Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Acrylic boronate: A multifunctional C3 building block for catalytic synthesis of rare organoborons and chemoselective heterobifunctional ligations

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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 or Acros Organics. 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 45 ºC unless otherwise mentioned. All reactions were performed in oven-dried glassware under an atmosphere of dry nitrogen/argon unless otherwise mentioned.

Apparatus

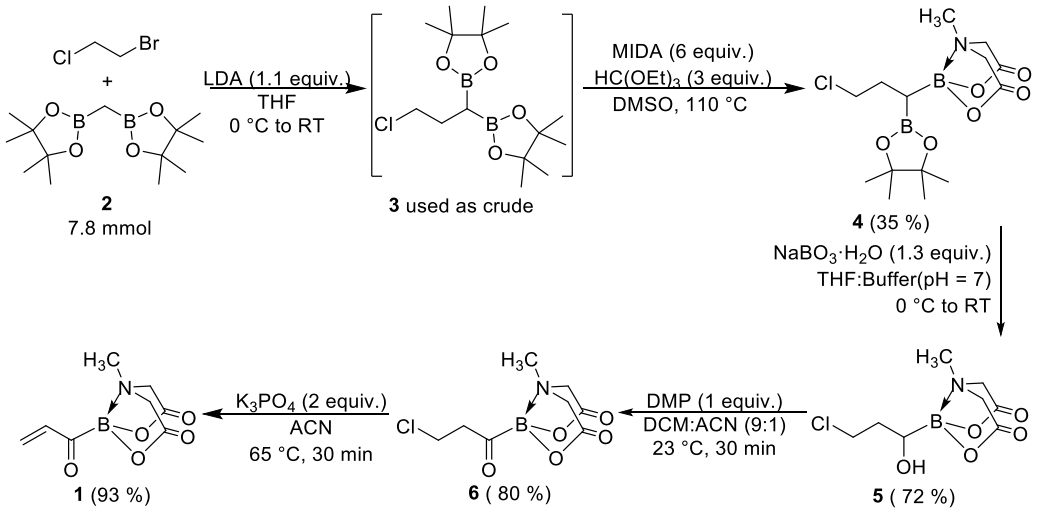
^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Varian-400 (400 MHz, ^{1}H; 100 MHz, ^{13}C, 128 MHz, ^{11}B) spectrometer. ^{19}F NMR were recorded on a Bruker Avance III 400 spectrometer (376 MHz,^{19}F). The ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) and referenced 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. FTIR analysis was carried out on a Bruker Tensor 27 Fourier transform infrared spectrometer. IR spectral data are given as follows: wavenumber (cm^{-1}); intensity (s-strong, m-medium, w-weak).

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. Synthesis of Acrylic Boronate 1



Scheme S1. Synthesis of Acrylic Boronate 1

Procedure for the synthesis of 6

To an oven dried 100 mL round bottom flask equipped with a stir bar, diborylmethane **2** (2.1 g, 7.8 mmol) and THF (20 mL) were added. The flask was evacuated and filled with nitrogen (three cycles). LDA (1.1 equiv.) was added via syringe at 0 ºC. The mixture was stirred for 5 min while maintaining at 0 ºC, then 1-Bromo-2-chloroethane (1 equiv.) was added.[7] 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 (saturated aq.). The organic layer was dried over Na_2SO_4, filtered and concentrated on vacuo, resulting crude **3** was used for next step without purification.

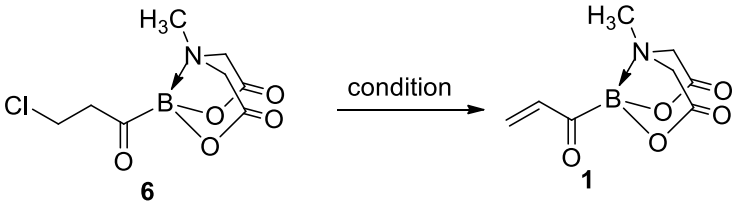
To a solution of **3** in DMSO (20 mL) was added methyliminodiacetic acid (MIDA, 6 equiv.) and $HC(OEt)_3$ (3 equiv.). The resulting mixture was stirred at 110 ºC for 14 h. The reaction mixture was then cooled to room temperature and filtered to recover unreacted methyliminodiacetic acid. Resulting filtrate was diluted with 100 ml of H_2O and extracted with EtOAc (3 x 200 mL). The combined organic phase was 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 **4** (1 g, 35%).

To a stirred mixture of **4** (1 g, 2.7 mmol) in THF (12 mL) and buffer (KH_2PO_4/NaOH, pH = 7, 1M, 8 mL) at 0 °C, $NaBO_3·H_2O$ (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 **5** (500mg, 72%).

To a solution of **5** (500 mg, 2 mmol) in 20 mL mixture of DCM/Acetonitrile (9:1), Dess-Martin periodinane (DMP, 1.0 equiv.) was added. The resulting mixture was stirred for 30 min and then celite was added. Solvent was removed on vacuo under room temperature, resulting crude solid was further purified using flash column chromatography (EtOAc/hexanes 0:10 to 10:0) to afford the pure product **6** (400 mg, 80 %).

Table S1. Optimization of conditions for dehydrochlorination of 6



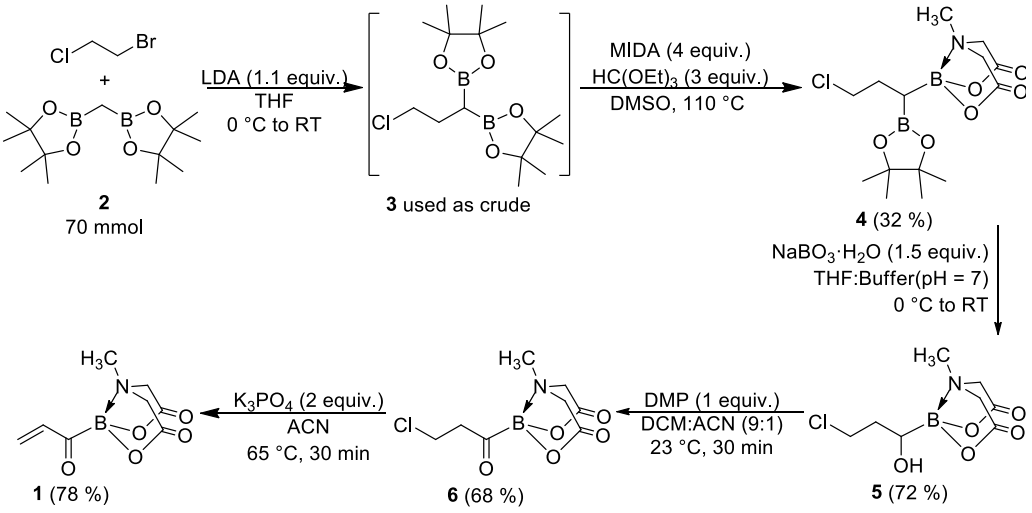
Entry	Condition	Isolated Yield%
1	DBU (1.1 equiv), ACN, 0 ºC, 30 min	ND[a]
2	NaOAc (1.1 equiv), DCM, RT, 30 min	0
3	Et_3N (1.1 equiv), ACN, RT, 50 min	20
4	Et_3N (1.1 equiv), ACN, 0 ºC, 20 min	14
5	NaOAc (3 equiv), DCM, RT, o/n	10
7	K_3PO_4 (2 equiv), ACN, RT, o/n	90
8	K_3PO_4 (2 equiv), ACN, 50 ºC, 1 h	90
9	K_3PO_4 (2 equiv), ACN, 65 ºC, 30 min	93
10	95 ºC, Toluene/DME	ND[a]

[a]: not detected.

Procedure for the synthesis of Acrylic Boronate 1

To a solution of **6** (400 mg, 1.6 mmol) in acetonitrile, K_3PO_4 (2 equiv.) was added. The reaction mixture was allowed to stir at 65 ºC. The completion of the reaction was confirmed by taking NMR of an aliquot of reaction crude. Upon complete conversion (usually completed in 30 min), the reaction crude was filtered through a short pad of celite and rinsed with acetonitrile. Filtrate was concentrated in vacuo to afford acrylic boronate **1** (315 mg, 93 %).

Procedure for large scale synthesis of Acrylic Boronate 1



Scheme S2. Large scale synthesis of 1

To an oven dried 250 mL round bottom flask equipped with a stir bar, diborylmethane **2** (19 g, 70 mmol) and THF (60 mL) were added. The flask was evacuated and filled with nitrogen (three cycles). LDA (1.1 equiv.) was added via syringe at 0 ºC. The mixture was stirred for 15 min while maintaining at 0 ºC, then 1-Bromo-2-chloroethane (1 equiv.) was added.[7] The reaction mixture was allowed to reach room temperature (23 ºC) while stirring for 14 h, then diluted with EtOAc and washed with NH_4Cl (saturated aq.). The organic layer was dried over Na_2SO_4, filtered and concentrated on vacuo, resulting crude **3** was used for next step without purification.

To a solution of **3** in DMSO (50 mL) was added methyliminodiacetic acid (MIDA, 4 equiv.) and $HC(OEt)_3$ (3 equiv.). The resulting mixture was stirred at 110 ºC for 14 h. The reaction mixture was then cooled to room temperature and filtered to recover unreacted methyliminodiacetic acid. Resulting filtrate was diluted with 500 mL of H_2O and extracted with EtOAc (3 x 200 mL). The combined organic phase was washed with brine, and then dried over Na_2SO_4, filtered, and concentrated. To the resulting residue, H_2O (200 ml), Hexane (100 ml) and DCM (5 ml) were added sequentially leading to the precipitation of a solid which was collected after filtration to give pure **4** (8 g, 32 % over two steps).

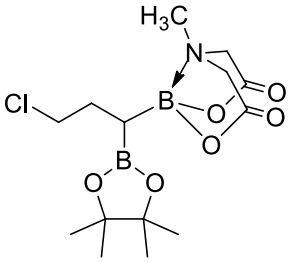
To a stirred mixture of **4** (8 g, 22 mmol) in THF (40 mL) and buffer (KH_2PO_4/NaOH, pH = 7, 1M, 25 mL) at 0 °C, $NaBO_3·H_2O$ (1.5 equiv.) was added. The reaction mixture was allowed to reach room temperature (23 ºC) over 6 h. Thereafter, the reaction mixture was diluted with EtOAc and then sequentially washed with 100 mL of H_2O and brine, then dried over Na_2SO_4. After filtration, residue was concentrated and subjected to flash column chromatography (silica gel; EtOAc/hexanes, 0:10 to 10:0) to obtain the pure product **5** (4 g, 72%)

To a solution of **5** (4 g, 16 mmol) in 50 mL mixture of DCM/Acetonitrile (9:1), Dess-Martin

periodinane (DMP, 1.0 equiv.) was added. The resulting mixture was stirred for 30 min and then celite was added. Solvent was removed on vacuo under room temperature, resulting crude solid was further purified using flash column chromatography (EtOAc/hexanes 0:10 to 10:0) to afford the pure product **6** (2.7 g, 68 %).

To a solution of **6** (2.7 g, 10.9 mmol) in acetonitrile, K_3PO_4 (2 equiv.) was added. The reaction mixture was allowed to stir at 65 ºC. The completion of the reaction was confirmed by taking NMR of an aliquot of reaction crude. Upon complete conversion (usually completed in 30 min), the reaction crude was filtered through a short pad of celite and rinsed with acetonitrile. Filtrate was concentrated in vacuo to afford acrylic boronate **1** (1.8 g, 78 %).

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



White solid; 1 g, 35 % yield; Melting point: 183 – 187 ºC

Rf (EtOAc) = 0.5

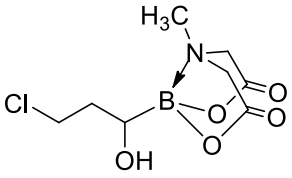
^{1}H NMR (400 MHz, CD_3CN) δ 3.99 – 3.79 (m, 4H), 3.73 – 3.63 (m, 1H), 3.63 – 3.52 (m, 1H), 2.97 (s, 3H), 1.94 – 1.83 (m, 2H), 1.20 (s, 12H), 0.65 – 0.58 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 168.9, 84.2, 63.8, 63.6, 47.9, 47.2, 31.0, 25.2, 25.0.

^{11}B NMR (128 MHz, CD_3CN) 34.27, 13.11.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{25}B_2ClNO_6$, calculated 360.1551; observed 360.1565.

2-(3-chloro-1-hydroxypropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5)



Sticky solid; 500 mg, 72 % yield.

Rf (EtOAc) = 0.2.

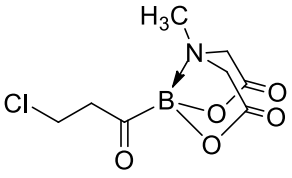
^{1}H NMR (400 MHz, CD_3CN) δ 4.00 – 3.90 (m, 2H), 3.87 – 3.78 (m, 2H), 3.76 – 3.67 (m, 2H), 3.47 (s, 1H), 3.03 (s, 3H), 2.59 (s, 1H), 1.95 – 1.90 (m, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.7, 168.9, 63.3, 63.1, 46.3, 43.7, 37.4.

^{11}B NMR (128 MHz, CD_3CN) 11.35

HRMS-ESI: m/z $[M+H]^+$ for $C_8H_{14}BClNO_5$, calculated 250.0650; observed 250.0650.

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



White solid; 400 mg, 80 % yield. Melting point: 117 – 120 ºC

Rf (EtOAc) = 0.4.

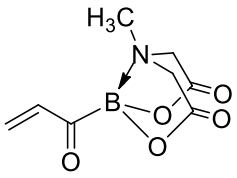
^{1}H NMR (400 MHz, CD_3CN) δ 4.05 (d, *J* = 16.9 Hz, 2H), 3.91 (d, *J* = 16.9 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 2H), 3.14 (t, *J* = 6.3 Hz, 2H), 2.83 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 63.1, 49.5, 47.6, 38.7

^{11}B NMR (128 MHz, CD_3CN) 4.89.

HRMS-ESI: m/z $[M+H]^+$ for $C_8H_{12}BClNO_5$, calculated 248.0494; observed 248.0492.

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



Yellow solid; 315 mg, 93 % yield. Melting point: 172 – 175 ºC

Rf (EtOAc) = 0.4.

IR (solid) cm^{-1}: 1752 (s), 1653 (m), 1286 (m), 1075 (s), 1053 (s), 1032 (s), 898 (m)

^{1}H NMR (400 MHz, CD_3CN) δ 6.56 (dd, *J* = 17.9, 10.8 Hz, 1H), 6.41 (dd, *J* = 17.9, 1.7 Hz, 1H).5.97 (dd, *J* = 10.8, 1.7 Hz, 1H), 4.05 (d, *J* = 16.9 Hz, 2H), 3.91 (d, *J* = 16.9 Hz, 2H), 2.84 (s, 3H).

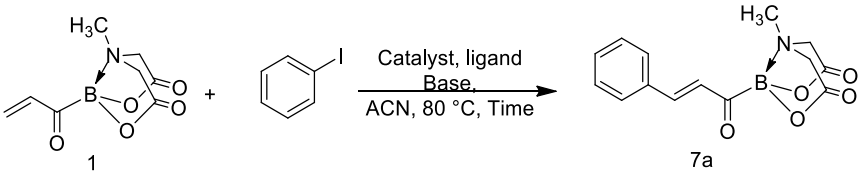
^{13}C NMR (100 MHz, DMSO) δ 168.6, 139.5, 128.8, 61.6, 46.3.

^{11}B NMR (128 MHz, CD_3CN) 4.83.

HRMS-ESI: m/z $[M+Na]^+$ for $C_8H_{10}BNO_5Na$, calculated 234.0551; observed 234.0551.

2. Synthesis of α,β and α,β,γ,δ-unsaturated MIDA acylboronates via Heck coupling

Table S2. Optimization of reaction conditions for Heck cross-coupling of Acrylic Boronate 1 and Iodobenzene



1 7a

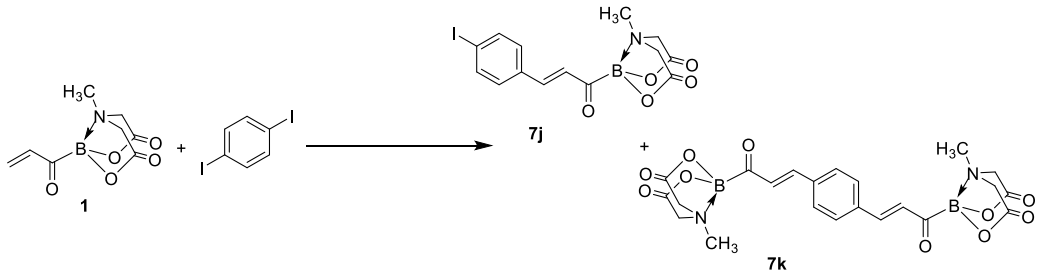
Entry	Amount of Iodobenzene (equiv.)	Catalyst (mol %) / Ligand (mol %)	Base (equiv.)	Time (h)	Isolated Yield of 7a (%)
1	3	$Pd_2(dba)_3$ (0.5) / PPh_3 (2)	Et_3N (2)	1.5	30
2	1.5	$Pd(OAc)_2$ (5)	AgOAc (1.5)	14	48
3	3	$Pd_2(dba)_3$ (0.5) / PPh_3 (2)	AgOAc (2)	14	ND[a]
4	1.5	$Pd(OAc)_2$ (5)	Et_3N (2)	1.5	40
5	1.5	$Pd(PPh_3)_4$ (2.5)	AgOAc (1.5)	14	42
6	1.5	$PdCl_2(PPh_3)_2$ (2.5)	AgOAc (1.5)	14	29

[a]: not detected.

General Procedure A: Synthesis of α,β and α,β,γ,δ-unsaturated MIDA acylboronates (7a - 7o) via Heck coupling

In a high pressure reaction tube, acrylic boronate **1** (100 mg, 0.47 mmol), AgOAc (1.5 equiv.), $Pd(OAc)_2$ (5 mol%), halide partner (1.5 equiv.) and acetonitrile (4 mL) were added. The reaction tube was then sealed and allowed to stir at 80 ºC for 14 h. Upon completion, the reaction crude was filtered through pad of celite and purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) using solid loading to afford α,β and α,β,γ,δ-unsaturated MIDA acylboronates **7**.

Table S3. Synthesis of compound 7j and compound 7k using 1,4-diiodobenzene

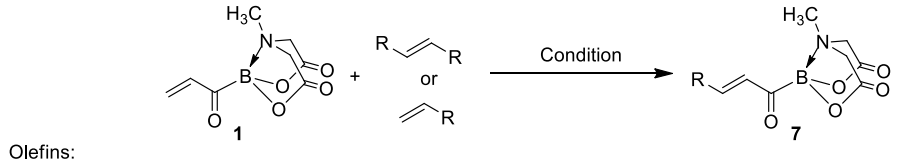


Condition	Isolated Yield of 7j	Isolated Yield of 7k
general procedure A	51%	9%
Modified general procedure A: **1** (3 equiv.), 1,4-diiodobenzene (1 equiv.), $Pd(OAc)_2$ (15 mol%), AgOAc (2.5 equiv), ACN, 80 ºC, 18 h	trace	82%

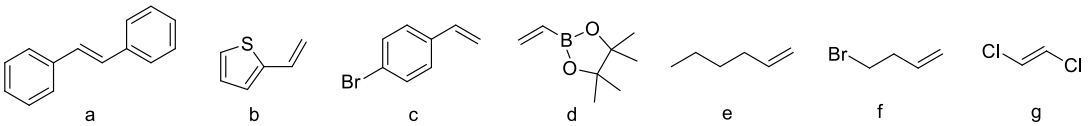
Modified general procedure A: In a thick wall high pressure reaction tube acrylic boronate **1** (3 equiv.), AgOAc (2.5 equiv.), $Pd(OAc)_2$ (15 mol%), 1,4-diiodobenzene (0.24 mmol) and acetonitrile (4 mL) were added. The reaction tube was then sealed and allowed to stir at 80 ºC for 18 h. Upon completion, the reaction crude was filtered through pad of celite and purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) to afford **7k** (82%).

3. Synthesis of α,β-unsaturated MIDA acylboronates via Cross Metathesis

Table S4. Screening of conditions for Cross Metathesis of 1 using various olefins



Olefins:



a b c d e f g

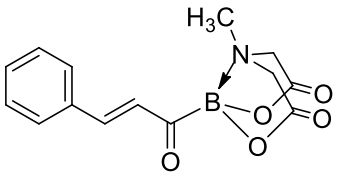
Entry	Olefin partner	Condition	Yield (7/unreacted 6)
1	a	Hoyeda-Grubbs 2nd , DCE, 55 ˚C, 14 h	60%[a]
2	b	Hoyeda-Grubbs 2nd , DCE, 55 ˚C, 14 h	20%[b] / 50%[b]
3		Hoyeda-Grubbs 2nd , DCE, 80 ˚C, 14 h	ND[c]
4	c	Hoyeda-Grubbs 2nd , DCE, 55 ˚C, 14 h	11%[b]
5	d	Hoyeda-Grubbs 2nd, DCE, 55 ˚C, 14 h	ND[c]
6		Grubbs 2nd, CuI, Et_2O, 35 ˚C, 14 h	ND[c]
7		Hoyeda-Grubbs 2nd, DCE, 55 ˚C, 48 h	ND[c]
8	e	Zhan Catalyst-1C, DCE/Toluene (1:1), 55 ˚C, 14 h	ND[c]
9		Hoyeda-Grubbs 2nd , DCE/Toluene (1:1), 55 ˚C, 14 h	ND[c] /50%[b]
10		Hoyeda-Grubbs 2nd , DCE, 55 ˚C, 14 h	48%[a]
11	f	Grubbs 2nd, DCE, 55 ˚C, 14 h	ND[c]
12	g	Hoyeda-Grubbs 2nd , DCE/Toluene (1:1), 55 ˚C, 14 h	ND[c]
13		Hoyeda-Grubbs 2nd , DCE/Toluene (1:1), 80 ˚C, 14 h	ND[c]

[a]: isolated yield; [b]: calculated based on NMR; [c]: not detected.

General Procedure B: Synthesis of α,β-unsaturated MIDA acylboronates (7a, 7b, 7i', 7p, 7q, 7r) via Cross Metathesis of 1

To a solution of acrylic boronate **1** (100 mg, 0.47 mmol) in DCE (0.2 M), Hoveyda-Grubbs Catalyst 2nd Generation (15 mol%) and alkene coupling partner (2 equiv.) were added. The resulting mixture was stirred for 14 h at 55 ºC. Upon completion, the reaction crude was filtered through pad of celite and rinse with DCM and then purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) using solid loading to afford α,β-unsaturated MIDA acylboronate **7.**

2-cinnamoyl-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7a)



Synthesized by general procedure A or B

Yellow sticky liquid; 65 mg, 48 % yield from general procedure A; 81 mg, 60 % yield from general procedure B;

Rf (ACN : EtOAc = 1 : 20) = 0.5.

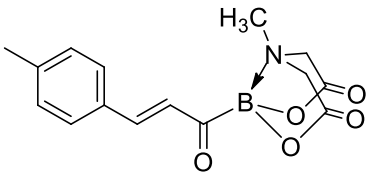
^{1}H NMR (400 MHz, CD_3CN) δ 7.75 (d, *J* = 16.4 Hz, 1H), 7.67 (s, 2H), 7.46 – 7.39 (m, 3H), 7.08 (d, *J* = 16.4 Hz, 1H), 4.06 (d, *J* = 16.9 Hz, 2H), 3.94 (d, *J* = 16.3 Hz, 2H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 143.9, 136.1, 131.6, 130.9, 130.0, 129.5, 62.9, 47.5.

^{11}B NMR (128 MHz, CD_3CN) 5.01.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{15}BNO_5$, calculated 288.1041; observed 288.1055

(E)-6-methyl-2-(3-(p-tolyl)acryloyl)-1,3,6,2-dioxazaborocane-4,8-dione (7b)



Synthesized by general procedure A or B.

Yellow sticky liquid; 71 mg, 50 % yield from general procedure A; 57 mg, 40 % yield from general procedure B;

Rf (ACN : EtOAc = 1 : 20) = 0.5.

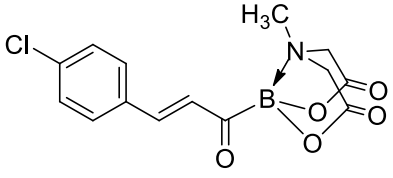
^{1}H NMR (400 MHz, CD_3CN) δ 7.73 (d, *J* = 16.2 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 6.4 Hz, 2H), 7.04 (d, *J* = 16.5 Hz, 1H), 4.06 (d, *J* = 16.9 Hz, 2H), 3.93 (d, *J* = 16.6 Hz, 2H), 2.85 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 144.1, 142.3, 133.3, 131.1, 130.6, 129.5, 62.9, 47.5, 21.5.

^{11}B NMR (128 MHz, CD_3CN) 5.08.

HRMS-ESI: m/z $[M+H]^+$ for $C_{15}H_{17}BNO_5$, calculated 302.1197; observed 302.1201.

(E)-2-(3-(4-chlorophenyl)acryloyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dion (7c)



Synthesized by general procedure A .

Yellow sticky liquid; 63 mg, 42 % yield.

Rf (ACN : EtOAc = 1 : 20) = 0.5

^{1}H NMR (400 MHz, CD_3CN) δ 7.74 – 7.63 (m, 3H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 16.4 Hz, 1H), 4.07 (d, *J* = 16.7 Hz, 2H),

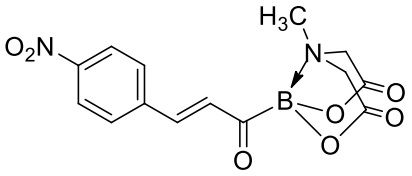
3.94 (d, *J* = 17.1 Hz, 2H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 142.3, 136.7, 134.9, 131.3, 131.0, 130.0, 62.9, 47.5.

^{11}B NMR (128 MHz, CD_3CN) 4.77.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{14}BClNO_5$, calculated 322.0651; observed 322.0655.

(E)-6-methyl-2-(3-(4-nitrophenyl)acryloyl)-1,3,6,2-dioxazaborocane-4,8-dione (7d)



Synthesized by general procedure A.

Yellow solid; 70 mg, 45 % yield. Melting point: 229 – 232 ºC

Rf (ACN : EtOAc = 1 : 20) = 0.5

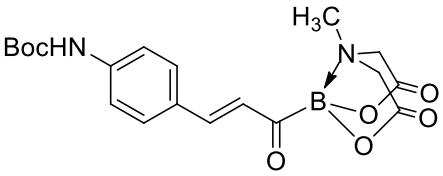
^{1}H NMR (400 MHz, CD_3CN) δ 8.24 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 16.2 Hz, 1H), 7.20 (d, *J* = 16.3 Hz, 1H), 4.08 (d, *J* = 16.8 Hz, 2H), 3.95 (d, *J* = 16.9 Hz, 2H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 149.6, 142.5, 140.6, 130.3, 130.0, 125.0, 63.0, 47.6.

^{11}B NMR (128 MHz, CD_3CN) δ 4.64.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{14}BN_2O_7$, calculated 333.0897; observed 333.0612.

(E)-tert-butyl-(4-(3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-oxoprop-1-en-1-yl)phenyl)carbamate (7e)



Synthesized by general procedure A.

Yellow sticky liquid; 48 mg, 25 % yield.

Rf (ACN : EtOAc = 1 : 20) = 0.5

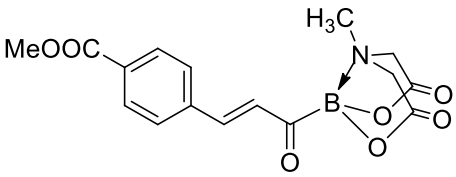
^{1}H NMR (400 MHz, CD_3CN) δ 7.75 (broad s, 1H), 7.71 (d, *J* = 16.4 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 16.3 Hz, 1H), 4.06 (d, *J* = 17.0 Hz, 2H), 3.94 (d, *J* = 16.9 Hz, 2H), 2.85 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 153.6, 143.8, 142.7, 130.5, 130.1, 119.1, 81.0, 62.9, 47.4, 28.5

^{11}B NMR (128 MHz, CD_3CN) 4.92.

HRMS-ESI: m/z $[M+H]^+$ for $C_{19}H_{24}BN_2O_7$, calculated 403.1675; observed 403.1669

(E)-methyl-4-(3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-oxoprop-1-en-1-yl)benzoate (7f)



Synthesized by general procedure A.

Yellow sticky liquid; 84 mg, 52 % yield.

Rf (ACN : EtOAc = 1 : 20) = 0.5

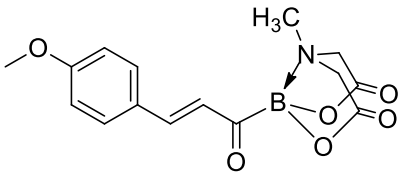
^{1}H NMR (400 MHz, CD_3CN) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.80 – 7.72 (m, 3H), 7.16 (d, *J* = 16.3 Hz, 1H), 4.08 (d, *J* = 16.9 Hz, 2H), 3.95 (d, *J* = 16.9 Hz, 2H), 3.88 (s, 3H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 167.2, 142.1, 140.5, 132.6, 132.5, 130.8, 129.5, 63.0, 52.9, 47.5.

^{11}B NMR (128 MHz, CD_3CN) δ 5.06.

HRMS-ESI: m/z $[M+H]^+$ for $C_{16}H_{17}BNO_7$, calculated 346.1096; observed 346.1097

(E)-2-(3-(4-methoxyphenyl)acryloyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7g)



Synthesized by general procedure A.

Yellow solid; 67 mg, 45 % yield. Melting point: 80 – 82 ºC

Rf (ACN : EtOAc = 1 : 20) = 0.5

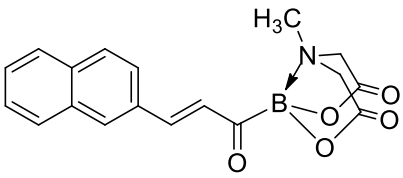
^{1}H NMR (400 MHz, CD_3CN) δ 7.73 (d, *J* = 16.3 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.02 – 6.95 (m, 3H), 4.06 (d, *J* = 16.8 Hz, 2H), 3.93 (d, *J* = 17.7 Hz, 2H), 3.83 (s, 3H), 2.85 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 162.8, 143.9, 131.3, 128.9, 128.5, 115.4, 62.9, 56.1, 47.4.

^{11}B NMR (128 MHz, CD_3CN) 5.06.

HRMS-ESI: m/z $[M+H]^+$ for $C_{15}H_{17}BNO_6$, calculated 318.1147; observed 318.1140.

(E)-6-methyl-2-(3-(naphthalen-2-yl)acryloyl)-1,3,6,2-dioxazaborocane-4,8-dione (7h)



Synthesized by general procedure A.

Yellow solid; 72 mg, 45% yield; 124mg, 35% yield from 1.2 mmol scale reaction.

Melting point: 82 – 84 ºC

Rf (ACN : EtOAc = 1 : 20) = 0.5

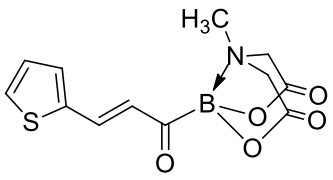
^{1}H NMR (400 MHz, CD_3CN) δ 8.69 (d, *J* = 16.0 Hz, 1H), 8.30 – 8.24 (m, 1H), 8.04 – 7.93 (m, 3H), 7.68 – 7.53 (m, 3H), 7.14 (d, *J* = 16.9 Hz, 1H), 4.11 (d, *J* = 16.6 Hz, 2H), 3.99 (d, *J* = 17.4 Hz, 2H), 2.91 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 141.0, 134.7, 133.6, 133.0, 132.6, 131.7, 129.8, 128.1, 127.3, 126.7, 126.0, 124.0, 63.0, 47.6.

^{11}B NMR (128 MHz, CD_3CN) 5.01.

HRMS-ESI: m/z $[M+H]^+$ for $C_{18}H_{17}BNO_5$, calculated 338.1198; observed 338.1194.

(E)-6-methyl-2-(3-(thiophen-2-yl)acryloyl)-1,3,6,2-dioxazaborocane-4,8-dione (7i)



Synthesized by general procedure A.

Yellow sticky liquid; 55 mg, 40 % yield.

Rf (ACN : EtOAc = 1 : 20) = 0.5

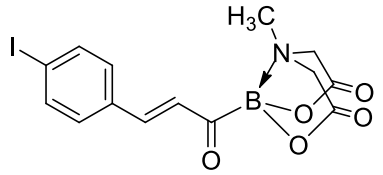
1H NMR (400 MHz, CD_3CN) δ 7.89 (d, *J* = 16.1 Hz, 1H), 7.56 (d, *J* = 5.1 Hz, 1H), 7.47 (d, *J* = 3.7 Hz, 1H), 7.13 (m, 1H), 6.84 (d, *J* = 16.1 Hz, 1H), 4.06 (d, *J* = 16.9 Hz, 2H), 3.93 (d, *J* = 17.0 Hz, 2H), 2.85 (s, 3H).

13C NMR (100 MHz, CD_3CN) δ 169.2, 141.4, 138.4, 136.5, 133.6, 130.6, 129.7, 62.9, 47.5.

11B NMR (128 MHz, CD_3CN) 4.96.

HRMS-ESI: m/z $[M+H]^+$ for $C_{12}H_{13}BNO_5S$, calculated 294.0605; observed 294.0606.

(E)-2-(3-(4-iodophenyl)acryloyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7j)



Yellow sticky liquid; 99 mg, 51 % yield from general procedure A.

Rf (ACN : EtOAc = 1 : 20) = 0.5

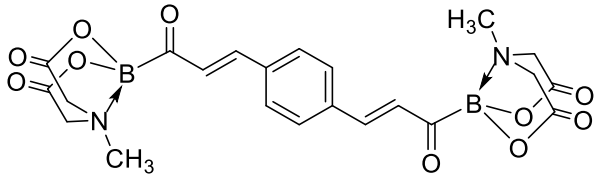
^{1}H NMR (400 MHz, CD_3CN) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 16.5 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 16.5 Hz, 1H), 4.06 (d, *J* = 16.9 Hz, 2H), 3.94 (d, *J* = 17.0 Hz, 2H), 2.85 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 142.5, 139.1, 135.8, 132.6, 131.1, 97.1, 63.0, 47.5.

^{11}B NMR (128 MHz, CD_3CN) δ 4.90.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{14}BINO_5$, calculated 414.0007; observed 414.0039.

6-methyl-2-((E)-4-(4-((E)-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-oxoprop-1-en-1-yl)phenyl)but-2-enoyl)-1,3,6,2-dioxazaborocane-4,8-dione (7k)



Yellow solid; Melting point: > 250 ºC.

21 mg, 9 % yield from general procedure A; *98 mg, 82 %* from *modified general procedure A.*

Rf (ACN : EtOAc = 1 : 20) = 0.2

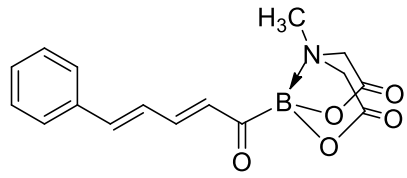
^{1}H NMR (400 MHz, CD_3CN) δ 7.77 – 7.70 (m, 6H), 7.14 (d, *J* = 16.1 Hz, 2H), 4.07 (d, *J* = 17.2 Hz, 4H), 3.94 (d, *J* = 17.4 Hz, 4H), 2.86 (s, 6H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 142.6, 138.1, 131.5, 130.0, 62.9, 47.5.

^{11}B NMR (128 MHz, CD_3CN) 4.82.

HRMS-ESI: m/z $[M+Na]^+$ for $C_{22}H_{22}B_2N_2O_{10}Na$, calculated 519.1358; observed 519.1365.

6-methyl-2-((2E,4E)-5-phenylpenta-2,4-dienoyl)-1,3,6,2-dioxazaborocane-4,8-dione (7m)



Synthesized by general procedure A.

Yellow solid; 66 mg, 45 % yield. Melting point: 92 – 95 ºC

Rf (ACN : EtOAc = 1 : 20) = 0.5

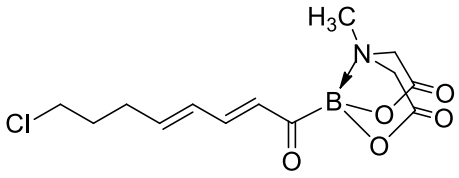
^{1}H NMR (400 MHz, CD_3CN) δ 7.62 – 7.52 (m, 3H), 7.44 – 7.31 (m, 3H), 7.17 – 7.02 (m, 2H), 6.59 (d, *J* = 15.6 Hz, 1H), 4.07 (d, *J* = 16.3 Hz, 2H), 3.93 (d, *J* = 12.5 Hz, 2H), 2.85 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 144.4, 142.7, 137.3, 134.6, 130.1, 129.9, 128.7, 128.2, 62.9, 47.4.

^{11}B NMR (128 MHz, CD_3CN) 5.93.

HRMS-ESI: m/z $[M+H]^+$ for $C_{16}H_{17}BNO_5$, calculated 314.1198; observed 314.1195.

2-((2E,4E)-8-chloroocta-2,4-dienoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7n)



Synthesized by general procedure A.

Yellow sticky liquid; 62 mg, 42 % yield.

Rf (ACN : EtOAc = 1 : 20) = 0.5

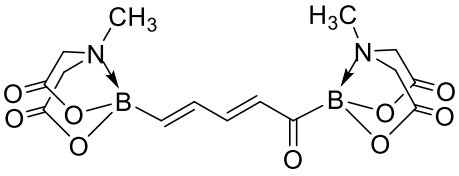
^{1}H NMR (400 MHz, CD_3CN) δ 7.42 – 7.32 (m, 1H), 6.38 (d, *J* = 15.3 Hz, 1H), 6.34 – 6.27 (m, 2H), 4.03 (d, *J* = 16.7 Hz, 2H), 3.91 (d, *J* = 16.7 Hz, 2H), 3.60 (t, *J* = 6.7 Hz, 2H), 2.82 (s, 3H), 2.38 – 2.30 (m, 2H), 1.93 – 1.87 (m, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 145.5, 144.7, 133.4, 131.4, 62.8, 47.3, 45.5, 32.1, 30.9.

^{11}B NMR (128 MHz, CD_3CN) 4.87.

HRMS-ESI: m/z $[M+H]^+$ for $C_{13}H_{18}BClNO_5$, calculated 314.0964; observed 314.0957.

2,2'-((2E,4E)-penta-2,4-dienoyl)bis(6-methyl-1,3,6,2-dioxazaborocane-4,8-dione) (7o)



Synthesized by general procedure A.

Yellow solid; 100 mg, 54 % yield. Melting point: 164 – 168 ºC

Rf (ACN : EtOAc = 1 : 20) = 0.5

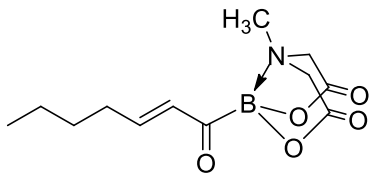
^{1}H NMR (400 MHz, CD_3CN) δ 7.45 – 7.34 (m, 1H), 6.81 – 6.71 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.27 (d, *J* = 17.4 Hz, 1H), 4.07 – 3.80 (m, 8H), 2.84 (s, 3H), 2.80 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.2, 169.0, 145.6, 142.5, 62.9, 62.6, 47.8, 47.4.

^{11}B NMR (128 MHz, CD_3CN) 10.38, 5.08.

HRMS-ESI: m/z $[M+H]^+$ for $C_{15}H_{19}B_2N_2O_9$, calculated 393.1272; observed 393.1274.

(E)-2-(hept-2-enoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7p)



Synthesized by general procedure B.

Yellow sticky liquid; 60 mg, 48 % yield.

Rf (ACN : EtOAc = 1 : 20) = 0.5

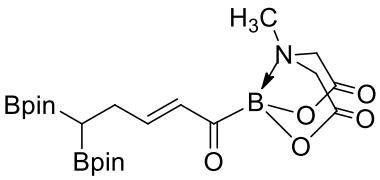
^{1}H NMR (400 MHz, CD_3CN) δ 7.02 – 6.90 (m, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 3.89 (d, *J* = 16.9 Hz, 2H), 3.76 (d, *J* = 16.9 Hz, 2H), 2.68 (s, 3H), 2.11 (q, *J* = 6.5 Hz, 2H), 1.36 – 1.27 (m, 2H), 1.26 – 1.15 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.1, 151.0, 135.8, 62.8, 47.3, 33.3, 30.9, 23.0, 14.1.

^{11}B NMR (128 MHz, CD_3CN) 4.89.

HRMS-ESI: m/z $[M+H]^+$ for $C_{12}H_{19}BNO_5$, calculated 268.1354; observed 268.1360.

(E)-2-(5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-enoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7q)



Synthesized by general procedure B.

Yellow solid; 92 mg, 40 % yield. Melting point: 78 – 81 ºC

Rf (ACN : EtOAc = 1 : 20) = 0.5

^{1}H NMR (400 MHz, CD_3CN) δ 7.20 – 7.10 (m, 1H), 6.23 (d, *J* = 16.3 Hz, 1H), 4.01 (d, *J* = 16.9 Hz, 2H), 3.89 (d, *J* = 16.9 Hz, 2H), 2.81 (s, 3H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.20 (s, 24H), 0.80 (t, *J* = 8.1 Hz, 1H).

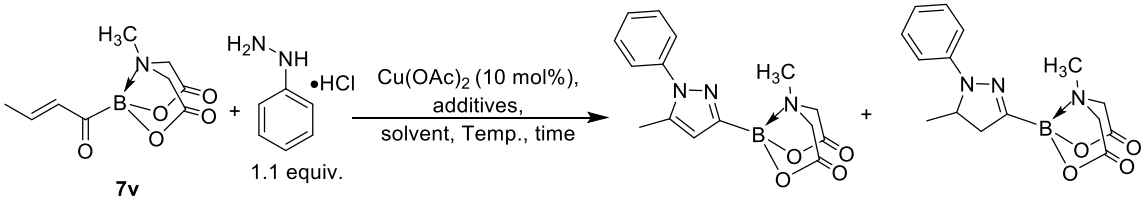
^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 152.8, 135.1, 84.2, 62.7, 47.2, 30.0, 25.2, 24.9.

^{11}B NMR (128 MHz, CD_3CN) 34.65, 5.09.

HRMS-ESI: m/z $[M+Na]^+$ for $C_{22}H_{36}B_3NO_9Na$, calculated 514.2562; observed 514.2568.

4. Synthesis of 3-boryl pyrazoles 8

Table S5. Optimization of reaction conditions for synthesis of 3-boryl pyrazole.



7v **8a** **8ab**

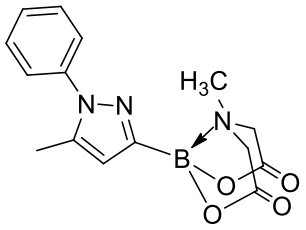
Entry	Condition / Additives (equiv.)	Solvent	Temp. (ºC)	Time (h)	Yield of 8a (%)[a]	Yield of 8ab (%)[b]
1	O_2 balloon	DMSO	85	2	9	13
2	O_2 balloon	DMSO	45	5.5	35	ND[c]
3	O_2 balloon	DMSO	45	14	23	ND[c]
4	O_2 balloon	DMSO	50	4.5	45	ND[c]
5	O_2 balloon, MS 4Å	DMSO	45	14	23	ND[c]
6	O_2 balloon, Na_2SO_4 (2 equiv.)	DMSO	45	14	31	ND[c]
7	O_2 balloon	DME/DMF (1:1)	55	14	ND[c]	ND[c]
8	O_2 balloon	DMF	50	15	33	ND[c]
9	O_2 balloon	AcOH	50	3	24	ND[c]
10	O_2 balloon, AcOH (2 equiv.)	DMSO	50	2	45	ND[c]
11	AcOH (3 equiv.)	DMSO	50	2	45	ND[c]
12	HCl (0.3 euiqv.)	DMSO	50	-	ND[c]	ND[c]

[a]: isolated yield; [b]: determined by NMR; [c]: not detected

General Procedure for the synthesis of 3-boryl pyrazoles 8

To a reaction vial, α,β or α,β,γ,δ-unsaturated MIDA acylboronate **7**, phenylhydrazine hydrochloride (1.1 equiv.), $Cu(OAc)_2$ (10 mol%), AcOH (3 equiv.) and DMSO (1.5 mL) were added. The reaction mixture was stirred at 55 ºC for 2-6 h (completion of reaction was monitored by thin layer chromatography (TLC)) then diluted with EtOAc (50 mL) and successively washed with H_2O (20 mL) and brine. The organic part was then dried over Na_2SO_4, filtered and concentrated on vacuo. The resulting crude was purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) to afford pyrazoles **8.**

6-methyl-2-(5-methyl-1-phenyl-1H-pyrazol-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (8a)



Starting material 2-acryloyl-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione **7v** was synthesized following reported procedure.[7]

Brown liquid; from 0.4 mmol scale, 45 % yield, 56 mg;

Reaction time: 2 h.

Rf (EtOAc) = 0.4

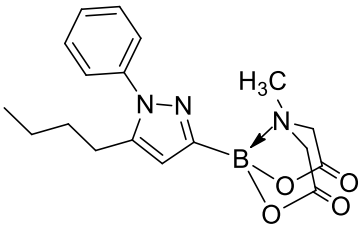
^{1}H NMR (400 MHz, CD_3CN) δ 7.53 – 7.46 (m, 4H), 7.44 – 7.39 (m, 1H), 6.36 (s, 1H), 4.05 (d, *J* = 16.9 Hz, 2H), 3.89 (d, *J* = 16.8 Hz, 2H), 2.67 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.5, 141.2, 140.1, 130.0, 128.5, 125.7, 112.9, 62.4, 48.1, 12.5.

^{11}B NMR (128 MHz, CD_3CN) 10.19.

HRMS-ESI: m/z $[M+H]^+$ for $C_{15}H_{17}BN_3O_4$, calculated 314.1310; observed 314.1316

2-(5-butyl-1-phenyl-1H-pyrazol-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8b)



Brown liquid; from 0.28 mmol scale, 31 % yield, 31 mg;

Reaction time: 4 h.

Rf (EtOAc) = 0.4

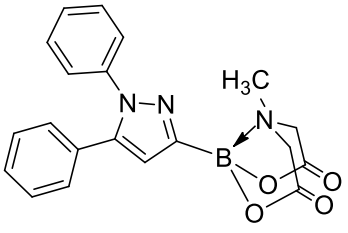
^{1}H NMR (400 MHz, CD_3CN) δ 7.56 – 7.38 (m, 5H), 6.39 (s, 1H), 4.05 (d, *J* = 17.0 Hz, 2H), 3.89 (d, *J* = 17.0 Hz, 2H), 2.66 (s, 5H), 1.58 – 1.47 (m, 2H), 1.32 – 1.20 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.5, 145.1, 141.3, 130.0, 128.7, 126.3, 111.4, 62.4, 48.0, 31.6, 26.4, 22.9, 14.0.

^{11}B NMR (128 MHz, CD_3CN) 10.17.

HRMS-ESI: m/z $[M+H]^+$ for $C_{18}H_{23}BN_3O_4$, calculated 356.1780; observed 356.1782.

2-(1,5-diphenyl-1H-pyrazol-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8c)



Brown liquid; from 0.68 mmol scale, 40 % yield, 100 mg;

Reaction time: 5 h.

Rf (EtOAc) = 0.4

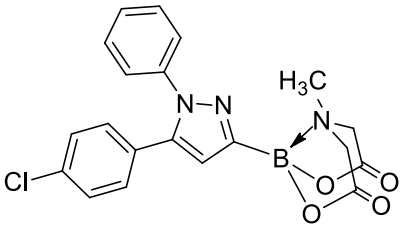
^{1}H NMR (400 MHz, CD_3CN) δ 7.41 – 7.35 (m, 3H), 7.34 – 7.22 (m, 7H), 6.71 (s, 1H), 4.09 (d, *J* = 17.1 Hz, 2H), 3.94 (d, *J* = 16.9 Hz, 2H), 2.73 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.5, 144.3, 141.5, 131.8, 129.8, 129.6, 129.4, 129.1, 128.6, 126.4, 113.8, 62.4, 48.2.

^{11}B NMR (128 MHz, CD_3CN) 10.58.

HRMS-ESI: m/z $[M+H]^+$ for $C_{20}H_{19}BN_3O_4$, calculated 376.1467; observed 376.1466.

2-(5-(4-chlorophenyl)-1-phenyl-1H-pyrazol-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8d)



Brown liquid; from 0.25 mmol scale, 37 % yield, 38 mg; Reaction time: 5 h.

Rf (EtOAc) = 0.4

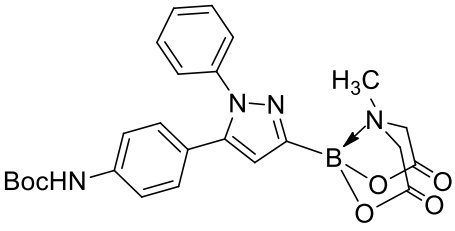
^{1}H NMR (400 MHz, CD_3CN) δ 7.41 – 7.36 (m, 3H), 7.34 – 7.27 (m, 4H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.73 (s, 1H), 4.10 (d, *J* = 16.9 Hz, 2H), 3.94 (d, *J* = 17.1 Hz, 2H), 2.73 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.4, 143.1, 141.2, 134.5, 131.2, 130.5, 129.9, 129.5, 128.7, 126.5, 114.0, 62.4, 48.2,

^{11}B NMR (128 MHz, CD_3CN) δ 9.87.

HRMS-ESI: m/z $[M+H]^+$ for $C_{20}H_{18}BClN_3O_4$, calculated 410.1077; observed 410.1078.

tert-butyl-(4-(3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenyl-1H-pyrazol-5-yl)phenyl)carbamate (8e)



Brown liquid; from 0.17 mmol scale, 40 % yield, 32mg; Reaction time: 5 h.

Rf (EtOAc) = 0.4

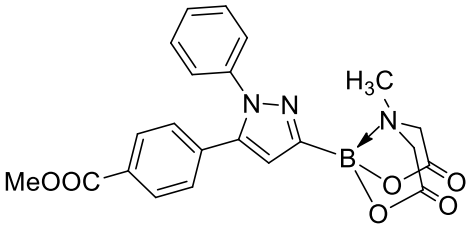
^{1}H NMR (400 MHz, CD_3CN) δ 7.58 (s, 1H), 7.41 – 7.26 (m, 7H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.65 (s, 1H), 4.09 (d, *J* = 16.8 Hz, 2H), 3.93 (d, *J* = 17.5 Hz, 2H), 2.73 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.5, 153.8, 144.1, 141.6, 140.2, 130.2, 129.8, 128.5, 126.4, 125.8, 119.0, 113.3, 80.8, 62.4, 48.2, 28.5.

^{11}B NMR (128 MHz, CD_3CN) 10.01.

HRMS-ESI: m/z $[M+H]^+$ for $C_{25}H_{28}BN_4O_6$, calculated 491.2101; observed 491.2094.

Methyl-4-(3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenyl-1H-pyrazol-5-yl)benzoate (8f)



Brown liquid; from 0.2 mmol scale, 42 % yield 35 mg; Reaction time: 6 h.

Rf (EtOAc) = 0.4

^{1}H NMR (400 MHz, CD_3CN) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.27 (m, 7H), 6.81 (s, 1H), 4.11 (d, *J* = 16.8 Hz, 2H), 3.95 (d, *J* = 17.0 Hz, 2H), 3.85 (s, 3H), 2.74 (s, 3H).

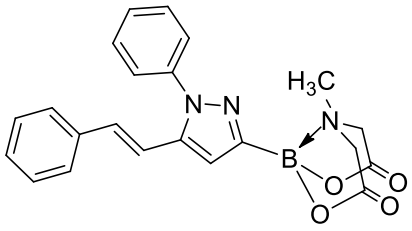
^{13}C NMR (100 MHz, CD_3CN) δ 169.4, 167.2, 143.2, 141.2, 136.1, 130.6, 130.3, 130.0, 129.7, 128.8,

126.5, 114.5, 62.5, 52.8, 48.2.

^{11}B NMR (128 MHz, CD_3CN) 9.96.

HRMS-ESI: m/z $[M+H]^+$ for $C_{22}H_{21}BN_3O_6$, calculated 434.1522; observed 434.1519.

(E)-6-methyl-2-(1-phenyl-5-styryl-1H-pyrazol-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (8g)



Brown liquid; from 0.28 mmol scale, 26 % yield, 30 mg; Reaction time: 4 h.

Rf (EtOAc) = 0.4

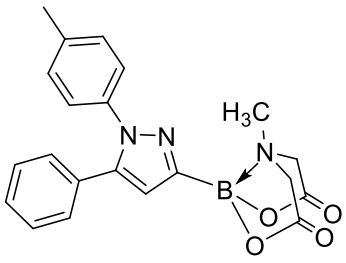
^{1}H NMR (400 MHz, CD_3CN) δ 7.59 – 7.43 (m, 7H), 7.37 – 7.31 (m, 2H), 7.30 – 7.19 (m, 2H), 6.99 – 6.91 (m, 2H), 4.09 (d, *J* = 17.0 Hz, 2H), 3.93 (d, *J* = 16.9 Hz, 2H), 2.71 (s, 3H).

^{13}C NMR (100 MHz, CD3CN) δ 169.5, 142.5, 140.8, 137.6, 132.7, 130.2, 129.8, 129.2, 129.0, 127.5, 126.4, 116.5, 110.2, 62.5, 48.2.

^{11}B NMR (128 MHz, CD_3CN) 10.12.

HRMS-ESI: m/z $[M+Na]^+$ for $C_{22}H_{20}BN_3O_4$, calculated 402.1624; observed 402.1620.

6-methyl-2-(5-phenyl-1-(p-tolyl)-1H-pyrazol-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (8h)



Brown liquid; from 0.24 mmol scale, 42 % yield, 40 mg;

Reaction time: 4 h.

Rf (EtOAc) = 0.4

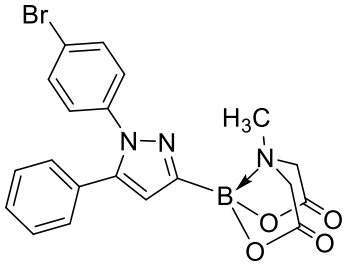
^{1}H NMR (400 MHz, CD_3CN) δ 7.35 – 7.28 (m, 3H), 7.28 – 7.22 (m, 2H), 7.17 (d, *J* = 3.2 Hz, 4H), 6.69 (s, 1H), 4.09 (d, *J* = 16.9 Hz, 2H), 3.93 (d, *J* = 16.9 Hz, 2H), 2.73 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.50, 144.3, 139.1, 138.7, 131.9, 130.3, 129.7, 129.4, 129.0, 126.4, 113.6, 62.4, 48.2, 21.1.

^{11}B NMR (128 MHz, CD_3CN) δ 10.7.

HRMS-ESI: m/z $[M+H]^+$ for $C_{21}H_{21}BN_3O_4$, calculated 390.1624; observed 390.1623.

2-(1-(4-bromophenyl)-5-phenyl-1H-pyrazol-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8i)



Brown liquid; from 0.24 mmol scale, 28 % yield, 30 mg;

Reaction time: 4 h.

Rf (EtOAc) = 0.4

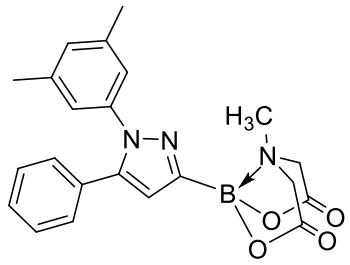
^{1}H NMR (400 MHz, CD_3CN) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.24 (m, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.71 (s, 1H), 4.09 (d, *J* = 17.0 Hz, 2H), 3.93 (d, *J* = 16.9 Hz, 2H), 2.72 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.4, 144.4, 140.7, 132.9, 131.6, 129.7, 129.5, 129.3, 128.1, 121.6, 114.2, 62.4, 48.2.

^{11}B NMR (128 MHz, CD_3CN) δ 10.3.

HRMS-ESI: m/z $[M+H]^+$ for $C_{20}H_{18}BBrN_3O_4$, calculated 454.0572; observed 454.0574.

2-(1-(3,5-dimethylphenyl)-5-phenyl-1H-pyrazol-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8j)



Yellowish sticky liquid; from 0.26 mmol scale, 45 % yield, 45 mg; Reaction time: 5 h.

Rf (EtOAc) = 0.4

^{1}H NMR (400 MHz, CD_3CN) δ 7.33 – 7.28 (m, 3H), 7.27 – 7.23 (m, 2H), 7.16 – 7.13 (m, 1H), 7.12 – 7.08 (m, 1H), 6.95 – 6.88 (m, 1H), 6.68 (s, 1H), 4.09 (d, *J* = 16.9 Hz, 2H), 3.93 (d, *J* = 17.0 Hz, 2H), 2.72 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.5, 144.2, 139.4, 138.5, 137.4, 130.6, 129.6, 129.3, 129.0, 127.5, 123.8, 113.5, 62.4, 48.2, 19.8, 19.4.

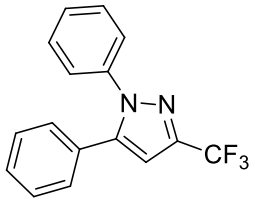
^{11}B NMR (128 MHz, CD_3CN) δ 10.5.

HRMS-ESI: m/z $[M+H]^+$ for $C_{22}H_{23}BN_3O_4$, calculated 404.1781; observed 404.1784.

Procedure for synthesis of Celecoxib analog 9

To a stirred mixture of **8c** (100mg, 0.27 mmol) in MeOH (1.5 mL)/DCM (1.5 mL)/H_2O (1.2 mL) $NaHCO_3$ (3 equiv.), CuCl (1 equiv.) and $NaSO_2CF_3$[8] (3 equiv.) were added. The reaction was then cooled to 0 ºC before adding TBHP (70%, 5 equiv.) dropwise. Resulting reaction mixture was allowed to warm up to RT (23 ºC) and stirred for 14 h, then filtered through a short pad of celite. Filtrate was evaporated under vacuo and subjected to flash chromatography purification on silica gel (EtOAc/hexanes 0:10 to 1:9) to afford Celecoxib derivatives **9** in 20 % yield.

1,5-diphenyl-3-(trifluoromethyl)-1H-pyrazole (9)



Colorless oil; 15 mg, 20 % yield.

Rf (Hexane/EtOAc = 1:9) = 0.6.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 8H), 7.30 – 7.20 (m, 2H), 6.76 (s, 1H).

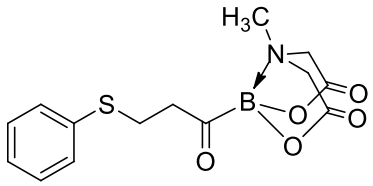
^{13}C NMR (100 MHz, $CDCl_3$) δ 129.3, 129.1, 129.0, 128.8, 128.6, 125.7, 105.7.

HRMS-ESI: m/z $[M+H]^+$ for $C_{16}H_{12}F_3N_2$, calculated 289.0947; observed 289.0952.

5. Procedure for Michael addition of thiols to Acrylic Boronate 1

To a stirred solution of acrylic boronate **1** (100 mg, 0.47 mmol) in acetonitrile (3 mL) thiol partner (1 equiv.) was added. Reaction mixture was stirred at 23 ºC for 15 min. Upon completion, the reaction crude was concentrated to dryness and then purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) to afford sulfide **10.**

6-methyl-2-(3-(phenylthio)propanoyl)-1,3,6,2-dioxazaborocane-4,8-dione (10a)



Pale yellow sticky liquid; 95 mg, 63 % yield.

Rf (EtOAc) = 0.6.

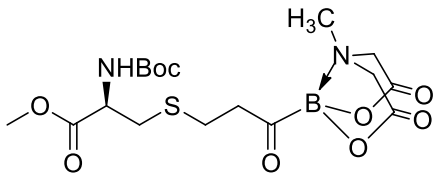
^{1}H NMR (400 MHz, CD_3CN) δ 7.35 – 7.26 (m, 4H), 7.20 (s, 1H), 4.03 (d, *J* = 16.9 Hz, 2H), 3.89 (d, *J* = 16.9 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.81 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.0, 137.5, 130.0, 129.4, 126.8, 63.1, 47.5, 46.8, 26.2.

^{11}B NMR (128 MHz, CD_3CN) 4.09.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{17}BNO_5S$, calculated 322.0918; observed 322.0922.

(R)-methyl-2-((tert-butoxycarbonyl)amino)-3-((3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-oxopropyl)thio)propanoate (10b)



Pale yellow solid; 151 mg, 72 % yield. Melting point: 85 – 90 ºC

Rf (EtOAc) = 0.5.

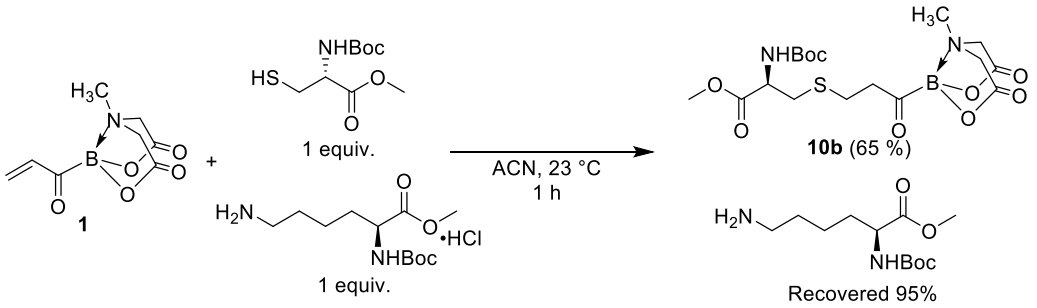
^{1}H NMR (400 MHz, CD_3CN) δ 5.70 (broad s, 1H), 4.33 (s, 1H), 4.08 – 3.96 (m, 2H), 3.94 – 3.84 (m, 2H), 3.68 (s, 3H), 2.99 – 2.79 (m, 7H), 2.70 (d, *J* = 2.7 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN) δ 172.6, 169.0, 63.1, 62.7, 54.6, 52.9, 47.6, 47.5, 34.8, 28.5, 25.4.

^{11}B NMR (128 MHz, CD_3CN) 4.75.

HRMS-ESI: m/z $[M+H]^+$ for $C_{17}H_{28}BN_2O_9S$, calculated 447.1612; observed 447.1608.

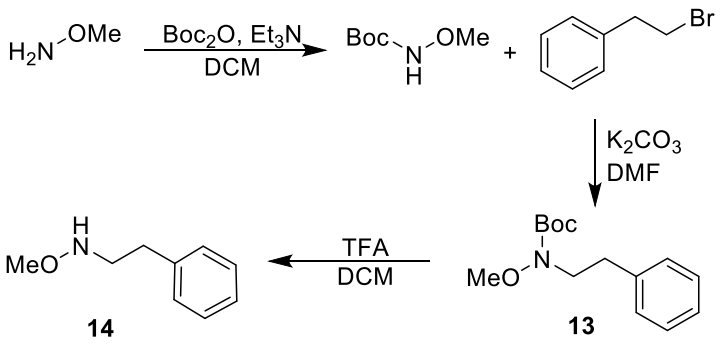
Procedure for competition experiment for Michael addition of Lysine and Cysteine to 1



Scheme S3. Competition experiment for Michael addition of 1

To a solution of **1** (100 mg, 0.47 mmol) in acetonitrile (3 mL) *N*-Boc-L-lysine methyl ester hydrochloride (1 equiv.) and *N*-Boc-L-cysteine methyl ester (1 equiv.) were added at the same time. The resulting mixture was stirred at 23 ºC for 1 h and then evaporated under vacuo, followed by flash chromatography purification on silica gel (EtOAc/hexanes 0:10 to 10:0) to afford **10b** (65 % yield) and the unreacted Lysine (95 % recovered).

6. Procedure for synthesis of *O*-methyl-*N*-phenethylhydroxylamine 14



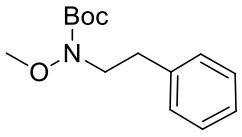
Scheme S4. Synthesis of *O*-methyl-*N*-phenethylhydroxylamine 14

O-methyl-*N*-phenethylhydroxylamine **14** was prepared according to reported procedure.[9] To a stirred solution of *O*-methylhydroxylamine (17 mmol) in DCM (15 mL) Boc_2O (1.3 equiv.) and Et_3N (3 equiv.) were added. The resulting reaction mixture was allowed to stir at 23 ºC for 14 h, then diluted with H_2O (20 mL) and extracted with DCM (30 mL x 3). Combined organic part was washed with brine and dried over Na_2SO_4, then concentrated to dryness to afford crude product ***N*-Boc-*O*-methylhydroxylamine**, which was used as such for next step.

A 50 mL round bottom flask equipped with magnetic bar, was charged with ***N*-Boc-*O*-methylhydroxylamine** (4 mmol) and K_2CO_3 (3 equiv.). Then DMF (10 mL) was added followed by the addition of (2-bromoethyl)benzene (1.2 equiv.). The reaction was stirred at 23 ºC for 14 h and then diluted with H_2O (15 mL) and extracted with EtOAc (20 mL x 3). Combined organic part was washed with brine and dried over Na_2SO_4 and concentrated on vacuo, followed by flash chromatography purification (EtOAc/hexanes 0:10 to 10:0) to afford compound **13**

To a solution of compound **13** (2.4 mmol) in DCM (6 mL) trifluoroacetic acid (TFA, 3 mL) was added. Reaction was stirred for 1 h at 23 ºC. Upon completion, reaction was quenched with saturated $NaHCO_3$(aq) at 0 ºC, resulting mixture was extracted with EtOAc (30 mL x 3). Combined organic part was further washed with brine and dried over Na_2SO_4. Compound **14** was obtained in 50 % yield after column purification on silica gel. (EtOAc/hexanes 0:10 to 2:3)

tert-butyl methoxy(phenethyl)carbamate (13)



Colorless oil; 954 mg, 95 % yield.

