Supporting Information

for

Electrochemical deconstruction of alkyl substituted boron clusters to produce alkyl boronate esters

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Materials and Methods

1. General information

General considerations

Reactions were performed using standard Schlenk techniques under N_2 atmosphere. DME, 1,4-dioxane and toluene were distilled over sodium in the presence of benzophenone and stored in a Straus flask. Acetonitrile was distilled over calcium hydride under N_2 atmosphere and stored in a Straus flask. Anhydrous diglyme, TCE, BF_3•Et_2O were prepared by distilling over calcium hydride under the reduced pressure. K_3PO_4, *t*-BuOLi, NaHMDS and KHMDS were purchased from J&K Scientific and used without further purification. Et_3N was purchased from BOER. LiHMDS and DABCO were purchased from Energy Chemical. *t*-BuOK was purchased from TCI. *t*-BuONa was purchased from TCI and Energy Chemical. $NaBH_4$ was purchased from Alfa Aesar and Acros. Substrates were purchased from Bidepharm and Adamas-beta. $TBAPF_6$ was purchased from Leyan and recrystallized in 200 proof ethanol three times before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and Energy Chemical. All other reagents were purchased from commercial vendors and used without further purification.

Instrumentations

^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, ^{11}B and $^{19}F\{^1H\}$ NMR spectra were recorded on a AVANCE III 400 and Ascend 600v spectrometers. MestReNova (Version 14.2.1 Build 27684 x64) software was used to process the NMR data. ^1H and $^{13}C\{^1H\}$ spectra were referenced to residual solvent resonances in deuterated solvents ($CDCl_3$: ^1H, δ 7.26; ^{13}C, δ 77.00; note: due to humidity, residual H_2O signals are often present). Mass spectrometry data was acquired using GCT Premier and Xevo G2 TOF mass spectrometer by direct injection. Agilent high-resolution mass spectrometry was used to collect mass data for the final products. Both IKA ElectraSyn 2.0 and customized electrochemical cells with DC power supply were used for the bulk electrolysis experiments described.

2. Preparation of *closo*-hexaborate anion 1 precursor

Synthesis of *n*-$Bu_4N(B_6H_7)$ (1)[1]

A 1 L round bottom, three-neck flask was charged with 15 g (397 mmol) of $NaBH_4$. The flask was tightly sealed by the rubber stoppers and was evaluated and backfilled with N_2 three times. 200 mL of dry diglyme were added to the reaction flask with stirring. The reaction mixture was then heated in an oil bath at 60 ºC for 30 minutes. Holding the oil bath at 60 ºC, $BF_3 \cdot Et_2O$ (24 mL, 187 mmol based on BF_3, diluted with 25 mL dry diglyme) was then added dropwise over 60-90 minutes, resulting in bubbling and dissolution of any solids remaining in the reaction flask. After the addition of $BF_3 \cdot Et_2O$ was complete, the reaction mixture was heated to 100 ºC for 1 hr. and then heated to 185 ºC for 36 hr. During the course of the reaction, $Na_2B_6H_6$ and other borates precipitated out of the diglyme solution. The reaction mixture was then allowed to cool to approximately room temperature before being filtered and washed with an additional 100 mL of diglyme to remove $Na_2B_{12}H_{12}$. The collected solids were then stirred with 150 mL of water for 30 min. to hydrolyze lower boranes. Precipitated borates were then removed by filtration and the water was removed by rotary evaporation under reduced pressure. Additional amounts of borates can be removed by concentrating the water solution and performing a second filtration. The dried $Na_2B_6H_6$ was then washed 3 × 20 mL with acetonitrile and then 3 × 20 mL with acetone before being further dried *in vacuo* and gave 3.2580 g $Na_2B_6H_6$. A 200 mL round flask was charged with $Na_2B_6H_6$ (2.5499 g, 22 mmol) and H_2O (25 mL). Under stirring, an aqueous solution of *n*-Bu_4NBr (6.3491 g, 19.7 mmol) in 25 mL of H_2O was added. A large amount of white precipitate formed immediately. The reaction mixture was stirred for another two hours. The white precipitate was collected by filtration and washed with H_2O (3 × 10 mL), then the white solid was dried *in vacuo* to remove residual water. Recrystallization from hot EtOH/MeOH (1:1, v/v) gave white crystals (2.0213 g, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 – 3.19 (m, 8H), 1.68 – 1.58 (m, 8H), 1.44 (h, *J* = 7.3 Hz, 8H), 1.00 (t, *J* = 7.3 Hz, 12H), -5.29 (s, *facial proton*, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 59.02, 24.07, 19.68, 13.65.

^{11}B NMR (128 MHz, $CDCl_3$) -13.46 (d, *J* = 146.3 Hz, 6B).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -13.47.

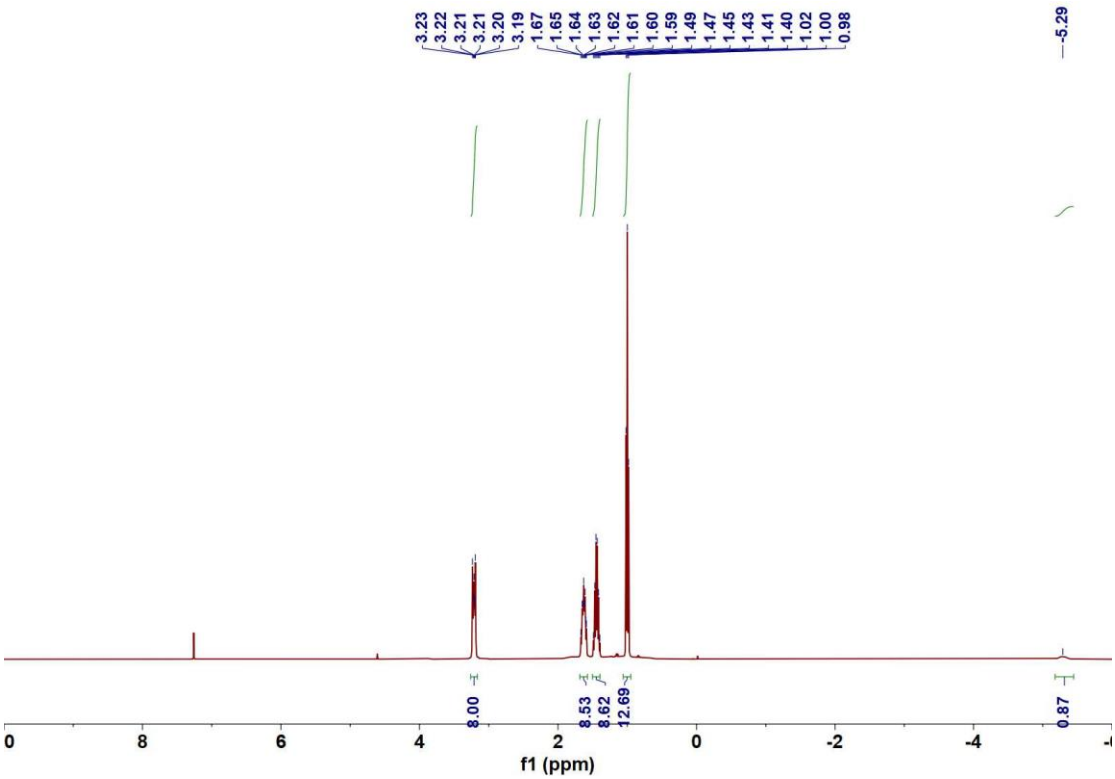


Figure S1. ^{1}H NMR spectrum of ***n*-$Bu_4N(B_6H_7)$** in $CDCl_3$ at 298K

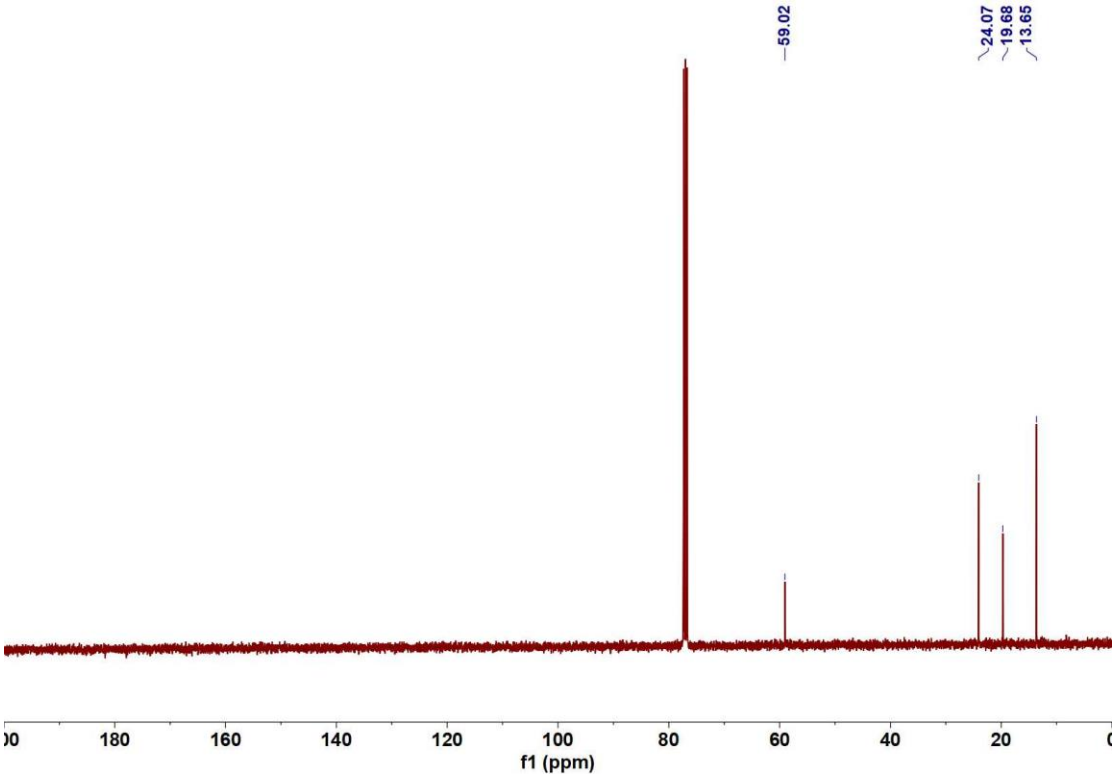


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of ***n*-$Bu_4N(B_6H_7)$** in $CDCl_3$ at 298K

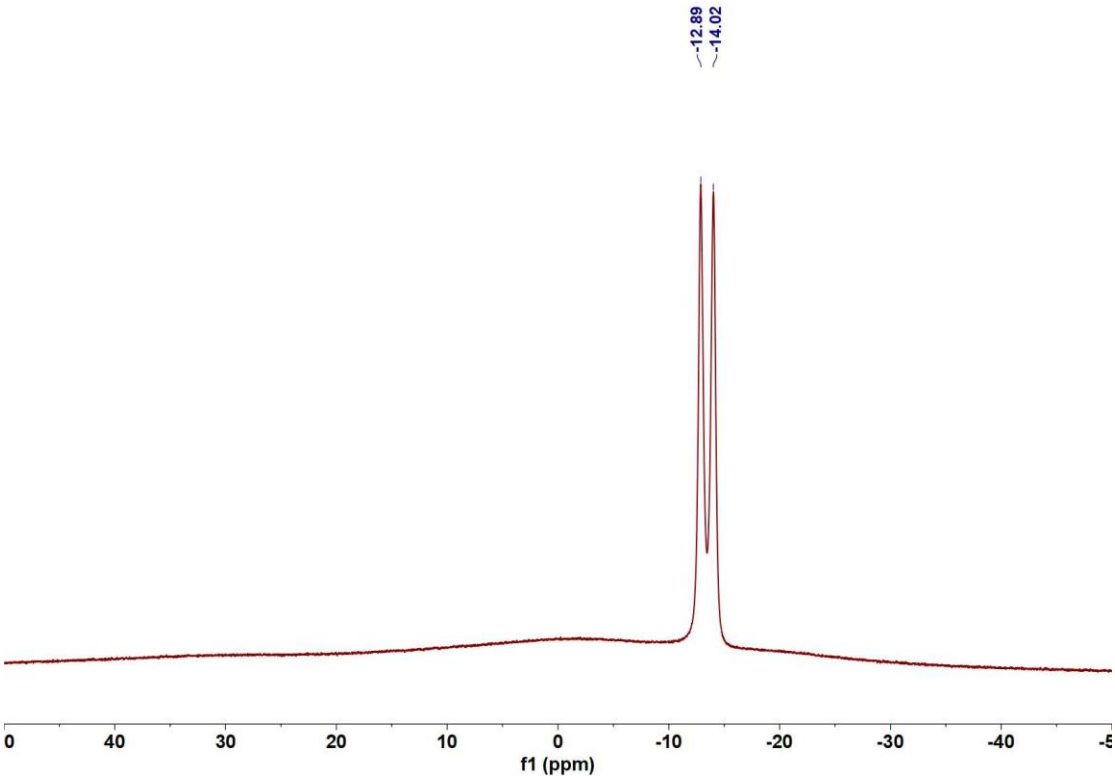


Figure S3. ^{11}B NMR spectrum of ***n*-Bu$_4$N(B$_6$H$_7$)** in $CDCl_3$ at 298K

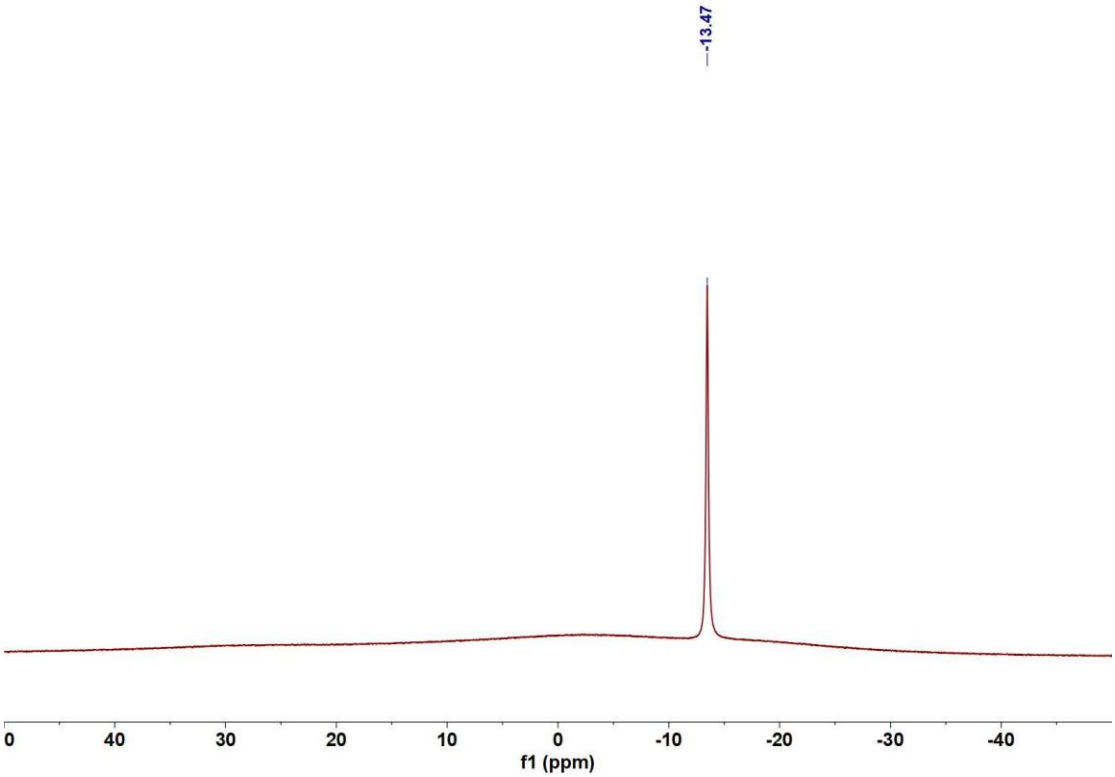


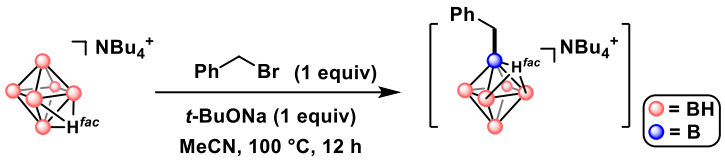
Figure S4. $^{11}B\{^1H\}$ NMR spectrum of ***n*-Bu$_4$N(B$_6$H$_7$)** in $CDCl_3$ at 298K

3. Optimization of reaction conditions for alkylation of *closo*-hexaborate anion

General procedures for optimization of reaction conditions

To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (31.2 mg, 0.1 mmol, 1 equiv), and *t*-BuONa (9.6 mg, 0.1 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (0.5 mL) was added via syringe. Then the solution of benzyl bromide (17.1 mg, 0.1 mmol, 1 equiv) in dry MeCN (0.5 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. The flask was cooled to room temperature and aliquot sample was subjected to spectroscopic analysis. ^{11}B NMR spectroscopy was used to determine conversion.

Table S1 Optimization of reaction conditions for alkylation of *closo*-hexaborate anion



Entry	Deviation from standard reaction condition	conversion (%)[a]
1	None	85
2	K_3PO_4 instead of *t*-BuONa	38
3	1.2 equiv of K_3PO_4 instead of 1.0 equiv of *t*-BuONa	50
4	1.5 equiv of K_3PO_4 instead of 1.0 equiv of *t*-BuONa	54
5	*t*-BuOK instead of *t*-BuONa	85
6	*t*-BuOLi instead of *t*-BuONa	13
7	LiHMDS instead of *t*-BuONa	53
8	NaHMDS instead of *t*-BuONa	trace
9	KHMDS instead of *t*-BuONa	44
10	DABCO instead of *t*-BuONa	trace
11	80 ℃ instead of 100 ℃	85
12	120 ℃ instead of 100 ℃	84
13	Toluene instead of MeCN	79
14	1,4-Dioxane instead of MeCN	83

[a] ^{11}B NMR conversion

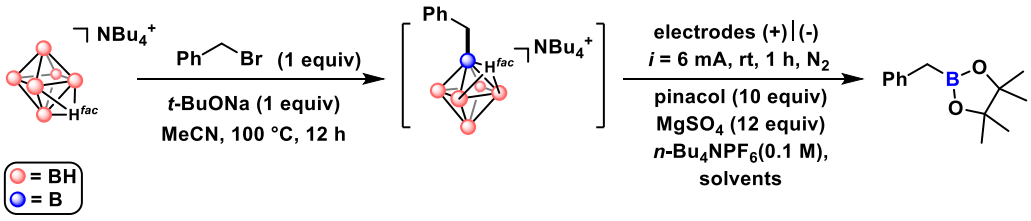
4. Optimization of reaction conditions for the bulk electrolysis

General procedures for optimization of reaction conditions

To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (31.2 mg, 0.1 mmol, 1 equiv), and *t*-BuONa (9.6 mg, 0.1 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (0.5 mL) was added via syringe. Then the solution of benzyl bromide (17.1 mg, 0.1 mmol, 1 equiv) in dry MeCN (0.5 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature.

To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, pinacol (118.2 mg, 1 mmol, 10 equiv), $MgSO_4$ (144.4 mg, 1.2 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as both the anode and cathode and then backfilled with N_2 atmosphere. The mixture was pre-stirred for five minutes, and then subjected to the bulk electrolysis under constant current mode of 6 mA until passing 2.20 F/mol of total charge (1 hour) at room temperature. ^{1}H NMR spectroscopic yields were determined using 1,3,5-trimethoxybenzene as the internal standard, and isolated yields are based on the two-step protocol.

Table S2 Optimization of reaction conditions for electrolysis



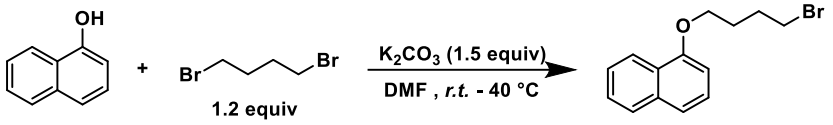
Entry	Solvents	electrodes	Yield (%)[b]
1	MeCN	RVC(+)|RVC(-)	29
3	MeCN:DCE = 1:1(v/v)	RVC(+)|RVC(-)	73
4	MeCN:DCM = 1:1(v/v)	RVC(+)|RVC(-)	74
5	MeCN:MeOH = 1:1(v/v)	RVC(+)|RVC(-)	46
2	MeCN:TCE = 1:1(v/v)	RVC(+)|RVC(-)	83
6	MeCN:TCE = 2:1(v/v)	RVC(+)|RVC(-)	77
7	MeCN:TCE = 5:1(v/v)	RVC(+)|RVC(-)	80
8	MeCN:TCE = 1:1(v/v)	RVC(+)|RVC(-)	69[c]
9	MeCN:TCE = 1:1(v/v)	Glassy C; Glassy C	65
10	MeCN:TCE = 1:1(v/v)	GF(+)|GF(-)	28
11	MeCN:TCE= 1:1(v/v)	RVC(+)|RVC(-)	79[d]
12	MeCN:TCE= 1:1(v/v)	RVC(+)|RVC(-)	63[e]

13	MeCN:TCE= 1:1(v/v)	RVC(+)|RVC(-)	trace[f]

[b] ^{1}H NMR yields were determined by using 1,3,5-trimethoxybenzene as the internal standard, yields are based on the two-step protocol. [c] 12 mA current. [d] 0.5 h electrolysis. [e] $LiPF_6$ as the electrolyte. [f] LiCl as the electrolyte.

5. Preparation of alkyl halides and alkyl pseudohalides

Majority of the benzyl and alkyl bromides used in the studies are commercially available and were used as received.

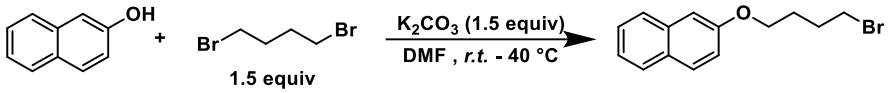


1-Naphthol (434.7 mg, 3 mmol, 1 equiv), potassium carbonate (626.3 mg, 4.5 mmol, 1.5 equiv) and a magnetic stir bar were added to a 50 mL three-neck bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DMF (10 mL) was added. The mixture was stirred for 5 min, then the solution of 1,4-dibromobutane (775.1 mg, 3.6 mmol, 1.2 equiv) in dry DMF (5 mL) was added. The reaction solution was stirred in a 40 ºC oil bath for 6 hours. Full consumption of the starting material was confirmed by TLC. Water (20 mL) was added to the mixture and extracted with DCM (20 mL), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (332.0 mg, 40%) (Petroleum: EtOAc = 10:1, R_f = 0.7).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.26 (m, 1H), 7.84 – 7.79 (m, 1H), 7.53 – 7.47 (m, 2H), 7.45 – 7.36 (m, 2H), 6.81 (d, J = 7.47 Hz, 1H), 4.18 (t, J = 5.8 Hz, 2H), 3.56 (t, J = 6.5 Hz, 2H), 2.23 – 2.16 (m, 2H), 2.14 – 2.07 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.52, 134.44, 127.43, 126.35, 125.81, 125.57, 125.14, 121.88, 120.20, 104.47, 66.92, 33.53, 29.65, 27.85.

The NMR spectra are consistent with literature report.[2] CAS registry No. 87723-21-5

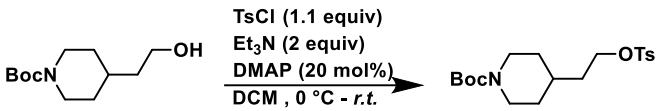


2-Naphthol (435.0 mg, 3 mmol, 1 equiv), potassium carbonate (625.1 mg, 4.5 mmol, 1.5 equiv) and a magnetic stir bar were added to a 50 mL three-neck bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DMF (10 mL) was added. The mixture was stirred for 5 min, then the solution of 1,4-dibromobutane (983.6 mg, 4.5 mmol, 1.5 equiv) in dry DMF (5 mL) was added. The reaction solution was stirred in a 40 ºC oil bath for 6 hours. Full consumption of the starting material was confirmed by TLC. Water (20 mL) was added to the mixture and extracted with DCM (20 mL), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (377.6 mg, 45%) (Petroleum, R_f = 0.28).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 3H), 7.44 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.34 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.13 – 7.16 (m, 2H), 4.12 (t, *J* = 6.0 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.08 – 2.18 (m, 2H), 2.07 – 1.97 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.79, 134.52, 129.39, 128.95, 127.62, 126.68, 126.35, 123.59, 118.85, 106.55, 66.80, 33.46, 29.51, 27.85.

The NMR spectra are consistent with literature report.[3] CAS registry No. 87723-22-6

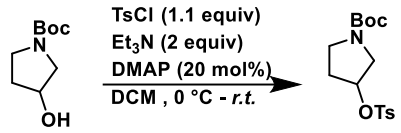


TsCl (442.7 mg, 2.31 mmol, 1.1 equiv), DMAP (51.4 mg, 0.42 mmol, 0.2 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then DCM (10 mL) and Et_3N (0.6 mL, 4.2 mmol, 2 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of 1-Boc-4-(2-hydroxyethyl)piperidine (481.1 mg, 2.1 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the ice bath was removed and the mixture was kept stirring for 14 hours. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (566.3 mg, 70%) (Petroleum: EtOAc = 4:1, R_f = 0.46).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.39 – 7.30 (m, 2H), 4.06 (t, *J* = 6.2 Hz, 2H), 4.06 – 3.98 (m, 2H), 2.67 – 2.53 (m, 2H), 2.45 (s, 3H), 1.61 – 1.47 (m, 5H), 1.43 (s, 9H), 1.12 – 0.93 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.73, 144.81, 132.95, 129.83, 127.86, 79.31, 67.93, 43.68, 35.21, 32.12, 31.58, 28.40, 21.60.

The NMR spectra are consistent with literature report.[4] CAS registry No. 89151-45-1

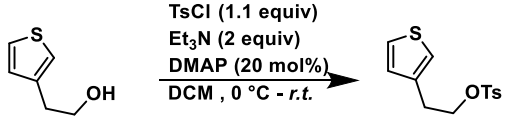


TsCl (630.7 mg, 3.3 mmol, 1.1 equiv), DMAP (73.1 mg, 0.6 mmol, 0.2 equiv) and a magnetic stir bar were added to a 100 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (10 mL) and Et_3N (0.84 mL, 6 mmol, 2 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of 1-(tert-butoxycarbonyl)-3-pyrrolidinol (566.3 mg, 3 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the ice bath was removed and the mixture was kept stirring for 14 hours. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (610.5 mg, 60%) (Petroleum: EtOAc = 3:1, R_f = 0.41).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 5.11 – 4.92 (m, 1H), 3.54 – 3.31 (m, 4H), 2.43 (s, 3H), 2.20 – 1.87 (m, 2H), 1.41 (s, 9H).

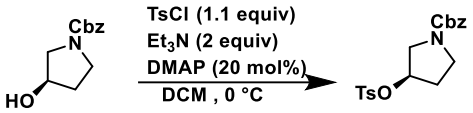
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.14, 145.02, 134.32, 129.97, 127.69, 80.72, 80.00, 79.74, 51.83, 51.36, 43.56, 32.37, 31.33, 28.39, 21.64.

The NMR spectra are consistent with literature report.[5] CAS registry No. 371240-55-0



TsCl (629.3 mg, 3.3 mmol, 1.1 equiv), DMAP (74.7 mg, 0.6 mmol, 0.2 equiv) and a magnetic stir bar were added to a 100 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (10 mL) and Et_3N (0.84 mL, 6 mmol, 2 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of thiophene-3-ethanol (388.5 mg, 3 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the ice bath was removed and the mixture was kept stirring for 14 hours. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (643.9 mg, 77%) (Petroleum: EtOAc = 3:1, R_f = 0.75).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.90 – 6.87 (m, 1H), 6.80 – 6.77 (m, 1H), 4.13 (t, *J* = 6.9 Hz, 2H), 2.91 (t, *J* = 6.9 Hz, 2H), 2.36 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.71, 136.38, 132.97, 129.80, 128.02, 127.83, 125.83, 122.13, 69.92, 29.82, 21.63.
The NMR spectra are consistent with literature report.[6] CAS registry No. 40412-09-7

6. Preparation of chiral alkyl pseudohalides



TsCl (417.9 mg, 2.2 mmol, 1.1 equiv), DMAP (48.3 mg, 0.4 mmol, 0.2 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.6 mL, 4 mmol, 2 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (*R*)-(+)-1-Cbz-3-pyrrolidinol (421.5 mg, 2 mmol, 1 equiv) in dry DCM (2 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with DCM (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (498.9 mg, 70%, >99:1 *e.r.*, $[\alpha]_D^{22.5}$ = 6.4 (c = 0.8, $CHCl_3$)) (Petroleum: EtOAc = 4:1, R_f = 0.27).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.2 Hz, 2H), 7.37 – 7.29 (m, 7H), 5.20 – 4.98 (m, 3H), 3.64 – 3.45 (m, 4H), 2.44 (d, *J* = 6.3 Hz, 3H), 2.24 – 1.94 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.47, 154.37, 145.05, 136.47, 133.56, 129.96, 129.93, 128.40, 127.96, 127.83, 127.61, 80.39, 79.67, 66.89, 51.91, 51.65, 43.76, 43.42, 32.27, 31.28, 21.57.

The NMR spectra are consistent with literature report.[7] CAS registry No. 158654-83-2

Chiral HPLC conditions: IF column (30% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S6): t_1 = 18.632 min (major), t_2 = 24.104 min (minor).

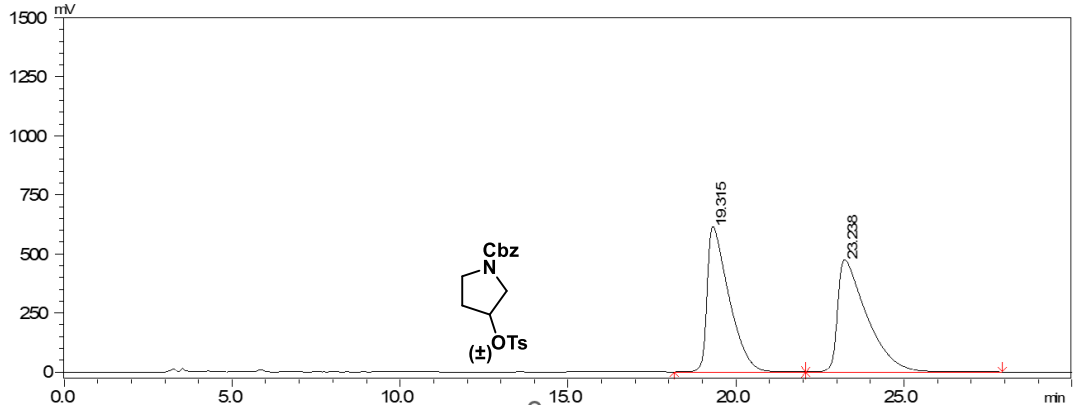


Figure S5. HPLC trace of benzyl 3-(tosyloxy)pyrrolidine-1-carboxylate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	19.315	615824	27781643	49.226
2	23.238	474986	28655583	50.774
total		1090810	56437226	100.000

Table S3. HPLC trace of benzyl 3-(tosyloxy)pyrrolidine-1-carboxylate.

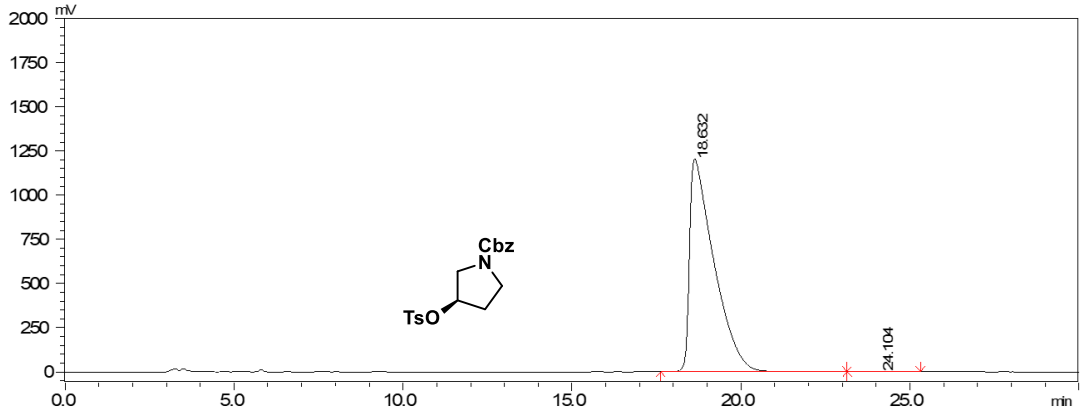
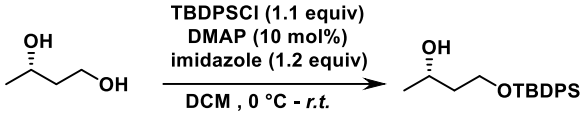


Figure S6. HPLC trace of benzyl (*R*)-3-(tosyloxy)pyrrolidine-1-carboxylate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	18.632	1204771	60500806	99.952
2	24.104	585	29150	0.048
total		1205356	60529956	100.000

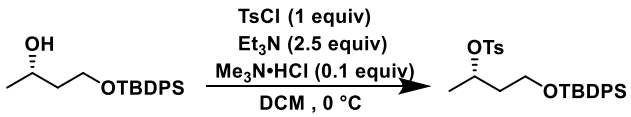
Table S4. HPLC trace of benzyl (*R*)-3-(tosyloxy)pyrrolidine-1-carboxylate.



Imidazole (407.1 mg, 6 mmol, 1.2 equiv), DMAP (60.6 mg, 0.5 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (15 mL) was added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (*S*)-(+)-1,3-butaneiol (458.5 mg, 5 mmol, 1 equiv) and TBDPSCl (1511.7 mg, 5.5 mmol, 1.1 equiv) in dry DCM (10 mL) was added. After addition, the ice bath was removed and the mixture was kept stirring for 12 hours. Full consumption of the starting material was confirmed by TLC. Water (15 mL) was added to the mixture and extracted with DCM (15 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (1398.5 mg, 84%) (Petroleum: EtOAc = 8:1, R_f = 0.27).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.48 – 7.36 (m, 6H), 4.12 – 4.07 (m, 1H), 3.91 – 3.82 (m, 2H), 3.25 (s, 1H), 1.79 – 1.71 (m, 1H), 1.68 – 1.60 (m, 1H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.06 (s, 9H).

The NMR spectra are consistent with literature report.[8] CAS registry No. 1240290-96-3



TsCl (812.2 mg, 4.25 mmol, 1 equiv), Me_3N•HCl (44.0 mg, 0.43 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL)

and Et_3N (1.5 mL, 10.6 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (2*S*)-4-[[(1,1-dimethylethyl)diphenylsilyl]oxy]-2-butanol (1395.4 mg, 4.25 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (1263.7 mg, 62%, 98.5:1.5 *e.r.*, $[\alpha]_D^{22.6}$ = -1.4 (c = 0.8, $CHCl_3$)) (Petroleum: EtOAc = 20:1, R_f = 0.26).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.47 – 7.41 (m, 2H), 7.41 – 7.34 (m, 4H), 7.27 – 7.22 (m, 2H), 4.90 – 4.80 (m, 1H), 3.56 (t, *J* = 6.1 Hz, 2H), 2.39 (s, 3H), 1.94 – 1.83 (m, 1H), 1.73 – 1.63 (m, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.01 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.32, 135.48, 135.45, 134.39, 133.50, 133.46, 129.70, 129.67, 127.70, 127.67, 127.65, 77.95, 59.70, 39.26, 26.75, 21.59, 20.97, 19.09.

The NMR spectra are consistent with literature report.[9]

Chiral HPLC conditions: AS column (5% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S8): t_1 = 8.595 min (major), t_2 = 11.010 min (minor).

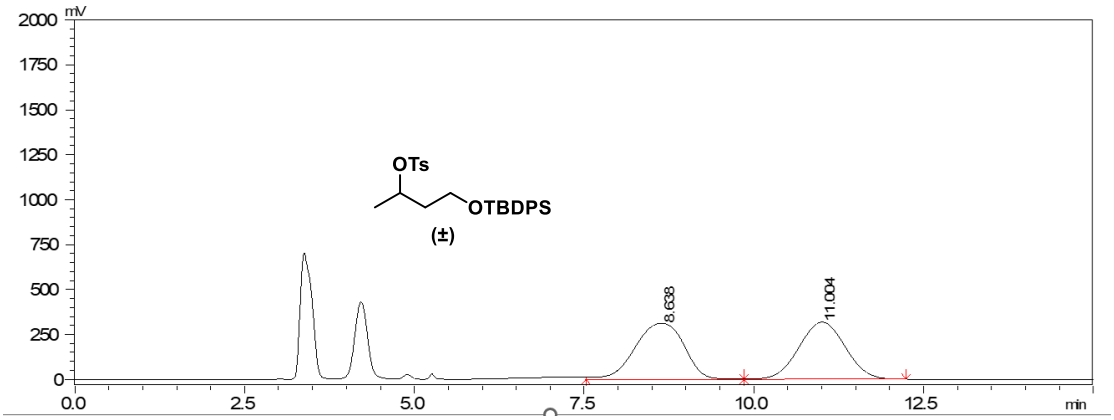


Figure S7. HPLC trace of 4-((tert-butyldiphenylsilyl)oxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.638	311373	15600823	50.956
2	11.004	316899	15015615	49.044
total		628272	30616438	100.000

Table S5. HPLC trace of 4-((tert-butyldiphenylsilyl)oxy)butan-2-yl 4-methylbenzenesulfonate.

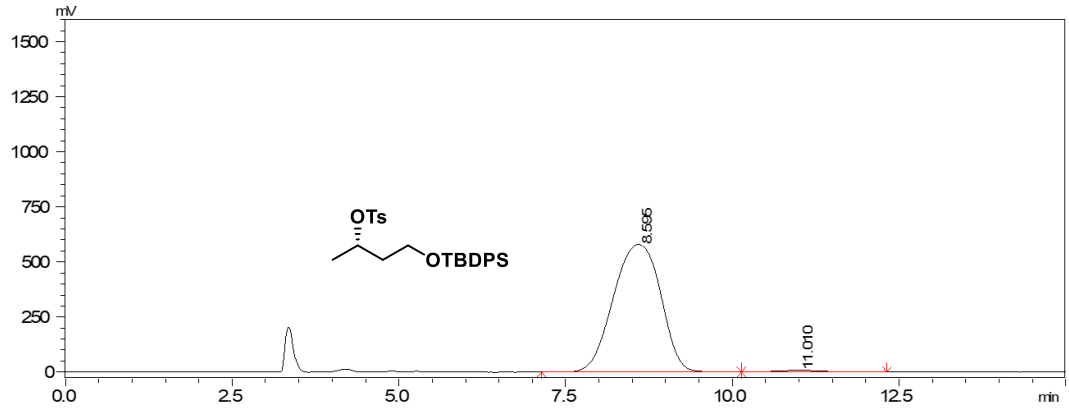
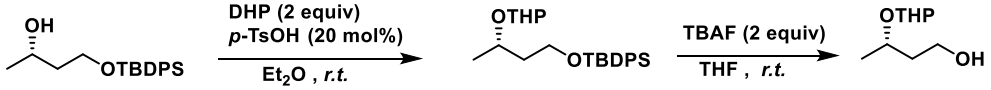


Figure S8. HPLC trace of (*S*)-4-((tert-butyldiphenylsilyl)oxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.595	579383	28704926	98.559
2	11.010	8412	419814	1.441
total		587795	29124740	100.000

Table S6. HPLC trace of (*S*)-4-((tert-butyldiphenylsilyl)oxy)butan-2-yl 4-methylbenzenesulfonate.



