Supporting Information

Facile synthesis of alkyl and aryl boronate esters enabled by carbon nanotubes supported copper catalyst

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I. General Information

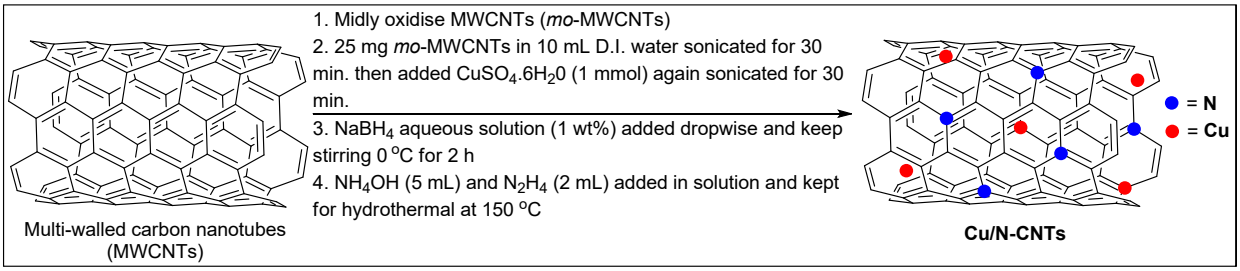
All reagents were purchased from Avra, SDFCL or Aldrich and were used as received. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and were dried using molecular sieves and deoxygenated using the freezepump-thaw method. Commercially available, pre-coated TLC sheets ALUGRAM® Xtra Sil G/UV254 was purchased from MACHEREY-NAGEL GmbH & Co. The removal of solvent was performed on a rotary evaporator in vacuum at a maximum temperature of 40 ˚C. All NMR spectra were recorded at ambient temperature using a Bruker Avance 400 NMR spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz). ^{1}H 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) whereas ^{13}C NMR spectra are 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 $BF_3{\cdot}Et_2O$. All ^{11}B and ^{13}C NMR spectra were broad-band ^{1}H decoupled. The IR spectra were obtained with a BRUKER ALPHA spectrometer in the range of 400 to 4000 cm^{-1} using KBr windows. GC-MS data were acquired using SHIMADZU GC-MS QP 2010SE system.

The microstructure of the nanoparticle was studied by Rigaku Ultima IV powder X-ray diffractometer using Cu Kα radiation (scan rate of 3˚ min^{-1}). Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopic (EDX) spectra were performed on a JSM 7100F JEOL FESEM with EDS, and TEM was carried out using FEI Tecnai T20 transmission electron microscope operating at 200 kV after casting a drop of nanoparticle dispersion in isopropyl alcohol over Cu grid. X-ray photoelectron spectroscopy was carried out on Axis Ultra DLD. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) measurements were carried out on BELSORP-max instrument. AAS analysis was performed on Shimadzu AA-7000 instrument. The alkyl halide 1-(6-chlorohexyl)-1H-indole was prepared according to literature procedure.[1]

II. Synthesis and Characterization of Cu/N-CNT Catalyst

Synthesis of copper-based composite catalyst

For the synthesis of Cu/N-CNT (Scheme S1), mildly oxidized multi-walled carbon nanotubes (MWCNTs; 25 mg, OD: 30-50 nm, Length: 10-30 μm, Sisco Research Laboratories Pvt. Ltd.; mildly oxidized through the modified Hummers method[2]) were dispersed in deionized water (10 mL) via sonication for 30 min. After that, $CuSO_4{\cdot}5H_2O$ (0.249 g, 1 mmol) was added to the MWCNT suspension and sonicated for another 30 min. The suspension was transferred to a flask placed in an ice-water bath. Then freshly prepared ice-cold $NaBH_4$ aqueous solution (1 wt%, 10 mL, ~2.5 mmol) was added dropwise. After reaction at 0 ˚C for 2 h, the suspension was transferred to a 50 mL Teflon-lined stainless steel autoclave. Ammonium hydroxide solution (28-30% NH_3 basic, 5 mL) and hydrazine hydrate solution (78–82%, 2 mL) were added, and then the autoclave was sealed and kept for hydrothermal treatment at 150 °C for 4 h. The precipitate was collected by centrifugation at 3500 r.p.m. for 10 min, washed with deionized water (30 mL x 3) and ethanol (10 mL x 2). The obtained Cu/N-CNTs composite was dried overnight at 80 ˚C and finally calcinated at 400 ˚C for 2 h.



Scheme S1: Synthesis of Cu/N-CNT.

FT-IR and TGA:

The FT-IR spectrum of synthesized Cu/N-CNT nanoparticles is shown in Figure S1a. IR spectrum showed a broad peak at around 3423 cm^{-1} which is related to N-H stretching vibration. The typical vibrations of C−N heterocycles at 1116−1369 cm^{-1} indicates C−N bond in sample. Peaks observed in the 1475−1624 cm^{-1} region consist with that of C=N bond in the sample. The absorption peaks at 2927 and 2849 cm^{-1} resulted from the stretching vibration of C−H bond. A small peak in the spectrum at 625 cm^{-1} confirms the presence of Cu–O bond in the material.

The thermogravimetric analysis (TGA) was performed under air atmosphere (Figure S1b), showing that N-CNTs were burned off and Cu was oxidized to CuO and C_2O. The weight remained after the TGA test is 71 wt%.

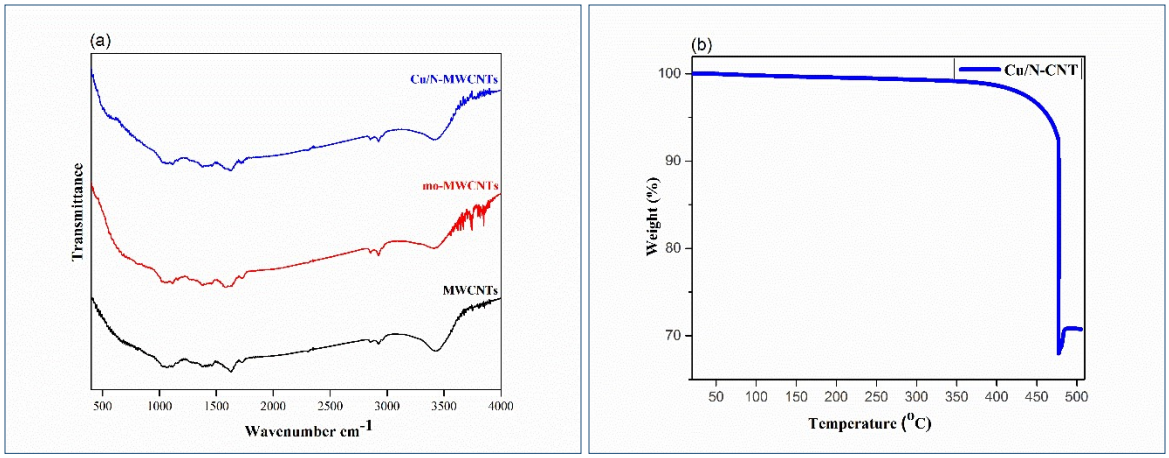


Figure S1: (a) FT-IR spectrum of MWCNT, mildly oxidized-CNT and Cu/N-CNT NPs. (b) TGA curve of the Cu/N-CNT NPs.

PXRD Analysis:

Powder X-ray diffraction (PXRD) results confirms (Figure S2) the presence of the mixture of CuO and Cu_2O in Cu/N-CNT and Cu/CNT NPs. The diffraction peaks at 32.49, 35.50, 38.73, 46.21, 48.66, 53.43, 58.37, 66.18 and 67.96 in the Cu/N-CNT can be assigned to the planes: 110, 002, 111, 112, -202, 020, 202, -311, 113 (JCPDS card number 80-1917; for CuO) also peaks at 36.44, 42.32, 61.40, 73.55 and 77.41 in the Cu/N-CNT can be assigned to the planes: 111, 200, 220, 311, 222 (JCPDS card number 78-2076; for Cu_2O) in NPs material.

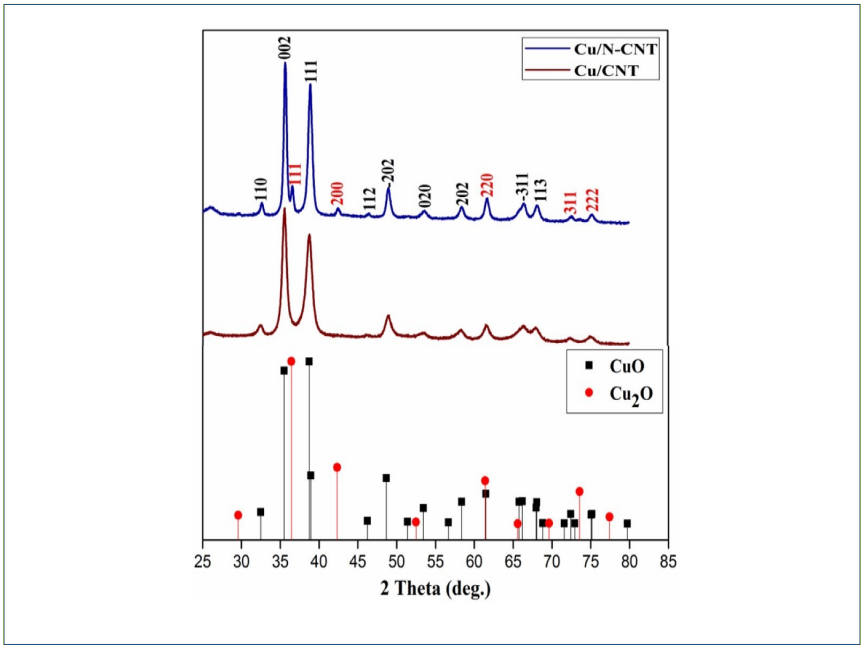


Figure S2: PXRD analysis of Cu/N-CNT and Cu/CNT.

FE-SEM and EDS:

Field emission scanning electron microscopy (FE-SEM) was used to observe the morphologies of the samples (Figure S3). FE-SEM images shows agglomerated spherical morphology of the Cu/N-CNT (a and b) and Cu/CNT NPs (c and d). Energy-dispersive X-ray spectroscopy (EDS) confirms the presence of Cu, O, N and C elements in the Cu/N-CNT NPs (Figure S4a) and presence of Cu, O and C elements in the Cu/CNT NPs (Figure S4b). There are white bright agglomerated spherical spots on the carbon nanotubes, which can be determined to be Cu nanoparticles by EDS.

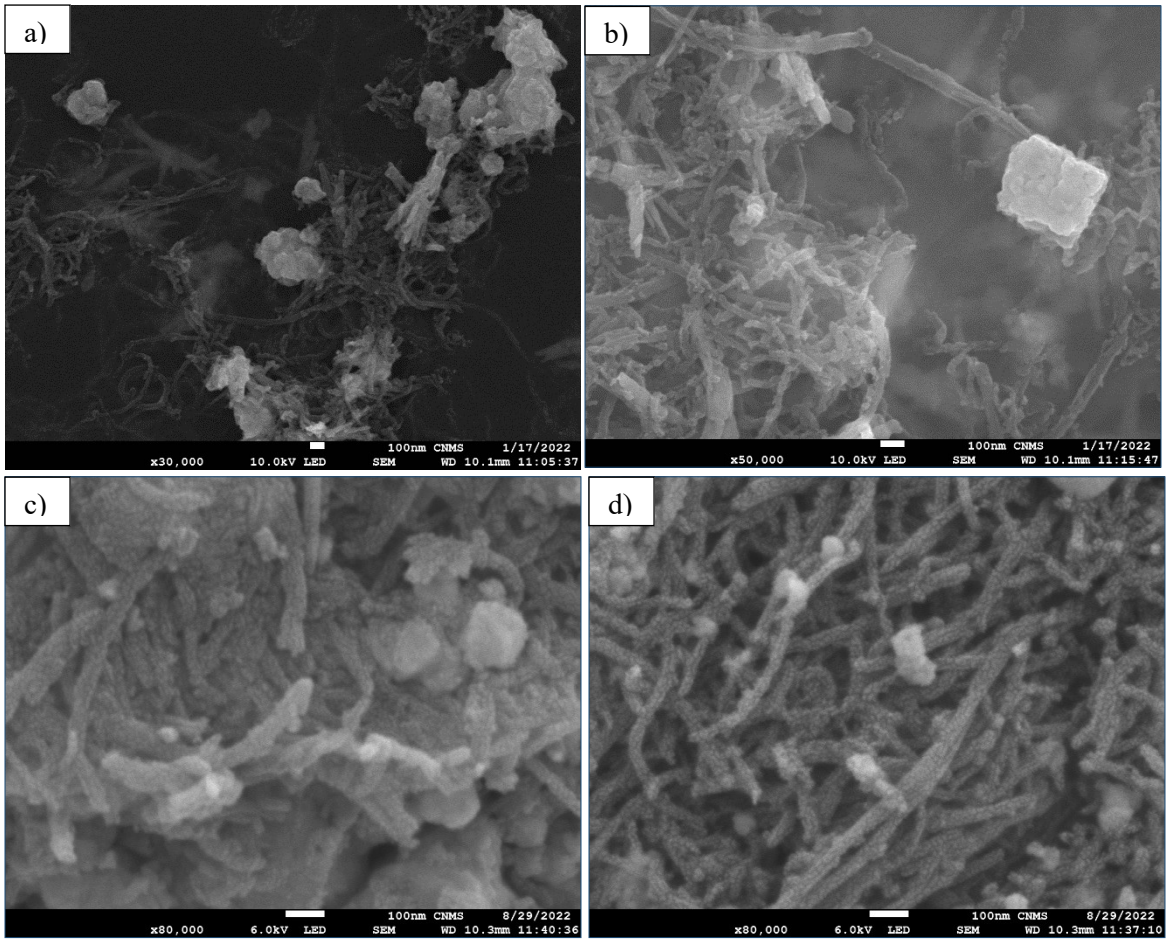


Figure S3: Scanning electron microscopy (SEM) images of Cu/N-CNT (a and b) and Cu/CNT (c and d) size at 100 nm.

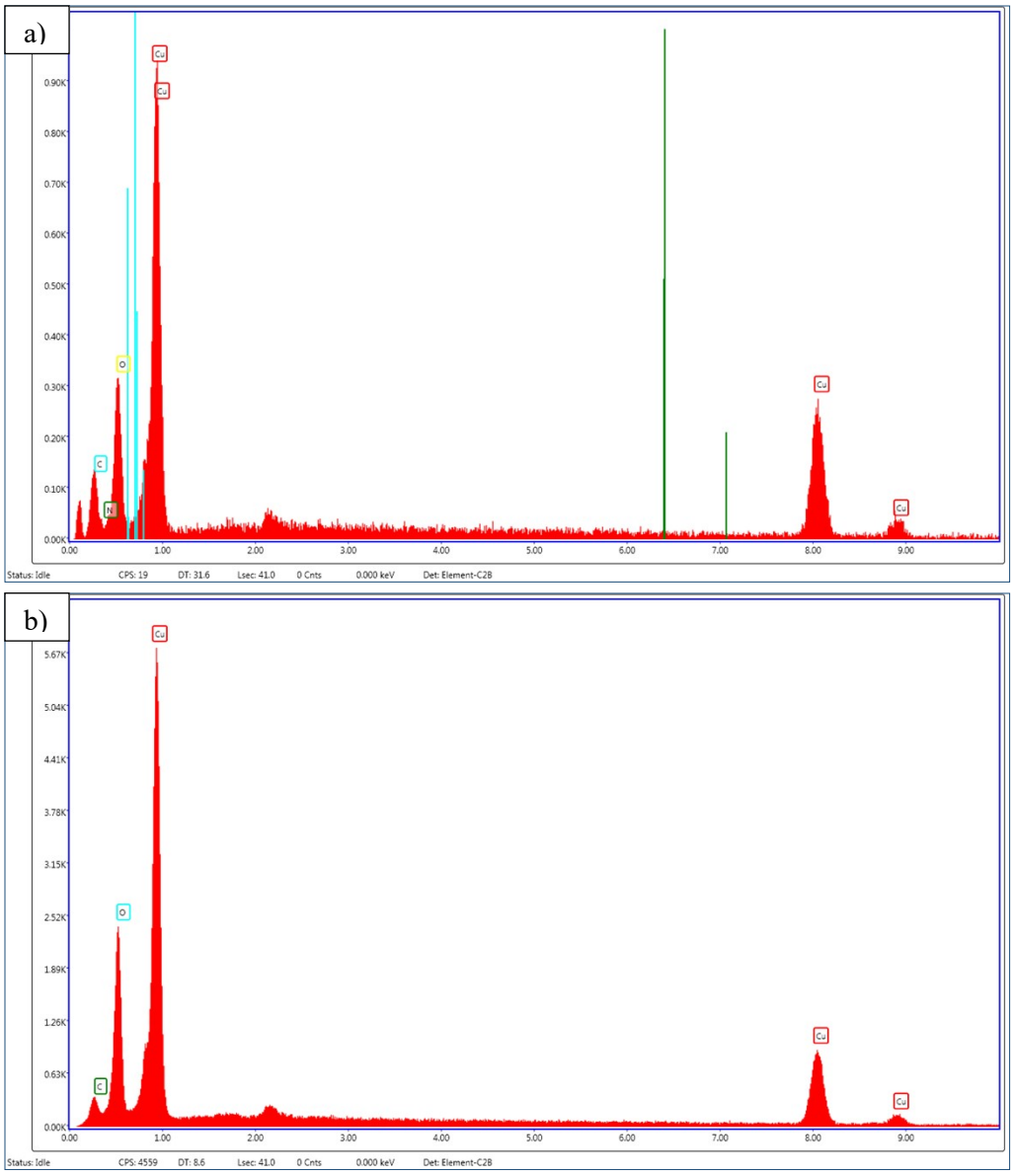


Figure S4: EDX spectra of Cu/N-CNT (a) and Cu/CNT (b) NPs.

TEM images of Cu/N-CNT:

The TEM analysis of Cu/N-CNTs (Figure S5) shows that the nanoparticles were having particle size in the range of 5-35 nm and an average particle size of 18.84 nm. HRTEM image indicates the high crystallinity of the material along with clear lattice fringes. The lattice fringe corresponds to a d-spacing value of 0.225 nm.

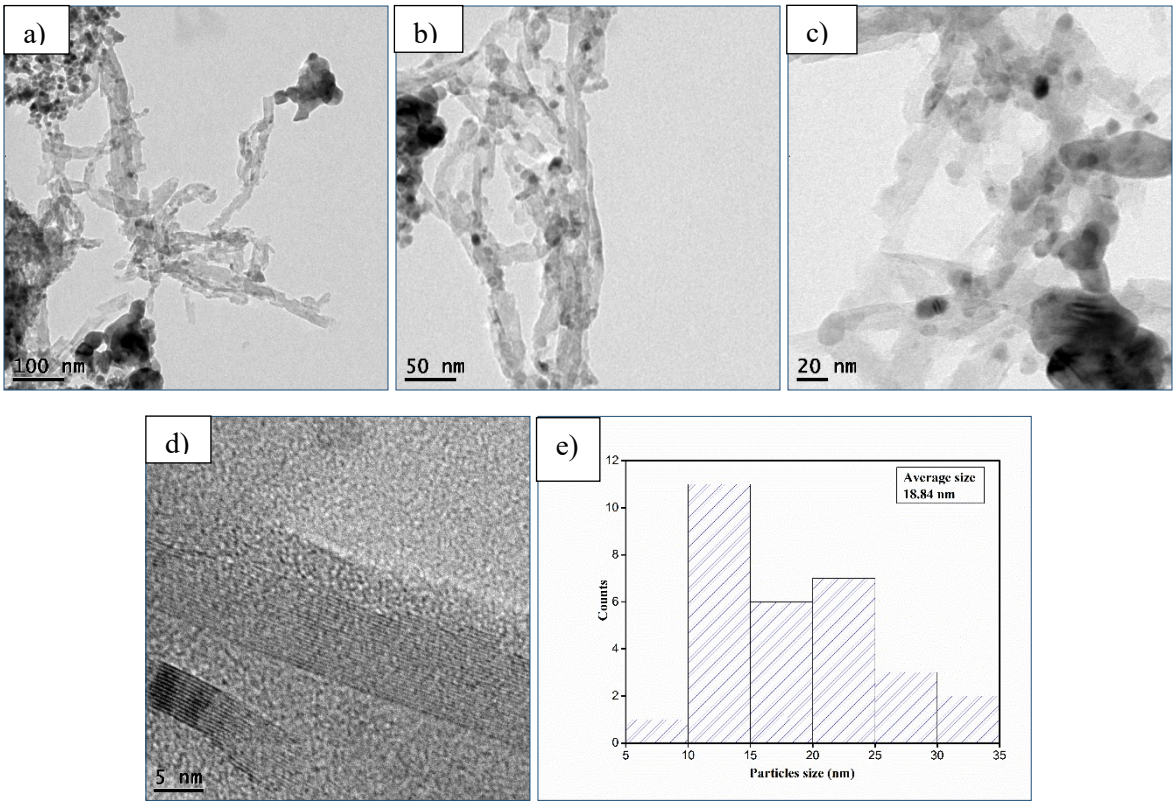


Figure S5: (a-c) TEM images of Cu/N-CNTs nanoparticles. (d) HRTEM image of Cu/N-CNTs. (e) Particle size distribution chart of Cu/N-CNTs nanoparticles.

BET analysis:

Surface modification, specific surface area, pore diameter and pore volume of freshly synthesized Cu/N-CNTs were studied using N_2 adsorption desorption isotherms at a liquid nitrogen temperature of 77 K. Based on the isotherm as displayed in Figure S6, the Cu/N-CNTs material reflect Type II BET isotherm with hysteresis loop, which confirms to the general characteristic behavior of typical mesoporous materials and the strong interaction between the prepared Cu/N-CNTs catalyst (adsorbents) and N_2 gas (adsorbate). According to the isotherm, BET surface area for Cu/N-CNTs was found to be 26.359 m^2g^{-1} with a pore volume of P/P_0 = 0.043 cm^3g^{-1}. In addition, to confirm the mesoporous nature of the catalyst we checked the pore diameter using BJH pore distribution curve and the obtained pore diameter for synthesized Cu/N-CNTs is 6.61 nm. Based on this observation, the decreased surface area of carbon nanotubes indicates successful decoration of Cu NPs on MWCNTs.

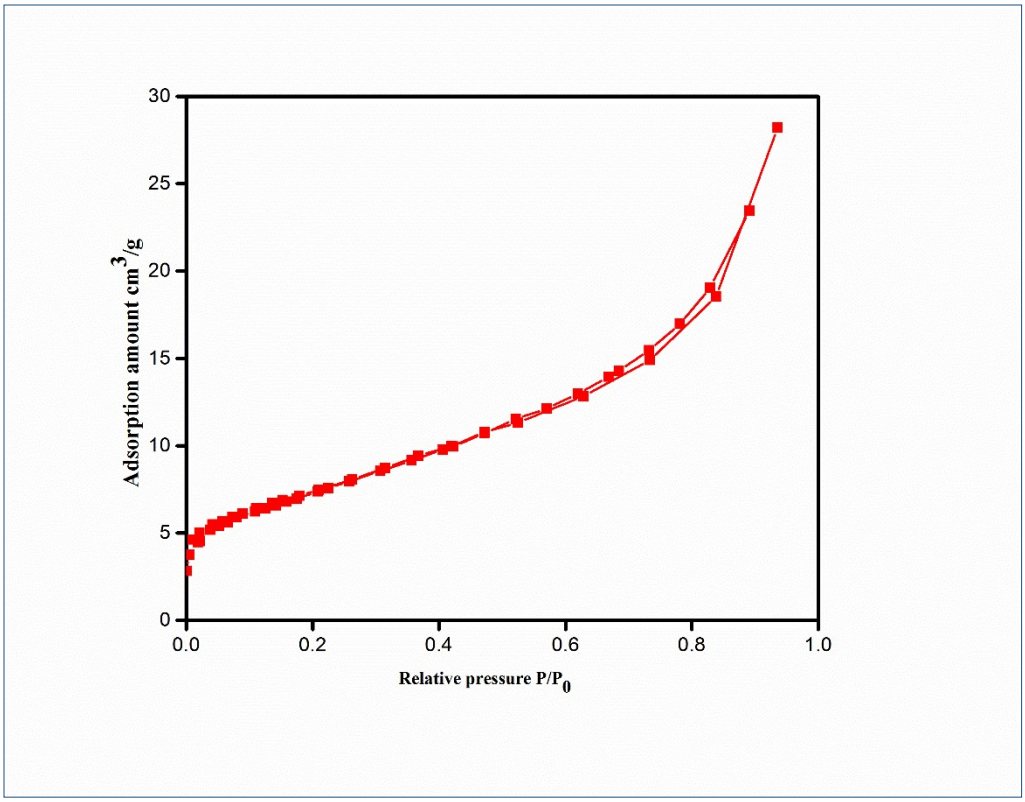


Figure S6: N_2 physisorption graph of Cu/N-CNT nanoparticle.

X-ray photoelectron spectroscopy (XPS) analysis:

Cu/N-CNT nanoparticles were analyzed by X-ray photoelectron spectroscopy (XPS) to know the composition of the surface elements present and oxidation of metal in the catalyst (Figure S7). Results of the XPS showed a peak of Cu $2p^{3/2}$ at 934.03 eV which is accompanied by two satellite peaks at about 941.16 eV and 943.84 eV, which suggests the existence of Cu(+2) along with peak of Cu $2p^{1/2}$ at 953.98 eV and its satellite peak at 962.28 eV confirm the presence of Cu(+2). XPS results confirms the presence of Cu(II) on the surface of the material which probably acting as an active catalyst site for catalyzing the reaction.

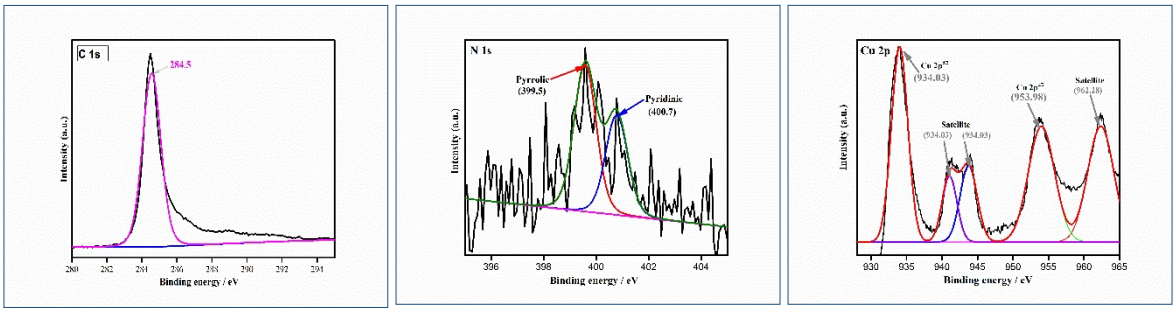


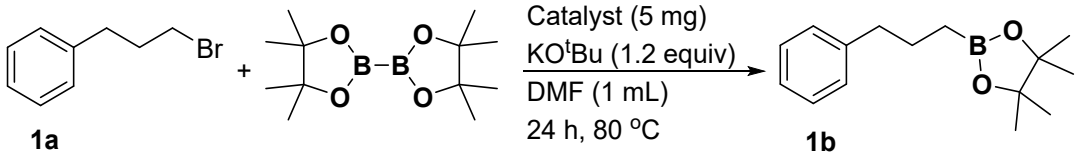
Figure S7: XPS analysis result of Cu/N-CNT.

III. Optimization of the Reaction Conditions for the Nanoparticles Catalyzed Borylation of Alkyl Halides

Experimental procedure for examples described in Table 1.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT NPs catalyst (5 mg; 13.12 mol % based on Cu), B_2pin_2 (76 mg, 0.3 mmol), base (0.3 mmol), (3-bromopropyl) benzene (**1a**, 49 mg, 0.25 mmol) and solvent (1 mL) were added. The reaction mixture was stirred at 80 ºC for the indicated amount of time. The crude reaction was dissolved in Et_2O (10 mL) and then transferred to a separatory funnel followed by the addition of H_2O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

Table S1: Screening of catalyst and Cu loading for the borylation of (3-bromopropyl)benzene (**1a**).

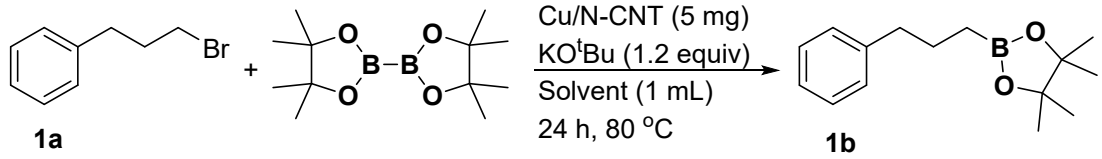


1a **1b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (ºC)	Time (h)	Yield (%)
1	-	DMF	KO^{t}Bu	1.2	80	24	9
2	Cu/CNT	DMF	KO^{t}Bu	1.2	80	24	88
3	**Cu/N-CNT[a]**	**DMF**	**KO^{t}Bu**	**1.2**	**80**	**24**	**96**
4	Cu/N-CNT[b]	DMF	KO^{t}Bu	1.2	80	24	83
5	Cu/N-CNT[c]	DMF	KO^{t}Bu	1.2	80	24	80

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), catalyst, KO^{t}Bu (1.2 equiv), DMF (1 mL) for 24 h at 80 ˚C. [a]Midly oxidized carbon nanotubes was used. Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard. [a] The Cu loading was 54.5 wt% (5 mg; 17 mol %, based on Cu). [b] The Cu loading was 26 wt% (5 mg; 6 mol %, based on Cu). [c] The Cu loading was 12 wt% (5 mg; 3 mol %, based on Cu).

Table S2. Screening of solvents for the Cu/N-CNT NPs catalysed borylation of (3-bromopropyl)benzene (**1a**).

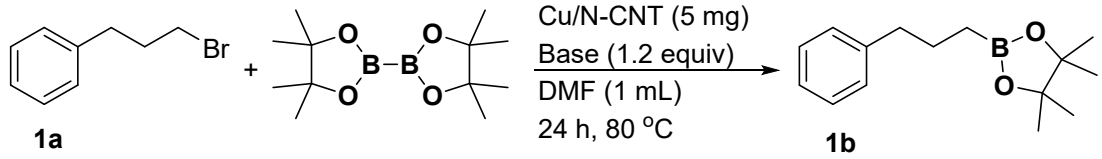


1a **1b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (°C)	Time (h)	Yield (%)
1	Cu/N-CNT	Acetonitrile	KO^{t}Bu	1.2	80	24	47
2	Cu/N-CNT	Toluene	KO^{t}Bu	1.2	80	24	0
3	Cu/N-CNT	Benzene	KO^{t}Bu	1.2	80	24	0
4	**Cu/N-CNT**	**DMF**	**KO^{t}Bu**	**1.2**	**80**	**24**	**96**
5	Cu/N-CNT	THF	KO^{t}Bu	1.2	80	24	0

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), Cu/N-CNTs (5 mg), KO^{t}Bu (1.2 equiv), solvent (1mL) for 24 h at 80 ˚C. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S3. Screening of bases for Cu/N-CNT NPs catalysed borylation of (3-bromopropyl)benzene (**1a**).

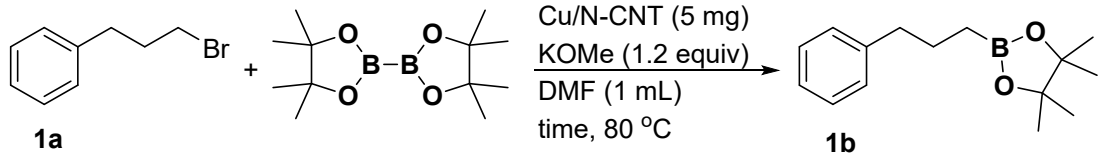


1a **1b**

entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (°C)	Time (h)	Yield (%)
1	Cu/N-CNT	DMF	NaO^{t}Bu	1.2	80	24	85
2	Cu/N-CNT	DMF	NaOMe	1.2	80	24	98
3	Cu/N-CNT	DMF	KO^{t}Bu	1.2	80	24	96
4	**Cu/N-CNT**	**DMF**	**KOMe**	**1.2**	**80**	**24**	**99**
5	Cu/N-CNT	DMF	LiO^{t}Bu	1.2	80	24	98
6	Cu/N-CNT	DMF	-	1.2	80	24	0

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), Cu/N-CNT (5 mg), Base (1.2 equiv), DMF (1 mL) for 24 h at 80 ˚C. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S4. Screening of reaction time for Cu/N-CNT NPs catalysed borylation of (3-bromopropyl)benzene (**1a**).

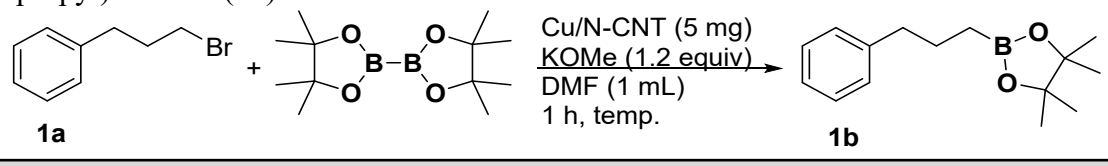


1a **1b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (°C)	Time	Yield (%)
1	Cu/N-CNT	DMF	KOMe	1.2	80	18 h	99
2	Cu/N-CNT	DMF	KOMe	1.2	80	12 h	99
3	Cu/N-CNT	DMF	KOMe	1.2	80	8 h	99
4	Cu/N-CNT	DMF	KOMe	1.2	80	2 h	99
5	Cu/N-CNT	DMF	KOMe	1.2	80	1 h	99
6	**Cu/N-CNT**	**DMF**	**KOMe**	**1.2**	**80**	**30 min**	**99**

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), Cu/N-CNT (5 mg), KOMe (1.2 equiv), in DMF (1 mL) at 80 ˚C. Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard.

Table S5. Screening of reaction temperature for Cu/N-CNT NPs catalysed borylation of (3-bromopropyl)benzene (**1a**).

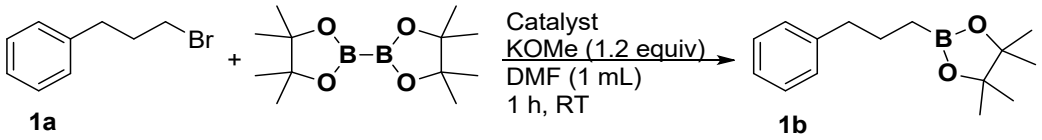


1a **1b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (°C)	Time (h)	Yield (%)
1	Cu/N-CNT	DMF	KOMe	1.2	RT	30 min	96
2	**Cu/N-CNT**	**DMF**	**KOMe**	**1.2**	**RT**	**1 h**	**99**
3	Cu/N-CNT	DMF	KOMe	1.2	50	30 min	99
4	Cu/N-CNT	DMF	KOMe	1.2	80	30 min	99

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), Cu/N-CNT (5 mg), KOMe (1.2 equiv), in DMF (1 mL). Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard.

Table S6. Control experiments for NPs catalyzed borylation of (3-bromopropyl)benzene (**1a**).



1a **1b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (^oC)	Time (h)	Yield (%)
1	CNT [a]	DMF	KOMe	1.2	RT	1h	Trace
2	N-CNT	DMF	KOMe	1.2	RT	1 h	Trace
3	Cu/N-CNT	DMF	KOMe	1.2	RT	1 h	99
4	CuO+CNT [b]	DMF	KOMe	1.2	RT	1 h	15
5	CuO+N-CNT[c]	DMF	KOMe	1.2	RT	1 h	19
6	CuO	DMF	KOMe	1.2	RT	1 h	59

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), catalyst (5 mg), KOMe (1.2 equiv), DMF (1 mL). Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard. [a] Mildly oxidized carbon nanotubes (5 mg) were used. [b] CuO (1.9 mg; 10 mol%) and mildly oxidized carbon nanotubes (5 mg) were used. [c] CuO (2 mg; 10 mol%) and N-CNT (5 mg) were used.

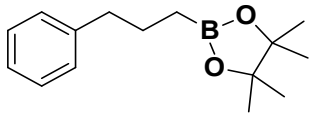
IV. Substrate Scope of Alkyl Halides Borylation Reaction

Experimental Procedure for Examples Described in Tables 2 and 3.

General Procedure A. In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol), DMF (5 mL) and alkyl halide/benzyl halide (1 mmol) were added and the reaction was stirred vigorously at room temperature for 1 h. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 15 mL). The combined organics were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography.

General Procedure B. In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B2pin2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol), DMF (5 mL), alkyl chloride (1 mmol) and NBu4I (1 mmol) were added and the reaction was stirred vigorously at 80 ˚C for 24 h. The crude reaction was dissolved in Et2O (20 mL) and then transferred to a separatory funnel followed by the addition of H2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et2O (3 x 15 mL). The combined organics were dried (Na2SO4) and concentrated. The residue was purified by column chromatography.

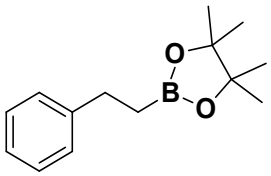
4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2 dioxaborolane (1b).[3]



Following general procedure A, a colorless liquid in 84% yield (206 mg) from 3-phenylpropyl bromide (**1a**, 199 mg, 1 mmol) was obtained. Following general procedure B, using (3-chloropropyl)benzene as a substrate, 77% yield of **1b** was determined by ^{1}H NMR using nitromethane as internal standard. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.20-7.15 (m, 3H), 2.63 (t, J = 8 Hz, 2H), 1.75 (qn, J = 8Hz, 2H), 1.26 (s, 12H), 0.84 (t, J = 8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.71, 128.60, 128.21, 125.61, 82.95, 38.64, 26.18, 24.88. The

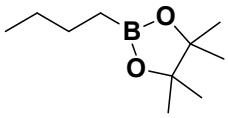
carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.91. GC-MS: m/z 246 (M+).

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolan (2b).[3]



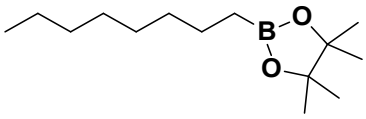
Following general procedure A, a colorless liquid in 81% yield (187 mg) from (2-bromoethyl)benzene (**2a**, 185 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 7.28–7.21 (m, 4 H), 7.15 (t, *J* = 8Hz, 1 H), 2.75 (t, J = 8 Hz, 2H), 1.22 (s, 12 H), 1.15 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 144.88, 128.64, 128.46, 125.95, 83.55, 30.41, 25.27. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl3): *δ* 34.35. GC-MS: m/z 232 (M+).

2-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b).[4]



Following general procedure A, a colorless liquid in 83% yield (153 mg) from 1-bromobutane (**3a**, 137 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): 1.41-1.35 (m, 2H), 1.32-1.28 (m, 2H), 1.23 (s, 12H), 0.86 (t, *J* = 8 Hz, 3H), 0.76 (t, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): *δ* 83.25, 26.65, 25.85, 25.23, 14.32, 11.87 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl3): *δ* 33.94. GC-MS: m/z 184 (M+).

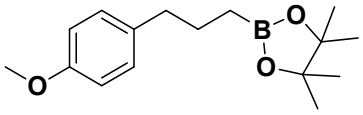
4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane (4b).[5]



Following general procedure A, a colorless liquid in 86% yield (206 mg) from 1-bromooctane (**4a**, 193 mg, 1 mmol) was obtained. Following general procedure B, using 1-chlorooctane as a substrate, 89% yield of **4b** was determined by ^{1}H NMR using nitromethane as internal standard.

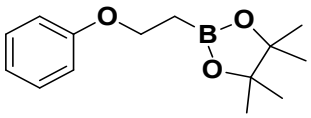
^{1}H NMR (400 MHz, CDCl3): δ 1.36-1.33 (m, 2H), 1.24-1.21 (m, 10 H), 1.19 (s, 12H), 0.82 (t, *J* = 8 Hz, 3H), 0.71 (t, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 83.17, 32.84, 32.31, 29.79, 29.67, 25.18, 24.40, 23.08, 14.50, 11.72 (very broad, low intensity). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.34. GC-MS: m/z 240 (M+).

2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b).[4]



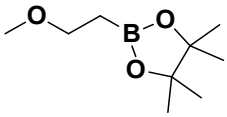
Following general procedure A, a colorless liquid in 81% yield (223 mg) from 1-(3- bromopropyl)-4-methoxybenzene (**5a**, 229 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.08 (m, 2H), 6.82-6.80 (m, 2H), 3.78 (s, 3H), 2.55 (t, *J* = 8 Hz, 2H), 1.70 (t, *J* = 8Hz, 2H), 1.24 (s, 12H), 0.81 (t, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.09, 135.31, 129.85, 114.08, 83.37, 55.70, 38.10, 26.74, 25.28. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.88. GC-MS: m/z 276 (M+).

4,4,5,5-Tetramethyl-2-(2-phenoxyethyl)-1,3,2-dioxaborolane (6b).[5]



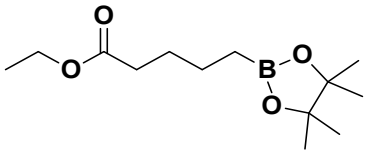
Following general procedure A, a colorless liquid in 80% yield (198 mg) from (2-bromoethoxy)benzene (**6a**, 201 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 7.33-7.19 (m, 2H), 6.97-6.84 (m, 3H), 4.11 (t, *J* = 8Hz, 2H), 1.38 (t, *J* = 8Hz, 2H), 1.26 (s, 12H). ^{13}C NMR (100 MHz, CDCl3): δ 159.50, 129.79, 120.85, 115.10, 83.82, 65.23, 25.26, 13.21 (broad peak). ^{11}B NMR (128 MHz, CDCl3): δ 33.51. GC-MS: m/z 248 (M+).

2-(2-Methoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b).[5]



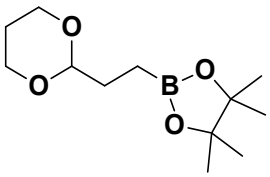
Following general procedure A, a colorless liquid in 87% yield (161 mg) from 1-bromo-2 methoxyethane (**7a**, 139 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 3.47 (t, *J* = 8Hz, 2H), 3.26 (s, 3H), 1.20 (s, 12H), 1.12 (t, *J* = 10Hz, 2H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{13}C NMR (100 MHz, CDCl3): δ 83.58, 69.67, 58.52, 25.18. ^{11}B NMR (128 MHz, CDCl3): *δ* 33.12. GC-MS: m/z 186 (M+).

Ethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (8b).[4]



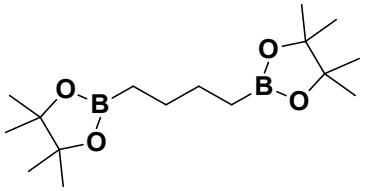
Following general procedure A, colorless liquid in 84% yield (215 mg) from ethyl 5-bromopentanoate (**8a**, 209 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 4.09 (q, *J* = 7 Hz, 2H), 2.27 (t, *J* = 8 Hz, 2H), 1.65-1.57 (m, 2H), 1.46-1.38 (m, 2H), 1.25-1.21 (m, 15H), 0.77 (t, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): *δ* 174.32, 83.40, 60.56, 34.67, 28.02, 25.25, 24.08, 14.68, 11.40 (br). ^{11}B NMR (128 MHz, CDCl3): *δ* 34.08 ppm. GC-MS: m/z 241 (M^{+}–CH3).

2-(2-(1,3-Dioxan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b).[3]



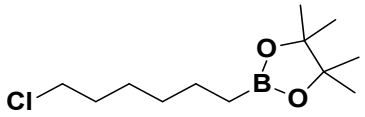
Following general procedure A, colorless liquid in 89% yield (215 mg) from 2-(2-bromoethyl)-1,3-dioxane (**9a**, 195 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 4.44 (t, *J* = 4Hz, 1H), 4.07-4.03 (m, 2H), 3.76-3.67 (m, 2H), 2.09-1.96 (m, 1H), 1.71-1.66 (m, 2H), 1.30-1.25 (m, 1H), 1.20 (s, 12H), 0.79 (t, *J* = 8Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 103.59, 83.35, 67.20, 29.91, 26.26, 25.19, 5.68. ^{11}B NMR (128 MHz, CDCl3): δ 34.0 GC-MS: m/z 242 (M^{+}).

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane (10b).[7]



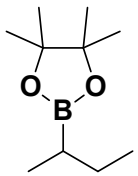
Following general procedure A using 2.3 equiv of B_2pin_2 and KO^{t}Bu, a colorless liquid in 76% yield (235 mg) from 1,4-dibromobutane (**10a**, 215 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3) δ 1.40-1.37 (m, 4H), 1.22 (s, 24H), 0.75 (br, 4H). ^{13}C NMR (100 MHz, CDCl3) δ 82.78, 26.85, 24.80, 11.0 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl3): δ 34.58. GC-MS: m/z 309 (M+).

2-(6-Chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b).[5]



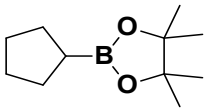
Following general procedure A, a colorless liquid in 81% yield (199 mg) from 1-bromo-6-chlorohexane (**11a**, 199 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 3.50 (t, J = 6Hz, 2H), 1.75 (t, J = 6Hz, 2H), 1.43-1.39 (m, 4H), 1.33-1.30 (m, J = 8, 2H), 1.23 (s, 12H) 0.76 (*t*, J = 8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.86, 45.08, 32.51, 31.50, 26.60, 24.79, 23.76, 10.94. (very broad, low intensity). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.08. GC-MS: m/z 246 (M+).

2-(sec-Butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b). [6]



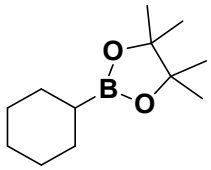
Following general procedure A, colorless liquid in 65% yield (119 mg) from 2-bromobutane (**12a**, 137 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 1.55-1.49 (m, 1H), 1.38-1.33 (m, 1H), 1.24 (s, 12H), 0.93-0.90 (m, 4H), 0.85 (t, J = 4Hz, 3H). ^{13}C NMR (100 MHz, CDCl3): 83.22, 27.36, 26.58, 15.64, 11.86. ^{11}B NMR (128 MHz, CDCl3): δ 35.17 GC-MS: m/z 184 (M+).

2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b).[6]



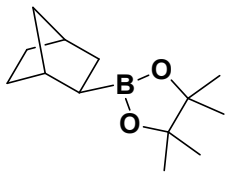
Following general procedure A, a colorless liquid in 82% yield (160 mg) from bromocyclopentane (**13a**, 149 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 1.79-1.69 (m, 2H), 1.60-1.47 (m, 6H), 1.23 (s, 12H), 1.18-1.14 (M, 1H). ^{13}C NMR (100 MHz, CDCl3): δ 83.23, 28.96, 27.28, 25.17, 23.11. ^{11}B NMR (128 MHz, CDCl3): δ 34.85. GC-MS: m/z 196 (M+).

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14b).[6]



Following general procedure A, a colorless liquid in 88% yield (184 mg) from bromocyclohexane (**14a**, 163 mg, 1.0 mmol) was obtained. Following general procedure B, using chlorocyclohexane as a substrate, 24% amount of **14b** was determined by GC-MS analysis. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.64-1.54 (m, 5H), 1.33-1.24 (m, 5H), 1.21 (s, 12H), 0.96-0.93 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.71, 27.95, 27.12, 26.75, 24.73, 22.08 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl3): δ 34.06. GC-MS: m/z 210 (M+).

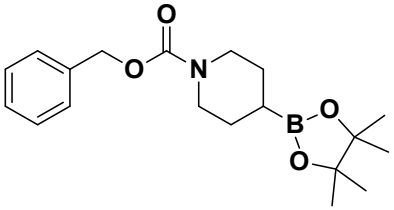
***exo*-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b).**[6]



Following general procedure A, colorless liquid in 70% yield (155 mg; a mixture containing an *exo*:*endo* ratio of ca. 74:26 of **15b** determined by averaging the ratio of carbon resonances in the ^{13}C NMR) was obtained from *exo*-2-bromonorbornane (*exo*-**15a**, 175 mg, 1 mmol). ^{1}H NMR (400 MHz, CDCl3): δ 2.36-2.17 (m, 2H), 1.55-1.42 (m, 3H), 1.38-1.33 (m, 1H), 1.24-1.22 (m, 14H), 1.18-1.13 (m, 2H), 0.91-0.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 83.24, 39.17, 38.59, 37.10, 32.64, 29.73, 28.33, 25.15 (*exo*); 83.33, 41.41, 39.37, 37.51, 32.67, 32.27, 30.30, 25.37, 25.32

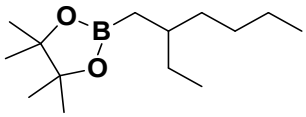
(*endo*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.13. GC-MS: m/z 222 (M+).

Benzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (16b).[6]



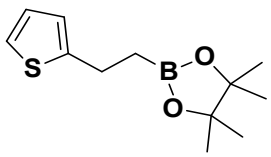
Following general procedure A, a colorless liquid in 80% yield (276 mg) from benzyl 4-bromopiperidine-1-carboxylate (**16a**, 298 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.26 (m, 5H), 5.11 (s, 2H), 3.86 (br, 2H), 3.01 (t, *J* = 10Hz, 2H), 1.65 (br, 2H), 1.51-1.49 (m, 2H), 1.22 (s, 12H), 1.16-1.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.77, 137.50, 128.88, 128.29, 128.23, 83.66, 67.29, 45.50, 27.32, 25.20. ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.15. GC-MS: m/z 345 (M^+)

2-(2-Ethylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)



Following general procedure B, a colorless liquid in 42% yield (100 mg) from 3-(bromomethyl)heptane (**18a**, 193 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63-1.47 (m, 5H), 1.45-1.32 (m, 4H), 1.29-1.25 (m, 6H), 1.24 (s, 12H), 0.78-0.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 83.19, 36.23, 36.06, 32.00, 29.56, 29.38, 27.33, 25.25, 23.50, 14.55, 11.55. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 34.57. GC-MS: m/z 240 (M^+).

