Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Transition-metal-free $PhI(OAc)_2$-promoted highly selective hydroboration of terminal alkynes under air

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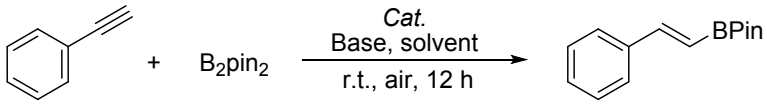
Contents

1. General information

All chemicals and solvents were purchased from Aldrich, J&K and Alfa Aesar Chemical Company as reagent grade and used without further purification unless otherwise stated. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Bruker Avance 400 spectrometer at room temperature. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were collected in $CDCl_3$ (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F) spectrometer with TMS as internal standard. Carbons with directly attached boron atoms were not observed, most likely due to quadrupolar relaxation.[1] HRMS were performed on a Brucker Daltonics Bio-TOF-Q mass spectrometer by the ESI method and LC-MS were obtained on a on a Waters Xevo TQ (Waters, Manchester, UK) equipped with an ESI source. The products were purified by flash column chromatography on silica gel (200-300 mesh).

2. Screening with different parameters

Table S1. Optimization of catalysts[a]



1a **2** **3a**

Entry	Catalyst	Base	Solvent	Yield(%)[b]
1	NaI	*t*-BuONa	EtOH	17
2	KI	*t*-BuONa	EtOH	18
3	TBAI	*t*-BuONa	EtOH	13
4	PhI	*t*-BuONa	EtOH	17
5	KIO_3	*t*-BuONa	EtOH	35
6	1-Hydroxy-1,2-benziodoxole-3-one	*t*-BuONa	EtOH	12
7	$PhI(OPiv)_2$	*t*-BuONa	EtOH	25
8	$PhI(OTFA)_2$	*t*-BuONa	EtOH	36
9	Ph_2IBF_4	*t*-BuONa	EtOH	18
10	**$PhI(OAc)_2$**	***t*-BuONa**	**EtOH**	**90**
11	Dess-Martin	*t*-BuONa	EtOH	12

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), catalyst (15 mol%), *t*-BuONa (2 equiv), EtOH (4 mL), r.t., air, 12 h. [b] Isolated yields based on **1a**.

Table S2. Optimization of bases[a].

Entry	Catalyst	Base	Solvent	Yield(%)[b]
1	$PhI(OAc)_2$	-	EtOH	0
2	$PhI(OAc)_2$	K_2CO_3	EtOH	17
3	$PhI(OAc)_2$	Cs_2CO_3	EtOH	16
4	$PhI(OAc)_2$	KOH	EtOH	31
5	$PhI(OAc)_2$	LiOH	EtOH	43
6	$PhI(OAc)_2$	DBU	EtOH	7
7	$PhI(OAc)_2$	Et_3N	EtOH	9
8	$PhI(OAc)_2$	DIPEA	EtOH	n.d.

9	$PhI(OAc)_2$	Pyridine	EtOH	n.d.
10	$PhI(OAc)_2$	DMAP	EtOH	n.d.
11	$PhI(OAc)_2$	MeONa	EtOH	50
12	$PhI(OAc)_2$	EtONa	EtOH	55
13	$PhI(OAc)_2$	*t*-BuOLi	EtOH	5
14	**$PhI(OAc)_2$**	***t*-BuONa**	**EtOH**	**90**
15	$PhI(OAc)_2$	*t*-BuOK	EtOH	62

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), $PhI(OAc)_2$ (15 mol%), base (2 equiv), EtOH (4 mL), r.t., air, 12 h; DBU: 1,5-diaza(5,4,0)undec-5-ene; DIPEA: N,N'-diisopropylethylamine; DMAP: 4-dimethylaminopyridine. [b] Isolated yields based on **1a**.

Table S3. Optimization of loading of catalyst[a].

Entry	$PhI(OAc)_2$	Base	Solvent	Yield(%)[b]
1	1%	*t*-BuONa	EtOH	32
2	5%	*t*-BuONa	EtOH	42
3	10%	*t*-BuONa	EtOH	73
4	12%	*t*-BuONa	EtOH	85
5	**15%**	***t*-BuONa**	**EtOH**	**90**
6	*18%*	*t*-BuONa	EtOH	89
7	20%	*t*-BuONa	EtOH	90

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), *t*-BuONa (2 equiv), EtOH (4 mL), r.t., air, 12 h. [b] Isolated yields based on **1a**.

Table S4. Optimization of solvents[a].

Entry	Catalyst	Base	Solvent	Yield(%)[b]
1	$PhI(OAc)_2$	*t*-BuONa	MeOH	40
2	**$PhI(OAc)_2$**	***t*-BuONa**	**EtOH**	**90**
3	$PhI(OAc)_2$	*t*-BuONa	*n*-PrOH	71
4	$PhI(OAc)_2$	*t*-BuONa	*i*-PrOH	55
5	$PhI(OAc)_2$	*t*-BuONa	*t*-BuOH	25
6	$PhI(OAc)_2$	*t*-BuONa	EtOH	35[c]

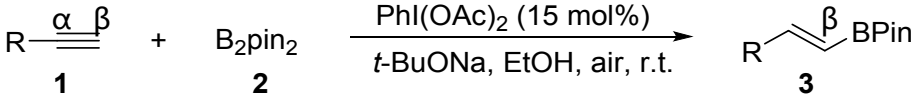
[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), $PhI(OAc)_2$ (15 mol%), *t*-BuONa (2 equiv), solvent (4 mL), r.t., air, 12 h. [b] Isolated yields based on **1a**. [c] 95% EtOH.

Table S5. Optimization of loading of bases[a].

Entry	Catalyst	Base	Solvent	Yield(%)[b]
1	$PhI(OAc)_2$	0.2	EtOH	15
2	$PhI(OAc)_2$	0.5	EtOH	39
3	$PhI(OAc)_2$	1.0	EtOH	60
4	$PhI(OAc)_2$	1.3	EtOH	69
5	$PhI(OAc)_2$	1.5	EtOH	82
6	**$PhI(OAc)_2$**	**1.8**	**EtOH**	**90**
7	$PhI(OAc)_2$	2.0	EtOH	90
8	$PhI(OAc)_2$	2.5	EtOH	91

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), $PhI(OAc)_2$ (15 mol%), *t*-BuONa, EtOH (4 mL), r.t., air, 12 h. [b] Isolated yields based on **1a**.

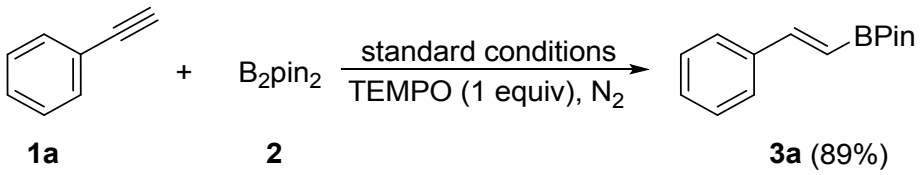
3. Typical experimental procedure



Alkyne **1** (0.5 mmol), B_2Pin_2 **2** (0.75 mmol, 191 mg), *t*-BuONa (0.9 mmol, 87 mg), $PhI(OAc)_2$ (0.075 mmol, 24 mg) were added to a round-bottom flask with EtOH (4 mL). Then, the reaction mixture was stirred at room temperature under air for 12 h. After completion of the reaction, the reaction mixture was concentrated in vaccum. The residue was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate) to afford the corresponding product **3**.

4. Preliminary mechanistic studies

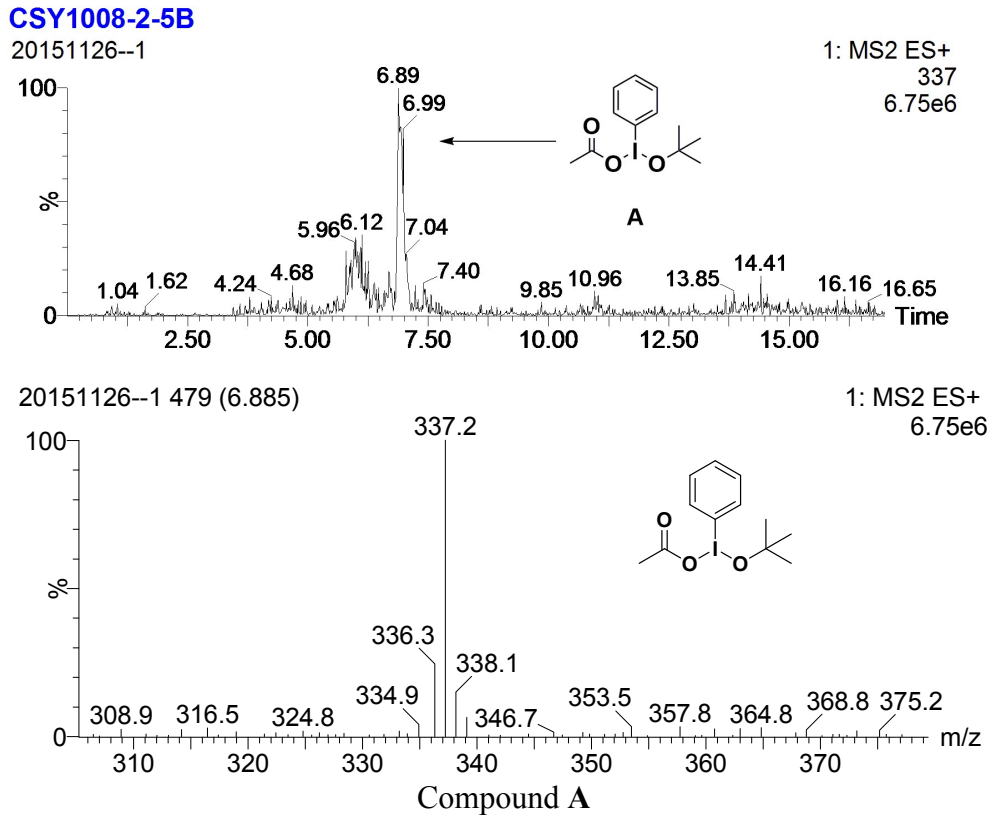
(1) Radical trapping experiment



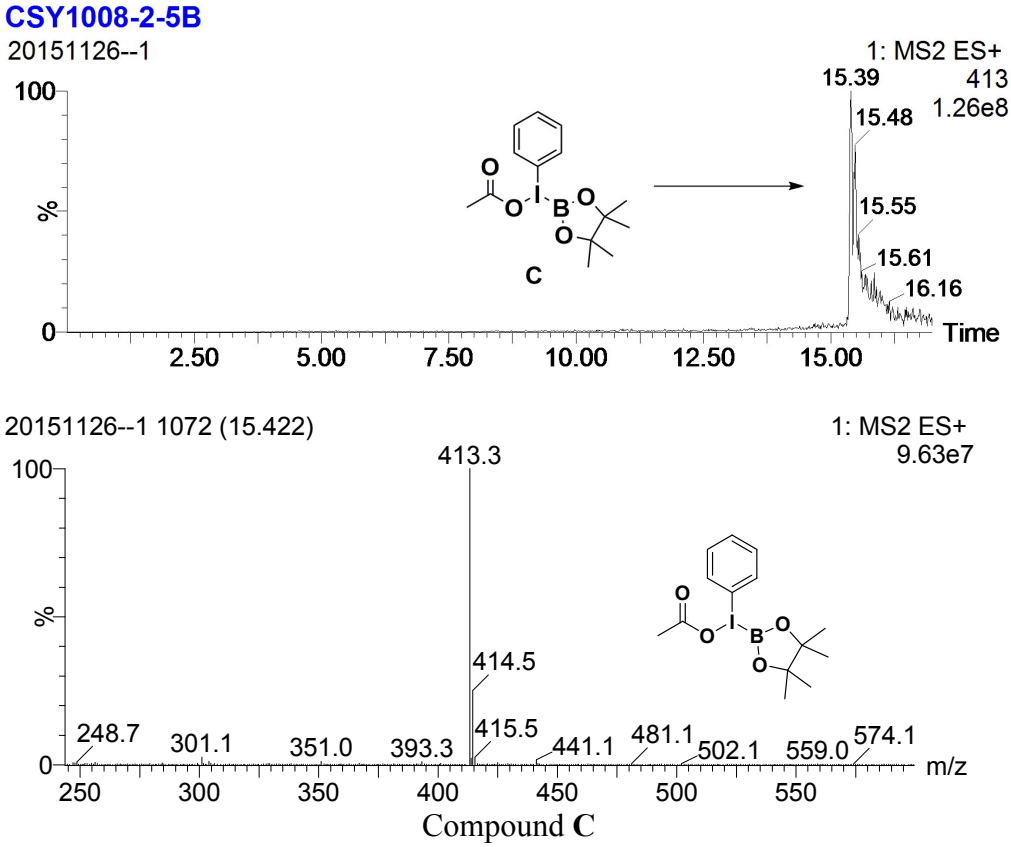
Phenylacetylene **1a** (0.5 mmol), B_2Pin_2 **2** (0.75 mmol, 191 mg), *t*-BuONa (0.9 mmol, 87 mg), TEMPO (0.5 mmol, 78 mg), and $PhI(OAc)_2$ (0.075 mmol, 24 mg) were added to a round-bottom flask with EtOH (4 mL), then the reaction mixture was stirred under at room temperature N_2 atmosphere for 12 h. The corresponding product **3a** was still obtained in 89% yield.

(2) LC-MS analysis

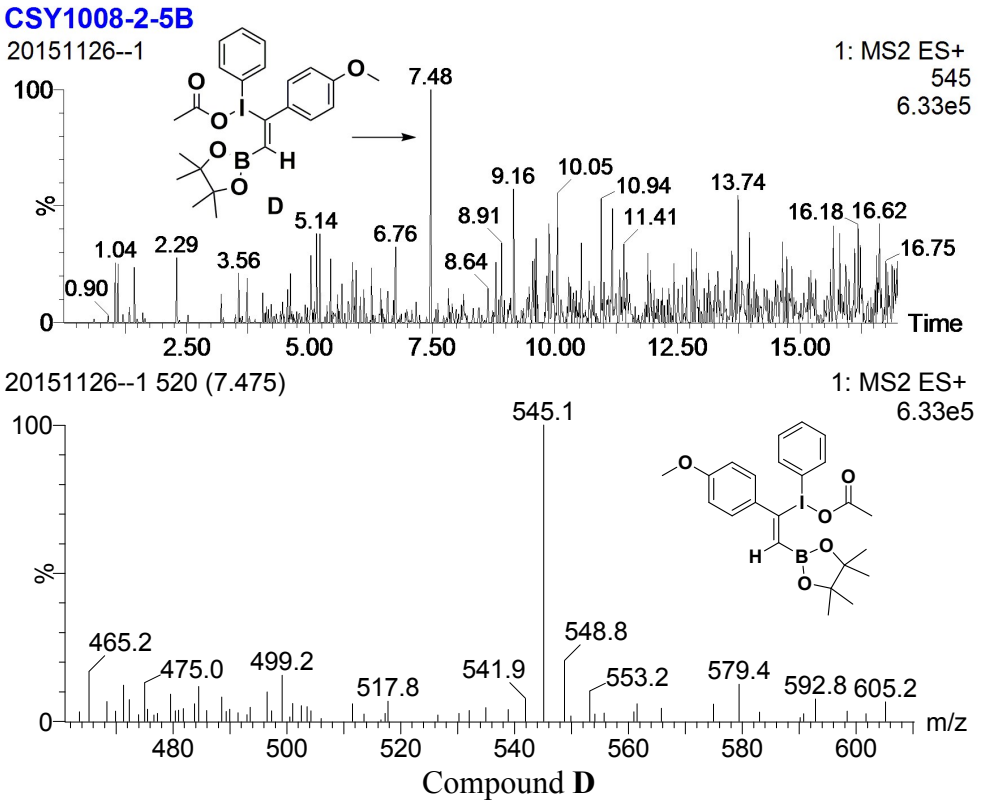
B_2Pin_2 **2** (0.75 mmol, 191mg), $PhI(OAc)_2$ (0.075 mmol, 24 mg), *t*-BuONa (0.9 mmol, 87 mg), 1-ethynyl-4-methoxybenzene **1b** (0.5 mmol), and EtOH (4 mL) were added to a round-bottom flask equipped with a magnetic stirrer. Then, the reaction mixture was stirred at room temperature under air atmosphere for 4 h. This reaction mixture was directly analyzed by LC-MS. In addition to the desired product **3b**, the $[M+H]^+$ ion peaks (m/z = 337.2, 309.1) for intermediates **A** and **E** and the $[M+Na]^+$ ion peaks (m/z = 413.3, 545.1) for intermediate **C** and **D** were detected.



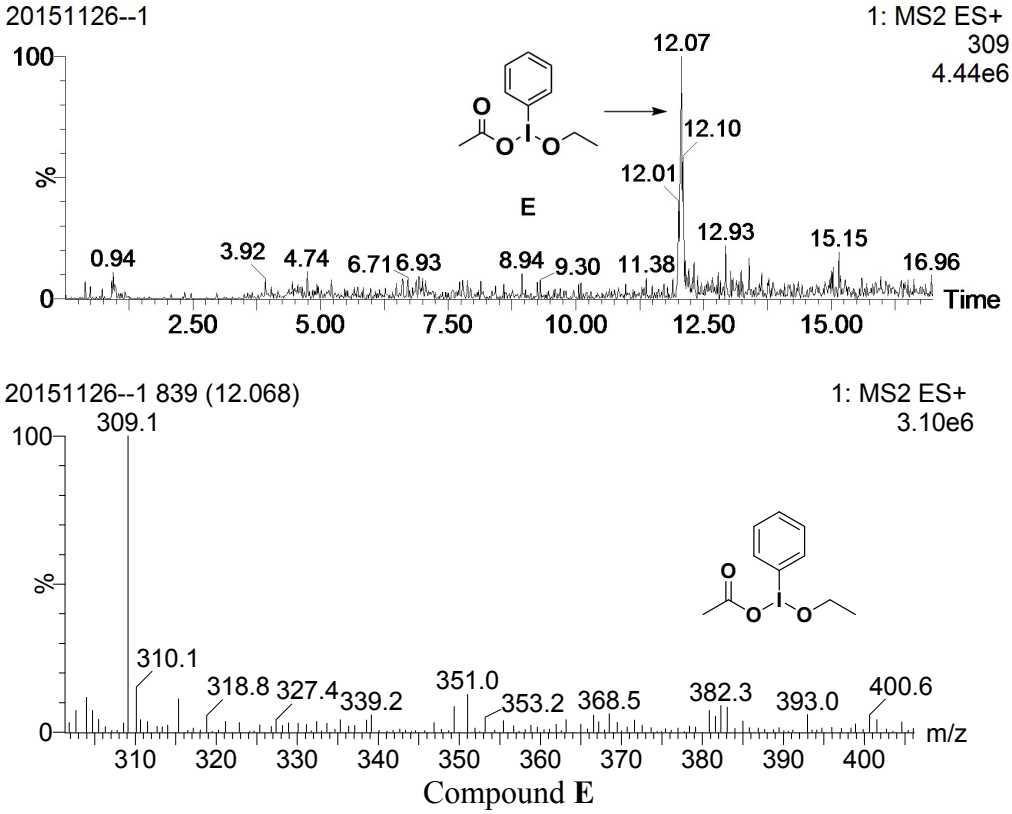
Compound **A**



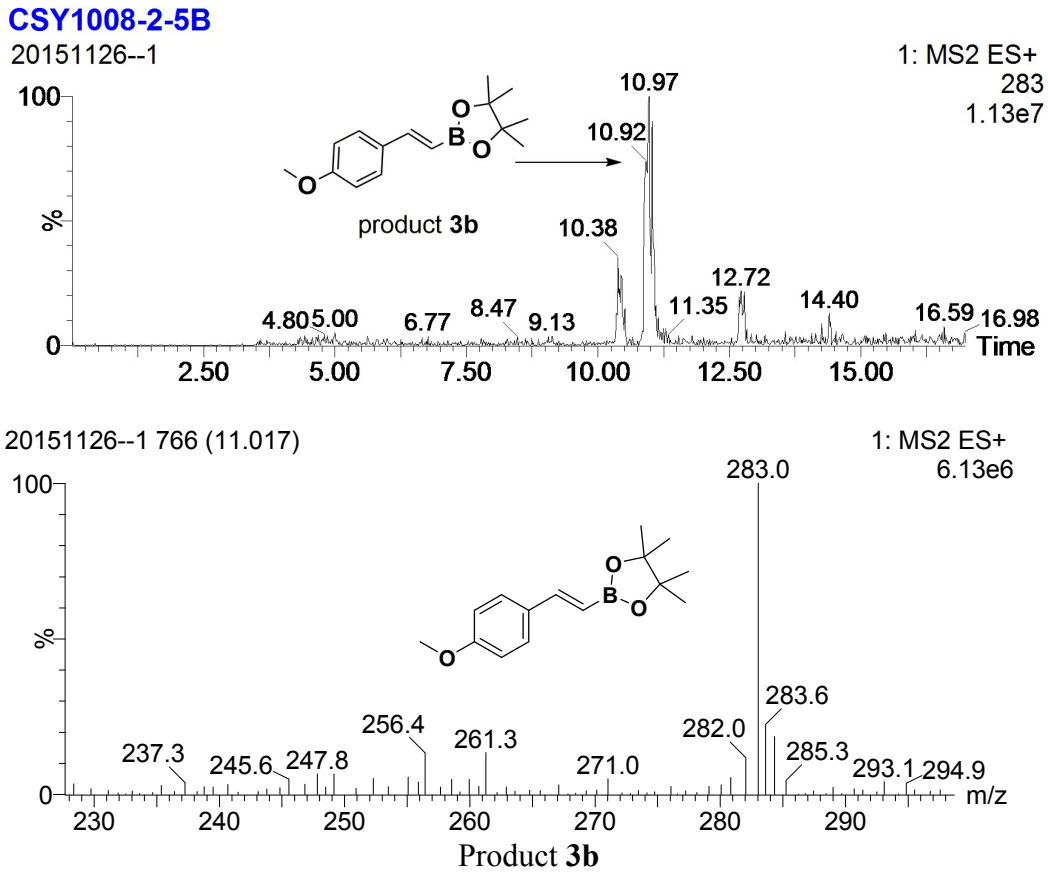
Compound **C**



Compound **D**

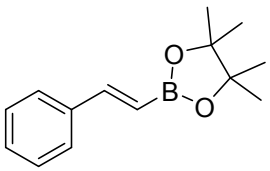


Compound **E**



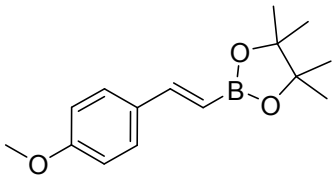
5. Characterization data of products (3a-3t)

***(E)*-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a)[2]:**



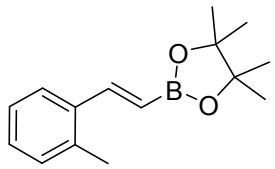
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 18.5 Hz, 1H), 7.35 (ddd, J = 12.3, 8.4, 4.2 Hz, 3H), 6.19 (d, J = 18.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.53, 137.47, 128.92, 128.59, 127.08, 83.38, 24.84.

***(E)*-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)[3]:**



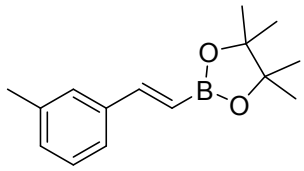
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 18.4 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 6.04 (d, J = 18.4 Hz, 1H), 3.83 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.29, 149.08, 130.38, 128.47, 113.97, 83.22, 55.28, 24.83. HR-MS(M+H)$^+$ calculated for $C_{15}H_{22}BO_3$ 261.1657, found 261.1657.

***(E)*-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane (3c)[2]:**



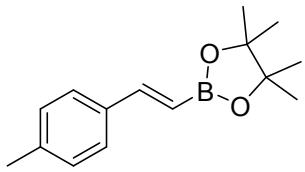
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 18.3 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.21 (dd, J = 6.2, 2.8 Hz, 2H), 7.19 – 7.13 (m, 1H), 6.11 (d, J = 18.3 Hz, 1H), 2.45 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.14, 136.33, 134.75, 130.41, 128.59, 126.12, 125.78, 83.32, 24.84, 19.85. HR-MS(M+H)$^+$ calculated for $C_{15}H_{22}BO_2$ 245.1707, found 245.1717.