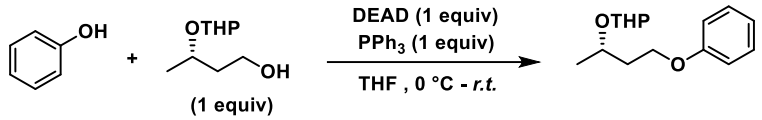
p-TsOH (603.9 mg, 3.2 mmol, 0.2 equiv) and a magnetic stir bar were added to a 250 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry Et_2O (70 mL) was added. The mixture was stirred for 5 min, then the solution of (2*S*)-4-[[(1,1-dimethylethyl)diphenylsilyl]oxy]-2-butanol (5228.0 mg, 16 mmol, 1 equiv) and DHP (2706.4 mg, 32 mmol, 2 equiv) in dry Et_2O (20 mL) was added. After addition, the mixture was kept stirring for 16 hours. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with EtOAc (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (3841.5 mg, 58%) (Petroleum: EtOAc = 9:1, R_f = 0.63).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 8H), 7.46 – 7.34 (m, 12H), 4.76 – 4.72 (m, 1H), 4.64 – 4.59 (m, 1H), 4.08 – 3.89 (m, 3H), 3.88 – 3.66 (m, 5H), 3.51 – 3.40 (m, 2H), 1.93 – 1.39 (m, 16H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.1 Hz, 3H), 1.05 (d, *J* = 1.7 Hz, 18H).

Tert-butyldiphenyl((3*S*)-3-((tetrahydro-2*H*-pyran-2-yl)oxy)butoxy)silane (3841.5 mg, 9.3 mmol) and a magnetic stir bar were added to a 100 mL bottle. The bottle was tightly sealed with the rubber stoppers, then dry THF (45 mL) was added. The mixture was stirred for 5 min, then TBAF (1.0 M in THF, 18.6 mmol, 18.6 mL, 2 equiv) was added. After addition, the mixture was kept stirring for 3 hours. Full consumption of the starting material was confirmed by TLC. the organic layers were concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (1398.2 mg, 86%) (Petroleum: EtOAc =

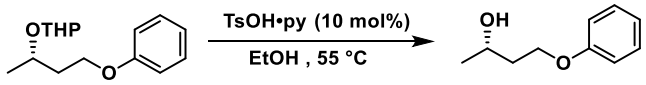
1:1, R_f = 0.23).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 – 4.60 (m, 1H), 4.56 – 4.48 (m, 1H), 4.01 – 3.81 (m, 4H), 3.79 – 3.58 (m, 4H), 3.48 – 3.39 (m, 2H), 3.27 (s, 1H), 2.65 (s, 1H), 1.78 – 1.59 (m, 8H), 1.51 – 1.37 (m, 8H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H).



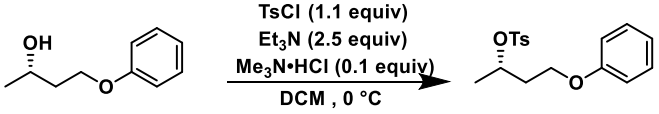
Phenol (384.0 mg, 4 mmol), PPh_3 (1088.8 mg, 4 mmol, 1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry THF (4 mL) was added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (3*S*)-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (696.5 mg, 4 mmol, 1 equiv) in dry THF (2 mL) was added. The solution of DEAD (705.9 mg, 4 mmol, 1 equiv) in dry THF (2 mL) was added dropwise and the reaction was warmed to room temperature and stirred for 18 hours. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with EtOAc (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (548.5 mg, 55%) (Petroleum: EtOAc = 20:1, R_f = 0.29).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 4H), 6.98 – 6.86 (m, 6H), 4.78 – 4.72 (m, 1H), 4.66 – 4.60 (m, 1H), 4.19 – 3.90 (m, 7H), 3.84 – 3.74 (m, 1H), 3.54 – 3.39 (m, 2H), 2.06 – 1.88 (m, 4H), 1.88 – 1.61 (m, 4H), 1.61 – 1.40 (m, 8H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 3H).



TsOH•py (56.3 mg, 0.2 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry EtOH (3 mL) was added. The mixture was stirred for 5 min, then the solution of tetrahydro-2-[(1*S*)-1-methyl-3-phenoxypropoxy]-2*H*-pyran (548.5mg, 2.19 mmol, 1 equiv) in dry EtOH (2 mL) was added . After addition, the mixture was heated to 55 ºC and kept stirring for 12 hours. Full consumption of the starting material was confirmed by TLC. the organic layers were concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (306.9 mg, 83%) (Petroleum: EtOAc = 4:1, R_f = 0.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.00 – 6.88 (m, 3H), 4.22 – 4.04 (m, 3H), 2.16 (s, 1H), 1.97 – 1.88 (m, 2H), 1.27 (d, *J* = 6.2 Hz, 3H).



TsCl (389.8 mg, 2 mmol, 1.1 equiv), Me_3N•HCl (21.4 mg, 0.2 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber

stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.7 mL, 4.6 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (2*S*)-4-phenoxy-2-butanol (306.9 mg, 1.83 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (364.9 mg, 62%, 98.5:1.5 *e.r.*, $[\alpha]_D^{22.2} = 43.8$ (c = 0.8, $CHCl_3$)) (Petroleum: EtOAc = 8:1, $R_f = 0.5$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, 2H), 7.28 – 7.19 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 1.1 Hz, 1H), 6.70 – 6.63 (m, 2H), 4.93 – 4.81 (m, 1H), 3.86 – 3.77 (m, 1H), 3.70 – 3.60 (m, 1H), 2.27 (s, 3H), 2.08 – 1.91 (m, 2H), 1.44 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.34, 144.52, 133.79, 129.65, 129.27, 127.53, 120.69, 114.19, 77.25, 62.84, 36.18, 21.58, 21.53.

The NMR spectra are consistent with literature report.[10]

Chiral HPLC conditions: OJ column (10% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S10): t_1 = 25.372 min (major), t_2 = 28.398 min (minor).

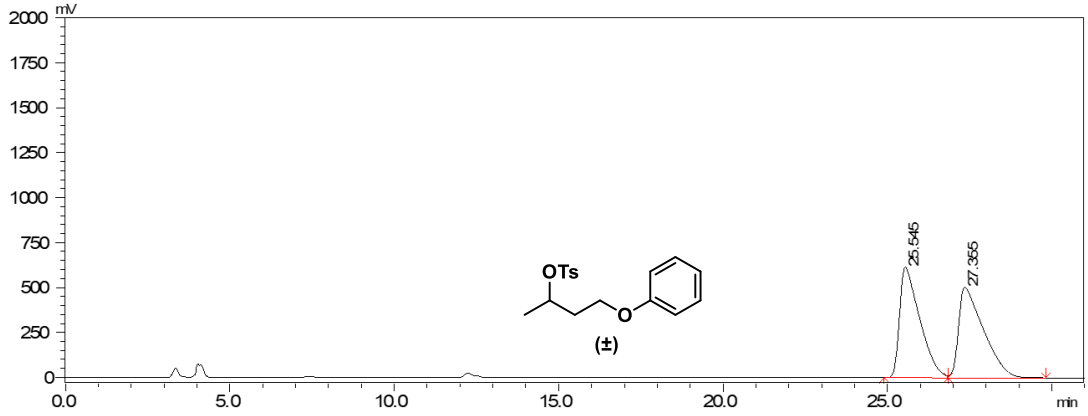


Figure S9. HPLC trace of 4-phenoxybutan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	25.545	614685	26234104	49.850
2	27.355	503957	26391817	50.150
total		1118641	52625921	100.000

Table S7. HPLC trace of 4-phenoxybutan-2-yl 4-methylbenzenesulfonate.

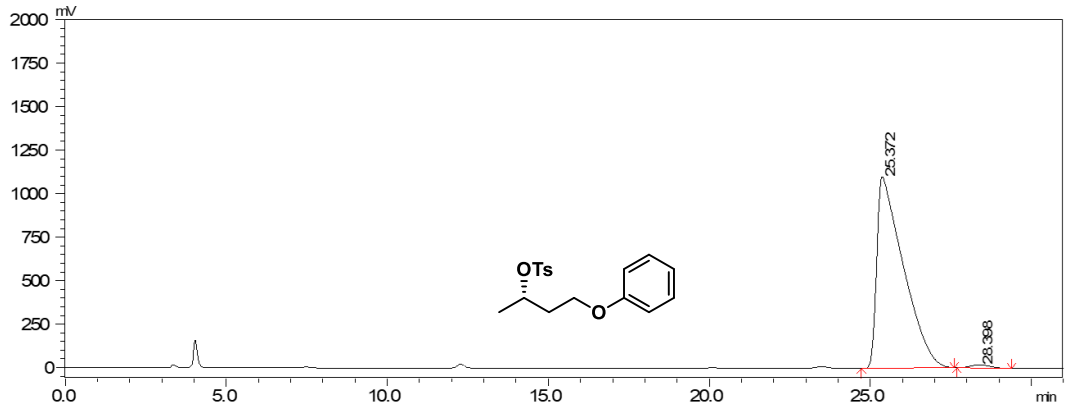
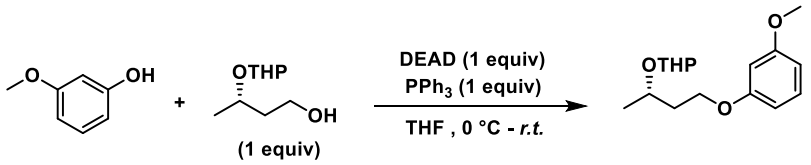


Figure S10. HPLC trace of (*S*)-4-phenoxybutan-2-yl 4-methylbenzenesulfonate.

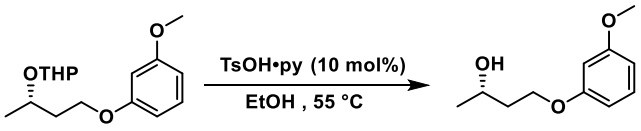
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	25.372	1100698	63045659	98.746
2	28.398	18762	800763	1.254
total		1119461	63846422	100.000

Table S8. HPLC trace of (*S*)-4-phenoxybutan-2-yl 4-methylbenzenesulfonate.



Guaiacol (498.4 mg, 4.0 mmol), PPh_3 (1047.5 mg, 4 mmol, 1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry THF (4 mL) was added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (3*S*)-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (696.5 mg, 4 mmol, 1 equiv) in dry THF (2 mL) was added. The solution of DEAD (699.6 mg, 4 mmol, 1 equiv) in dry THF (2 mL) was added dropwise and the reaction was warmed to room temperature and stirred for 18 hours. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with EtOAc (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (471.7 mg, 42%) (Petroleum: EtOAc = 9:1, R_f = 0.83).

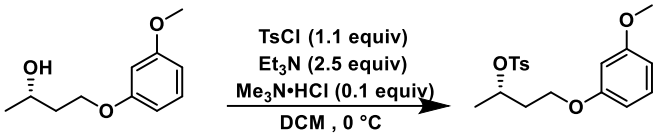
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.56 – 6.42 (m, 6H), 4.78 – 4.71 (m, 1H), 4.66 – 4.59 (m, 1H), 4.13 – 3.88 (m, 7H), 3.82 – 3.74 (m, 7H), 3.54 – 3.39 (m, 2H), 2.05 – 1.87 (m, 4H), 1.87 – 1.74 (m, 2H), 1.76 – 1.62 (m, 2H), 1.61 – 1.42 (m, 8H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H).



TsOH•py (59.1 mg, 0.2 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL

Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry EtOH (3 mL) was added. The mixture was stirred for 5 min, then the solution of 2-(((*S*)-4-(3-methoxyphenoxy)butan-2-yl)oxy)tetrahydro-2*H*-pyran (471.1 mg, 1.68 mmol, 1 equiv) in dry EtOH (2 mL) was added . After addition, the mixture was heated to 55 ºC and kept stirring for 12 hours. Full consumption of the starting material was confirmed by TLC. the organic layers were concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (247.3 mg, 77%) (Petroleum: EtOAc = 4:1, R_f = 0.29).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.2 Hz, 1H), 6.54 – 6.49 (m, 2H), 6.48 – 6.45 (m, 1H), 4.19 – 4.03 (m, 3H), 3.78 (s, 3H), 2.22 (s, 1H), 1.95 – 1.87 (m, 2H), 1.26 (d, *J* = 6.3 Hz, 3H).



TsCl (303.0 mg, 1.43 mmol, 1.1 equiv), Me_3N•HCl (12.9 mg, 0.13 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.5 mL, 3.25 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (2*S*)-4-(3-methoxyphenoxy)-2-butanol (247.3 mg, 1.3 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated i*n vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (246.4 mg, 54%, 98.5:1.5 *e.r.*, $[\alpha]_D^{22.1}$ = 20.5 (c = 0.8, $CHCl_3$)) (Petroleum: EtOAc = 8:1, R_f = 0.27).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.05 (m, 3H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 2.4 Hz, 1H), 6.22 (s, 1H), 4.92 – 4.77 (m, 1H), 3.87 – 3.72 (m, 4H), 3.67 – 3.57 (m, 1H), 2.28 (s, 3H), 2.09 – 1.89 (m, 2H), 1.44 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.67, 159.62, 144.56, 133.78, 129.68, 129.66, 127.52, 106.50, 106.16, 100.74, 77.21, 62.97, 55.20, 36.13, 21.60, 21.47.

HR-MS (EI) for $C_{18}H_{22}O_5S$ [M] *m/z* $[M]^+$: calculated: 350.1185 found: 350.1190

Chiral HPLC conditions: AD column (10% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S12): t_1 = 9.830 min (major), t_2 = 10.858 min (minor).

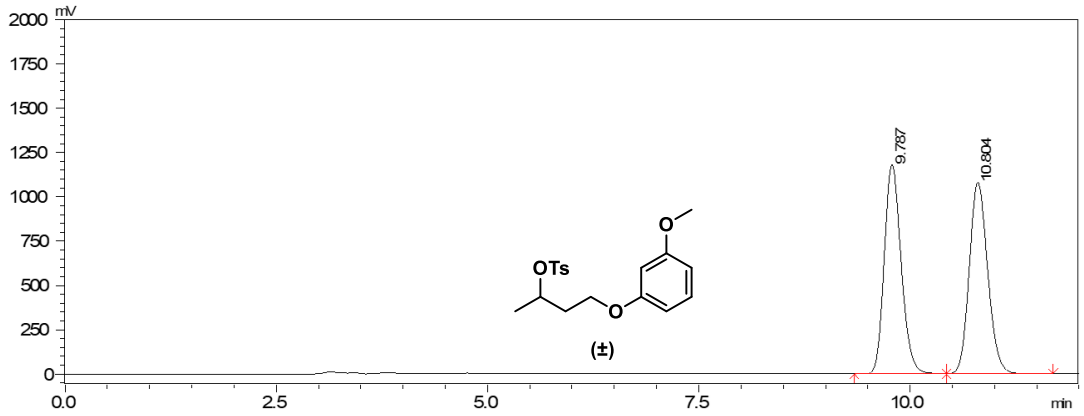


Figure S11. HPLC trace of 4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.787	1180255	16418597	50.035
2	10.804	1078756	16395476	49.965
total		2259011	32814073	100.000

Table S9. HPLC trace of 4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate.

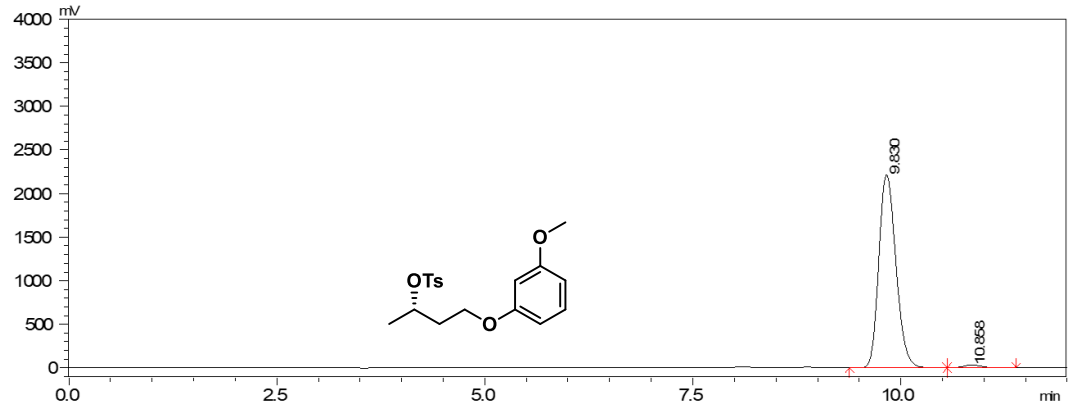
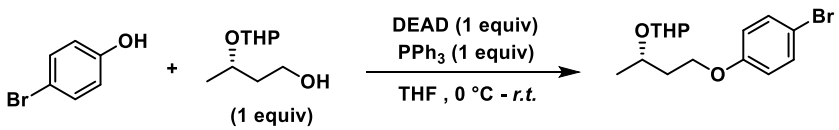


Figure S12. HPLC trace of (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.830	2215863	31806574	98.414
2	10.858	33549	512705	1.586
total		2249412	32319279	100.000

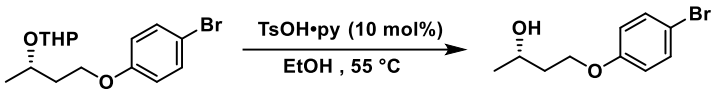
Table S10. HPLC trace of (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate.



4-Bromophenol (569.7 mg, 3.12 mmol), PPh_3 (802.5 mg, 3.12 mmol, 1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber

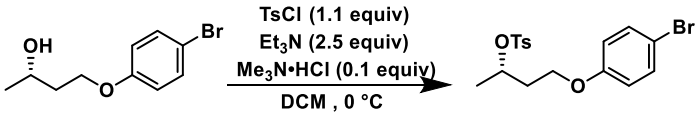
stoppers and was evaluated and backfilled with N_2 three times, then dry THF (4 mL) was added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (3*S*)-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (543.4 mg, 3.12 mmol, 1 equiv) in dry THF (2 mL) was added. The solution of DEAD (551.3 mg, 3.12 mmol, 1 equiv) in dry THF (2 mL) was added dropwise and the reaction was warmed to room temperature and stirred for 18 hours. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with EtOAc (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (593.3 mg, 58%) (Petroleum: EtOAc = 9:1, R_f = 0.83).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 6.80 – 6.73 (m, 4H), 4.73 – 4.69 (m, 1H), 4.63 – 4.57 (m, 1H), 4.08 – 3.88 (m, 7H), 3.80 – 3.71 (m, 1H), 3.52 – 3.37 (m, 2H), 1.99 – 1.86 (m, 4H), 1.84 – 1.60 (m, 4H), 1.58 – 1.41 (m, 8H), 1.30 (d, *J* = 6.3 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H).



TsOH•py (59.3 mg, 0.2 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry EtOH (3 mL) was added. The mixture was stirred for 5 min, then the solution of 2-(((*S*)-4-(4-bromophenoxy)butan-2-yl)oxy)tetrahydro-2*H*-pyran (593.3 mg, 1.8 mmol, 1 equiv) in dry EtOH (2 mL) was added . After addition, the mixture was heated to 55 ºC and kept stirring for 12 hours. Full consumption of the starting material was confirmed by TLC. the organic layers were concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (374.0 mg, 85%) (Petroleum: EtOAc = 4:1, R_f = 0.29).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 6.82 – 6.75 (m, 2H), 4.17 – 4.02 (m, 3H), 1.97 – 1.83 (m, 3H), 1.27 (d, *J* = 6.2 Hz, 3H).



TsCl (324.8 mg, 1.68 mmol, 1.1 equiv), Me_3N•HCl (14.8 mg, 0.15 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.54 mL, 3.83 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (2*S*)-4-(4-bromophenoxy)-2-butanol (374.0 mg, 1.53 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (347.3 mg, 57%, 98.5:1.5 *e.r.*, $[\alpha]_D^{22.1}$ = 3.8 (c = 0.4, $CHCl_3$)) (Petroleum: EtOAc = 8:1, R_f = 0.27).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.34 – 7.28 (m, 2H), 7.13 – 7.11 (m, 2H),

6.56 – 6.51 (m, 2H), 4.90 – 4.79 (m, 1H), 3.80 – 3.73 (m, 1H), 3.64 – 3.57 (m, 1H), 2.28 (s, 3H), 2.06 – 1.90 (m, 2H), 1.44 (d, J = 6.3 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.48, 144.60, 133.78, 132.09, 129.69, 127.55, 115.99, 112.89, 76.98, 63.20, 36.10, 21.69, 21.61.

HR-MS (EI) for $C_{17}H_{19}{}^{79}BrO_4S$ [M] *m/z* $[M]^+$: calculated: 398.0187 found: 398.0189

Chiral HPLC conditions: IB column (5% EtOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S14): t_1 = 8.631 min (major), t_2 = 9.402 min (minor).

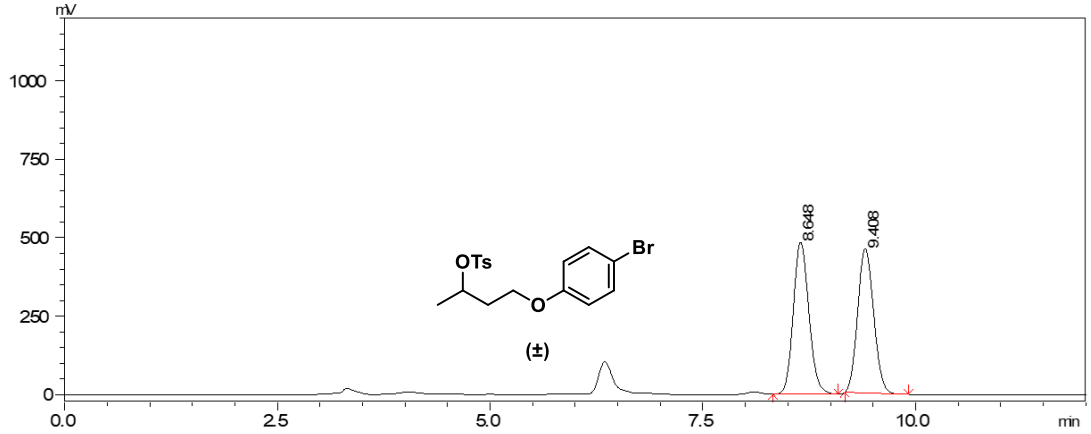


Figure S13. HPLC trace of 4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.648	484516	6173689	50.603
2	9.408	460937	6026498	49.397
total		945453	12200187	100.000

Table S11. HPLC trace of 4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate.

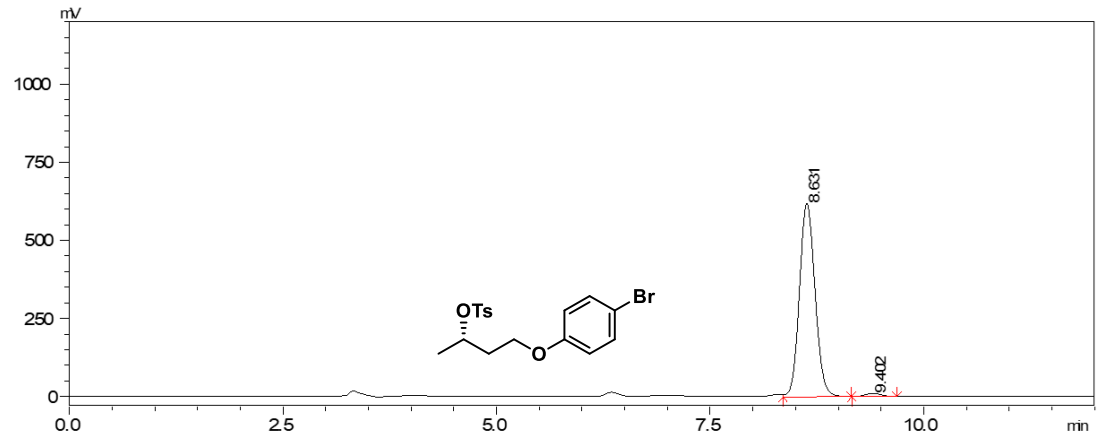
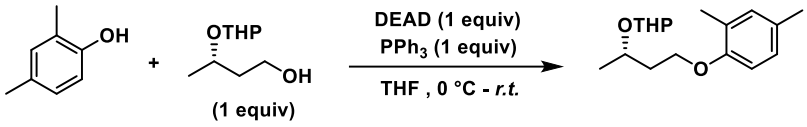


Figure S14. HPLC trace of (*S*)-4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate.

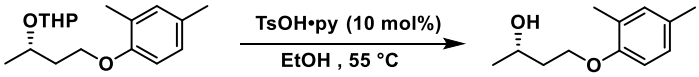
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.631	619175	7883269	98.409
2	9.402	10085	127453	1.591
total		629261	8010721	100.000

Table S12. HPLC trace of (*S*)-4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate.



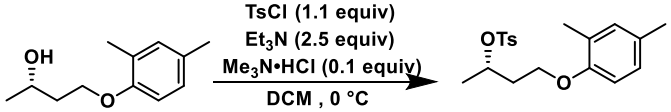
2,4-Dimethylphenol (696.0 mg, 5 mmol), PPh_3 (1322.8 mg, 5 mmol, 1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry THF (6 mL) was added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (3*S*)-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (870.7 mg, 5 mmol, 1 equiv) in dry THF (2 mL) was added. The solution of DEAD (873.5 mg, 5 mmol, 1 equiv) in dry THF (2 mL) was added dropwise and the reaction was warmed to room temperature and stirred for 12 hours. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with EtOAc (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (490.3 mg, 35%) (Petroleum: EtOAc = 20:1, R_f = 0.25).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.81 (m, 4H), 6.67 – 6.60 (m, 2H), 4.70 – 4.65 (m, 1H), 4.57 – 4.52 (m, 1H), 4.07 – 3.81 (m, 7H), 3.75 – 3.66 (m, 1H), 3.44 – 3.31 (m, 2H), 2.17 (s, 6H), 2.11 (s, 6H), 1.96 – 1.81 (m, 4H), 1.78 – 1.67 (m, 2H), 1.66 – 1.54 (m, 2H), 1.53 – 1.33 (m, 8H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H).



TsOH•py (50.9 mg, 0.2 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers, then dry EtOH (3 mL) was added. The mixture was stirred for 5 min, then the solution of 2-(((*S*)-4-(2,4-dimethylphenoxy)butan-2-yl)oxy)tetrahydro-2*H*-pyran (490.3 mg, 1.8 mmol, 1 equiv) in dry EtOH (2 mL) was added . After addition, the mixture was heated to 55 ºC and kept stirring for 12 hours. Full consumption of the starting material was confirmed by TLC. the organic layers were concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (292.9 mg, 84%) (Petroleum: EtOAc = 6:1, R_f = 0.31).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.92 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.21 – 4.03 (m, 3H), 2.43 (s, 1H), 2.27 (s, 3H), 2.20 (s, 3H), 2.00 – 1.90 (m, 2H), 1.28 (d, *J* = 6.2 Hz, 3H).



TsCl (221.2 mg, 1.16 mmol, 1.1 equiv), Me_3N•HCl (9.5 mg, 0.11 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.4 mL, 2.6 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (2*S*)-4-(2,4-dimethylphenoxy)-2-butanol (292.9 mg, 1.05 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were

dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (209.5 mg, 57%, 98.5:1.5 *e.r.*, $[\alpha]_D^{22.5}$ = 16.7 (c = 0.4, $CHCl_3$)) (Petroleum: EtOAc = 8:1, R_f = 0.42).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 2.3 Hz, 1H), 6.88 – 6.84 (m, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 4.92 – 4.82 (m, 1H), 3.81 – 3.73 (m, 1H), 3.66 – 3.58 (m, 1H), 2.26 (s, 6H), 2.06 (s, 3H), 2.04 – 1.92 (m, 2H), 1.46 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.28, 144.42, 133.76, 131.32, 129.59, 129.32, 127.44, 126.73, 126.06, 110.25, 77.34, 62.81, 36.36, 21.59, 21.47, 20.38, 16.04.

HR-MS (EI) for $C_{19}H_{24}O_4S$ [M] *m/z* $[M]^+$: calculated: 348.1395 found: 348.1393

Chiral HPLC conditions: OJ column (10% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S16): t_1 = 14.655 min (major), t_2 = 19.612 min (minor).

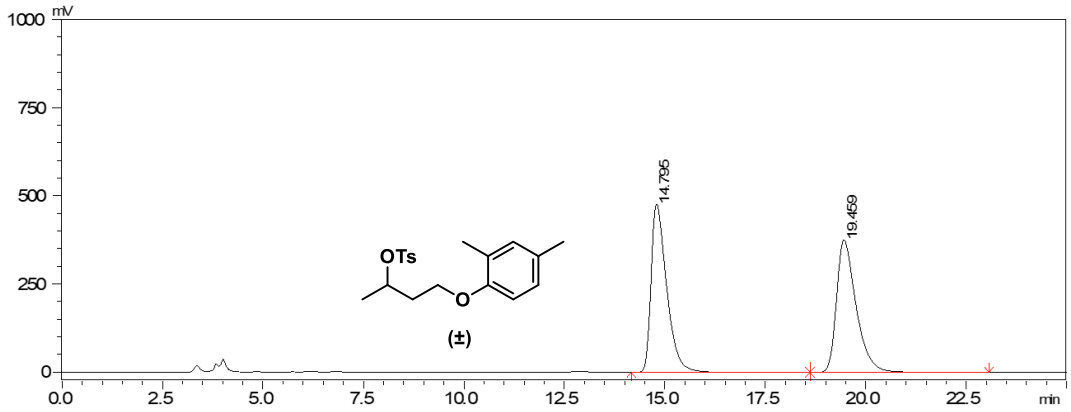


Figure S15. HPLC trace of 4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	14.795	477437	12912989	50.268
2	19.459	375509	12775303	49.732
total		852946	25688292	100.000

Table S13. HPLC trace of 4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate.

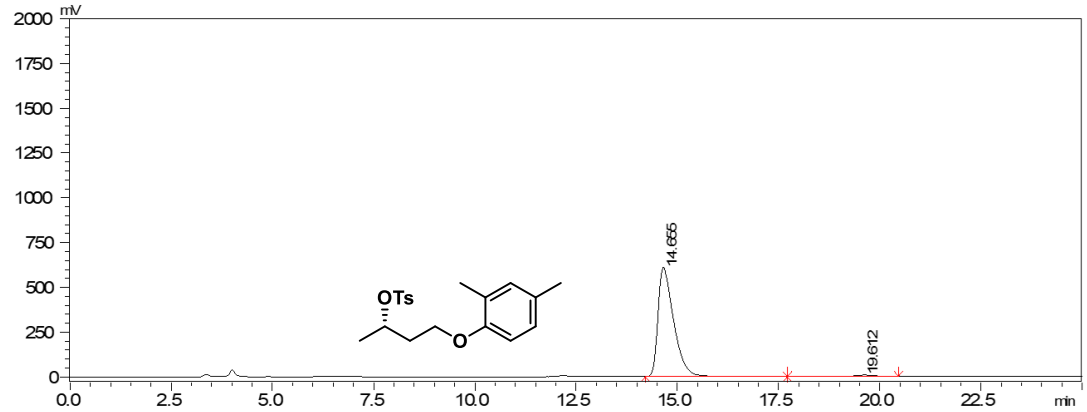
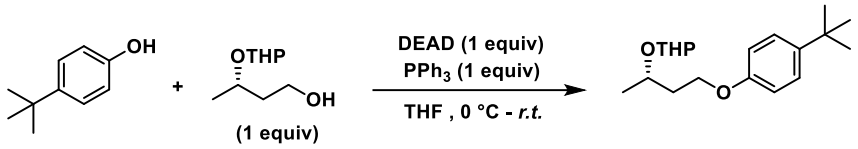


Figure S16. HPLC trace of (*S*)-4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate.

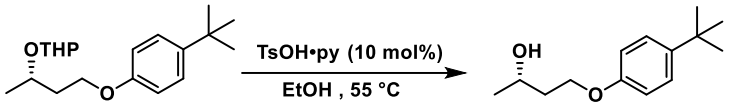
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	14.655	609104	16340704	98.493
2	19.612	7910	250098	1.507
total		617014	16590802	100.000

Table S14. HPLC trace of (*S*)-4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate.



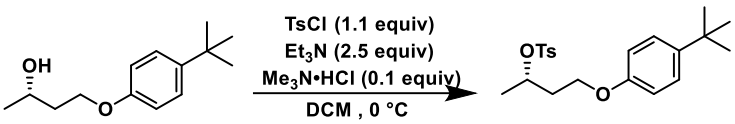
4-Tert-butylphenol (760.6 mg, 5 mmol), PPh_3 (1306.3 mg, 5 mmol, 1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry THF (6 mL) was added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (3*S*)-3-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (870.7 mg, 5 mmol, 1 equiv) in dry THF (2 mL) was added. The solution of DEAD (873.5 mg, 5 mmol, 1 equiv) in dry THF (2 mL) was added dropwise and the reaction was warmed to room temperature and stirred for 12 hours. Full consumption of the starting material was confirmed by TLC. Water (5 mL) was added to the mixture and extracted with EtOAc (5 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (464.3 mg, 30%) (Petroleum: EtOAc = 20:1, R_f = 0.25).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 6.88 – 6.81 (m, 4H), 4.79 – 4.72 (m, 1H), 4.68 – 4.59 (m, 1H), 4.11 – 3.90 (m, 7H), 3.85 – 3.78 (m, 1H), 3.55 – 3.41 (m, 2H), 2.04 – 1.89 (m, 4H), 1.86 – 1.77 (m, 2H), 1.73 – 1.62 (m, 2H), 1.60 – 1.42 (m, 8H), 1.33 – 1.29 (m, 21H), 1.19 (d, *J* = 6.1 Hz, 3H).



TsOH•py (57.0 mg, 0.2 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers, then dry EtOH (3 mL) was added. The mixture was stirred for 5 min, then the solution of 2-(((*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl)oxy)tetrahydro-2*H*-pyran (464.3 mg, 1.5 mmol, 1 equiv) in dry EtOH (3 mL) was added. After addition, the mixture was heated to 55 ºC and kept stirring for 12 hours. Full consumption of the starting material was confirmed by TLC. the organic layers were concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a colorless oil (250.3 mg, 75%) (Petroleum: EtOAc = 6:1, R_f = 0.34).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 6.89 – 6.82 (m, 2H), 4.20 – 4.05 (m, 3H), 2.15 (d, *J* = 3.8 Hz, 1H), 1.96 – 1.88 (m, 2H), 1.30 (s, 9H), 1.27 (d, *J* = 6.2 Hz, 3H).



TsCl (167.6 mg, 0.9 mmol, 1.1 equiv), Me_3N•HCl (9.1 mg, 0.08 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.3 mL, 2.1 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (2*S*)-4-[4-(1,1-dimethylethyl)phenoxy]-2-butanol (250.3 mg, 0.8 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (192.3 mg, 63%, 98:2 *e.r.*, $[\alpha]_D^{22.5}$ = 21.7 (c = 0.4, $CHCl_3$)) (Petroleum: EtOAc = 8:1, R_f = 0.37).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 2H), 7.27 – 7.23 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.62 – 6.59 (m, 2H), 4.91 – 4.83 (m, 1H), 3.80 – 3.75 (m, 1H), 3.65 – 3.59 (m, 1H), 2.26 (s, 3H), 2.05 – 1.90 (m, 2H), 1.43 (d, *J* = 6.3 Hz, 3H), 1.30 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.11, 144.46, 143.27, 133.79, 129.65, 127.57, 126.04, 113.62, 77.35, 62.87, 36.23, 34.03, 31.52, 21.58.

HR-MS (EI) for $C_{21}H_{28}O_4S$ [M] *m/z* $[M]^+$: calculated: 376.1708 found: 376.1711

Chiral HPLC conditions: AD column (5% EtOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S18): t_1 = 8.547 min (major), t_2 = 9.681 min (minor).

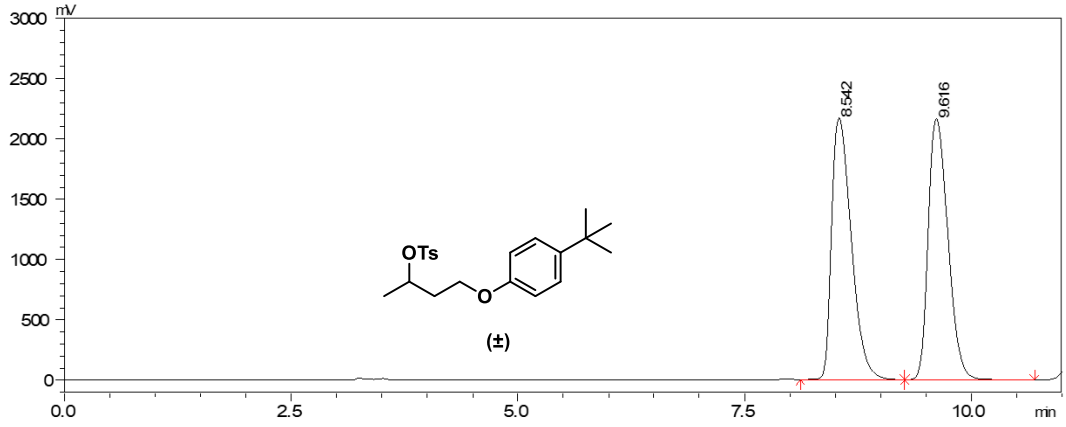


Figure S17. HPLC trace of 4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.542	2169145	32879595	50.066
2	9.616	2164333	32792949	49.934
total		4333478	65672544	100.000

Table S15. HPLC trace of 4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate.

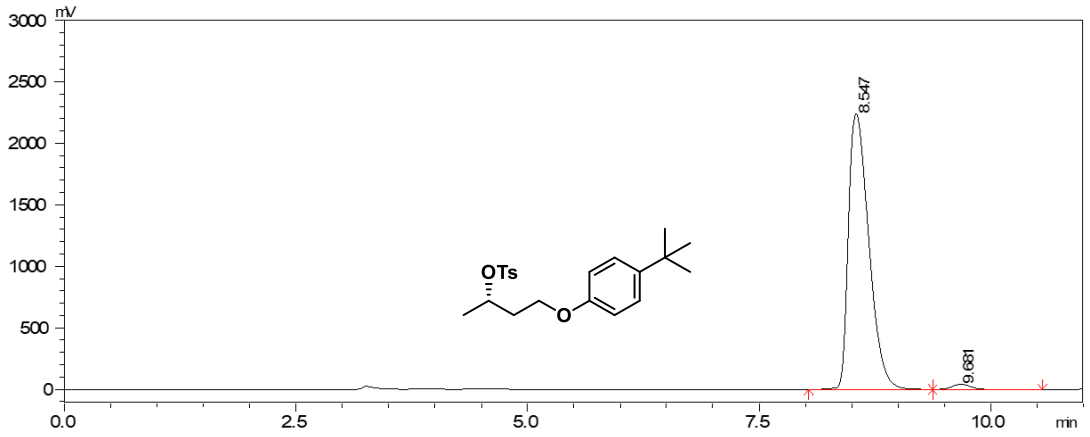
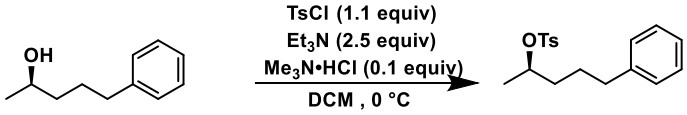


Figure S18. HPLC trace of (*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.547	2243723	34491369	98.164
2	9.681	43907	645109	1.836
total		2287630	35136478	100.000

Table S16. HPLC trace of (*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate.



