Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Lewis acid catalysis: regioselective hydroboration of alkynes and alkenes promoted by scandium triflate

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I. General considerations

Unless otherwise noted all the reactions were performed in an argon filled MBRAUN glove box or using standard Schlenk technique. All chemicals were purchased either from Sigma Aldrich or Alfa Aesar and used without further purification. Scandium triflate (99.995% trace metal basis), $NaBHEt_3$, and pinacol borane (HBpin) were purchased from Sigma Aldrich. HBpin for bulk reactions was prepared from B_2pin_2 according to literature procedure.[1] Reagent grade solvents were purchased form SD Fine Chemicals (India), distilled and deoxygenated by freeze pump thaw cycle (three times) before using. Deuterated solvents $CDCl_3$, C_6D_6, toluene-d_8, D_2O were purchased from Cambridge Isotope Laboratories and deoxygenated by freeze pump thaw cycle and stored over molecular sieves before use.

GC-MS data were acquired using GCMS-QP2010 SE SHIMADZU system. Commercially available, pre-coated TLC-sheets ALUGRAM® Xtra Sil G/UV254 were purchased from MACHEREY-NAGEL GmbH & Co. KG. The removal of solvent was performed on a rotary evaporator in vacuo at a maximum temperature of 40 °C.

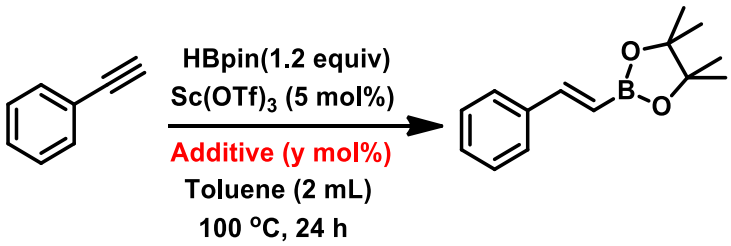
All NMR spectra (^1H (400 MHz), $^{13}C\{^1H\}$ (100 MHz), ^{11}B (128 MHz)) were recorded by a Bruker Avance 400 MHz NMR spectrometer and ^{19}F (470 MHz) was recorded in a 500 MHz Jeol NMR spectrometer at an ambient temperature. ^1H NMR chemical shifts were reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm) whereas ^{13}C NMR spectra were reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm). ^{11}B NMR signals were quoted relative to $BF_3{\cdot}Et_2O$ and ^{19}F NMR signals were quoted using $FCCl_3$ as an internal standard. ^1H NMR yields were calculated using CH_3NO_2 (nitromethane) as an internal standard. Peak values were reported downfield to TMS in ppm (parts per million) and following notation has been used to assign the peaks (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad, dd: doublet of a doublet, dt: doublet of a triplet, td: triplet of a doublet). Coupling constants values were given in Hertz's (Hz) and rounded up to the nearest whole number.

II. Optimization of the Reaction Conditions

Experimental Procedure for Examples Described in Table 1.

In a microwave vial equipped with magnetic stirring bar, scandium triflate (6 mg, 0.0125 mmol), $NaBHEt_3$ (1M in THF, 12 µl, 0.0125 mmol), pinacol borane (44 µl, 0.3 mmol), phenylacetylene (27 µl, 0.25 mmol) and 2 mL of solvent were added. The reaction mixture was stirred at 100 °C for the indicated amount of time, and then eluted with Et_2O: hexane (3:7) mixture through a plug of celite (Ø 3 mm × 8 mm). The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from ^1H NMR using nitromethane as an internal standard.

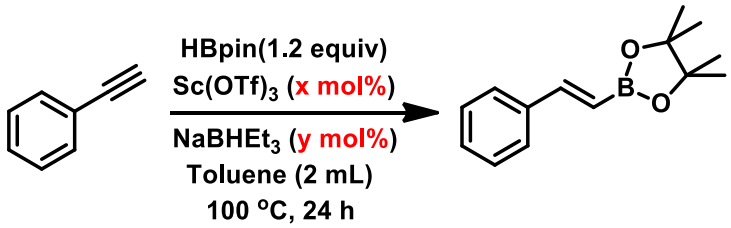
Table S1: Screening of additives for hydroboration of phenyl acetylene (1a).



Entry	Catalyst (5 mol %)	Additive (y mol %)	Solvent	Temp (^oC)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$	$NaBHEt_3$ (20)	toluene	100	24	65
2	$Sc(OTf)_3$	$NaBH_4$ (20)	toluene	100	24	74
3	$Sc(OTf)_3$	$NaBH_4$ (5)	toluene	100	24	51
4	$Sc(OTf)_3$	NaH (20)	toluene	100	24	41
5	$Sc(OTf)_3$	MeOH (20)	toluene	100	24	trace
6	$Sc(OTf)_3$	$SiHMe_2Cl$ (5)	toluene	100	24	28
7	$Sc(OTf)_3$	NaO^tBu (5)	toluene	100	24	51

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (1.2 equiv, 0.3 mmol), $Sc(OTf)_3$ (5 mol %, 0.0125 mmol), additives (y mol %) and toluene (2 mL) at 100 °C for 24 h in N_2 atmosphere. [a] Yields were determined by ^1H NMR using nitromethane as an internal standard.

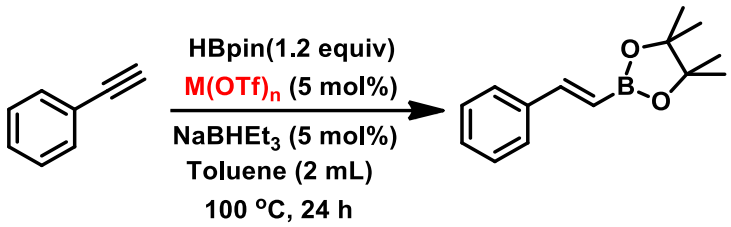
Table S2: Screening of catalyst and additive loading for hydroboration of phenyl acetylene (1a).



Entry	Catalyst (x mol %)	Additive (y mol %)	Solvent	Temp (^{o}C)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$ (2.5)	$NaBHEt_3$ (2.5)	toluene	100	24	90
2	$Sc(OTf)_3$ (2.5)	$NaBHEt_3$ (5)	toluene	100	24	87
3	$Sc(OTf)_3$ (5)	$NaBHEt_3$ (2.5)	toluene	100	24	58
4	$Sc(OTf)_3$ (5)	$NaBHEt_3$ (5)	toluene	100	24	99
5	$Sc(OTf)_3$ (5)	$NaBHEt_3$ (10)	toluene	100	24	96
6	$Sc(OTf)_3$ (10)	$NaBHEt_3$ (10)	toluene	100	24	>99

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (1.2 equiv, 0.3 mmol), $Sc(OTf)_3$ (x mol %), $NaBHEt_3$ (y mol %) and toluene (2 mL) at 100 °C for 24 h in N_2 atmosphere. [a] Yields were determined by ^{1}H NMR using nitromethane as an internal standard.

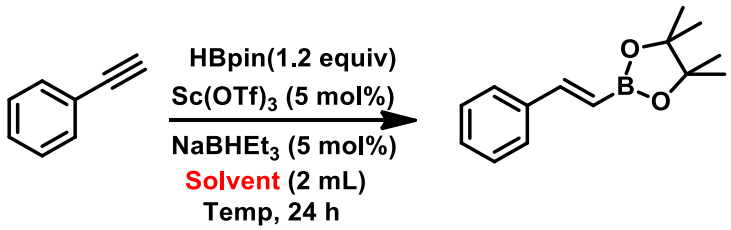
Table S3: Screening of metal salts for hydroboration of phenyl acetylene (1a).



Entry	Catalyst $M(OTf)_n$ (5 mol%)	Additive (5 mol%)	Solvent	Temp (^oC)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	24	99
2	$Bi(OTf)_3$	$NaBHEt_3$	toluene	100	24	11
3	$In(OTf)_3$	$NaBHEt_3$	toluene	100	24	36
4	$Cu(OTf)_2$	$NaBHEt_3$	toluene	100	24	27

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (1.2 equiv, 0.3 mmol), $M(OTf)_n$ (5 mol %, 0.0125 mmol), $NaBHEt_3$ (5 mol %, 0.0125 mmol) and toluene (2 mL) at 100 °C for 24 h in N_2 atmosphere. [a] Yields were determined by ^1H NMR using nitromethane as an internal standard.

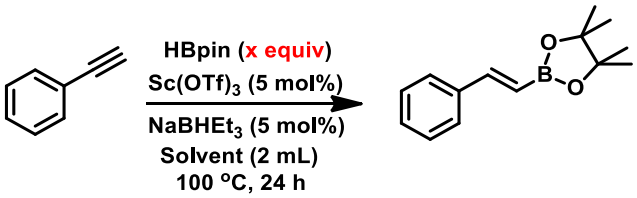
Table S4: Screening of solvents for hydroboration of phenyl acetylene (1a).



Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (^{o}C)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$	$NaBHEt_3$	DCM	40	24	40
2	$Sc(OTf)_3$	$NaBHEt_3$	THF	70	24	77
3	$Sc(OTf)_3$	$NaBHEt_3$	CH_3CN	85	24	17
4	$Sc(OTf)_3$	$NaBHEt_3$	benzene	85	24	94
5	$Sc(OTf)_3$	$NaBHEt_3$	dioxane	110	24	66
6	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	24	99
7	$Sc(OTf)_3$	$NaBHEt_3$	DMF	110	24	trace

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (1.2 equiv, 0.3 mmol), $Sc(OTf)_3$ (5 mol %, 0.0125 mmol), $NaBHEt_3$ (5 mol %, 0.0125 mmol) and solvent (2 mL) for 24 h in N_2 atmosphere. [a] Yields were determined by ^{1}H NMR using nitromethane as an internal standard.

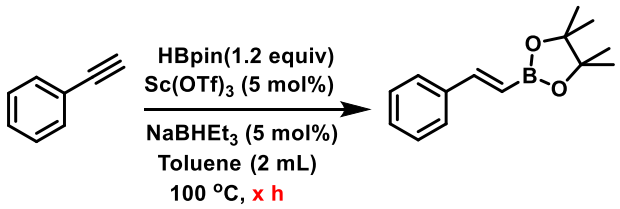
Table S5: Screening of HBpin equivalents for hydroboration of phenyl acetylene (1a).



Entry	Catalyst	Additive (y mol%)	HBpin	Solvent	Temp(°C)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$	$NaBHEt_3$ (5)	1	toluene	100	24	78
2	$Sc(OTf)_3$	$NaBHEt_3$ (5)	1.2	toluene	100	24	99

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (x equiv), $Sc(OTf)_3$ (5 mol %, 0.0125 mmol), $NaBHEt_3$ (5 mol %) and toluene (2 mL) at 100 °C for 24 h in N_2 atmosphere. [a] Yields were determined by ^1H NMR using nitromethane as an internal standard.

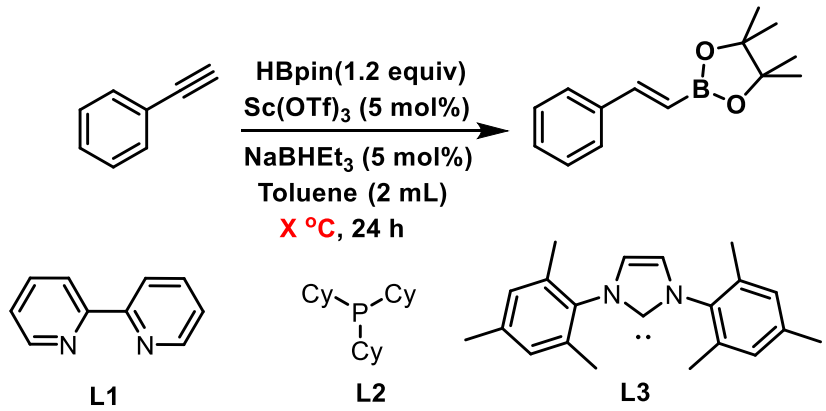
Table S6: Screening of reaction time for hydroboration of phenyl acetylene (1a).



Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	2	38
2	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	8	57
3	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	12	77
4	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	18	83
5	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	24	99

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (1.2 equiv, 0.3 mmol), $Sc(OTf)_3$ (5 mol %, 0.0125 mmol), $NaBHEt_3$ (5 mol %, 0.0125 mmol) and toluene (2 mL) at 100 °C for mentioned amount of time in N_2 atmosphere. [a] Yields were determined by ^1H NMR using nitromethane as an internal standard.

Table S7: Screening of reaction temperature for hydroboration of phenyl acetylene (1a).



Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%)[a]
1	$Sc(OTf)_3$	$NaBHEt_3$	toluene	RT	24	14
2	$Sc(OTf)_3$	$NaBHEt_3$	toluene	50	24	29
3	$Sc(OTf)_3$	$NaBHEt_3$	toluene	60	24	38
4[b]	$Sc(OTf)_3$	$NaBHEt_3$	toluene	60	24	20
5[c]	$Sc(OTf)_3$	$NaBHEt_3$	toluene	60	24	21
6[d]	$Sc(OTf)_3$	$NaBHEt_3$	toluene	60	24	5
7	$Sc(OTf)_3$	$NaBHEt_3$	toluene	80	24	89
8	$Sc(OTf)_3$	$NaBHEt_3$	toluene	90	24	92
9	$Sc(OTf)_3$	$NaBHEt_3$	toluene	100	24	99

Reaction conditions: Phenyl acetylene (0.25 mmol), pinacol borane (1.2 equiv, 0.3 mmol), $Sc(OTf)_3$ (5 mol %, 0.0125 mmol), $NaBHEt_3$ (5 mol %, 0.0125 mmol) and toluene (2 mL) at mentioned temperature for 24 h in N_2 atmosphere. [a] Yields were determined by ^1H NMR using nitromethane as an internal standard. [b] Reaction was performed in the presence of **L1** (2,2'-bipyridyl, 10 mol %). [c] Reaction was performed in the presence of **L2** (tricyclohexylphosphine, 10 mol %). [d] Reaction was performed in the presence of **L3** (IMes, 10 mol %).

III. Substrate Scope

General procedure A: for small scale catalytic reactions.

A microwave vial equipped with a magnetic stirring bar was charged with scandium triflate (5 mol %, 6 mg, 0.0125 mmol), $NaBHEt_3$ (1M in THF, 5 mol %, 12 µL, 0.0125 mmol), pinacol borane (1.2 equiv, 44 µL, 0.3 mmol), alkynes (1 equiv, 0.25 mmol) and 2 mL of toluene. The reaction mixture was heated at 100 ºC for 24 h. After completion, the reaction mixture was eluted with Et_2O:hexane (3:7) mixture through a plug of celite (Ø 3 mm × 8 mm). The solvent was removed in vacuo and the crude reaction mixture was subjected to ^1H NMR. The product yield was determined from ^1H NMR using nitromethane as an internal standard and average of two runs.

General Procedure B: for larger scale catalytic reactions.

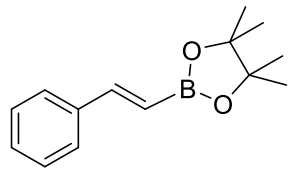
In a screw capped long vial or in a Schlenk tube equipped with a magnetic stirring bar, scandium triflate (5 mol %, 25 mg, 0.05 mmol), $NaBHEt_3$ (1M in THF, 5 mol %, 50 µL, 0.05 mmol), pinacol borane (1.2 equiv, 174 µL, 1.2 mmol), alkynes (1 equiv, 1 mmol) and 6 mL of toluene were added. The reaction mixture was heated at 100 °C for 24 h. After completion, the reaction mixture was eluted with Et_2O:hexane (3:7) mixture through a short plug of celite; the filtrate was analyzed by GC-MS. The product was purified by silica gel column chromatography eluted with mostly EtOAc:hexane (02:98) mixture.

General Procedure C: for gram scale synthesis

In a schlenk tube equipped with a magnetic stirring bar, scandium triflate (5 mol %, 250 mg, 0.5 mmol), $NaBHEt_3$ (1M in THF, 5 mol%, 0.5 mL, 0.5 mmol), pinacol borane (1.2 equiv, 1.74 mL, 12 mmol), phenyl acetylene (**1a**, 1.02 g, 10 mmol) and 20 mL of toluene were added. The reaction mixture was heated at 100 °C for 24 h. After completion, the reaction mixture was eluted with Et_2O:hexane (3:7) mixture through a short plug of celite. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (02:98) mixture. (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane was obtained as a colourless oil in 82% yield (1.8 g, 8.2 mmol).

Spectral Data

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (1b)



Following general procedure B, colourless liquid in 95% (218 mg, 0.95 mmol) yield from phenyl acetylene (**1a**, 102 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[2]

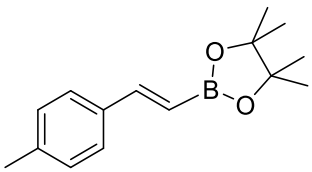
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51–7.48 (m, 2H), 7.41 (d, *J* = 19 Hz, 1H), 7.36 – 7.29 (m, 3H), 6.18 (d, *J* = 18 Hz, 1H), 1.32 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.2.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.7, 137.6, 129.0, 128.7, 127.2, 116.9 (br, *C-B*) 83.5, 25.0.

GC-MS: m/z 230 (M^+)

(*E*)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)



Following general procedure B, yellowish liquid in 94% (229 mg, 0.94 mmol) yield from 4-methylphenylacetylene (**2a**, 116 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[2]

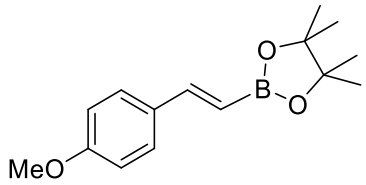
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.36 (m, 3H), 7.14 (d, *J* = 8 Hz, 2H), 6.11 (d, *J* = 19 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.4.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.6, 139.0, 135.0, 129.4, 127.1, 115.4 (br *C-B*), 83.4, 24.9, 21.5.

GC-MS: m/z 244 (M^+)

(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



Following general procedure B, yellowish liquid in 94% (244 mg, 0.94 mmol) yield from 4-methoxyphenylacetylene (**3a**, 132 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[2]

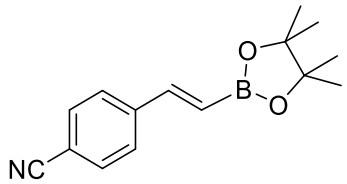
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45–7.42 (m, 2H), 7.35 (d, *J* = 18 Hz, 1H), 6.86 (d, *J* = 9 Hz, 2H), 6.01 (d, *J* = 18 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.4, 149.2, 130.6, 128.6, 114.1, 83.4, 55.4, 25.0.

GC-MS: m/z 260 (M^+)

(*E*)-4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (4b)



Following general procedure B, brown solid in 86% (219 mg, 0.86 mmol) yield from 4-ethynylbenzonitrile (**4a**, 127 mg, 1 mmol) was obtained using 5% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[3]

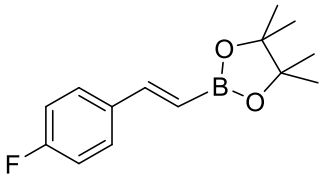
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62–7.60 (m, 2H), 7.54 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 18 Hz, 1H), 6.27 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.4.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.2, 141.8, 132.6, 127.5, 121.2 (br, *C-B*), 118.9, 112.1, 83.9, 24.9.

GC-MS: m/z 255 (M^+)

(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)



Following general procedure B, colourless liquid in 92% (228 mg, 0.92 mmol) yield from 4-fluoro phenylacetylene (**5a**, 120 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46 (dd, *J* = 8, 6 Hz, 2H), 7.35 (d, *J* = 18 Hz, 1H), 7.02 (t, *J* = 9 Hz, 2H), 6.07 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H).

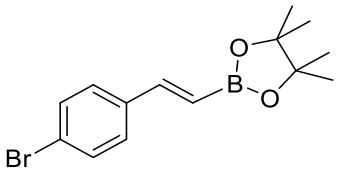
^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.5, 148.3, 133.9, 128.9 (d, J = 8 Hz), 115.7 (d, J = 22 Hz), 83.6, 25.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -112.29

GC-MS: m/z 248 (M^+)

(*E*)-2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6b)



Following general procedure B, yellow solid in 94% (275 mg, 0.94 mmol) yield from 4-bromoethynylbenzene (**6a**, 181 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[5]

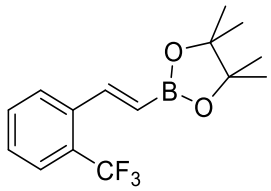
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50–7.47 (m,2H), 7.38 – 7.36 (m, 2H), 7.30 (d, *J* = 13 Hz, 1H), 6.17 (d, *J* = 18 Hz, 1H), 1.34 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.2.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.2, 136.6, 131.9, 128.7, 123.0, 83.6, 25.0.

GC-MS: m/z 309 (M^+)

(*E*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7b)



Following general procedure B, red solid in 42% (125 mg, 0.42 mmol) yield from 1-ethynyl-2-(trifluoromethyl)benzene (**7a**, 170 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (dd, *J* = 18, 2 Hz, 1H), 7.71 (d, *J* = 8 Hz, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 1H), 7.36 (t, *J* = 8 Hz, 1H), 6.18 (d, *J* = 18 Hz, 1H), 1.31 (s, 12 H).

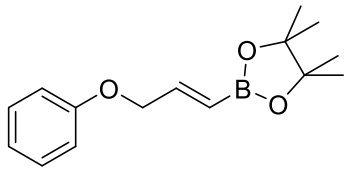
^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.6.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.9, 137.1, 132.0, 128.3, 127.6, 126.6, 125.8 (q, J = 6 Hz), 123.0, 83.7, 24.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -58.82.

GC-MS: m/z 283 $(M\text{-}CH_3)^+$

(*E*)-4,4,5,5-Tetramethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (8b)



Following general procedure B, colourless oil in 59% (153 mg, 0.59 mmol) yield from phenyl propargyl ether (**8a**, 132 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[7]

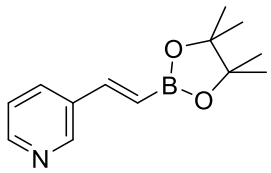
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.24 (t, *J* = 8 Hz, 2H), 6.94 – 6.85 (m, 3H), 6.75 (dt, *J* = 18, 4 Hz, 1H), 5.82 (dt, *J* = 18, 2 Hz, 1H), 4.58 (dd, *J* = 4, 2 Hz, 2H), 1.25 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.6, 147.4, 129.5, 120.9, 114.7, 83.4, 69.2, 24.9.

GC-MS: m/z 260 (M^+)

(*E*)-3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9b)



Following general procedure B, colourless oil in 21% (48 mg, 0.21 mmol) yield from 3-ethynylpyridine (**9a**, 103 mg, 1 mmol) was obtained using EtOAc as eluent.

The NMR is consistent with literature data. [7]

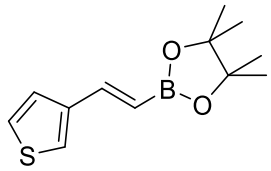
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.69 (d, *J* = 3 Hz, 1H), 8.52 (d, *J* = 2 Hz, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.37 (d, *J* = 19 Hz, 1H), 7.29 (dd, *J* = 8, 5 Hz, 1H), 6.25 (d, *J* = 19 Hz, 1H), 1.31 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.3.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.7, 150.0, 145.7, 133.5, 125.0, 123.8, 83.8, 24.9.

GC-MS: m/z 231 (M^+)

(*E*)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (10b)



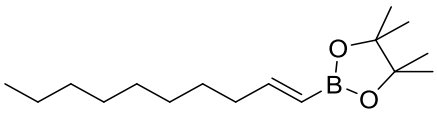
Following general procedure A, colourless oil in 63% NMR yield from 3-ethynylthiophene (**10a**, 27 mg, 0.25 mmol) was obtained.

The NMR is consistent with literature data. [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 18 Hz, 1H), 7.28 – 7.27 (m, 1H), 7.26 – 7.24 (m, 1H), 7.25 – 7.22 (m, 1H), 5.91 (d, *J* = 18 Hz, 1H), 1.27 (s, 12H).

GC-MS: m/z 236 (M^+)

(*E*)-2-(Dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b)



Following general procedure B, colourless oil in 93% (247 mg, 0.93 mmol) yield from 1-decyne (**11a**, 138 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.
The NMR is consistent with literature data.[8]

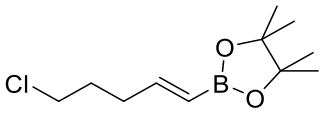
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.58 (dt, *J* = 18, 6 Hz, 1H), 5.37 (d, *J* = 18 Hz, 1H), 2.12 – 2.06 (m, 2H), 1.36 – 1.34 (m, 2H), 1.21 (s, 12H), 1.19 – 1.17 (m, 10H), 0.82 (t, *J* = 7 Hz, 3H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.9.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.8, 128.7, 118.7 (br, C-B), 83.0, 36.0, 32.0, 29.5, 29.3, 28.3, 24.8, 22.7, 14.2.

GC-MS: m/z 251 $(M\text{-}CH_3)^+$

(*E*)-2-(5-Chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b)



Following general procedure B, colourless oil in 60% (138 mg, 0.60 mmol) yield from 5-chloro-1-pentyne (**12a**, 103 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.
The NMR is consistent with literature data. (9)

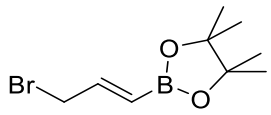
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.57 (dt, *J* = 18, 6 Hz, 1H), 5.47 (dt, *J* = 18, 1 Hz, 1H), 3.51 (t, *J* = 7 Hz, 2H), 2.29 (tt, *J* = 9, 4 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.25 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.2, 120.4 (br, C-B), 83.2, 44.4, 32.8, 31.1, 24.9.

GC-MS: m/z 230 (M^+).

(*E*)-2-(3-Bromoprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b)



Following general procedure B, colourless oil in 42% (103 mg, 0.42 mmol) yield from propargyl bromide (**13a**, 119 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[10]

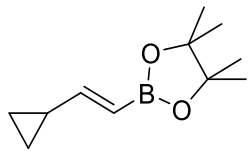
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.67 (dt, *J* = 18, 7 Hz, 1H), 5.67 (d, *J* = 18 Hz, 1H), 3.97 (d, *J* = 7 Hz, 2H), 1.26 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.5.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.9, 83.7, 33.8, 24.9.

GC-MS: m/z 248 (M+2)

(*E*)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14b)



Following general procedure B, colourless oil in 52% (101 mg, 0.52 mmol) yield from cyclopentylacetylene (**14a**, 66 mg, 1 mmol) was obtained without any further purification.

The NMR is consistent with literature data.[2]

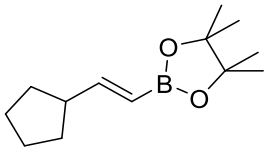
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.06 (dd, *J* = 18, 9 Hz, 1H), 5.48 (d, *J* = 18 Hz, 1H), 1.50 (tdd, *J* = 17, 11, 6 Hz, 1H), 1.24 (s, 12H), 0.85 – 0.74 (m, 2H), 0.56 – 0.49 (m, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.5.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.7, 115.0 (br, C-B), 83.1, 24.9, 17.1, 8.0.

GC-MS: m/z 194 (M^+)

(*E*)-2-(2-Cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b)



Following general procedure B, colourless oil in 65% (144 mg, 0.65 mmol) yield from cyclopentylacetylene (**15a**, 94 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data. [11]

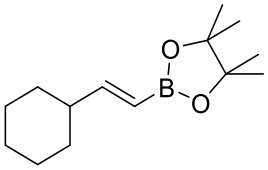
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.60 (dd, *J* = 18, 7 Hz, 1H), 5.39 (dd, *J* = 18, 1 Hz, 1H), 2.58 – 2.43 (m, 1H), 1.82 – 1.73 (m, 2H), 1.68 – 1.59 (m, 2H), 1.58 – 1.50 (m, 2H), 1.42 – 1.31 (m, 2H), 1.26 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 29.6.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.1, 83.1, 46.3, 32.5, 25.4, 24. 9.

GC-MS: m/z 222 (M^+)

(*E*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16b)



Following general procedure B, colourless oil in 90% (212 mg, 0.90 mmol) yield from cyclohexylacetylne (**16a**, 108 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[12]

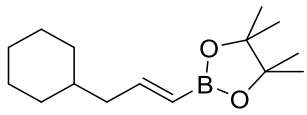
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.56 (dd, *J* = 18, 6 Hz, 1H), 5.36 (dd, *J* = 18, 1 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.78 – 1.67 (m, 4H), 1.65 – 1.59 (m, 2H), 1.25 (s, 12H), 1.15 – 1.01 (m, 4H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.0

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.0, 83.1, 43.4, 32.1. 29.9, 26.1, 24.9.

GC-MS: m/z 236 (M^+)

(*E*)-2-(3-Cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17b)



Following general procedure B, colourless oil in 83% (207 mg, 0.83 mmol) yield from 3-cyclohexyl-1-propyne (**17a**, 122 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[7]

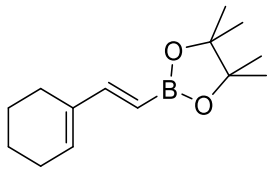
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.59 (dt, *J* = 18, 7 Hz, 1H), 5.38 (d, *J* = 18 Hz, 1H), 2.03 (t, *J* = 7 Hz, 2H), 1.71 - 1.64 (m, 4H), 1.41 – 1.31 (m, 1H), 1.25 (s, 12H), 1.23 – 1.08 (m, 4H), 0.94 – 0.79 (m, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.0.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 83.1, 44.3, 37.4, 33.3, 26.7, 26.4, 25.0.

GC-MS: m/z 235 $(M\text{-}CH_3)^+$

(*E*)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)



Following general procedure B, colourless oil in 80% (187 mg, 0.80 mmol) yield from ethynylcyclohexene (**18a**, 106 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[2]

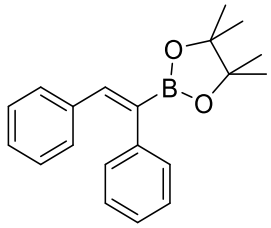
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.01 (d, *J* = 18 Hz, 1H), 5.97 – 5.94 (m, 1H), 5.41 (d, *J* = 18 Hz, 1H), 2.14 – 2.11 (m, 4H), 1.73 – 1.61 (m, 2H), 1.61 – 1.53 (m, 2H), 1.26 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.0.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 137.3, 134.4, 112.0 (br, *C-B*), 83.1, 26.3, 24.9, 23.9, 22.5, 22.5.

GC-MS: m/z 234 (M^+)

(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19b)



Following general procedure B, white solid in 73% (223 mg, 0.73 mmol) yield from diphenylacetylene (**19a**, 178 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent. The NMR is consistent with literature data.[2]

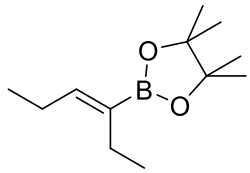
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (s, 1H), 7.42 – 7.38 (m, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.18 (m, 5H), 1.44 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.6.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.3, 140.5, 137.0, 131.0, 128.9, 128.3, 127.9, 127.7, 126.3, 83.8, 24.8.

GC-MS: m/z 291 $(M\text{-}CH_3)^+$

(*Z*)-2-(Hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20b)



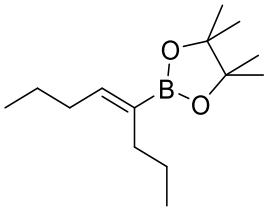
Following general procedure A, colourless oil in 74% NMR yield from 3-hexyne (**20a**, 20 mg, 0.25 mmol) was obtained.

The NMR is consistent with literature data.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.25 (t, J = 7 Hz, 1H), 2.14 – 2.08 (m, 4H), 1.25 (s, 12H), 0.99 (t, J = 8 Hz, 3H), 0.93 (t, J = 8 Hz, 3H).

GC-MS: m/z 210 (M^+)

(*Z*)-4,4,5,5-Tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (21b)



Following general procedure B, colourless oil in 82% (195 mg, 0.82 mmol) yield from 4-octyne (**22a**, 110 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[2]

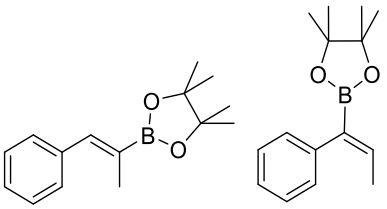
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.28 (t, *J* = 7 Hz, 1H), 2.08 (ddd, *J* = 11, 7, 4 Hz, 4H), 1.44 – 1.29 (m, 4H), 1.23 (s, 12H), 0.89 (t, *J* = 7 Hz, 3H), 0.86 (t, *J* = 7 Hz, 3H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.4.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.1, 132.3 (br, *C*-*B*), 83.0, 30.8, 30.7, 24.8, 23.4, 22.5, 14.2, 14.2.

GC-MS: m/z 223 $(M\text{-}CH_3)^+$

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (22b)



22b **22c**

Following general procedure B, colourless oil in 78% (190 mg, mixture of two isomers) yield from 1-phenyl-1-propyne (**23a**, 116 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[2] NMR data for major isomer is given below. (for minor isomer, the peaks has been assigned by asterisk (*) in ^{1}H NMR spectrum)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42–7.29 (m, 4H), 7.28–7.14 (m, 2H), 2.00 (d, *J* = 2 Hz, 3H), 1.32 (s, 12H).

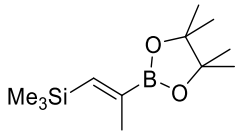
^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 30.7.

^{13}C NMR for 22b (100 MHz, $CDCl_3$) δ (ppm) 142.9, 138.1, 129.5, 128.2, 127.2, 83.6, 25.0, 16.1.

^{13}C NMR for 22c (100 MHz, $CDCl_3$) δ (ppm) 142.50, 129.22, 127.88, 126.00, 83.56, 24.88, 16.03 (peak for quaternary carbon was not observed).

GC-MS: m/z 229 $(M\text{-}CH_3)^+$

(*Z*)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (23b)



Following general procedure B, colourless oil in 52% (130 mg, 0.52 mmol) yield from 1-trimethylsilylpropyne (**23a**, 112 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data. [8] The NMR data for the major isomer.

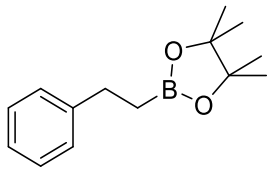
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.09 (q, *J* = 7 Hz, 1H), 1.89 (d, *J* = 7 Hz, 3H), 1.24 (s, 12H), 0.17 (s, 9H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 31.5.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 156.1, 83.2, 24.9, 0.9.

GC-MS: m/z 225 $(M\text{-}CH_3)^+$

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (24b)



Following general procedure B, colourless oil in 70% (162 mg, 0.70 mmol) yield from styrene (**24a**, 104 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.[13]

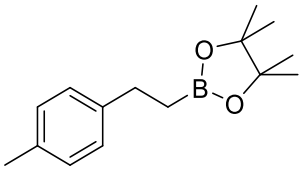
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34 – 7.25 (m, 4H), 7.24 – 7.17 (m, 1H), 2.80 (t, *J* = 8 Hz, 2H), 1.27 (s, 12H), 1.20 (t, *J* = 8 Hz, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 33.9.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.6, 128.3, 128.1, 125.6, 83.2, 30.1, 24.9, 13.2 (br, *C-B*).

GC-MS: m/z 232 (M^+)

4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (25b)



Following general procedure B, colourless oil in 94% (231 mg, 0.94 mmol) yield from 4-methylstyrene (**25a**, 116 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.
The NMR is consistent with literature data.[13]

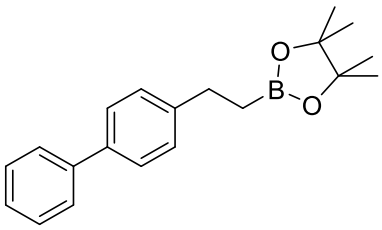
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 2.73 (t, *J* = 8 Hz, 2H), 2.32 (s, 3H), 1.25 (s, 12H), 1.18 – 1.11 (m, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 33.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.5, 135.0, 129.0, 128.0, 83.2, 29.6, 24.9, 21.1, 13.5 (br, *C-B*).

GC-MS: m/z 231$(M\text{-}CH_3)^+$

2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26b)



Following general procedure B, white solid in 82% (253 mg, 0.82 mmol) yield from 4-vinylbiphenyl (**26a**, 180 mg, 1 mmol) was obtained using 1% EtOAc in hexane as eluent.
The NMR is consistent with literature data. [14]

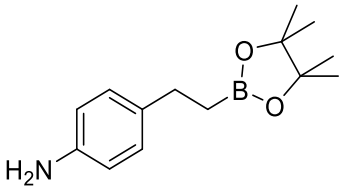
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 7.44 (t, *J* = 5 Hz, 2H), 7.36 – 7.28 (m, 3H), 2.81 (t, *J* = 8 Hz, 2H), 1.25 (s, 12H), 1.20 (t, *J* = 8 Hz, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 33.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.7, 141.4, 138.6, 128.8, 128.6, 127.1, 127.1, 127.0, 83.3, 29.7, 25.0, 13.1 (br *C-B*).

GC-MS: m/z 308 (M^+)

4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (27b)



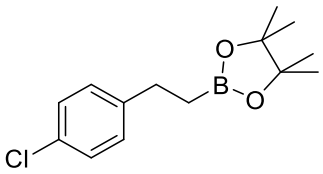
Following general procedure A, off white solid in 43% NMR yield from 4-vinylaniline (**27a**, 30 mg, 1 mmol) was obtained.

The NMR is consistent with literature data.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.00 (d, *J* = 8 Hz, 2H), 6.61 (d, *J* = 8 Hz, 2H), 2.64 (t, *J* = 9 Hz, 2H), 1.22 (s, 12H), 1.09 (t, *J* = 8 Hz, 2H).

GC-MS: m/z 247 (M^+)

2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28b)



Following general procedure A, colorless oil in 96% (64 mg, 0.96 mmol) yield from 4-chlorostyrene (**28a**, 35 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data. [13]

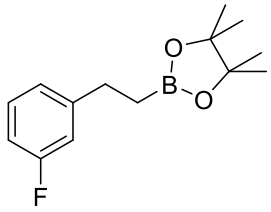
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 2.71 (t, *J* = 8 Hz, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 8 Hz, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 33.7.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.9, 131.3, 129.5, 128.3, 83.3, 29.4, 24.9, 15.4 (br, *C-B*).

GC-MS: m/z 251 $(M\text{-}CH_3)^+$

2-(3-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29b)



Following general procedure B, colourless oil in 65% (162 mg, 0.65 mmol) yield from 3-fluorostyrene (**29a**, 122 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.
The NMR is consistent with literature data.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.10 (td, *J* = 8, 6 Hz, 1H), 6.88 (d, *J* = 8 Hz, 1H), 6.82 (d, *J* = 10 Hz, 1H), 6.74 (td, *J* = 8, 2 Hz, 1H), 2.64 (t, J = 8 Hz 2H), 1.12 (s, 12H), 1.05 (t, *J* = 8 Hz, 2H).

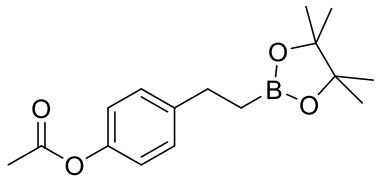
^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 33.9.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.0 (d, *J* = 245 Hz), 147.1 (d, *J* = 5 Hz), 129.7 (d, *J* = 8 Hz), 123.8, 115.0 (d, *J* = 21 Hz), 112.4 (d, *J* = 21 Hz), 83.3, 29.9, 24.9, 12.7 (br, *C-B*).

^{19}F NMR (470 MHz, $CDCl_3$) δ (ppm) -114.13.

GC-MS: m/z 225 $(M\text{-}CH_3)^+$

4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (30b)



Following general procedure B, white solid in 55% (159 mg, 0.55 mmol) yield from 4-acetoxystyrene (**30a**, 162 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.
The NMR is consistent with literature data.[17]

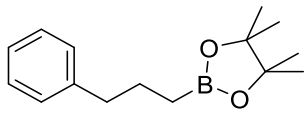
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 8 Hz, 2H), 2.73 (t, *J* = 8 Hz, 2H), 2.28 (s, 3H), 1.21 (s, 12H), 1.13 (t, *J* = 8 Hz, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 34.1.

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 169.8, 148.7, 142.1, 129.0, 121.2, 83.3, 29.5, 24.9, 21.2, 13.2 (br, *C-B*).

GC-MS: m/z 275 $(M\text{-}CH_3)^+$

4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (31b)



Following general procedure B, colourless oil in 95% (234 mg, 0.95 mmol) yield from ethynylcyclohexene (**31a**, 118 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data. [13]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29 (dd, *J* = 10, 5 Hz, 2H), 7.23 – 7.16 (m, 3H), 2.65 (t, *J* = 8 Hz, 2H), 1.78 (pentet, *J* = 8 Hz, 2H), 1.28 (s, 12H), 0.87 (t, *J* = 8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.8, 128.6, 128.2, 125.6, 83.0, 38.7, 26.2, 24.9, 11.1 (br, *C*-*B*).

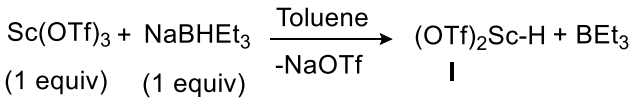
^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) 34.1.

GC-MS: m/z 231 $(M\text{-}CH_3)^+$

IV. Mechanistic Investigation

To gain insight for the proposed catalytic cycle a series of stoichiometric reactions have been performed. The reactions were monitored by ^{1}H and ^{11}B NMR spectroscopy.