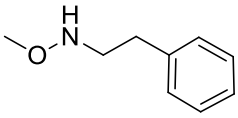
Rf (Hexane : EtOAc = 3 :7) = 0.6

^{1}H NMR (400 MHz, CD_3CN) δ 7.32 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 3.68 – 3.63 (m, 2H), 3.61 (s, 3H), 2.86 (t, *J* = 7.3 Hz, 2H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, CD_3CN) δ 140.3, 129.9, 129.4, 127.2, 81.5, 62.4, 50.9, 34.0, 28.4.

HRMS-ESI: m/z $[M+Na]^+$ for $C_{14}H_{21}NO_3Na$, calculated 274.1412; observed 274.1415.

O-methyl-N-phenethylhydroxylamine (14)[10]



brown oil; 286 mg, 50 % yield.

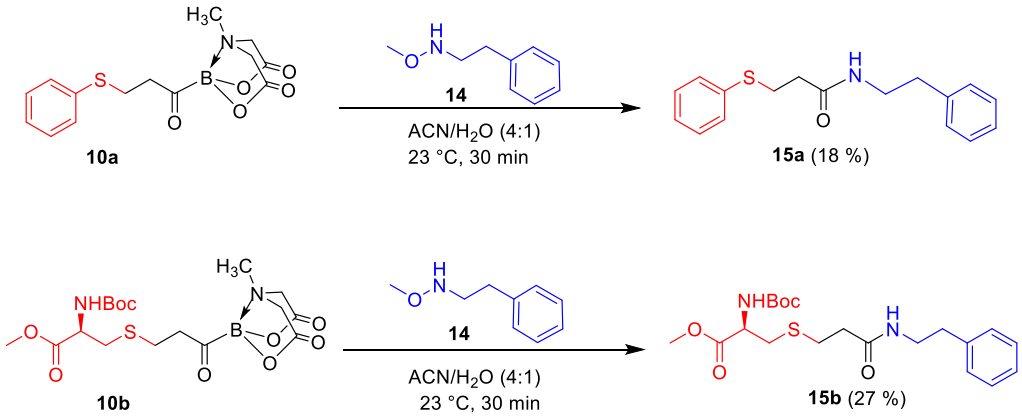
Rf (Hexane : EtOAc = 2 :3) = 0.5

^{1}H NMR (400 MHz, CD_3CN) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 3.46 (s, 3H), 3.08 (m, 2H), 2.78 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 141.2, 129.8, 129.7, 129.3, 127.0, 61.7, 53.8, 34.4.

HRMS-ESI: m/z $[M+H]^+$ for $C_9H_{14}NO$, calculated 152.1070; observed 152.1070.

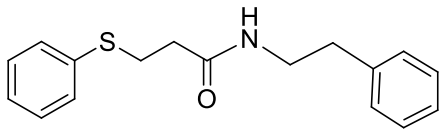
7. Procedure for ligation of Acylboron 10 with *N*-hydroxyamine 14



Scheme S5. Ligation of Acylboron 10

To a solution of **10** in acetonitrile/H_2O (4:1, 2 mL) compound **14** (1 equiv.) was added followed by stirring at 23 ºC for 30 min.[9] Reaction mixture was then evaporated to dryness under vacuo and purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 2:3).

N-phenethyl-3-(phenylthio)propenamide (15a)



Colorless oil; from 0.31 mmol scale, 18% yield, 15 mg.

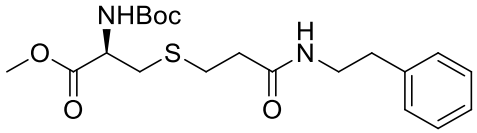
Rf (Hexane : EtOAc = 2 :3) = 0.4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 10H), 5.55 (br s, 1H), 3.52 (q, *J* = 6.5 Hz, 2H), 3.19 (t, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 138.9, 129.7, 129.2, 128.9, 128.8, 126.7, 126.5, 40.8, 36.3, 35.7, 29.6.

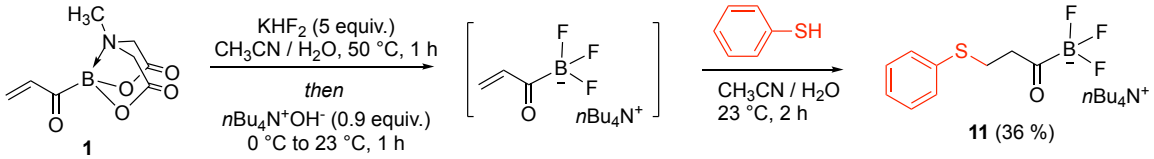
HRMS-ESI: m/z $[M+H]^+$ for $C_{17}H_{20}NOS$, calculated 286.1265; observed 286.1261.

(R)-methyl-2-((tert-butoxycarbonyl)amino)-3-((2-(phenethylamino)ethyl)thio)propanoate (15b)



Colorless oil; from 0.22 mmol scale, 22% yield, 20 mg.
Rf (Hexane : EtOAc = 2 :3) = 0.4
^{1}H NMR (400 MHz, CD_3CN) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 6.45 (br s, 1H), 5.79 (br s, 1H), 4.32 (s, 1H), 3.68 (s, 3H), 3.37 (q, *J* = 6.8 Hz, 2H), 2.96 – 2.69 (m, 6H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.41 (s, 9H).
^{13}C NMR (100 MHz, CD_3CN) δ 172.6, 171.6, 140.6, 129.8, 129.4, 127.2, 54.7, 52.9, 41.4, 37.0, 36.3, 34.4, 28.8, 28.5.
HRMS-ESI: m/z $[M+Na]^+$ for $C_{20}H_{30}N_2O_5SNa$, calculated 433.1768; observed 433.1768

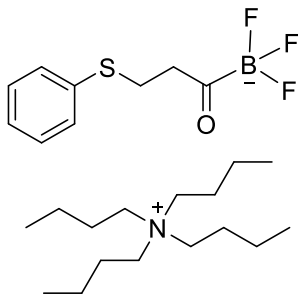
8. Conversion of 1 into tetrabutylammonium acrylic trifluoroborate followed by thia-Michael addition



Scheme S6. Synthesis and thia-Michael reaction of tetrabutylammonium acrylic trifluoroborate

To a solution of **1** (0.7 mmol) in ACN/H_2O (6 mL, 2: 1) KHF_2 (5 equiv.) was added. Resulting reaction crude was stirred at 50 ºC for 1 h. Upon completion, reaction crude was cooled to 0 ºC, tetrabutylammonium hydroxide[13] (1 M in MeOH, 0.9 equiv.) was added dropwise over 5 min and the reaction mixture stirred for 1 h at 23 ºC. The reaction was then diluted with 20 mL of H_2O and extracted with DCM (50 mL x 2). Combined organic part was washed with brine and dried over Na_2SO_4, then concentrated on vacuo. The resulting residue was dissolved in ACN/H_2O (3 mL, 2:1) and thiophenol (1.1 equiv.) was added. The reaction mixture was stirred at 23 ºC for 1 h, then diluted with H_2O (20 mL) and extracted with DCM (50 mL x 2). The combined organic part was washed with H_2O (20 mL) and brine (20 ml), then dried over Na_2SO_4. This crude reaction mixture was purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) to afford compound **11** in 36 % yield (over three steps).

Tetra-n-butylammonium trifluoro(3-(phenylthio)propanoyl)borate (11)

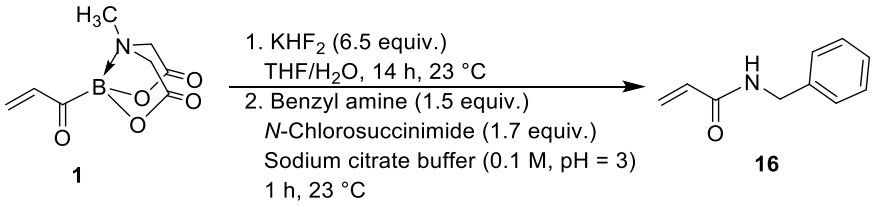


Brown crystalline solid; 110 mg, 36% yield. Melting point: 73 – 75 º C
Rf (EtOAc) = 0.5
^{1}H NMR (400 MHz, CD_3CN) δ 7.32 – 7.26 (m, 4H), 7.16 (ddd, *J* = 8.6, 6.1, 2.6 Hz, 1H), 3.12 – 3.00 (m, 10H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.66 – 1.53 (m, 8H), 1.35 (h, *J* = 7.5 Hz, 8H), 0.96 (t, *J* = 7.3 Hz, 12H).
^{13}C NMR (100 MHz, CD_3CN) δ 138.6, 129.9, 128.9, 126.3, 59.3, 26.8, 24.3, 20.3, 13.8.
^{11}B NMR (128 MHz, CD_3CN) δ -1.47 (q, *J* = 54.2 Hz).

^{19}F NMR (377 MHz, CD_3CN) δ -145.10.

HRMS-ESI: m/z [M-TBA]$^-$ for $C_9H_9BF_3OS$, calculated 233.0426; observed 233.0419.

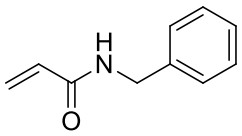
9. One-pot conversion of 1 into acrylic trifluoroborate and ligation with amine



Scheme S7. One-pot acrylic trifluoroborate formation and ligation with amine

To a solution of **1** (0.94 mmol) in THF/H_2O (3 mL, 2: 1) KHF_2 (6.5 equiv.) was added.[9] Resulting reaction crude was stirred at 23 ºC for 14 h, then sodium citrate buffer (citric acid/sodium citrate, 0.1 M, pH=3, 7 mL), *N*-Chlorosuccinimide[11] (1.7 equiv.) and benzylamine (1.5 equiv.) were added. After stirring for 1 h at 23 ºC, the reaction was diluted with 15 mL of H_2O and extracted with EtOAc (30 mL x 3). Combined organic part was washed with brine and dried over Na_2SO_4, and further purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 2:3) to afford compound **16** in 18 % yield over two steps.

***N*-benzyl acrylamide (16)**[12]



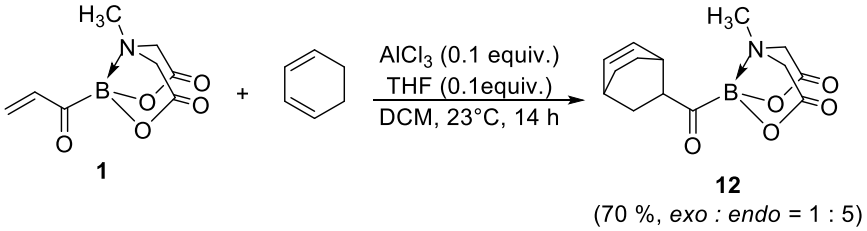
White solid; 25 mg, 18% yield. Melting point: 72 – 75 º C

Rf (Hexane : EtOAc = 2 :3) = 0.4

^{1}H NMR (400 MHz, CD_3CN) δ 7.37 – 7.21 (m, 5H), 6.97 (br s, 1H), 6.28 – 6.12 (m, 2H), 5.65 – 5.57 (m, 1H), 4.41 (d, *J* = 6.1 Hz, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 166.0, 140.3, 132.3, 129.4, 128.4, 128.0, 126.2, 43.6.

10. Diels-Alder reaction of 1 with 1,3-cyclohexadiene

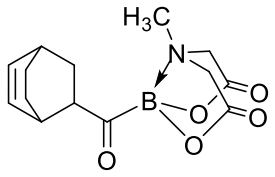


Scheme S8. Diels-Alder reaction of 1

In a reaction vial charged with $AlCl_3$ (0.1 equiv.), DCM (2 mL) and THF (0.1 equiv.) were added. The resulting mixture was stirred at 23 ºC for 15 min, then **1** (0.47 mmol) was added and stirred for another 15 min before addition of 1,3-cyclohexadiene.[14] Reaction was allowed to stir at 23 ºC for

14 h, then concentrated on vacuo and purified by flash chromatography on silica gel (EtOAc/hexanes 0:10 to 10:0) to afford compound **12** in 70 % yield.

2-(bicyclo[2.2.2]oct-5-ene-2-carbonyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (12)



White solid; 90 mg, 70% yield, *exo : endo* = 1 : 5. The *exo/endo* ratio was determined by ^{1}H NMR spectroscopy.[15]

Melting point: 211 – 214 º C

Rf (EtOAc) = 0.5;

^{1}H NMR (400 MHz, CD_3CN) δ 6.43 (t, *J* = 8.1 Hz, 0.2H), 6.35 – 6.30 (m, 0.2H), 6.18 (t, *J* = 7.5 Hz, 1H), 5.94 (t, *J* = 7.3 Hz, 1H), 4.04 – 3.97 (m, 2.4H), 3.93 – 3.85 (m, 2.4H), 3.08 (ddd, *J* = 9.6, 5.5, 1.9 Hz, 1H), 3.04 – 3.00 (m, 1H), 2.95 (s, 0.2H), 2.92 – 2.87 (m, 0.2H), 2.80 (s, 0.6H), 2.77 (s, 3H), 2.59 – 2.51 (m, 1.3H), 1.74 – 1.65 (m, 2.2H), 1.60 – 1.44 (m, 2.5H), 1.35 – 1.18 (m, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 169.4, 169.2, 169.0, 168.8, 136.2, 135.7, 135.2, 132.2, 64.1, 63.0, 62.98, 62.94, 54.3, 47.35, 47.31, 33.3, 31.2, 30.8, 30.5, 26.7, 26.5, 25.8, 25.5, 25.4, 21.5

^{11}B NMR (128 MHz, CD_3CN) δ 5.1.

HRMS-ESI: m/z $[M+H]^+$ for $C_{14}H_{18}BNO_5$, calculated 292.1359; observed 292.1353.

11. X-ray Data

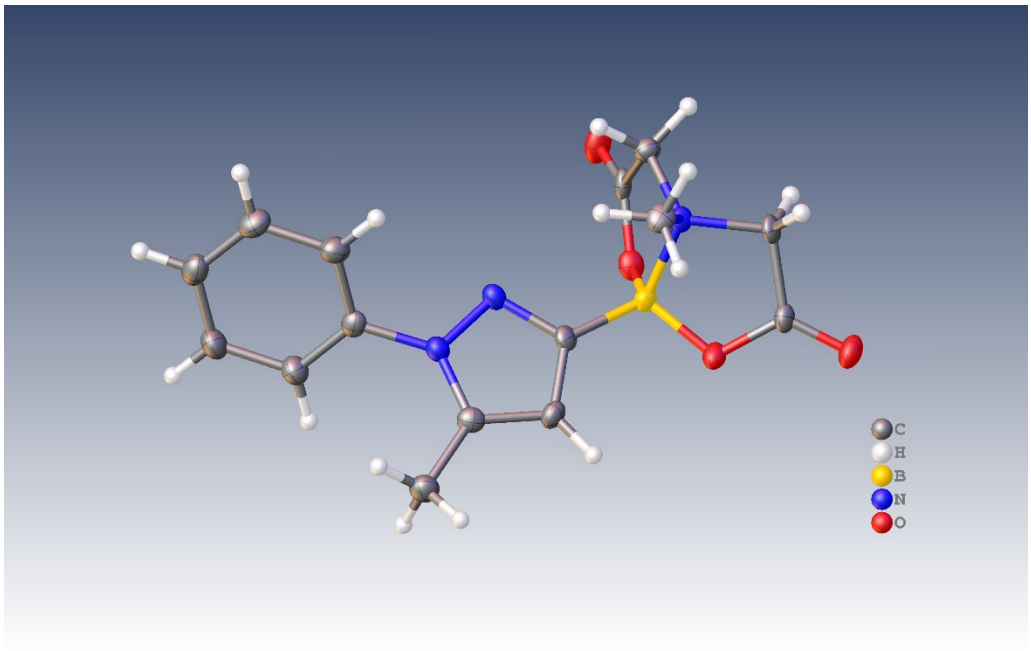


Figure S1. Molecular structure of **8a**.[16]

Crystal data of 8a

Compound	8a
Formula	$C_{15}H_{16}BN_3O_4$
MW	313.12
Space group	$P2_1/c$
***a* (Å)**	11.1651(7)
***b* (Å)**	10.4907(6)
***c* (Å)**	12.5832(6)
***α* (°)**	90
***β* (°)**	94.045(6)
***γ* (°)**	90
V (Å^3)	1470.20(14)
Z	4
ρ_{calc} (g cm^{-3})	1.415
T (K)	100
λ (Å)	1.54184
$2\theta_{min}$, $2\theta_{max}$	8, 145
Nref	9449
R(int), R(σ)	.074, .186
μ(mm^{-1})	0.853
Size (mm)	.08 x .03 x .02
T_{max} / T_{min}	1.03
Data	3232
Restraints	0
Parameters	211
R_1(obs)	0.0531
wR_2(all)	0.0991
S	1.024
Peak, hole (e$^-$ Å^{-3})	0.33, -0.29

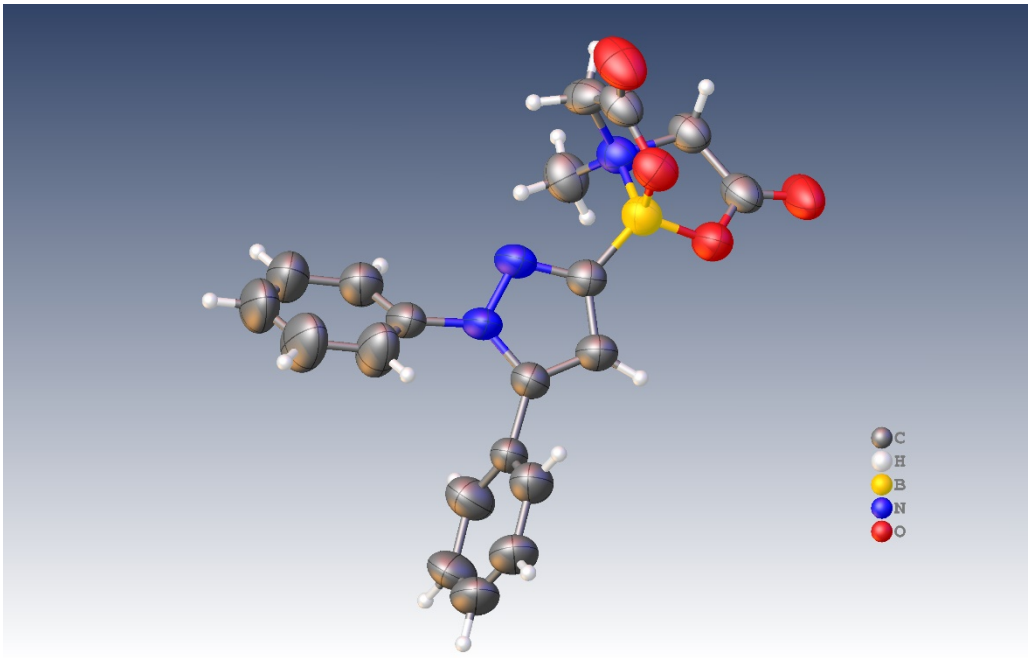


Figure S2. Molecular structure of **8c**.[16]

Crystal data of 8c

Compound	8c
Formula	$C_{20}H_{18}BN_3O_4$
MW	375.18
Space group	$P2_1/c$
***a* (Å)**	17.1144(19)
***b* (Å)**	9.3148(9)
***c* (Å)**	12.0484(17)
***α* (°)**	90
***β* (°)**	94.910(11)
***γ* (°)**	90
V (Å^3)	1913.7(4)
Z	4
ρ_{calc} (g cm^{-3})	1.302
T (K)	292.9(5)
$2\theta_{min}$, $2\theta_{max}$	10.376, 154.432
R(int), R(σ)	0.0577, 0.0979
μ(mm^{-1})	0.750
Size (mm)	.15 x .04 x .01
Data/Restraints/Parameters	3826/0/255
Peak, hole (e$^-$ Å^{-3})	0.39, -0.28
F(000)	784.0
Radiation	CuKa (λ = 1.54184)
Reflection collected	7012
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ(I)]	R_1 = 0.0929, wR_2 = 0.2320
Final R indexes [all data]	R_1 = 0.1838, wR_2 = 0.2818
Index ranges	-19 ≤ h ≤ 21, -8 ≤ h ≤ 11, -14 ≤ h ≤ 14

12. References

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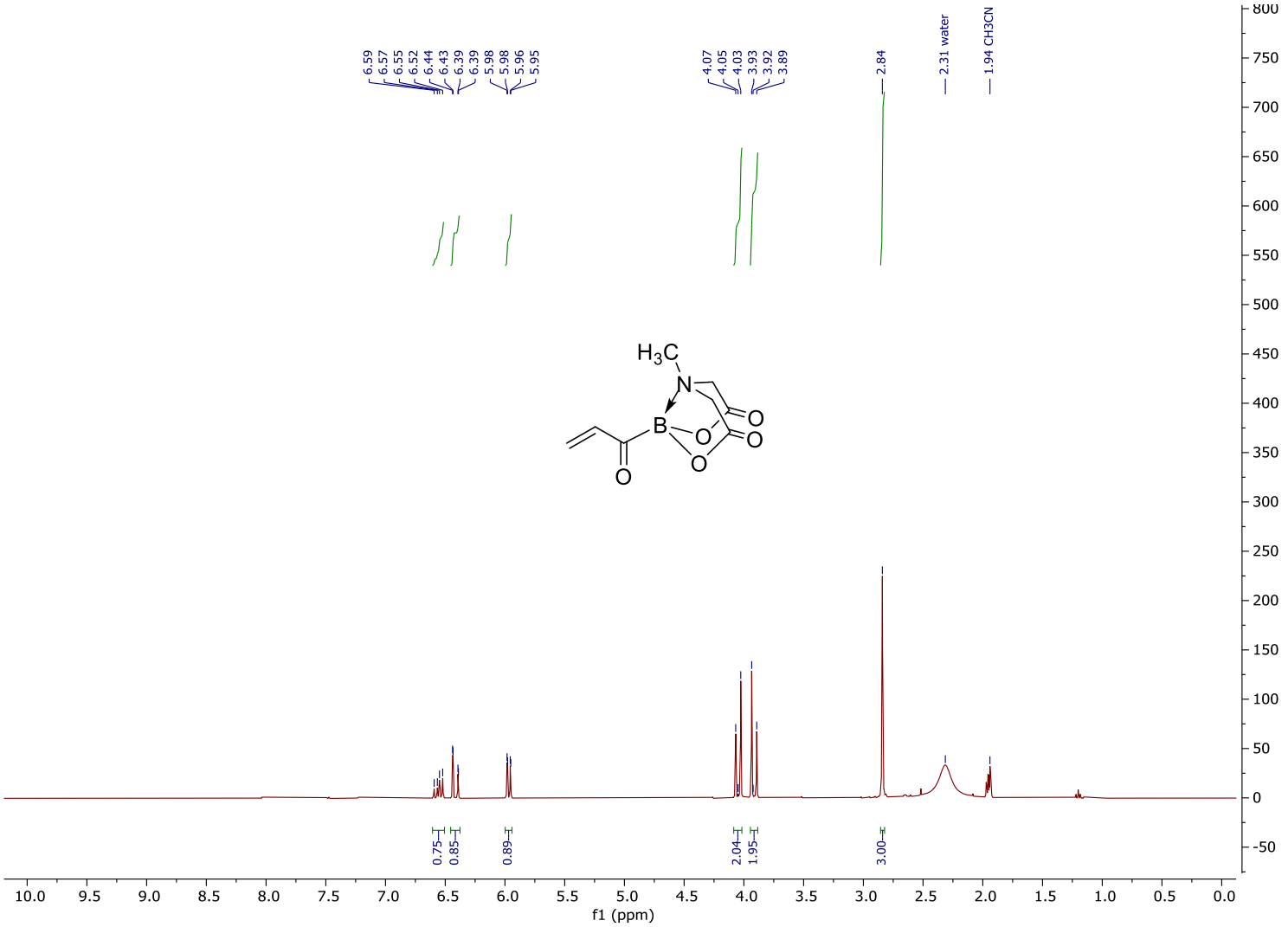
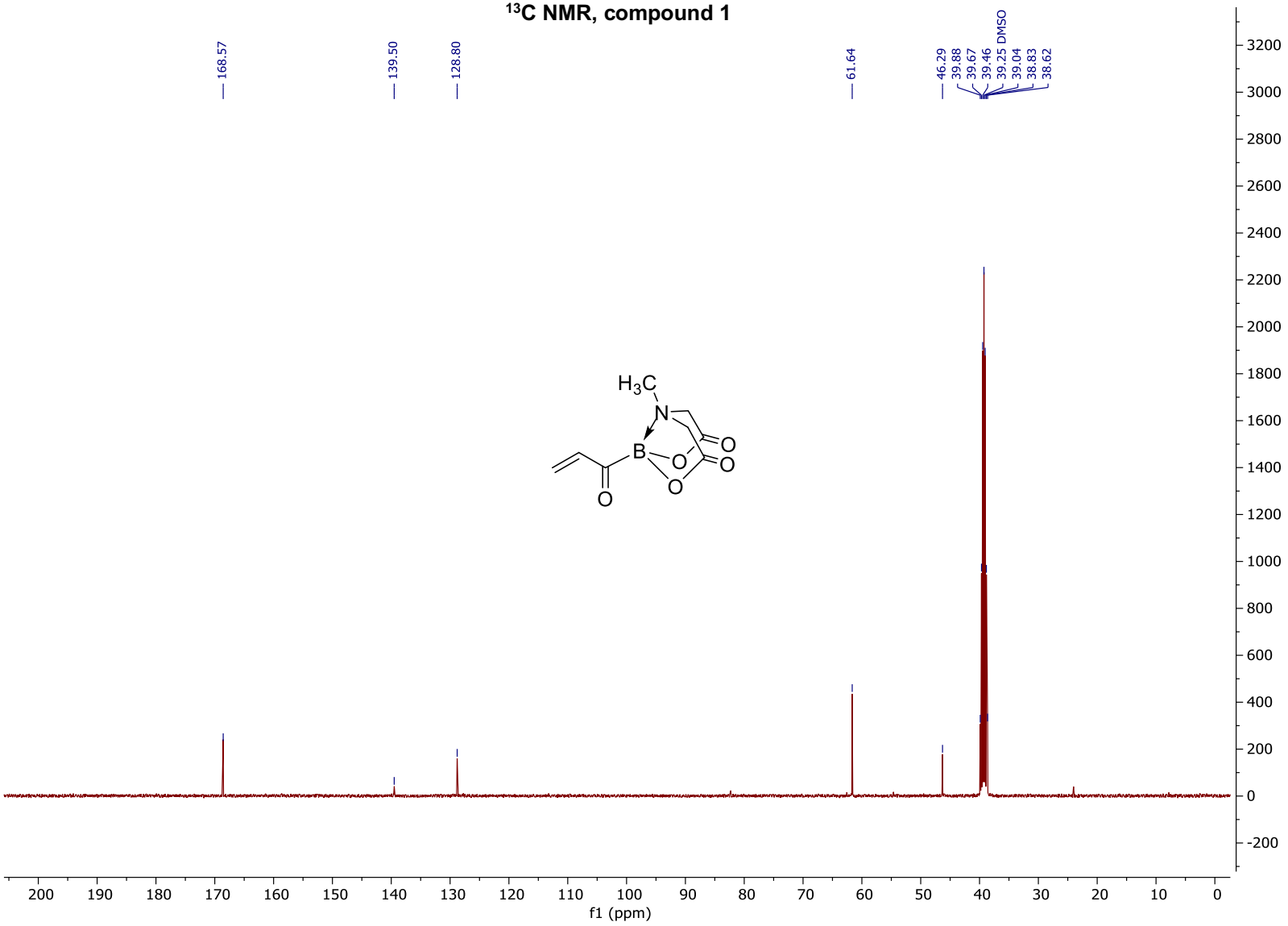
15) a) J. C. Davis Jr. and T. V. Van Auken, *J. Am. Chem. Soc.*, 1965, **87**, 3900–3905; b) J. H. Cooley and R. V. Williams, *J. Chem. Educ.*, 1997, **74**, 582-585.
16) CCDC 2061438 (**8a**) and 2061439 (**8c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk

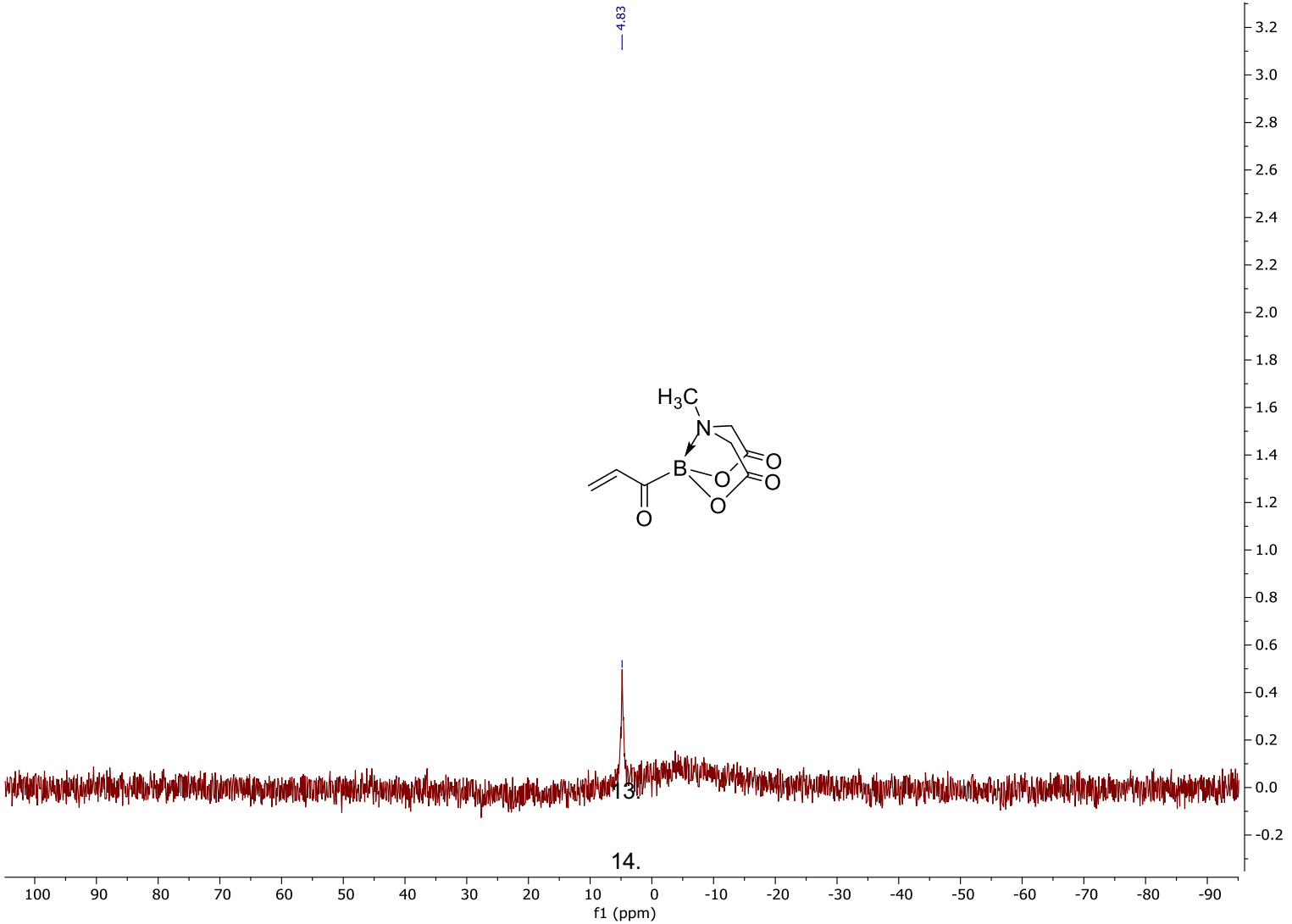
^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra

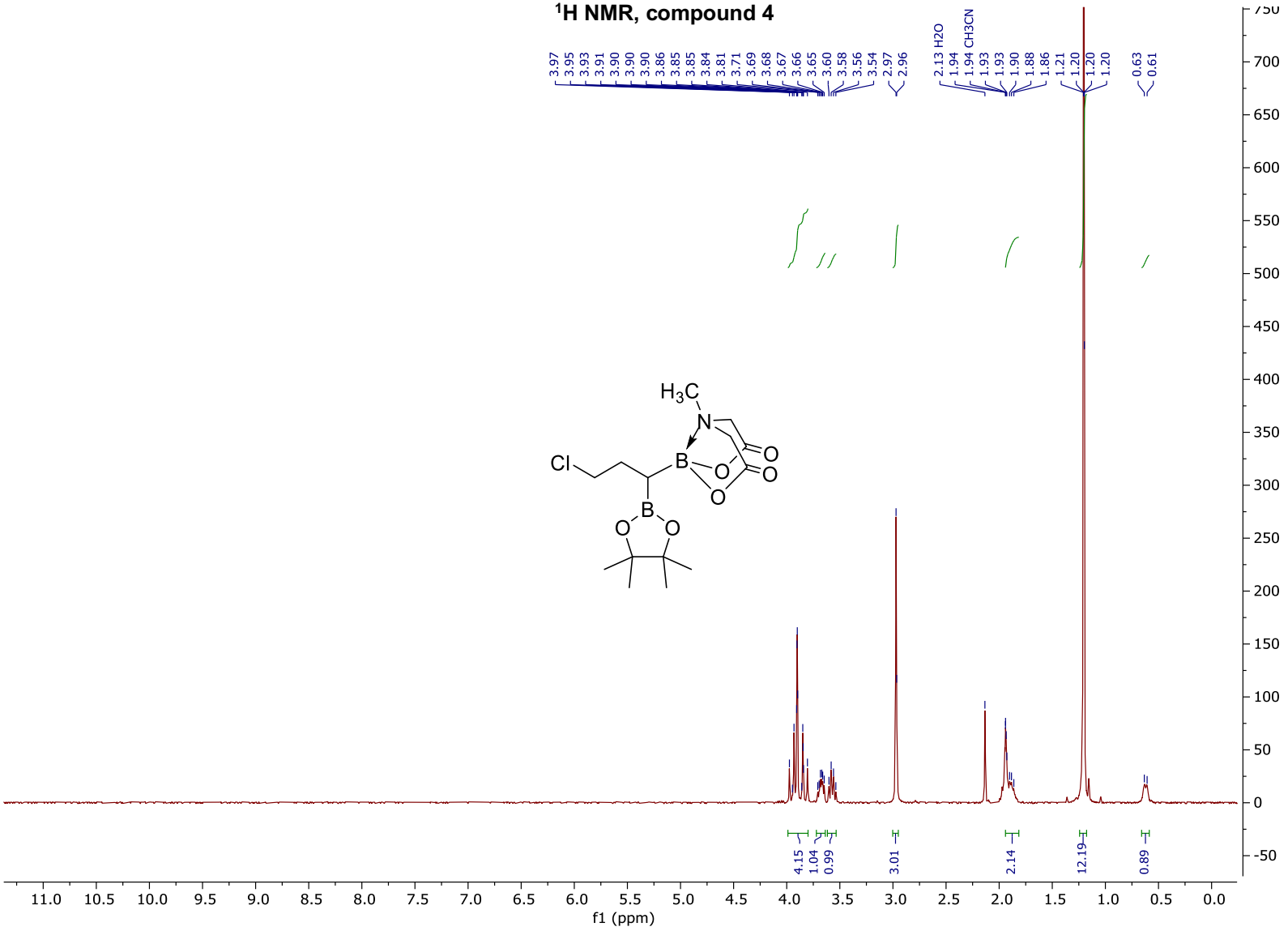
^{1}H NMR, compound 1



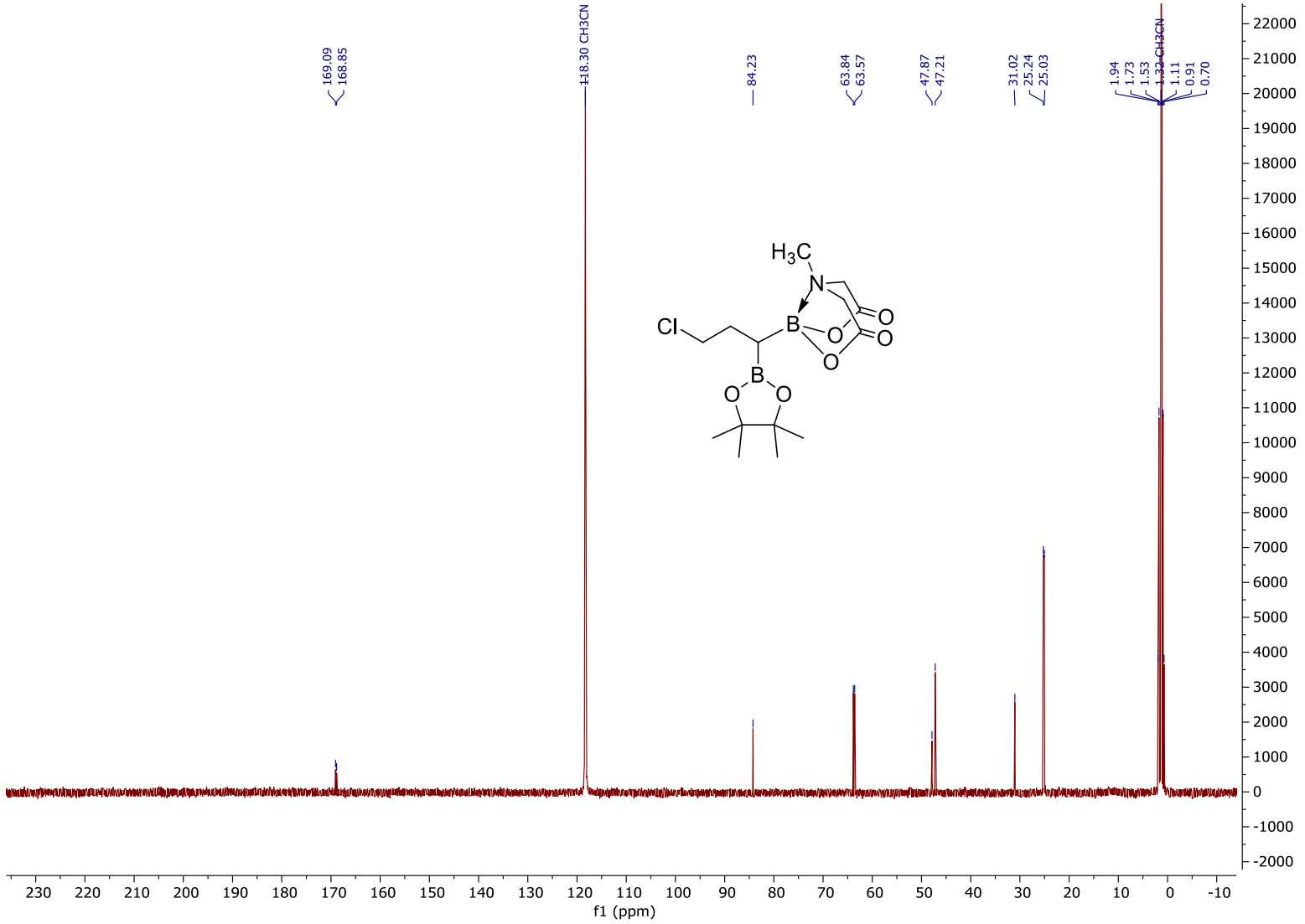

13C NMR, compound 1
168.57
139.50
128.80
61.64
46.29
39.88
39.67
39.46
39.25 DMSO
39.04
38.83
38.62
H3C
N
B
O
O
O
O
O
f1 (ppm)

^{11}B NMR, compound 1

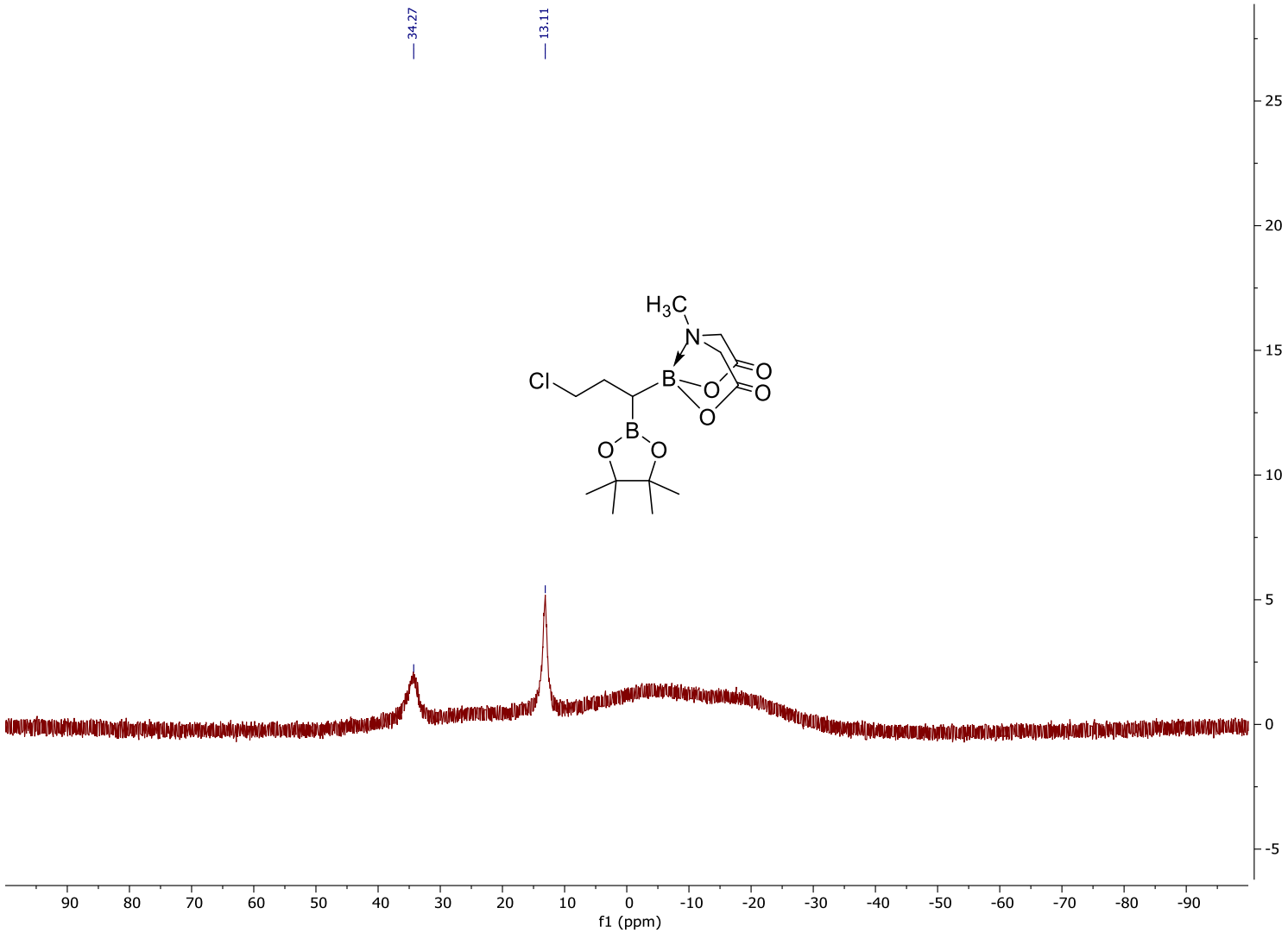


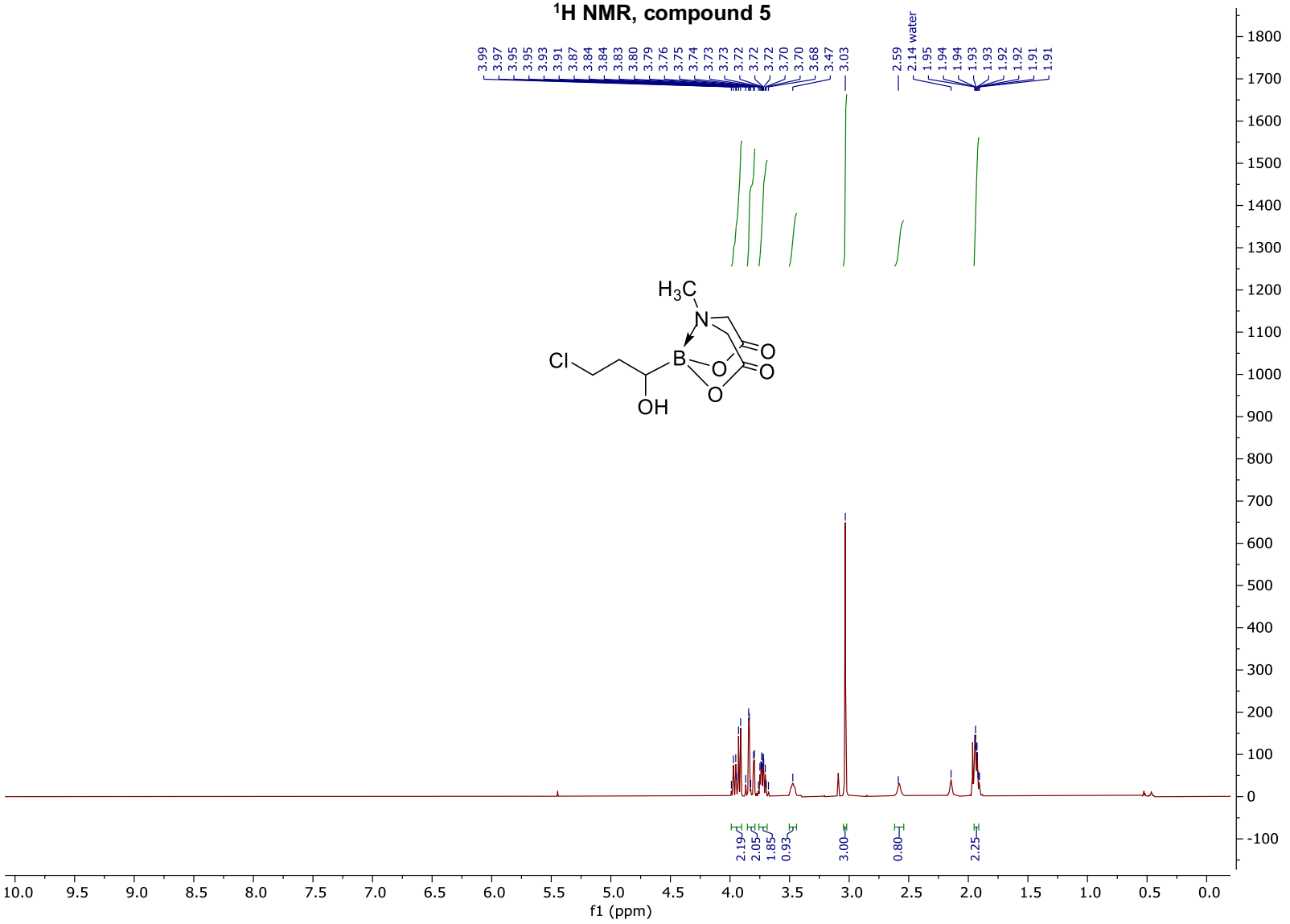

¹H NMR, compound 4
3.97
3.95
3.93
3.91
3.90
3.90
3.90
3.86
3.85
3.85
3.84
3.81
3.71
3.69
3.68
3.67
3.66
3.65
3.60
3.58
3.56
3.54
2.97
2.96
2.13 H2O
1.94
1.94 CH3CN
1.93
1.93
1.90
1.88
1.86
1.21
1.20
1.20
1.20
0.63
0.61
H3C
N
Cl
B
O
O
O
B
O
O
4.15
1.04
0.99
3.01
2.14
12.19
0.89
f1 (ppm)

^{13}C NMR, compound 4

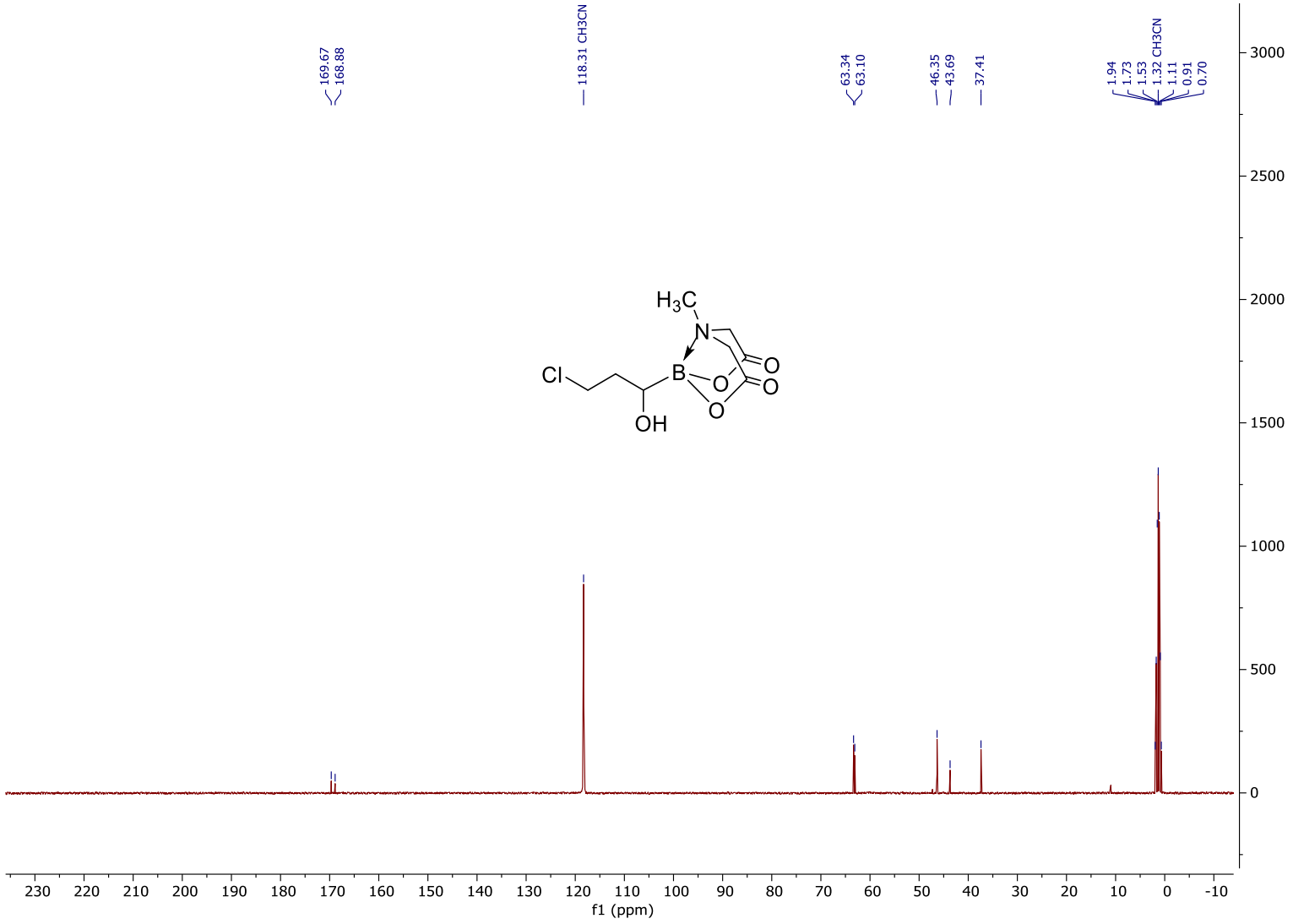


^{11}B NMR, compound 4

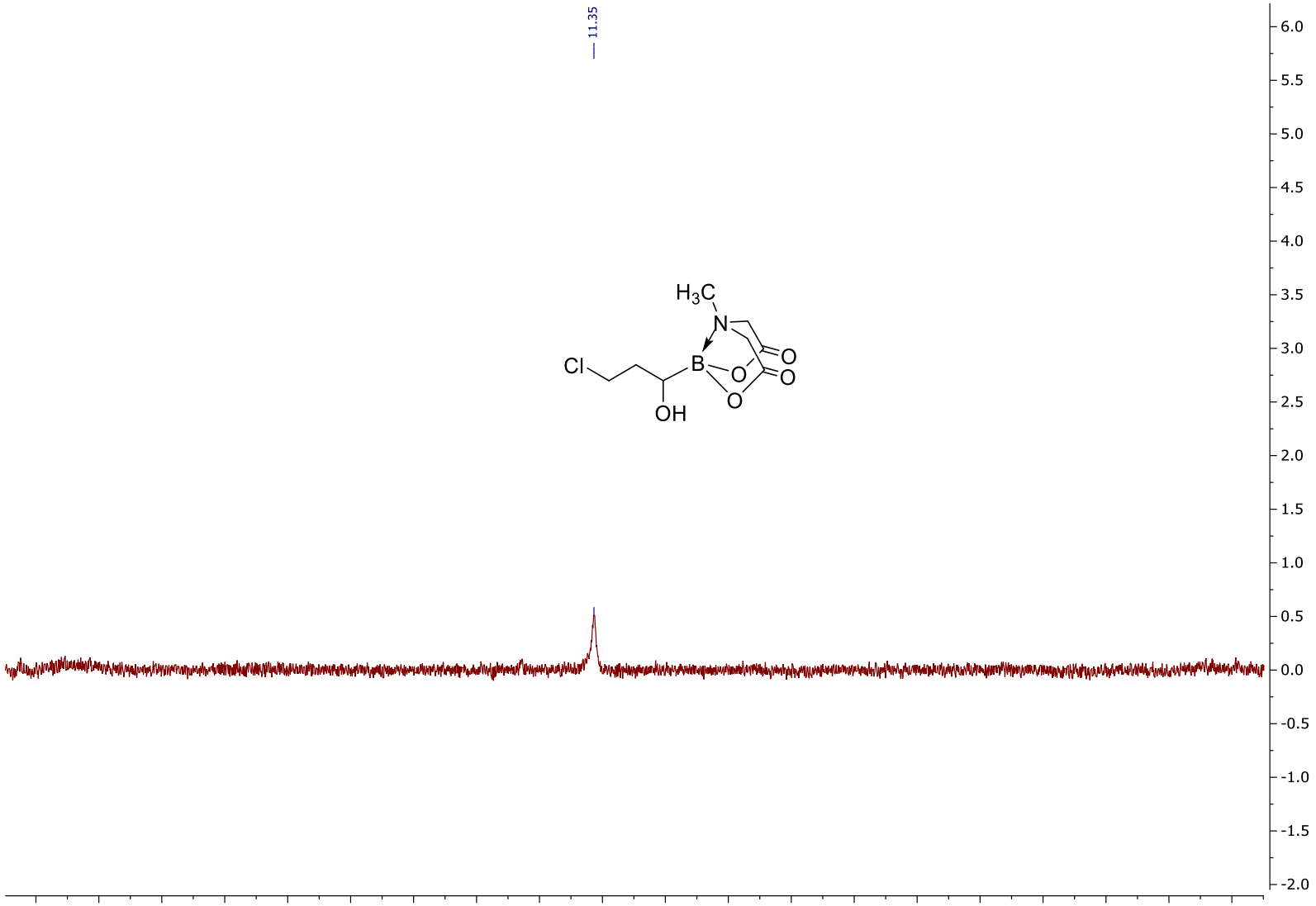



1H NMR, compound 5
3.99
3.97
3.95
3.95
3.93
3.91
3.87
3.84
3.84
3.83
3.80
3.79
3.76
3.75
3.74
3.73
3.73
3.72
3.72
3.72
3.70
3.70
3.68
3.47
3.03
2.59
2.14 water
1.95
1.94
1.94
1.93
1.93
1.92
1.92
1.91
1.91
H3C
N
B
O
O
O
O
Cl
OH
2.19
2.05
1.85
0.93
3.00
0.80
2.25
f1 (ppm)