TsCl (210.8 mg, 1.1 mmol, 1.1 equiv), Me_3N•HCl (10.8 mg, 0.1 mmol, 0.1 equiv) and a magnetic stir bar were added to a 50 mL Schlenk bottle. The bottle was tightly sealed with the rubber stoppers and was evaluated and backfilled with N_2 three times, then dry DCM (5 mL) and Et_3N (0.4 mL, 2.5 mmol, 2.5 equiv) were added. The mixture was stirred for 5 min and cooled to 0 ºC, then the solution of (*R*)-5-phenylpentan-2-ol (151.4 mg, 1 mmol, 1 equiv) in dry DCM (5 mL) was added. After addition, the mixture was kept stirring for 2 hours at 0 ºC. Full consumption of the starting material was confirmed by TLC. Water (10 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Subsequent purification via a silical gel column chromatography afforded a white solid (146.2 mg, 46%, >99:1 *e.r.*, $[\alpha]_D^{22.6}$ = 0.7 (c = 0.8, $CHCl_3$)) (Petroleum: EtOAc = 16:1, R_f = 0.26).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 2H), 4.72 – 4.60 (m, 1H), 2.69 – 2.57 (m, 1H), 2.55 – 2.48 (m, 1H), 2.46 (s, 3H), 2.01 – 1.89 (m, 1H), 1.87 – 1.76 (m, 1H), 1.31 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.47, 140.80, 134.47, 129.74, 128.41, 128.23, 127.70, 126.01, 79.84, 38.12, 31.13, 21.60, 20.82.

The NMR spectra are consistent with literature report.[10]

Chiral HPLC conditions: OJ column (10% EtOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for chiral compound (Fig. S20): t_1 = 17.197 min (major), t_2 = 20.481 min (minor).

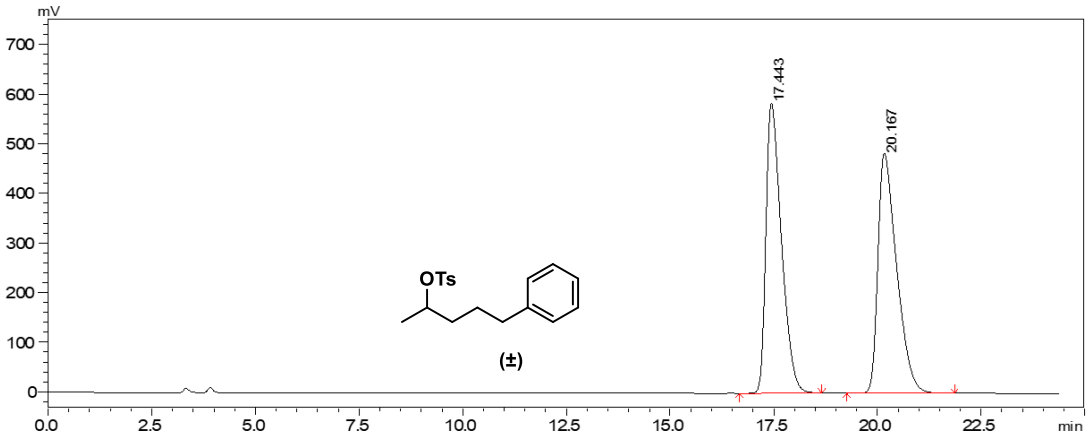


Figure S19. HPLC trace of 5-phenylpentan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	17.443	584602	15131184	50.007
2	20.167	483315	15127216	49.993
total		1067917	30258401	100.000

Table S17. HPLC trace of 5-phenylpentan-2-yl 4-methylbenzenesulfonate.

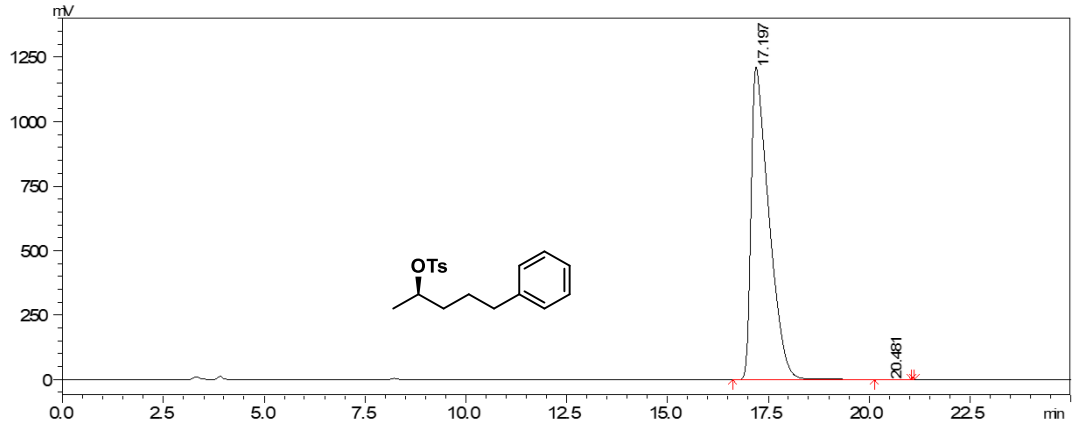
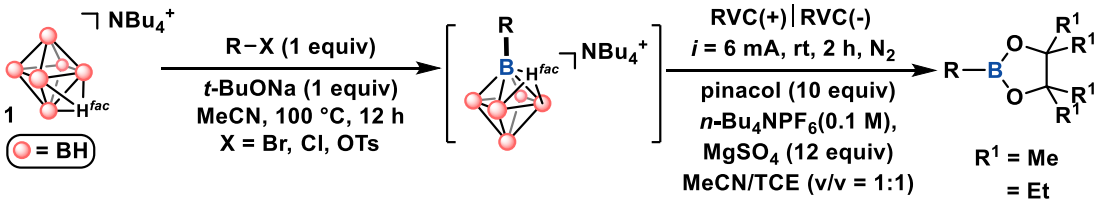


Figure S20. HPLC trace of (*R*)-5-phenylpentan-2-yl 4-methylbenzenesulfonate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	17.197	1212741	37205342	99.975
2	20.481	358	9294	0.025
total		1213099	37214636	100.000

Table S18. HPLC trace of (*R*)-5-phenylpentan-2-yl 4-methylbenzenesulfonate.

7. Reaction procedures for the nucleophilic substitutions and electrochemical deconstruction of alkyl substituted hexaborate clusters, and product characterization data



Method A (Electrolysis set up 1, ElectraSyn 2.0): To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol, 1 equiv), and *t*-BuONa (19.2 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of benzyl bromides or alkyl bromides (0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, pinacol (236.3 mg, 2 mmol, 10 equiv), $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method B (Electrolysis set up 1, ElectraSyn 2.0): To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol, 1 equiv), and *t*-BuONa (19.2 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **benzyl chlorides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, pinacol (236.3 mg, 2 mmol, 10 equiv), $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with

RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method C (Electrolysis set up 1, ElectraSyn 2.0)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol, 1 equiv), and *t*-BuONa (19.2 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **alkyl pseudohalides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, pinacol (236.3 mg, 2 mmol, 10 equiv), $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method D (Electrolysis set up 1, ElectraSyn 2.0)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol, 1 equiv), and *t*-BuONa (19.2 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **alkyl bromides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, pinacol (236.3 mg, 2 mmol, 10 equiv), $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for

five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing **1.10 F/mol of charge (1 hours)** at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method E (Electrolysis set up 1, ElectraSyn 2.0)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol, 1 equiv), and *t*-BuONa (19.2 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **benzyl bromides or alkyl bromides or alkyl pseudohalides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, **3,4-Diethyl-3,4-hexanediol (278.8 mg, 1.6 mmol, 8 equiv)**, $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

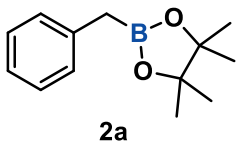
Method F (Electrolysis set up 2)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol, 1 equiv), and *t*-BuONa (19.2 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **benzyl bromides or alkyl bromides or alkyl pseudohalides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a **20 mL** electrochemical reaction cell equipped with a magnetic stir bar, **3,4-Diethyl-3,4-hexanediol (278.8 mg, 1.6 mmol, 8 equiv)**, $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and **$TBAPF_6$ (155.0 mg, 0.4 mmol, 0.1 M)** were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry **MeCN (2 mL)** was added. Then the solution of the crude product of the substituted cluster in dry **TCE (2 mL)** was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids

were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method G (Electrolysis set up 1, ElectraSyn 2.0)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, ***n*-$Bu_4N(B_6H_7)$ (1) (124.9 mg, 0.4 mmol, 2 equiv)**, and ***t*-BuONa (38.4 mg, 0.4 mmol, 2 equiv)** were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **alkyl bromides or alkyl pseudohalides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, **3,4-Diethyl-3,4-hexanediol (278.8 mg, 1.6 mmol, 8 equiv)**, $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method H (Electrolysis set up 1, ElectraSyn 2.0)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, ***n*-$Bu_4N(B_6H_7)$ (1) (93.7 mg, 0.3 mmol, 1.5 equiv)**, and ***t*-BuONa (28.8 mg, 0.3 mmol, 1.5 equiv)** were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **alkyl bromides or alkyl pseudohalides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for 12 hours. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, **3,4-Diethyl-3,4-hexanediol (278.8 mg, 1.6 mmol, 8 equiv)**, $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

Method I (Electrolysis set up 1, ElectraSyn 2.0)： To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, ***n*-$Bu_4N(B_6H_7)$ (1) (93.7 mg, 0.3 mmol, 1.5 equiv)**, and ***t*-BuONa (28.8 mg, 0.3 mmol, 1.5 equiv)** were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of **alkyl bromides (0.2 mmol, 1 equiv)** in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath at 100 ºC for **36 hours**. Then the heating bath was removed and the flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, **3,4-Diethyl-3,4-hexanediol (278.8 mg, 1.6 mmol, 8 equiv)**, $MgSO_4$ (288.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (116.3 mg, 0.3 mmol, 0.1 M) were added sequentially. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.



2a

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. Benzyl bromide (35.1 mg, 0.2 mmol), *t*-BuONa (19.2 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.7 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step:

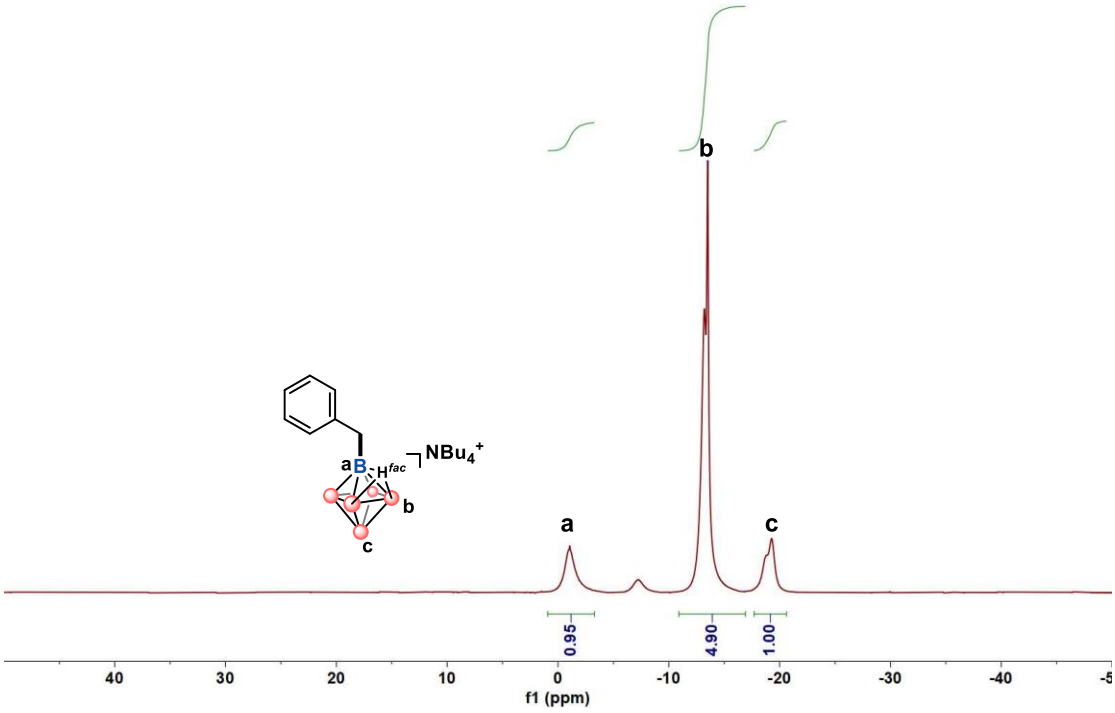


Figure S21. $^{11}B\{^1H\}$ NMR spectrum after substitution step with benzyl bromide.

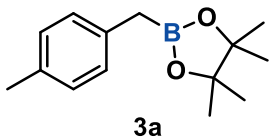
The assignment of boron signals is shown here. The signal c corresponds to boron atom B_c of substituted cluster, unreacted *closo*-hexaborate anion signal overlapped with signal b corresponds to equatorial boron B_b. The ratio of substituted cluster/hexaborate = 1/{(4.90-1×4)/6}=1/0.15, the conversion = 1/(1+0.15)×100% = 87%.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.43 (Petroleum: EtOAc = 25:1). For method A, 28.0 mg (64%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 4H), 7.19 – 7.14 (m, 1H), 2.34 (s, 2H), 1.27 (s, 12H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 138.63, 128.97, 128.24, 124.80, 83.40, 24.73.

The NMR spectra are consistent with literature report.[11] CAS registry No. 87100-28-5



3a

4,4,5,5-Tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane

Method A are applied. 4-Methylbenzyl bromide (38.1 mg, 0.2 mmol), *t*-BuONa (19.0 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.8 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (72% conversion):

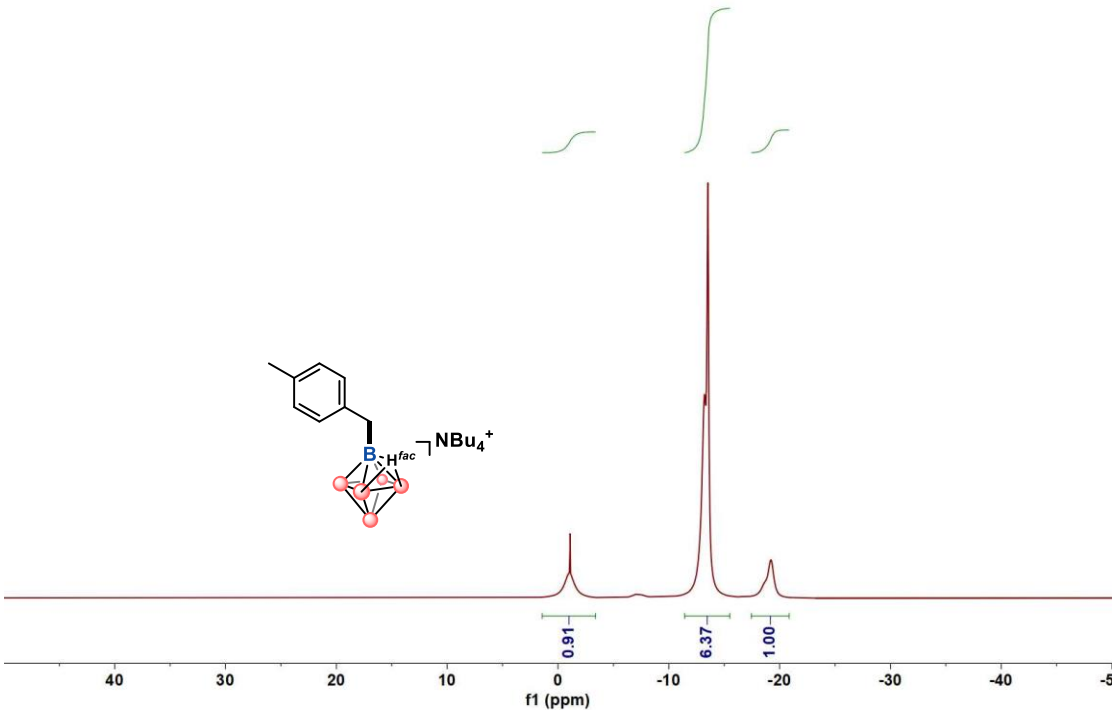


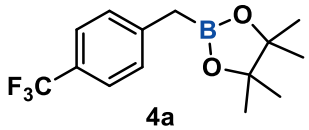
Figure S22. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 4-methylbenzyl bromide.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 20:1) to give a colorless oil. R_f = 0.7 (Petroleum: EtOAc = 20:1). For method A, 22.5 mg (48%) of product was obtained.

^1H NMR (600 MHz, $CDCl_3$) δ 7.09 -7.05 (m, 4H), 2.30 (s, 3H), 2.26 (s, 2H), 1.24 (s, 12H).

$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 135.34, 134.08, 128.95, 128.82, 83.32, 24.70, 20.93.

The NMR spectra are consistent with literature report.[11] CAS registry No. 356570-52-0



4a

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane

Method A are applied. 4-(Trifluoromethyl)benzyl bromide (49.9 mg, 0.2 mmol), *t*-BuONa (19.2 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.2 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (76% conversion):

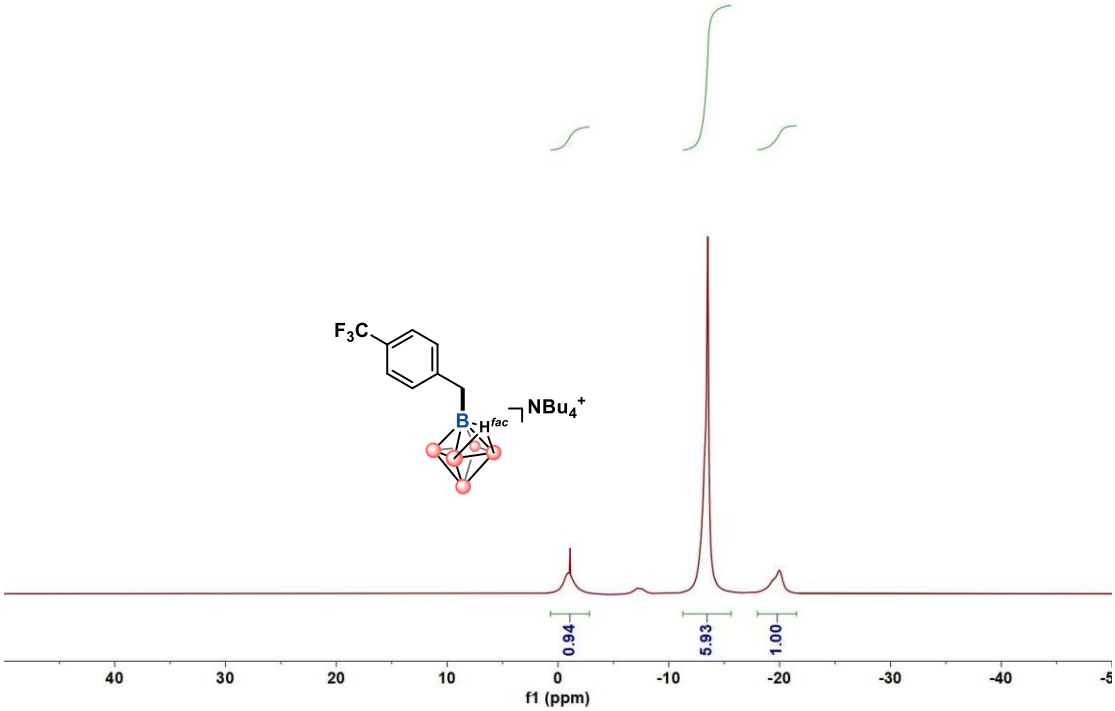


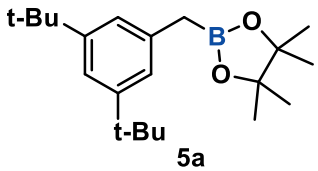
Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 4-(trifluoromethyl)benzyl bromide.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 20:1) to give a colorless oil. R_f = 0.63 (Petroleum: EtOAc = 20:1). For method A, 23.4 mg (41%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 2H), 1.23 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 143.10, 129.15, 127.15 (q, ^{2}J = 31.9 Hz), 125.12 (q, ^{3}J = 4.1 Hz), 124.51 (q, ^{1}J = 271.9 Hz, CF_3), 83.66, 24.69.

The NMR spectra are consistent with literature report.[11] CAS registry No. 475250-46-5



5a

2-(3,5-Bis(1,1-dimethylethyl)phenyl]methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. 3,5-Bis(1,1-dimethylethyl)phenyl]methyl bromide (57.7 mg, 0.2 mmol), *t*-BuONa (19.6 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.0 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (84% conversion):

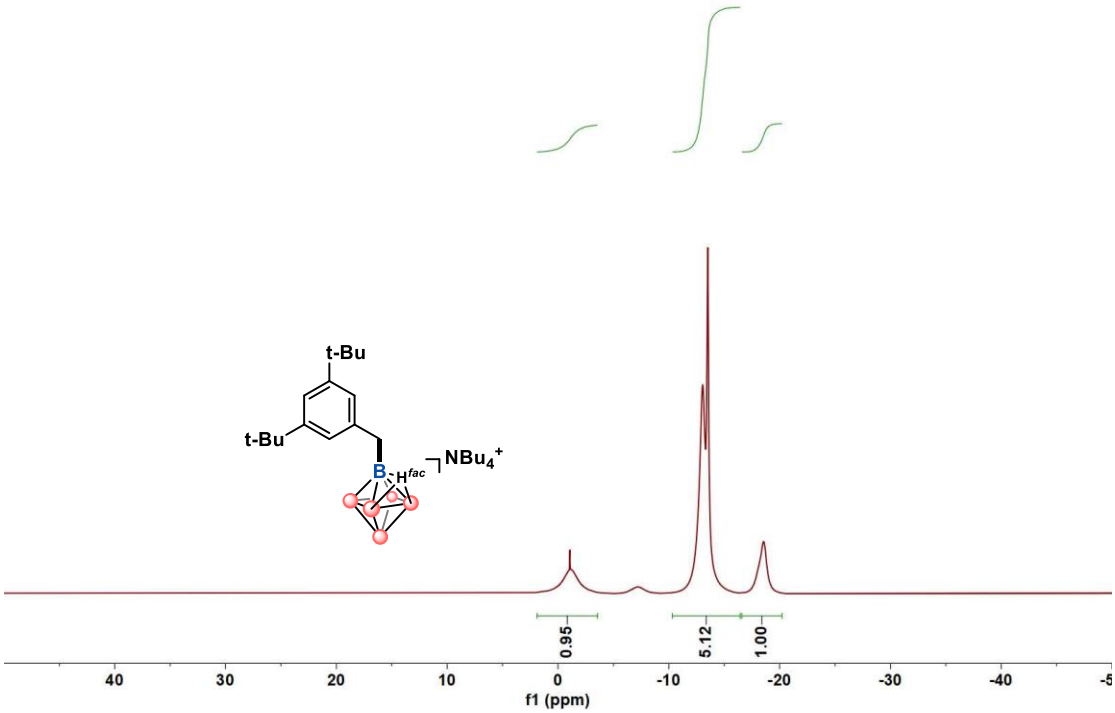


Figure S24. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 3,5-bis(1,1-dimethylethyl)phenyl]methyl.

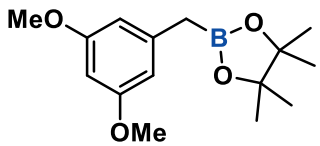
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 30:1) to give a colorless oil. R_f = 0.76 (Petroleum: EtOAc = 30:1). For method A, 35.7 mg (54%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19– 7.18 (m, 1H), 7.05 – 7.04 (m, 2H), 2.29 (s, 2H), 1.31 (s, 18H), 1.26 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.29, 137.21, 123.47, 118.81, 83.28, 34.70, 31.49, 24.75.

$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ 33.23.

HR-MS (ESI) for $C_{21}H_{35}{}^{11}BO_2Na$ [M] *m/z* $[M+Na]^+$: calculated: 353.2628, found: 353.2628



6a

2-(3,5-dimethoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. 3,5-Dimethoxybenzyl bromide (46.7 mg, 0.2 mmol), *t*-BuONa (19.7 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.5 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (72% conversion):

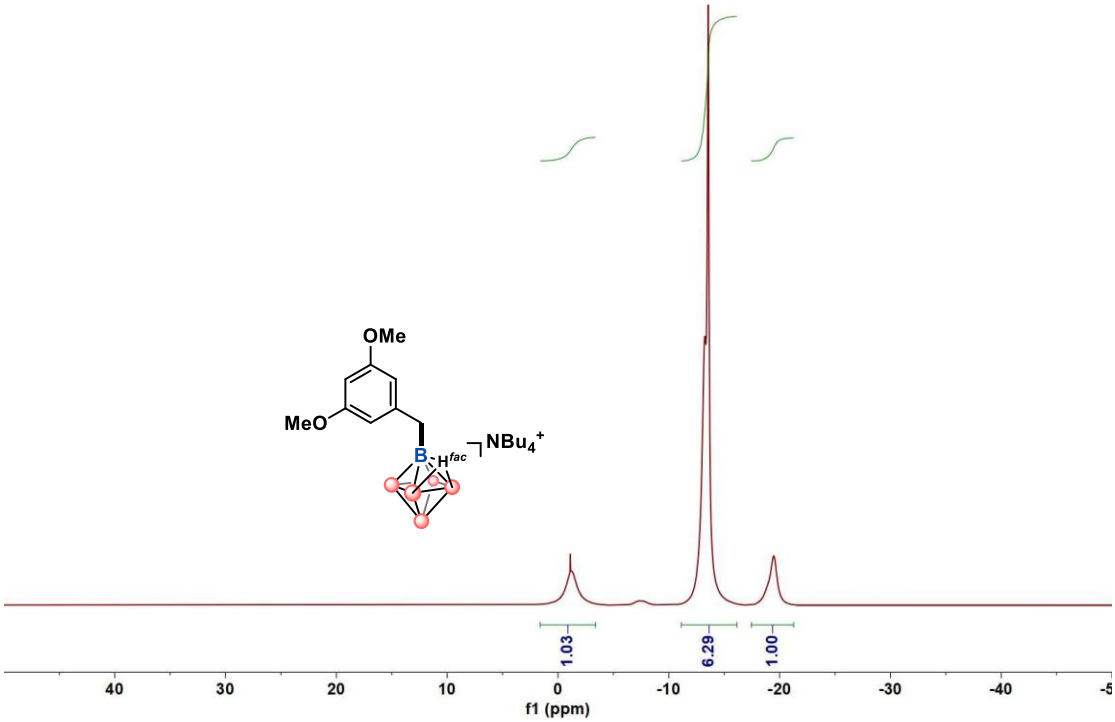


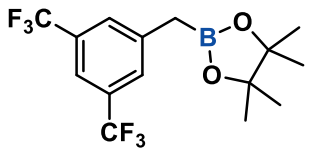
Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 3,5-dimethoxybenzyl bromide.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 30:1) to give a colorless oil. R_f = 0.32 (Petroleum: EtOAc = 20:1). For method A, 17.9 mg (32%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, *J* = 2.2 Hz, 2H), 6.25 (t, *J* = 2.3 Hz, 1H), 3.76 (s, 6H), 2.24 (s, 2H), 1.24 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.58, 140.89, 107.06, 97.27, 83.44, 55.17, 24.70.

The NMR spectra are consistent with literature report.[12] CAS registry No. 1854115-26-6



7a

2-(3,5-bis(trifluoromethyl)benzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. 3,5-Bis(trifluoromethyl)benzyl bromide (62.4 mg, 0.2 mmol), *t*-BuONa (19.8 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol) are used for substitution step.

For method A, the ^{11}B NMR after substitution step (68% conversion):

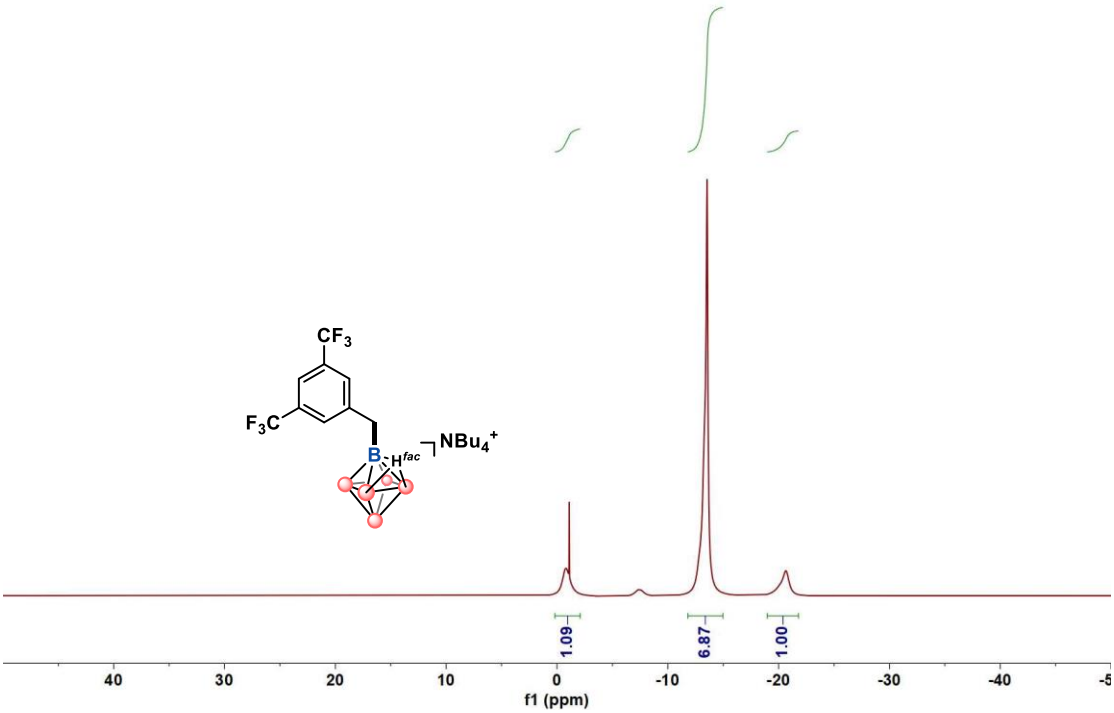


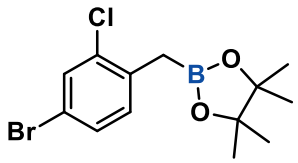
Figure S26. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 3,5-bis(trifluoromethyl)benzyl bromide.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 30:1) to give a colorless oil. R_f = 0.06 (Petroleum). For method A, 38.1 mg (53%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 3H), 2.42 (s, 2H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 141.31, 131.22 (q, ^{2}J = 32.8 Hz), 129.1, 124.82 (q, ^{1}J = 271.7 Hz, CF_3), 119.0 (q, ^{3}J = 3.8 Hz), 83.97, 24.65.

The NMR spectra are consistent with literature report.[12] CAS registry No. 1854115-27-7



8a

2-[(2-Chloro-4- bromide)methyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. 4-Bromo-1-(bromomethyl)-2-chloro-bromide (56.1 mg, 0.2 mmol), *t*-BuONa (19.1 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.2 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (77% conversion):

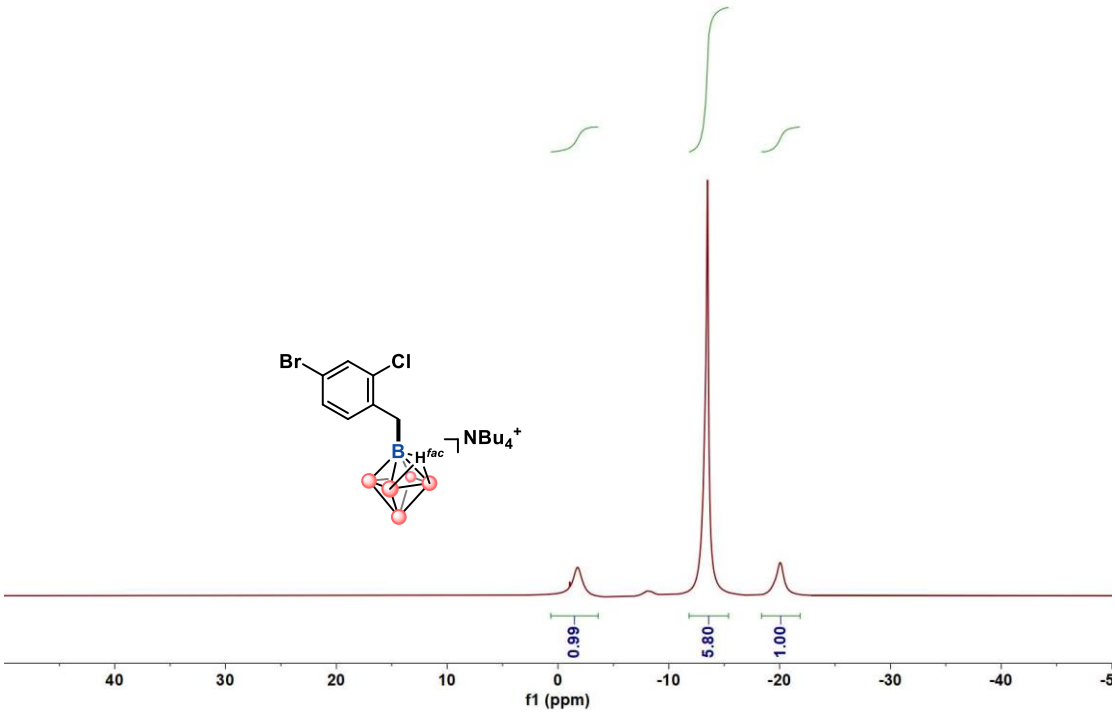


Figure S27. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 4-bromo-1-(bromomethyl)-2-chloro-bromide.

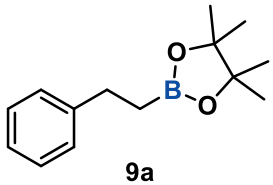
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.31 (Petroleum: EtOAc = 25:1). For method A, 33.2 mg (50%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 1H), 7.28 – 7.25 (m, 1H), 7.10 – 7.08 (m, 1H), 2.33 (s, 2H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 136.72, 134.71, 131.85, 131.51, 129.79, 118.73, 83.68, 24.69.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 32.74.

HR-MS (EI) for $C_{13}H_{17}{}^{11}BO_2{}^{35}Cl{}^{81}Br$ [M] *m/z* $[M]^+$: calculated: 332.0173, found: 332.0171



9a

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane

Method A are applied. (2-Bromoethyl)benzene (37.5 mg, 0.2 mmol), *t*-BuONa (19.9 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (63.0 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (54% conversion):

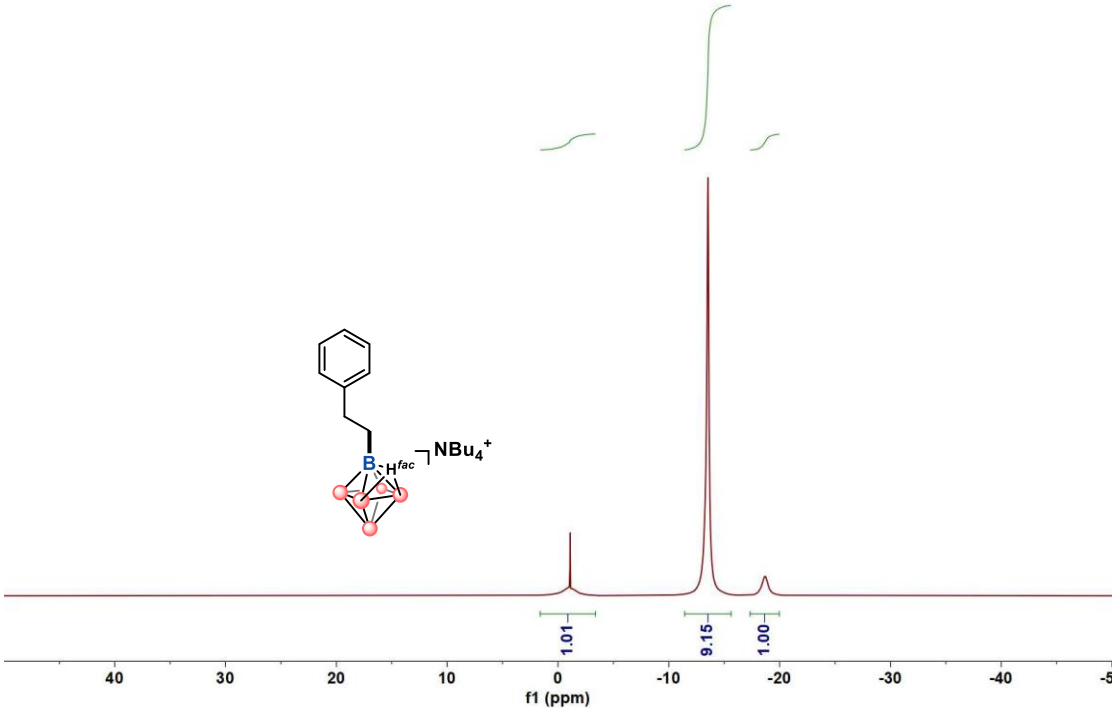


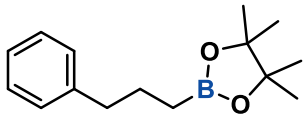
Figure S28. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with (2-bromoethyl)benzene.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.6 (Petroleum: EtOAc = 25:1). For method A, 19.0 mg (41%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 7.17 – 7.13 (m, 1H), 2.75 (t, *J* = 7.95, 2H), 1.22 (s, 12H), 1.17 – 1.13 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.41, 128.17, 127.99, 125.48, 83.09, 29.93, 24.79.

