

Supporting Information

**Markovnikov Selective Co(I) Catalyzed Hydroboration of
Vinylarenes and Carbonyl Compounds**

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I. General information

Unless otherwise noted all the reactions are performed in nitrogen filled MBRAUN glove box or using standard Schlenk technique. All chemicals are purchased either from Sigma Aldrich, Alfa Aesar and Avra-chemicals and used without further purification unless mentioned. Pinacol borane (HBpin) was purchased from Sigma Aldrich. HBpin for bulk reactions was prepared from Bispinacolatodiborane (B_2pin_2) according to literature procedures.¹ B_2pin_2 was obtained from AllyChem Co. Ltd., China, and was used after further purification by sublimation process. Reagent grade solvents are purchased from SD Fine Chemicals (India), distilled and deoxygenated by freeze pump thaw cycle (three to four times) before using. $CDCl_3$ and C_6D_6 were purchased from either Cambridge Isotope Laboratories or Sigma Aldrich and deoxygenated by freeze pump thaw cycle and stored over molecular sieves before use. IMes (1,3-bis-(2,4,6-trimethylphenyl)imidazole-2-ylidene)^{2a} and $Co(IMes)_2Cl^{2b}$ were prepared according to literature procedures.

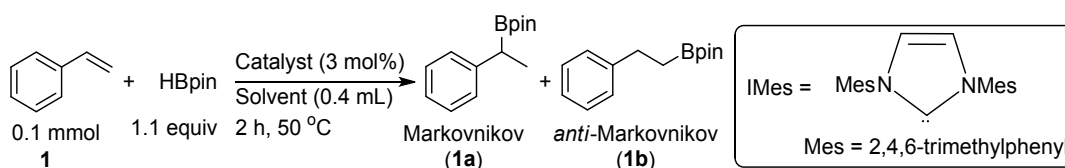
All NMR spectra (1H (400 MHz), $^{13}C\{^1H\}$ (100 MHz), ^{11}B (128 MHz), ^{19}F (376 MHz)) were recorded by a Bruker Avance 400MHz NMR spectrometer at an ambient temperature. 1H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6 : 7.16 ppm, C_4D_8O : 3.58 ppm), whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm). ^{11}B NMR signals are quoted relative to $BF_3 \cdot Et_2O$ and ^{19}F NMR signals are quoted using $FCCl_3$ as internal standard. 1H NMR yield was calculated as CH_3NO_2 (nitromethane) as an internal standard. GC-MS data were acquired using GCMS-QP2010 SE SHIMADZU system. For Electrospray ionization (ESI) mass spectral analysis, Agilent 6538 Ultra high definition (UHD) accurate Mass-Q-TOF (LC-HRMS) and Bruker Daltonics make Esquire 300 Plus ESI model mass spectrometers were used. Commercially available, pre-coated TLC-sheets ALUGRAM[®] Xtra Sil G/UV₂₅₄ was purchased from MACHEREY-NAGEL GmbH & Co. KG. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 55 °C.

II Optimization of the Reaction Conditions

Experimental procedure described in Table 1.

In a glass vial equipped with magnetic stirring bar, Co(IMes)₂Cl (3 mol %, 0.003 mmol), HBpin (1.1 equiv, 0.11 mmol), styrene (1 equiv, 0.1 mmol) were added followed by 0.4 mL of solvent. The reaction mixture was stirred at 50 °C for the indicated amount of time, then eluted with Et₂O:hexane (3:7) mixture through a plug of celite (Ø 3 mm × 8 mm). The solvent was removed in vacuum, further dried and nitromethane was added as an internal standard. The product yield was determined from ¹H NMR using nitromethane as an internal standard.

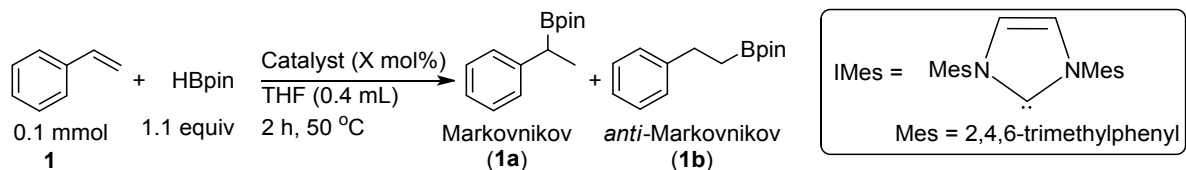
Table S1. Screening of solvents for the Hydroboration of styrene, 1.^a



Entry	Catalyst	Solvent	Yield (%) ^b	Ratio (1a : 1b) ^c
1.	Co(IMes) ₂ Cl	THF	97	95:5
2.	Co(IMes) ₂ Cl	1,2-DME	95	95:5
3.	Co(IMes) ₂ Cl	MTBE	78	83:17
4.	Co(IMes) ₂ Cl	Toluene	45	68:32
5.	Co(IMes) ₂ Cl	DMF	53	83:17
6.	Co(IMes) ₂ Cl	-	76	58:42

^a Reaction conditions: **1** (0.1 mmol), HBpin (0.11 mmol), Co(IMes)₂Cl (3 mol%) in 0.4 mL of solvent at 50 °C for 2 h unless otherwise stated. ^b Combined yields (**1a**+**1b**) were determined by ¹H NMR analysis using nitromethane as an internal standard. ^c Product ratios determined from ¹H NMR of crude reaction mixtures.

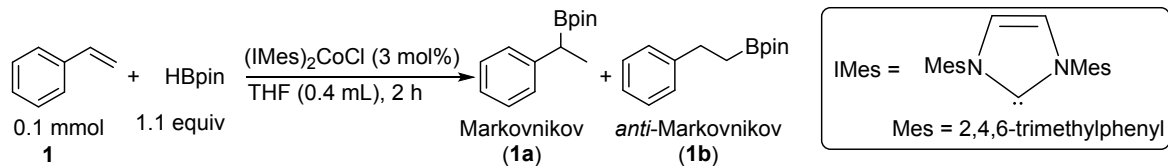
Table S2. Screening of catalyst and catalyst loading for the Hydroboration of styrene, 1.^a



Entry	Catalyst	Catalyst loading	Solvent	Yield (%) ^b	Ratio (1a : 1b) ^c
1.	Co(IMes) ₂ Cl ₂	5 mol %	THF	--	--
2.	CoCl ₂	5 mol %	THF	--	--
3.	Imes	5 mol %	THF	--	--
4.	--	--	THF	--	--
5.	Co(IMes) ₂ Cl	1 mol %	THF	70	96:4
6.	Co(IMes) ₂ Cl ^d	1 mol %	THF	80	93:7
7.	Co(IMes) ₂ Cl	3 mol %	THF	97	95:5
8.	Co(IMes) ₂ Cl ^e	3 mol %	THF	58	25:75
9.	Co(IMes) ₂ Cl	5 mol %	THF	97	95:5

^a Reaction conditions: **1** (0.1 mmol), HBpin (0.11 mmol), catalyst (X mol %) in 0.4 mL of THF at 50 °C for 2 h unless otherwise stated. ^b Combined yields (**1a**+**1b**) were determined by ¹H NMR analysis using nitromethane as an internal standard. ^c Product ratios determined from ¹H NMR of crude reaction mixtures. ^d Reaction was carried out for 8 h. ^e Catecholborane (HBcat) was used as a boron reagent.

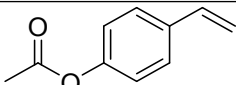
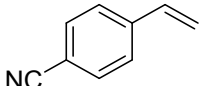
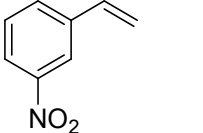
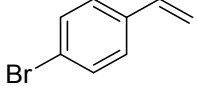
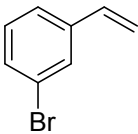
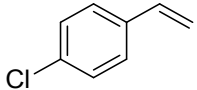
Table S3. Screening of reaction temperature for the Hydroboration of styrene, **1.^a**



Entry	Catalyst	T (°C)	Solvent	Yield (%) ^b	Ratio (1a : 1b) ^c
1.	Co(IMes) ₂ Cl	RT	THF	92	96:4
2.	Co(IMes) ₂ Cl	50 °C	THF	97	95:5
3.	Co(IMes) ₂ Cl	80 °C	THF	97	85:15

^a Reaction conditions: **1** (0.1 mmol), HBpin (0.11 mmol), Co(IMes)₂Cl (3 mol %) in 0.4 mL of THF for 2 h unless otherwise stated. ^b Combined yields (**1a**+**1b**) were determined by ¹H NMR analysis using nitromethane as an internal standard. ^c Product ratios determined from ¹H NMR of crude reaction mixtures.

Table S4: Examples of substrates which are incompatible for hydroboration by HBpin in presence of Co(IMes)₂Cl.^a

entry	substrates	Temp, time	outcome
1.		rt, 12 h	Mixture of carbonyl, branched and linear hydroborated product along with vinylboronate.
2.		rt, 12 h	Mixture of alkene and nitrile hydroboration product.
3.		rt, 12 h	Hydroboration of N=O bond to give 95% of borylated product. No hydroboration of alkene.
4.		50 °C, 24 h	4-Bpin-styrene – 21% by Ar-Br activation. No hydroboration of alkene. Rest, unreacted starting material.
5.		50 °C, 24 h	3-Bpin-styrene – 12% by Ar-Br activation. No hydroboration of alkene. Rest, unreacted starting material.
6.		50 °C, 6 h	4-Bpin-styrene – 23% by Ar-Cl activation. Hydroboration of alkene: Branched product 37%, Linear product: 24%.

^a Reaction conditions: Alkene (0.1 mmol), HBpin (0.11 mmol), Co(IMes)₂Cl (3 mol %) in 0.4 mL of THF unless otherwise stated. Analysis is based on NMR spectra and GCMS.

III. Substrate Scope

General procedure A, for small scale reaction to get NMR yield:

In a glass vial equipped with magnetic stirring bar, alkene (0.1 mmol), HBpin (1.1 equiv, 0.11 mmol), Co(IMes)₂Cl (3 mol%, 0.003 mmol), were added followed by 0.4 mL of solvent. The reaction mixture was stirred at 50 °C for the indicated amount of time, then eluted with Et₂O: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.

General procedure B, for larger scale catalytic reactions:

In a glass vial equipped with magnetic stirring bar, alkene (1.0 mmol), HBpin (1.1 equiv, 1.1 mmol), Co(IMes)₂Cl (3 mol%, 0.03 mmol), were added followed by 1.2 mL of THF. The reaction mixture was stirred at 50°C for the indicated amount of time. After completion, the reaction mixture was eluted with Et₂O: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.

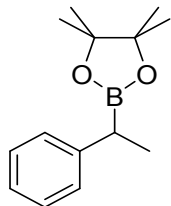
General Procedure C, for NMR scale catalytic reaction of aldehyde and ketone:

In a glass vial equipped with magnetic stirring bar, aldehyde or ketone (0.5 mmol), HBpin (1.1 equiv, 0.55 mmol), Co(IMes)₂Cl (1 mol%, 0.005 mmol), were added followed by 0.8 mL of THF. The reaction mixture was stirred at room temperature for 2 h. 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.

Spectral Data

Co(I)-catalyzed Markovnikov selective hydroboration of alkenes:

2-(1-Phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**).



The product was obtained following general procedure B as colourless oil in 86% yield (199 mg) from **1** (104 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.³

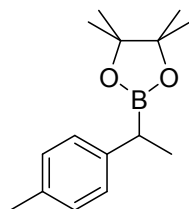
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.30-7.24 (m, 4H), 7.18-7.14 (m, 1H), 2.47 (q, J = 7.5 Hz, 1H), 1.37 (d, J = 7.5 Hz, 3H), 1.27 (s, 6H), 1.24 (s, 6H).

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.7.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 145.1, 128.4, 127.9, 125.2, 83.4, 30.6 (br, *C-B*), 24.73, 24.69, 17.2.

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

4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)ethyl)-1,3,2-dioxaborolane (**2a**).



The product was obtained following general procedure B as colourless oil in 91% yield (224 mg) from **2** (118 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.⁴

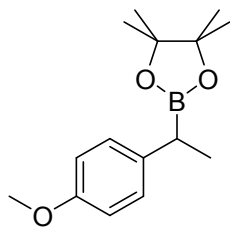
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.13-7.05 (m, 4H), 2.39 (q, J = 7.5 Hz, 1H), 2.30 (s, 3H), 1.31 (d, J = 7.5 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H).

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.6.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 141.8, 134.3, 129.0, 127.7, 83.8, 29.5 (br, *C-B*), 24.64, 24.61, 20.9, 17.3.

GC-MS: m/z 246 (M^+)

2-(1-(4-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a).



The product was obtained following general procedure B as colourless oil in 82% yield (215 mg) from **3** (134 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.³

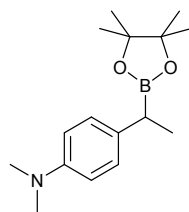
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.20-7.17 (m, 2H), 6.87-6.85 (m, 2H), 3.80 (s, 3H), 2.42 (q, J = 7.4 Hz, 1H), 1.33 (d, J = 7.5 Hz, 3H), 1.26 (s, 6H), 1.24 (s, 6H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.7

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 157.7, 137.4, 129.1, 114.2, 83.7, 55.6, 29.7 (br, *C-B*), 25.1, 17.9

GC-MS: m/z 262 (M^+)

4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N,N*-dimethylbenzenamine (4a).



The product was obtained following general procedure A as colourless oil from **4** in 86% yield (NMR).

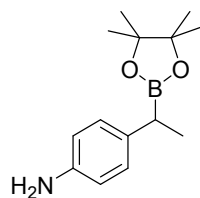
The spectroscopic data is consistent with literature data.³

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.14 (d, J = 7.5 Hz, 2H), 6.73 (d, J = 7.6 Hz, 2H), 2.94 (s, 6H), 2.36 (br, 1H), 1.33 (d, J = 7.6 Hz, 3H), 1.26 (s, 6H), 1.24 (s, 6H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.9

GC-MS: m/z 275 (M^+)

4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzenamine (5a).



In a glass vial equipped with magnetic stirring bar, 4-vinylaniline (1.0 mmol), HBpin (2.2 equiv, 2.2 mmol), Co(IMes)₂Cl (3 mol%, 0.3 mmol), were added followed by 1.2 mL of THF. The reaction mixture was stirred at 50 °C for 24 h. Without exposing the reaction mixture to air, the solvent was evaporated under vacuum to remove unreacted HBpin. The crude mixture was then extracted with hexane, passed through cotton (product was unstable in silica or celite) and solvent was removed under vacuum. Product was obtained as a colourless oil in 74% (183 mg) yield.

The spectroscopic data is consistent with literature data.³

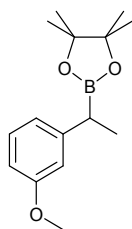
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.04 – 6.97 (m, 2H), 6.66 – 6.58 (m, 2H), 3.58 (br-s, 2H), 2.55 (q, J = 7.60 Hz, 1H), 1.30 (br, 3H), 1.27 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 34.5

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 114.2, 134.1, 128.4, 115.2, 83.0, 24.5, 15.9.

GC-MS: m/z 247 (M⁺).

2-[1-(3-Methoxyphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a).



The product was obtained following general procedure B as colourless oil in 79% yield (207 mg) from **5** (134 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.⁵

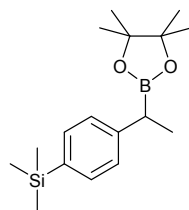
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.19 (t, J = 7.9 Hz, 1H), 6.83-6.79 (m, 2H), 6.70-6.68 (m, 1H), 3.79 (s, 3H), 2.3 (q, J = 7.4 Hz, 1H), 1.34 (d, J = 7.5 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.7

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.7, 146.7, 129.3, 120.4, 113.6, 110.6, 83.4, 55.1, 24.71, 24.69, 17.11

GC-MS: m/z 262 (M⁺)

2-(1-(4-Trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a)



The product was obtained following general procedure B as colourless oil in 55% yield (167 mg) from **6** (176 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.³

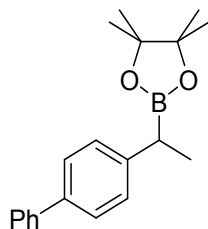
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.47-7.45 (m, 2H), 7.27-7.25 (m, 2H), 2.47 (q, J = 7.5 Hz, 1H), 1.37 (d, J = 7.5 Hz, 3H), 1.26 (s, 6H), 1.24 (s, 6H), 0.27 (s, 9H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.3

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 145.7, 136.3, 133.5, 127.4, 83.3, 30.0 (br, *C-B*), 24.7, 17.2, -0.87

GC-MS: m/z 304 (M⁺)

2-(1-(1,1'-Biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a).



The product was obtained following general procedure B as white solid in 71% yield (216 mg) from **7** (180 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.³

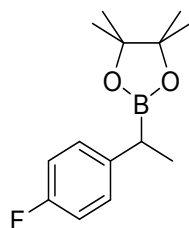
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.63-7.60 (m, 2H), 7.55-7.53 (m, 2H), 7.46-7.42 (m, 2H), 7.35-7.32 (m, 3H), 2.51 (q, J = 7.5 Hz, 1H), 1.40 (d, J = 7.5 Hz, 3H), 1.26 (s, 6H), 1.25 (s, 6H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.9.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 144.3, 141.4, 138.1, 128.8, 128.3, 127.1, 127.0, 126.9, 83.5, 24.77, 24.74, 17.2

GC-MS: m/z 308 (M⁺)

2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a).



The product was obtained following general procedure B as colourless oil in 83% yield (207 mg) from **8** (122 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.³

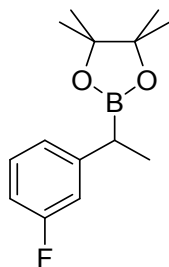
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.19-7.15 (m, 2H), 6.96-6.92 (m, 2H), 2.42 (q, J = 7.5 Hz, 1H), 1.31 (d, J = 7.5 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.4.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 161.0 (d, J = 240.8 Hz), 140.6 (d, J = 2.8 Hz), 129.1 (d, J = 7.6 Hz), 115.0 (d, J = 20.8 Hz), 83.4, 24.69, 24.65, 17.3

GC-MS: m/z 250 (M⁺)

2-(1-(3-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10a).



The product was obtained following general procedure B as colourless oil in 80% yield (200 mg) from **9** (122 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.³

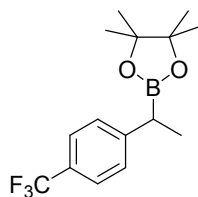
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.23-7.14 (m, 1H), 7.00-6.98 (m, 1H), 6.96-6.93 (m, 1H), 6.86-6.79 (m, 1H), 2.45 (q, J = 7.4 Hz, 1H), 1.33 (d, J = 7.5 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.5.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.4 (d, J = 243.0 Hz), 148.1 (d, J = 7.1 Hz), 129.98 (d, J = 8.3 Hz), 123.9 (d, J = 2.4 Hz), 115.0 (d, J = 20.9 Hz), 112.6 (d, J = 21.0 Hz), 83.9, 25.06, 25.01, 17.2.

GC-MS: m/z 250 (M^+).

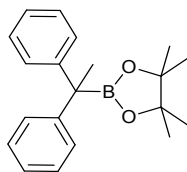
2-(1-(4-Trifluoromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11a).



The spectroscopic data is consistent with literature data.³ Since the two isomers could not be separated, the integration was not possible in ¹H NMR.

GC-MS: m/z 300 (M^+).

2-(1,1-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12a).



The new product was obtained following general procedure B as white solid in 83% yield (271 mg) from **10** (180 mg, 1.0 mmol).

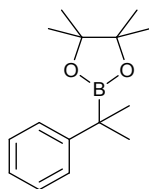
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.28-7.20 (m, 8H), 7.19-7.15 (m, 2H), 1.71 (s, 3H), 1.22 (s, 12H).

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

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 147.8, 128.7, 128.1, 125.5, 83.9, 25.9, 24.6.

GC-MS: m/z 308 (M^+), HRMS: m/z 331.3667 [$\text{M}+\text{Na}$] $^+$.

4,4,5,5-Tetramethyl-2-(2-phenylpropan-2-yl)-1,3,2-dioxaborolane (13a).



The product was obtained following general procedure B as colourless oil in 75% yield (184 mg) from **11** (118 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.⁶

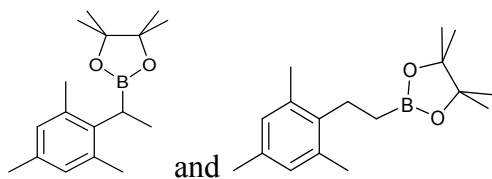
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.42-7.34 (m, 4H), 7.23-7.19 (m, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 1.28 (s, 6H), 1.27 (s, 6H).

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 34.4.

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 148.6, 128.1, 126.3, 125.0, 83.3, 35.9, 25.7, 24.5.

GC-MS: m/z 246 (M^+)

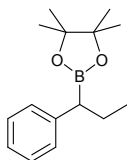
2-(1-Mesitylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14a).



The spectroscopic data is consistent with literature data.^{6,7} Since the two isomers could not be separated, the integration was not possible in ¹H NMR.

GC-MS: m/z 274 (M⁺).

4,4,5,5-Tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (15a).



The product was obtained following general procedure B as colourless oil in 92% yield (226 mg) from **15** (118 mg, 1.0 mmol).

The product **15a** was obtained following general procedure B as colourless oil in 70% yield (226 mg) from **22** (118 mg, 1.0 mmol). The formation of **15a** from **22** is due to the isomerization hydroboration reaction. The other isomer was anti-Markovnikov hydroborated product.

The spectroscopic data is consistent with literature data.⁸

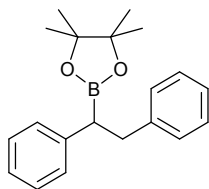
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.32-7.26 (m, 4H), 7.20-7.16 (m, 1H), 2.28 (t, *J* = 7.8 Hz, 1H), 1.95-1.93 (m, 1H), 1.75-1.73 (m, 1H), 1.27 (s, 6H), 1.25 (s, 6H), 0.97 (t, *J* = 7.3 Hz, 3H).

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.7.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 143.4, 128.4, 128.3, 125.2, 83.3, 29.5 (br, *C-B*), 25.9, 24.7, 24.6, 14.0.

GC-MS: m/z 246 (M⁺)

2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-Dioxaborolane (16a).



The product was obtained following general procedure B as white solid in 74% yield (228 mg) from **14** (180 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.⁷

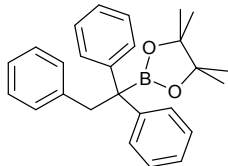
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.38-7.21 (m, 10H), 3.27 (dd, $J = 13.4$ Hz, $J = 9.8$ Hz, 1H), 3.08 (dd, $J = 13.4$ Hz, $J = 9.8$ Hz, 1H), 2.8 (dd, $J = 9.7$ Hz, $J = 9.8$ Hz, 1H), 1.21 (s, 6H), 1.19 (s, 6H).

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 32.8.

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.6, 141.7, 128.9, 128.7, 128.4, 128.4, 128.1, 125.8, 125.4, 83.3, 38.9, 34.4 (br, C-B), 24.6, 24.5.

GC-MS: m/z 308 (M⁺)

2-(1,1,2-triphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17a).



The new product was obtained following general procedure B as white solid in 68% yield (261 mg) from **15** (256 mg, 1.0 mmol).

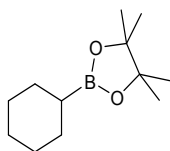
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43-7.21 (m, 13H), 7.01-7.1 (m, 2H), 3.71 (s, 2H), 1.32 (s, 12H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 34.3

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 146.6, 140.6, 131.2, 130.5, 129.0, 128.7, 128.3, 127.8, 126.3, 126.2, 100.4, 84.4, 44.6, 25.0.

GC-MS: m/z 384 (M⁺), HRMS: m/z 349.1654 [(M-C₆H₅)+H+CH₃CN]⁺.

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18a).



The product was obtained following general procedure B as colourless oil in 89% yield (186 mg) from **16** (82 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.⁷

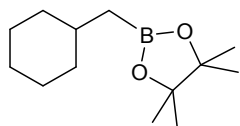
¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.71–1.49 (m, 6H), 1.38–1.28 (m, 4H), 1.22 (s, 12H), 1.02–0.90 (m, 1H).

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 34.0

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 82.9, 28.1, 27.3, 26.9, 24.9, 22.6 (br, *C-B*).

GC-MS: *m/z* 210 (*M*⁺)

2-(Cyclohexylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19b).



The product was obtained following general procedure B as colourless oil in 80% yield (179 mg) from **17** (96 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.⁹

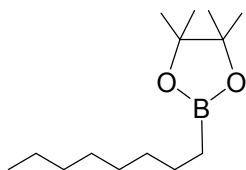
¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.67–1.60 (m, 6H), 1.49–1.41 (m, 1H), 1.21 (s, 12H), 1.11–1.03 (m, 1H), 0.93–0.80 (m, 3H), 0.67 (d, *J* = 7.16 Hz, 2H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.9

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 82.9, 36.0, 34.3, 26.7, 26.4, 24.9, 20.4 (br, *C-B*)

GC-MS: *m/z* 224 (*M*⁺)

4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (20b)



The product was obtained following general procedure B as colourless oil in 83% yield (199 mg) from **18** (96 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.¹⁰

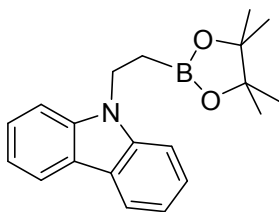
¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.41-1.36 (m, 3H), 1.26-1.19 (m, 20H), 0.89-0.85m (m, 4H), 0.78-0.74 (m, 2H)

¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 34.1

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 82.8, 32.5, 32.0, 29.5, 29.3, 24.9, 24.1, 22.7, 14.2

GC-MS: m/z 240 (M⁺)

9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-9H-carbazole (21b)



The product was obtained following general procedure B as white solid in 76% yield (244 mg) from **19** (193 mg, 1.0 mmol).

The spectroscopic data is consistent with literature data.¹¹

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.20-8.15 (m, 2H), 7.58-7.51 (m, 4H), 7.33-7.29 (m, 2H), 4.54 (t, J = 8.0 Hz, 2H), 1.52 (t, J = 7.16 Hz, 2H), 1.27 (s, 12H)

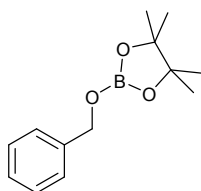
¹¹B NMR (128 MHz, CDCl₃): δ (ppm) 33.4

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 140.0, 125.5, 123.0, 120.3, 118.7, 109.1, 83.6, 38.8, 24.9

GC-MS: m/z 321 (M⁺)

Co(I)-catalyzed hydroboration of carbonyl compounds:

2-(Benzyloxy)pinacolborane (24a).



Following general procedure C, the product yield (97%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

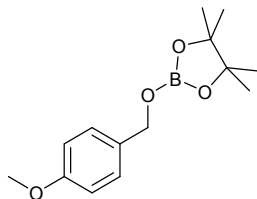
The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.36-7.26 (m, 5H), 4.94 (s, 2H), 1.28 (s, 12H).

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 22.4.

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 139.3, 128.3, 127.4, 126.8, 83.0, 66.7, 24.7.

2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24b).



Following general procedure C, the product yield (88%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

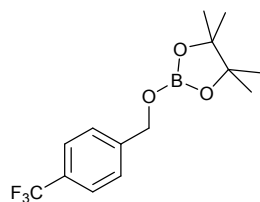
The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.31-7.26 (d, $J = 8.4$ Hz, 2H), 6.89-6.87 (d, $J = 8.4$ Hz, 2H), 4.87 (s, 2H), 3.79 (s, 2H), 1.28 (s, 12H)

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 22.4

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.5, 129.0, 114.1, 83.3, 66.9, 54.7, 25.1

2-((4-Trifluoromethyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24c).



Following general procedure C, the product yield (91%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

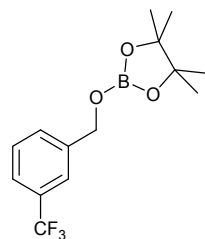
The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.60 (d, $J = 7.9$ Hz, 2H), 7.47 (d, $J = 7.9$ Hz, 2H), 5.00 (s, 2H), 1.29 (s, 12H)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 143.2, 129.7 (q, $J = 31.6$ Hz), 126.5, 125.1 (q, $J = 3.6$ Hz), 82.1, 65.8, 24.4

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 22.2

2-((3-Trifluoromethyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24d).



Following general procedure C, the product yield (93%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

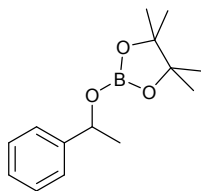
^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.66 (s, 1H), 7.55-7.46 (m, 3H), 4.99 (s, 2H), 1.29 (s, 12H)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 140.2, 129.9, 128.7, 124.1 (q, $J = 3.5$ Hz), 123.4 (q, $J = 3.7$), 83.2, 65.9, 24.5

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 21.1

Note: Due to the instability of borate ester (**22d**) HRMS/elemental analysis was not obtained.

4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (24e).



Following general procedure C, the product yield (87%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

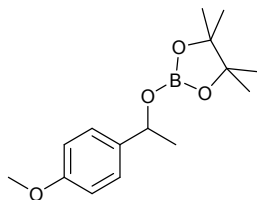
The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.40-7.32 (m, 4H), 7.29-7.24 (m, 1H), 5.27 (q, $J = 6.4$ Hz, 1H), 1.51 (d, $J = 6.4$ Hz, 3H), 1.26 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 144.5, 128.2, 127.1, 125.3, 82.7, 72.6, 25.4, 24.54, 24.50

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 21.3

2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24f).



Following general procedure C, the product yield (91%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

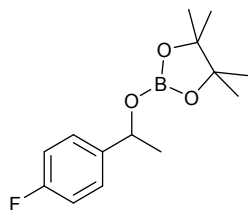
The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.31 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 5.22 (q, $J = 6.4$ Hz, 2H), 3.79 (s, 3H), 1.49 (d, $J = 6.4$ Hz, 3H), 1.26 (s, 6H), 1.23 (s, 6H)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 158.6, 136.6, 126.4, 113.3, 82.5, 72.0, 55.0, 25.1, 24.4, 24.3.

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 21.2

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24g).



Following general procedure C, the product yield (97%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

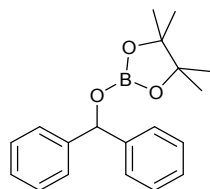
The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.33-7.30 (m, 2H), 7.00-6.95 (m, 2H), 5.21 (q, $J = 6.4\text{ Hz}$, 1H), 1.45 (d, $J = 6.4\text{ Hz}$, 3H), 1.22 (s, 6H), 1.19 (s, 6H)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 161.9 (d, $J = 243.2\text{ Hz}$), 140.3 (d, $J = 2.8\text{ Hz}$), 127.0 (d, $J = 7.95\text{ Hz}$), 115.0, 114.8, 82.8, 71.8, 25.4, 24.50, 24.45

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 21.1

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24h).



Following general procedure C, the product yield (97%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

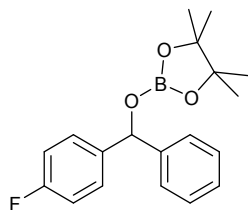
The spectroscopic data is consistent with literature data.¹³

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.46 (d, $J = 7.2\text{ Hz}$, 2H), 7.38-7.34 (m, 4H), 7.31-7.26 (m, 2H), 6.27 (s, 1H), 1.27 (s, 12H)

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 143.0, 128.2, 127.2, 126.4, 82.9, 77.8, 24.4

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 22.4

2-(1-(4-Fluorophenyl)benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24i).



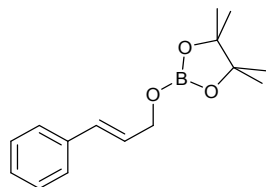
Following general procedure C, the new product yield (94%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.43-7.27 (m, 8H), 7.02 (t, $J = 8.7$ Hz, 2H), 6.22 (s, 1H), 1.25 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 161.7 (d, $J = 244.5$ Hz), 142.5, 138.7, 138.6, 127.9, 127.1, 126.1, 114.8, 114.6, 82.7, 76.9, 24.2

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 22.4

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24j).



Following general procedure C, the product yield (94%) was determined by ^1H NMR spectroscopy of the crude reaction mixture (nitromethane as internal standard).

The spectroscopic data is consistent with literature data.¹²

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.39 (d, $J = 7.4$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.26-7.22 (t, $J = 7.0$ Hz, 1H), 6.65 (d, $J = 15.9$ Hz, 1H), 6.31 (dt, $J = 15.9$ Hz, 5.3 Hz, 1H), 4.56 (dd, $J = 5.3$ Hz, $J = 1.4$ Hz, 2H), 1.29 (s, 12H)

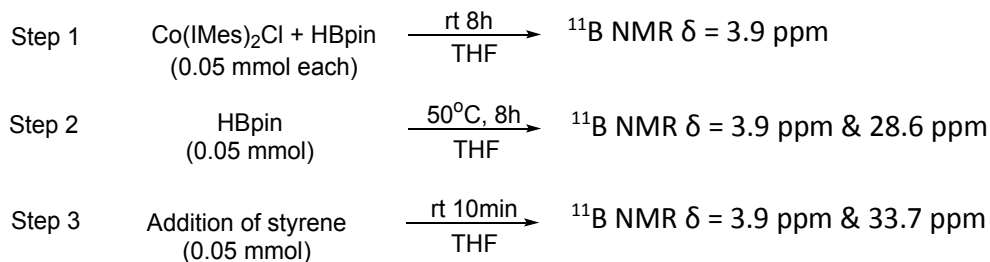
^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 136.9, 130.6, 129.1, 128.6, 127.5, 126.5, 82.9, 65.3, 24.6

^{11}B NMR (128 MHz, CDCl_3): δ (ppm) 22.3

IV. Preliminary Mechanistic Investigations

To get insight into operative mechanistic cycle, several stoichiometric reactions were performed:

Experiment S1:



Equimolar amount (0.05 mmol) of Co(IMes)₂Cl (35.2 mg) and HBpin (7.1 μ l) were mixed in THF (0.6 ml). The reaction mixture was stirred at room temperature for 8 h. Addition of another equivalent of HBpin in the step 2 could not produce any change in the ¹¹B NMR. However, addition of styrene (0.05 mmol, 5.7 μ l) in step 3 immediately resulted in the product. The mixture was further monitored by ¹¹B NMR at 10 min interval.

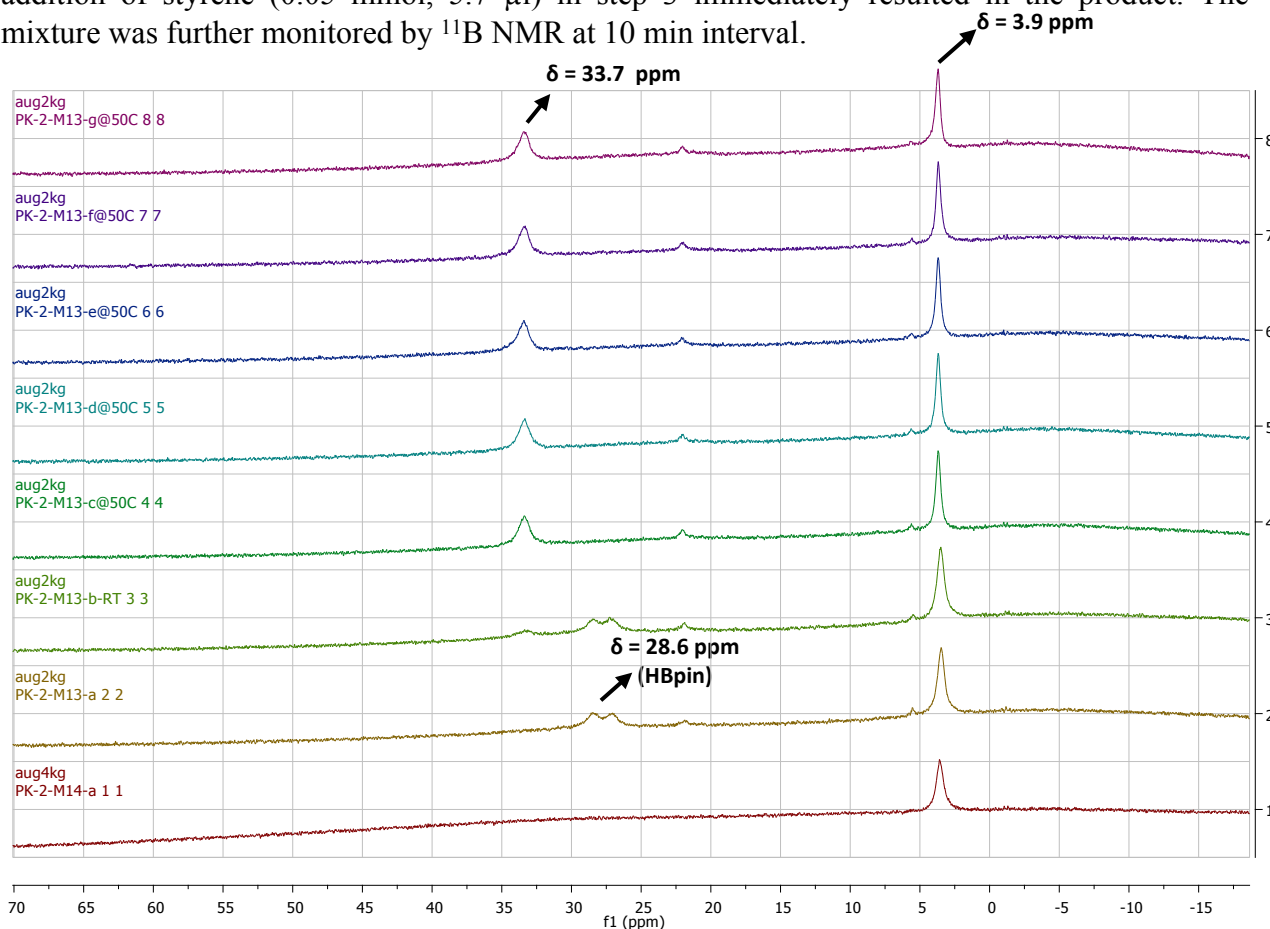


Figure S1. ¹¹B NMR spectra of (1) Equimolar amount (0.05 mmol) of Co(IMes)₂Cl and HBpin in THF for 8 h at rt, (2) 0.05 mmol of HBpin in (1) after 8 h, (3) 0.05 mmol of styrene at T = 0 min, (4) after T = 10 min, (5) after T = 20 min, (6) after T = 30 min, (7) after T = 40 min, (8) after T = 50 min.