Control Experiments:



Experimental Procedure: In a NMR tube equimolar amount of $Sc(OTf)_3$ (9 mg, 0.02 mmol) and $NaBHEt_3$ (1 M in THF, 20 µL, 0.02 mmol) was taken and 0.4 mL of benzene-d_6 was added. Immediately ^{1}H and ^{11}B NMR of resulting mixture has been recorded. As seen from Figure S1 the ^{11}B resonance of boron in $NaBHEt_3$ shifts from -11.71 ppm to 86.73 which has been assigned to BEt_3.[4] The ^{1}H NMR spectrum of the reaction mixture did not show the Sc-H resonance at room temperature, however when it was cooled to 213 K (-60 ˚C) a broad peak at δ = 6.55 ppm was observed may corresponds to Sc-H (Figure S2).[18]

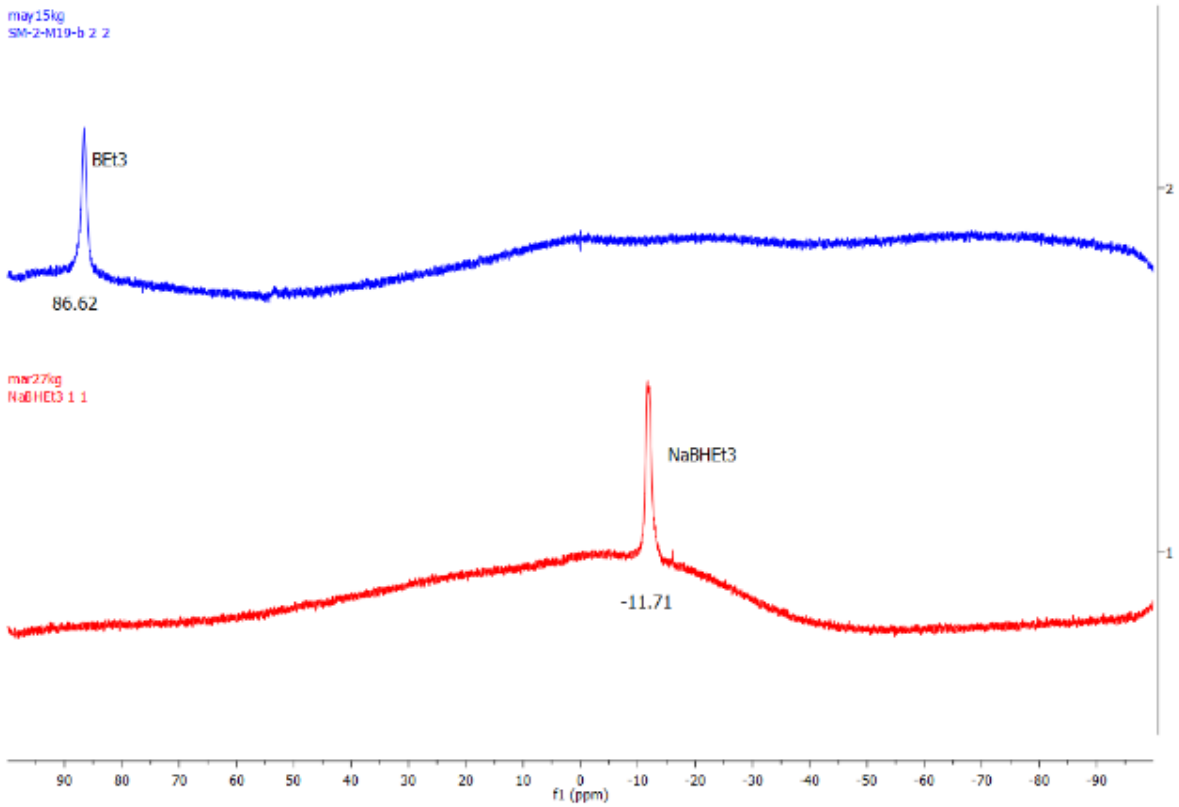


Figure S1: ^{11}B NMR spectra of: 1) $NaBHEt_3$, 2) Crude reaction mixture of $Sc(OTf)_3$ and $NaBHEt_3$ (1:1) at RT.

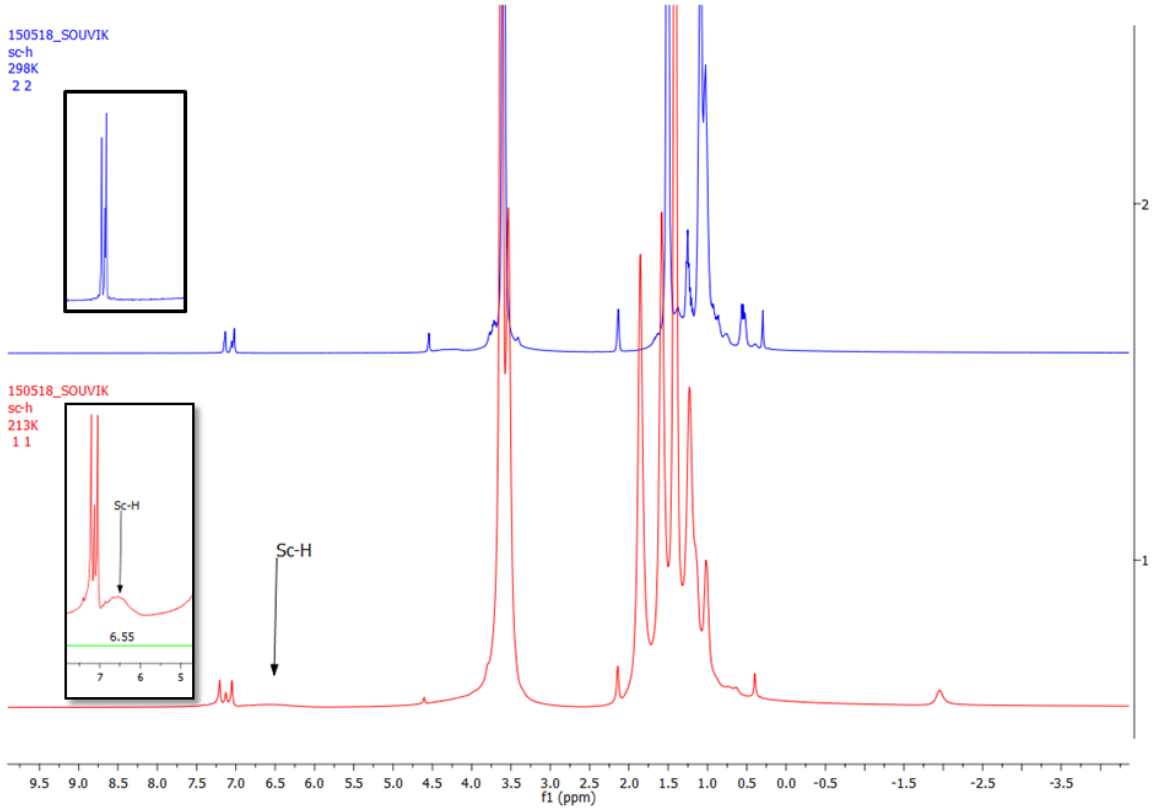
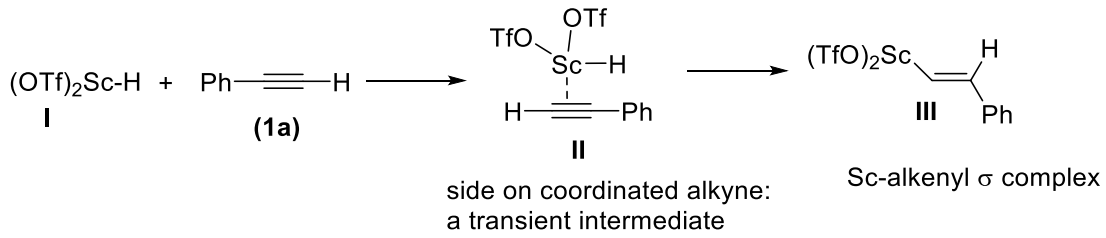


Figure S2: Stacked ^{1}H NMR spectra of crude reaction mixture of $Sc(OTf)_3$ and $NaBHEt_3$ (1:1), recorded at: 1) 213 K (-60 ºC); 2) 298 K.

Subsequent addition of phenyl acetylene (**1a**, 2.2 µL, 0.02 mmol) to the above reaction mixture showed an upfield shift for acetylenic proton of **1a** from 2.99 ppm to 2.73 ppm, which implies the side on coordination of **1a** with scandium centre (Figure S3).



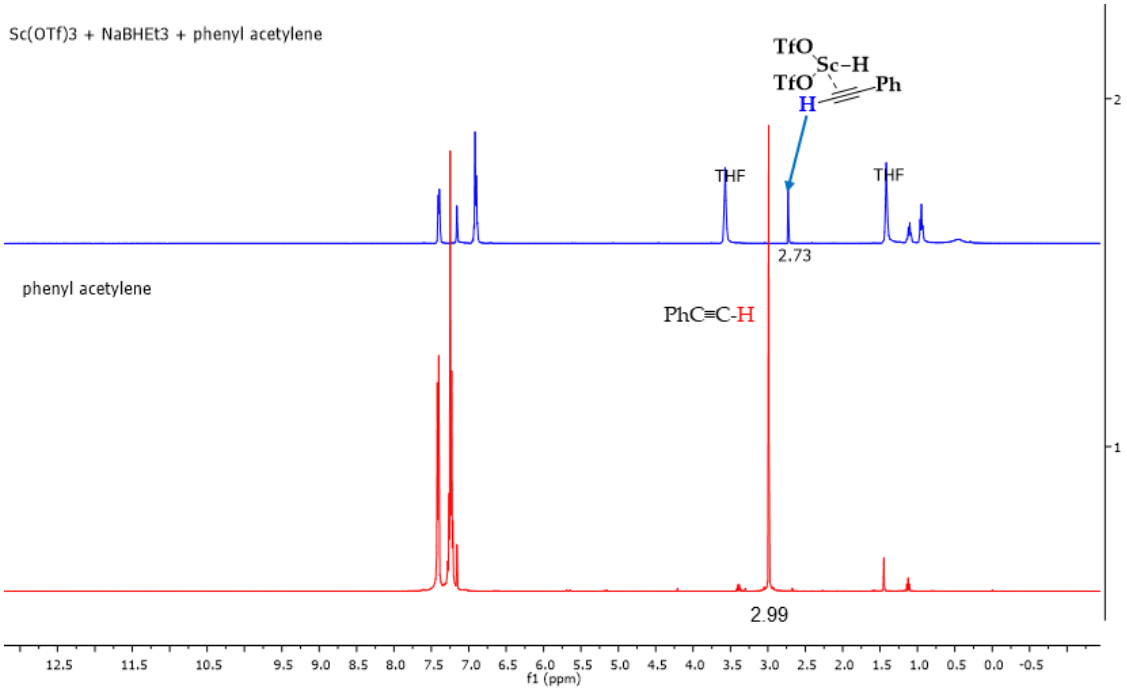


Figure S3: Stacked ^{1}H NMR spectra of: 1) Phenyl acetylene (**1a**), 2) $Sc(OTf)_3$+ $NaBHEt_3$ + phenyl acetylene (1:1:1) (both spectra have been recorded in C_6D_6).

After careful observation of ^{1}H NMR spectrum of "*Sc(OTf)$_3$ + NaBHEt$_3$ + phenyl acetylene*" (Figure S4) reveals two set of distinct doublets at δ = 5.60 and 5.05 ppm, which is growing in intensity upon increasing the time. The transient doublets can be assigned to Sc-alkenyl σ complex which may formed because of hydride migration from scandium centre to alkyne. Further addition of pinacol borane (2.9 µL, 0.02 mmol) to the reaction mixture, intensity of the doublets at 5.6 ppm and 5.05 ppm reduced and product doublet at 7.76 ppm and 6.46 ppm has started to form (see inset of Figure S5).

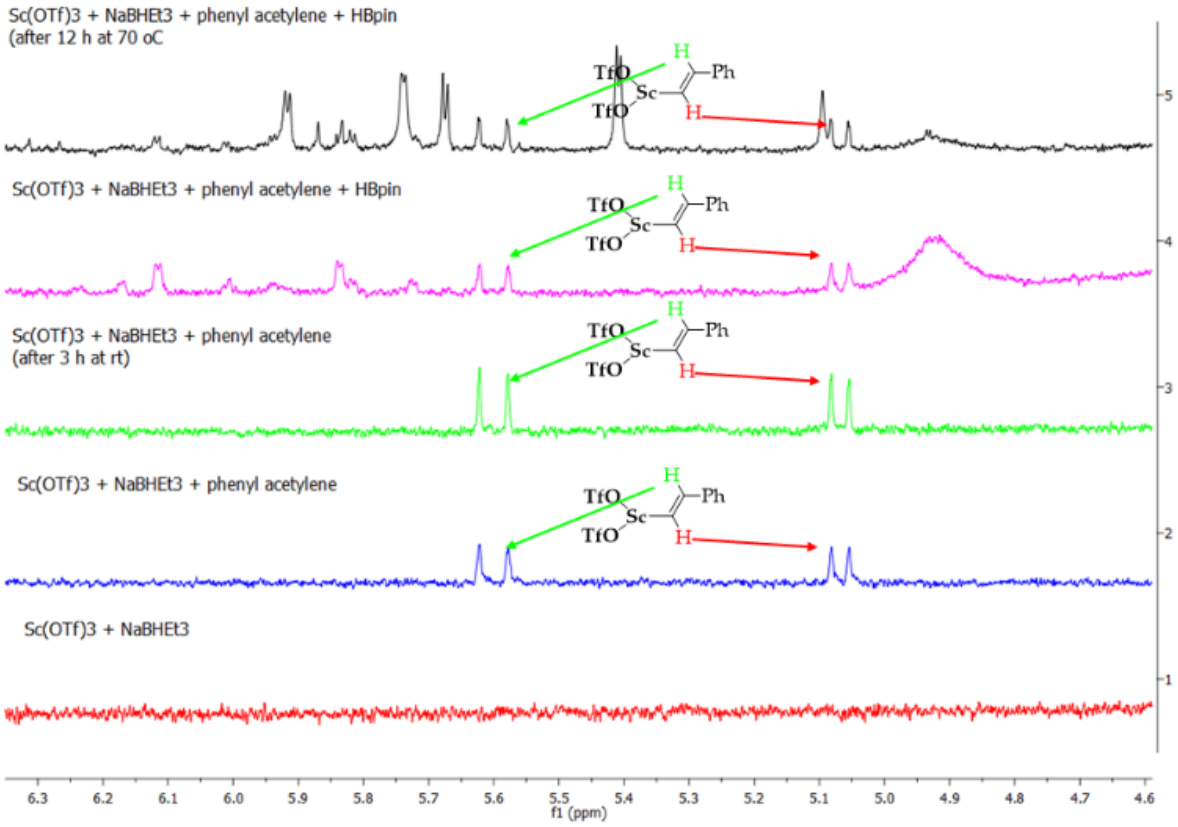


Figure S4: Stacked ^{1}H NMR spectra of sequential addition of reagents (expanded region from 6.3 ppm to 4.6 ppm): 1) $Sc(OTf)_3$ + $NaBHEt_3$, 2) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a**, 3) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** (stirred at RT for 3h), 4) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** + HBpin, 5) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** + HBpin (after 12 h, at 70 ºC).

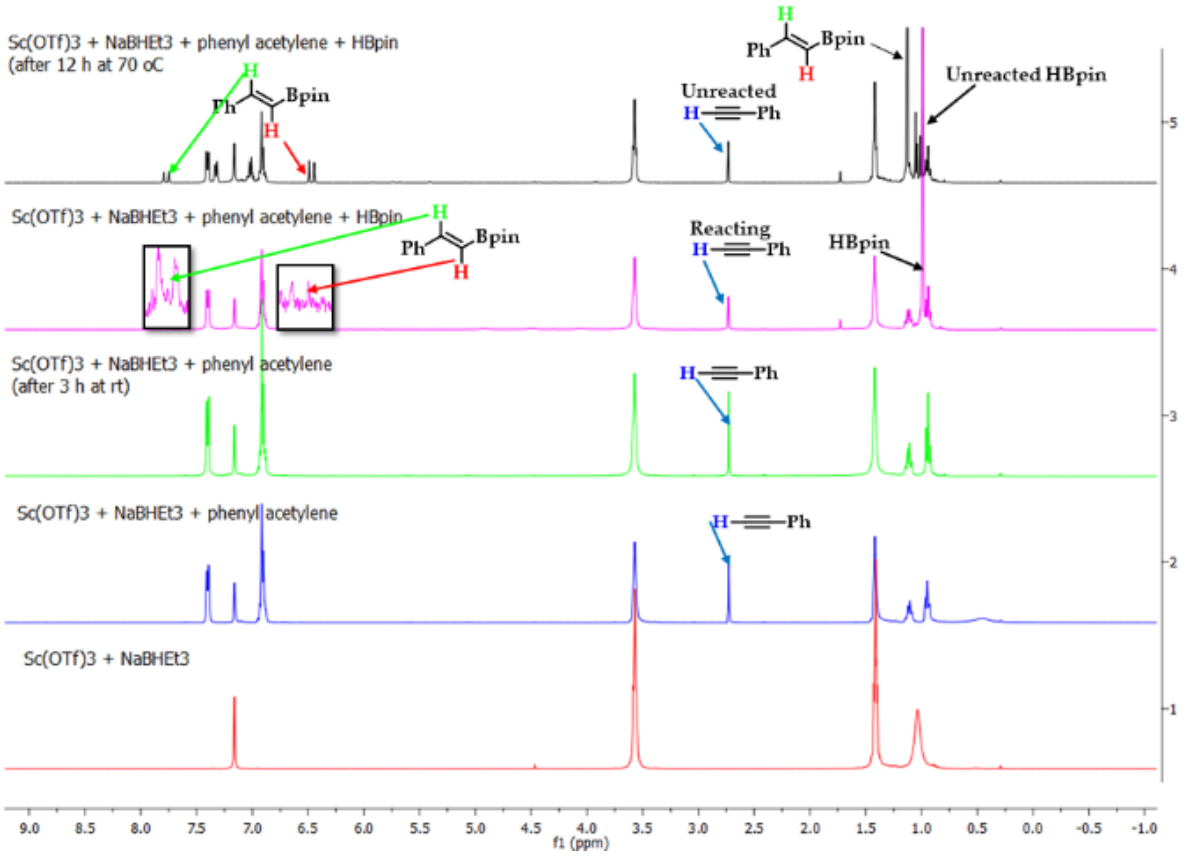
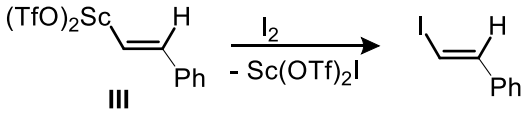


Figure S5: Stacked ^{1}H NMR spectra of sequential addition of reagents: 1) $Sc(OTf)_3$ + $NaBHEt_3$, 2) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a**, 3) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** (stirred at RT for 3h), 4) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** + HBpin, 5) $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** + HBpin (after 12 h, at 70 ºC).

I_2 quenching experiment:

In order to confirm the existence of Sc-alkenyl intermediate, I_2 quenching experiment was carried out. In a NMR tube I_2 solution in C_6D_6 (100 µL, 50.6 mM) was added to the reaction mixture of $Sc(OTf)_3$ + $NaBHEt_3$ + **1a**. The ^{1}H NMR shows the formation of (2-iodovinyl)benzene[19] at δ = 7.4 and 6.4 ppm. GC-MS analysis of the reaction mixture further confirmed the formation of (2-iodovinyl)benzene, m/z = 229 (M^+).

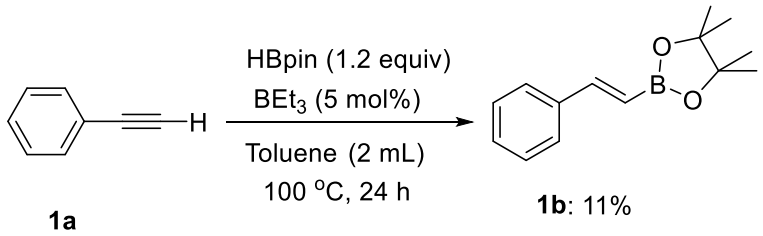


Insights for deprotonation mechanism:

Further, when we performed the reaction of **I** with phenylacetylene (**1a**) in a sealed NMR tube, no H_2 production was observed in the ^1H NMR spectrum, suggesting that reaction may not proceed *via* deprotonation of the alkyne by the Sc-H intermediate, as reported for the catalytic hydroboration of alkynes using a N,N'-bis-2,6-diisopropylphenyl diketiminate (NacNac)-supported aluminum dihydride.[20]

Experimental procedure for catalytic reaction using BEt_3

A microwave vial equipped with a magnetic stirring bar was charged with BEt_3[21] (5 mol %, 3 µL, 0.02 mmol), HBpin (1.2 equiv, 65 µL, 0.48 mmol), phenyl acetylene (**1a**, 1 equiv, 44 µL, 0.4 mmol) and 2 mL of toluene. The reaction mixture was heated at 100 °C for 24 h and then eluted with Et_2O: hexane (3:7) mixture through a plug of celite (Ø 3 mm × 8 mm). The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product (**1b**) yield of 11% was obtained from ^1H NMR using nitromethane as an internal standard.



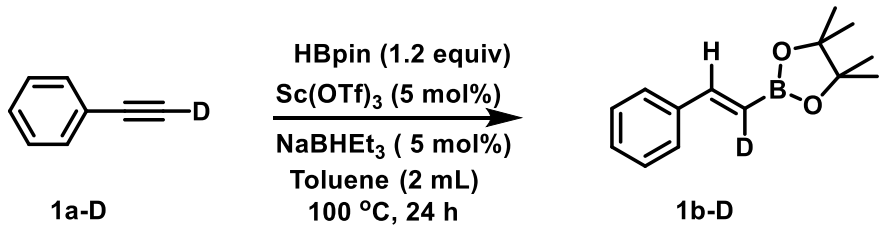
Under the standard conditions, treatment of $Sc(OTf)_3$ with $NaBHEt_3$ and HBpin, in the absence of alkyne, show additional signals in ^{11}B NMR at δ = 57 and 34.6 ppm for Et_2BH, EtBpin alongside Et_3B.

$$\underset{(1\ \text{equiv})}{Sc(OTf)_3} + \underset{(1\ \text{equiv})}{NaHBEt_3} + \underset{(1\ \text{equiv})}{HBpin} \xrightarrow[-NaOTf]{Toluene} \underset{\text{proposed}}{(OTf)_nSc\text{-}H} + BEt_3 + HBEt_2 + HBpin$$

Deuterium labelling Experiments:

Experimental procedure:

Phenyl acetylene-d_1[22] and pinacolborane-d_1[23] (DBpin) was synthesized according to the reported literature and used for the following reaction.



1a-D 1b-D

A microwave vial equipped with a magnetic stirring bar was charged with scandium triflate (5 mol %, 6 mg, 0.0125 mmol), $NaBHEt_3$ (1M in THF, 5 mol %, 12.5 µL, 0.0125 mmol), pinacol borane (1.2 equiv, 44 µL, 0.3 mmol), phenyl acetylene-d_1 (1 equiv, 0.25 mmol) and 2 mL of toluene. The reaction mixture was heated at 100 ^{o}C for 24 hours. The ^{2}H NMR of the crude reaction mixture shows peak at δ = 6.25 ppm (Figure S6), which indicates a *cis* orientation of deuterium and phenyl group in **1b-D**.

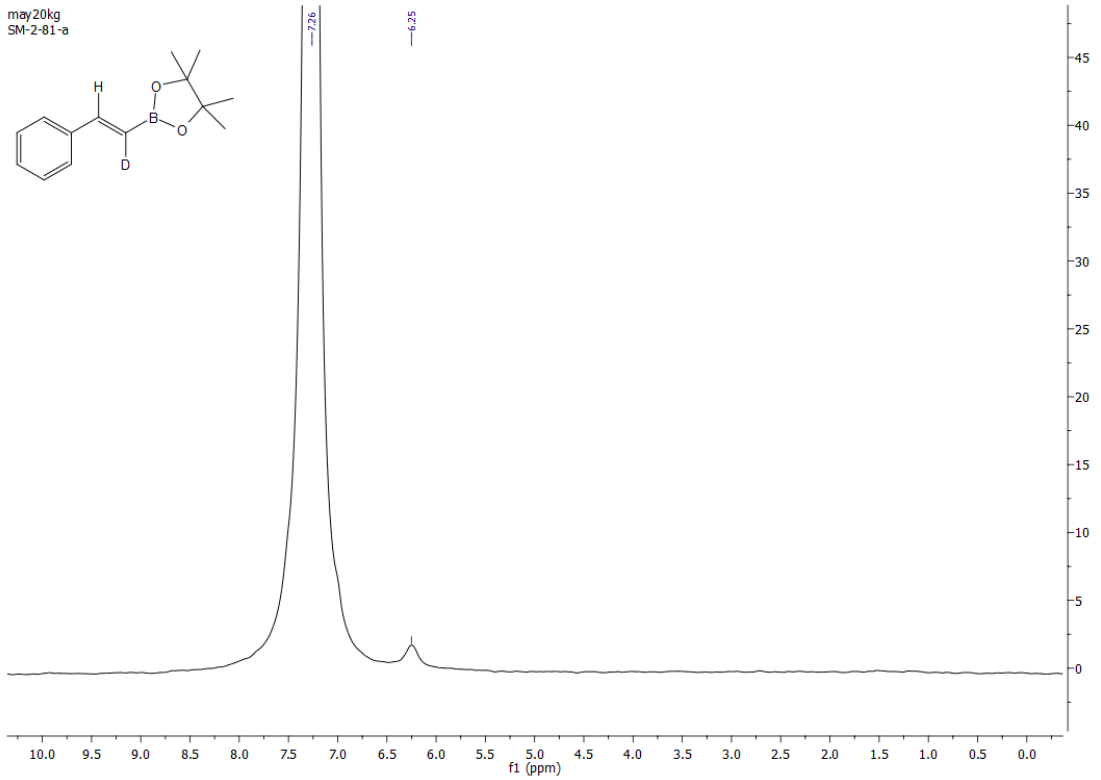
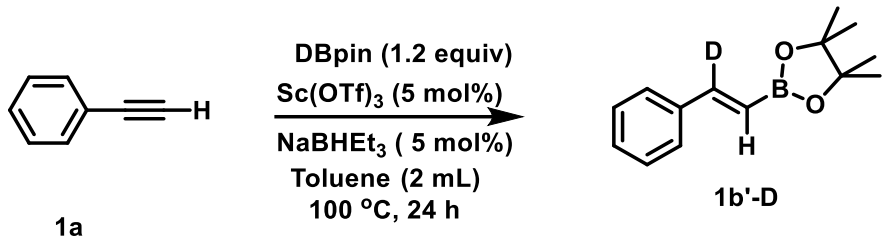


Figure S6: ^{2}H NMR ($CDCl_3$, 62 MHz) spectra of crude reaction mixture of $Sc(OTf)_3$ + $NaBHEt_3$ + **1a-D** + HBpin.



A microwave vial equipped with a magnetic stirring bar was charged with $Sc(OTf)_3$ (5 mol %, 6 mg, 0.0125 mmol), $NaBHEt_3$ (1M in THF, 5 mol%, 12 µL, 0.0125 mmol), pinacol borane-d_1 (1.2 equiv, 0.3 mmol), **1a** (1 equiv, 27 µL, 0.25 mmol) and 2 mL of toluene. The reaction mixture was heated at 100 °C for 24 h. The ^2H NMR of the crude reaction mixture shows peak at δ = 7.32 ppm (Figure S7), which indicates a *cis* orientation of deuterium and Bpin unit in **1b'-D**.

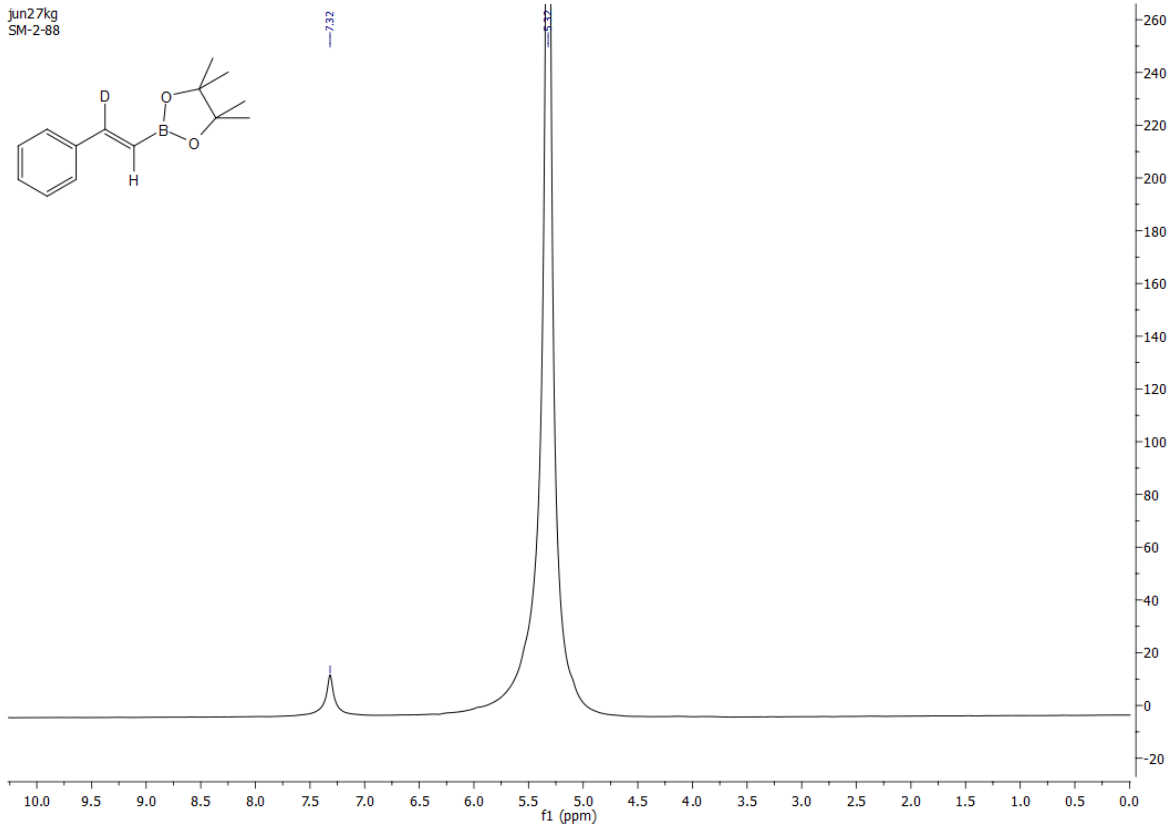


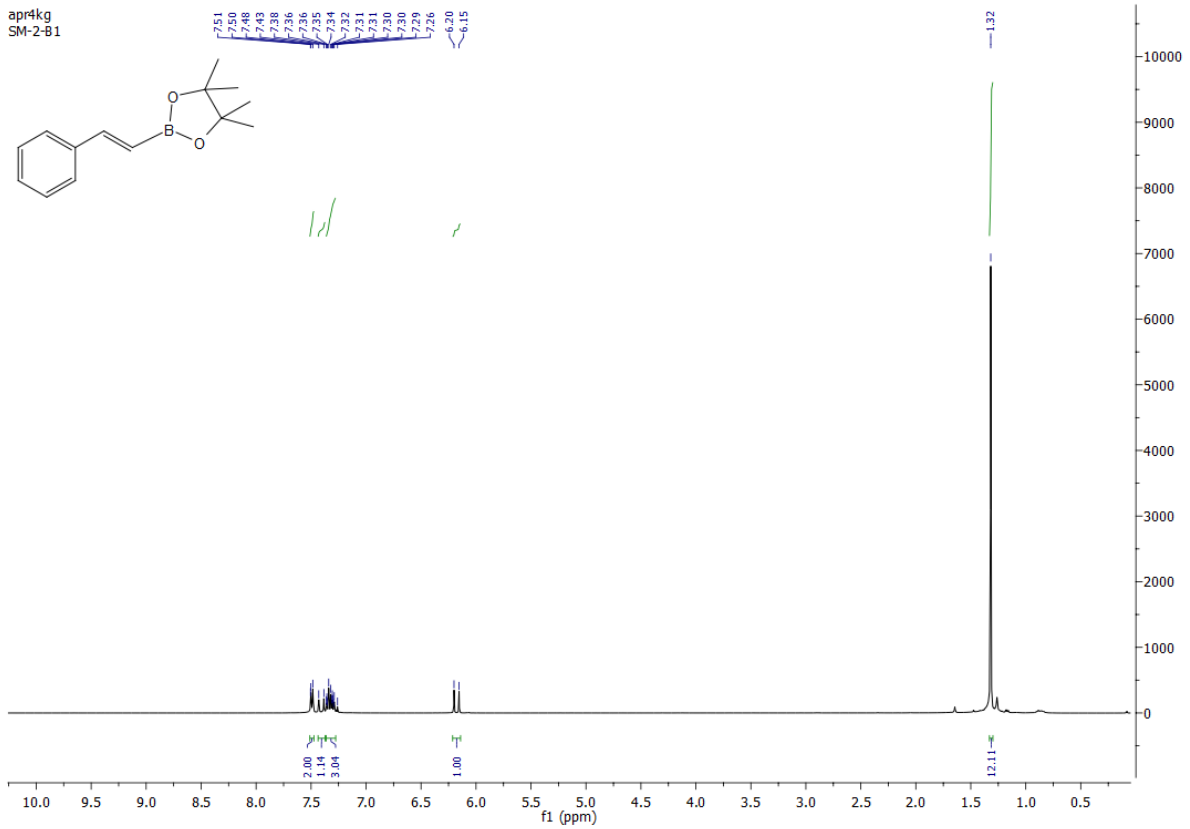
Figure S7: ^2H NMR (CD_2Cl_2, 62 MHz) spectra of crude reaction mixture of $Sc(OTf)_3$ + $NaBHEt_3$ + **1a** + DBpin.

V. NMR Spectra

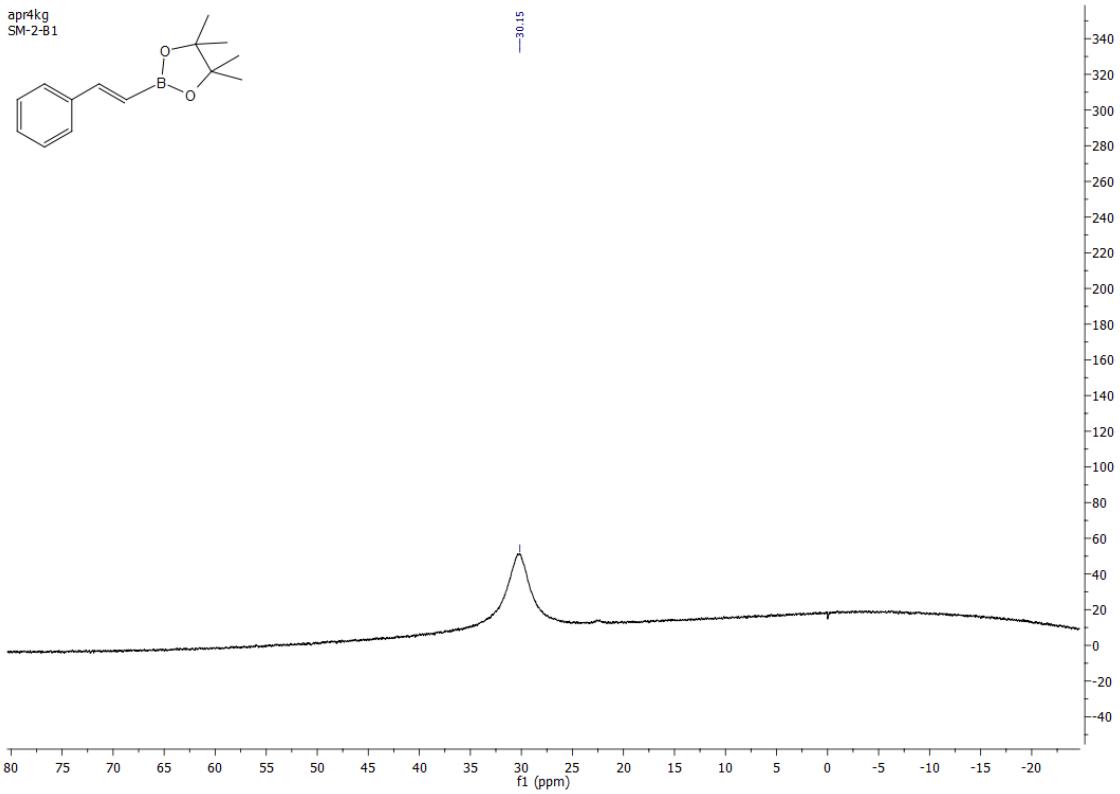
The ^{1}H, ^{11}B, ^{13}C and ^{19}F spectra of the isolated compounds were given below. The impurities in the spectra have been marked using (#), Characteristics peak for isomers has been assigned using asterisk (*). In ^{1}H NMR spectra (for yield calculation), the internal standard nitromethane peak (δ = 4.32 ppm) has been denoted with (■).

