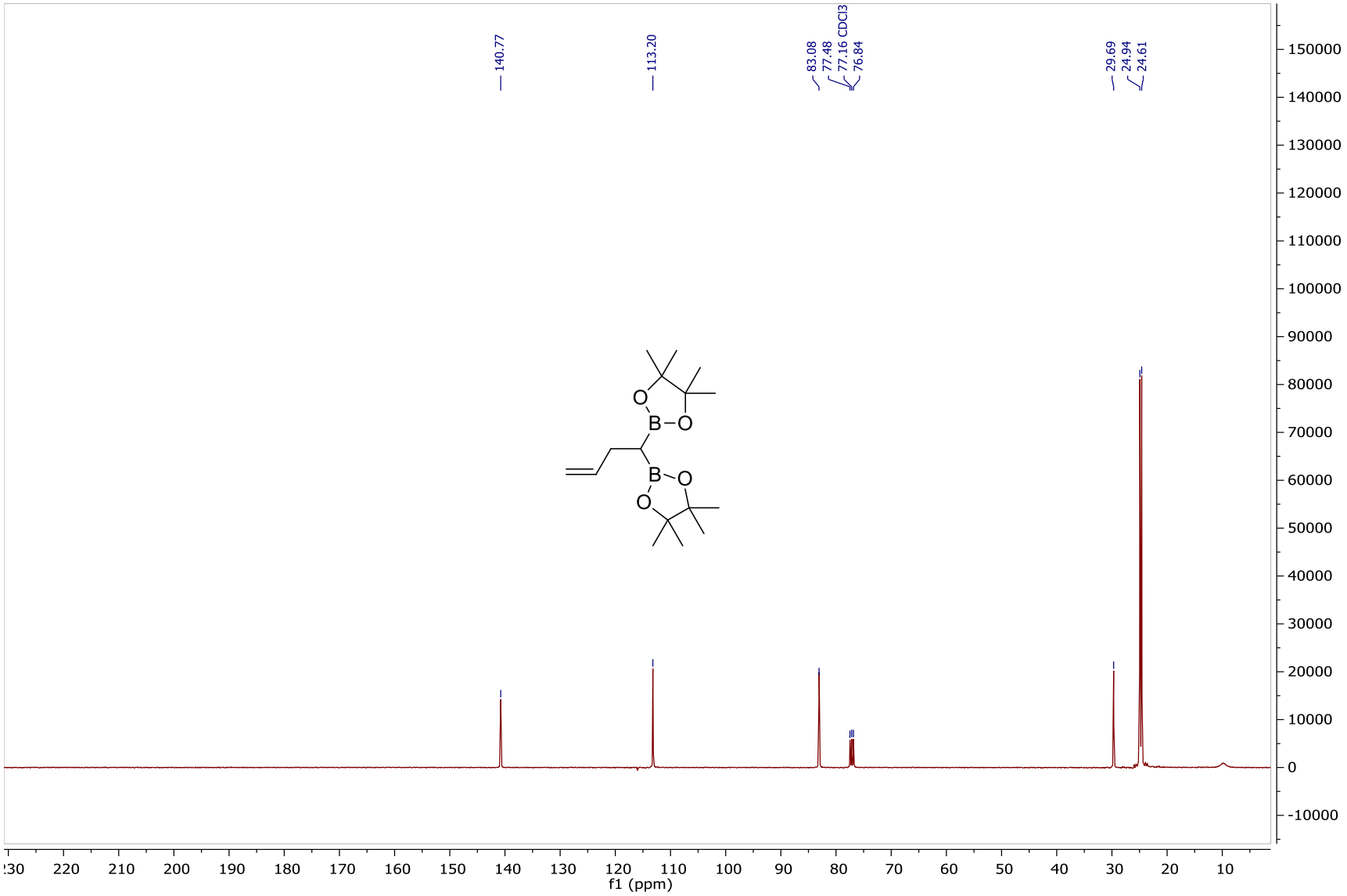
^{11}B NMR, compound 2p



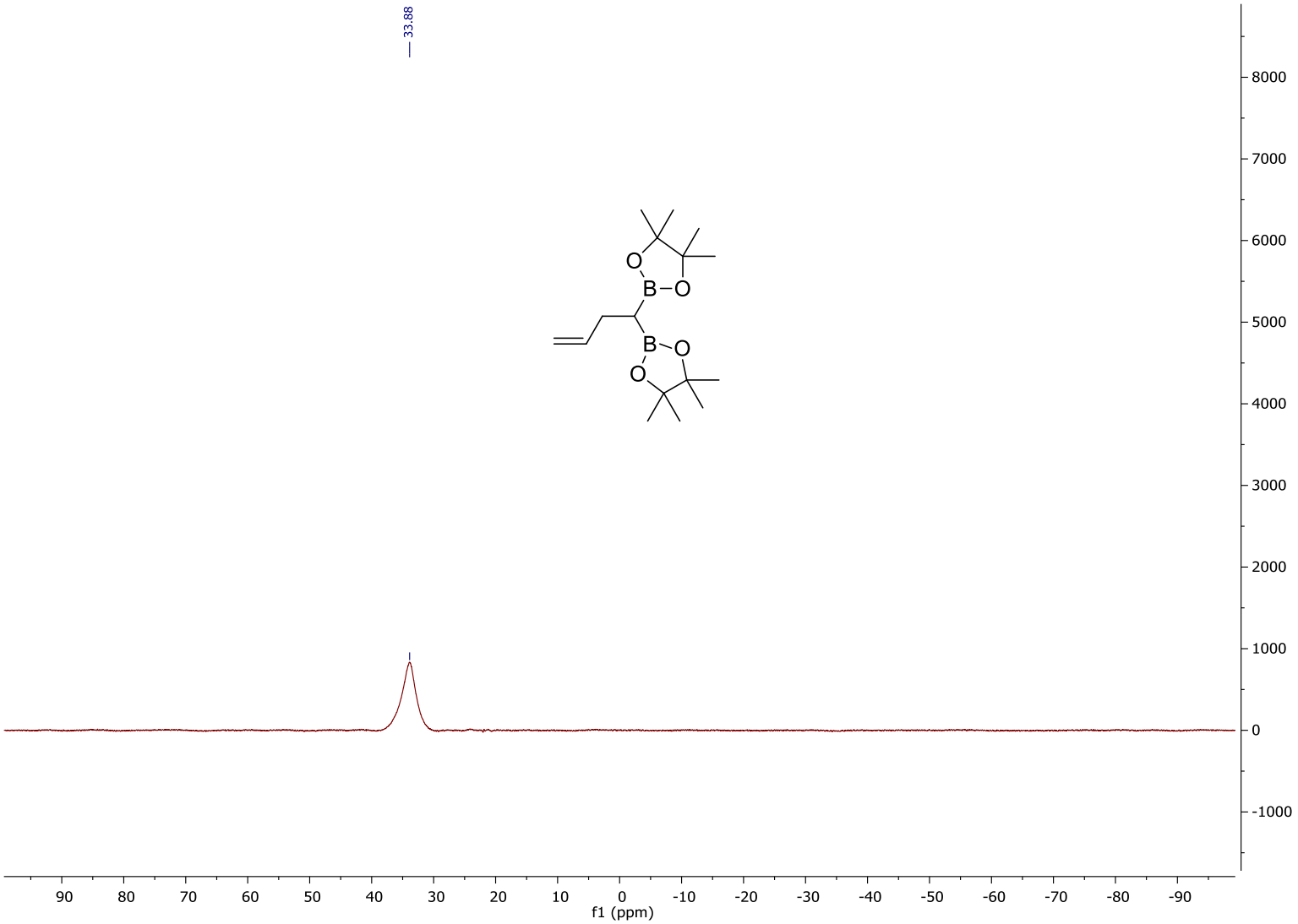
^{1}H NMR, compound 2q



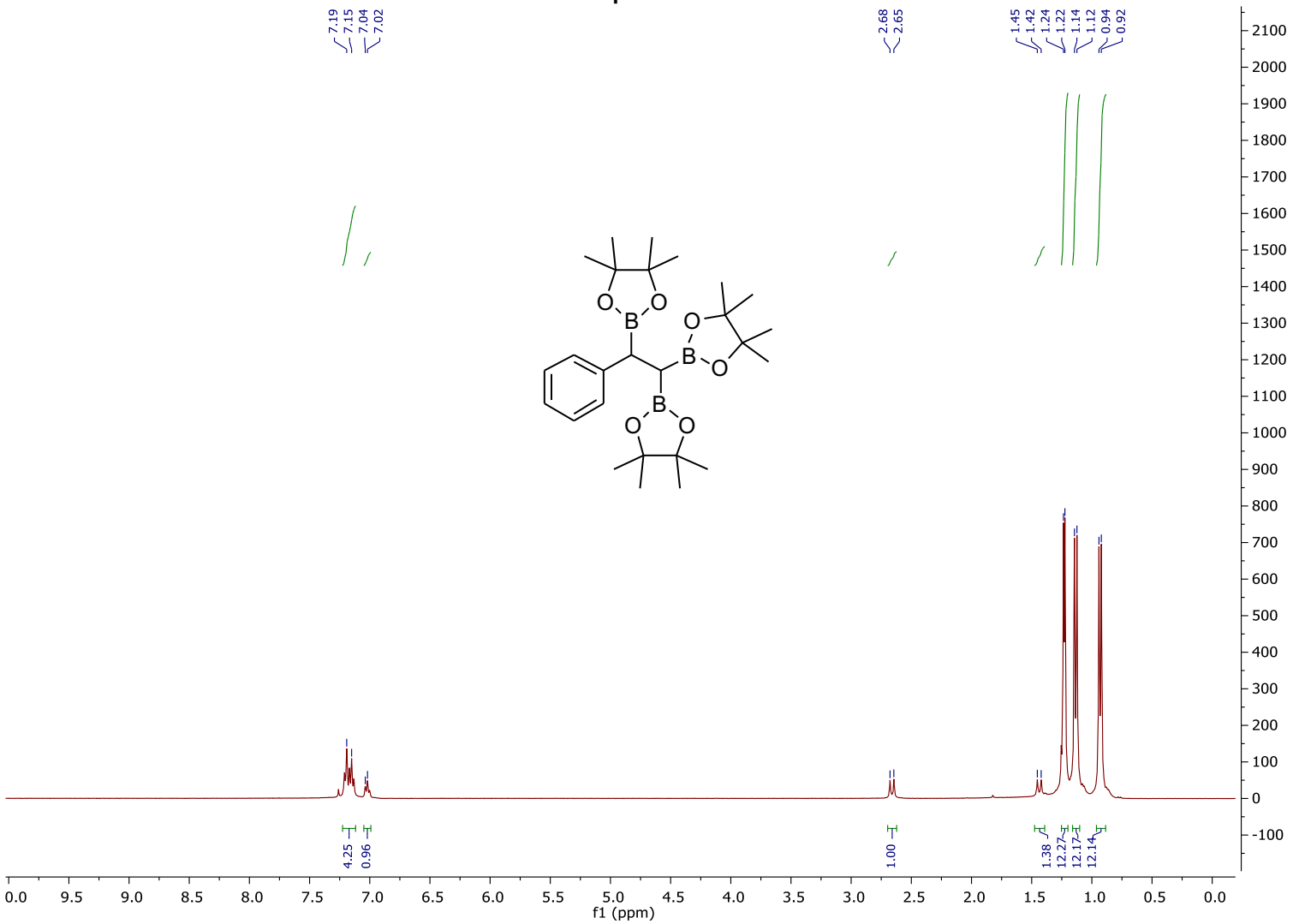
^{13}C NMR, compound 2q



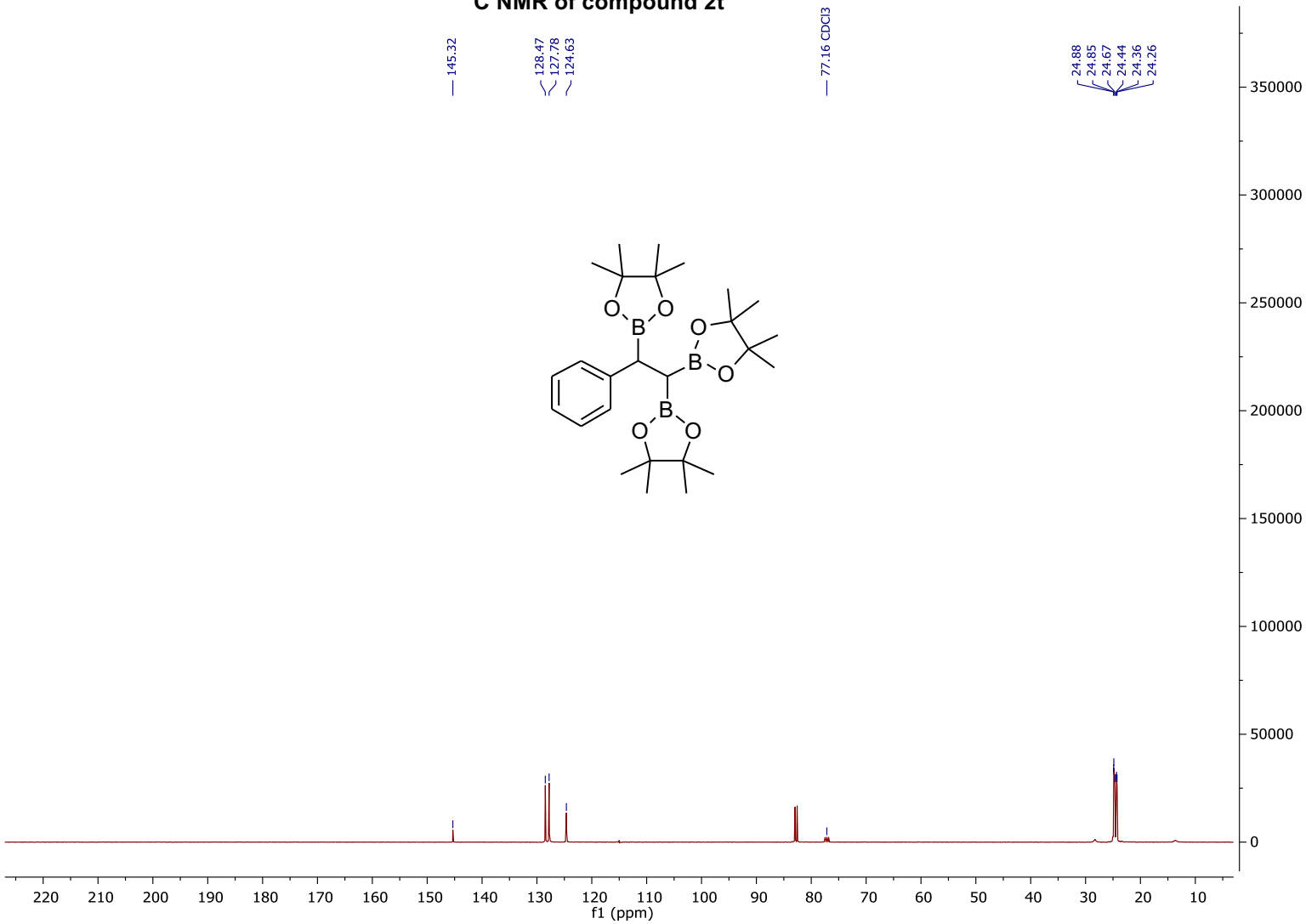
^{11}B NMR, compound 2q



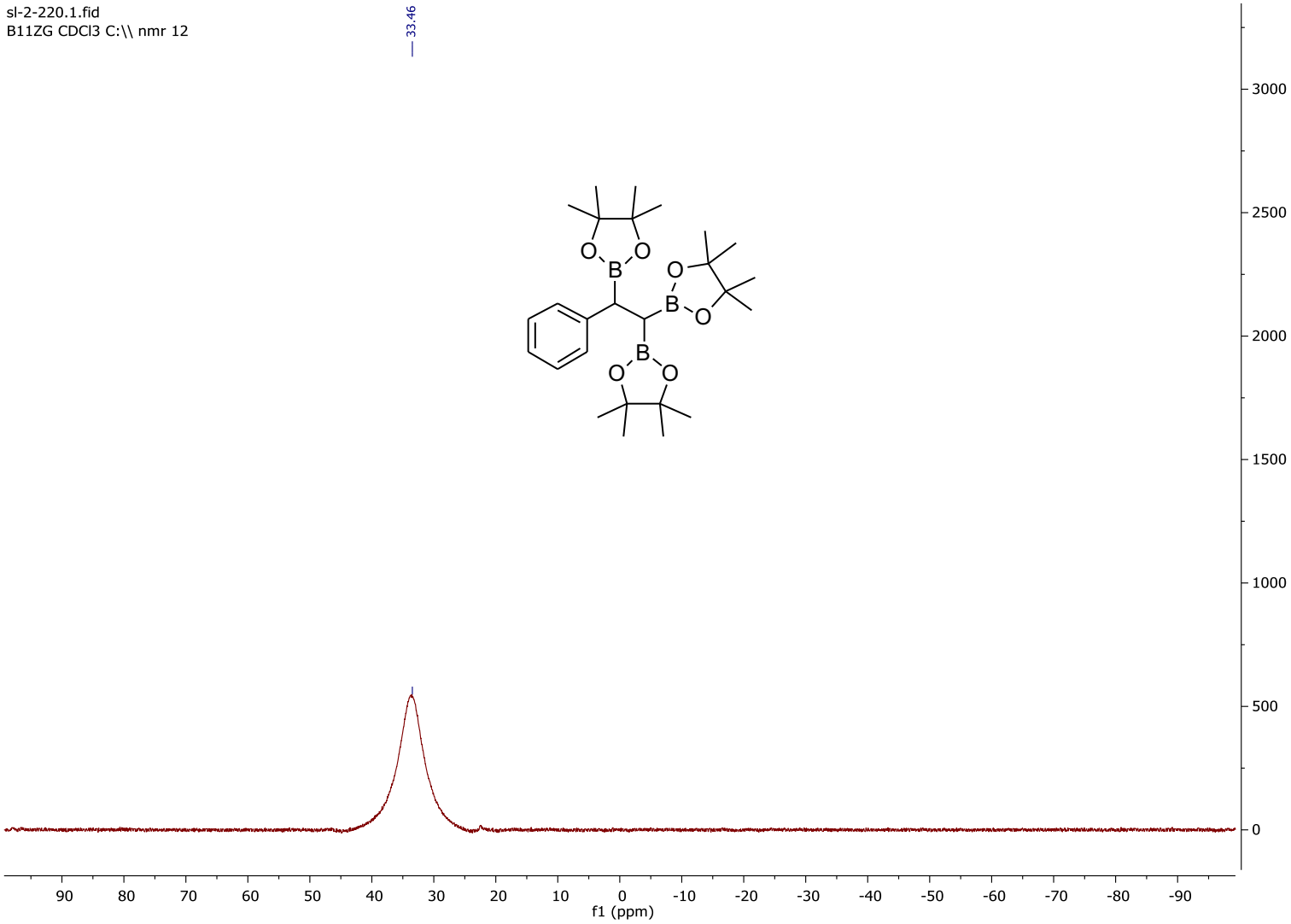
^{1}H NMR of compound 2t



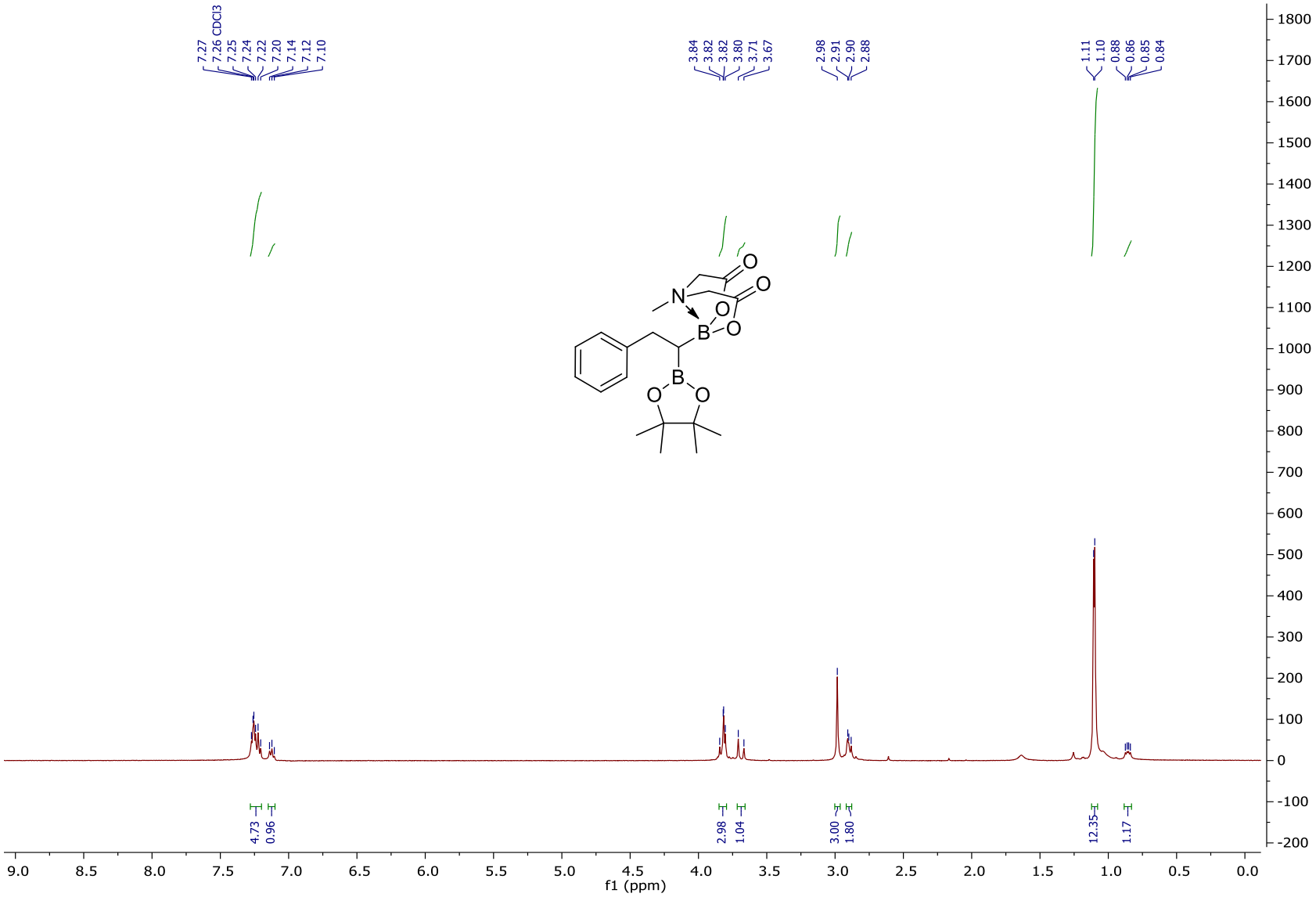
^{13}C NMR of compound 2t



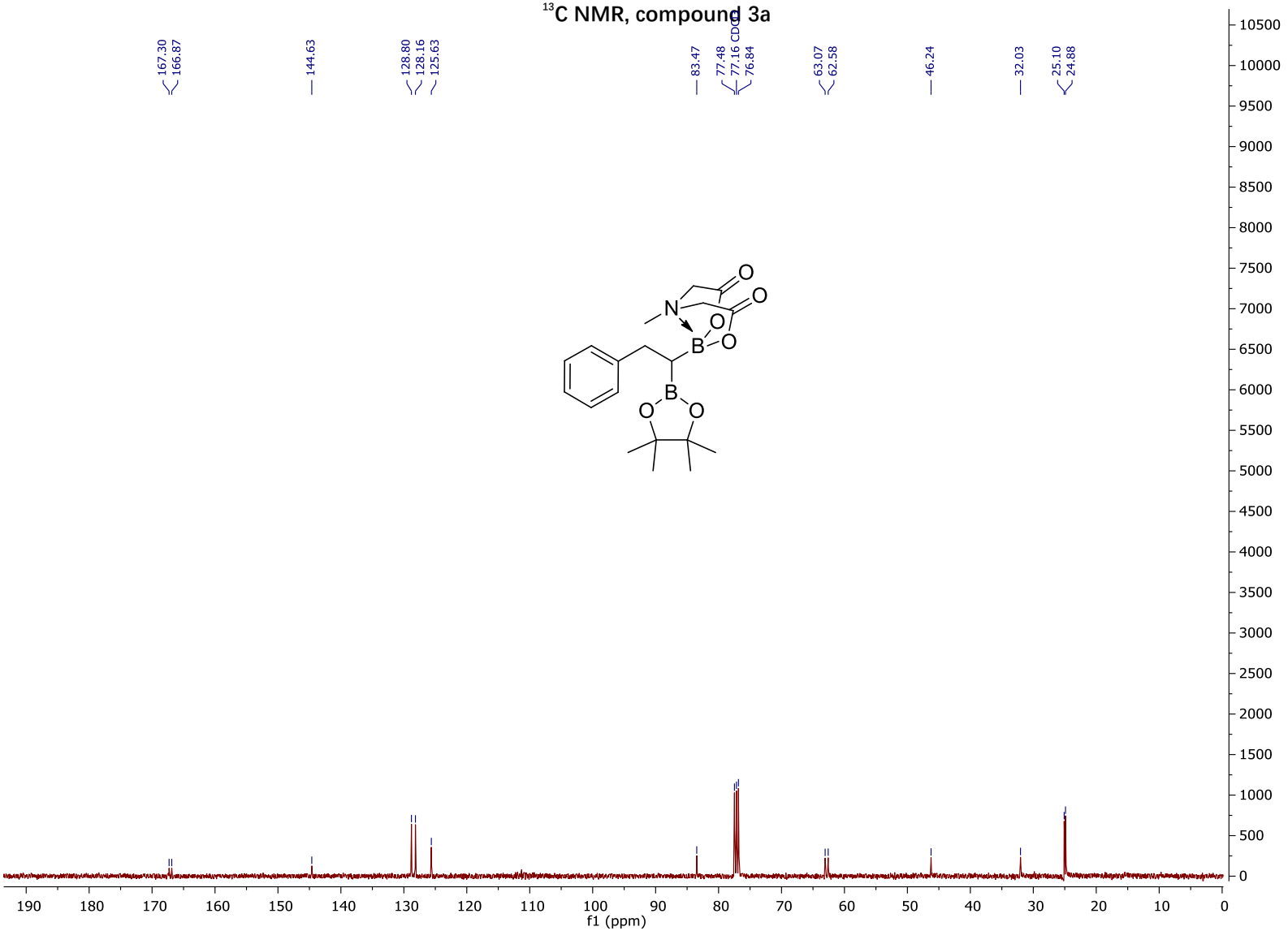
^{11}B NMR of compound 2t



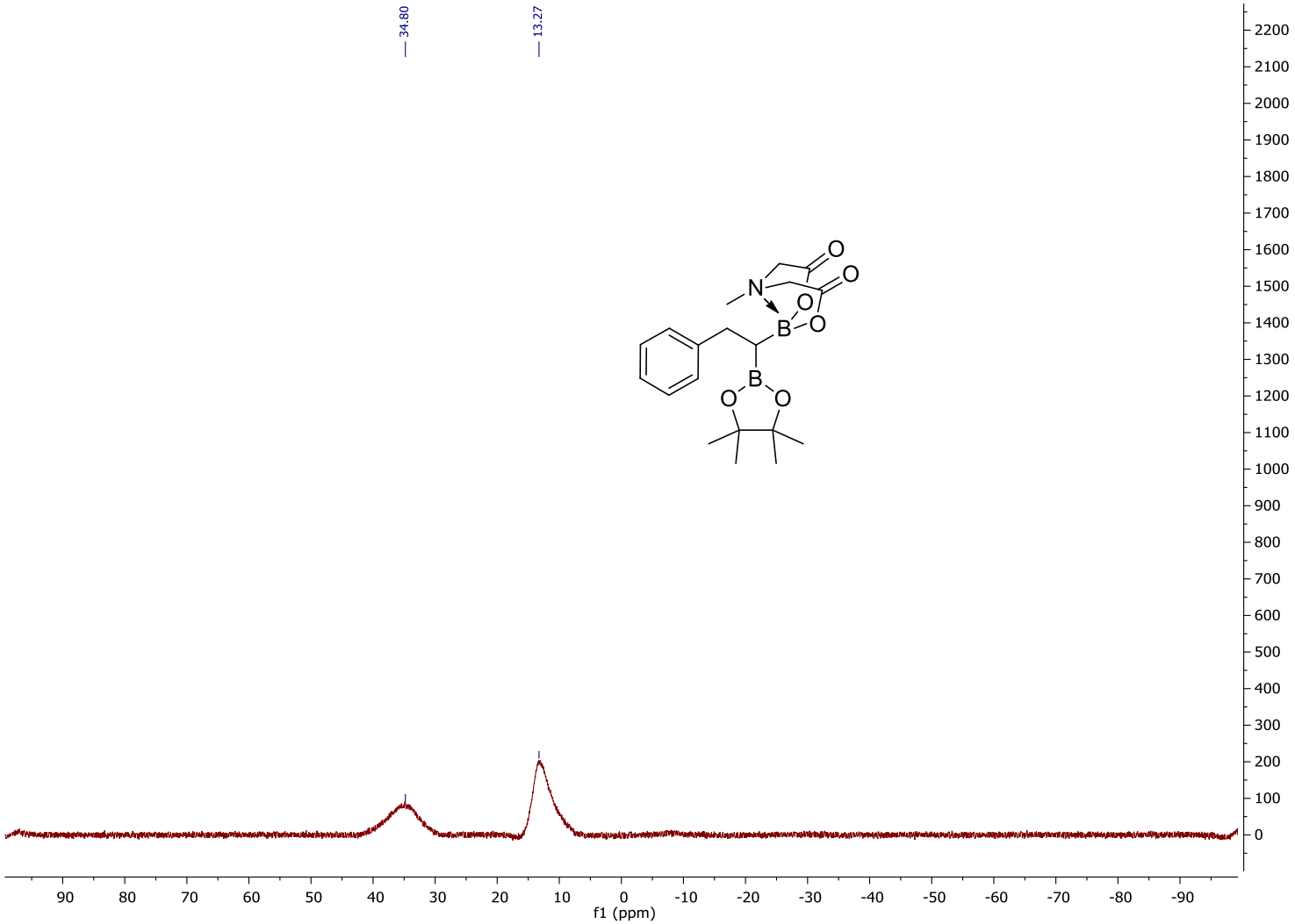
^{1}H NMR, compound 3a



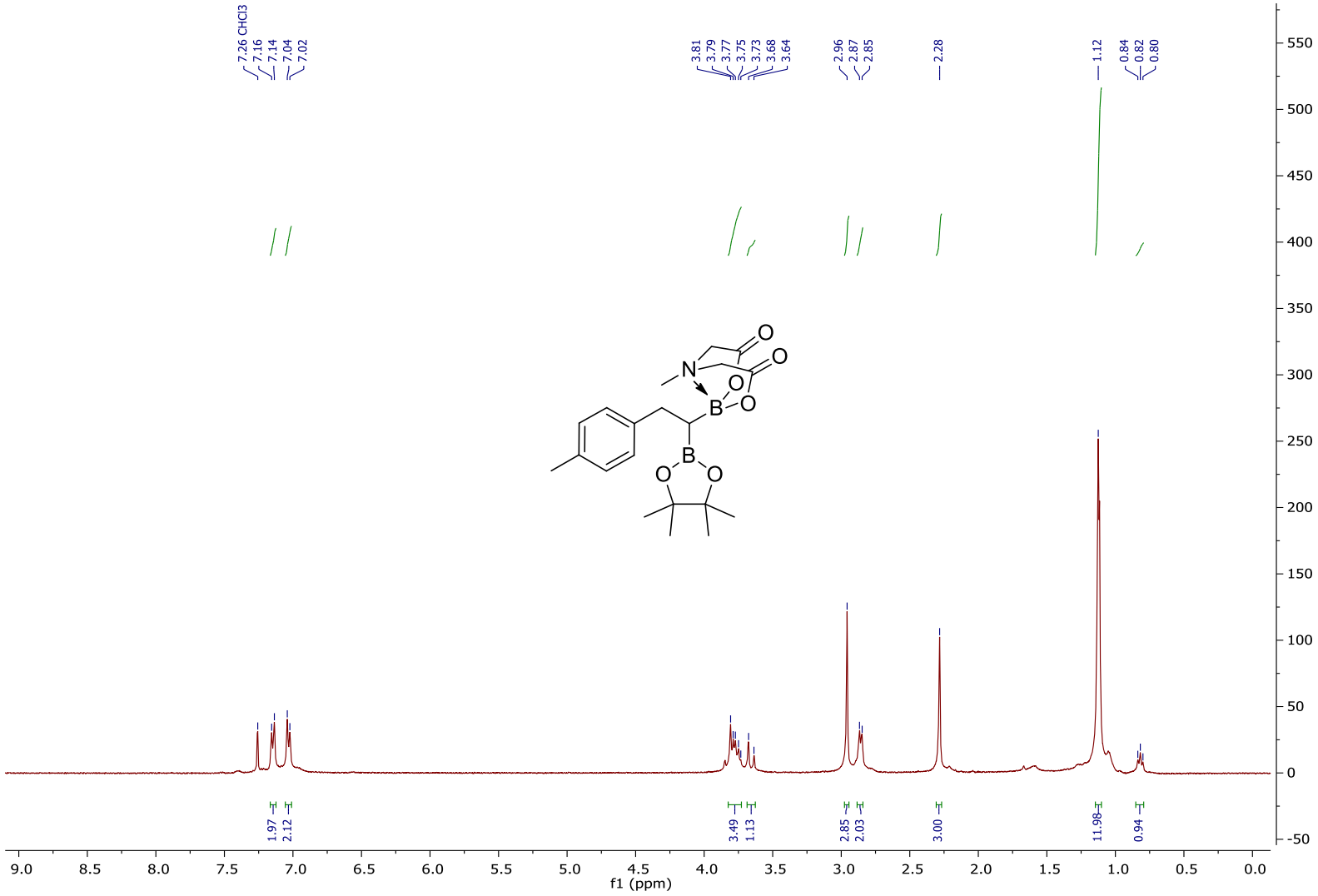
^{13}C NMR, compound 3a

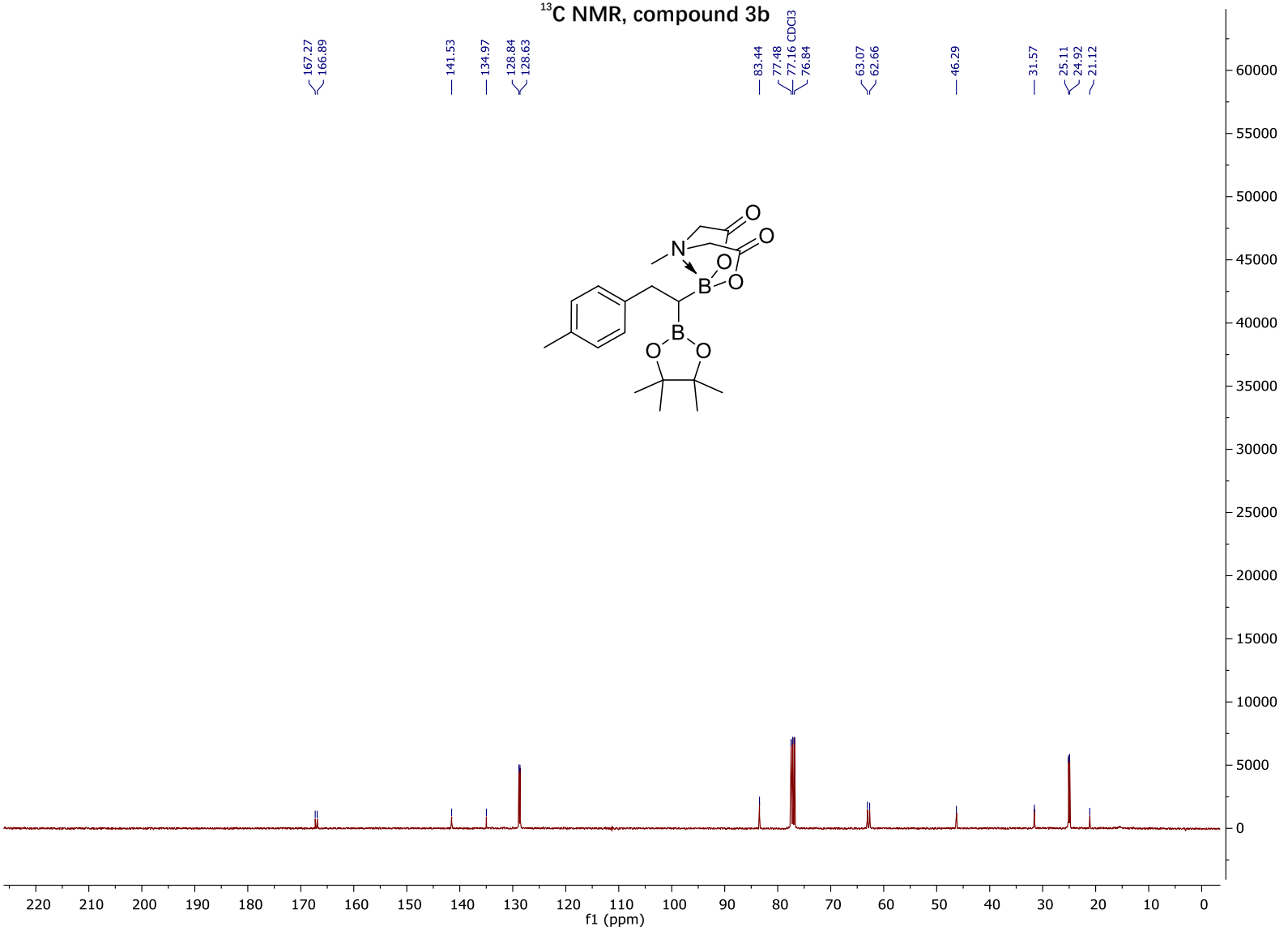


^{11}B NMR, compound 3a

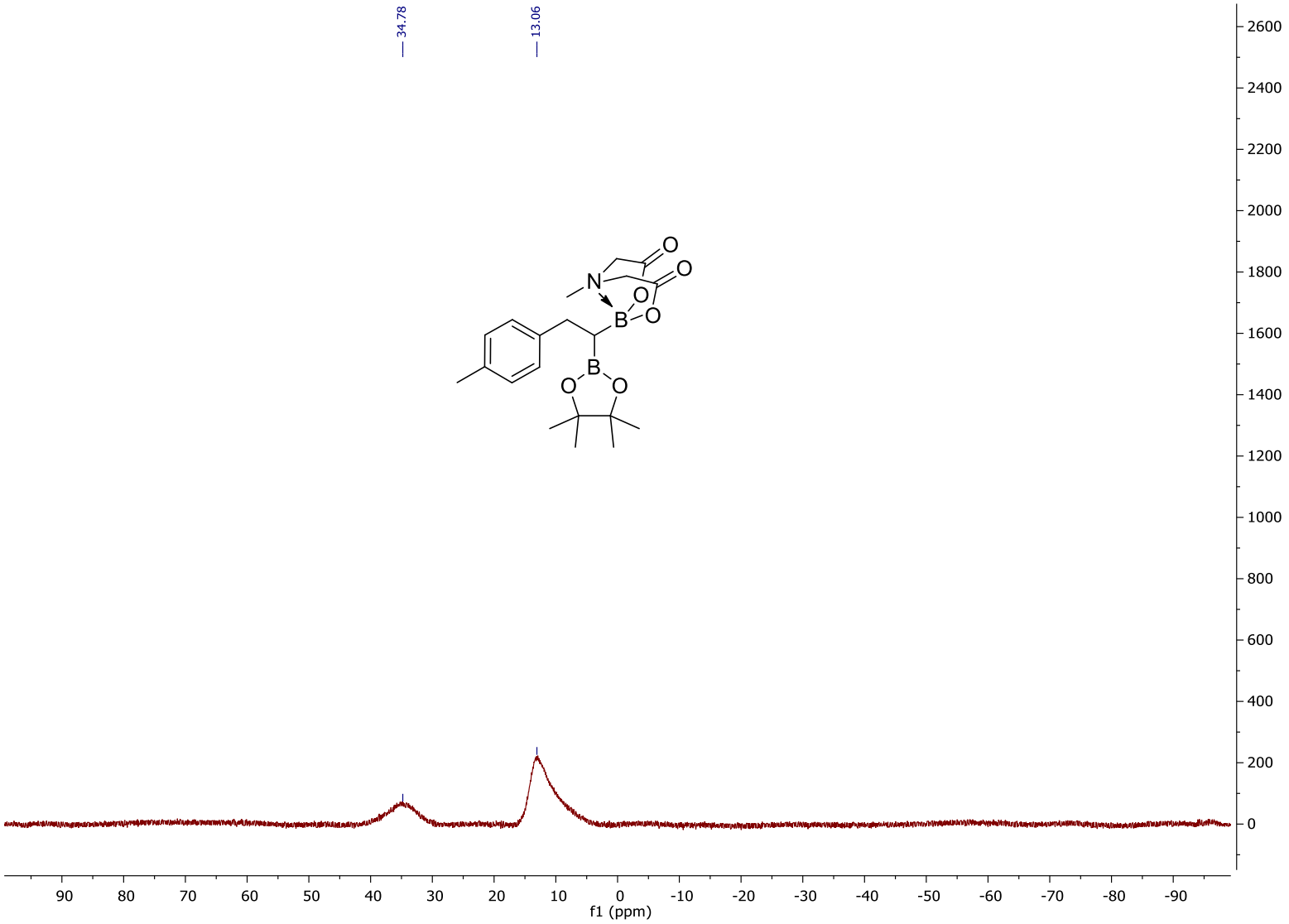


^{1}H NMR, compound 3b

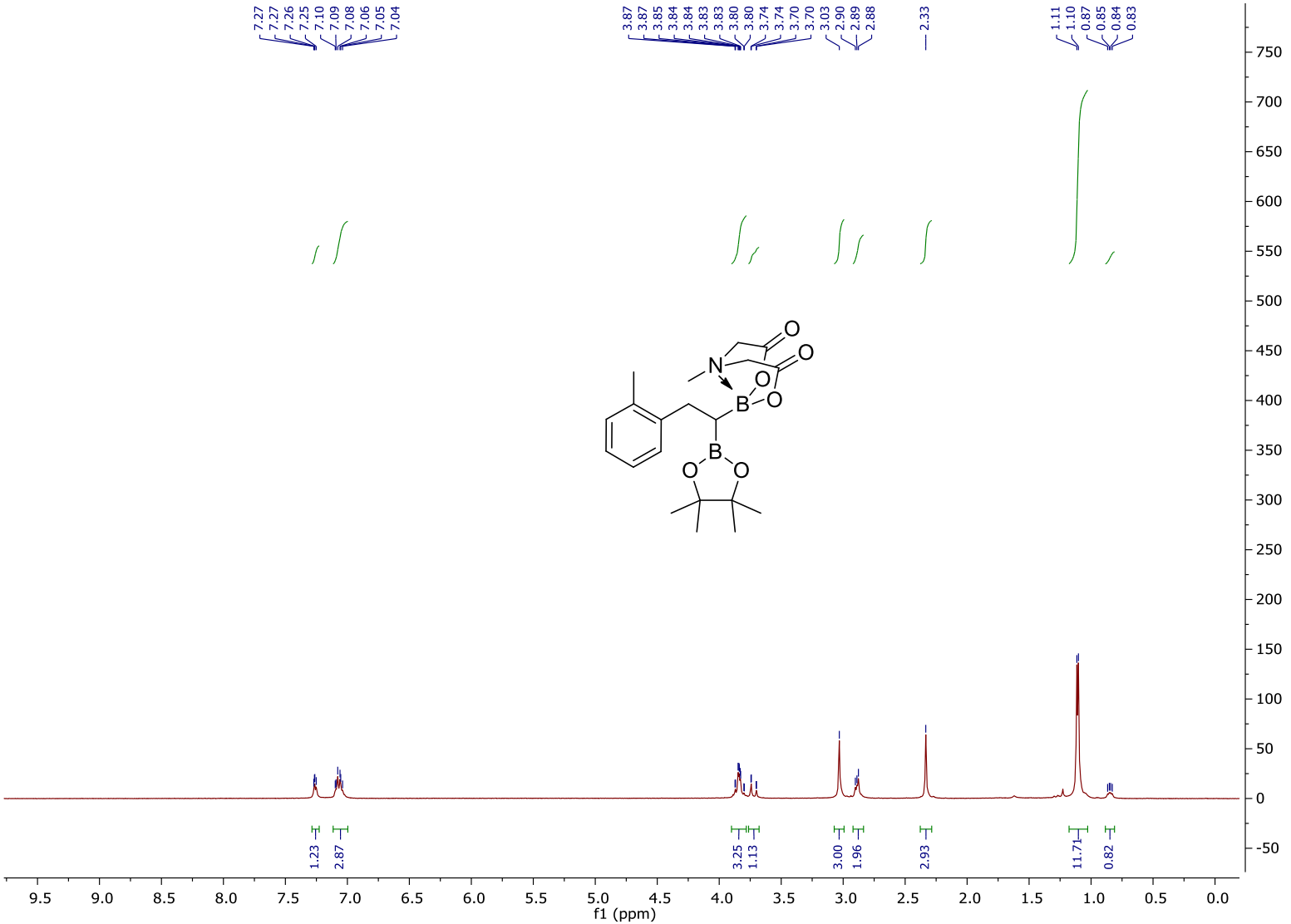


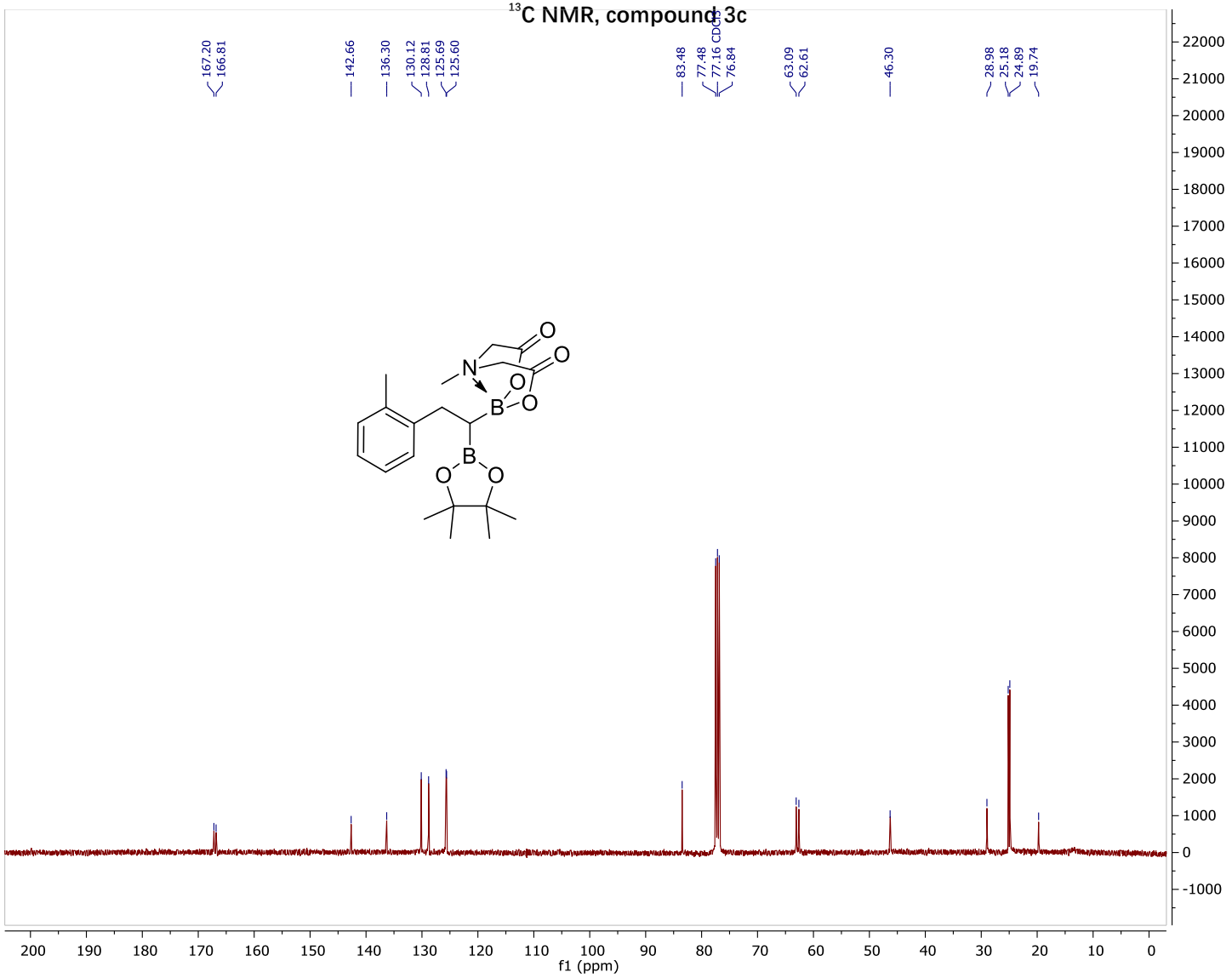

13C NMR, compound 3b
167.27
166.89
141.53
134.97
128.84
128.63
83.44
77.48
77.16 CDCl3
76.84
63.07
62.66
46.29
31.57
25.11
24.92
21.12
O
O
N
O
B
O
B
O
O
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{11}B NMR, compound 3b

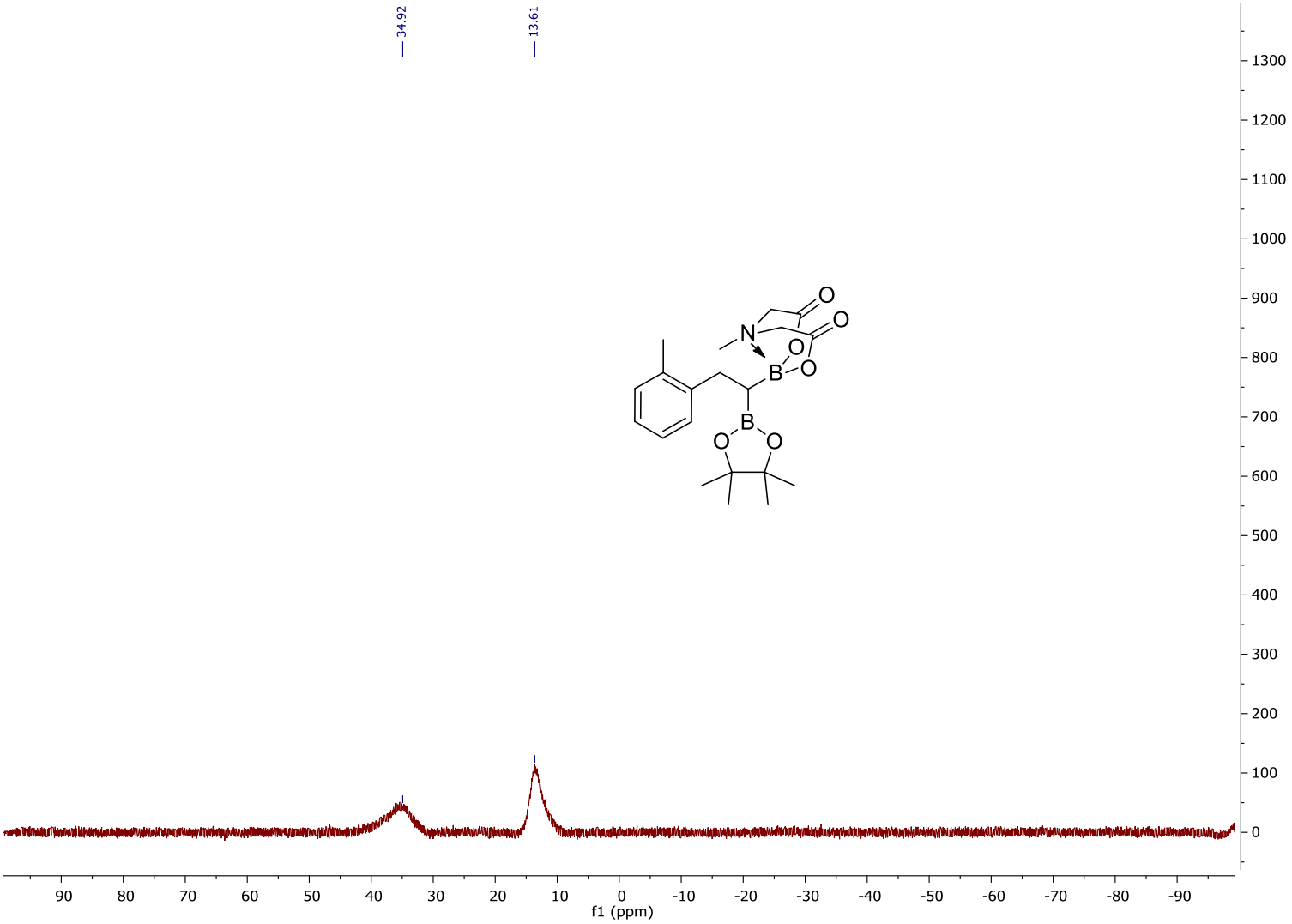


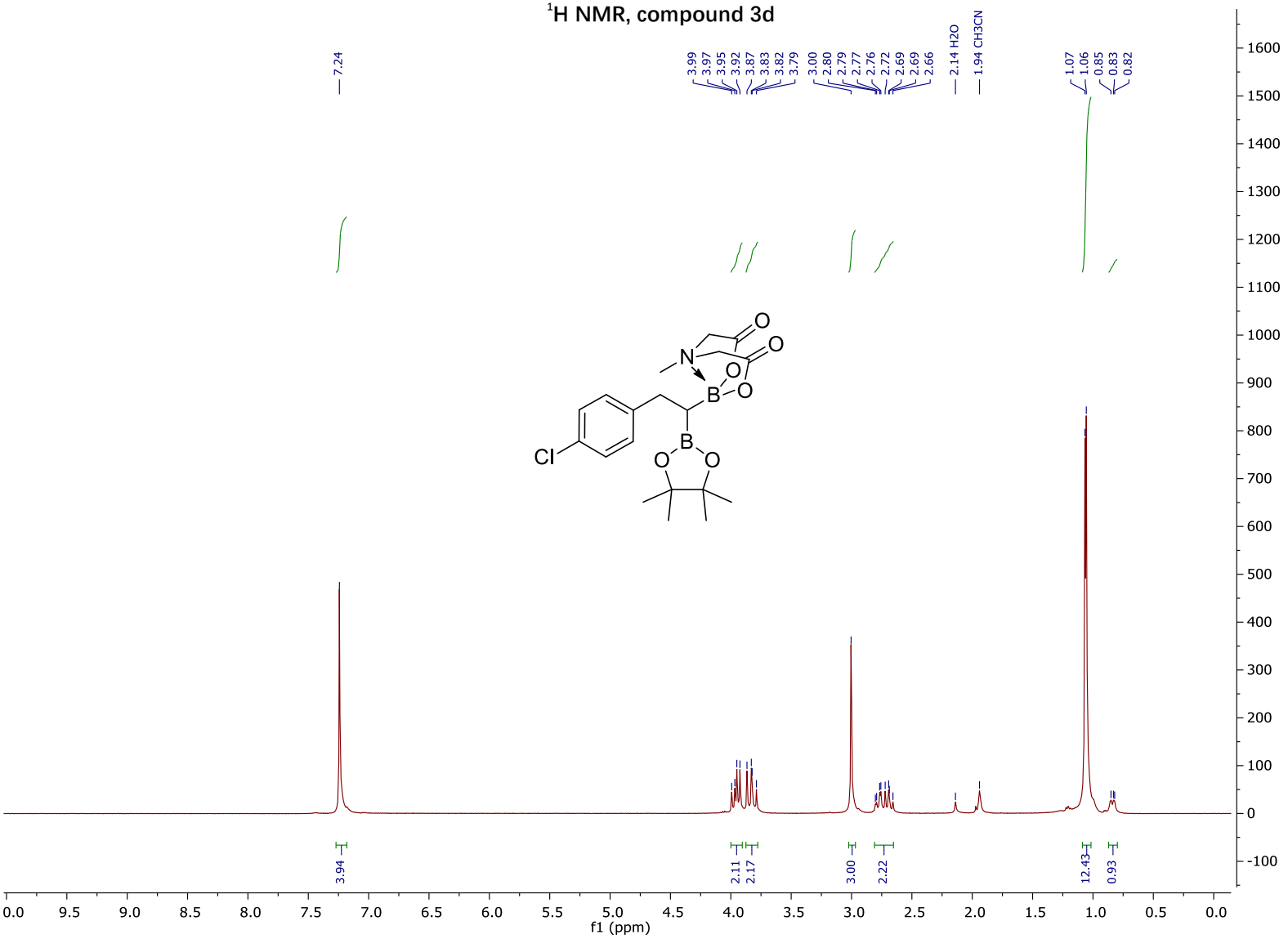
^{1}H NMR, compound 3c

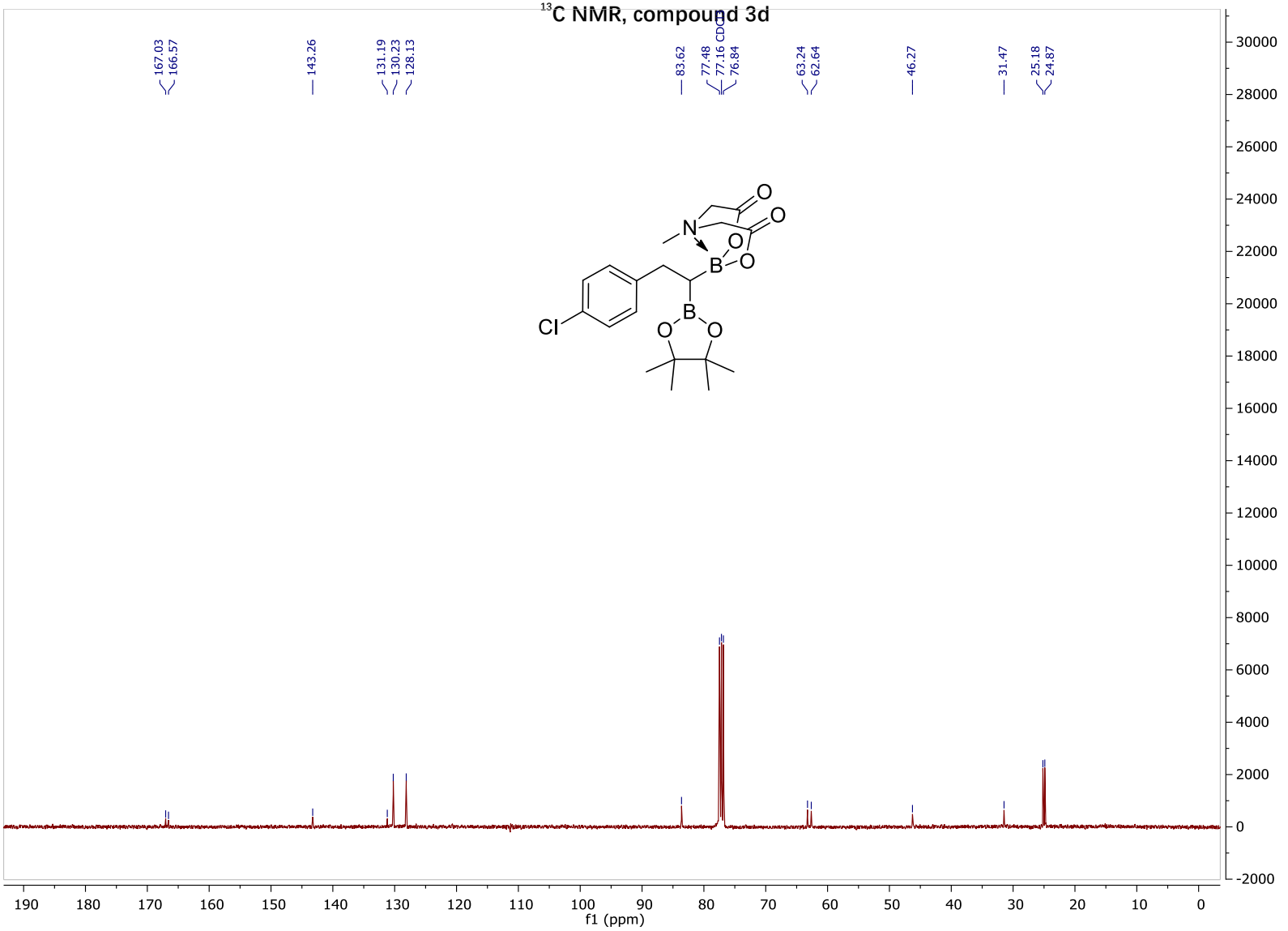



13C NMR, compound 3c
167.20
166.81
142.66
136.30
130.12
128.81
125.69
125.60
83.48
77.48
77.16 CDCl3
76.84
63.09
62.61
46.30
28.98
25.18
24.89
19.74
f1 (ppm)

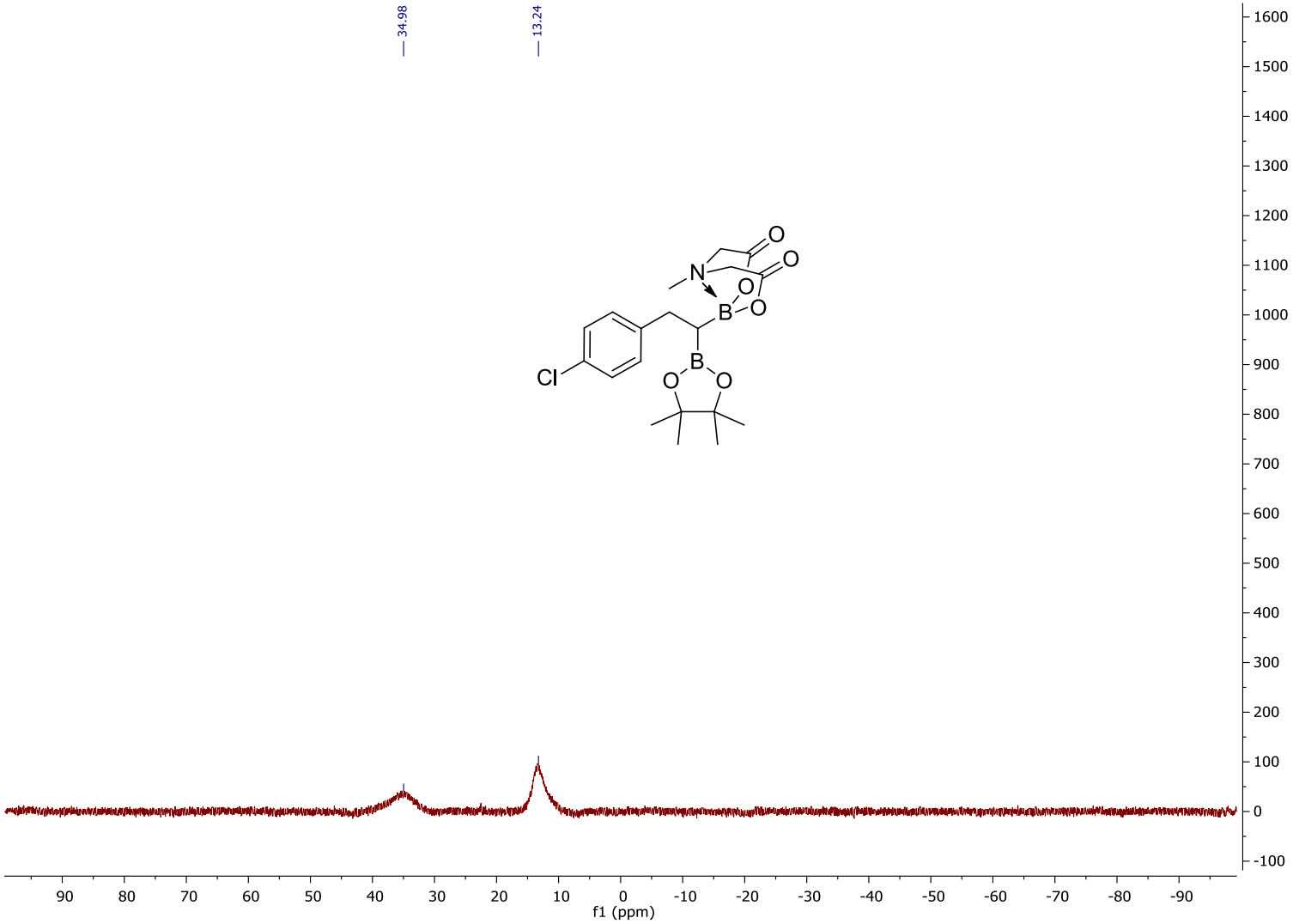
^{11}B NMR, compound 3c



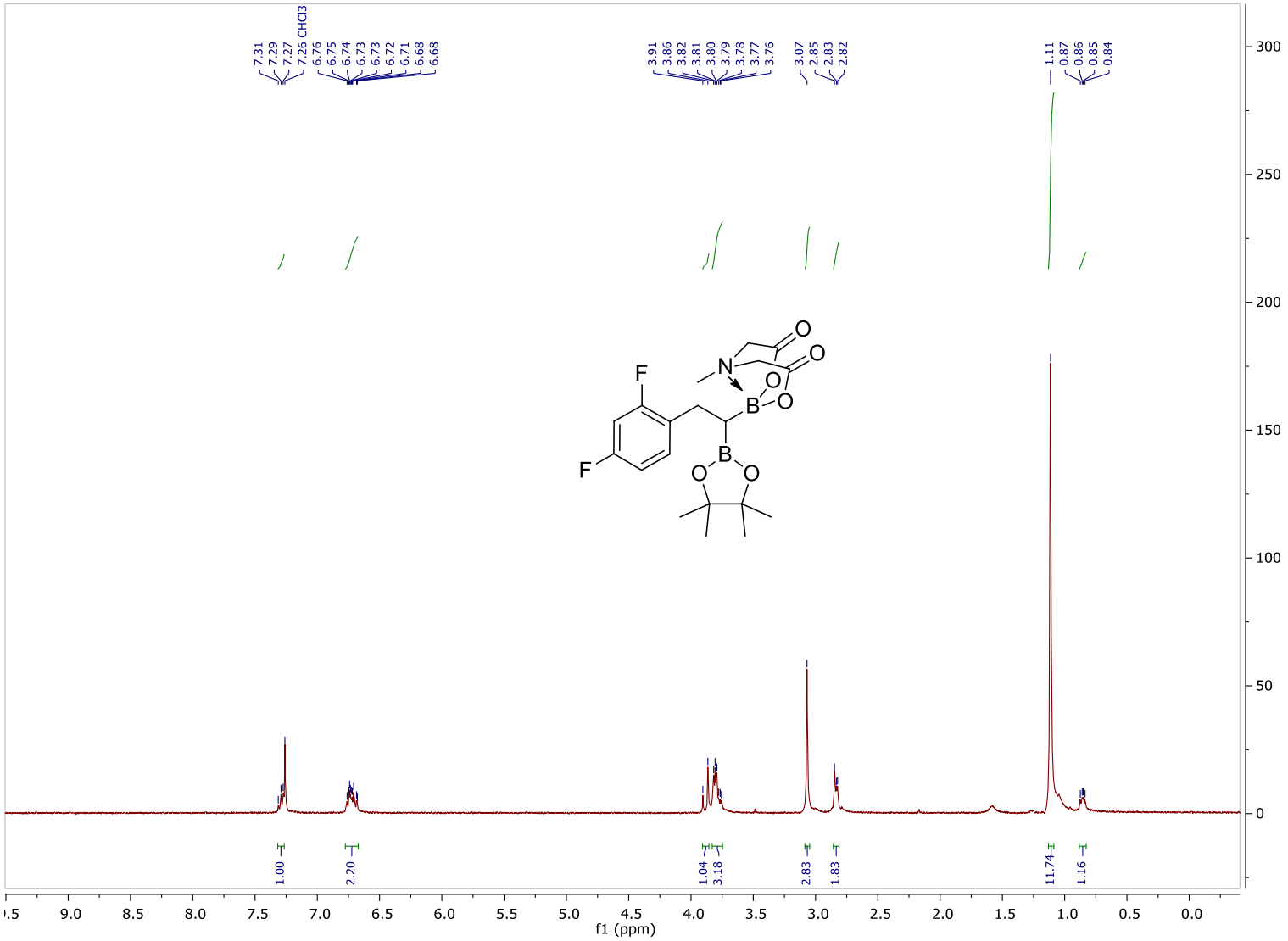

1H NMR, compound 3d
7.24
3.99
3.97
3.95
3.92
3.87
3.83
3.82
3.79
3.00
2.80
2.79
2.77
2.76
2.72
2.69
2.69
2.66
2.14 H2O
1.94 CH3CN
1.07
1.06
0.85
0.83
0.82
Cl
N
O
B
3.94
2.11
2.17
3.00
2.22
12.43
0.93
f1 (ppm)

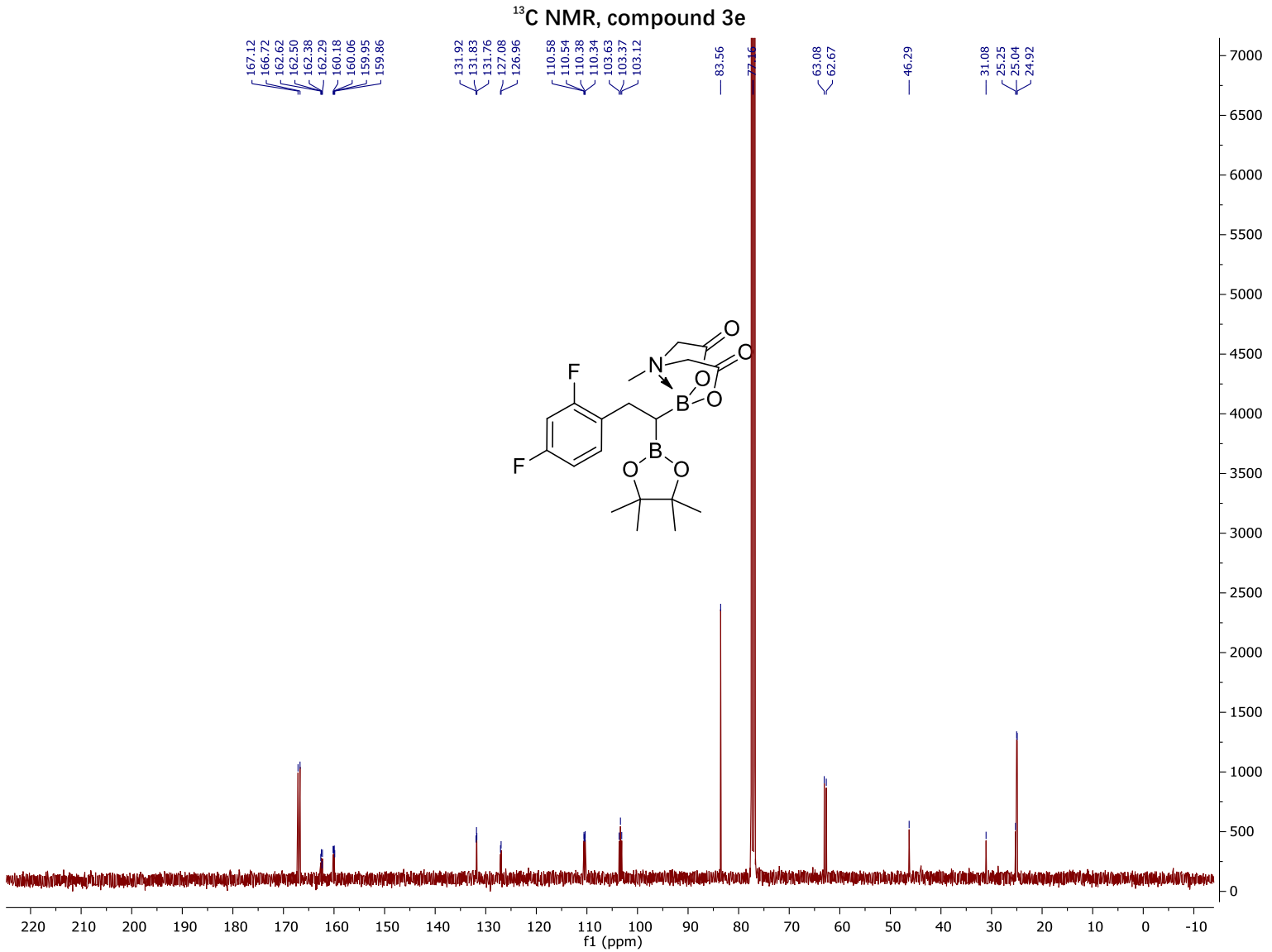

13C NMR, compound 3d
167.03
166.57
143.26
131.19
130.23
128.13
83.62
77.48
77.16 CDCl3
76.84
63.24
62.64
46.27
31.47
25.18
24.87
Cl
f1 (ppm)

^{11}B NMR, compound 3d

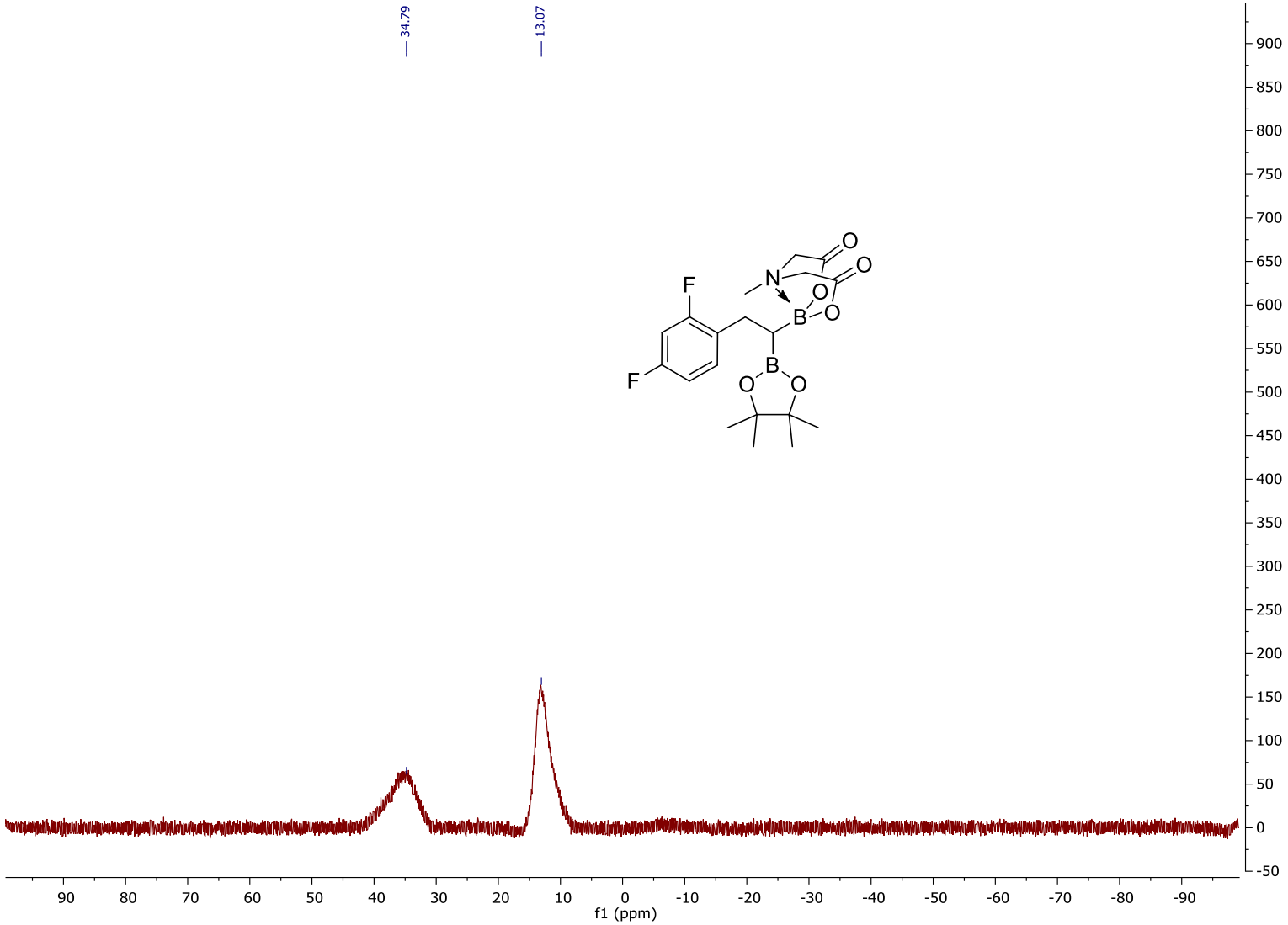


^{1}H NMR, compound 3e

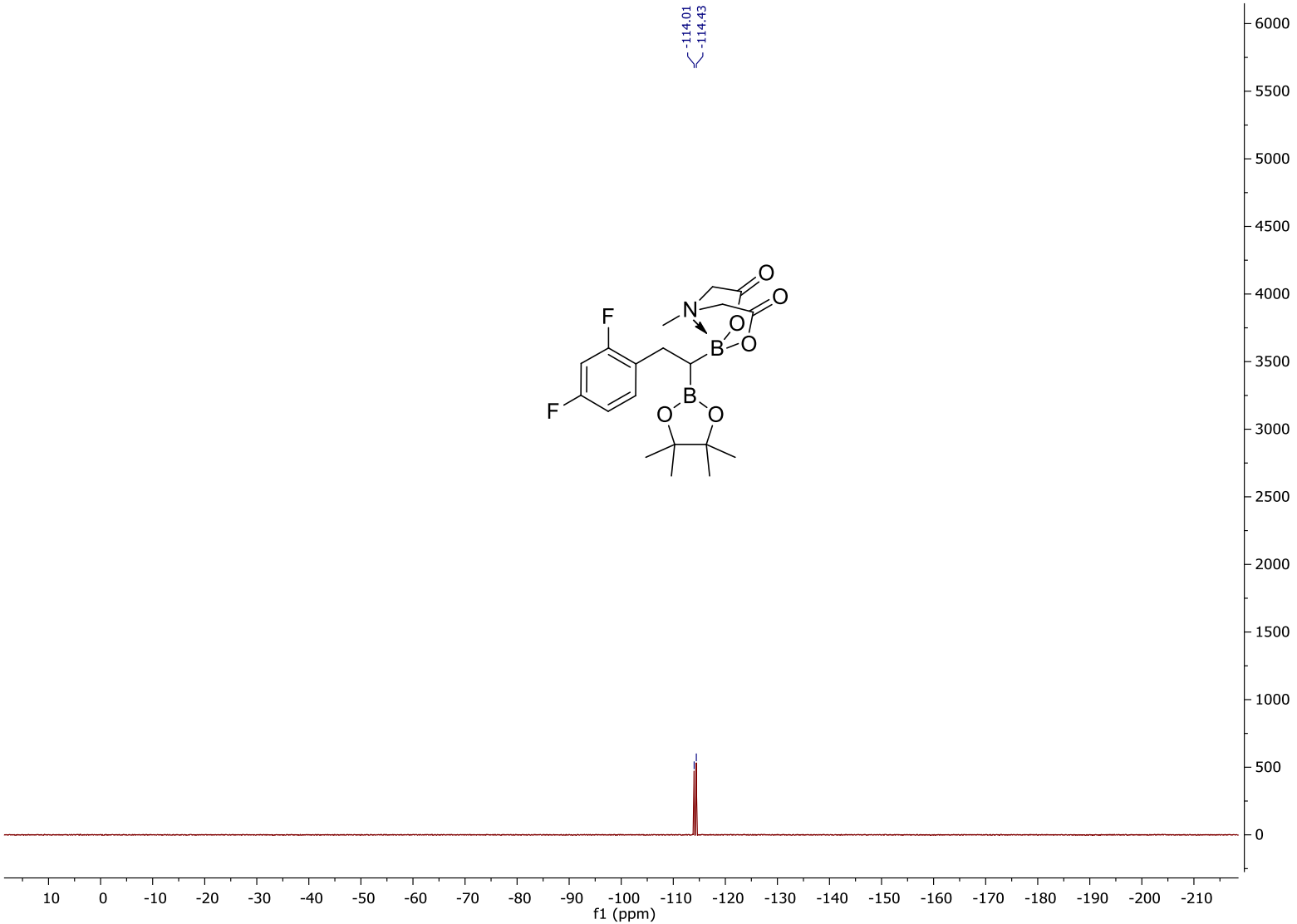



13C NMR, compound 3e
167.12
166.72
162.62
162.50
162.38
162.29
160.18
160.06
159.95
159.86
131.92
131.83
131.76
127.08
126.96
110.58
110.54
110.38
110.34
103.63
103.37
103.12
83.56
77.16
63.08
62.67
46.29
31.08
25.25
25.04
24.92
F
F
N
O
O
O
O
B
O
B
O
O
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