The spectra show that reaction between $\text{Co}(\text{IMes})_2\text{Cl}$ and HBpin produced a boron containing entity, which is unaffected throughout the reaction. Removal of THF and recrystallization in benzene afforded a colourless crystal of compound **I**. It was further verified by HRMS of the reaction mixture of $\text{Co}(\text{IMes})_2\text{Cl}$ and HBpin in THF.

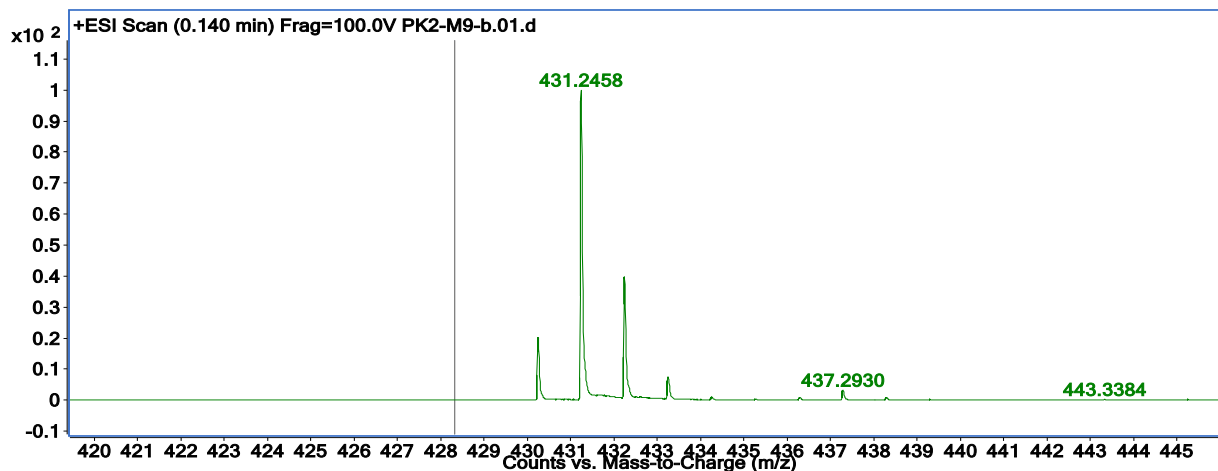


Figure S2. Mass Spectrum of complex **I** (IMes.Bpin) in THF, showing the ion peak at 431.2458 (m/z) which corresponds to $[\text{M}+\text{H}]^+$ of compound **I**. Calculated mass of the complex **I** (IMes.Bpin) is 431.2869 u.

Experiment S2:

The comparison of ^1H NMR of the catalyst, $\text{Co}(\text{IMes})_2\text{Cl}$ and mixture of $\text{Co}(\text{IMes})_2\text{Cl}$ and HBpin in d_8 -THF shows the disappearance of characteristic peaks corresponding to $\text{Co}(\text{IMes})_2\text{Cl}^{14}$, which also supports the formation of compound **I** and active catalyst.

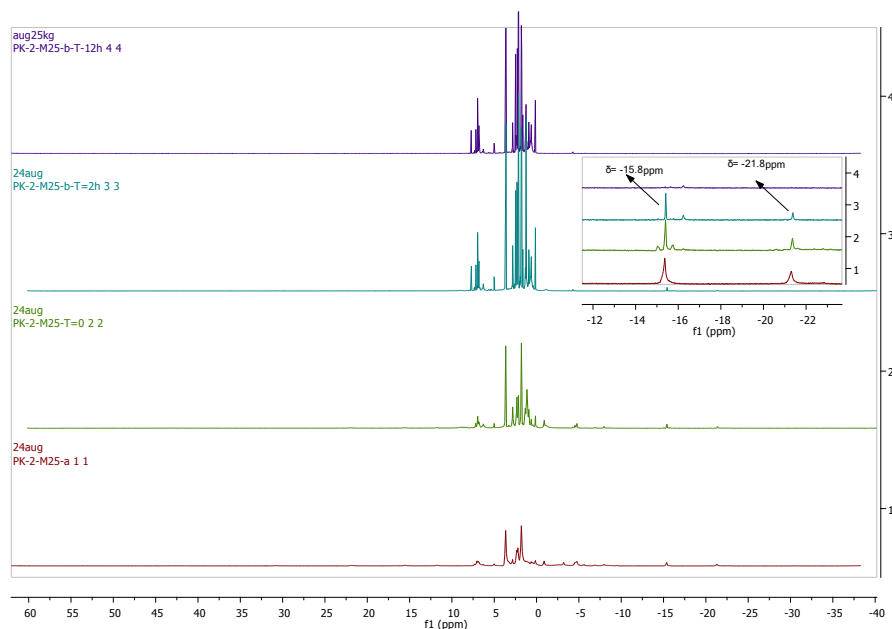
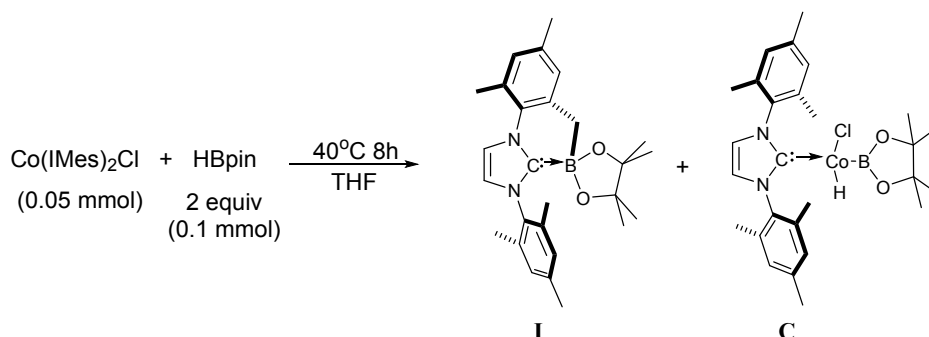


Figure S3. ^1H NMR spectra of (1) $\text{Co}(\text{IMes})_2\text{Cl}$, (2) Equimolar amount (0.025 mmol) of $\text{Co}(\text{IMes})_2\text{Cl}$ (17.5 mg) and HBpin (3.5 μl) in d_8 -THF after (2) $T=15$ min, (3) 2h, (4) $T=12$ h.

Experiment S3:



To find the possible *in situ* generating catalyst upon reaction between $\text{Co(Imes)}_2\text{Cl}$ and HBpin, 0.05 mmol of $\text{Co(Imes)}_2\text{Cl}$ (35.2 mg) and HBpin (7.1 μl) each were mixed in THF for 12 h and then analysed by HR-MS (ESI). Only compound **I** could be detected by HRMS. However, when 0.05 mmol of $\text{Co(Imes)}_2\text{Cl}$ and 2 equiv of HBpin (0.10 mmol, 14.2 μl) were reacted in THF for 8 h at 40 $^\circ\text{C}$, HRMS of the reaction mixture shows the peaks corresponding to both **I** and **C**.

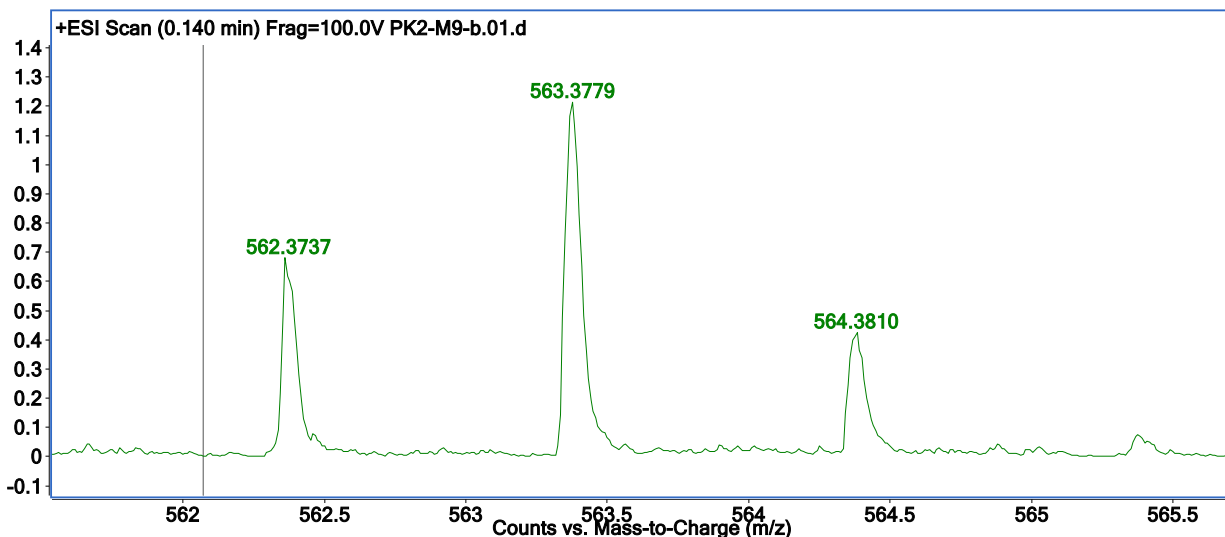


Figure S4. Mass Spectrum of complex **C**, Co(Imes)HBpinCl in THF, showing the ion peak at 563.3779 (m/z) which corresponds to $[(\text{M-Cl})+\text{C}_4\text{H}_8\text{O}]^+$. Calculated mass of the $[(\text{M-Cl})+\text{C}_4\text{H}_8\text{O}]^+$ is 563.2855 u.

Observation of the complex **C** reveals that first equivalent of HBpin reacts with $\text{Co(Imes)}_2\text{Cl}$ to give **I** and Co(Imes)Cl . Addition of another equivalent of HBpin undergoes oxidative addition on the *in situ* generated catalyst Co(Imes)Cl to give the Co(III) complex **C**, Co(Imes)HBpinCl .

Experiment S4:

Equimolar amount (0.025 mmol) of $\text{Co}(\text{IMes})_2\text{Cl}$ (17.5 mg) and HBpin (2.5 μl) were mixed in d_8 -THF (0.4 ml). The reaction mixture was stirred at room temperature for 8 h. Addition of 0.025 mmol of styrene (2.75 μl) in step 2 did not produce any change in the ^1H NMR spectrum. In step 3, addition of one equivalent of HBpin (0.025 mmol, 2.5 μl) immediately produced the product.

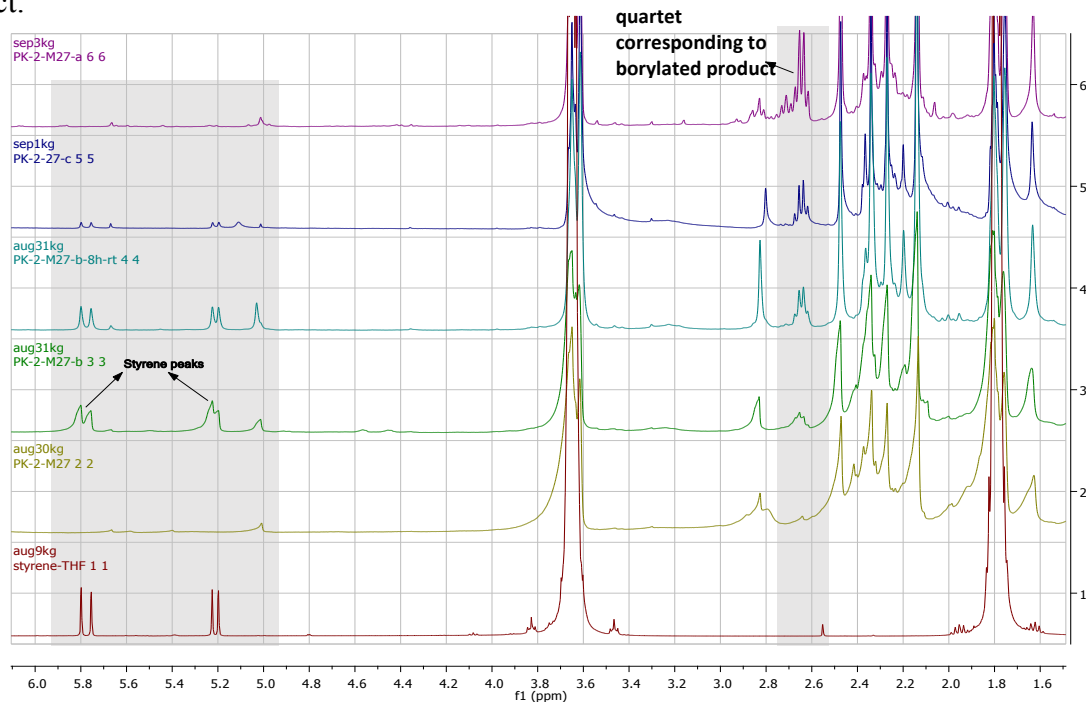


Figure S5. ^1H NMR spectra of (1) Styrene in THF, (2) Equimolar amount (0.025 mmol) of $\text{Co}(\text{IMes})_2\text{Cl}$ and HBpin in d_8 -THF after 8 h at rt, (3) addition of 0.025 mmol of styrene, T = 10 min (4) at T = 30 min, (5) at T = 1 h (6) T = 2 h.

Experiment S5:

Equimolar amount of $\text{Co}(\text{IMes})_2\text{Cl}$ (0.05 mmol, 35.2 mg) and styrene (0.05 mmol, 5.7 μl) were mixed in THF. One equivalent of HBpin was added to the reaction mixture and stirred for 8 h at rt. Then another equivalent of HBpin was added. The reaction was followed by ^{11}B NMR. The spectra show that with one equivalent of $\text{Co}(\text{IMes})_2\text{Cl}$, styrene and HBpin, both the product and compound **I** formed. Next addition of HBpin to this mixture further increased the intensity of the peak corresponding to the product and **I**. The spectra shows that formation of **I** is accompanied by the formation of product; which further point out that HBpin reacts with $\text{Co}(\text{IMes})_2\text{Cl}$ to generate active catalyst and a by-product, compound **I**.

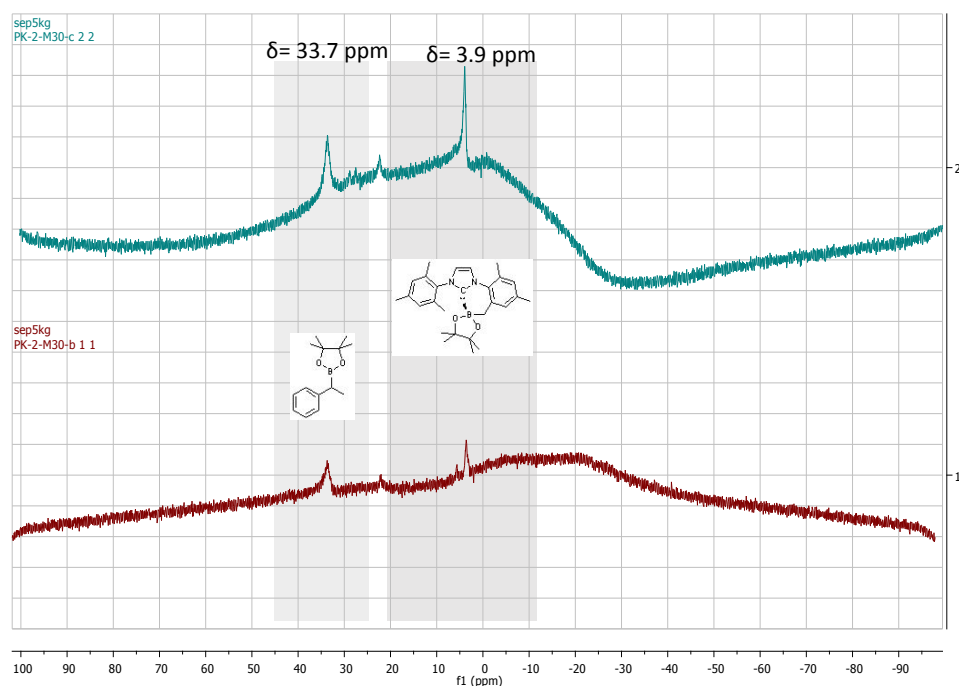


Figure S6. ^{11}B NMR spectra of (1) Equimolar amount (0.05 mmol) of $\text{Co}(\text{IMes})_2\text{Cl}$, styrene and HBpin in THF after 8 h, (2) addition of next 0.05 mmol of HBpin, after 8 h.

V. X-ray Crystallographic Data

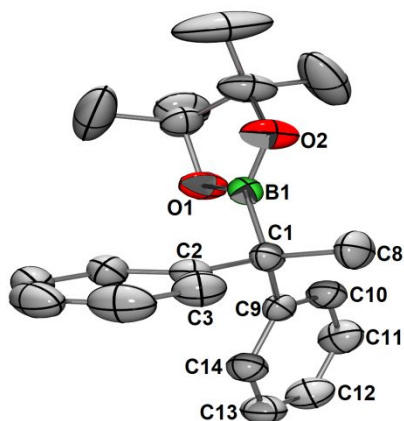


Figure S7. Crystal structure of 12a

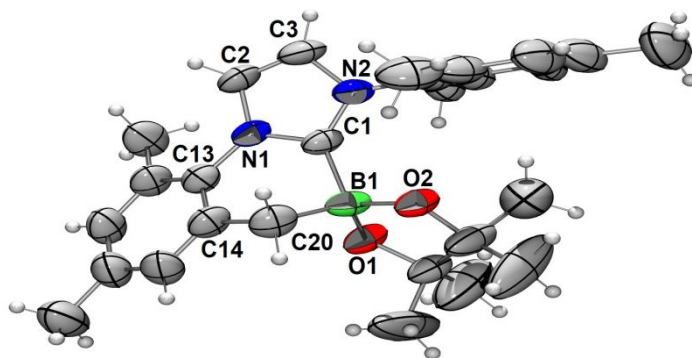


Figure S8. Crystal structure of I

Table S6. X-ray crystallographic data for Compound 12a and Compound I*.

	Compound 12a	Compound I
Empirical formula	C ₂₀ H ₂₅ BO ₂	C ₂₇ H ₃₅ BN ₂ O ₂
Formula weight	308.21	430.38
Temperature/K	296.15	100
Crystal system	triclinic	orthorhombic
Space group	P-1	Pna2 ₁
a/Å	7.774(3)	10.300(6)
b/Å	10.137(3)	21.709(13)
c/Å	12.705(4)	11.269(7)
α/°	100.143(8)	90
β/°	106.960(8)	90
γ/°	101.963(8)	90
Volume/Å ³	906.4(5)	2520(3)
Z	2	4
ρ _{calc} /g/cm ³	1.129	1.134
μ/mm ⁻¹	0.070	0.070
F(000)	332.0	928.0
Crystal size/mm ³	0.02 × 0.016 × 0.012	0.21 × 0.17 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.698 to 57.434	5.678 to 54.976
Reflections collected	58245	74793
Independent reflections	4616 [R _{int} = 0.0612, R _{sigma} = 0.0357]	5756 [R _{int} = 0.1217, R _{sigma} = 0.0538]
Data/restraints/parameters	4616/0/213	5756/1/298
Goodness-of-fit on F ²	1.020	1.055
Final R indexes [I>=2σ (I)]	R ₁ = 0.0631, wR ₂ = 0.1328	R ₁ = 0.0915, wR ₂ = 0.2271
Final R indexes [all data]	R ₁ = 0.1157, wR ₂ = 0.1579	R ₁ = 0.1444, wR ₂ = 0.2610
Bond distances (Å)	C1-B1 = 1.592(3), C2-C1 = 1.533(2), C1-C8 = 1.548(2), C9-C1 = 1.530(2)	C1-B1 = 1.674(7), C20-B1 = 1.618(11), C1-N1 = 1.365(8), C1-N2 = 1.378(8), C13-N1 = 1.445(8), C20-C14 = 1.490(9), C13-C14 = 1.399(8)

* The poor quality of this crystal resulted in weak data at higher angles, resulting in higher R-factor (R = 0.0915).

VI. Kinetic Study

Kinetic Experiments

Kinetics of hydroboration reaction was studied by performing NMR scale reactions. *trans*- β -methyl-styrene (**15**) was used as substrate for the kinetic study because no other isomeric product was found with HBpin and catalyst **A**, in benzene- d_6 as solvent. The reaction was monitored by ^1H NMR analysis at time interval of 25 min. Reactions were performed at 60°C temperature and long-time interval (25min) was chosen due to very slow progress of reaction in absence of stirring and benzene- d_6 as a solvent. The kinetic data were obtained by following the increment in the proton integral of $\beta\text{C-H}$ (**13a**) relative to aromatic-H of mesitylene (internal standard).

General procedure for the rate determination:

In nitrogen atmosphere, required amount of Co- catalyst **A** and alkene **15** were taken along with mesitylene (5 μl) and 0.5 ml benzene- d_6 . Required amount of HBpin was then transferred to the NMR tube and the reaction mixture was kept immediately in the ice bath. NMR was recorded at room temperature considering it at $T = 0$ min (no product was observed). Then NMR tube was kept in oil bath, 60°C temperature and spectra was recorded at the interval of 25 min.

Catalyst rate order assessment:

Varying concentration of catalyst **A** while keeping HBpin and alkene (**15**) concentration constant.

[Catalyst] (M)	[HBpin] (M)	[Alkene] (M)	Rate M/min	R ²
0.0060	0.20	0.20	$5.76 \times 10^{-4} \pm 1.64 \times 10^{-5}$	0.99674
0.0150	0.20	0.20	$7.80 \times 10^{-4} \pm 1.97 \times 10^{-5}$	0.99743
0.0300	0.20	0.20	$1.10 \times 10^{-3} \pm 2.68 \times 10^{-5}$	0.99761
0.0450	0.20	0.20	$1.39 \times 10^{-3} \pm 1.03 \times 10^{-4}$	0.98916

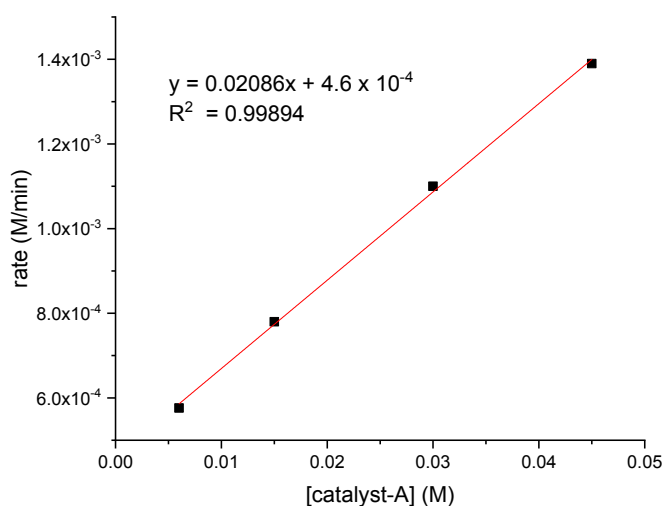


Figure S9: Plot of [Catalyst] vs. reaction rate, the reaction follows first order dependence over Catalyst.

HBpin rate order assessment:

Varying concentration of HBpin while keeping Catalyst **A** and alkene (**15**) concentration constant.

[HBpin] (M)	[Catalyst] (M)	[Alkene] (M)	Rate M/min	R ²
0.14	0.0075	0.20	$5.27 \times 10^{-4} \pm 1.99 \times 10^{-5}$	0.99573
0.20	0.0075	0.20	$5.76 \times 10^{-4} \pm 1.64 \times 10^{-5}$	0.99743
0.30	0.0075	0.20	$1.16 \times 10^{-3} \pm 1.22 \times 10^{-5}$	0.99967
0.40	0.0075	0.20	$1.62 \times 10^{-3} \pm 1.39 \times 10^{-4}$	0.98544

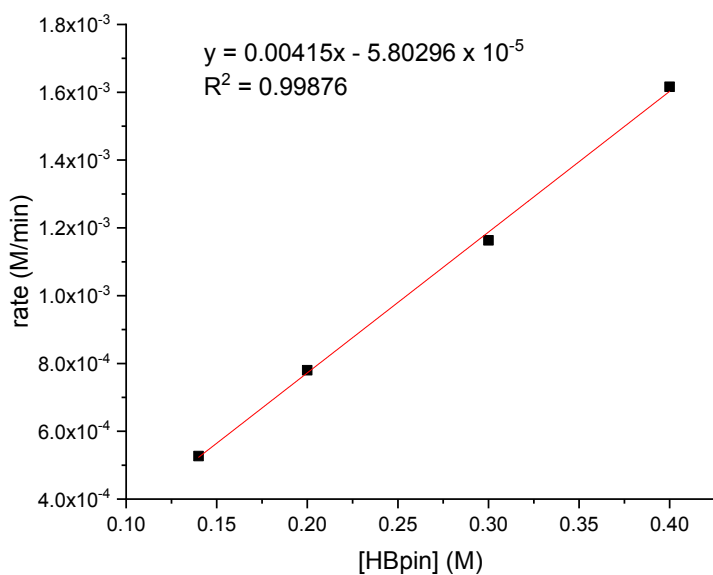


Figure S10: Plot of [HBpin] vs. reaction rate, the reaction follows first order dependence over HBpin.

Alkene rate order assessment:

Varying concentration of alkene (**15**) while keeping Catalyst **A** and HBpin concentration constant.

[Alkene] (M)	[HBpin] (M)	[Catalyst] (M)	Rate M/min	R ²
0.14	0.20	0.0075	$7.18 \times 10^{-4} \pm 2.18 \times 10^{-5}$	0.99634
0.20	0.20	0.0075	$5.27 \times 10^{-4} \pm 1.99 \times 10^{-5}$	0.99743
0.40	0.20	0.0075	$8.17 \times 10^{-4} \pm 1.02 \times 10^{-5}$	0.99953
0.60	0.20	0.0075	$7.54 \times 10^{-4} \pm 3.17 \times 10^{-5}$	0.99295

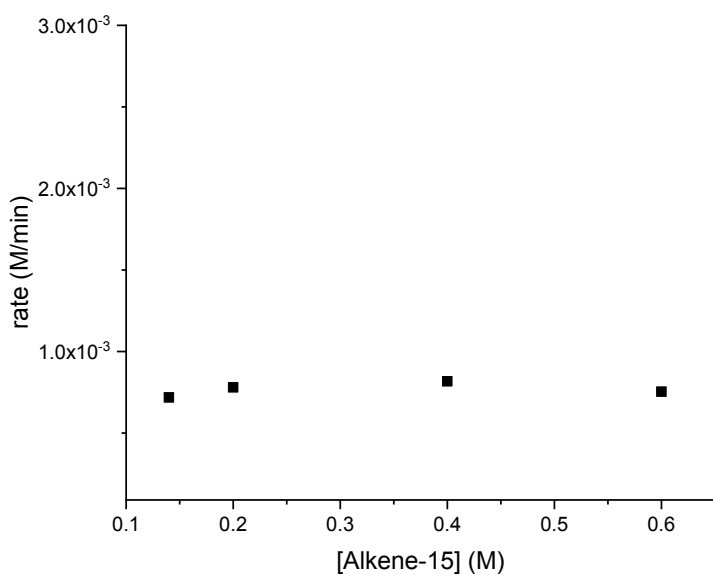
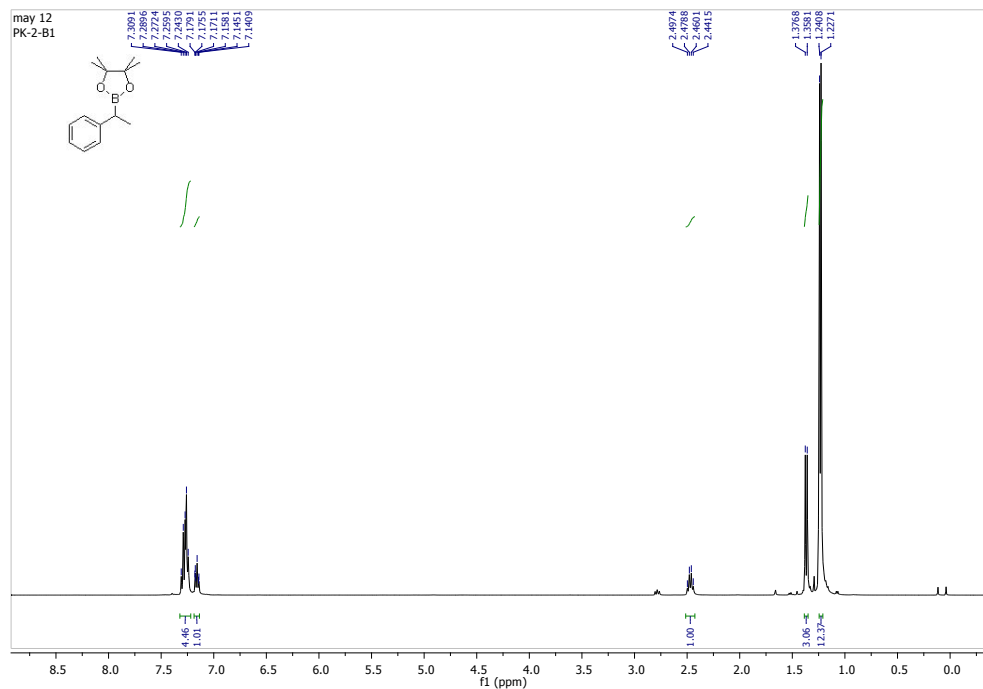


Figure S11: Plot of [Catalyst] vs. reaction rate, the reaction follows zero order dependence over alkene.

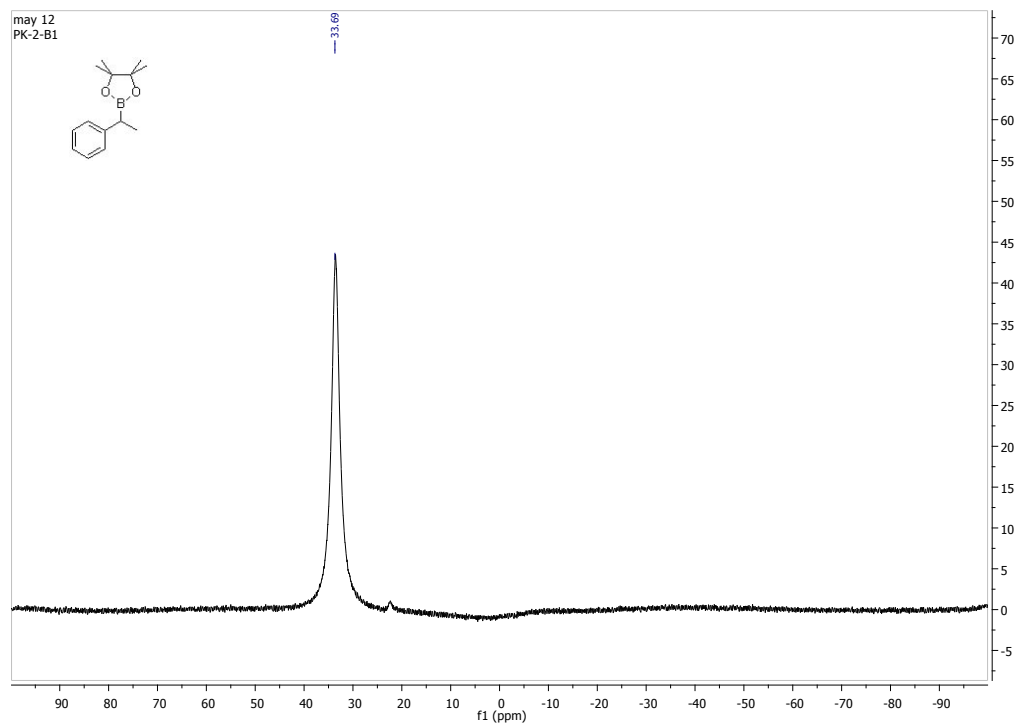
VII. NMR Spectra

2-(1-Phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**).