***(E)*-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (3d)[2]:**



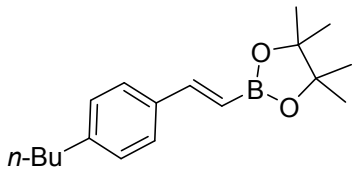
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 18.5 Hz, 1H), 7.32 (d, J = 5.7 Hz, 2H), 7.25 (t, J = 7.8 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 6.18 (d, J = 18.4 Hz, 1H), 2.37 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.71, 138.09, 137.48, 129.72, 128.47, 127.80, 124.26, 83.33, 24.82, 21.40. HR-MS(M+H)$^+$ calculated for$C_{15}H_{22}BO_2$ 245.1707, found 245.1714.

***(E)*-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (3e)[3]:**



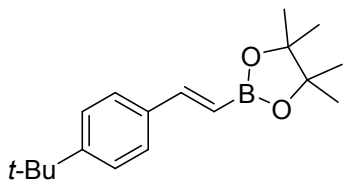
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H), 7.17 (d, J = 7.9 Hz, 2H), 6.13 (d, J = 18.4 Hz, 1H), 2.37 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.49, 138.99, 134.80, 129.31, 127.04, 83.30, 24.83, 21.35. HR-MS(M+H)$^+$ calculated for $C_{15}H_{22}BO_2$ 245.1707, found 245.1716.

***(E)*-4,4,5,5-tetramethyl-2-(4-pentylstyryl)-1,3,2-dioxaborolane (3f)[2]:**



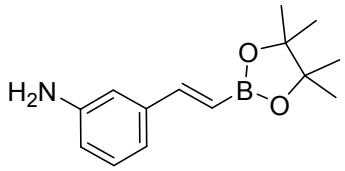
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 18.5 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 6.15 (d, J = 18.4 Hz, 1H), 2.61 (m, 2H), 1.63 (m, 2H), 1.34 (s, 16H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.57, 144.06, 135.03, 128.65, 127.05, 83.28, 35.77, 31.50, 31.01, 24.82, 22.54, 14.03. HR-MS(M+H)$^+$ calculated for $C_{19}H_{30}BO_2$ 301.2333, found 301.2332.

***(E)*-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)[4]:**



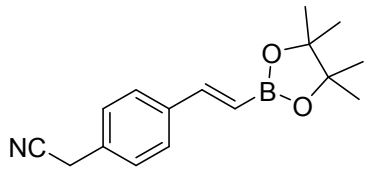
^{1}H NMR (400 MHz, CDCl3) δ 7.46 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 18.4 Hz, 1H), 7.39 (d, J = 8.3 Hz, 3H), 6.15 (d, J = 18.4 Hz, 1H), 1.34 (s, 21H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.13, 149.40, 134.78, 126.84, 125.51, 83.29, 34.71, 31.25, 24.83. HR-MS(M+H)$^+$ calculated for $C_{19}H_{30}BO_2$ 301.2333, found 301.2334.

***(E)*-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (3h)[3]:**



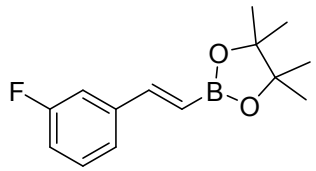
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 18.4 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.70 – 6.62 (m, 1H), 6.12 (d, *J* = 18.4 Hz, 1H), 3.71 (s, 2H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.72, 146.45, 138.57, 129.46, 117.97, 115.93, 113.40, 83.32, 24.82. HR-MS(M+H)$^+$ calculated for $C_{14}H_{21}BNO_2$ 246.1660, found 246.1657.

***(E)*-2-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (3i)[5]:**



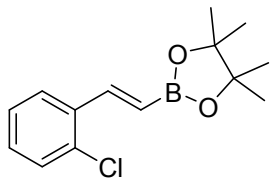
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 18.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.19 (d, *J* = 18.4 Hz, 1H), 3.76 (s, 2H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.32, 137.35, 132.82, 130.34, 128.21, 127.70, 117.69, 83.48, 24.83, 23.45. HR-MS(M+H)$^+$ calculated for $C_{16}H_{21}BNO_2$ 270.1660, found 270.1657.

***(E)*-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)[2]:**



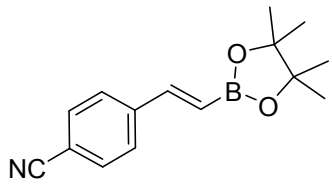
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 18.5 Hz, 1H), 7.32 (m, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.04 – 6.97 (m, 1H), 6.18 (d, *J* = 18.4 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.07 (d, *J* = 245.6 Hz), 148.07 (d, *J* = 2.5 Hz), 139.84 (d, *J* = 7.5 Hz), 130.02 (d, *J* = 8.3 Hz), 123.00 (d, *J* = 2.7 Hz), 115.68 (d, *J* = 21.5 Hz), 113.29 (d, *J* = 21.5 Hz), 83.52, 24.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.48.

***(E)*-2-(2-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)[3]:**



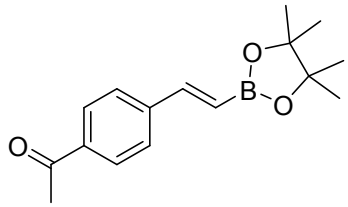
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 18.4 Hz, 1H), 7.65 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.37 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.27 – 7.21 (m, 2H), 6.19 (d, *J* = 18.3 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.96, 135.58, 133.85, 129.79, 129.70, 127.01, 126.87, 83.50, 24.84. HR-MS(M+H)$^+$ calculated for $C_{14}H_{19}BClO_2$ 265.1161, found 245.1166.

***(E)*-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (3l)[5]:**



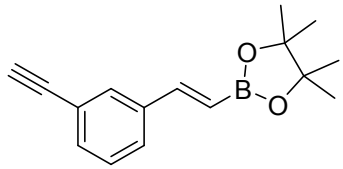
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 18.4 Hz, 1H), 6.29 (d, J = 18.4 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.20, 141.65, 132.45, 127.42, 118.81, 111.97, 83.74, 24.81. HR-MS(M+Na)$^+$ calculated for $C_{15}H_{18}BNNaO_2$ 278.1323, found 278.1319.

***(E)*-1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)ethan-1-one (3m)[6]:**



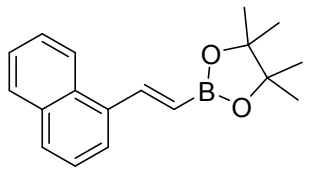
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 18.4 Hz, 1H), 6.30 (d, J = 18.4 Hz, 1H), 2.61 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.64, 148.00, 141.82, 136.98, 128.74, 127.12, 83.62, 26.70, 24.83.

***(E)*-2-(3-ethynylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)[3]:**



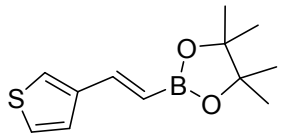
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.34 (m, 2H), 6.20 (d, J = 18.4 Hz, 1H), 3.10 (s, 1H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.30, 137.66, 132.37, 130.75, 128.61, 127.38, 122.43, 83.48, 83.37, 77.24, 24.82.

***(E)*-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (3o)[7]:**



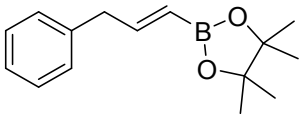
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.3 Hz, 1H), 8.24 (d, J = 18.2 Hz, 1H), 7.90 – 7.83 (m, 3H), 7.76 (d, J = 7.2 Hz, 1H), 7.53 (m, 4H), 6.29 (d, J = 18.2 Hz, 1H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.45, 135.37, 133.62, 131.11, 129.02, 128.49, 126.17, 125.79, 125.59, 124.08, 123.79, 83.43, 24.88.

***(E)*-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (3p)[2]:**



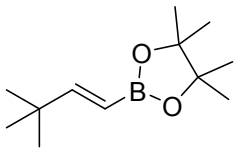
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 18.4 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.29 (dd, J = 4.7, 3.1 Hz, 1H), 5.97 (d, J = 18.4 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.16, 141.22, 126.13, 125.03, 124.89, 83.33, 24.81.

***(E)*-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3q)[3]:**



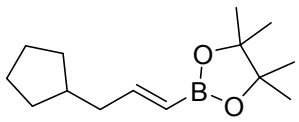
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.4 Hz, 2H), 7.21 (dd, J = 12.7, 7.4 Hz, 3H), 6.79 (dt, J = 17.8, 6.3 Hz, 1H), 5.47 (d, J = 17.8 Hz, 1H), 3.50 (d, J = 5.8 Hz, 2H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.47, 139.07, 128.94, 128.44, 126.15, 83.13, 42.29, 24.80. HR-MS(M+H)$^+$ calculated for $C_{15}H_{22}BO_2$ 245.1707, found 245.1715.

***(E)*-2-(3,3-dimethylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)[8]:**



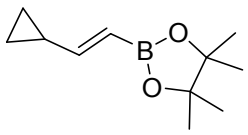
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (d, J = 18.3 Hz, 1H), 5.34 (d, J = 18.3 Hz, 1H), 1.27 (s, 13H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.36, 82.95, 34.98, 28.78, 24.79. HR-MS(M+Na)$^+$ calculated for $C_{12}H_{23}BNaO_2$ 233.1684, found 233.1696.

***(E)*-2-(3-cyclopentylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)[9]:**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (dt, J = 17.8, 6.7 Hz, 1H), 5.43 (d, J = 17.9 Hz, 1H), 2.18 (t, J = 6.9 Hz, 2H), 1.92 (dt, J = 15.0, 7.6 Hz, 1H), 1.77 (dt, J = 11.3, 6.8 Hz, 2H), 1.66 – 1.45 (m, 4H), 1.29 (s, 12H), 1.14 (dt, J = 19.2, 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.21, 82.98, 42.48, 39.01, 32.42, 25.07, 24.79. HR-MS(M+Na)$^+$ calculated for $C_{14}H_{25}BNaO_2$ 259.1840, found 259.1830.

***(E)*-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)[2]:**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (dd, J = 17.8, 9.3 Hz, 1H), 5.52 (d, J = 17.8 Hz, 1H), 1.56 – 1.51 (m, 1H), 1.28 (s, 12H), 0.83 (dt, J = 6.3, 4.3 Hz, 2H), 0.61 – 0.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.58, 82.93, 24.76, 17.02, 7.90.

6. References

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[4] M. Fleige, J. Möbus, T. vom Stein, F. Glorius and D. W. Stephan, *Chem. Commun.*, 2016, **52**, 10830-10833.
[5] C. Feng, H. Wang, L. Xu and P. Li, *Org. Biomol. Chem.*, 2015, **13**, 7136-7139.
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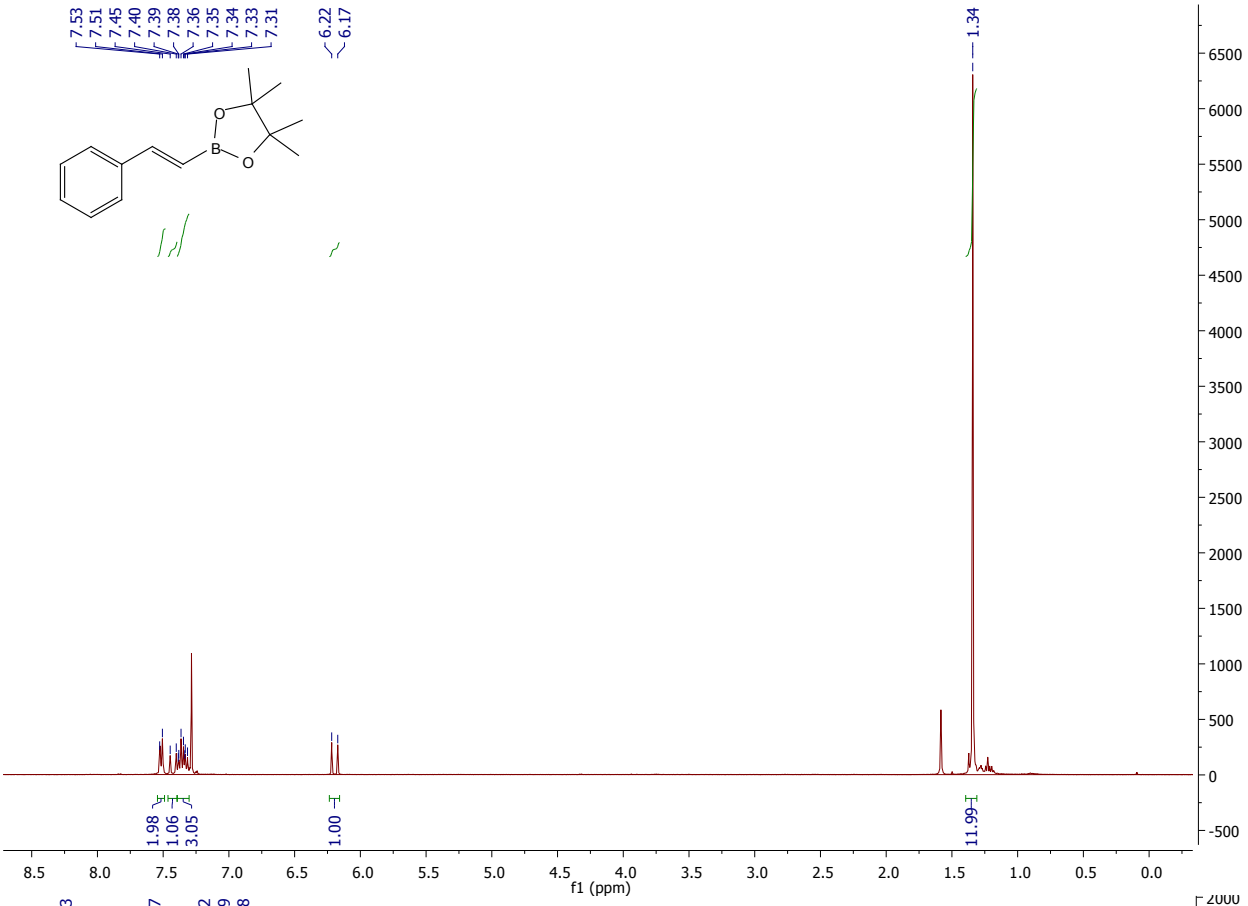
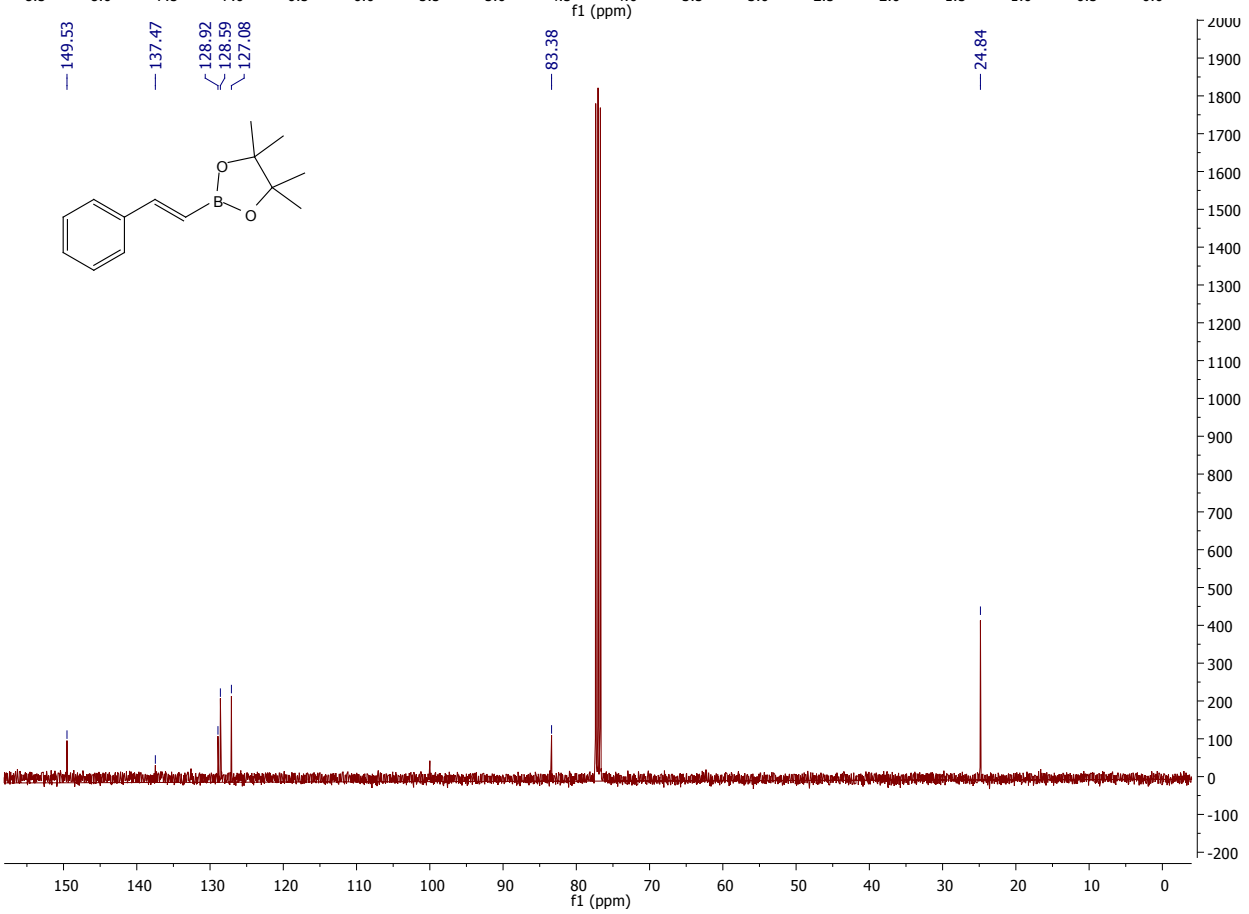
[8] A. Bismuto, S. P. Thomas and M. J. Cowley, *Angew. Chem. Int. Ed.*, 2016, **55**, 15356-15359.
[9] H. Jang, A. R. Zhugralin, Y. Lee and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2011, **133**, 7859-7871.

