Supporting Information

Efficient Synthesis of Alkylboronic Esters *via* Magnetically Recoverable Copper Nanoparticle-Catalyzed Borylation of Alkyl Chlorides and Bromides

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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. KG. 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 JEOL transmission electron microscope operating at 200 kV after casting a drop of nanoparticle dispersion in isopropyl alcohol over Cu grid. ICP-MS data were obtained with a Thermo Scientific™ iCAP Q ICP-MS. 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. The alkyl halides, 1-(6-chlorohexyl)-1H-indole,[1] 1-(3-bromobutyl)-4-methoxybenzene[2] and 9-(6-chlorohexyl)-9H-carbazole[3] were prepared according to literature procedures.

II. Synthesis and Characterization of Fe-DOPA-Cu Catalyst

Synthesis of Fe-DOPA-Cu Catalyst
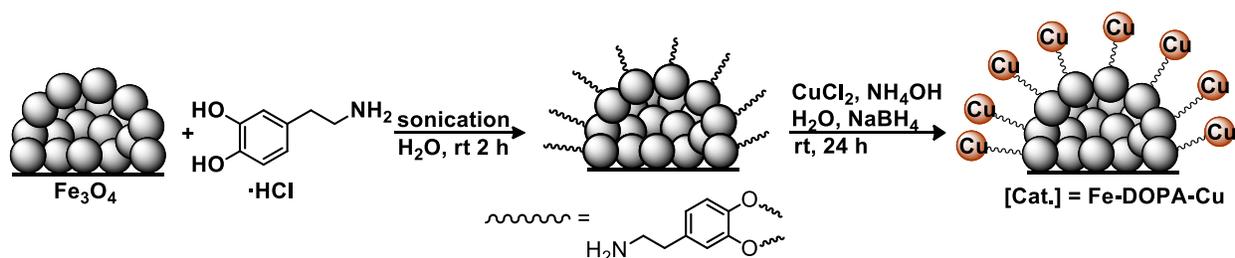
Scheme S1: Synthesis of nano-ferrite copper catalyst (Fe-DOPA-Cu).[4]

Step I: Preparation of magnetic ferrites/Fe₃O₄:

$FeSO_4 \cdot 7H_2O$ (13.9 g) and $Fe_2(SO_4)_3$ (20 g) were dissolved in 500 mL water in 1000 mL beaker in this ammonium hydroxide (25%) was added dropwise to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 60 °C. The precipitated nanoparticles were separated magnetically, washed with water until the pH reached 7, and then dried under vacuum at 60 °C for 2 h gives magnetic nano-ferrite (Fe_3O_4). The FE-SEM image shown in Figure S1 (a), displayed quite uniform spherical morphology of nanoparticles and the EDX analysis confirms presence of Fe and O elements only (Figure S1 (b)). The IR spectrum of prepared Fe_3O_4 nanoparticles is shown in Figure S2 (a). A strong peak at around 590 cm^{-1} is related to Fe-O stretching frequency and XRD pattern confirms the formation of single-phase Fe_3O_4 nanoparticles (Figure S2 (b)).
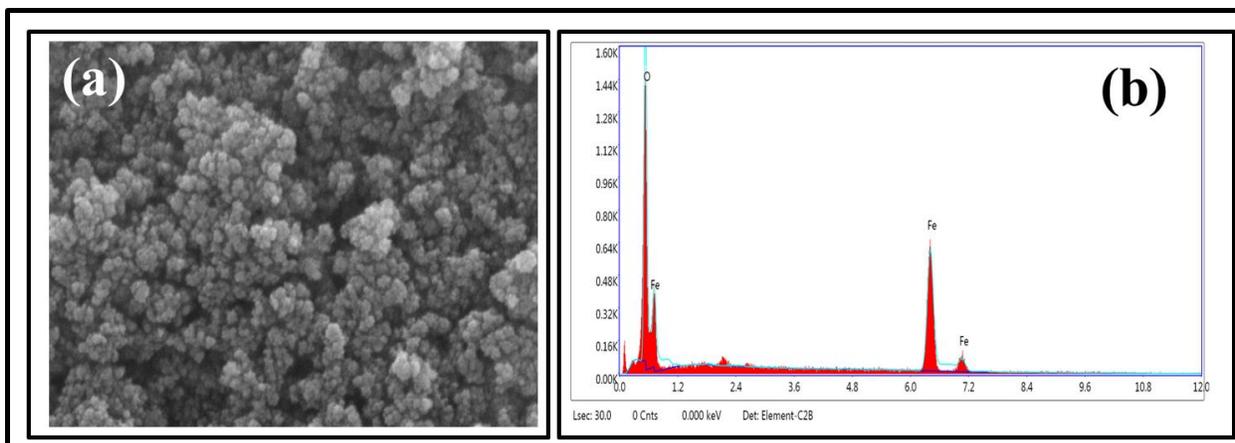
Figure S1: (a) Scanning Electron Microscopy (SEM) images of Fe_3O_4 catalyst size at 100 nm, (b) EDX spectrum of Fe_3O_4 NPs.
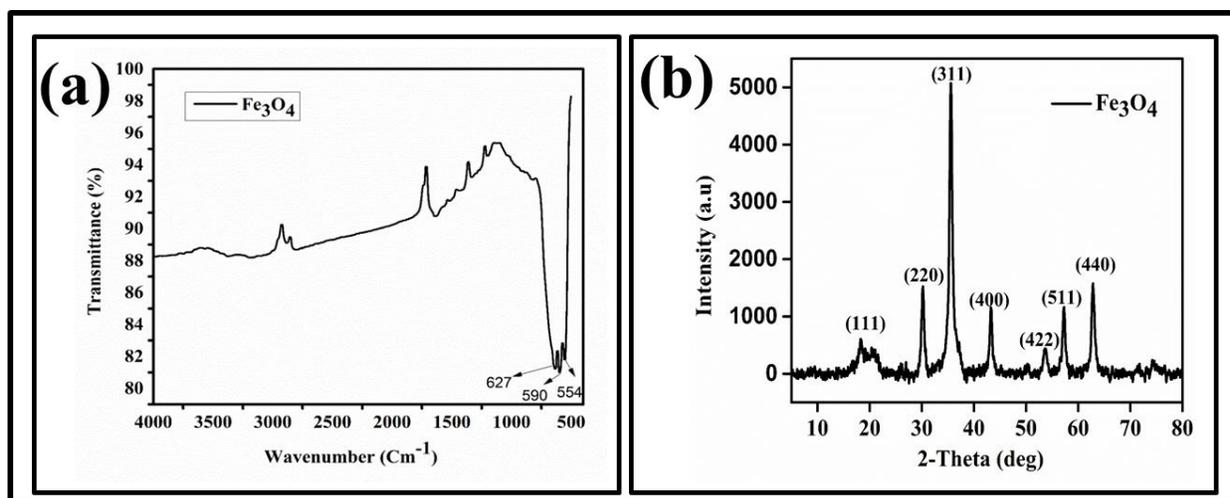
Figure S2: (a) FT-IR spectrum of Fe_3O_4 NPs, (b) Powder XRD pattern of Fe_3O_4 nanoparticles.

Step II: Preparation of Nano-Fe-DOPA:

Fe_3O_4 (2 g) magnetic nanoparticles were dispersed in 25 ml of distilled water by sonication for 30 min. The dopamine hydrochloride (1 g) was dissolved in 5 mL of distilled water and was added to the dispersed ferrite magnetic nanoparticle, followed by sonicated the mixture for 2 h. The nanomaterial was then precipitated using acetone. The nano-Fe-DOPA magnetic nanoparticle was then isolated by centrifugation and successively washed with water and ethanol and dried in vacuum at 60 °C for 2 h. The amine functionalized nano-Fe_3O_4 was characterised by FT-IR spectroscopy (Figure S3(b)). FT-IR spectra confirmed the anchoring of DOPA on ferrite surfaces (Scheme S3).[5]
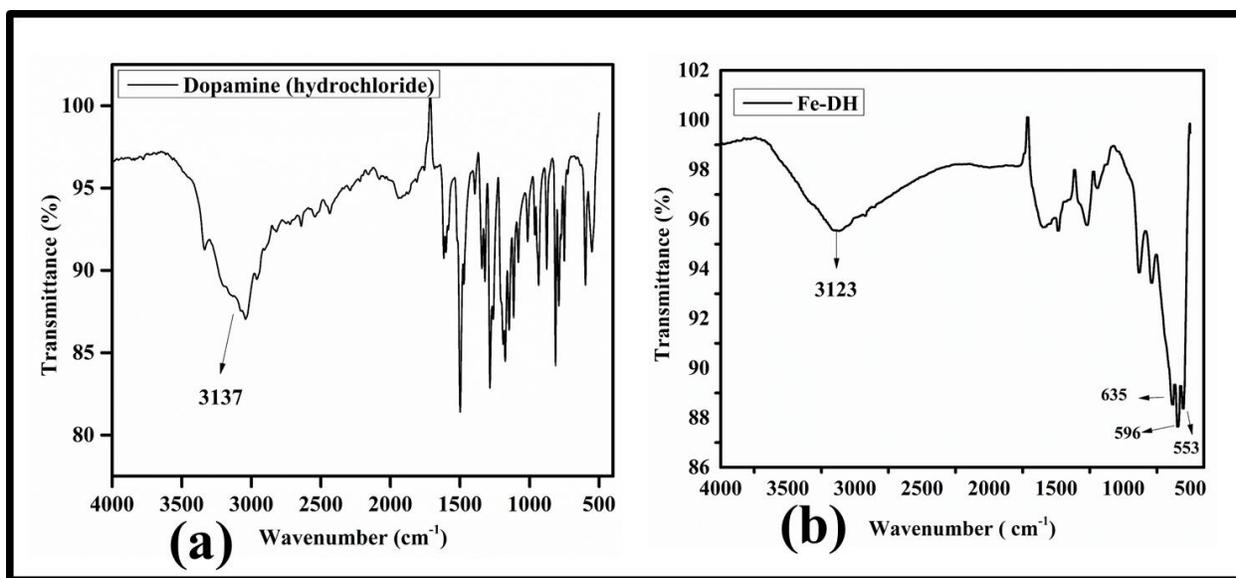
Figure S3: (a) FT-IR spectrum of dopamine hydrochloride. (b) FT-IR spectrum of nano-Fe-DOPA (Fe-DOPA).

Step III: Preparation of Fe-DOPA-Cu catalyst:

Amine functionalized nano-Fe_3O_4 (Fe-DOPA; 1g) was dispersed in water and methanol mixture in 1:1 ratio. A water solution of $CuCl_2 \cdot 2H_2O$ (100 mg) was added to the above mixture. Hydrazine monohydrate solution in water was added drop wise to bring the pH of this mixture to 9, followed by the addition of 0.1 gm of $NaBH_4$ in small portions. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle down and washed several times with water and acetone, dried in a vacuum at 60 °C for 2 h. The Fe-DOPA-Cu nanoparticles were characterised by using field emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectroscopy (EDX) and powder XRD (X-ray diffraction).[4]

Characterization of Fe-DOPA-Cu Catalyst.

The nano-ferrite copper catalyst (Fe-DOPA-Cu NPs) were characterised by using field emission scanning electron microscope (Figure S4). EDX analysis confirmed the presence of Fe, O and Cu elements and mapping analysis shows the well dispersion of copper (Figure S5). The signals of Cu metal were not detected in XRD, indicating that the Cu species is highly dispersed on ferrites (Figure S6).
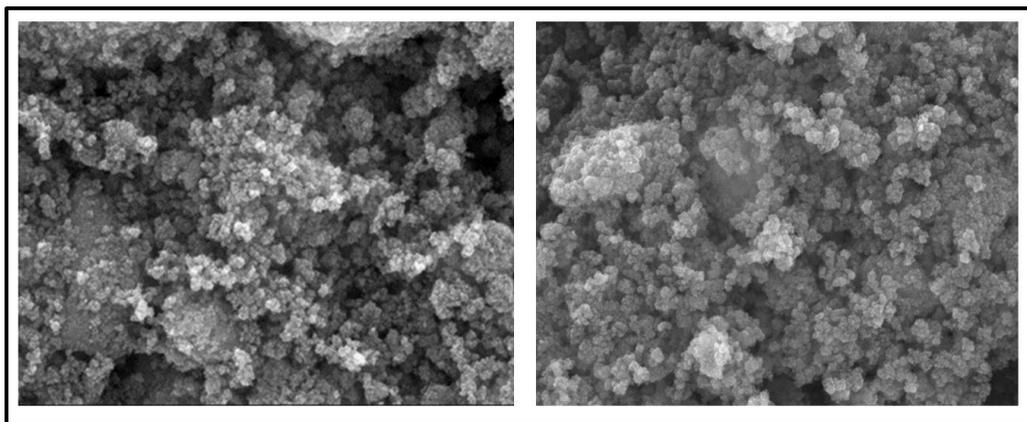
Figure S4: FESEM image of Fe-DOPA-Cu NPs.
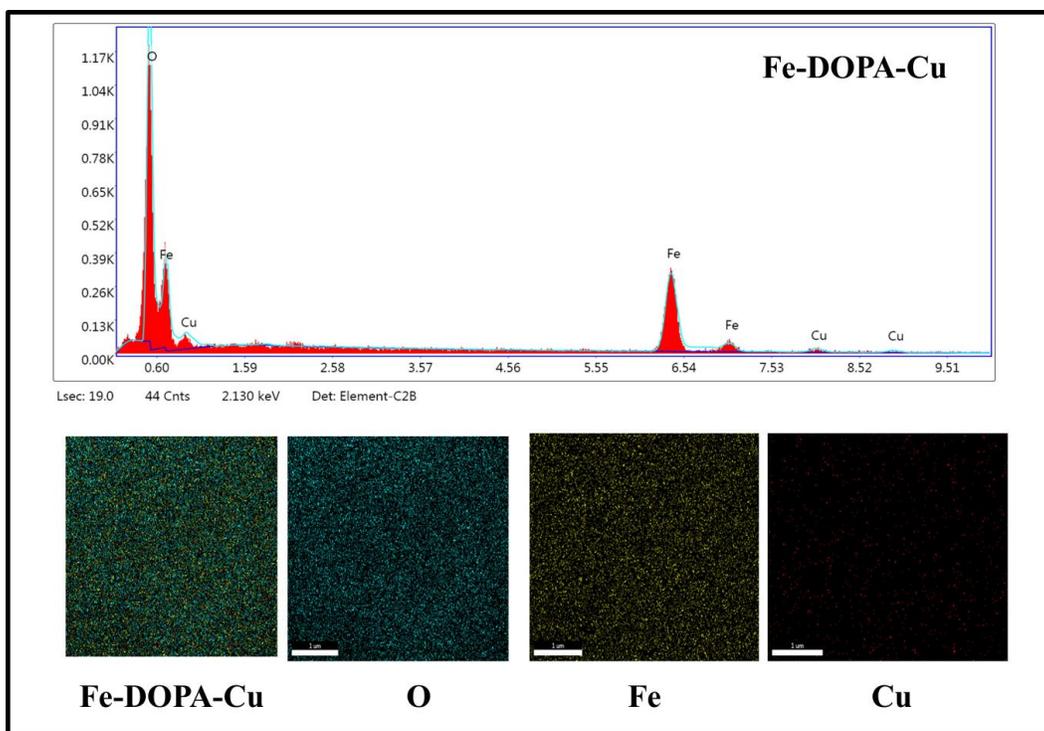
Figure S5: EDX analysis and mapping of Fe-DOPA-Cu NPs.
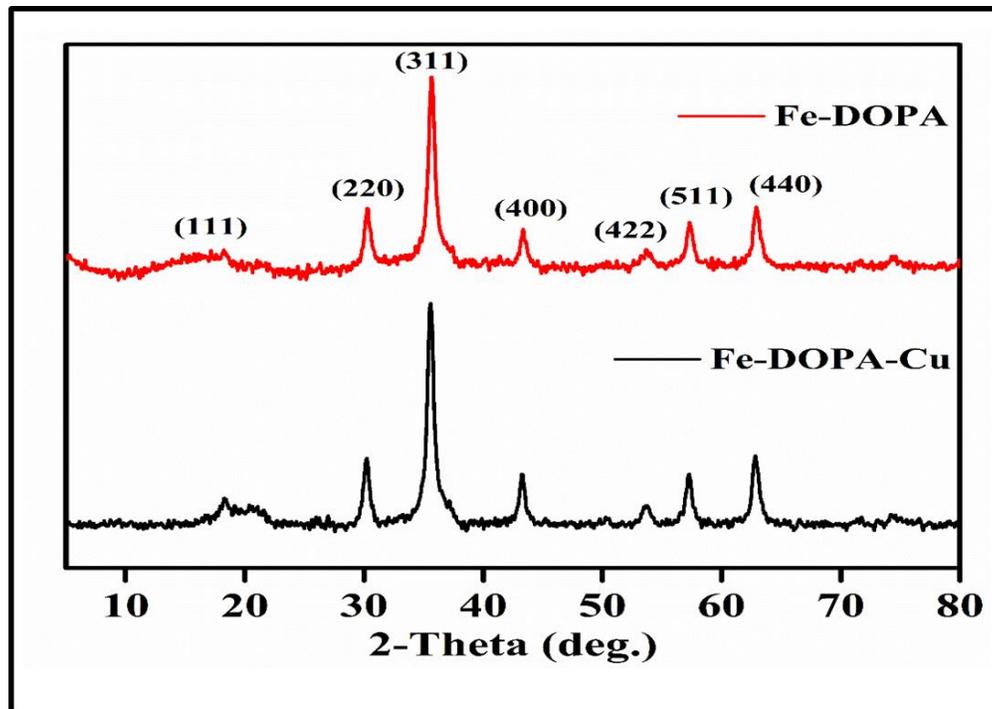
Figure S6: XRD analysis of Fe-DOPA-Cu NPs.

TEM images and particle size distributions of Fe-DOPA-Cu NPs

The TEM analysis of Fe-DOPA-Cu nanoparticle (Figure S7) shows that the nanoparticles were having particle size in the range of 4-30 nm and an average particle size of 13.5 ±0.2 nm. HRTEM image of indicates the high crystallinity of the material along with clear lattice fringes. The lattice fringe corresponds to a d-spacing value of 0.22 nm.
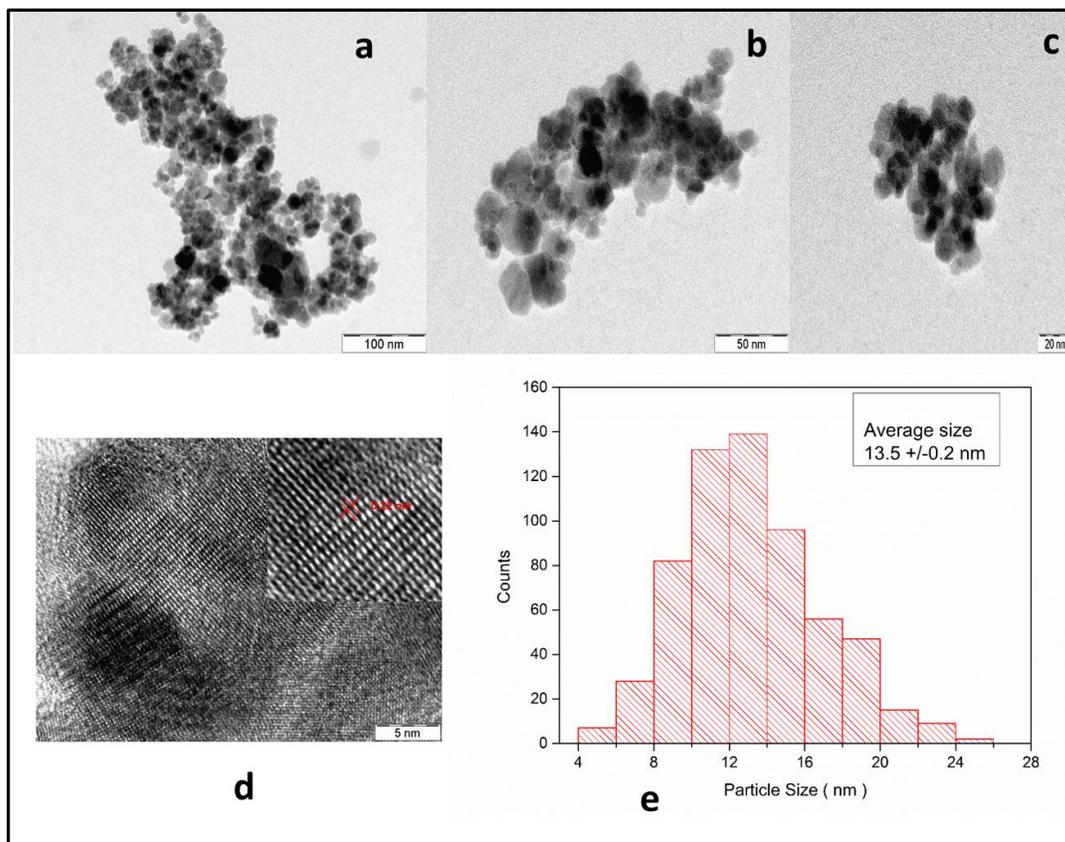
Figure S7: (a-c) TEM images of Fe-DOPA-Cu nanoparticles. (d) HRTEM image of Fe-DOPA-Cu nanoparticle. (e) Size distribution of particles is determined from measurement of 615 particles from representative TEM images.

BET analysis

The functionalized magnetic nanoparticles have holds key importance in deciding its providence in enhancing catalytic activities. BET analysis results (Figure S8) based on the N_2 adsorption

desorption isotherms, it could be seen that the materials reflect Type IV isotherms with hysteresis loop, which corroborates to the general characteristic traits of mesoporous materials. It was seen that of Fe-DOPA-Cu nanoparticles possesses a BET surface area of 88.834 m^2 g^{-1} with a pore volume of 0.137 cm^3 g^{-1}. Furthermore, in order to validate these observations, the related BJH pore distribution revealed the presence of mesopores with a pore diameter of 3.77 nm.
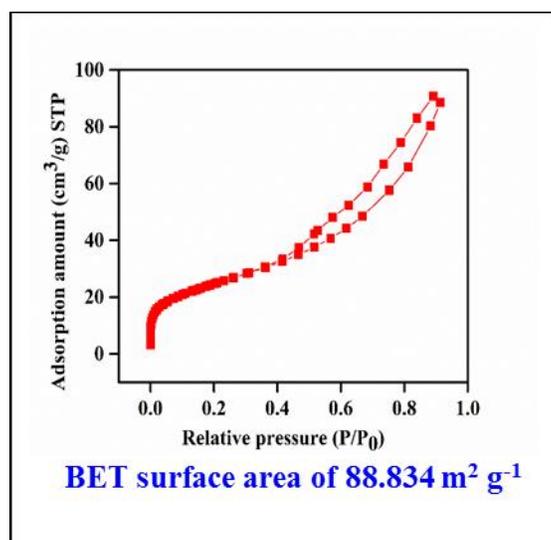
Figure S8: N_2 physisorption graphs of Fe-DOPA-Cu nanoparticle.

X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed in order to investigate the composition of surface elements and corresponding metallic states present in Fe-DOPA-Cu nanoparticles (Figure S9), which notably revealed the presence of the peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ assigned at 933.6 eV and 953 eV, respectively with spin-orbit component of 19.4 eV. The strong satellite peaks at 942 and 962 eV confirms the presence of Cu in +2 oxidation state.
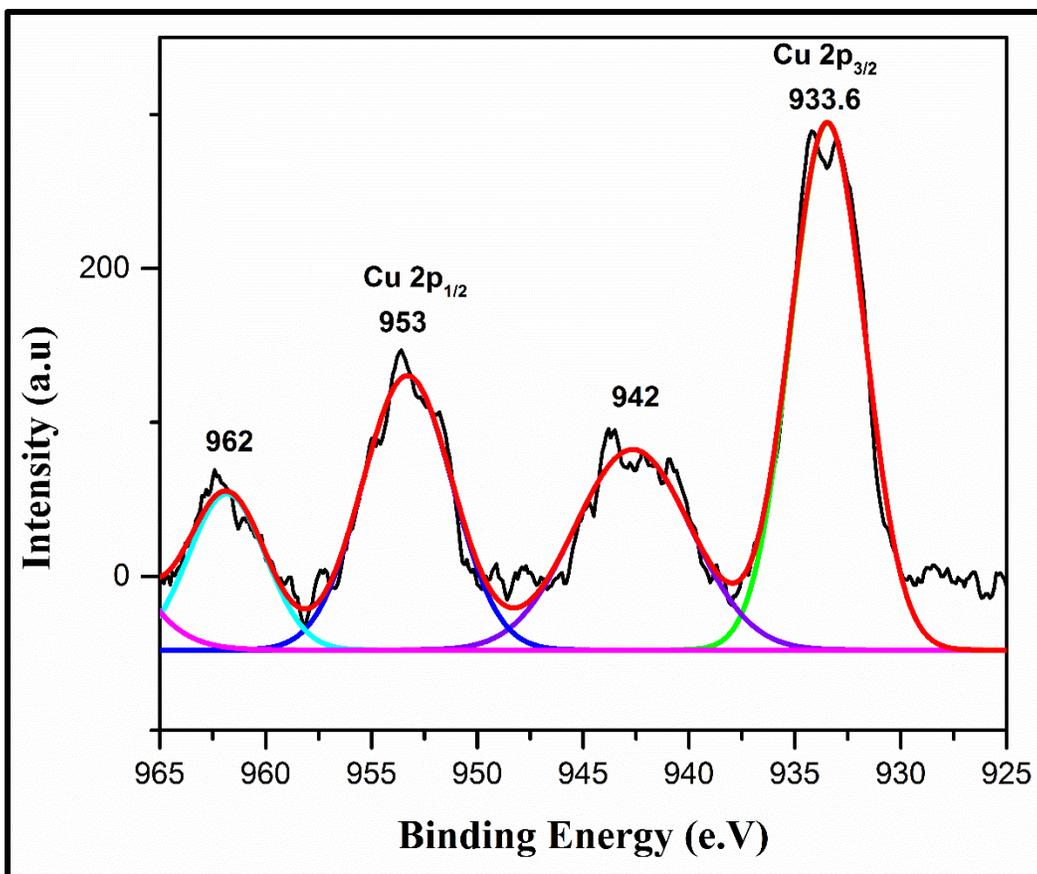
Figure S9: Copper region of the X-ray photoelectron spectrum of Fe-DOPA-Cu nanoparticles.

Inductively coupled plasma mass spectrometer (ICP-MS) analysis

The inductively coupled plasma mass spectrometer (ICP-MS) analysis showed that in Fe-DOPA-Cu NPs catalyst the Cu loading is 3.45 wt%.

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, Fe-DOPA-Cu-NPs catalyst (25 mg; 5.4 mol % based on Cu), B_2pin_2 (0.3 mmol), base (0.3 mmol), (2-bromoethyl) benzene (**1a**, 0.25 mmol) and solvent (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 ^{1}H NMR spectroscopy using nitromethane as an internal standard.

Table S1: Screening of catalyst for the borylation of (2-bromoethyl)benzene (**1a**).
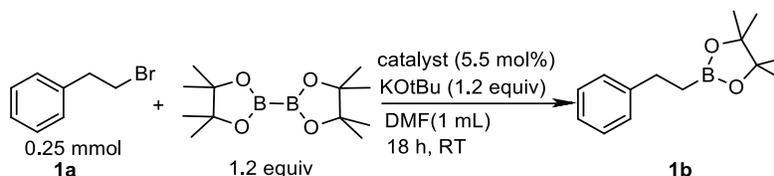
entry	Catalyst (NPs)	solvent	base	B_2pin_2 (equiv)	Temp (°C)	yield (%)
1	**Fe-DOPA-**	**DMF**	**KO^{t}Bu**	**1.2**	**RT**	**94**
2	Fe_3O_4	DMF	KO^{t}Bu	1.2	RT	10
3	Fe_3O_4-DH	DMF	KO^{t}Bu	1.2	RT	14
4	-	DMF	KO^{t}Bu	1.2	RT	5

Reaction condition: 0.25 mmol **1a**, B_2pin_2 (1.2 equiv), catalyst (5.4 mol %), KO^{t}Bu (1.2 equiv), DMF (1 mL) for 18 h at RT. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S2. Screening of bases for the Fe-DOPA-Cu NPs catalyzed borylation of (2-bromoethyl)benzene (**1a**).

entry	catalyst	solvent	base	B$_2$pin$_2$ (equiv)	temp (℃)	yield (%)
1	Fe-DOPA-Cu	DMF	NaOtBu	1.2	RT	52
2	Fe-DOPA-Cu	DMF	NaOMe	1.2	RT	24
3	Fe-DOPA-Cu	DMF	KOtBu	1.2	RT	94
4	Fe-DOPA-Cu	DMF	KOMe	1.2	RT	40
5	Fe-DOPA-Cu	DMF	LiO^{t}Bu	1.2	RT	50
6	Fe-DOPA-Cu	DMF	-	1.2	RT	0

Reaction condition: 0.25 mmol **1a**, B$_2$pin$_2$ (1.2 equiv), Fe-DOPA-Cu (25 mg), base (1.2 equiv), DMF (1 mL) for 18 h at RT. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S3. Screening of solvents for Fe-DOPA-Cu NPs catalyzed borylation of (2-bromoethyl)benzene (**1a**).

entry	catalyst	solvent	base	B$_2$pin$_2$ (equiv)	temp (℃)	yield (%)
1	Cu-DH	DMF	KO^{t}Bu	1.2	RT	94
2	Cu-DH	THF	KO^{t}Bu	1.2	RT	16
3	Cu-DH	MTBE	KO^{t}Bu	1.2	RT	23
4	Cu-DH	Toluene	KO^{t}Bu	1.2	RT	3
5	Cu-DH	DMA	KO^{t}Bu	1.2	RT	60
6	Cu-DH	CH$_3$CN	KO^{t}Bu	1.2	RT	72

Reaction condition: 0.25 mmol **1a**, B$_2$pin$_2$ (1.2 equiv), Fe-DOPA-Cu (25 mg), KOtBu (1.2 equiv), solvent (1 mL) for 18 h at RT. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S4. Effect of reaction time on the Fe-DOPA-Cu NPs catalyzed borylation of (2-bromoethyl)benzene (**1a**).
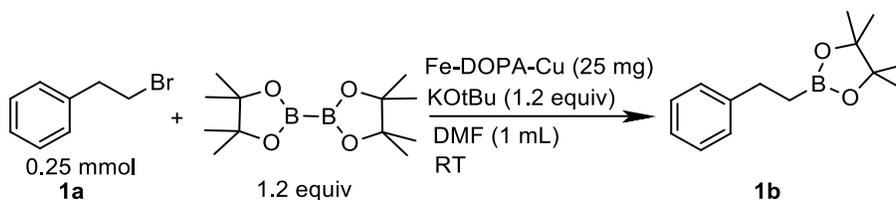
entry	catalyst	solvent	base	B$_2$pin$_2$ (equiv)	time(hrs)	yield (%)
1	Fe-DOPA-Cu	DMF	KO^{t}Bu	1.2	8	31
2	Fe-DOPA-Cu	DMF	KO^{t}Bu	1.2	12	84
3	Fe-DOPA-Cu	DMF	KO^{t}Bu	1.2	18	94

Reaction condition: 0.25 mmol **1a**, B$_2$pin$_2$ (1.2 equiv), Fe-DOPA-Cu (25 mg), KOtBu (1.2 equiv), DMF (1 mL) at RT. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

Table S5. Screening of different ratios of B$_2$pin$_2$/KOtBu for Fe-DOPA-Cu NPs catalyzed borylation of (2-bromoethyl)benzene (**1a**).
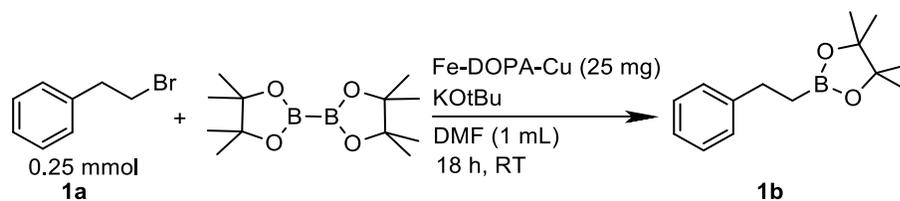
entry	catalyst	solvent	KO^{t}Bu	B$_2$pin$_2$	temp (˚C)	yield (%)
1	Fe-DOPA-Cu	DMF	1.2	1.2	RT	94
2	Fe-DOPA-Cu	DMF	1.3	1.3	RT	99

Reaction condition: 0.25 mmol **1a**, B$_2$pin$_2$, Fe-DOPA-Cu (25 mg), KOtBu, DMF (1 mL) for 18 h at RT. Yields were determined by ^{1}H NMR analysis, using nitromethane as an internal standard.

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, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KO^tBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL) and alkyl halide/benzyl 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 (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 chromatography.

General Procedure B. In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KO^tBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL), alkyl chloride (1 mmol) and NBu_4I (1 mmol) were added and the reaction was stirred vigorously at 80 °C for 24 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 chromatography.

General Procedure for the Gram Scale Reaction.

In a 100 mL Schlenk flask equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (600 mg, 5.4 mol % of Cu), B_2Pin_2 (1.3 equiv, 1.980 g, 7.8 mmol), KO^{t}Bu (1.3 equiv, 0.870 g, 7.8 mmol), DMF (30 mL) and (2-bromoethyl)benzene (**1a**, 1.11 g, 6 mmol,) were added and the reaction mixture was stirred vigorously at room temperature for 24 h. The crude reaction was dissolved in Et_2O (50 mL) and then transferred to a separatory funnel followed by the addition of H_2O (50 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 30 mL). The combined organics were dried (Na_2SO_4) and concentrated. The residue was purified by chromatography (isolated yield **1b**: 1.14 g, 82%).

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolan (1b).[6]
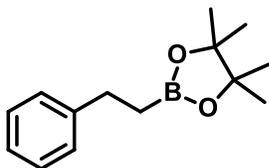
Following general procedure A, a colorless liquid in 85% yield (197 mg) from (2-bromoethyl)benzene (**1a**, 185 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.32–7.20 (m, 4 H), 7.19-7.14 (m, 1 H), 2.77 (t, J = 8 Hz, 2H), 1.24 (s, 12 H), 1.17 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.4, 128.1, 128.0, 125.5, 83.0, 29.9, 24.82, 13.0 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.1. GC-MS: m/z 232 (M[+]).

4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2b).[6]
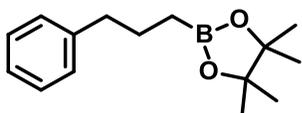
Following general procedure A, a colorless liquid in 82% yield (202 mg) from 3-phenylpropyl bromide (**2a**, 199 mg, 1 mmol) was obtained. Following general procedure B, using (3-chloropropyl)benzene as a substrate, 77% yield of **2b** was determined by ^{1}H NMR using nitromethane as internal standard. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28-7.25 (m, 2H), 7.19-7.16 (m, 3H), 2.62 (t, J = 8 Hz, 2H),), 1.79-1.71 (m, 2H), 1.25 (s, 12H), 0.84 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.8, 128.6, 128.3, 125.7, 83.0, 38.7, 26.2, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.2. GC-MS: m/z 246 (M[+]).

4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane (3b).[7]
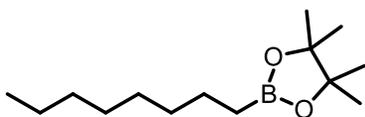
Following general procedure A, a colorless liquid in 88% yield (211 mg) from 1-bromooctane (**3a**, 193 mg, 1 mmol) was obtained. Following general procedure B, using 1-chlorooctane as a

substrate, 89% yield of **3b** was determined by ^{1}H NMR using nitromethane as internal standard. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.39-1.35 (m, 2H), 1.30-1.23 (m, 10 H), 1.20 (s, 12H), 0.84 (t, J = 7 Hz, 3H), 0.72 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.8, 32.5, 32.0, 29.5, 29.4, 24.9, 24.1, 22.8, 14.2, 11.5 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl3): δ 33.8. GC-MS: m/z 240 (M$^+$).

2-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b).[8]
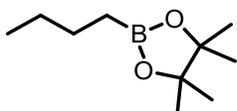
Following general procedure A, a colorless liquid in 80% yield (147 mg) from 1-bromobutane (**4a**, 137 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): 1.36 (dd, J = 15.7, 8 Hz, 2H), 1.27 (dd, J = 15.2, 7.3 Hz, 2H), 1.22 (s, 12H), 0.86 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.9, 26.3, 25.5, 24.9, 13.9, 11.7 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.6. GC-MS: m/z 184 (M$^+$).

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5b).[9]
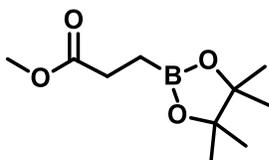
Following general procedure A, colorless liquid in 75% yield (160 mg) from methyl 3-bromopropanoate (**5a**, 167 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.63 (s, 3H), 2.41 (t, J = 8 Hz, 2H), 1.21 (s, 12H), 0.99 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 175.1, 83.3, 51.5, 28.7, 24.8, 5.2 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.7 ppm. GC-MS: m/z 214 (M$^+$).

Ethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (6b).[8]
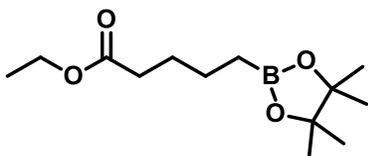
Following general procedure A, colorless liquid in 80% yield (205 mg) from ethyl 5-bromopentanoate (**6a**, 209 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.10 (q, J = 8 Hz, 2H), 2.27 (t, J = 8 Hz, 2H), 1.64-1.60 (m, 2H), 1.43-1.42 (m, 2H), 1.28-1.23 (m, 15H), 0.78 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.9, 83.1, 60.2, 34.3, 27.7, 24.9, 23.7, 14.04. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.1 ppm. GC-MS: m/z 241 (M$^+$−CH$_3$).

2-(2-(1,3-Dioxan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b).[6]
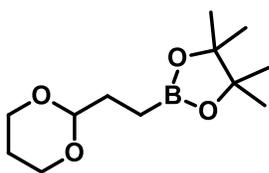
Following general procedure A, colorless liquid in 79% yield (191 mg) from 2-(2-bromoethyl)-1,3-dioxane (**7a**, 195 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.44 (t, J = 5 Hz, 1H), 4.05-4.01 (m, 2H), 3.77-3.68 (m, 2H), 2.07-1.97 (m, 1H), 1.74-1.67 (m, 2H), 1.30-1.26 (m, 1H), 1.20 (s, 12H), 0.79 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 103.2, 83.0, 66.8, 29.5, 25.9, 25.0, 5.4 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.7. GC-MS: m/z 227 (M$^+$−CH$_3$).

2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b).[10]
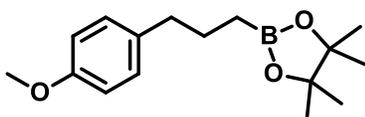
Following general procedure A, a colorless liquid in 69% yield (190 mg) from 1-(3-bromopropyl)-4-methoxybenzene (**8a**, 229 mg, 1 mmol) was obtained. Following general procedure B, using 1-(3-chloropropyl)-4-methoxybenzene as a substrate, 74% yield of **8b** was determined by ^{1}H NMR using nitromethane as internal standard. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.11-7.07 (m, 2H), 6.84-6.79 (m, 2H), 3.78 (s, 3H), 2.55 (t, J = 8 Hz, 2H), 1.74-1.66 (m, 2H), 1.24 (s, 12H), 0.81 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.8, 135.0, 129.5, 113.8,

83.1, 55.4, 37.8, 26.4, 25.0, 10.4 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.6. GC-MS: m/z 276 (M$^+$).

2-(6-Chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b).[1]
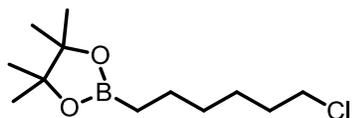
Following general procedure A, a colorless liquid in 70% yield (172 mg) from 1-bromo-6-chlorohexane (**9a**, 199 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.51 (t, J = 7 Hz, 2H), 1.79-1.72 (m, 2H), 1.44-1.37 (m, 4H), 1.36-1.28 (m, 2H), 1.24 (s, 12H), 0.77 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.9, 45.2, 32.6, 31.6, 26.7, 24.9, 23.9, 10.9 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.1. GC-MS: m/z 231 (M$^+$-CH$_3$).

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane (10b).[11]
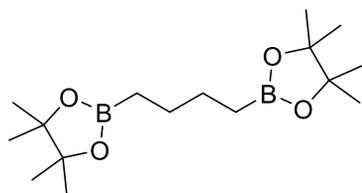
Following general procedure A using 2.3 equiv of B$_2$pin$_2$ and KOtBu, a colorless liquid in 69% yield (214 mg) from 1,4-dibromobutane (**11a**, 215 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.41-1.37 (m, 4H), 1.22 (s, 24H), 0.74 (br, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 82.9, 27.0, 24.9, 11.2 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.4. GC-MS: m/z 310 (M$^+$).

(±)-2-*sec*-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b).[10]
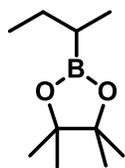
Following general procedure A, a colorless liquid in 70% yield (129 mg) from 2-bromobutane (**12a**, 137 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.48-1.39 (m, 1H), 1.38-

1.28 (m, 1H), 1.22 (s, 12H), 1.02-0.94 (m, 4H), 0.88 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 83.2, 26.5, 25.2, 25.1, 15.6, 13.8. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.4. GC-MS: m/z 184 (M[+]).

2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b).[10]
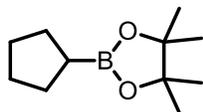
Following general procedure A, a colorless liquid in 80% yield (157 mg) from bromocyclopentane (**13a**, 149 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.75-1.67 (m, 2H), 1.60-1.38 (m, 6H), 1.20 (s, 12H), 1.16-1.11 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.8, 28.6, 26.9, 24.8, 22.7 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.7. GC-MS: m/z 196 (M[+]).

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b).[10]
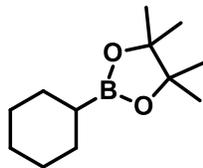
Following general procedure A, a colorless liquid in 84% yield (176 mg) from bromocyclohexane (**14a**, 163 mg, 1.0 mmol) was obtained. Following general procedure A, a colorless liquid in 80% yield (168 mg) from iodocyclohexane (210 mg, 1.0 mmol) was obtained. Following general procedure A, using chlorocyclohexane as a substrate, trace amount of **14b** was determined by GC-MS analysis. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.68-1.58 (m, 5H), 1.38-1.25 (m, 5H), 1.23 (s, 12H), 1.01-0.95 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.8, 28.1, 27.3, 26.9, 24.9, 22.3 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.9. GC-MS: m/z 210 (M[+]).

exo-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(14b).[10]
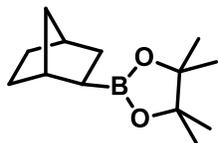
Following general procedure A, a colorless liquid in 81% yield (180 mg; a mixture containing an exo:endo ratio of ca. 88:12 of **15b** determined by averaging the ratio of carbon resonances in the ^{13}C NMR) was obtained from exo-2-bromonorbornane (exo-**15a**, 175 mg, 1 mmol). ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.26-2.19 (br, 1H), 2.19 (br, 1H), 1.48-1.46 (m, 3H), 1.34-1.29 (m, 1H), 1.20 (br, 14H), 1.15-1.11 (m, 2H), 0.88-0.84 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.9, 38.9, 38.2, 36.8, 32.4, 32.3, 29.4, 24.8 (exo); 83.0, 41.1, 39.0, 37.2, 32.0, 31.7, 30.0, 25.03, 25.00 (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 34.1. GC-MS: m/z 222 (M$^+$).

Benzyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (15b).[10]
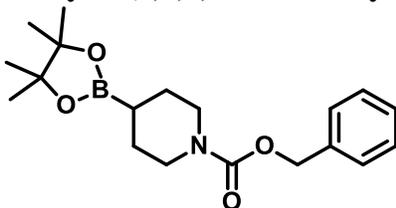
Following general procedure A, a colorless liquid in 64% yield (221 mg) from benzyl 4-bromopiperidine-1-carboxylate (**16a**, 298 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37-7.26 (m, 5H), 5.14 (s, 2H), 3.95 (m, 2H), 3.57-3.54 (m, 2H), 2.13 (br, 2H), 1.58-1.38 (m, 2H), 1.25 (s, 12H), 0.90-0.84 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.4, 136.8, 128.4, 127.9, 127.8, 83.4, 66.9, 43.4, 26.9, 24.9, 19.9 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.8.

2-(Cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16b).[10]
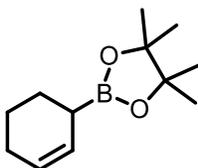
Following general procedure A, a colorless liquid in 72% yield (150 mg) from 3-bromocyclohexene (**17a**, 161 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.75-5.62 (m, 2H), 1.98-1.95 (m, 2H), 1.77-1.61 (m, 5H), 1.23 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 127.7, 126.1, 83.3, 25.1, 24.9, 24.8, 24.2, 22.7. ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.8. GC-MS: m/z 208 (M[+]).

2-Adamantan-1-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17b).[10]
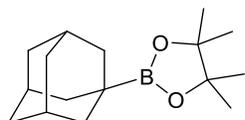
Following general procedure A, using 1-bromoadamantane (**18a**) as a substrate, 1.3 equiv of B$_2$cat$_2$ as a boron source instead of B$_2$pin$_2$, followed by transesterification with pinacol at 80 °C for 24 h, 5% yield of **18b** was determined by ^{1}H NMR using nitromethane as internal standard. Following general procedure B, using 1-bromoadamantane (**18a**) as a substrate, 11% yield of **18b** was determined by ^{1}H NMR using nitromethane as internal standard and was not been readily isolated.

4,4,5,5-Tetramethyl-2-((7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)-1,3,2-dioxaborolane (18b)[12]
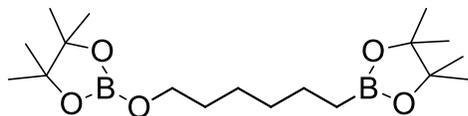
Following general procedure B, a yellowish liquid in 82% yield (290 mg) from 6-chlorohexan-1-ol (**18a**, 136 mg, 1.0 mmol) was obtained. ^{1}H NMR (CDCl$_3$): δ 3.62-3.57 (m, 2H), 1.56-1.50 (m, 4H), 1.41-1.38 (m, 2H), 1.23-1.21 (m, 24H), 0.87-0.83 (m, 2H), 0.75 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 82.9, 82.6, 62.8, 32.6, 32.1, 25.5, 24.8, 24.6, 23.9, 11.5 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$) δ 34.1, 21.8. GC-MS: m/z 354 (M[+]), 339 (M[+]-CH$_3$).

1-(6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1H-indole (19b).[1]
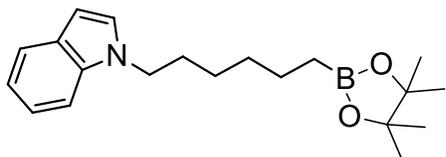
Following general procedure B, white solid in 80% yield (261 mg) from 1-(6-chlorohexyl)-1H-indole (**19a**, 235 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63 (d, J = 8 Hz, 1H), 7.35 (d, J = 8 Hz, 1H), 7.24–7.17 (m, 1H), 7.14-7.06 (m, 2H), 6.49 (d, J = 3 Hz, 1H), 4.11 (t, J = 7 Hz, 2H), δ 1.87-1.80 (m, 2H), 1.36-1.27 (m, 6H), 1.25 (s, 12H), 0.77 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 135.0, 128.6, 127.9, 121.3, 121.0, 119.2, 109.5, 100.9, 83.0, 46.5, 32.0, 30.2, 26.8, 24.9, 23.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.9. GC-MS: m/z 327 (M$^+$).

9-(6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-9*H*-carbazole (20b).
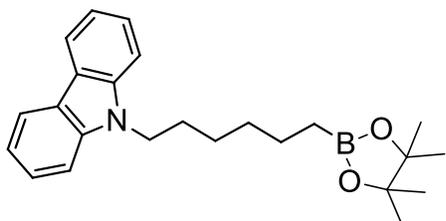
Following general procedure B, a yellowish liquid in 49% yield (184 mg) from 9-(6-chlorohexyl)-9H-carbazole (**20a**, 286 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.12-8.09 (m, 2H), 7.49-7.44 (m, 2H), 7.42-7.40 (m, 2H), 7.25-7.20 (m, 2H), 4.29 (t, J = 7 Hz, 2H), 1.90-1.83 (m, 2H), 1.41-1.34 (m, 6H), 1.24 (s, 12H), 0.77 (t, J = 7 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.5, 125.7, 122.9, 120.4, 118.7, 108.8, 83.0, 43.2, 32.2, 29.0, 27.2, 24.9, 24.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 34.2. GC-MS: m/z 377 (M$^+$). HRMS (ESI) m/z: [M+H]$^+$ calculated for C$_{24}$H$_{33}$BNO$_2$: 378.2604; Found: 378.2696.

4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (21b)[1]
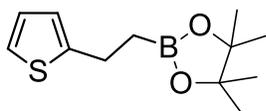
Following general procedure B, a colorless oil in 62% yield (147 mg) from 2-(2-chloroethyl)thiophene (**21a**, 146 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.05 (dd, J = 5, 1 Hz, 1H), 6.88 (dd, J = 5, 3 Hz, 1H), 6.79-6.78 (m, 1H), 2.95 (t, J = 8 Hz, 2H), 1.23-1.22 (m, 14H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 147.8, 126.6, 123.5, 122.7, 83.3, 25.0, 24.9, 14.2 (br); ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.6. GC-MS: m/z 238 (M$^+$).

Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (22b)[10]
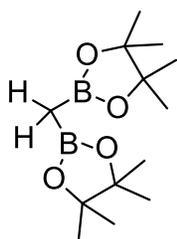
Following general procedure B using 2.3 equiv of B$_2$pin$_2$/KO^{t}Bu, and 2.0 equiv of (Bu$_4$N)I, a white solid in 70% yield (188 mg) from dichloromethane (**22a**, 85 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.22 (s, 24H), 0.35 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 83.1, 24.8. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.5. GC-MS: m/z 268 (M$^+$), 253 (M$^+$-CH$_3$).

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23b).[1]
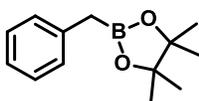
Following general procedure A, a colorless liquid in 86% yield (187 mg) from (bromomethyl)benzene (**23a**, 171 mg, 1 mmol) was obtained. Following general procedure A, a colorless liquid in 84% yield (183 mg) from (chloromethyl)benzene (**23a**, 126 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28-7.13 (m, 5H), 2.32 (s, 2H), 1.26 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): $δ$ 139.1, 129.5, 128.7, 125.3, 83.9, 25.17. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): $δ$ 33.1. GC-MS: m/z 218 (M$^+$).

4,4,5,5-Tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (24b).[10]
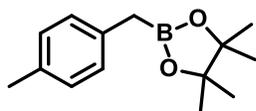
Following general procedure A, a colorless liquid in 65% yield (151 mg) from 1-(chloromethyl)-4-methylbenzene (**24a**, 140 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.11-7.05 (m, 4H), 2.31 (s, 3H), 2.27 (s, 2H), 1.25 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 135.5, 134.2, 129.1, 128.9, 83.5, 24.8, 21.1, 19.3 (very broad, low intensity). ^{11}B NMR (128 MHz, CDCl$_3$): δ 32.7. GC-MS: m/z 232 (M$^+$).

4,4,5,5-Tetramethyl-2-(2-methylbenzyl)-1,3,2-dioxaborolane (25b).[13]
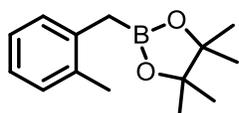
Following general procedure A, a colorless liquid in 50% yield (116 mg) from 1-(chloromethyl)-2-methylbenzene (**25a**, 140 mg, 1.0 mmol) was obtained. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16-7.03 (m, 4H), 2.28 (s, 3H), 2.26 (s, 2H), 1.23 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.6, 136.0, 129.9, 129.5, 125.9, 125.3, 83.4, 24.8, 20.2. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.8. GC-MS: m/z 232 (M$^+$).

Experimental Procedure for the Example Described in Scheme 1: Borylation of (2-Bromoethyl)benzene (1a) Using *Bis*(neopentylglycolato)diboron (B₂neop₂).
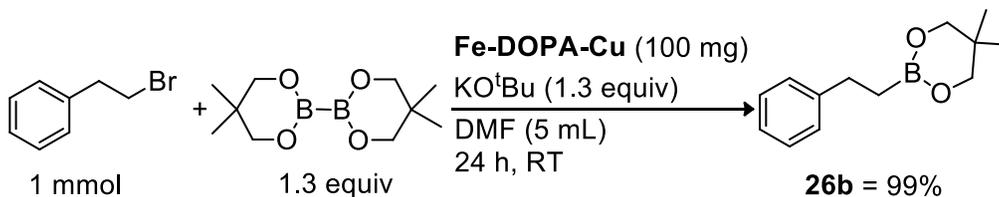
In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2neop_2 (1.3 equiv, 294 mg, 1.3 mmol), KO^tBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL) and (2-bromoethyl)benzene (**1a**, 1 mmol, 185 mg) were added and the reaction was stirred vigorously at room temperature for 24 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-phenethyl-1,3,2-dioxaborinane (26b)[8]

A colorless liquid in 88% yield (191 mg) from (2-bromoethyl)benzene (**1a**, 185 mg, 1.0 mmol) was obtained. From (2-bromoethyl)benzene (**1a**, 46 mg, 0.25 mmol) 99% yield of **26b** was determined by ^{1}H NMR using nitromethane as internal standard. ^{1}H NMR (400 MHz, CDCl₃): δ 7.26-7.16 (m, 5H), 3.60 (s, 4H), 2.71 (t, $J = 8$, 2H), 1.08 (t, $J = 8$, 2H), 0.93 (s, 6H). ^{13}C NMR (100 MHz, CDCl₃): δ 145.1, 128.3, 128.1, 125.4, 72.1, 31.7, 30.2, 29.8, 21.9. ^{11}B NMR (128 MHz, CDCl₃): δ 30.8. GC-MS: m/z 218 (M⁺).

Unsuccessful Substrates

Table S6. Screening of secondary and tertiary alkyl chlorides and benzyl chlorides for the **Fe-DOPA-Cu NPs** catalyzed borylation reaction.[a]
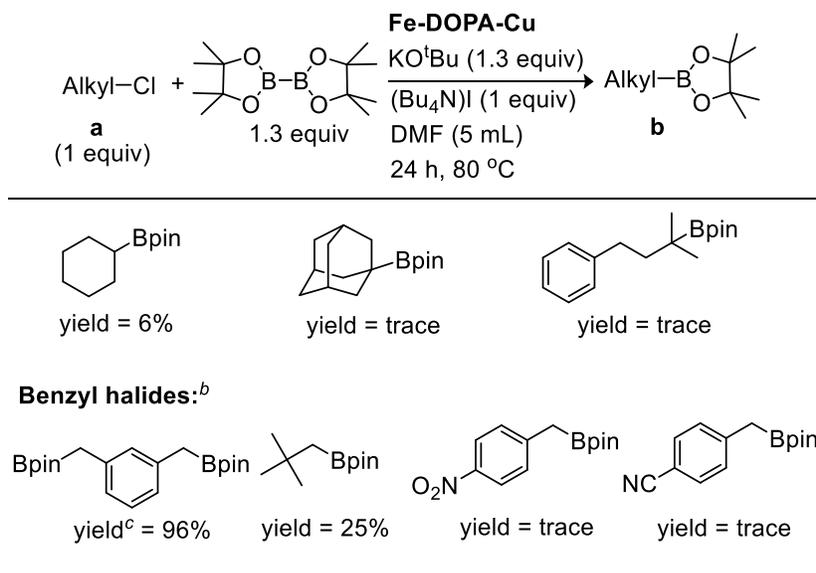
[a]Reaction conditions: Alkyl chloride (1.0 mmol, 1 equiv), **Fe-DOPA-Cu NPs** (100 mg), B_2pin_2 (1.3 equiv), KOtBu (1.3 equiv), 1.0 equiv of $(Bu_4N)I$ in DMF at 80 °C for 24 h unless otherwise stated. Yields were determined by ^{1}H NMR using nitromethane as internal standard. [b]Reaction was performed in the absence of $(Bu_4N)I$ at RT for 18 h. [c]Reaction was performed using 2.3 equiv of B_2pin_2 and KOtBu at RT for 18 h.

This heterogeneous Cu catalyzed borylation protocol has some substrate restrictions (Table S6). When the reaction was performed using cyclohexyl chloride with added $(Bu_4N)I$ yielded cyclohexyl boronate in 6% yield. Even higher temperature and longer reaction time did not improve the reaction outcome. Also, (3-chloro-3-methylbutyl)benzene and 1-chloroadamantane produced only trace amount of alkyl boronates. Neopentyl chloride afforded low yield of borylated product and was not readily isolated. When benzyl chlorides containing a nitro and cyano functional group were used, the desire product was detected in only trace amounts by GC-MS analysis.

Borylation of primary alkyl pseudohalides:
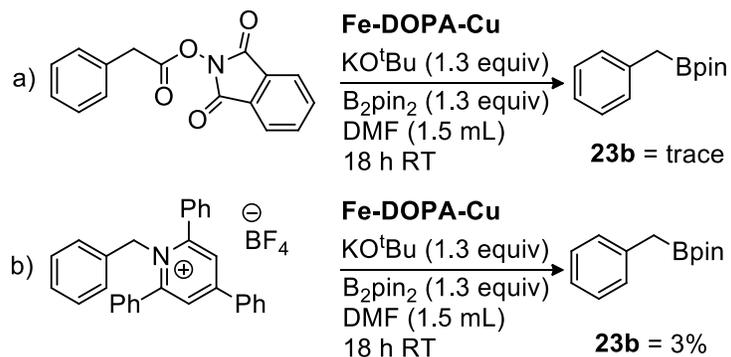
Scheme S2. Fe-DOPA-Cu NPs catalyzed borylation reactions of: a) *N*-hydroxyphthalimide ester[14a] and b) *N*-alkylpyridinium/Katritzsky salt.[14b]

The borylation of readily available pseudohalides, such as primary *N*-hydroxyphthalimide (NHPI) ester (Scheme S2a) and Katritzky *N*-alkylpyridinium salt (Scheme S2b) gave **23b** in trace amount and 3% yields, respectively (Scheme S2). Therefore, alkyl pseudohalides, such as the NHPI esters and Katritzky salts could not be used in this heterogeneous Cu catalyzed borylation protocol.

1,3-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzene[15]
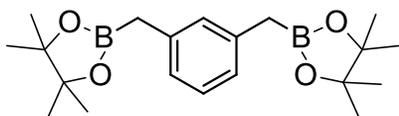
Yield: 96%

Following general procedure A, using 1,3-bis(chloromethyl)benzene as a substrate, 96% yield of diboryl product was determined by ^{1}H NMR using nitromethane as internal standard and confirm by GC-MS analysis. GC-MS: m/z 358 (M$^+$).

After several attempt also we were not able to isolate the pure product due to the decomposition of the desire diboryl during chromatography processes.

GC-MS

— 33.16

¹¹B NMR (128 MHz, CDCl₃)

7.11
7.10
7.10
7.09
7.08
7.06
7.06
7.05

2.27
2.24
2.18
2.16

1.23

#

#

4.63

4.37

24.00
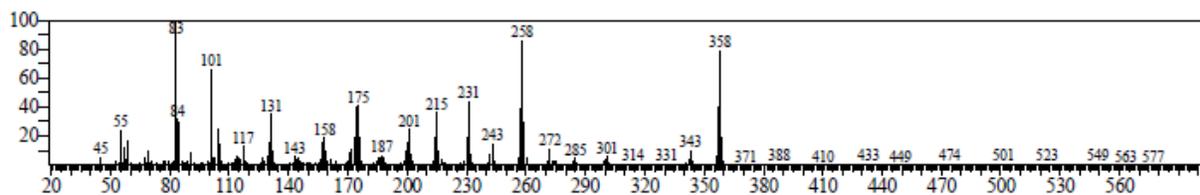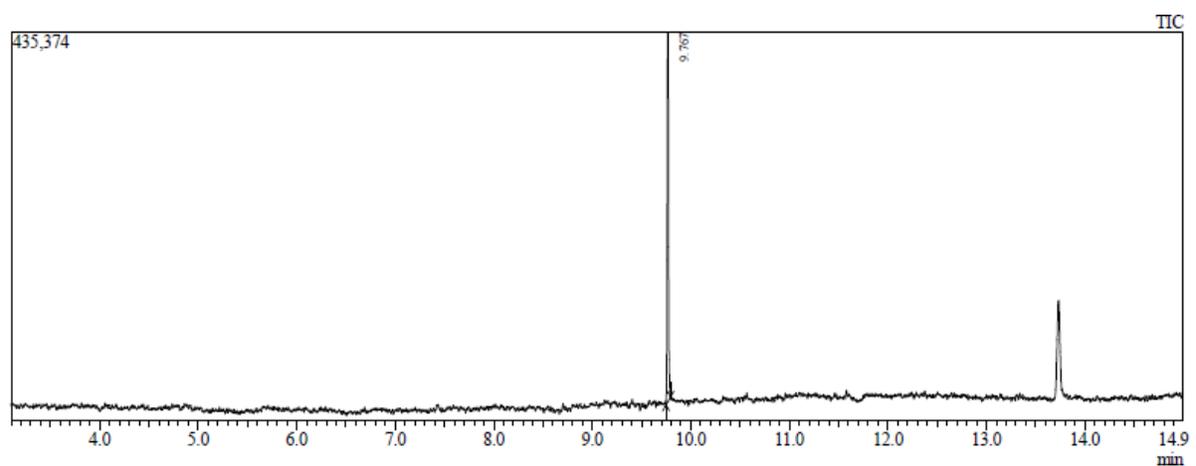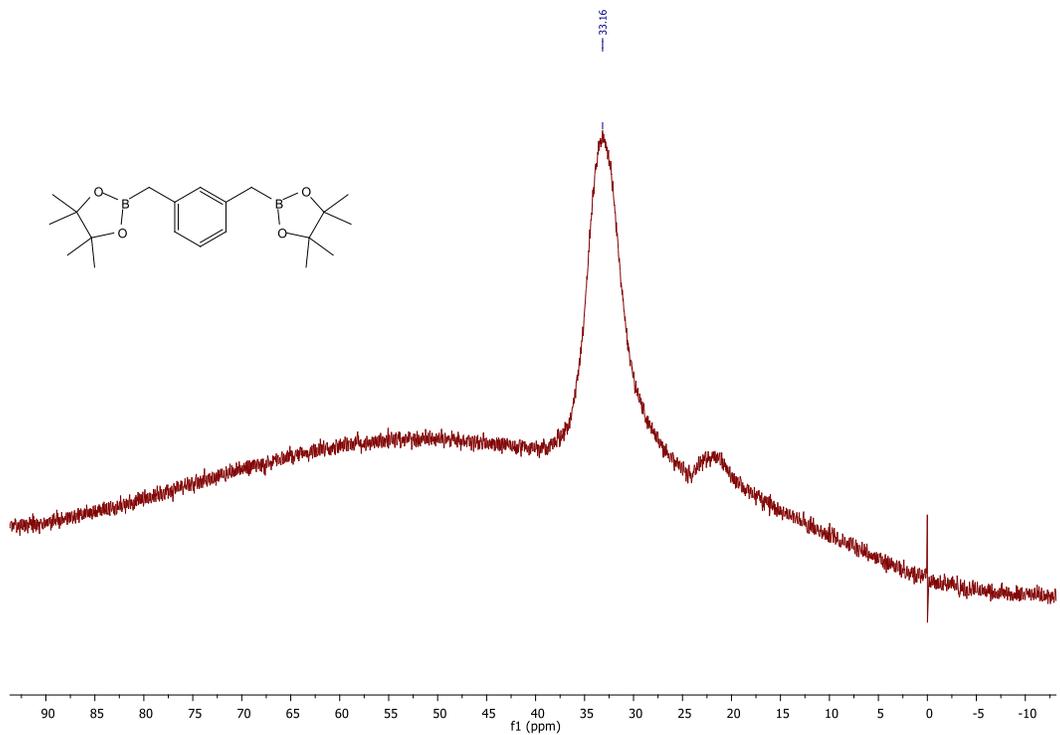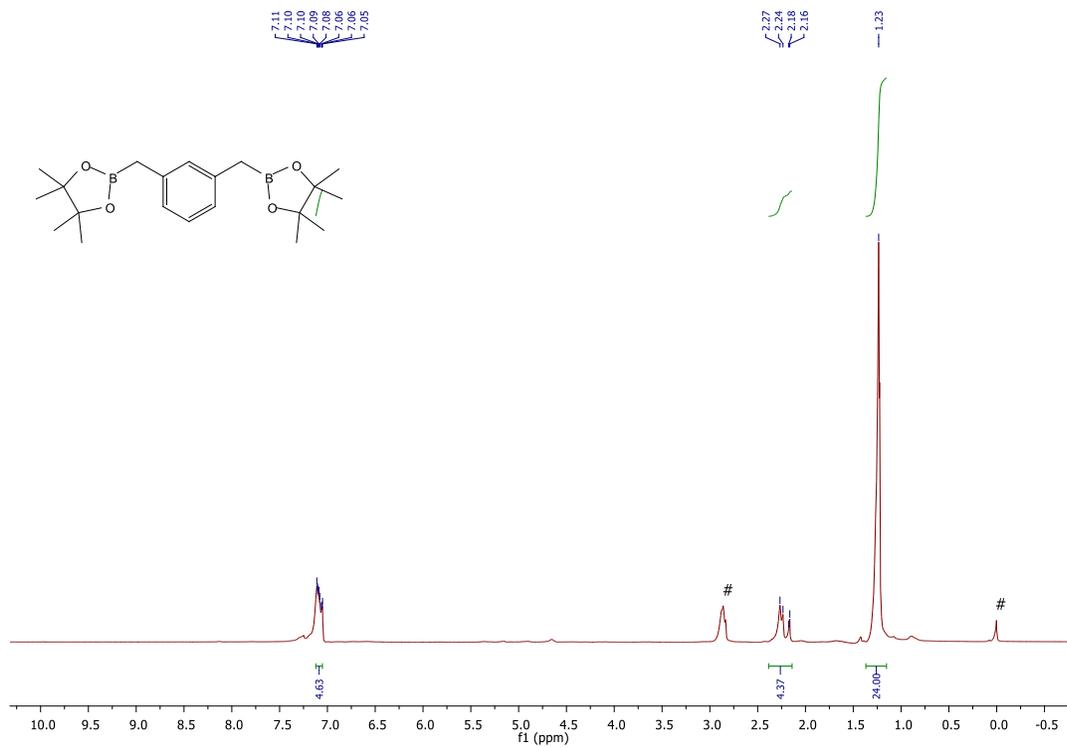
¹H NMR (400 MHz, CDCl₃)

V. Mechanistic Investigations

Experimental Procedure for the Example Described in Scheme 2: Borylation of Cyclopropylmethyl bromide (27a).[10]
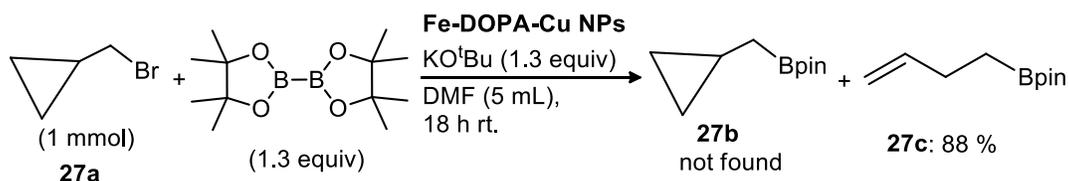
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KO^tBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL) were added and the reaction mixture was stirred for 10 min. To this reaction mixture, cyclopropylmethyl bromide (**27a**, 135 mg, 1.0 mmol) was added. The resulting reaction mixture was stirred vigorously at room temperature for 18 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 ^{1}H NMR spectroscopy. Further the residue was purified by chromatography.

2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27c).[10]
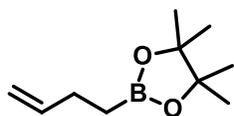
A colorless liquid in 88% yield (160 mg) from (bromomethyl)cyclopropane (**27a**, 135 mg, 1 mmol) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93-5.83 (m, 1H), 5.01-4.87 (m, 2H), 2.19-2.13 (m, 2H), 1.23 (s, 12H), 0.88 (t, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 113.2, 83.1, 28.1, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.9 ppm. GC-MS: m/z 182 (M^+).

Experimental Procedures for the Example Described in Scheme 2: Borylation of 6- bromohex-1-ene (28a).[10]
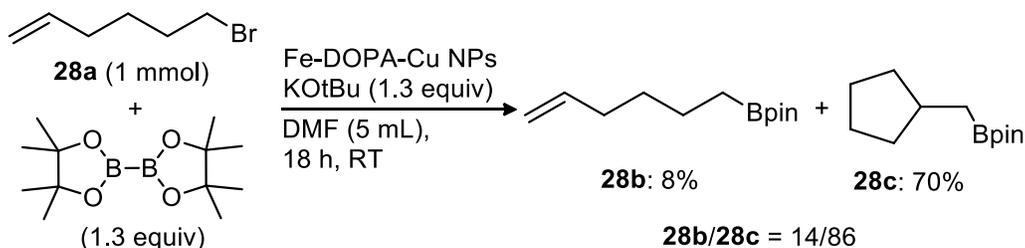
28a (1 mmol)

+

(1.3 equiv)

Fe-DOPA-Cu NPs
KOtBu (1.3 equiv)
DMF (5 mL),
18 h, RT

28b: 8%   28c: 70%

28b/28c = 14/86

In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KO^tBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL) were added and the reaction mixture was stirred for 10 min. To this reaction mixture, 6-bromohex-1-ene (**28a**, 163 mg, 1.0 mmol) was added. The resulting reaction mixture was stirred vigorously at room temperature for 18 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 chromatography.

2-(Cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28c).[10]

28b   28c
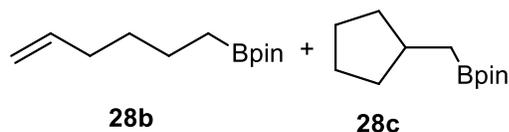
Chromatography yielded an inseparable 22:78 mixture of **28b** and **28c** (130 mg, 62% yield) as a clear liquid from 6-bromohex-1-ene (**28a**, 163 mg, 1 mmol). **28c**:[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01-1.89 (m, 1H), 1.80-1.76 (m, 2H), 1.65-1.46 (m, 4H), 1.23 (s, 12H), 1.06-1.01 (m, 2H), 0.83 (d, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 83.2, 36.6, 35.5, 25.6, 25.2. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.1 ppm. GC-MS: m/z 210 (M+).

Radical Scavenging Experiments

Experiment S1:
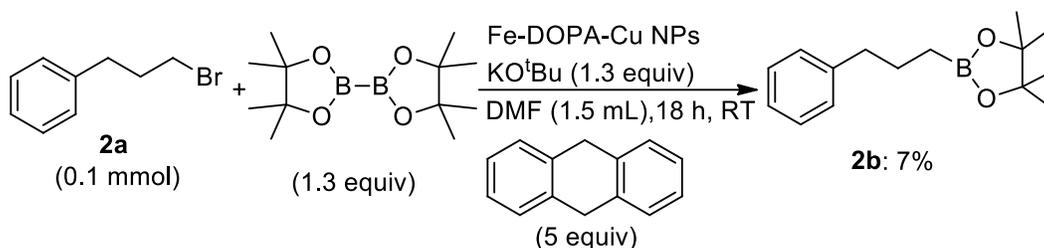
In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, Fe-DOPA-Cu NPs (10 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 33 mg, 0.13 mmol), KO^tBu (1.3 equiv, 15 mg, 0.13 mmol) and 5 equiv of 9,10-dihydroanthracene (90.1 mg) were added, followed by 1.5 mL of solvent and reaction mixture was kept under stirring for 18h 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. An internal standard nitromethane was added to the residue. The yield of the product was determined by ^1H NMR spectroscopy.

Experiment S2:
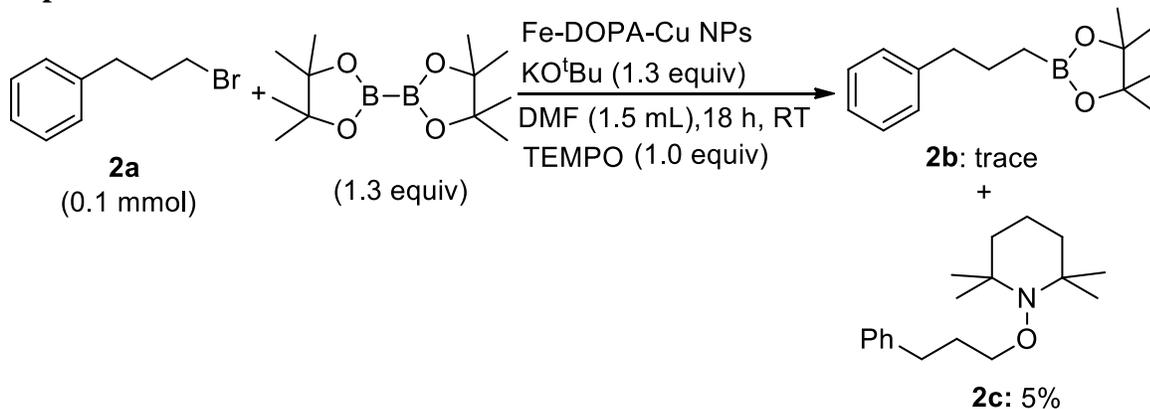
In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, Fe-DOPA-Cu NPs (10 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 33 mg, 0.13 mmol), KO^tBu (1.3 equiv, 15 mg, 0.13 mmol) and 1 equiv of TEMPO (16 mg) were added, followed by 1.5 ml of solvent and reaction mixture was kept under stirring h for 18 h room temperature. The crude reaction was dissolved in

Et$_2$O (20 mL) and then transferred to a separatory funnel followed by the addition of H$_2$O (20 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et$_2$O (3 x 10 mL). The combined organics were dried (Na$_2$SO$_4$) and concentrated. An internal standard nitromethane was added to the residue. The crude reaction mixture was examined by ^{1}H NMR spectroscopy and GC-MS analysis.

Trace amount of borylated product **2b** was observed by ^{1}H NMR spectroscopy and GC-MS analysis. 3-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-propane (**2c**)[10] was observed in only small amount and was not readily isolated.

Mercury Poisoning Experiments

a) In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KO^tBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL), (3-bromopropyl)benzene (**2a**, 199 mg, 1 mmol) and Hg (300 equiv) we added and the reaction was stirred vigorously at room temperature for 18 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.

b) In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KOtBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL), (3-bromopropyl)benzene (**2a**, 199 mg, 1 mmol) were added and the reaction was stirred vigorously at room temperature for 8 h. After 8 h reaction process, the reaction was interrupted and 300 equiv of Hg was added. After stirring for about 10 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. An internal standard nitromethane was added to the residue. The yield of the product was determined by ^1H NMR spectroscopy.
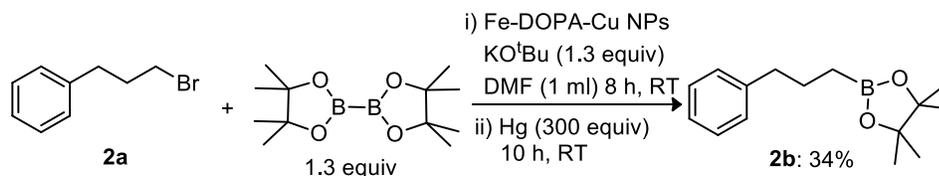
Filtration Experiment

In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KOtBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (5 mL), (2-bromoethyl)benzene (**1a**, 185 mg, 1 mmol) were added and the reaction was stirred vigorously at room temperature for 8 h. After 8 h reaction process, the Fe-DOPA-Cu NPs catalyst was separated by applying an external magnet, and the filtrate was stirred for another 10 h under identical conditions. Gratifyingly, there was no further increase in the yield of **1b** after the removal of the catalyst. Further addition of the removed 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 Fe-DOPA-Cu NPs catalyst.
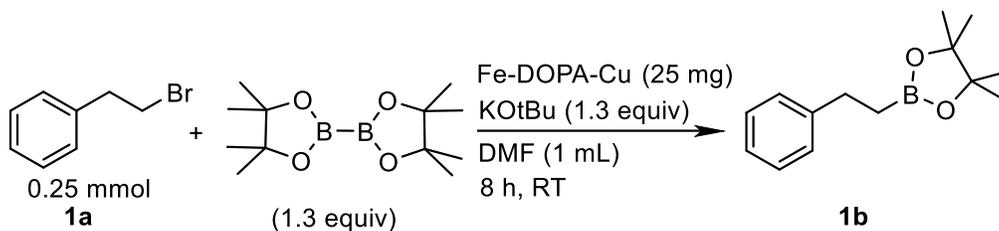
Recyclability Experiment for Alkyl Halide Borylation Reaction.
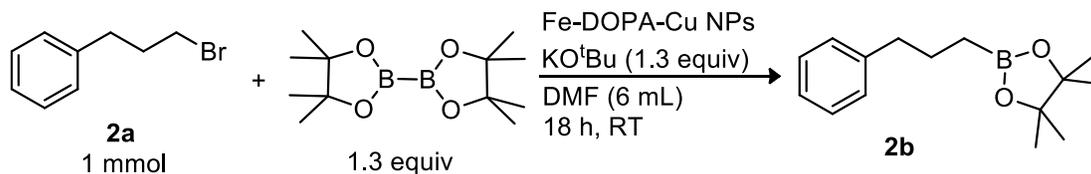
In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, Fe-DOPA-Cu NPs (100 mg, 5.4 mol % of Cu), B_2pin_2 (1.3 equiv, 330 mg, 1.3 mmol), KOtBu (1.3 equiv, 146 mg, 1.3 mmol), DMF (6 mL) and (3-bromopropyl)benzene (**2a**, 199 mg, 1 mmol) were added and the reaction was stirred vigorously at room temperature for 18 h. Cu-DH catalyst was separated by applying an external magnet and washed thoroughly MeOH (2 x 10 ml) and dried at 60 °C for 4 h, and same catalyst used for further cycles. Yields were determined by GC-MS analysis using *n*-dodecene as an internal standard.

Yields: 1st cycle to 10th cycle **2b** = 96%
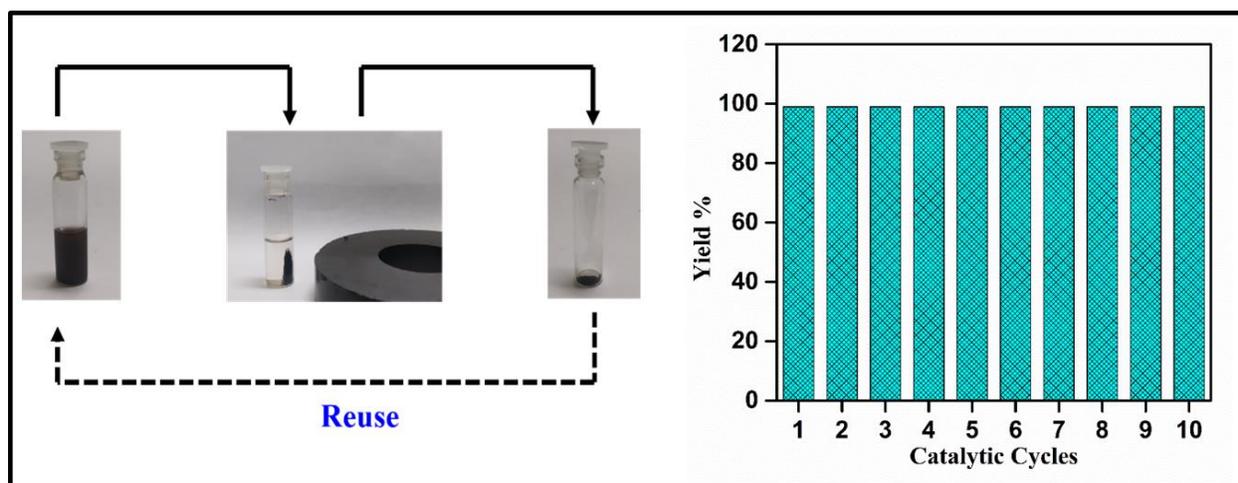
Figure S10: Catalyst recovery and recyclability for the borylation of (3-bromopropyl)benzene (**2a**).
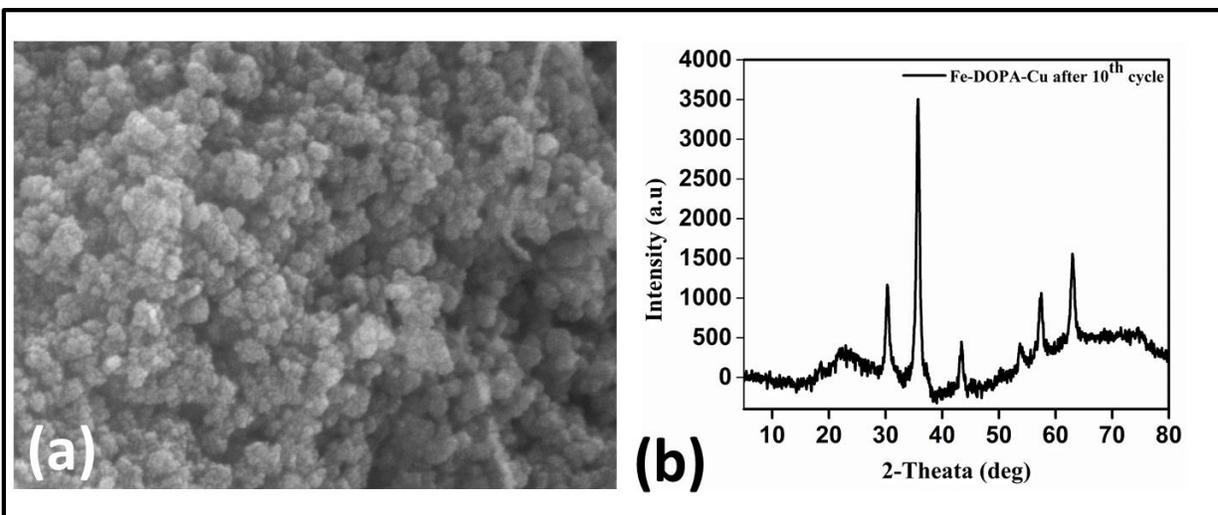
Figure S11: (a) FESEM image and (b) XRD pattern of catalyst after recovery.
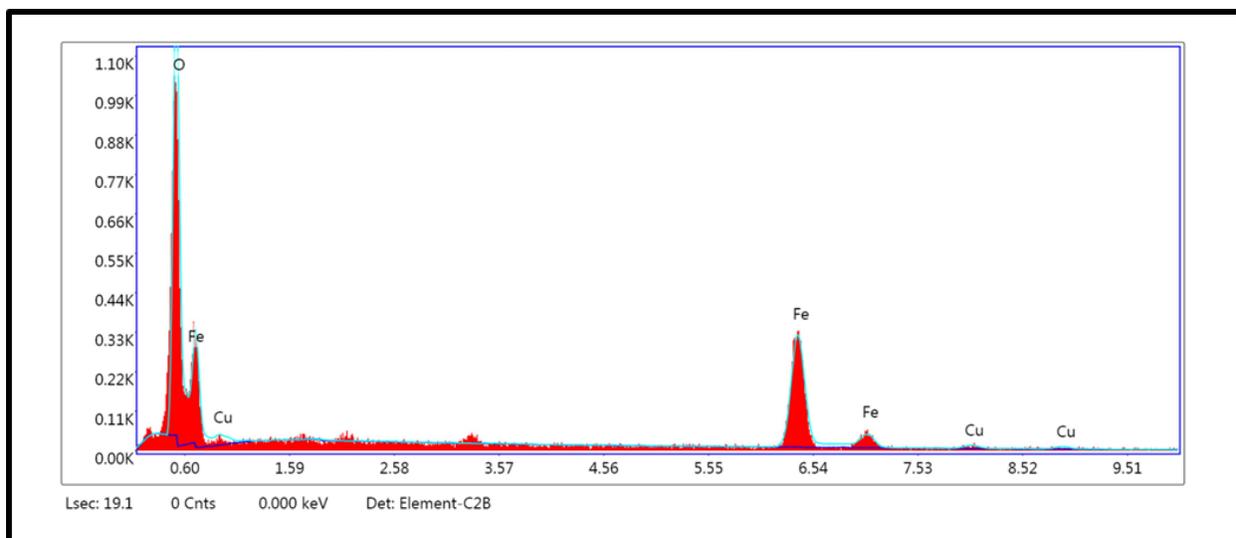
Figure S12: EDX analysis of catalyst after recovery.