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (1b)

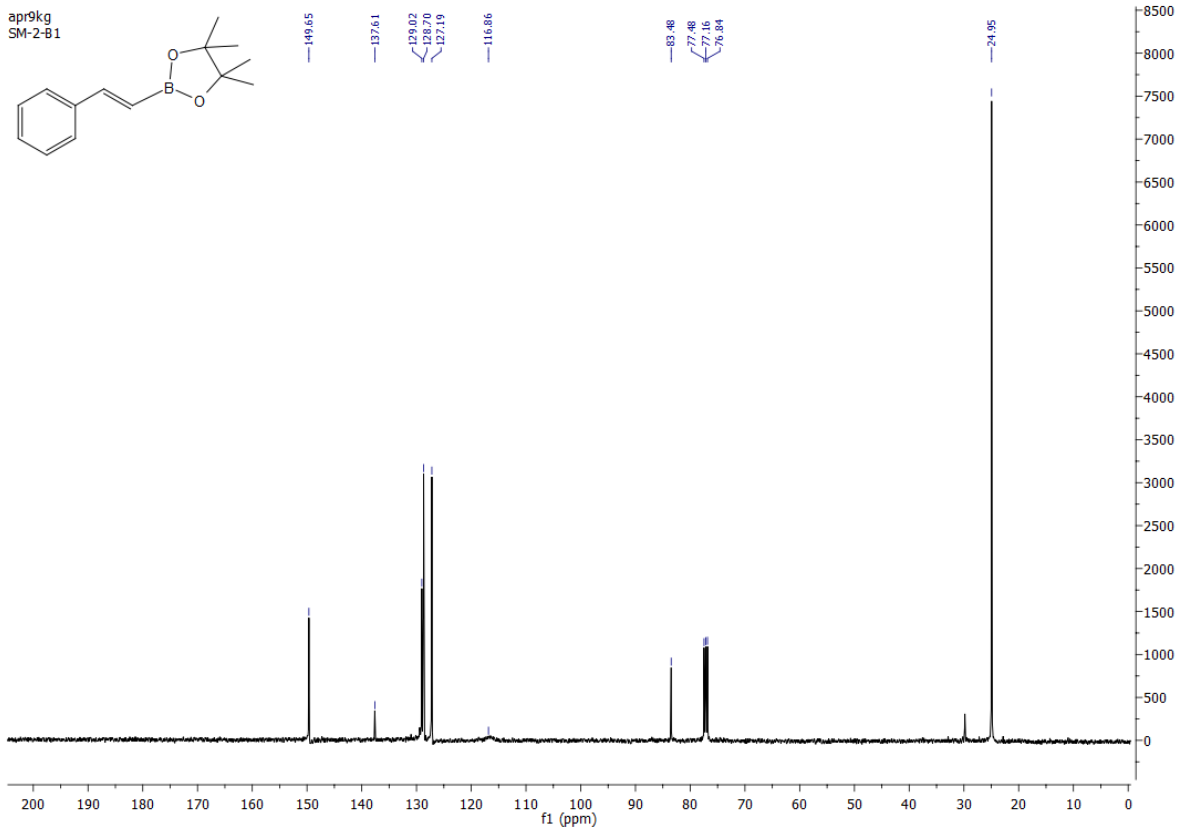
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

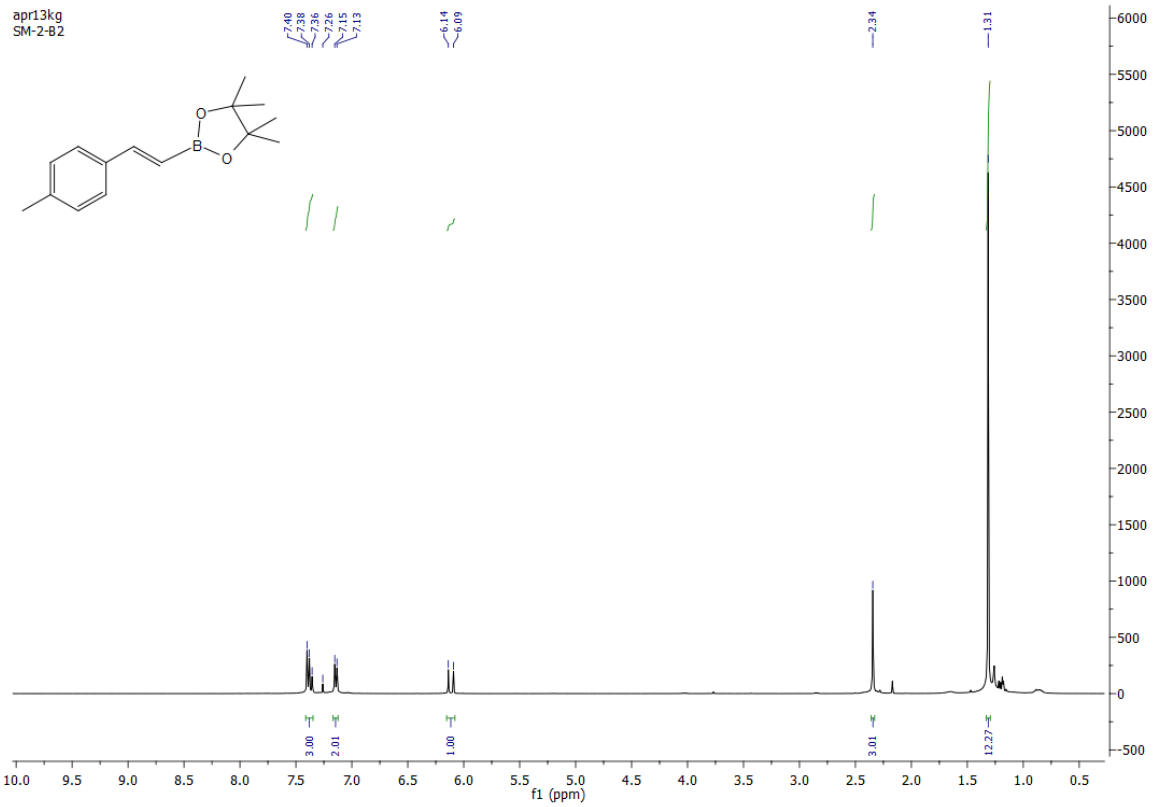


^{13}C NMR, $CDCl_3$, 100 MHz:

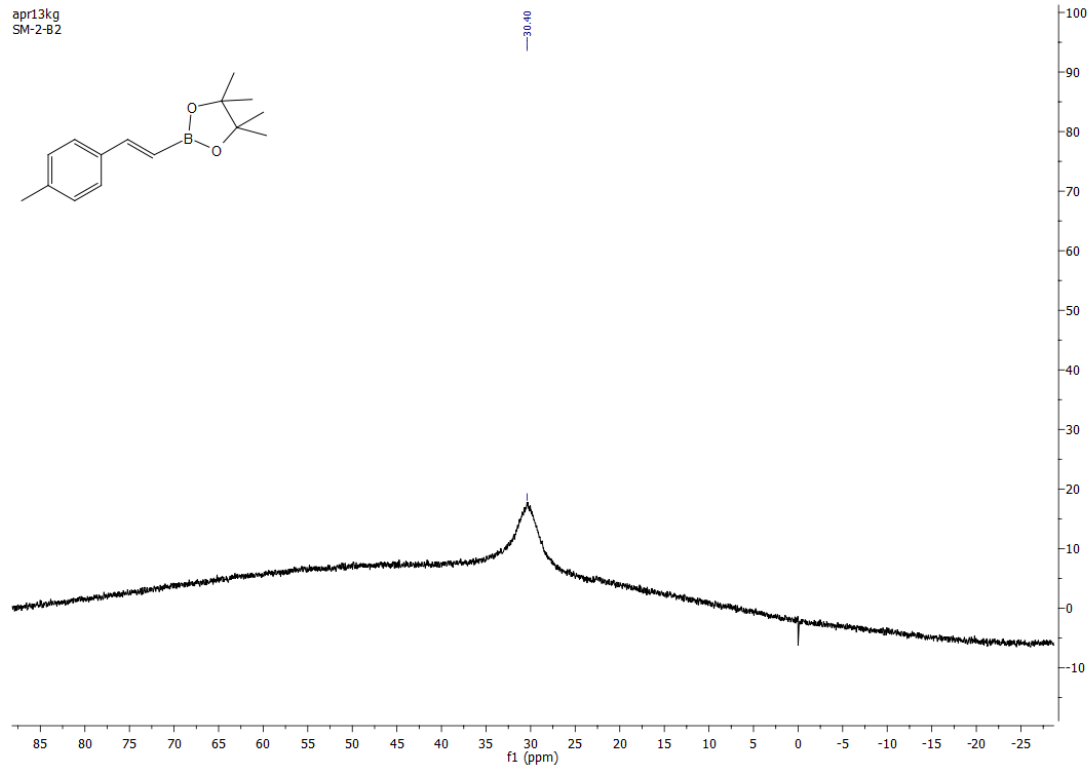


(*E*)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)

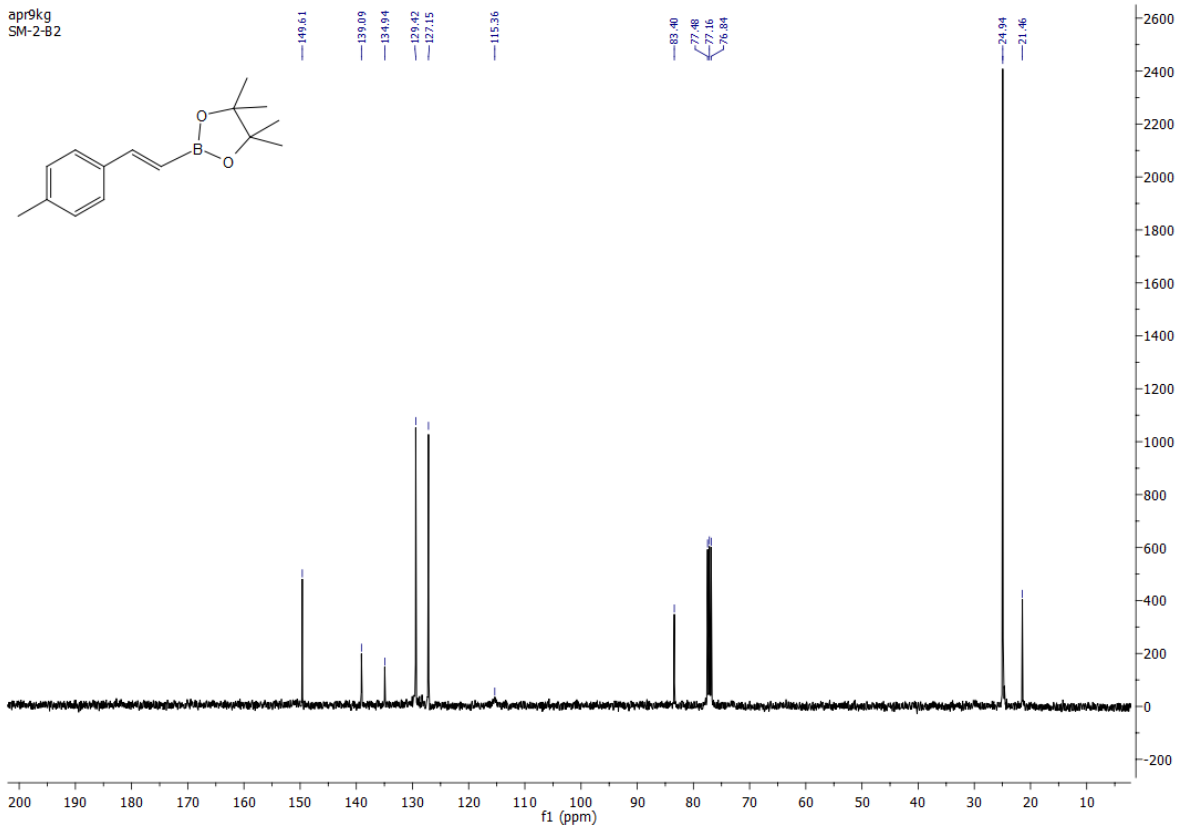
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

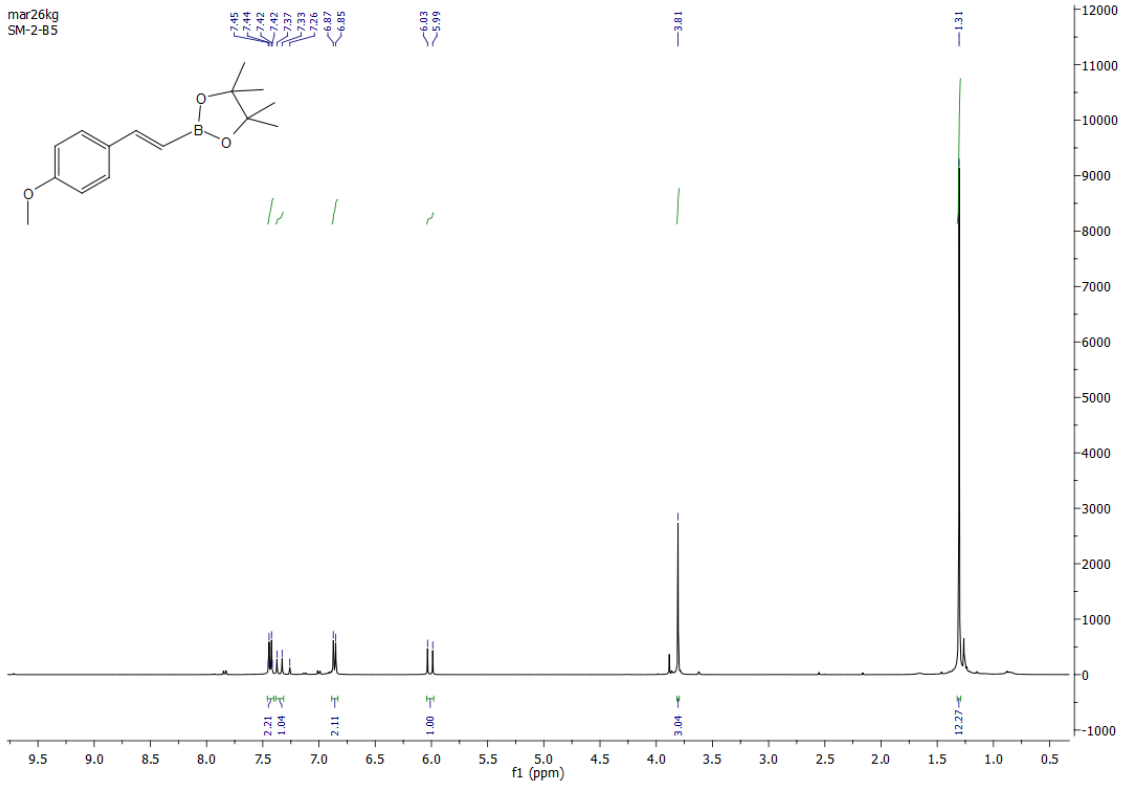


^{13}C NMR, $CDCl_3$, 100 MHz:

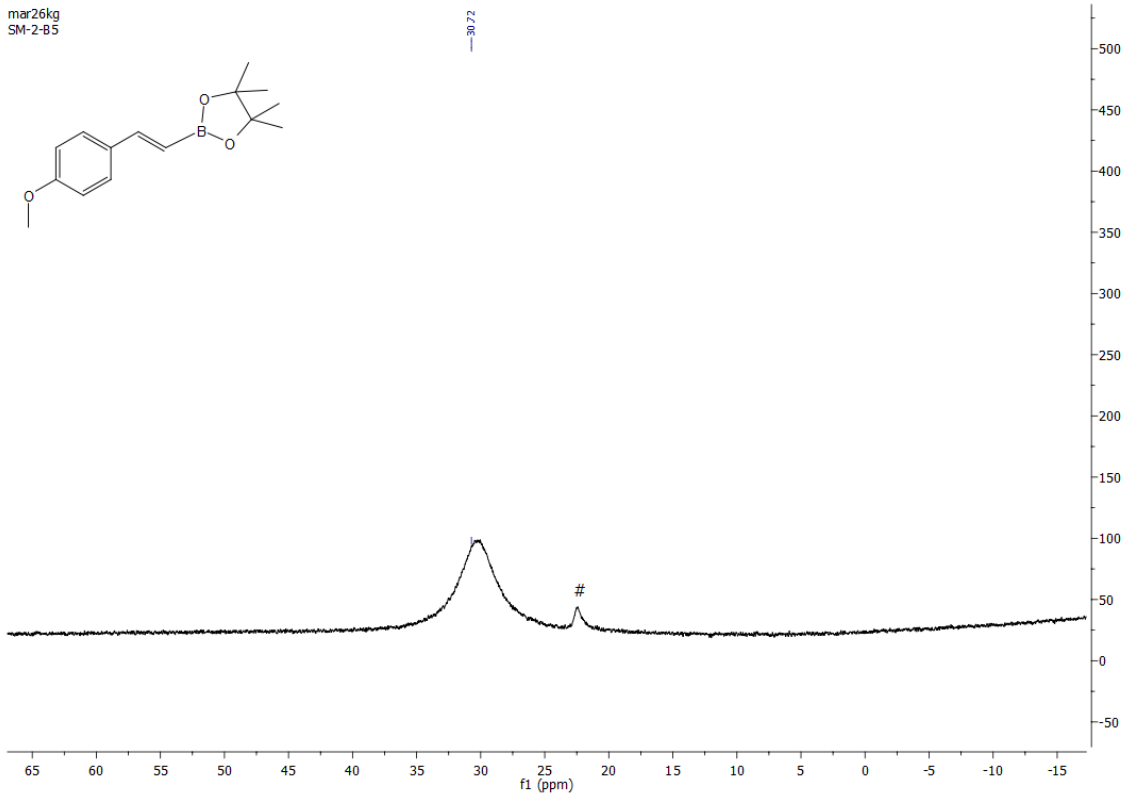


(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

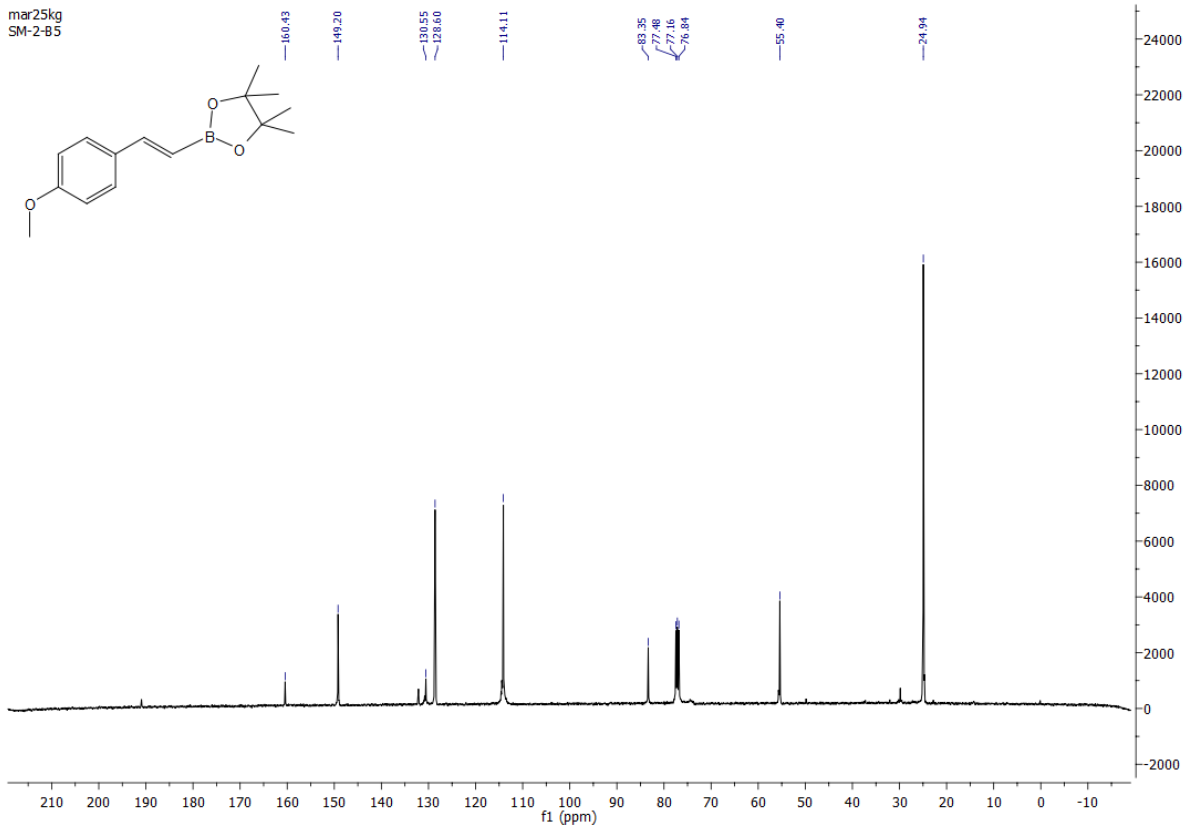
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

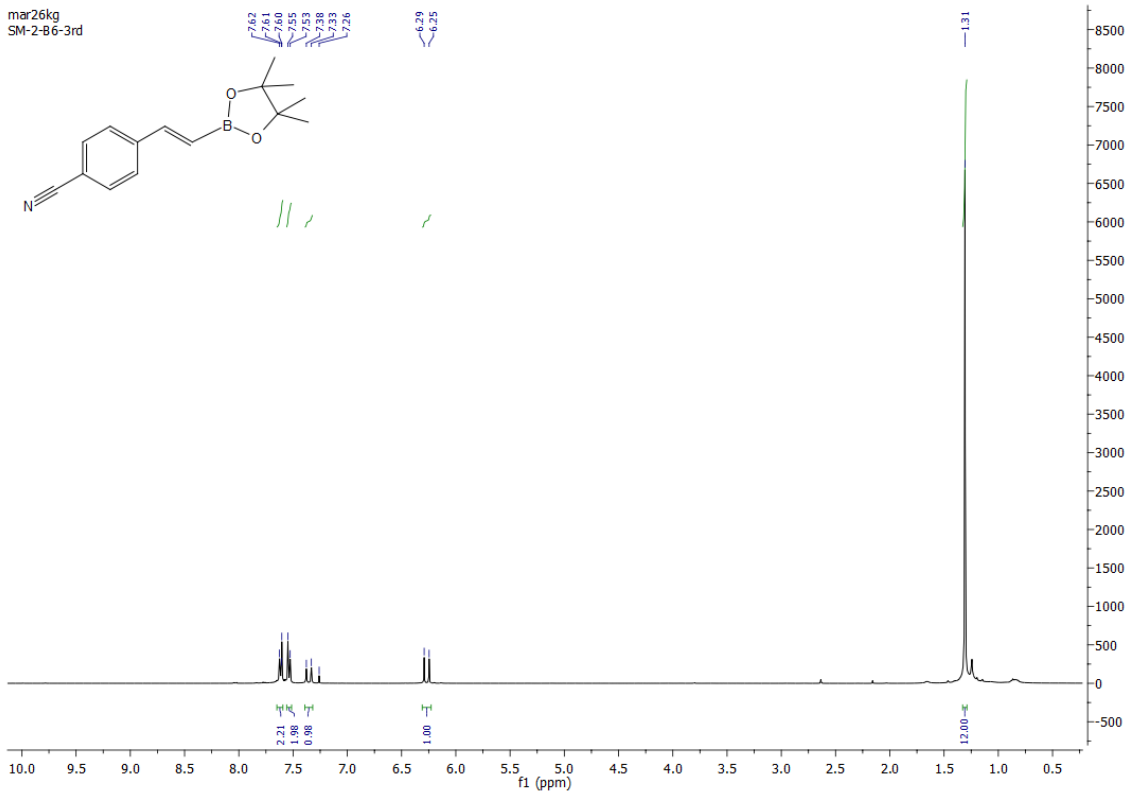


^{13}C NMR, $CDCl_3$, 100 MHz:

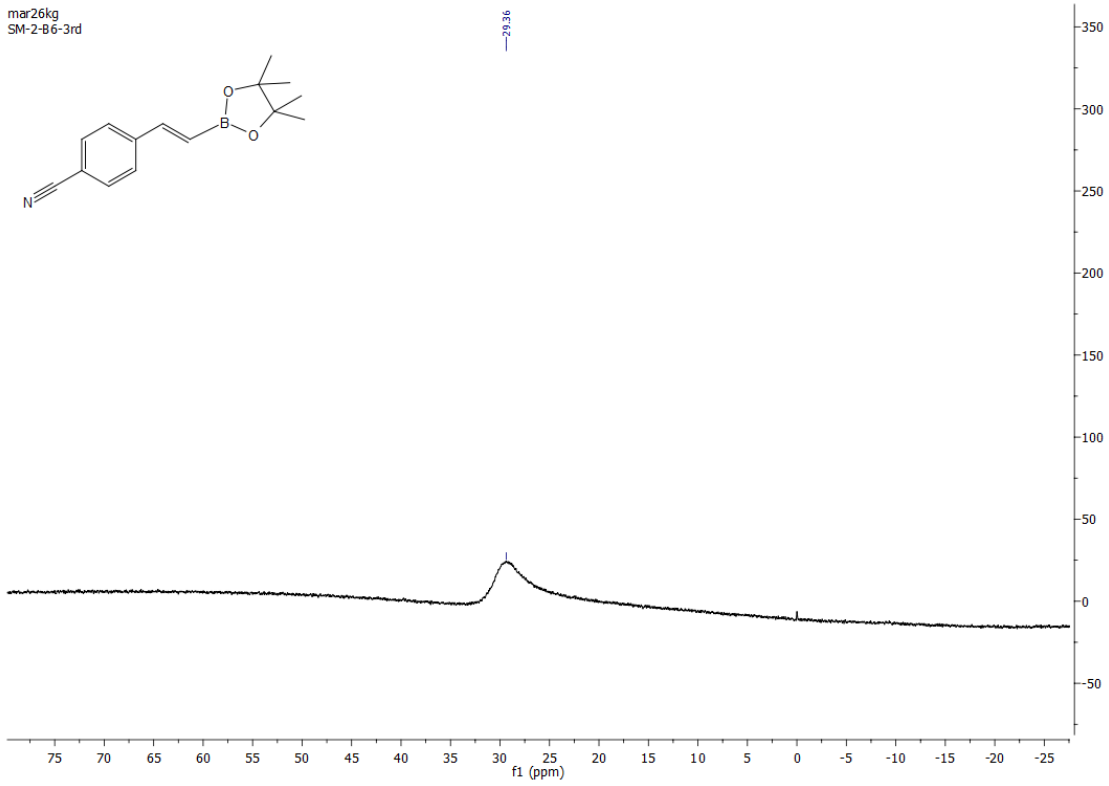


(*E*)-4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (4b)

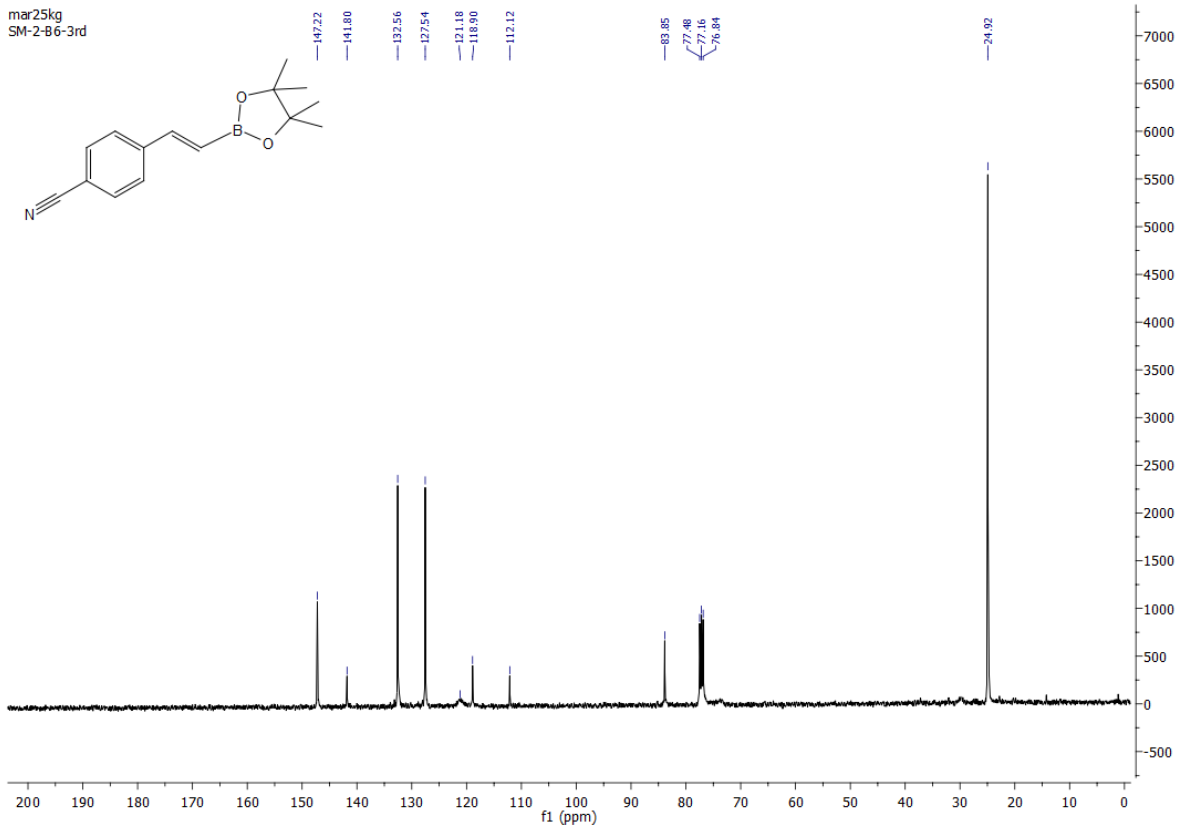
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

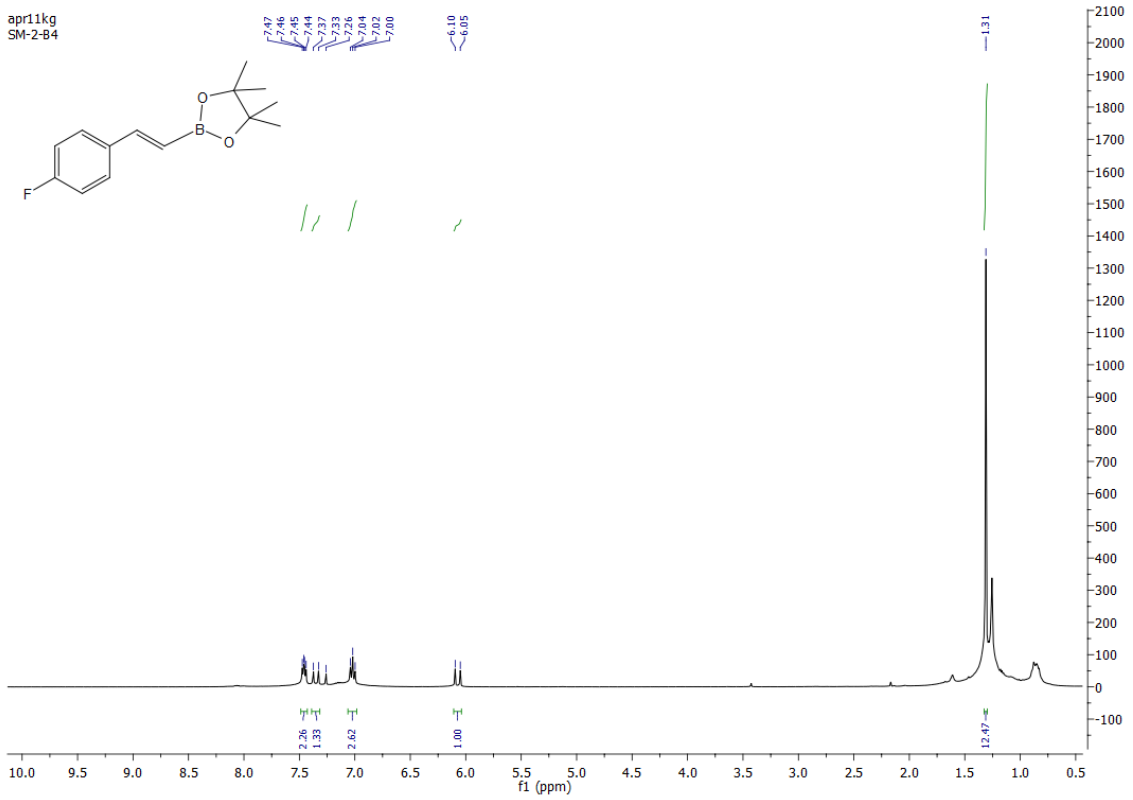


^{13}C NMR, $CDCl_3$, 100 MHz:

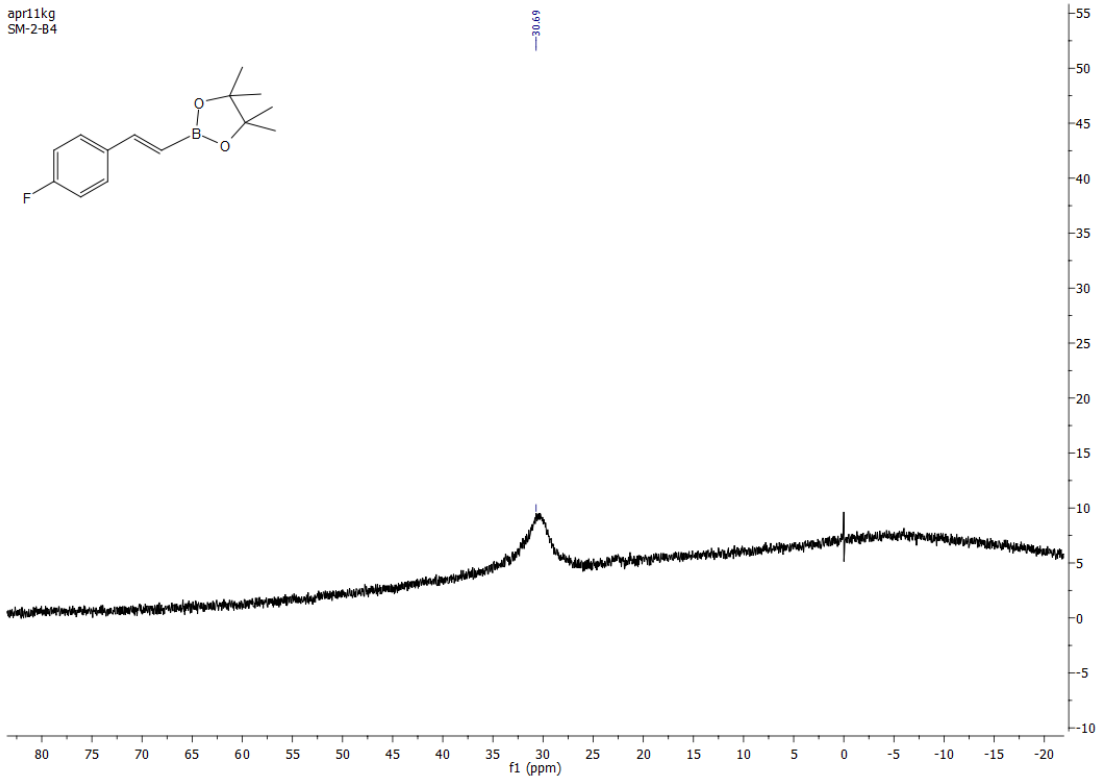


(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

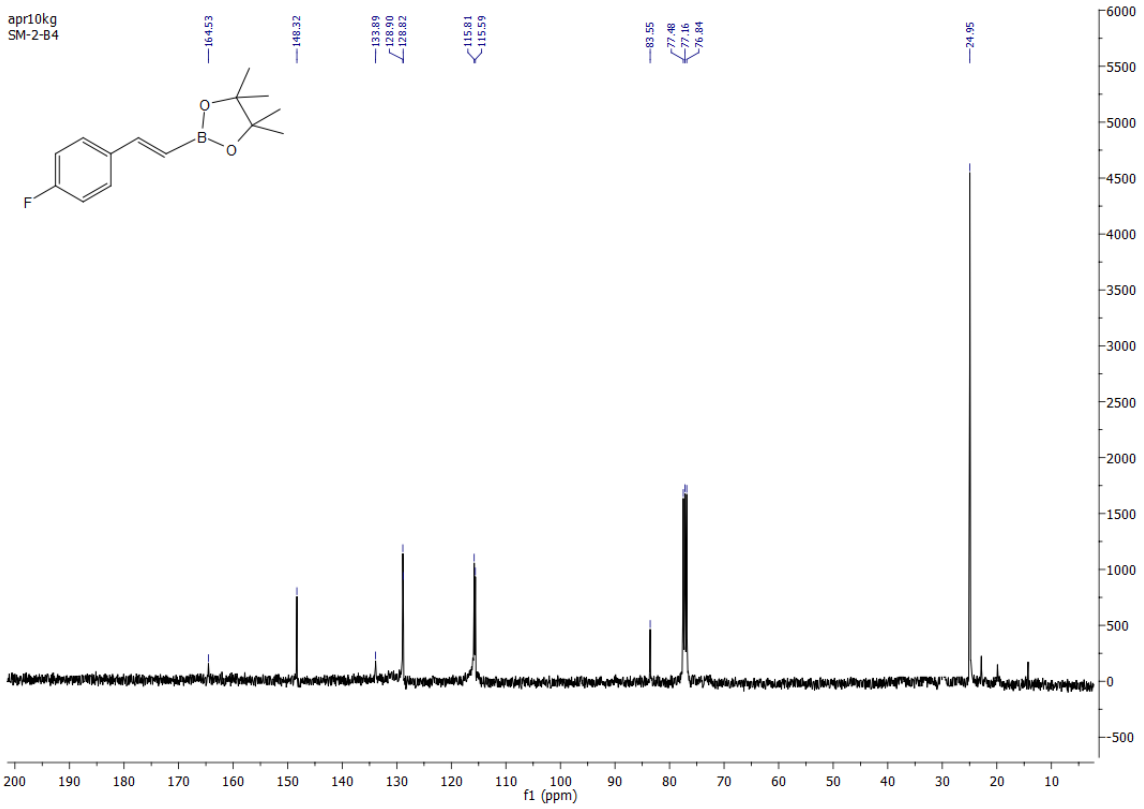
^{1}H NMR, $CDCl_3$ 400 MHz:



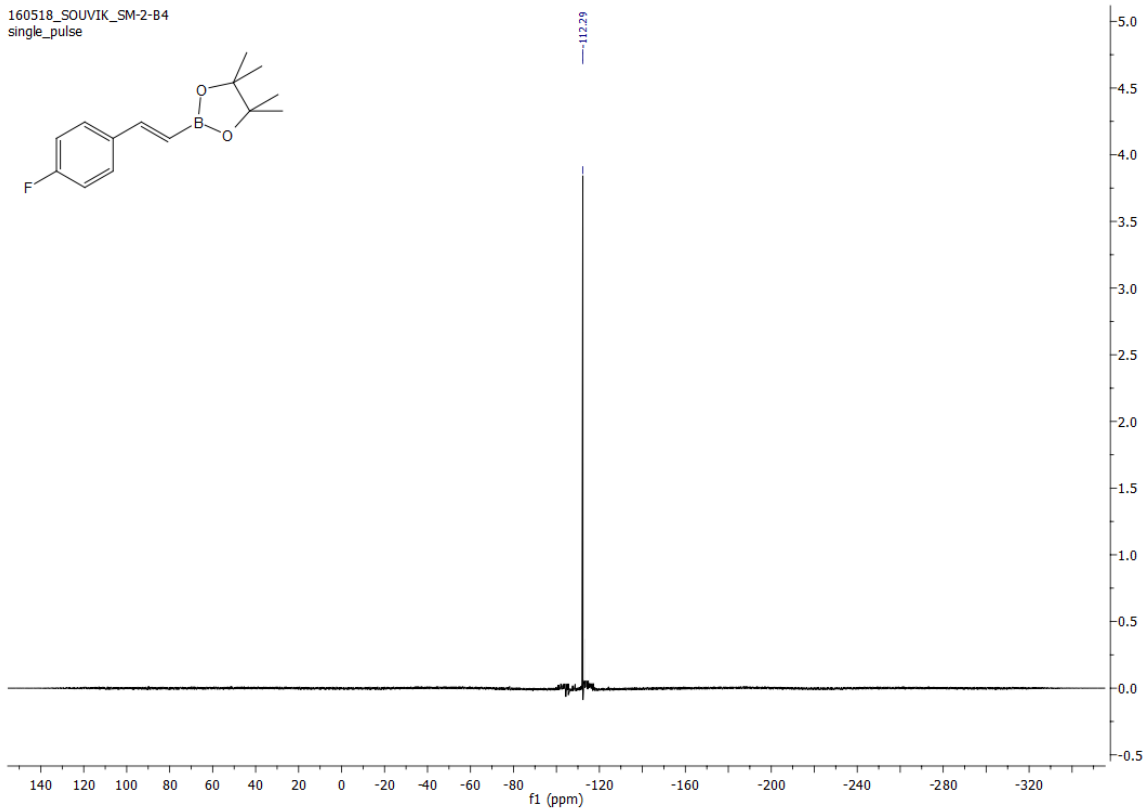
^{11}B NMR, $CDCl_3$, 128 MHz:



^{13}C NMR, $CDCl_3$, 100 MHz:

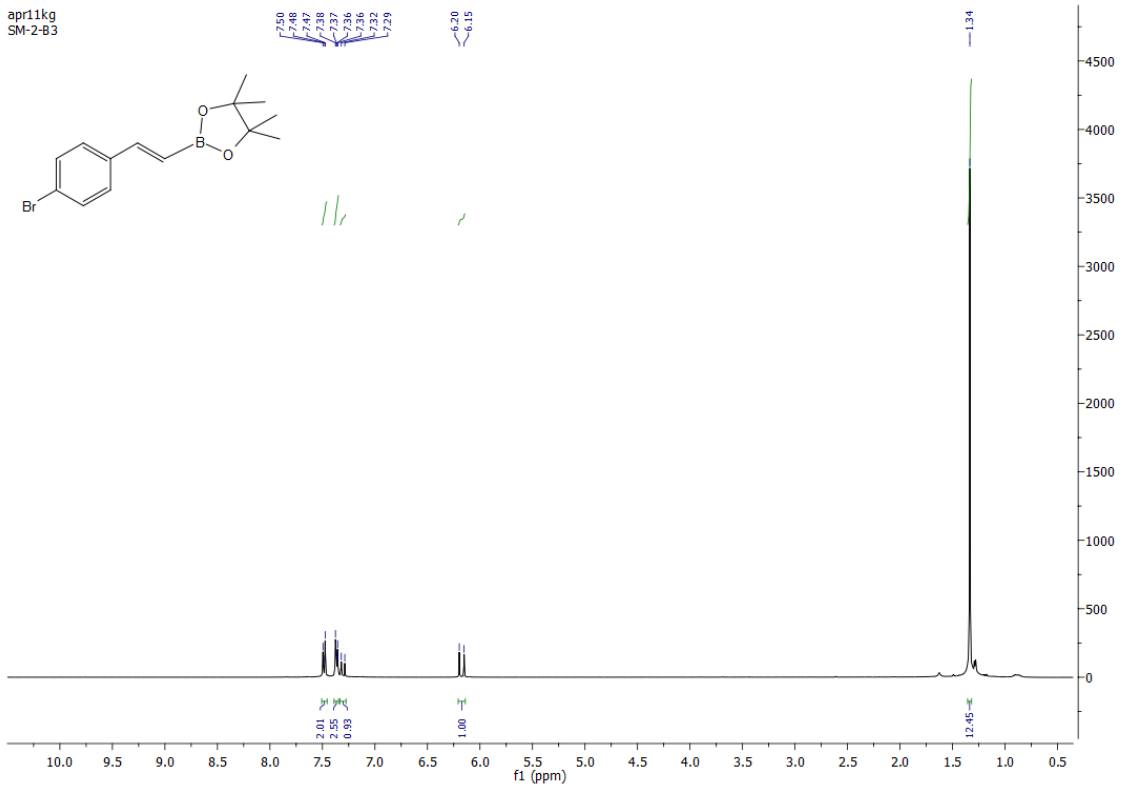


^{19}F NMR, $CDCl_3$, 470 MHz:

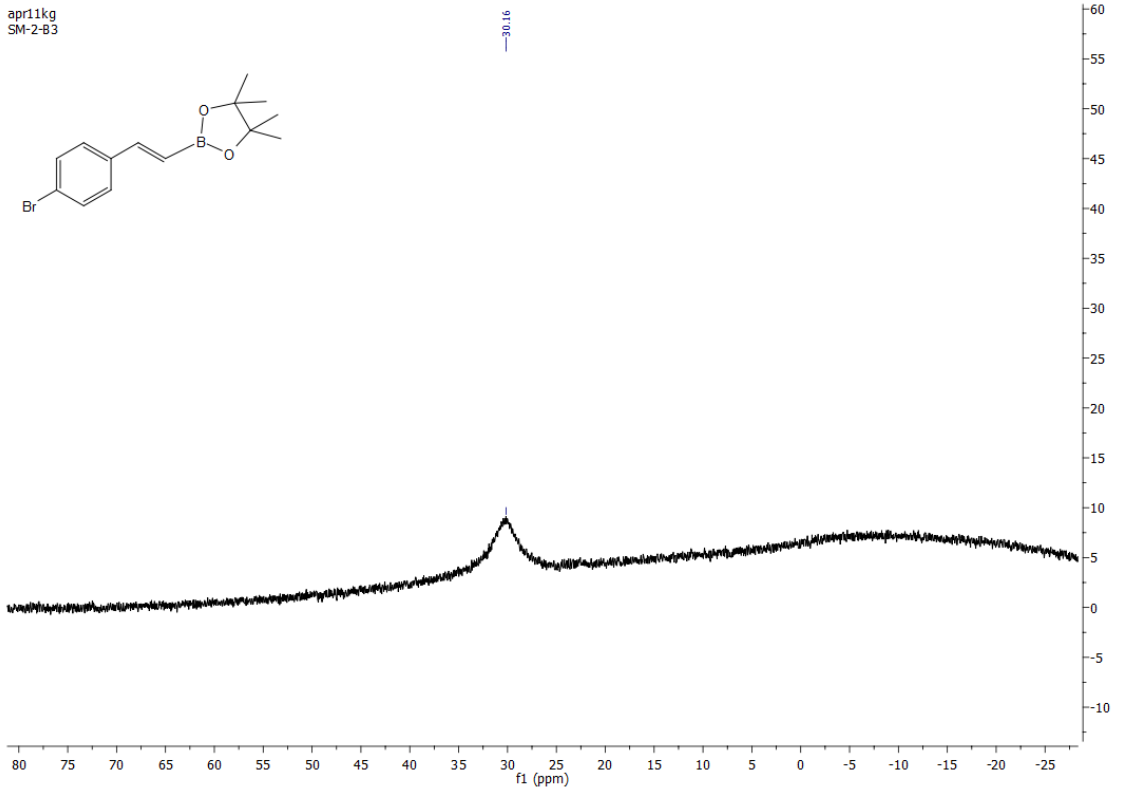


(*E*)-2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6b)