The NMR spectra are consistent with literature report.[11] CAS registry No. 165904-22-3



10a

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

Method A are applied. 1-Bromo-3-phenylpropane (40.6 mg, 0.2 mmol), *t*-BuONa (19.6 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.6 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (76% conversion):

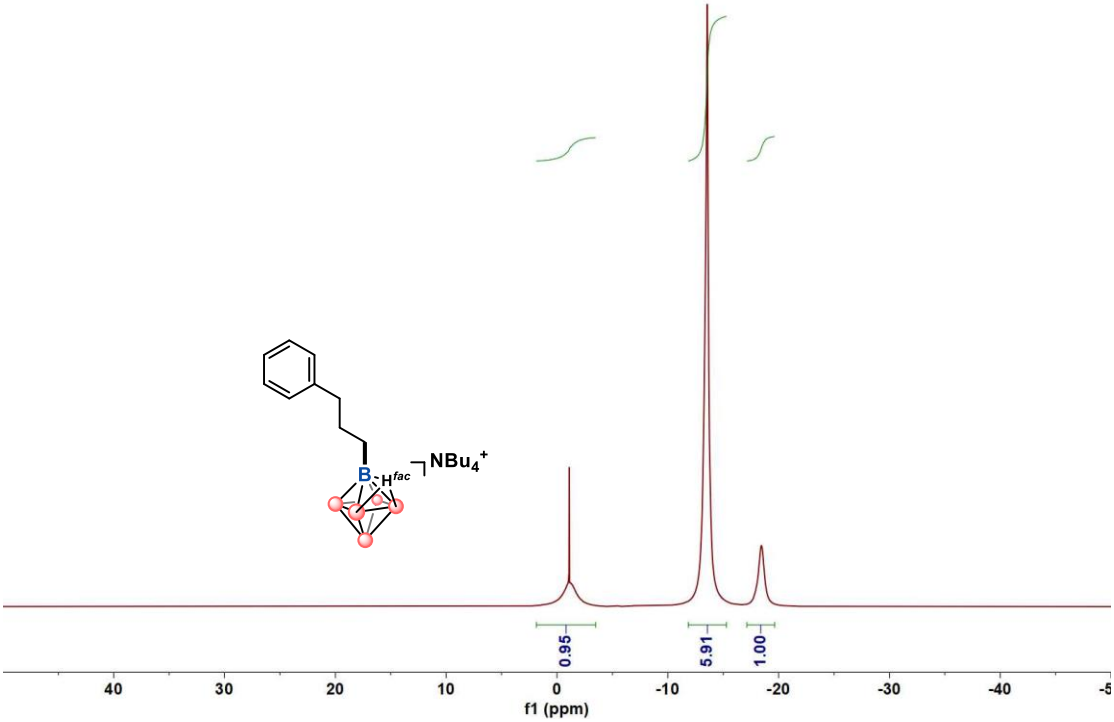


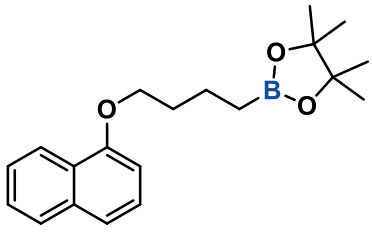
Figure S29. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 1-bromo-3-phenylpropane.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 40:1) to give a colorless oil. R_f = 0.6 (Petroleum: EtOAc = 20:1). For method A, 25.8 mg (52%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 2.62 (t, *J* = 7.78, 2H), 1.79 – 1.71 (m, 2H), 1.26 (s, 12H), 0.84 (t, *J* = 7.93 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 142.68, 128.53, 128.15, 125.54, 82.92, 38.58, 26.09, 24.81.

The NMR spectra are consistent with literature report.[13] CAS registry No. 329685-40-7



11a

2-[4-(1-naphthalenyloxy)butyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. 1-(4-Bromobutoxy)naphthalene (57.4 mg, 0.2 mmol), *t*-BuONa (19.3 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.5 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (95% conversion):

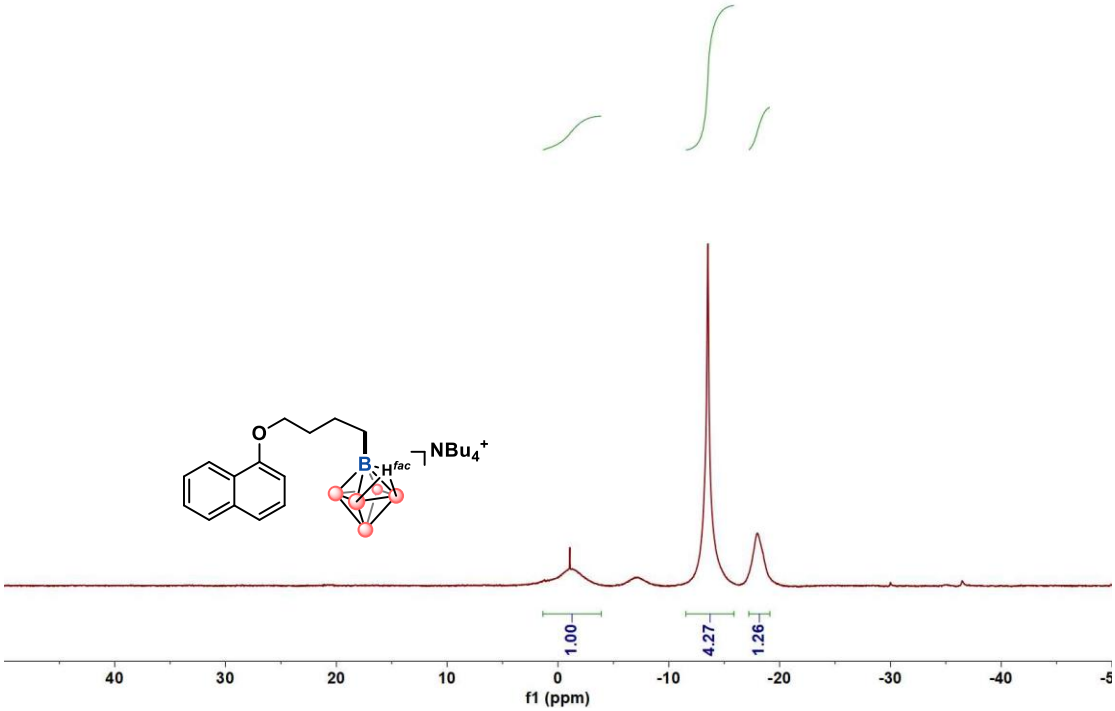


Figure S30. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 1-(4-bromobutoxy)naphthalene.

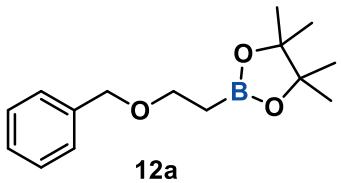
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 40:1) to give a colorless oil. R_f = 0.59 (Petroleum: EtOAc = 16:1). For method A, 36.9 mg (57%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.28 (m, 1H), 7.80 – 7.76 (m, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.34 (m, 2H), 6.80 – 6.78 (m, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 1.99 – 1.91 (m, 2H), 1.75 – 1.67 (m, 2H), 1.26 (s, 12H), 0.92 (t, *J* = 7.8 Hz, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.88, 134.45, 127.33, 126.24, 125.88, 124.95, 122.19, 119.82, 104.44, 82.99, 67.87, 31.82, 24.81, 20.80.

$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ 34.08.

HR-MS (EI) for $C_{20}H_{27}{}^{11}BO_3$ [M] *m/z* $[M]^+$: calculated: 326.2053, found: 326.2055



12a

2-(2-(Benzyloxy)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method A are applied. Benzyl 2-bromoethyl ether (44.4 mg, 0.2 mmol), *t*-BuONa (19.8 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (63.3 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (67% conversion):

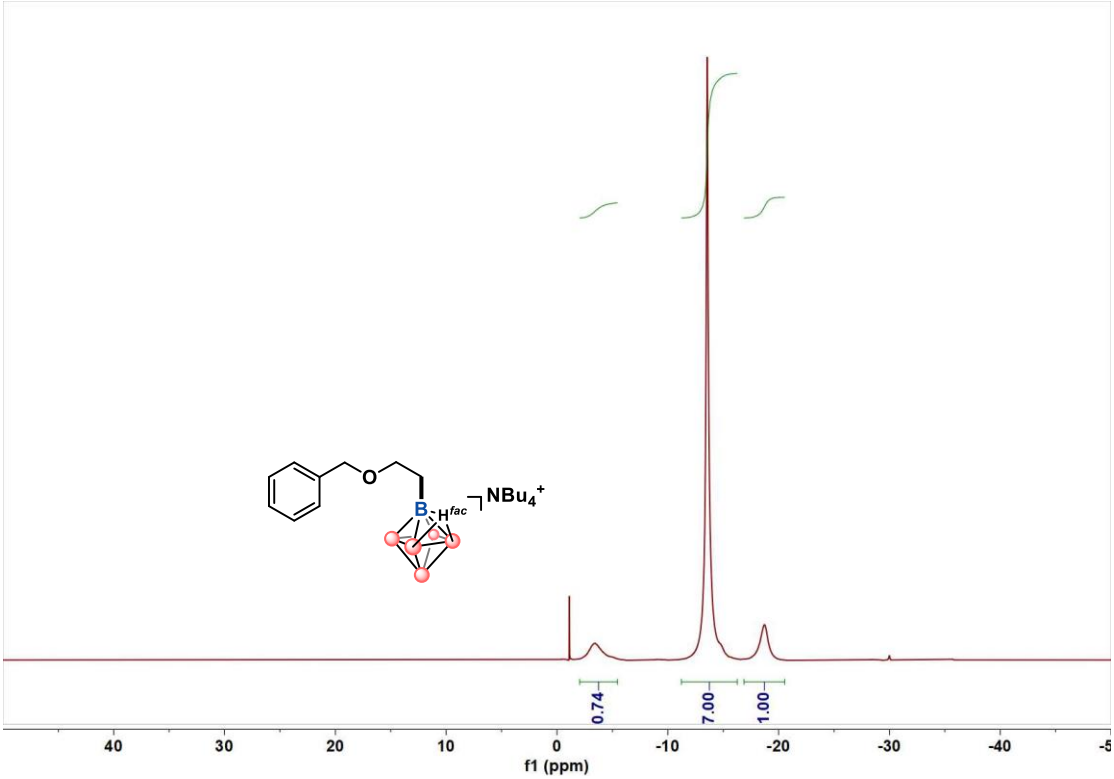
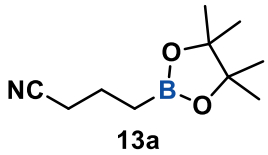


Figure S31. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with benzyl 2-bromoethyl ether. The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.2 (Petroleum: EtOAc = 30:1). For method A, 19.1 mg (36%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 4H), 7.27 – 7.26 (m, 1H), 4.51 (s, 2H), 3.63 (t, *J* = 7.9 Hz, 2H), 1.26 – 1.23(m, 14H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 138.78, 128.26, 127.60, 127.34, 83.15, 72.58, 67.04, 24.80.

The NMR spectra are consistent with literature report.[14] CAS registry No. 137297-51-9



13a

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile

Method D are applied. 3-Bromopropyl cyanide (30.5 mg, 0.2 mmol), *t*-BuONa (19.5 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.7 mg, 0.2 mmol) are used for substitution step. **For method D**, the ^{11}B NMR after substitution step (61% conversion):

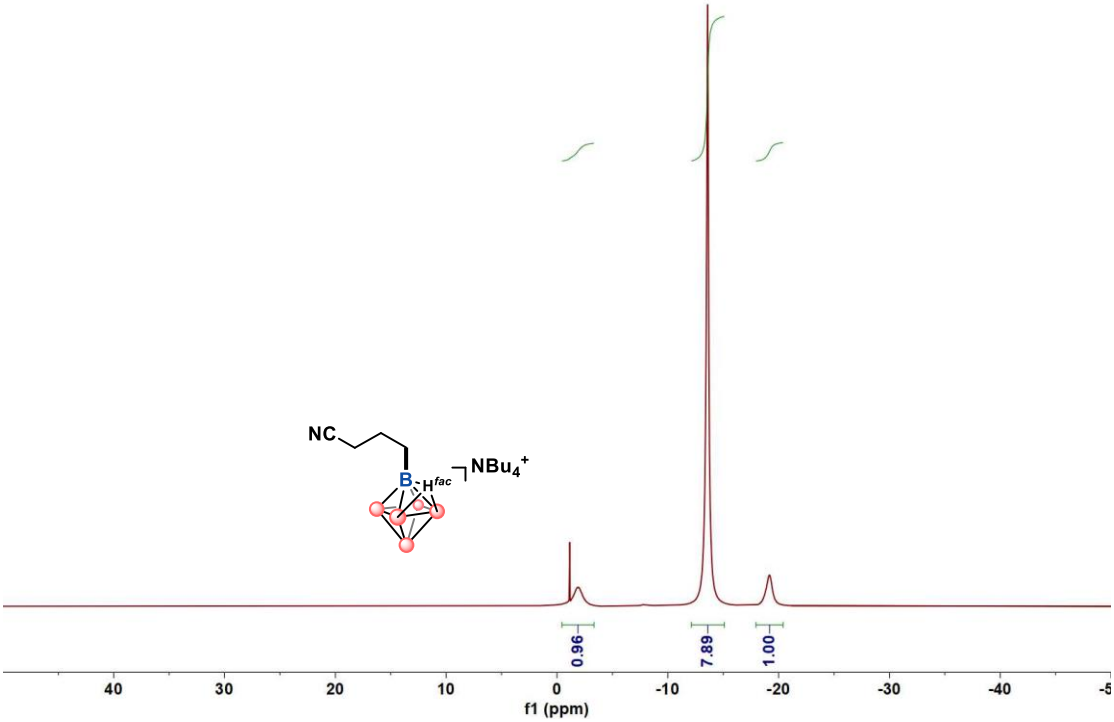


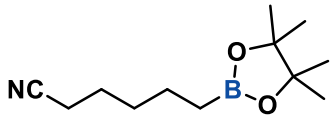
Figure S32. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 3-bromopropyl cyanide.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 8:1) to give a colorless oil. R_f = 0.56 (Petroleum: EtOAc = 4:1). For method A, 19.4 mg (50%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (t, *J* = 7.2 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.24 (s, 12H), 0.94 (t, *J* = 7.8 Hz, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 119.87, 83.35, 24.80, 20.36, 19.15.

The NMR spectra are consistent with literature report.[15] CAS registry No. 2238088-16-9



14a

6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanenitrile

Method A are applied. 6-Bromohexanenitrile (37.2 mg, 0.2 mmol), *t*-BuONa (18.9 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.4 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (93% conversion):

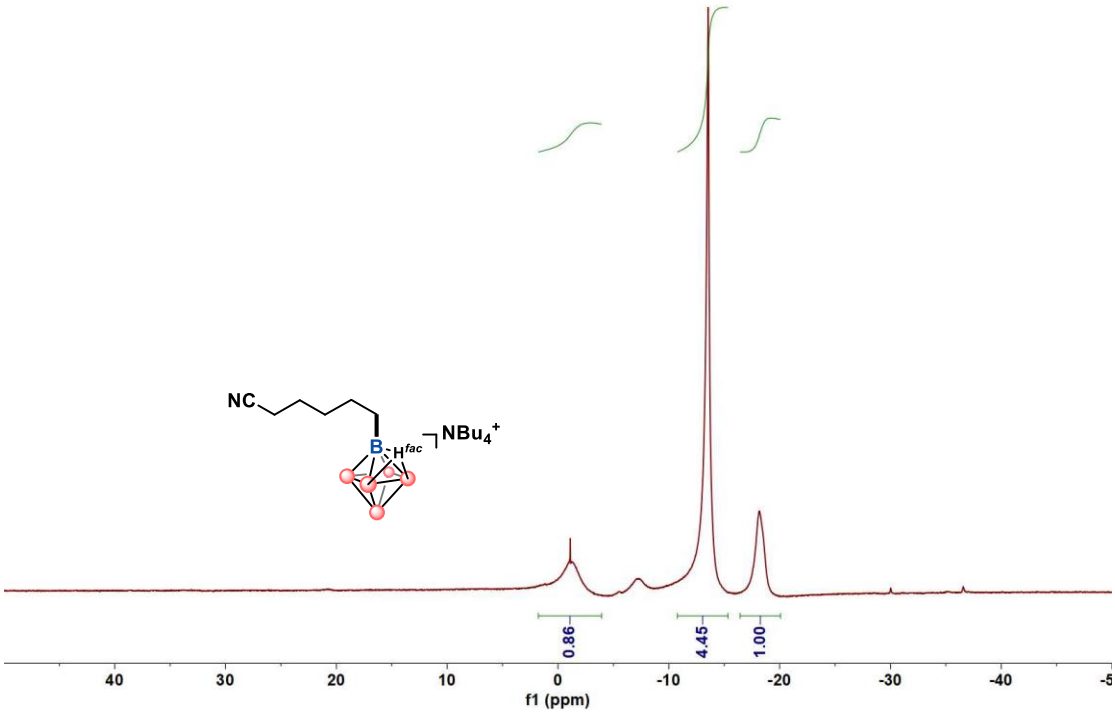


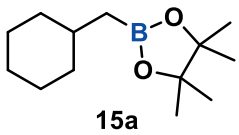
Figure S33. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 6-bromohexanenitrile.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 8:1) to give a colorless oil. R_f = 0.65 (Petroleum: EtOAc = 4:1). For method A, 24.2 mg (54%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.62 (m, 2H), 1.47 – 1.43 (m, 4H), 1.25 (s, 12H), 0.81 – 0.77 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 119.86, 83.02, 31.18, 29.68, 25.13, 24.80, 23.11, 17.02.

The NMR spectra are consistent with literature report.[3] CAS registry No. 1361022-65-2



15a

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

Method A are applied. Cyclohexylmethyl bromide (35.1 mg, 0.2 mmol), *t*-BuONa (20.1 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.3 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (74% conversion):

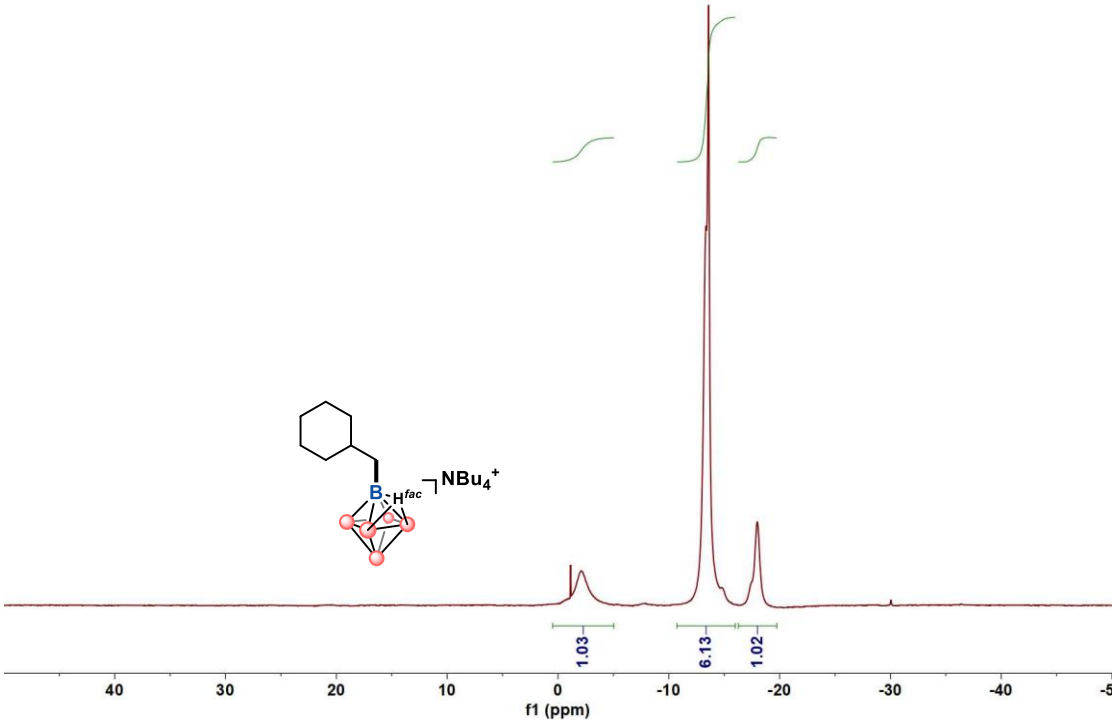
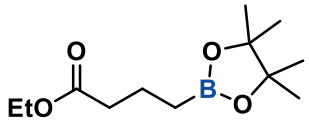


Figure S34. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with cyclohexylmethyl bromide. The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 20:1) to give a colorless oil. R_f = 0.88 (Petroleum: EtOAc = 20:1). For method A, 19.3 mg (43%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.70 – 1.59 (m, 5H), 1.50 – 1.46 (m, 1H), 1.26 – 1.22(m, 14H), 1.13 – 1.08 (m, 1H), 0.95 – 0.88 (m, 2H), 0.71 (d, *J* = 7.2 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 82.79, 35.91, 34.19, 26.54, 26.28, 24.82.

The NMR spectra are consistent with literature report.[14] CAS registry No. 123706-53-6



16a

Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate

Method A are applied. Ethyl 4-bromobutyrate (40.5 mg, 0.2 mmol), *t*-BuONa (19.1 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.5 mg, 0.2 mmol) are used for substitution step. **For method A**, the ^{11}B NMR after substitution step (47% conversion):

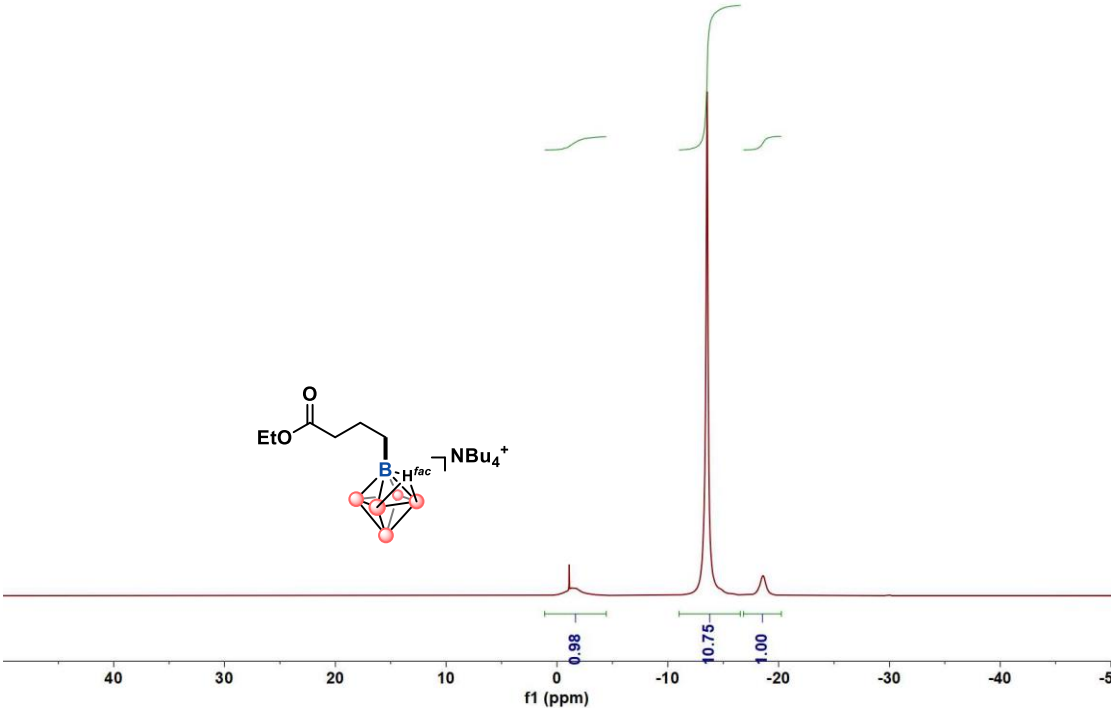


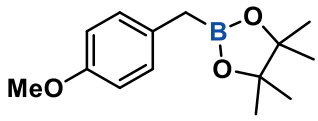
Figure S35. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with ethyl 4-bromobutyrate.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.39 (Petroleum: EtOAc = 16:1). For method A, 11.3 mg (23%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (q, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.27 – 1.23 (m, 15H), 0.82 (t, *J* = 7.9 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 173.72, 83.04, 60.08, 36.60, 24.80, 19.64, 14.24.

The NMR spectra are consistent with literature report.[15] CAS registry No. 1392140-97-4



17a

2-(4-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method B are applied. 4-Methoxybenzylchloride (31.8 mg, 0.2 mmol), *t*-BuONa (19.4 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.5 mg, 0.2 mmol) are used for substitution step. **For method B**, the ^{11}B NMR after substitution step (88% conversion):

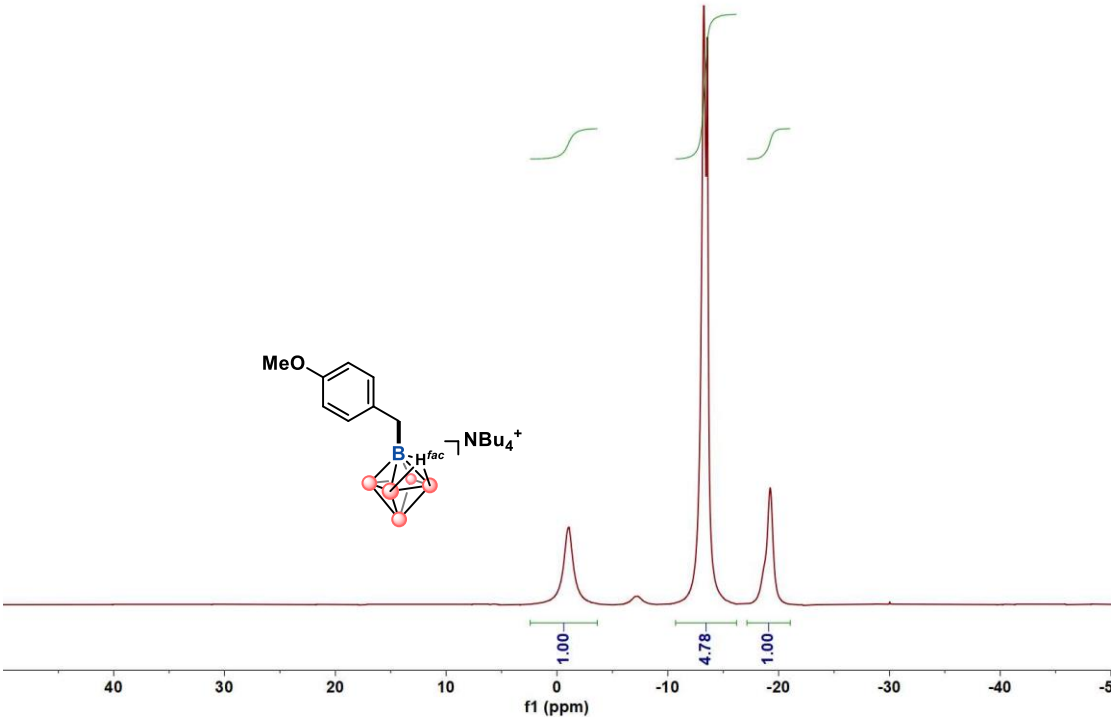


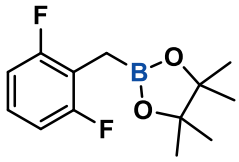
Figure S36. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 4-methoxybenzylchloride.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 20:1) to give a colorless oil. R_f = 0.23 (Petroleum: EtOAc = 25:1). For method A, 25.3 mg (51%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 – 7.09 (m, 2H), 6.80 – 6.78 (m, 2H), 3.77 (s, 3H), 2.23 (s, 2H), 1.23 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 157.08, 130.45, 129.78, 113.73, 83.33, 55.18, 24.71.

The NMR spectra are consistent with literature report.[15] CAS registry No. 475250-52-3



18a

2-(2,6-difluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method B are applied. 2,6-Difluorobenzyl chloride (33.2 mg, 0.2 mmol), *t*-BuONa (19.8 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.8 mg, 0.2 mmol) are used for substitution step. **For method B**, the ^{11}B NMR after substitution step (85% conversion):

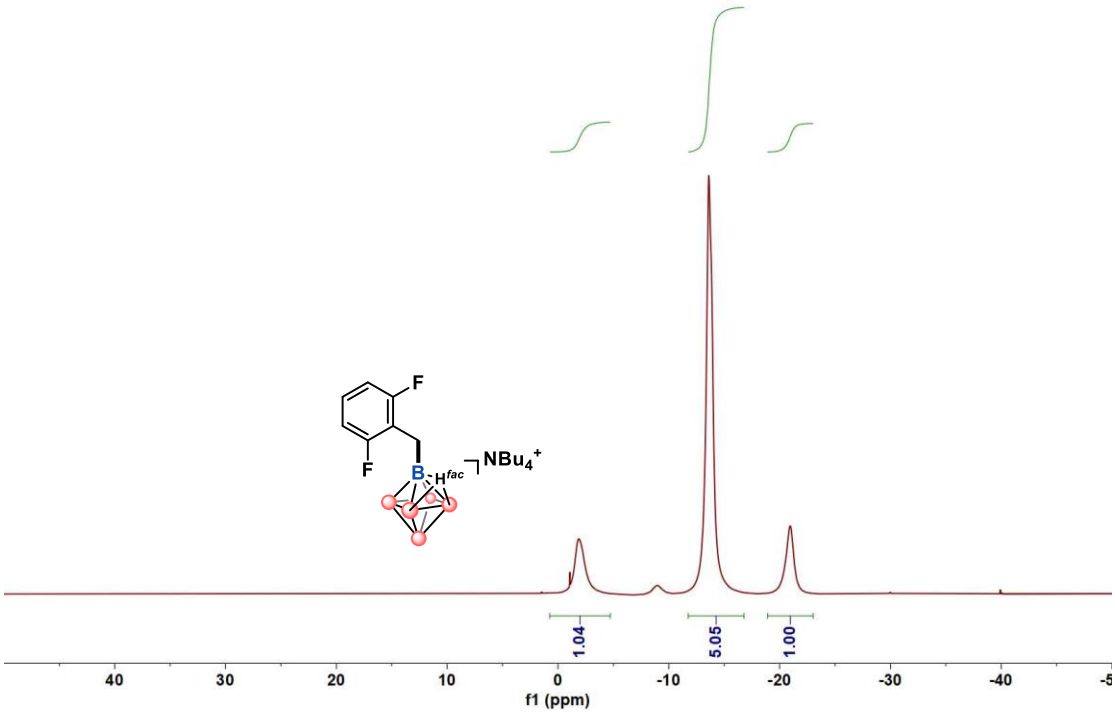


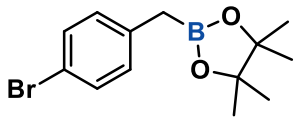
Figure S37. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 2,6-difluorobenzyl chloride.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.25 (Petroleum: EtOAc = 25:1). For method A, 31.9 mg (62%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 – 7.04 (m, 1H), 6.84 – 6.79 (m, 2H), 2.23 (s, 2H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ161.36 (d, ^{1}J = 244.4 Hz), δ161.3 (d, ^{1}J = 244.8 Hz), 126.09(t, ^{3}J = 10.8 Hz), 114.04(t, ^{2}J = 21.1 Hz), 110.66(m, ^{2}J = 20.5 Hz), 83.68, 24.62.

The NMR spectra are consistent with literature report.[12] CAS registry No. 2052955-28-7



19a

2-(4-bromobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Method B are applied. 4-Bromobenzyl chloride (41.9 mg, 0.2 mmol), *t*-BuONa (19.1 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.1 mg, 0.2 mmol) are used for substitution step. **For method B**, the ^{11}B NMR after substitution step (75% conversion):

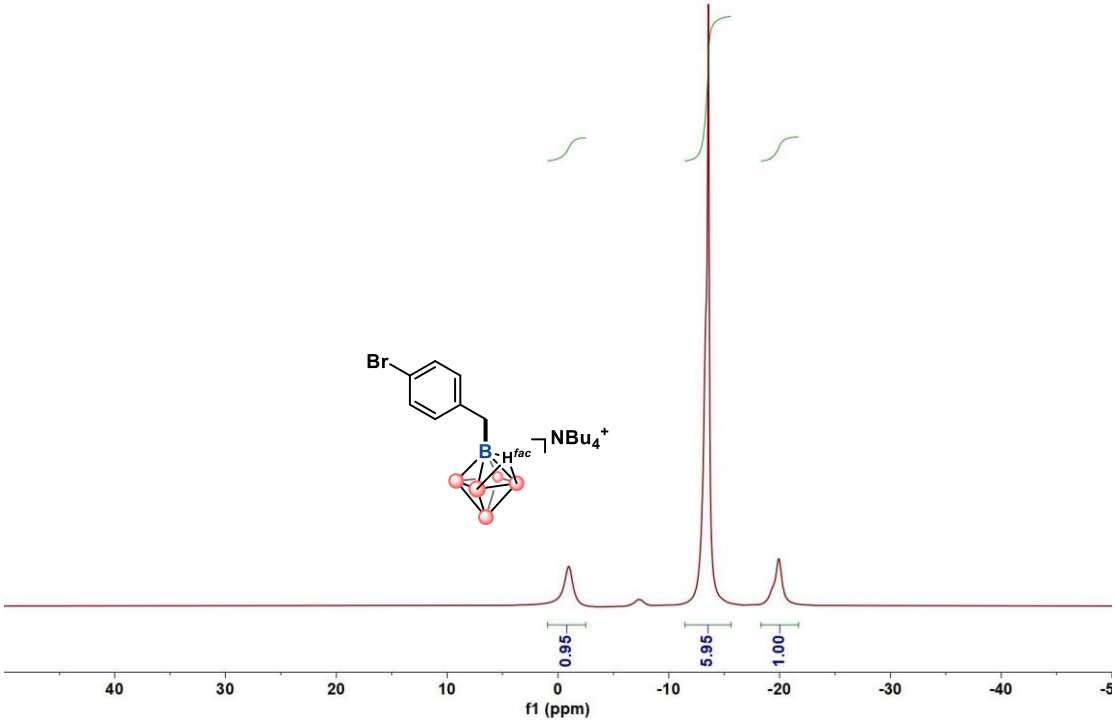


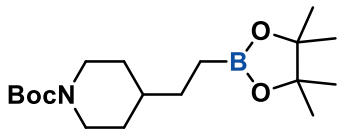
Figure S38. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 4-bromobenzyl chloride.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.2 (Petroleum: EtOAc = 25:1). For method A, 25.0 mg (42%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 7.06 – 7.04 (m, 2H), 2.23 (s, 2H), 1.23 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 137.68, 131.22, 130.71, 118.54, 83.55, 24.69.

The NMR spectra are consistent with literature report.[3] CAS registry No. 477841-90-0



20a

1-Piperidinecarboxylic acid, 4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-,1,1-dimethylethyl ester

Method C are applied. N-tert-butoxycarbonyl-4-[2-(4-toluenesulfonyloxy)ethyl] (76.8 mg, 0.2 mmol), *t*-BuONa (19.2 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.8 mg, 0.2 mmol) are used for substitution step. **For method C**, the ^{11}B NMR after substitution step (83% conversion):

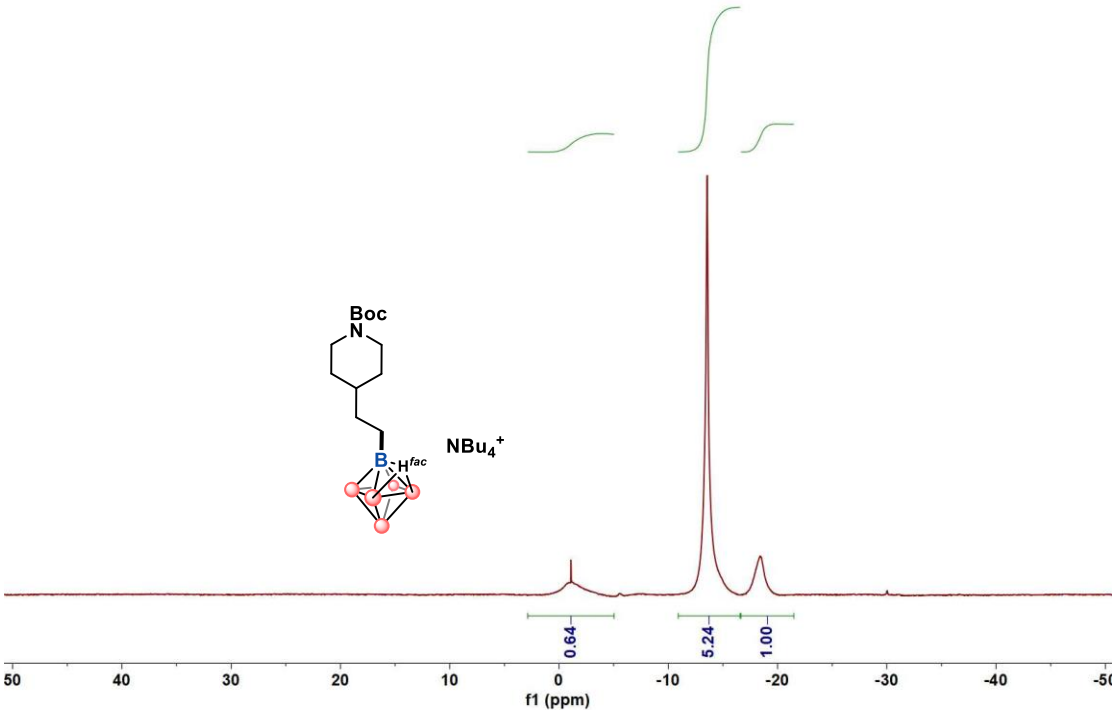


Figure S39. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with N-tert-butoxycarbonyl-4-[2-(4-toluenesulfonyloxy)ethyl].

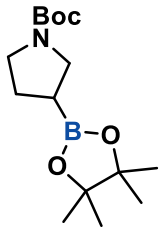
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 10:1) to give a colorless oil. R_f = 0.45 (Petroleum: EtOAc = 10:1). For method A, 27.1 mg (40%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 2H), 2.67 – 2.61 (m, 2H), 1.72 – 1.59 (m, 3H), 1.44 (s, 9H), 1.37 – 1.32 (m, 2H), 1.24 (s, 12H), 1.08 – 0.98 (m, 2H), 0.78 – 0.74 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 154.92, 82.94, 79.07, 44.01, 38.18, 31.77, 30.43, 28.44, 24.77.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 34.21.

HR-MS (EI) for $C_{18}H_{34}{}^{11}BNO_4$ [M] *m/z* $[M]^+$: calculated: 339.2581, found: 339.2583



21a

1-Boc-pyrrolidine-3-boronic acid pinacol ester

Method C are applied. 1-Boc-3-tosyloxypyrrolidine (69.0 mg, 0.2 mmol), *t*-BuONa (19.2 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.2 mg, 0.2 mmol) are used for substitution step. **For method C**, the ^{11}B NMR after substitution step (64% conversion):

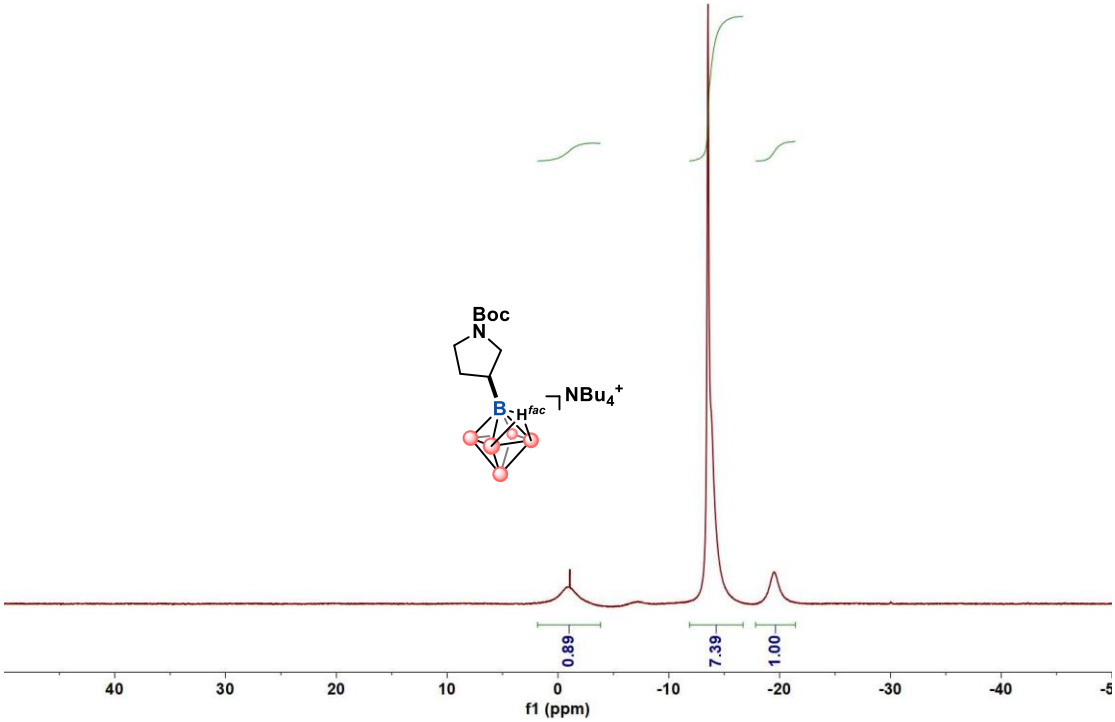
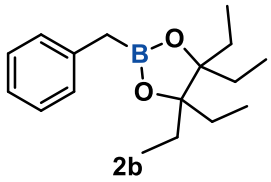


Figure S40. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 1-Boc-3-tosyloxypyrrolidine. The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 7:1) to give a colorless oil. R_f = 0.51 (Petroleum: EtOAc = 7:1). For method A, 21.8 mg (37%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 – 3.45 (m, 2H), 3.22 – 3.15 (m, 2H), 2.02 – 1.95 (m, 1H), 1.82 – 1.72 (m, 1H), 1.57 – 1.52 (m, 1H), 1.45 (s, 9H), 1.24 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 154.57, 83.45, 78.83, 47.90, 46.61, 28.57, 24.72.