VI. NMR Spectra and GC-MS Analyses of Alkyl Boronates

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

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolan (1b).[6]
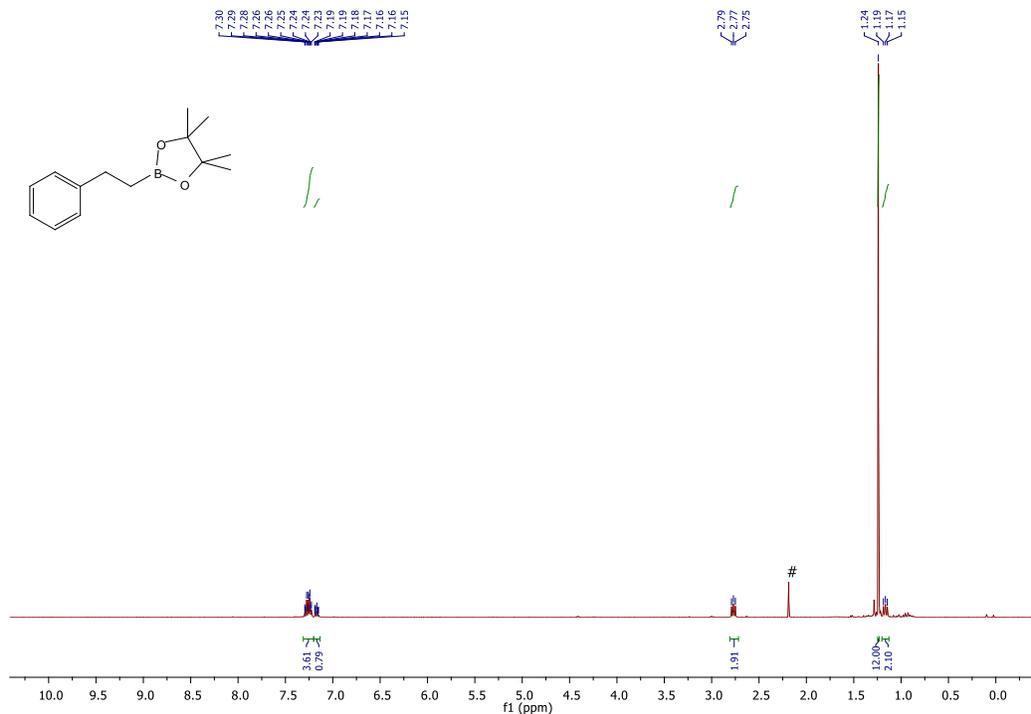
^{1}H NMR of 1b (400 MHz, CDCl$_3$)
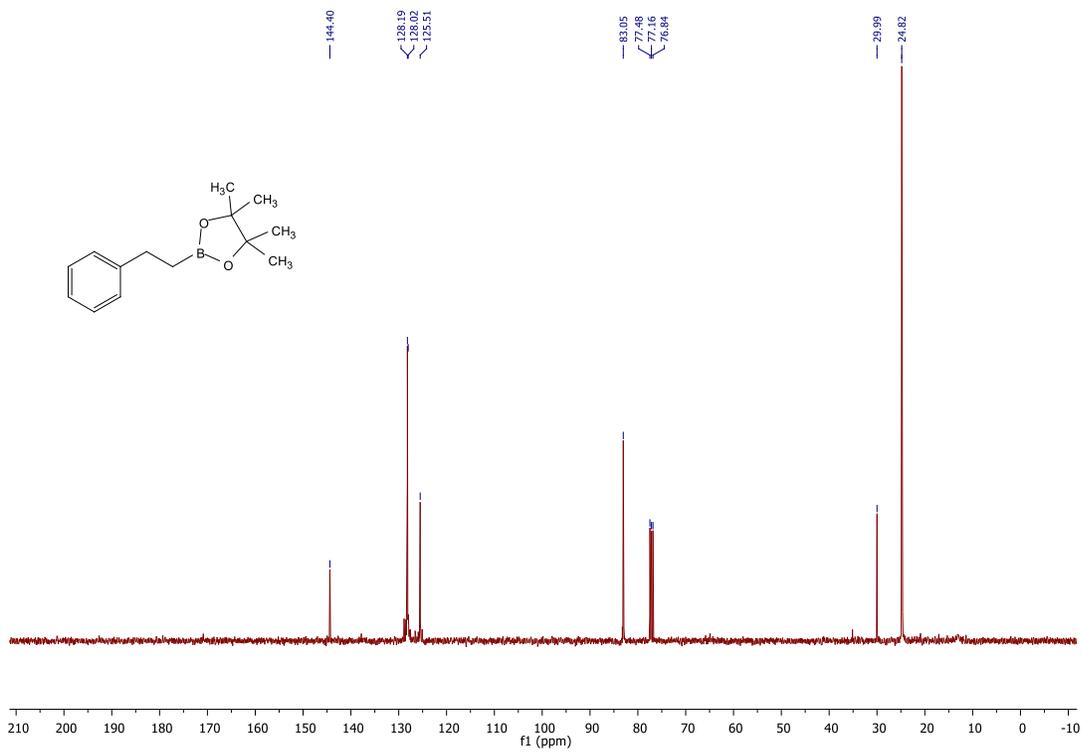
^{13}C NMR of 1b (100 MHz, CDCl$_3$)
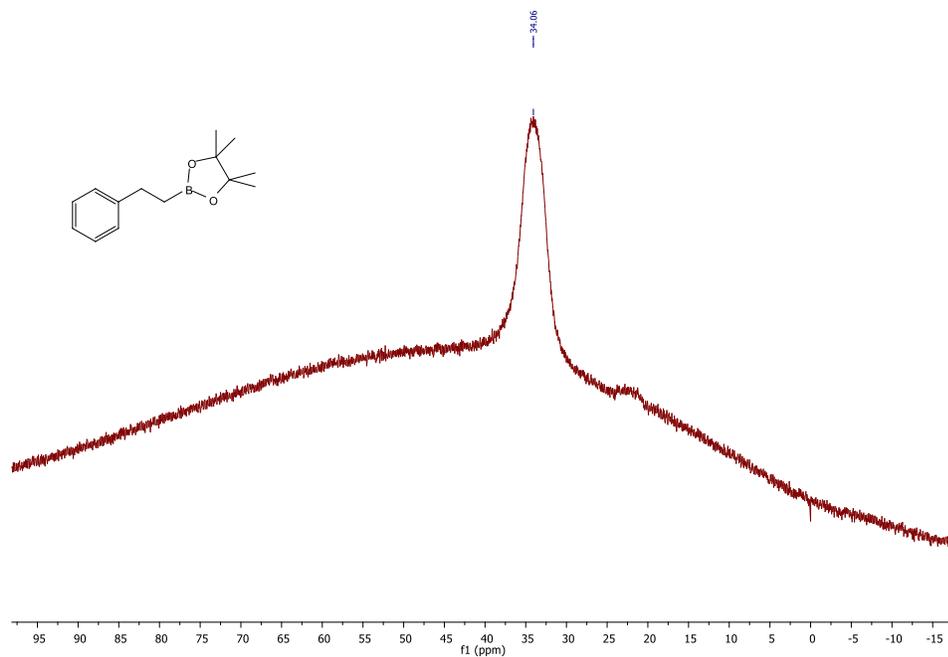
^{11}B NMR of 1b (128 MHz, CDCl$_3$)
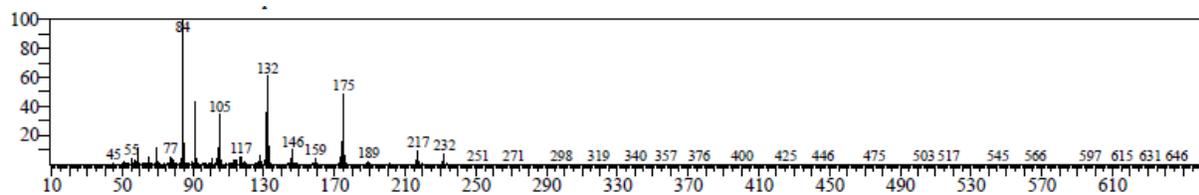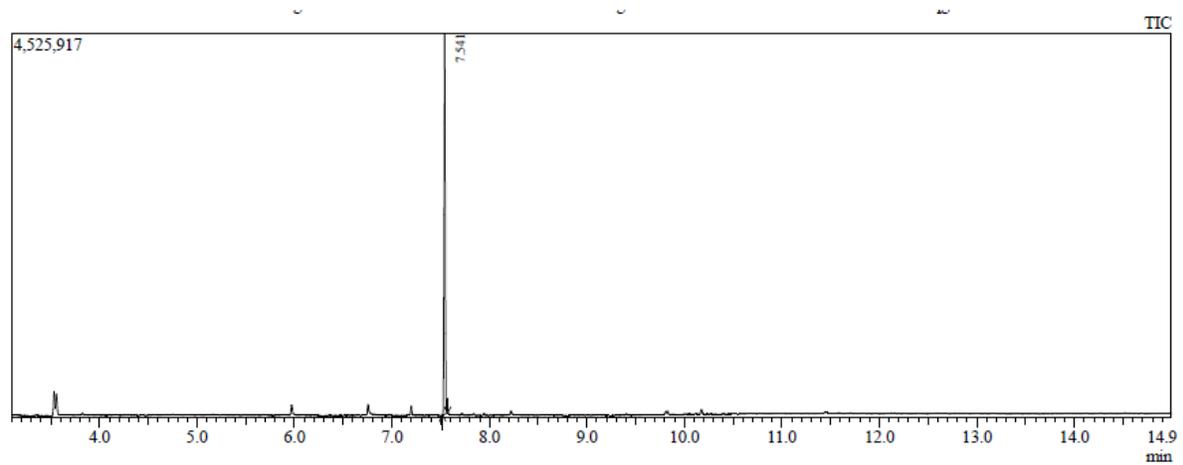
GC-MS data 1b

4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2b).[6]
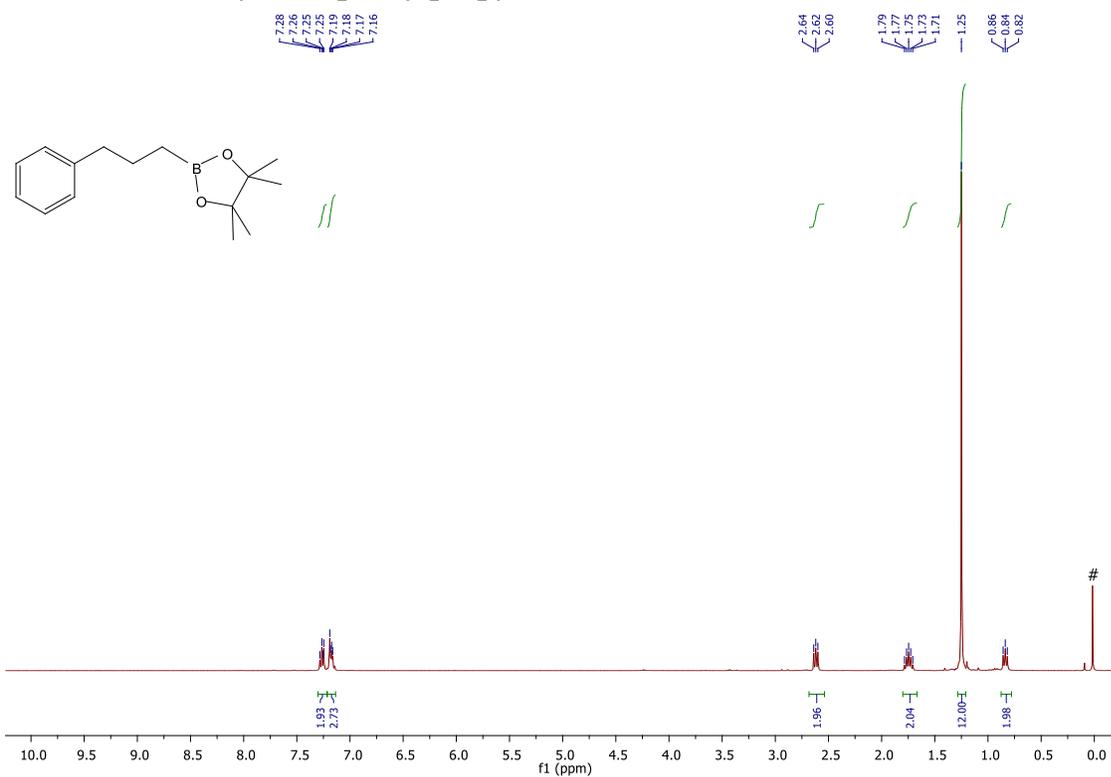
^{1}H NMR of 2b (400 MHz, CDCl$_3$)
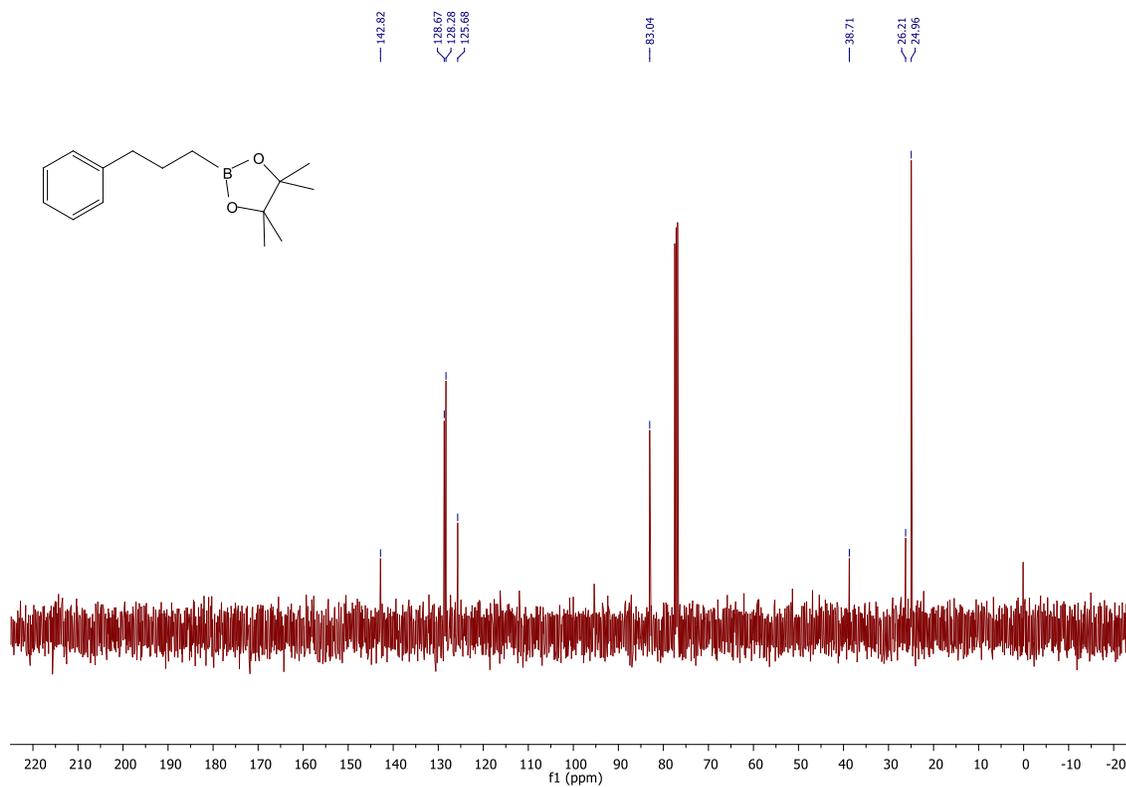
^{13}C NMR of 2b (100 MHz, CDCl$_3$)
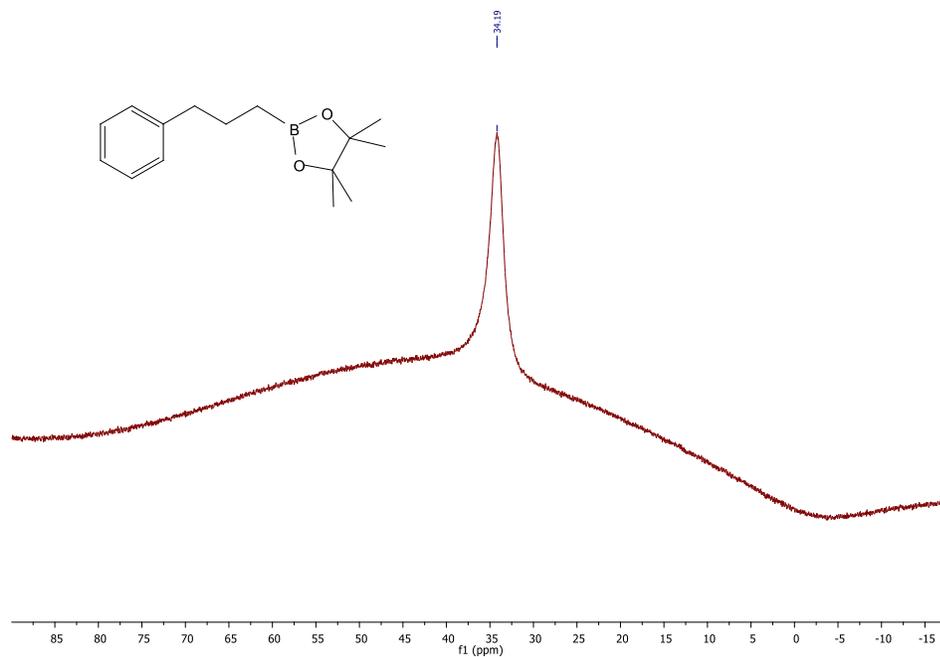
^{11}B NMR of 2b (128 MHz, CDCl₃)
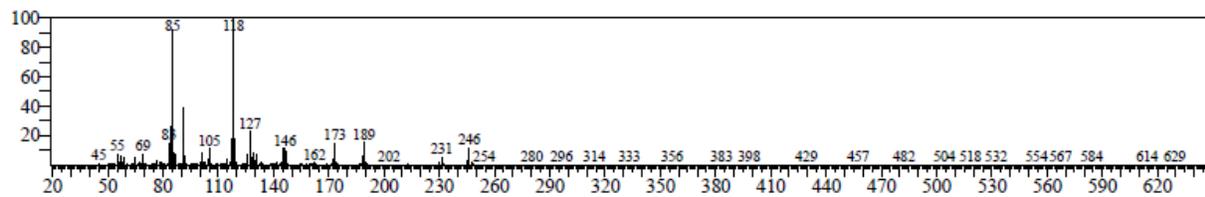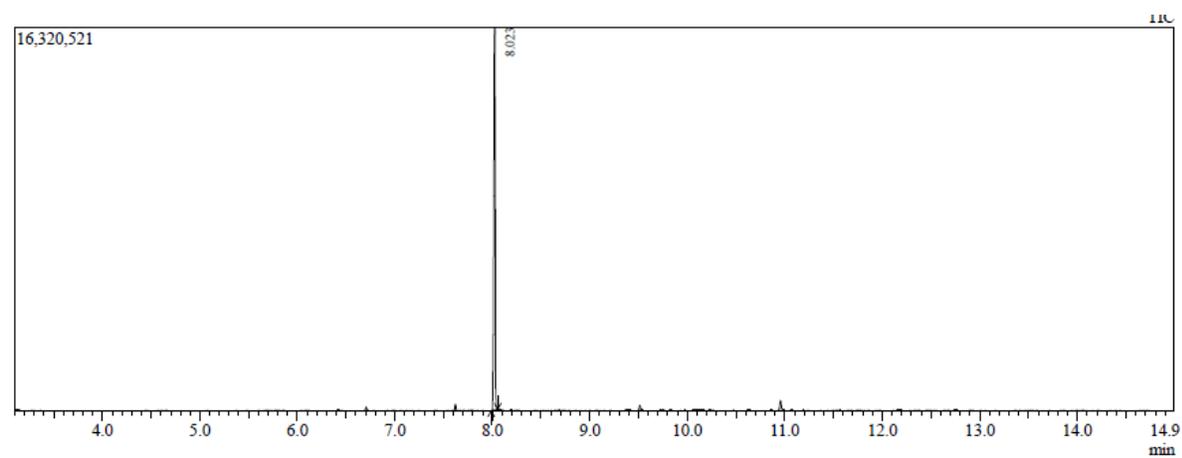
GC-MS data 2b

4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane (3b).[7]
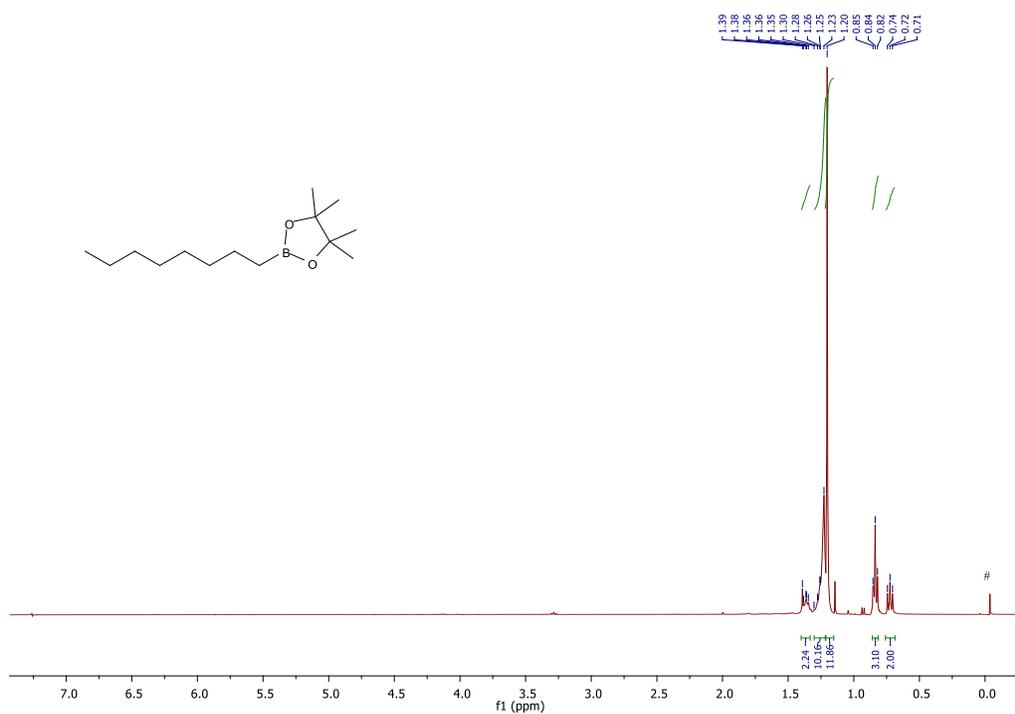
^{1}H NMR of 3b (400 MHz, CDCl$_3$)
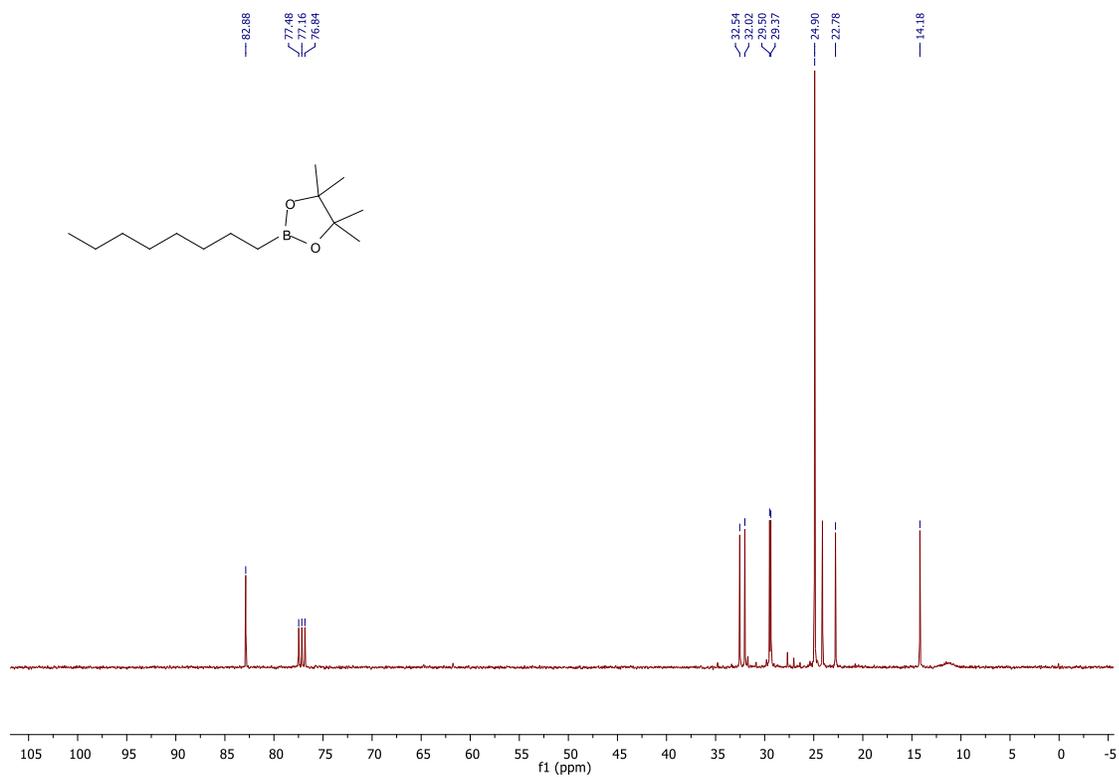
^{13}C NMR of 3b (100 MHz, CDCl$_3$)

−33.85
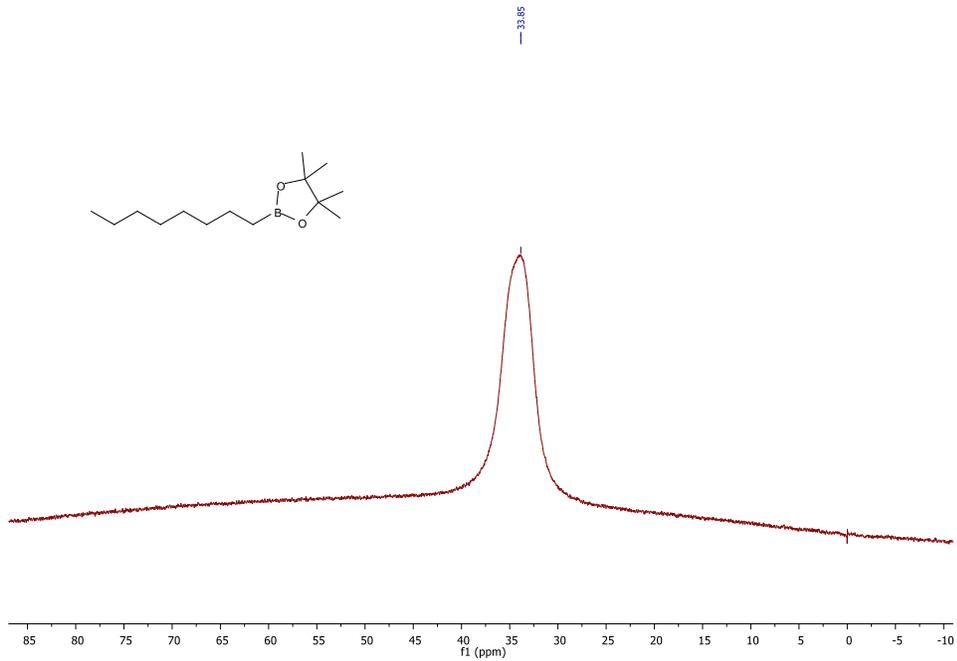
^{11}B NMR of 3b (128 MHz, CDCl$_3$)

24,334,545

7.209

TIC
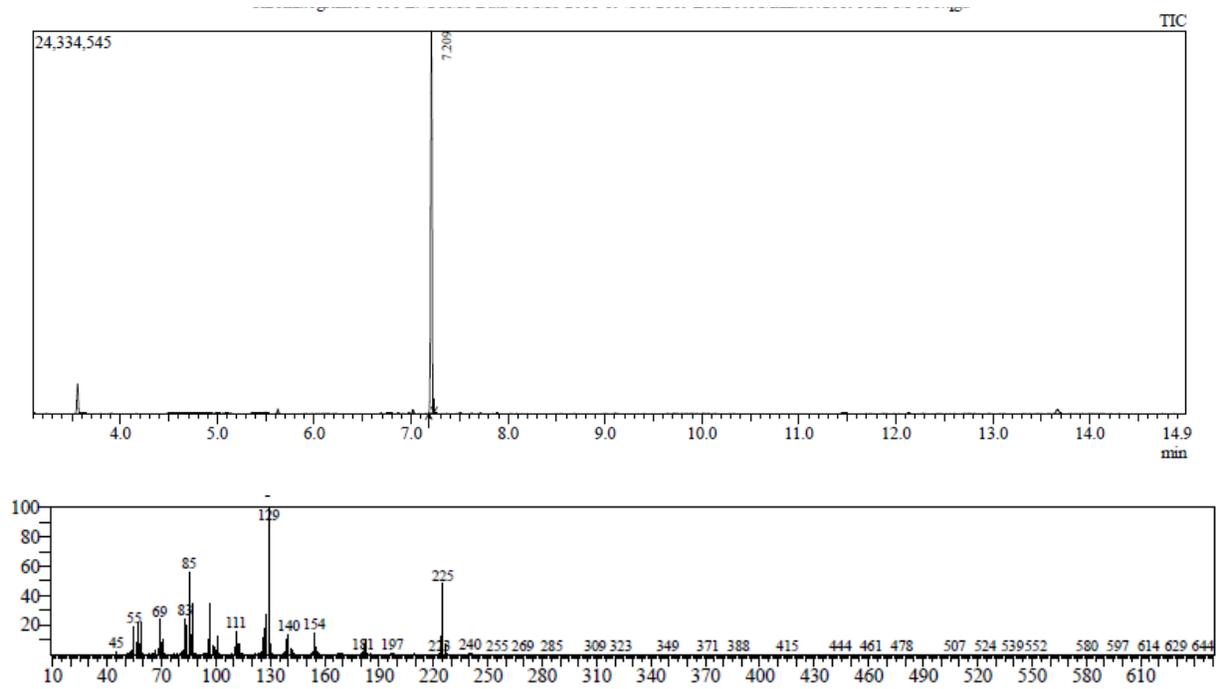
GC-MS data 3b

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

^{1}H NMR of 4b (400 MHz, CDCl$_3$)
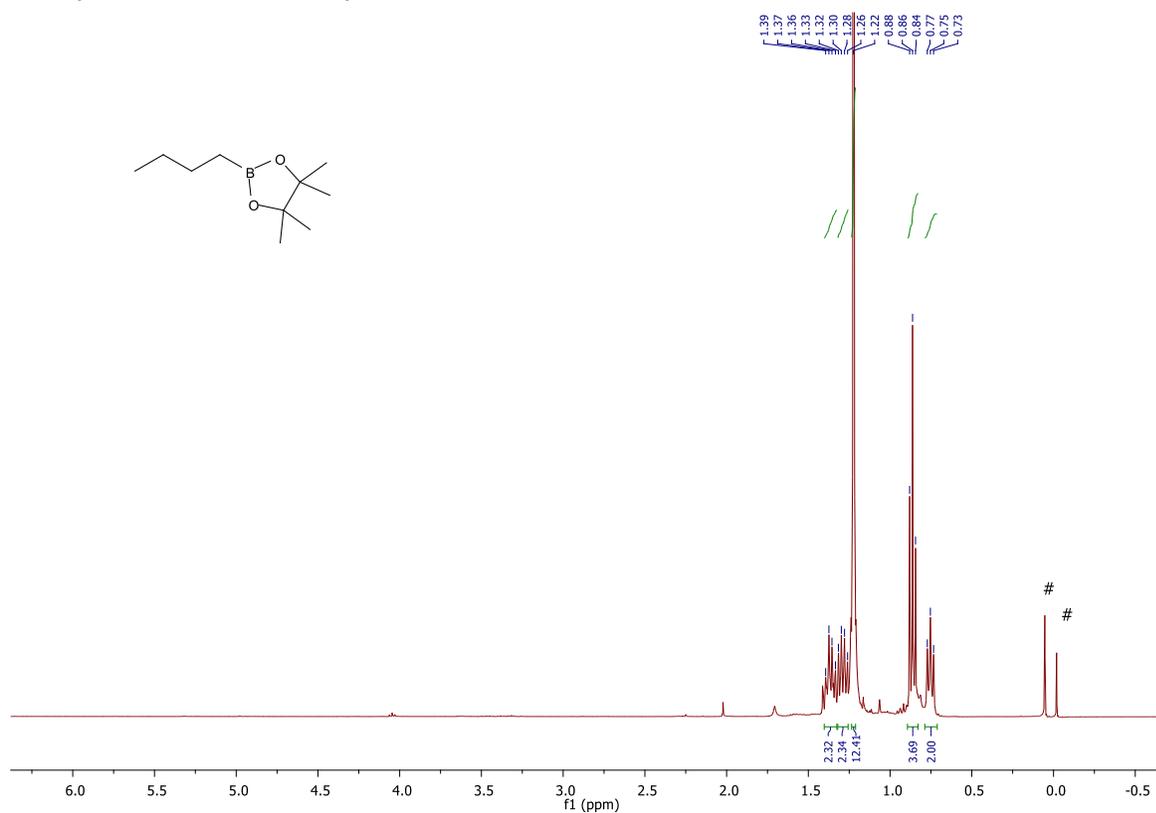
^{13}C NMR of 4b (100 MHz, CDCl$_3$)
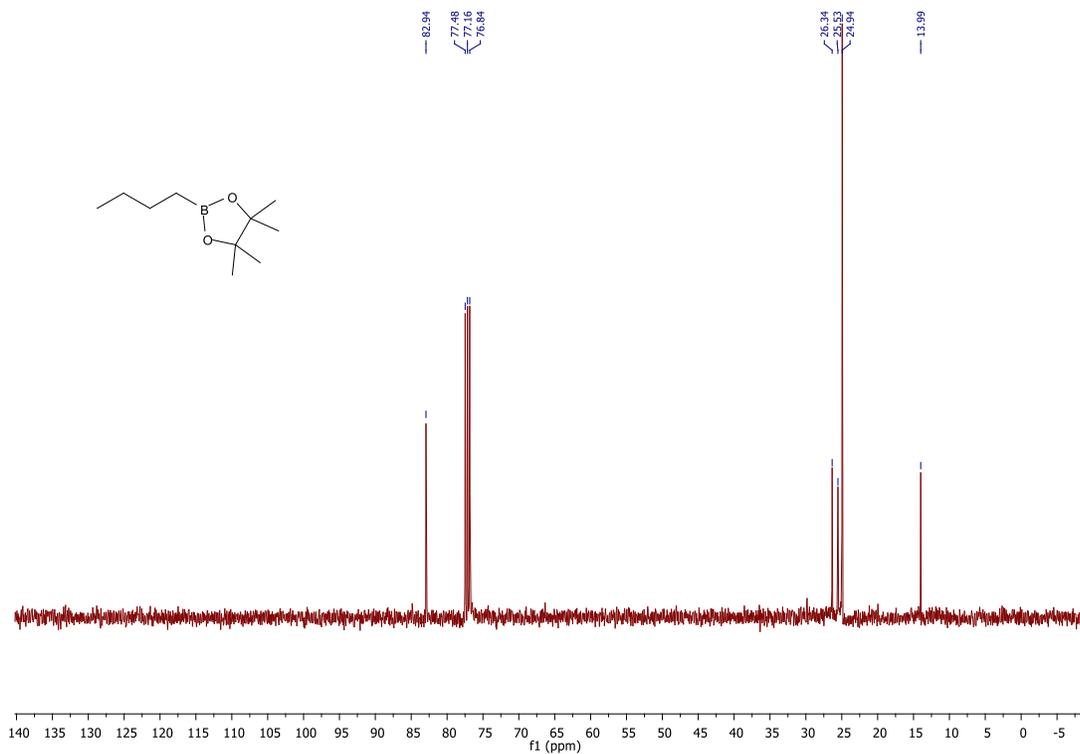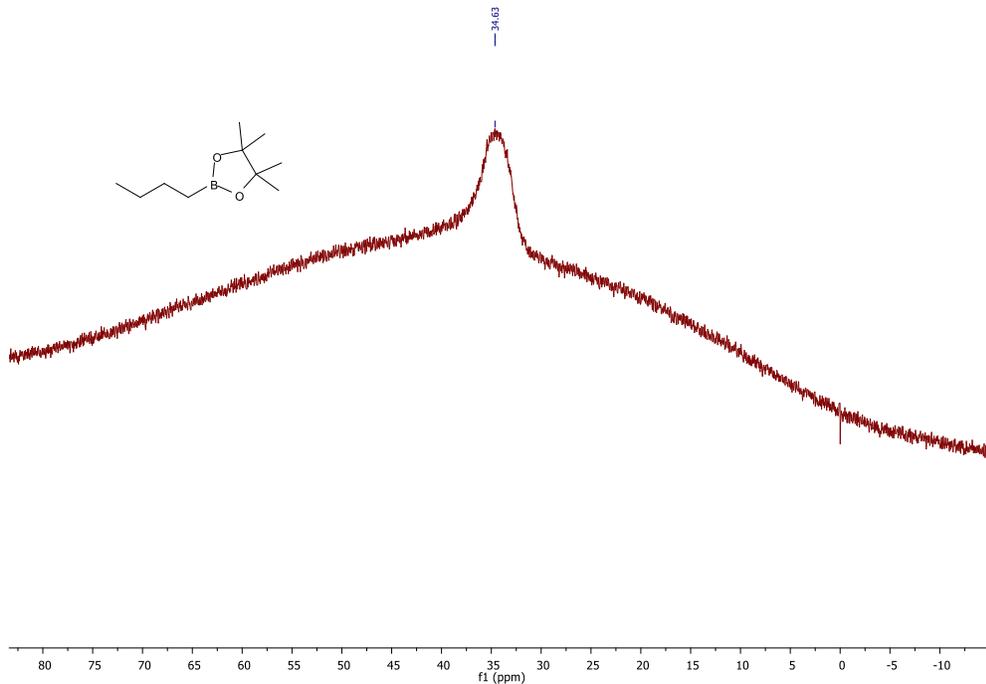
^{11}**B NMR of 4b (128 MHz, CDCl$_3$)**
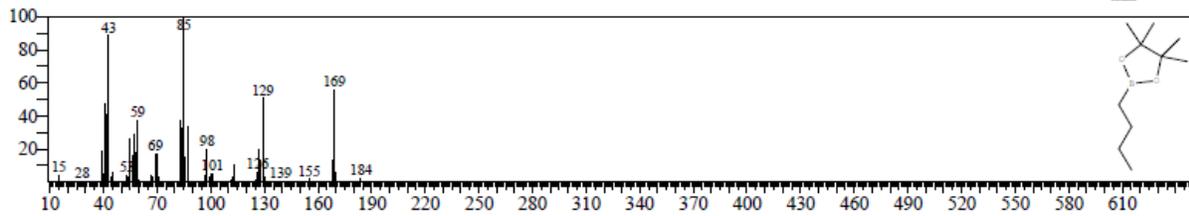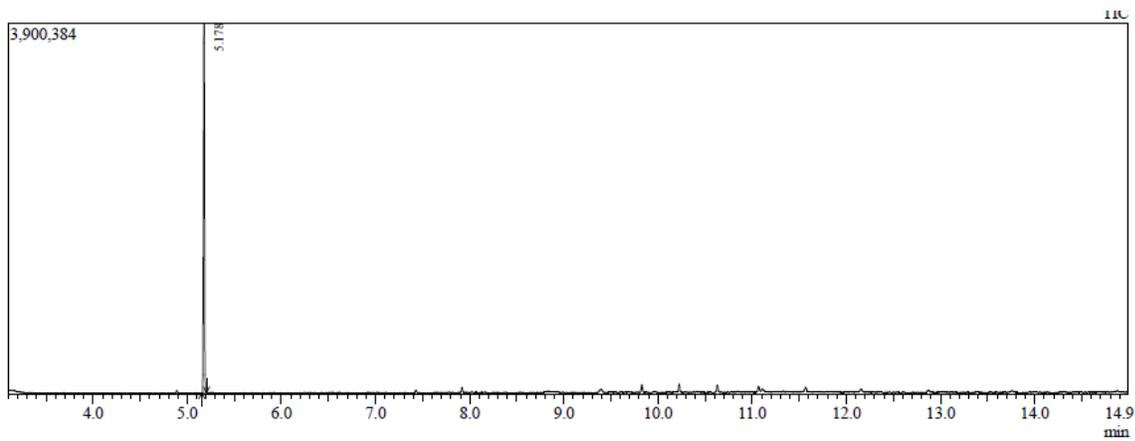
GC-MS data 4b

Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (5b).[9]

^{1}H NMR of 5b (400 MHz, CDCl$_3$)
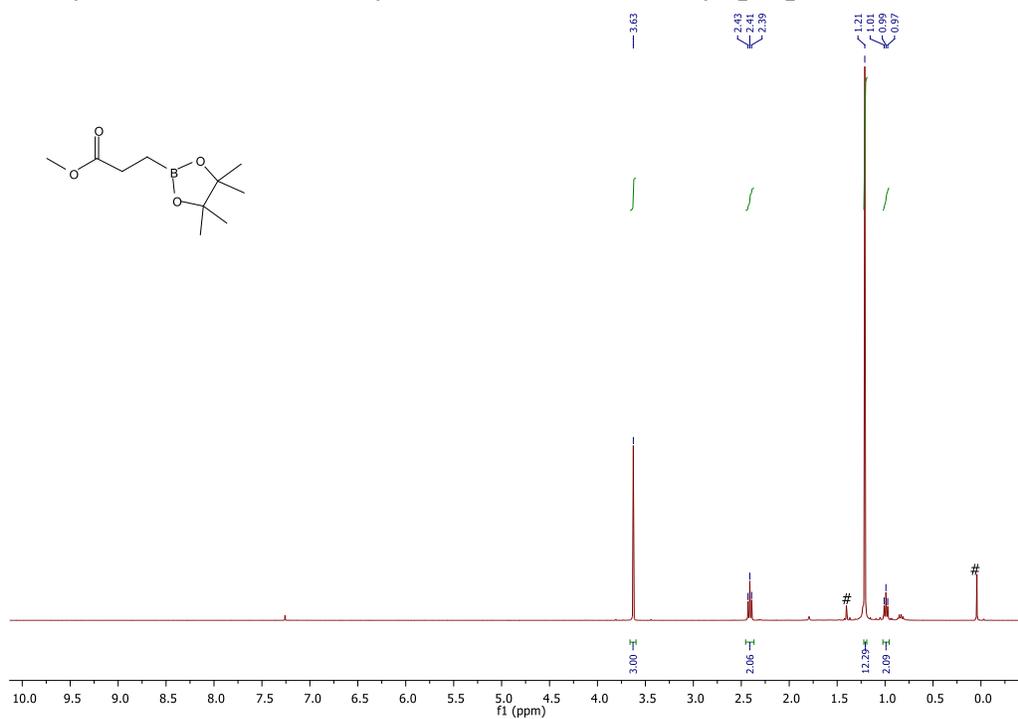
^{13}C NMR of 5b (100 MHz, CDCl$_3$)

