Supporting Information

Organocatalytic hydroboration of olefins in pyrrolidinium ionic liquids

Paweł Huninik,[a,b] Jakub Szyling,[a] Agnieszka Czapik[b] and Jędrzej Walkowiak*[a]

[a]Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland.

[b]Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland.

*E-mail: jedrzejw@amu.edu.pl

Outline

1. General information:

1.1. NMR analyzes

^{1}H, ^{11}B and ^{13}C NMR spectra were recorded at 25 °C on Bruker UltraShield 300, Bruker Ascend™ 400 MHz NANOBAY or Bruker Ascend™ 600 MHz with a number of scans (NS) for ^{1}H NMR = 16 or 32, ^{13}C NMR = 512 or 1024 (unless otherwise stated). Chemical shifts were reported in ppm with the reference to the residue portion solvent peak for ^{1}H, ^{13}C NMR or BF_3-Et_2O for ^{11}B, respectively. Chloroform-d_1, Benzene-d_6 were used as solvents and for internal deuterium lock. The multiplicities were reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), pentet (p), multiplet (m).

1.2. GC-MS analysis

The mass spectra of the products were obtained by GC-MS analysis on a Bruker Scion 436-GC with a 30m Varian DB-5 0.25mm capillary column and a Scion SQ-MS mass spectrometry detector giving fragment ions in *m*/*z* with relative intensities (%) in parentheses. Temperature program used: 60 °C (3 min), 10 °C/min, 250 °C (30 min).

1.3. MALDI-TOF-MS analysis

MALDI-TOF mass spectra were recorded on a UltrafleXtreme mass spectrometer (Bruker Daltonics), equipped with a SmartBeam II laser (355 nm) in 1-4000 m/z range. 2,5-Dihydroxybenzoic acid (DHB, Bruker Daltonics, Bremen, Germany) served as matrix and was prepared in TA30 solvent (30:70 v/v acetonitrile: 0.1% TFA in water) at a concentration of 20 mg/mL. Studied samples were dissolved in dichloromethane (2 mg/mL) and then mixed in a ratio 1:1 v/v with matrix solution. Matrix/sample mixtures (1 μL) were spotted onto the MALDI target and dried in air. Mass spectra were measured in reflection mode.

1.4. FT-IR analysis

FT-IR spectra were measured on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) equipped with a built-in ATR accessory with ATR diamond unit. In all experiments, 16 scans at a resolution of 2 cm^{-1} were performed

1.5. Elemental analysis

Elemental analyses were performed using the Vario EL III instrument.

1.6. X-Ray crystallography analysis

A colourless crystals of **2v** suitable for X-ray structural analysis were obtained by slow evaporation of *n*-heptane. The diffraction data were collected at 100 K with Rigaku XtaLAB Synergy-R diffractometer, using Cu Kα radiation (λ = 1.54184 Å). The intensity data were collected and processed using CrysAlis PRO software.[1] The structures were solved by direct methods with the program SHELXT 2018/2 and refined by full-matrix least-squares method on F^2 with SHELXL 2018/3.[2, 3] The carbon-bound hydrogen atoms were refined as riding on their carriers and their displacement parameters were set equal to 1.5Ueq(C) for the methyl groups and 1.2Ueq(C) for the remaining H atoms. The hydrogen atoms of OH groups were located in electron-density dierence maps. In the final cycles of refinement, they were included in the calculated position and treated as riding atoms. Absolute structures of the compounds were specified by the synthetic procedure and confirmed using Flack parameter.[4]

A summary of the crystallographic data is given in **Table S4**. Molecular graphics were generated with Olex2 and Mercury CSD 4.3.1 software.[5, 6] ORTEP representation of the molecular structure of the reported compound is presented in **Figures S104**.

Asymmetric unit consist two symmetrically independent molecules slightly different conformation (**Figure S105a**). The crystal packing of the molecules is shown in **Figure S105b-c**. In a crystal, symmetrically independent molecules interact *via* O-H···O hydrogen bonds, forming a chain stretched in the x-axis direction (**Figure S105d**). The chain structure is stabilized by C-H···O interactions between the methoxy group and the oxygen atom of the OH group of symmetrically dependent molecules. The 1D structure is additionally stabilized by the interaction of the methoxy group and the π-electron system of the phenyl ring of symmetrically independent molecules. The 3D structure is stabilized by C-H···O interactions between adjacent chains. The parameters of selected hydrogen bonds are summarized in **Table S5**.

CCDC **2216859** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

2. Materials

Styrene (99%, Sigma-Aldrich), 4-chlorostyrene (98%,Fluorochem), 2,4,6-trimethylstyrene (95%, Alfa Aesar), 4-*tert*-butylstyrene (94%, Thermo Scientific), 4-fluorostyrene (95%, AmBeed), 4-bromostyrene (95%, Apollo Scientific), 4-vinylaniline (97%, Sigma-Aldrich), 4-methoxystyrene (97%, Sigma-Aldrich), methyl 4-vinylbenzoate (98%, Angene), 4-vinylbenzylchloride (90%, Sigma-Aldrich), 4-vinylbiphenyl (98%, Angene), 2-vinylnaphtalene (98%, J&K), 4-(trifluoromethyl)styrene (98%, Apollo Scientific), α-methylstyrene (99%, Thermo Scientific), *p*,α-dimethylstyrene (96%, Thermo Scientific), 4-chloro-α-methylstyrene (97%, AmBeed), dimethylphenylvinylsilane (98%, Sigma-Aldrich), allylbenzene (98%, Thermo Scientific), 1-allyltoluene (97%, Sigma-Aldrich), 1-allyl-4-fluorobenzene (97%, Sigma-Aldrich), 1-allyl-4-methoxybenzene (98, Thermo Scientific), 4-allyl-1,2-dimethoxybenzene (95%, Angene), allylpentafluorobenzene (97%, Sigma-Aldrich), 4-allyl-2-methoxyphenol (98%, Sigma-Aldrich), 1,1-diphenylethylene (97%, Sigma-Aldrich), 2-methyl-3-phenyl-1-propene (99%, Thermo Scientific), pinacolborane (99%, TCI), 1-butyl-3-methylimidazolium chloride (98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium acetate (98%, Iolitec), choline acetate (98%, Iolitec), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (99%, Iolitec), 1-ethyl-1-methylpyrrolidinium bromide (99%, Iolitec), 1-ethyl-1-methylpyrrolidinium triflate (99%, Iolitec), 1-ethyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (99%, Iolitec), choline chloride (98%, Angene), 1-butyl-3-methylimidazolium tetrafluoroborate (98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium triflate (99%, Iolitec), 4-iodotoluene (99%, Sigma-Aldrich), magnesium sulfate (anhydrous, 99%, Sigma-Aldrich), cesium carbonate (99%, Sigma-Aldrich), potassium hydrogenfluoride (99%, Sigma-Aldrich), vinylmagnesium bromide solution 1.0 M in THF (Sigma-Aldrich), sodium thiosulfate (99%, Merck), sodium perborate tetrahydrate (Sigma-Aldrich), *p*-toluenesulfonyl chloride (98%, Sigma-Aldrich), sodium methoxide (95%, Sigma-Aldrich), iodine (99%, Sigma-Aldrich), 5-hexen-1-ol (98%, Sigma-Aldrich), methyltriphenylphosphonium iodide (97%, AmBeed), *n*-butyllithium solution (1.6 M in hexanes, Sigma-Aldrich), 2-methoxybenzaldehyde (98%, AcrosOrganics), trimethylsilyl trifluoromethanesulfonate, (99%, Alfa Aesar), 1-(2-chlorophenyl) ethanone (97%, AmBeed), *N*,*N*,*N*',*N*-tetramethylethylenediamine (>99.5%, Sigma-Aldrich), 1,4-diazabicyclo[2.2.2]octane (>99%, Sigma-Aldrich), silica gel (MN-Kieselgel 60, 0.04-0.063 mm (230-400 mesh ASTM; Sigma-Aldrich)) were used as received. Toluene, tetrahydrofurane, *n*-hexane, hexanes, *n*-heptane ethyl acetate, dichloromethane,

acetone, diethyl ether, methanol were purchased from Avantor Performance Materials Poland. The chloroform-d_1 and benzene-d_6 were purchased from Deutero and dried over molecular sieves (4Å) prior use.

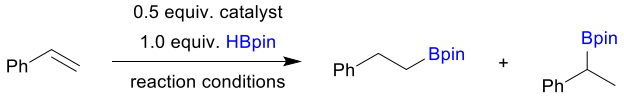
The THF used in the reactions was distilled over Na/benzophenone mixture, deoxygenated with standard Schlenk line procedure and stored under argon atmosphere. Argon (99,999%) was purchased from Messer. Ionic liquids were dried over 24 h under vacuum (10^{-3} mbar) at 70 °C prior use.

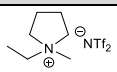
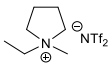
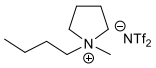
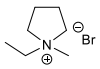
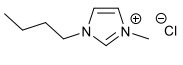
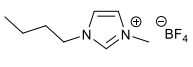
3. Optimization procedures.

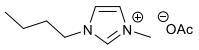
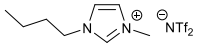
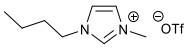
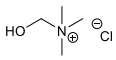
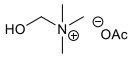
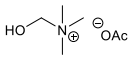
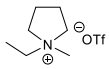
A Schlenk's vessel was charged with dried ionic liquid in an argon atmosphere. Subsequently, pinacolborane (1.0 mmol) and styrene (**1a**, 1.0 mmol) were added (both distilled prior before use) in argon atmosphere. The reactions were carried out in the reaction conditions listed in Tables S1, S2, S3. The reaction mixture was cooled down and the products were extracted with *n*-heptane (3 × 5 mL). Extracts were combined and solvent was evaporated. After evaporation, the extracts were weighed and characterized by GC–MS and ^{1}H NMR analyses.

3.1. Catalysts and condition screening.

Table S1. Screening of catalysts selected for hydroboration of styrene.

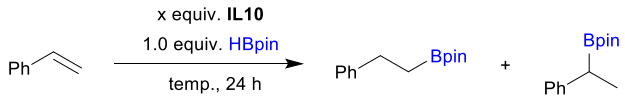


entry	catalyst	conv. of **1a** [%][a]	temp. [°C]	yield of **2a** [%][a]	selectivity (**2a**/**3a**)[b]
1	 [EMPyrr][NTf$_2$] IL1	26	60	25	98/2
2	 [EMPyrr][NTf$_2$] IL1	95	110	95	>99/0
3	 [BMPyrr][NTf$_2$] IL2	80	110	78	98/2
4	 [EMPyrr][Br] IL3	82	110	81	99/1
5	 [BMIM][Cl] IL4	11	110	10	94/6
6	 [BMIM][BF$_4$] IL5	48	110	45	94/6

7	 [BMIM][OAc] IL6	56	110	53	96/4
8	 [BMIM][NTf_2]	60	110	59	98/2
9	 [BMIM][OTf] IL7	59	110	56	95/5
10	 [Chol][Cl] IL8	10	110	10	99/1
11	 [Chol][OAc] IL9	11	90	8	68/32
12	 [Chol][OAc] IL9	15	110	15	98/2
13	 [EMPyrr][OTf] IL10	>99	110	>99	>99/0
14	NaOTf	78	110	75	94/6
15	Me_3SiOTf	n.r	110	-	-
16	none	8	110	7	93/7

Reaction conditions: [**IL**]:[**1a**]:[**HBpin**] = 0.5:1:1, neat, inert atmosphere, 24 h. [a]Determined by GC-MS analysis. [b]Determined by GC-MS and ^1H NMR analyses.

Table S2. Screening of temperature and ionic liquid loadings for [EMPyrr][OTf] **IL10** catalyzed hydroboration of styrene.

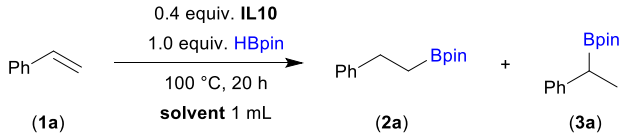


(**1a**) (**2a**) (**3a**)

entry	**IL10** [equiv.]	conv. of **1a** [%][a]	temp. [°C]	yield of **2a** [%][a]	selectivity (**2a**/**3a**)[b]
1	0.5	>99	110	>99	>99/0
2	0.5	91	80	89	98/2
3	0.5	>99	100	>99	>99/0
4	0.3	90	100	90	>99/0
5	0.4	>99	100	>99	>99/0
6[c]	0.4	>99	100	>99	>99/0
7[d]	0.4	96	100	96	>99/0
8[e]	0.05	41	70	41	>99/0

[a]Determined by GC-MS analysis. [b]Determined by GC-MS and ^1H NMR analyses.[c]20 h [d]18 h. [e][**IL**]:[**1a**]:[**HBpin**] = 0.05:1:1.2, inert atmosphere, 12 h.

Table S3. Screening of solvents for [EMPyrr][OTf] **IL10** catalyzed hydroboration of styrene.



entry	**solvent**	conv. of **1a** [%][a]	yield of **2a** [%][a]	selectivity (**2a**/**3a**)[b]
1	neat	>99	>99	>99/0
2	THF	22	22	99/1
3	MeCN	47	46	98/2
4	Toluene	45	44	98/2
5	Benzene	54	53	99/1
6	Chloroform	50	50	>99/0
7	DMSO	n.r.	-	-
8[c]	H_2O	n.r.	-	-
9[c,d]	neat	16	~ 16	98/2

[a]Determined by GC-MS analysis. [b]Determined by GC-MS and ^{1}H NMR analyses.
[c] Formation of pinBOBpin was observed. [d] 10μL of H_2O were added.

4. General procedures

4.1. Hydroboration of alkenes (1a – 1ae) in IL10 under optimized reaction/extraction conditions.

A Schlenk's vessel was charged with dried **IL10** (0.4 equiv.) in an argon atmosphere. Subsequently, pinacolborane (1.0 mmol) and olefin (**1a** – **1ae**, 1.0 mmol) were added. The reaction was carried out for 20 h at 100 °C. The reaction mixture was cooled down and the extractant soluble components were extracted with *n*-heptane (3 × 5 mL). Extracts were combined and solvent was evaporated. After evaporation, the extracts were weighed and characterized by GC–MS and ^{1}H NMR analyses. The products (**2a**–**2ae**) were purified on silica by flash chromatography (Biotage IsoleraOne chromatograph) with a UV detector (λ1 = 254 nm, λ2 = 280 nm). Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 12 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100% by 3 CV, step 2: gradient 10%/CV by 7 CV, step 3: hexane 50% by 2 CV). The products were characterized by GC-MS, ^{1}H ^{13}C and ^{11}B NMR analyses.

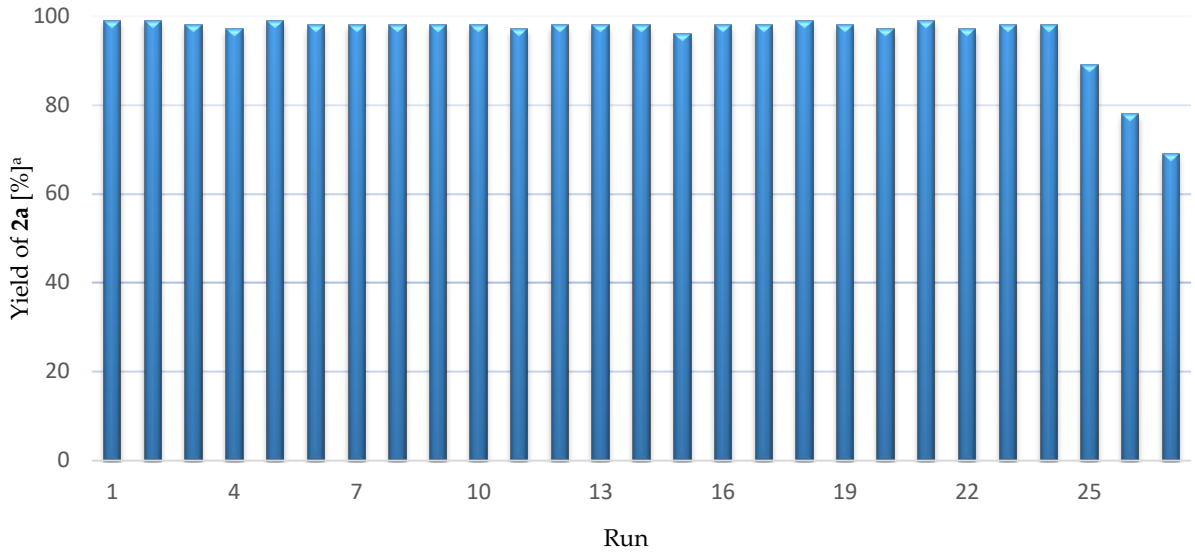
*Gram-scale hydroboration of **2a**:*
[EMPyrr][OTf] (**IL10**) (5 mmol, 0.4 equiv.), pinacolborane (10 mmol) and **1a** (10 mmol) were added into Schlenk vessel under argon atmosphere and stirred for 20 h at 100 °C. The reaction mixture was cooled down and the extractant soluble components were extracted with *n*-heptane. Extracts were combined and solvent was evaporated to afford the **2a** (2.25 g, 98%) as a white solid. Crude reaction mixture was analyzed by GC-MS and ^{1}H NMR analyses.

4.2. Hydroboration of styrene (1a) in repetitive batch mode.

*Repetitive hydroboration of styrene (**1a**) using **IL 10** (0.5 equiv.):*
A Schlenk's vessel was charged with dried **IL10** (0.5 equiv.) in an argon atmosphere. Subsequently, pinacolborane (1.0 mmol) and styrene (**1a**, 1.0 mmol) were added. The reaction was carried out for 20 h at 100 °C. The reaction mixture was cooled down and the extractant soluble components were extracted with *n*-heptane (3 × 5 mL). Extracts were combined and solvent was evaporated. After evaporation, the

extracts were weighed and characterized by GC–MS and ^{1}H NMR analyses. **IL10** was recovered and used in the next reaction.

*Repetitive hydroboration of styrene (**1a**) using **IL 10** (0.4 equiv.):*
The procedure with the application of 0.4 equiv. of **IL10** was analogous to the protocol described above with 0.5 equiv. of **IL10**.



Plot S1. Hydroboration of styrene (**1a**) with HBpin under repetitive batch mode using [EMPyrr][OTf] (0.4 equiv.) at 100 °C for 20 h.[a] Determined by GC-MS analysis. Selectivity of anti-Markovnikov/Markovnikov products was determined by GC-MS and ^{1}H NMR analyses.

4.3. Synthesis of alkenes 1l and 1ac (Wittig reaction).

To a solution of methyltriphenylphosphonium iodide (2.83 g, 7 mmol, 2.0 equiv.) in THF (10 mL) at 0 °C was added 1.6 M *n*-butyllithium solution in hexanes (3.38 mL, 7 mmol, 2.0 equiv.) dropwise over 30 minutes. The reaction mixture was stirred for 1 hour at room temperature. The corresponding ketone or aldehyde (3.5 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise to the cooled reaction mixture at 0 °C *via* syringe. The reaction was then stirred at room temperature for 24 hours. Afterwards, the resulting mixture was quenched with saturated NH_4Cl (20 mL), diluted with water (15 mL) and extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (2 x 15 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved in hexane and triphenylphosphine oxide was filtered off. The filtrate solution was then concentrated under reduced pressure. The products **1l** and **1ac** were isolated by flash column chromatography. Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 4 CV (CV = column volume), phase: hexanes. The products were characterized by GC-MS and ^{1}H NMR analyses.[7, 8]

4.4. Synthesis of hex-5-en-1-yl 4-methylbenzenesulfonate (1w).

To a solution of 5-hexen-1-ol (1.00 g, 10.0 mmol) in CH_2Cl_2 (25 mL) were added Et_3N (1.95 mL, 13.9 mmol) and TsCl (2.22 g, 11.6 mmol) at 0 °C. The reaction mixture was stirred at room temperature over 5 h before adding water (30 mL). The resulting mixture was extracted with CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and combined organic phases were washed with saturated sodium bicarbonate and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The product was purified on silica by flash chromatography to afford the hex-5-en-1-yl 4-methylbenzenesulfonate **1w** (2.30 g, 96%) as a pale-yellow oil. Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 12 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100% by 3 CV, step 2: gradient

10%/CV by 7 CV, step 3: hexane 50% by 2 CV). The product was characterized by GC-MS and ^{1}H NMR analyses.[9]

4.5. One-pot Suzuki coupling. Synthesis of 1-methyl-4-(2-phenylethyl)benzene (4).

[EMPyrr][OTf] (**IL10**) (0.5 mmol, 0.4 equiv.), pinacolborane (1 mmol) and styrene **1a** (1 mmol) were added into Schlenk vessel under argon atmosphere and stirred for 20 h at 100 °C. The reaction mixture was cooled down and volatiles were evaporated. Subsequently, [$Pd(PPh_3)_4$] (0.005 mmol), and 4-iodotoluene (1.2 mmol) were placed in the Schlenk vessel and evacuated. Then THF (1 mL) and aqueous solution of Cs_2CO_3 (3M, 1mL) were added under argon atmosphere and stirred for 24 h at 70 °C. Afterwards, the mixture was cooled to room temperature. Then, water was added (10.0 mL), and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and solvent was evaporated under vacuo. Product was purified on silica by flash chromatography to afford the **4** (150 mg, 76%) as a white solid. Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 10 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100% by 3 CV, step 2: gradient 5%/CV by 5 CV, step 3: hexane 50% by 2 CV). The product was characterized by GC-MS and ^{1}H NMR analyses.

4.6. One-pot oxidation. Synthesis of 2-phenylethanol (5).

[EMPyrr][OTf] (**IL10**) (0.5 mmol, 0.4 equiv.), pinacolborane (1 mmol) and styrene **1a** (1 mmol) were added into Schlenk vessel under argon atmosphere and stirred for 20 h at 100 °C. The reaction mixture was cooled down and volatiles were evaporated. $NaBO_3 \times 4H_2O$ (3 mmol) was added. Then THF (1 mL) and water (1 mL) were added and stirred for 5 h at room temperature. Afterwards, the reaction was quenched with water and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and solvent was evaporated under vacuo. Product was purified on silica by flash chromatography to afford the **5** (115 mg, 94%) as a colorless oil. Purification details: cartridge 10 g, flow rate: 12 mL/min, length: 12 CV (CV = column volume), phase: hexane/ethyl acetate (step 1: hexane 100% by 2 CV, step 2: gradient 5%/CV by 3 CV, step 3: hexane 80%/CV by 7 CV). The product was characterized by GC-MS and ^{1}H NMR analyses.

4.7. Synthesis of potassium trifluoroborate salt (6).

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane **2a** (1 mmol) was placed in a round bottom flask, then KHF_2 (5 mmol, 390 mg) and water (2 mL) were added and stirred for 24 h at room temperature. Afterwards, the reaction mixture was evaporated and washed with acetone. The solution was concentrated and precipitated with toluene to obtain the corresponding potassium trifluoroborate salt **6** (205 mg, 97%) as white solid. The product was characterized by ^{1}H NMR analysis.

4.8. Zweifel olefination. Synthesis of but-3-enylbenzene (7).

To a solution of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane **2a** (1.0 mmol) in anhydrous THF (10 mL) at room temperature was added a vinylmagnesium bromide (1.0 M in THF, 4.0 mmol) dropwise. The resulting mixture was stirred at room temperature for 30 min and cooled down to –78 °C. A solution of I_2 (4.0 mmol) in MeOH (4 mL) was added dropwise. Reaction mixture was stirred for 30 min and a solution of MeONa (8.0 mmol) in MeOH (8 mL) was added. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 2 hours, then quenched with a 20% aqueous solution of $Na_2S_2O_3$ (5 mL), extracted with EtOAc (3 × 10 mL), washed with brine, dried over Na_2SO_4 and solvent was evaporated under vacuo. Product was purified on silica by flash chromatography to afford the **7** (112 mg, 85%) as a colorless oil. The product was characterized by GC-MS and ^{1}H NMR analyses.

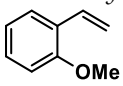
4.9. Mechanistic studies

General procedure for NMR studies:
To the screw cap NMR tube, dry [EMPyrr][OTf] (**IL10**) (26.3 mg, 0.1 mmol) and the HBpin (25.6mg, 0.2 mmol) (or in 2:1 ratio) were added under argon atmosphere. After that, the 0.6 mL of deuterated solvent ($CDCl_3$ or C_6D_6) was added under argon atmosphere. Then, NMR analyses were performed according to section **1.1**. and information provided in section **7**.

General procedure for reactions with TMEDA or DABCO:
A Schlenk's vessel was charged with dried [EMPyrr][OTf] (**IL10**) (0.4 equiv.), pinacolborane (1 mmol), styrene **1a** (1 mmol) and TMEDA (1.0 or 0.4, or 0.1 equiv.) or DABCO (1.0 or 0.4 equiv.) under argon atmosphere and stirred for 20 h at 100 °C. The reaction mixture was cooled down and the extractant soluble components were extracted with *n*-heptane. Extracts were combined and solvent was evaporated. Crude reaction mixture was analyzed by GC-MS and ^{1}H NMR analyses.

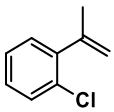
4. Product characterization.

1-Methoxy-2-vinylbenzene (**1l**)



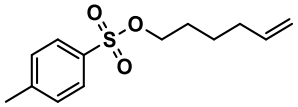
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.48 (1H, dd, $J_{H\text{-}H}$ = 7.6 Hz, 1.8Hz), 7.29–7.20 (2H, m), 7.07 (1H, dd, $J_{H\text{-}H}$ = 17.8 Hz, 11.2Hz), 6.95 (1H, t, $J_{H\text{-}H}$ = 7.5 Hz), 6.89 (1H, d, $J_{H\text{-}H}$ = 8.2 Hz), 5.75 (1H, dd, $J_{H\text{-}H}$ = 17.1, 1.6 Hz), 5.27 (1H, dd, $J_{H\text{-}H}$ = 11.1, 1.6 Hz), 3.86 (3H, s, ArOC$\underline{H}_3$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 156.89, 128.97, 126.94, 126.68, 120.76, 114.58, 111.01, 55.61. **MS** (EI, m/z): 134(M^+, 100), 121(15), 119(99), 103(10), 91(52), 65(13). Colorless oil. Isolated yield: (286mg, 60%). Analytical data are in agreement with the literature.[7]

1-Chloro-2-isopropenylbenzene (**1ac**)



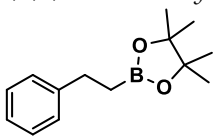
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.38–7.33 (1H, m), 7.23–7.15 (3H, m), 5.27–5.22 (1H, m), 5.00–4.95 (1H, m), 2.12 (3H, dd, $J_{H\text{-}H}$ = 1.6, 0.9 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 144.51, 142.92, 131.98, 129.95, 129.73, 128.32, 126.77, 116.31, 23.48. **MS** (EI, m/z): 152 (M^+, 100), 137(15), 117(67), 102(15), 75(10), 63(10), 51(10). Colorless oil. Isolated yield: (281mg, 52%). Analytical data are in agreement with the literature.[8]

Hex-5-en-1-yl 4-methylbenzenesulfonate (**1w**)



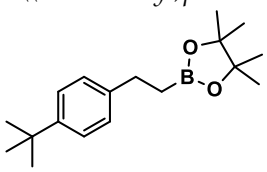
^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.76 (2H, d, $J_{H\text{-}H}$ = 8.4 Hz, Ar), 7.32 (2H, d, $J_{H\text{-}H}$ = 8.0 Hz, Ar), 5.68(1H, ddt, $J_{H\text{-}H}$ = 16.9, 10.2, 6.7 Hz), 4.98–4.86 (2H, m), 4.00 (2H, t, $J_{H\text{-}H}$ = 6.4 Hz), 2.41 (3H, s, ArC$\underline{H}_3$), 2.02–1.91 (2H, m), 1.68–1.56 (2H, m), 1.44–1.31 (2H, m). **MS** (EI, m/z): 254(M^+, 6), 172(100), 155(73), 127(65), 82(48), 54(11). Colorless oil. Isolated yield: (2.3 g, 96%). Analytical data are in agreement with the literature.[9]

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**2a**)



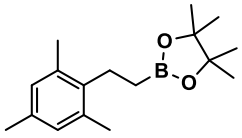
^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.29 – 7.20 (4H, m, Ar), 7.19 – 7.12 (1H, m, Ar), 2.75 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, Ar$C\underline{H}_2CH_2$Bpin) 1.22 (12H, s, C($C\underline{H}_3$)$_2$), 1.15 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, Ar$CH_2C\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 144.54, 128.30, 128.13, 125.62, 83.21 ($\underline{C}(CH_3)_2$), 30.08 (Ar$\underline{C}H_2CH_2$Bpin), 24.93 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 34.05. **MS** (EI, m/z): 232 (M^+, 8), 217(7), 175(30), 159(3), 146(6), 132(45), 131(30), 117(5), 105(33), 91(56), 84(100). White solid. Isolated yield: (222 mg, 96%). Analytical data are in agreement with the literature.[10]

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



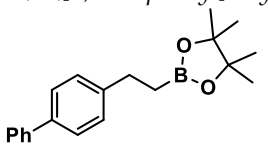
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.29 (2H, d, $J_{H\text{-}H}$ = 8.0 Hz, Ar), 7.16 (2H, d, $J_{H\text{-}H}$ = 8.0 Hz, Ar), 2.72 (1H, t, $J_{H\text{-}H}$ = 8.0 Hz, Ar$C\underline{H}_2CH_2$Bpin), 1.31 (9H, s, C($C\underline{H}_3$)$_3$), 1.23 (12H, s, C($C\underline{H}_3$)$_2$), 1.13 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, Ar$CH_2C\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 148.38, 141.50, 127.78, 125.19, 83.20 ($\underline{C}(CH_3)_2$), 34.45, 31.58, 29.51, 24.95 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 288 (M^+, 28), 273(100), 272(25), 231(19), 173(37), 160(56), 145(43), 131(34), 117(20), 85(27), 84(96), 57(37). Colorless oil. Isolated yield: (265 mg, 92%). Analytical data are in agreement with the literature.[11]

2-(2,4,6-Trimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**)



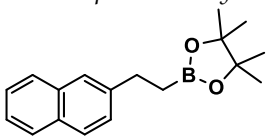
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.86 (2H, s, Ar), 2.78 – 2.66 (2H, m, Ar$C\underline{H}_2CH_2$Bpin), 2.34 (6H, s), 2.28 (3H, s), 1.31 (12H, s, C($C\underline{H}_3$)$_2$), 1.05 – 0.97 (2H, m, Ar$CH_2C\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 138.59, 135.71, 134.70, 128.92, 83.17 ($\underline{C}(CH_3)_2$), 24.96, 23.35, 20.89, 19.74. Cα to boron atom was not observed. **MS** (EI, m/z): 274(M^+, 28), 273(7), 174(45), 173(15), 159(29), 158(10), 146(17), 134(10), 133(100), 120(7), 105(9), 84(13). Colorless oil. Isolated yield: (255 mg, 93%). Analytical data are in agreement with the literature.[12]

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



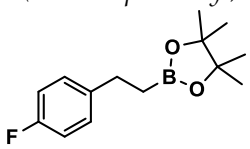
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.60 – 7.27 (9H, m, Ar), 2.80 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, Ar$C\underline{H}_2CH_2$Bpin), 1.23 (12H, s, C($C\underline{H}_3$)$_2$), 1.18 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, Ar$CH_2C\underline{H}_2$Bpin).**^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 143.74, 141.40, 138.62, 128.82, 128.58, 127.13, 127.09, 127.05, 83.29 ($\underline{C}(CH_3)_2$), 29.75, 24.97 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 308(M^+, 34), 307(9), 251(10), 207(15), 192(12), 180(100), 167(55), 84(75). White solid. Isolated yield: (290 mg, 94%). Analytical data are in agreement with the literature.[13]

2-(2-(Naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**)



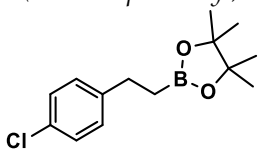
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.84 – 7.73 (3H, m), 7.66 (1H, s), 7.48 – 7.35 (3H, m), 2.94 (2H, t, $J_{H\text{-}H}$ = 8.1 Hz, $ArC\underline{H}_2CH_2Bpin$), 1.28 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, $ArCH_2C\underline{H}_2Bpin$), 1.23 (12H, s, $C(C\underline{H}_3)_2$). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 142.09, 133.77, 132.04, 127.80, 127.68, 127.55, 127.39, 125.83, 125.81, 125.03, 83.25 ($\underline{C}(CH_3)_2$), 30.25, 24.94 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 282(M^+, 45), 281(11), 225(14), 182(26), 181(22), 166(24), 165(9), 164(13), 155(30), 154(100), 153(9), 141(50), 115(15), 84(67). Colorless oil. Isolated yield: (265 mg, 94%). Analytical data are in agreement with the literature.[14]

2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**)



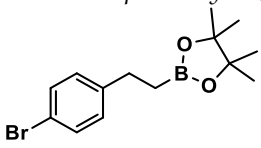
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.20 – 7.12 (2H, m), 6.97 – 6.89 (2H, m), 2.72 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, $ArC\underline{H}_2CH_2Bpin$), 1.21 (12H, s, $C(C\underline{H}_3)_2$), 1.12 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, $ArCH_2C\underline{H}_2Bpin$). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 161.23 (d, $J^1_{C\text{-}F}$ = 242.5 Hz), 140.06 (d, $J^4_{C\text{-}F}$ = 3.3 Hz), 129.42 (d, $J^3_{C\text{-}F}$ = 7.6 Hz), 114.90 (d, $J^2_{C\text{-}F}$ = 21.0 Hz). 83.11 ($\underline{C}(CH_3)_2$), 29.17, 24.78 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 250(M^+, 7), 235(6), 193(23), 150(29), 149(23), 109(45), 84(100), 69(12), 59(23). Colorless oil. Isolated yield: (232 mg, 93%). Analytical data are in agreement with the literature.[14]

2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2g**)



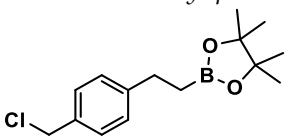
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.25 – 7.08 (4H, m), 2.71 (2H, t, $J_{H\text{-}H}$ = 8.1 Hz, $ArC\underline{H}_2CH_2Bpin$), 1.21 (12H, s, $C(C\underline{H}_3)_2$), 1.11 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, $ArCH_2C\underline{H}_2Bpin$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 142.99, 131.32, 129.54, 128.38, 83.33 ($\underline{C}(CH_3)_2$), 29.48, 24.96 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 266(M^+, 6), 251(3), 211(6), 210(4), 209(20), 167(10), 165(18), 165(9), 150(6), 139(10), 131(21), 127(7), 125(29), 85(14), 84(100), 59(22). Colorless oil. Isolated yield: (248 mg, 93%). Analytical data are in agreement with the literature.[11]

2-(4-Bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**)



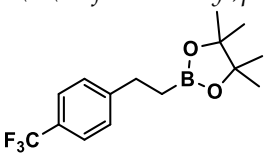
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.41 – 7.33 (2H, m), 7.12 – 7.04 (2H, m), 2.69 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz), 1.21 (12H, s, $C(C\underline{H}_3)_2$), 1.11 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 143.47, 131.30, 129.94, 119.30, 83.30 ($\underline{C}(CH_3)_2$), 29.52, 24.93 ($C(\underline{C}H_3)_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 312(M^++2, 4), 310(M^+, 4), 295(2), 255(12), 171(13), 131(21), 84(100), 69(10), 59(20). Colorless oil. Isolated yield: (283 mg, 91%). Analytical data are in agreement with the literature.[14]

2-(4-(Chloromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2i**)



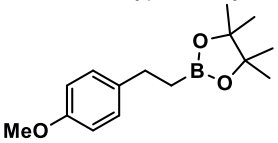
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.31 – 7.18 (4H, m, Ar), 4.56 (2H, s, ClC$\underline{H}_2$Ar), 2.75 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, ArC$\underline{H}_2$CH$_2$Bpin), 1.22 (12H, s, C(C$\underline{H}_3$)$_2$), 1.11 (2H, t, $J_{H\text{-}H}$ = 8.3 Hz, ArCH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 145.02, 134.83, 128.67, 128.53, 83.29 ($\underline{C}$(CH$_3$)$_2$), 46.47, 29.82, 24.95. Cα to boron atom was not observed. **MS** (EI, m/z): 280(M$^+$, 3), 223(21), 145(35), 131(16), 84(100), 69(8), 59(13). Colorless oil. Isolated yield: (258mg, 92%). Analytical data are in agreement with the literature.[15, 16]

2-(4-(Trifluoromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2j**)



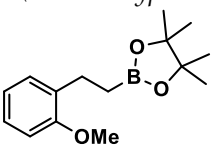
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.51 (2H, d, $J_{H\text{-}H}$ = 7.9 Hz, Ar), 7.32 (2H, d, $J_{H\text{-}H}$ = 8.0 Hz, Ar), 2.80 (2H, t, $J_{H\text{-}H}$ = 8.1 Hz, ArC$\underline{H}_2$CH$_2$Bpin), 1.22 (12H, s, C(C$\underline{H}_3$)$_2$), 1.15 (2H, t, $J_{H\text{-}H}$ = 8.2 Hz, ArCH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 148.51, 128.32, 128.06 (q, $J^2_{C\text{-}F}$ = 32.2 Hz), 125.25 (q, $J^4_{C\text{-}F}$ = 3.9 Hz), 124.59 (q, $J^1_{C\text{-}F}$ = 271.7 Hz), 83.26 ($\underline{C}$(CH$_3$)$_2$), 29.84, 24.80 (C($\underline{C}$H$_3$)$_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 300 (M$^+$, 3), 285(20), 243(52), 200(40), 181(42), 159(53), 84(79), 59(100). Colorless oil. Isolated yield: (279 mg, 93%). Analytical data are in agreement with the literature.[17]

2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k**)



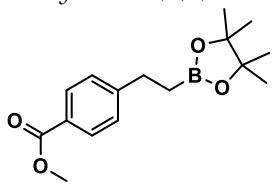
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.20 – 7.09 (2H, m, Ar), 6.85 – 6.76 (2H, m, Ar), 3.77 (3H, s, ArOC$\underline{H}_3$), 2.70 (2H, t, $J_{H\text{-}H}$ = 7.9 Hz, ArC$\underline{H}_2$CH$_2$Bpin), 1.23 (12H, s, C(C$\underline{H}_3$)$_2$), 1.12 (2H, t, $J_{H\text{-}H}$ = 8.2 Hz, ArCH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 157.67, 136.65, 128.94, 113.69, 83.12 ($\underline{C}$(CH$_3$)$_2$), 55.30, 29.14, 24.90 (C($\underline{C}$H$_3$)$_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 262(M$^+$, 26), 205(5), 161(16), 146(12), 134(90), 121(100), 84(47), 78(9), 69(7). Colorless oil. Isolated yield: (241 mg, 92%). Analytical data are in agreement with the literature.[12]

2-(2-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**)



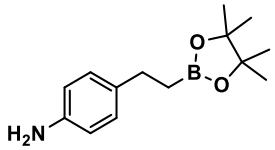
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.22 – 7.11 (2H, m, Ar), 6.91 – 6.79 (2H, m, Ar), 3.82 (3H, s, ArOC$\underline{H}_3$), 2.74 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, ArC$\underline{H}_2$CH$_2$Bpin), 1.24 (12H, s, C(C$\underline{H}_3$)$_2$), 1.13 (2H, t, $J_{H\text{-}H}$ = 8.2 Hz, ArCH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 157.52, 132.92, 129.24, 126.79, 120.36, 110.18, 83.08 $\underline{C}$(CH$_3$)$_2$), 55.29, 24.96, 24.50 (C($\underline{C}$H$_3$)$_2$. **MS** (EI, m/z): 262(M$^+$, 14), 204(5), 189(100), 163(5), 147(9), 121(8), 91(10), 77(5), 41(8). Colorless oil. Isolated yield: (220 mg, 84%). Analytical data are in agreement with the literature. [18]

Methyl 4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzoate (**2m**)



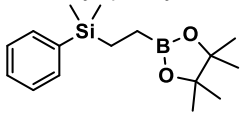
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.93 (2H, d, $J_{H\text{-}H}$ = 8.2 Hz, Ar), 7.28 (2H, d, $J_{H\text{-}H}$ = 8.2 Hz, Ar), 3.89 (3H, s, C(O)OC$\underline{H}_3$), 2.80 (2H, t, $J_{H\text{-}H}$ = 8.1 Hz, ArC$\underline{H}_2$CH$_2$Bpin), 1.21 (12H, s, C(C$\underline{H}_3$)$_2$), 1.15 (2H, t, $J_{H\text{-}H}$ = 8.2 Hz, ArCH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 167.40, 150.13, 129.74, 128.21, 127.68, 83.37 (C(CH$_3$)$_2$), 52.07, 30.17, 24.95 (C($\underline{C}$H$_3$)$_2$). Cα to boron atom was not observed. **MS** (EI, m/z): 290(M$^+$, 4), 275(5), 259(6), 233(43), 190(25), 159(50), 131(25), 84(100), 59(21). Colorless oil. Isolated yield: (258 mg, 89%). Analytical data are in agreement with the literature.[19]

4-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]aniline (**2n**)



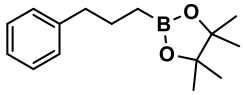
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.14 – 7.06 (2H, m, Ar), 6.97 – 6.88 (2H, m, Ar), 2.67 (2H, t, $J_{H\text{-}H}$ = 8.1 Hz, ArC$\underline{H}_2$CH$_2$Bpin), 1.21 (12H, s, C(C$\underline{H}_3$)$_2$), 1.08 (2H, t, $J_{H\text{-}H}$ = 8.3 Hz, ArCH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 142.94, 135.47, 128.84, 115.87, 83.05, 29.16, 24.91. Cα to boron atom was not observed. **MS** (EI, m/z): 247(M$^+$, 16), 146(6), 119(16), 106(100), 107(8), 84(5), 77(3). Pale-yellow oil. Isolated yield: (203 mg, 82%). Analytical data are in agreement with the literature.[19]

Dimethyl-phenyl-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]silane (**2o**)



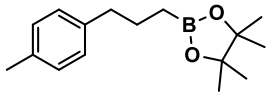
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.60 – 7.48 (2H, m, Ar), 7.41 – 7.30 (3H, m, Ar), 1.25 (12H, s, C(C$\underline{H}_3$)$_2$), 0.88 – 0.75 (4H, m), 0.28 (6H, s, Si(C$\underline{H}_3$)$_2$) **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 139.49, 133.79, 128.81, 127.74, 83.03 (C(CH$_3$)$_2$), 24.92 (C($\underline{C}$H$_3$)$_2$), 8.58, -3.39. Cα to boron atom was not observed. **MS** (EI, m/z): 290(M$^+$, 2). 275(72), 233(3), 213(33), 193(11), 175(5), 161(8), 147(8). 137(10), 135(100), 115(136), 84(18), 55(25). Colorless oil. Isolated yield: (264 mg, 91%). Analytical data are in agreement with the literature.[20]

4,4,5,5-Tetramethyl-2-[3-(2-methylphenyl)propyl]-1,3,2-dioxaborolane (**2p**)



^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.30 – 7.23 (2H, m, Ar), 7.23 – 7.12 (3H, m, Ar), 2.62 (2H, t, $J_{H\text{-}H}$ = 7.8 Hz, ArC$\underline{H}_2$CH$_2$CH$_2$Bpin), 1.75 (2H, p, $J_{H\text{-}H}$ = 7.8 Hz, ArCH$_2$C$\underline{H}_2$CH$_2$Bpin), 1.25 (12H, s, C(C$\underline{H}_3$)$_2$), 0.84 (2H, t, $J_{H\text{-}H}$ = 7.9 Hz, ArCH$_2$CH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 142.84, 128.69, 128.30, 125.69, 83.06 (C(CH$_3$)$_2$), 38.73, 26.24, 24.97. Cα to boron atom was not observed. **MS** (EI, m/z): 246(M$^+$, 13), 231(5), 189(12), 127(18), 118(91), 91(42), 85(100), 55(11). Colorless oil. Isolated yield: (233 mg, 95%). Analytical data are in agreement with the literature.[21]

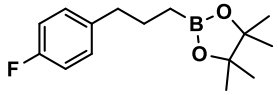
4,4,5,5-Tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane (**2q**)



^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.15 – 7.07 (4H, m, Ar), 2.60 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, ArC$\underline{H}_2$CH$_2$CH$_2$Bpin), 2.31 (3H, s, ArC$\underline{H}_3$), 1.69 (2H, p, $J_{H\text{-}H}$ = 7.8 Hz, ArCH$_2$C$\underline{H}_2$CH$_2$Bpin), 1.25 (12H, s, C(C$\underline{H}_3$)$_2$), 0.87 (2H, t, $J_{H\text{-}H}$ = 7.8 Hz, ArCH$_2$CH$_2$C$\underline{H}_2$Bpin). **^{13}C NMR** (151 MHz, $CDCl_3$, δ, ppm): 139.77,

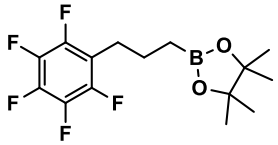
135.07, 128.99, 128.56, 83.05 (C(CH3)2), 38.23, 26.36, 24.97, 21.12. **MS** (EI, m/z): 260(M^+, 12), 245(5), 203(4), 187(8), 160(33), 145(12), 132(100), 129(56), 112(15), 105(63), 84(44), 57(34). Colorless oil. Isolated yield: (247 mg, 95%). Analytical data are in agreement with the literature.[22]

2-(3-(4-Fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2r**)



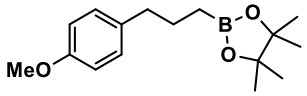
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.16 – 7.07 (2H, m, Ar), 6.98 – 6.89 (2H, m, Ar), 2.57 (2H, t, J_{H-H} = 7.7 Hz, ArC$\underline{H}_2$CH2CH2Bpin), 1.70 (2H, p, J_{H-H} = 7.7 Hz, ArCH2C$\underline{H}_2$CH2Bpin), 1.24 (12H, s, C(C$\underline{H}_3$)2), 0.80 (2H, t, J_{H-H} = 8.0 Hz, ArCH2CH2C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 161.29 (d, $^1J_{C-F}$ = 242.8 Hz), 138.36 (d, $^4J_{C-F}$ = 3.3 Hz), 129.93 (d, $^3J_{C-F}$ = 7.9 Hz), 114.95 (d, $^2J_{C-F}$ = 21.0 Hz), 83.08 (C(CH3)2), 37.82, 26.32, 24.94. Cα to boron atom was not observed. **MS** (EI, m/z): 264(M^+, 7), 249(4), 207(6), 136(64), 129(33), 109(46), 85(100), 55(26). Colorless oil. Isolated yield: (241 mg, 94%). Analytical data are in agreement with the literature.[23]

4,4,5,5-Tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane (**2s**)



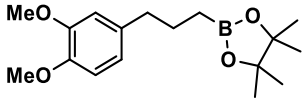
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.69 (2H, t, J_{H-H} = 7.8 Hz, ArC$\underline{H}_2$CH2CH2Bpin), 1.69 (2H, p, J_{H-H} = 7.7 Hz, ArCH2C$\underline{H}_2$CH2Bpin), 1.23 (12H, s, C(C$\underline{H}_3$)2), 0.80 (2H, t, J_{H-H} = 7.9 Hz, ArCH2CH2C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 145.05 (dm, J^1_{C-F} = 243.8 Hz), 139.18 (dm, J^1_{C-F} = 251.7 Hz), 137.44 (dm, J^1_{C-F} = 250.9 Hz), 115.54 (t, J^2_{C-F} = 19.1 Hz), 83.12 (C(CH3)2), 24.74, 24.52, 23.87. Cα to boron atom was not observed. **MS** (EI, m/z): 336(M^+, 5), 321(18), 279(7), 237(5), 208(5), 181(24), 169(11), 155(6), 151(13), 129(35), 127(15), 85(100), 59(41). Colorless oil. Isolated yield: (309 mg, 92%). Analytical data are in agreement with the literature.[24]

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



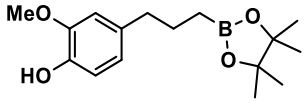
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.14 – 7.05 (2H, m, Ar), 6.85 – 6.78 (2H, m, Ar), 3.78 (3H, s, ArOCH3), 2.56 (2H, t, J_{H-H} = 8.0 Hz, ArC$\underline{H}_2$CH2CH2Bpin), 1.71 (2H, p, J_{H-H} = 7.8 Hz, ArCH2C$\underline{H}_2$CH2Bpin), 1.25 (12H, s, C(C$\underline{H}_3$)2), 0.82 (2H, t, J_{H-H} = 7.9 Hz, ArCH2CH2C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 157.74, 134.91, 129.49, 113.71, 82.98 (C(CH3)2), 55.30, 37.74, 26.40, 24.92. Cα to boron atom was not observed. **MS** (EI, m/z): 276(M^+, 27), 260(3), 192(21), 160(14), 148(50), 121(100), 85(27). Colorless oil. Isolated yield: (251 mg, 91%). Analytical data are in agreement with the literature.[25]

2-(3-(3,4-Dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**)



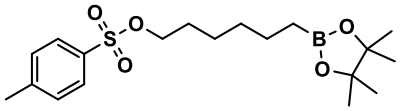
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.81 – 6.66 (3H, m, Ar), 3.86 (3H, s, ArOC$\underline{H}_3$), 3.84 (3H, s, ArOC$\underline{H}_3$), 2.55 (2H, t, J_{H-H} = 8.0 Hz, ArC$\underline{H}_2$CH2CH2Bpin), 1.70 (2H, p, J_{H-H} = 7.7 Hz, ArCH2C$\underline{H}_2$CH2Bpin), 1.23 (12H, s, C(C$\underline{H}_3$)2), 0.81 (2H, t, J_{H-H} = 7.9 Hz, ArCH2CH2C$\underline{H}_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 148.82, 147.15, 135.53, 120.44, 112.07, 111.30, 83.03 (C(CH3)2), 56.04, 55.88, 38.30, 26.37, 24.94. Cα to boron atom was not observed. **MS** (EI, m/z): 306(M^+, 45), 222(8), 206(9), 189(9), 178(25), 151(100), 107(7), 85(11), 55(5). Colorless oil. Isolated yield: (276 mg, 90%). Analytical data are in agreement with the literature.[26]

2-Methoxy-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol (**2v**)



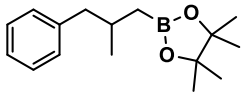
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.95 – 6.58 (3H, m, Ar), 3.87 (3H, s, $ArOC\underline{H}_3$), 2.53 (2H, t, $J_{H\text{-}H}$ = 8.0 Hz, $ArC\underline{H}_2CH_2CH_2Bpin$), 1.69 (2H, p, $J_{H\text{-}H}$ = 7.8 Hz, $ArCH_2C\underline{H}_2CH_2Bpin$), 1.24 (12H, s, $C(C\underline{H}_3)_2$), 0.81 (2H, t, $J_{H\text{-}H}$ = 8.1Hz, $ArCH_2CH_2C\underline{H}_2Bpin$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 146.37, 143.67, 134.85, 121.24, 114.17, 111.29, 83.09 ($\underline{C}(CH_3)_2$), 55.98, 38.45, 26.52, 24.99. Cα to boron atom was not observed. **^{11}B NMR** (128 MHz, $CDCl_3$, δ, ppm): 34.27. **MS** (EI, m/z): 292 (M^+, 38), 277(3), 208(16), 192(15), 176(24), 164(44), 149(4), 138(11), 137(100), 85(21), 55(9). **MALDI TOF MS** (m/z): 292.2401 (M^+). **FT-IR** (neat, cm^{-1}): 3379, 2980, 2944, 1605, 1518, 1453, 1431, 1417, 1371, 1344, 1316, 1302, 1266, 1233, 1201, 1170, 1139, 1032, 969, 850, 826, 641, 560. **Elemental Anal.** For $C_{16}H_{25}BO_4$ (%): calcd.: C, 65.77; H, 8.62; found: 65.71; H, 8.54. Colorless solid. Isolated yield: (236 mg, 81%).