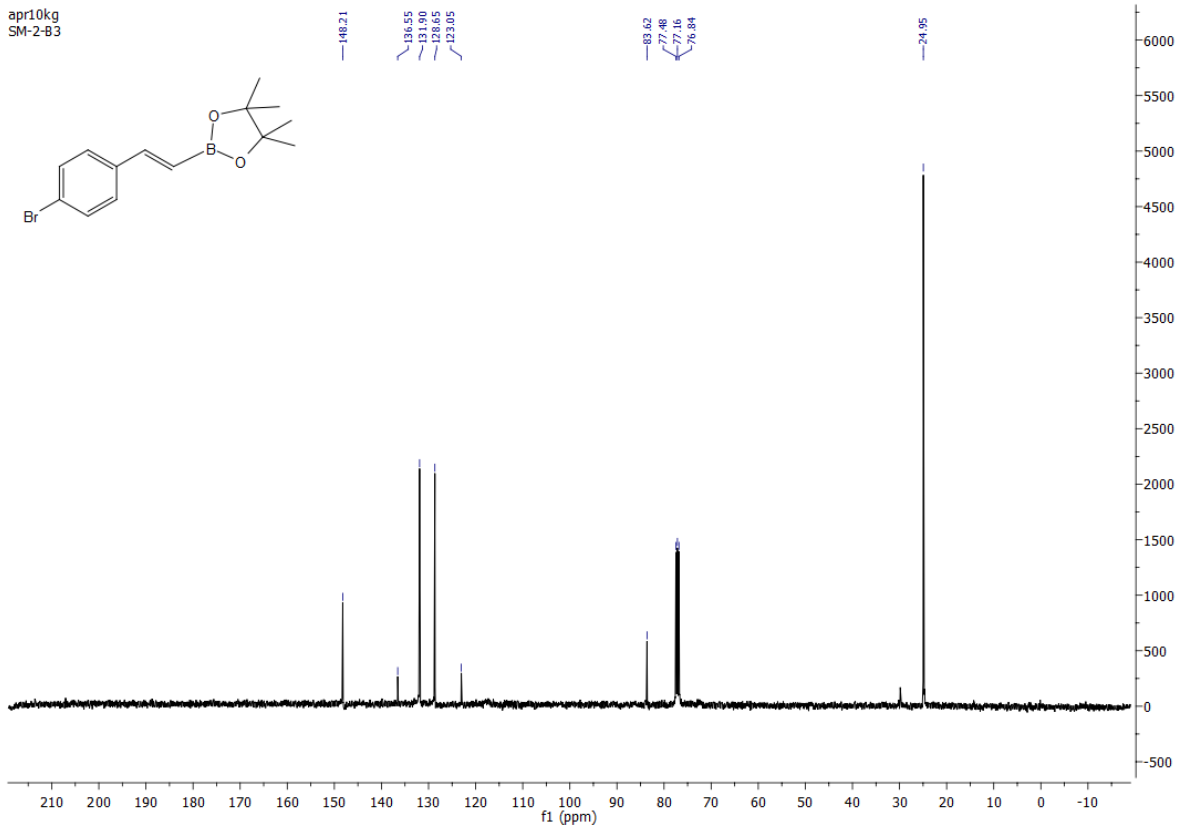
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

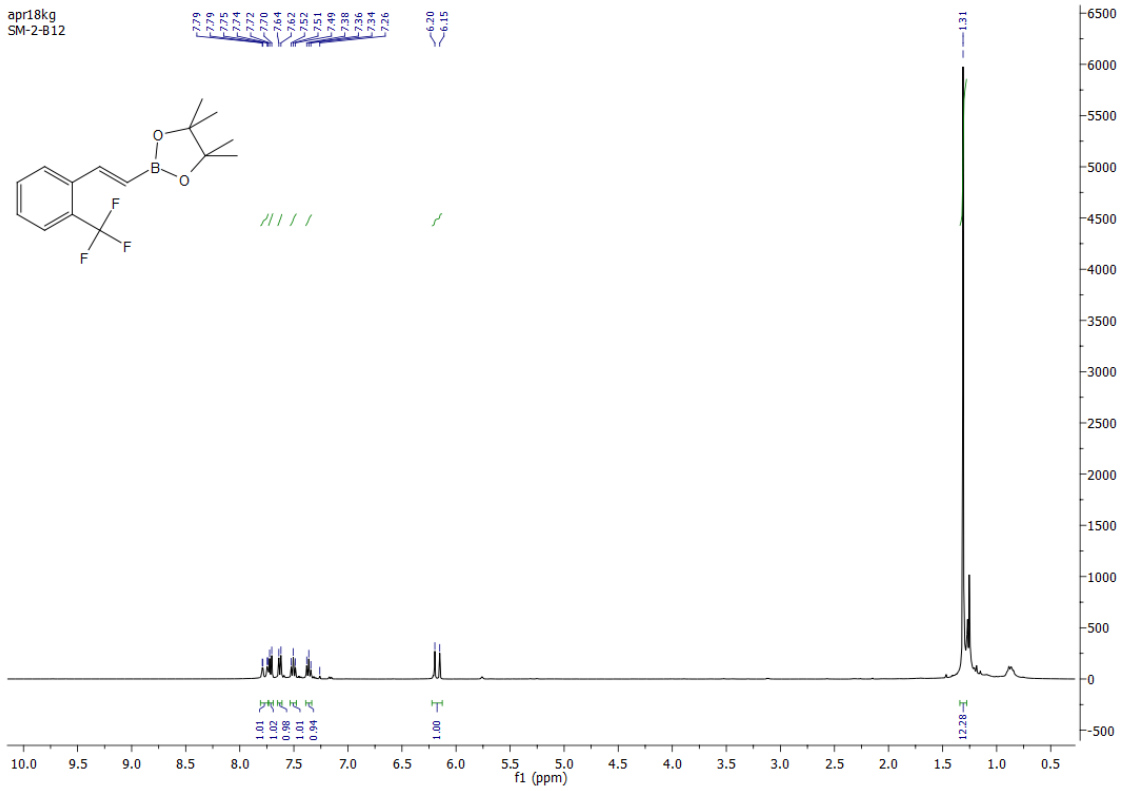


^{13}C NMR, $CDCl_3$, 100 MHz:

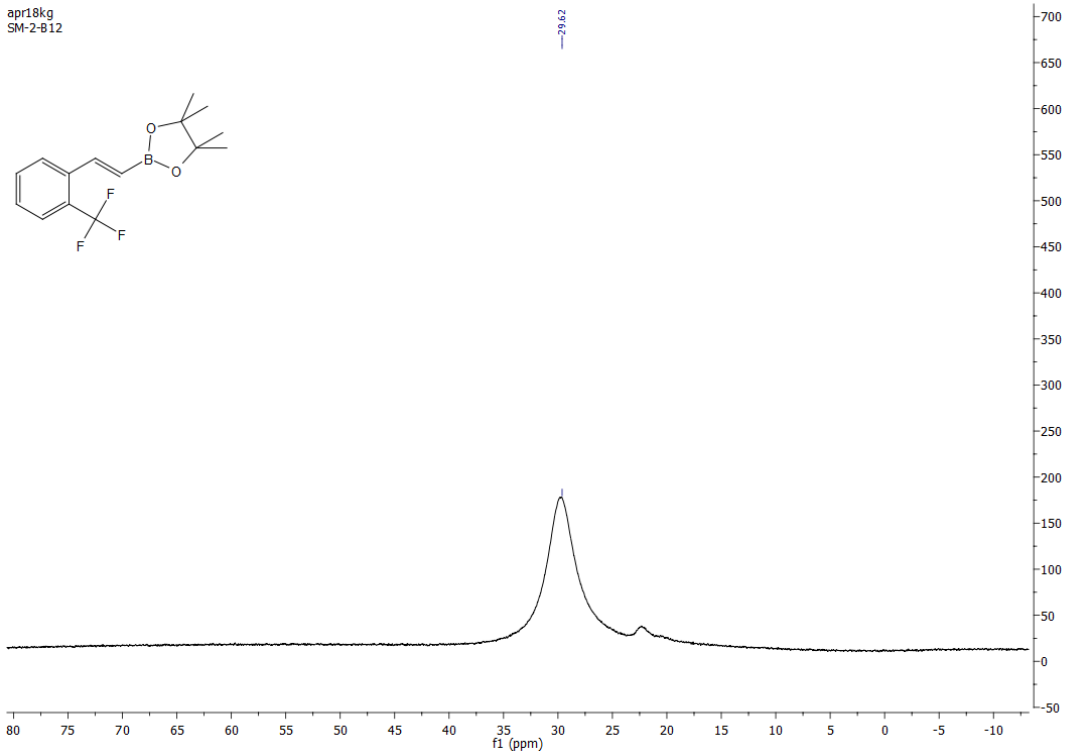


(*E*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (7b)

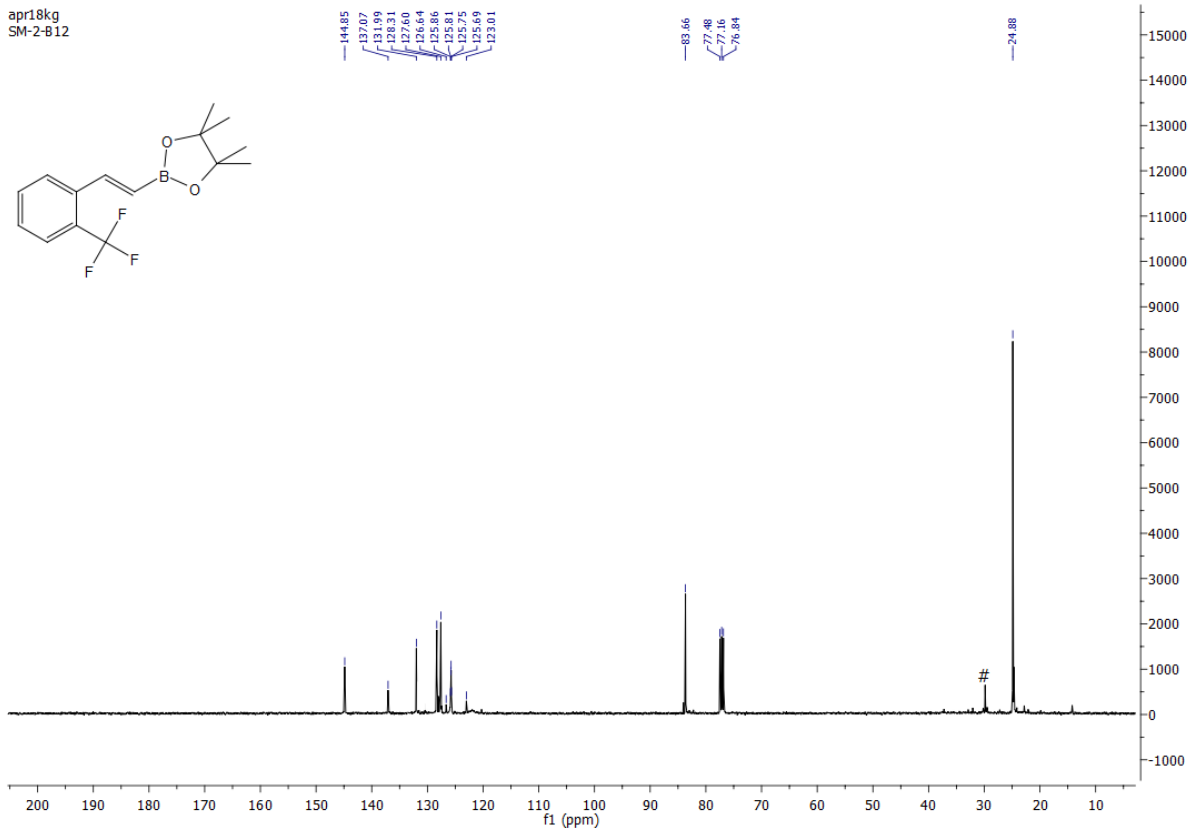
^{1}H NMR, $CDCl_3$ 400 MHz:



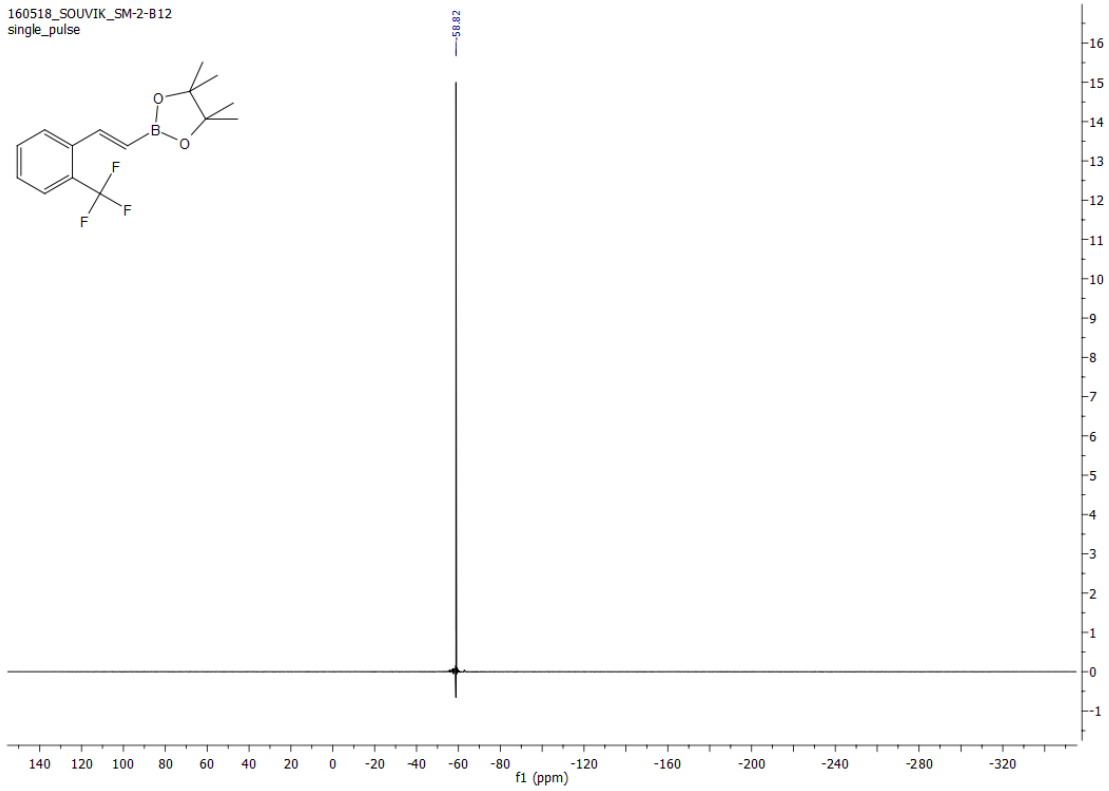
^{11}B NMR, $CDCl_3$, 128 MHz:



^{13}C NMR, $CDCl_3$, 100 MHz:

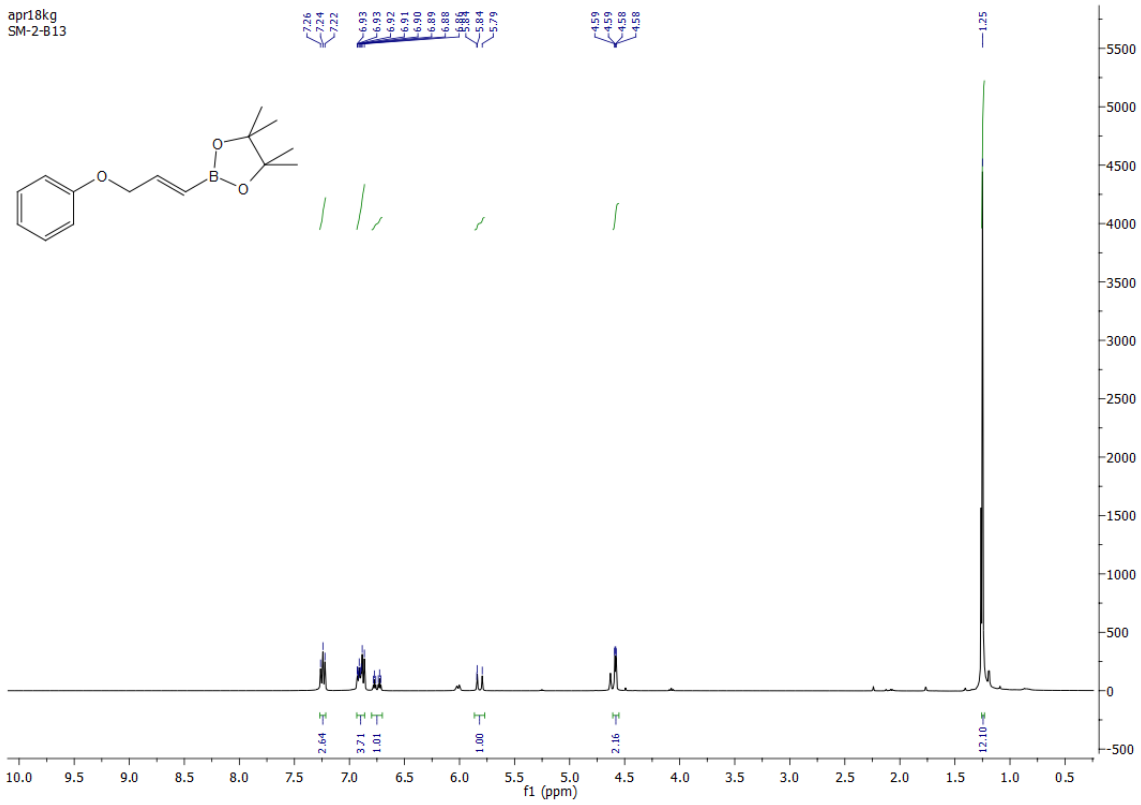


^{19}F NMR, $CDCl_3$, 470 MHz:

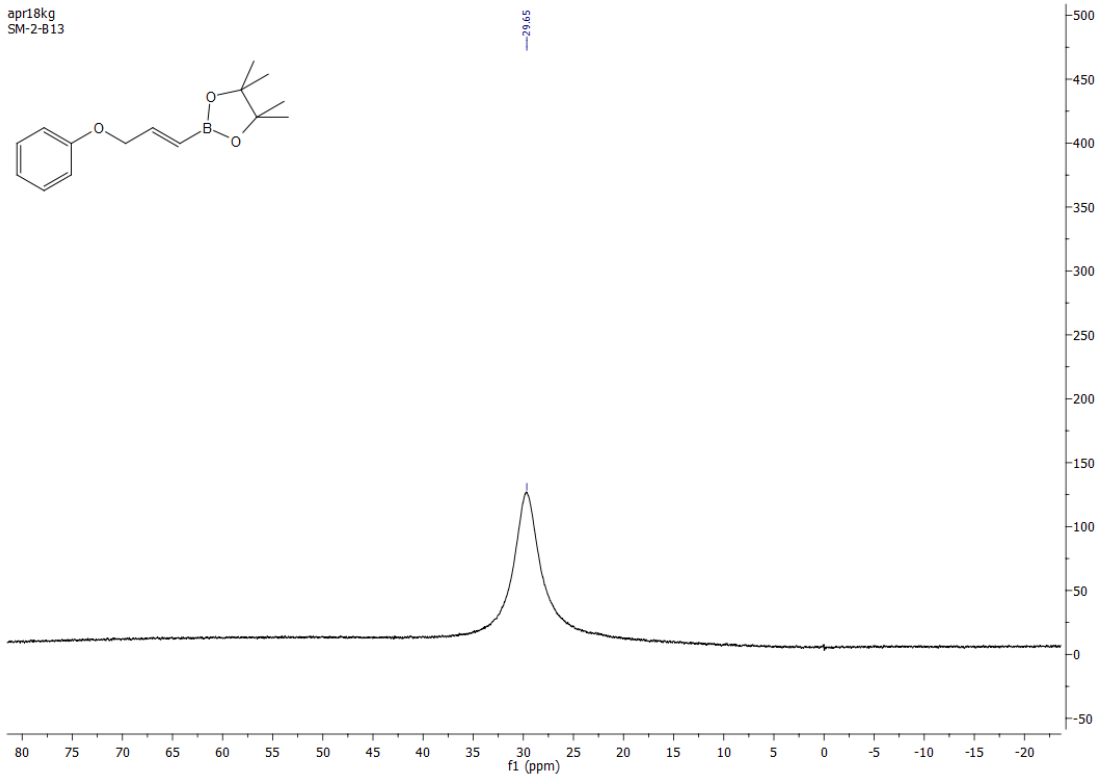


(*E*)-4,4,5,5-Tetramethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (8b)

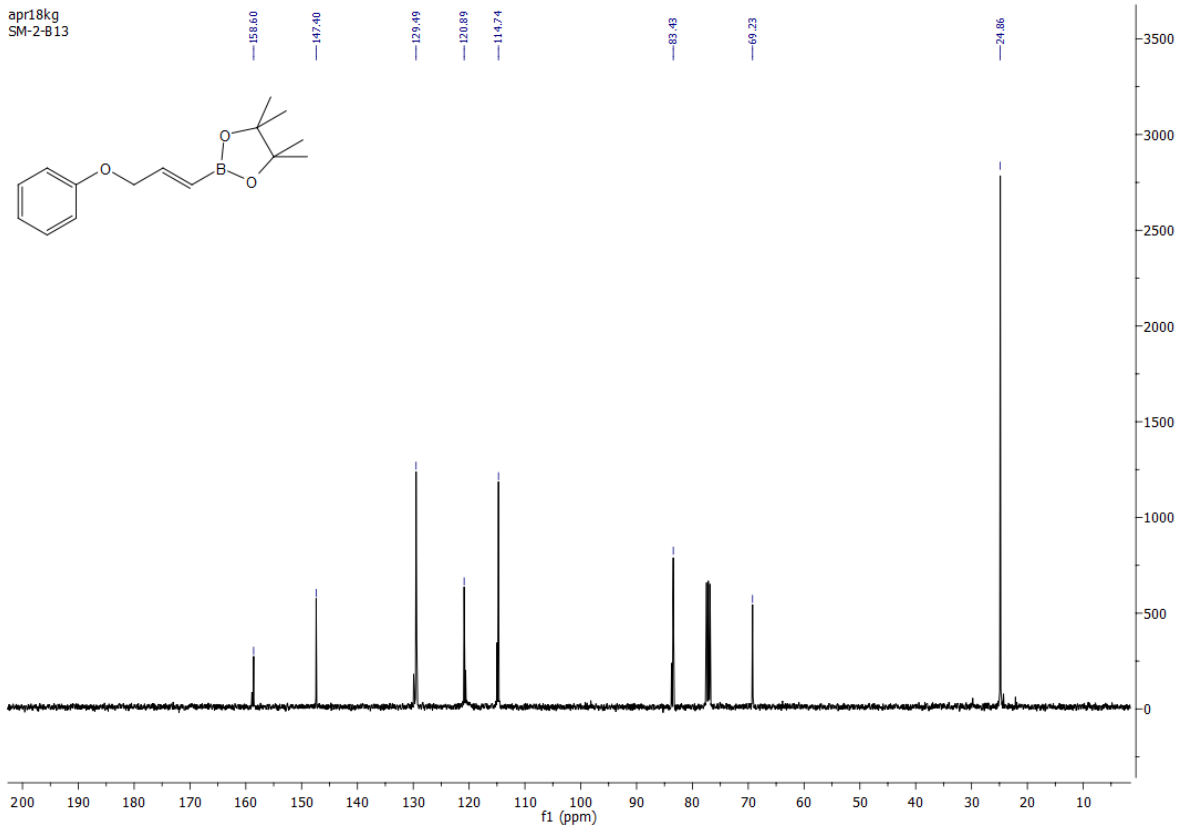
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

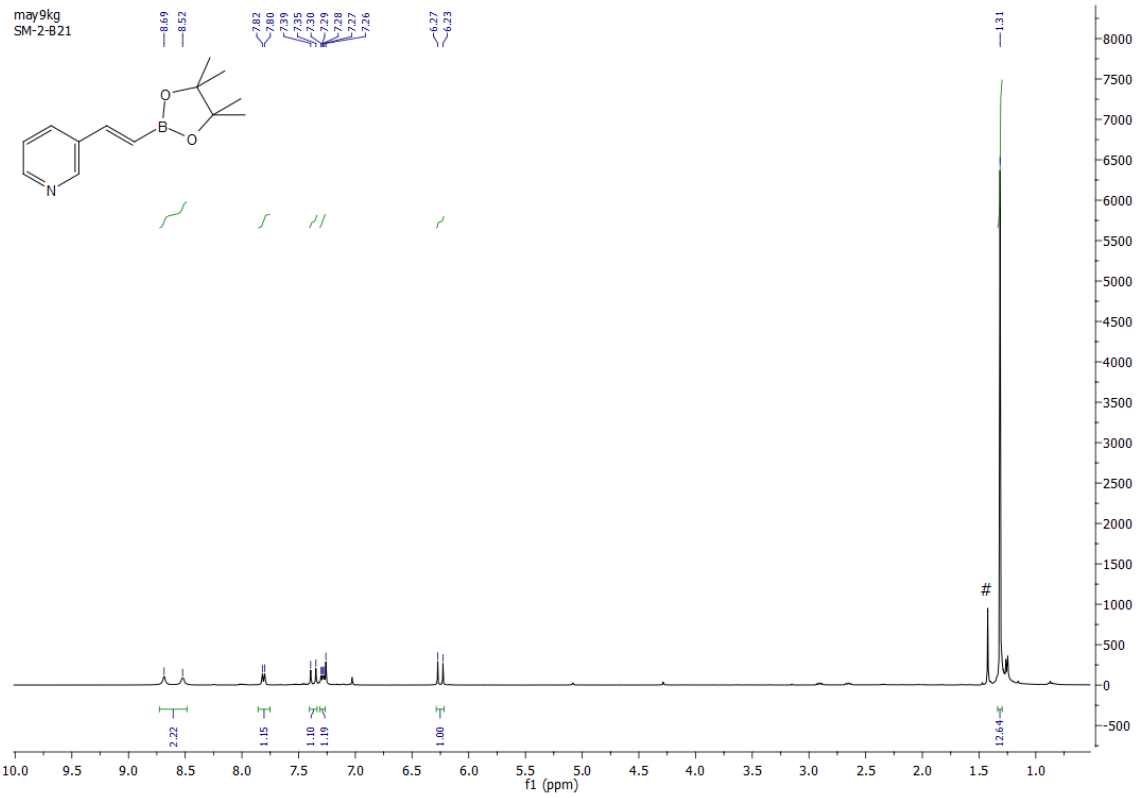


^{13}C NMR, $CDCl_3$, 100 MHz:

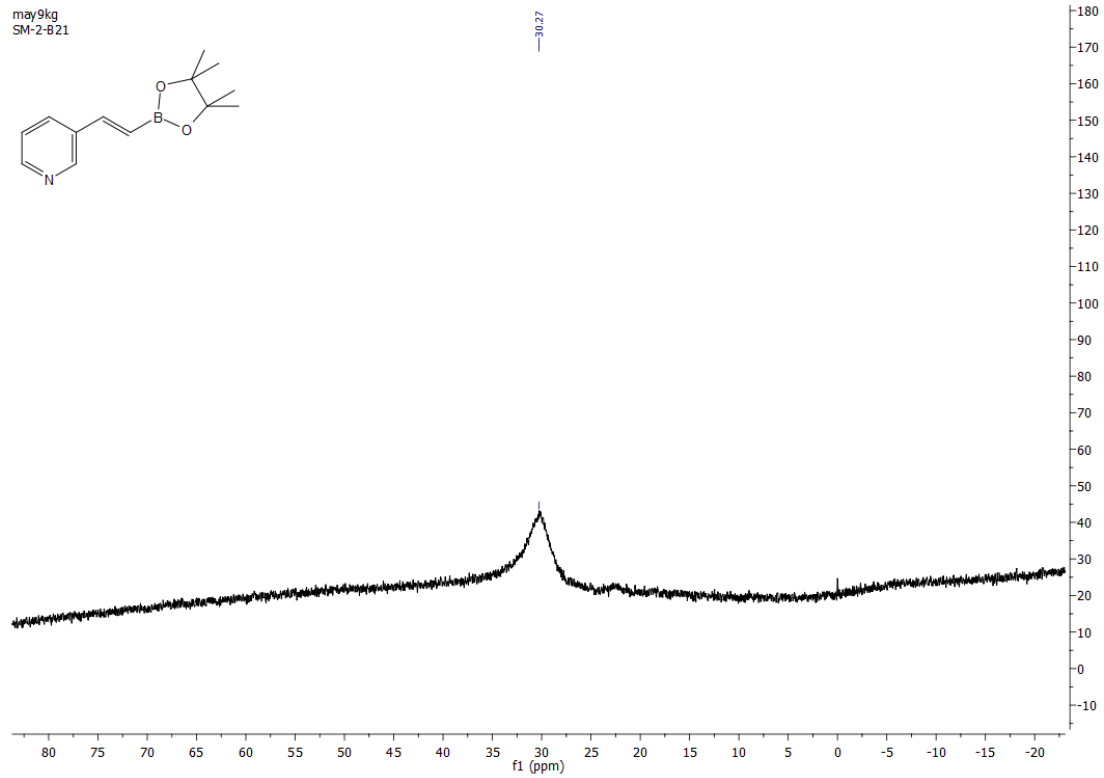


(*E*)-3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (9b)

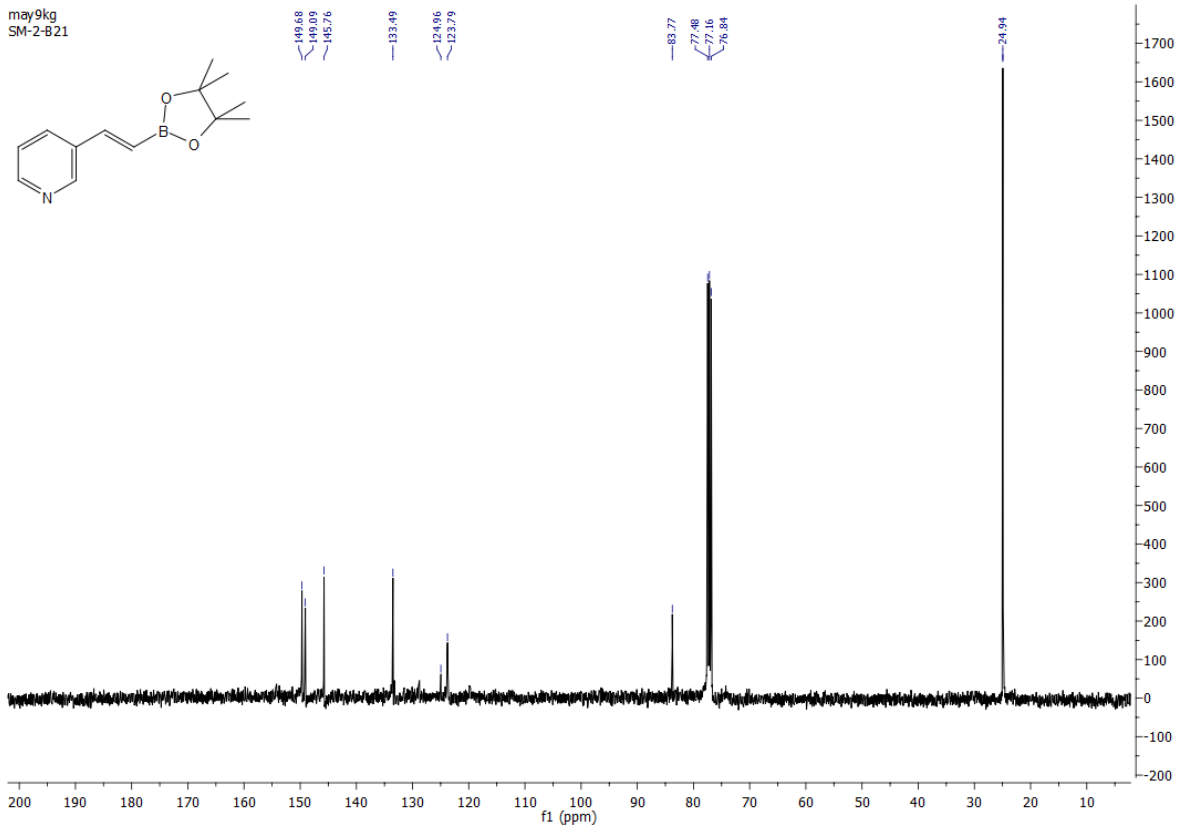
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

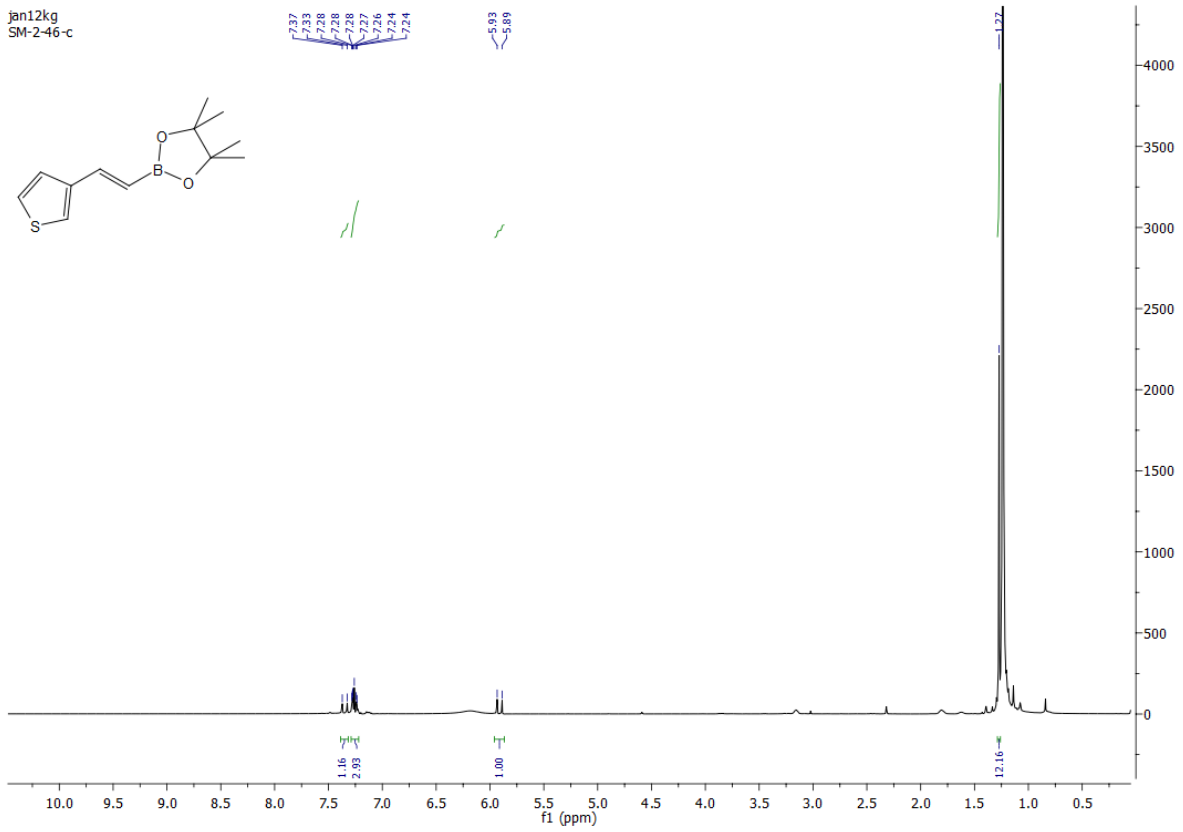


^{13}C NMR, $CDCl_3$, 100 MHz:



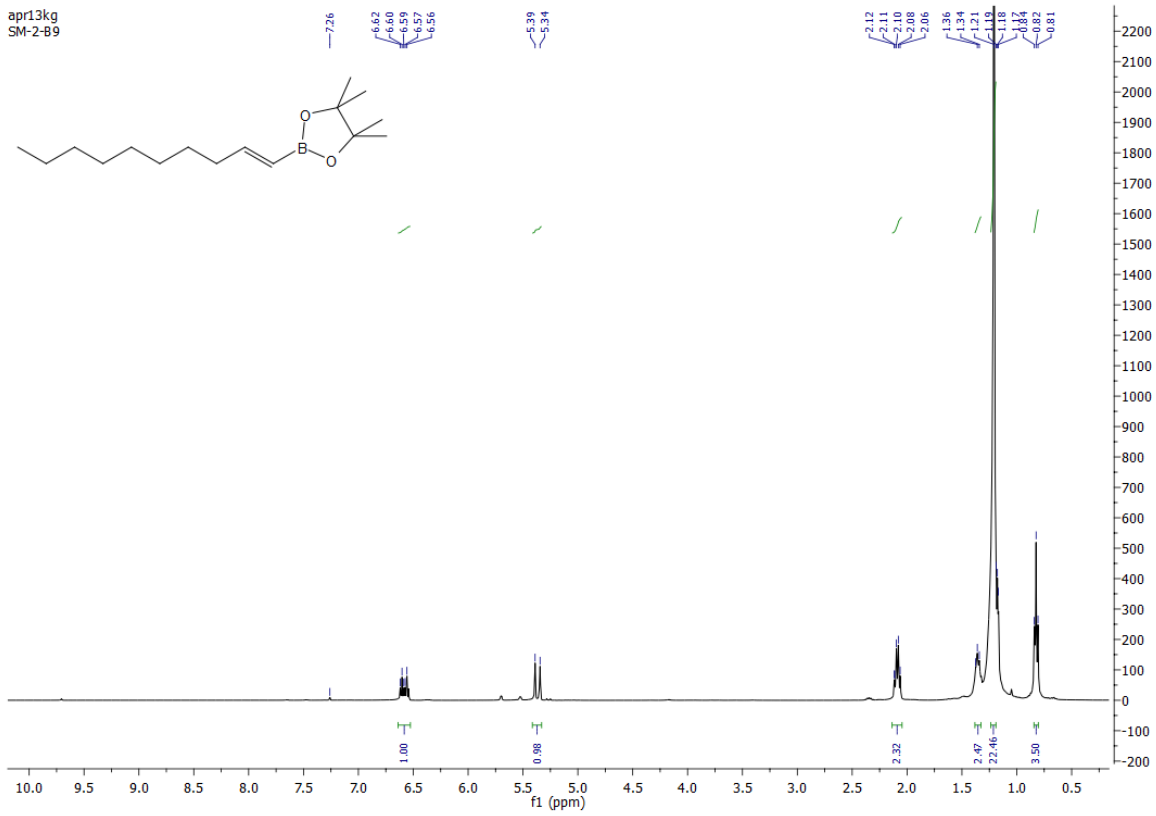
(*E*)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (10b)

^{1}H NMR, $CDCl_3$ 400 MHz:

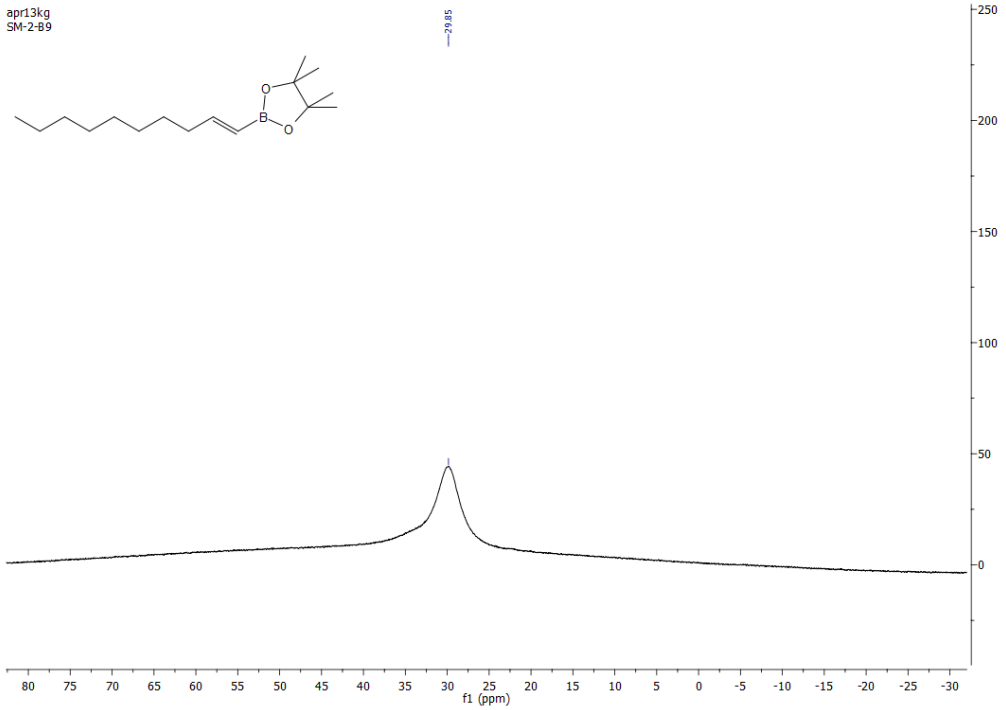


(*E*)-2-(Dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b)

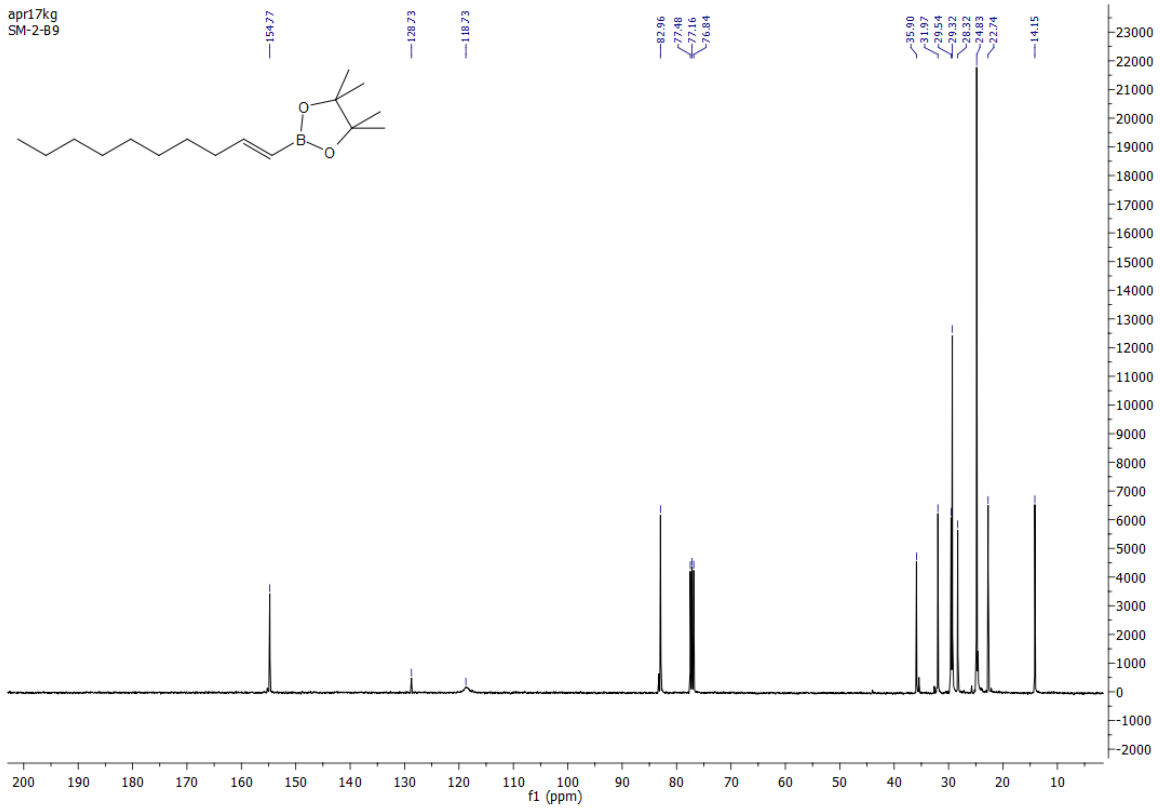
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