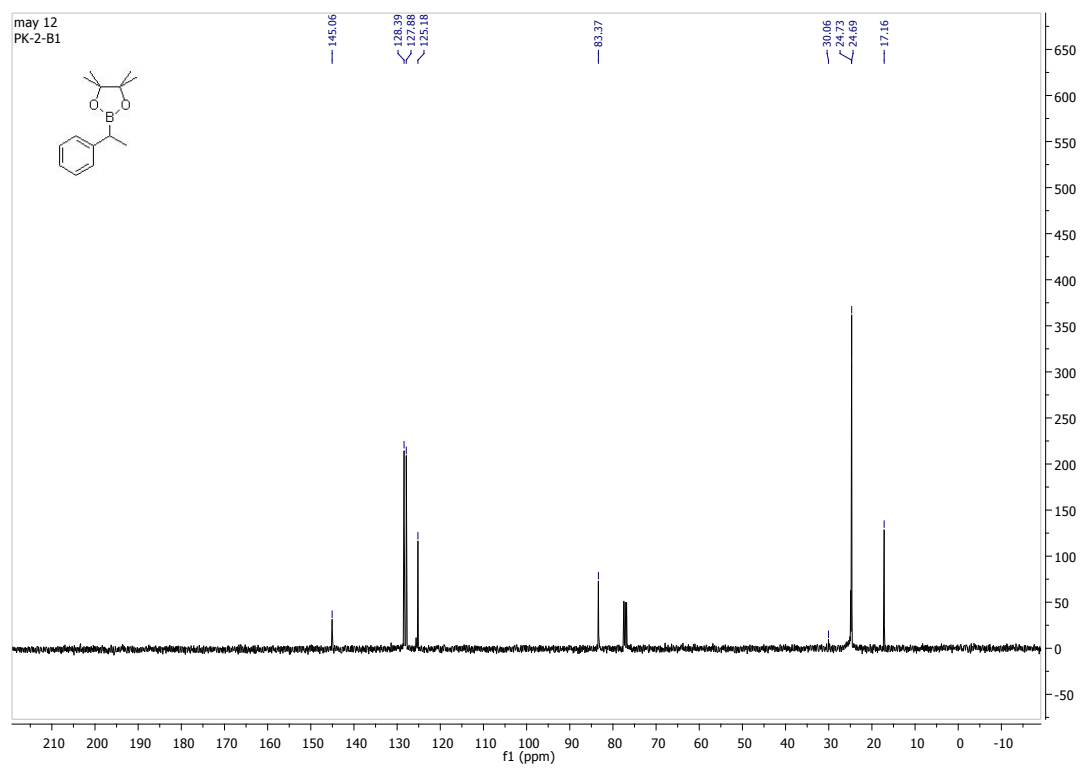
^1H NMR, CDCl_3 , 400 MHz:



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

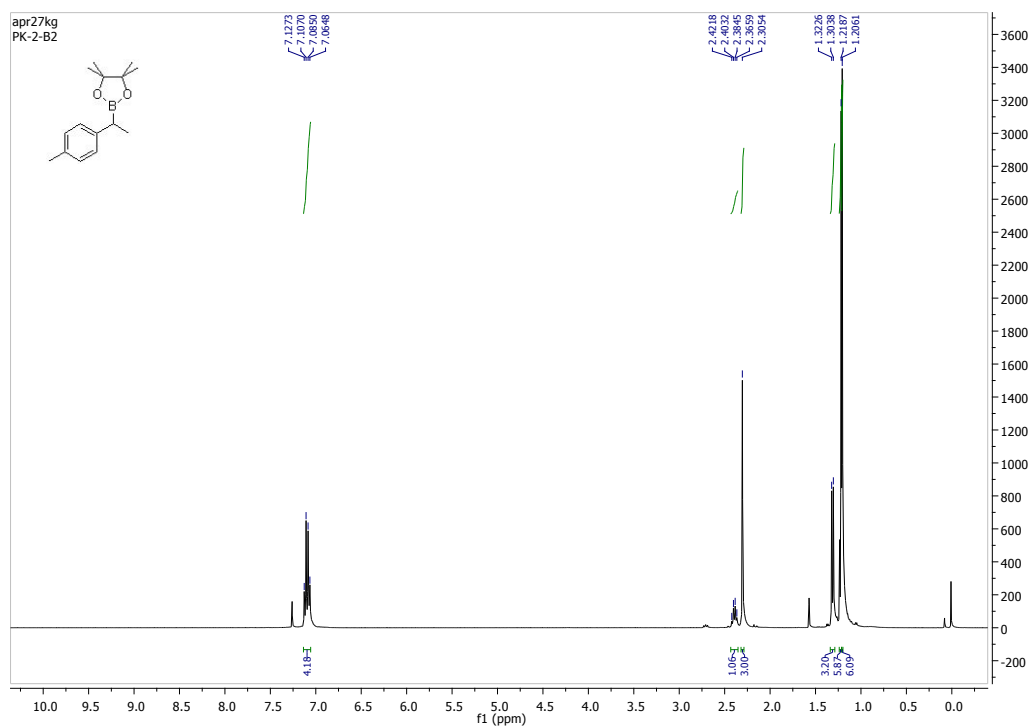


^{13}C NMR, CDCl_3 , 100 MHz:

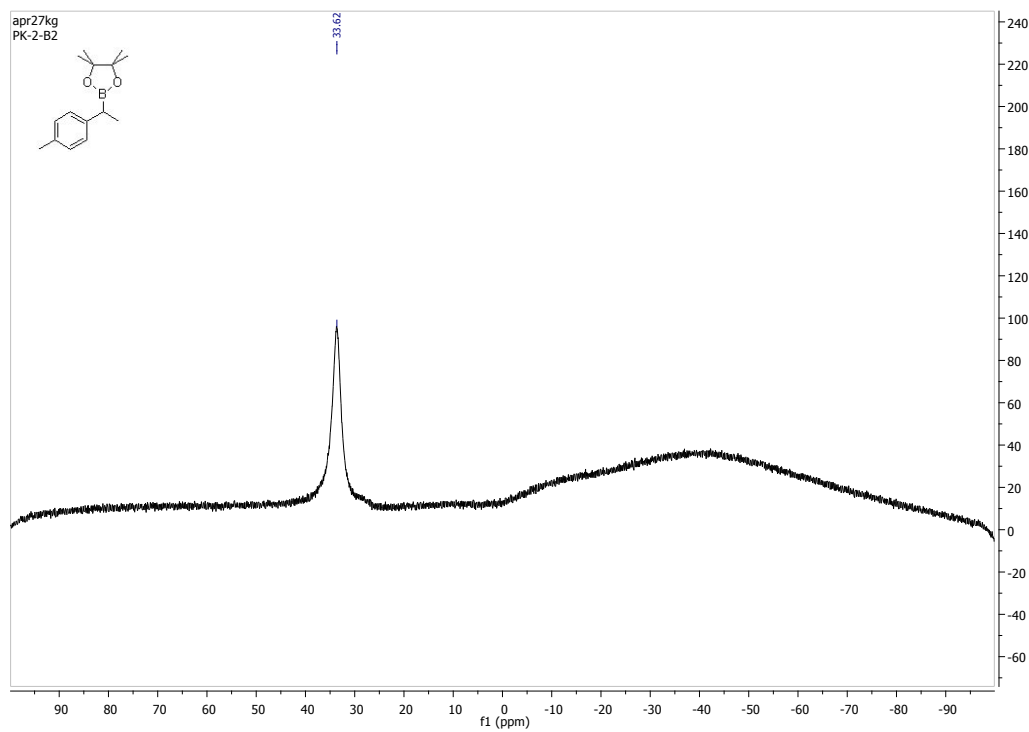


4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethyl)-1,3,2-dioxaborolane (2a).

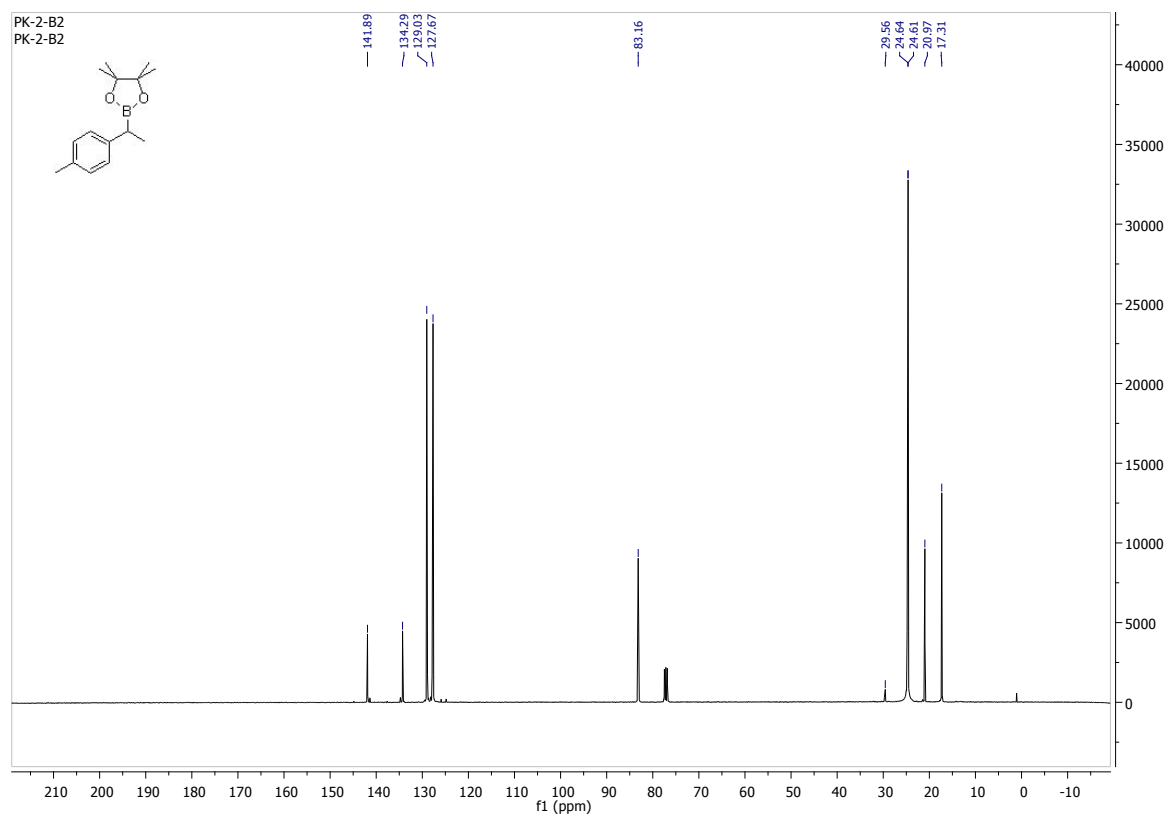
^1H NMR, CDCl_3 , 400 MHz:



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

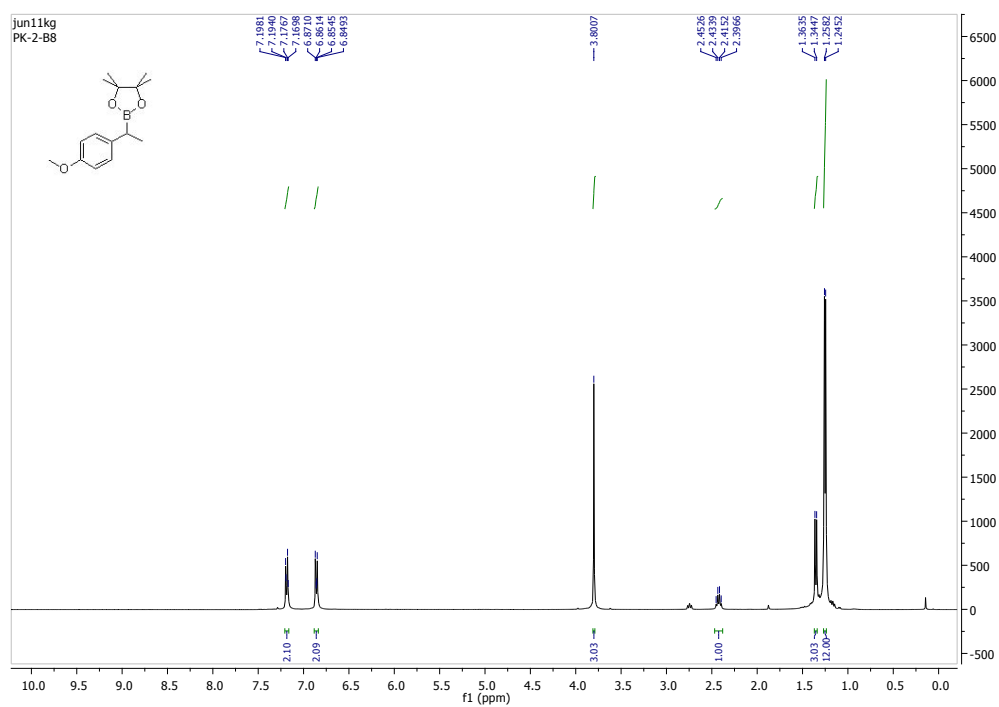


^{13}C NMR, CDCl_3 , 100 MHz:

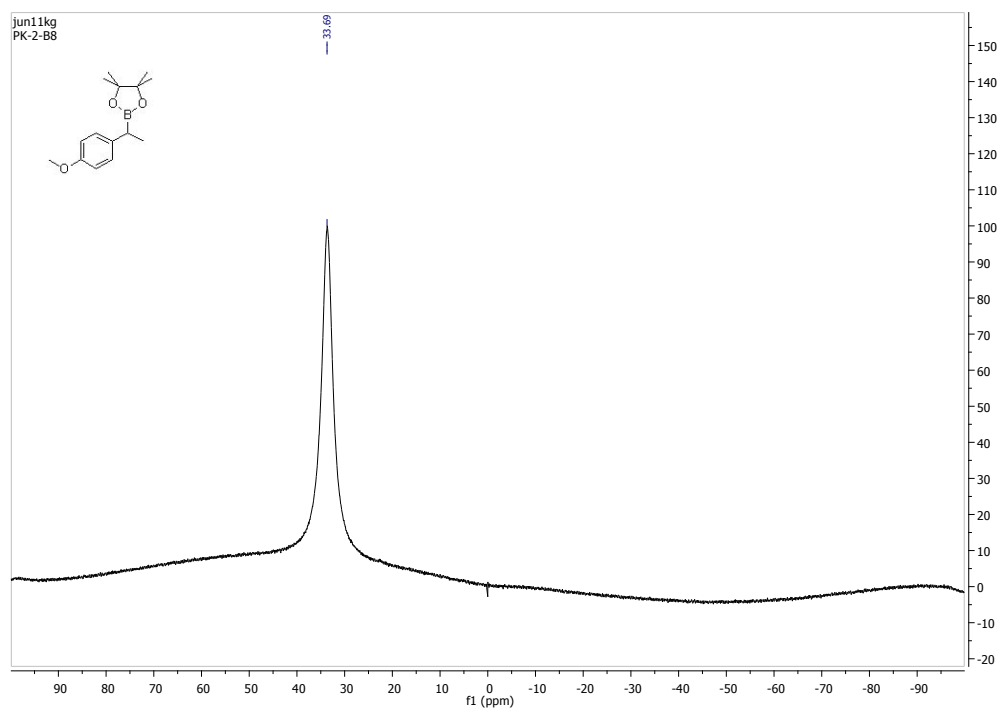


2-(1-(4-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a).

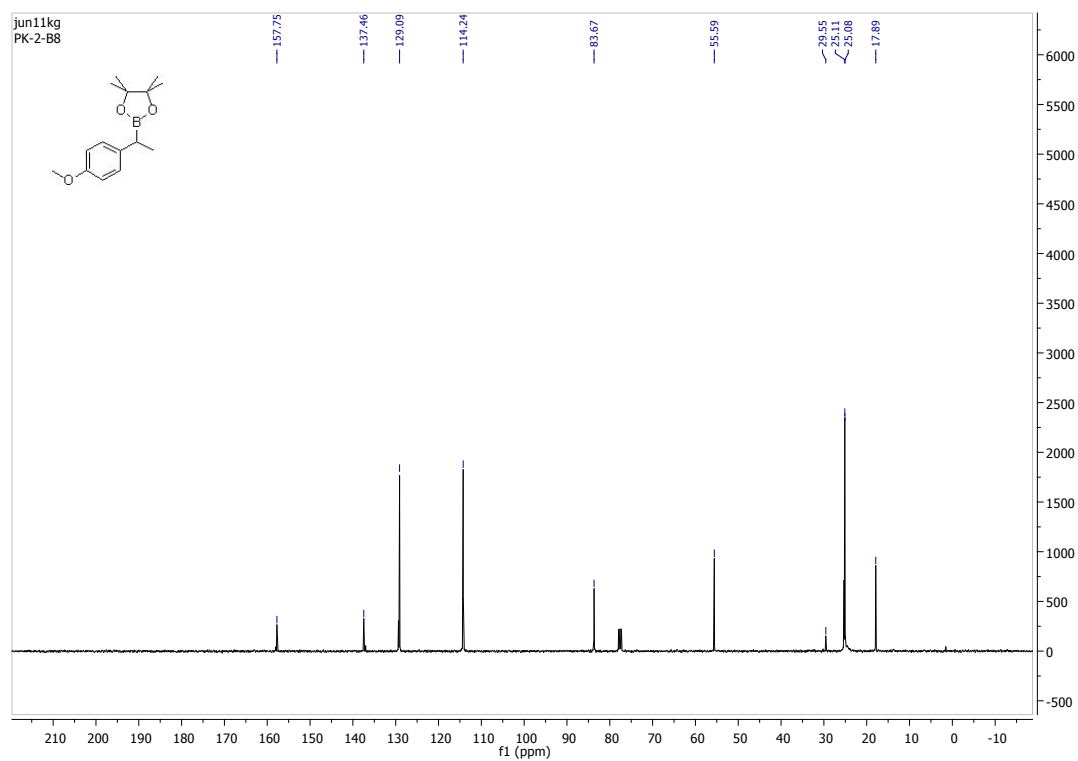
^1H NMR, CDCl_3 , 400 MHz:



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

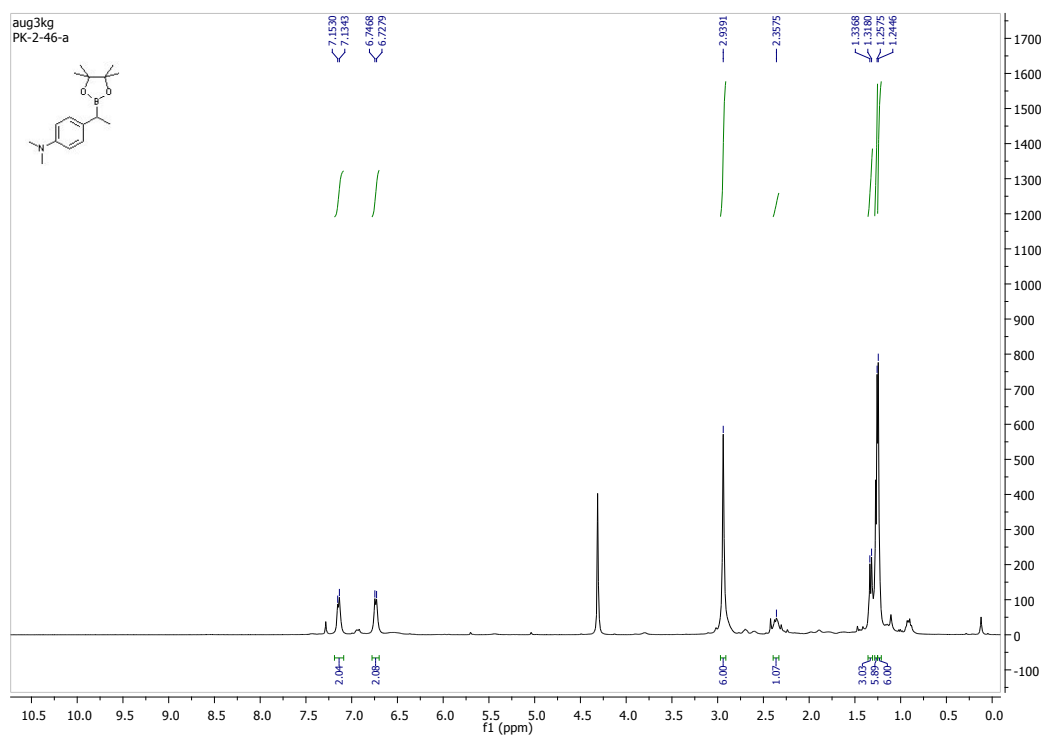


^{13}C NMR, CDCl_3 , 100 MHz:

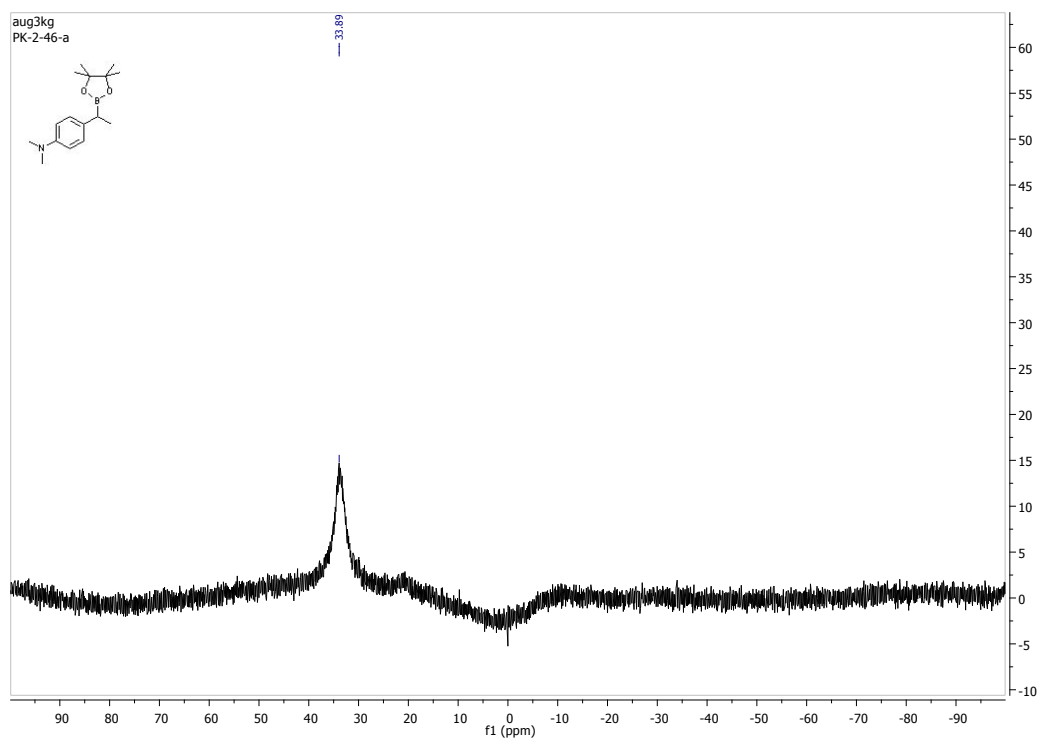


4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-*N,N*-dimethylbenzenamine (4a).

^1H NMR, CDCl_3 , 400 MHz:

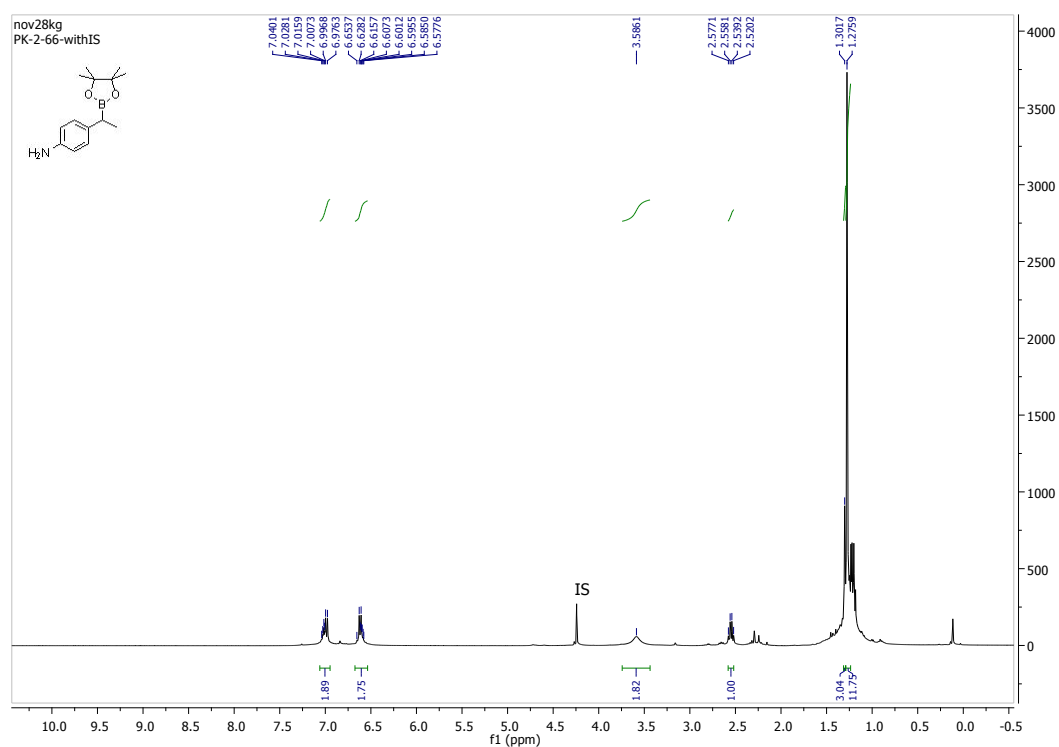


^{11}B NMR, CDCl_3 , 128 MHz:

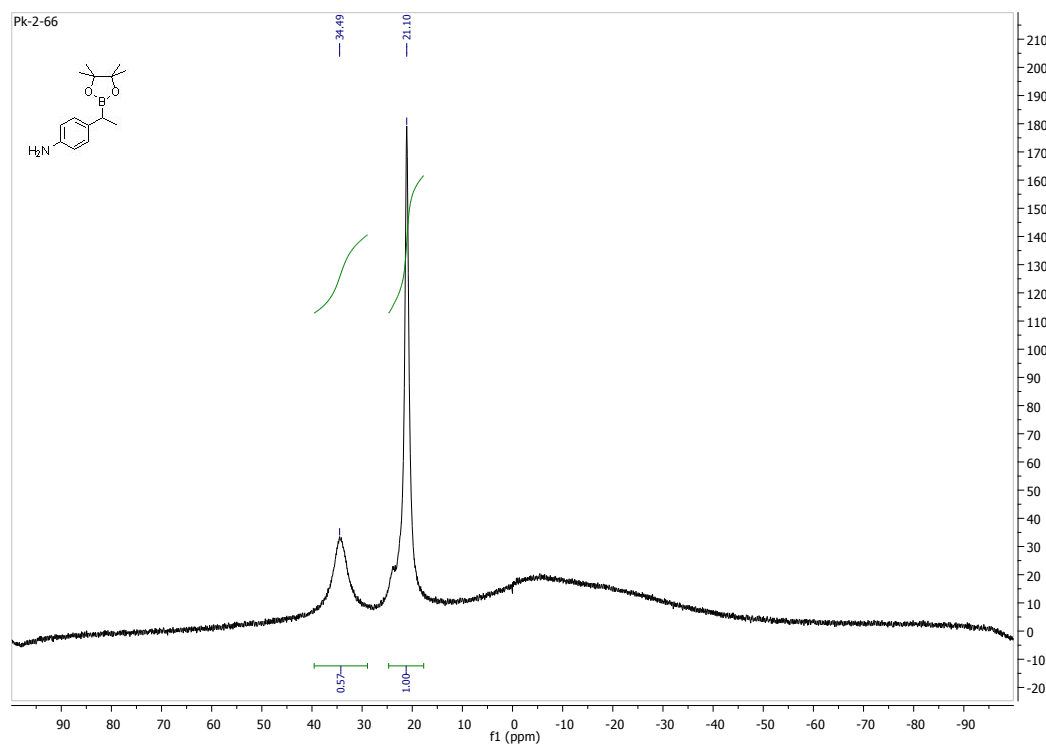


4-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzenamine (5a).

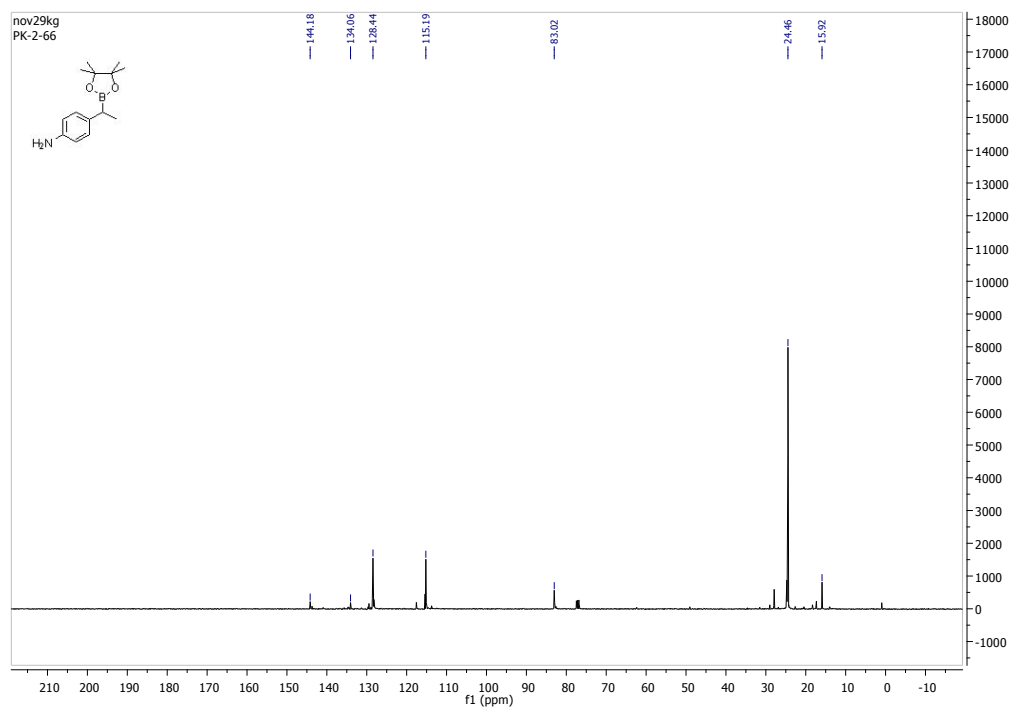
^1H NMR, CDCl_3 , 400 MHz:



^{11}B NMR, CDCl_3 , 128 MHz: The peak at δ 21.1 ppm is due to unreacted HBpin,

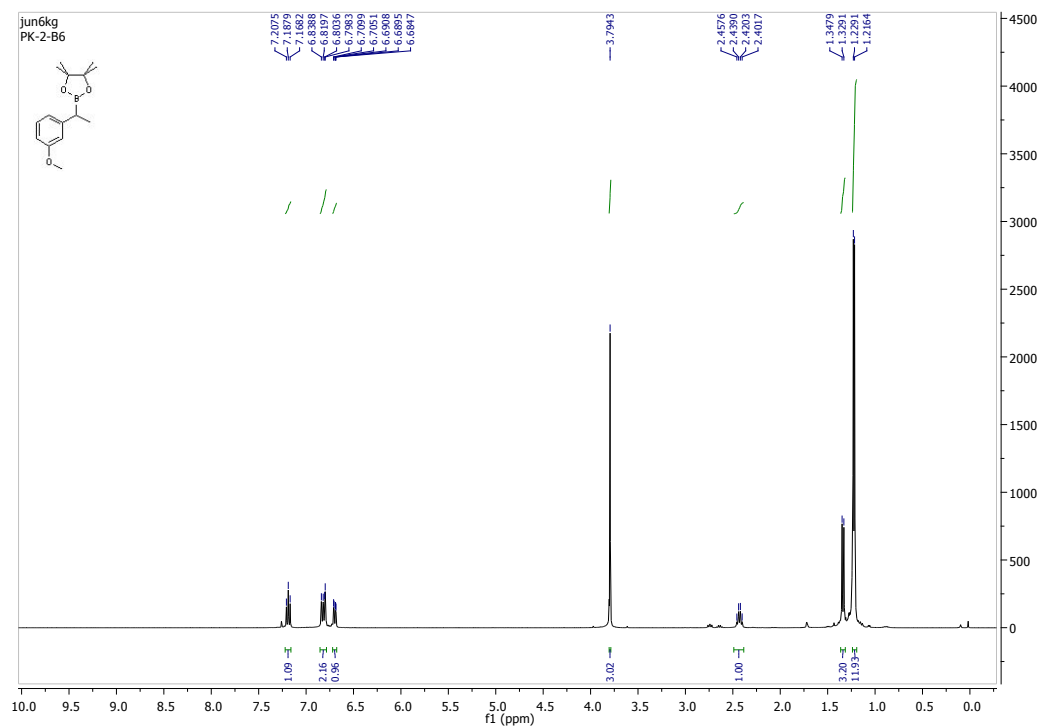


^{13}C NMR, CDCl_3 , 100 MHz:

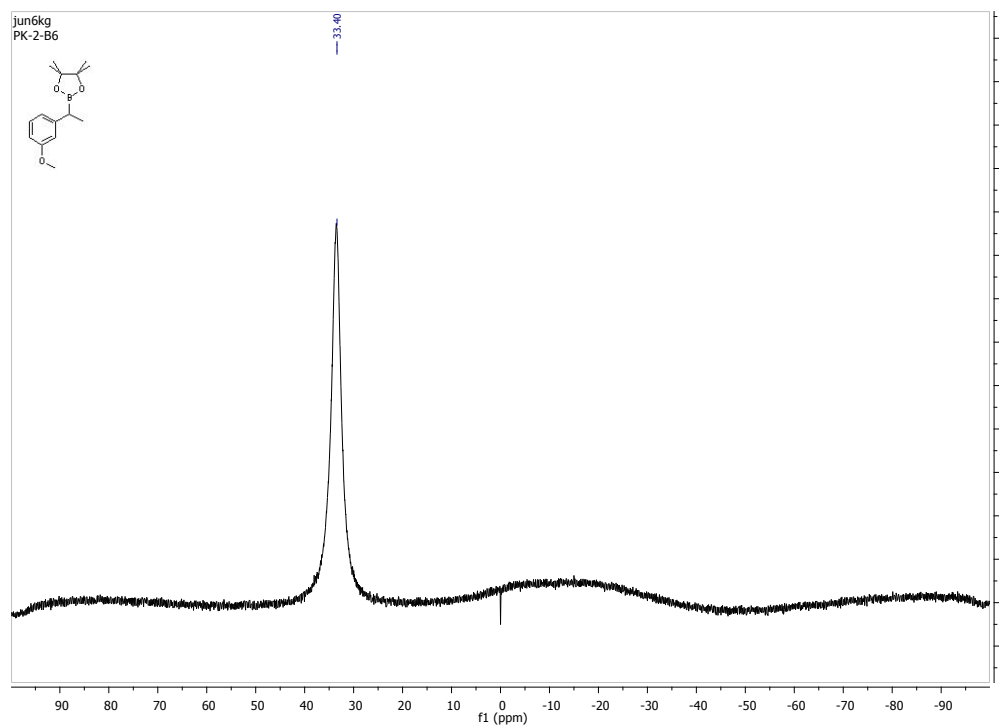


2-[1-(3-Methoxyphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a).

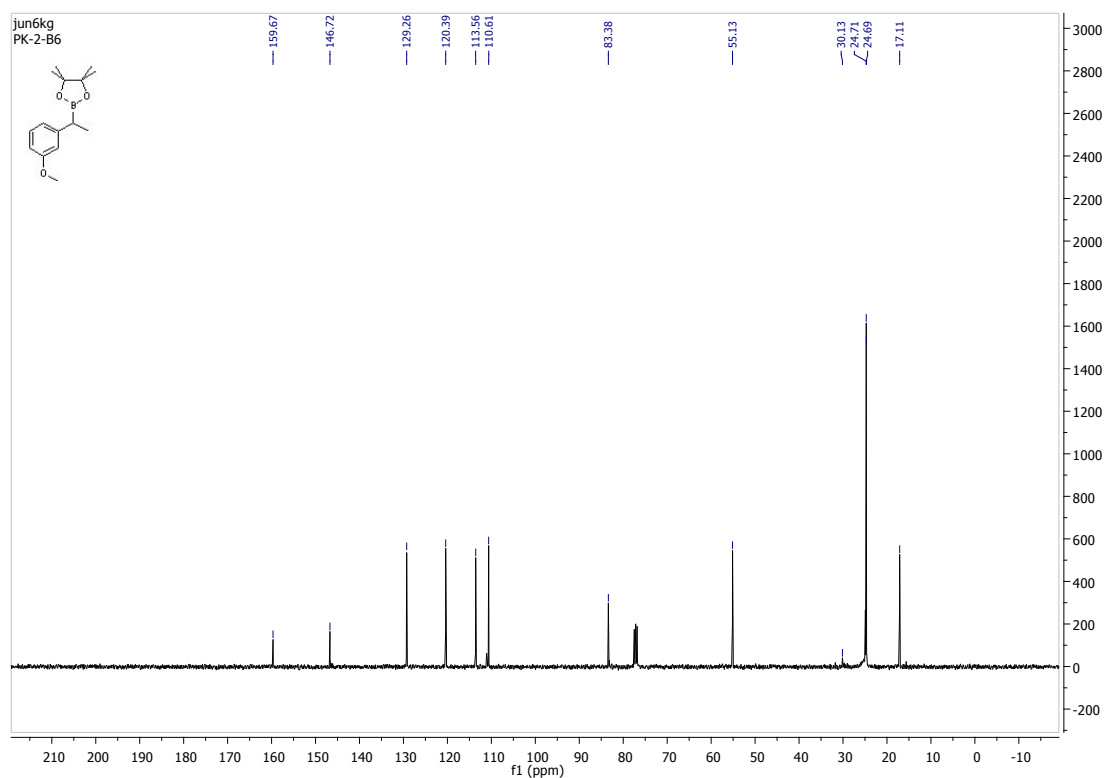
^1H NMR, CDCl_3 , 400 MHz:



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

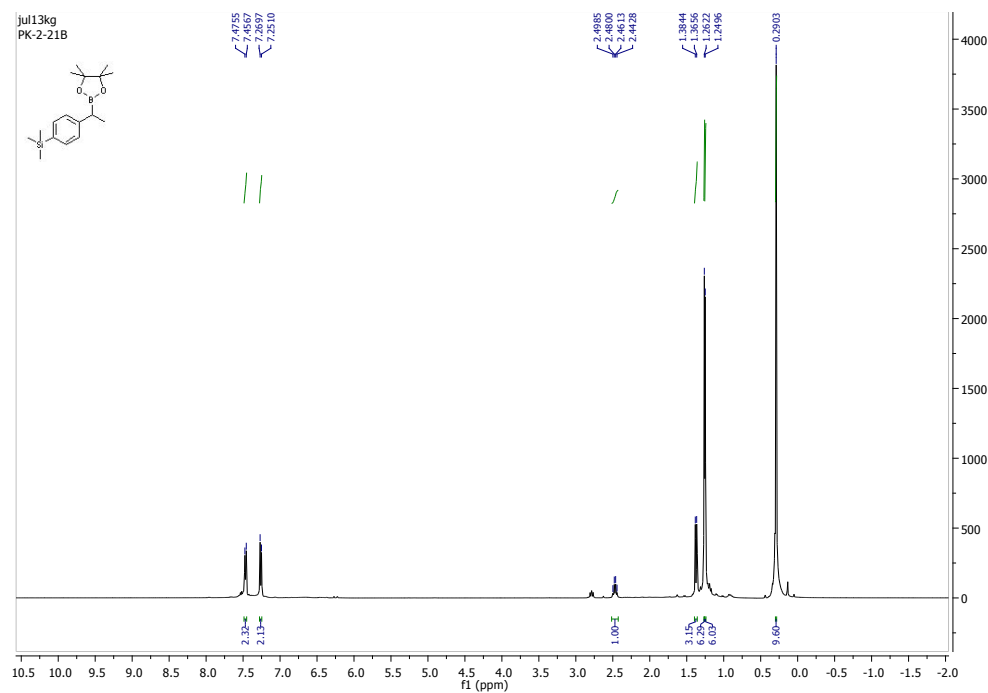


^{13}C NMR, CDCl_3 , 100 MHz:

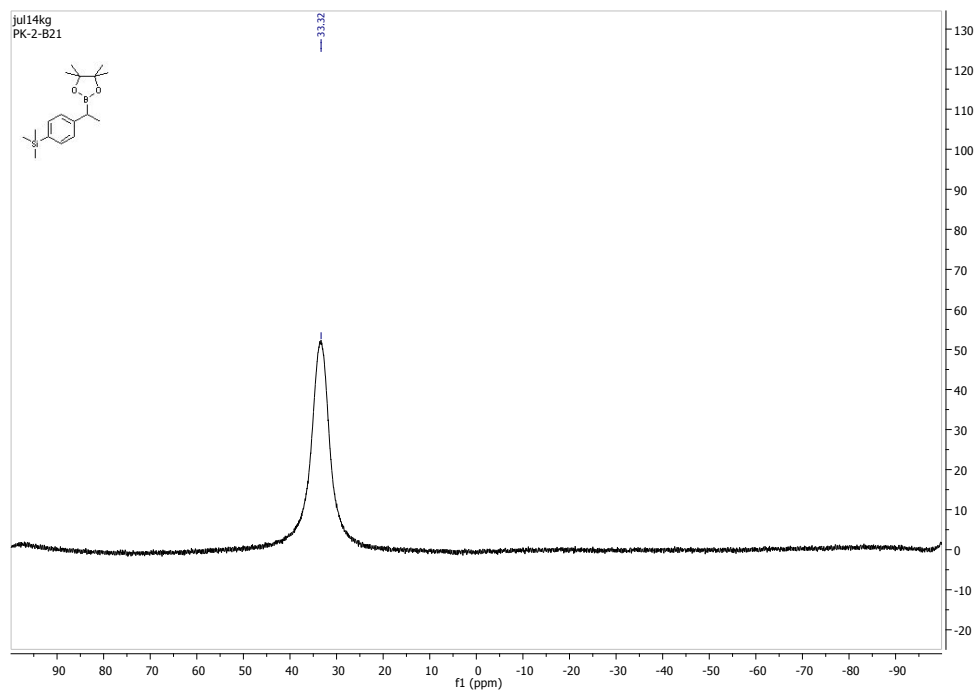


2-(1-(4-Trimethylsilylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a).