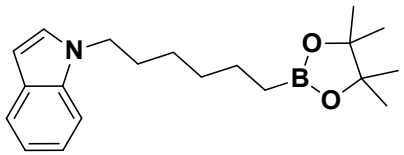
4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (19b).[5]



Following general procedure B, a colorless liquid in 42% yield (100 mg) from 1-(2-bromoethyl)cyclopenta-1,3-diene (**19a**, 173 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz,

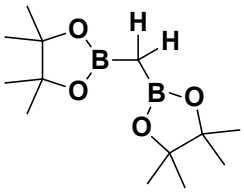
$CDCl_3$): δ 7.07 (dd, *J* = 5.2Hz, 1.2 Hz, 1H), 6.89 (dd, *J* = 5Hz, 3.4 Hz, 1H), 6.81-6.80 (m, 1H), 2.97 (t, *J* = 8 Hz, 2H), 1.31-1.27 (m, 2H), 1.24 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.19, 126.98, 123.86, 123.06, 83.67, 25.27, 24.82, 14.56. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 33.85.

1-(6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1H-indole (20b).[1]



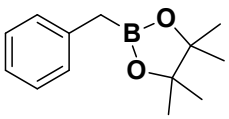
Following general procedure B, white solid in 70% yield (228 mg) from 1-(6-chlorohexyl)-1H-indole (**20a**, 235 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.68 (m, 1H), 7.40 (d, *J* = 8 Hz, 1H), 7.29–7.24 (m, 1H), 7.19-7.14 (m, 2H), 6.56-6.54 (m, 1H), 4.14 (t, *J* = 8 Hz, 2H), 1.92-1.87 (m, 2H), 1.41-1.40 (m, 6H), 1.31 (s, 12H), 0.86 (t, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.49, 129.12, 128.31, 121.79, 121.43, 119.64, 109.92, 101.34, 83.42, 46.84, 32.42, 30.66, 27.28, 25.36, 25.25, 24.39, 15.99. ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.38. GC-MS: m/z 327 (M^+).

2,2'-(Propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (21b).[6]



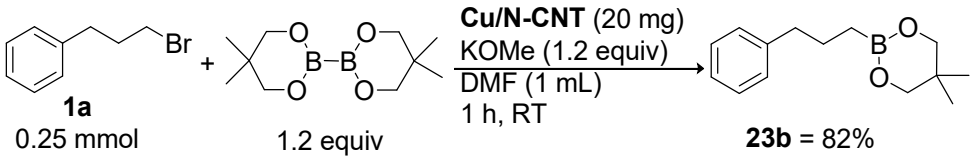
Following general procedure A, a colorless liquid in 70% yield (186 mg) from dichloromethane (**21a**, 85 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 (s, 24H), 0.22 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 82.81, 24.56. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): *δ* 33.60. GC-MS: m/z 267 (M+).

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22b).[1]



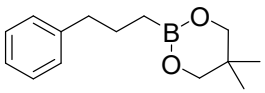
Following general procedure A, a colorless liquid in 75% yield (163 mg) from (bromomethyl)benzene (**22a**, 171 mg, 1 mmol) was obtained. Following general procedure B, a colorless liquid in 85% yield from (chloromethyl)benzene (126 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.14 (m, 5H), 2.75 (t, J = 8Hz 2H), 1.22 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.42, 128.18, 128.00, 125.49, 83.10, 29.95, 24.81, 12.97.
^{11}B NMR (128 MHz, $CDCl_3$): δ 34.07. GC-MS: m/z 218 (M+).

Experimental Procedure for the Example Described in Scheme 2: Borylation of (3-Bromopropyl)benzene (1a) Using *Bis*(neopentylglycolato)diboron (B_2neop_2).



In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT NPs (20 mg, 13.12 mol % of Cu), B_2neop_2 (271 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol), DMF (5 mL) and (3-bromopropyl)benzene (**1a**, 199 mg, 1 mmol) were added and the reaction was stirred vigorously at room temperature for 1 h. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. The residue was purified by chromatography.

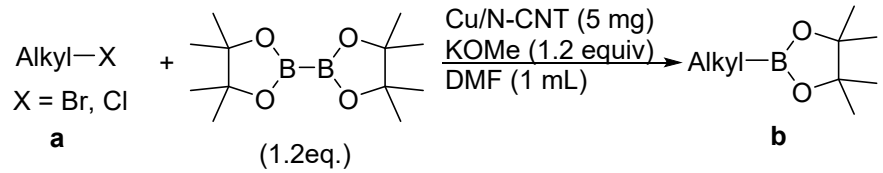
5,5-Dimethyl-2-(3-phenylpropyl)-1,3,2-dioxaborinane (23b).[5]



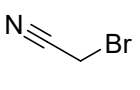
A colorless liquid in 82% yield (190 mg) from (3-bromopropyl)benzene (**1a**, 199 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.15 (m, 5H), 3.59 (s, 4H), 2.61 (t, J = 7.6 Hz, 2H), 1.76-1.67 (m, 2H), 0.97 (s, 6H), 0.78 (t, J = 8.2 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.38. GC-MS: m/z 232 (M^+).

Unsuccessful Substrates

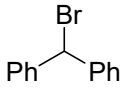
Table S7: Screening of alkyl bromide, chlorides and benzyl chlorides for the Cu/N-CNTs catalyzed borylation reaction.[a]



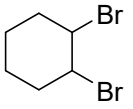
Alkyl Bromide:



Yield = 0%



Yield = 0%

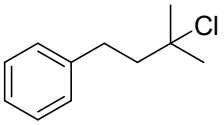


Yield = 0%

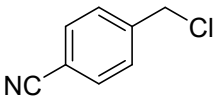
Yield = 0%

Yield = 0%

Alkyl Chloride:[b]



Yield = 0%



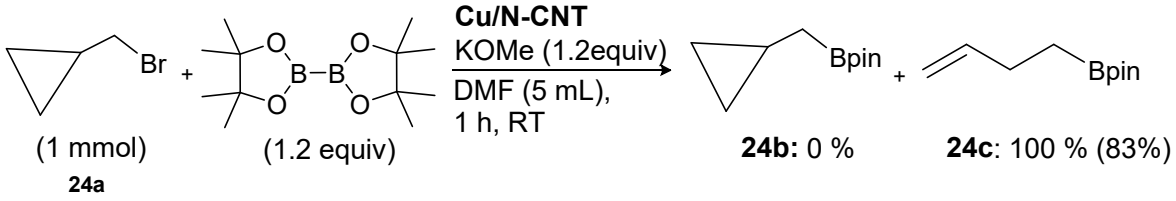
Yield = 0%

[a]Reaction conditions: Alkyl halide (0.25 mmol, 1 equiv), Cu/N-CNT NPs (5 mg), B_2pin_2 (76 mg, 1.2 equiv), KOMe (21 mg, 1.2 equiv), in DMF at RT for 1 h unless otherwise stated. Yields were determined by ^{1}H NMR using nitromethane as internal standard. [b]Reaction was performed in the presence of 1 equiv of $(Bu_4N)I$ at 80 ˚C for 24 h.

This heterogeneous Cu catalyzed borylation protocol has some substrate restrictions. When the reaction was performed using 2-bromoacetonitrile, (bromomethylene)dibenzene, 1,2-dibromocyclohexane, 1-bromobicyclo[2.2.1]heptane and 2-bromo-2-methylpropane as a substrate there were no product formation. When (3-chloro-3-methylbutyl)benzene and 4-(chloromethyl)benzonitrile were used as a substrate in the presence of $(Bu_4N)I$ (1 equiv), no product formation was observed by GC-MS analysis.

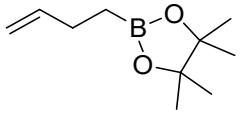
V. Mechanistic Investigations of Alkyl Halides Borylation Reaction

Experimental Procedure for the Example Described in Scheme 3: Borylation of Cyclopropylmethyl bromide (24a).



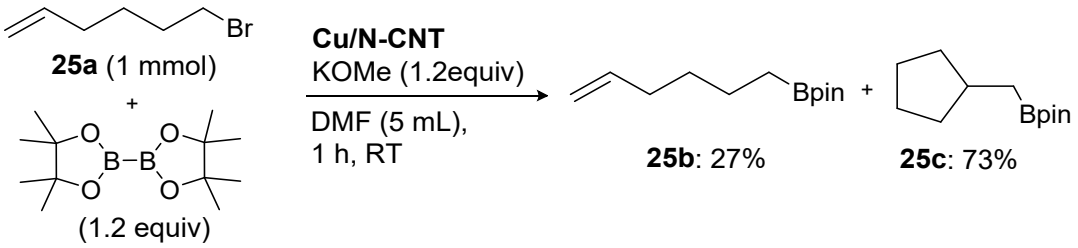
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol) and DMF (5 mL) were added and the reaction mixture was stirred for 10 min. To this reaction mixture, cyclopropylmethyl bromide (**24a**, 135 mg, 1.0 mmol) was added. The resulting reaction mixture was stirred vigorously at room temperature for 1 h. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. The yield of the product was determined by ^1H NMR spectroscopy. Further the residue was purified by column chromatography.

2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24c).[6]



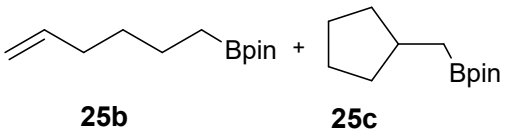
A colorless liquid in 83% yield (151 mg) from (bromomethyl)cyclopropane (**24a**, 135 mg, 1 mmol) was obtained. ^1H NMR (400 MHz, $CDCl_3$): δ 5.90-5.79 (m, 1H), 4.98-4.84 (m, 2H), 2.16-2.10 (m, 2H), 1.20 (s, 12H), 0.84 (t, J = 6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.03, 113.55, 83.39, 28.38, 25.23. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.89 ppm. GC-MS: m/z 182 (M^+).

Experimental Procedures for the Example Described in Scheme 3: Borylation of 6-bromohex-1-ene (25a).



In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol) and DMF (5 mL) were added and the reaction mixture was stirred for 10 min. To this reaction mixture, 6-bromohex-1-ene (**25a**, 163 mg, 1.0 mmol) was added. The resulting reaction mixture was stirred vigorously at room temperature for 1 h. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. An internal standard nitromethane was added to the residue. The yields and the ratio of the products were determined by ^{1}H NMR spectroscopy. Further the residue was purified by column chromatography.

2-(Cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25c).[6]

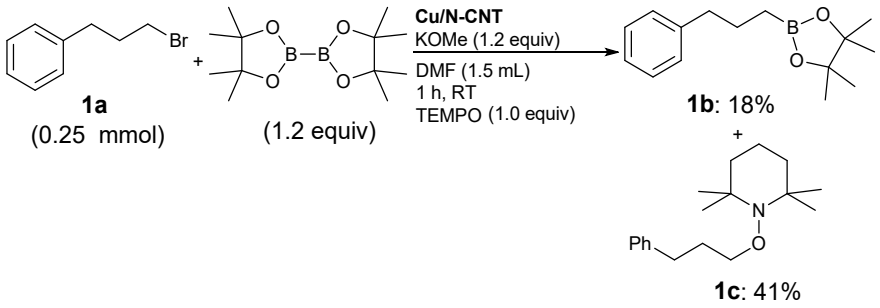


Chromatography yielded an inseparable 27:73 mixture of **25b** and **25c** as a clear liquid from 6-bromohex-1-ene (**25a**).

25c: ^{1}H NMR (400 MHz, CDCl3): δ 5.80-5.70 (m, **25b**), 4.95-4.84 (m, **25b**), 2.00-1.83 (m, 1H), 1.74-1.35 (m, 6H), 1.19 (s, 12H), 1.06-0.91 (m, 2H), 0.78 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.49 (**25b**), 114.44 (**25b**), 83.15, 36.52, 35.45, 25.52, 25.18. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl3) δ 33.94 ppm. GC-MS: m/z 210 (M^+).

Radical Scavenging Experiments

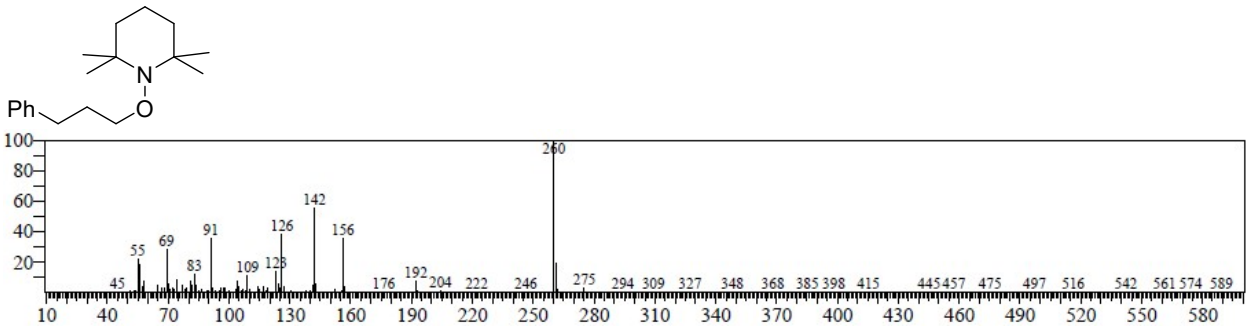
Experiment S1:



In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol) and 1 equiv of TEMPO (156 mg) were added, followed by 5 mL of solvent and reaction mixture was kept under stirring for 1 h room temperature. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. The yields and the ratio of the products were determined by ^1H NMR spectroscopy using nitromethane as an internal standard. The crude reaction mixture was also examined by GC-MS analysis.

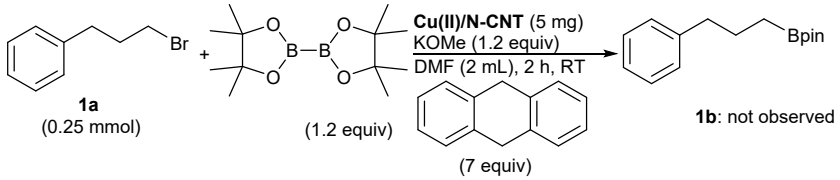
4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2 dioxaborolane (1b) and 2,2,6,6-Tetramethyl-1-(3-phenylpropoxy)piperidine (1c).

A yellow liquid was obtained. ^1H NMR (500 MHz, $CDCl_3$): δ 7.23-7.07 (m, 5H), 3.70 (t, J = 6 Hz, 2H), 2.63 (t, J = 8 Hz, 2H), 1.84-1.74 (m, 2H), 1.54-1.20 (m, 6H), 1.06 (s, 6H), 1.04 (s, 6H).



GC-MS Analysis of 1c

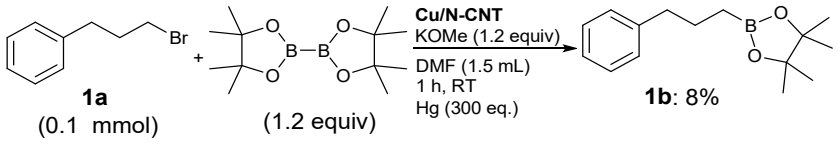
Experiment S2:



In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, Cu/N-CNT (5 mg, 13.12 mol % of Cu), B_2pin_2 (76 mg, 1.2 equiv, 0.3 mmol), KOMe (21 mg, 1.2 equiv, 0.3 mmol), 1a (49 mg, 0.25 mmol) and 7 equiv of 9,10-dihydroanthracene (1.75 mmol, 315 mg) were added, followed by 2 mL of DMF and reaction mixture was kept under stirring for 2 h at room temperature. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated, and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. The yields and the ratio of the products were determined by ^1H NMR spectroscopy. The crude reaction mixture was also examined by GC-MS analysis.

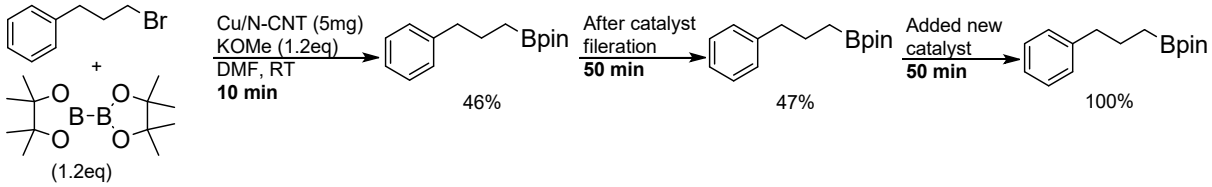
Mercury Poisoning Experiments

In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol), DMF (1 mL), (3-bromopropyl)benzene (**1a**, 19.9 mg, 1 mmol) and Hg (300 equiv) were added and the reaction was stirred vigorously at room temperature for 1 h. The crude reaction was dissolved in Et_2O (20 mL) and then transferred to a separatory funnel followed by the addition of H_2O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. An internal standard nitromethane was added to the residue. The yield of the product was determined by ^1H NMR spectroscopy.



Filtration Experiment

In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol), DMF (5 mL) and (3-bromopropyl)benzene (**1a**, 199 mg, 1 mmol) were added and the reaction was stirred vigorously at room temperature for 10 minutes. After 10 minutes reaction process, the Cu/N-CNT catalyst was separated and the filtrate was stirred for another 50 minutes under identical conditions. Gratifyingly, there was no further increase in the yield of **1b** after the removal of the catalyst. Further addition of the new catalyst to the filtrate led to the full conversion of **1a**. These results show that copper leaching from the catalyst is negligible during the reaction process, which can be attributed to the excellent stability of the Cu/N-CNT catalyst.



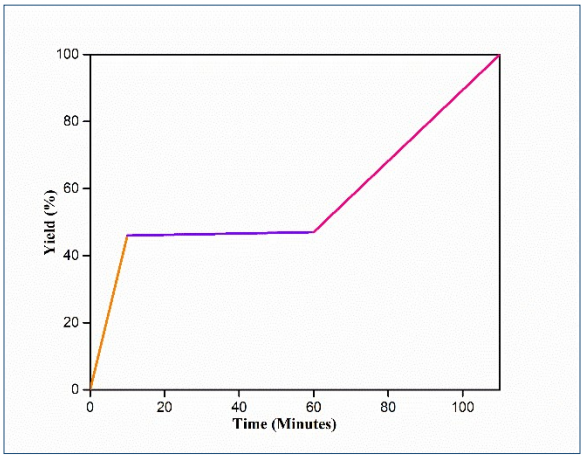
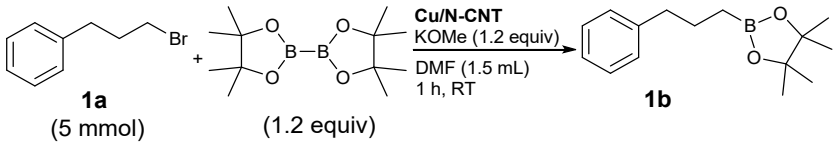


Fig. S8. Cu/N-CNT nanoparticle catalyst filtration experiment for the borylation of (3-bromopropyl)benzene (**1a**).

Recyclability Experiment for Alkyl Halide Borylation Reaction



In a 100 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (100 mg, 13.12 mol % of Cu), B_2pin_2 (1.52 g, 1.2 equiv, 6 mmol), KOMe (420 mg, 1.2 equiv, 6 mmol), DMF (25 mL) and (3-bromopropyl)benzene (**1a**, 995 mg, 5 mmol) were added and the reaction was stirred vigorously at room temperature for 1 h. Cu/N-CNT catalyst was separated by centrifuge and washed thoroughly EtOH (2 x 50 mL) and dried at 80 ˚C overnight, and same catalyst used for further cycles. An internal standard nitromethane was added to the residue. The yield of the product was determined by ^{1}H NMR spectroscopy.

Yields: 1st cycle = >96%, 2nd cycle = >93%, 3rd cycle = 89%, 4th cycle = 89 %, 5th cycle = 93%, 6th cycle = 92%, 7th cycle = 91%, 8th cycle = 88%, 9th cycle = 95 %, 10th cycle = 93%.

To lessen yield variability, the recover catalyst was heated at 200 ˚C for 2 hours after the fifth cycle and reused. After tenth cycle of catalyst recovery, the catalyst was analyzed by FE-SEM, EDX and PXRD [Fig. S9 (b), (c) and (d)].

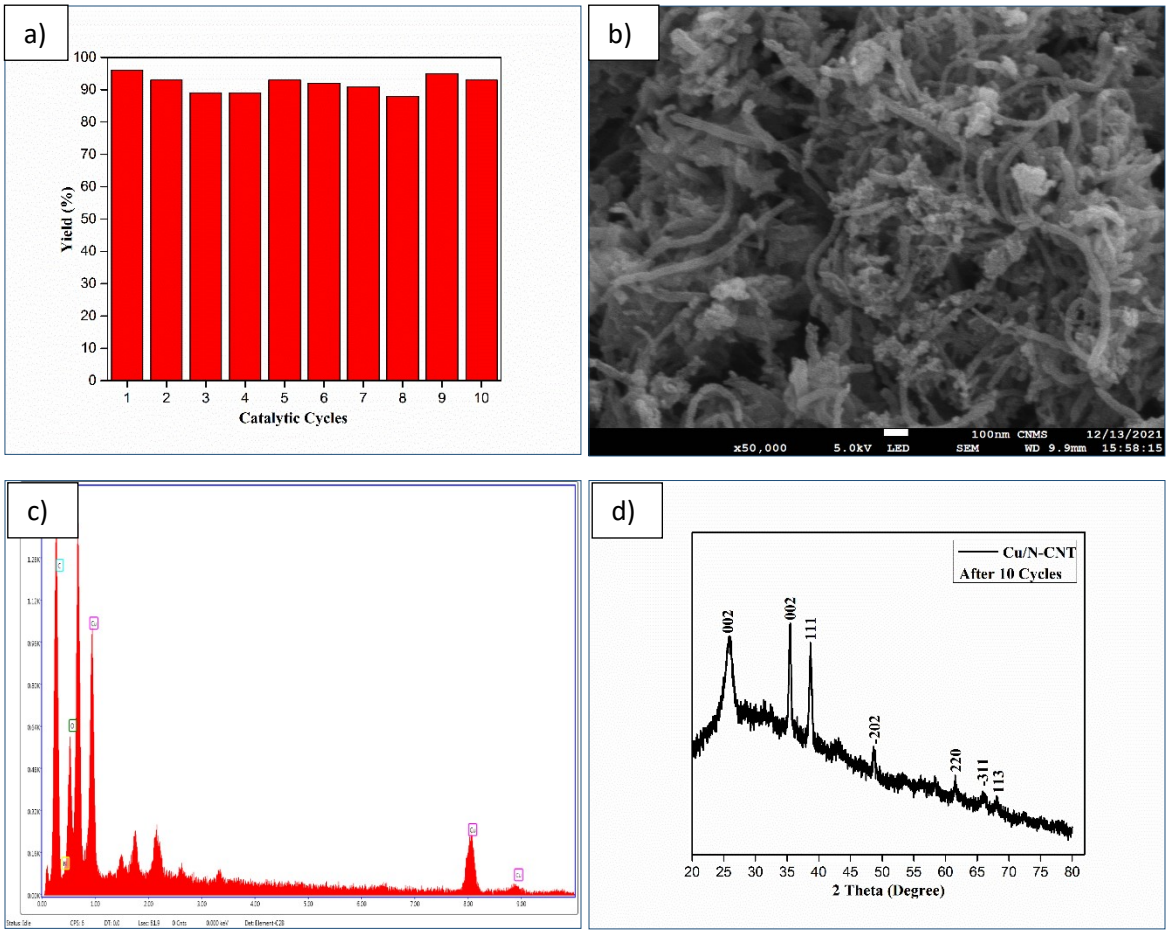
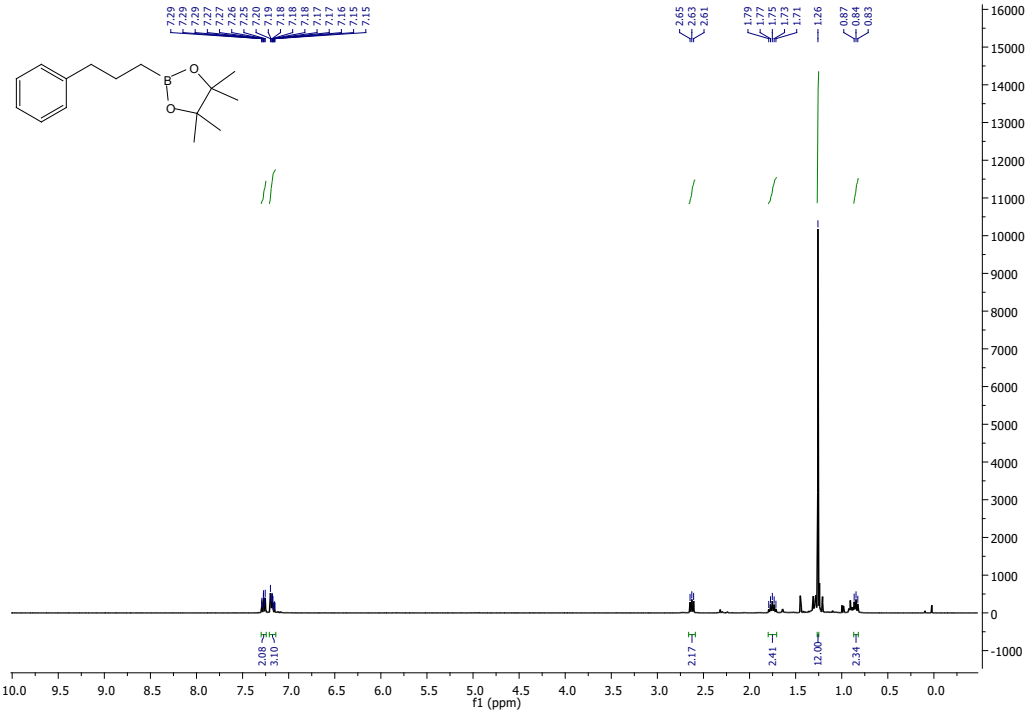


Fig. S9. (a) Cu/N-CNT nanoparticle catalyst recovery and recyclability experiments for the borylation of (3-bromopropyl)benzene (**1a**). (b) FE-SEM image of catalyst after recovery from 10th cycle. (c) EDX spectrum of Cu/N-CNT NPs after catalyst recovered from 10th cycle. (d) PXRD analysis of Cu/N-CNT after catalyst recovered from 10th cycle.

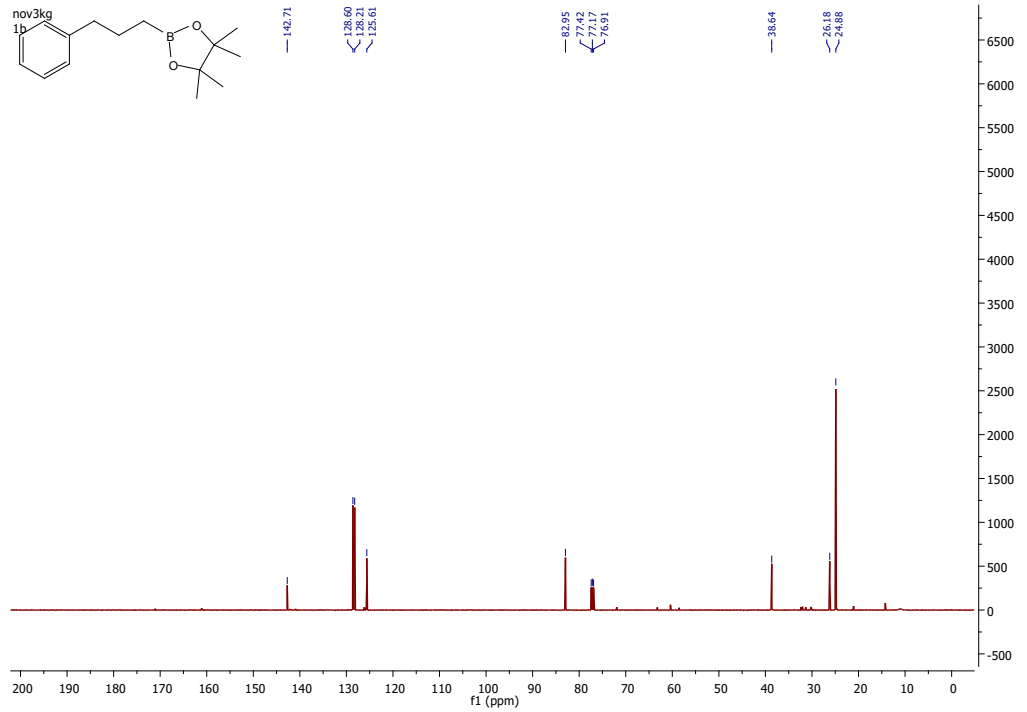
VI. NMR Spectra of Alkyl Halides Borylation Products

***Note*:** Resonances denoted by (#) corresponds to solvent/grease.

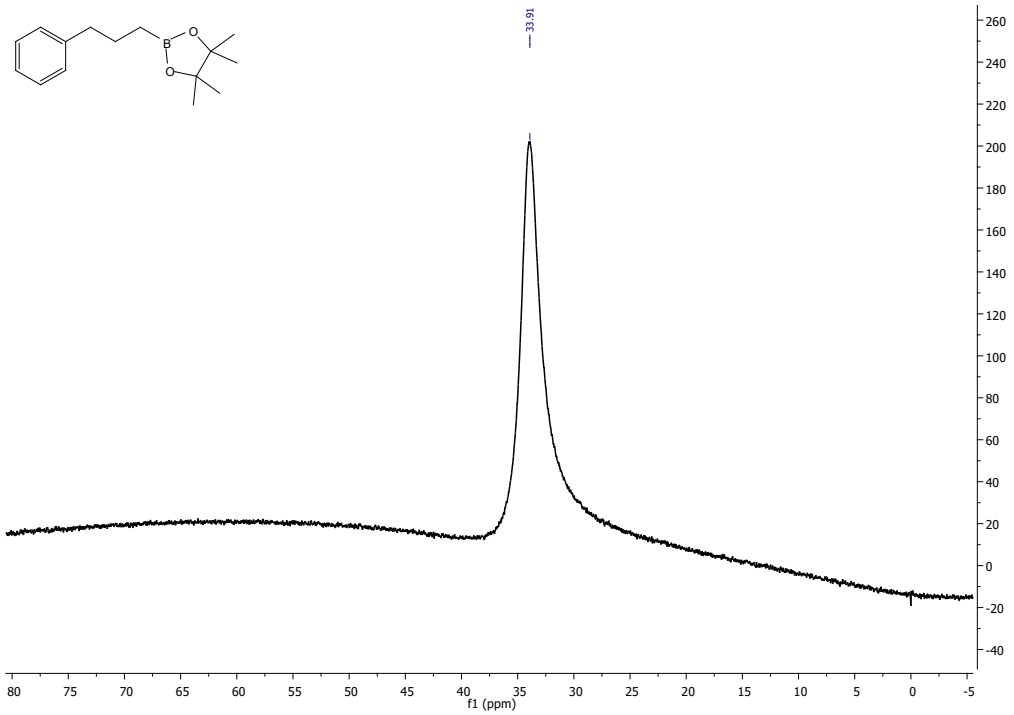
4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2 dioxaborolane (1b)



^{1}H NMR of 1b (400 MHz, $CDCl_3$)

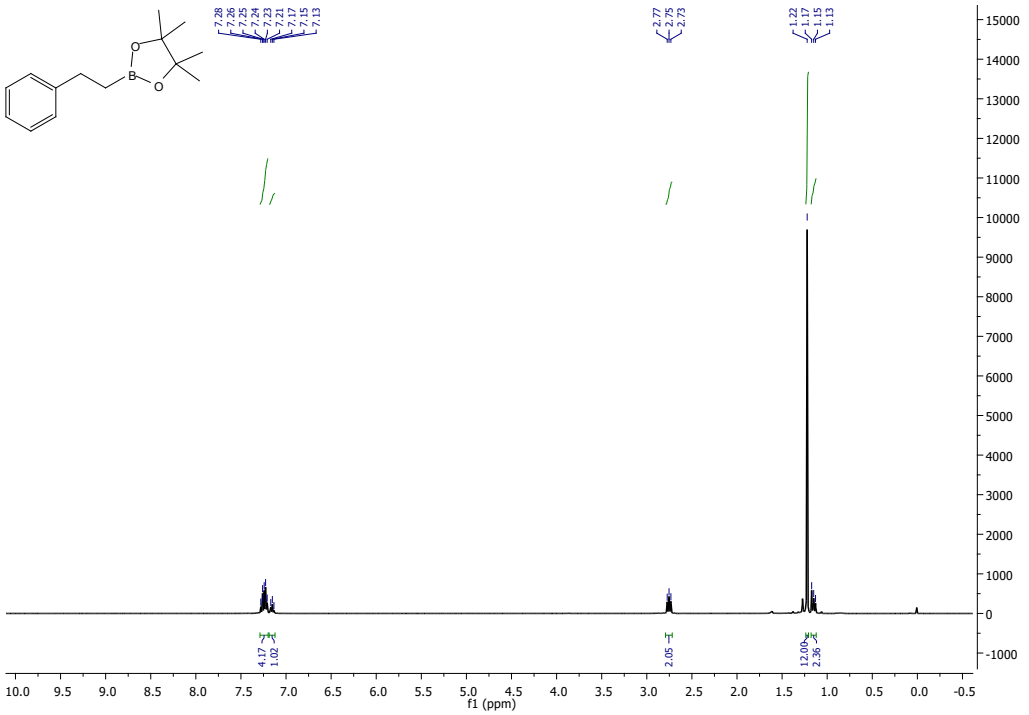


^{13}C NMR of 1b (125 MHz, $CDCl_3$)

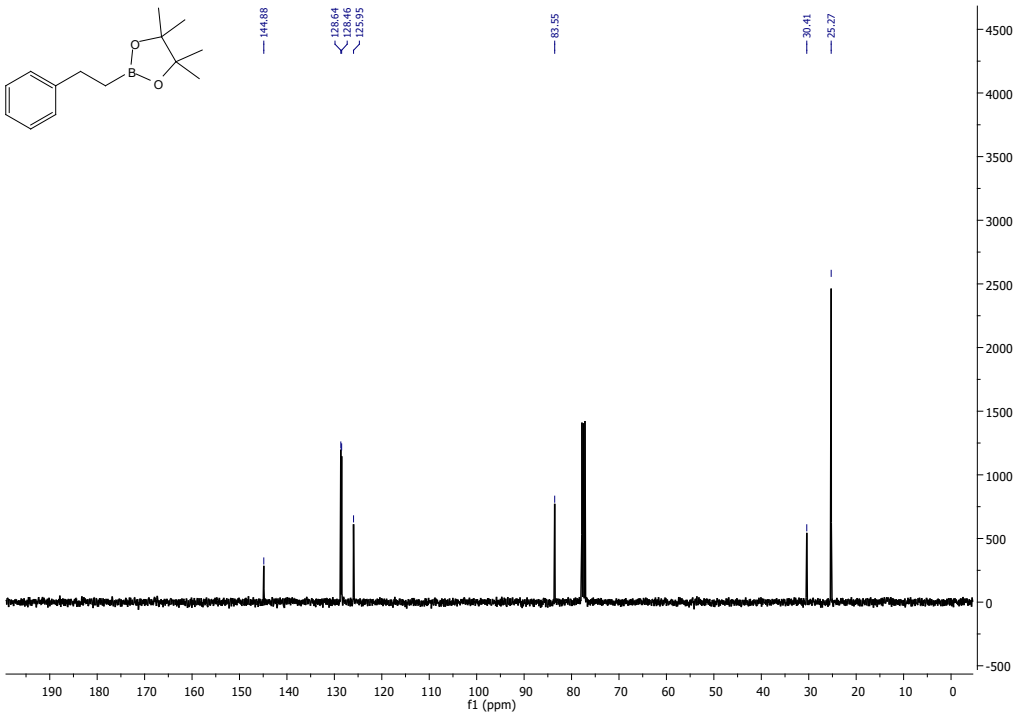


^{11}B NMR of 1b (128 MHz, $CDCl_3$)

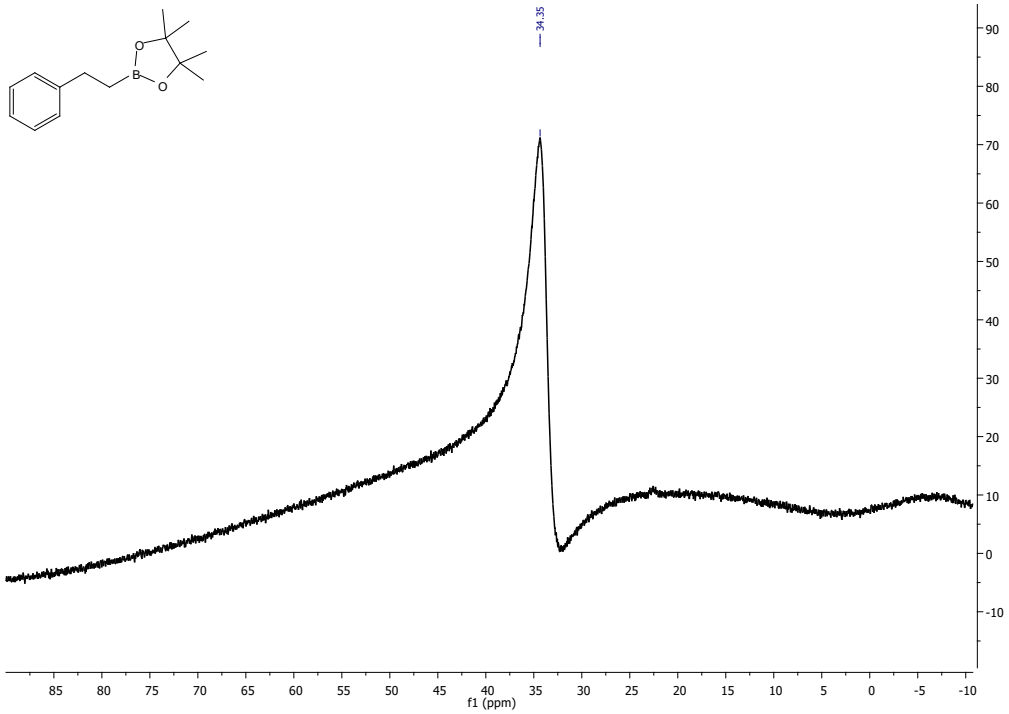
4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolan (2b)



^{1}H NMR of 2b (400 MHz, $CDCl_3$)

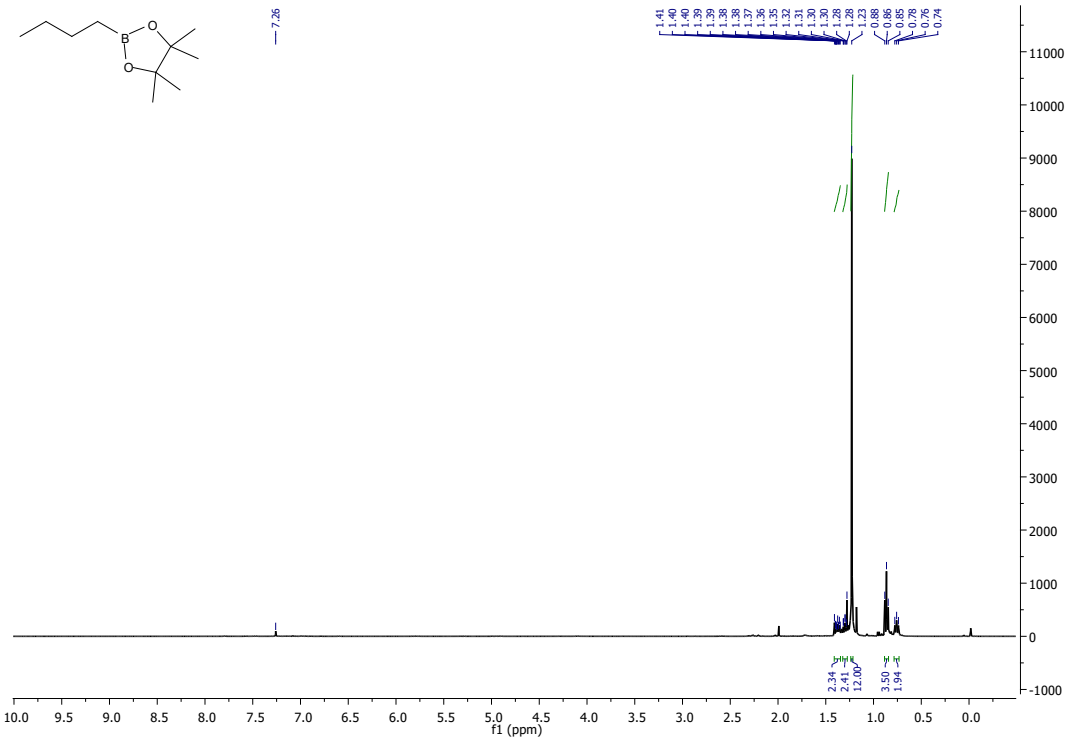


^{13}C NMR of 2b (100 MHz, $CDCl_3$)

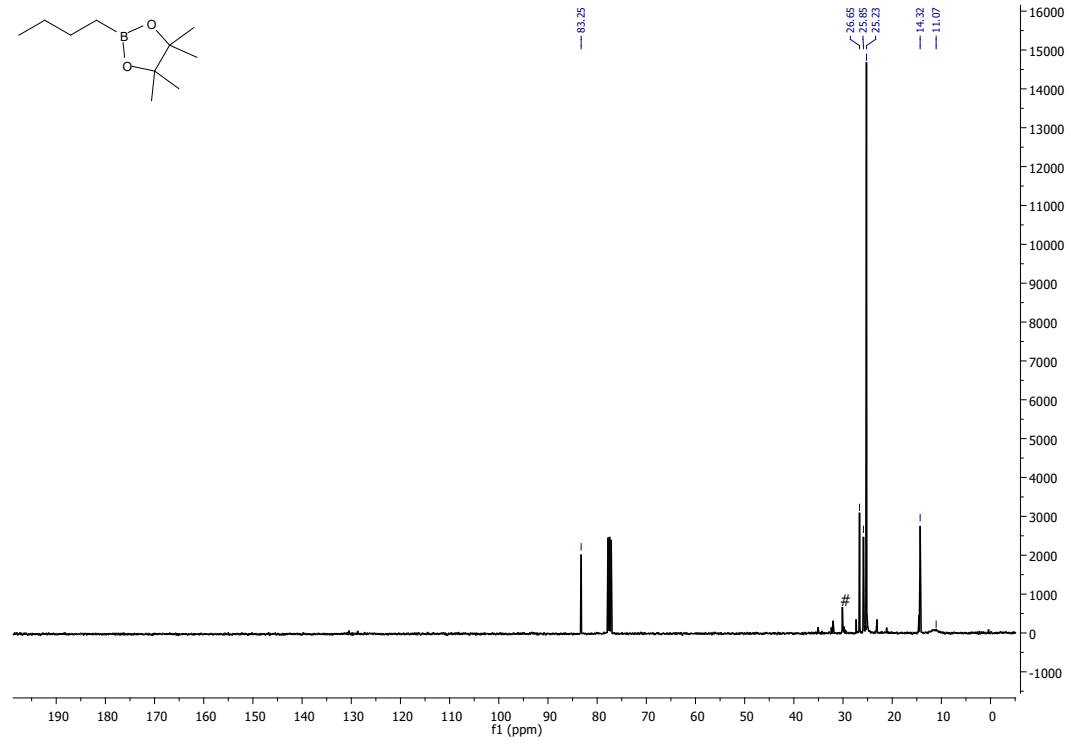


^{11}B NMR of 2b (128 MHz, $CDCl_3$)

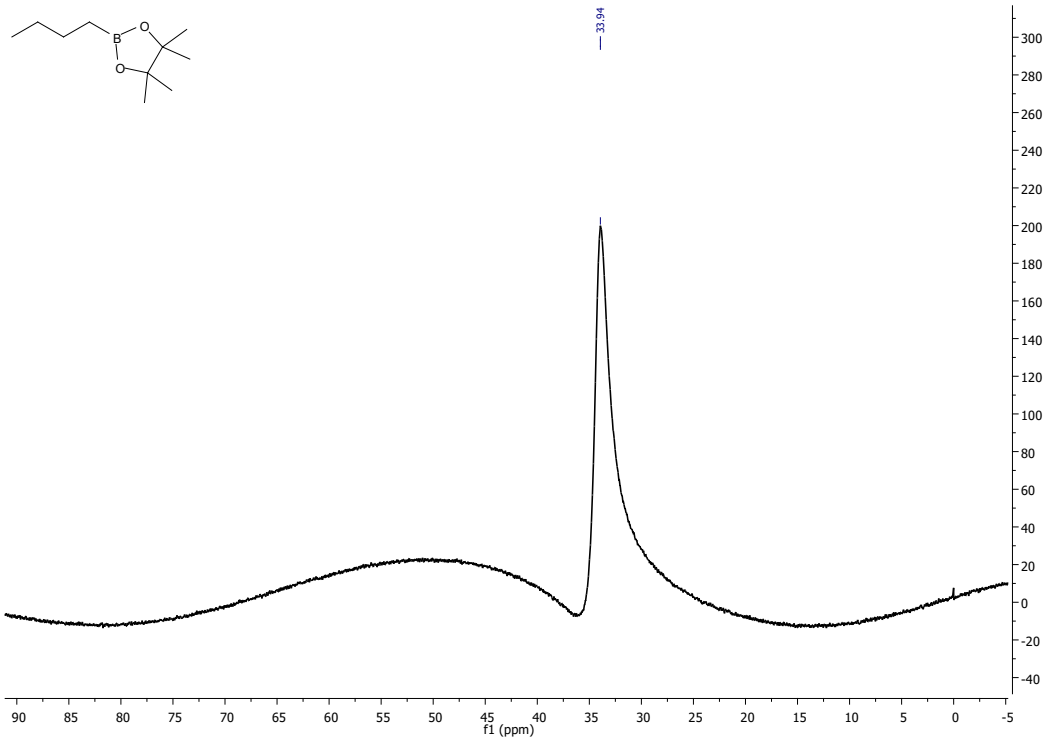
2-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



^{1}H NMR of 3b (400 MHz, $CDCl_3$)

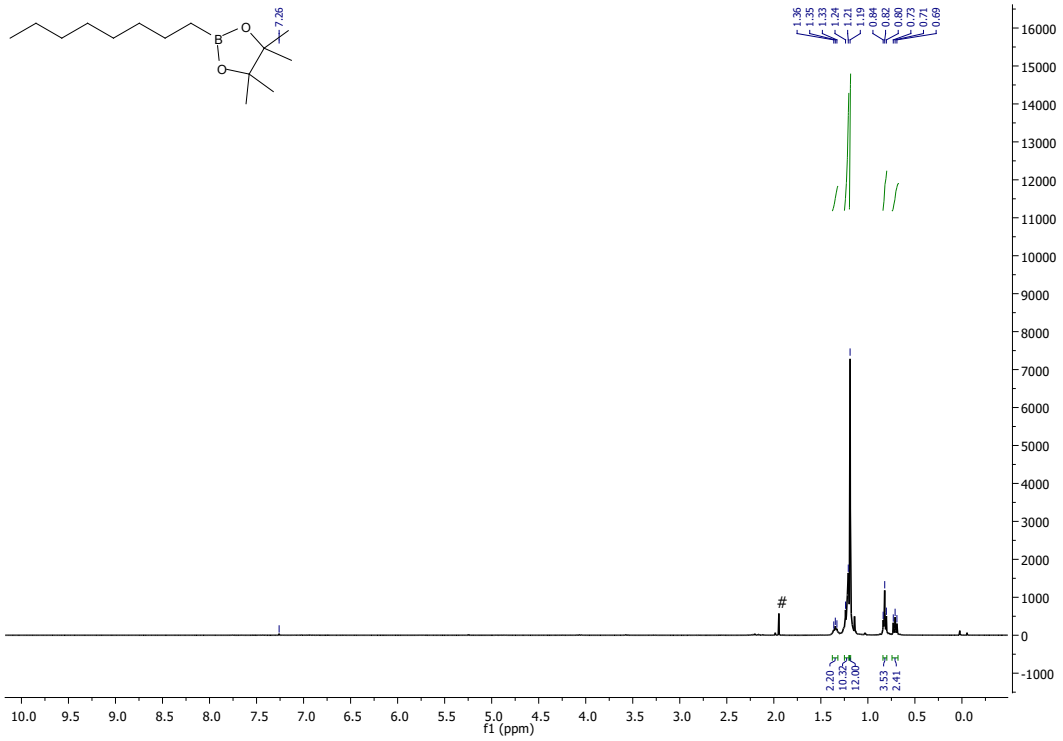


^{13}C NMR of 3b (100 MHz, $CDCl_3$)