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl-4-methylbenzenesulfonate (**2w**)



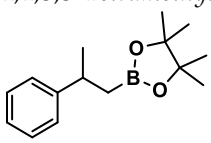
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.77 (2H, d, $J_{H\text{-}H}$ = 8.3 Hz, Ar), 7.32 (2H, d, $J_{H\text{-}H}$ = 7.9 Hz, Ar), 4.06 – 3.94 (2H, m), 2.43 (3H, s, $ArC\underline{H}_3$), 1.65 – 1.55 (2H, m), 1.39 – 1.22 (6H, m), 1.22 (12H, s, $C(C\underline{H}_3)_2$), 0.70 (2H, t, $J_{H\text{-}H}$ = 7.6 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 144.71, 133.47, 129.92, 128.02, 83.04, 70.83, 31.75, 28.86, 25.22, 24.95, 23.86, 21.76. Cα to boron atom was not observed. **MS** (EI, m/z): 382(M^+, 2), 323(3), 309(2), 283(3), 266(8), 245(17), 241(19), 199(100), 169(33), 155(81), 91(77), 83(55), 69(44), 55(33). Colorless oil. Isolated yield: (344 mg, 90%). Analytical data are in agreement with the literature.[27]

4,4,5,5-Tetramethyl-2-(2-methyl-3-phenylpropyl)-1,3,2-dioxaborolane (**2x**)



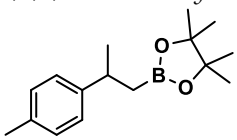
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.31 – 7.23 (2H, m, Ar), 7.22 – 7.11 (3H, m, Ar), 2.62 (1H, dd, $J_{H\text{-}H}$ = 13.2, 6.4 Hz, $ArC\underline{H}_2CH(CH_3)CH_2Bpin$), 2.44 (1H, dd, $J_{H\text{-}H}$ = 13.2, 7.8 Hz, $ArC\underline{H}_2CH(CH_3)CH_2Bpin$), 2.09 – 1.93 (1H, m, $ArCH_2C\underline{H}(CH_3)CH_2Bpin$), 1.25 (12H, s, $C(C\underline{H}_3)_2$), 0.92 (3H, d, $J_{H\text{-}H}$ = 6.6 Hz, $ArCH_2CH(C\underline{H}_3)CH_2Bpin$), 0.90 – 0.84 (1H, m, $ArCH_2CH(CH_3)C\underline{H}_2Bpin$), 0.70 (1H, dd, $J_{H\text{-}H}$ = 15.6, 8.6 Hz, $ArCH_2CH(CH_3)C\underline{H}_2Bpin$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 141.80, 129.44, 128.15, 125.71, 83.03, 46.17, 31.85, 25.05, 24.94, 22.14. Cα to boron atom was not observed. **MS** (EI, m/z): 260(M^+, 100), 203(11), 176(12), 160(12), 132(40), 125(20), 101(33), 91(47), 83(49), 69(51), 57(100). Colorless oil. Isolated yield: (244 mg, 94%). Analytical data are in agreement with the literature.[28]

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



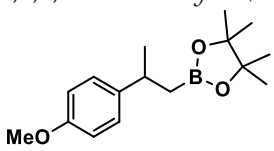
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.32 – 7.22 (4H, m, Ar), 7.20 – 7.13 (1H, m, Ar), 3.13 – 2.98 (1H, m, $ArC\underline{H}(CH_3)CH_2Bpin$), 1.30 (3H, d, $J_{H\text{-}H}$ = 6.9 Hz, $ArCH(C\underline{H}_3)CH_2Bpin$), 1.22 – 1.13 (14H, m). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 149.38, 128.30, 126.77, 125.80, 83.12 ($\underline{C}(CH_3)_2$), 35.95, 25.03, 24.91, 24.83. Cα to boron atom was not observed. **MS** (EI, m/z): 246(M^+, 4), 231(7), 202(5), 146(16), 145(11), 131(17), 130 (8), 128(14), 118(5), 105(62), 104(7), 101(9), 84 (100). Colorless oil. Isolated yield: (239 mg, 92%). Analytical data are in agreement with the literature.[29]

4,4,5,5-Tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane (**2z**)



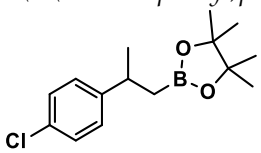
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.18 (2H, d, $J_{H\text{-}H}$ = 8.3 Hz, Ar), 7.11 (2H, d, $J_{H\text{-}H}$ = 7.9 Hz, Ar), 3.14 – 2.98 (1H, m, ArC<u>H</u>(CH_3)CH_2Bpin), 2.34 (3H, s, ArC<u>H</u>$_3$), 1.31 (3H, d, $J_{H\text{-}H}$ = 6.9 Hz, ArCH(C<u>H</u>$_3$)CH_2Bpin), 1.28 – 1.12 (14H, m). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 146.35, 134.99, 128.89, 126.52, 82.97 (<u>C</u>(CH_3)$_2$), 35.40, 24.97, 24.85, 24.76, 21.01. Cα to boron atom was not observed. **MS** (EI, m/z): 260(M^+, 11), 245(13), 216(6), 159(11), 145(17), 132(54), 119(100), 91(19), 84(75), 55(7). Colorless oil. Isolated yield: (252 mg, 92%). Analytical data are in agreement with the literature.[30]

4,4,5,5-Tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane (**2aa**)



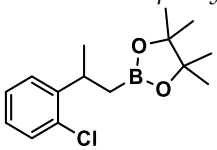
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.16 (2H, d, $J_{H\text{-}H}$ = 8.3 Hz, Ar), 6.81 (2H, d, $J_{H\text{-}H}$ = 8.9 Hz, Ar), 3.77 (3H, s, ArOC<u>H</u>$_3$), 3.08 – 2.93 (1H, m, ArC<u>H</u>(CH_3)CH_2Bpin), 1.26 (3H, d, $J_{H\text{-}H}$ = 6.9 Hz, ArCH(C<u>H</u>$_3$)CH_2Bpin), 1.17 (14H, m). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 157.71, 141.56, 127.55, 113.64, 83.04 (<u>C</u>(CH_3)$_2$), 55.31, 35.07, 25.23, 24.87, 24.80. Cα to boron atom was not observed. **MS** (EI, m/z): 276(M^+, 27), 261(26), 275(11), 148(10), 136(12), 135(100), 134(11), 105(6), 41(6). Colorless oil. Isolated yield: (229 mg, 83%). Analytical data are in agreement with the literature.[31]

2-(2-(4-Chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ab**)



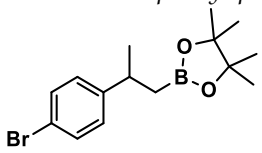
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.26 – 7.10 (4H, m, Ar), 3.10 – 2.92 (1H, m, ArC<u>H</u>(CH_3)CH_2Bpin), 1.24 (3H, d, $J_{H\text{-}H}$ = 7.0 Hz, ArCH(C<u>H</u>$_3$)CH_2Bpin), 1.16 (12H, s, C(C<u>H</u>$_3$)$_2$), 1.12 (2H, d, $J_{H\text{-}H}$ = 7.9 Hz, ArCH(CH_3)C<u>H</u>$_2$Bpin). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 147.82, 131.33, 128.35, 128.17, 83.20 (<u>C</u>(CH_3)$_2$), 35.40, 24.97, 24.88, 24.84. **MS** (EI, m/z): 280(M^+, 4), 265(5), 179(4), 145(11), 141(13), 139(38), 128(14), 103(12), 84(100), 59(8). Colorless oil. Isolated yield: (271 mg, 92%). Analytical data are in agreement with the literature.[30]

2-(2-(2-Chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ac**)



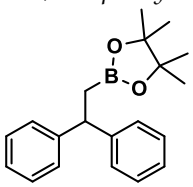
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.30 – 7.25 (2H, m, Ar), 7.20 – 7.14 (1H, m, Ar), 7.09 – 7.01 (1H, m, Ar), 3.61 – 3.46 (1H, m, ArC<u>H</u>(CH_3)CH_2Bpin), 1.23 (3H, d, $J_{H\text{-}H}$ = 6.8 Hz, ArCH(C<u>H</u>$_3$)CH_2Bpin), 1.17 – 1.10 (14H, m). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 146.28, 133.46, 129.44, 127.20, 83.15 (<u>C</u>(CH_3)$_2$), 31.76, 24.84, 24.78, 23.57. **MS** (EI, m/z): 280(M^+, 3), 265(69), 245(100), 187(40), 179(37), 145(30), 139(55), 103(36), 84(59), 41(33). Colorless oil. Isolated yield: (210 mg, 75%). Analytical data are in agreement with the literature.[32]

2-(2-(4-Bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ad**)



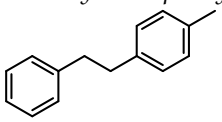
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.37 (2H, d, $J_{H\text{-}H}$ = 8.5 Hz, Ar), 7.11 (2H, d, $J_{H\text{-}H}$ = 8.4 Hz, Ar), 3.07 – 2.90 (1H, m, ArC<u>H</u>(CH_3)CH_2Bpin), 1.24 (3H, d, $J_{H\text{-}H}$ = 6.9 Hz, ArCH(C<u>H</u>$_3$)CH_2Bpin), 1.16 (12H, s, C(C<u>H</u>$_3$)$_2$), 1.11 (2H, d, $J_{H\text{-}H}$ = 8.0 Hz, ArCH(CH_3)C<u>H</u>$_2$Bpin). **^{13}C NMR** (101 MHz, $CDCl_3$, δ, ppm): 148.36, 131.32, 128.61, 119.36, 83.23 (<u>C</u>(CH_3)$_2$), 35.47, 24.92, 24.90, 24.85. **MS** (EI, m/z): 325(M^+, 5), 311(6), 309(7), 243(5), 185(25), 145(14), 104(12), 84(100), 69(15), 41(10). Colorless oil. Isolated yield: (269 mg, 83%). Analytical data are in agreement with the literature.[32]

2-(2,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2ae**)



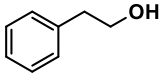
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.29 – 7.22 (8H, m, Ar), 7.17 – 7.11 (2H, m, Ar), 4.29 (1H, t, $J_{H\text{-}H}$ = 8.5 Hz, ArC<u>H</u>CH_2Bpin), 1.61 (1H, d, $J_{H\text{-}H}$ = 8.4 Hz, ArCHC<u>H</u>$_2$Bpin), 1.06 (12H, s, C(C<u>H</u>$_3$)$_2$). **^{13}C NMR** (75 MHz, $CDCl_3$, δ, ppm): 146.74, 128.36, 127.82, 126.02, 83.25 (<u>C</u>(CH_3)$_2$), 46.68, 24.71 Cα to boron atom was not observed.. **MS** (EI, m/z): 308(M^+, 6), 293(3), 264(7), 208(8), 180(37), 167(100), 152(12), 84(61), 69(6). Colorless oil. Isolated yield: (290 mg, 90%). Analytical data are in agreement with the literature.[33]

1-Methyl-4-(2-phenylethyl)benzene (**4**)



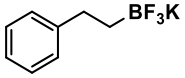
^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.33 – 7.25 (2H, m, Ar), 7.24 – 7.17 (3H, m, Ar), 7.10 (4H, s, Ar), 2.90 (4H, s, ArC<u>H</u>$_2$C<u>H</u>$_2$Ar), 2.33 (3H, s, ArC<u>H</u>$_3$). **MS** (EI, m/z): 196(M^+, 19), 105(100), 91(19), 77(14), 65(10). Colorless oil. Isolated yield: (150 mg, 76%). Analytical data are in agreement with the literature.[34]

2-Phenylethanol (**5**)



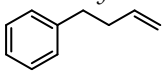
^{1}H NMR (300 MHz, DMSO, δ, ppm): 7.41 – 7.30 (2H, m, Ar), 7.30 – 7.22 (3H, m, Ar), 3.87 (2H, t, $J_{H\text{-}H}$ = 6.6 Hz, ArCH_2C<u>H</u>$_2$OH), 2.89 (2H, t, $J_{H\text{-}H}$ = 6.6 Hz, ArC<u>H</u>$_2$$CH_2$OH), 1.66 (1H, s, CH_2O<u>H</u>). **MS** (EI, m/z): 122(M^+, 22), 102(9), 92(23), 91(100), 65(8), 51(9). Colorless liquid. Isolated yield: (115 mg, 94%). Analytical data are in agreement with the literature.[35]

Potassium phenethyltrifluoroborate (**6**)



^{1}H NMR (300 MHz, DMSO, δ, ppm): 7.23 – 7.09 (4H, m, Ar), 7.09 – 7.00 (1H, m, Ar), 2.48 – 2.37 (2H, m), 0.40 – 0.23 (2H, m). **^{13}C NMR** (75 MHz, DMSO, δ, ppm): 148.09, 127.97, 127.78, 124.50, 32.14. White solid. Isolated yield: (205 mg, 97%). Analytical data are in agreement with the literature.[36]

But-3-enylbenzene (**7**)



^{1}H NMR (300 MHz, DMSO, δ, ppm): 7.39 – 7.30 (2H, m, Ar), 7.30 – 7.20 (3H, m, Ar), 5.92 (1H, ddt, $J_{H\text{-}H}$ = 16.9, 10.2, 6.6 Hz), 5.15 – 5.01 (2H, m), 2.84 – 2.69 (2H, m), 2.53 – 2.35 (2H, m). **MS** (EI, m/z): 132(M^+, 18), 104(14), 91(100), 65(12). Colorless oil. Isolated yield: (112 mg, 85%). Analytical data are in agreement with the literature.[37]

5. NMR spectra

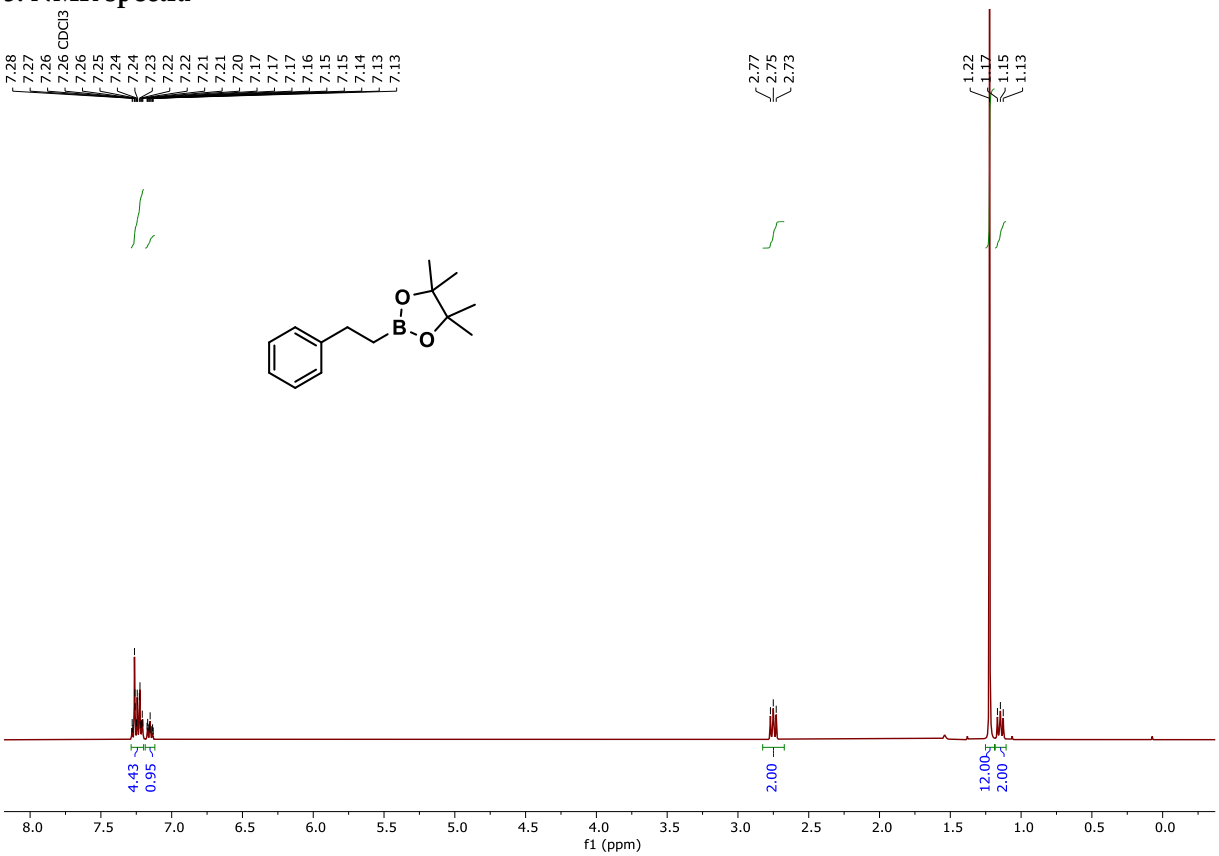


Figure S1. ^{1}H NMR spectrum of *4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane* (**2a**).

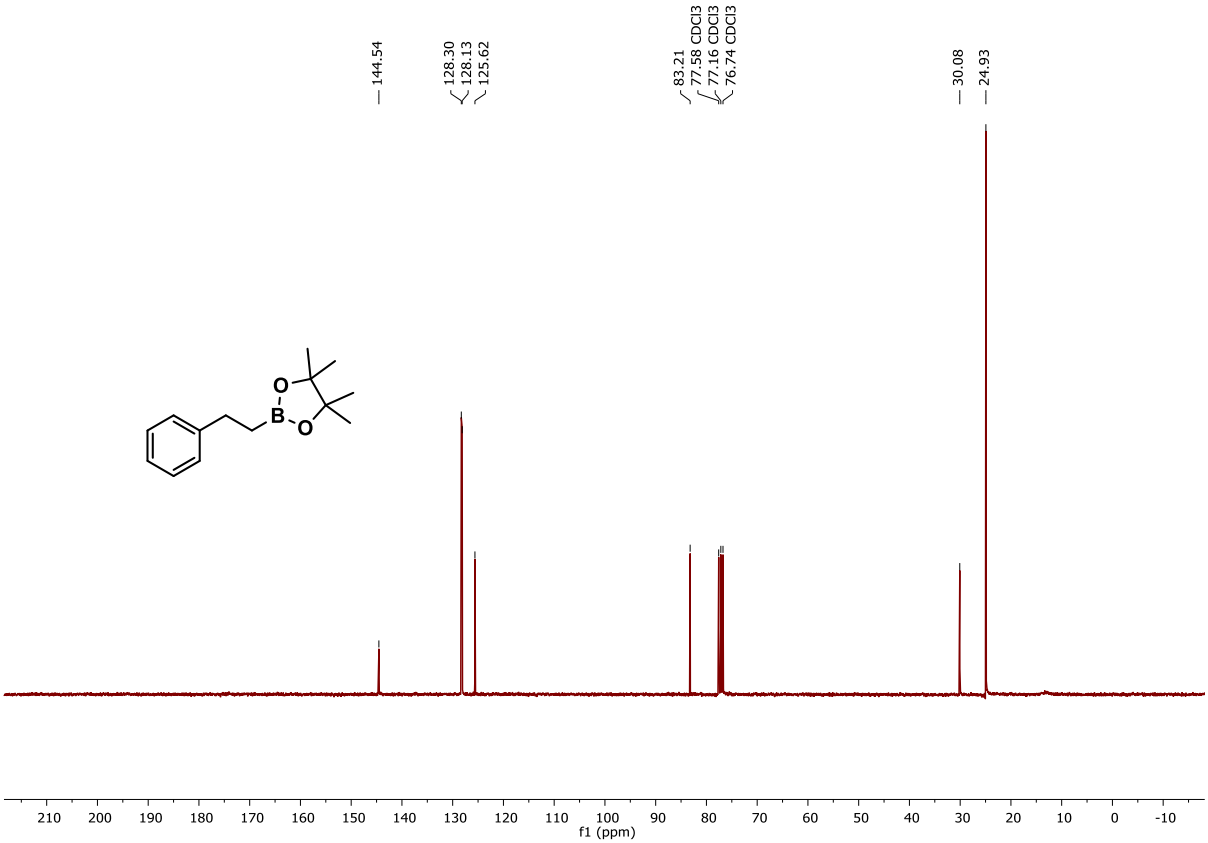


Figure S2. ^{13}C NMR spectrum of *4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane* (**2a**).

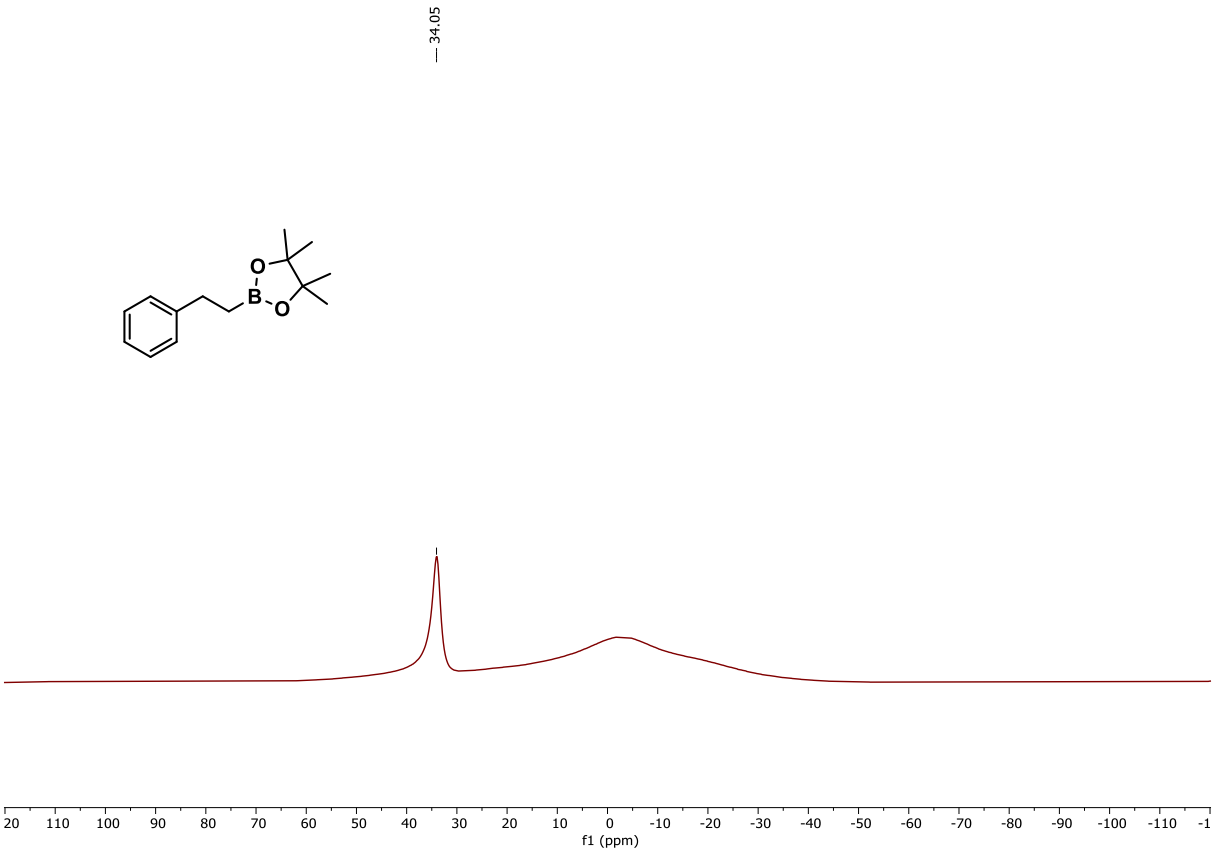


Figure S3. ^{11}B NMR spectrum of *4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane* (**2a**).

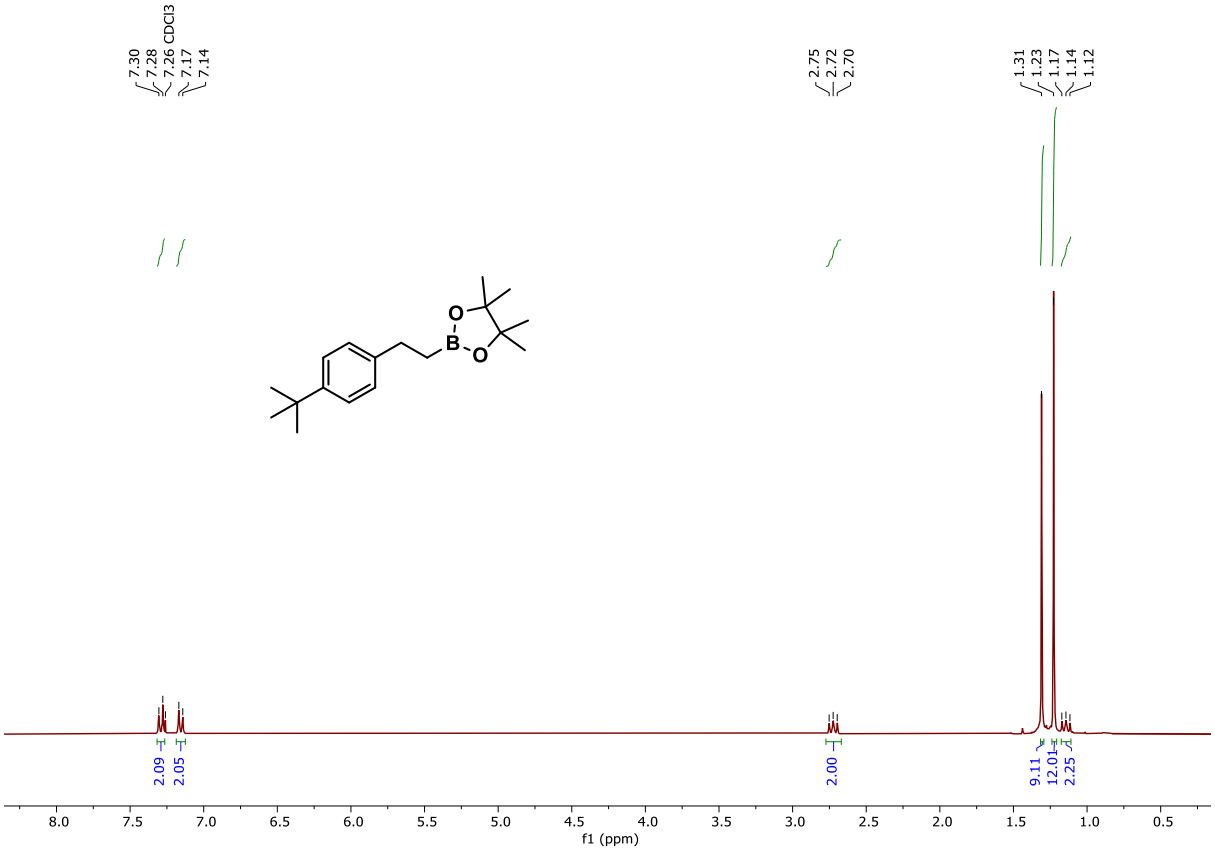


Figure S4. ^{1}H NMR spectrum of *2-((4-tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2b**).

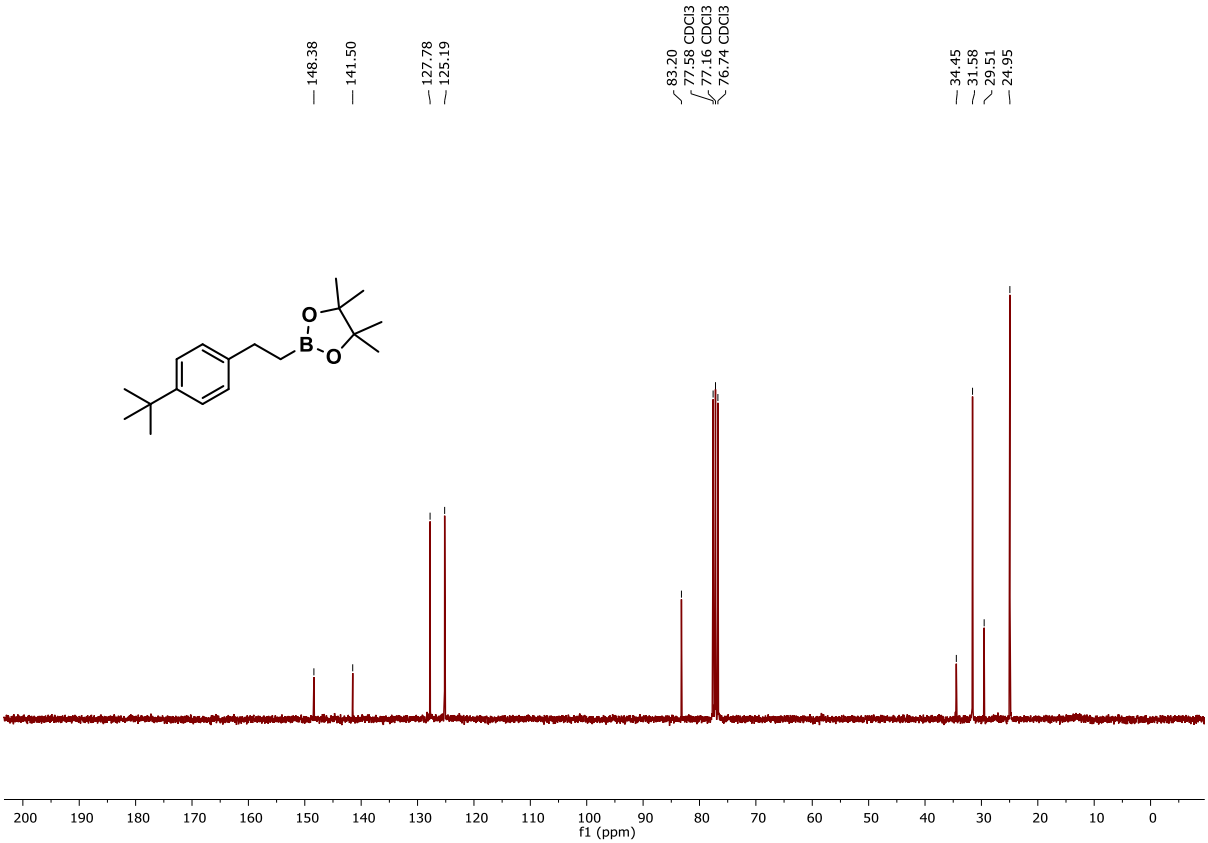


Figure S5. ^{13}C NMR spectrum of *2-((4-tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2b**).

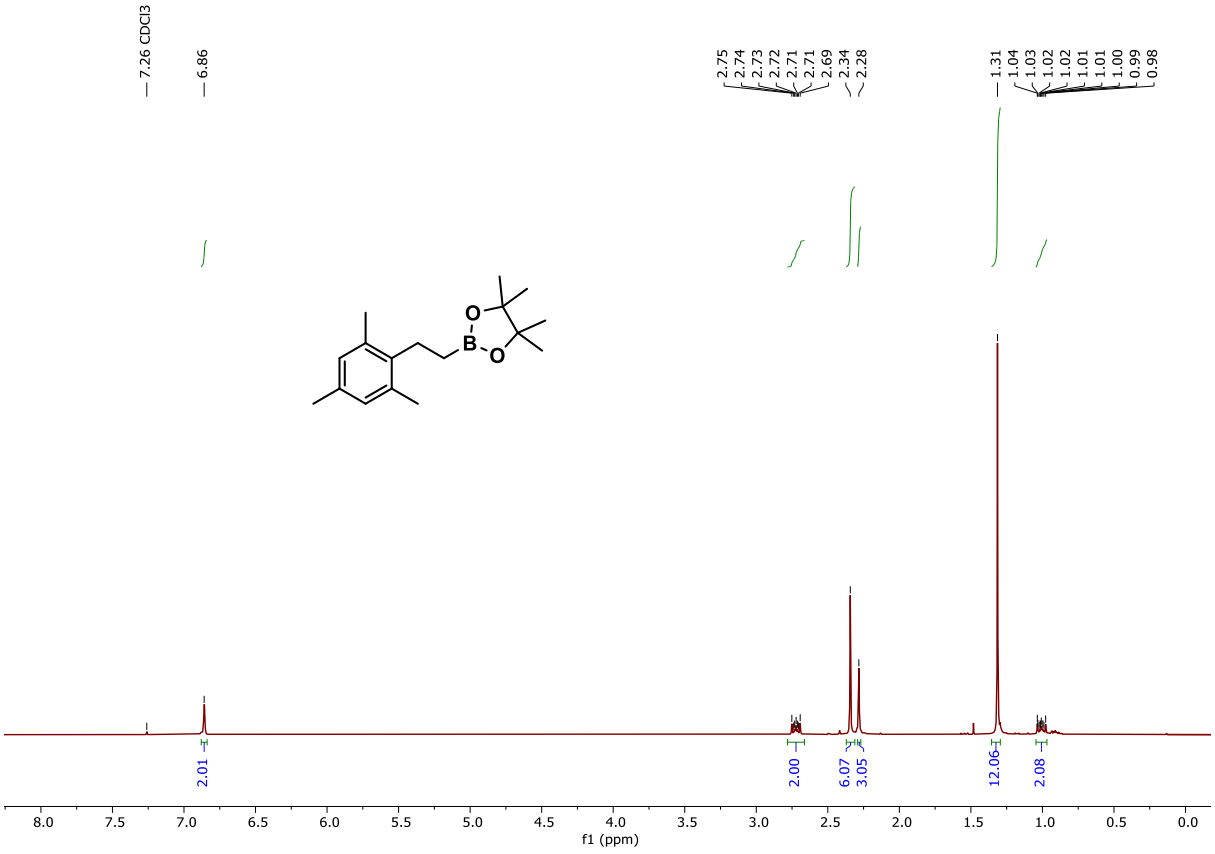


Figure S6. ^{1}H NMR spectrum of *2-(2,4,6-trimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2c**).

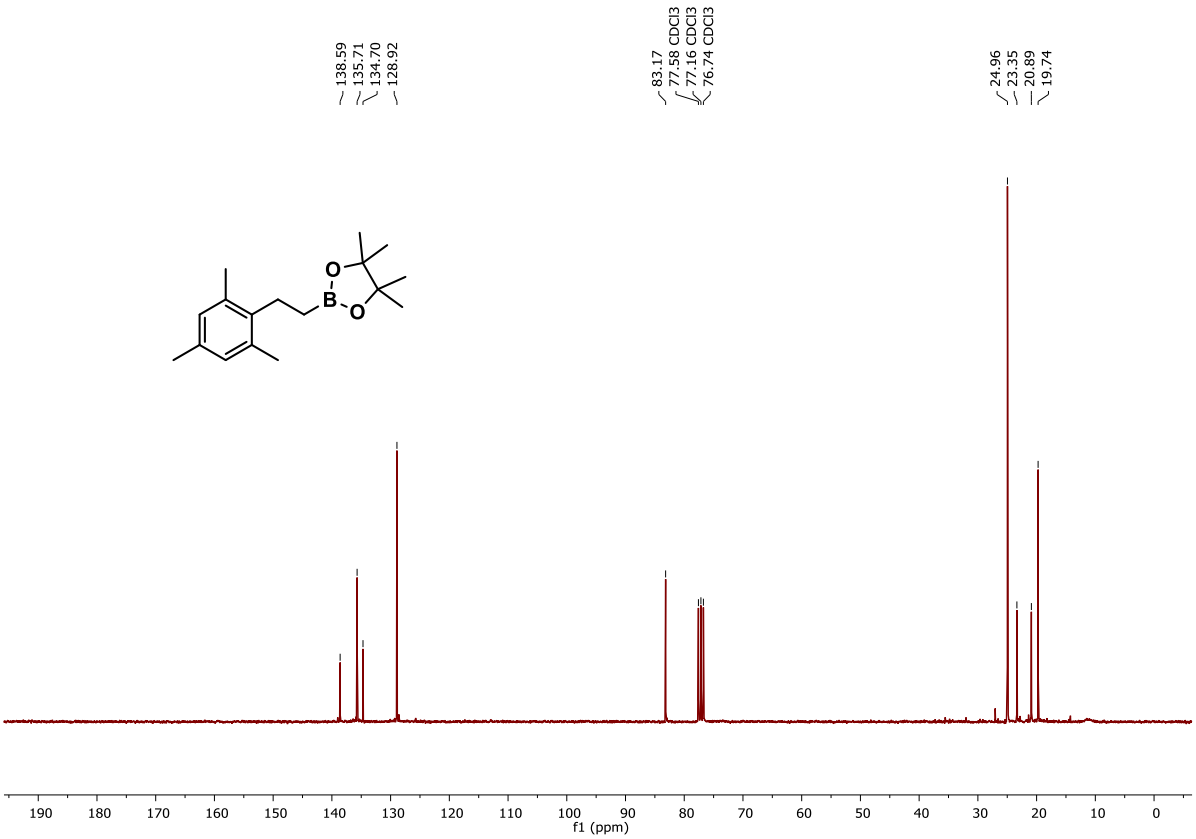


Figure S7. ^{13}C NMR spectrum of *2-(2,4,6-trimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2c**).

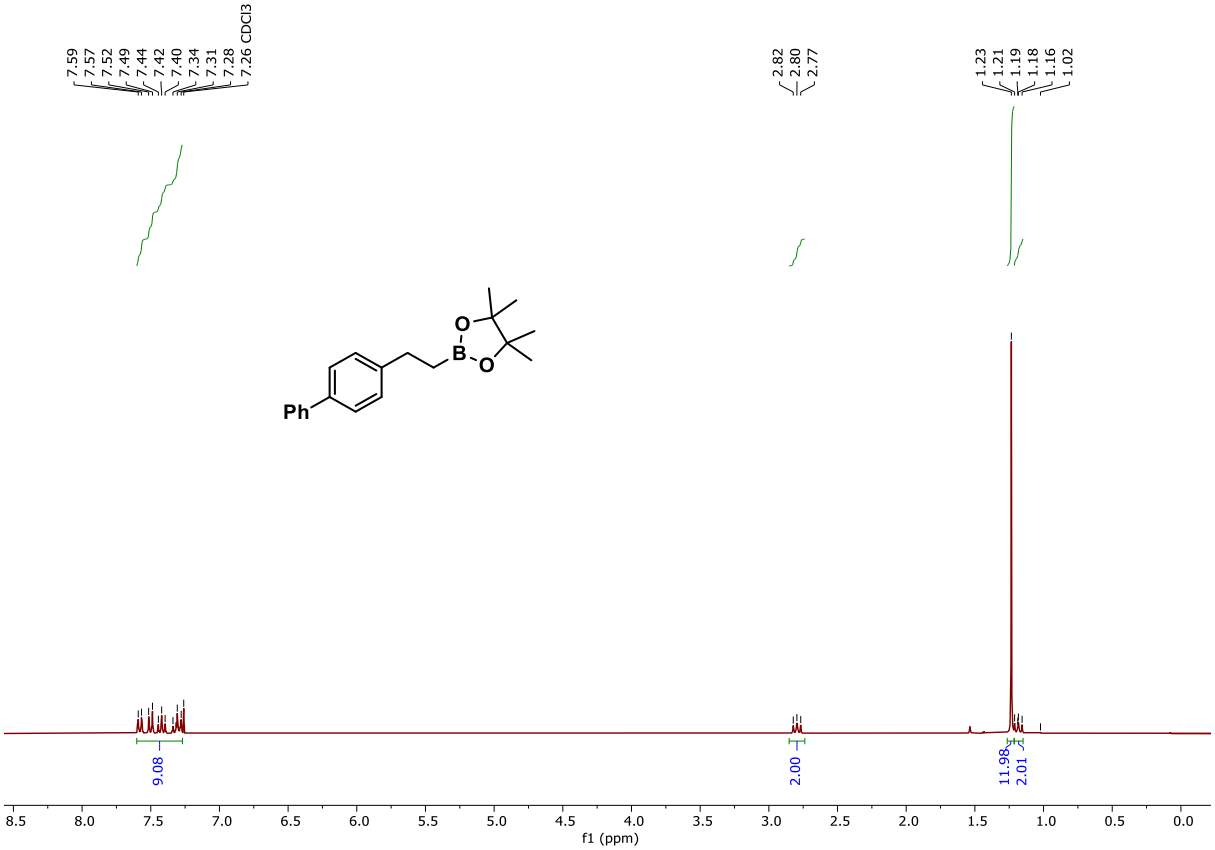


Figure S8. ^{1}H NMR spectrum of *2-(2-([1,1'-biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2d**).

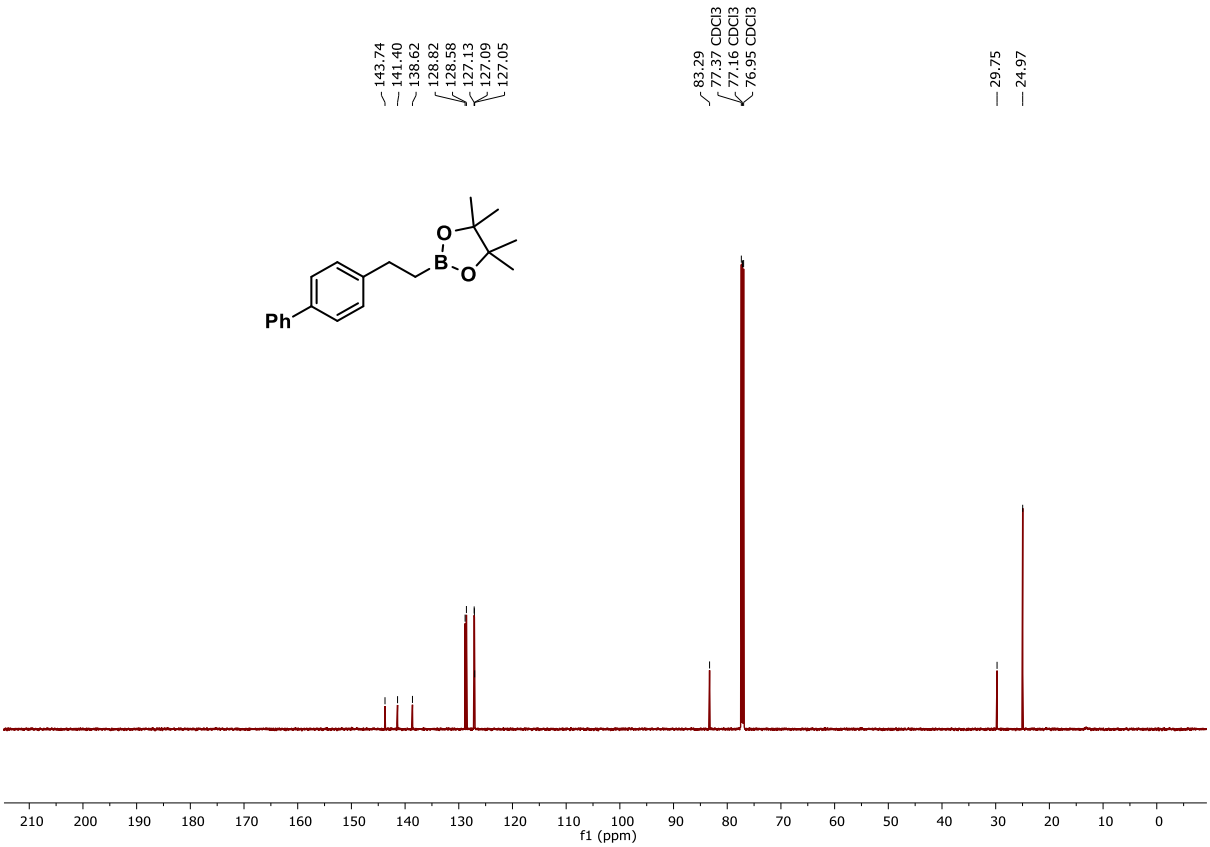


Figure S9. ^{13}C NMR spectrum of *2-(2-([1,1'-biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2d**).

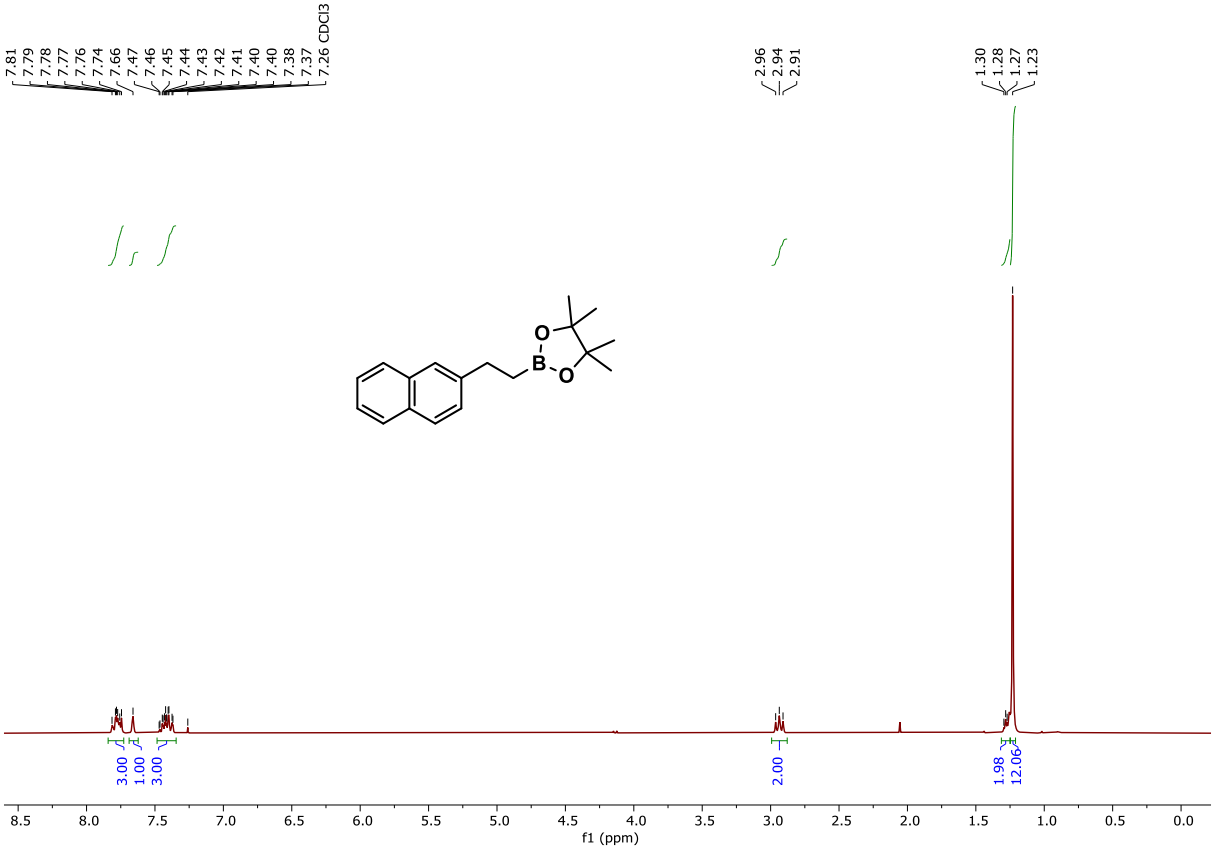


Figure S10. ^{1}H NMR spectrum of *2-(2-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2e**).

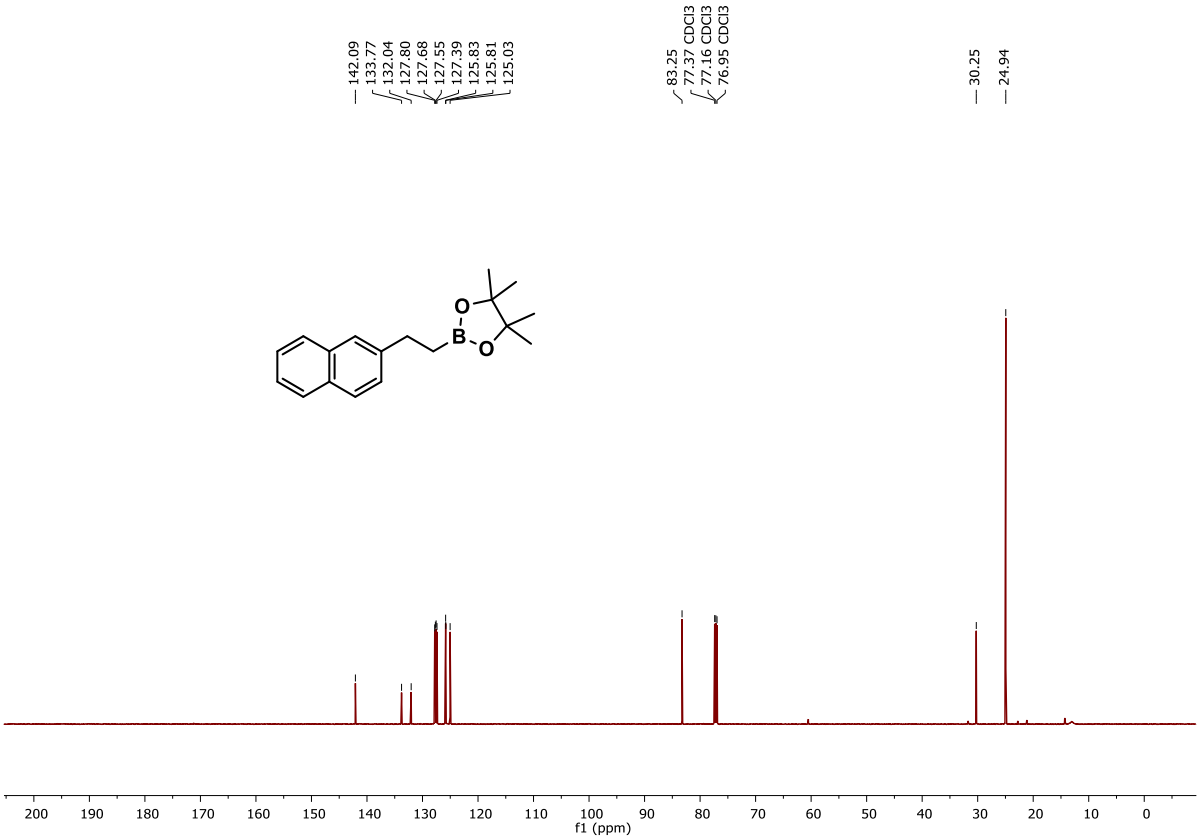


Figure S11. [13]C NMR spectrum of *2-(2-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2e**).

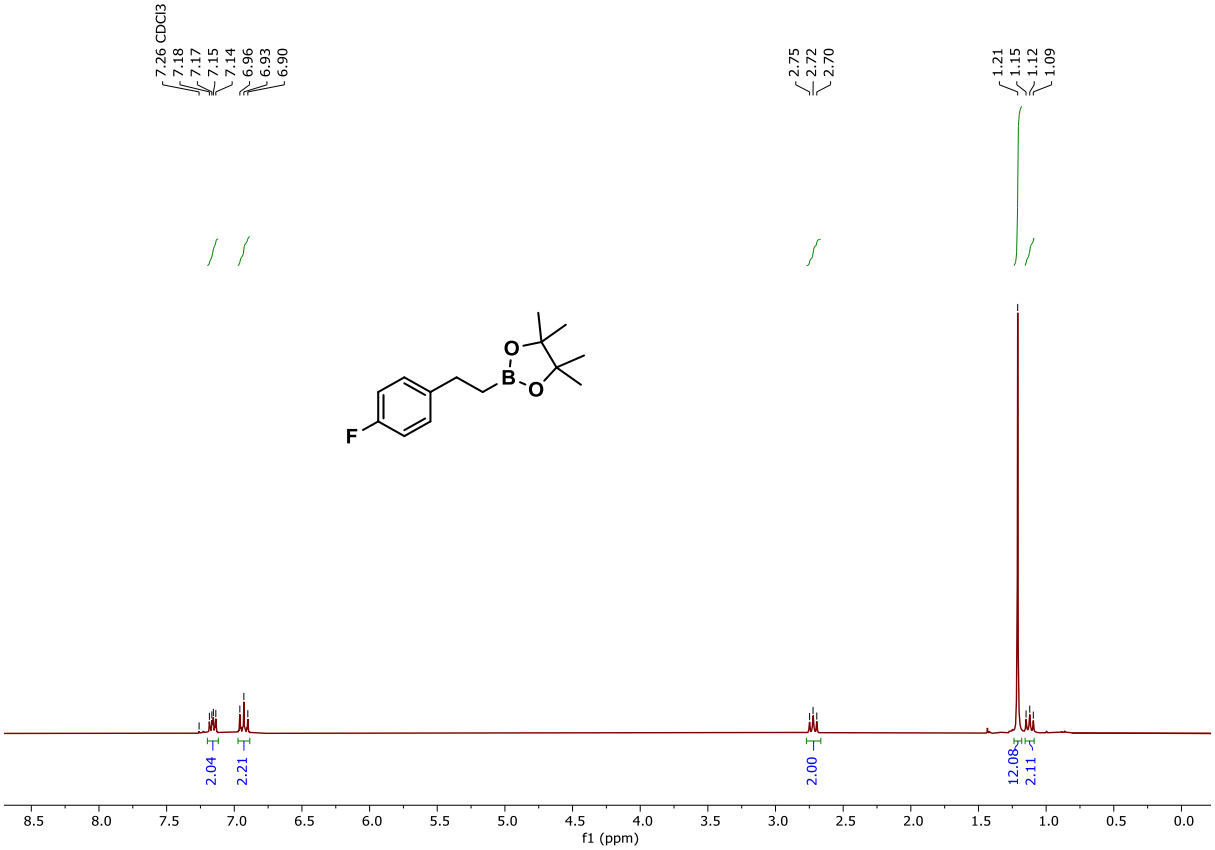


Figure S12. [1]H NMR spectrum of *2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2f**).