The NMR spectra are consistent with literature report.[16] CAS registry No. 1312712-22-3



2-benzyl-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

Method E are applied. Benzyl bromide (35.3 mg, 0.2 mmol), *t*-BuONa (19.2 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.7 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (86% conversion):

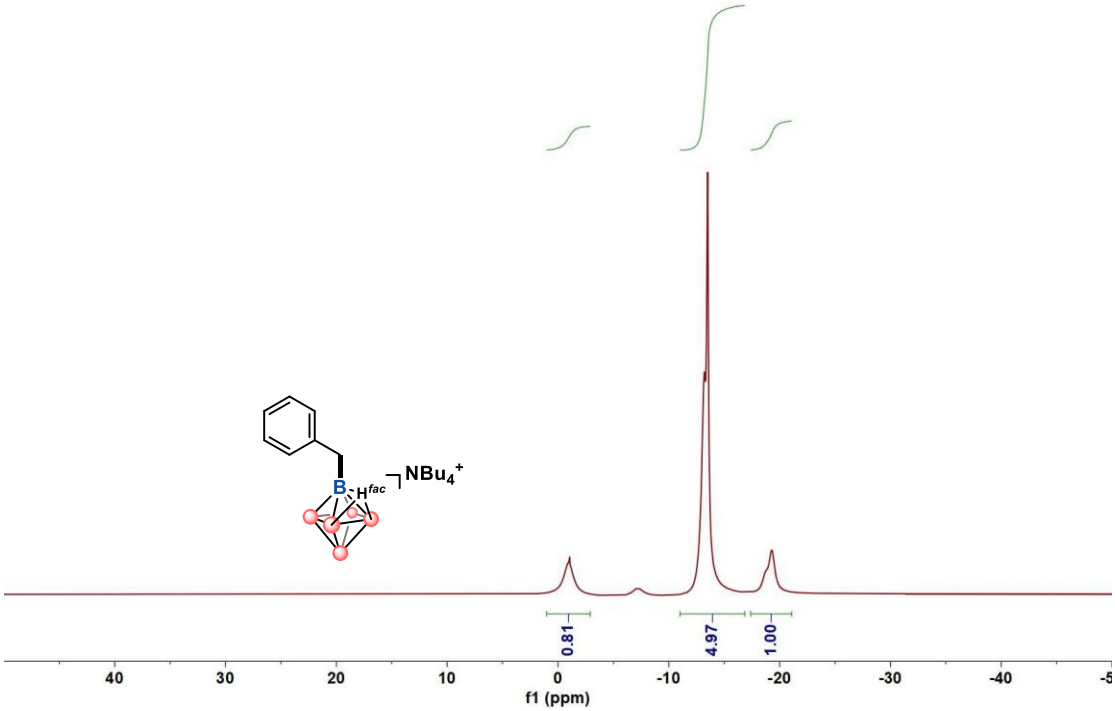


Figure S41. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with benzyl bromide.

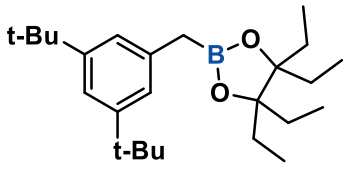
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 40:1) to give a colorless oil. R_f = 0.7 (Petroleum: EtOAc = 20:1). For method E, 33.8 mg (71%) of product was obtained.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 7.13 – 7.09 (m, 1H), 2.30 (s, 2H), 1.69 – 1.59 (m, 8H), 0.87 (t, *J* = 7.5 Hz, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 139.03, 129.00, 128.07, 124.63, 88.41, 26.26, 8.72.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 32.48.

HR-MS (EI) for $C_{17}H_{27}{}^{11}BO_2$ [M] *m/z* $[M]^+$: calculated: 274.2104, found: 274.2106



5b

2-(3,5-di-tert-butylbenzyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

Method E are applied. 3,5-Bis(1,1-dimethylethyl)phenyl]methyl bromide (56.1 mg, 0.2 mmol), *t*-BuONa (18.9 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.5 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (84% conversion):

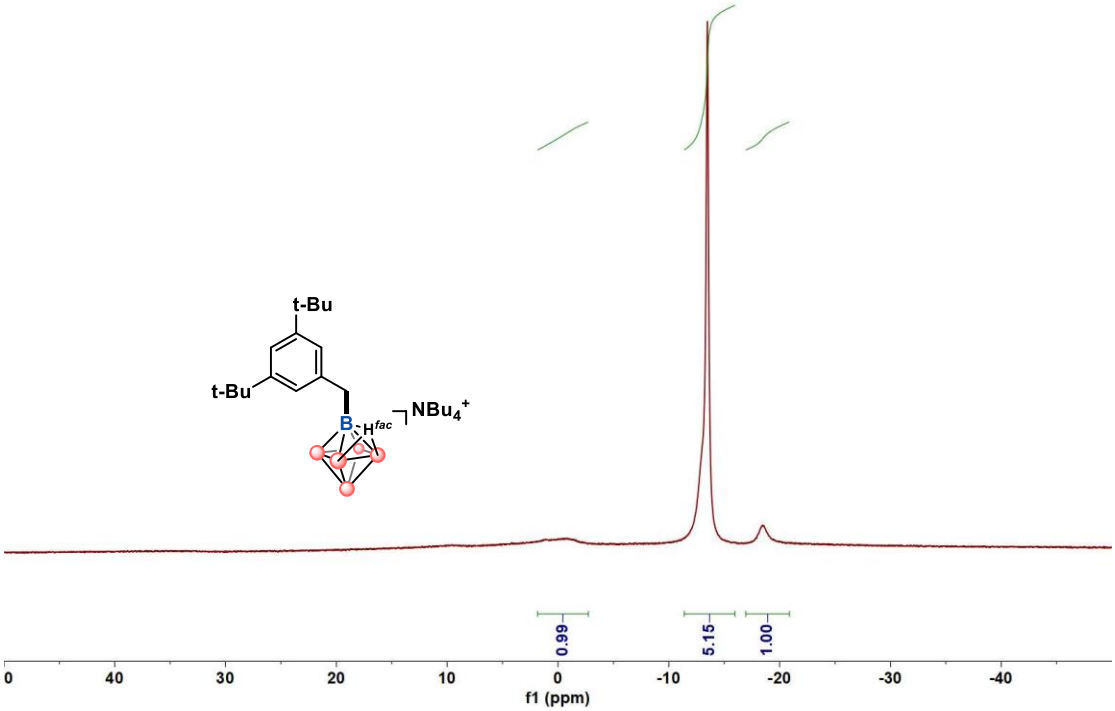


Figure S42. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 3,5-bis(1,1-dimethylethyl)phenyl]methyl bromide.

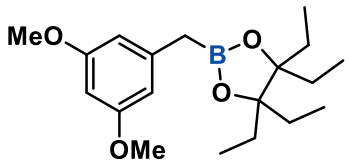
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 80:1) to give a colorless oil. R_f = 0.66 (Petroleum: EtOAc = 20:1). For method E, 49.0 mg (63%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.16 (m, 1H), 7.07 – 7.06 (m, 2H), 2.30 (s, 2H), 1.71 – 1.58 (m, 8H), 1.31 (s, 18H), 0.89 (t, *J* = 7.5 Hz, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.17, 137.64, 123.42, 118.60, 88.29, 34.68, 31.49, 26.26, 8.76.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 32.66.

HR-MS (EI) for $C_{25}H_{43}{}^{11}BO_2$ [M] *m/z* $[M]^+$: calculated: 386.3356, found: 386.3359



6b

2-(3,5-dimethoxybenzyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

Method E are applied. 3,5-Dimethoxybenzyl bromide (48.5 mg, 0.2 mmol), *t*-BuONa (18.5 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (61.9 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (72% conversion):

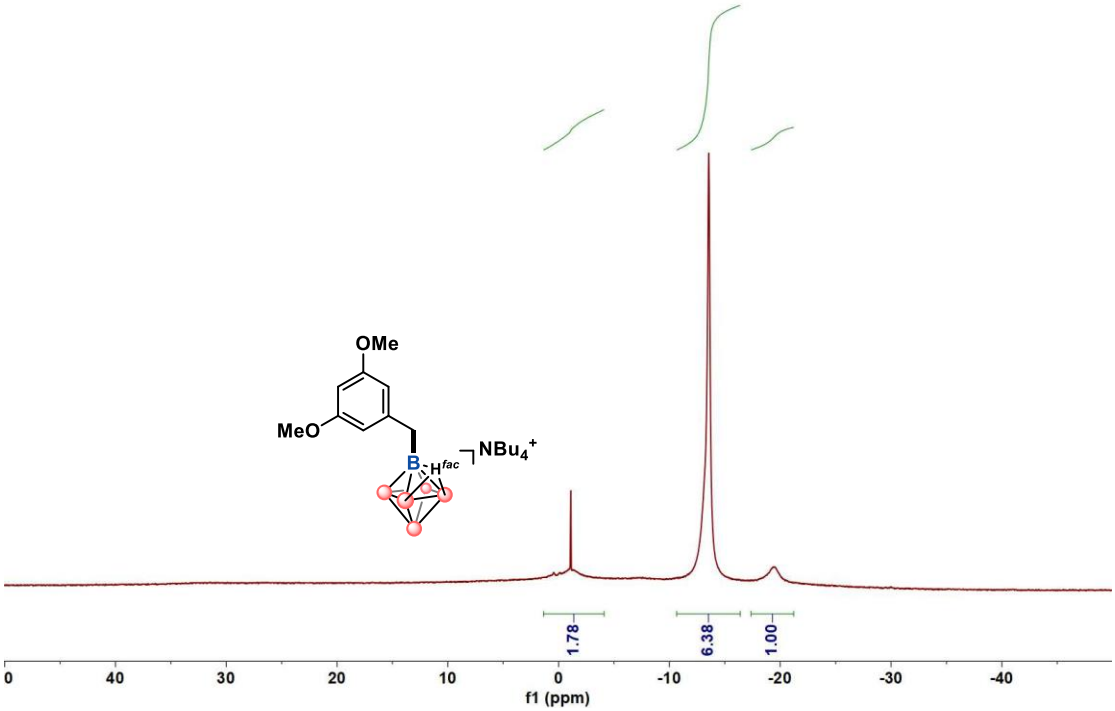


Figure S43. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 3,5-dimethoxybenzyl bromide.

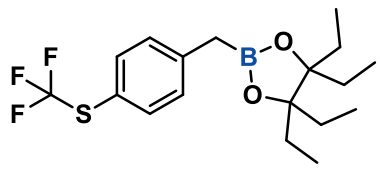
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 25:1) to give a colorless oil. R_f = 0.45 (Petroleum: EtOAc = 25:1). For method E, 49.0 mg (63%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 – 6.37 (m, 2H), 6.25 – 6.24 (m, 1H), 3.76 (s, 6H), 2.25 (s, 2H), 1.71 – 1.57 (m, 8H), 0.88 (t, *J* = 7.5 Hz, 12H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 160.48, 141.31, 107.02, 97.28, 88.46, 55.17, 26.25, 8.75.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 32.36.

HR-MS (EI) for $C_{19}H_{31}{}^{11}BO_4$ [M] *m/z* $[M]^+$: calculated: 334.2315, found: 334.2319



22b

4,4,5,5-tetraethyl-2-(4-((trifluoromethyl)thio)benzyl)-1,3,2-dioxaborolane

Method F are applied. 1-Bromomethyl-4-trifluoromethylsulfanylbenzene (54.8 mg, 0.2 mmol), *t*-BuONa (21.4 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (63.2 mg, 0.2 mmol) are used for substitution step. **For method F**, the ^{11}B NMR after substitution step (66% conversion):

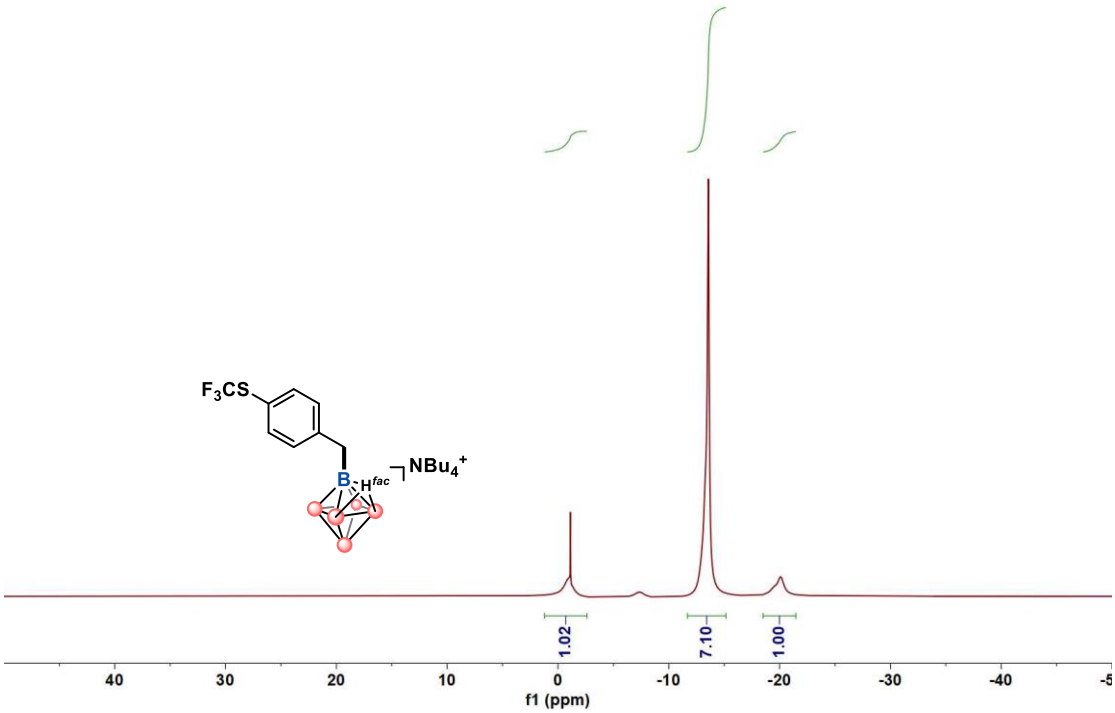


Figure S44. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 1-bromomethyl-4-trifluoromethylsulfanylbenzene.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: DCM = 10:1) to give a colorless oil. R_f = 0.88 (Petroleum: EtOAc = 20:1). For method F, 40.4 mg (53%) of product was obtained.

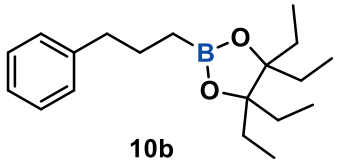
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H), 7.25 – 7.23 (m, 2H), 2.33 (s, 2H), 1.70 – 1.56 (m, 8H), 0.86 (t, *J* = 7.5 Hz, 12H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 142.92, 136.28, 130.13,129.69(q, ^{1}J = 307.4 Hz, CF_3), 119.95(q, ^{3}J = 2.2 Hz), 88.71, 29.70, 26.26, 8.68.

$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$) δ -43.31.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 32.30.

HR-MS (EI) for $C_{18}H_{26}{}^{11}BF_3O_2S$ [M] *m/z* $[M]^+$: calculated: 374.1699, found: 374.1697



10b

4,4,5,5-tetraethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane

Method E are applied. 1-Bromo-3-phenylpropane (41.0 mg, 0.2 mmol), *t*-BuONa (19.4 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (61.7 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (77% conversion):

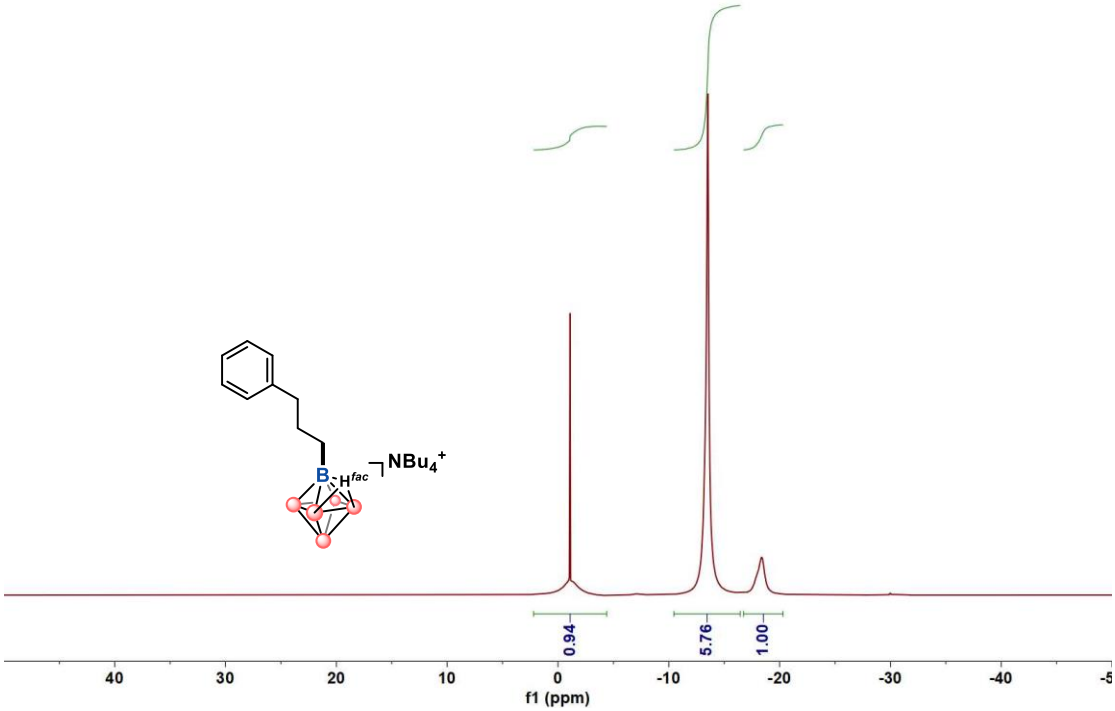


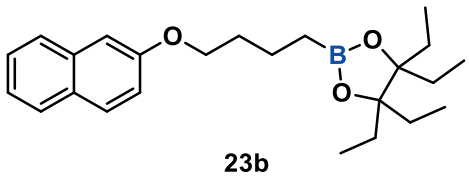
Figure S45. $^{11}B\{^1H\}$ NMR spectrum after substitution step with1-bromo-3-phenylpropane. The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 80:1) to give a colorless oil. R_f = 0.7 (Petroleum: EtOAc = 20:1). For method E, 34.2 mg (57%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 2.64 – 2.60 (m, 2H), 1.78 – 1.71 (m, 2H), 1.71 – 1.59 (m, 8H), 0.92 (t, *J* = 7.5 Hz, 12H), 0.84 (t, *J* = 7.7 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.87, 128.54, 128.14, 125.51, 87.94, 38.63, 26. 36, 8.80.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.51.

HR-MS (EI) for $C_{19}H_{31}{}^{11}BO_2$ [M] *m/z* $[M]^+$: calculated: 302.2417, found: 302.2419



23b

4,4,5,5-tetraethyl-2-(4-(naphthalen-2-yloxy)butyl)-1,3,2-dioxaborolane

Method E are applied. 2-(4-Bromobutoxy)naphthalene (57.1 mg, 0.2 mmol), *t*-BuONa (20.7 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.9 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (76% conversion):

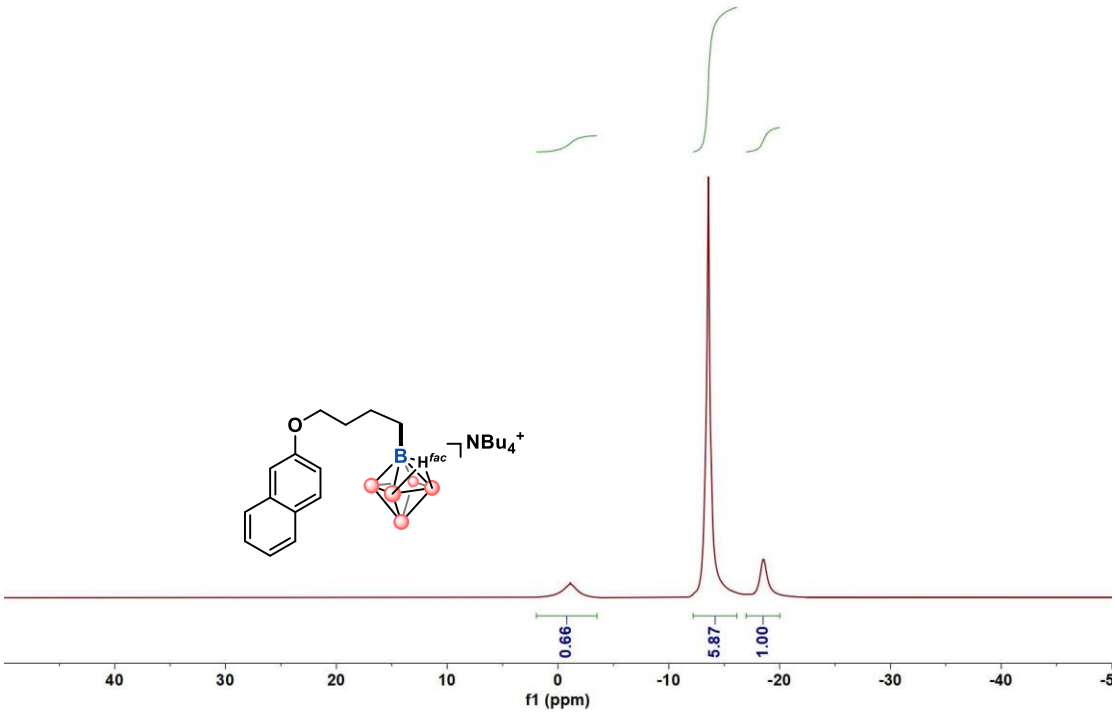


Figure S46. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 2-(4-bromobutoxy)naphthalene.

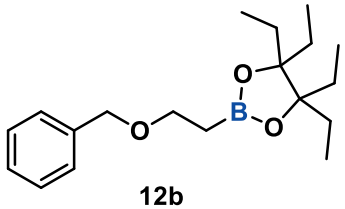
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 80:1) to give a colorless oil. R_f = 0.8 (Petroleum: EtOAc = 20:1). For method E, 49.1 mg (64%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 3H), 7.45 – 7.40 (m, 1H), 7.34 – 7.30 (m, 1H), 7.16 – 7.12 (m, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 1.90 – 1.86 (m, 2H), 1.72 – 1.60 (m, 10H), 0.94 – 0.87 (m, 14H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.12, 134.61, 129.20, 128.81, 127.58, 126.66, 126.19, 123.35, 119.08, 106.49, 88.00, 67.83, 31.76, 26.36, 20.81, 8.80.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 33.49.

HR-MS (EI) for $C_{24}H_{35}{}^{11}BO_3$ [M] *m/z* $[M]^+$: calculated: 382.2679, found: 382.2675



12b

2-(2-(benzyloxy)ethyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

Method E are applied. Benzyl 2-bromoethyl ether (43.7 mg, 0.2 mmol), *t*-BuONa (19.0 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (61.2 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (66% conversion):

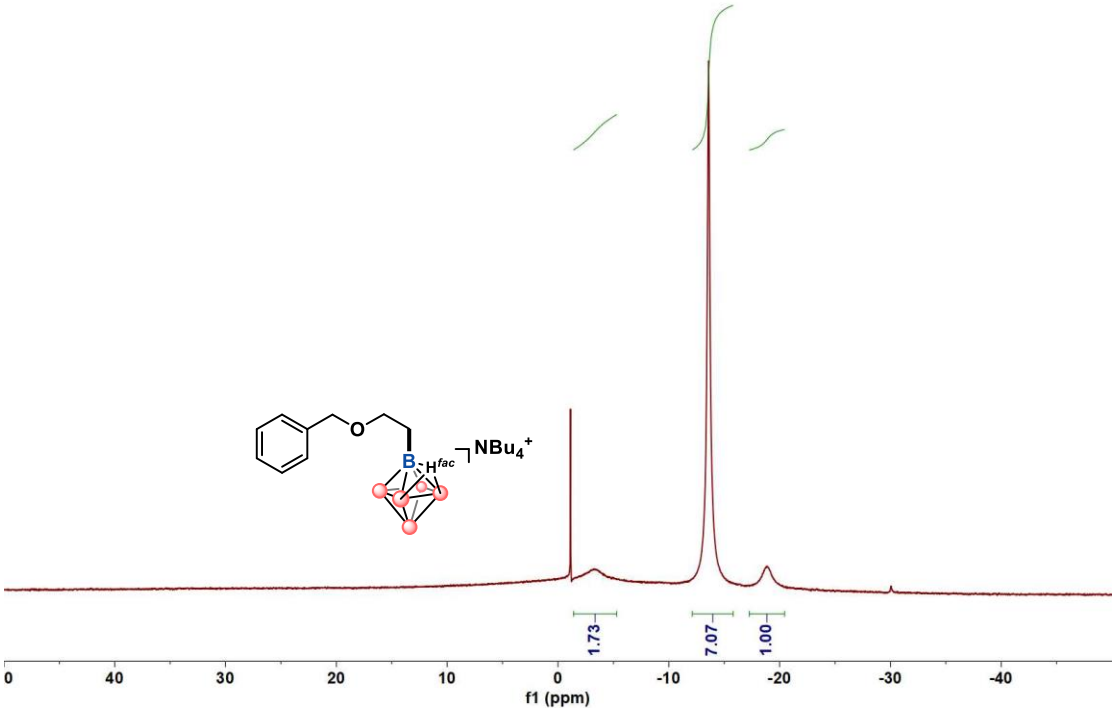


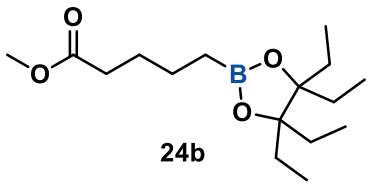
Figure S47. $^{11}B\{^1H\}$ NMR spectrum after substitution step with benzyl 2-bromoethyl ether. The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 30:1) to give a colorless oil. R_f = 0.23 (Petroleum: EtOAc = 30:1). For method E, 24.9 mg (40%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 4.50 (s, 2H), 3.64 (t, *J* = 7.9 Hz, 2H), 1.72 – 1.58 (m, 8H), 1.26 – 1.22 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.83, 128.23, 127.55, 127.29, 88.17, 72.52, 67.30, 26.32, 8.76.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 32.79.

HR-MS (EI) for $C_{19}H_{31}{}^{11}BO_3$ [M] *m/z* $[M]^+$: calculated: 318.2366 found: 318.2364



24b

methyl 5-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pentanoate

Method F are applied. 5-Bromo-pentanoicacimethylester (38.2 mg, 0.2 mmol), *t*-BuONa (20.1 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.3 mg, 0.2 mmol) are used for substitution step. **For method F**, the ^{11}B NMR after substitution step (46% conversion):

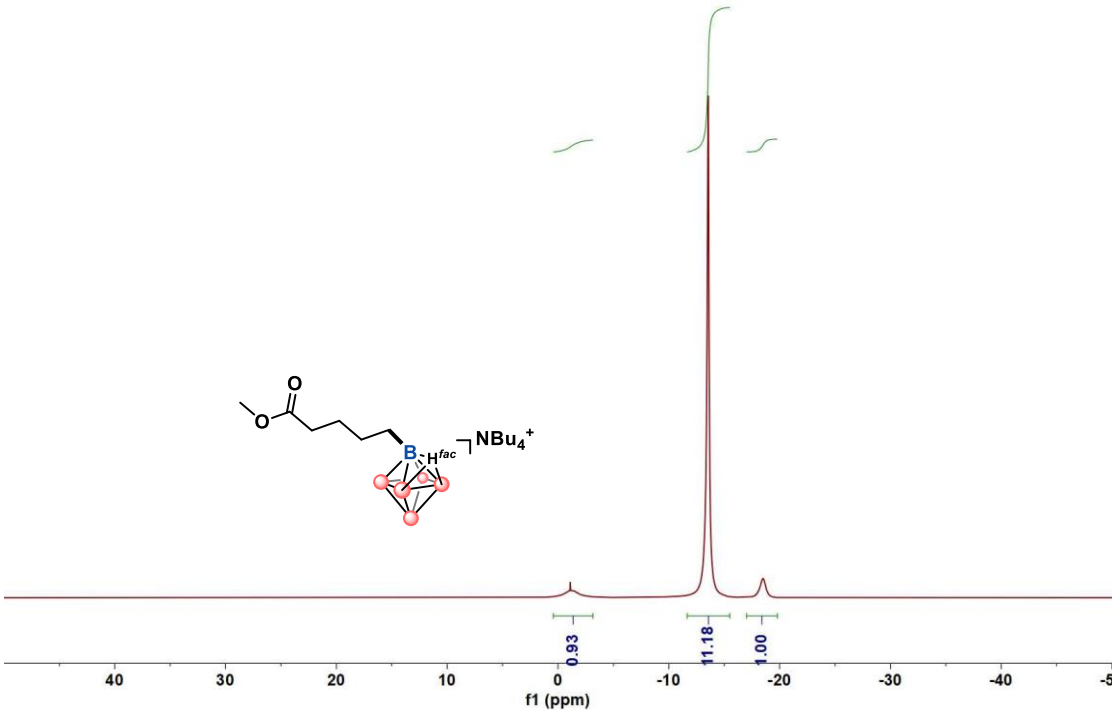


Figure S48. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 5-bromo-pentanoicacimethylester.

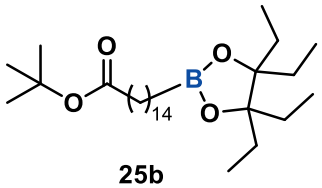
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 20:1) to give a colorless oil. R_f = 0.47 (Petroleum: EtOAc = 20:1). For method F, 24.5 mg (41%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.70 – 1.57 (m, 10H), 1.47 – 1.40 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 12H), 0.79 (t, *J* = 7.9 Hz, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.34, 87.98, 51.39, 33.98, 27.57, 26.38, 26.35, 23.80, 8.77.

$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ 33.53.

HR-MS (EI) for $C_{14}H_{26}{}^{11}BO_4$ [M] *m/z* $[M\text{-}CH_2CH_3]^+$: calculated: 269.1924, found: 269.1921



25b

tert-butyl 15-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pentadecanoate

Method F are applied. *Tert*-butyl 15-bromopentadecanoate (76.0 mg, 0.2 mmol), *t*-BuONa (20.0 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.8 mg, 0.2 mmol) are used for substitution step. **For method F**, the ^{11}B NMR after substitution step (64% conversion):

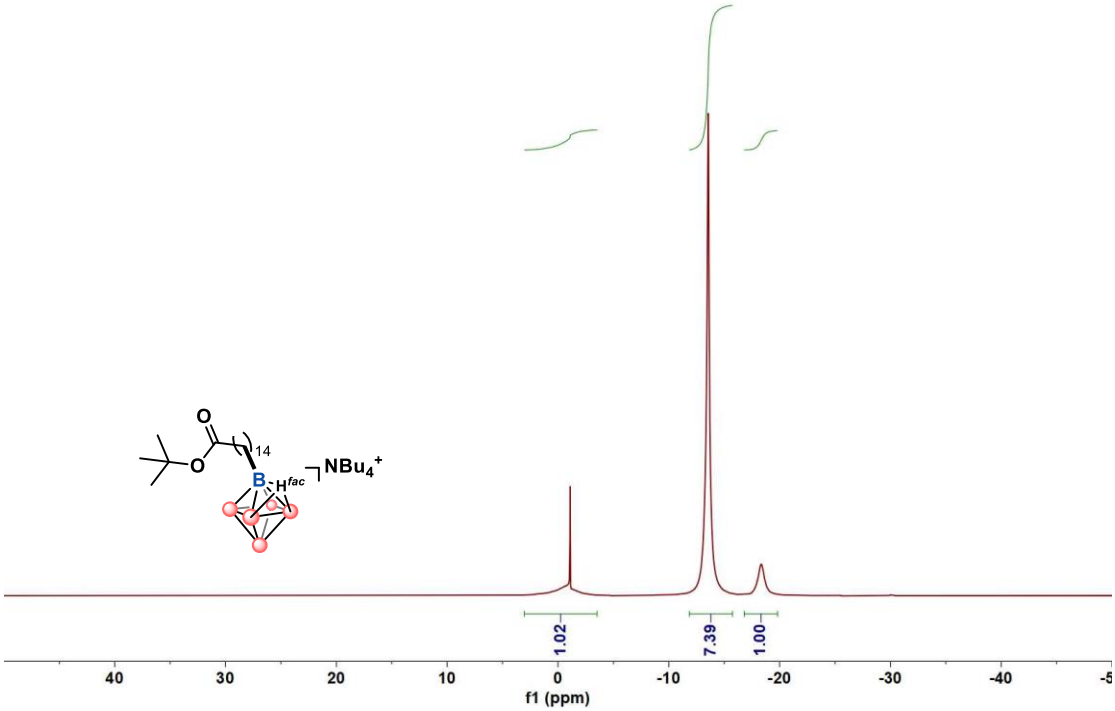


Figure S49. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with *tert*-butyl 15-bromopentadecanoate.

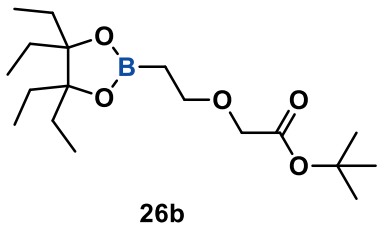
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: DCM = 5:1) to give a colorless oil. R_f = 0.33 (Petroleum: DCM = 5:1). For method F, 37.0 mg (38%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.61 (m, 8H), 1.58 – 1.53 (m, 2H), 1.44 (s, 9H), 1.42 – 1.37 (m, 2H), 1.28 – 1.24 (m, 20H), 0.90 (t, *J* = 7.5 Hz, 12H), 0.76 (t, *J* = 7.7 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.37, 87.81, 79.86, 35.63, 32.45, 29.66, 29.60, 29.48, 29.45, 29.30, 29.09, 28.10, 26.34, 25.12, 24.21, 8.79.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 31.12.

HR-MS (ESI) for $C_{29}H_{57}{}^{11}BO_4Na$ [M] *m/z* $[M+Na]^+$: calculated: 503.4248, found: 503.4245



26b

tert-butyl 2-(2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethoxy)acetate

Method I are applied. *Tert*-butyl 2-(2-bromoethoxy)acetate (48.3 mg, 0.2 mmol), *t*-BuONa (32.4 mg, 0.3 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (92.6 mg, 0.3 mmol) are used for substitution step. **For method I**, the ^{11}B NMR after substitution step (52% conversion):

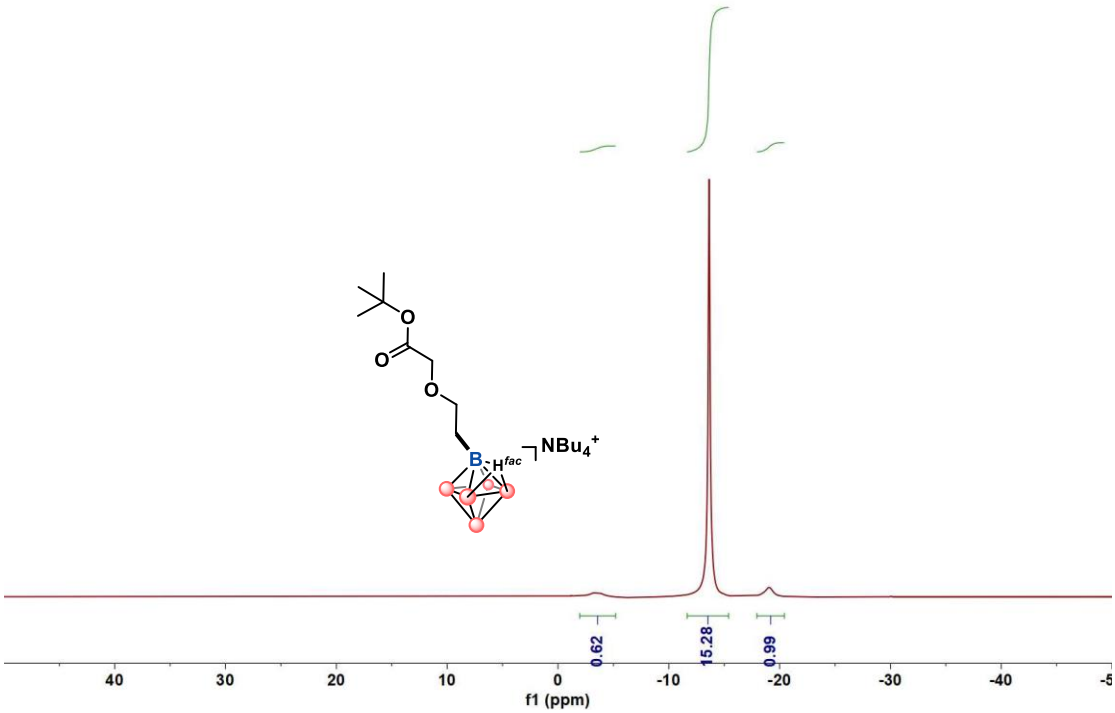


Figure S50. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with *tert*-butyl 2-(2-bromoethoxy)acetate.

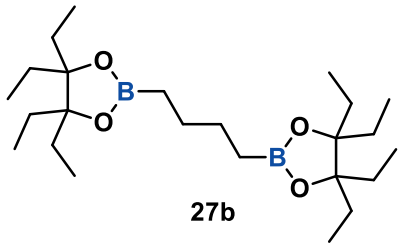
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 20:1) to give a colorless oil. R_f = 0.5 (Petroleum: EtOAc = 10:1). For method I, 31.5 mg (45%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 2H), 3.65 (t, *J* = 8.2 Hz, 2H), 1.71 – 1.64 (m, 8H), 1.47 (s, 9H), 1.24 (t, *J* = 8.2 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 12H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.90, 88.21, 81.31, 81.29, 68.48, 68.46, 28.10, 26.31, 8.76.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 32.61.