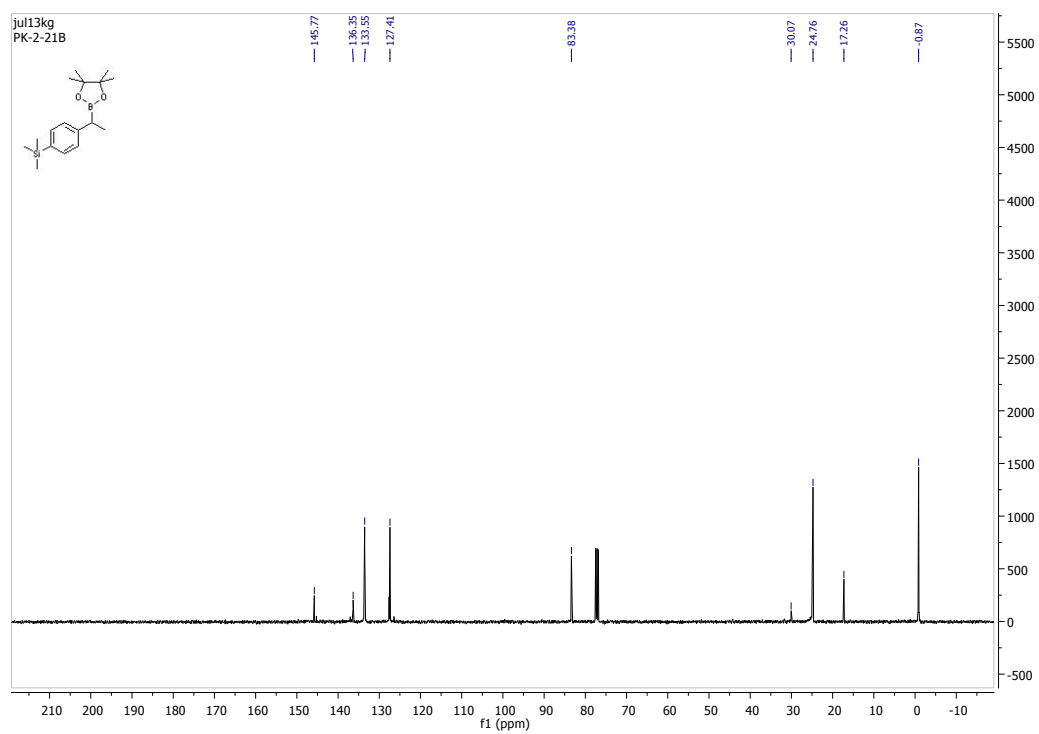
^1H NMR, CDCl_3 , 400 MHz:



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

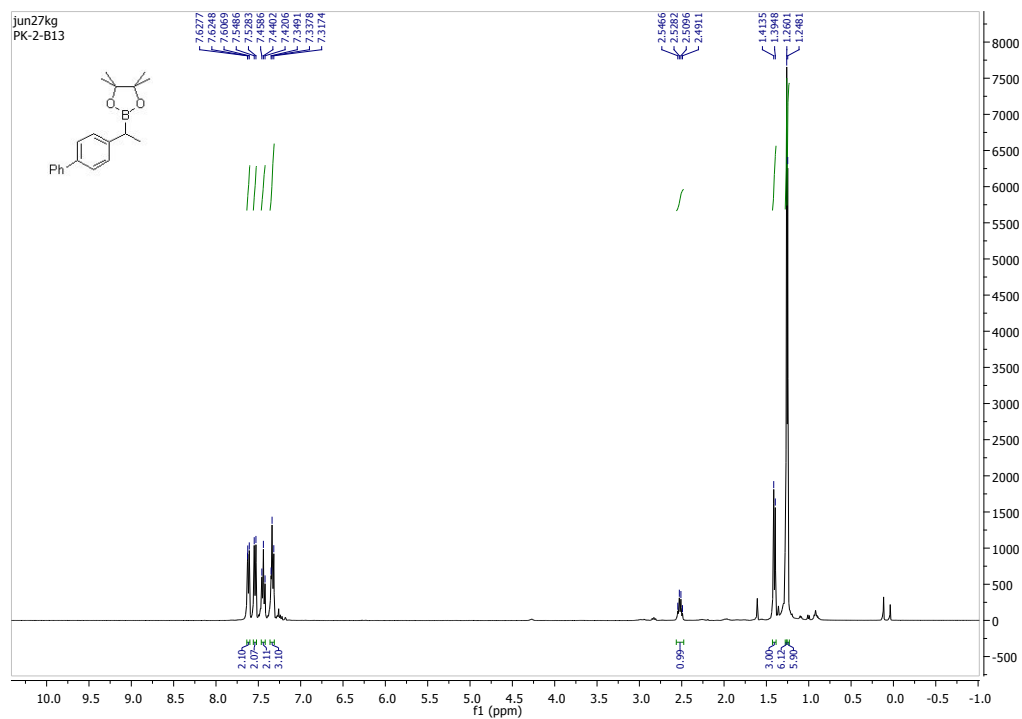


^{13}C NMR, CDCl_3 , 100 MHz:

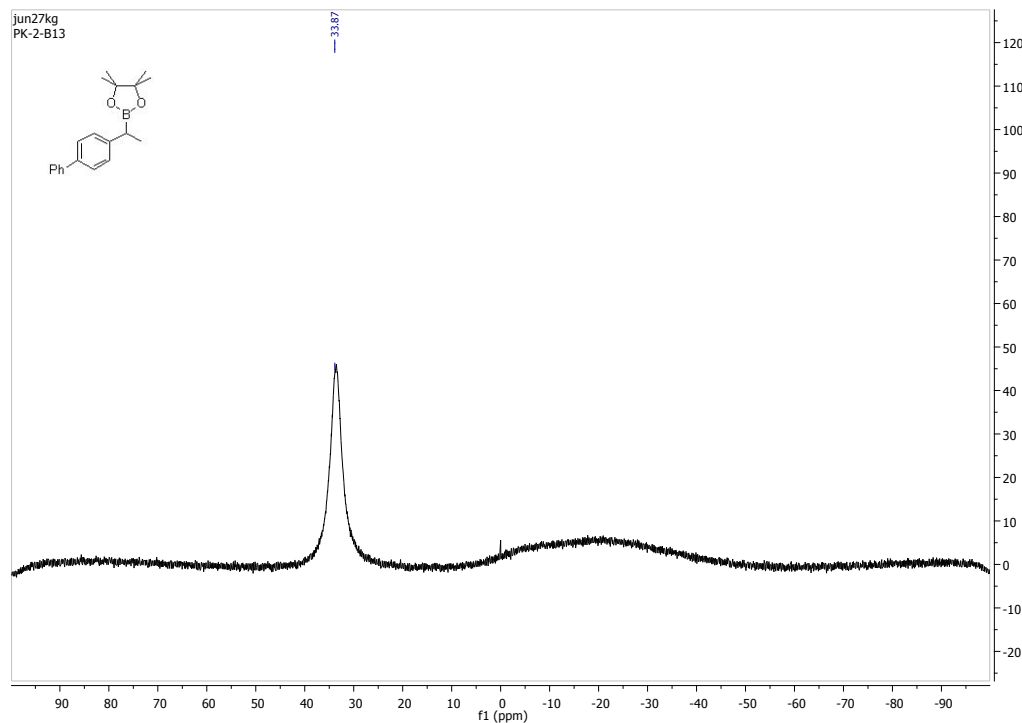


2-(1-(1,1'-Biphenyl)-4-ylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a).

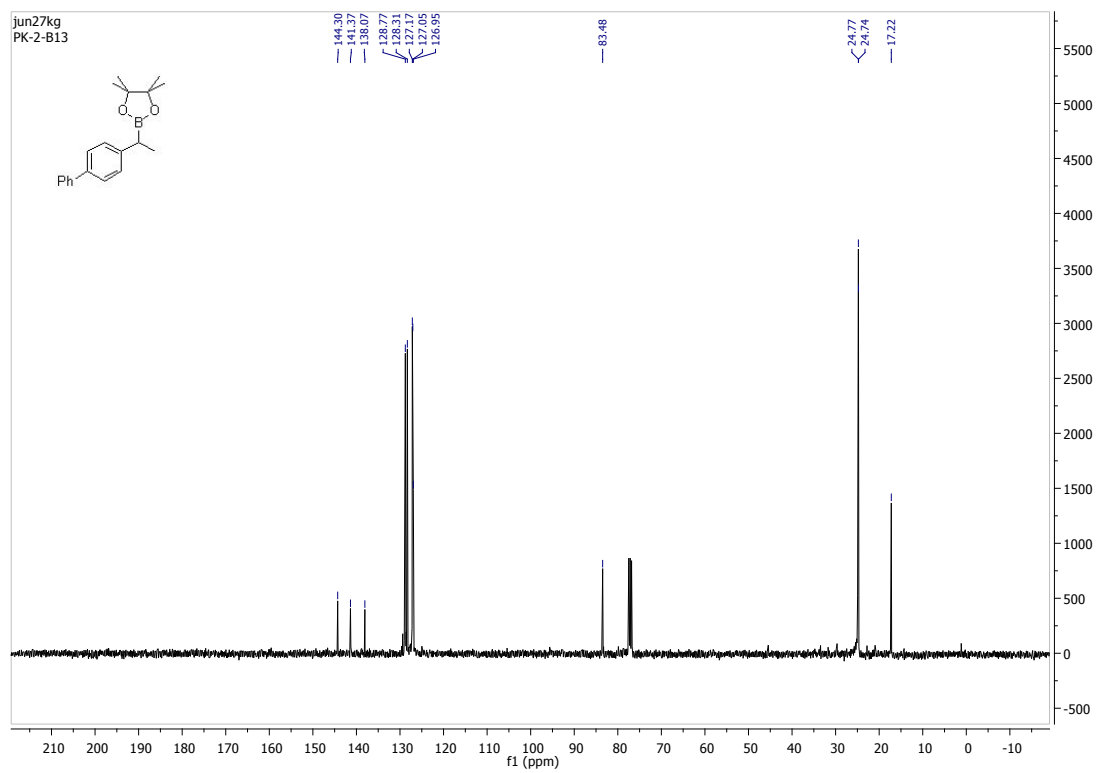
^1H NMR, CDCl_3 , 400 MHz:



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

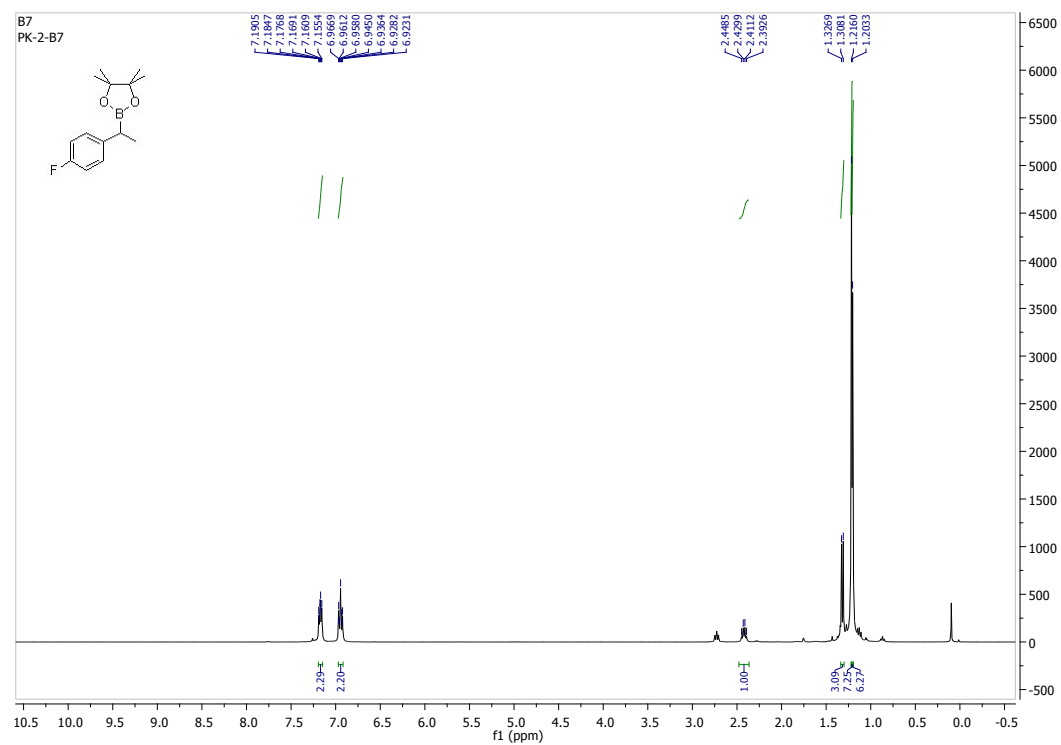


^{13}C NMR, CDCl_3 , 100 MHz:

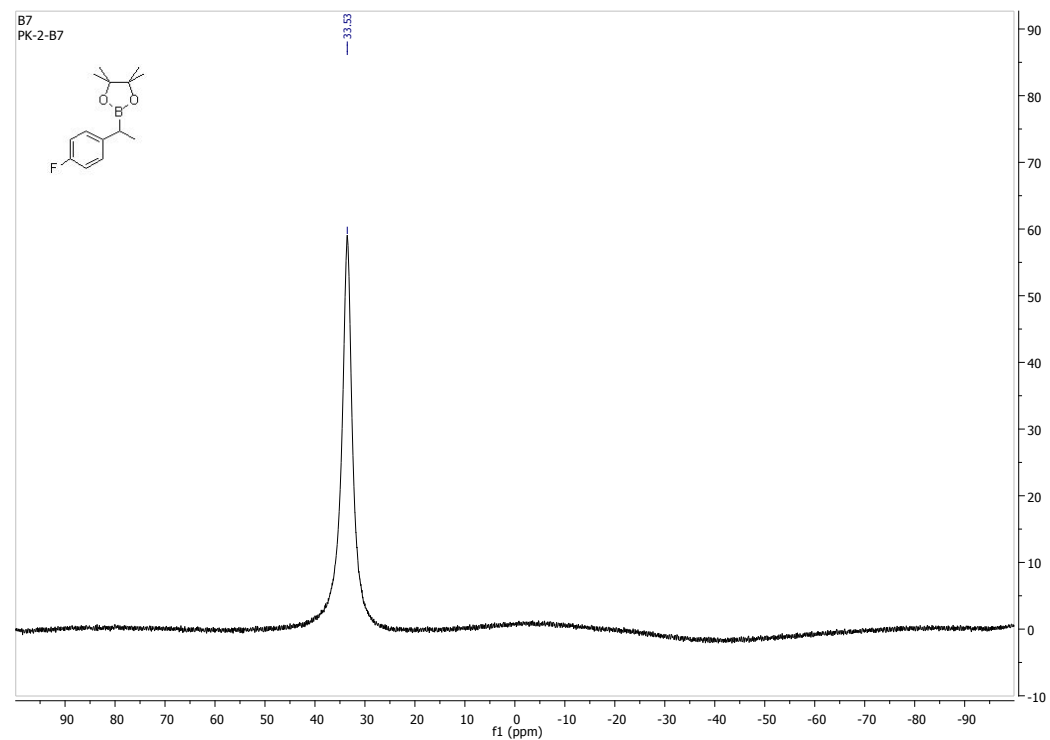


2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a).

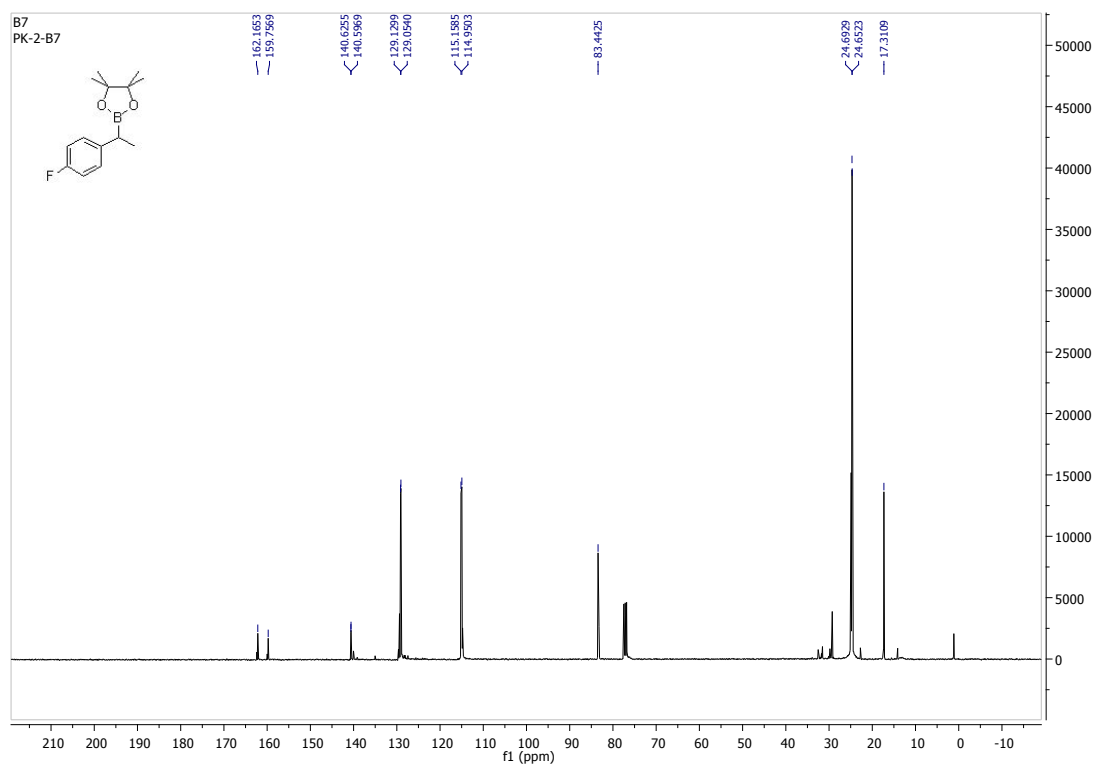
^1H NMR, CDCl_3 , 400 MHz:



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

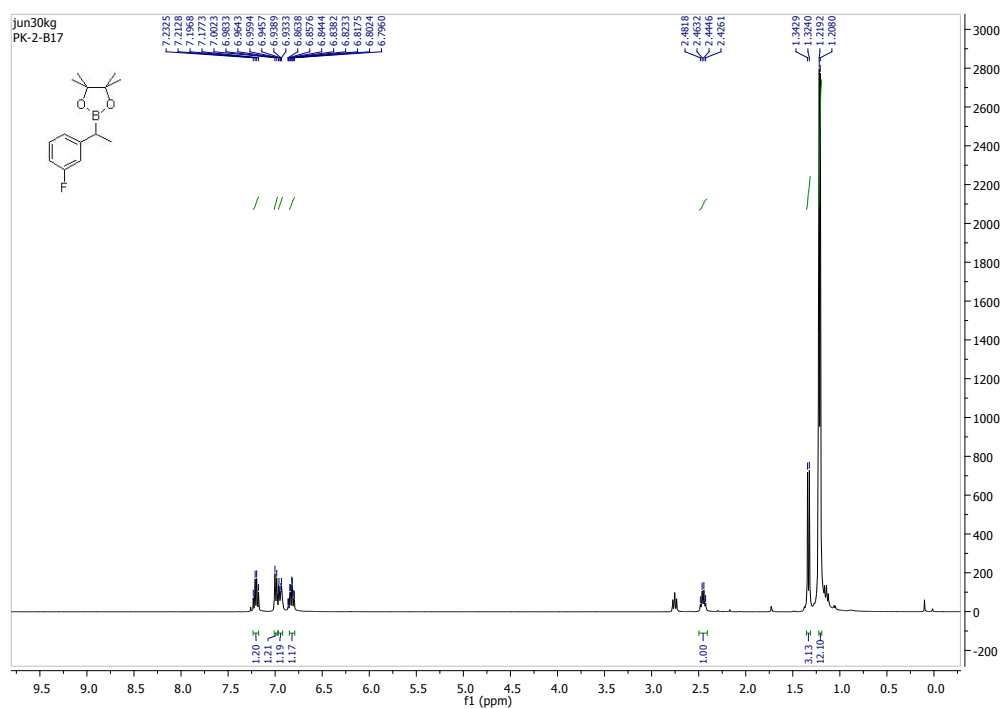


^{13}C NMR, CDCl_3 , 100 MHz:

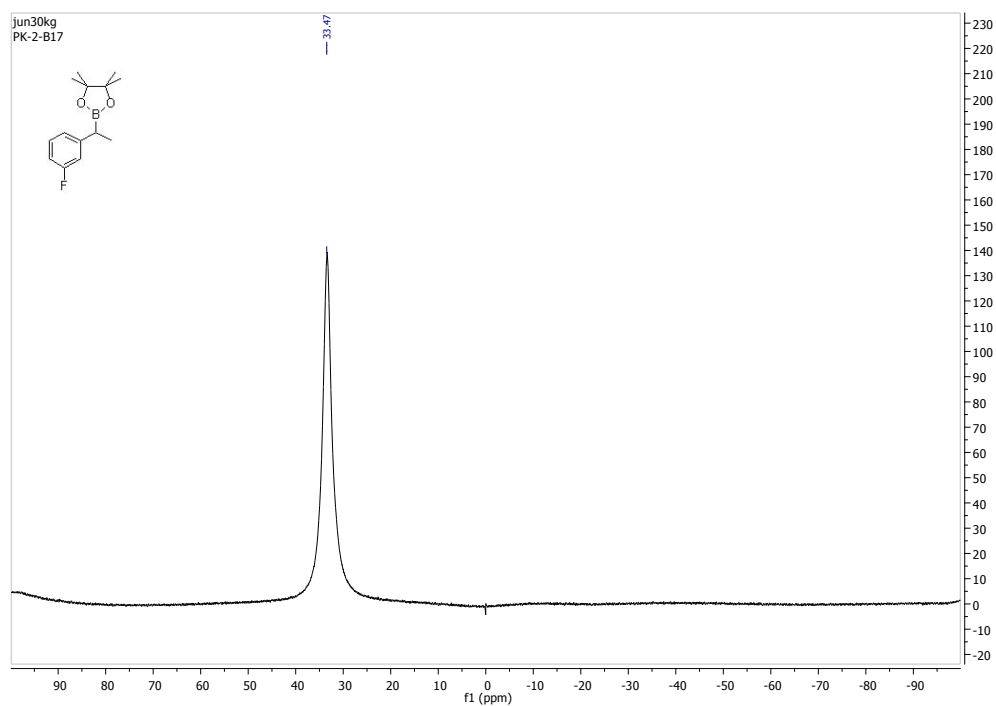


2-(1-(3-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10a).

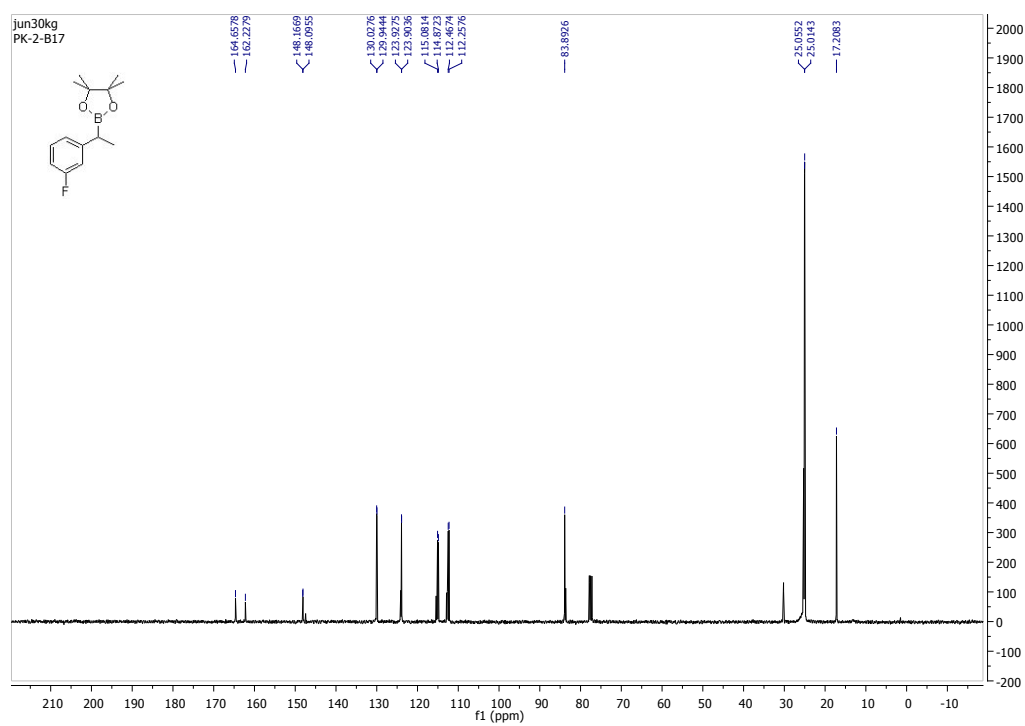
^1H NMR, CDCl_3 , 400 MHz:



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

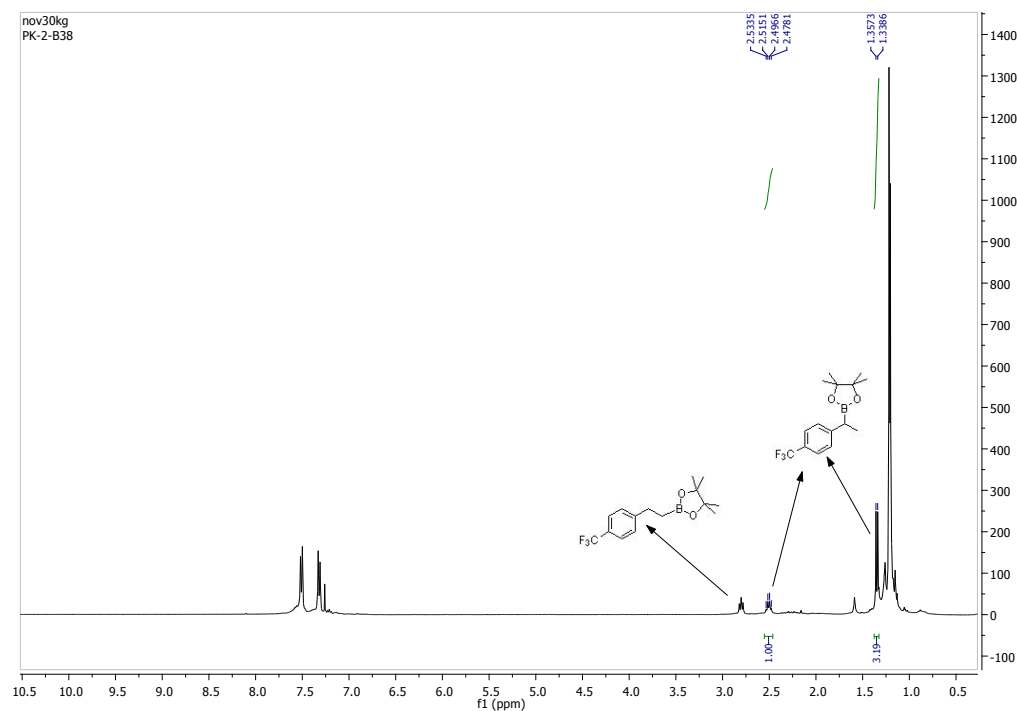


^{13}C NMR, CDCl_3 , 100 MHz:

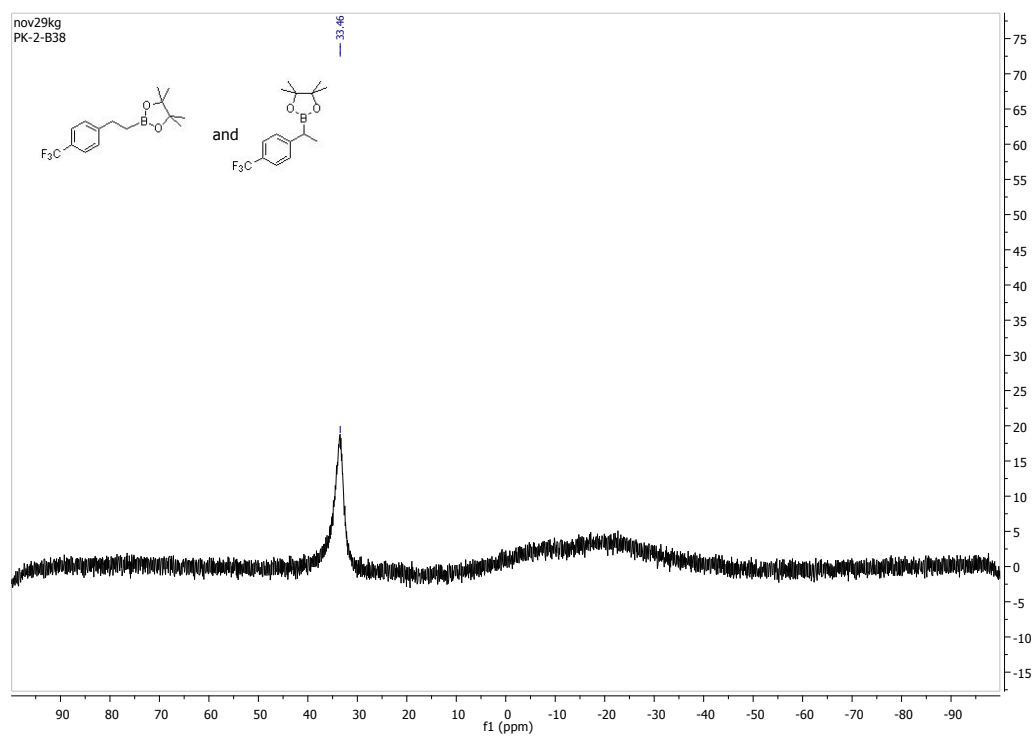


2-(1-(4-Trifluoromethylphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11a).

^1H NMR, CDCl_3 , 400 MHz:

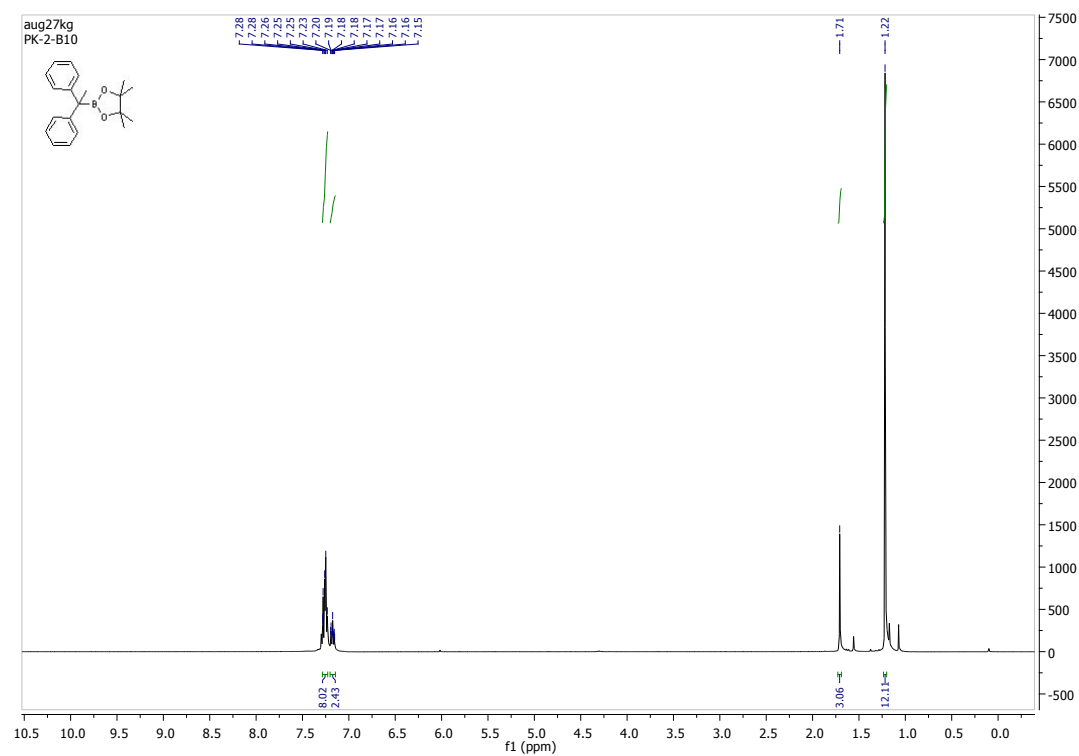


^{11}B NMR, CDCl_3 , 128 MHz:

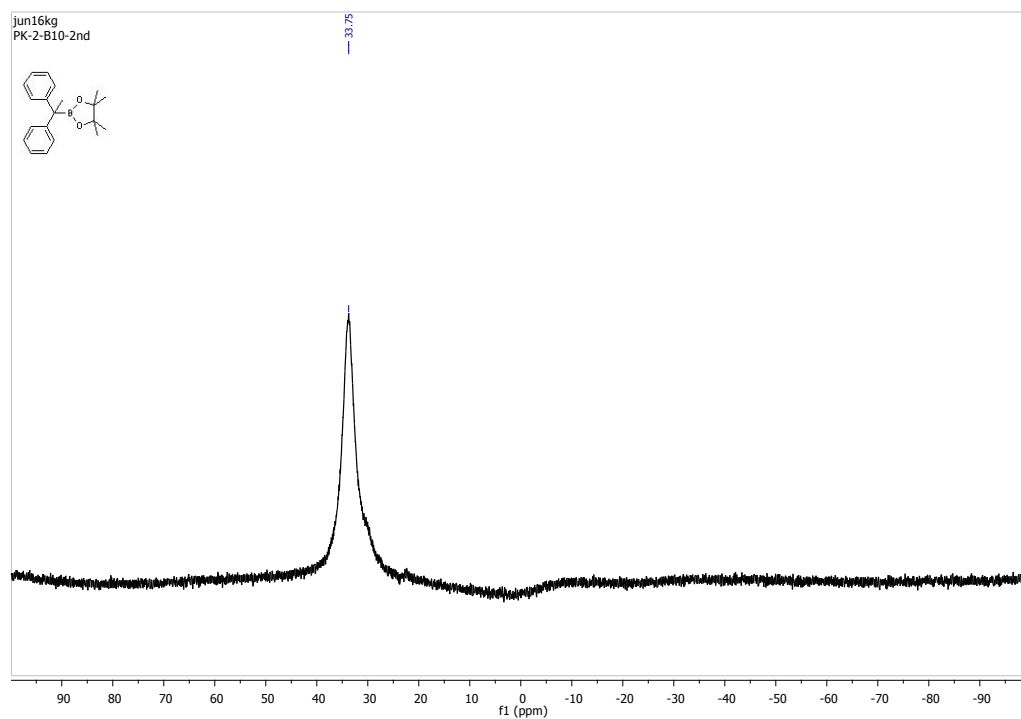


2-(1,1-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12a).