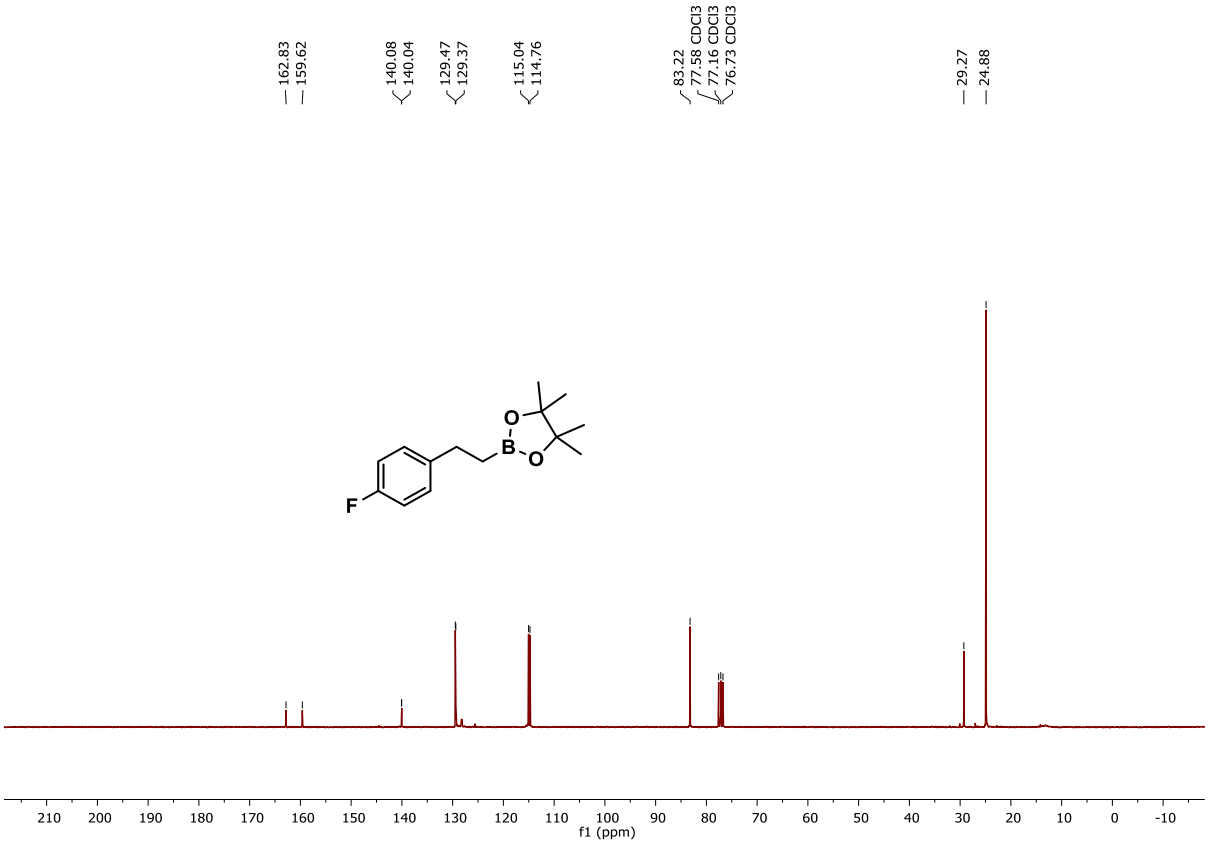


Figure S13. [13]C NMR spectrum of *2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2f**).

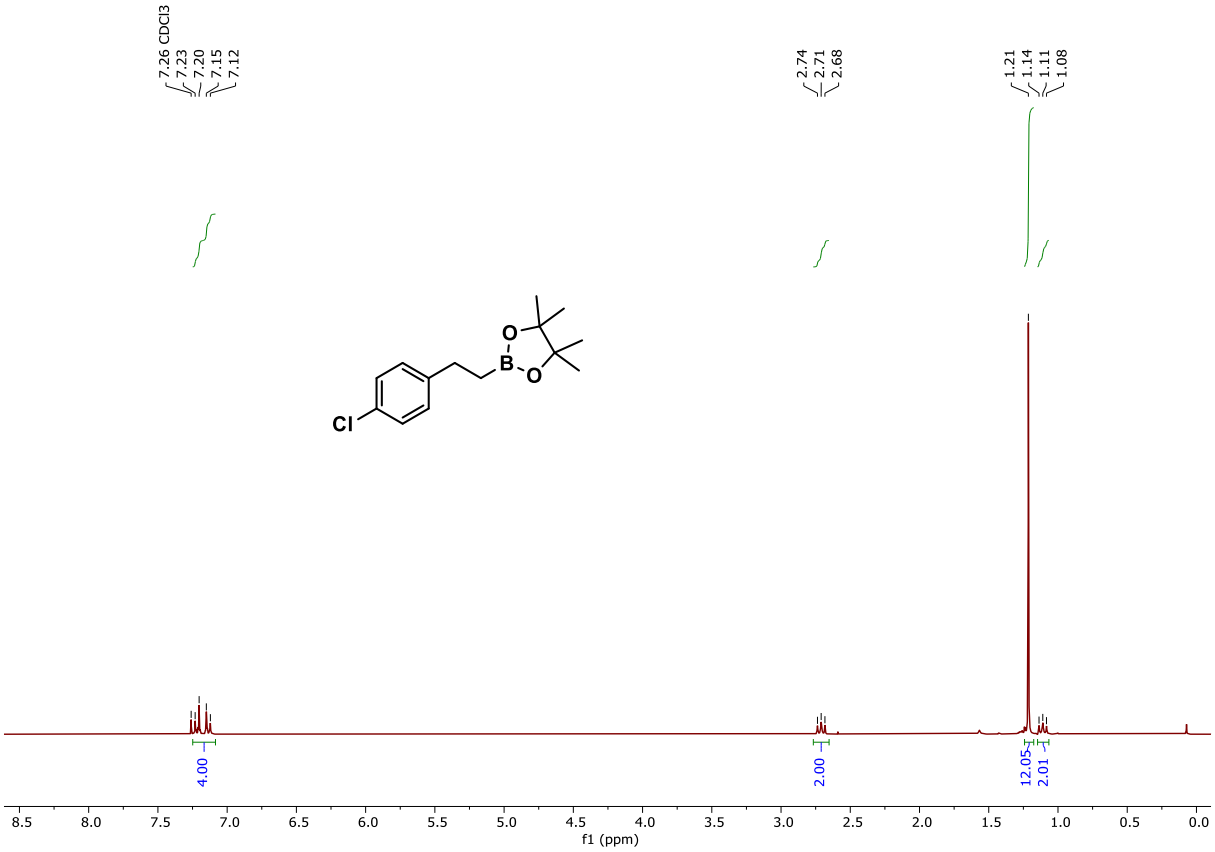


Figure S14. [1]H NMR spectrum of *2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2g**).

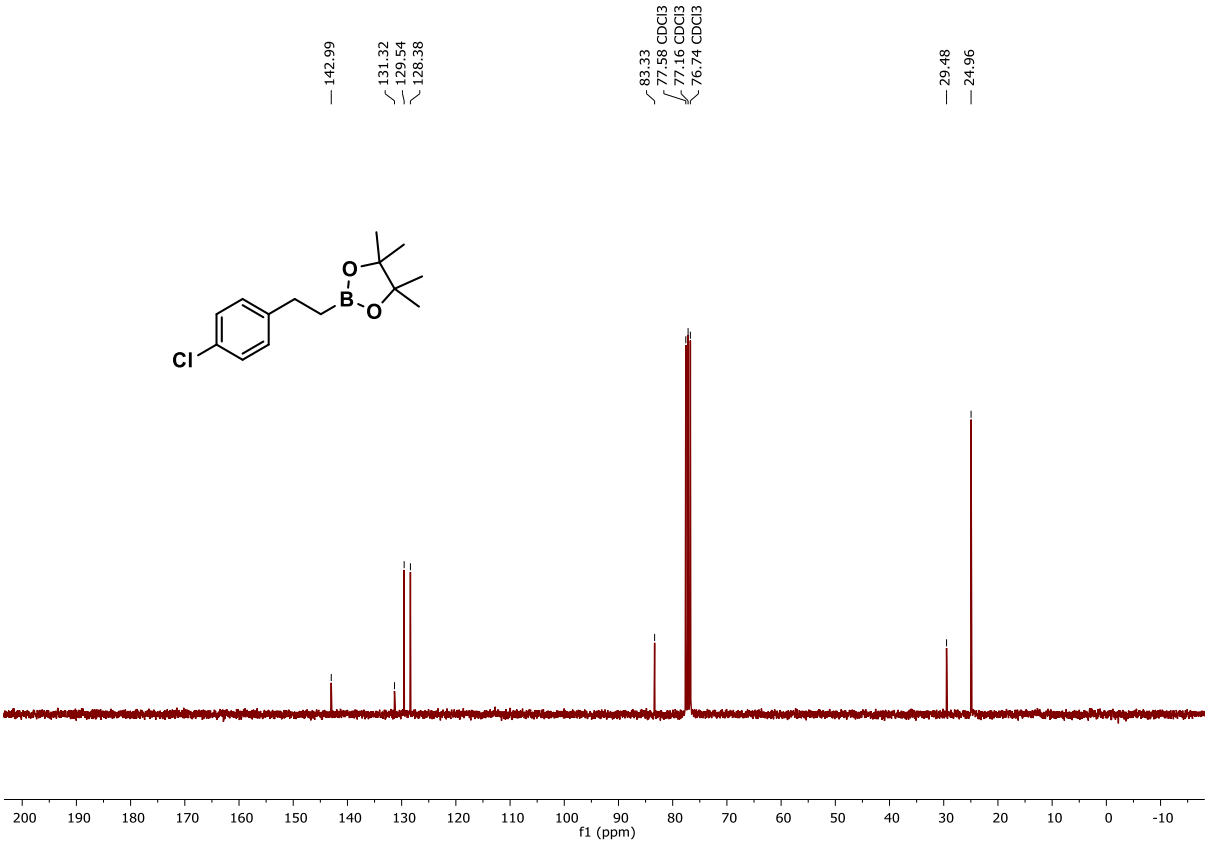


Figure S15. [13]C NMR spectrum of *2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2g**).

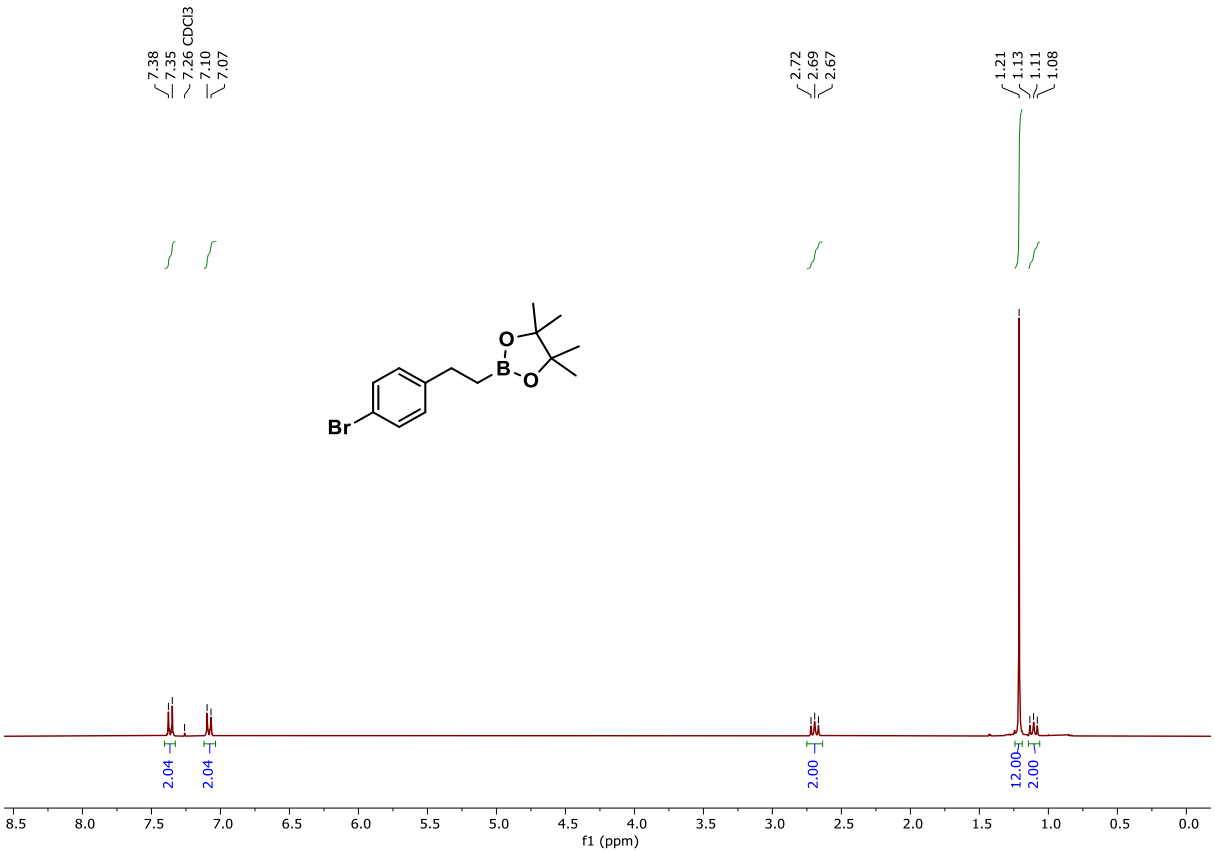


Figure S16. [1]H NMR spectrum of *2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2h**).

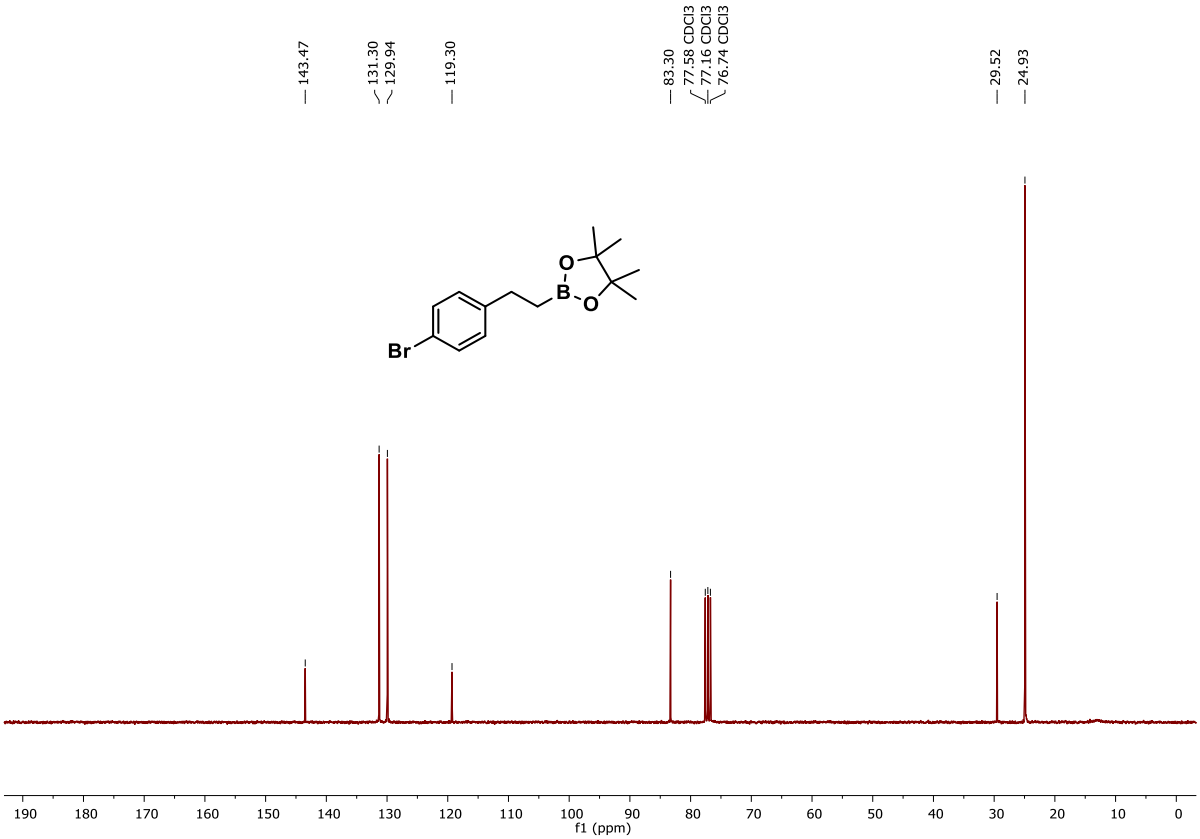


Figure S17. [13]C NMR spectrum of *2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2h**).

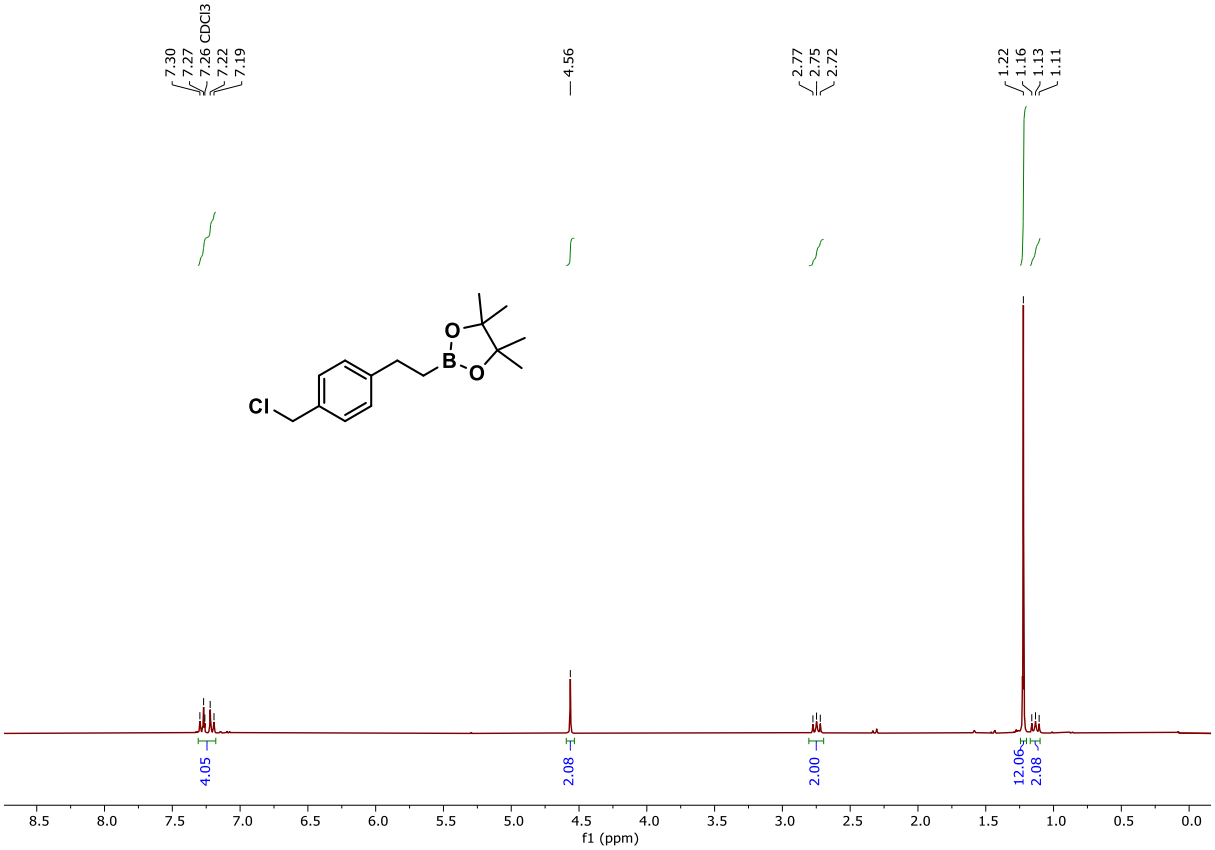


Figure S18. [1]H NMR spectrum of *2-(4-(chloromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2i**).

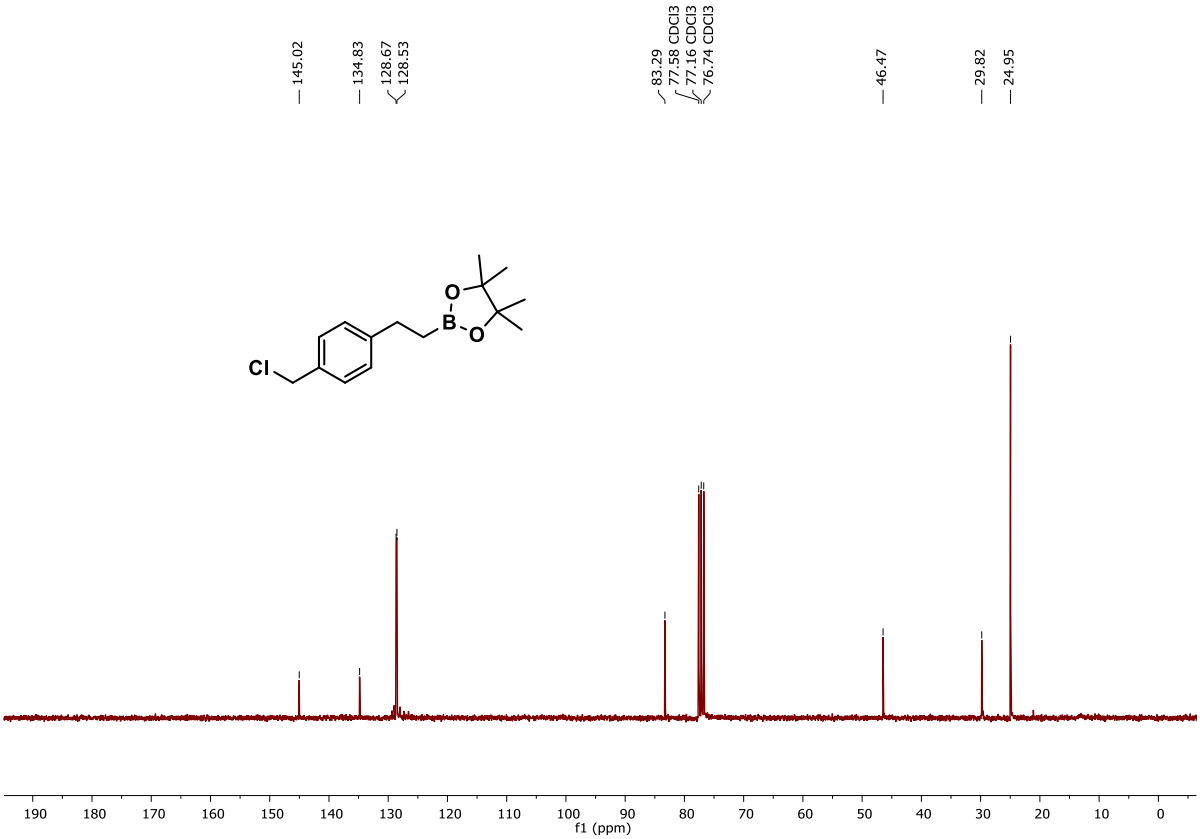


Figure S19. ^{13}C NMR spectrum of *2-(4-(chloromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2i**).

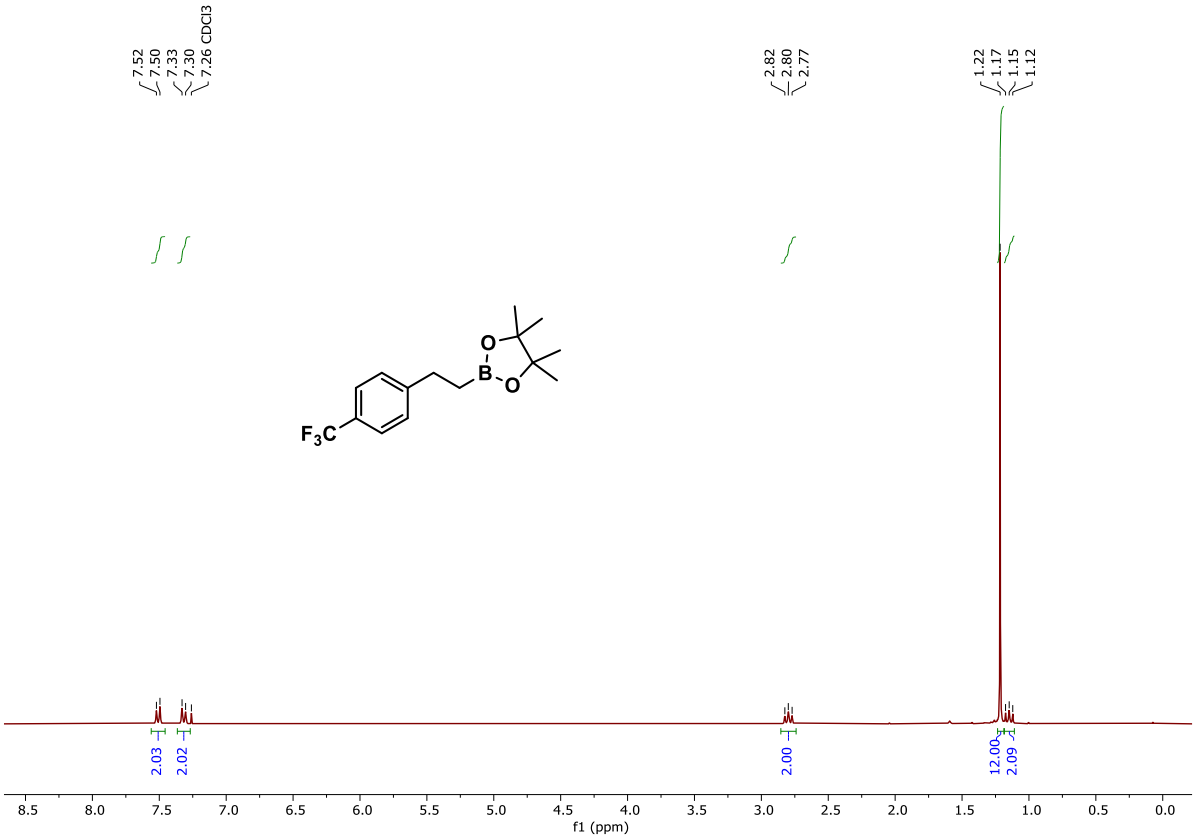


Figure S20. ^{1}H NMR spectrum of *2-(4-(trifluoromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2j**).

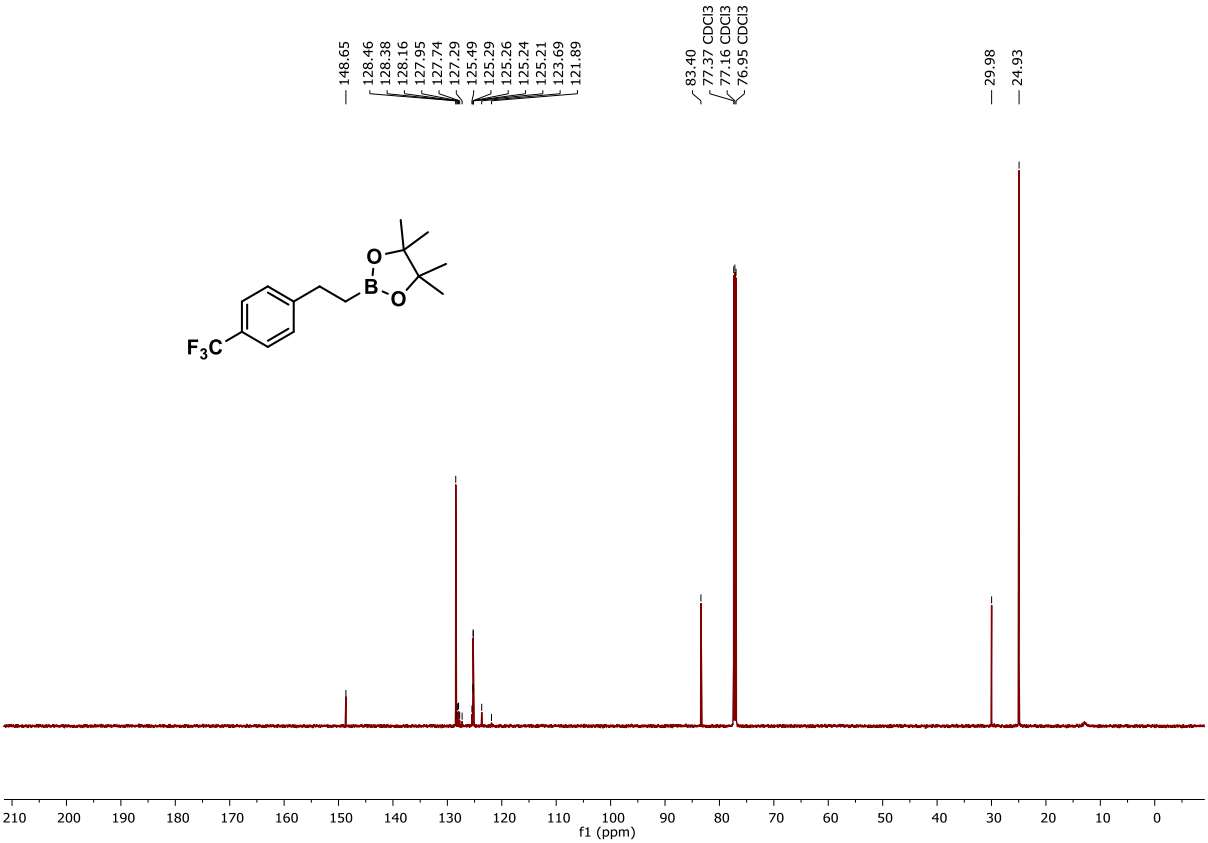


Figure S21. ^{13}C NMR spectrum of *2-(4-(trifluoromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2j**).

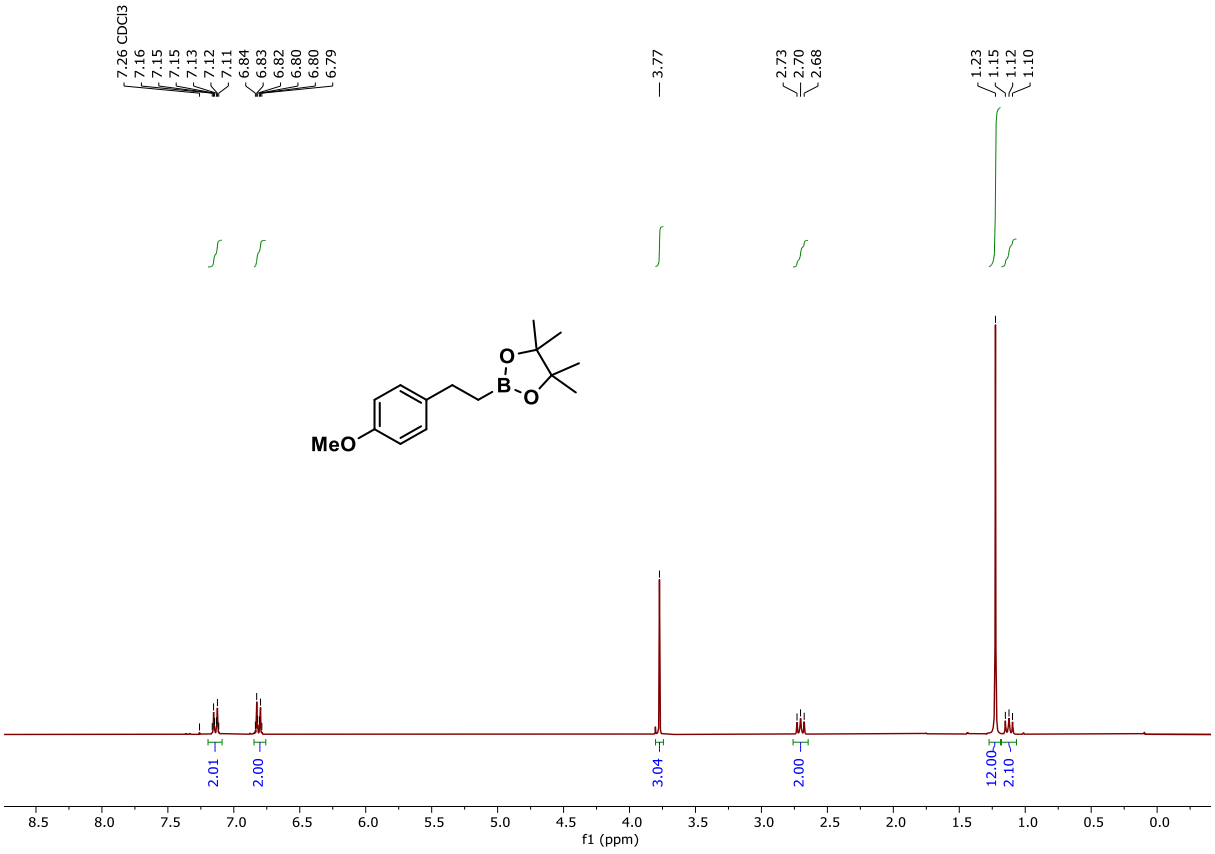


Figure S22. ^{1}H NMR spectrum of *2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2k**).

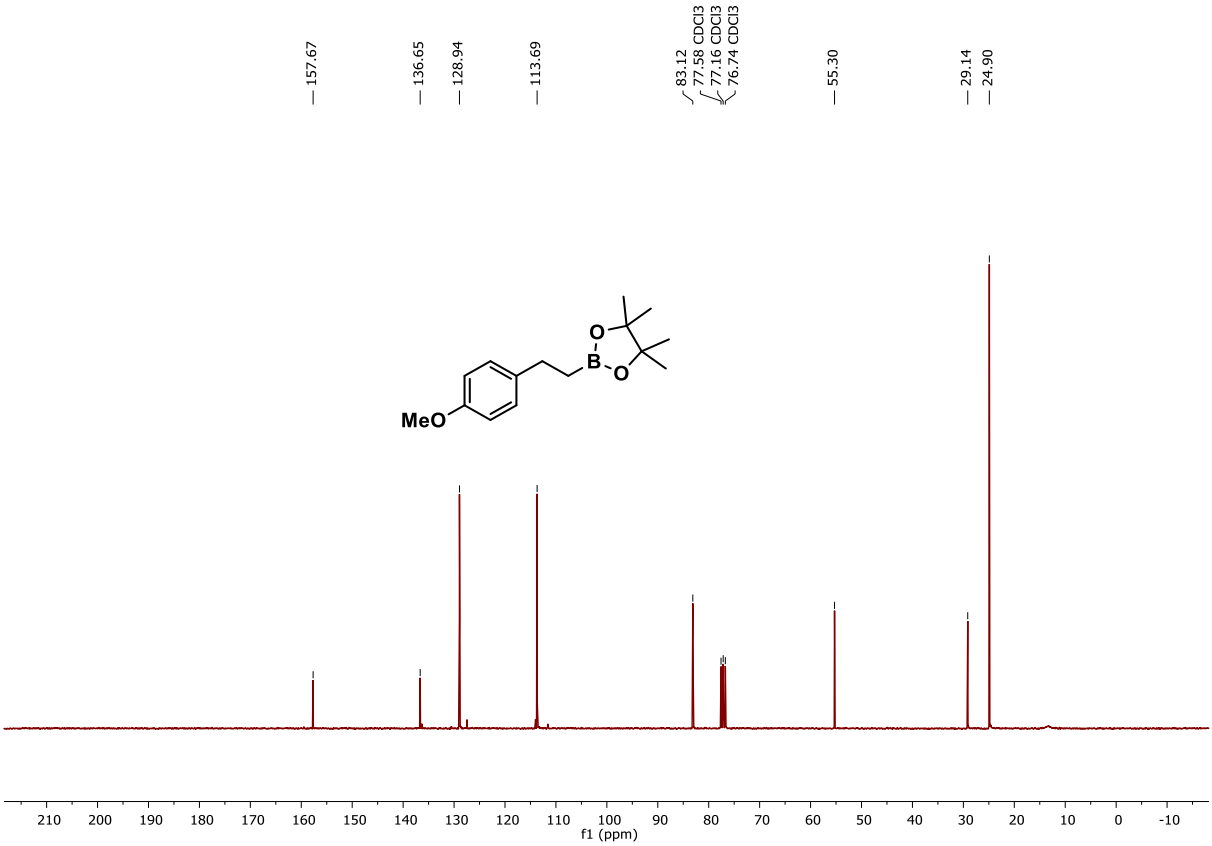


Figure S23. ^{13}C NMR spectrum of *2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2k**).

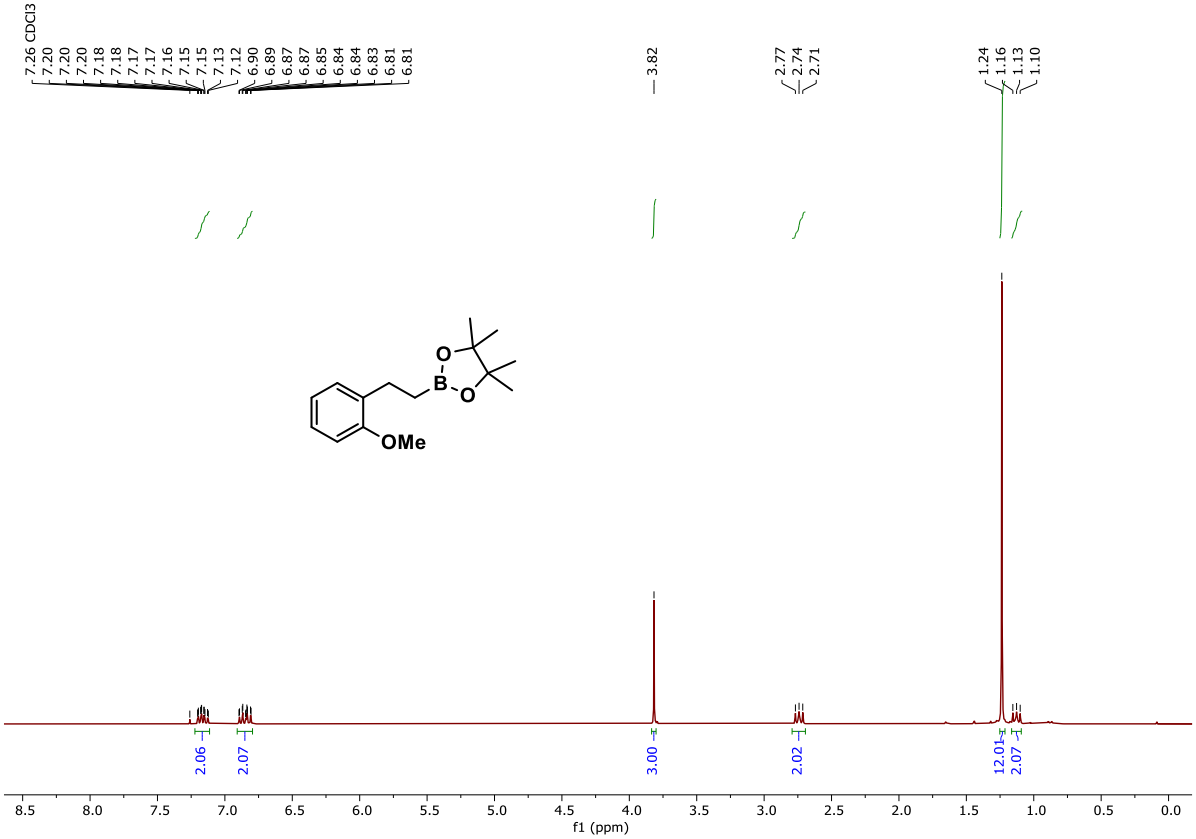


Figure S24. ^{1}H NMR spectrum of *2-(2-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2l**).

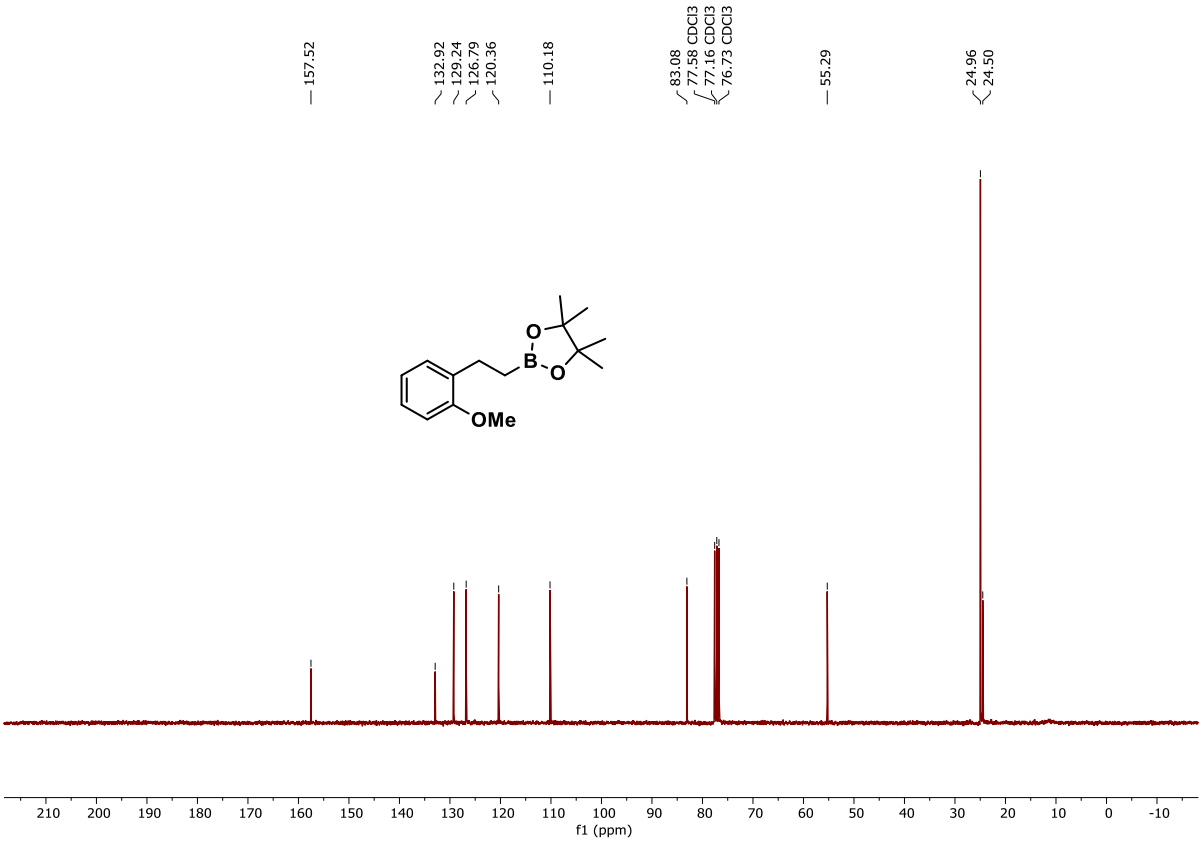


Figure S25. [13]C NMR spectrum of *2-(2-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2l**).

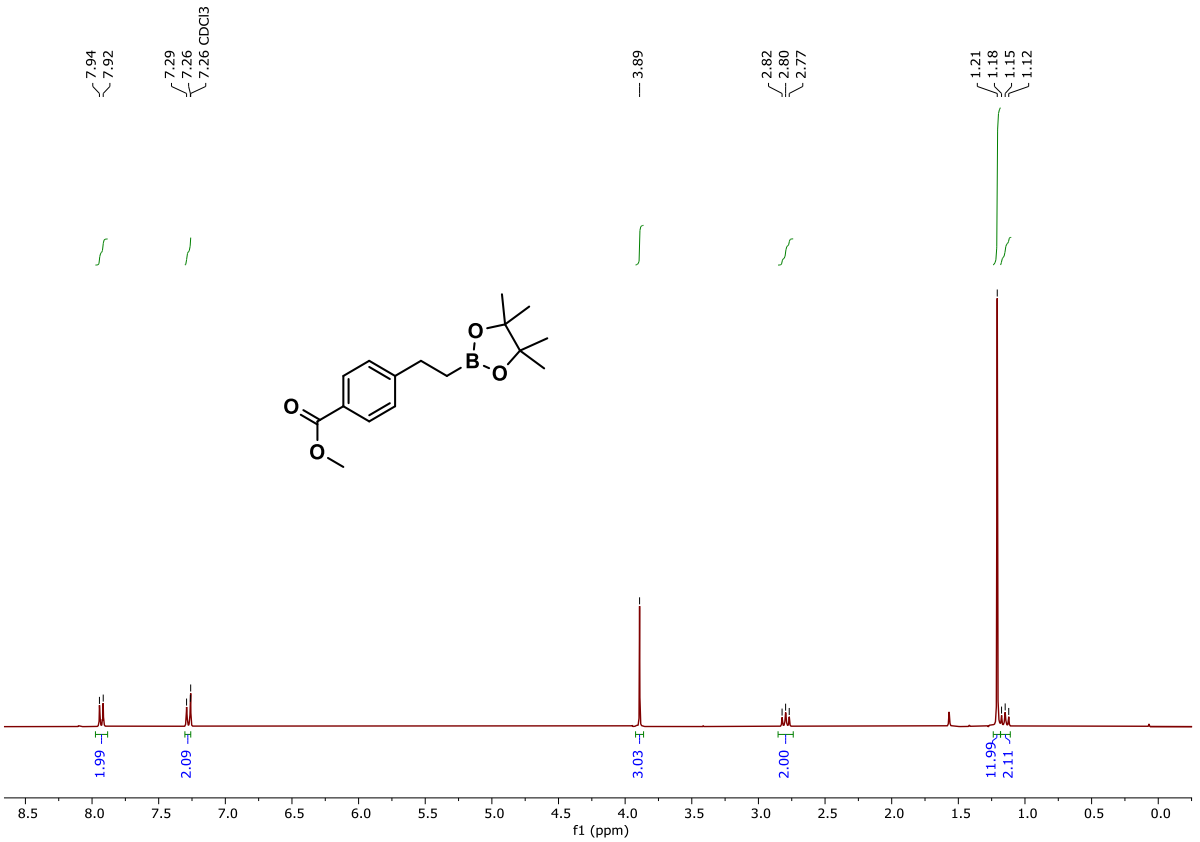


Figure S26. [1]H NMR spectrum of *methyl 4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzoate* (**2m**).

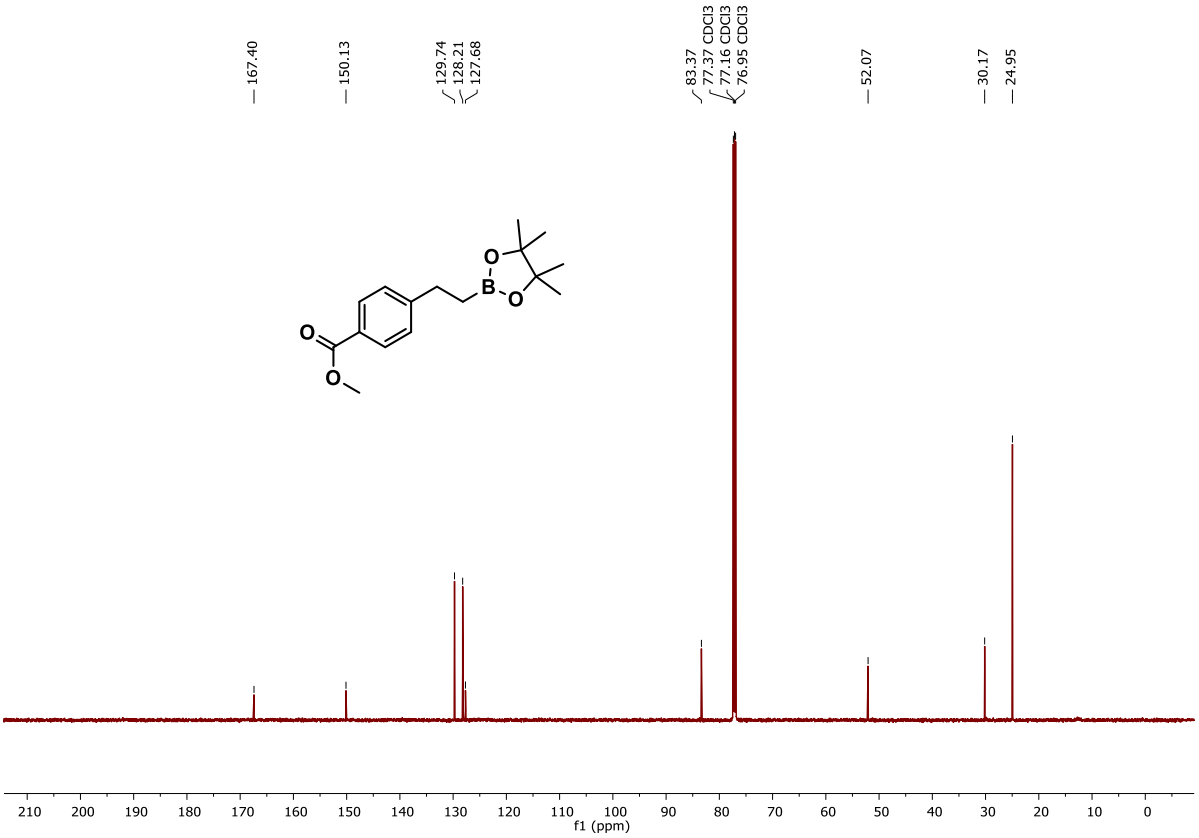


Figure S27. ^{13}C NMR spectrum of *methyl 4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]benzoate* (**2m**).

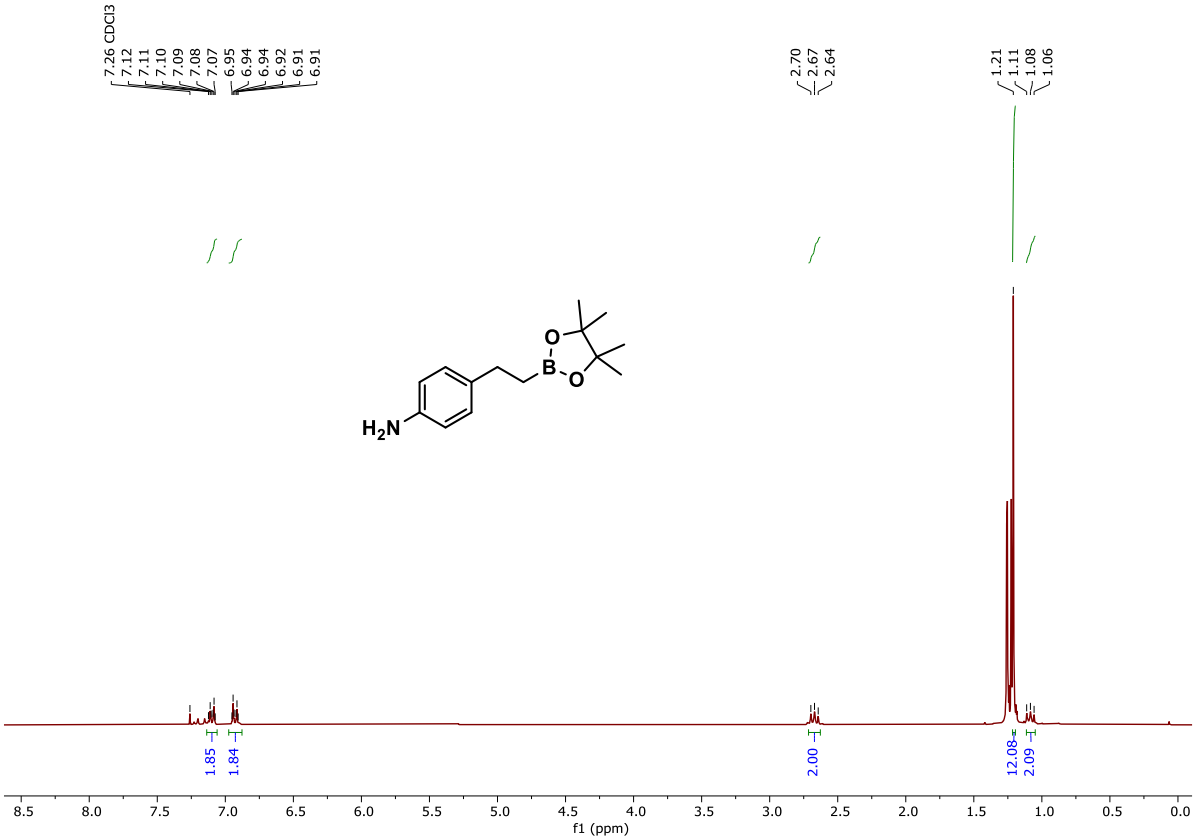


Figure S28. ^{1}H NMR spectrum of *4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]aniline* (**2n**).