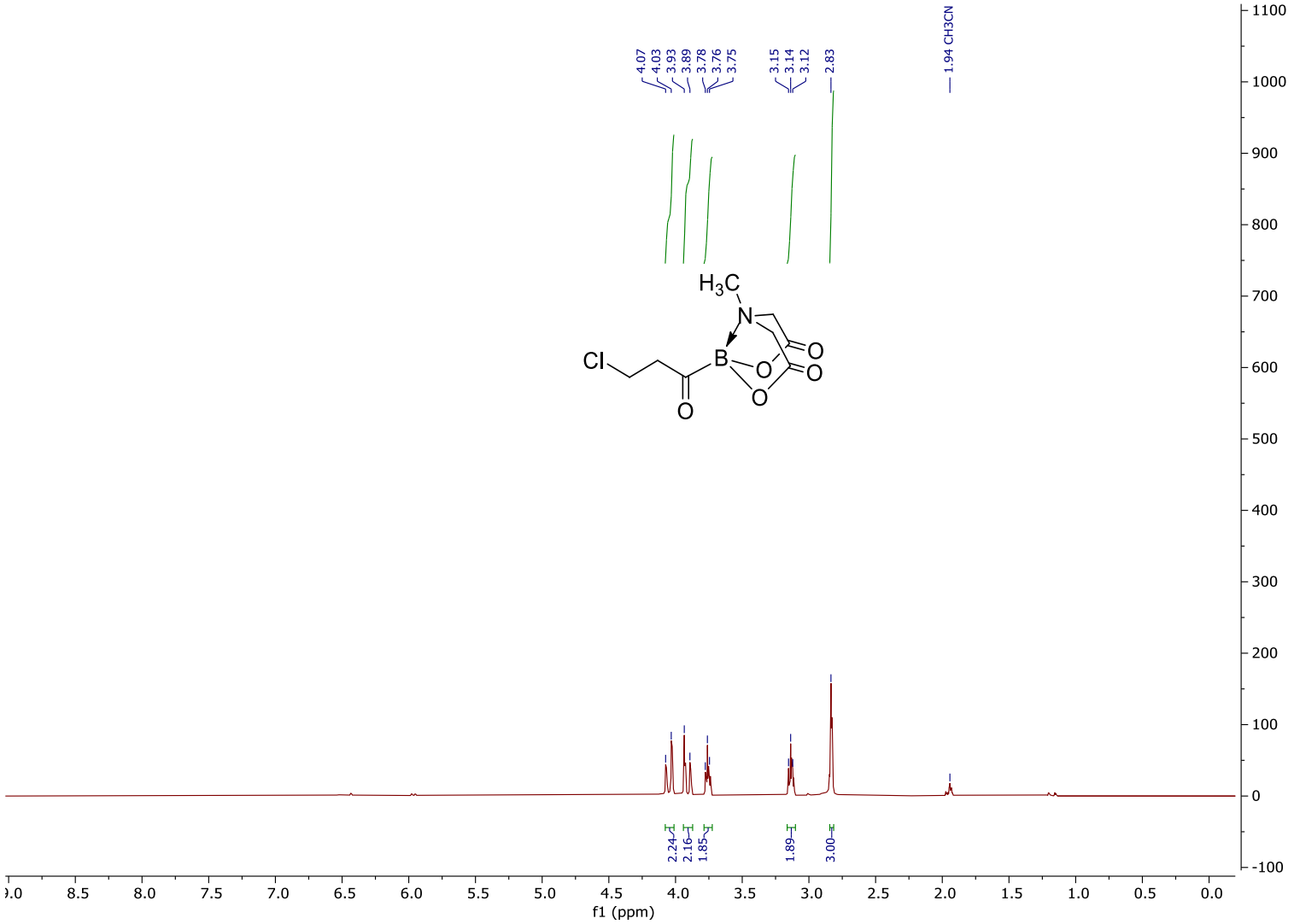
^{13}C NMR, compound 5



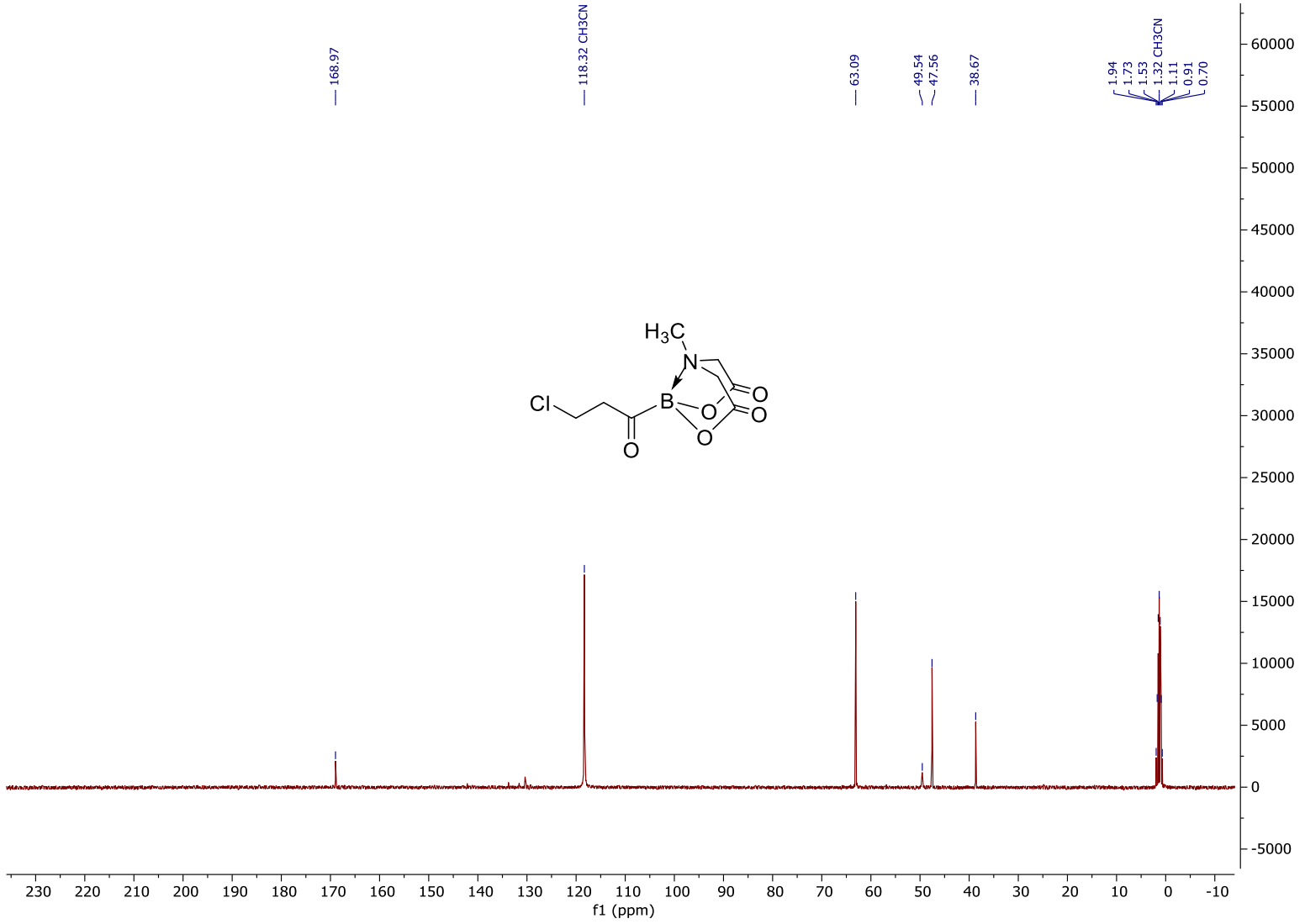
^{11}B NMR, compound 5



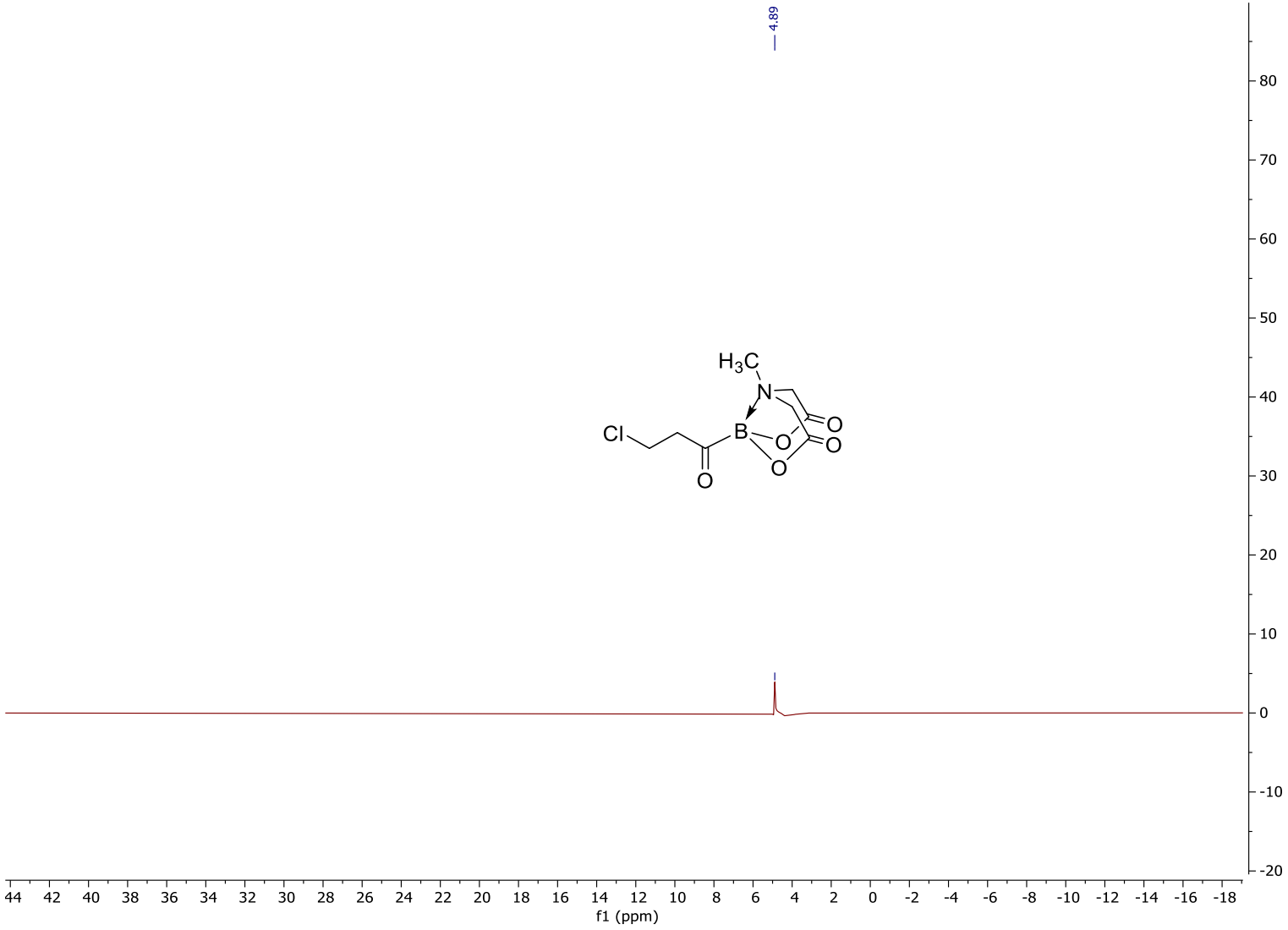
^{1}H NMR, compound 6



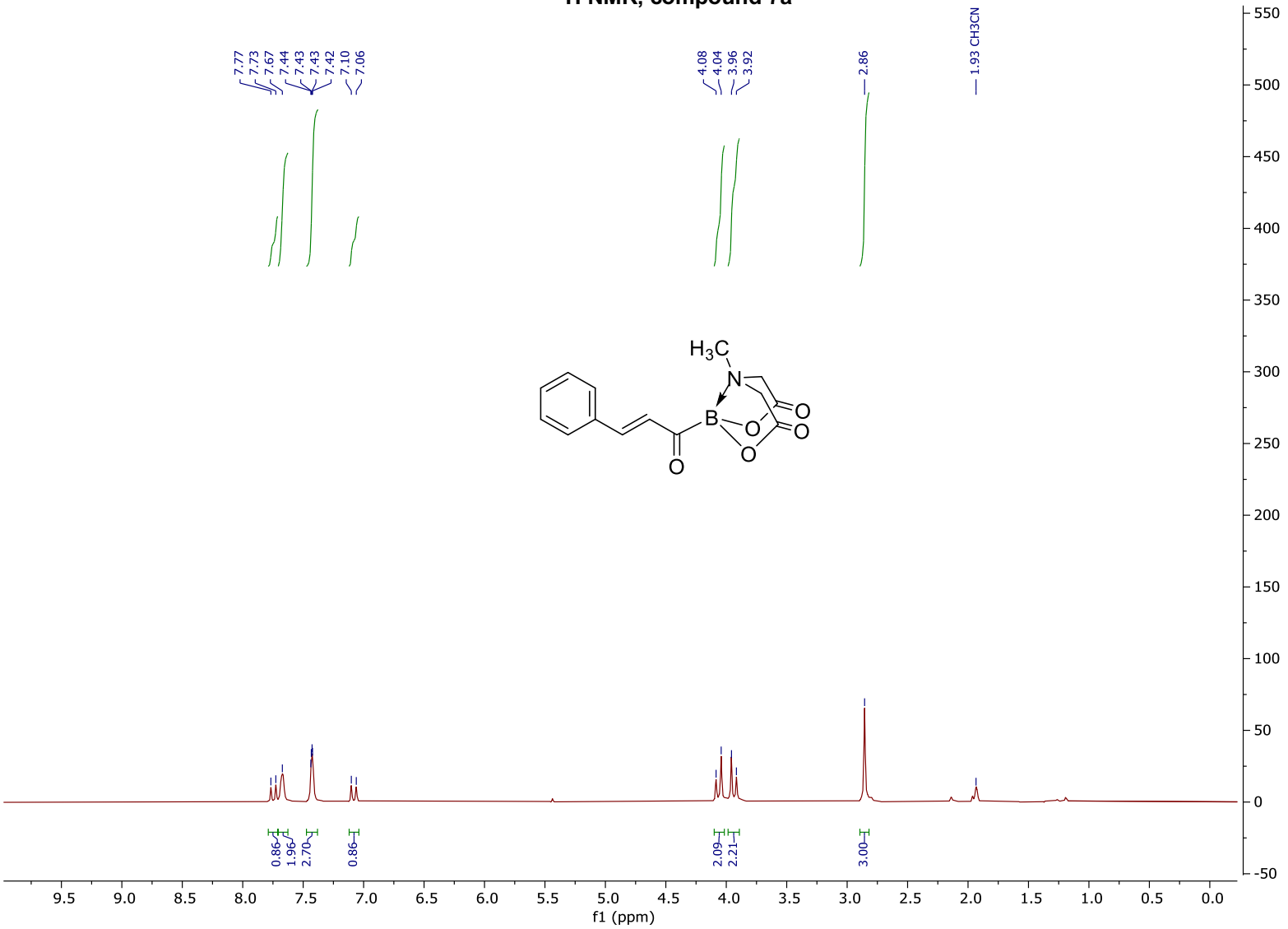
^{13}C NMR, compound 6



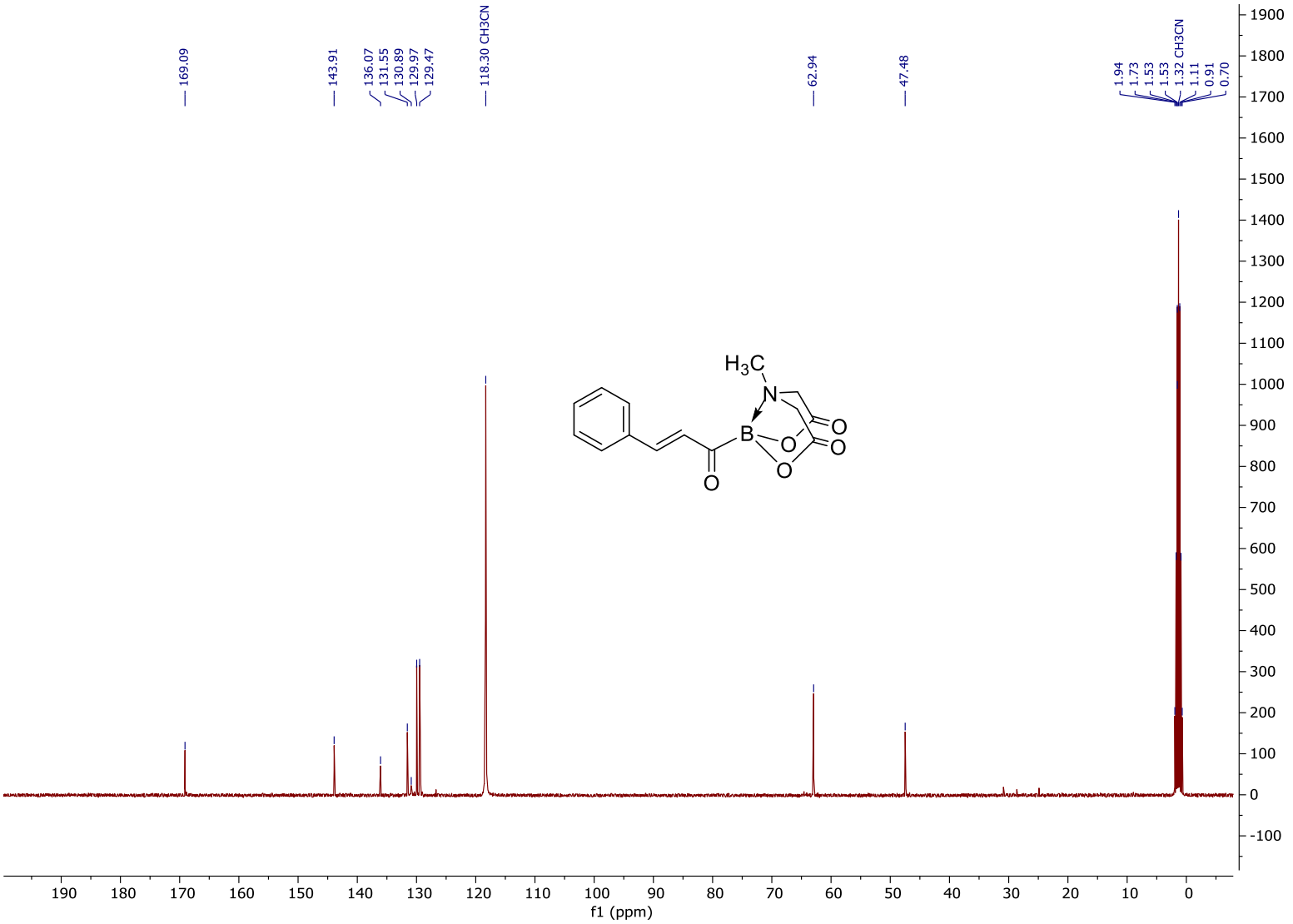
^{11}B NMR, compound 6



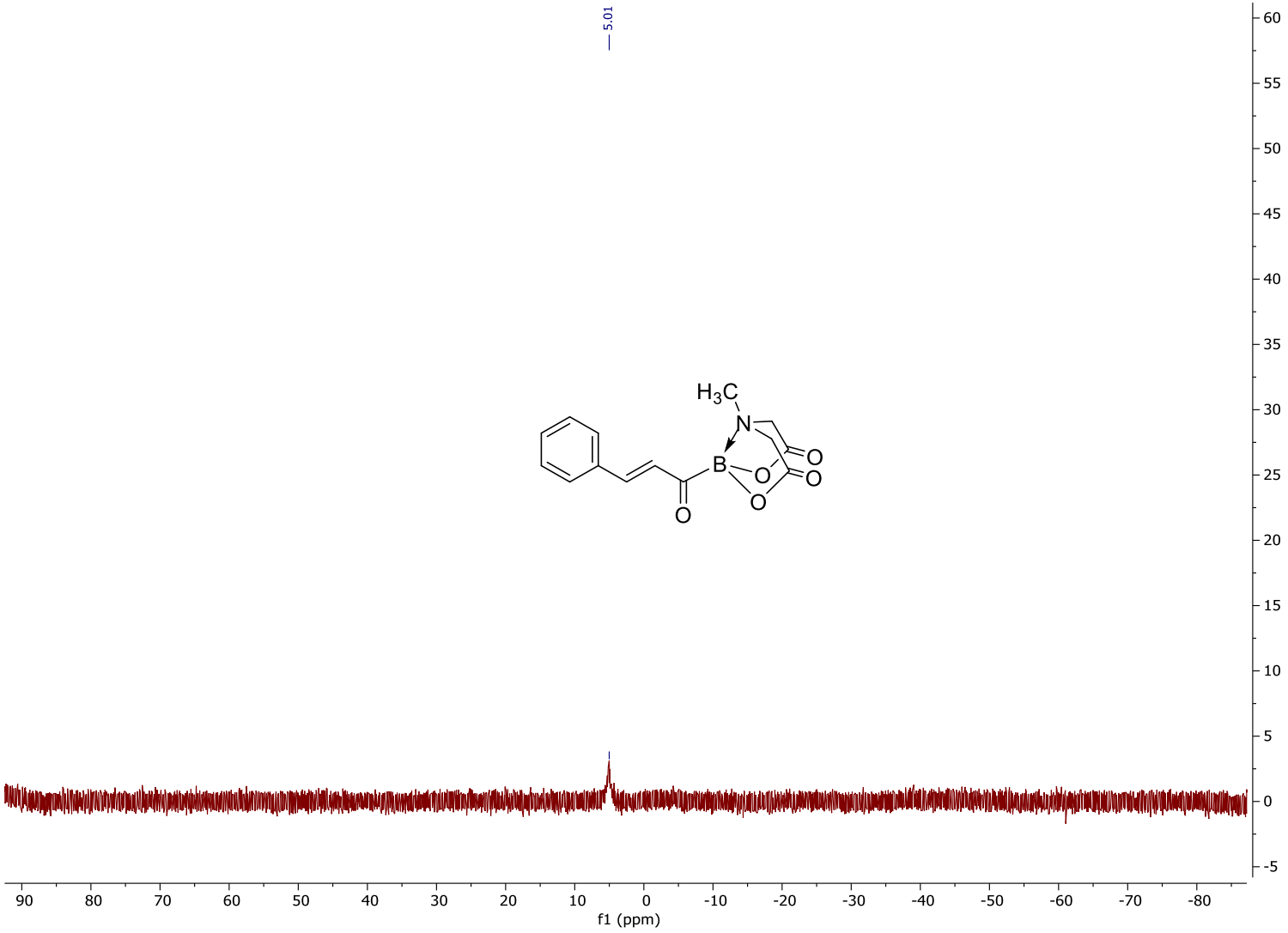
^{1}H NMR, compound 7a

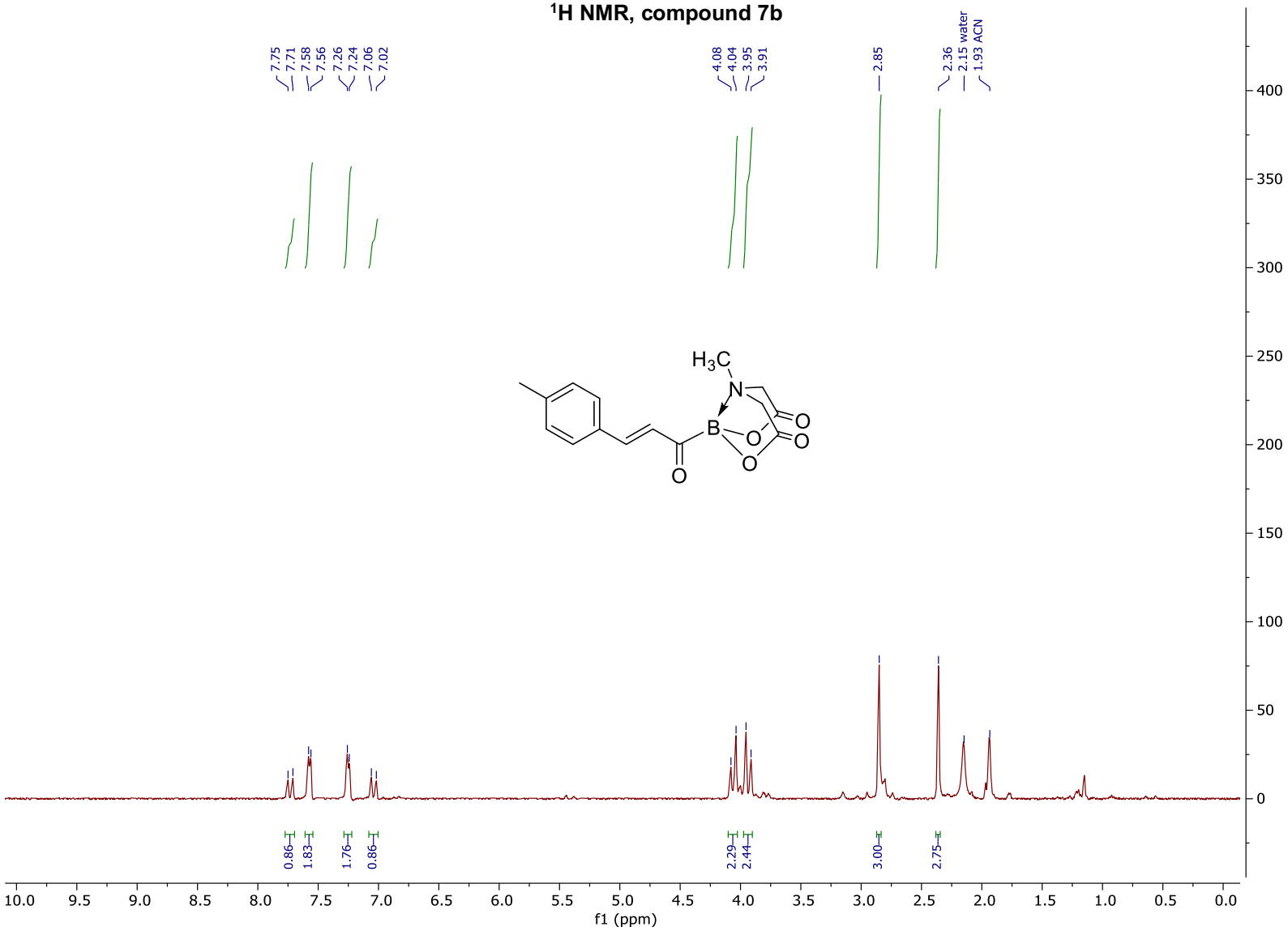


^{13}C NMR, compound 7a

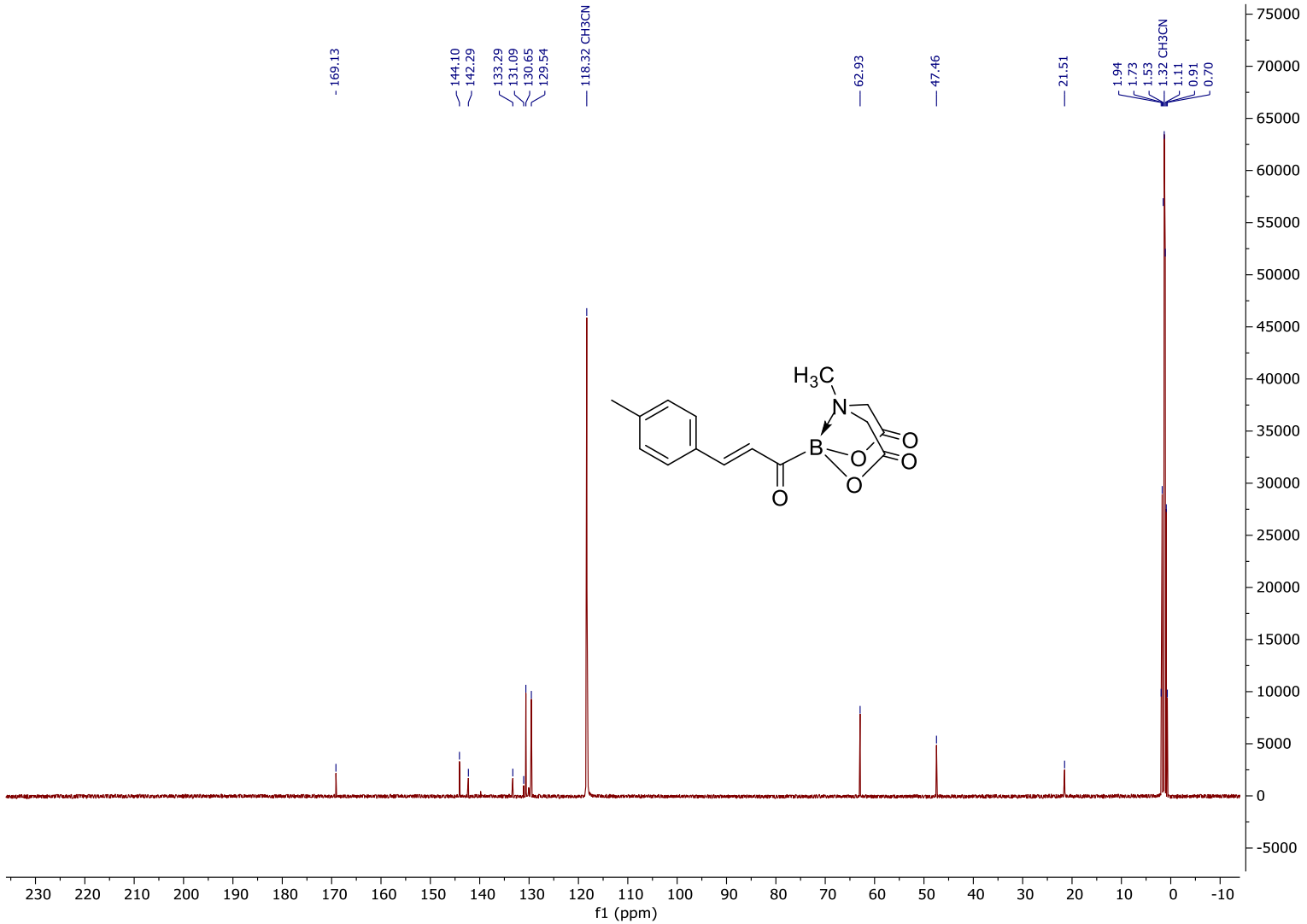


^{11}B NMR, compound 7a

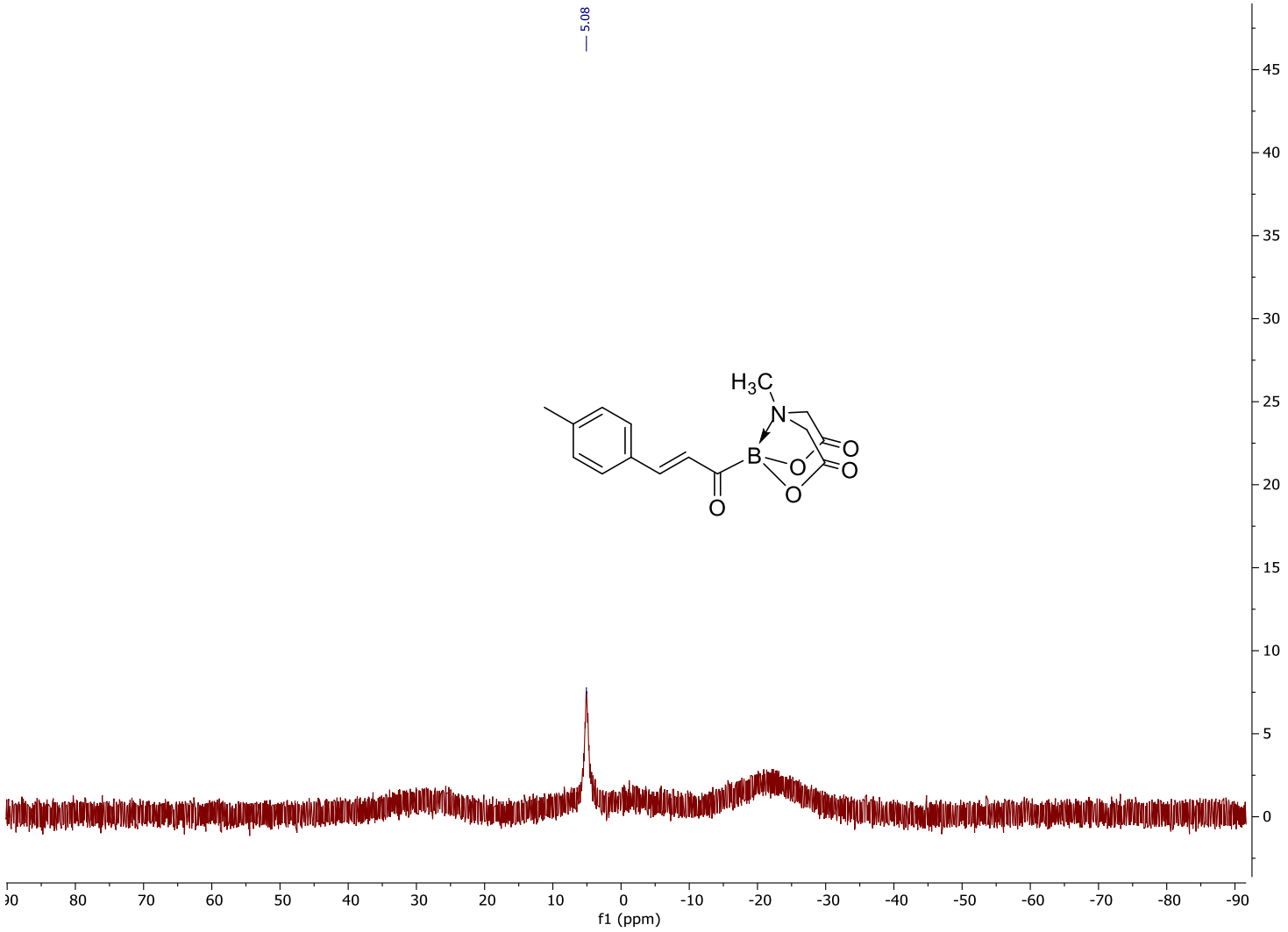



¹H NMR, compound 7b
7.75
7.71
7.58
7.56
7.26
7.24
7.06
7.02
4.08
4.04
3.95
3.91
2.85
2.36
2.15 water
1.93 ACN
H3C
N
B
O
O
O
O
O
0.86
1.83
1.76
0.86
2.29
2.44
3.00
2.75
f1 (ppm)

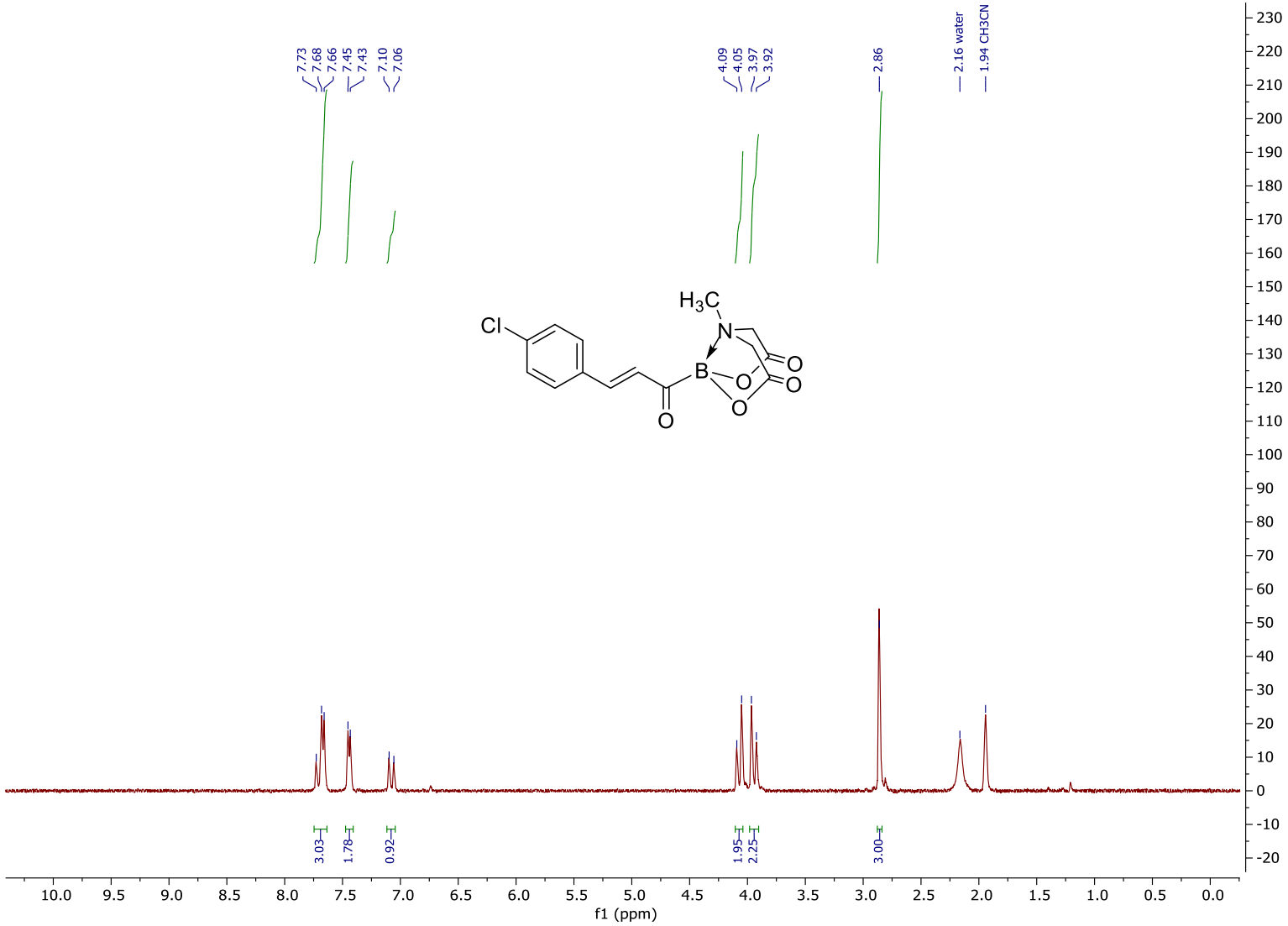
^{13}C NMR, compound 7b



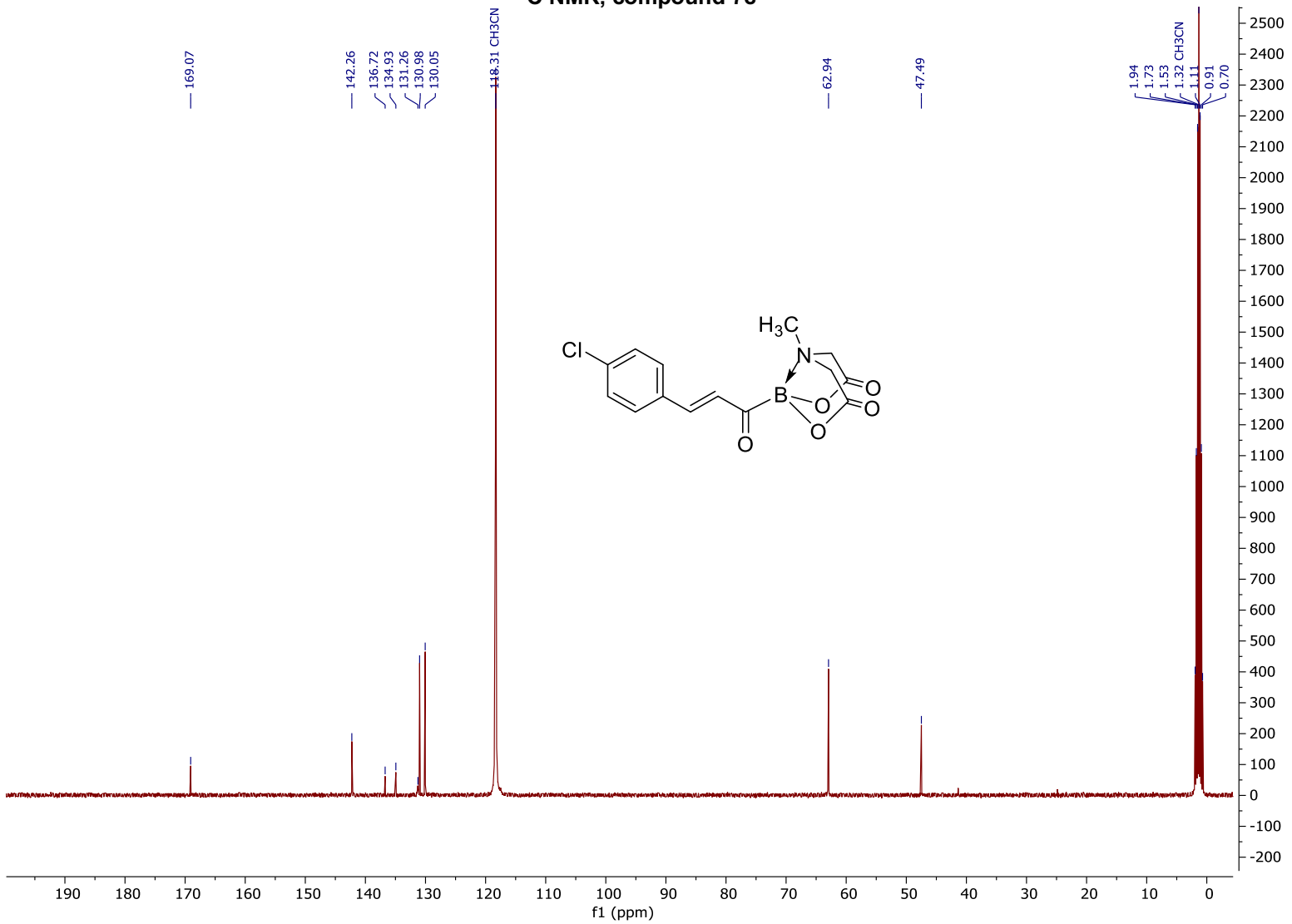
^{11}B NMR, compound 7b



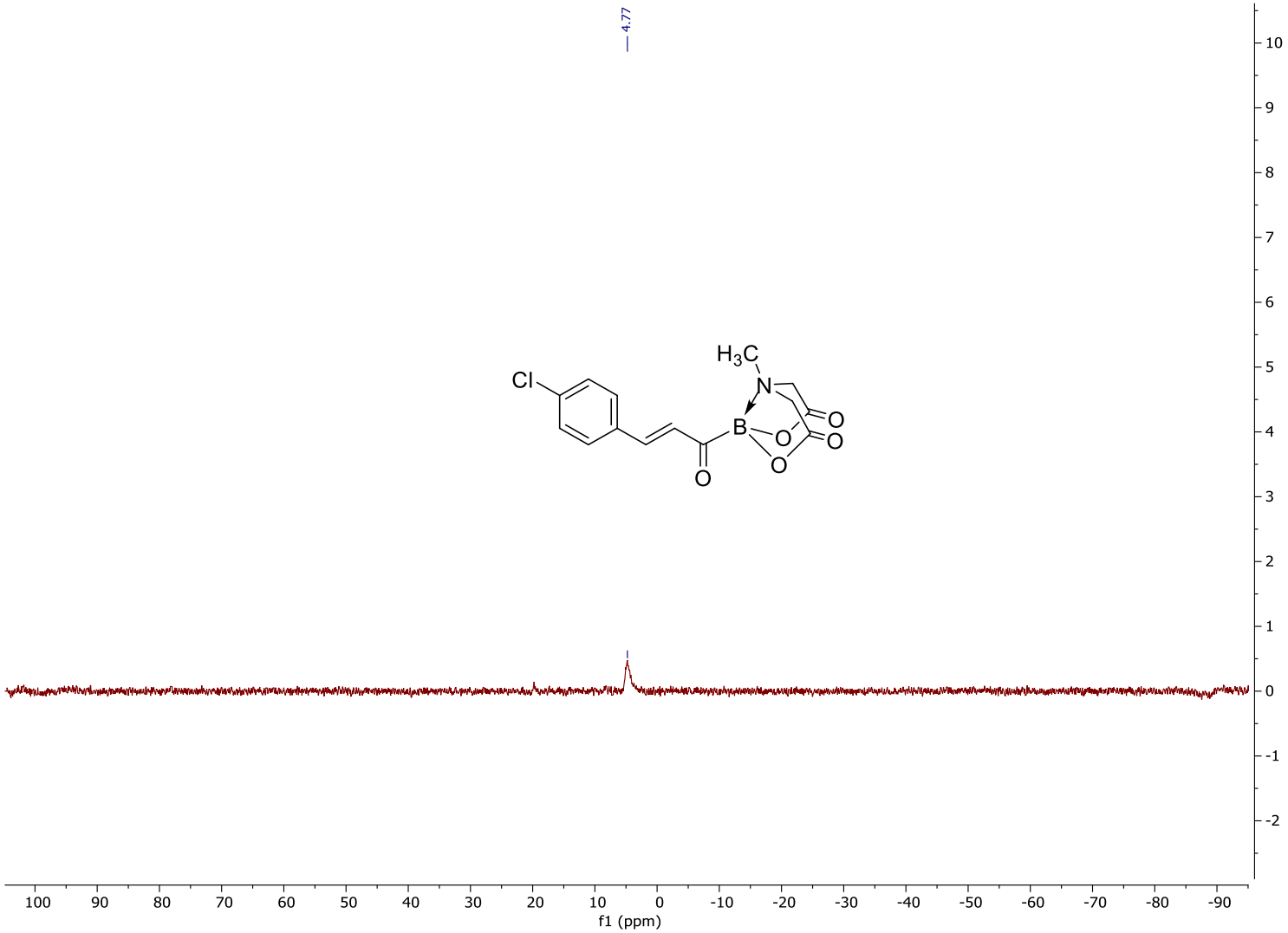
^{1}H NMR, compound 7c



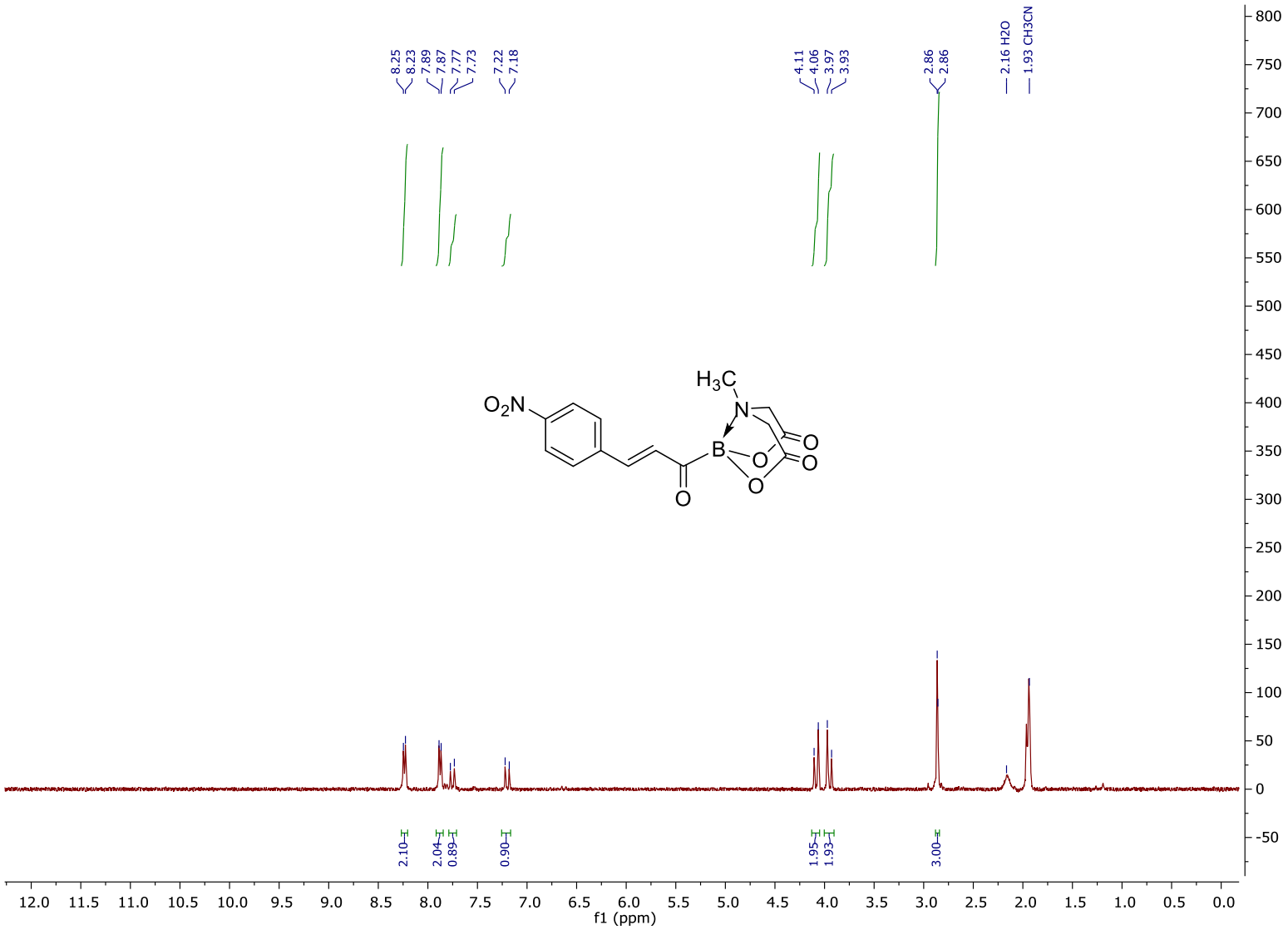
^{13}C NMR, compound 7c



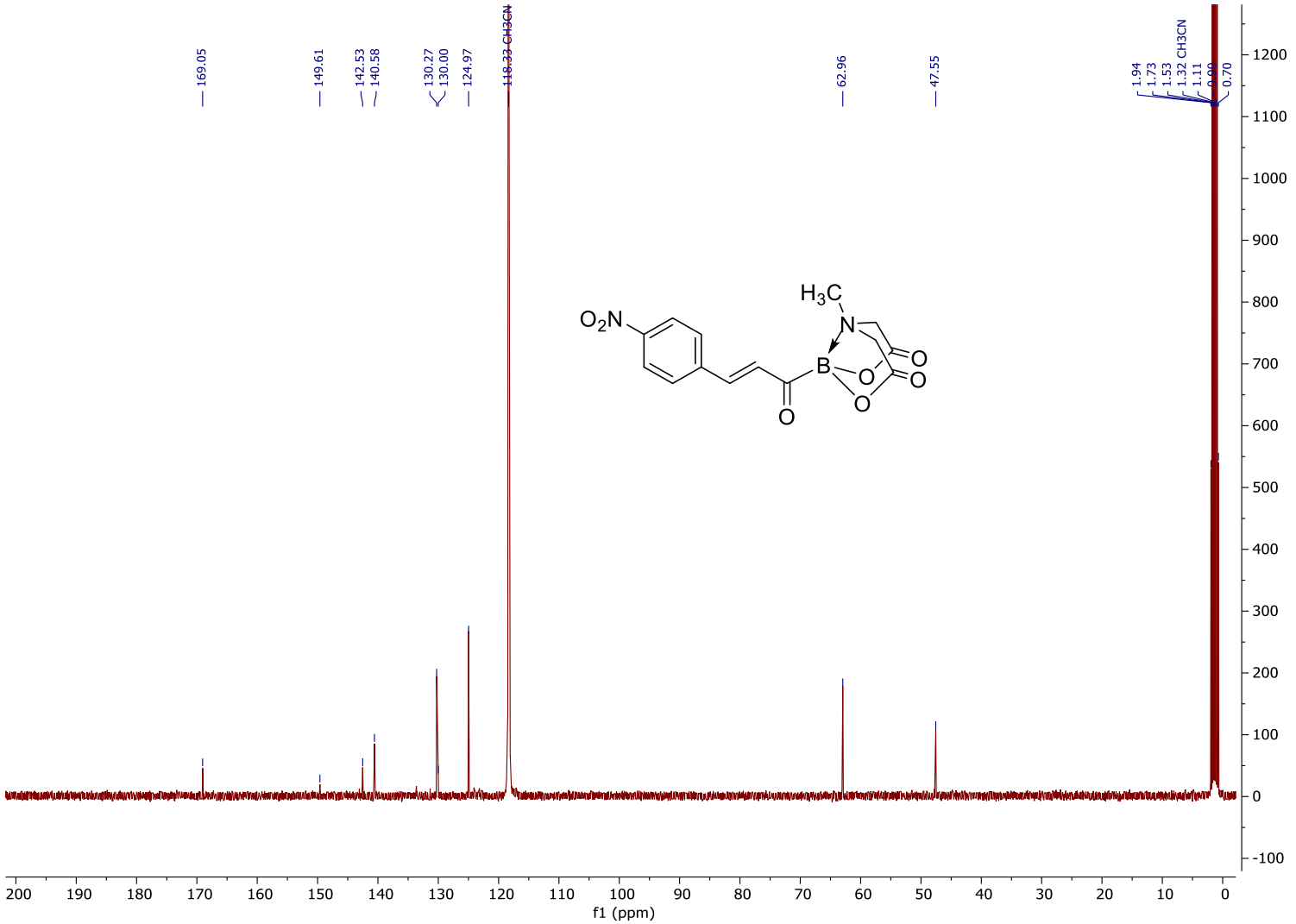
^{11}B NMR, compound 7c



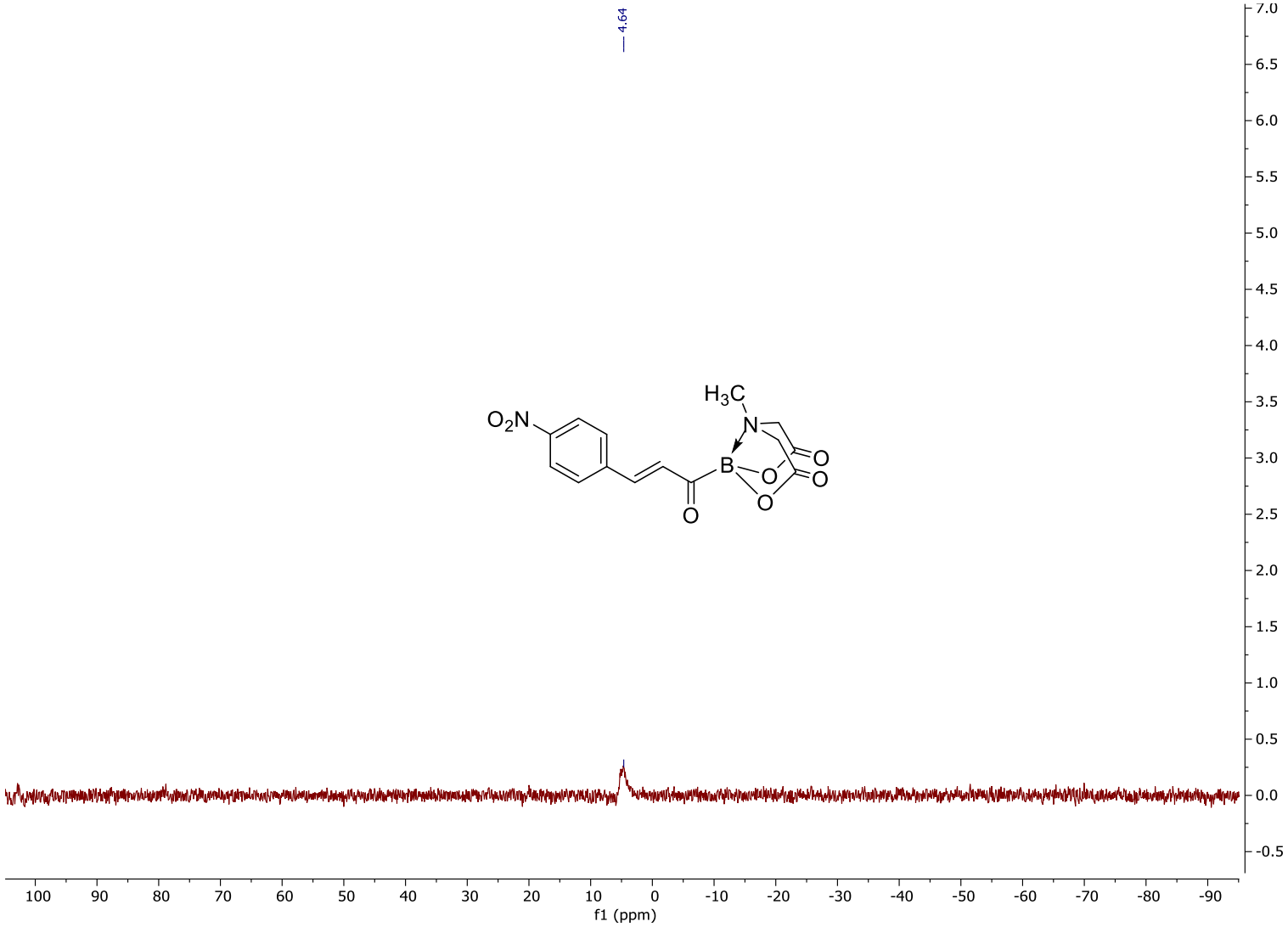
^{1}H NMR, compound 7d



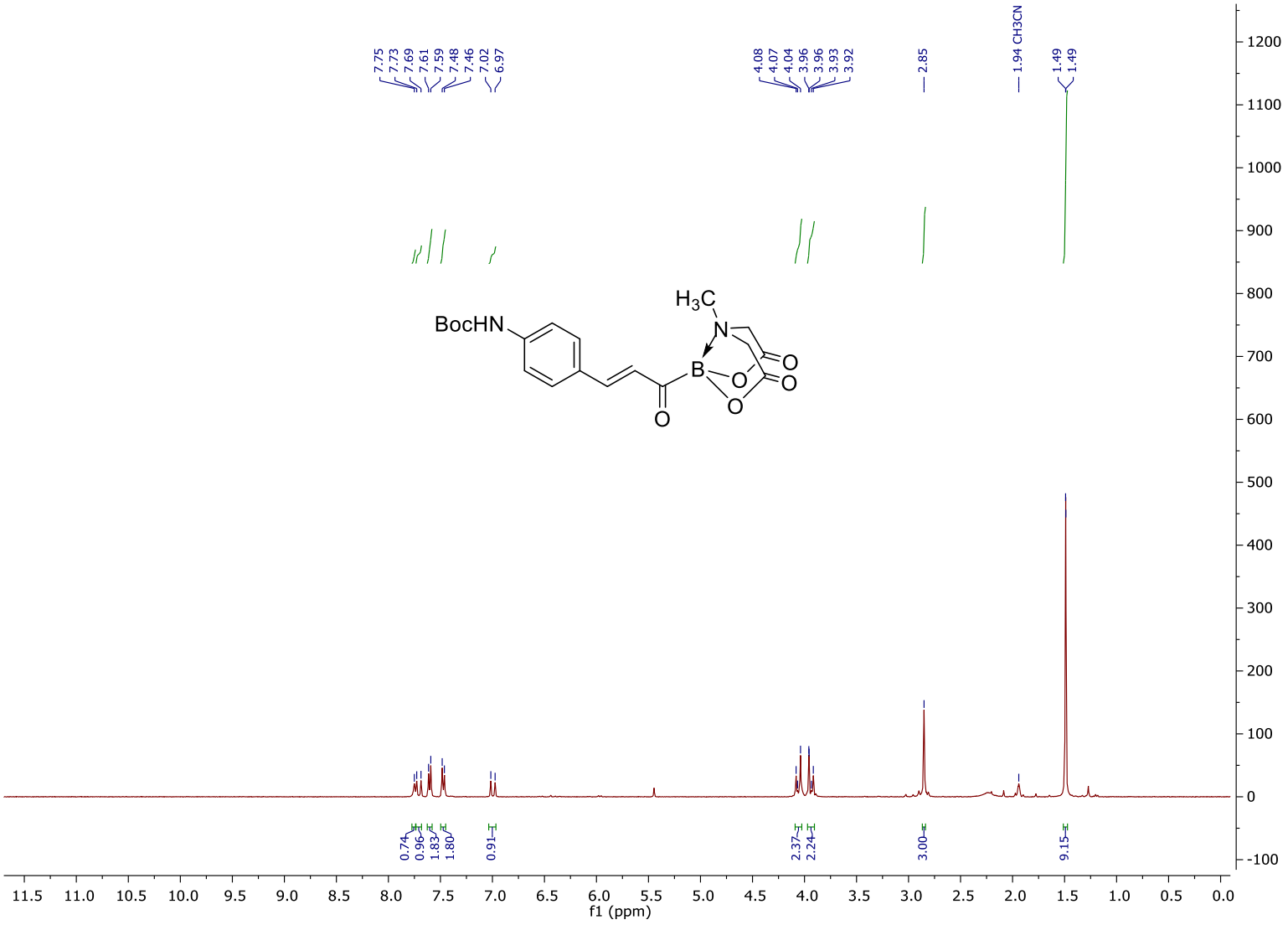
^{13}C NMR, compound 7d



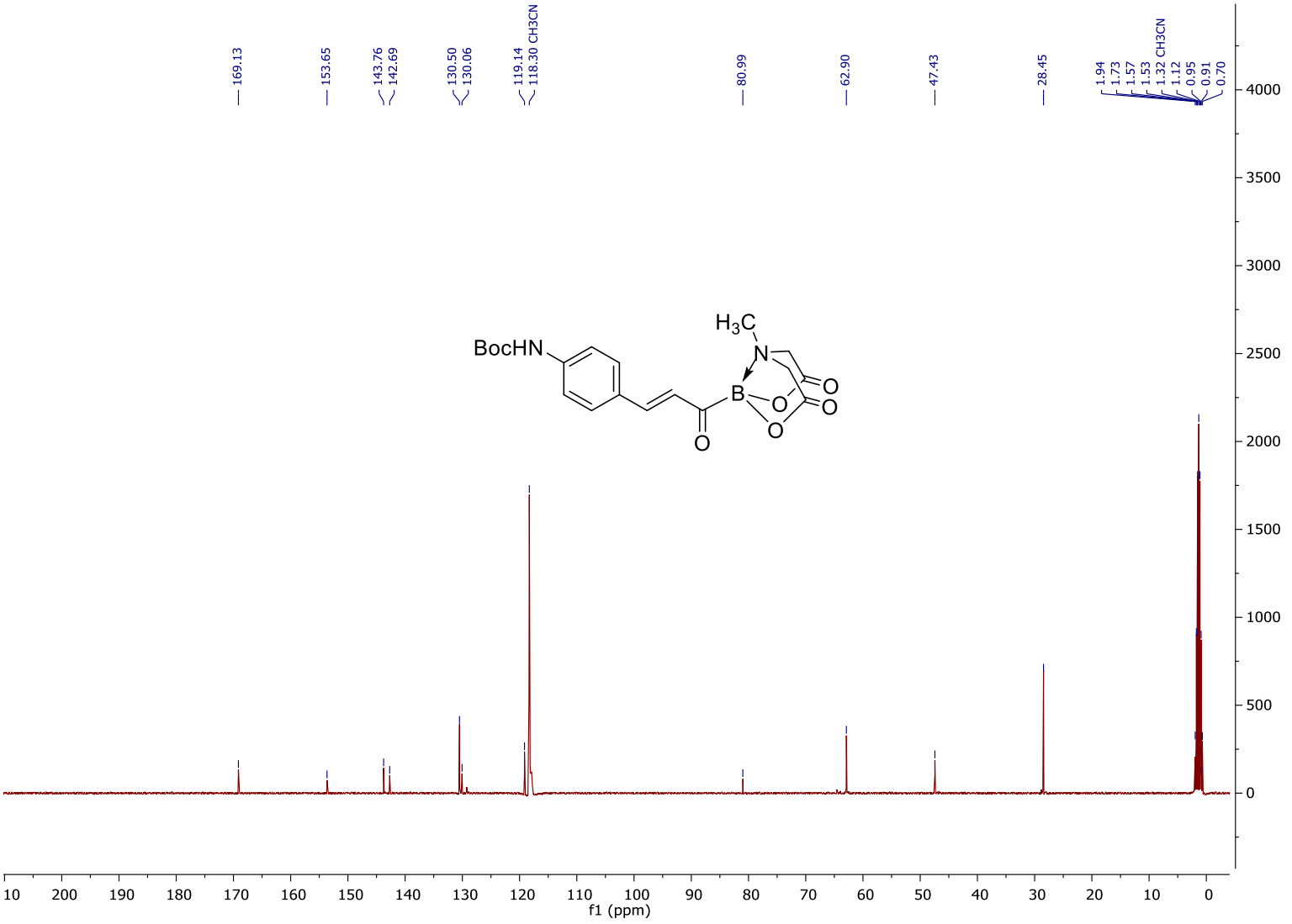
^{11}B NMR, compound 7d



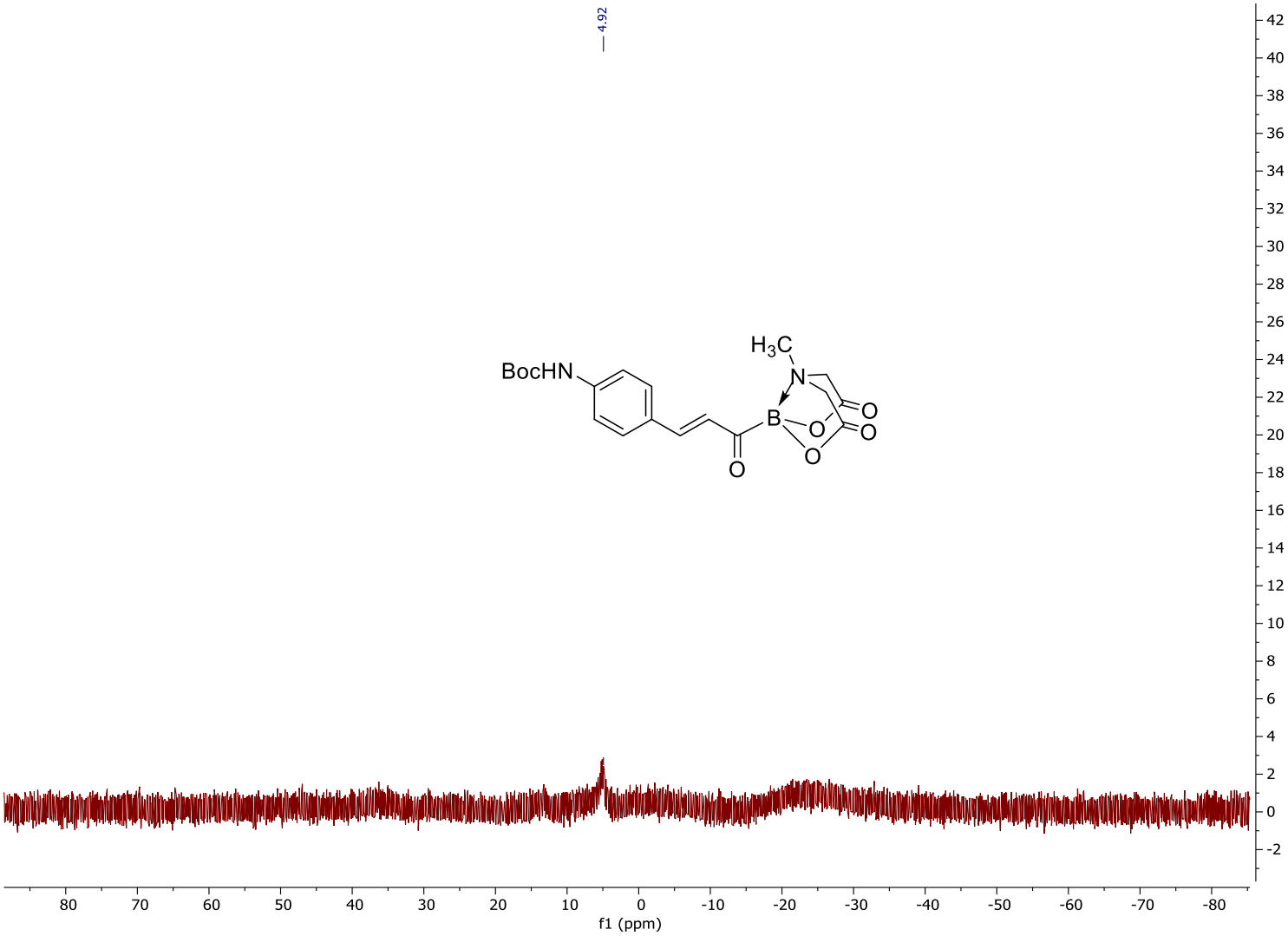
^{1}H NMR, compound 7e

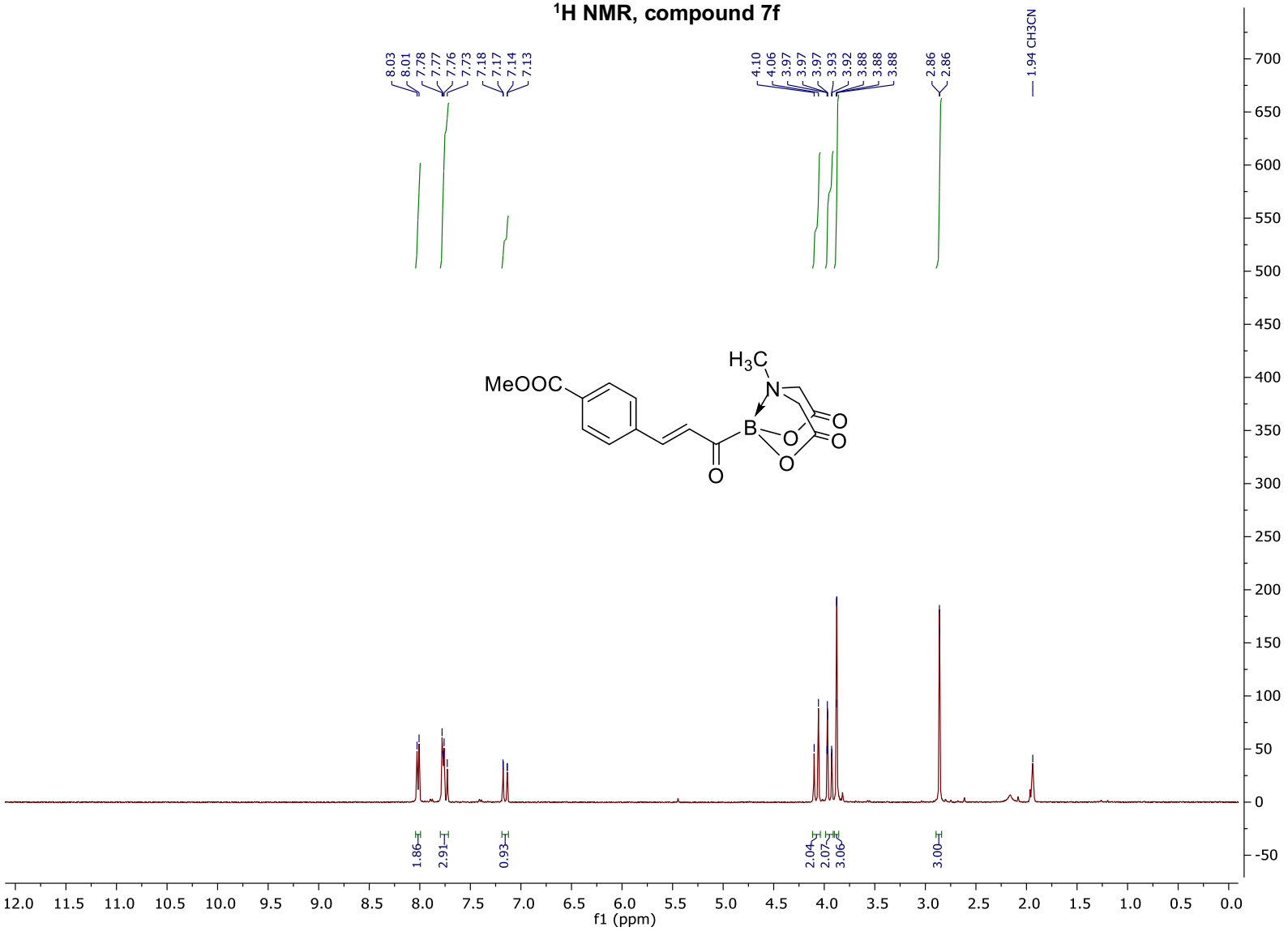


^{13}C NMR, compound 7e

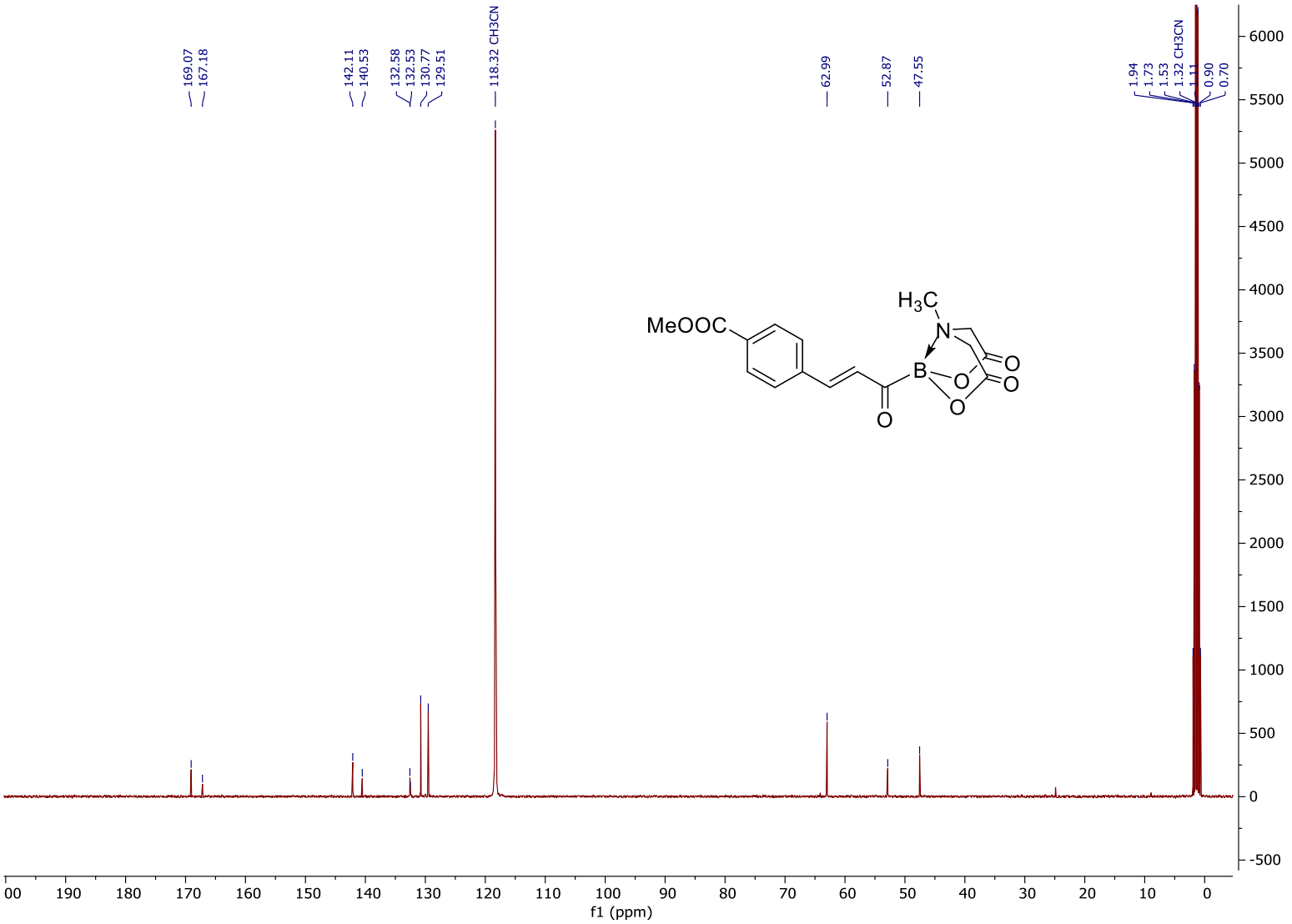


^{11}B NMR, compound 7e

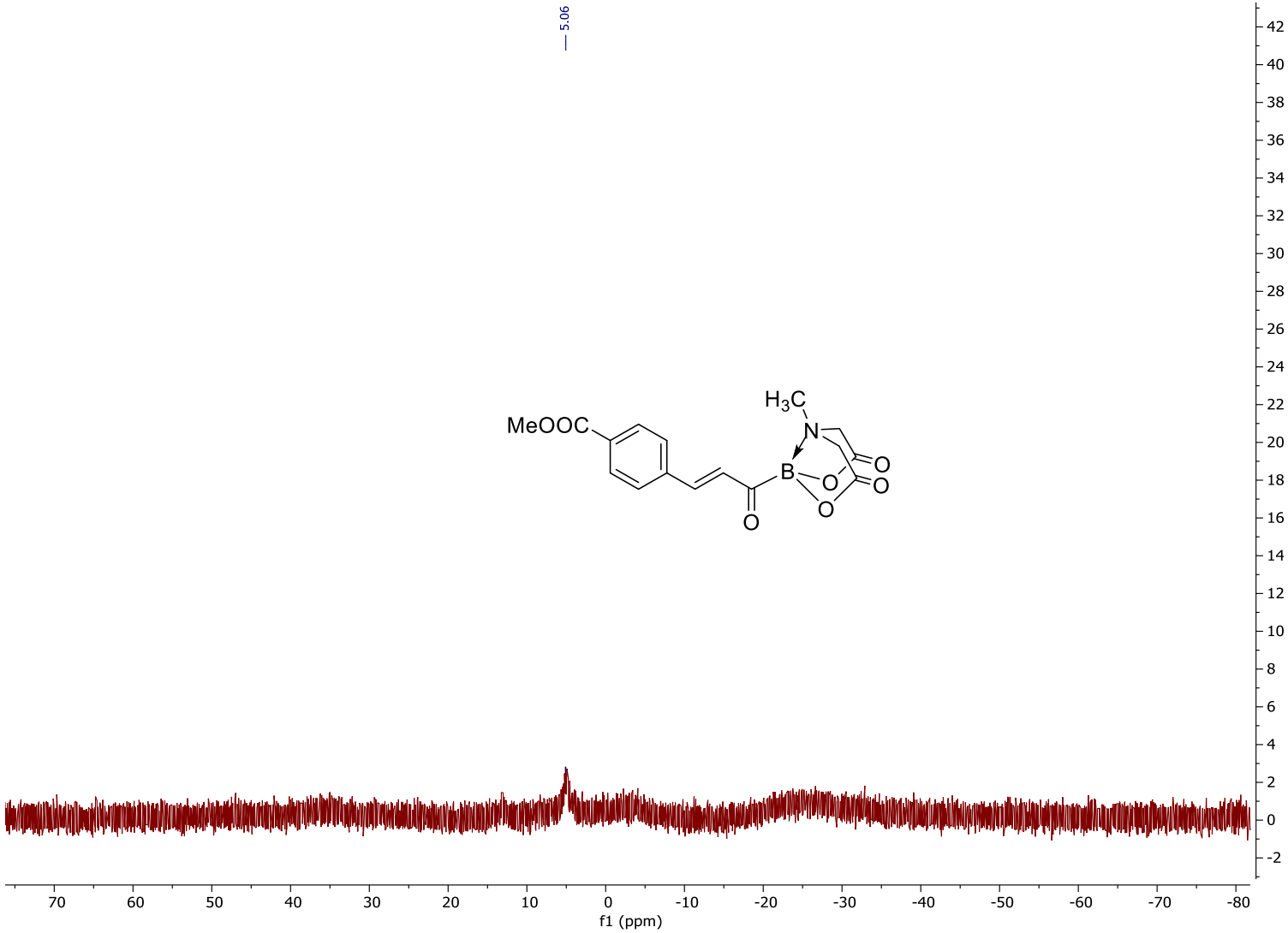



1H NMR, compound 7f
8.03
8.01
7.78
7.77
7.76
7.73
7.18
7.17
7.14
7.13
4.10
4.06
3.97
3.97
3.97
3.93
3.92
3.88
3.88
3.88
2.86
2.86
1.94 CH3CN
MeOOC
H3C
N
B
O
O
O
O
O
1.86
2.91
0.93
2.04
2.07
3.06
3.00
f1 (ppm)