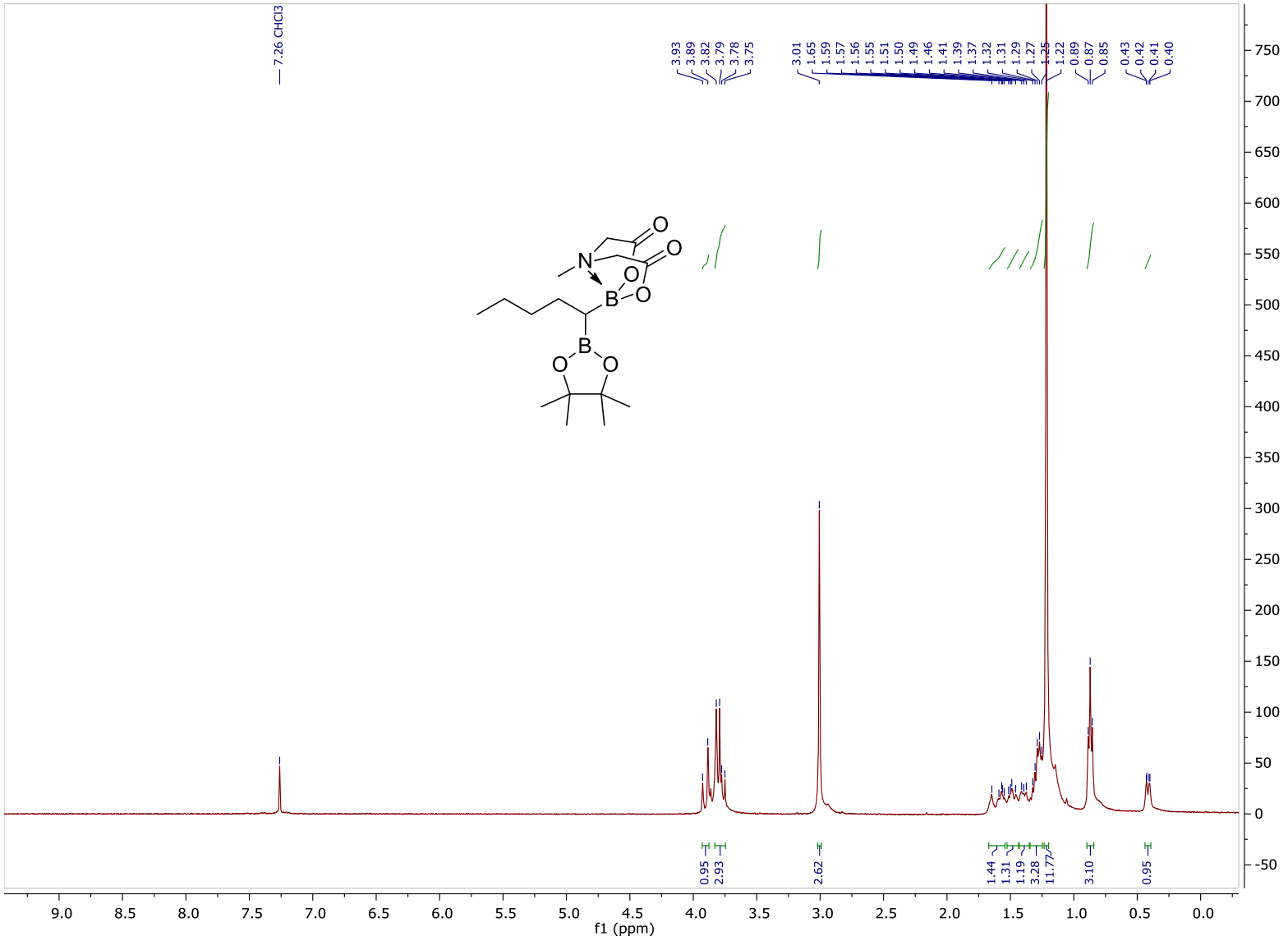
^{11}B NMR, compound 3e



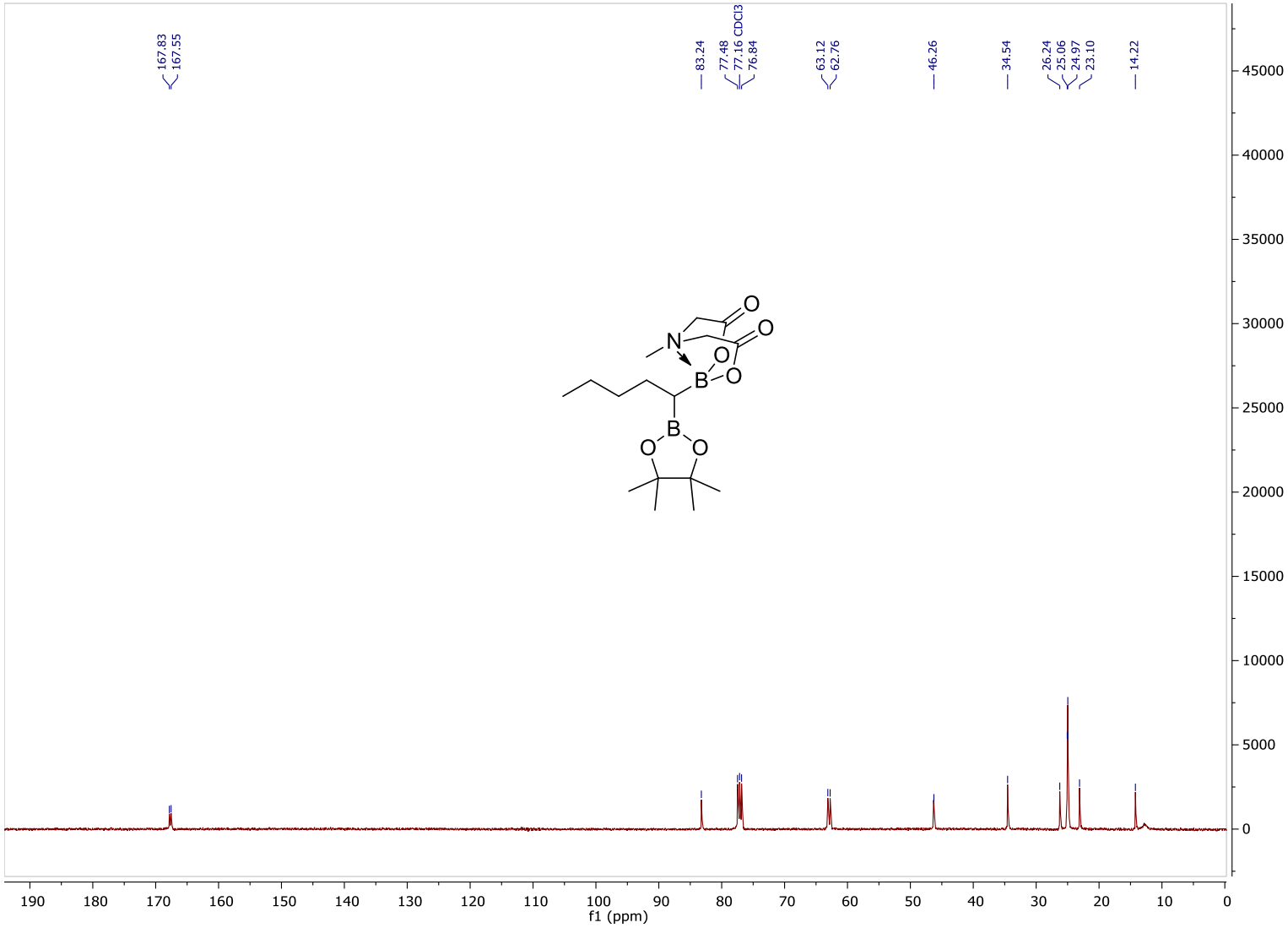
^{19}F NMR, compound 3e



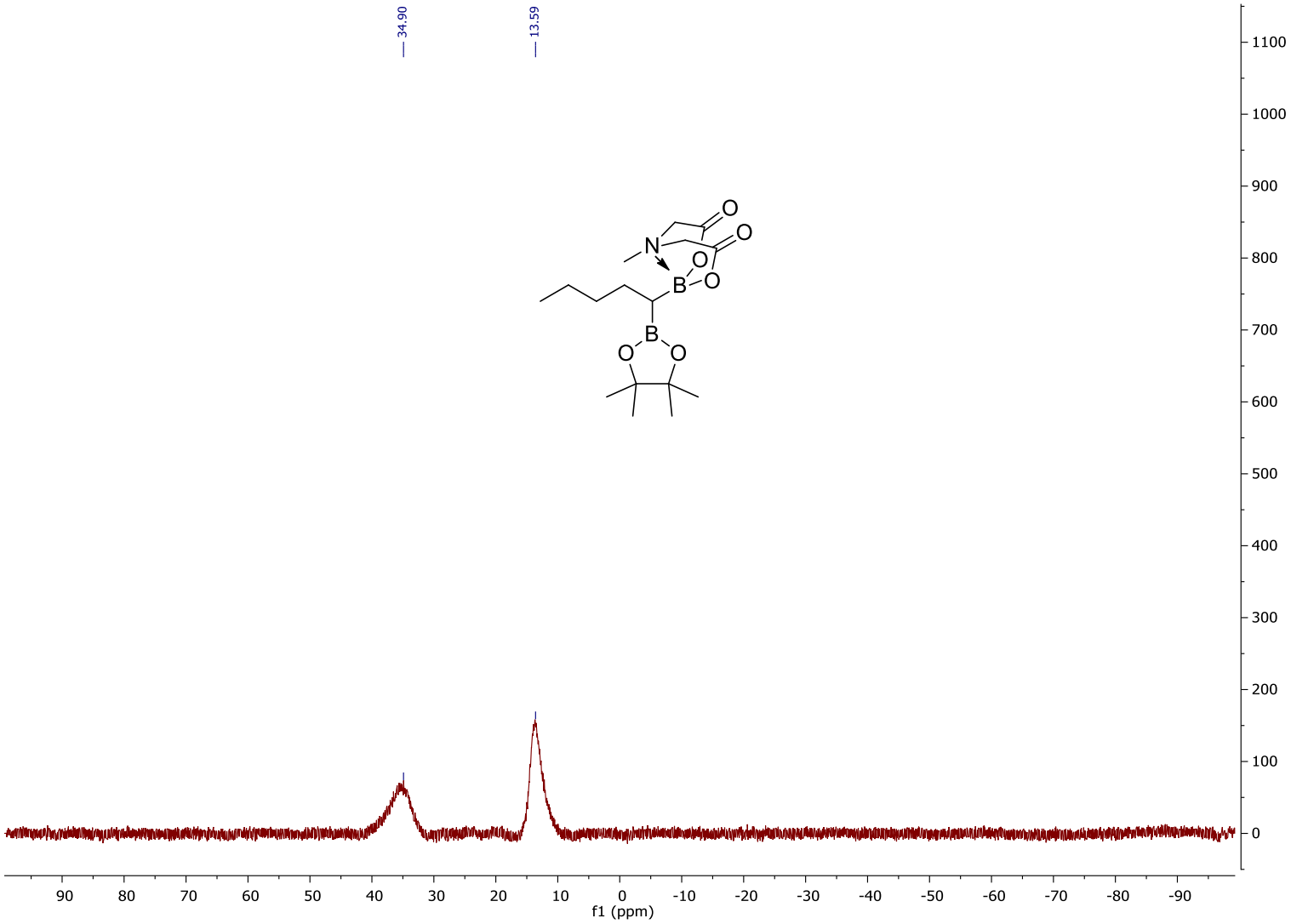
^{1}H NMR, compound 3f



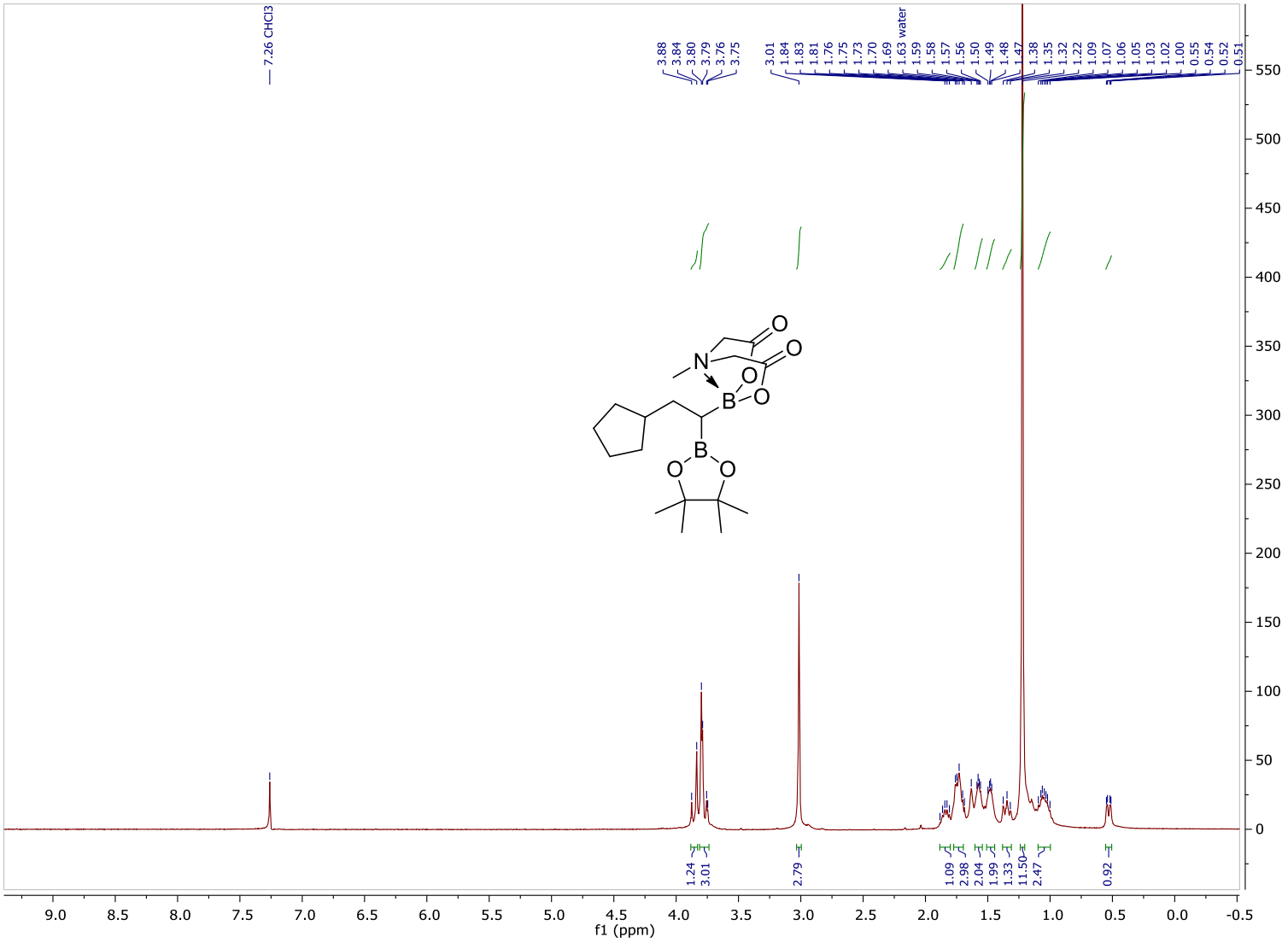
^{13}C NMR, compound 3f



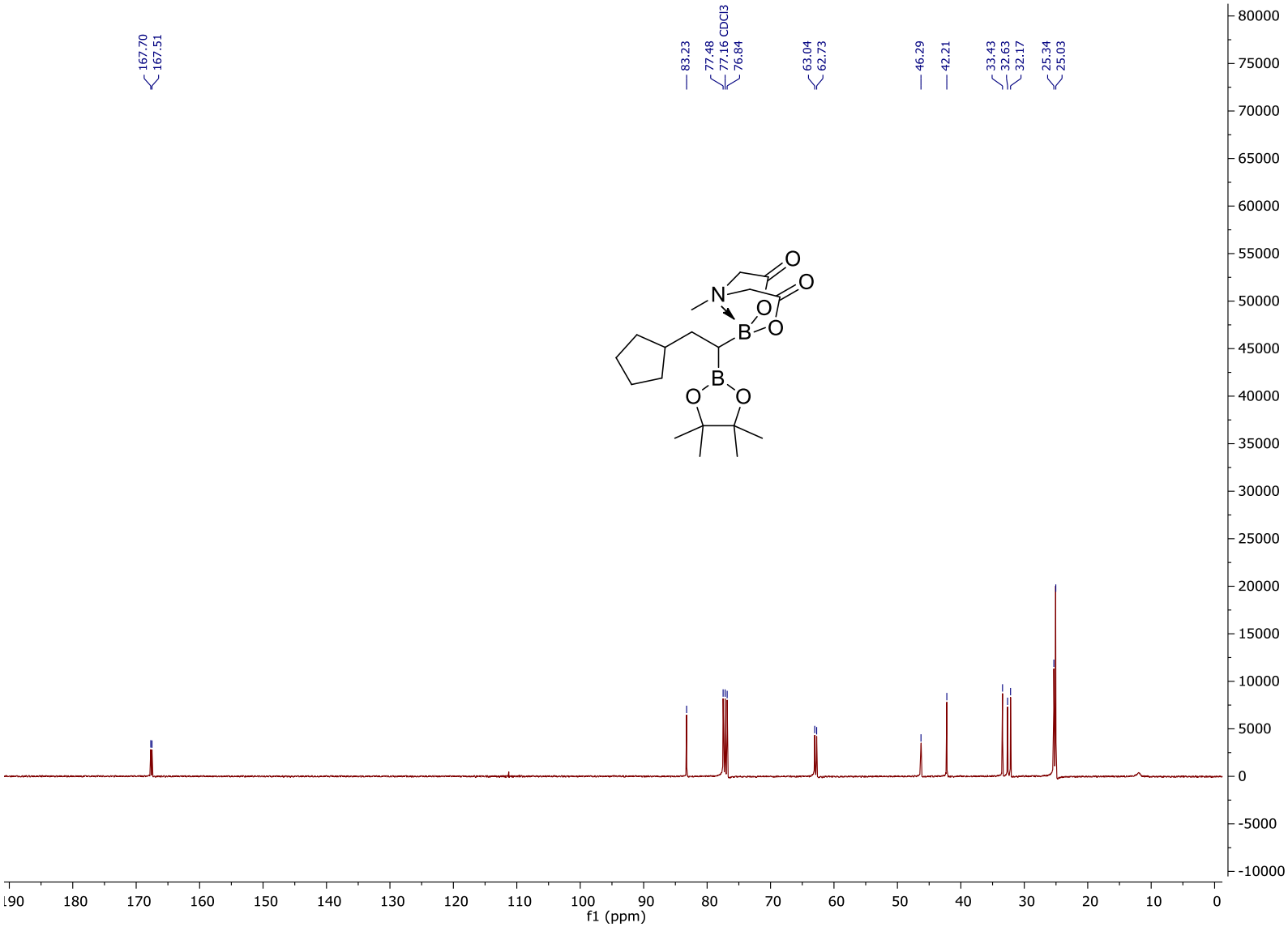
^{11}B NMR, compound 3f



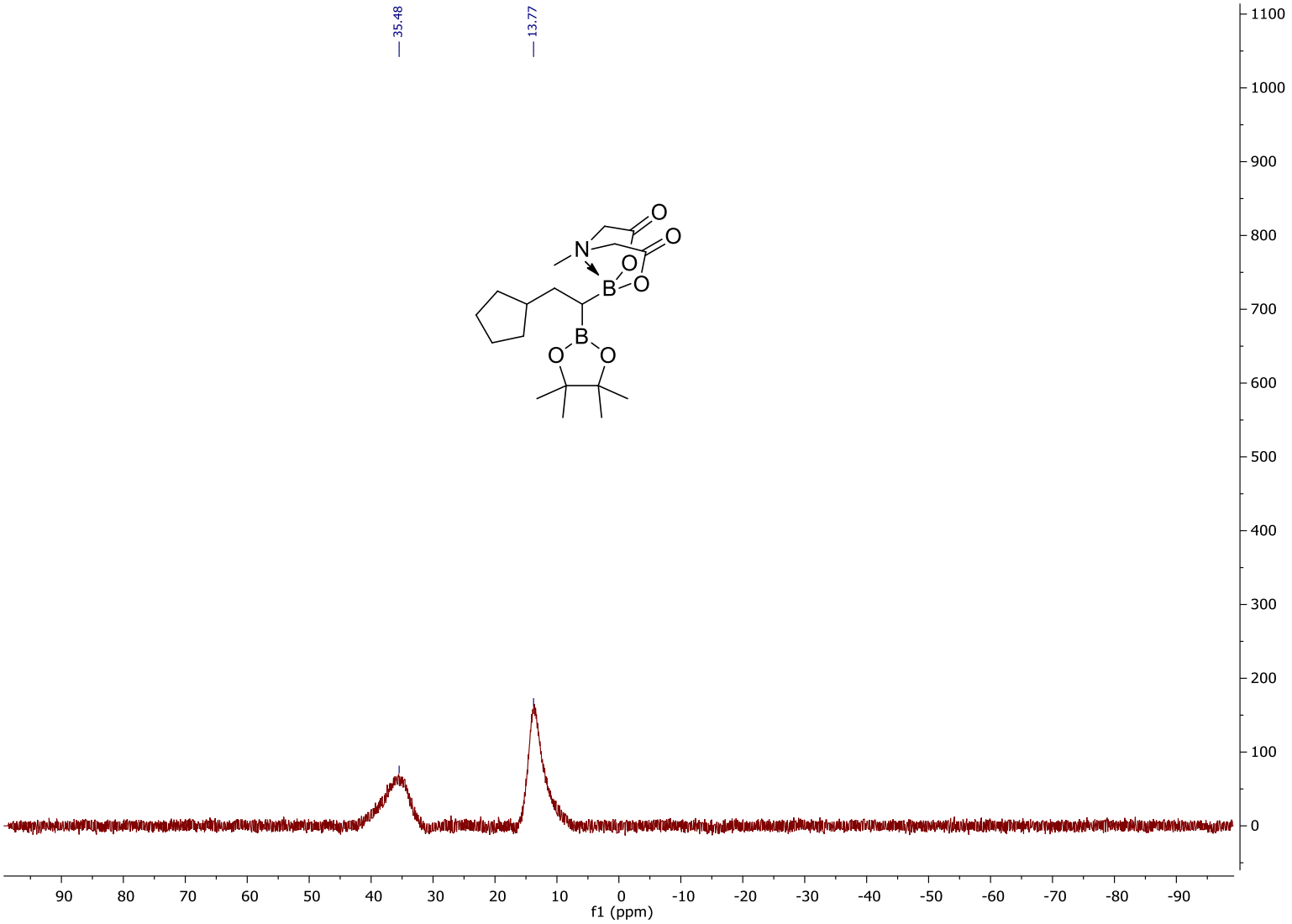
^{1}H NMR, compound 3g



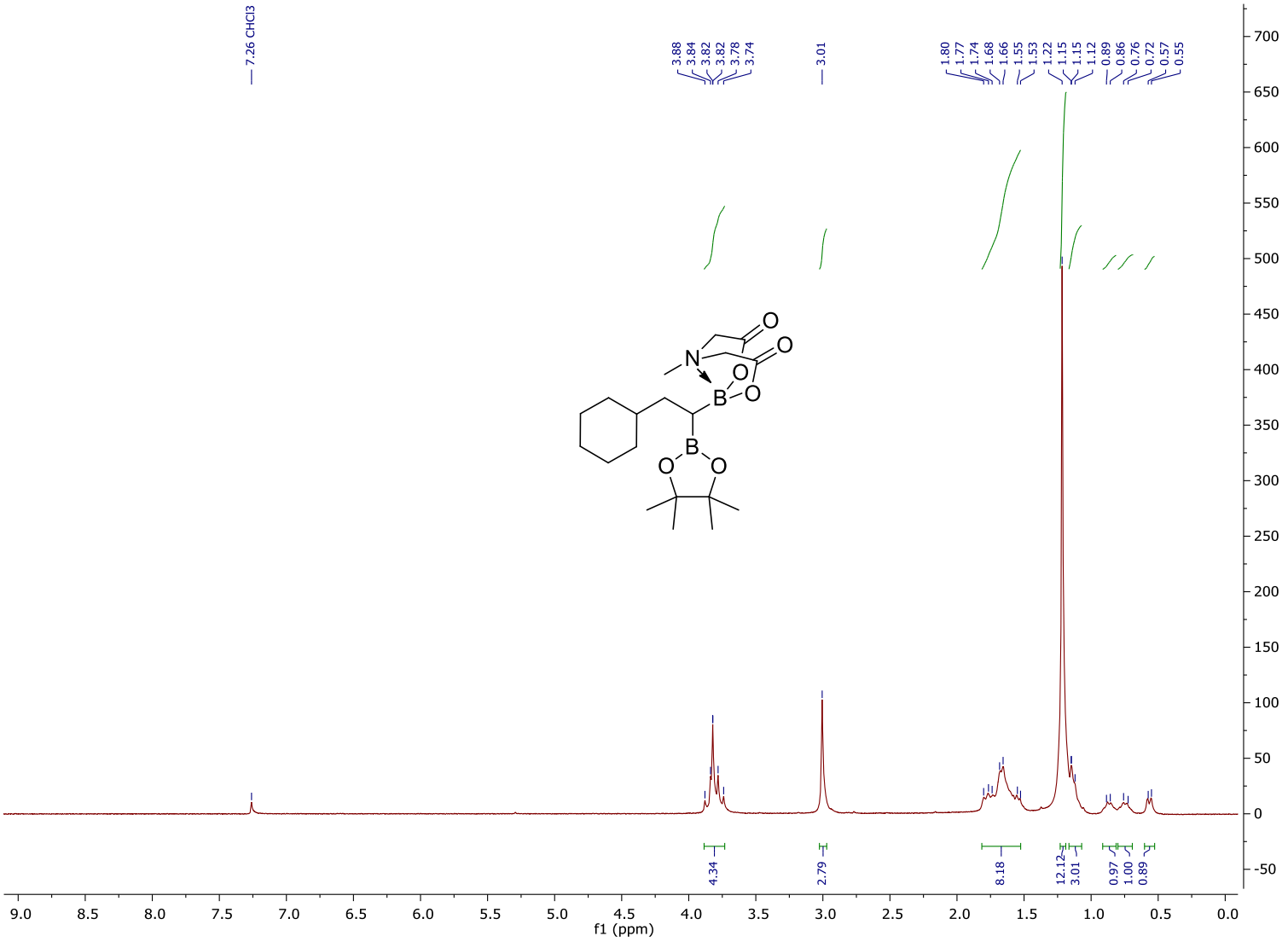
^{13}C NMR, compound 3g

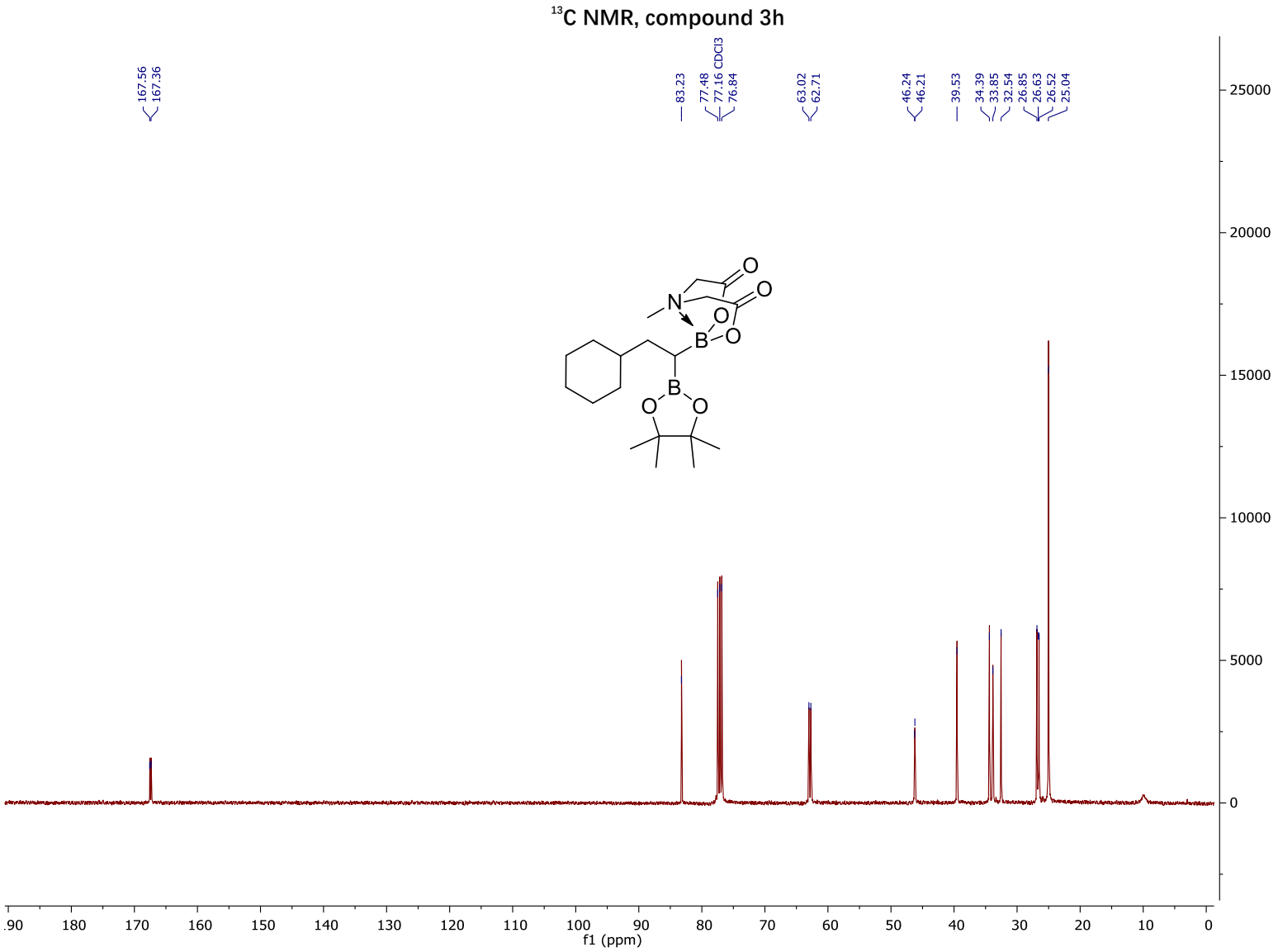


^{11}B NMR, compound 3g

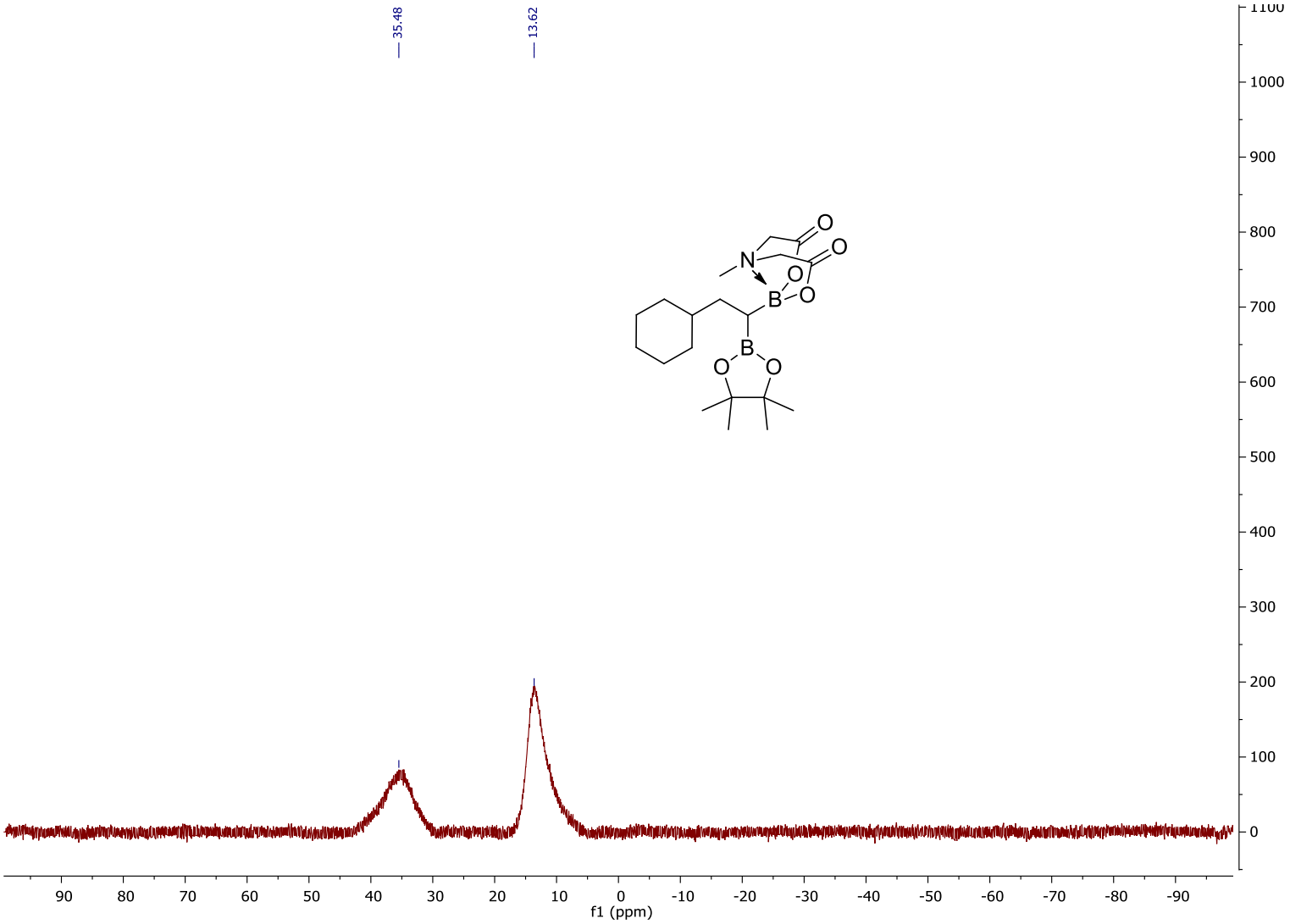


^{1}H NMR, compound 3h

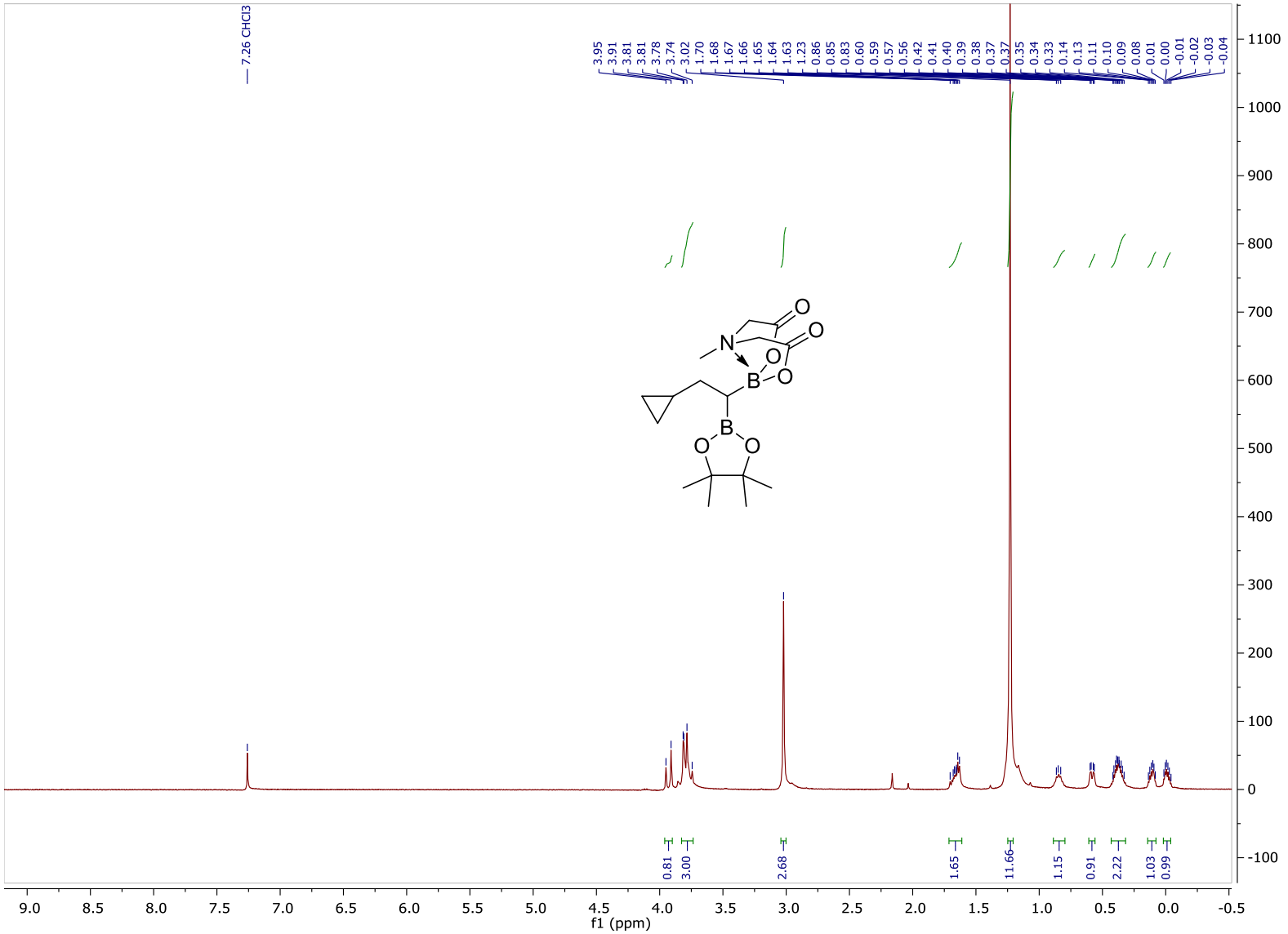



13C NMR, compound 3h
167.56
167.36
83.23
77.48
77.16 CDCl3
76.84
63.02
62.71
46.24
46.21
39.53
34.39
33.85
32.54
26.85
26.63
26.52
25.04
25000
20000
15000
10000
5000
0
f1 (ppm)

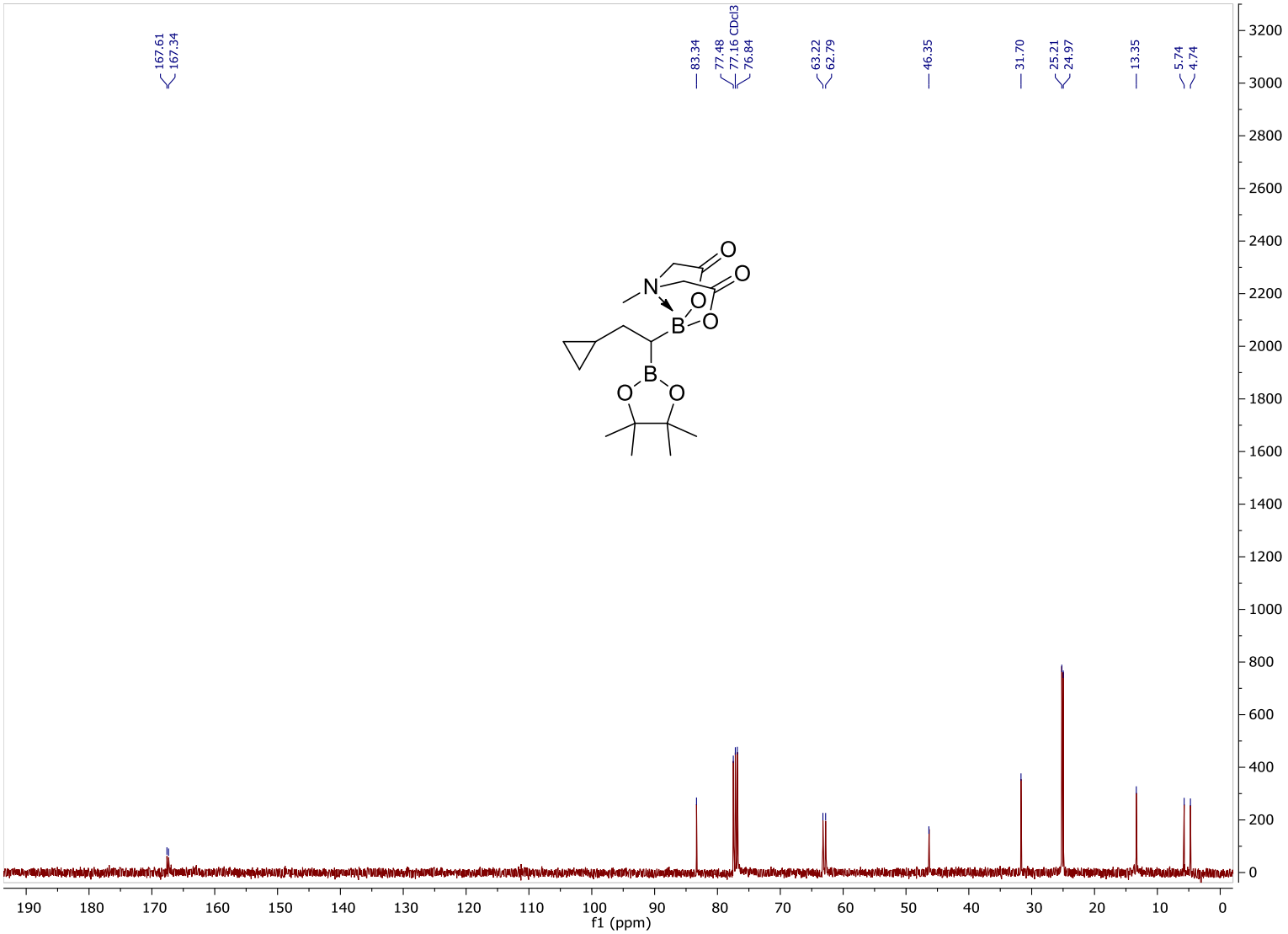
^{11}B NMR, compound 3h



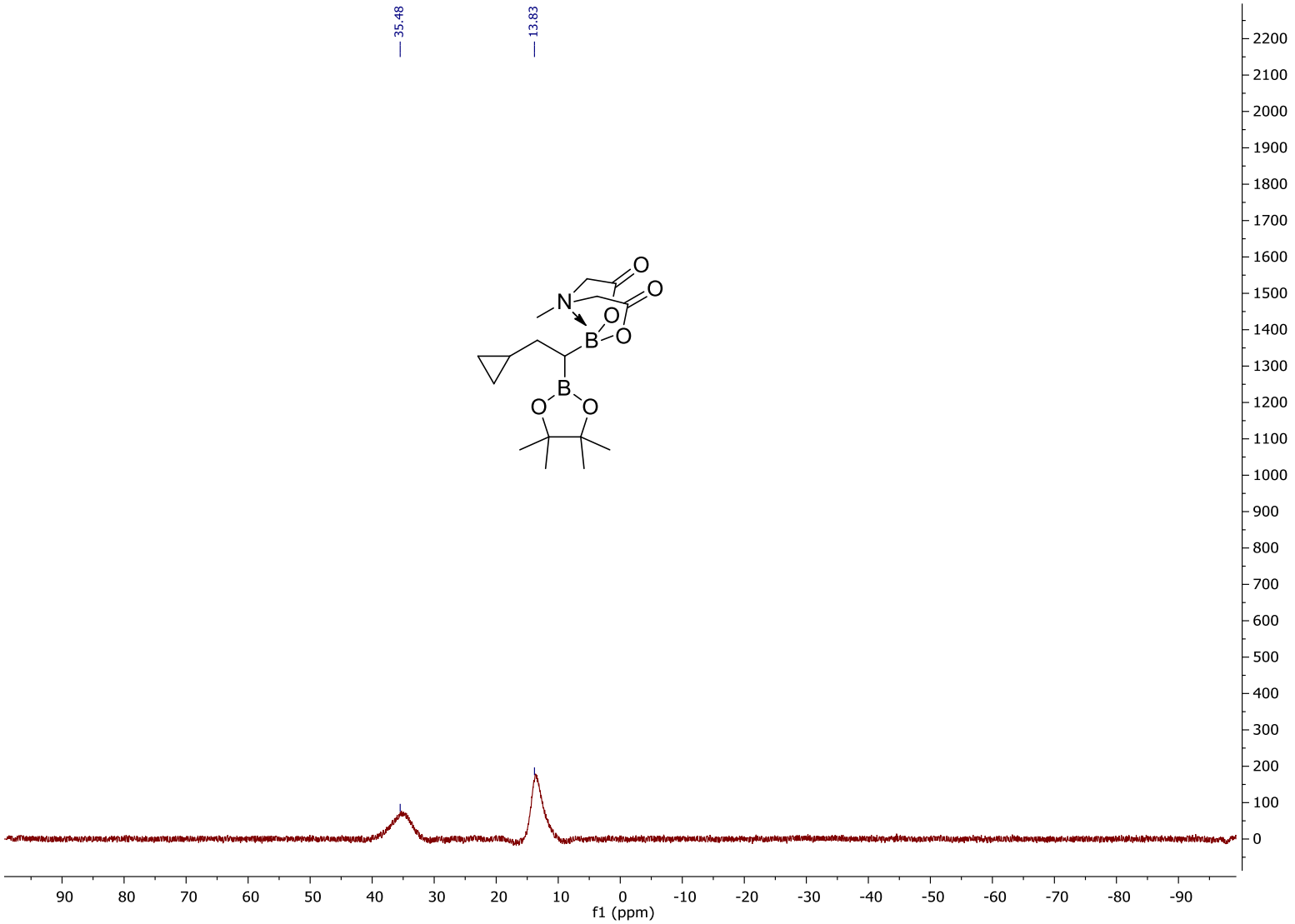
^{1}H NMR, compound 3i



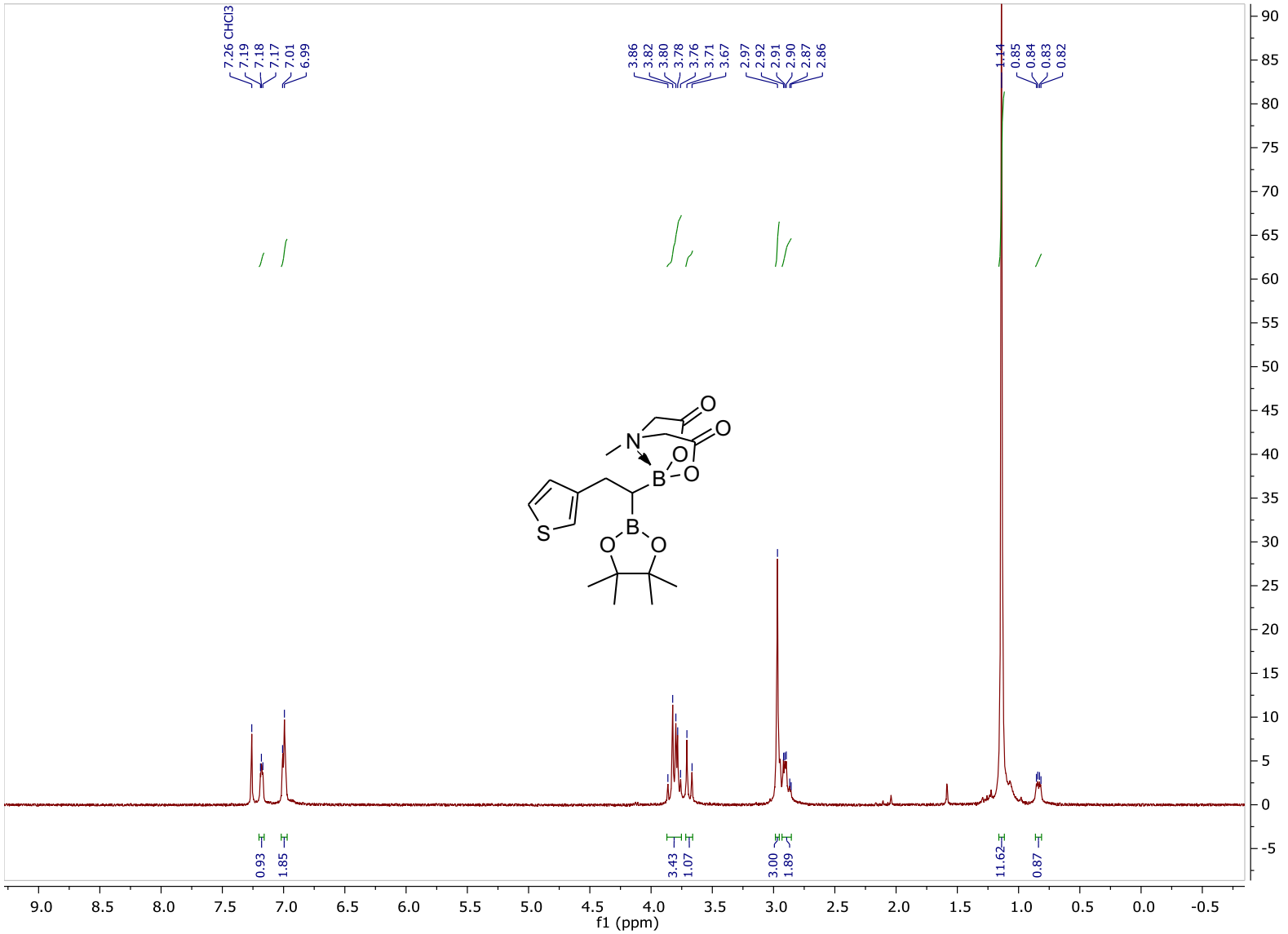
^{13}C NMR, compound 3i

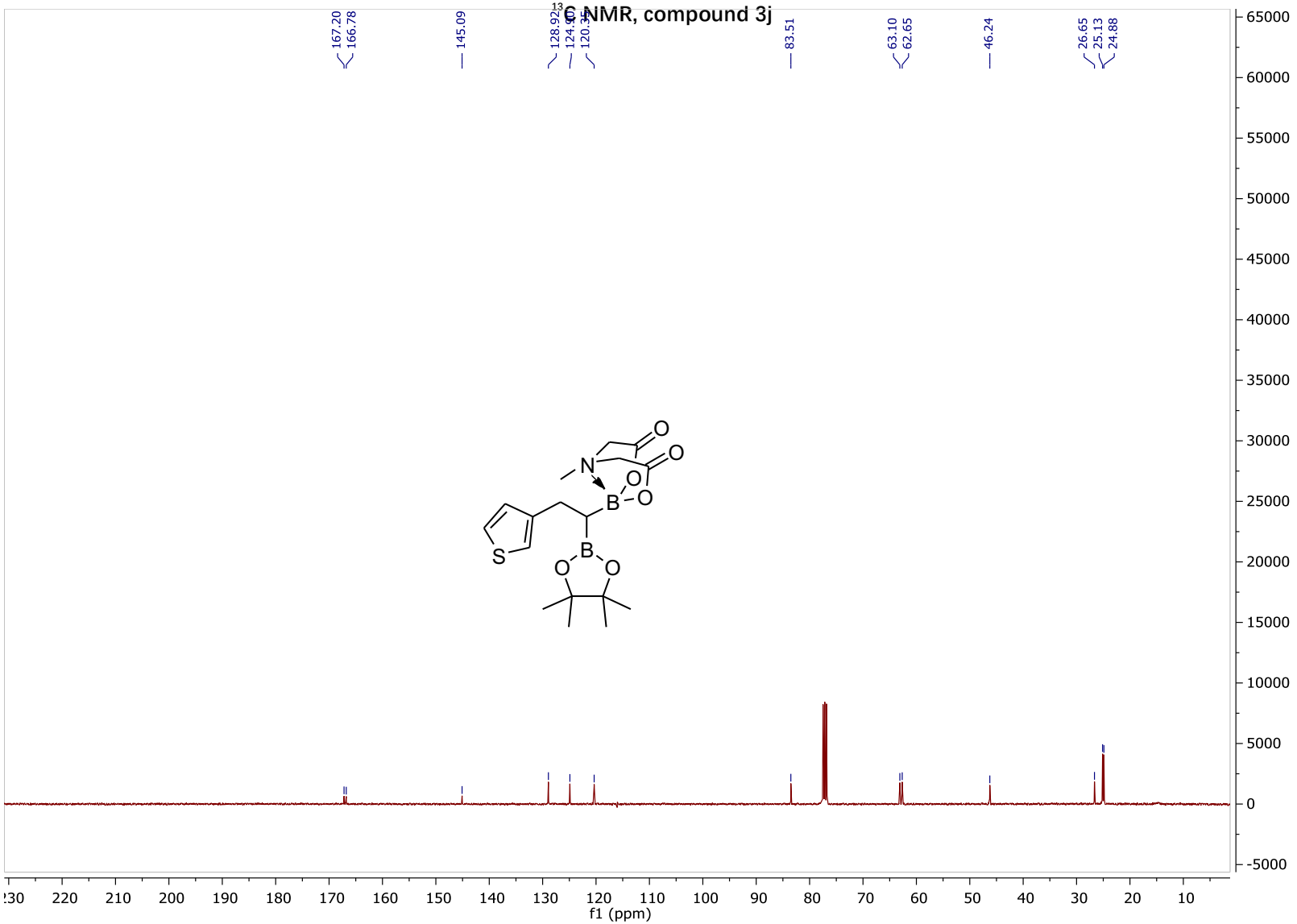


^{11}B NMR, compound 3i

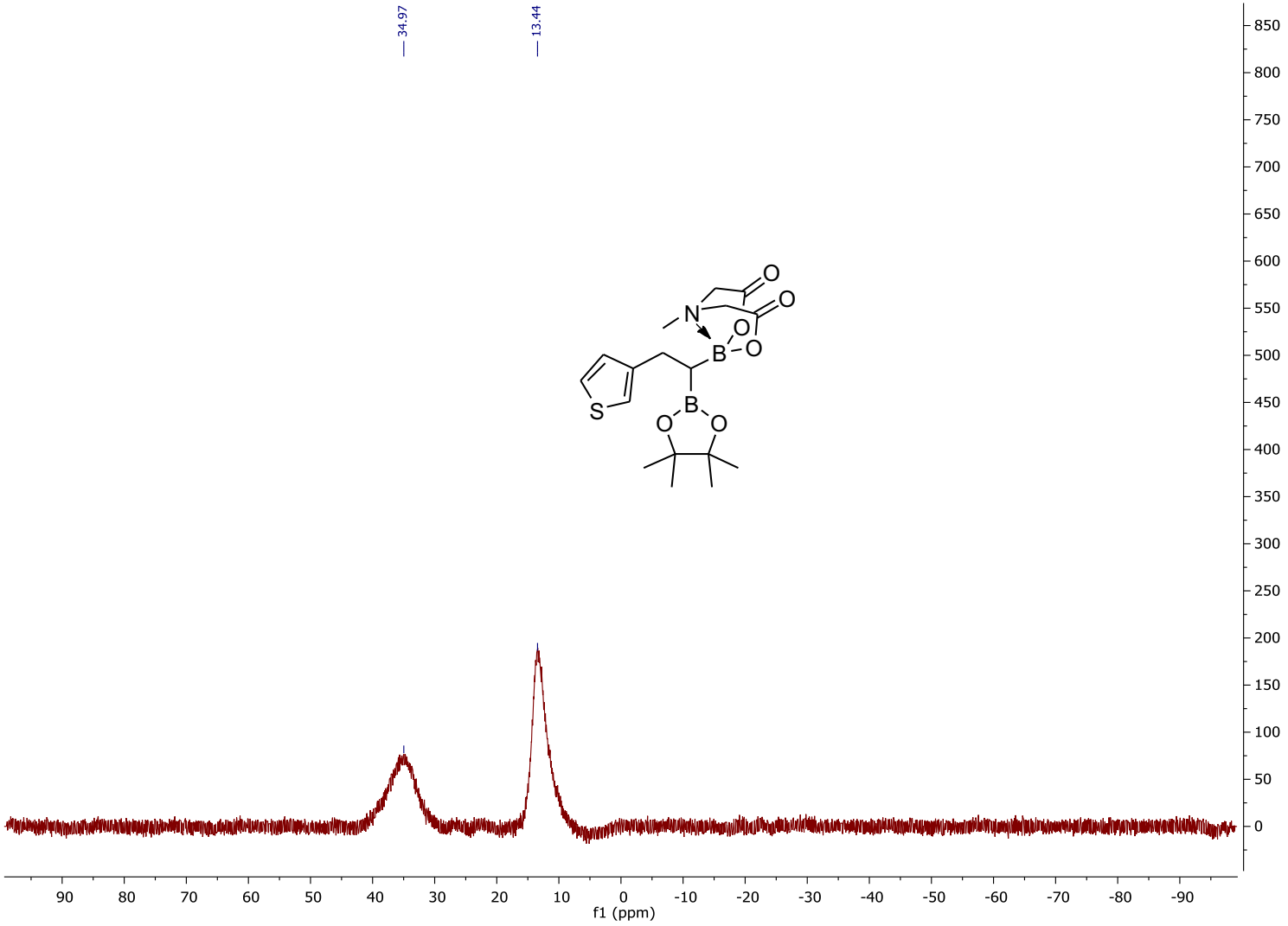


^{1}H NMR, compound 3j

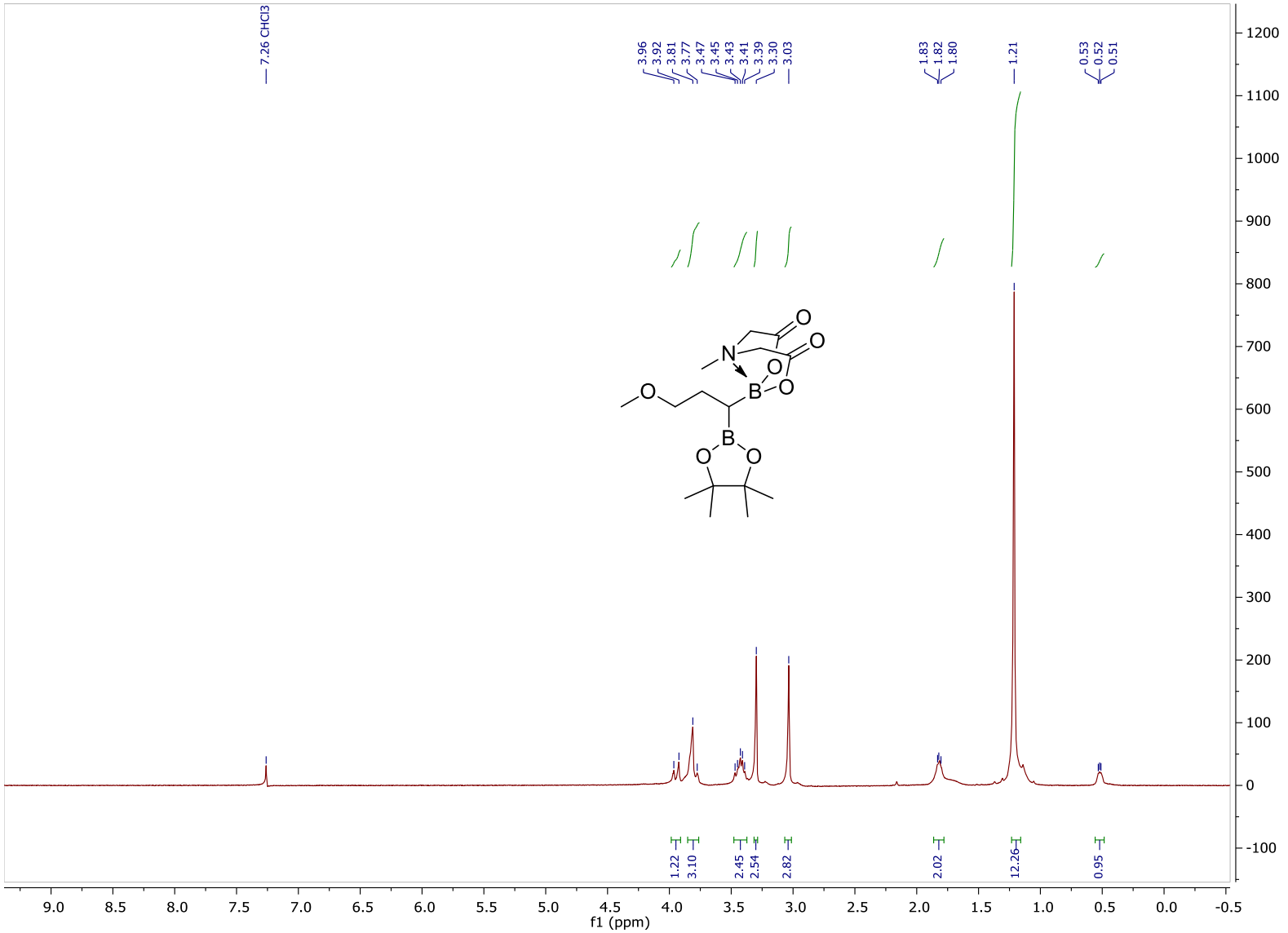


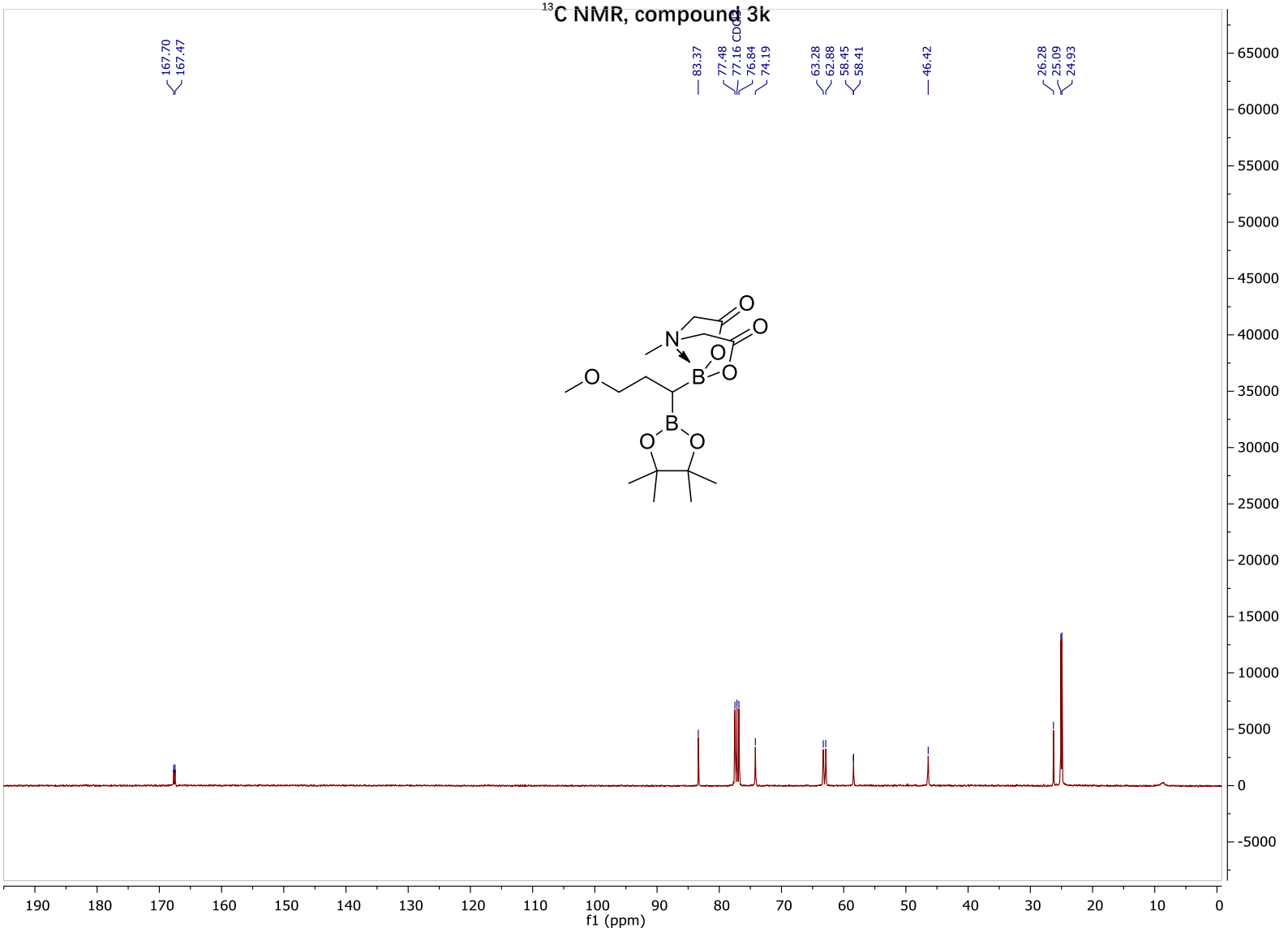

13C NMR, compound 3j
167.20
166.78
145.09
128.92
124.40
120.34
83.51
63.10
62.65
46.24
26.65
25.13
24.88
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{11}B NMR, compound 3j

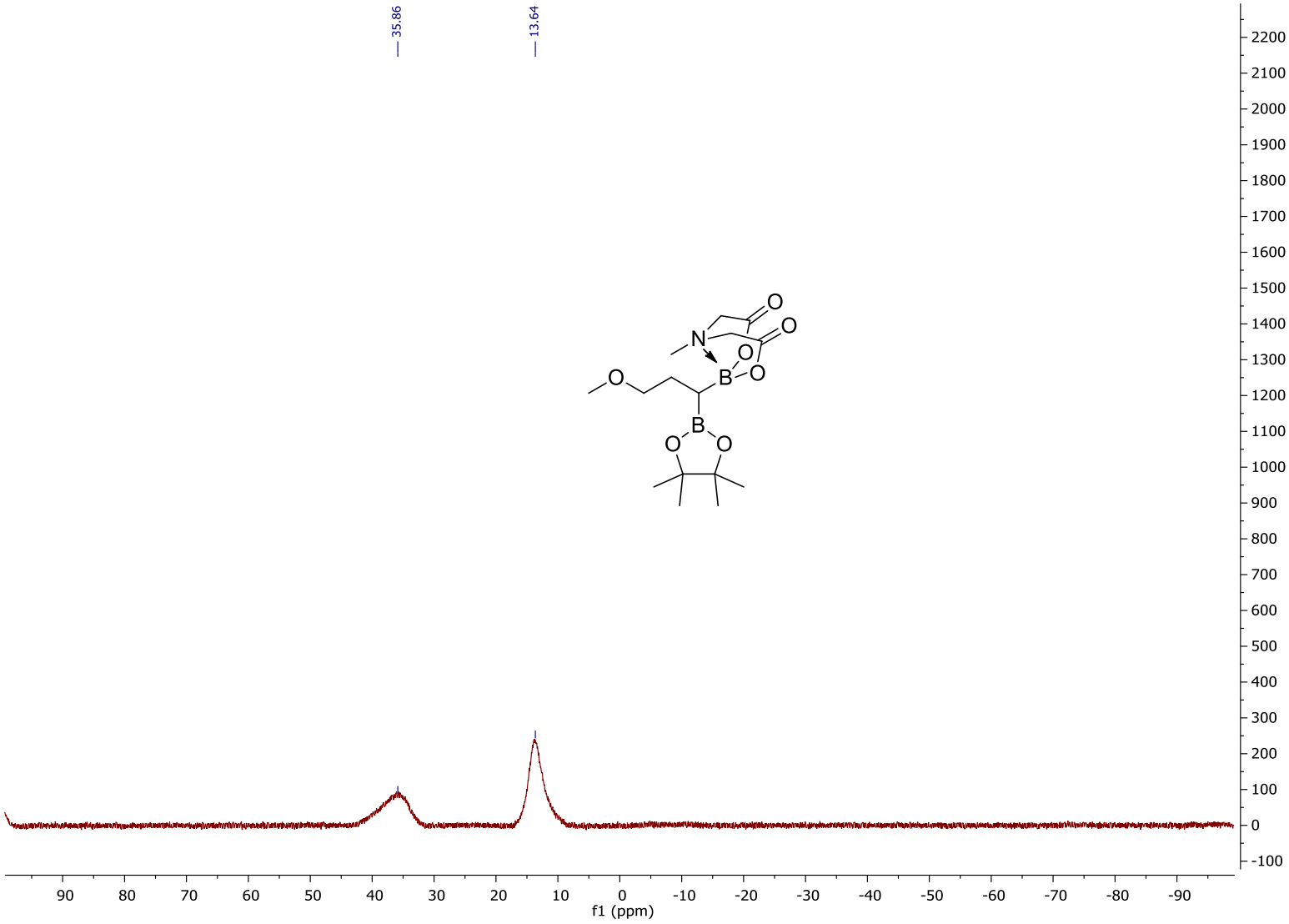


^{1}H NMR, compound 3k

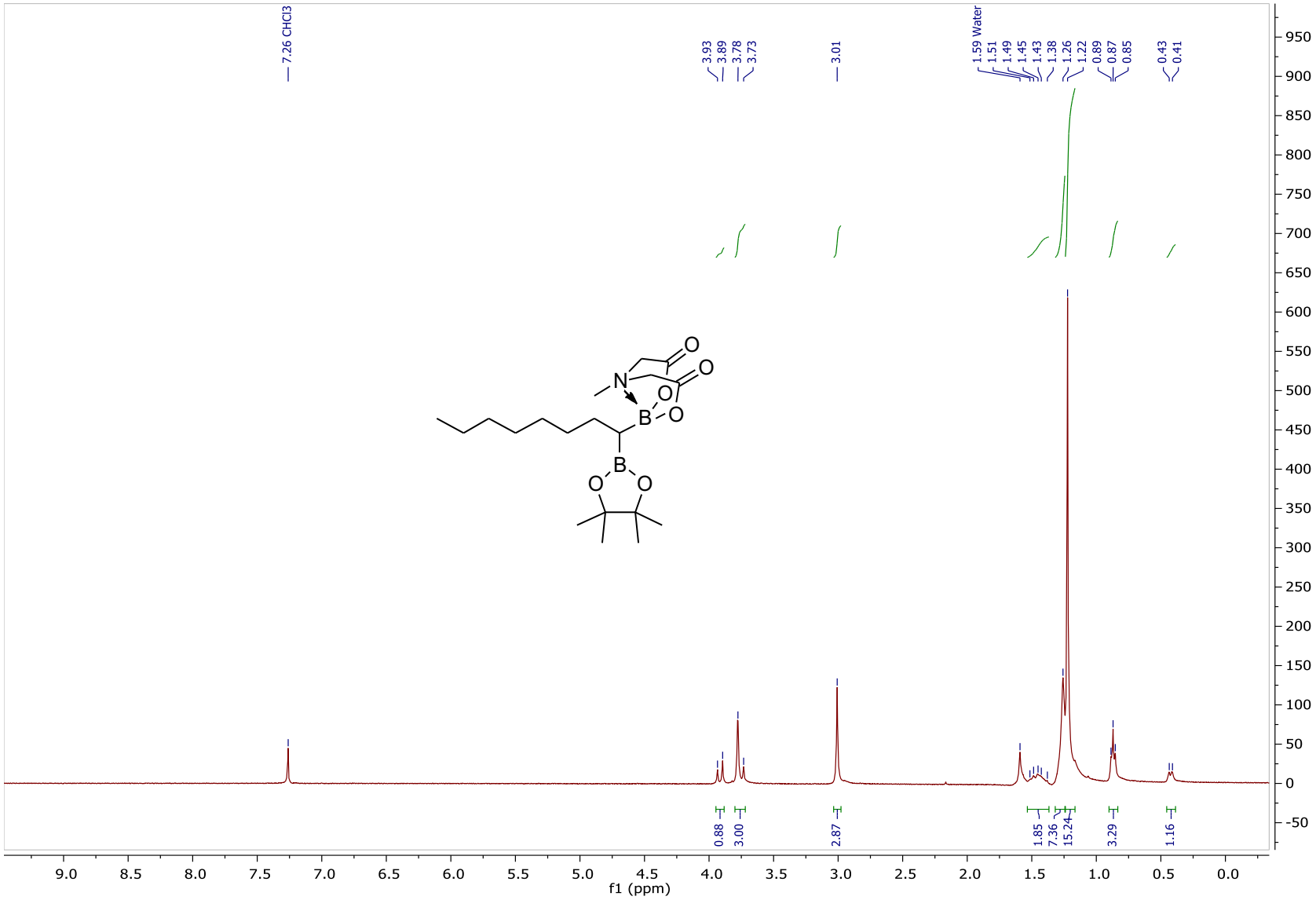


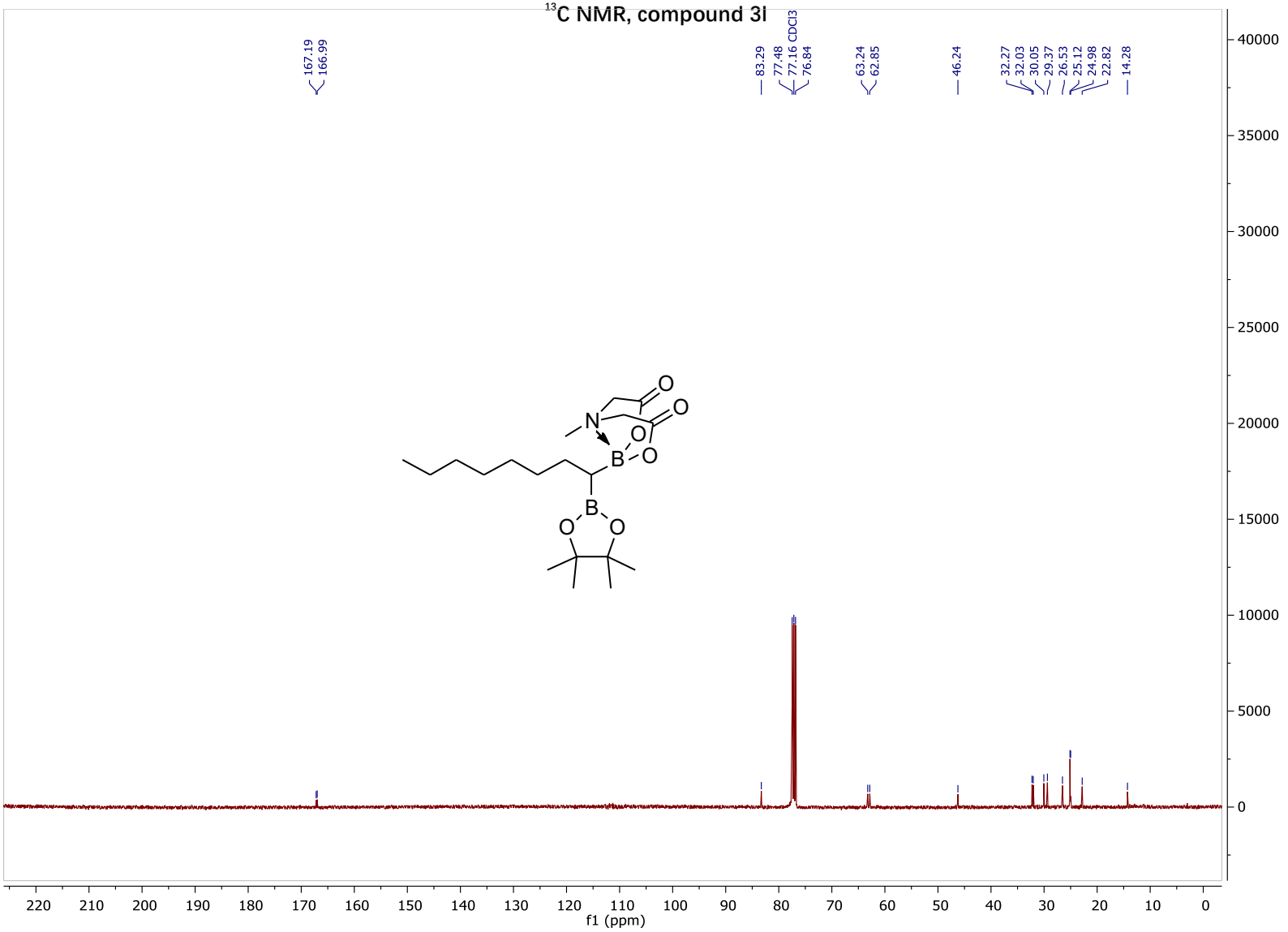

13C NMR, compound 3k
167.70
167.47
83.37
77.48
77.16 CDCl3
76.84
74.19
63.28
62.88
58.45
58.41
46.42
26.28
25.09
24.93
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
N
O
B
O
O
O
B
O
O

^{11}B NMR, compound 3k

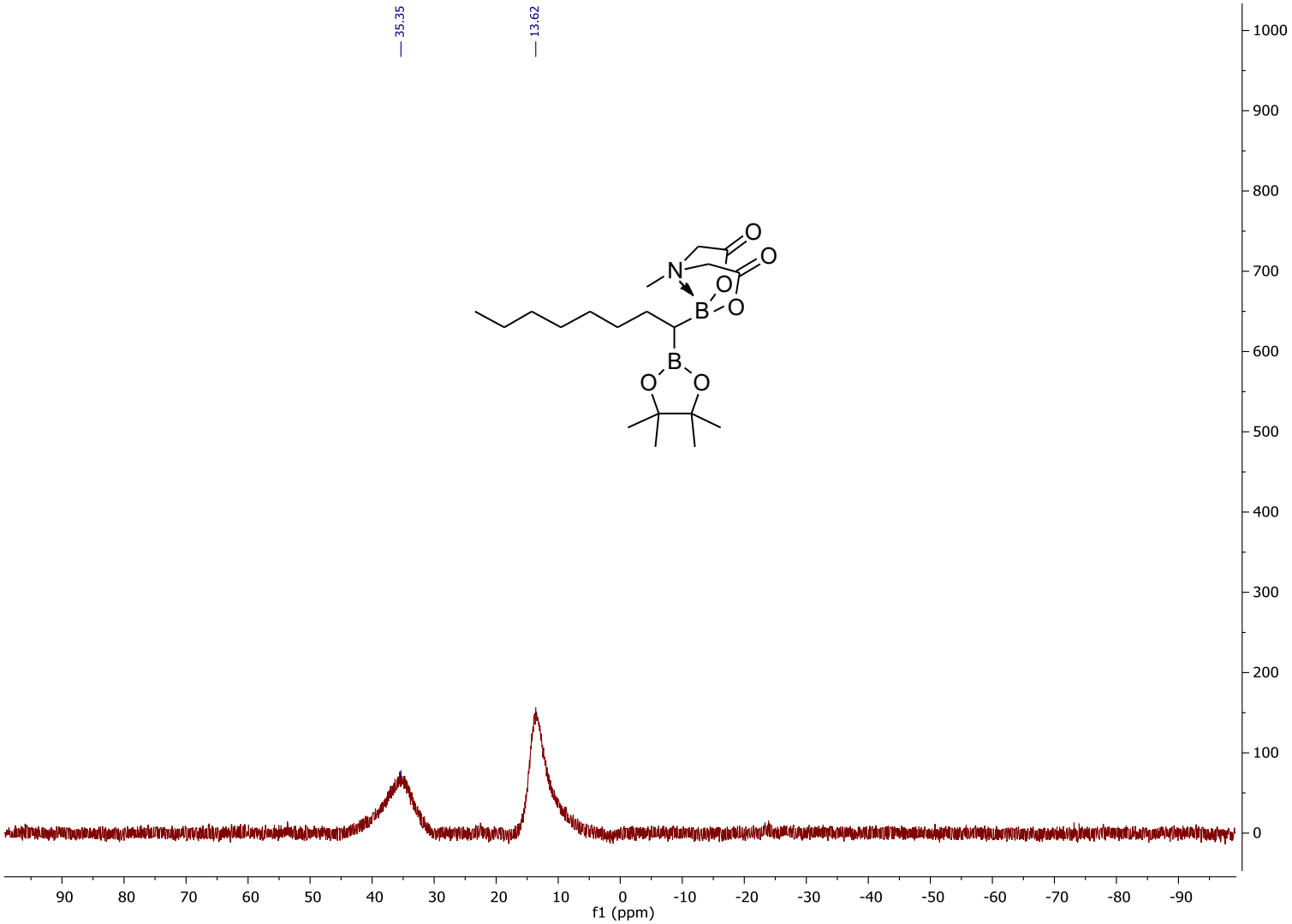


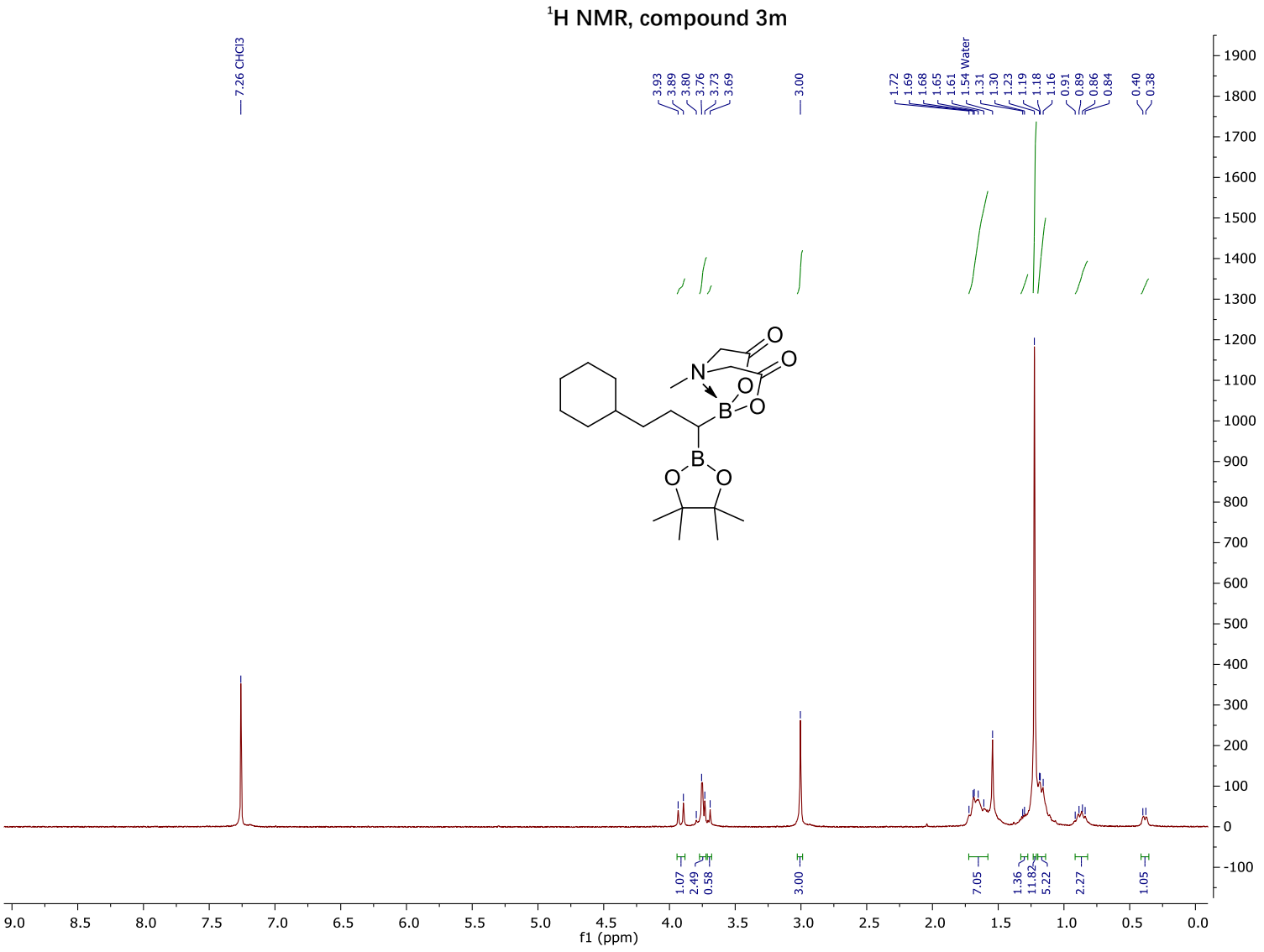
^{1}H NMR, compound 3l

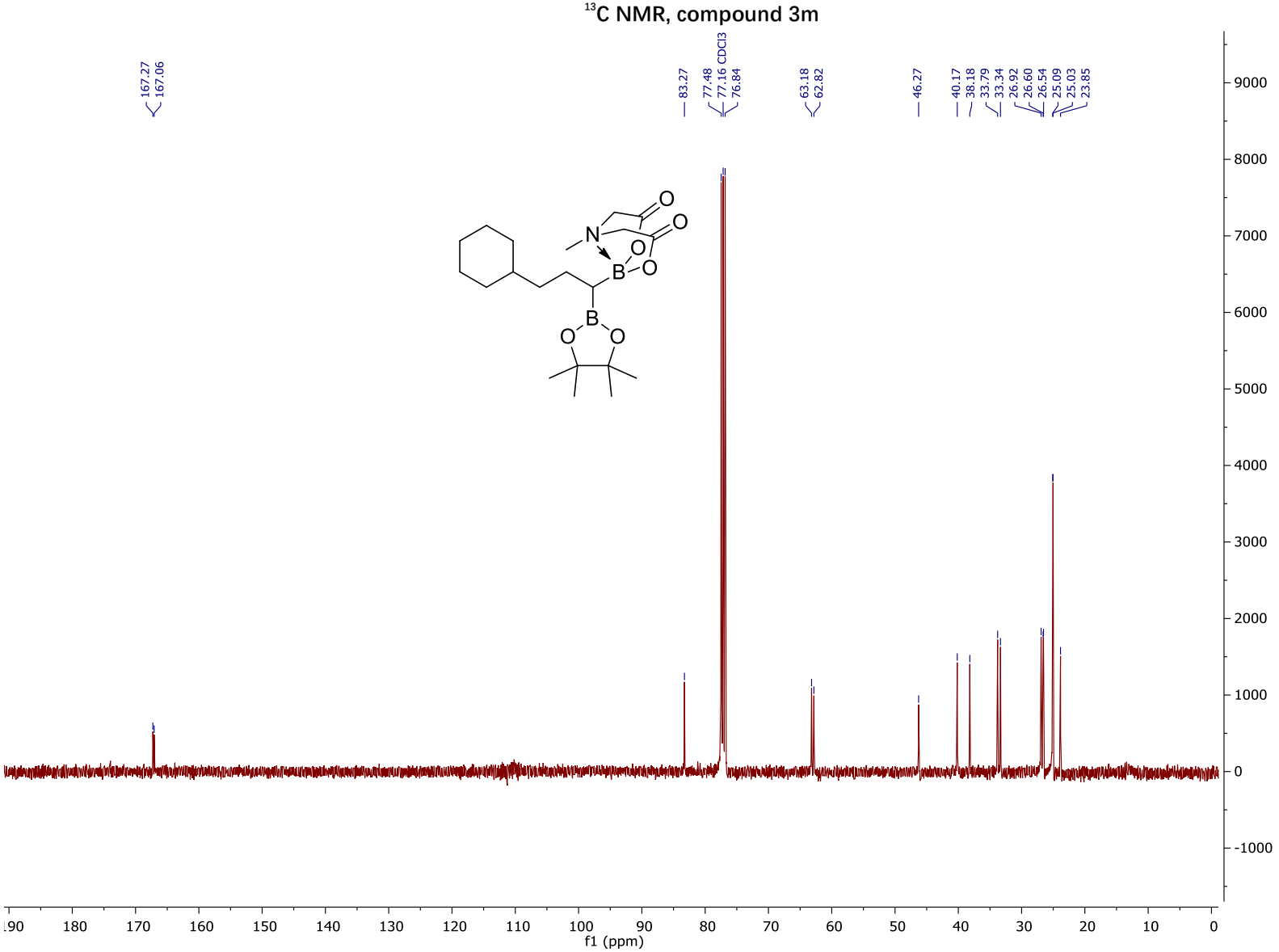



13C NMR, compound 3l
167.19
166.99
83.29
77.48
77.16 CDCl3
76.84
63.24
62.85
46.24
32.27
32.03
30.05
29.37
26.53
25.12
24.98
22.82
14.28
40000
35000
30000
25000
20000
15000
10000
5000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