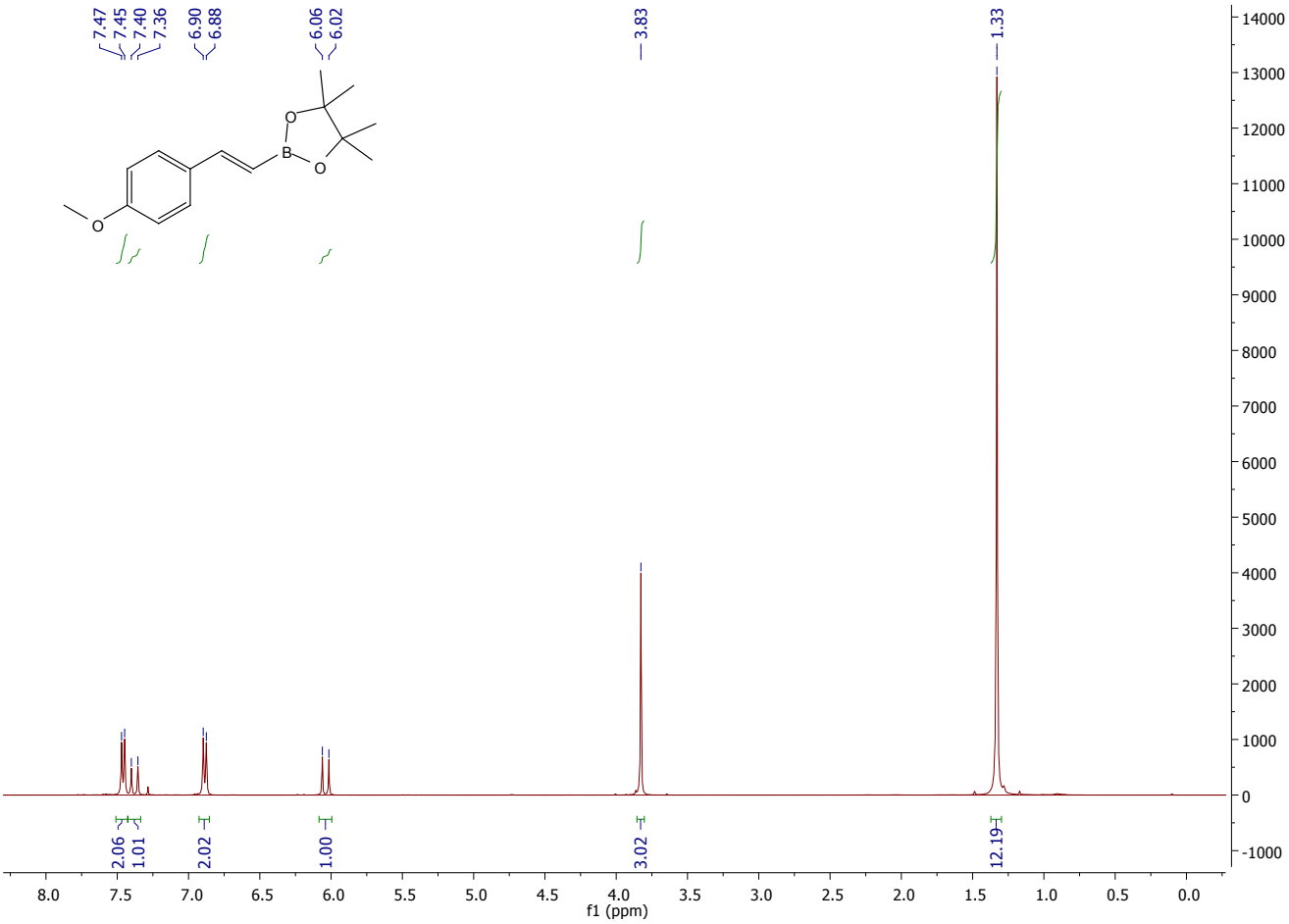
7. Copies of NMR spectra for products

3a





3b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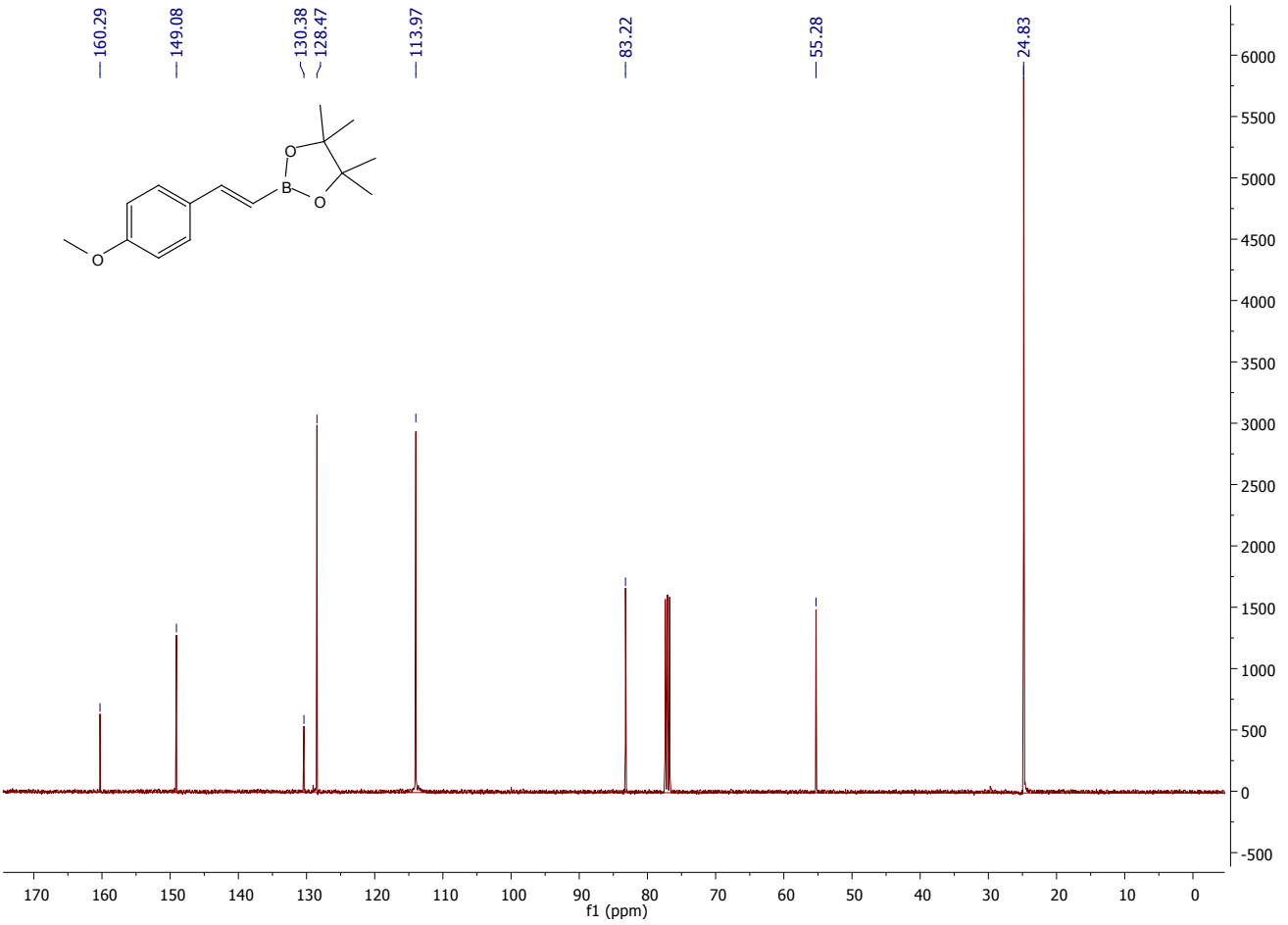
7.40
7.36
6.90
6.88
6.06
6.02
3.83
1.33
O
B
O
O
2.06
1.01
2.02
1.00
3.02
12.19
f1 (ppm)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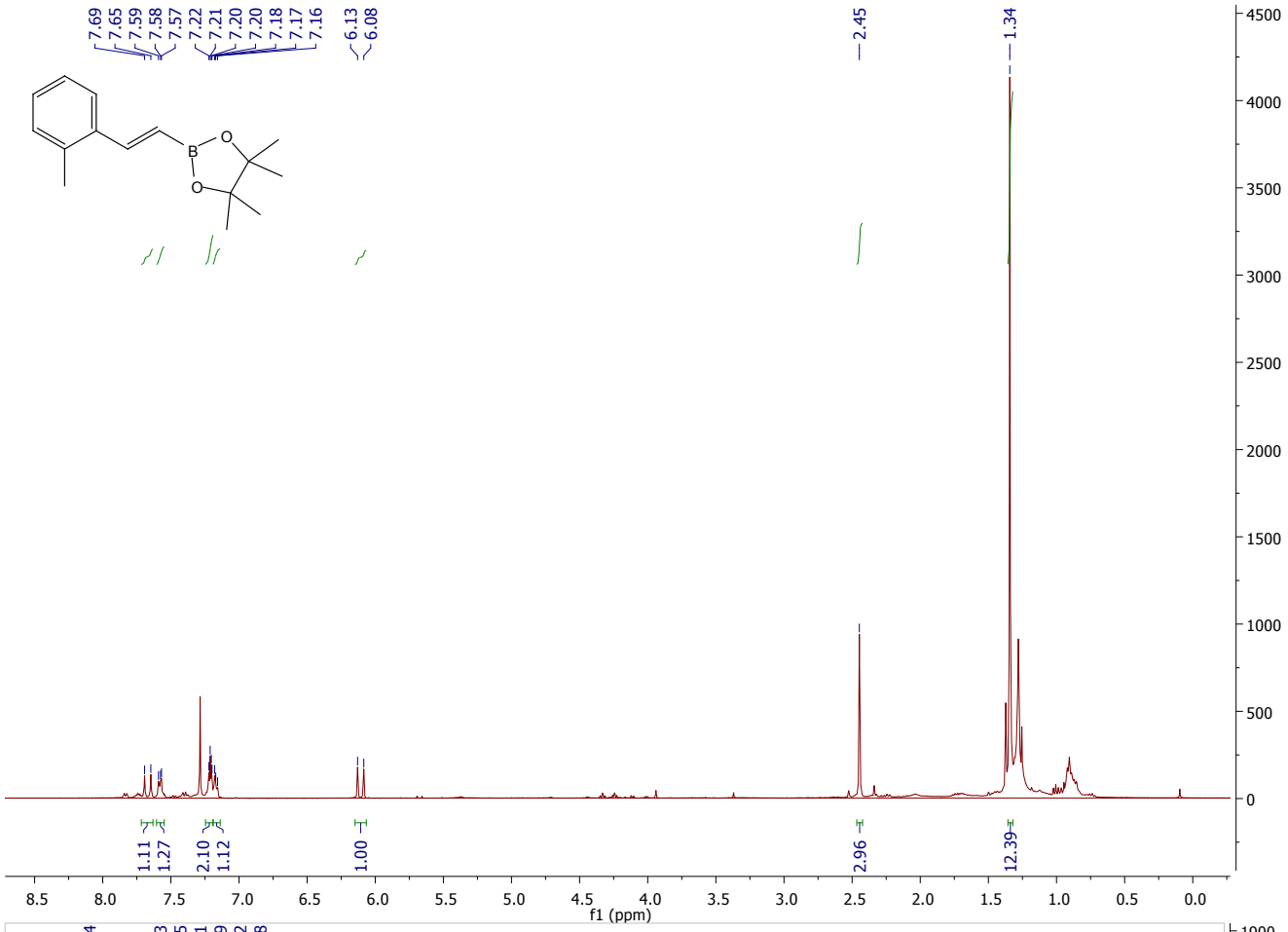
B
O
O
f1 (ppm)

3c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7.20
7.20
7.18
7.17
7.16
6.13
6.08
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1.34
1.11
1.27
2.10
1.12
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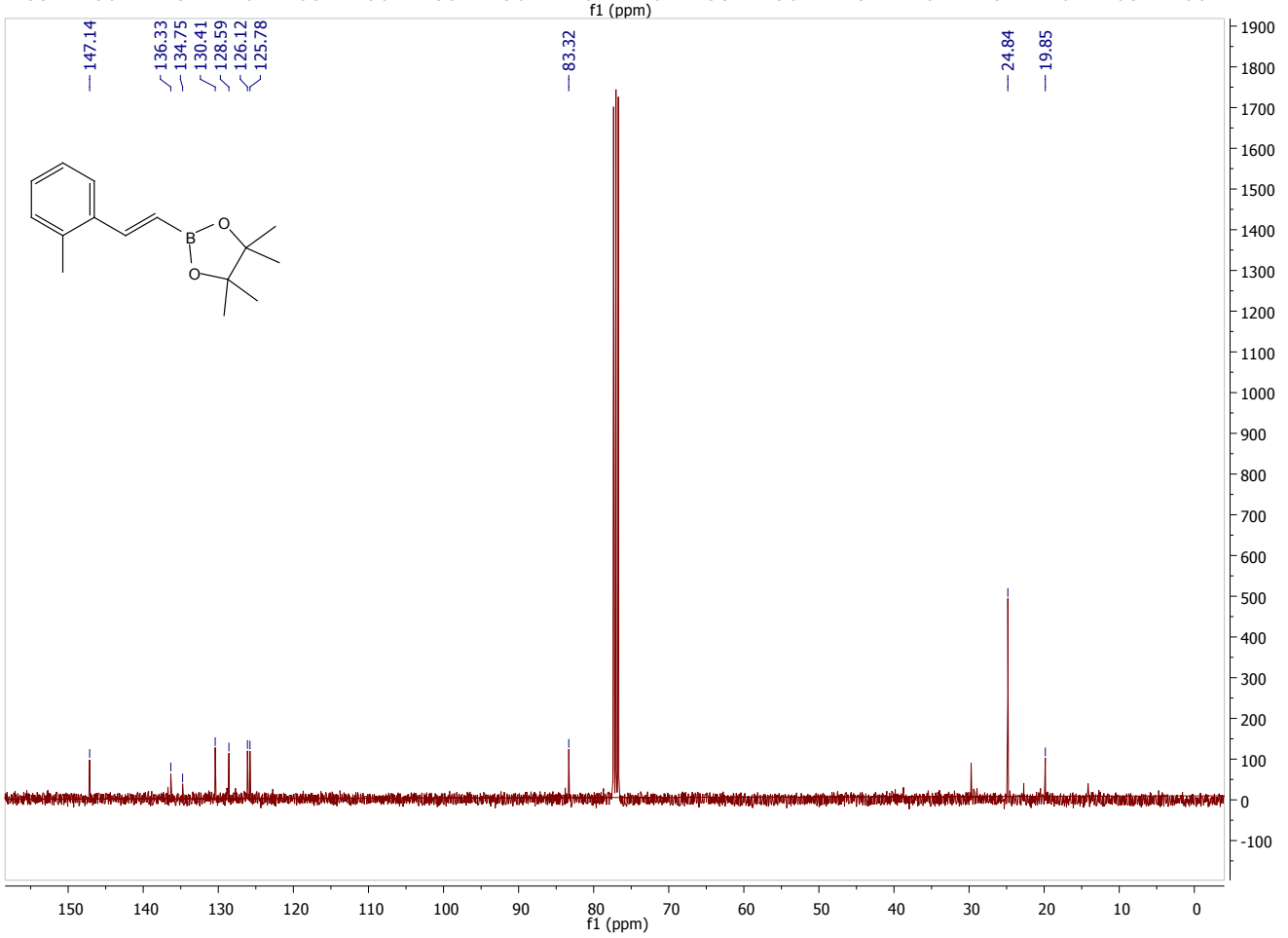
12.39
f1 (ppm)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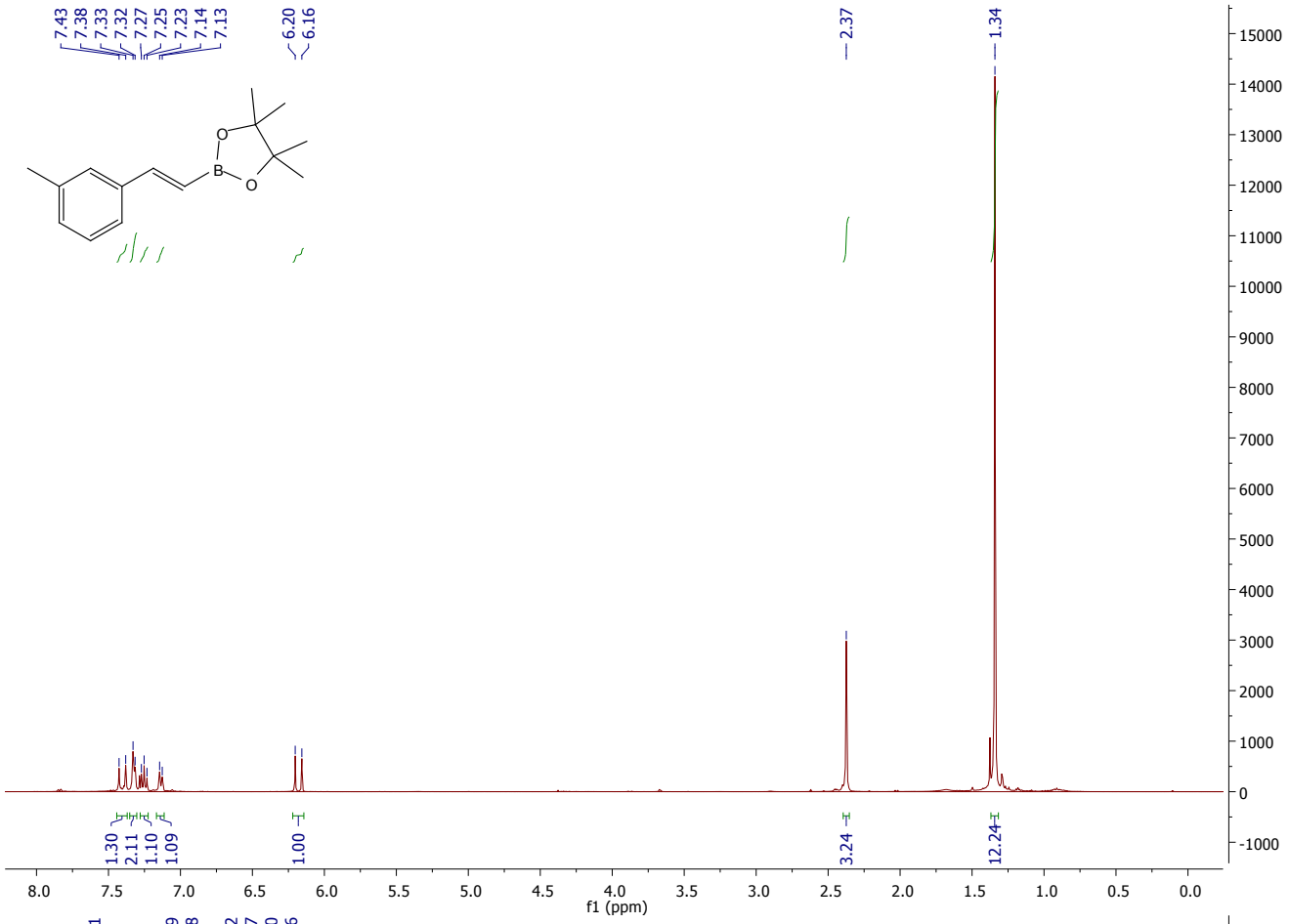
3d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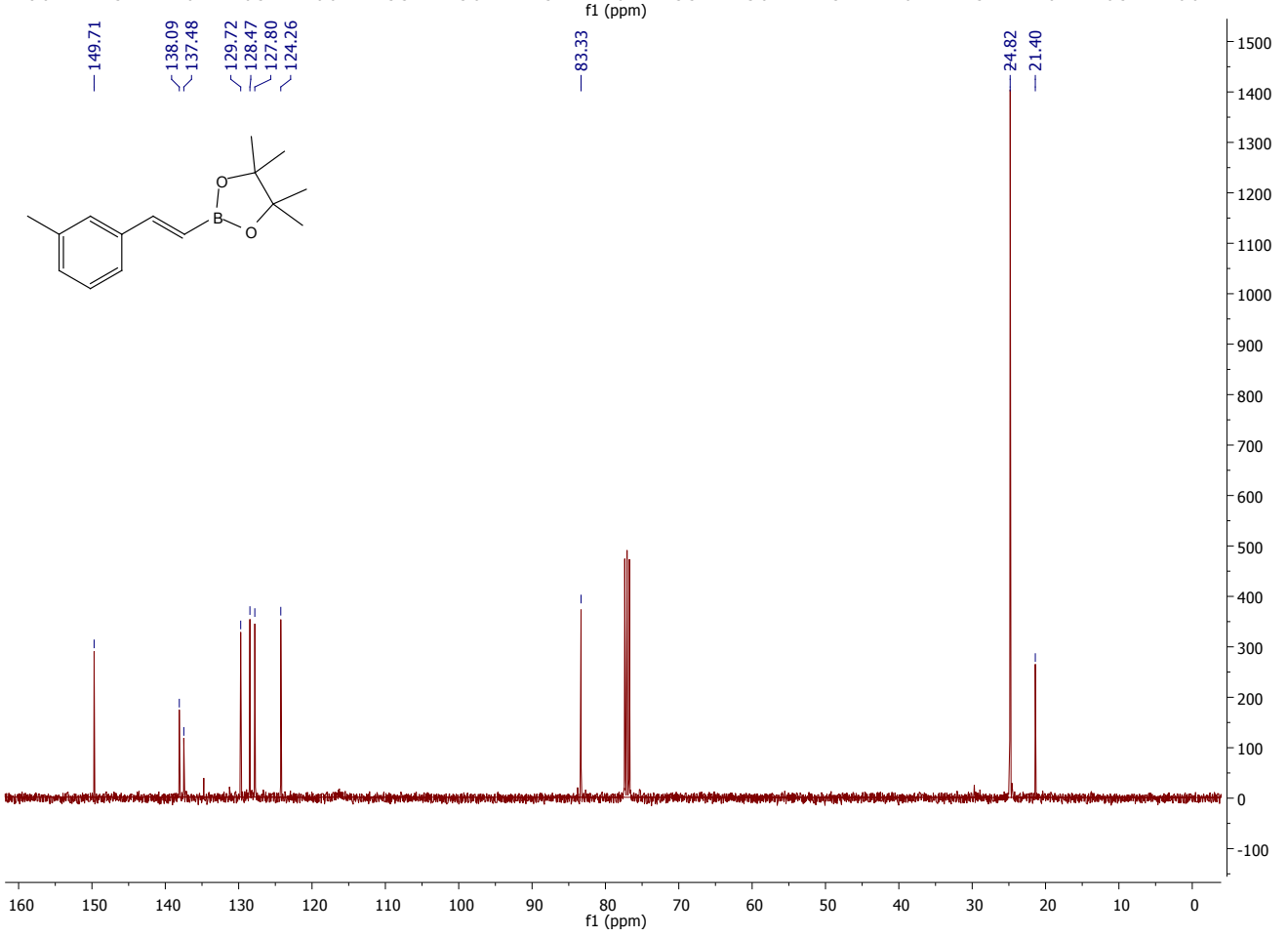
7.23
7.14
7.13
6.20
6.16
2.37
1.34
O
B
O
1.30
2.11
1.10
1.09
1.00
3.24
12.24
f1 (ppm)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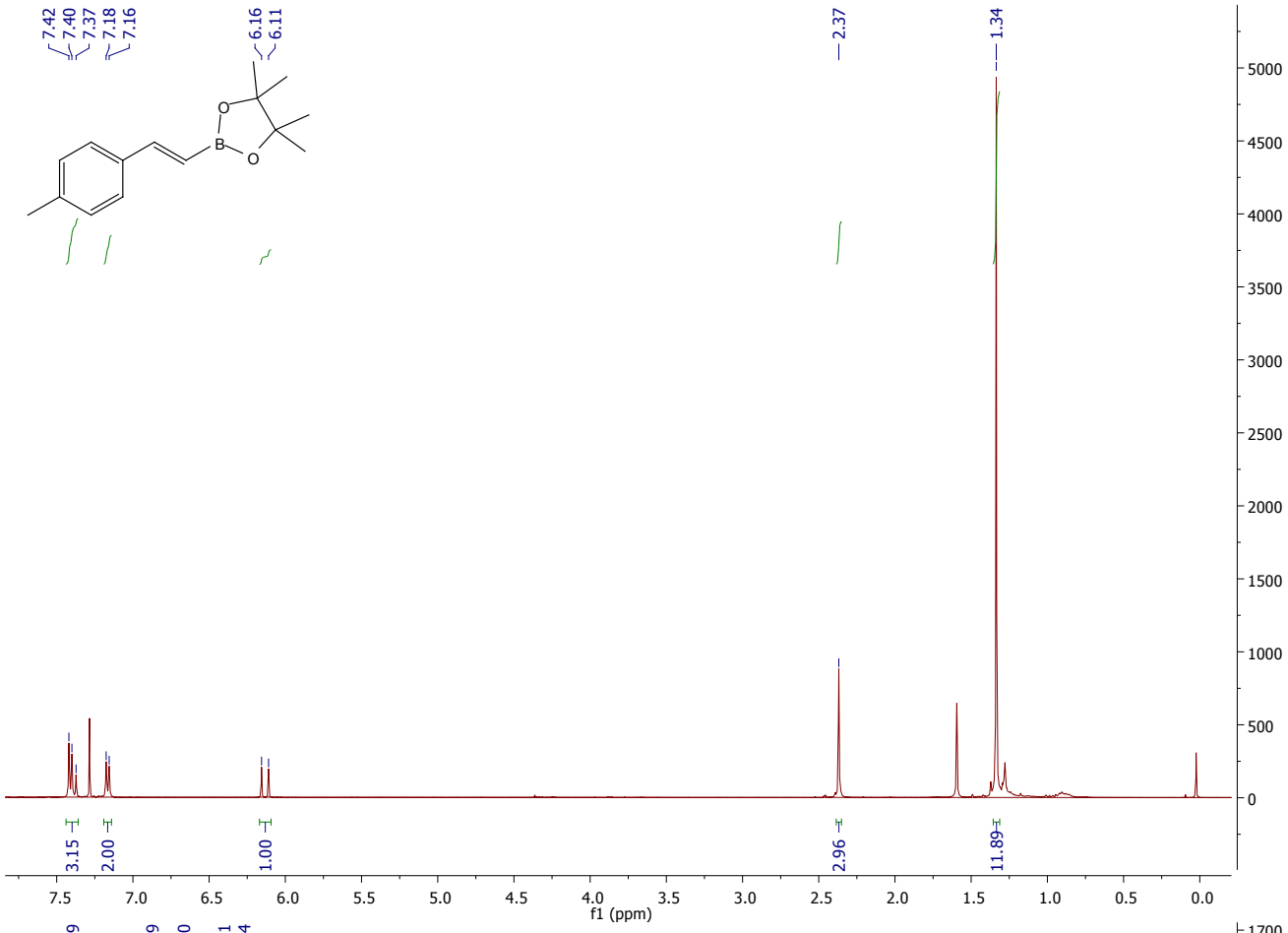
B
O
f1 (ppm)