33.73
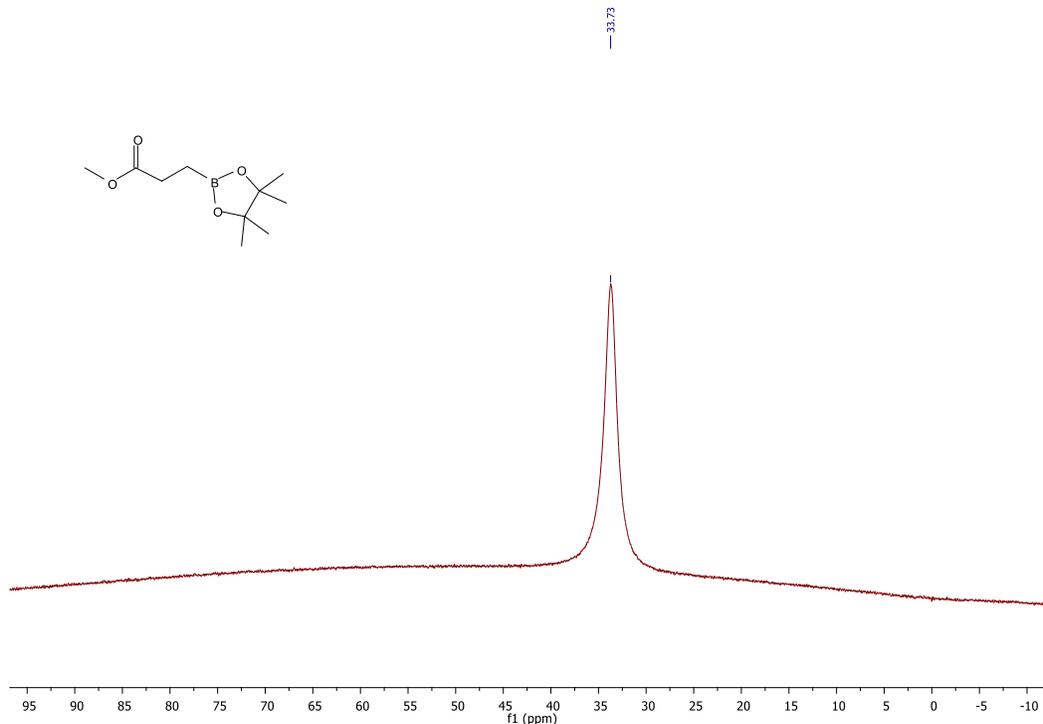
¹¹B NMR of 5b (128 MHz, CDCl₃)
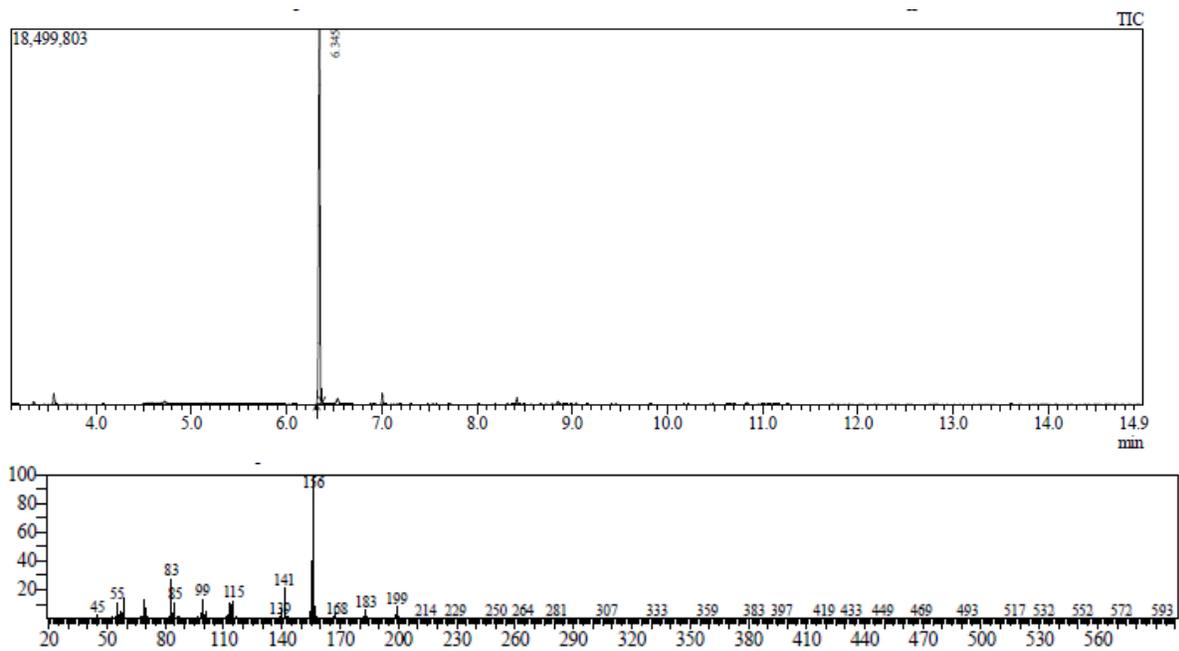
GC-MS data 5b

Ethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (6b).[8]

^{1}H NMR of 6b (400 MHz, CDCl$_3$)
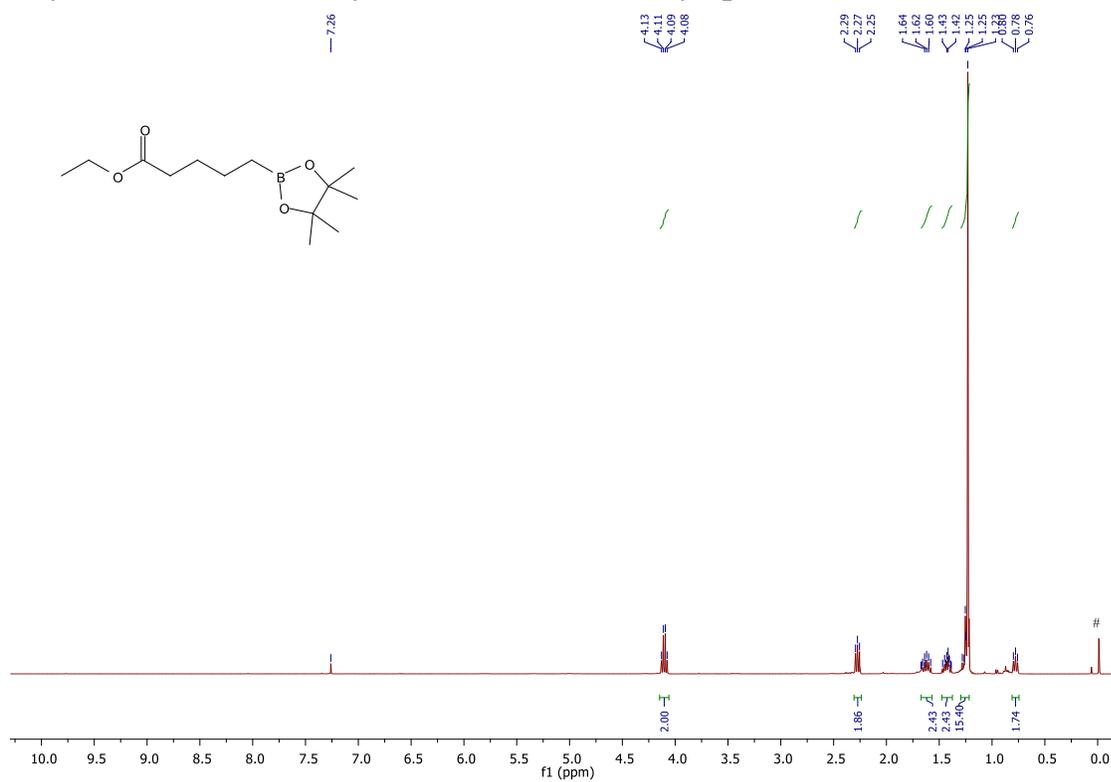
^{13}C NMR of 6b (100 MHz, CDCl$_3$)
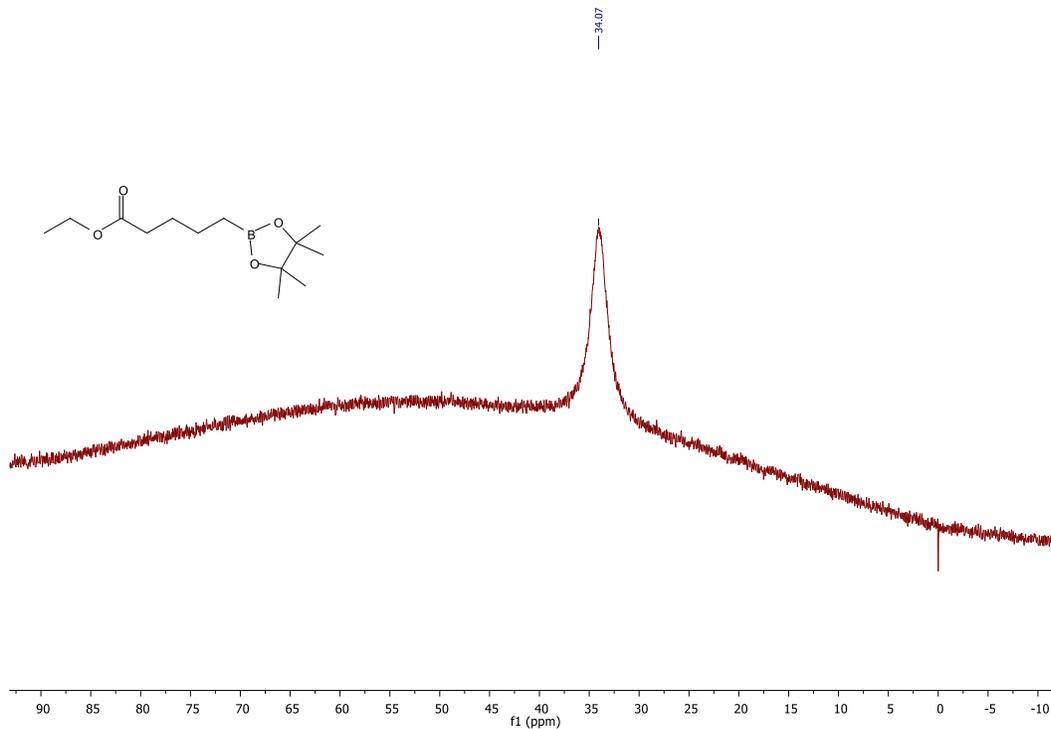
^{11}B NMR of 6b (128 MHz, CDCl$_3$)
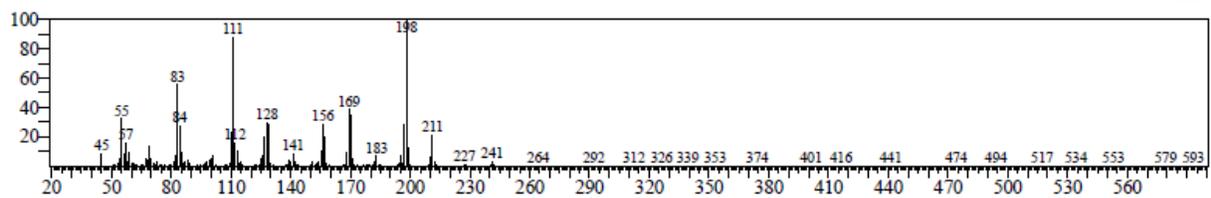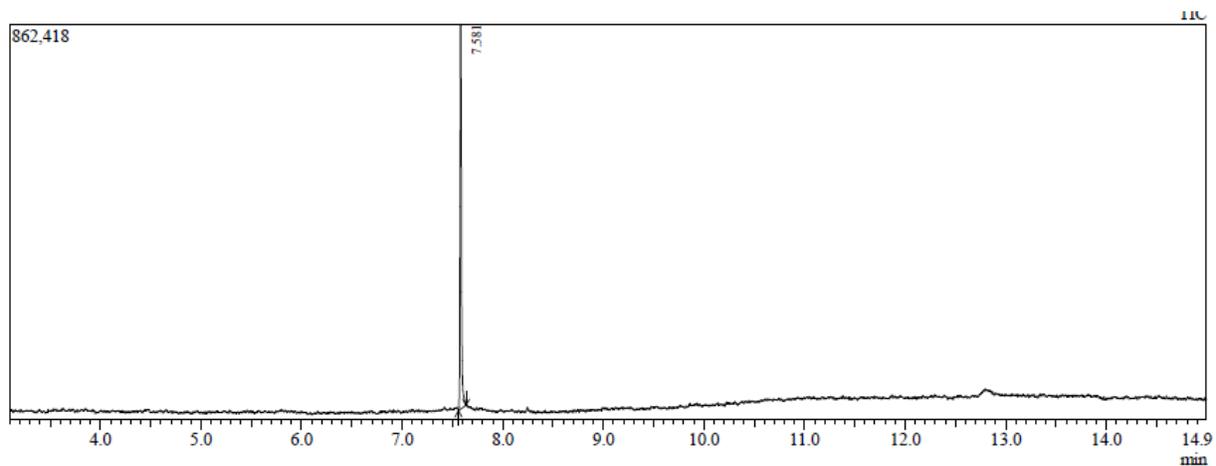
GC-MS data 6b

2-(2-(1,3-Dioxan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b).[6]
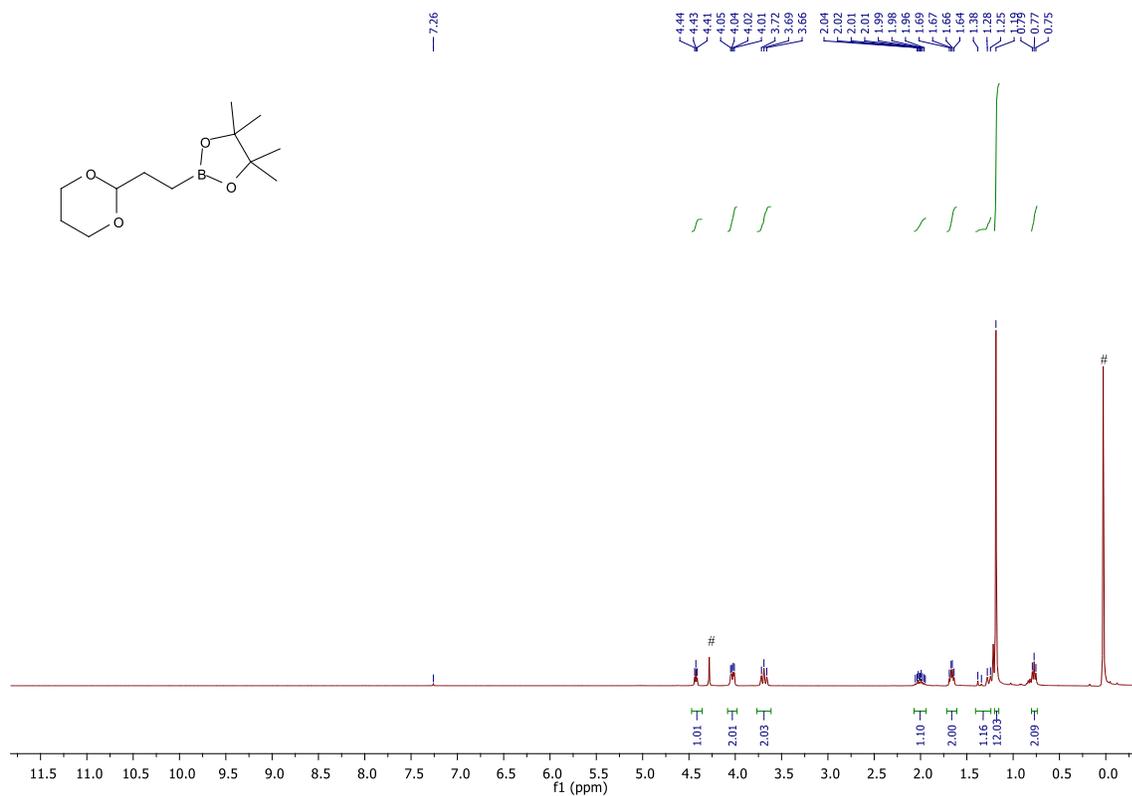
^{1}H NMR of 7b (400 MHz, CDCl[3])
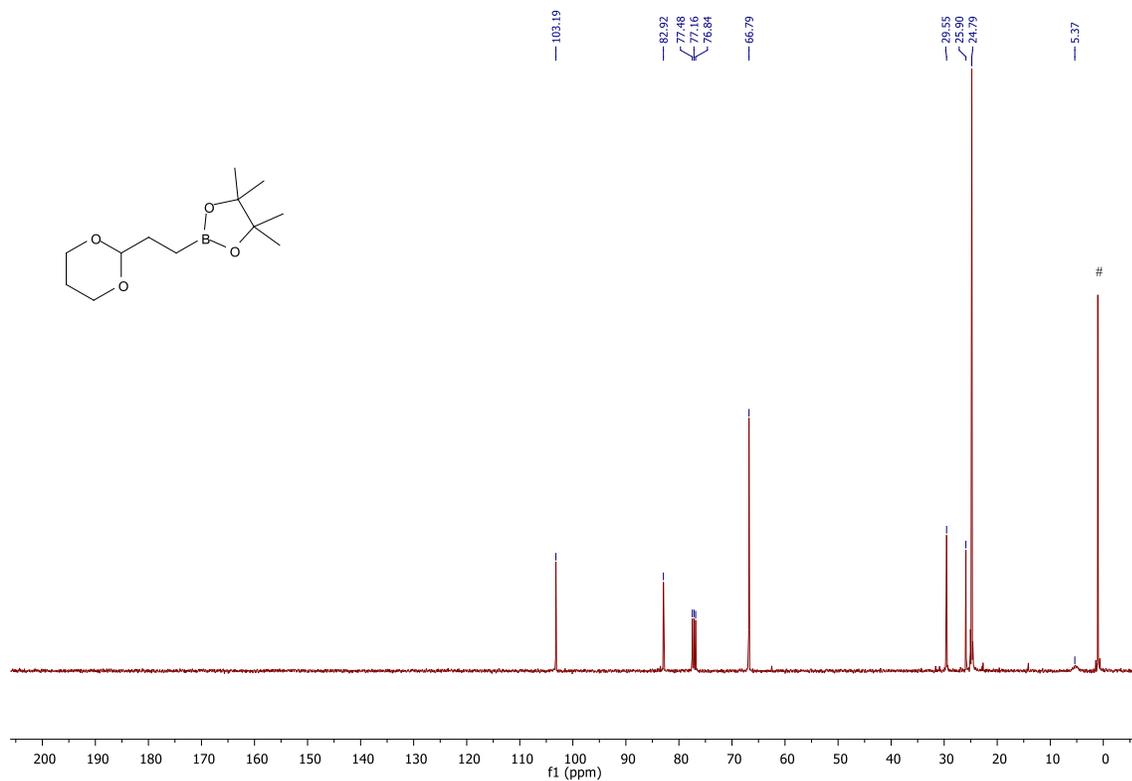
^{13}C NMR of 7b (100 MHz, CDCl[3])

—33.72
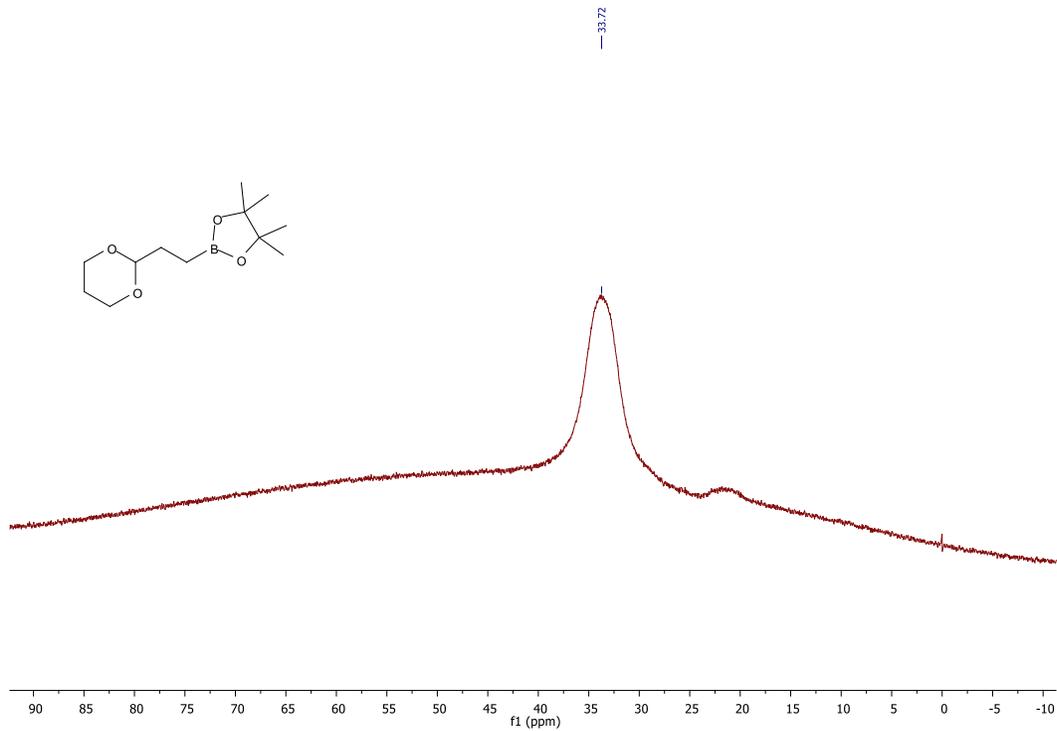
^{11}B NMR of 7b (128 MHz, CDCl$_3$)
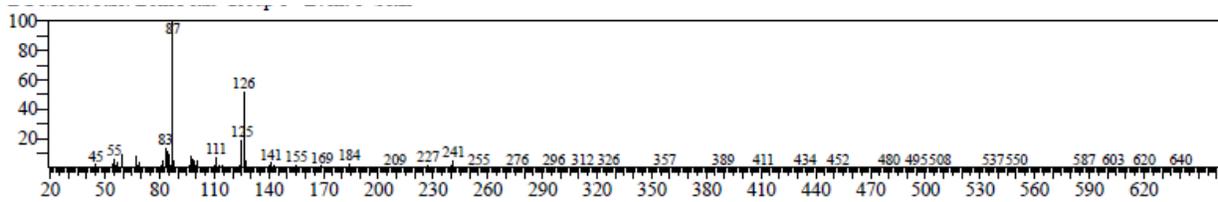
GC-MS data 7b

2-(3-(4-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b).[10]

^{1}H NMR of 8b (400 MHz, CDCl$_3$)

^{13}C NMR of 8b (100 MHz, CDCl$_3$)
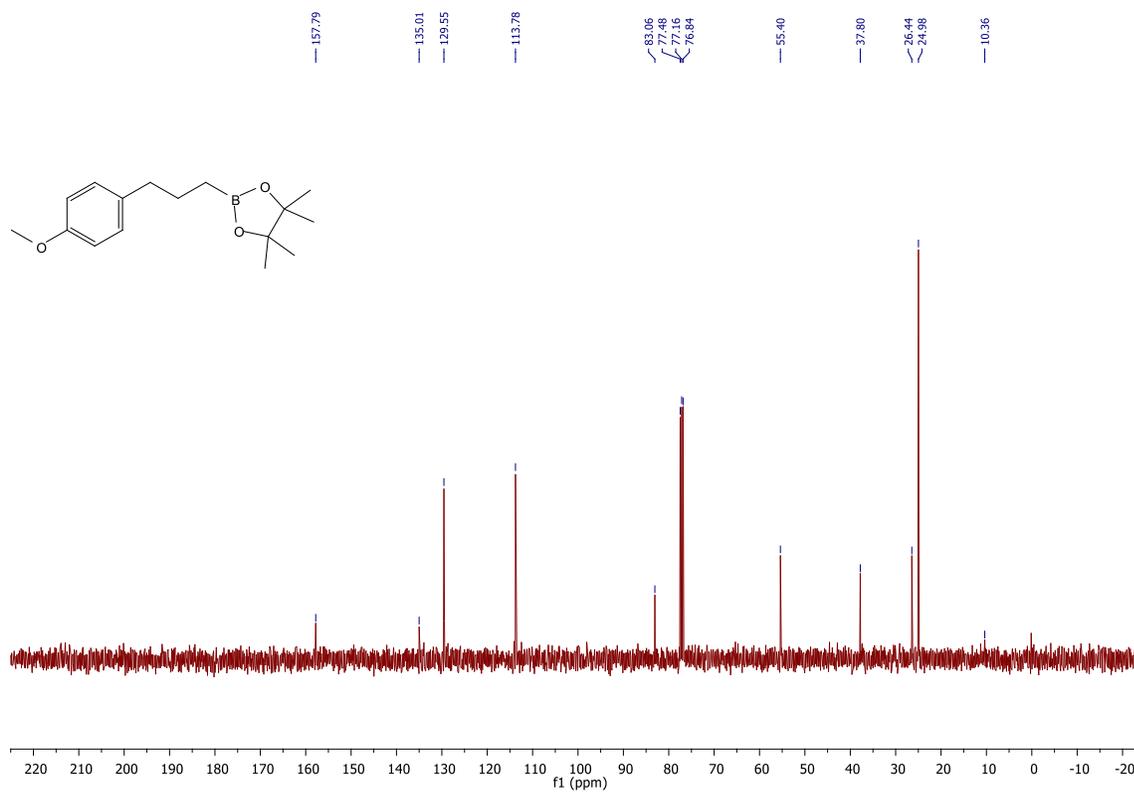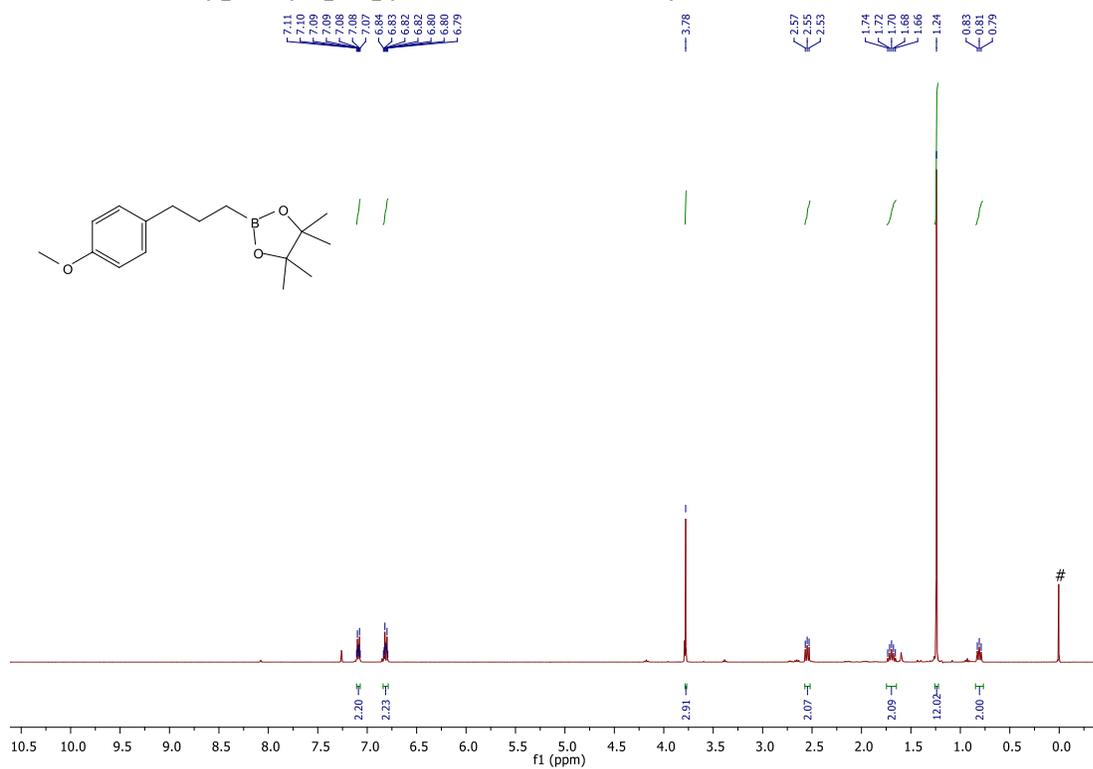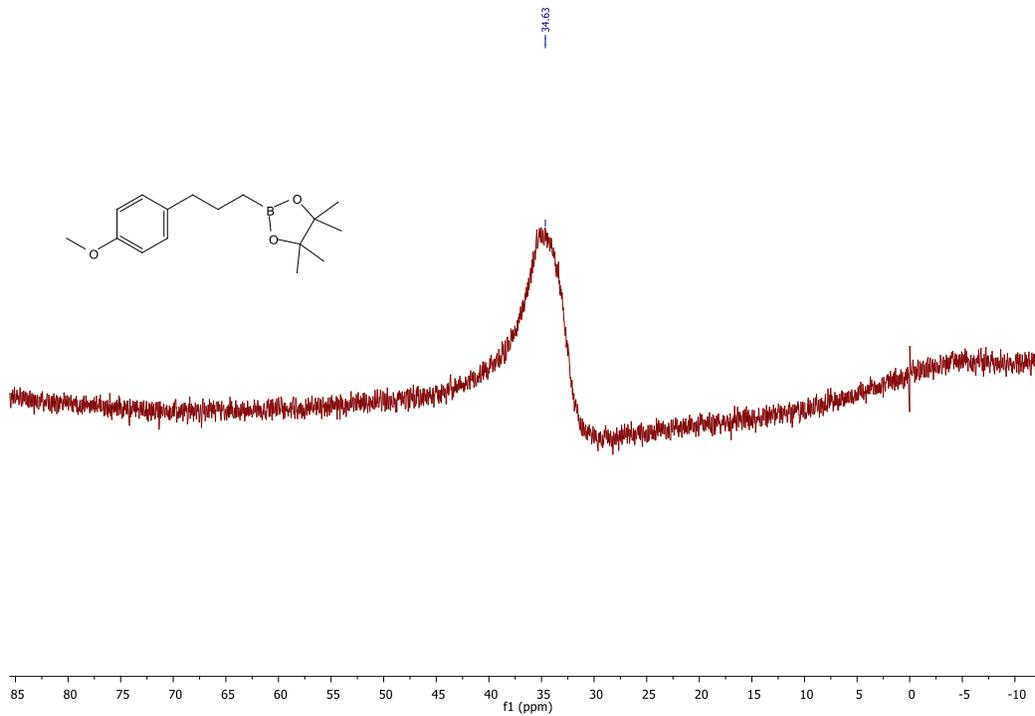
11B NMR of 8b (128 MHz, CDCl3)

GC-MS data 8b.

2-(6-Chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9b).[1]

¹H NMR of 9b (400 MHz, CDCl₃)
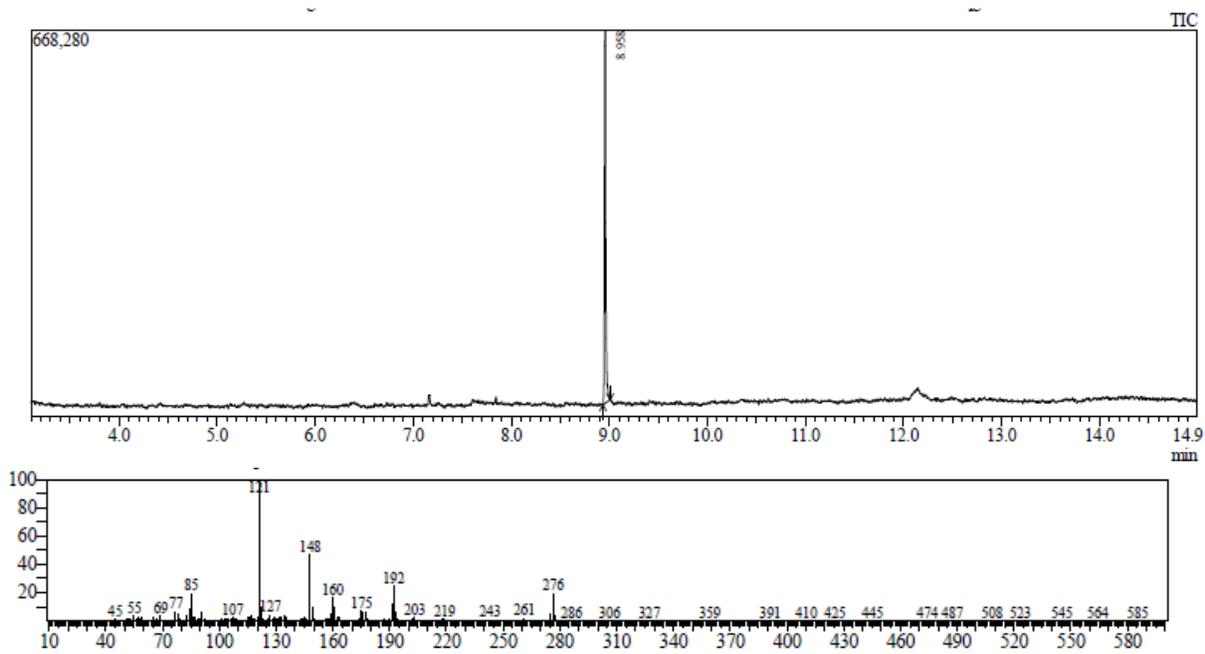
¹³C NMR of 9b (100 MHz, CDCl₃)
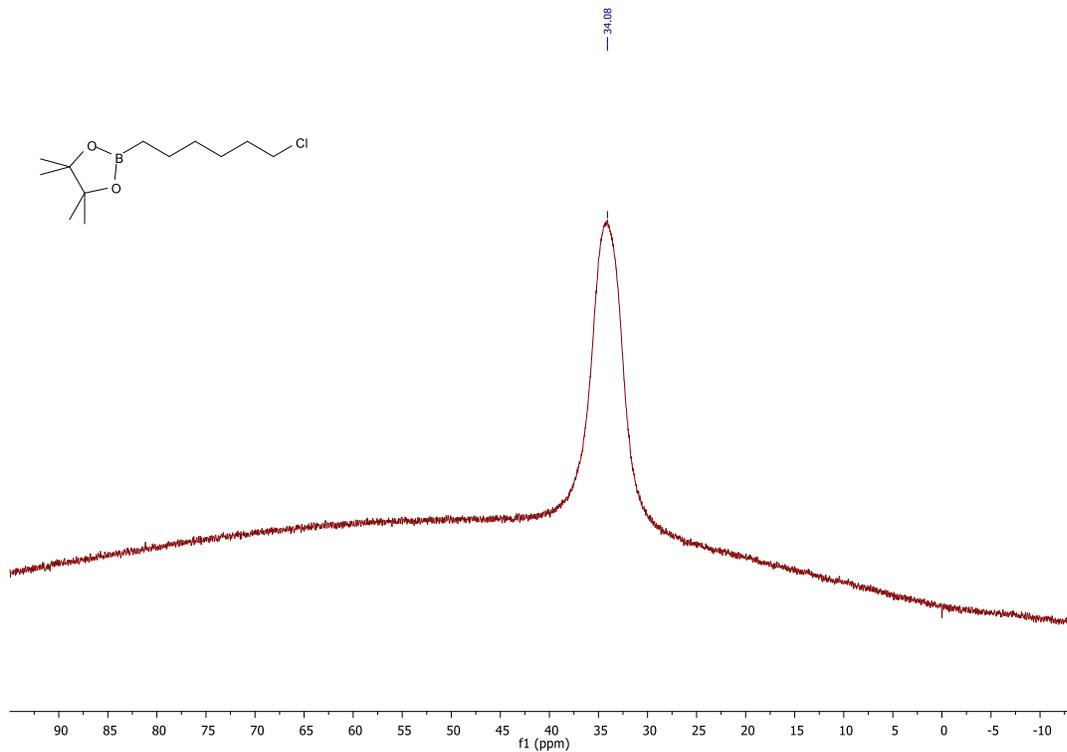
^{11}B NMR of 9b (128 MHz, CDCl$_3$)
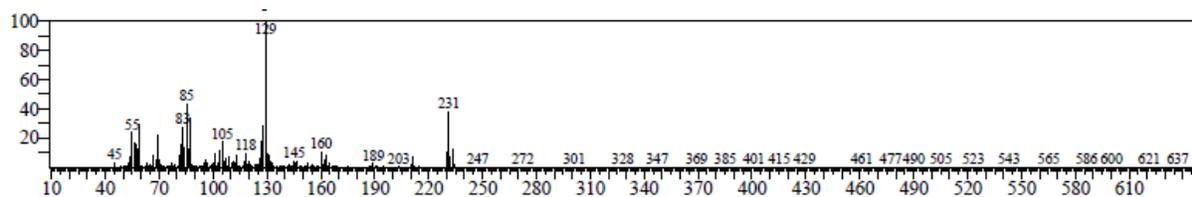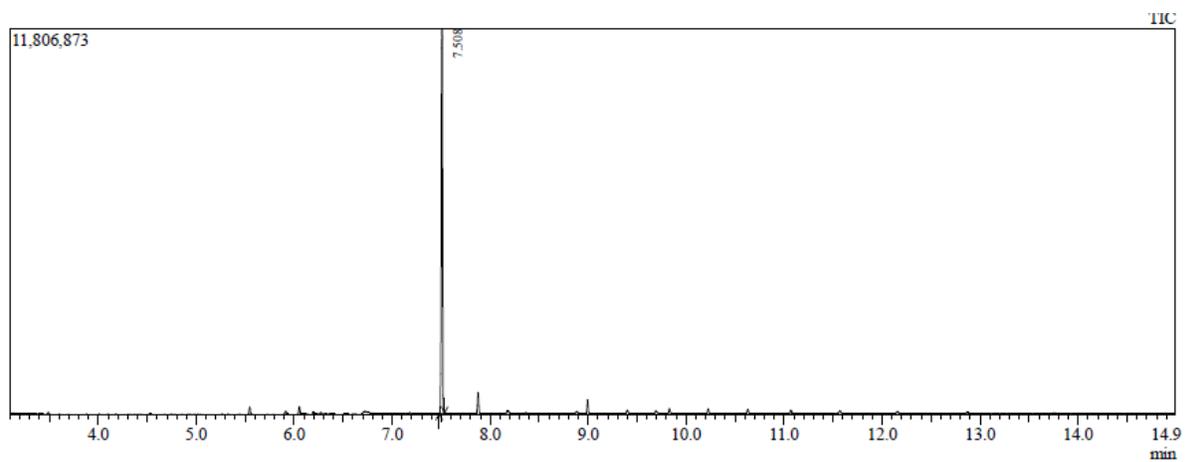
GC-MS data 9b

1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane (10b).[11]

^{1}H NMR of 10b (400 MHz, CDCl$_3$)

^{13}C NMR of 10b (100 MHz, CDCl$_3$)
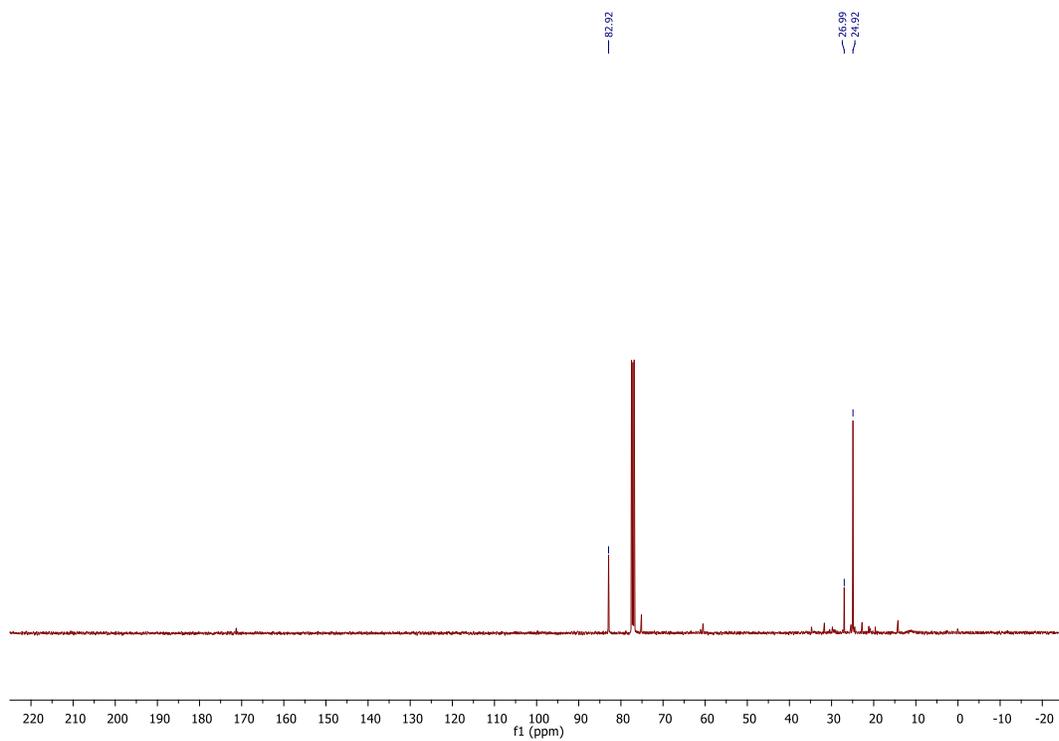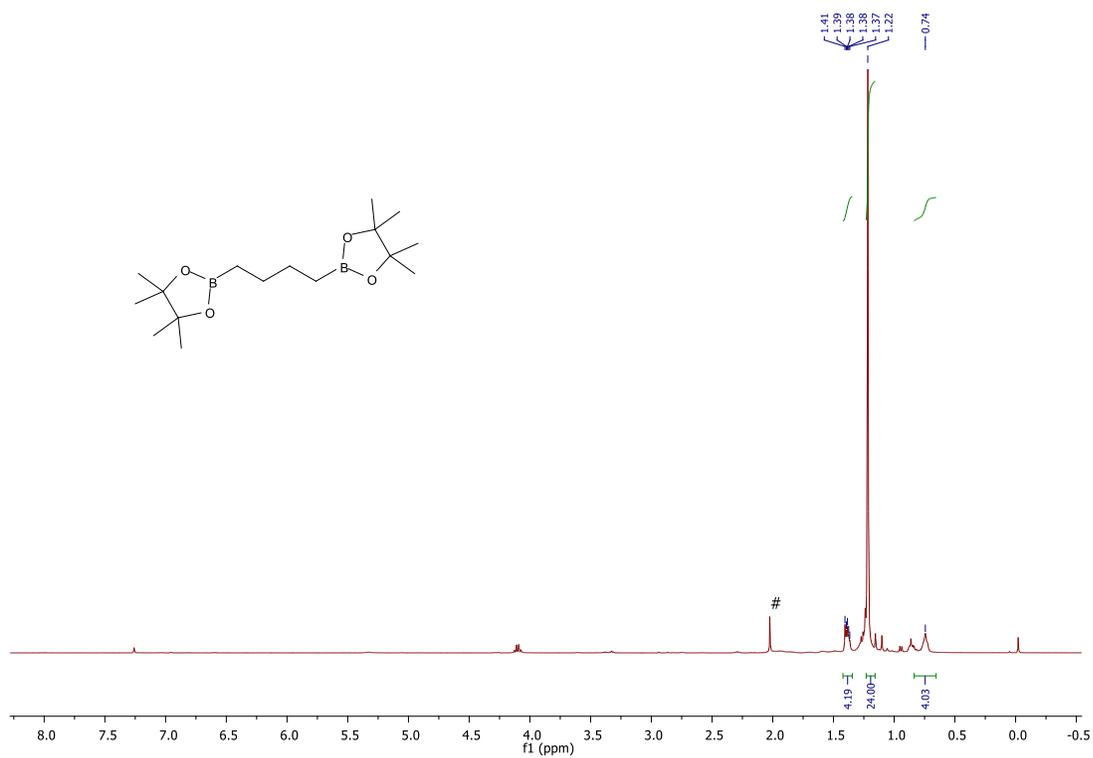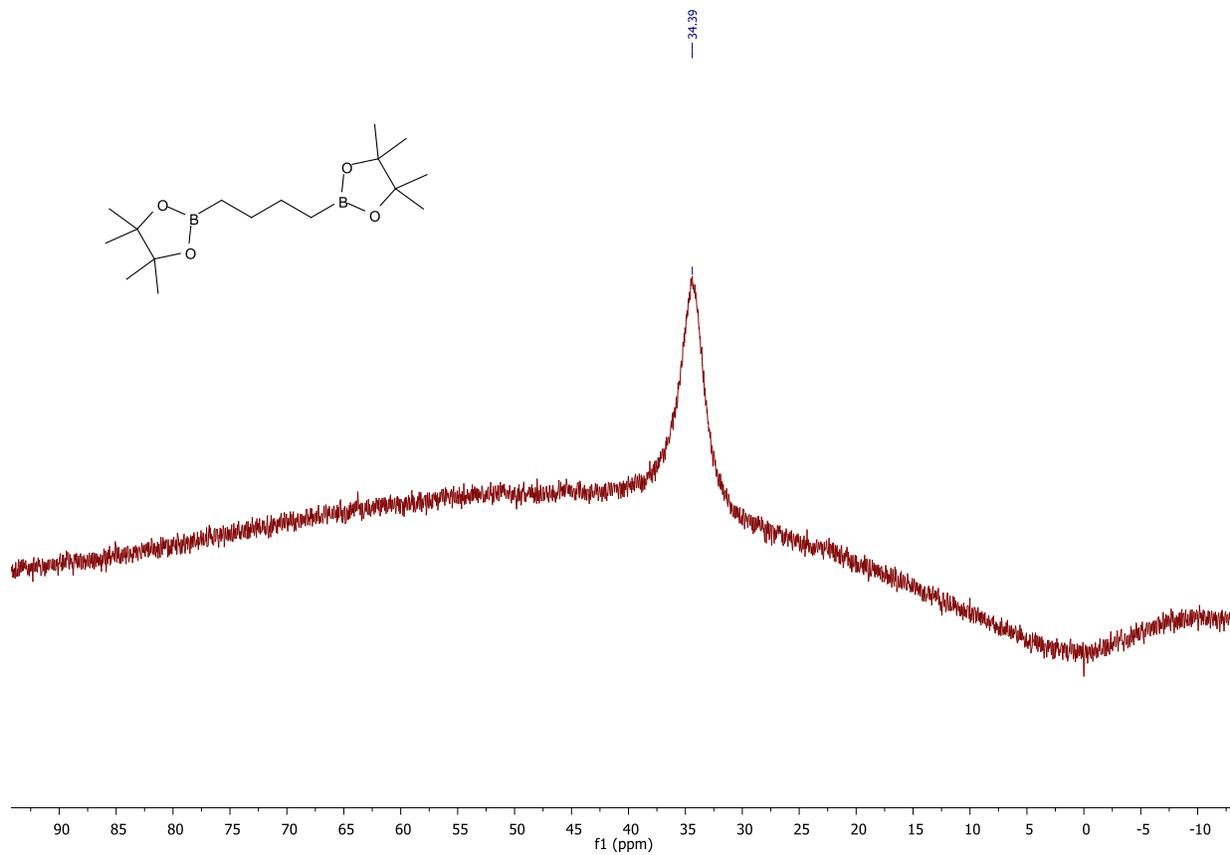
^{11}B NMR of 10b (128 MHz, CDCl$_3$)
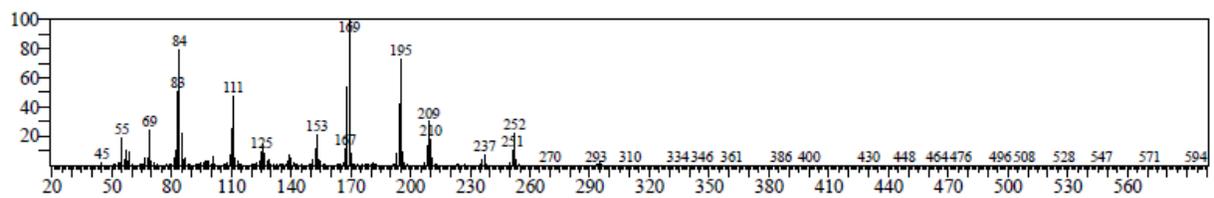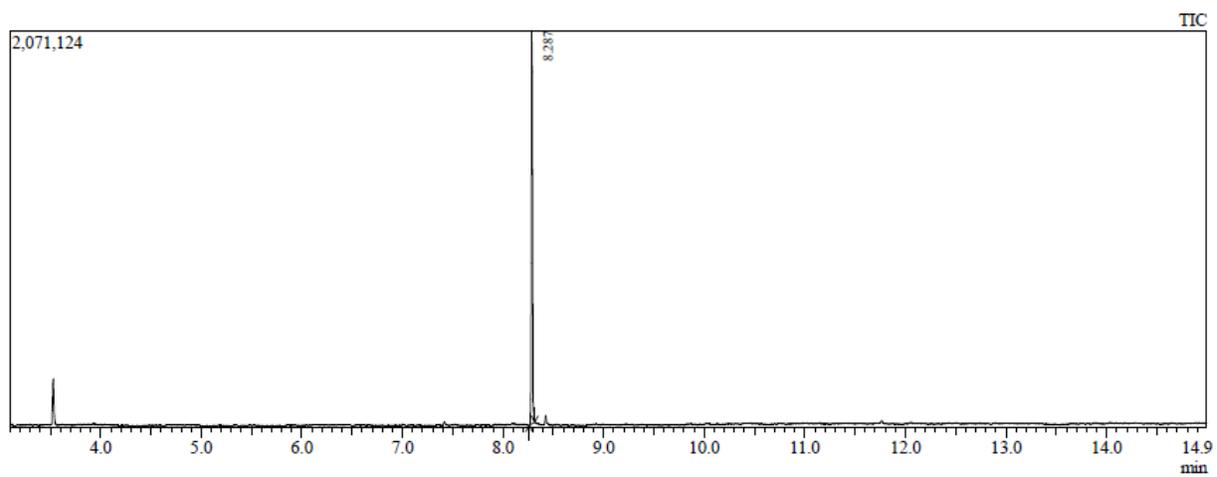
GC-MS data 10b