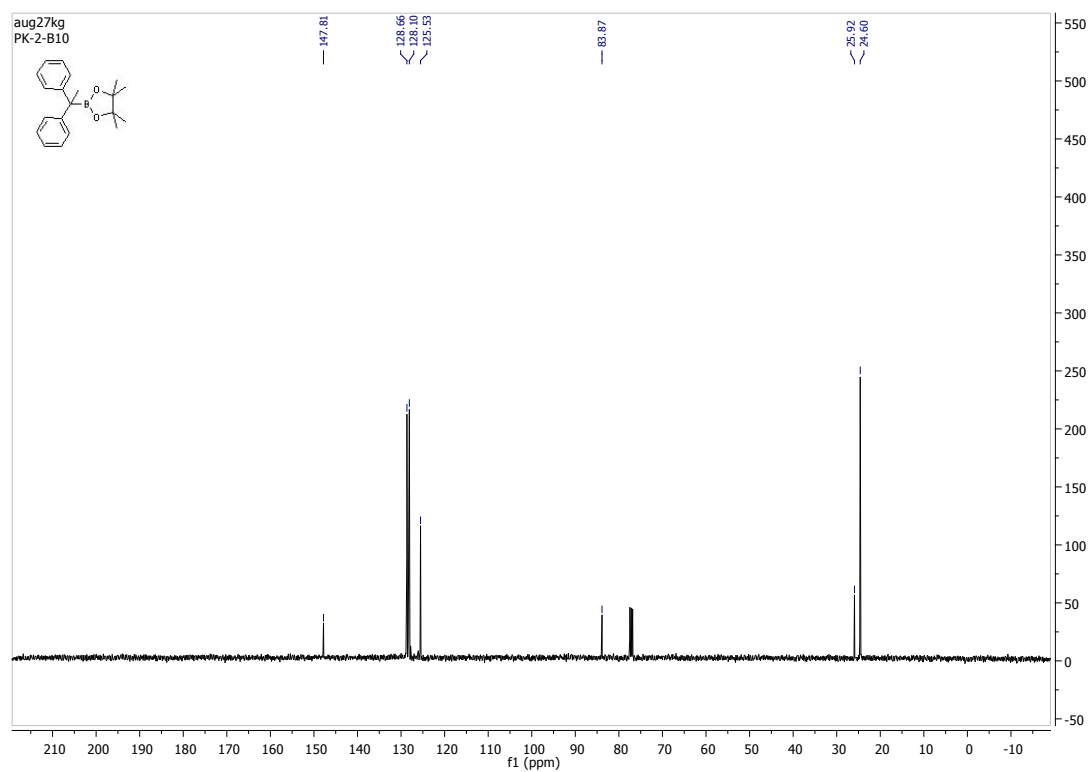
^1H NMR, CDCl_3 , 400 MHz:



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

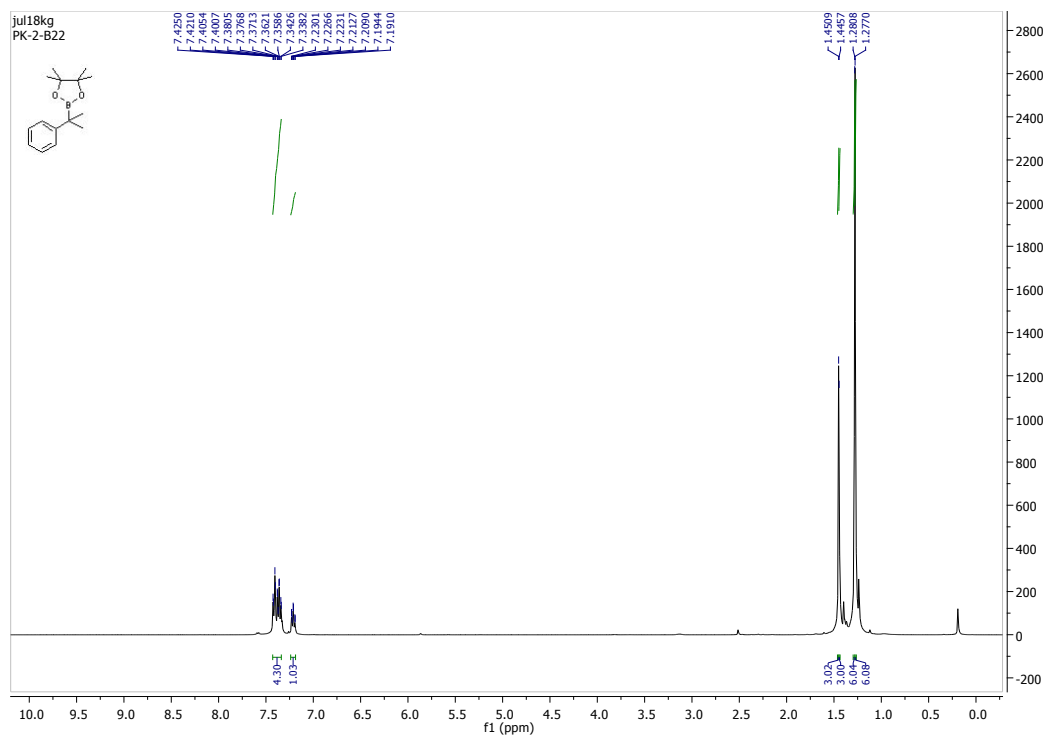


^{13}C NMR, CDCl_3 , 100 MHz:

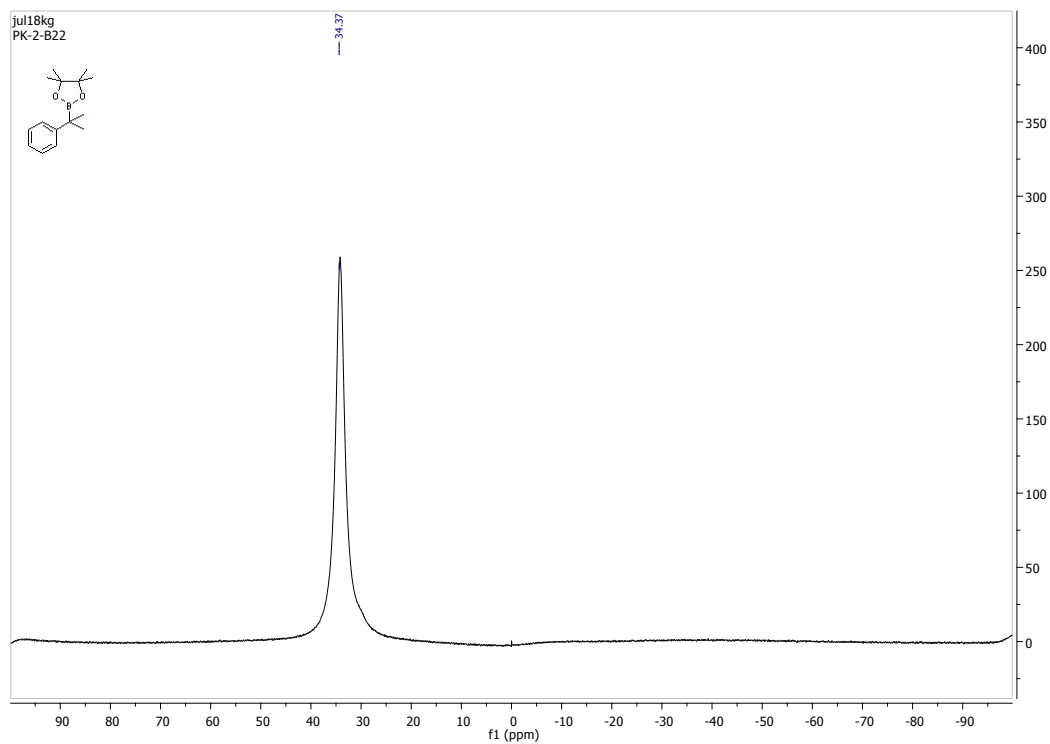


4,4,5,5-Tetramethyl-2-(2-phenylpropan-2-yl)-1,3,2-dioxaborolane (13a).

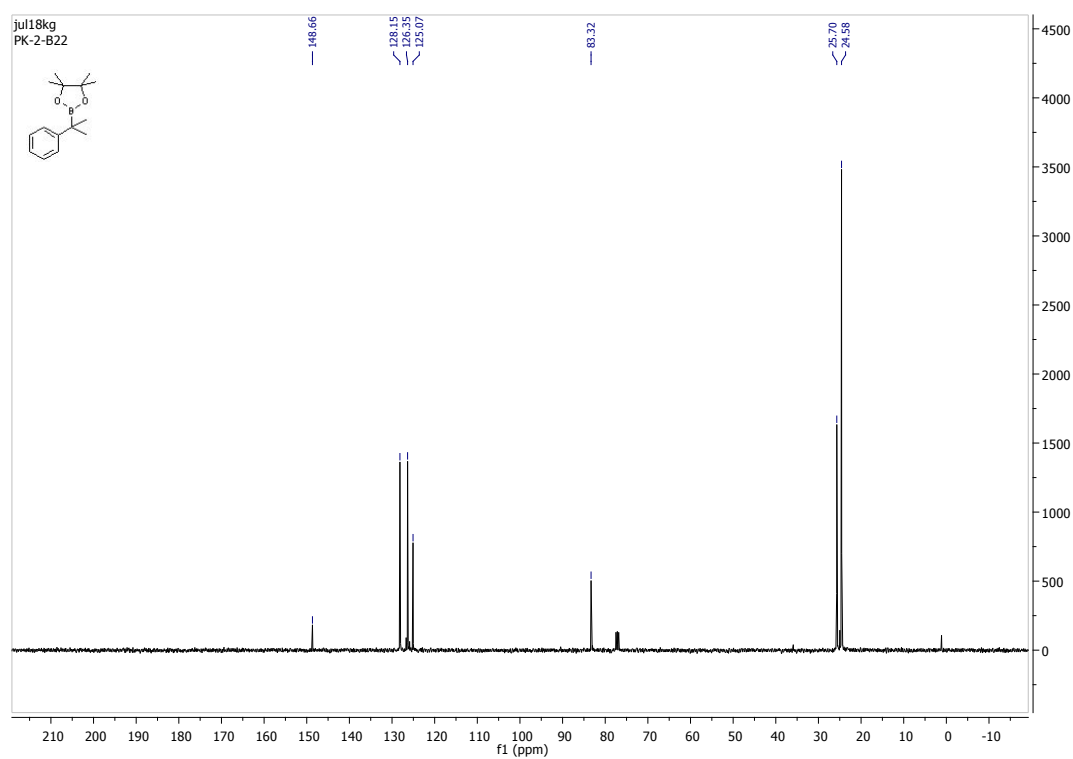
^1H NMR, CDCl_3 , 400 MHz:



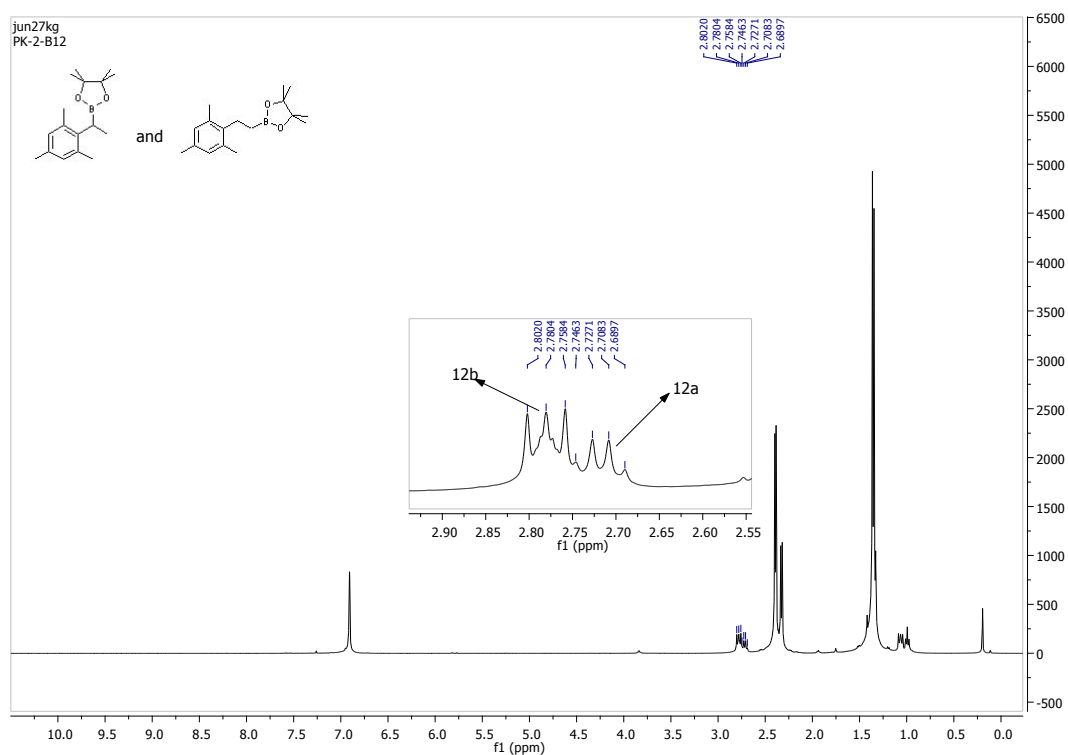
^{11}B NMR, CDCl_3 , 128 MHz:



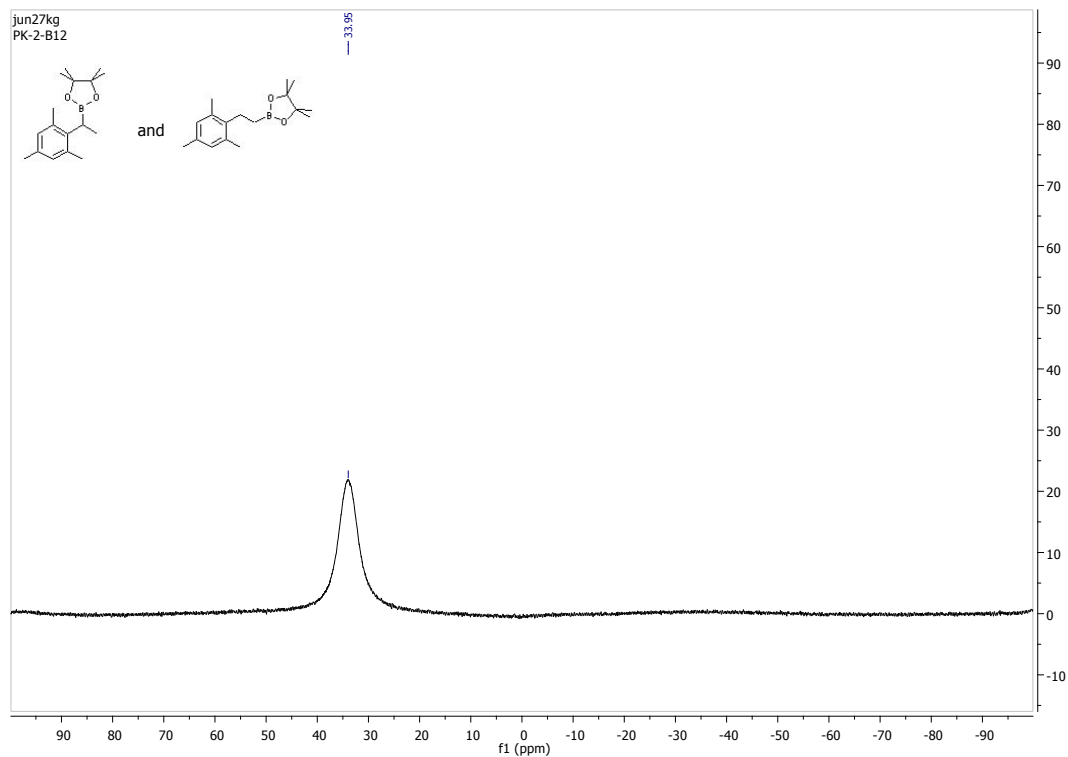
^{13}C NMR, CDCl_3 , 100 MHz:



2-(1-Mesitylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14a).

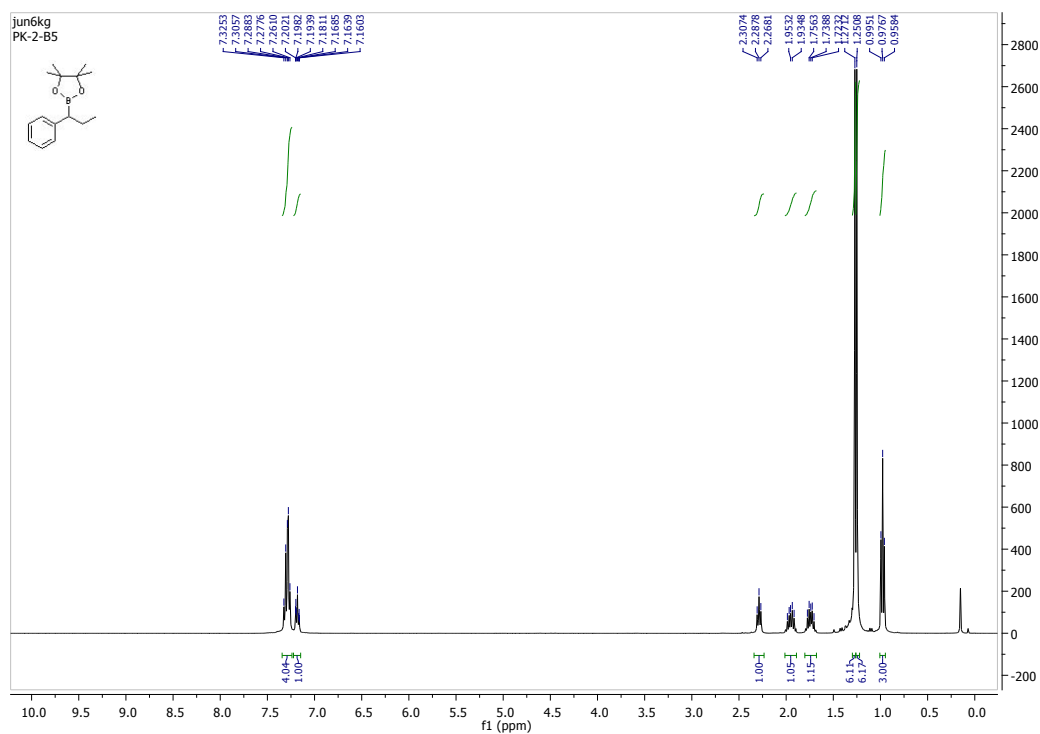


^{11}B NMR, CDCl_3 , 128 MHz:

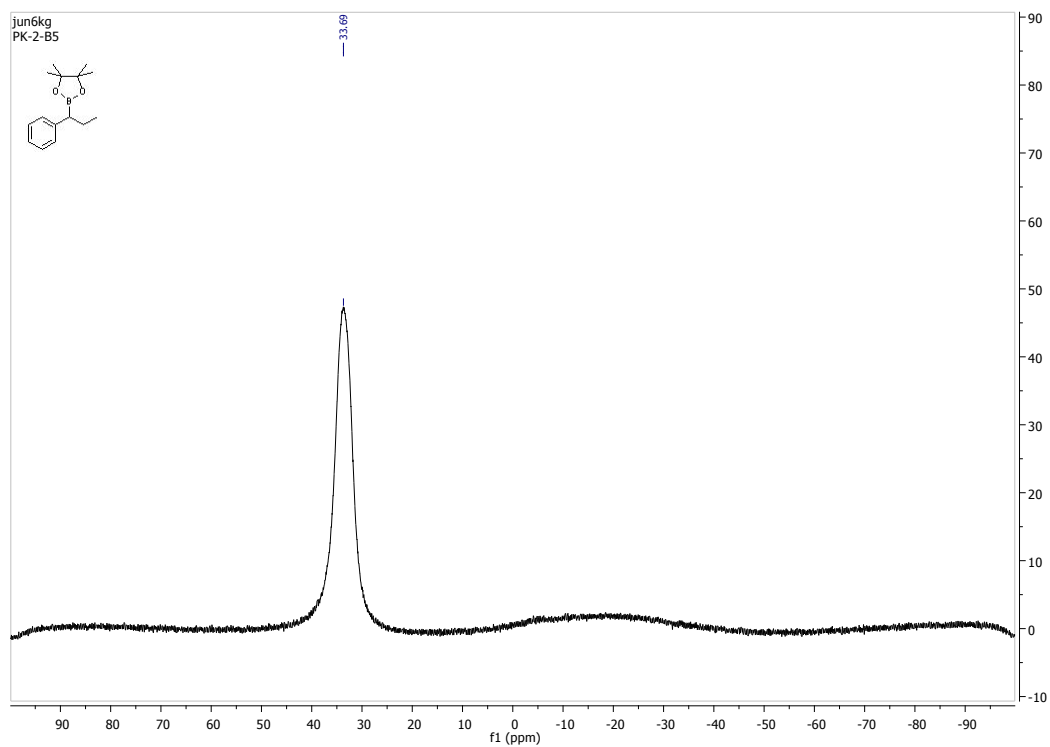


4,4,5,5-Tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (15a).

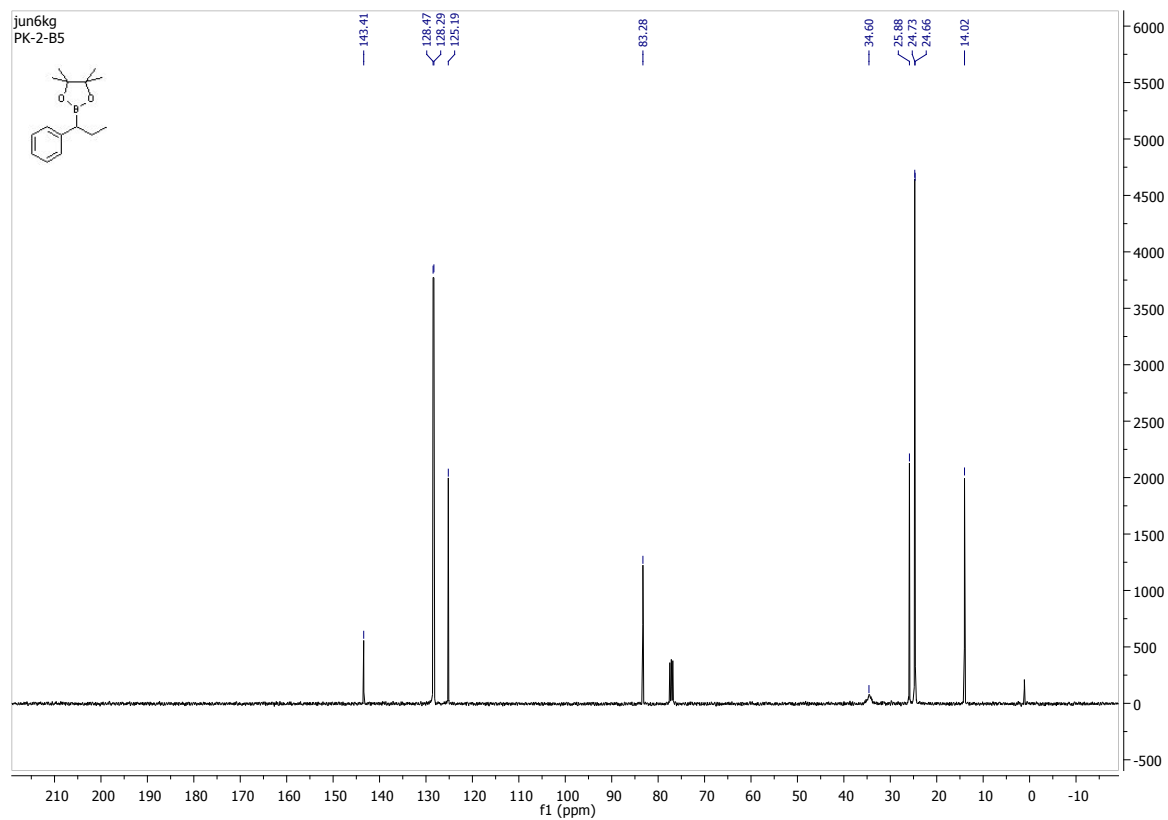
^1H NMR, CDCl_3 , 400 MHz:



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

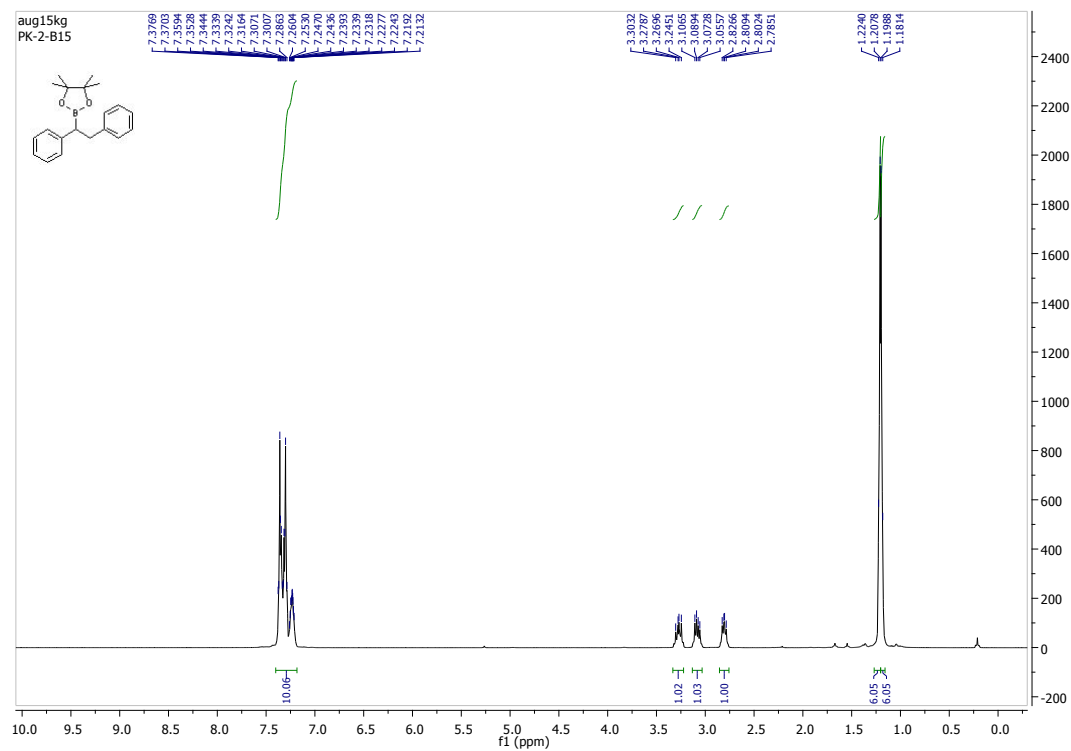


^{13}C NMR, CDCl_3 , 100 MHz:

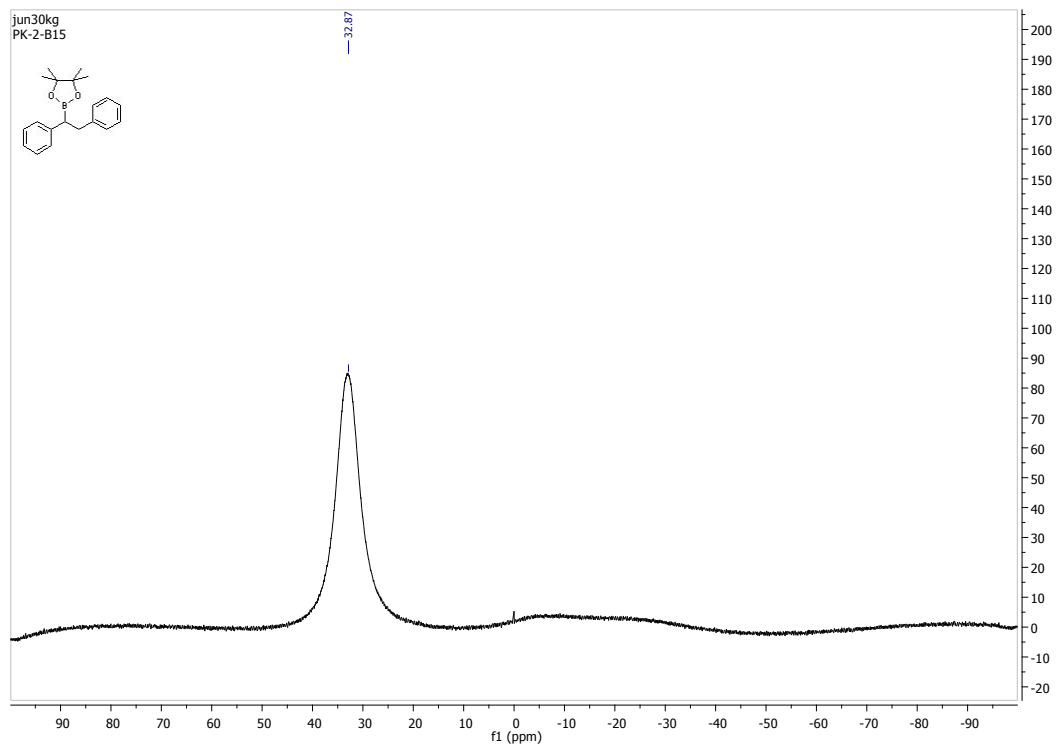


2-(1,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-Dioxaborolane (16a).

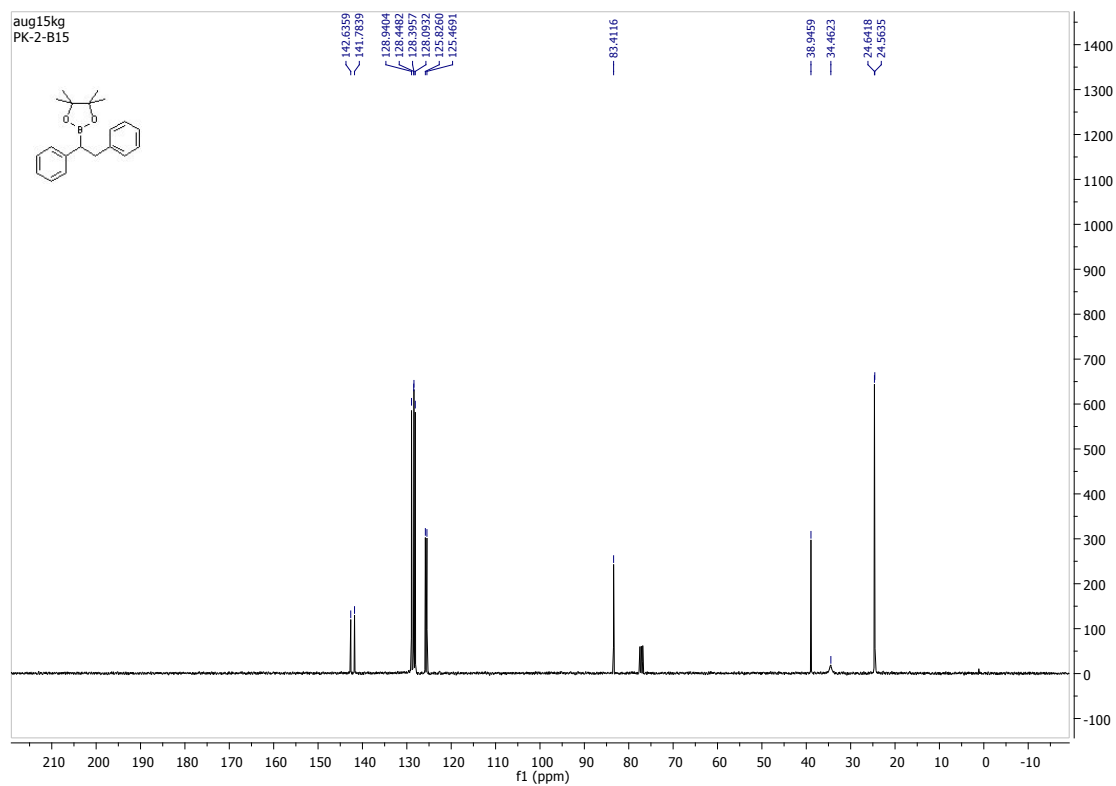
^1H NMR, CDCl_3 , 400 MHz:



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

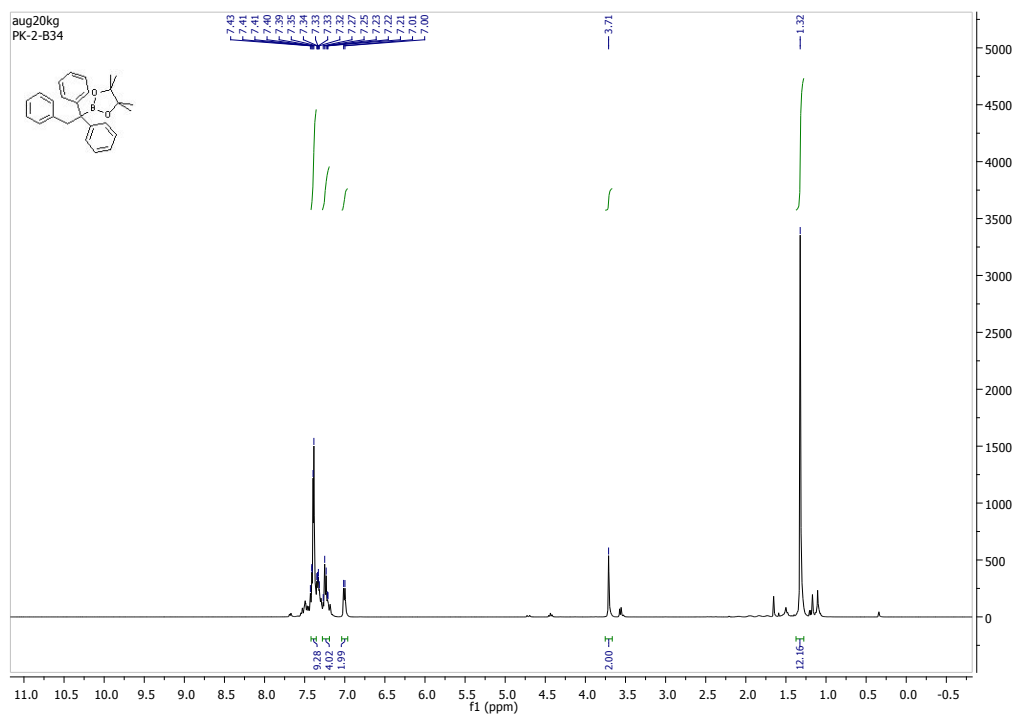


^{13}C NMR, CDCl_3 , 100 MHz:

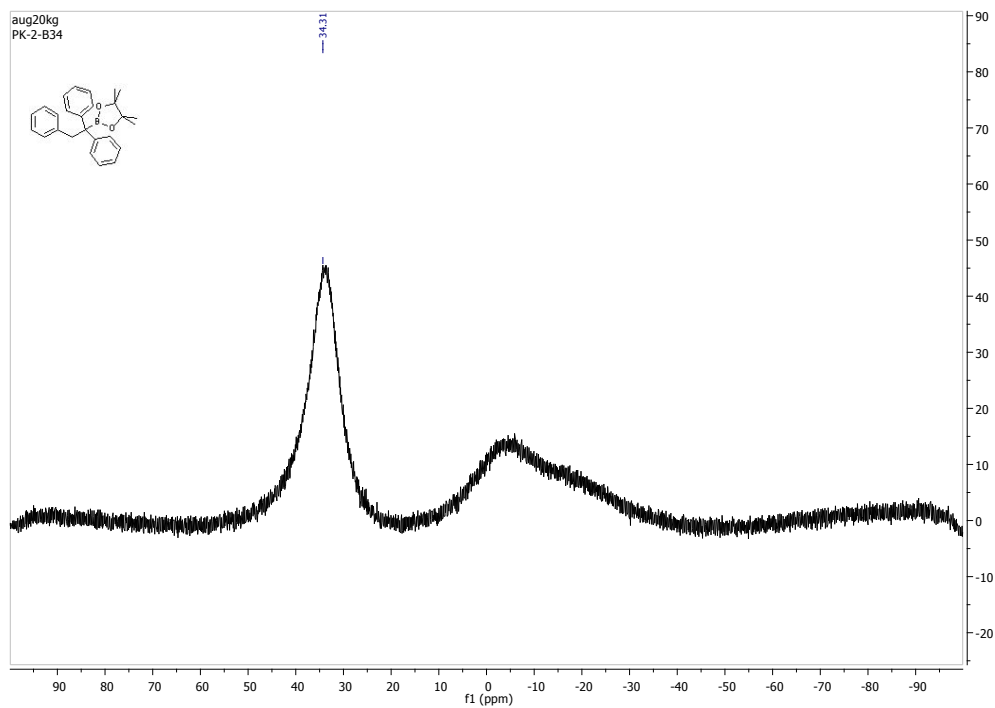


2-(1,1,2-triphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17a).