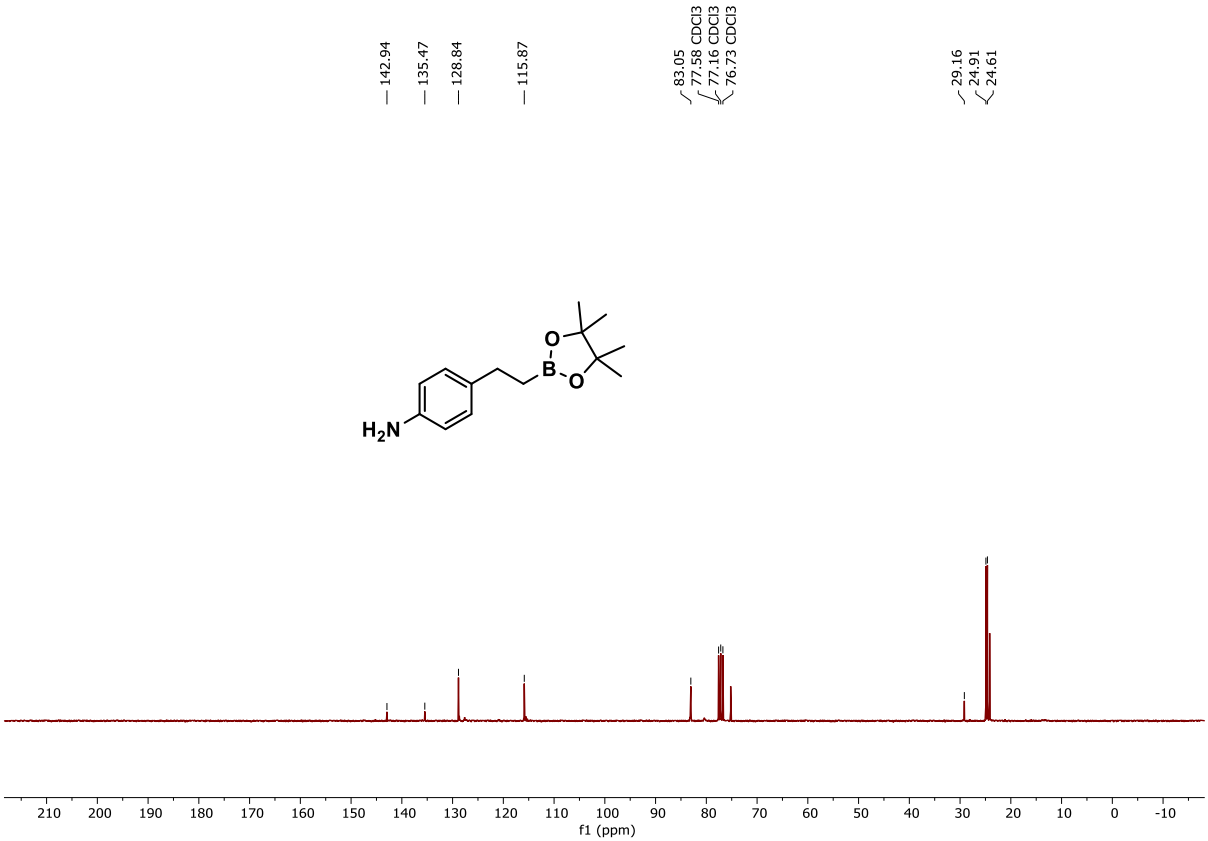


Figure S29. ^{13}C NMR spectrum of *4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]aniline* (**2n**).

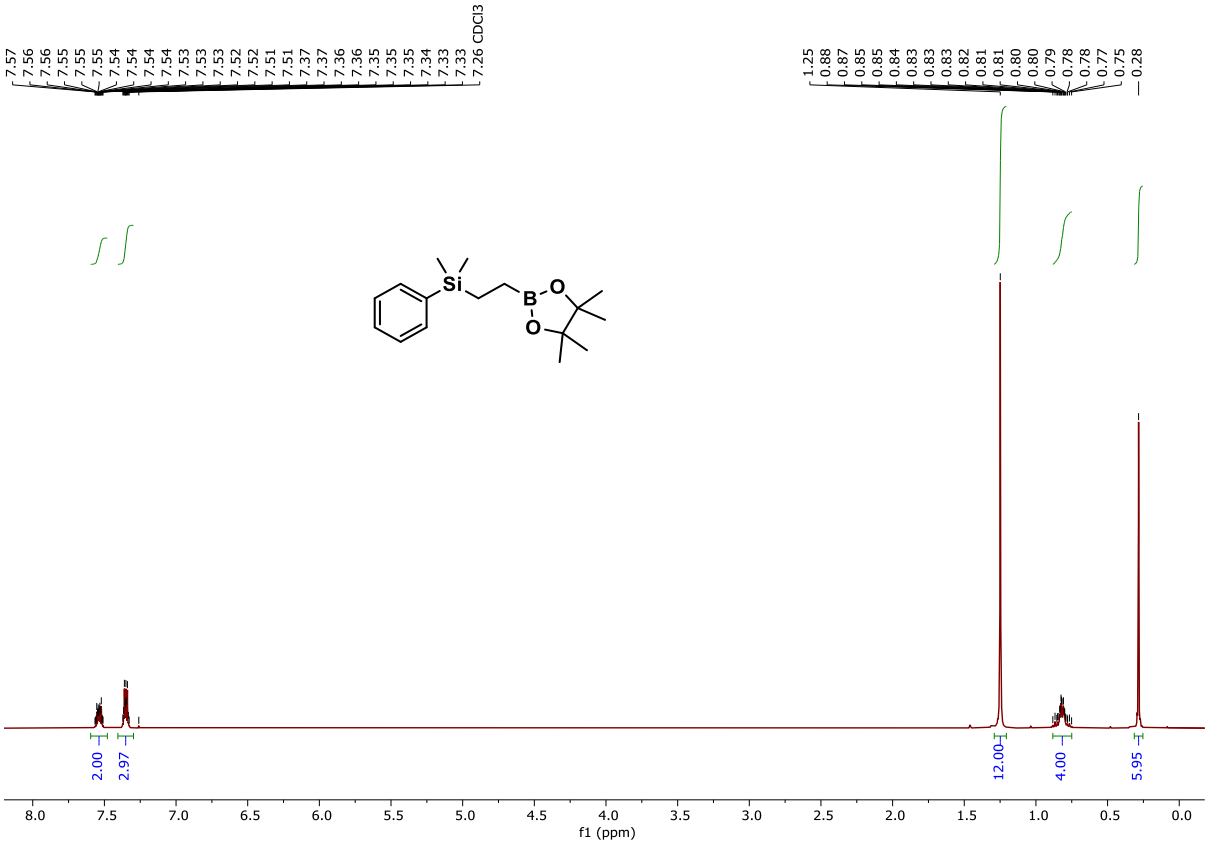


Figure S30. ^{1}H NMR spectrum of *dimethyl-phenyl-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]silane* (**2o**).

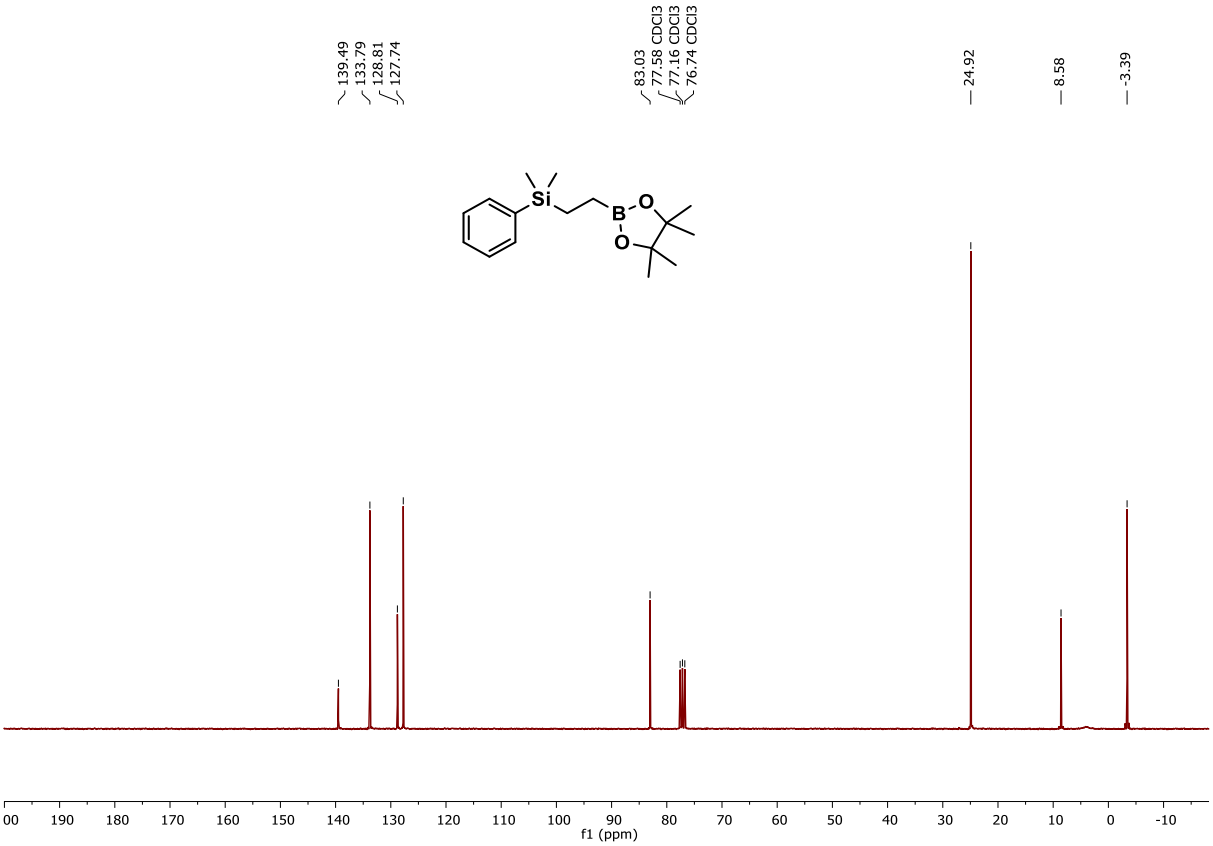


Figure S31. ^{13}C NMR spectrum of *dimethyl-phenyl-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]silane* (**2o**).

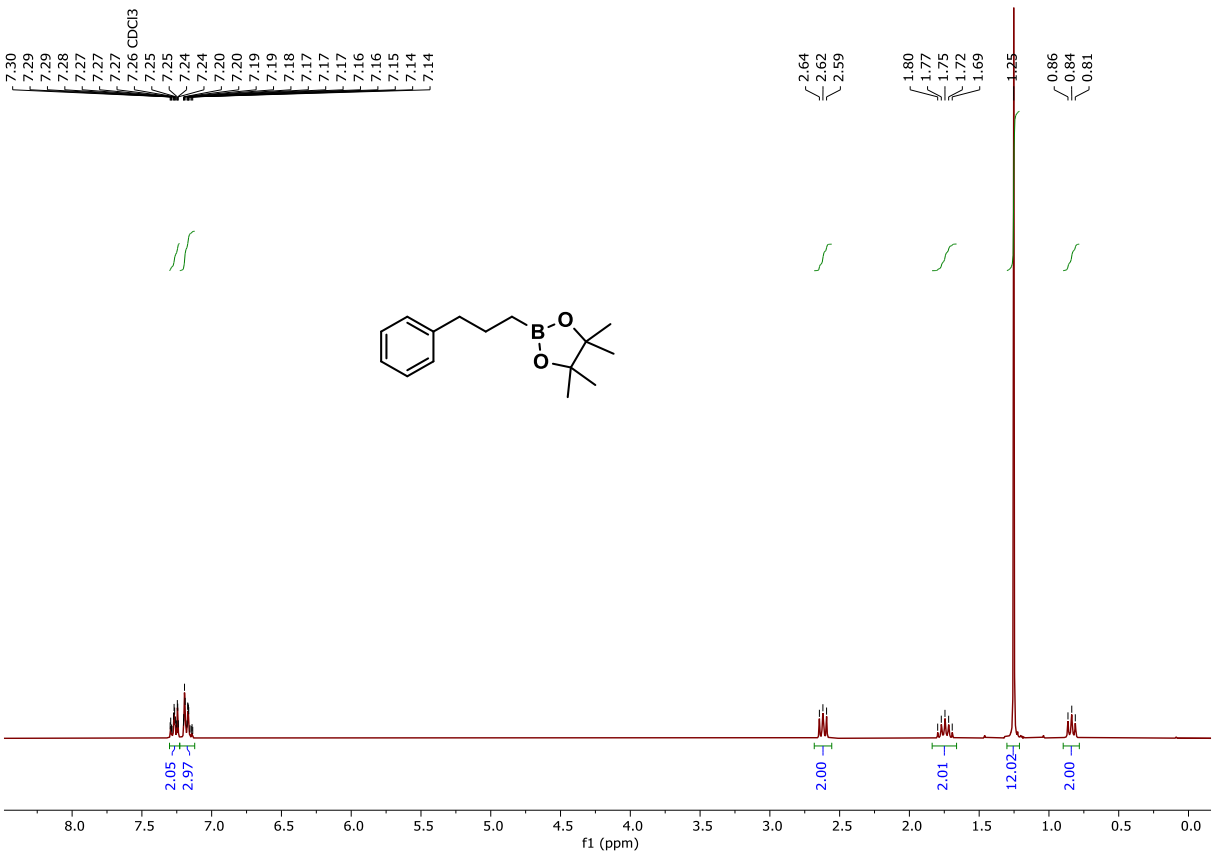


Figure S32. ^{1}H NMR spectrum of *4,4,5,5-tetramethyl-2-[3-(2-methylphenyl)propyl]-1,3,2-dioxaborolane* (**2p**).

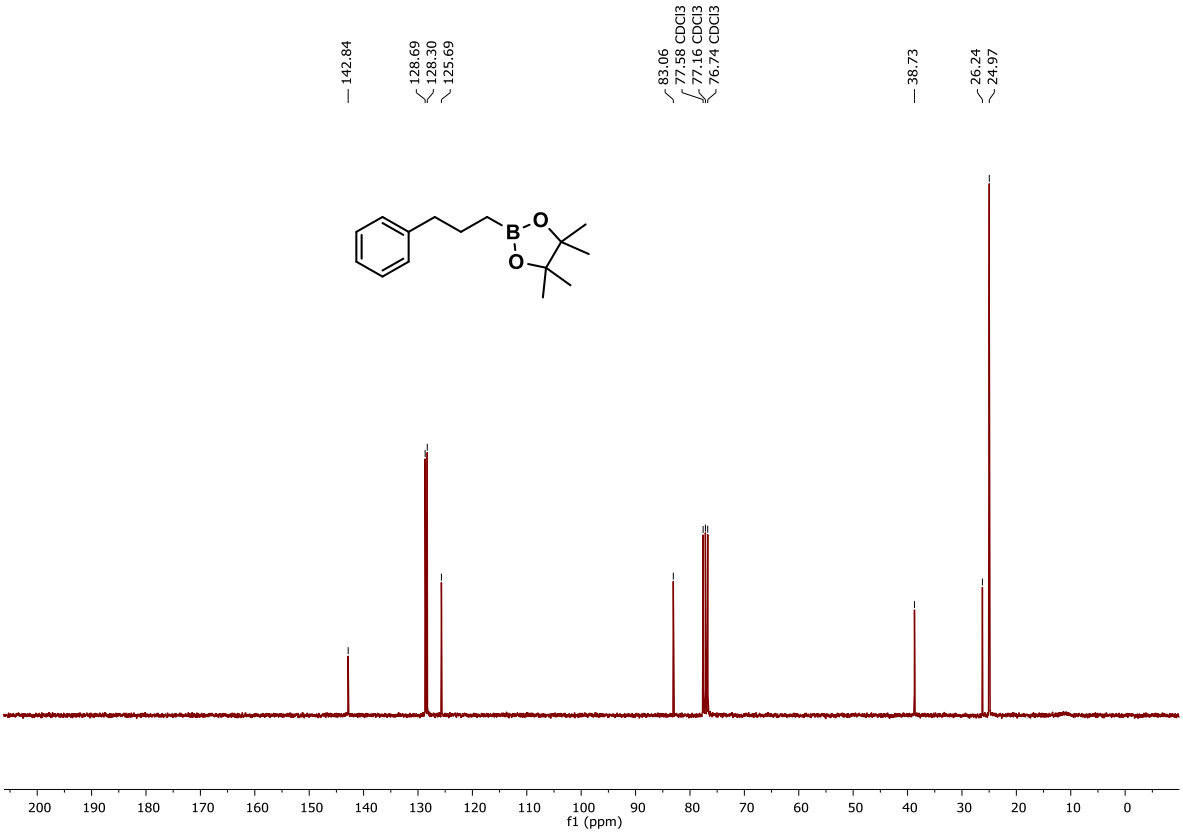


Figure S33. [13]C NMR spectrum of *4,4,5,5-tetramethyl-2-[3-(2-methylphenyl)propyl]-1,3,2-dioxaborolane* (**2p**).

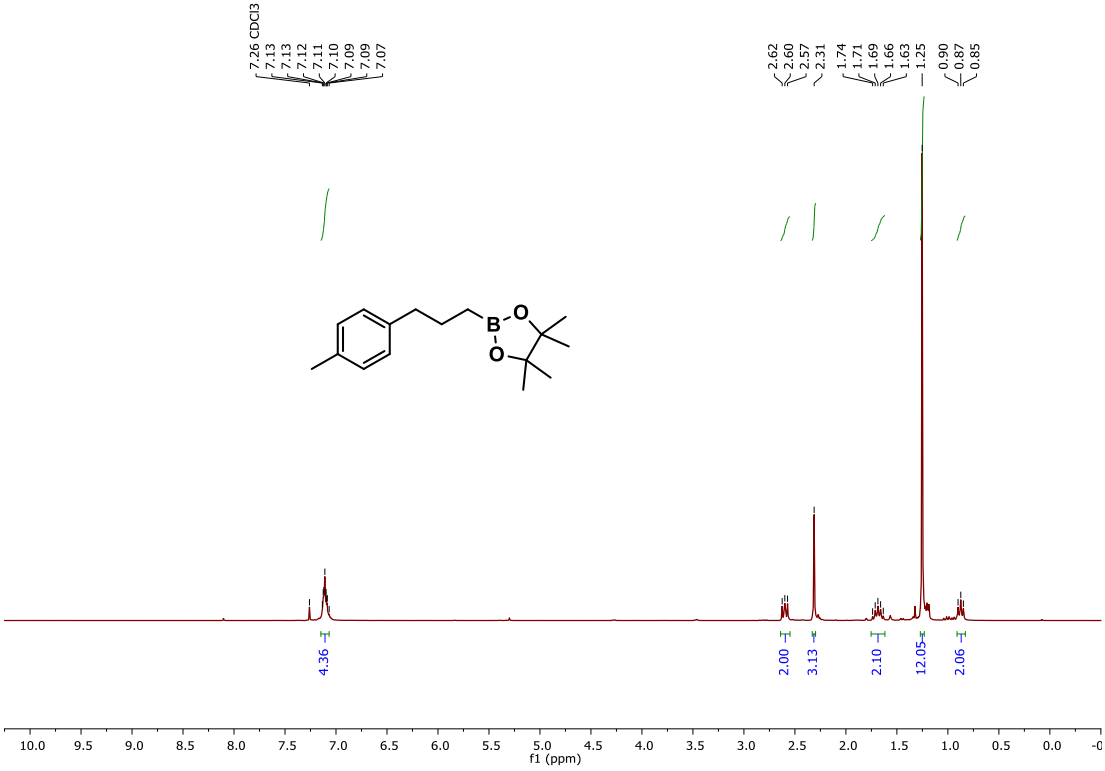


Figure S34. [1]H NMR spectrum of *4,4,5,5-tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane* (**2q**).

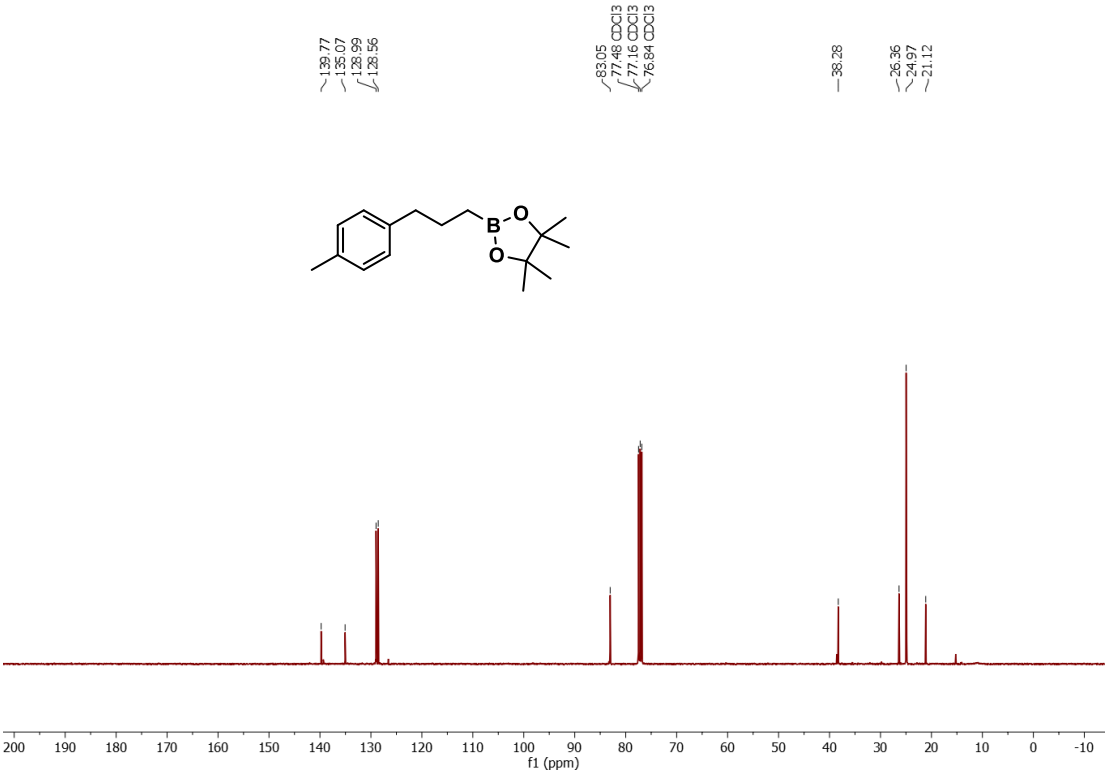


Figure S35. ^{13}C NMR spectrum of *4,4,5,5-tetramethyl-2-(3-p-tolylpropyl)-1,3,2-dioxaborolane* (**2q**).

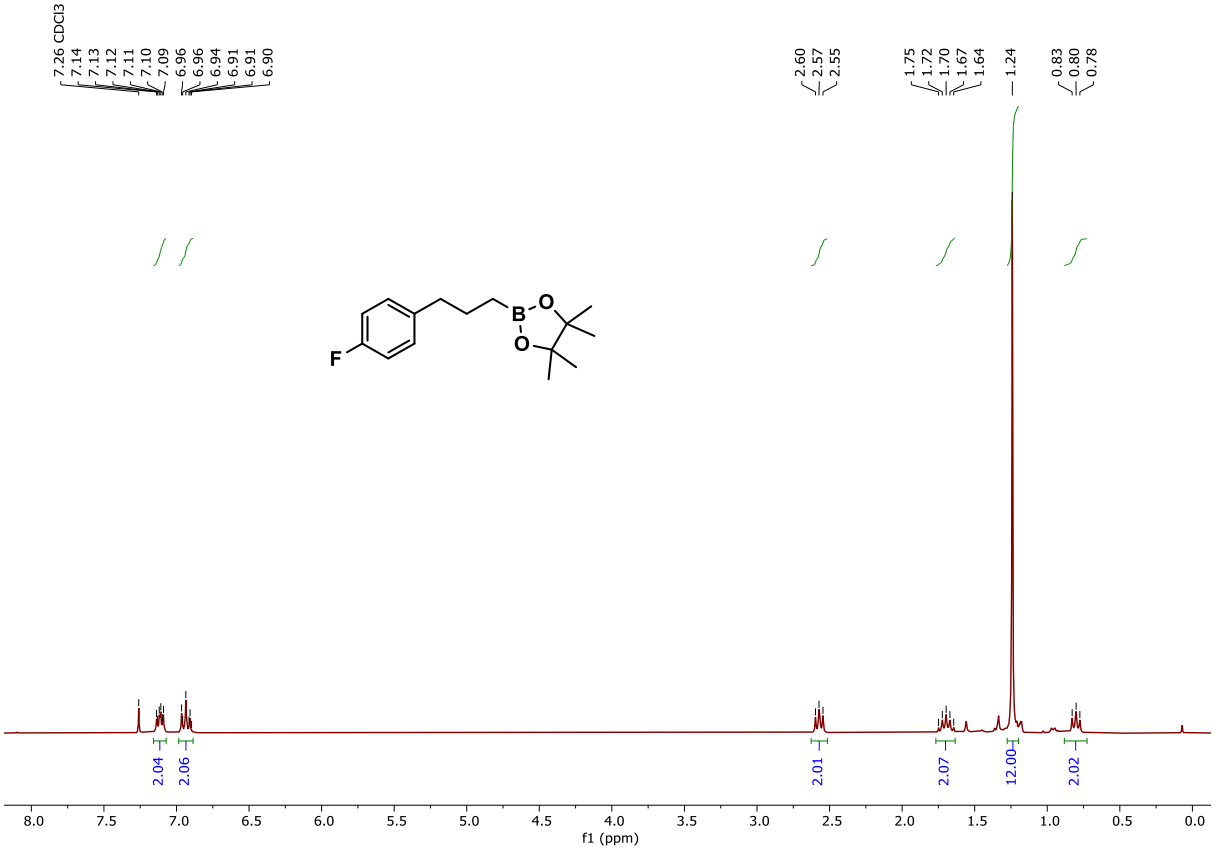


Figure S36. ^{1}H NMR spectrum of *2-(3-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2r**).

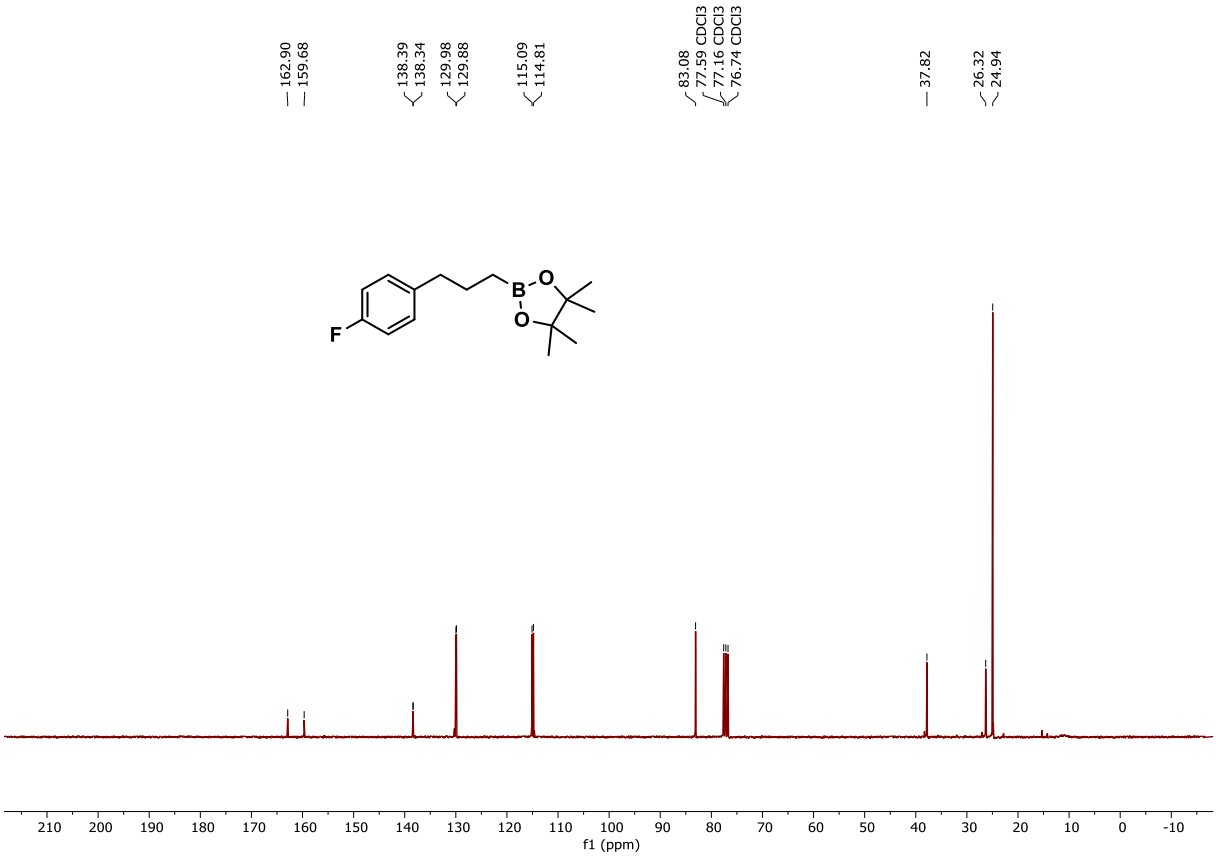


Figure S37. ^{13}C NMR spectrum of *2-(3-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2r**).

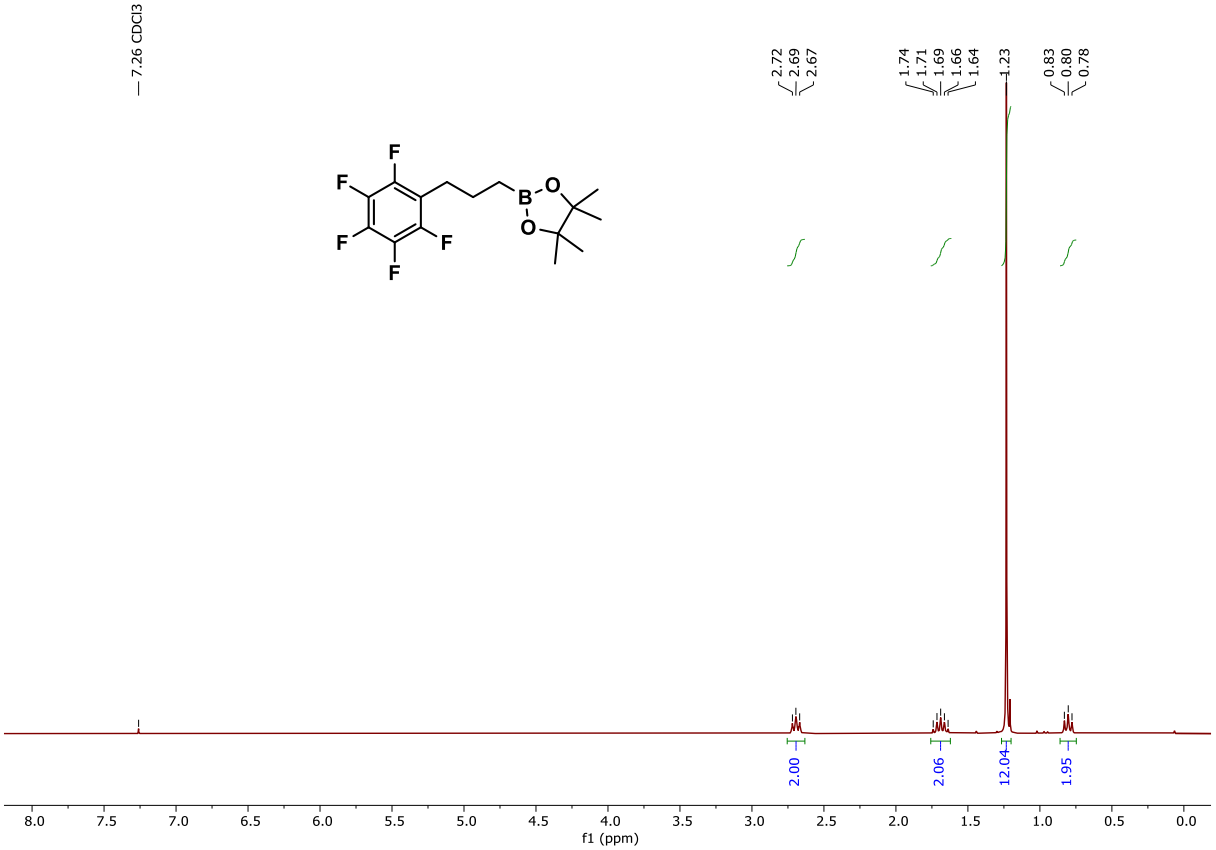


Figure S38. ^{1}H NMR spectrum of *4,4,5,5-tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane* (**2s**).

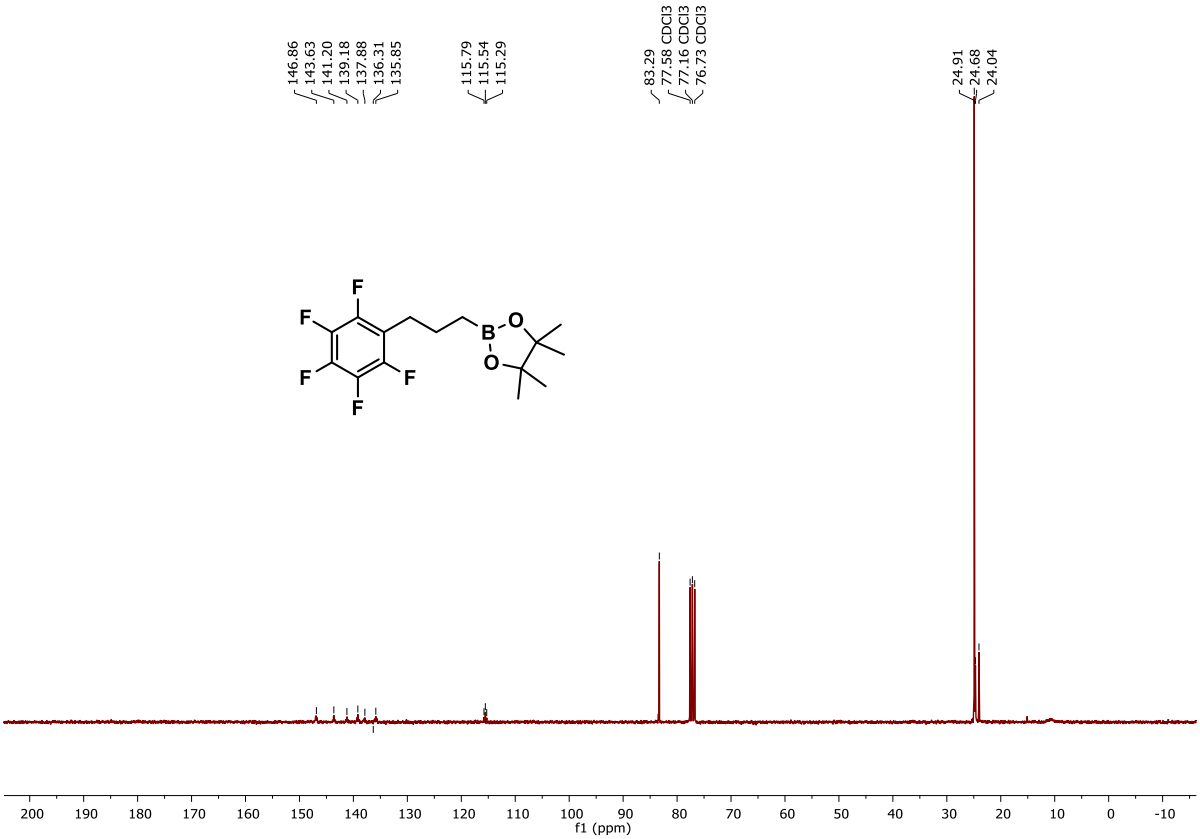


Figure S39. ^{13}C NMR spectrum of *4,4,5,5-tetramethyl-2-(3-(perfluorophenyl)propyl)-1,3,2-dioxaborolane* (**2s**).

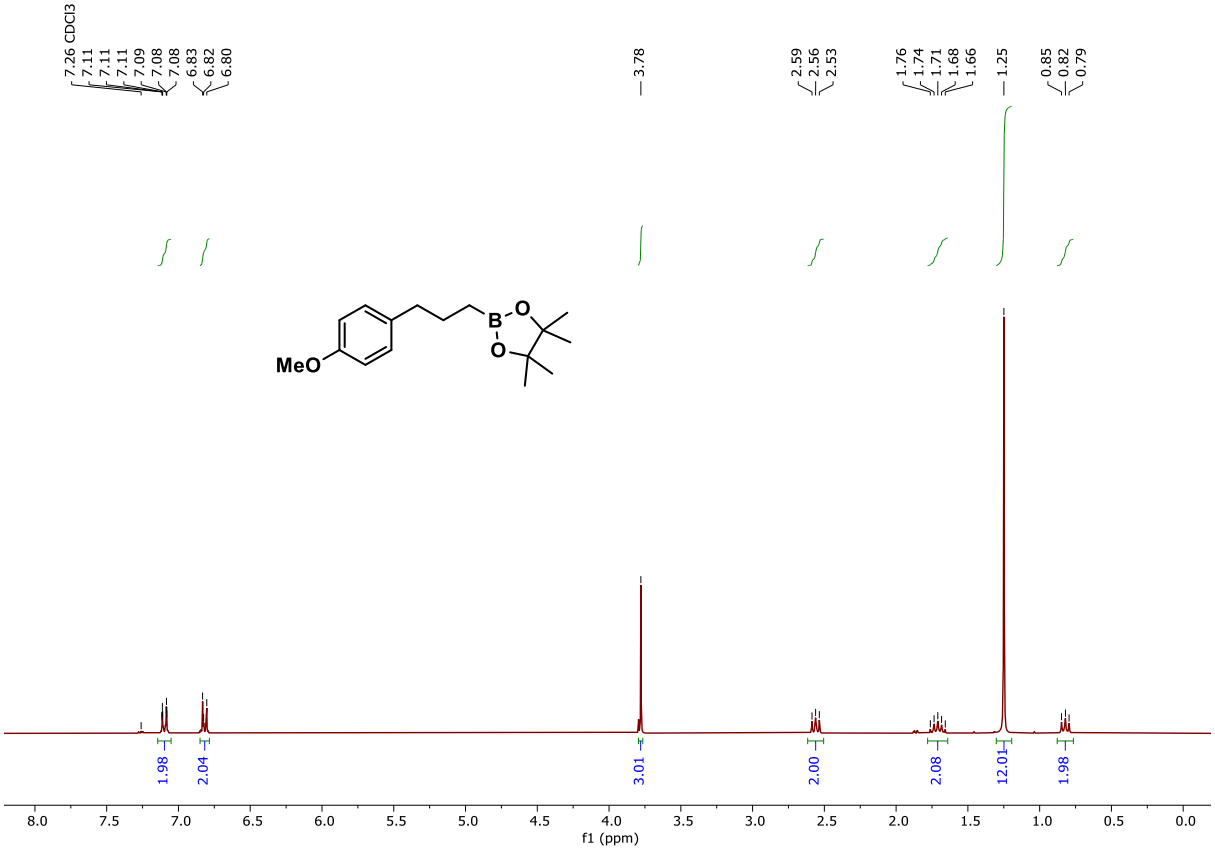


Figure S40. ^{1}H NMR spectrum of *2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2t**).

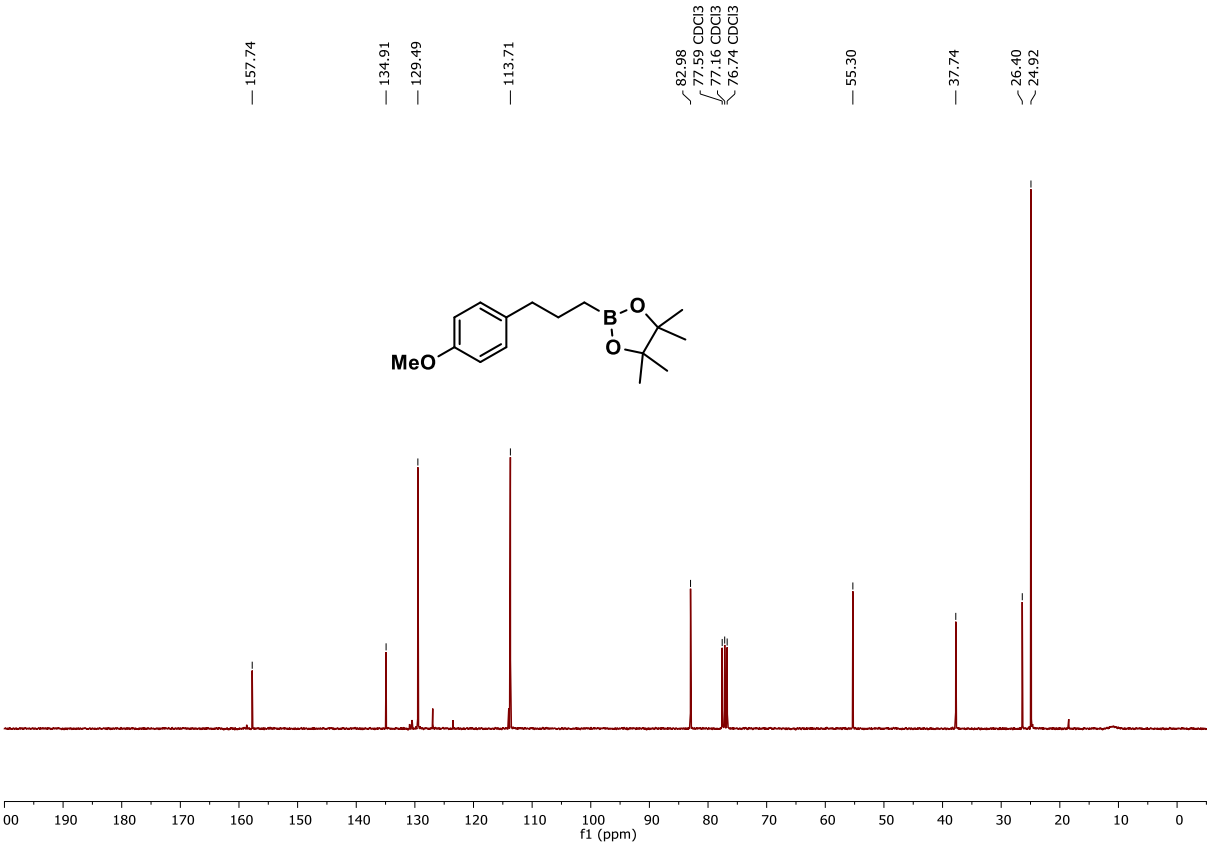


Figure S41. ^{13}C NMR spectrum of *2-(3-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2t**).

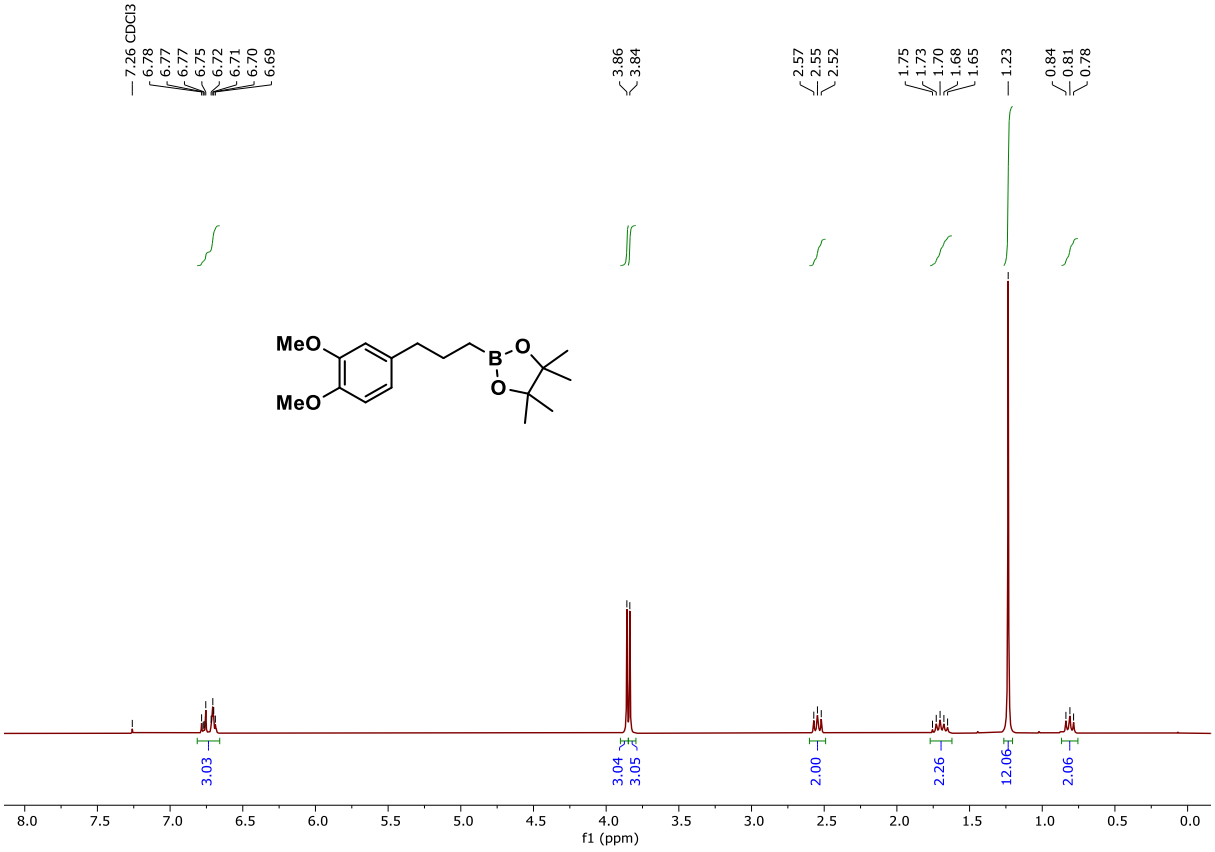


Figure S42. ^{1}H NMR spectrum of *2-(3-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2u**).

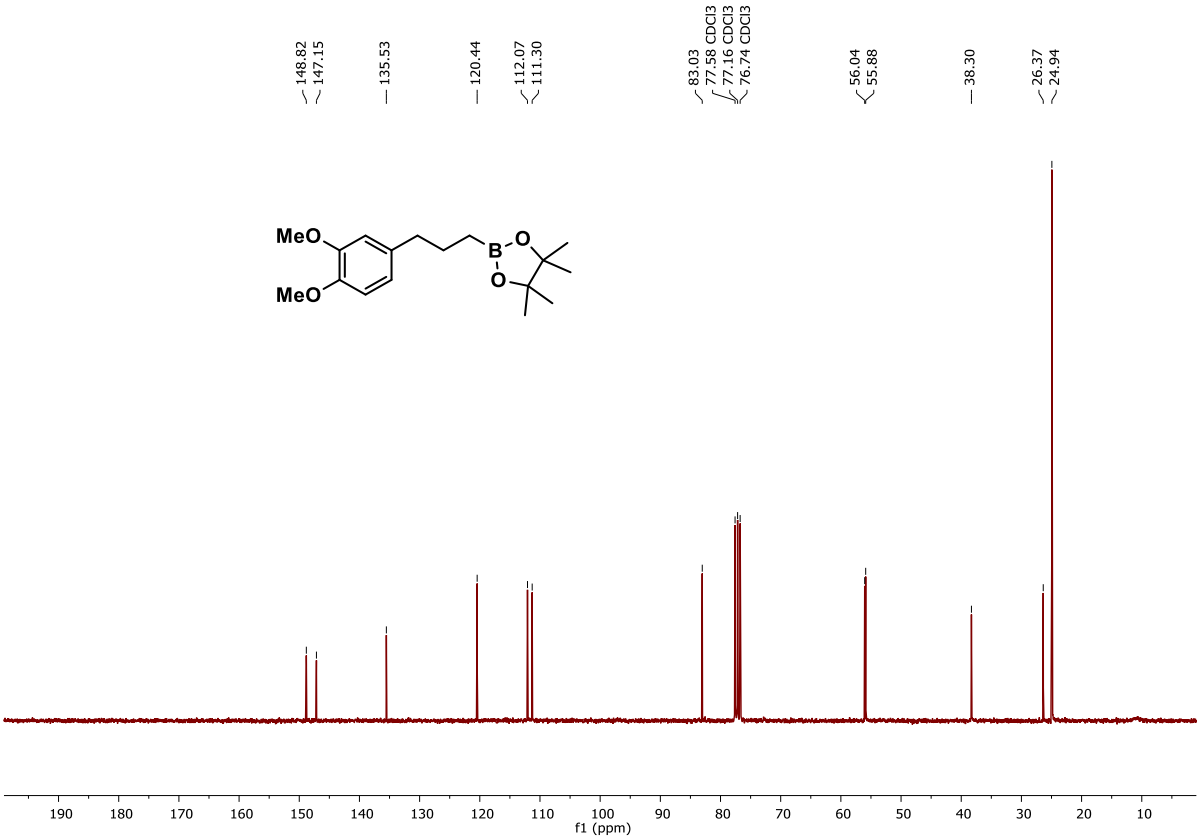


Figure S43. ^{13}C NMR spectrum of *2-(3-(3,4-dimethoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2u**).