HR-MS (ESI) for $C_{18}H_{35}{}^{11}BO_5Na$ [M] *m/z* $[M+Na]^+$: calculated: 365.2475, found: 365.2477



27b

1,4-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)butane

Method G are applied. 1,4-Dibromobutane (43.7 mg, 0.2 mmol), *t*-BuONa (38.3 mg, 0.4 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (124.1 mg, 0.4 mmol) are used for substitution step. **For method G**, the ^{11}B NMR after substitution step (>90% conversion):

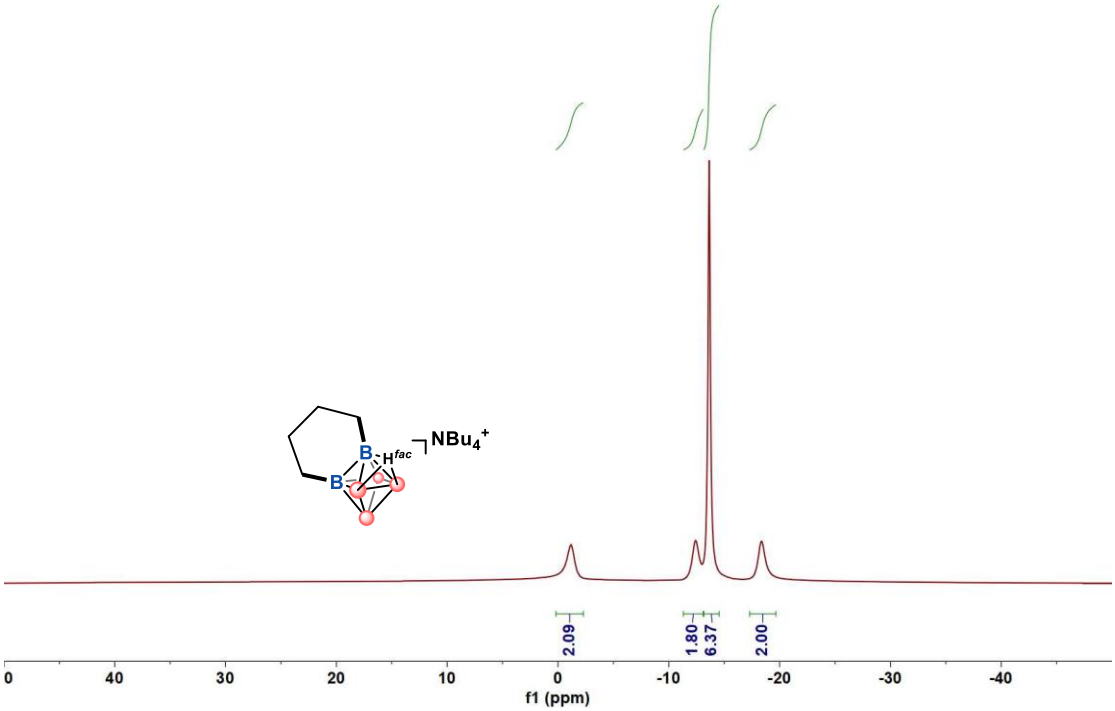


Figure S51. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 1,4-dibromobutane.

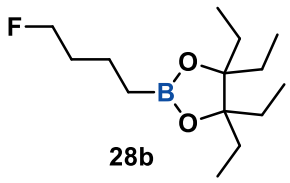
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 80:1) to give a colorless oil. R_f = 0.7 (Petroleum: EtOAc = 20:1). For method G, 46.4 mg (54%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 – 1.60 (m, 16H), 1.43 – 1.39 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 24H), 0.78 – 0.74 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 87.77, 27.04, 26.35, 8.79.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 33.68.

HR-MS (EI) for $C_{22}H_{43}{}^{11}B_2O_4$ [M] *m/z* $[M\text{-}CH_2CH_3]^+$: calculated: 393.3347, found: 393.3345



28b

4,4,5,5-tetraethyl-2-(4-fluorobutyl)-1,3,2-dioxaborolane

Method G are applied. 1-Bromo-4-fluorobutane (32.0 mg, 0.2 mmol), *t*-BuONa (40.4 mg, 0.4 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (123.3 mg, 0.4 mmol) are used for substitution step. **For method G**, the ^{11}B NMR after substitution step (95% conversion):

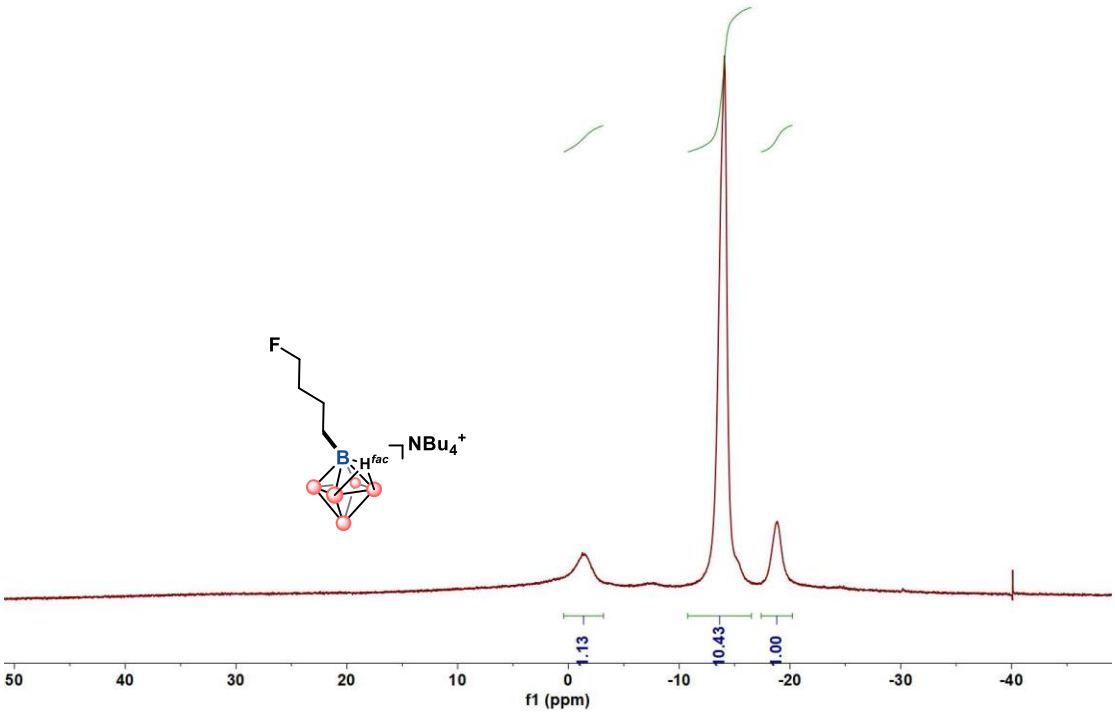


Figure S52. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 1-bromo-4-fluorobutane.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 80:1) to give a colorless oil. R_f = 0.49 (Petroleum: EtOAc = 38:1). For method G, 30.5 mg (57%) of product was obtained.

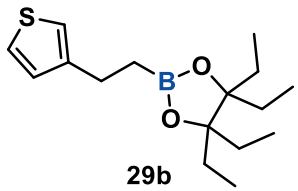
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (t, *J* = 6.2 Hz, 1H), 4.37 (t, *J* = 6.2 Hz, 1H), 1.77 – 1.59 (m, 10H), 1.55 – 1.48 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 12H), 0.81 (t, *J* = 7.9 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 87.99, 84.04 (d, ^{1}J = 162.5 Hz), 32.86 (d, ^{2}J = 19.5 Hz), 26.35, 19.80 (d, ^{3}J = 5.7 Hz), 8.76.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -218.22.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 33.34.

HR-MS (EI) for $C_{14}H_{28}{}^{11}BFO_2$ [M] *m/z* $[M]^+$: calculated: 258.2166 found: 258.2168



29b

4,4,5,5-tetraethyl-2-(2-(thiophen-3-yl)ethyl)-1,3,2-dioxaborolane

Method E are applied. 2-(Thiophen-3-yl)ethyl 4-methylbenzenesulfonate (57.1 mg, 0.2 mmol), *t*-BuONa (18.9 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (61.6 mg, 0.2 mmol) are used for substitution step. **For method E**, the ^{11}B NMR after substitution step (70% conversion):

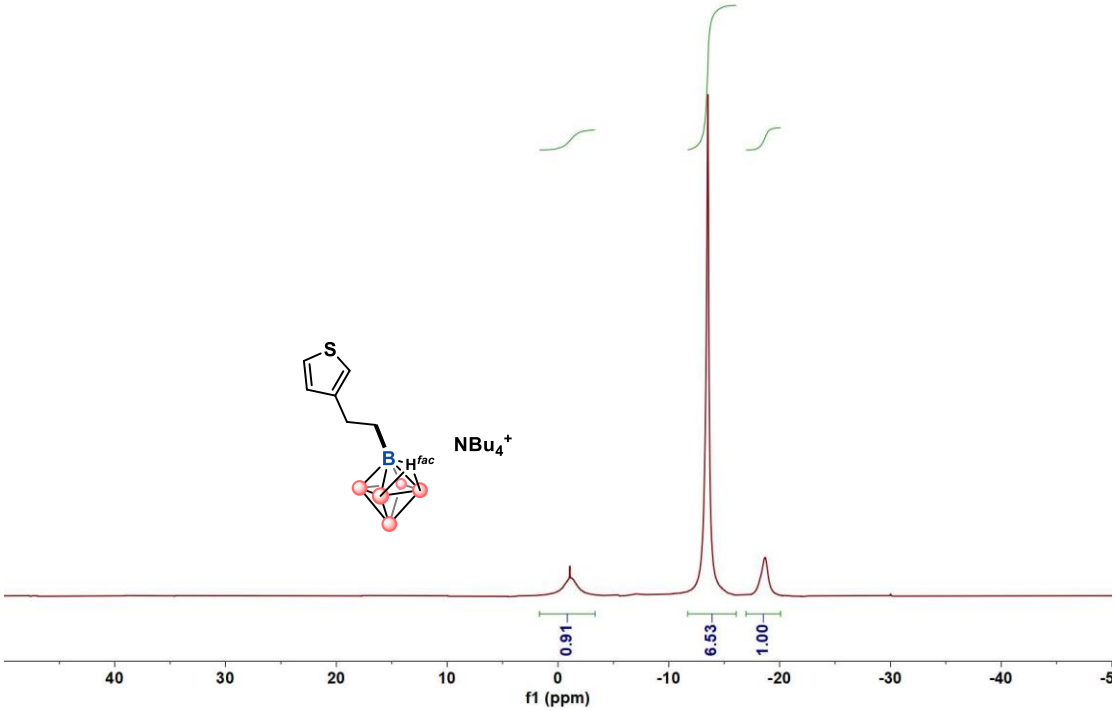


Figure S53. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 2-(thiophen-3-yl)ethyl 4-methylbenzenesulfonate.

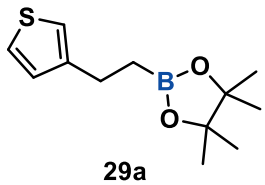
The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 120:1) to give a colorless oil. R_f = 0.14 (Petroleum: Diethyl ether = 120:1). For method E, 23.9 mg (41%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.20 (m, 1H), 6.97 – 6.95 (m, 1H), 6.95 – 6.93 (m, 1H), 2.76 (t, 2H), 1.69 – 1.56 (m, 8H), 1.17 (t, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 145.02, 128.17, 124.87, 119.27, 88.12, 26.30, 24.66, 8.75.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 33.23.

HR-MS (EI) for $C_{16}H_{27}{}^{11}BO_2S$ [M] *m/z* $[M]^+$: calculated: 294.1825 found: 294.1822



29a

4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)ethyl)-1,3,2-dioxaborolane

Method C are applied. 2-(Thiophen-3-yl)ethyl 4-methylbenzenesulfonate (57.5 mg, 0.2 mmol), *t*-BuONa (19.3 mg, 0.2 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (62.6 mg, 0.2 mmol) are used for substitution step. **For method C**, the ^{11}B NMR after substitution step (70% conversion):

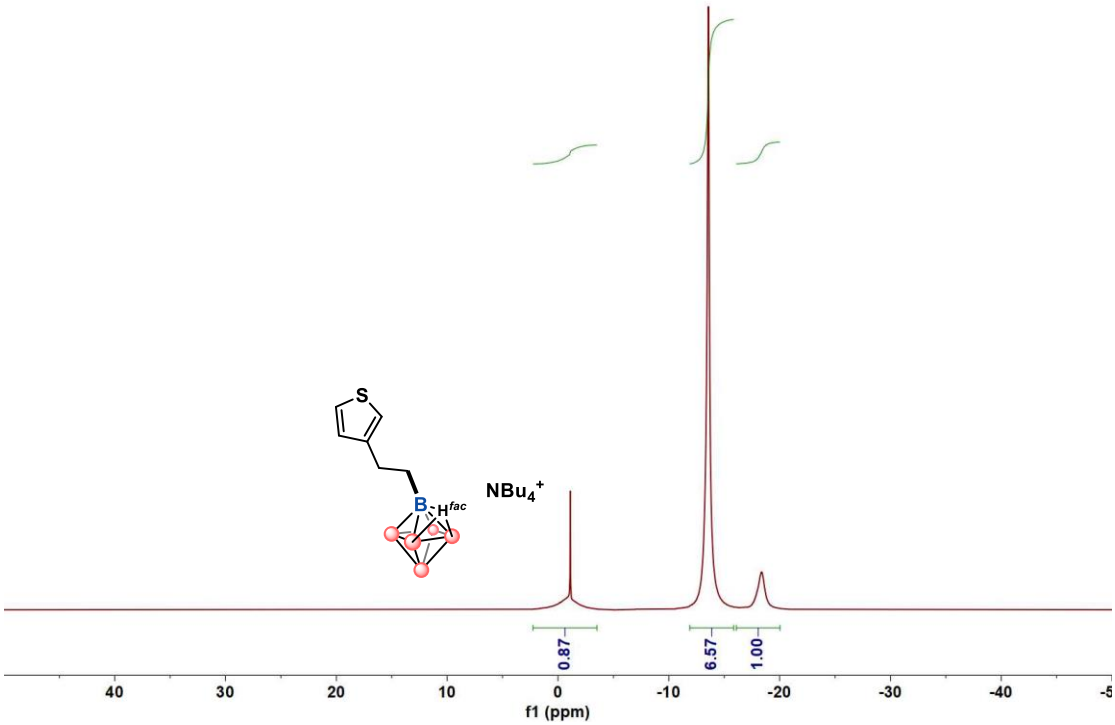


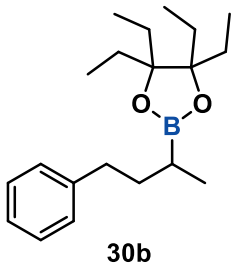
Figure S54. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 2-(thiophen-3-yl)ethyl 4-methylbenzenesulfonate.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: Diethyl ether = 80:1) to give a colorless oil. R_f = 0.78 (Petroleum: EtOAc = 16:1). For method A, 9.3 mg (19%) of product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 4.9, 3.0 Hz, 1H), 6.97 – 6.93 (m, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.17 – 1.13 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.86, 128.18, 124.95, 119.40, 83.10, 24.78, 24.52.

The NMR spectra are consistent with literature report.[17] CAS registry No. 280563-56-6



30b

4,4,5,5-tetraethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane

Method H are applied. 4-Phenylbutan-2-yl 4-methylbenzenesulfonate (61.2 mg, 0.2 mmol), *t*-BuONa (28.6 mg, 0.3 mmol) and *n*-$Bu_4N(B_6H_7)$ (**1**) (95.0 mg, 0.3 mmol) are used for substitution step. **For method H**, the ^{11}B NMR after substitution step (65% conversion):

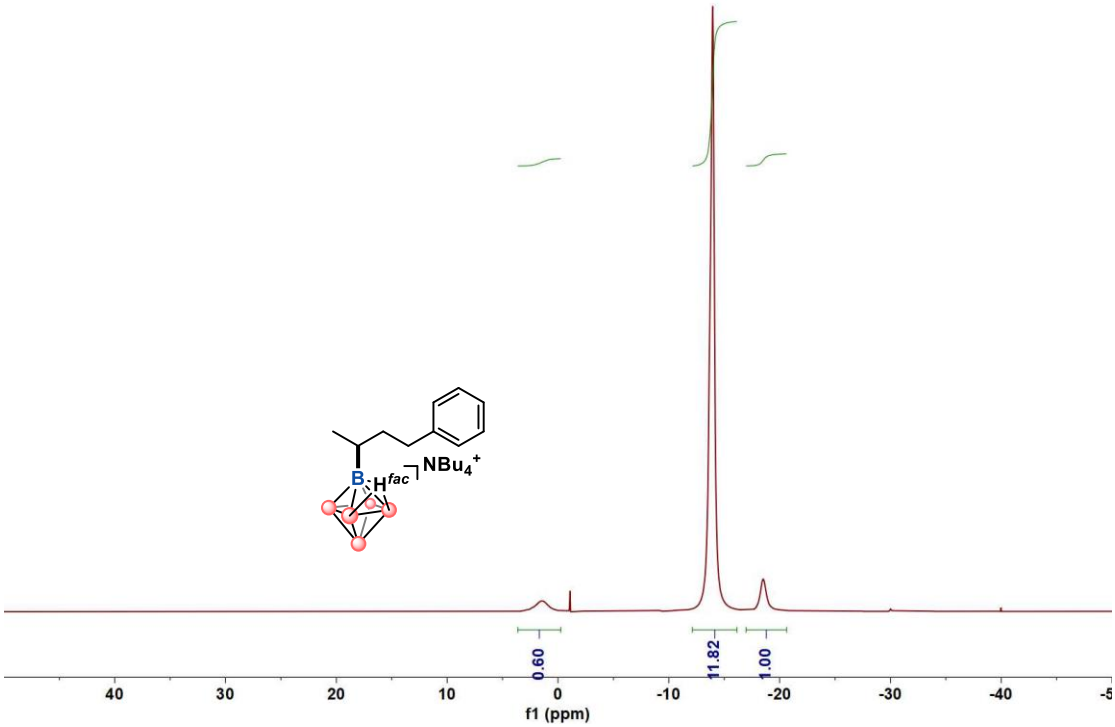


Figure S55. $^{11}B\{^{1}H\}$ NMR spectrum after substitution step with 4-phenylbutan-2-yl 4-methylbenzenesulfonate.

The title compound after the bulk electrolysis was purified by flash column chromatography (silica gel, Petroleum: EtOAc = 60:1) to give a colorless oil. R_f = 0.76 (Petroleum: EtOAc = 30:1). For method H, 28.9 mg (47%) of product was obtained.

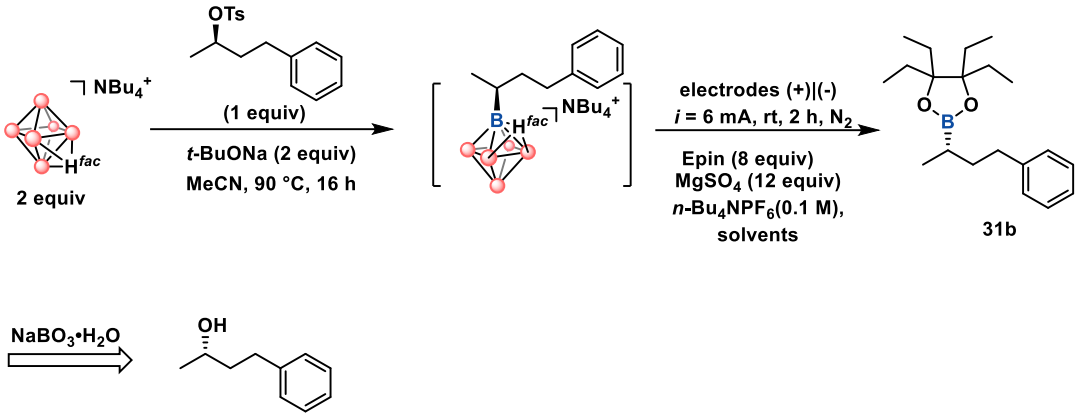
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 2.63 (t, *J* = 8.2 Hz, 2H), 1.82 – 1.73 (m, 1H), 1.73 – 1.61 (m, 8H), 1.59 – 1.54 (m, 1H), 1.10 – 1.06 (m, 1H), 1.05 – 1.00 (m, 3H), 0.94 – 0.90 (m, 12H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 143.30, 128.43, 128.17, 125.44, 87.87, 35.52, 35.32, 26.31, 26.26, 15.78, 8.81, 8.77.

$^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) δ 33.96.

HR-MS (EI) for $C_{20}H_{33}{}^{11}BO_2$ [M] *m/z* $[M]^+$: calculated: 316.2574 found: 316.2576

8. Substitutions of chiral electrophiles, electrochemical deconstruction procedures and characterization data



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (124.8 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (37.8 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*R*)-4-phenylbutan-2-yl 4-methylbenzenesulfonate (60.9 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. he mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 89%.

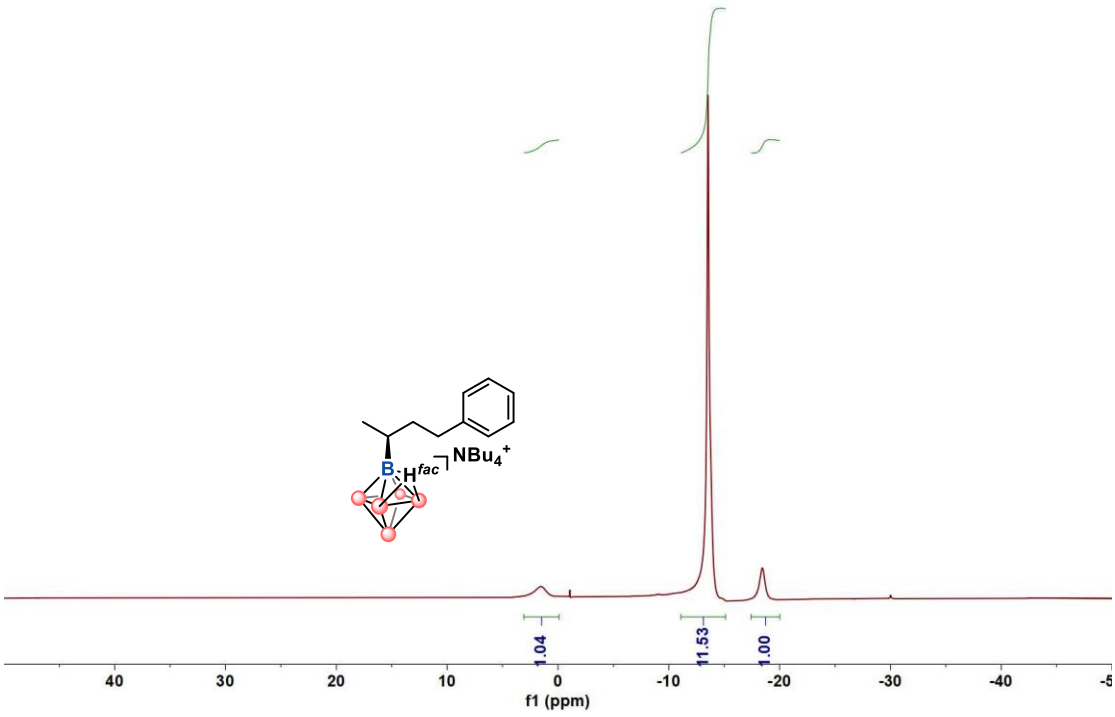
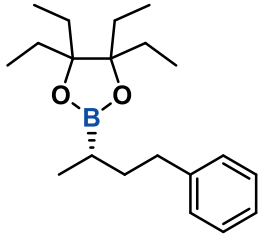


Figure S56. $^{11}B\{^1H\}$ NMR spectrum after substitution step with (*R*)-4-phenylbutan-2-yl 4-methylbenzenesulfonate.

Electrolysis set up 1(IKA: ElectraSyn 2.0) is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (279.6mg, 1.6 mmol, 8 equiv), $MgSO_4$ (290.2 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (114.3 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the product (23.9 mg, $[\alpha]_D^{22.8}$ = -0.6 (c = 0.1, $CHCl_3$)) in 46% yield. R_f = 0.64 (Petroleum: EtOAc = 30:1).



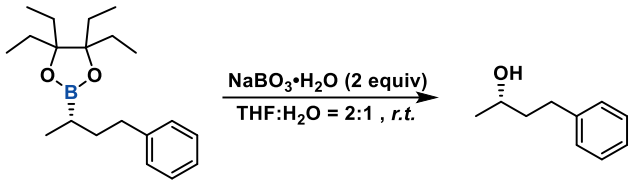
31b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 2.63 (t, *J* = 8.2 Hz, 2H), 1.84 – 1.73 (m, 1H), 1.73 – 1.61 (m, 8H), 1.55 – 1.53 (m, 1H), 1.13 – 1.05 (m, 1H), 1.03 – 1.01 (m, 3H), 0.95 – 0.90 (m, 12H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.23, 128.43, 128.17, 125.44, 87.87, 35.52, 35.32, 26.31, 26.26, 15.78, 8.81, 8.77.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.94.

HR-MS (EI) for $C_{20}H_{33}{}^{11}BO_2$ [M] *m/z* $[M]^+$: calculated: 316.2574 found: 316.2576



31b

(*S*)-4,4,5,5-tetraethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (29.4 mg, 0.09 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (22.5 mg, 0.2 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (Petroleum: EtOAc =5:1) afforded a colorless oil (10.7 mg, 77%, 94:6 *e.r.*). The *e.r.* was determined on HPLC system with IB column (5% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for compound (Fig. S58): t_1 = 6.976 min (major), t_2 = 9.177 min (minor).

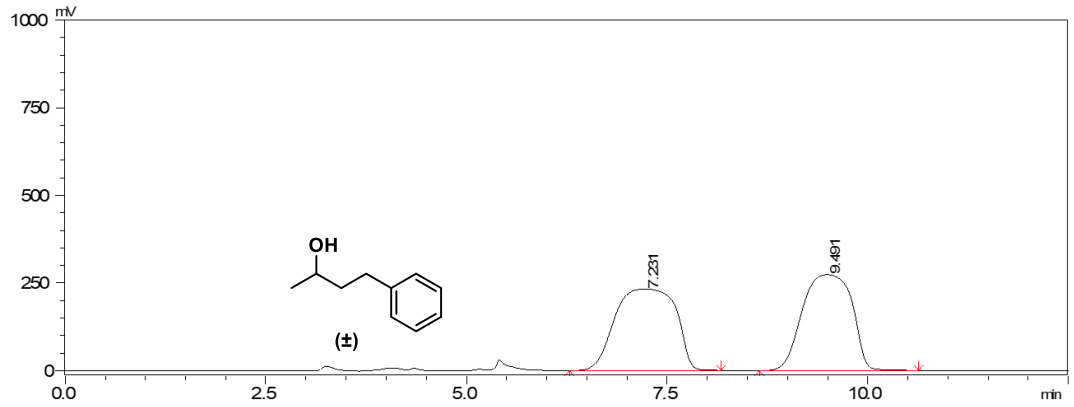


Figure S57. HPLC trace of 4-phenylbutan-2-ol

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.231	232369	12210839	50.955
2	9.491	273592	11753162	49.045
total		505961	23964001	100.000

Table S19. HPLC trace of 4-phenylbutan-2-ol

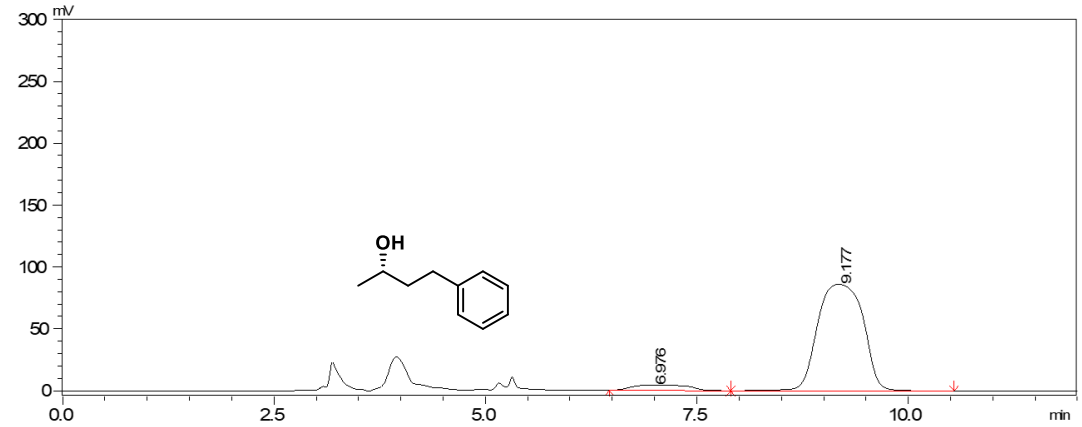
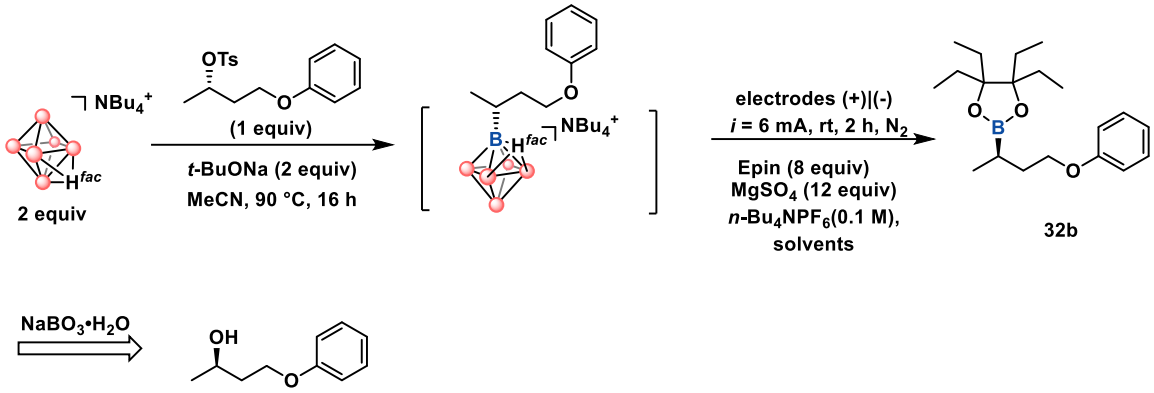


Figure S58. HPLC trace of (*S*)-4-phenylbutan-2-ol

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.976	4327	202089	5.910
2	9.177	86098	3217454	94.090
total		90426	3419543	100.000

Table S20. HPLC trace of (*S*)-4-phenylbutan-2-ol



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (128.7 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (38.9 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*S*)-4-phenoxybutan-2-yl 4-methylbenzenesulfonate (67.0 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 91%.

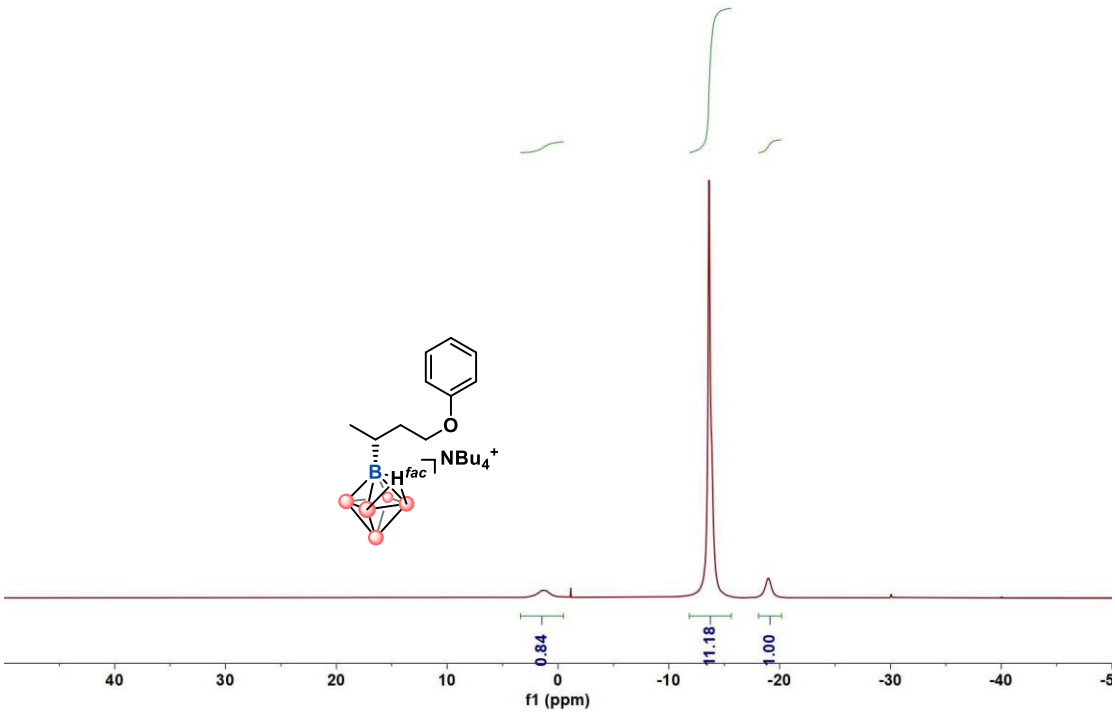
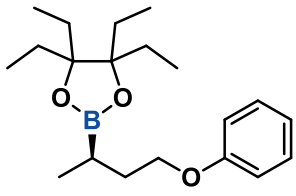


Figure S59. $^{11}B\{^1H\}$ NMR spectrum after substitution step with (*S*)-4-phenoxybutan-2-yl 4-methylbenzenesulfonate

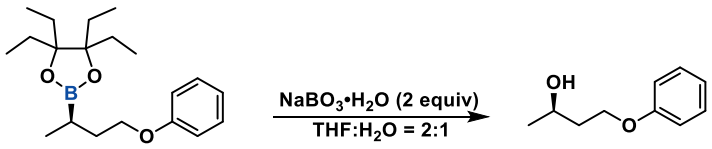
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (291.1 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (284.9 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (117.1 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the

crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afforded the product (38.8 mg, $[\alpha]_D^{22.8}$ = -4.8 (c = 0.8, $CHCl_3$)) in 56% yield. R_f = 0.7 Petroleum: EtOAc = 20:1).



32b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 6.93 – 6.89 (m, 3H), 4.10 – 3.96 (m, 2H), 2.02 – 1.93 (m, 1H), 1.80 – 1.70 (m, 1H), 1.70 – 1.58 (m, 8H), 1.29 – 1.19 (m, 1H), 1.08 (d, *J* = 7.5 Hz, 3H), 0.88 (td, *J* = 7.5, 2.6 Hz, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.19, 129.31, 120.28, 114.56, 88.02, 67.28, 32.51, 26.29, 26.24, 15.79, 8.77, 8.75.
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.76.
HR-MS (EI) for $C_{20}H_{33}{}^{11}BO_3$ [M] *m/z* $[M]^+$: calculated: 332.2523 found: 332.2520



32b

(*R*)-4,4,5,5-tetraethyl-2-(4-phenoxybutan-2-yl)-1,3,2-dioxaborolane (38.8 mg, 0.12 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (23.9 mg, 0.24 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 4:1) afforded a colorless oil (15.7 mg, 80%, 93:7 *e.r.*). The *e.r.* was determined on HPLC system with AD column (5% EtOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for compound (Fig. S61): t_1 = 10.294 min (minor), t_2 = 11.436 min (major).

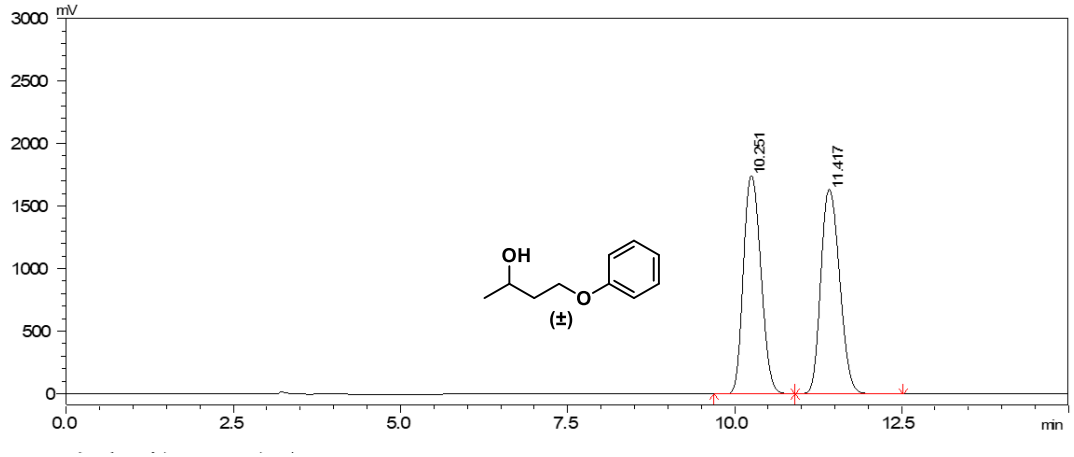


Figure S60. HPLC trace of 4-phenoxybutan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.251	1746984	31917745	49.782
2	11.417	1637483	32197411	50.218
total		3384466	64115156	100.000

Table S21. HPLC trace of 4-phenoxybutan-2-ol.

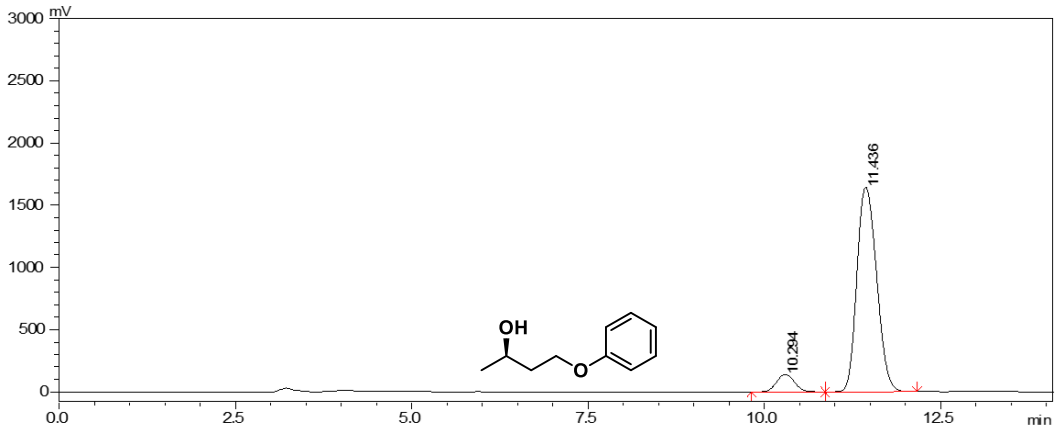
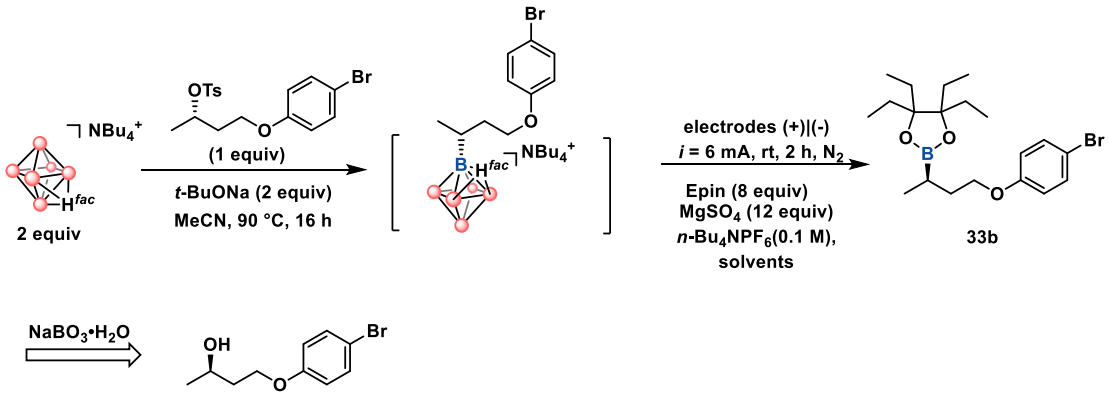


Figure S61. HPLC trace of (*R*)-4-phenoxybutan-2-ol

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	10.294	139394	2465324	7.151
2	11.436	1643408	32010931	92.849
total		1782802	34476255	100.000

Table S22. HPLC trace of (*R*)-4-phenoxybutan-2-ol



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (121.0 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (40.2 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*S*)-4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate (80.2 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. T The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 90%.