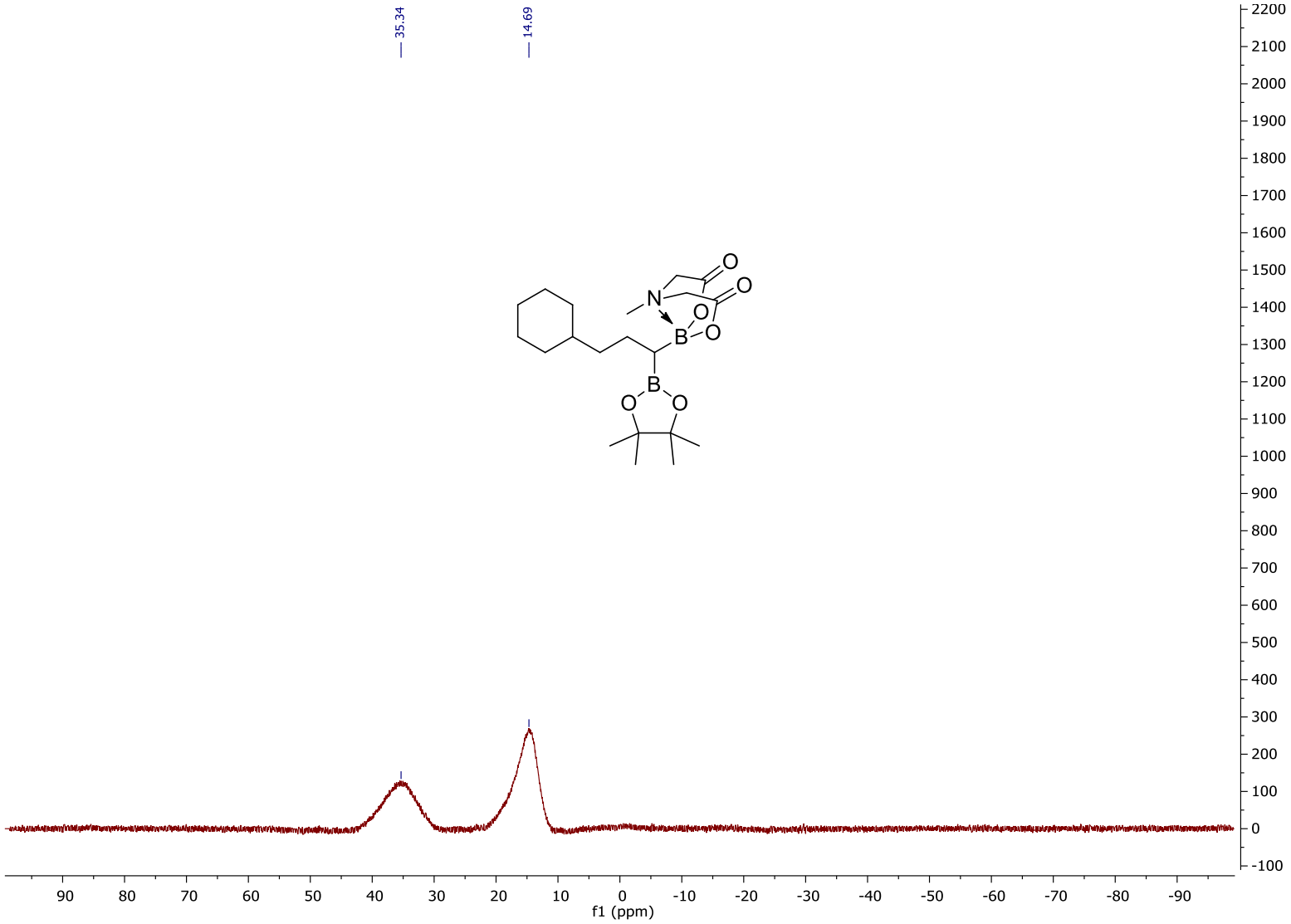
^{11}B NMR, compound 3l

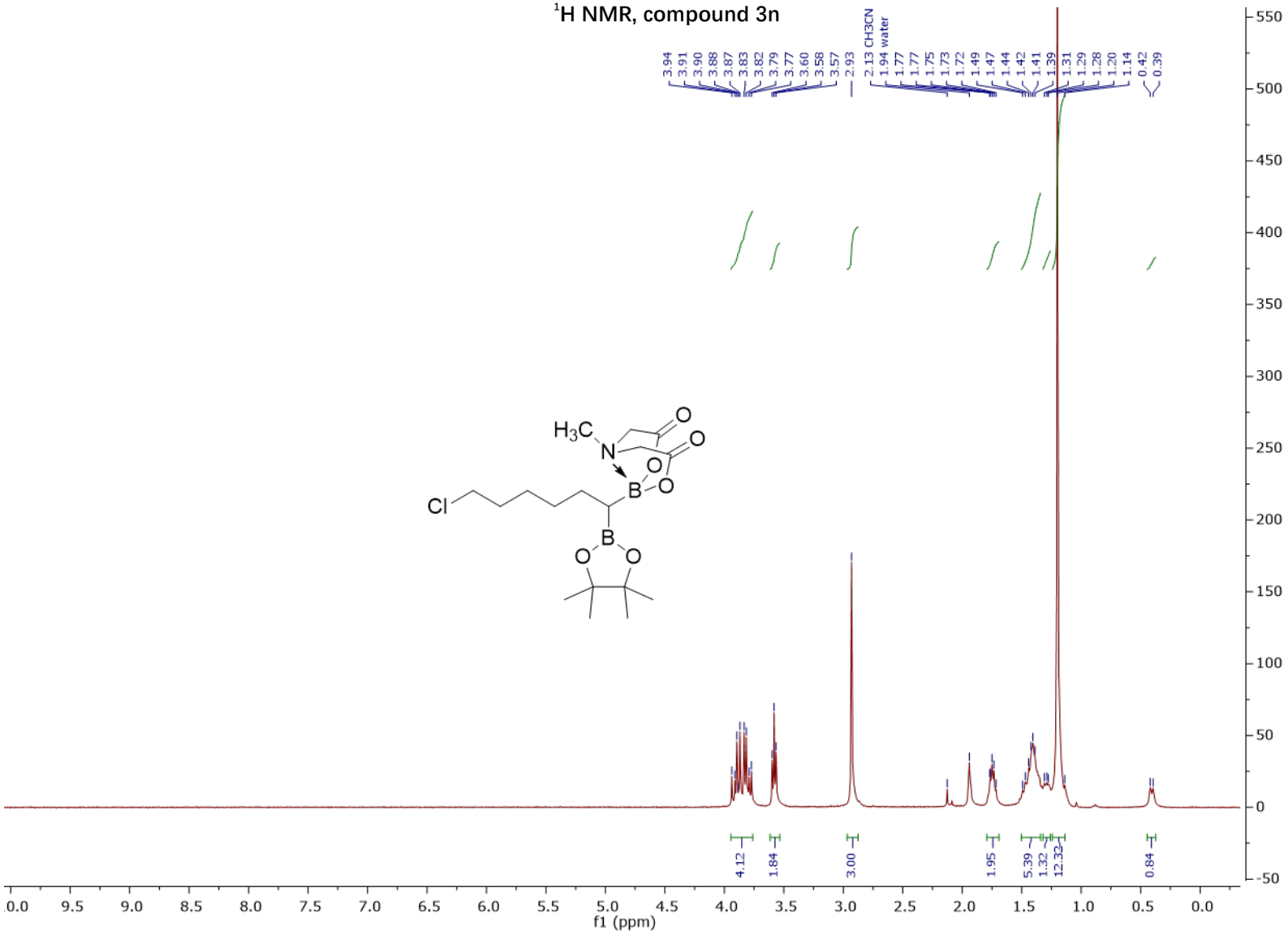


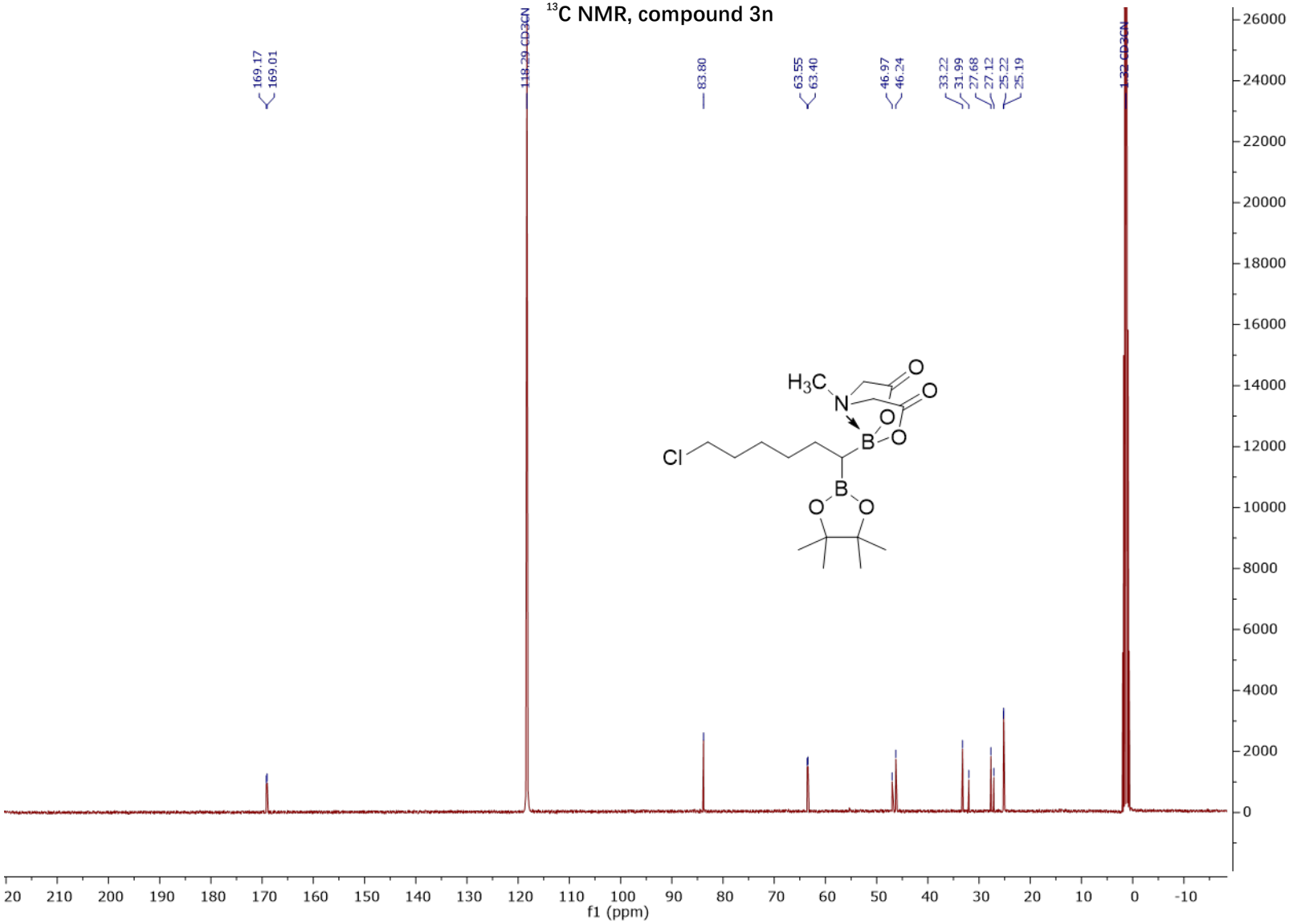

1H NMR, compound 3m
7.26 CHCl3
3.93
3.89
3.80
3.76
3.73
3.69
3.00
1.72
1.69
1.68
1.65
1.61
1.54 Water
1.31
1.30
1.23
1.19
1.18
1.16
0.91
0.89
0.86
0.84
0.40
0.38
1.07
2.49
0.58
3.00
7.05
1.36
11.82
5.22
2.27
1.05
f1 (ppm)


13C NMR, compound 3m
167.27
167.06
83.27
77.48
77.16 CDCl3
76.84
63.18
62.82
46.27
40.17
38.18
33.79
33.34
26.92
26.60
26.54
25.09
25.03
23.85
f1 (ppm)

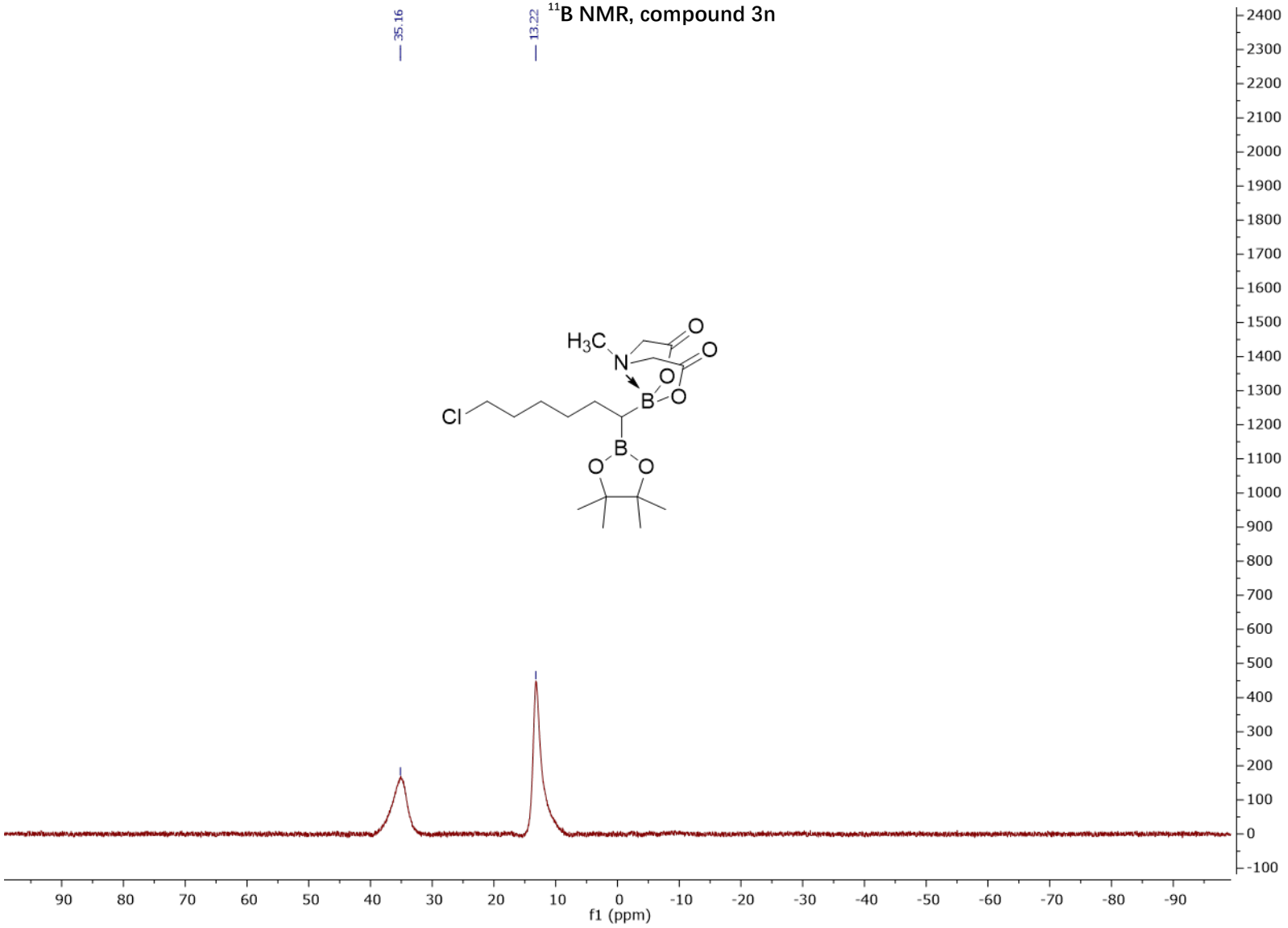
^{11}B NMR, compound 3m

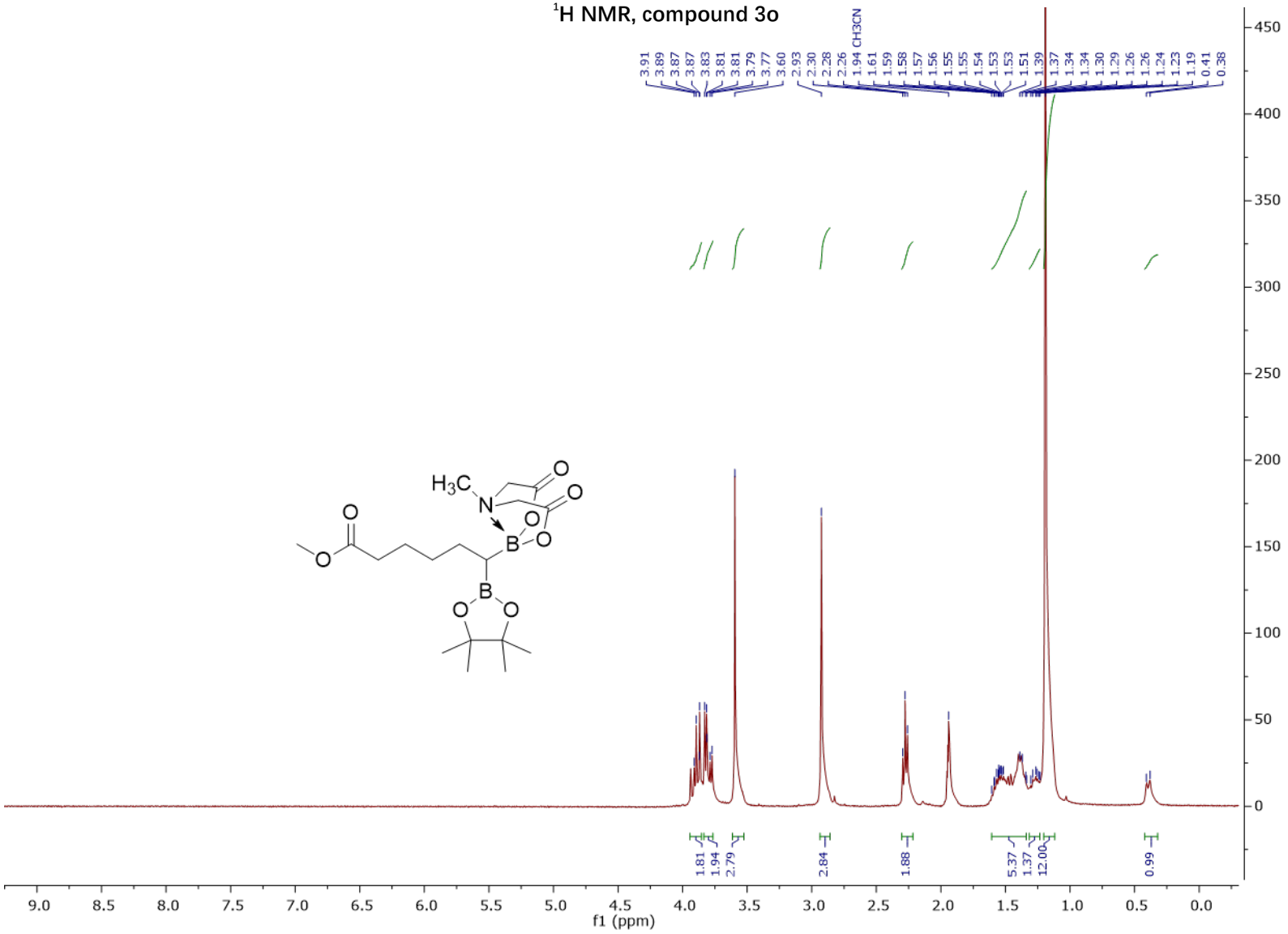



1H NMR, compound 3n
3.94
3.91
3.90
3.88
3.87
3.83
3.82
3.79
3.77
3.60
3.58
3.57
2.93
2.13 CH3CN
1.94 water
1.77
1.77
1.75
1.73
1.72
1.49
1.47
1.44
1.42
1.41
1.39
1.31
1.29
1.28
1.20
1.14
0.42
0.39
H3C
N
O
O
O
O
B
O
Cl
B
O
O
4.12
1.84
3.00
1.95
5.39
1.32
12.32
0.84
f1 (ppm)

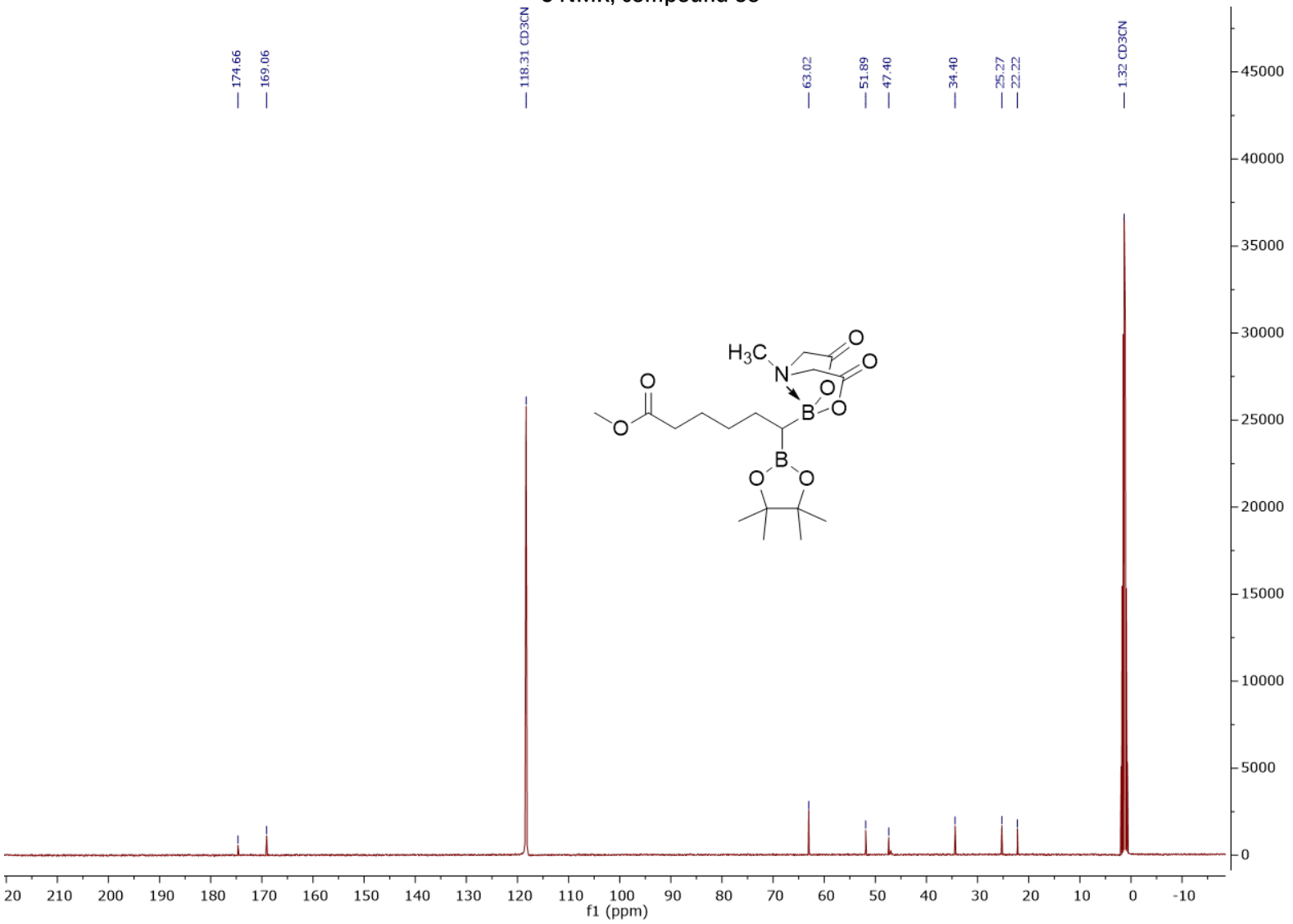

13C NMR, compound 3n
169.17
169.01
118.29 CD3CN
83.80
63.55
63.40
46.97
46.24
33.22
31.99
27.68
27.12
25.22
25.19
1.32 CD3CN
H3C
N
O
O
O
B
O
Cl
B
O
O
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{11}B NMR, compound 3n

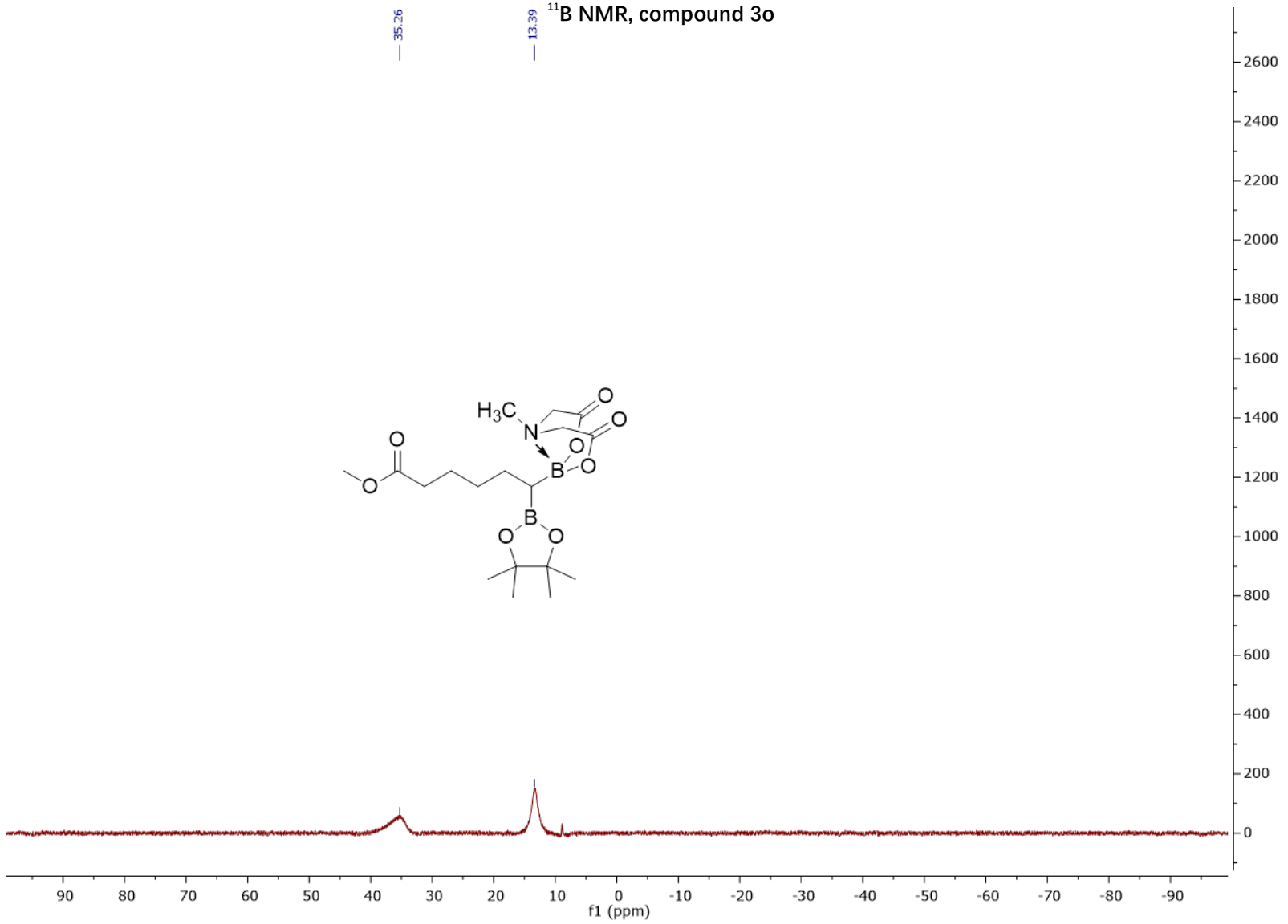



1H NMR, compound 3o
CH3CN
f1 (ppm)

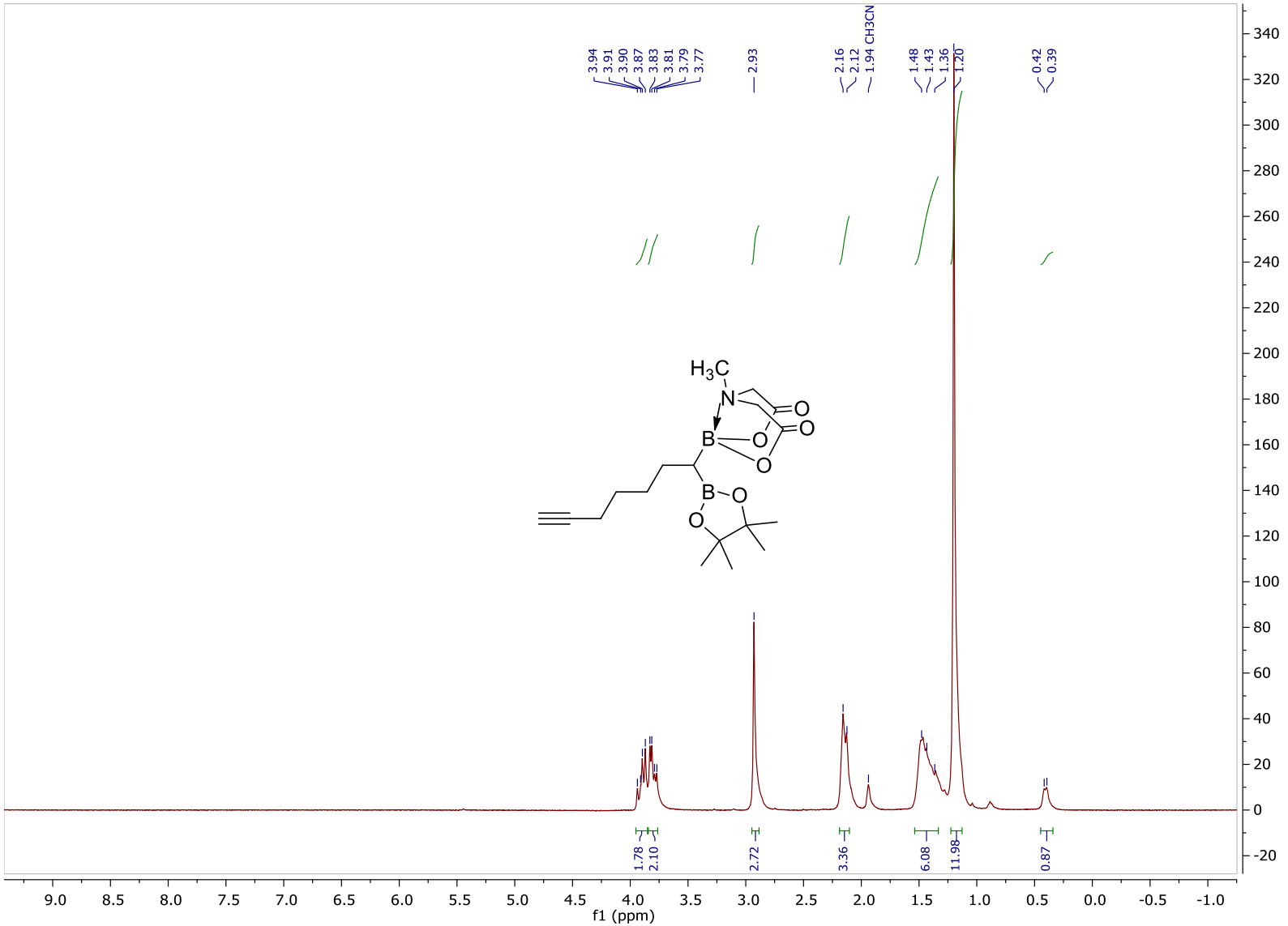
^{13}C NMR, compound 3o



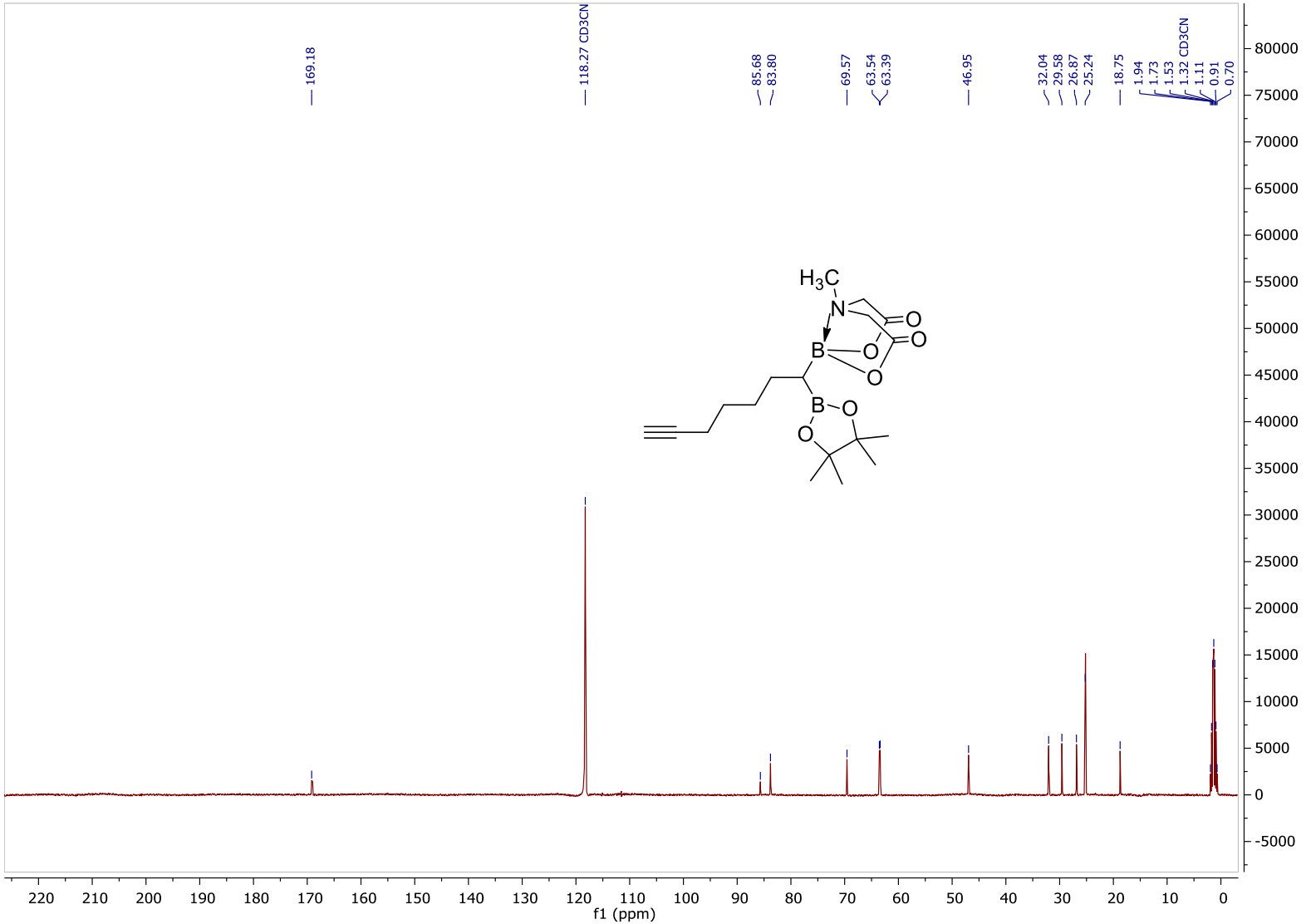
^{11}B NMR, compound 3o



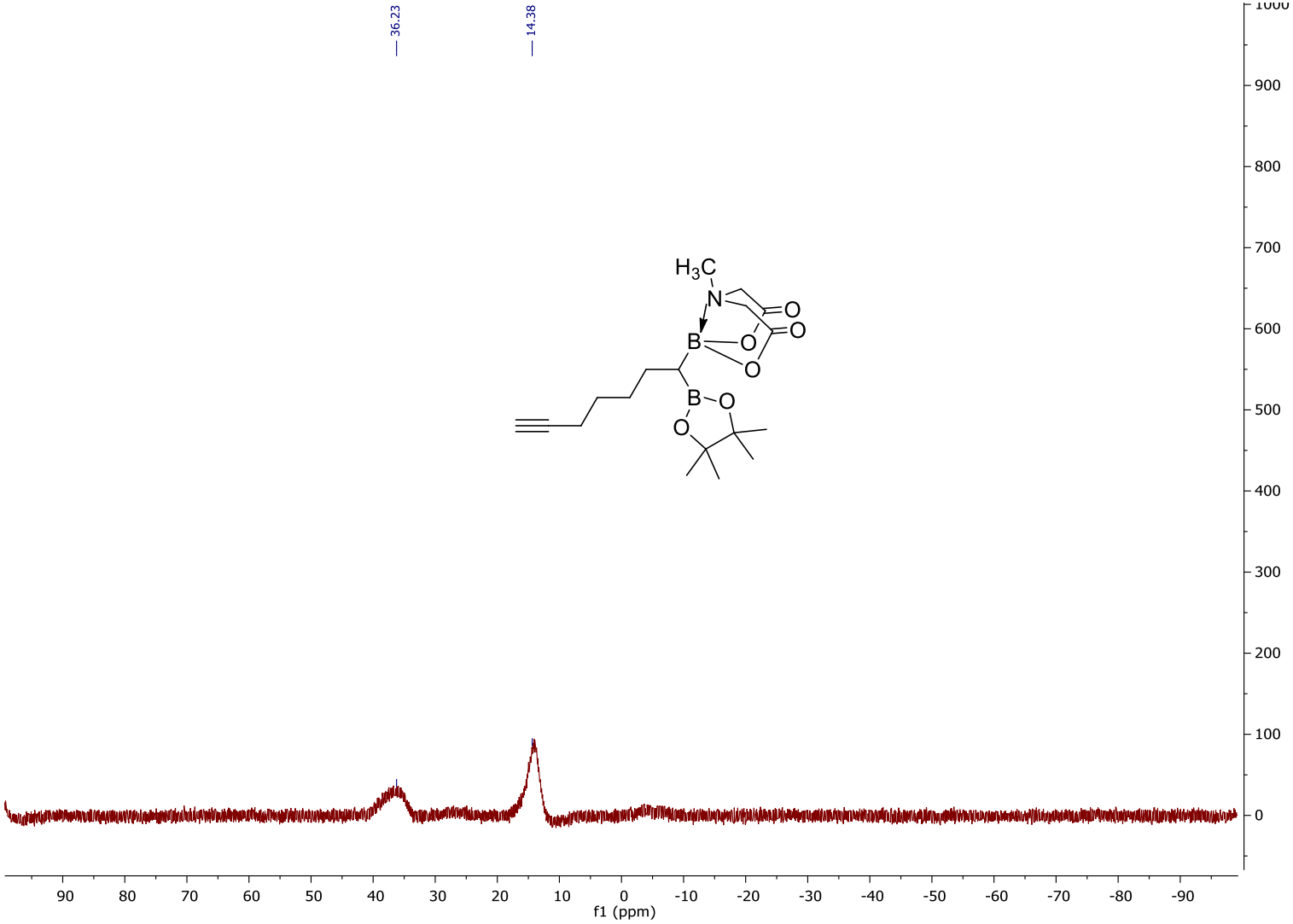
^{1}H NMR, compound 3p



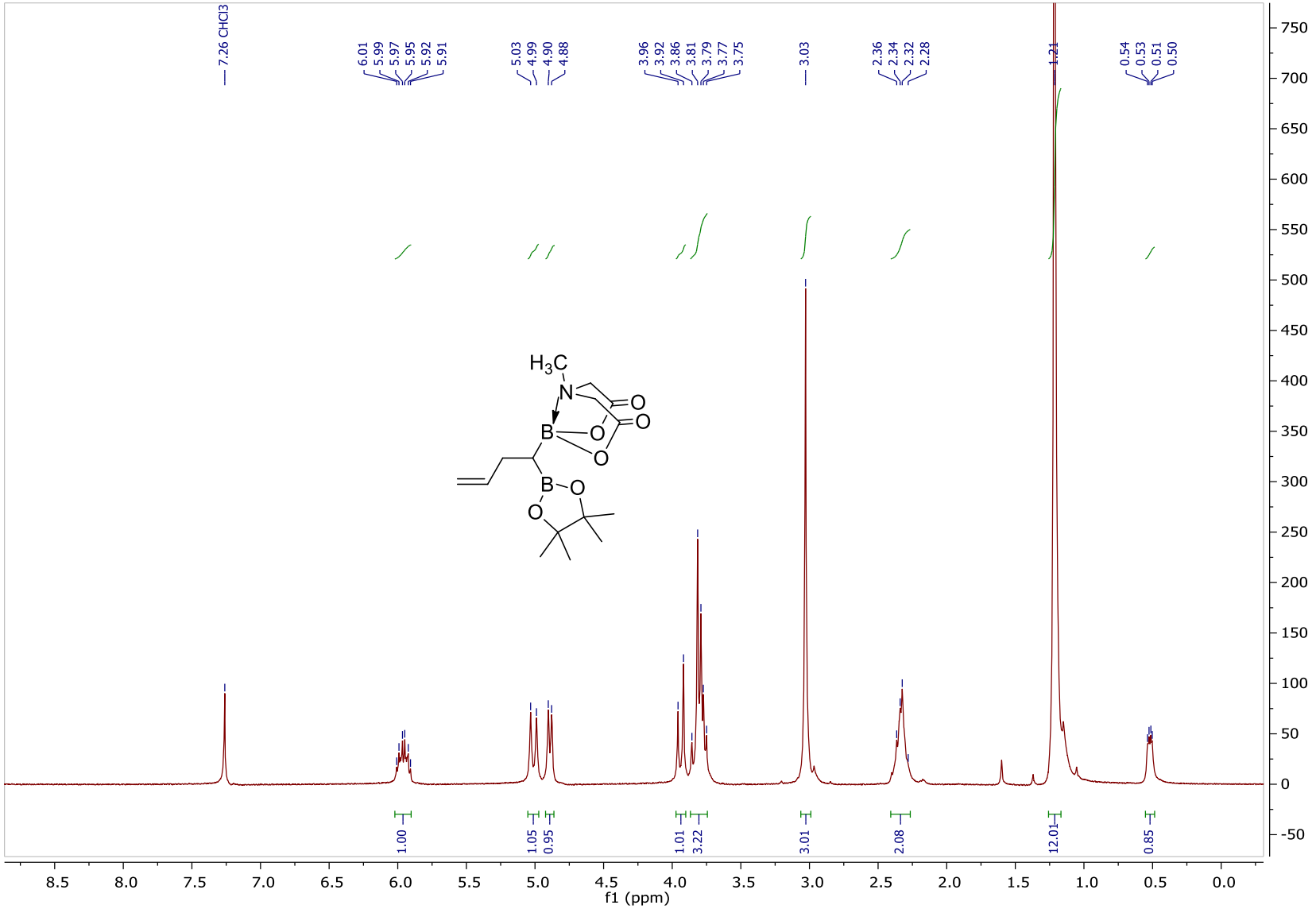
^{13}C NMR, compound 3p



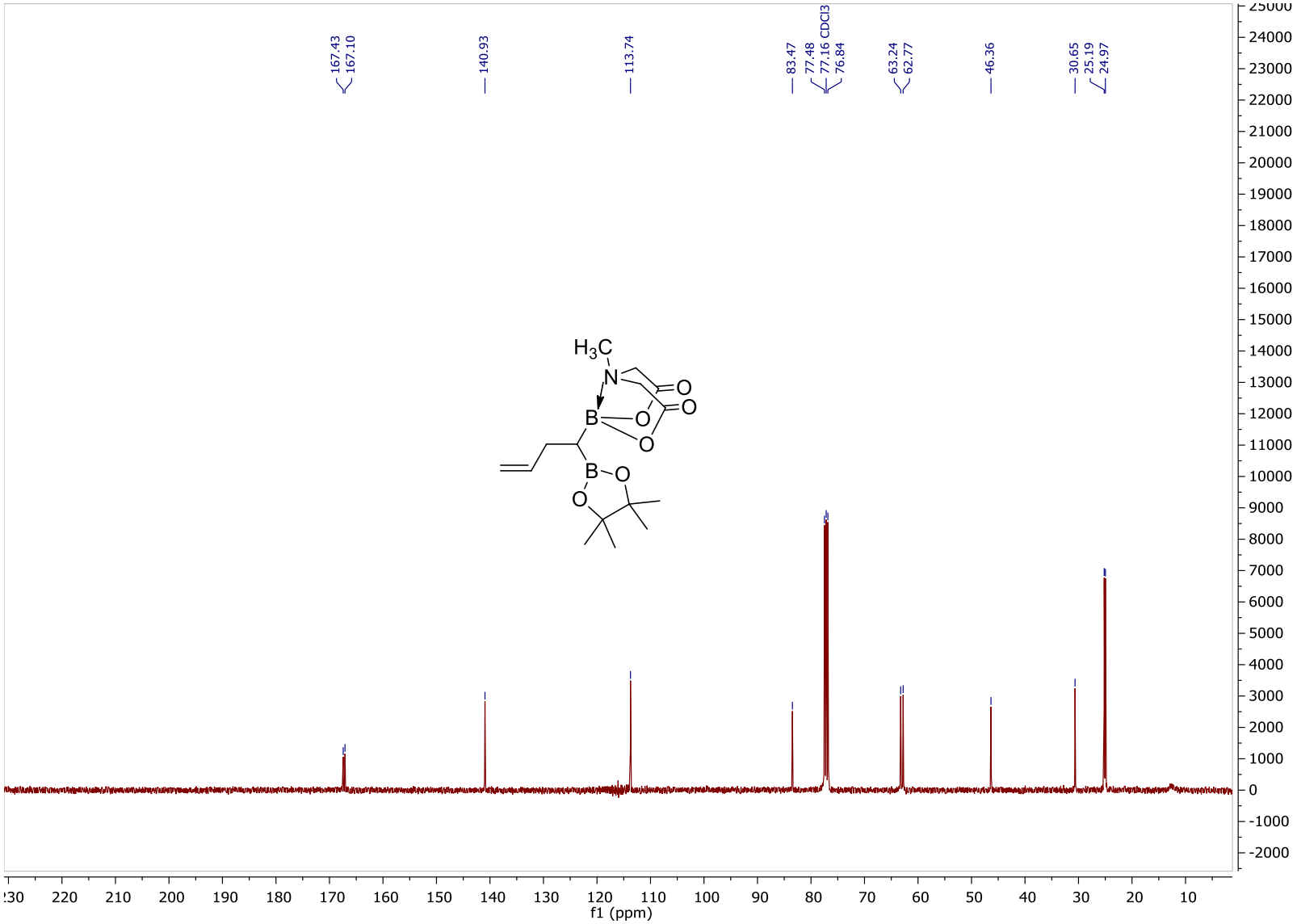
^{11}B NMR, compound 3p



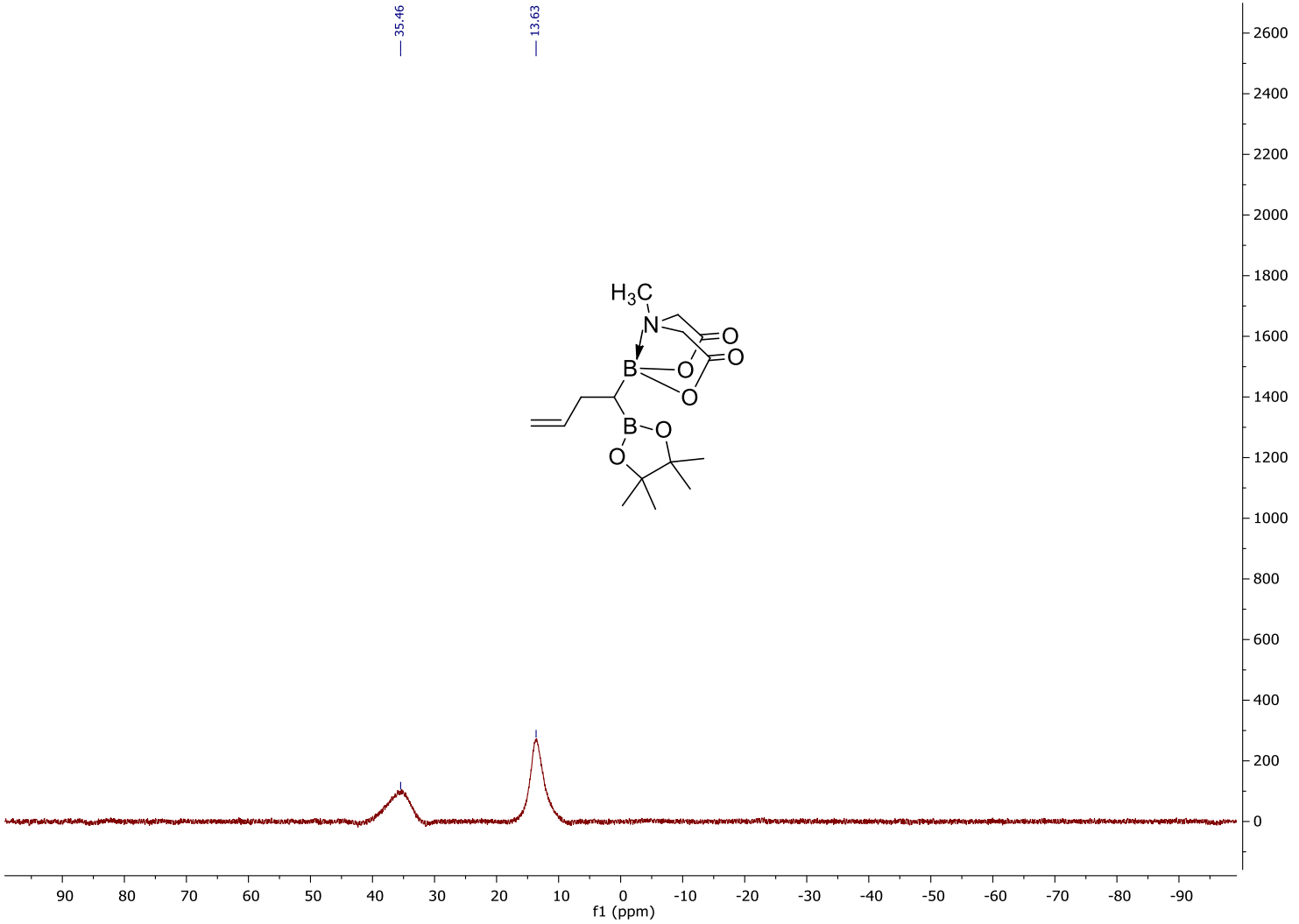
^{1}H NMR, compound 3q

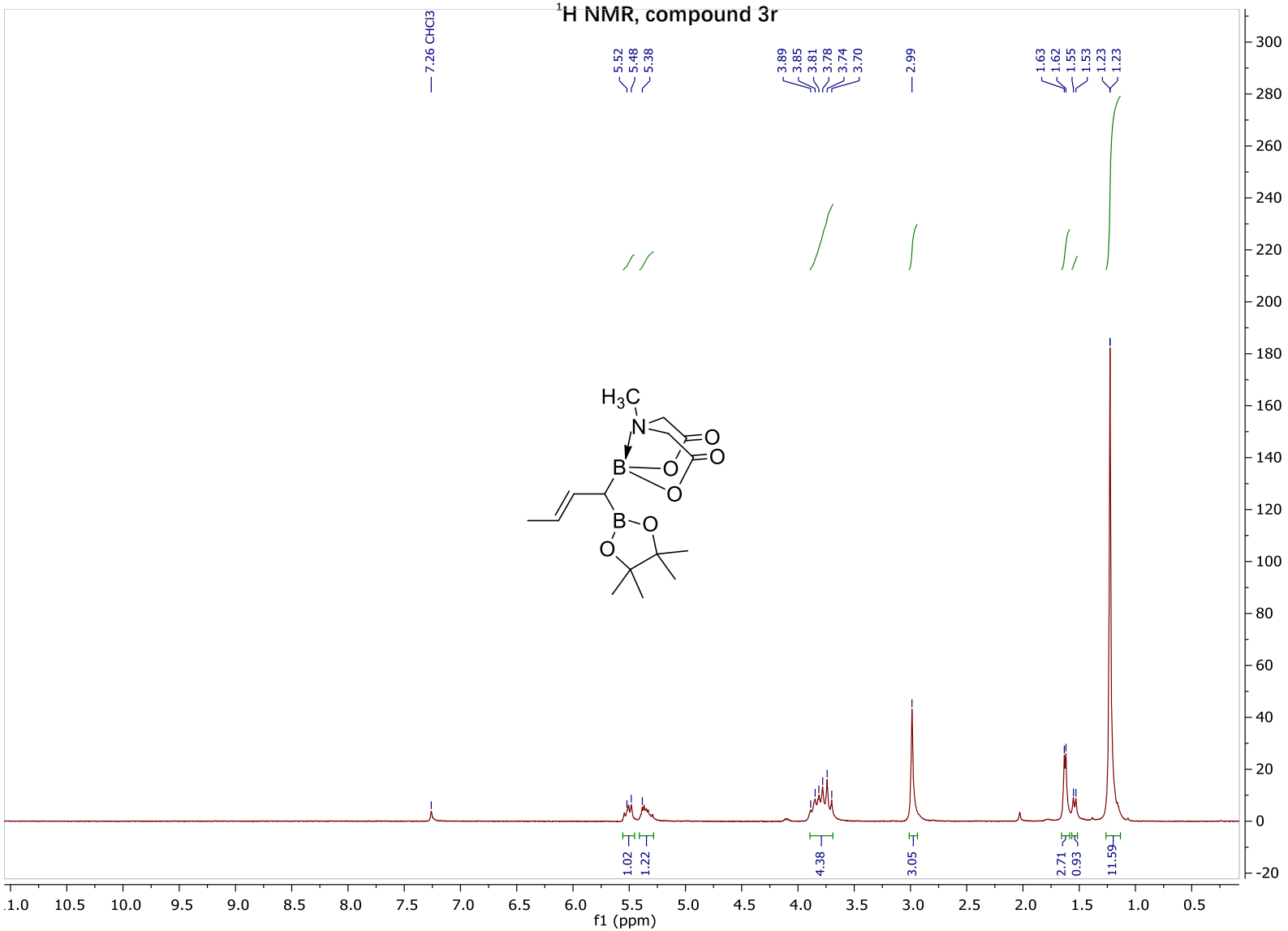


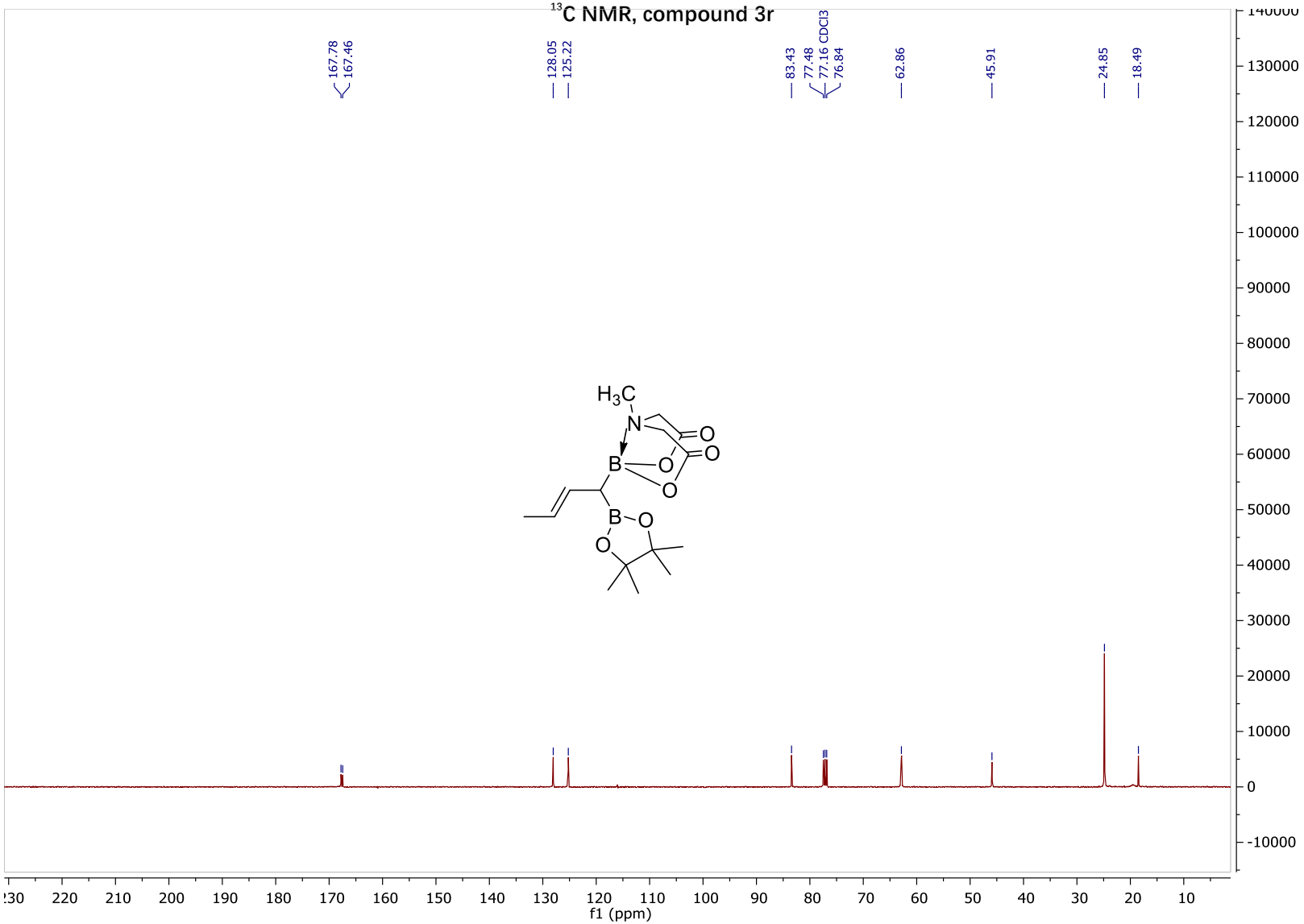
^{13}C NMR, compound 3q



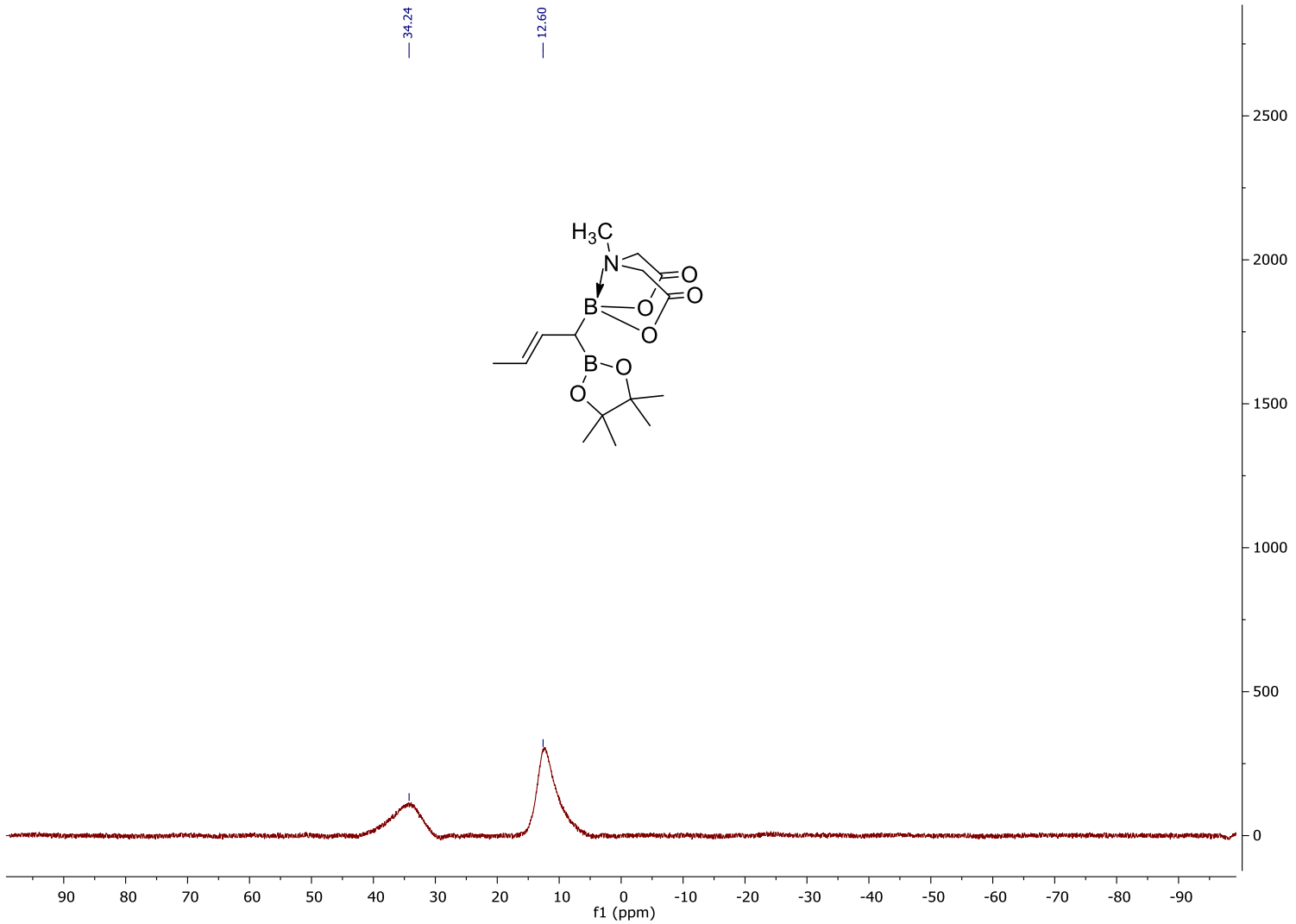
^{11}B NMR, compound 3q

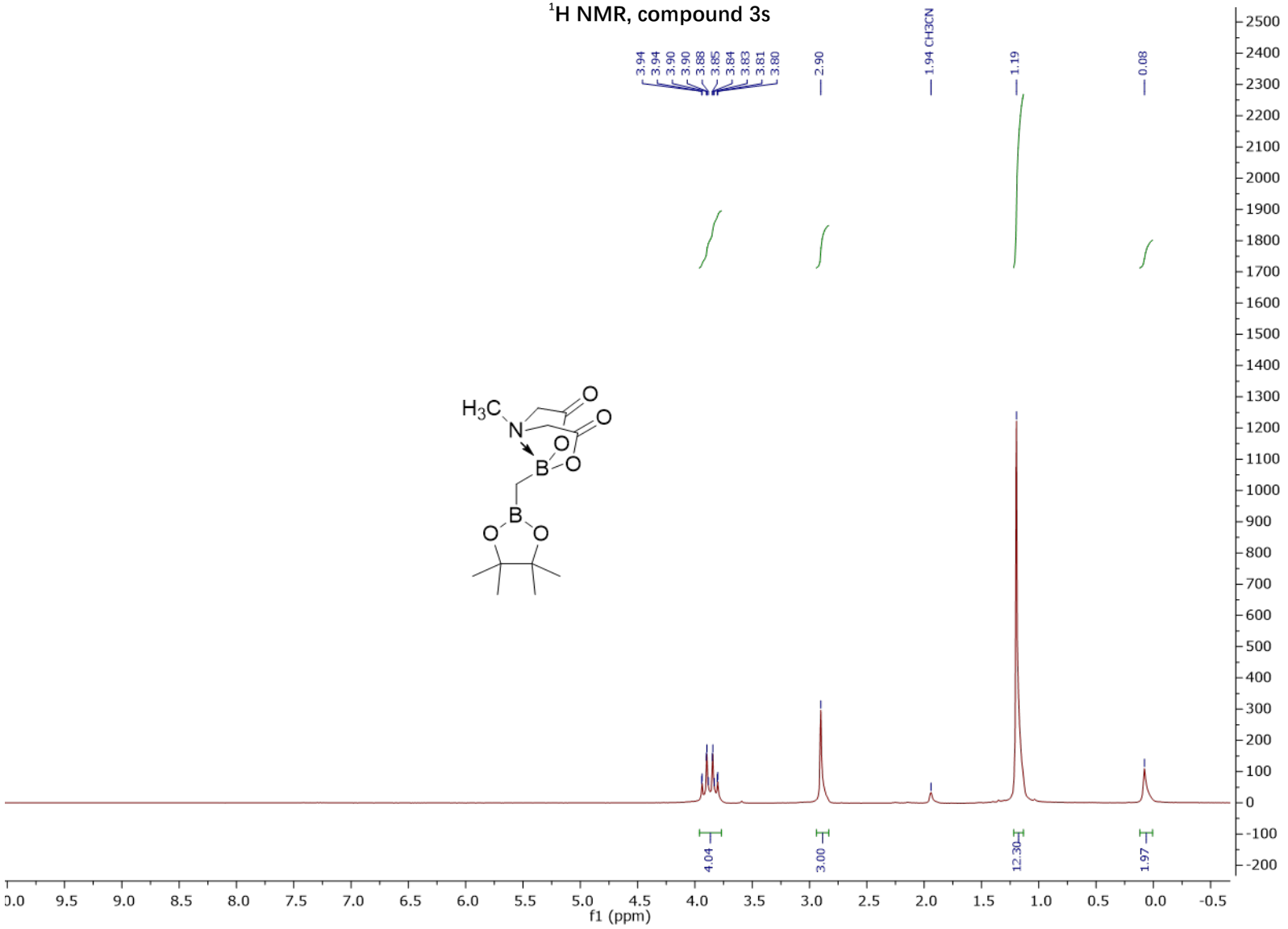


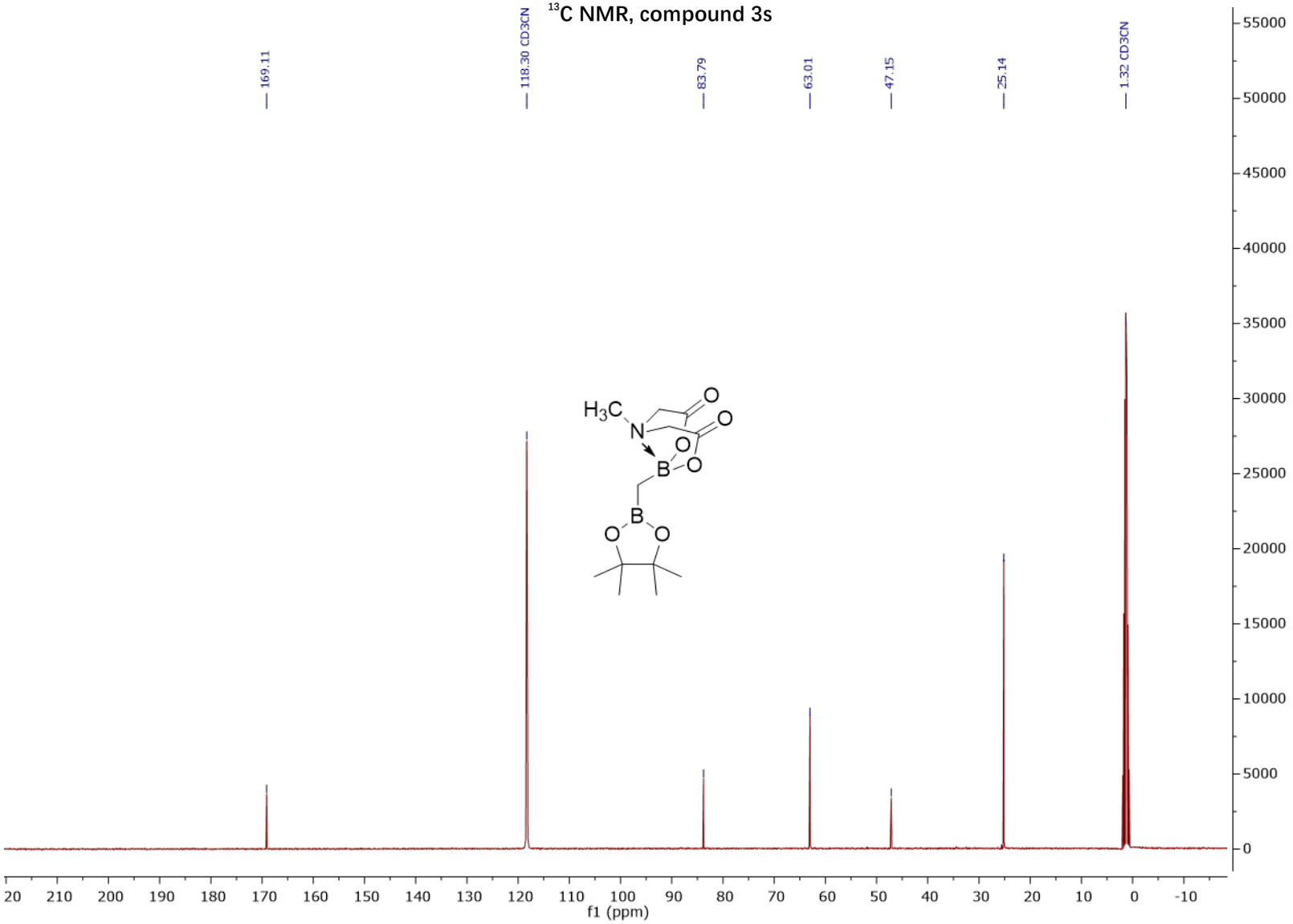

1H NMR, compound 3r
7.26 CHCl3
5.52
5.48
5.38
3.89
3.85
3.81
3.78
3.74
3.70
2.99
1.63
1.62
1.55
1.53
1.23
1.23
H3C
N
B
O
O
O
O
B
O
O
1.02
1.22
4.38
3.05
2.71
0.93
11.59
f1 (ppm)


13C NMR, compound 3r
167.78
167.46
128.05
125.22
83.43
77.48
77.16 CDCl3
76.84
62.86
45.91
24.85
18.49
H3C
N
B
O
B
O
O
f1 (ppm)

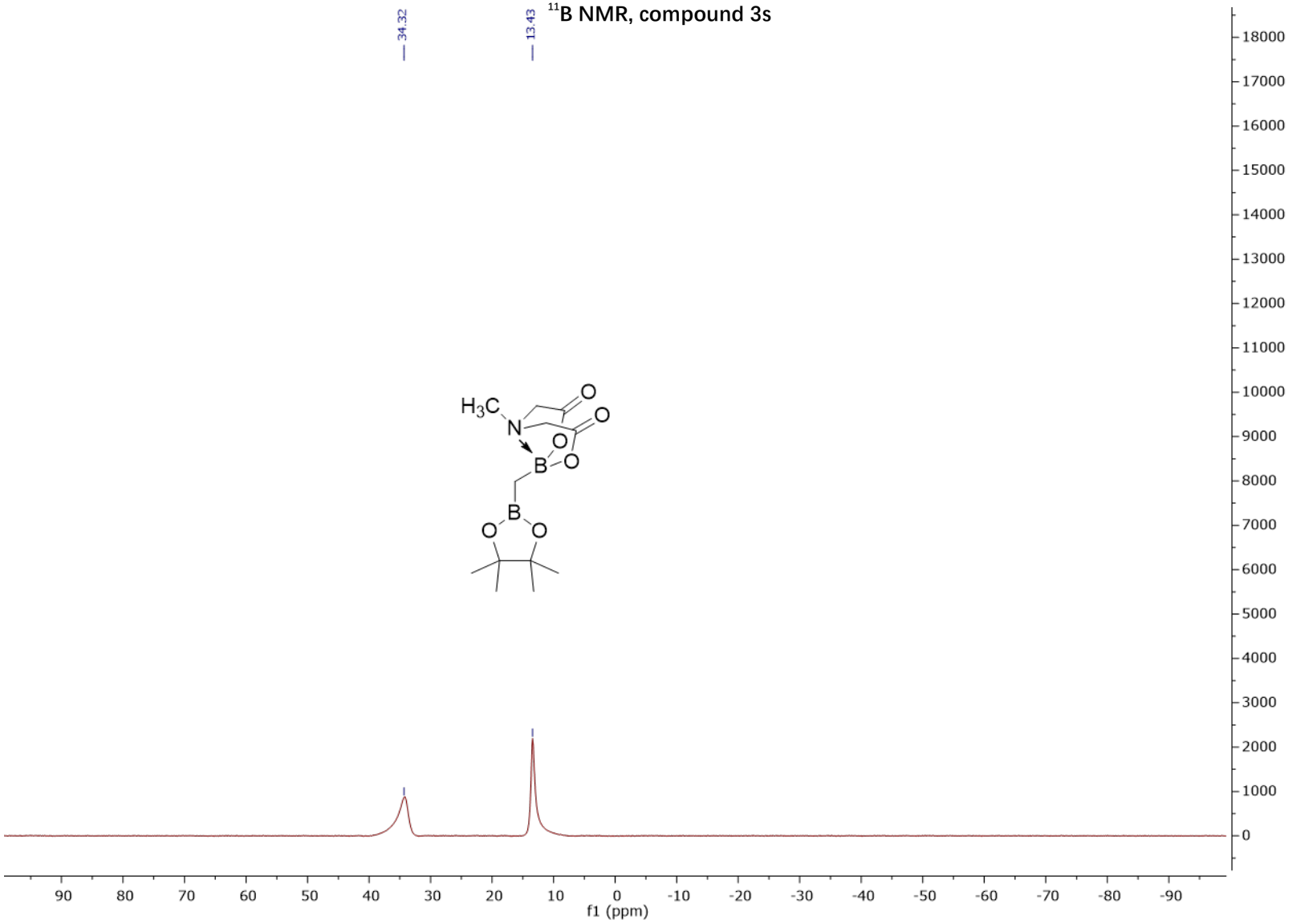
^{11}B NMR, compound 3r

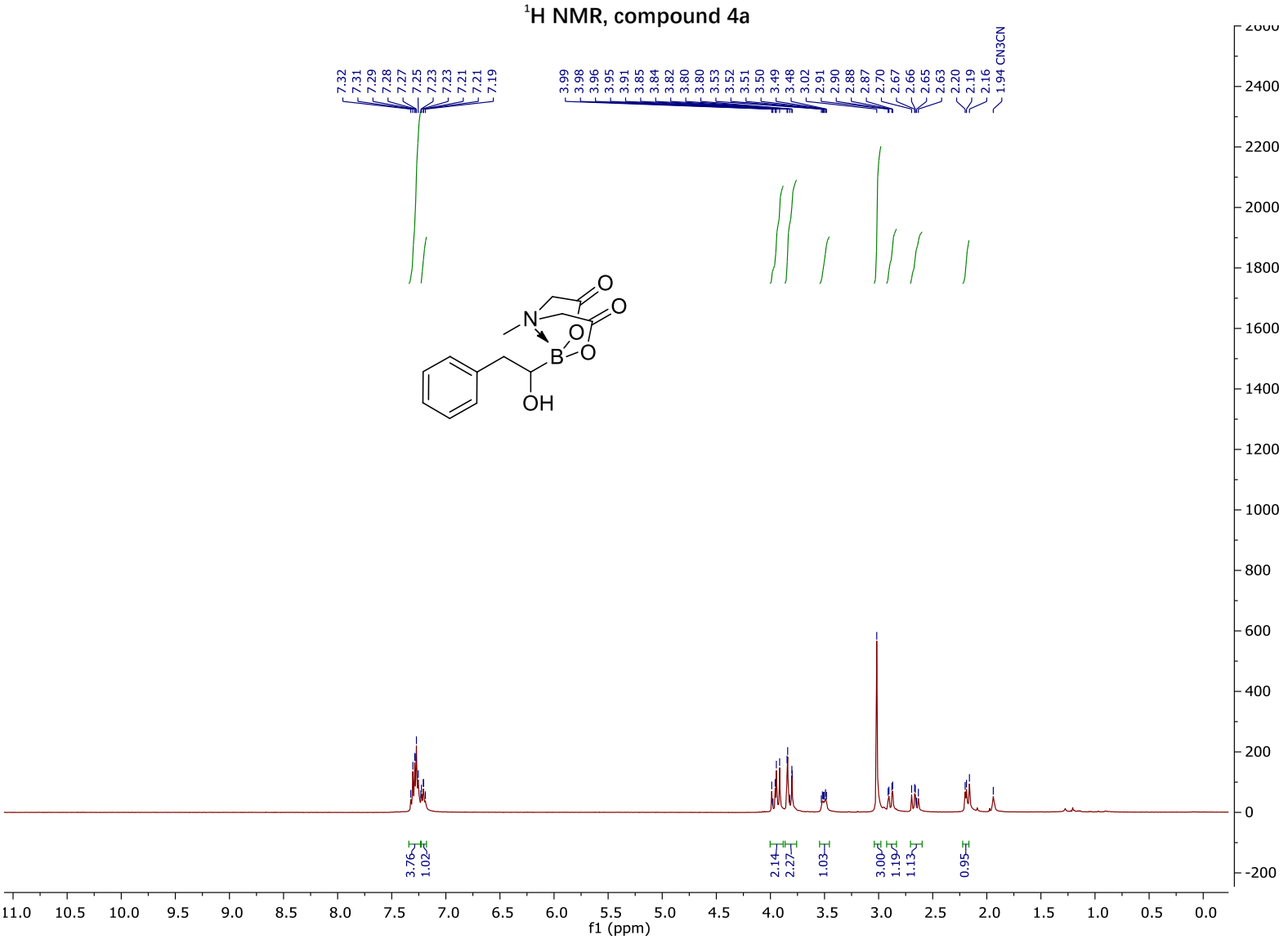



1H NMR, compound 3s
3.94
3.94
3.90
3.90
3.88
3.85
3.84
3.83
3.81
3.80
2.90
1.94 CH3CN
1.19
0.08
H3C
N
O
O
O
B
O
B
O
O
4.04
3.00
12.30
1.97
f1 (ppm)

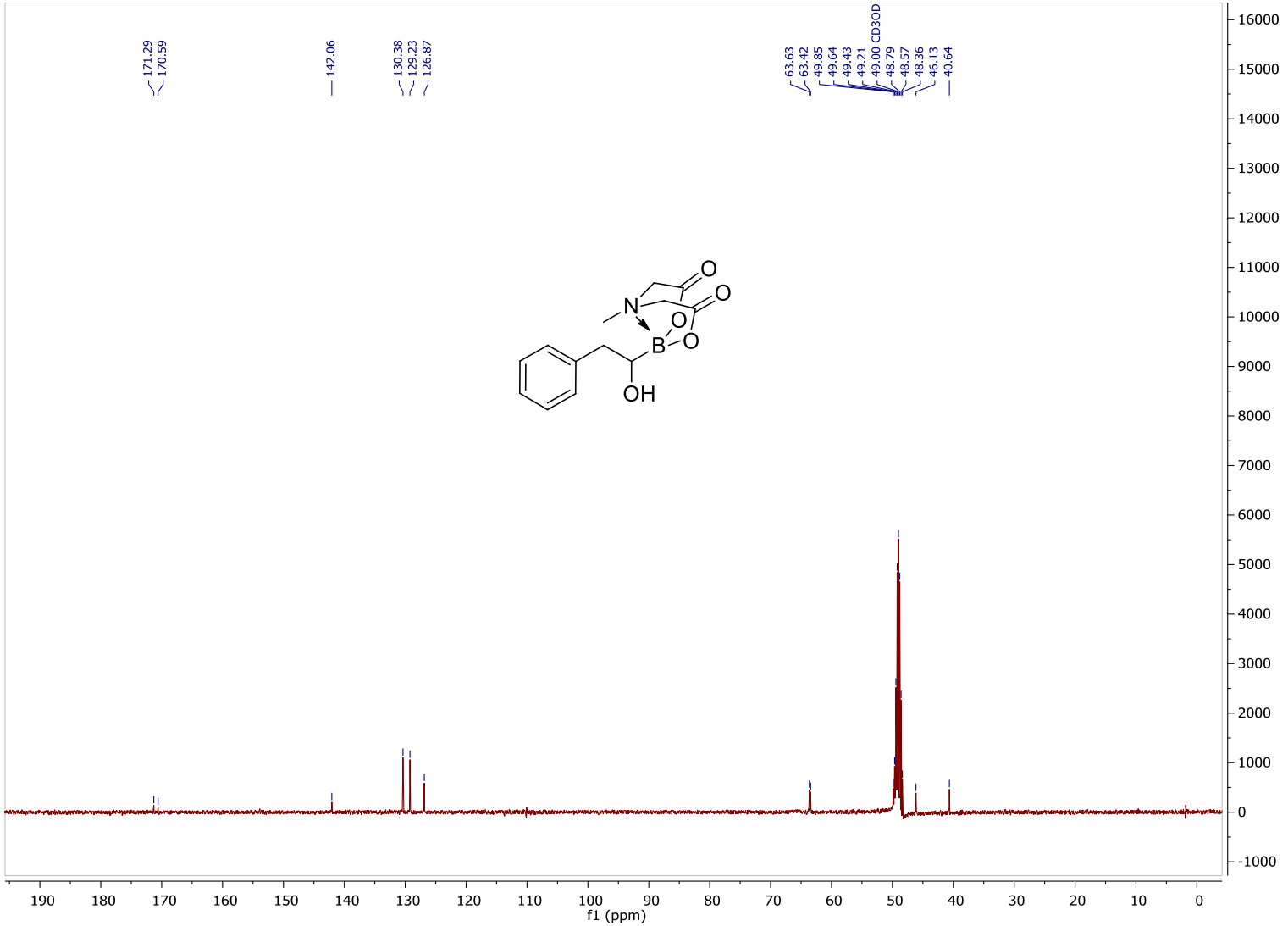

^{13}C NMR, compound 3s
169.11
118.30 CD3CN
83.79
63.01
47.15
25.14
1.32 CD3CN
H3C
N
O
O
O
B
O
B
O
O
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{11}B NMR, compound 3s