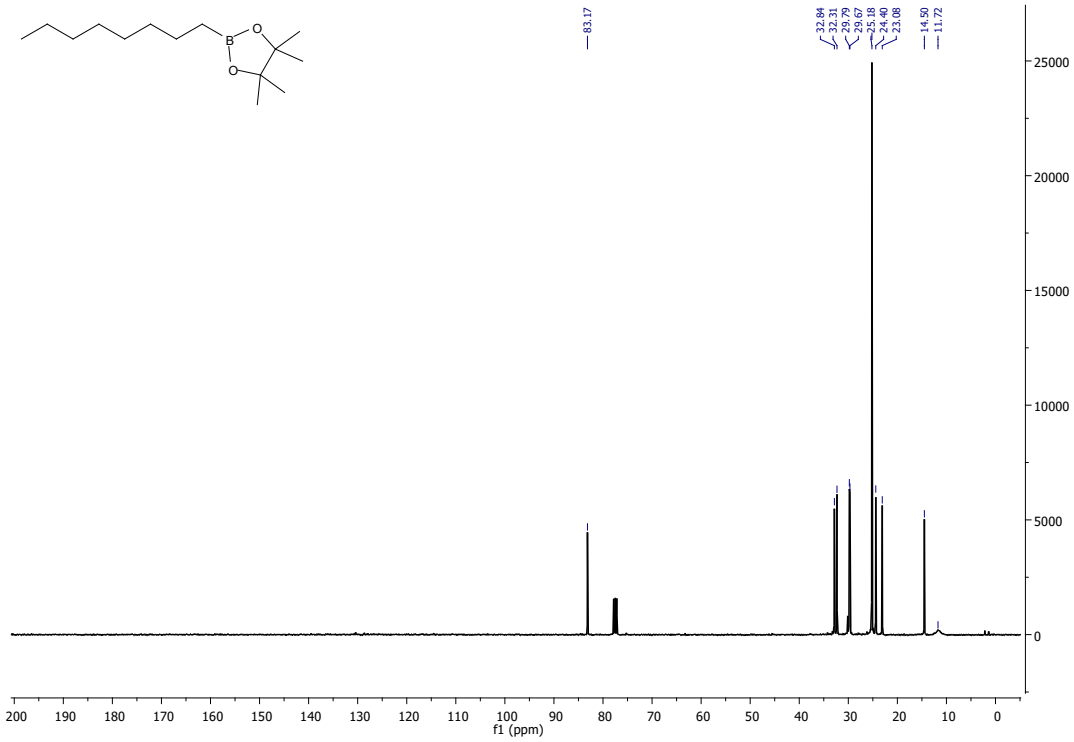


^{11}B NMR of 3b (128 MHz, $CDCl_3$)

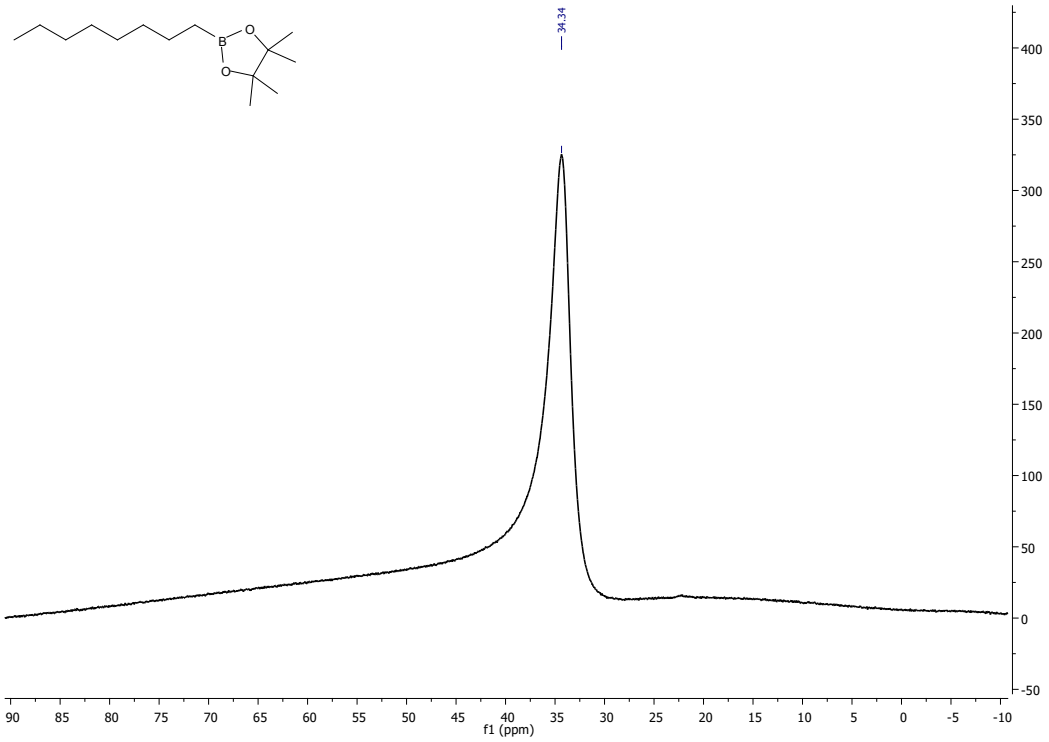
4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane (4b)



^{1}H NMR of 4b (400 MHz, $CDCl_3$)

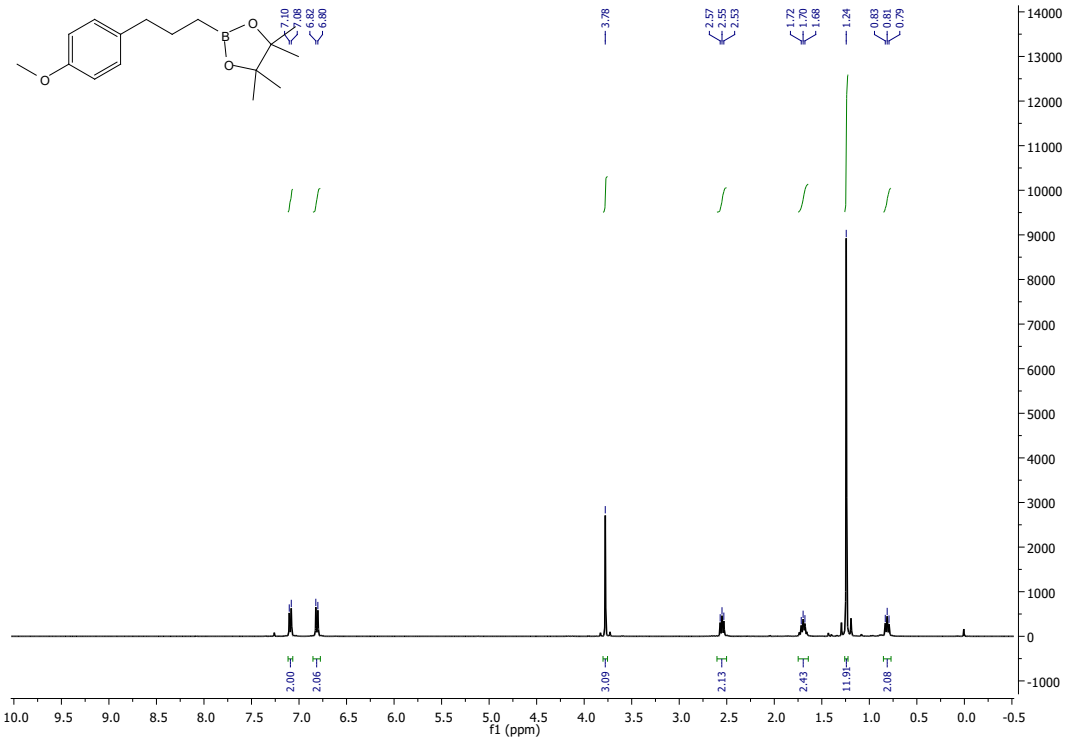


^{13}C NMR of 4b (100 MHz, $CDCl_3$)

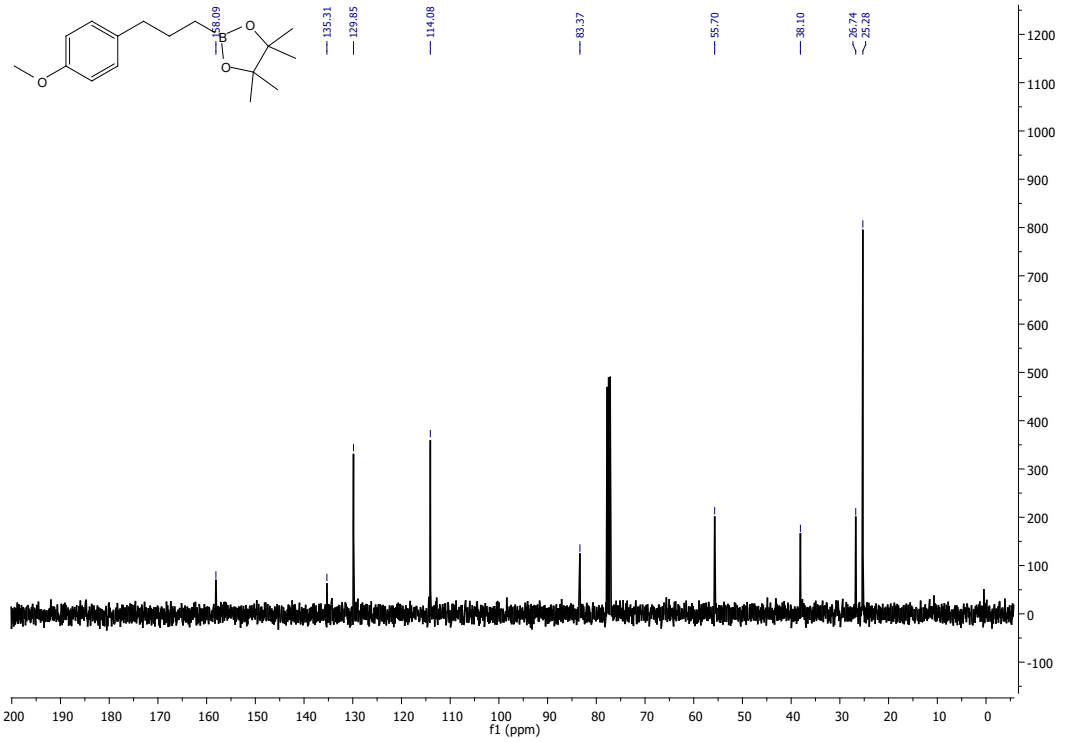


^{11}B NMR of 4b (128 MHz, $CDCl_3$)

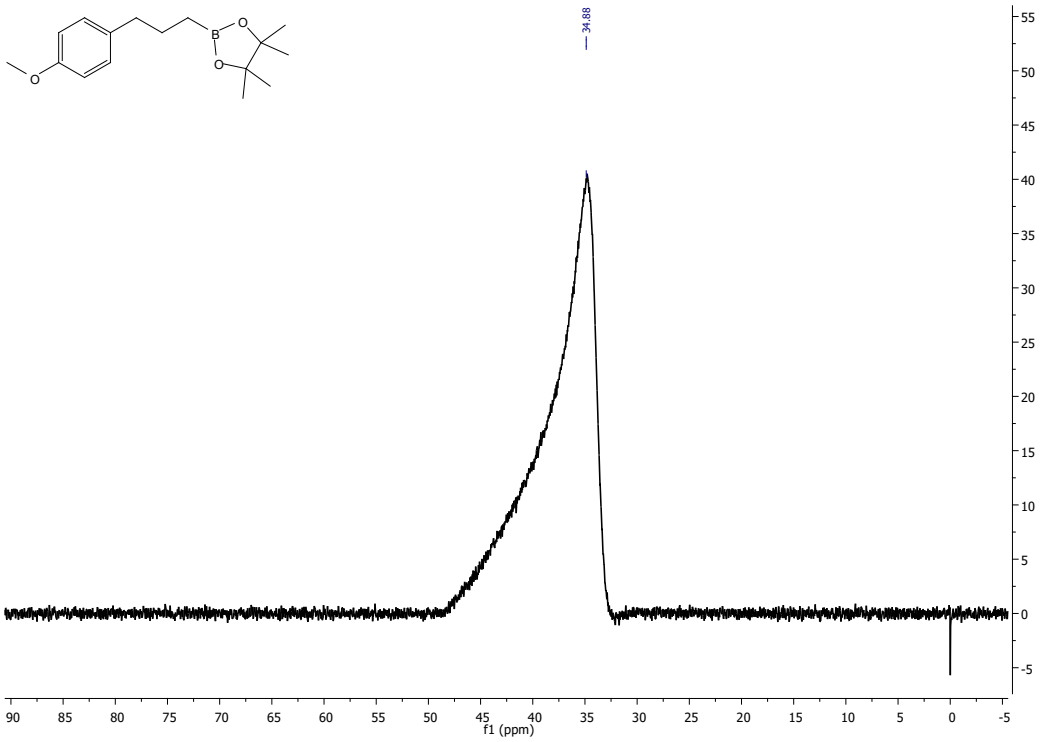
2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)



^{1}H NMR of 5b (400 MHz, $CDCl_3$)

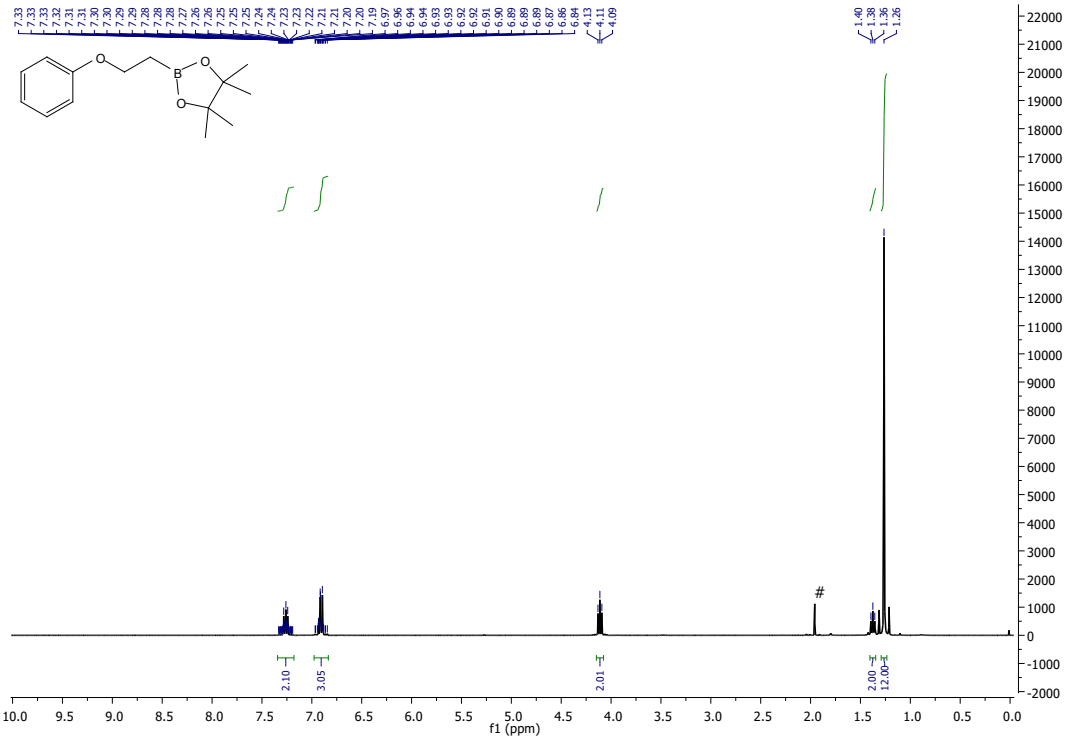


^{13}C NMR of 5b (100 MHz, $CDCl_3$)

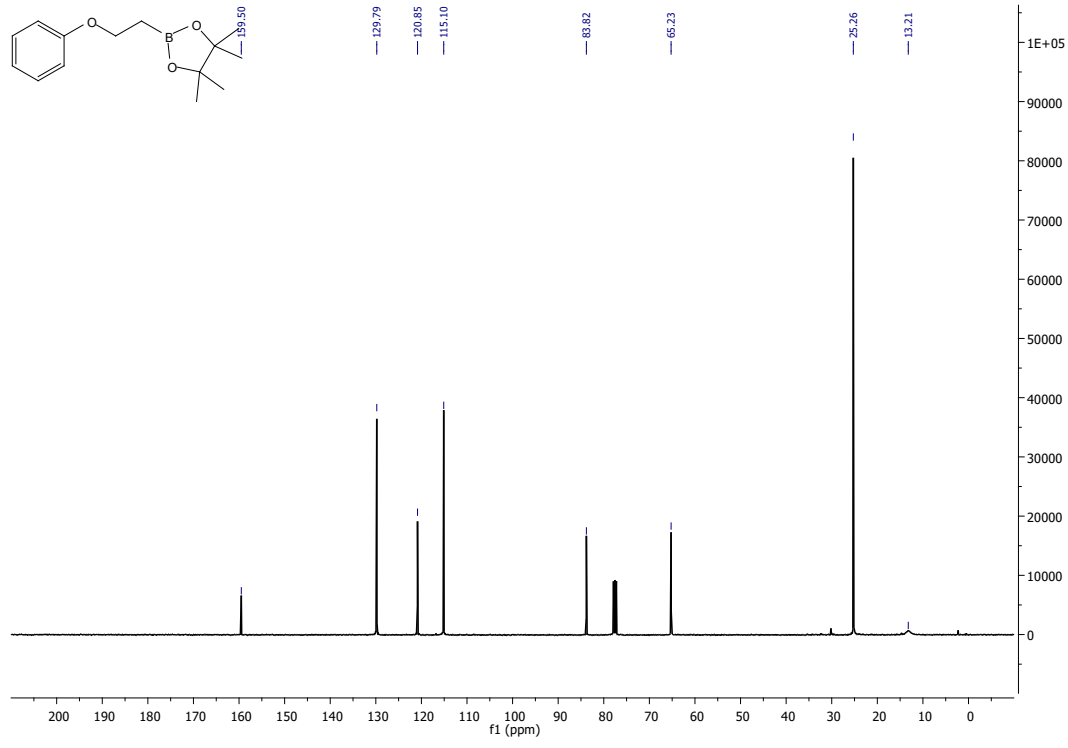


^{11}B NMR of 5b (128 MHz, $CDCl_3$)

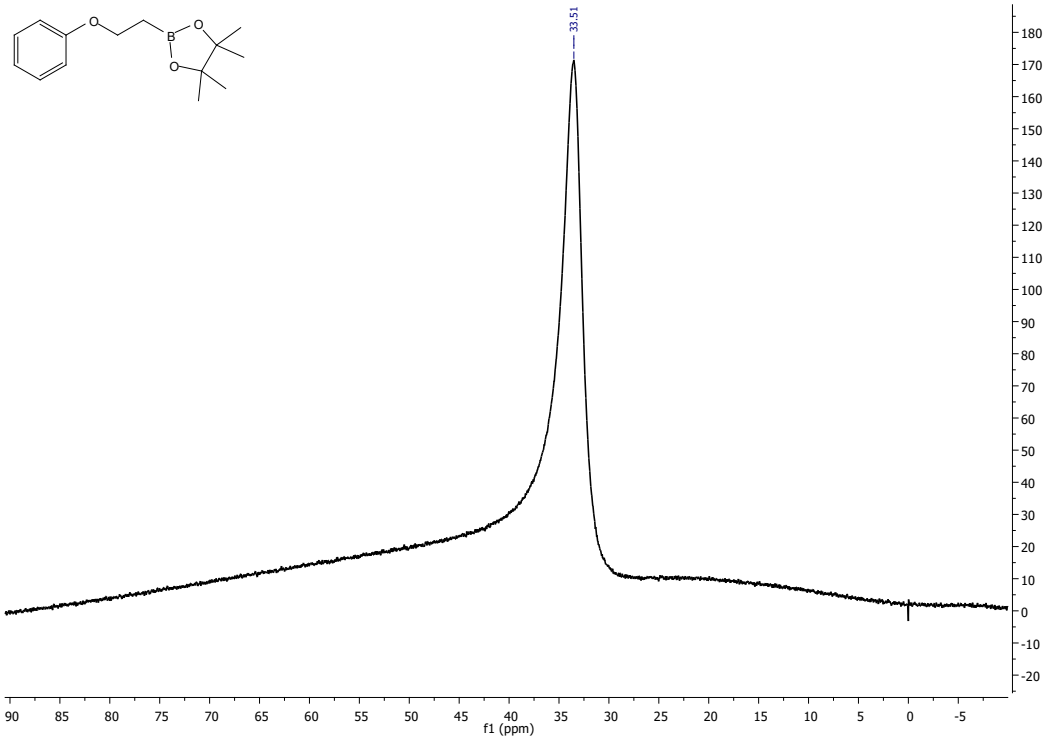
4,4,5,5-Tetramethyl-2-(2-phenoxyethyl)-1,3,2-dioxaborolane (6b)



^{1}H NMR of 6b (400 MHz, $CDCl_3$)

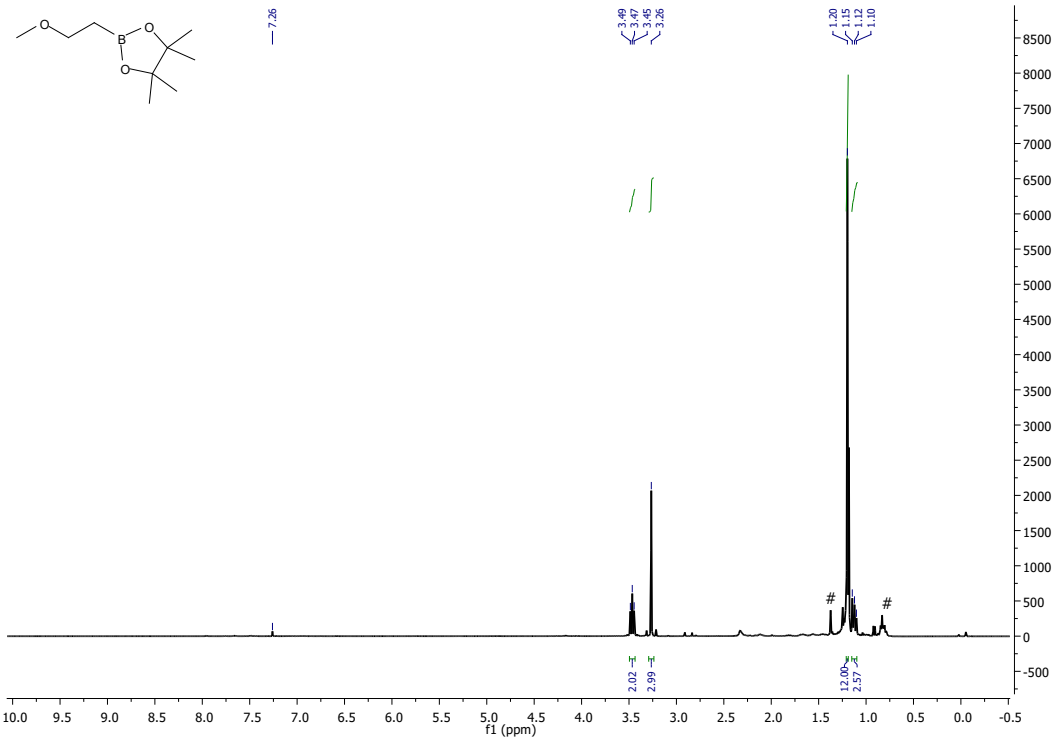


^{13}C NMR of 6b (100 MHz, $CDCl_3$)

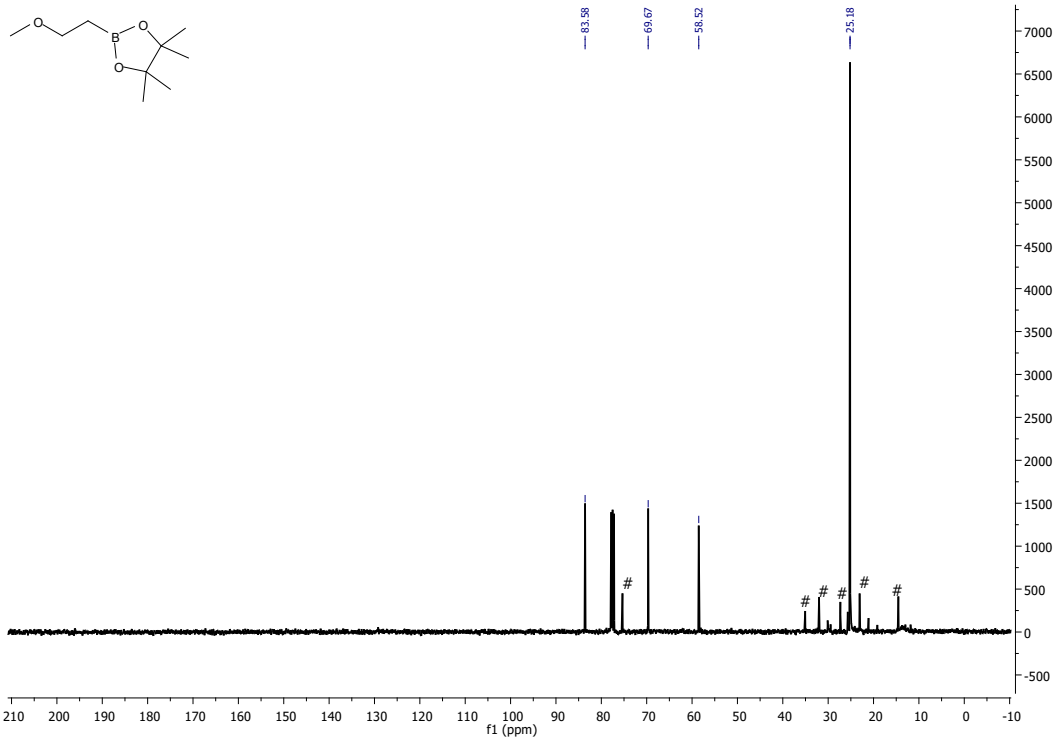


^{11}B NMR of 6b (128 MHz, $CDCl_3$)

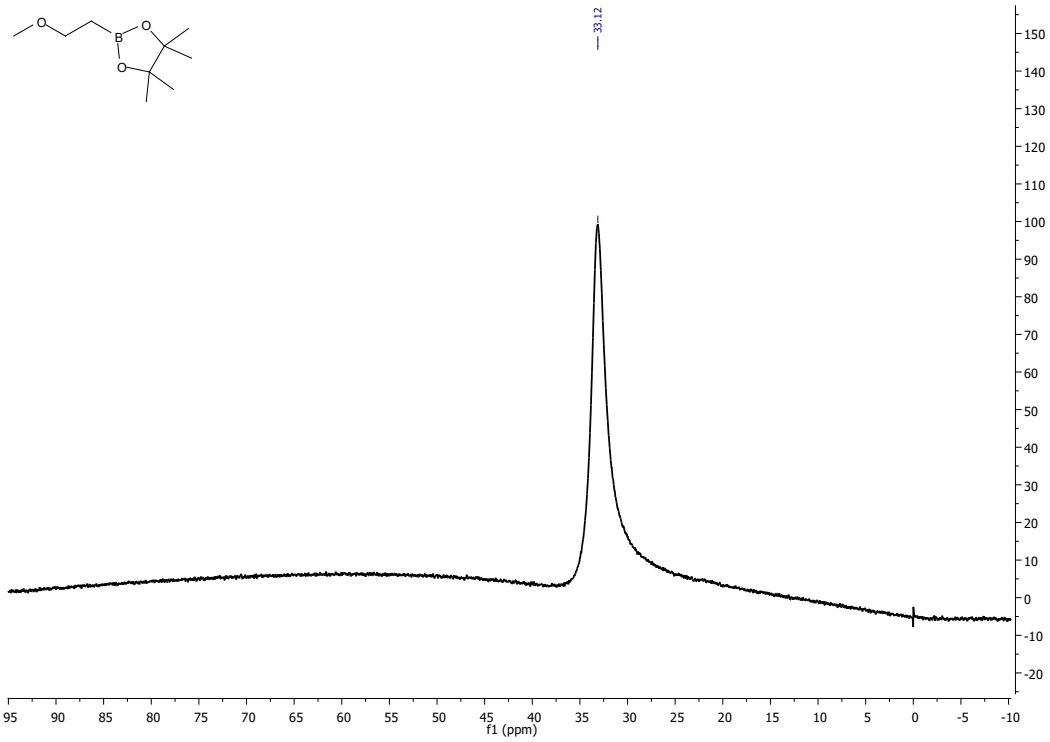
2-(2-Methoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b)



^{1}H NMR of 7b (400 MHz, $CDCl_3$)

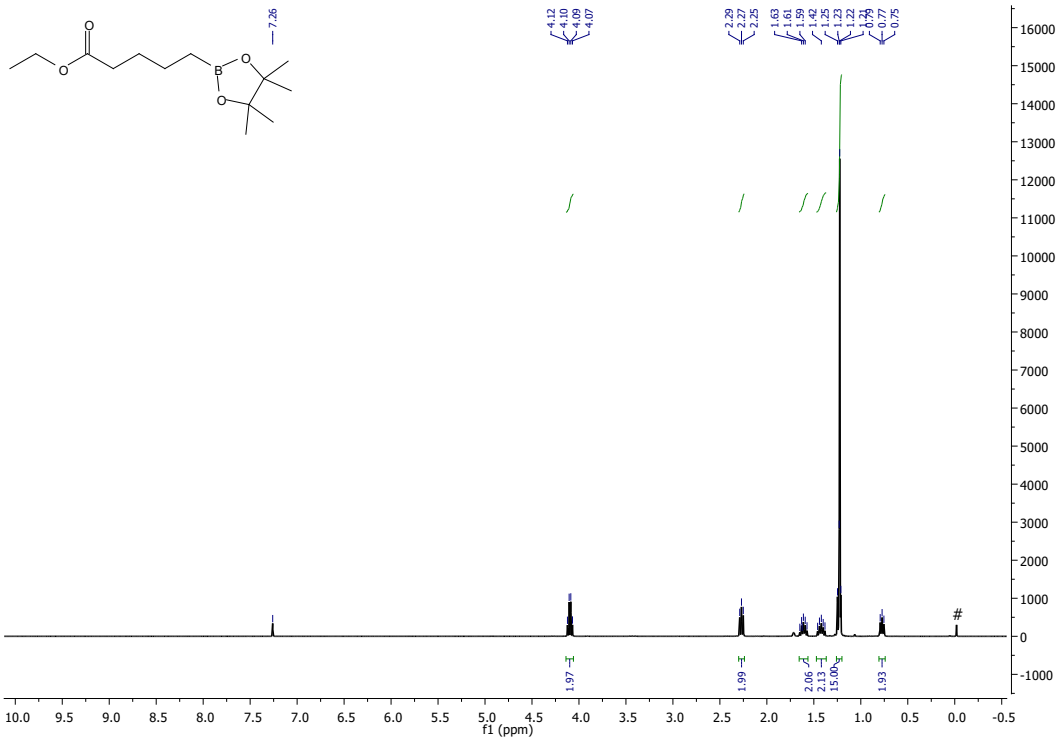


^{13}C NMR of 7b (100 MHz, $CDCl_3$)

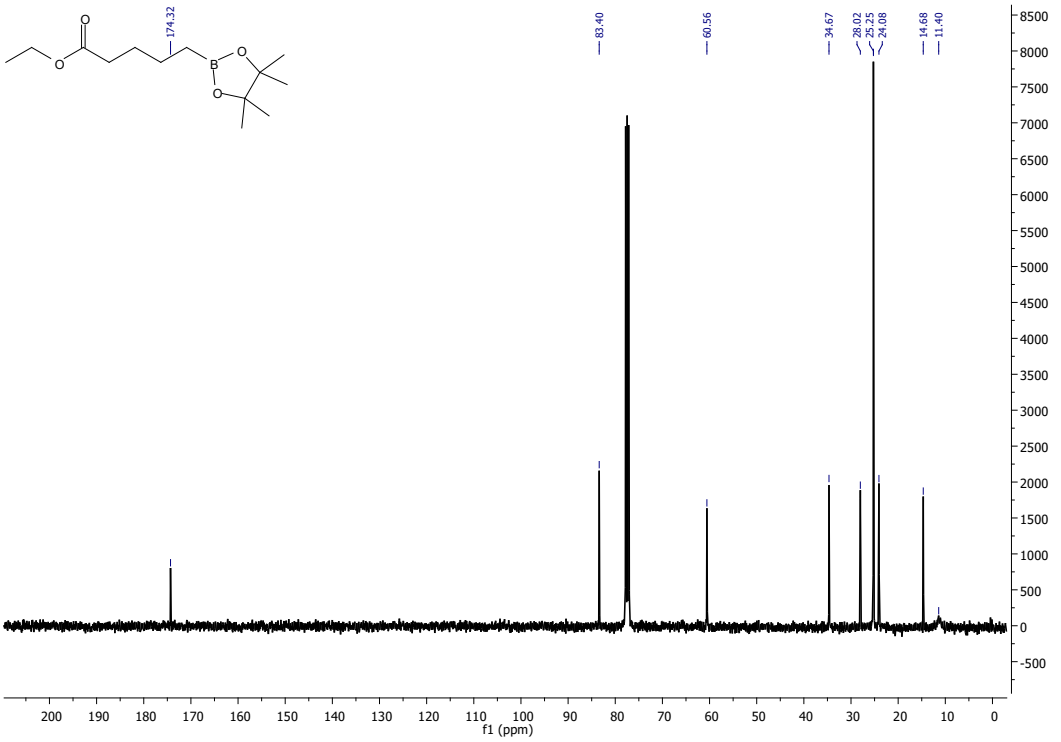


^{11}B NMR of 7b (128 MHz, $CDCl_3$)

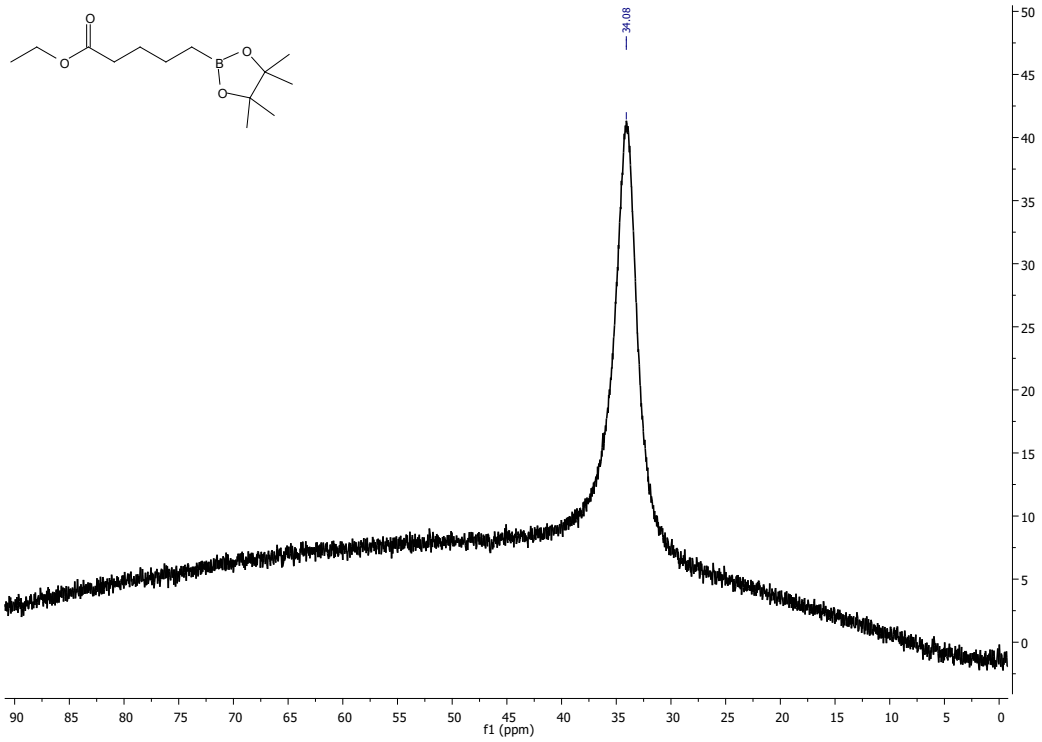
Ethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (8b)



^{1}H NMR of 8b (400 MHz, $CDCl_3$)

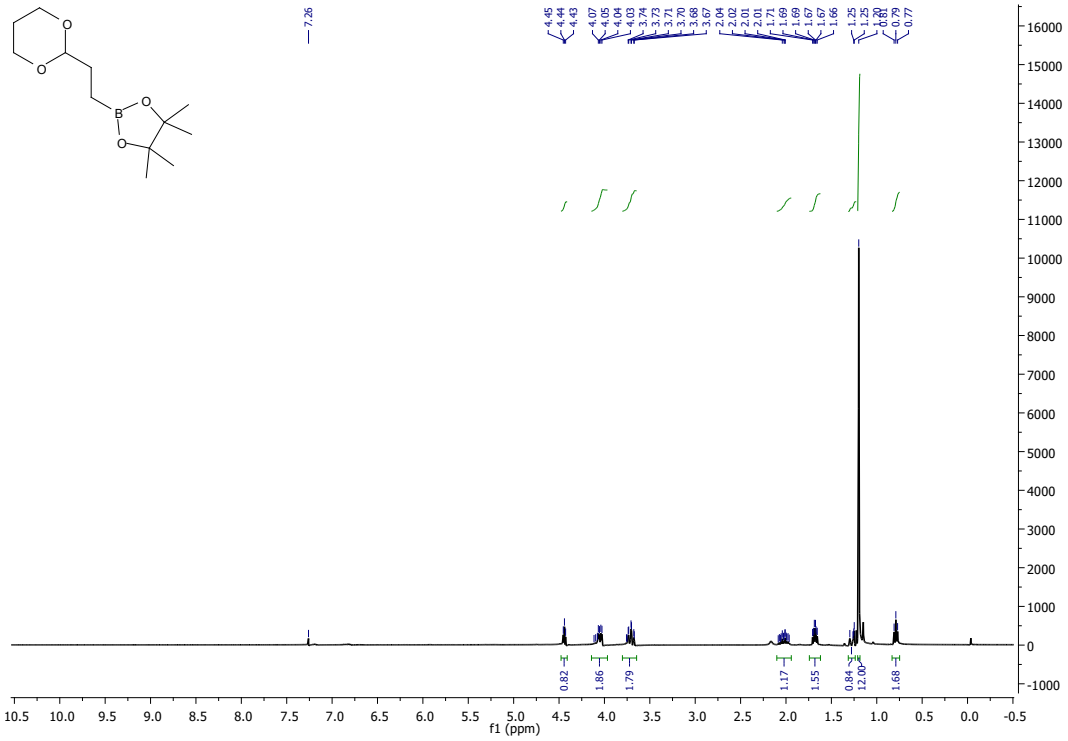


^{13}C NMR of 8b (100 MHz, $CDCl_3$)

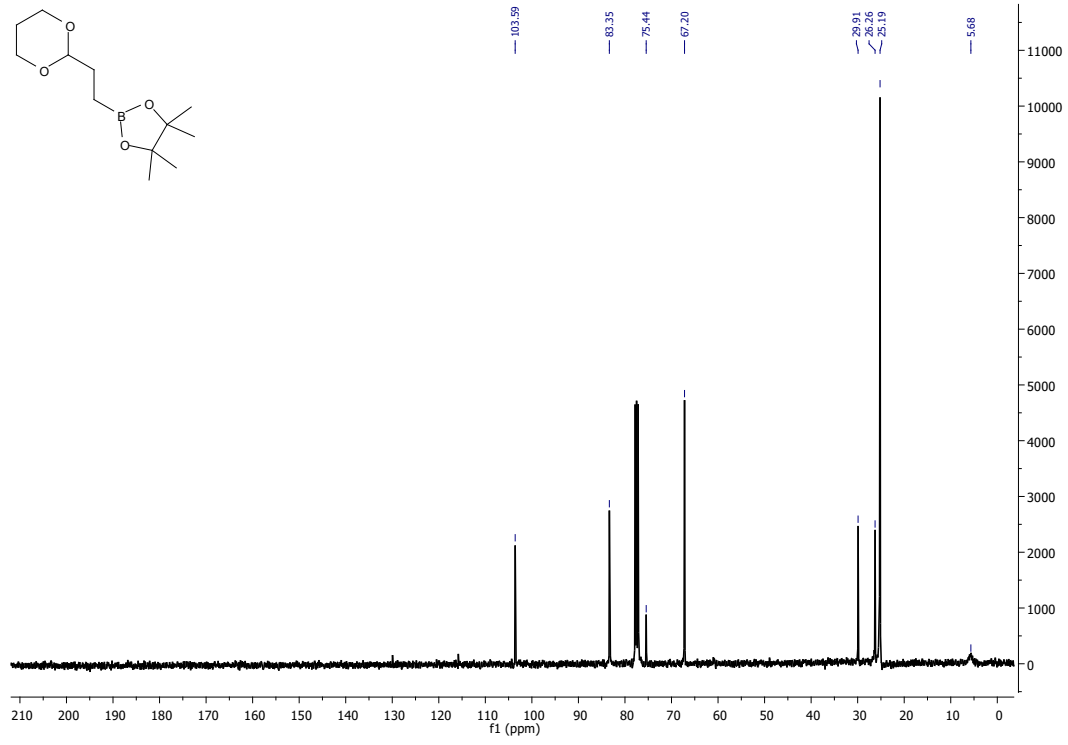


^{11}B NMR of 8b (128 MHz, $CDCl_3$)

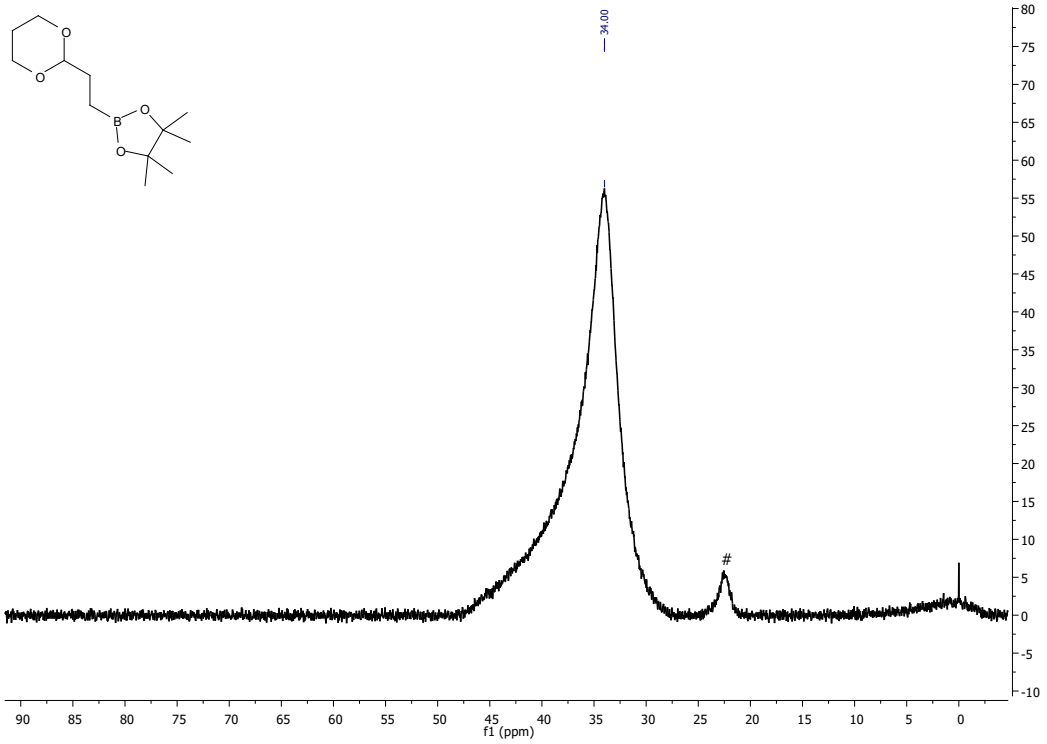
2-(2-(1,3-Dioxan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b)



^{1}H NMR of 9b (400 MHz, $CDCl_3$)

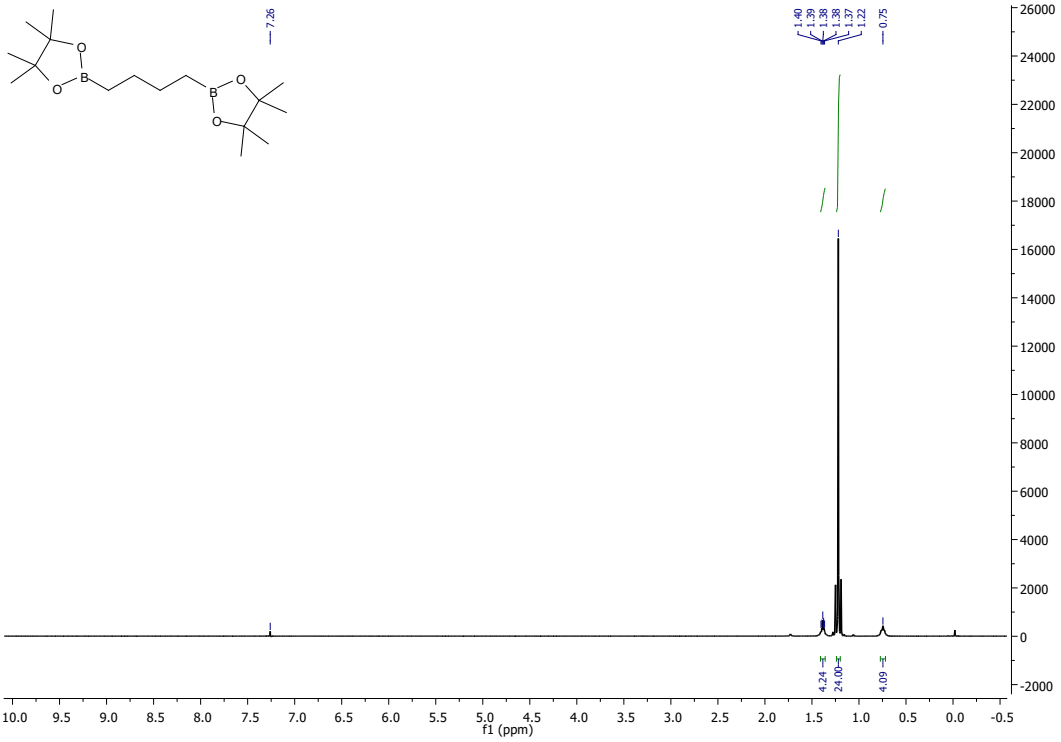


^{13}C NMR of 9b (100 MHz, $CDCl_3$)

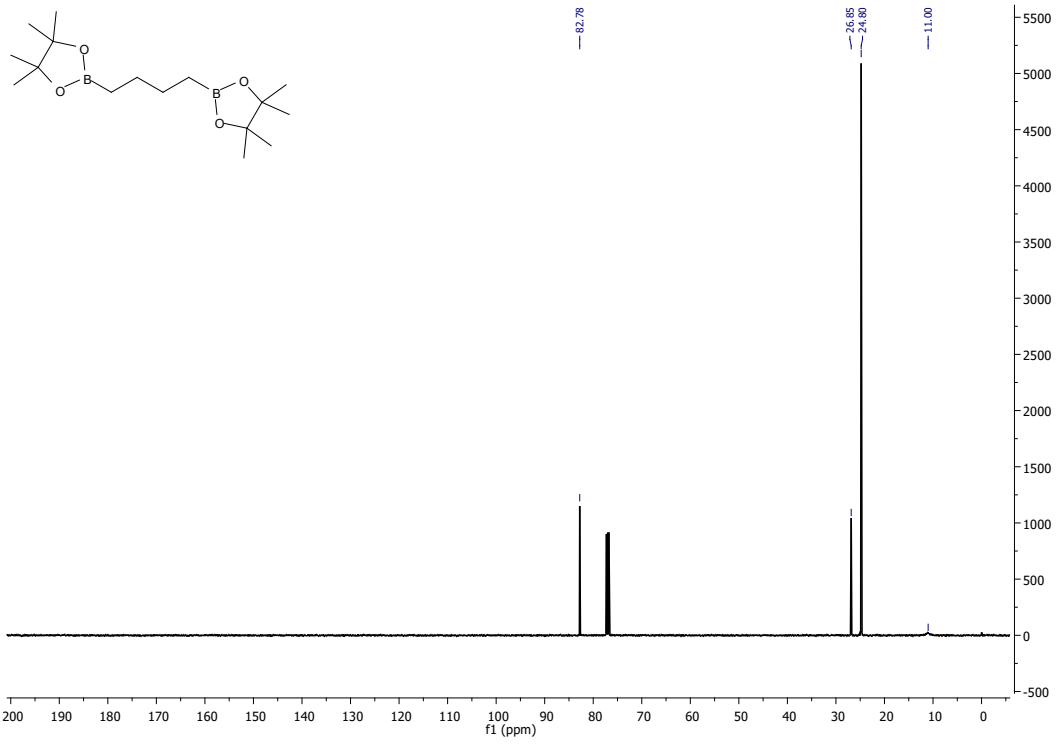


^{11}B NMR of 9b (128 MHz, $CDCl_3$)