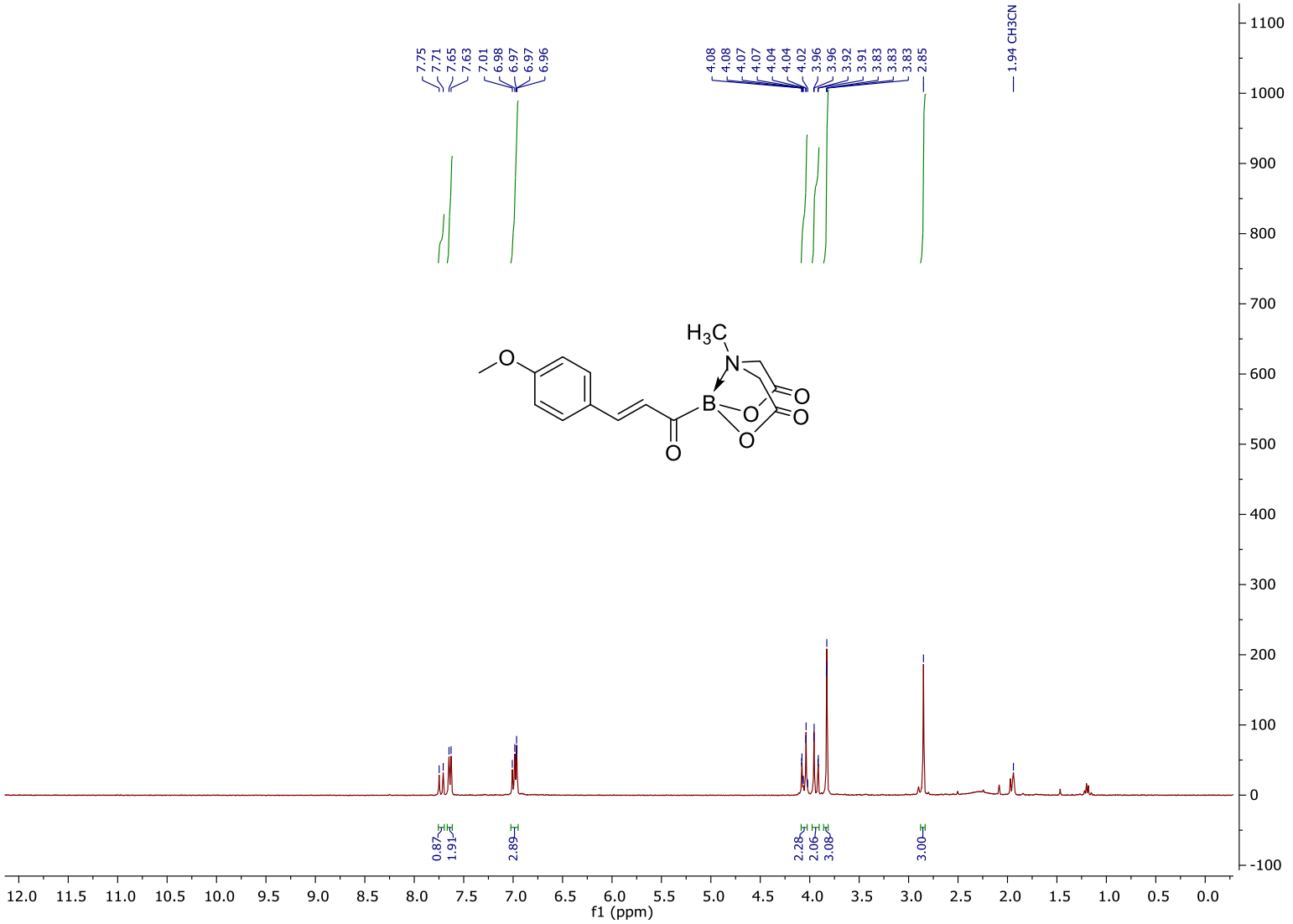
^{13}C NMR, compound 7f



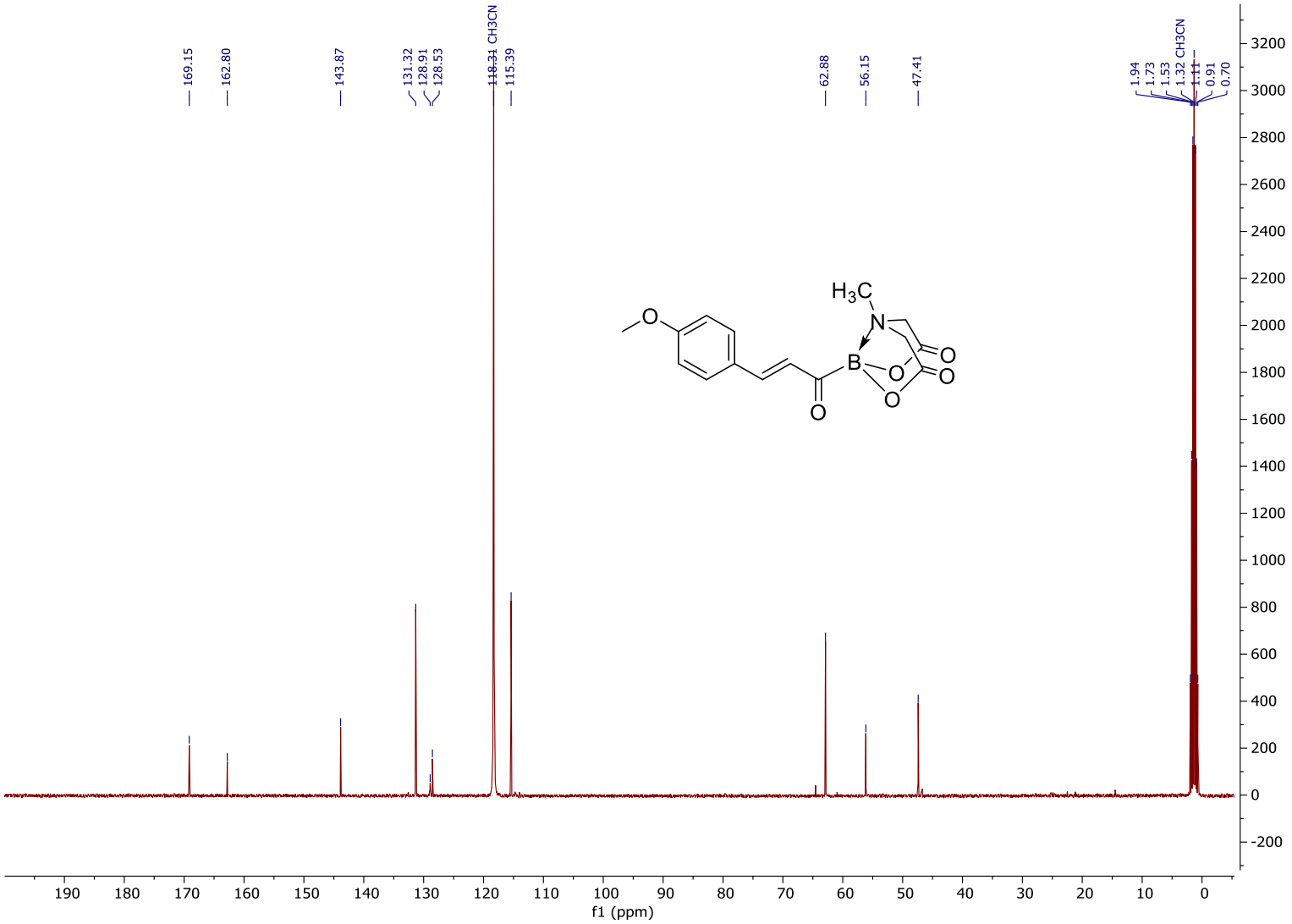
^{11}B NMR, compound 7f



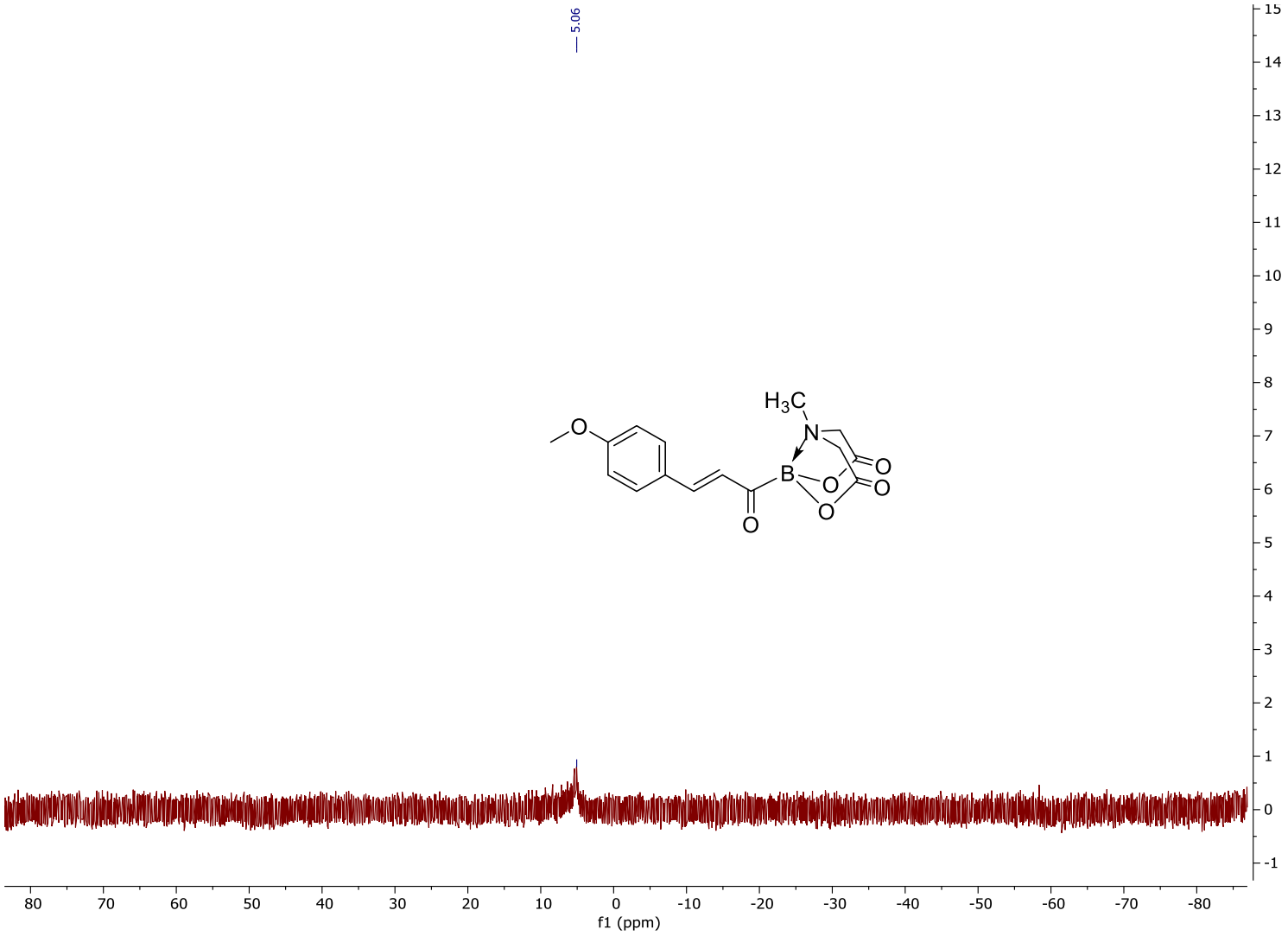
^{1}H NMR, compound 7g



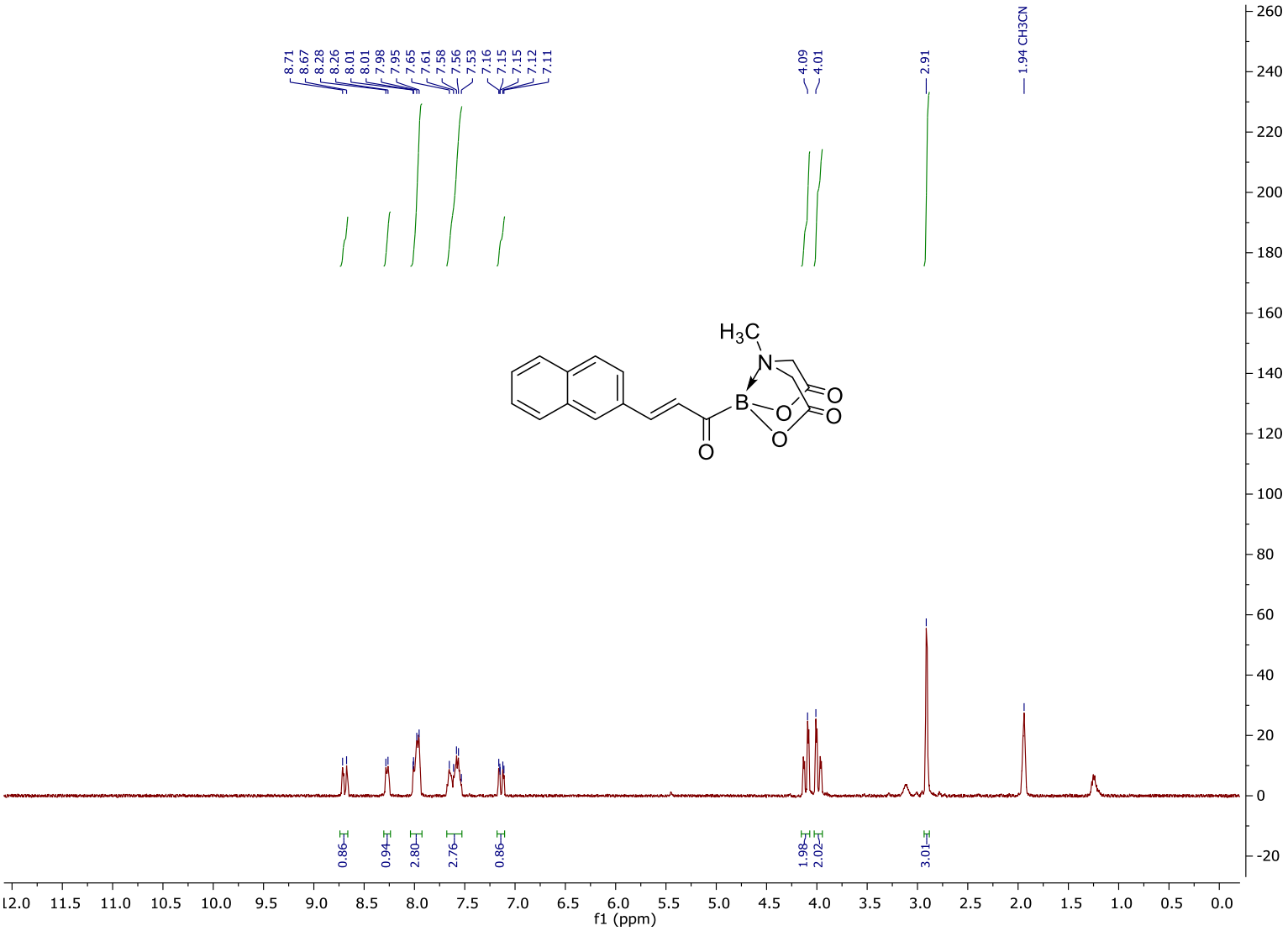
^{13}C NMR, compound 7g



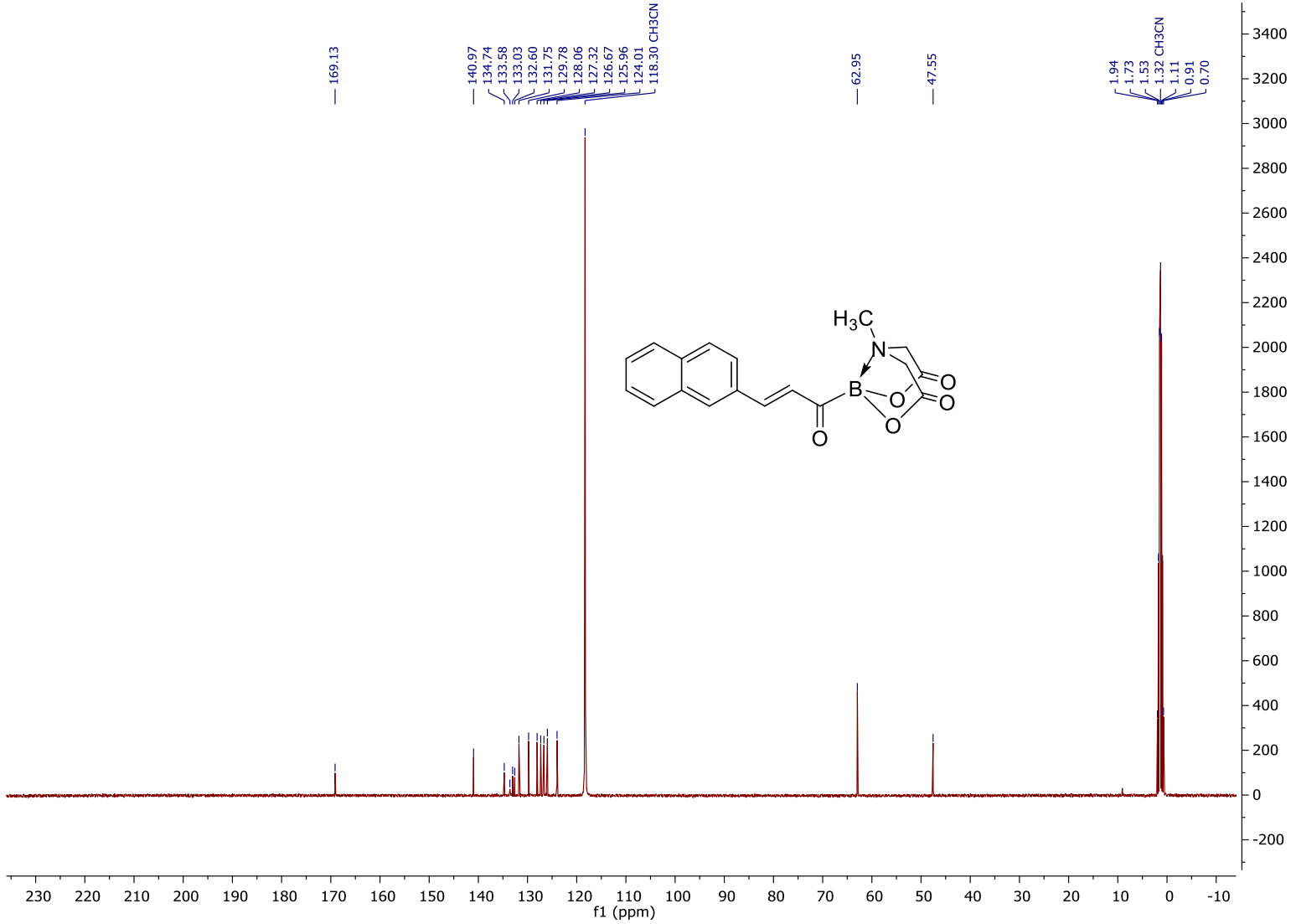
^{11}B NMR, compound 7g



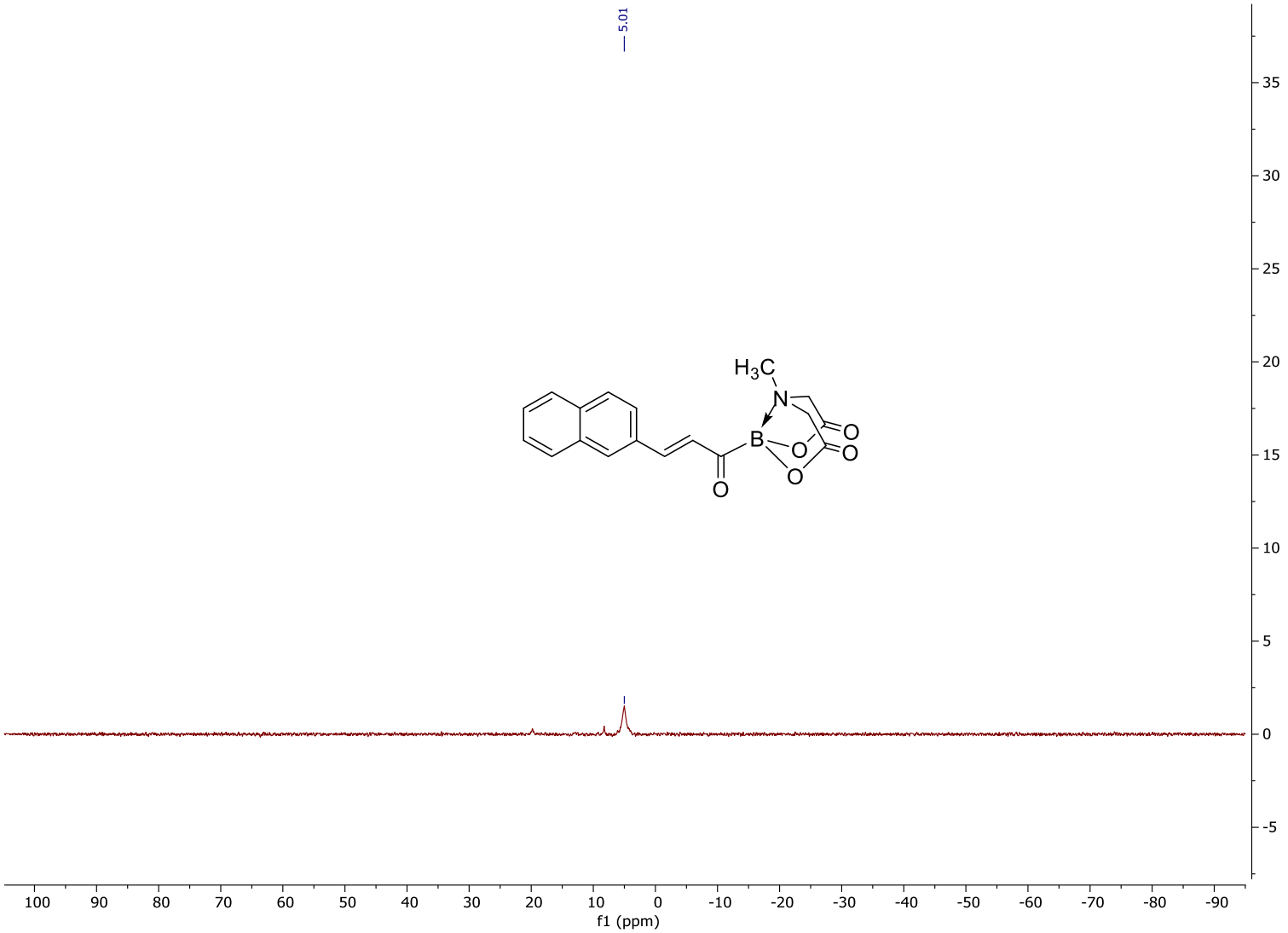
^{1}H NMR, compound 7h

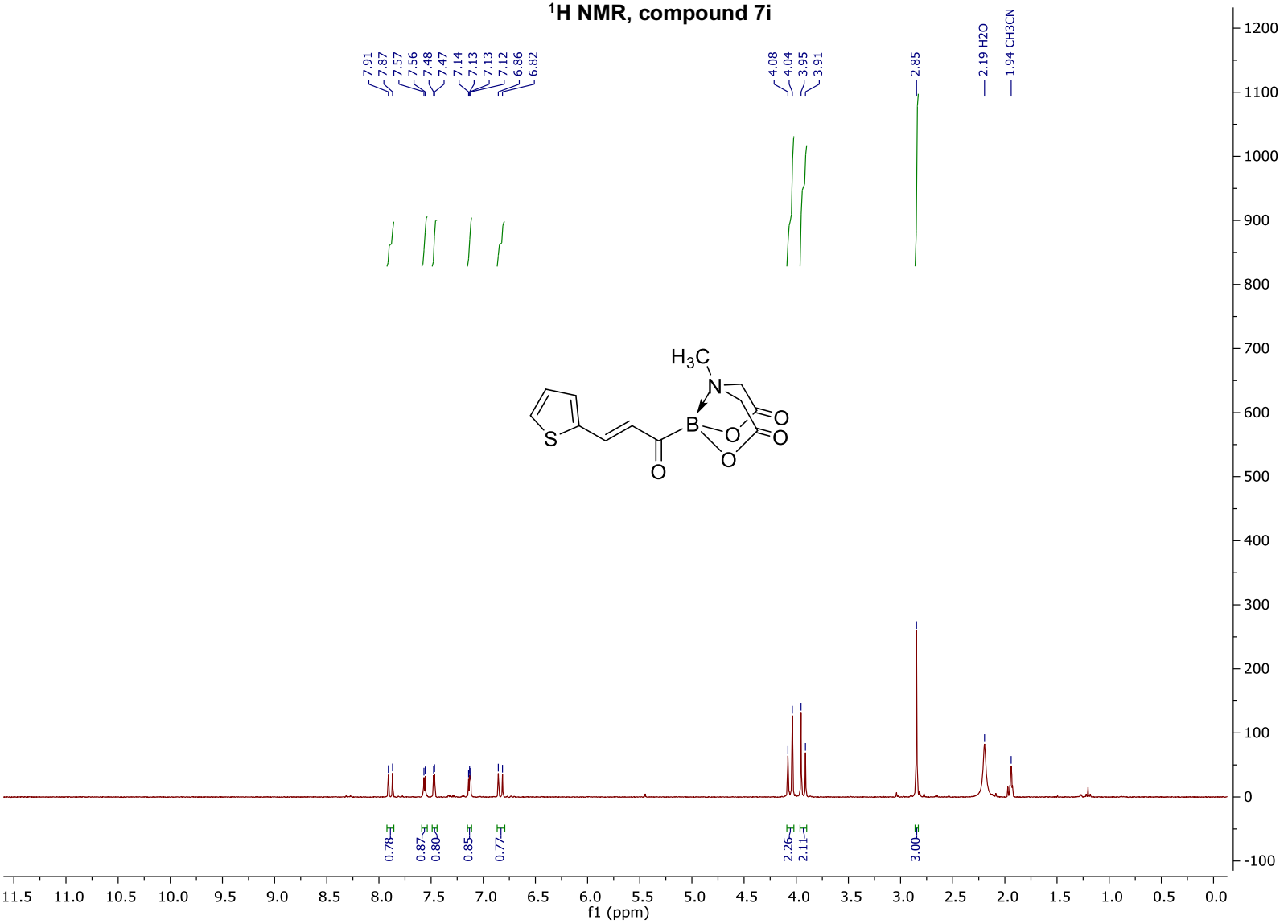


^{13}C NMR, compound 7h

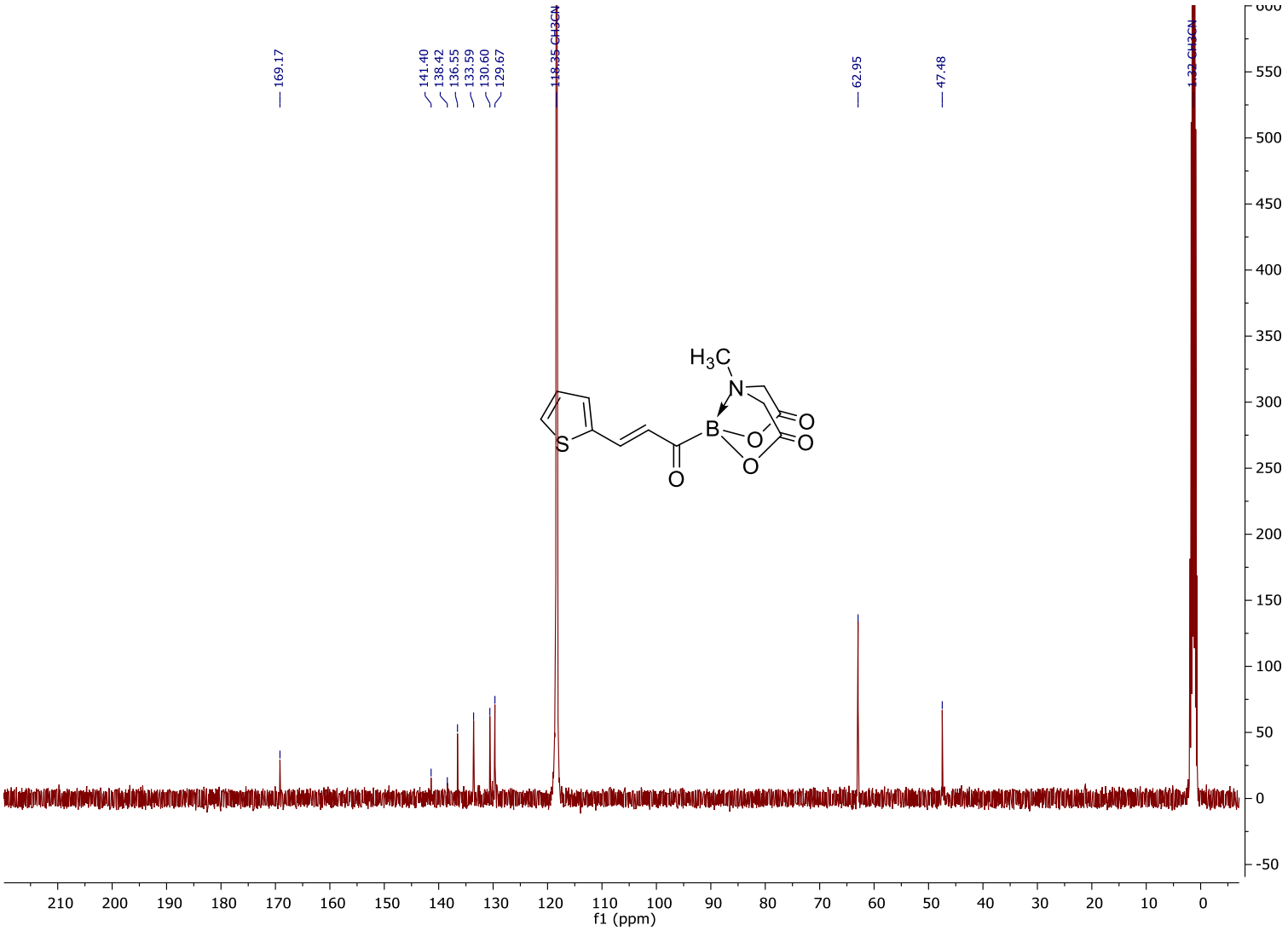


^{11}B NMR, compound 7h

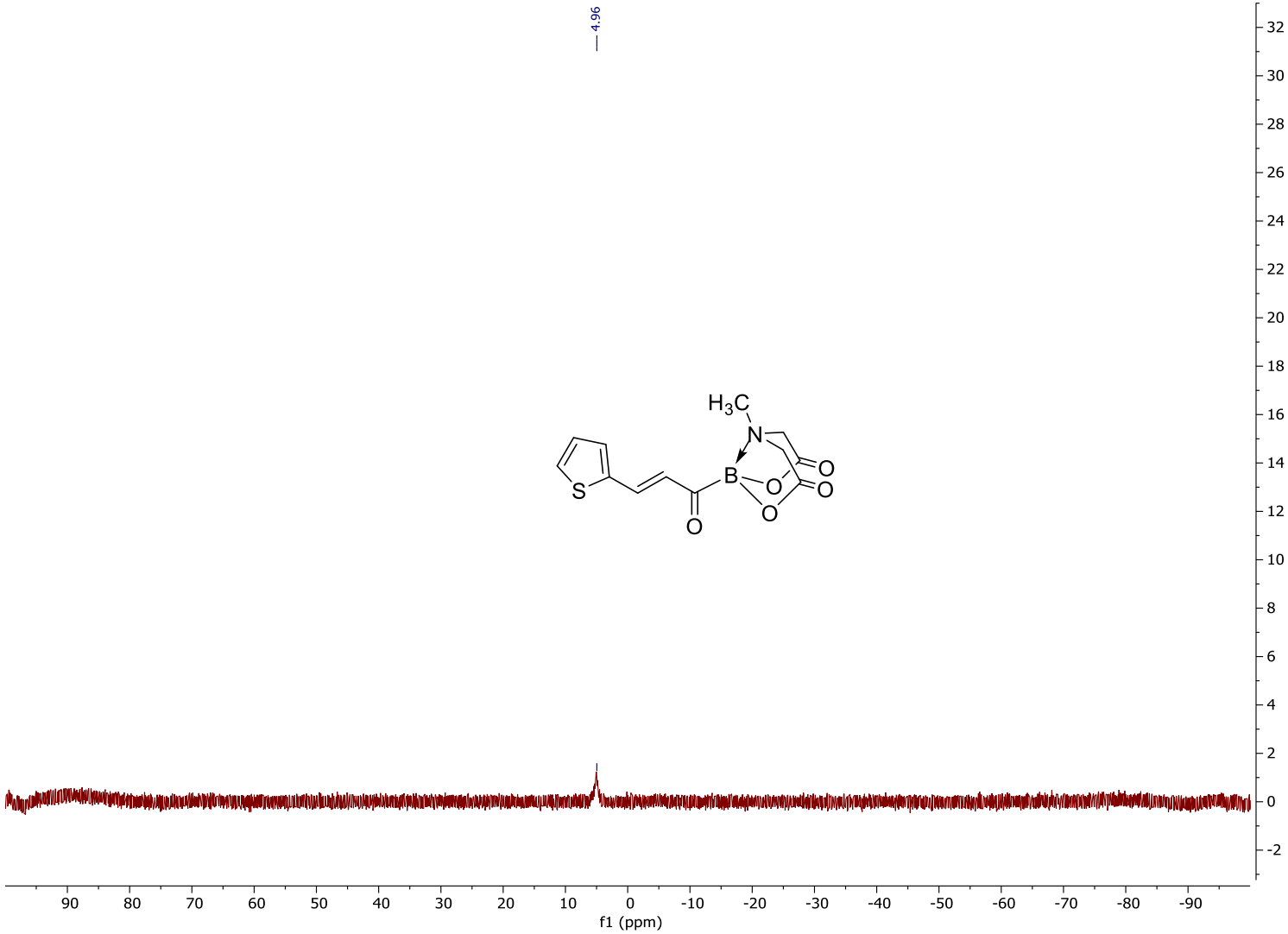


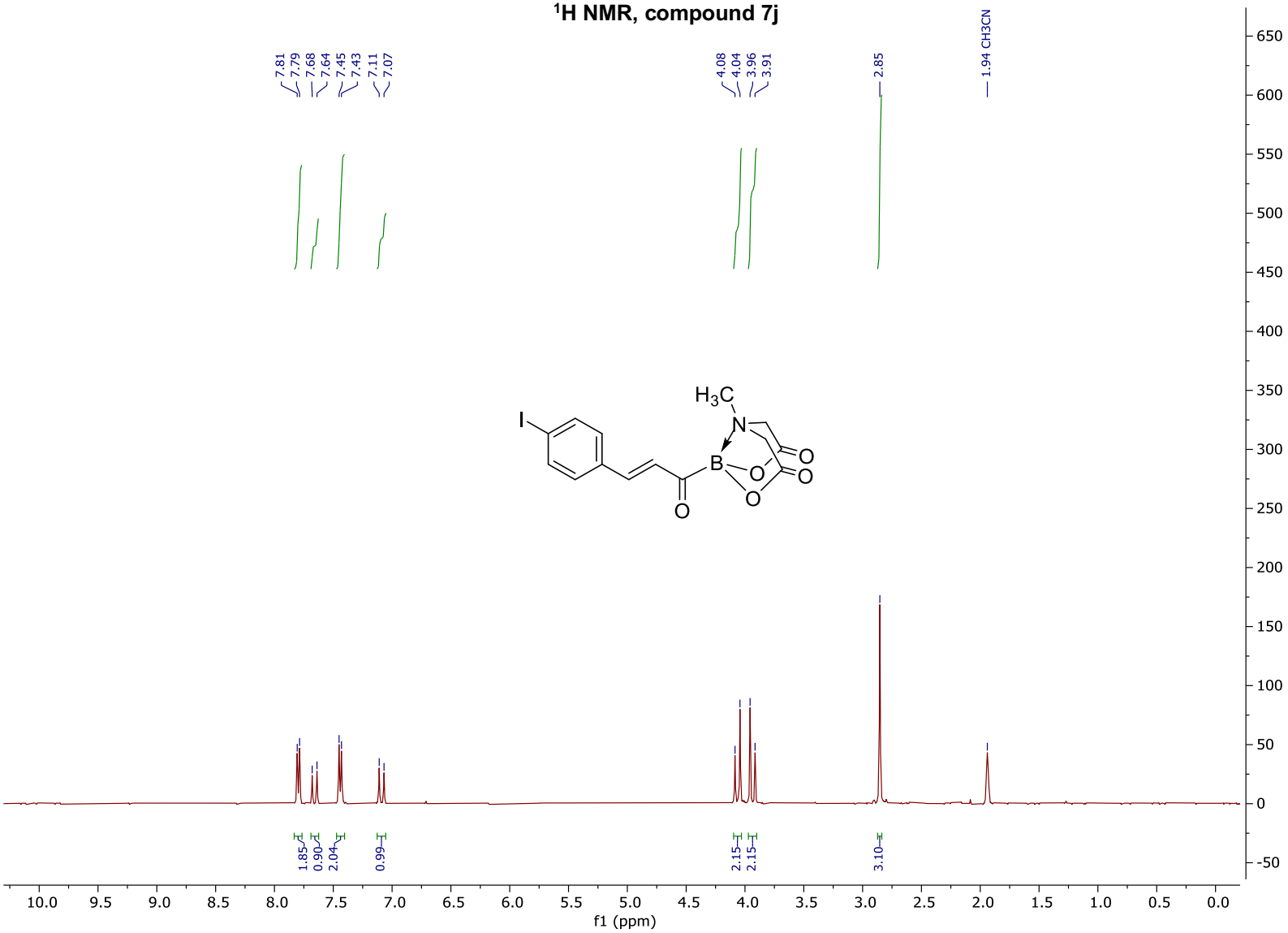

¹H NMR, compound 7i
7.91
7.87
7.57
7.56
7.48
7.47
7.14
7.13
7.13
7.12
6.86
6.82
4.08
4.04
3.95
3.91
2.85
2.19 H2O
1.94 CH3CN
H3C
N
B
O
O
O
O
S
O
0.78
0.87
0.80
0.85
0.77
2.26
2.11
3.00
f1 (ppm)

^{13}C NMR, compound 7i

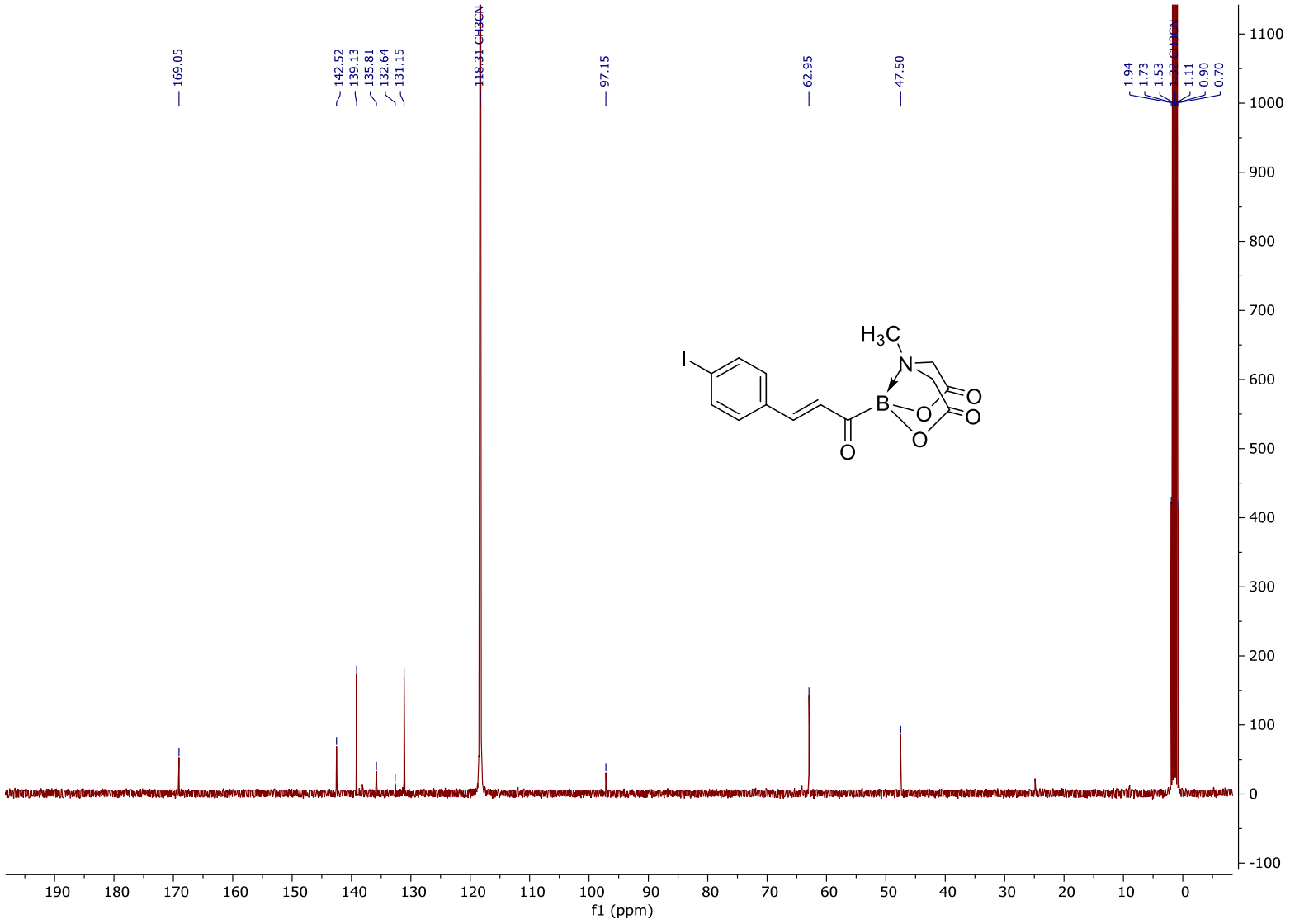


^{11}B NMR, compound 7i

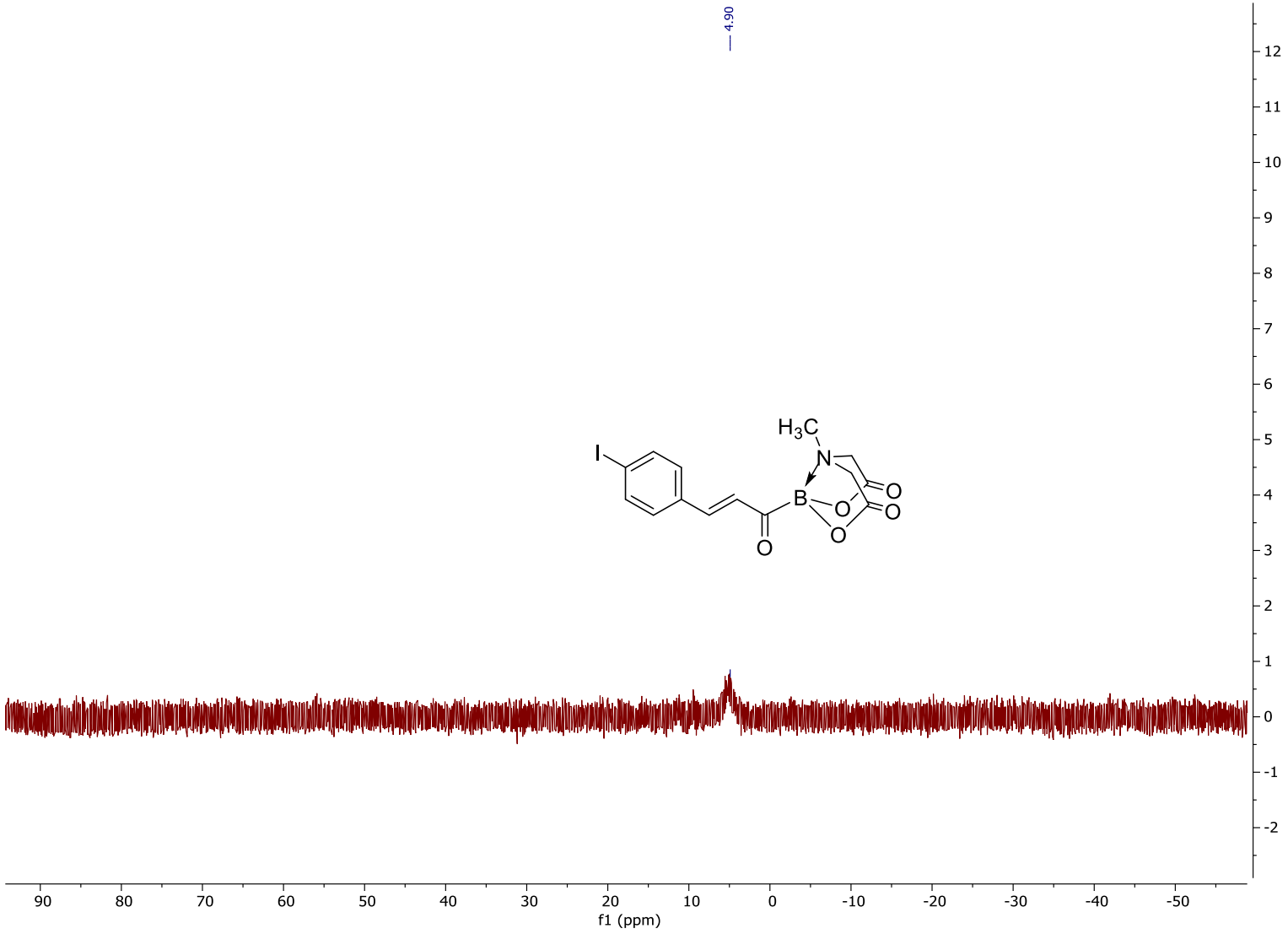


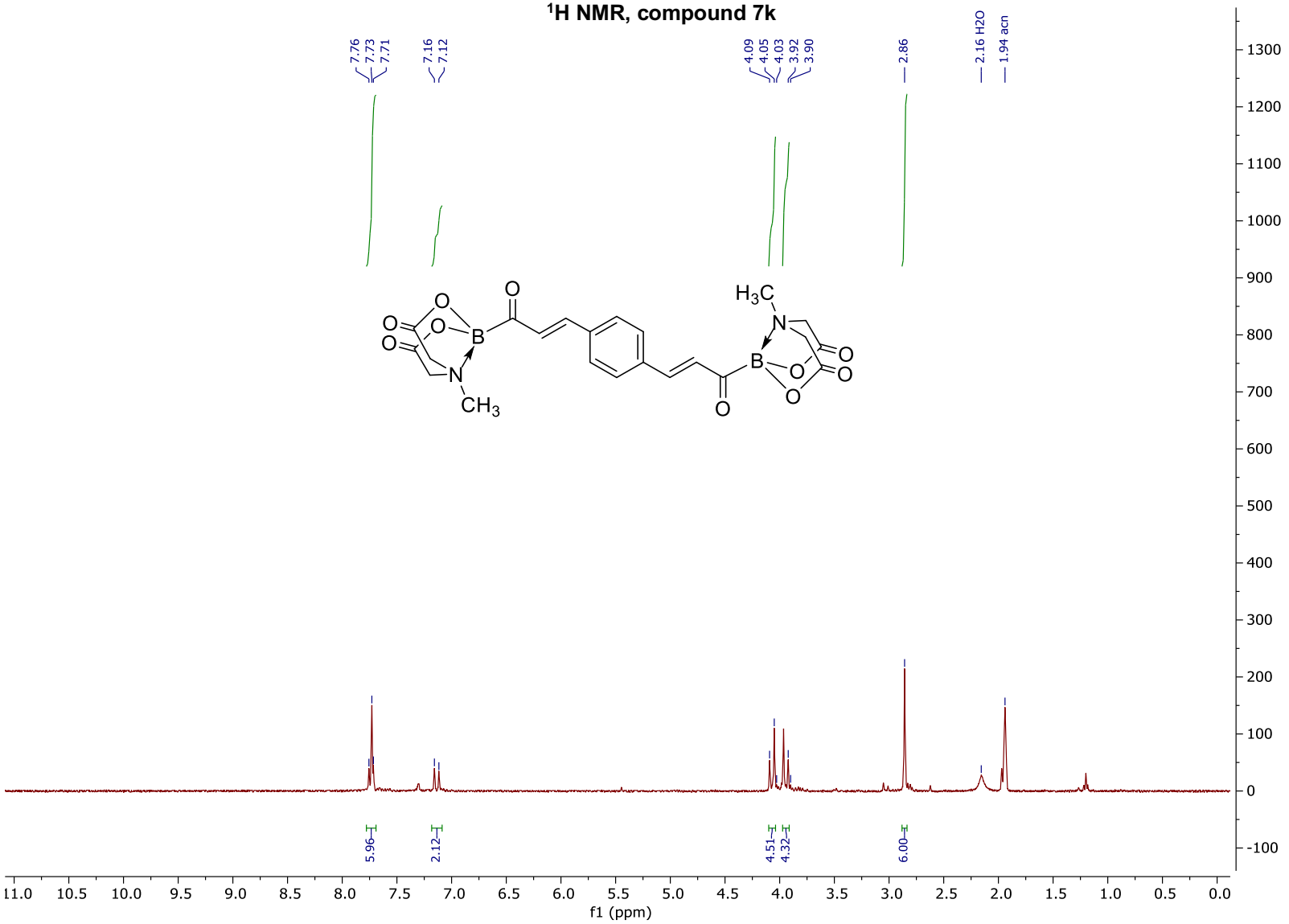

¹H NMR, compound 7j
7.81
7.79
7.68
7.64
7.45
7.43
7.11
7.07
4.08
4.04
3.96
3.91
2.85
1.94 CH3CN
H3C
N
I
B
O
O
O
O
O
1.85
0.90
2.04
0.99
2.15
2.15
3.10
f1 (ppm)

^{13}C NMR, compound 7j

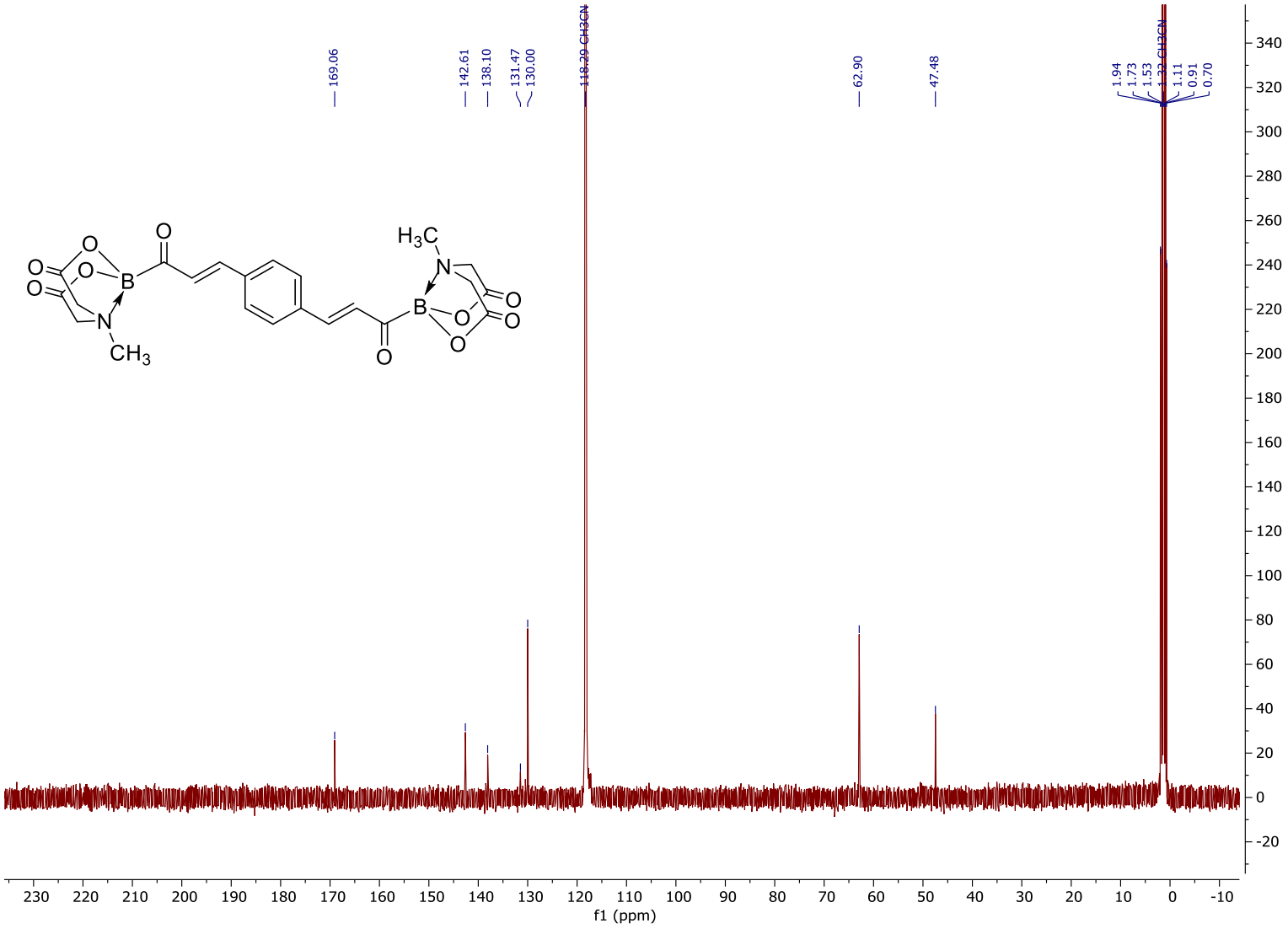


^{11}B NMR, compound 7j

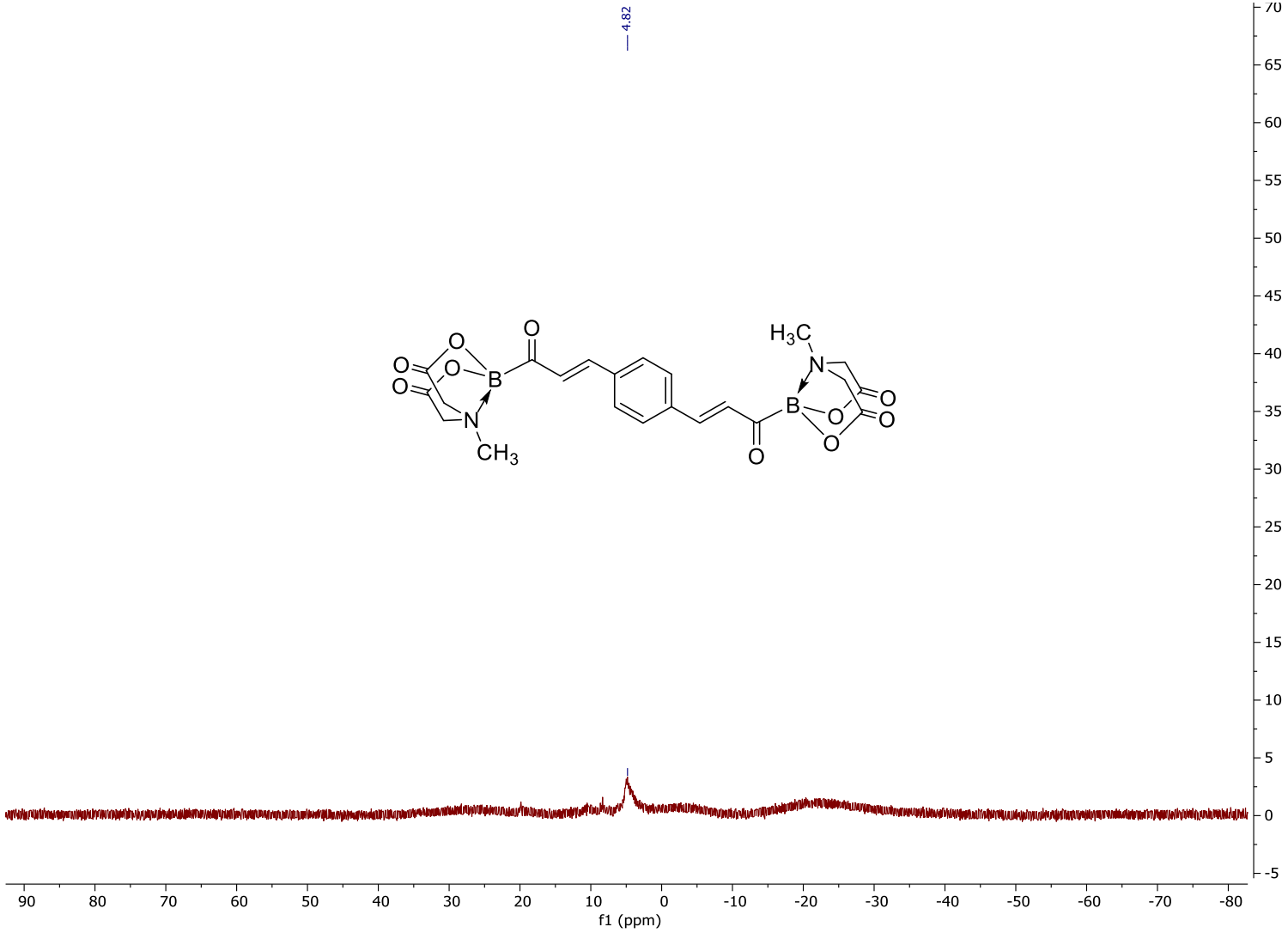


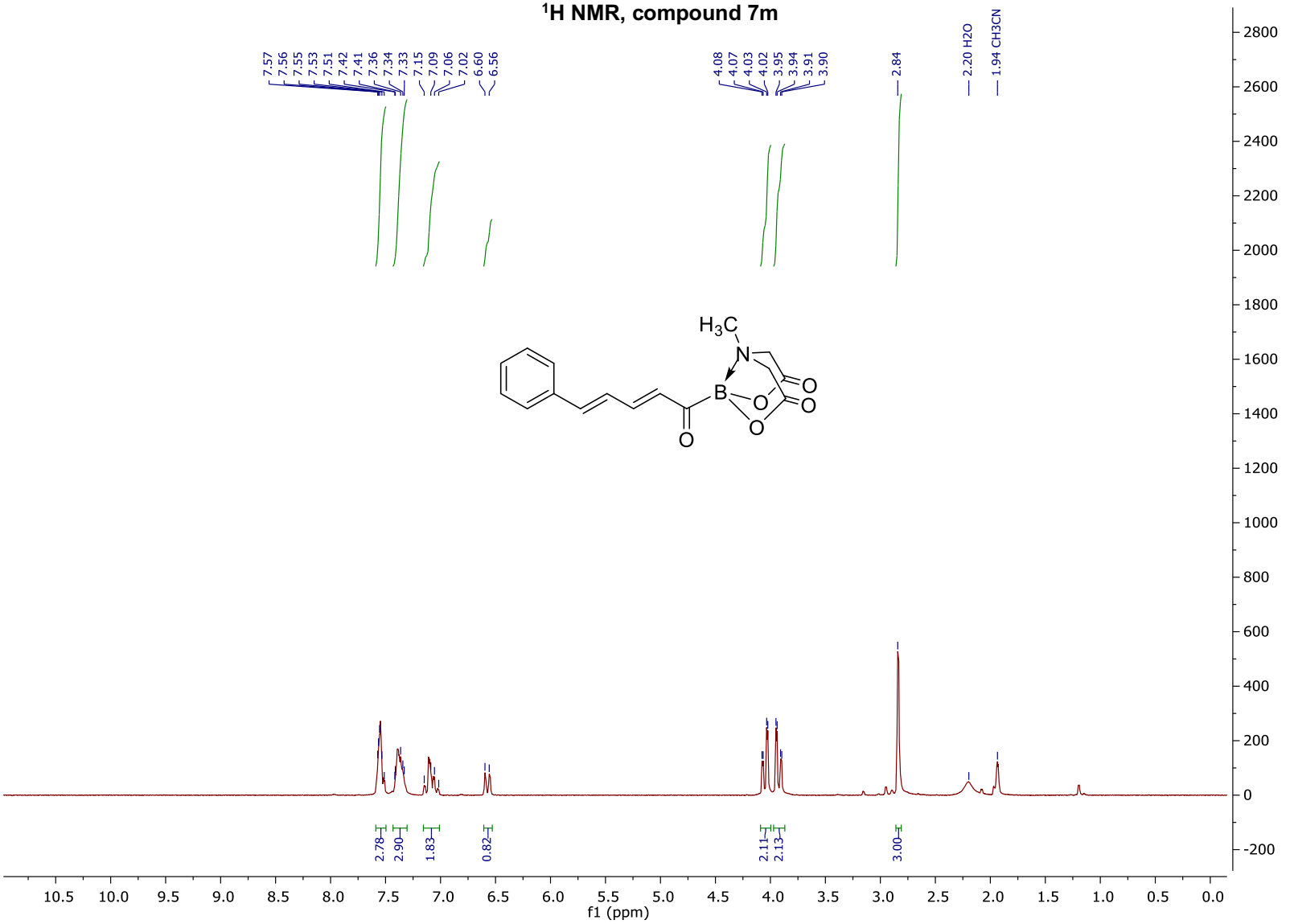

1H NMR, compound 7k
7.76
7.73
7.71
7.16
7.12
4.09
4.05
4.03
3.92
3.90
2.86
2.16 H2O
1.94 acn
5.96
2.12
4.51
4.32
6.00
f1 (ppm)