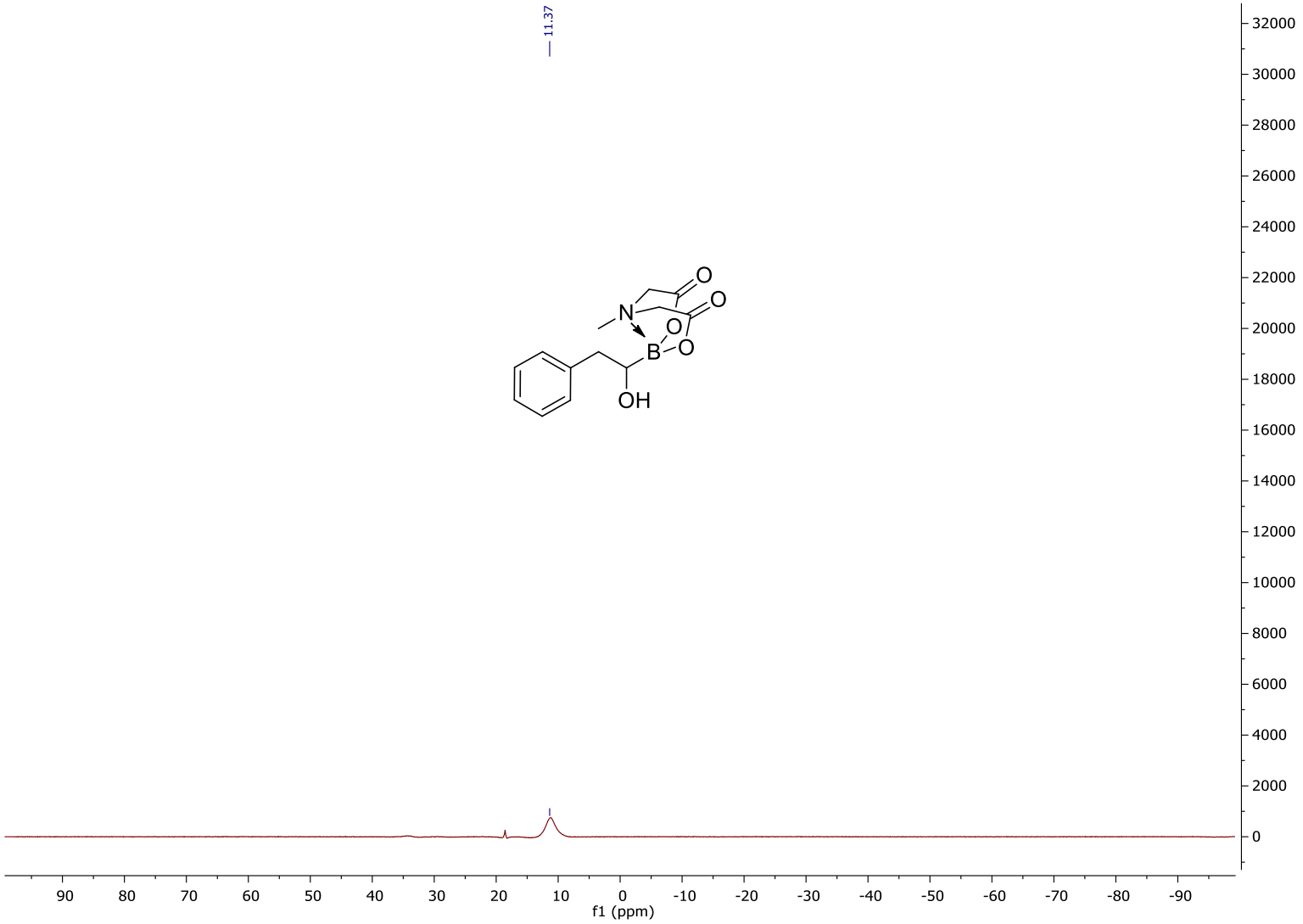


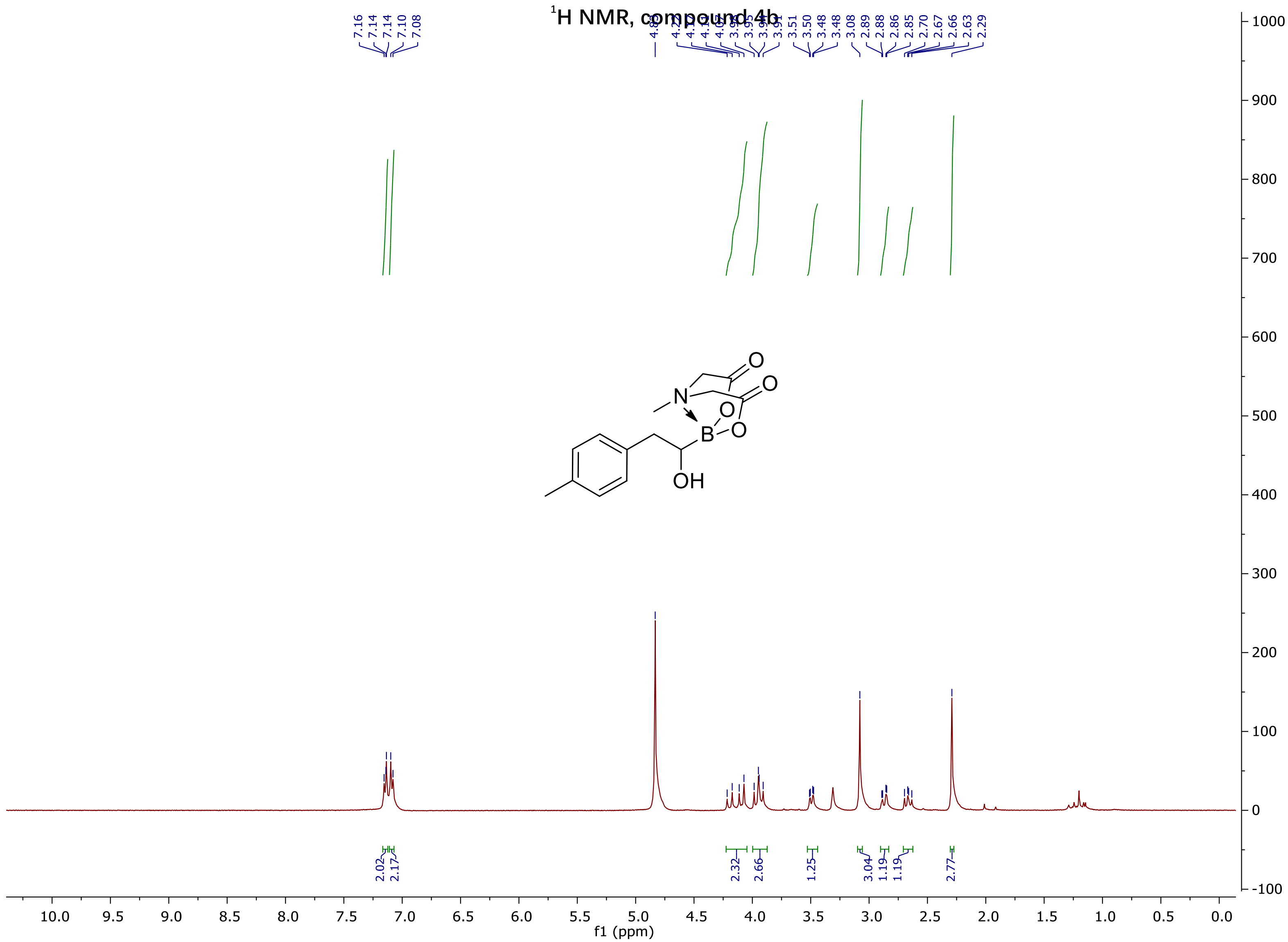

1H NMR, compound 4a
7.32
7.31
7.29
7.28
7.27
7.25
7.23
7.23
7.21
7.21
7.19
3.99
3.98
3.96
3.95
3.91
3.85
3.84
3.82
3.80
3.80
3.53
3.52
3.51
3.50
3.49
3.48
3.02
2.91
2.90
2.88
2.87
2.70
2.67
2.66
2.65
2.63
2.20
2.19
2.16
1.94 CN3CN
O
O
N
O
B
O
OH
3.76
1.02
2.14
2.27
1.03
3.00
1.19
1.13
0.95
f1 (ppm)

^{13}C NMR, compound 4a

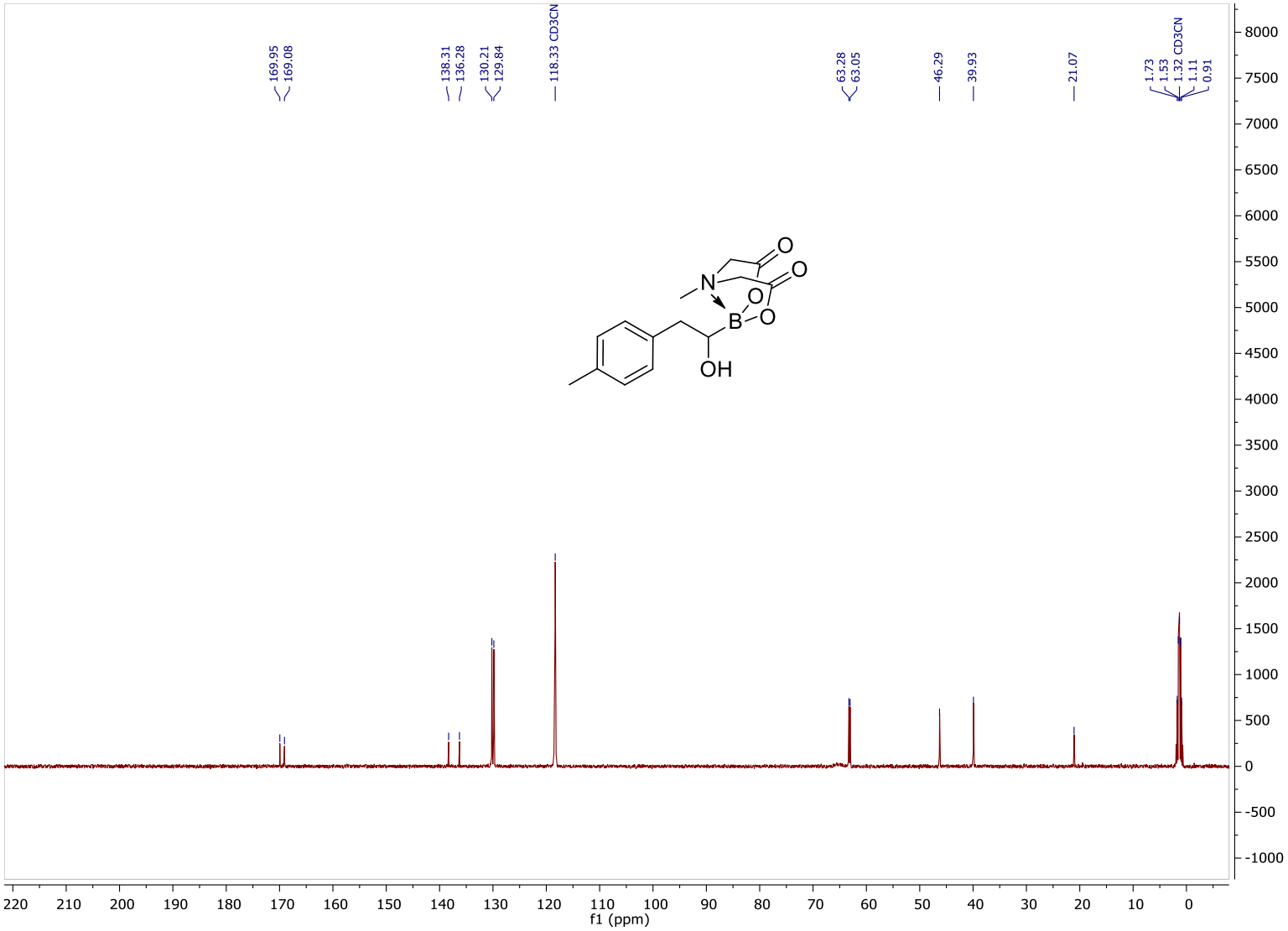


^{11}B NMR, compound 4a

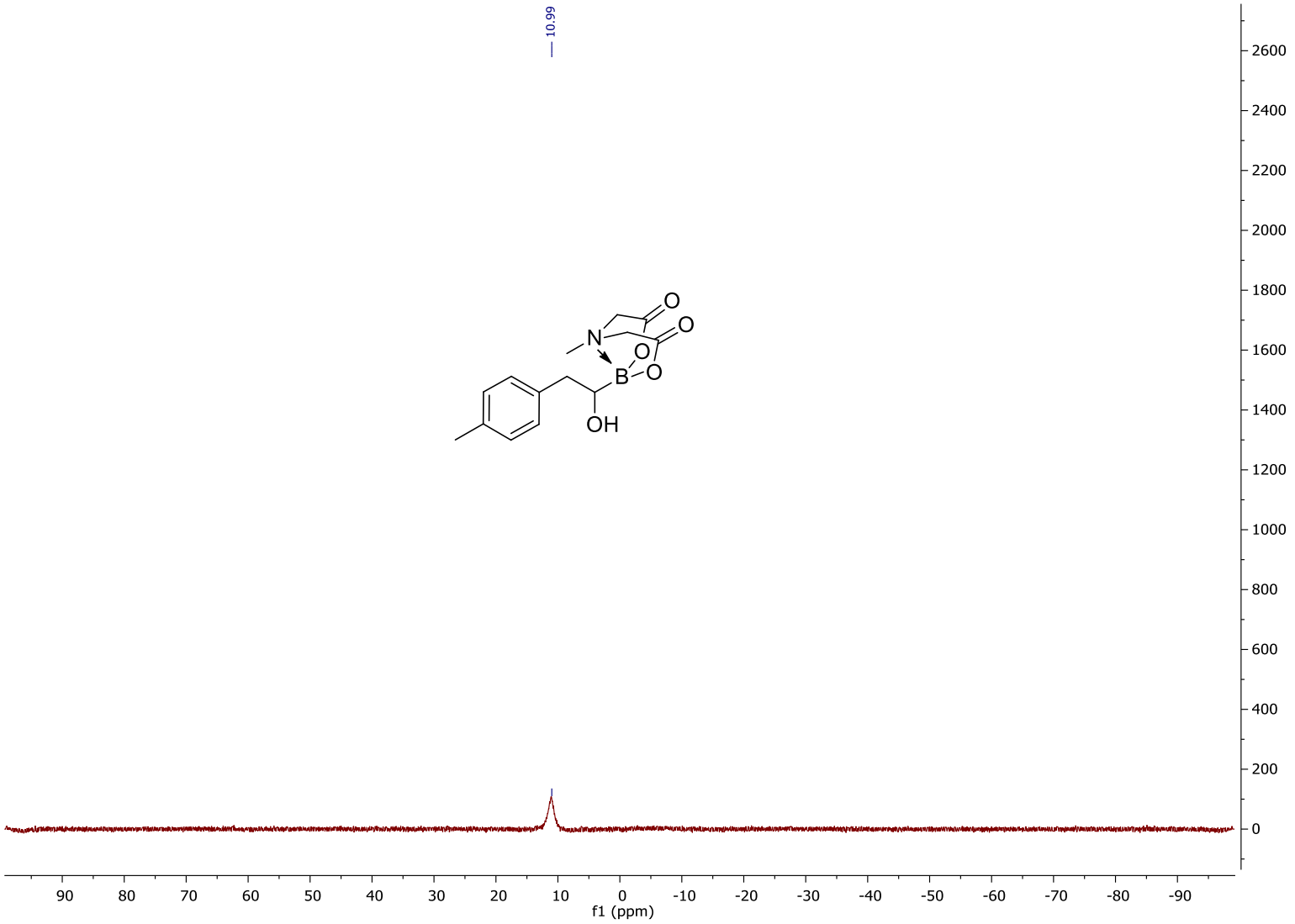


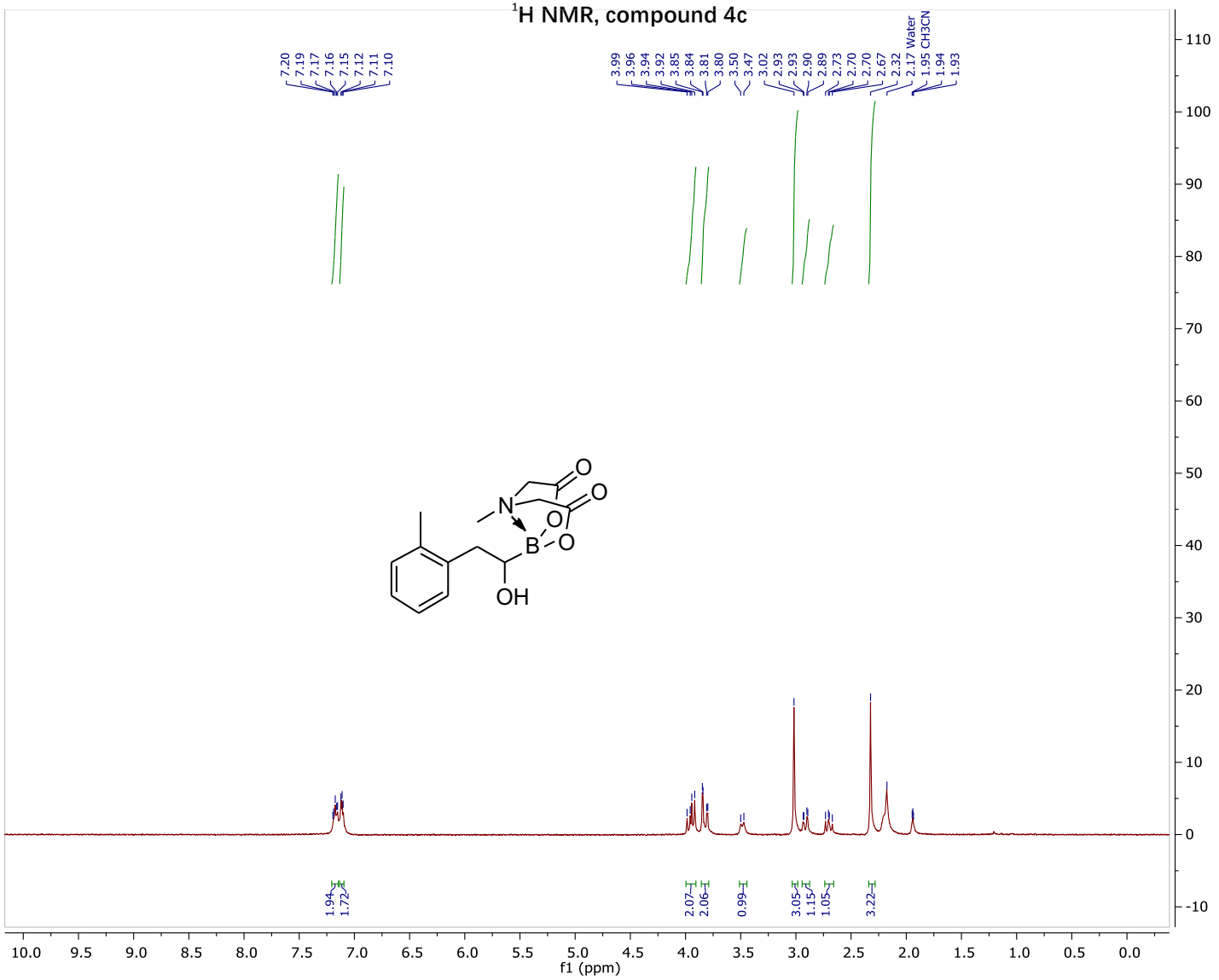

1H NMR, compound 4b
OH
B
N
O
f1 (ppm)

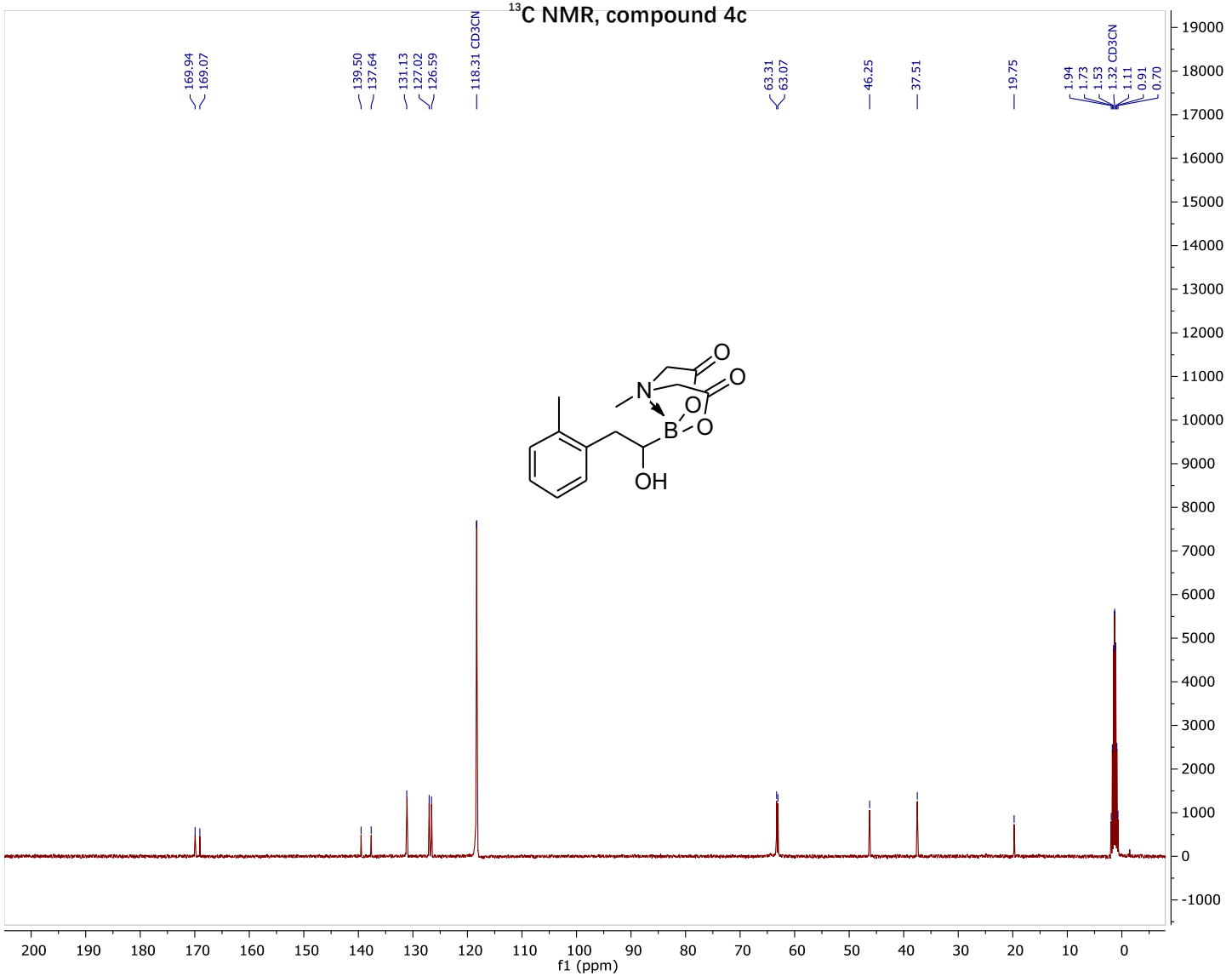
^{13}C NMR, compound 4b



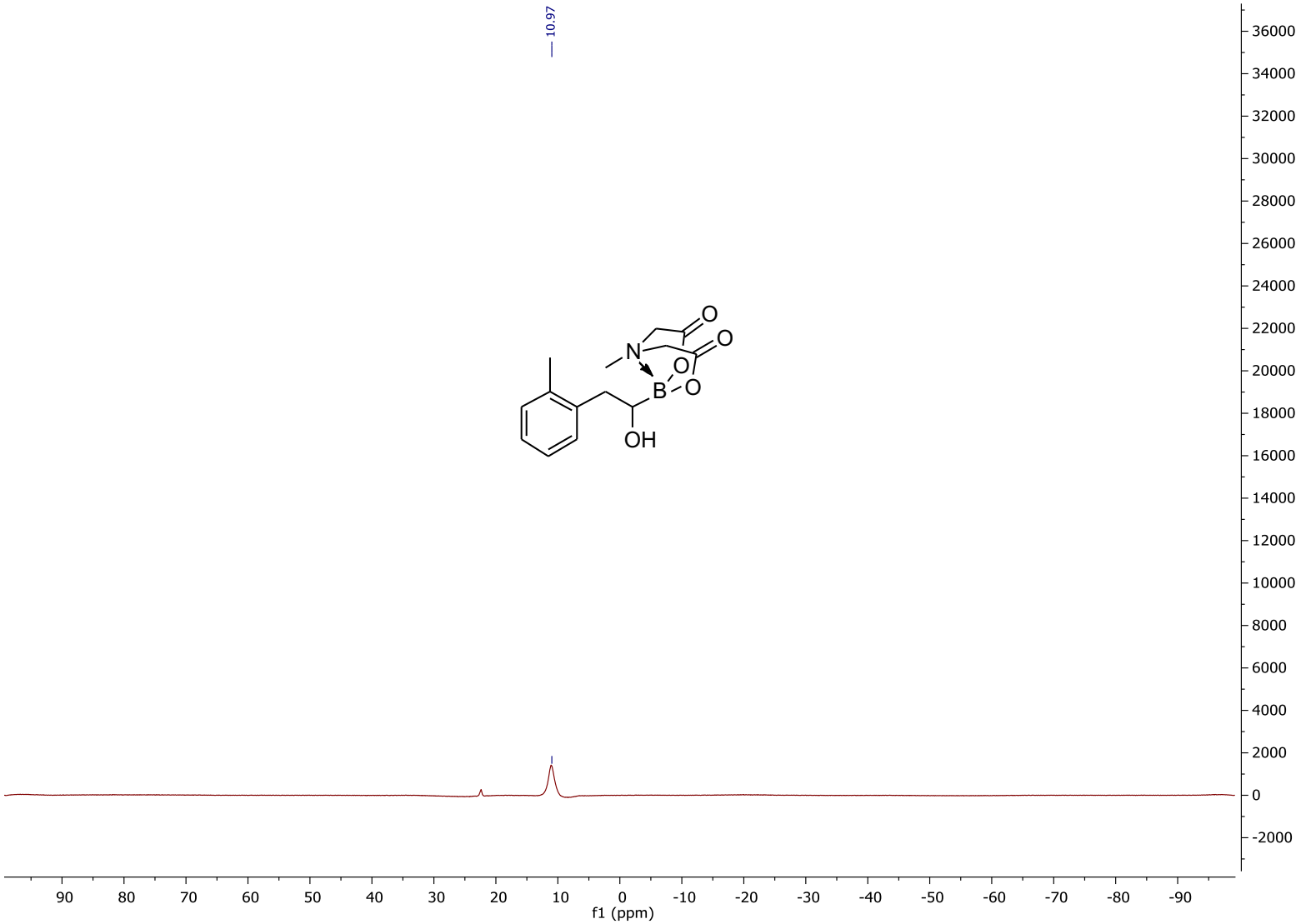
^{11}B NMR, compound 4b

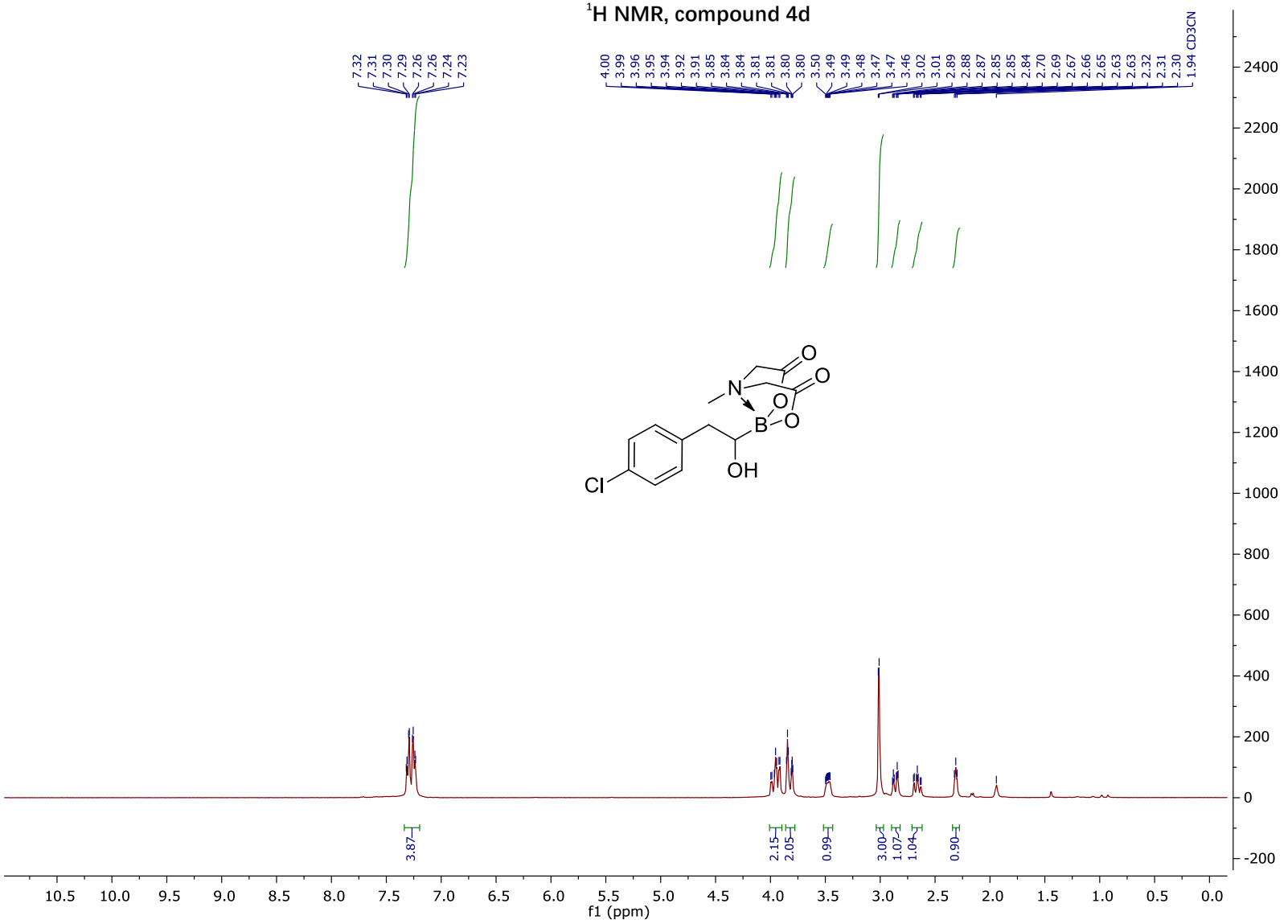



1H NMR, compound 4c
7.20
7.19
7.17
7.16
7.15
7.12
7.11
7.10
3.99
3.96
3.94
3.92
3.85
3.84
3.81
3.80
3.50
3.47
3.02
2.93
2.93
2.90
2.89
2.73
2.70
2.70
2.67
2.32
2.17 Water
1.95 CH3CN
1.94
1.93
O
O
N
O
B
O
OH
1.94
1.72
2.07
2.06
0.99
3.05
1.15
1.05
3.22
f1 (ppm)

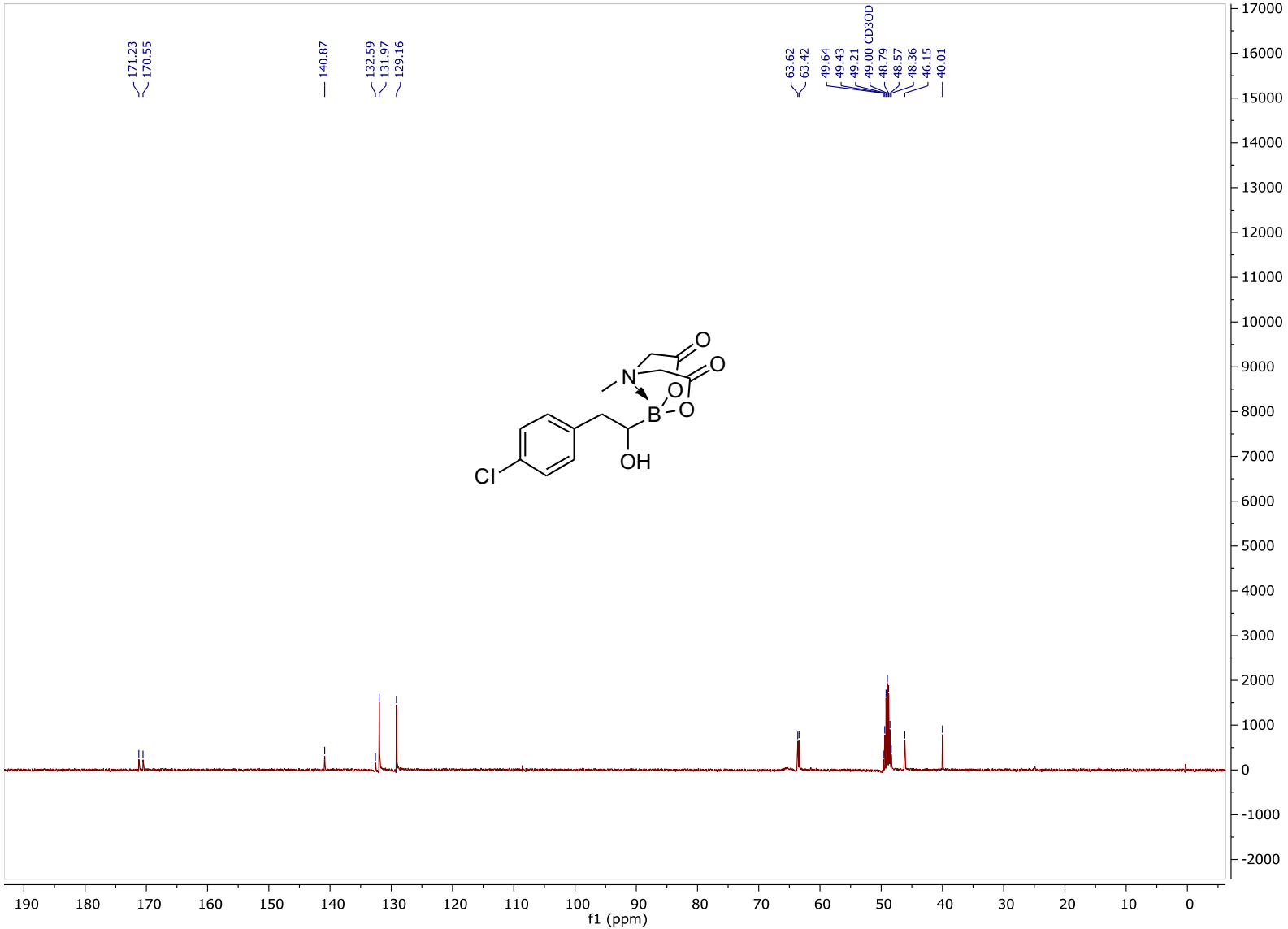

^{13}C NMR, compound 4c
169.94
169.07
139.50
137.64
131.13
127.02
126.59
118.31 CD3CN
63.31
63.07
46.25
37.51
19.75
1.94
1.73
1.53
1.32 CD3CN
1.11
0.91
0.70
O
O
N
O
B
O
OH
f1 (ppm)

^{11}B NMR, compound 4c

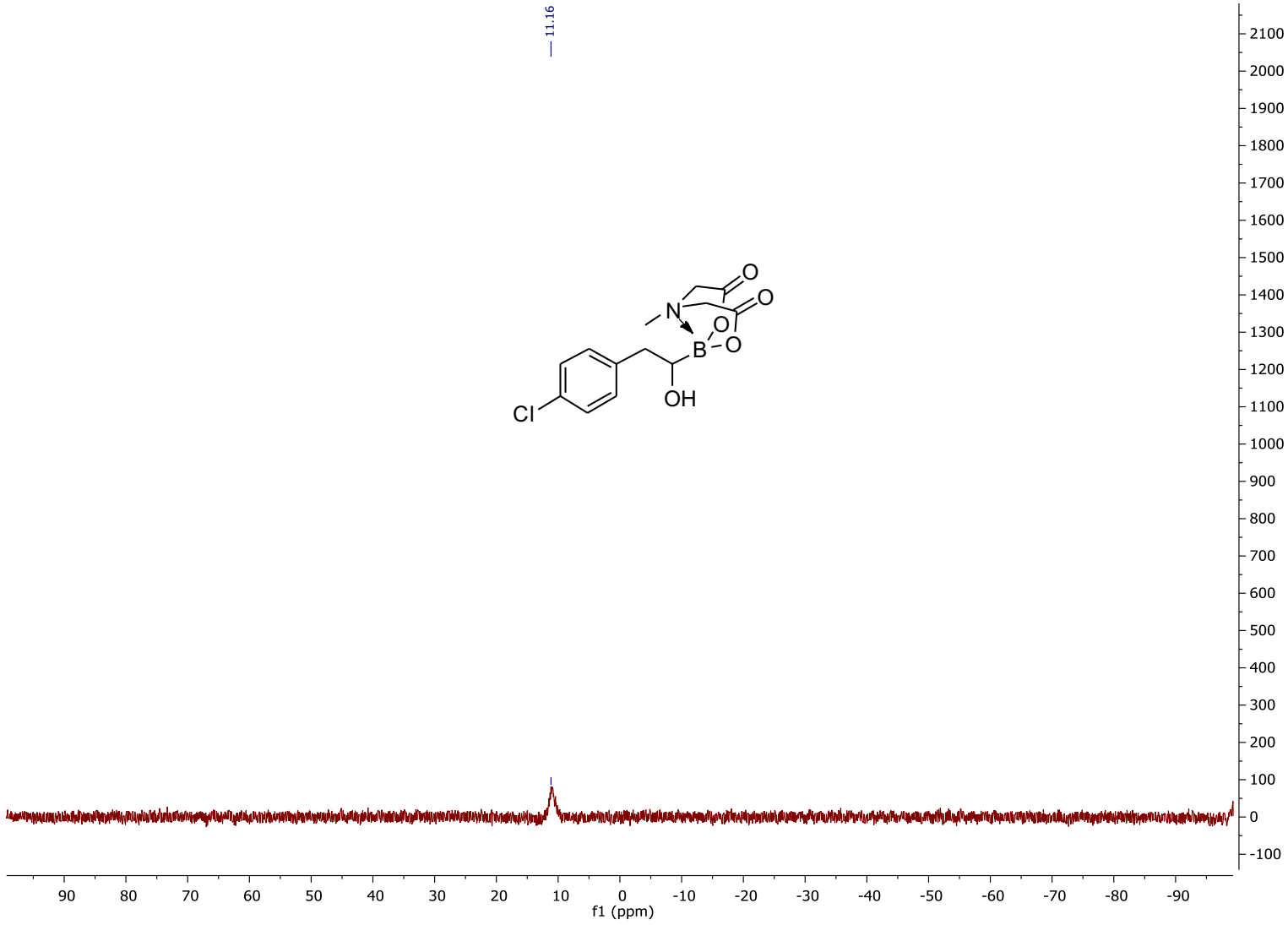



1H NMR, compound 4d
7.32
7.31
7.30
7.29
7.26
7.26
7.24
7.23
4.00
3.99
3.96
3.95
3.94
3.92
3.91
3.85
3.84
3.84
3.81
3.81
3.80
3.80
3.50
3.49
3.49
3.48
3.47
3.47
3.46
3.02
3.01
2.89
2.88
2.87
2.85
2.85
2.84
2.70
2.69
2.67
2.66
2.65
2.63
2.63
2.32
2.31
2.30
1.94 CD3CN
O
O
N
O
B
O
OH
Cl
3.87
2.15
2.05
0.99
3.00
1.07
1.04
0.90
f1 (ppm)

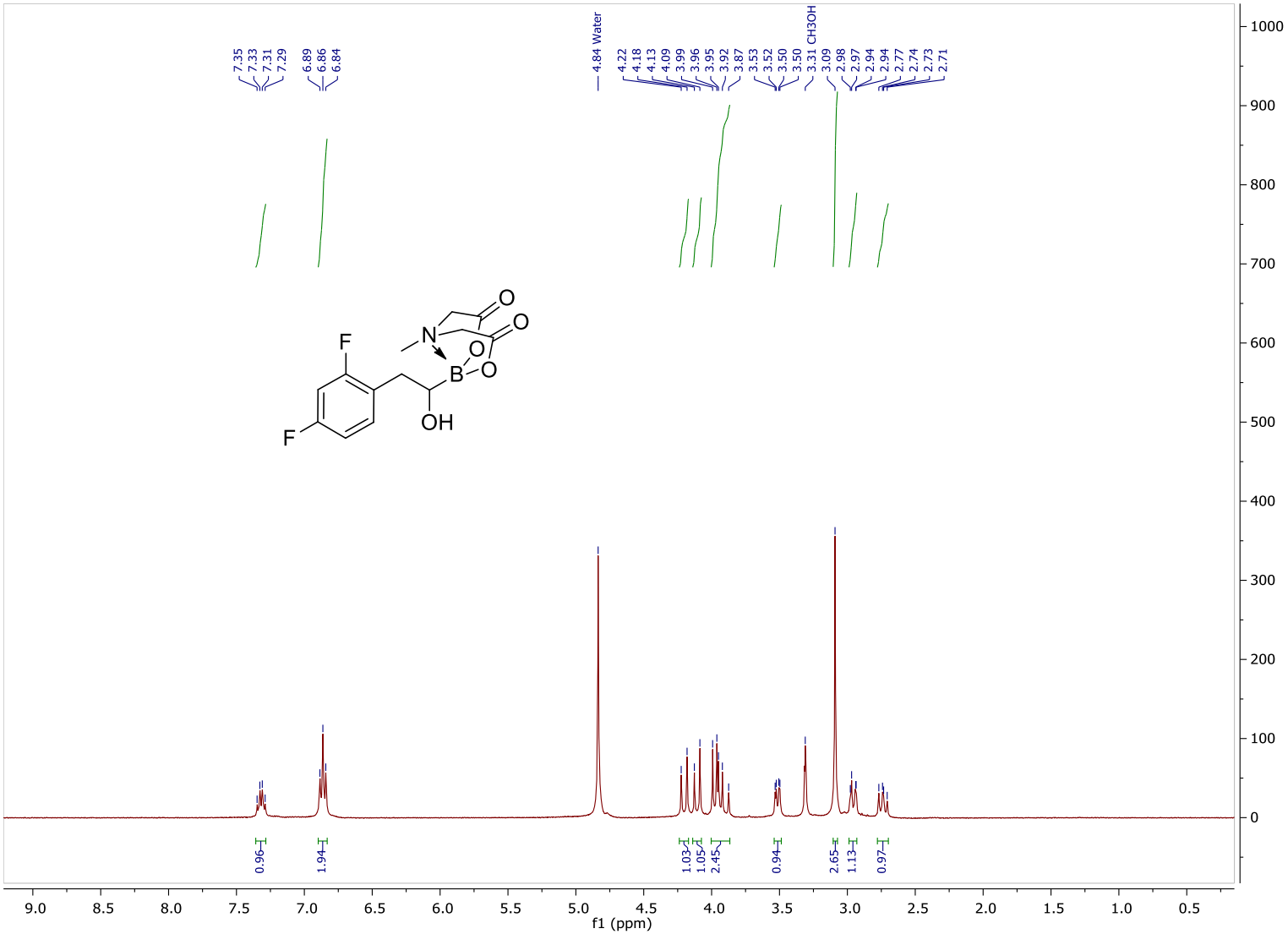
^{13}C NMR, compound 4d



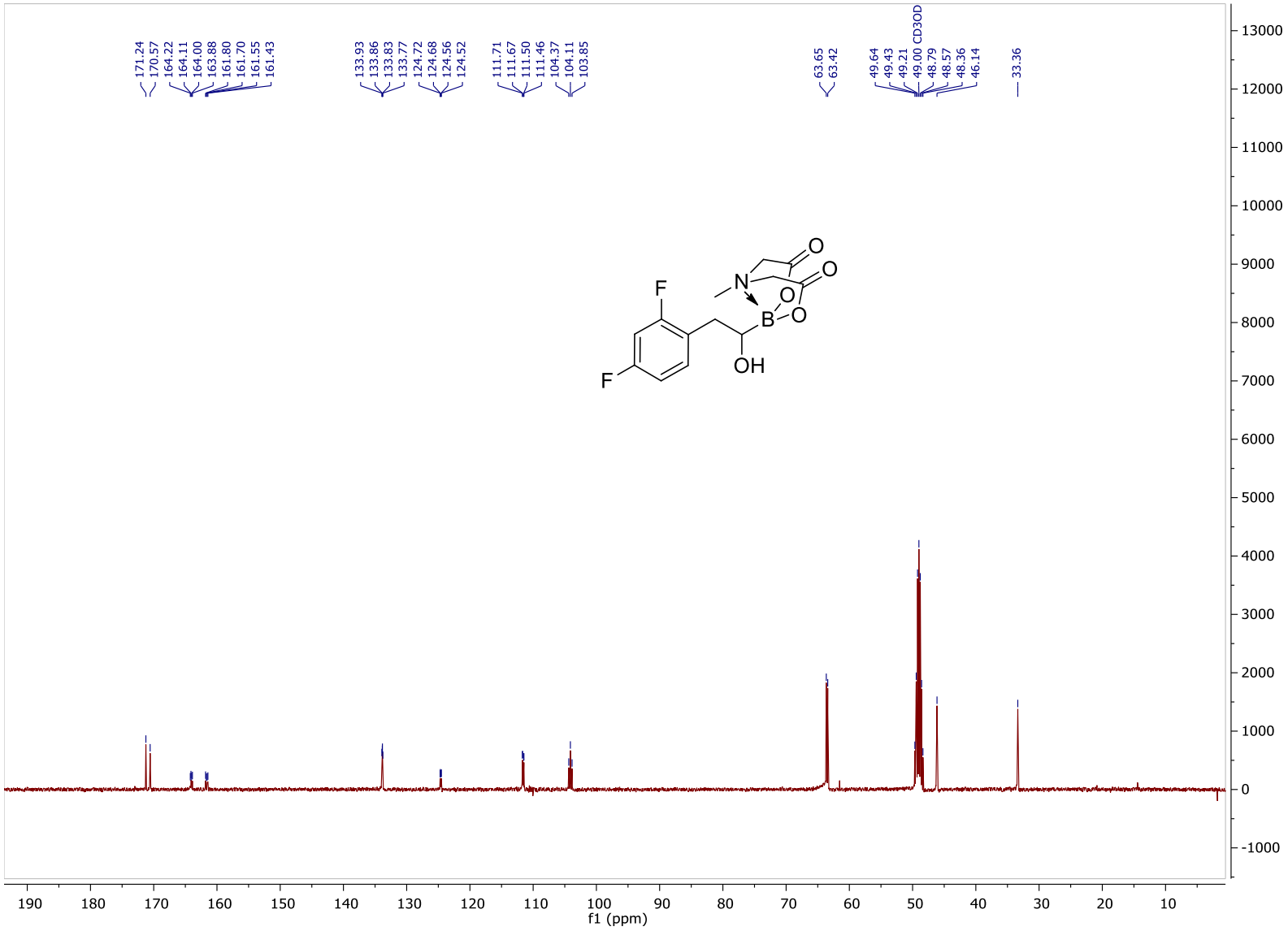
^{11}B NMR, compound 4d



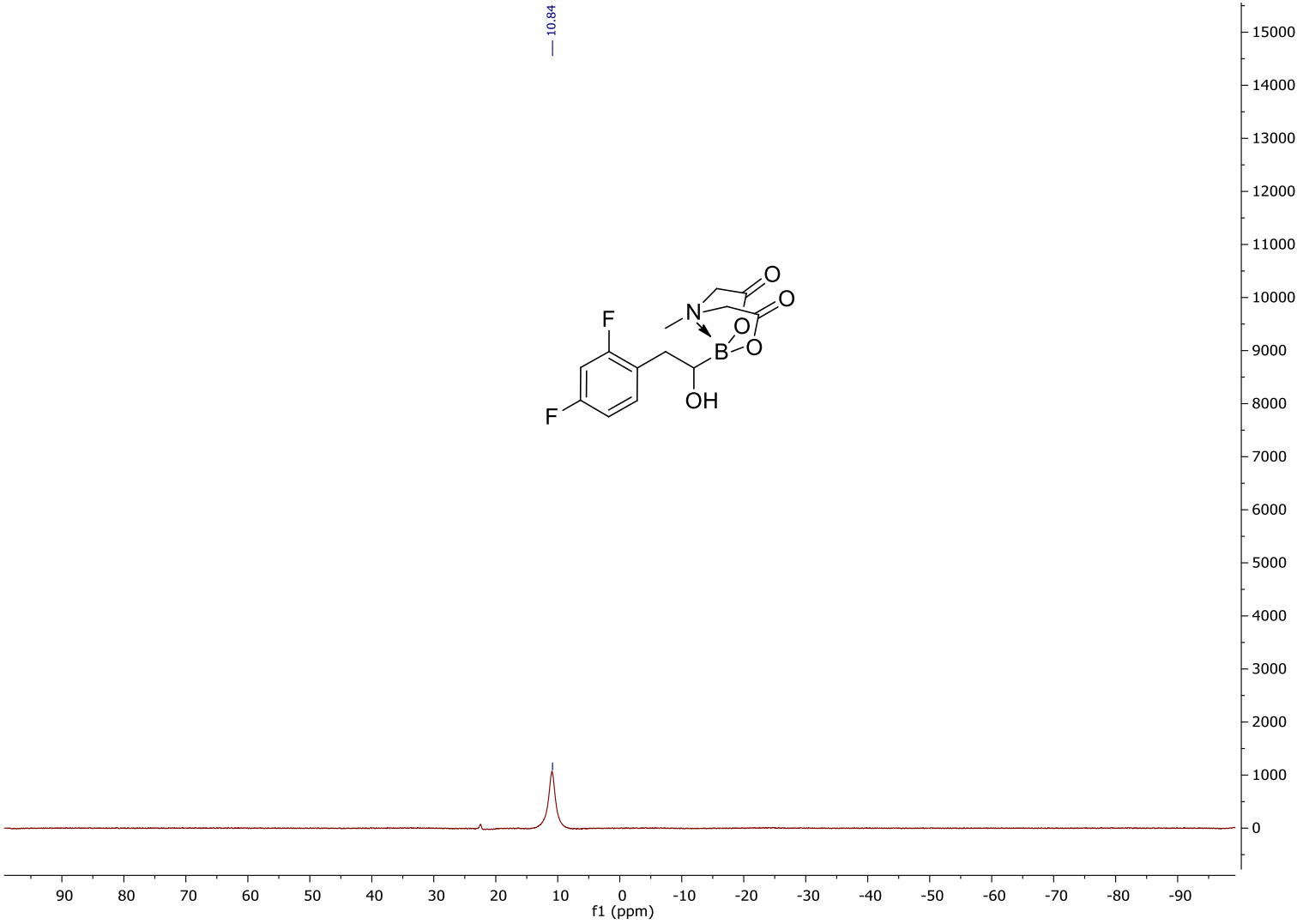
^{1}H NMR, compound 4e



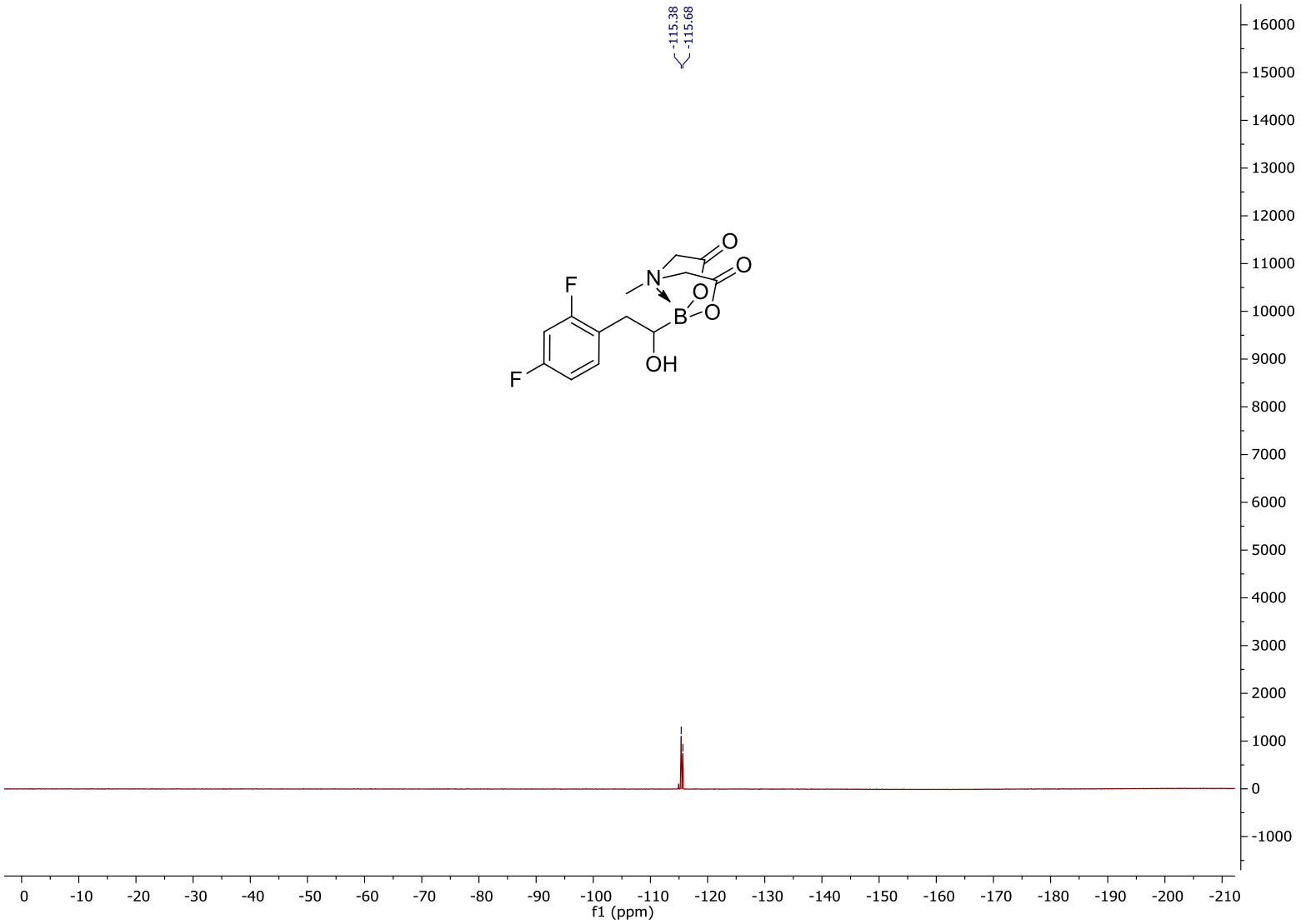
^{13}C NMR, compound 4e



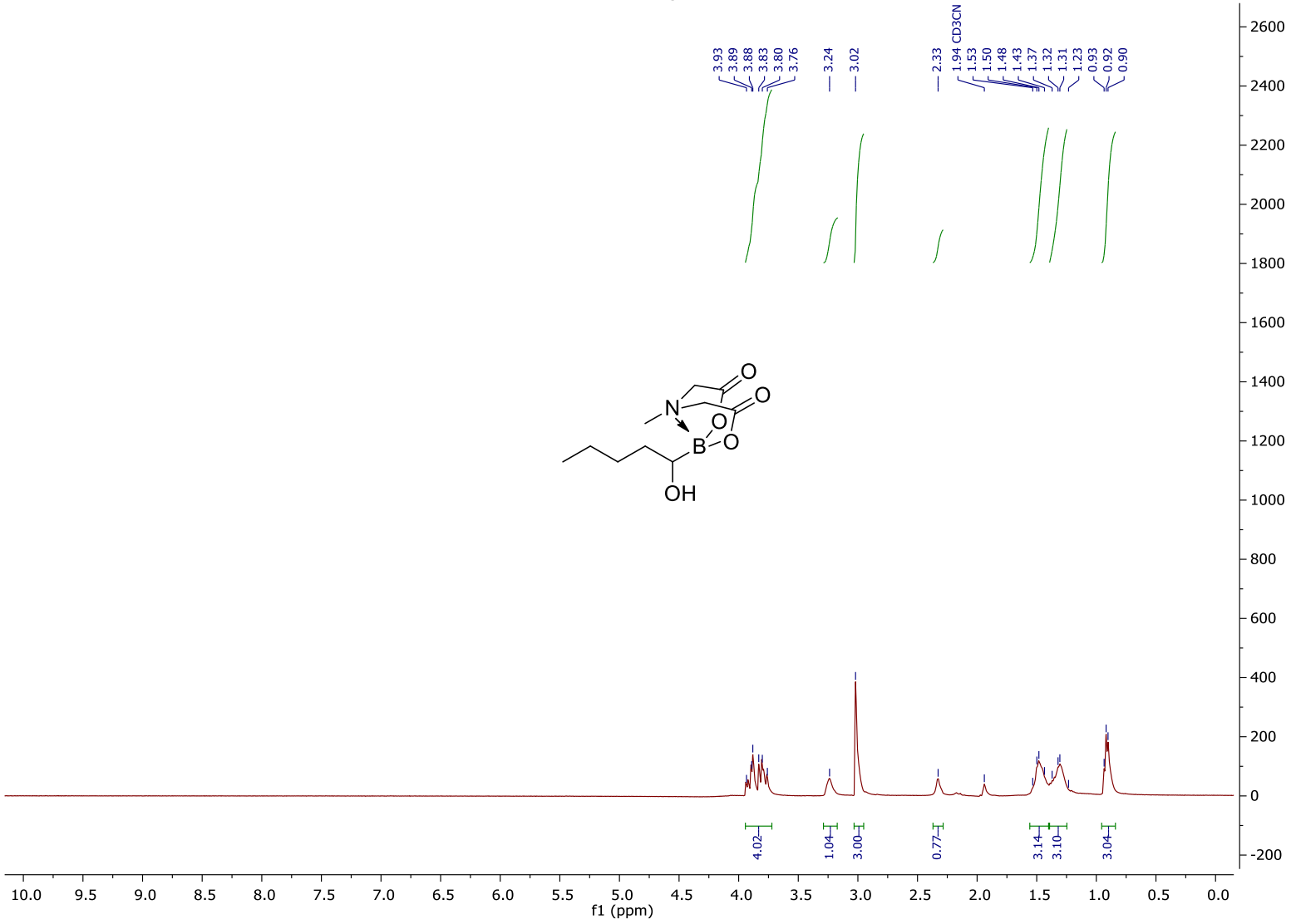
^{11}B NMR, compound 4e



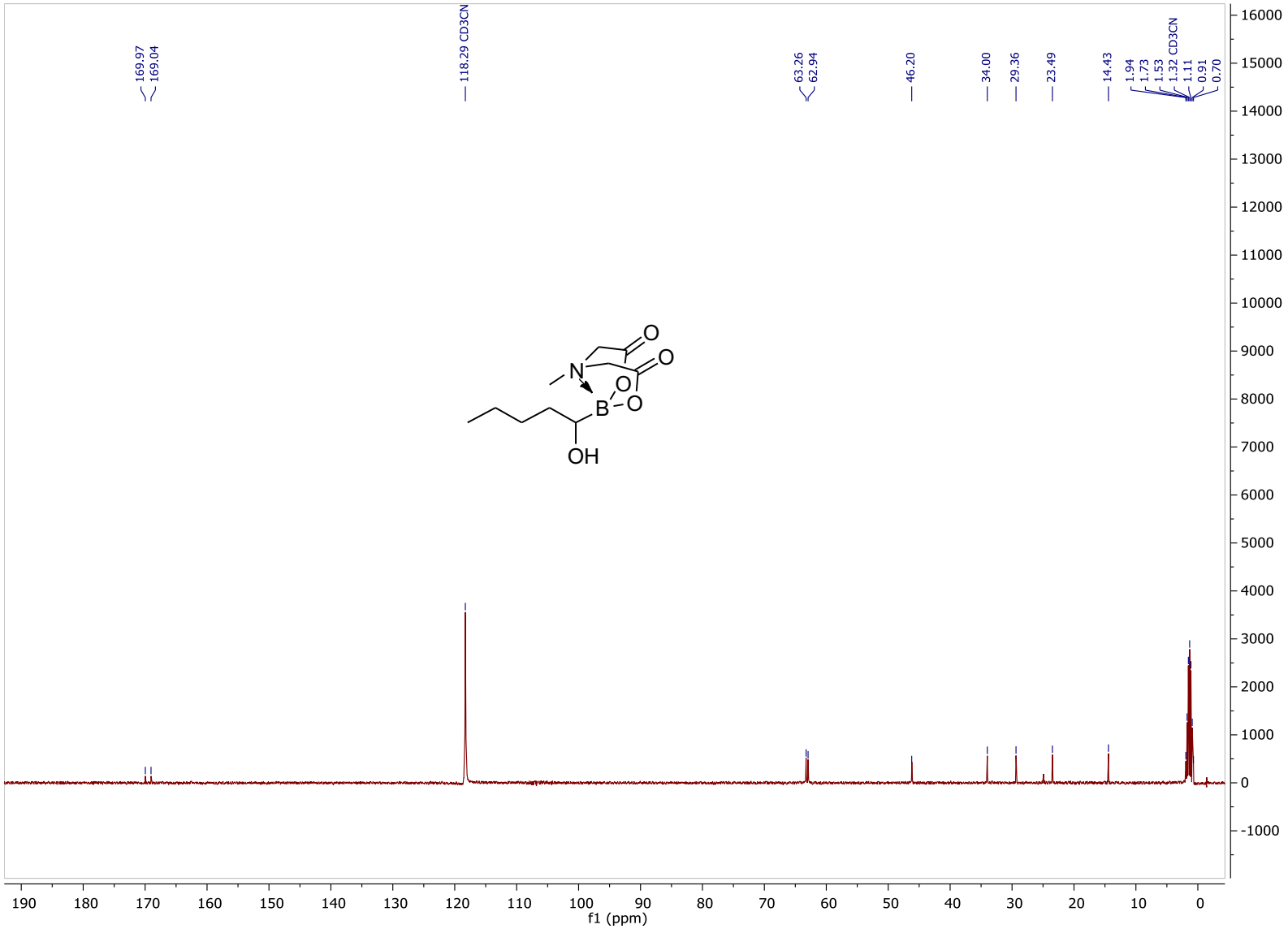
^{19}F NMR, compound 4e



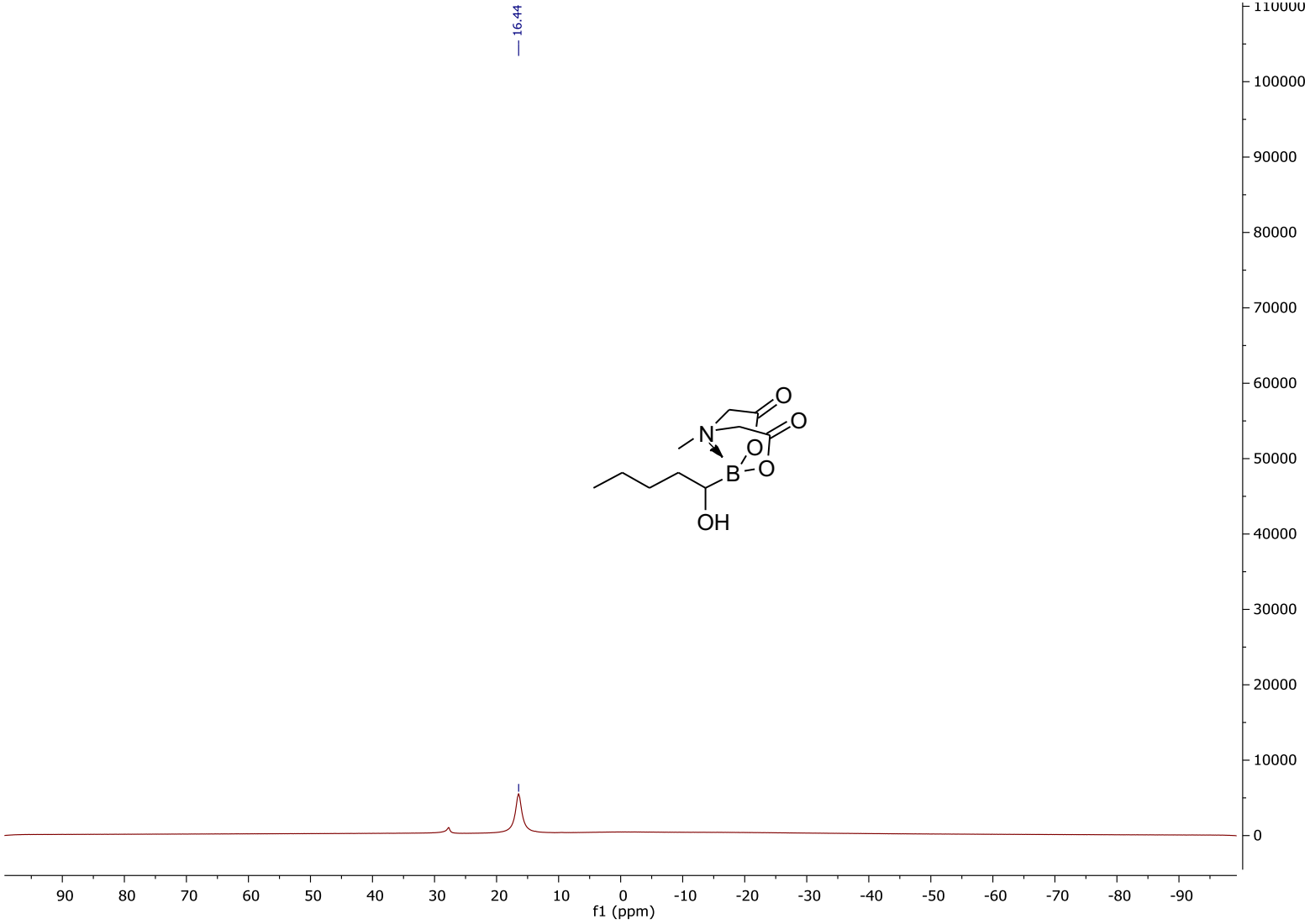
^{1}H NMR, compound 4f

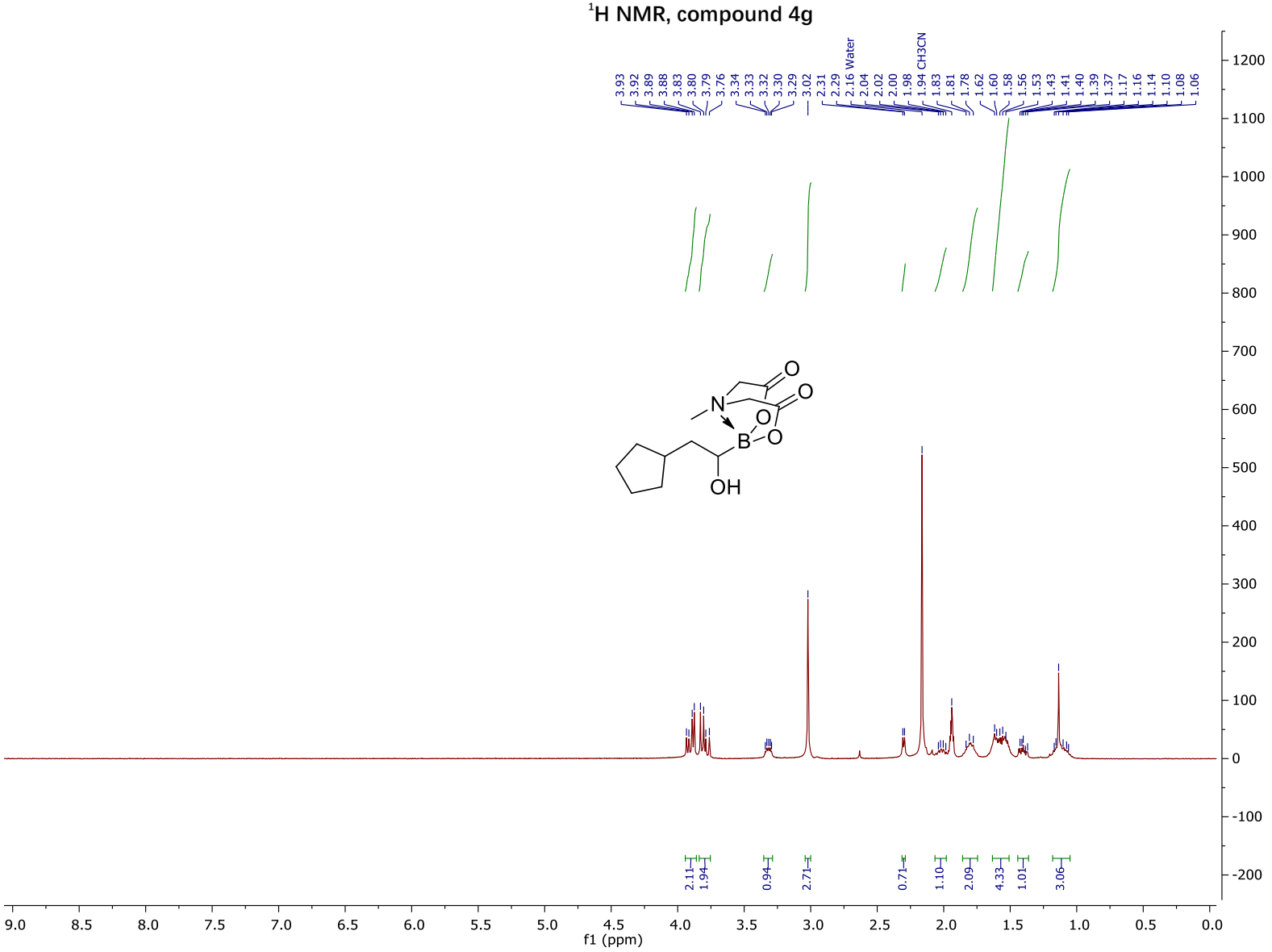


^{13}C NMR, compound 4f

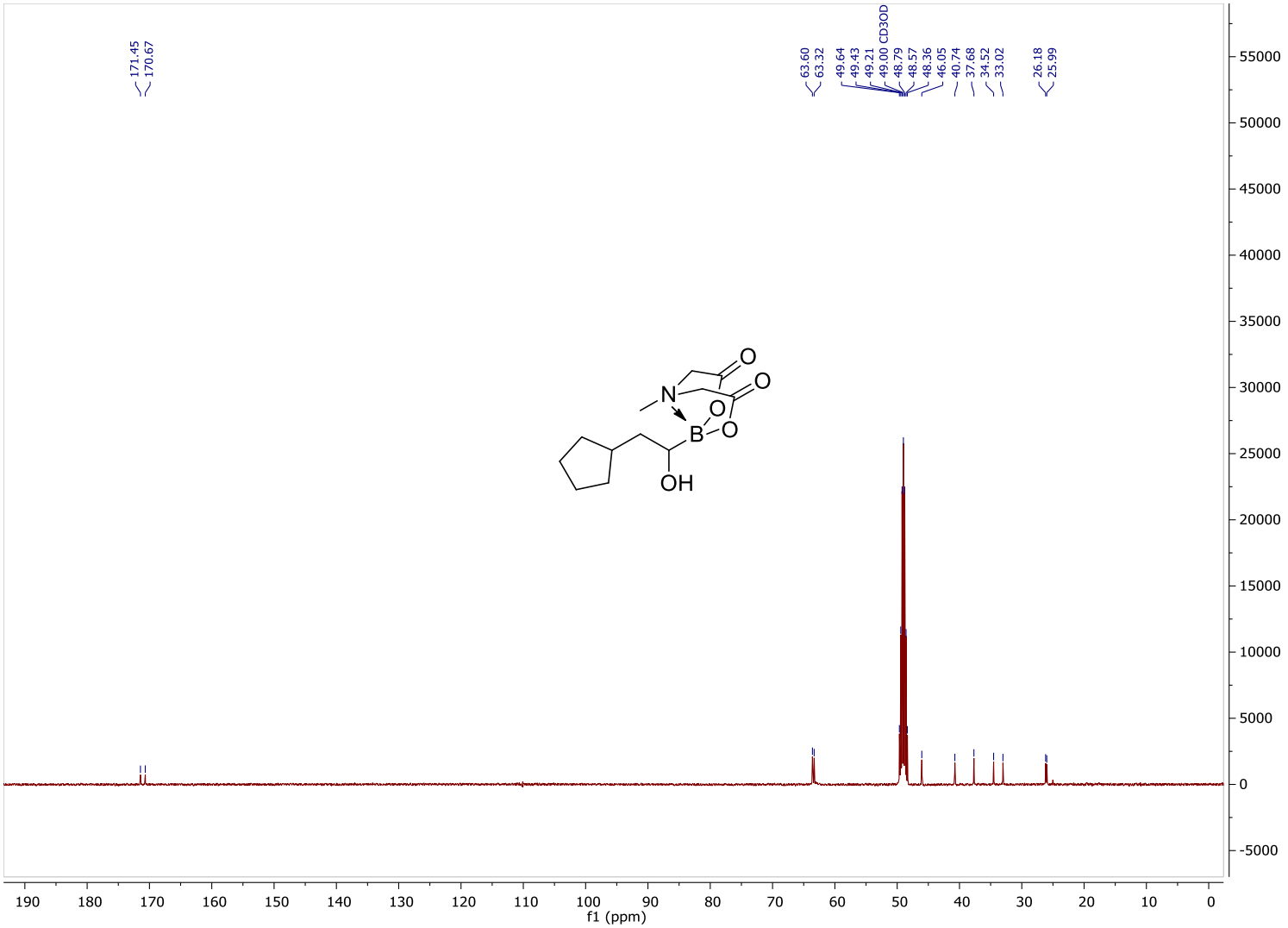


^{11}B NMR, compound 4f

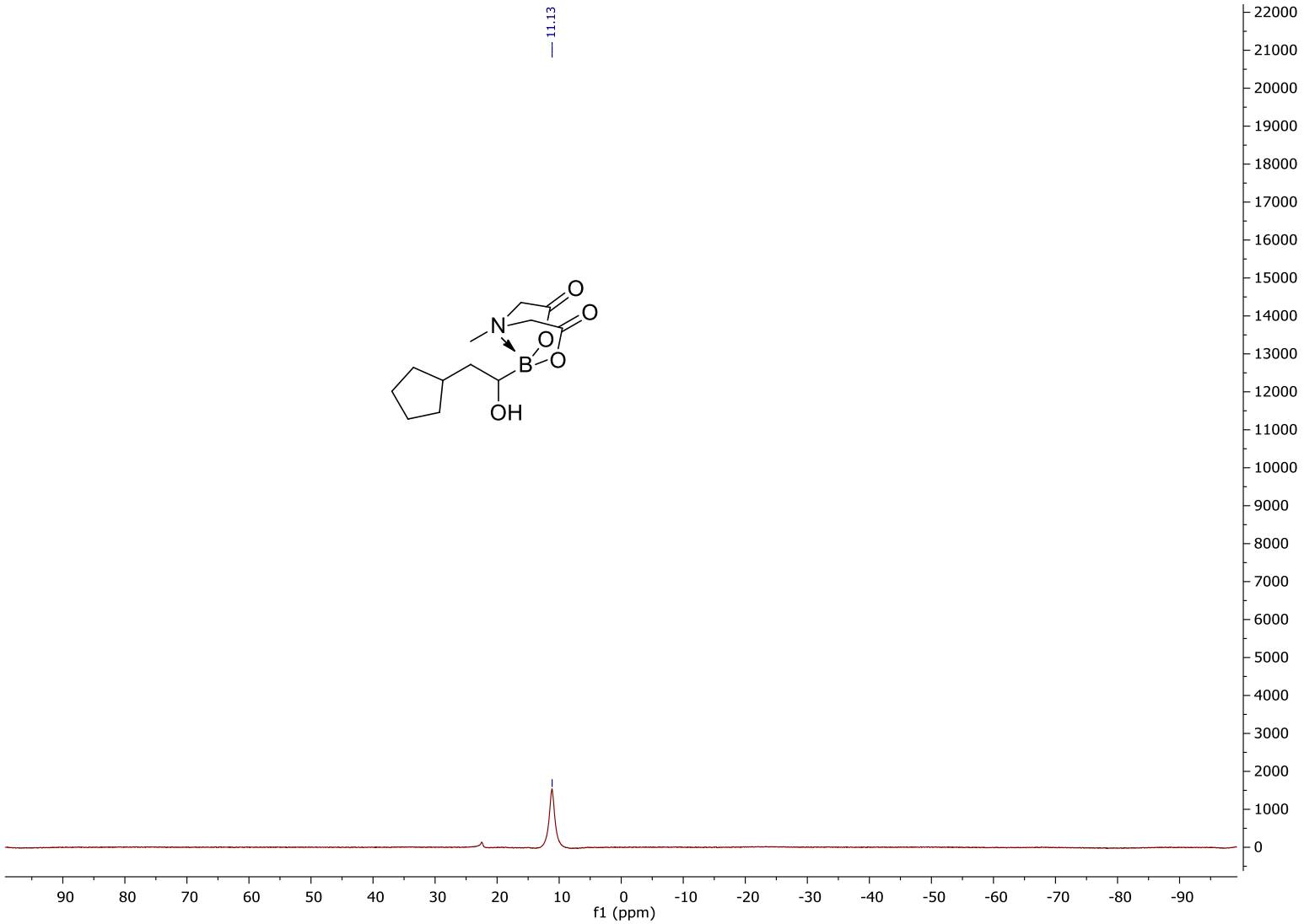


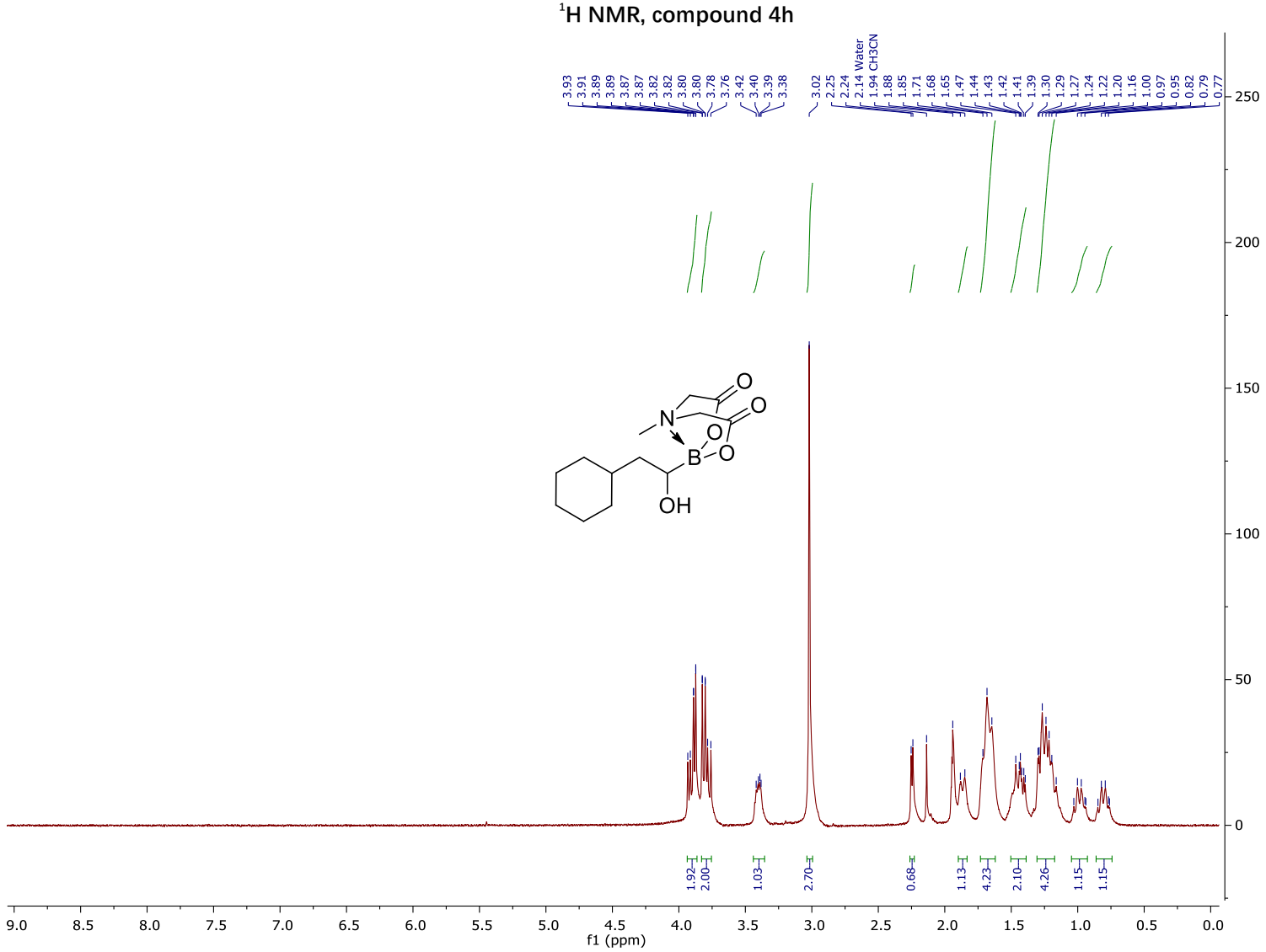

1H NMR, compound 4g
3.93
3.92
3.89
3.88
3.83
3.80
3.79
3.76
3.34
3.33
3.32
3.30
3.29
3.02
2.31
2.29
2.16 Water
2.04
2.02
2.00
1.98
1.94 CH3CN
1.83
1.81
1.78
1.62
1.60
1.58
1.56
1.53
1.43
1.41
1.40
1.39
1.37
1.17
1.16
1.14
1.10
1.08
1.06
O
O
N
O
B
O
OH
2.11
1.94
0.94
2.71
0.71
1.10
2.09
4.33
1.01
3.06
f1 (ppm)