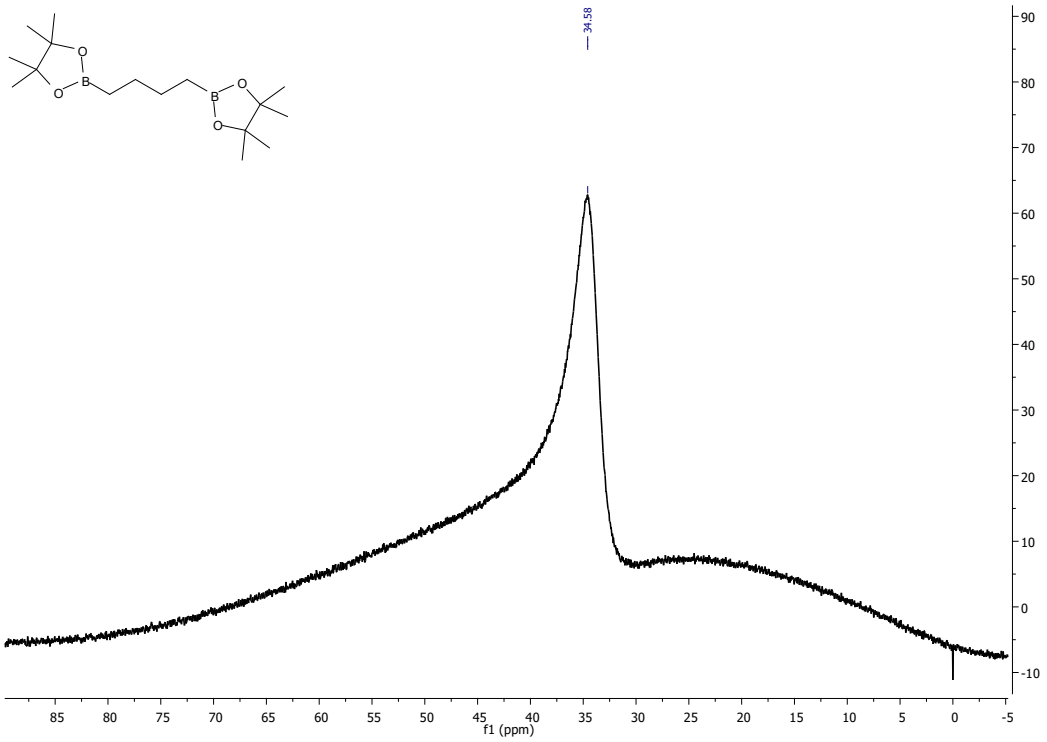
1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane (10b)



^{1}H NMR of 10b (400 MHz, $CDCl_3$)

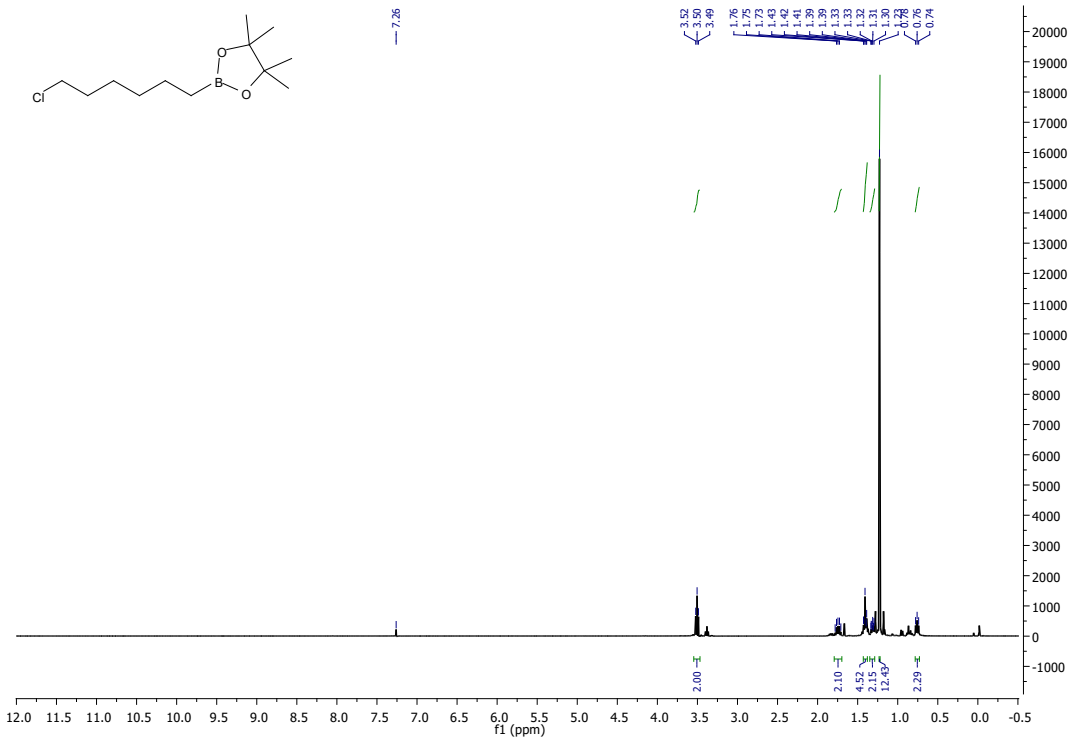


^{13}C NMR of 10b (100 MHz, $CDCl_3$)

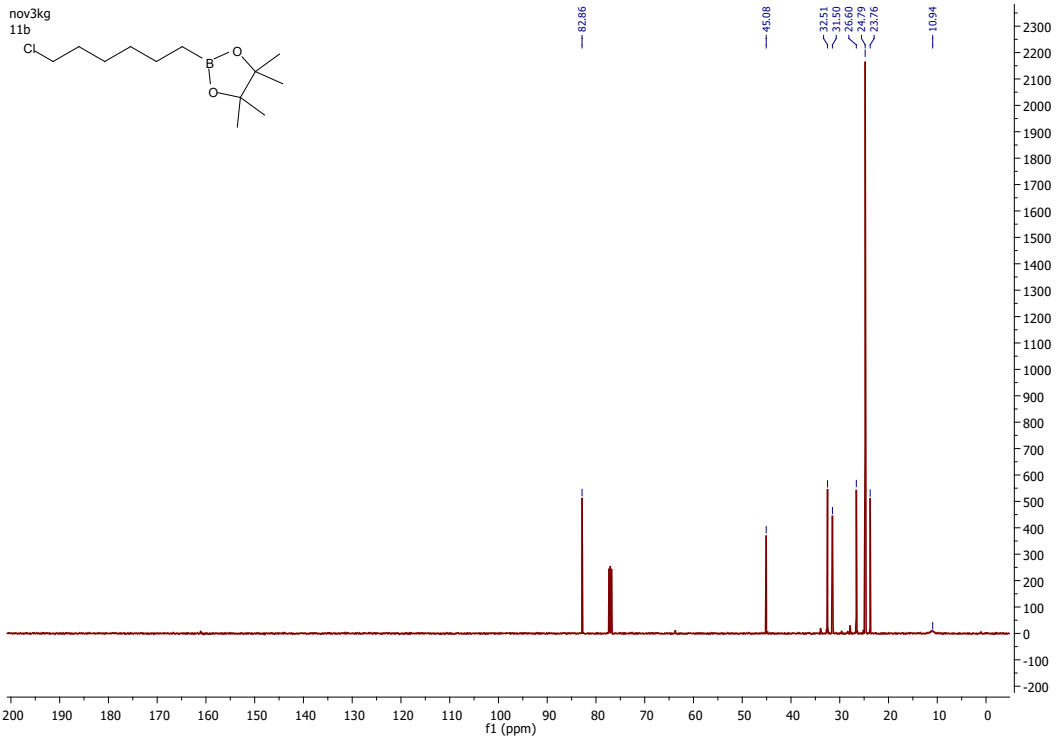


^{11}B NMR of 10b (128 MHz, $CDCl_3$)

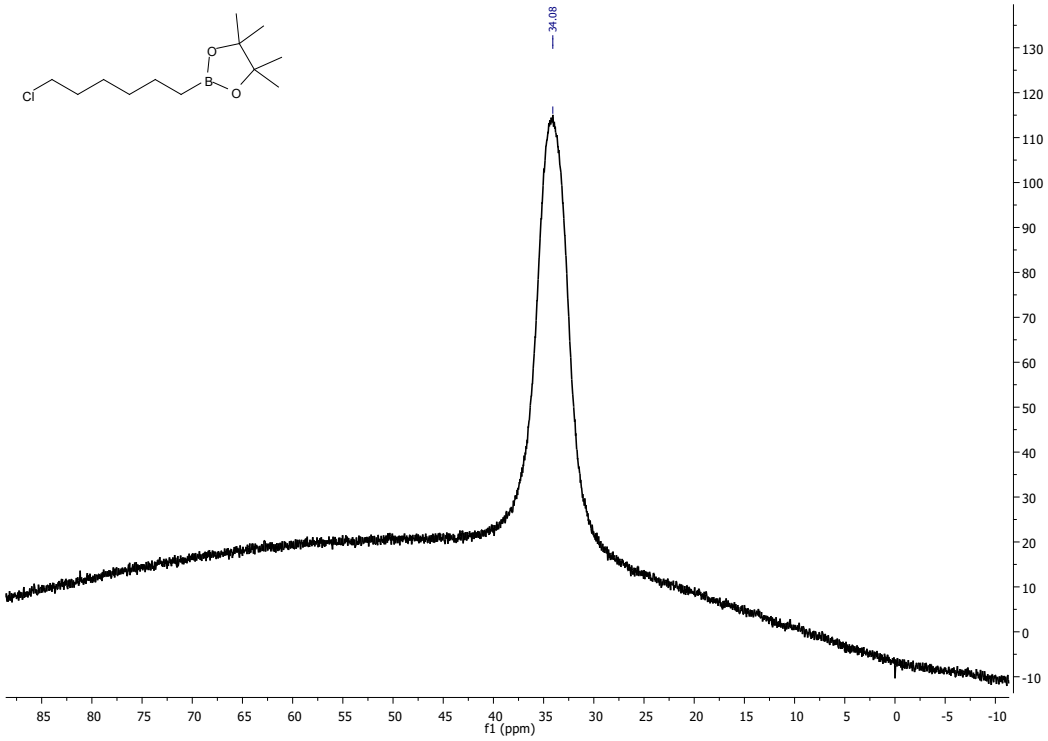
2-(6-Chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b)



^{1}H NMR of 11b (400 MHz, $CDCl_3$)

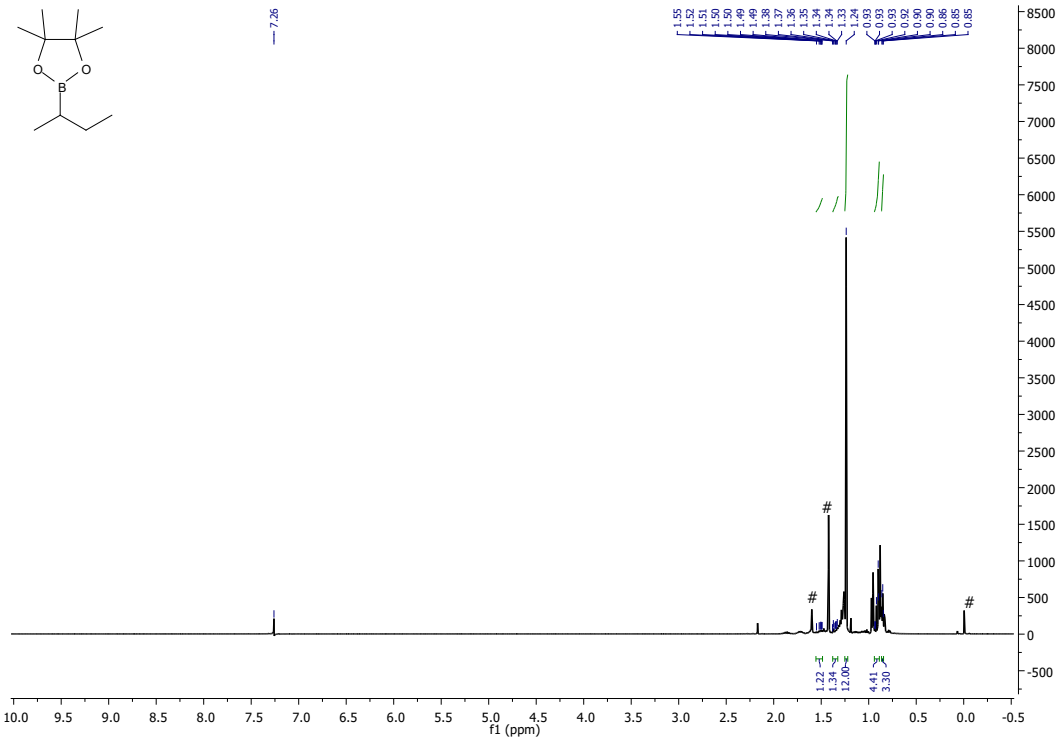


^{13}C NMR of 11b (125 MHz, $CDCl_3$)

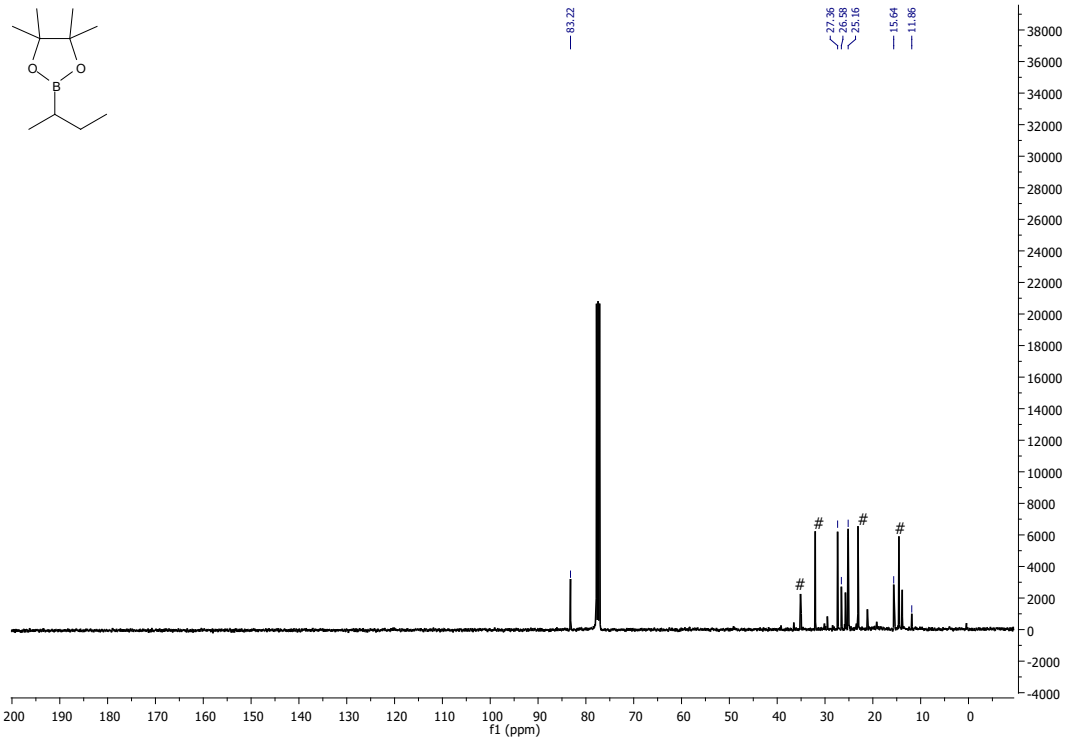


^{11}B NMR of 11b (128 MHz, $CDCl_3$)

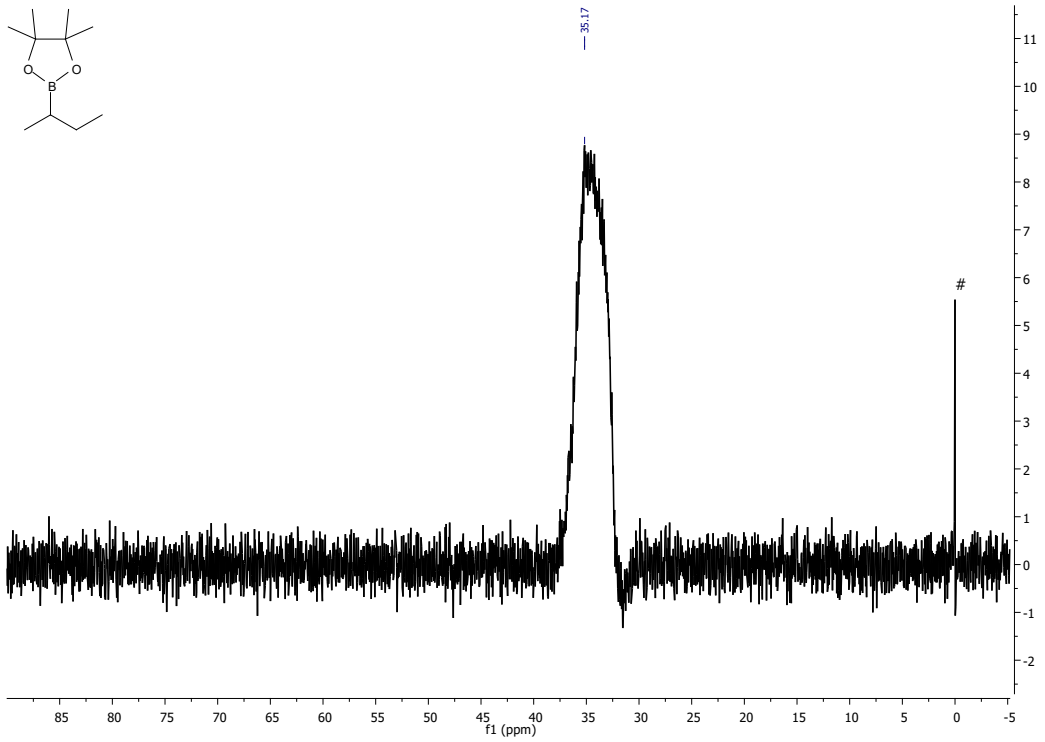
2-(sec-Butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b)



^{1}H NMR of 12b (400 MHz, $CDCl_3$)

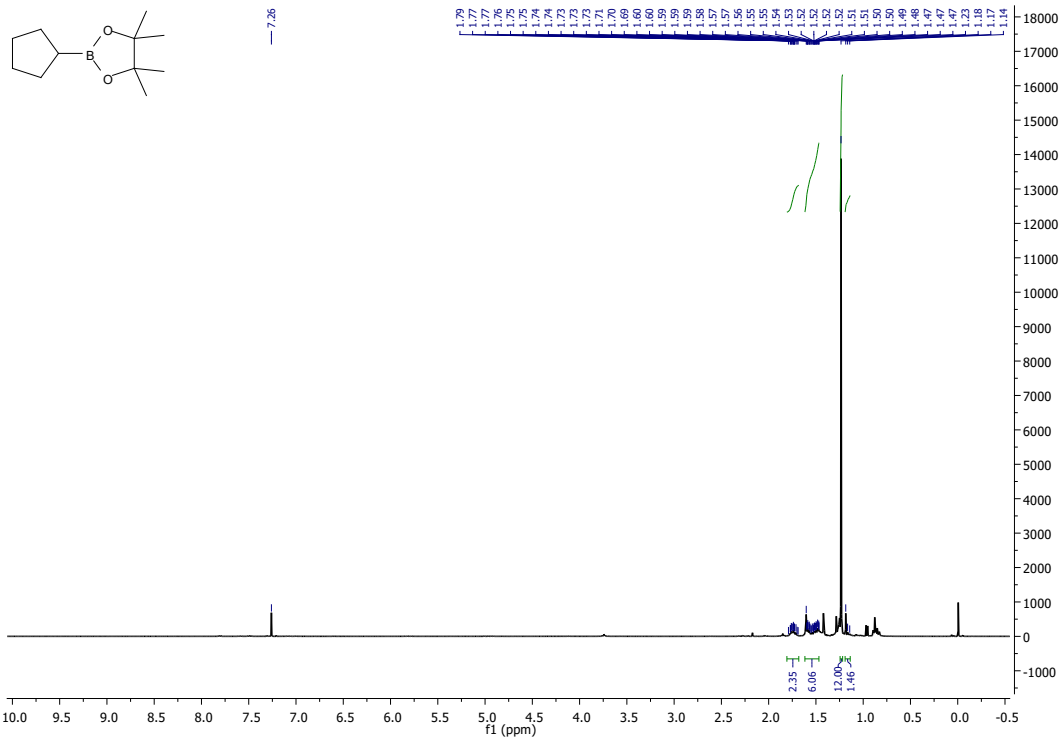


^{13}C NMR of 12b (100 MHz, $CDCl_3$)

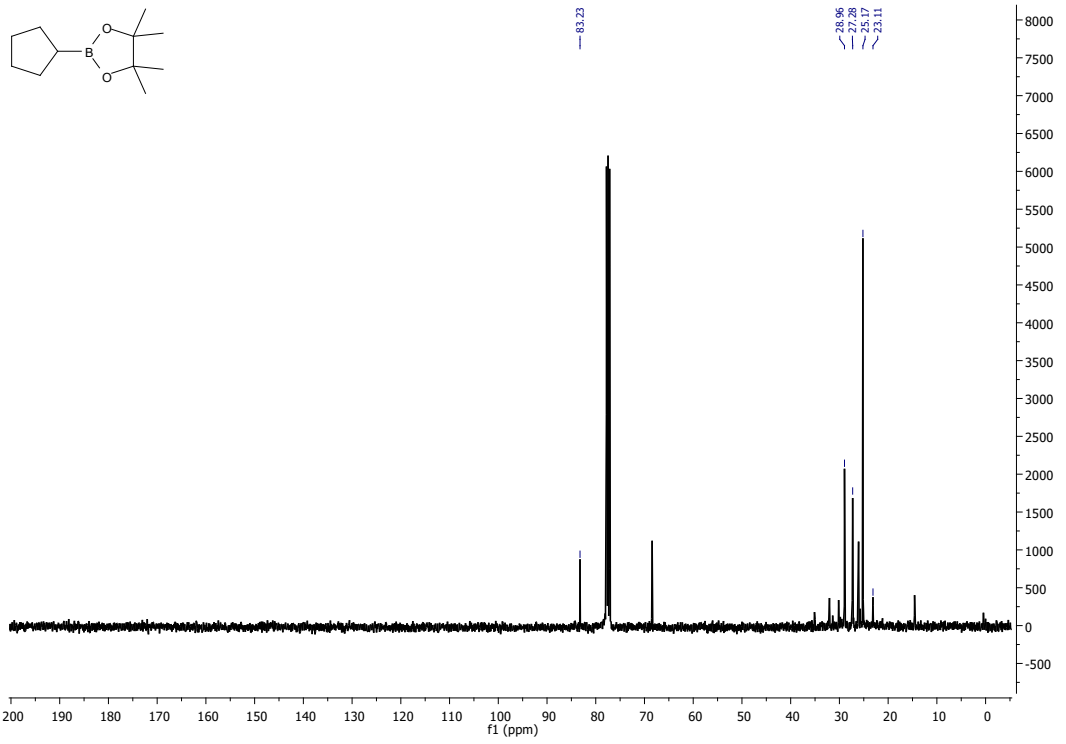


^{11}B NMR of 12b (128 MHz, $CDCl_3$)

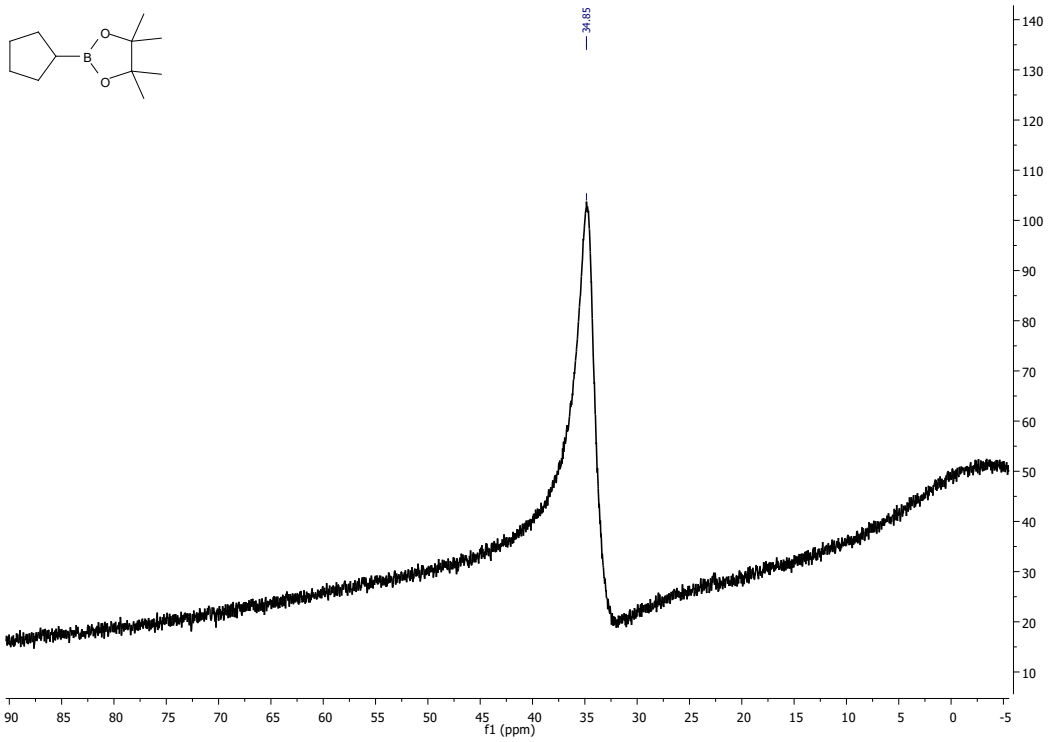
2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b)



^{1}H NMR of 13b (400 MHz, $CDCl_3$)

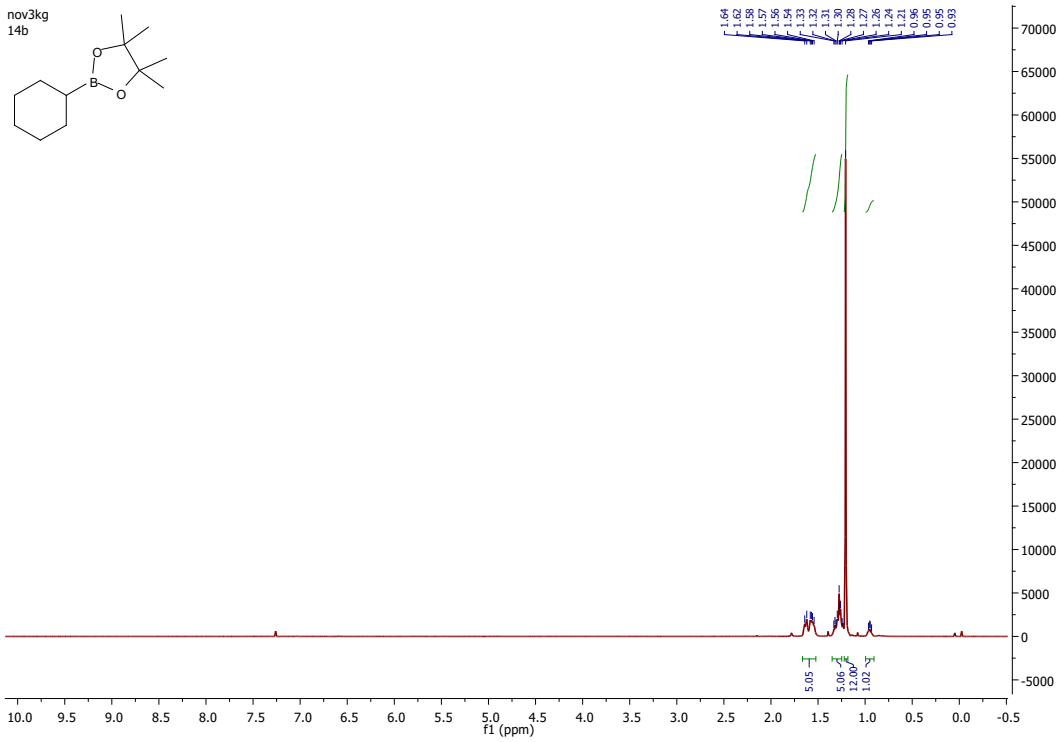


^{13}C NMR of 13b (100 MHz, $CDCl_3$)

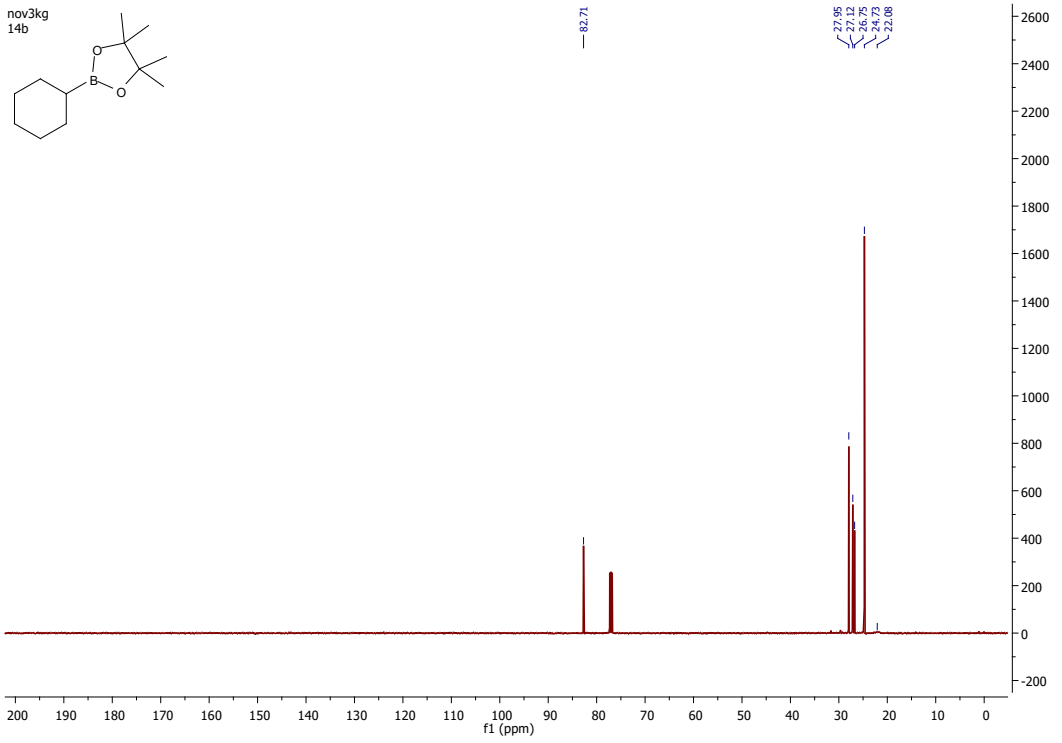


^{11}B NMR of 13b (128 MHz, $CDCl_3$)

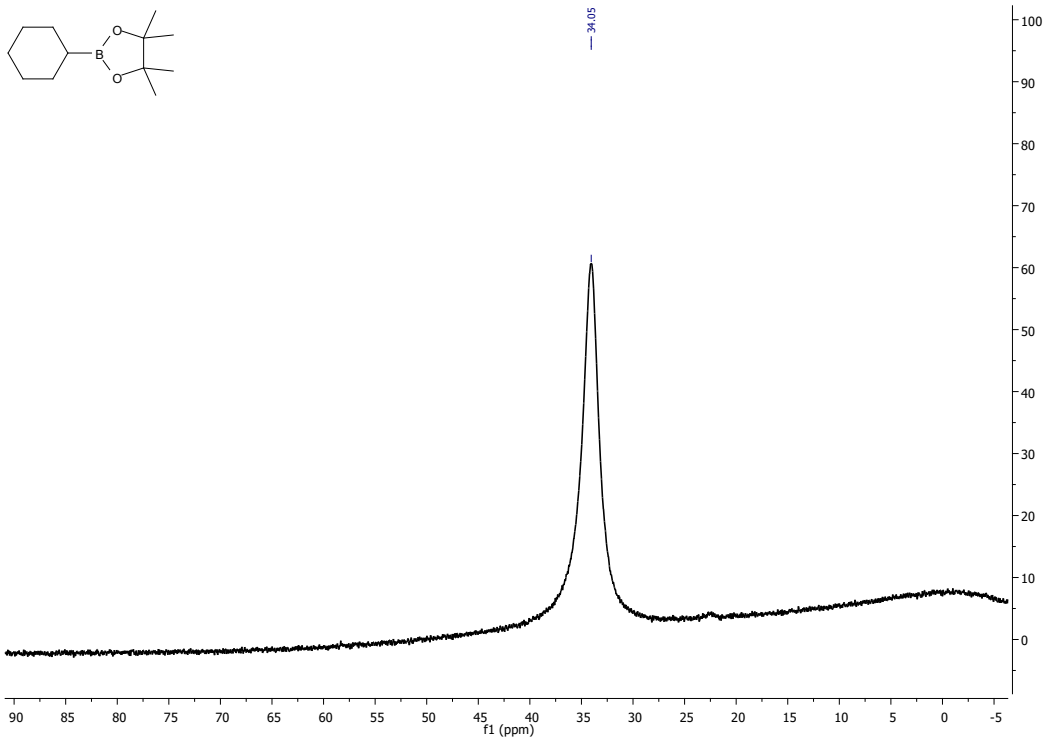
2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14b)



^{1}H NMR of 14b (500 MHz, $CDCl_3$)

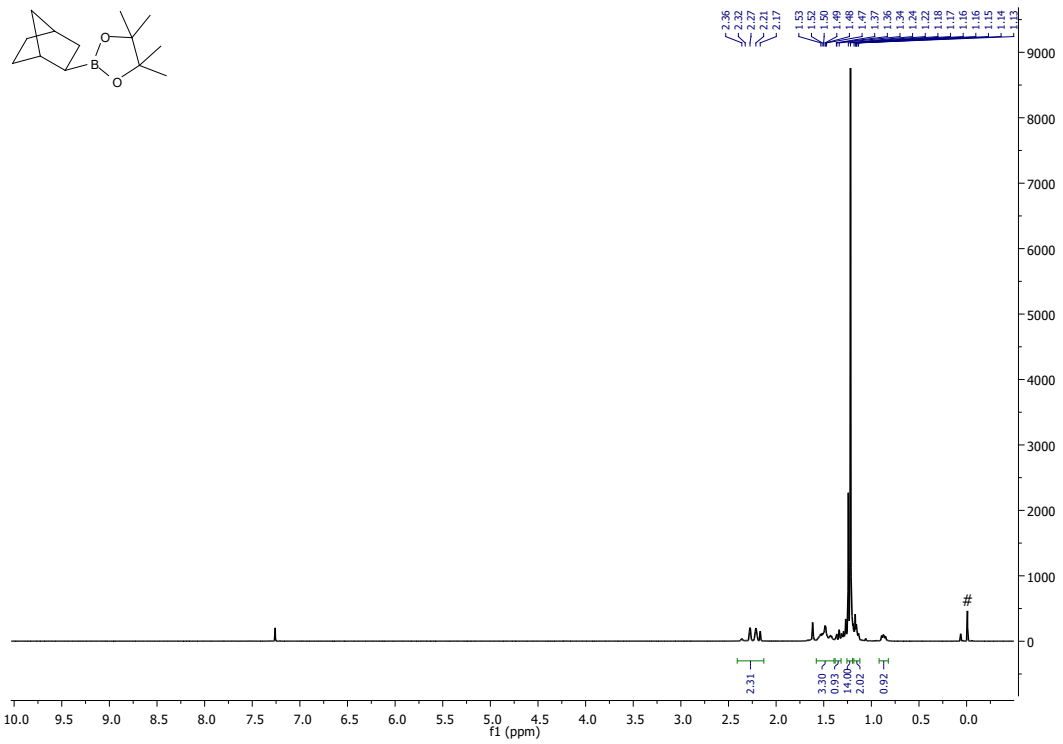


^{13}C NMR of 14b (125 MHz, $CDCl_3$)

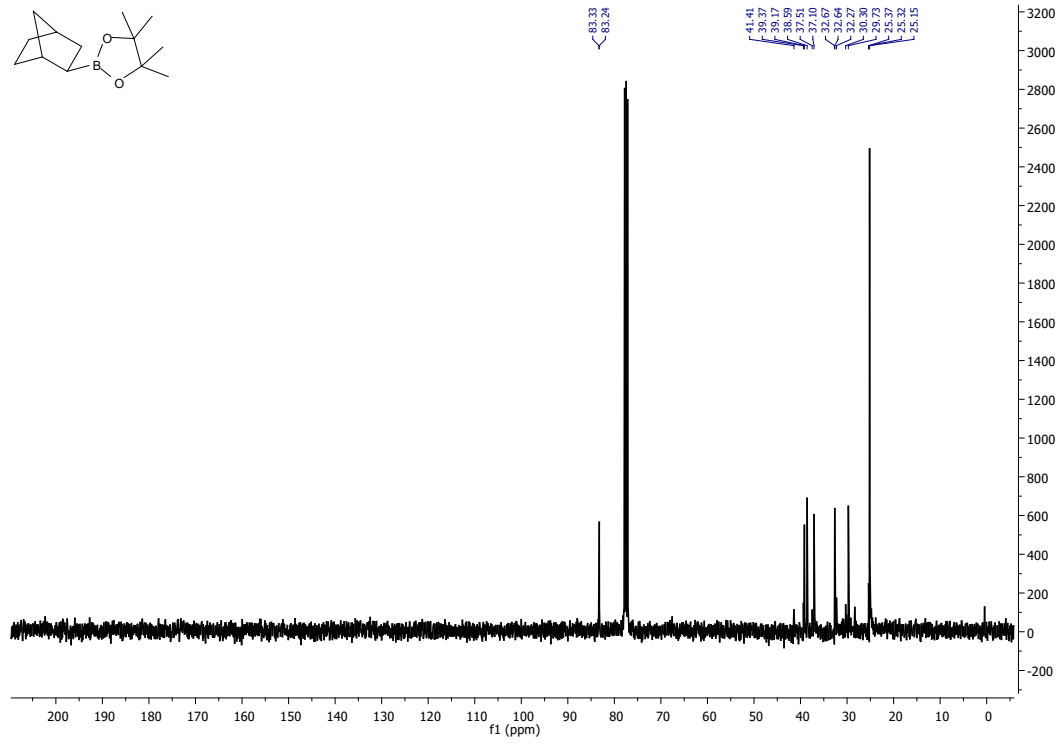


^{11}B NMR of 14b (128 MHz, $CDCl_3$)

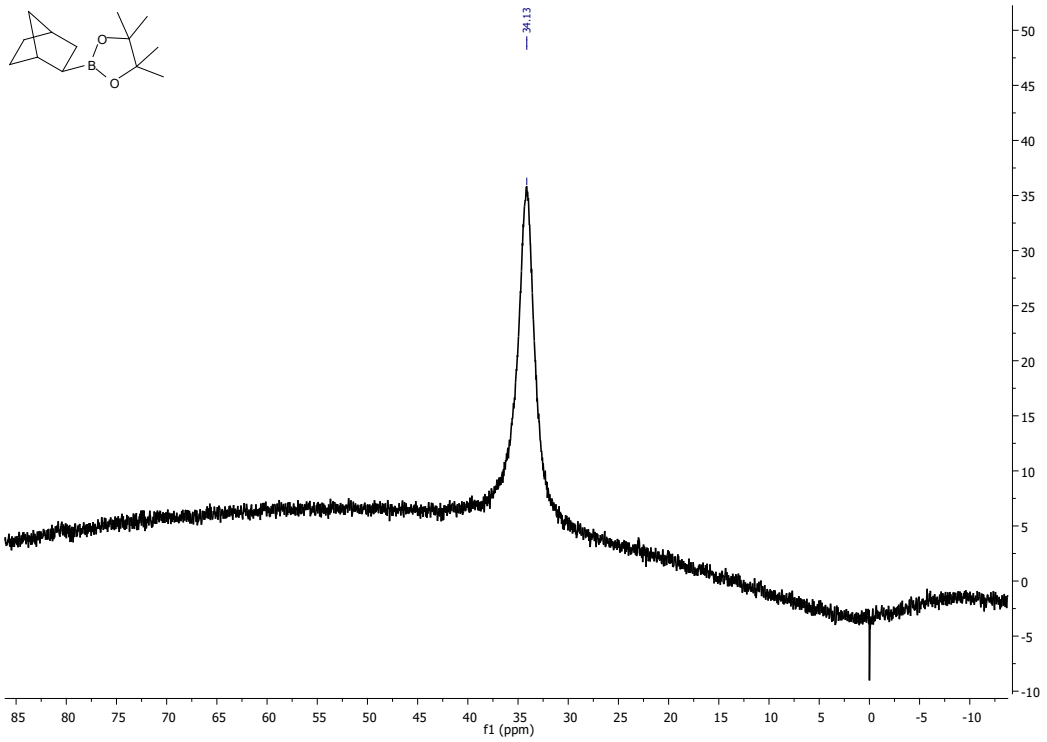
***exo*-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b)**



^{1}H NMR of 15b (400 MHz, $CDCl_3$)

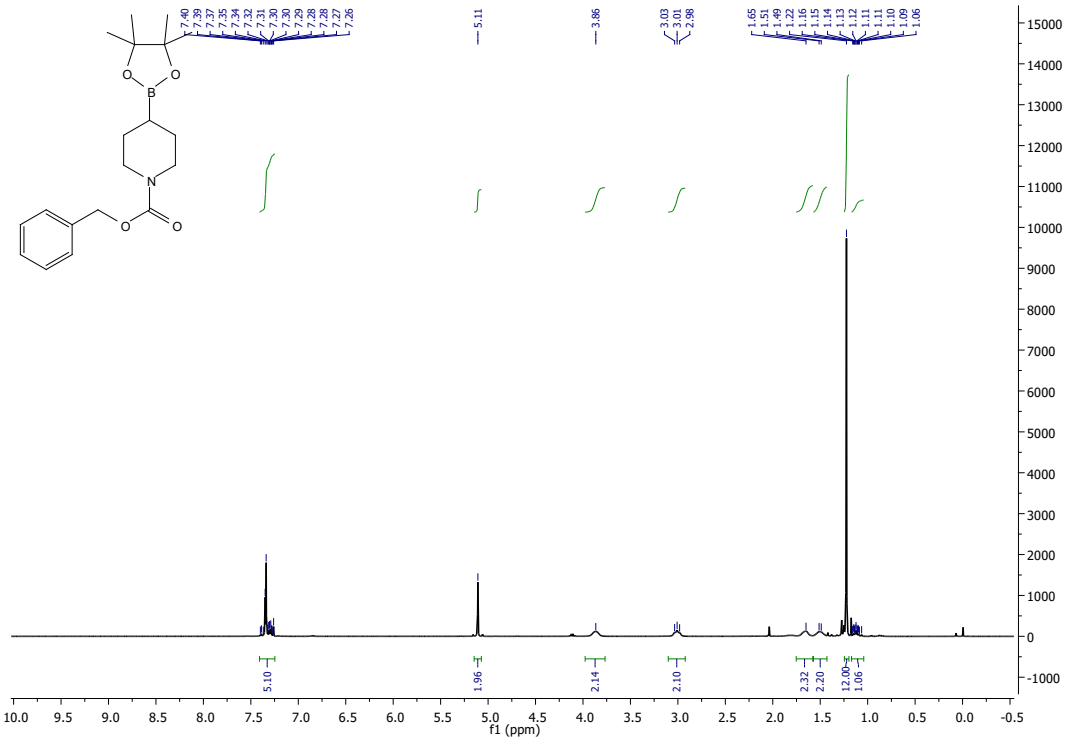


^{13}C NMR of 15b (100 MHz, $CDCl_3$)

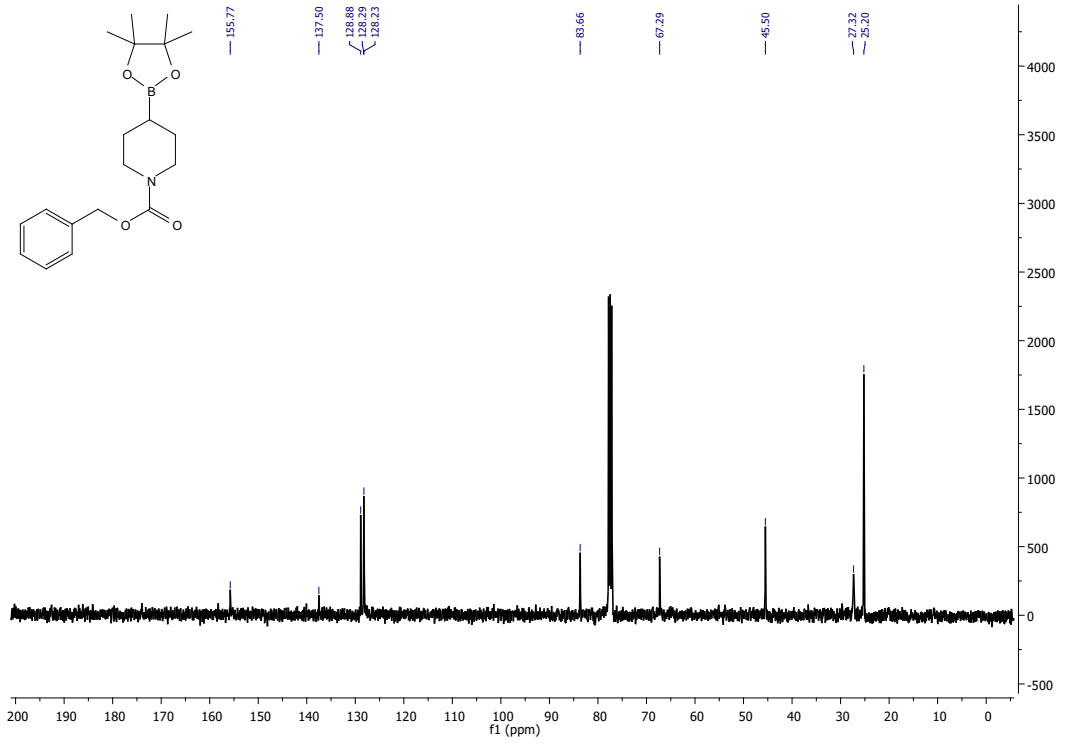


^{11}B NMR of 15b (128 MHz, $CDCl_3$)

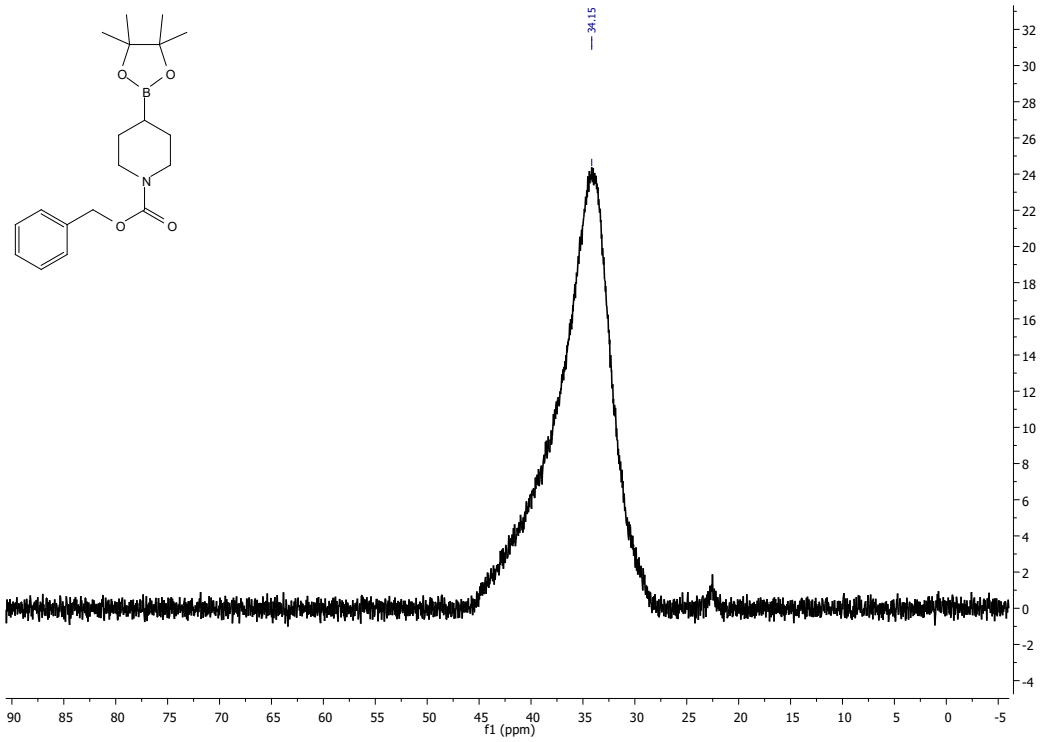
Benzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (16b)



^{1}H NMR of 16b (400 MHz, $CDCl_3$)