2-(sec-Butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b).[10]

¹H NMR of 11b (400 MHz, CDCl₃)
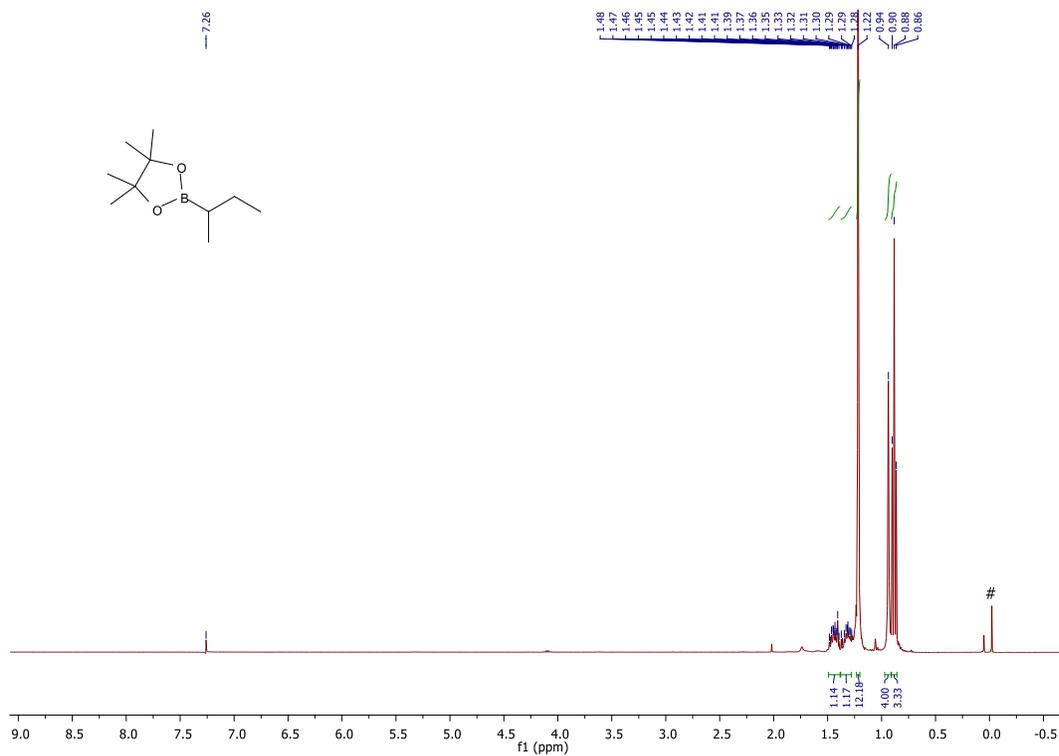
¹³C NMR of 11b (100 MHz, CDCl₃)

— 34.40
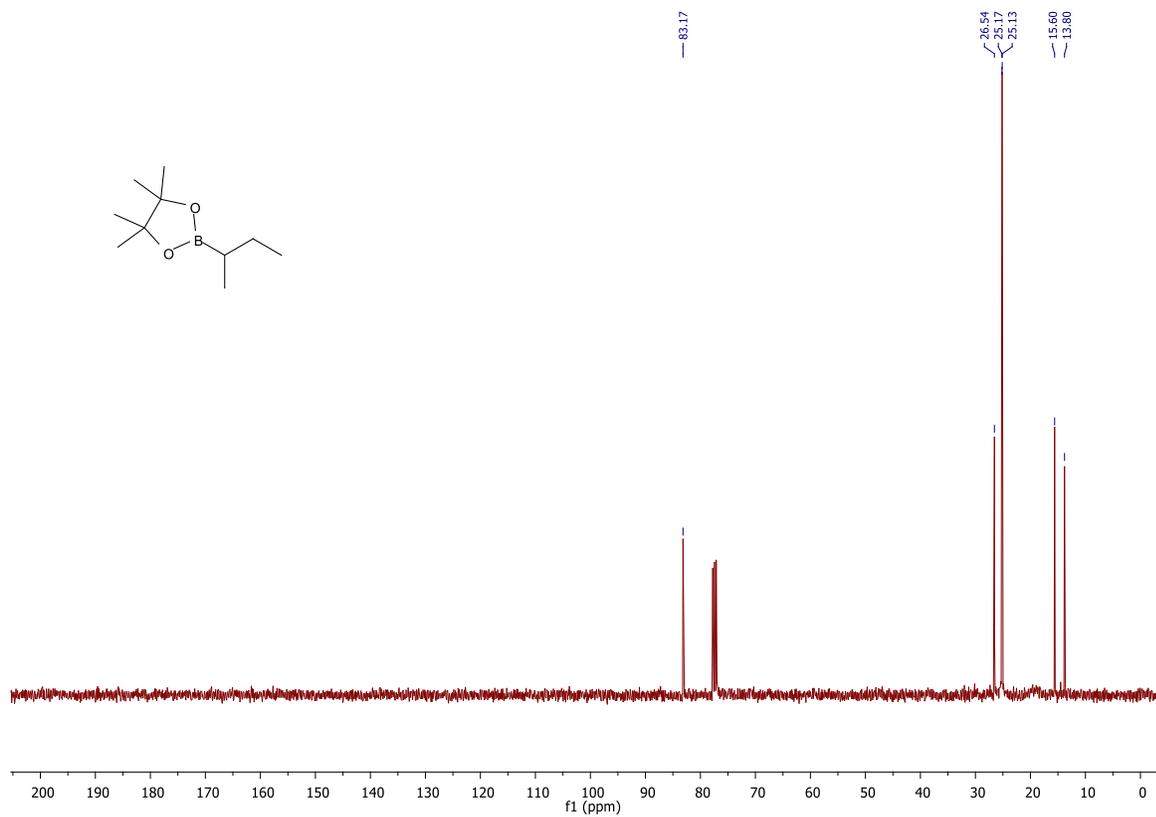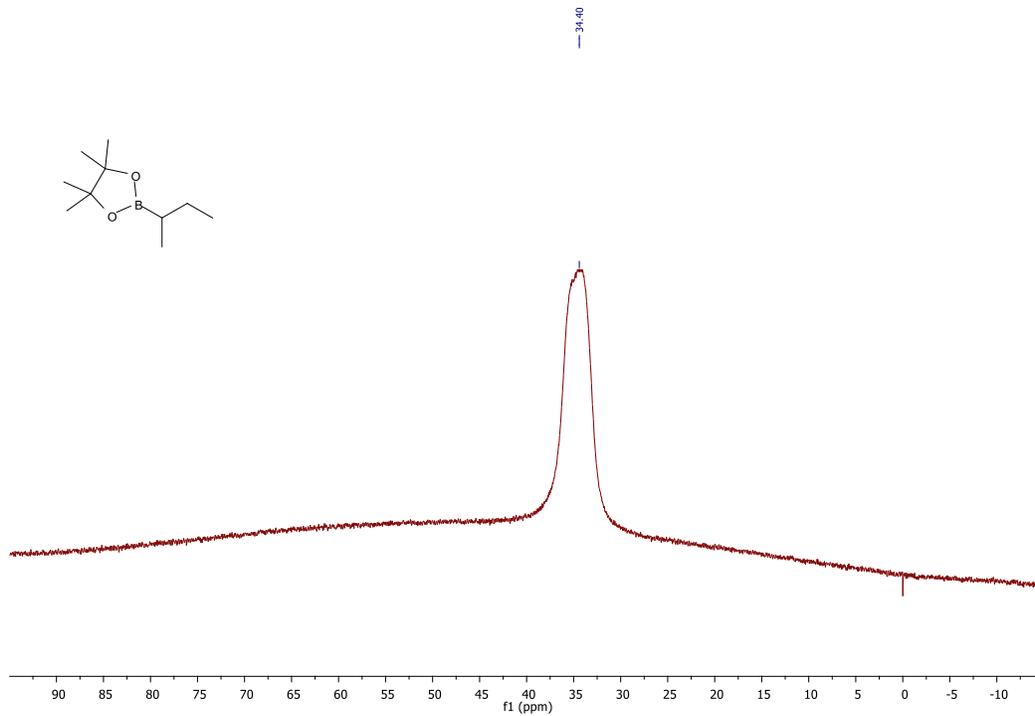
^{11}B NMR of 11b (128 MHz, CDCl$_3$)

2,409,267
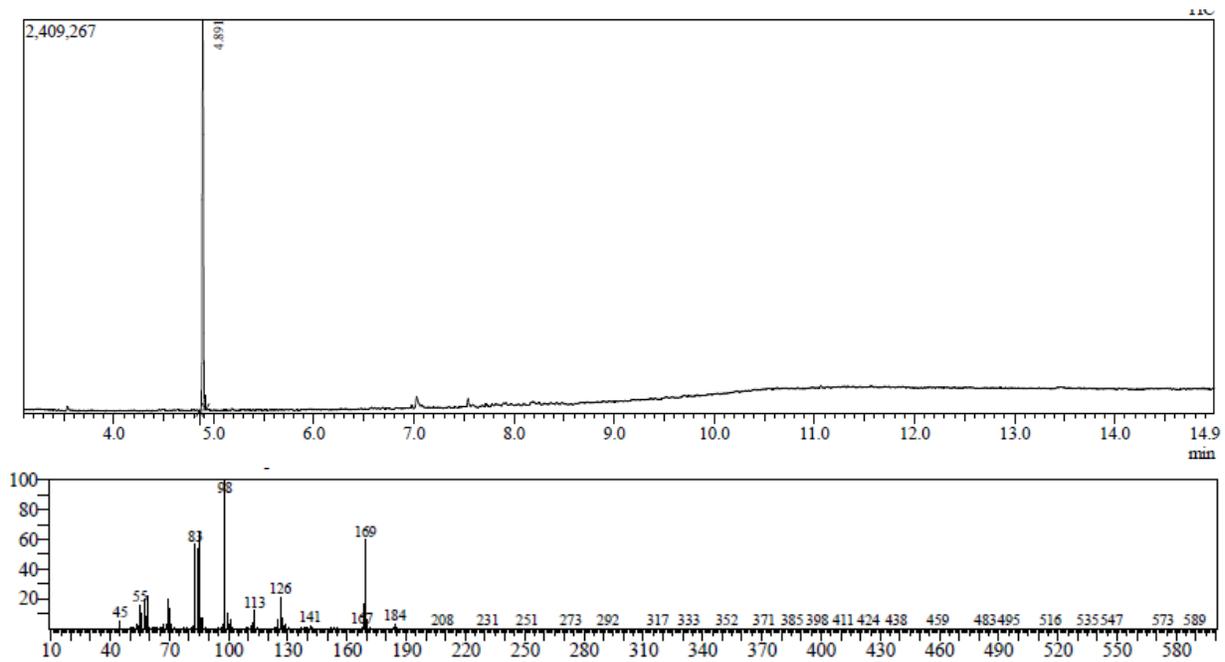
GC-MS data 11b

2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b).[10]
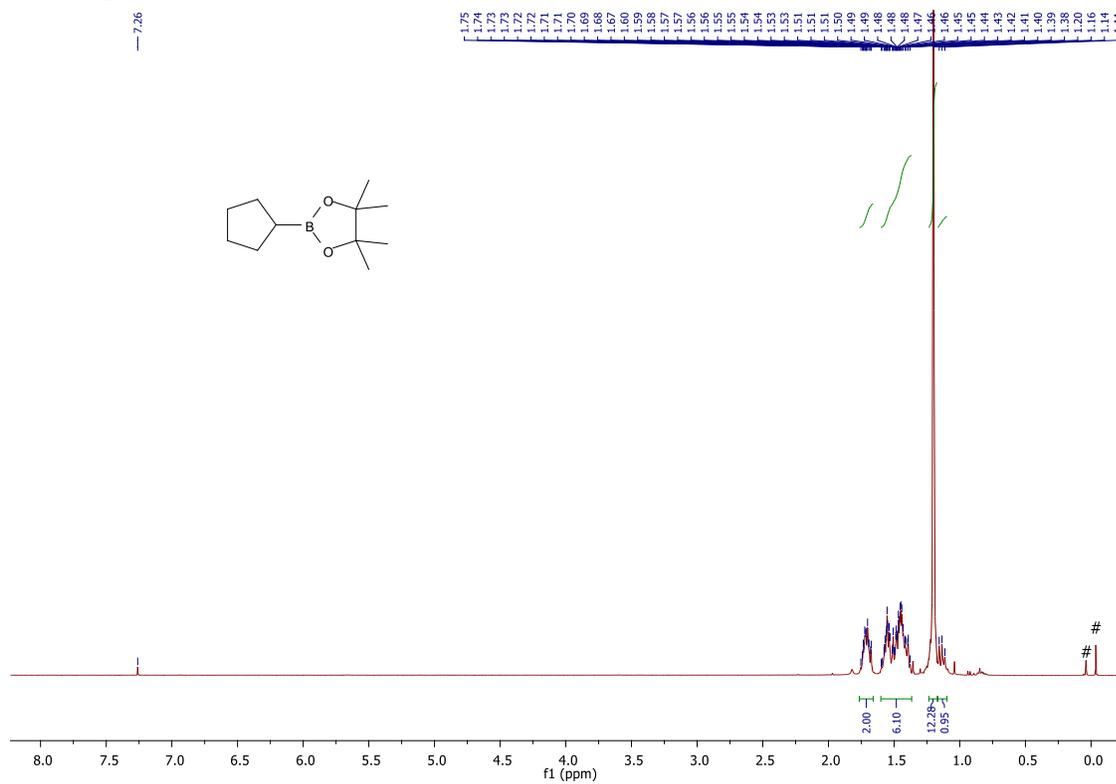
^{1}H NMR of 12b (400 MHz, CDCl$_3$)
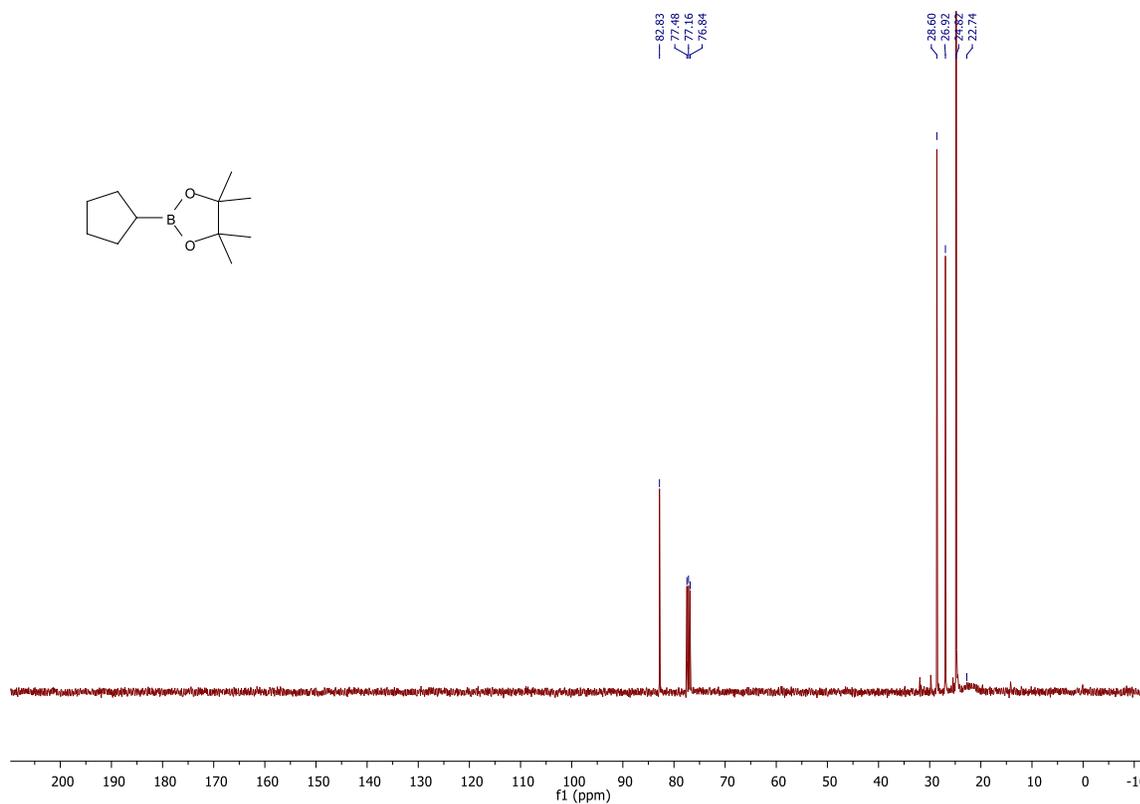
^{13}C NMR of 12b (100 MHz, CDCl$_3$)
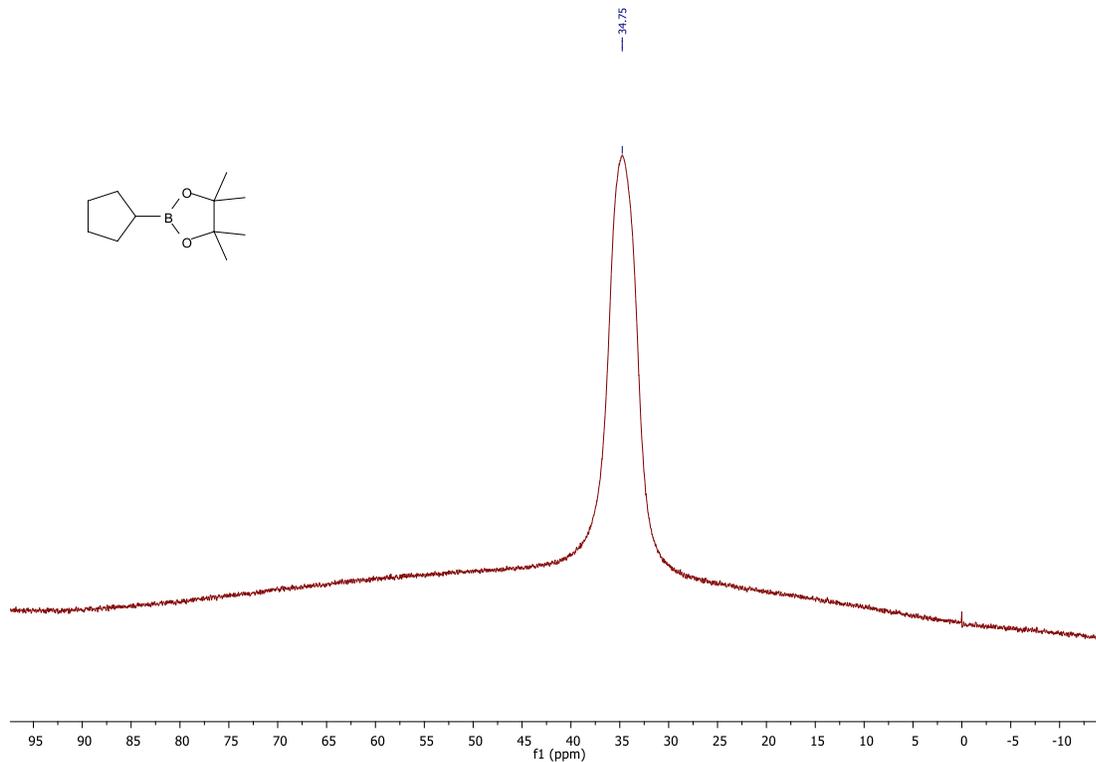
^{11}B NMR of 12b (128 MHz, CDCl$_3$)
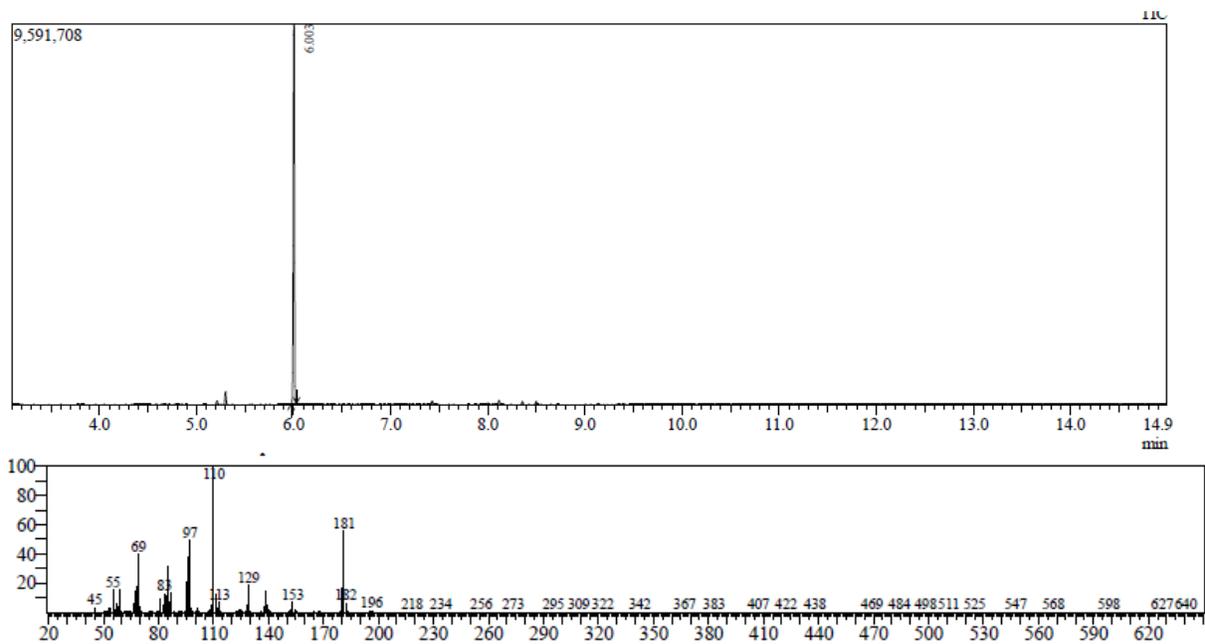
GC-MS data 12b

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b).[10]

^{1}H NMR of 13b (400 MHz, CDCl$_3$)
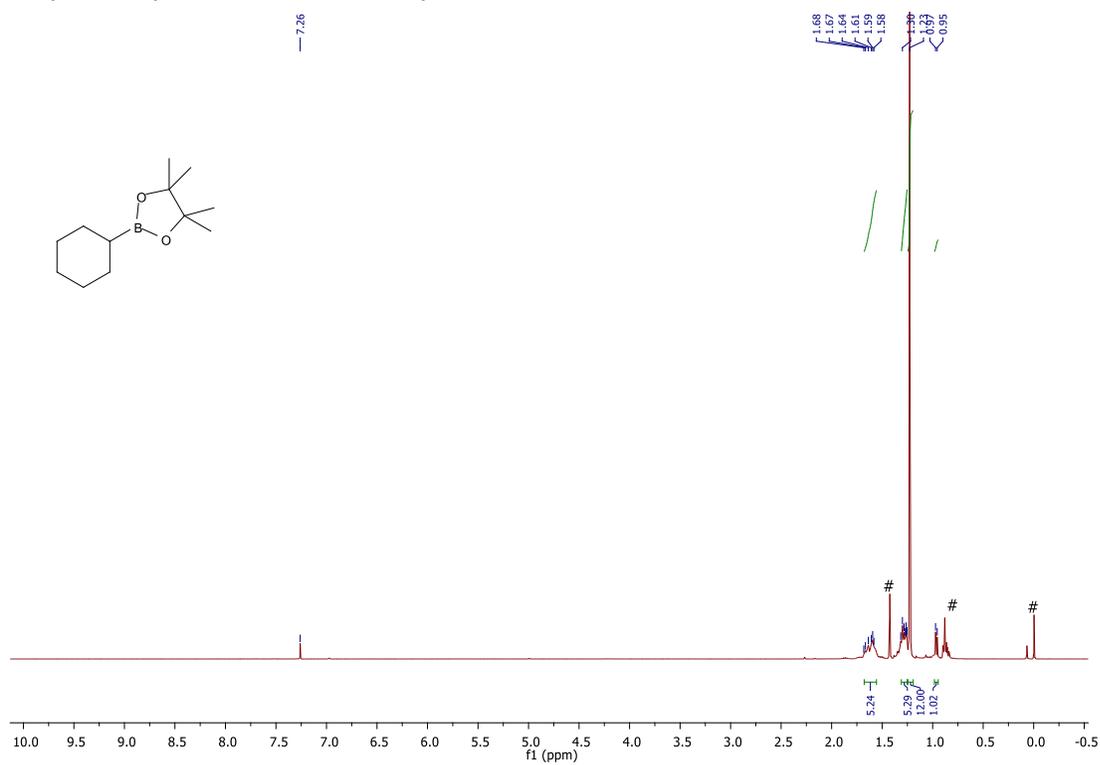
^{13}C NMR of 13b (100 MHz, CDCl$_3$)

— 34.93
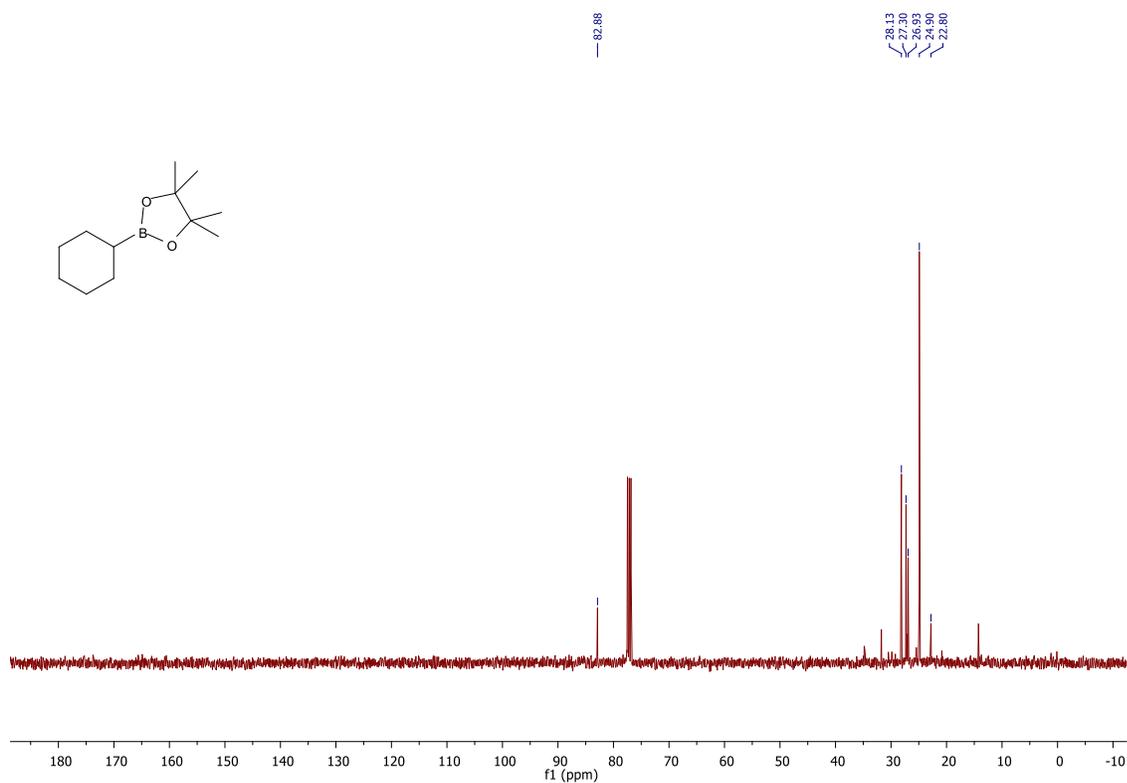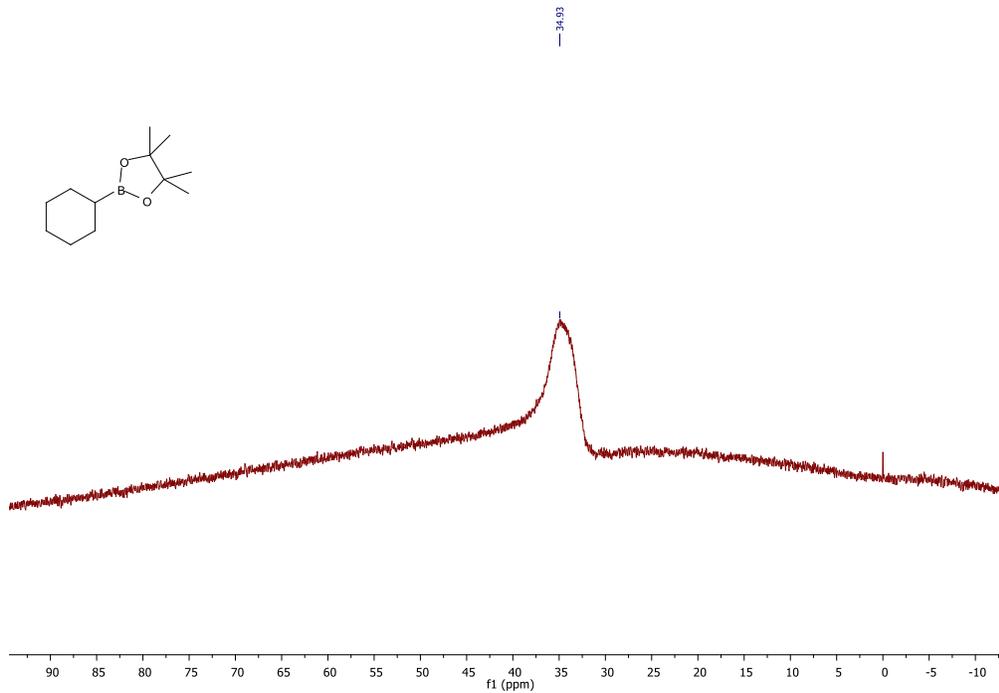
^{11}B NMR of 13b (128 MHz, CDCl$_3$)

TIC

299,176

6.517

100
80
60
40
20

114

69

82
110
129

195

45 55

152 167
196 210

234

258 271 286

307 320 335

355 370

388 404

425 440 457 472

491 505 523

552 571 591 604

625 641
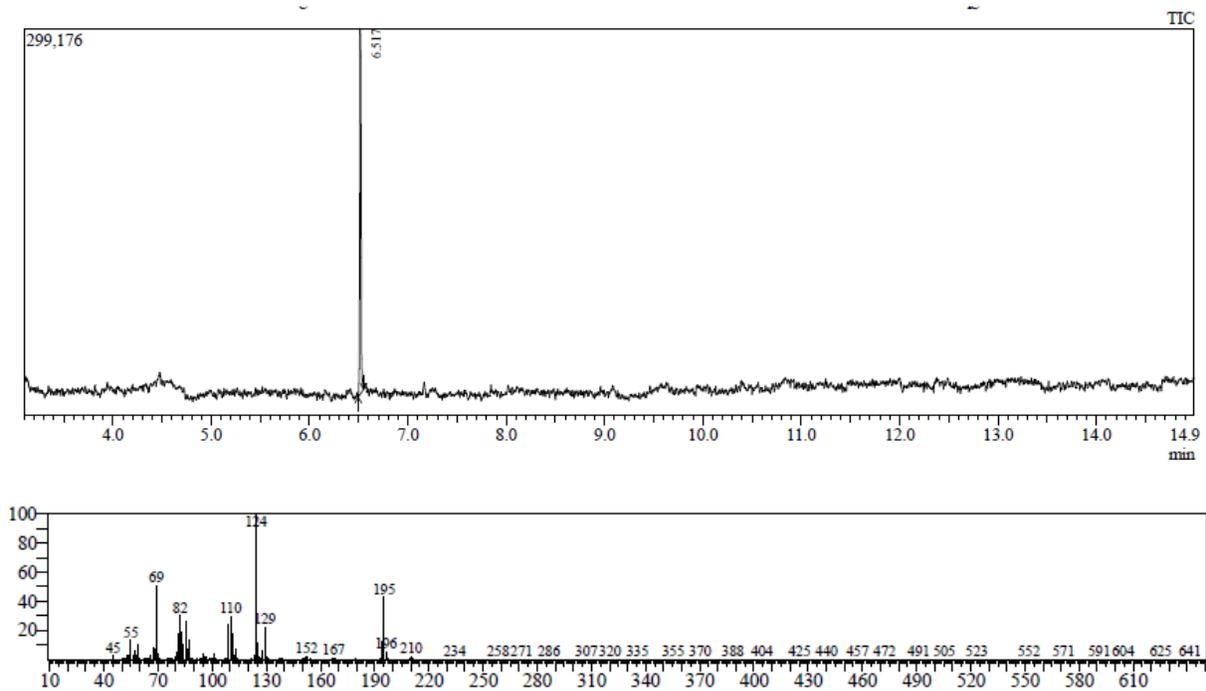
GC-MS data 13b

***exo*-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(14b).[10]**
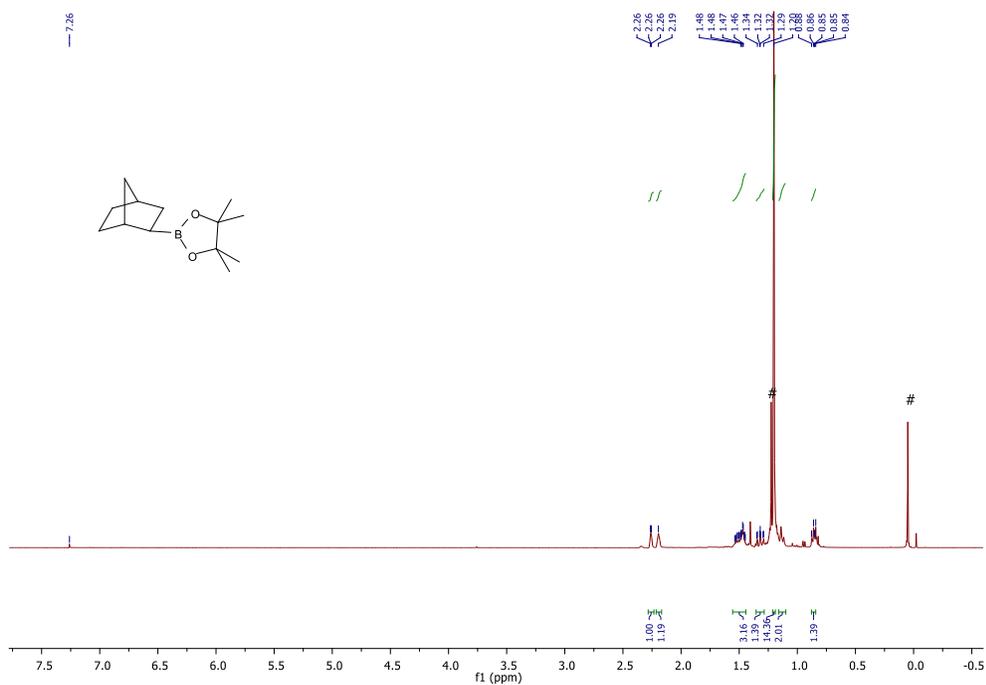
¹H NMR of 14b (400 MHz, CDCl₃)
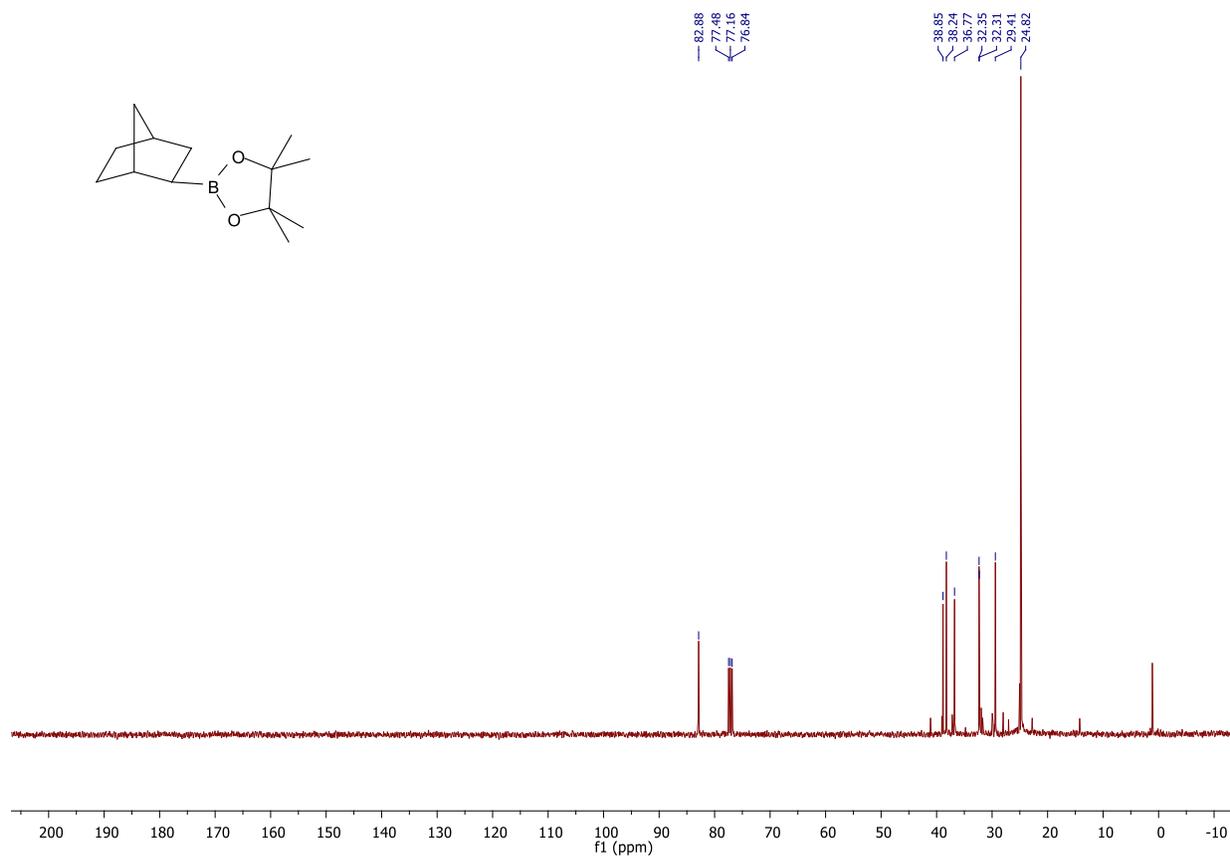
¹³C NMR of 14b (100 MHz, CDCl₃)
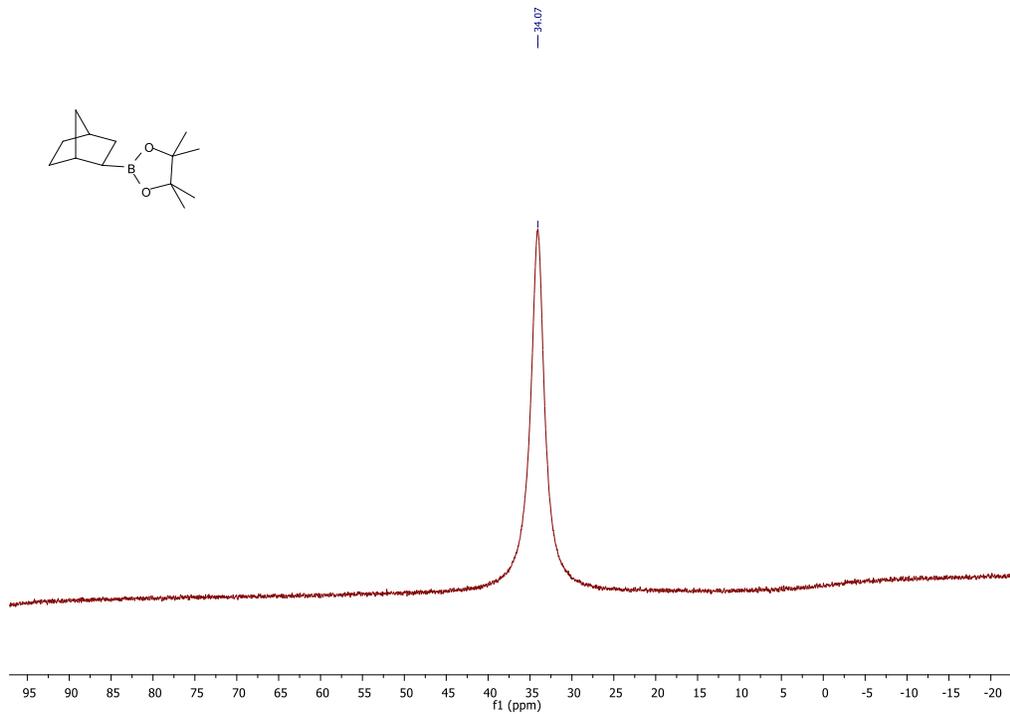
^{11}B NMR of 14b (128 MHz, CDCl$_3$)