^{13}C NMR, compound 7k

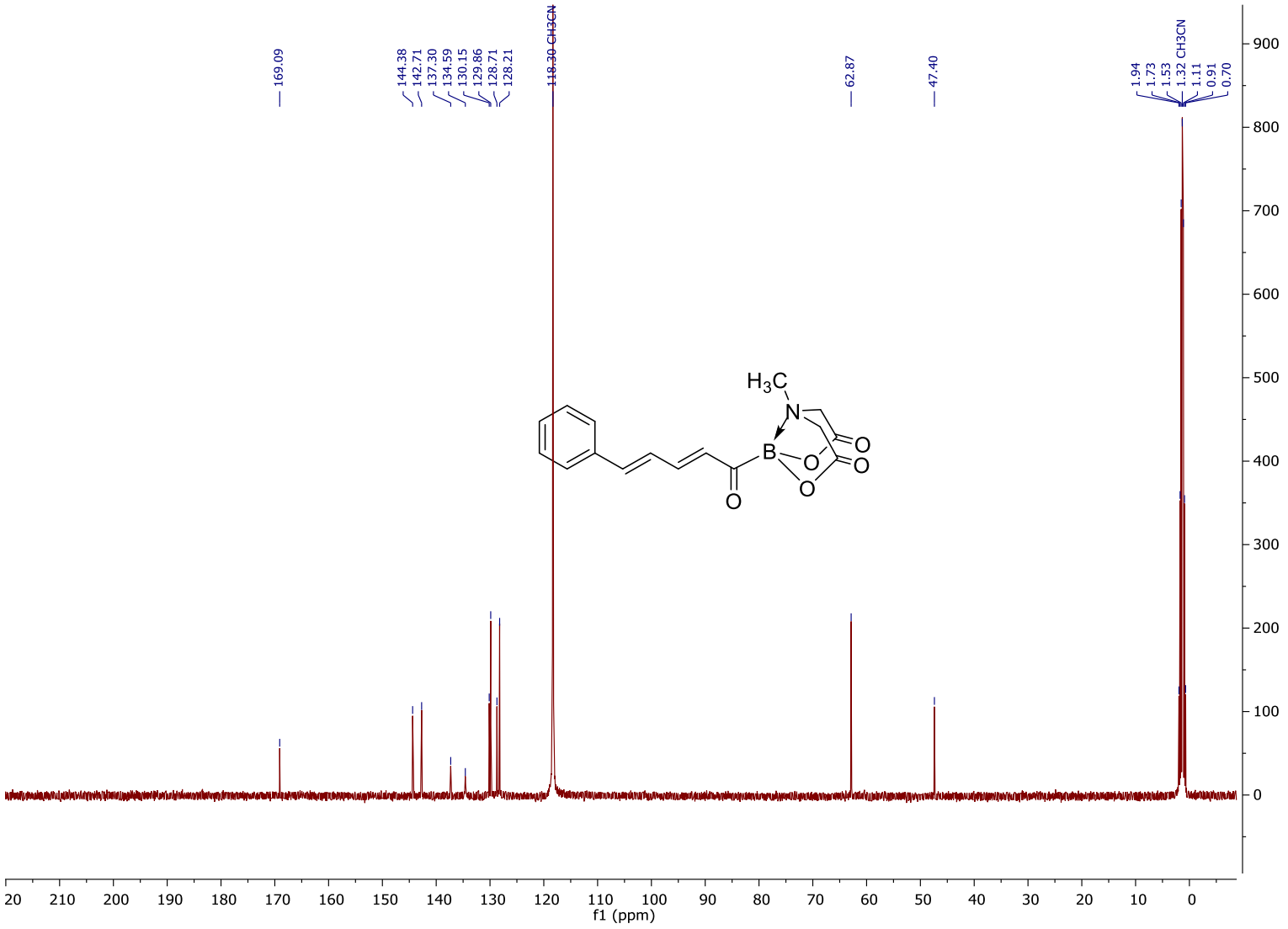


^{11}B NMR, compound 7k

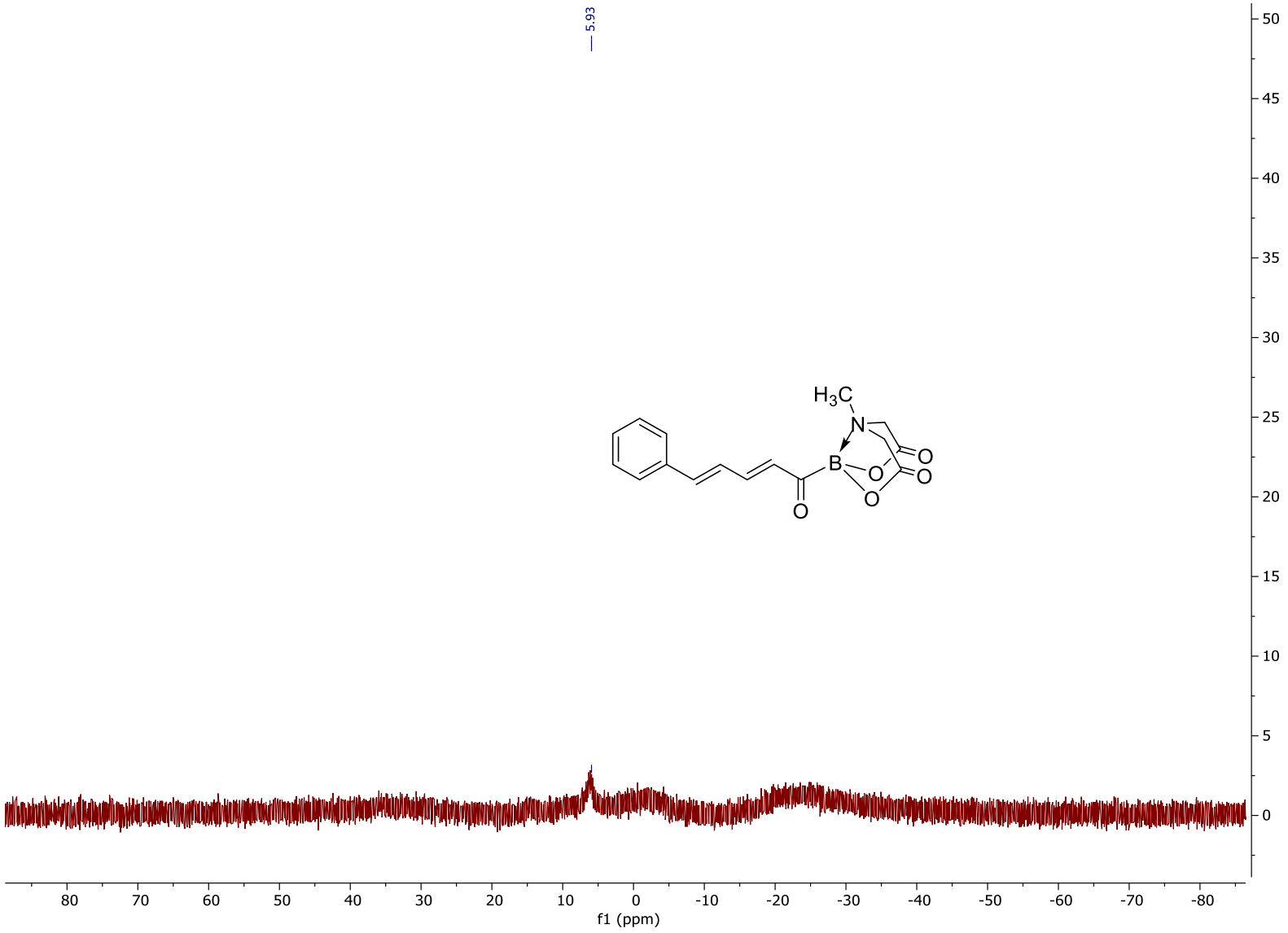


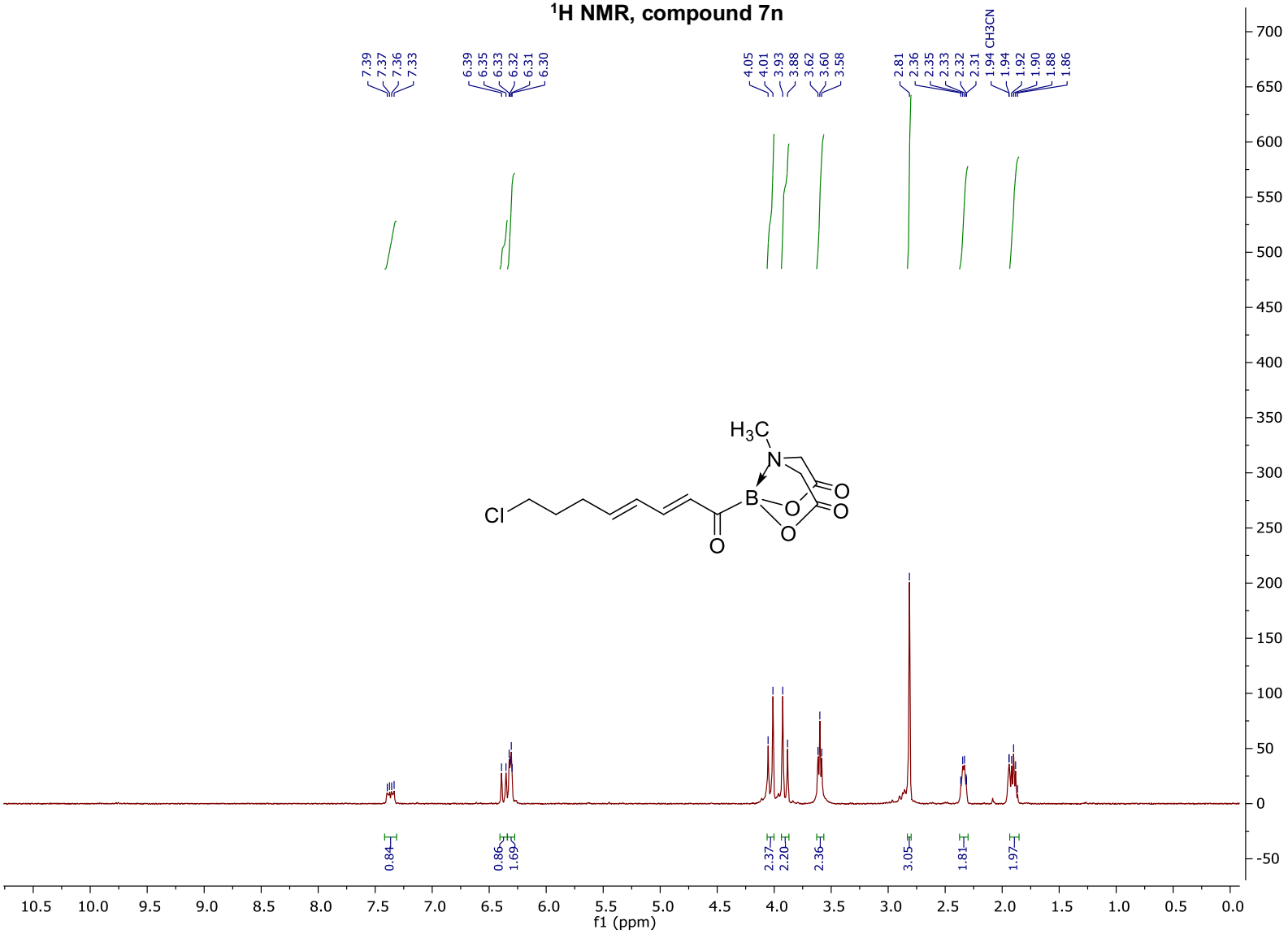

¹H NMR, compound 7m
7.57
7.56
7.55
7.53
7.51
7.42
7.41
7.36
7.34
7.33
7.15
7.09
7.06
7.02
6.60
6.56
4.08
4.07
4.03
4.02
3.95
3.94
3.91
3.90
2.84
2.20 H2O
1.94 CH3CN
H3C
N
B
O
O
O
O
O
2.78
2.90
1.83
0.82
2.11
2.13
3.00
f1 (ppm)

^{13}C NMR, compound 7m

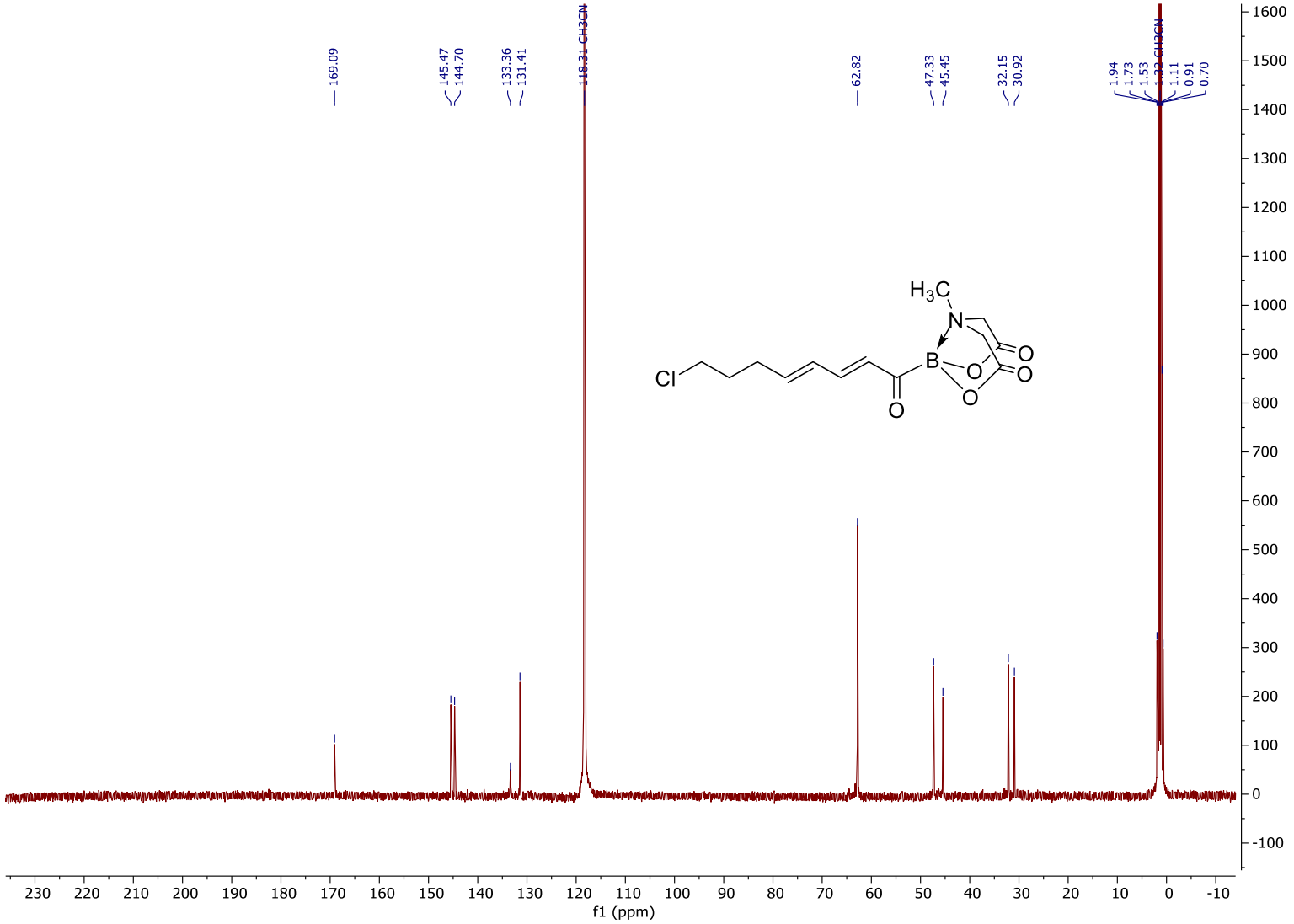


^{11}B NMR, compound 7m

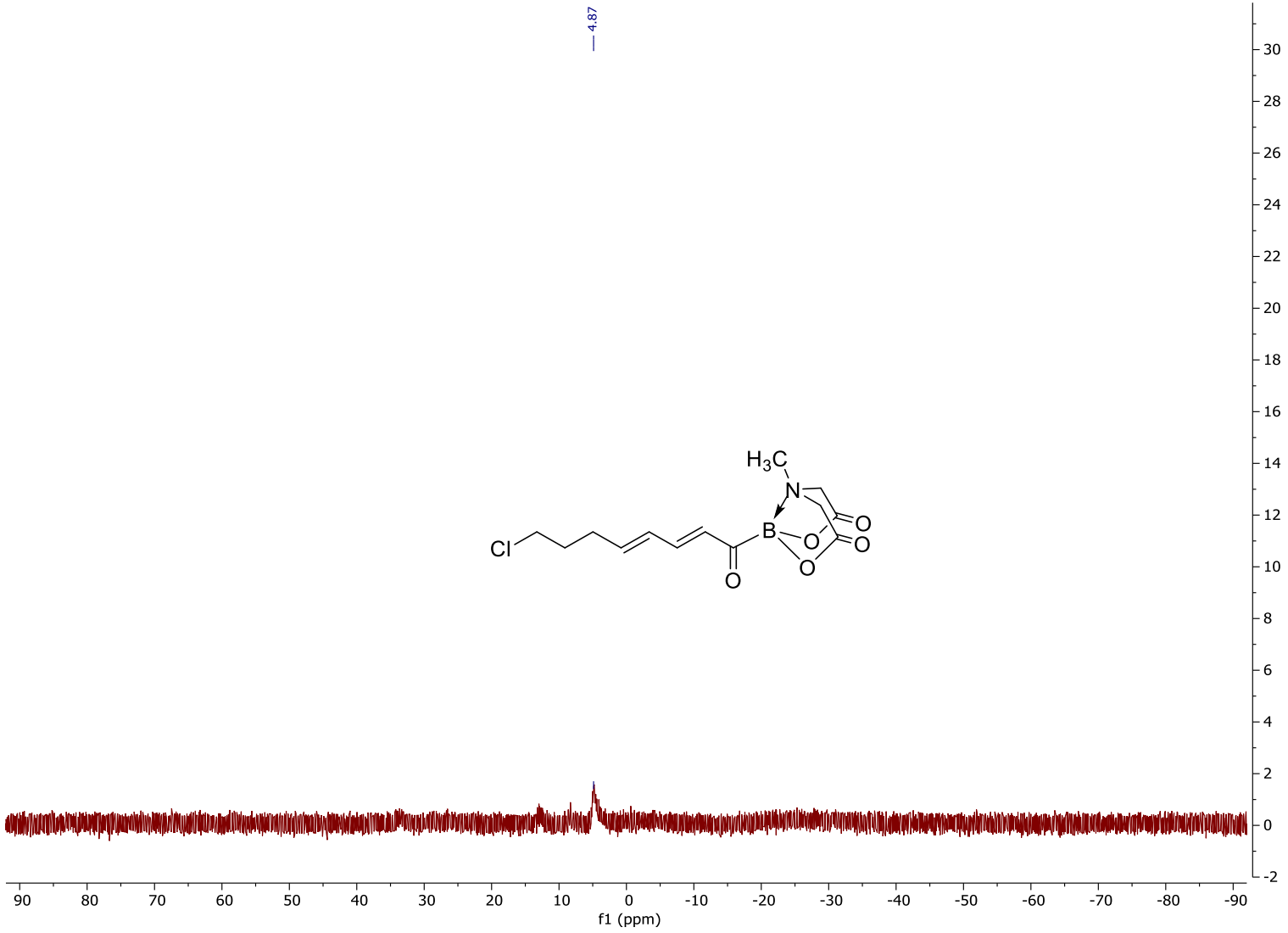


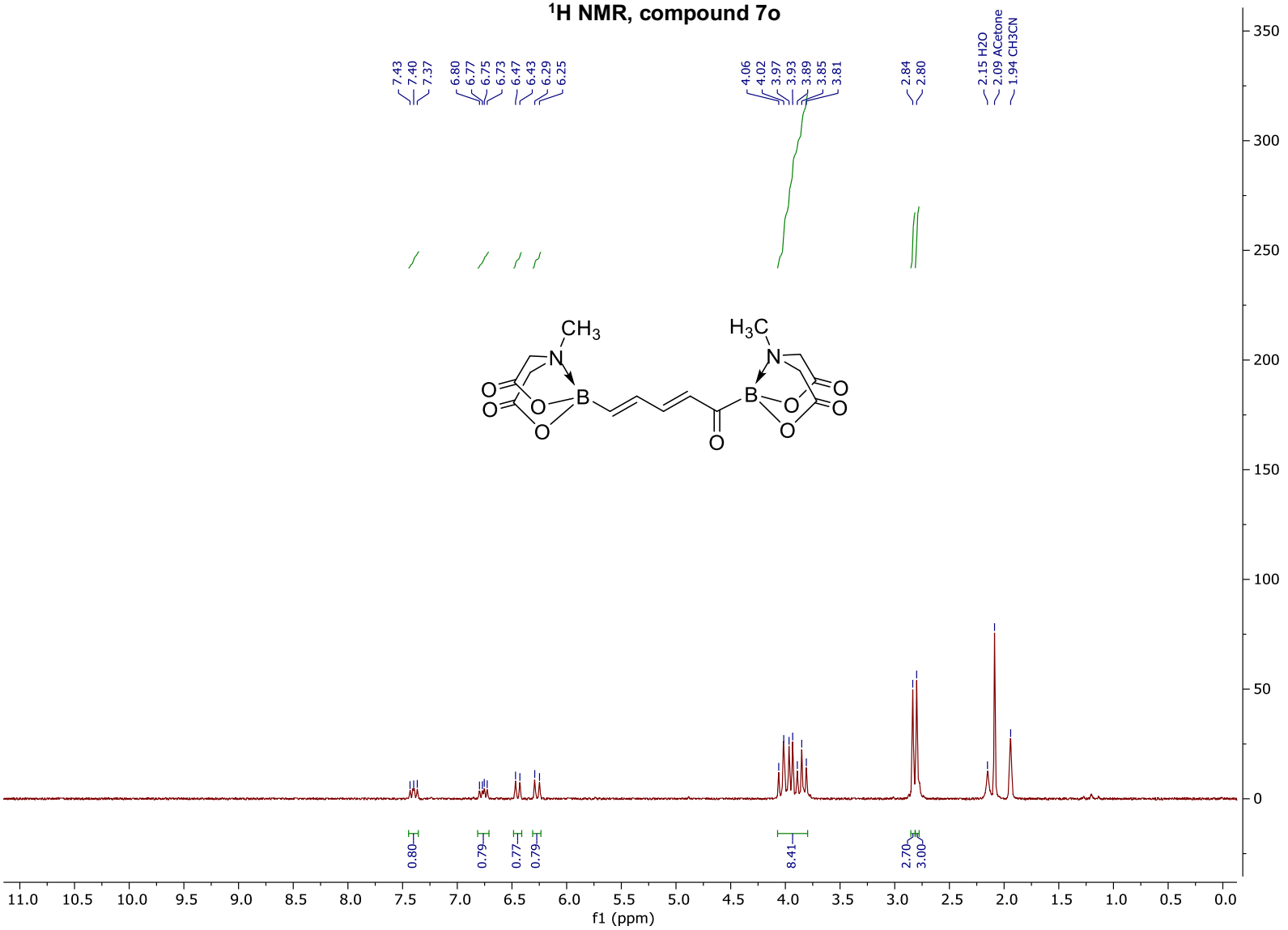

¹H NMR, compound 7n
7.39
7.37
7.36
7.33
6.39
6.35
6.33
6.32
6.31
6.30
4.05
4.01
3.93
3.88
3.62
3.60
3.58
2.81
2.36
2.35
2.33
2.32
2.31
1.94 CH3CN
1.94
1.92
1.90
1.88
1.86
H3C
N
B
O
O
O
O
O
Cl
0.84
0.86
1.69
2.37
2.20
2.36
3.05
1.81
1.97
f1 (ppm)

^{13}C NMR, compound 7n

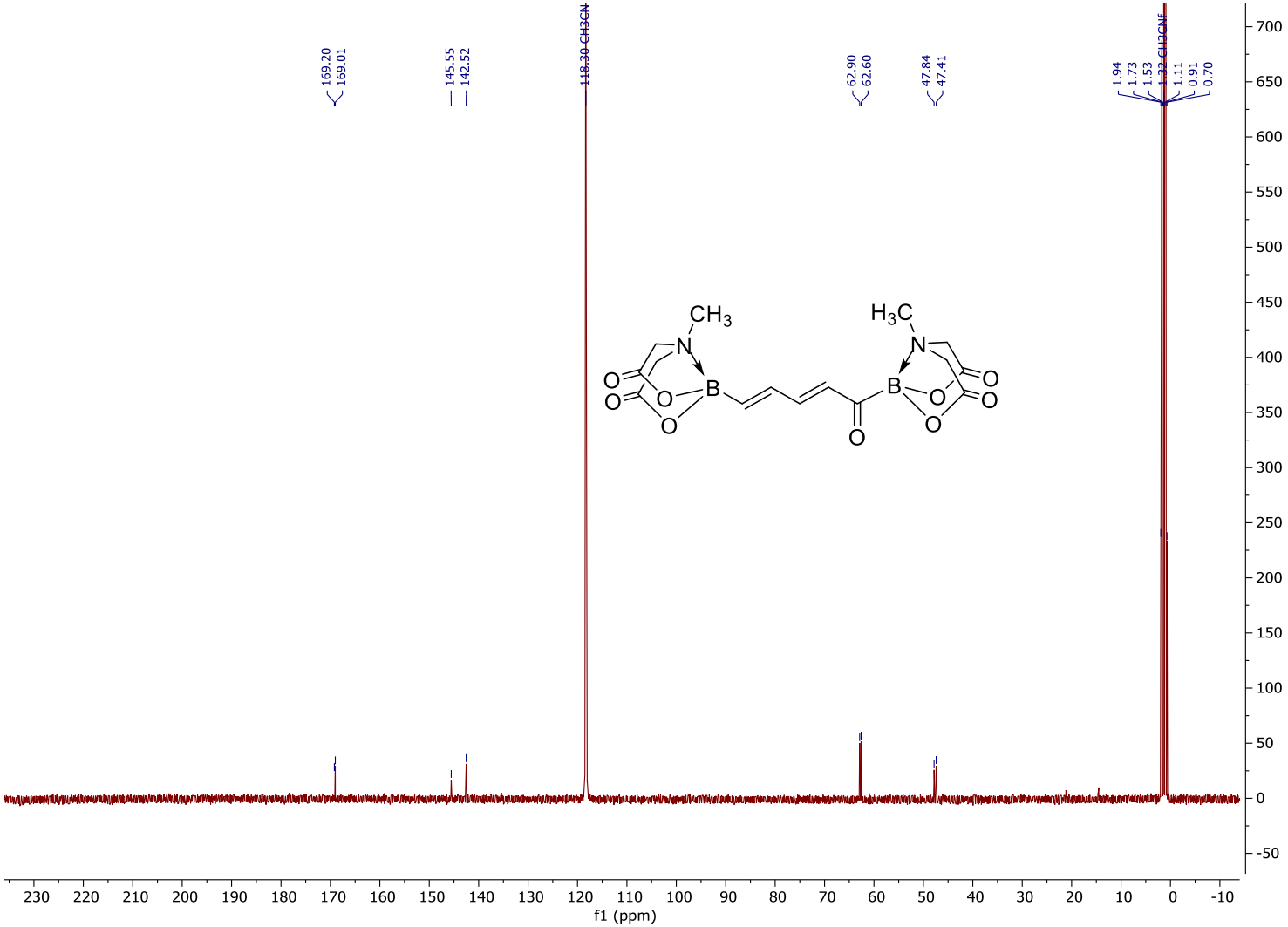


^{11}B NMR, compound 7n

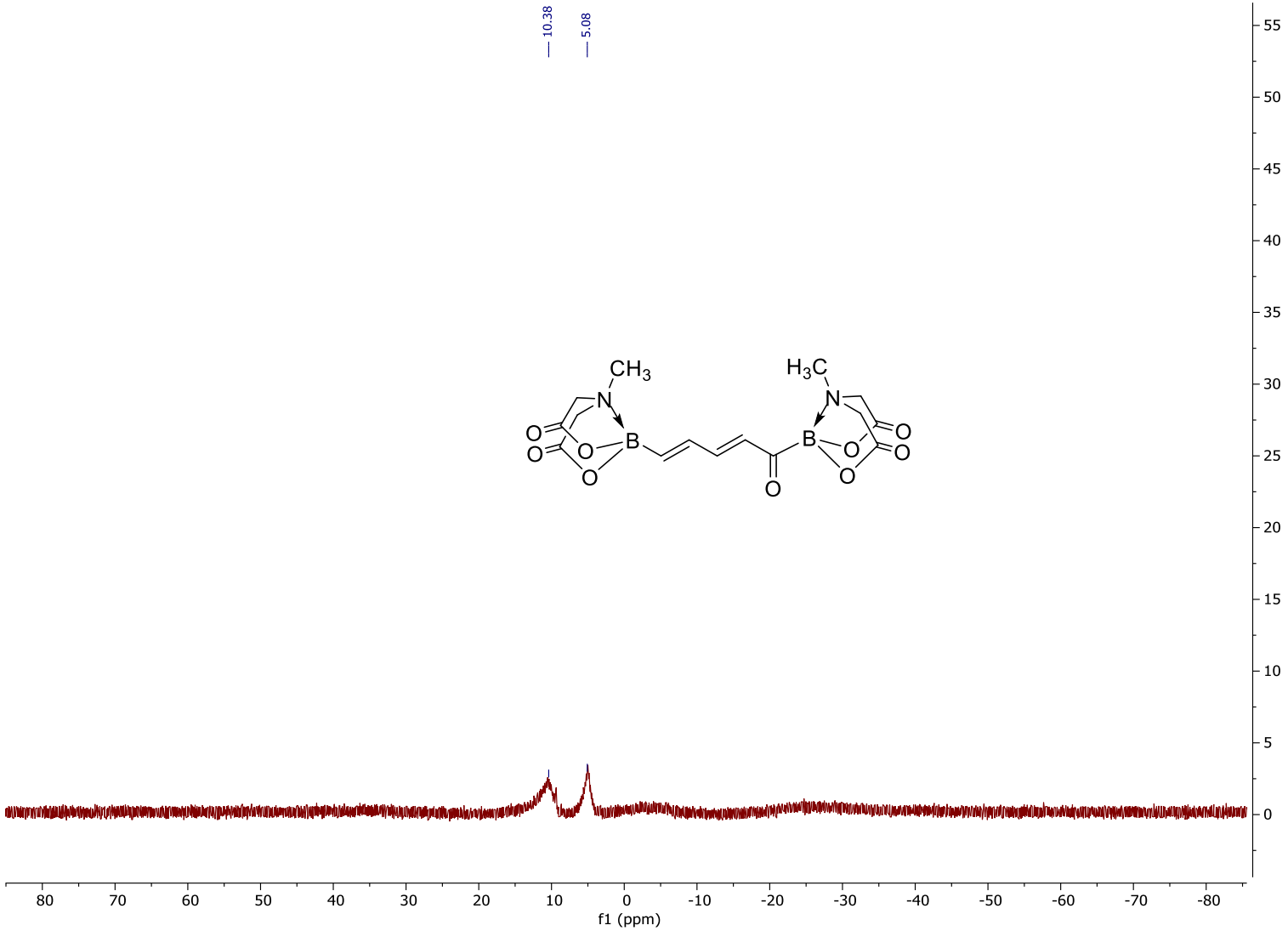



¹H NMR, compound 7o
7.43
7.40
7.37
6.80
6.77
6.75
6.73
6.47
6.43
6.29
6.25
4.06
4.02
3.97
3.93
3.89
3.85
3.81
2.84
2.80
2.15 H2O
2.09 ACetone
1.94 CH3CN
CH3
H3C
N
B
O
0.80
0.79
0.77
0.79
8.41
2.70
3.00
f1 (ppm)

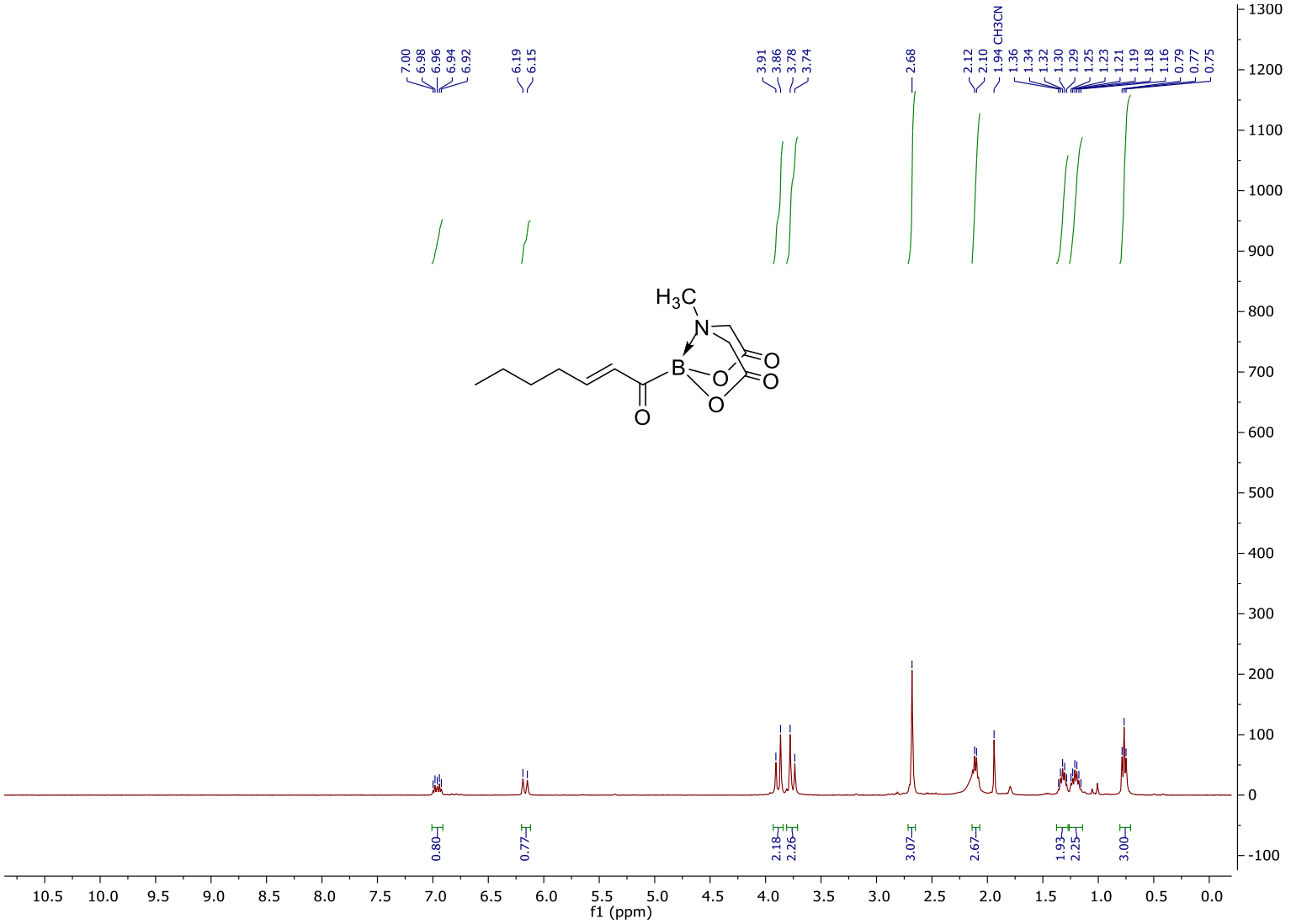
^{13}C NMR, compound 7o



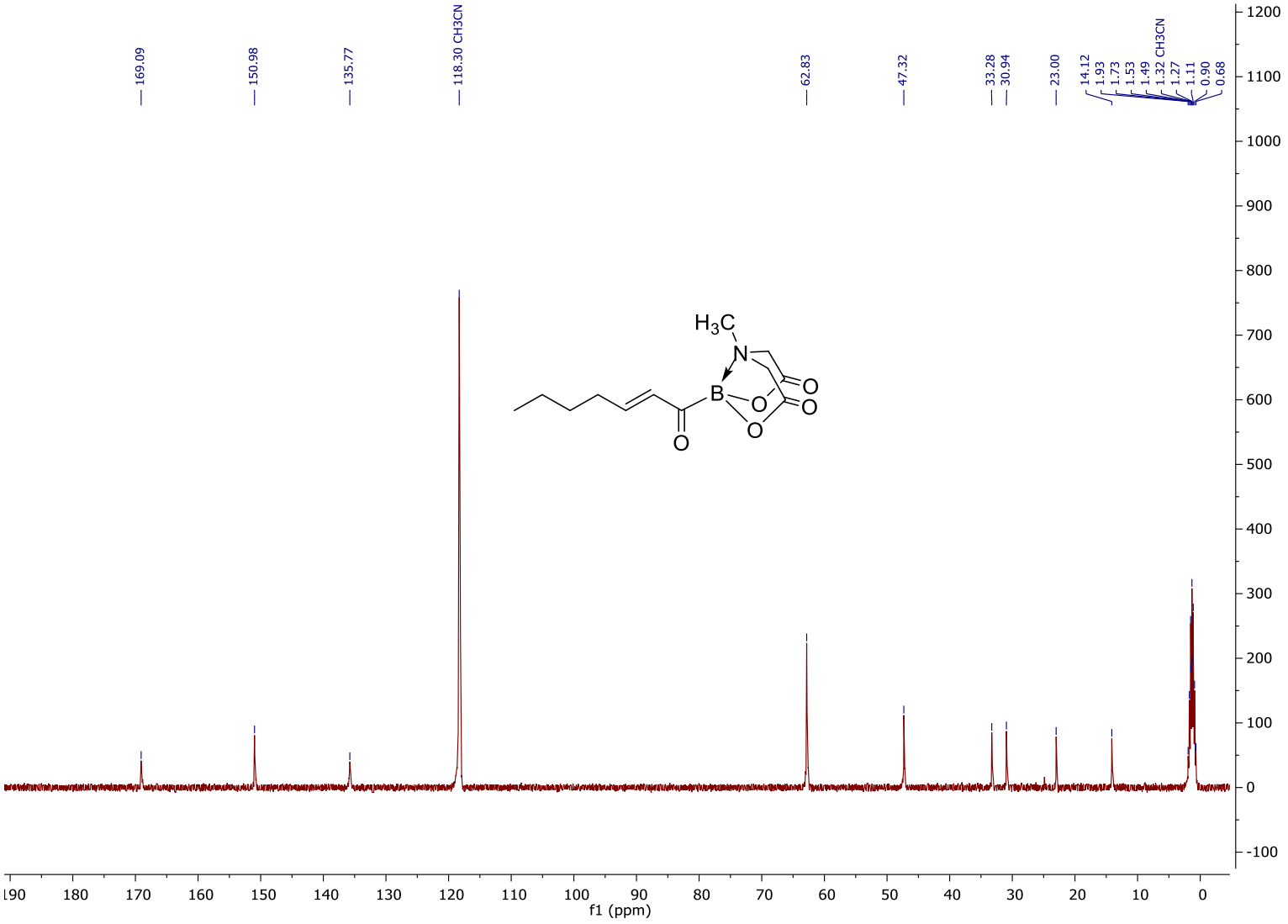
^{11}B NMR, compound 7o



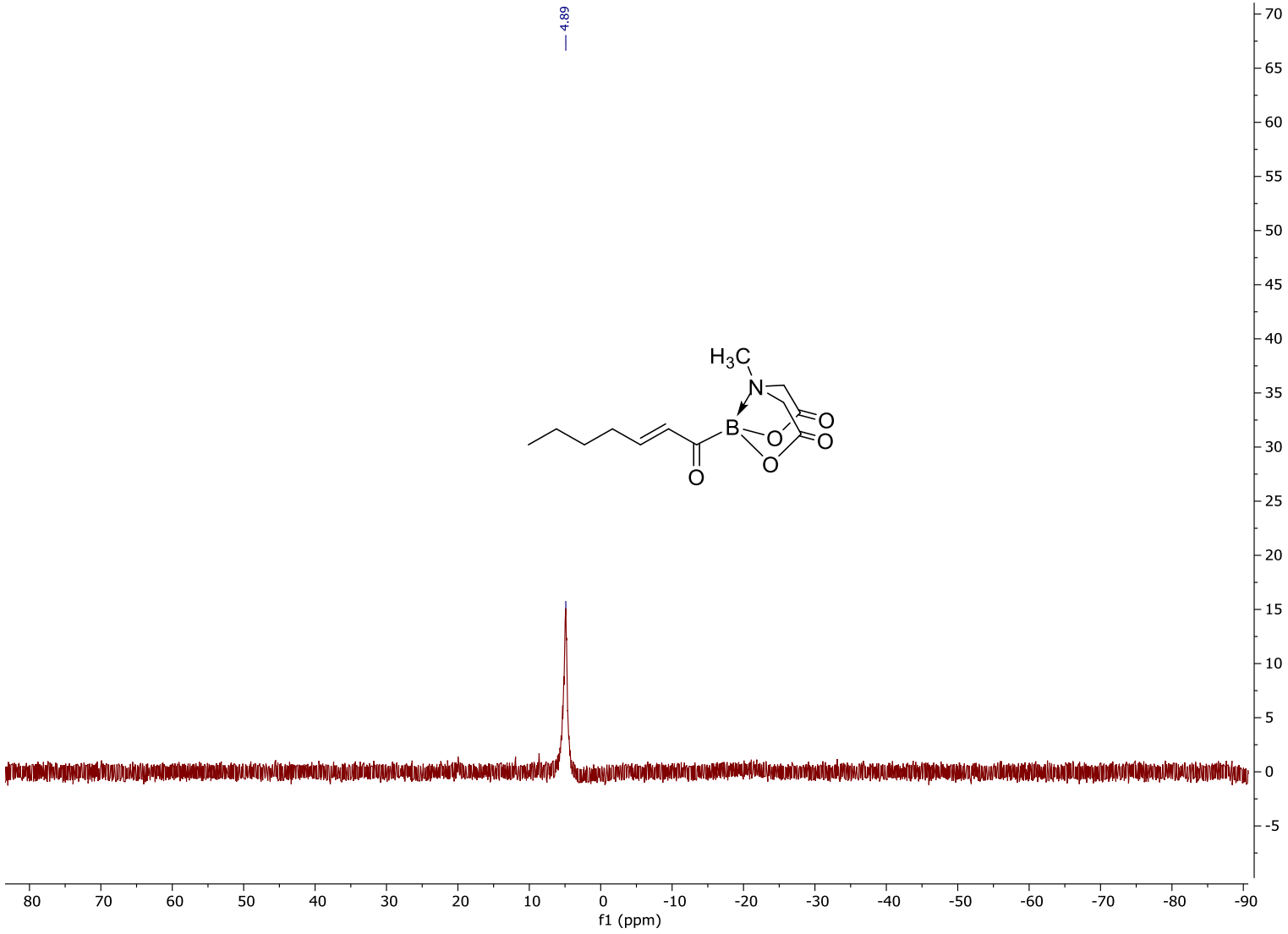
^{1}H NMR, compound 7p



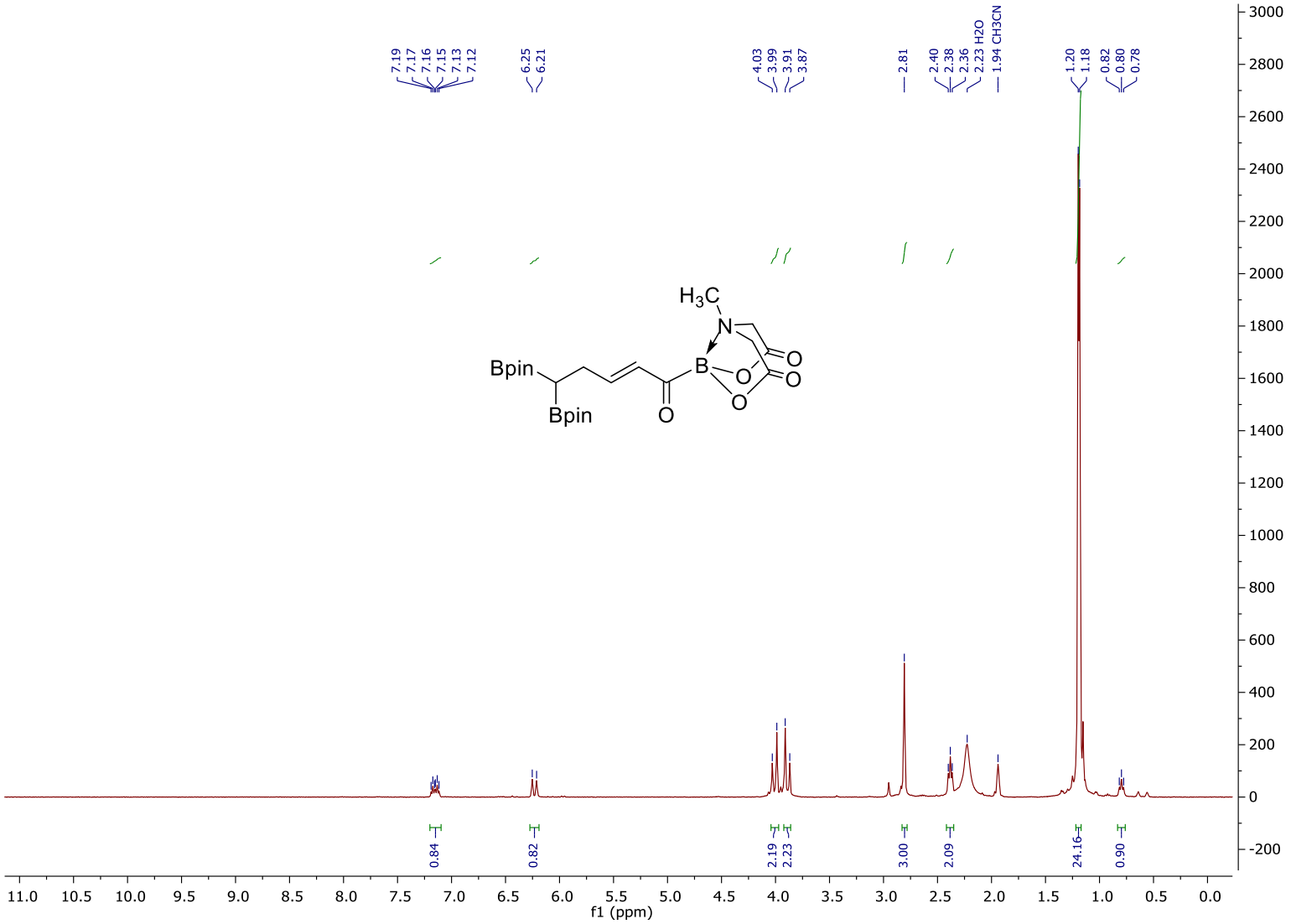
^{13}C NMR, compound 7p



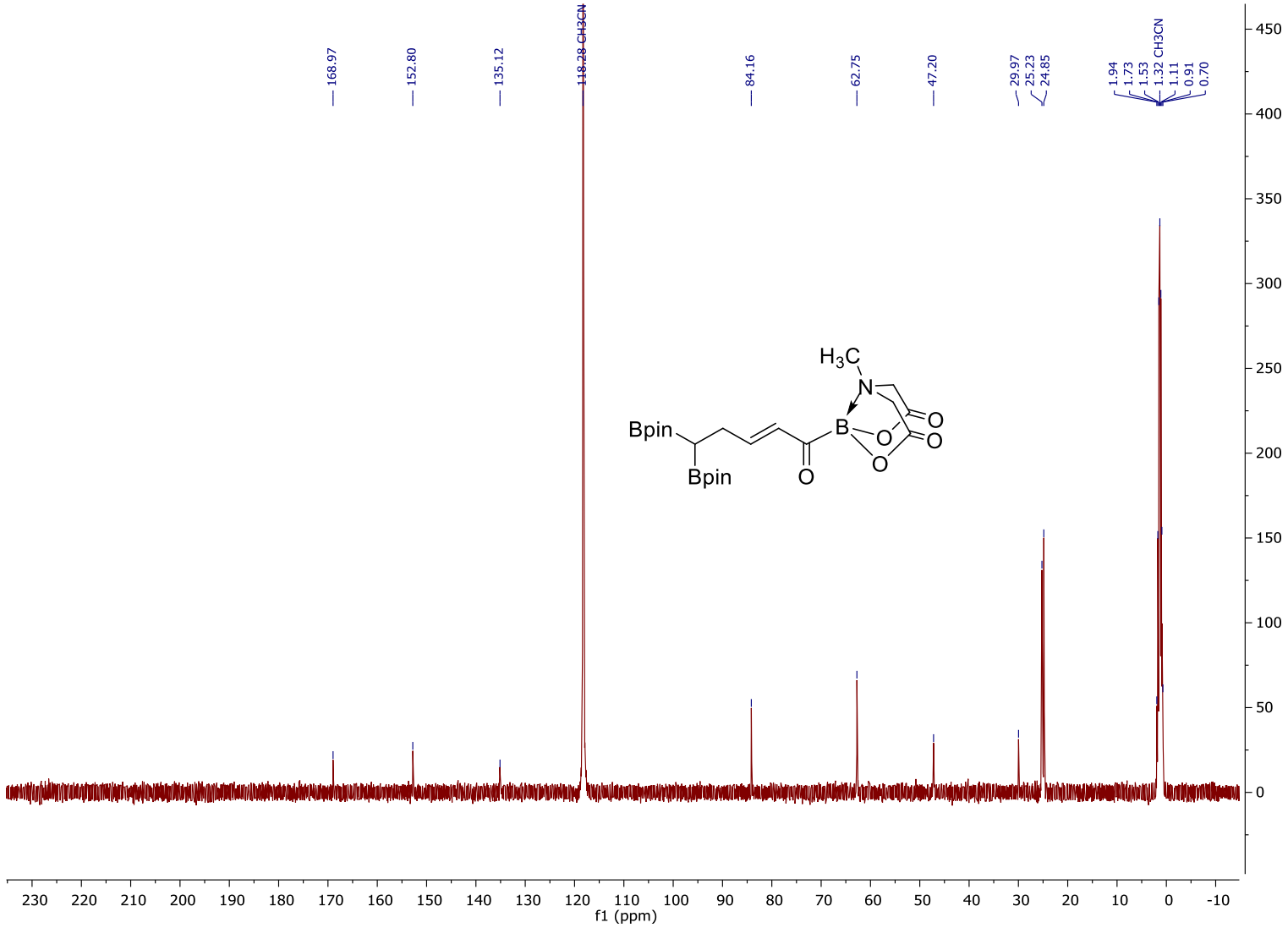
^{11}B NMR, compound 7p



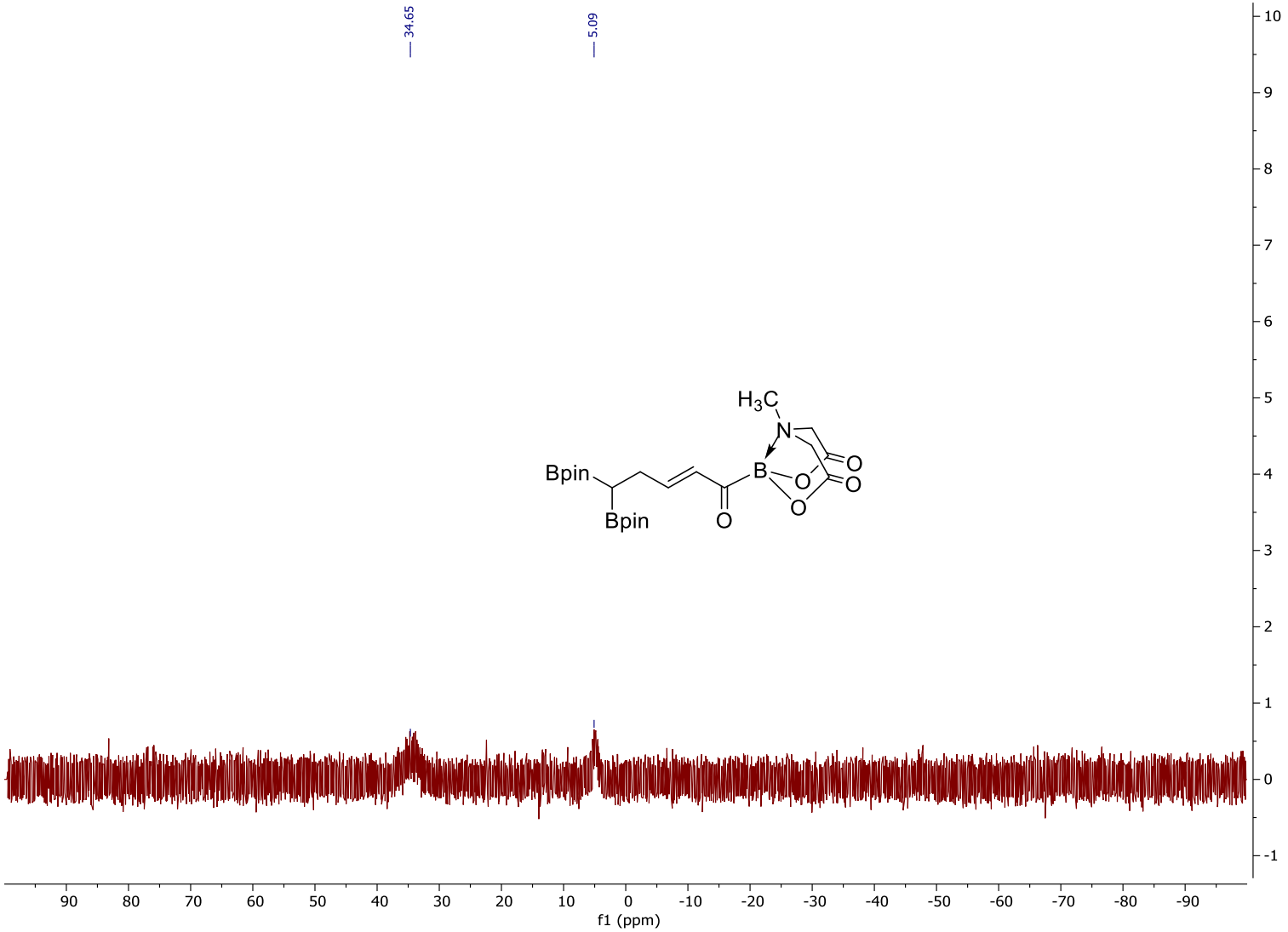
^{1}H NMR, compound 7q

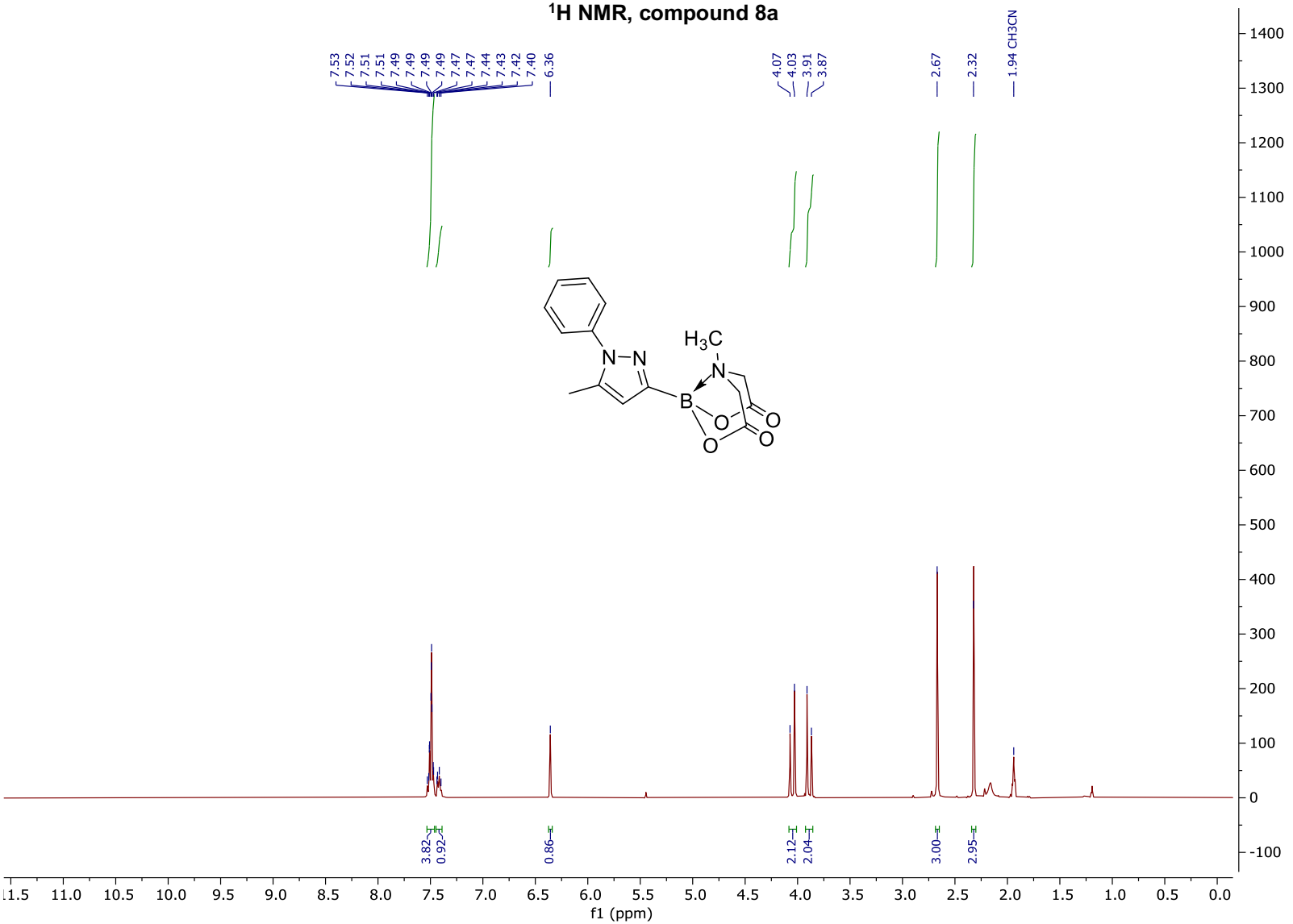


^{13}C NMR, compound 7q

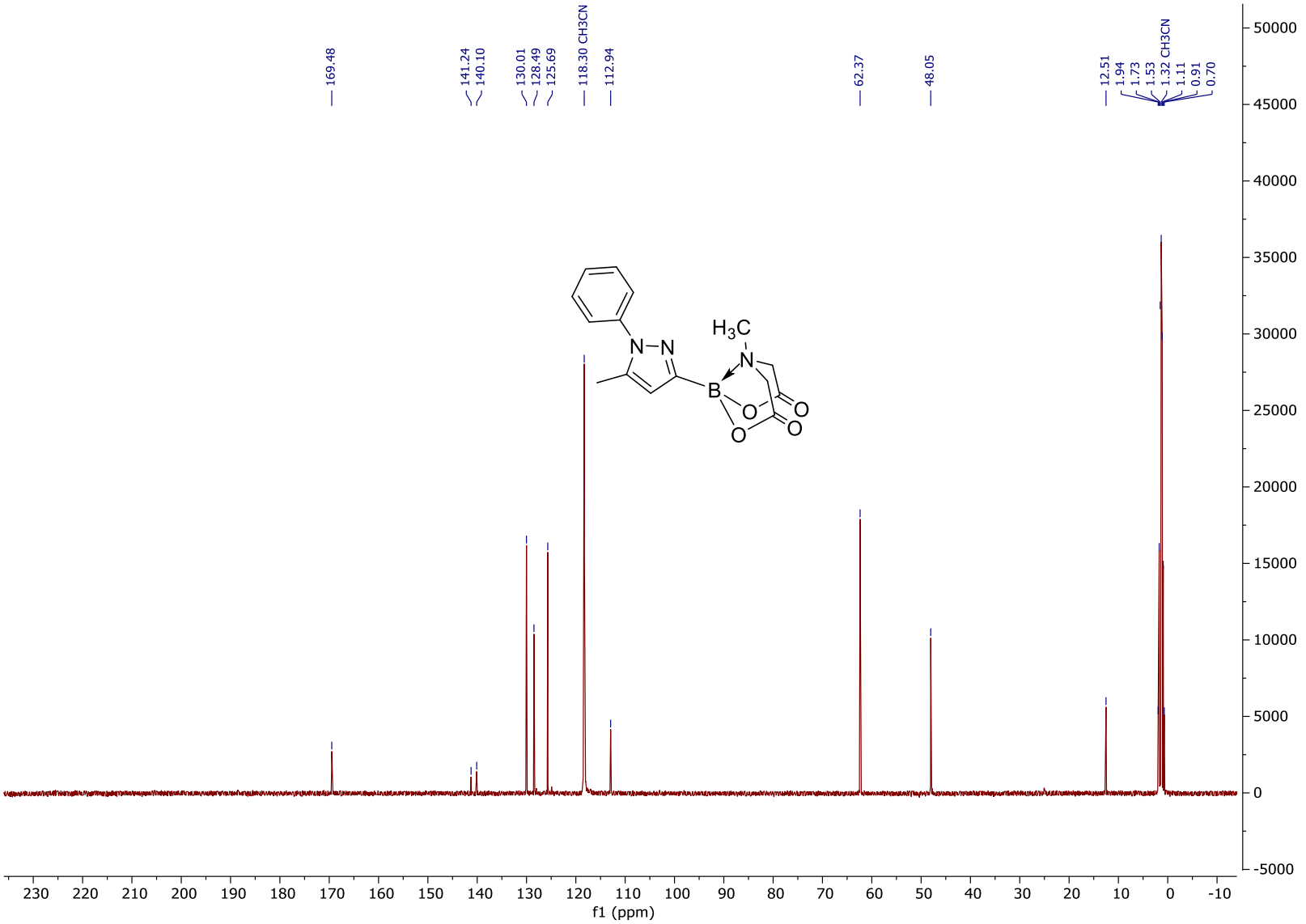


^{11}B NMR, compound 7q

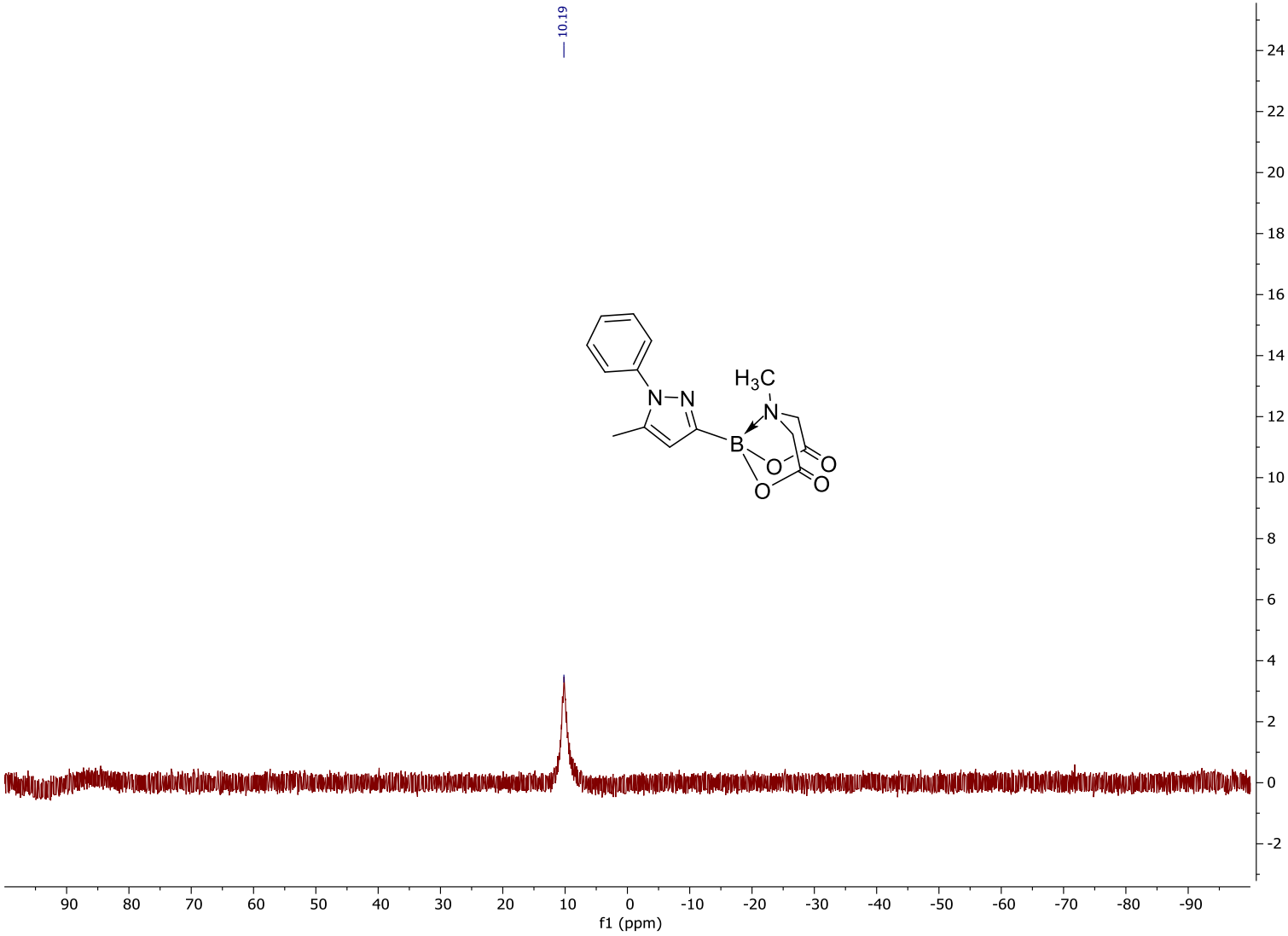



¹H NMR, compound 8a
7.53
7.52
7.51
7.51
7.49
7.49
7.49
7.49
7.47
7.47
7.44
7.43
7.42
7.40
6.36
4.07
4.03
3.91
3.87
2.67
2.32
1.94 CH3CN
H3C
N–N
N
B
O
O
O
O
3.82
0.92
0.86
2.12
2.04
3.00
2.95
f1 (ppm)