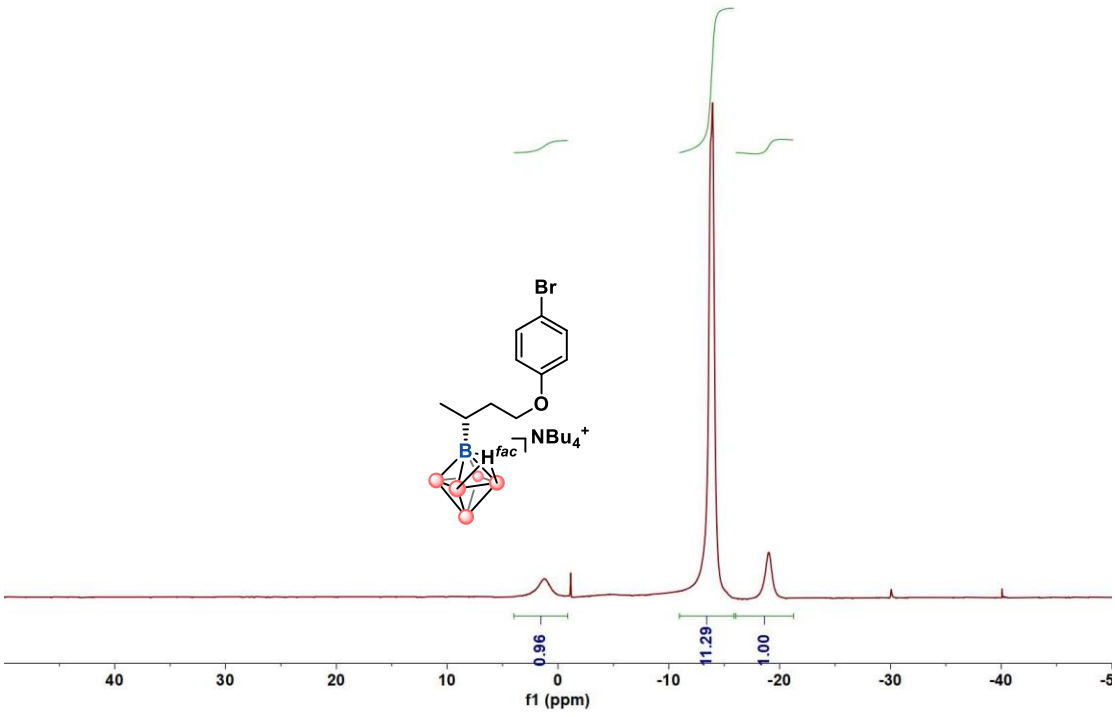
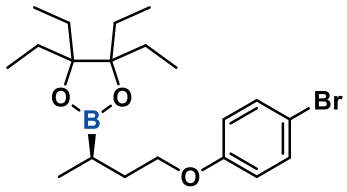


Figure S62. $^{11}B\{^1H\}$ NMR spectrum after substitution step with ((*S*)-4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate

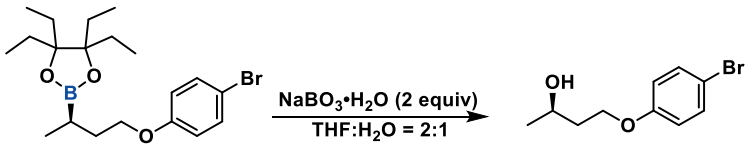
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (271.3 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (295.8 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (114.6 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the

solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the product (35.5 mg, $[\alpha]_D^{22.4}$ = -1.4 (c = 0.2, $CHCl_3$)) in 43% yield. R_f = 0.42(Petroleum: EtOAc = 20:1).



33b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 6.82 – 6.75 (m, 2H), 4.02 – 3.91 (m, 2H), 1.99 – 1.90 (m, 1H), 1.78 – 1.70 (m, 1H), 1.68 – 1.57 (m, 8H), 1.26 – 1.18 (m, 1H), 1.04 (d, *J* = 7.5 Hz, 3H), 0.92 – 0.88 (m, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.32, 132.10, 116.37, 112.38, 88.07, 67.68, 32.36, 26.30, 26.24, 15.81, 8.77, 8.74.
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.74.
HR-MS (EI) for $C_{20}H_{32}{}^{11}BO_3{}^{79}Br$ [M] *m/z* $[M]^+$: calculated: 410.1628 found: 410.1631



33b

(*R*)-2-(4-(4-bromophenoxy)butan-2-yl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (32.3 mg, 0.07 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (19.4 mg, 0.16 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 4:1) afforded a colorless oil (10.4 mg, 54%, 93:7 *e.r.*). The *e.r.* was determined on HPLC system with AS column (10% EtOH/hexanes, flow rate 1.0 mL/min, 25 °C); retention time for compound (Fig. S64): t_1 = 7.119 min (minor), t_2 = 12.463 min (major).

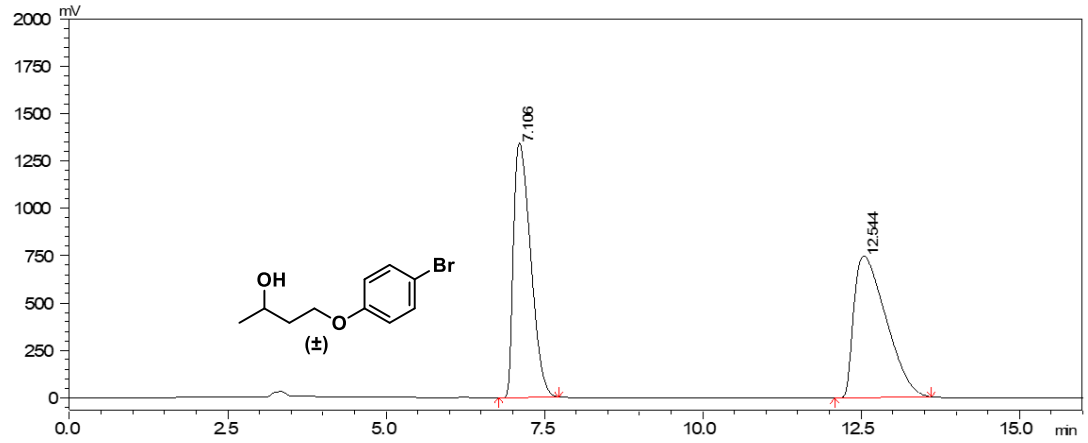


Figure S63. HPLC trace of 4-(4-bromophenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.106	1346073	25409184	49.017
2	12.544	748609	26427912	50.983
total		2094682	51837096	100.000

Table S23. HPLC trace of standard 4-(4-bromophenoxy)butan-2-ol.

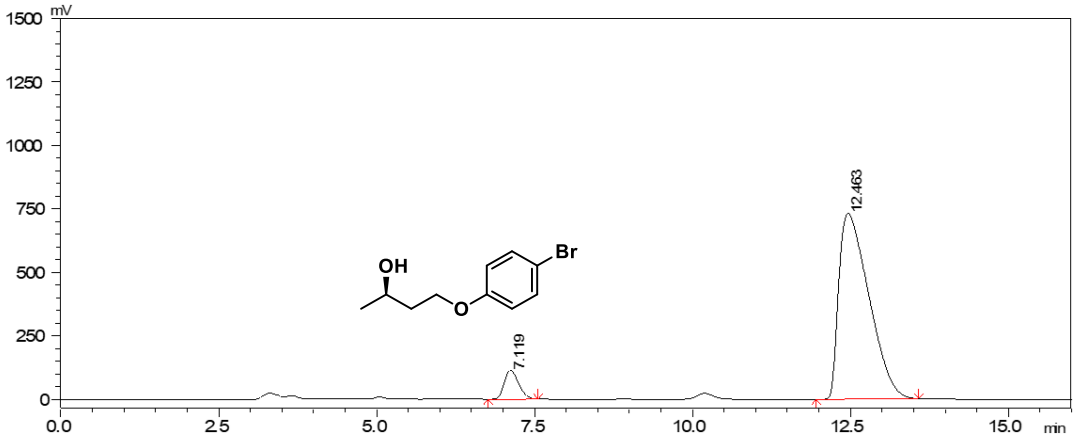
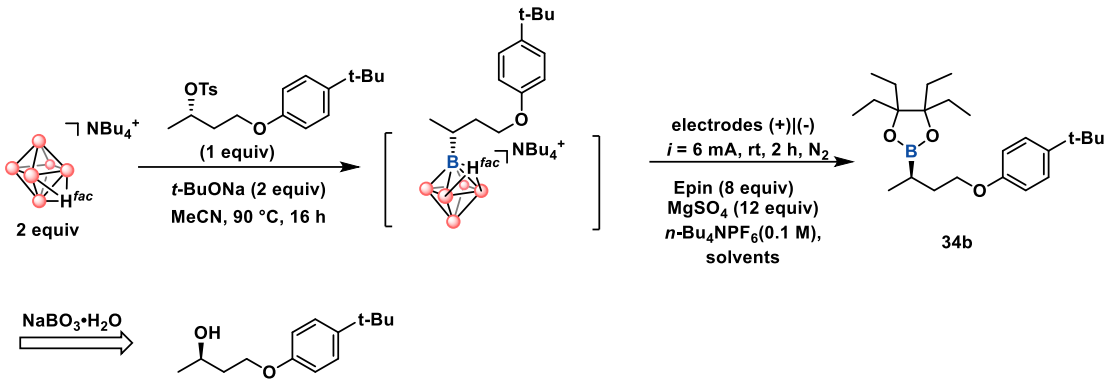


Figure S64. HPLC trace of (*R*)-4-(4-bromophenoxy)butan-2-ol

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.119	112741	1792121	6.878
2	12.463	731923	24262311	93.122
total		844664	26054431	100.000

Table S24. HPLC trace of (*R*)-4-(4-bromophenoxy)butan-2-ol



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (125.5 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (38.5 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate (75.7 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 83%.

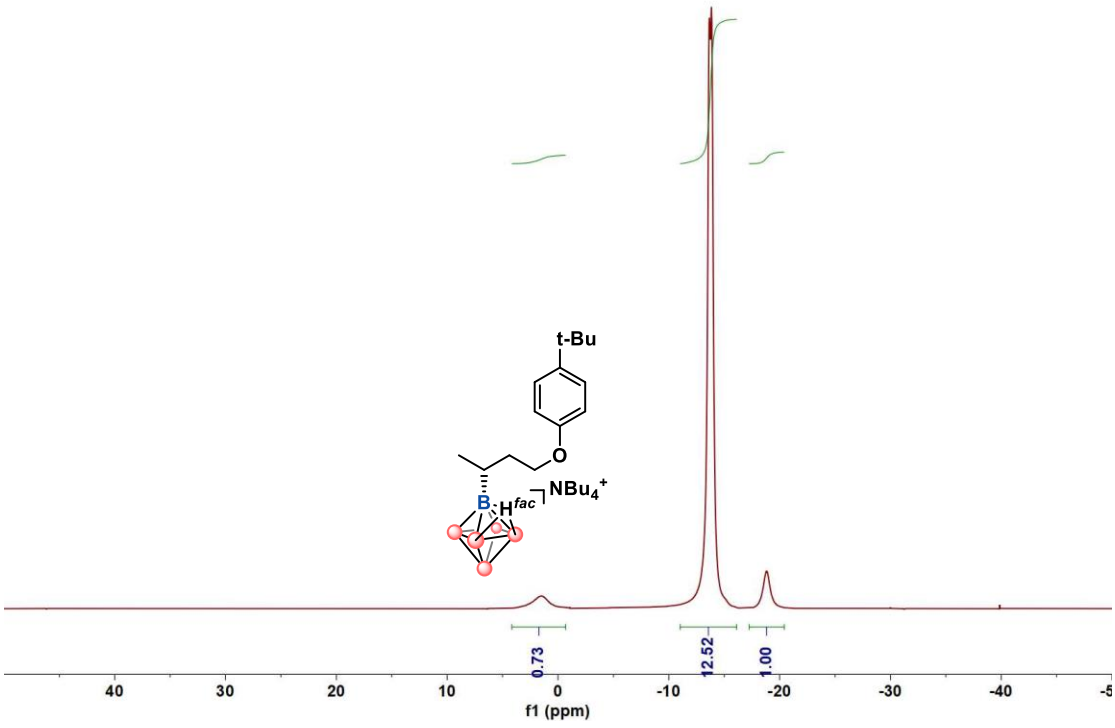
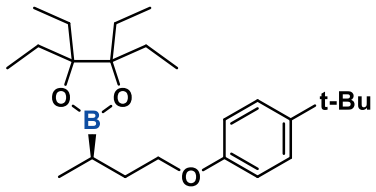


Figure S65. $^{11}B\{^1H\}$ NMR spectrum after substitution step with (*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate

Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (281.9 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (289.2 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (117.3 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the

crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the product (35.9 mg, $[\alpha]_D^{22.3}$ = -2.3 (c = 0.4, $CHCl_3$)) in 46% yield. R_f = 0.65 (Petroleum: EtOAc = 20:1).



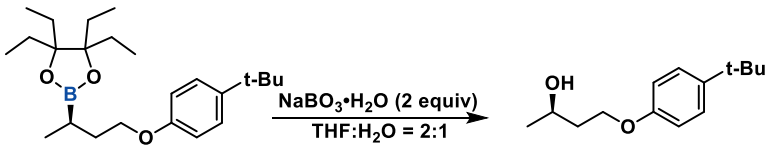
34b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 6.86 – 6.82 (m, 2H), 4.02 – 3.93 (m, 2H), 1.99 – 1.94 (m, 1H), 1.76 – 1.59 (m, 9H), 1.29 (s, 9H), 1.04 (d, *J* = 7.5 Hz, 3H), 0.90 (td, *J* = 7.5, 2.6 Hz, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.92, 142.89, 126.08, 113.95, 88.00, 67.29, 34.00, 32.56, 31.53, 26.27, 26.22, 15.76, 8.79, 8.76.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.67.

HR-MS (EI) for $C_{24}H_{41}{}^{11}BO_3$ [M] *m/z* $[M]^+$: calculated: 388.3149 found: 388.3147



34b

(*R*)-2-(4-(4-(tert-butyl)phenoxy)butan-2-yl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (29.3 mg, 0.08 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (17.3 mg, 0.16 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 4:1) afforded a colorless oil (9.0 mg, 54%, 94:6 *e.r.*). The *e.r.* was determined on HPLC system with OJ column (5% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for compound (Fig. S67): t_1 = 12.377 min (major), t_2 = 13.382 min (minor).

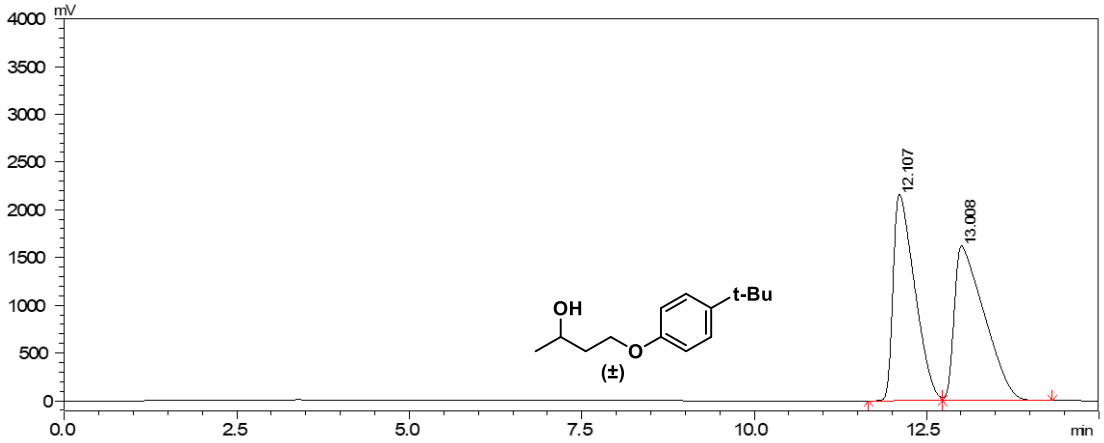


Figure S66. HPLC trace of 4-(4-(tert-butyl)phenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.107	2161789	47049753	48.901
2	13.008	1622788	49164206	51.099
total		3784577	96213959	100.000

Table S25. HPLC trace of 4-(4-(tert-butyl)phenoxy)butan-2-ol.

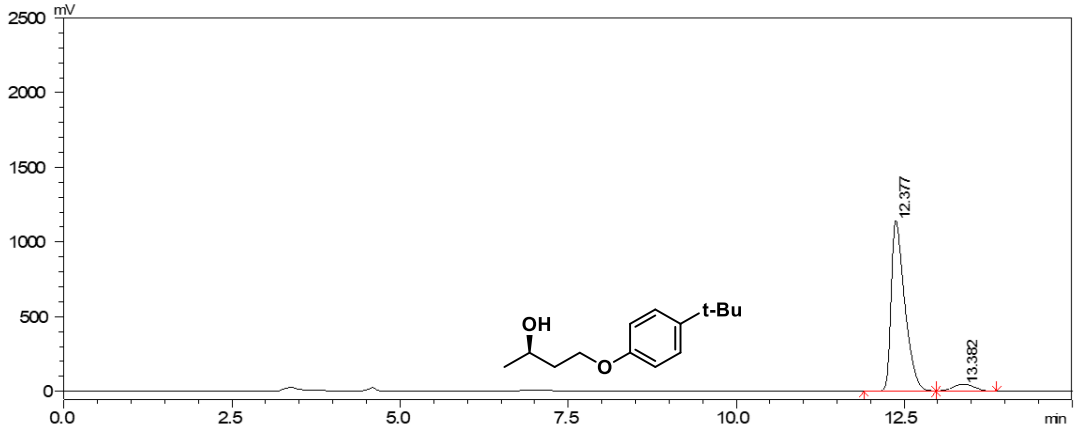
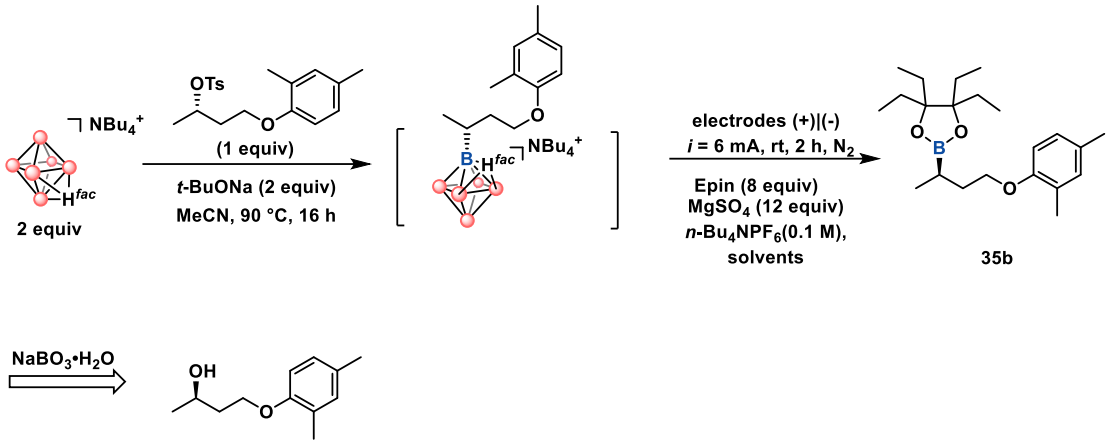


Figure S67. HPLC trace of (*R*)-4-(4-(tert-butyl)phenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.377	1146004	16131538	93.638
2	13.382	47711	1096041	6.362
total		1193715	17227579	100.000

Table S26. HPLC trace of (*R*)-4-(4-(tert-butyl)phenoxy)butan-2-ol.



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (125.1 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (39.6 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of benzyl (*S*)-4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate (69.9 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 90%.

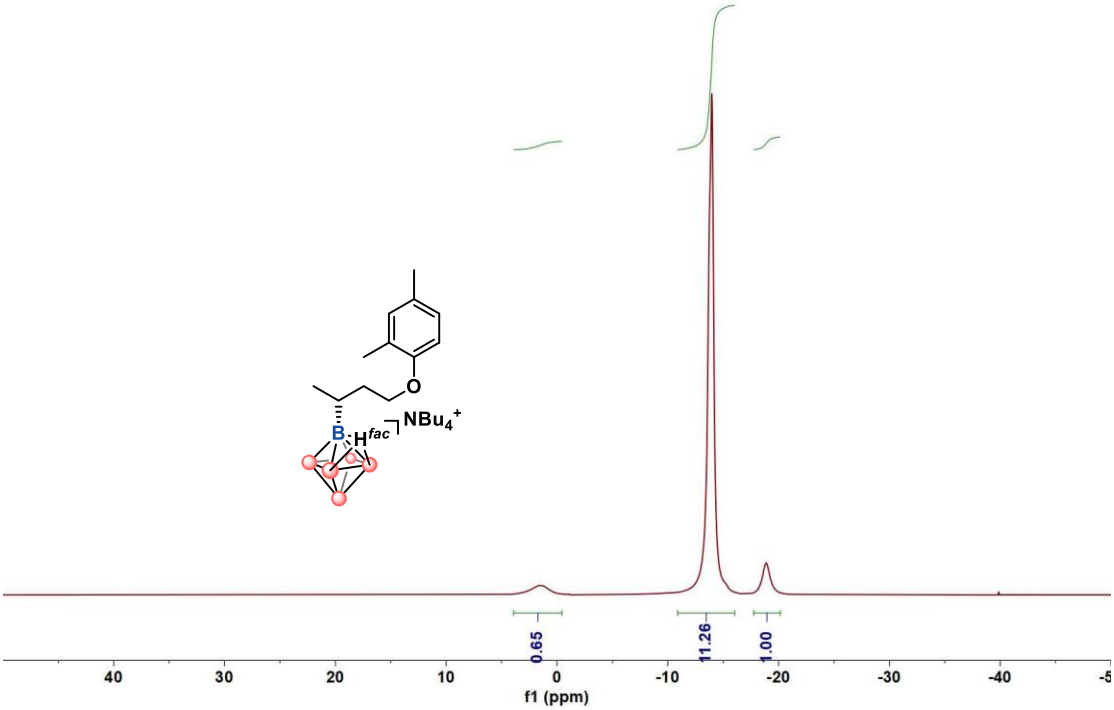
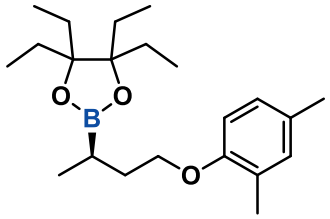


Figure S68. $^{11}B\{^1H\}$ NMR spectrum after substitution step with benzyl (*S*)-4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate.

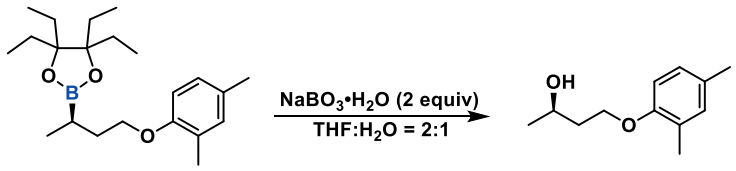
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (278.9 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (289.5 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (117.6 mg, 0.3 mmol, 0.1 M) were added. The cell

was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 100:1) to afford the product (46.0 mg, $[\alpha]_D^{21.7}$ = -3.2 (c = 0.4, $CHCl_3$)) in 63% yield. R_f = 0.75 (Petroleum: EtOAc = 20:1).



35b

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.90 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.01 – 3.94 (m, 2H), 2.25 (s, 3H), 2.19 (s, 3H), 2.00 – 1.95 (m, 1H), 1.78 – 1.74 (m, 1H), 1.70 – 1.59 (m, 8H), 1.28 – 1.24 (m, 1H), 1.05 (d, *J* = 7.5 Hz, 3H), 0.92 – 0.88 (m, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.19, 131.32, 129.05, 126.76, 126.69, 111.23, 87.98, 67.58, 32.59, 26.29, 26.23, 20.42, 16.18, 15.78, 8.79, 8.74.
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.81.
HR-MS (EI) for $C_{22}H_{37}{}^{11}BO_3$ [M] *m/z* $[M]^+$: calculated: 360.2836 found: 360.2834



35b

(*R*)-2-(4-(2,4-dimethylphenoxy)butan-2-yl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (21.8 mg, 0.06 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (13.2 mg, 0.12 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 4:1) afford a colorless oil (9.2 mg, 78%, 94:6 *e.r.*). The *e.r.* was determined on HPLC system with AD column (5% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 °C); retention time for compound (Fig. S70): t_1 = 8.360 min (minor), t_2 = 8.938 min (major).

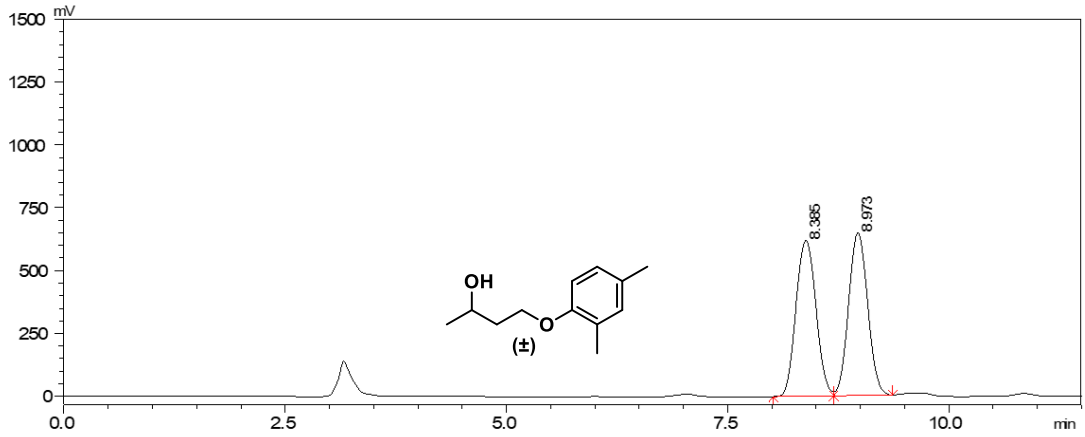


Figure S69. HPLC trace of 4-(2,4-dimethylphenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.385	620118	9754192	50.112
2	8.973	648124	9710696	49.888
total		1268242	19464888	100.000

Table S27. HPLC trace of 4-(2,4-dimethylphenoxy)butan-2-ol.

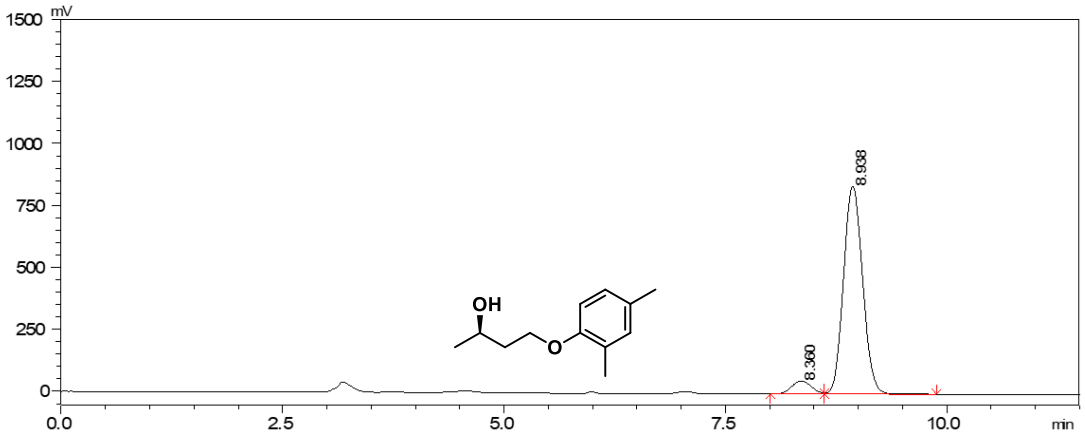
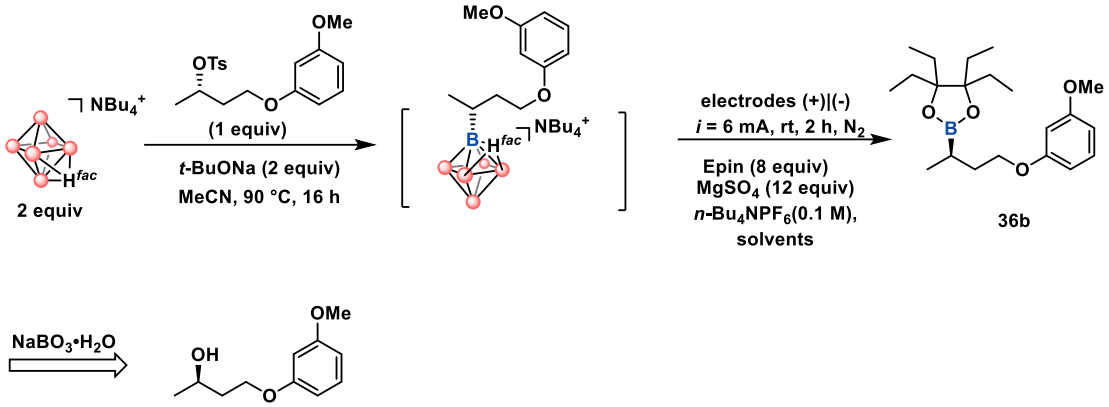


Figure S70. HPLC trace of (*R*)-4-(2,4-dimethylphenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.360	51405	800493	5.979
2	8.938	837283	12587903	94.021
total		888688	13388396	100.000

Table S28. HPLC trace of (*R*)-4-(2,4-dimethylphenoxy)butan-2-ol.



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (120.1 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (39.1 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate (69.8 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 98%.

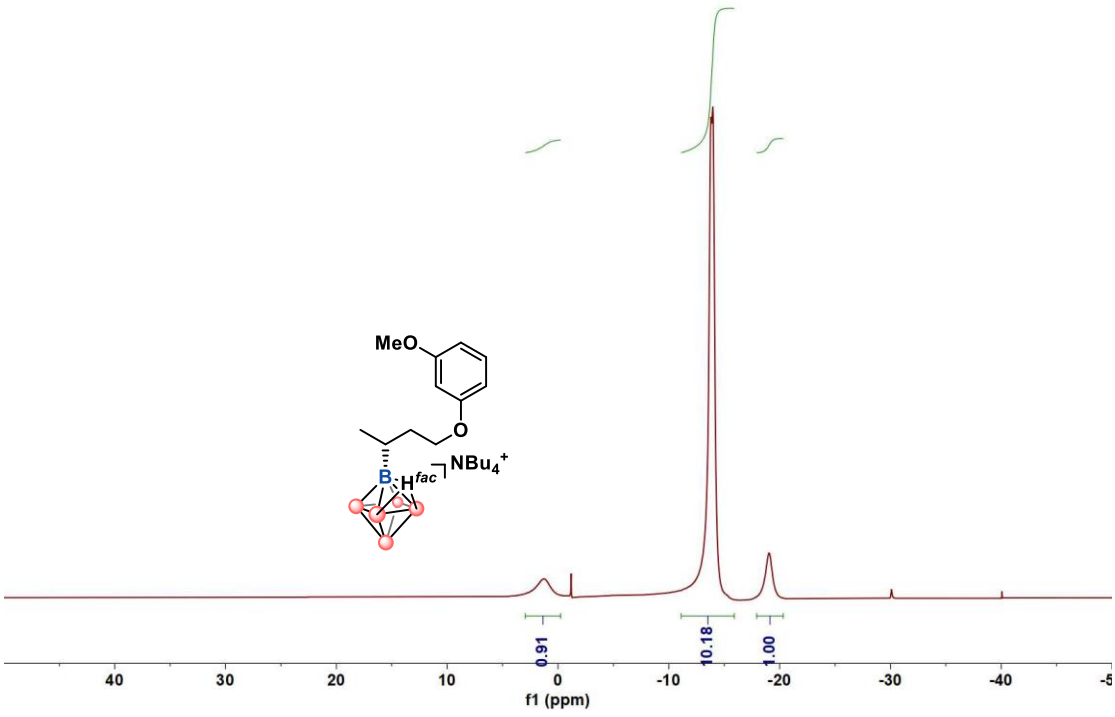
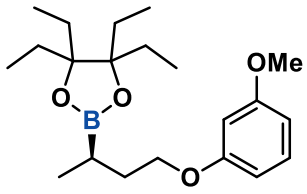


Figure S71. $^{11}B\{^1H\}$ NMR spectrum after substitution step with (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate

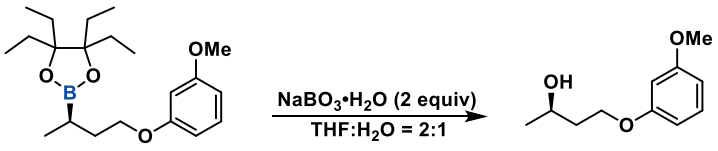
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (276.6 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (289.6 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (121.8 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the

solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the product (48.5 mg, $[\alpha]_D^{22.0}$ = -2.3 (c = 0.4, $CHCl_3$)) in 67% yield. R_f = 0.54 (Petroleum: EtOAc = 20:1).



36b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 6.52 – 6.46 (m, 3H), 4.01 – 3.96 (m, 2H), 3.78 (s, 3H), 1.97 – 1.95 (m, 1H), 1.77 – 1.71(m, 1H), 1.71 – 1.59 (m, 8H), 1.26 – 1.22 (m, 1H), 1.04 (d, *J* = 7.5 Hz, 3H), 0.94 – 0.88 (m, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.74, 160.48, 129.72, 106.69, 106.02, 100.93, 88.02, 67.37, 55.21, 32.47, 26.28, 26.22, 15.77, 8.78, 8.75.
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.74.
HR-MS (EI) for $C_{21}H_{35}{}^{11}BO_4$ [M] *m/z* $[M]^+$: calculated: 362.2628 found: 362.2630



36b

(*R*)-4,4,5,5-tetraethyl-2-(4-(3-methoxyphenoxy)butan-2-yl)-1,3,2-dioxaborolane (48.5 mg, 0.14 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (28.2 mg, 0.28 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 4:1) afforded a colorless oil (17.2 mg, 67%, 93:7 *e.r.*). The *e.r.* was determined on HPLC system with AD column (5% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for compound (Fig. S73): t_1 = 12.964 min (minor), t_2 = 15.152 min (major).

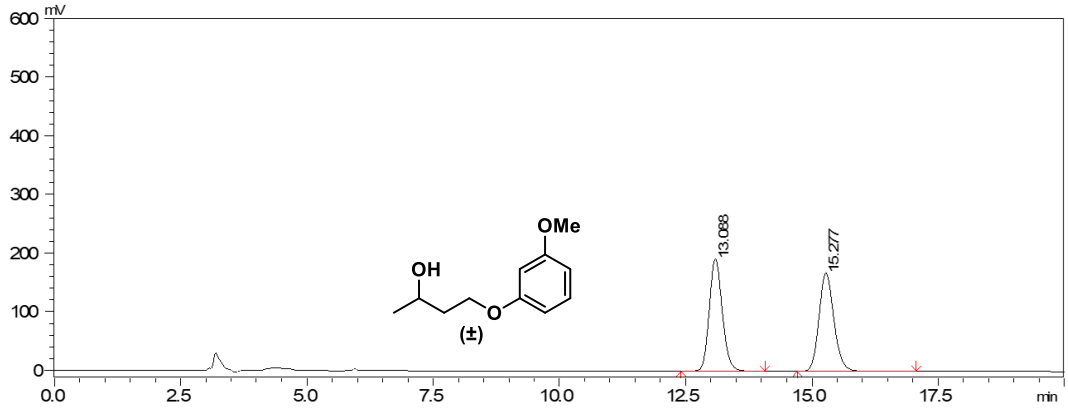


Figure S72. HPLC trace of 4-(3-methoxyphenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	13.088	191291	3450438	49.944
2	15.277	167519	3458219	50.056
total		358811	6908657	100.000

Table S29. HPLC trace of 4-(3-methoxyphenoxy)butan-2-ol.

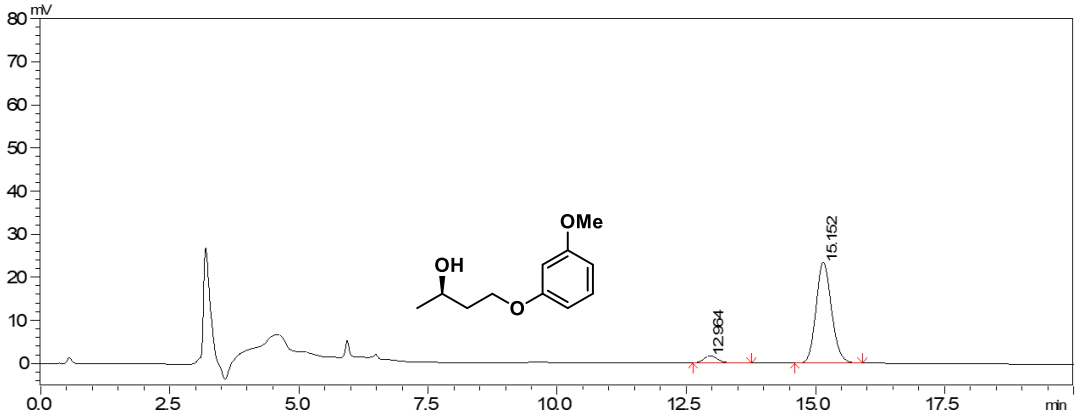
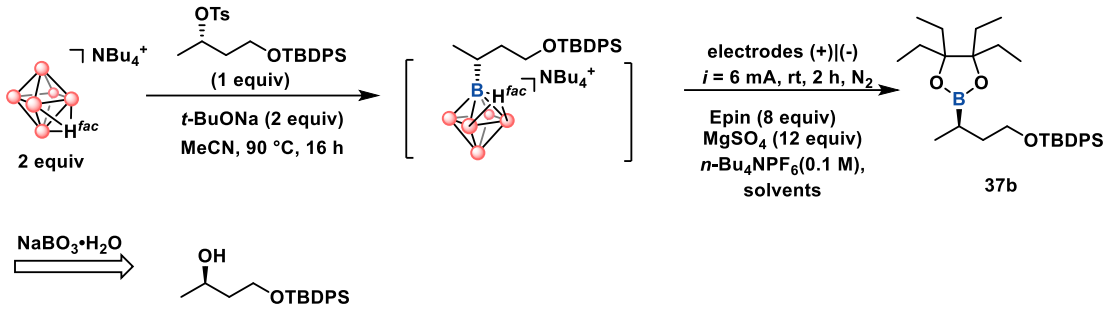


Figure S73. HPLC trace of (*R*)-4-(3-methoxyphenoxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.964	1691	32335	6.202
2	15.152	23455	489055	93.798
total		25146	521390	100.000

Table S30. HPLC trace of (*R*)-4-(3-methoxyphenoxy)butan-2-ol.