44,859,043
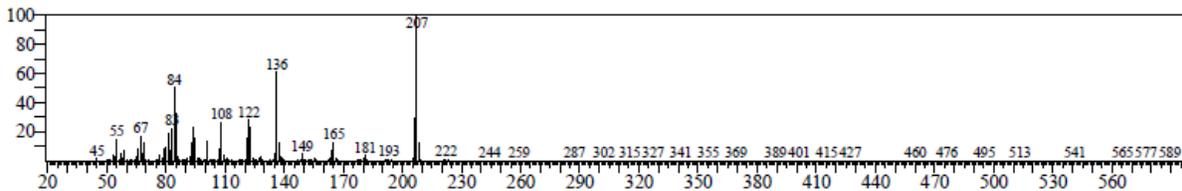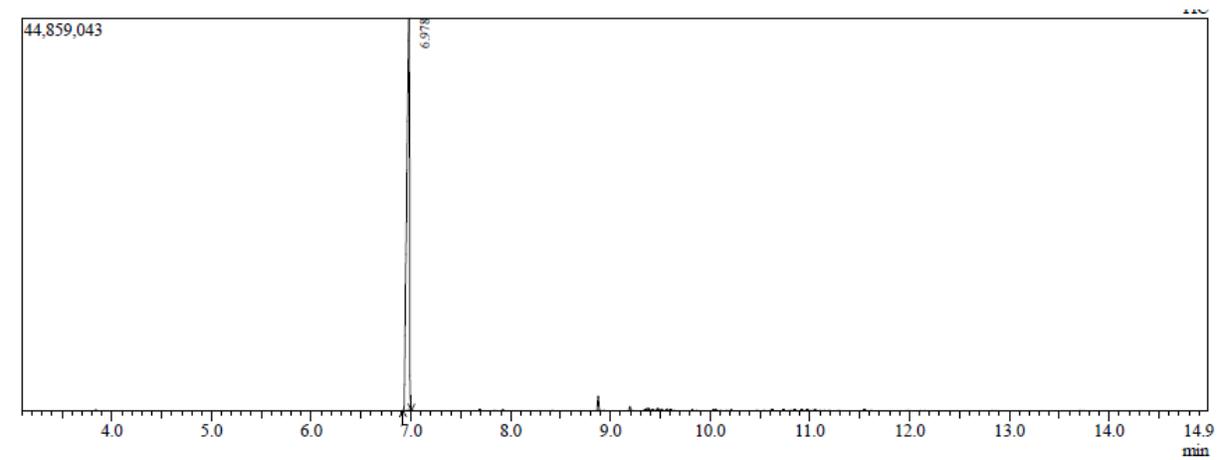
GC-MS data 14b

Benzyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (15b).[10]
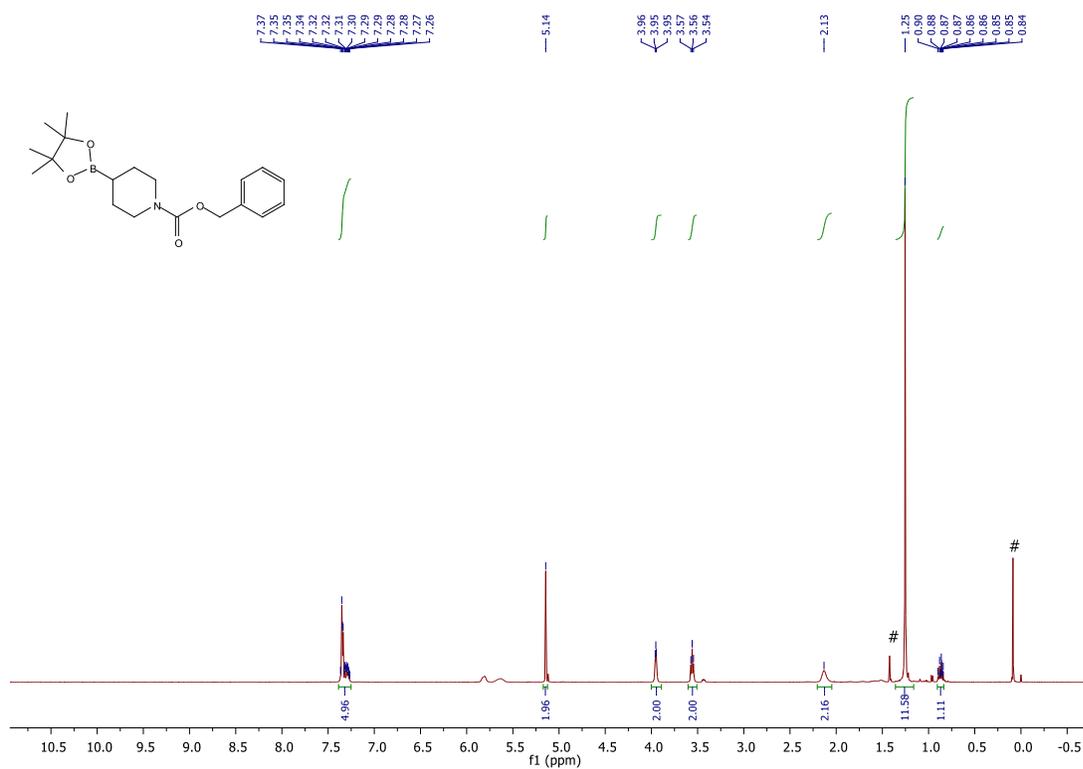
^{1}H NMR of 15b (400 MHz, CDCl$_3$)
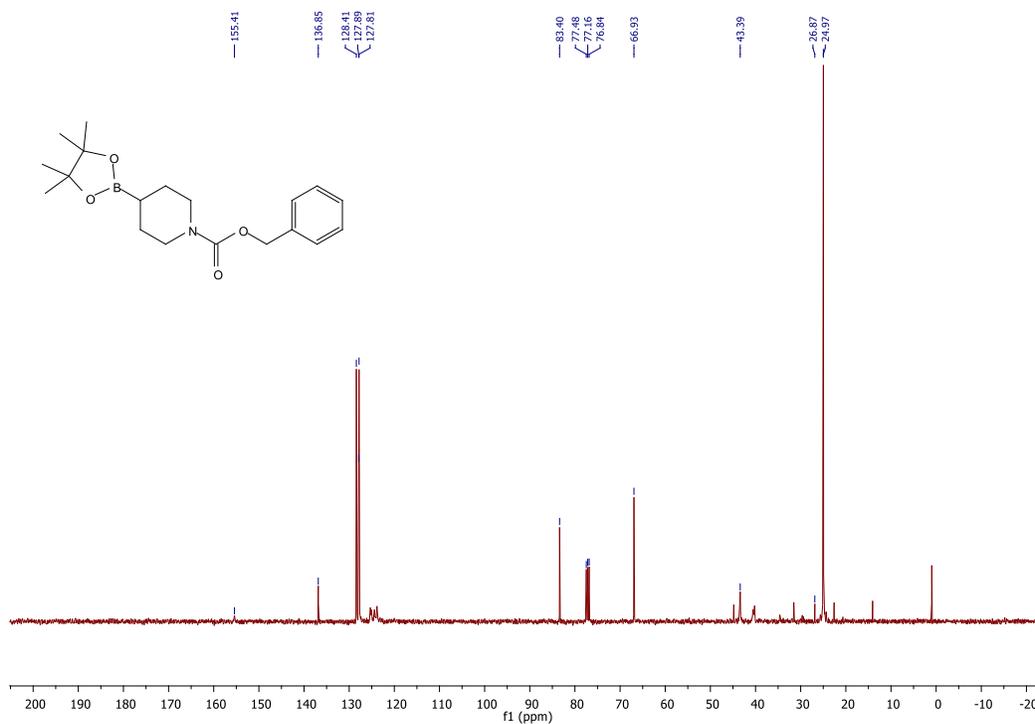
^{13}C NMR of 15b (100 MHz, CDCl$_3$)
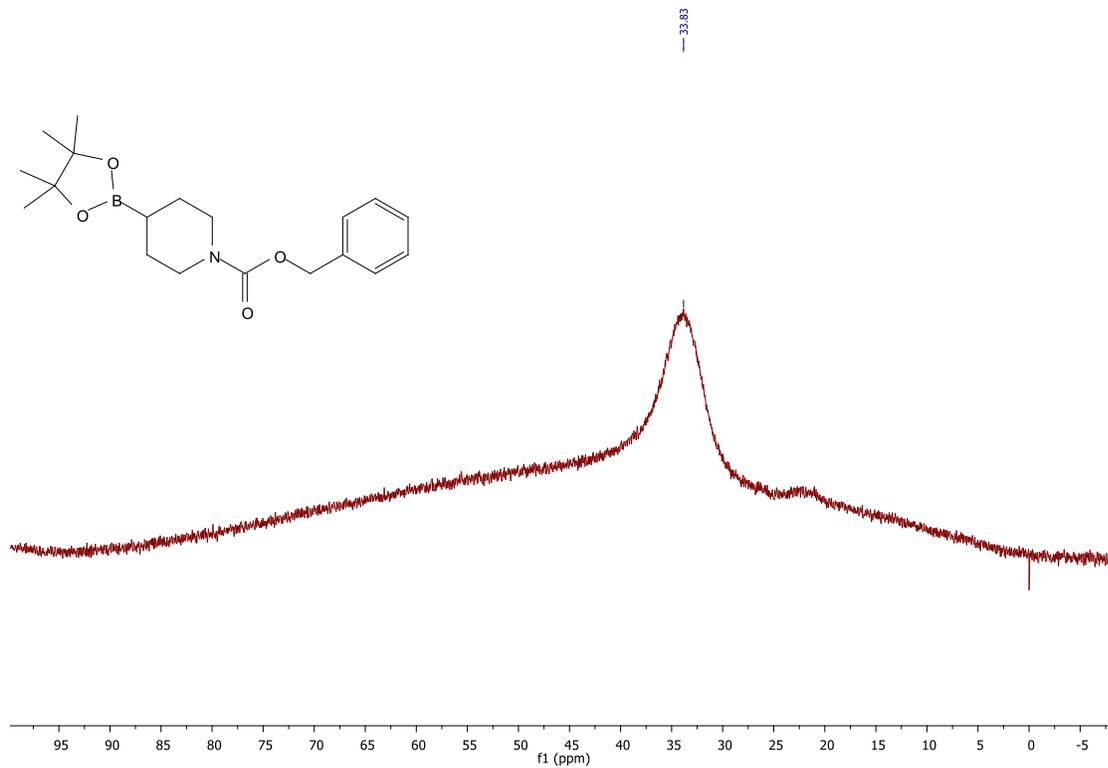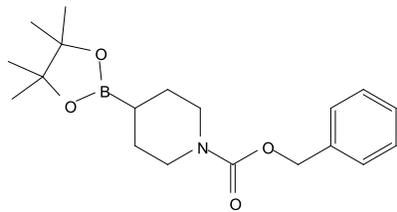
11B NMR of 15b (128 MHz, CDCl3)

33.83

2-(Cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16b).[10]
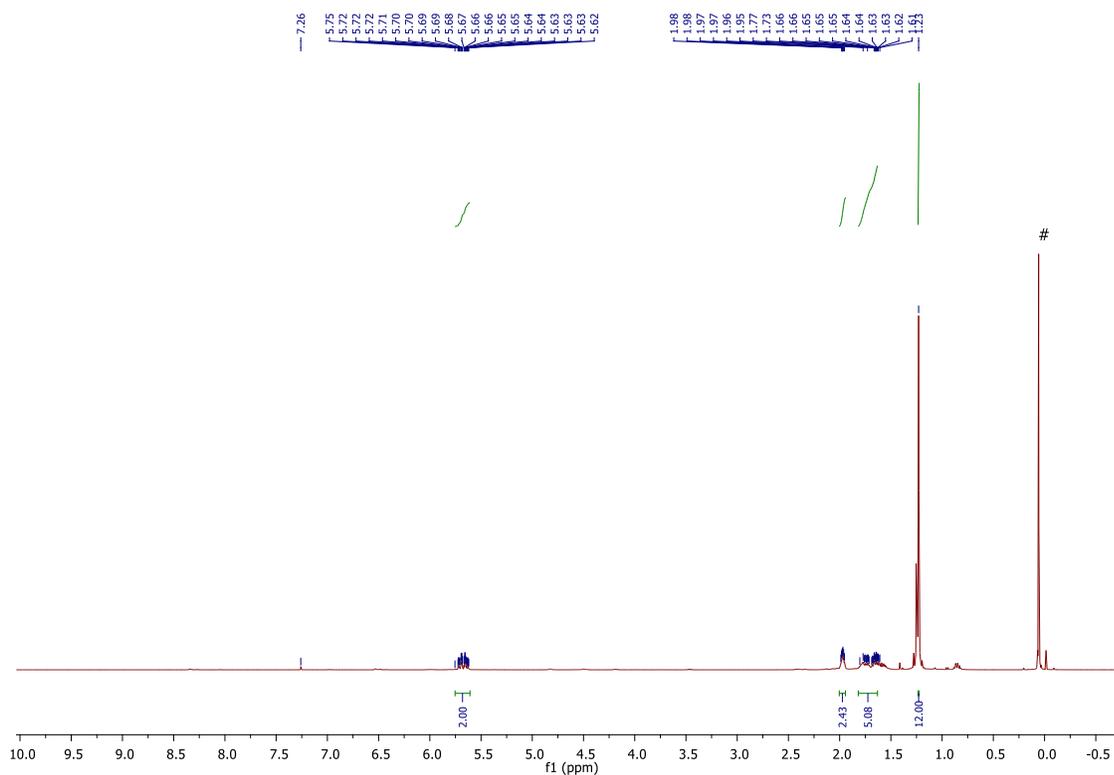
¹H NMR of 16b (400 MHz, CDCl₃)
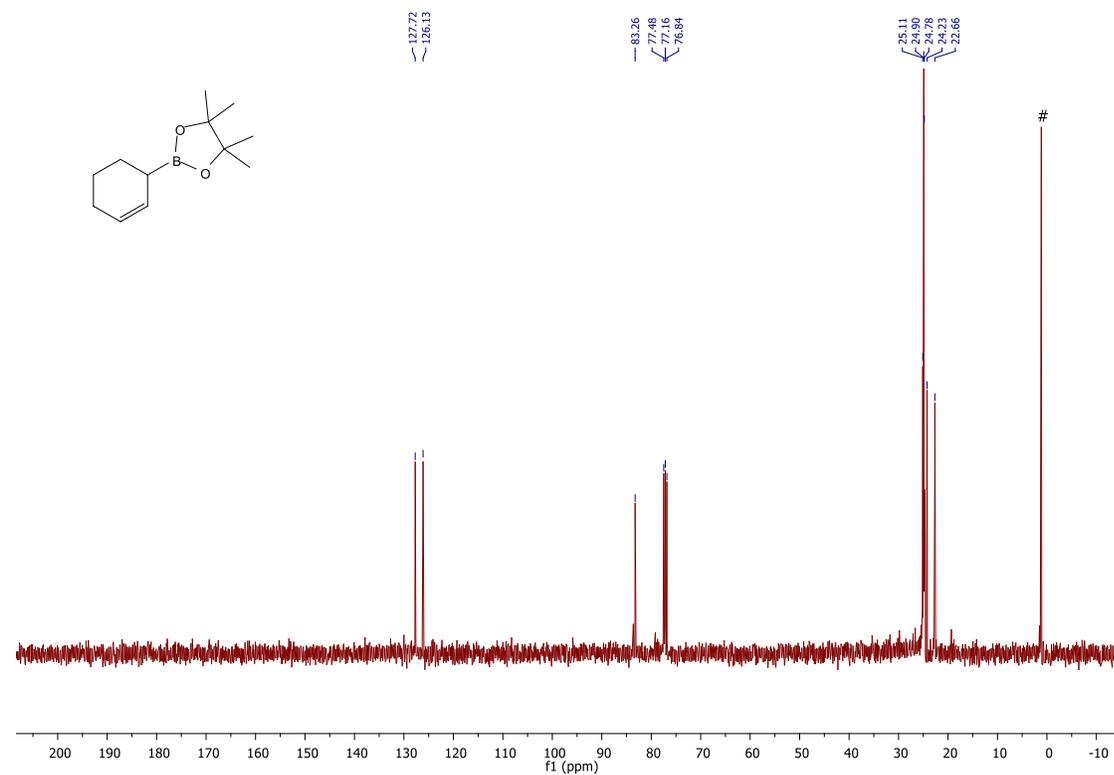
¹³C NMR of 16b (100 MHz, CDCl₃)
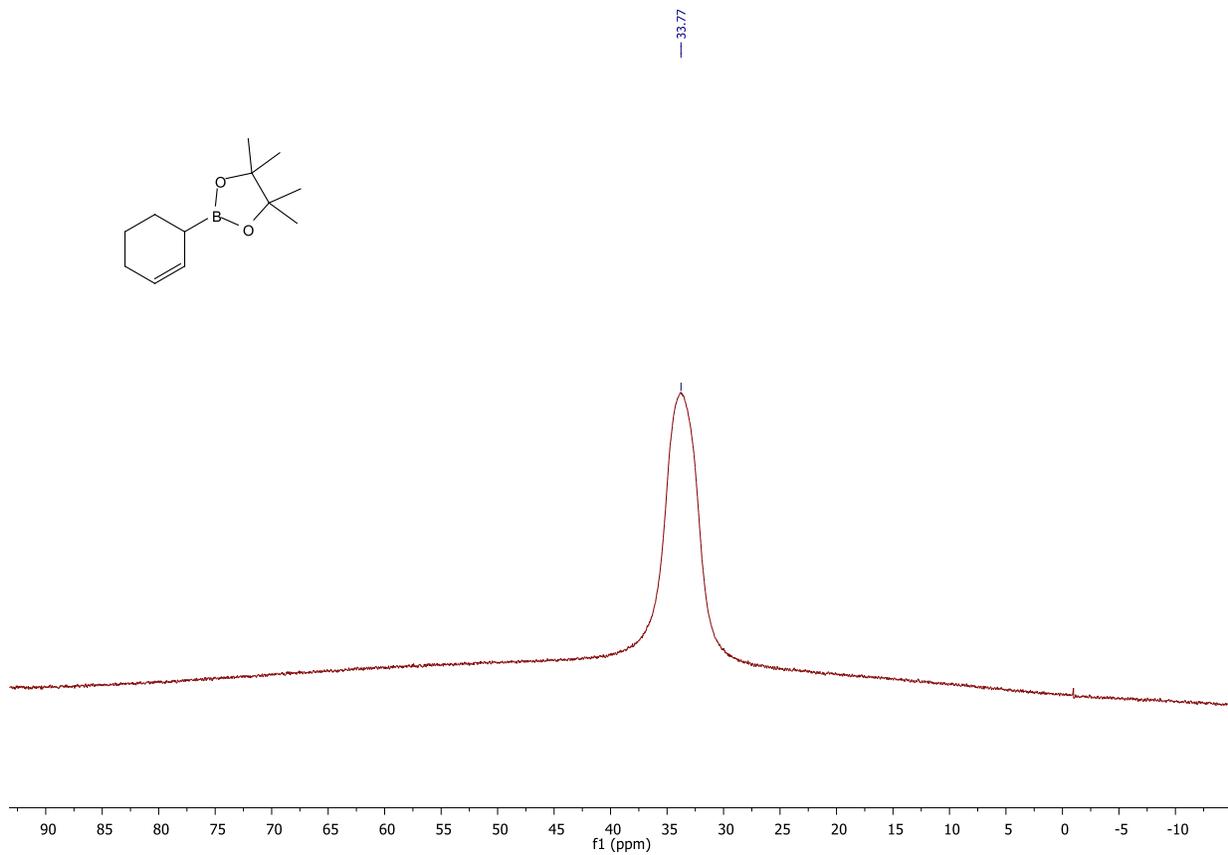
11B NMR of 16b (128 MHz, CDCl₃)

— 33.77
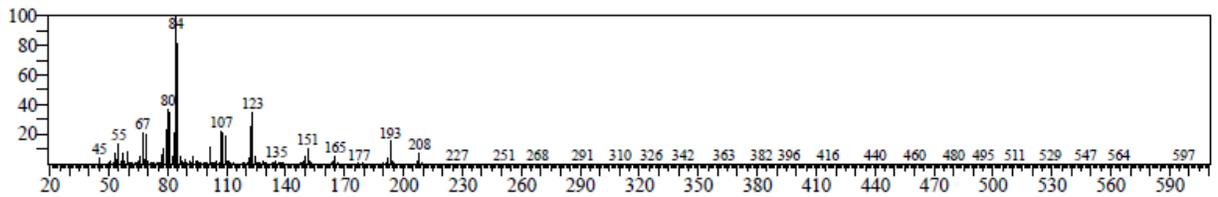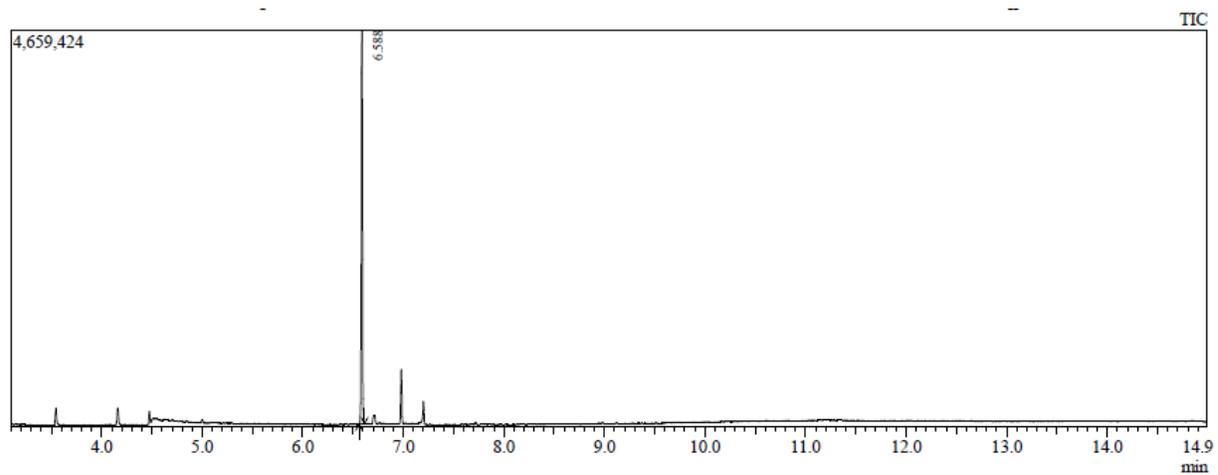
GC-MS data 16b

4,4,5,5-Tetramethyl-2-((7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)-1,3,2-dioxaborolane (18b).[12]

¹H NMR of 18b (400 MHz, CDCl₃)

¹³C NMR of 18b (100 MHz, CDCl₃)

— 34.14
— 21.85
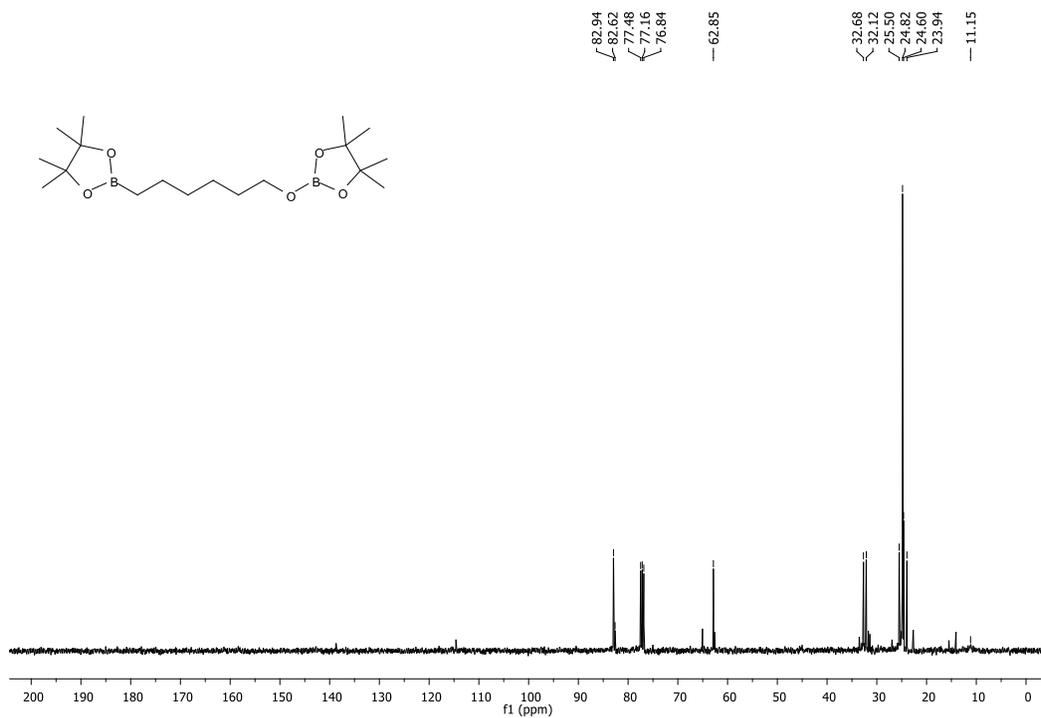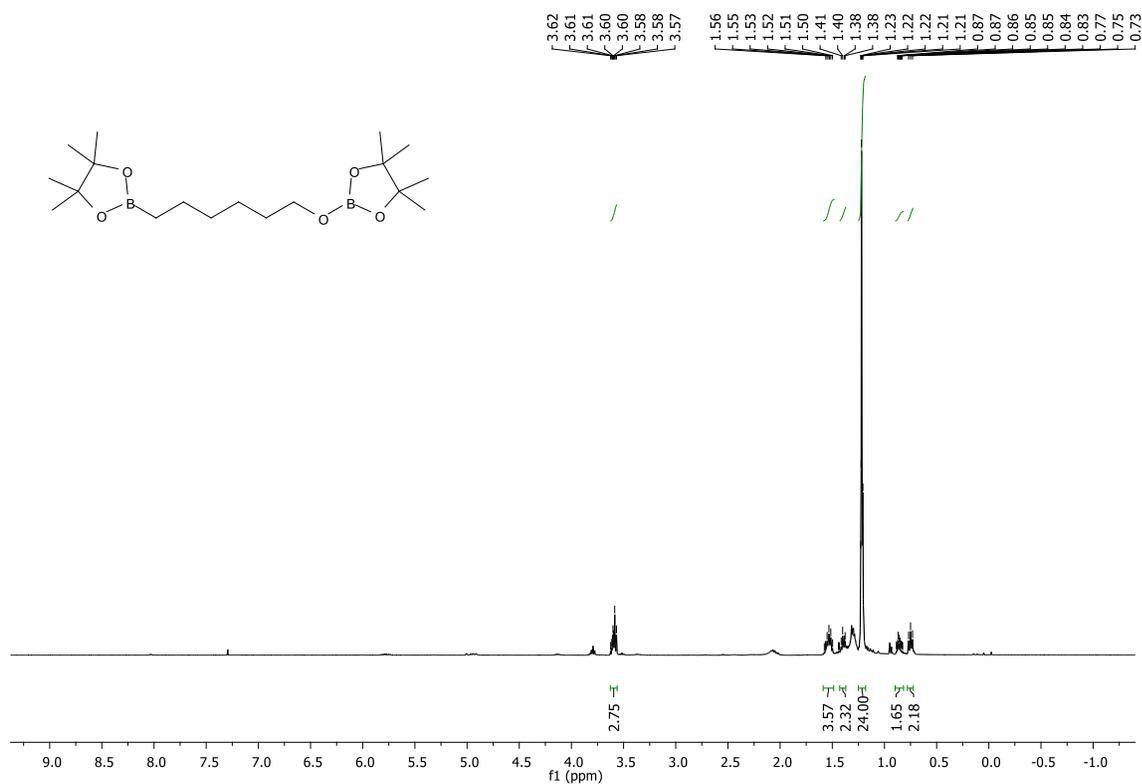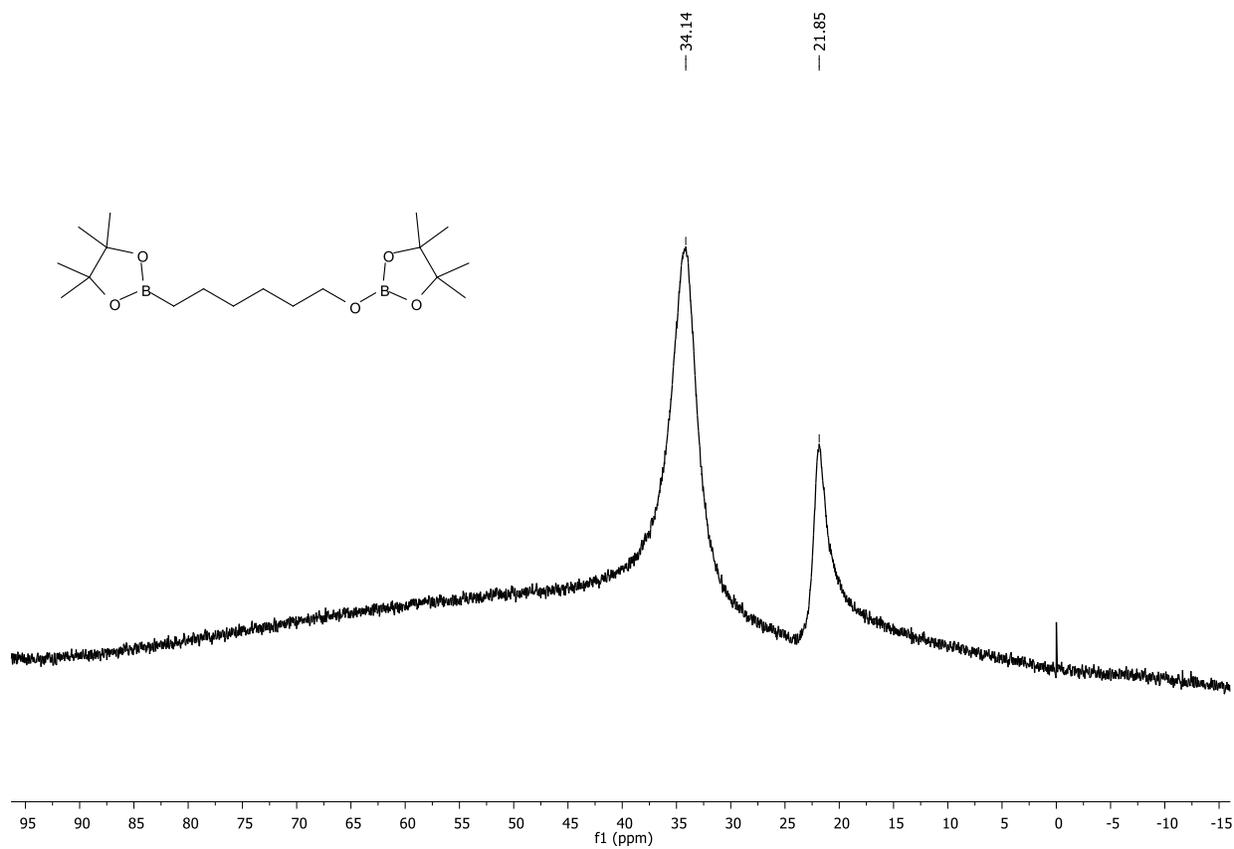
^{11}B NMR of 18b (128 MHz, CDCl$_3$)
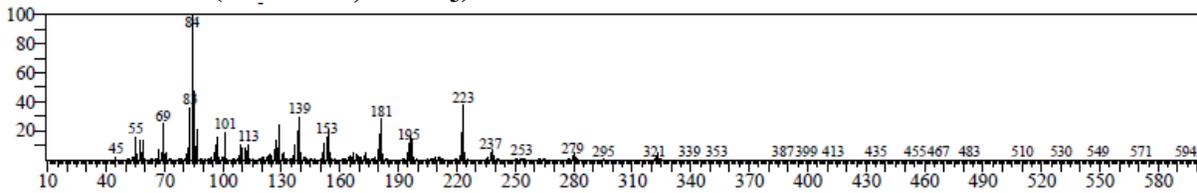
GC-MS data 18b

1-(6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1H-indole (19b).[1]

^{1}H NMR of 19b (400 MHz, CDCl₃)
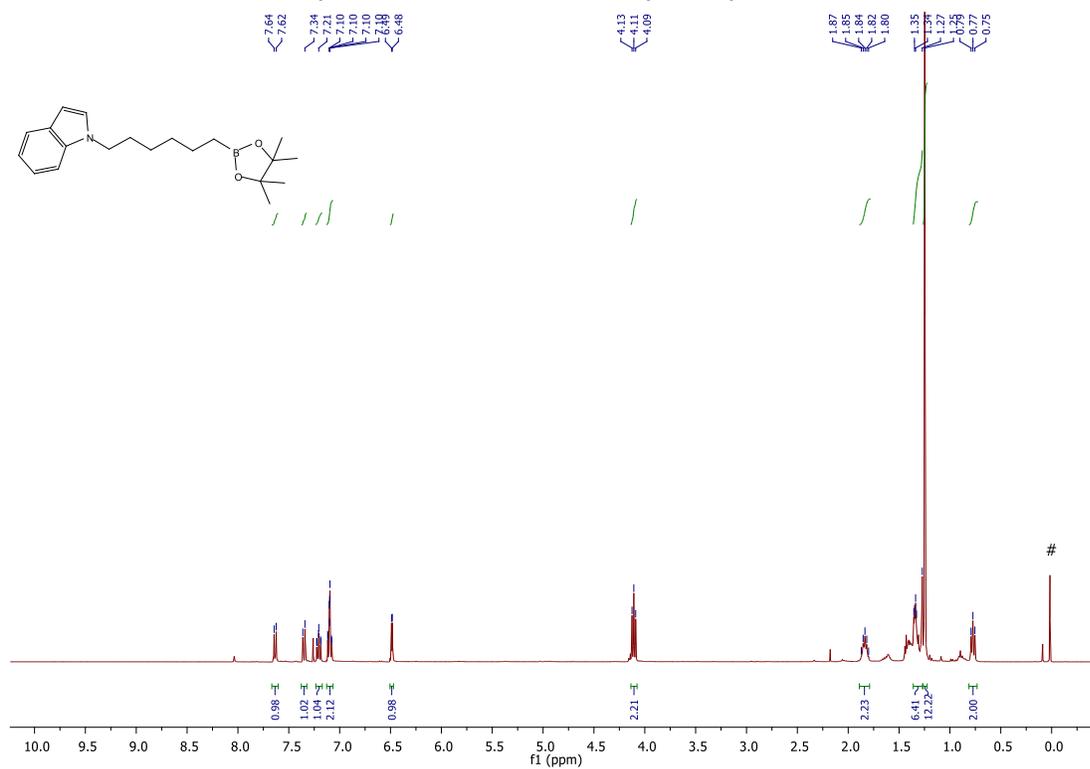
^{13}C NMR of 19b (100 MHz, CDCl₃)

— 33.97

95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)
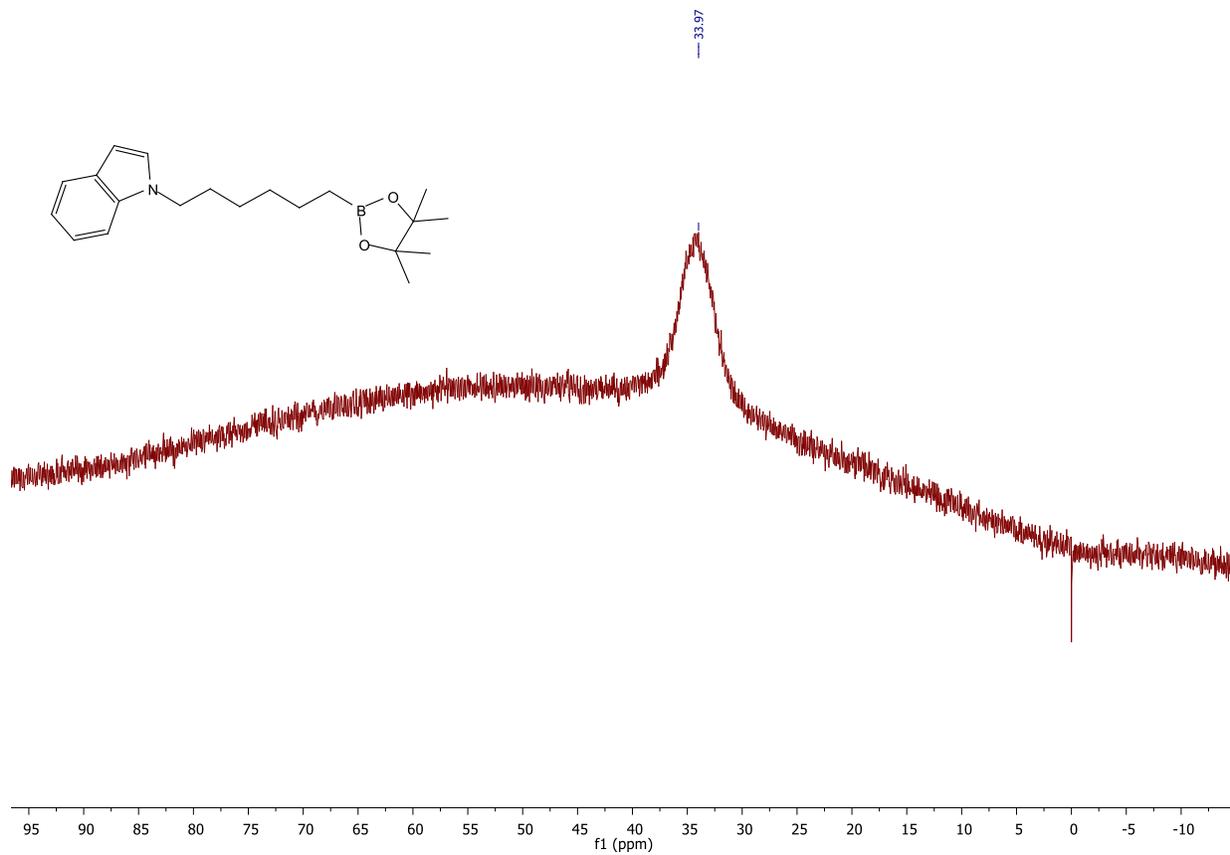
¹¹B NMR of 19b (128 MHz, CDCl₃)
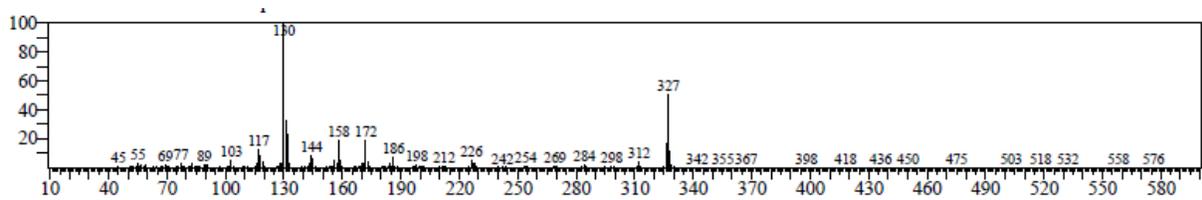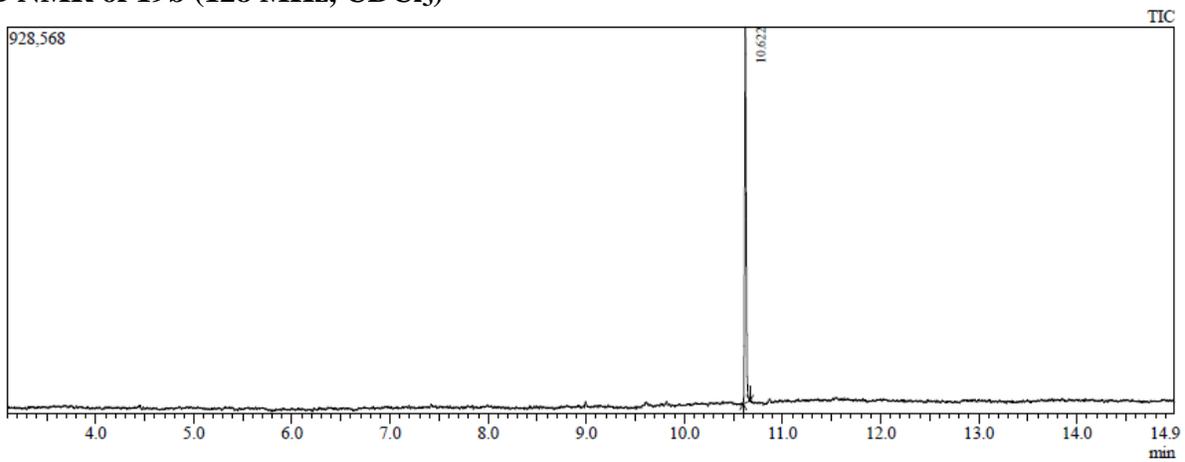
GC-MS data 19b

9-(6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-9H-carbazole (20b).