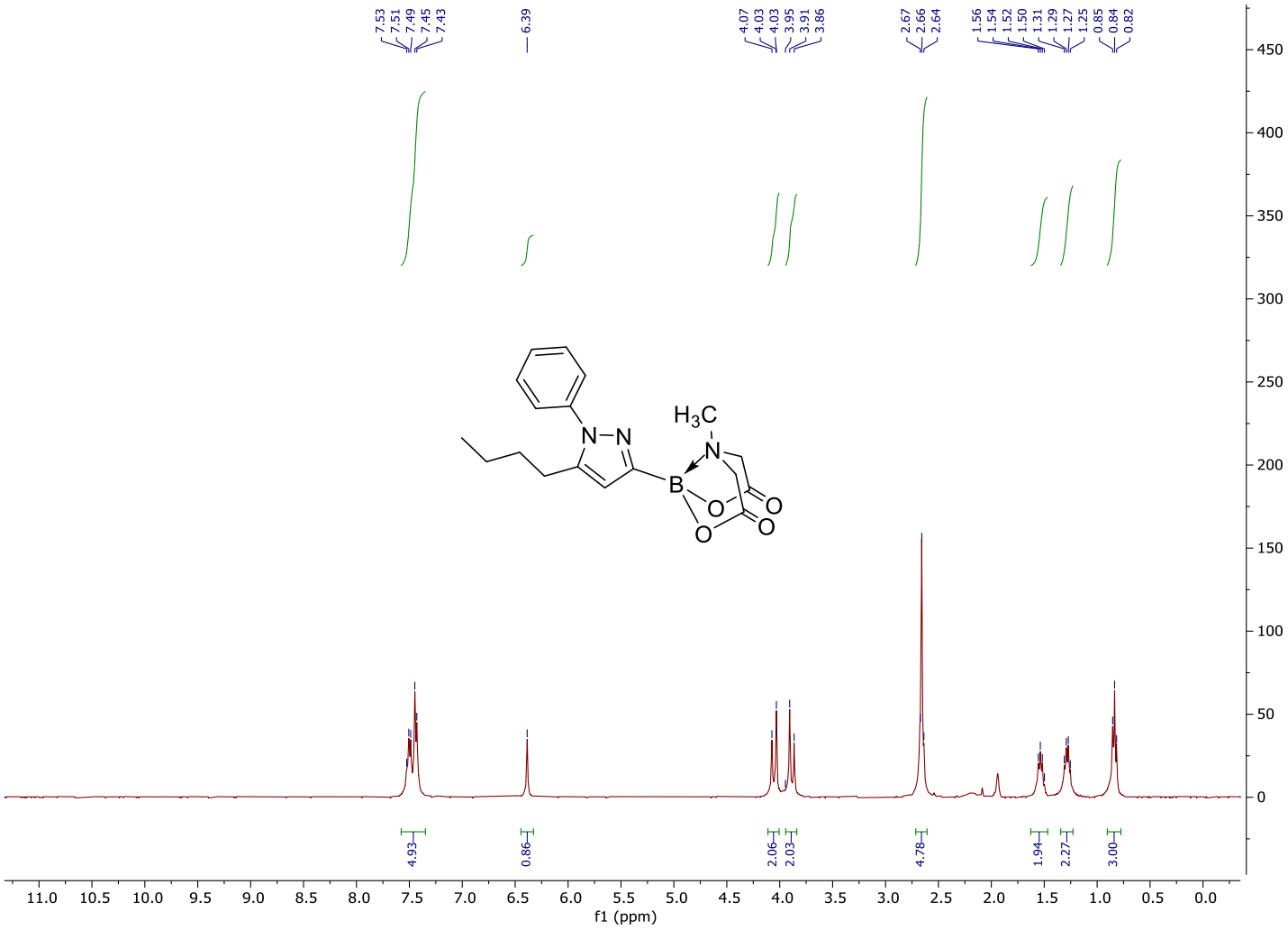
^{13}C NMR, compound 8a



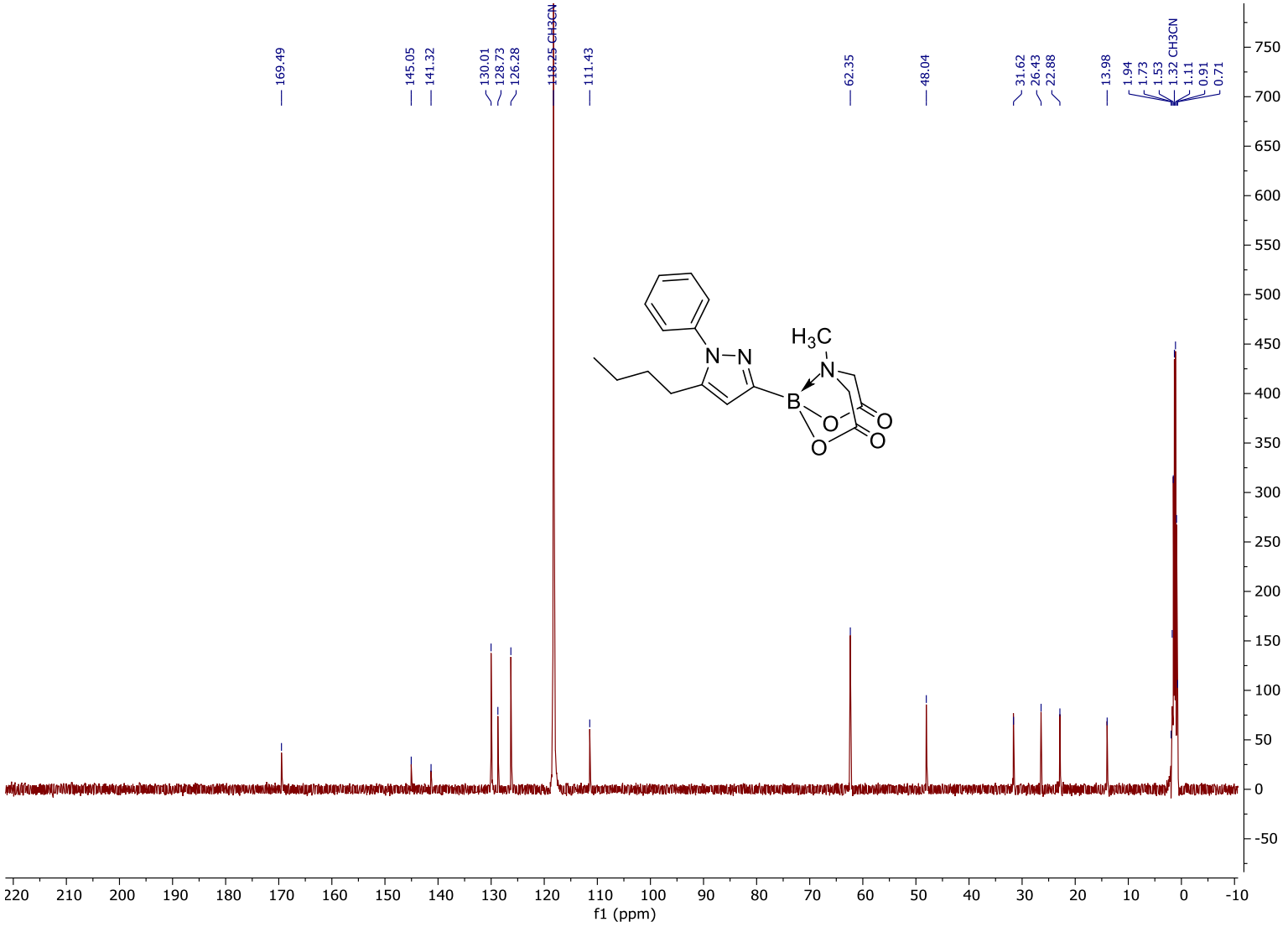
^{11}B NMR, compound 8a



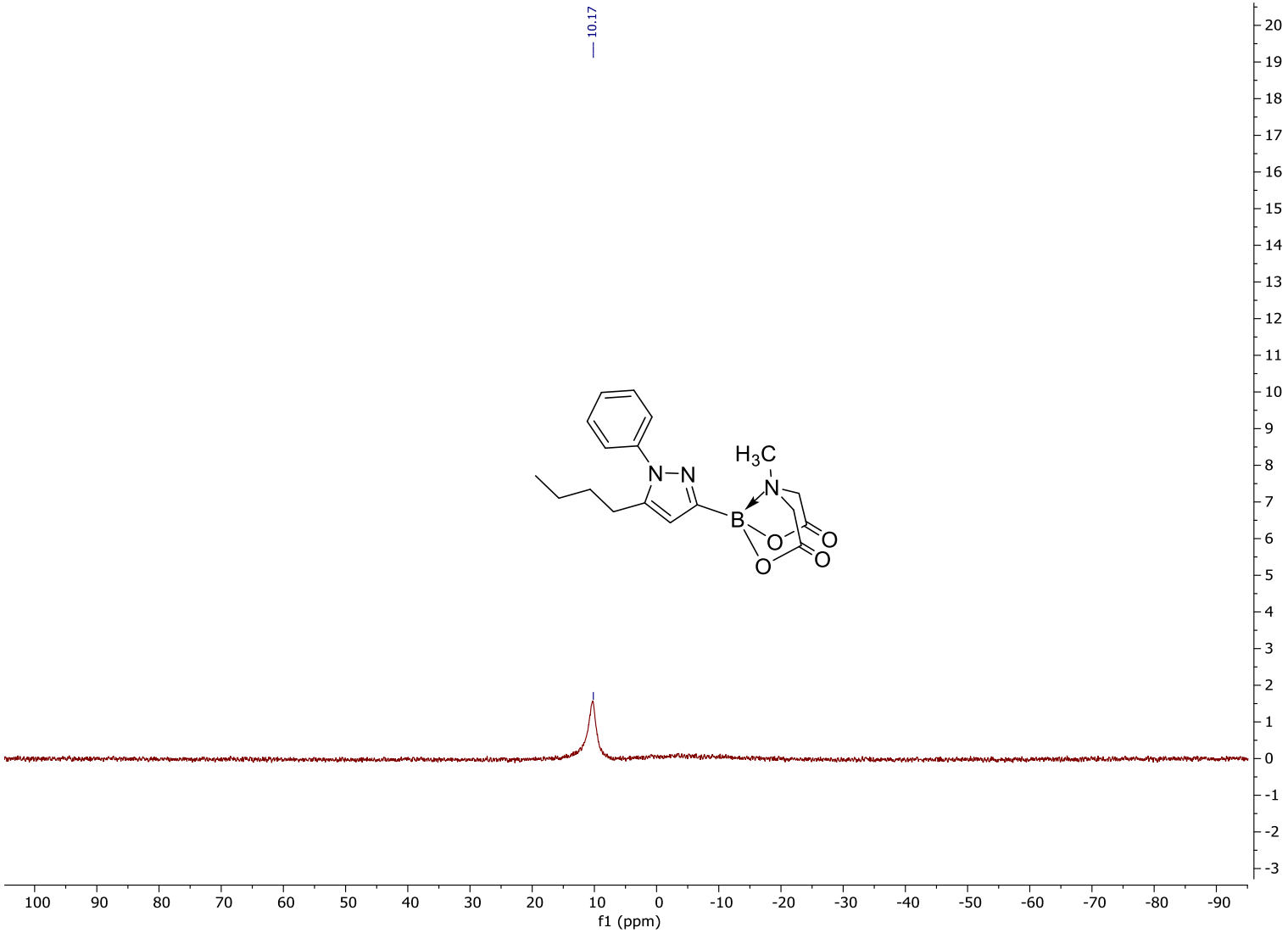
^{1}H NMR, compound 8b



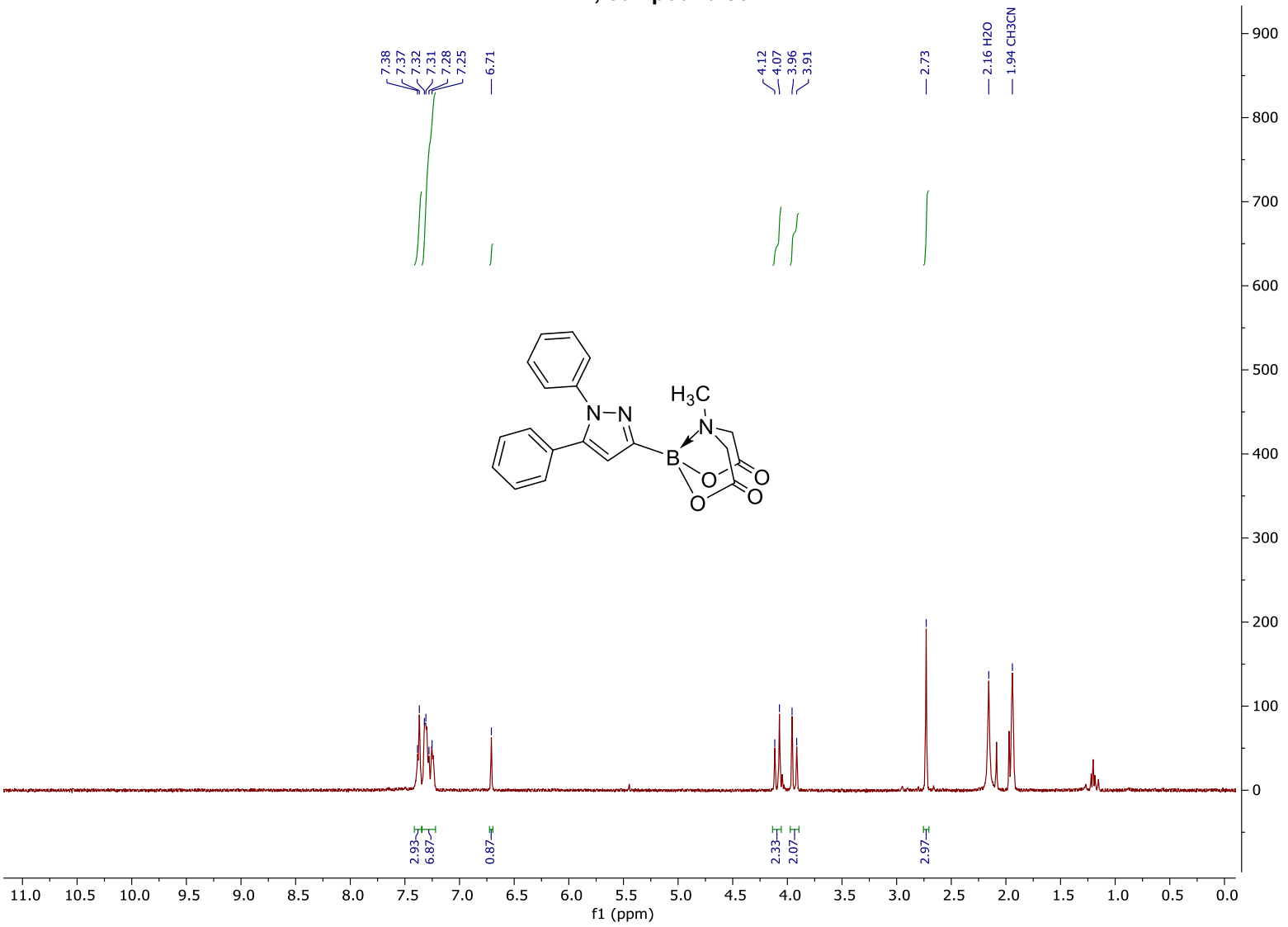
^{13}C NMR, compound 8b



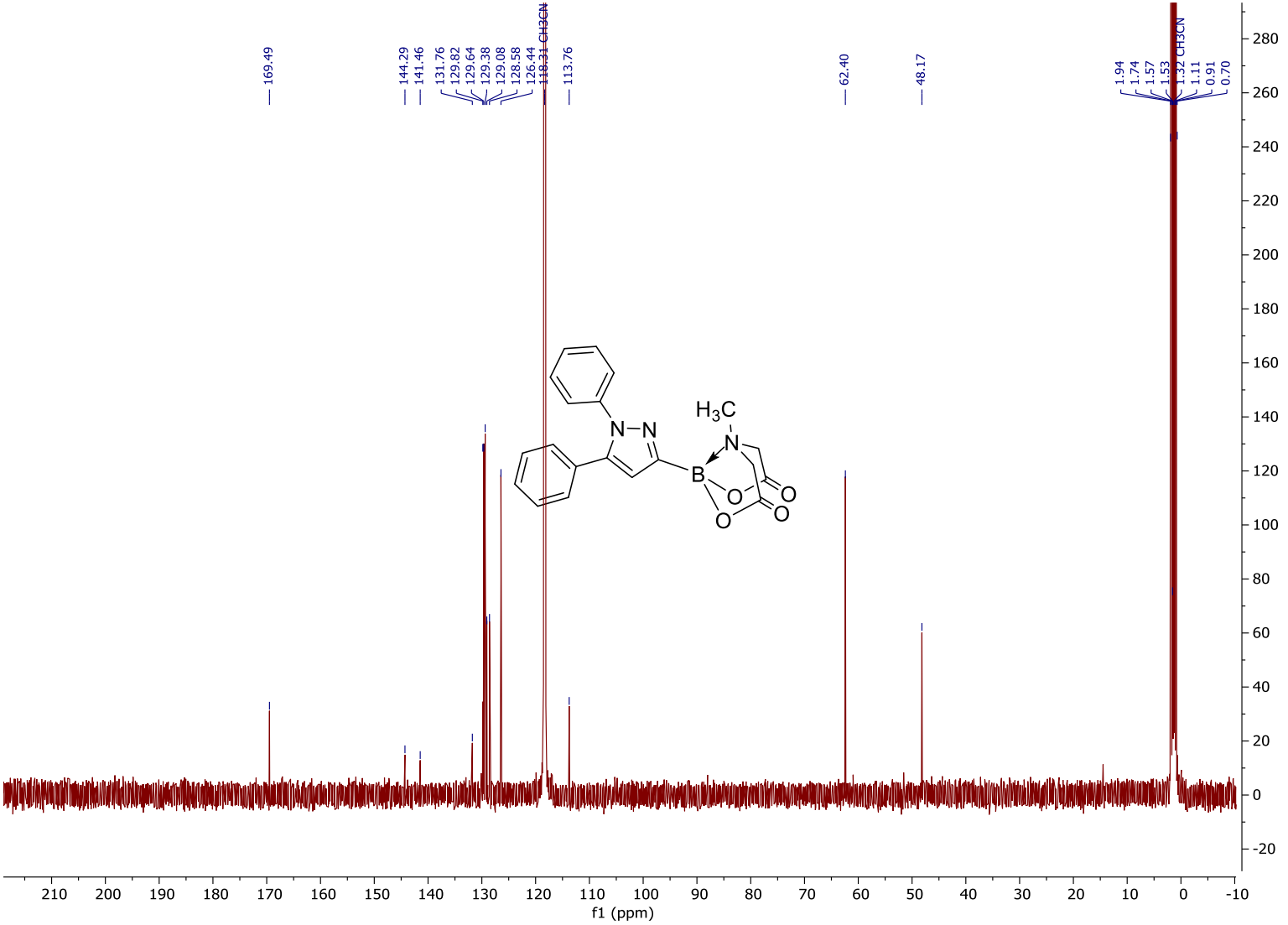
^{11}B NMR, compound 8b



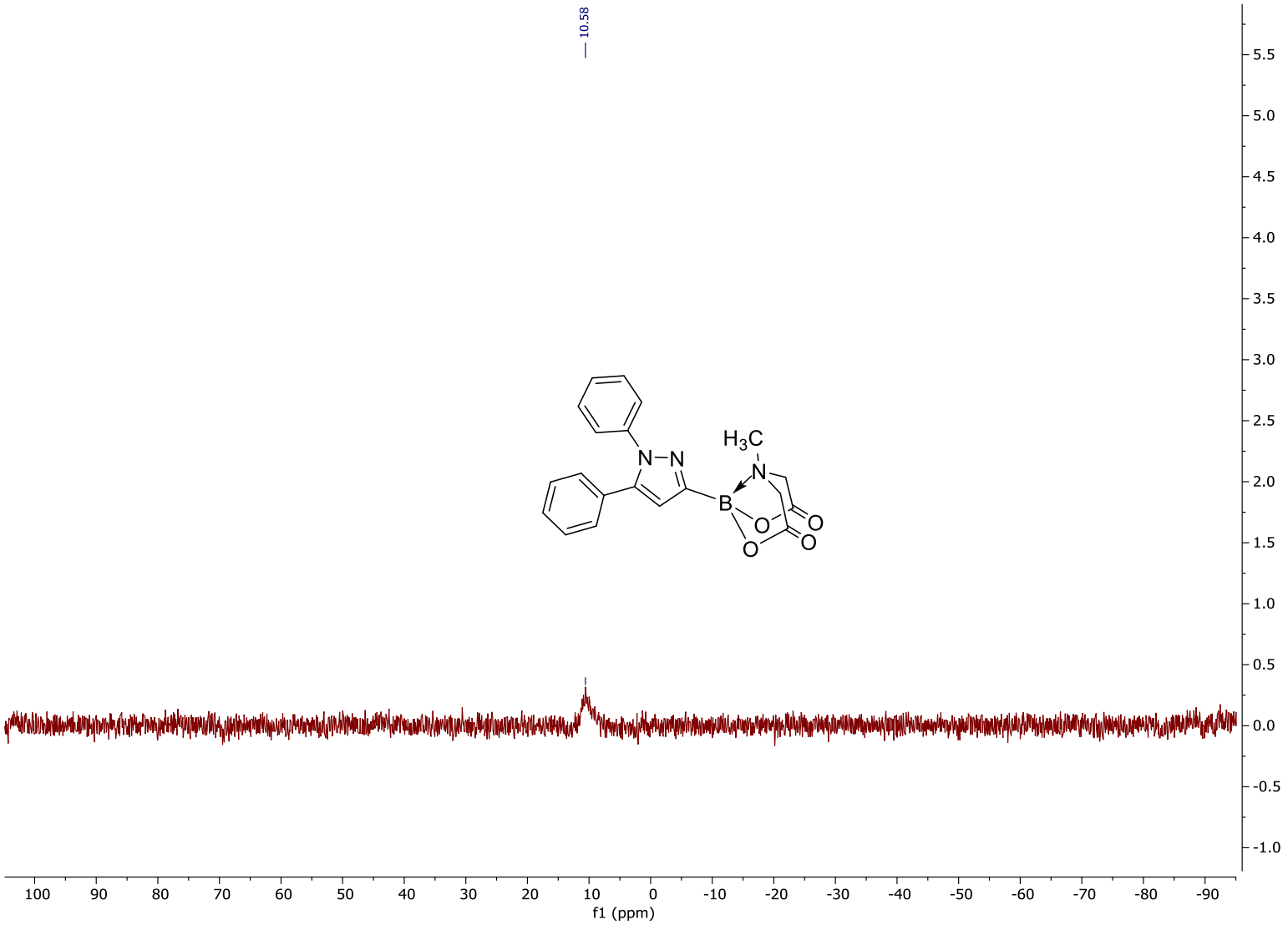
^{1}H NMR, compound 8c



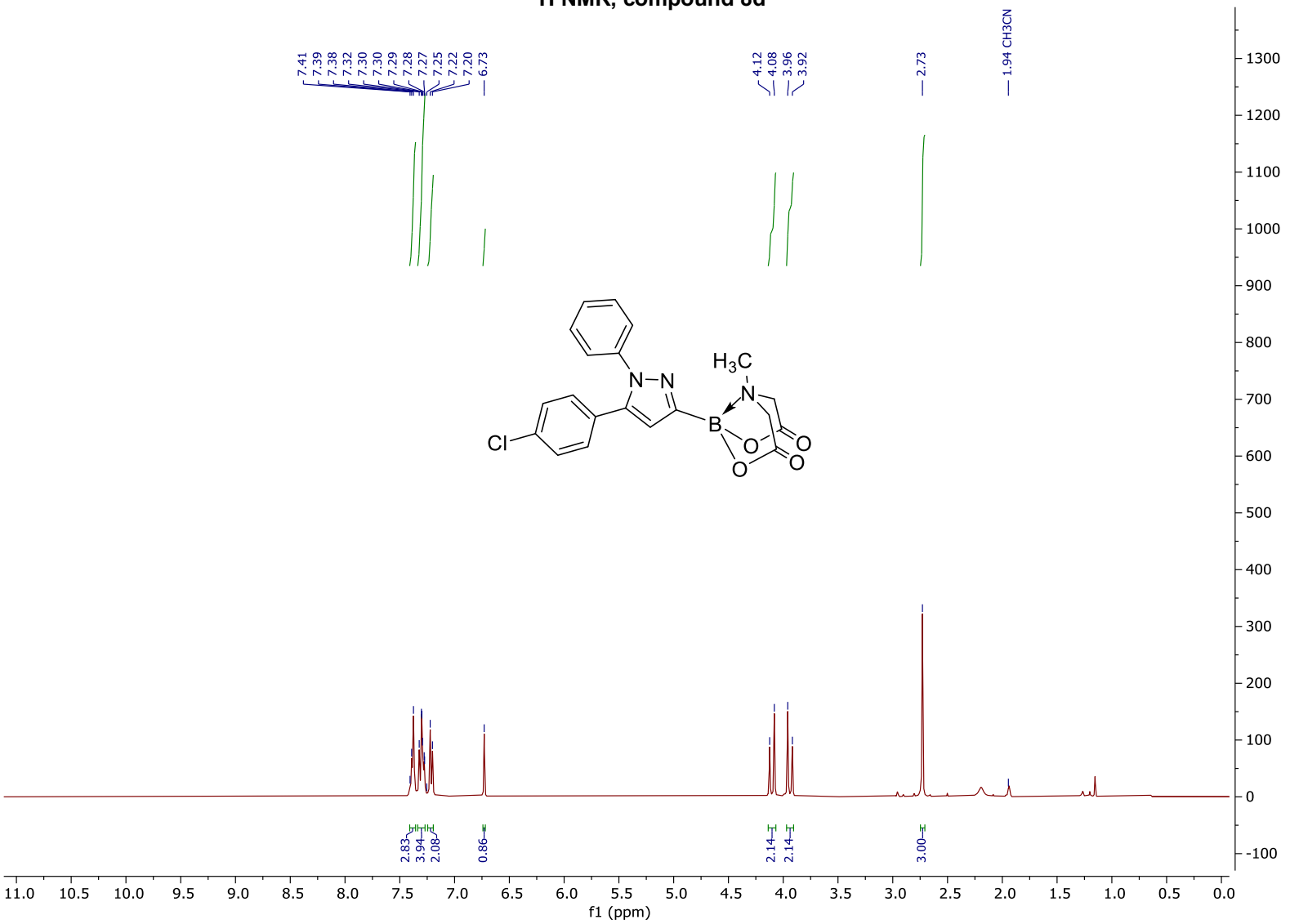
^{13}C NMR, compound 8c



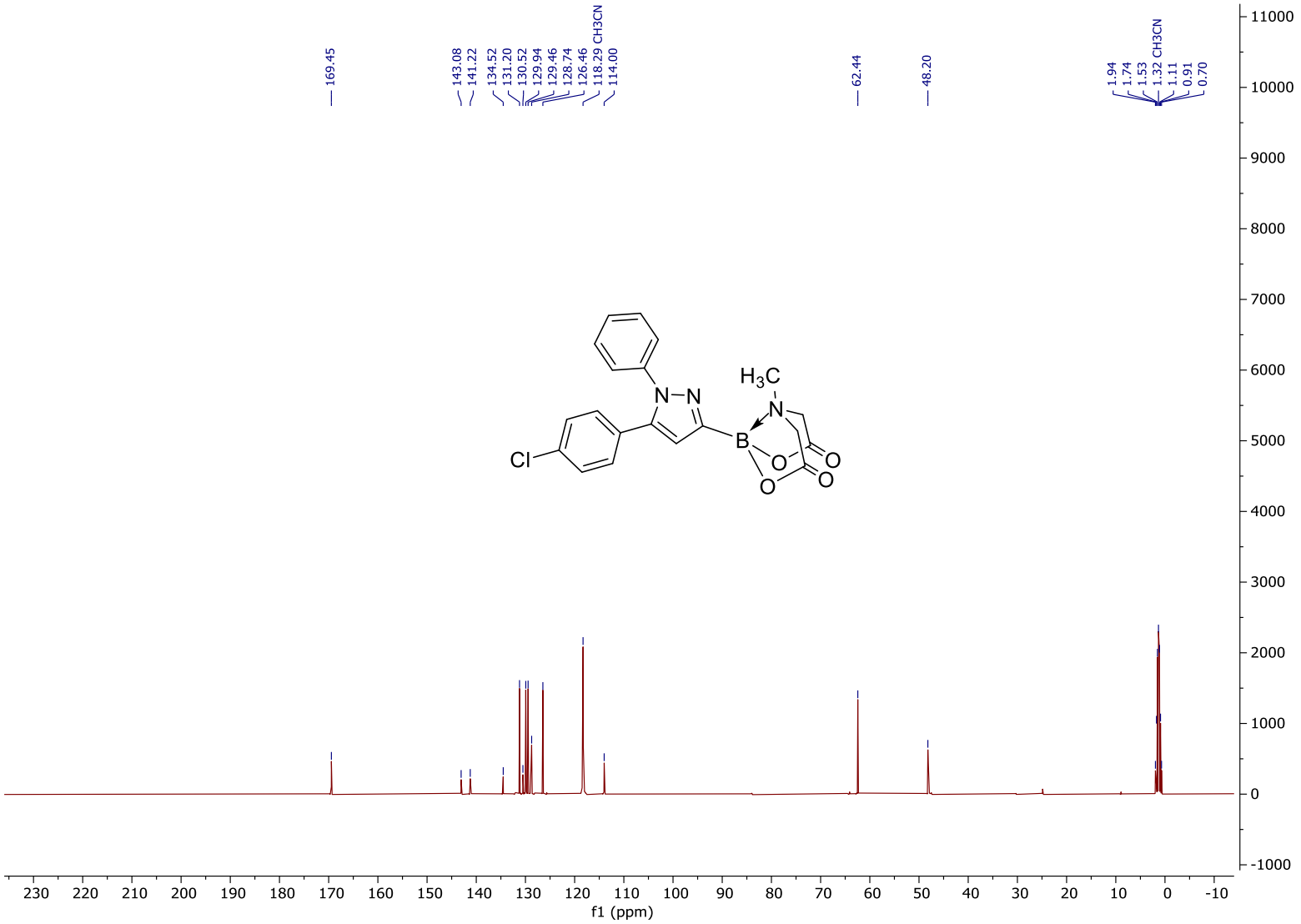
^{11}B NMR, compound 8c



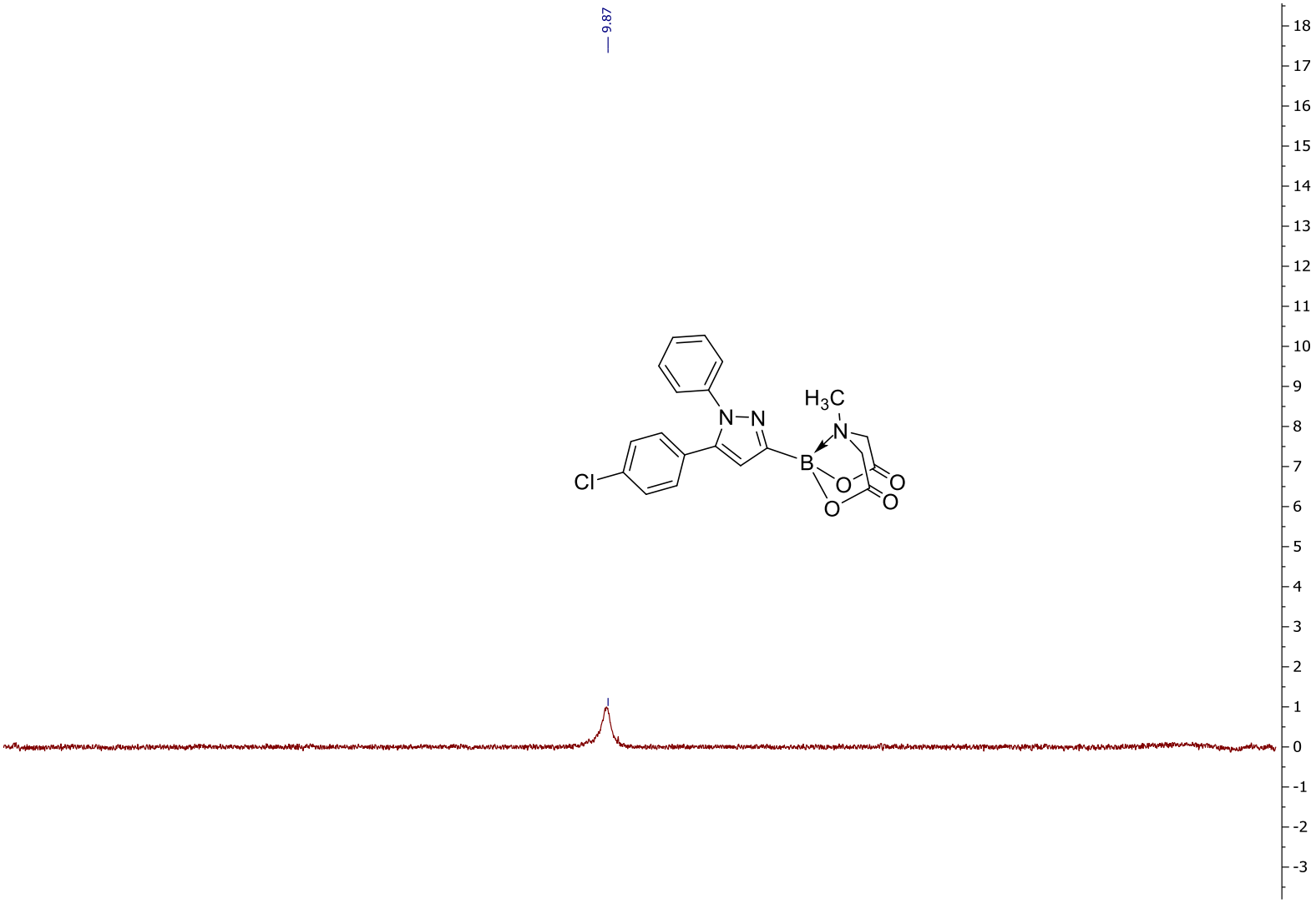
^{1}H NMR, compound 8d



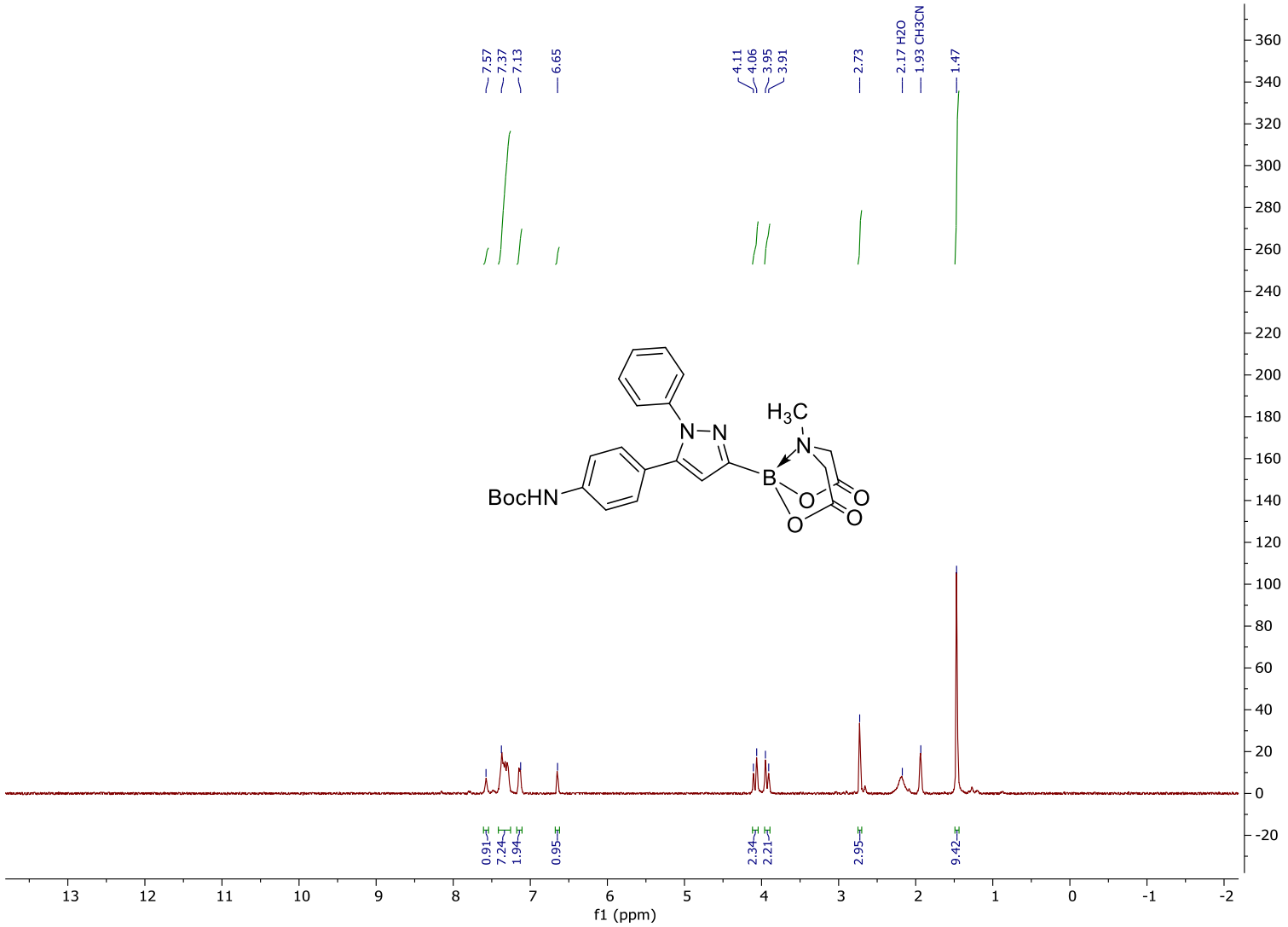
^{13}C NMR, compound 8d



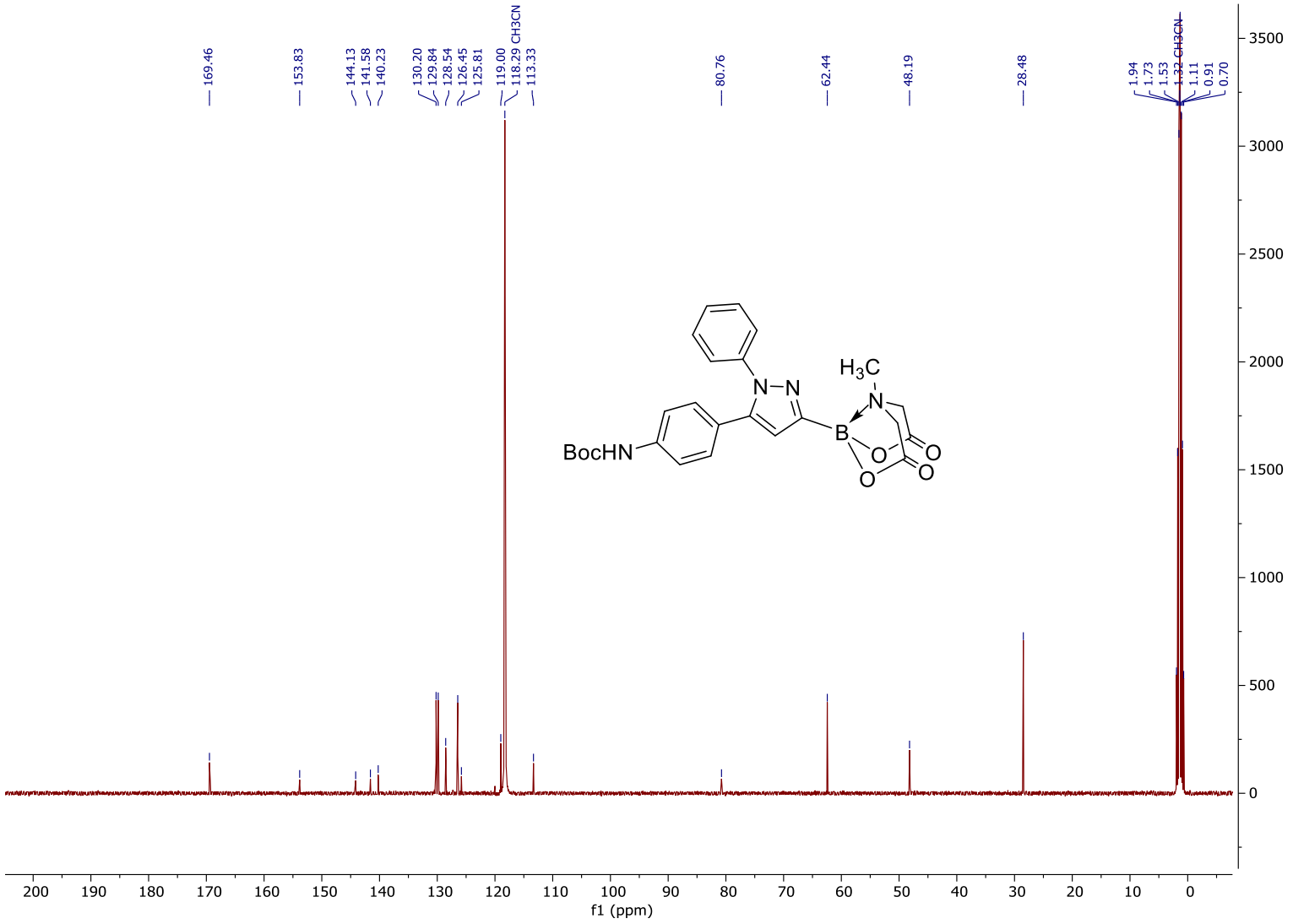
^{11}B NMR, compound 8d



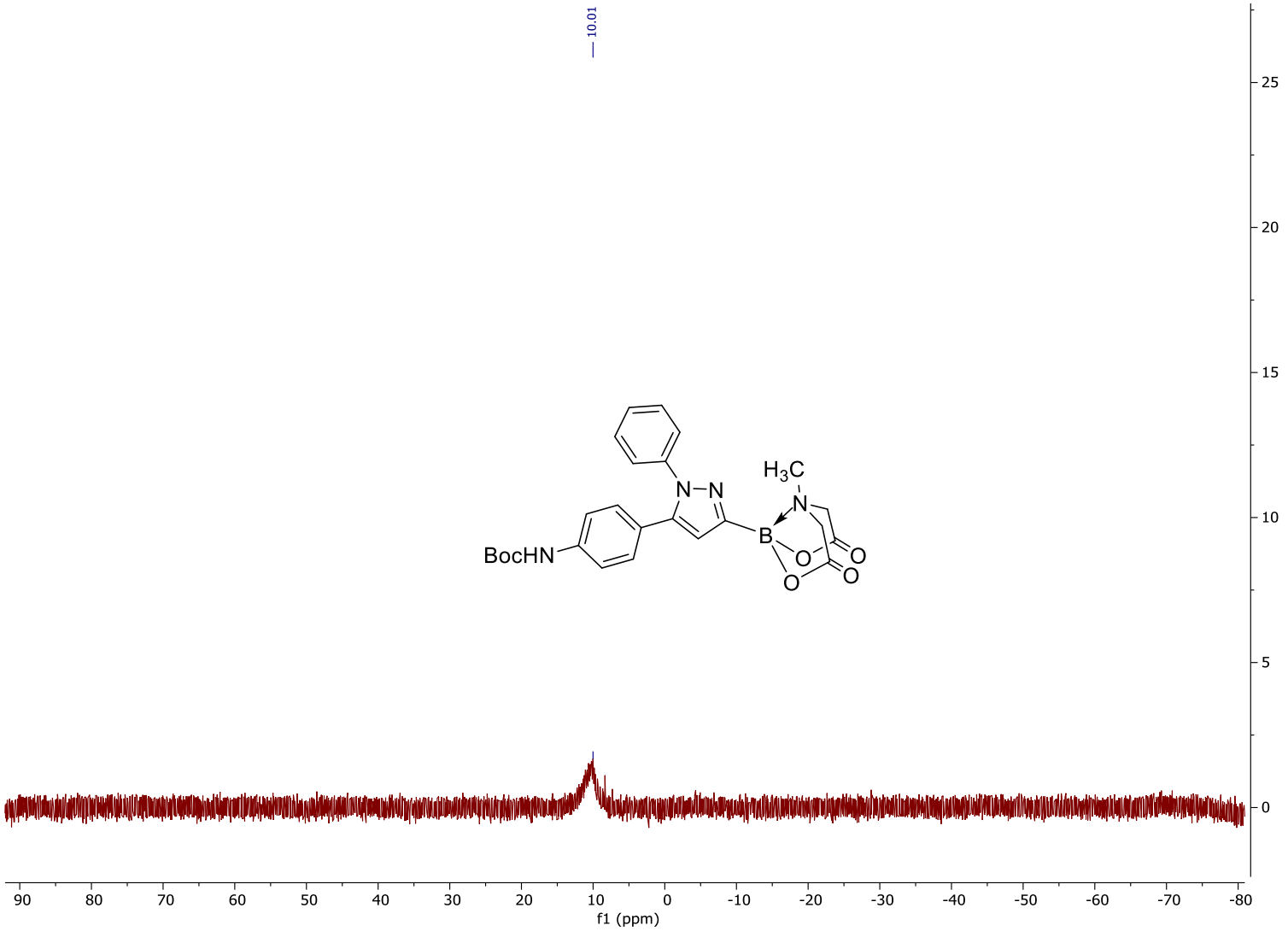
^{1}H NMR, compound 8e



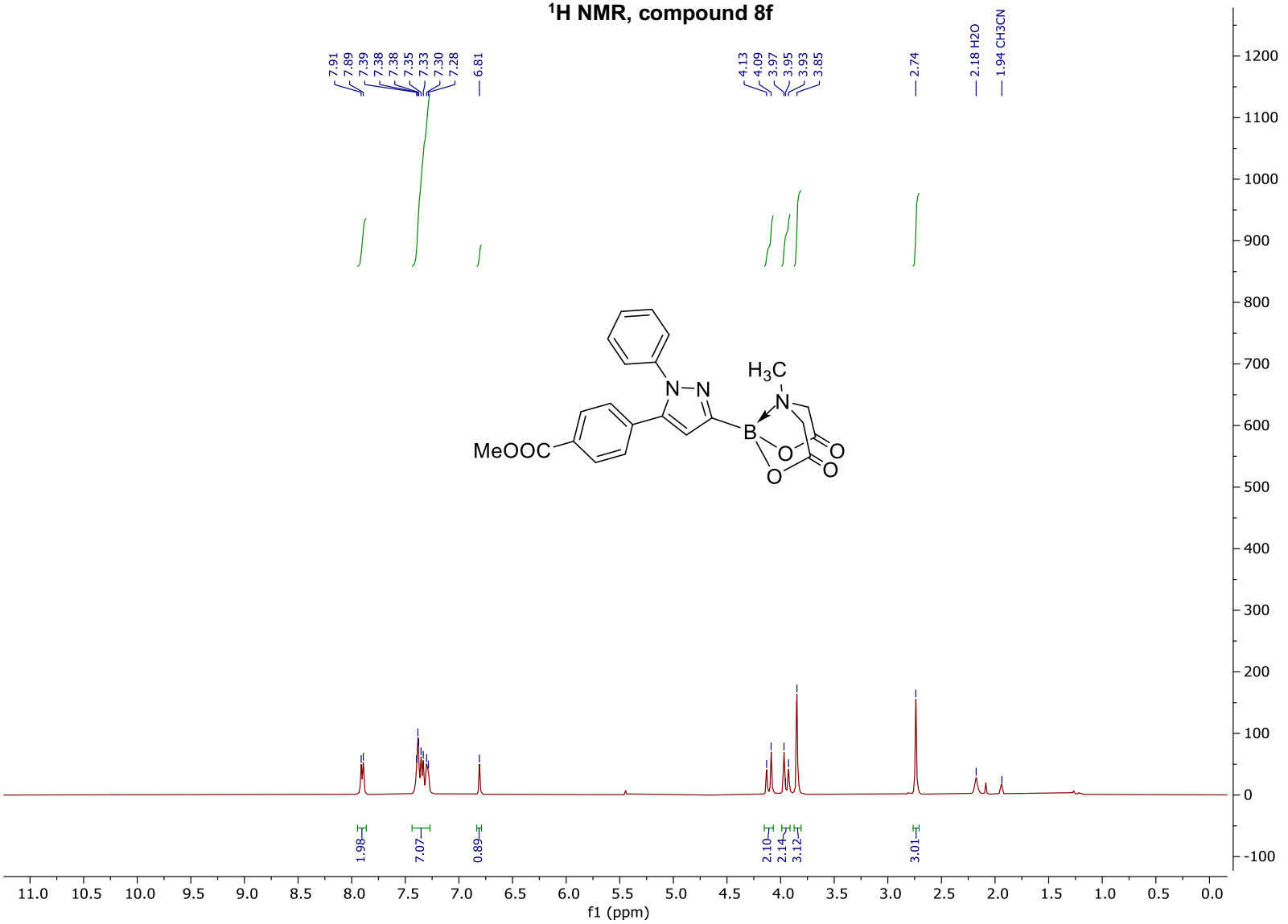
^{13}C NMR, compound 8e



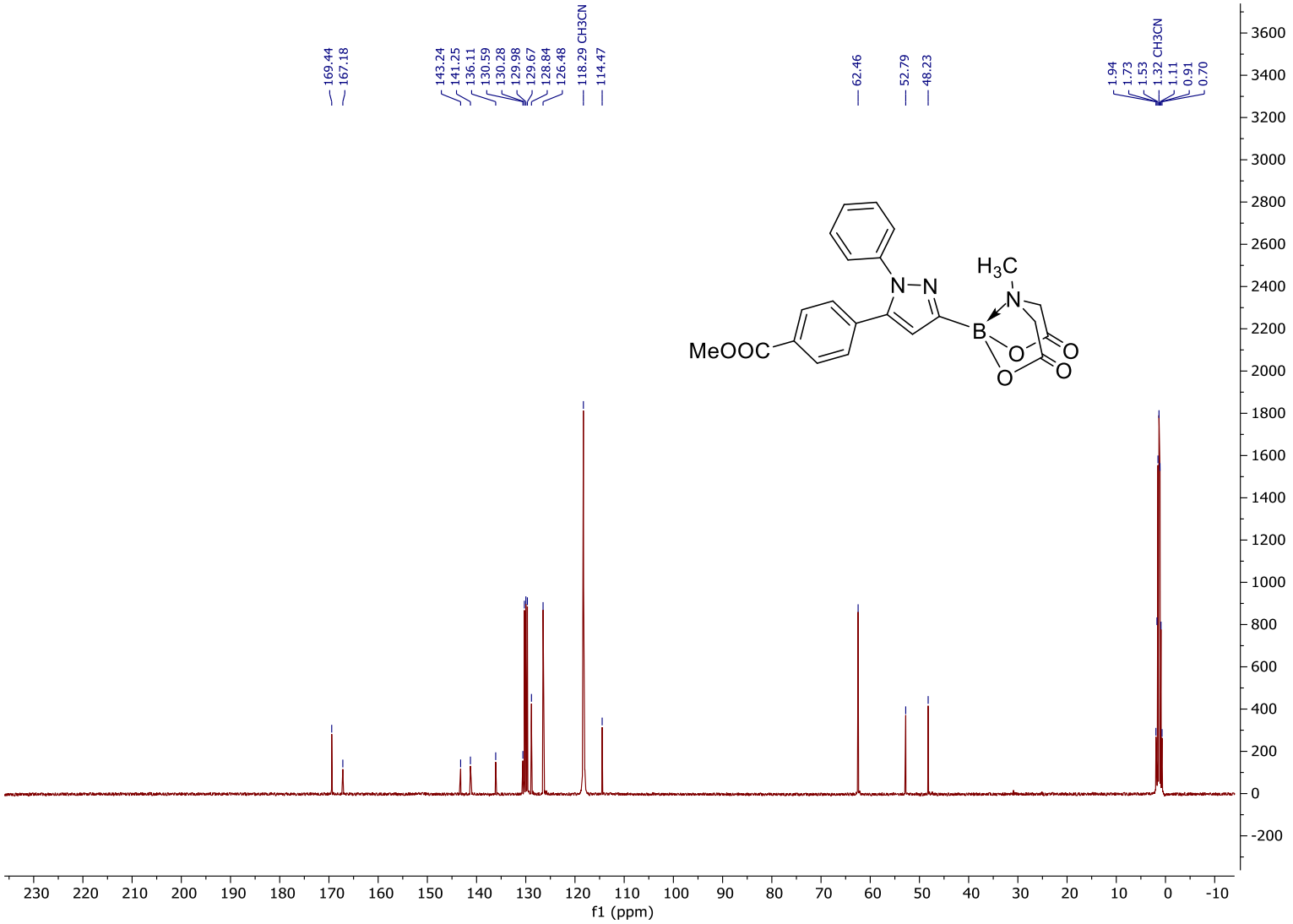
^{11}B NMR, compound 8e



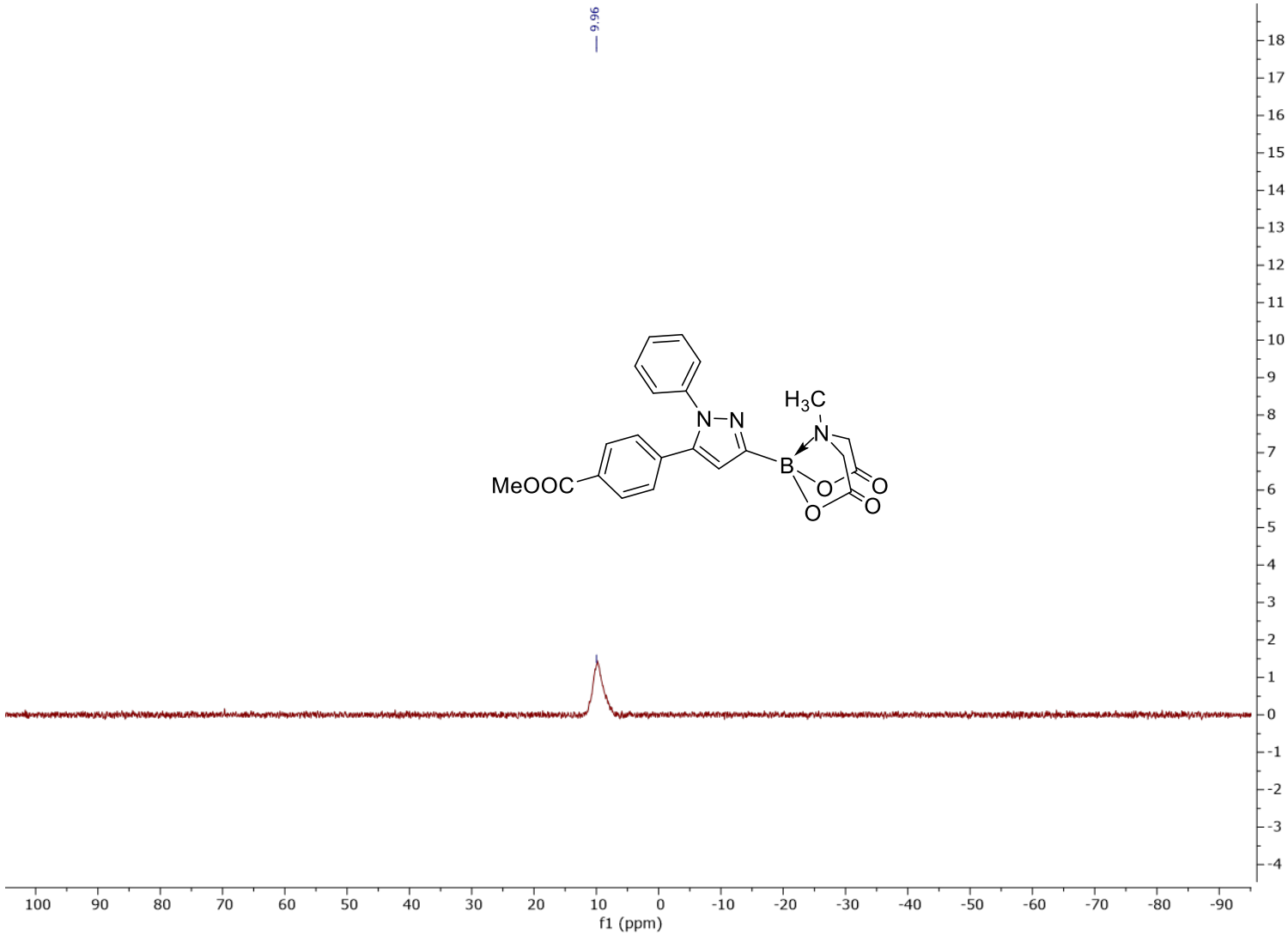
^{1}H NMR, compound 8f



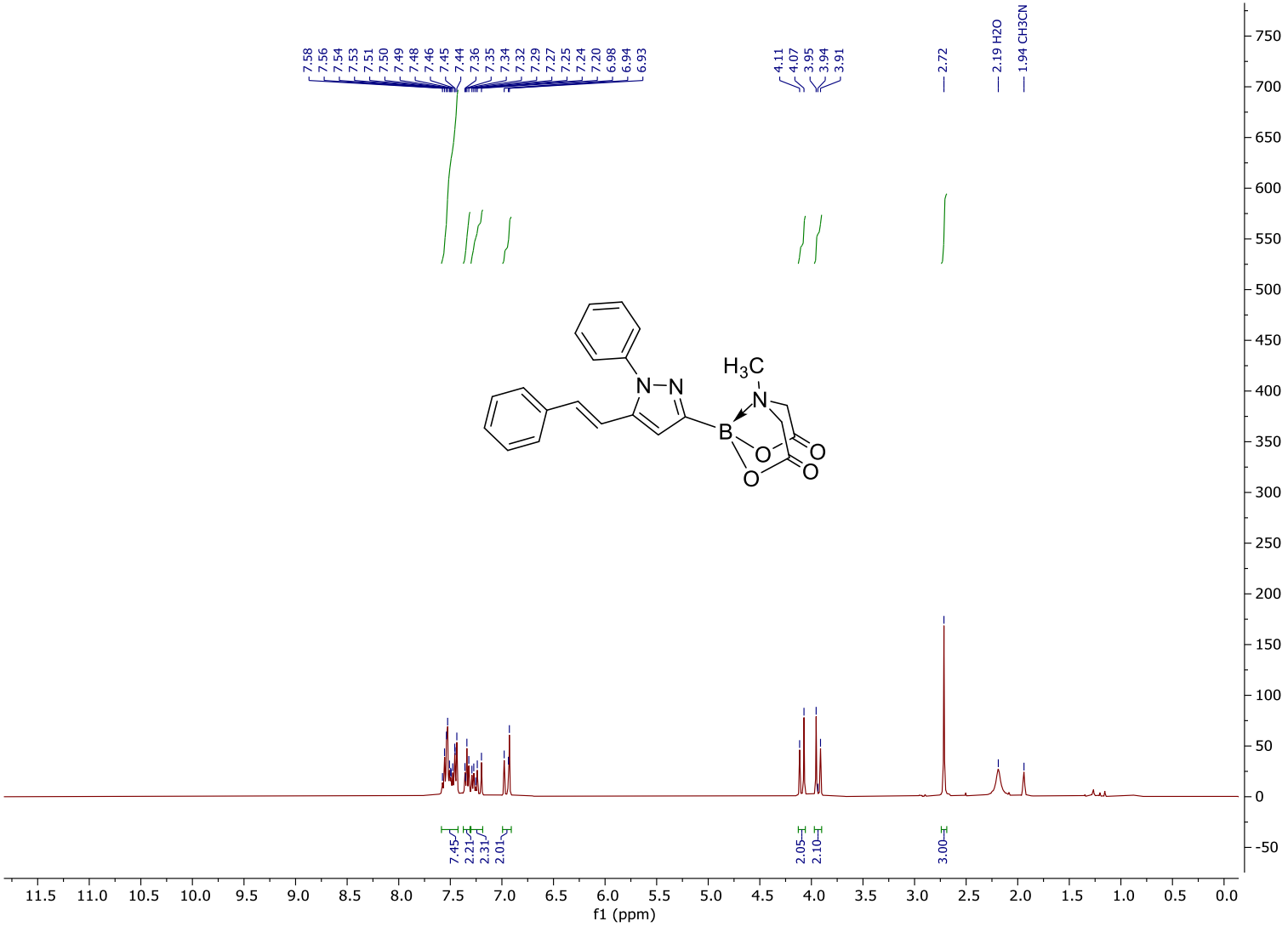
^{13}C NMR, compound 8f



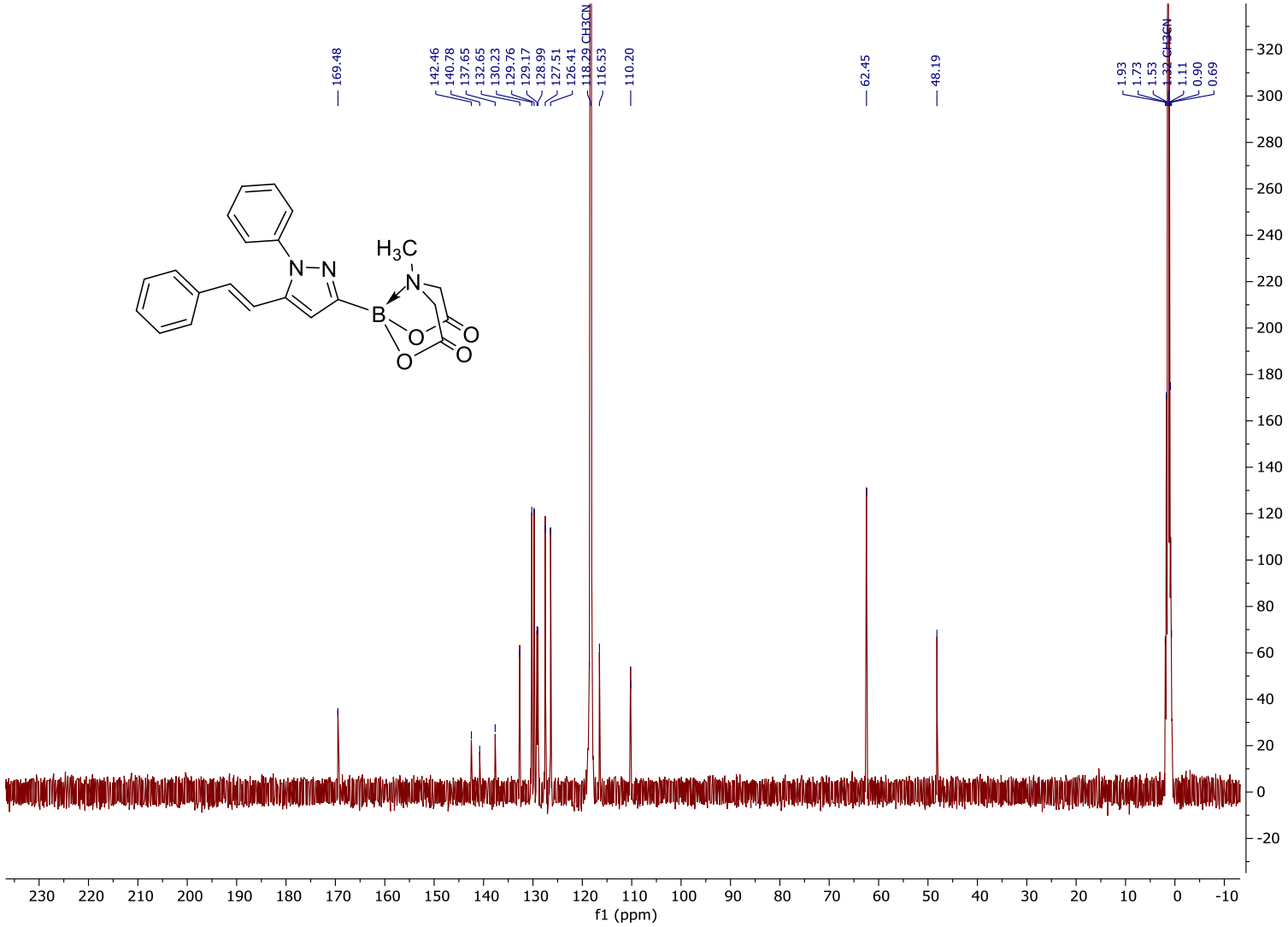
^{11}B NMR, compound 8f



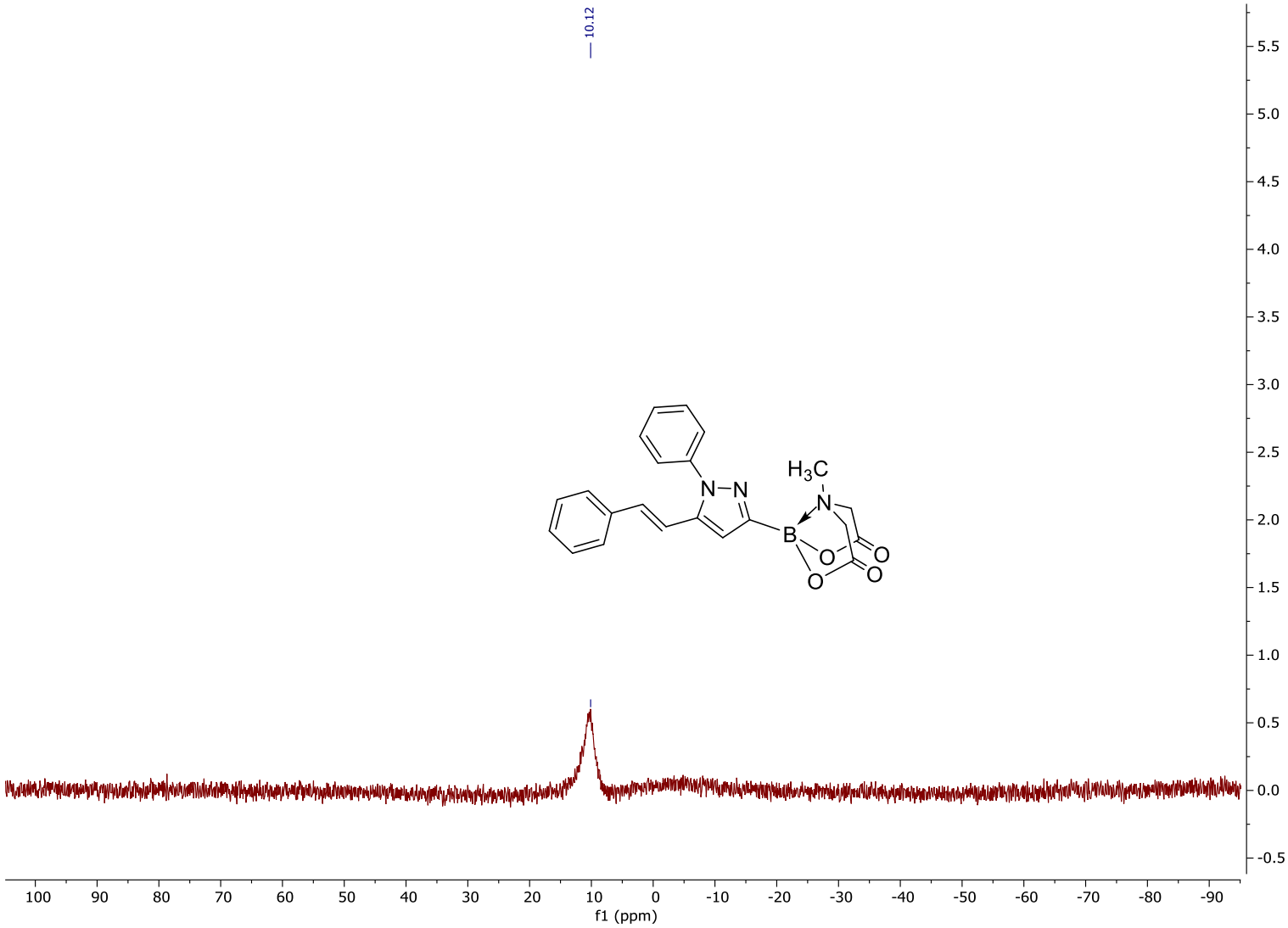
^{1}H NMR, compound 8g



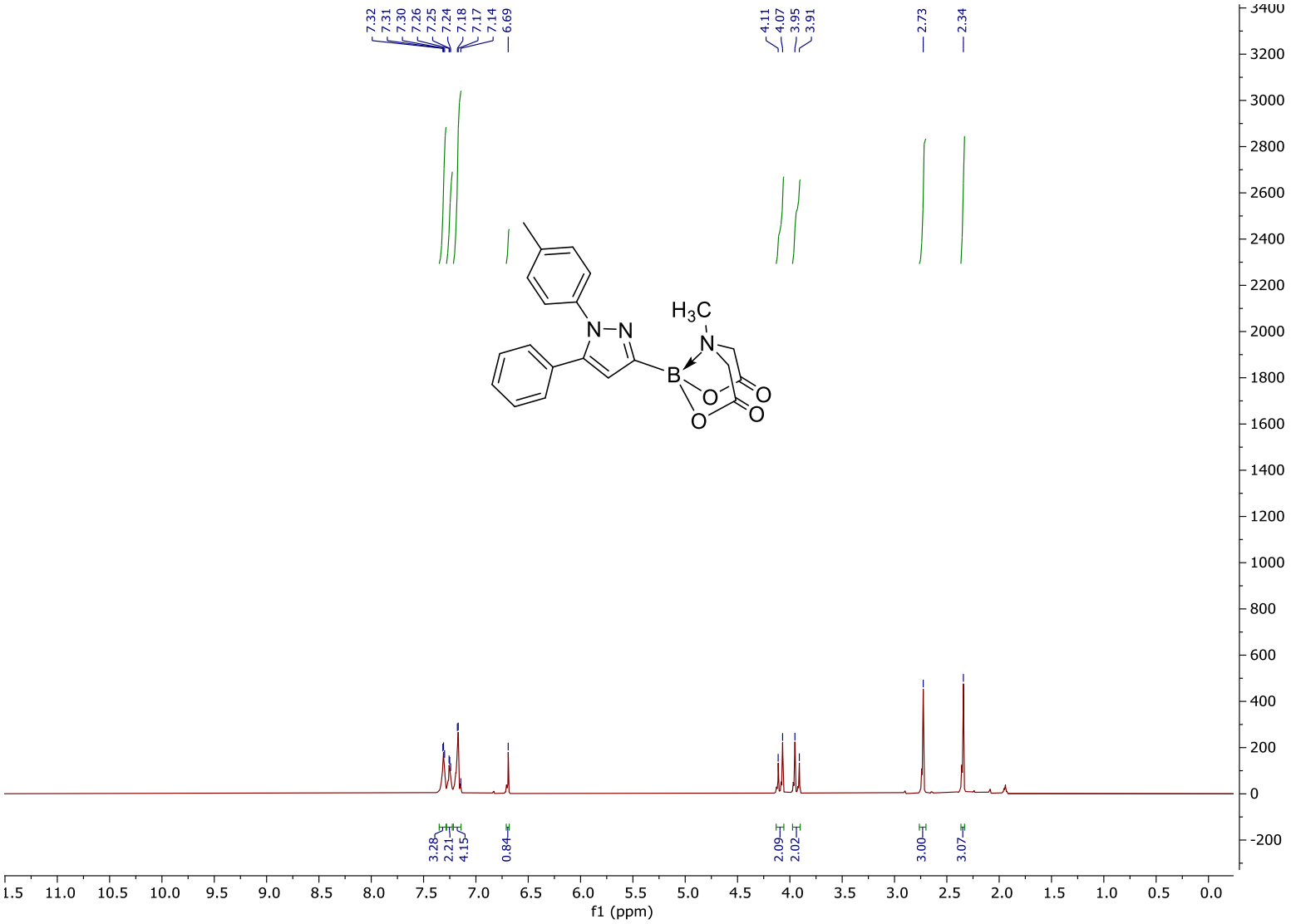
^{13}C NMR, compound 8g



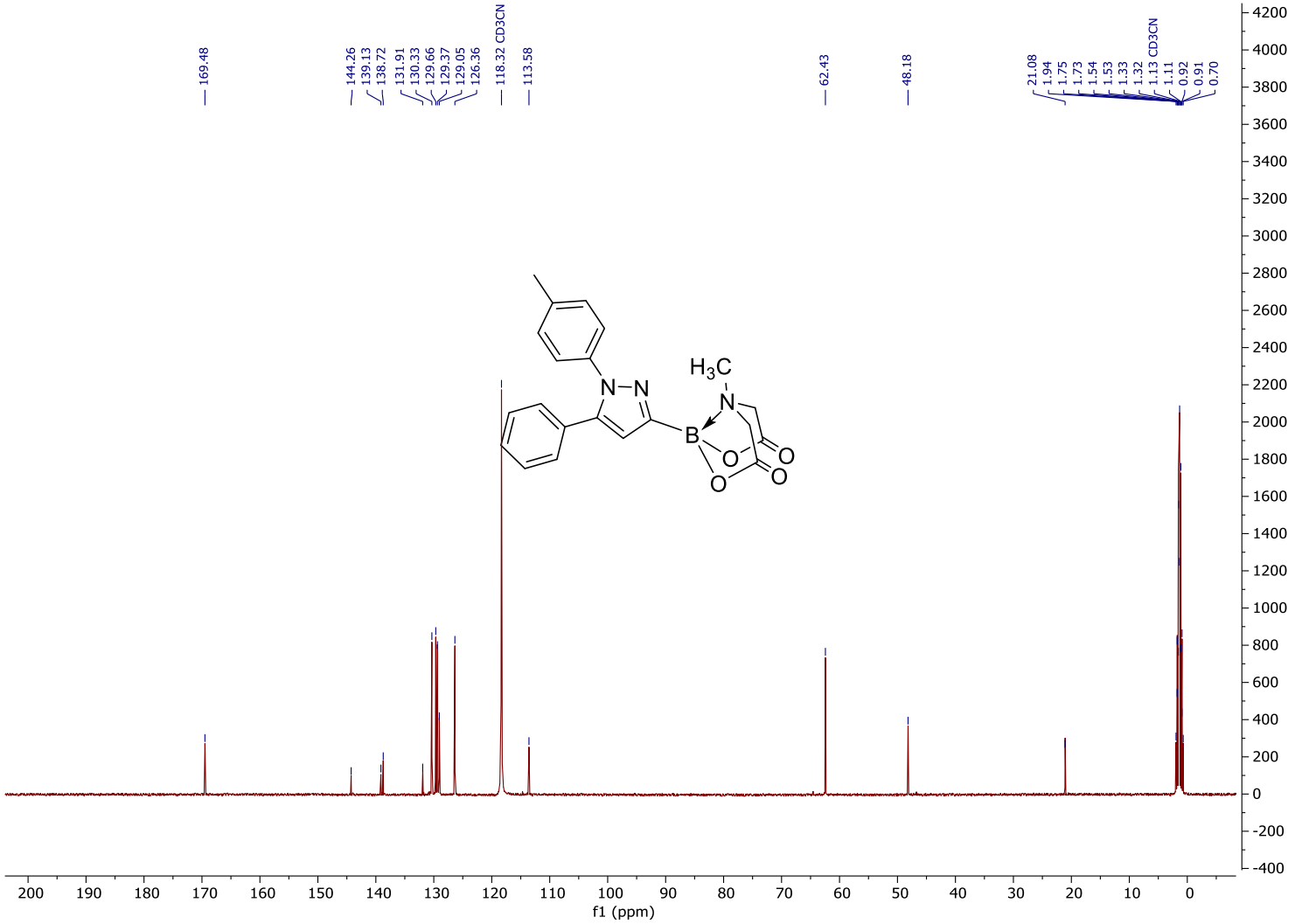
^{11}B NMR, compound 8g