3e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B
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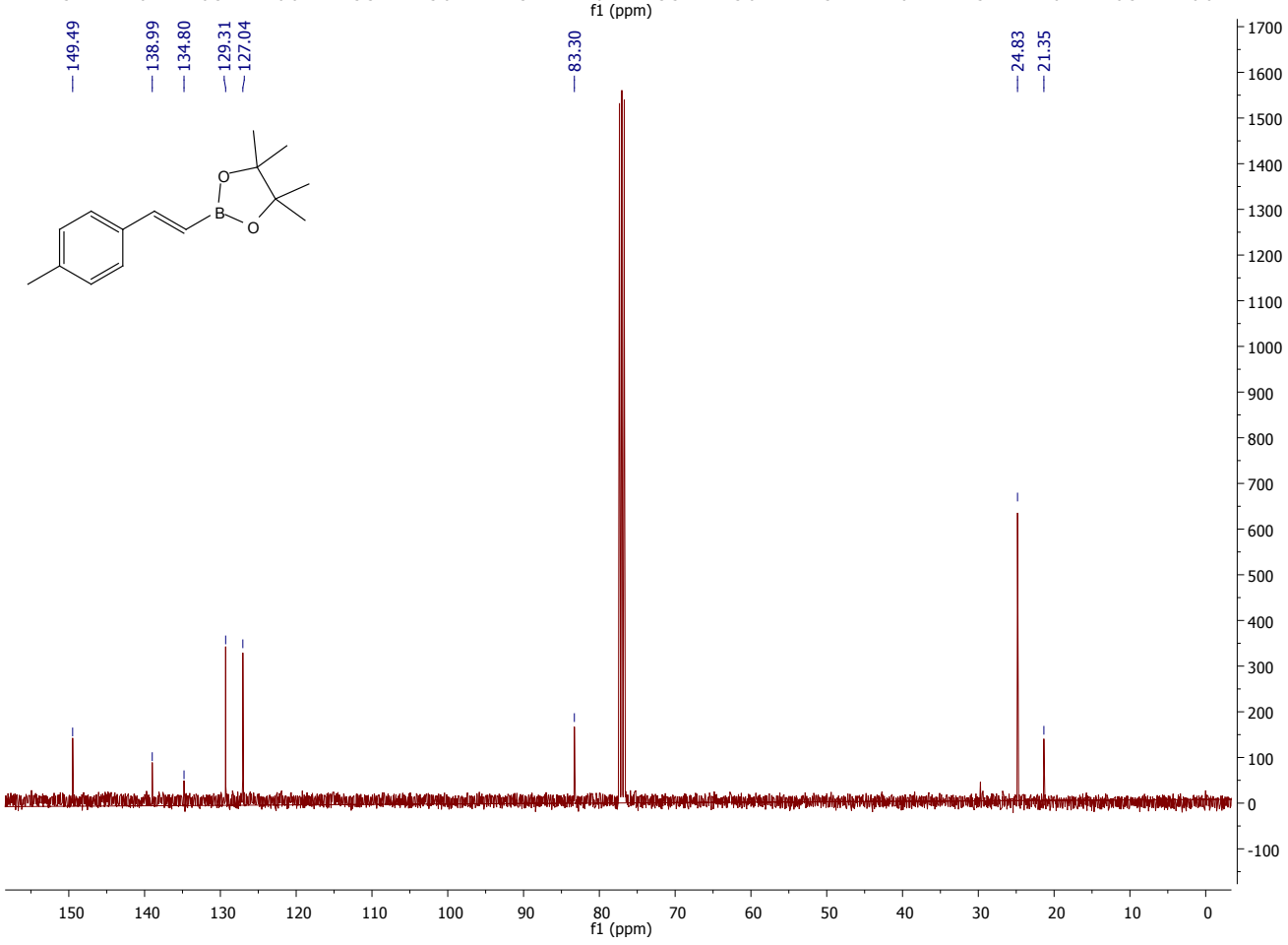
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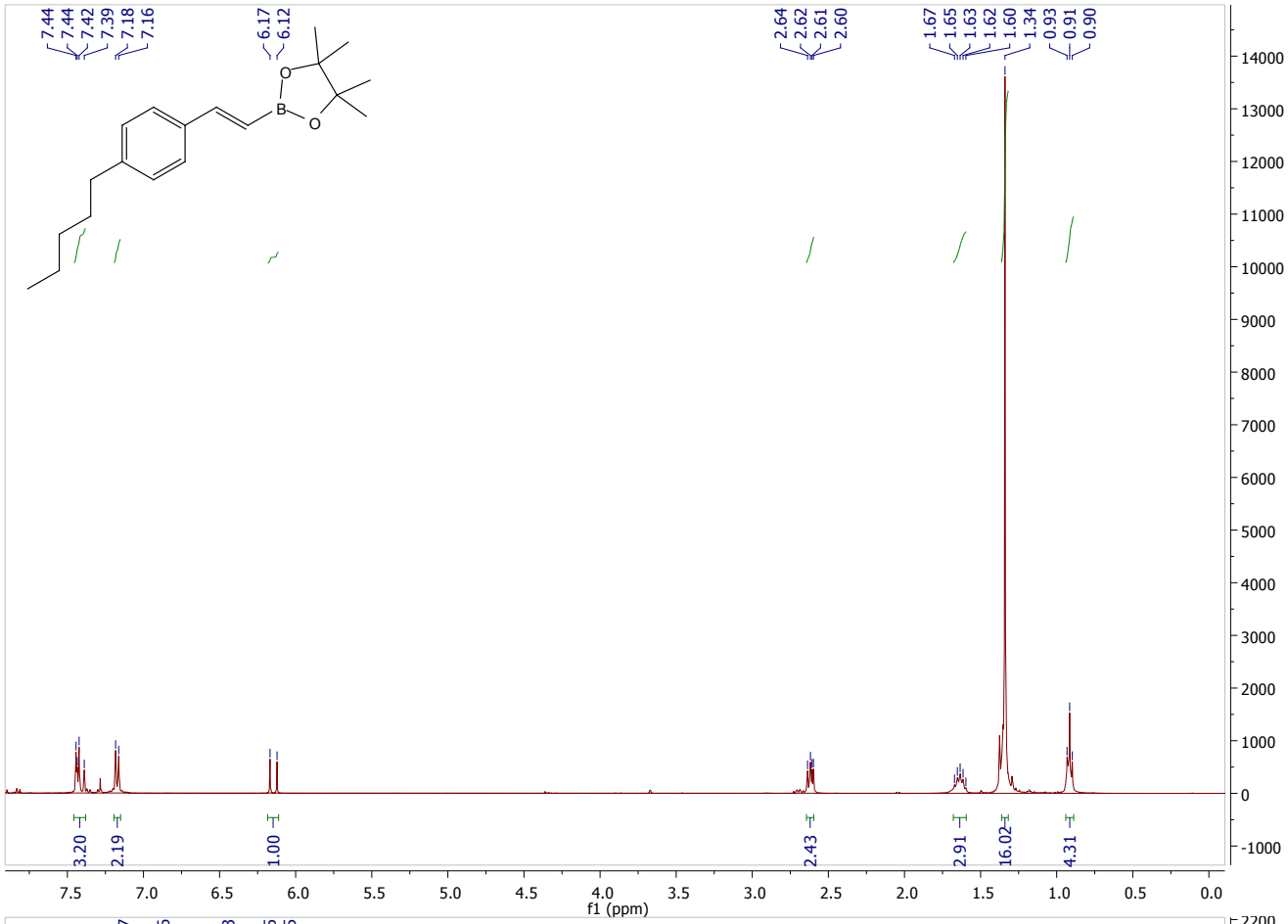
f1 (ppm)

3f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1.63
1.62
1.60
1.34
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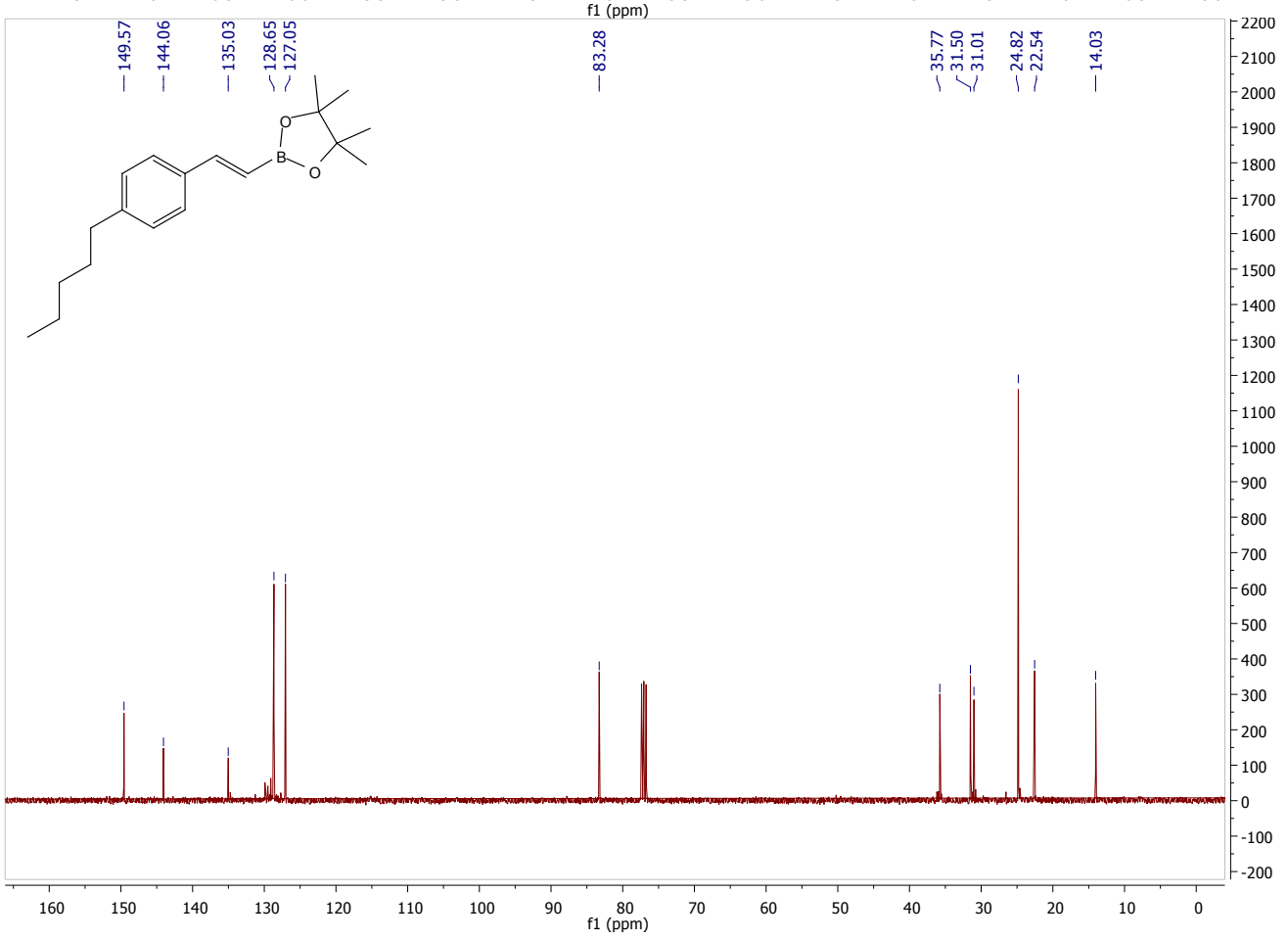
4.31
f1 (ppm)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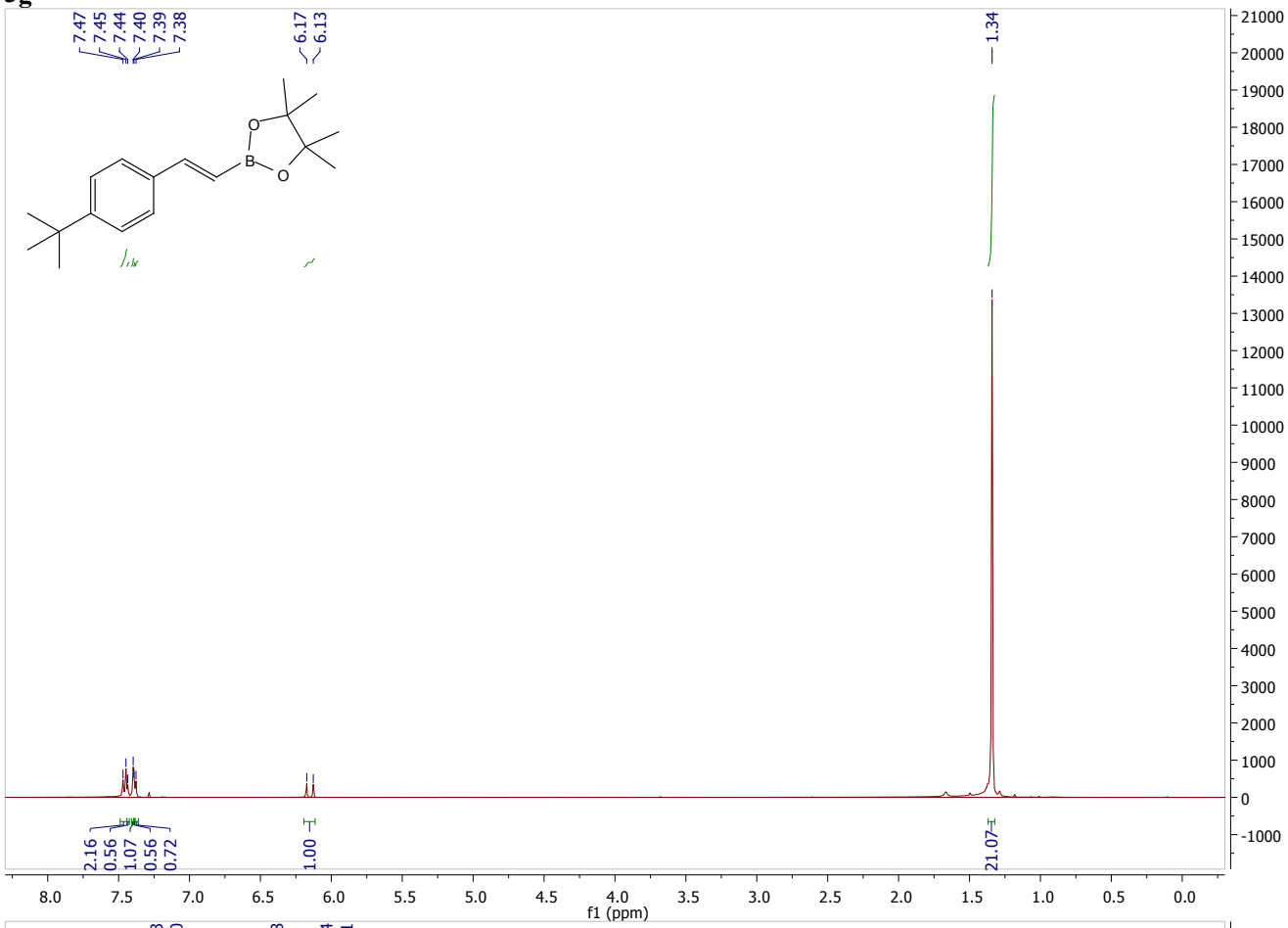
O
f1 (ppm)