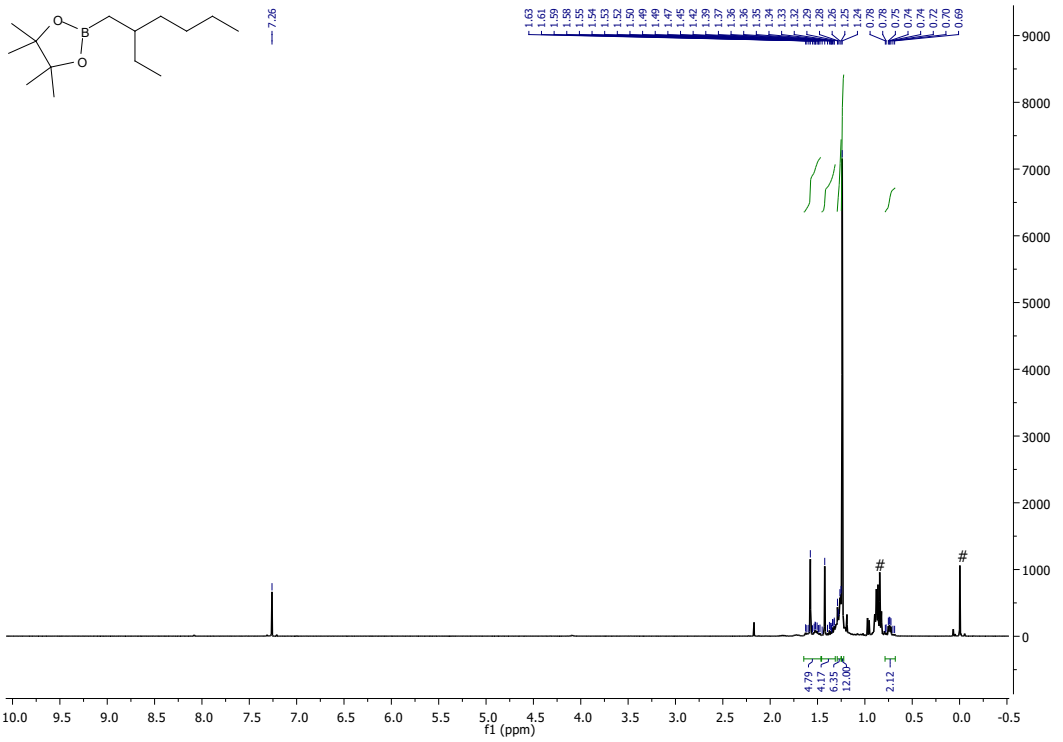


^{13}C NMR of 16b (100 MHz, $CDCl_3$)

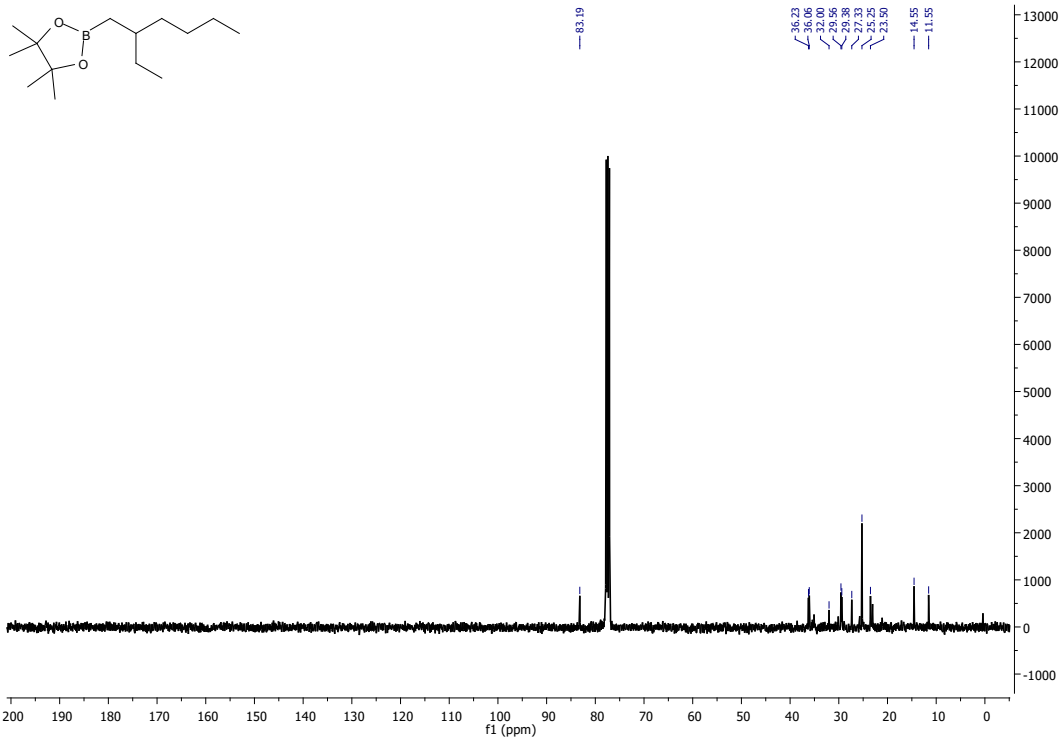


^{11}B NMR of 16b (128 MHz, $CDCl_3$)

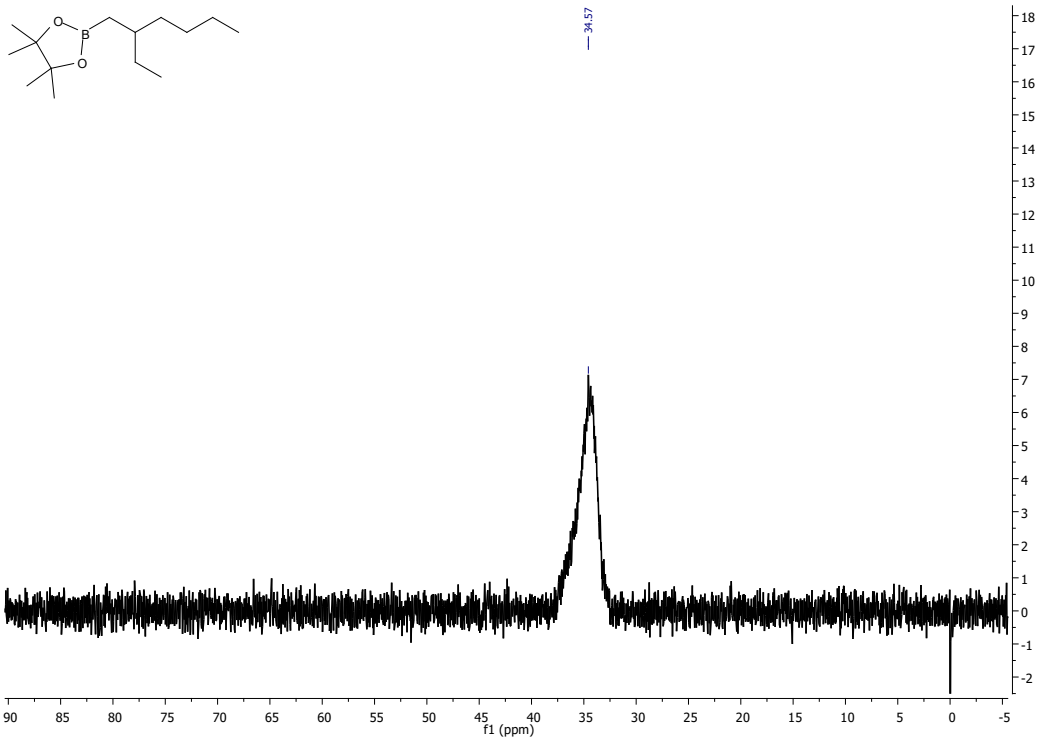
2-(2-Ethylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)



^{1}H NMR of 18b (400 MHz, $CDCl_3$)

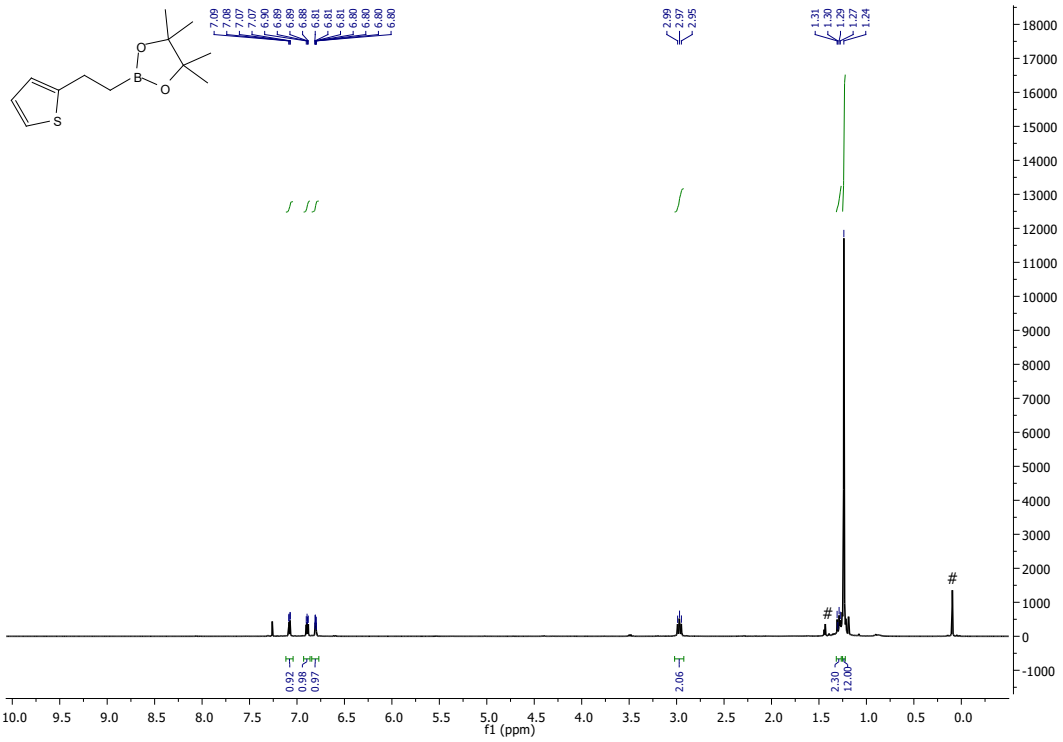


^{13}C NMR of 18b (100 MHz, $CDCl_3$)

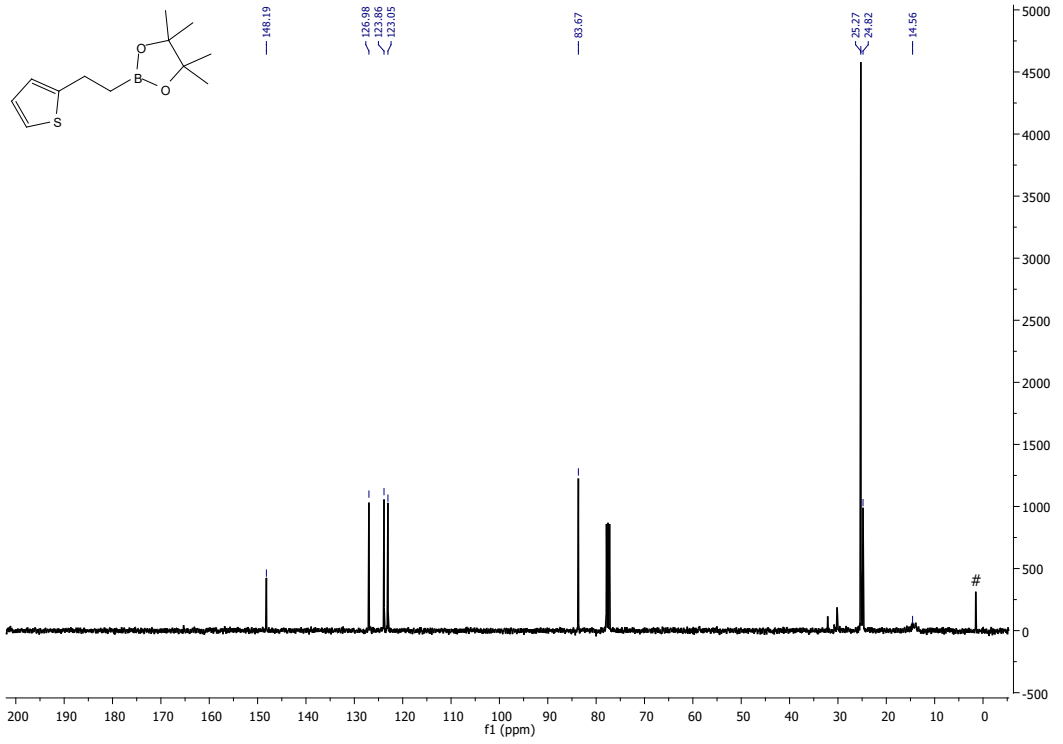


^{11}B NMR of 18b (128 MHz, $CDCl_3$)

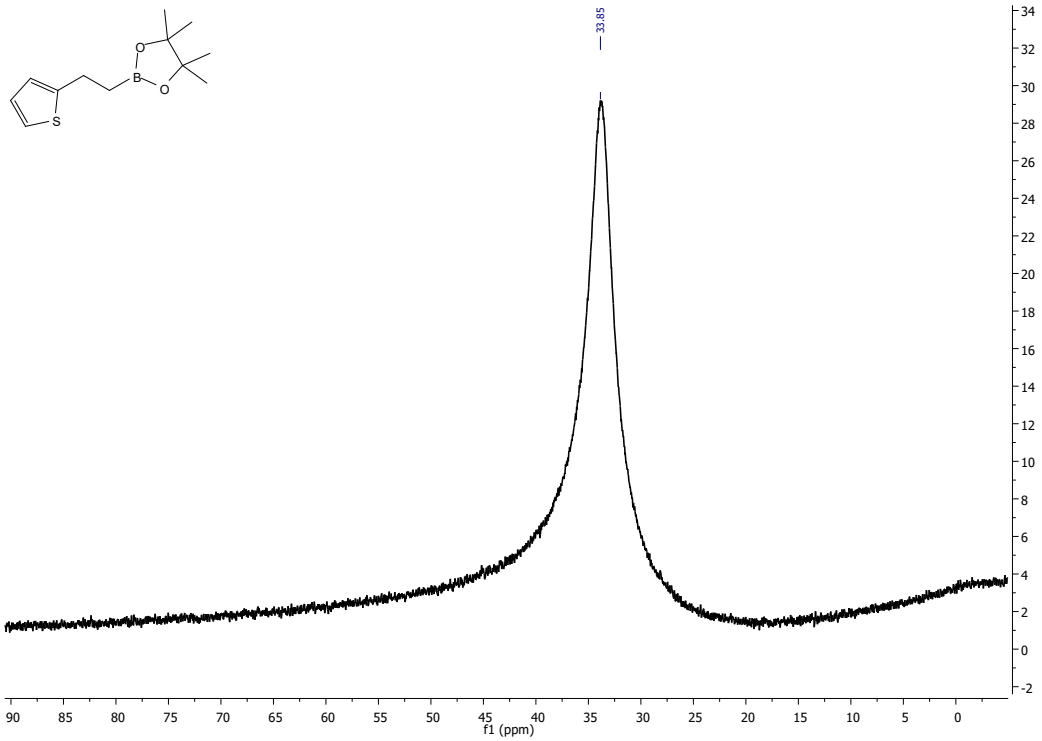
4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (19b)



^{1}H NMR of 19b (400 MHz, $CDCl_3$)

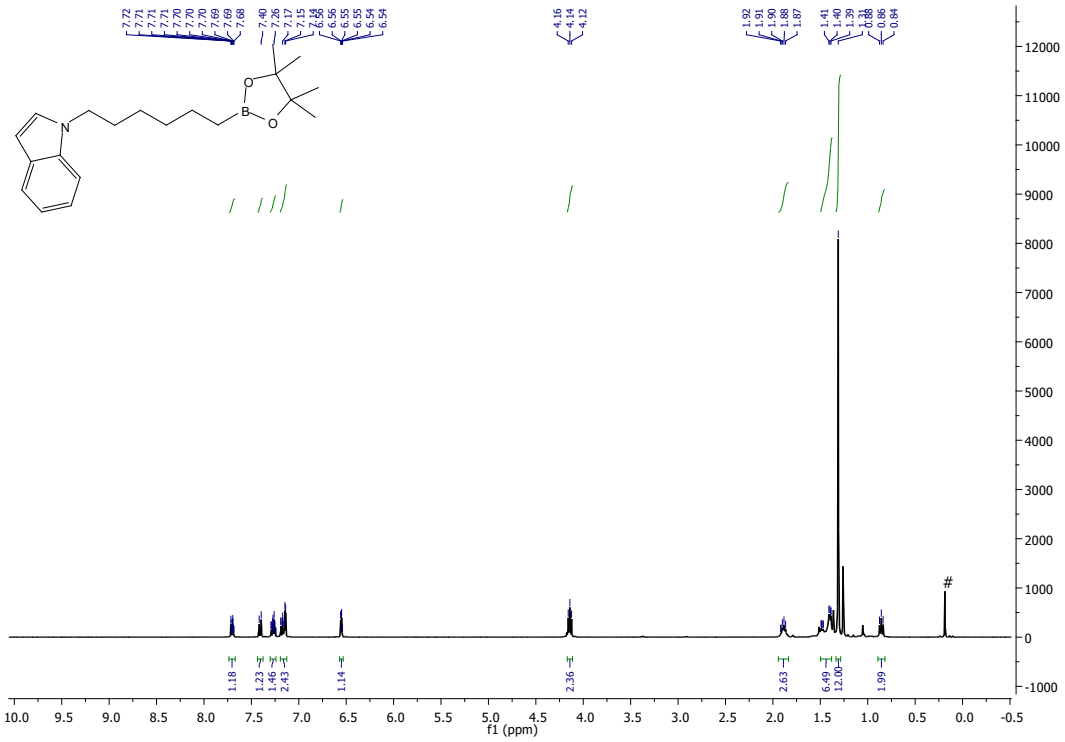


^{13}C NMR of 19b (100 MHz, $CDCl_3$)

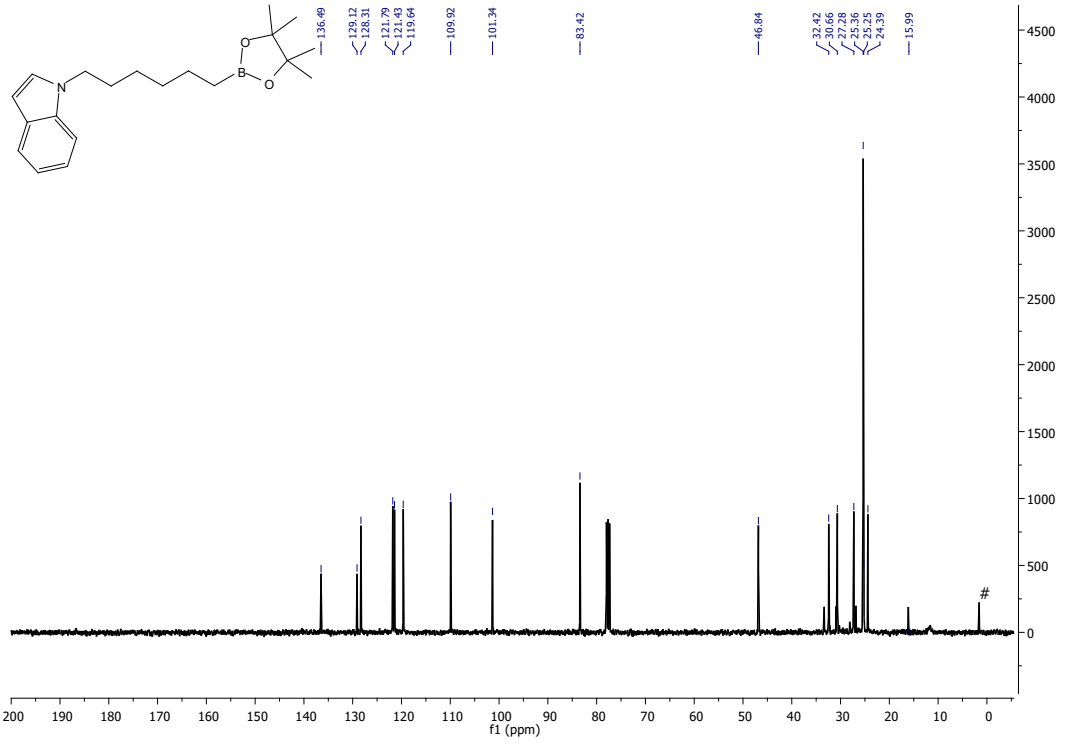


^{11}B NMR of 19b (128 MHz, $CDCl_3$)

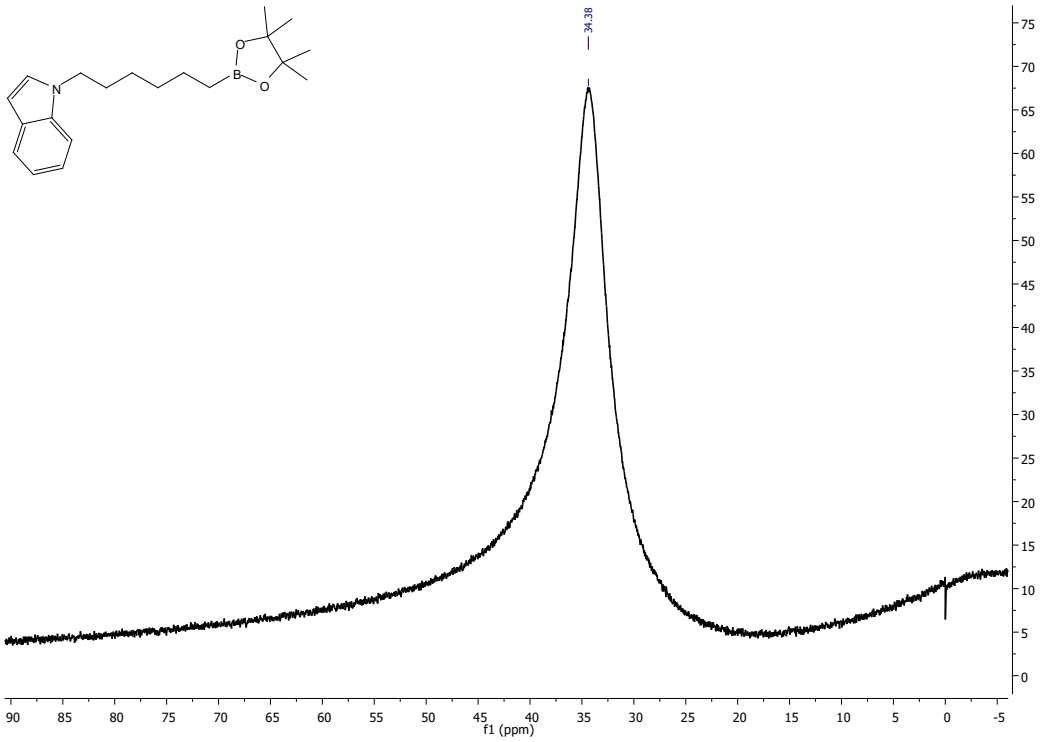
1-(6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1H-indole (20b)



^{1}H NMR of 20b (400 MHz, $CDCl_3$)

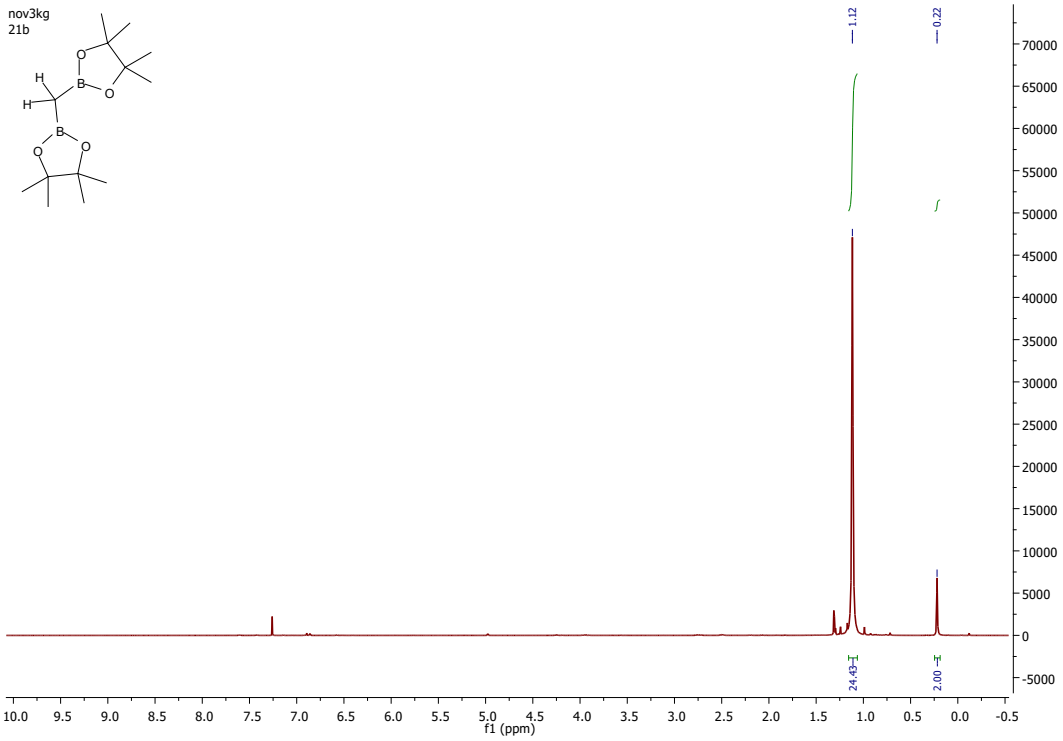


^{13}C NMR of 20b (100 MHz, $CDCl_3$)

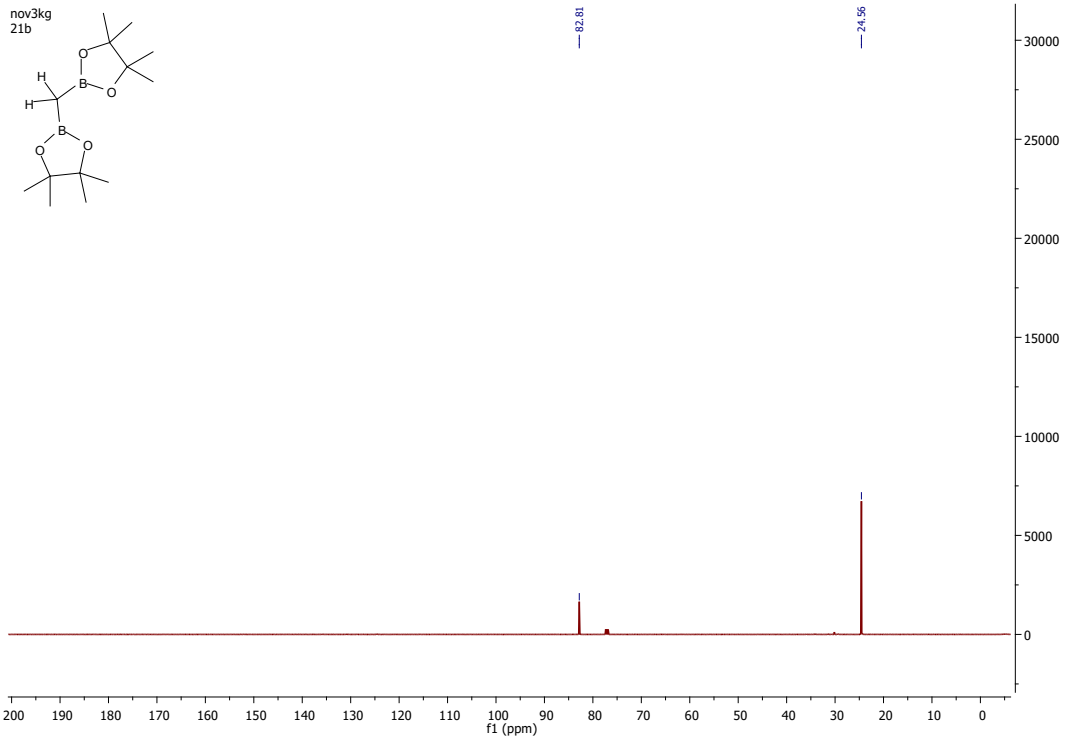


^{11}B NMR of 20b (128 MHz, $CDCl_3$)

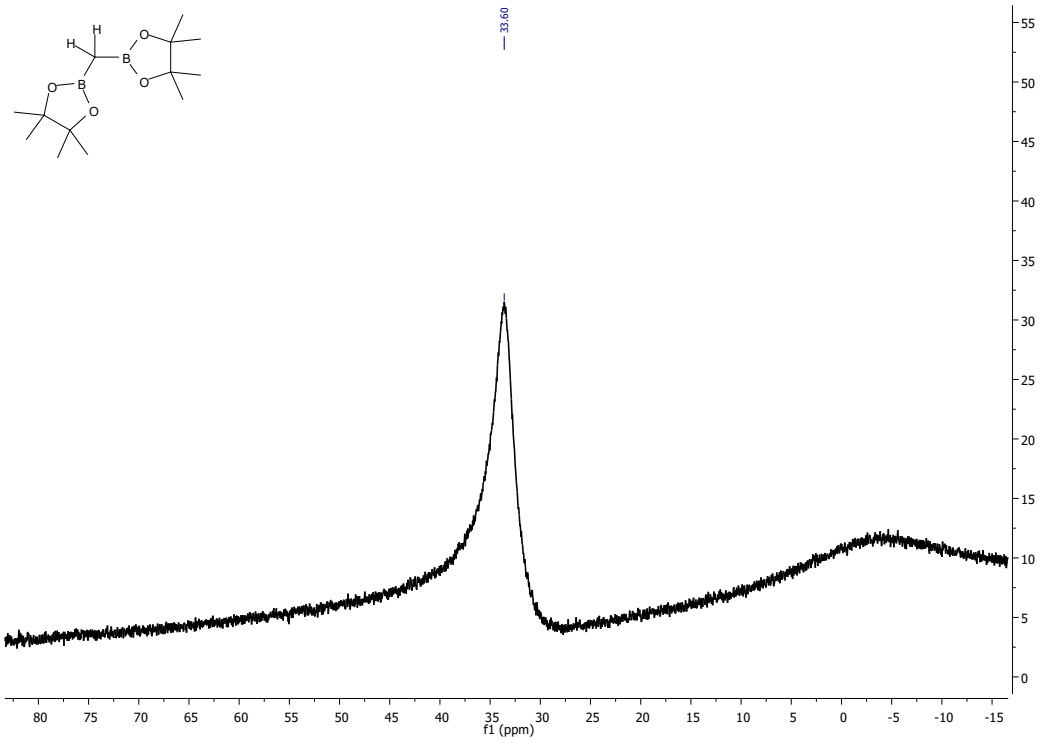
2,2'-(Propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (21b)



^{1}H NMR of 21b (500 MHz, $CDCl_3$)

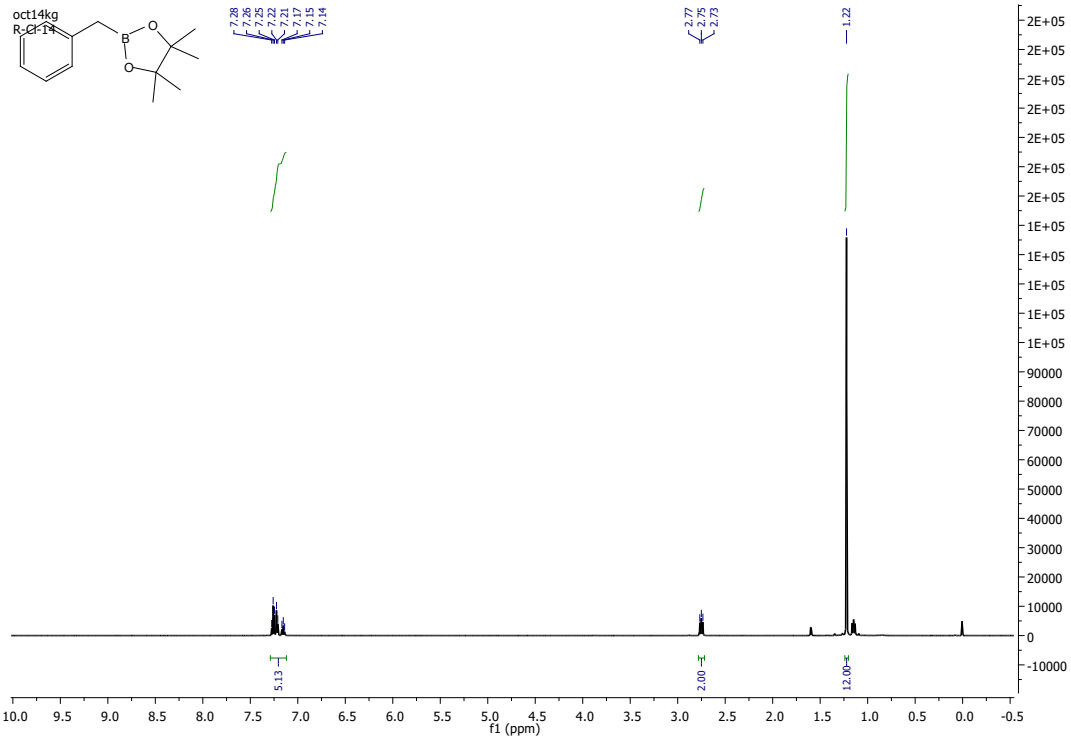


^{13}C NMR of 21b (125 MHz, $CDCl_3$)

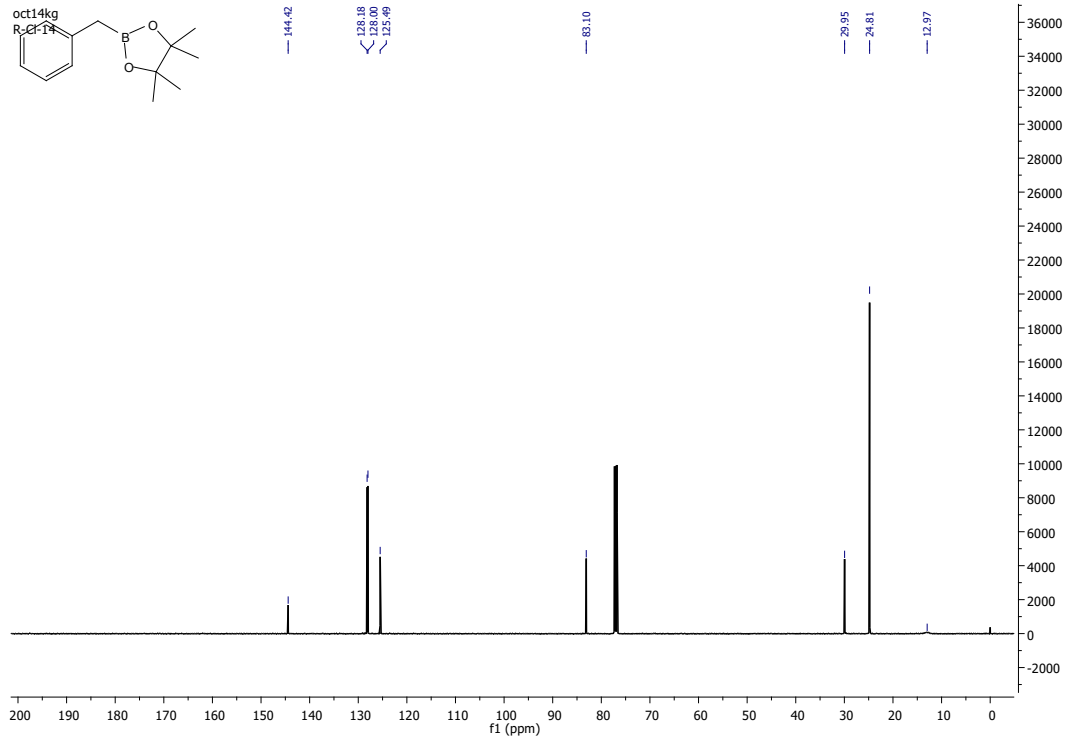


^{11}B NMR of 21b (128 MHz, $CDCl_3$)

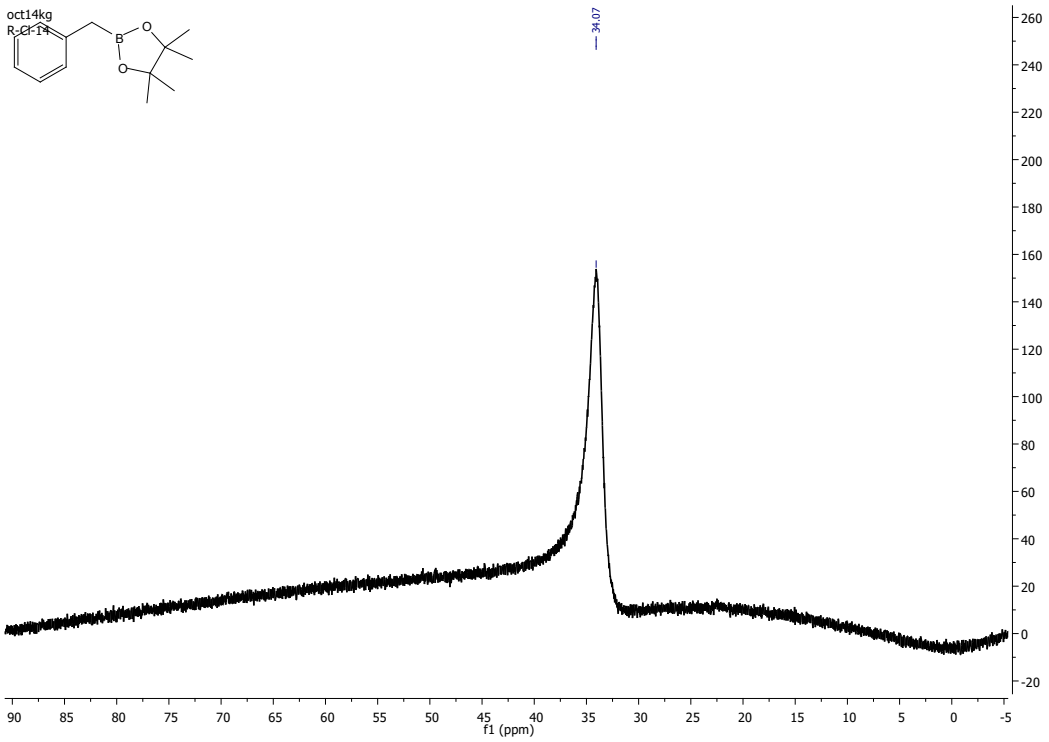
2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22b)



^{1}H NMR of 22b (400 MHz, $CDCl_3$)

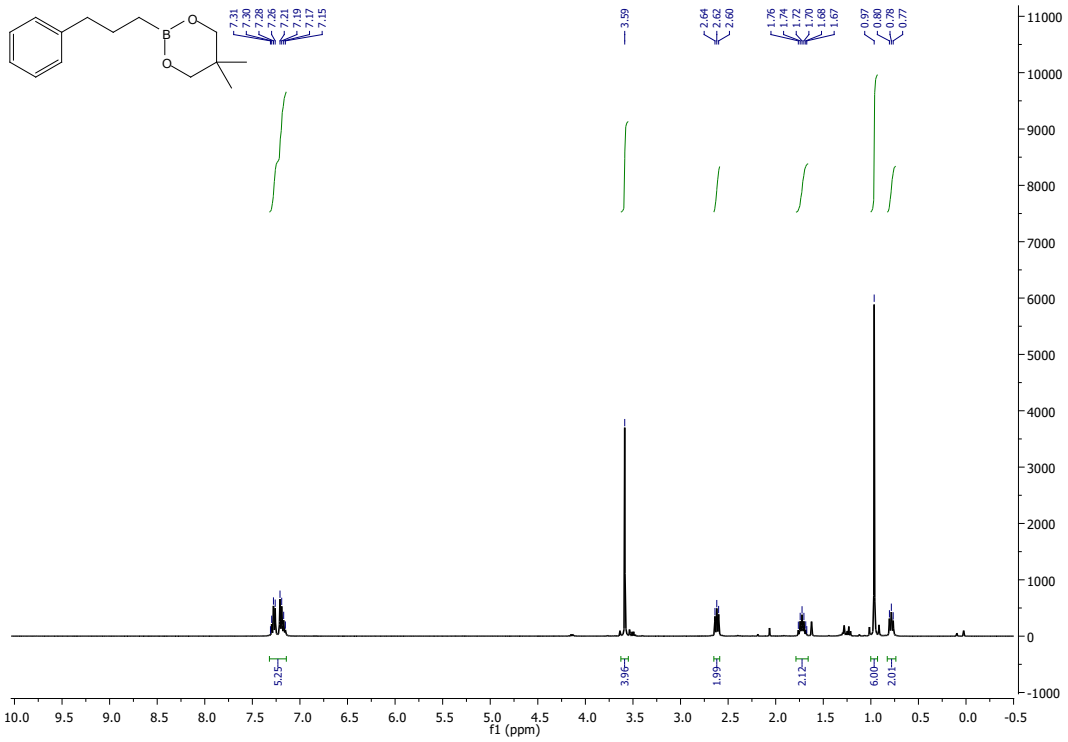


^{13}C NMR of 22b (100 MHz, $CDCl_3$)

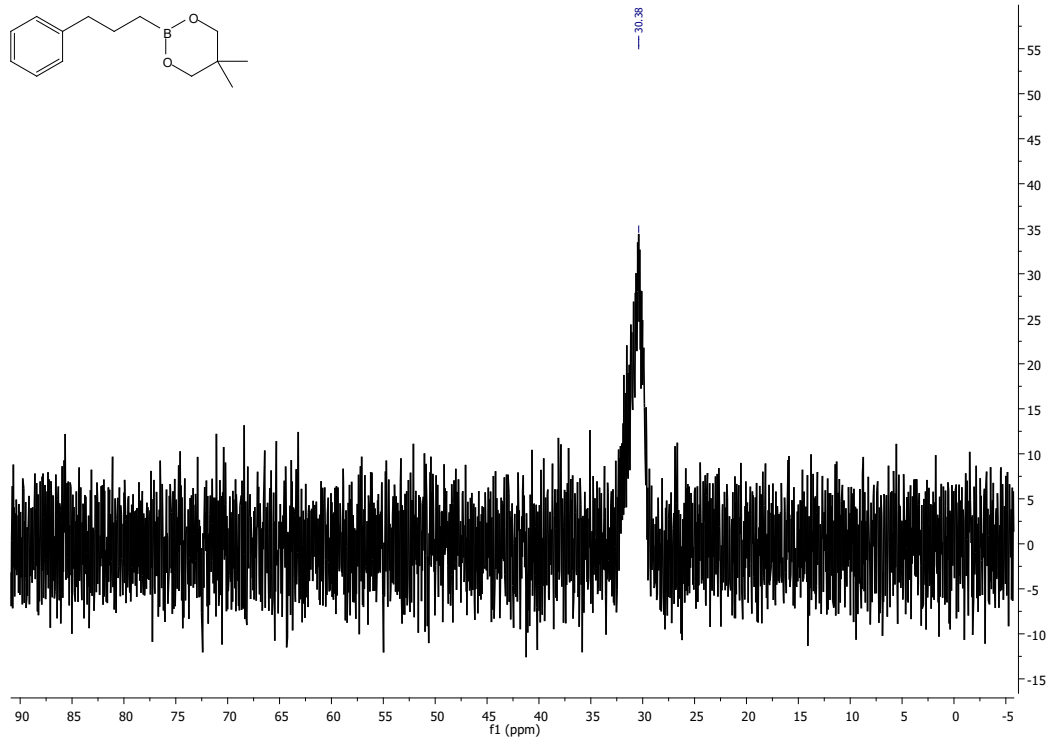


^{11}B NMR of 22b (128 MHz, $CDCl_3$)

5,5-Dimethyl-2-(3-phenylpropyl)-1,3,2-dioxaborinane (23b)

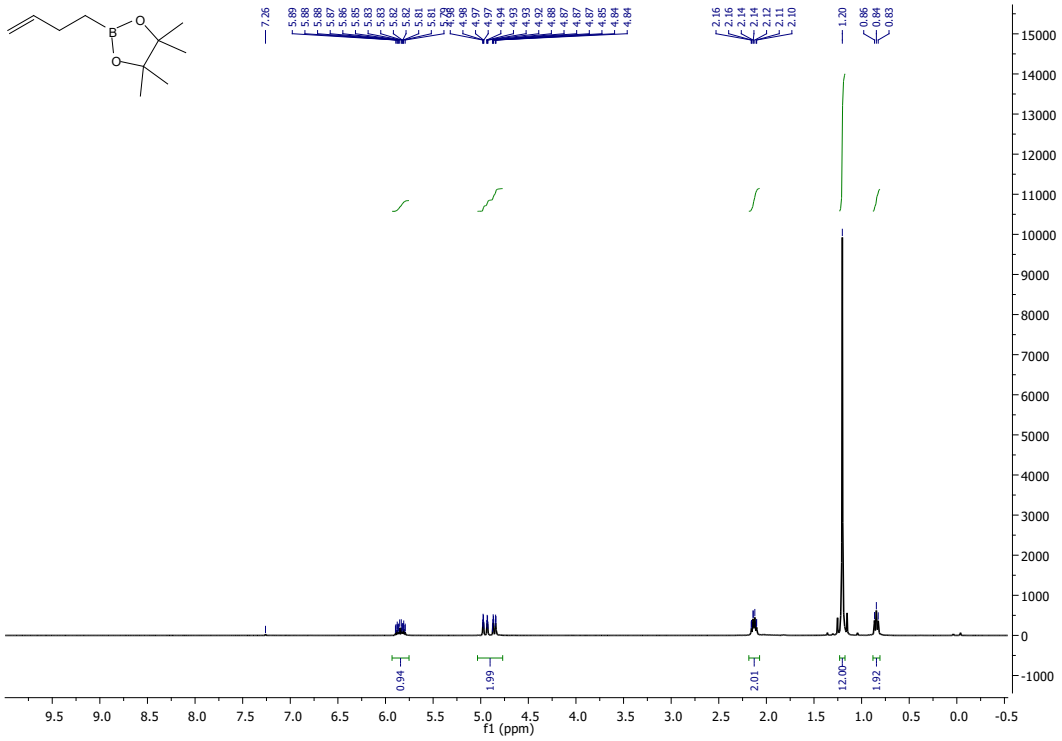


^{1}H NMR of 23b (400 MHz, $CDCl_3$)

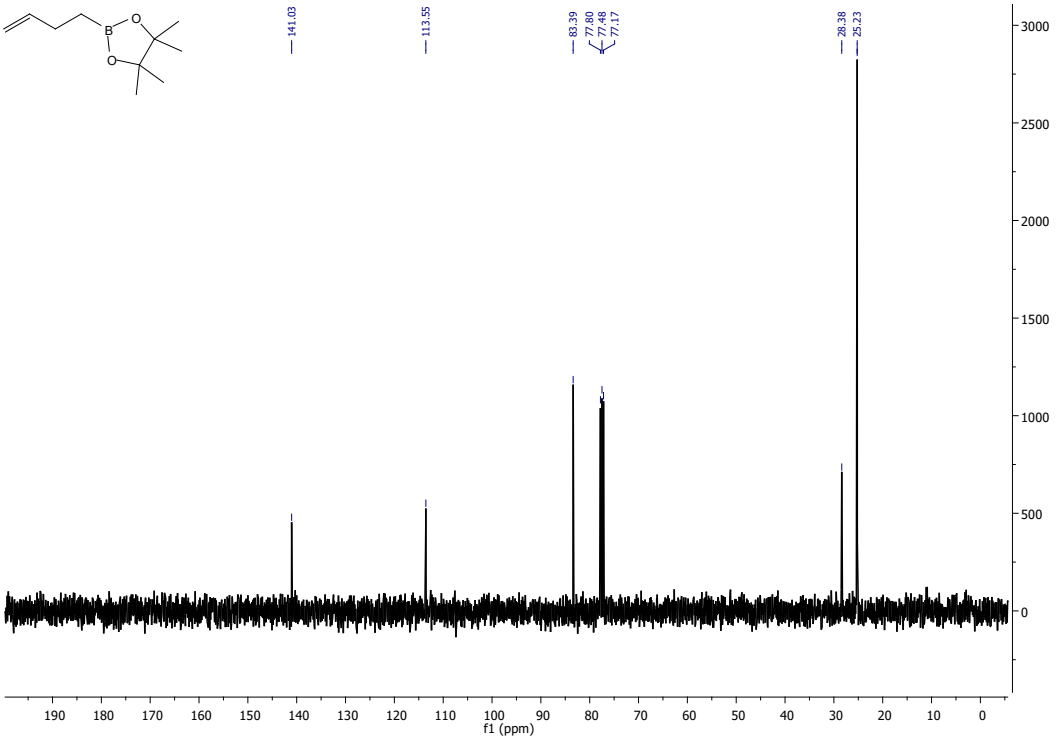


^{11}B NMR of 23b (128 MHz, $CDCl_3$)

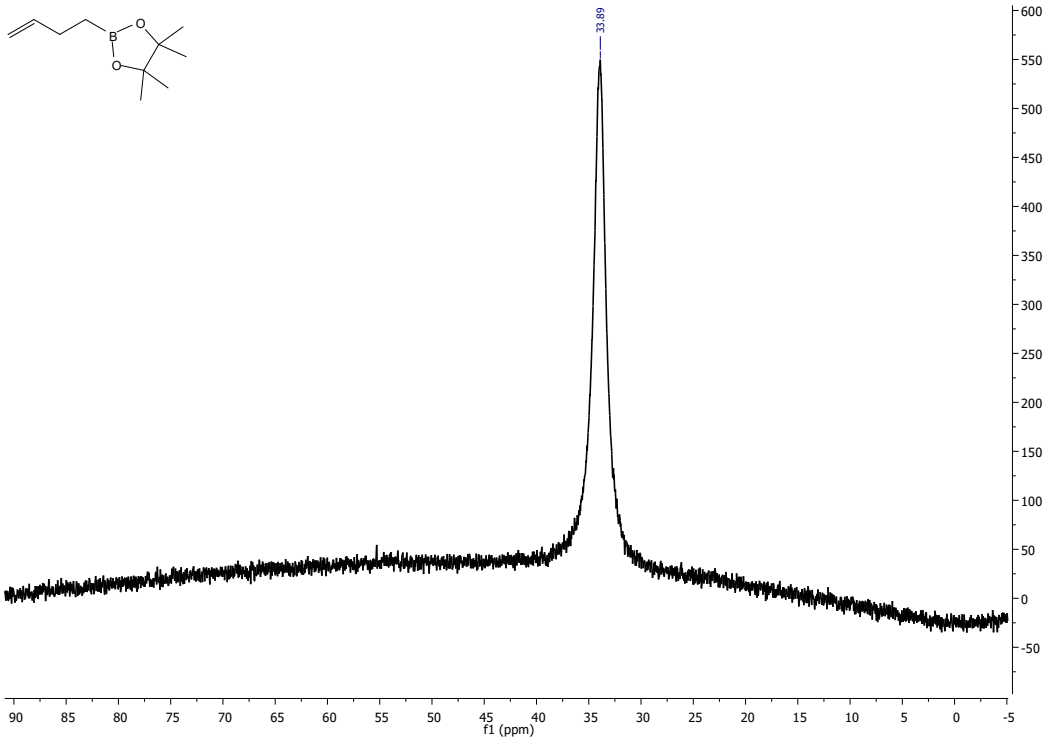
2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24c)