^{13}C NMR, compound 4g

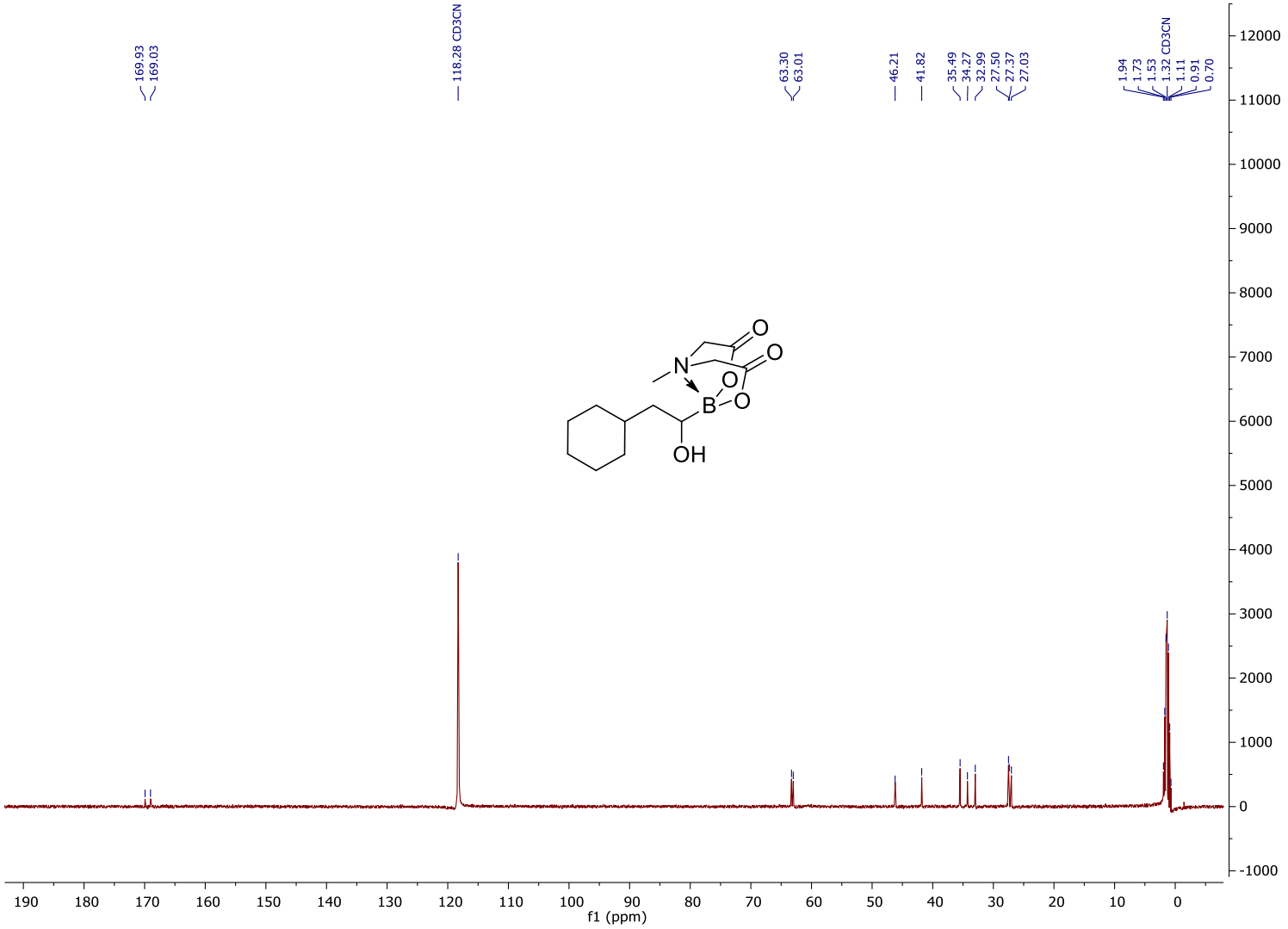


^{11}B NMR, compound 4g

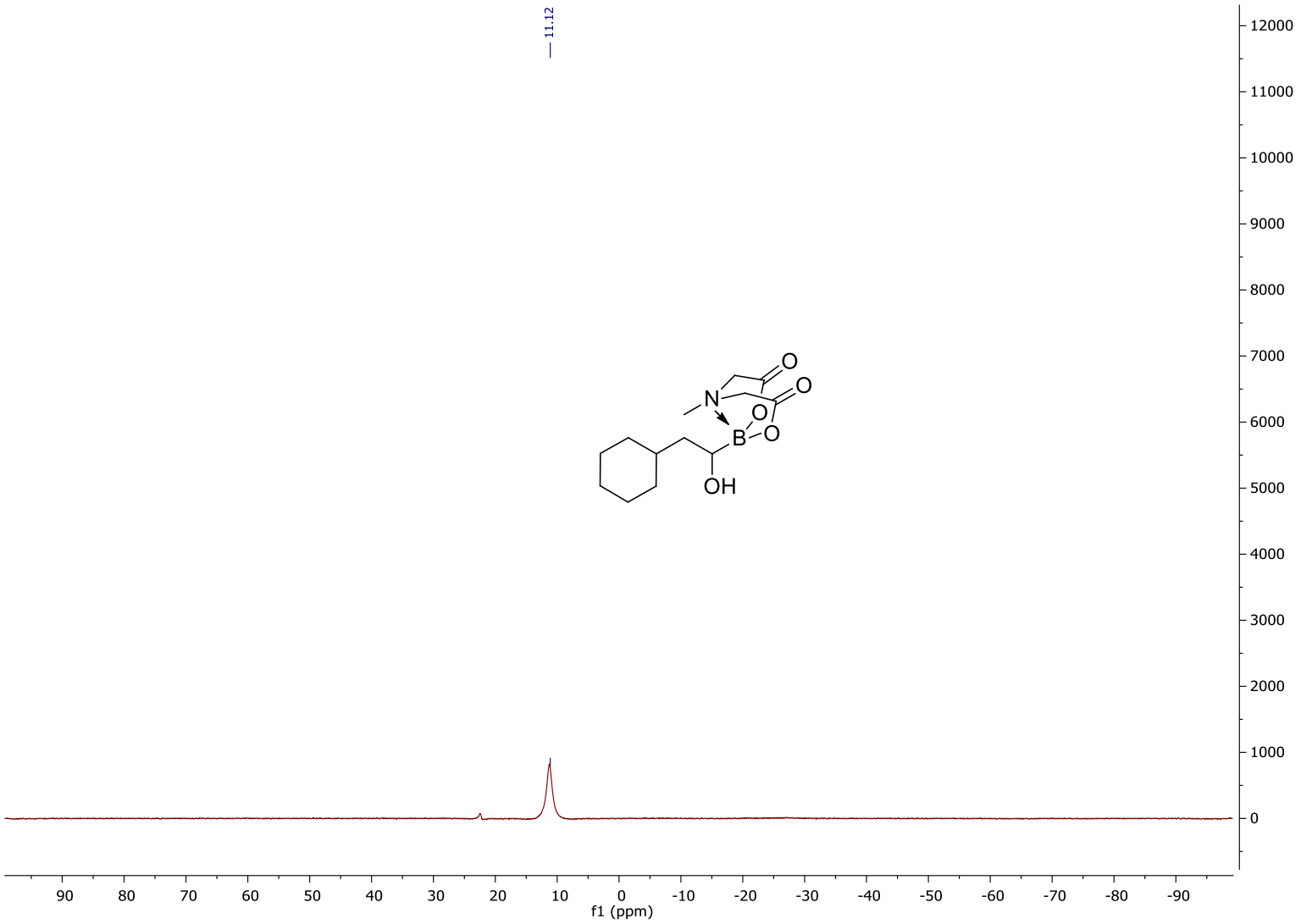


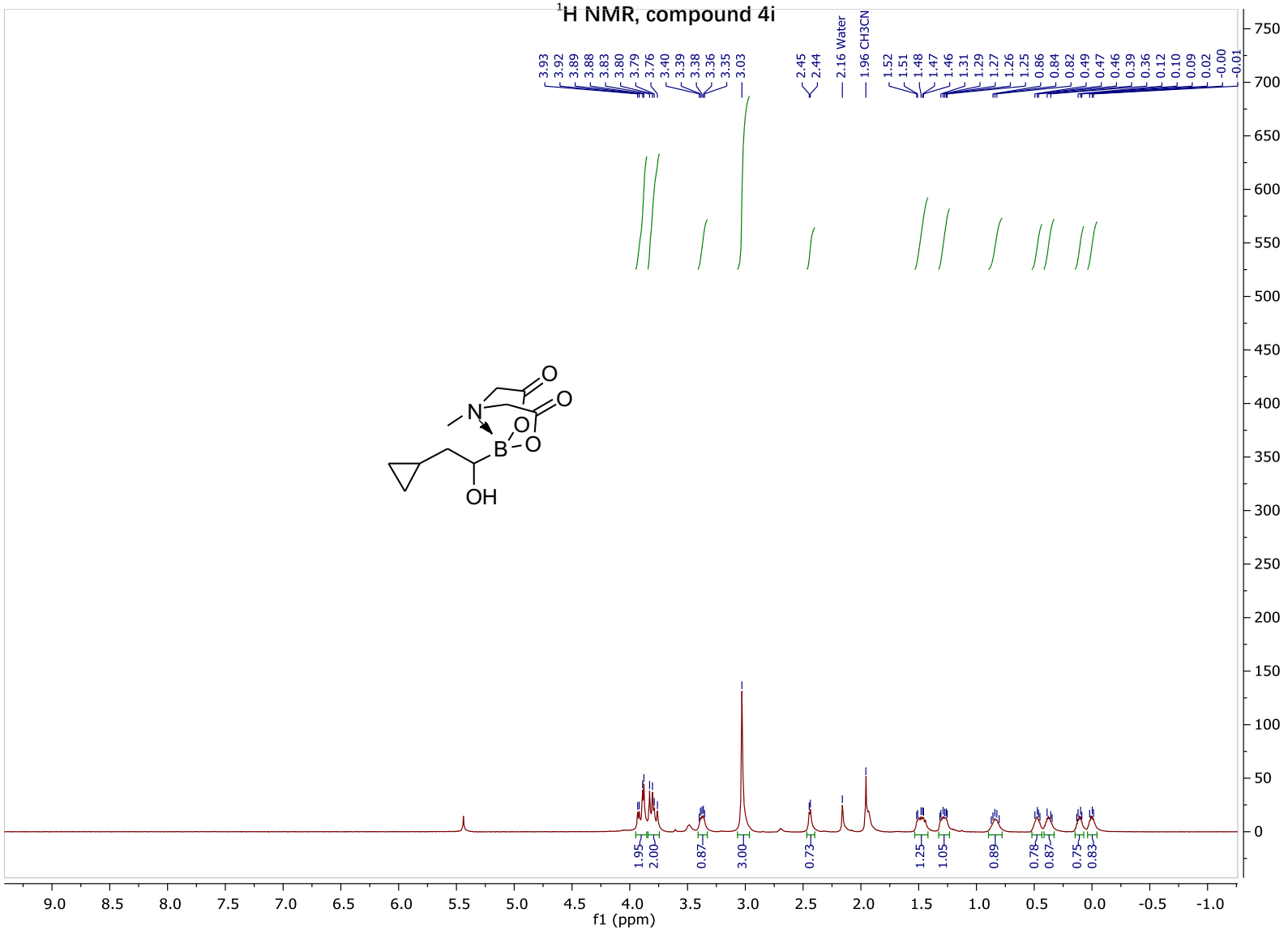

1H NMR, compound 4h
3.93
3.91
3.89
3.89
3.87
3.87
3.82
3.82
3.80
3.80
3.78
3.76
3.42
3.40
3.39
3.38
3.02
2.25
2.24
2.14 Water
1.94 CH3CN
1.88
1.85
1.71
1.68
1.65
1.47
1.44
1.43
1.42
1.41
1.39
1.30
1.29
1.27
1.24
1.22
1.20
1.16
1.00
0.97
0.95
0.82
0.79
0.77
O
O
N
O
B
O
OH
250
200
150
100
50
0
1.92
2.00
1.03
2.70
0.68
1.13
4.23
2.10
4.26
1.15
1.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{13}C NMR, compound 4h

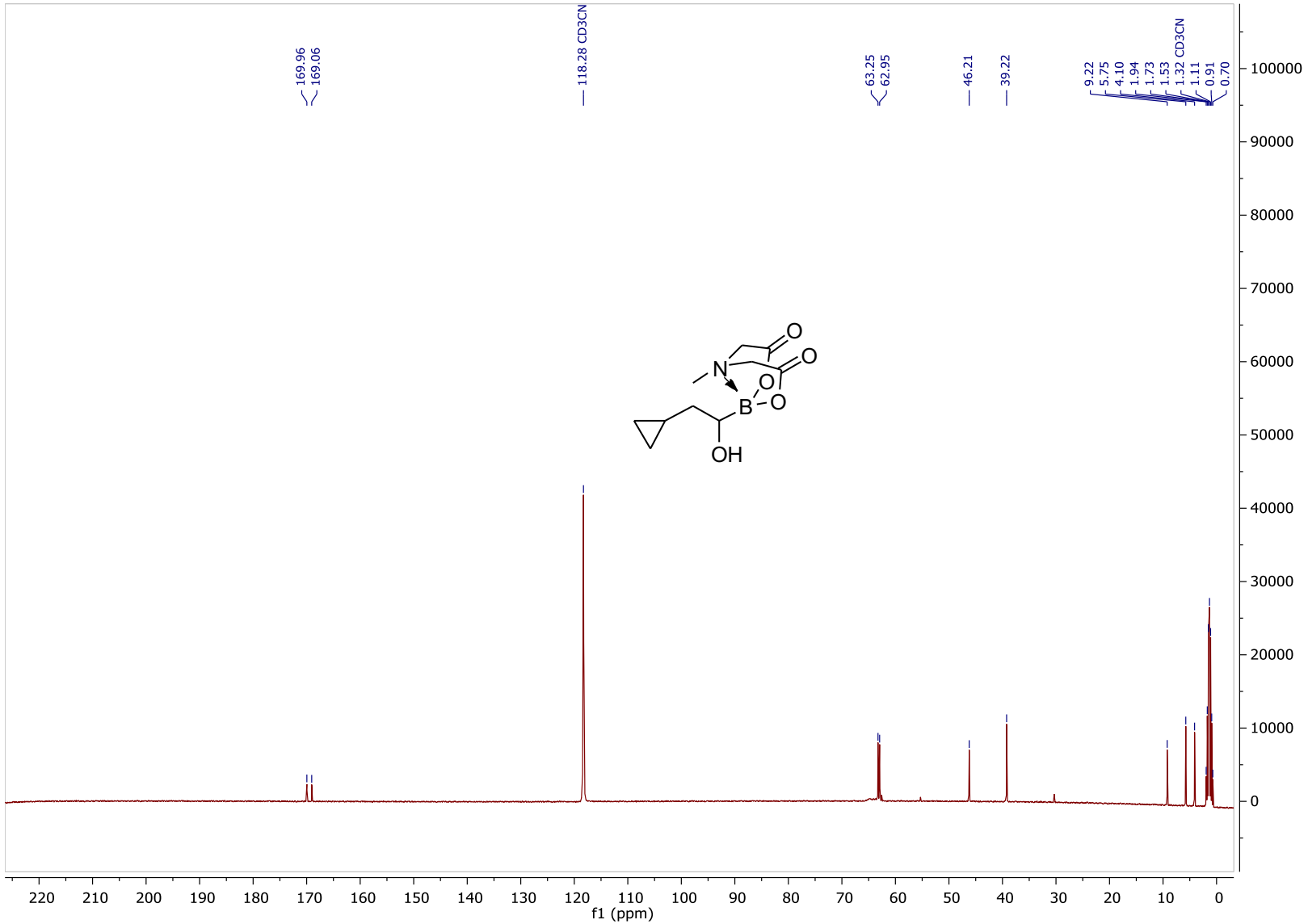


^{11}B NMR, compound 4h

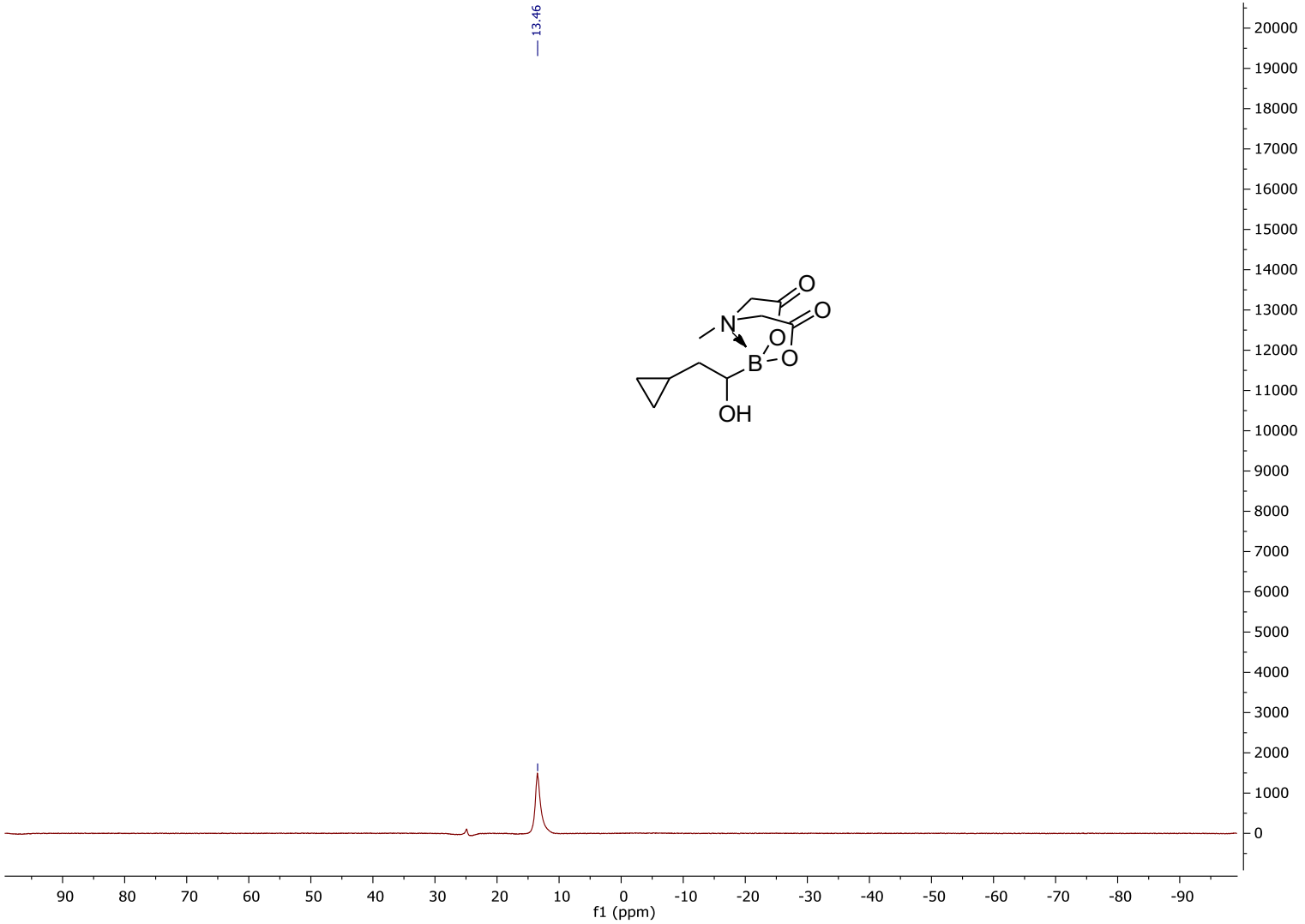



1H NMR, compound 4i
3.93
3.92
3.89
3.88
3.83
3.80
3.79
3.76
3.40
3.39
3.38
3.36
3.35
3.03
2.45
2.44
2.16 Water
1.96 CH3CN
1.52
1.51
1.48
1.47
1.46
1.31
1.29
1.27
1.26
1.25
0.86
0.84
0.82
0.49
0.47
0.46
0.39
0.36
0.12
0.10
0.09
0.02
-0.00
-0.01
O
O
N
O
B
O
OH
1.95
2.00
0.87
3.00
0.73
1.25
1.05
0.89
0.78
0.87
0.75
0.83
f1 (ppm)

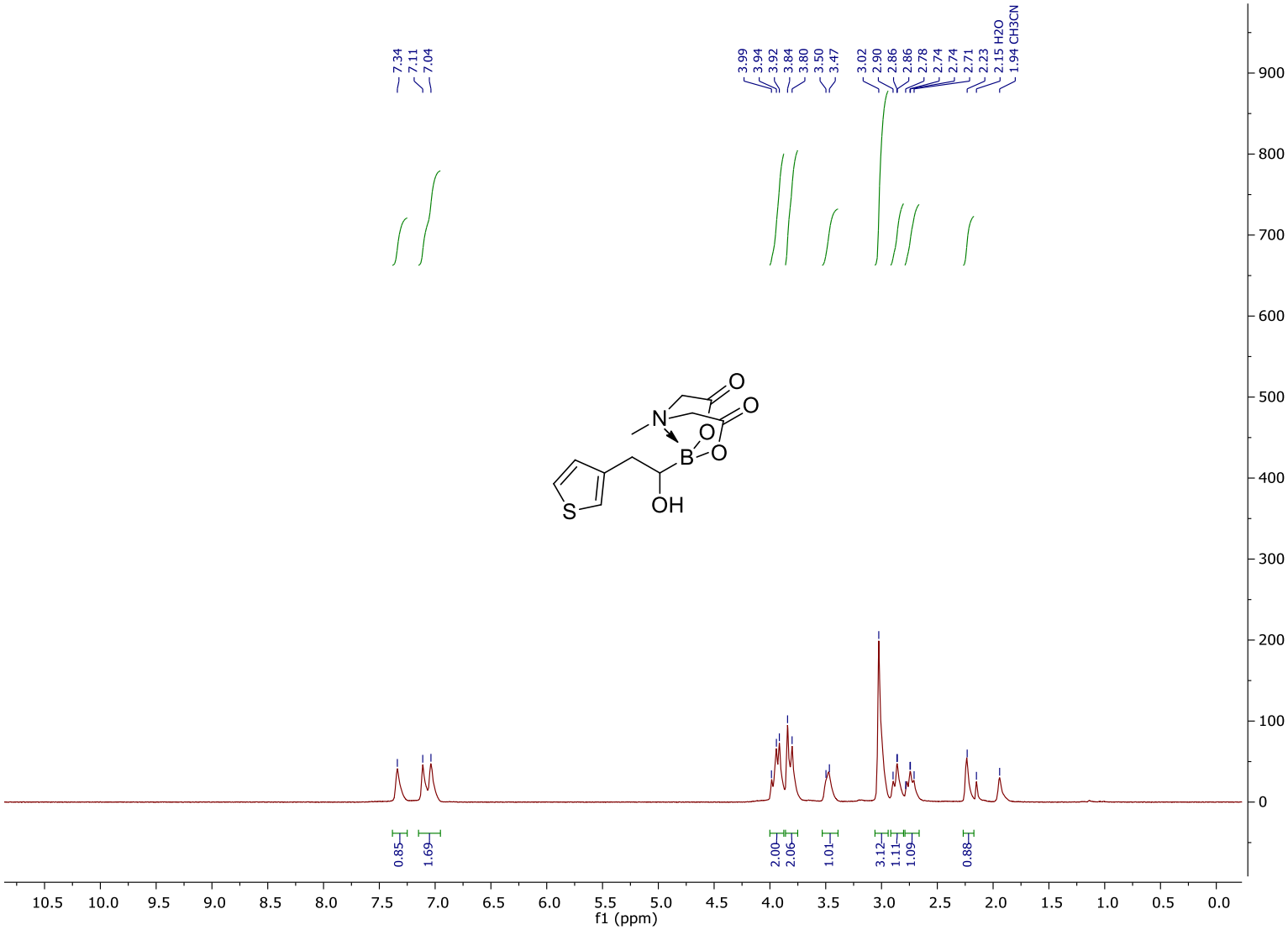
^{13}C NMR, compound 4i



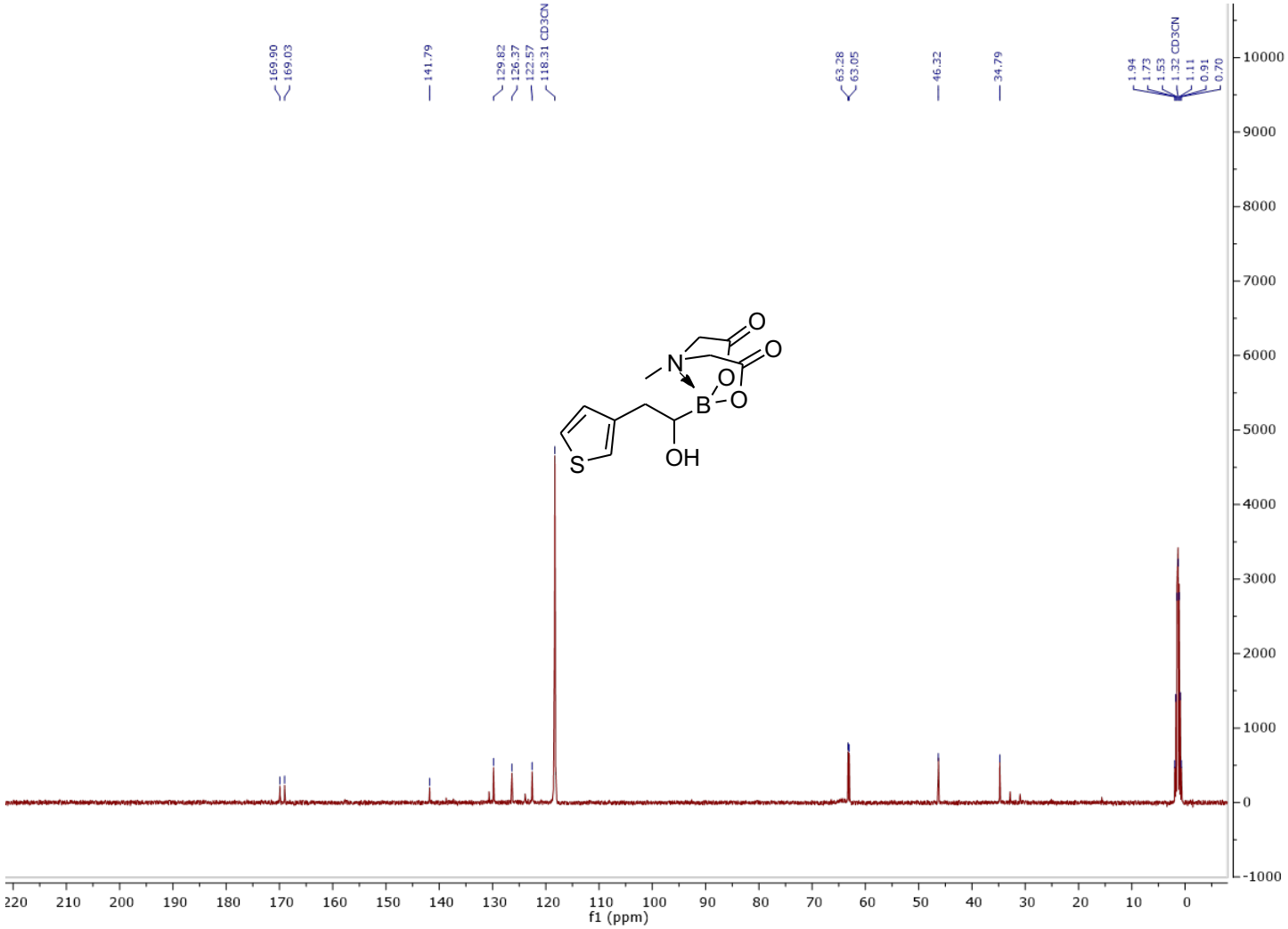
^{11}B NMR, compound 4i



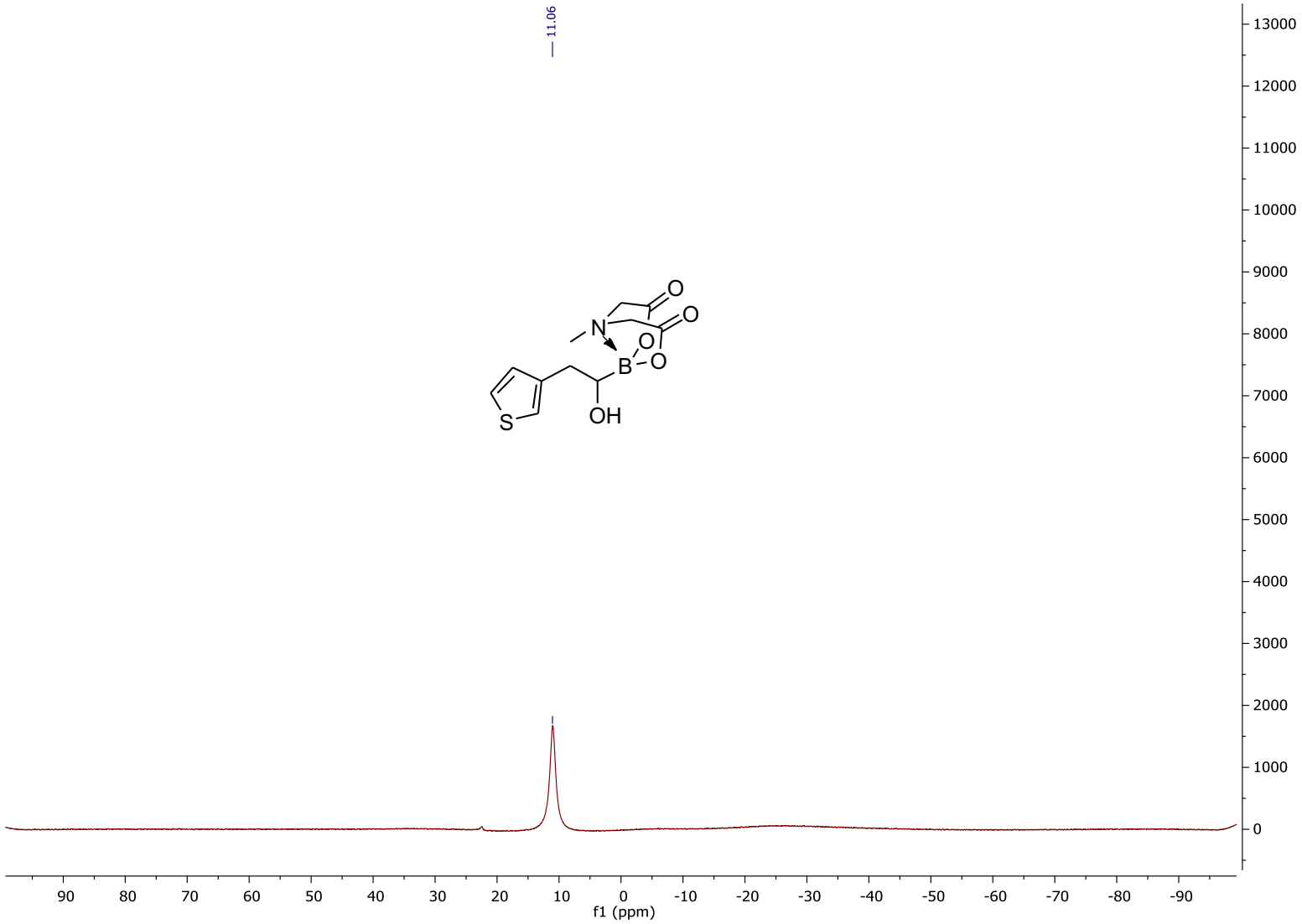
^{1}H NMR, compound 4j



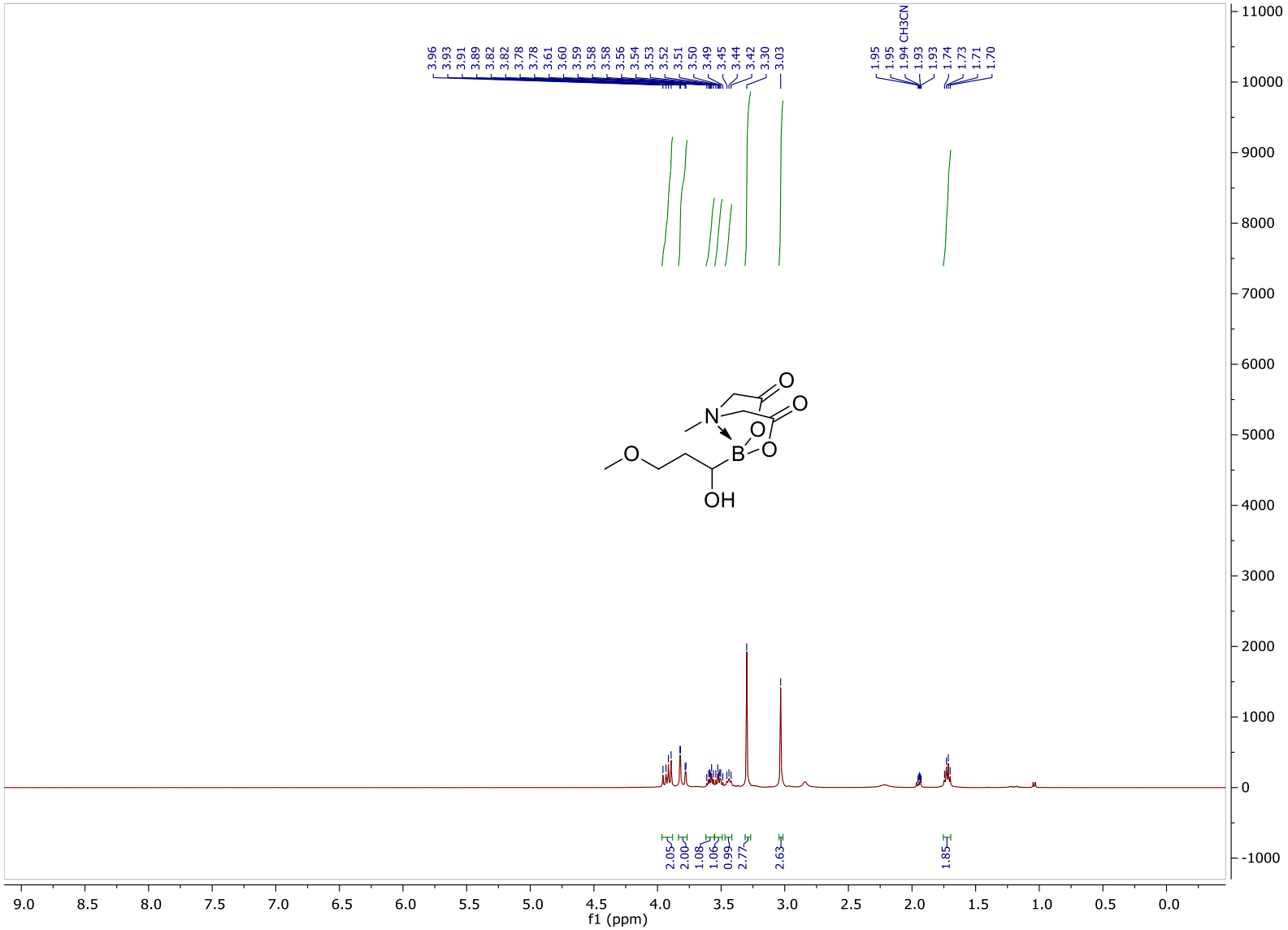
^{13}C NMR, compound 4j



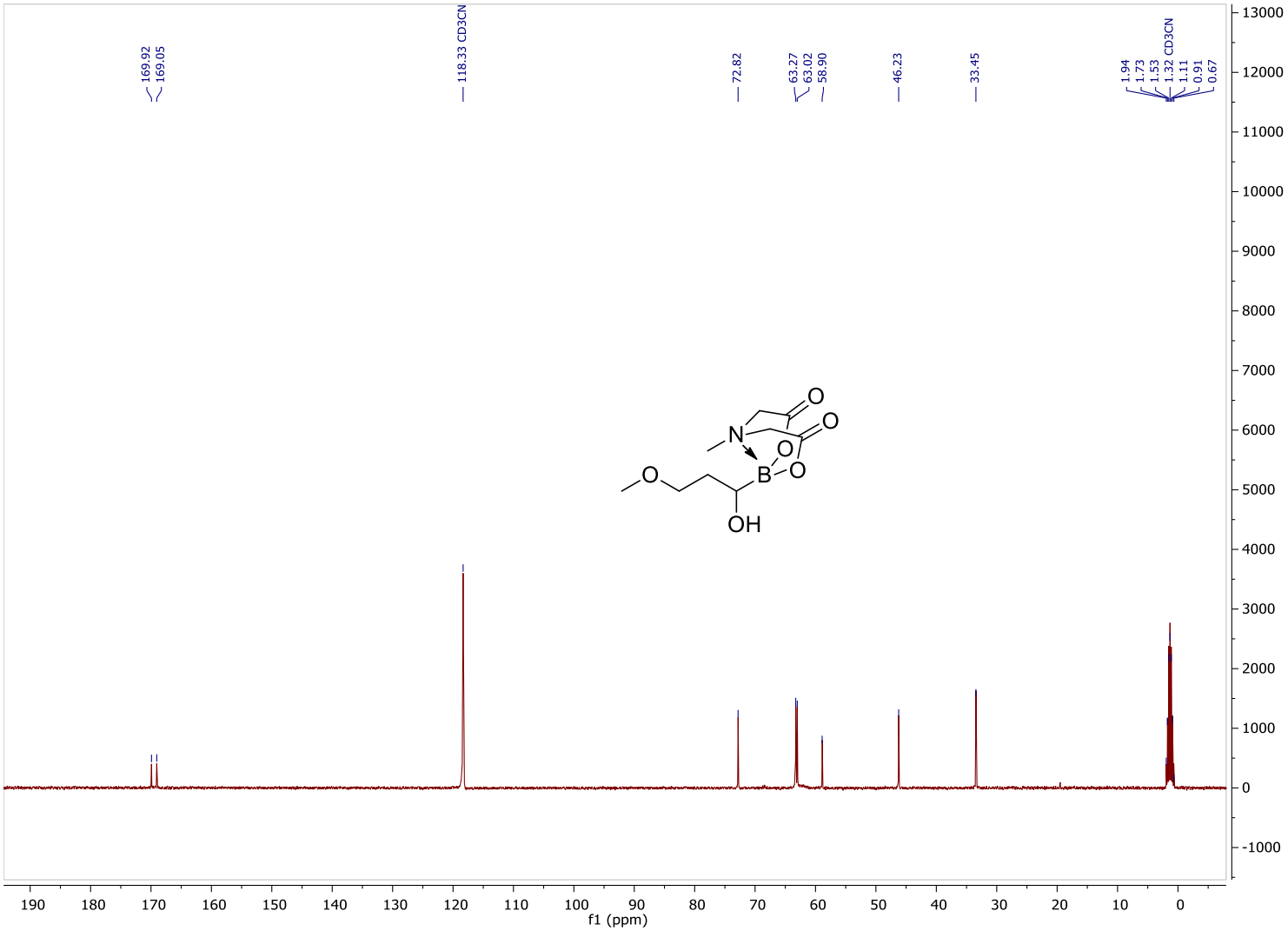
^{11}B NMR, compound 4j



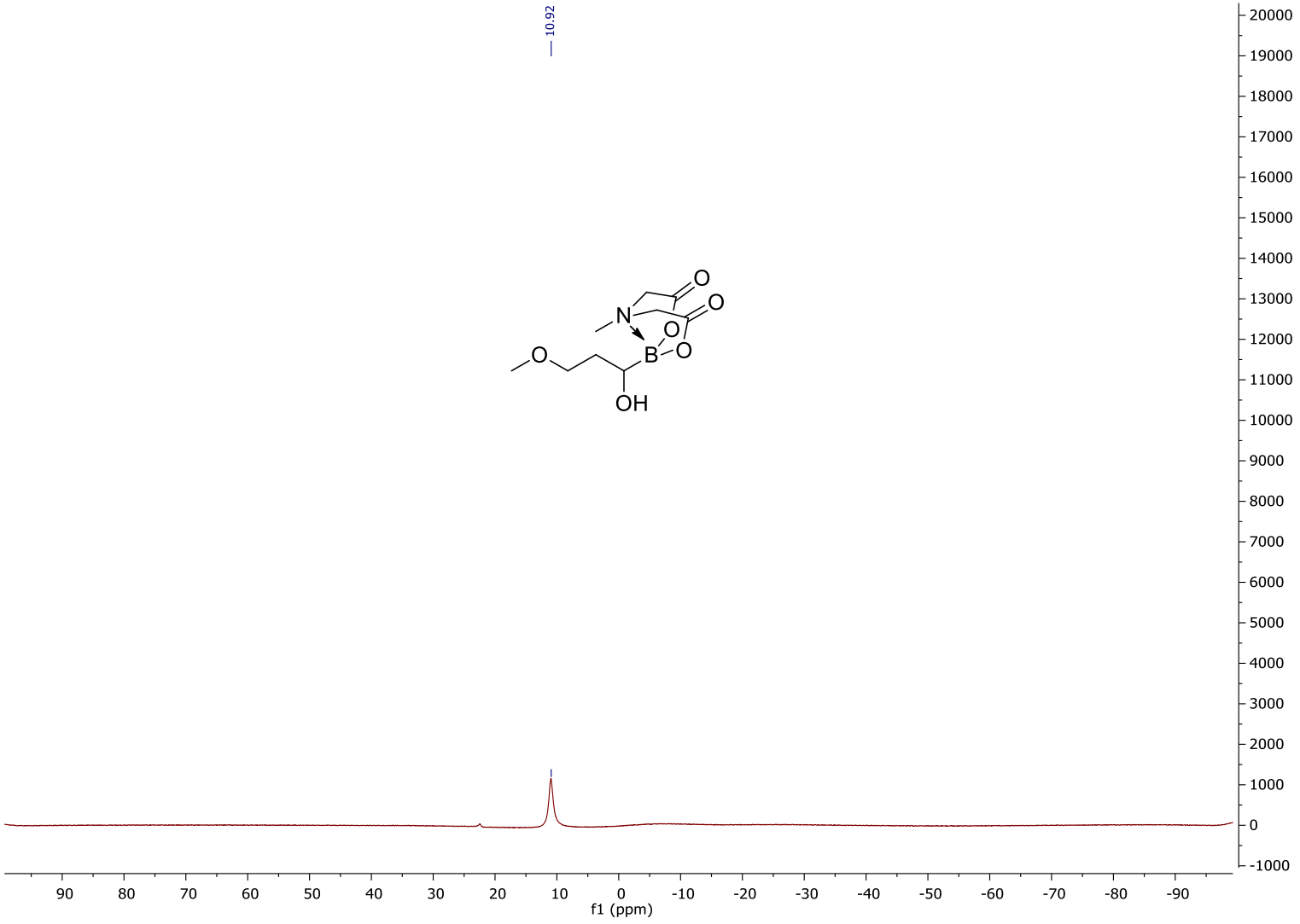
^{1}H NMR, compound 4k

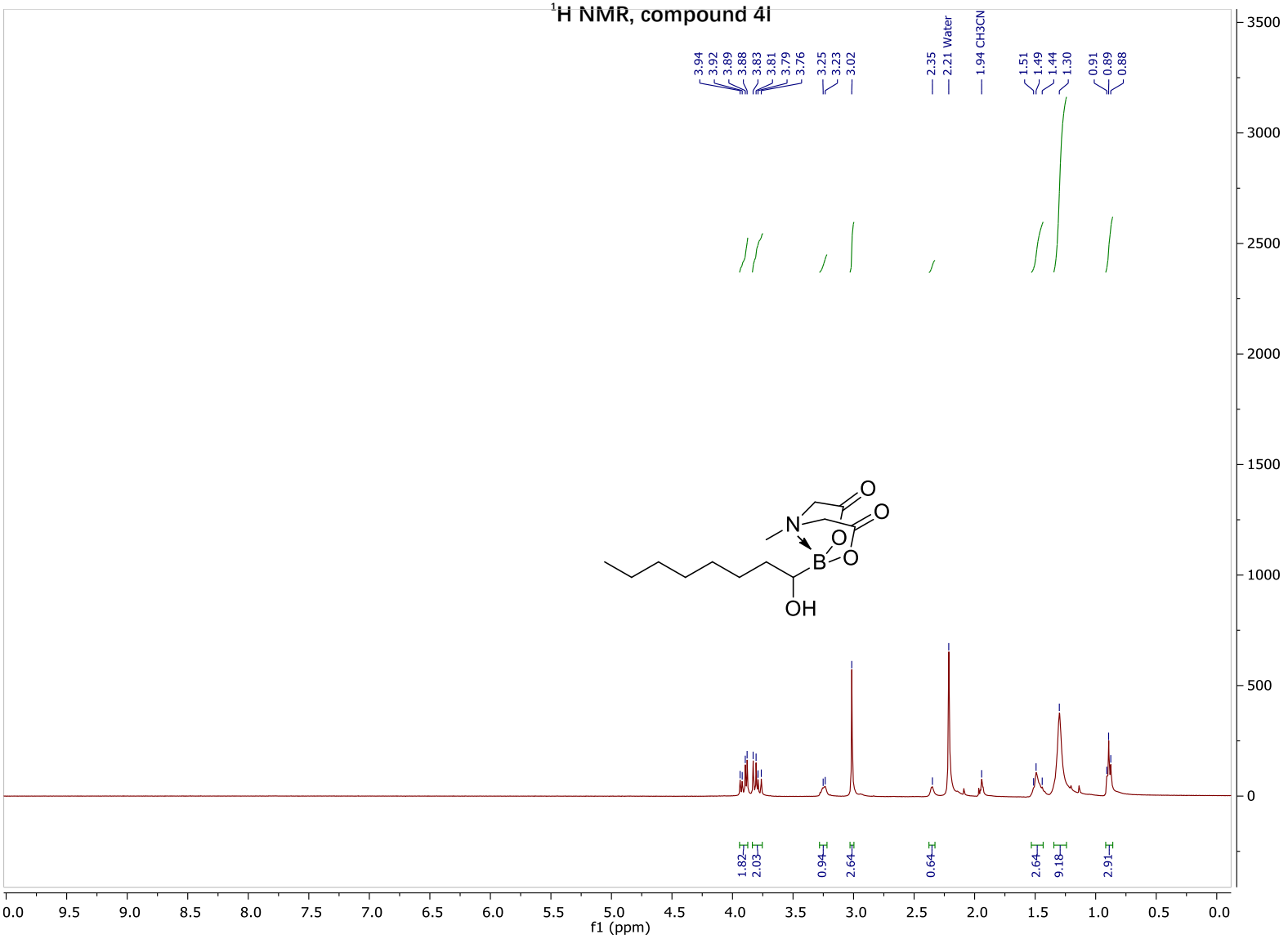


^{13}C NMR, compound 4k

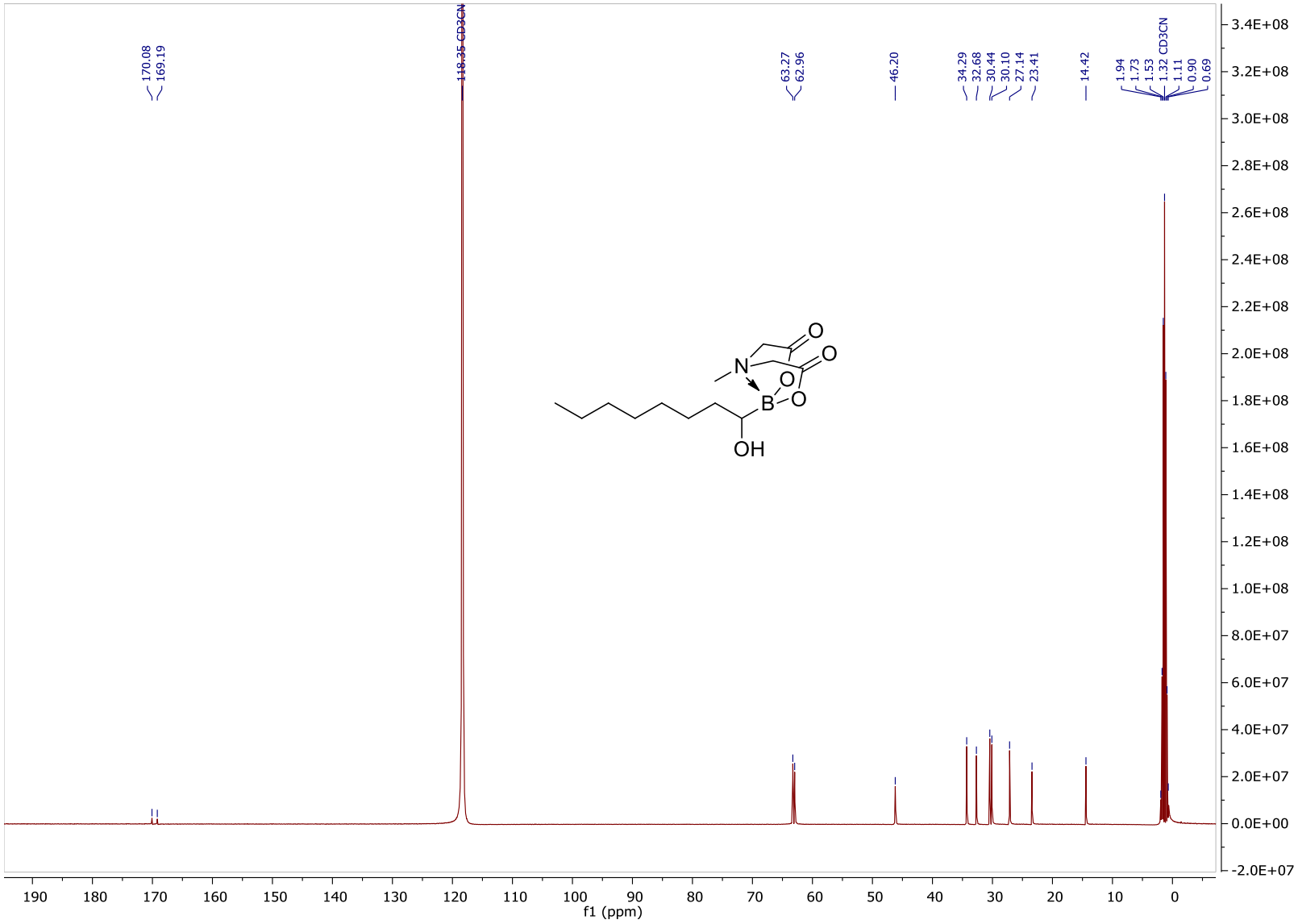


^{11}B NMR, compound 4k

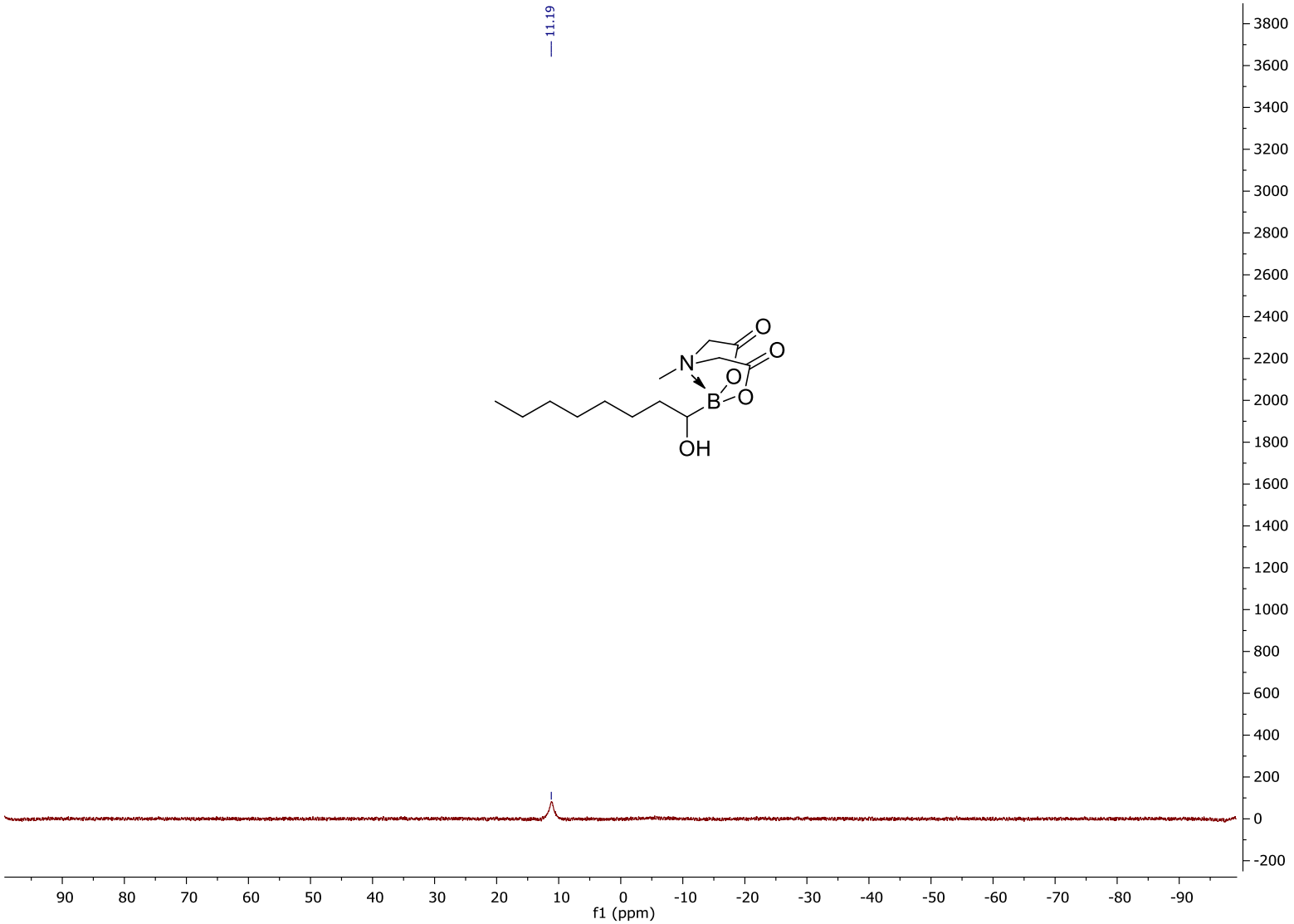


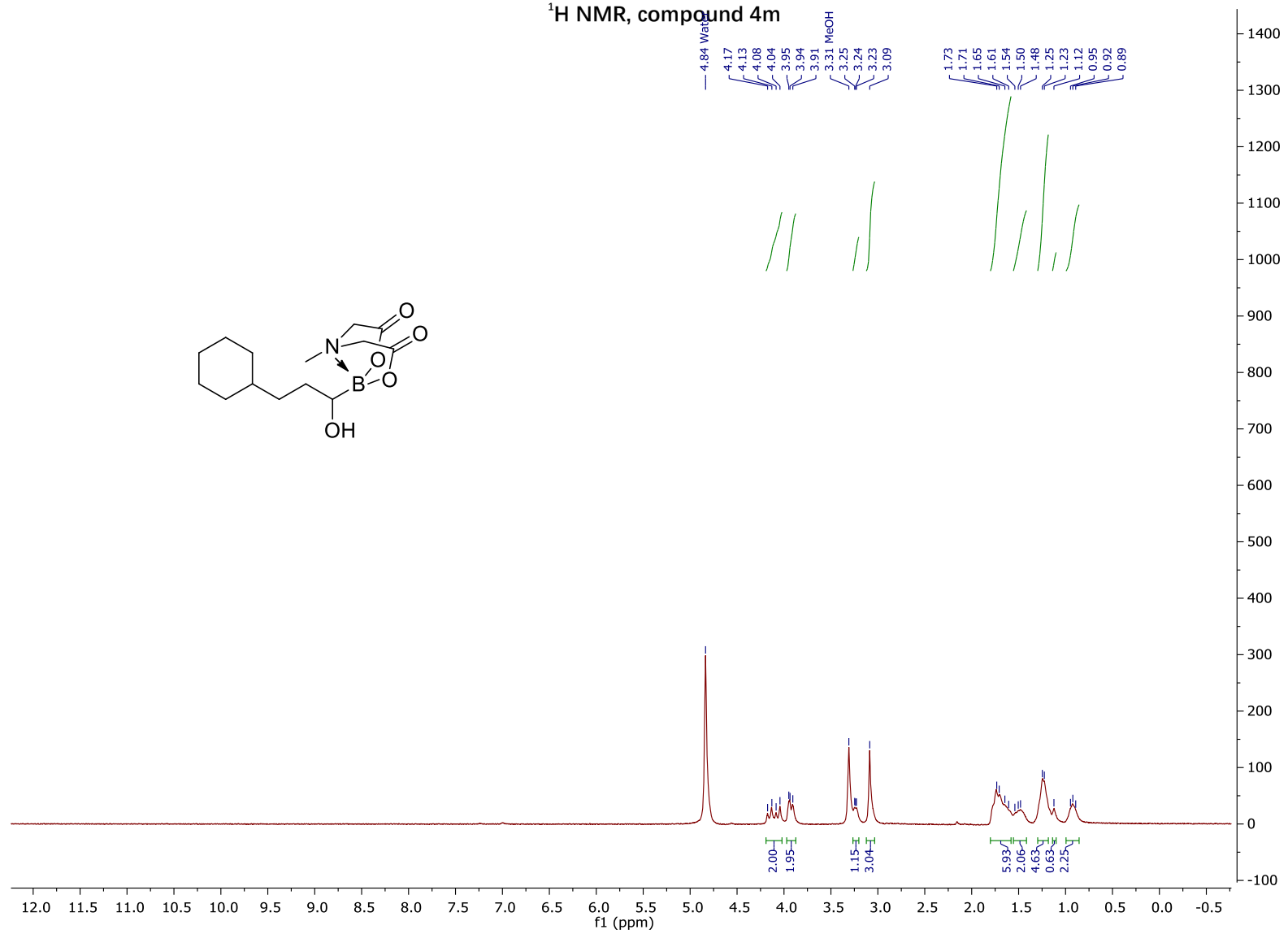

1H NMR, compound 4l
3.94
3.92
3.89
3.88
3.83
3.81
3.79
3.76
3.25
3.23
3.02
2.35
2.21 Water
1.94 CH3CN
1.51
1.49
1.44
1.30
0.91
0.89
0.88
O
O
N
O
B
O
OH
1.82
2.03
0.94
2.64
0.64
2.64
9.18
2.91
f1 (ppm)

^{13}C NMR, compound 4l

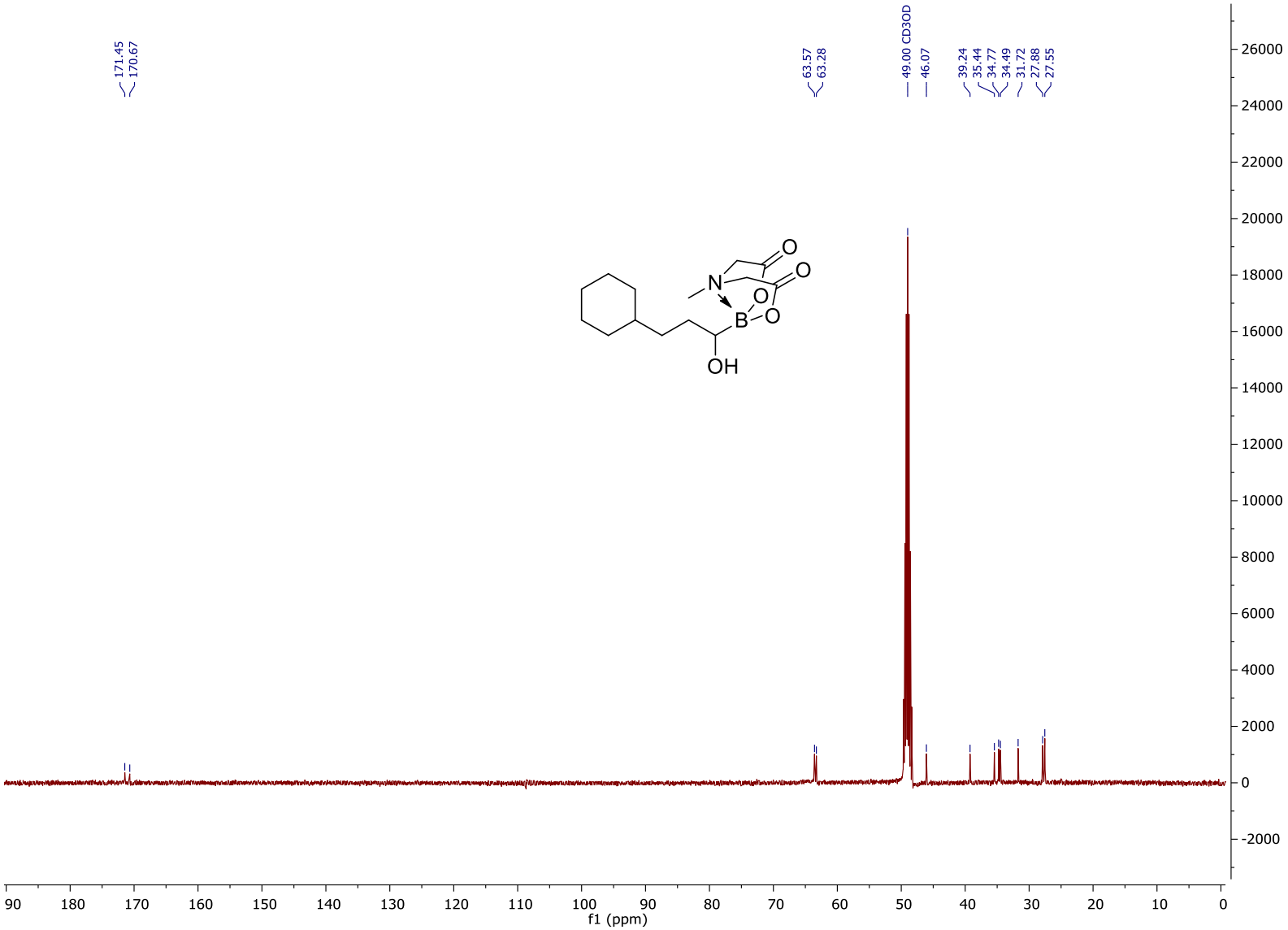


^{11}B NMR, compound 4l

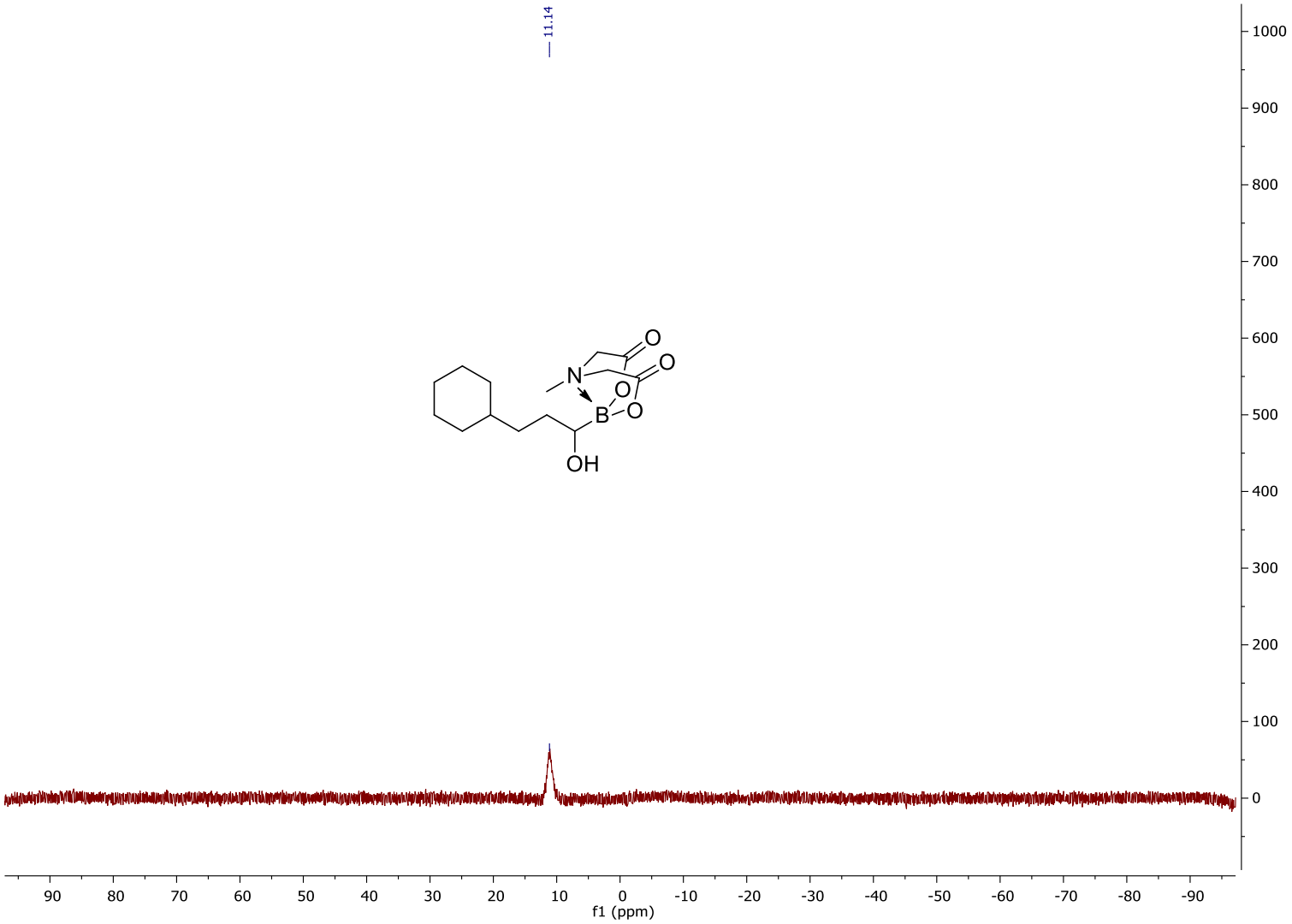


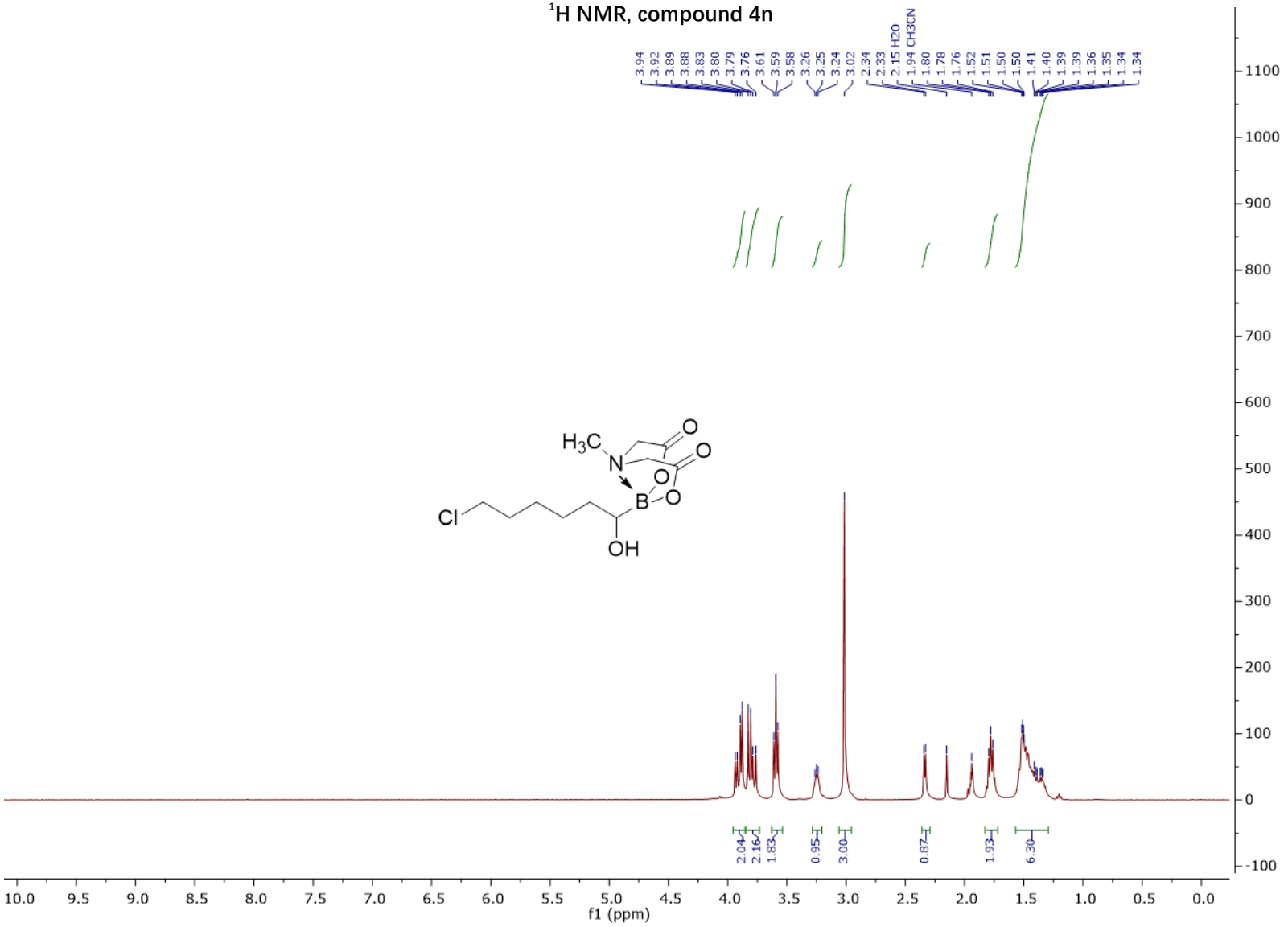

1H NMR, compound 4m
4.84 Wat
4.17
4.13
4.08
4.04
3.95
3.94
3.91
3.31 MeOH
3.25
3.24
3.23
3.09
1.73
1.71
1.65
1.61
1.54
1.50
1.48
1.25
1.23
1.12
0.95
0.92
0.89
2.00
1.95
1.15
3.04
5.93
2.06
4.63
0.63
2.25
f1 (ppm)

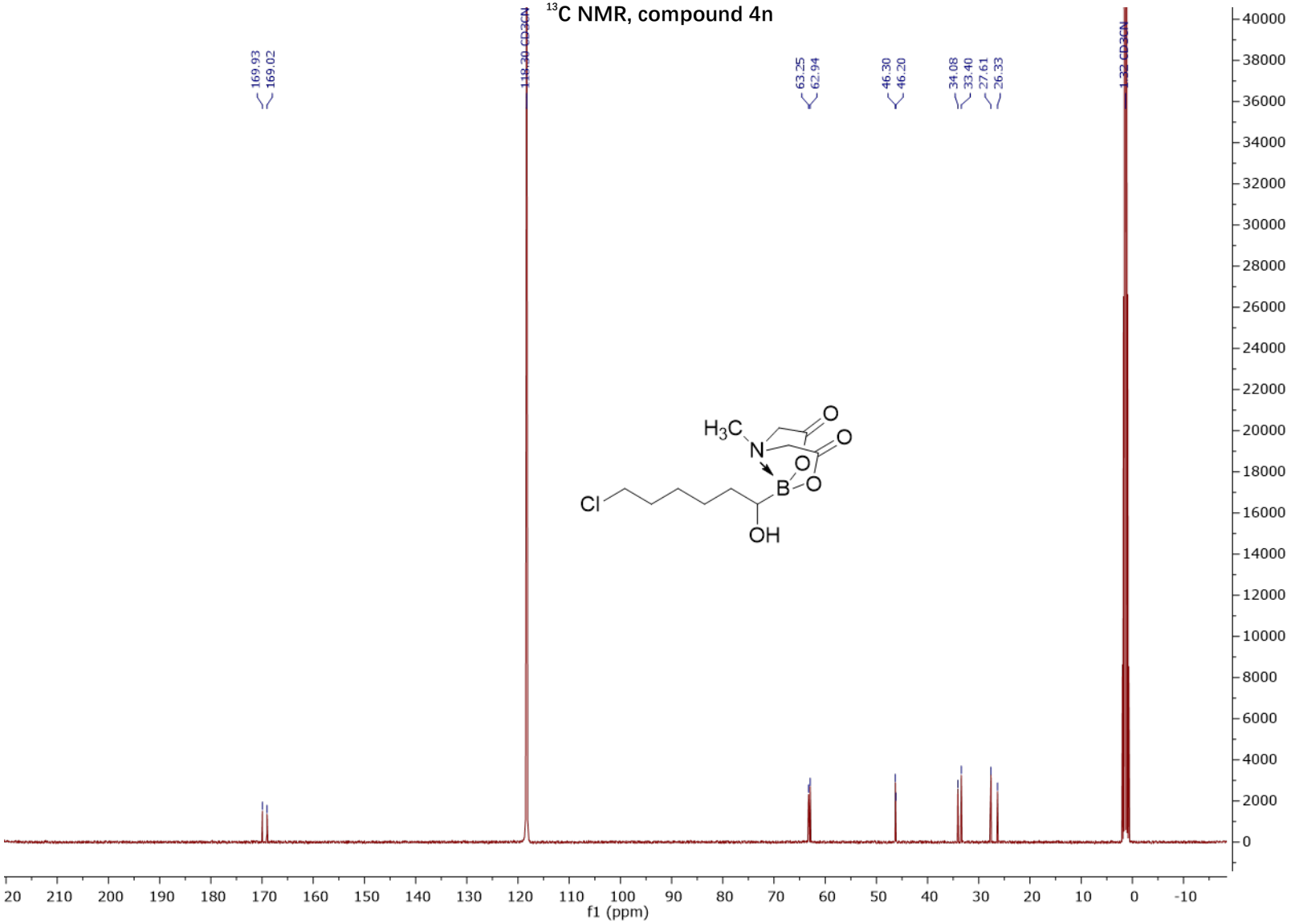
^{13}C NMR, compound 4m



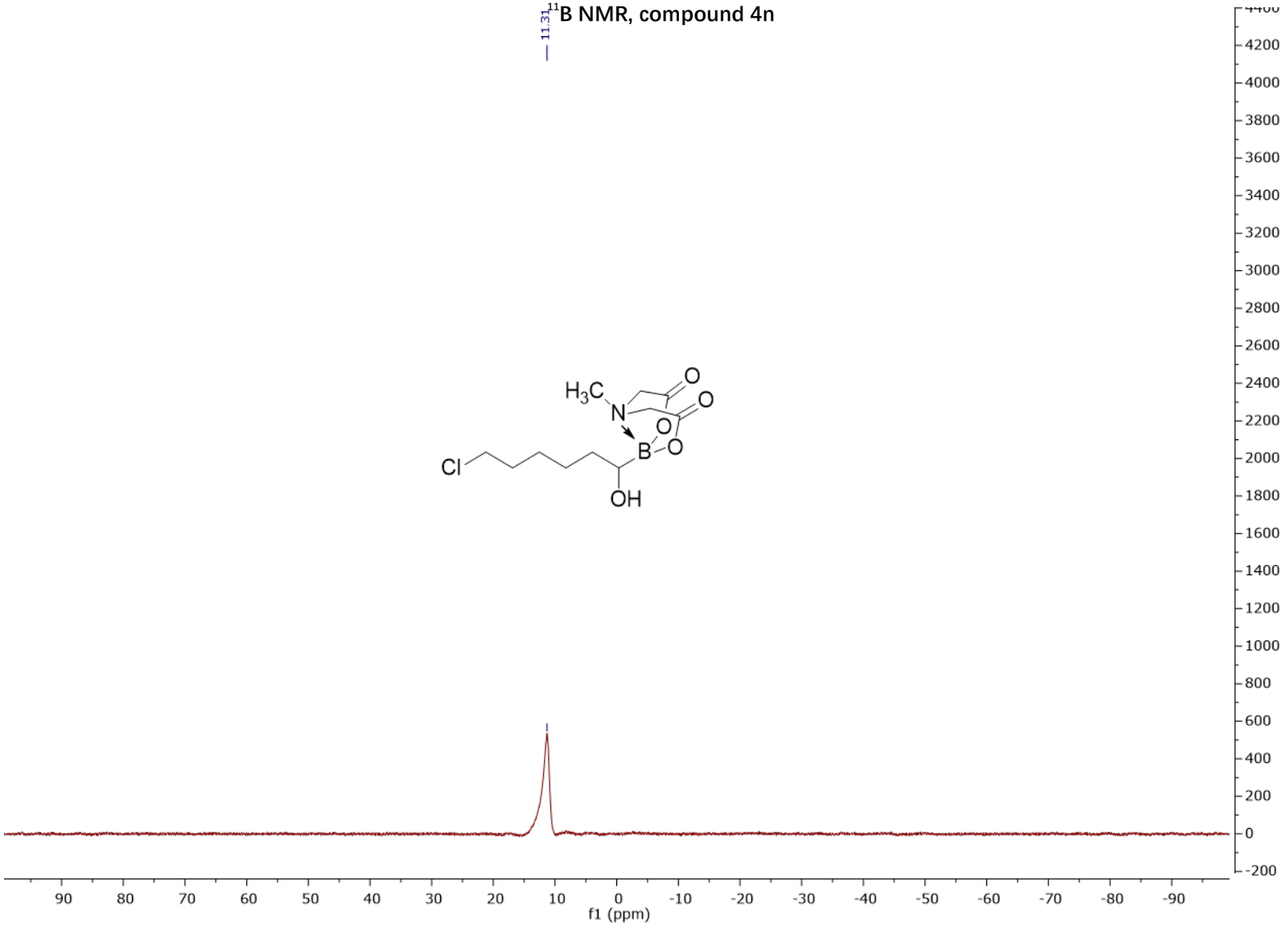
^{11}B NMR, compound 4m

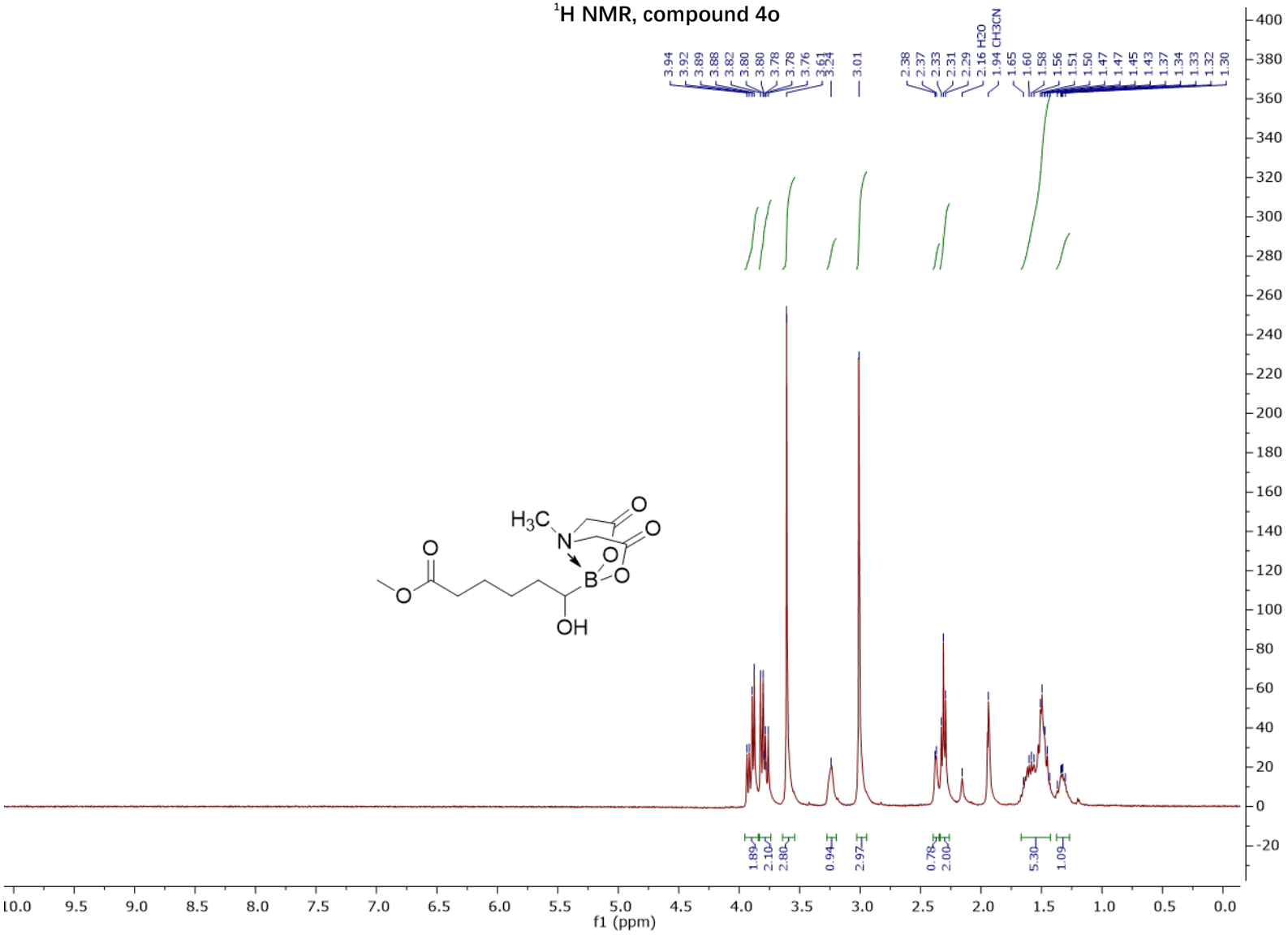


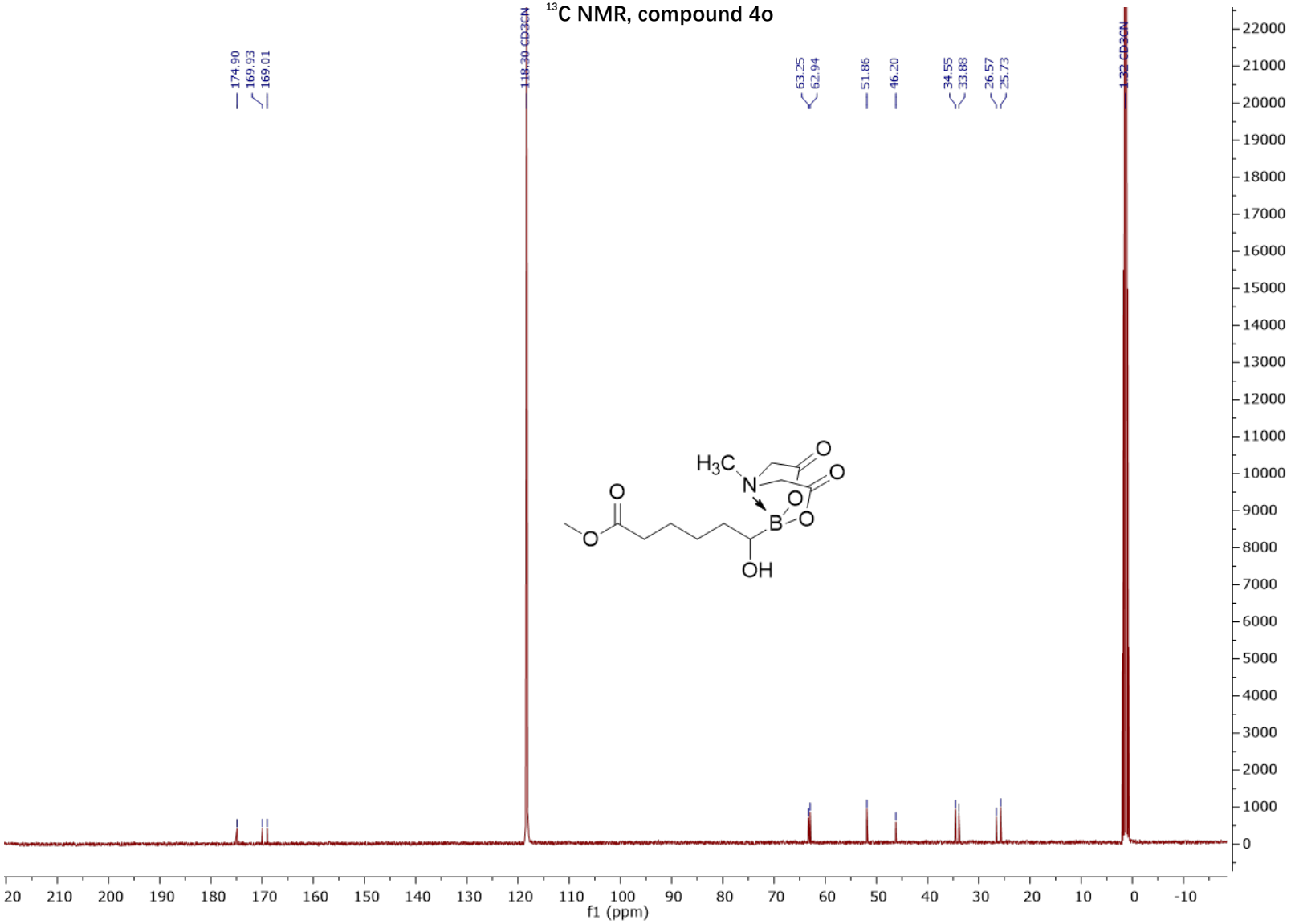

1H NMR, compound 4n
3.94
3.92
3.89
3.88
3.83
3.80
3.79
3.76
3.61
3.59
3.58
3.26
3.25
3.24
3.02
2.34
2.33
2.15 H2O
1.94 CH3CN
1.80
1.78
1.76
1.52
1.51
1.50
1.50
1.41
1.40
1.39
1.39
1.36
1.35
1.34
1.34
H3C
N
O
O
O
B
O
Cl
OH
2.04
2.16
1.83
0.95
3.00
0.87
1.93
6.30
f1 (ppm)