3g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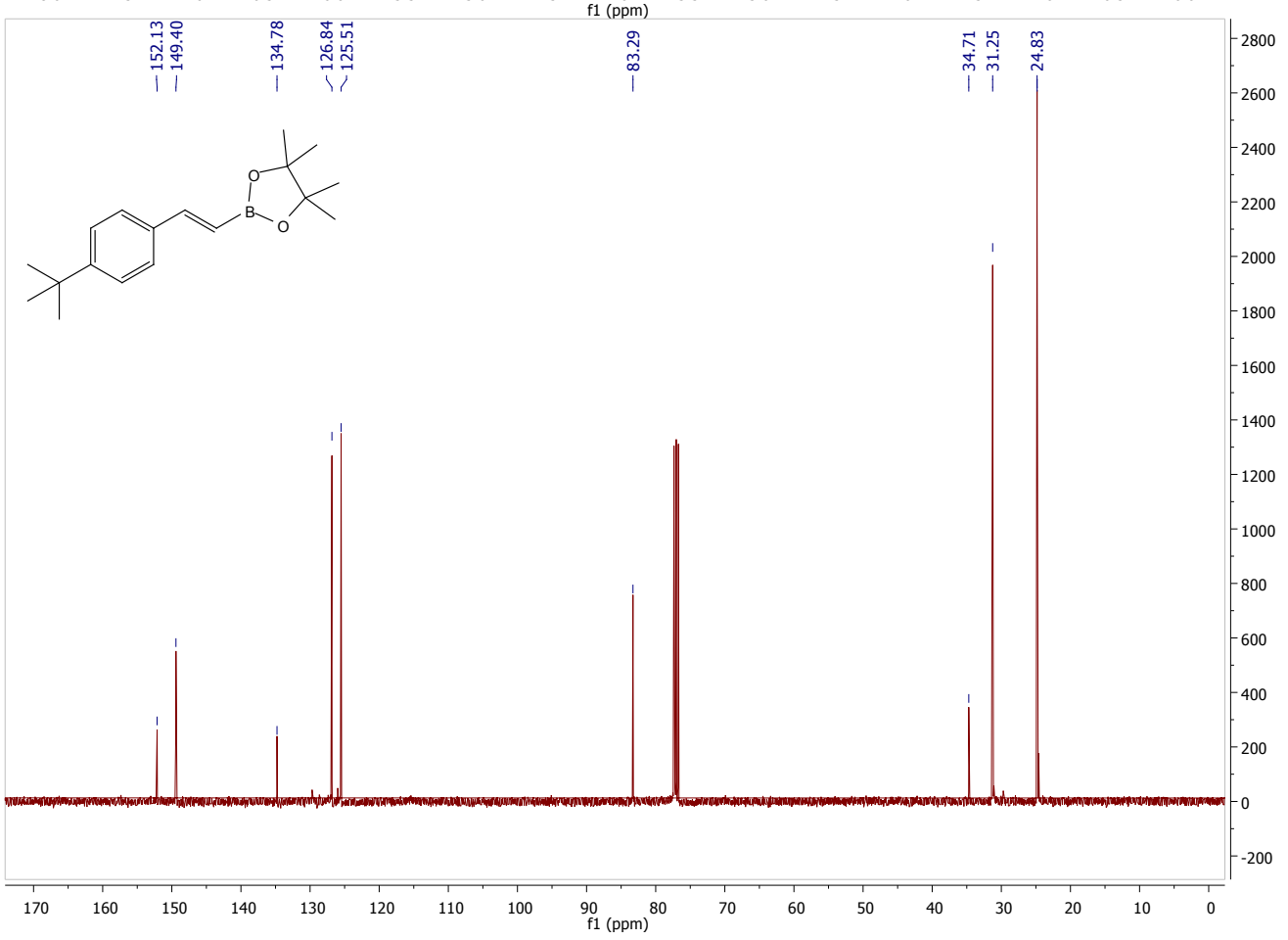
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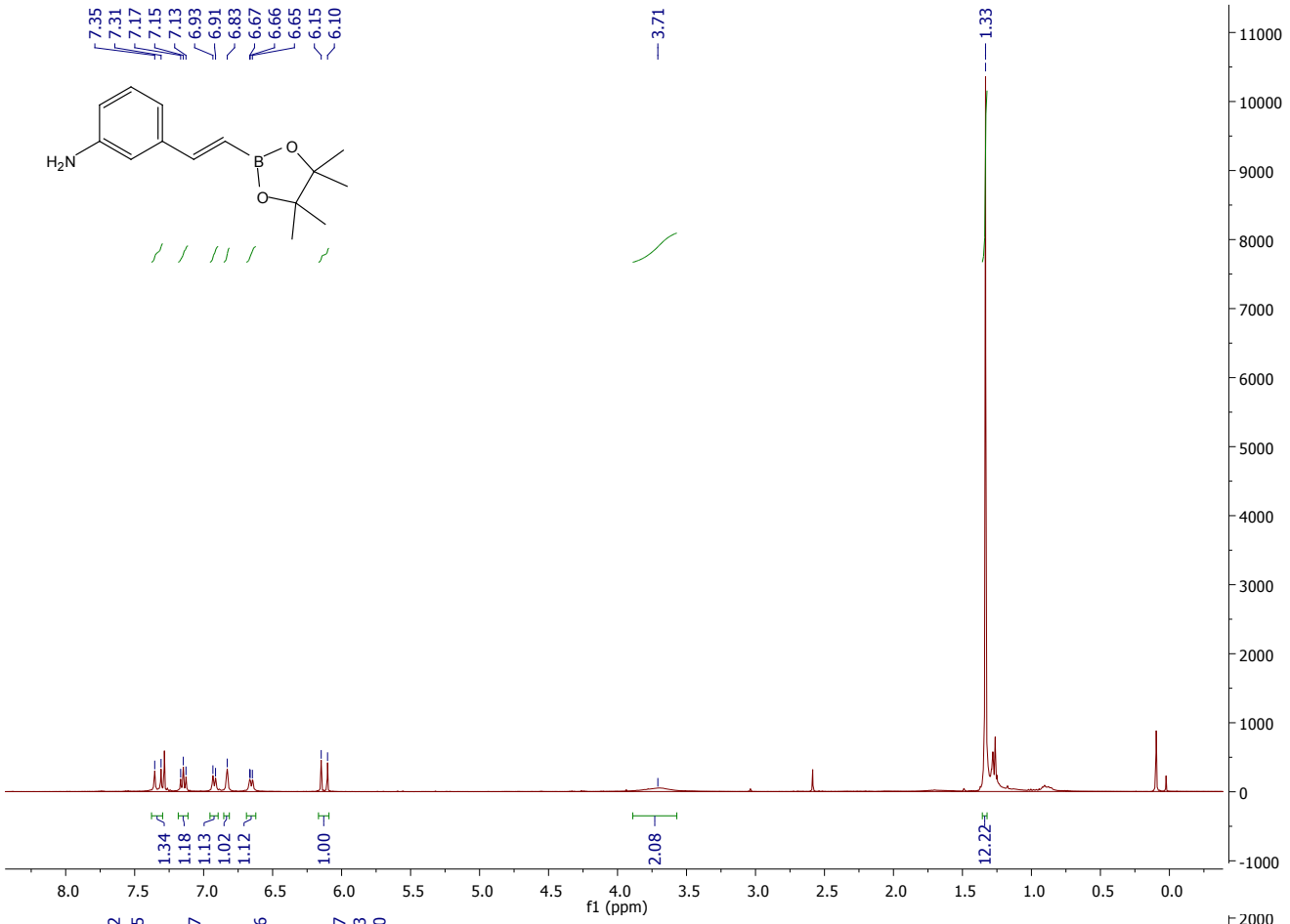
3h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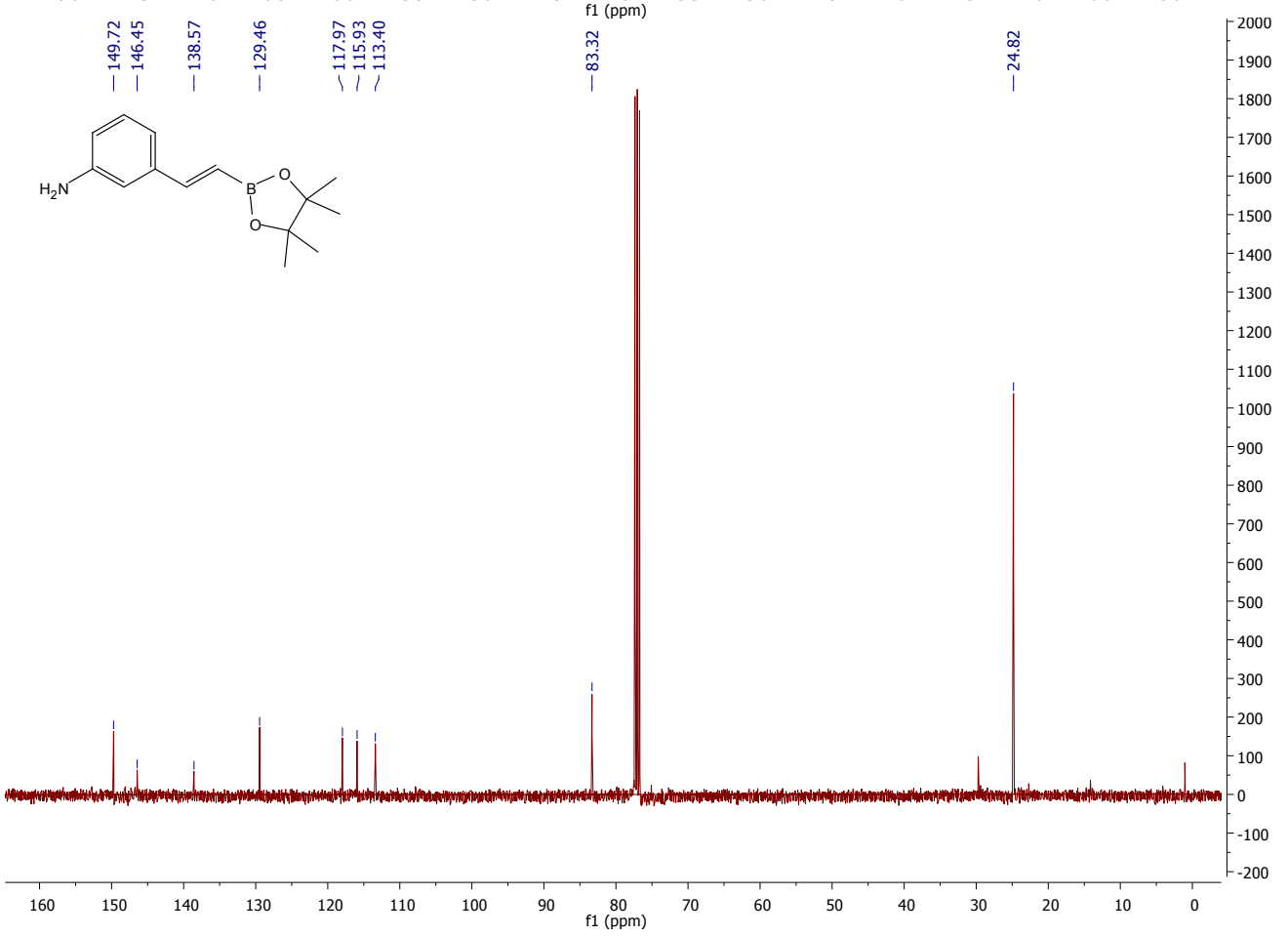
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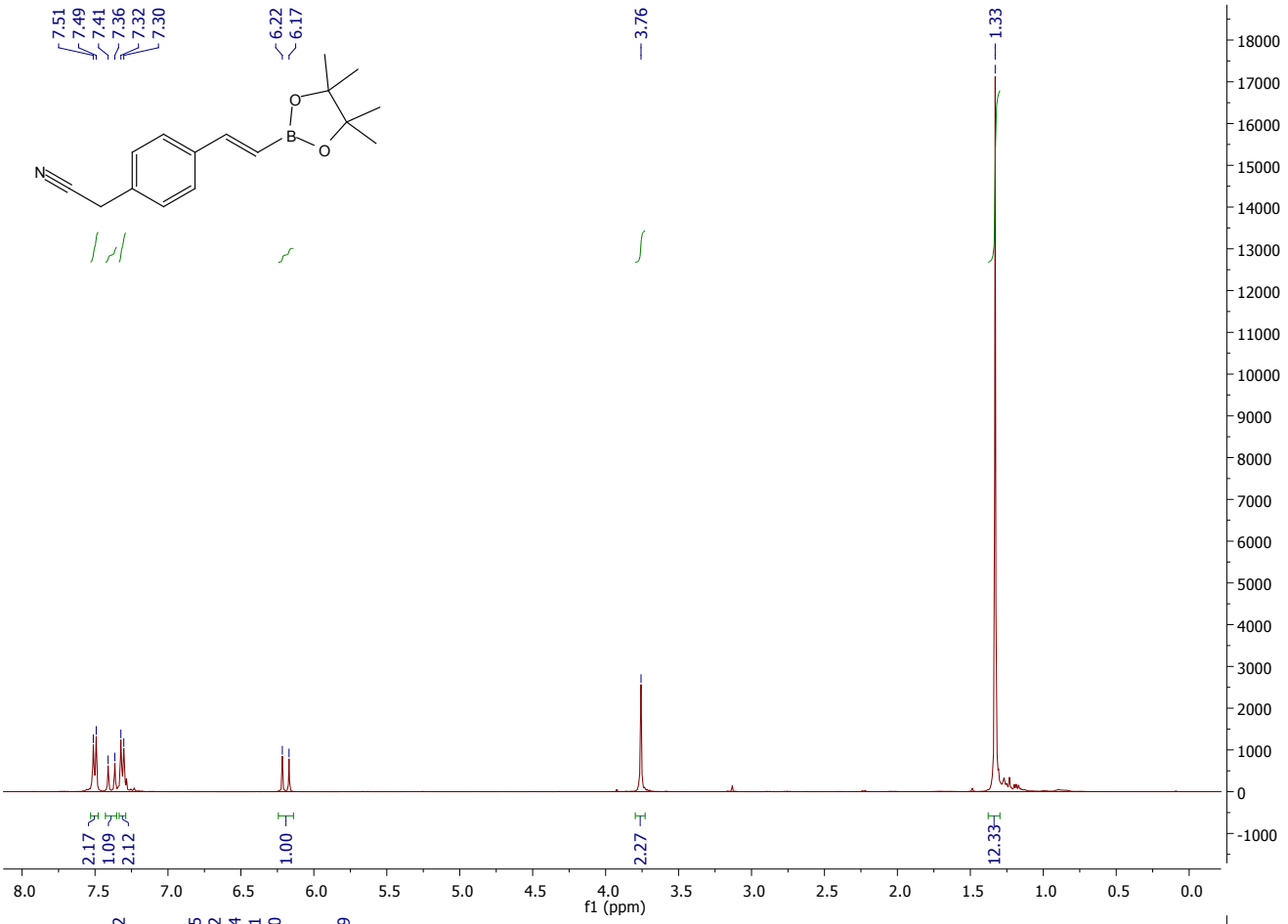
3i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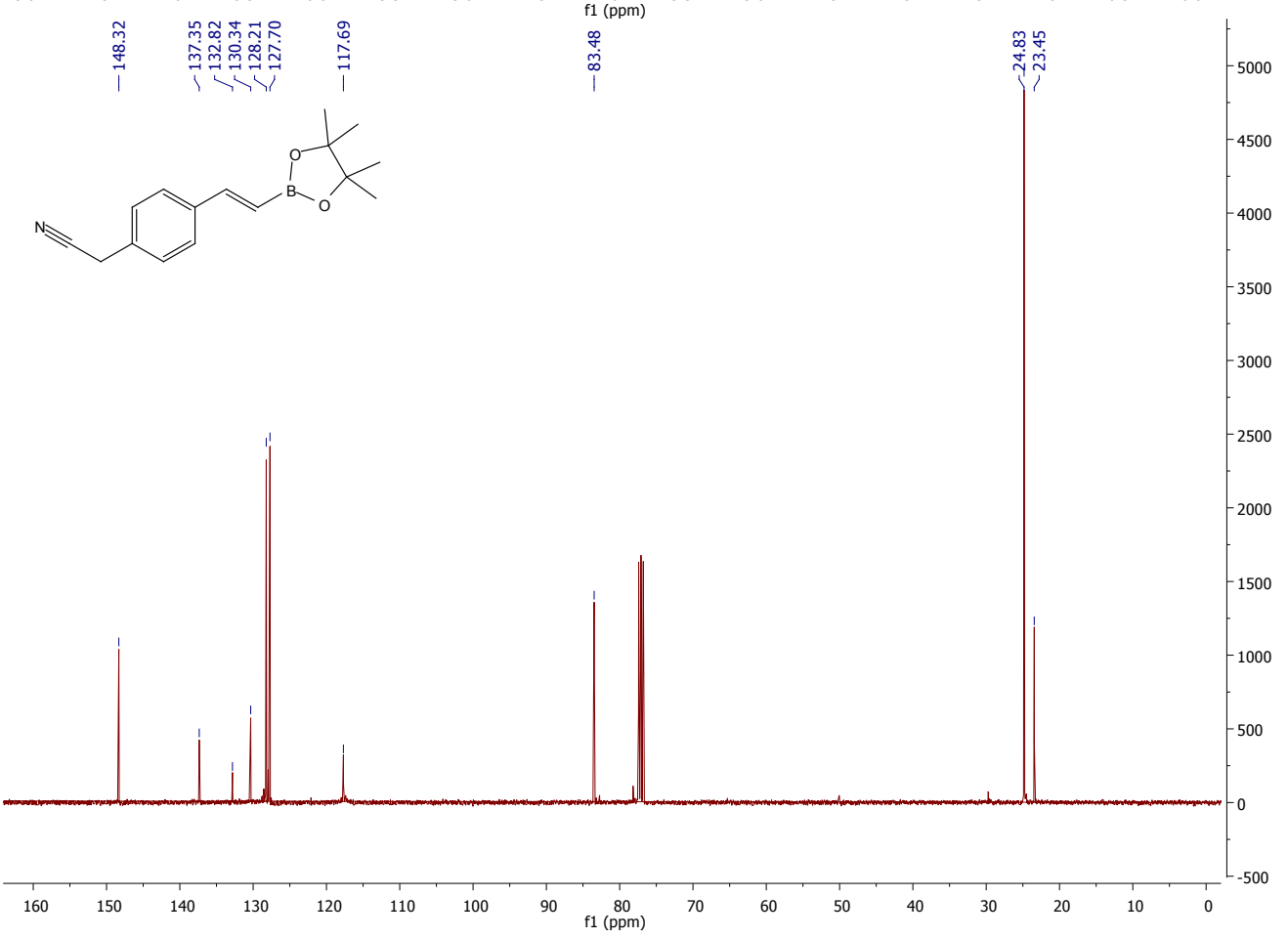
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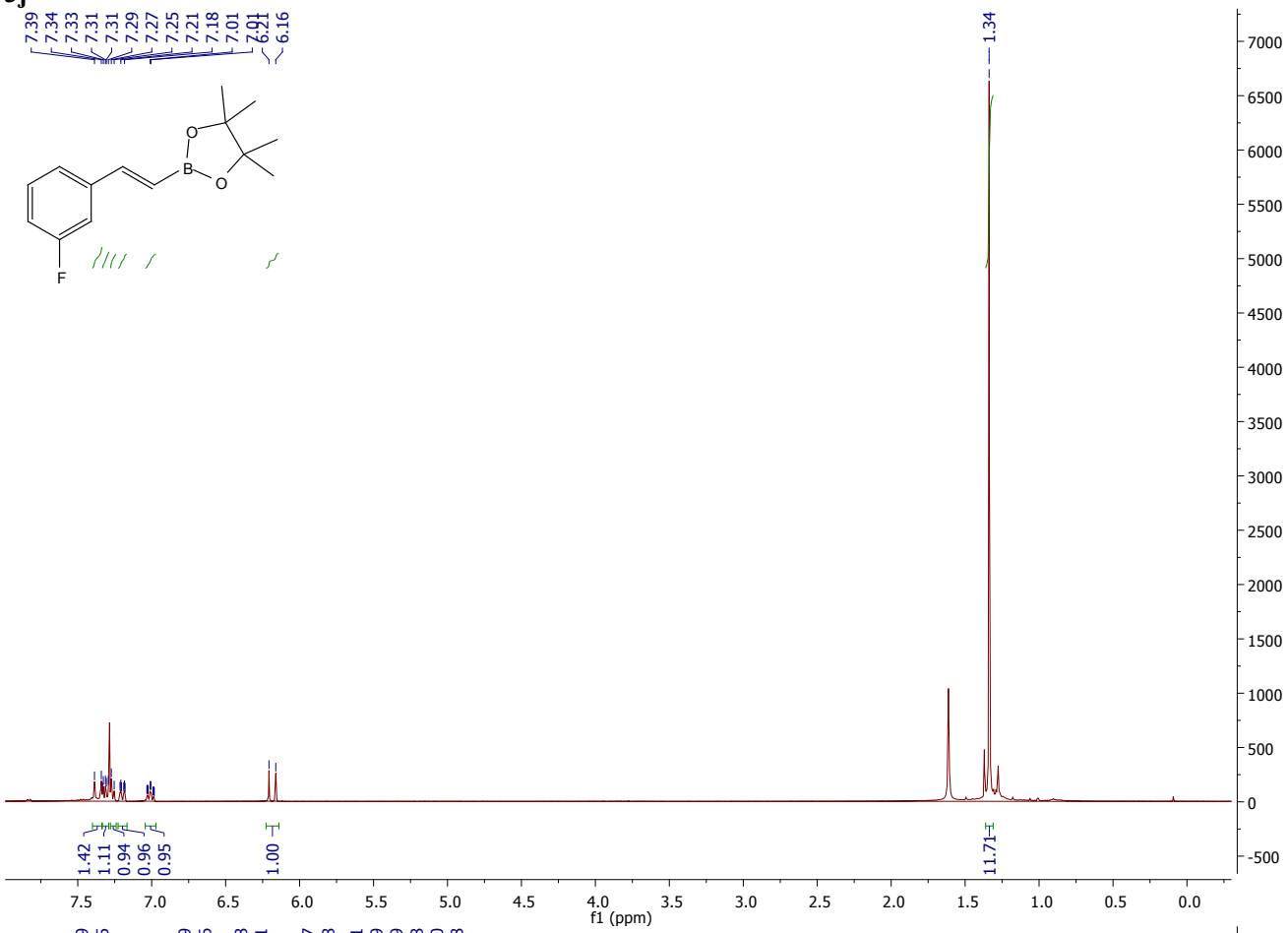
3j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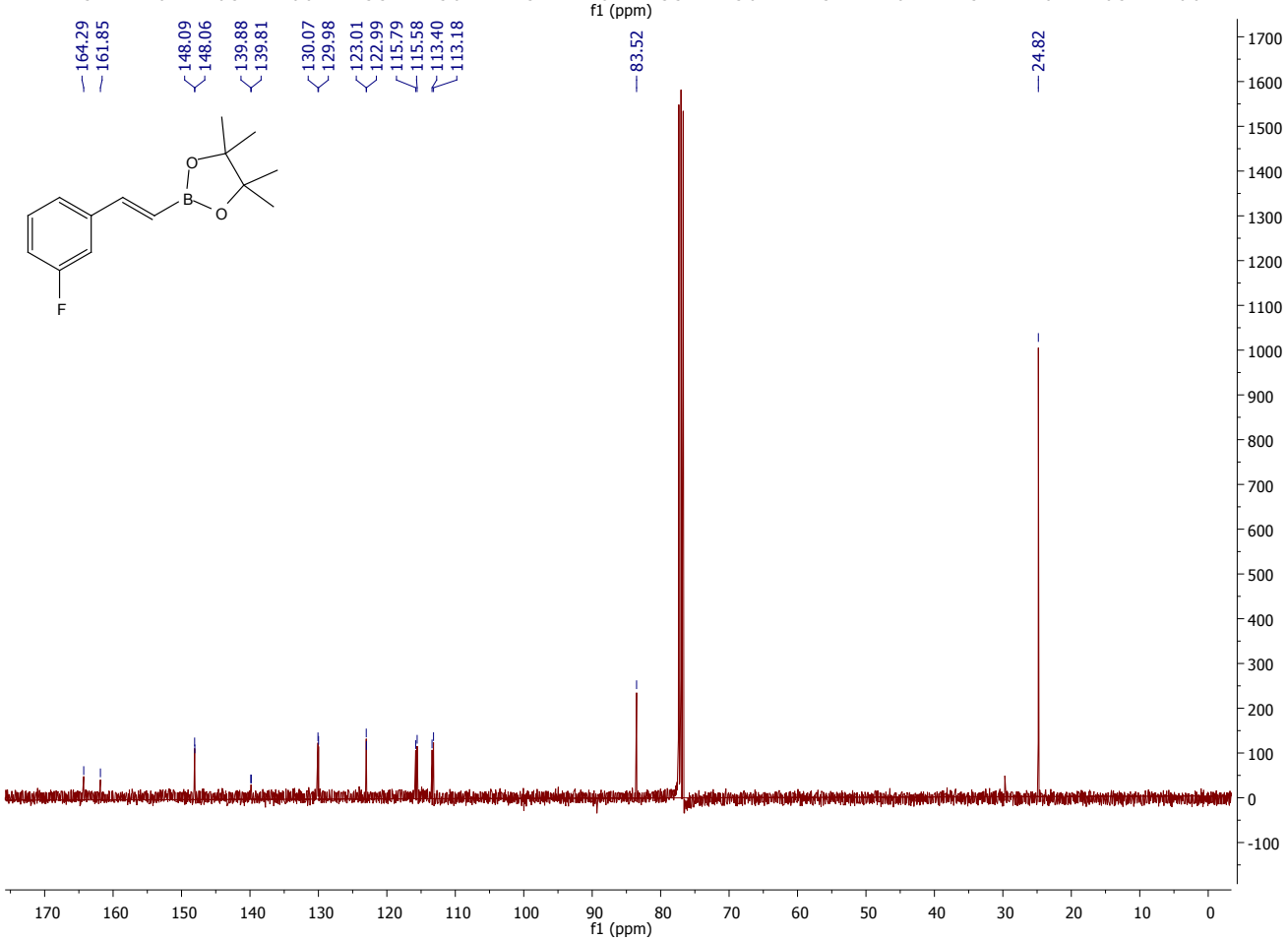
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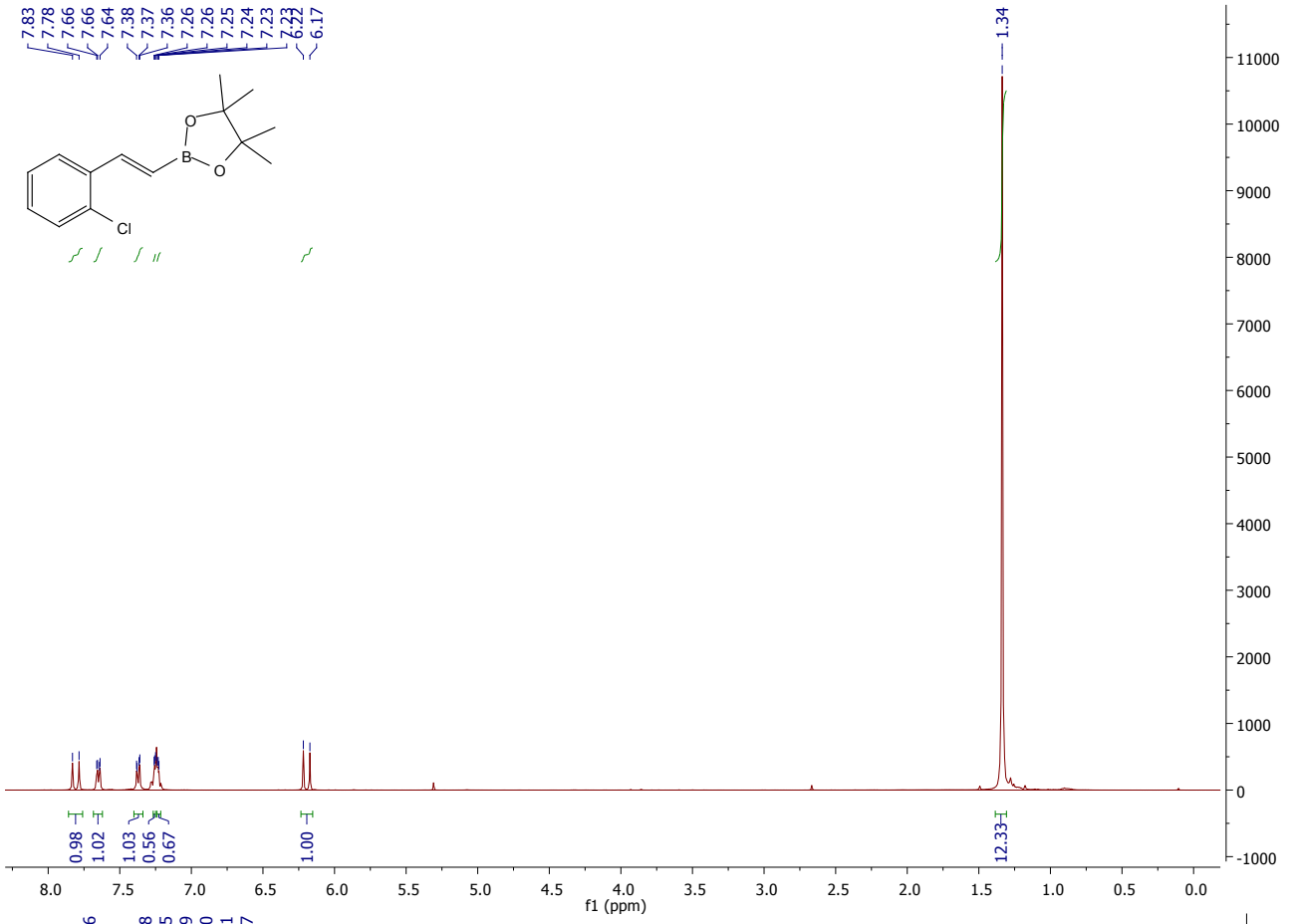
f1 (ppm)