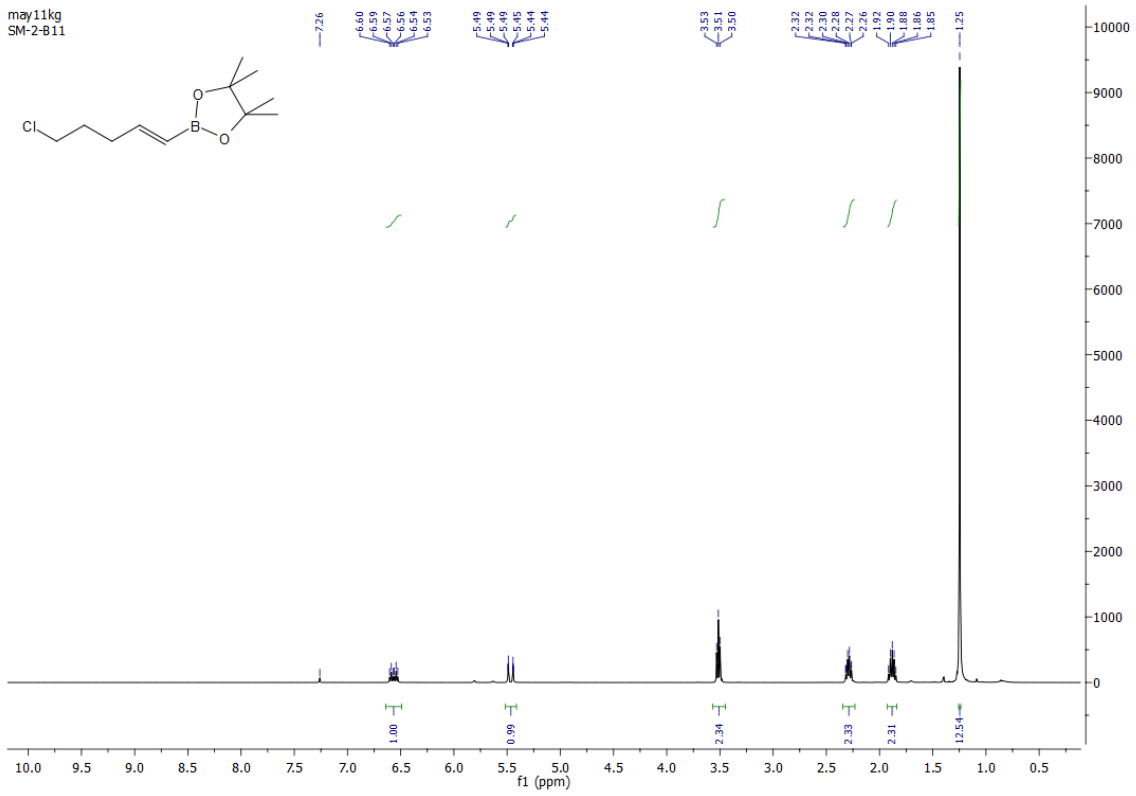


^{13}C NMR, $CDCl_3$, 100 MHz:

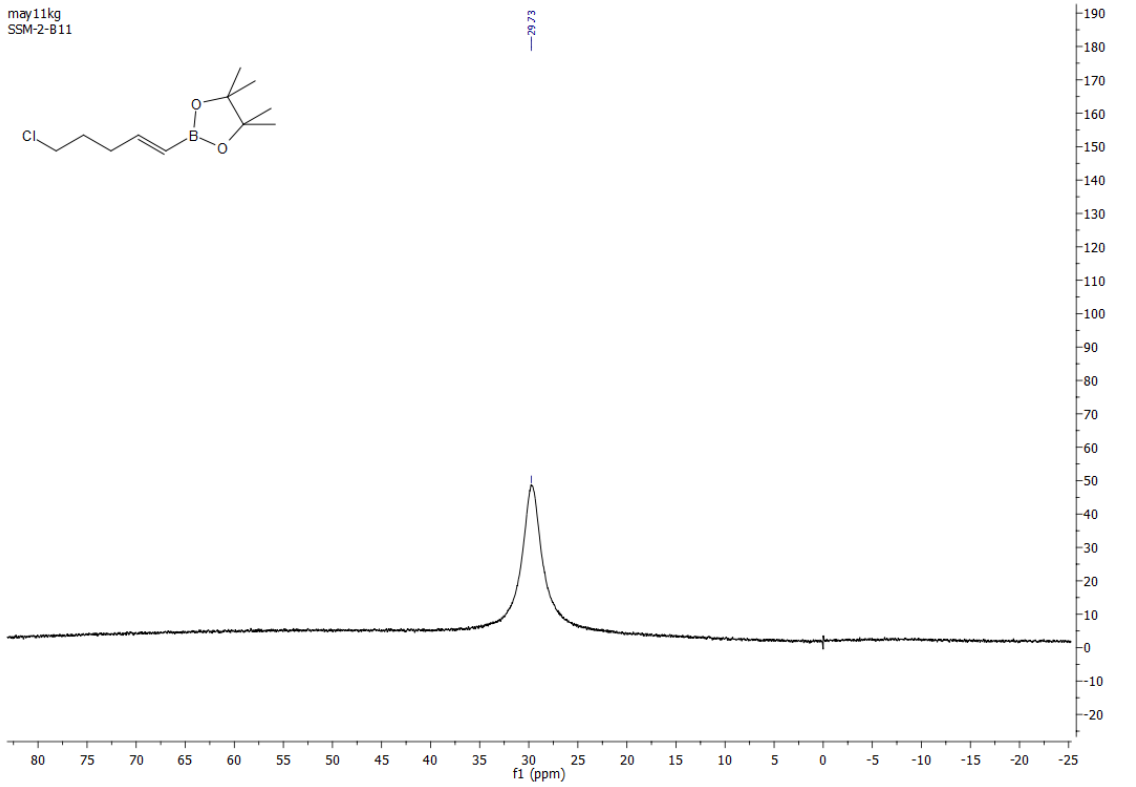


(*E*)-2-(5-Chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b)

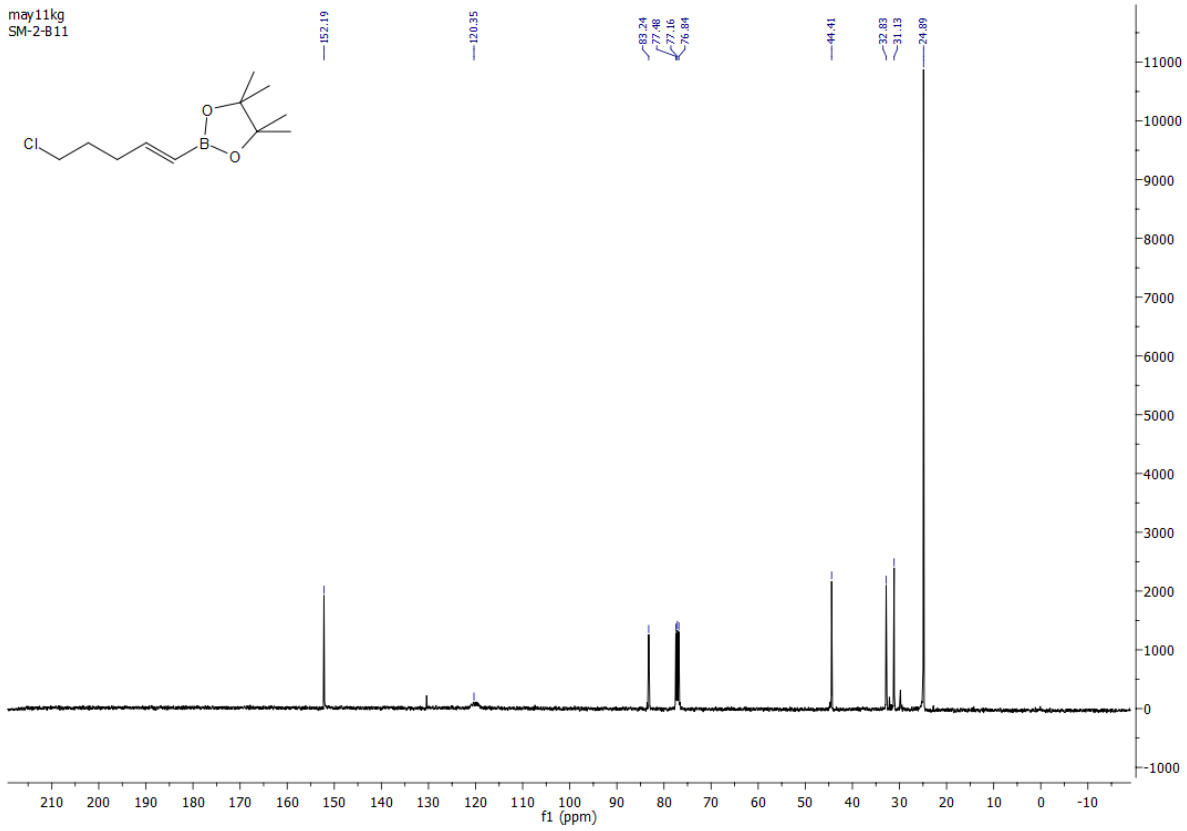
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

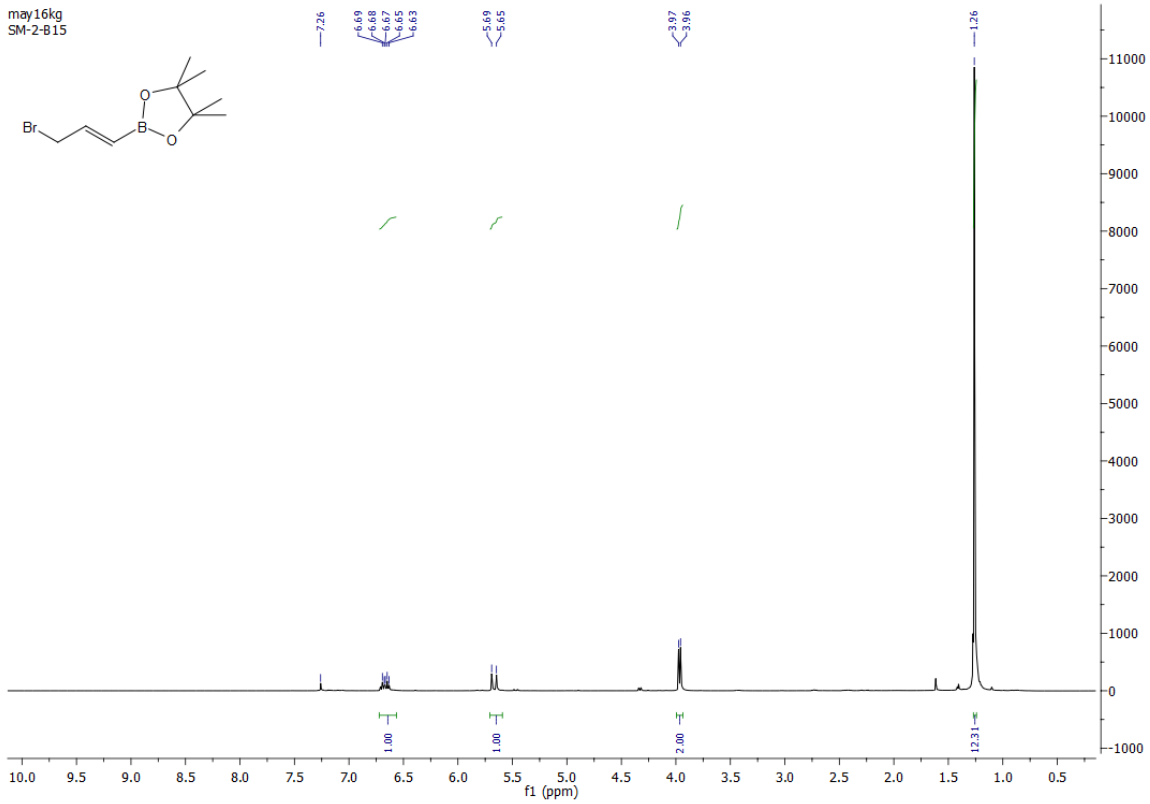


^{13}C NMR, $CDCl_3$, 100 MHz:

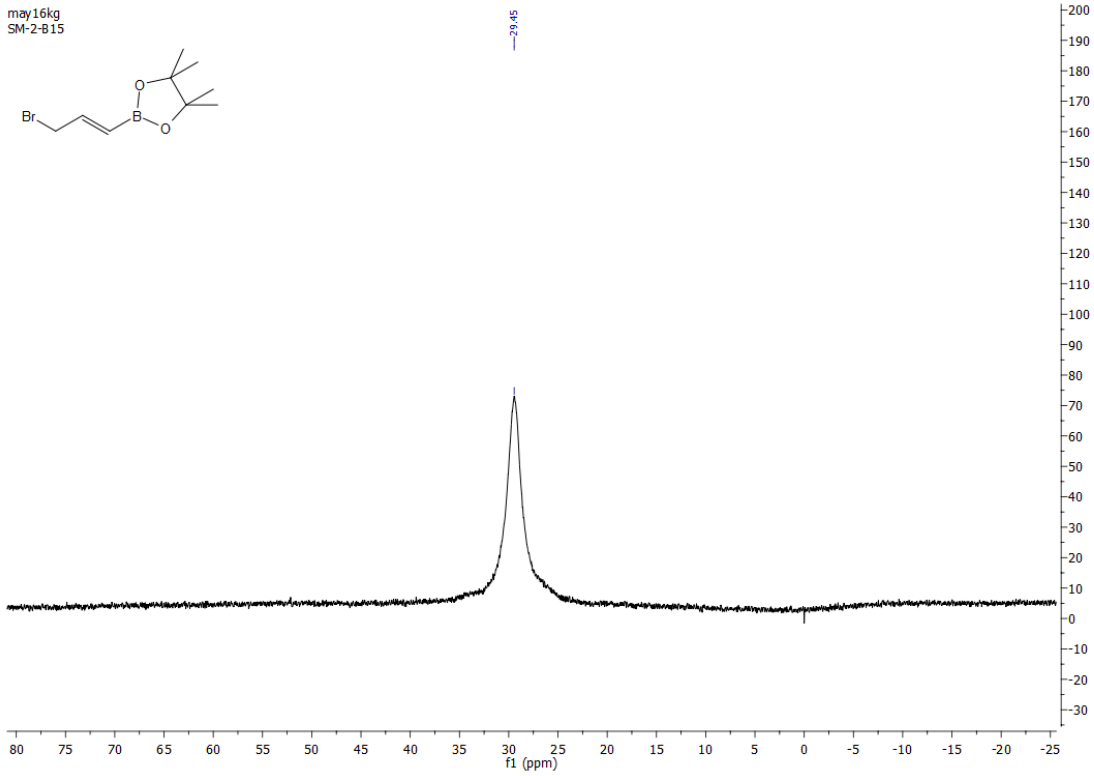


(*E*)-2-(3-Bromoprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b)

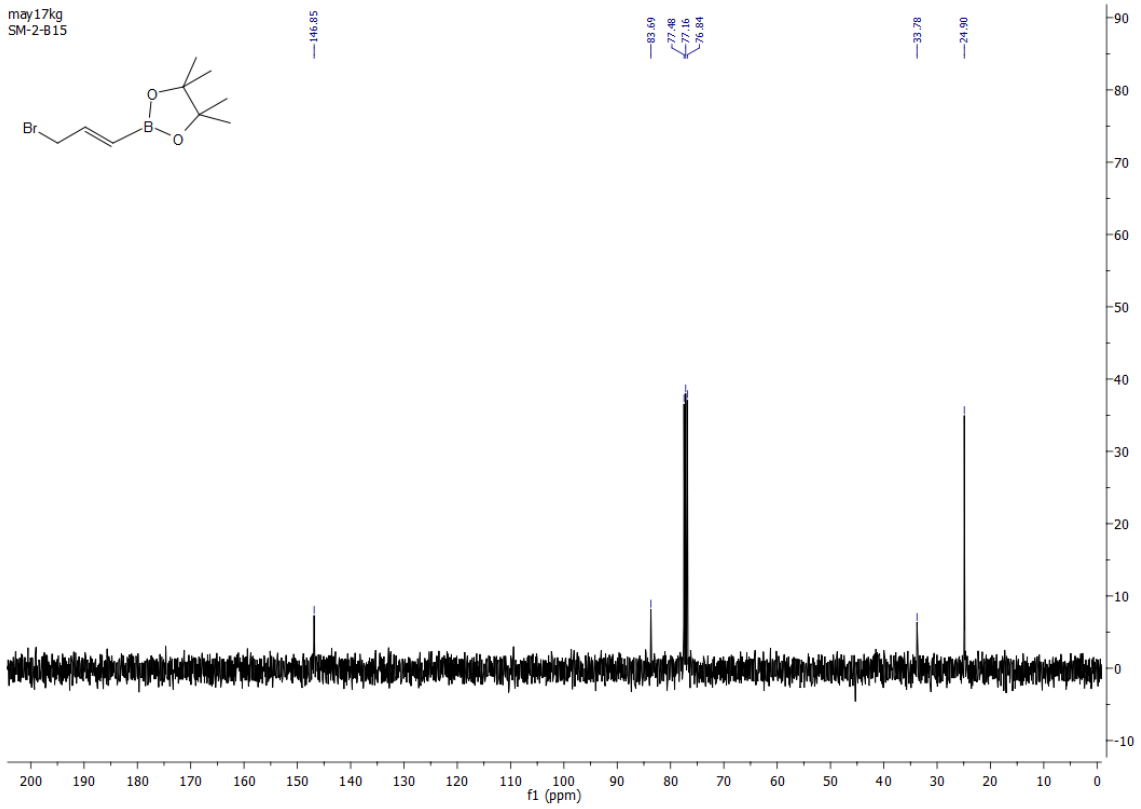
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

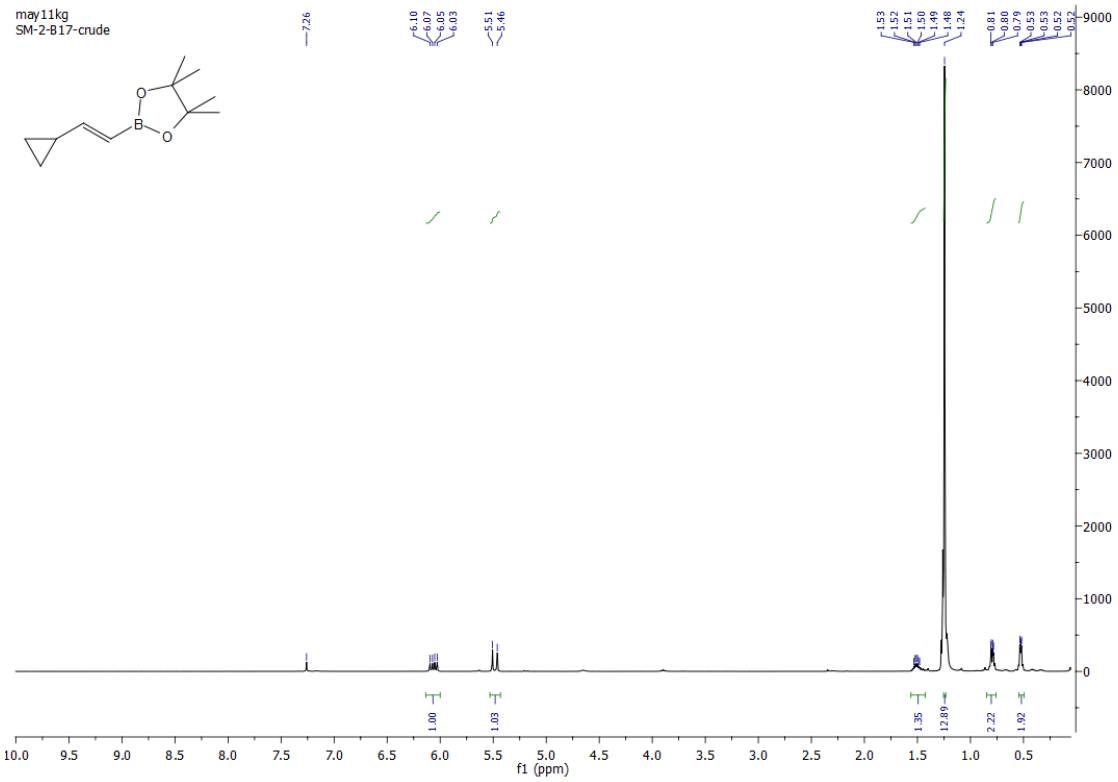


^{13}C NMR, $CDCl_3$, 100 MHz:

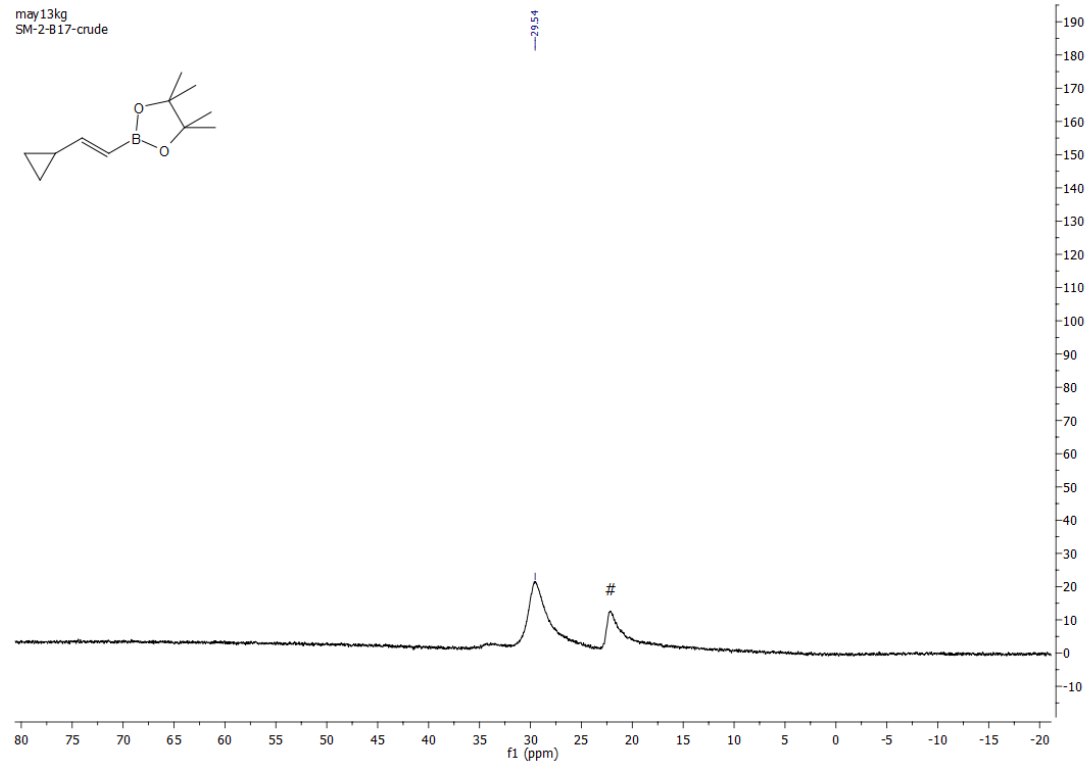


(*E*)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14b)

^{1}H NMR, $CDCl_3$ 400 MHz:

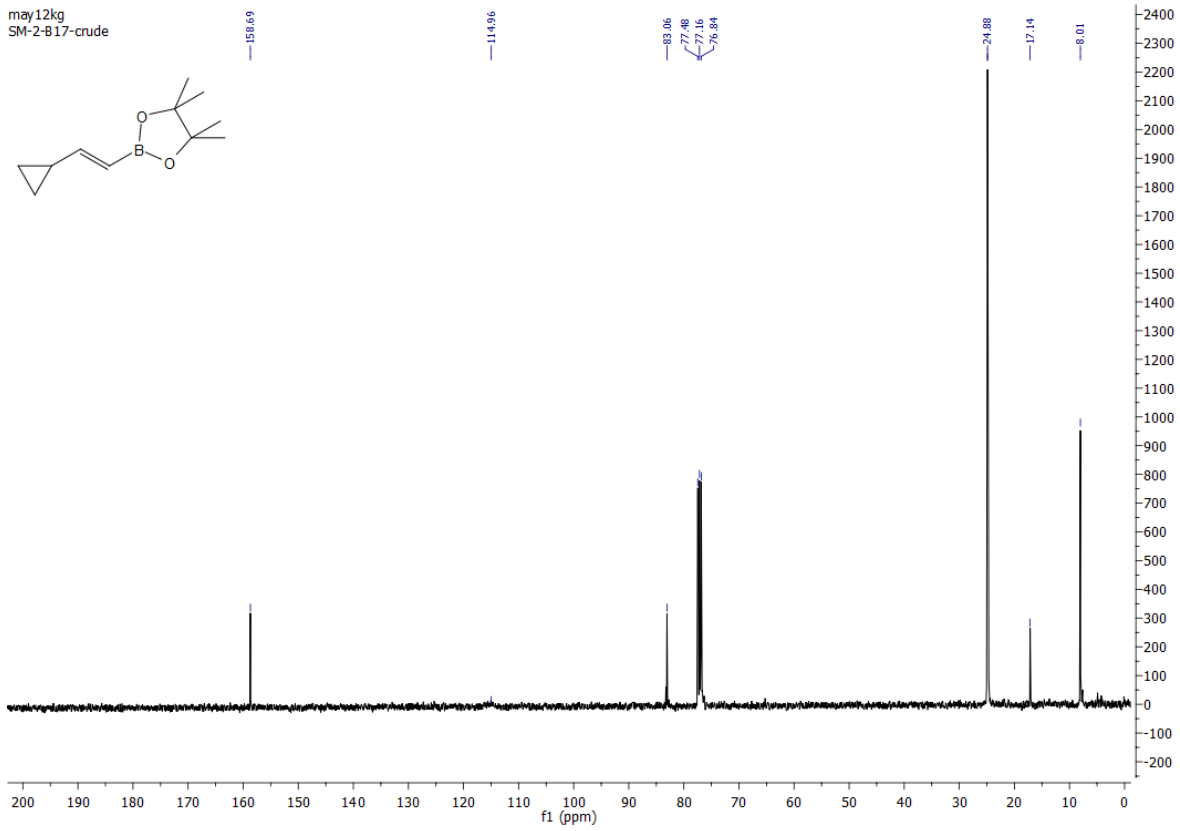


^{11}B NMR, $CDCl_3$, 128 MHz:



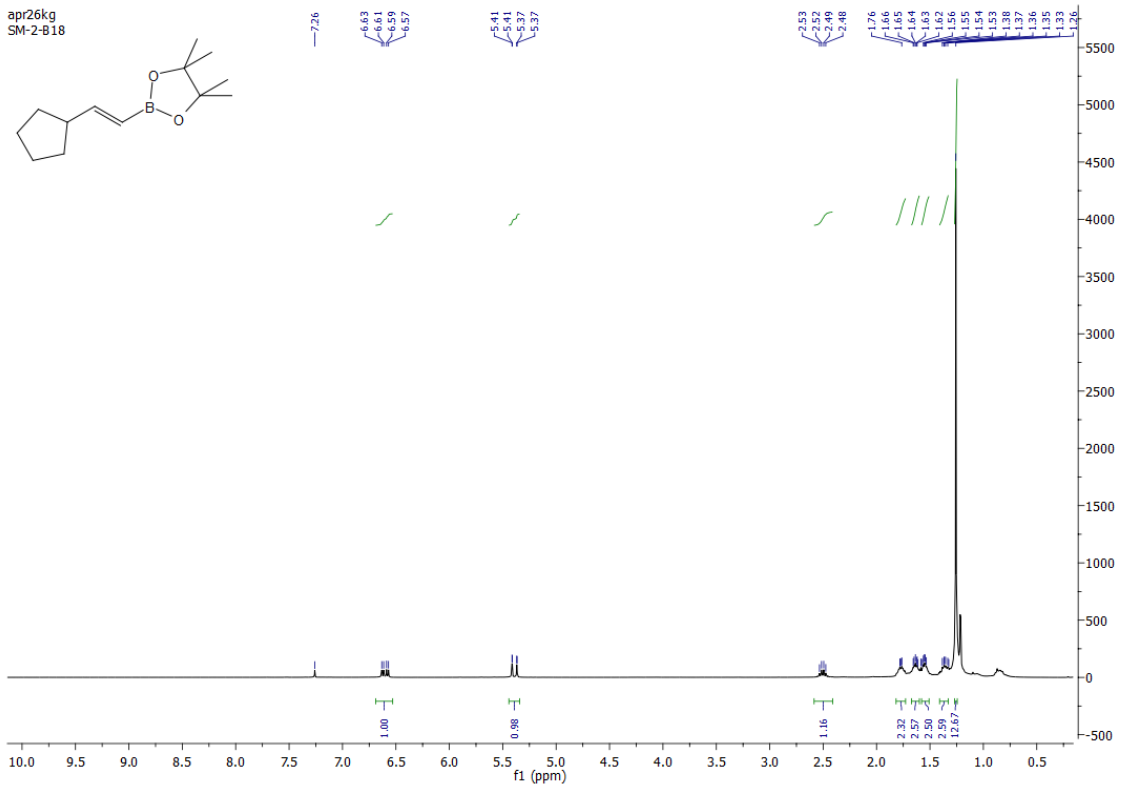
Note: #: Inpurity of Bpin-O-Bpin

^{13}C NMR, $CDCl_3$, 100 MHz:

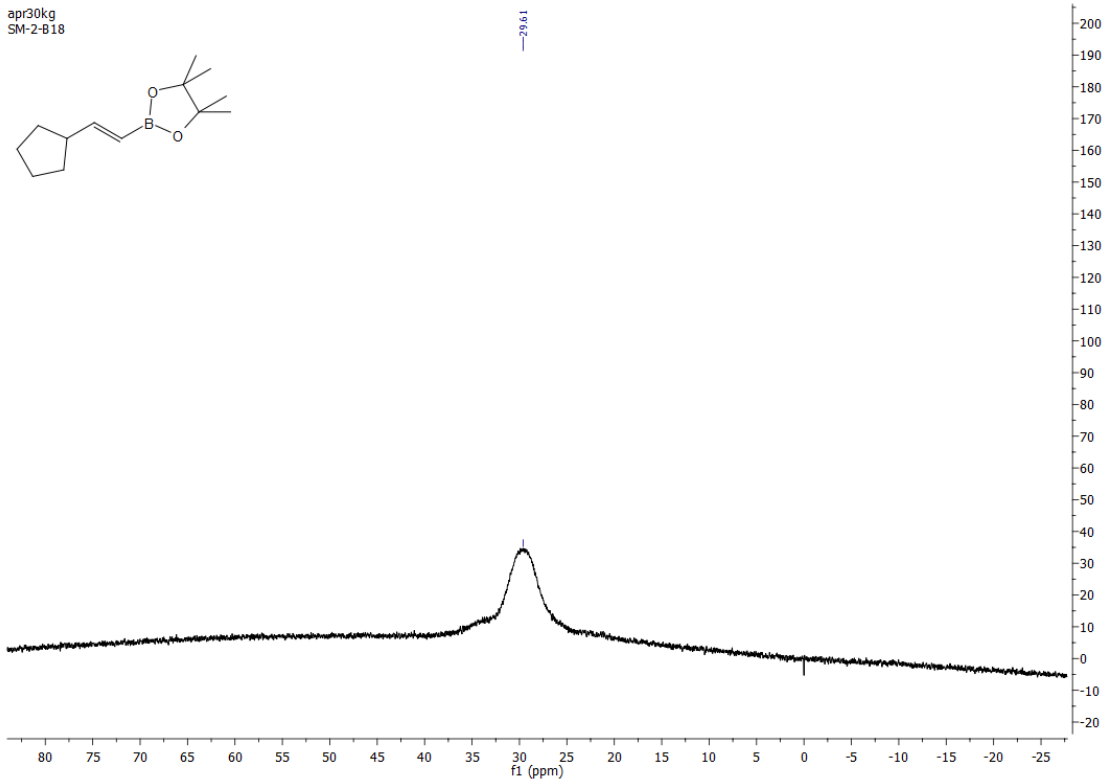


(*E*)-2-(2-Cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b)

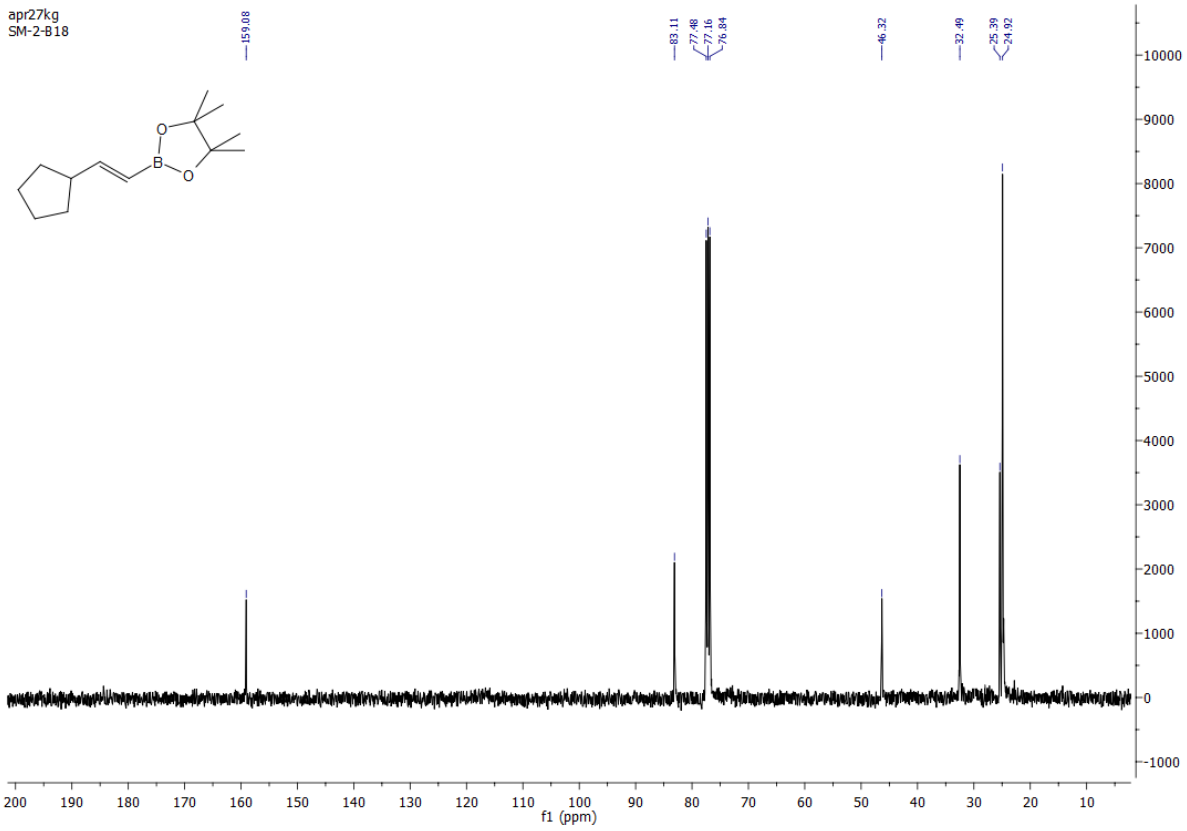
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

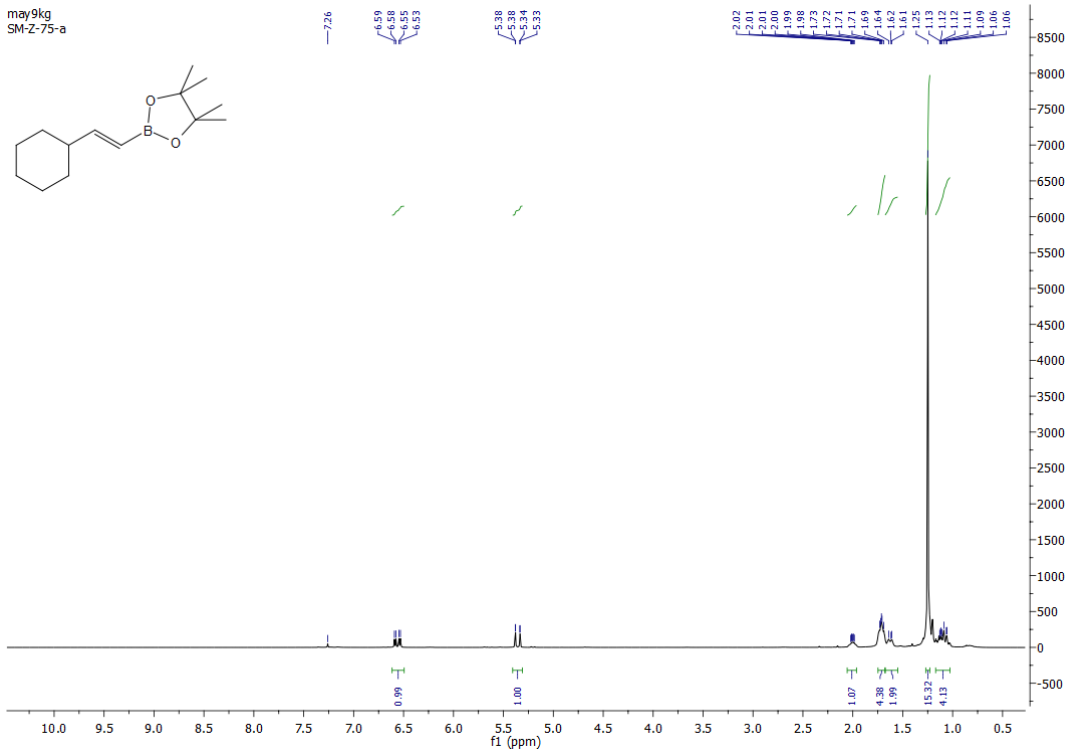


^{13}C NMR, $CDCl_3$, 100 MHz:

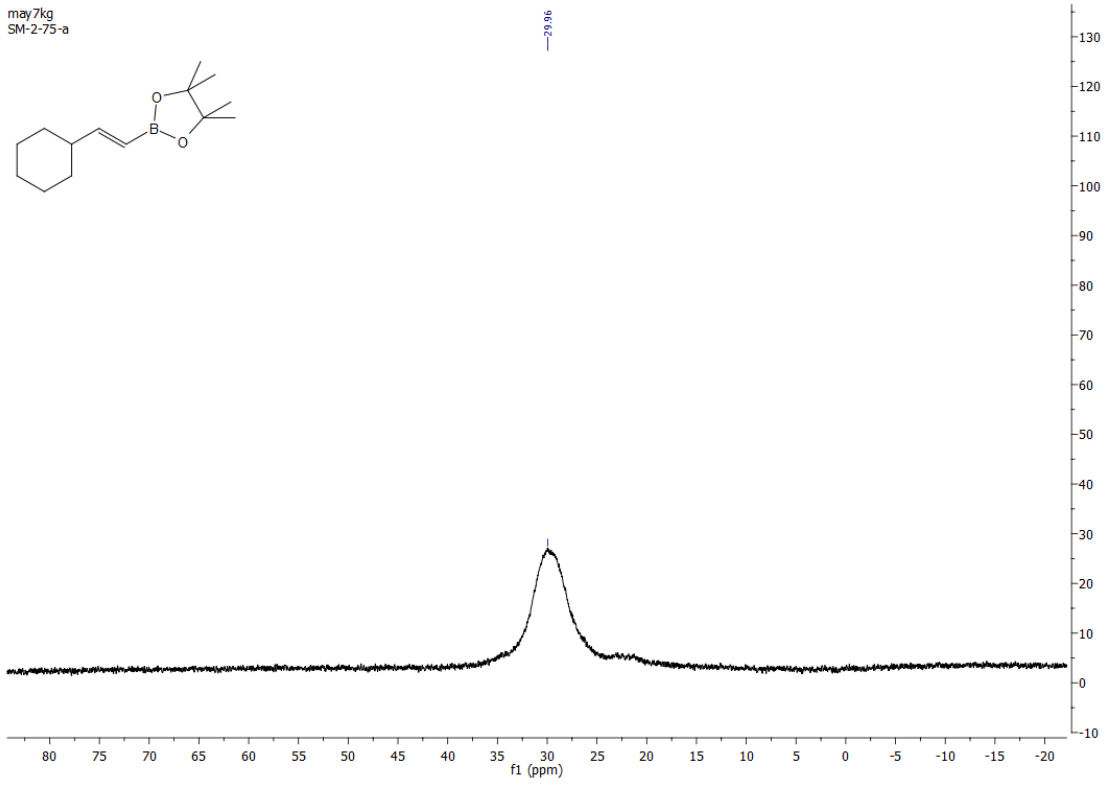


(*E*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16b)