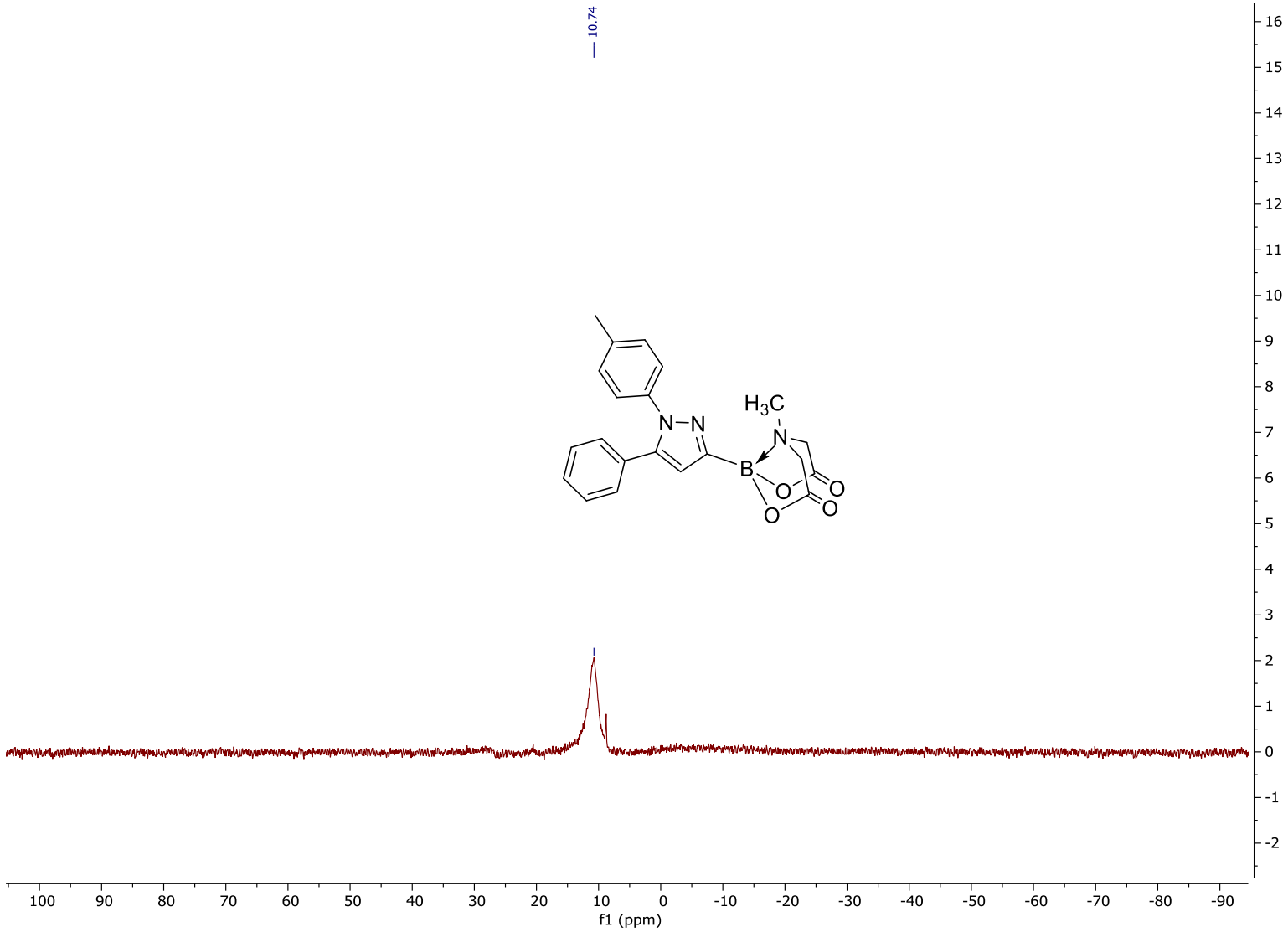
^{1}H NMR, compound 8h



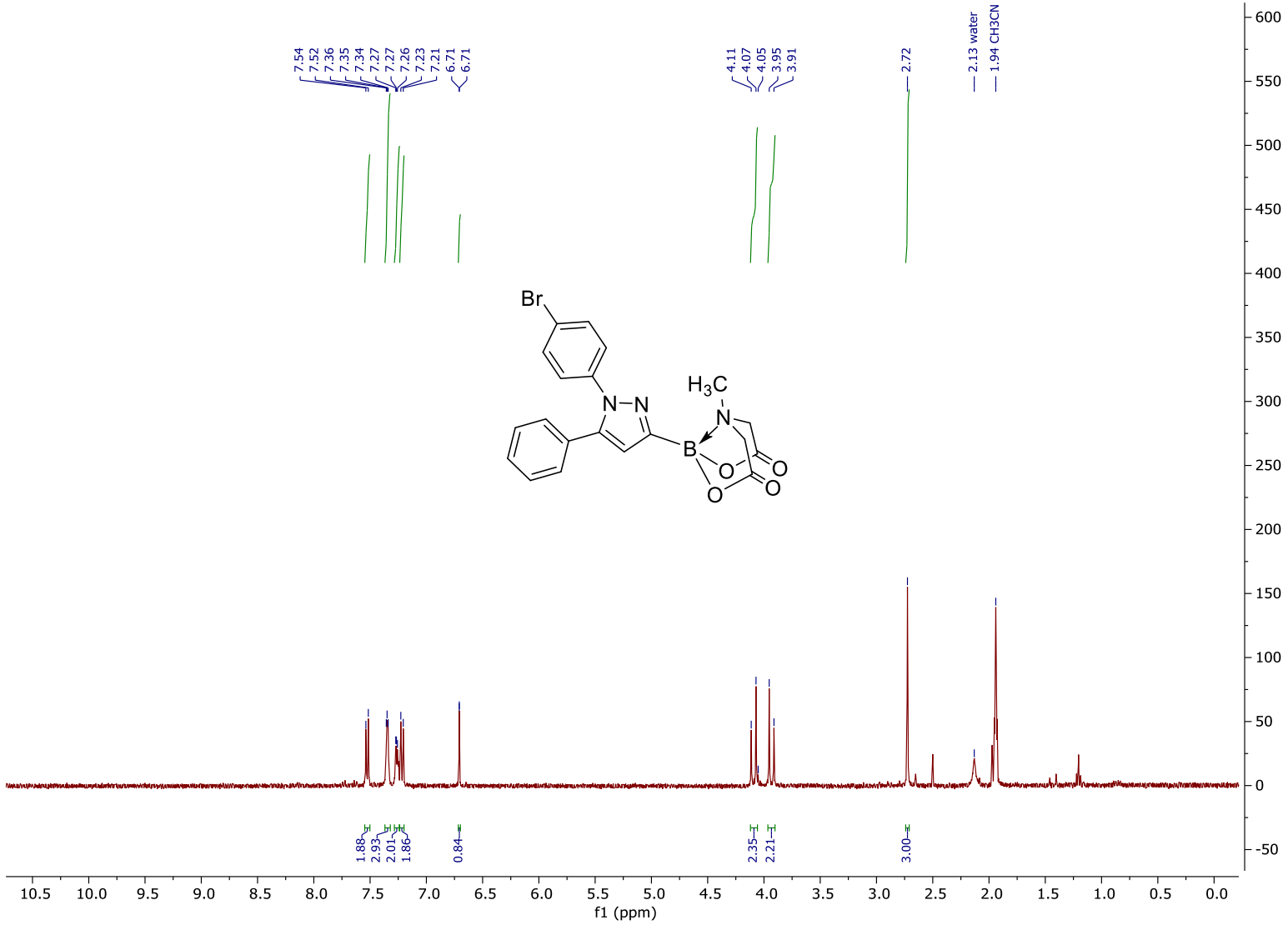
^{13}C NMR, compound 8h



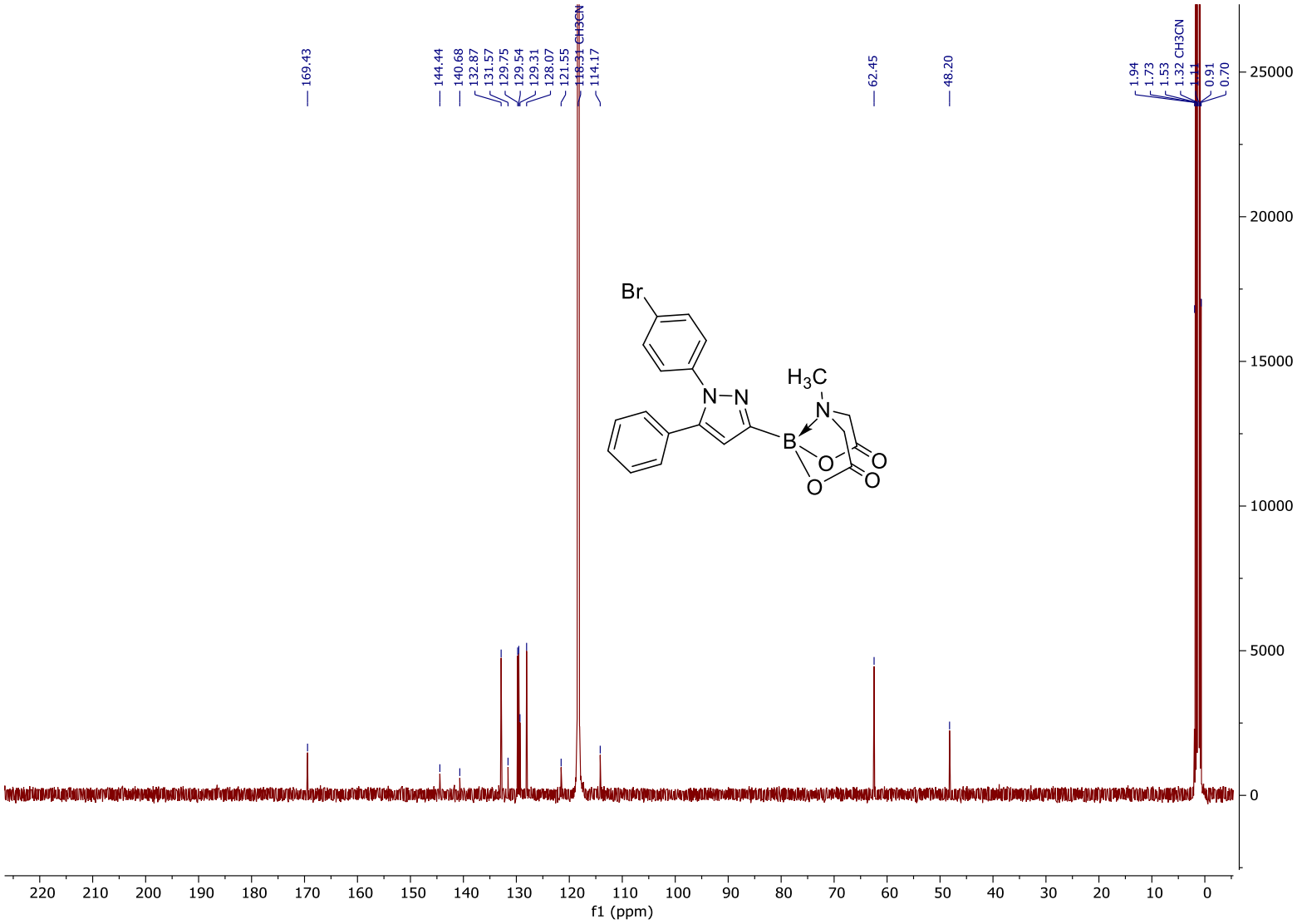
^{11}B NMR, compound 8h



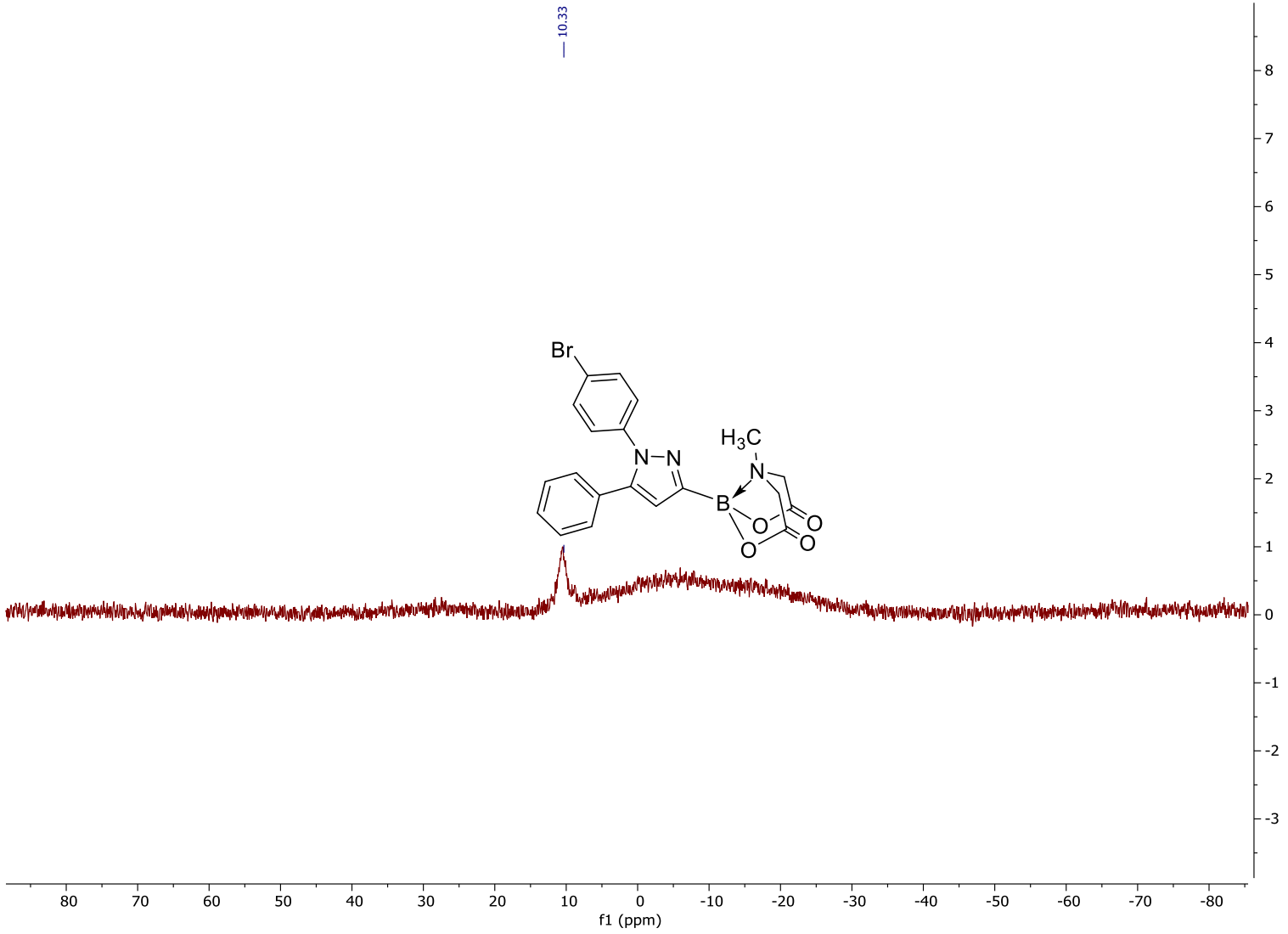
^{1}H NMR, compound 8i



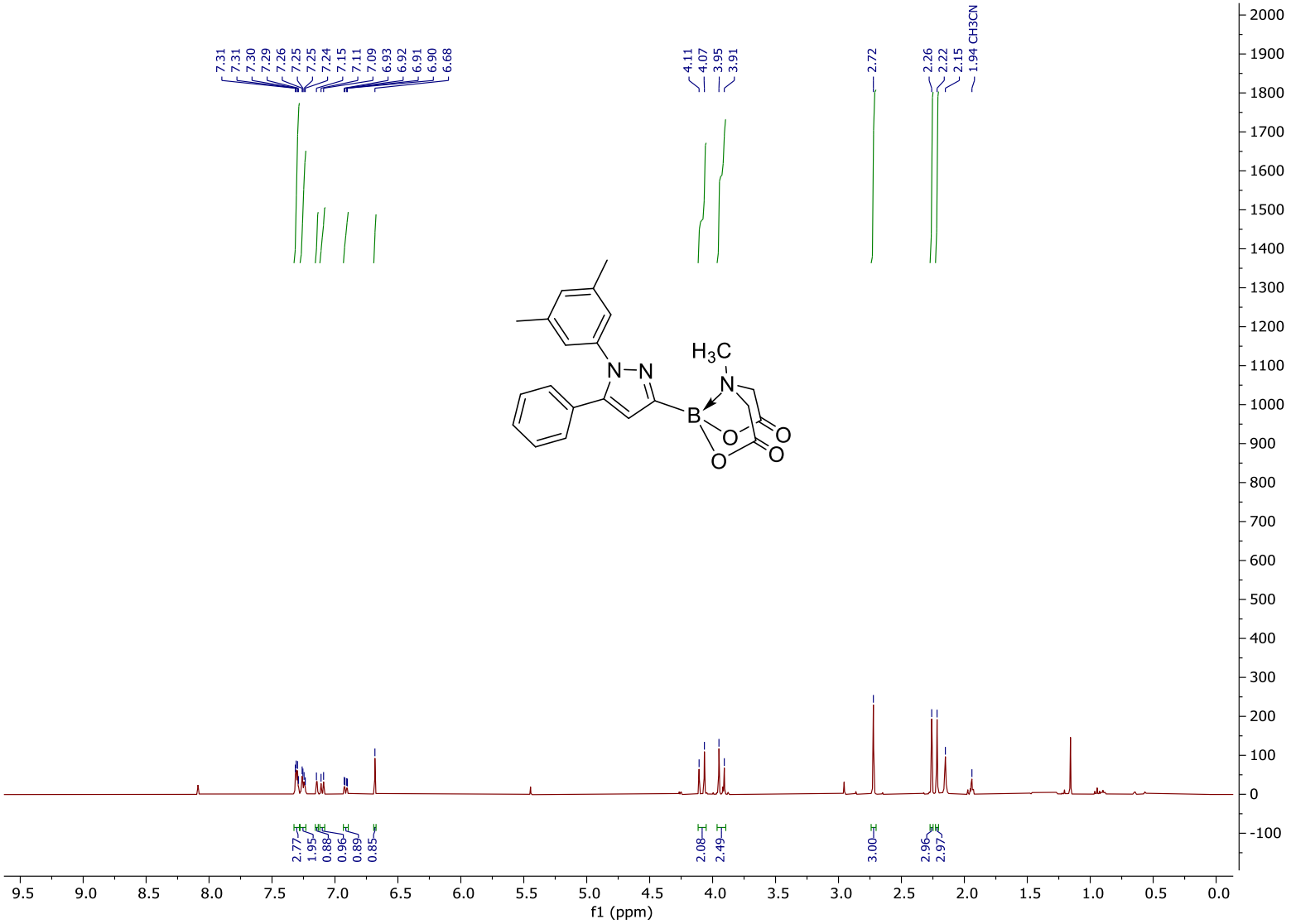
^{13}C NMR, compound 8i



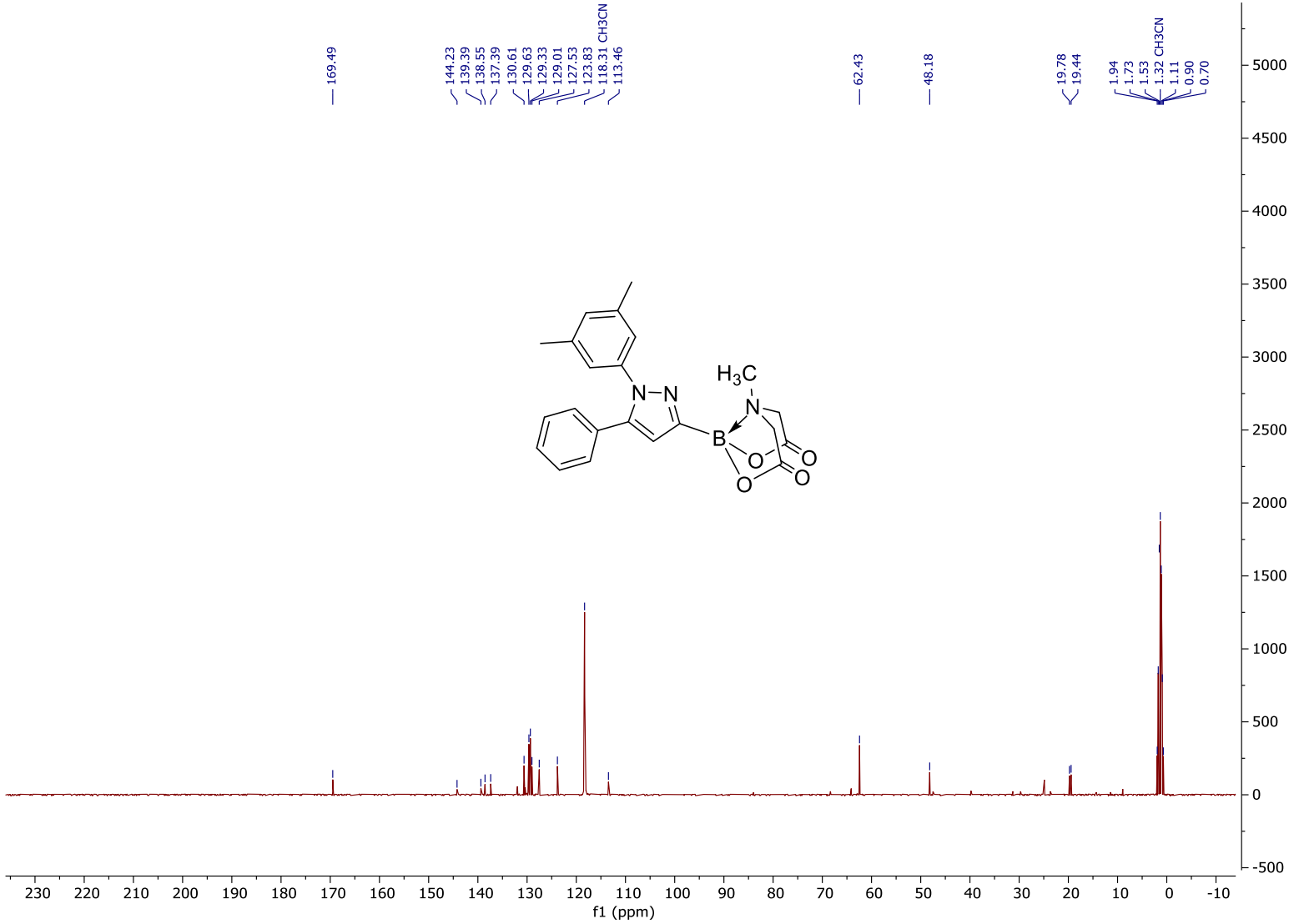
^{11}B NMR, compound 8i



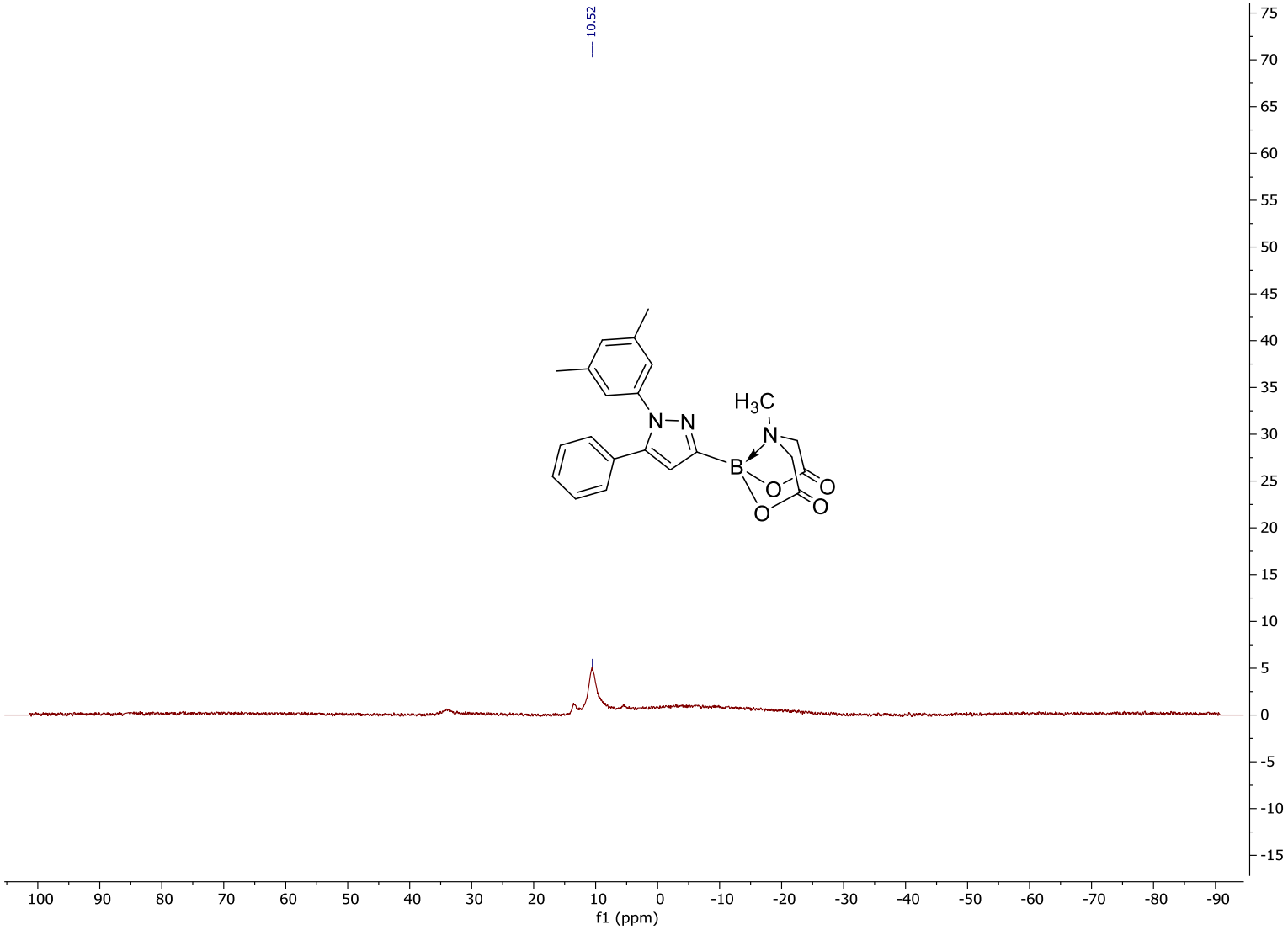
^{1}H NMR, compound 8j

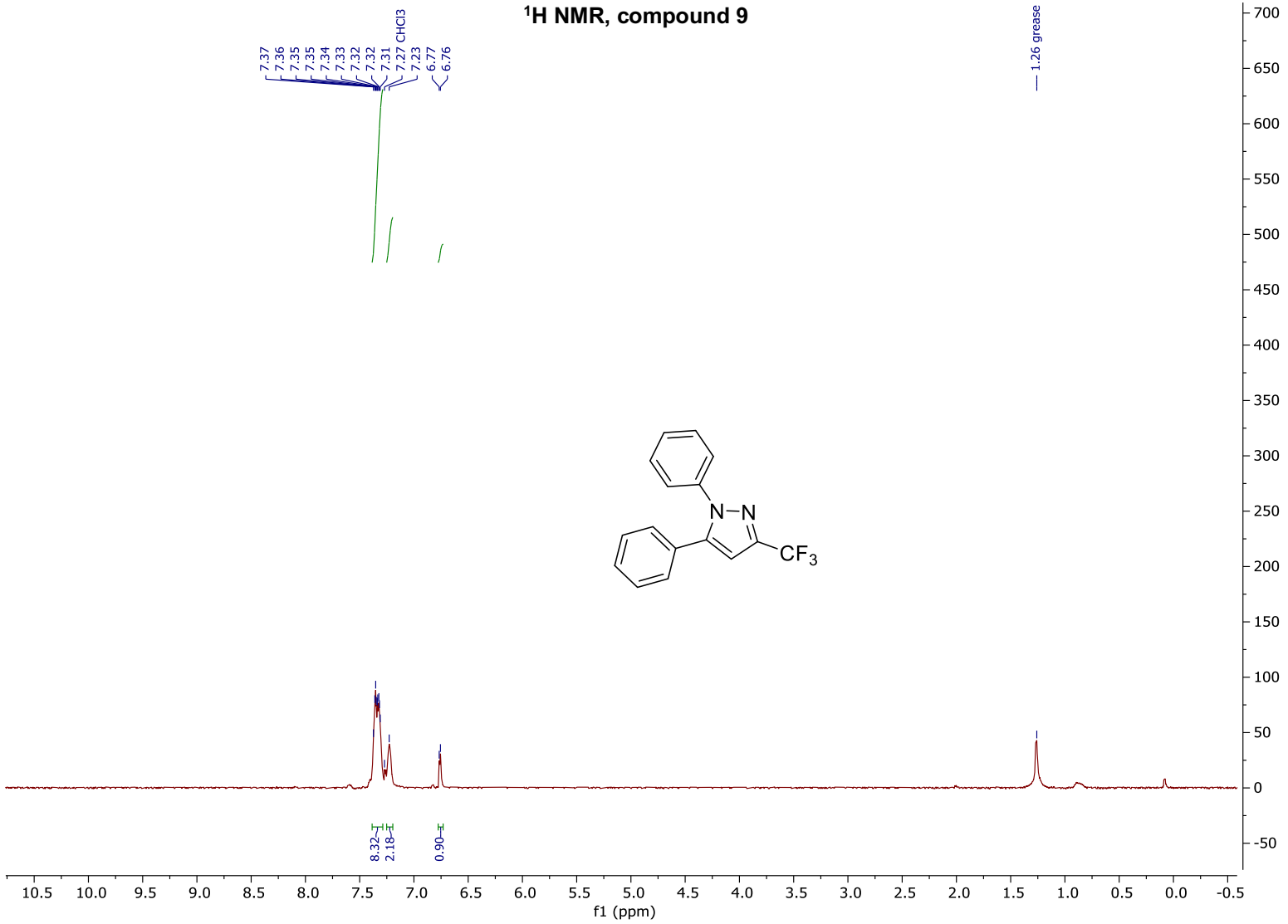


^{13}C NMR, compound 8j

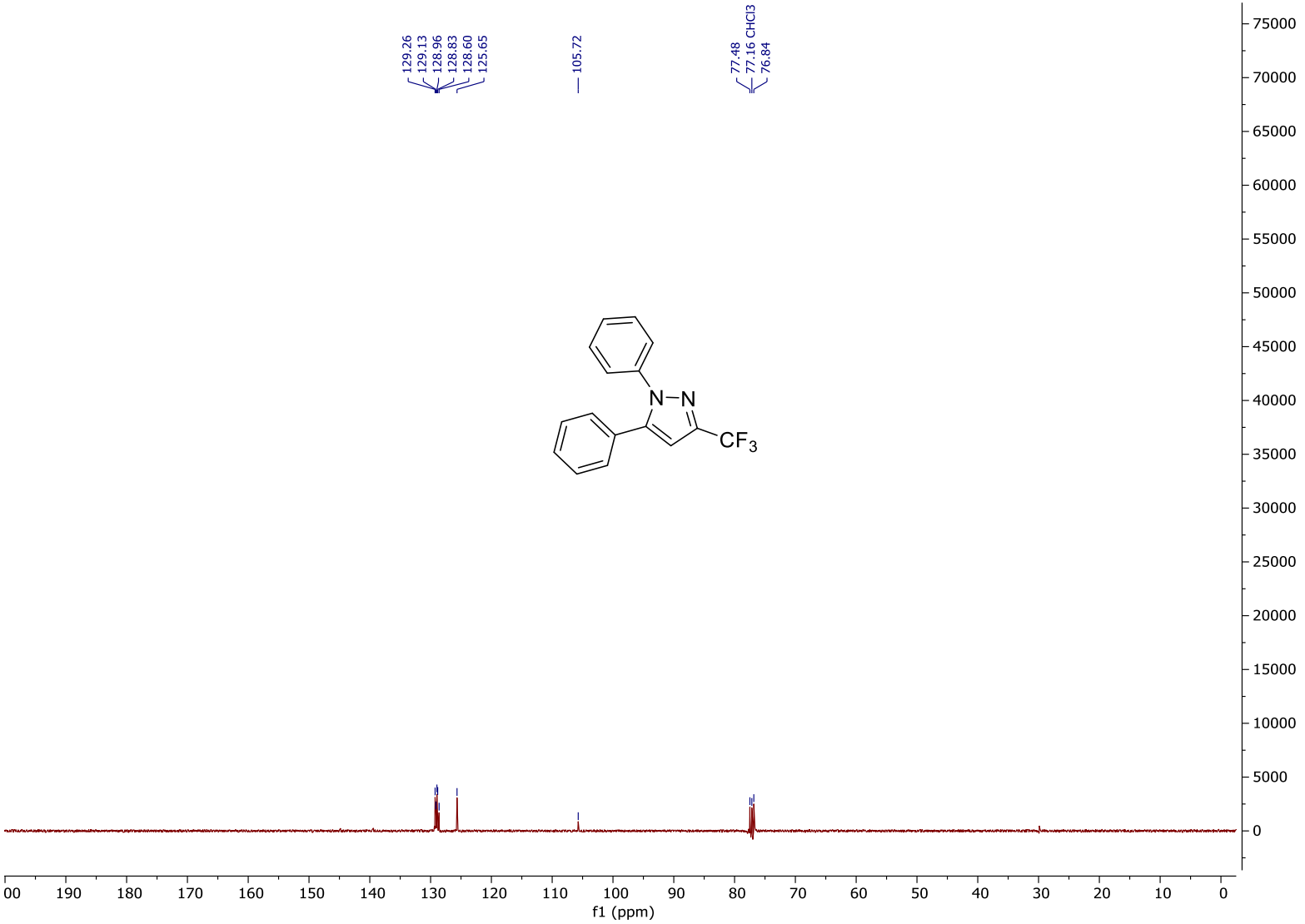


^{11}B NMR, compound 8j

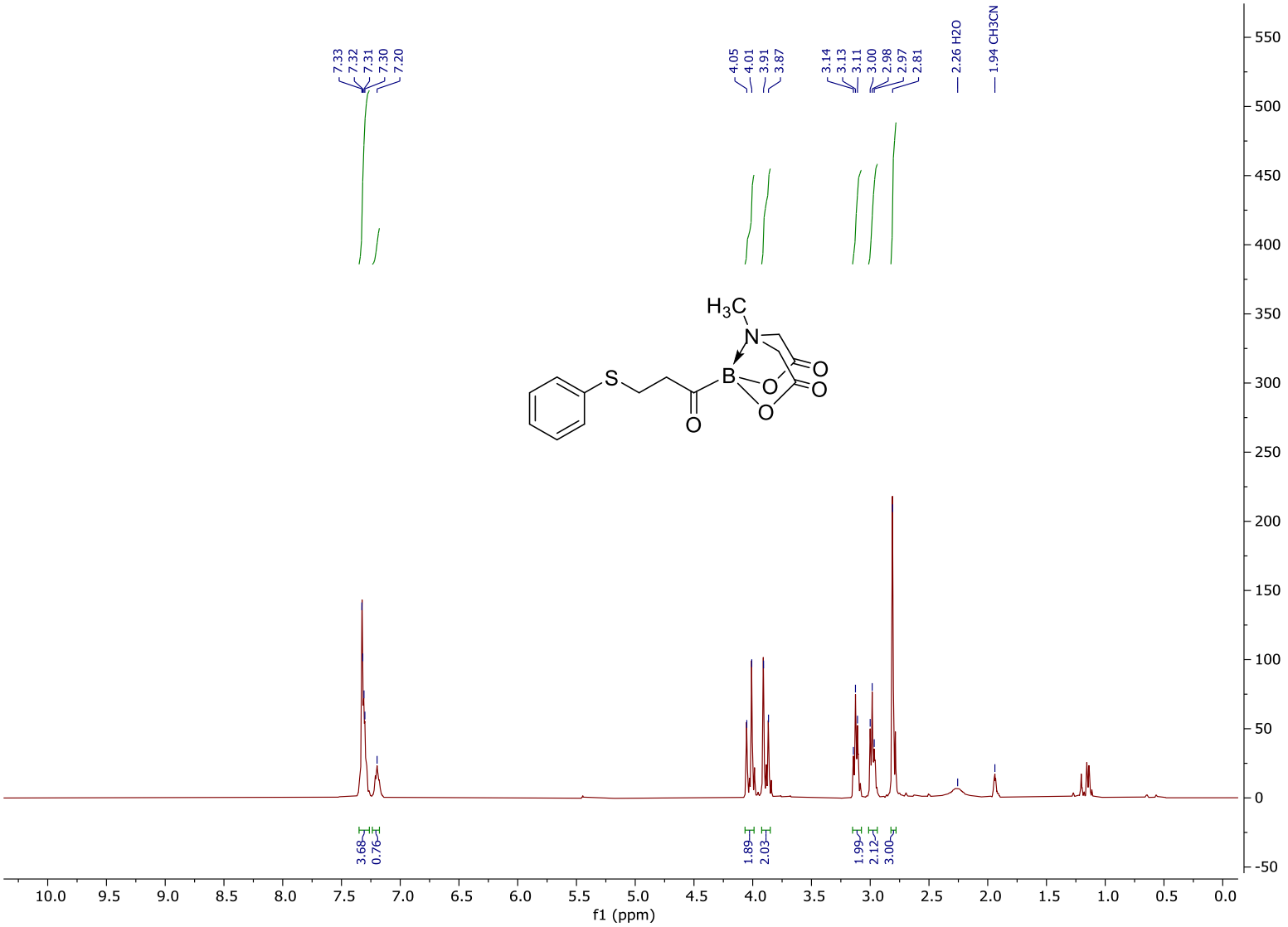



^{1}H NMR, compound 9
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.27 CHCl3
7.23
6.77
6.76
1.26 grease
N–N
CF3
8.32
2.18
0.90
f1 (ppm)

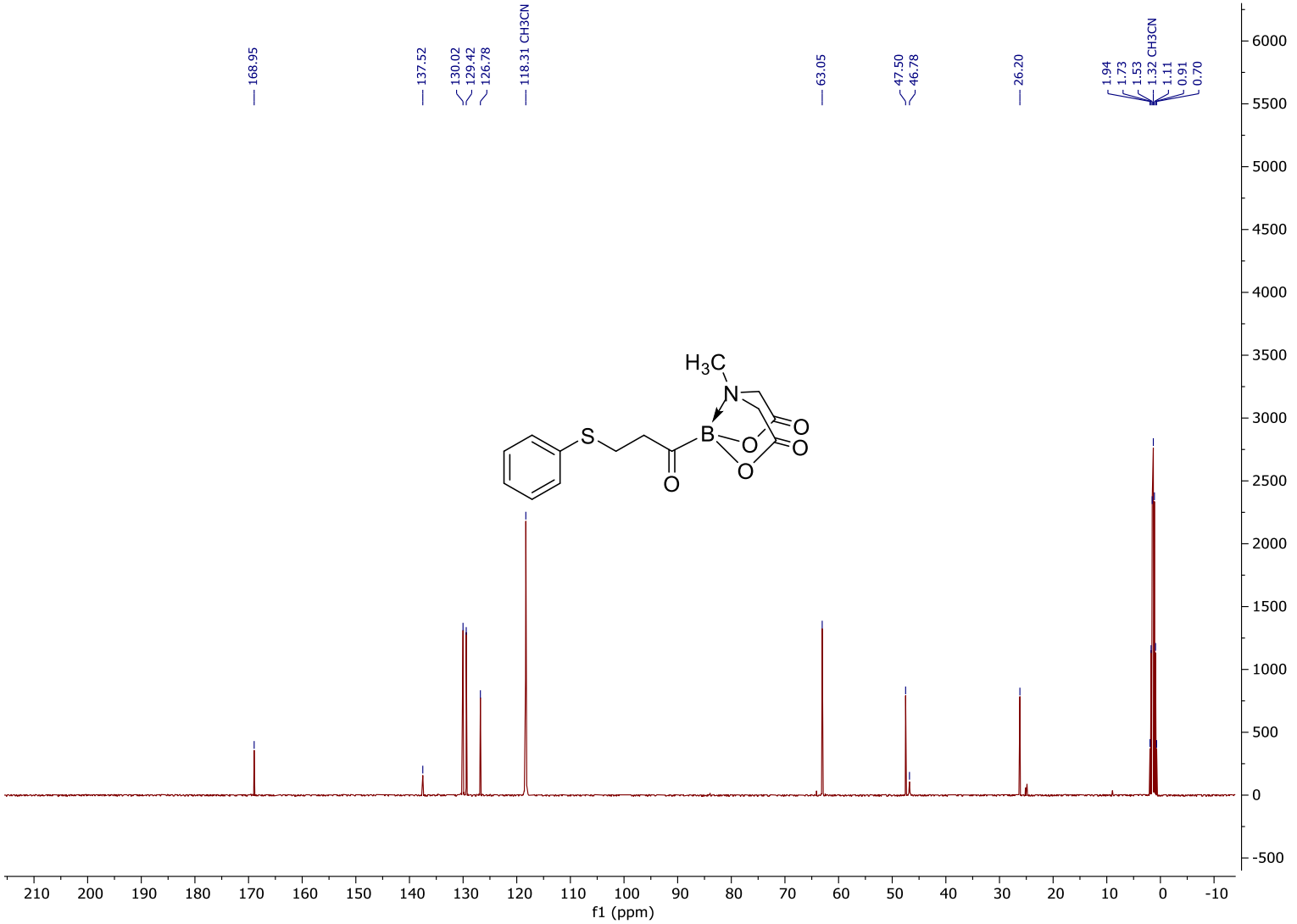
^{13}C NMR, compound 9



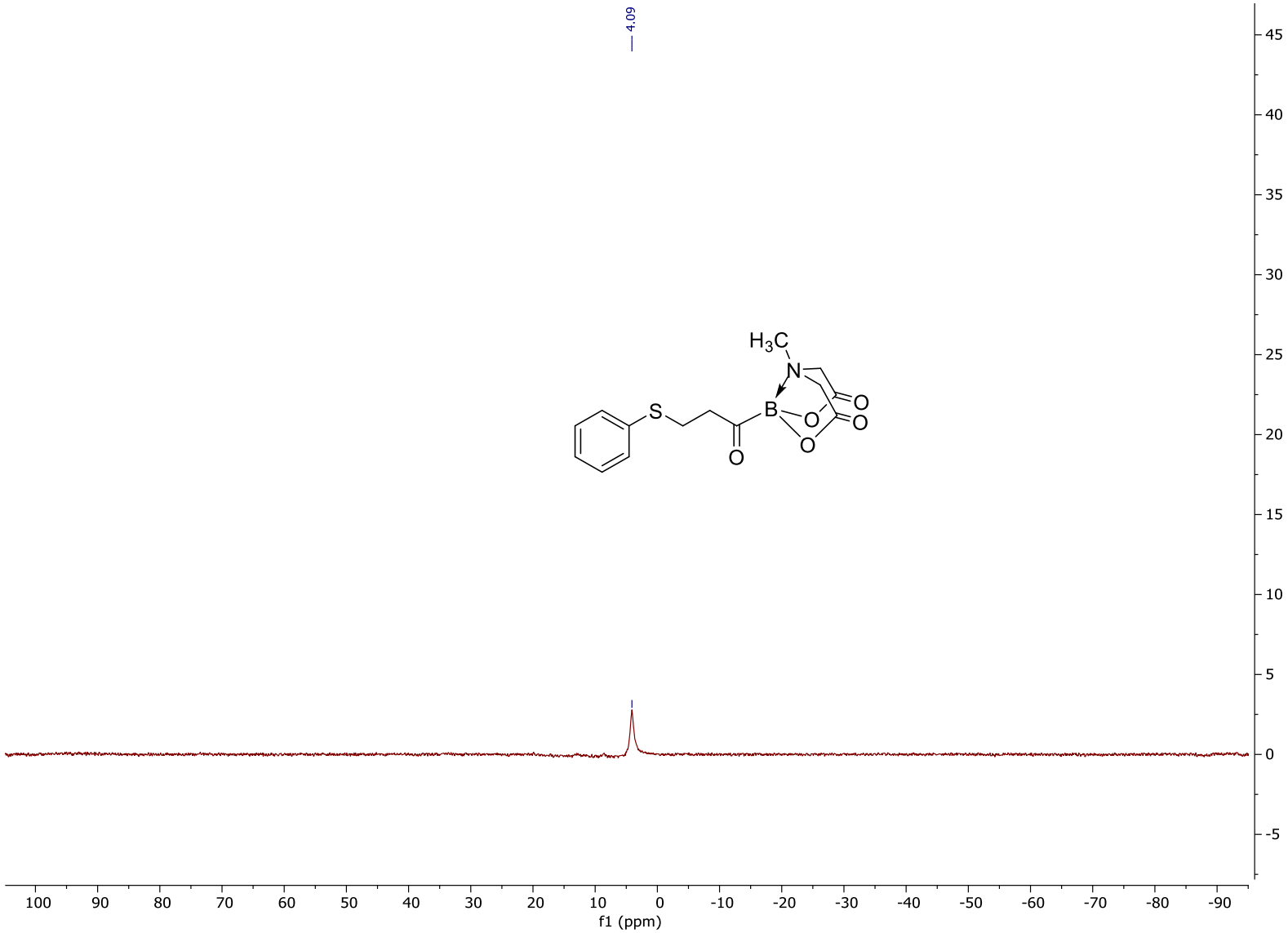
^{1}H NMR, compound 10a

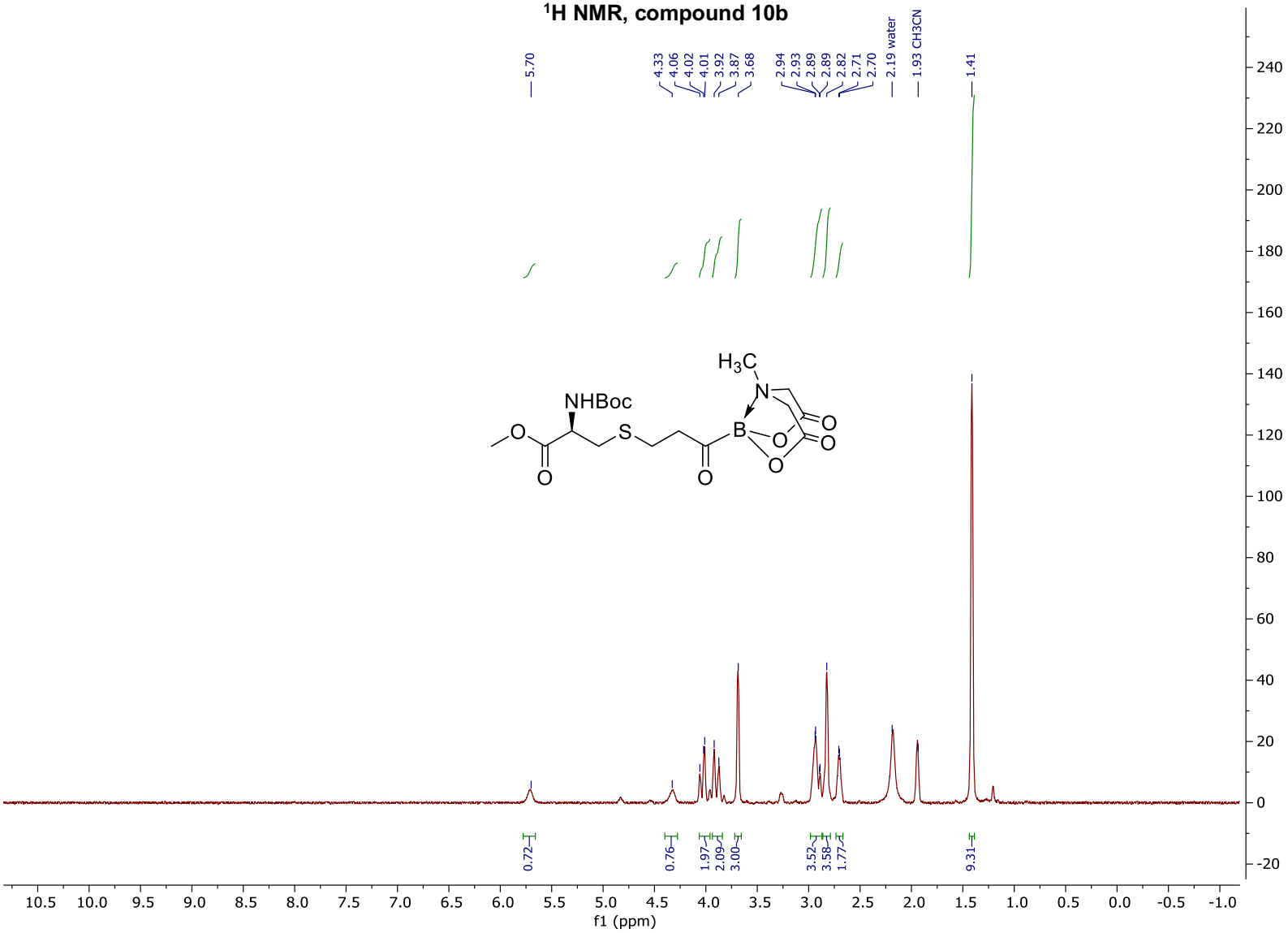


^{13}C NMR, compound 10a

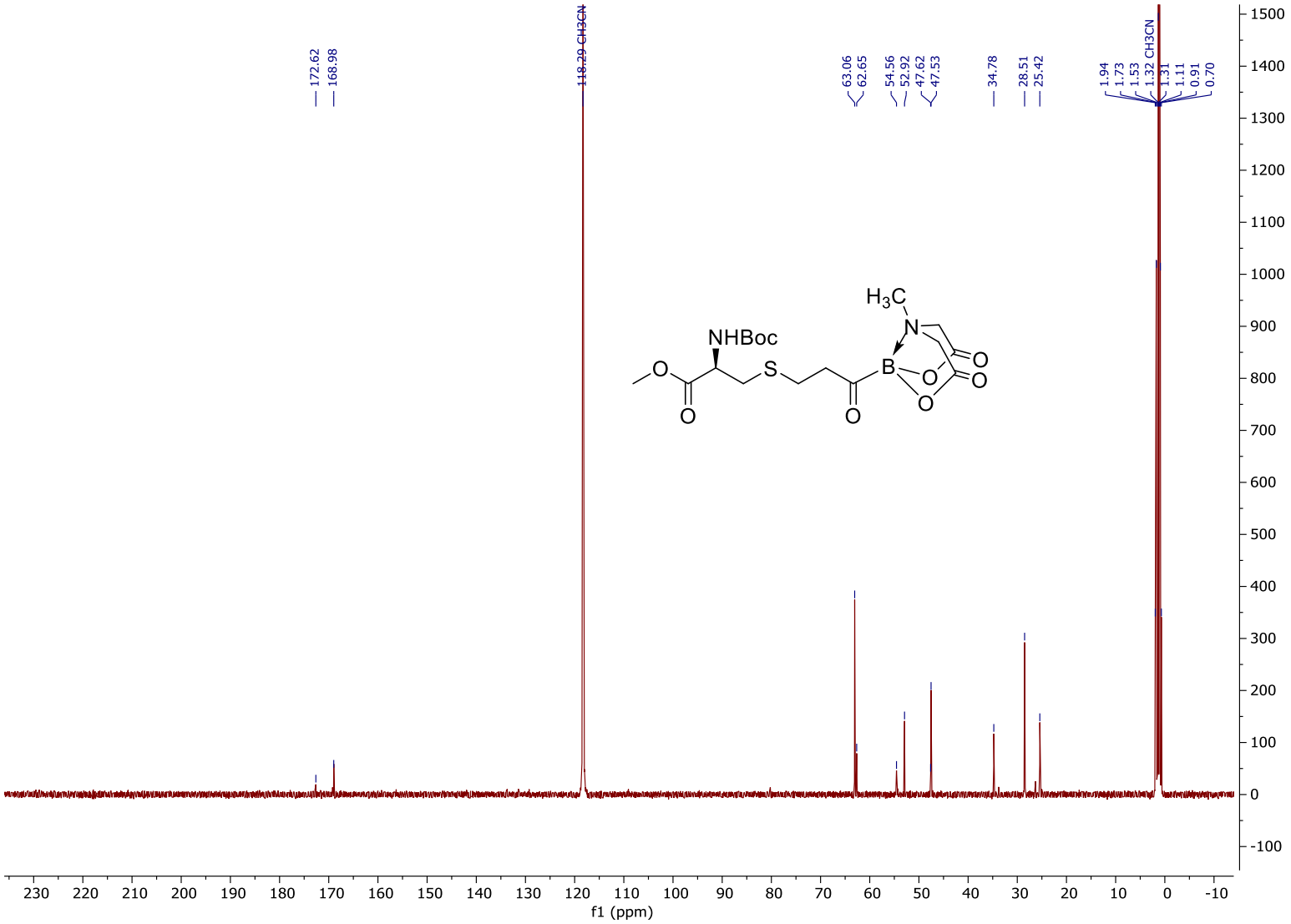


^{11}B NMR, compound 10a

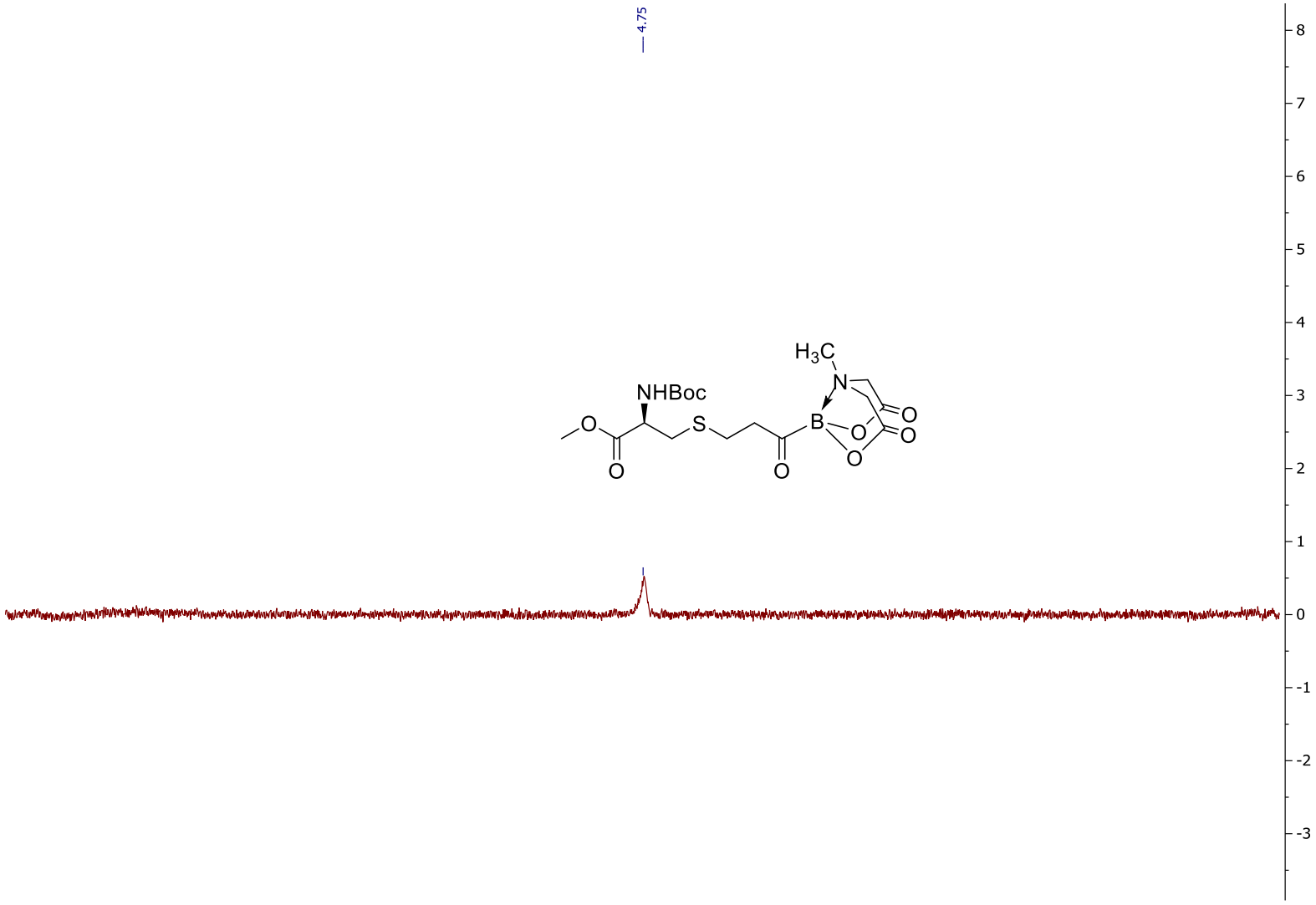


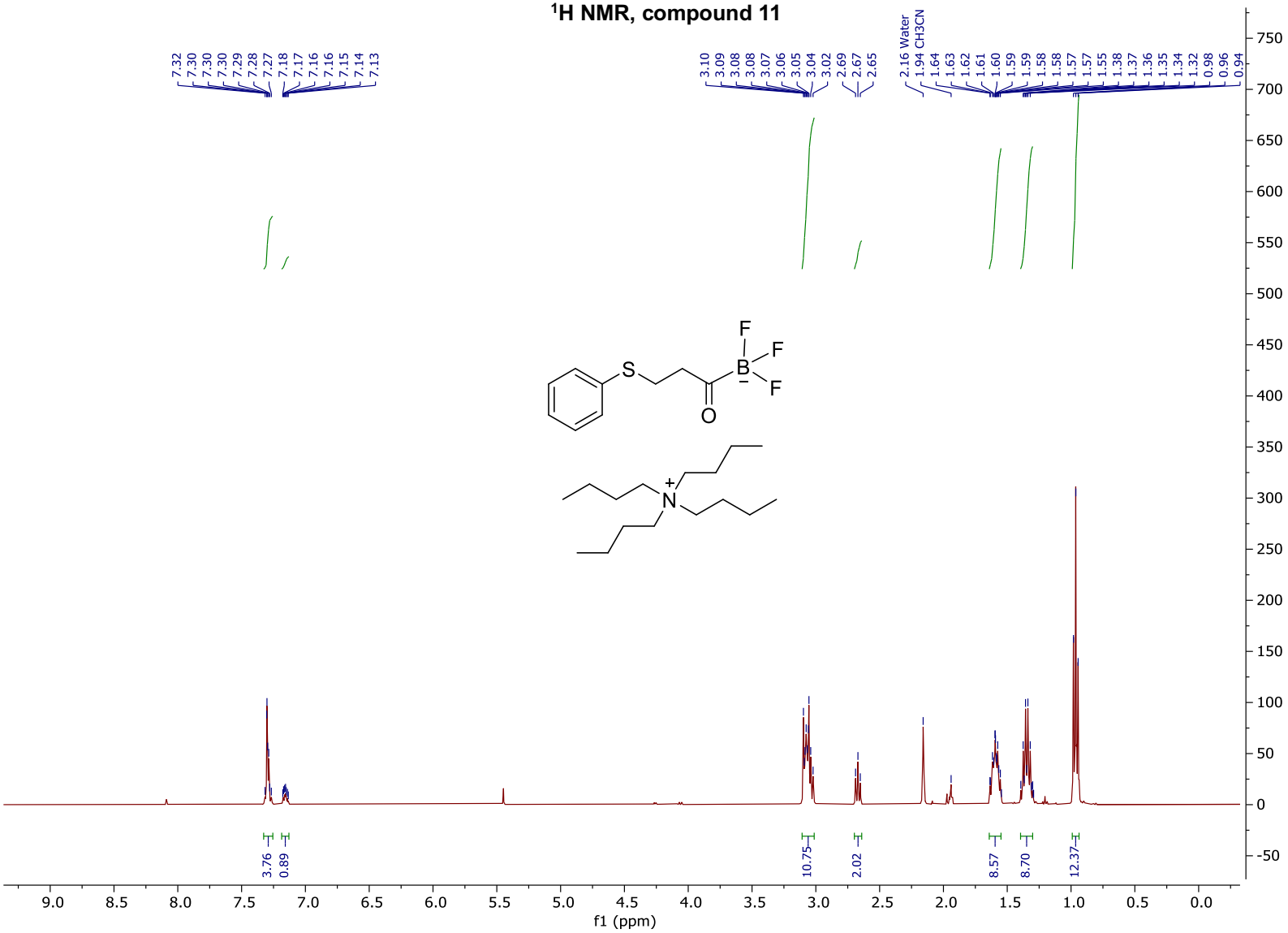

¹H NMR, compound 10b
5.70
4.33
4.06
4.02
4.01
3.92
3.87
3.68
2.94
2.93
2.89
2.89
2.82
2.71
2.70
2.19 water
1.93 CH3CN
1.41
NHBoc
H3C
N
O
S
B
0.72
0.76
1.97
2.09
3.00
3.52
3.58
1.77
9.31
f1 (ppm)