3k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6.17
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Cl
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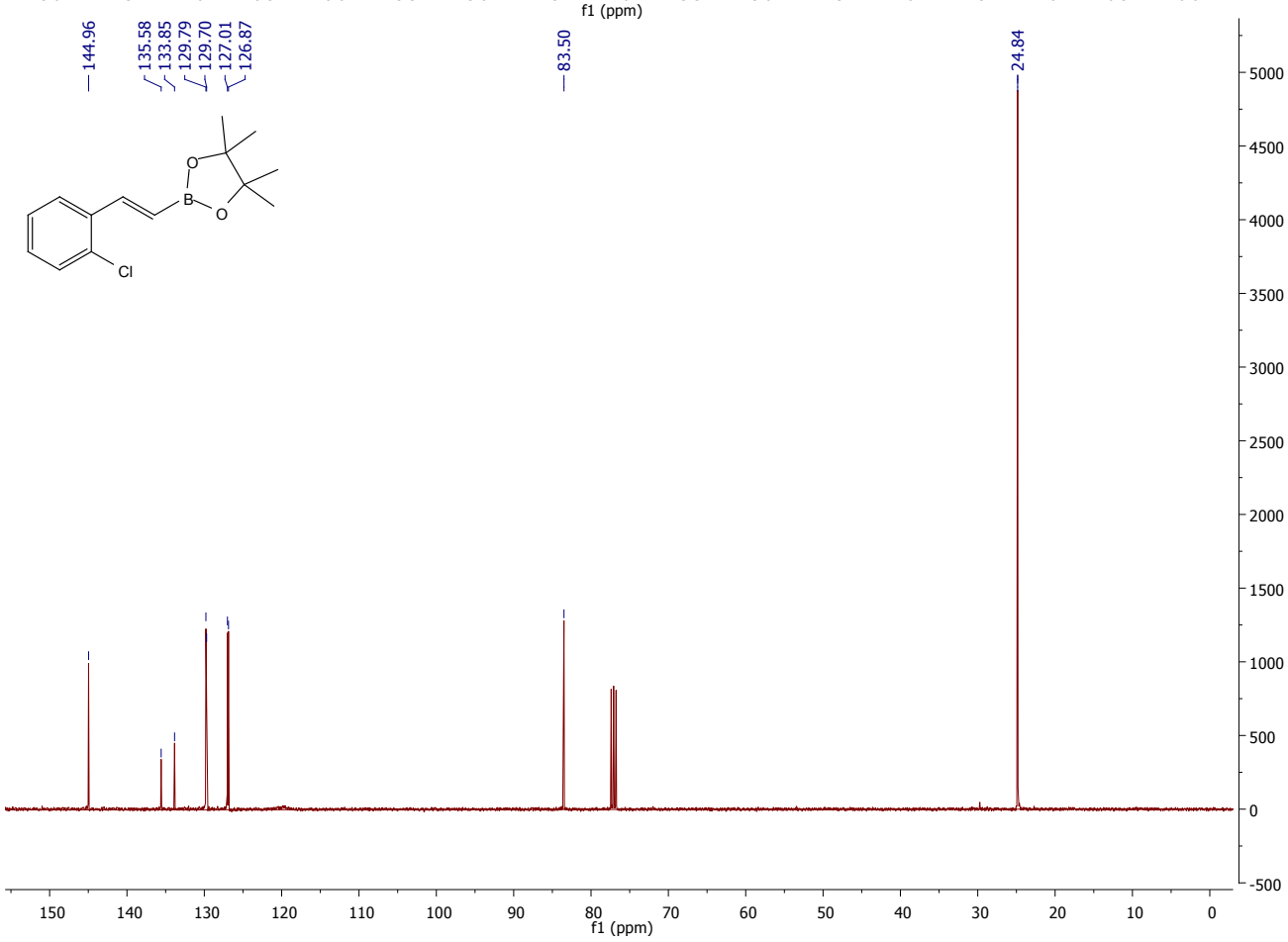
f1 (ppm)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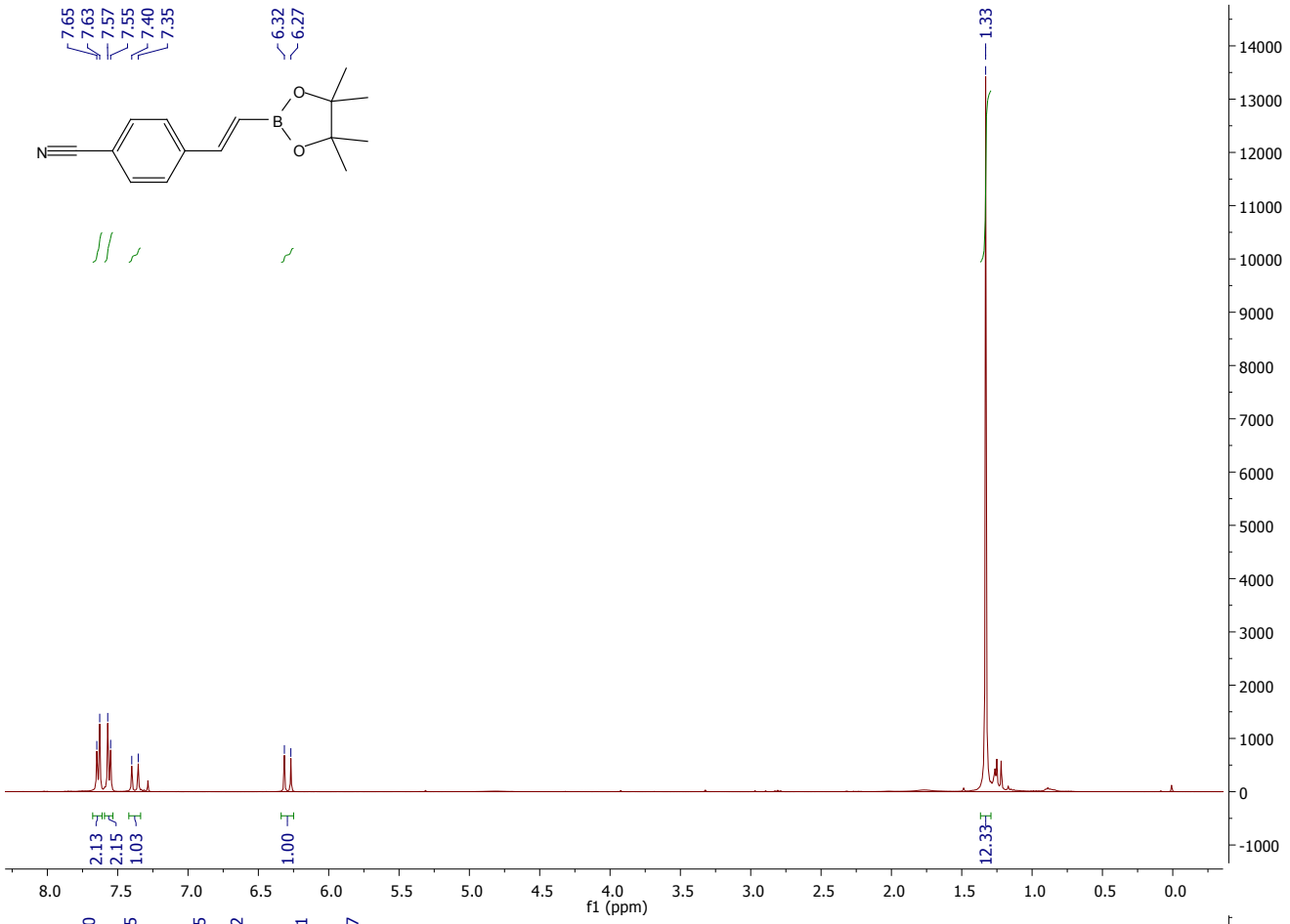
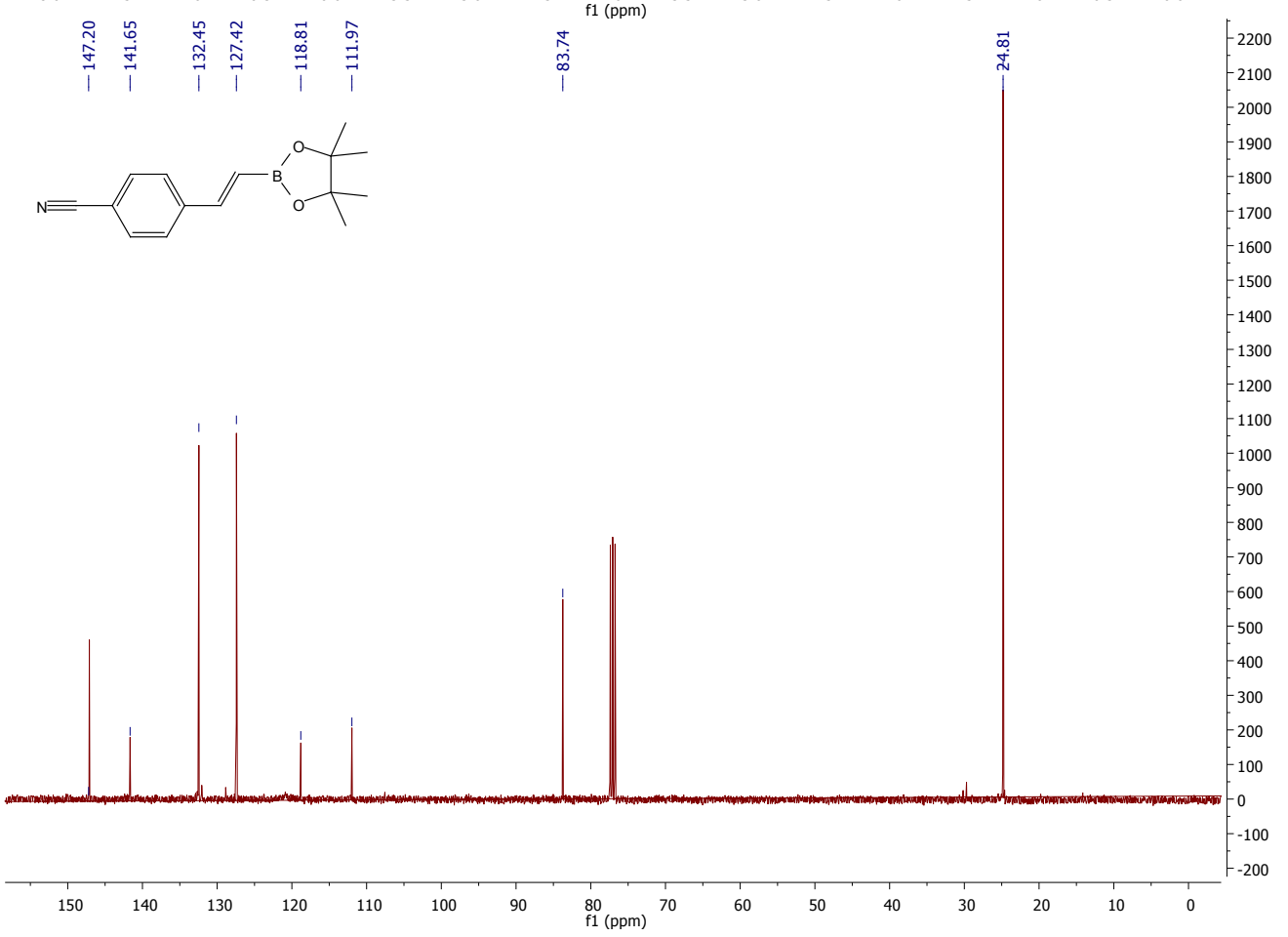
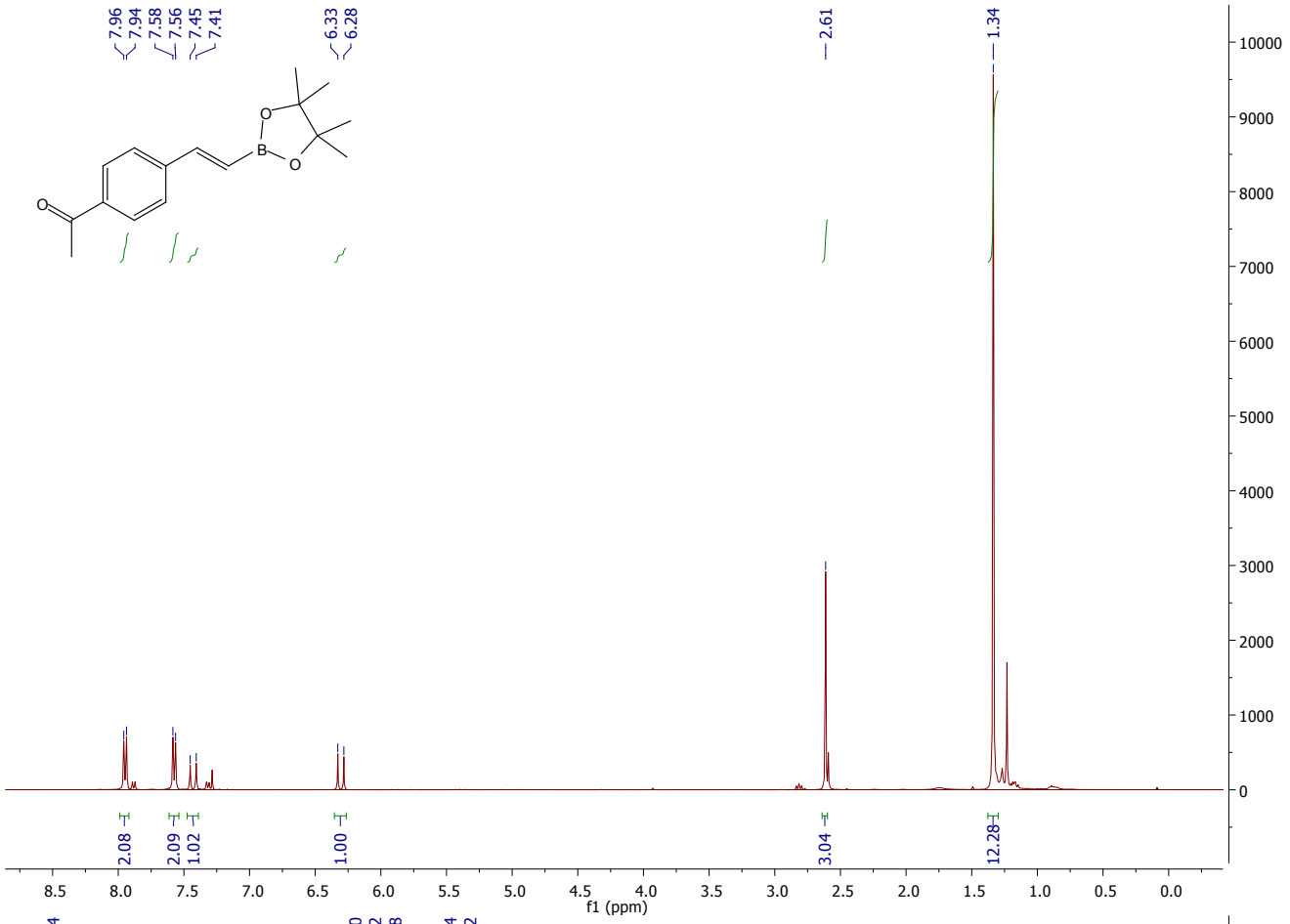
129.70
127.01
126.87
83.50
24.84
O
B
O
Cl
f1 (ppm)

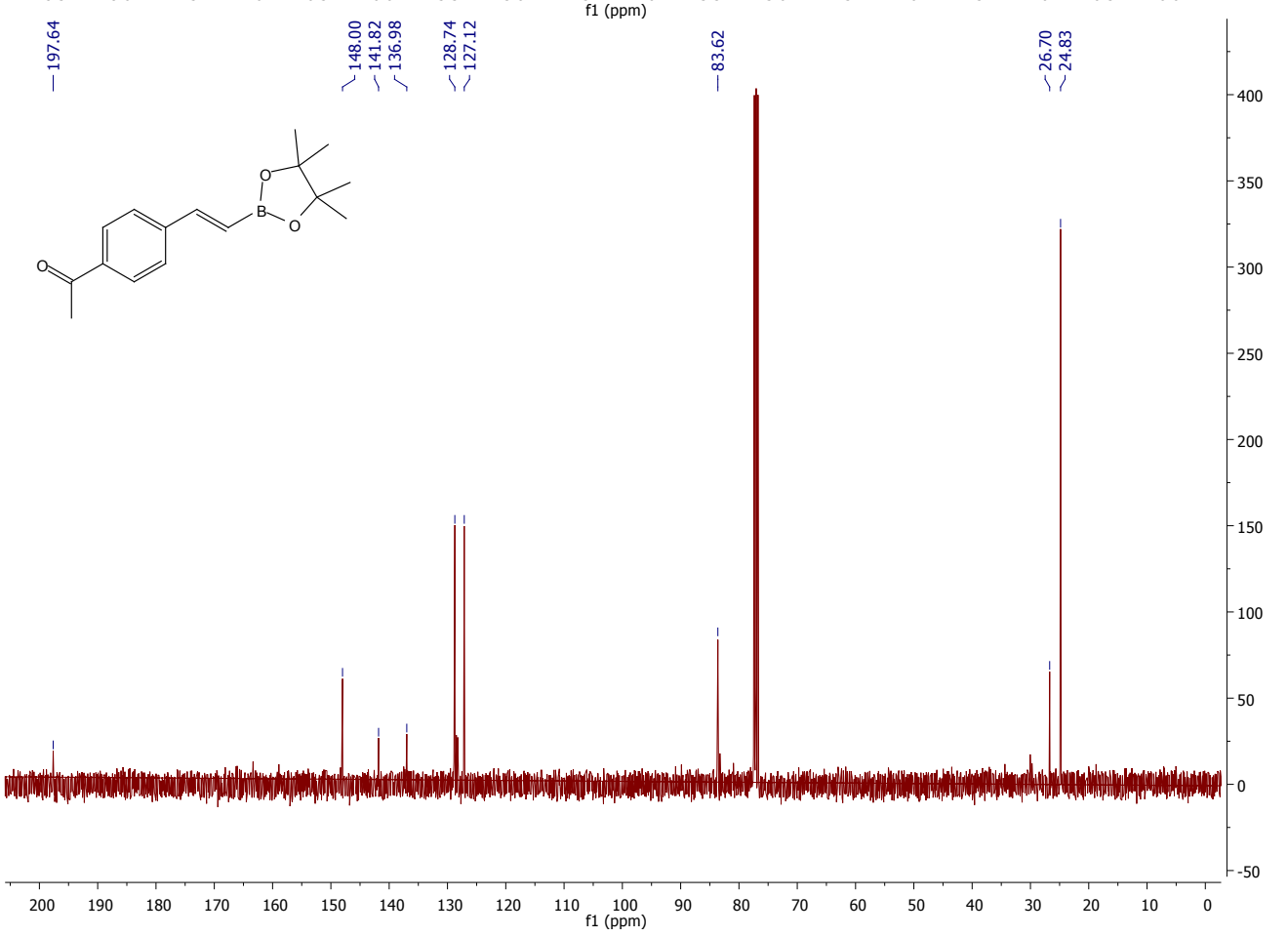
31


7.65
7.63
7.57
7.55
7.40
7.35
6.32
6.27
1.33
N
B
O
O
2.13
2.15
1.03
1.00
12.33
f1 (ppm)

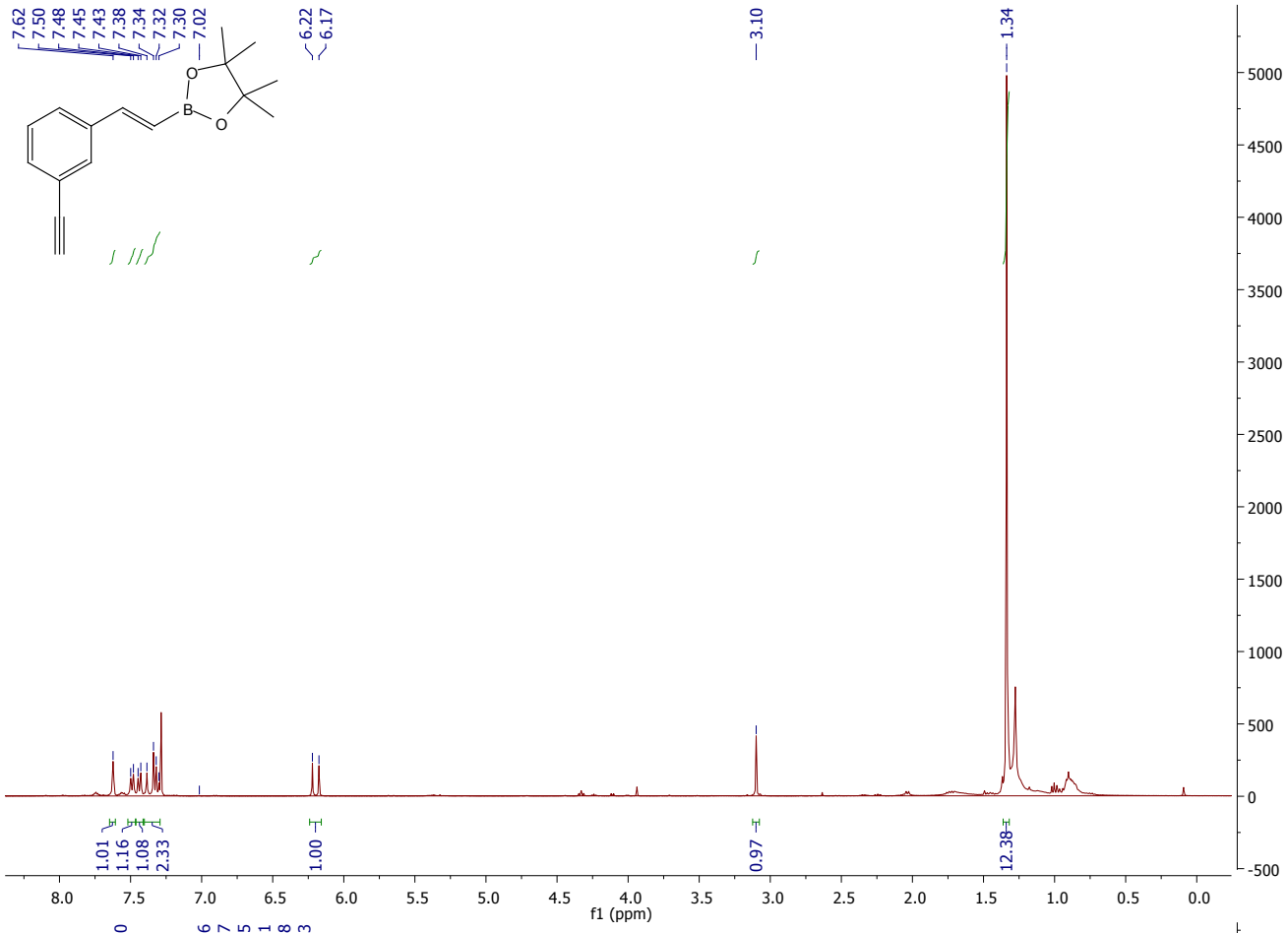

147.20
141.65
132.45
127.42
118.81
111.97
83.74
24.81
N
B
O
O
f1 (ppm)

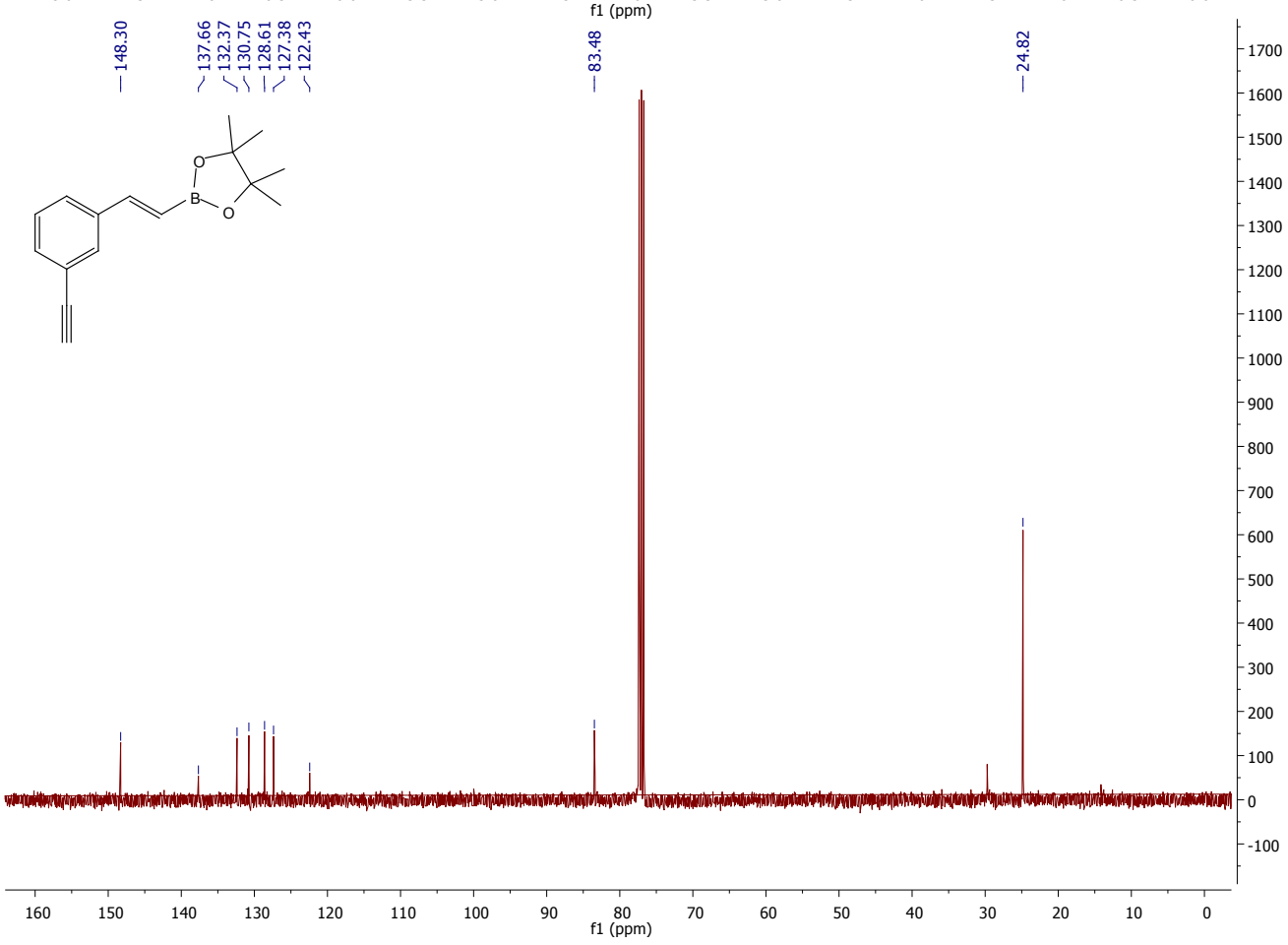
3m


7.96
7.94
7.58
7.56
7.45
7.41
6.33
6.28
2.61
1.34
O
B
O
O
2.08
2.09
1.02
1.00
3.04
12.28
f1 (ppm)

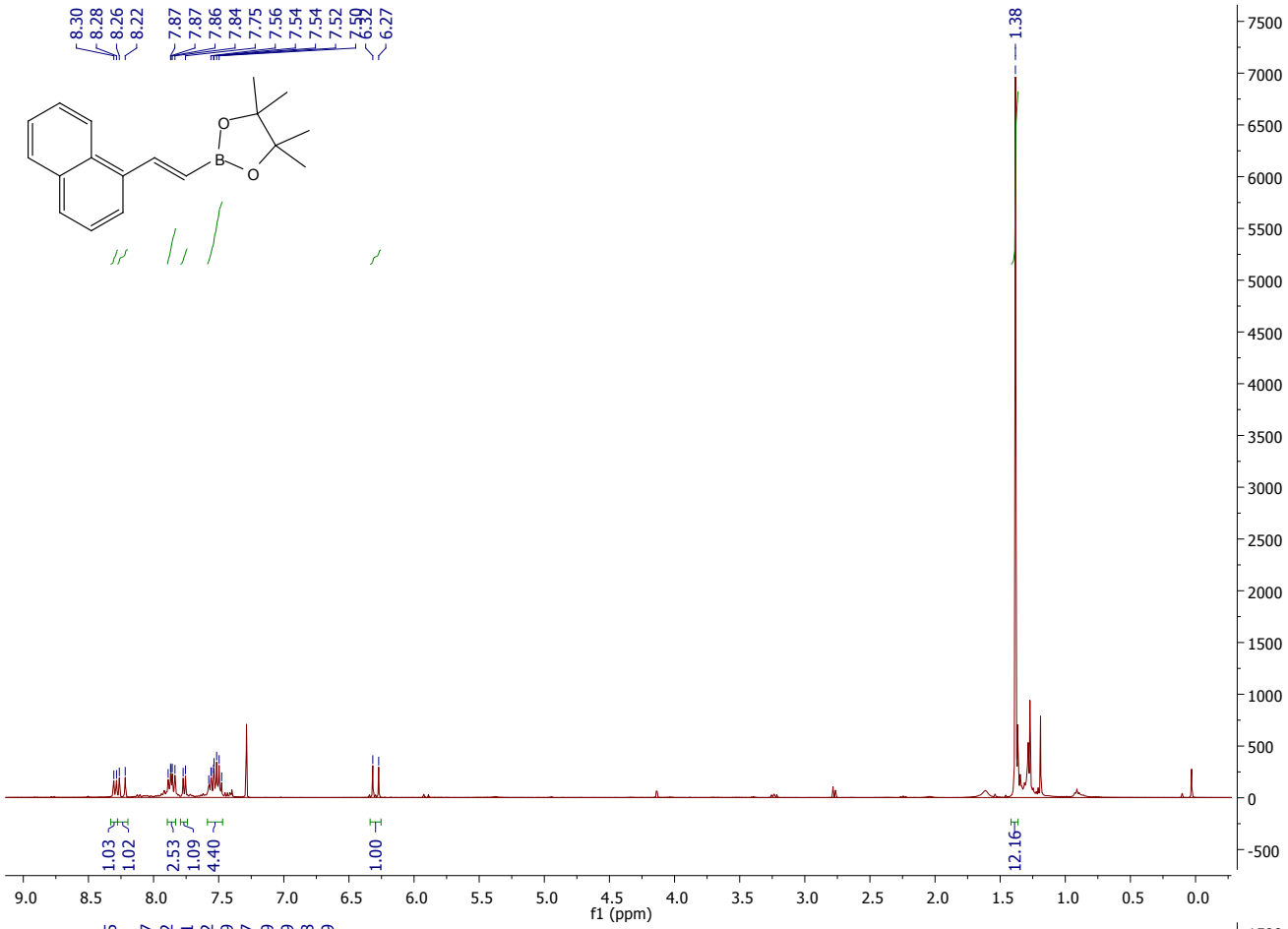

197.64
148.00
141.82
136.98
128.74
127.12
83.62
26.70
24.83
O
B
O
O
f1 (ppm)