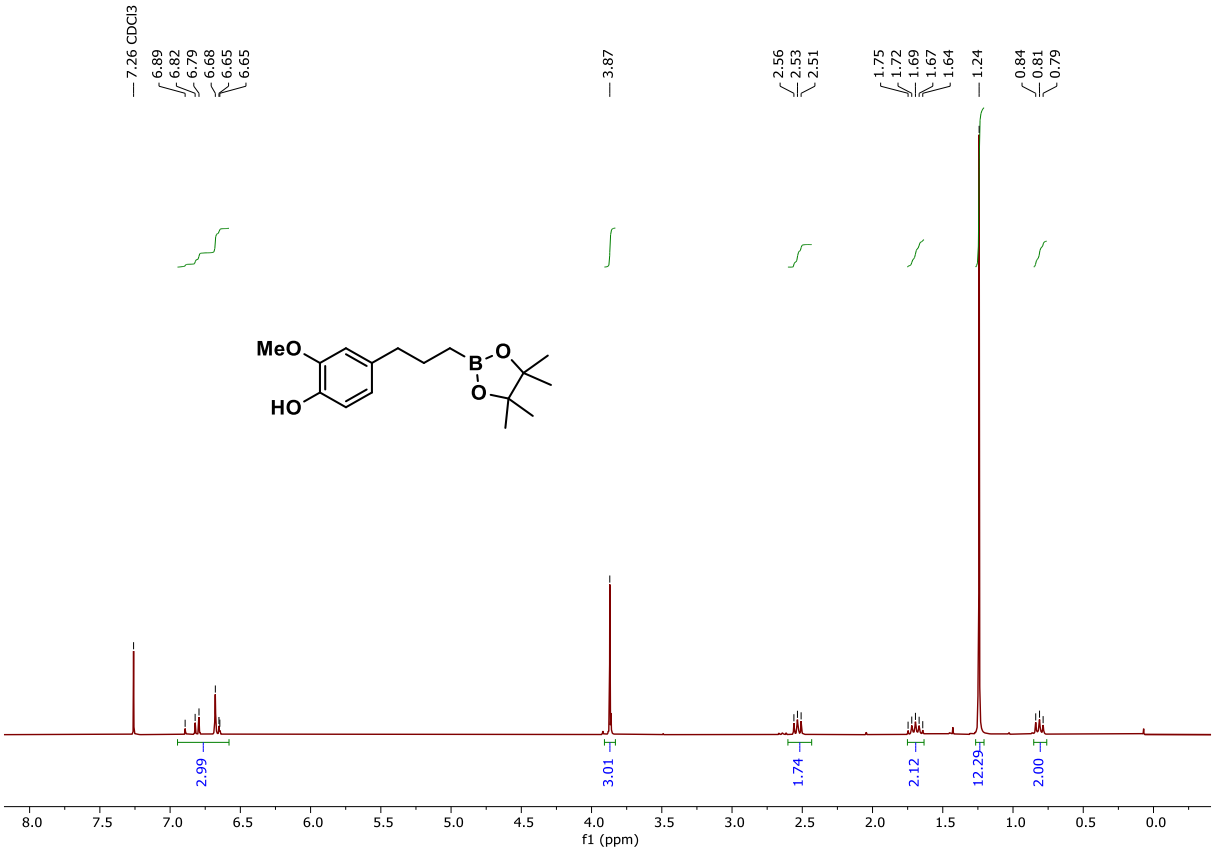


Figure S44. ^{1}H NMR spectrum of *2-methoxy-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol* (**2v**).

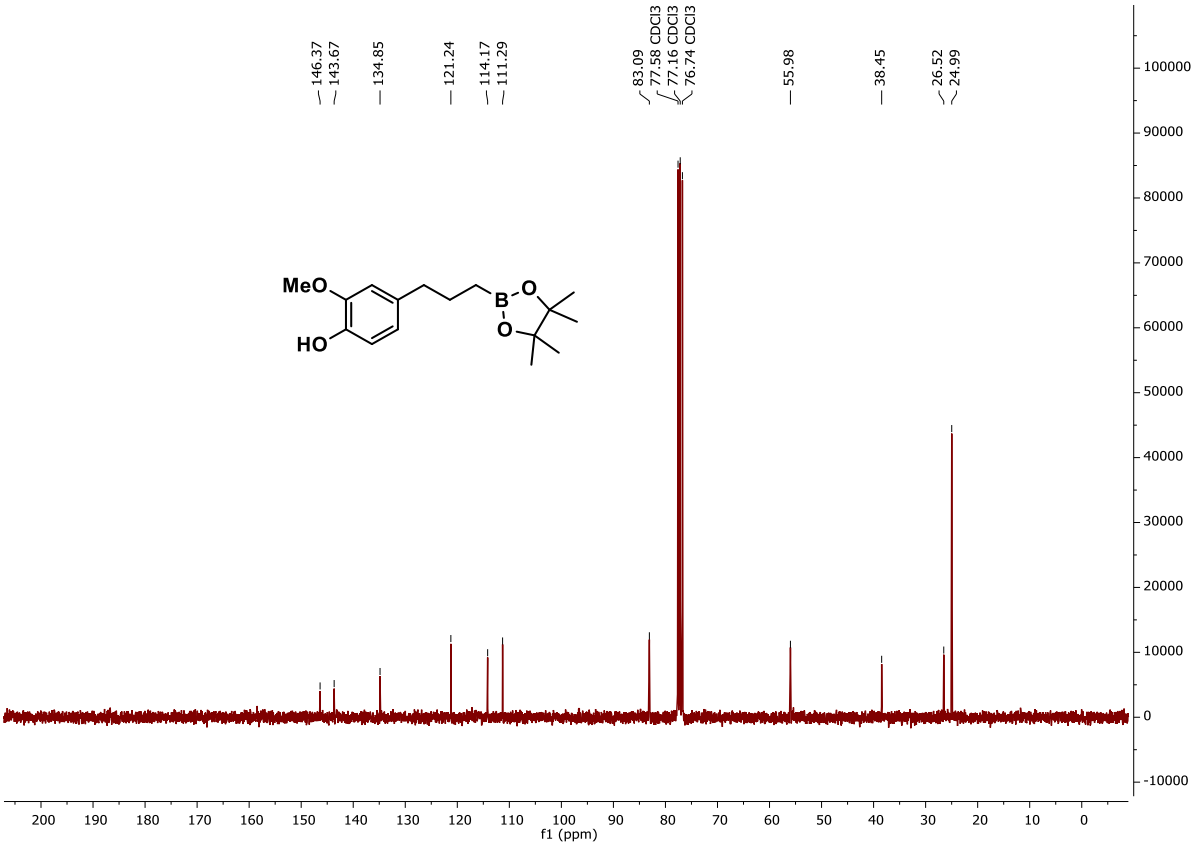


Figure S45. ^{13}C NMR spectrum of *2-methoxy-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol* (**2v**).

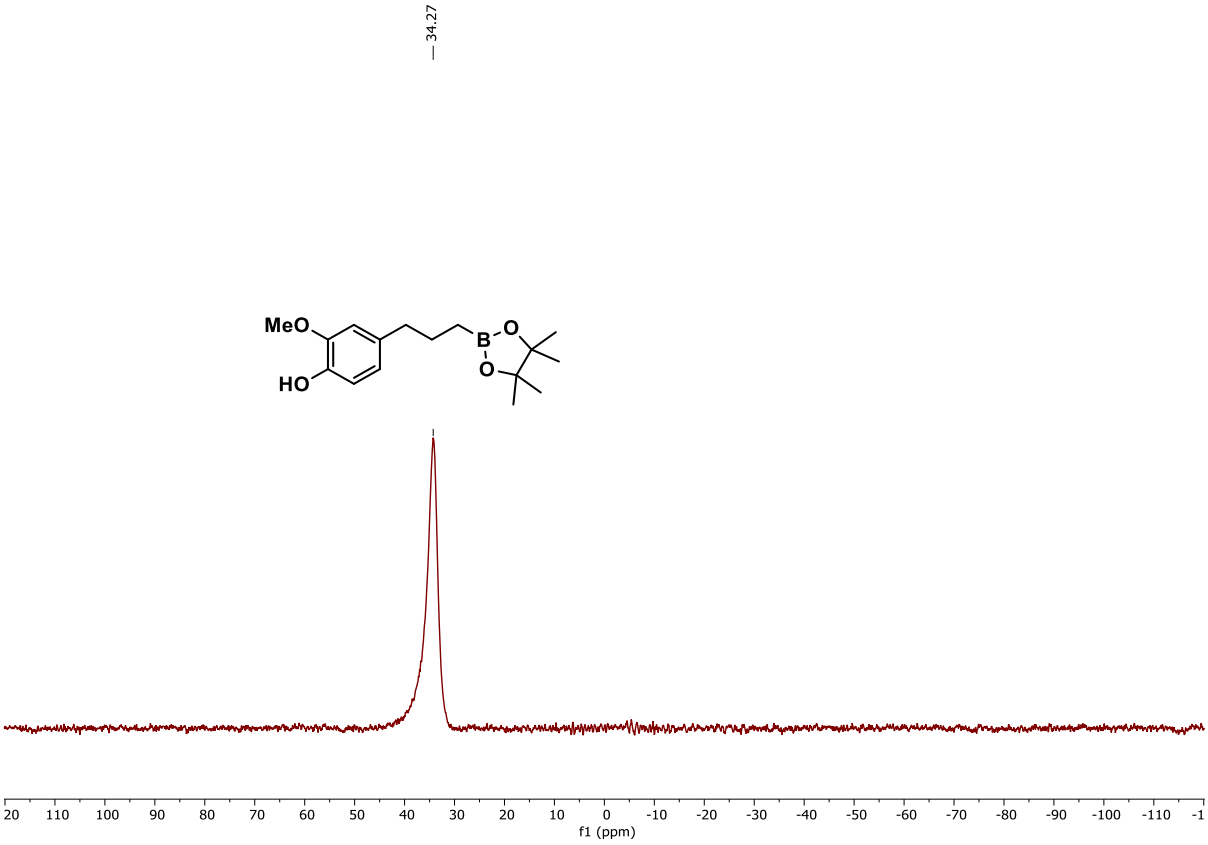


Figure S46. ^{11}B NMR spectrum of *2-methoxy-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenol* (**2v**).

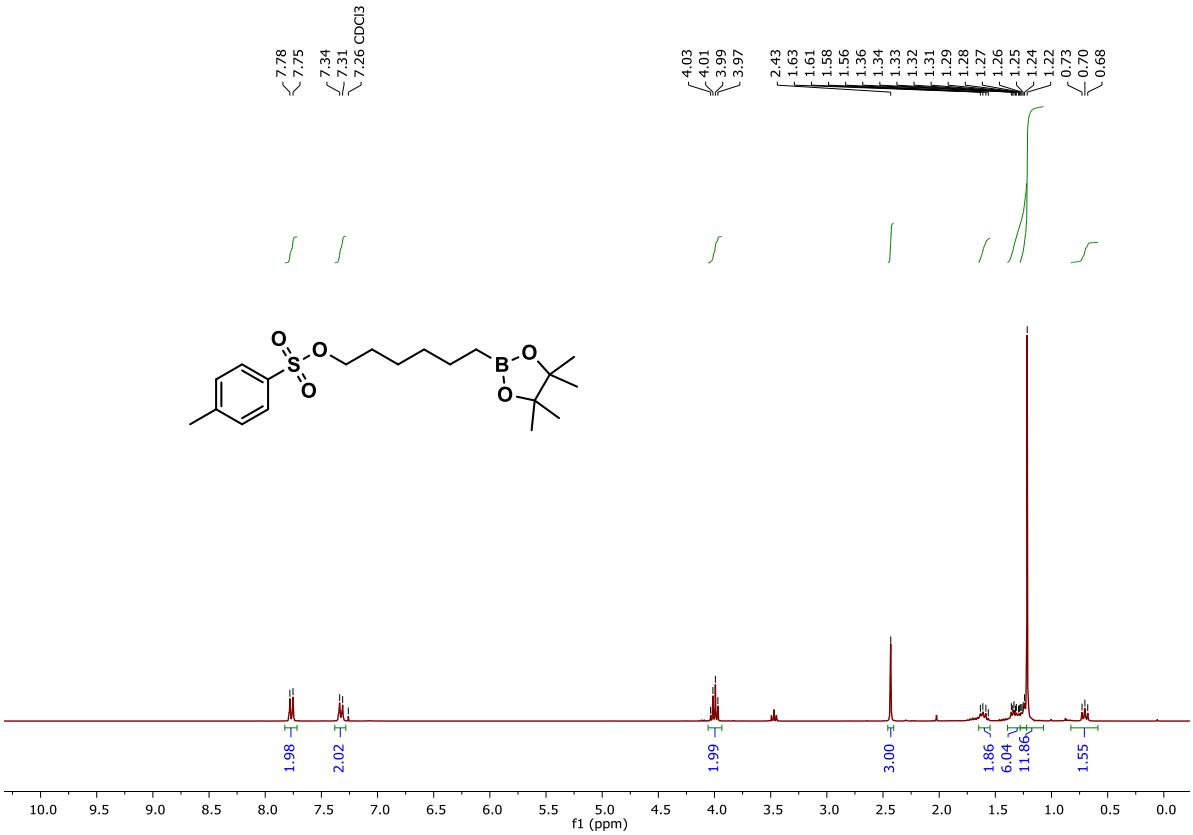


Figure S47. ^{1}H NMR spectrum of *6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl-4-methylbenzenesulfonate* (**2w**).

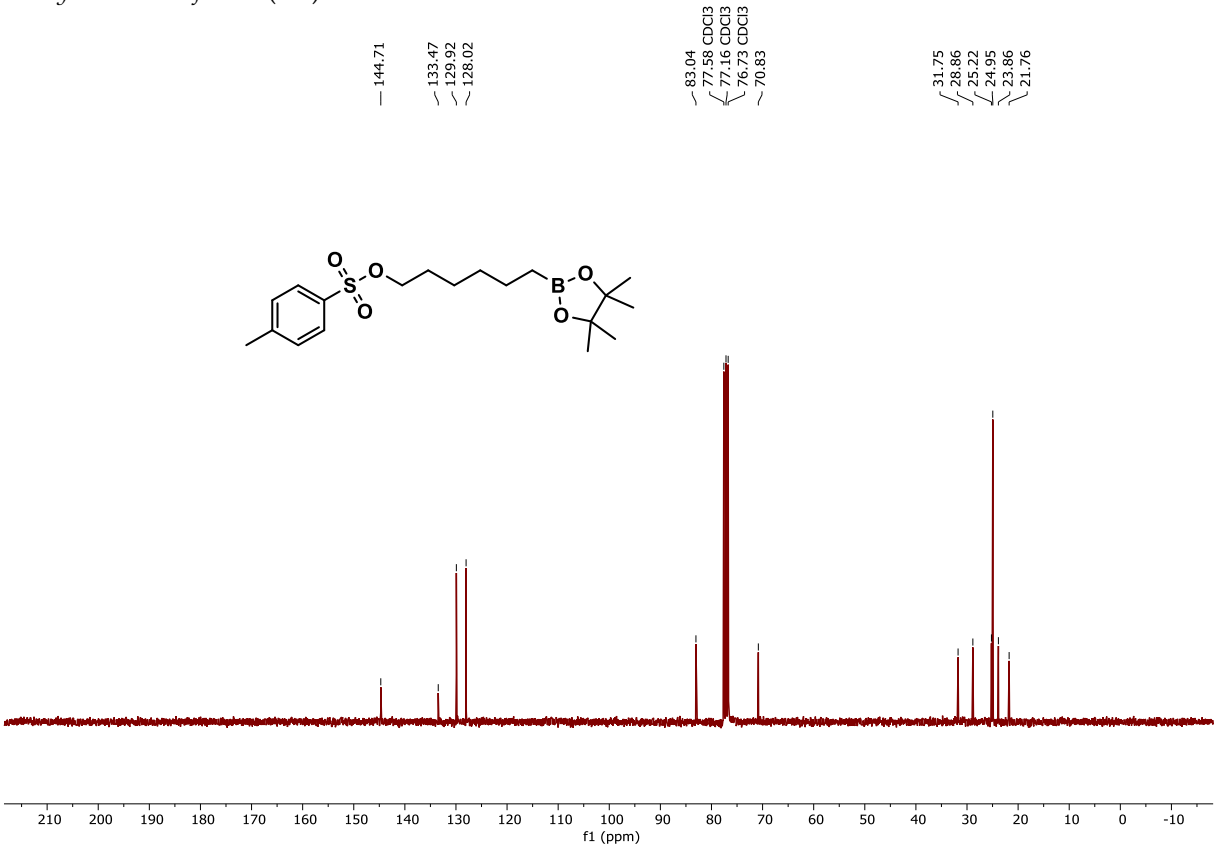


Figure S48. ^{13}C NMR spectrum of *6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl-4-methylbenzenesulfonate* (**2w**).

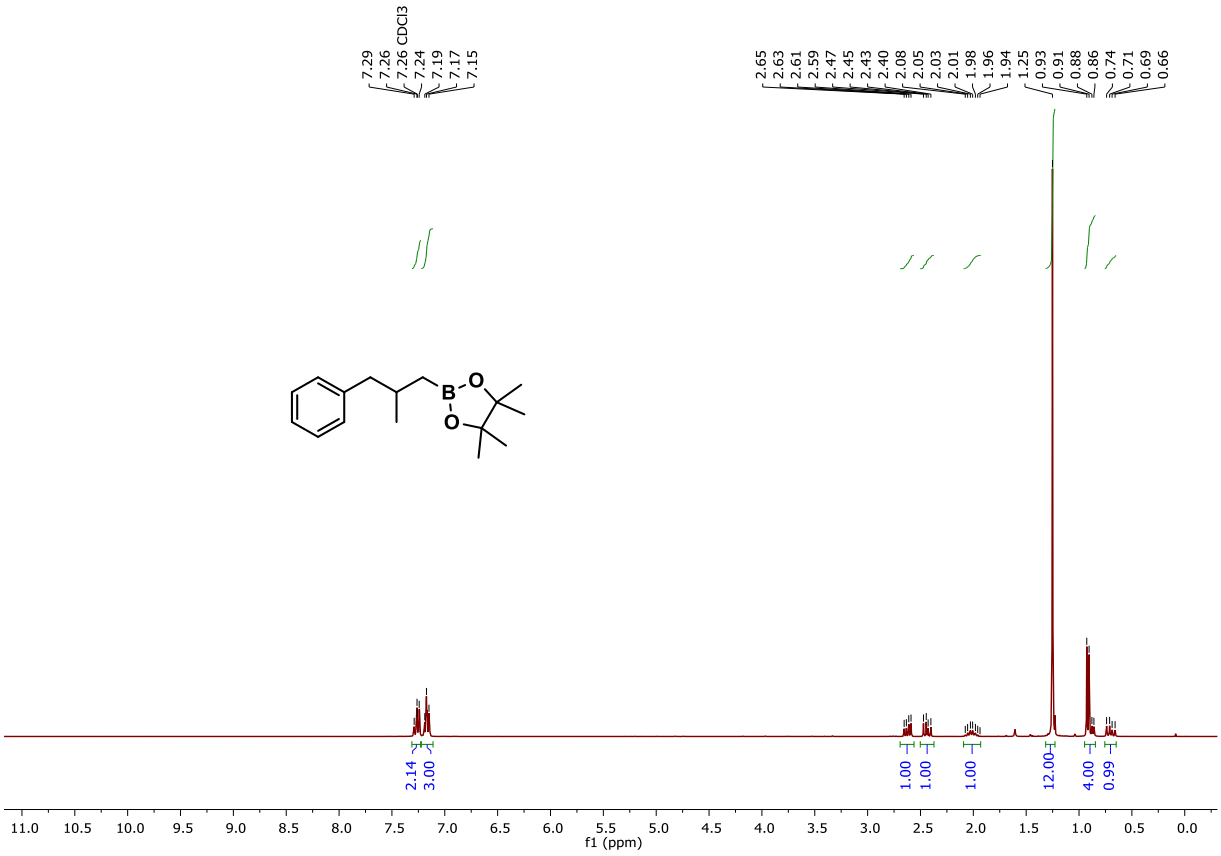


Figure S49. [1]H NMR spectrum of *4,4,5,5-tetramethyl-2-(2-methyl-3-phenylpropyl)-1,3,2-dioxaborolane* (**2x**).

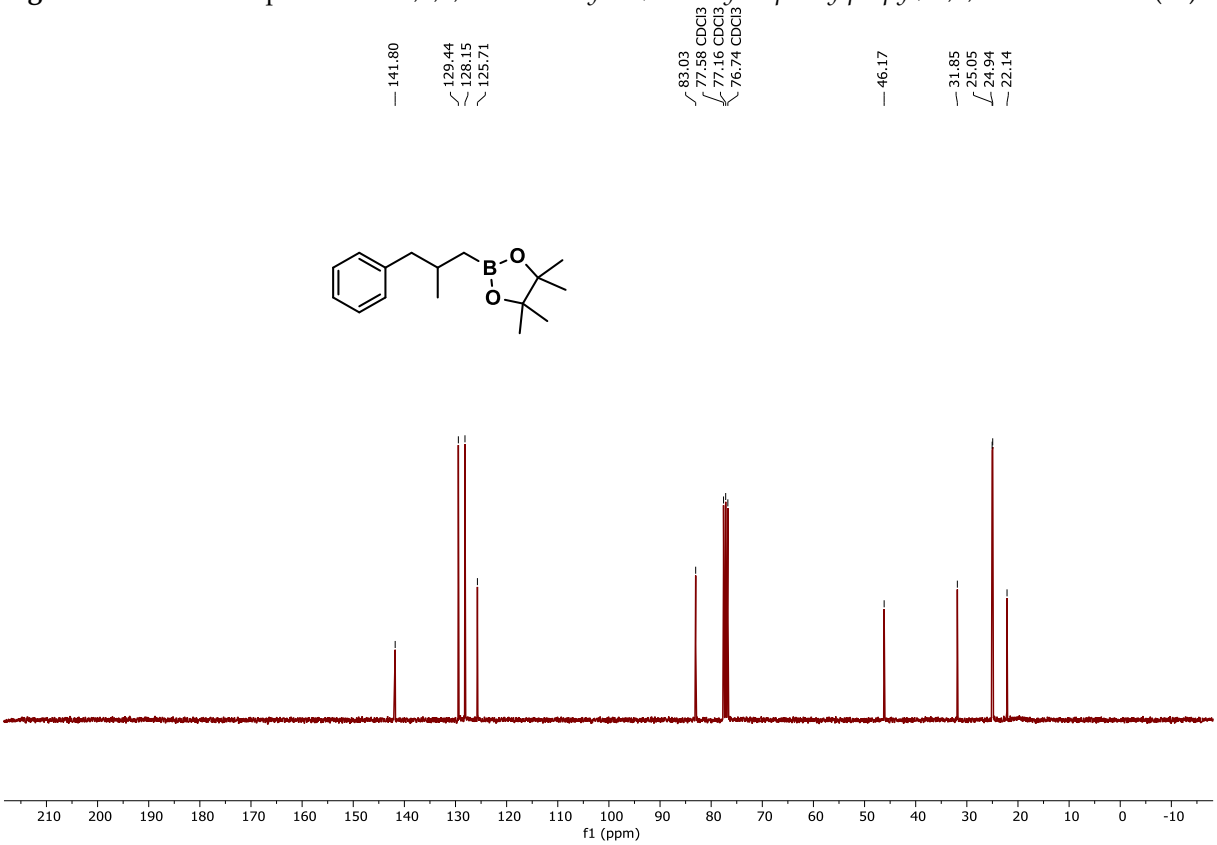


Figure S50. [13]C NMR spectrum of *4,4,5,5-tetramethyl-2-(2-methyl-3-phenylpropyl)-1,3,2-dioxaborolane* (**2x**).

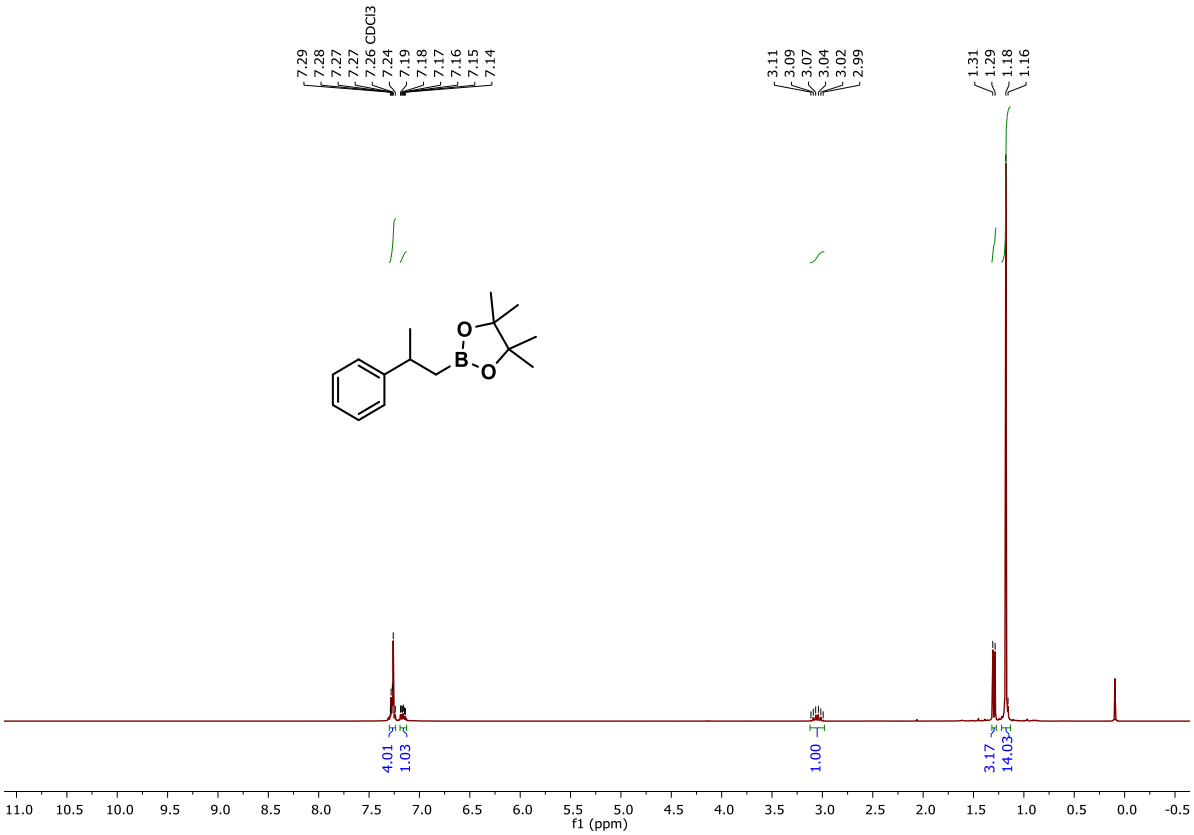


Figure S51. [1]H NMR spectrum of *4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane* (**2y**).

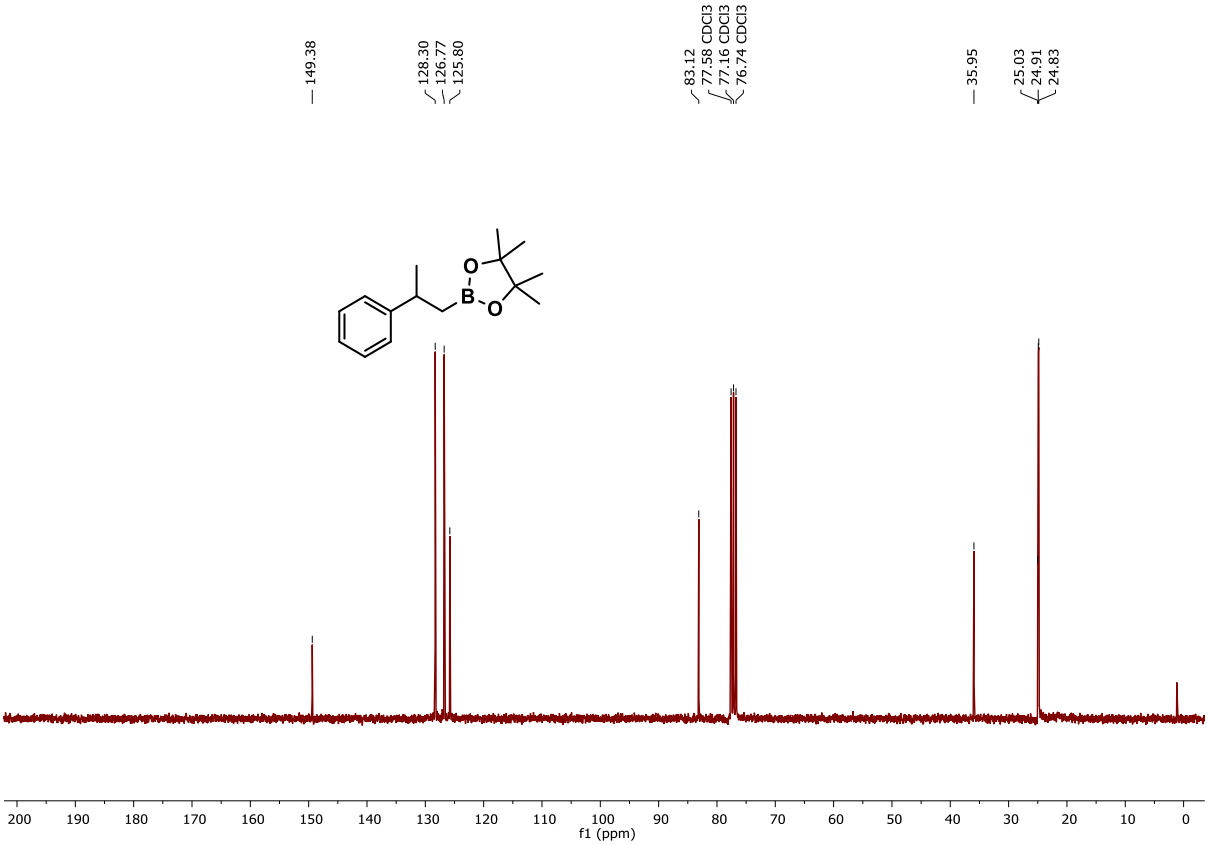


Figure S52. [13]C NMR spectrum of *4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane* (**2y**).

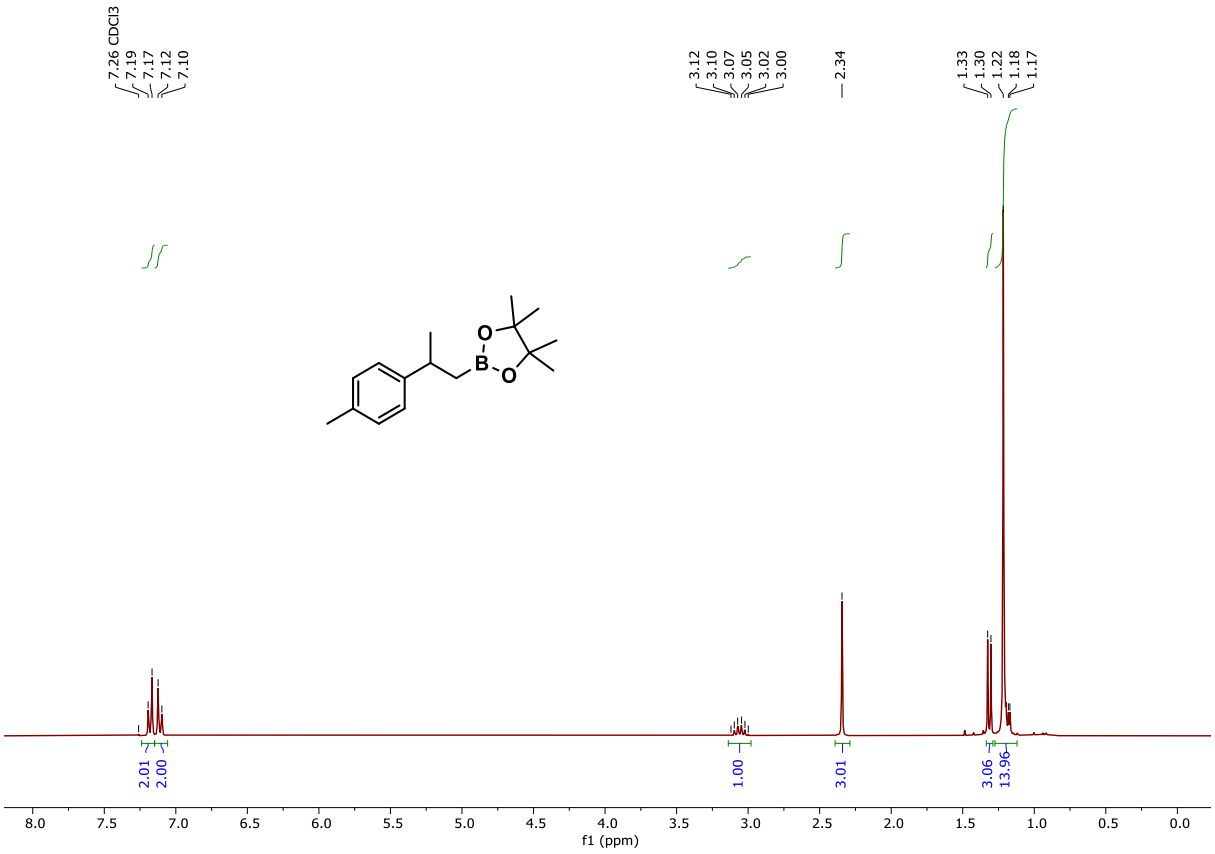


Figure S53. [1]H NMR spectrum of *4,4,5,5-tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane* (**2z**).

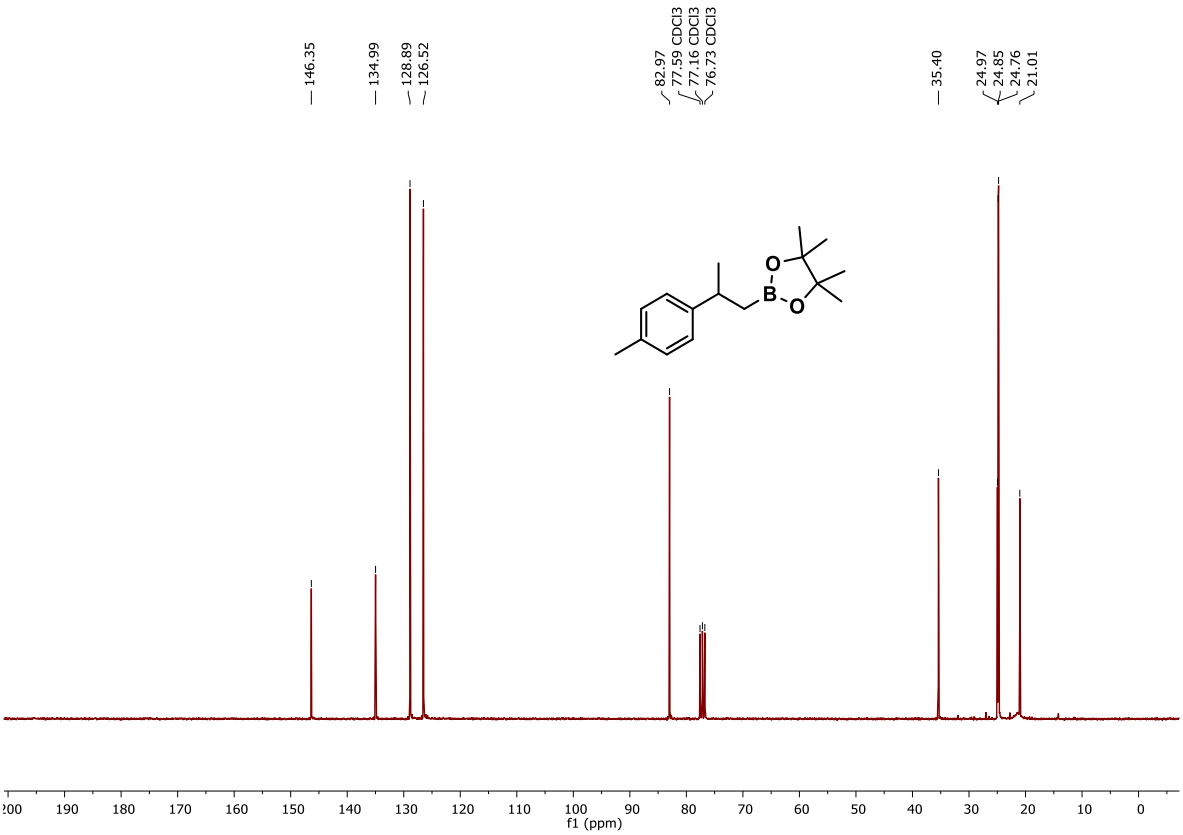


Figure S54. [13]C NMR spectrum of *4,4,5,5-tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane* (**2z**).

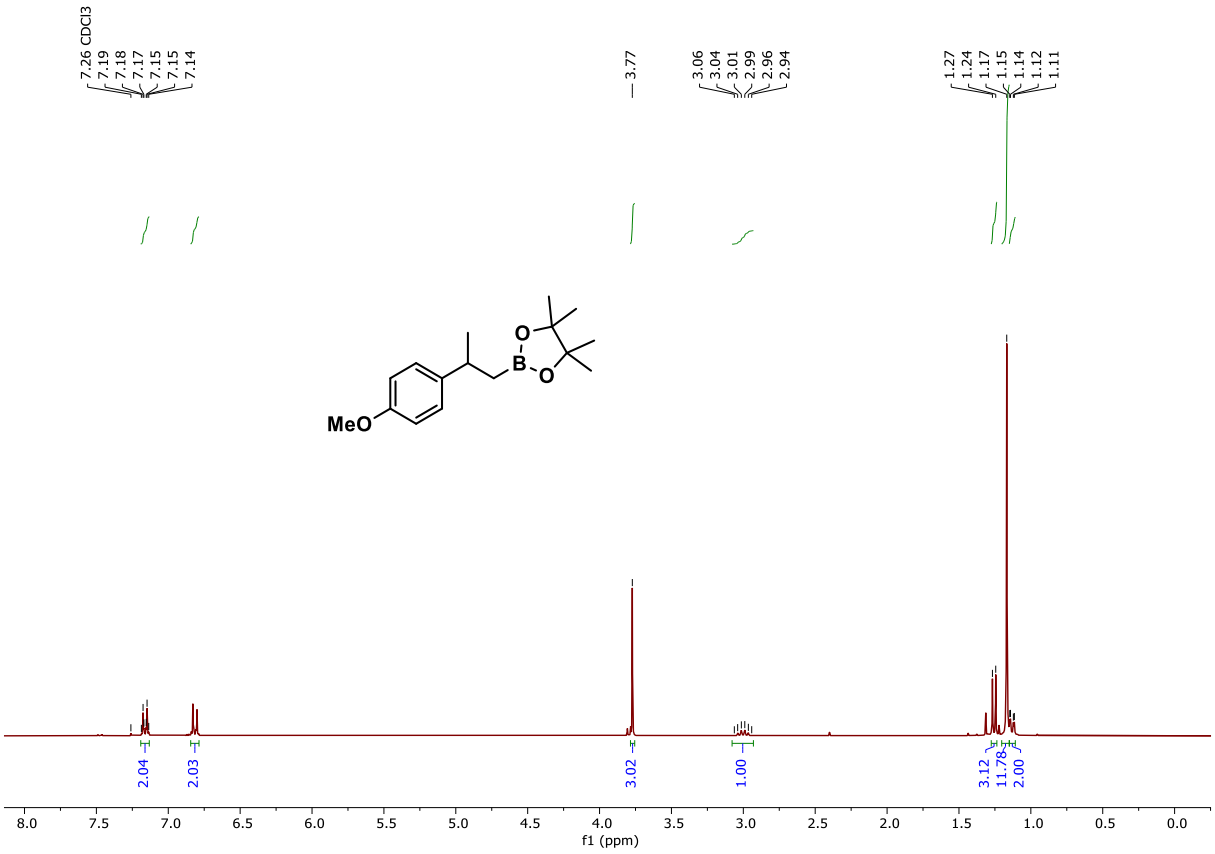


Figure S55. [1]H NMR spectrum of *4,4,5,5-tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane* (**2aa**).

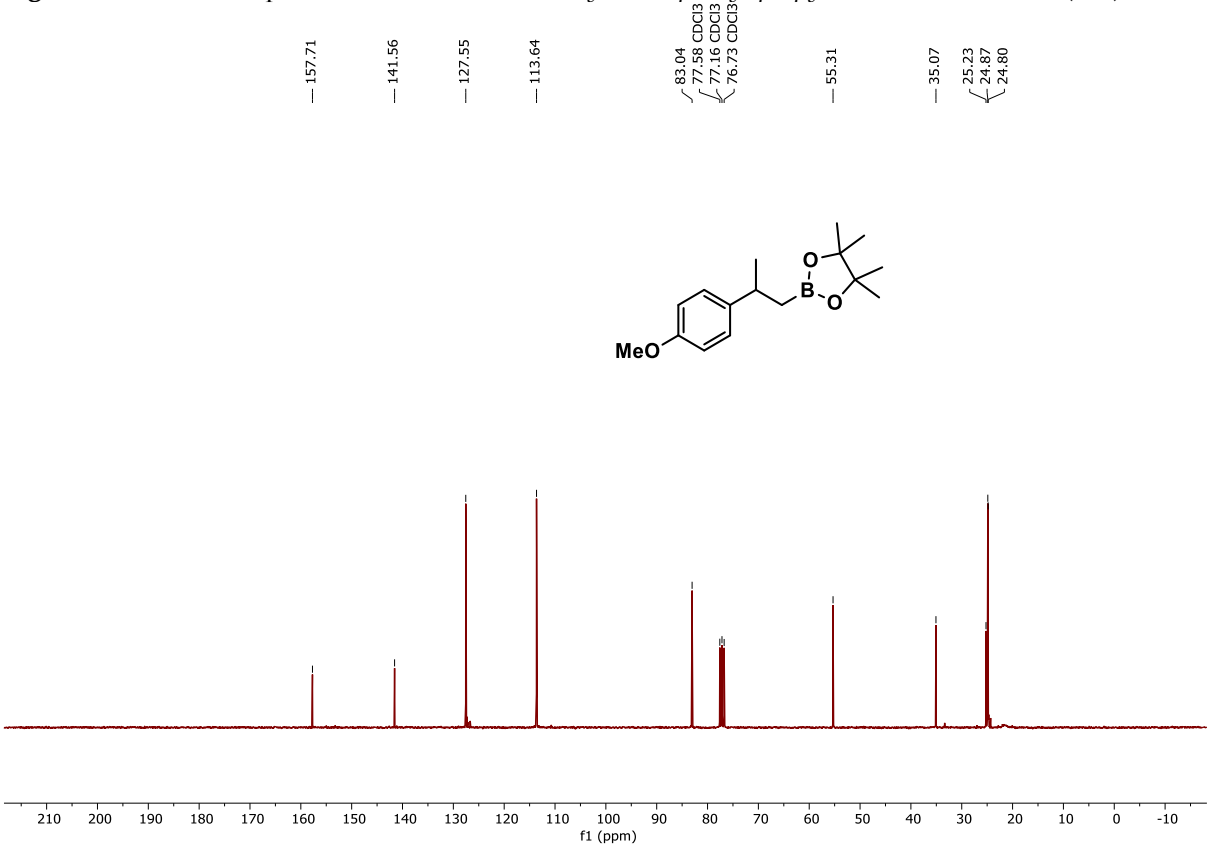


Figure S56. [13]C NMR spectrum of *4,4,5,5-tetramethyl-2-(2-(p-tolyl)propyl)-1,3,2-dioxaborolane* (**2aa**).

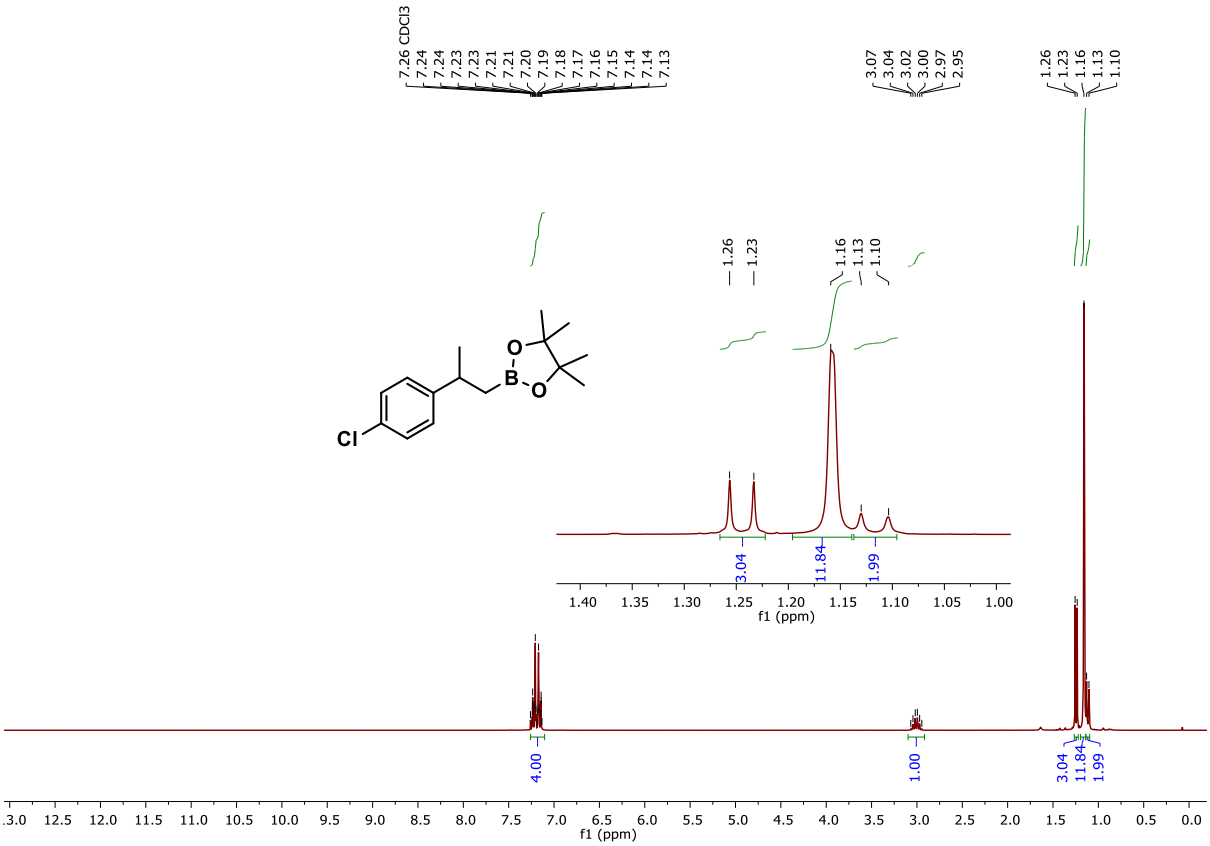


Figure S57. [1]H NMR spectrum of *2-(2-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ab**).

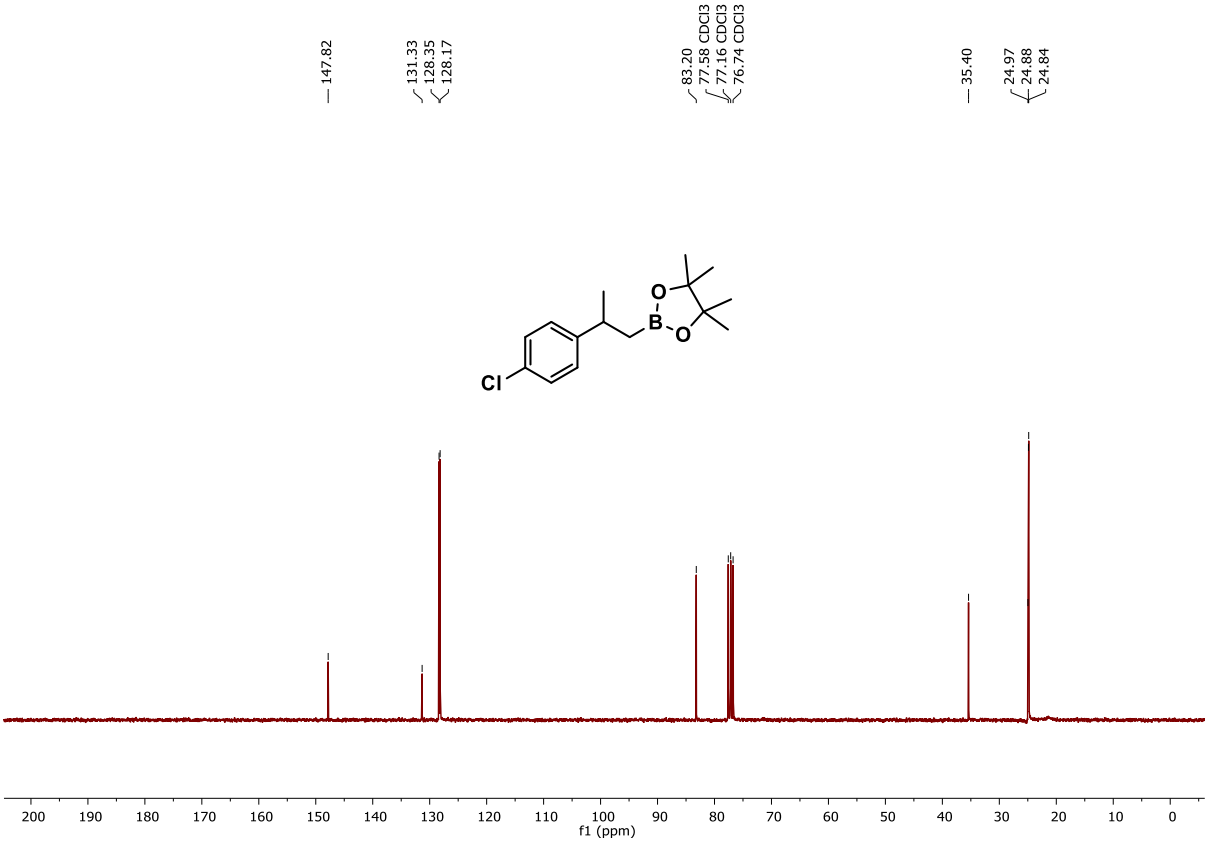


Figure S58. [13]C NMR spectrum of *2-(2-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ab**).

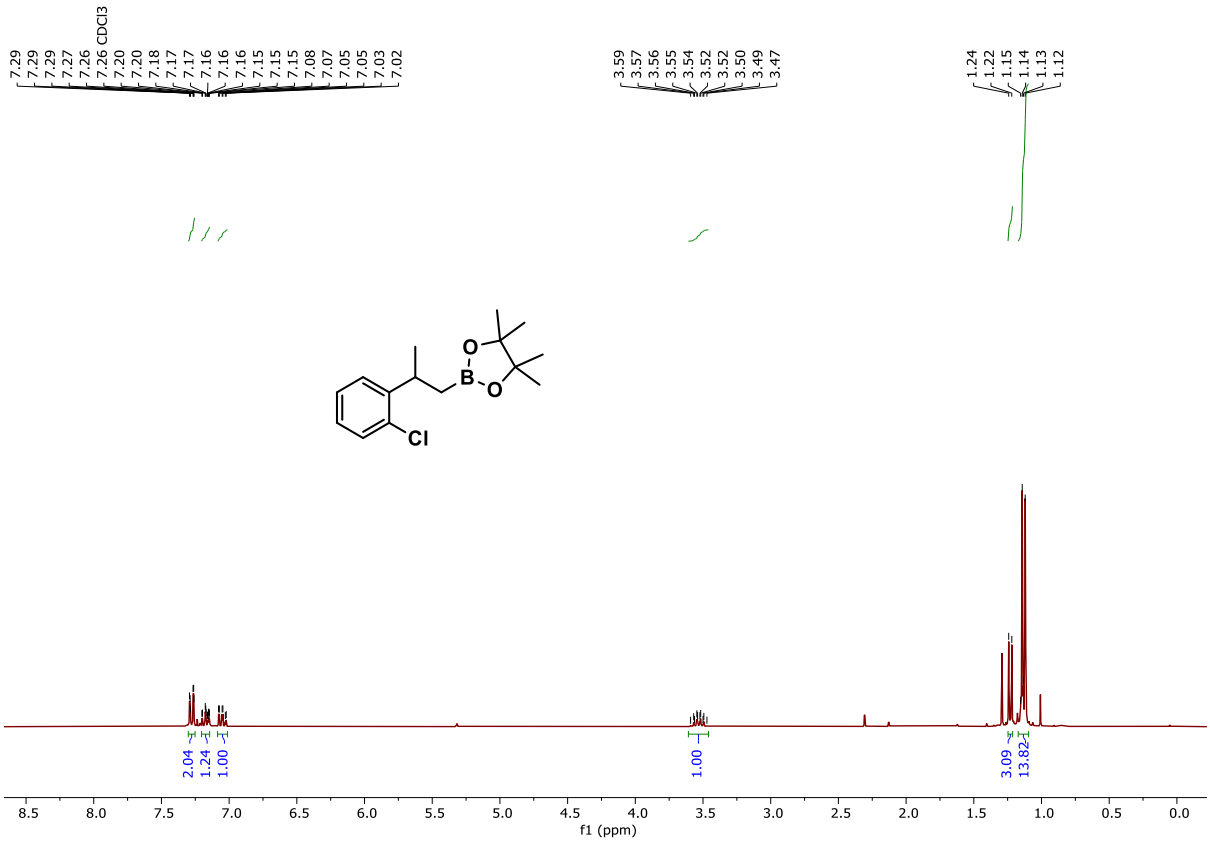


Figure S59. [1]H NMR spectrum of *2-(2-(2-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ac**).