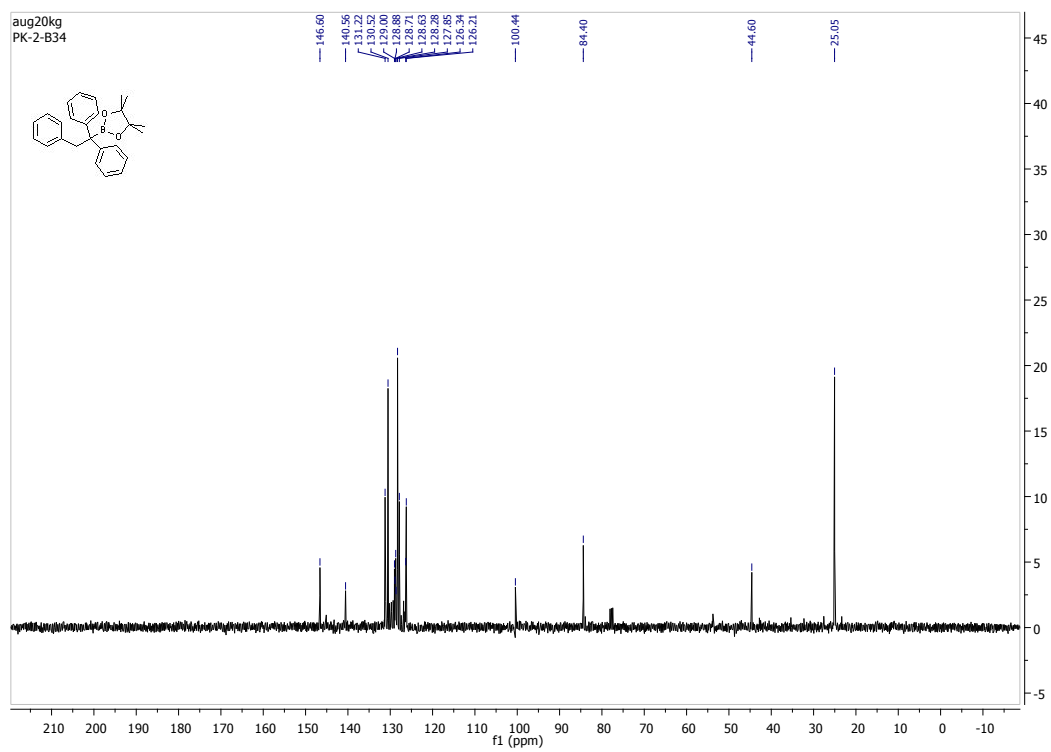
^1H NMR, CDCl_3 , 400 MHz:



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

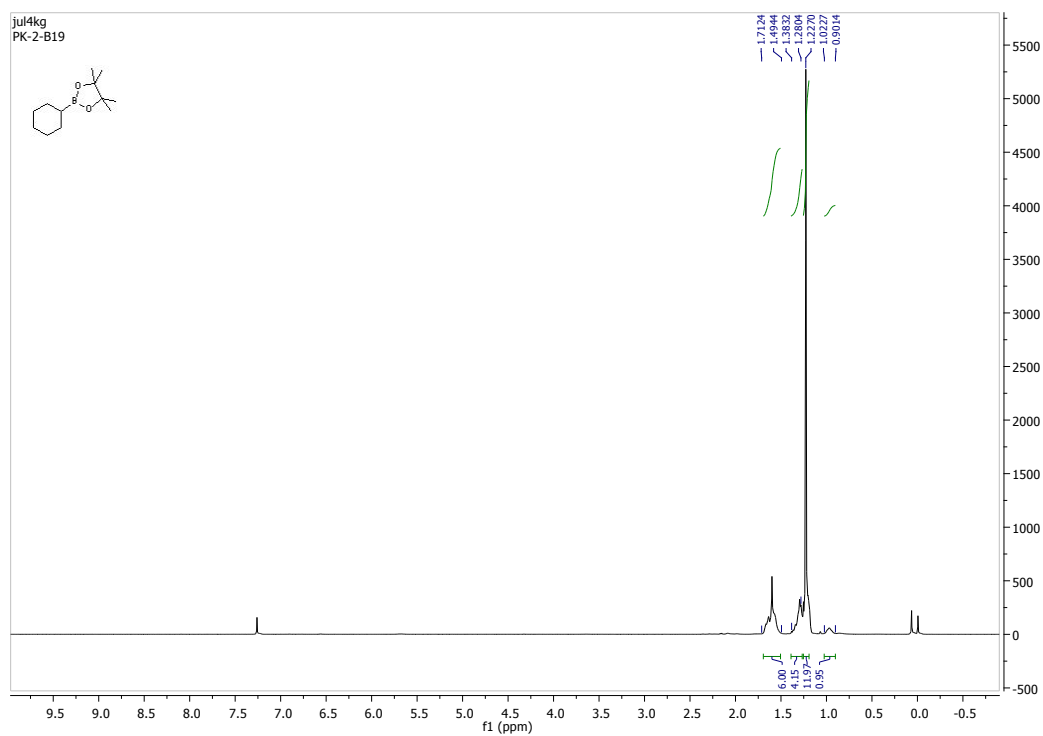


^{13}C NMR, CDCl_3 , 100 MHz:

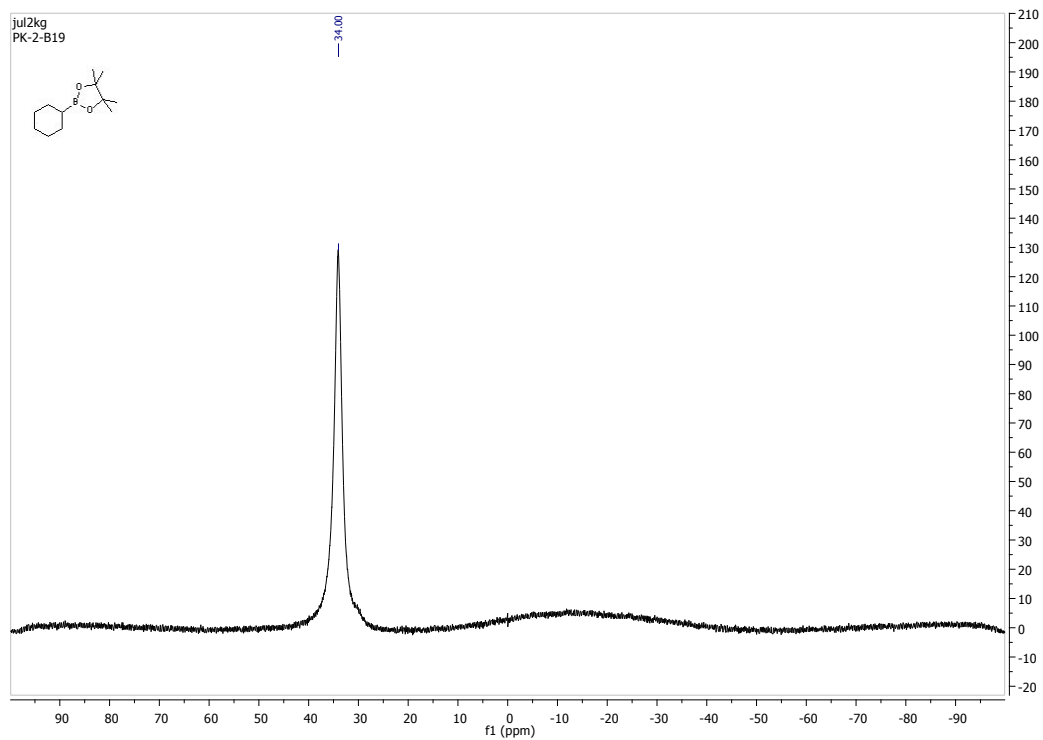


2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18a).

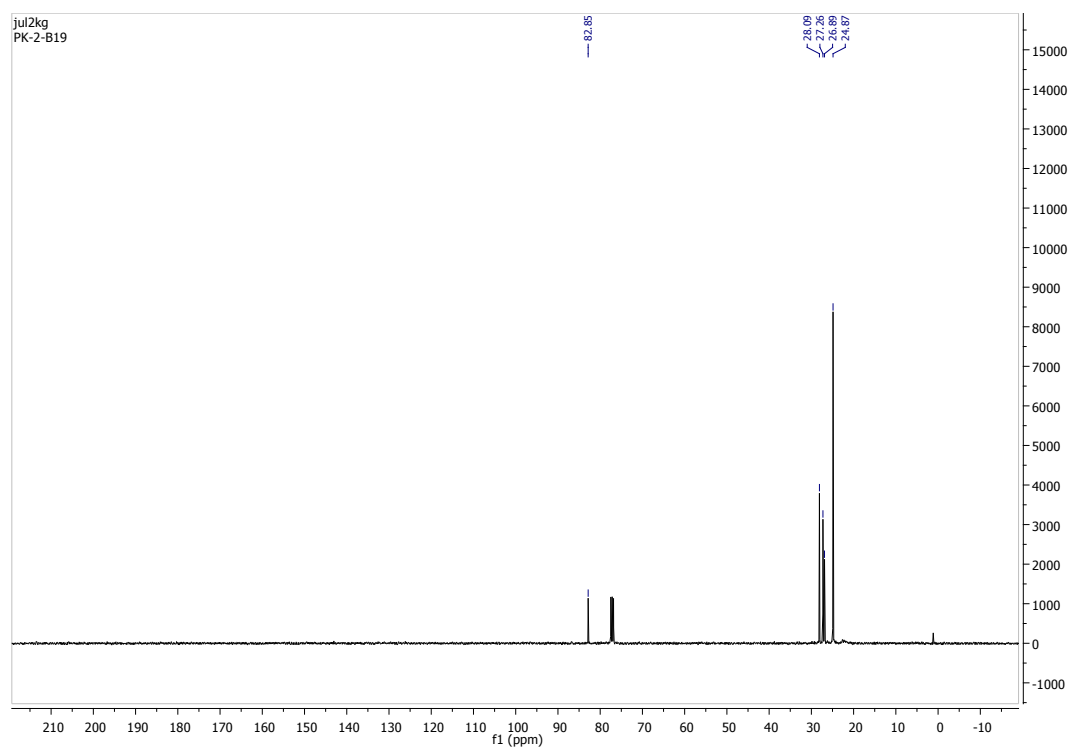
^1H NMR, CDCl_3 , 400 MHz:



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

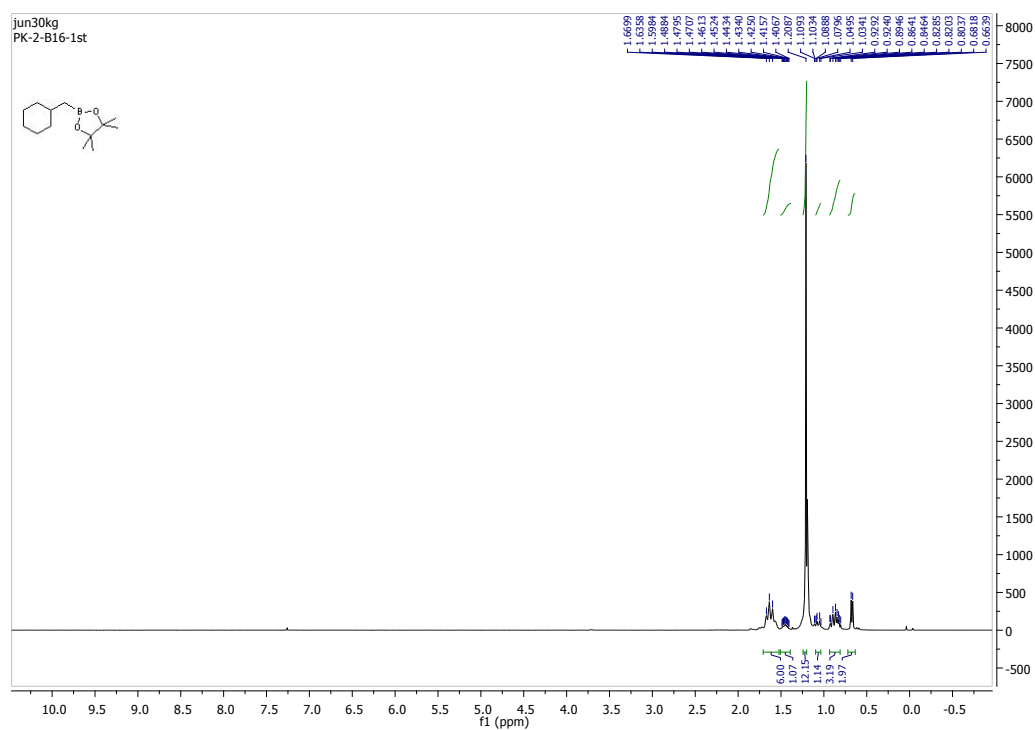


^{13}C NMR, CDCl_3 , 100 MHz:

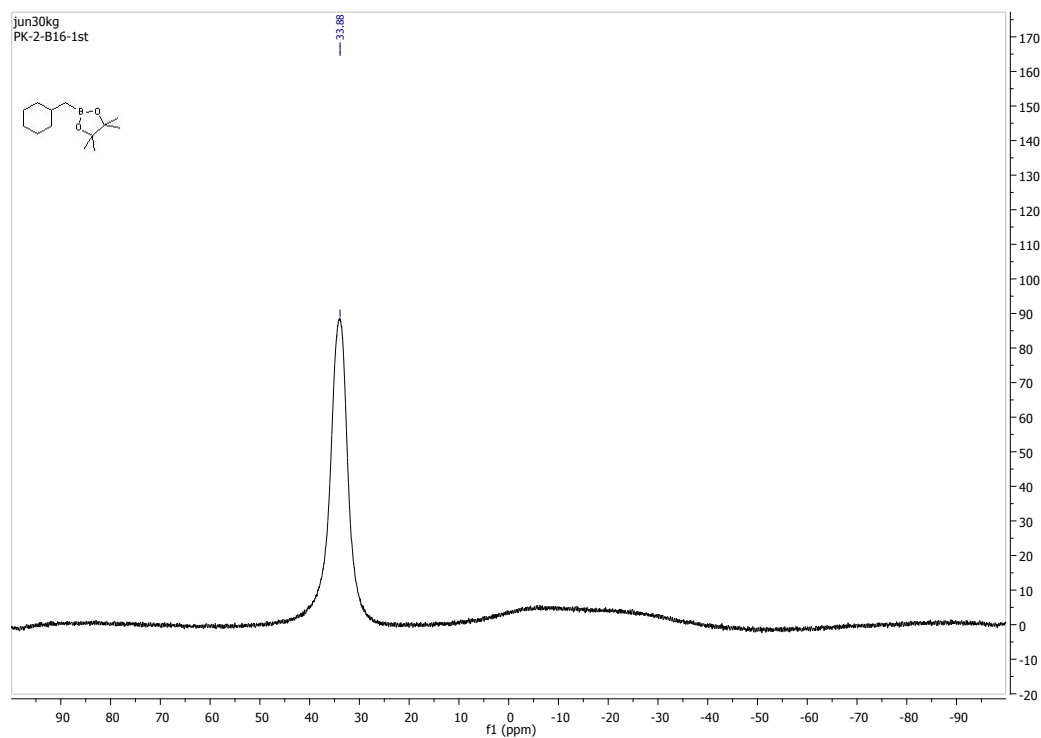


2-(Cyclohexylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19a).

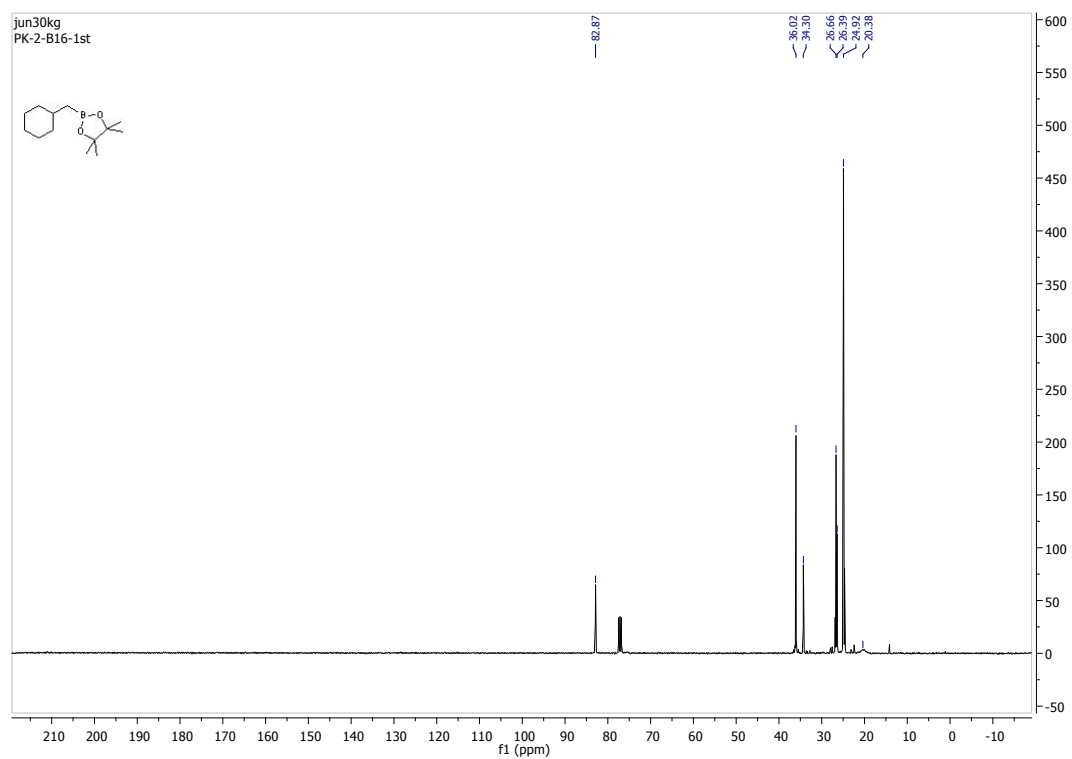
^1H NMR, CDCl_3 , 400 MHz:



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

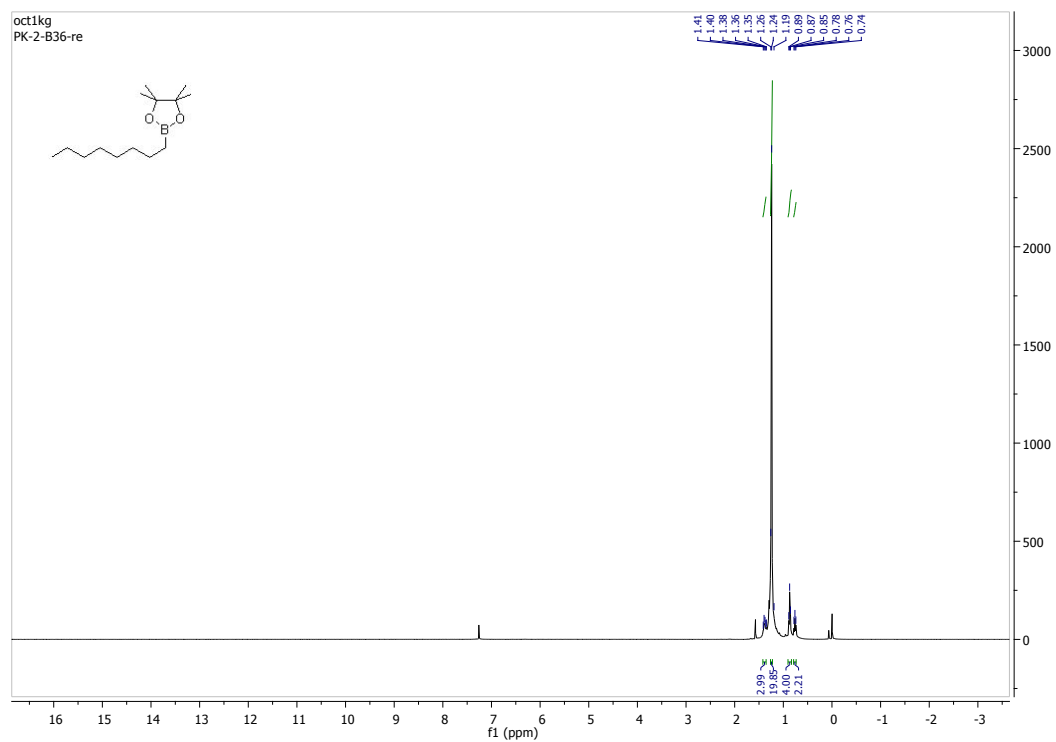


^{13}C NMR, CDCl_3 , 100 MHz:

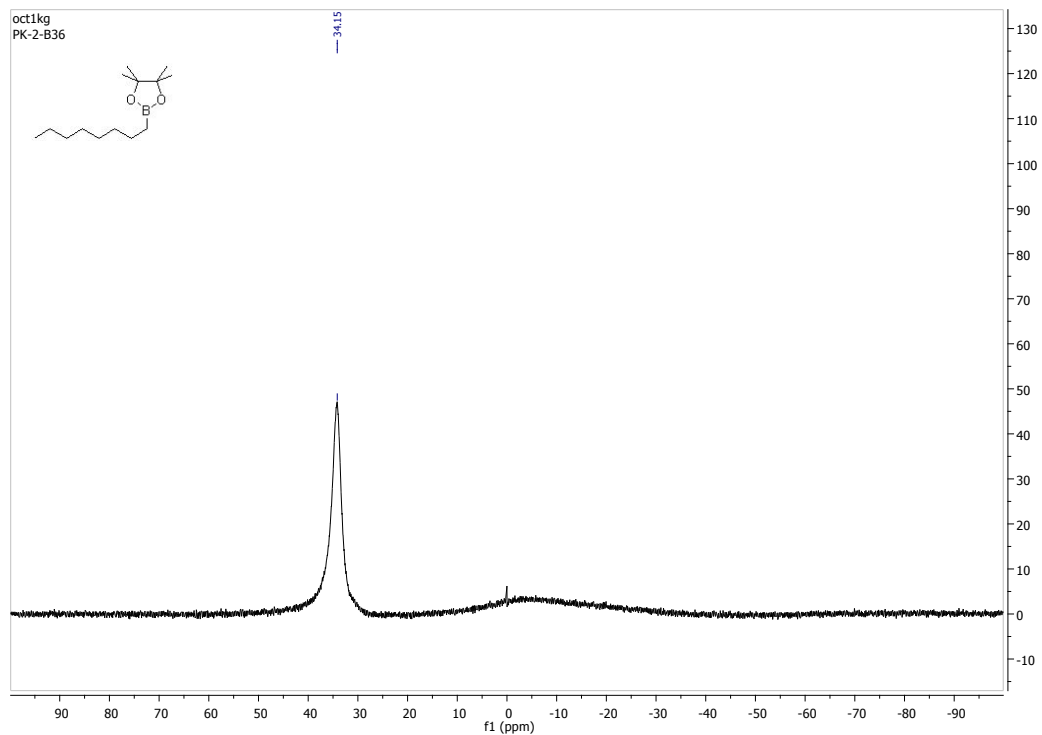


4,4,5,5-Ttramethyl-2-octyl-1,3,2-dioxaborolane (20a)

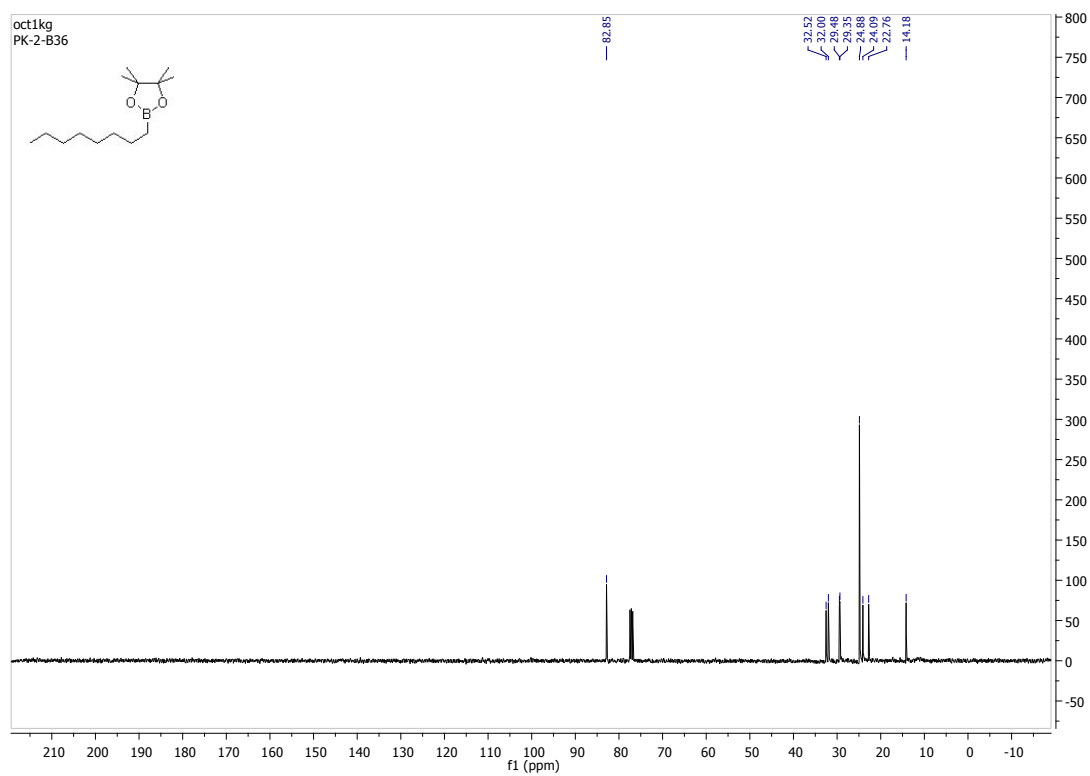
^1H NMR, CDCl_3 , 400 MHz:



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

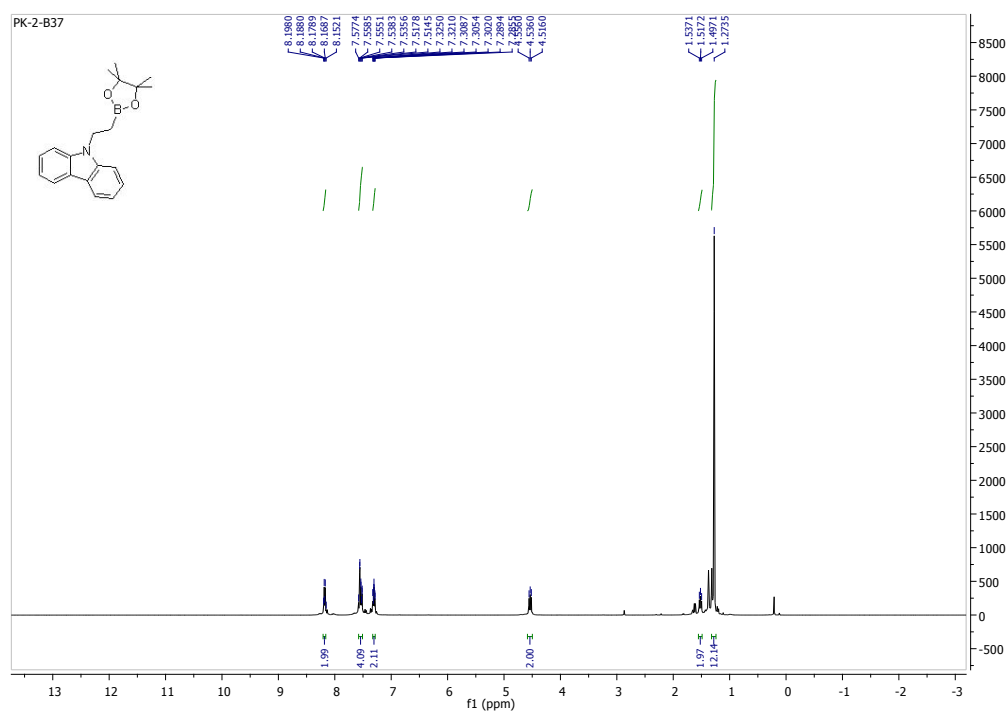


^{13}C NMR, CDCl_3 , 100 MHz:

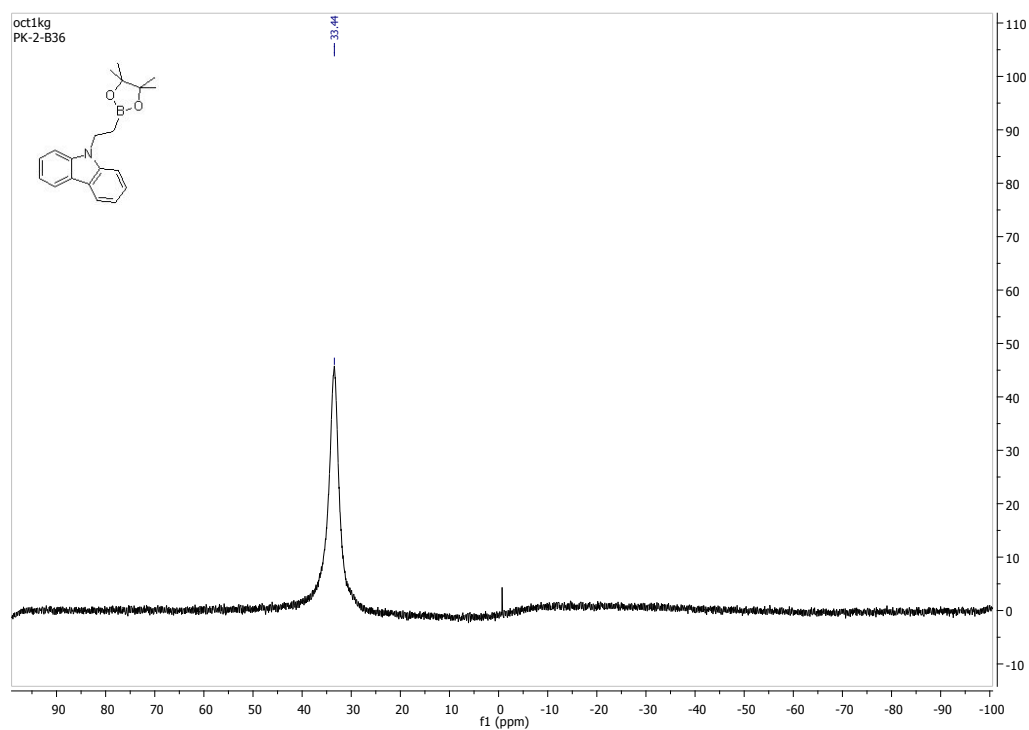


9-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-9H-carbazole (21a)

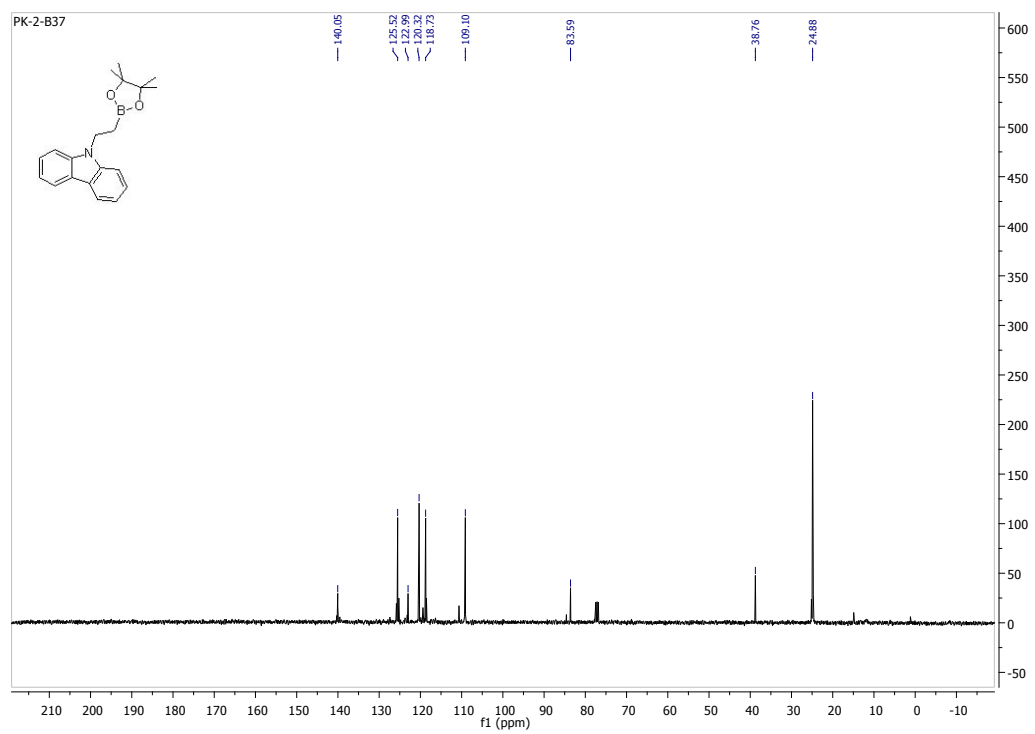
^1H NMR, CDCl_3 , 400 MHz:



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

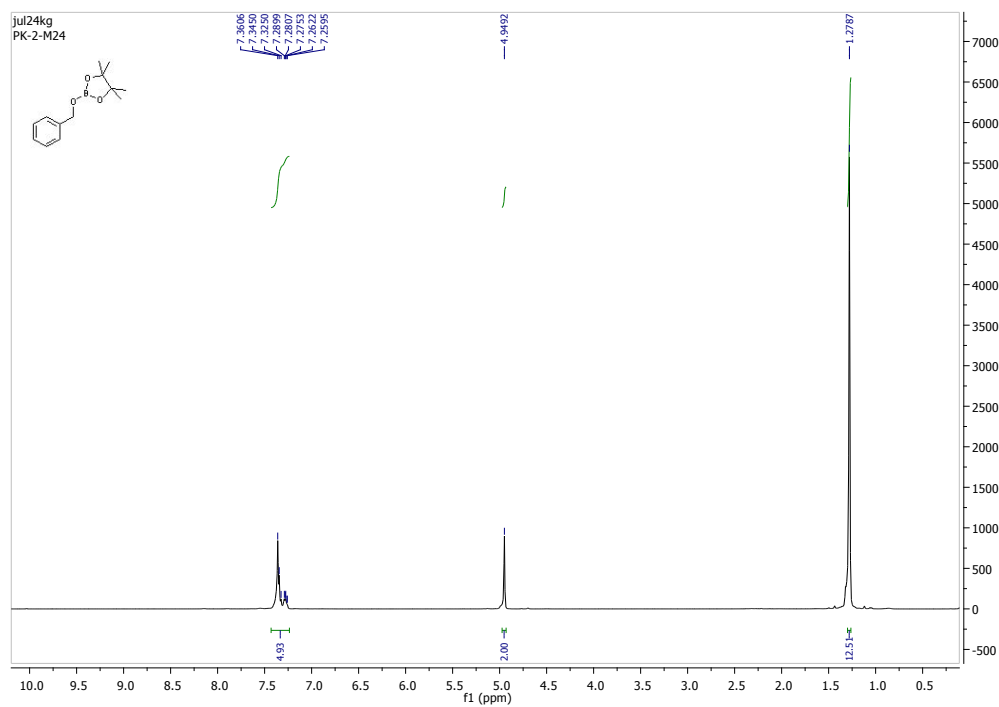


^{13}C NMR, CDCl_3 , 100 MHz:

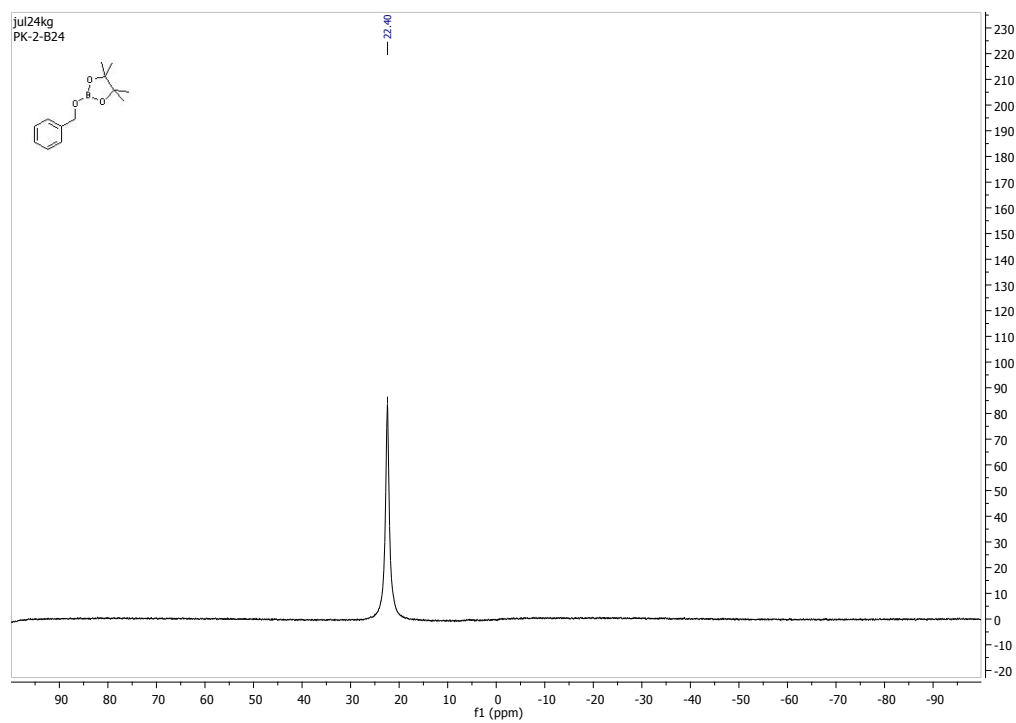


2-(Benzyloxy)pinacolborane (24a).