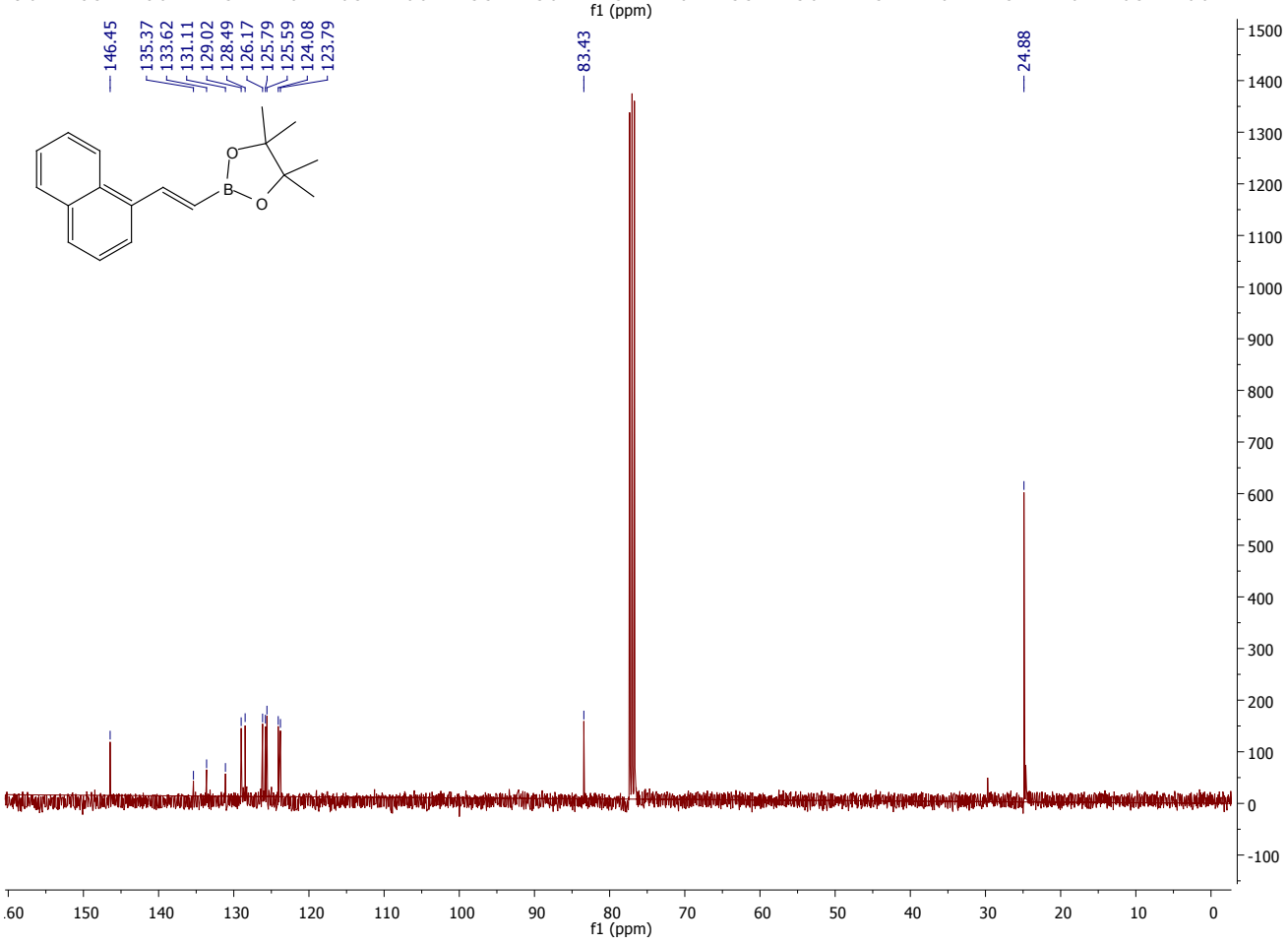
3n


7.62
7.50
7.48
7.45
7.43
7.38
7.34
7.32
7.30
7.02
6.22
6.17
3.10
1.34
O
B
O
1.01
1.16
1.08
2.33
1.00
0.97
12.38
f1 (ppm)

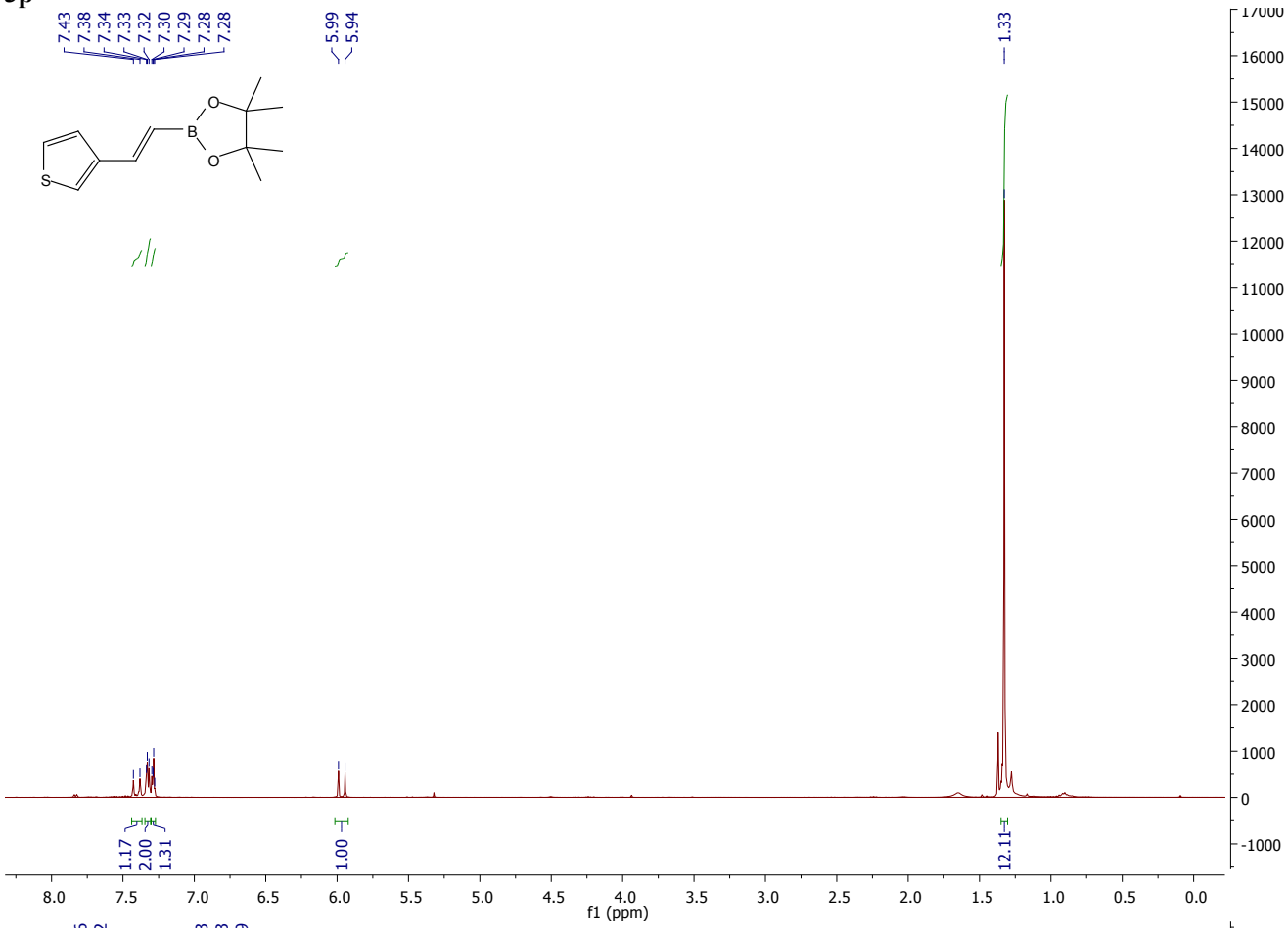

148.30
137.66
132.37
130.75
128.61
127.38
122.43
83.48
24.82
O
B
O
f1 (ppm)

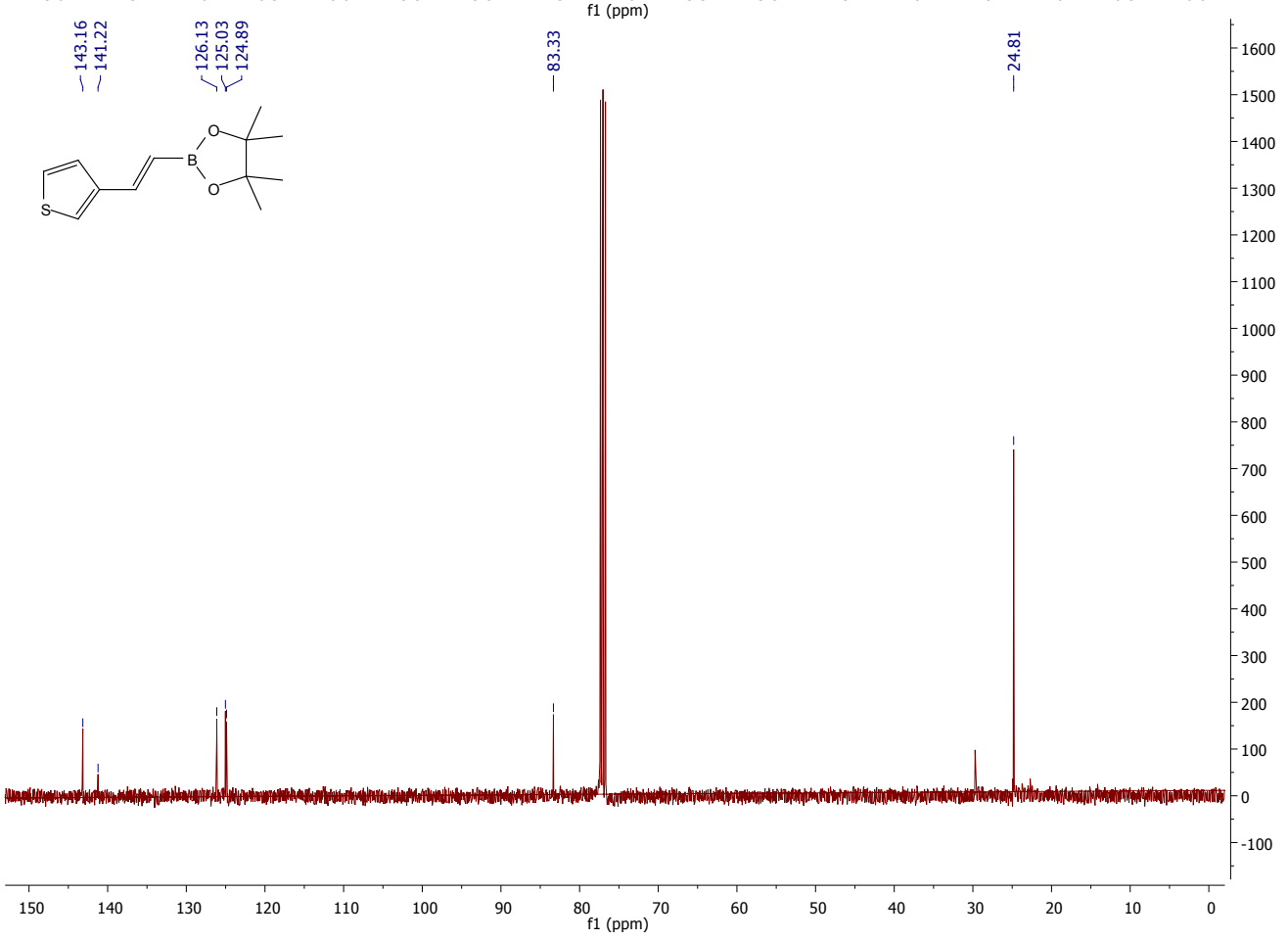
3o


8.30
8.28
8.26
8.22
7.87
7.87
7.86
7.84
7.75
7.56
7.54
7.54
7.52
7.50
6.32
6.27
1.38
O
B
O
1.03
1.02
2.53
1.09
4.40
1.00
12.16
f1 (ppm)

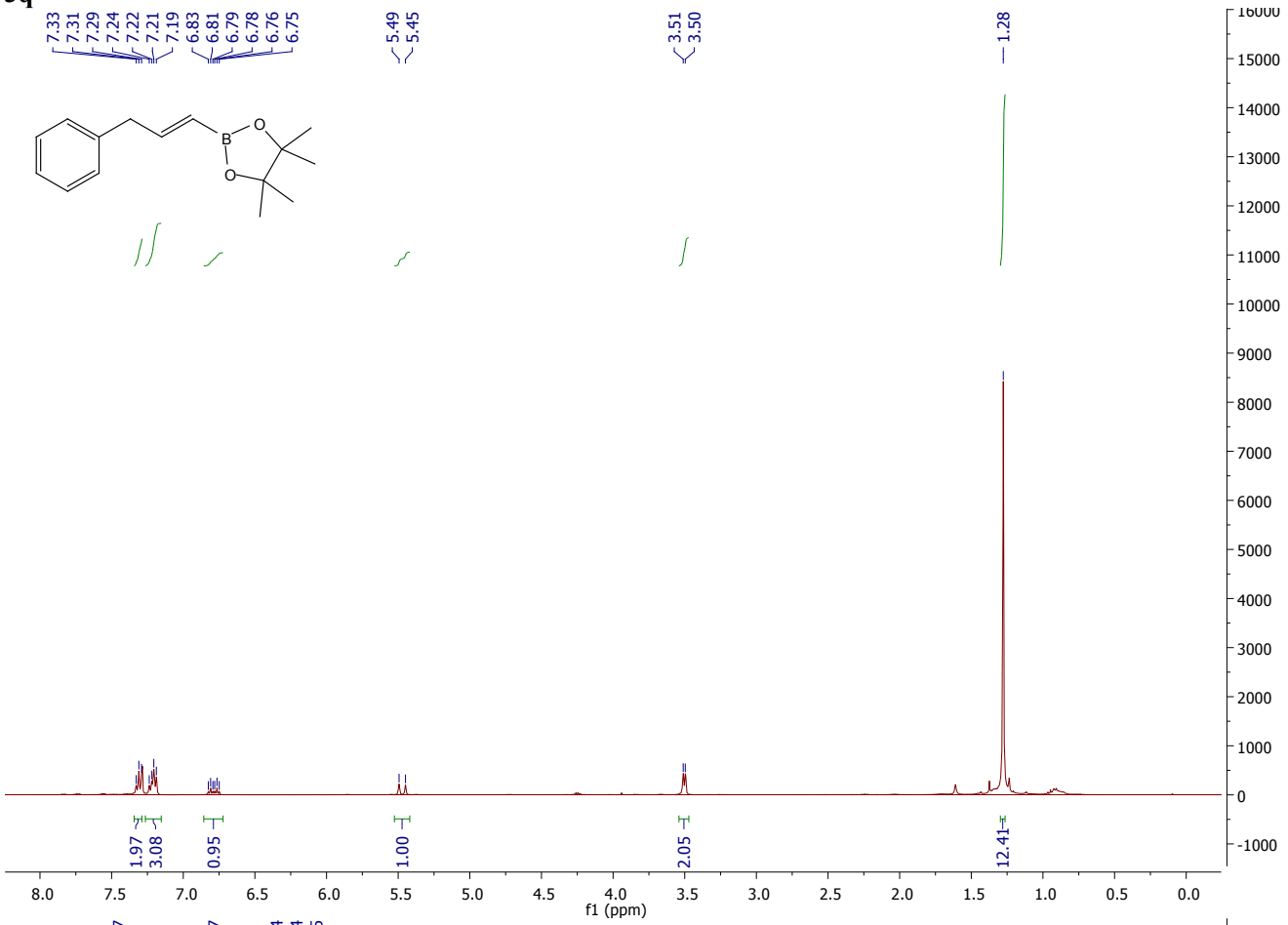

146.45
135.37
133.62
131.11
129.02
128.49
126.17
125.79
125.59
124.08
123.79
83.43
24.88
O
B
O
f1 (ppm)

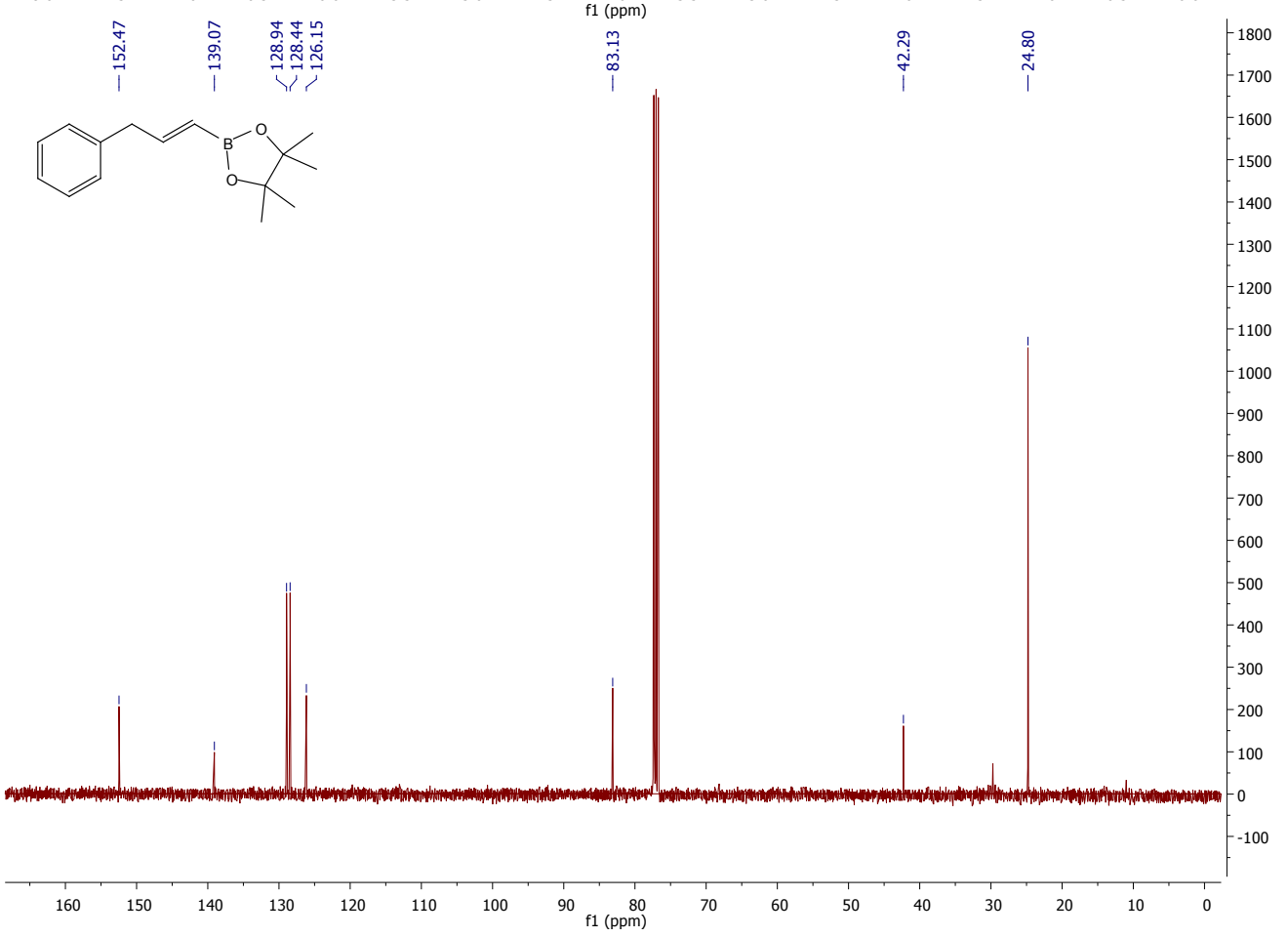
3p


7.43
7.38
7.34
7.33
7.32
7.30
7.29
7.28
7.28
5.99
5.94
1.33
O
B
O
S
1.17
2.00
1.31
1.00
12.11
f1 (ppm)

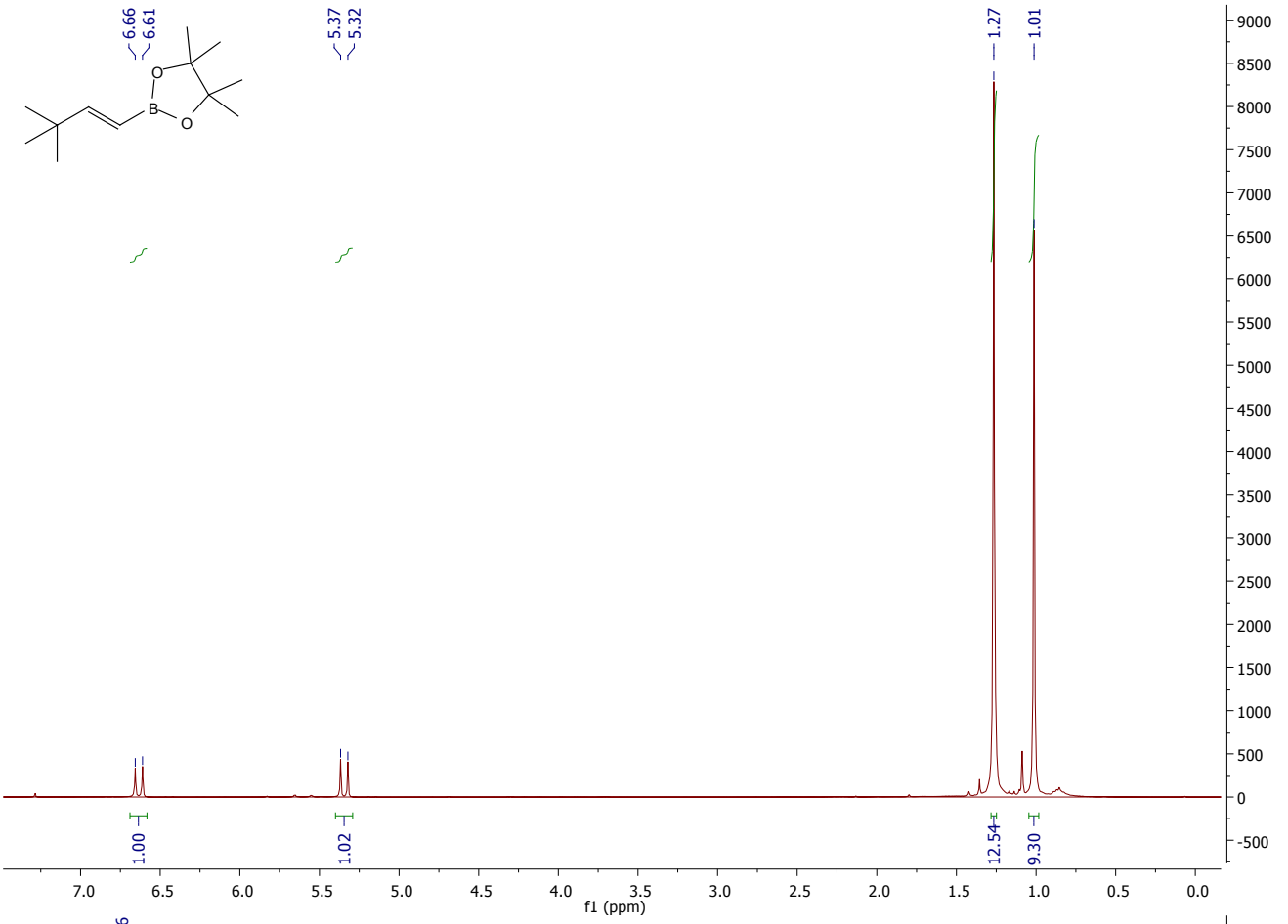

143.16
141.22
126.13
125.03
124.89
83.33
24.81
O
B
O
S
f1 (ppm)