13C NMR, compound 4n
169.93
169.02
118.30 CD3CN
63.25
62.94
46.30
46.20
34.08
33.40
27.61
26.33
1.32 CD3CN
H3C
N
O
O
O
O
B
O
Cl
OH
f1 (ppm)

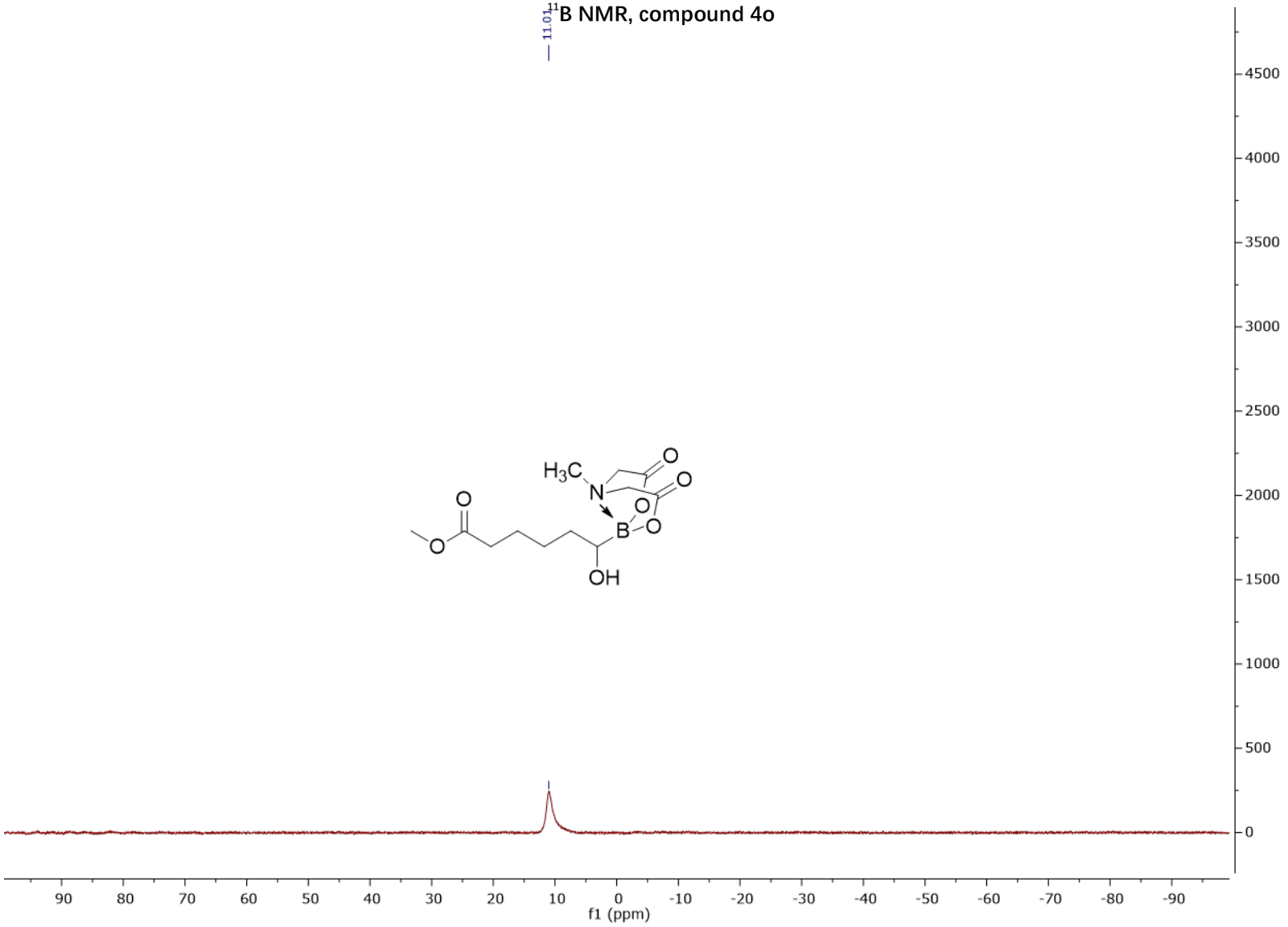
^{11}B NMR, compound 4n

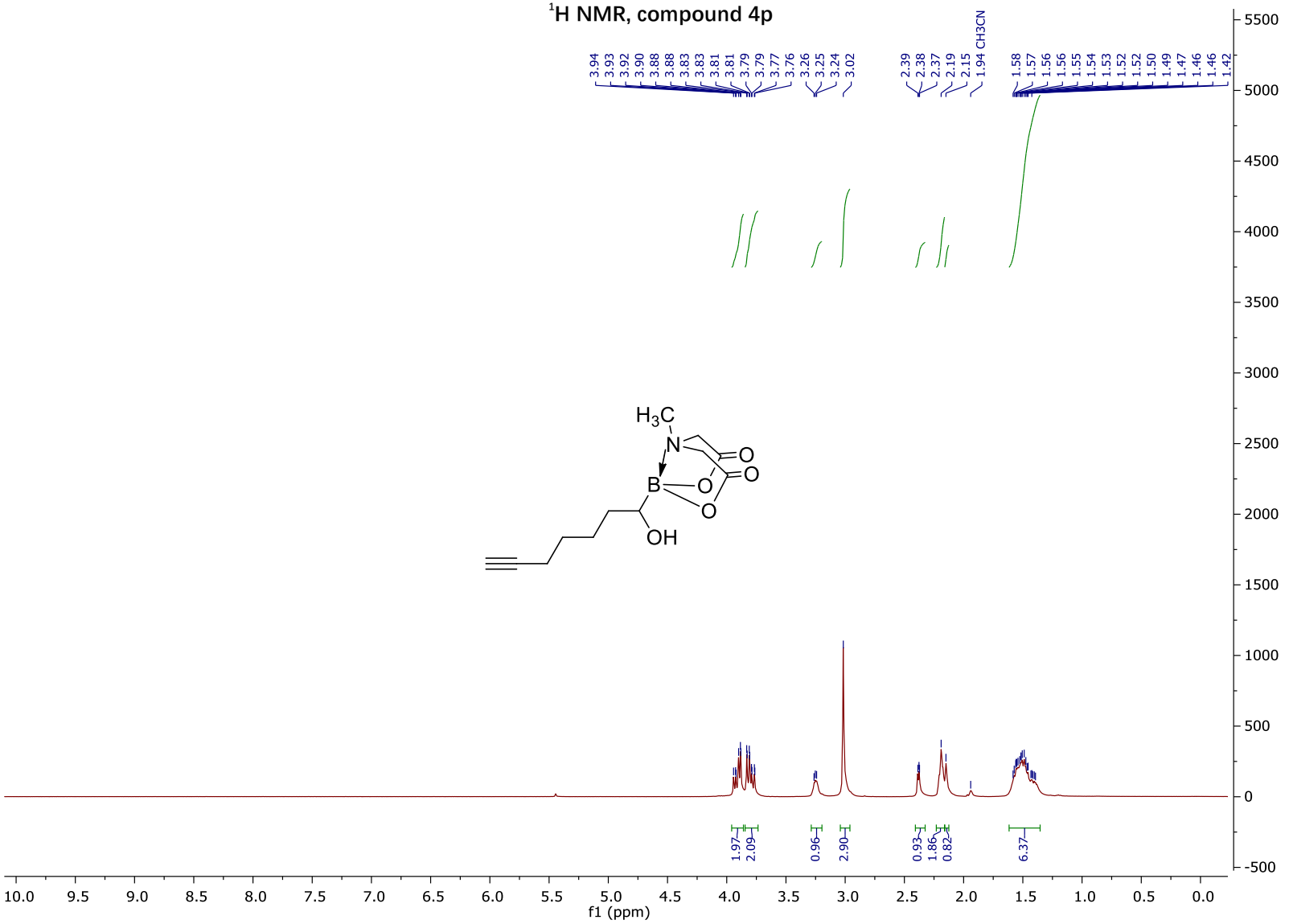



1H NMR, compound 4o
3.94
3.92
3.89
3.88
3.82
3.80
3.80
3.78
3.78
3.76
3.61
3.54
3.01
2.38
2.37
2.33
2.31
2.29
2.16 H2O
1.94 CH3CN
1.65
1.60
1.58
1.56
1.51
1.50
1.47
1.47
1.45
1.43
1.37
1.34
1.33
1.32
1.30
1.89
2.10
2.80
0.94
2.97
0.78
2.00
5.30
1.09
f1 (ppm)

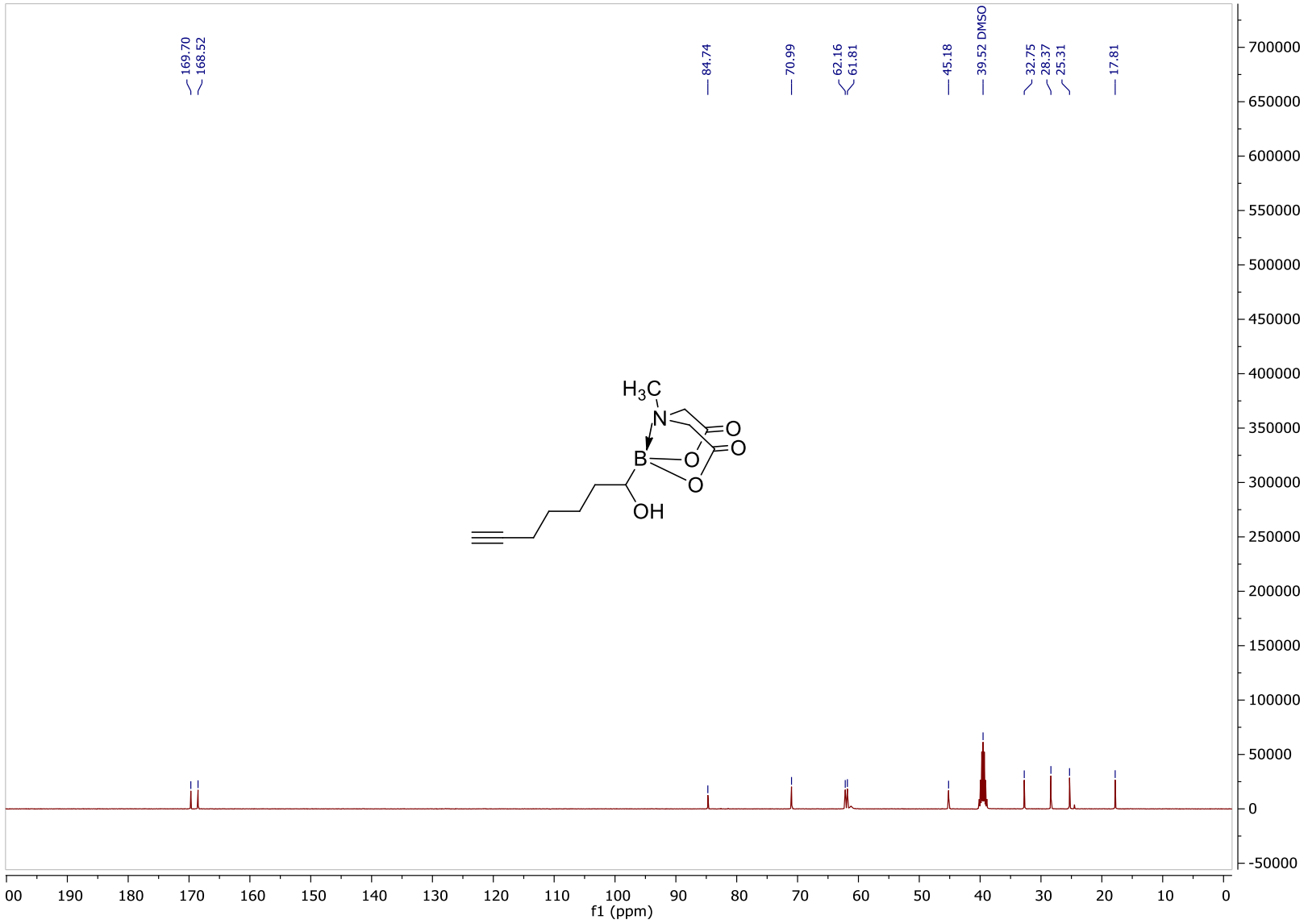

13C NMR, compound 4o
174.90
169.93
169.01
118.30 CD3CN
63.25
62.94
51.86
46.20
34.55
33.88
26.57
25.73
1.32 CD3CN
H3C
N
O
O
O
O
B
O
O
OH
f1 (ppm)

^{11}B NMR, compound 4o

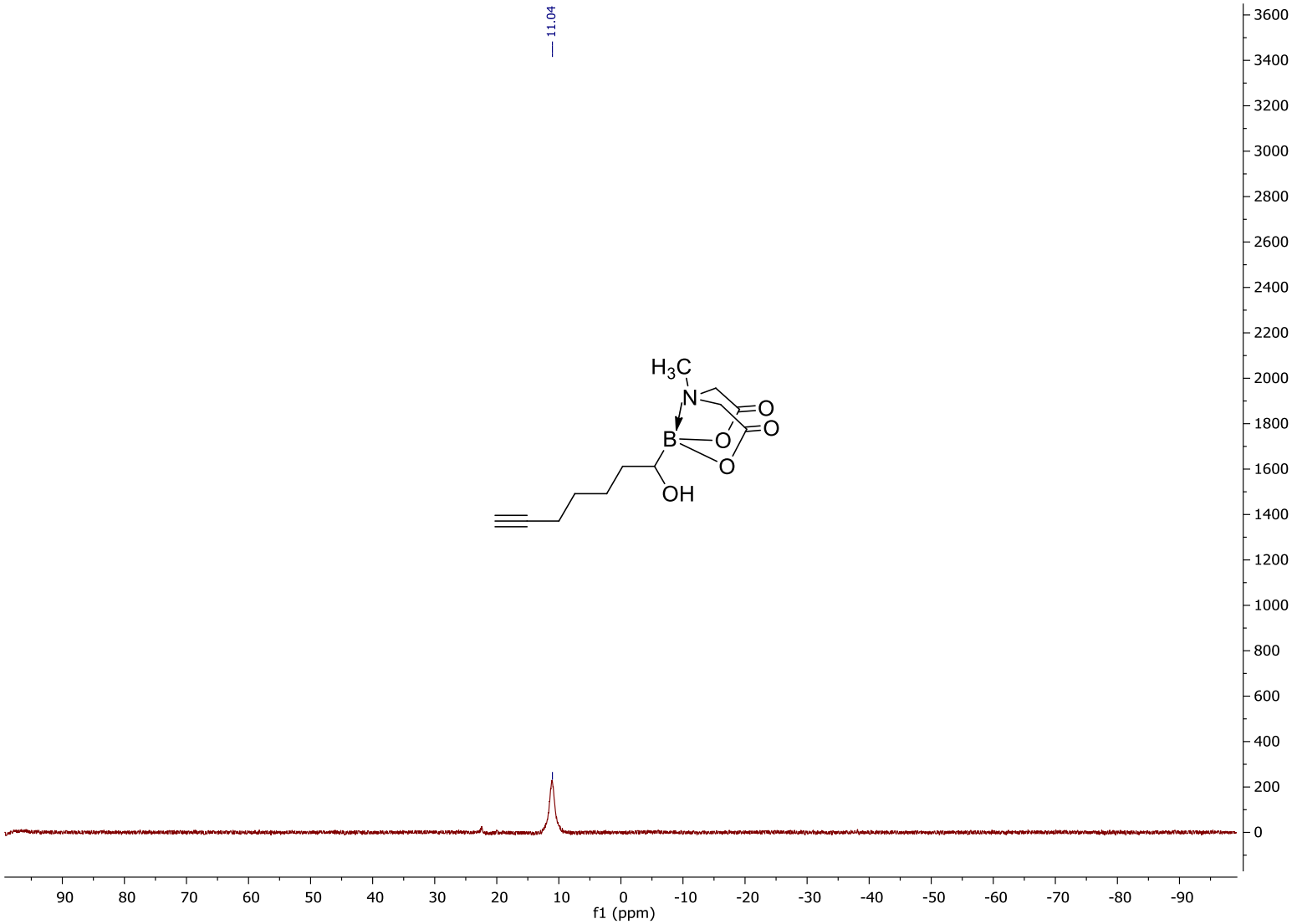


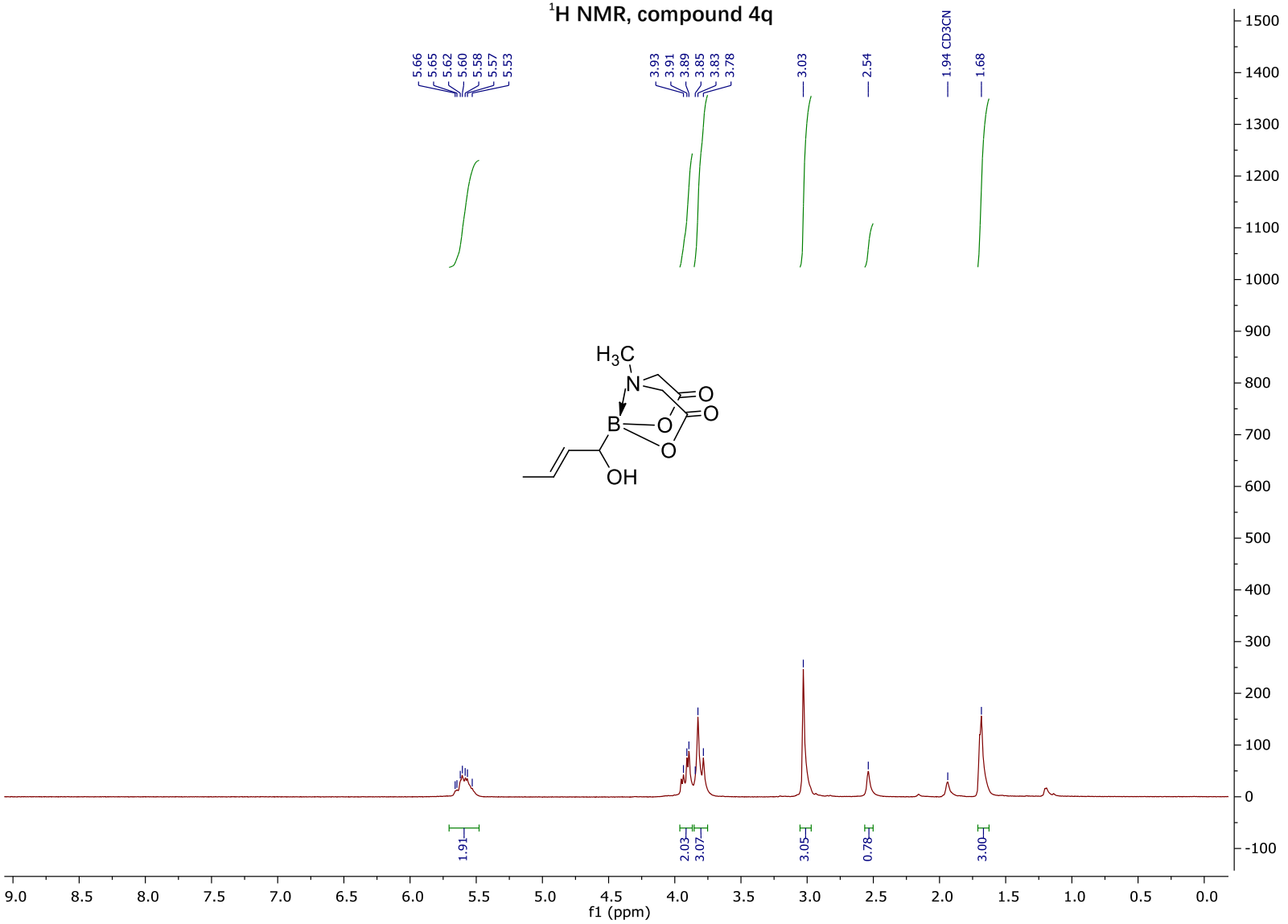

1H NMR, compound 4p
3.94
3.93
3.92
3.90
3.88
3.88
3.83
3.83
3.81
3.81
3.79
3.79
3.77
3.76
3.26
3.25
3.24
3.02
2.39
2.38
2.37
2.19
2.15
1.94 CH3CN
1.58
1.57
1.56
1.56
1.55
1.54
1.53
1.52
1.52
1.50
1.49
1.47
1.46
1.46
1.42
H3C
N
O
O
B
O
O
OH
1.97
2.09
0.96
2.90
0.93
1.86
0.82
6.37
f1 (ppm)

^{13}C NMR, compound 4p

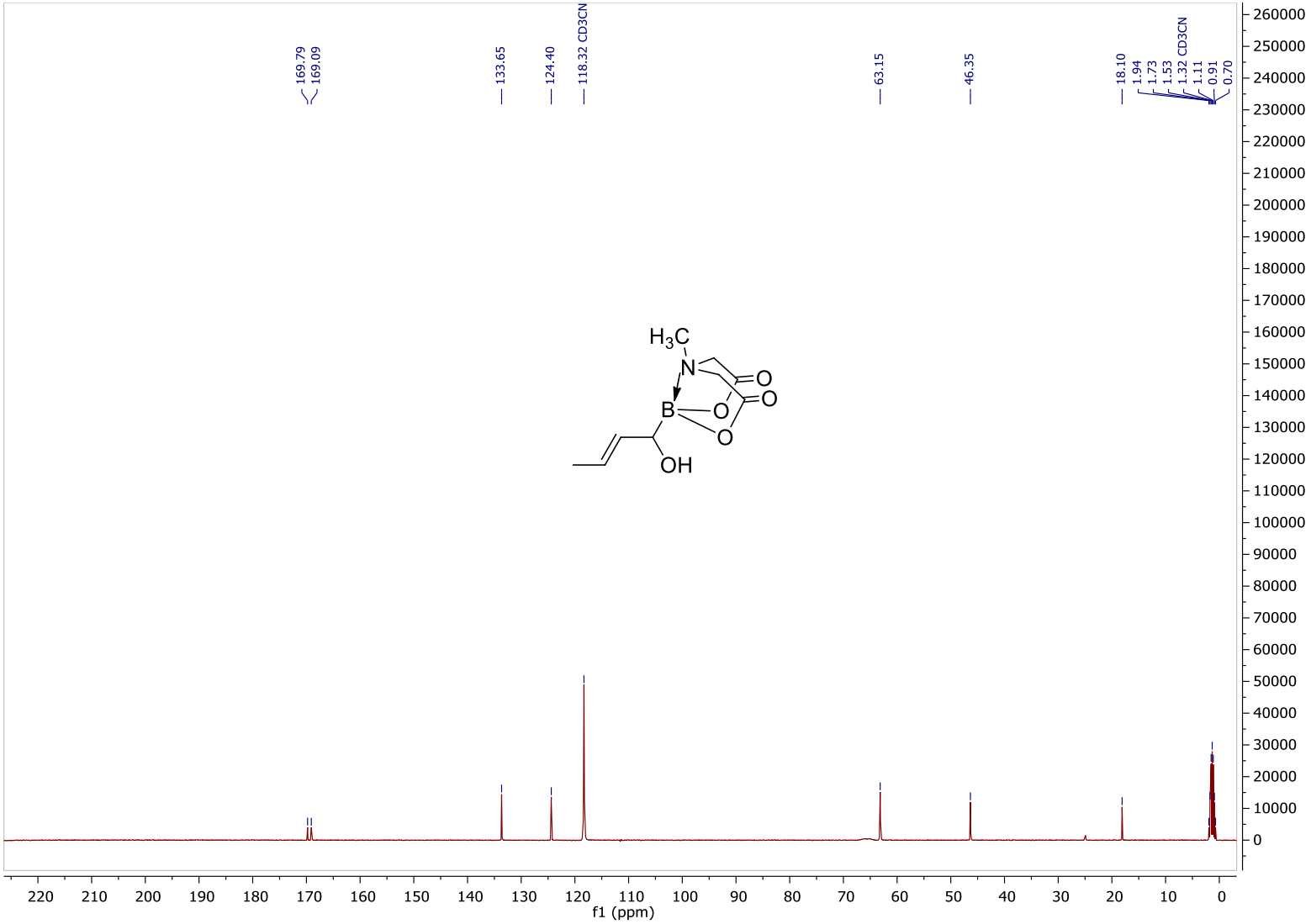


^{11}B NMR, compound 4p

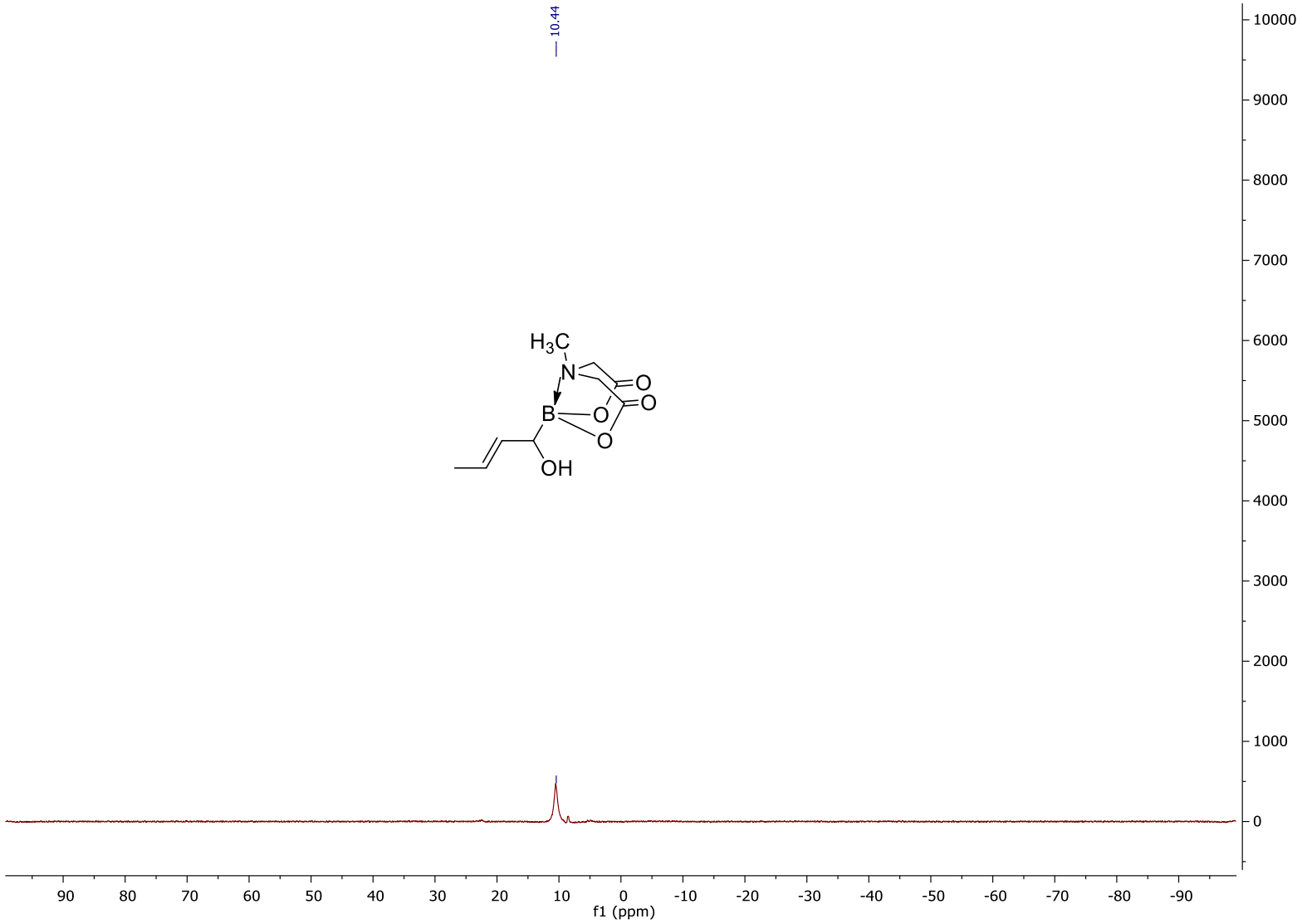


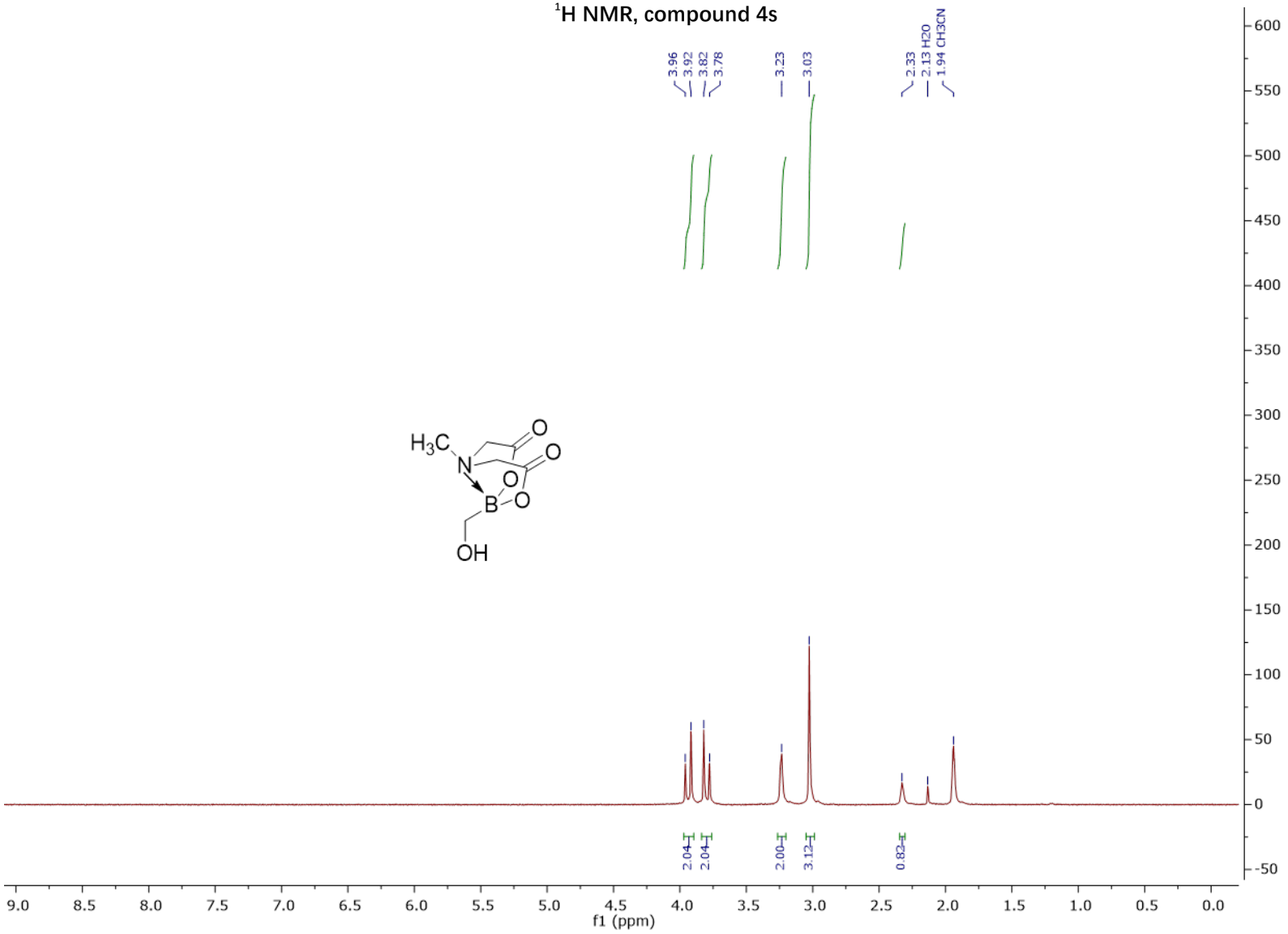

^{1}H NMR, compound 4q
5.66
5.65
5.62
5.60
5.58
5.57
5.53
3.93
3.91
3.89
3.85
3.83
3.78
3.03
2.54
1.94 CD3CN
1.68
H3C
N
B
O
O
O
O
OH
1.91
2.03
3.07
3.05
0.78
3.00
f1 (ppm)

^{13}C NMR, compound 4q

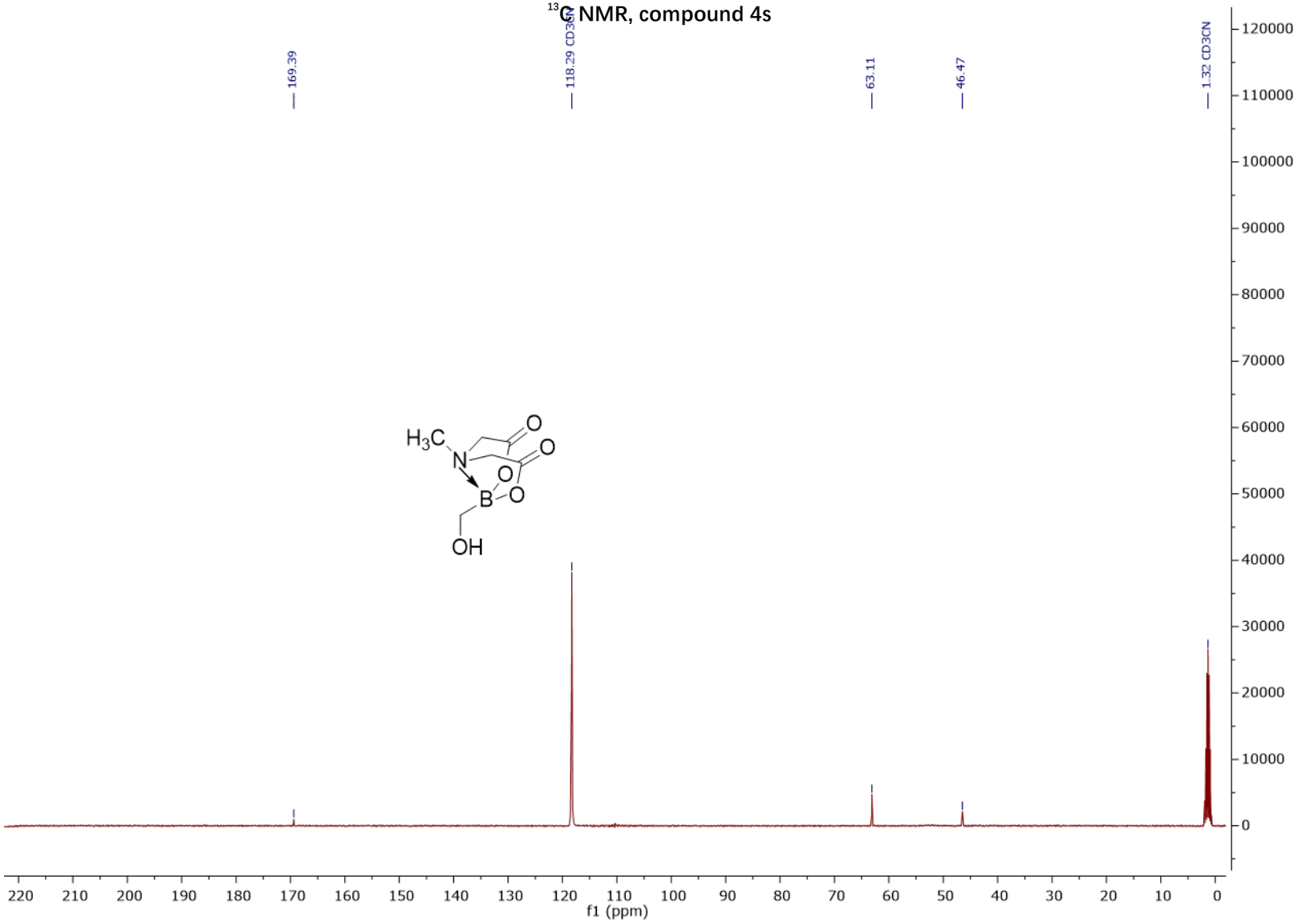


^{11}B NMR, compound 4q

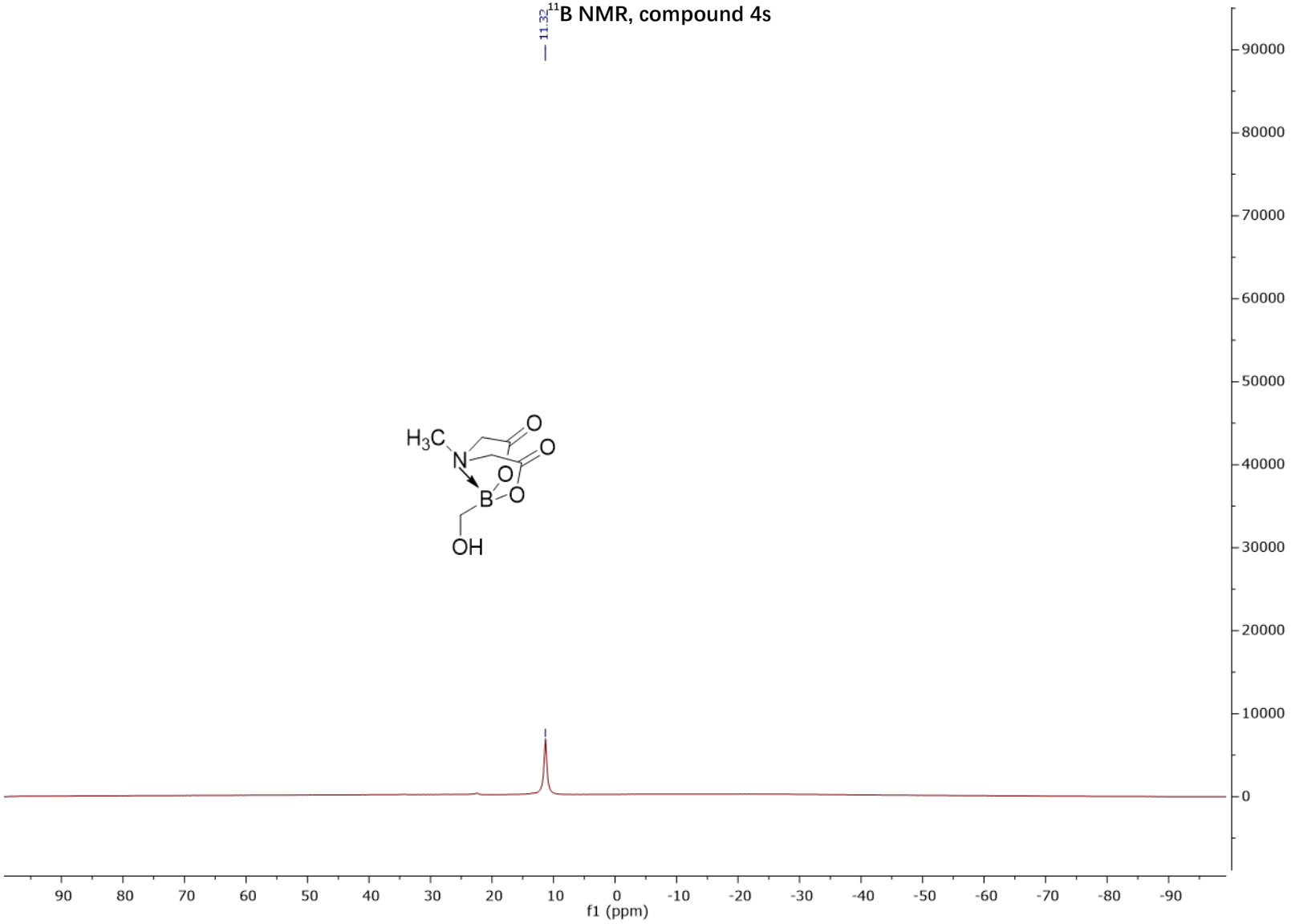



1H NMR, compound 4s
3.96
3.92
3.82
3.78
3.23
3.03
2.33
2.13 H2O
1.94 CH3CN
H3C
N
O
O
O
B
O
OH
2.04
2.04
2.00
3.12
0.82
f1 (ppm)

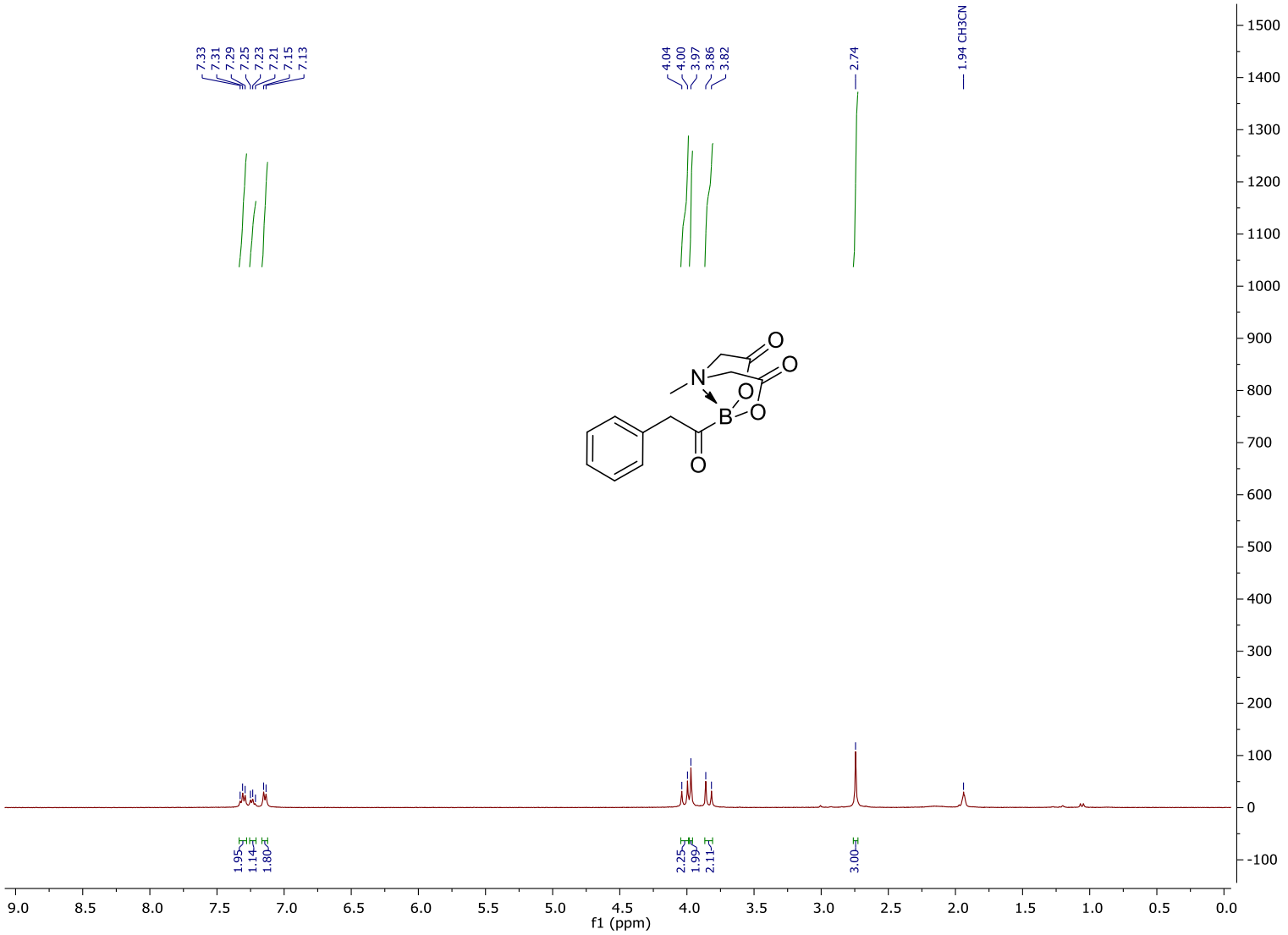
^{13}C NMR, compound 4s



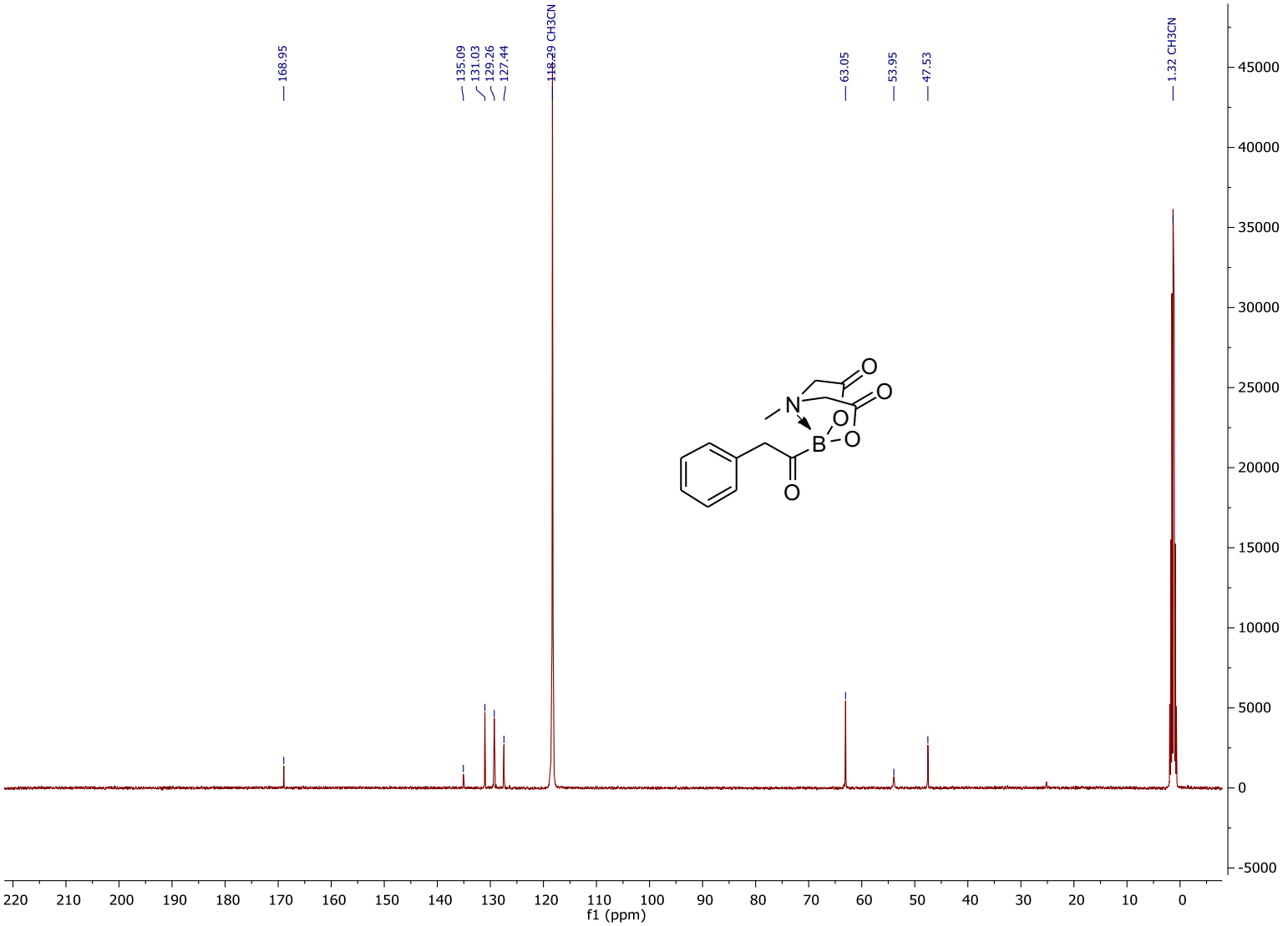
^{11}B NMR, compound 4s



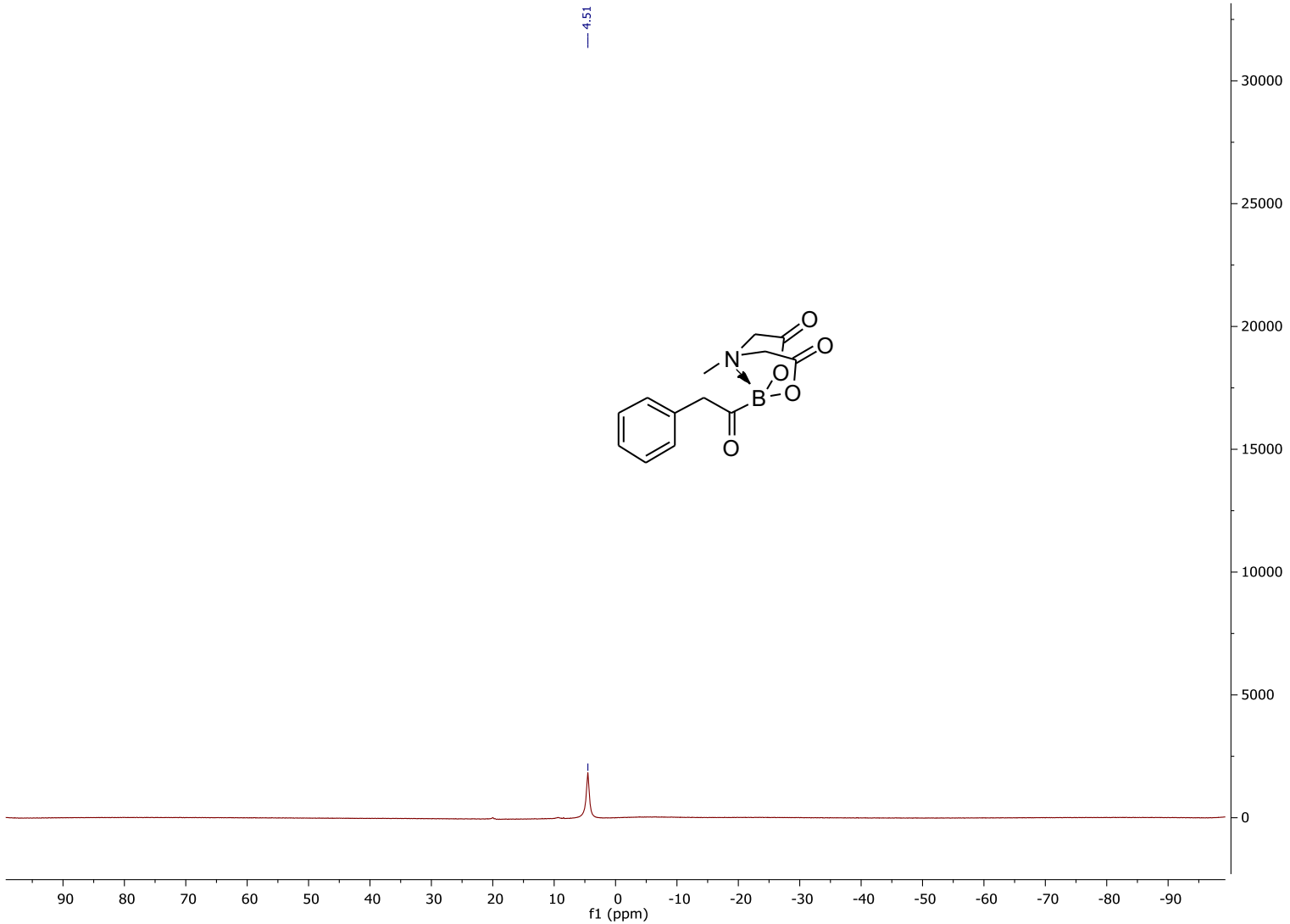
^{1}H NMR, compound 5a



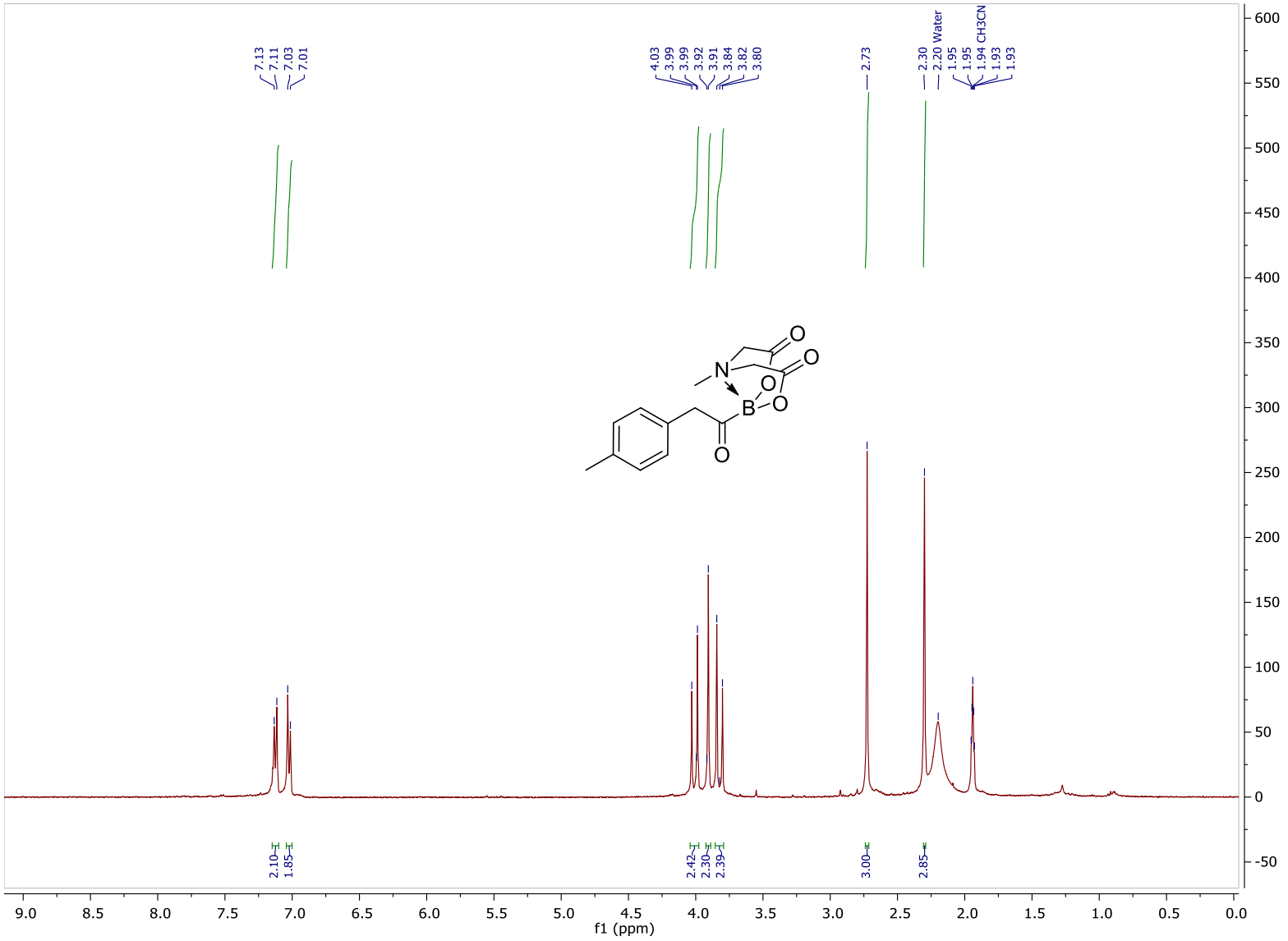
^{13}C NMR, compound 5a



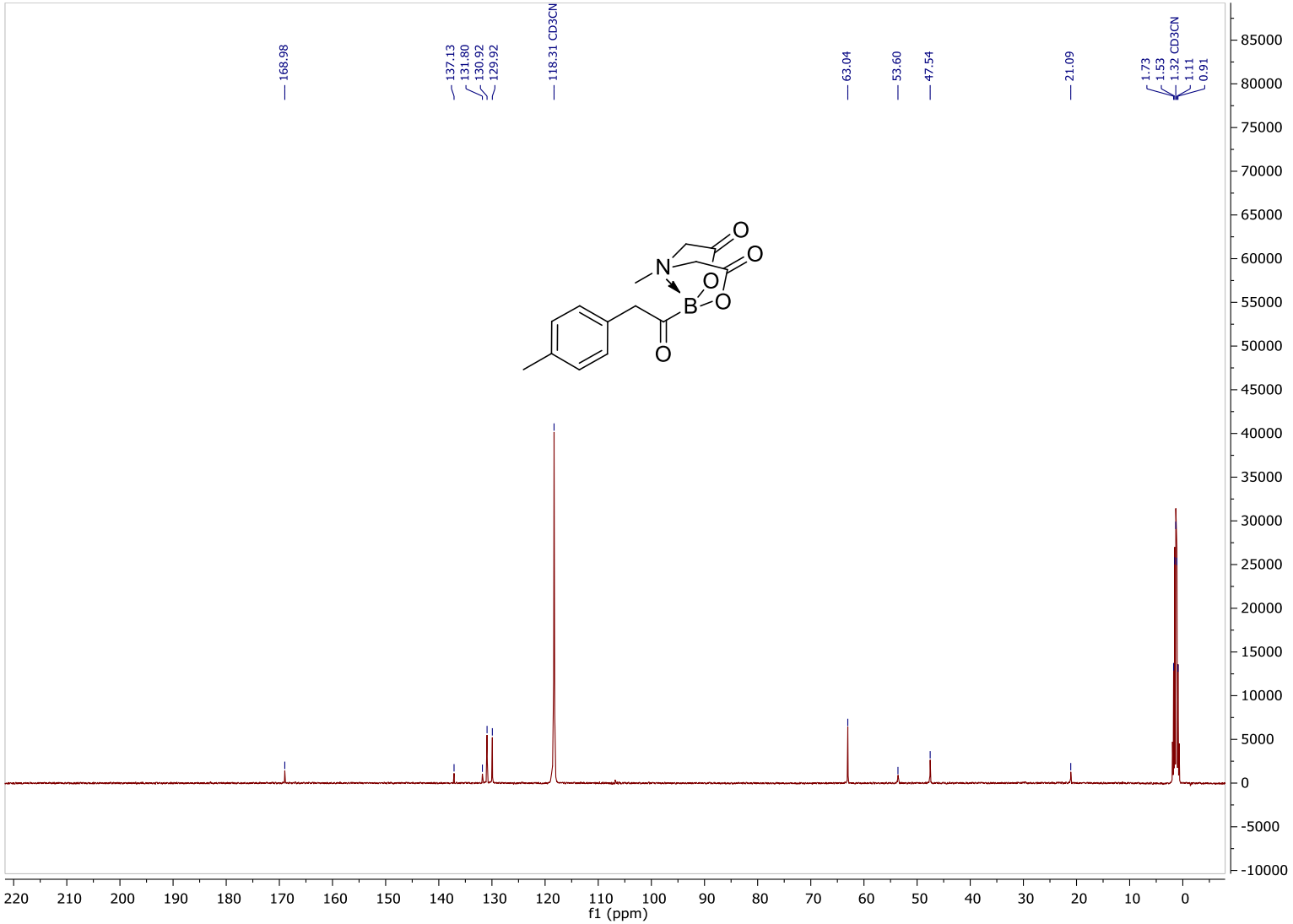
^{11}B NMR, compound 5a



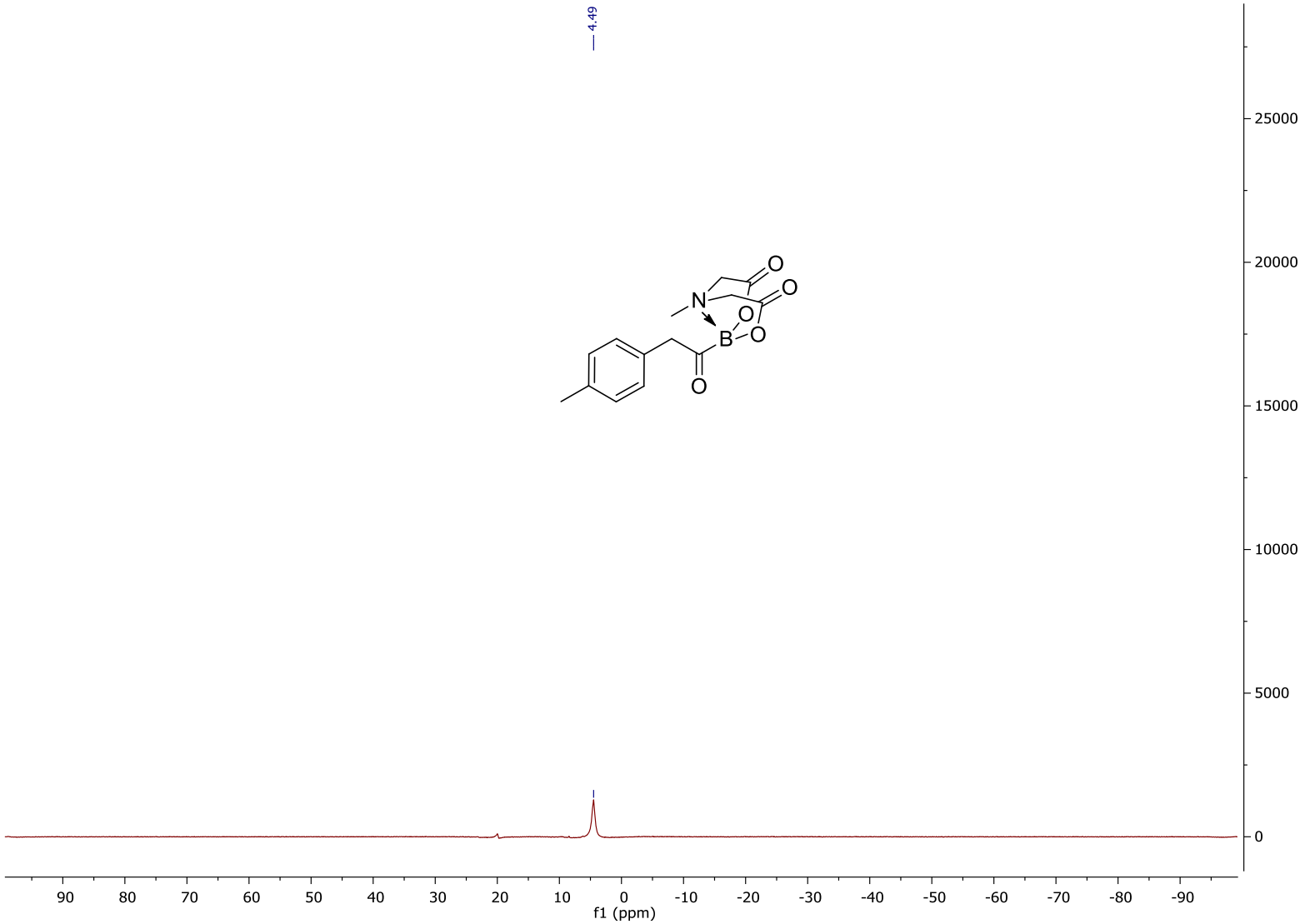
^{1}H NMR, compound 5b



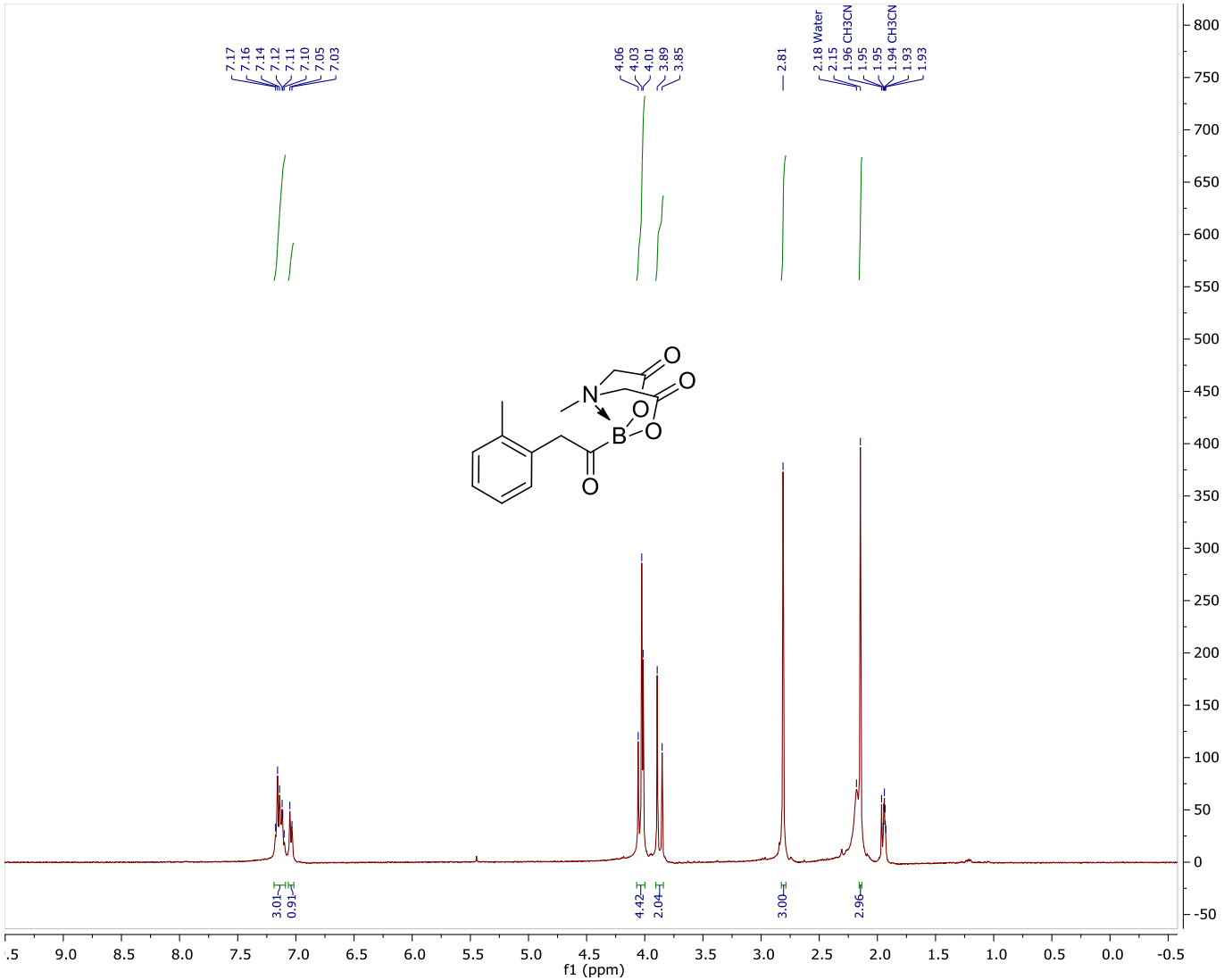
^{13}C NMR, compound 5b



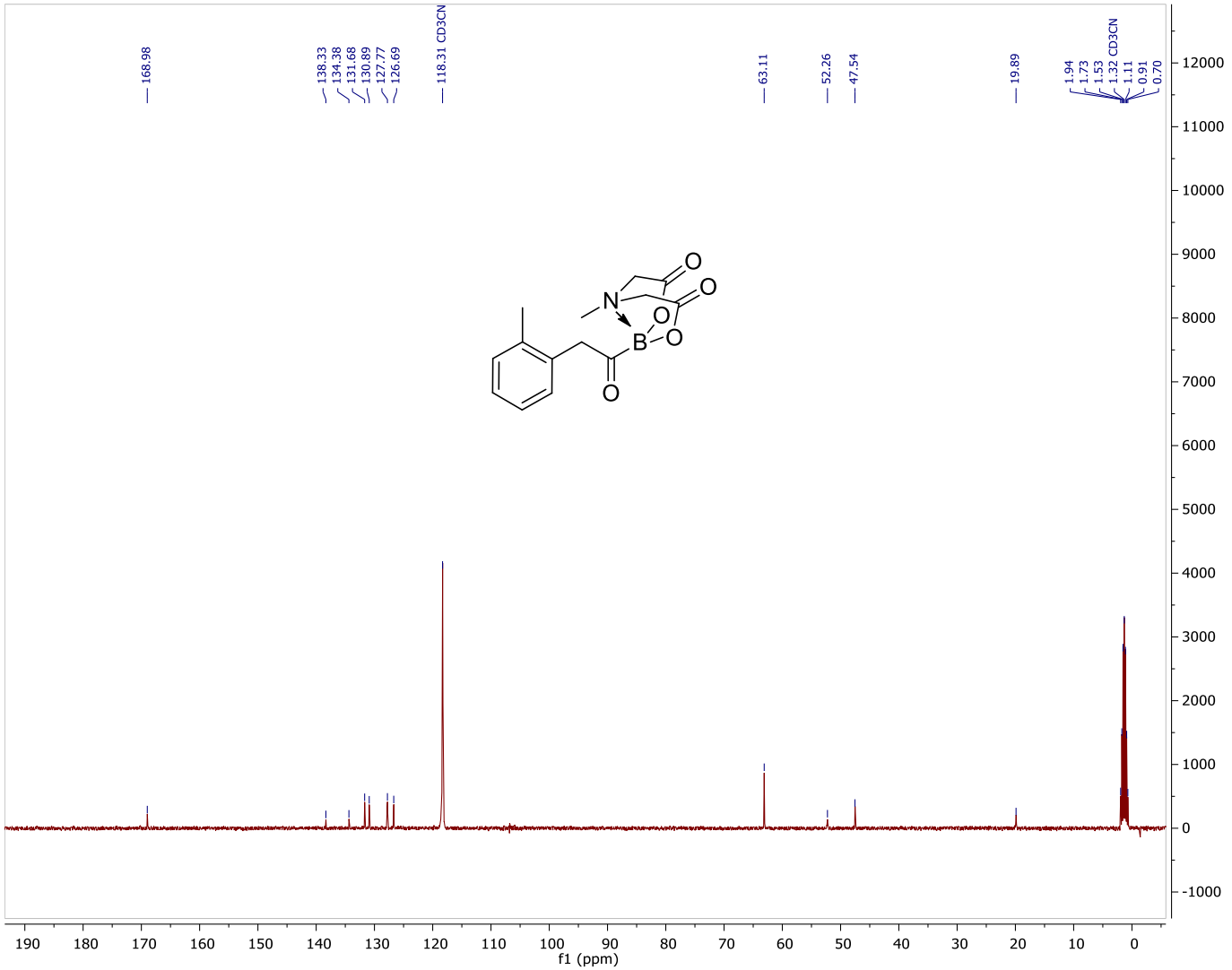
^{11}B NMR, compound 5b



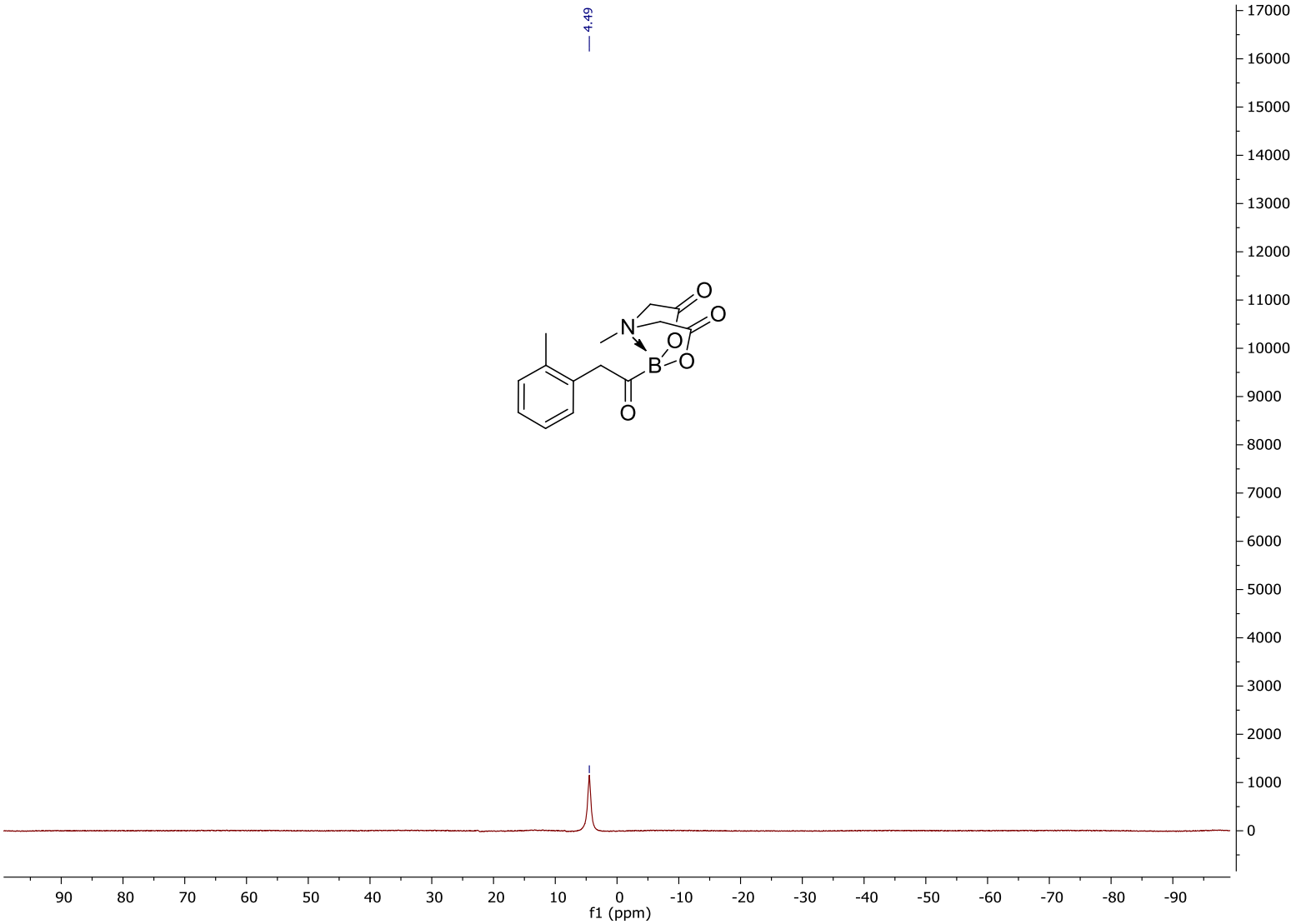
^{1}H NMR, compound 5c



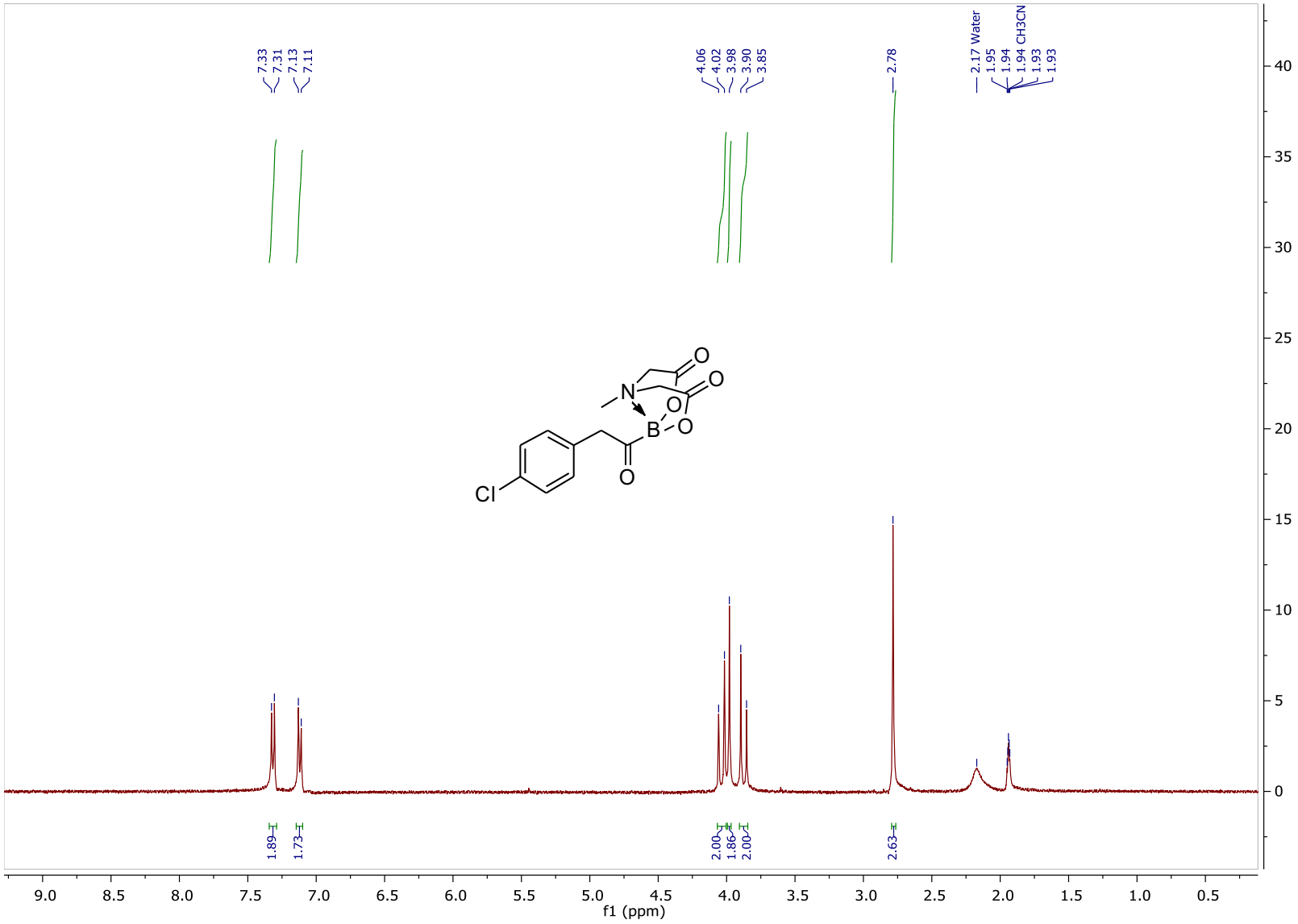
^{13}C NMR, compound 5c

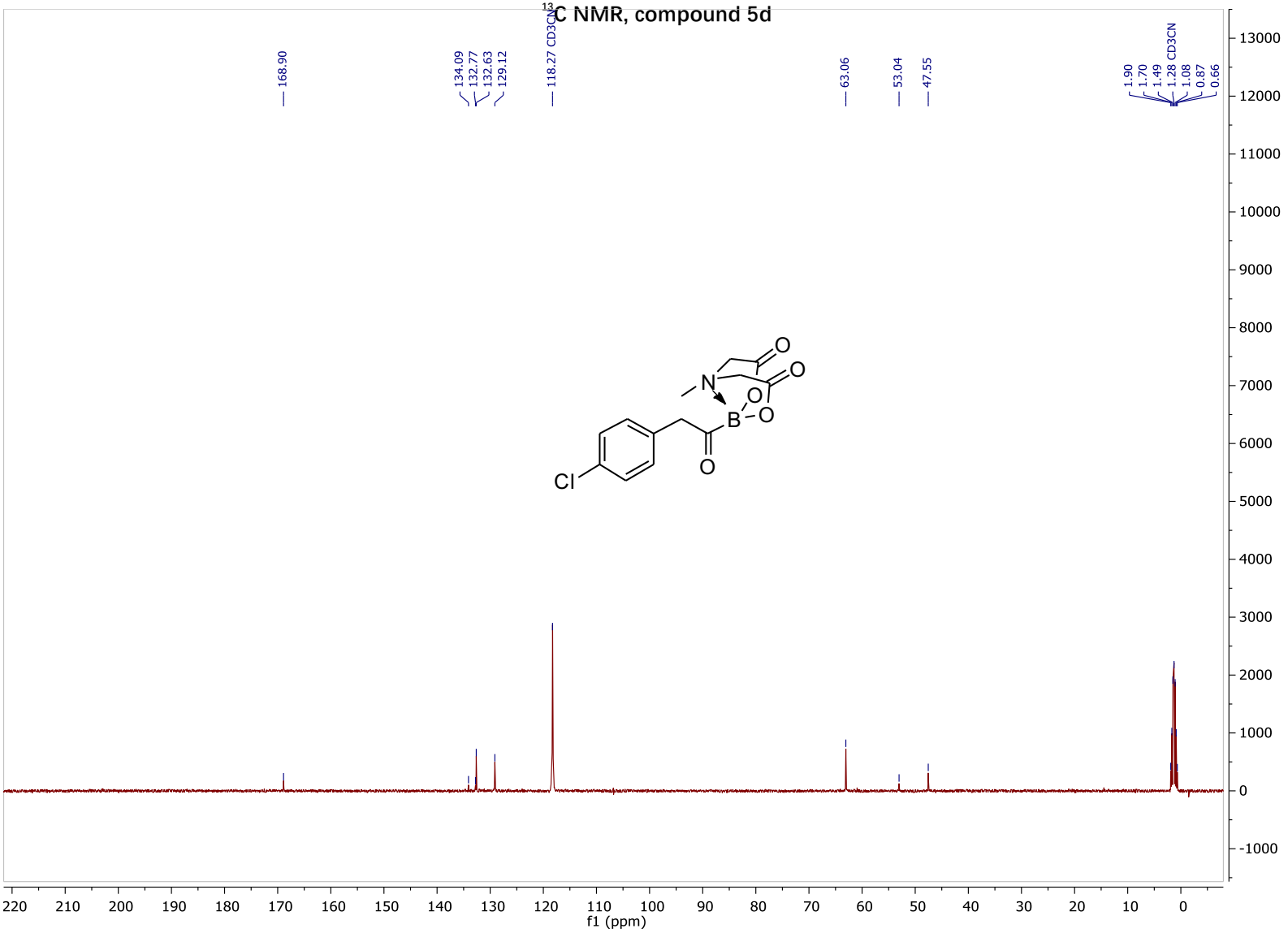


^{11}B NMR, compound 5c

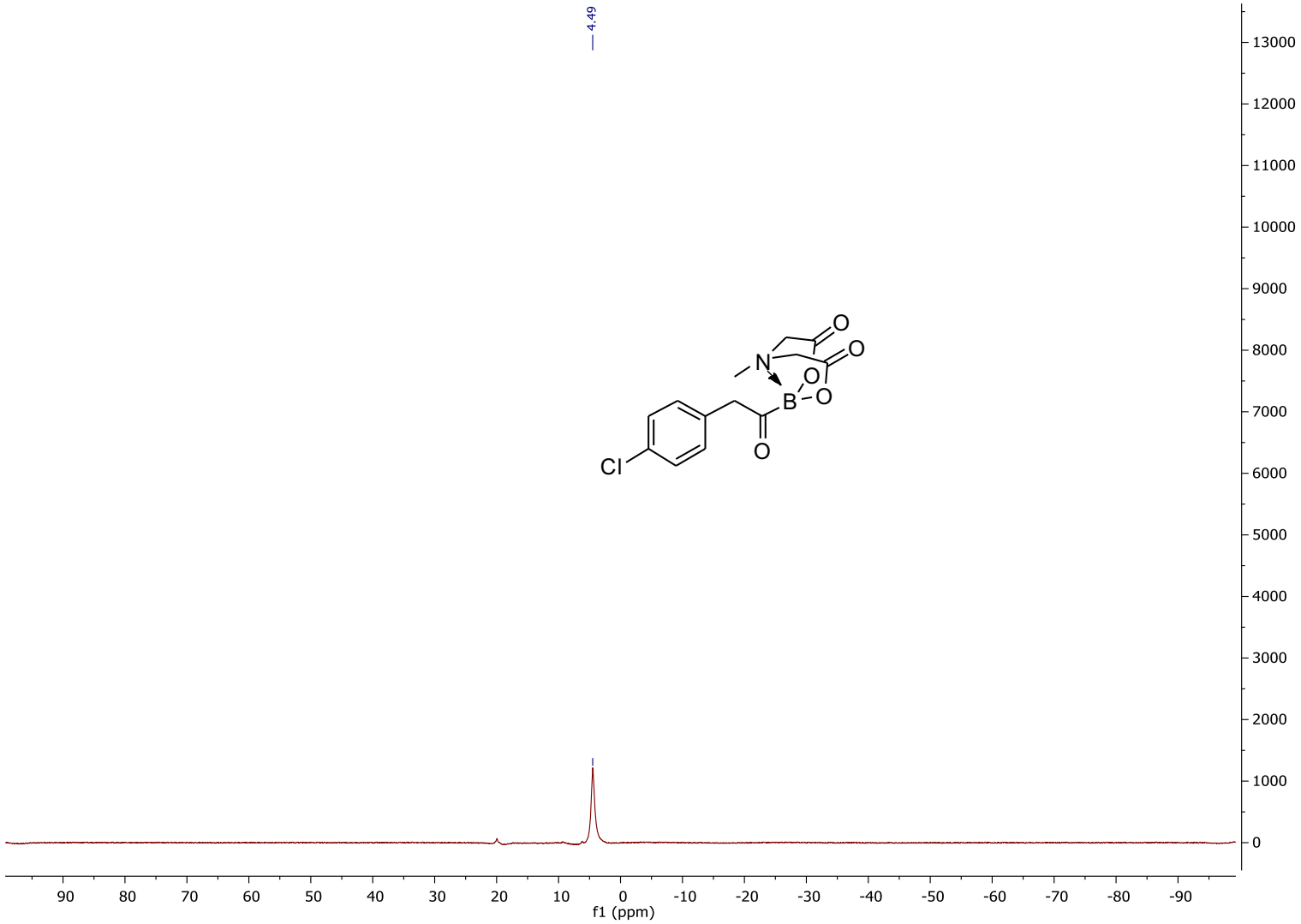


^{1}H NMR, compound 5d

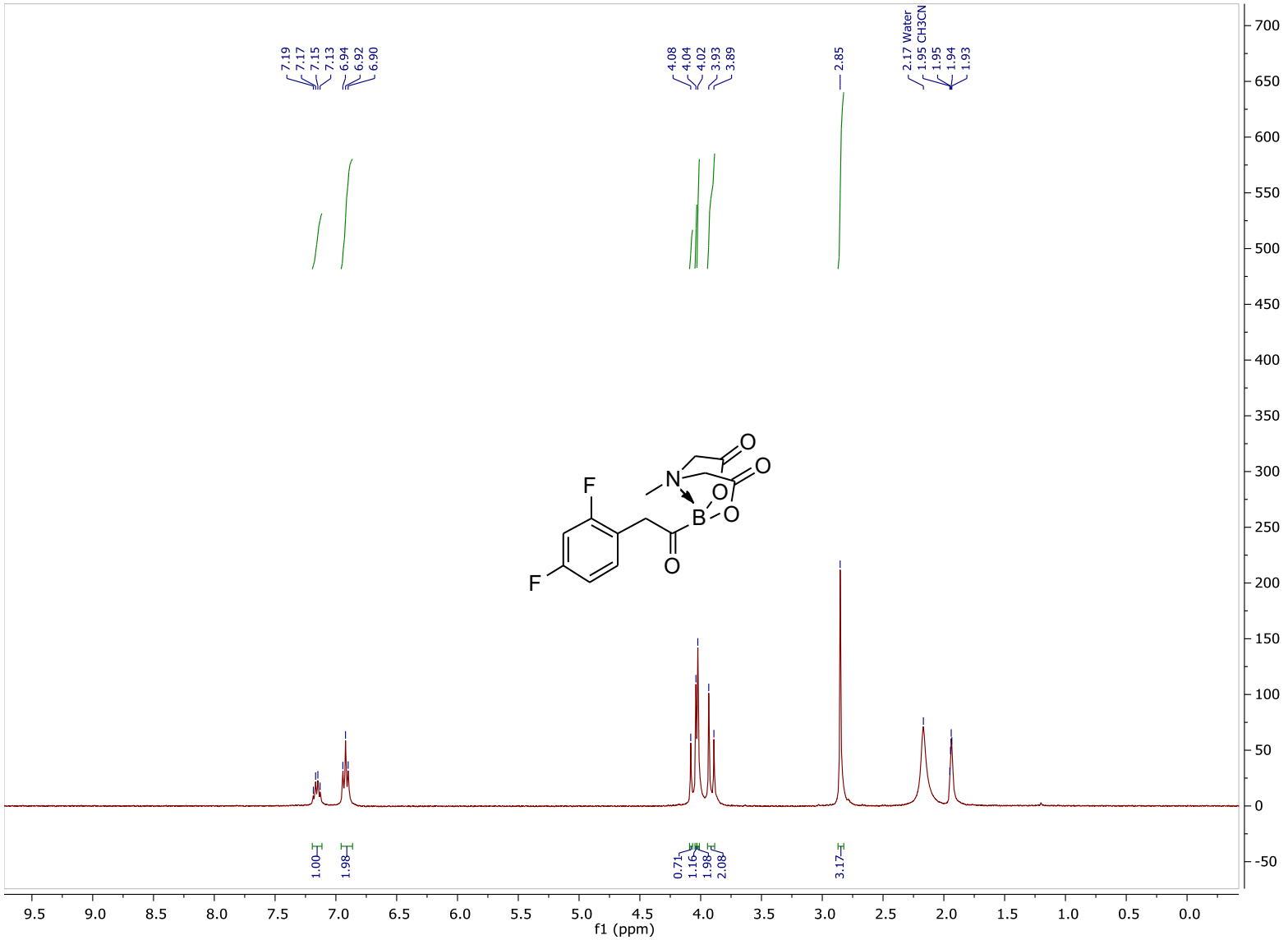



13C NMR, compound 5d
168.90
134.09
132.77
132.63
129.12
118.27 CD3CN
63.06
53.04
47.55
1.90
1.70
1.49
1.28 CD3CN
1.08
0.87
0.66
O
O
N
O
B
O
O
Cl
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