1H NMR of 20b (400 MHz, CDCl3)
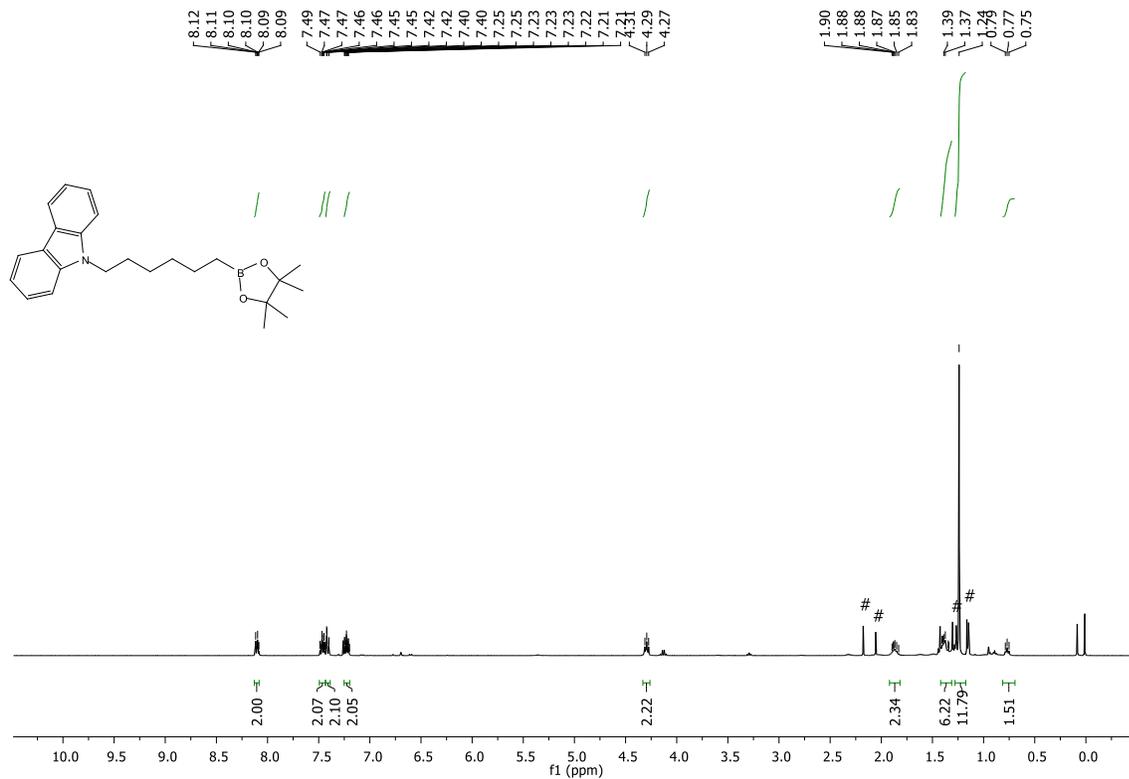
13C NMR of 20b (100 MHz, CDCl3)
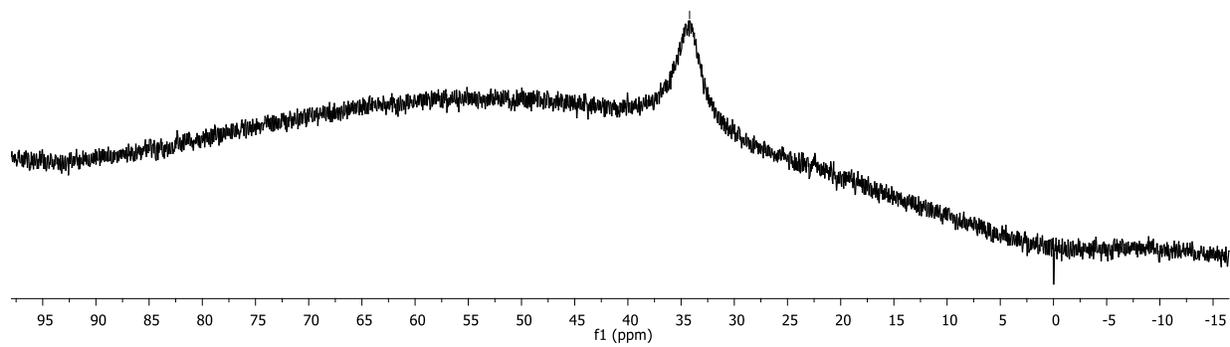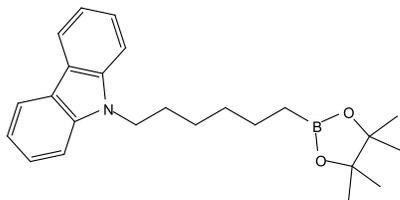
^{11}B NMR of 20b (128 MHz, CDCl$_3$)
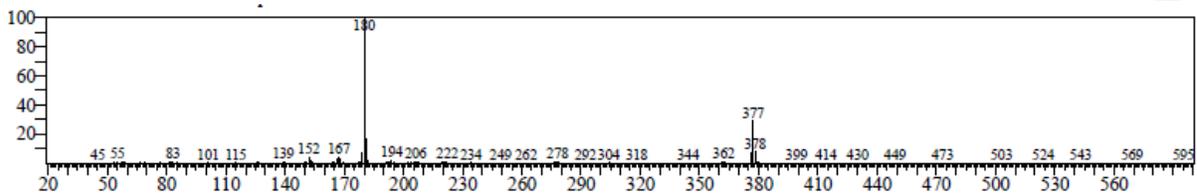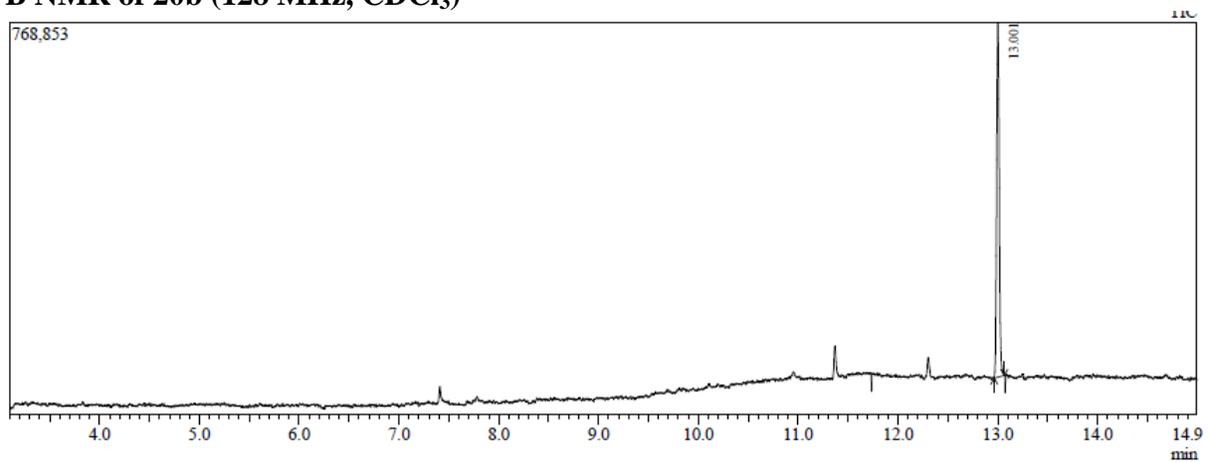
GC-MS data 20b

4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (21b).[1]

7.08
7.07
7.06
7.06
6.89
6.88
6.87
6.79
6.79
6.78
6.78
2.97
2.95
2.93
1.23
1.22

0.72
1.02
0.74
2.00
14.56

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
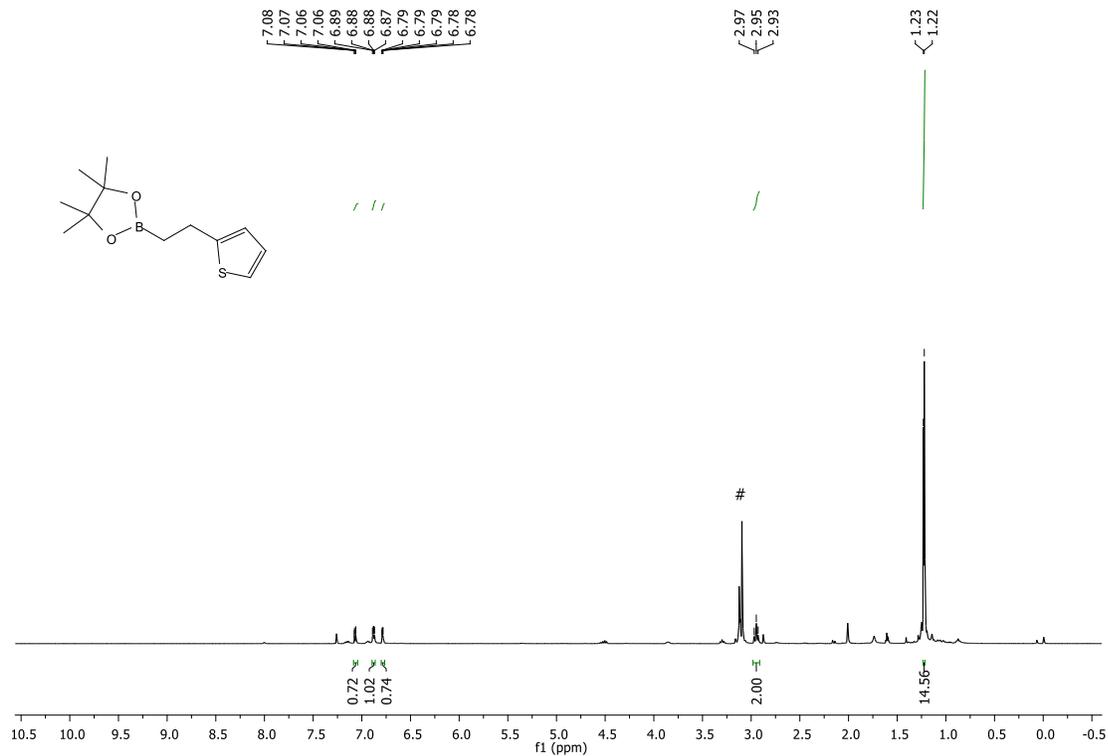
^{1}H NMR of 21b (400 MHz, CDCl₃)

147.87
126.65
123.52
122.72
83.35
77.48
77.16
76.84
24.98
24.92
14.26

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
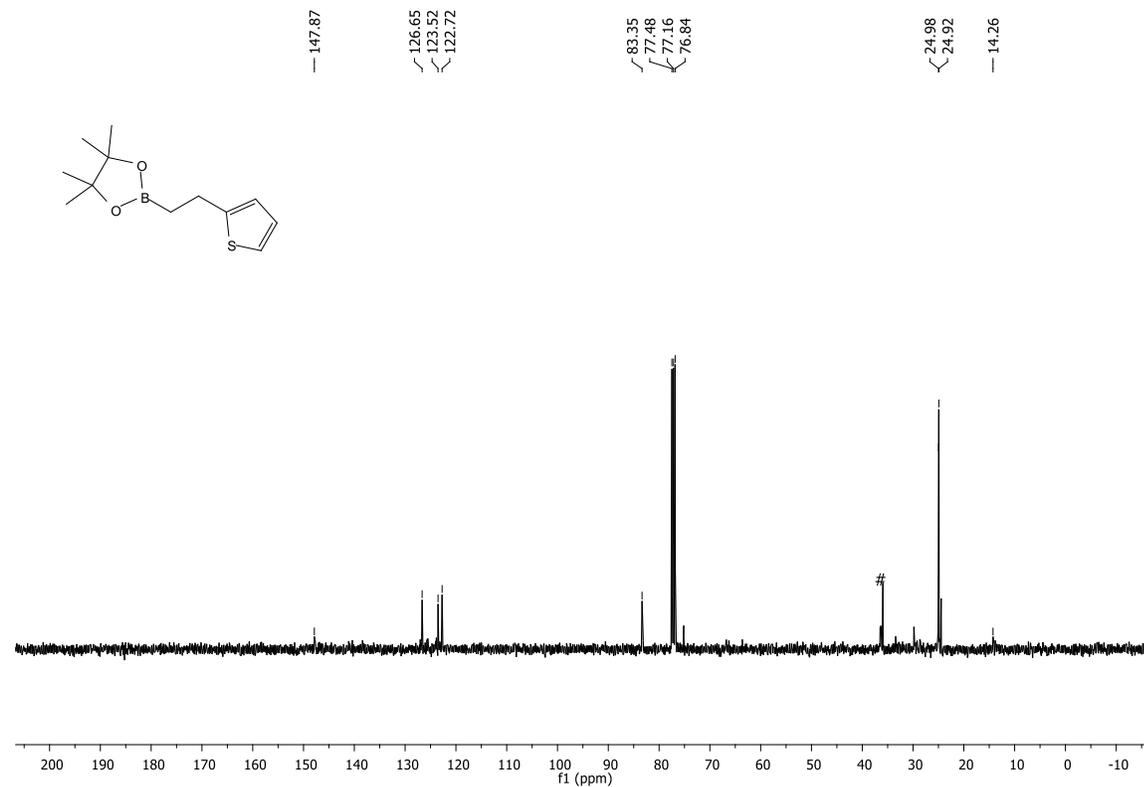
^{13}C NMR of 21b (100 MHz, CDCl₃)

— 33.62
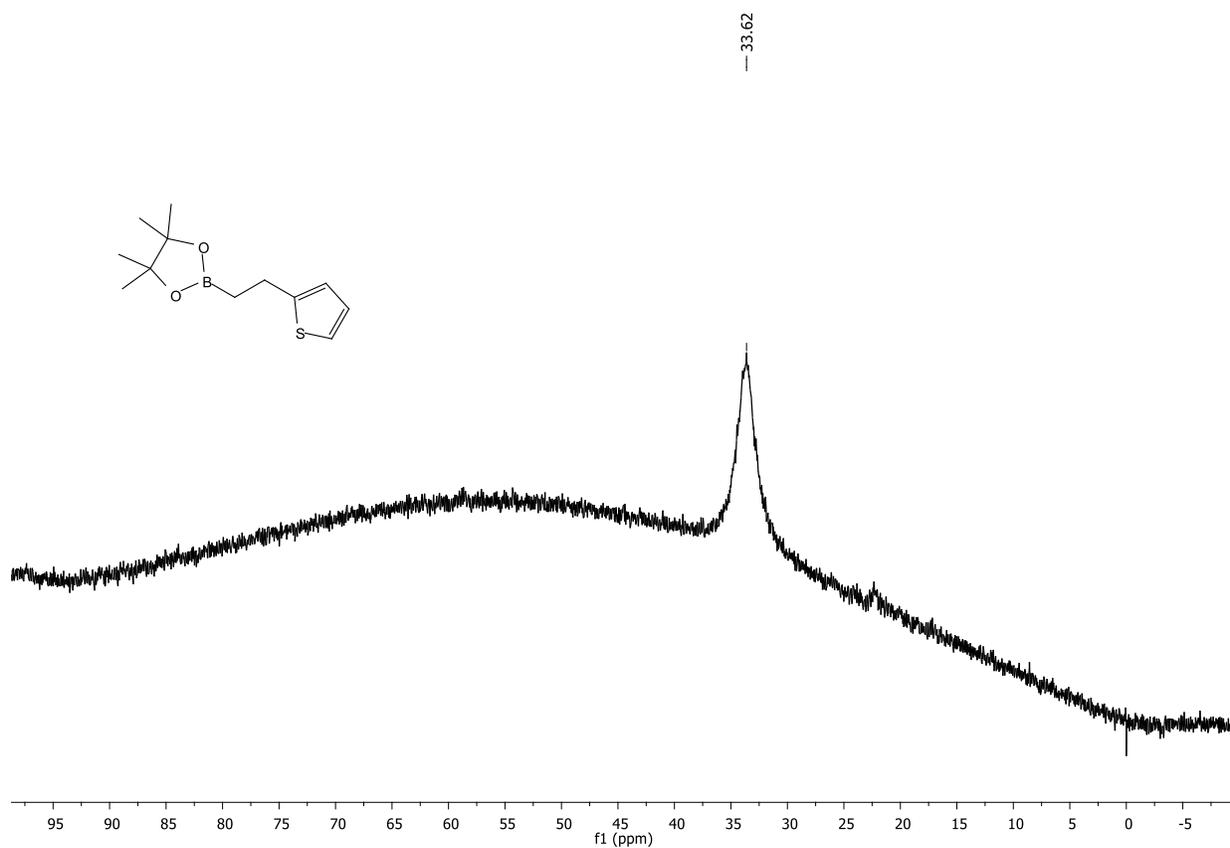
^{11}B NMR of 21b (128 MHz, CDCl$_3$)
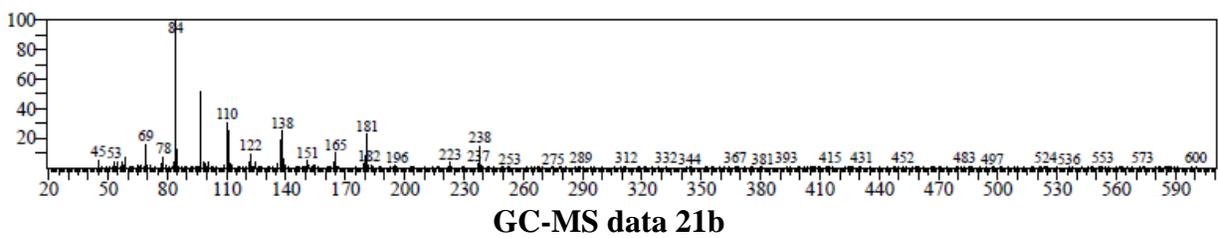
GC-MS data 21b

Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (22b).[10]
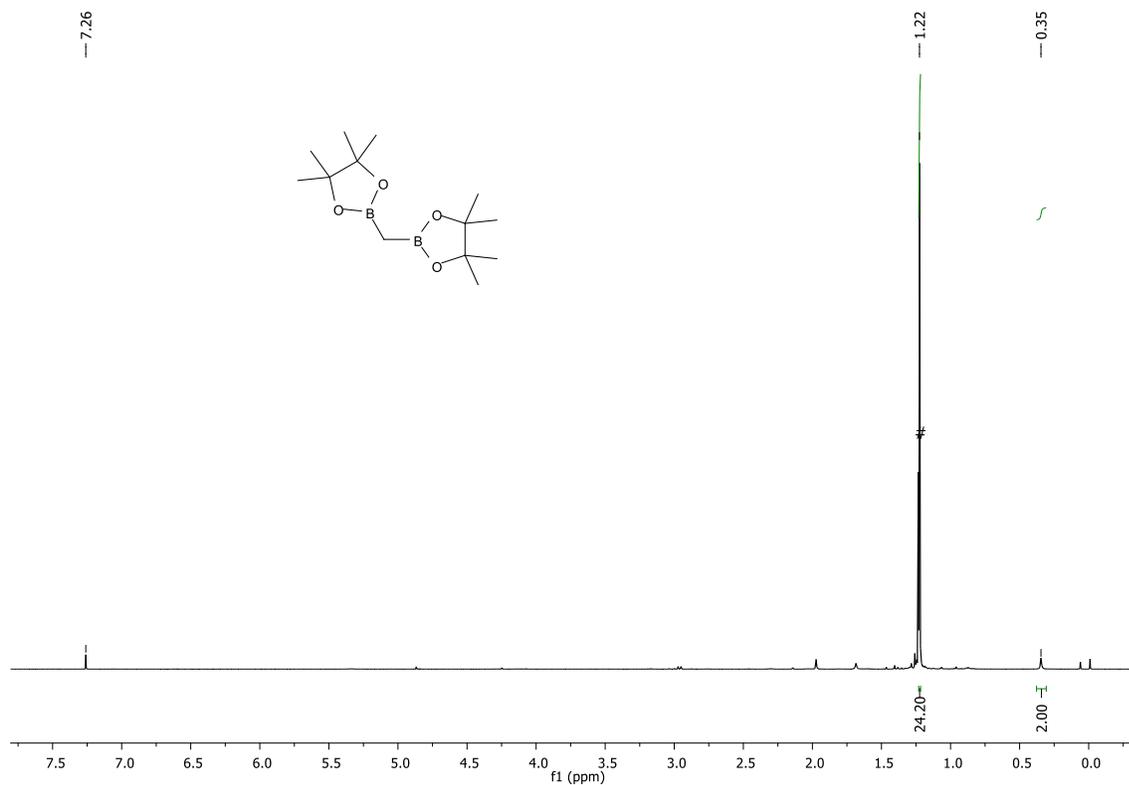
^{1}H NMR of 22b (400 MHz, CDCl$_3$)
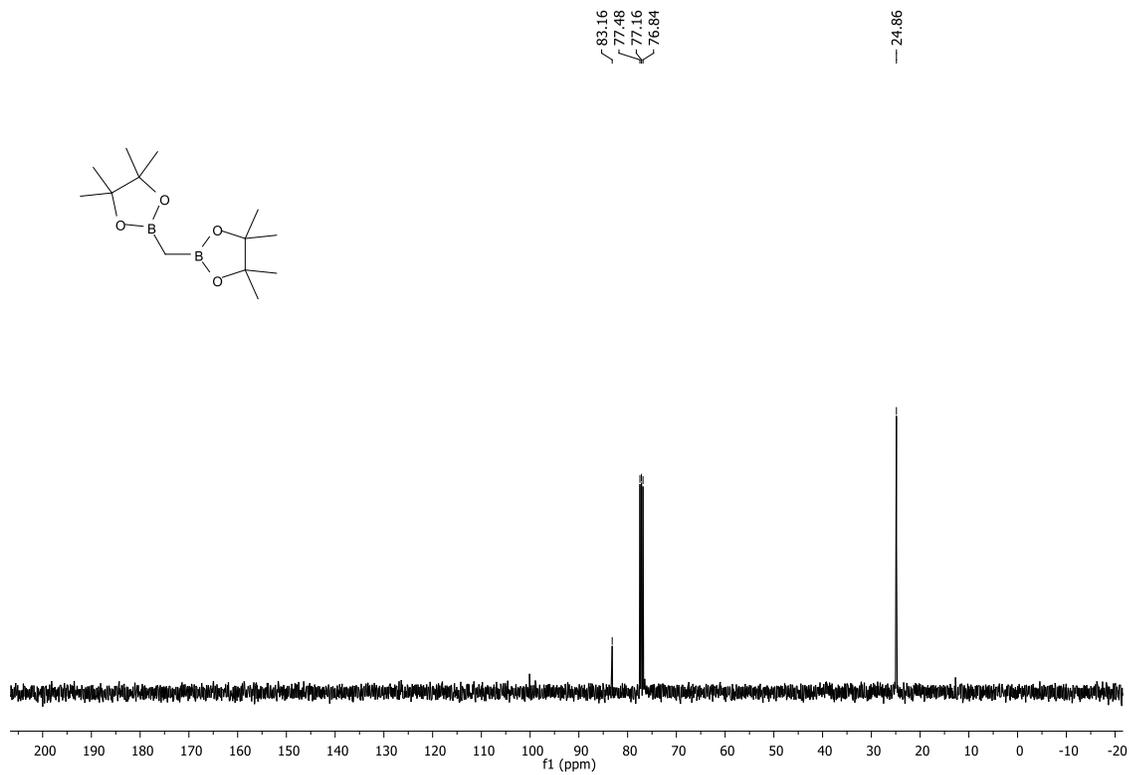
^{13}C NMR of 22b (100 MHz, CDCl$_3$)

— 33.51
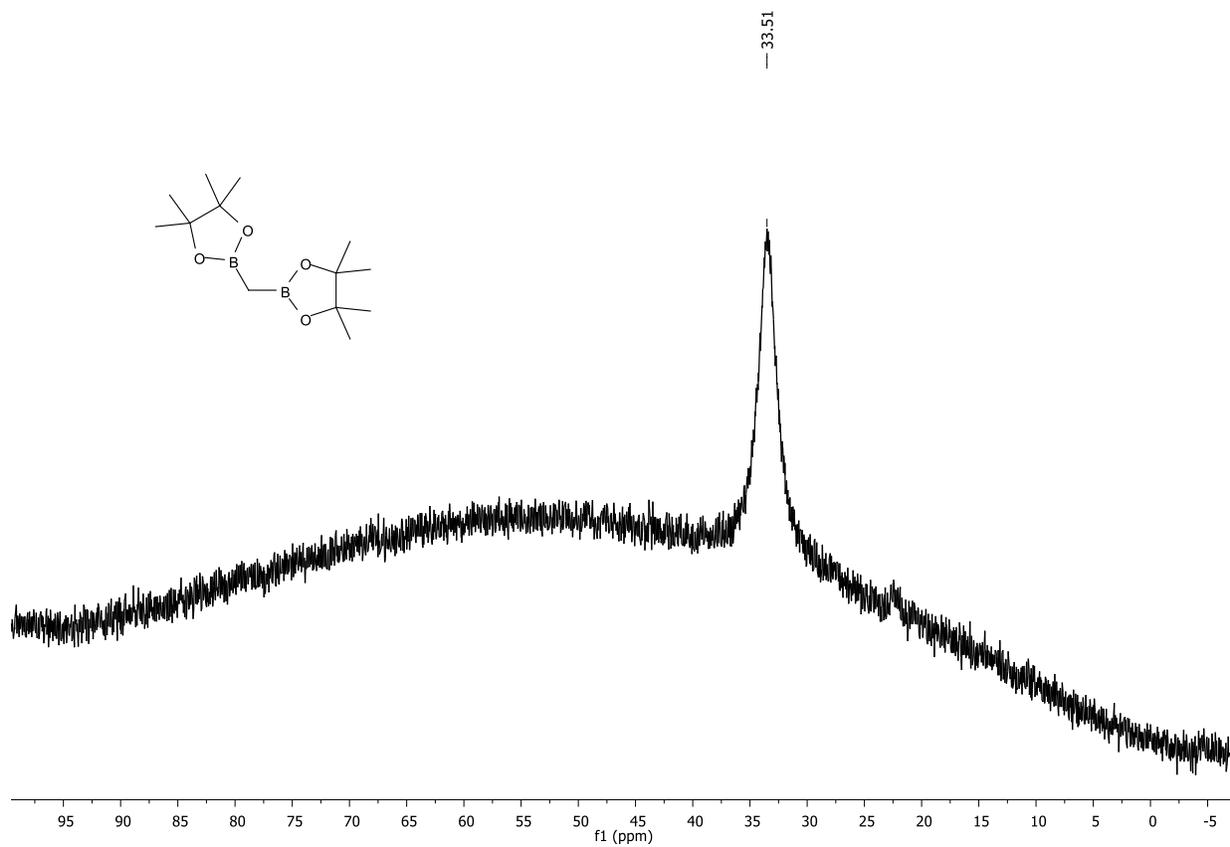
¹¹B NMR of 22b (128 MHz, CDCl₃)

1,456,391

7.027

TIC

4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.9

min

84
83
253
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45

10 40 70 100 130 160 190 220 250 280 310 340 370 400 430 460 490 520 550 580
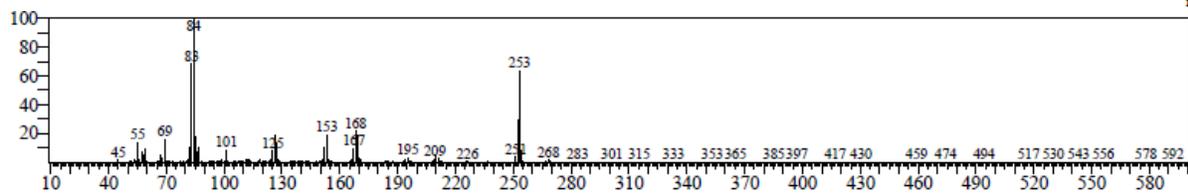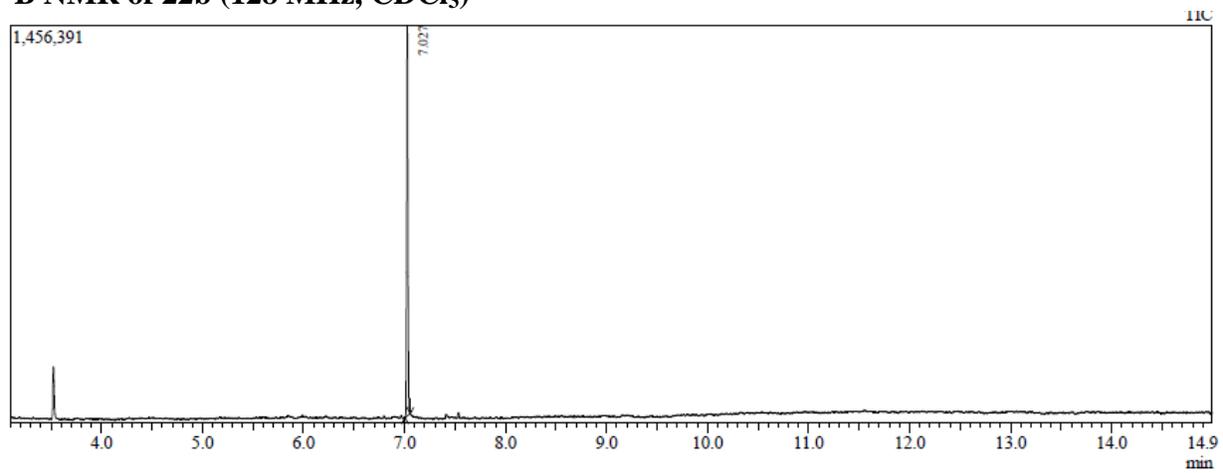
GC-MS data 22b

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23b).[1]
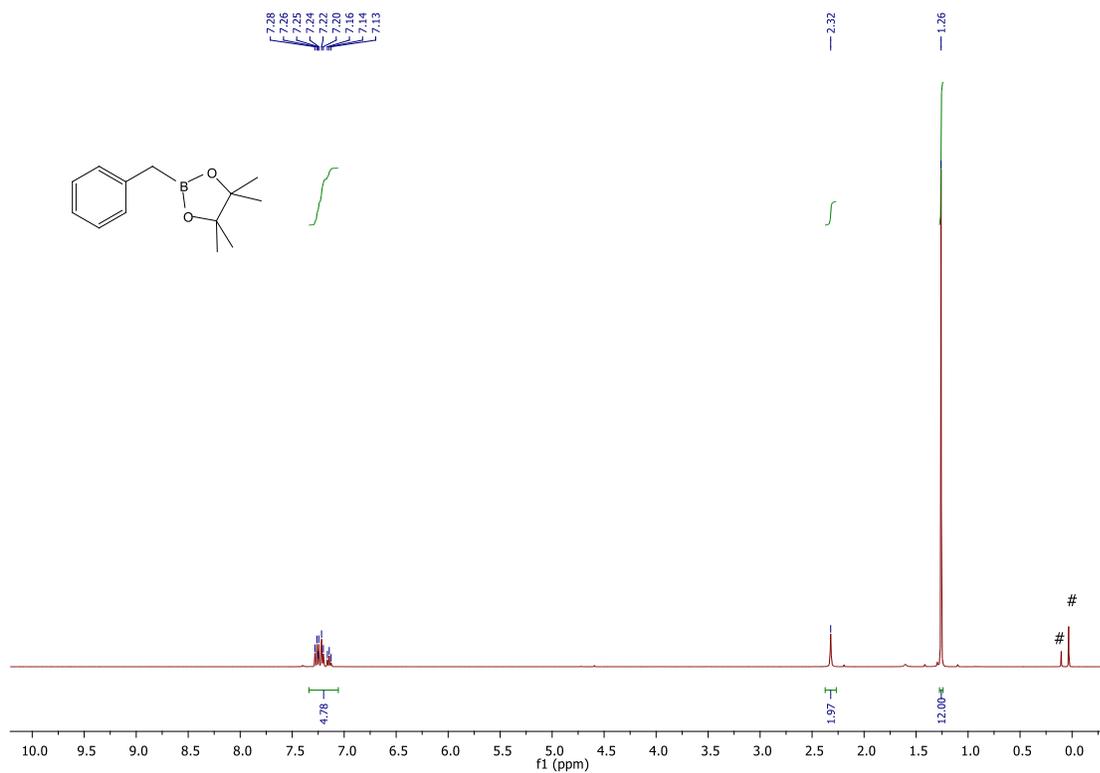
1H NMR of 23b (400 MHz, CDCl₃)
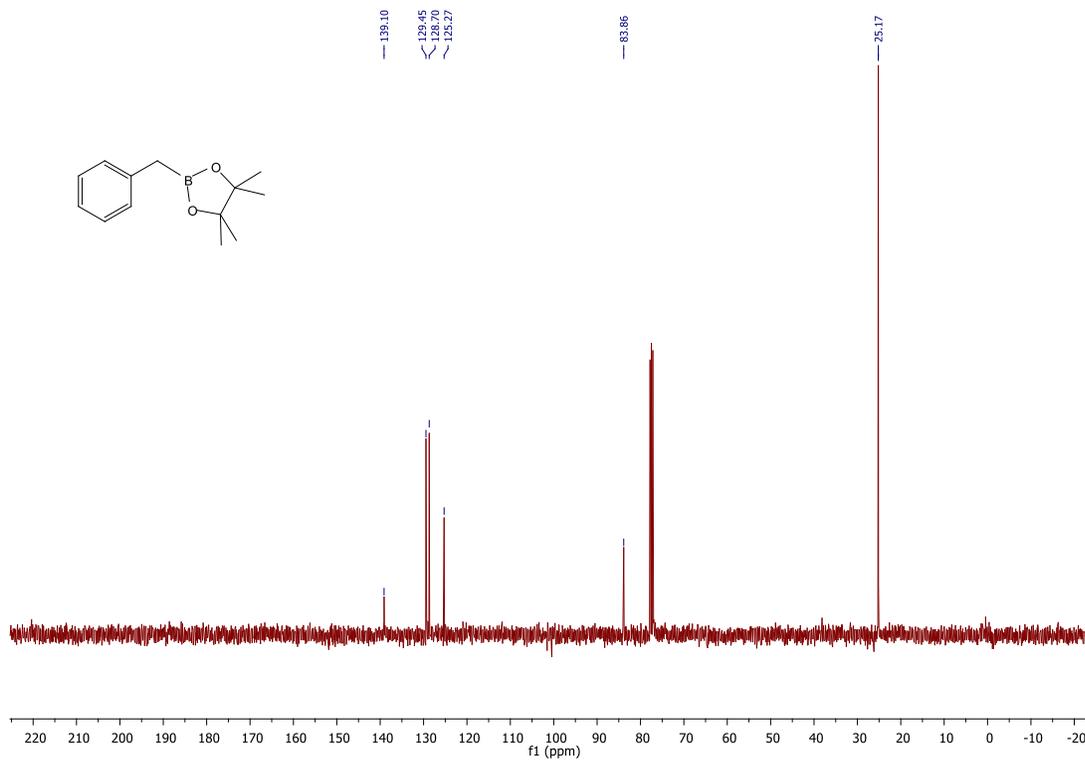
13C NMR of 23b (100 MHz, CDCl₃)

33.14

¹¹B NMR of 23b (128 MHz, CDCl₃)

¹¹B NMR of 23b (128 MHz, CDCl₃)

TIC

24,804,191

7.088

Library

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RawMode:Averaged 7.085-7.095(798-800) BasePeak:118.10(3222986)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

GC-MS data 23b

4,4,5,5-Tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (24b).[10]
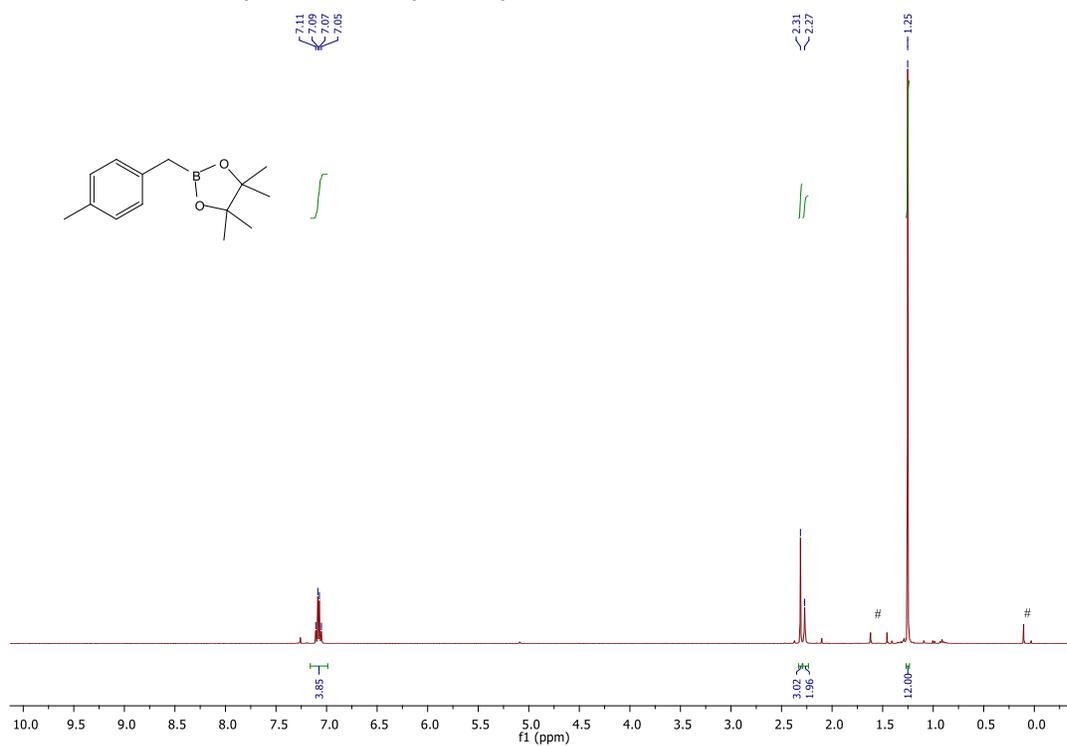
^{1}H NMR of 24b (400 MHz, CDCl$_3$)
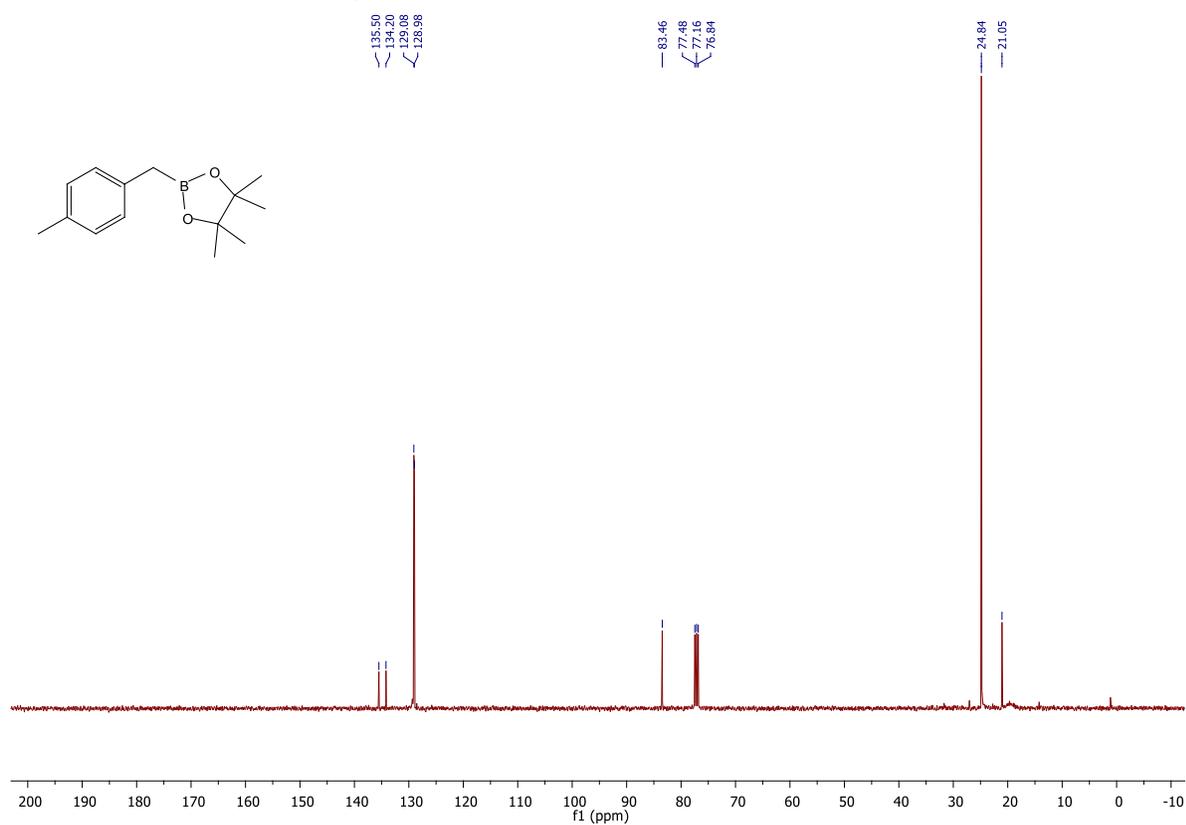
^{13}C NMR of 24b (100 MHz, CDCl$_3$)
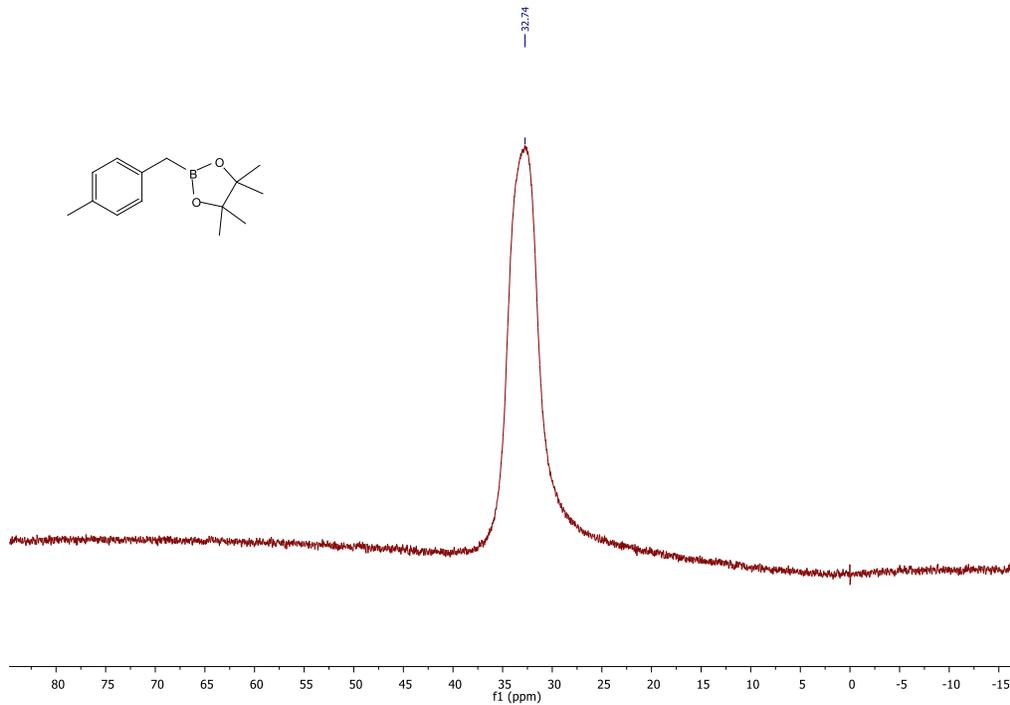
^{11}B NMR of 24b (128 MHz, CDCl$_3$)
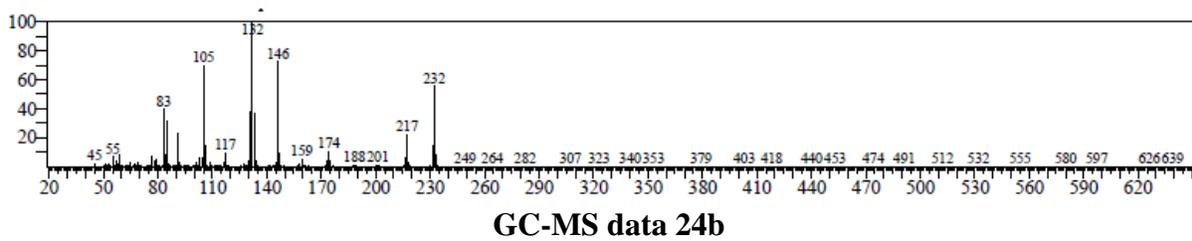
GC-MS data 24b