^{1}H NMR of 24c (400 MHz, $CDCl_3$)

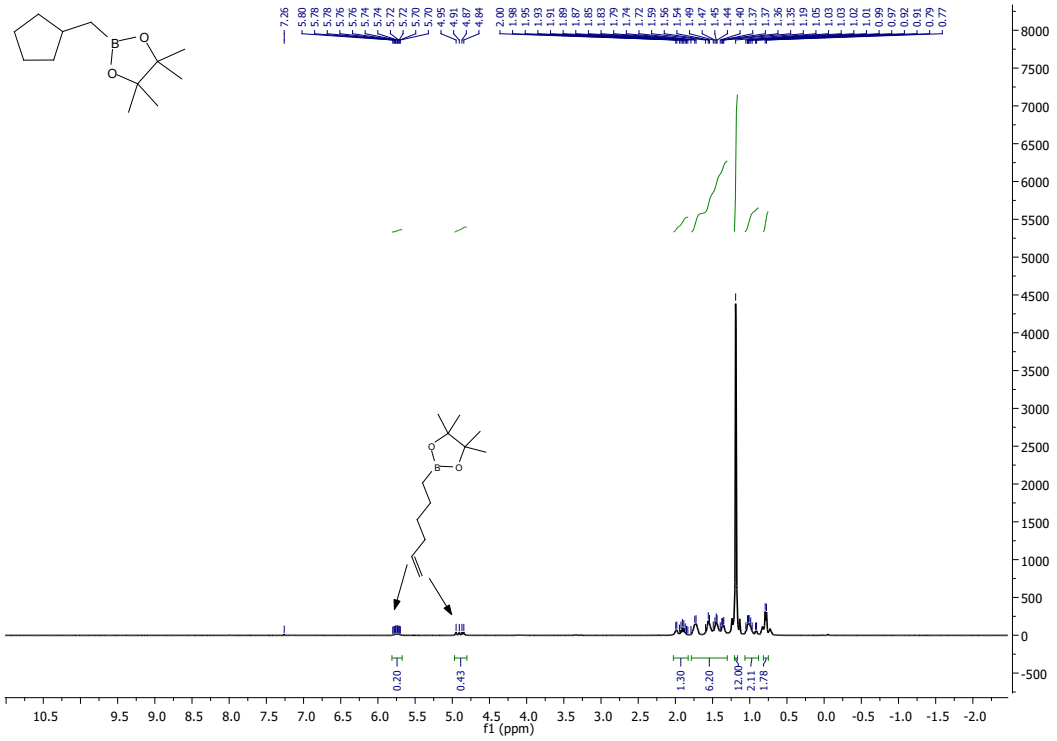


^{13}C NMR of 24c (100 MHz, $CDCl_3$)

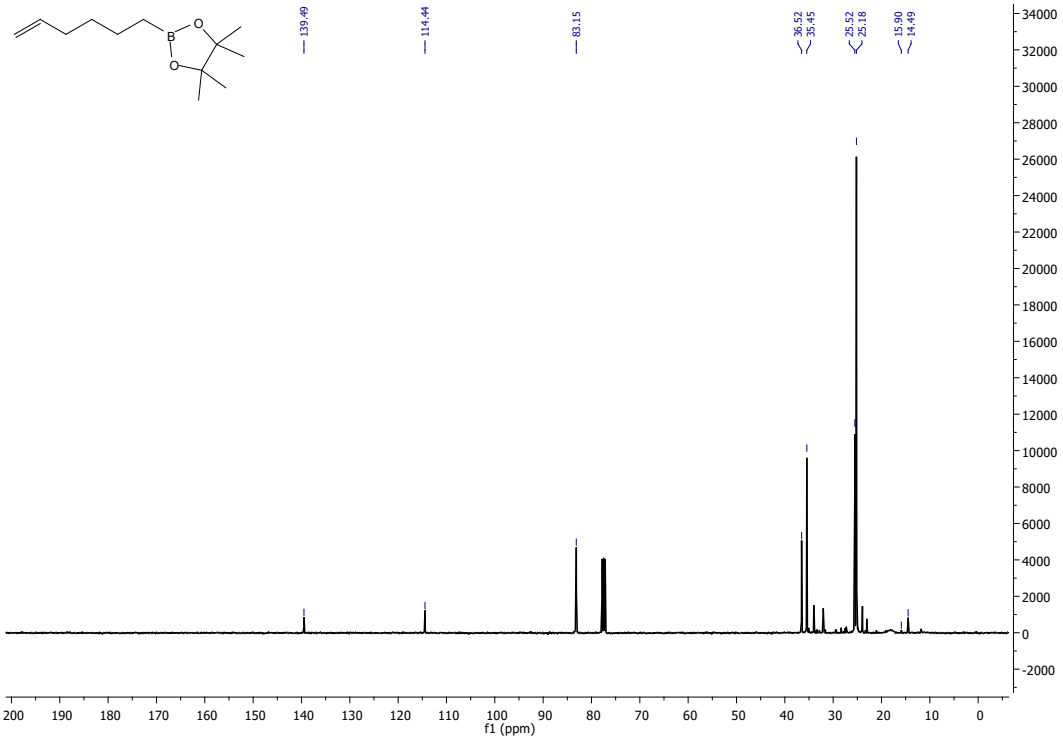


^{11}B NMR of 24c (128 MHz, $CDCl_3$)

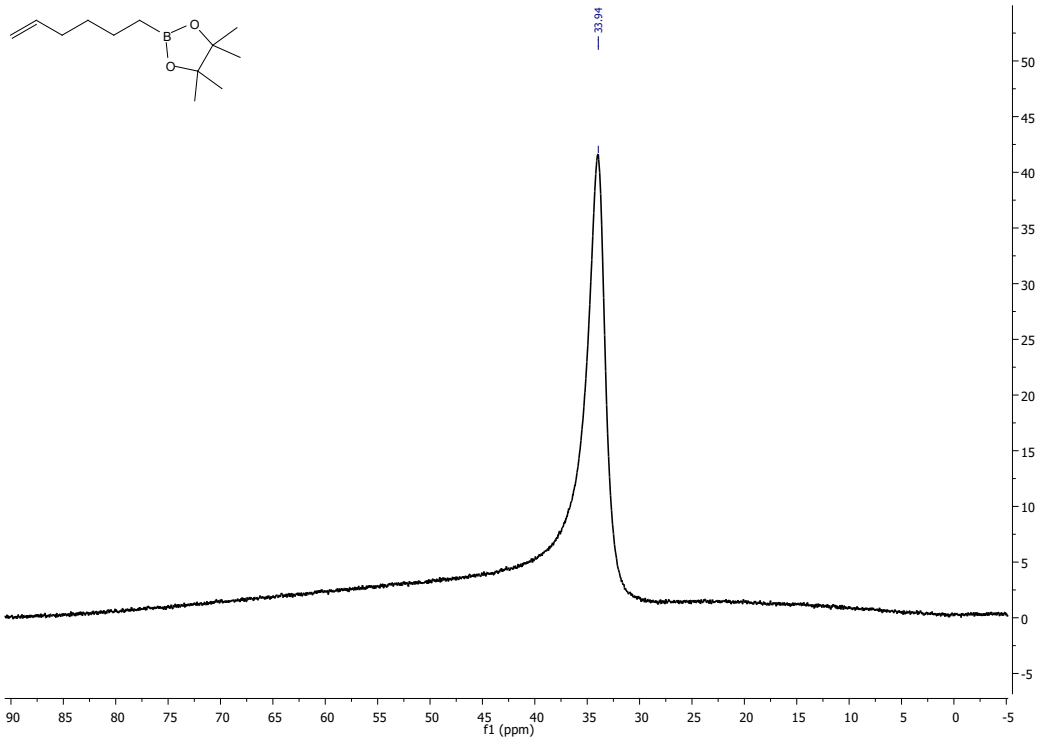
2-(Cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25c)



^{1}H NMR of 25c (400 MHz, $CDCl_3$)



^{13}C NMR of 25c (100 MHz, $CDCl_3$)



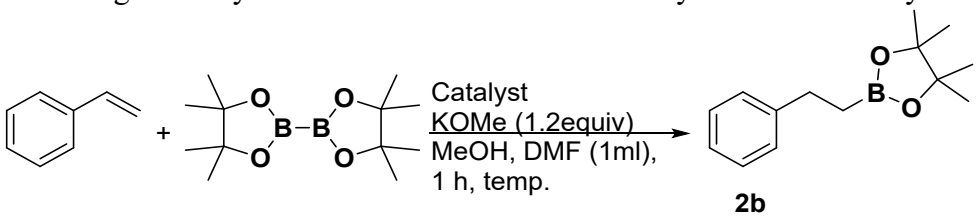
^{11}B NMR of 25c (128 MHz, $CDCl_3$)

VII. Hydroboration of Alkenes: Optimization of the Reaction Conditions

Experimental procedure for examples described in Table 4.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT NPs catalyst (5 mg; 13.12 mol % based on Cu), B_2pin_2 (76 mg, 0.3 mmol), base (1.2 equiv, 0.3 mmol), MeOH (5 equiv), styrene (26 mg, 0.25 mmol) and DMF (1 mL) were added. The reaction mixture was stirred at room temperature for the indicated amount of time. The crude reaction was dissolved in Et_2O (10 mL) and then transferred to a separatory funnel followed by the addition of H_2O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

Table S8. Screening of catalyst and amount of MeOH for the hydroboration of styrene.



2b

Entry	Catalyst (NPs)	solvent	base	B_2pin_2 (equiv)	MeOH (equiv)	Temp (^oC)	Time (h)	Yield (%)
1	-	DMF	KOMe	1.2	5	RT	1 h	Trace
2	Cu/N-CNT	DMF	-	1.2	5	RT	1 h	0
3	Cu/N-CNT	DMF	KOMe	1.2	5	RT	1 h	>99
4	**Cu/N-CNT**	**DMF**	**KOMe**	**1.2**	**2**	**RT**	**1 h**	**>99**

Reaction condition: 0.25 mmol styrene, B_2pin_2 (1.2 equiv), Cu/N-CNTs (5 mg), KOMe (1.2 equiv), MeOH and DMF (1 mL) for 1 h at room temperature. Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard.

VIII. Substrate Scope of Alkenes Hydroboration

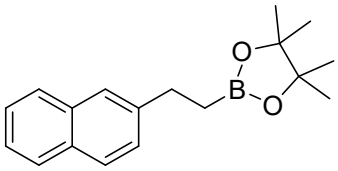
Experimental procedure for examples described in Table 5.

General Procedure C. In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT NPs (5 mg, 13.12 mol % of Cu), B_2pin_2 (76 mg, 1.2 equiv, 0.3 mmol), KOMe (21 mg, 1.2 equiv, 0.3 mmol), DMF (1 mL), MeOH (2 equiv, 25 μL, 0.6 mmol), and aryl alkene substrate (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 1 h. The crude reaction was dissolved in Et_2O (10 mL) and then transferred to a separatory funnel followed by the addition of H_2O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

General Procedure D. In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT NPs (20 mg, 13.12 mol % of Cu), B_2pin_2 (304 mg, 1.2 equiv, 0.3 mmol), KOMe (84 mg, 1.2 equiv, 0.3 mmol), DMF (5 mL), MeOH (2 equiv, 100 μL, 0.6 mmol), and aryl alkene (1 mmol) were added and the reaction was stirred vigorously at room temperature. The crude reaction was dissolved in Et_2O (30 mL) and then transferred to a separatory funnel followed by the addition of H_2O (30 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography.

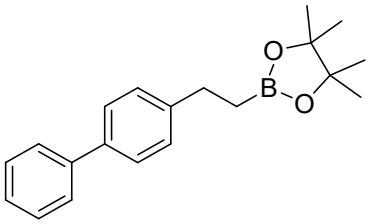
Spectroscopic data

4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (26b).[8]



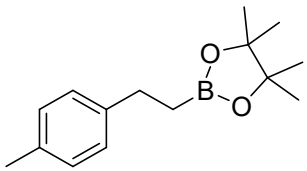
Following general procedure D, a colorless liquid in 86% yield (242 mg) from 2-vinylnaphthalene (**26a**, 154 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, CDCl3): δ 7.81 (dd, *J* = 17.5 Hz, 7.5 Hz, 3H), 7.72 (s, 1H), 7.50-7.43 (s, 3H), 3.02-2.98 (m, 2H), 1.34–1.27 (m, 14H). ^{13}C NMR (126 MHz, CDCl3): δ 142.03, 133.75, 132.02, 127.77, 127.64, 127.51, 127.35, 125.79, 124.99, 83.18, 30.22, 24.89, 13.01(br, C-B). ^{11}B NMR (160 MHz, $CDCl_3$): *δ* 34.49. GC-MS: m/z 282 (M^+).

2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27b). [9]



Following general procedure D, a colorless liquid in 89% yield (274 mg) from 4-vinyl-1,1'-biphenyl (**27a**, 180 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 7.60 (d, J = 8 Hz, 2H), 7.52 (d, *J* = 8Hz, 2H), 7.44 (t, *J* = 8Hz, 2H), 7.33 (t, *J* = 8Hz, 3H), 2.82 (t, J = 8 Hz, 2H), 1.25 (s, 12H), 1.21 (t, *J* = 8Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 144.07, 141.73, 138.96, 129.96, 128.92, 127.46, 127.42, 127.38, 83.62, 30.08, 25.30, 13.39 (br, C-B). ^{11}B NMR (128 MHz, CDCl3): *δ* 34.58. GC-MS: m/z 308 (M^+).

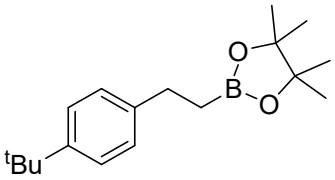
4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (28b).[8,9]



Following general procedure D, a colorless liquid in 90% yield (221 mg) from 1-methyl-4-vinylbenzene (**28a**, 118 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 7.15-7.08 (m, 4H), 2.74 (t, *J* = 8 Hz, 2H), 2.33 (s, 3H), 1.25 (s, 12H), 1.17–1.13 (m, 2H). ^{13}C NMR (100 MHz,

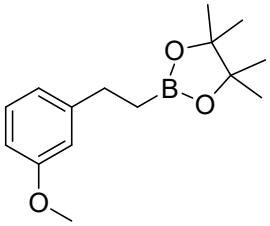
CDCl3): δ 141.87, 135.30, 129.35, 128.33, 83.53, 30.00, 25.30, 21.45, 13.74 (br, C-B). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.11. GC-MS: m/z 246 (M^+).

2-(4-(Tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29b).[8]



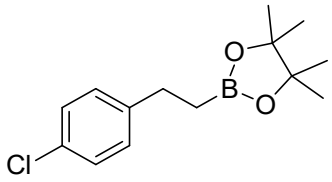
Following general procedure D, a colorless liquid in 72% yield (207 mg) from 1-(tert-butyl)-4-vinylbenzene (**29a**, 160 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, CDCl3): δ 7.29-7.25 (m, 2H), 7.15 (d, J = 5 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 1.30 (s, 9H), 1.22 (s, 12H), 1.13 (t, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3): δ 148.25, 141.36, 127.65, 125.06, 83.07, 34.31, 31.44, 29.38, 24.81, 22.70, 12.90 (br, C-B). ^{11}B NMR (160 MHz, $CDCl_3$): δ 33.57. GC-MS: m/z 288 (M^+).

2-(3-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30b).[9]



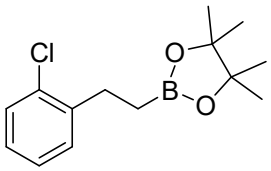
Following general procedure D, a colorless liquid in 91% yield (238 mg) from 1-methoxy-3-vinylbenzene (**30a**, 134 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 7.18 (t, J = 8 Hz, 1H), 6.84-6.80 (m, 2H), 6.73-6.70 (m, 1H), 3.78 (s, 3H), 2.75 (t, J = 8 Hz, 2H), 1.24 (s, 12H), 1.16 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 160.04, 146.52, 129.58, 120.86, 114.10, 111.45, 83.51, 55.44, 30.50, 25.27, 13.54 (br, C-B). ^{11}B NMR (128 MHz, CDCl3): δ 33.81. GC-MS: m/z 262 (M+).

2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31b). [8,9]



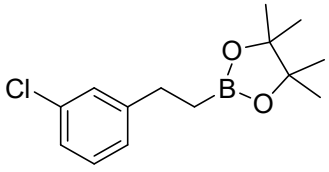
Following general procedure D, a colorless liquid in 53% yield (140 mg) from 1-chloro-4-vinylbenzene (**31a**, 138 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl3): δ 7.22 (d, *J* = 8 Hz, 2H), 7.14 (d, *J* = 8Hz, 2H), 2.71 (t, *J* = 8 Hz, 2H), 1.22 (s, 12H), 1.11 (t, *J* = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 143.26, 131.60, 129.83, 128.67, 83.62, 29.77, 25.24. The carbon directly attached to the boron atom was not detected, likely due to quadrpolar broadening. ^{11}B NMR (128 MHz, CDCl3): *δ* 33.90. GC-MS: m/z 266 (M+).

2-(2-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32b).[10]



Following general procedure D, a colorless liquid in 80% yield (212 mg) from 1-chloro-2-vinylbenzene (32a, 138 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, CDCl3): δ 7.32-7.26 (m, 4H), 7.18-7.08 (m, 2H), 2.85 (t, *J* = 10 Hz, 2H), 1.24 (s, 12H), 1.15 (t, *J* = 10 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3): δ 154.94, 142.30, 134.30, 130.20, 129.76, 127.41, 127.06, 83.60, 30.14, 28.24, 25.27, 11.54 (br, C-B). ^{11}B NMR (160 MHz, CDCl3): *δ* 33.67. GC-MS: m/z 266 (M+).

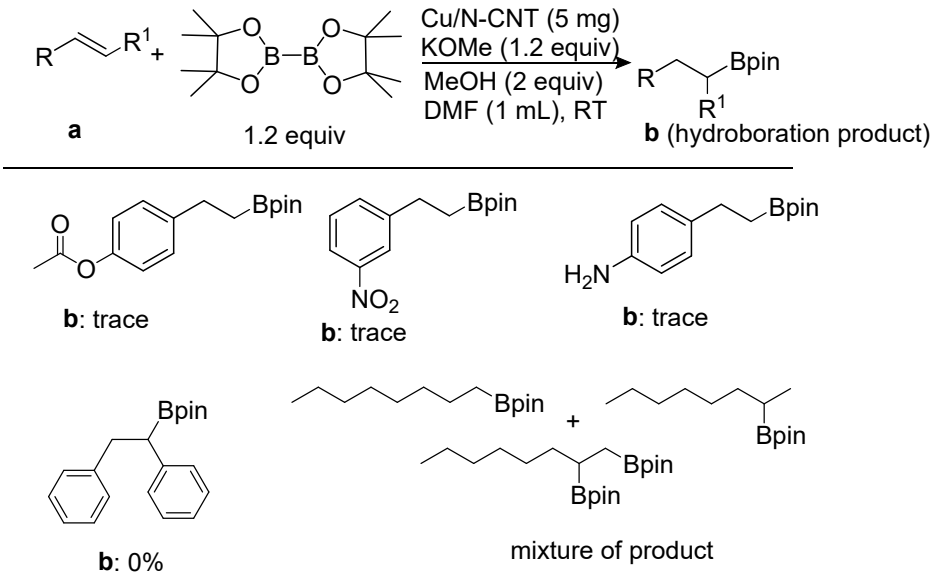
2-(3-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33b).[10]



Following general procedure D, a colorless liquid in 83% yield (220 mg) from 1-chloro-3-vinylbenzene (**33a**, 138 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, CDCl3): δ 7.26-7.07 (m, 4H), 2.72 (t, *J* = 10 Hz, 2H), 1.21 (s, 12H), 1.12 (t, *J* = 10 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3): δ 146.45, 133.89, 129.43, 128.28, 126.26, 125.67, 83.20, 29.70, 24.81, 12.75 (br, C-B). ^{11}B NMR (160 MHz, CDCl3): *δ* 33.83. GC-MS: m/z 266 (M+).

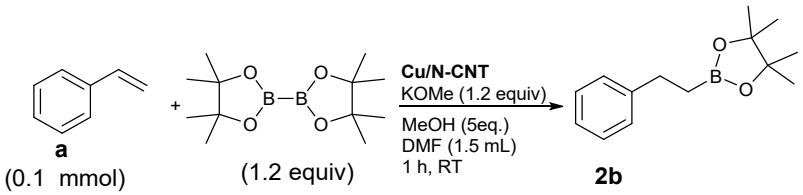
Unsuccessful Substrates

Table S9. Screening of **Cu/N-CNT** NPs catalyzed hydroboration of alkenes.[a]



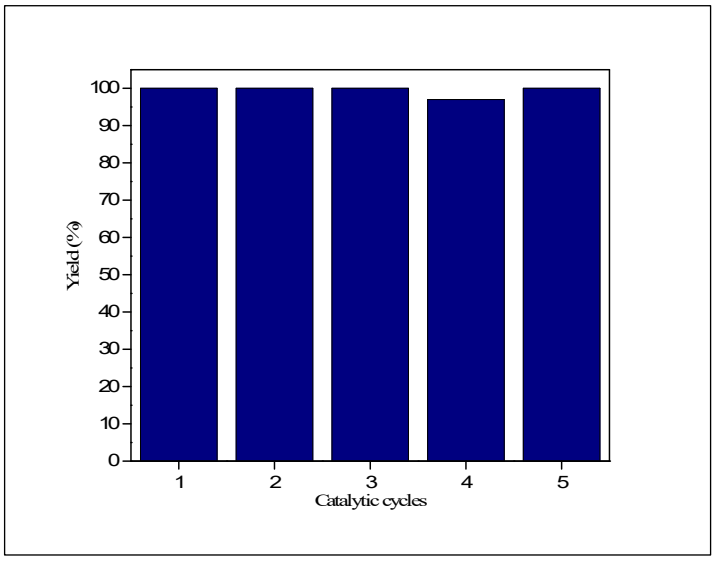
Reaction condition: 0.25 mmol alkene, B_2pin_2 (1.2 equiv), Cu/N-CNTs (5 mg), KOMe (1.2 equiv), MeOH 92 equiv) and DMF (1 mL) for 24 h at room temperature. Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard and product ratio were determined by GC-MS analysis.

IX. Recyclability Experiment for Alkenes Hydroboration Reaction



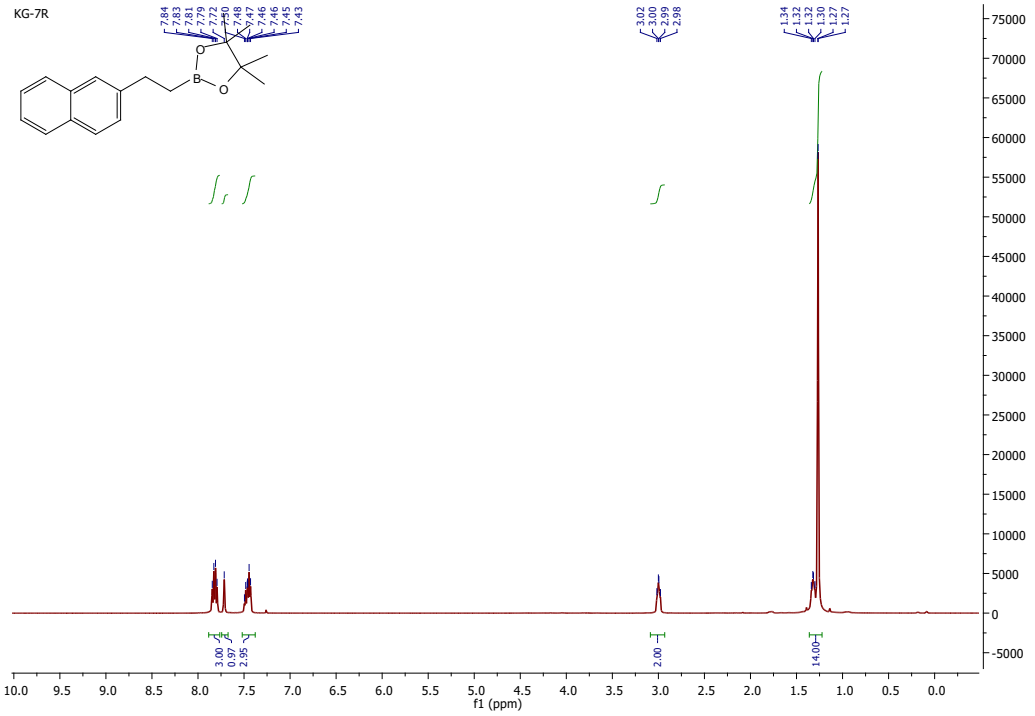
In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/N-CNT (20 mg, 13.12 mol % of Cu), B2pin2 (304 mg, 1.2 equiv, 1.2 mmol), KOMe (84 mg, 1.2 equiv, 1.2 mmol), DMF (5 mL) and styrene (104 mg, 1 mmol) were added and the reaction was stirred vigorously at room temperature for 1 h. Cu/N-CNT catalyst was separated by centrifuge washed thoroughly by EtOH (2 x 10 mL) and dried at 80 ˚C overnight, and same catalyst used for further cycles. The product yield was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

Yields: 1st cycle = 100%, 2nd cycle = 100%, 3rd cycle = 100%, 4th cycle = 97 %, 5th cycle = 100%

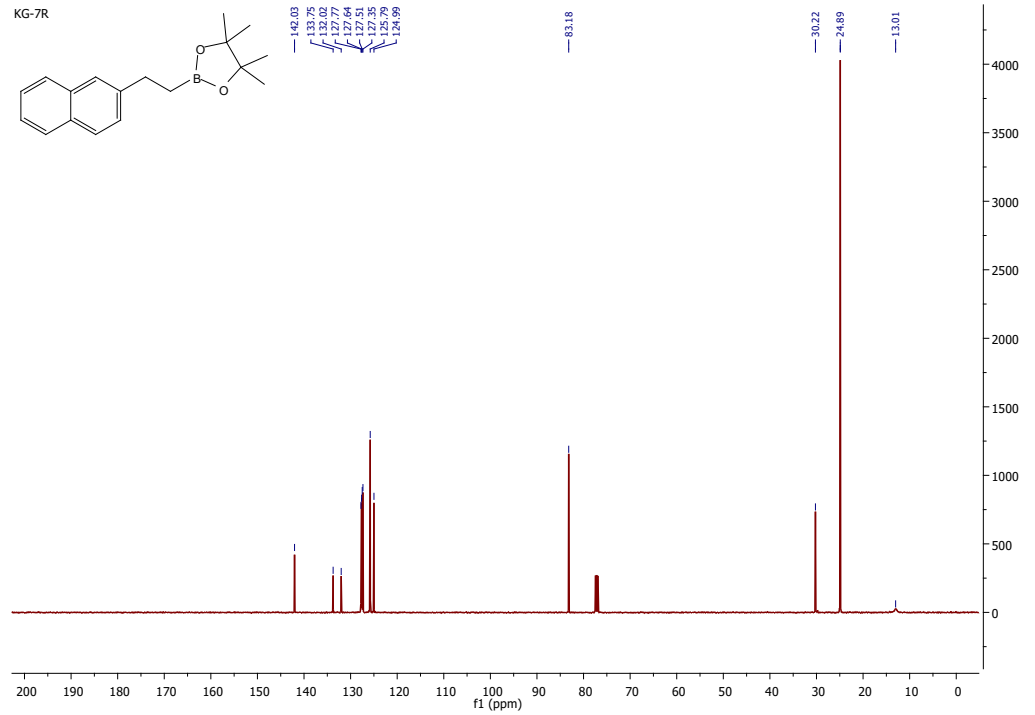


X. NMR Spectra of Alkenes Hydroboration Products

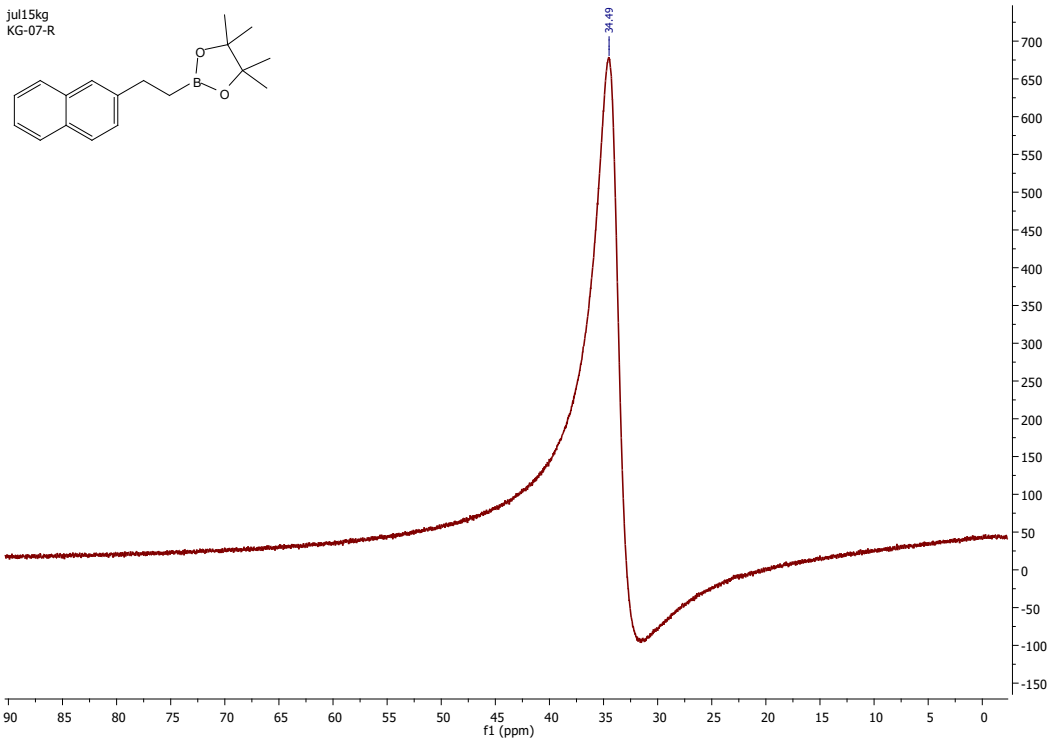
4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (26b)



^{1}H NMR of 26b (500 MHz, $CDCl_3$)

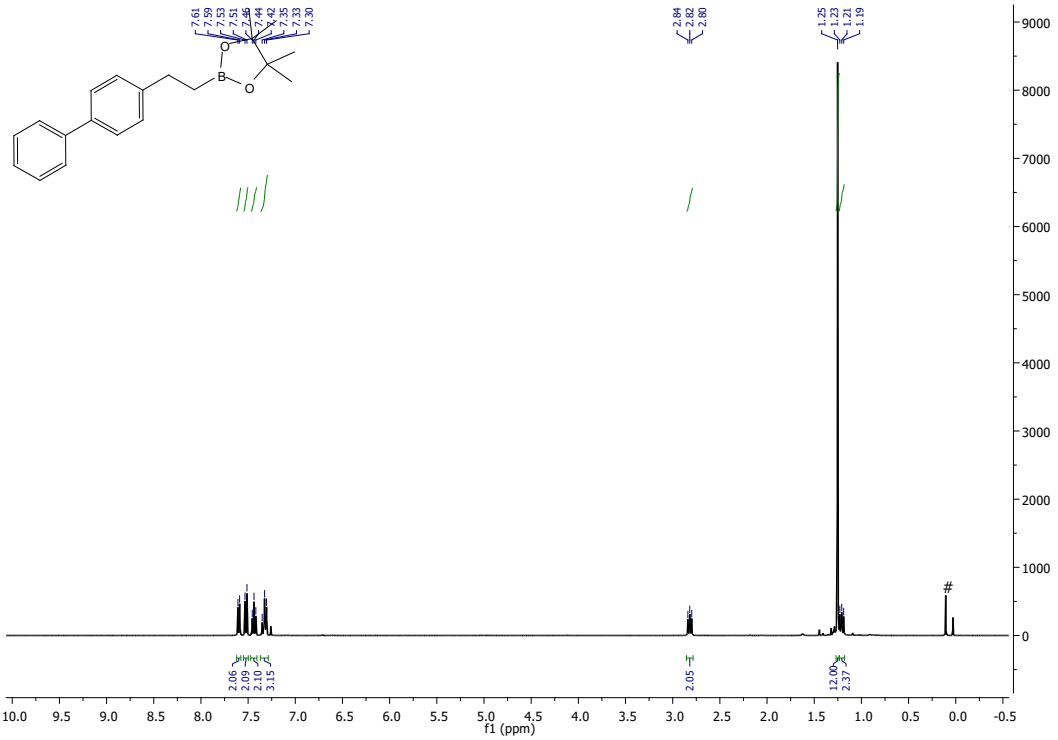


^{13}C NMR of 26b (126 MHz, $CDCl_3$)

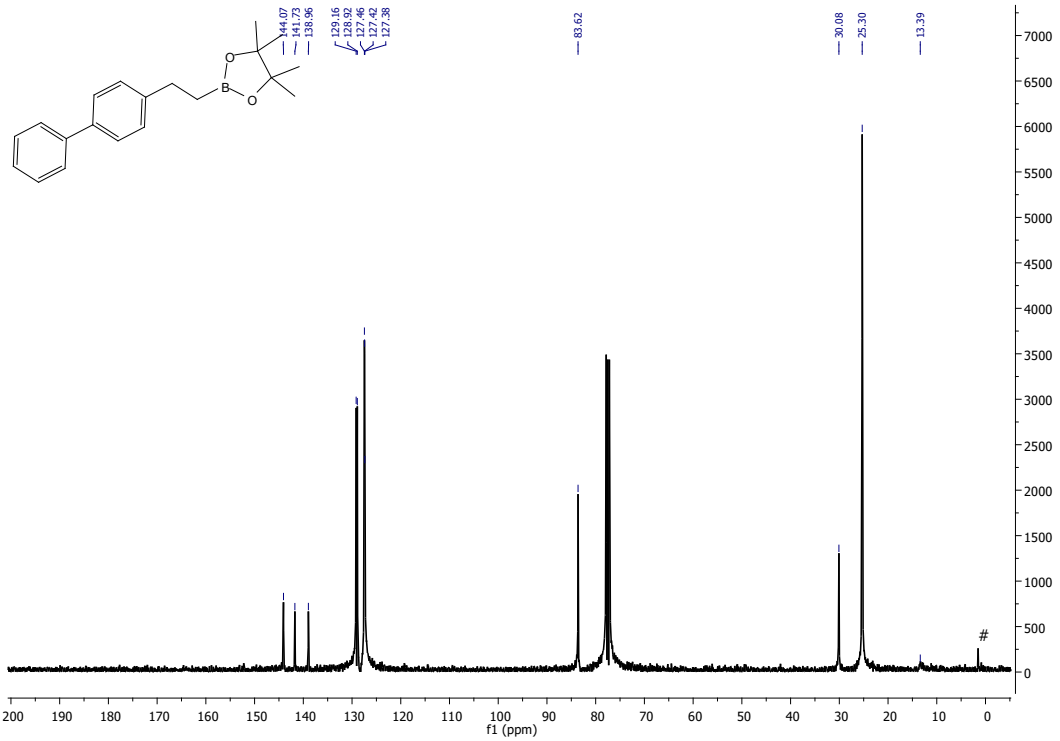


^{11}B NMR of 26b (160 MHz, $CDCl_3$)

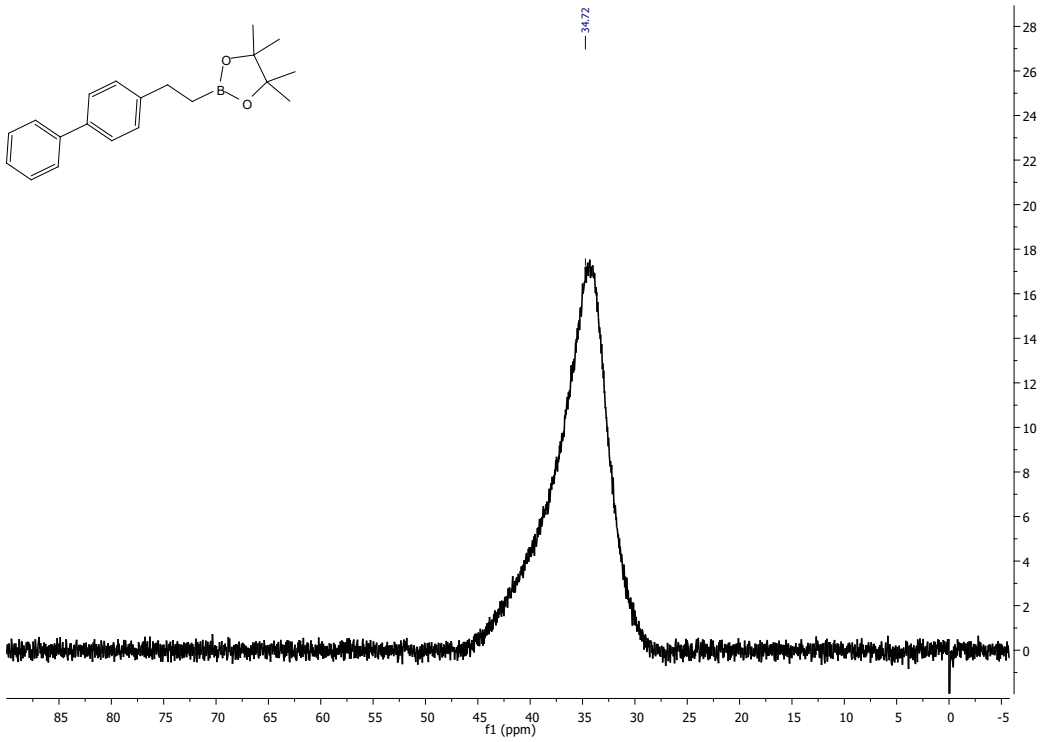
2-(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27b)



^{1}H NMR of 27b (400 MHz, $CDCl_3$)

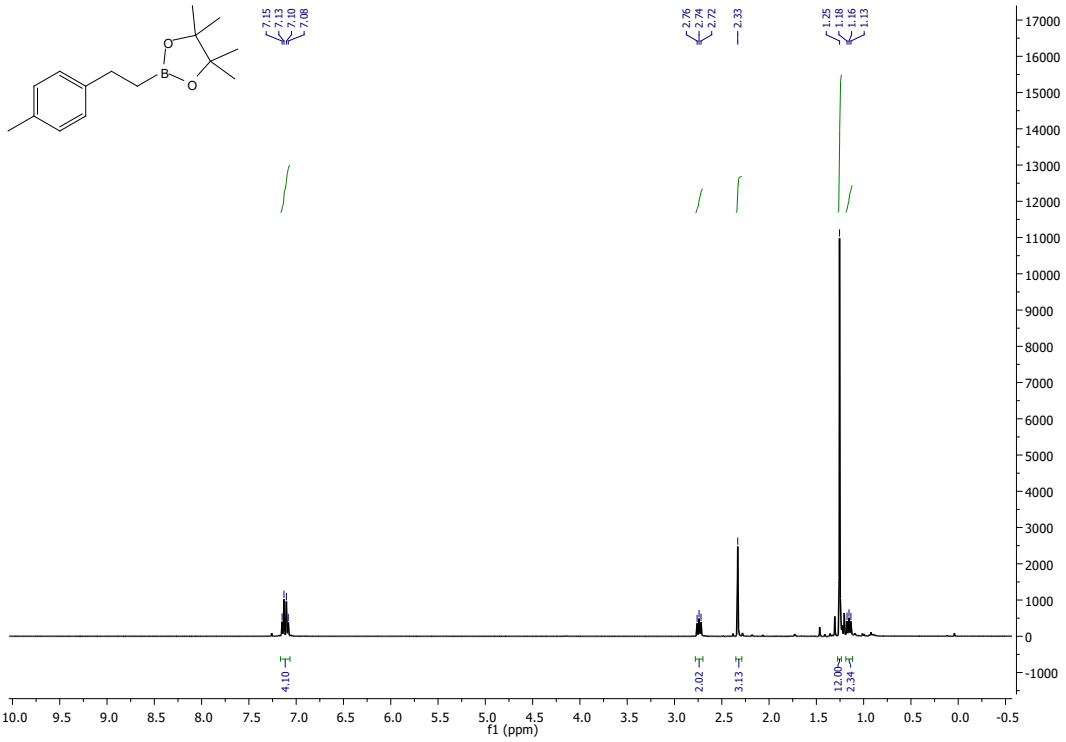


^{13}C NMR of 27b (100 MHz, $CDCl_3$)

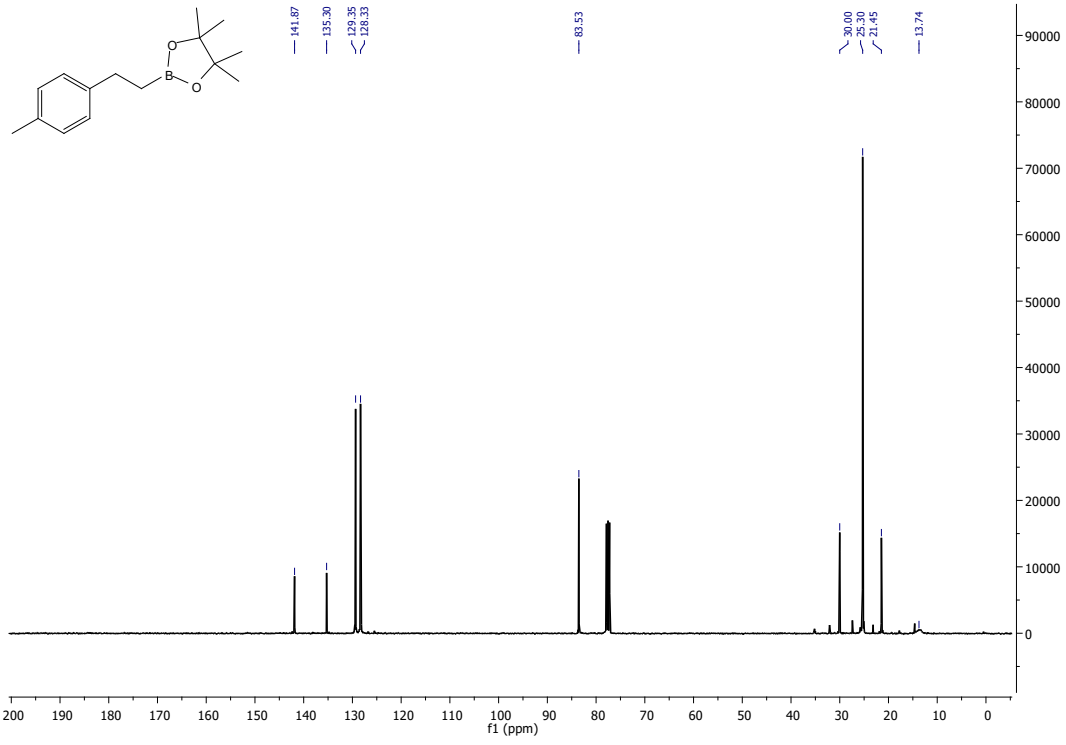


^{11}B NMR of 27b (128 MHz, $CDCl_3$)

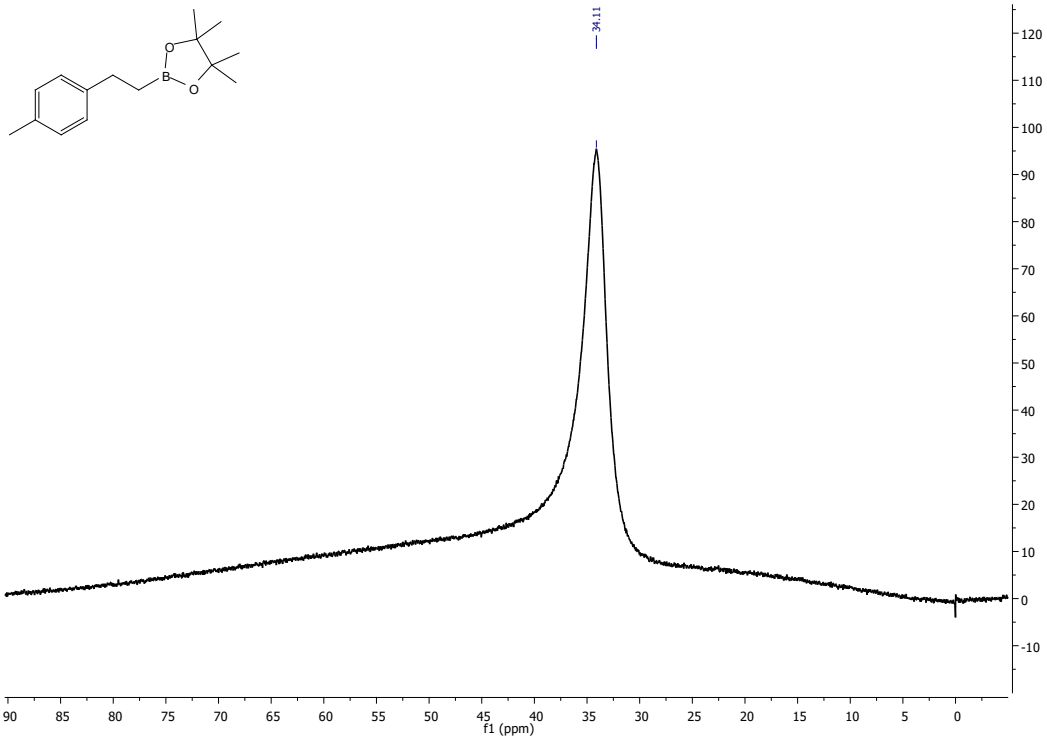
4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (28b)



^{1}H NMR of 28b (400 MHz, $CDCl_3$)

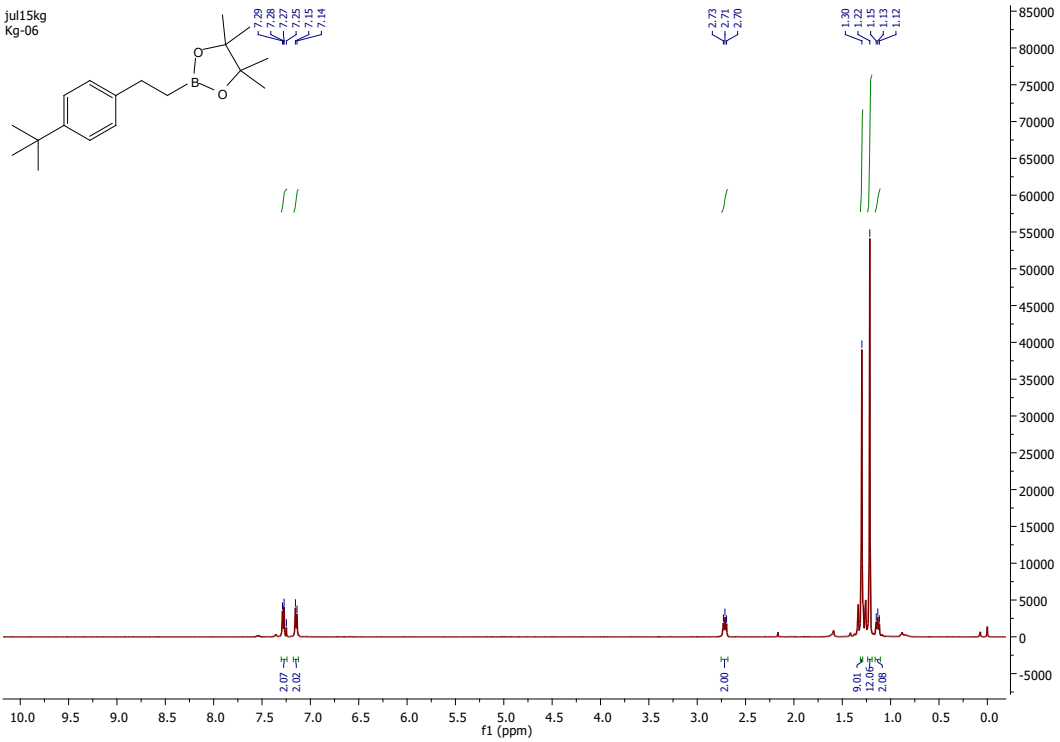


^{13}C NMR of 28b (100 MHz, $CDCl_3$)