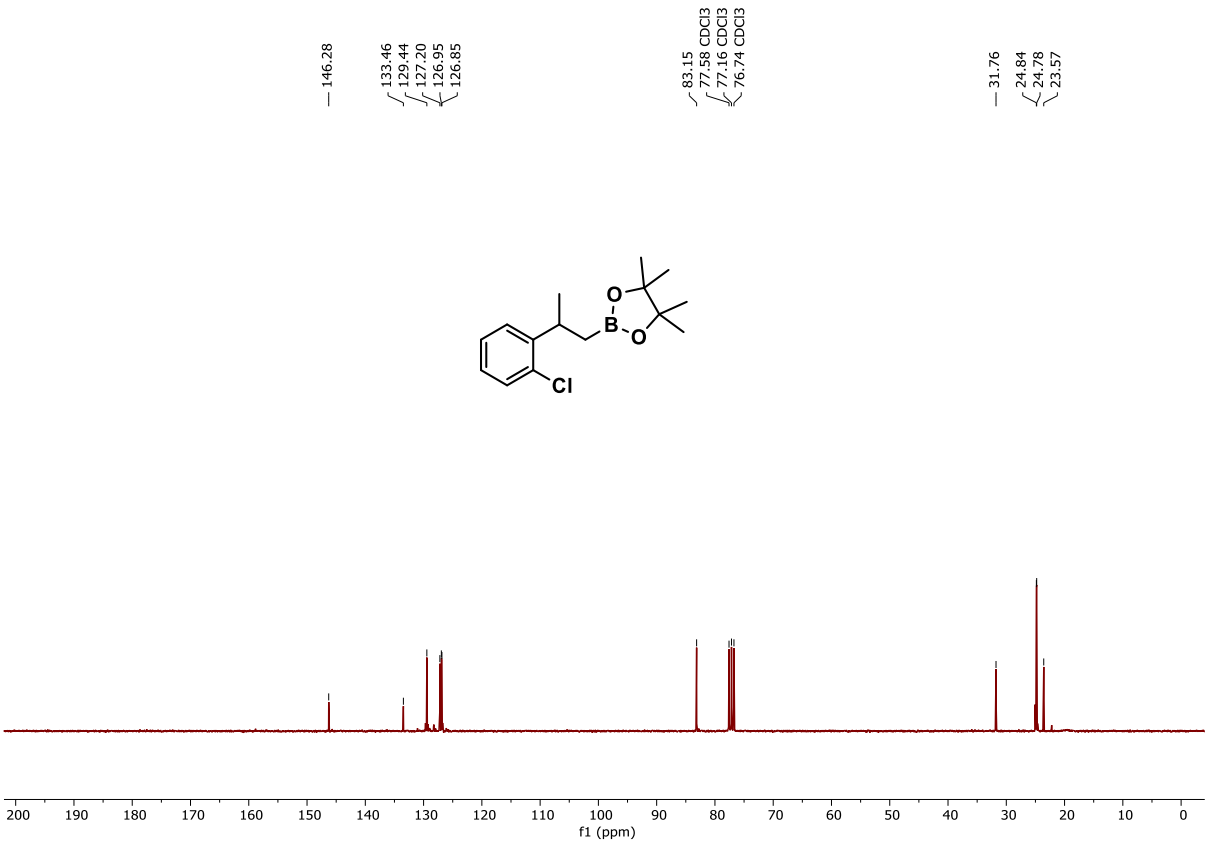


Figure S60. [13]C NMR spectrum of *2-(2-(2-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ac**).

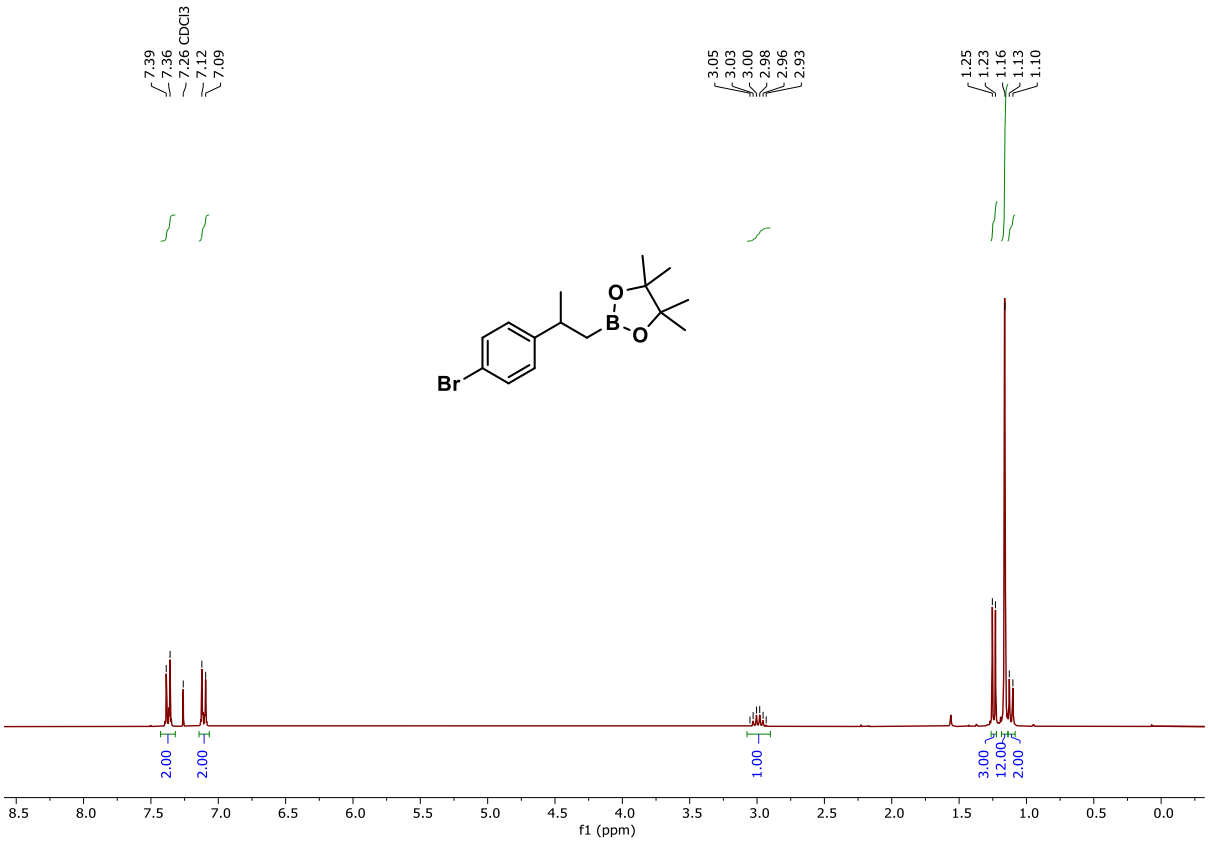


Figure S61. [1]H NMR spectrum of *2-(2-(4-bromoophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ad**).

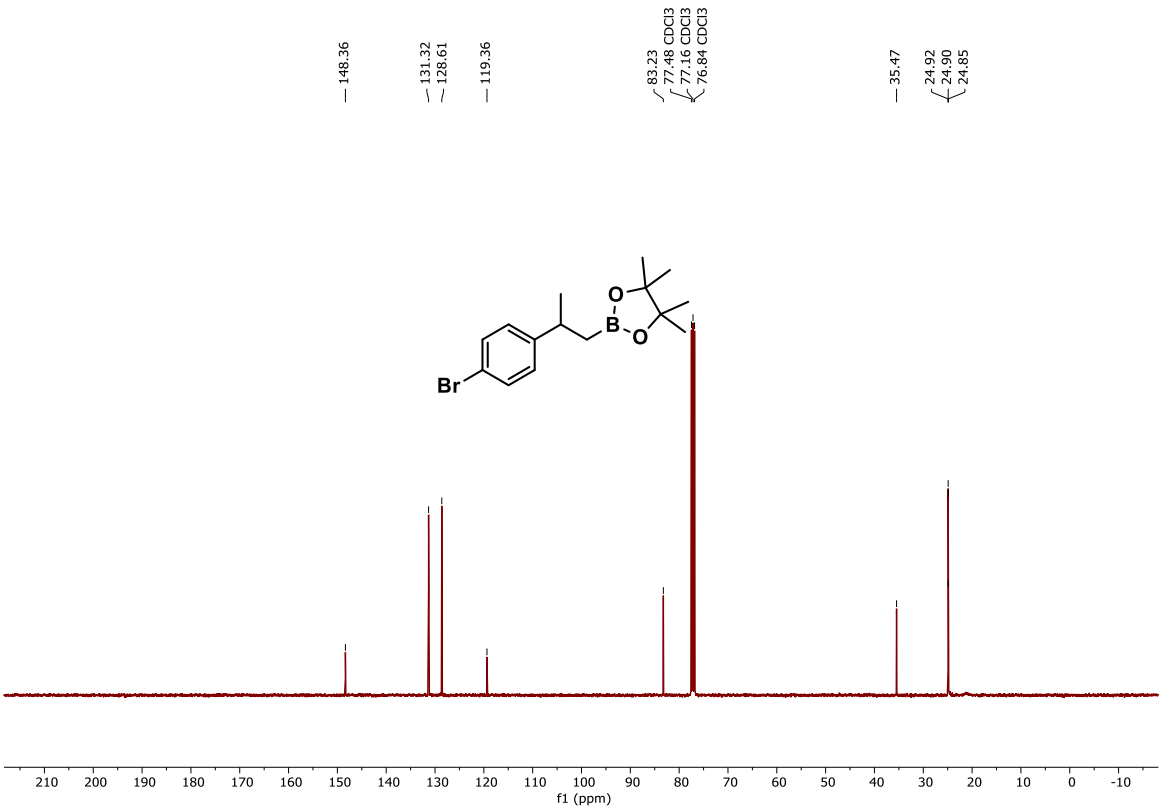


Figure S62. [13]C NMR spectrum of *2-(2-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ad**).

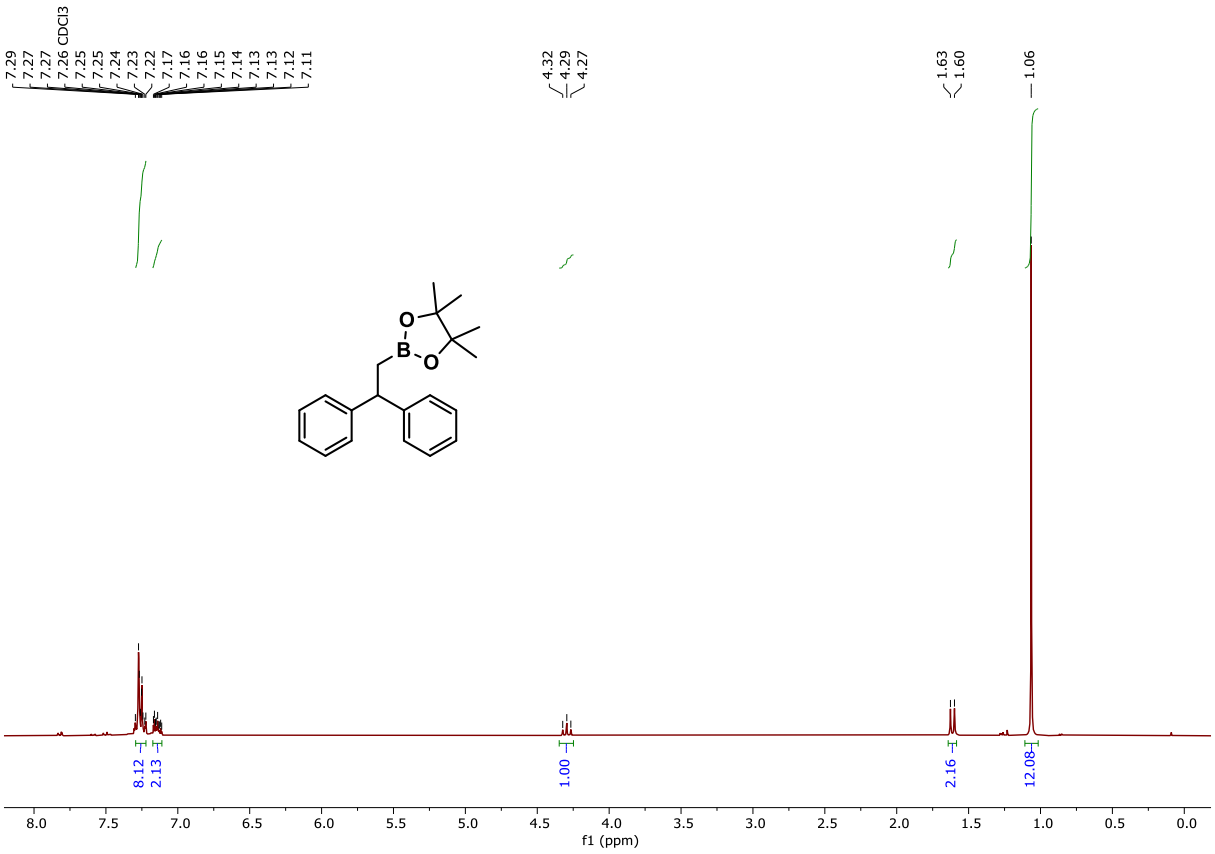


Figure S63. [1]H NMR spectrum of *2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ae**).

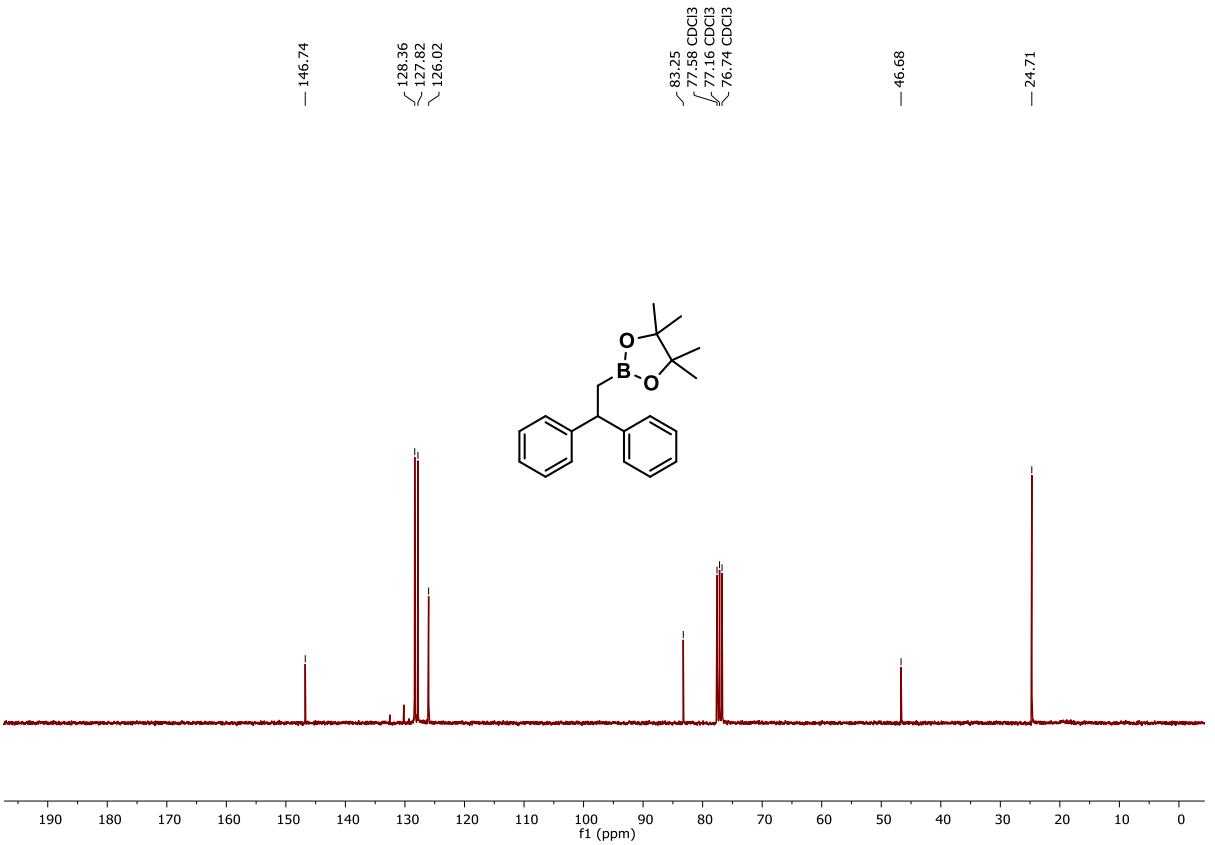


Figure S64. [13]C NMR spectrum of *2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**2ae**).

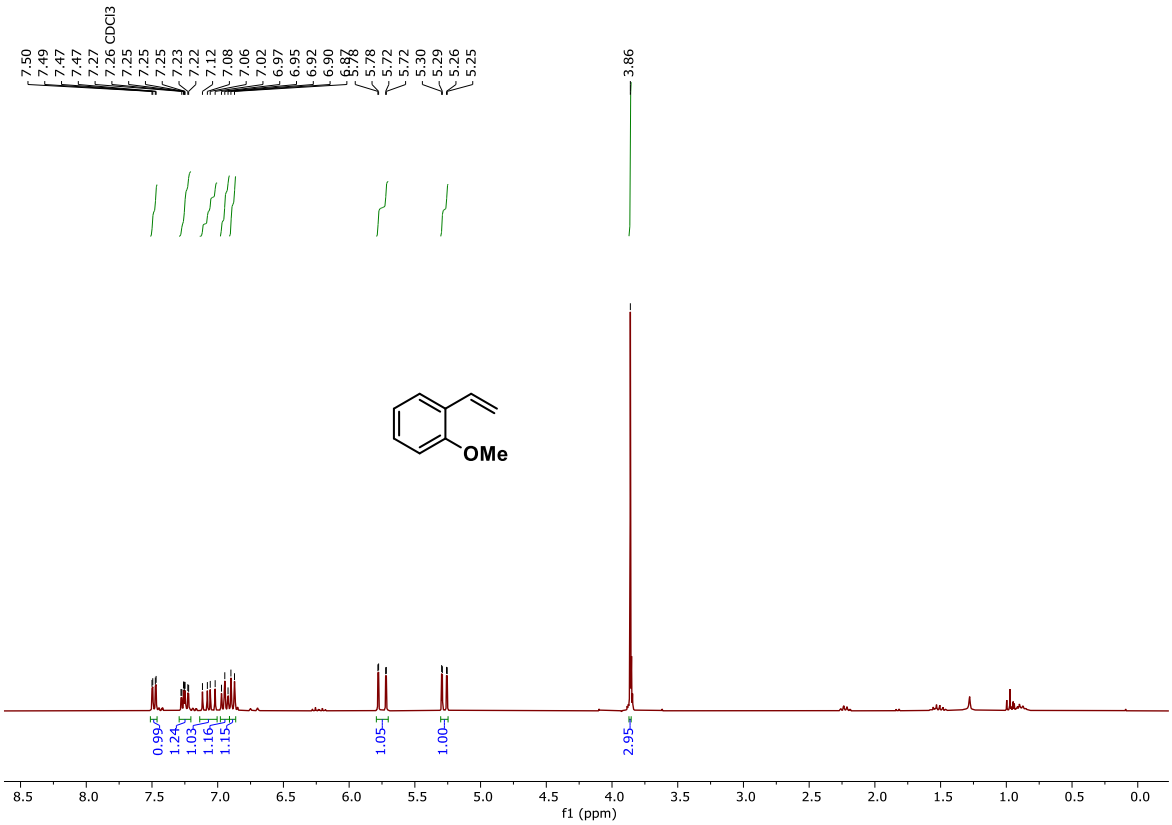


Figure S65. [1]H NMR spectrum of *1-methoxy-2-vinylbenzene* (**1l**).

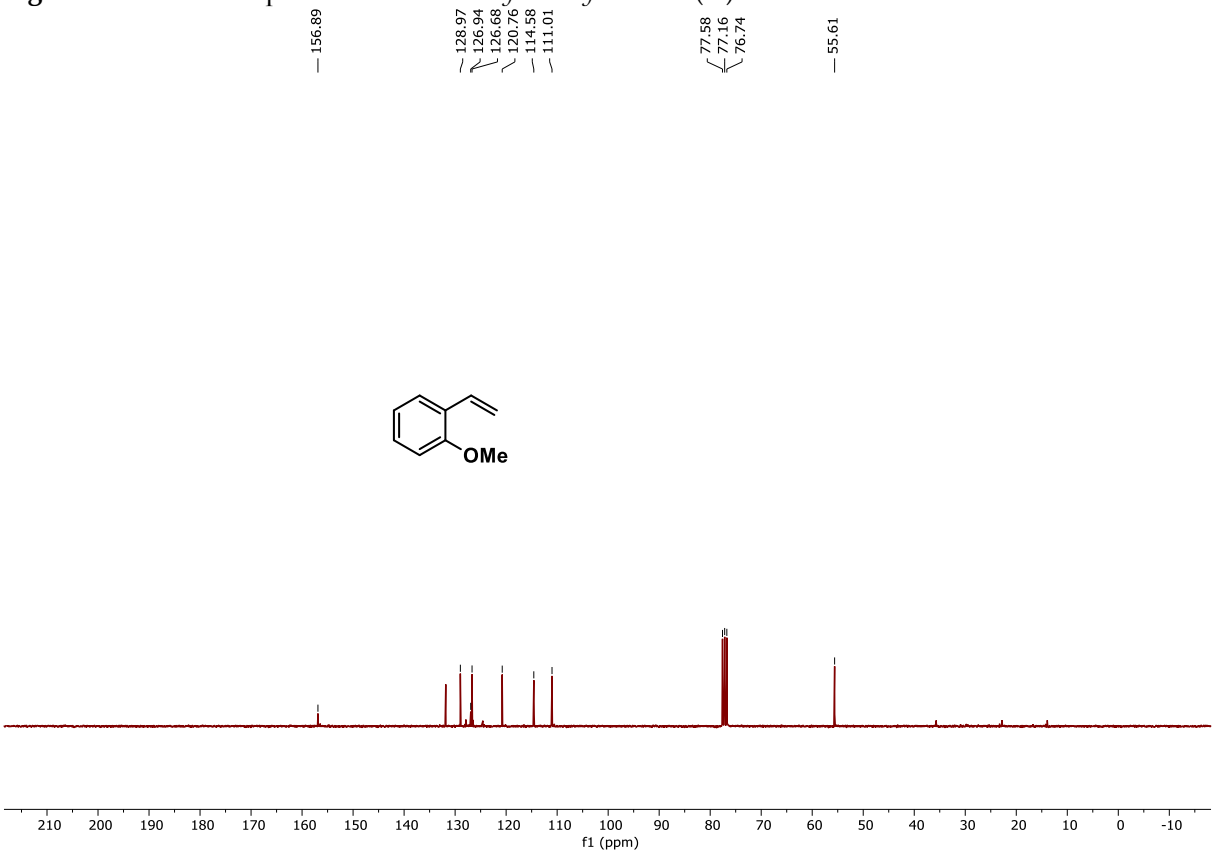


Figure S66. [13]C NMR spectrum of *1-methoxy-2-vinylbenzene* (**1l**).

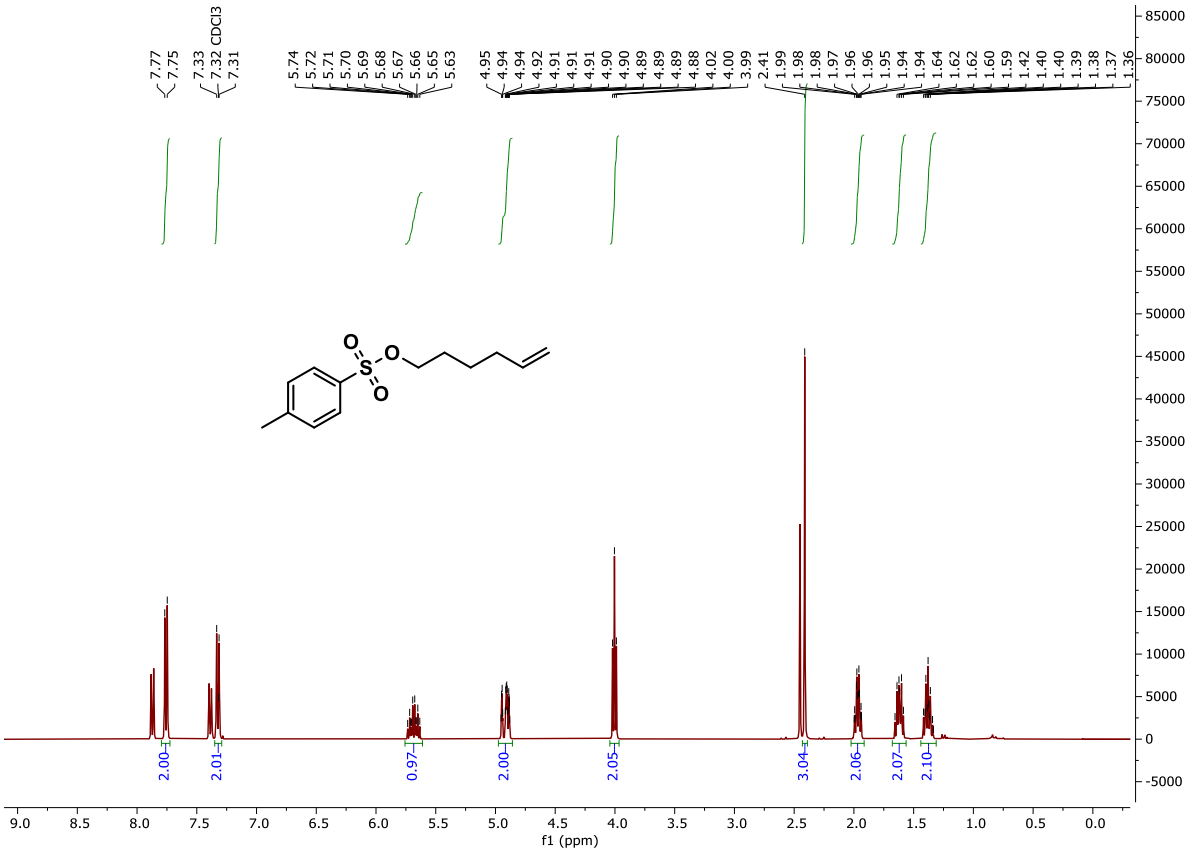


Figure S67. ^{1}H NMR spectrum of *hex-5-en-1-yl 4-methylbenzenesulfonate* (**1w**).

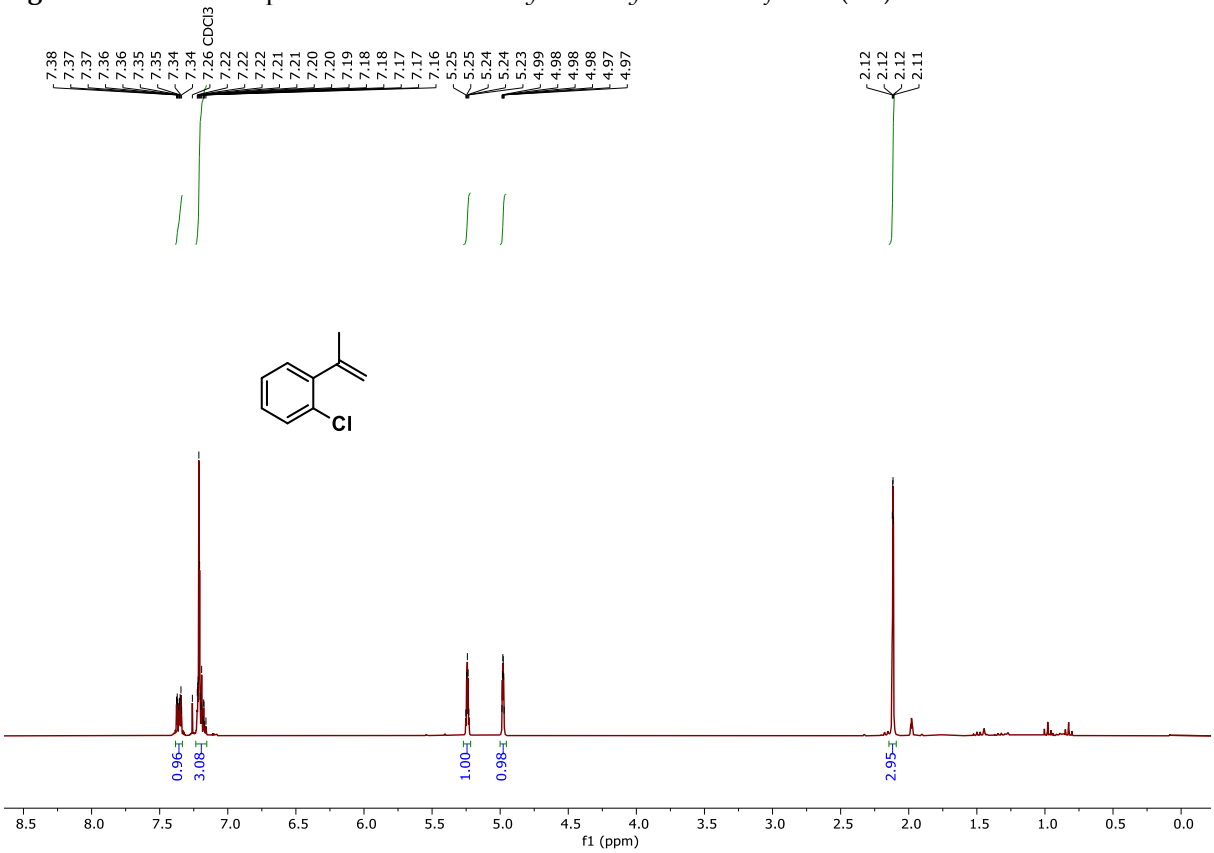


Figure S68. ^{1}H NMR spectrum of *1-chloro-2-isopropenylbenzene* (**1ac**).

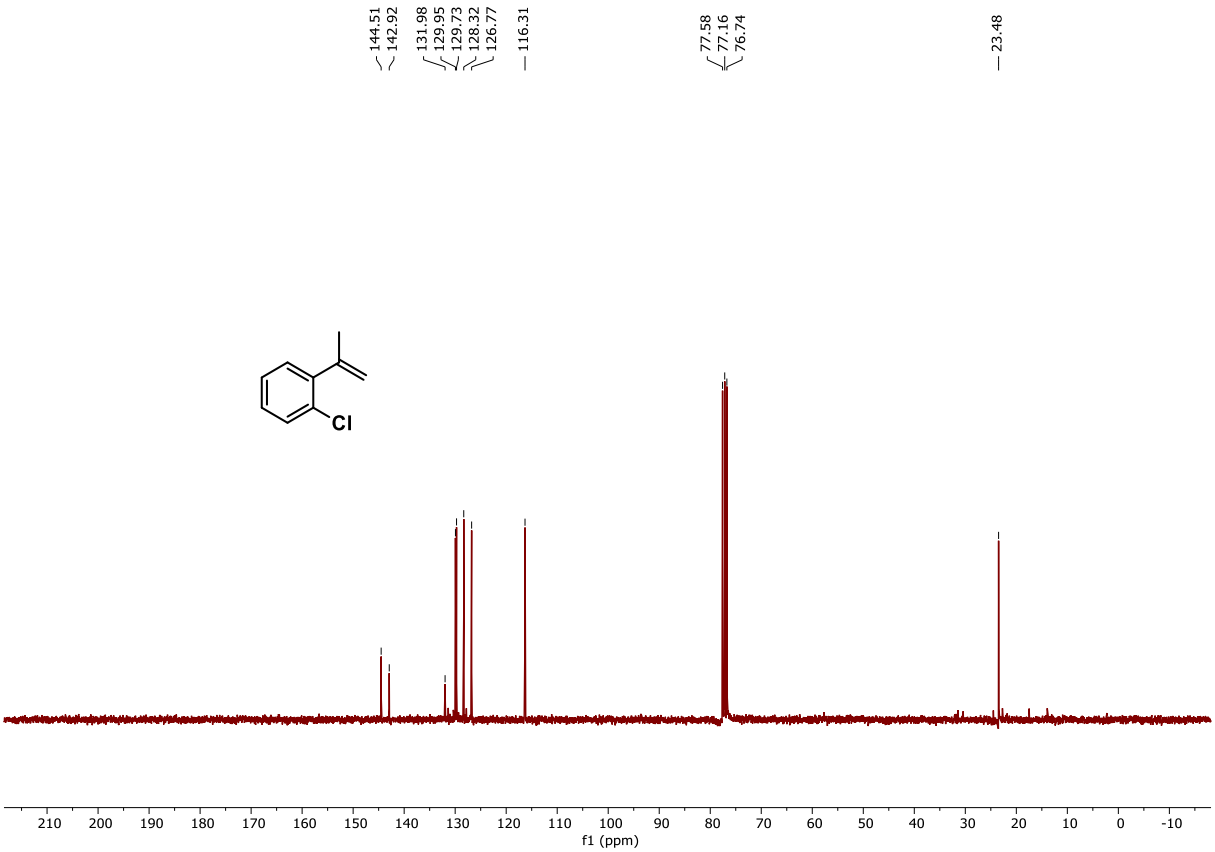


Figure S69. [13]C NMR spectrum of *1-chloro-2-isopropenylbenzene* (**1ac**).

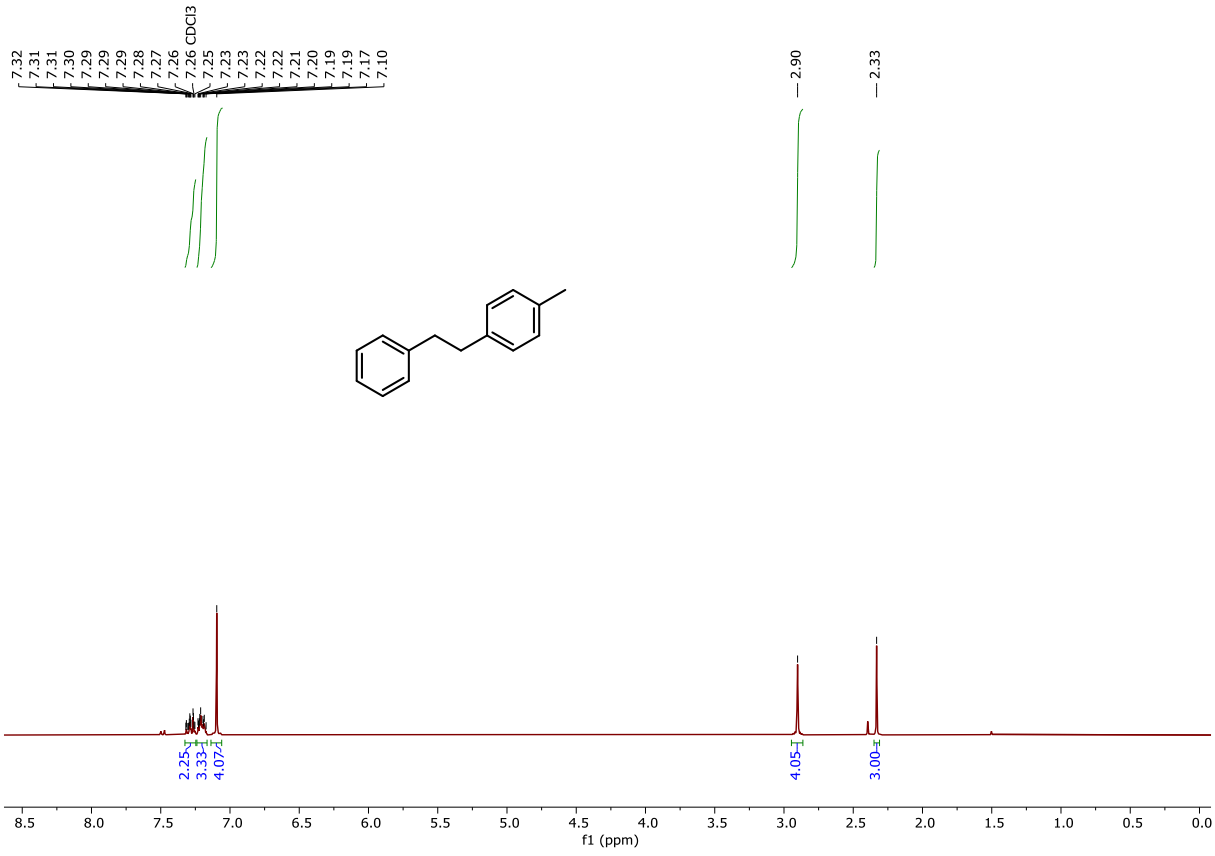


Figure S70. [1]H NMR spectrum of *1-methyl-4-(2-phenylethyl)benzene* (**4**).

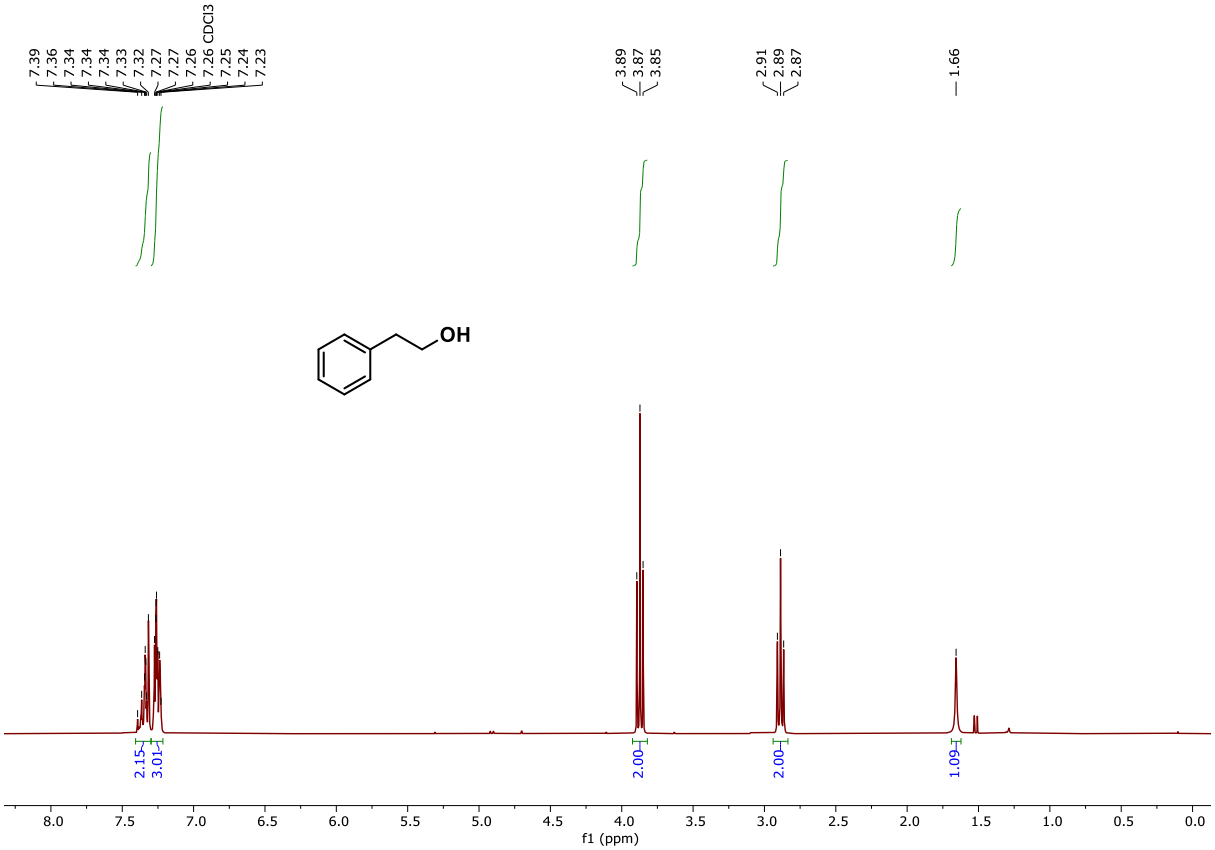


Figure S71. ^{1}H NMR spectrum of *2-Phenylethanol* (**5**).

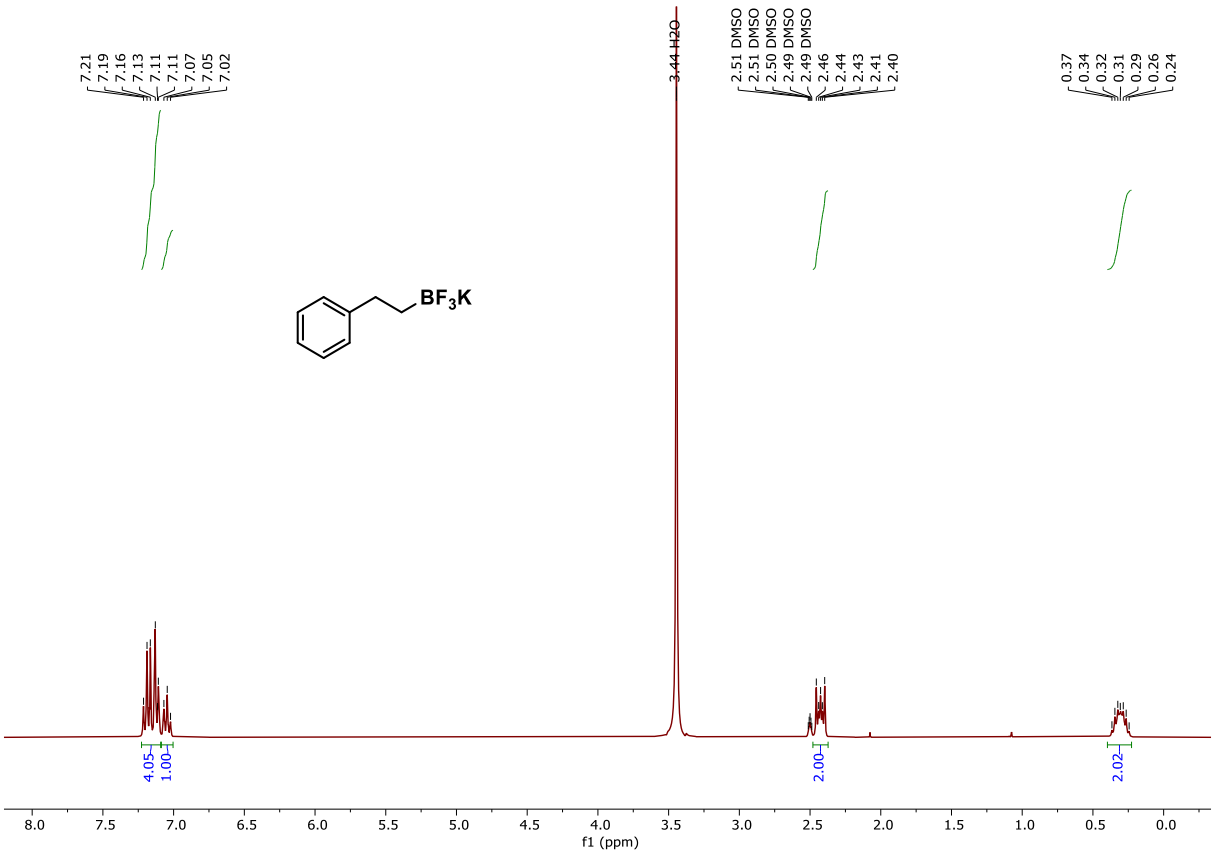


Figure S72. [1]H NMR spectrum of *potassium phenethyltrifluoroborate* (**5**).

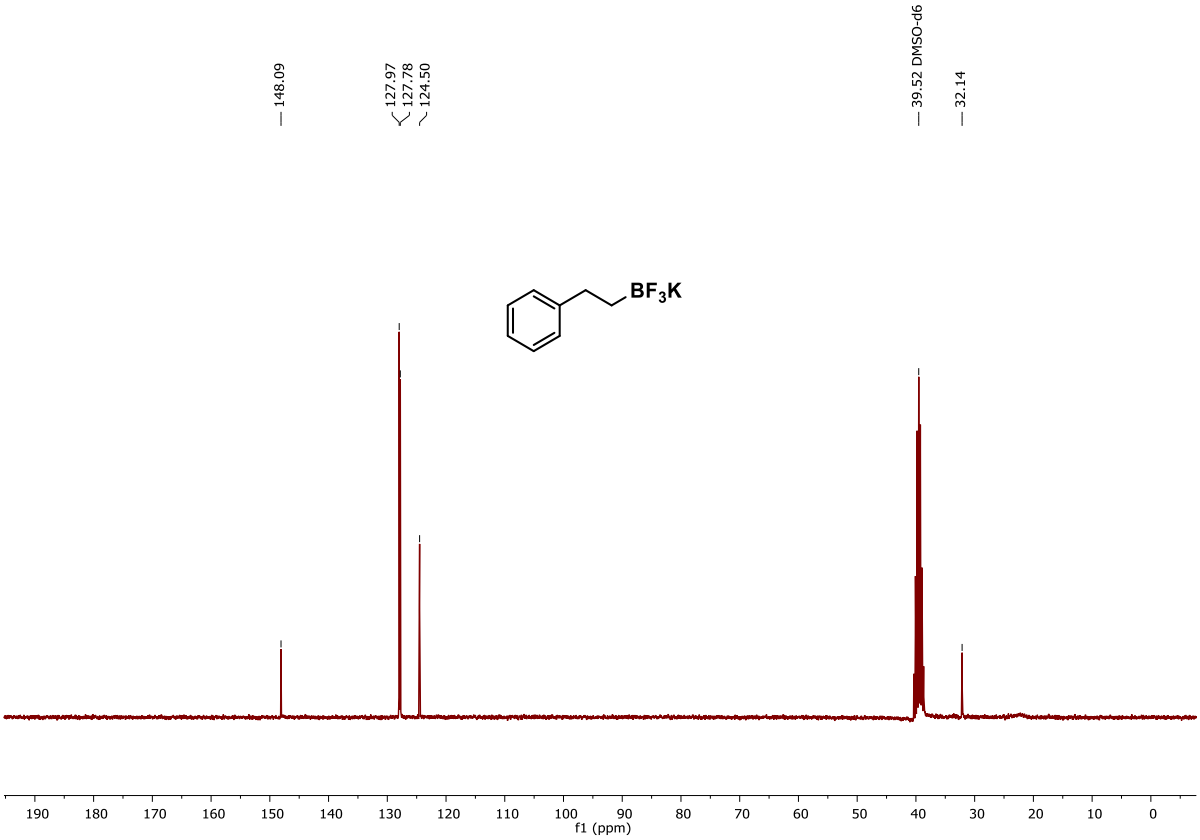


Figure S73. [13]C NMR spectrum of *potassium phenethyltrifluoroborate* (**6**).

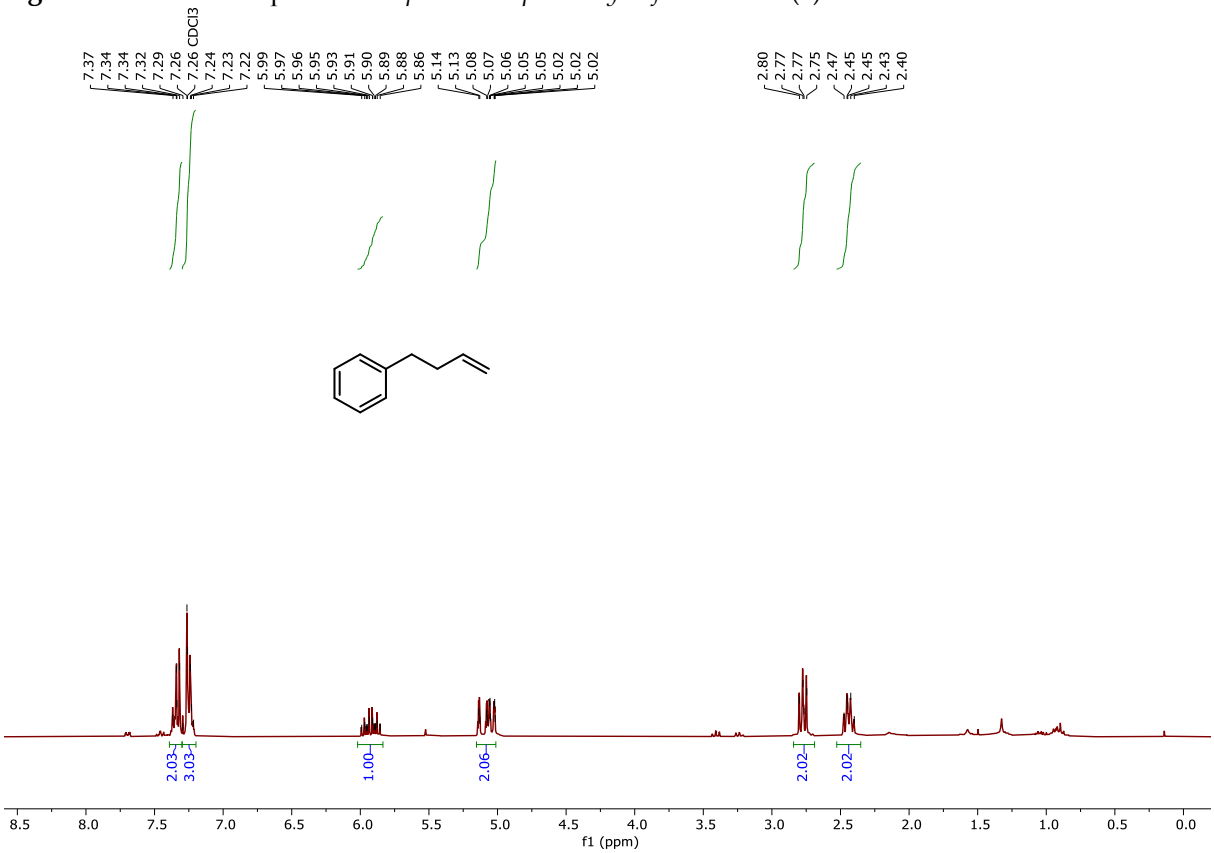


Figure S74. [1]H NMR spectrum of *but-3-enylbenzene* (**7**).

7. NMR spectra for mechanistic studies.

[EMPyrr][OTf] - 1-Ethyl-1-methylpyrrolidinium trifluoromethanesulfonate (IL10)

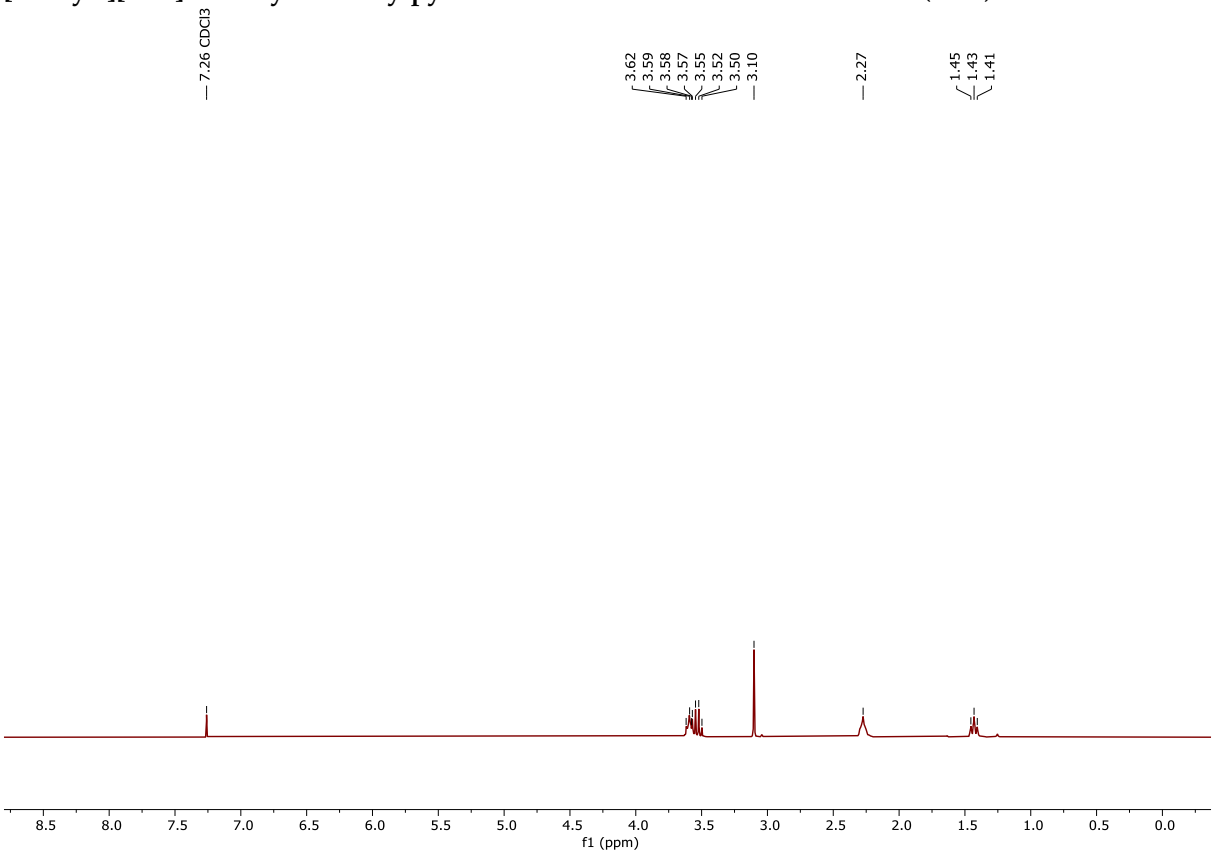


Figure S75. ^{1}H NMR (300MHz, $CDCl_3$, 25 °C). Spectrum of IL10.