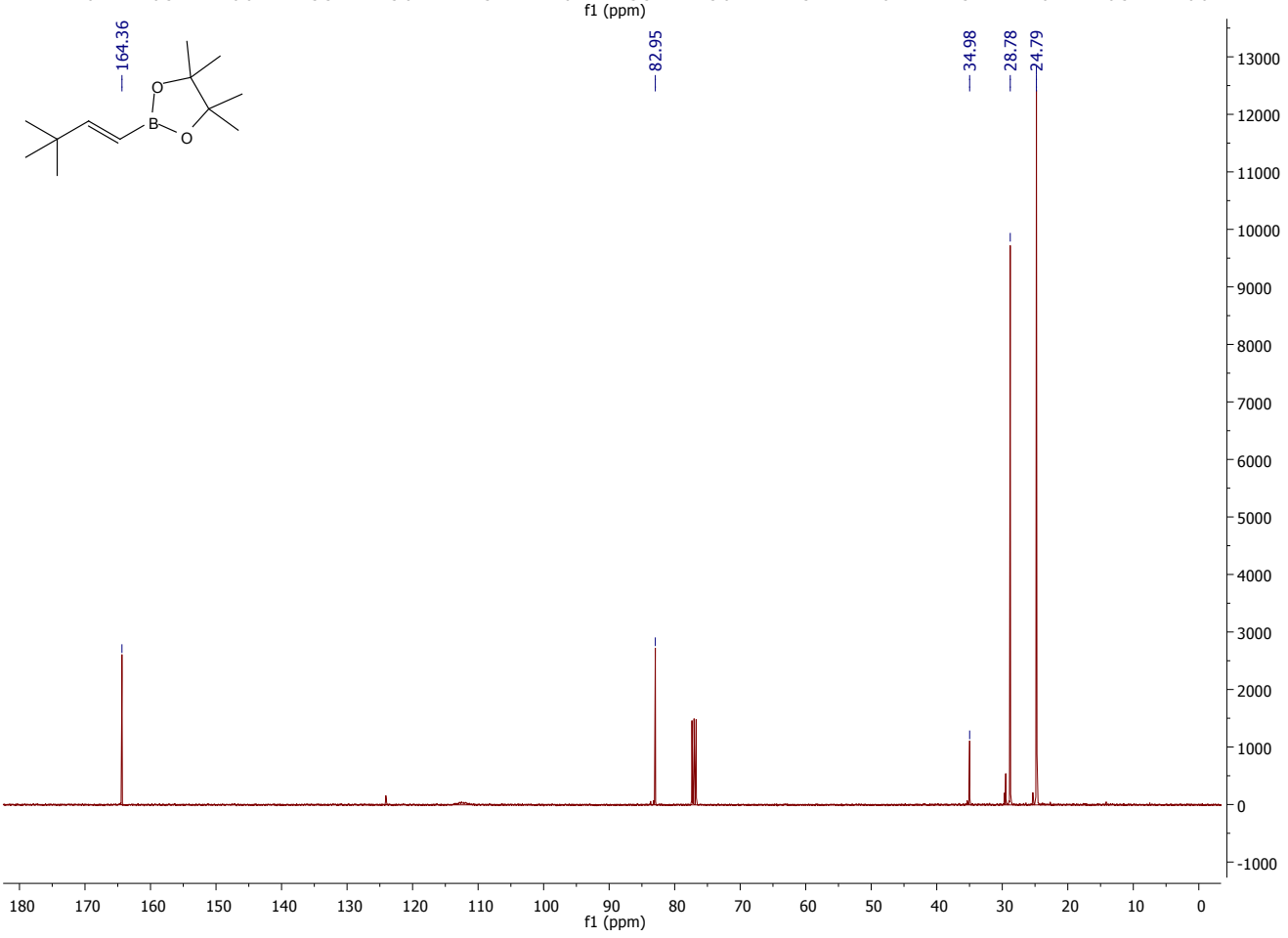
3q


7.33
7.31
7.29
7.24
7.22
7.21
7.19
6.83
6.81
6.79
6.78
6.76
6.75
5.49
5.45
3.51
3.50
1.28
B
O
O
1.97
3.08
0.95
1.00
2.05
12.41
f1 (ppm)

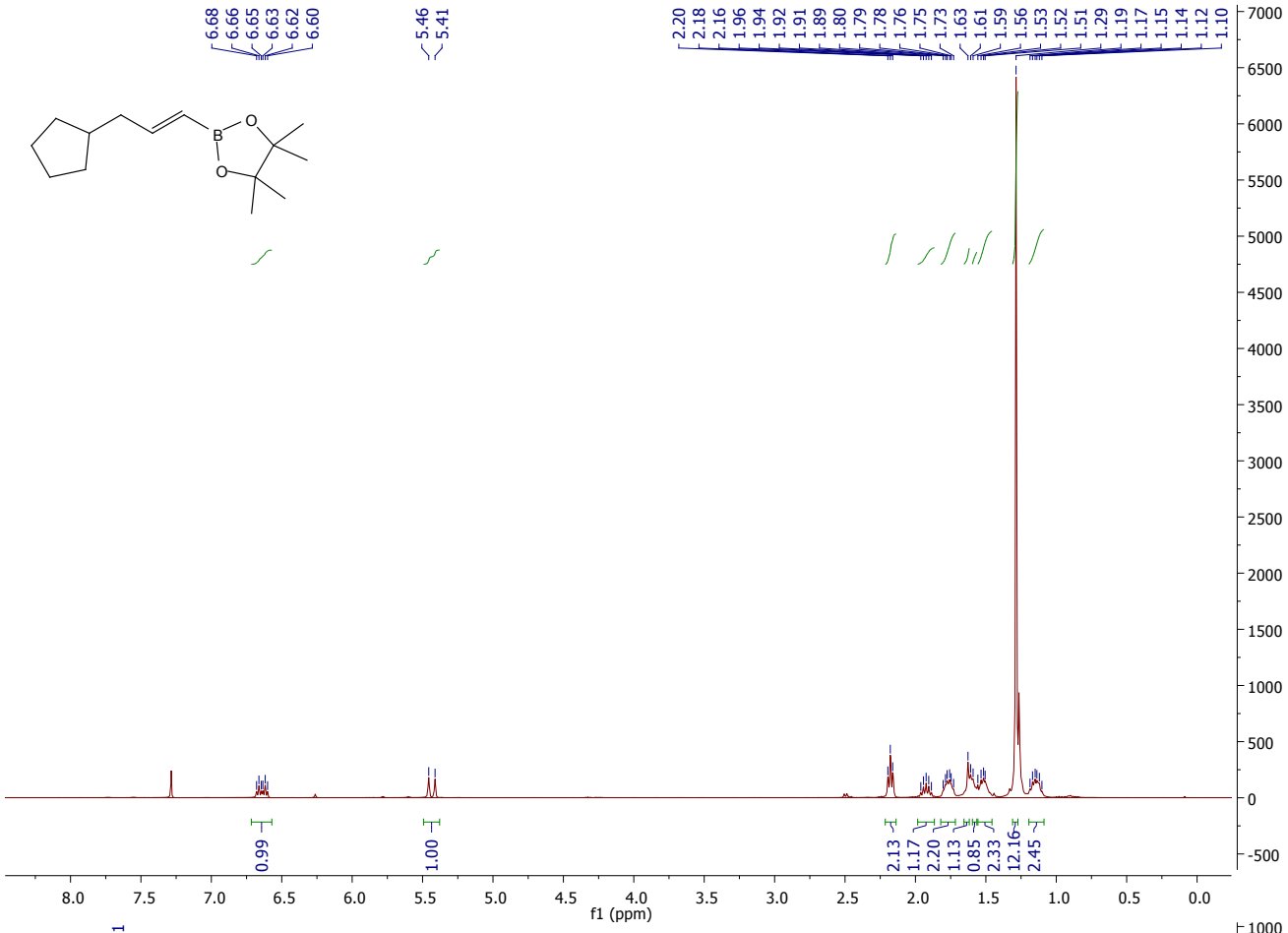

152.47
139.07
128.94
128.44
126.15
83.13
42.29
24.80
B
O
O
f1 (ppm)

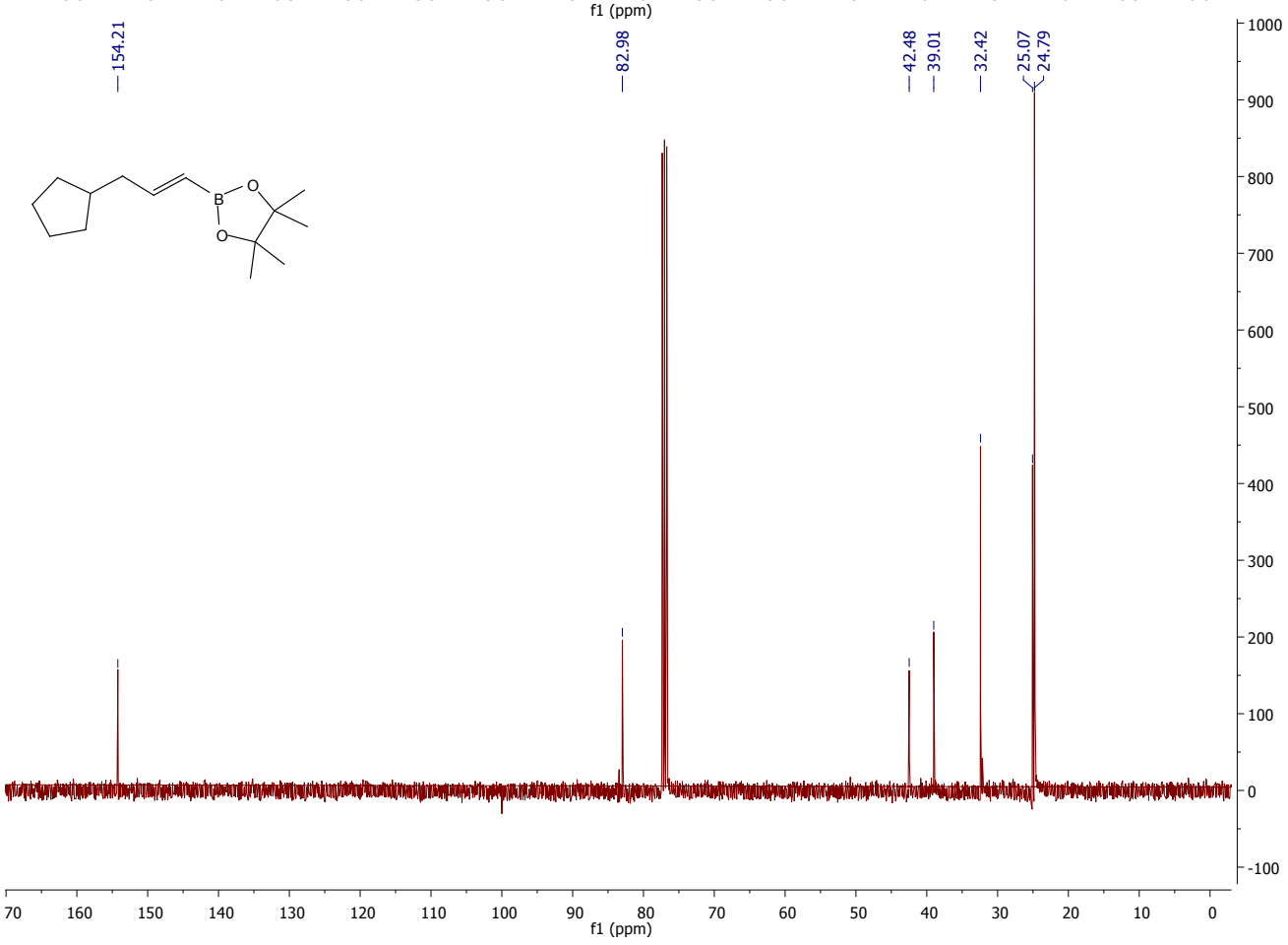
3r


6.66
6.61
5.37
5.32
1.27
1.01
1.00
1.02
12.54
9.30
f1 (ppm)

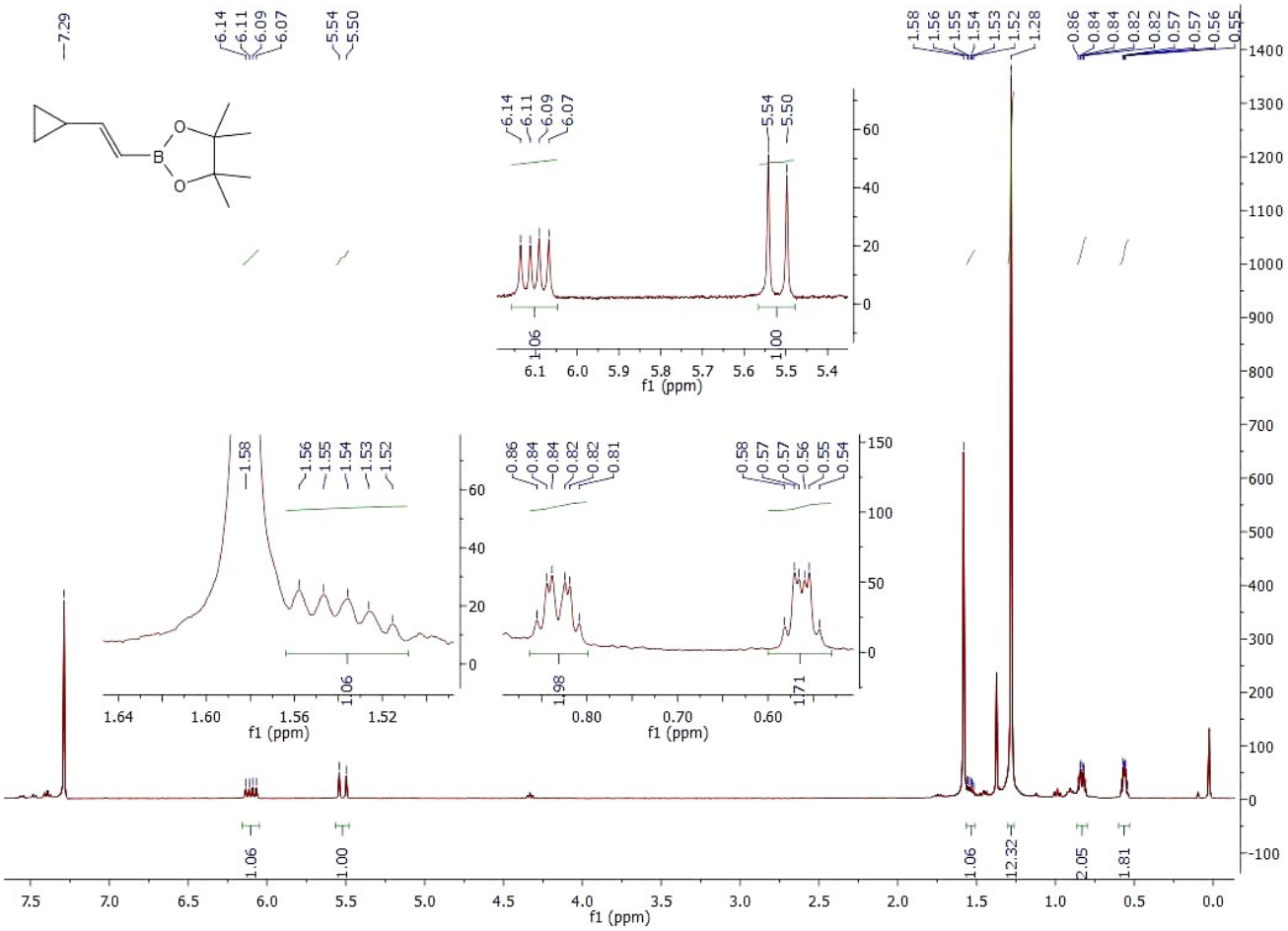

164.36
82.95
34.98
28.78
24.79
f1 (ppm)

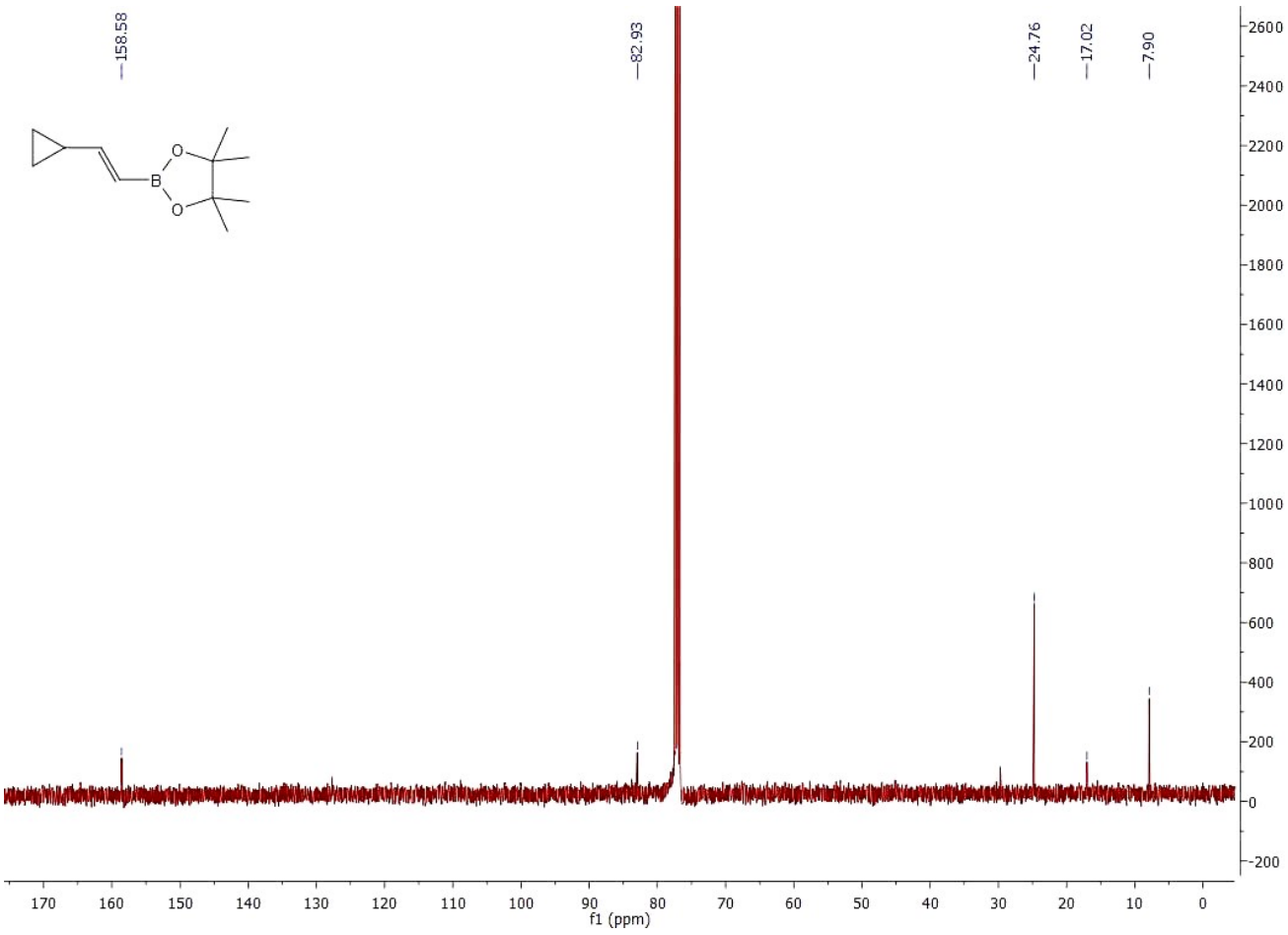
3s


6.68
6.66
6.65
6.63
6.62
6.60
5.46
5.41
2.20
2.18
2.16
1.96
1.94
1.92
1.91
1.89
1.80
1.79
1.78
1.76
1.75
1.73
1.63
1.61
1.59
1.56
1.53
1.52
1.51
1.29
1.19
1.17
1.15
1.14
1.12
1.10
O
B
O
0.99
1.00
2.13
1.17
2.20
1.13
0.85
2.33
12.16
2.45
f1 (ppm)

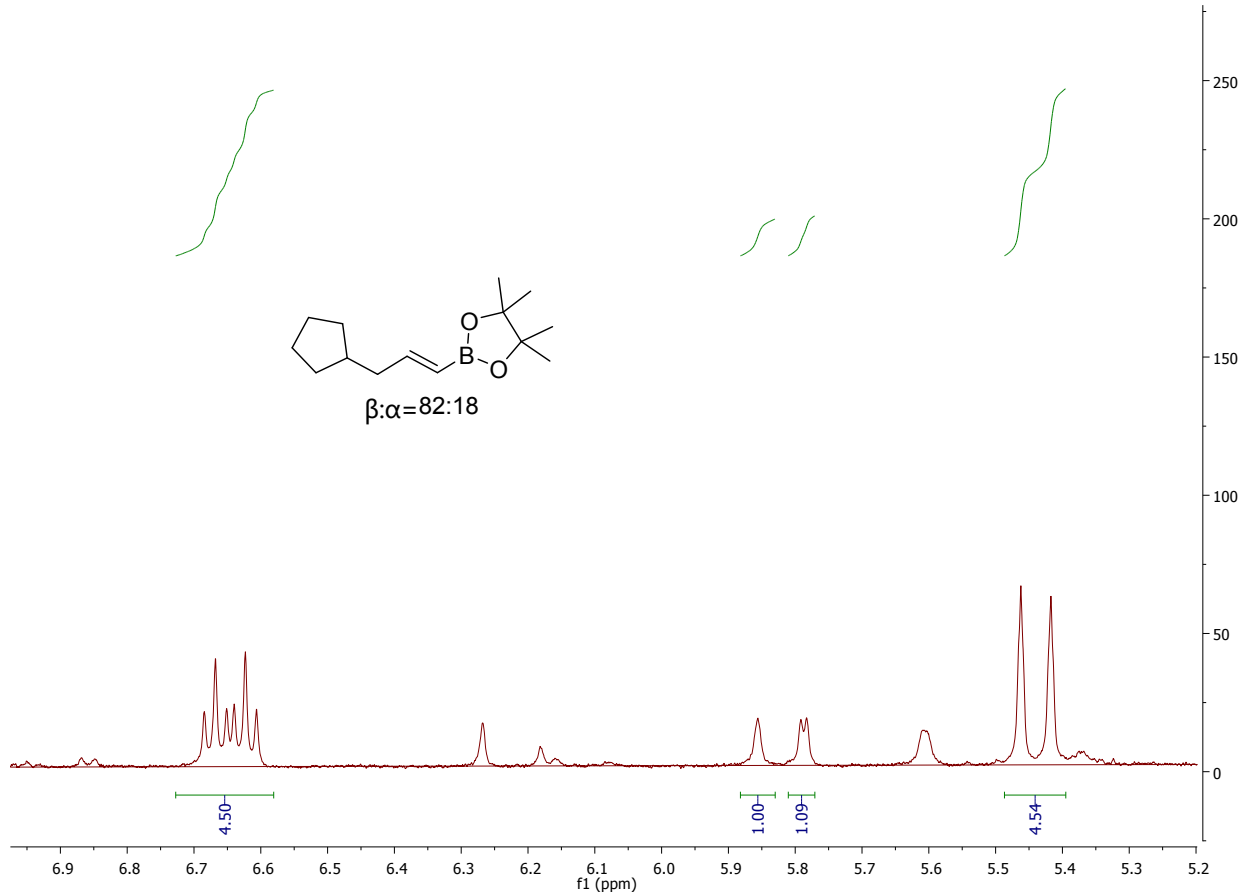

154.21
82.98
42.48
39.01
32.42
25.07
24.79
O
B
O
f1 (ppm)

3t


7.29
6.14
6.11
6.09
6.07
5.54
5.50
1.58
1.56
1.55
1.54
1.53
1.52
1.28
0.86
0.84
0.84
0.82
0.82
0.57
0.57
0.56
0.55
f1 (ppm)
1.06
1.00
12.32
2.05
1.81


158.58
82.93
24.76
17.02
7.90
f1 (ppm)

3s



3t