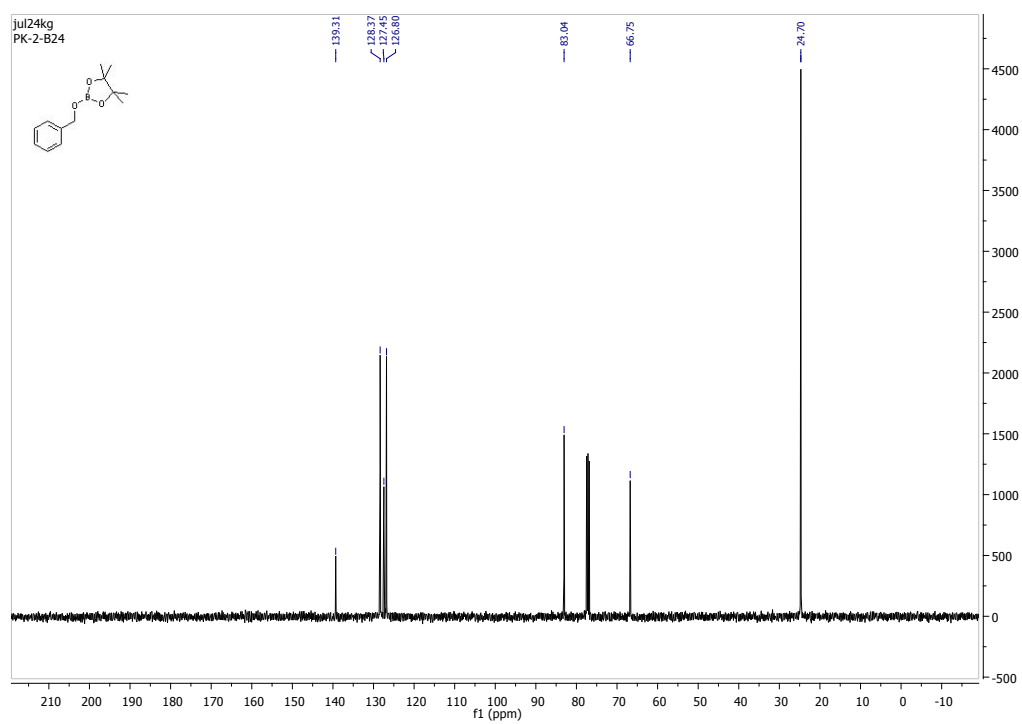
^1H NMR, CDCl_3 , 400 MHz:



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

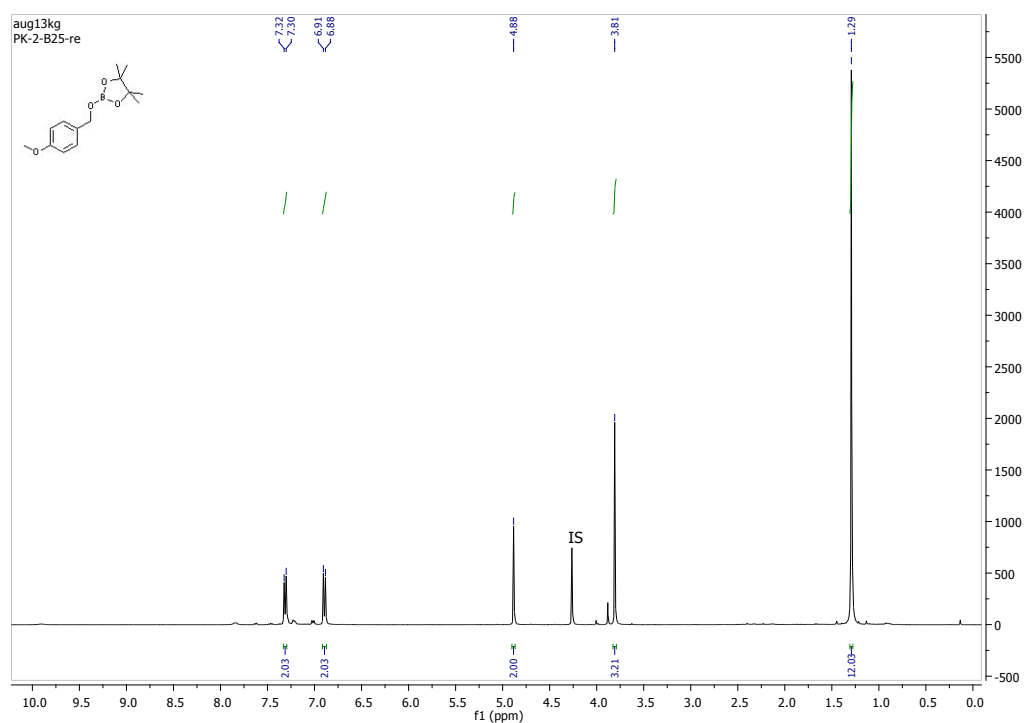


^{13}C NMR, CDCl_3 , 100 MHz:

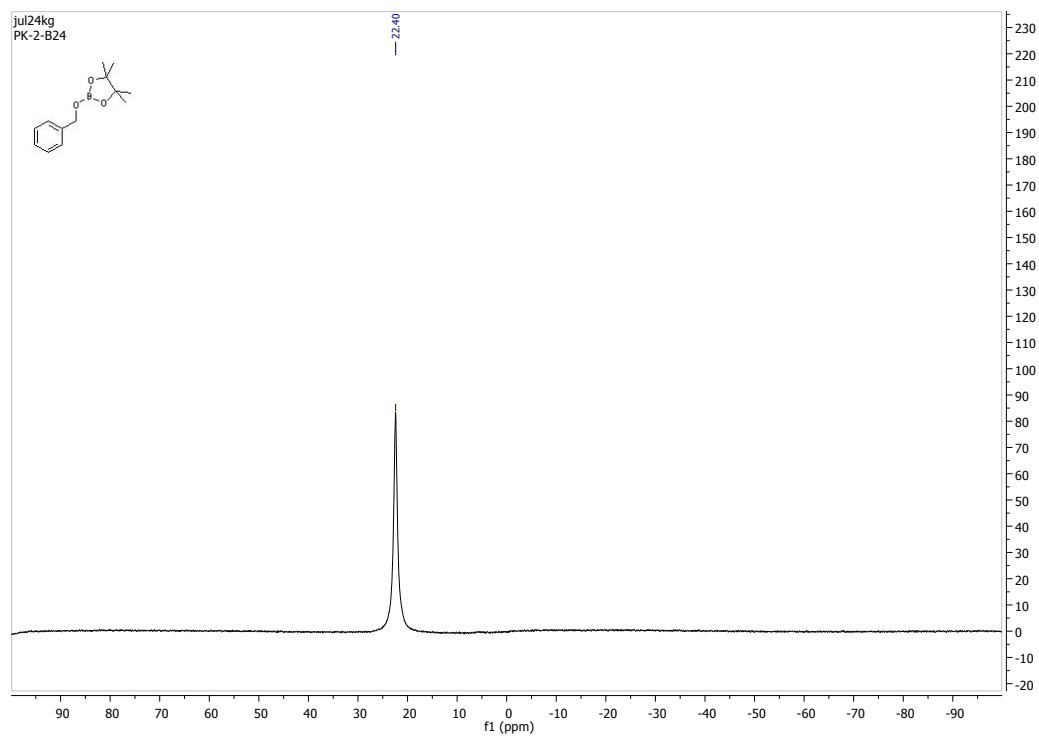


2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24b).

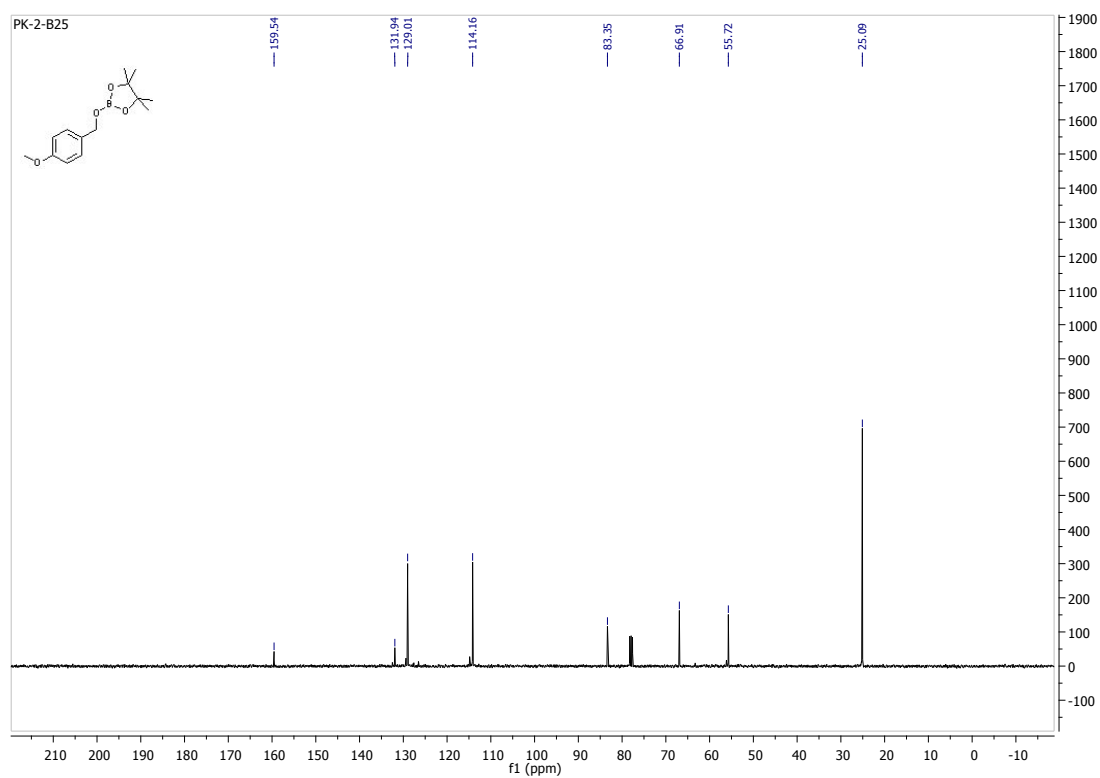
^1H NMR, CDCl_3 , 400 MHz:



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

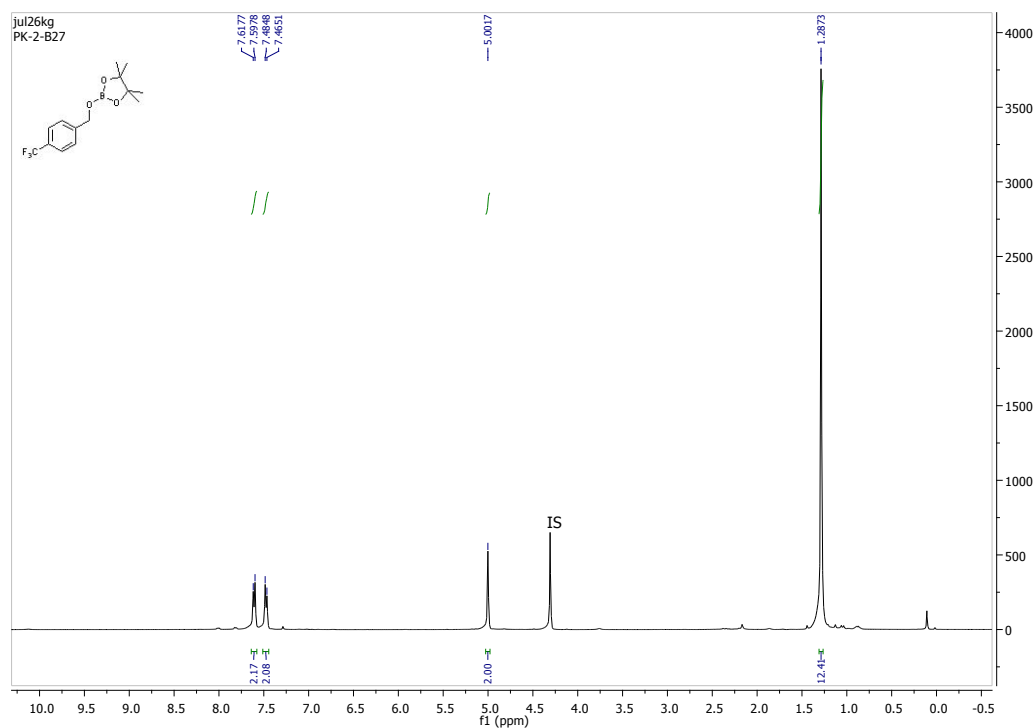


^{13}C NMR, CDCl_3 , 100 MHz:

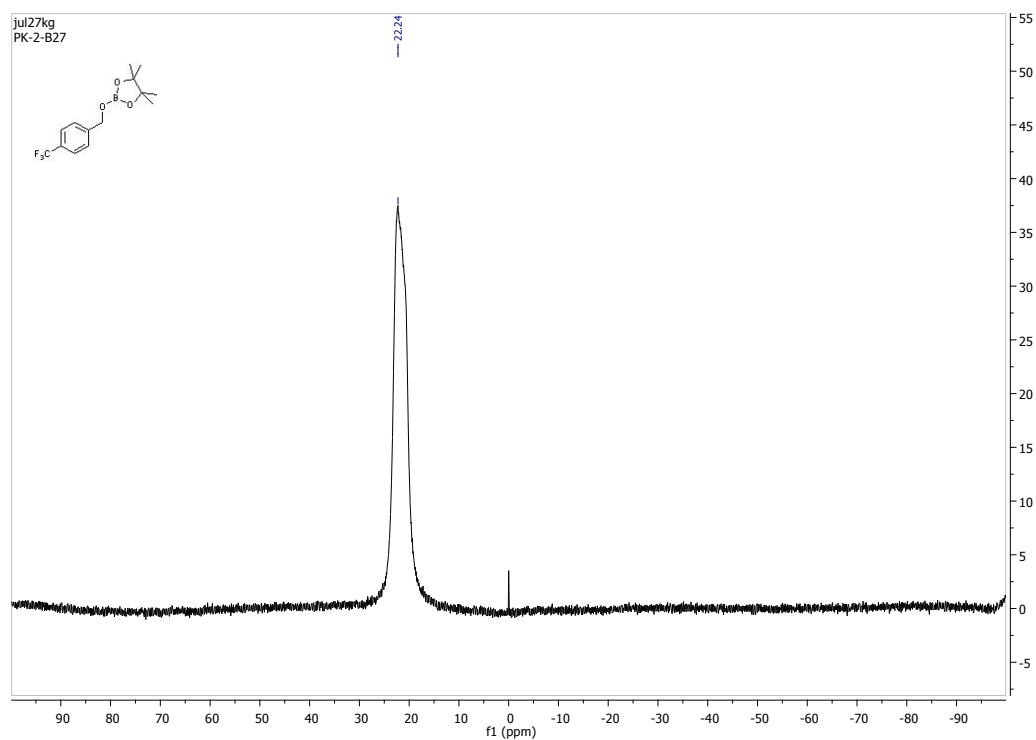


2-((4-Trifluoromethyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24c).

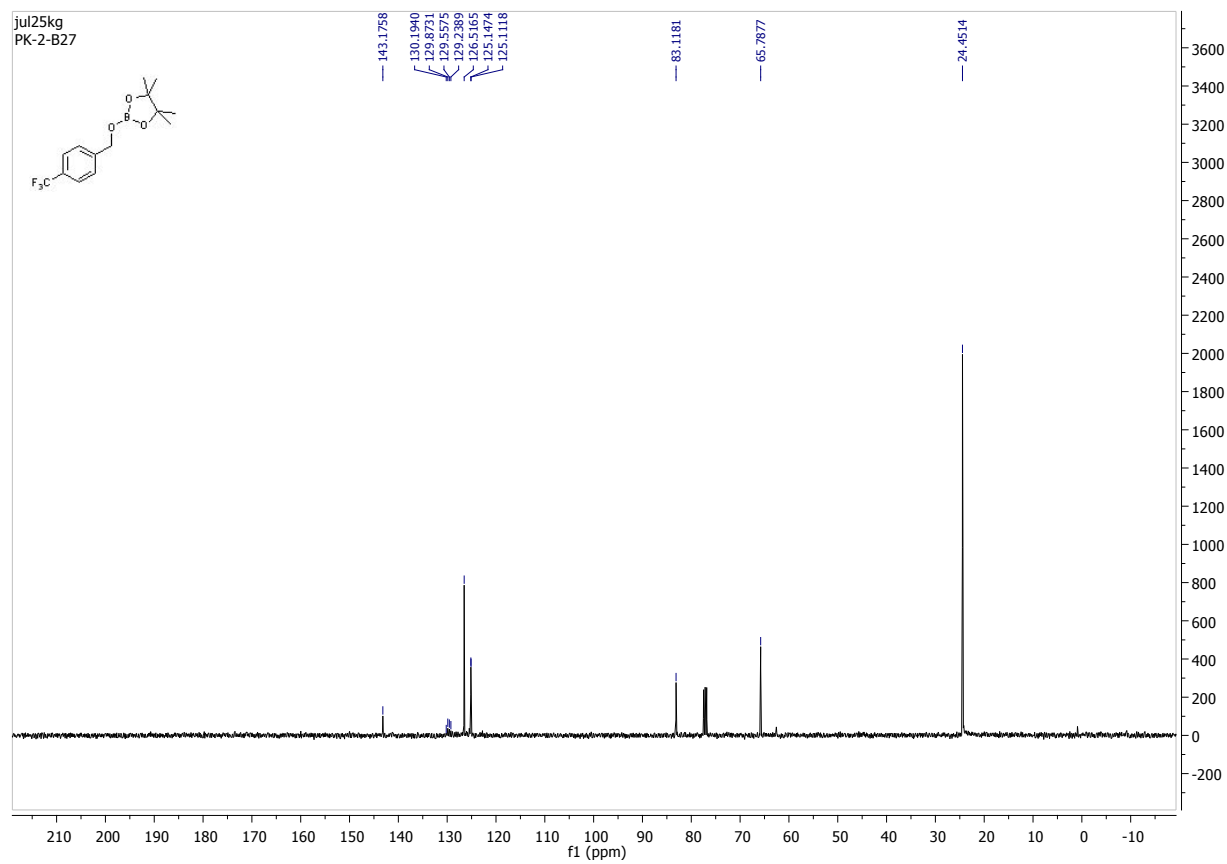
^1H NMR, CDCl_3 , 400 MHz:



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

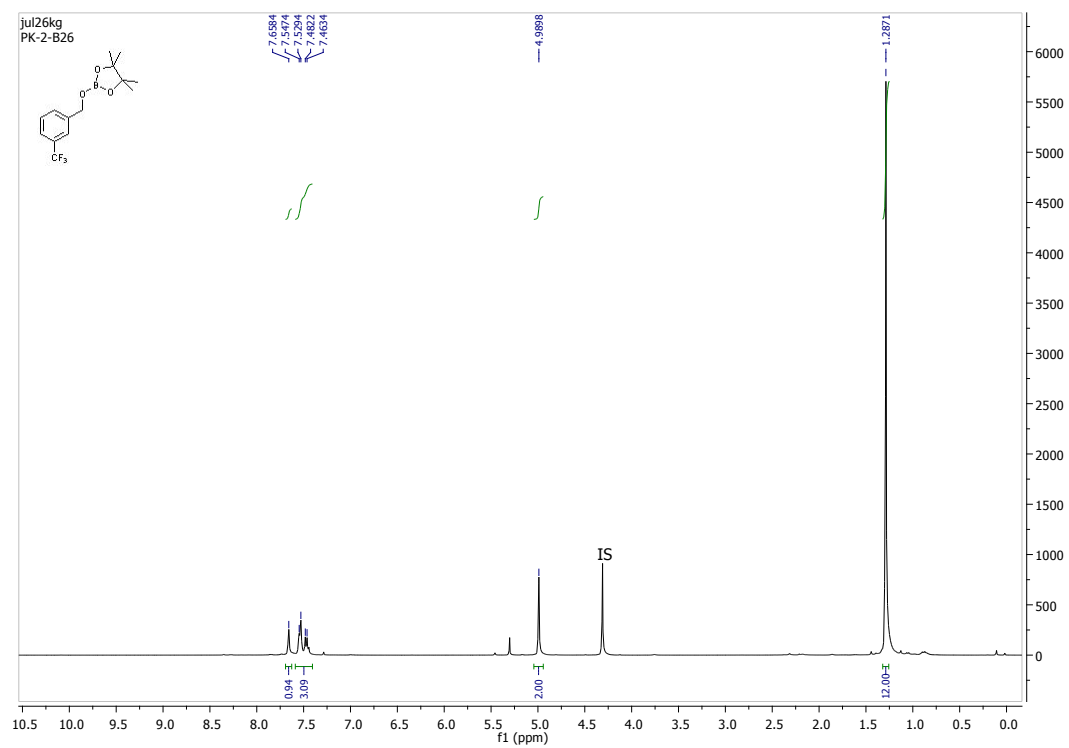


^{13}C NMR, CDCl_3 , 100 MHz:

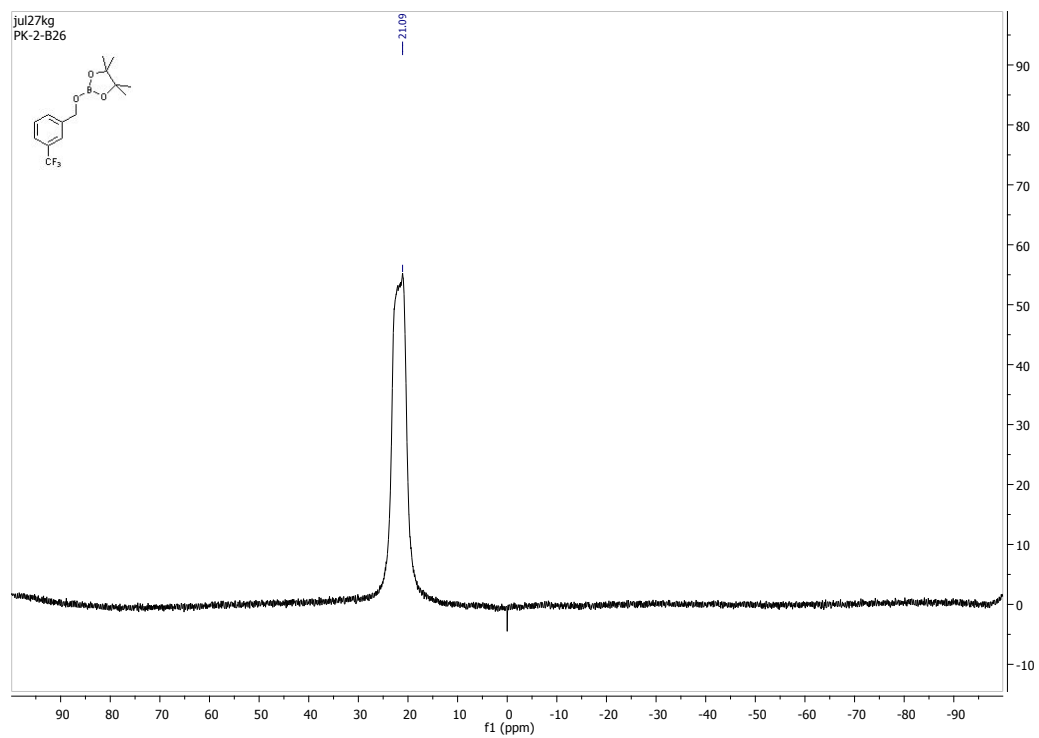


2-((3-Trifluoromethyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24d).

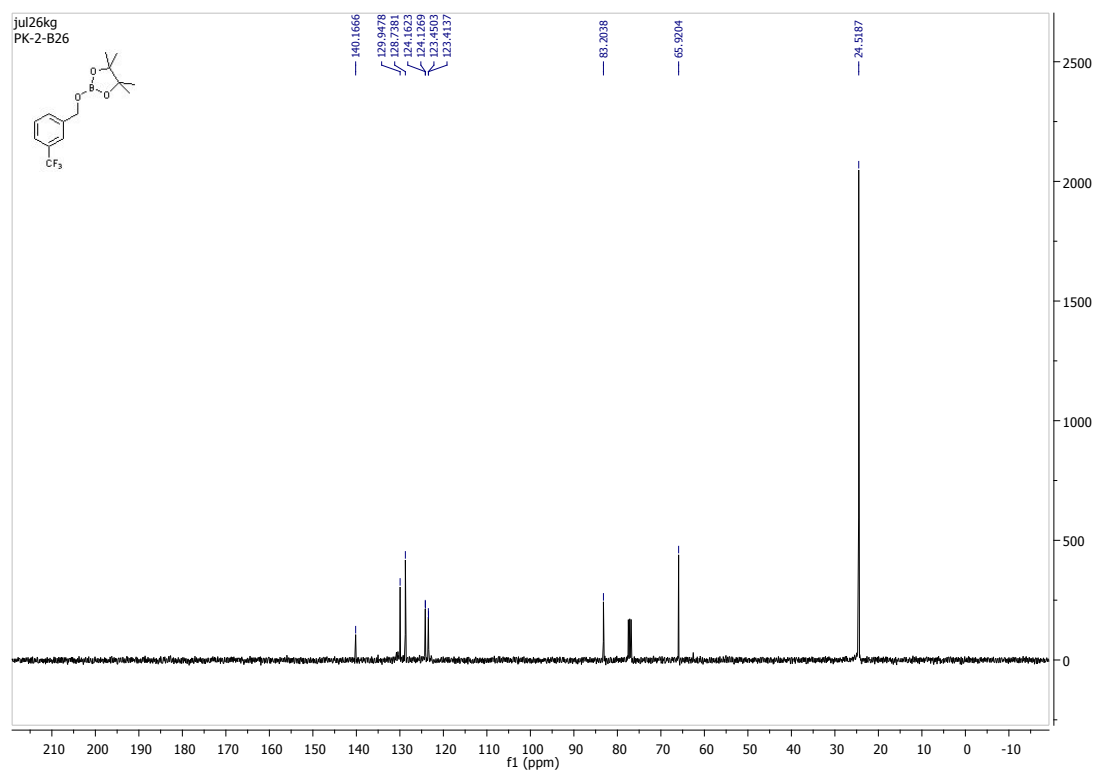
¹H NMR, CDCl₃, 400 MHz:



¹¹B NMR, CDCl₃, 128 MHz:

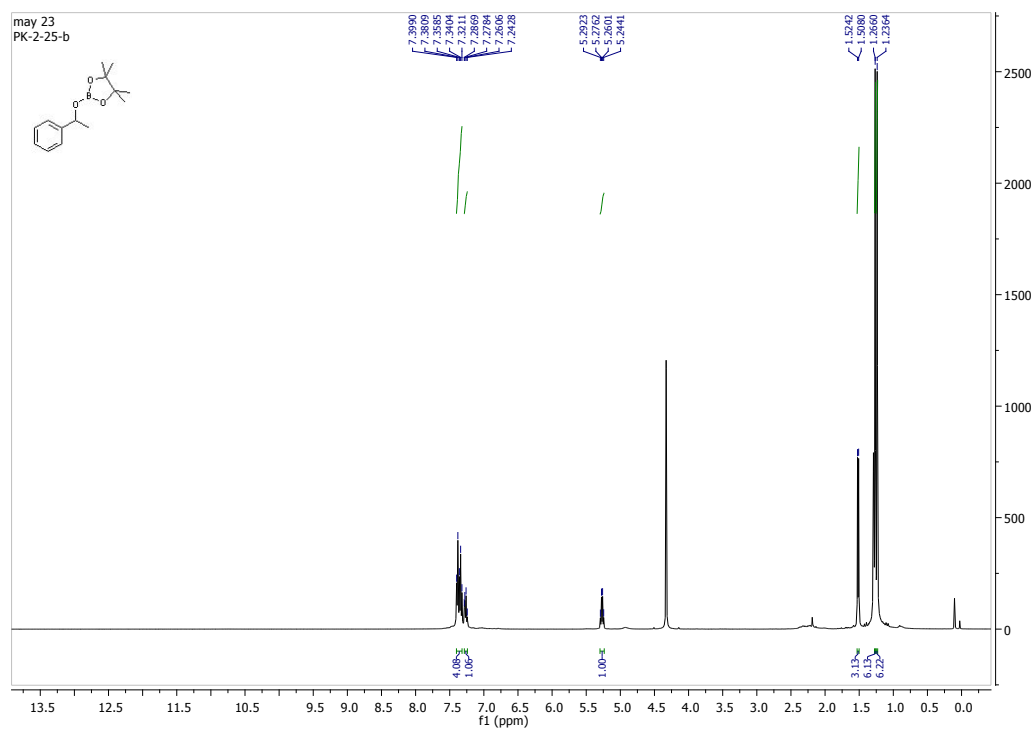


^{13}C NMR, CDCl_3 , 100 MHz:

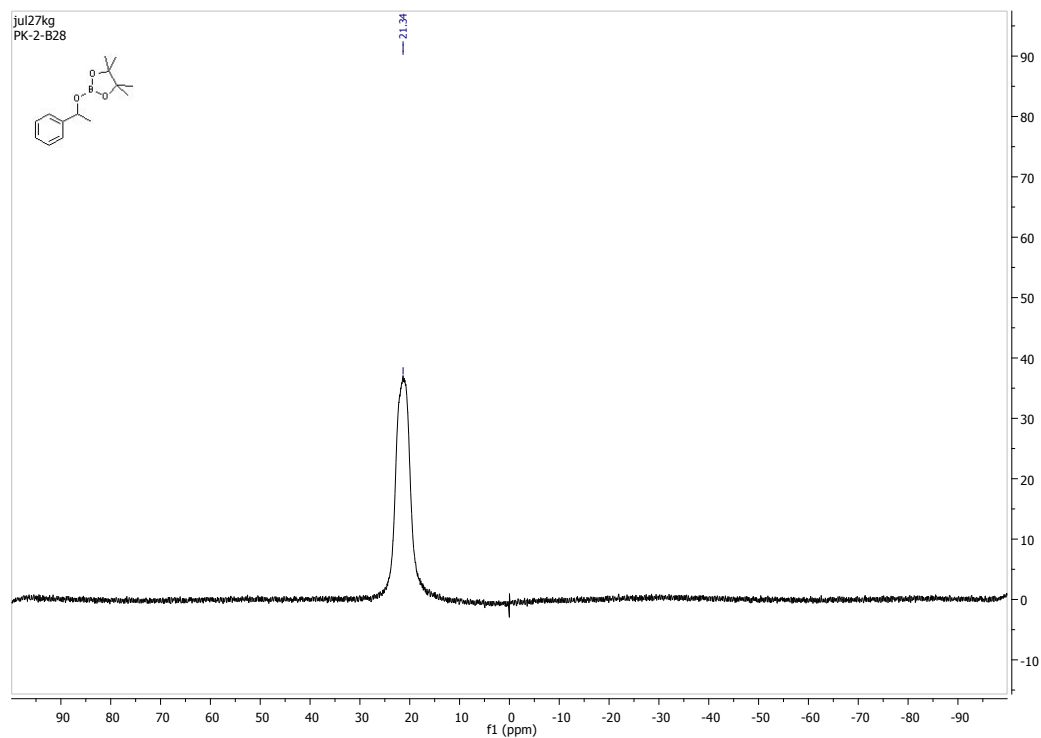


4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (24e).

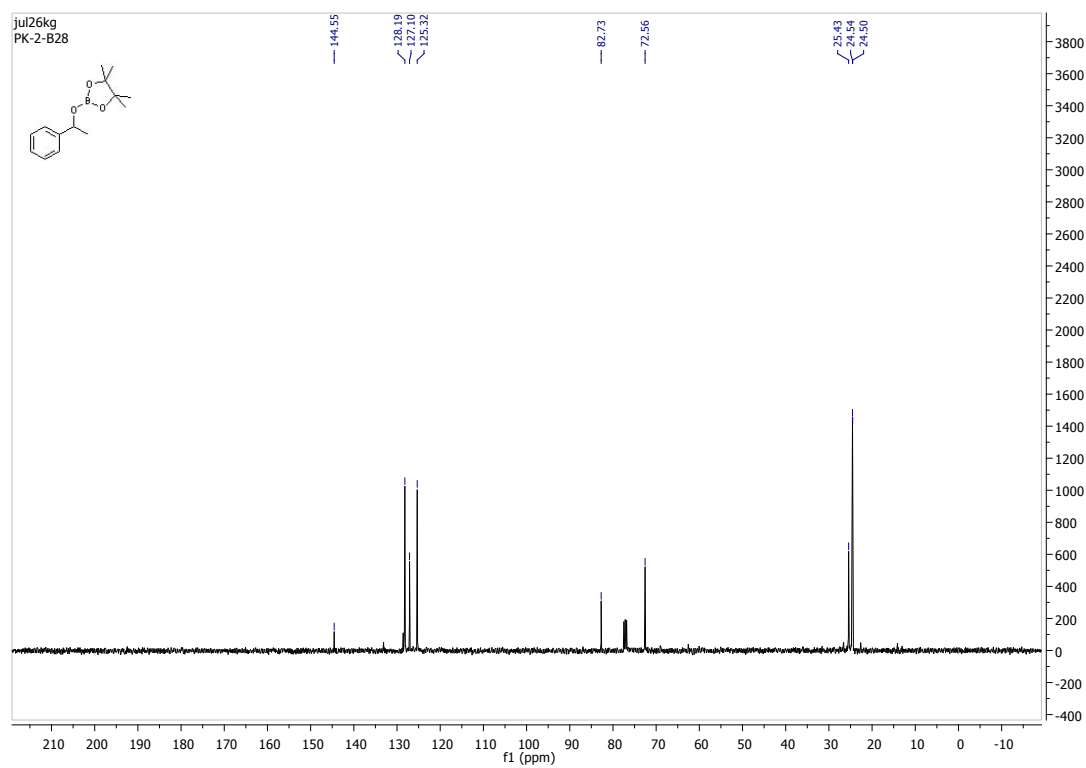
^1H NMR, CDCl_3 , 400 MHz:



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

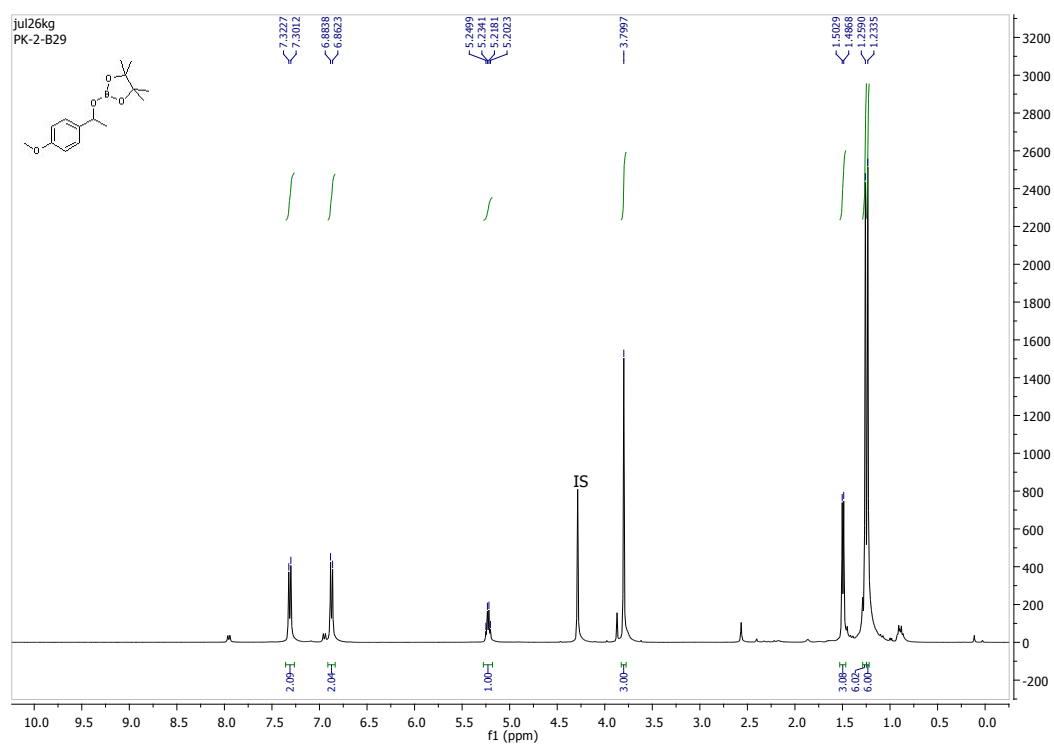


^{13}C NMR, CDCl_3 , 100 MHz:

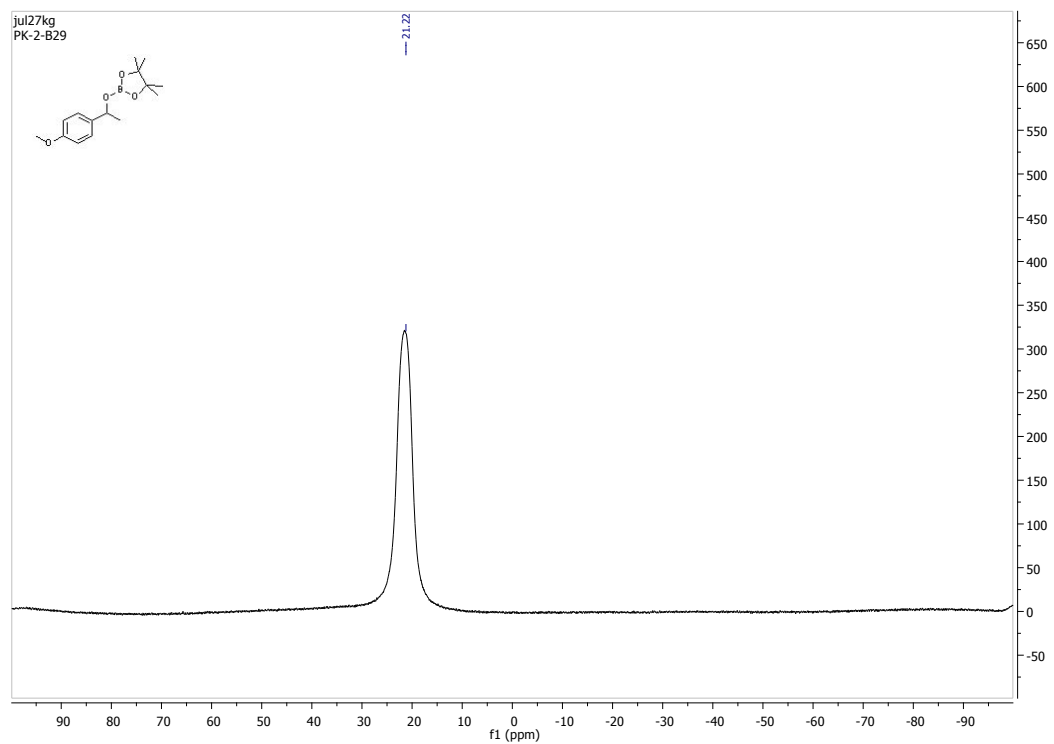


2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24f).