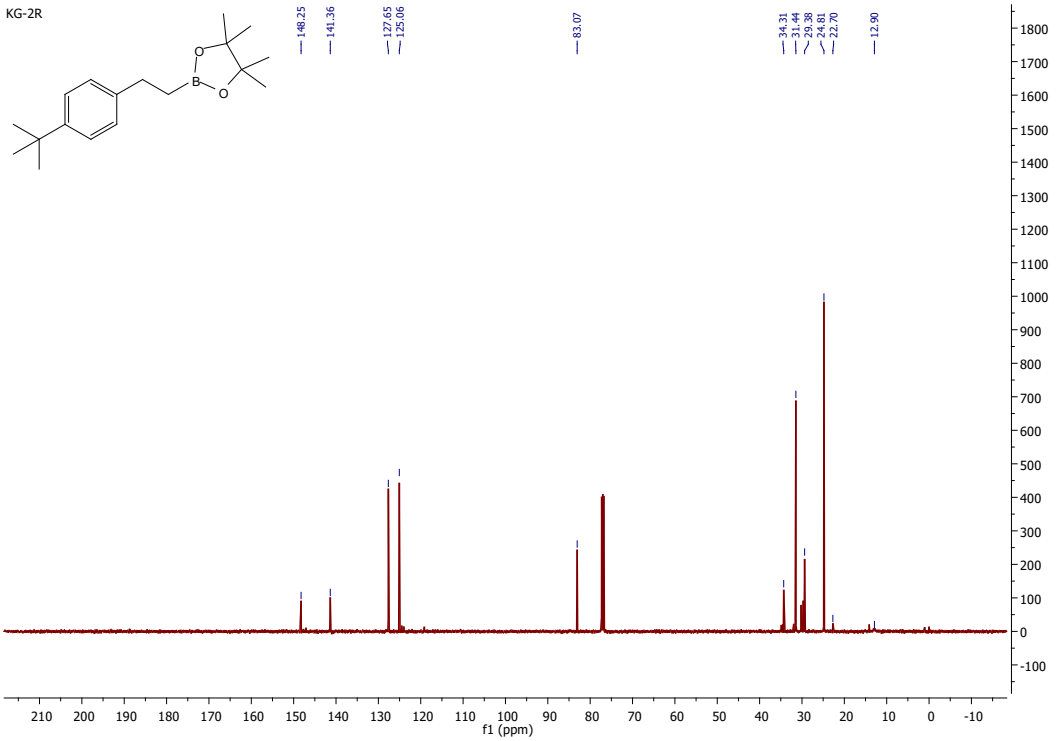


^{11}B NMR of 28b (128 MHz, $CDCl_3$)

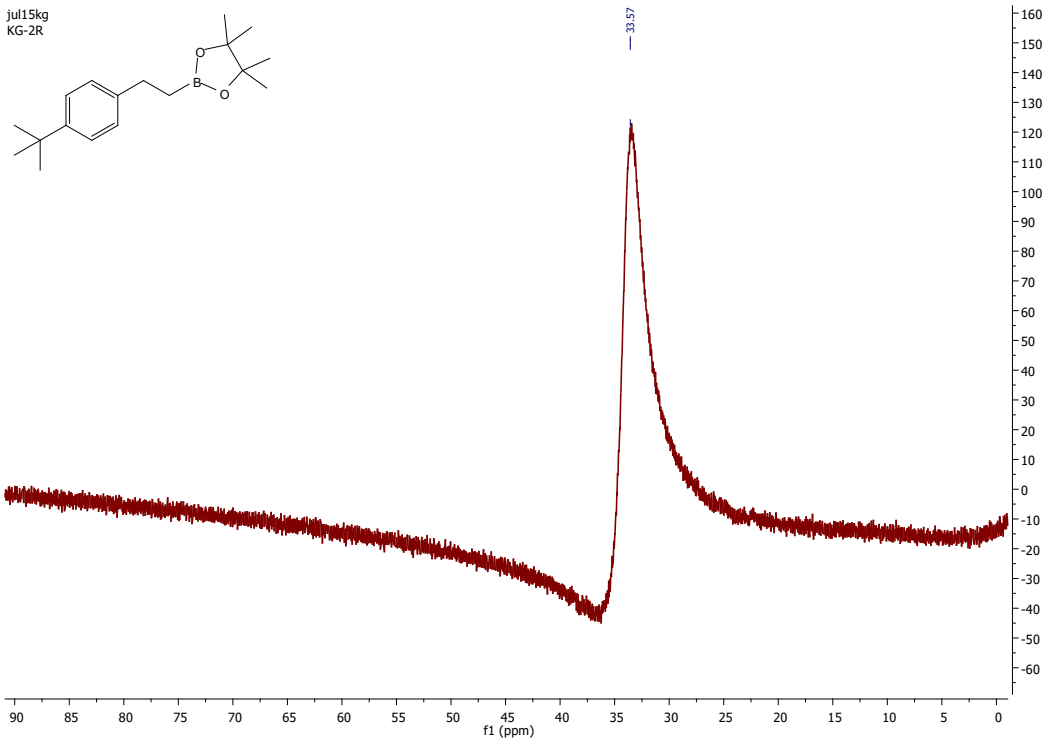
2-(4-(Tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29b)



^{1}H NMR of 29b (500 MHz, $CDCl_3$)

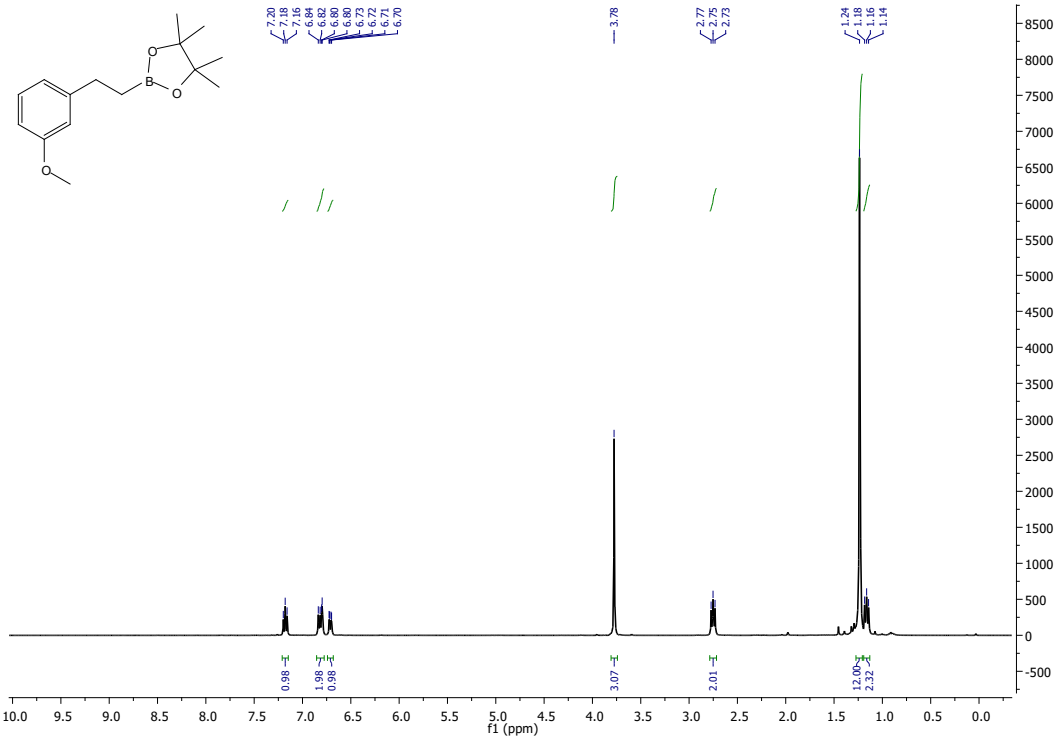


^{13}C NMR of 29b (126 MHz, $CDCl_3$)

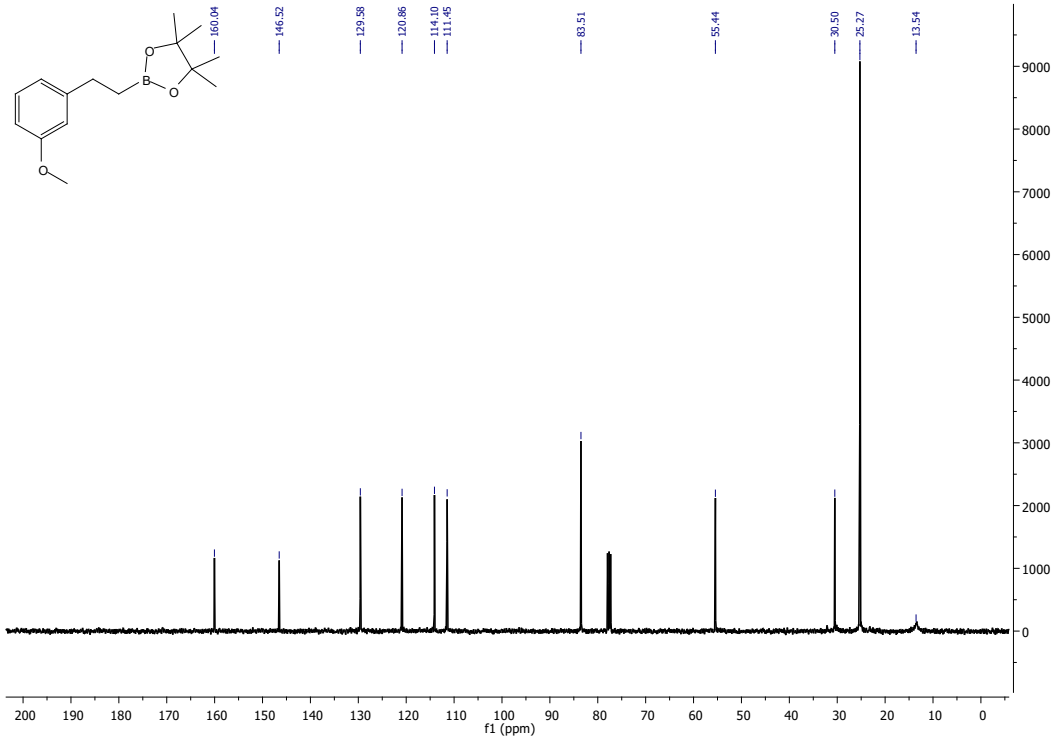


^{11}B NMR of 29b (160 MHz, $CDCl_3$)

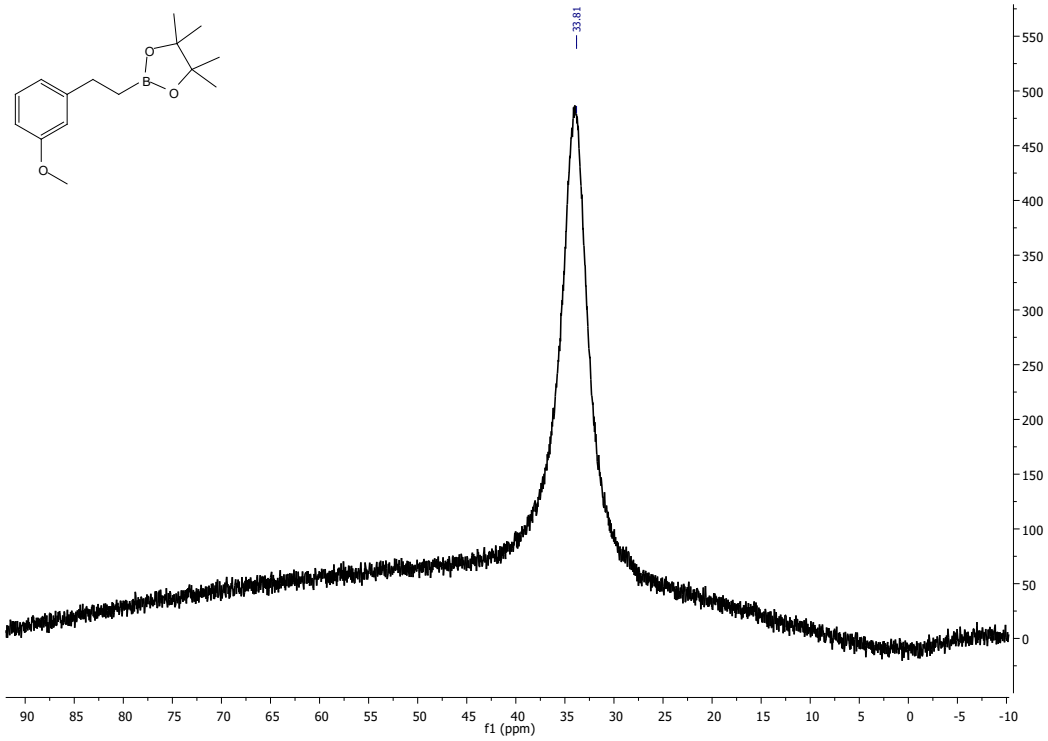
2-(2-Cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30b)



^{1}H NMR of 30b (400 MHz, $CDCl_3$)

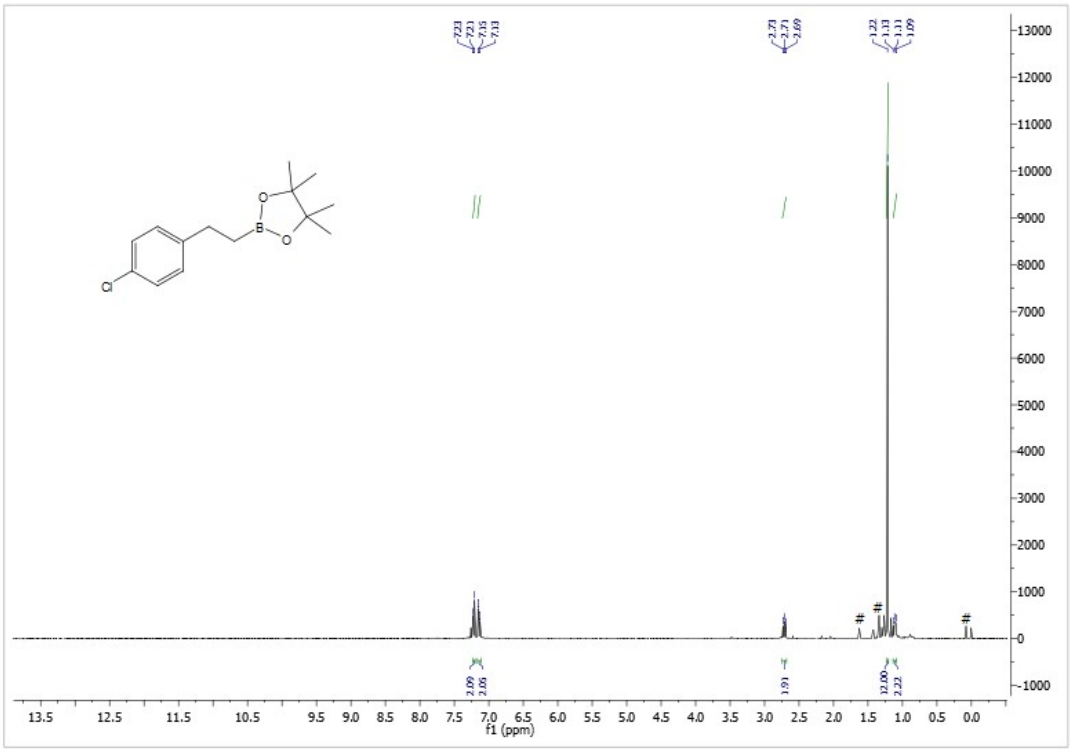


^{13}C NMR of 30b (100 MHz, $CDCl_3$)

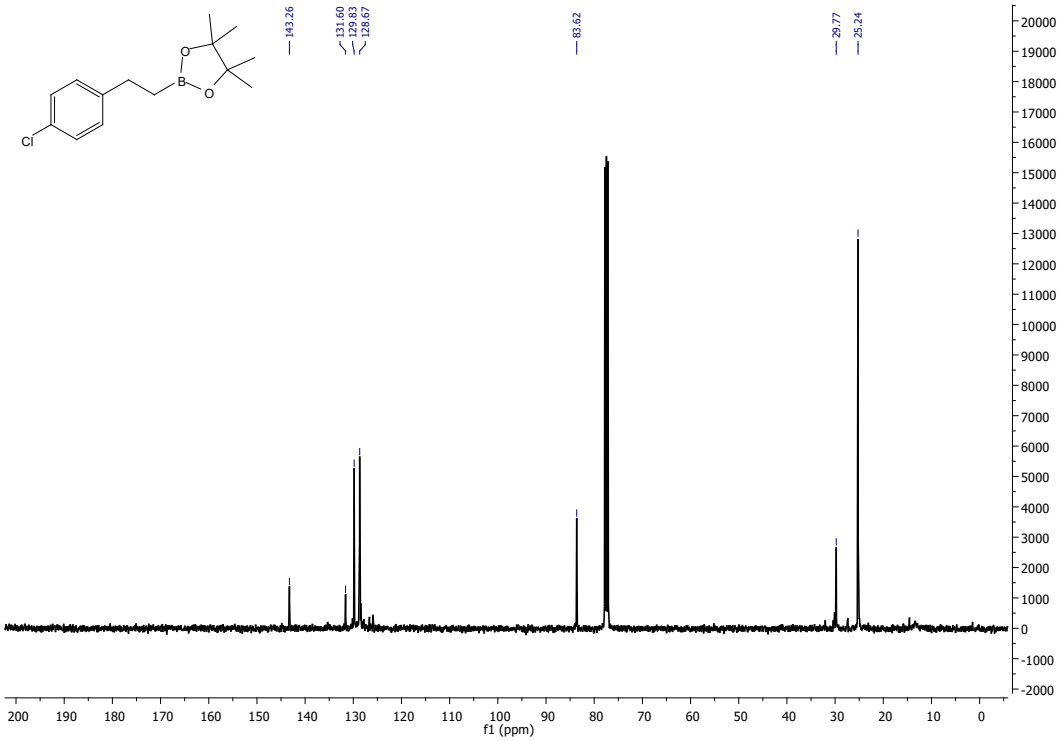


^{11}B NMR of 30b (128 MHz, $CDCl_3$)

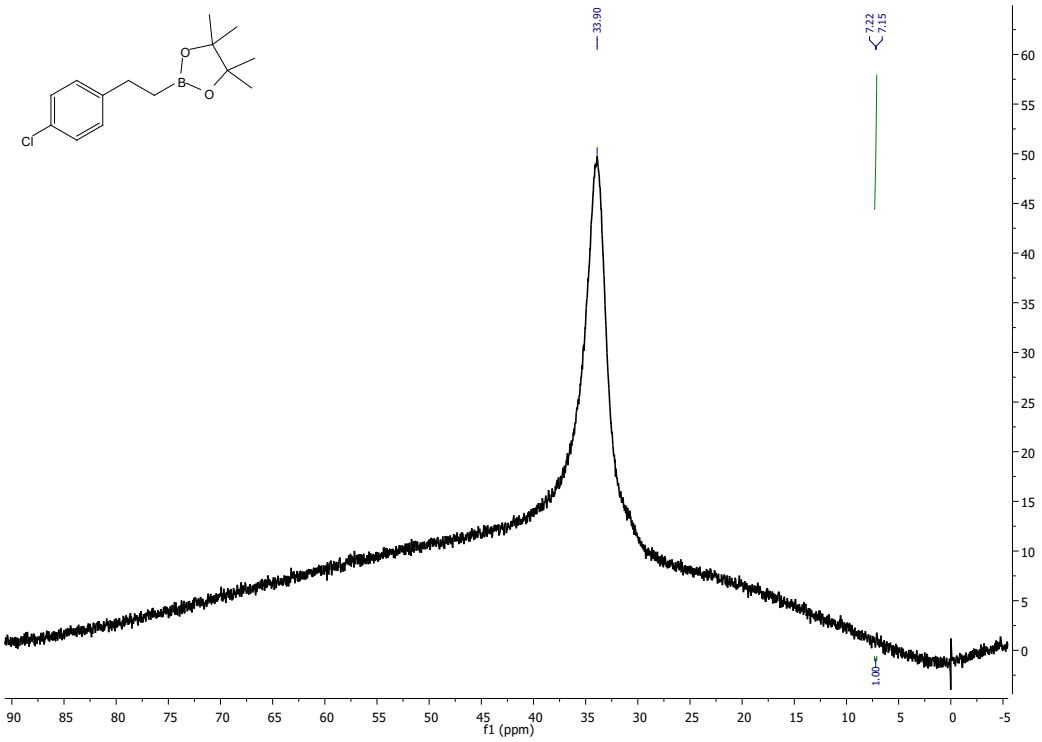
2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31b)



^{1}H NMR of 31b (400 MHz, $CDCl_3$)

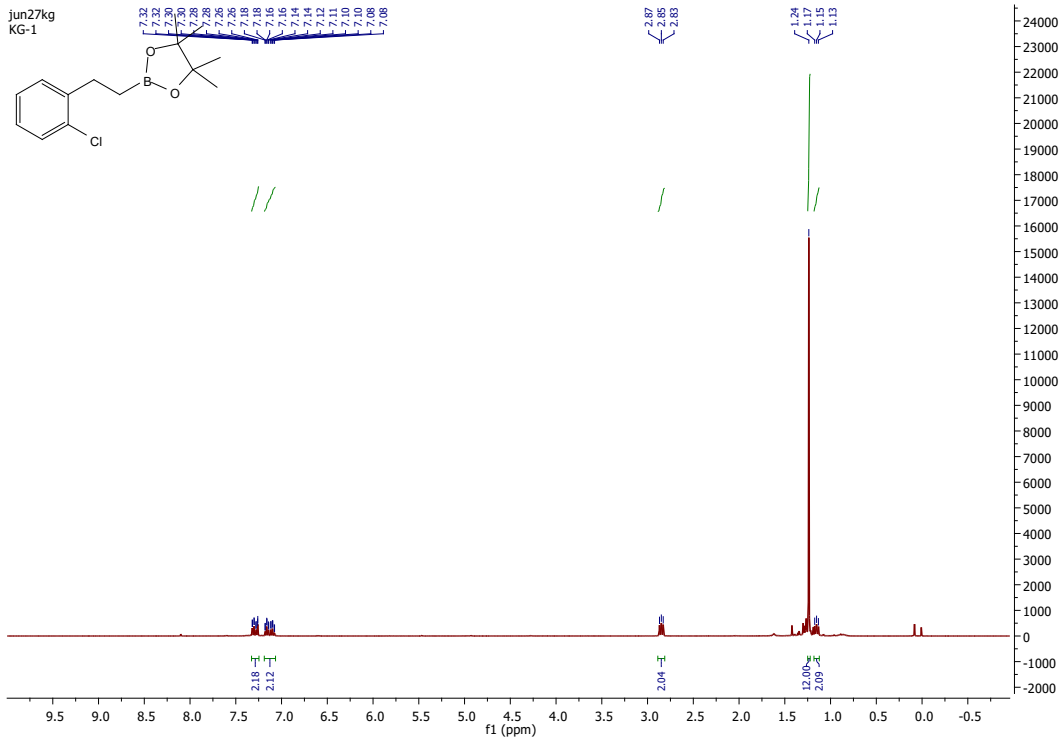


^{13}C NMR of 31b (100 MHz, $CDCl_3$)

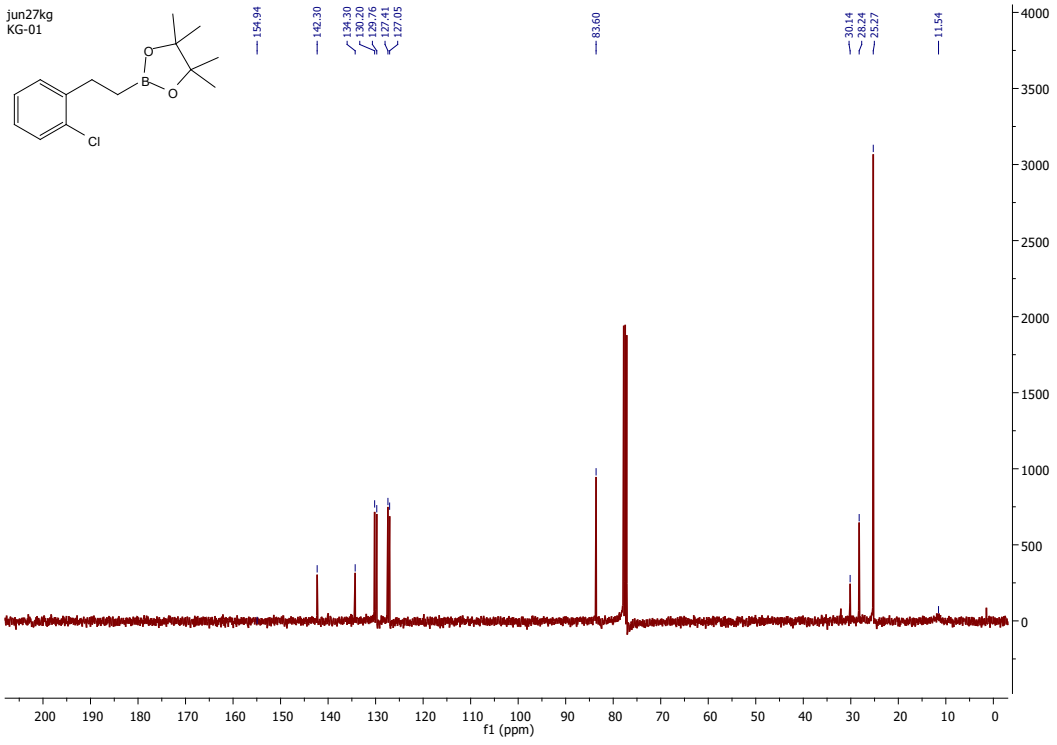


^{11}B NMR of 31b (128 MHz, $CDCl_3$)

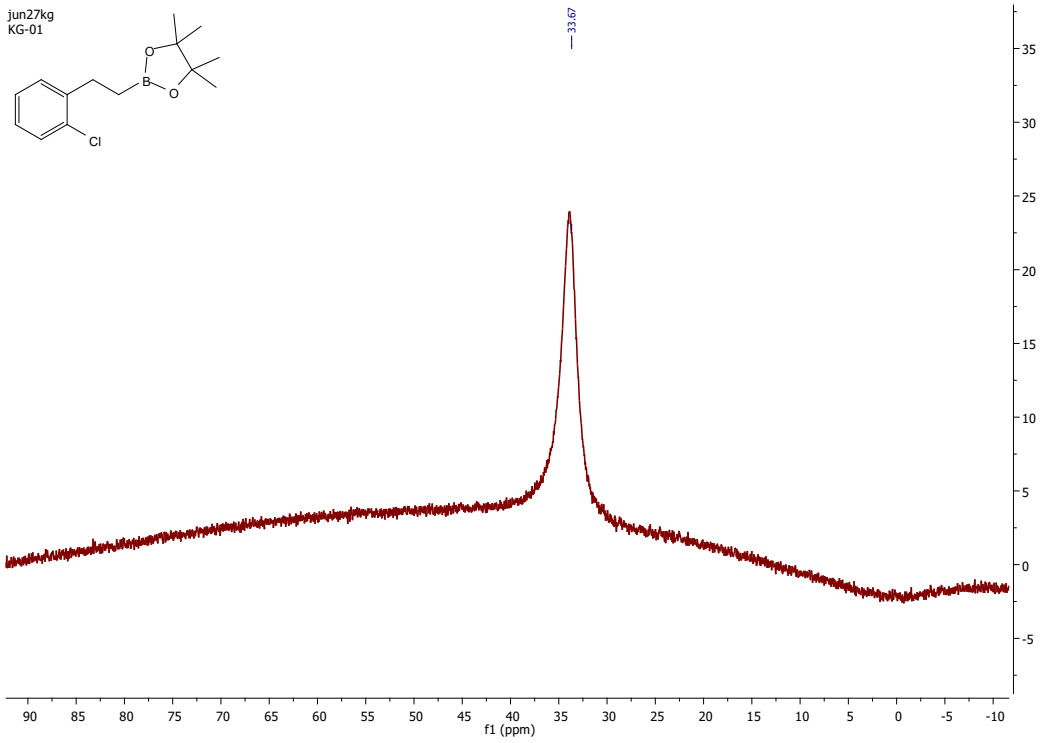
2-(2-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32b)



^{1}H NMR of 32b (500 MHz, $CDCl_3$)

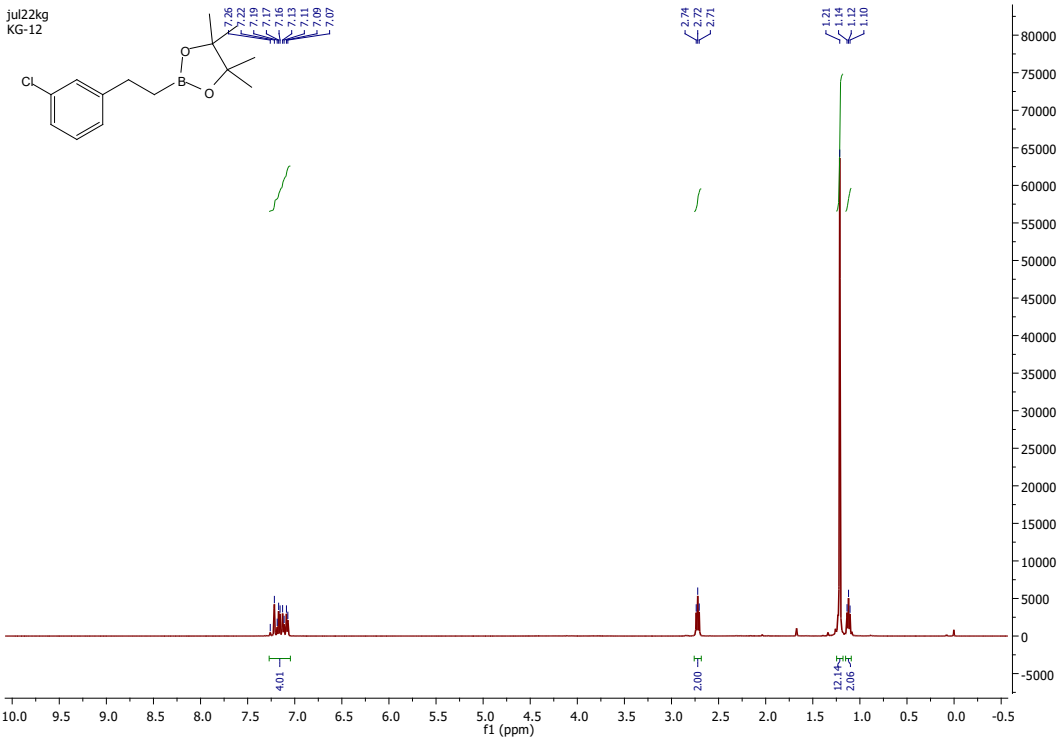


^{13}C NMR of 32b (126 MHz, $CDCl_3$)

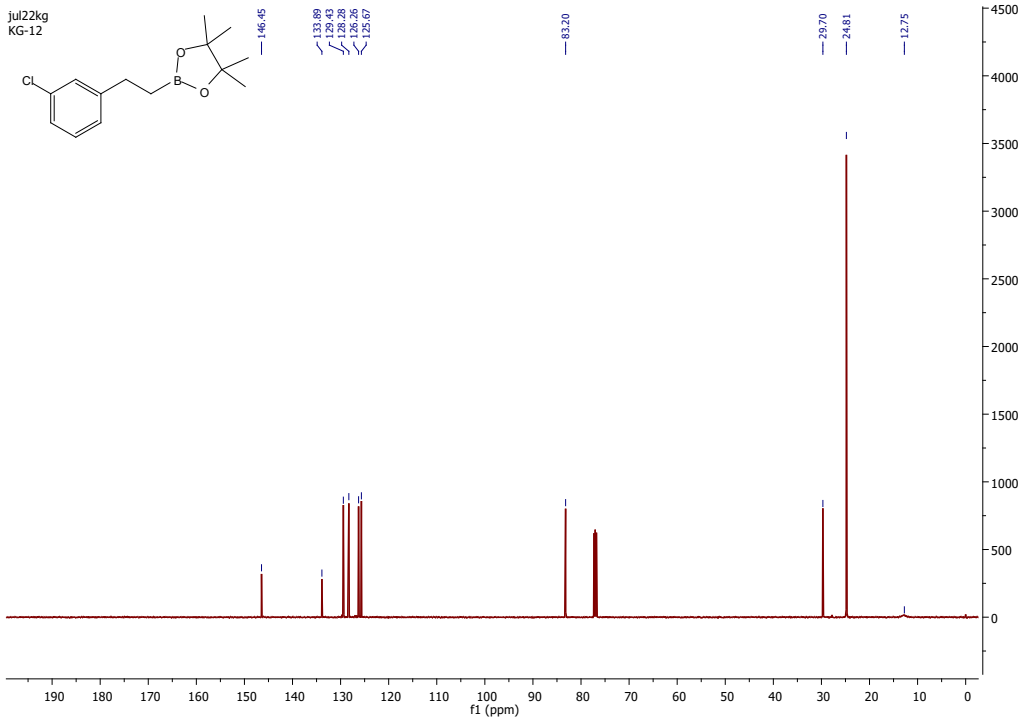


^{11}B NMR of 32b (160 MHz, $CDCl_3$)

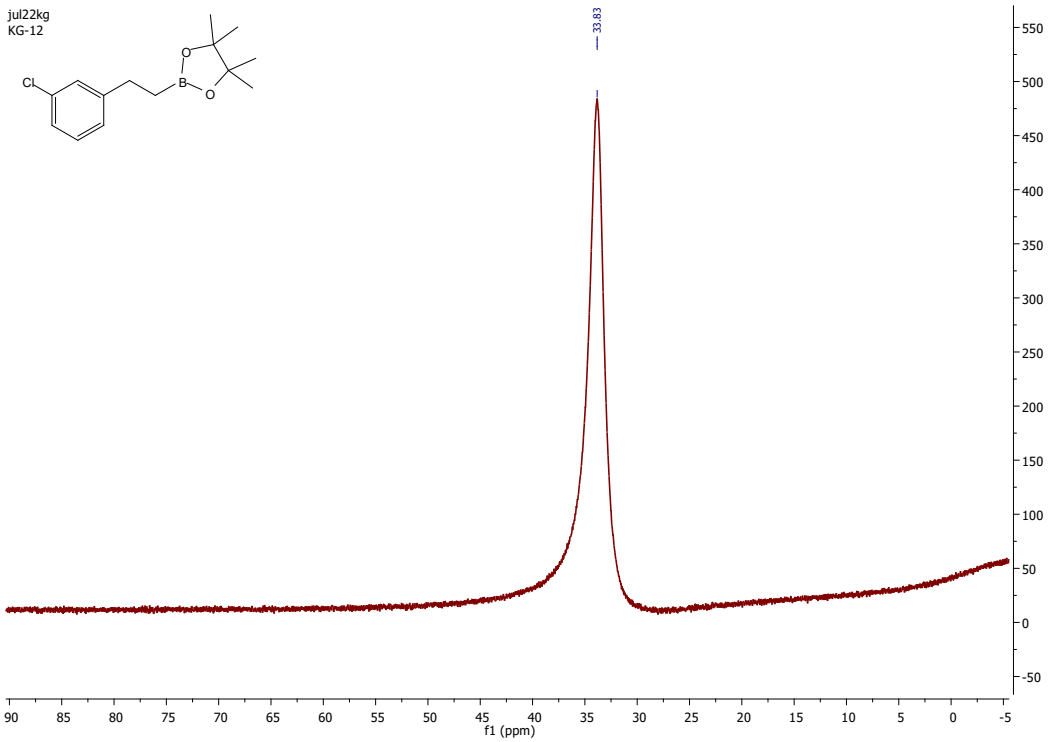
2-(3-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33b)



^{1}H NMR of 33b (500 MHz, $CDCl_3$)



^{13}C NMR of 33b (125 MHz, $CDCl_3$)



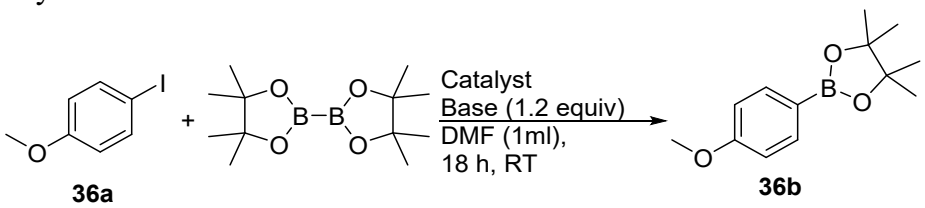
^{11}B NMR of 33b (160 MHz, $CDCl_3$)

XI. Optimization of the Reaction Conditions for Aryl Halides Borylation

Experimental procedure:

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/CNT NPs catalyst (5 mg), B_2pin_2 (76 mg, 0.3 mmol), base (1.2 equiv, 0.3 mmol), 1-iodo-4-methoxybenzene (58 mg, 0.25 mmol) and DMF (1 mL) were added. The reaction mixture was stirred at room temperature for the indicated amount of time. The crude reaction was dissolved in Et_2O (10 mL) and then transferred to a separatory funnel followed by the addition of H_2O (10 mL). The layers were separated, and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

Table S10. Screening of catalyst and base for the nanoparticles catalysed borylation of 1-iodo-4-methoxybenzene.

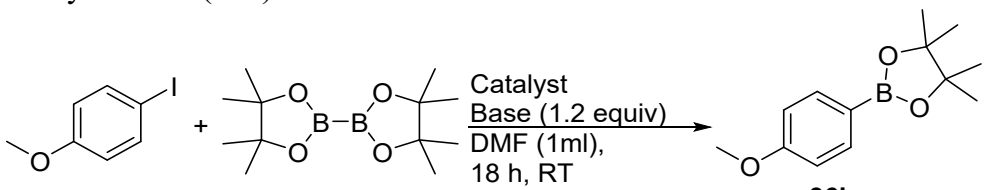


36a **36b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (^oC)	Time (h)	Yield (%)
1	-	DMF	KOMe	1.2	RT	18 h	Trace
2	Cu/CNT	DMF	-	1.2	RT	18 h	Trace
3	Cu/CNT	DMF	KO^{t}Bu	1.2	RT	18 h	47
4	Cu/CNT	DMF	KOEt	1.2	RT	18 h	35
5	Cu/N-CNT[a]	DMF	KOEt	1.2	RT	18 h	61
6	**Cu/CNT**	**DMF**	**KOMe**	**1.2**	**RT**	**18 h**	**62**[b]
7	Cu/CNT	DMF	NaOtBu	1.2	RT	18 h	54
8	Cu/CNT	DMF	NaOEt	1.2	RT	18 h	59
9	Cu/CNT	DMF	NaOMe	1.2	RT	18 h	35

Reaction condition: 0.25 mmol 1-iodo-4-methoxybenzene (**36a**), B_2pin_2 (1.2 equiv), catalyst (5 mg), base (1.2 equiv), DMF (1 mL) for 18 h at room temperature. Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard. [a] Reaction was performed using Cu/N-CNT (5 mg). b [c]Approximate 22% of anisole was estimated by GC-MS analysis.

Table S11. Screening of reaction temperature the nanoparticles catalysed borylation of 1-iodo-4-methoxybenzene (**36a**).



36a **36b**

Entry	Catalyst (NPs)	Solvent	Base	B_2pin_2 (equiv)	Temp (^oC)	Time (h)	Yield (%)
1	**Cu/CNT**	**DMF**	**KOMe**	**1.2**	**RT**	**18 h**	**62**
2	Cu/CNT	DMF	KOMe	1.2	50	18 h	62
3	Cu/CNT	DMF	KOMe	1.2	80	18 h	52

Reaction condition: 0.25 mmol 1-iodo-4-methoxybenzene (**36a**), B_2pin_2 (1.2 equiv), Cu/CNTs (5 mg), KOMe (1.2 equiv), DMF (1 mL) for 18 h at given temperature. Yields were determined by ^1H NMR analysis, using nitromethane as an internal standard.

XII. Substrate Scope of Aryl halides Borylation

Experimental procedure for examples described in Table 6.

General Procedure E. In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/CNT NPs (5 mg), B_2pin_2 (76 mg, 1.2 equiv, 0.3 mmol), KOMe (21 mg, 1.2 equiv, 0.3 mmol), DMF (1 mL) and aryl iodide substrate (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 18 h. The crude reaction was dissolved in Et_2O (10 mL) and then transferred to a separatory funnel followed by the addition of H_2O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

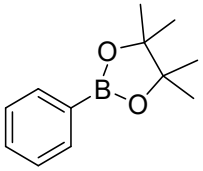
General Procedure F. In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/CNT NPs (5 mg), B_2pin_2 (76 mg, 1.2 equiv, 0.3 mmol), KOMe (21 mg, 1.2 equiv, 0.3 mmol), DMF (1 mL) and aryl bromide substrate (0.25 mmol) were added and the reaction was stirred vigorously at room temperature for 18 h. The crude reaction was dissolved in Et_2O (10 mL) and then transferred to a separatory funnel followed by the addition of H_2O (10 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

General Procedure G. In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu/CNT NPs (20 mg), B_2pin_2 (304 mg, 1.2 equiv, 0.3 mmol), KOMe (84 mg, 1.2 equiv, 0.3 mmol), DMF (5 mL) and aryl halide (1 mmol) were added and the reaction was stirred vigorously at room temperature for 18 h. The crude reaction was dissolved in Et_2O (30 mL) and then transferred to a separatory funnel followed by the addition of H_2O (30 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were

further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography.

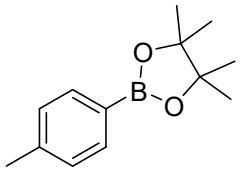
Spectroscopic data

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (34b).[11]



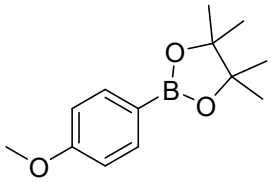
Following general procedure **G**, a colorless liquid in 62% yield (126 mg) from iodobenzene (**34a**, 204 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 10 Hz, 2H), 7.44 (d, J = 10 Hz, 1H), 7.38 (t, J = 7.5, 2H), 1.37 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 134.71, 131.21, 127.67, 83.72, 24.84, 14.10 (C-B; broad). ^{11}B NMR (160 MHz, $CDCl_3$): δ 30.94. GC-MS: m/z 204 (M^+).

4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (35b).[11]



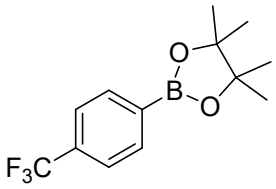
Following general procedure **G**, a colorless liquid in 77% yield (168 mg) from 1-iodo-4-methylbenzene (**35a**, 218 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 10 Hz, 2H), 7.21 (d, J = 5 Hz, 2H), 2.38 (s, 3H), 1.38 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.35, 134.78, 134.57, 128.48, 83.72, 83.57, 83.40, 24.82, 21.68, 14.09 (C-B; broad). ^{11}B NMR (160 MHz, $CDCl_3$): δ 30.69. GC-MS: m/z 218 (M^+).

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36b).[11]



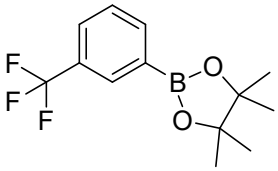
Following general procedure **G**, a colorless liquid in 51% yield (119 mg) from 1-iodo-4-methoxybenzene (**36a**, 234 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 10 Hz, 2H), 6.90 (d, *J* = 10 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.16, 136.52, 133.32, 83.56, 55.09, 24.87. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (160 MHz, $CDCl_3$): *δ* 30.70. GC-MS: m/z 234 (M^+).

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (37b).[11]



Following general procedure **G**, a colorless liquid in 67% yield (182 mg) from 1-iodo-4-(trifluoromethyl)benzene (**37a**, 272 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 5 Hz, 2H), 7.61 (d, *J* = 5 Hz, 2H), 1.36 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 135.00, 132.82 (q, *J* = 32.76 Hz), 124.30 (q, *J* = 3.78 Hz), 124.82 (q, *J* = 273.42 Hz), 84.26, 24.84, 14.10 (C-B; broad). ^{11}B NMR (160 MHz, $CDCl_3$): *δ* 30.29. GC-MS: m/z 272 (M^+).

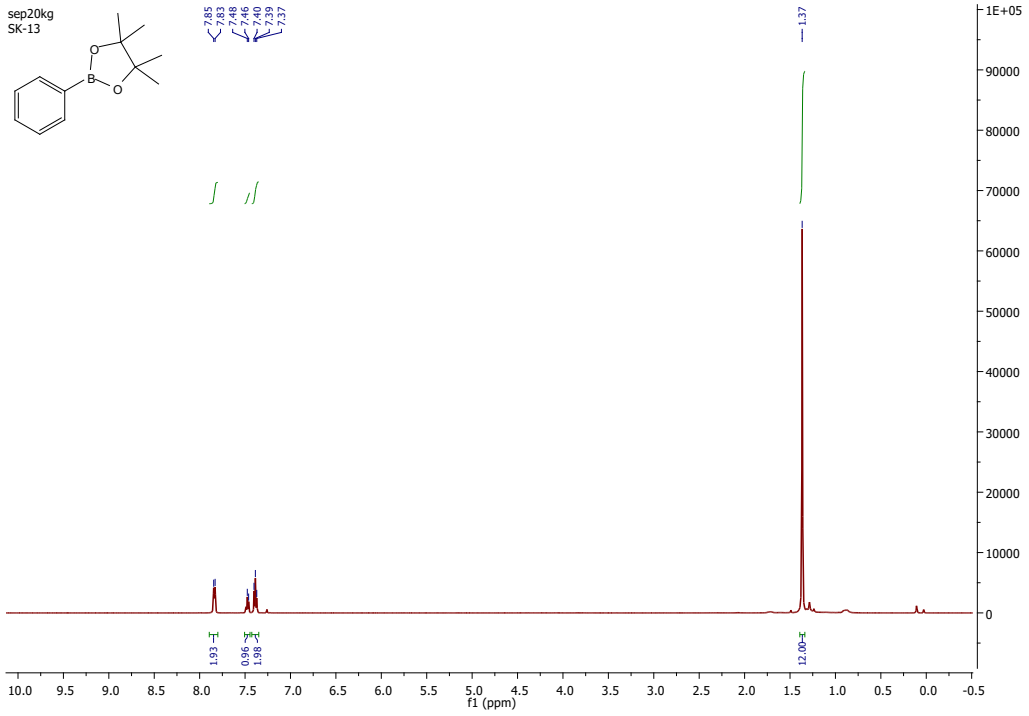
4,4,5,5-Tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (38b).[12]



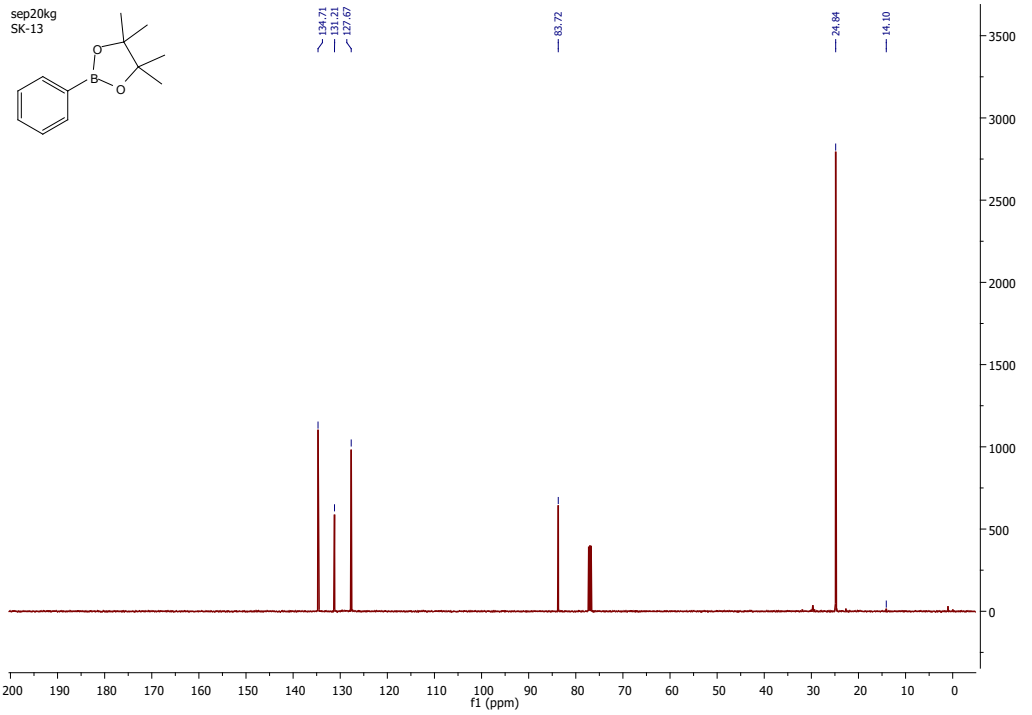
Following general procedure **G**, a colorless liquid in 71% yield (193 mg) from 1-iodo-3-(trifluoromethyl)benzene (**38a**, 272 mg, 1 mmol) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.98 (d, *J* = 10 Hz, 1H), 7.70 (d, *J* = 10 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H) 1.36 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): 13C NMR (126 MHz, $CDCl_3$) δ 137.99, 131.34 (q, *J* = 3.78 Hz), 130.03 (q, J = 31.5 Hz), 128.01, 127.76 (q, J = 3.78 Hz), 124.28 (q, J = 273.42 Hz), 84.26, 24.84, 14.10. (C-B; broad). ^{11}B NMR (160 MHz, CDCl3): *δ* 30.94. GC-MS: m/z 272 (M^+).