4,4,5,5-Tetramethyl-2-(2-methylbenzyl)-1,3,2-dioxaborolane (25b).[13]
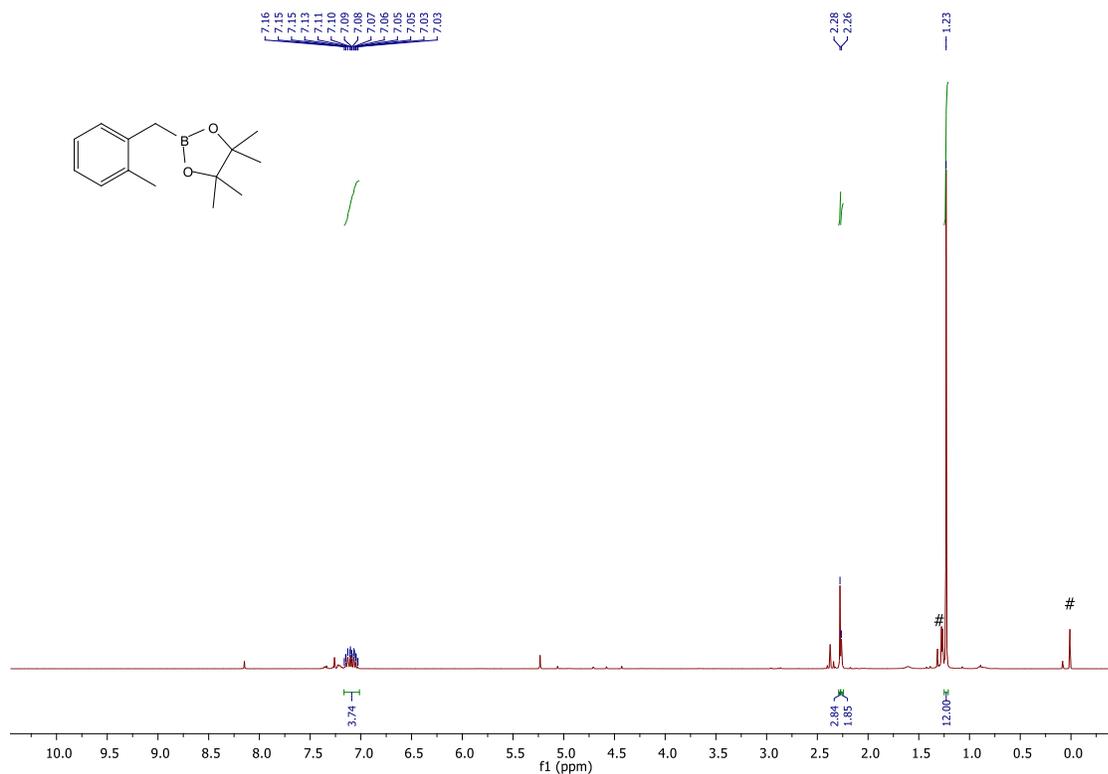
^{1}H NMR of 25b (400 MHz, CDCl$_3$)
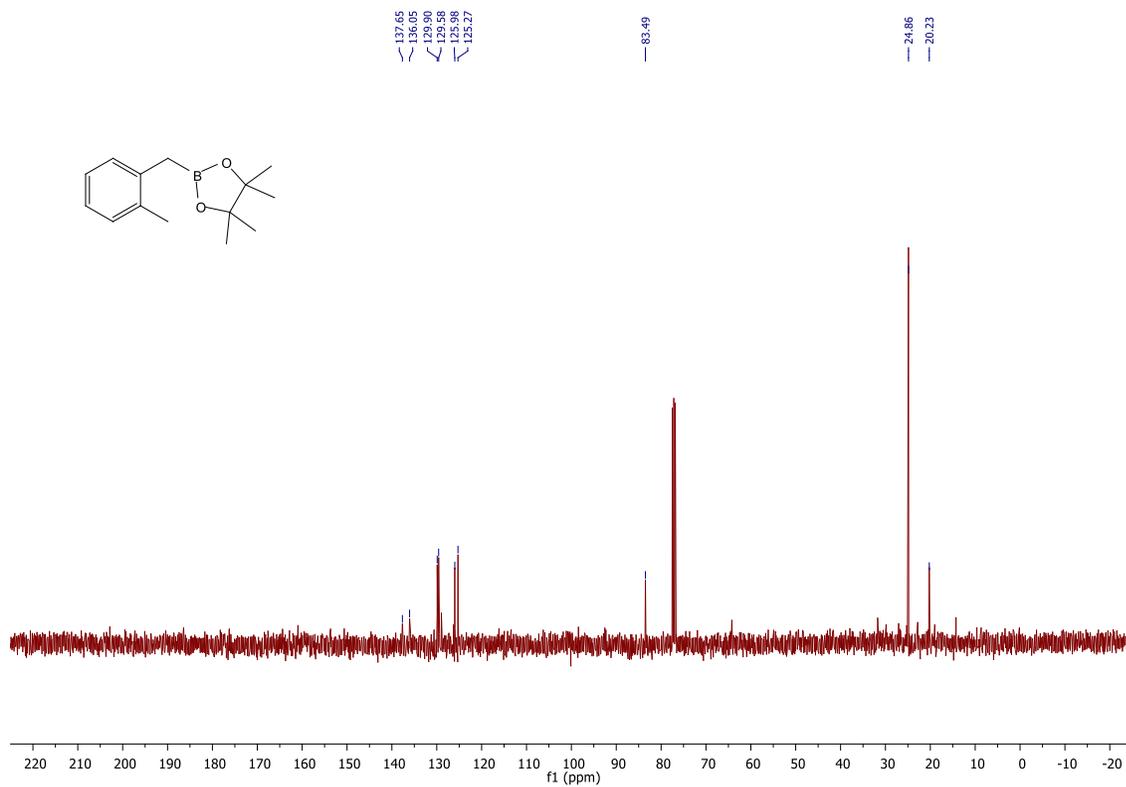
^{13}C NMR of 25b (100 MHz, CDCl$_3$)
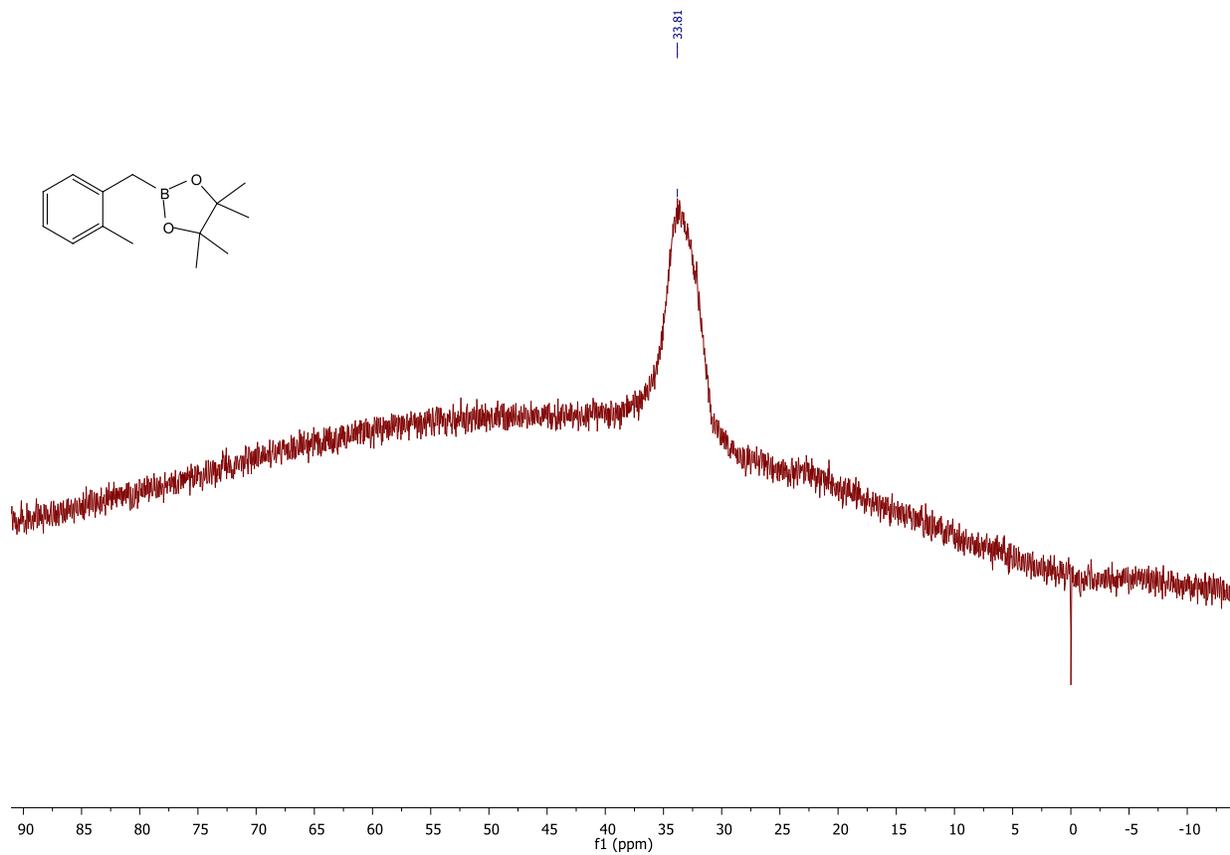
^{11}B NMR of 25b (128 MHz, CDCl$_3$)
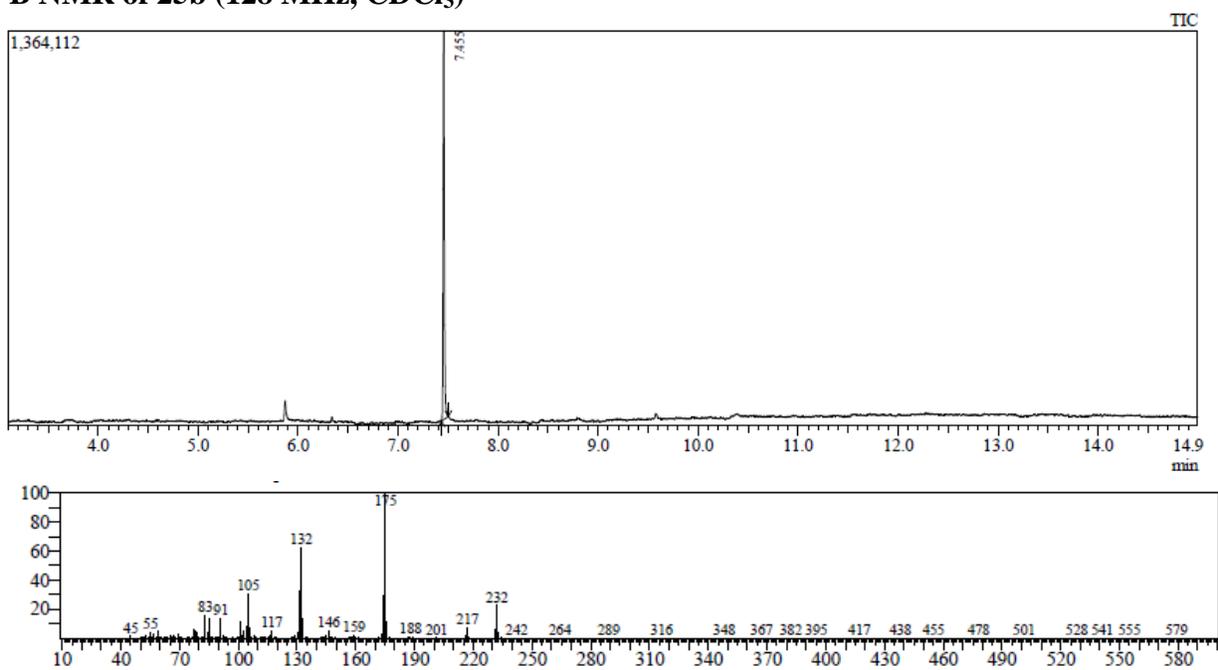
GC-MS data 25b

5,5-Dimethyl-2-phenethyl-1,3,2-dioxaborinane (26b).[8]
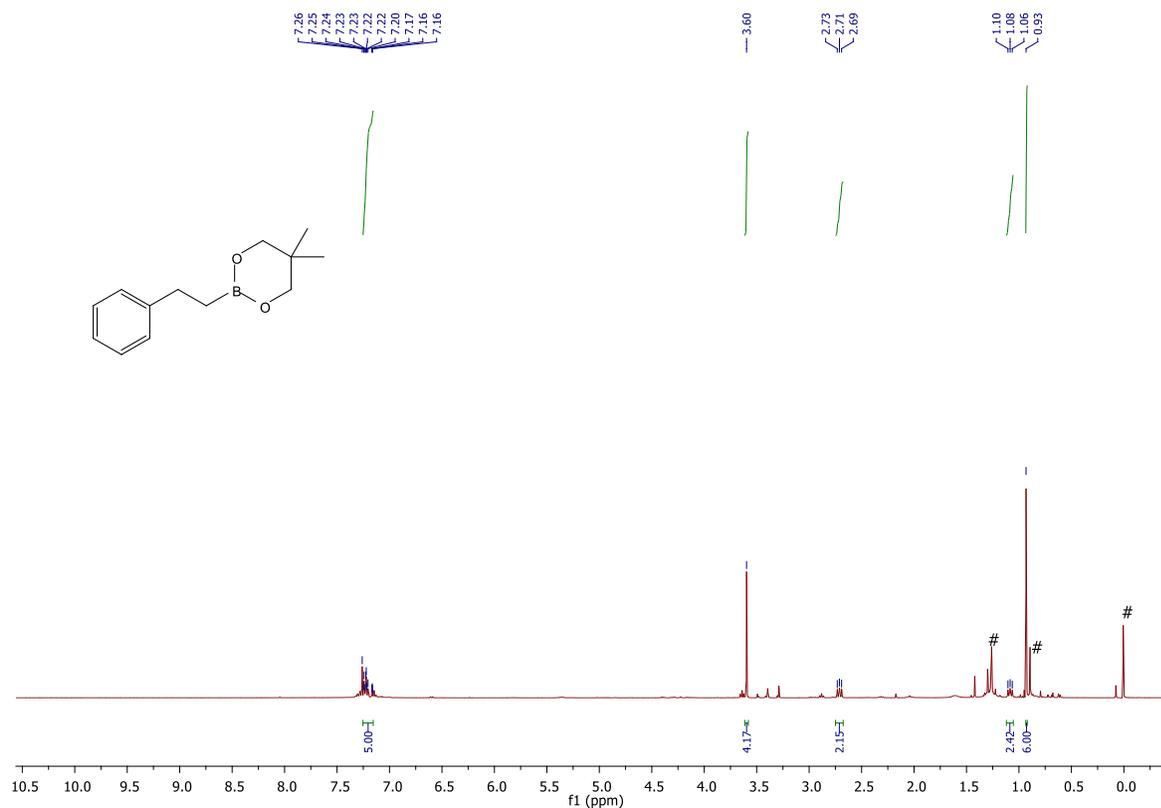
^{1}H NMR of 26b (400 MHz, CDCl$_3$)
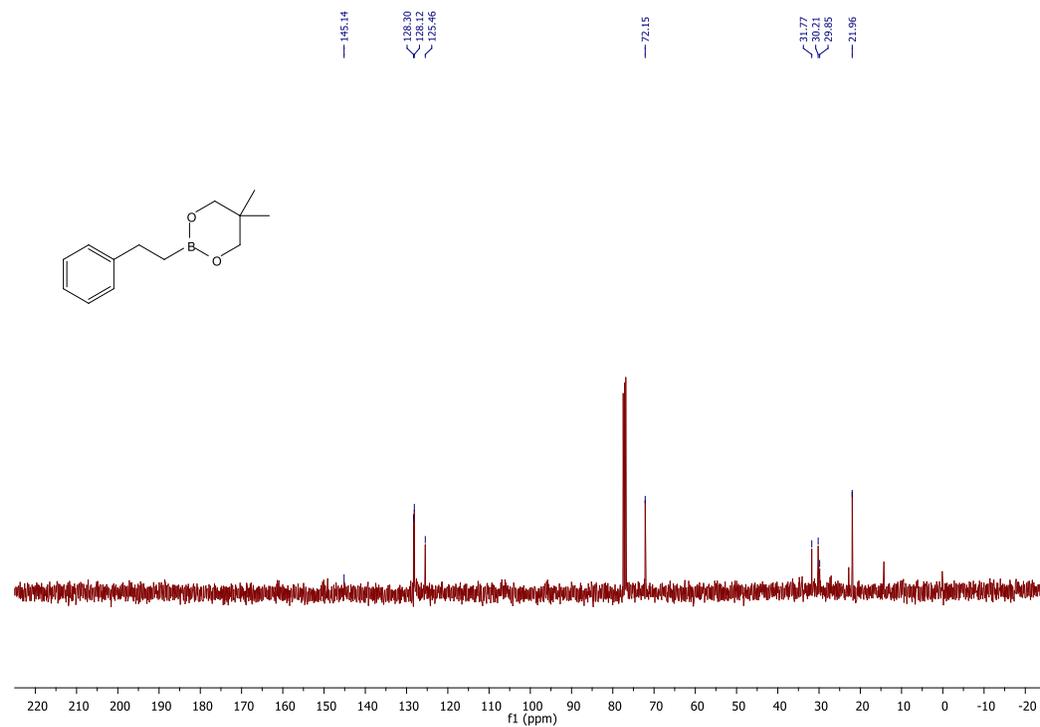
^{13}C NMR of 26b (100 MHz, CDCl$_3$)

— 30.83

95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)
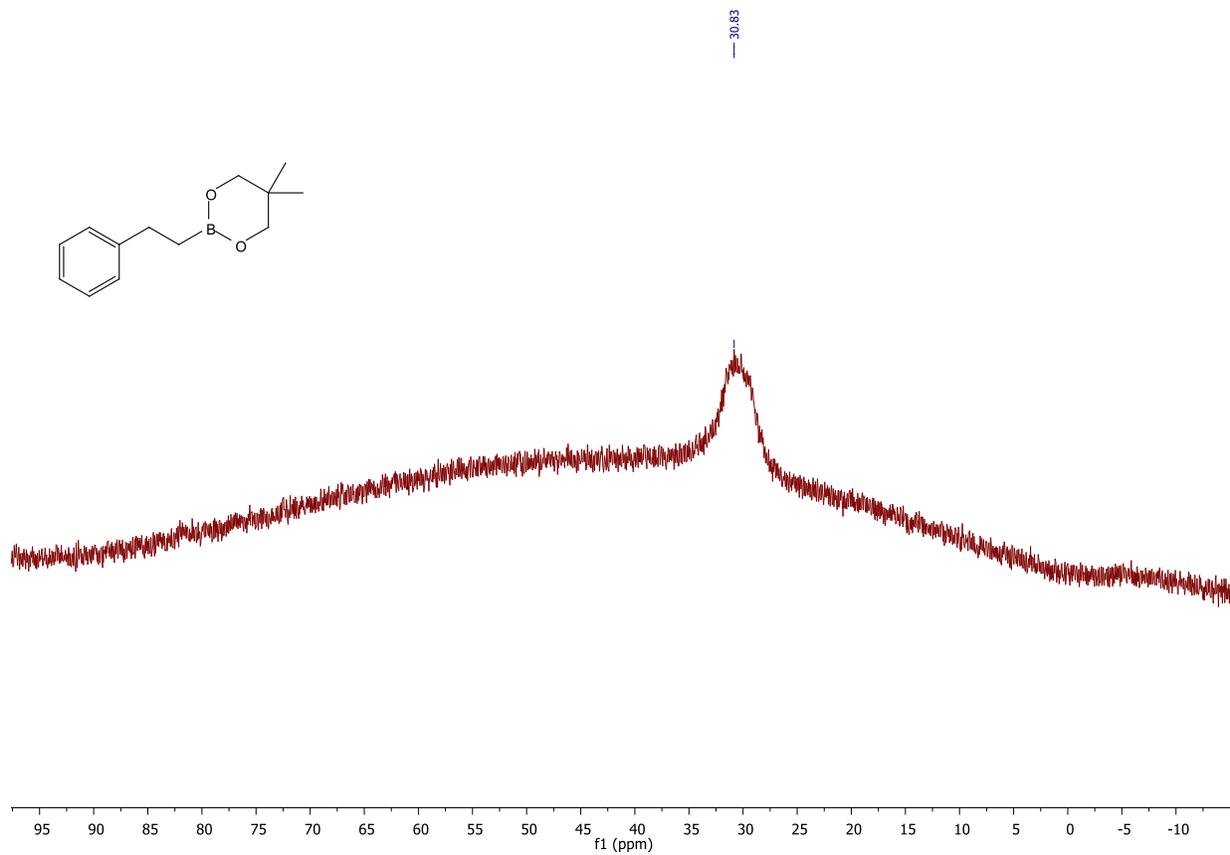
¹¹B NMR of 26b (128 MHz, CDCl₃)
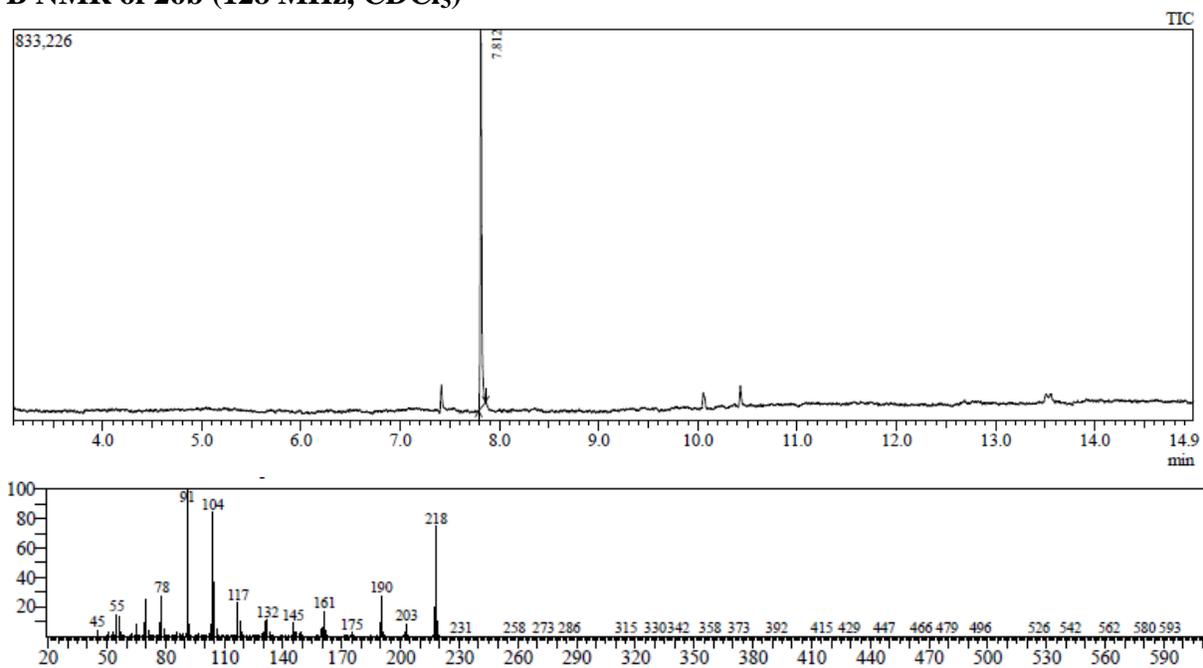
GC-MS data 26b

2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27c).[10]

^{1}H NMR of 27c (400 MHz, CDCl$_3$)
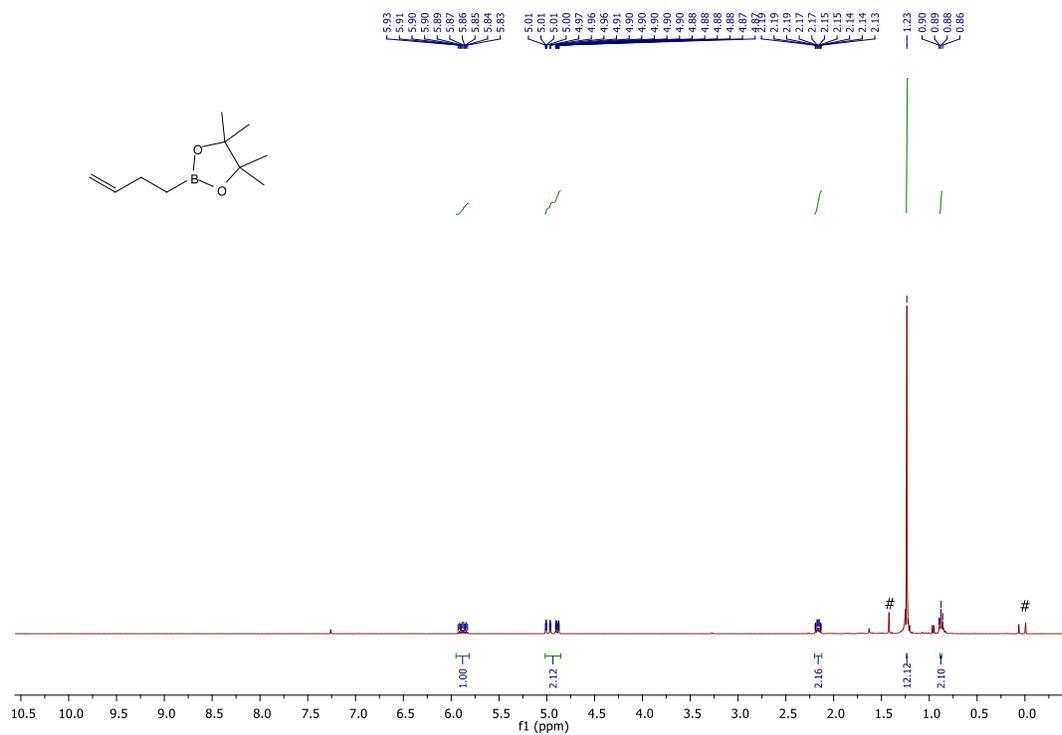
^{13}C NMR of 27c (100 MHz, CDCl$_3$)
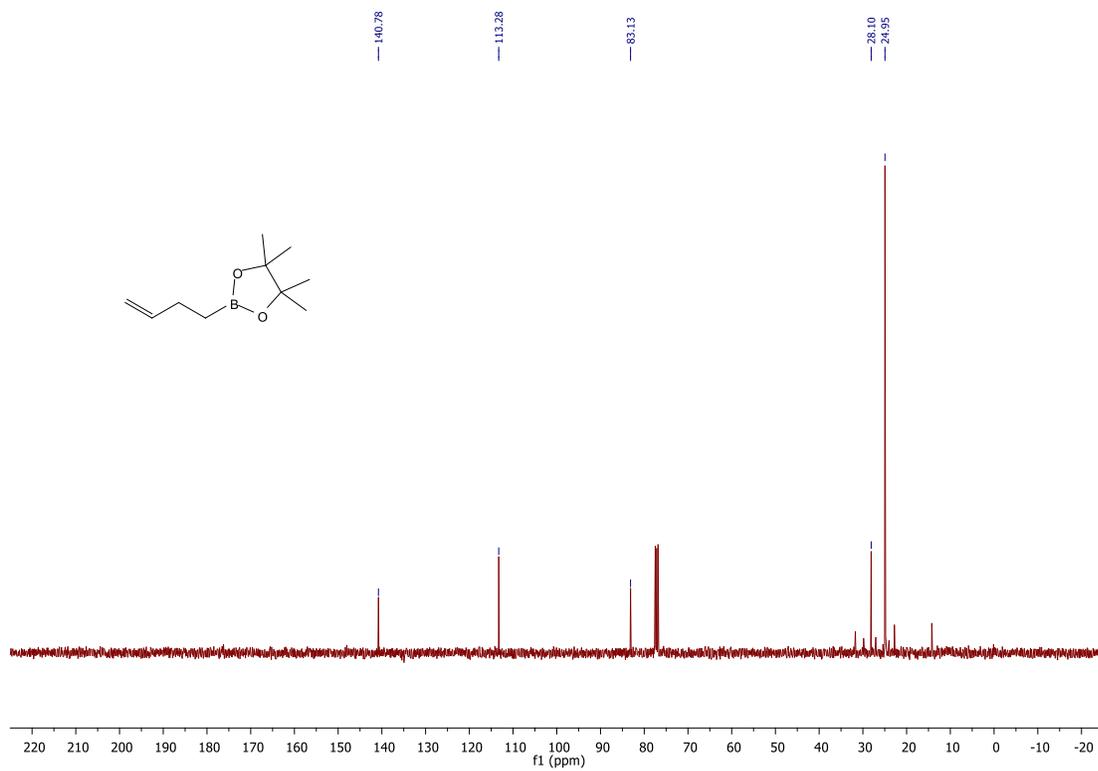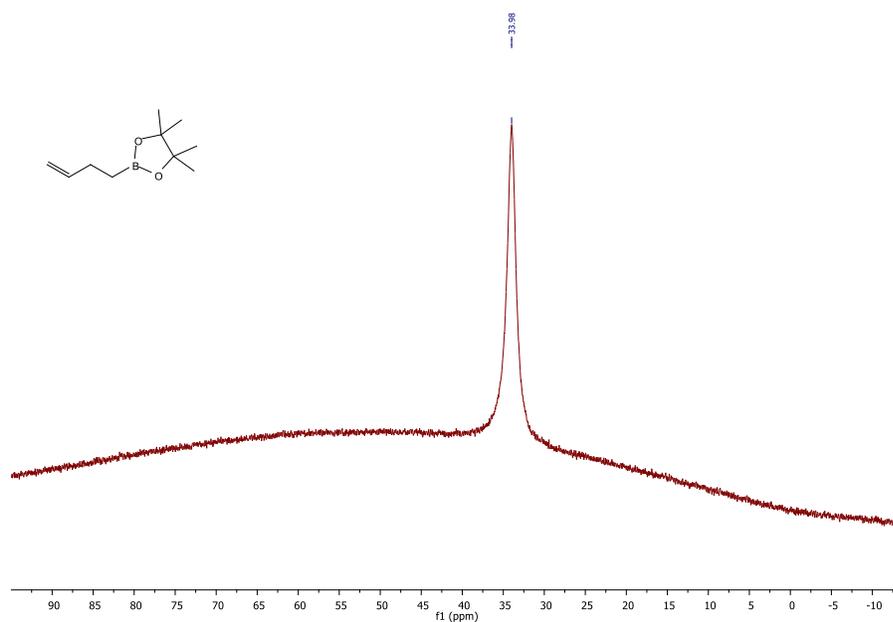
^{11}B NMR of 27c (128 MHz, CDCl$_3$)
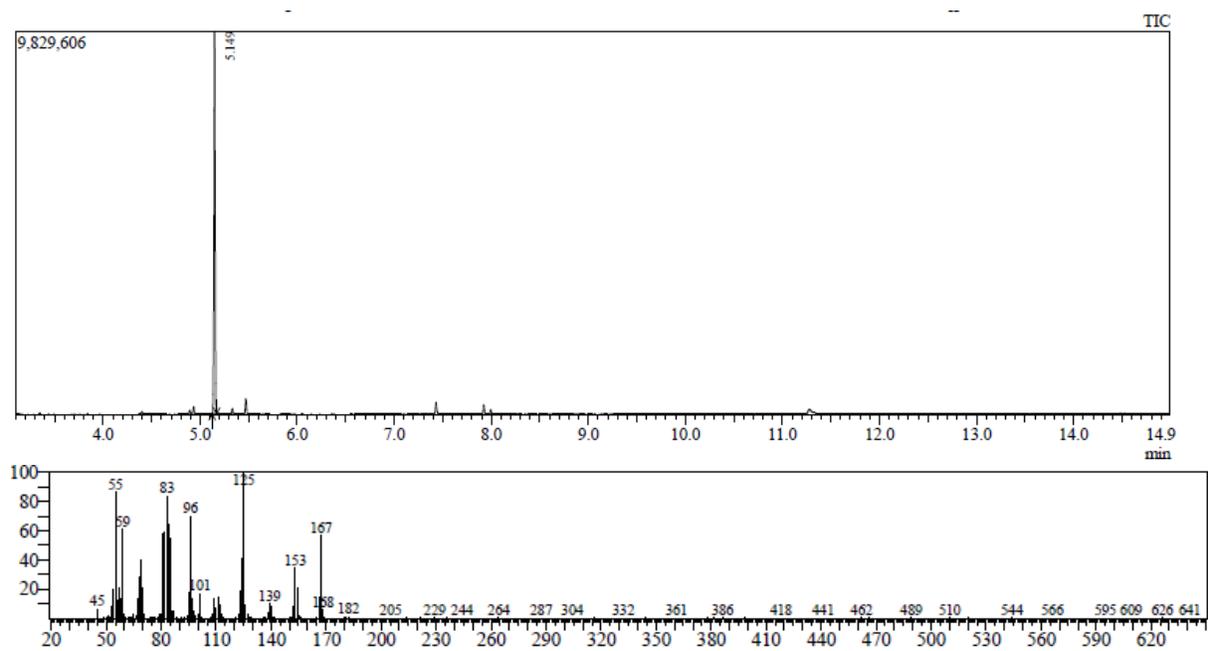
GC-MS data 27c

2-(Cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28c).[10]
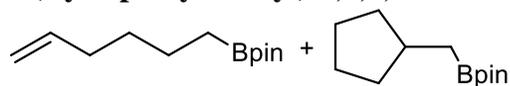
28b

28c

28b/28c = 22/78
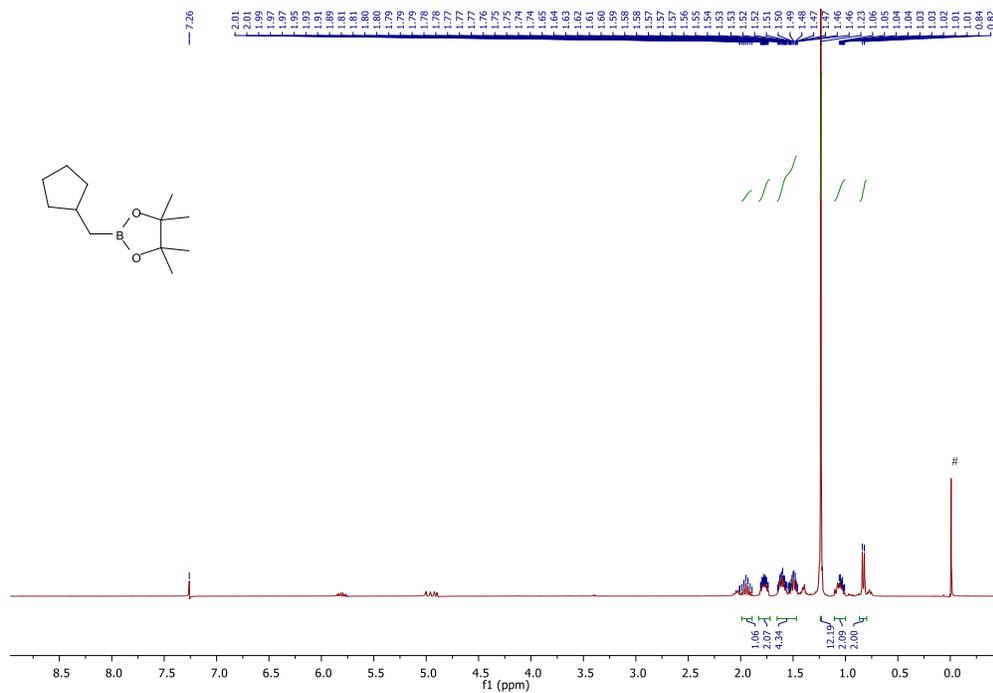
^{1}H NMR of 28c (400 MHz, CDCl$_3$)
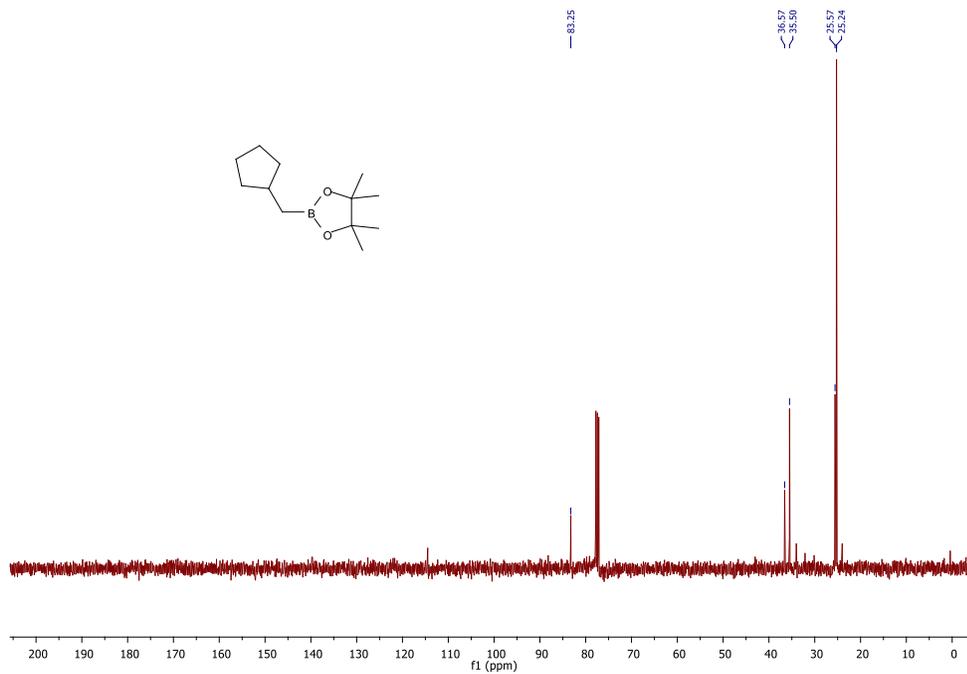
^{13}C NMR of 28c (100 MHz, CDCl$_3$)
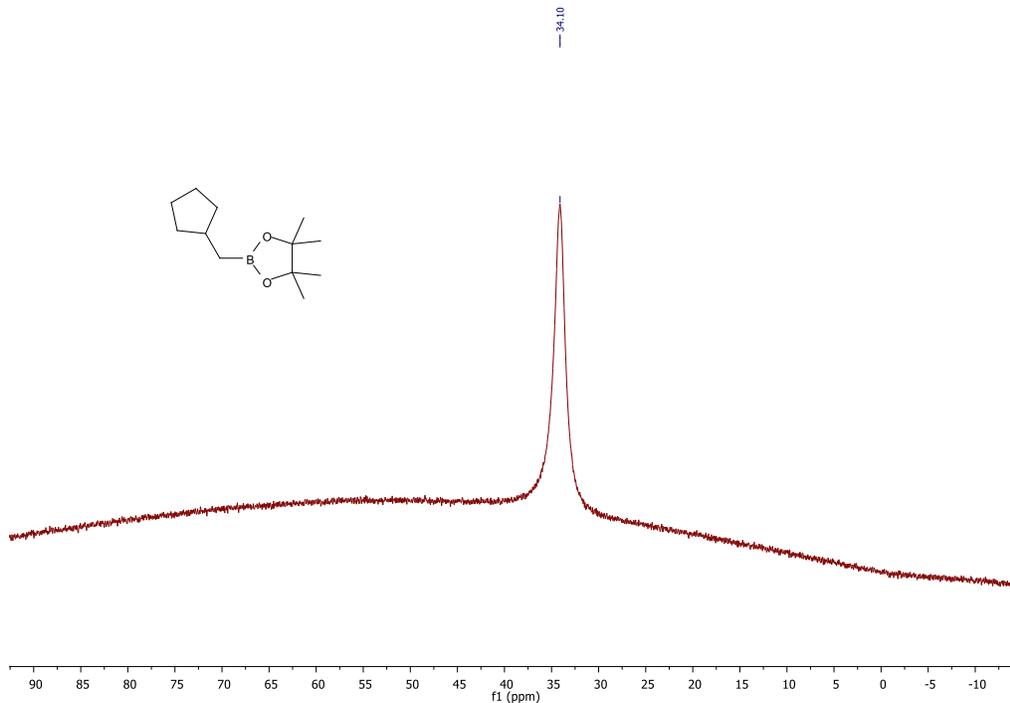
11B NMR of 28c (128 MHz, CDCl₃)
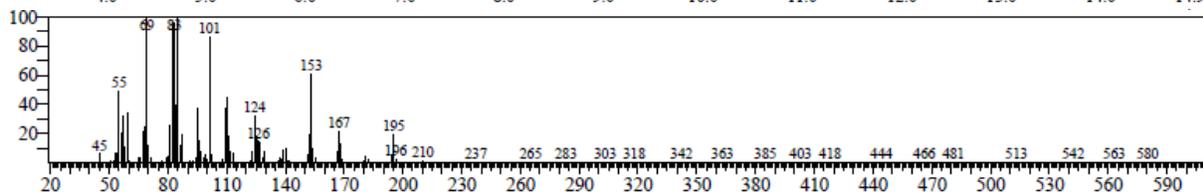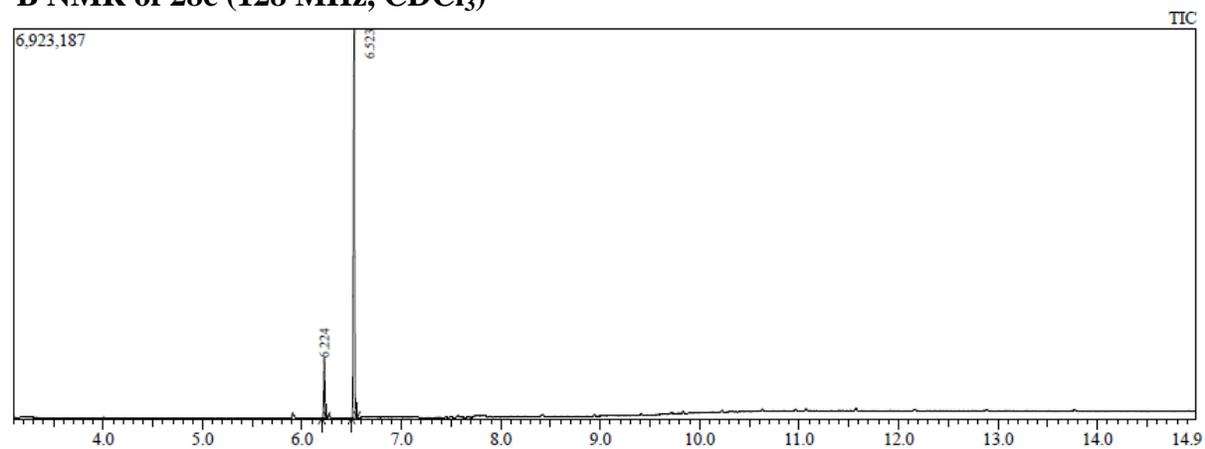
GC-MS data 28c

VII. References

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