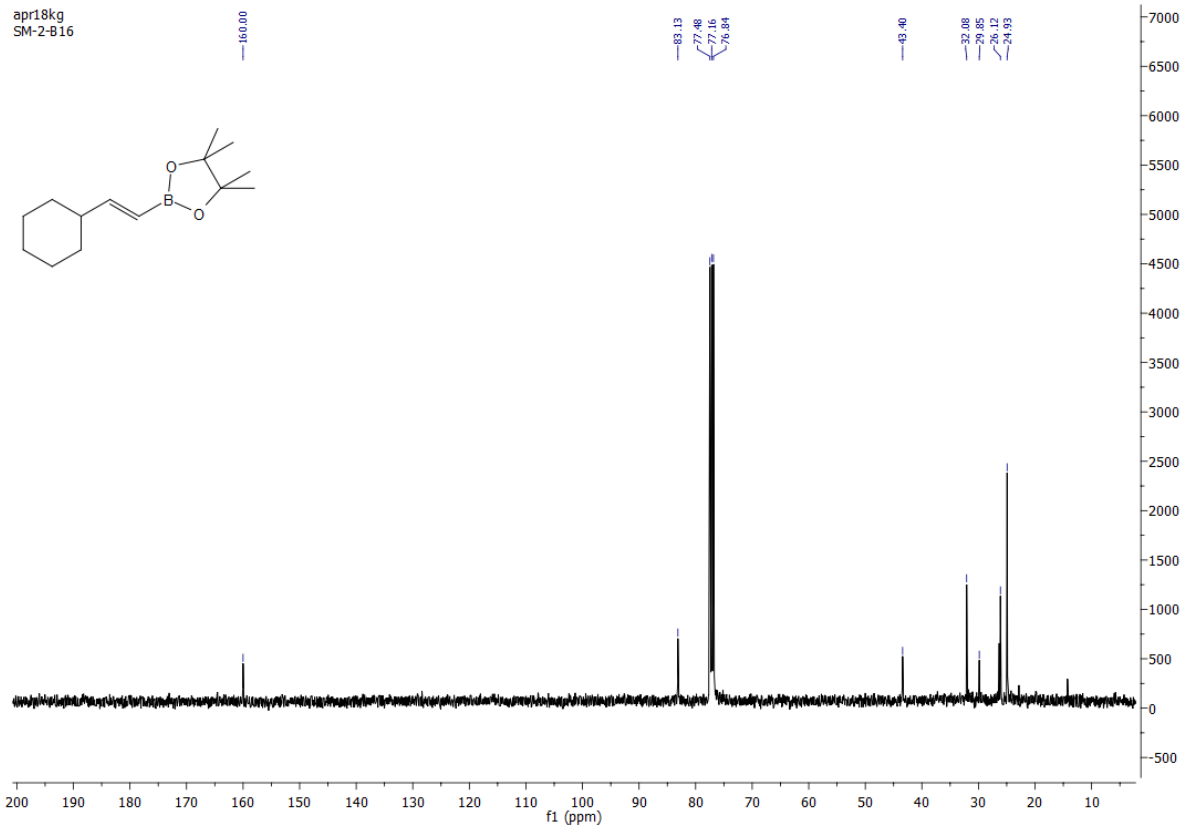
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

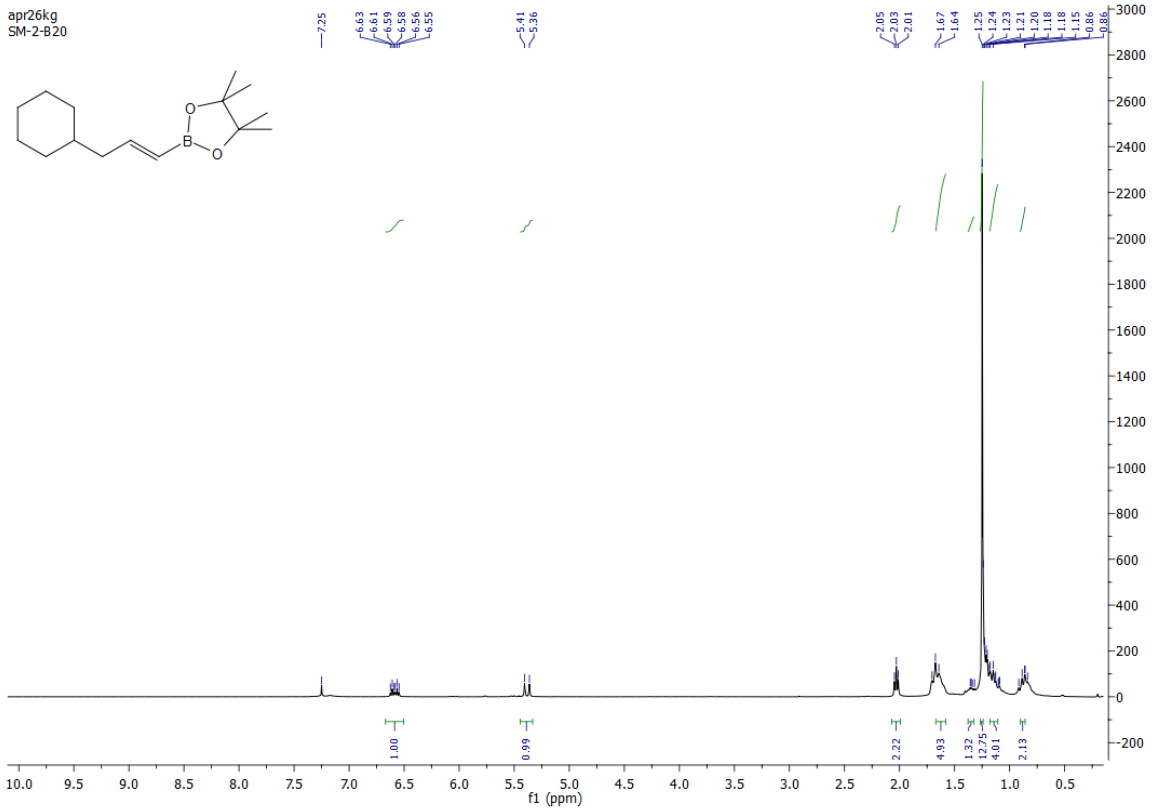


^{13}C NMR, $CDCl_3$, 100 MHz:

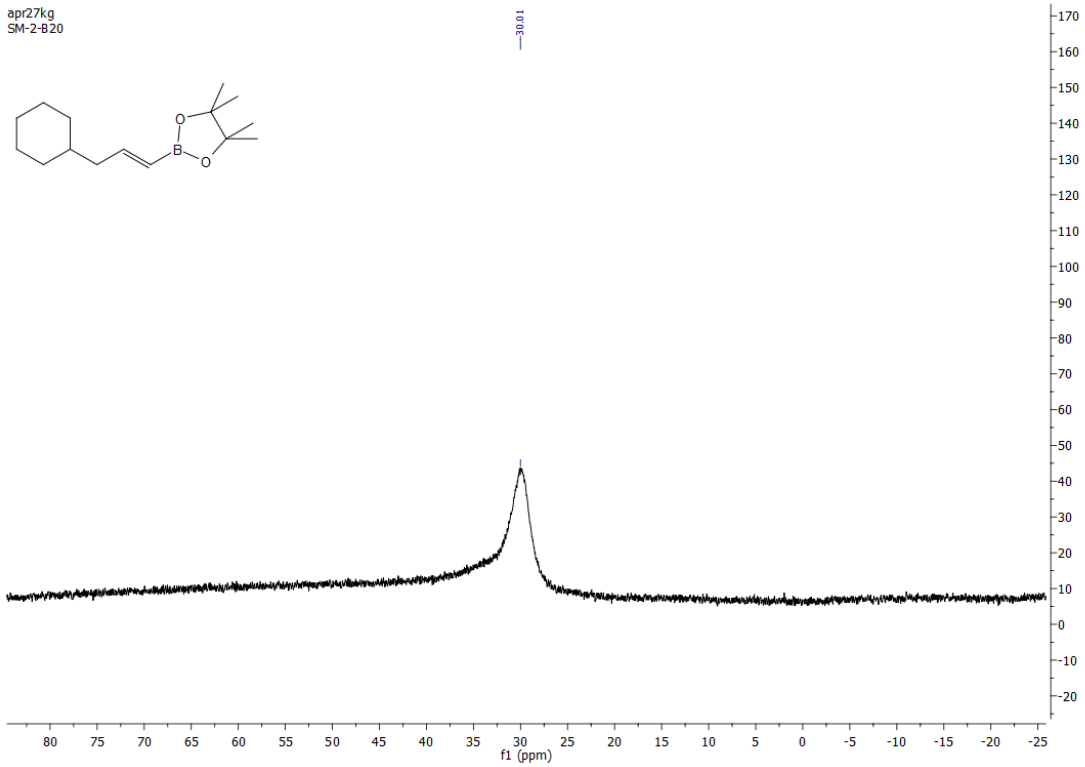


(*E*)-2-(3-Cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17b)

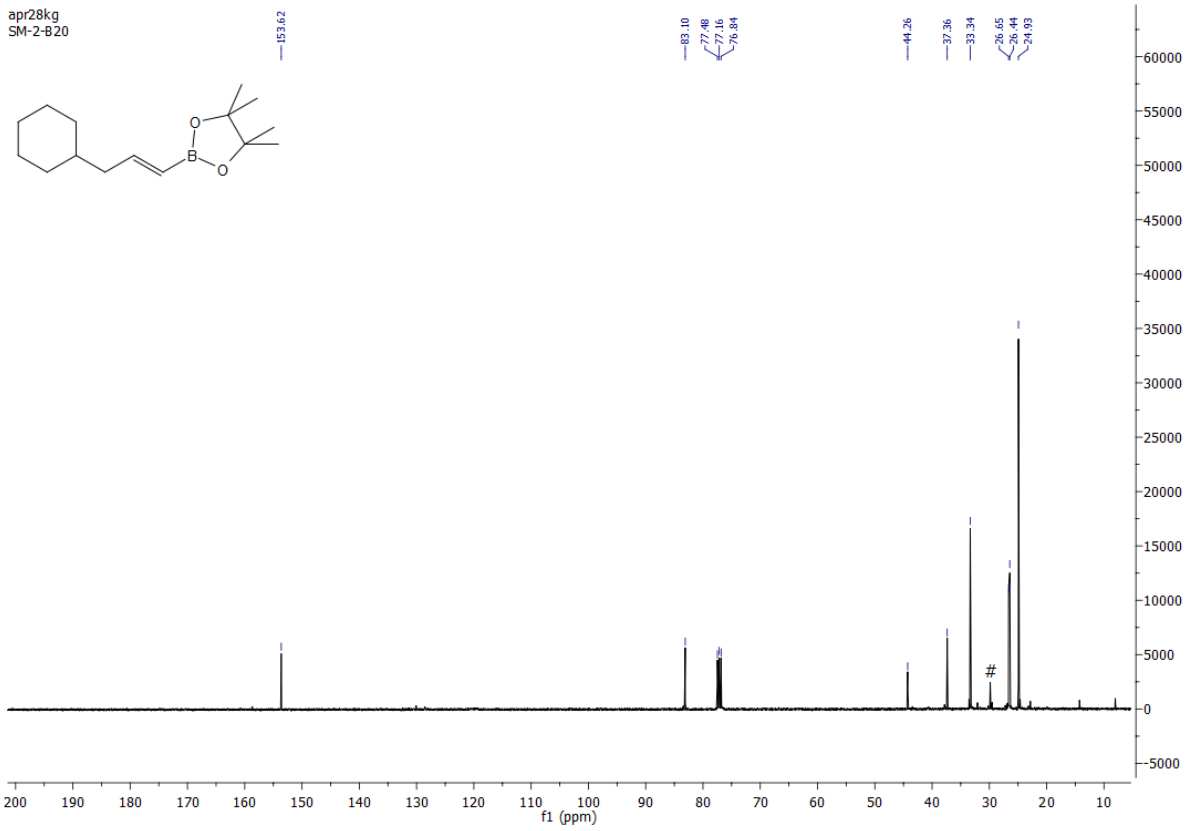
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

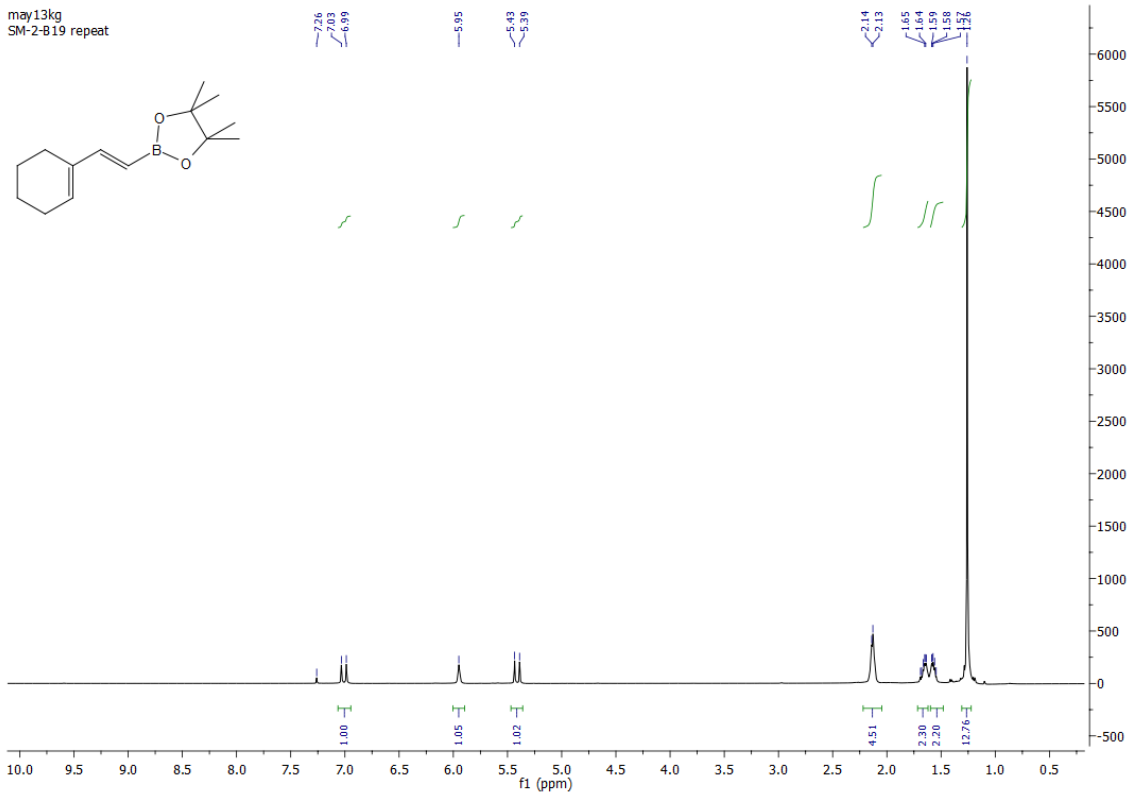


^{13}C NMR, $CDCl_3$, 100 MHz:

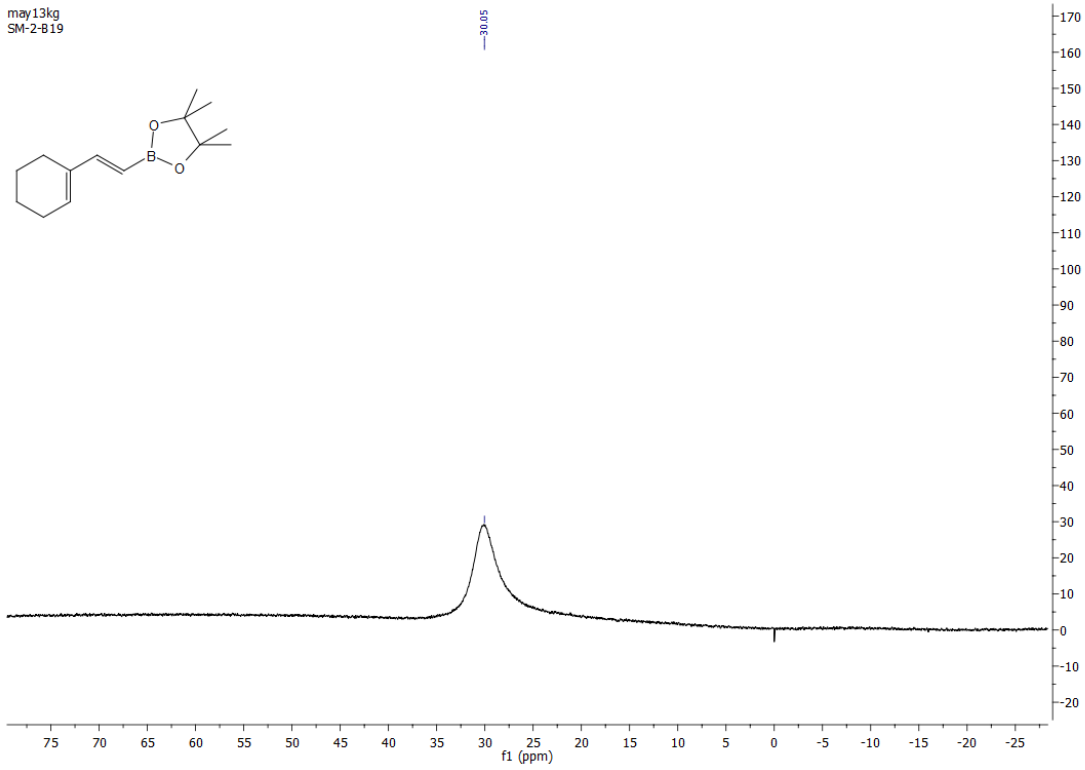


(*E*)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)

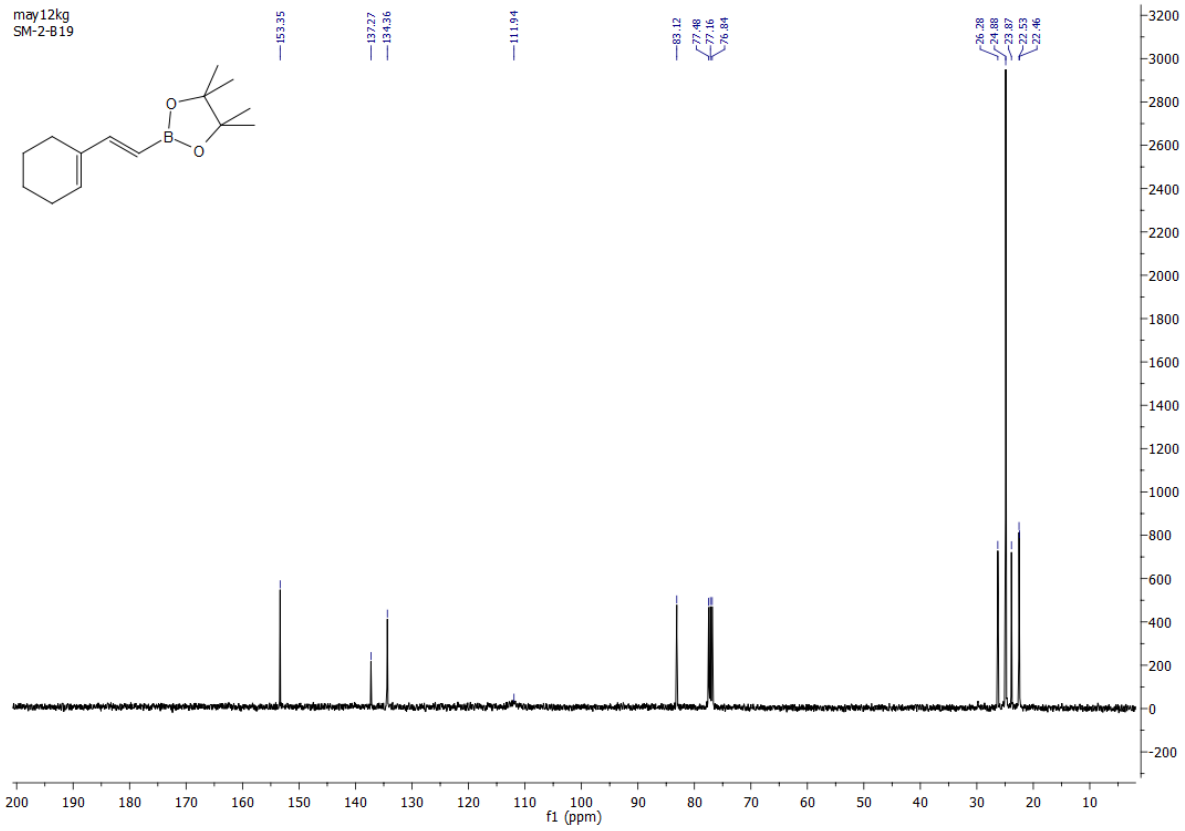
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

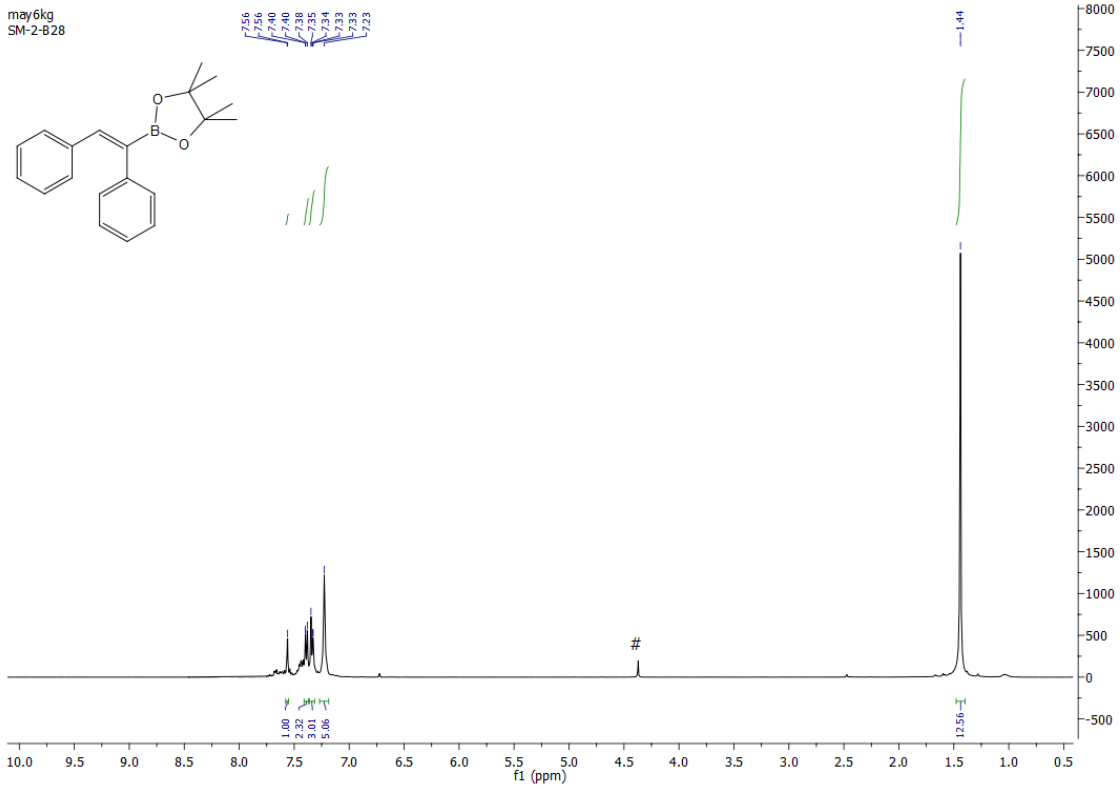


^{13}C NMR, $CDCl_3$, 100 MHz:

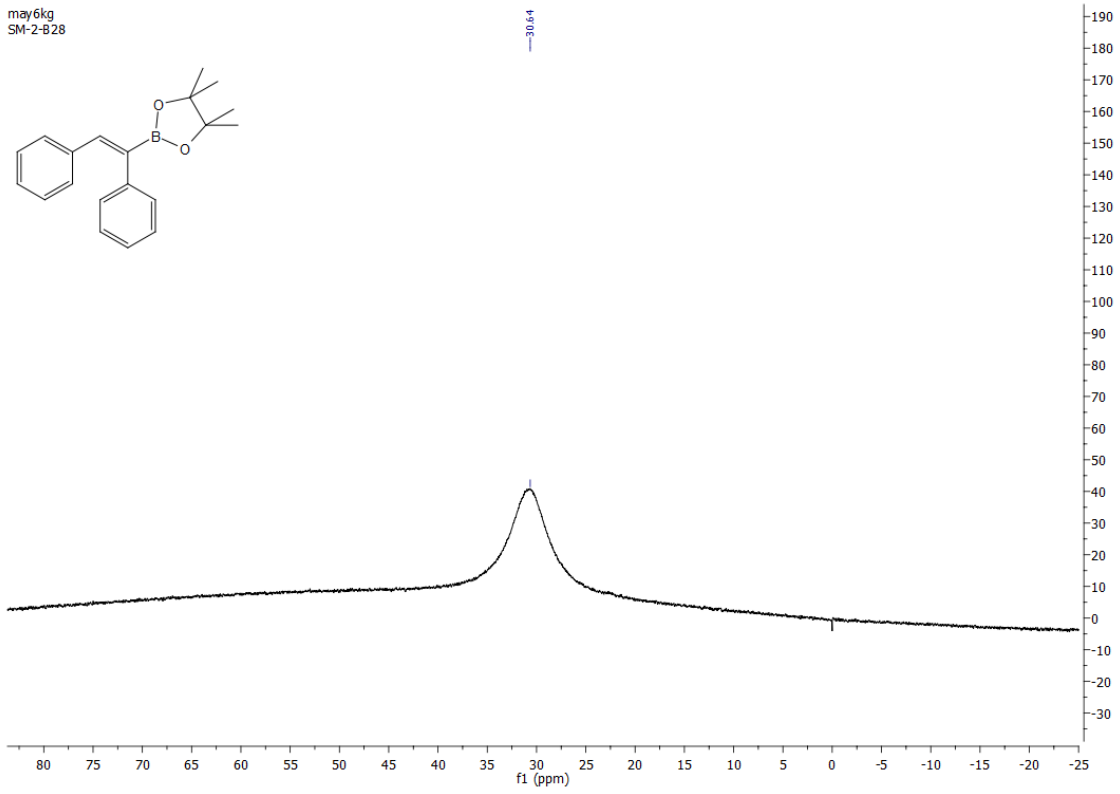


(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19b)

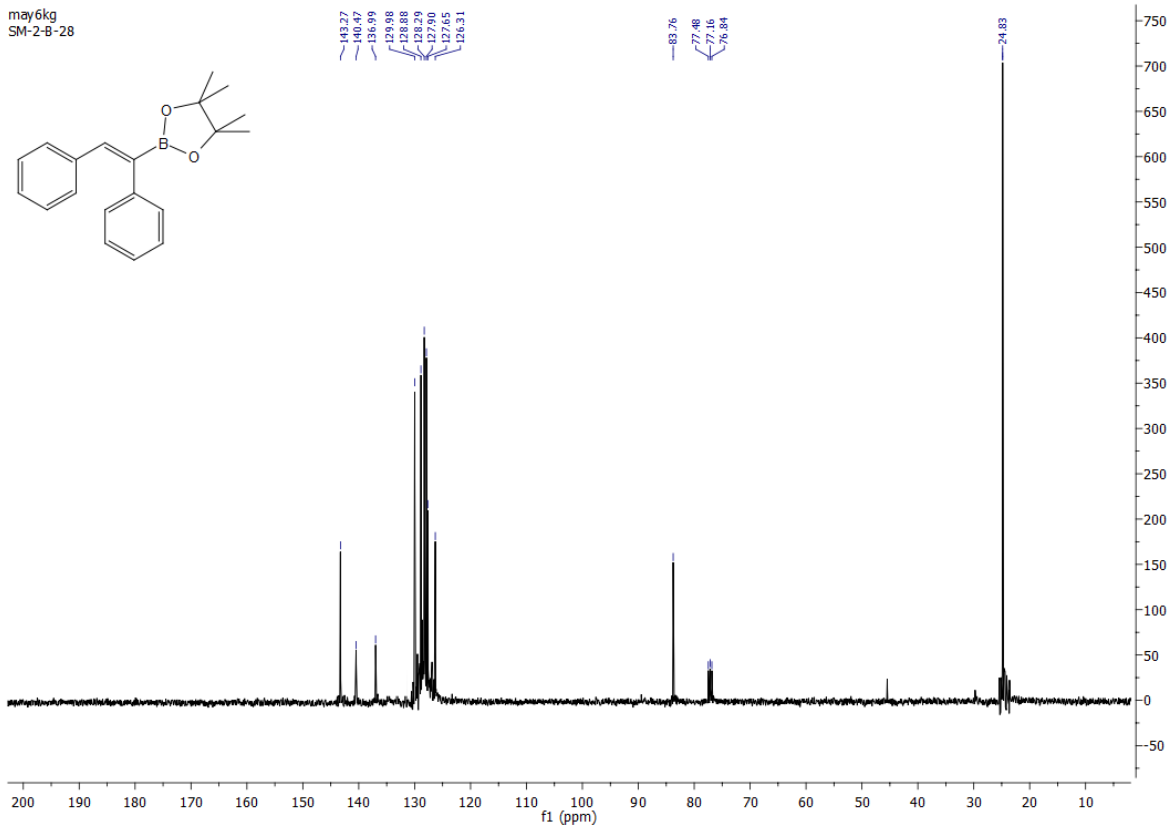
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

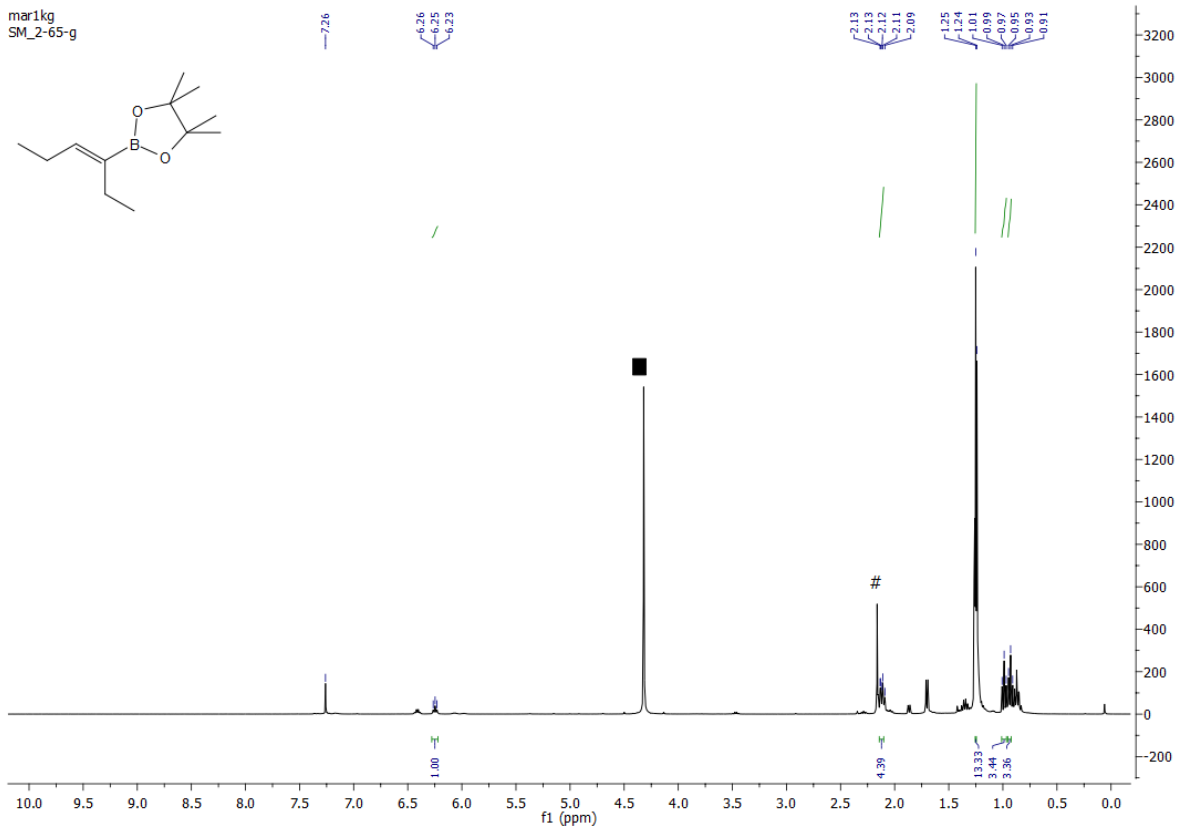


^{13}C NMR, $CDCl_3$, 100 MHz:



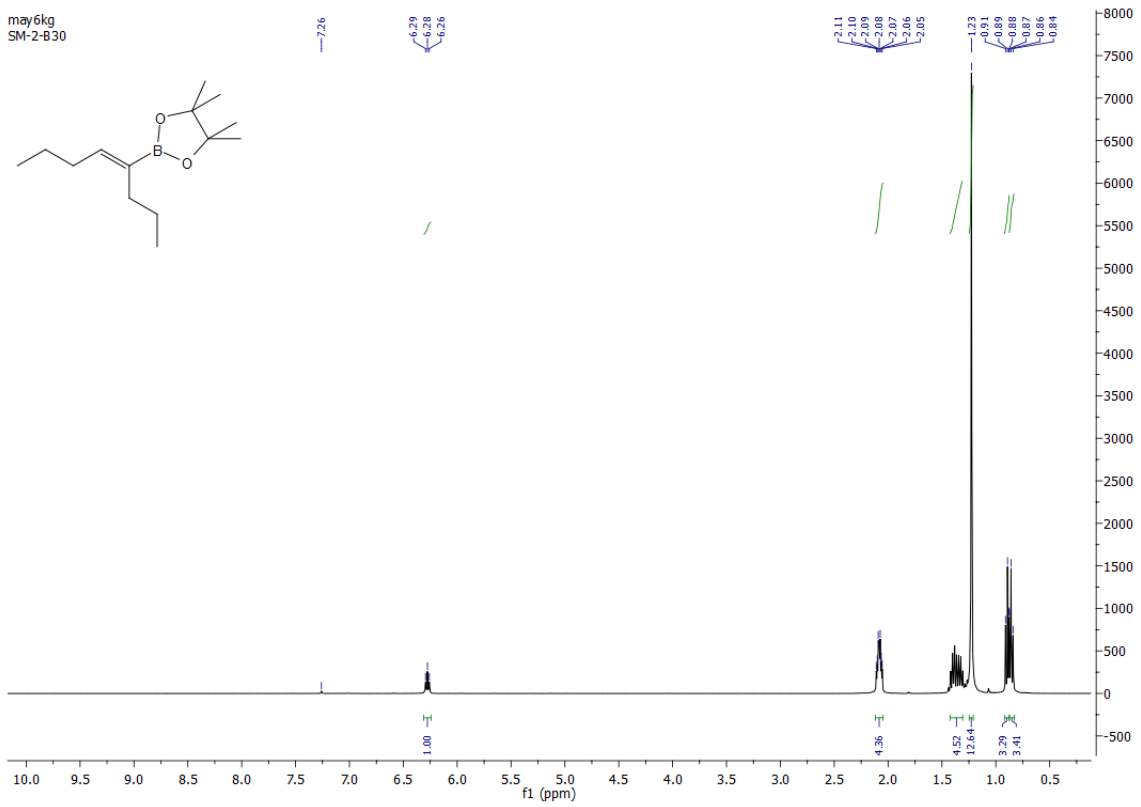
(*Z*)-2-(Hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [20b]

^{1}H NMR, $CDCl_3$ 400 MHz:

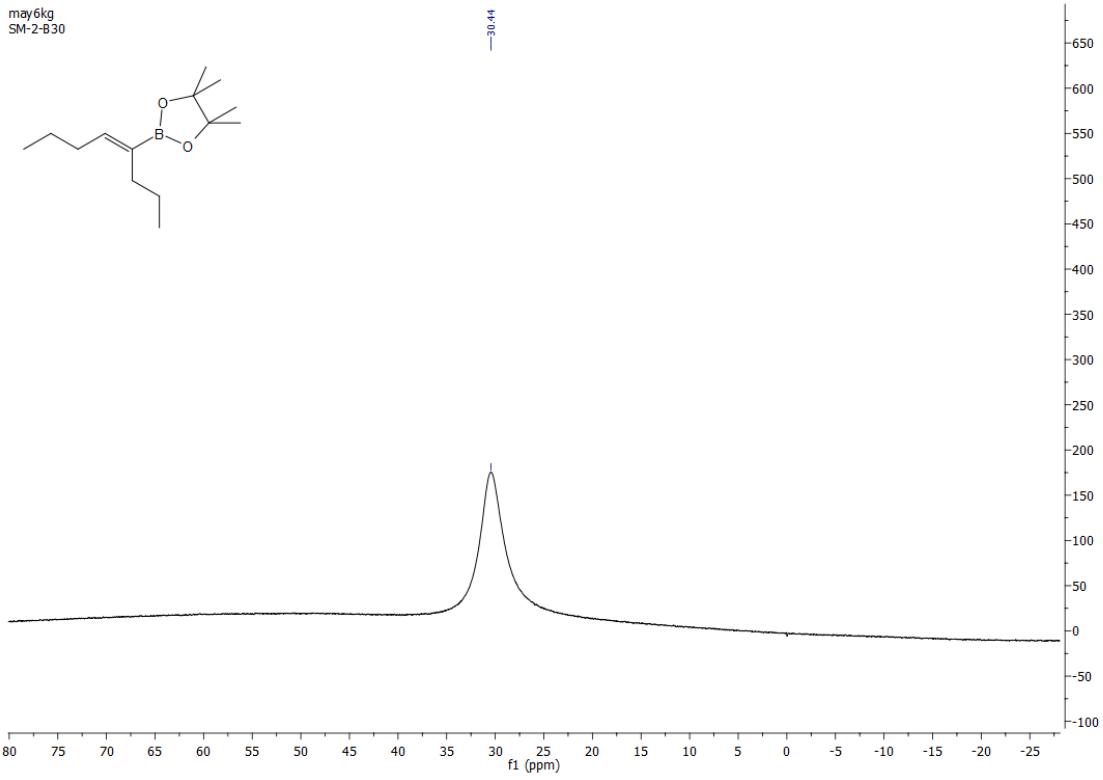


(*Z*)-4,4,5,5-Tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (21b)

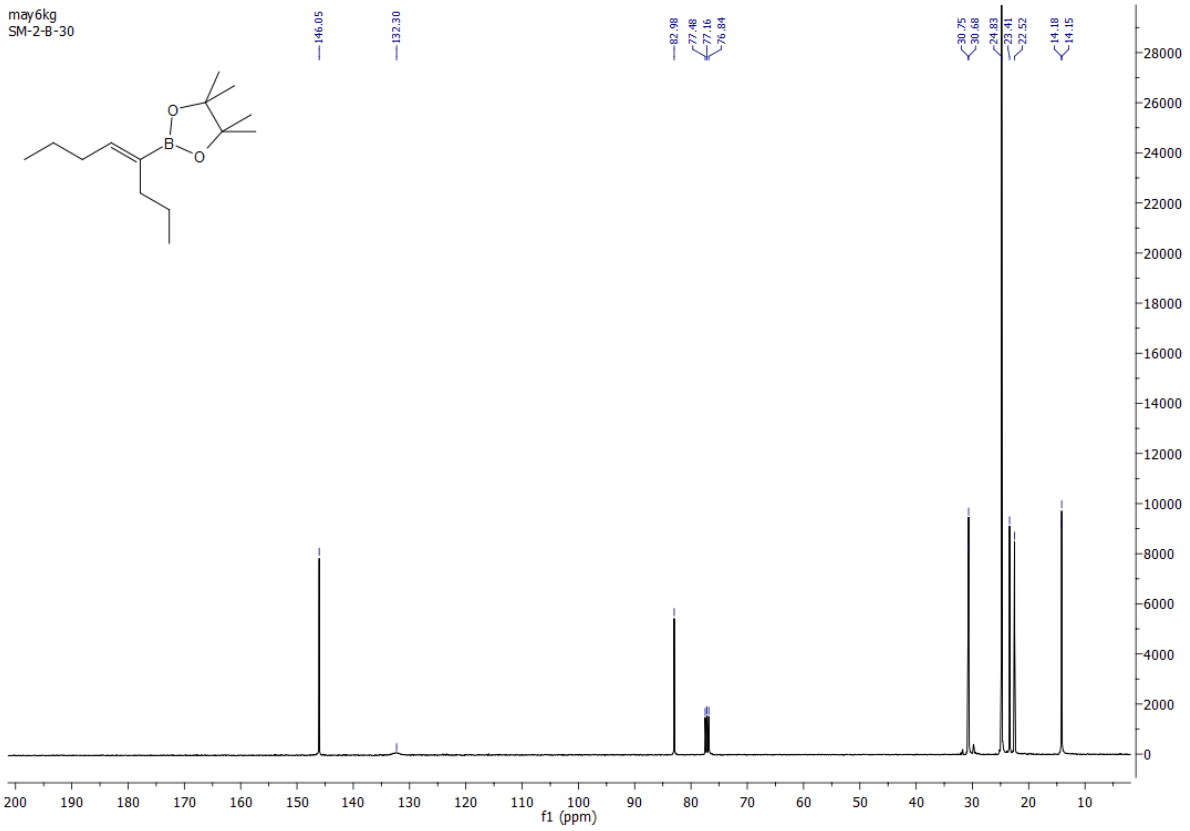
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