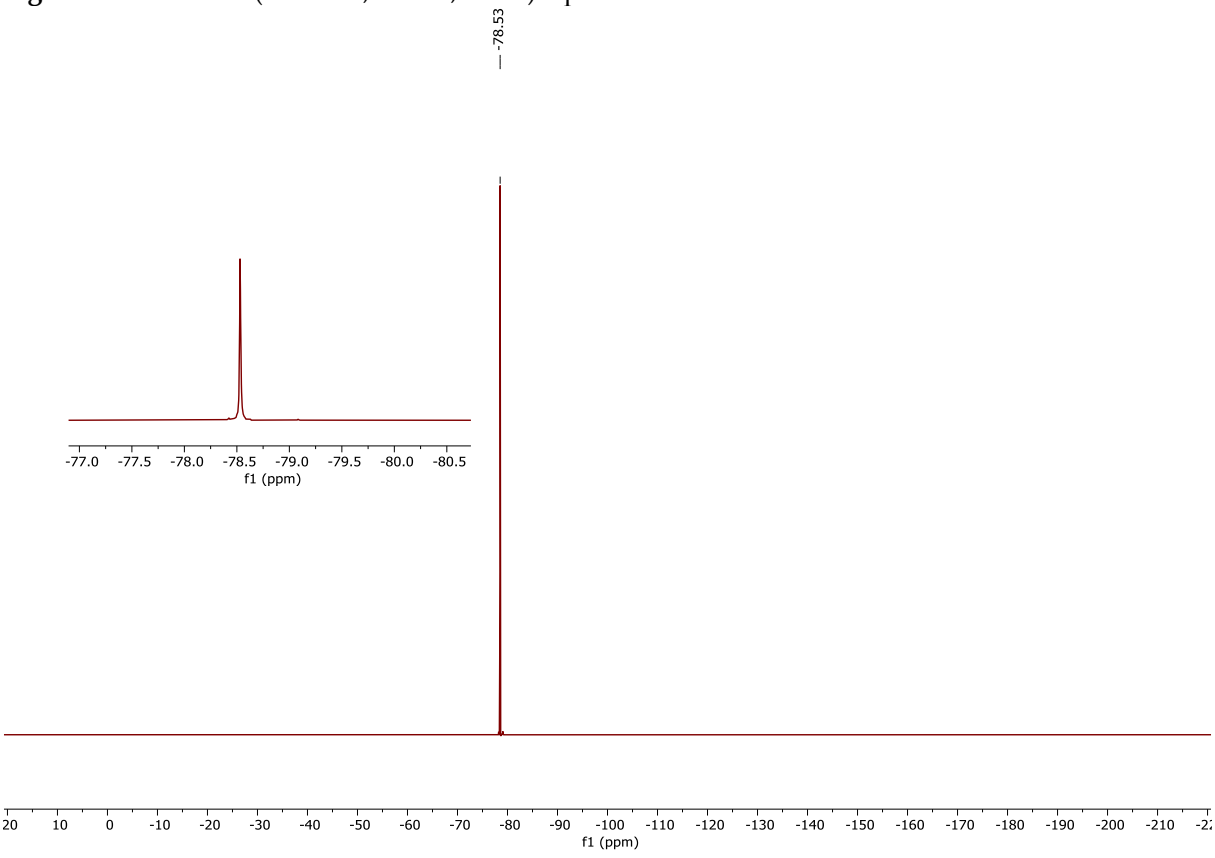


Figure S76. ^{19}F NMR (377MHz, $CDCl_3$, 25 °C). Spectrum of IL10.

HBpin

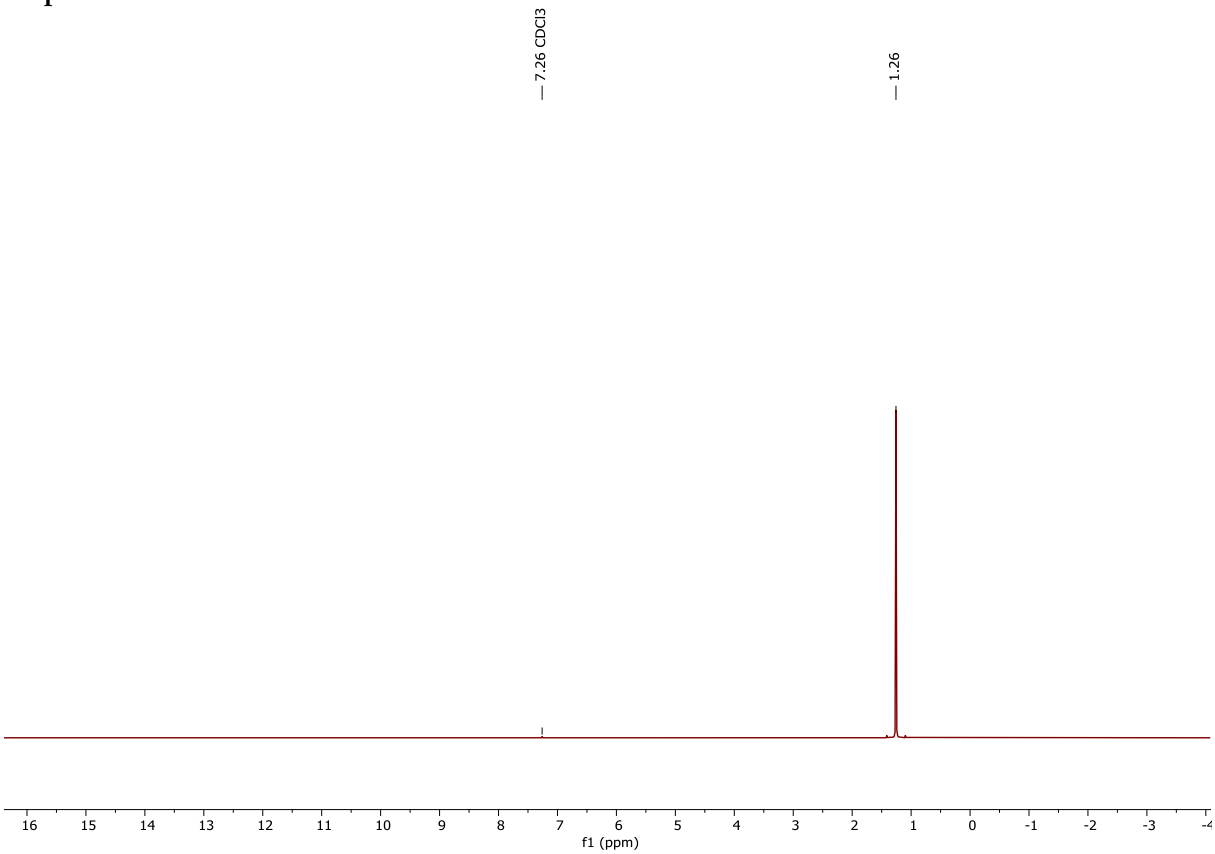


Figure S77. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). Spectrum of HBpin after distillation.

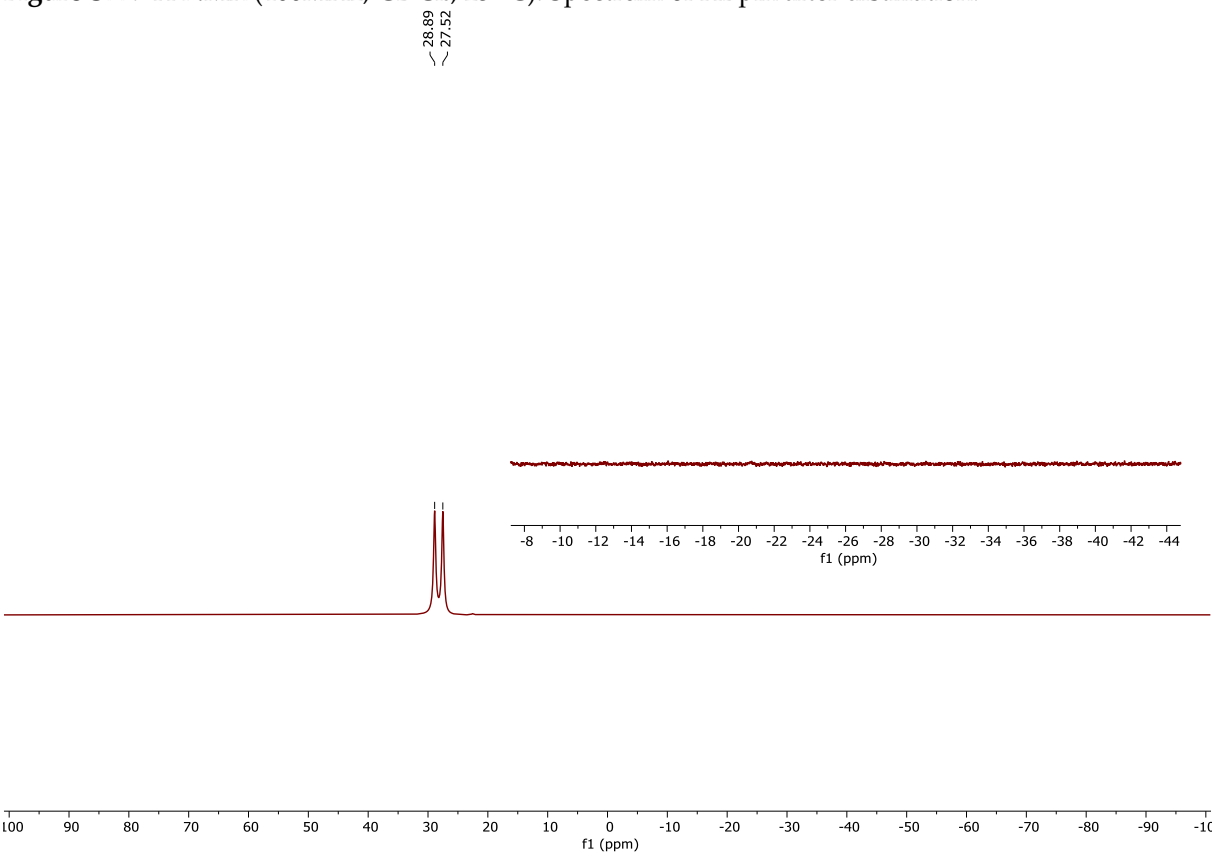


Figure S78. ^{11}B NMR (128MHz, $CDCl_3$, 25 °C). Spectrum of HBpin after distillation. BH_3, BH_3•SMe_2 or $[BH_4]^-$ was not observed.

TMEDA - *N,N,N',N'*-Tetramethylethylenediamine

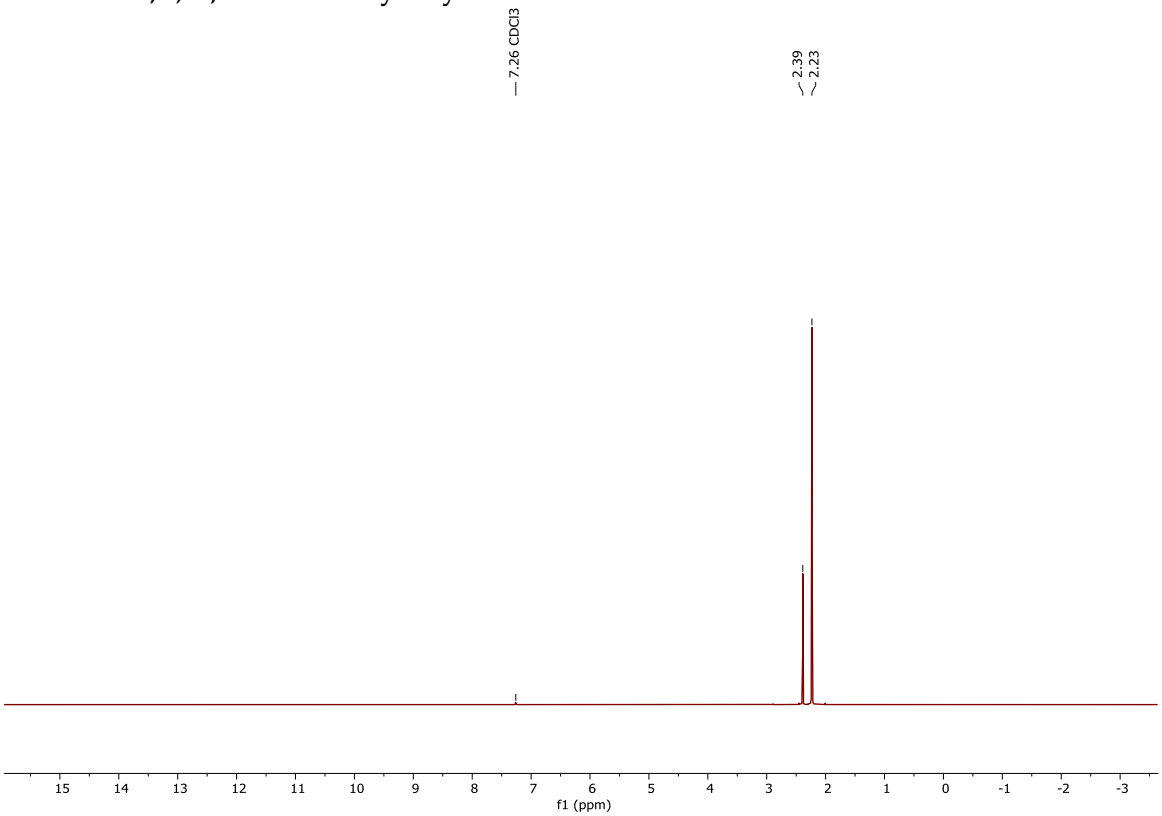


Figure S79. ^1H NMR (300MHz, $CDCl_3$, 25 °C). Spectrum of TMEDA.

IL10+Styrene(1a)+HBpin control experiment.

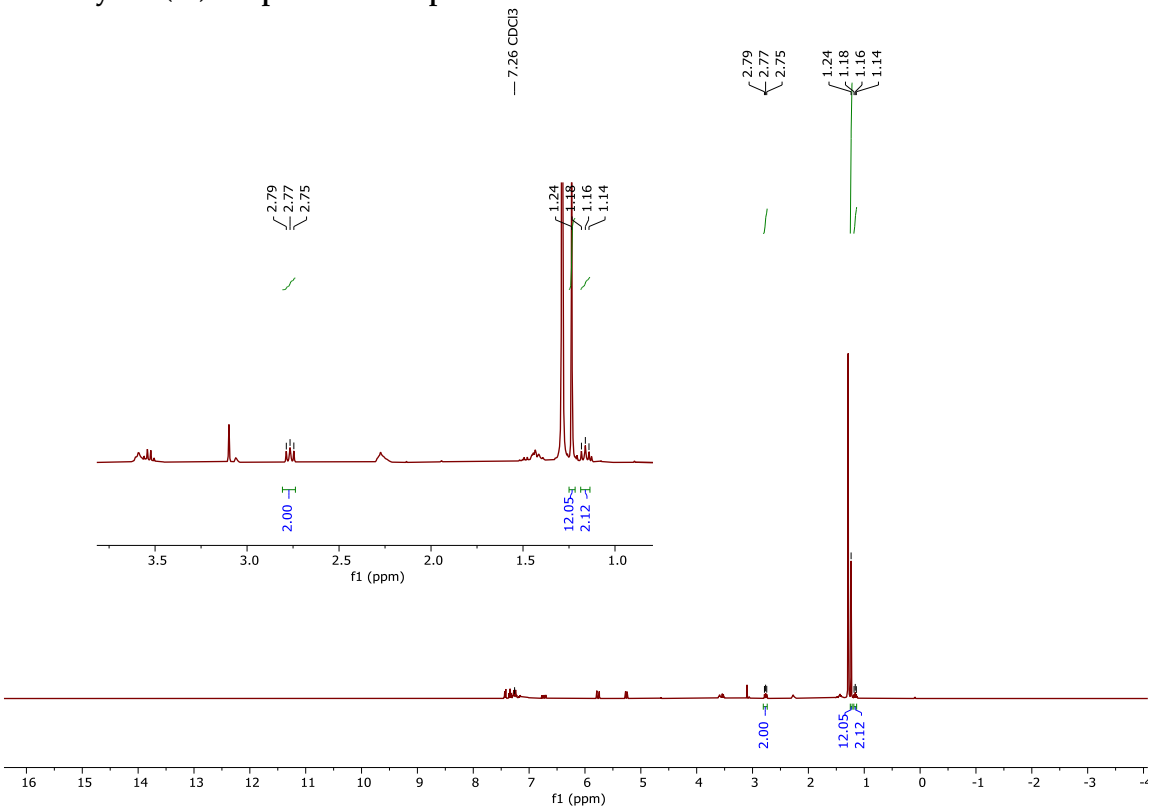


Figure S80. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). IL10+Styrene (**1a**)+HBpin control experiment**.** Reaction conditions: [IL]:[**1a**]:[HBpin] = 0.5:1:1, $CDCl_3$, inert atmosphere, 100 °C, 15 h. Reaction was performed in NMR tube. Formation of hydroboration product **2a** was observed.

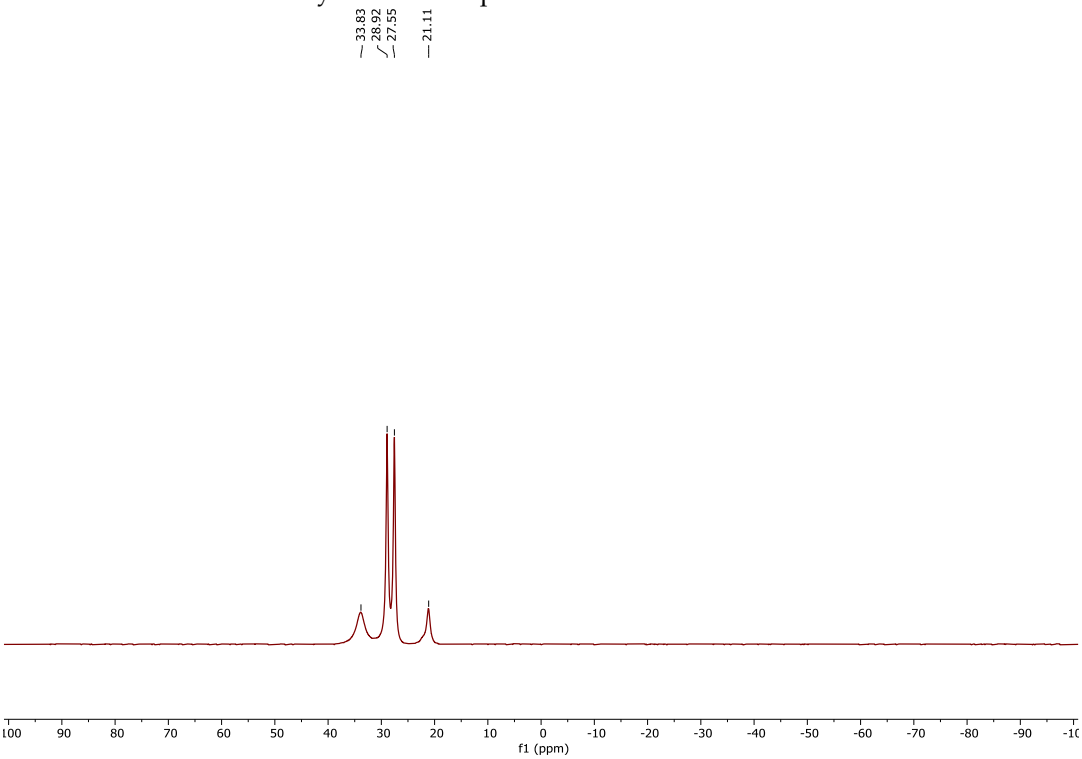


Figure S81. ^{11}B NMR (128MHz, $CDCl_3$, 25 °C). IL10+Styrene (**1a**)+HBpin control experiment**.** Reaction conditions: [IL]:[**1a**]:[HBpin] = 0.5:1:1, $CDCl_3$, inert atmosphere, 100 °C, 15 h. Reaction was performed in NMR tube. Signal at 33.83 ppm indicates hydroboration product **2a**. Signal at 21.11 ppm corresponds to pinBOTf.

IL10+HBpin (1:2) in room temperature (reactions were performed in NMR tube).

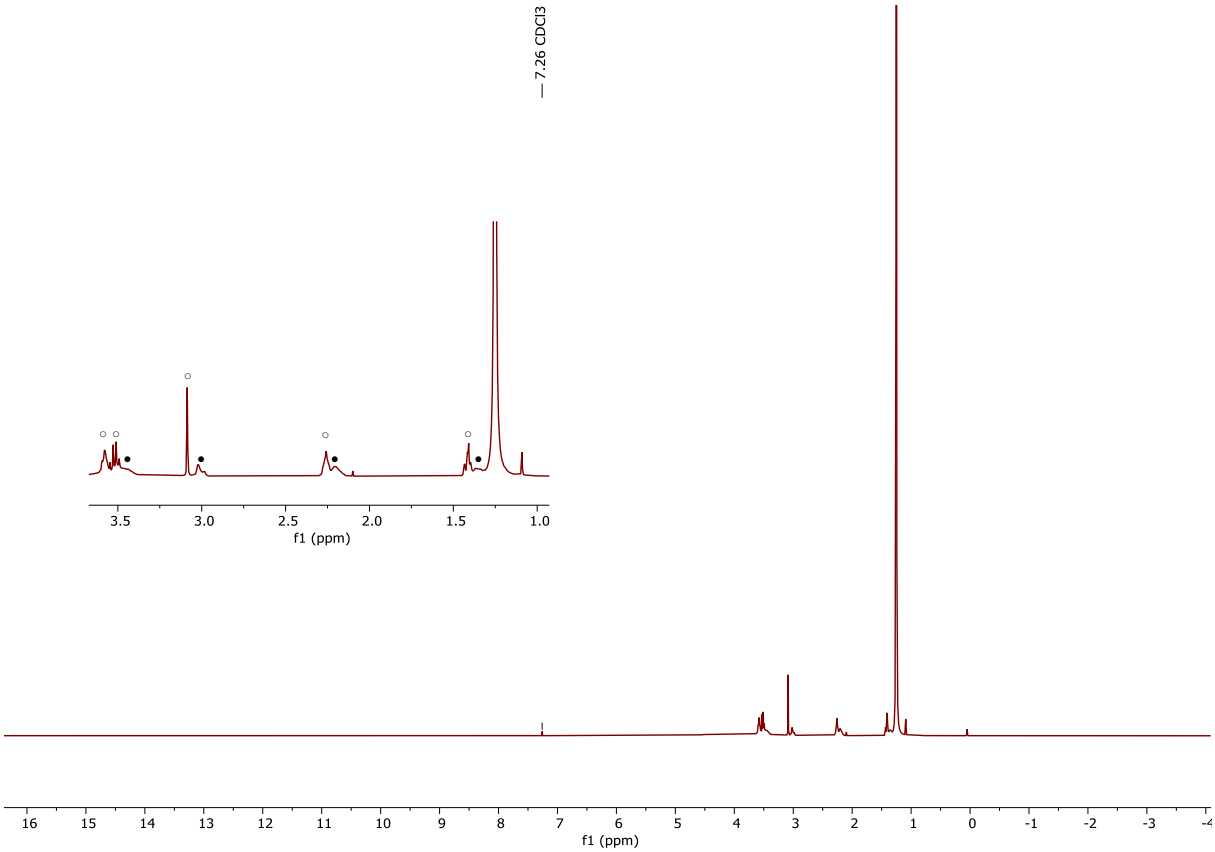


Figure S82. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (rt, 15 h). ○ Indicates IL10. ● Preasumbly indicates new signal originating from $[EMPyrr]^+$ ion.

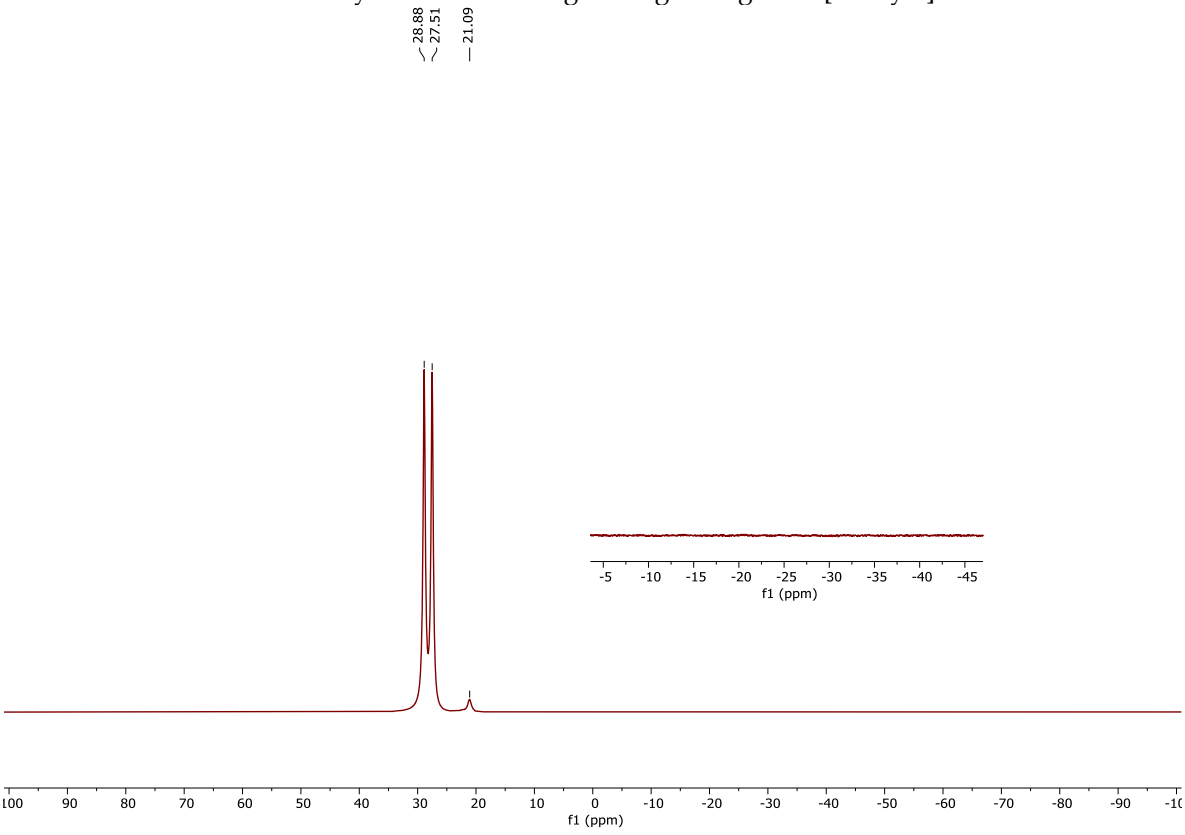


Figure S83. ^{11}B NMR (128MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (rt, 15 h). Doublet at 28.88 ppm and 27.51 ppm corresponds to HBpin. Signal at 21.09 ppm corresponds to pinBOTf. BH_3 or $[BH_4]^-$ was not observed.

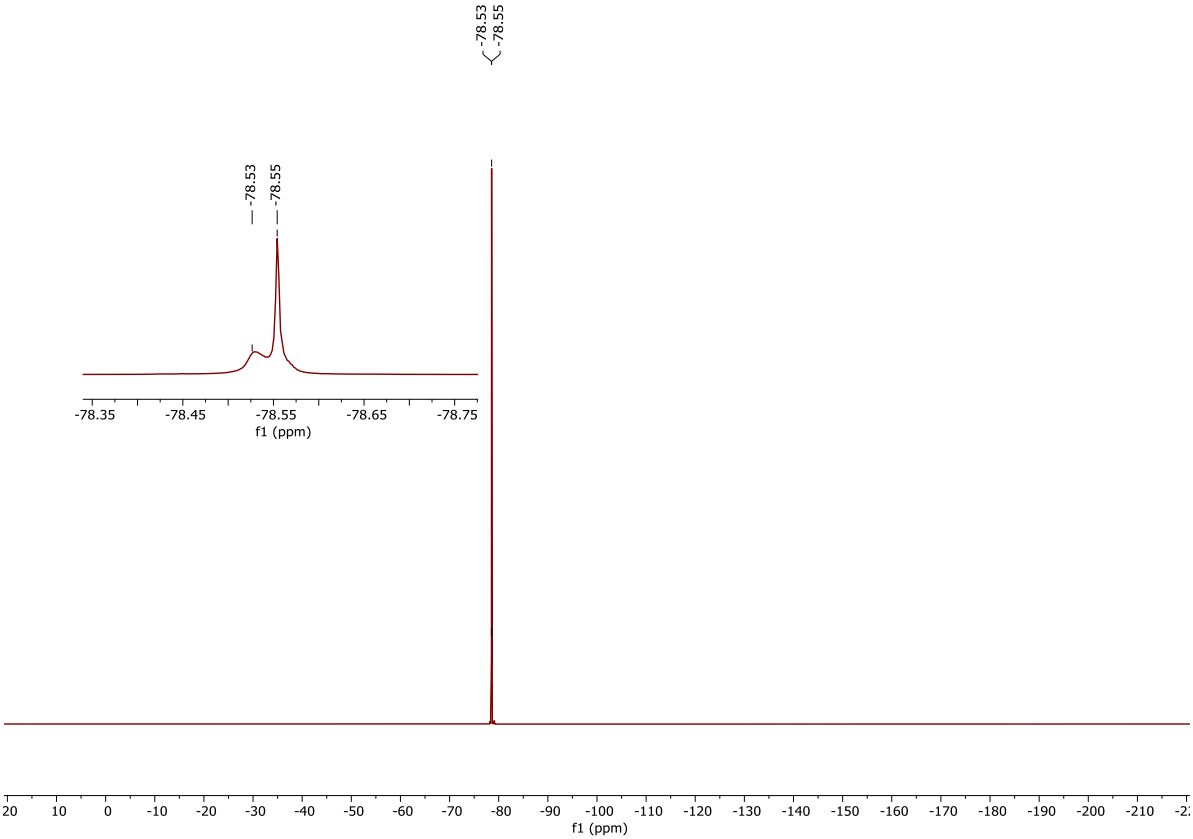


Figure S84. ^{19}F NMR (377MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (rt, 15 h).
IL10+HBpin (1:2) after heating in 100 °C for 15 hours (reactions were performed in NMR tube).

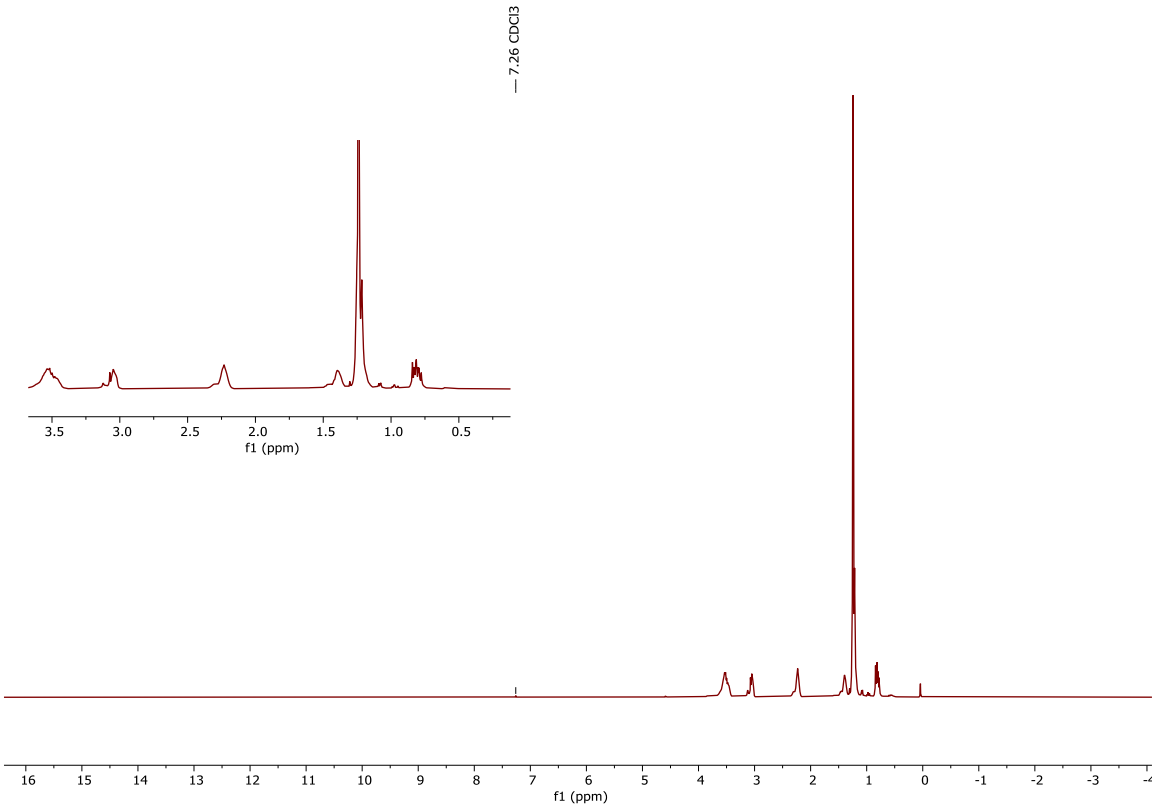


Figure S85. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h).

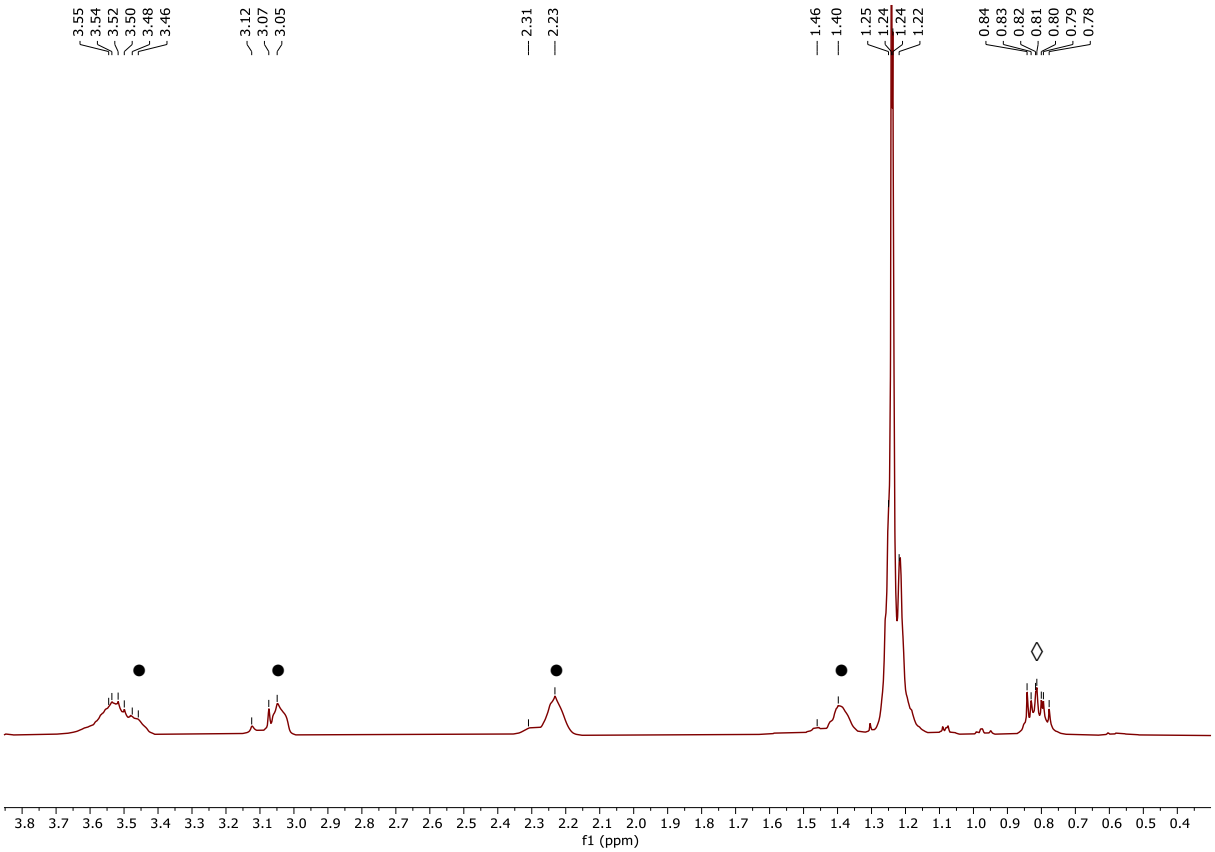


Figure S86. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h). ● Preasumbly indicates new signal originating from $[EMPyrr]^+$ ion. ◊ Indicates unknown new signal.

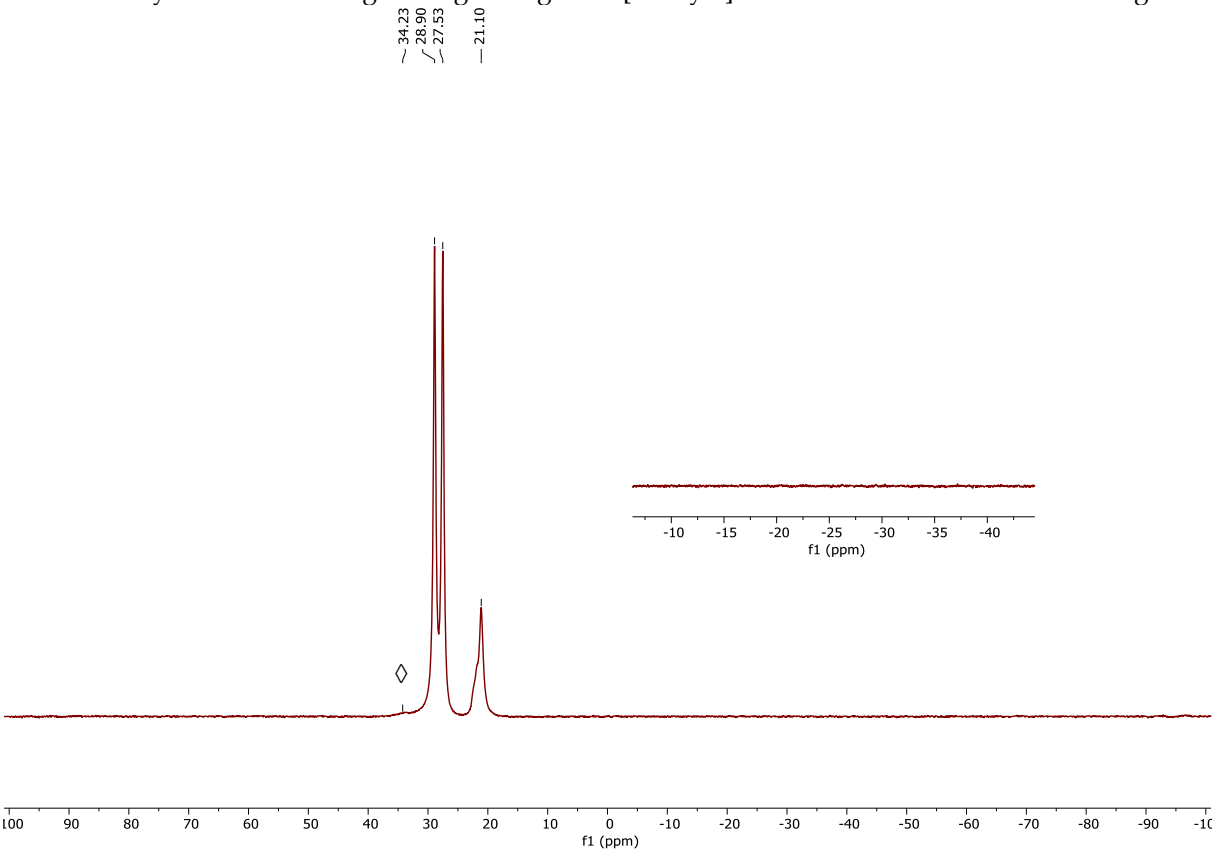


Figure S87. ^{11}B NMR (128MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h).

◊ indicates unknown new signal at 34.23 ppm. Doublet at 28.90 ppm and 27.53 ppm corresponds to HBpin. Signal at 21.10 ppm corresponds to pinBOTf. BH_3 or $[BH_4]^-$ were not observed.

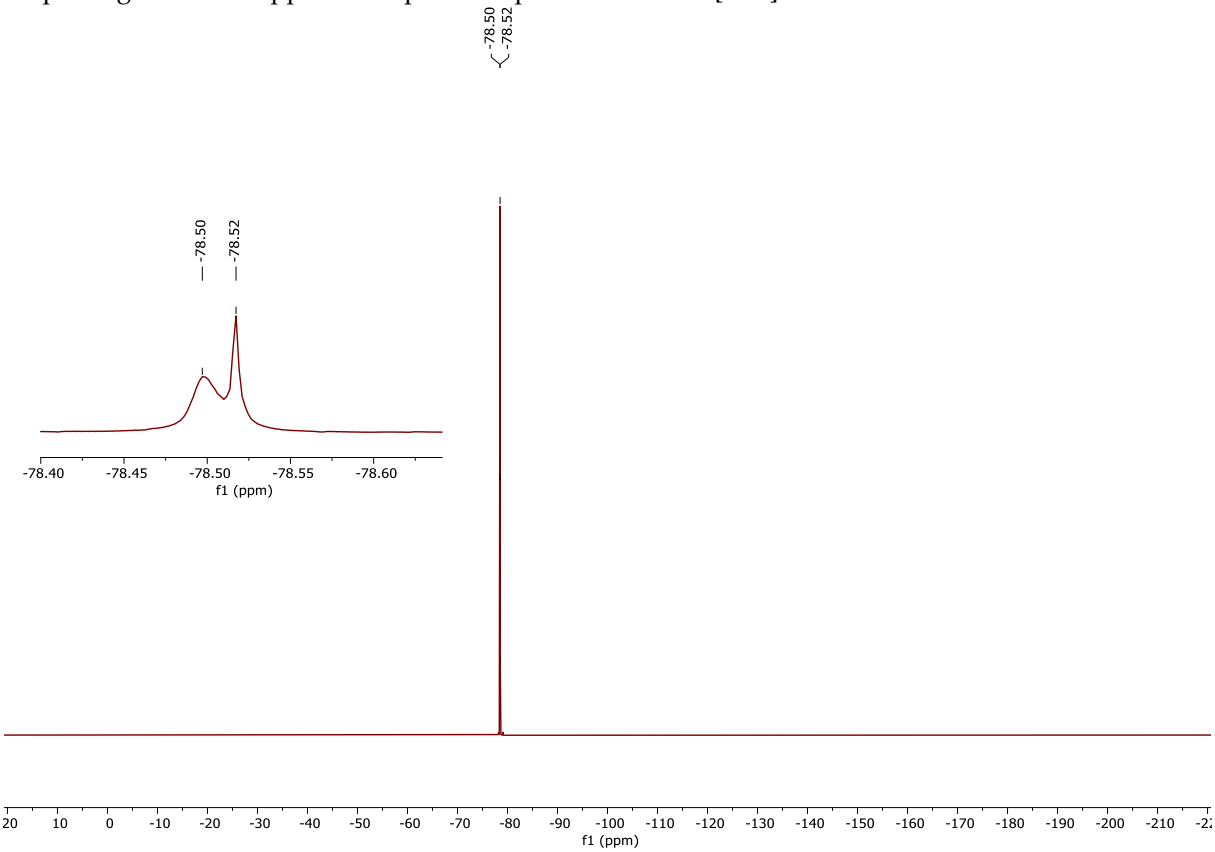


Figure S88. ^{19}F NMR (377MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h).

IL10+HBpin (2:1) after heating in 100 °C for 15 hours (reactions were performed in NMR tube).

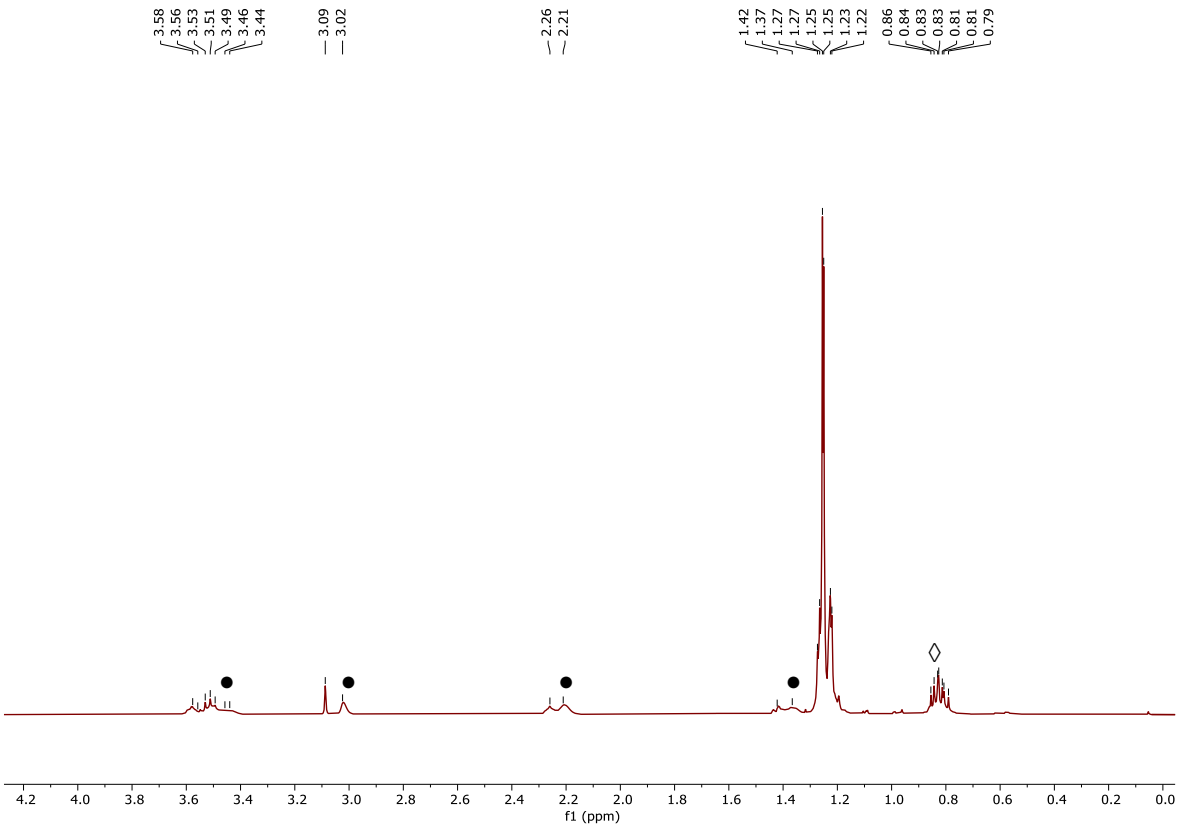


Figure S89. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 2:1 ratio (100 °C, 15 h). ● Preasumbly indicates new signal originating from $[EMPyrr]^+$ ion. ◊ Indicates unknown new signal.

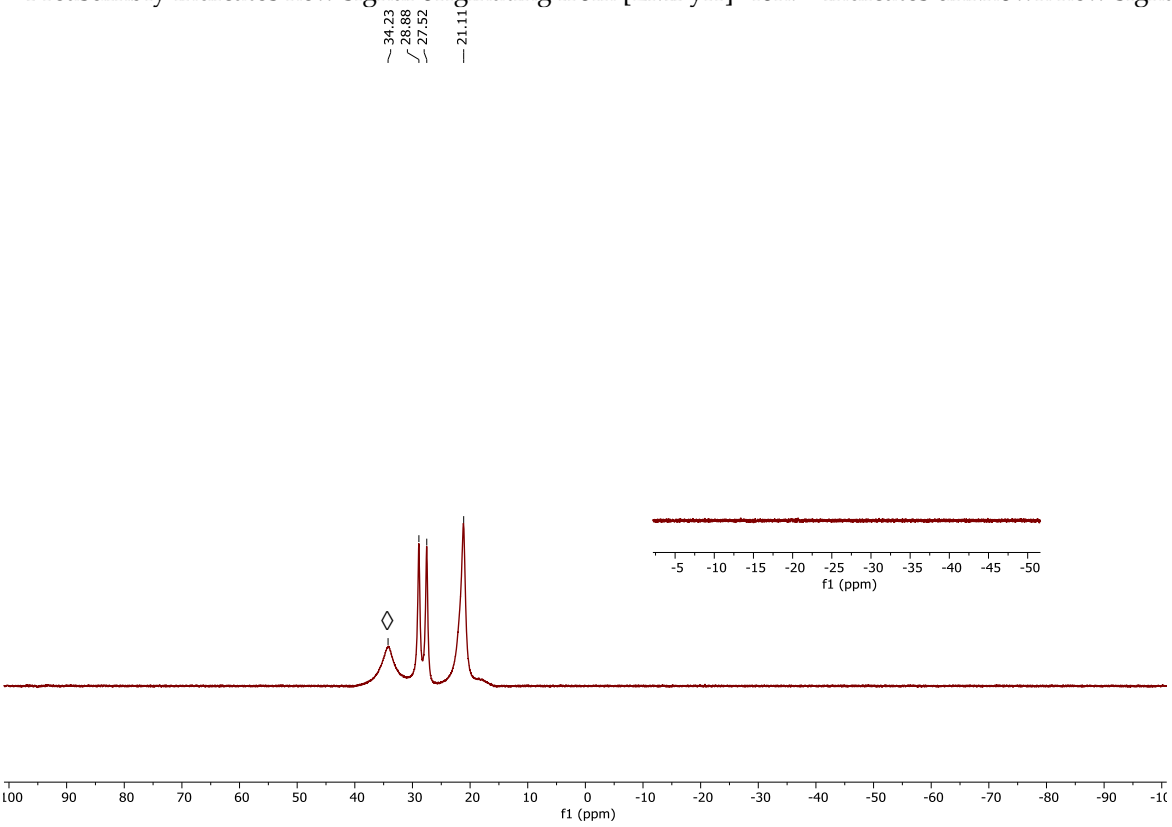


Figure S90. ^{11}B NMR (128MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 2:1 ratio (100 °C, 15 h).

◊ Indicates unknown new signal at 34.23 ppm. Doublet at 28.88 ppm and 27.52 ppm corresponds to HBpin. Signal at 21.11 ppm corresponds to pinBOTf. BH_3 or $[BH_4]^-$ were not observed.