^{13}C NMR, compound 10b

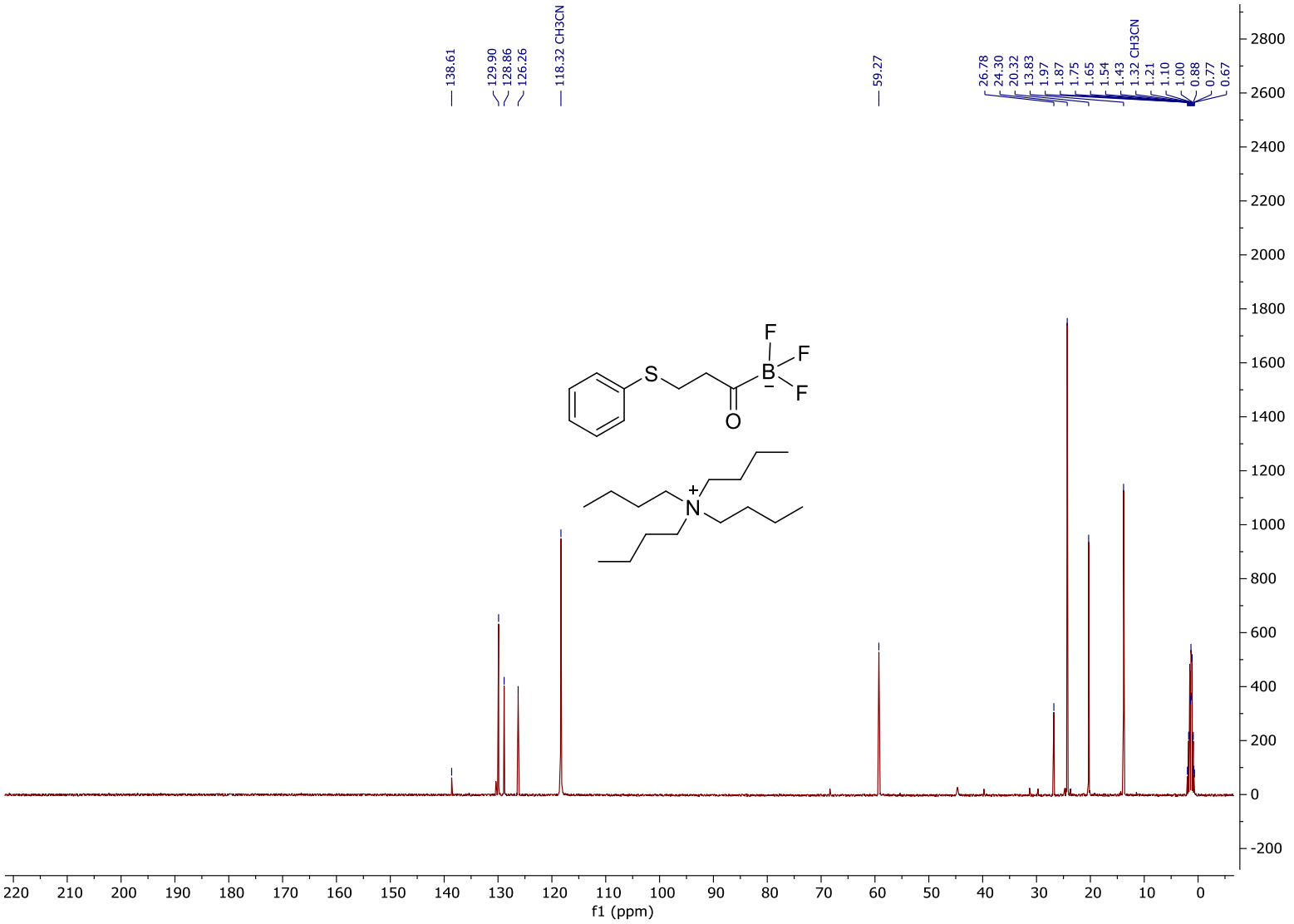


^{11}B NMR, compound 10b

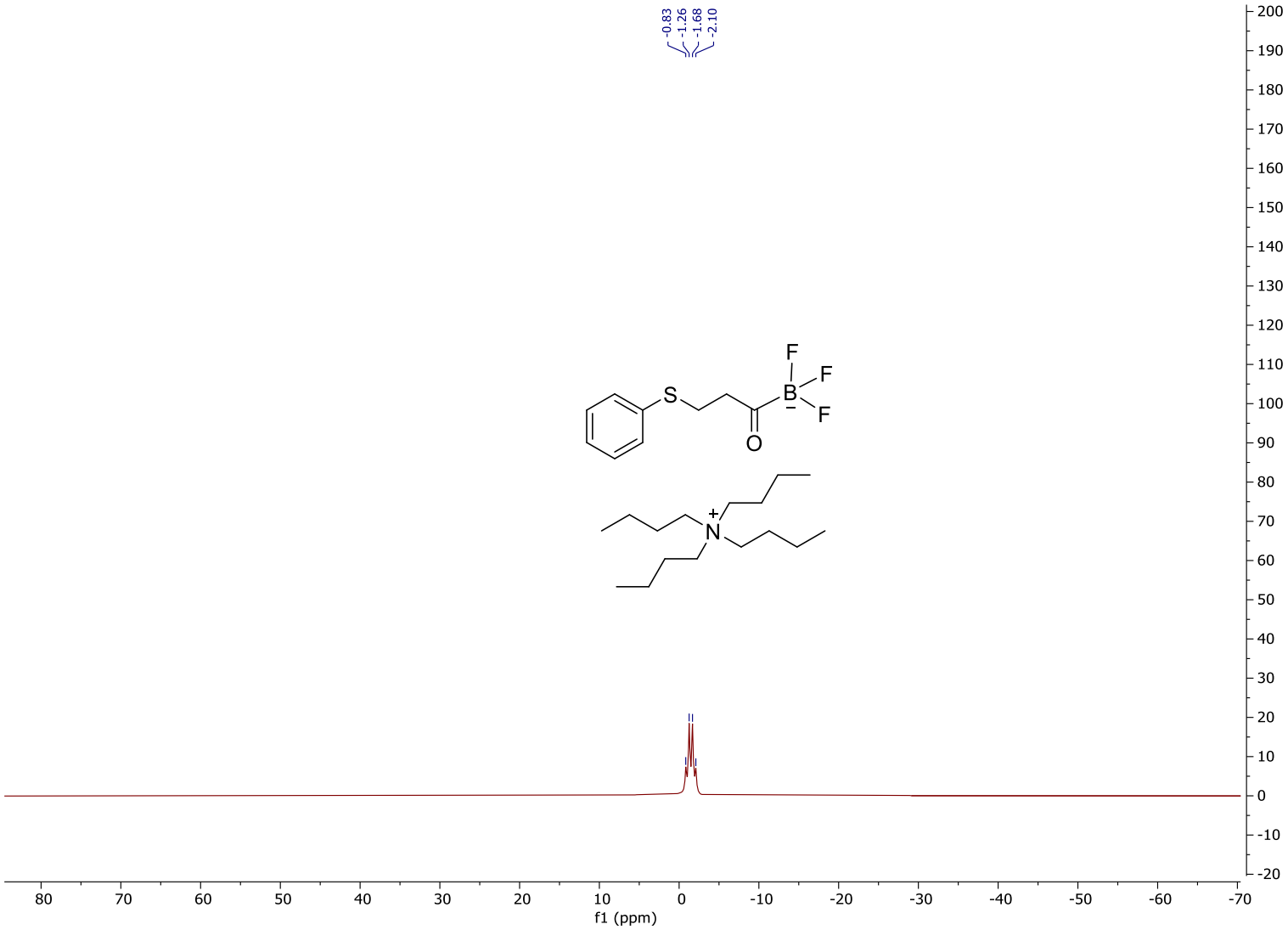



¹H NMR, compound 11
7.32
7.30
7.30
7.30
7.29
7.28
7.27
7.18
7.17
7.16
7.16
7.15
7.14
7.13
3.10
3.09
3.08
3.08
3.07
3.06
3.05
3.04
3.02
2.69
2.67
2.65
2.16 Water
1.94 CH3CN
1.64
1.63
1.62
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.55
1.38
1.37
1.36
1.35
1.34
1.32
0.98
0.96
0.94
F
F
F
B
S
O
N
3.76
0.89
10.75
2.02
8.57
8.70
12.37
f1 (ppm)

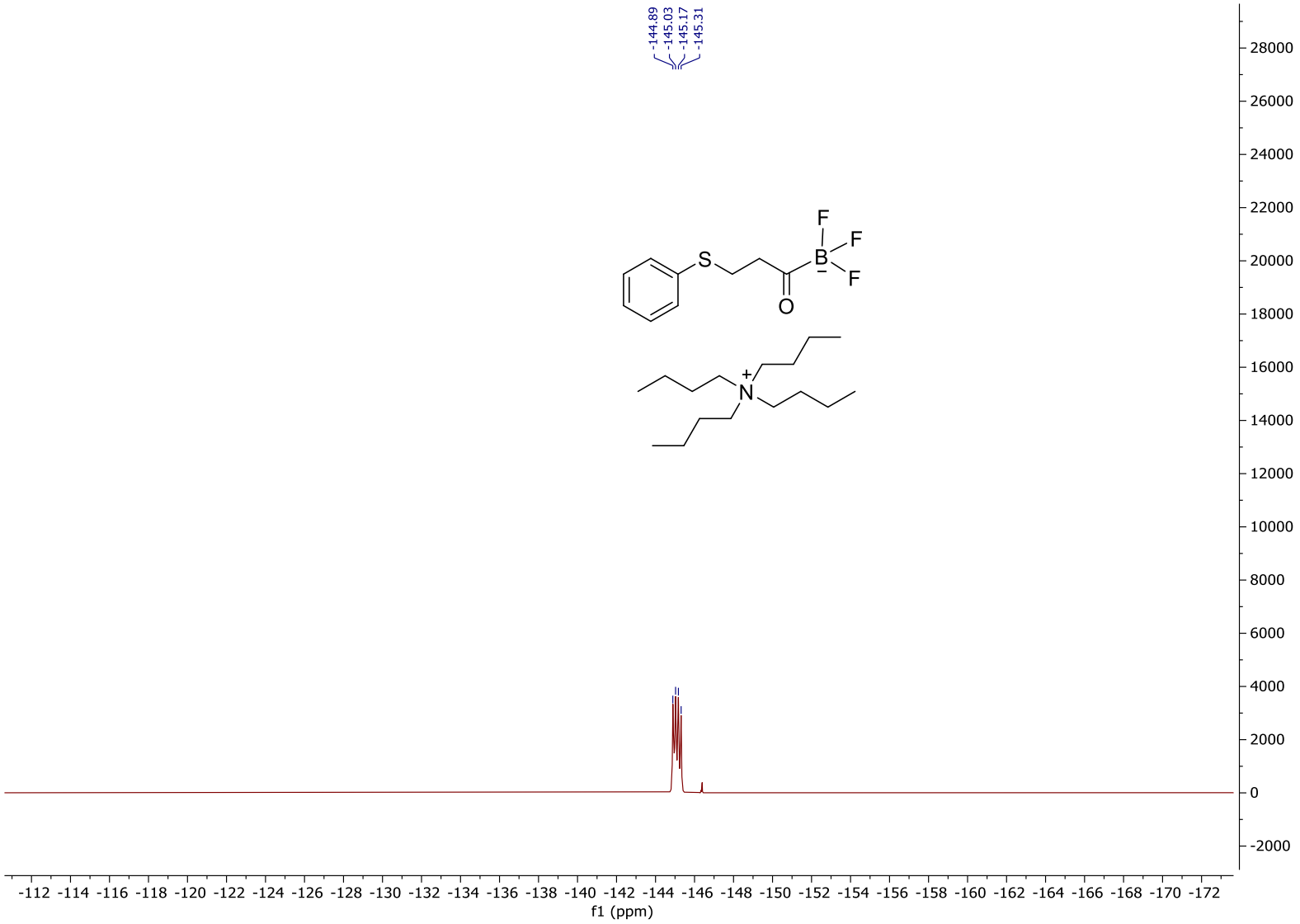
^{13}C NMR, compound 11



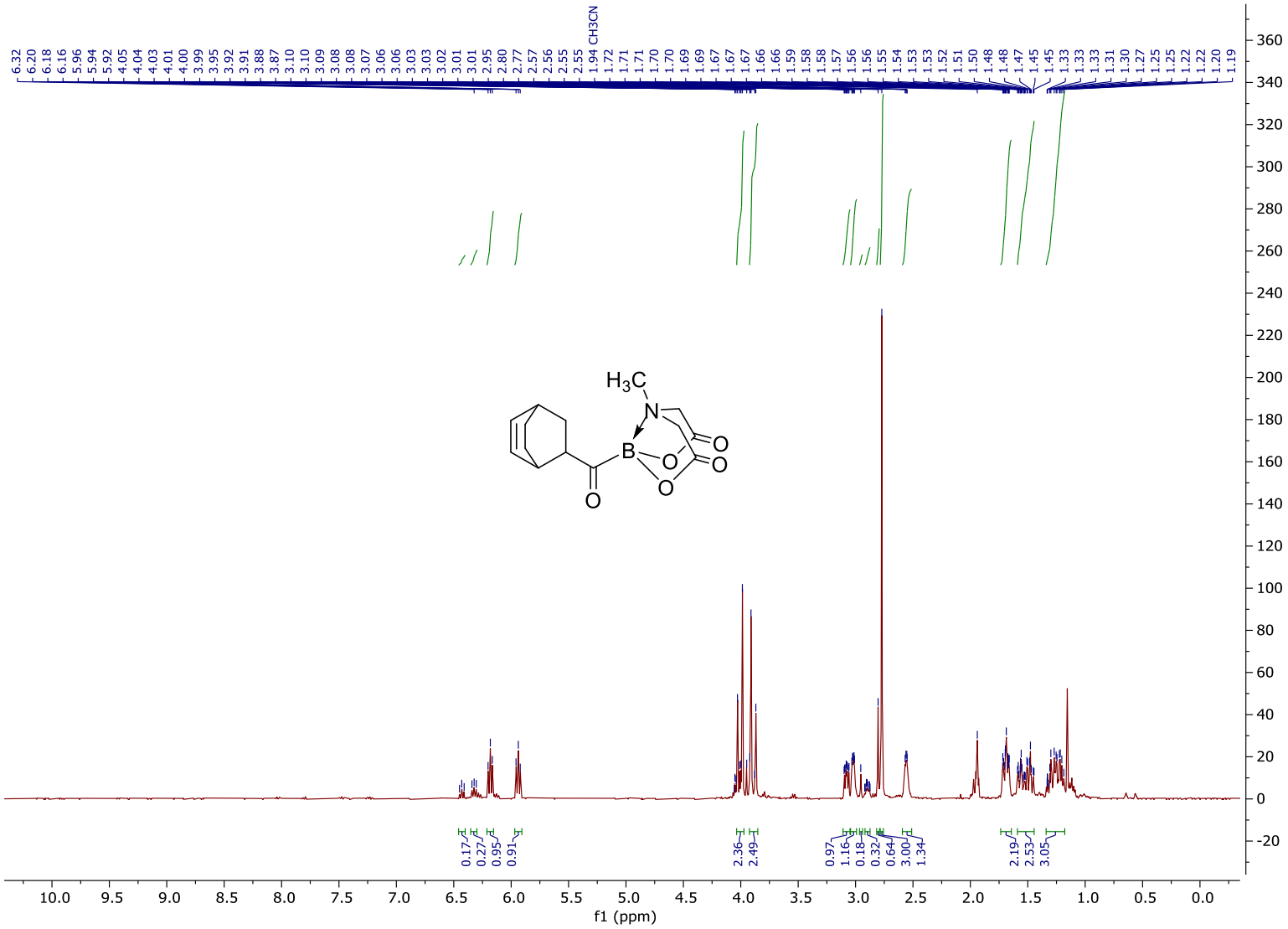
^{11}B NMR, compound 11

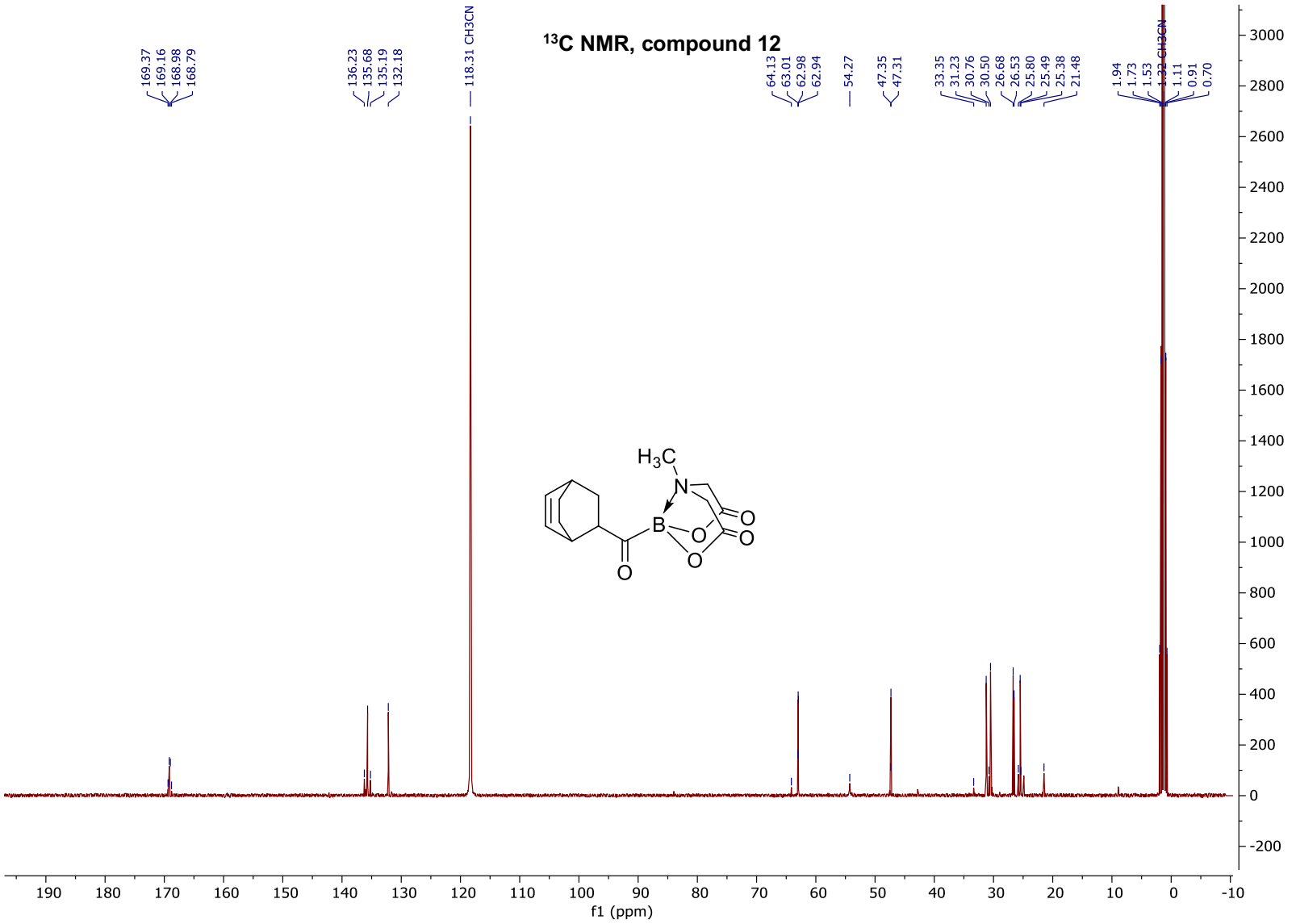


^{19}F NMR, compound 11

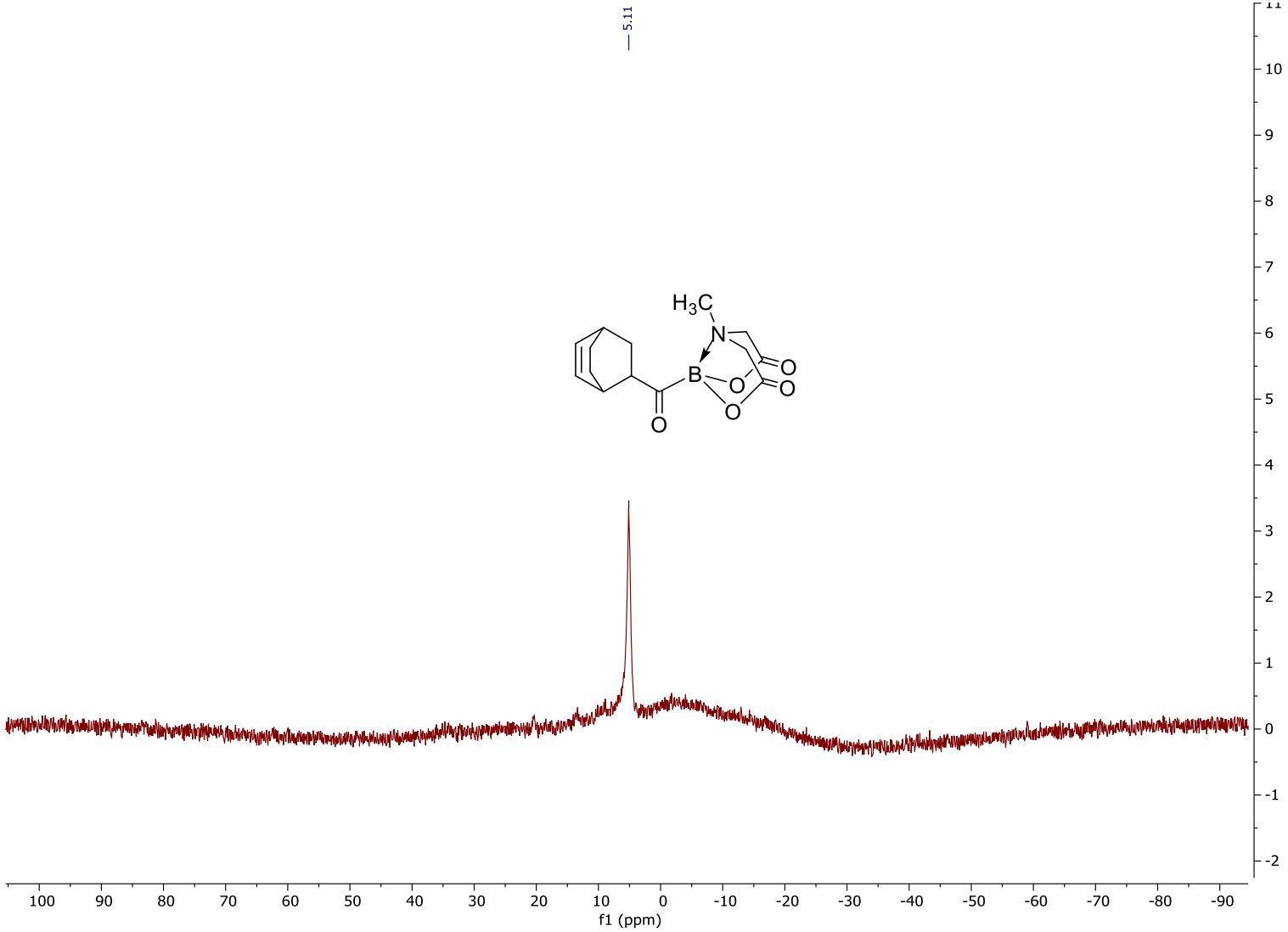


^{1}H NMR, compound 12

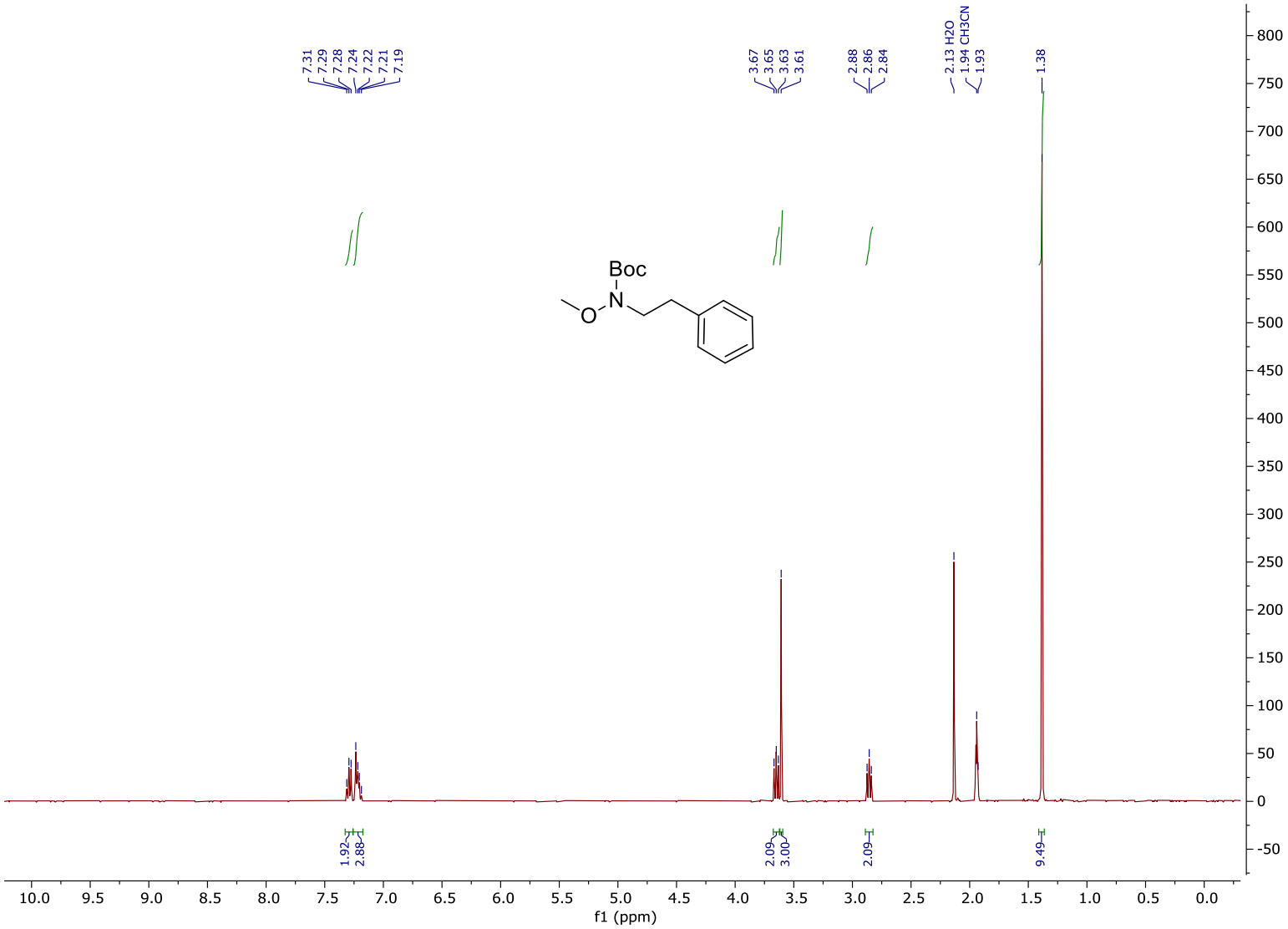



13C NMR, compound 12
169.37
169.16
168.98
168.79
136.23
135.68
135.19
132.18
118.31 CH3CN
64.13
63.01
62.98
62.94
54.27
47.35
47.31
33.35
31.23
30.76
30.50
26.68
26.53
25.80
25.49
25.38
21.48
1.94
1.73
1.53
1.32 CH3CN
1.11
0.91
0.70
H3C
N
B
O
O
O
O
O
f1 (ppm)

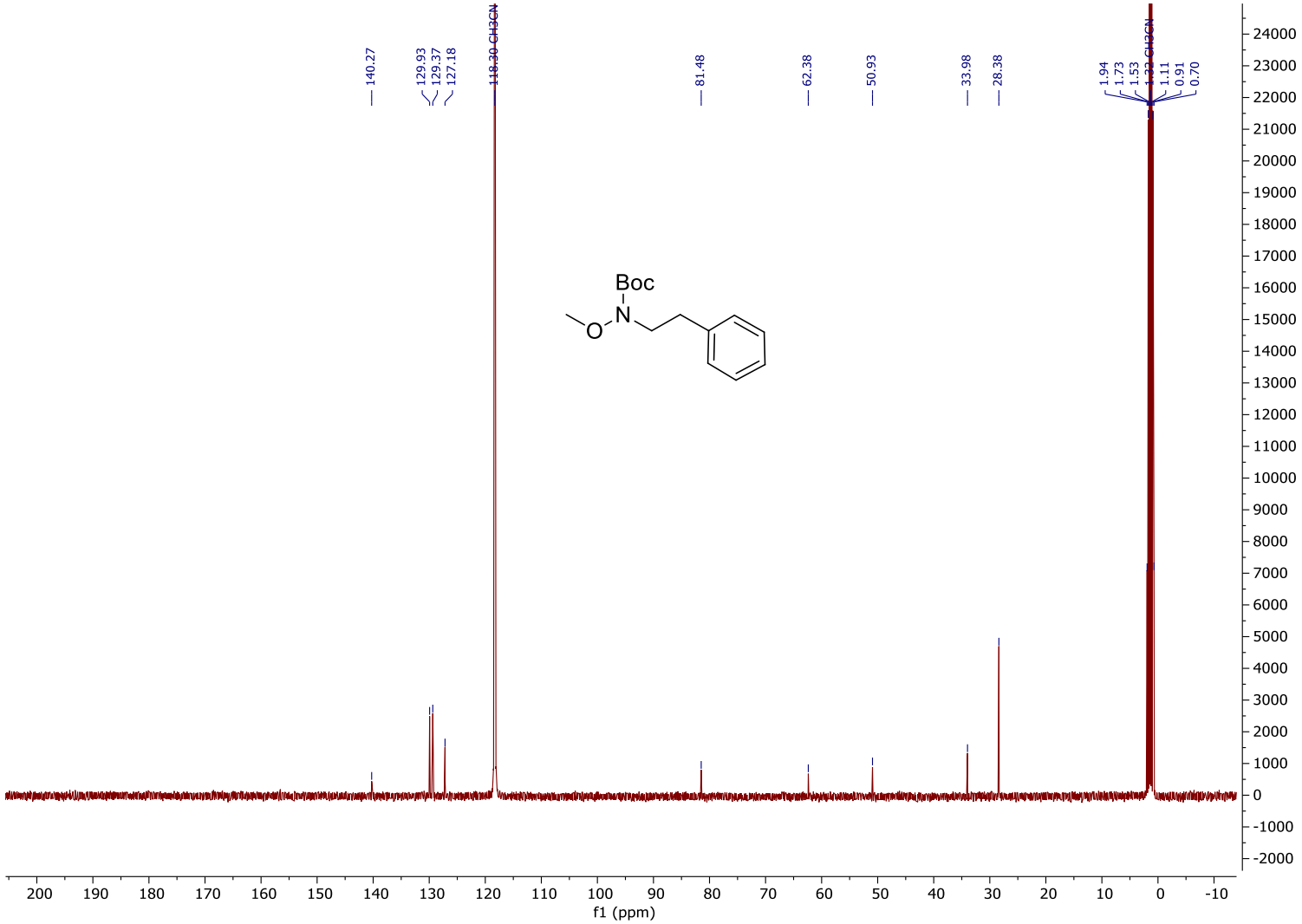
^{11}B NMR, compound 12



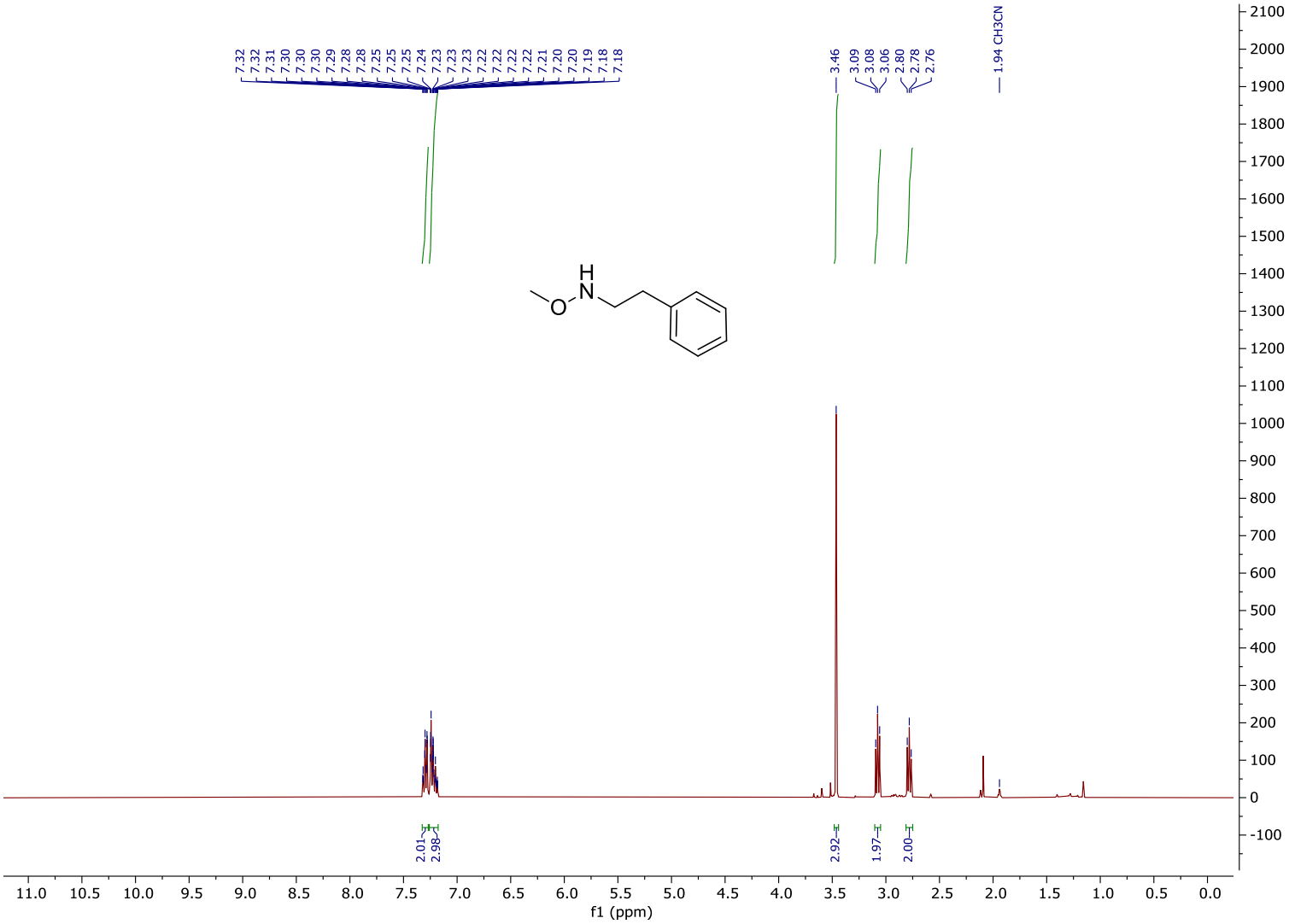
^{1}H NMR, compound 13



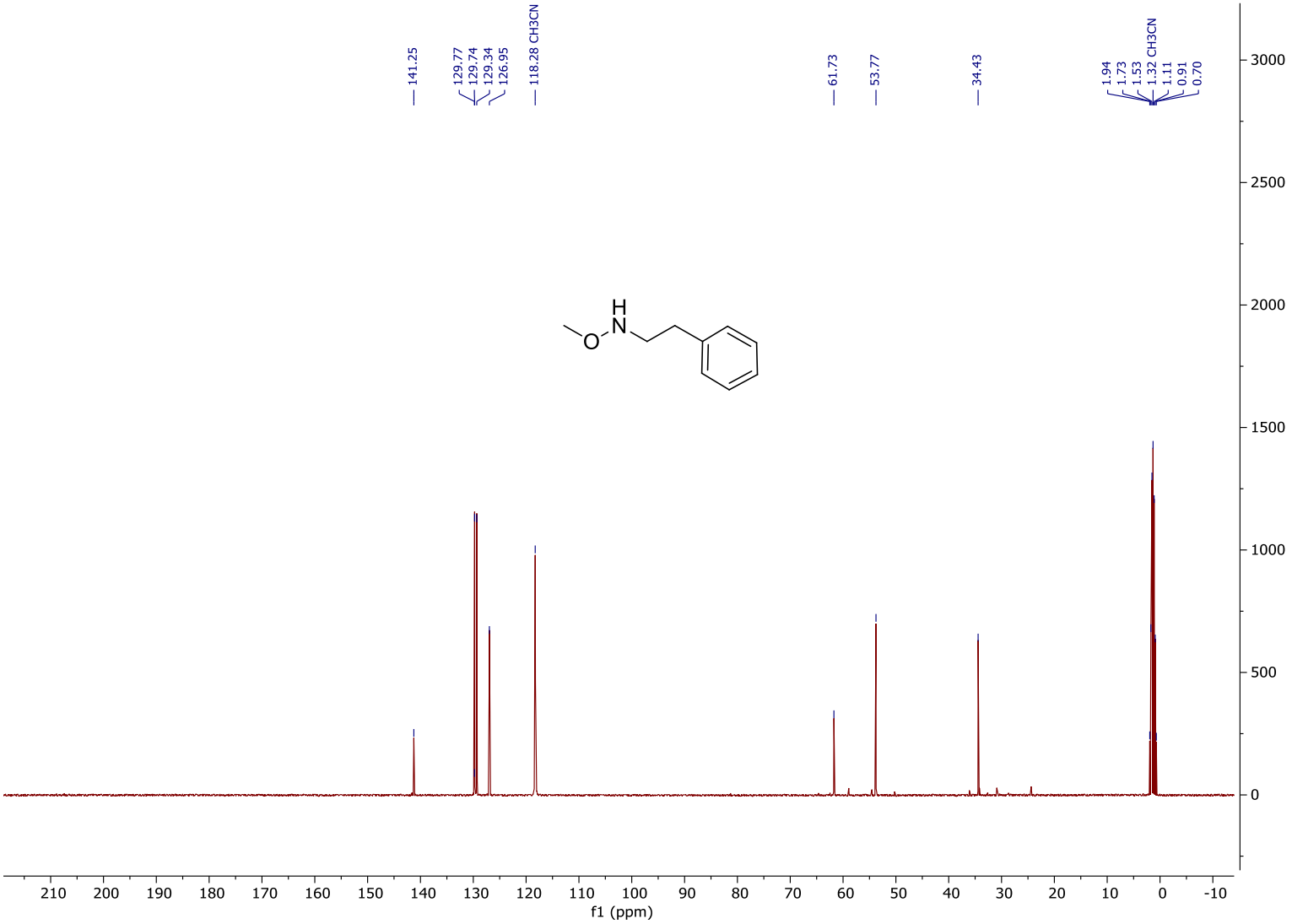
^{13}C NMR, compound 13



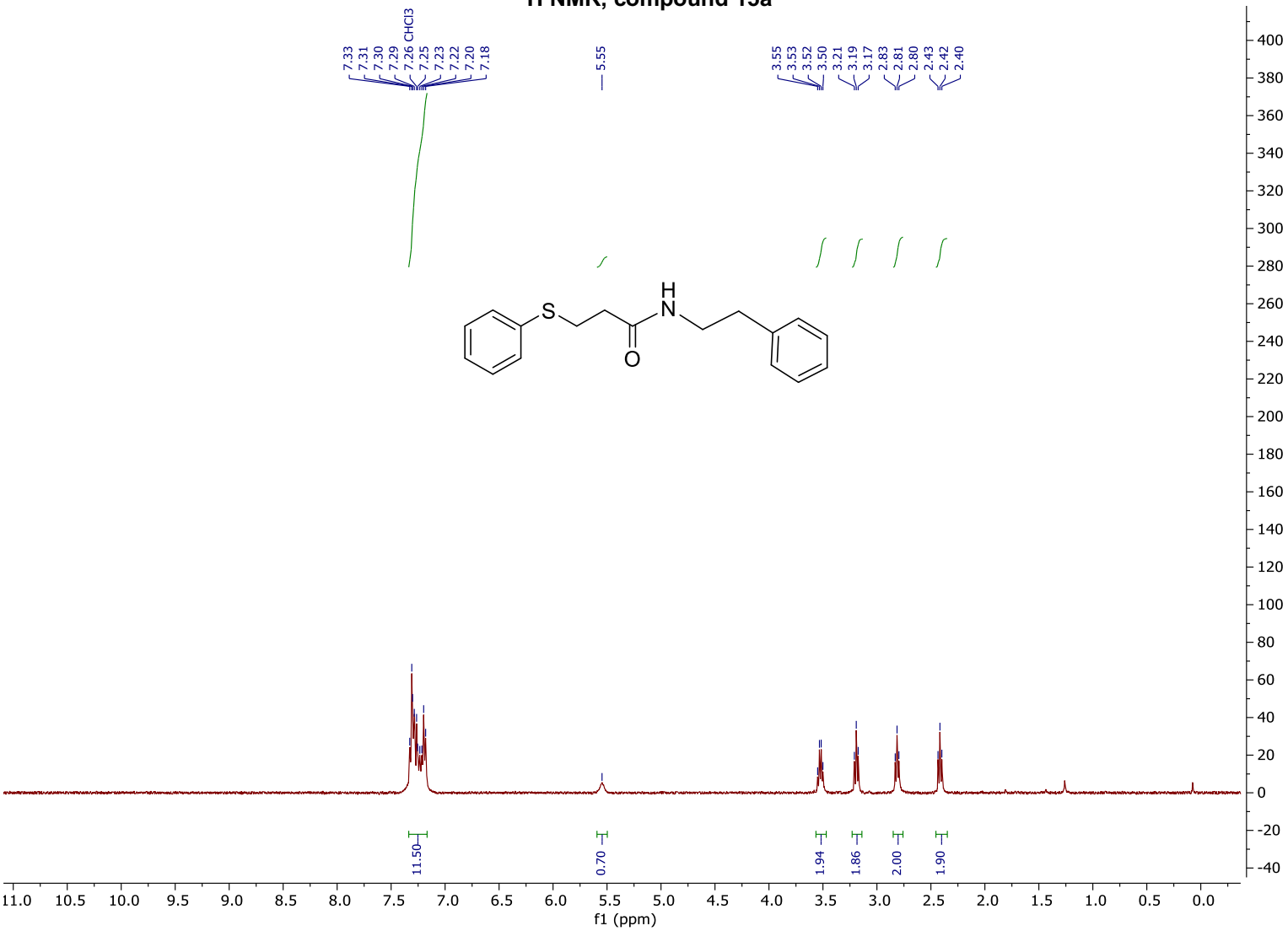
^{1}H NMR, compound 14



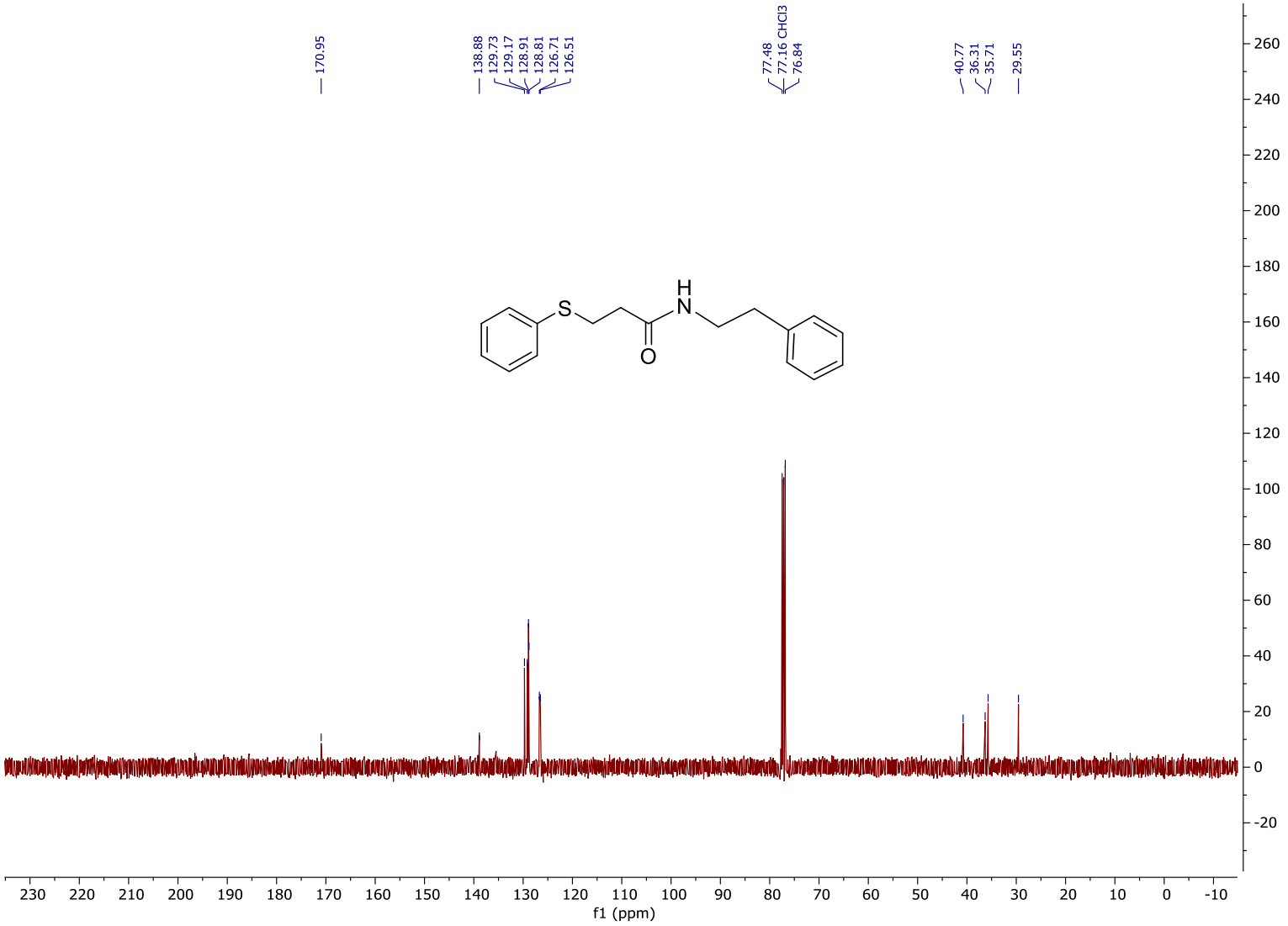
^{13}C NMR, compound 14

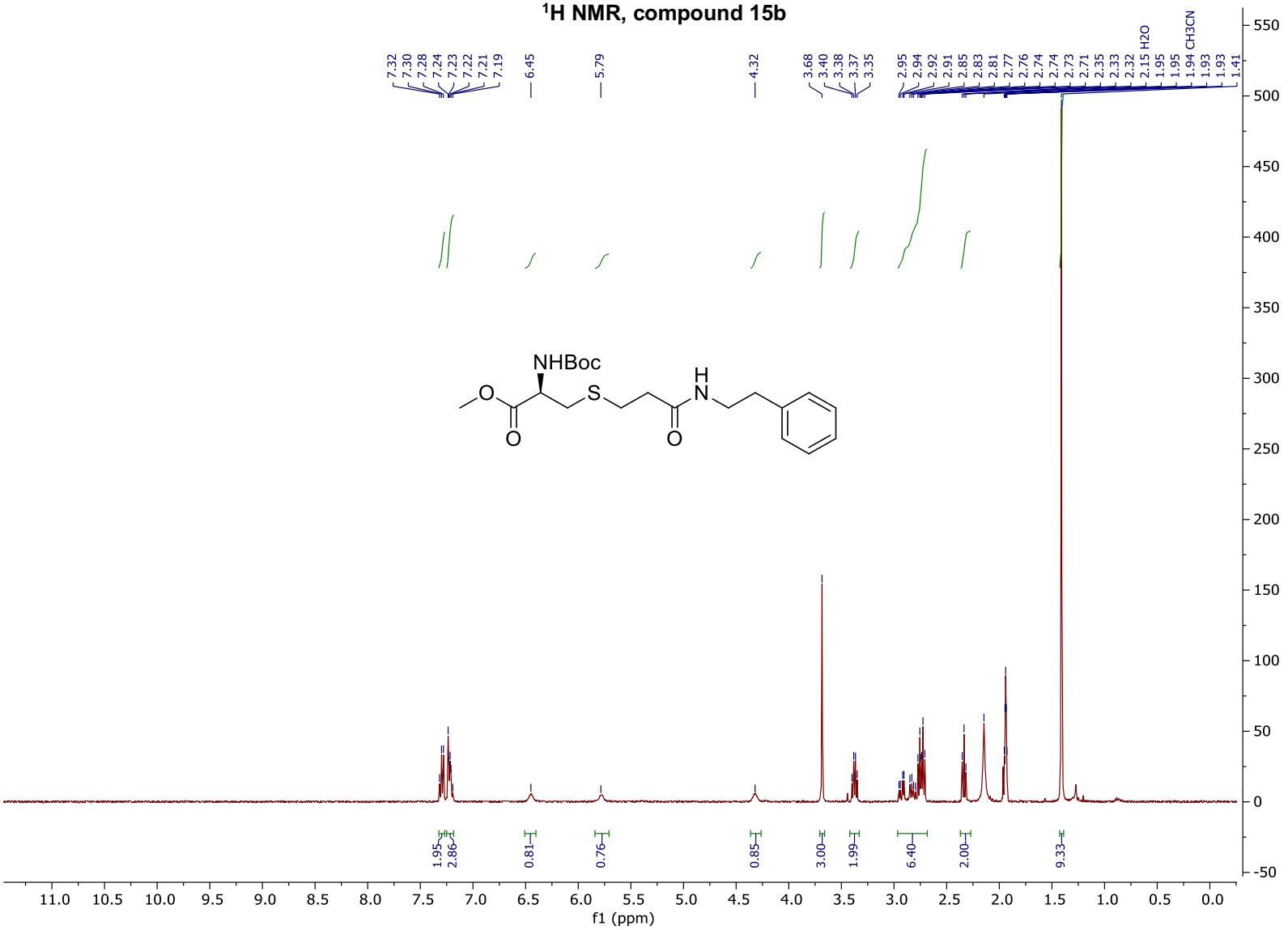


^{1}H NMR, compound 15a

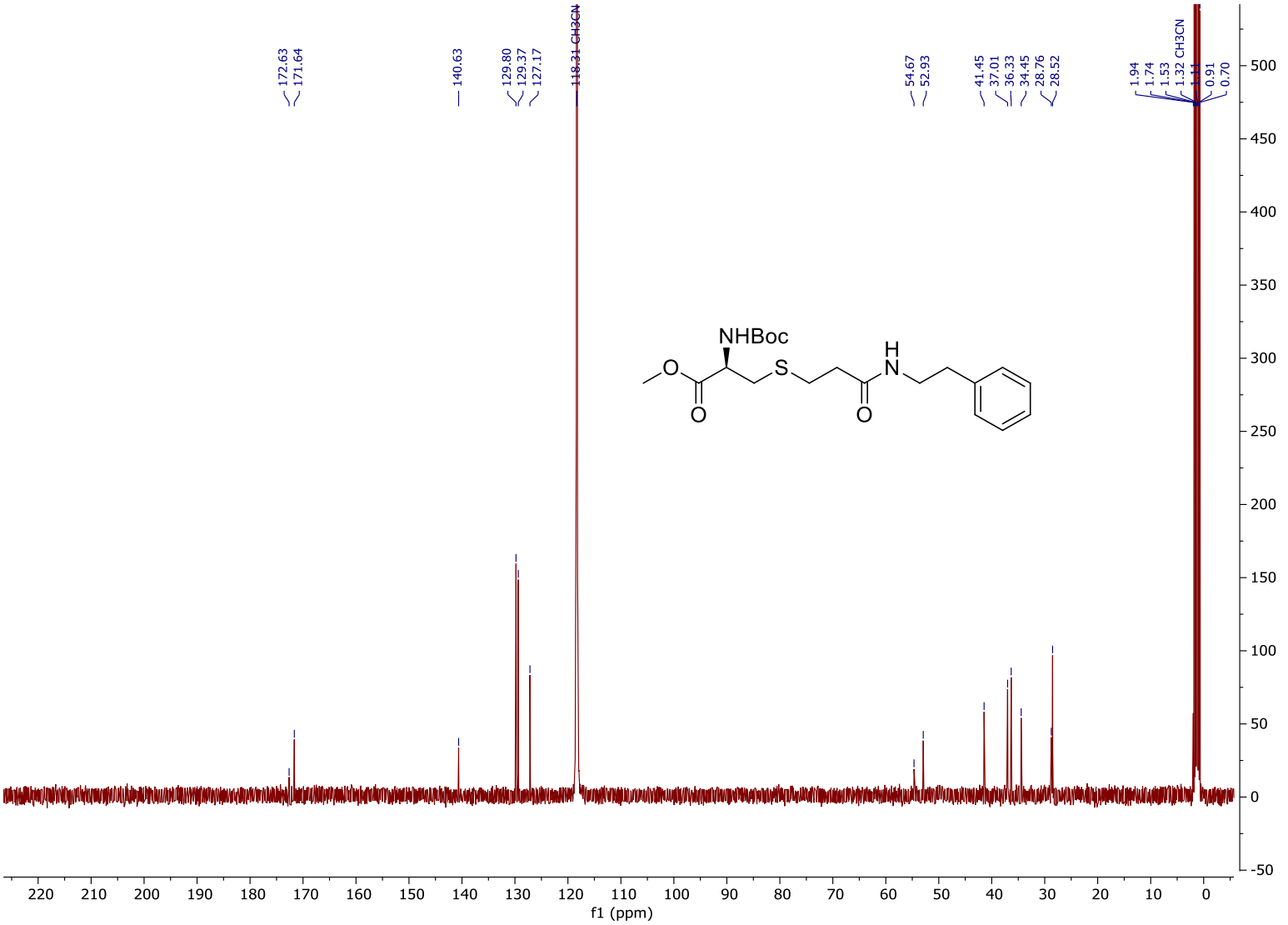


^{13}C NMR, compound 15a

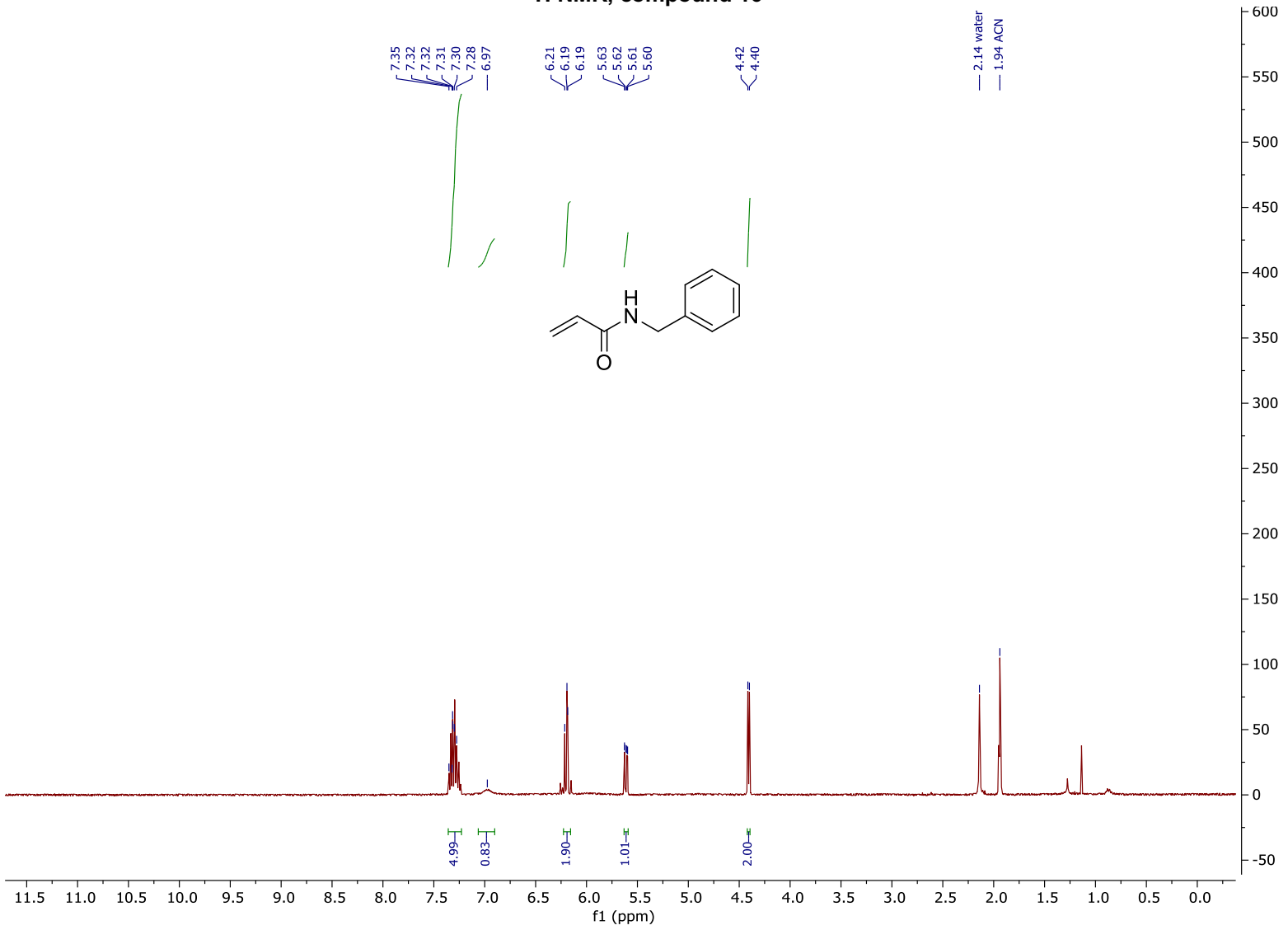



¹H NMR, compound 15b
7.32
7.30
7.28
7.24
7.23
7.22
7.21
7.19
6.45
5.79
4.32
3.68
3.40
3.38
3.37
3.35
2.95
2.94
2.92
2.91
2.85
2.83
2.81
2.77
2.76
2.74
2.74
2.73
2.71
2.35
2.33
2.32
2.15 H2O
1.95
1.95
1.94 CH3CN
1.93
1.93
1.41
NHBoc
O
S
H
N
O
O
1.95
2.86
0.81
0.76
0.85
3.00
1.99
6.40
2.00
9.33
f1 (ppm)

^{13}C NMR, compound 15b



^{1}H NMR, compound 16



^{13}C NMR, compound 16