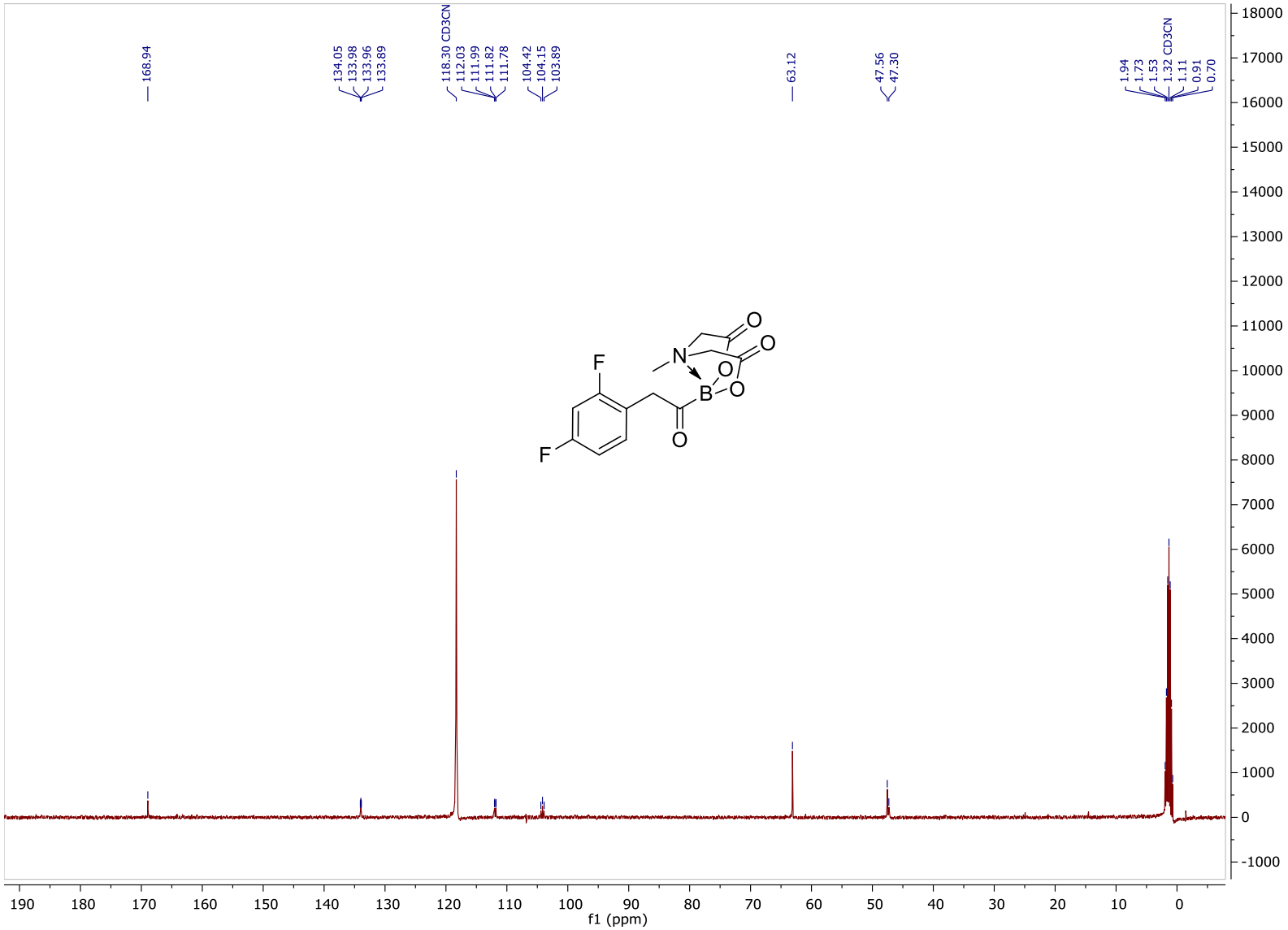
^{11}B NMR, compound 5d



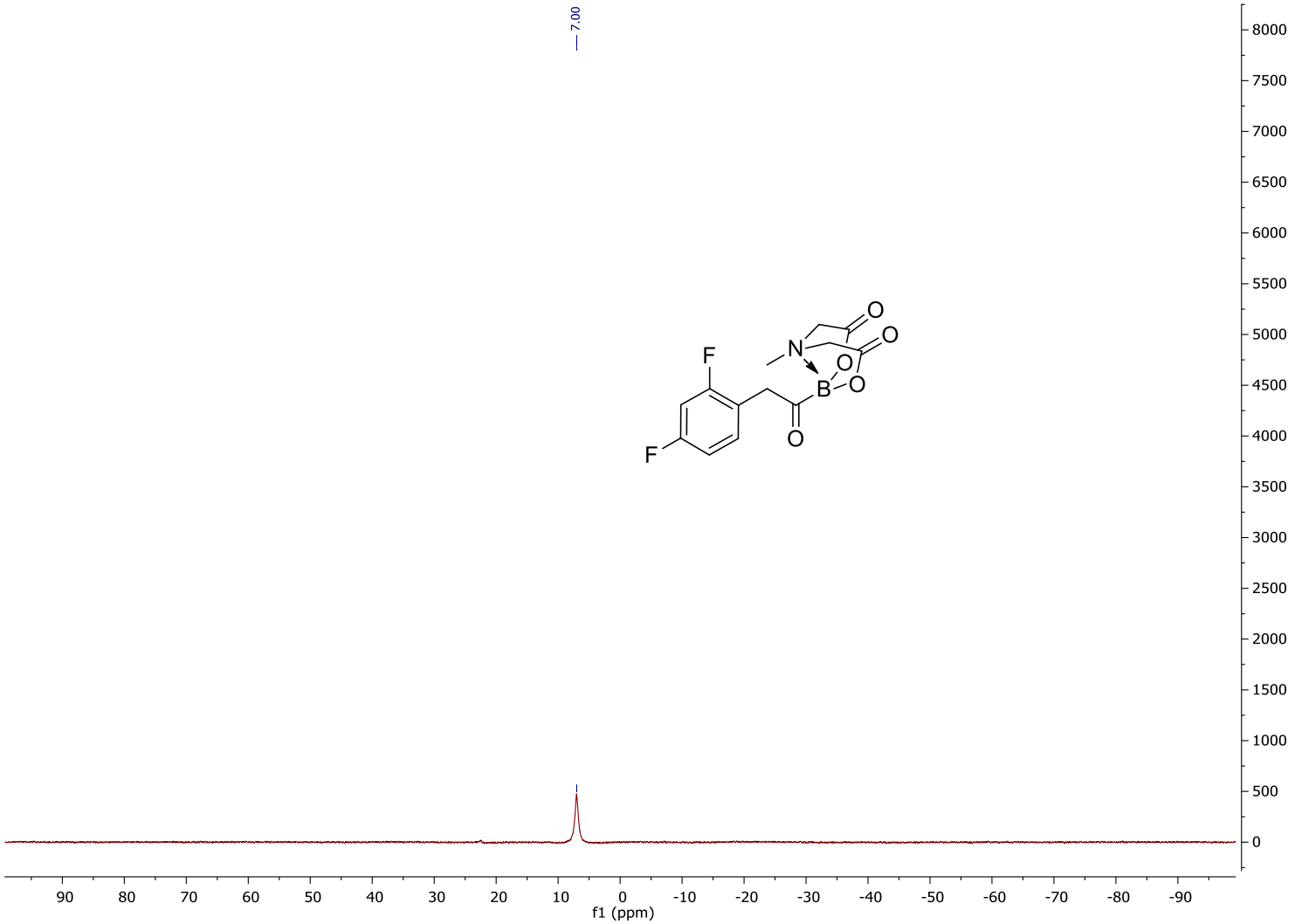
^{1}H NMR, compound 5e



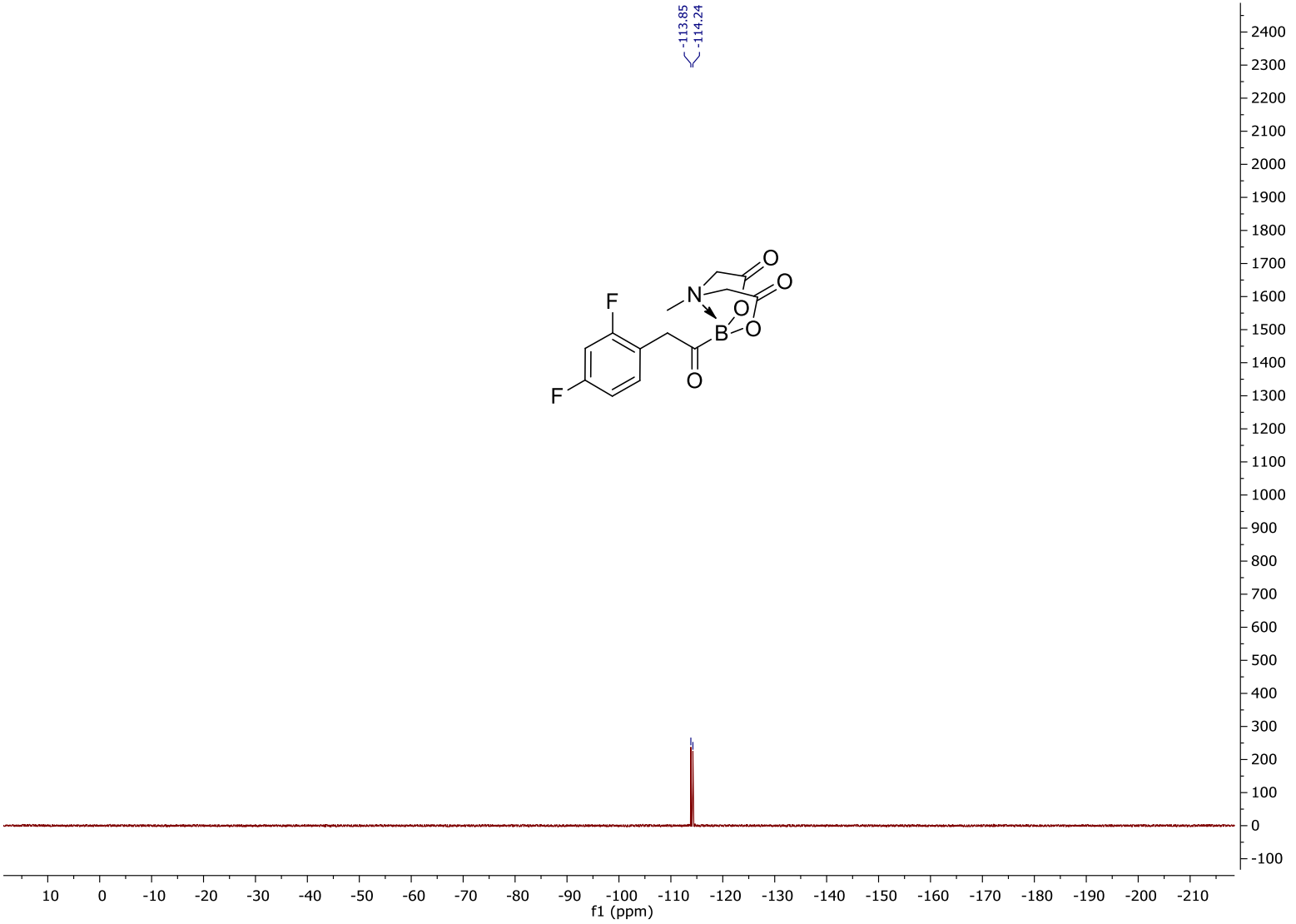
^{13}C NMR, compound 5e



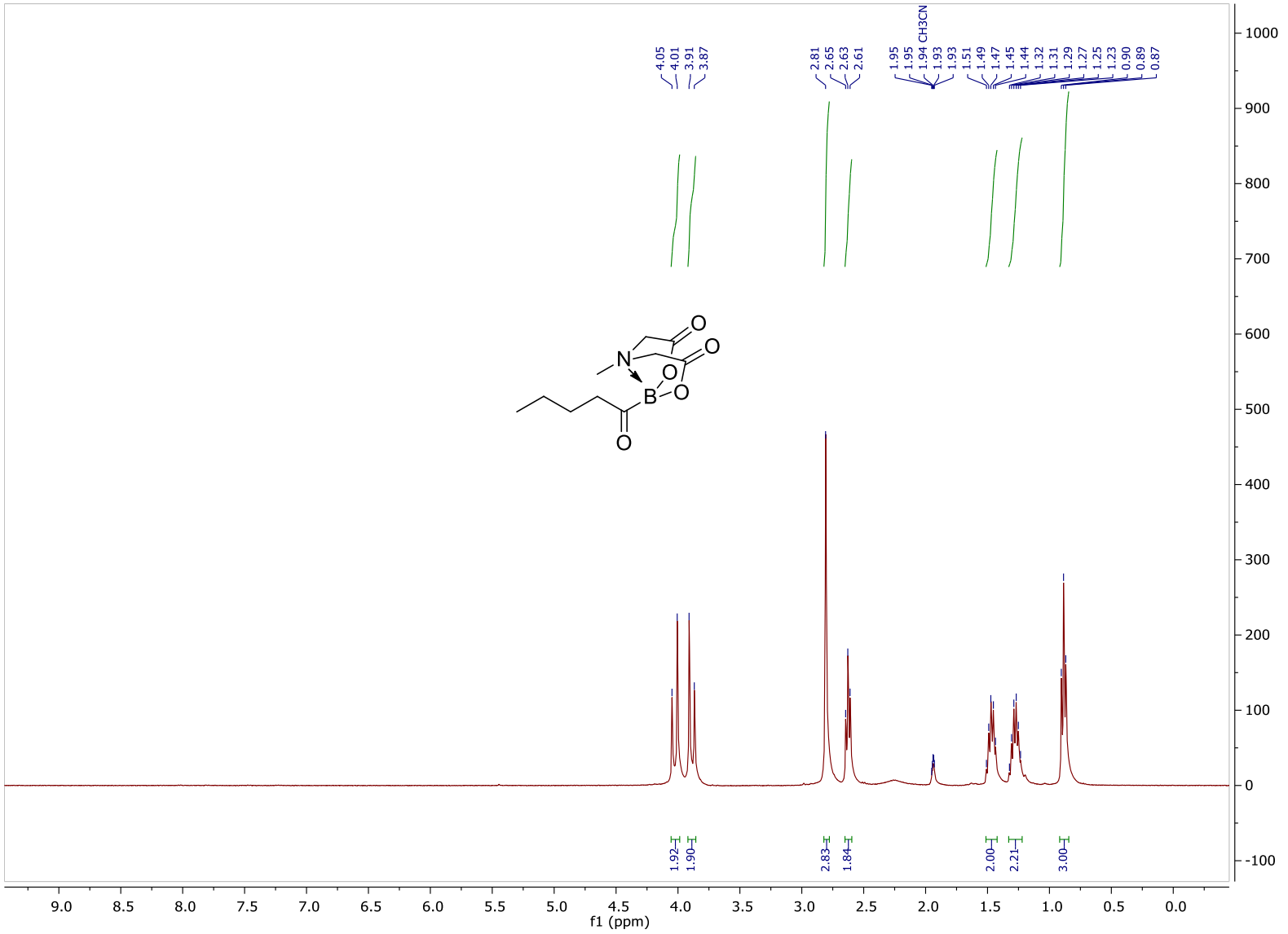
^{11}B NMR, compound 5e



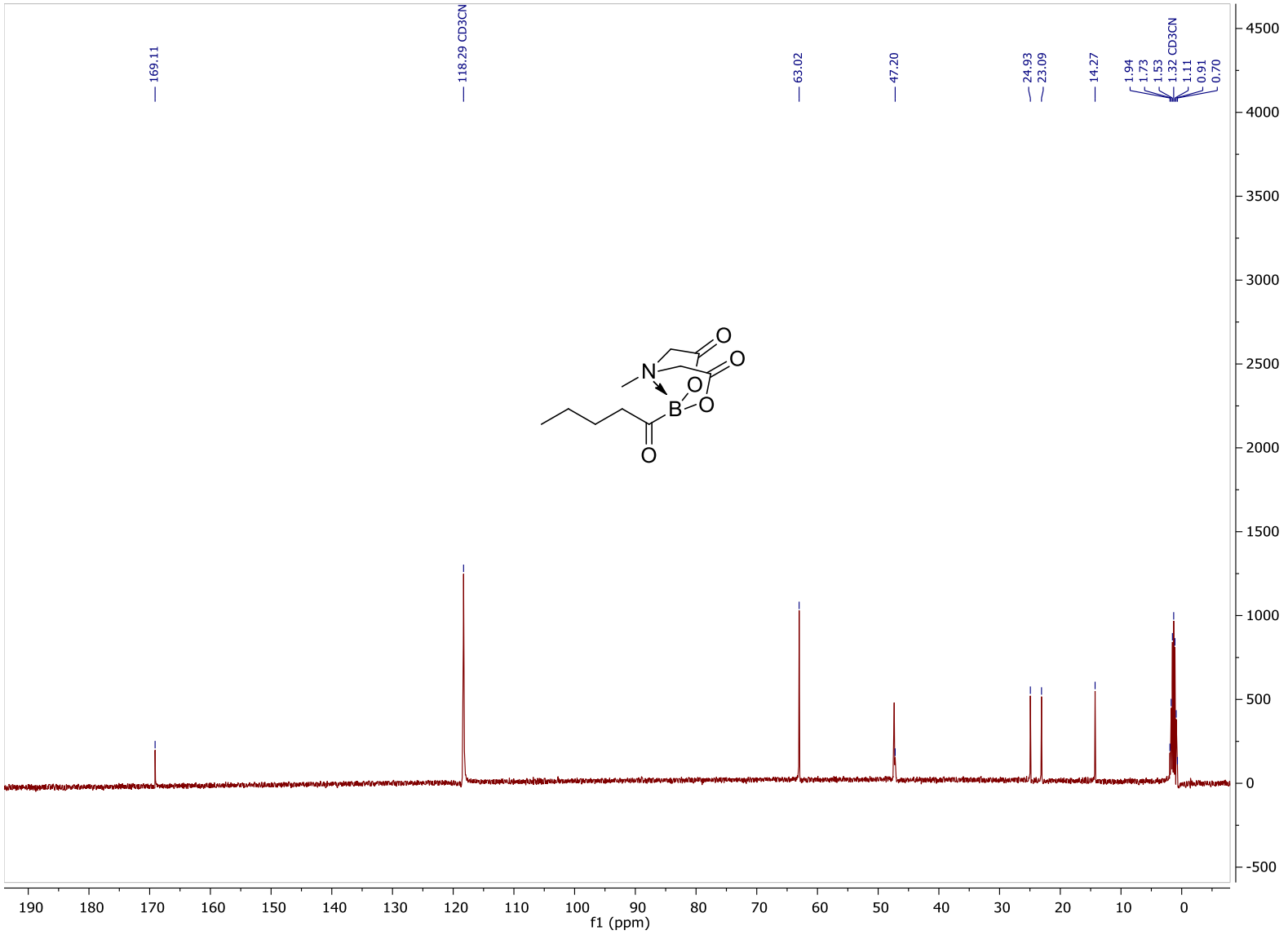
^{19}F NMR, compound 5e



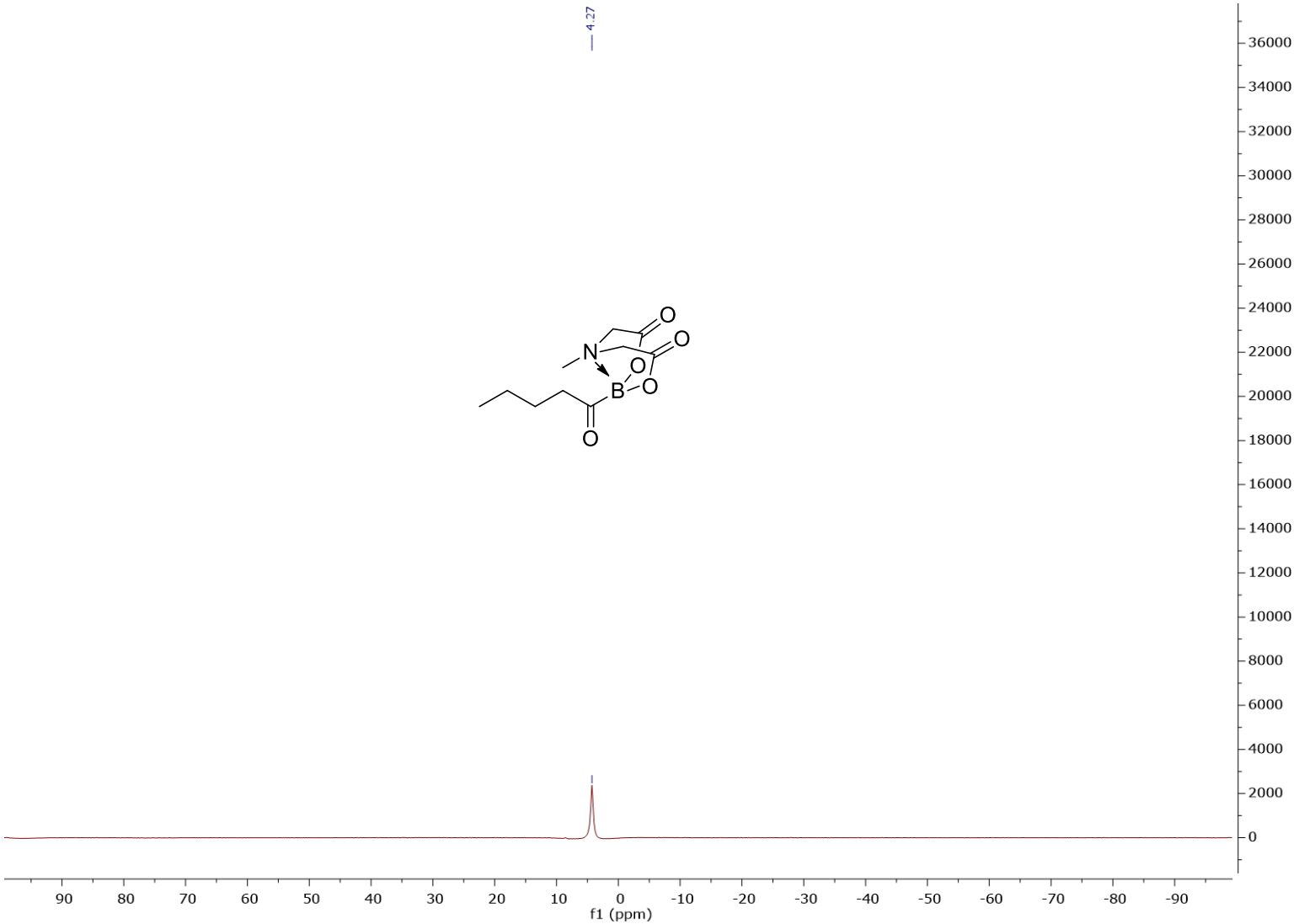
^{1}H NMR, compound 5f

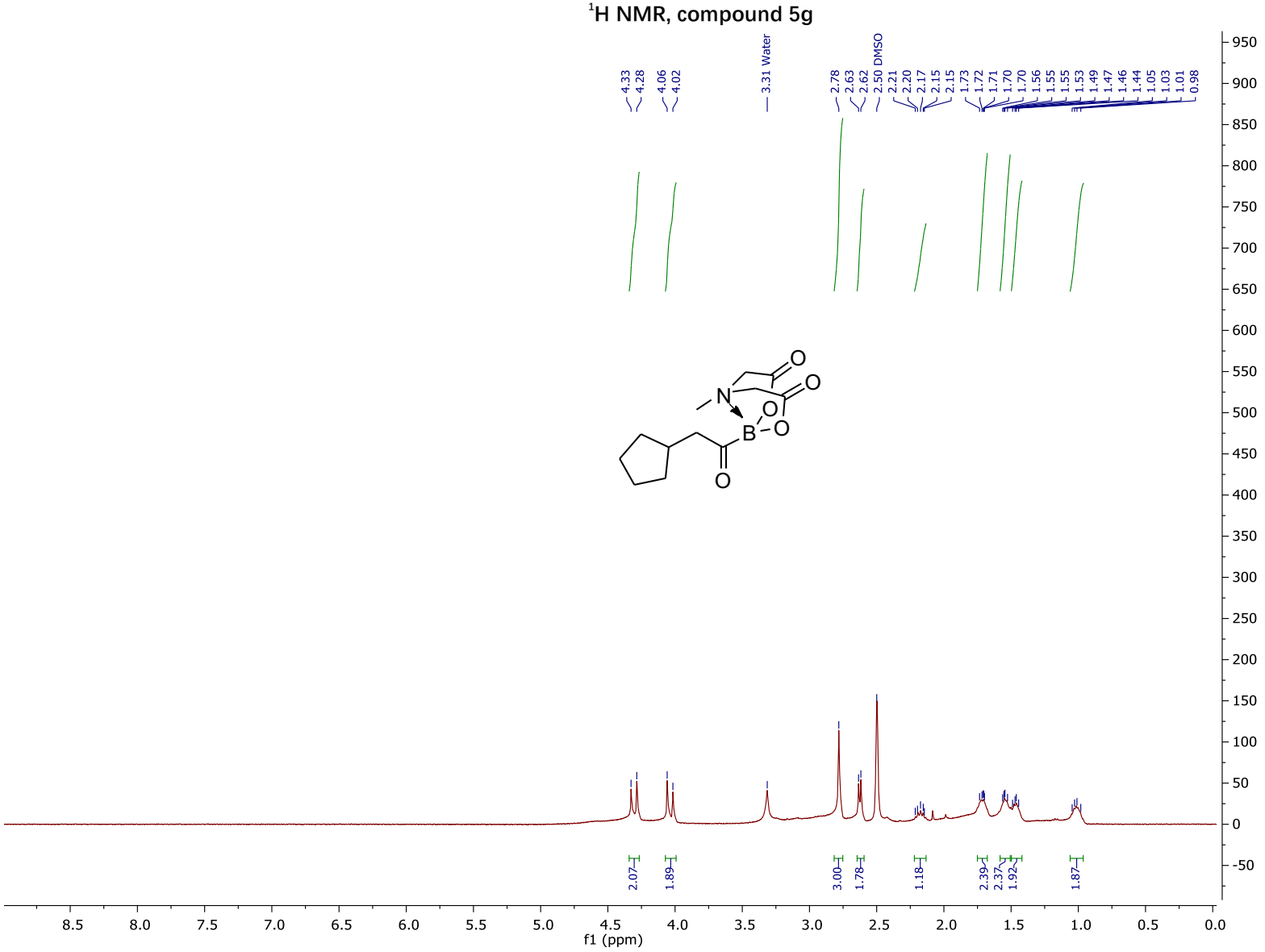


^{13}C NMR, compound 5f

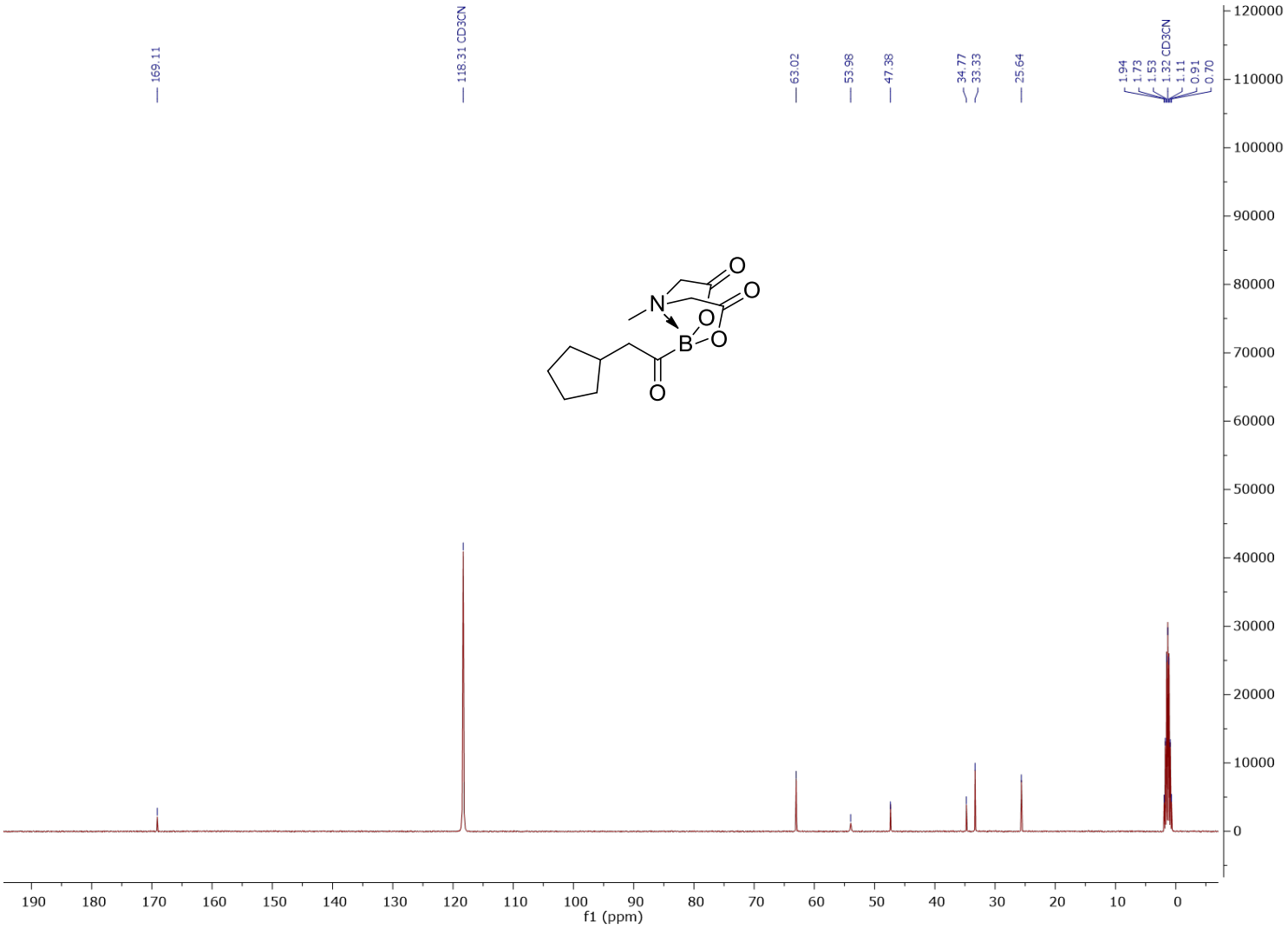


^{11}B NMR, compound 5f

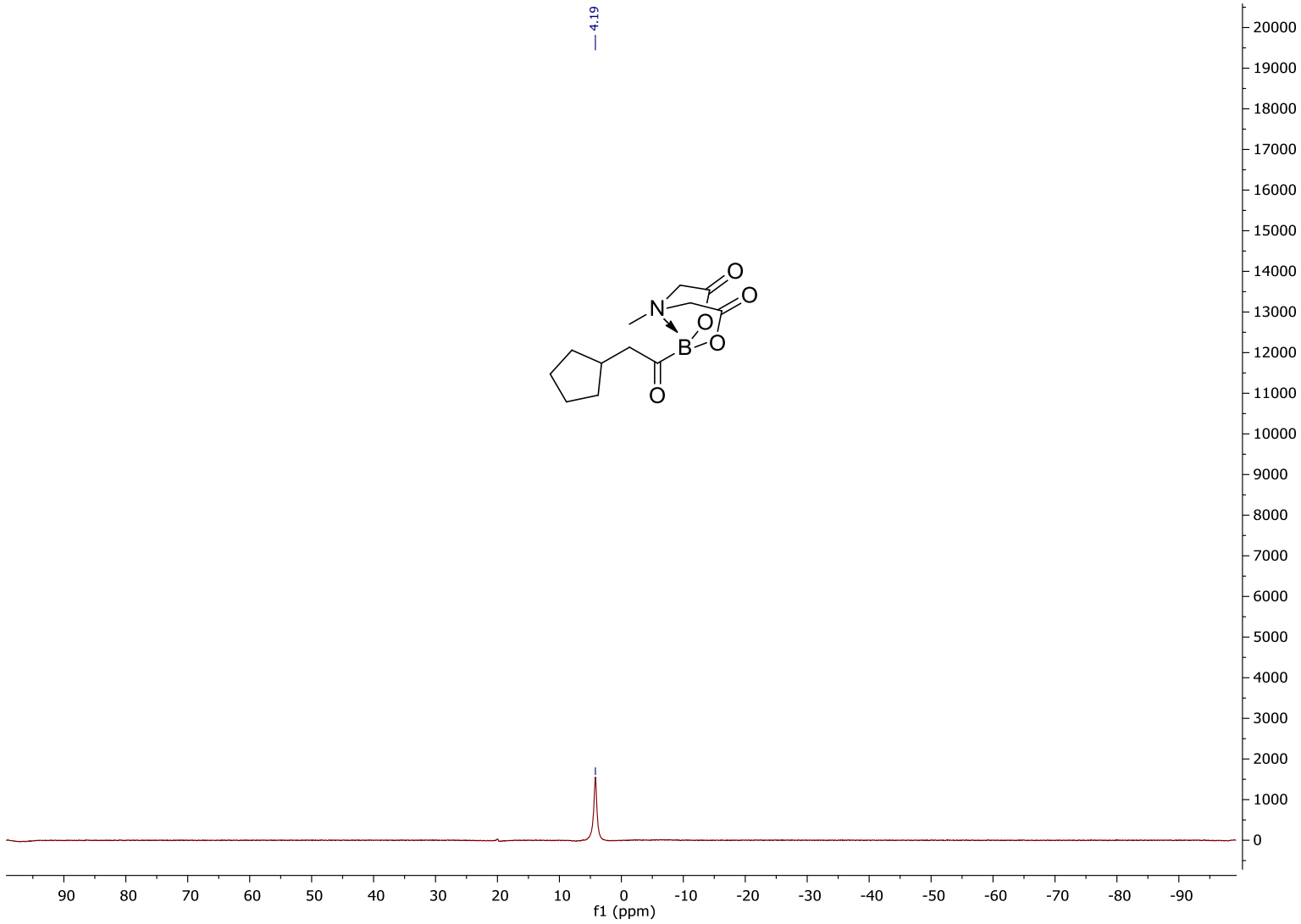



1H NMR, compound 5g
4.33
4.28
4.06
4.02
3.31 Water
2.78
2.63
2.62
2.50 DMSO
2.21
2.20
2.17
2.15
2.15
1.73
1.72
1.71
1.70
1.70
1.56
1.55
1.55
1.53
1.49
1.47
1.46
1.44
1.05
1.03
1.01
0.98
2.07
1.89
3.00
1.78
1.18
2.39
2.37
1.92
1.87
f1 (ppm)

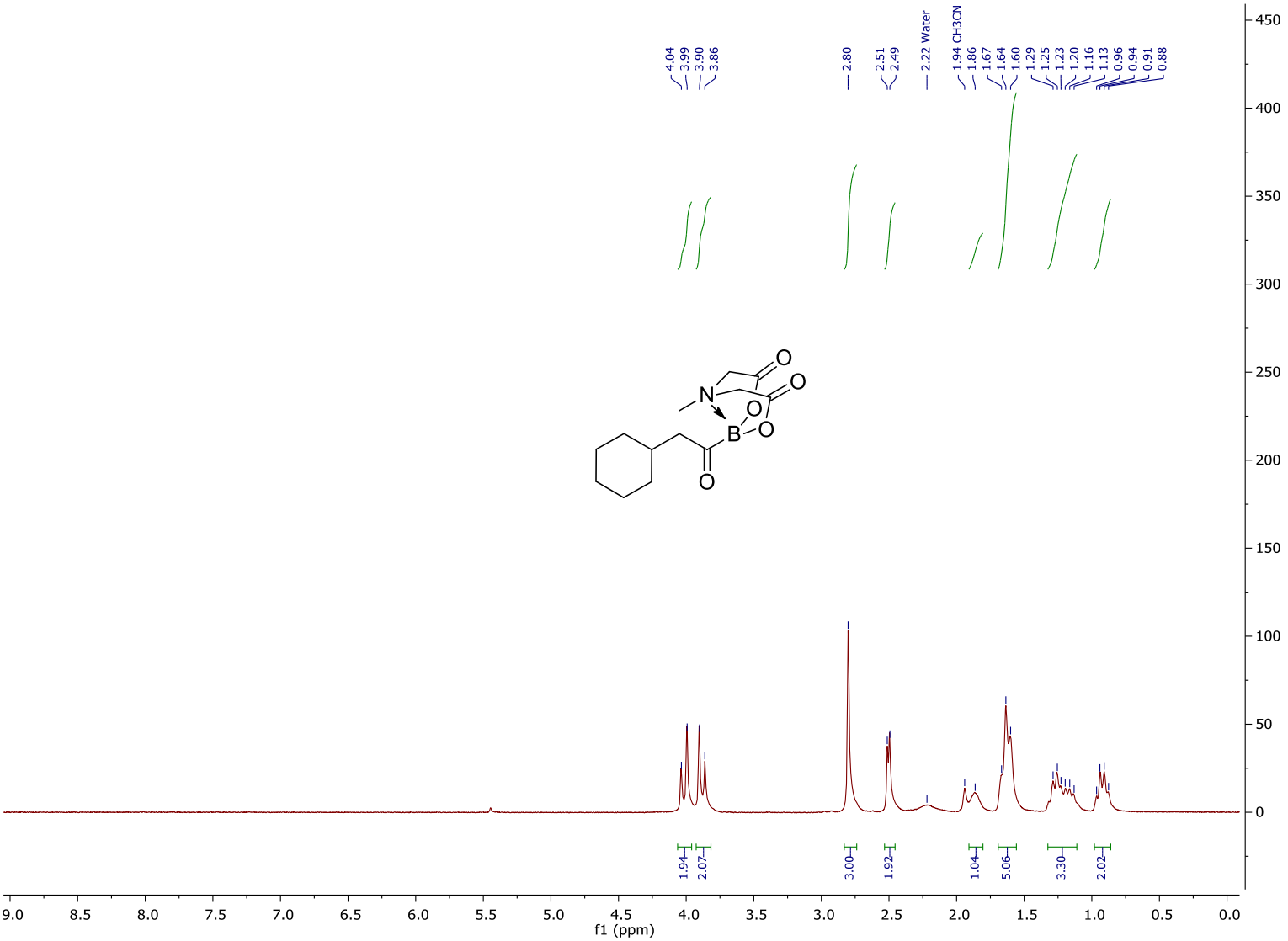
^{13}C NMR, compound 5g

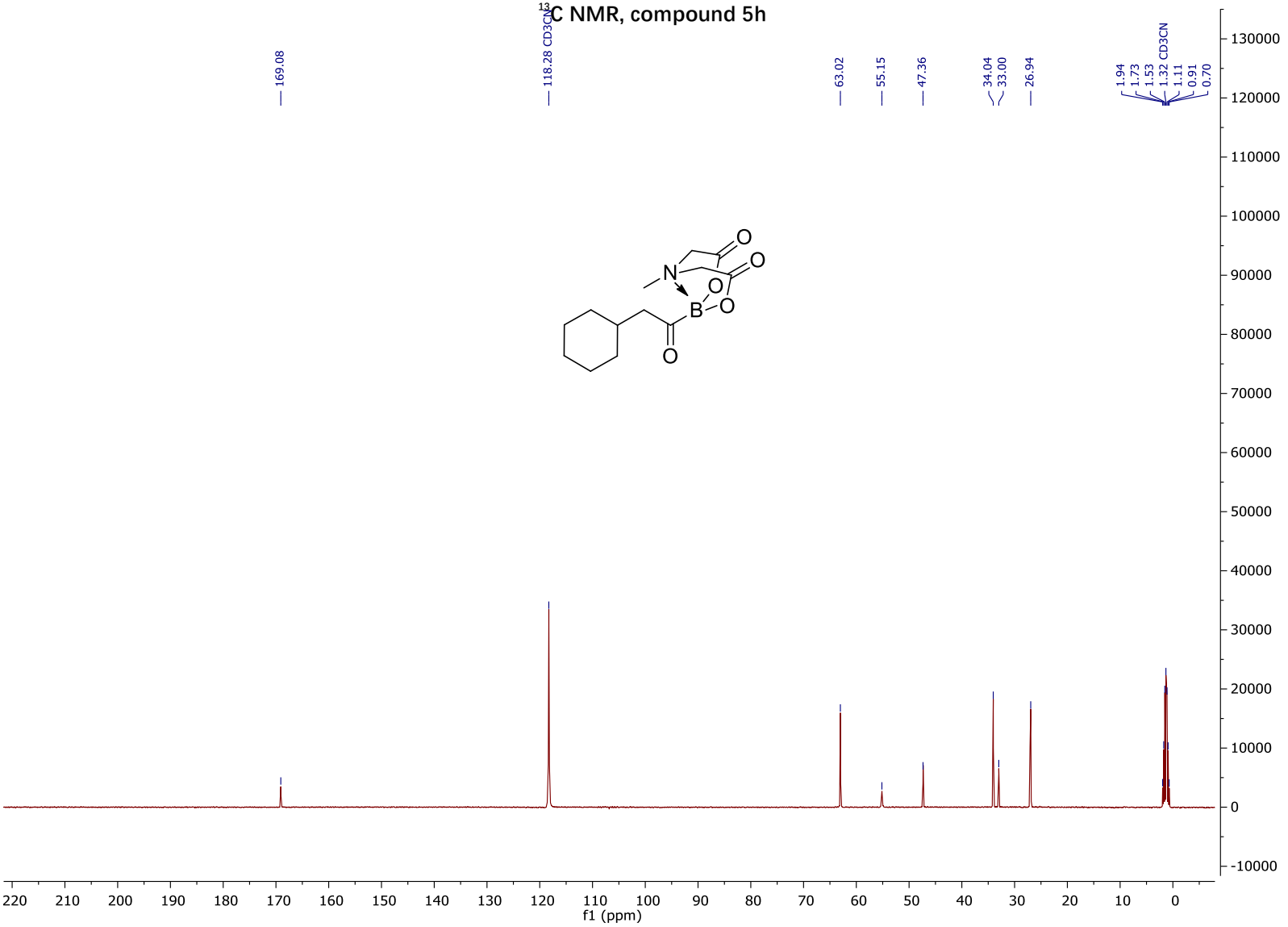


^{11}B NMR, compound 5g

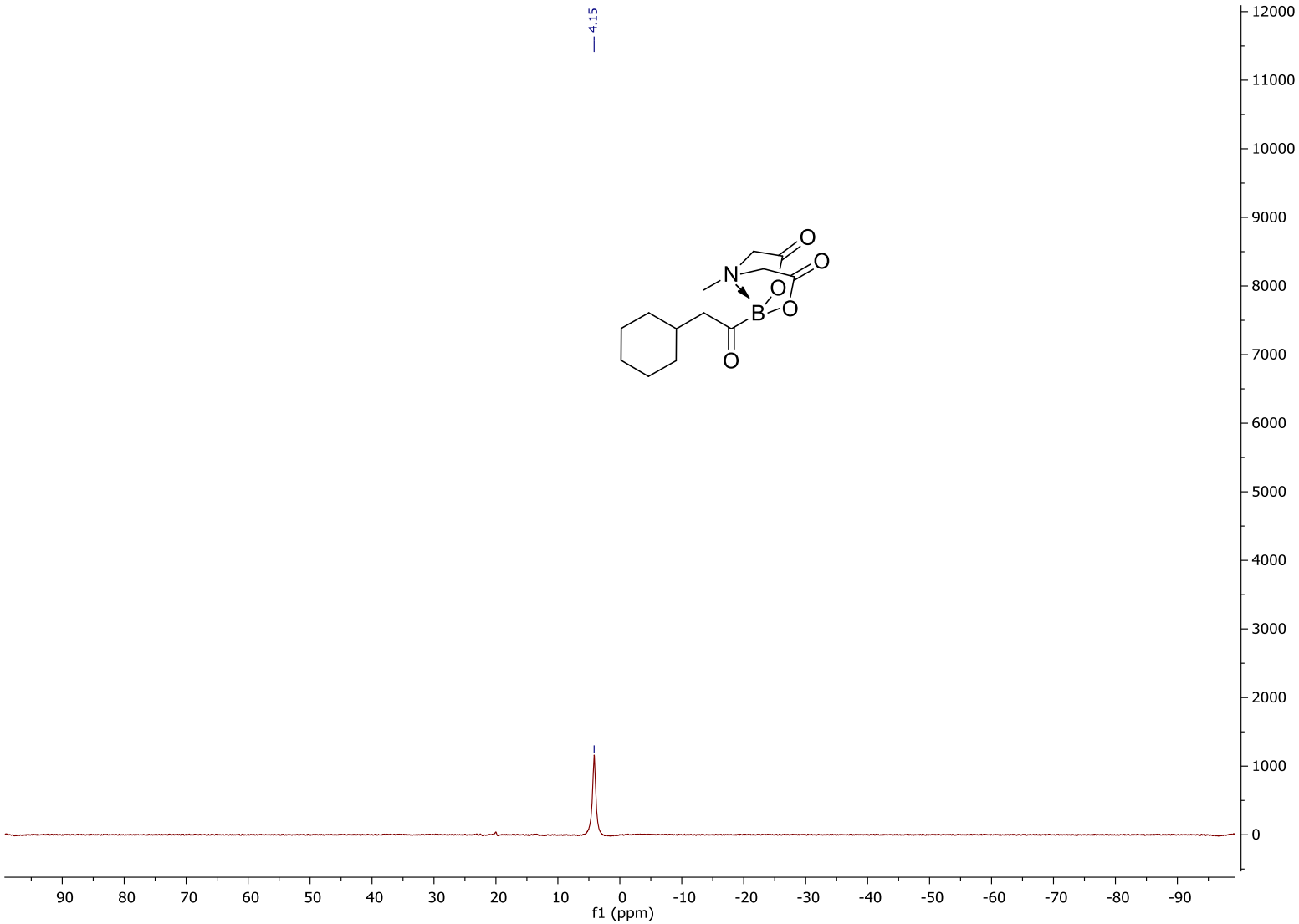


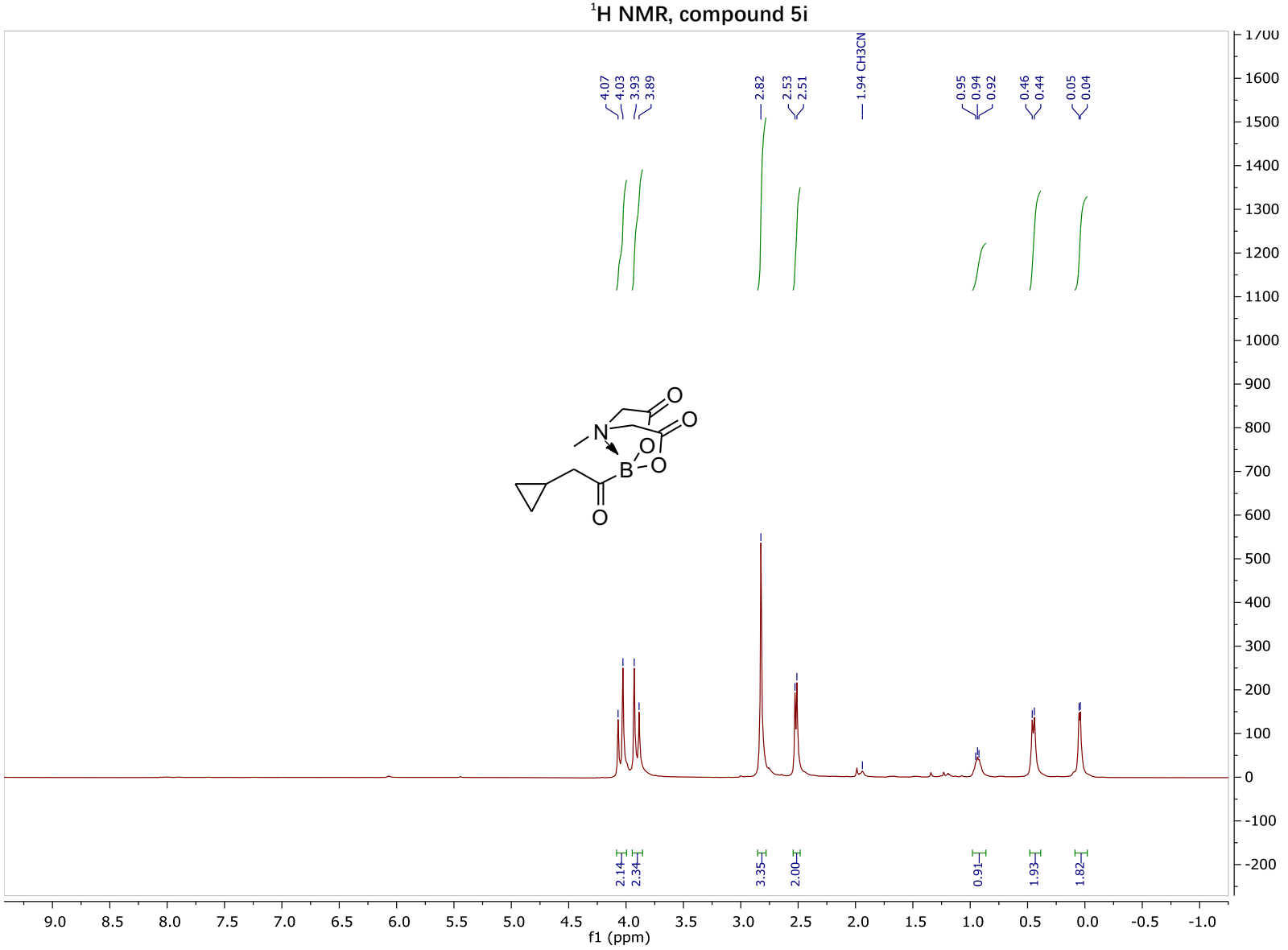
^{1}H NMR, compound 5h



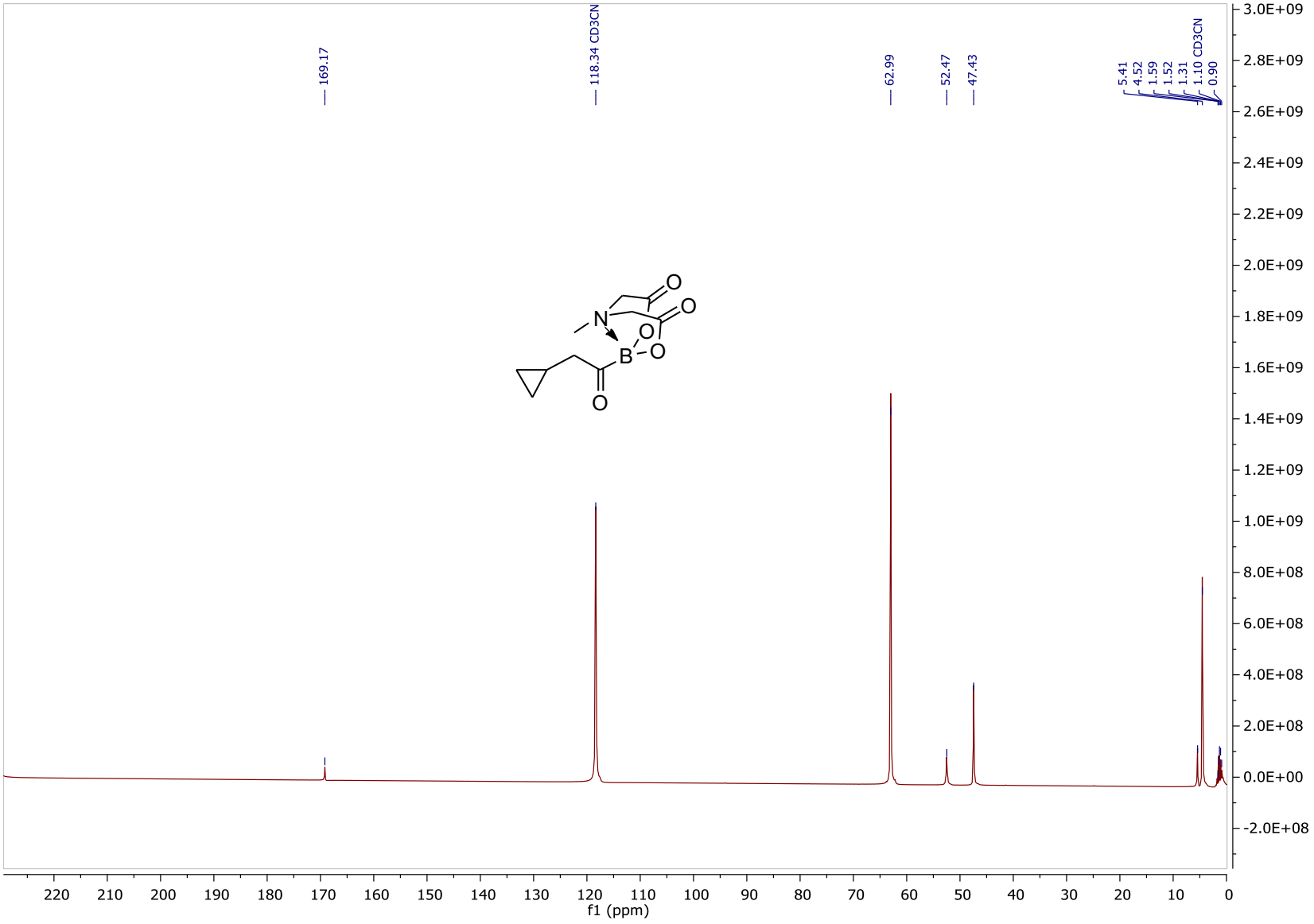

13C NMR, compound 5h
169.08
118.28 CD3CN
63.02
55.15
47.36
34.04
33.00
26.94
1.94
1.73
1.53
1.32 CD3CN
1.11
0.91
0.70
O
O
N
O
B
O
O
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{11}B NMR, compound 5h

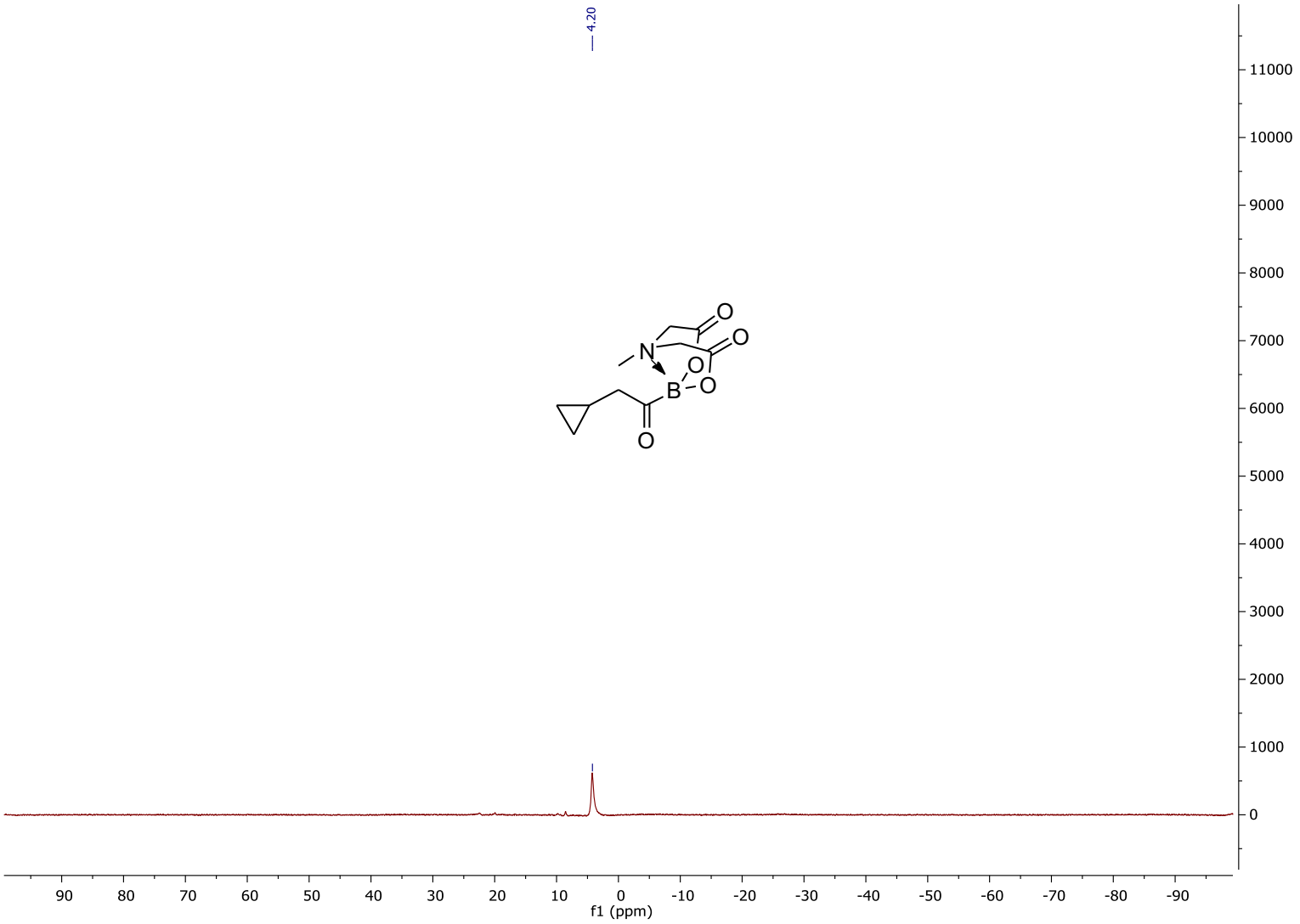



1H NMR, compound 5i
4.07
4.03
3.93
3.89
2.82
2.53
2.51
1.94 CH3CN
0.95
0.94
0.92
0.46
0.44
0.05
0.04
2.14
2.34
3.35
2.00
0.91
1.93
1.82
f1 (ppm)