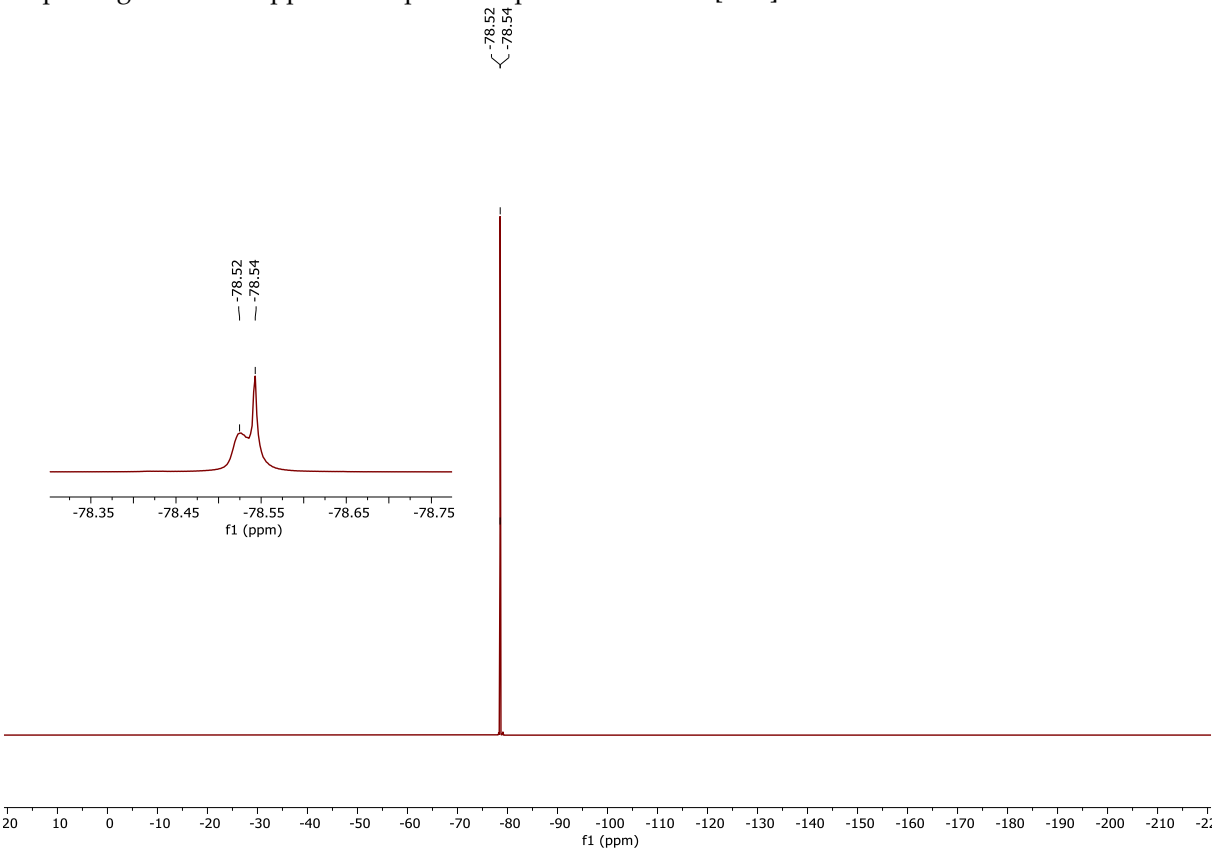


Figure S91. ^{19}F NMR (377MHz, $CDCl_3$, 25 °C). Spectrum of IL10 and HBpin in 2:1 ratio (100 °C, 15 h).

IL10+HBpin (1:2) after heating in 100°C for 15 hours in C_6D_6 in NMR tube.

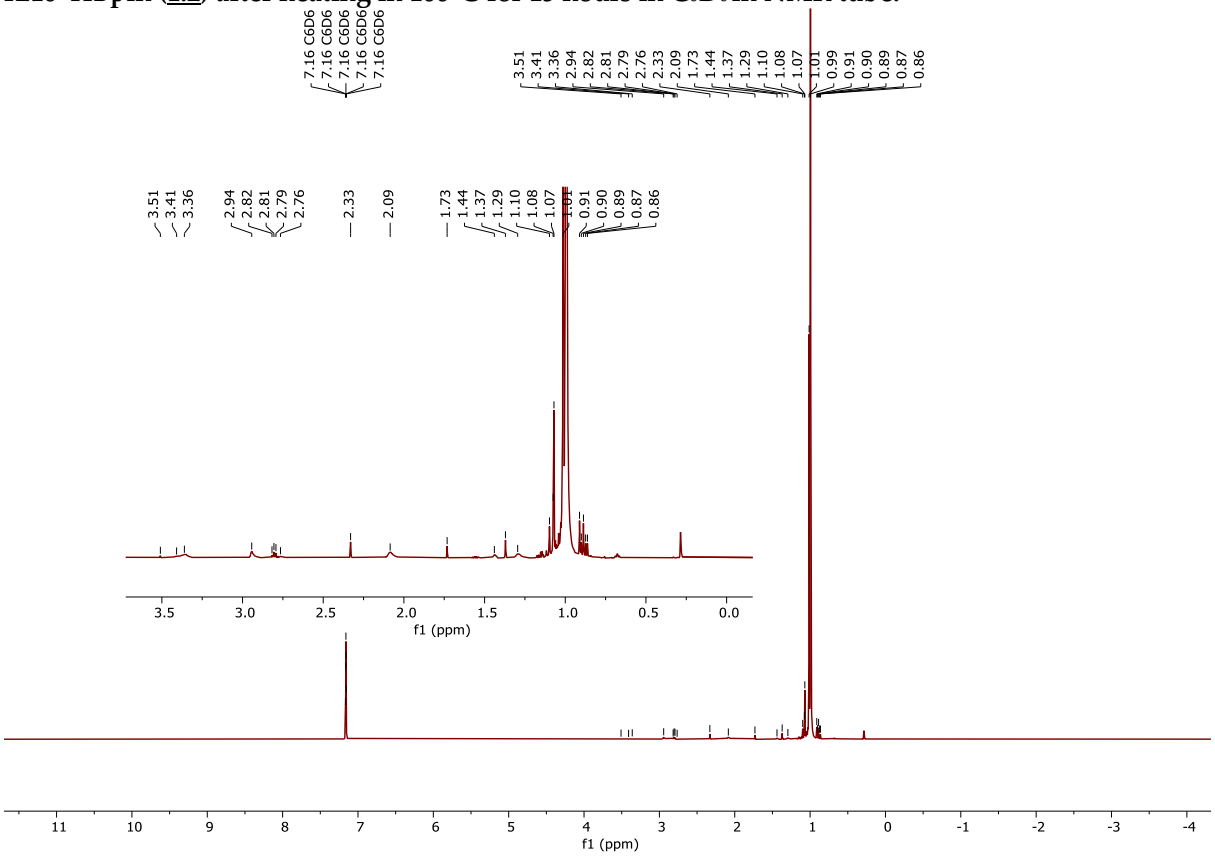


Figure S92. ^{1}H NMR (400MHz, C_6D_6, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h).

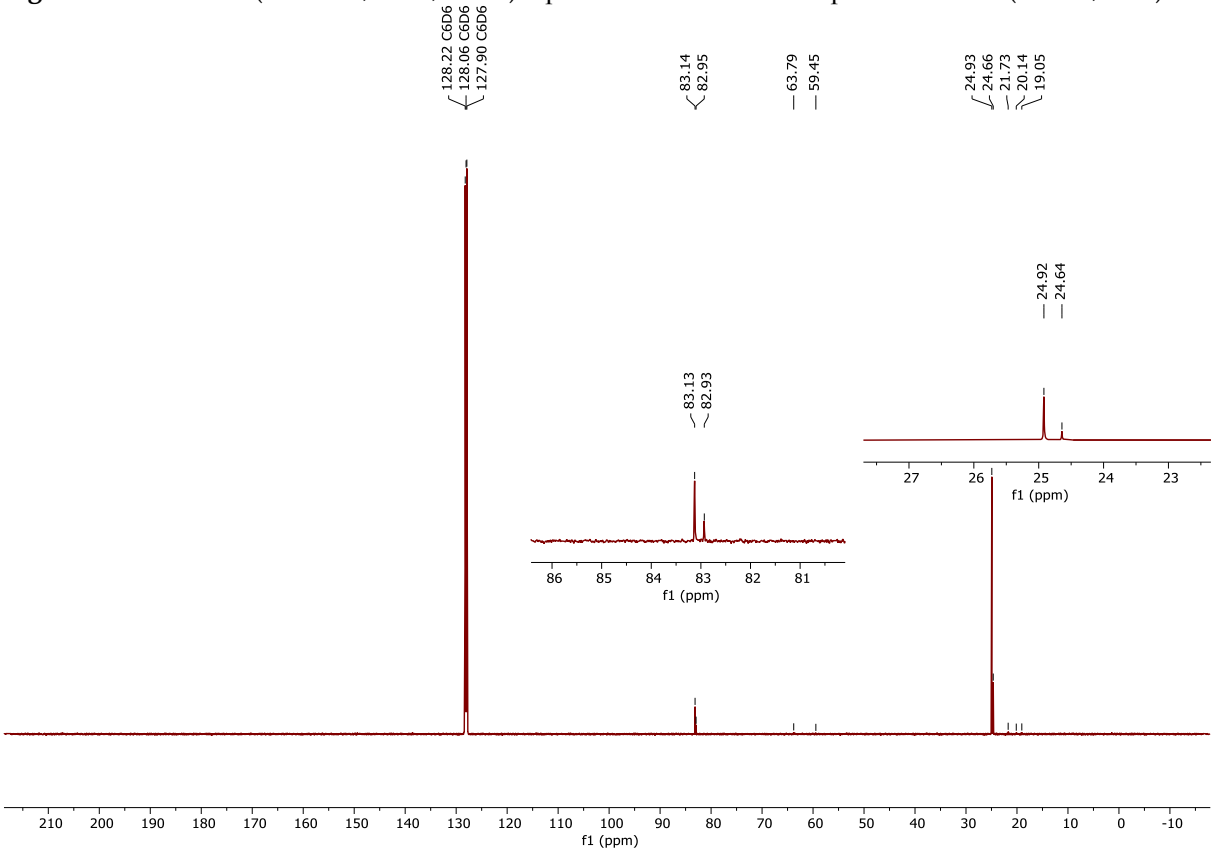


Figure S93. ^{13}C NMR (151MHz, C_6D_6, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h).

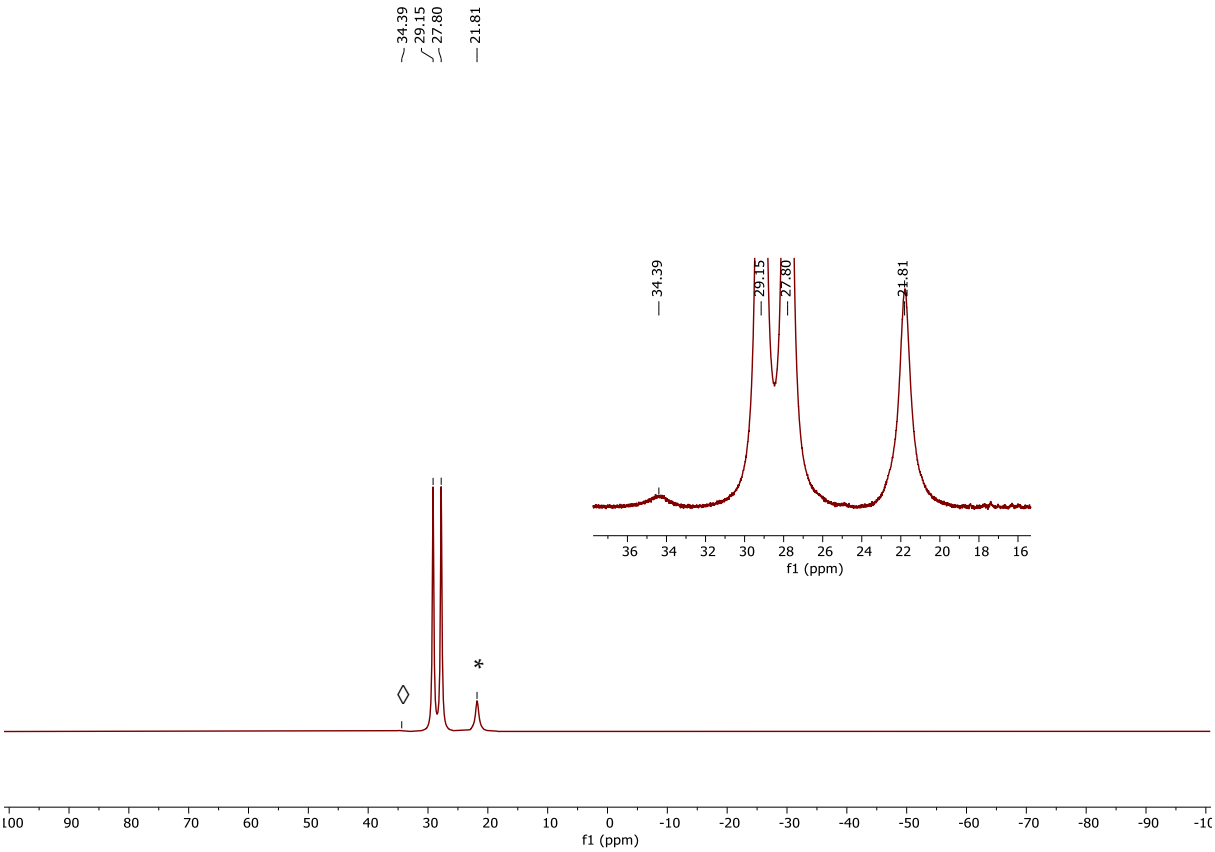


Figure S94. ^{11}B NMR (128MHz, C_6D_6, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h).

◊ Indicates unknown new signal at 34.39 ppm. Doublet at 29.15 ppm and 27.80 ppm corresponds to HBpin. *Signal at 21.81 ppm corresponds to pinBOTf which is in agreement with the literature.[38, 39]

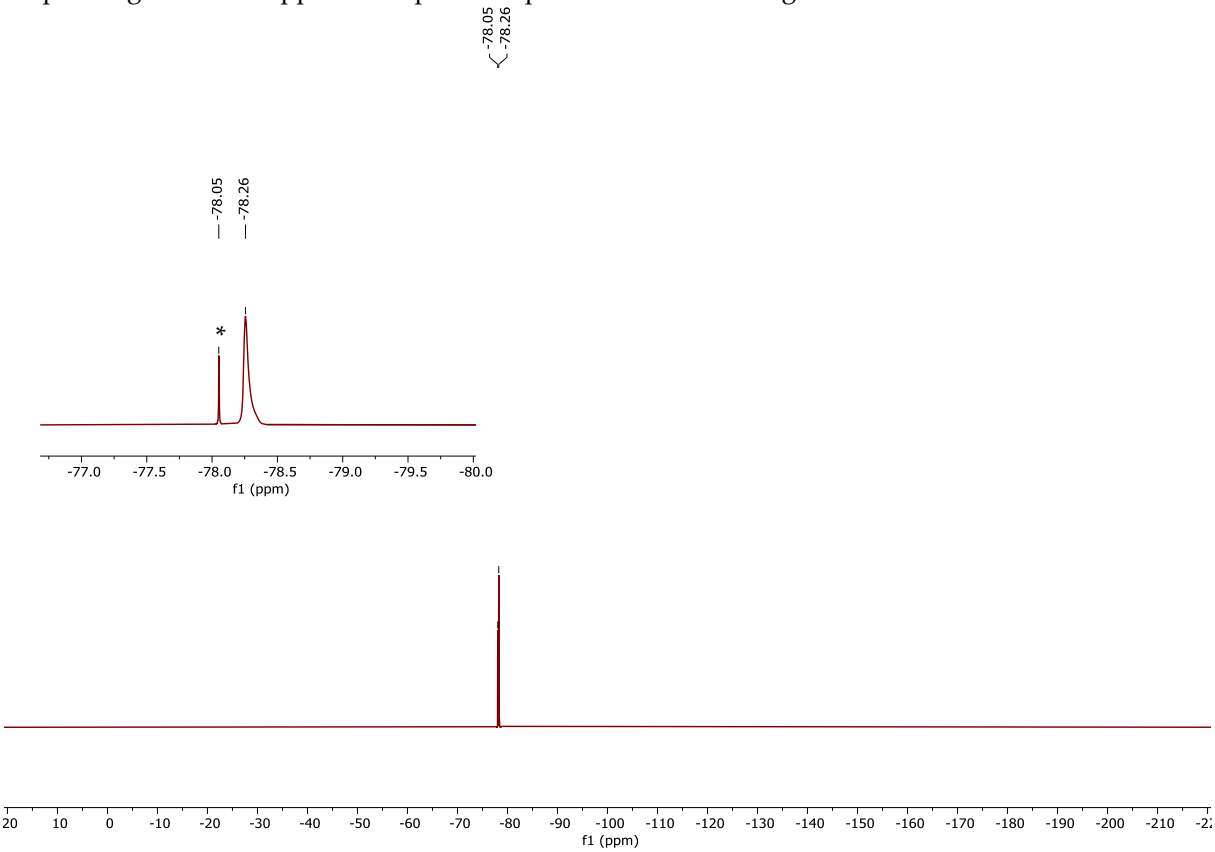


Figure S95. ^{19}F NMR (377MHz, C_6D_6, 25 °C). Spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h). *Signal at -78.05 ppm corresponds to pinBOTf which is in agreement with the literature.[38, 39]

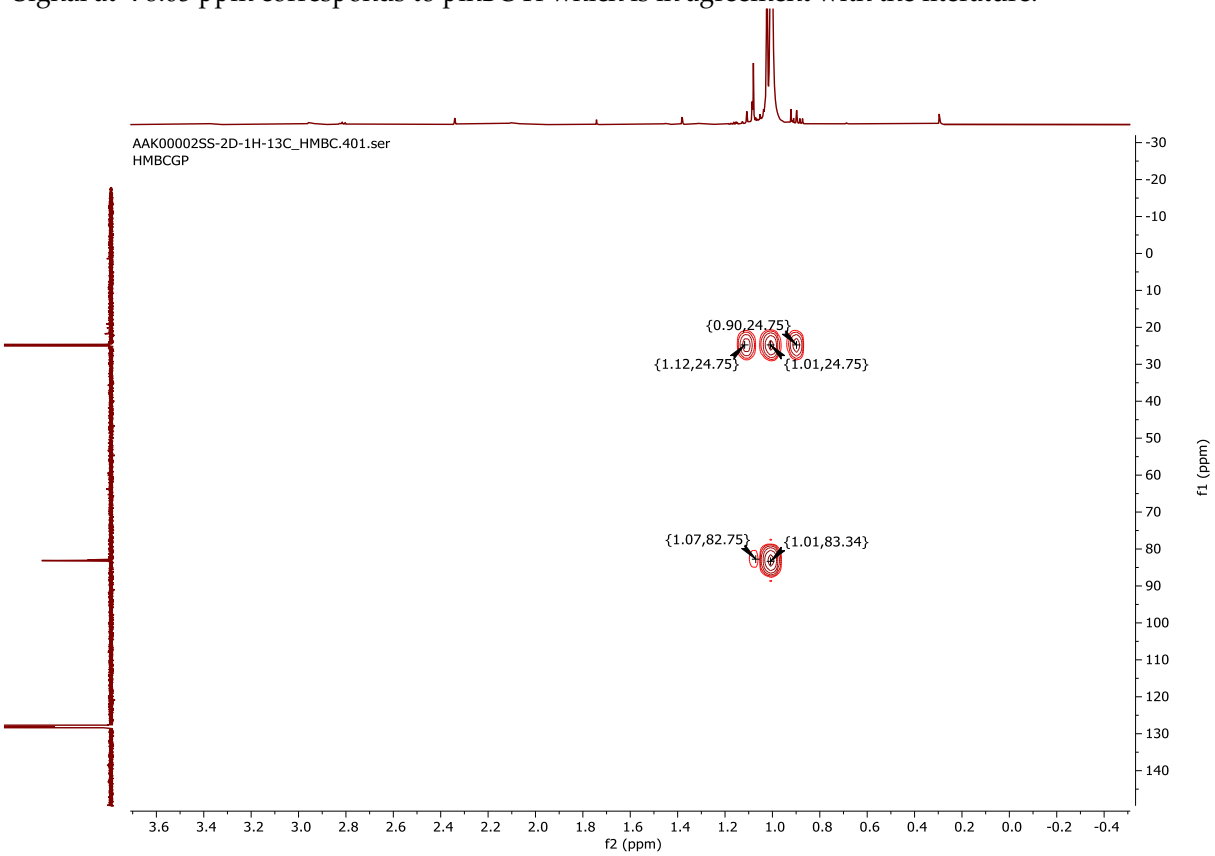


Figure S96. ^{1}H-^{13}C HMBCGP NMR (C_6D_6, 25 °C) spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h). New signals correlated to pinacol group of Bpin are observed.

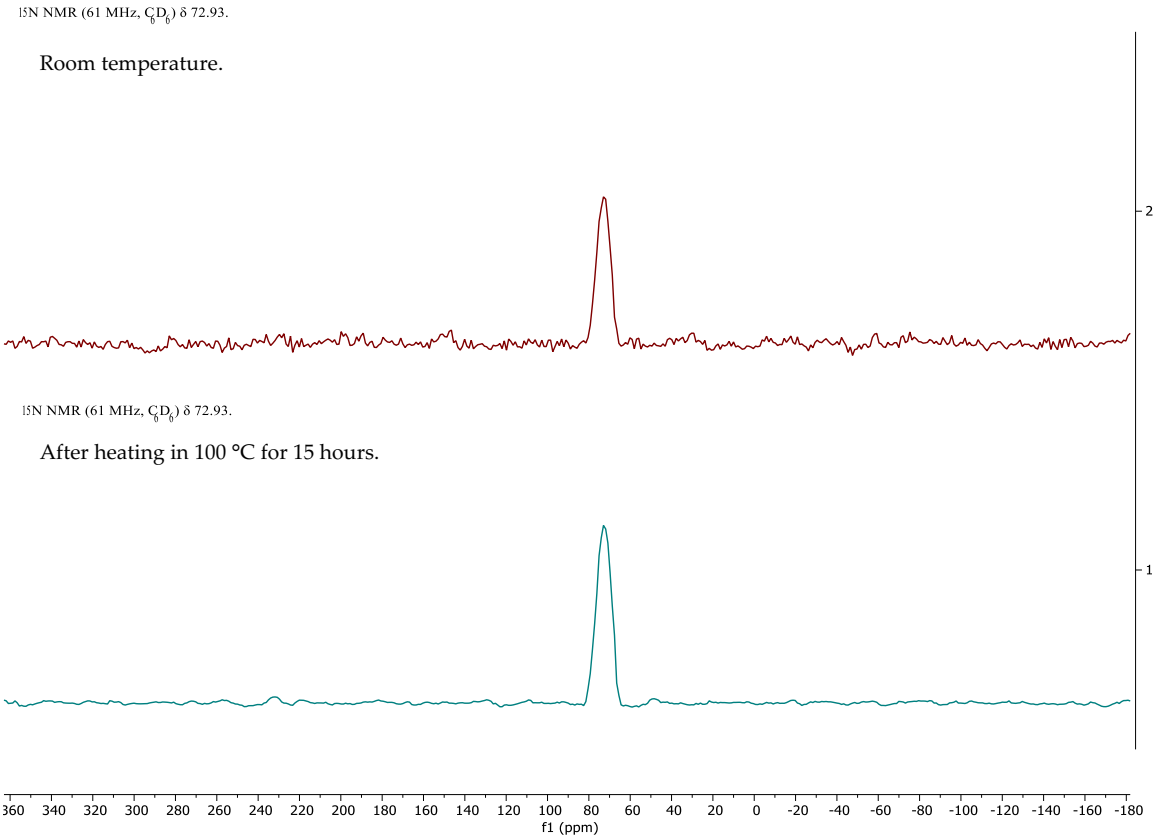


Figure S97. ^{15}N NMR (61 MHz, C_6D_6, 25 °C) spectrum of IL10 and HBpin in 1:2 ratio.

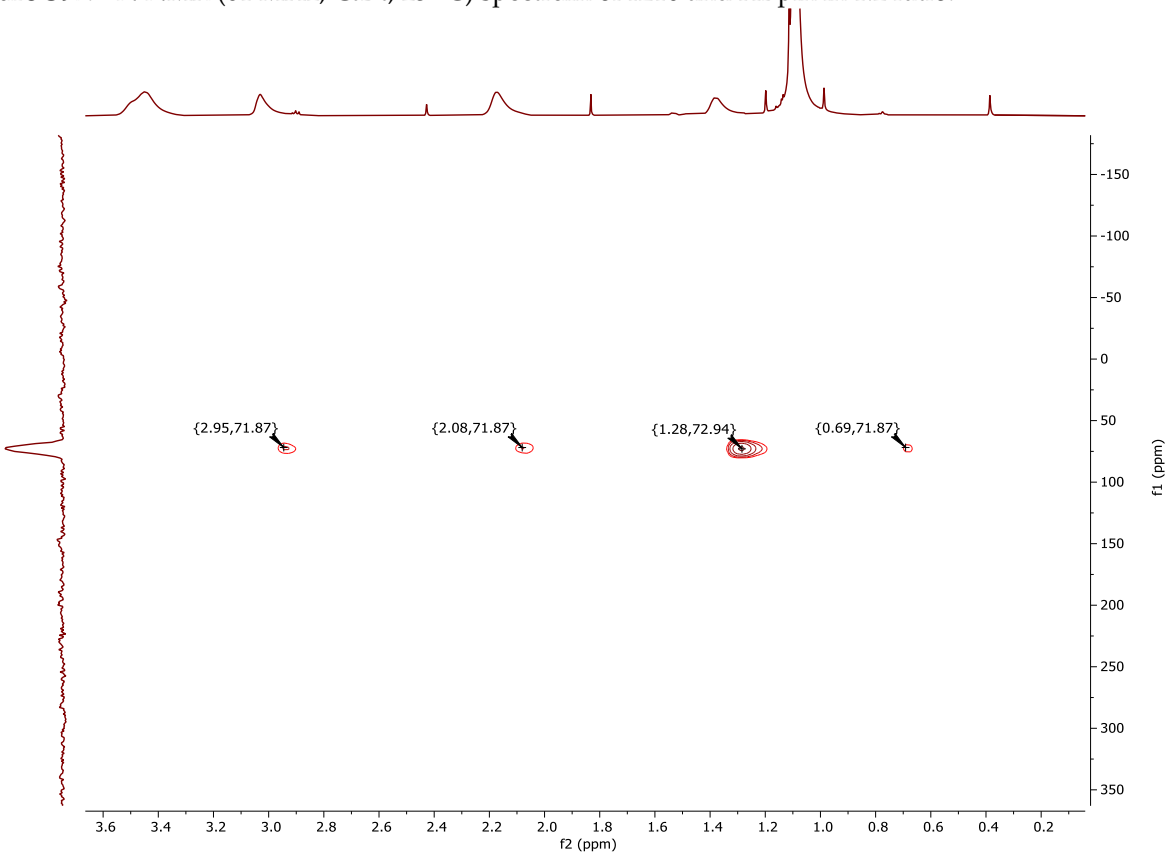


Figure S98. ^{1}H-^{15}N HMBC NMR (C_6D_6, 25 °C) spectrum of IL10 and HBpin in 1:2 ratio (rt, 15 h).

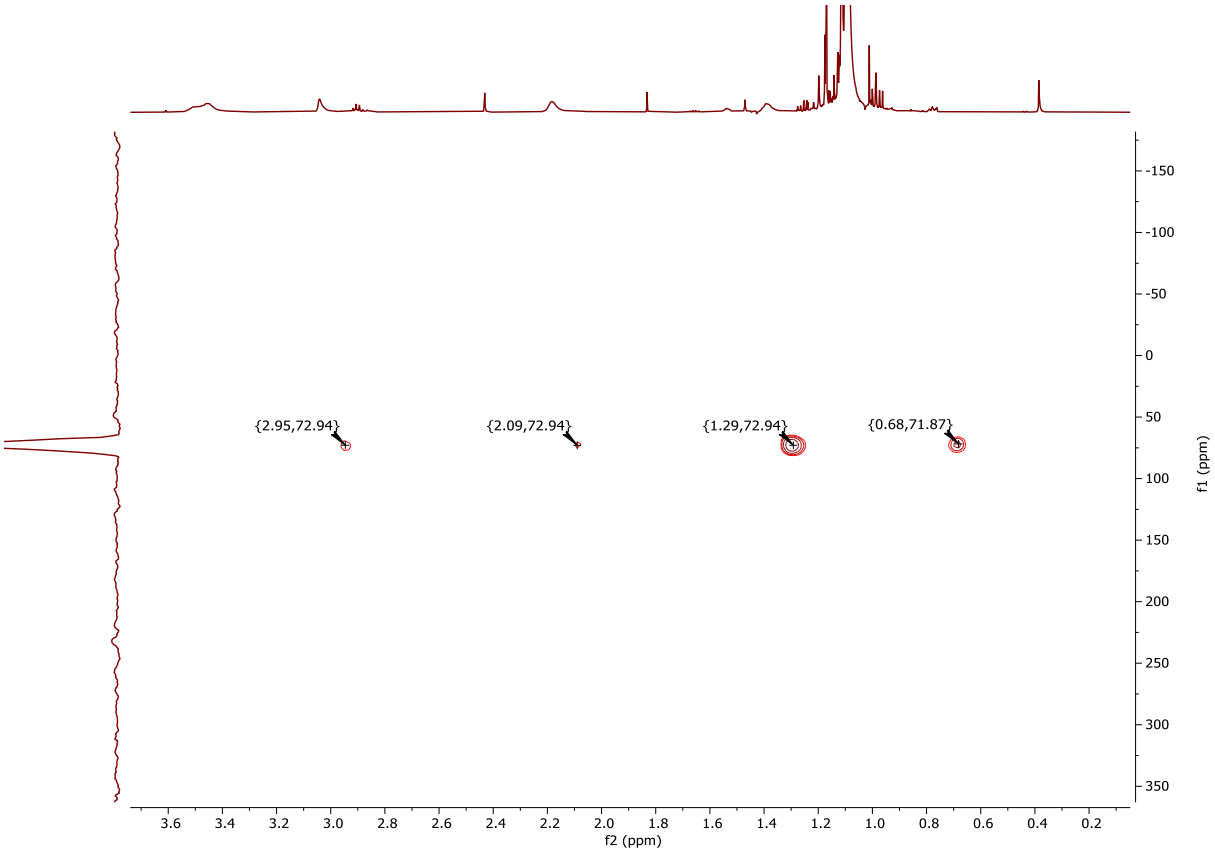


Figure S99. ^{1}H-^{15}N HMBC NMR (C_6D_6, 25 °C) spectrum of IL10 and HBpin in 1:2 ratio (100 °C, 15 h). Shifts of the signals corresponding to [EMPyrr][OTf] were observed.

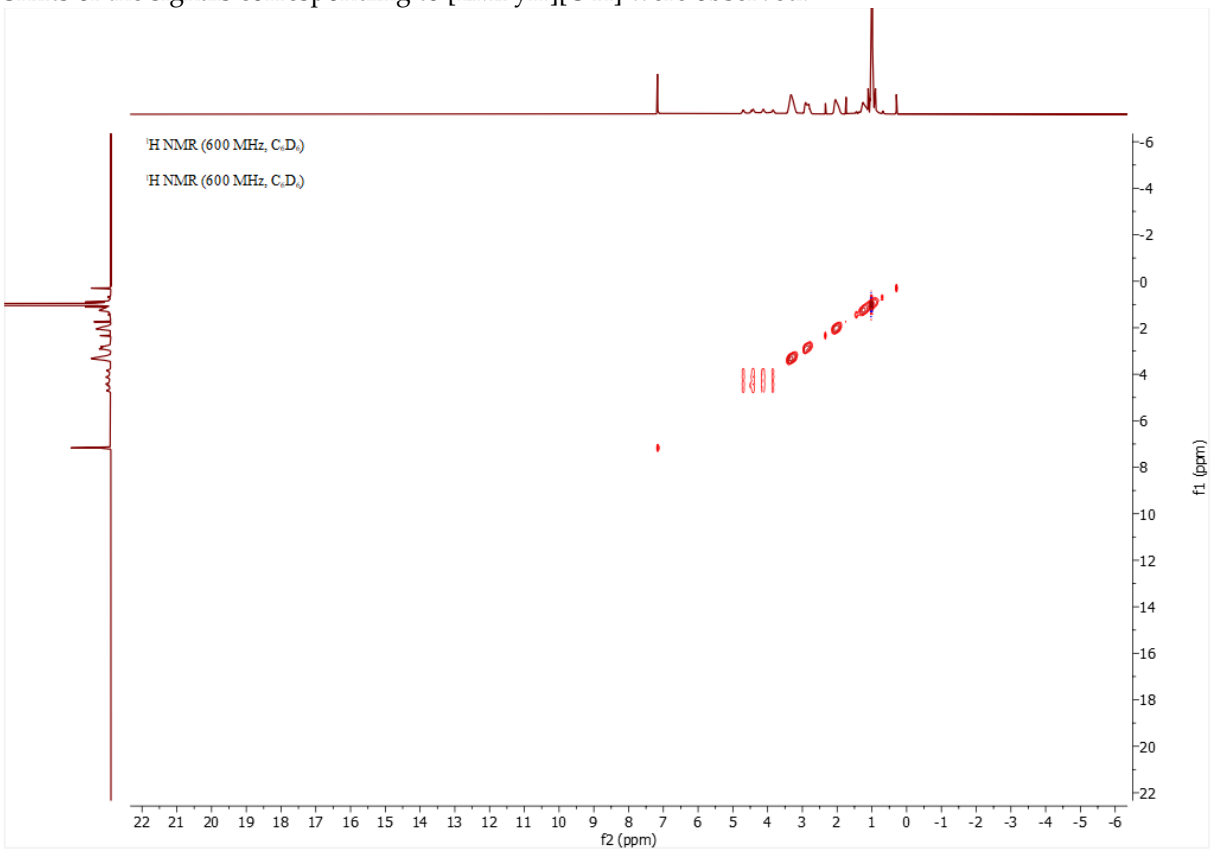


Figure S100. ^{1}H-^{1}H NOESY NMR (C_6D_6, 25 °C) spectrum of IL10 and HBpin in 1:2 ratio at room temperature.

IL10+TMEDA+HBpin (in 1:1:2 ratio) (reactions were performed in NMR tube).

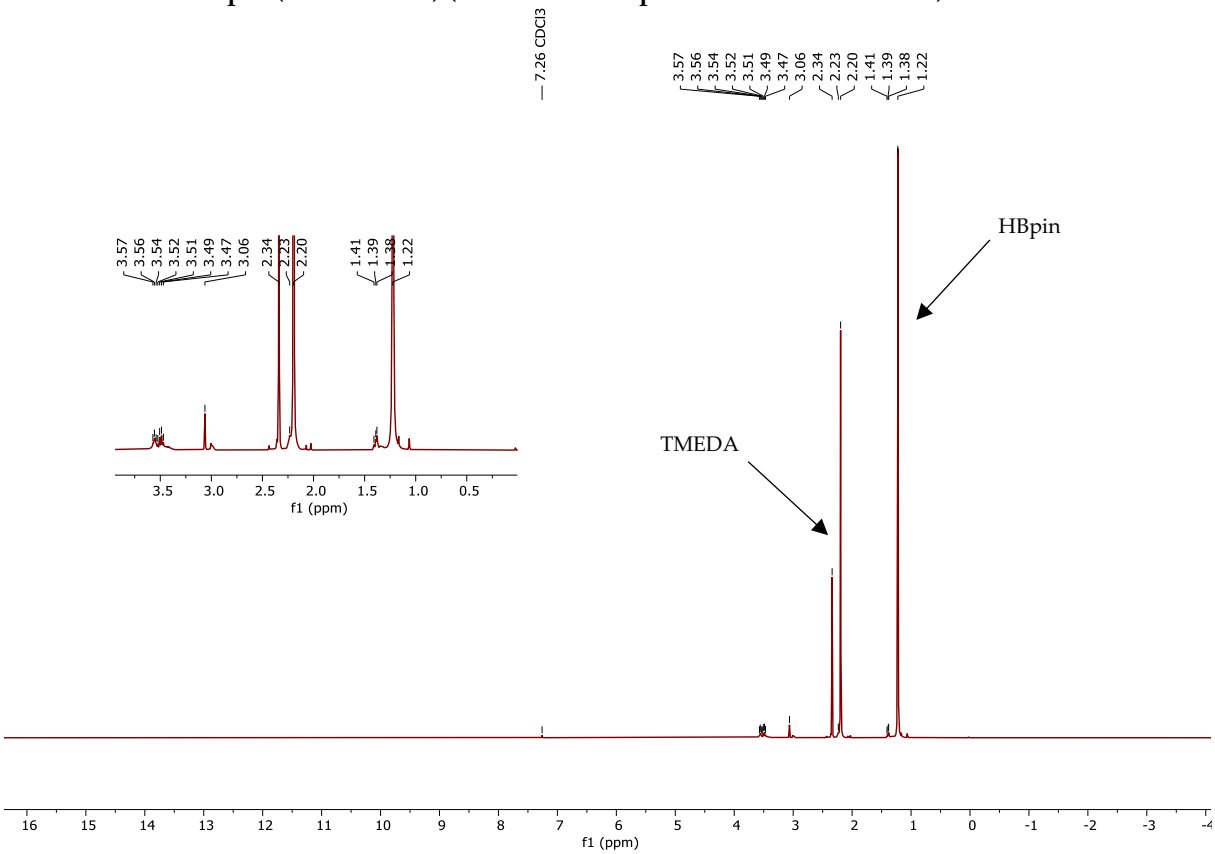


Figure S101. ^{1}H NMR (400MHz, $CDCl_3$, 25 °C). Spectrum of IL10+TMEDA+HBpin in 1:1:2 ratio (rt, 15 h).

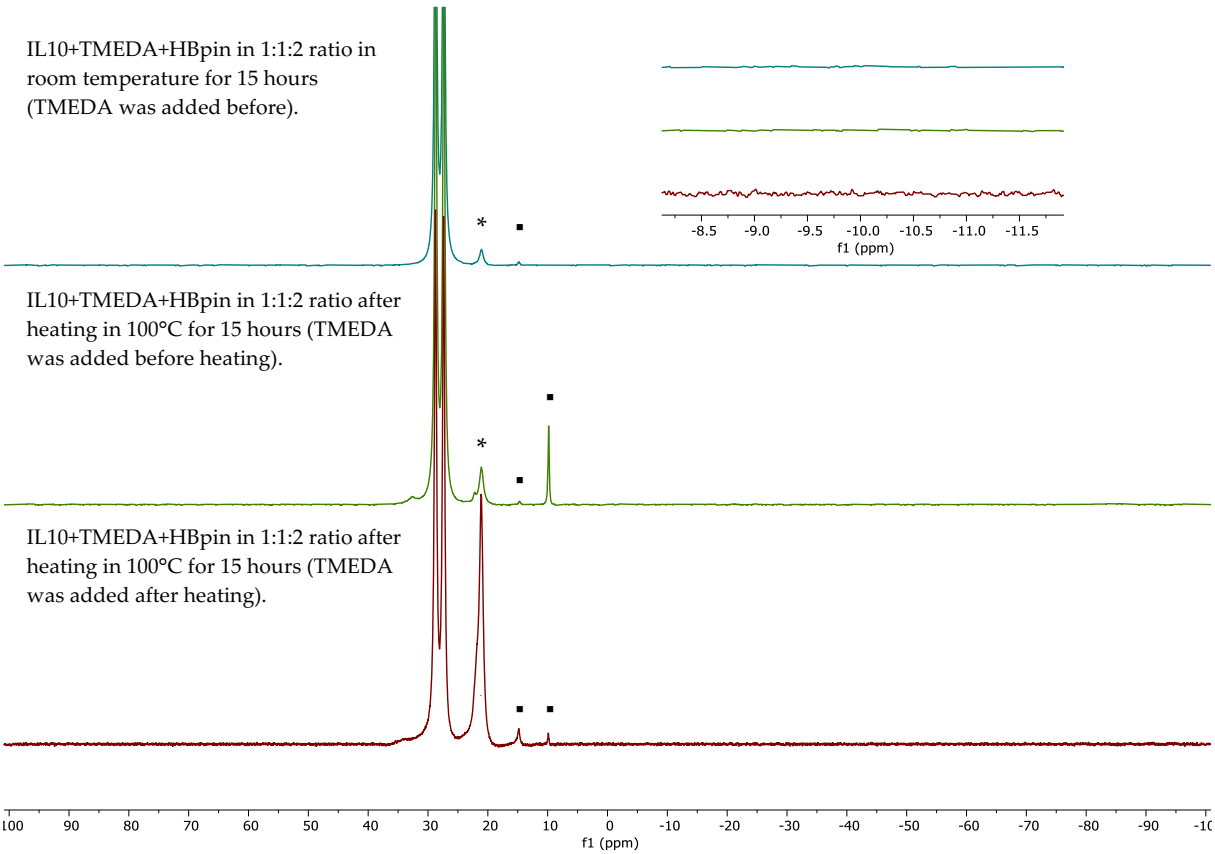


Figure S102. ^{11}B NMR (128MHz, $CDCl_3$, 25 °C). Stacked spectra of IL10 + TMEDA + HBpin in 1:1:2 ratio. *Indicates pinBOTf. ▪Indicates unknown boron species. There was no evidence of BH_3 being formed and coordinated to TMEDA, which normally appears at around -10 ppm, ruling out the possibility of the hidden borane catalysis.[40]

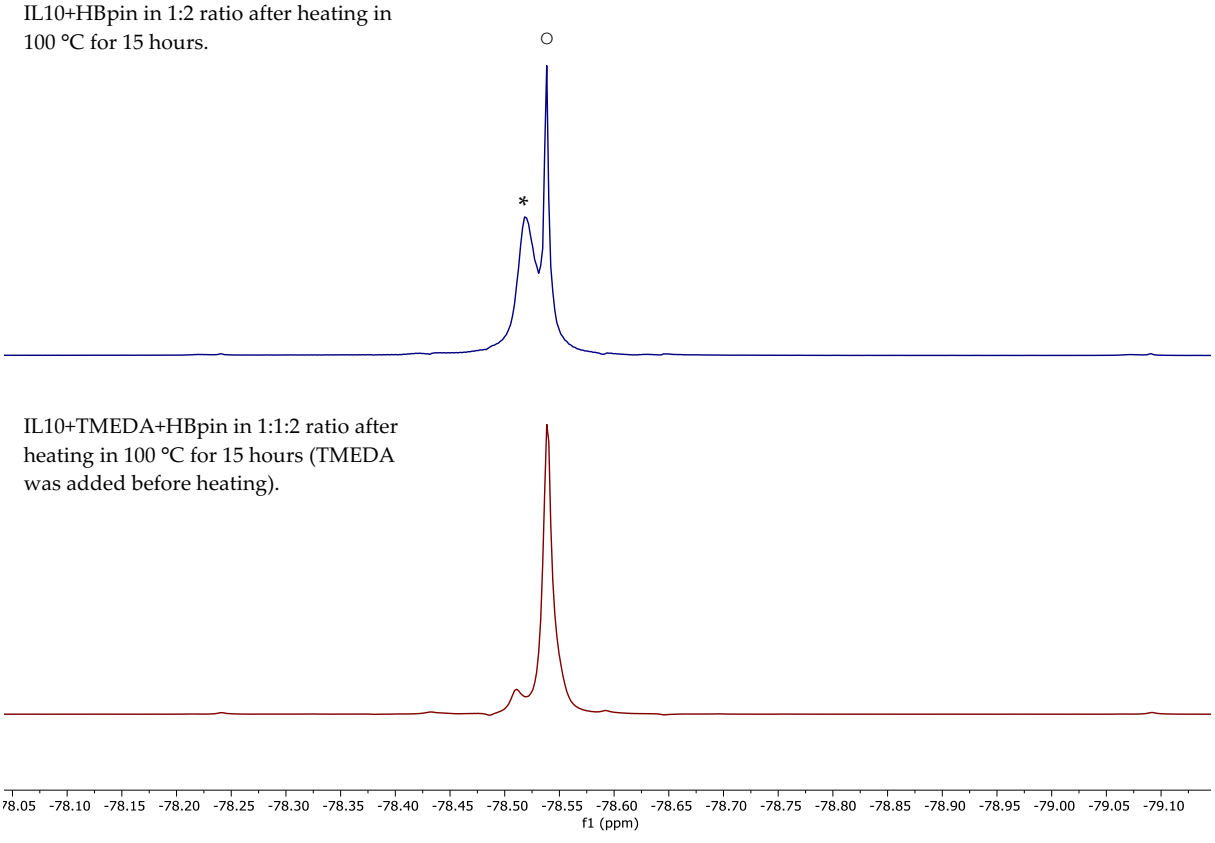


Figure S103. ^{19}F NMR (377MHz, $CDCl_3$, 25 °C). Stacked spectra. *Indicates pinBOTf. ○ Indicates [EMPyrr][OTf]. These ^{11}B and ^{19}F NMR spectra suggest that there is interaction between formed intermediates and TMEDA (presumably inhibiting its formation).

8. X-Ray crystallography data.

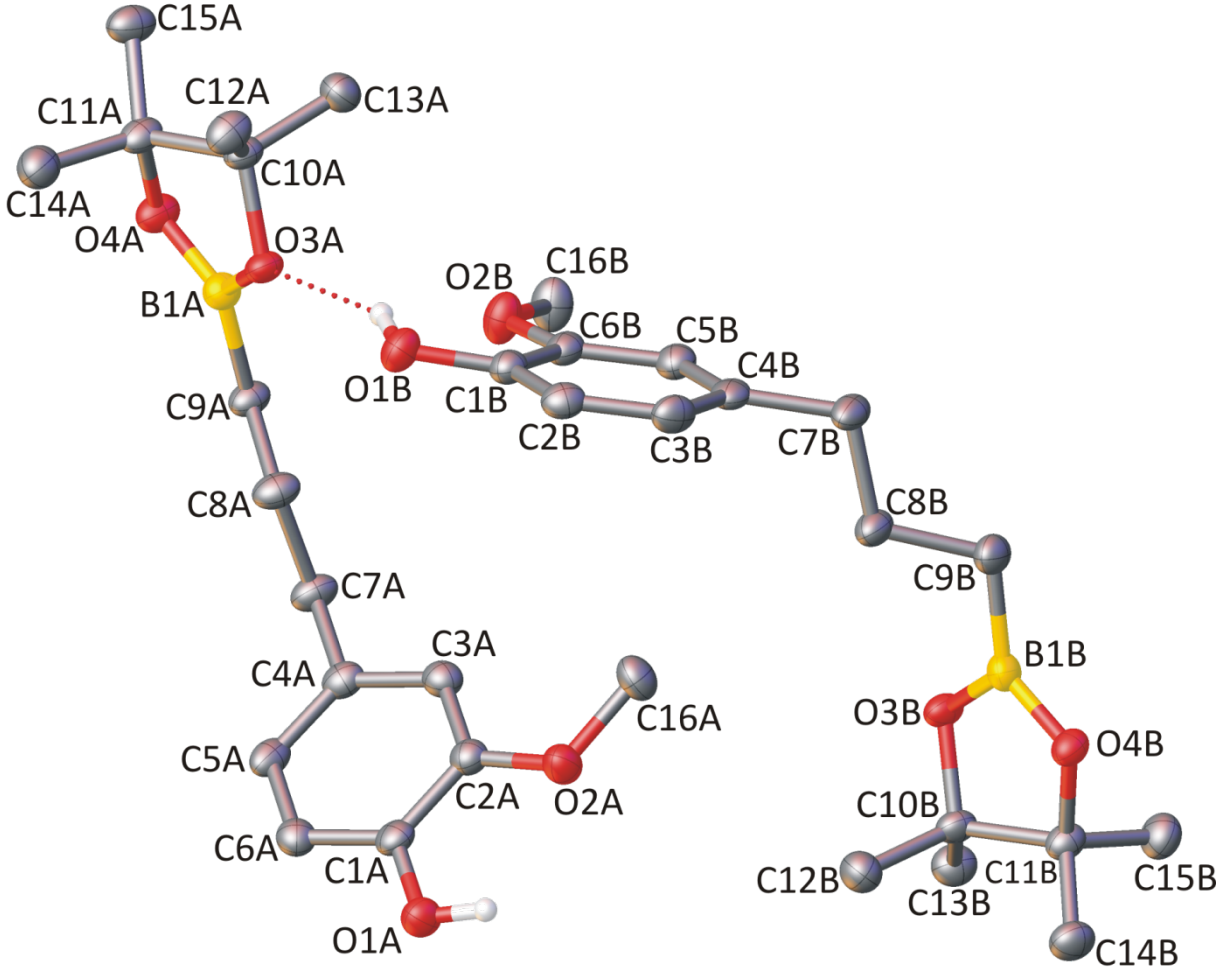


Figure S104. Molecular structure of asymmetric unit compound **2u** and atoms numbering scheme. The C-bound hydrogen atoms omitted for clarity. Displacement ellipsoids shown at the 50% probability level.

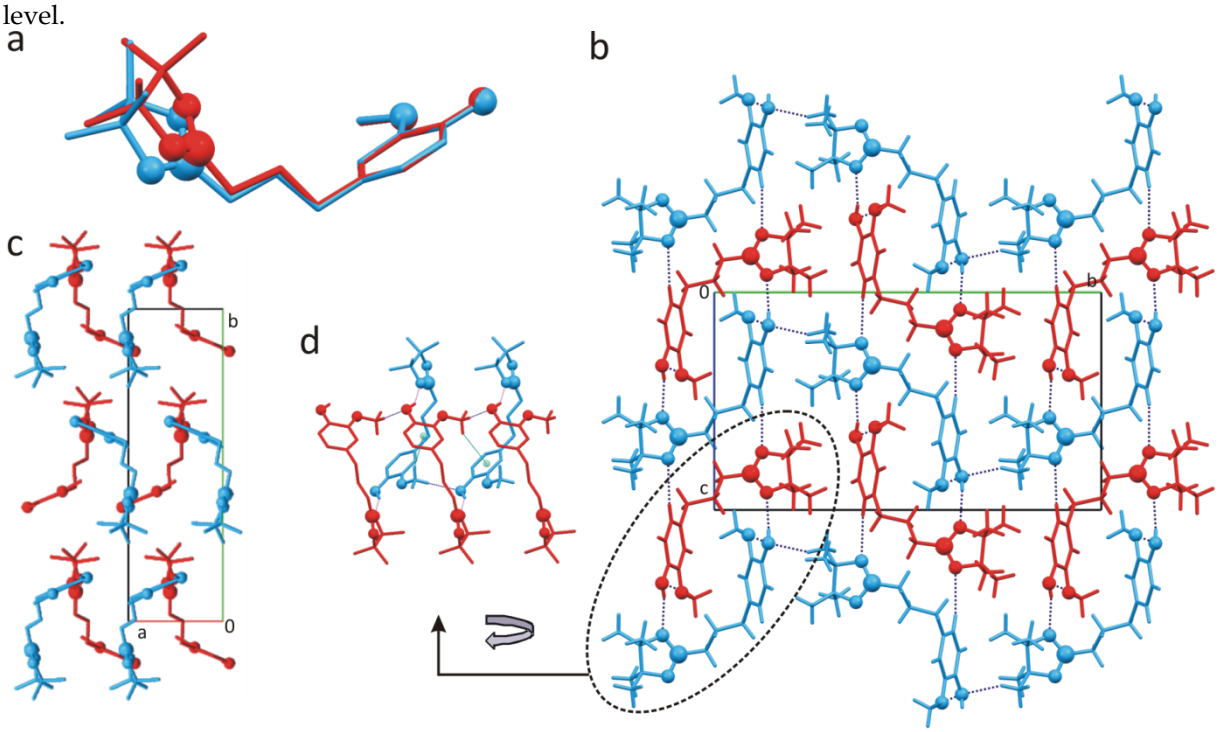


Figure S105. a) Comparison of the conformations of symmetrically independent molecules and the molecular packing in the crystal: b) view along c-axis and c) view along a-axis. d) intermolecular interaction in 1D supramolecular chain. Hydrogen atoms omitted for clarity. The O and B atoms showed as balls. Intermolecular interaction showed as dashed lines.

Table S4. Selected crystal data and structure refinement details.

	2v
CCDC number	2216859
Chemical formula	$C_{16}H_{25}BO_4$
Mr	292.17
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, *b*, *c* (Å)	6.4649 (2), 21.3198 (6), 11.9814 (3)
β (°)	91.894 (3)
V (Å^3)	1650.50 (8)
Z	4
D_x (Mg m^{-3})	1.176
Radiation type	Cu *K*α
μ (mm^{-1})	0.66
Crystal size (mm)	0.5 × 0.2 × 0.05
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5868, 5868, 5688
R_{int}	0.042
Range of *h*, *k*, *l*	*h* = -8→8, *k* = -26→26, *l* = -15→15
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.061, 0.163, 1.14
No. of parameters	392
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.57, -0.33
Absolute structure parameter	0.39 (10)

Table S5. Selected hydrogen bonds parameters.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O1A—H1A···O2A	0.84	2.19	2.651 (5)	114.1
O1A—H1A···O3B^{i}	0.84	2.15	2.898 (5)	148.3
O1B—H1B···O3A	0.84	2.10	2.868 (4)	151.5
O1B—H1B···O2B	0.84	2.22	2.649 (5)	111.9
C8B—H8BB···O3B	0.99	2.67	3.020 (6)	101.1

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