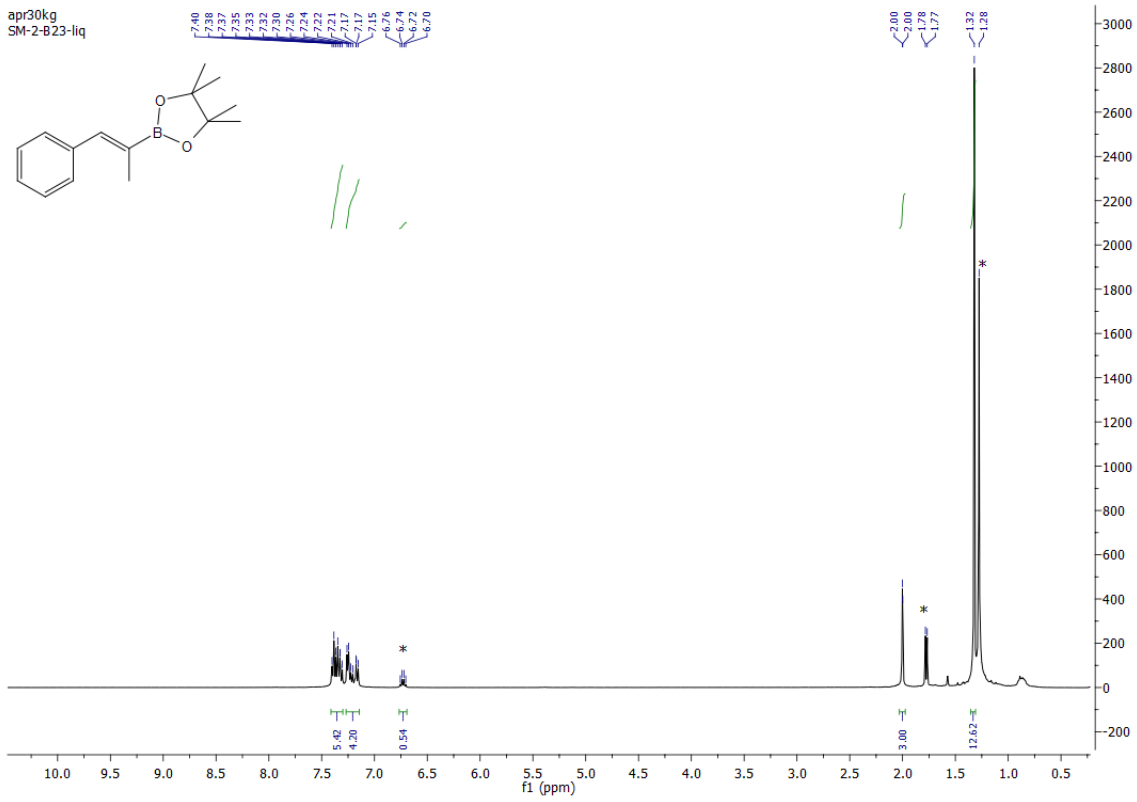


^{13}C NMR, $CDCl_3$, 100 MHz:

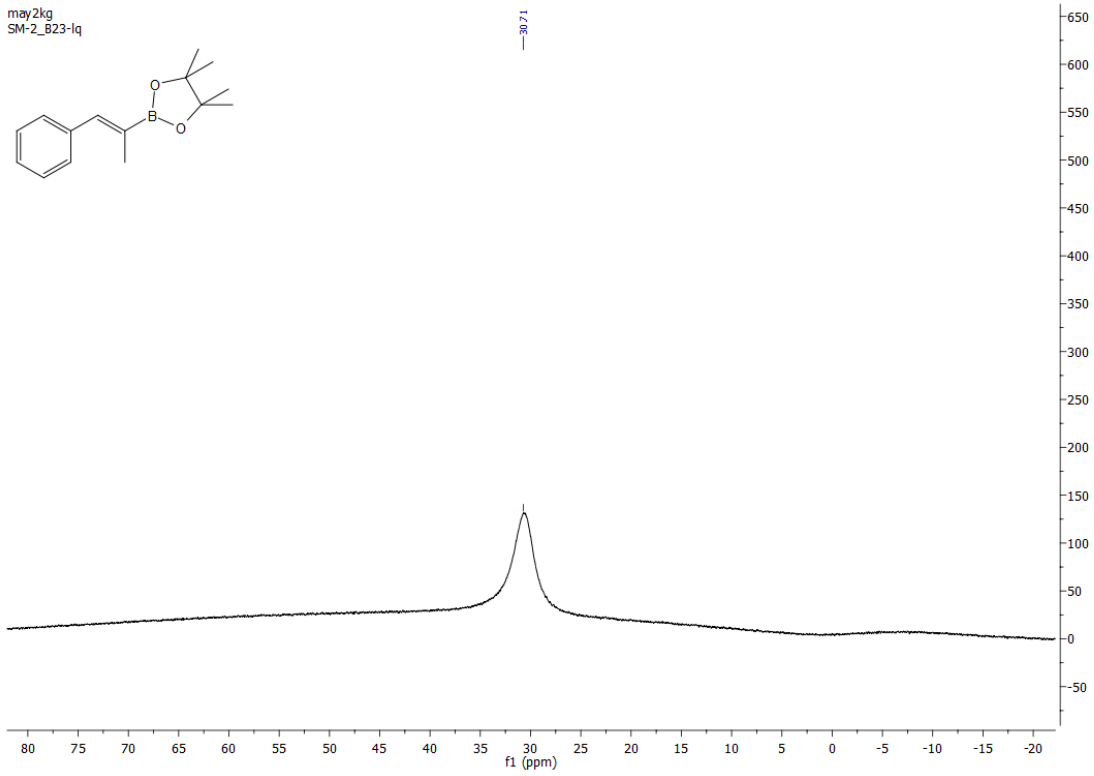


(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (22b)

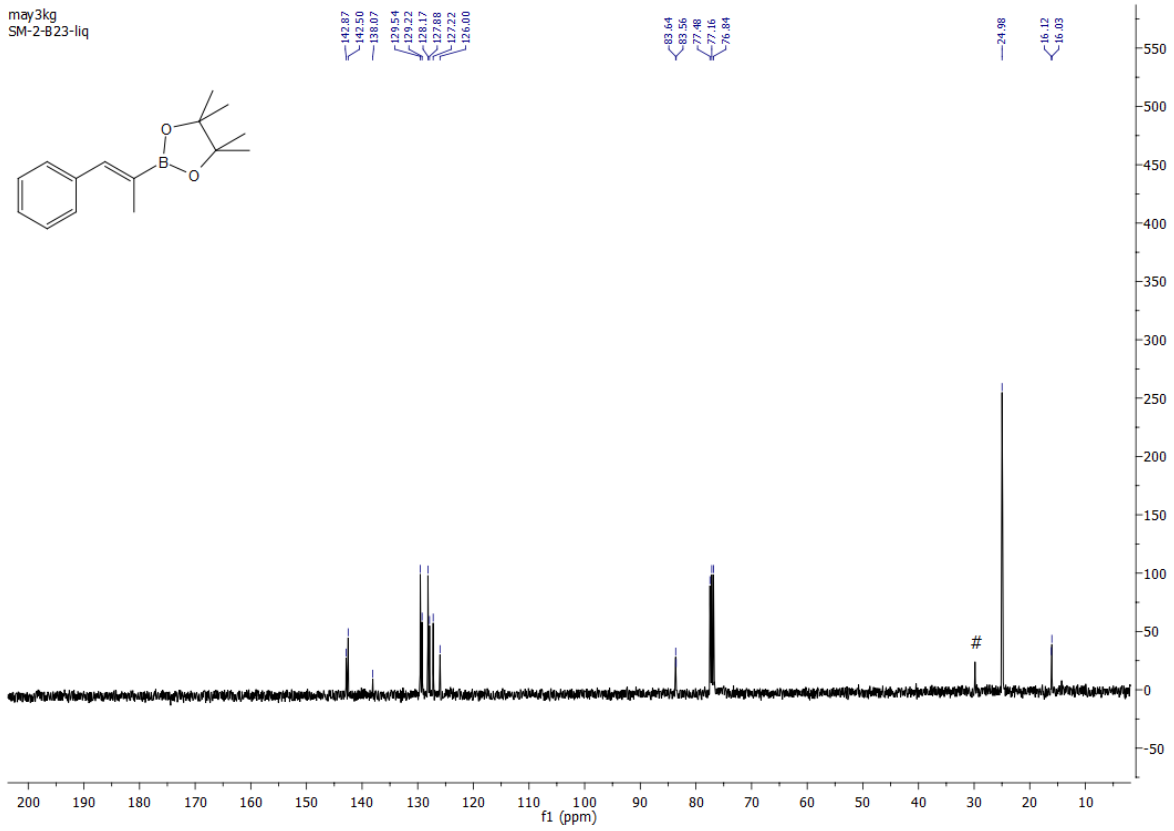
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

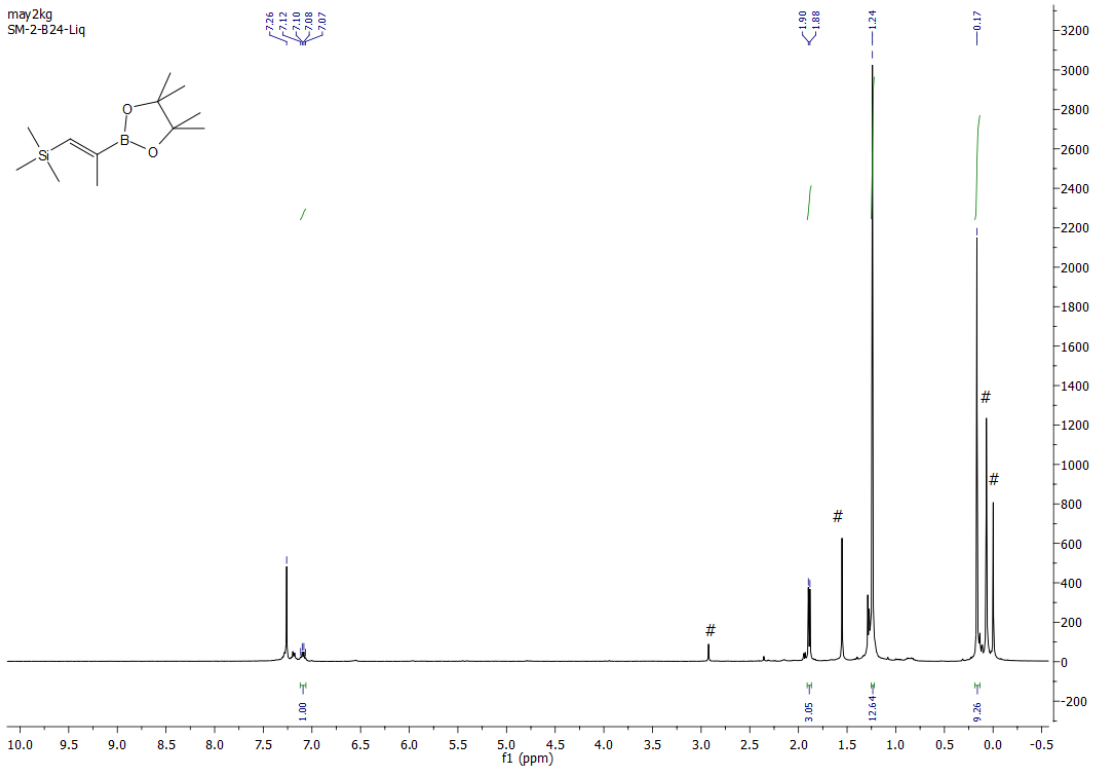


^{13}C NMR, $CDCl_3$, 100 MHz:

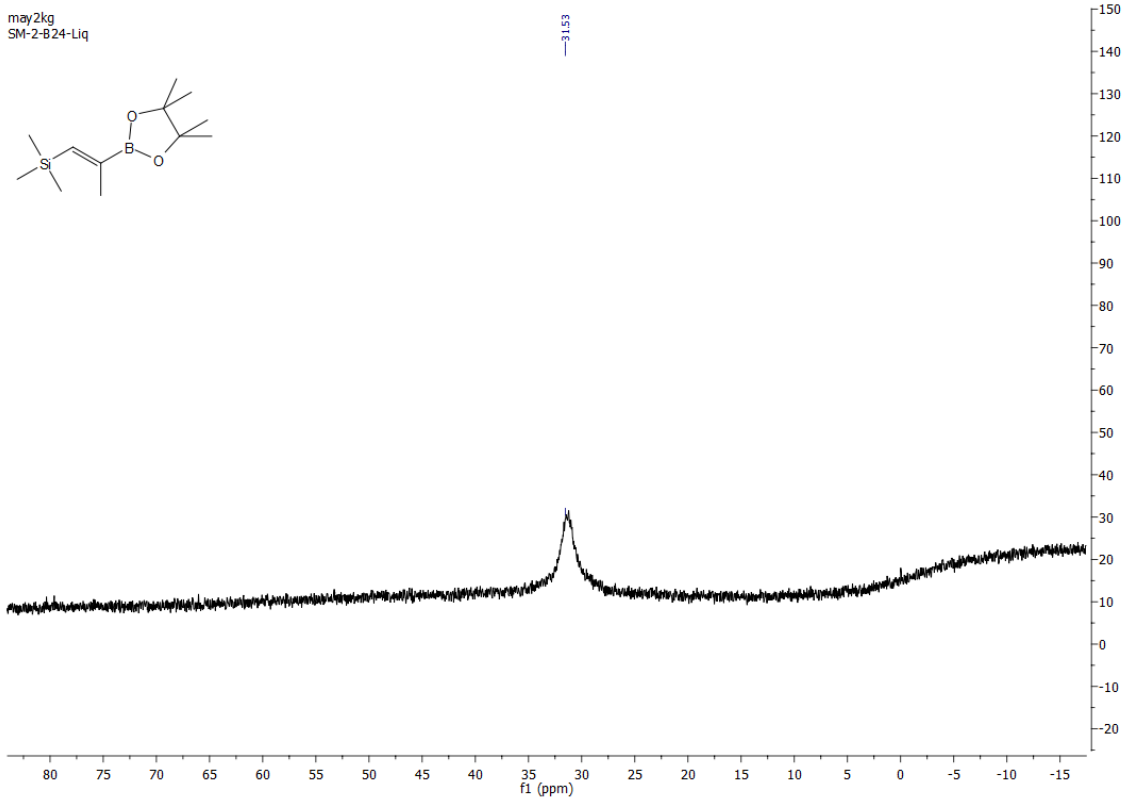


(*Z*)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (23b)

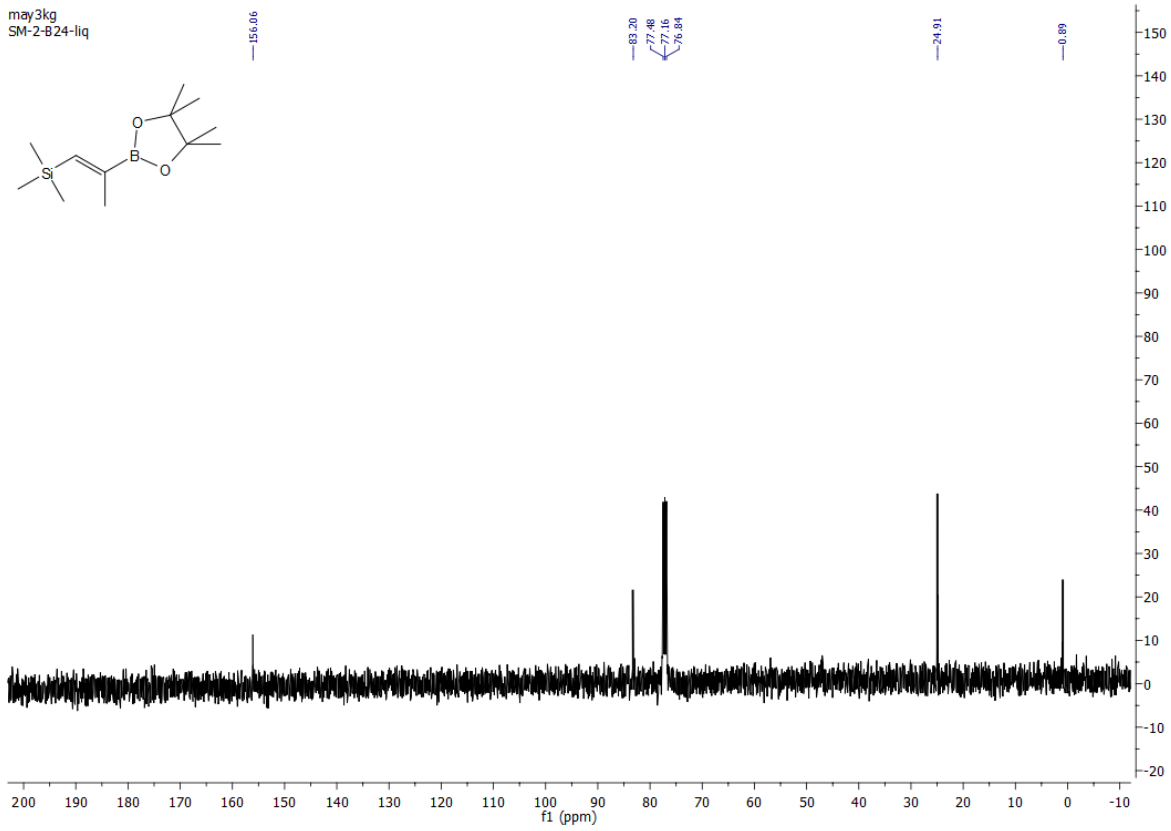
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

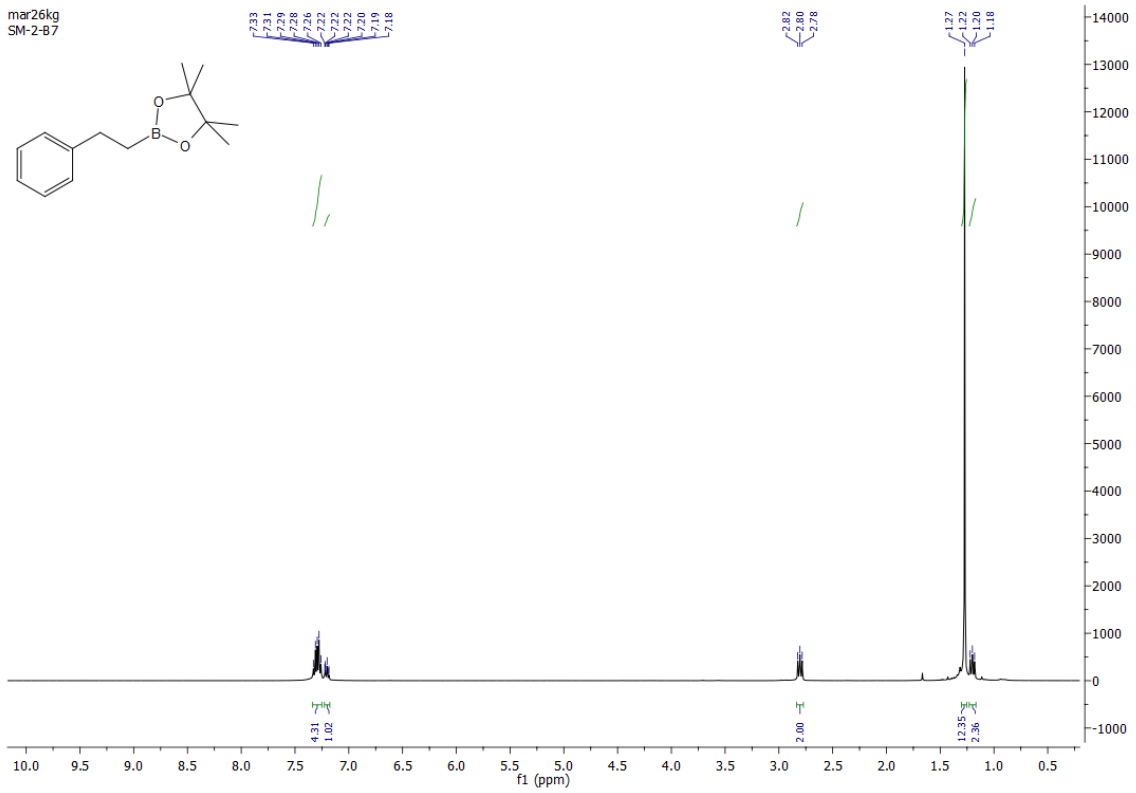


^{13}C NMR, $CDCl_3$, 100 MHz:

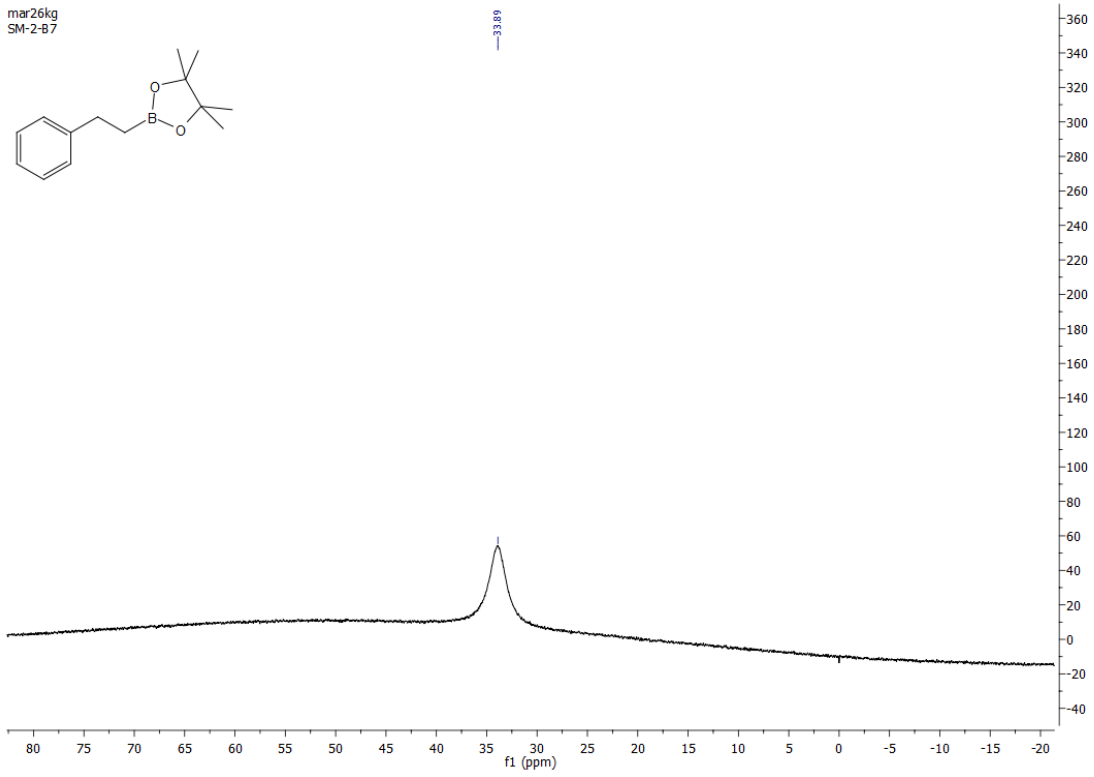


4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (24b)

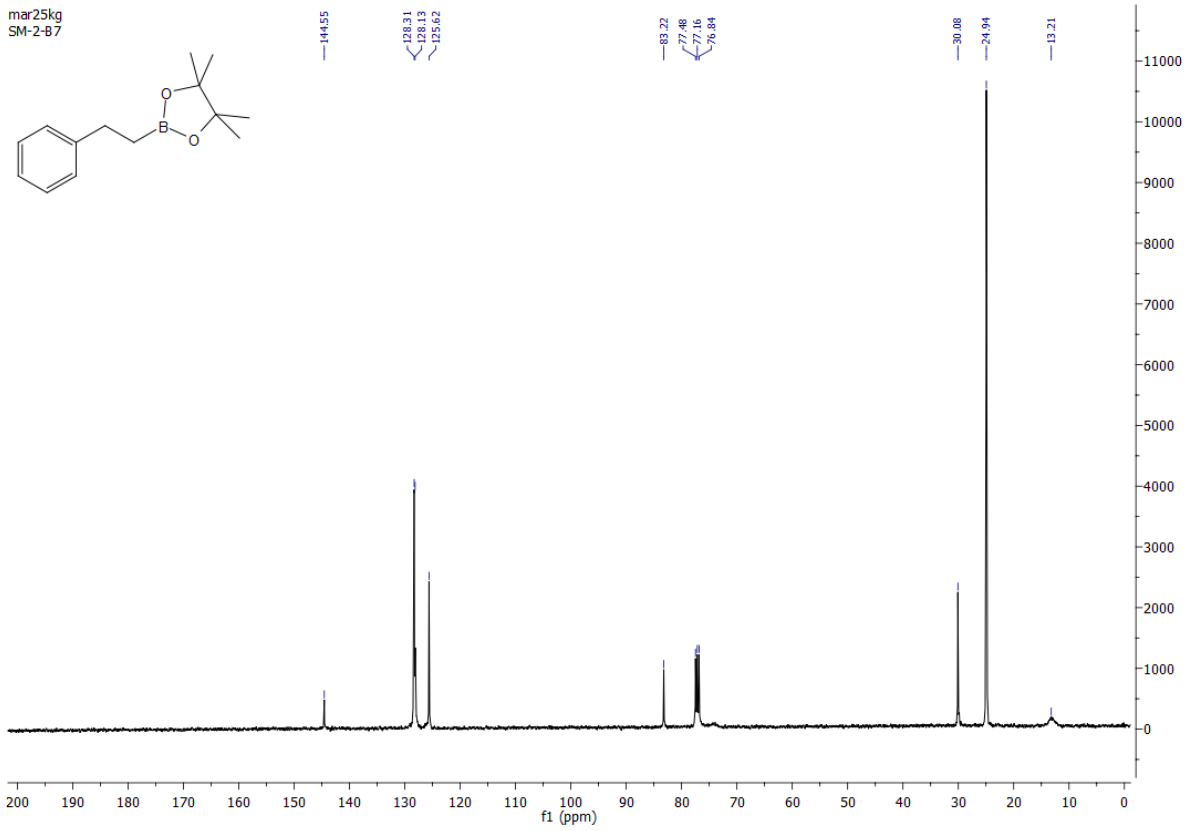
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

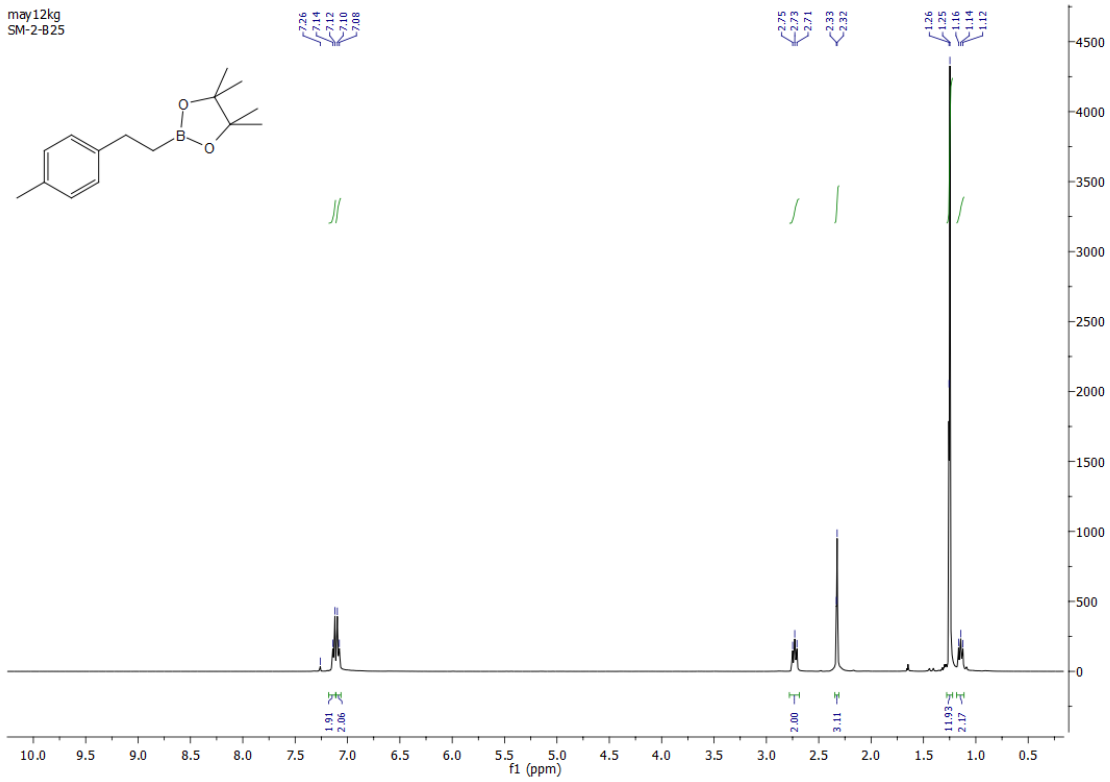


^{13}C NMR, $CDCl_3$, 100 MHz:

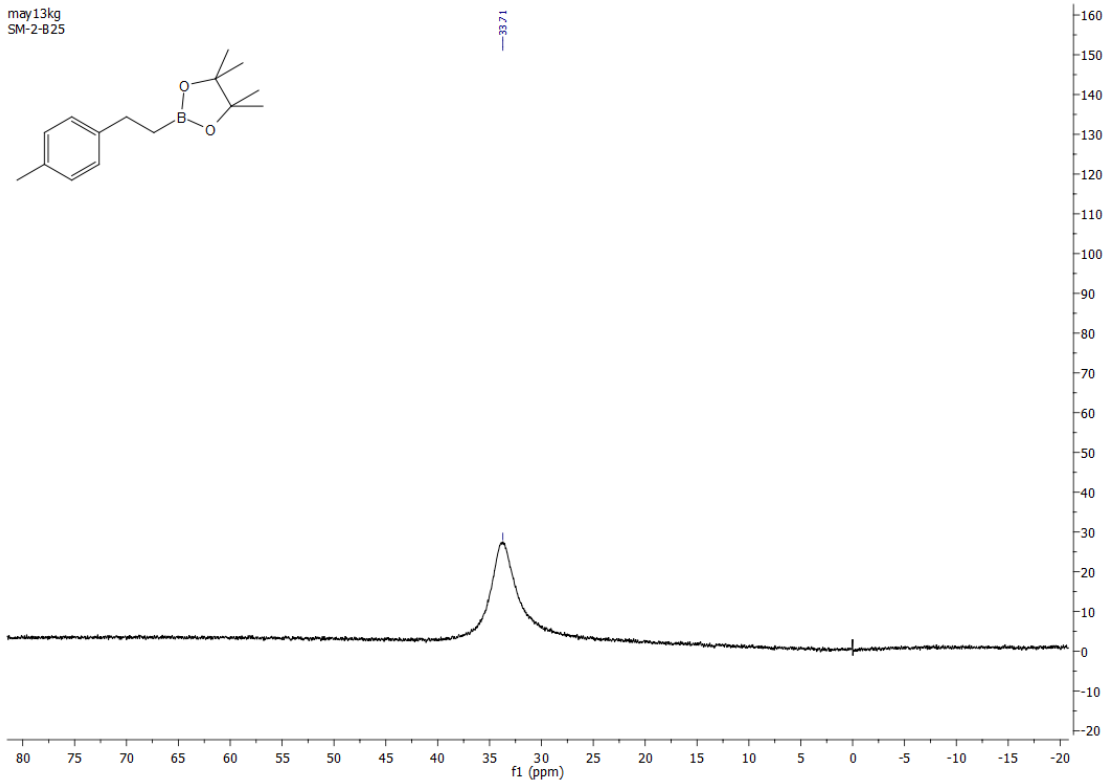


4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (25b)

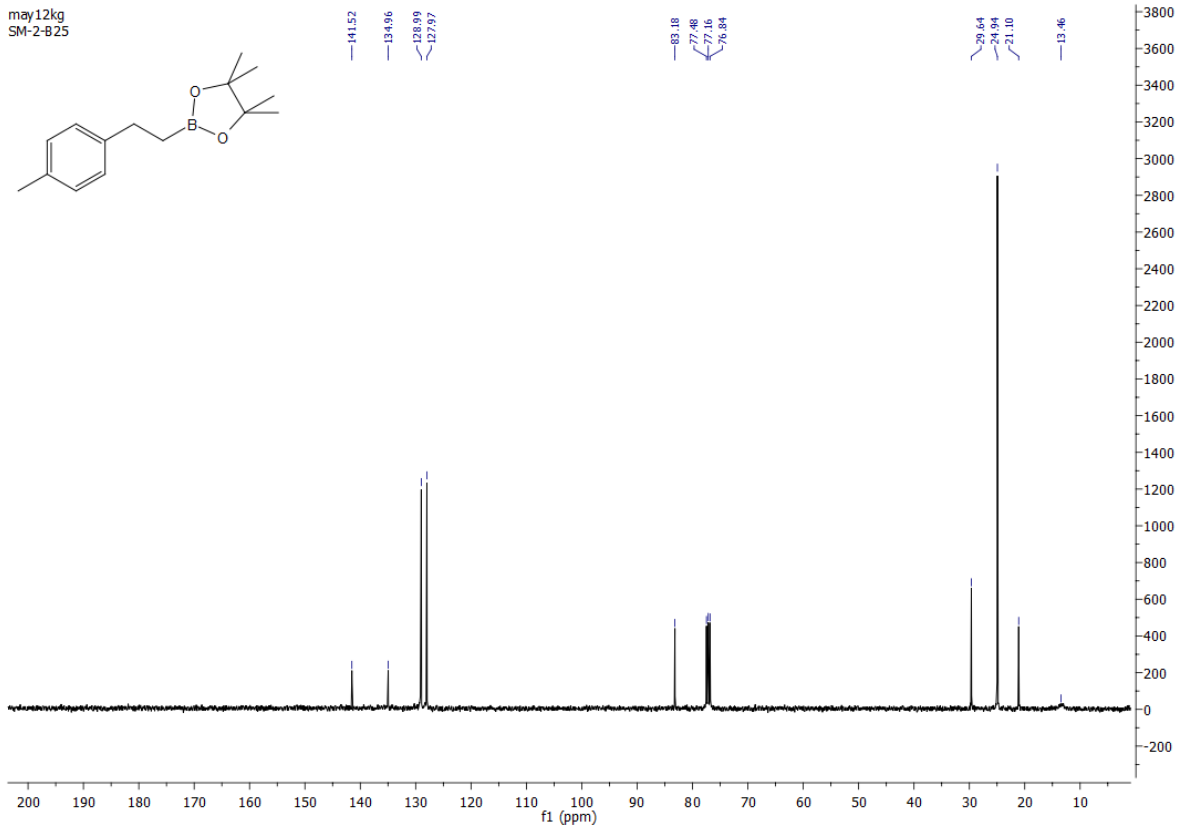
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

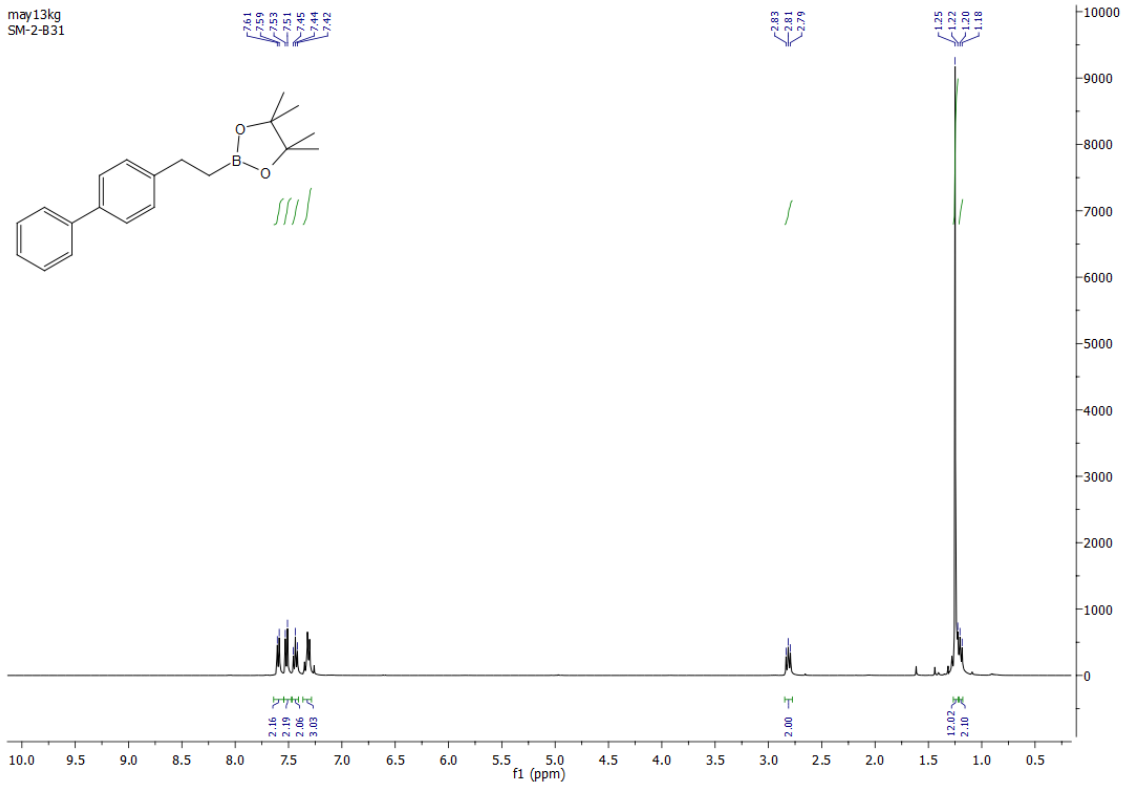


^{13}C NMR, $CDCl_3$, 100 MHz:

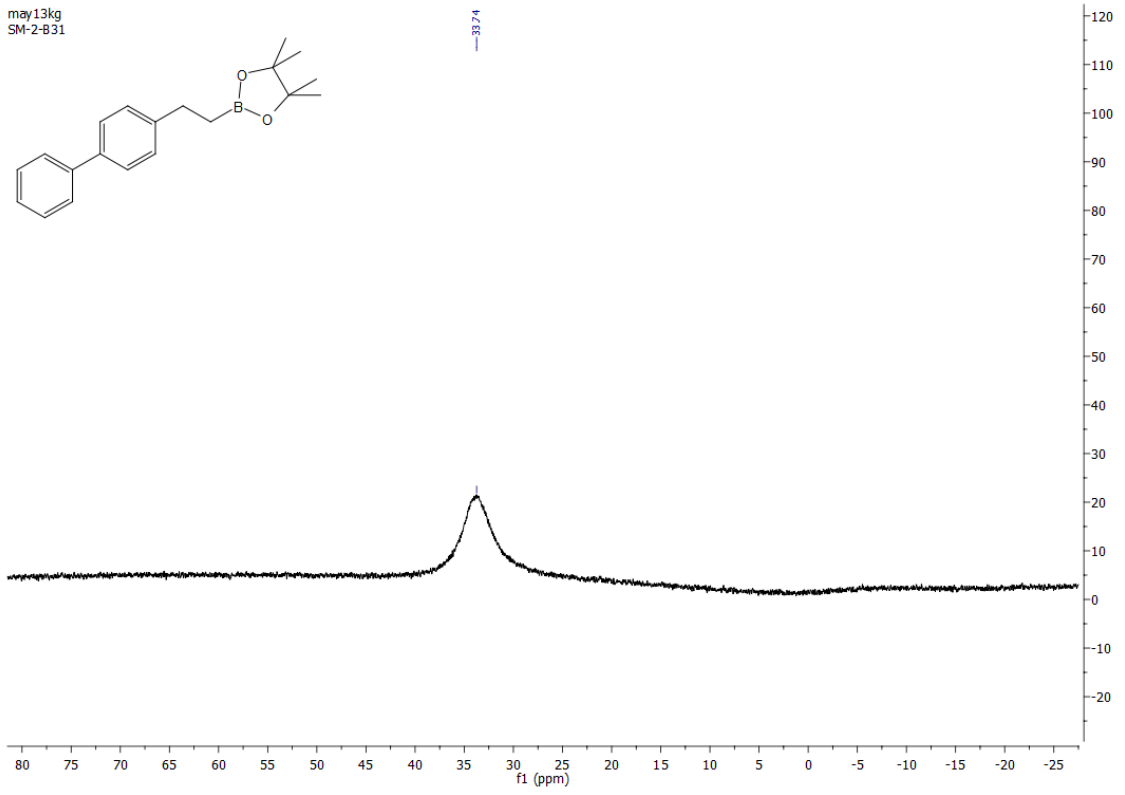


2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26b)

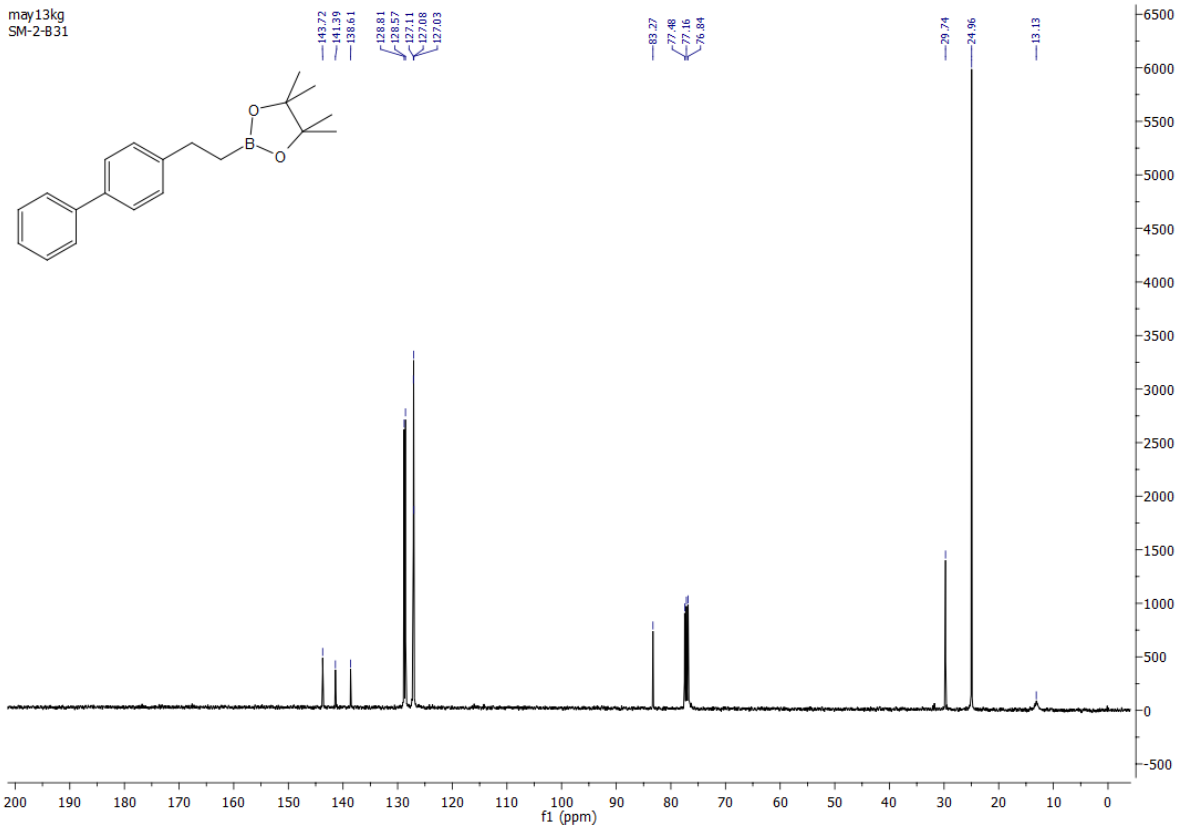
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