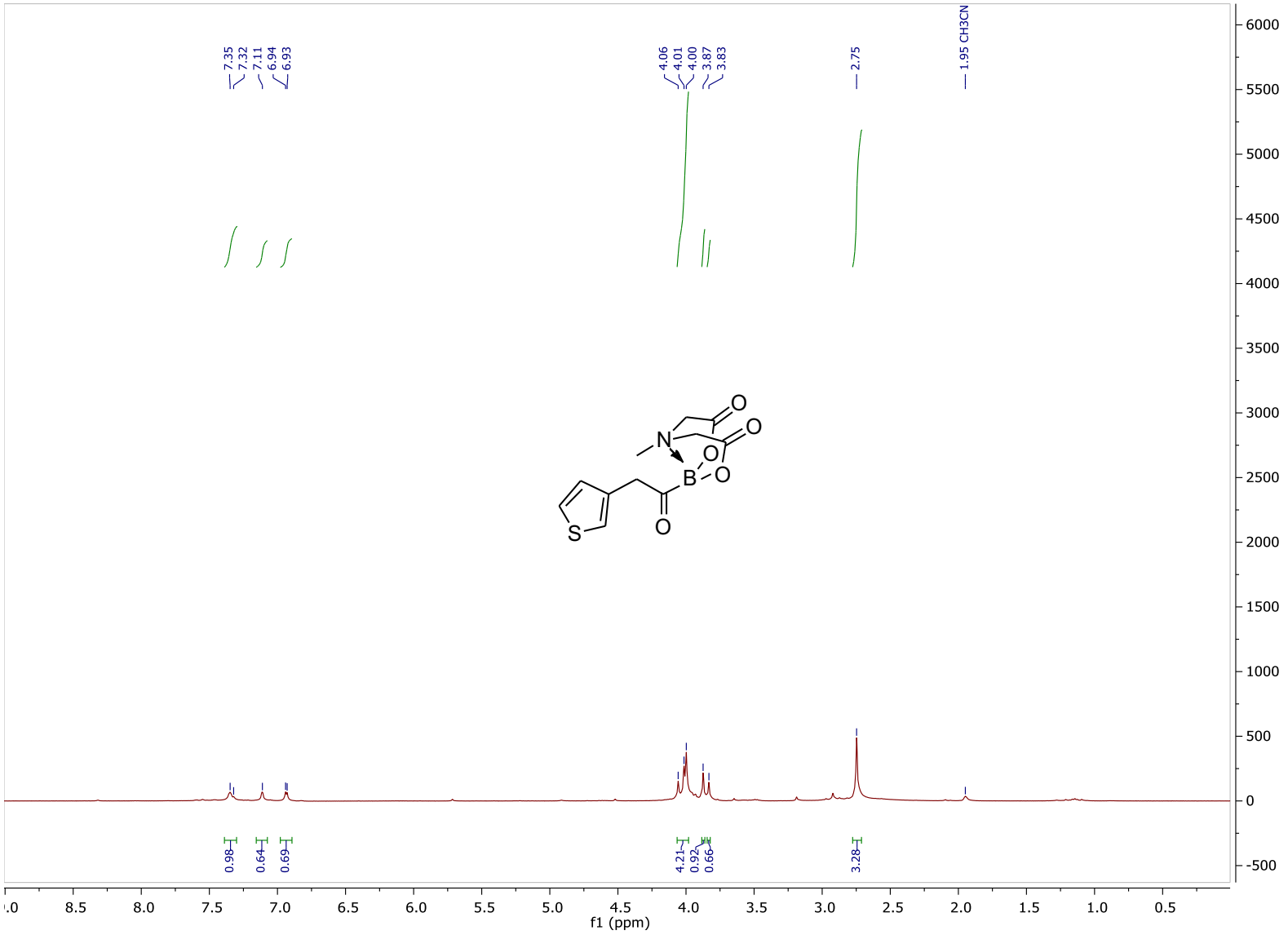
^{13}C NMR, compound 5i



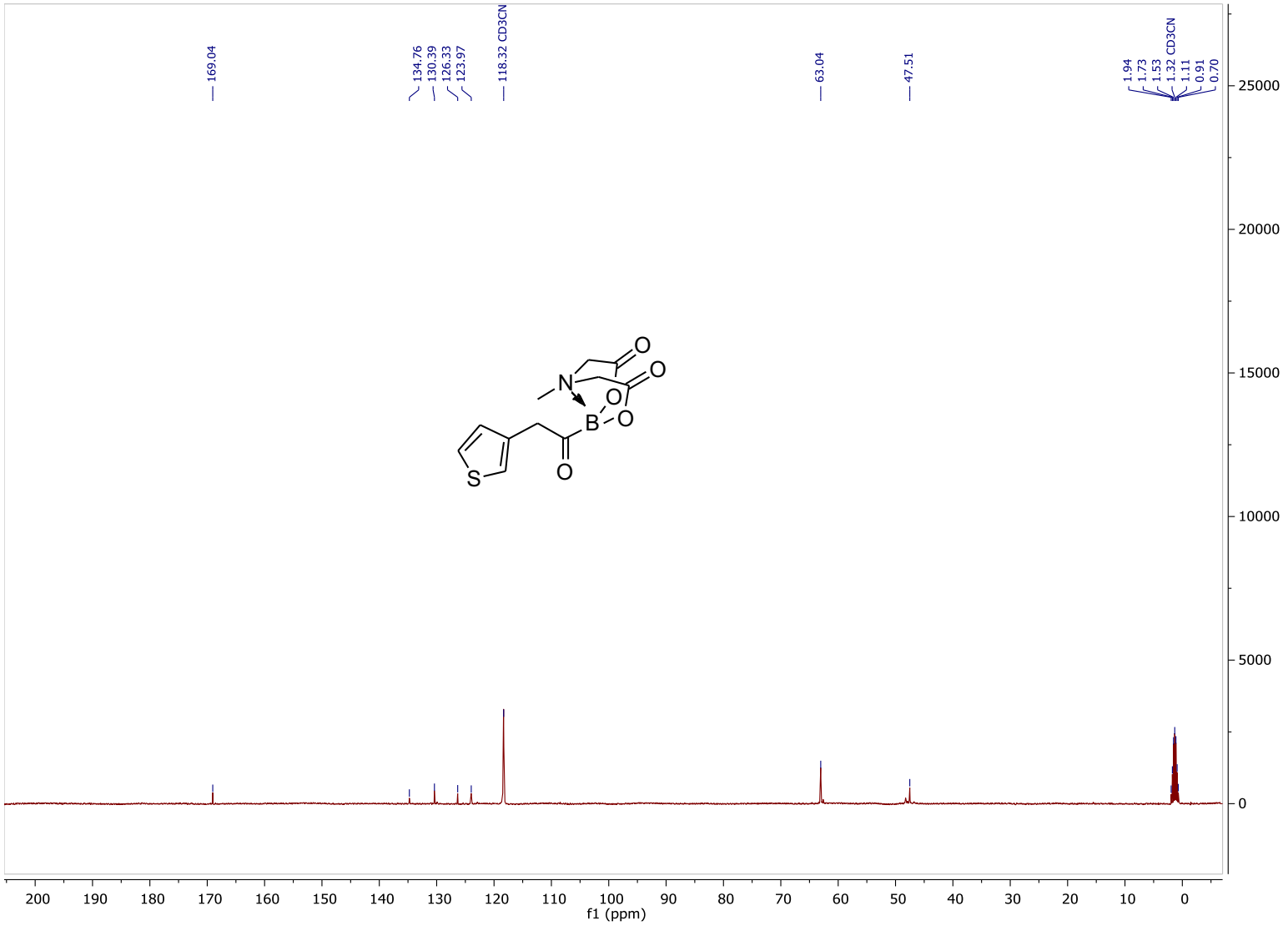
^{11}B NMR, compound 5i



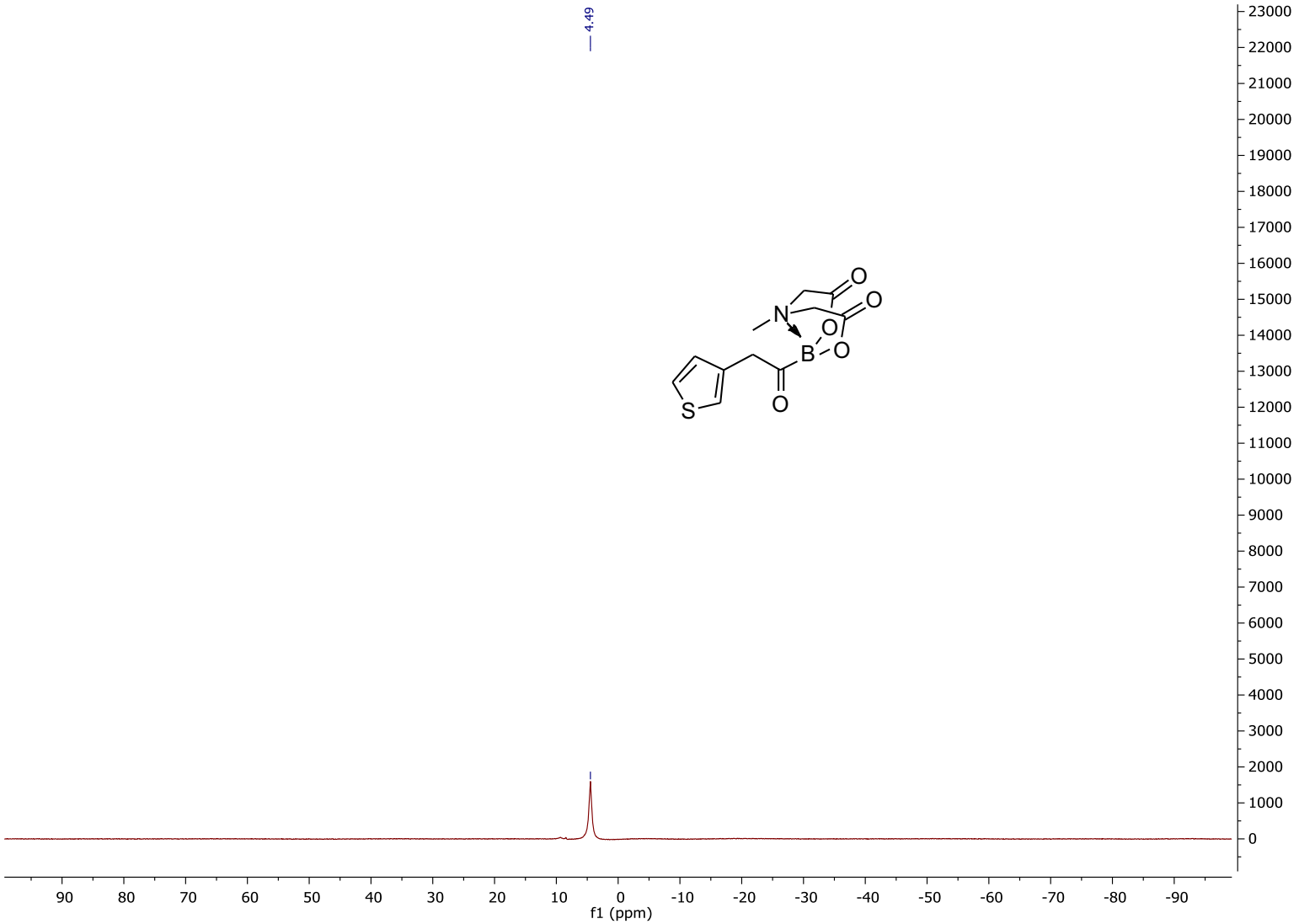
^{1}H NMR, compound 5j



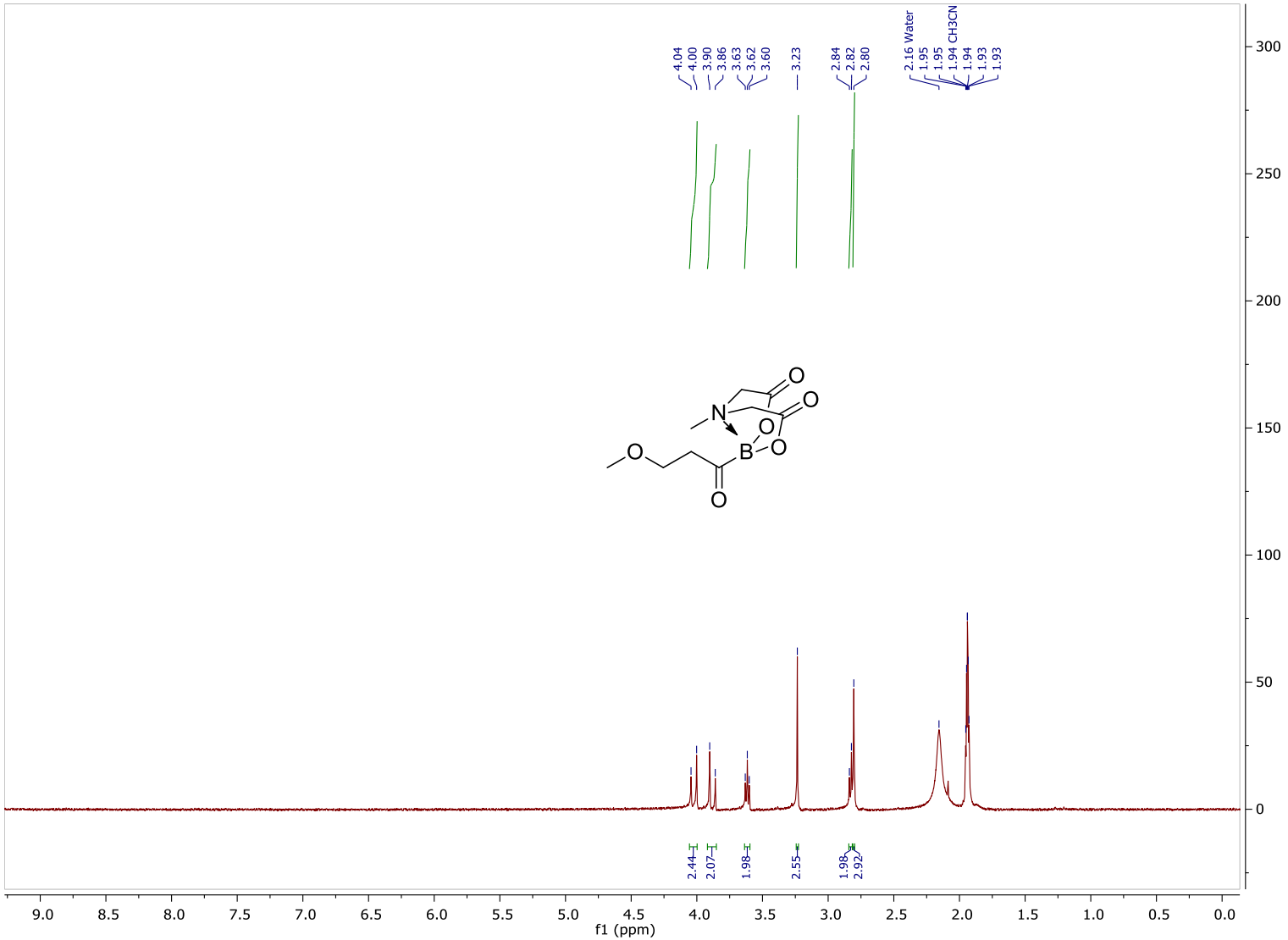
^{13}C NMR, compound 5j



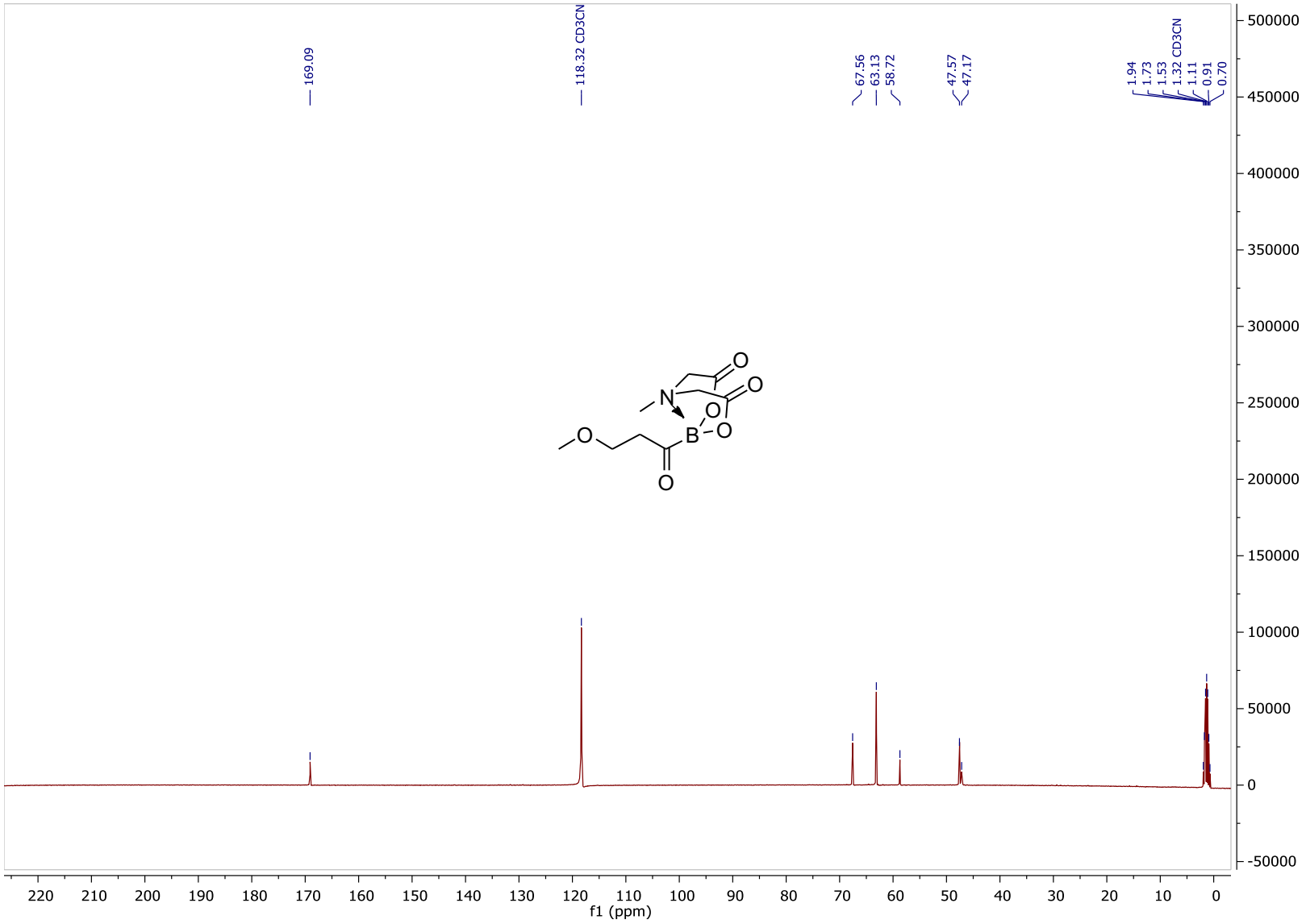
^{11}B NMR, compound 5j



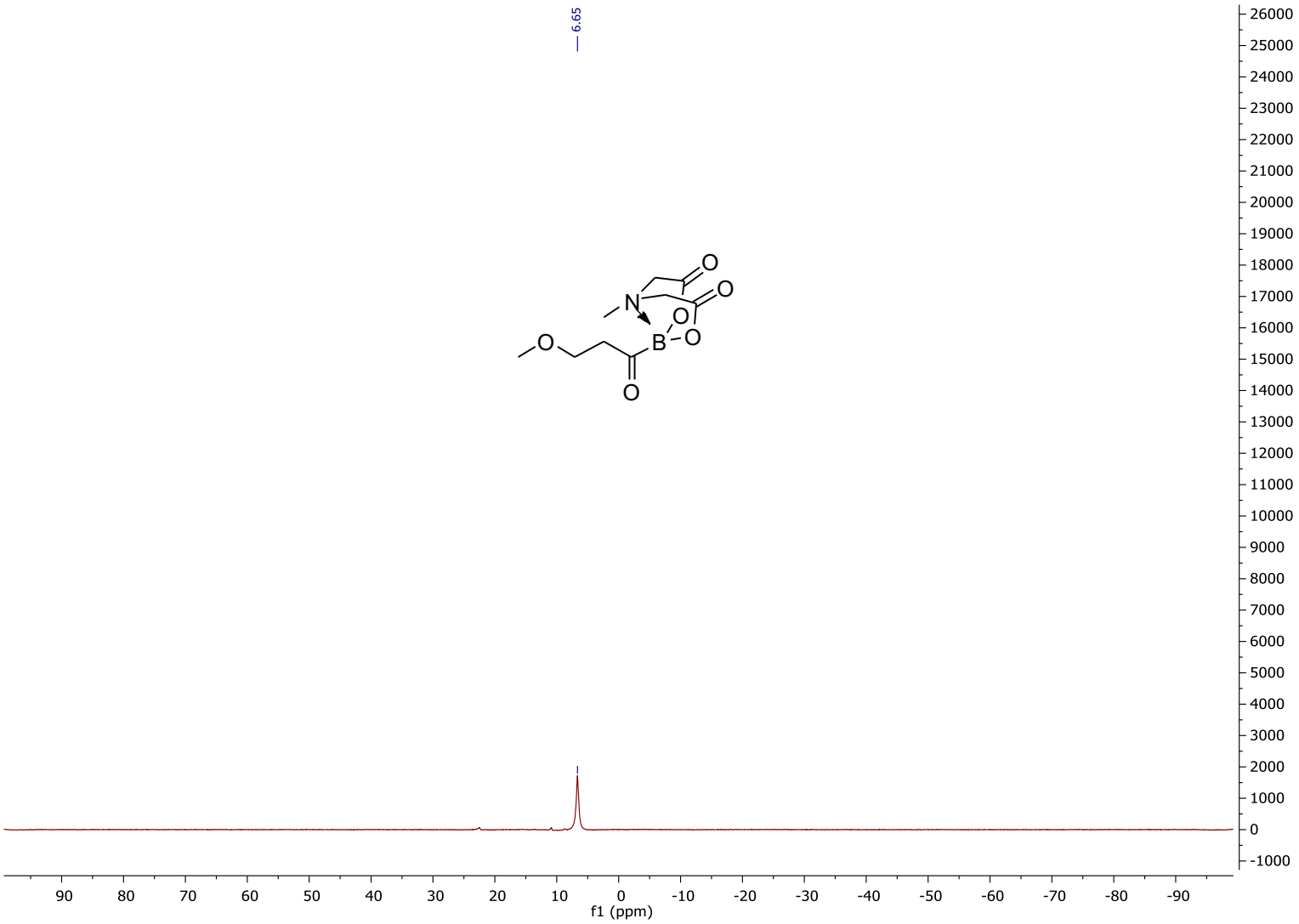
^{1}H NMR, compound 5k



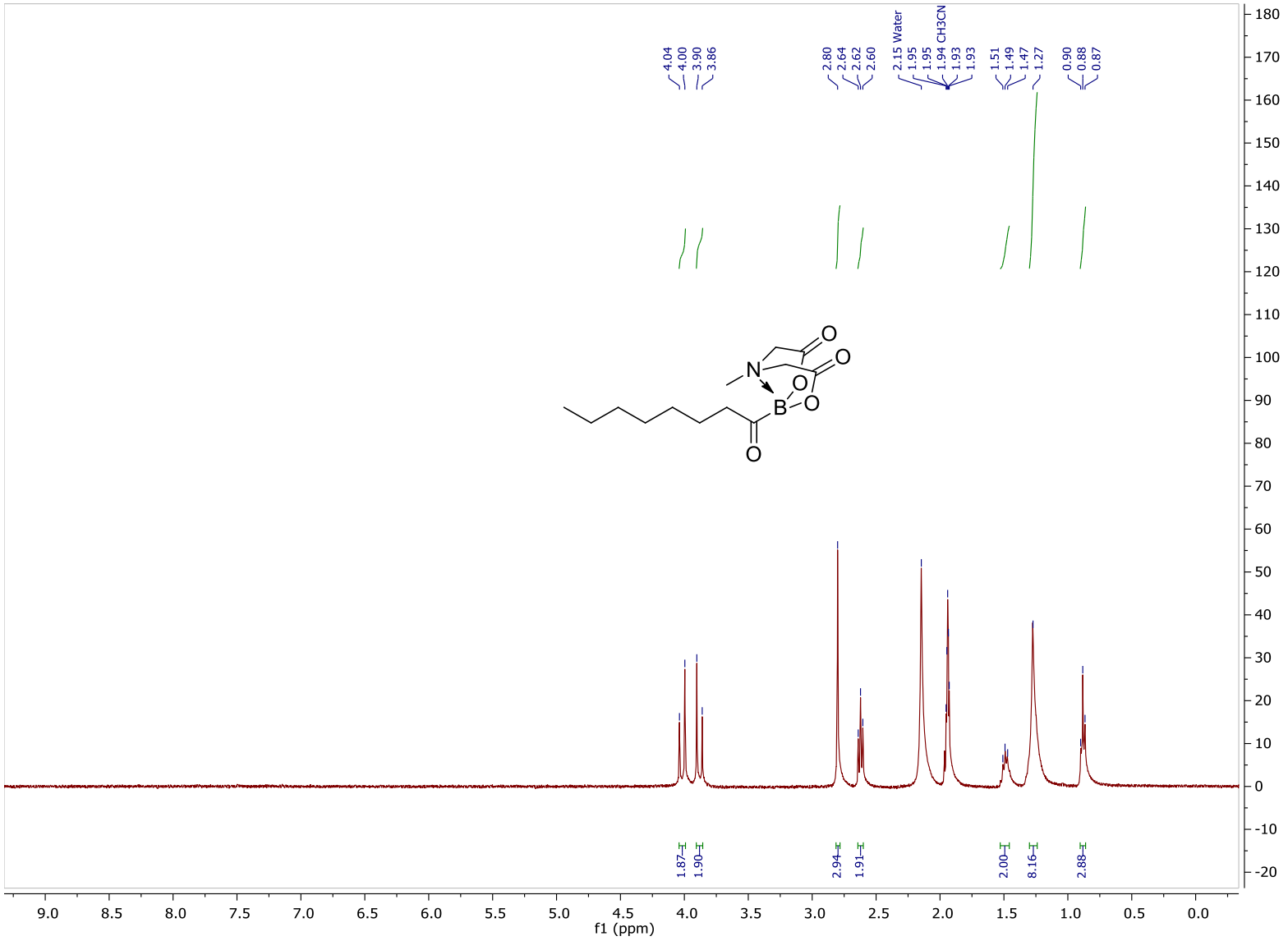
^{13}C NMR, compound 5k



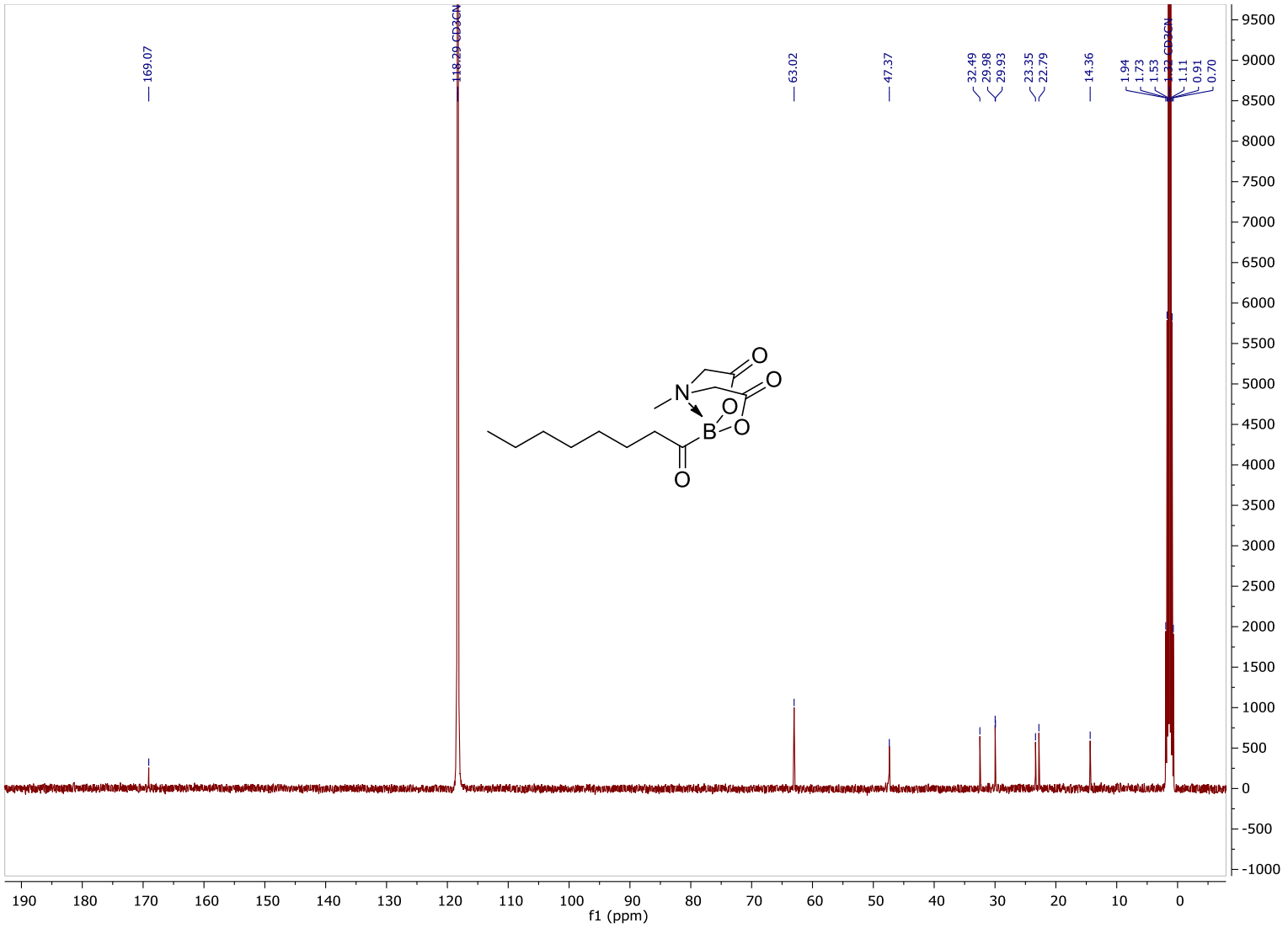
^{11}B NMR, compound 5k



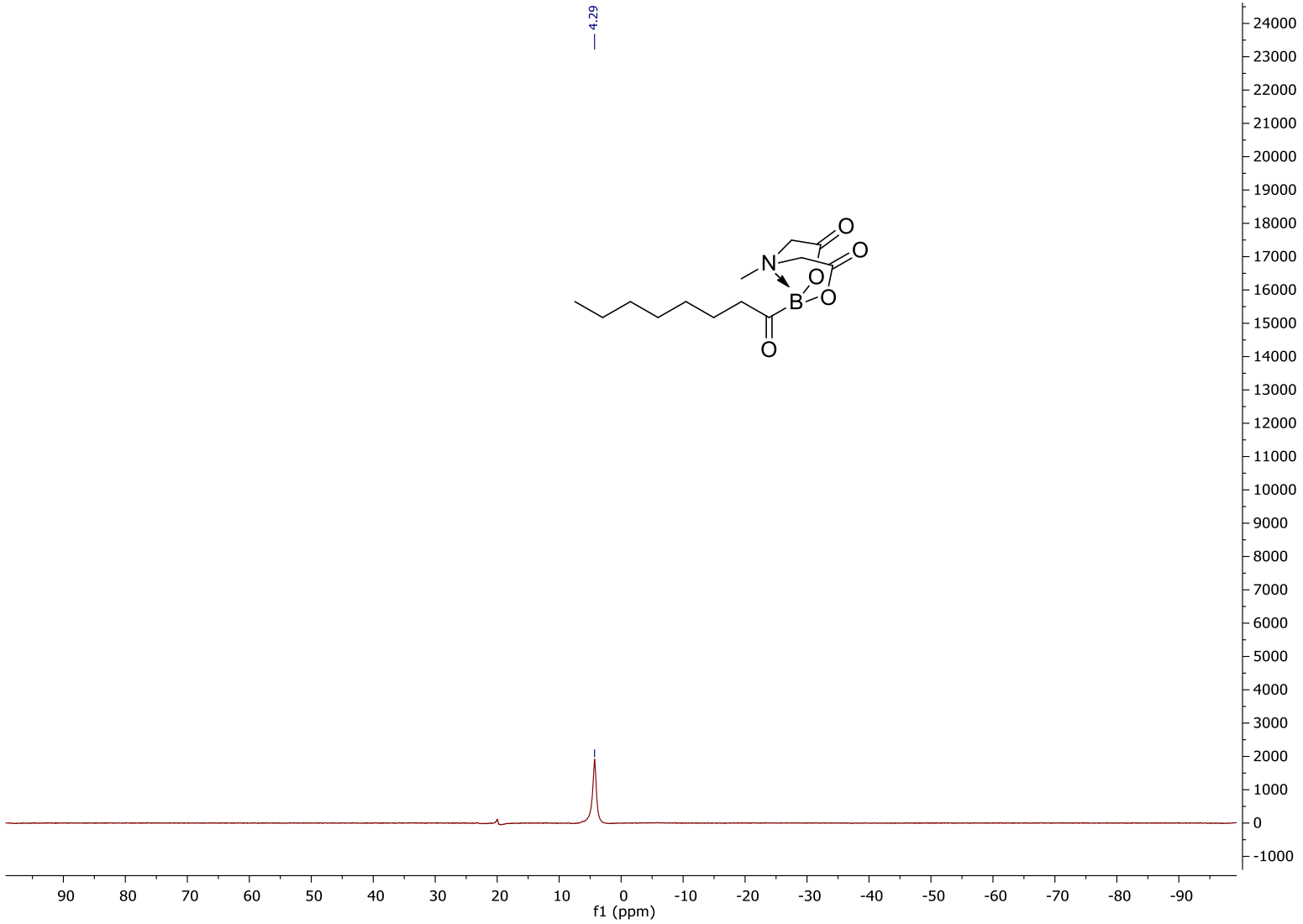
^{1}H NMR, compound 5l



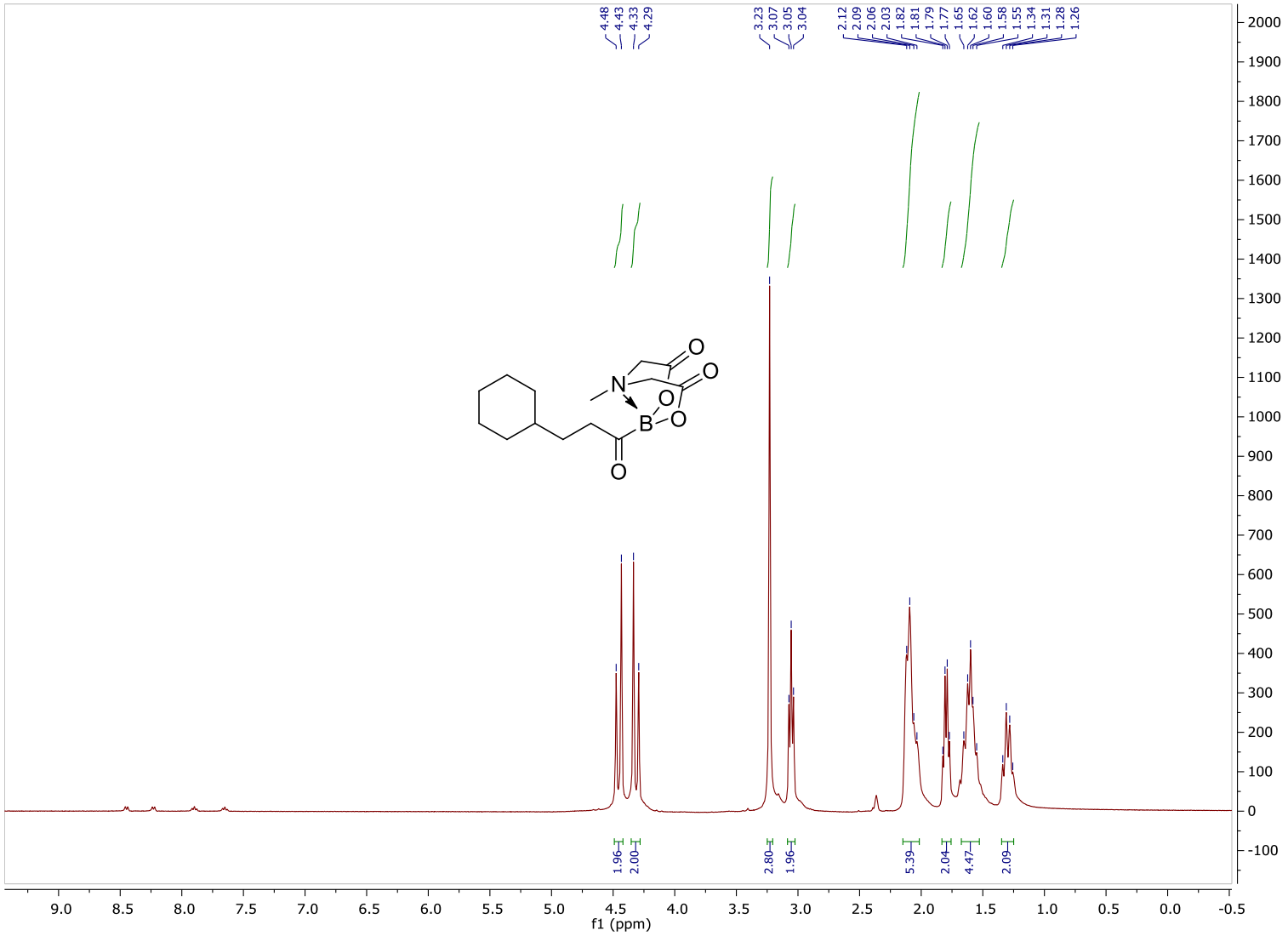
^{13}C NMR, compound 5l



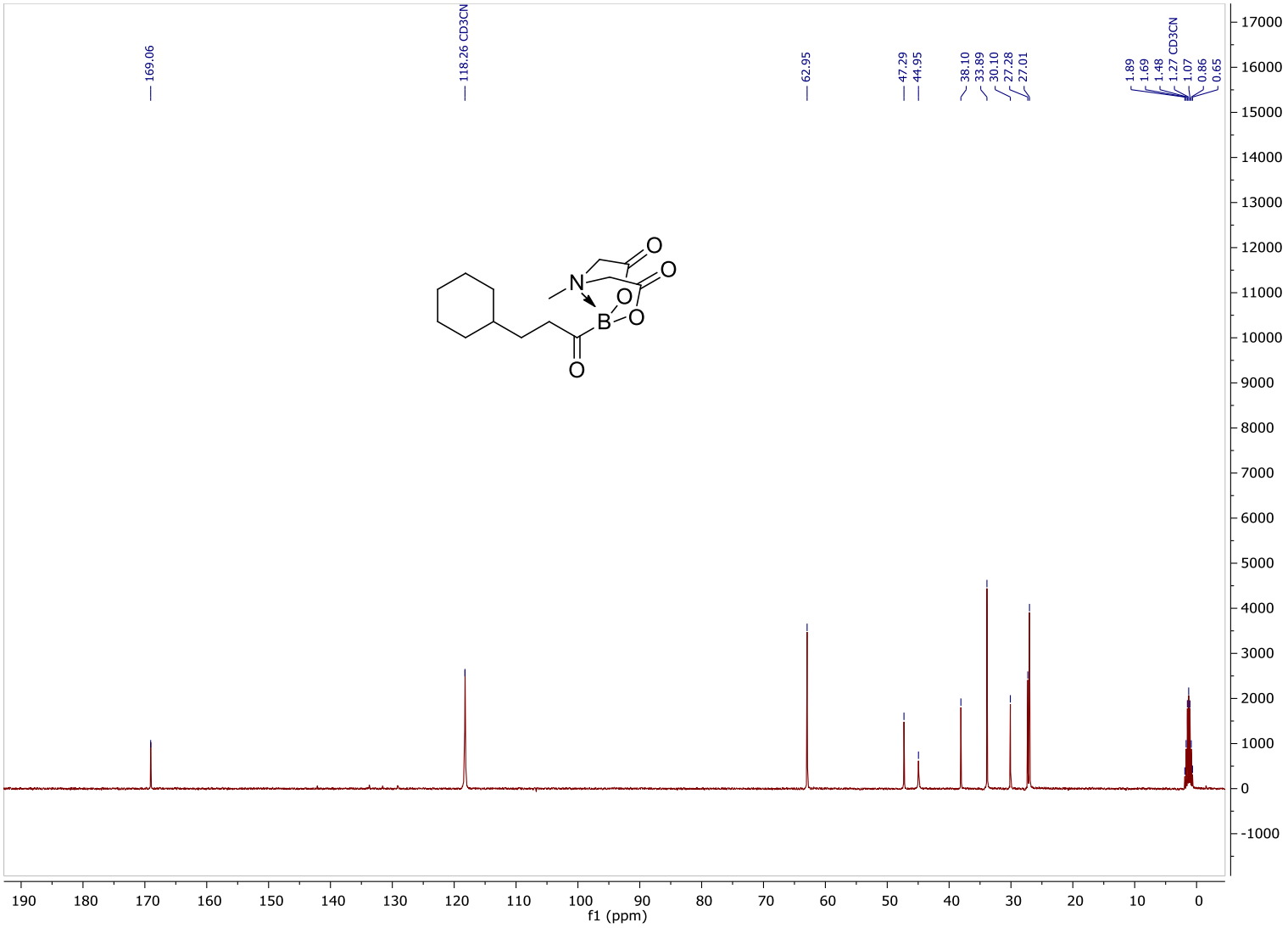
^{11}B NMR, compound 5l



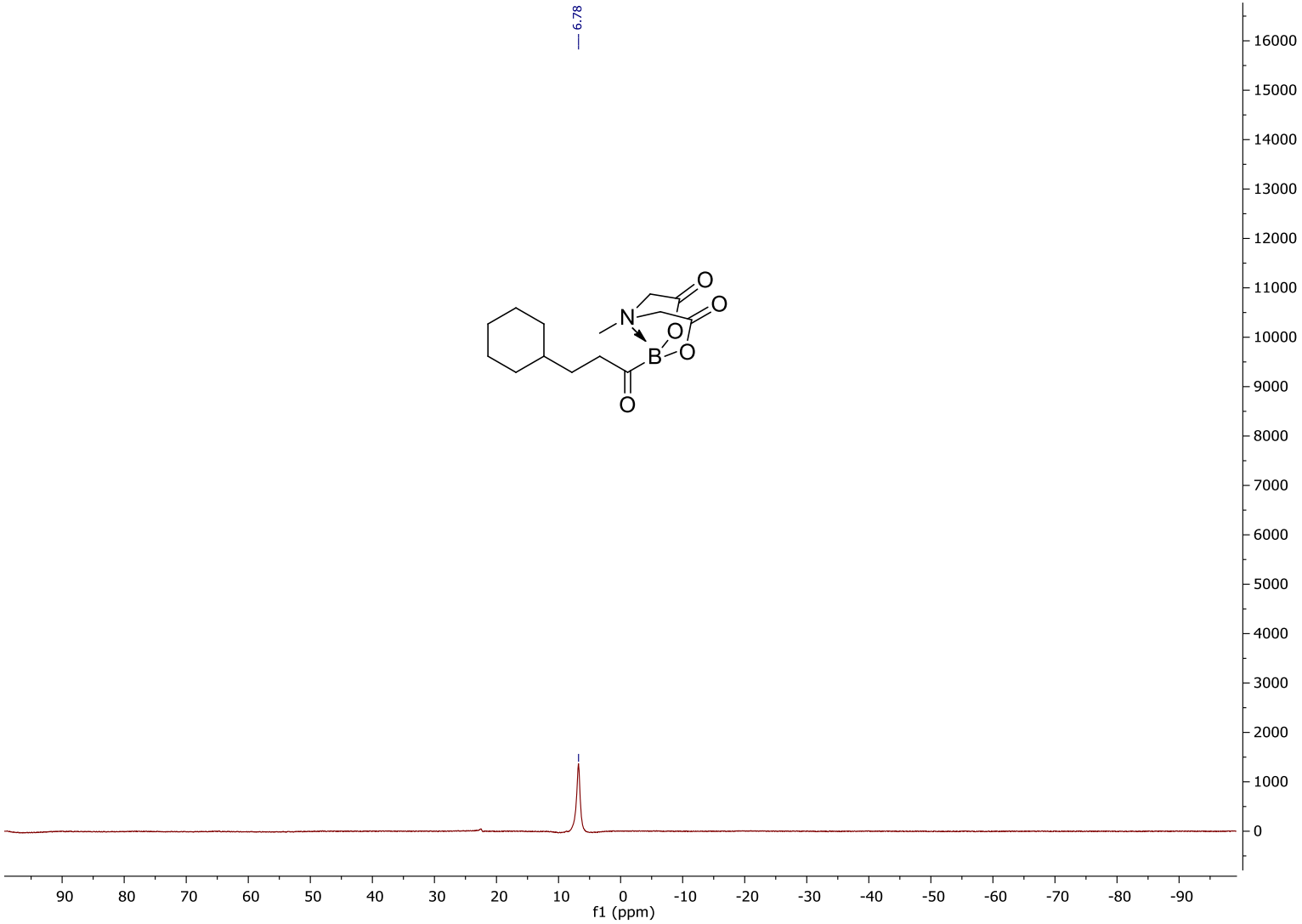
^{1}H NMR, compound 5m

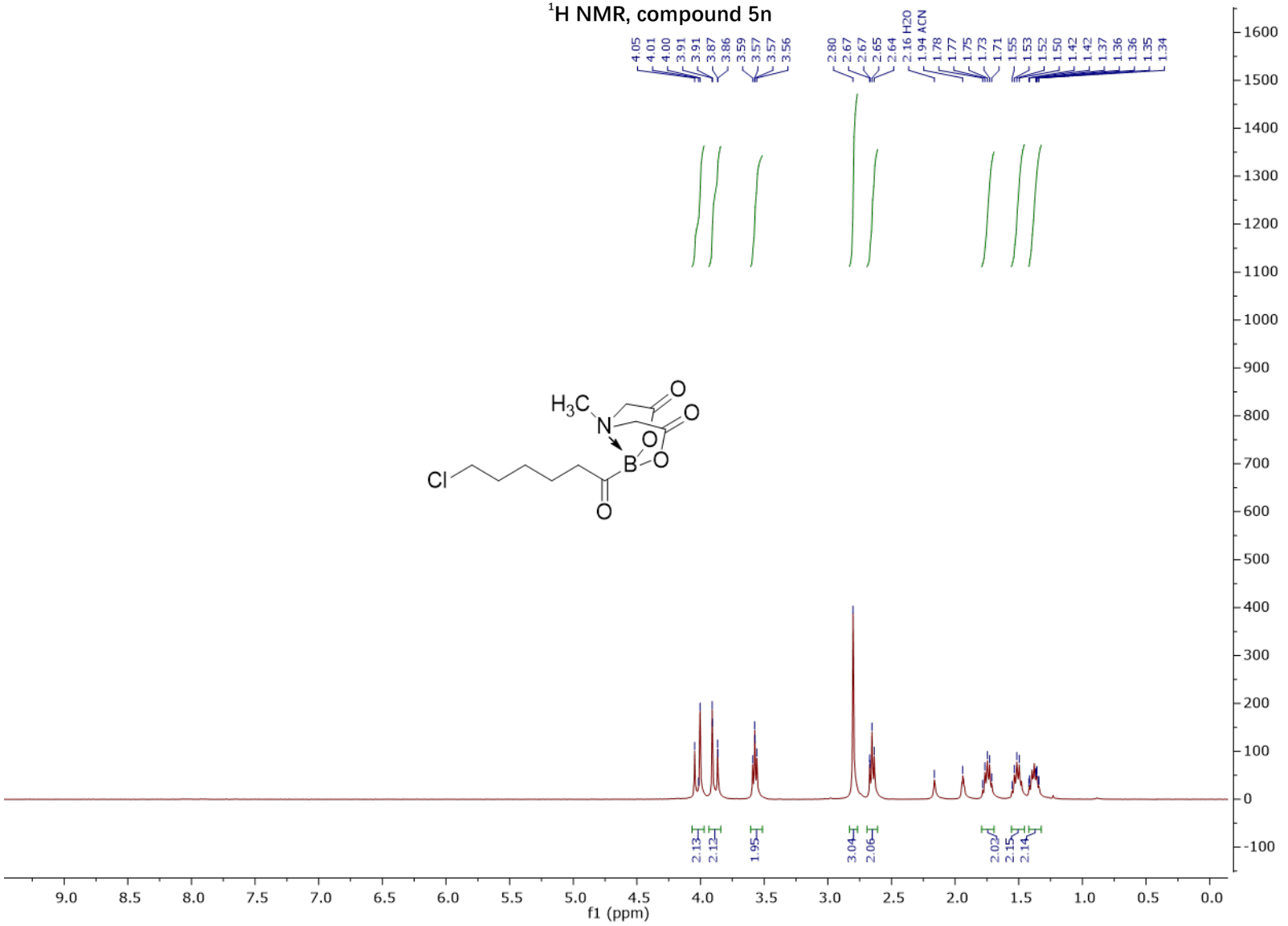


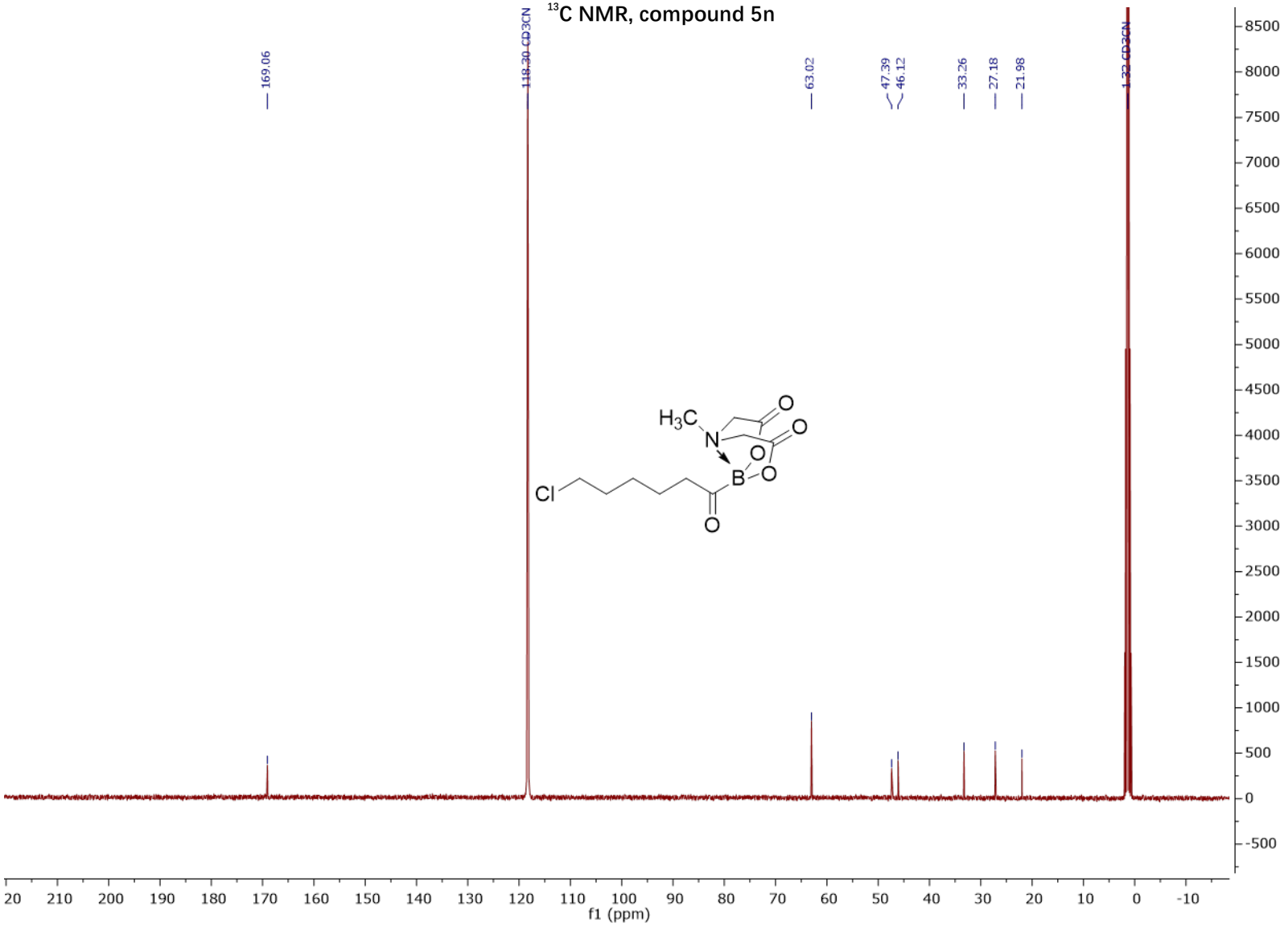
^{13}C NMR, compound 5m



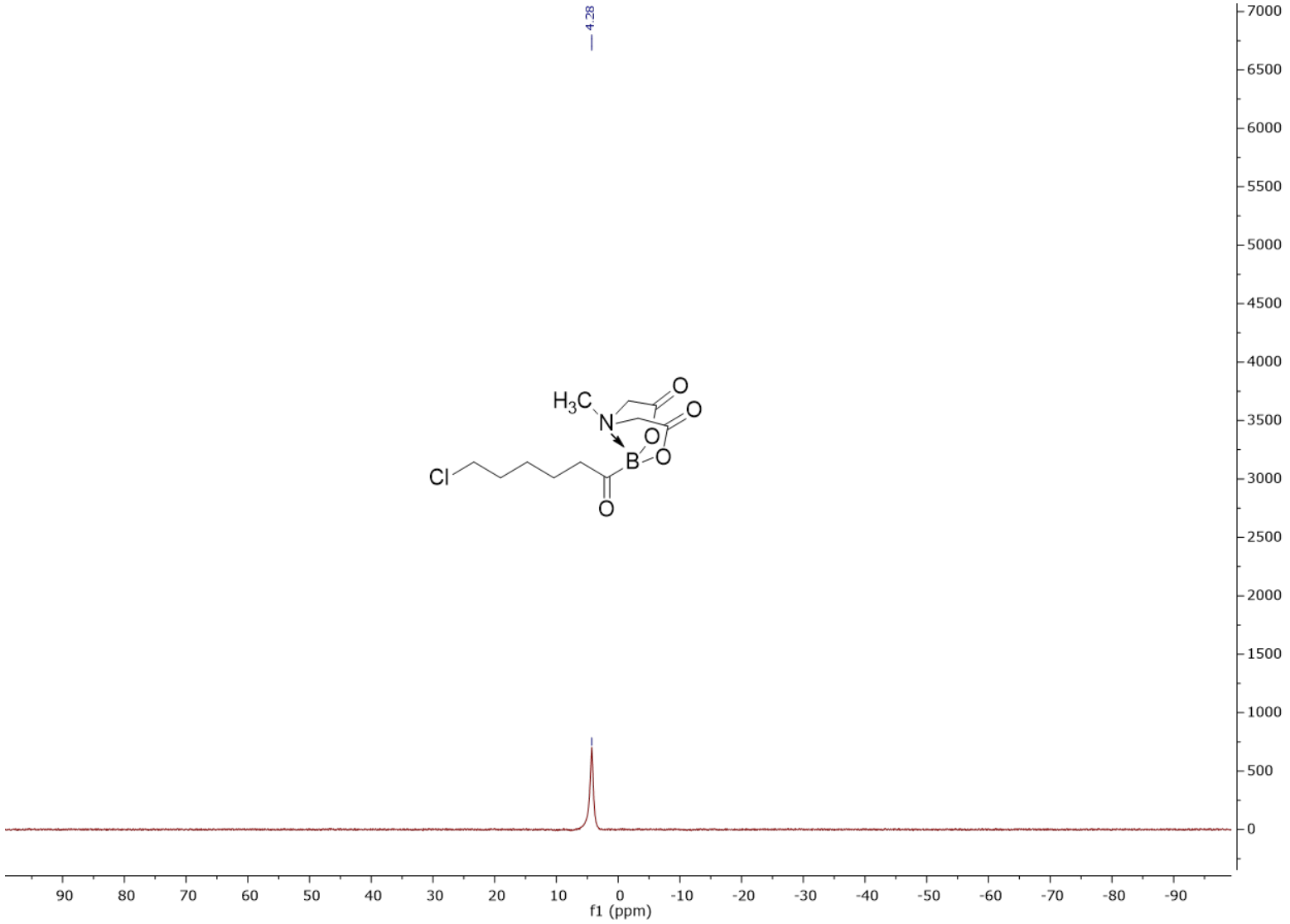
^{11}B NMR, compound 5m



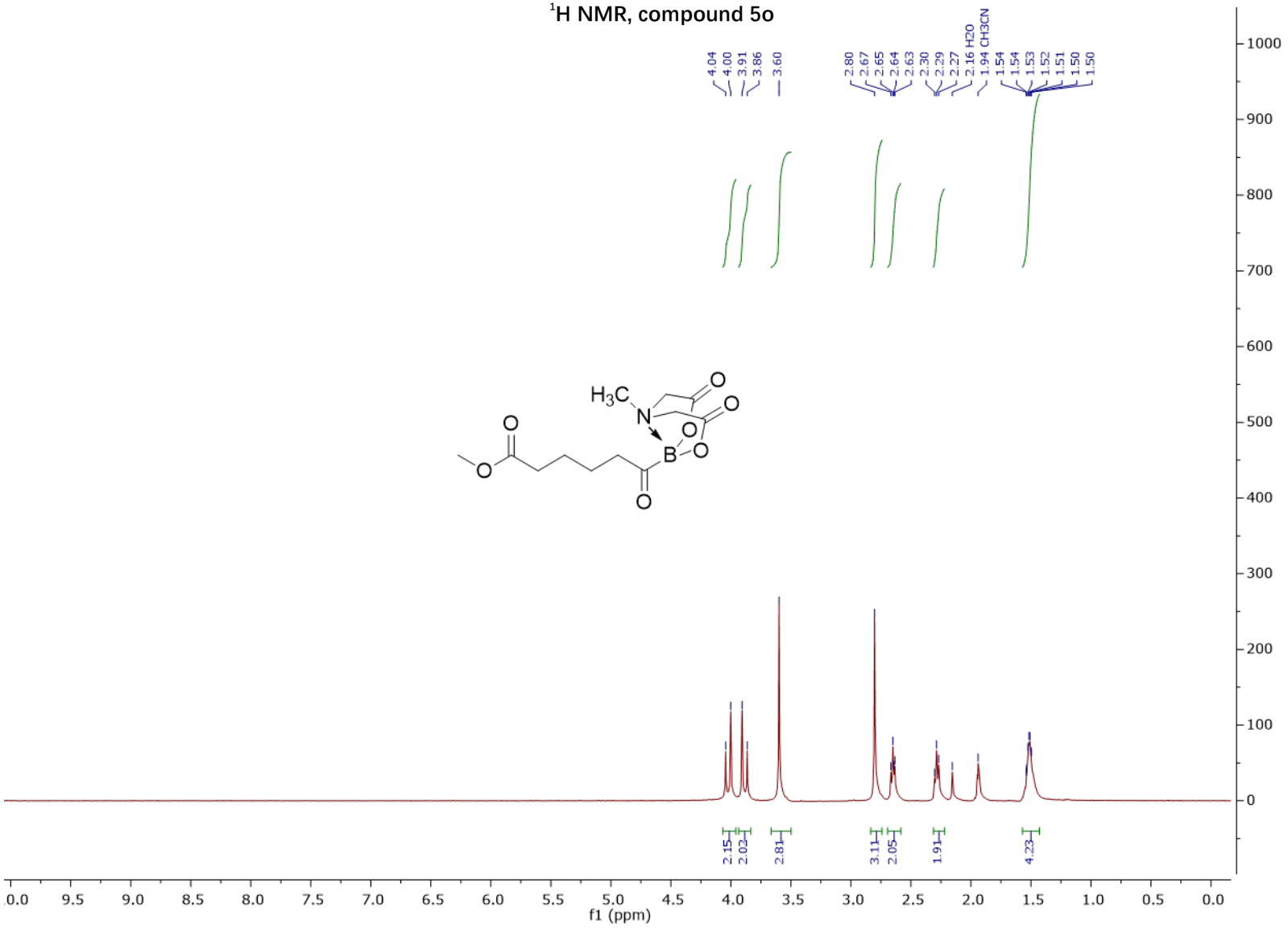

1H NMR, compound 5n
4.05
4.01
4.00
3.91
3.91
3.87
3.86
3.59
3.57
3.57
3.56
2.80
2.67
2.67
2.65
2.64
2.16 H2O
1.94 ACN
1.78
1.77
1.75
1.73
1.71
1.55
1.53
1.52
1.50
1.42
1.42
1.37
1.36
1.36
1.35
1.34
H3C
N
O
O
O
O
B
O
Cl
O
2.13
2.12
1.95
3.04
2.06
2.02
2.15
2.14
f1 (ppm)


^{13}C NMR, compound 5n
169.06
118.30 CD3CN
63.02
47.39
46.12
33.26
27.18
21.98
1.32 CD3CN
H3C
N
O
O
O
B
O
Cl
O
f1 (ppm)

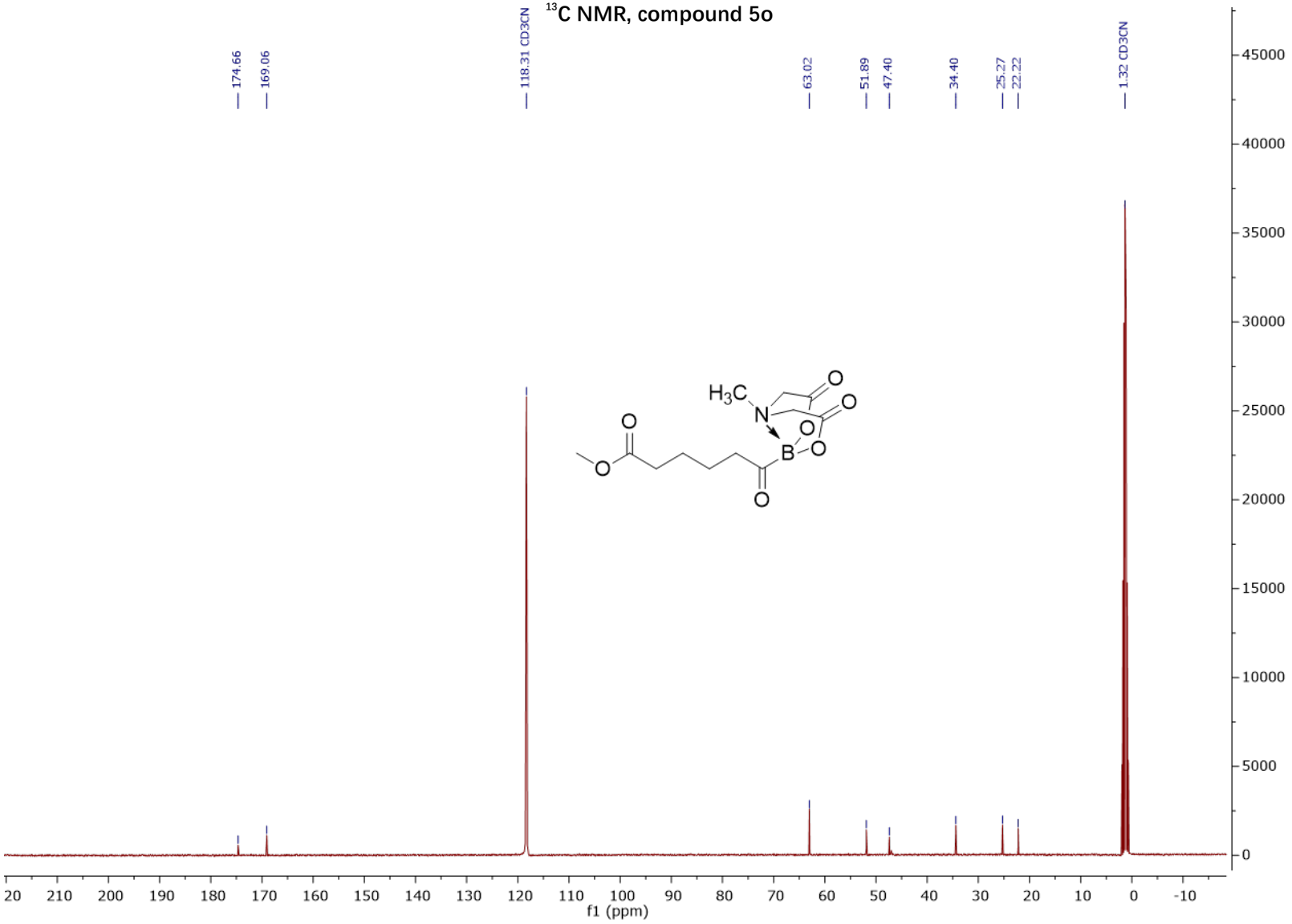
^{11}B NMR, compound 5n



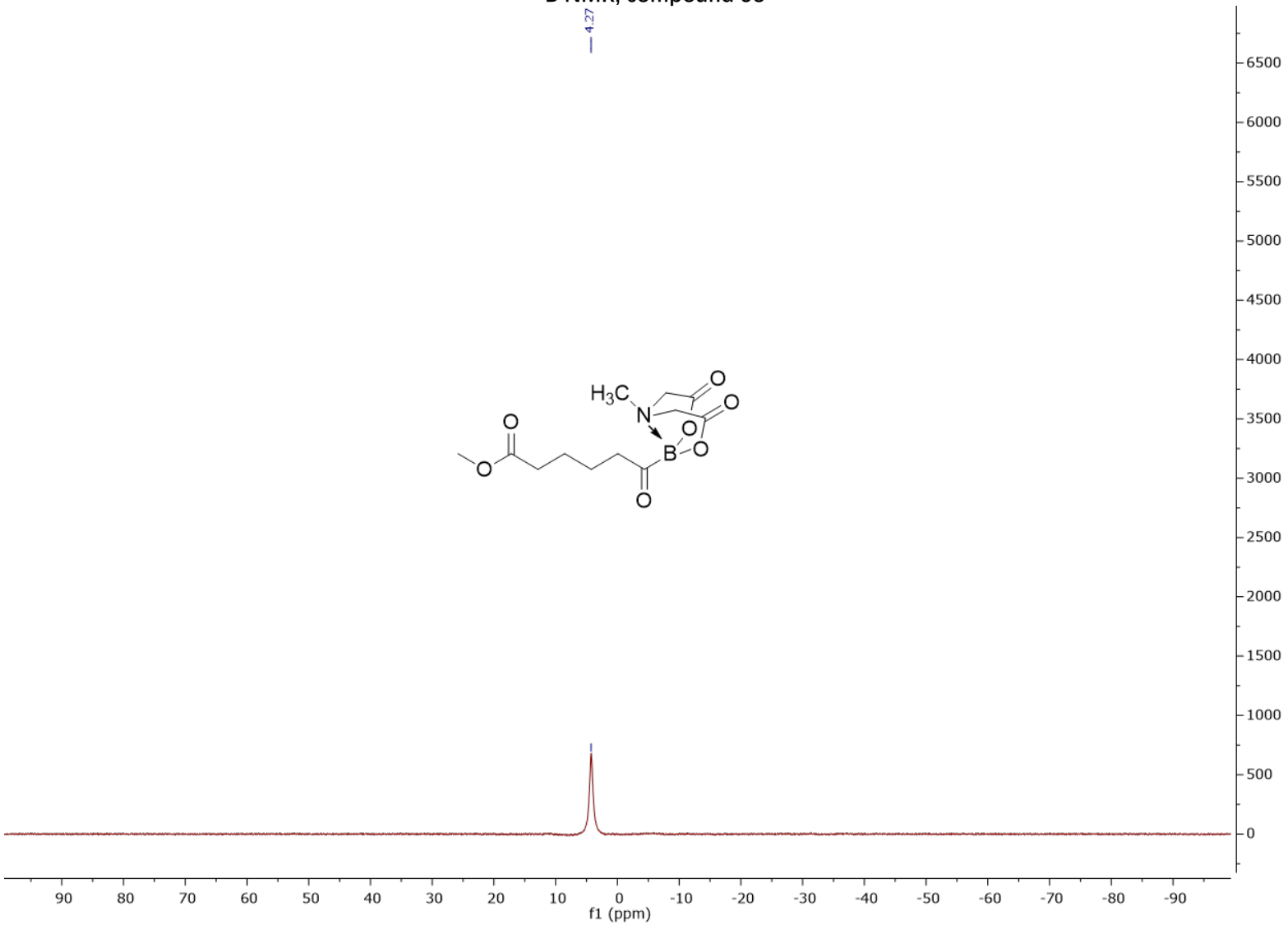
^{1}H NMR, compound 5o

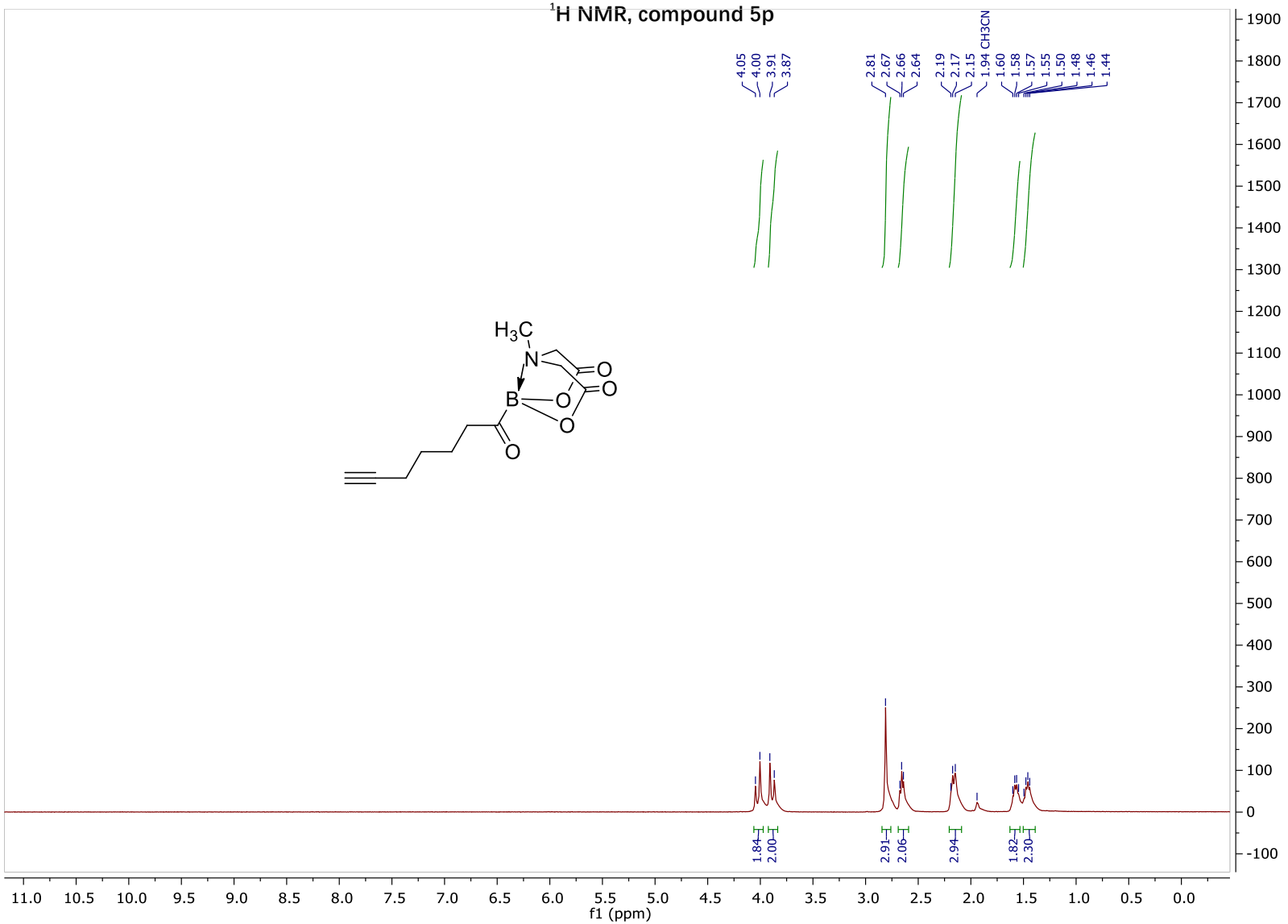


^{13}C NMR, compound 5o

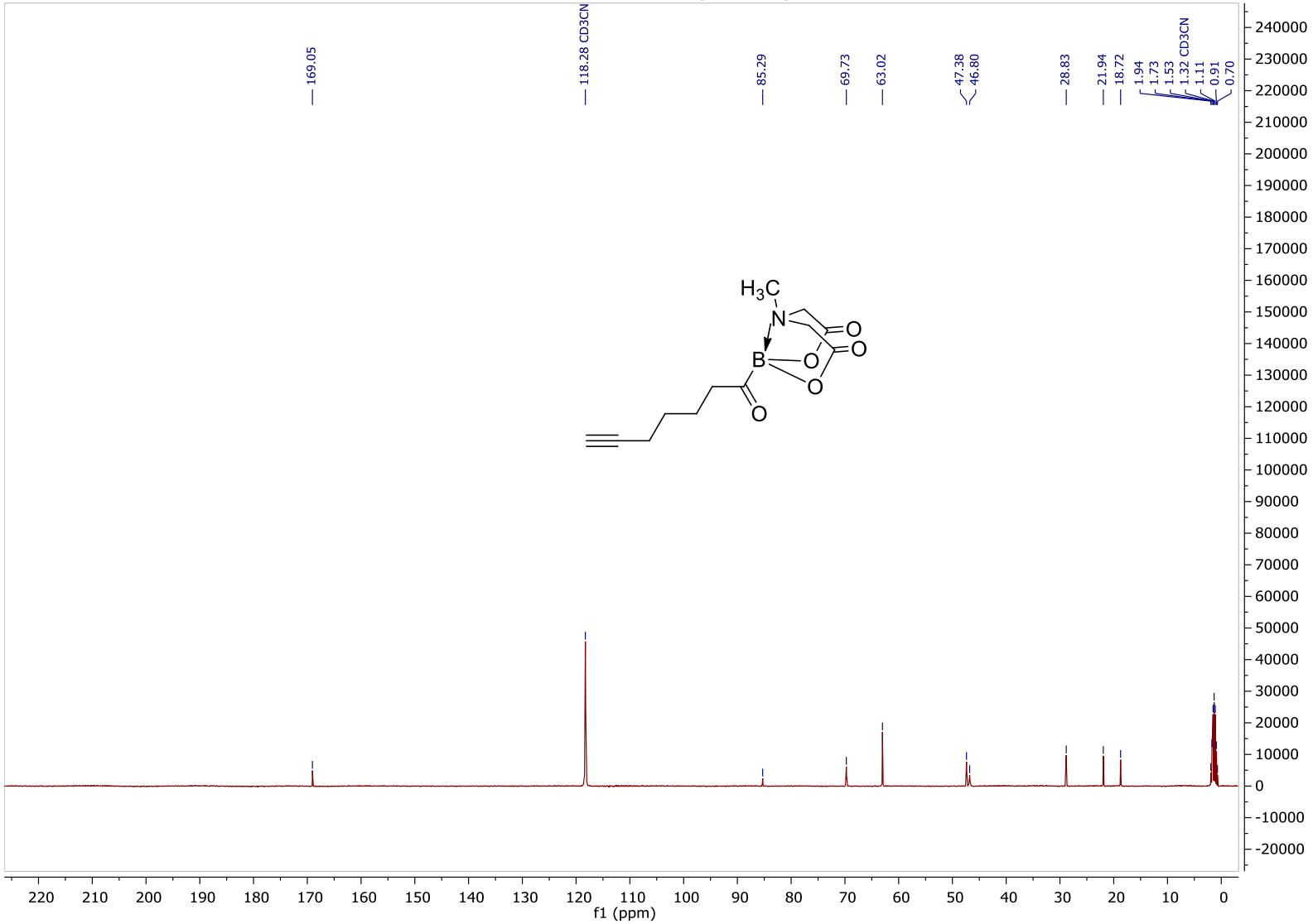


^{11}B NMR, compound 5o

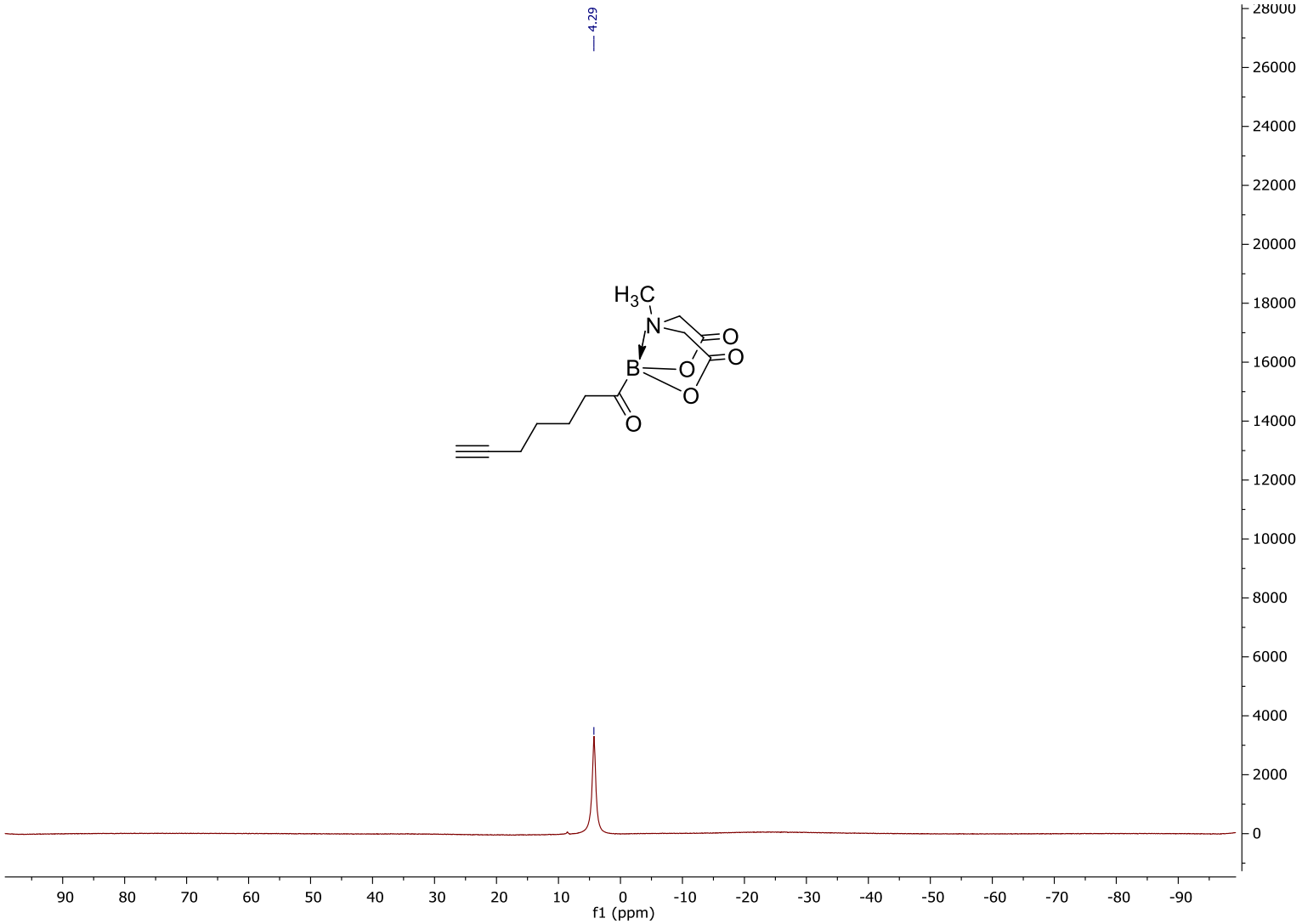



1H NMR, compound 5p
4.05
4.00
3.91
3.87
2.81
2.67
2.66
2.64
2.19
2.17
2.15
1.94 CH3CN
1.60
1.58
1.57
1.55
1.50
1.48
1.46
1.44
H3C
N
B
O
O
O
O
O
1.84
2.00
2.91
2.06
2.94
1.82
2.30
f1 (ppm)

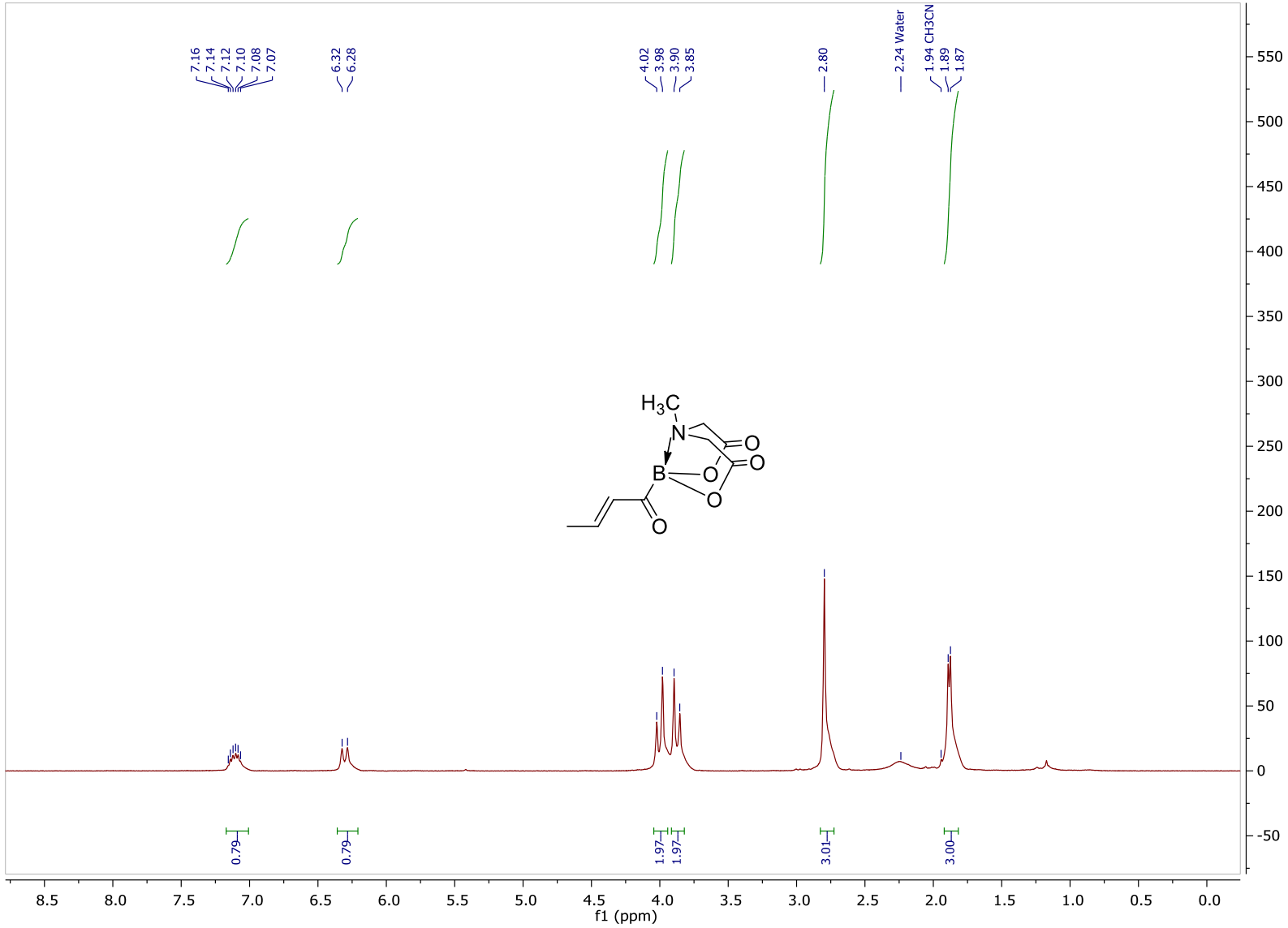
^{13}C NMR, compound 5p

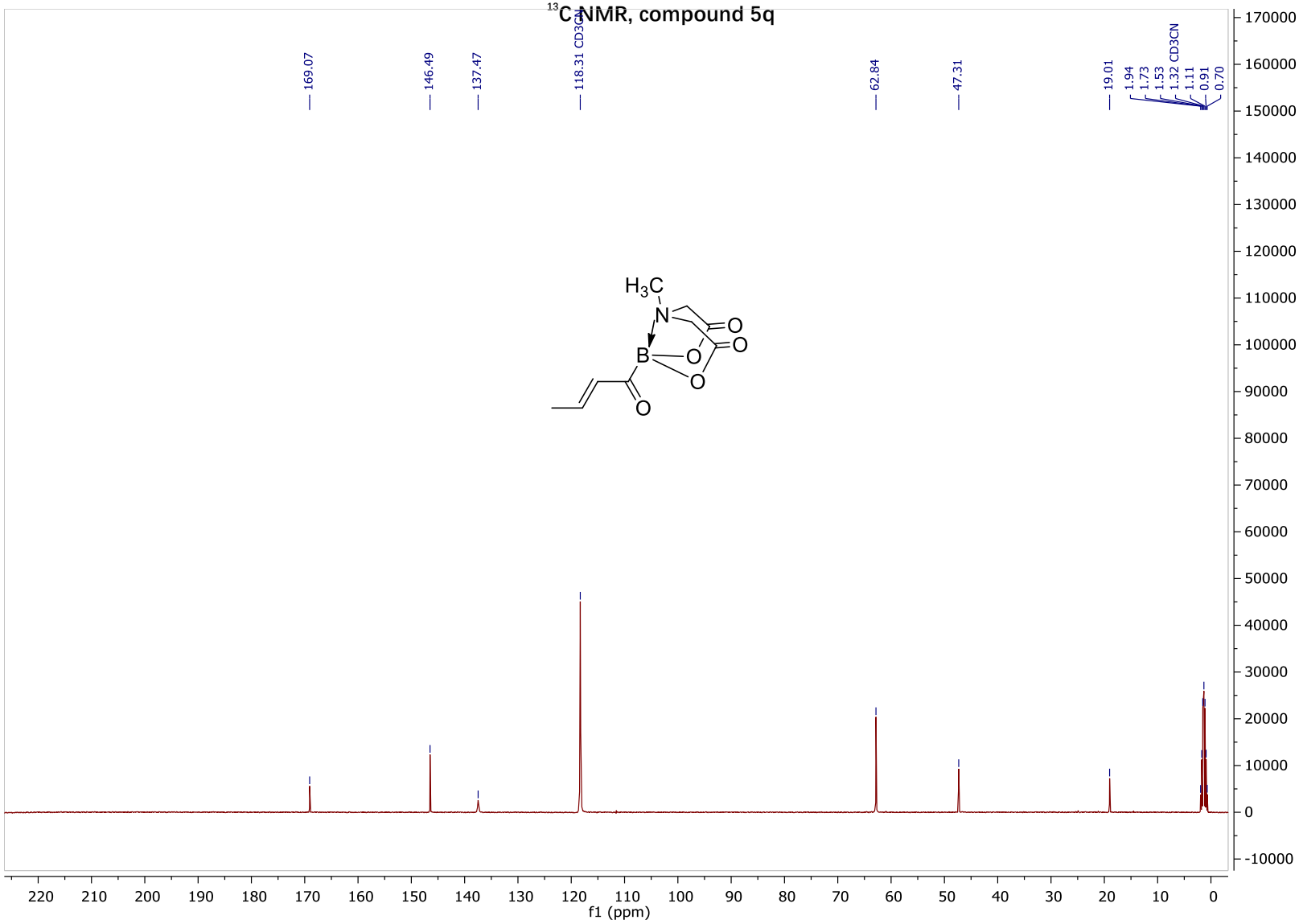


^{11}B NMR, compound 5p

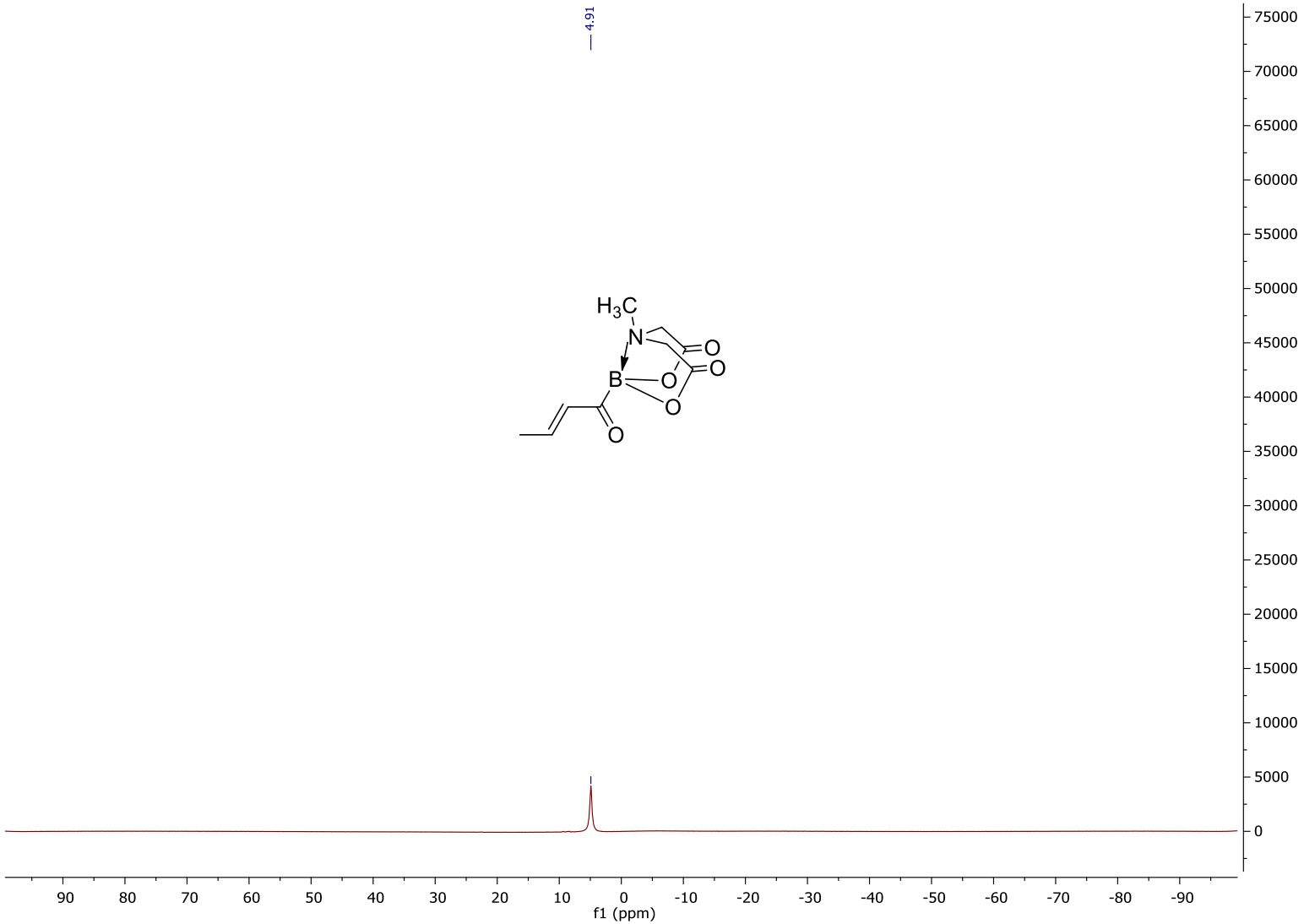


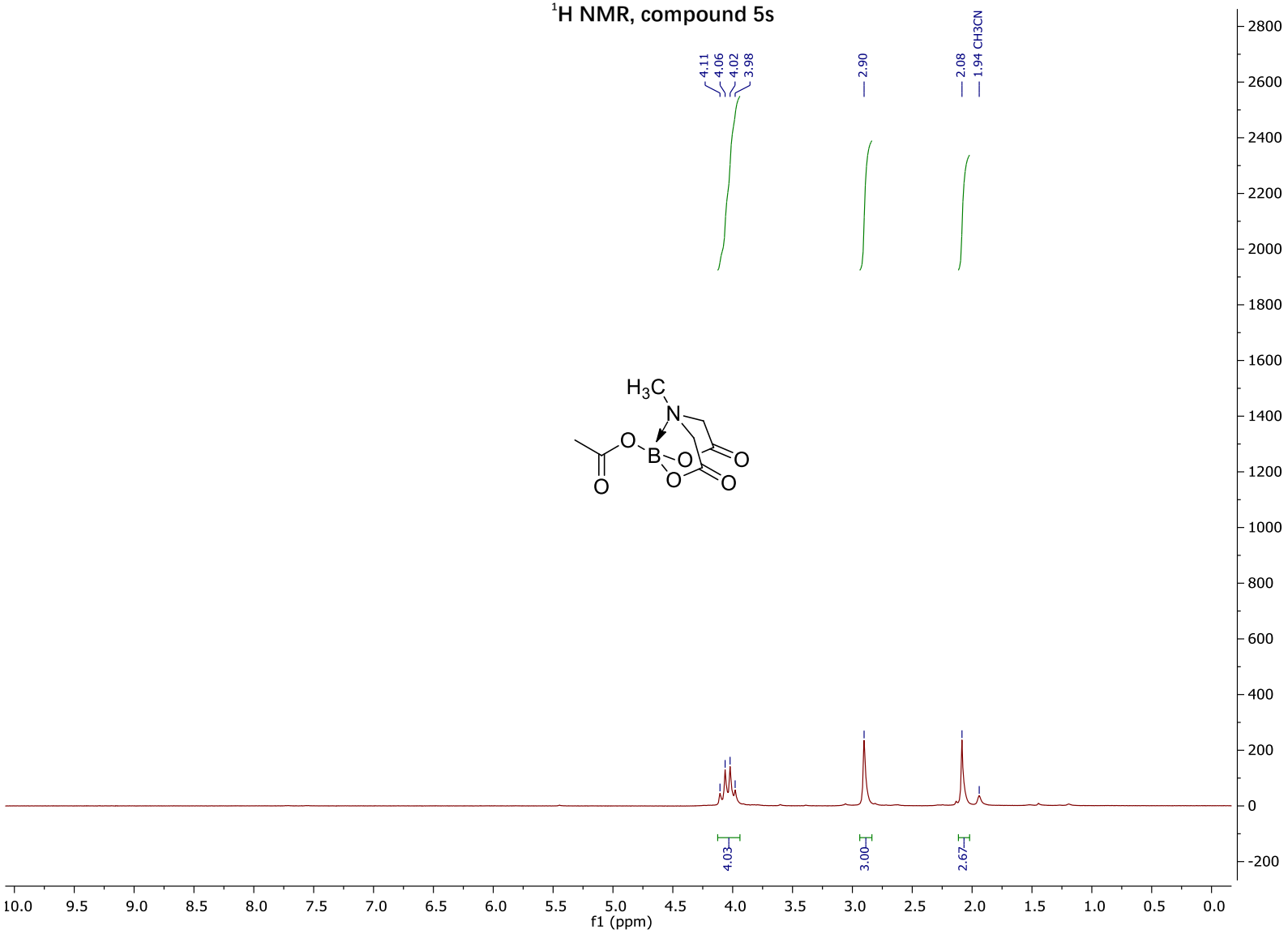
^{1}H NMR, compound 5q

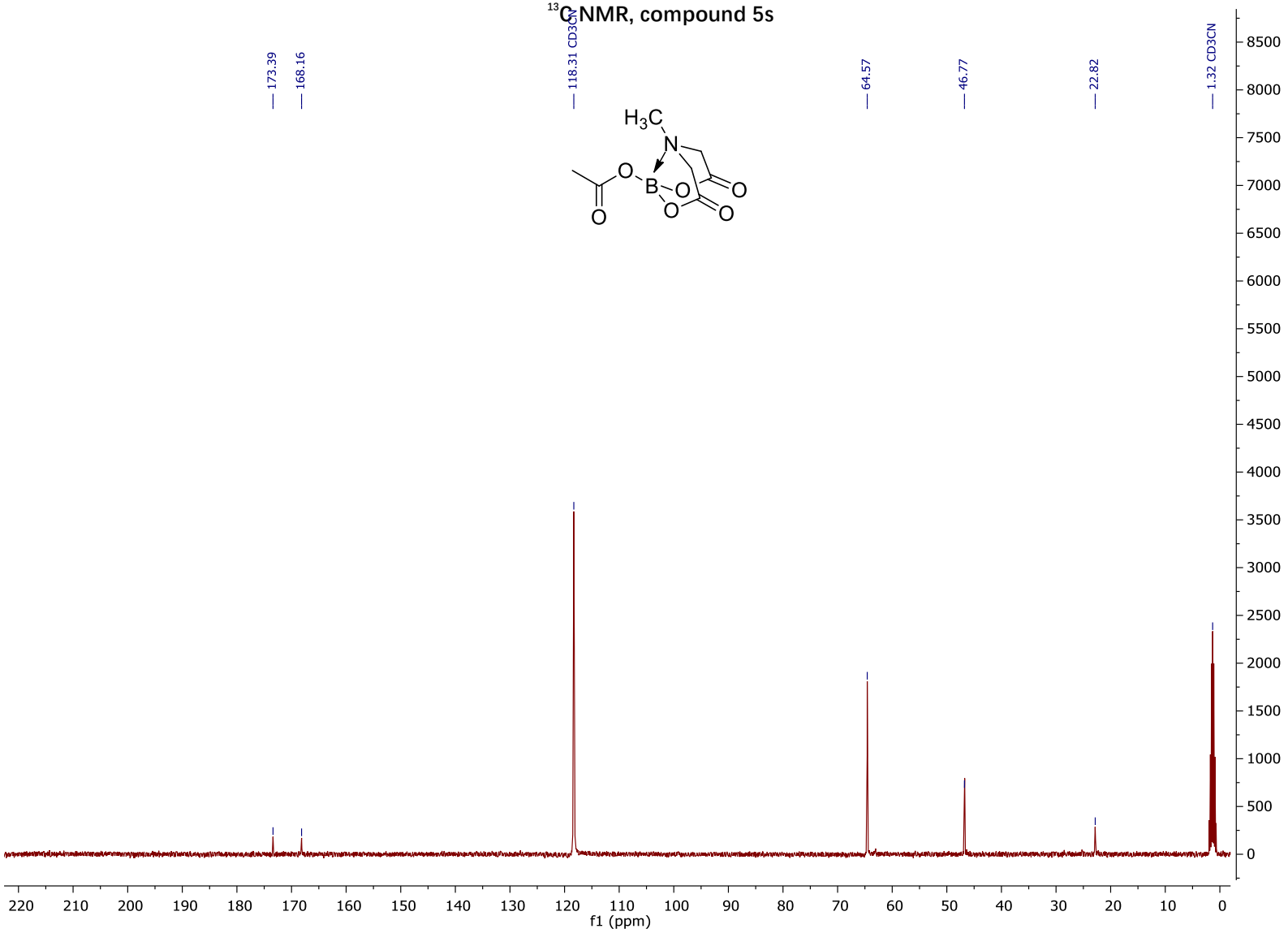



13C NMR, compound 5q
169.07
146.49
137.47
118.31 CD3CN
62.84
47.31
19.01
1.94
1.73
1.53
1.32 CD3CN
1.11
0.91
0.70
H3C
N
B
O
O
O
O
O
f1 (ppm)

^{11}B NMR, compound 5q




1H NMR, compound 5s
4.11
4.06
4.02
3.98
2.90
2.08
1.94 CH3CN
H3C
N
O
B
O
O
O
O
O
4.03
3.00
2.67
f1 (ppm)


13C NMR, compound 5s
173.39
168.16
118.31 CD3CN
64.57
46.77
22.82
1.32 CD3CN
H3C
N
O
B
O
O
O
O
O
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{11}B NMR, compound 5s