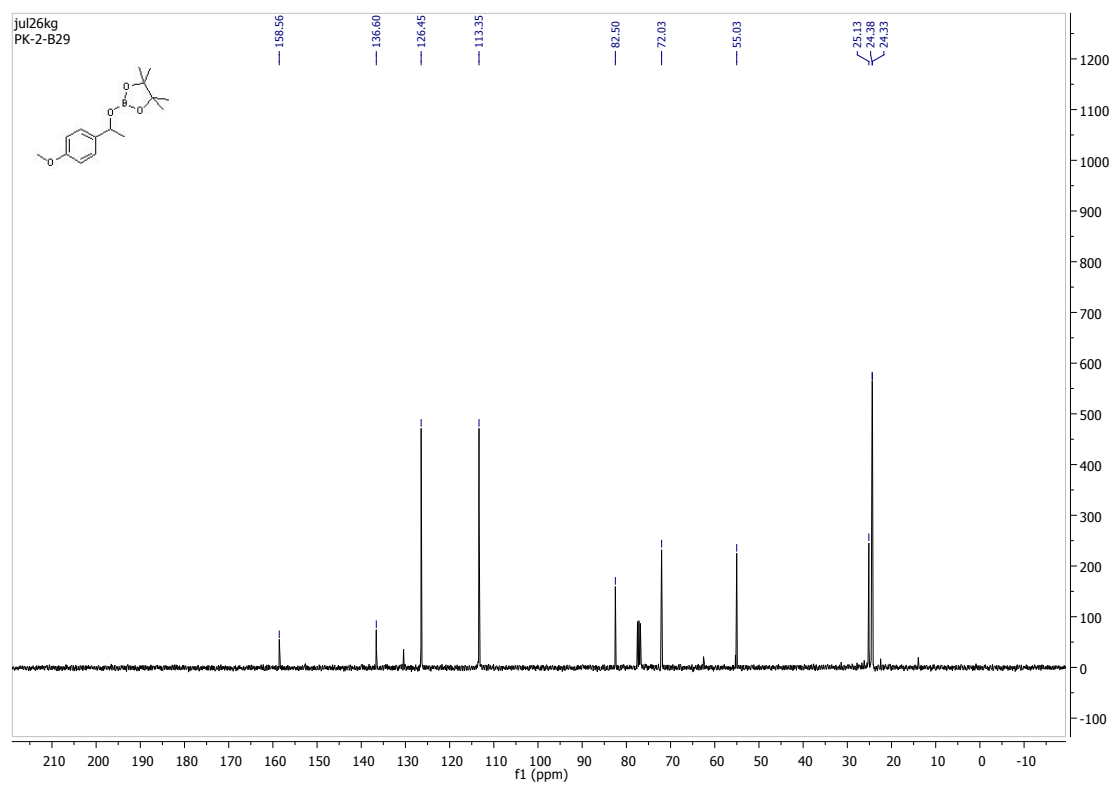
^1H NMR, CDCl_3 , 400 MHz:



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

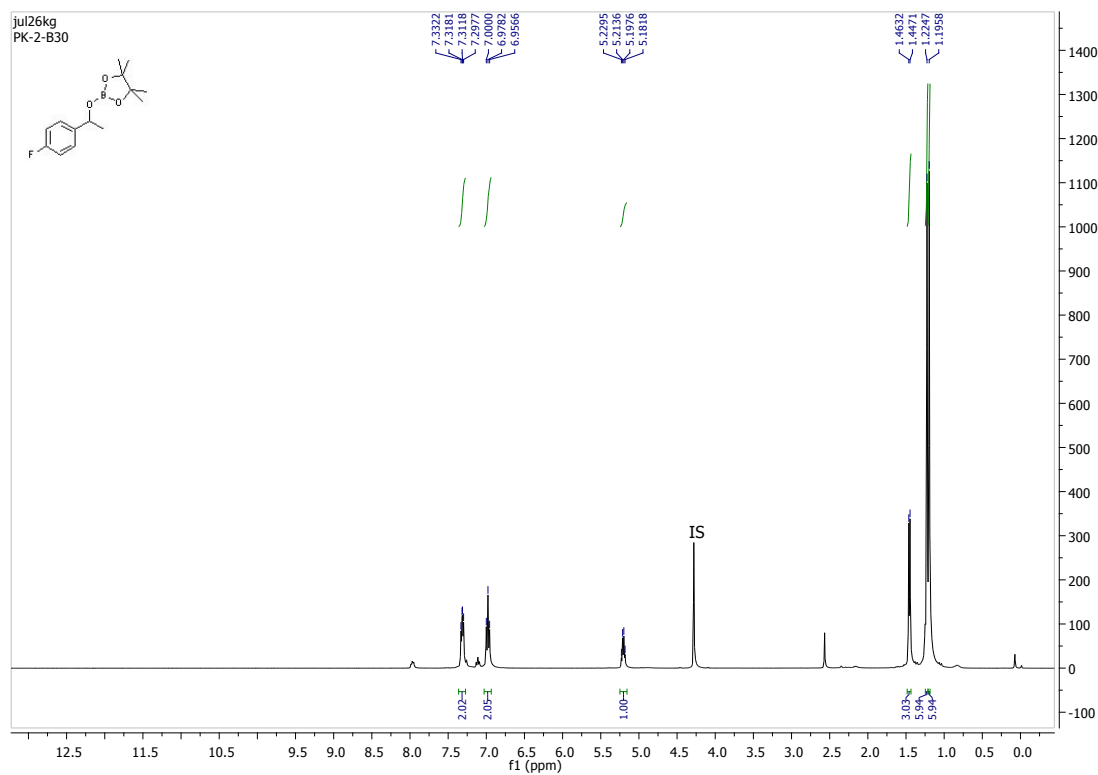


^{13}C NMR, CDCl_3 , 100 MHz:

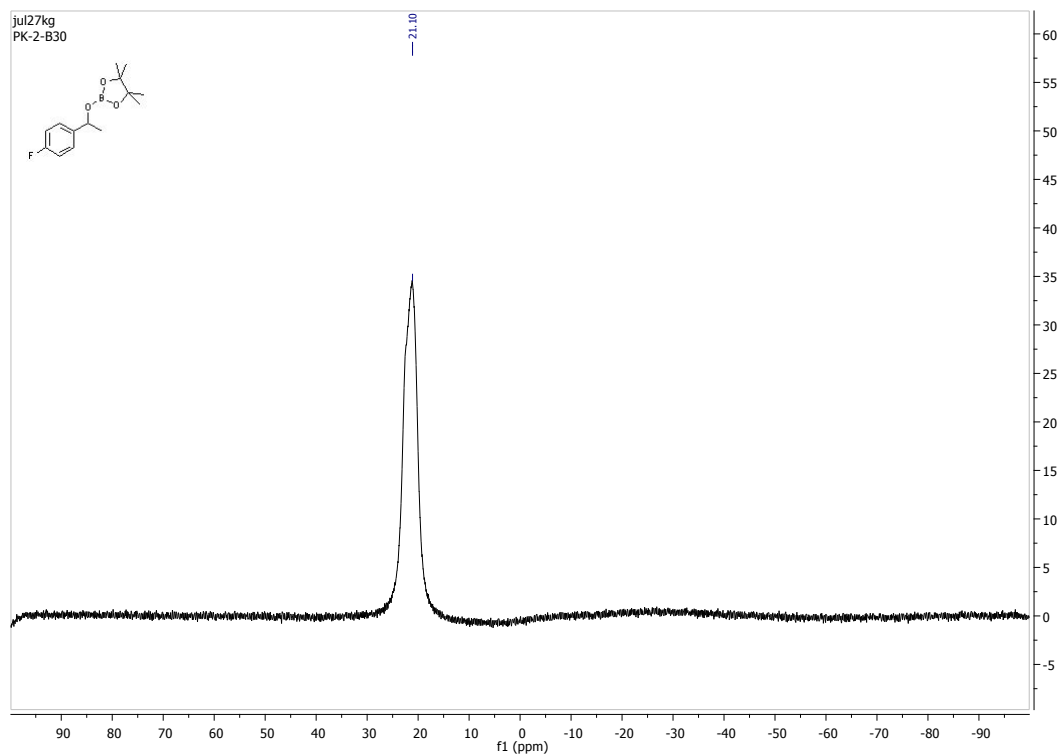


2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24g).

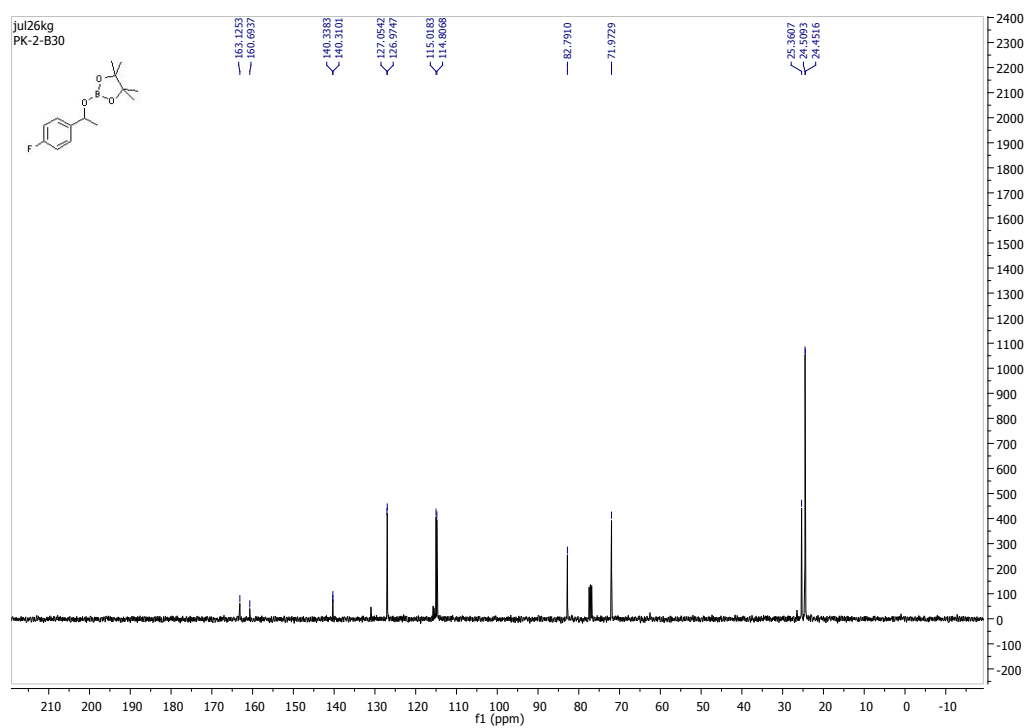
¹H NMR, CDCl₃, 400 MHz:



¹¹B NMR, CDCl₃, 128 MHz:

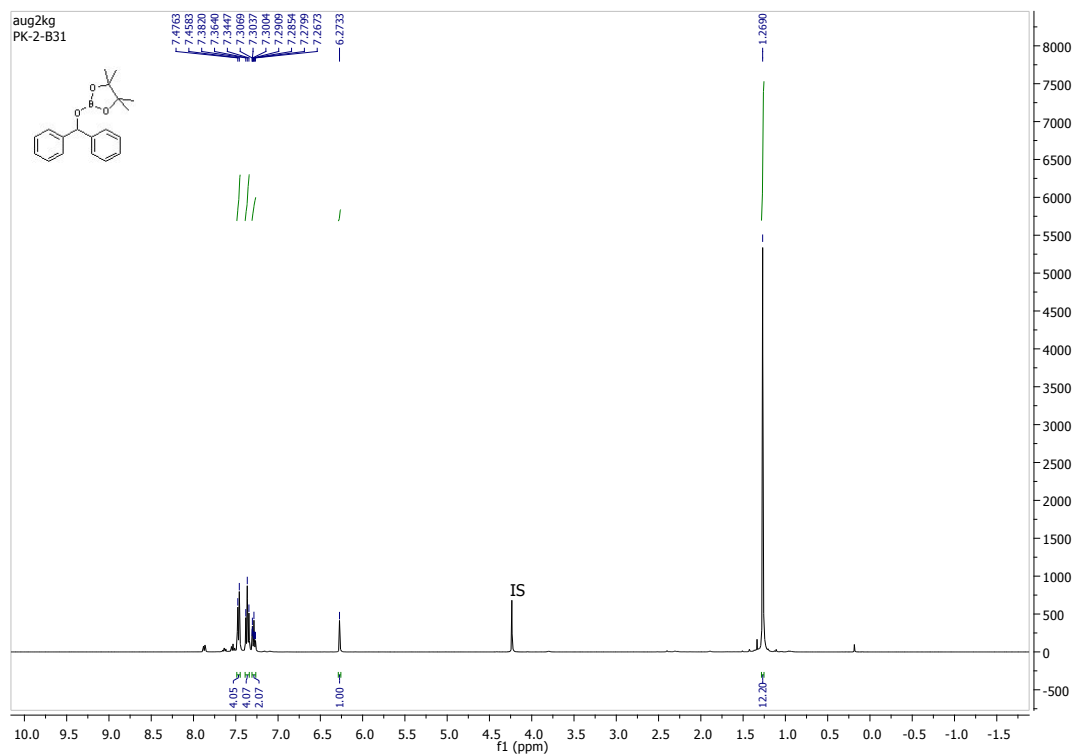


^{13}C NMR, CDCl_3 , 100 MHz:

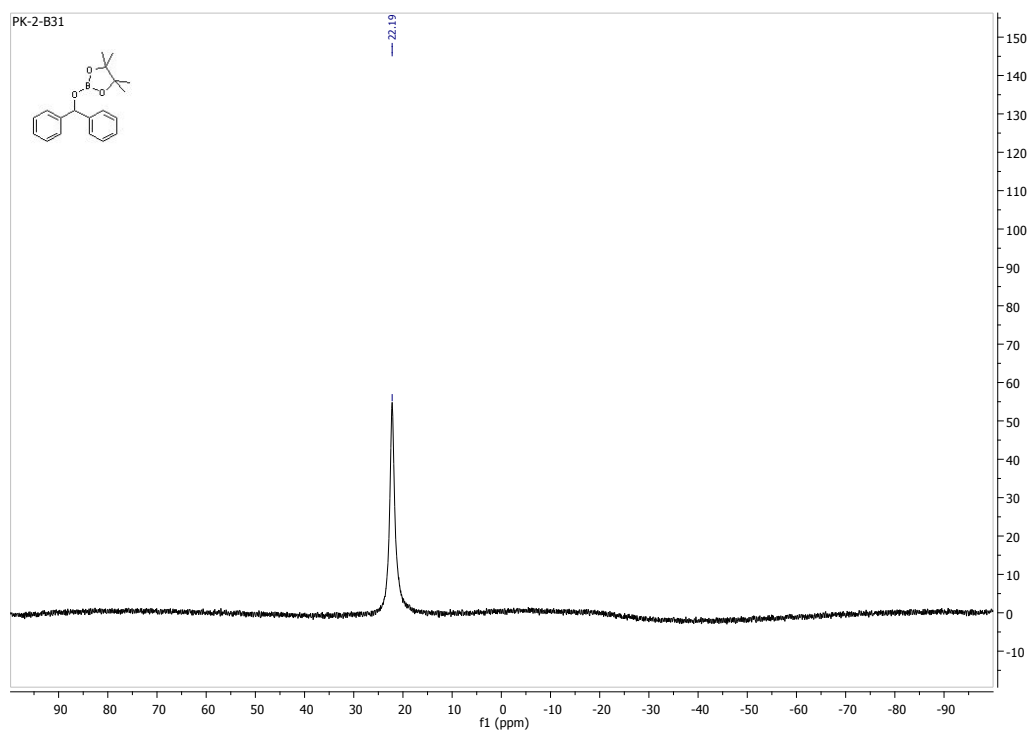


2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24h).

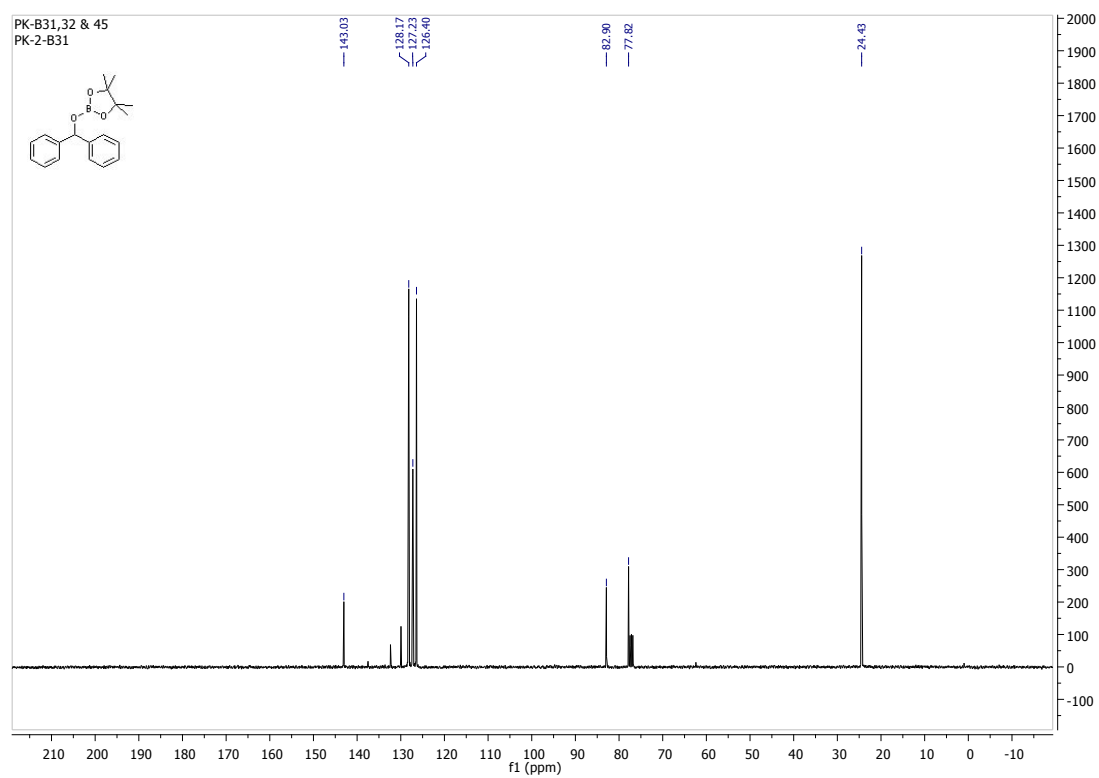
^1H NMR, CDCl_3 , 400 MHz:



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

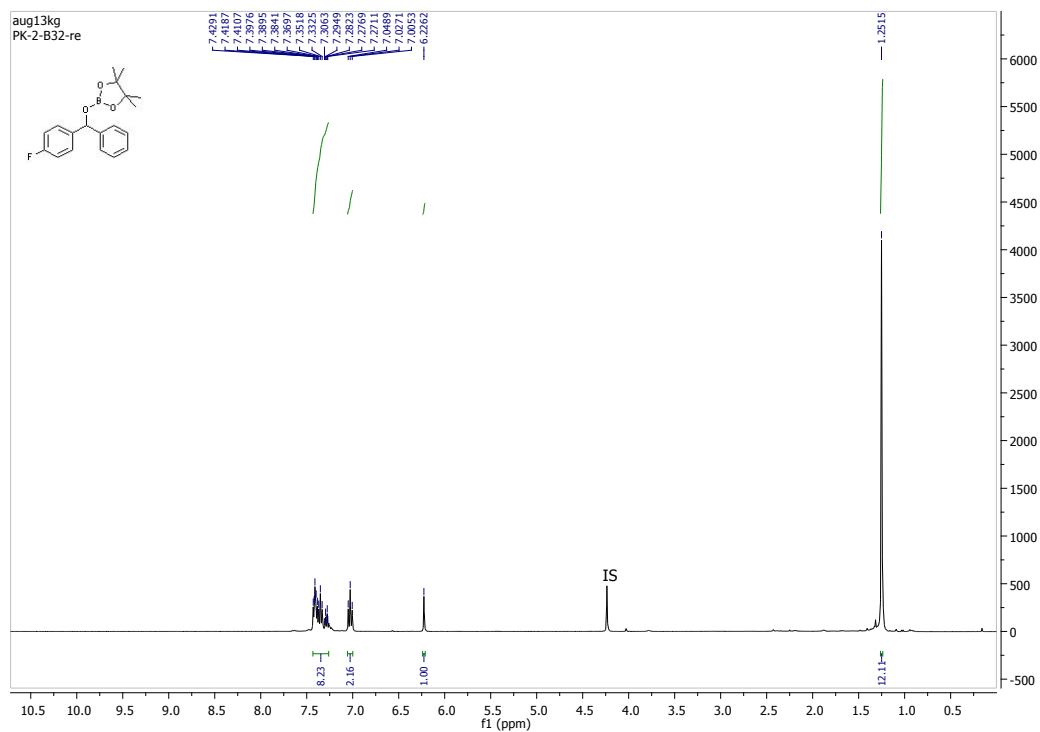


^{13}C NMR, CDCl_3 , 100 MHz:

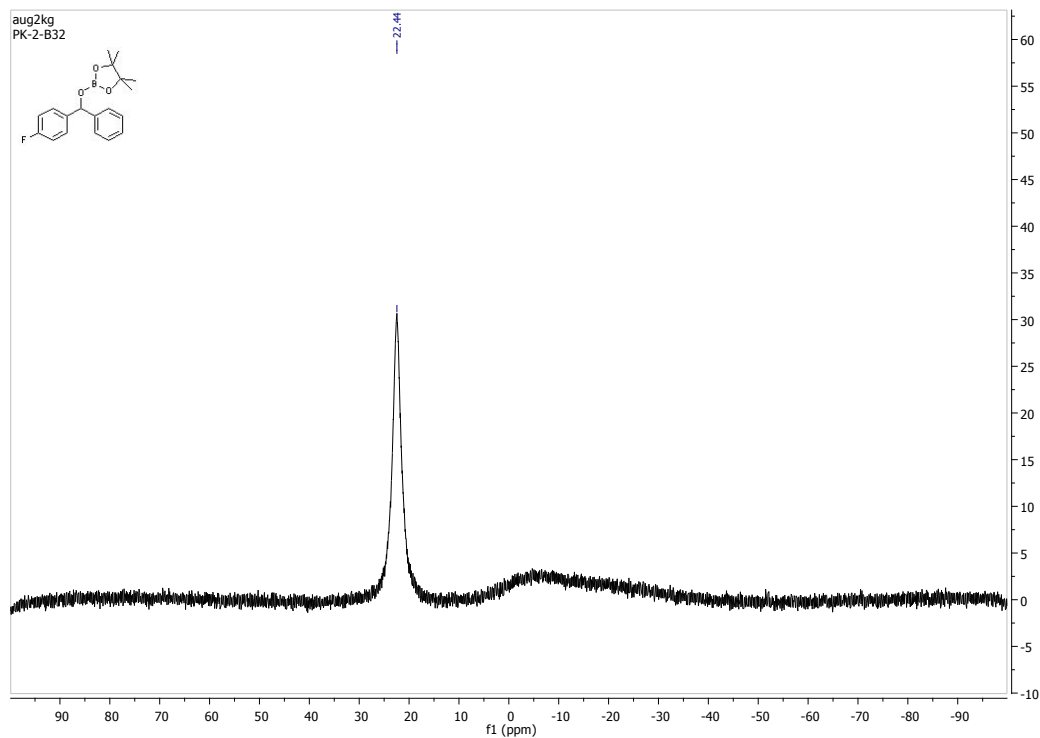


2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24i).

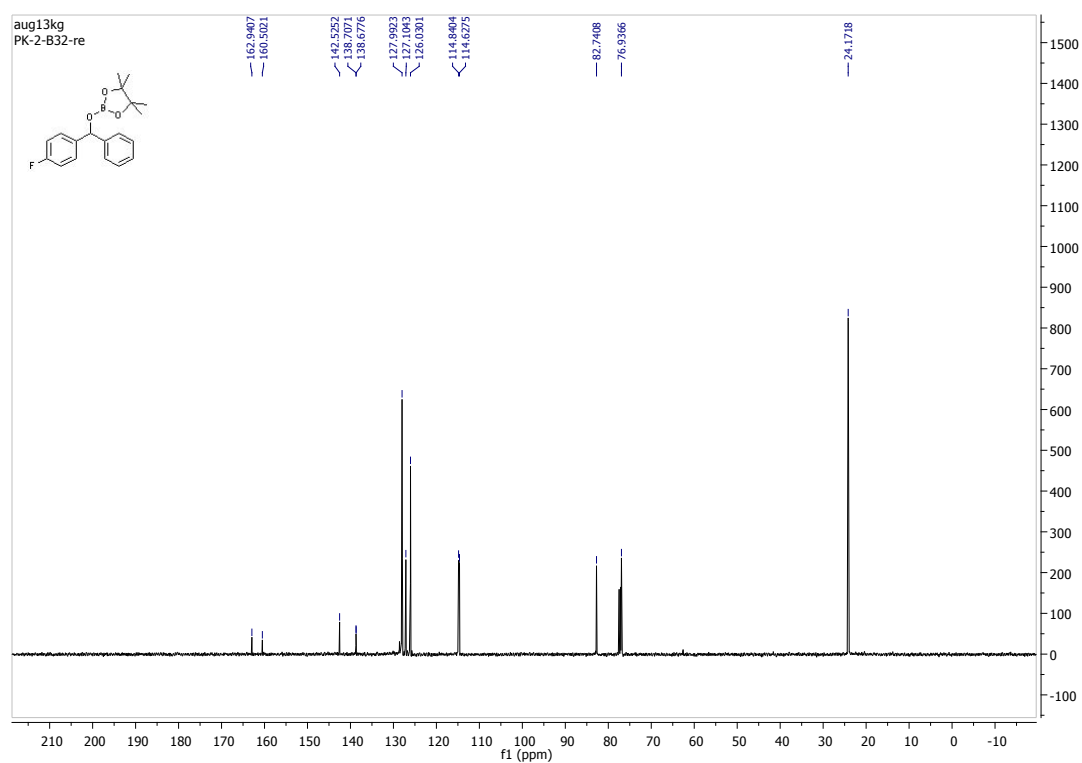
^1H NMR, CDCl_3 , 400 MHz:



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

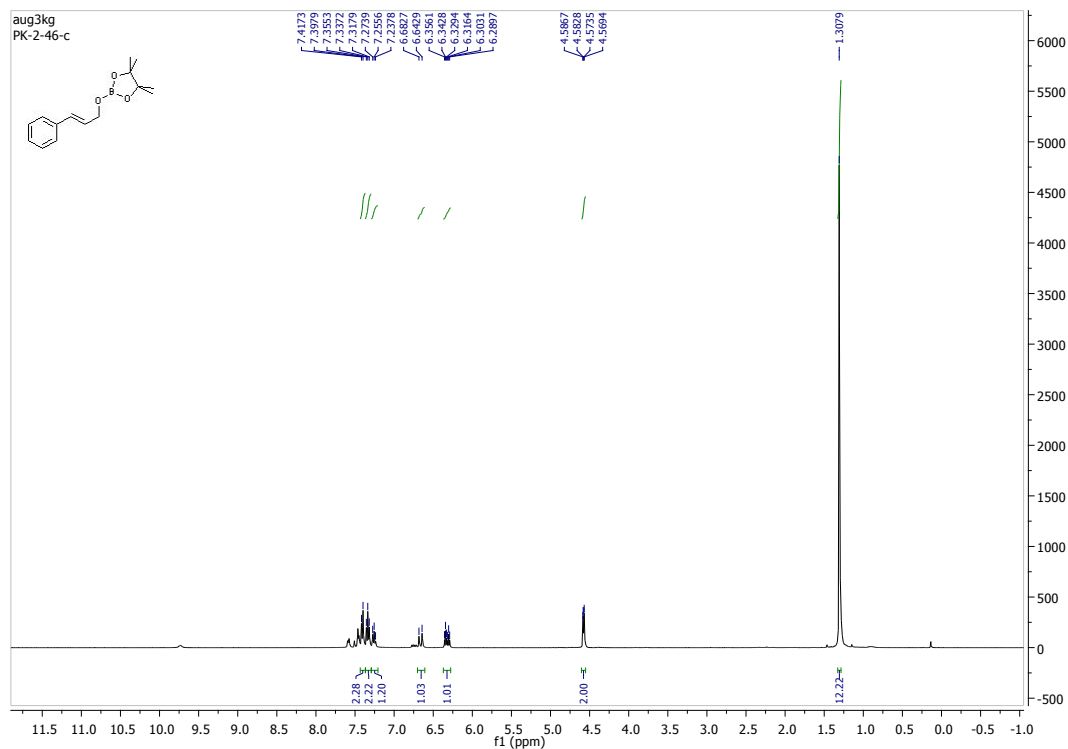


^{13}C NMR, CDCl_3 , 100 MHz:

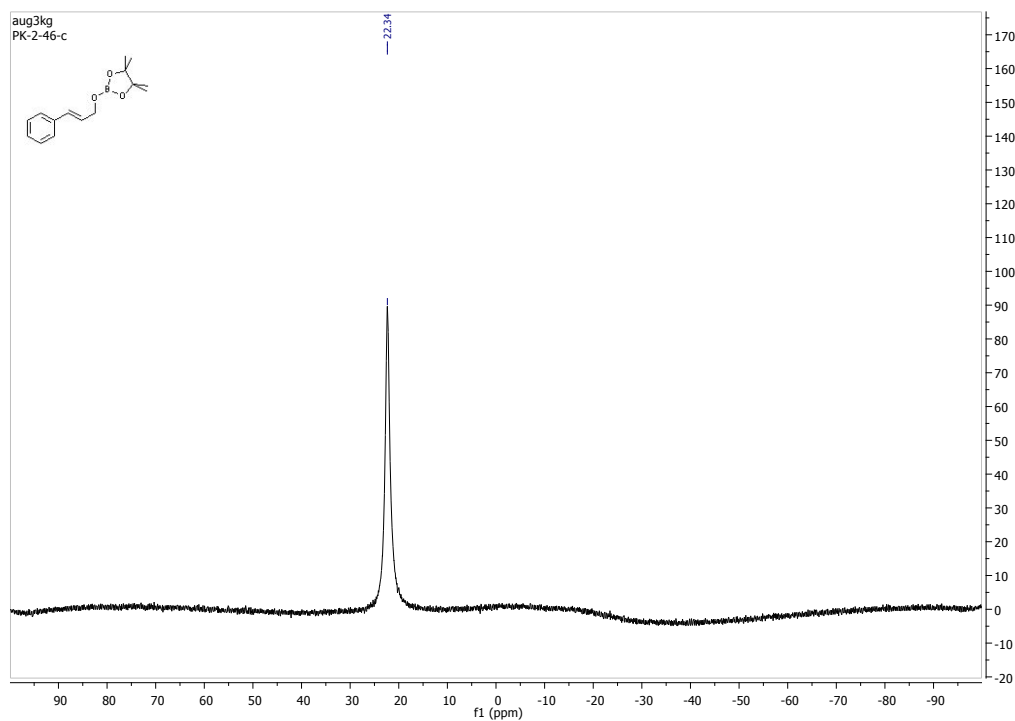


2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24j).

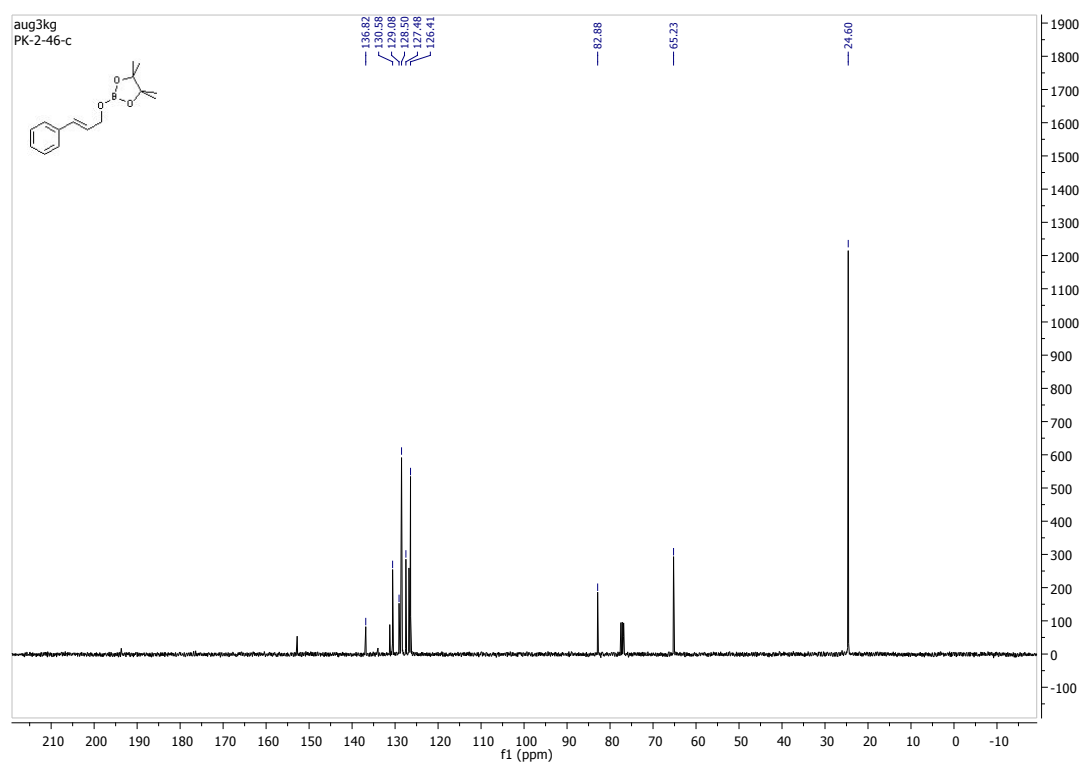
¹H NMR, CDCl₃, 400 MHz:



¹¹B NMR, CDCl₃, 128 MHz:



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



VIII. References

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