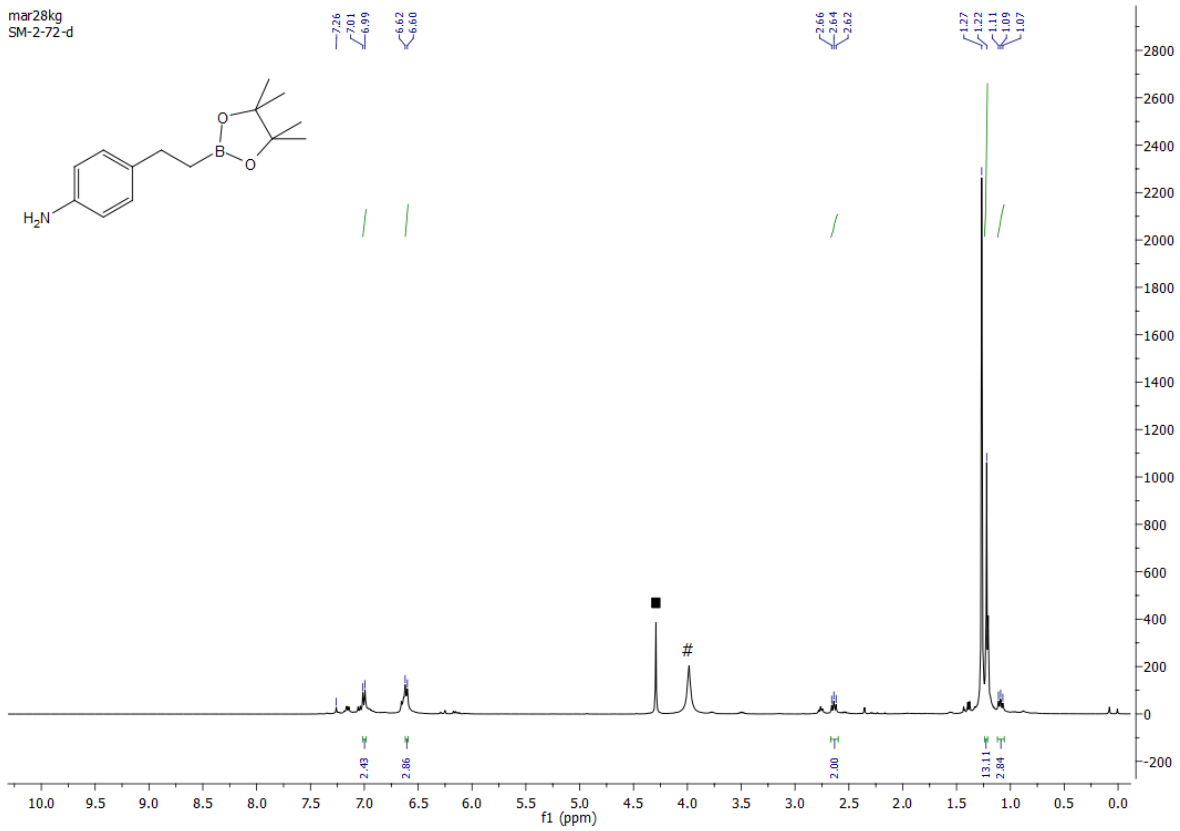


^{13}C NMR, $CDCl_3$, 100 MHz:



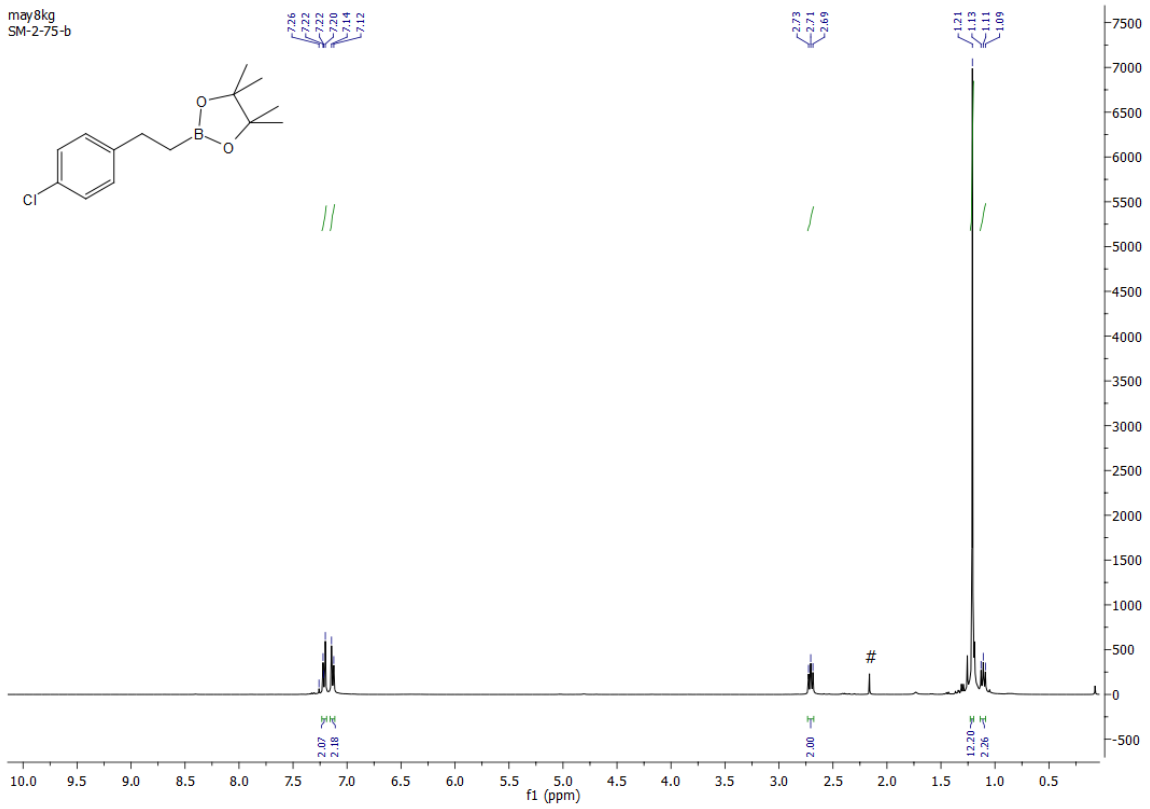
4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (27b)

^{1}H NMR, $CDCl_3$ 400 MHz:

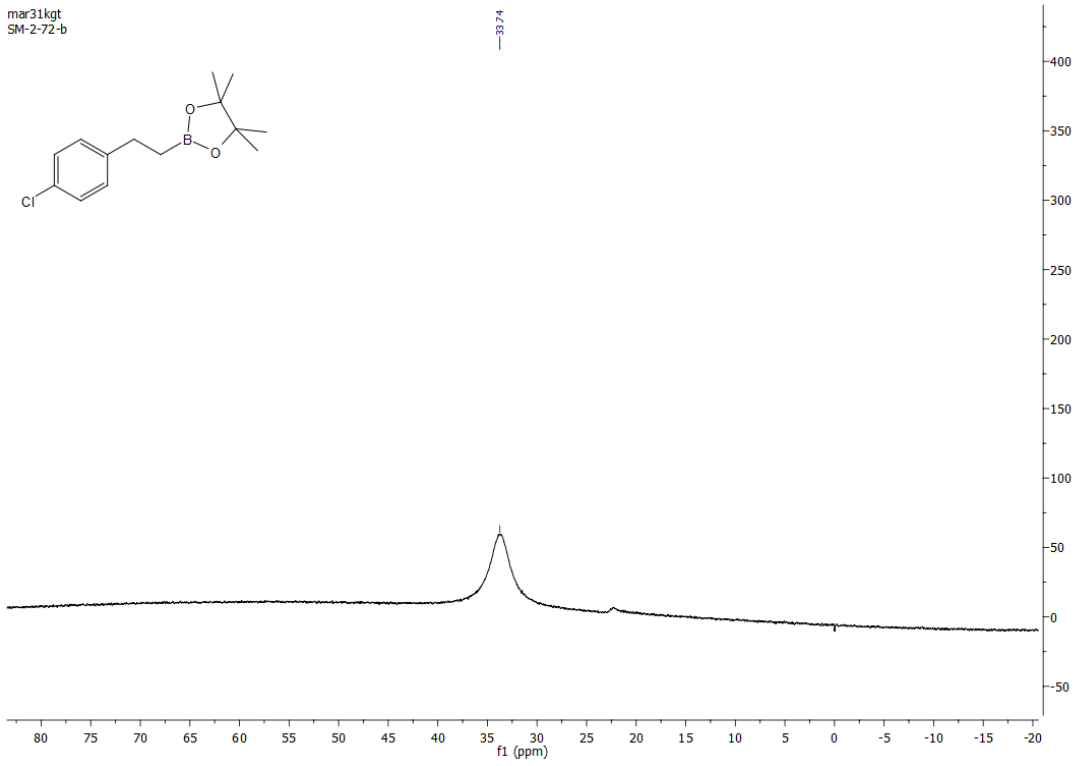


2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28b)

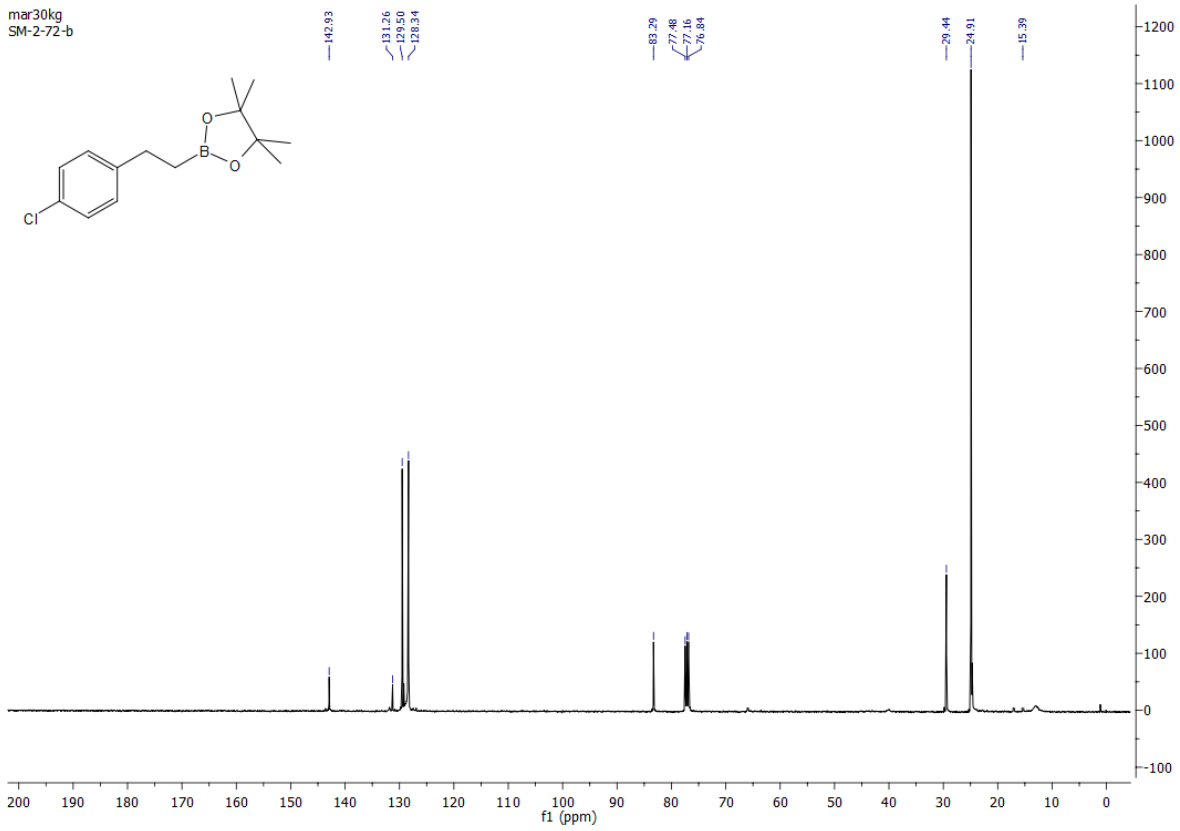
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

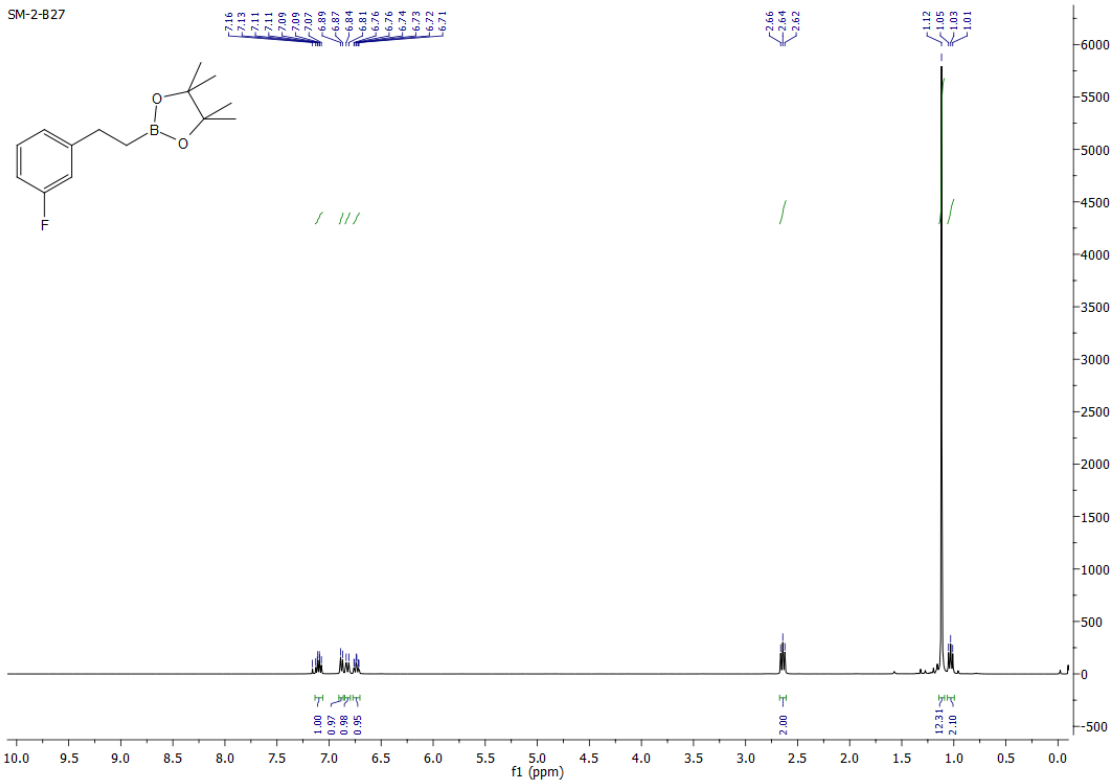


^{13}C NMR, $CDCl_3$, 100 MHz:

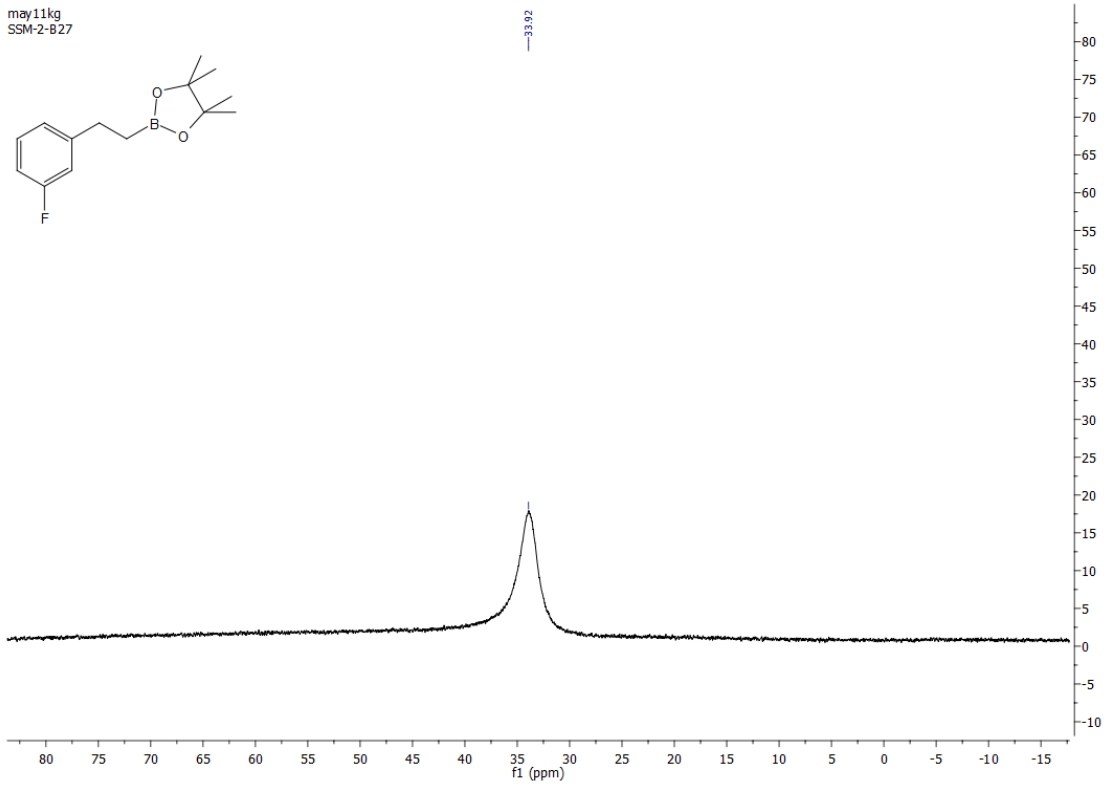


2-(3-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29b)

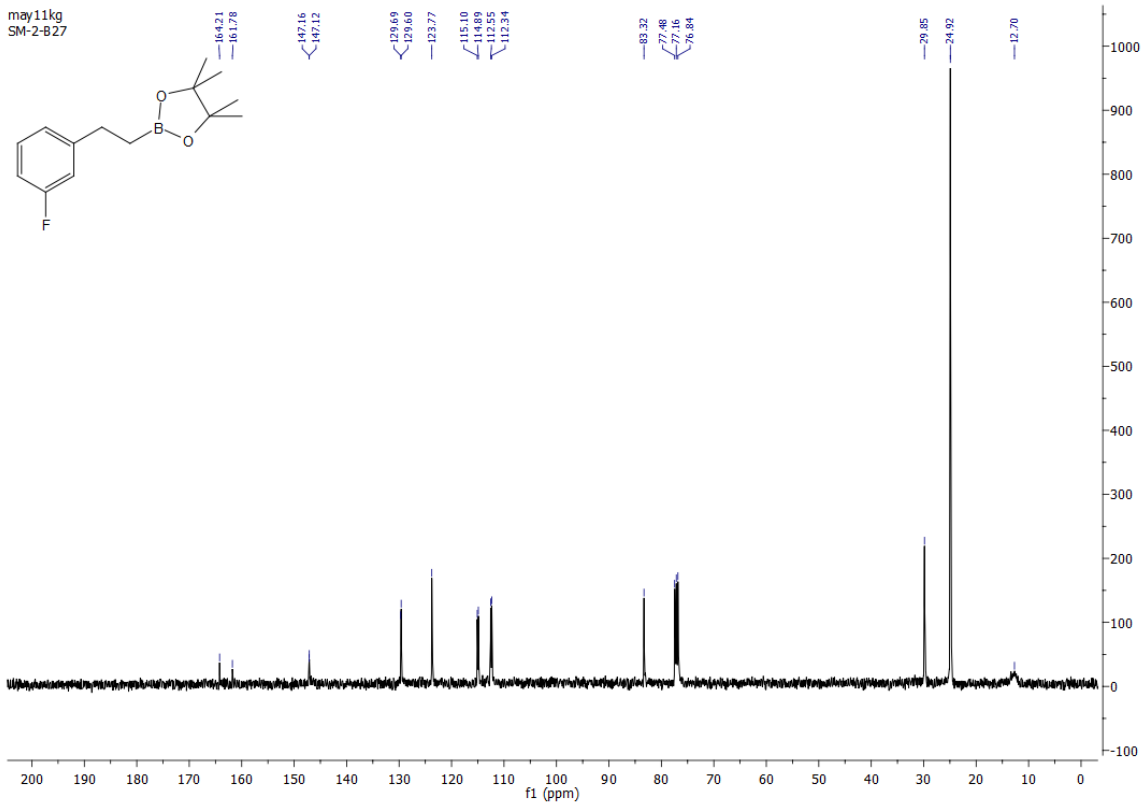
^{1}H NMR, $CDCl_3$ 400 MHz:



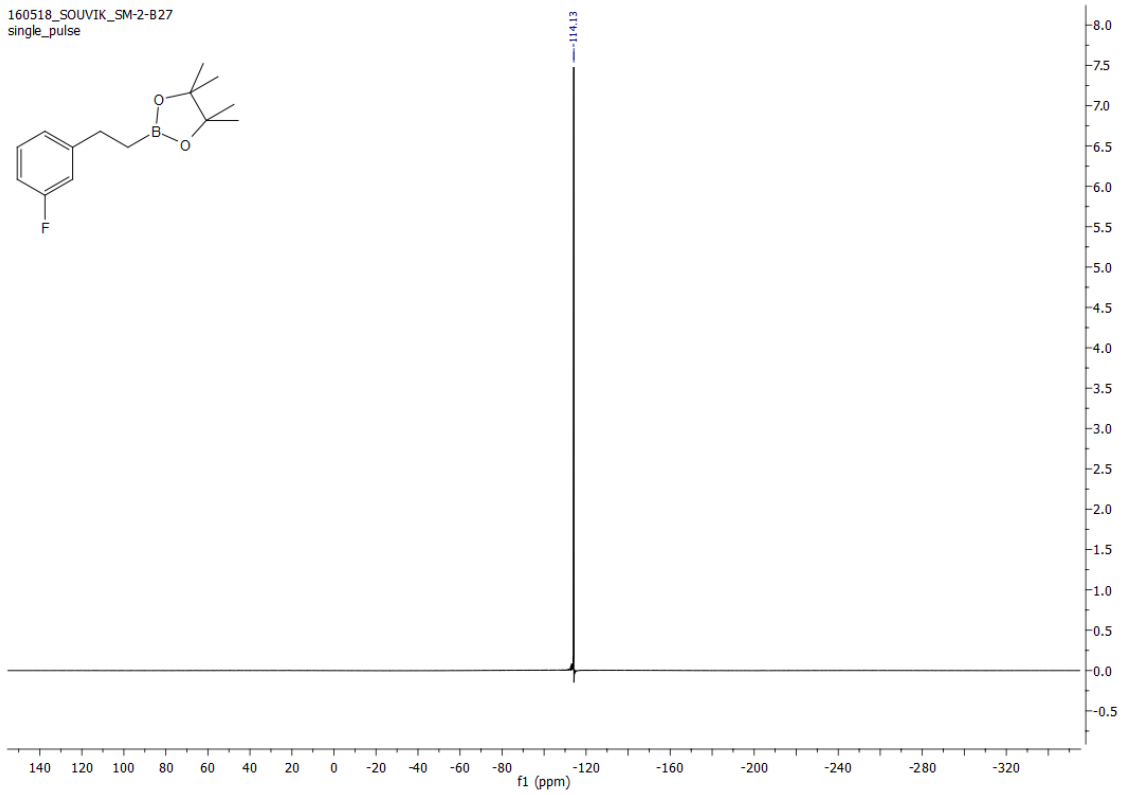
^{11}B NMR, $CDCl_3$, 128 MHz:



^{13}C NMR, $CDCl_3$, 100 MHz:

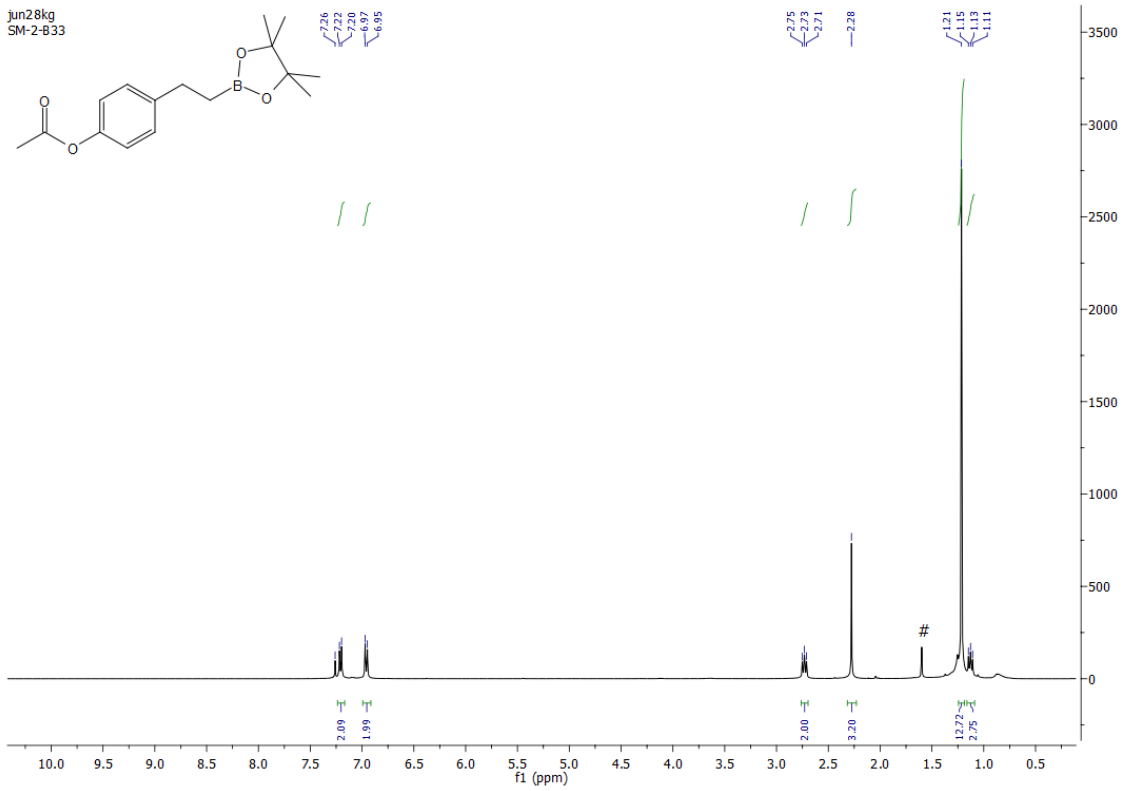


^{19}F NMR, $CDCl_3$, 407 MHz:

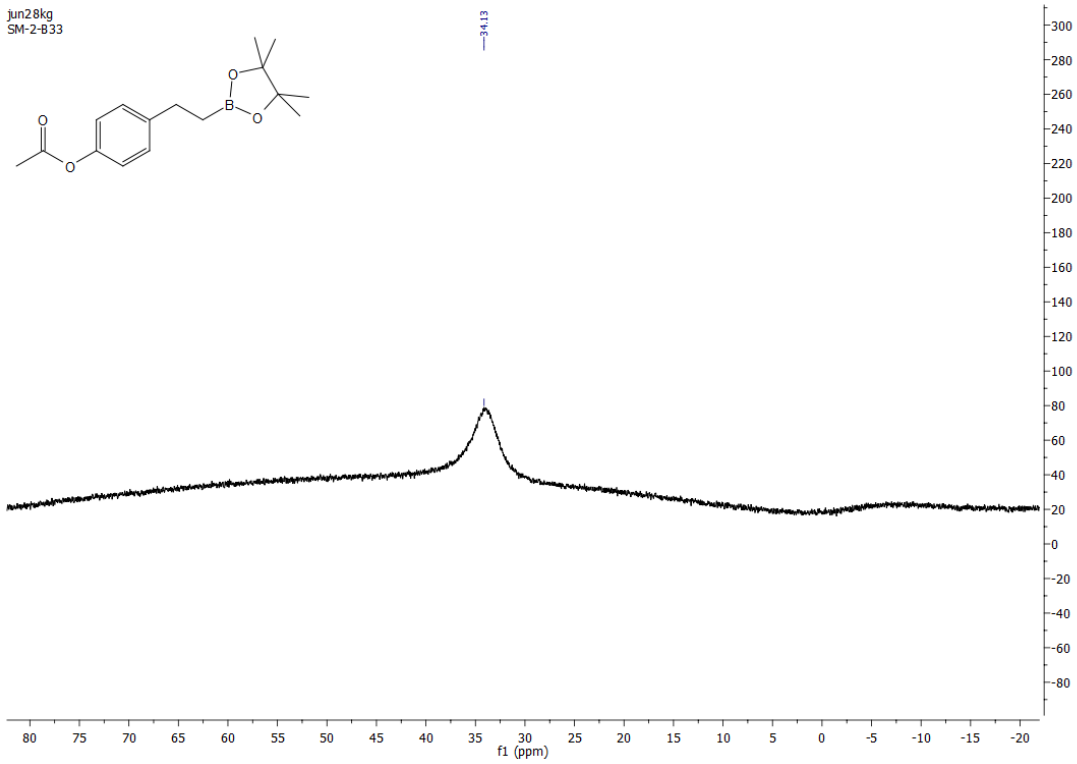


4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl acetate (30b)

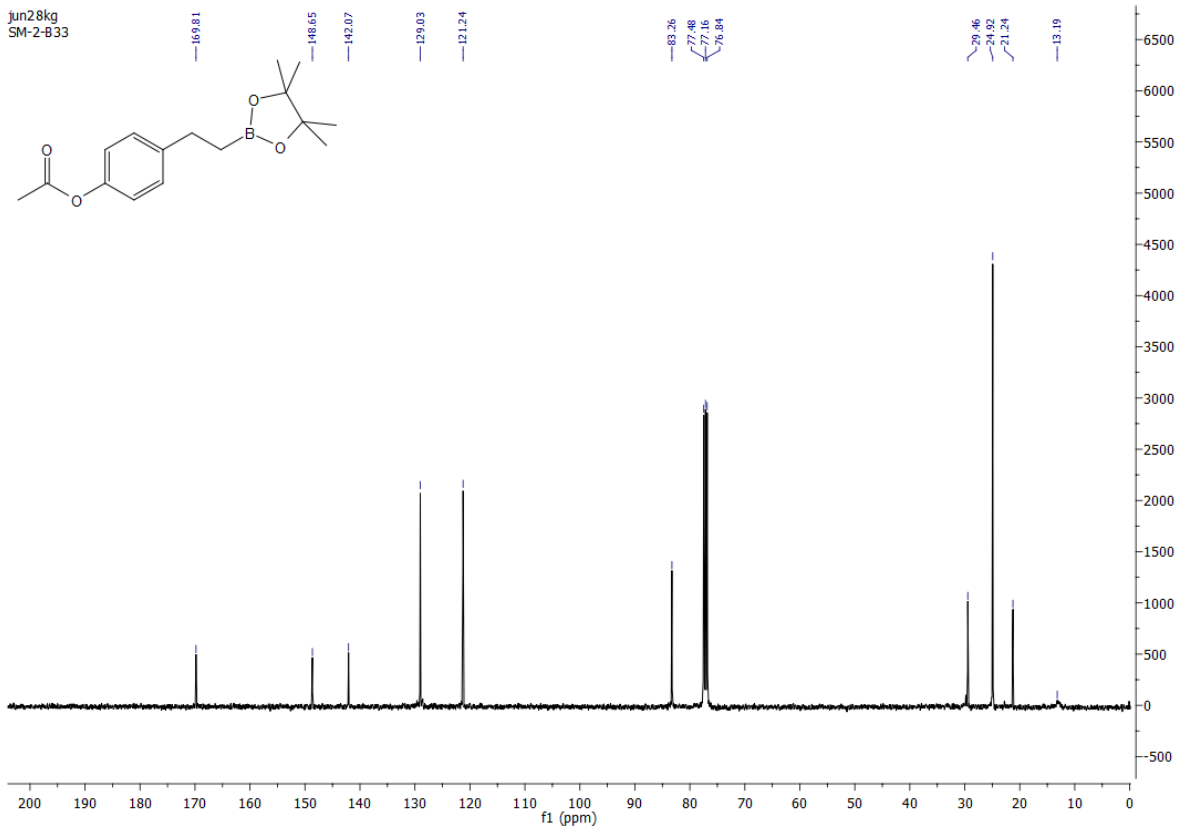
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:

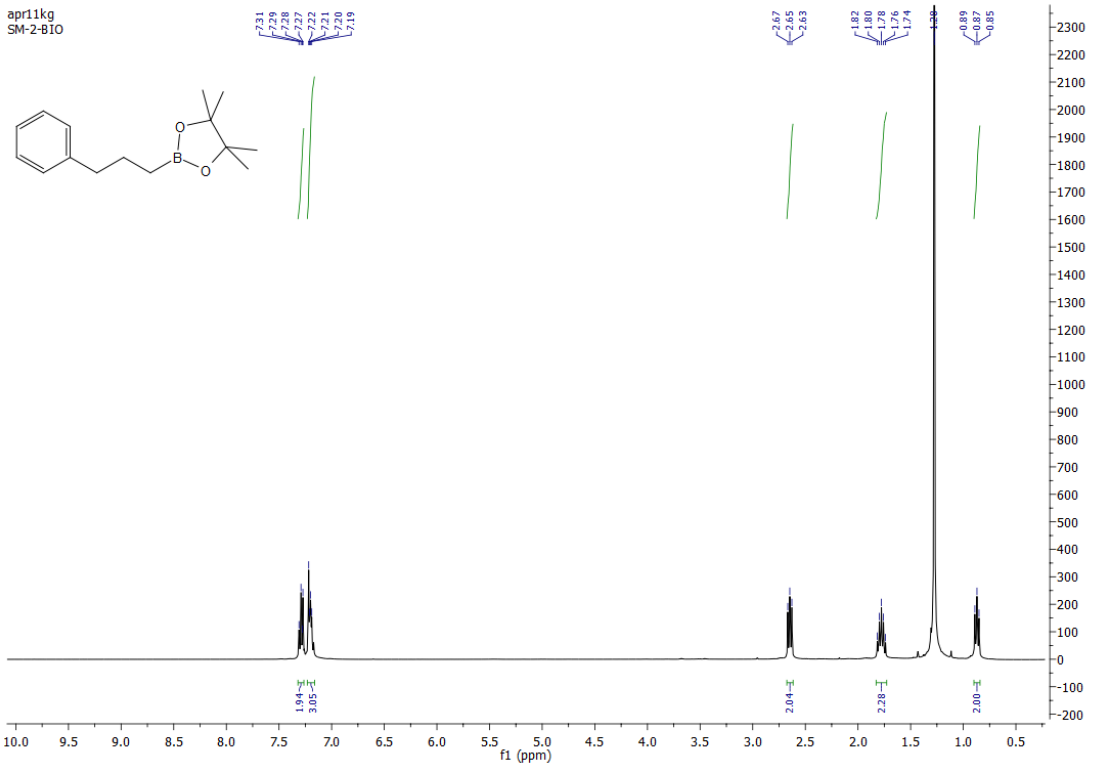


^{13}C NMR, $CDCl_3$, 100 MHz:

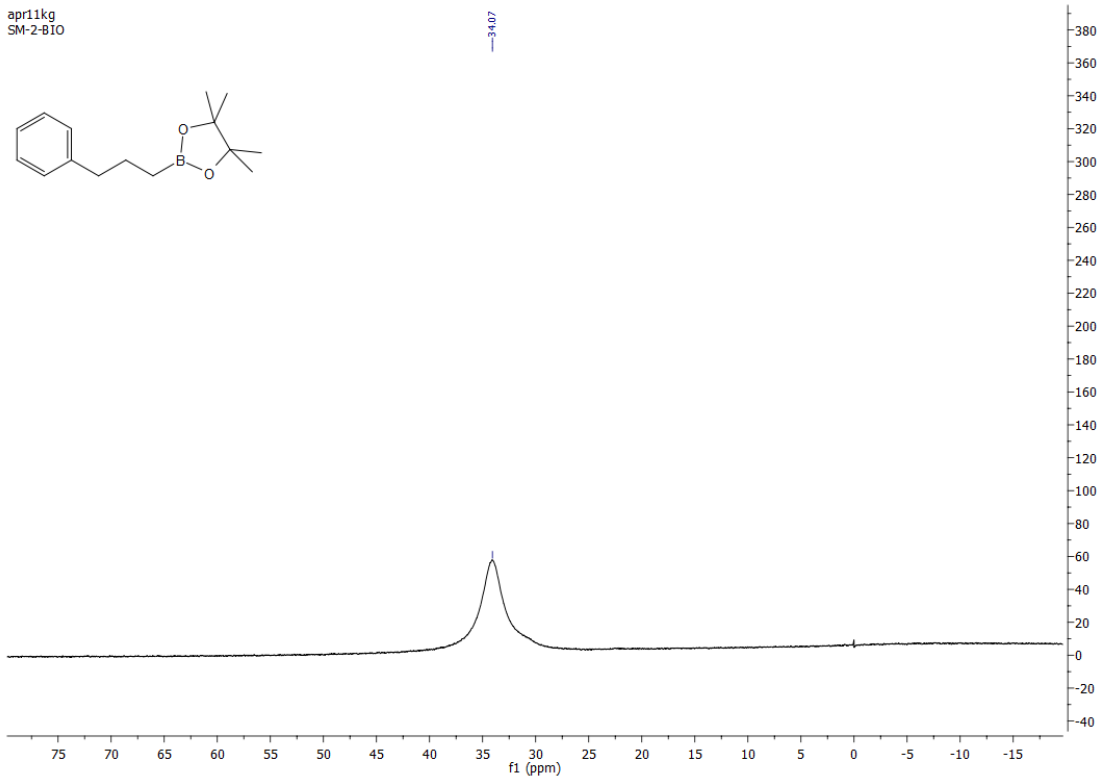


4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (31b)

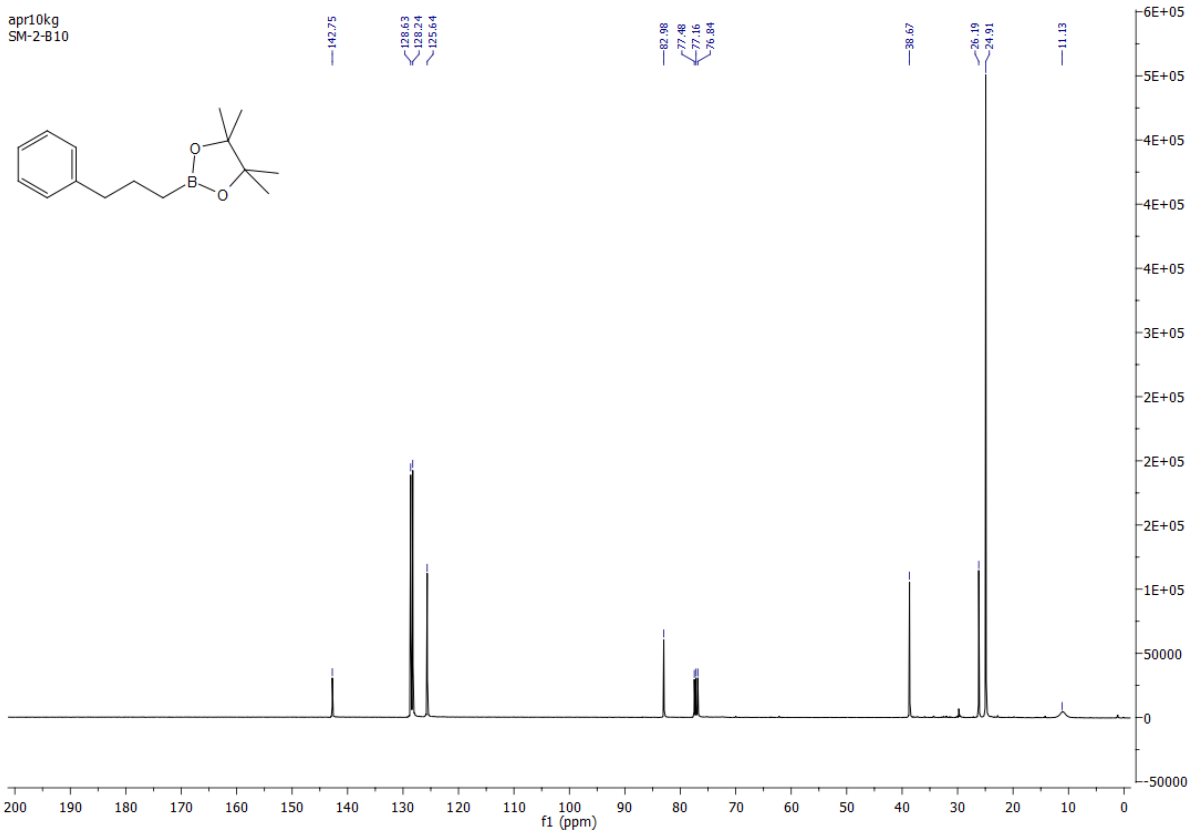
^{1}H NMR, $CDCl_3$ 400 MHz:



^{11}B NMR, $CDCl_3$, 128 MHz:



^{13}C NMR, $CDCl_3$, 100 MHz:



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