XIII. NMR Spectra of Aryl halides Borylation Products

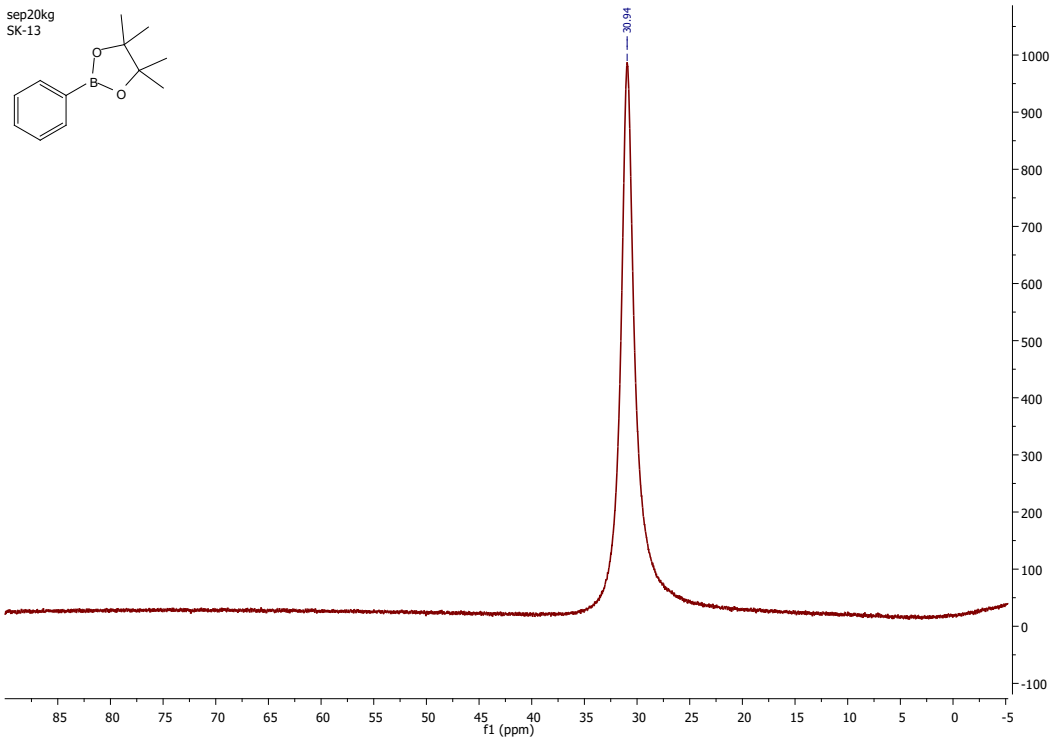
4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (34b)



^{1}H NMR of 34b (500 MHz, $CDCl_3$)

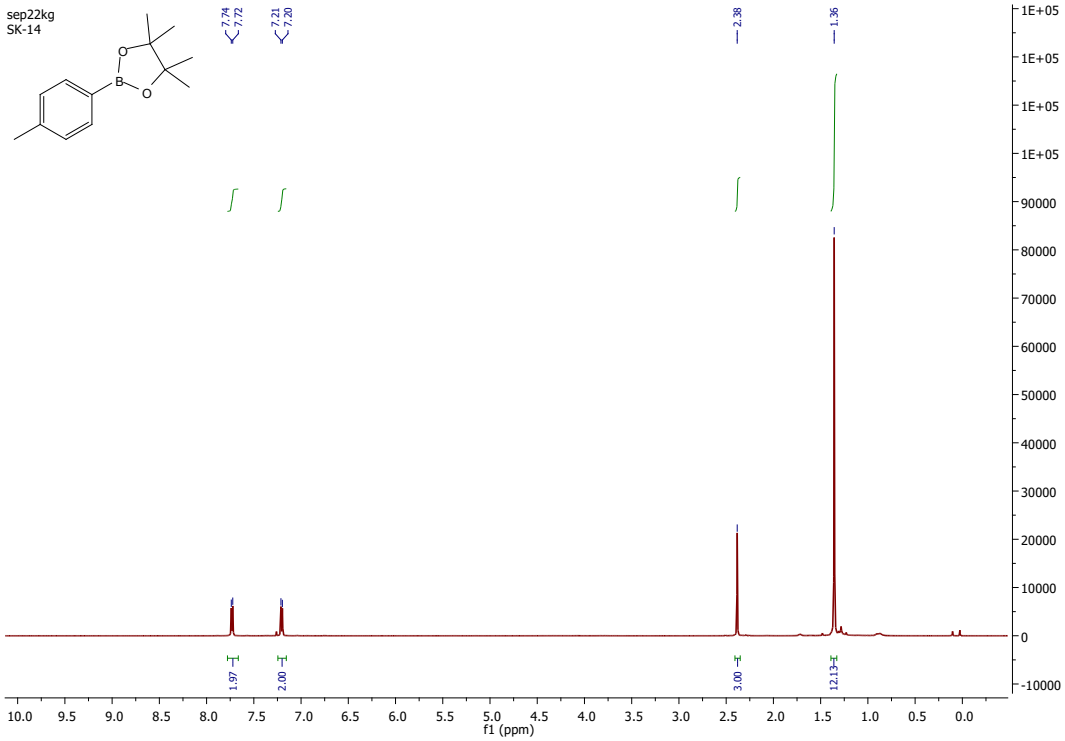


^{13}C NMR of 34b (126 MHz, $CDCl_3$)

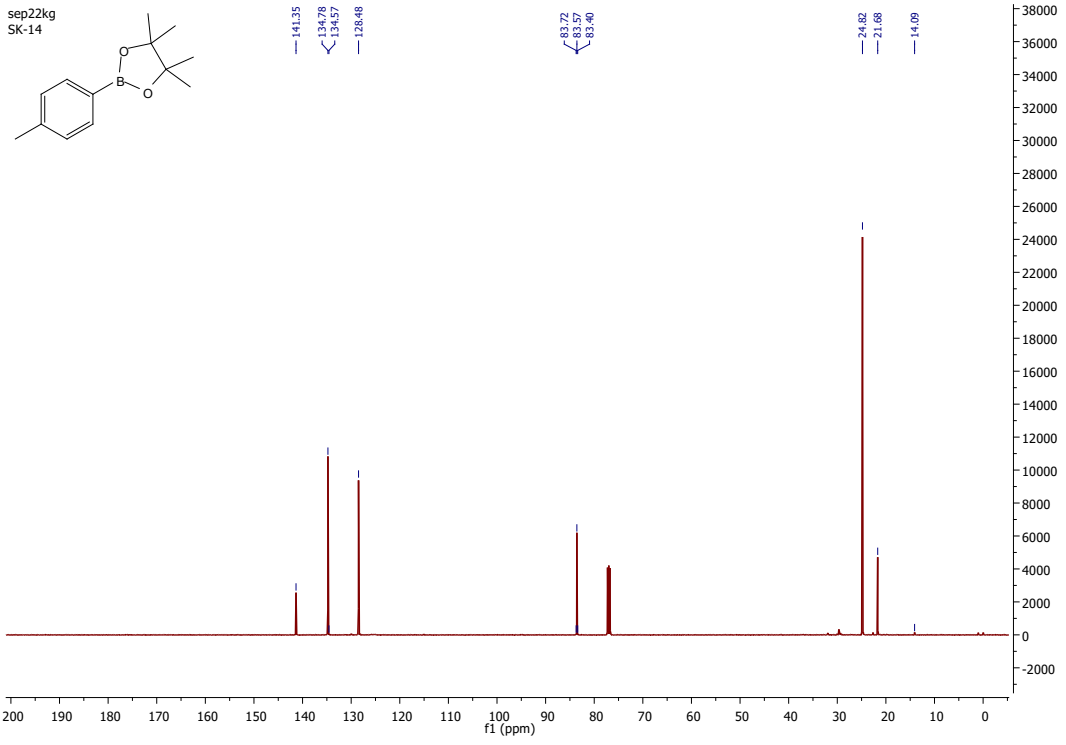


^{11}B NMR of 34b (160 MHz, $CDCl_3$)

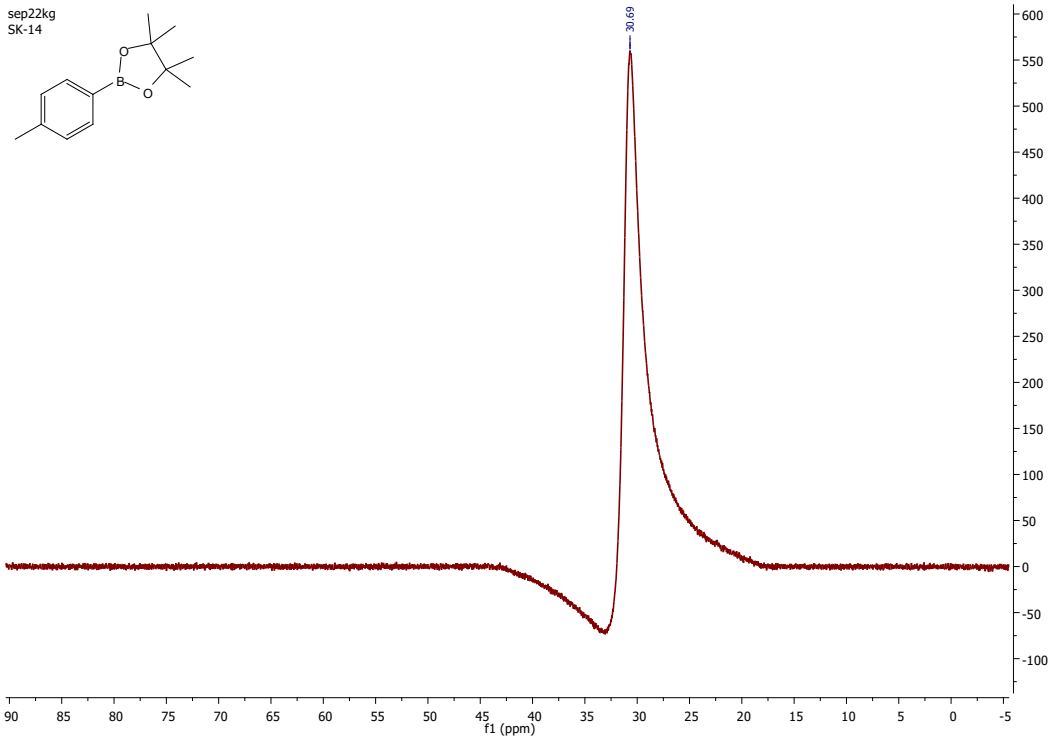
4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (35b)



^{1}H NMR of 35b (500 MHz, $CDCl_3$)

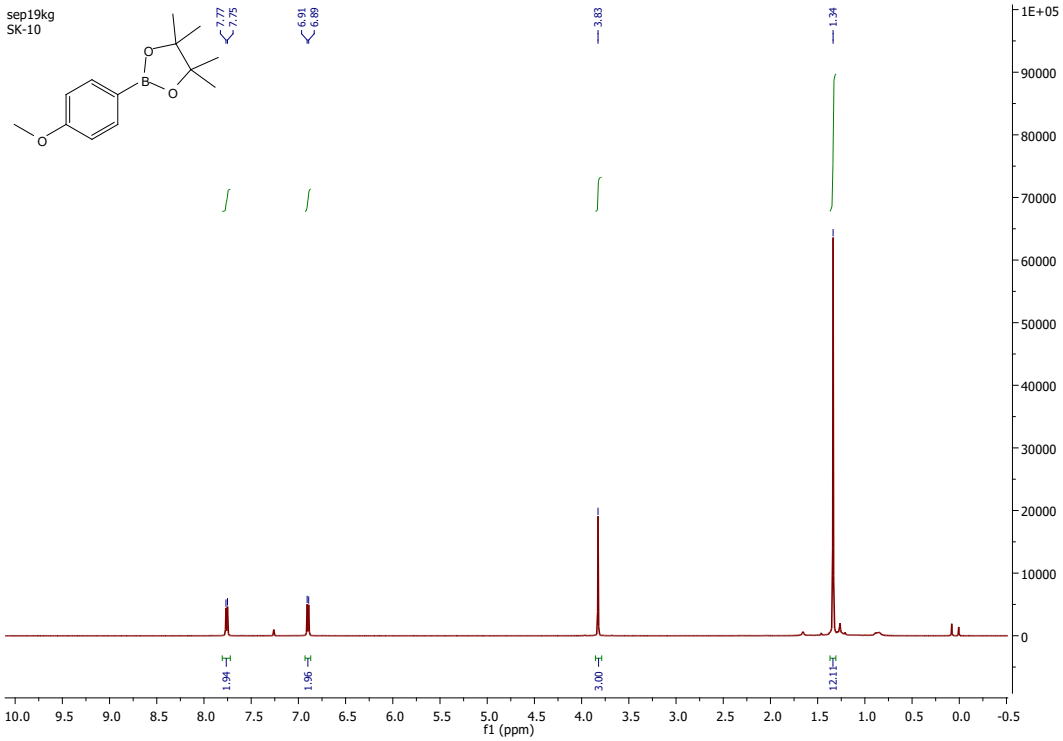


^{13}C NMR of 35b (126 MHz, $CDCl_3$)

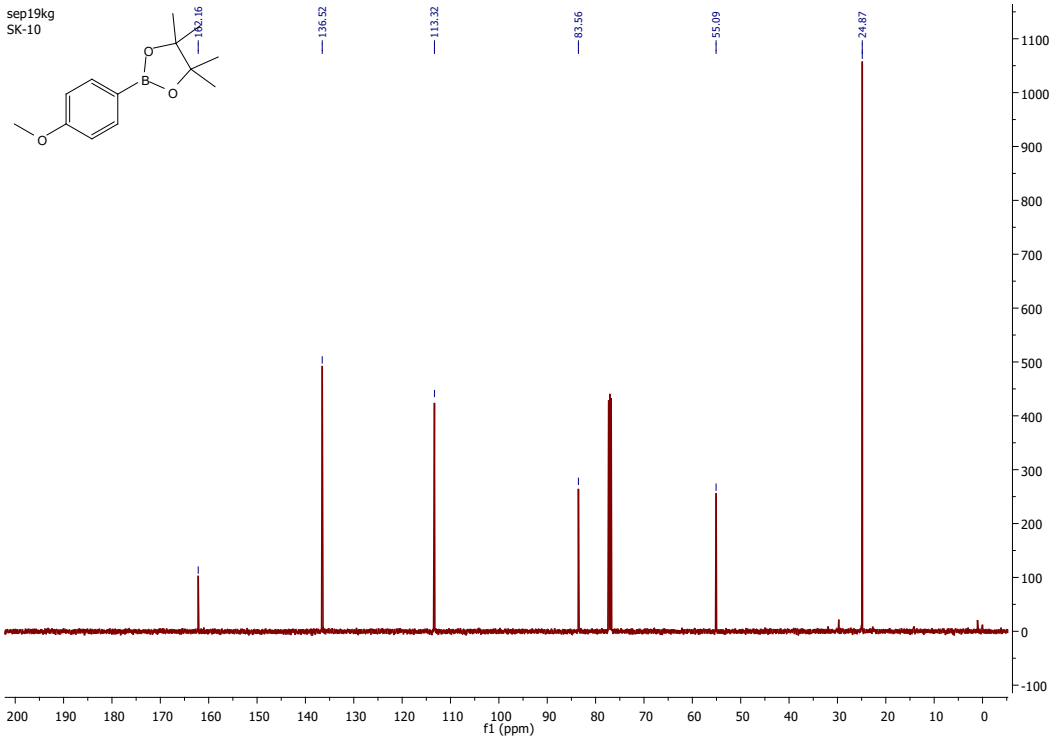


^{11}B NMR of 35b (160 MHz, $CDCl_3$)

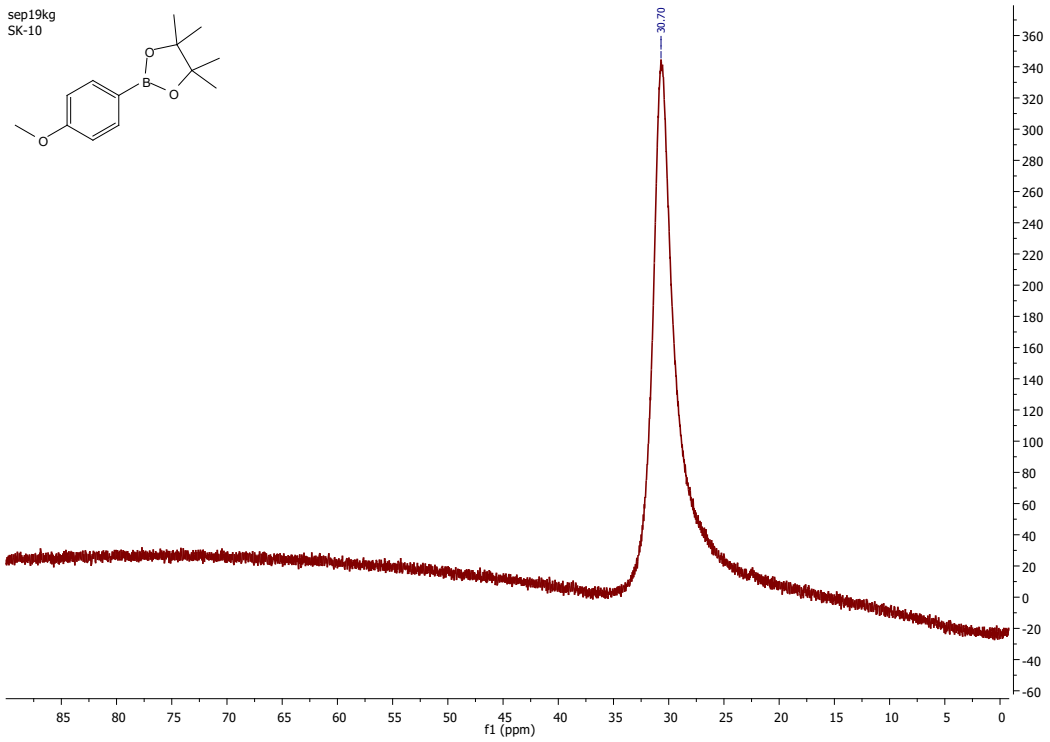
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36b)



^{1}H NMR of 36b (500 MHz, $CDCl_3$)

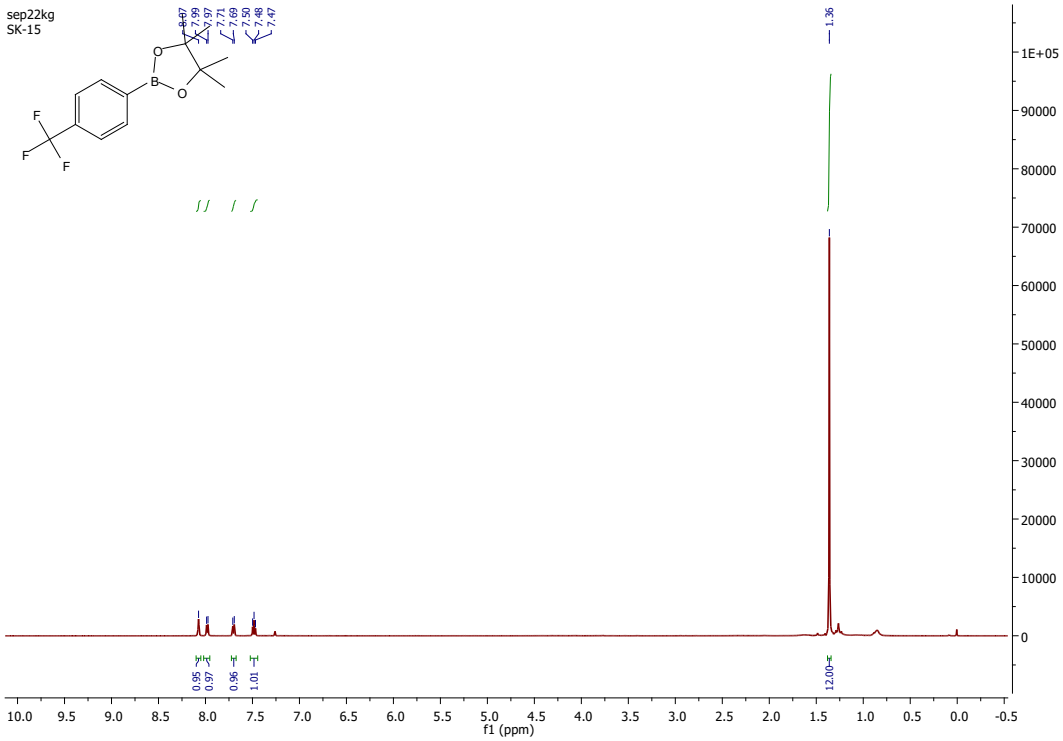


^{13}C NMR of 36b (126 MHz, $CDCl_3$)

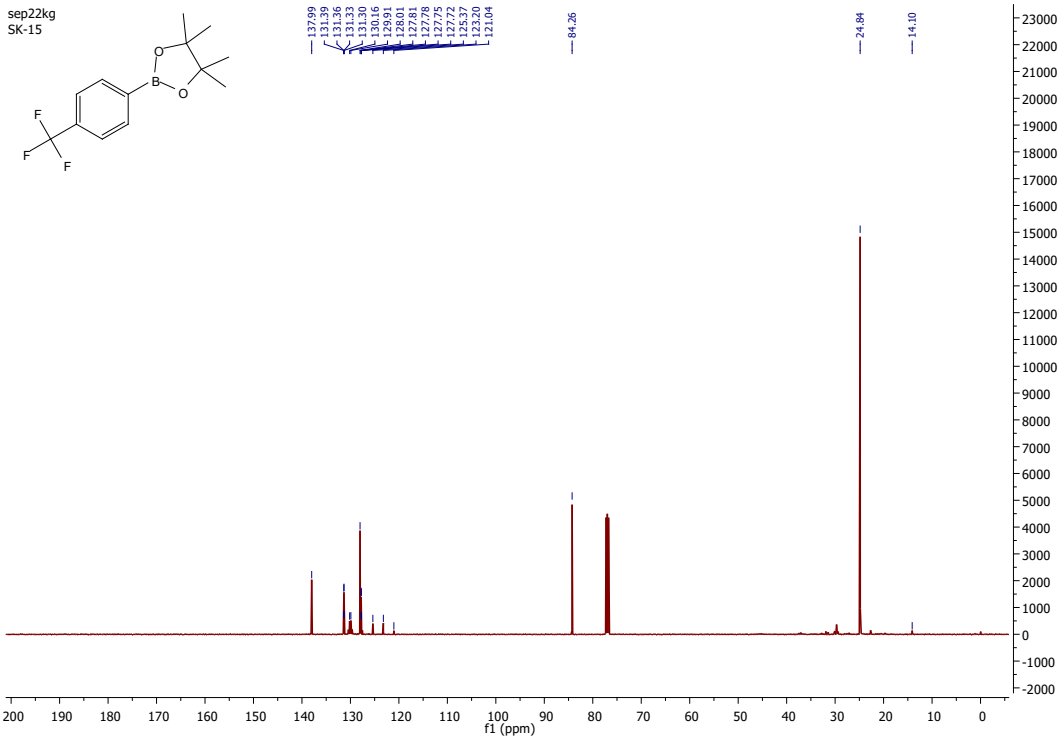


^{11}B NMR of 36b (160 MHz, $CDCl_3$)

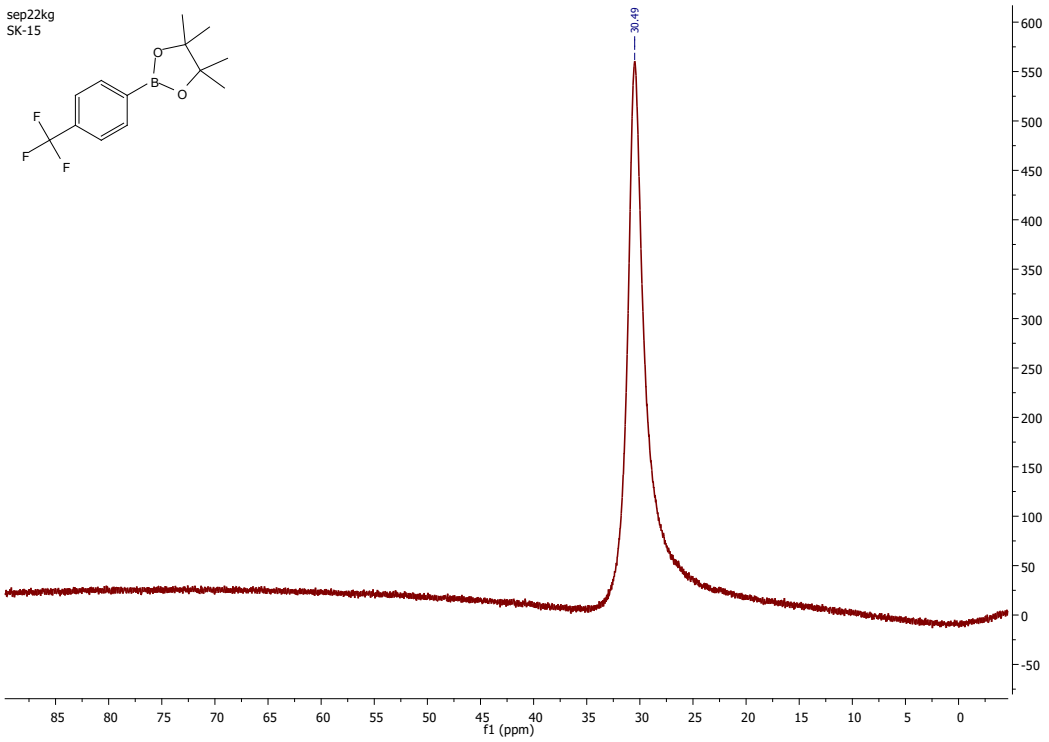
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (37b)



^{1}H NMR of 37b (500 MHz, $CDCl_3$)

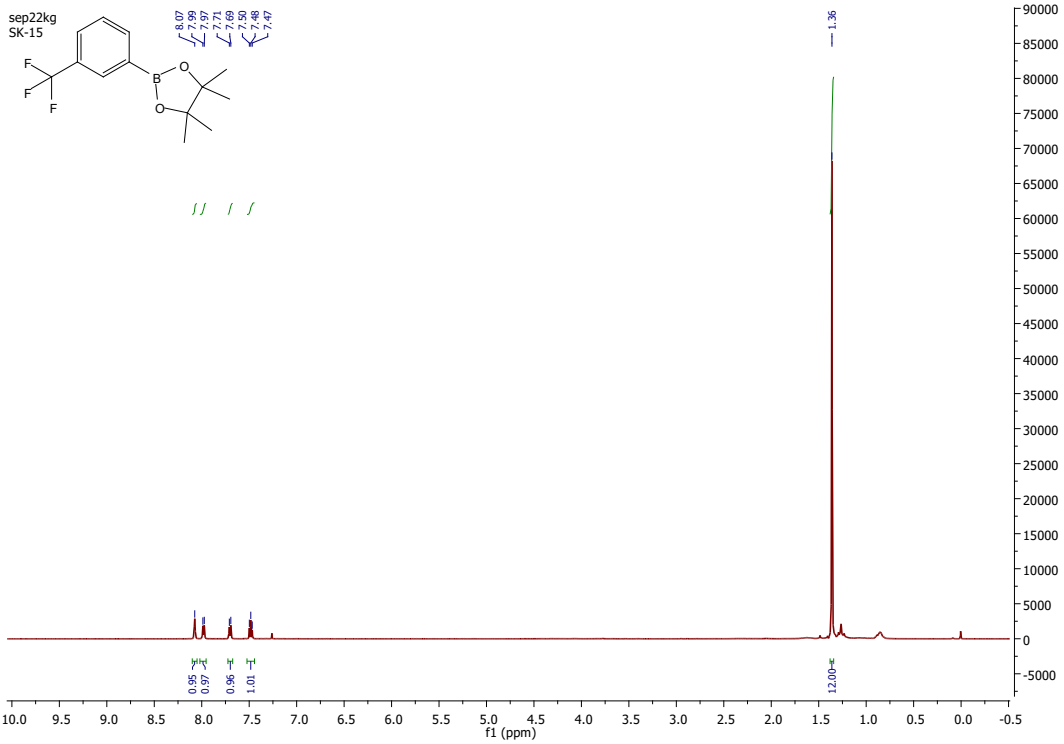


^{13}C NMR of 37b (126 MHz, $CDCl_3$)

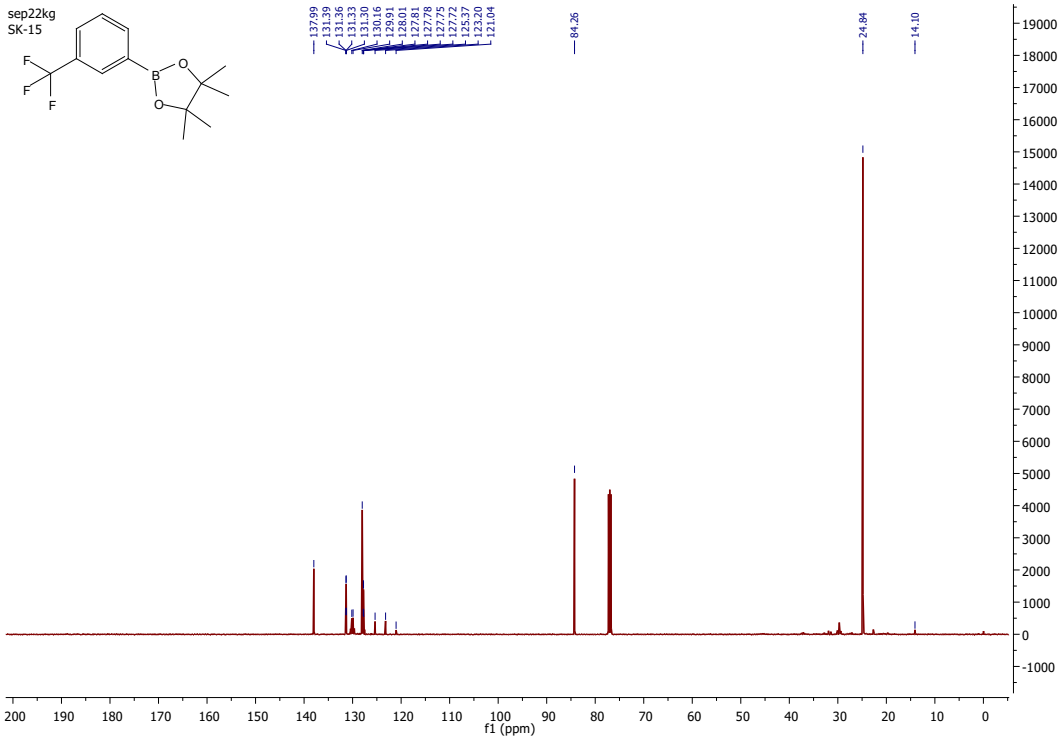


^{11}B NMR of 37b (160 MHz, $CDCl_3$)

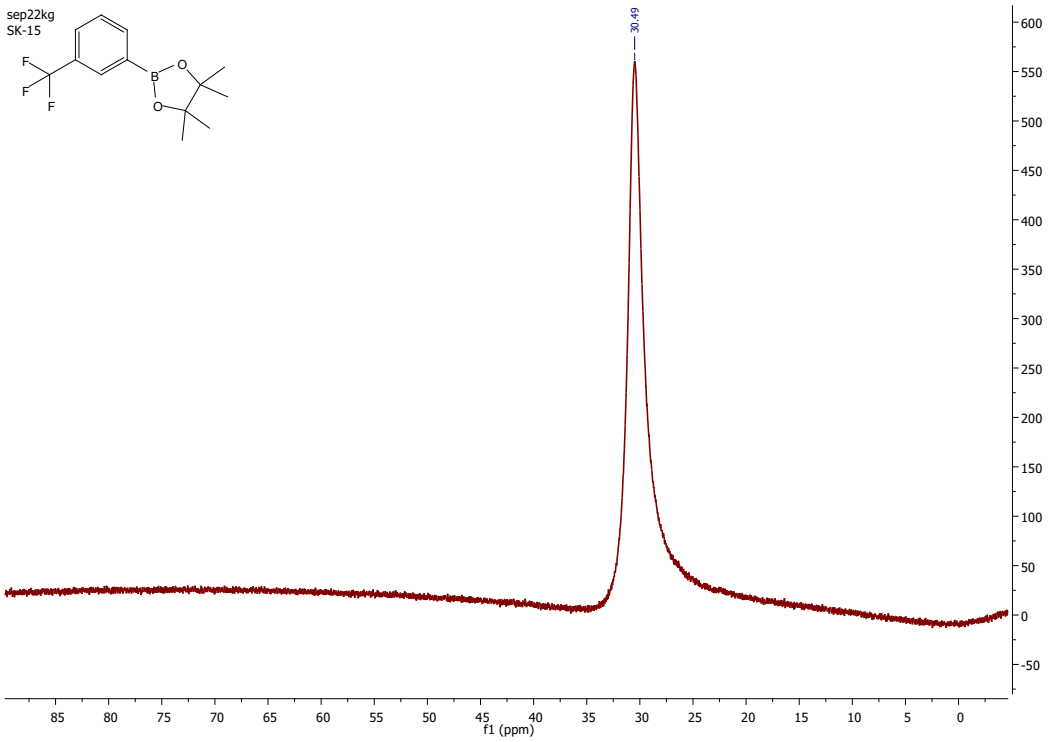
4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (38b)



^{1}H NMR of 38b (500 MHz, $CDCl_3$)



^{13}C NMR of 38b (125 MHz, $CDCl_3$)



^{11}B NMR of 38b (160 MHz, $CDCl_3$)

XIV. Computational Details

We have performed density functional theory (DFT) based calculations using Quantum Espresso Code.[10] We have used the following ultrasoft pseudopotential to define the atomic wavefunction, C.pbe-rrkjus.UPF, N.pbe-n-rrkjus_psl.1.0.0.UPF, O.pbe-n-rrkjus_psl.1.0.0.UPF, B.pbe-n-rrkjus_psl.1.0.0.UPF, Br.pbe-n-rrkjus_psl.1.0.0.UPF, H.pbe-rrkjus_psl.1.0.0.UPF and Cu.pbe-dn-rrkjus_psl.1.0.0.UPF. To define the exchange and correlation, Perdew–Burke – Ernzerh (PBE) functional is used.[11,12] For all the optimization and self-consistent field (scf) calculations, we have used energy cut-off (ecut) 35 Ry and ecutrho 350 Ry. We have optimized all the structures until the energy conversion threshold 10^{-6} Ry and force convergence of 10^{-5} Ry are achieved. To incorporate van-der-Waal's interaction, we have incorporated the DFT-D2 method.[13] We have used (7 x 7 x 1) Monkhorst Pack mesh to define the Brillion zone. To avoid the interaction with repeated image/layers, we have used 15 Å vacuum along the z-axis. Also, to calculate zero-point energy (ZPE) and entropy term (TS), we have performed the phonon calculation to know the vibrational frequency. The details of the ZPE and TS terms are given in supporting information.

We have calculated the zero-point energy (ZPE) and TS value are calculated using following formula:

Zero-point energy (ZPE) and entropy (S) obtained using single point calculations using the equations

$$\text{ZPE} = \sum_i \frac{\hbar \nu_i}{2} \qquad \ldots (1)$$

$$S = k_B T \sum_i \left[\frac{\hbar\nu_i}{k_B T(e^{\hbar\nu_i / k_B T} - 1)} - \ln\left(1 - e^{-\hbar\nu_i / k_B T}\right) \right] \quad \ldots (2)$$

Here ν_i , $\hbar$, k_B and T denote, vibrational frequencies, reduced Planck's constant, Boltzmann constant and temperature respectively; where we have considered T = 300°C.

Electron localization function (ELF)

The free molecule can be considered as free radical, due to its high reactivity towards any other species and the charge density and electron localization function (ELF) can infer this. To confirm the free lone pair, we have performed the ELF calculation for B_2pin_2, Bpin and Alkyl-Br. The plot of ELF clearly demonstrate that the Br is associated with lone pair, whereas Bpin and B_2pin_2 does not having any free lone pair. In the colour scale of ELF plot, blue and red colour indicates no electron and all electron associates with atom. Along with ELF, we have also shown the total charge density for the same structures (Fig. S10 (a), (b) and (c)).

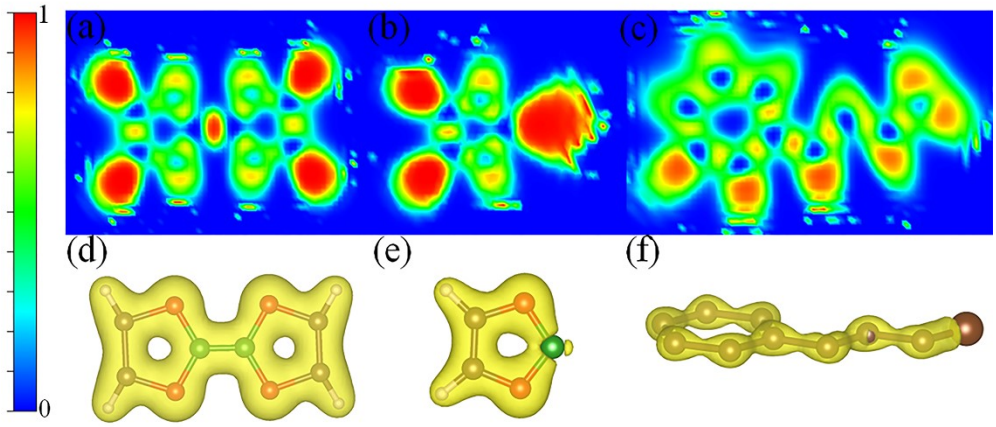


Figure S10. (a), (b) and (c) Demonstrate the electron localization function (ELF) plot for B_2Pin_2, PinB and Alkyl-Br, respectively. (d), (e) and (f) Demonstrate the charge density difference for the

same structure respectively. Here, in colour scale, blue and red colour indicates no electron and all electron localization around atoms.

DFT calculation using CuO cluster as a model:

In the formation of alkyl boronate ester, the main objective is the estimation of the potential determining step (PDS) and, required overpotential. For the formation of alkyl-Bpin product on copper nanoparticles, we have considered the CNT (5,5) as the host surface and alkyl bromide (alkyl-Br), and B_2pin_2 free radicals. The crystal structure of N-doped CNT is shown in the inset of Fig. S11 (step 1), where we have considered N-doped CNT along with alkyl-Br as a free radical and B_2pin_2 as molecule as a reference to plot the profile. We have observed that CuO cluster followed the chemisorption process and adsorbed strongly on the N-CNT surface with the free energy change of –0.19 eV (step 2) and is named CuO@N-CNT. The optimized structure of adsorbed CuO cluster on the N-CNT surface is shown in Fig. S11. In step 3, the adsorption of alkyl-Br (substrate) on CuO@N-CNT surface is considered, which follows endothermic process with a change in free energy of 0.24 eV. This step is found to be the potential determining step (PDS). In step 4, alkyl-Br* to (Bpin-Alkyl-Br)* is taken into account and we observed that the conversion reaction is exothermic (-0.08 eV), which could be the main reason for CuO@N-CNT as an excellent host for the borylation reaction. Finally, to get the desire product (alkyl-Bpin), the step 5 is exothermic in nature (-0.02 eV; step 5). Overall, the reaction energy for the borylation is exothermic and the free energy profile for all the steps is shown in Fig. S11.

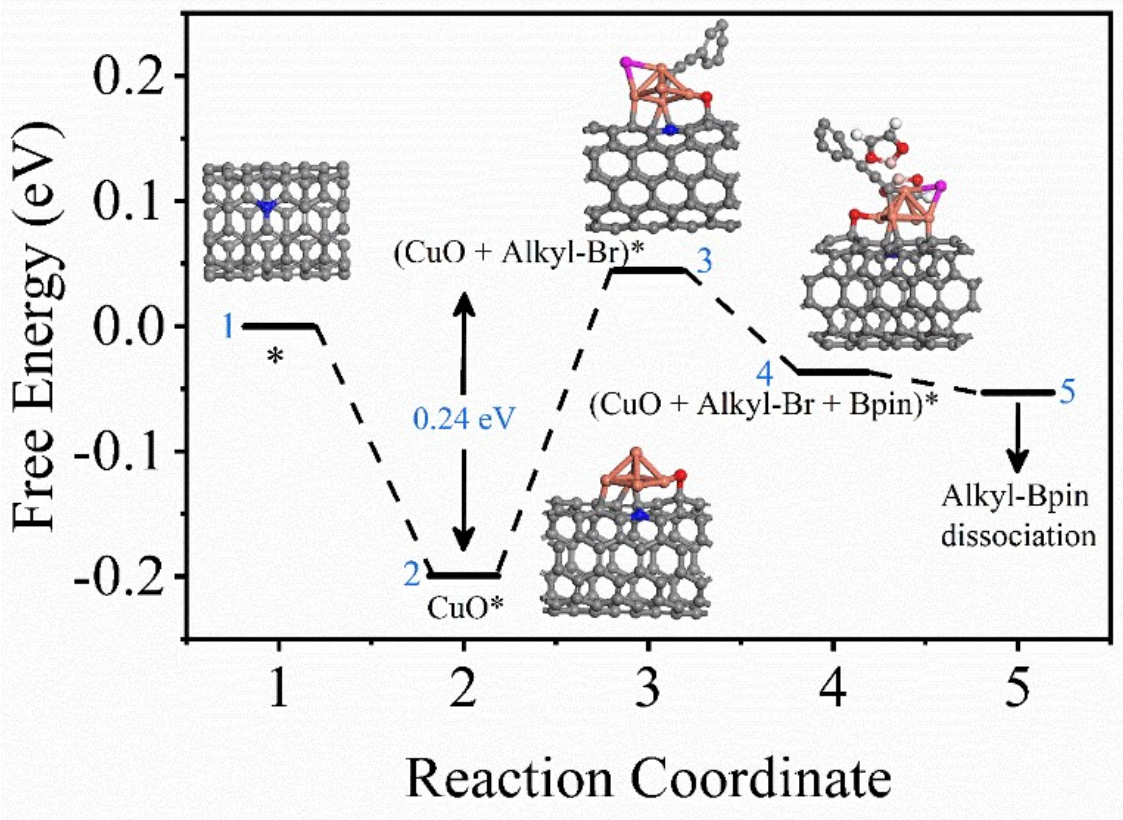


Fig. S11. The free energy profile for the formation of alkyl boronate ester on CuO cluster@N-CNT surface. Structures in the inset (N-CNT in Step 1, alkyl-Br in Step 3 and B_2pin_2 in Step 4) shows the N-doped CNT and free radical molecules.

The detailed mechanism about the reaction step which was followed in plotting complete free energy profile is as follows.

Step 1- * + CuO + B_2Pin_2 + Alkyl-Br

Step 2- CuO* + B_2Pin_2 + Alkyl-Br

Step 3- (CuO + Alkyl-Br)* + B_2pin_2

Step 4- (CuO + Alkyl-Br)* + Bpin + Bpin

Step 5- (CuO + Br)* + Alkyl-Bpin + Bpin

DFT calculation using single Cu atom as a model:

For the formation of alkyl-Bpin product on copper nanoparticles, we have considered the CNT (5,5) as the host surface and alkyl bromide (alkyl-Br), and B_2pin_2 free radicals. The crystal structure of N-doped CNT is shown in the inset of Fig. S12 (step 1), where we have considered N-doped CNT along with free radicals alkyl-Br, and B_2pin_2 as a reference to plot the profile. We have observed that CuO followed the chemisorption process and adsorbed strongly on the N-CNT surface with the free energy change of -1.19 eV (step 2) and is named CuO@N-CNT. The optimized structure of adsorbed CuO molecule on the N-CNT surface is shown in Fig. S13a. In step 3, the adsorption of B_2pin_2 free radical on CuO@N-CNT surface is considered, which follows endothermic process with a change in free energy of 0.81 eV. This step is found to be the potential determining step (PDS). In step 4, $B_2pin_2^*$ to (Bpin-Alkyl-Br)* is taken into account and we observed that this conversion needs very lower energy (0.54 eV), which could be the main reason for CuO@N-CNT as an excellent host for the borylation reaction. Finally, to get the desire product (alkyl-Bpin), the step 5 is exothermic in nature (-0.99 eV; step 5). Overall, the reaction energy for borylation is exothermic and the free energy profile for all the steps is shown in Fig. S12. The optimized crystal structures for step 2 to step 5 are demonstrated in Fig. S13.

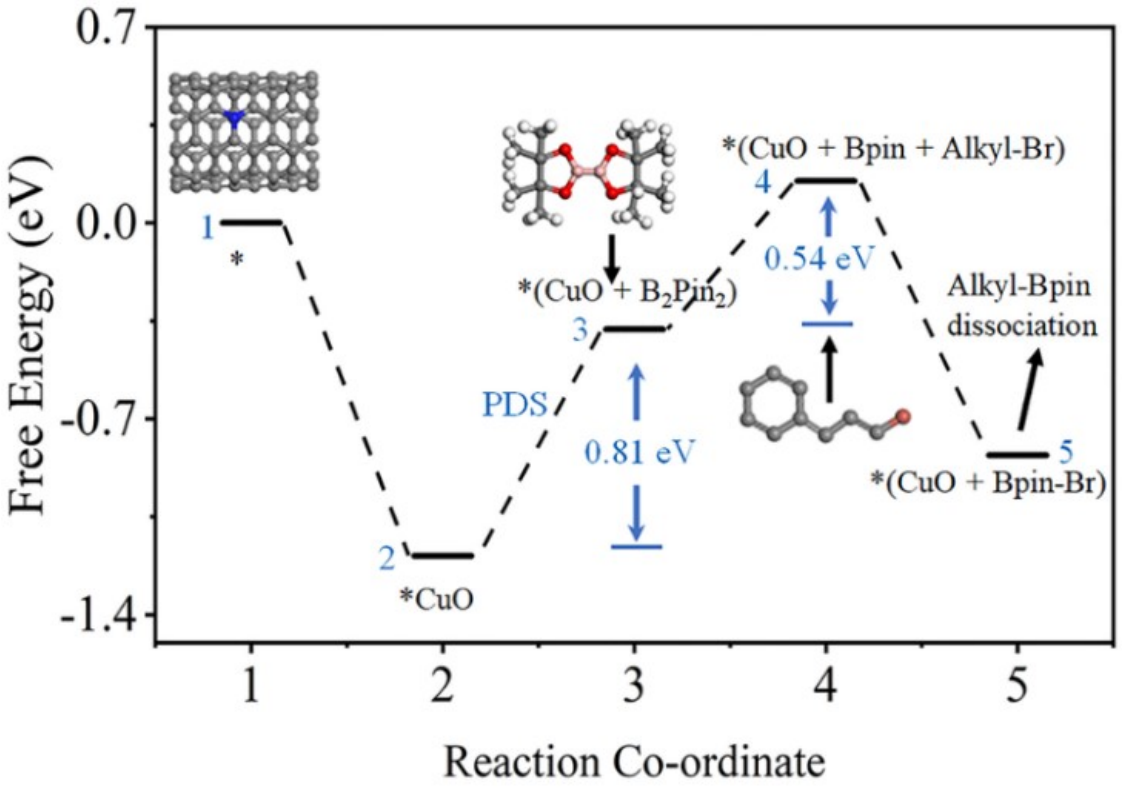


Fig. S12. The free energy profile for the formation of alkyl boronate ester on CuO@N-CNT surface. Structures in the inset (N-CNT in Step 1, B_2pin_2 in Step 3 and Alkyl-Br in Step 4) shows the N-doped CNT and free radical molecules.

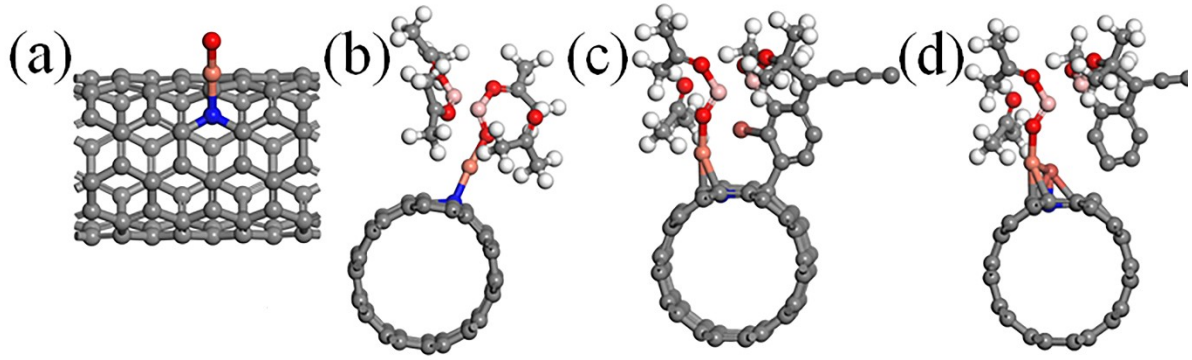


Figure S13. Optimized crystal structure for step 2 to step 5.

The detailed mechanism about the reaction step which was followed in plotting complete free energy profile is as follows.

Step 1- * + CuO + B_2pin_2 + Alkyl-Br

Step 2- CuO* + B_2pin_2 + Alkyl-Br

Step 3- (CuO + Bpin)* + Bpin + Alkyl-Br

Step 4- (CuO + Bpin + Alkyl-Br)* + Bpin

Step 5- (CuO + Bpin + Br)* + Alkyl-Bpin

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