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (125.3 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (39.4 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*S*)-4-((tert-butyldiphenylsilyl)oxy)butan-2-yl 4-methylbenzenesulfonate (95.2 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 72%.

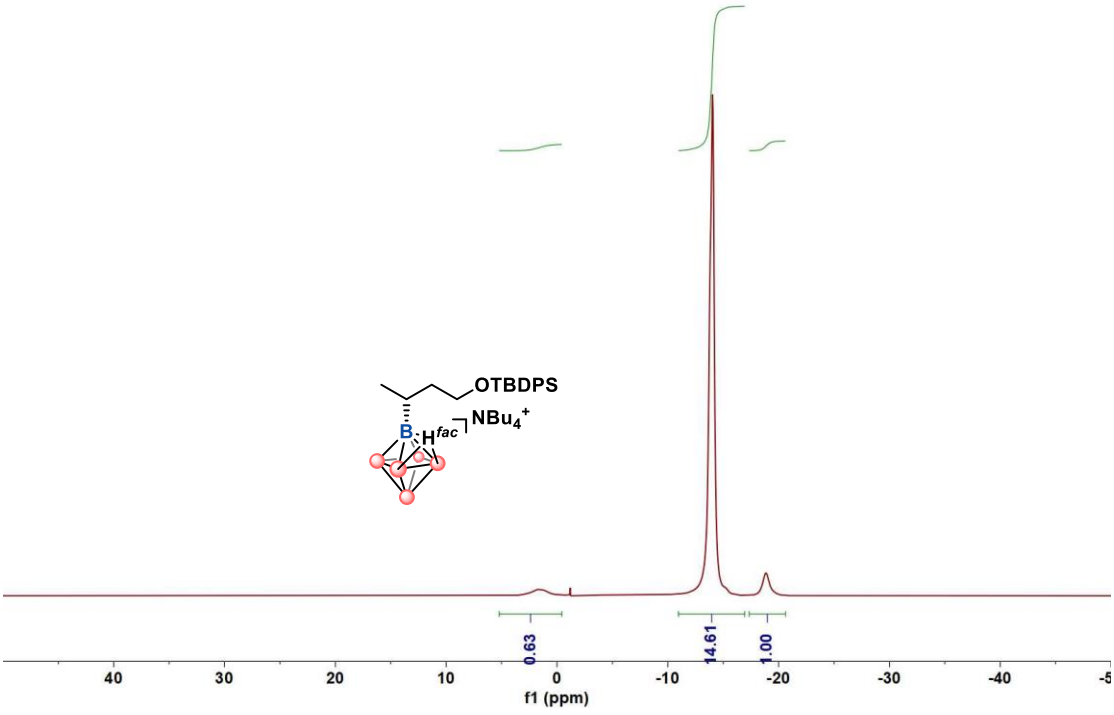
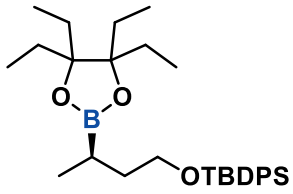


Figure S74. $^{11}B\{^1H\}$ NMR spectrum after substitution step with (*S*)-4-((tert-butyldiphenylsilyl)oxy)butan-2-yl 4-methylbenzenesulfonate

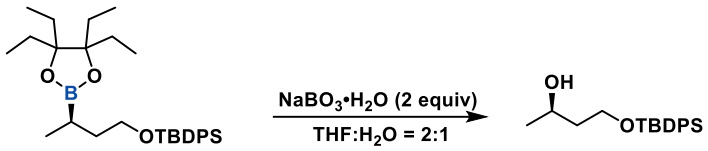
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (278.4 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (294.5 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (127.1 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5

mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the product (47.7 mg, $[\alpha]_D^{22.2}$ = -2.4 (c = 0.4, $CHCl_3$)) in 45% yield. R_f = 0.14(Petroleump: EtOAc = 40:1).



37b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 4H), 7.43 – 7.34 (m, 6H), 3.72 – 3.67 (m, 2H), 1.82 – 1.78 (m, 1H), 1.63 – 1.52 (m, 9H), 1.20 – 1.14 (m, 1H), 1.04 (s, 9H), 0.95 (d, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.55, 134.30, 129.37, 127.50, 87.78, 63.38, 35.97, 29.70, 26.87, 26.26, 26.20, 19.21, 15.73, 8.77, 8.71.
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.83.
HR-MS (EI) for $C_{28}H_{42}{}^{11}BO_3Si$ [M] *m/z* $[M\text{-}CH_2CH_3]^+$: calculated: 465.2996, found: 465.2992



37b

(*R*)-tert-butyldiphenyl(3-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane (47.7 mg, 0.1 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (21.1 mg, 0.2 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 8:1) afforded a colorless oil (13.5 mg, 43%, 92:8 *e.r.*). The *e.r.* was determined on HPLC system with IB column (1% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for compound (Fig. S76): t_1 = 7.267 min (minor), t_2 = 9.600 min (major).

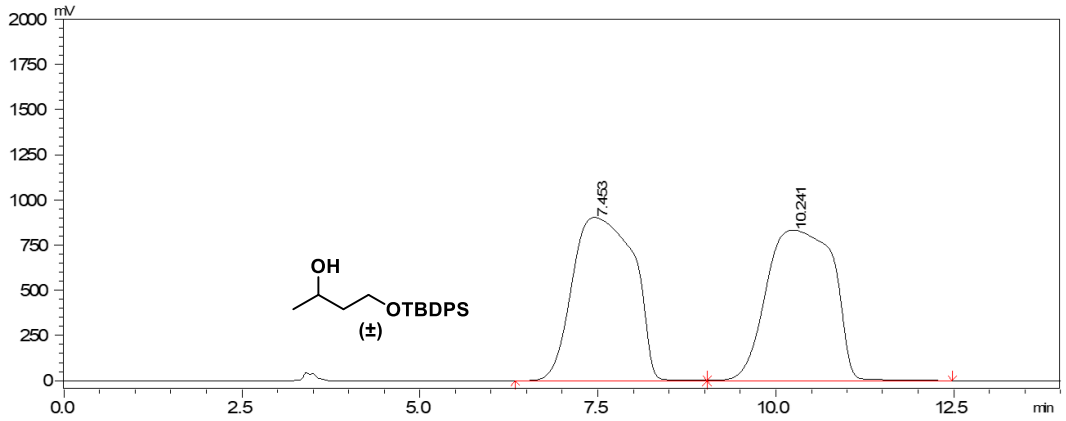


Figure S75. HPLC trace of 4-((tert-butyldiphenylsilyl)oxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.453	903338	54406623	49.765
2	10.241	833728	54920967	50.235
total		1737066	109327590	100.000

Table S31. HPLC trace of 4-((tert-butyldiphenylsilyl)oxy)butan-2-ol.

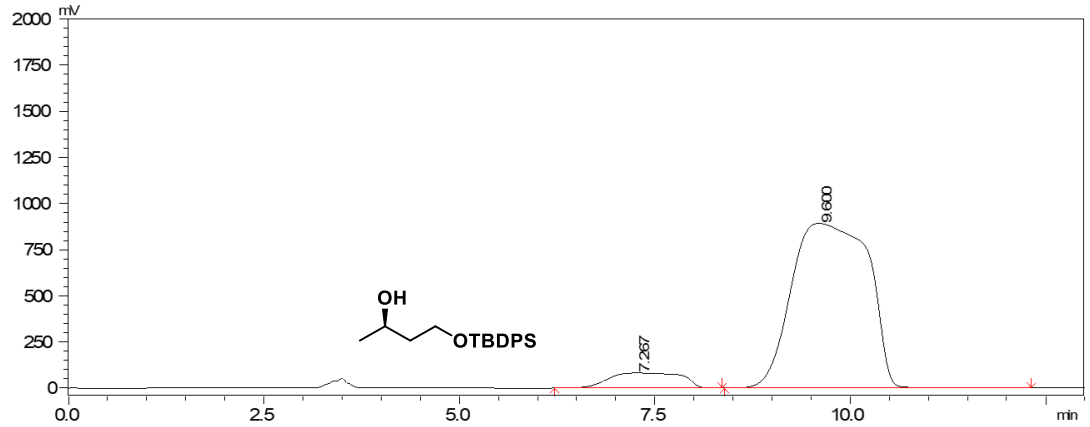
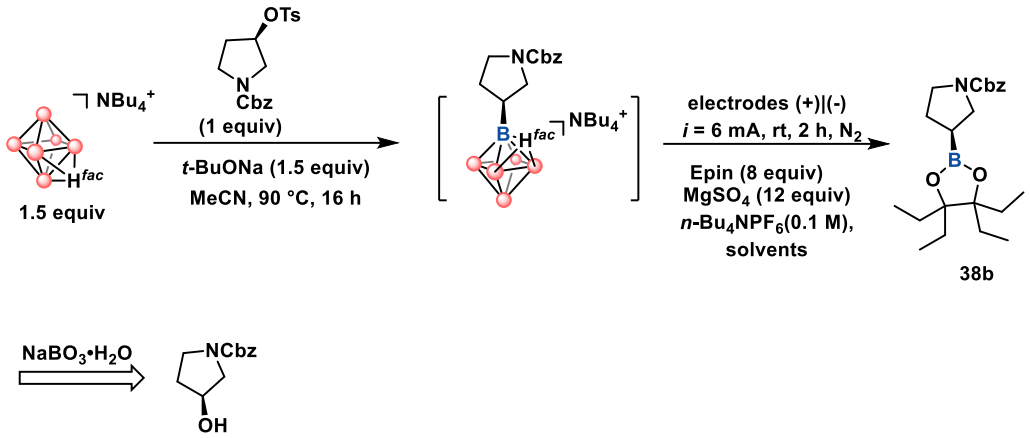


Figure S76. HPLC trace of (*R*)-4-((tert-butyldiphenylsilyl)oxy)butan-2-ol.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.267	81614	5311046	7.983
2	9.600	892271	61222397	92.017
total		973884	66533442	100.000

Table S32. HPLC trace of (*R*)-4-((tert-butyldiphenylsilyl)oxy)butan-2-ol.



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (92.6 mg, 0.3 mmol, 1.5 equiv), and *t*-BuONa (29.5 mg, 0.3 mmol, 1.5 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of benzyl (*R*)-3-(tosyloxy)pyrrolidine-1-carboxylate (75.3 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined as 76%.

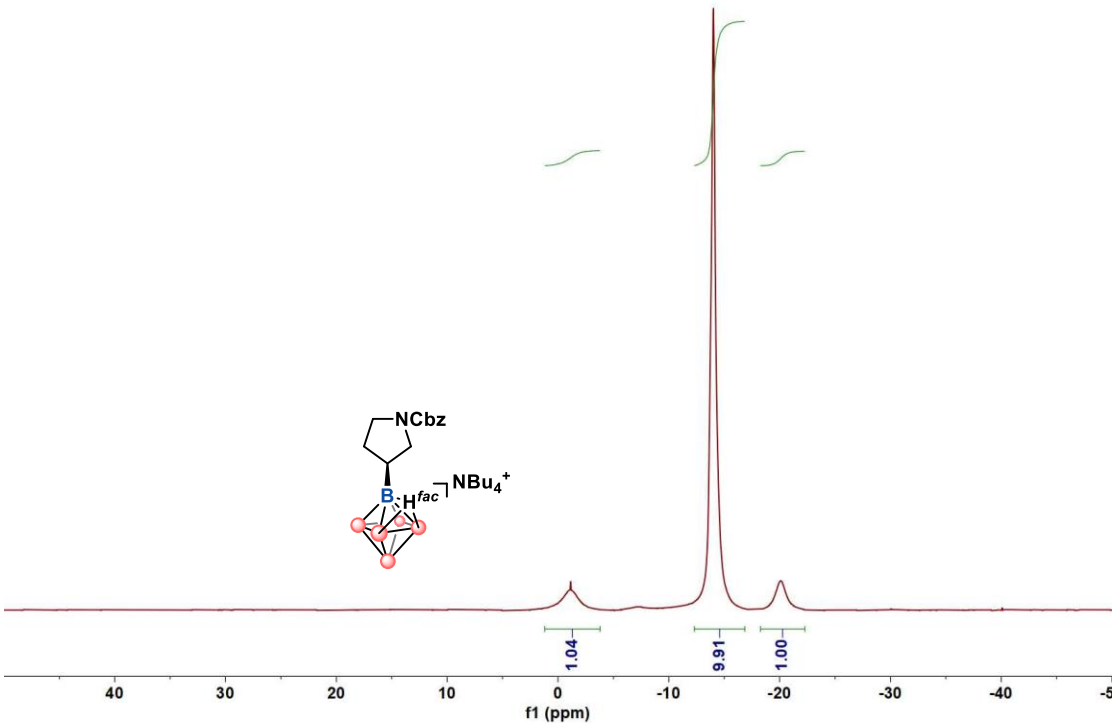
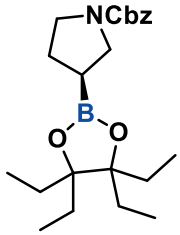


Figure S77. $^{11}B\{^1H\}$ NMR spectrum after substitution step with benzyl (*R*)-3-(tosyloxy)pyrrolidine-1-carboxylate.

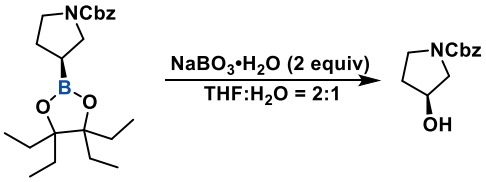
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (279.5 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (287.3 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (115.8 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated

and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: EtOAc= 15:1) to afford the product (46.9 mg, $[\alpha]_D^{21.4}$ = - 3.5 (c = 0.4, $CHCl_3$)) in 60% yield. R_f = 0.29 (Petroleum: EtOAc = 8:1).



38b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.17 – 5.09 (m, 2H), 3.63 – 3.52 (m, 2H), 3.35 – 3.25 (m, 2H), 2.04 – 1.98 (m, 1H), 1.83 – 1.80 (m, 1H), 1.69 – 1.57 (m, 9H), 0.89 (t, *J* = 7.5 Hz, 12H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.66, 137.21, 128.39, 127.77, 88.50, 66.51, 48.66, 47.09, 28.51, 26.37, 26.35, 8.75, 8.73.
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 32.88.
HR-MS (EI) for $C_{22}H_{34}{}^{11}BNO_4$ [M] *m/z* $[M]^+$: calculated: 387.2581 found: 387.2584



38b

Benzyl (*S*)-3-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (38.7 mg, 0.1 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$•H_2O (21.2 mg, 0.2 mmol) and H_2O (0.5 mL) were added and the mixture was stirred at room temperature for 4 hours. Upon complete consumption of the substrate, the mixture was extracted with Et_2O (3 mL×3) and dried over Na_2SO_4. Column separation (silica gel, Petroleum: EtOAc = 2:1) afforded a colorless oil (10.6 mg, 48%, 94:6 *e.r.*). The *e.r.* was determined on HPLC system with IF column (20% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 25 ºC); retention time for compound (Fig. S79): t_1 = 7.709 min (minor), t_2 = 9.066 min (major).

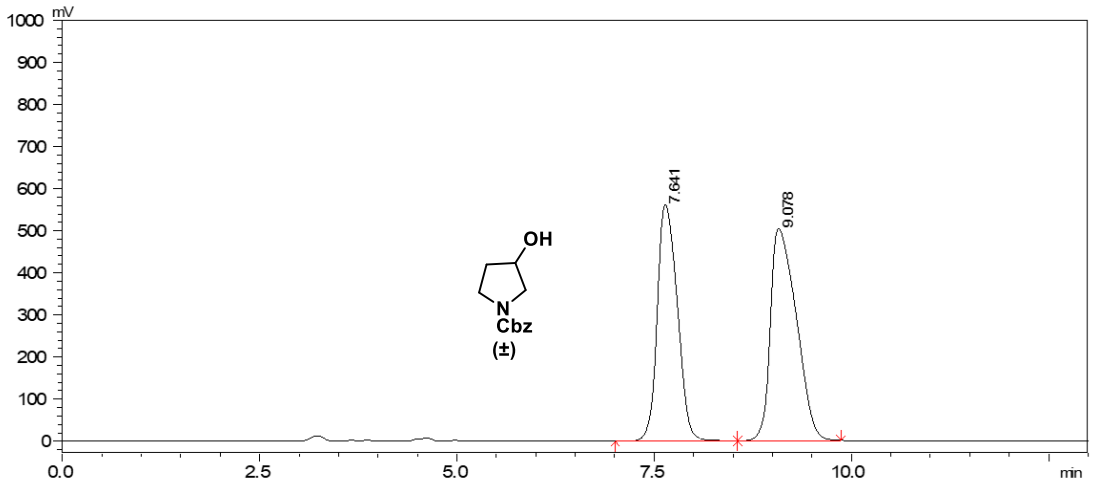


Figure S78. HPLC trace of benzyl 3-hydroxypyrrolidine-1-carboxylate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.641	562125	9955785	46.348
2	9.078	504502	11524549	53.652
total		1066627	21480334	100.000

Table S33. HPLC trace of benzyl 3-hydroxypyrrolidine-1-carboxylate.

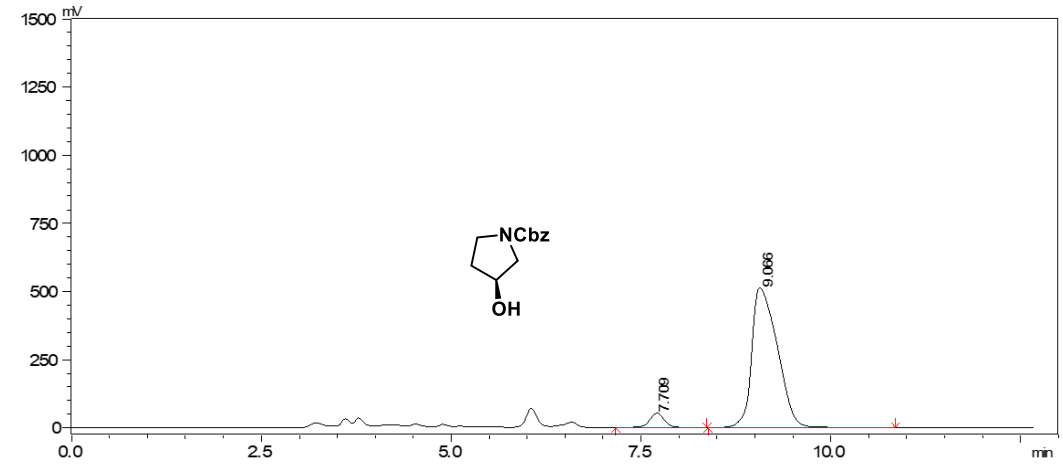
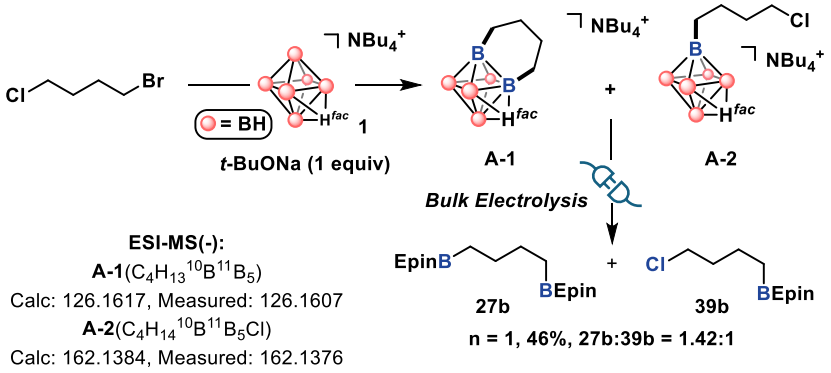


Figure S79. HPLC trace of benzyl (*S*)-3-hydroxypyrrolidine-1-carboxylate.

#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.709	52830	705793	5.544
2	9.066	513769	12024251	94.456
total		566599	12730044	100.000

Table S34. HPLC trace of benzyl (*S*)-3-hydroxypyrrolidine-1-carboxylate.

9. Intramolecular nucleophilic borylation of unactivated alkyl chloride



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (123.7 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (19.6 mg, 0.2 mmol, 1 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of 1-bromo-4-chlorobutane (37.3 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 100 ºC for 12 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined.

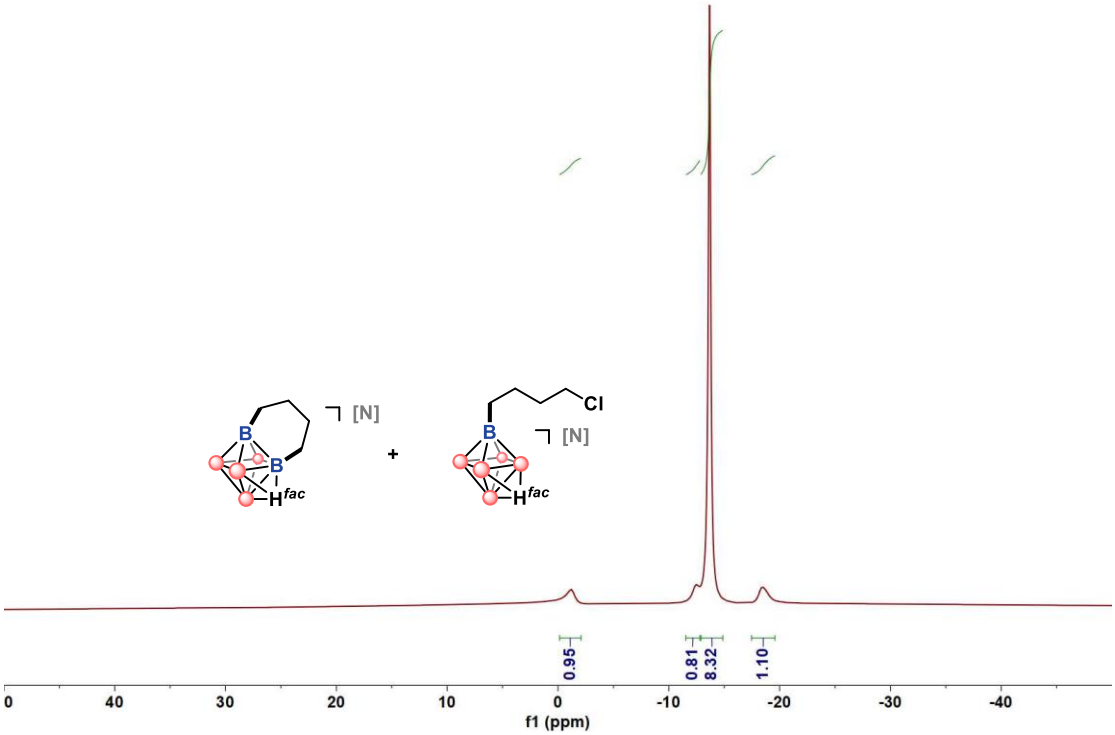


Figure S80. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 1-bromo-4-chlorobutane

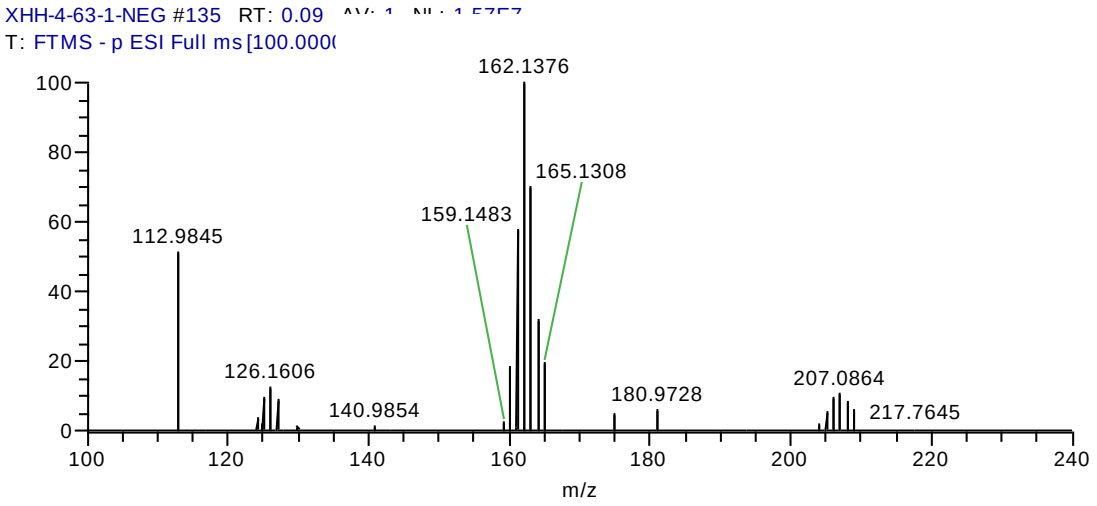
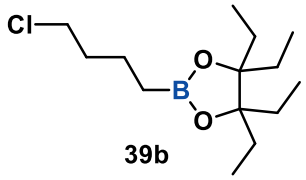


Figure S81. ESI-MS(-) of reaction mixture containing **A-1** and **A-2**.

Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (280.1 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (289.4 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (120.6 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL).

The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the 2-(4-chlorobutyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (11.1 mg) in 19% yield and 1,4-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)butane (24.6 mg) in 27% yield.



39b

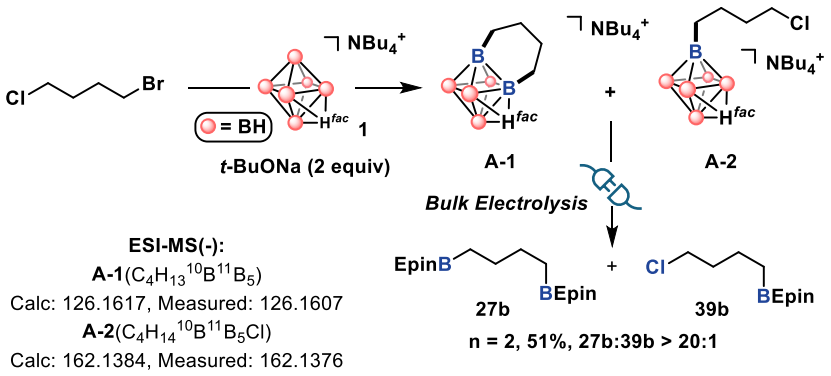
2-(4-chlorobutyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (t, *J* = 6.8 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.70 – 1.61 (m, 8H), 1.58 – 1.51 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 12H), 0.80 (t, *J* = 7.9 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 88.05, 44.95, 35.11, 26.35, 21.57, 8.78.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.35.

HR-MS (EI) for $C_{14}H_{28}{}^{11}BO_2Cl$ [M] *m/z* $[M]^+$: calculated: 274.1871, found: 274.1873



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (122.2 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (39.8 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of 1-Bromo-4-chlorobutane (37.3 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 100 ºC for 12 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3), from ^{11}B NMR the conversion could be determined.

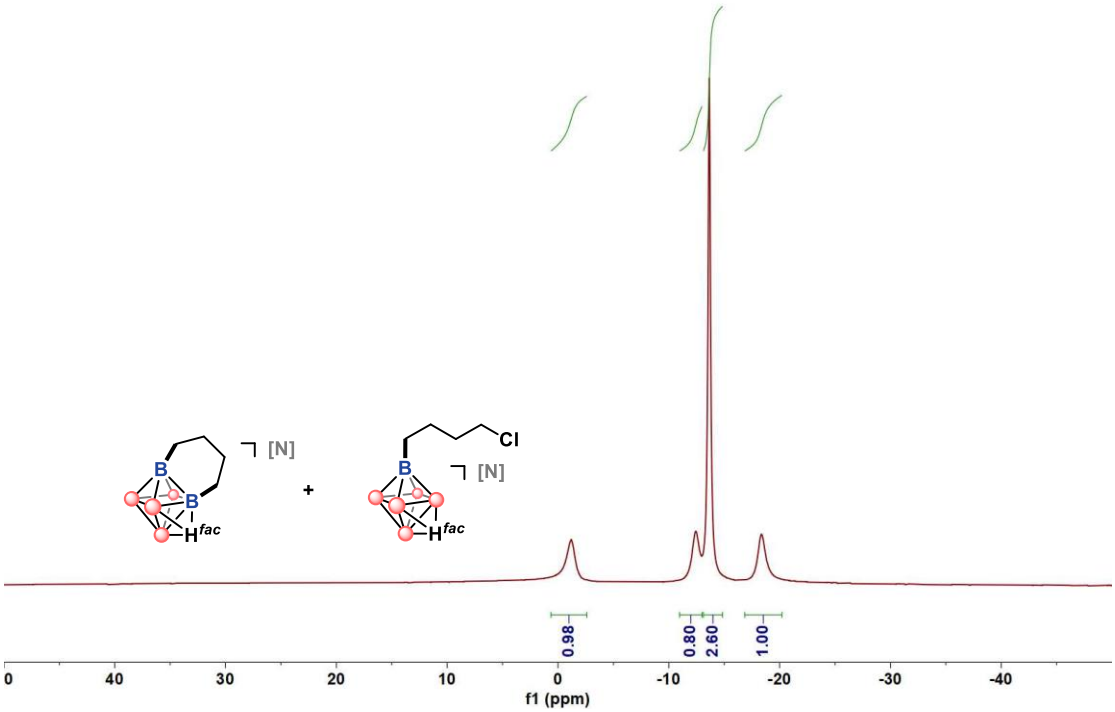


Figure S82. $^{11}B\{^1H\}$ NMR spectrum after substitution step with 1-bromo-4-chlorobutane

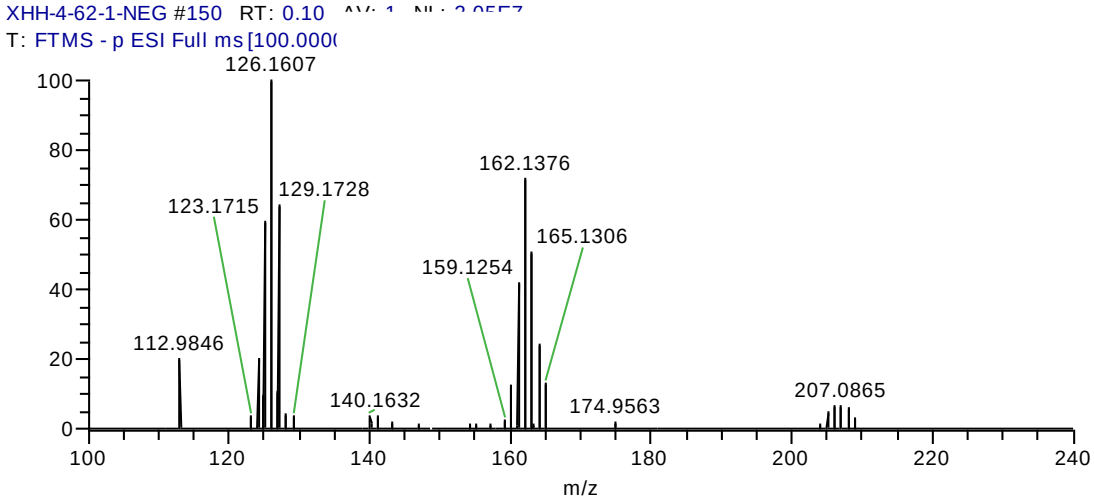
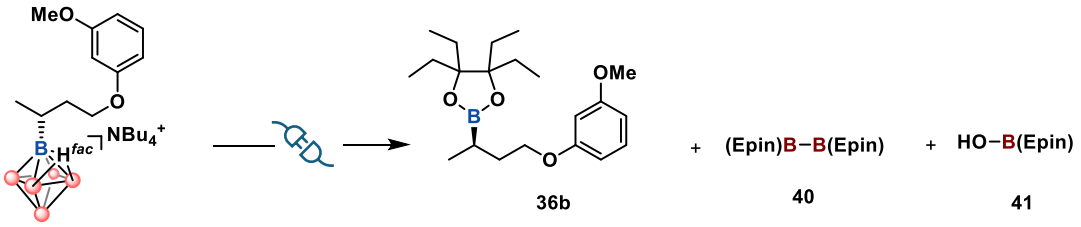


Figure S83. ESI-MS(-) of reaction mixture containing.

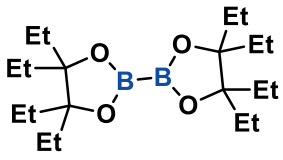
Electrolysis set up 1 is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (281.7 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (290.2 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (115.8 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1) to afford the 1,4-bis(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)butane (46.8mg) in 51% yield.

10. Investigations of the boron-containing fragments after the bulk electrolysis.



To a 10 mL oven dried Schlenk tube equipped with a magnetic stir bar, *n*-$Bu_4N(B_6H_7)$ (**1**) (120.1 mg, 0.4 mmol, 2 equiv), and *t*-BuONa (39.1 mg, 0.4 mmol, 2 equiv) were added sequentially. The tube was evacuated and backfilled with N_2 three times. Dry MeCN (1 mL) was added via syringe. Then the solution of (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate (69.8 mg, 0.2 mmol, 1 equiv) in dry MeCN (1 mL) was added. The mixture was then magnetically stirred while being heated in oil bath 90 ºC for 16 hours. Then the heating bath was removed and flask was cooled down to room temperature. The solvent was removed *in vacuo* and resulting oil was washed with hexane (3 mL×3).

Electrolysis set up 1(IKA ElectraSyn 2.0) is used. To a 5 mL electrochemical reaction cell equipped with a magnetic stir bar, 3,4-Diethyl-3,4-hexanediol (276.6 mg, 1.6 mmol, 8 equiv), $MgSO_4$ (289.6 mg, 2.4 mmol, 12 equiv), and $TBAPF_6$ (121.8 mg, 0.3 mmol, 0.1 M) were added. The cell was evacuated and backfilled with N_2 three times. Dry MeCN (1.5 mL) was added. Then the solution of the crude product of the substituted cluster in dry TCE (1.5 mL) was added. The undivided cell was equipped with RVC (3.5 mm×0.5 mm×0.4 mm) as the anode and RVC (3.5 mm×0.5 mm×0.4 mm) as the cathode and then backfilled with N_2 to replace air atmosphere. The mixture was pre-stirred for five minutes, and then the reaction mixture was electrolyzed at a constant current of 6 mA until passing 2.20 F/mol of total charge (2 hours) at room temperature. The solvent was removed under reduced pressure and the residual solids were extracted with ethyl acetate (10 mL). The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1 - Petroleum: EtOAc = 8:1) to afford the product (48.5 mg) in 67% yield, 4,4,4',4',5,5,5',5'-octaethyl-2,2'-bi(1,3,2-dioxaborolane) (6.2 mg) in 3% yield and 4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-ol (142.2 mg) in 71% yield.



40

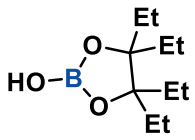
4,4,4',4',5,5,5',5'-octaethyl-2,2'-bi(1,3,2-dioxaborolane)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.59 (m, 16H), 0.90 (t, *J* = 7.5 Hz, 24H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 88.31, 26.39, 8.95.

$^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ 29.61.

HR-MS (EI) for $C_{20}H_{40}{}^{11}B_2O_4$ [M] *m/z* $[M]^+$: calculated: 366.3113, found: 366.3112



41

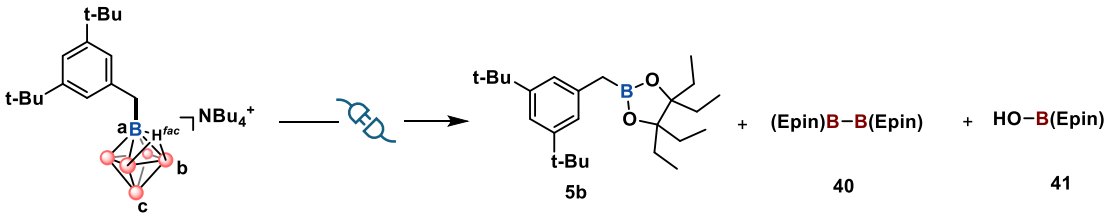
4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (s, 1H), 1.76 – 1.65 (m, 8H), 0.91 (t, *J* = 7.5 Hz, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 88.34, 26.21, 8.55.

^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 22.00.

HR-MS (EI) for $C_{20}H_{40}{}^{11}B_2O_5$ [M] *m/z* [(Epin)B-O-B(Epin)]$^{+}$: calculated: 382.3062, found: 382.3059



5b 40 41

Method E are applied. The extract was concentrated and subjected to column separation (silica gel, Petroleum: Diethyl ether= 80:1 - Petroleum: EtOAc = 8:1) to afford the product (49.0 mg) in 63% yield, 4,4,4',4',5,5,5',5'-octaethyl-2,2'-bi(1,3,2-dioxaborolane) (13.6 mg) in 7% yield and 4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-ol (101.8 mg) in 51% yield.

11. References and notes

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12. NMR spectra of chiral alkyl pseudohalides

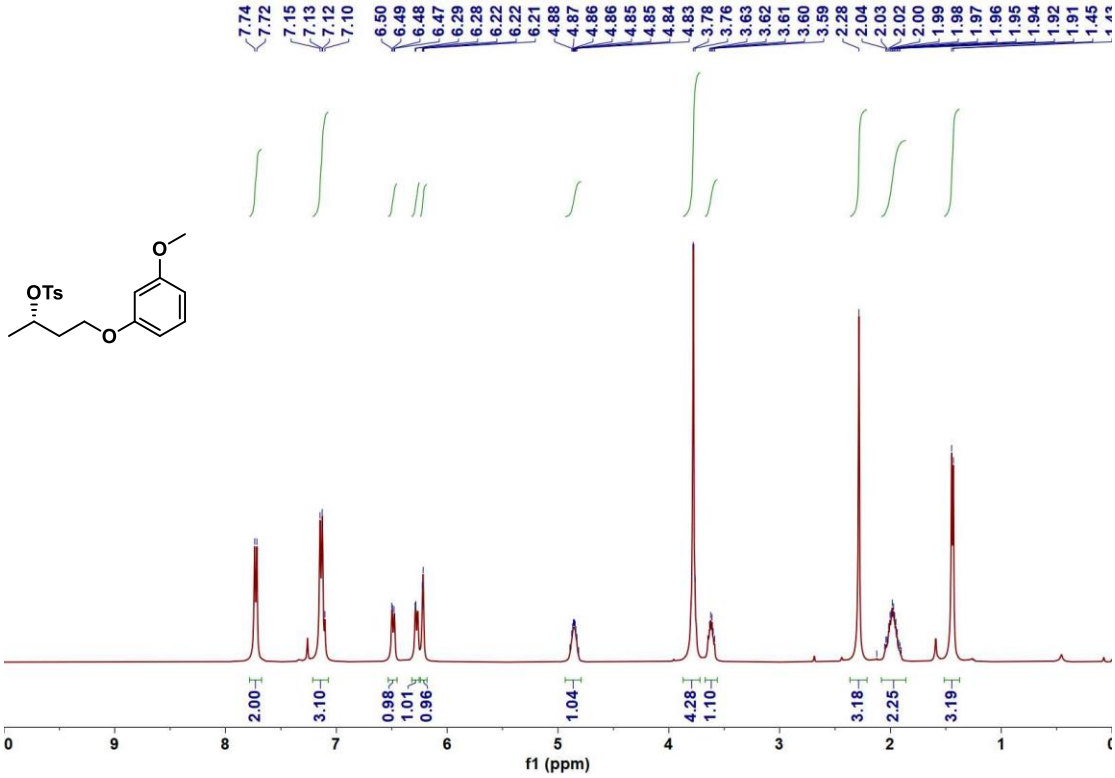


Figure S84. ^{1}H NMR spectrum of (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

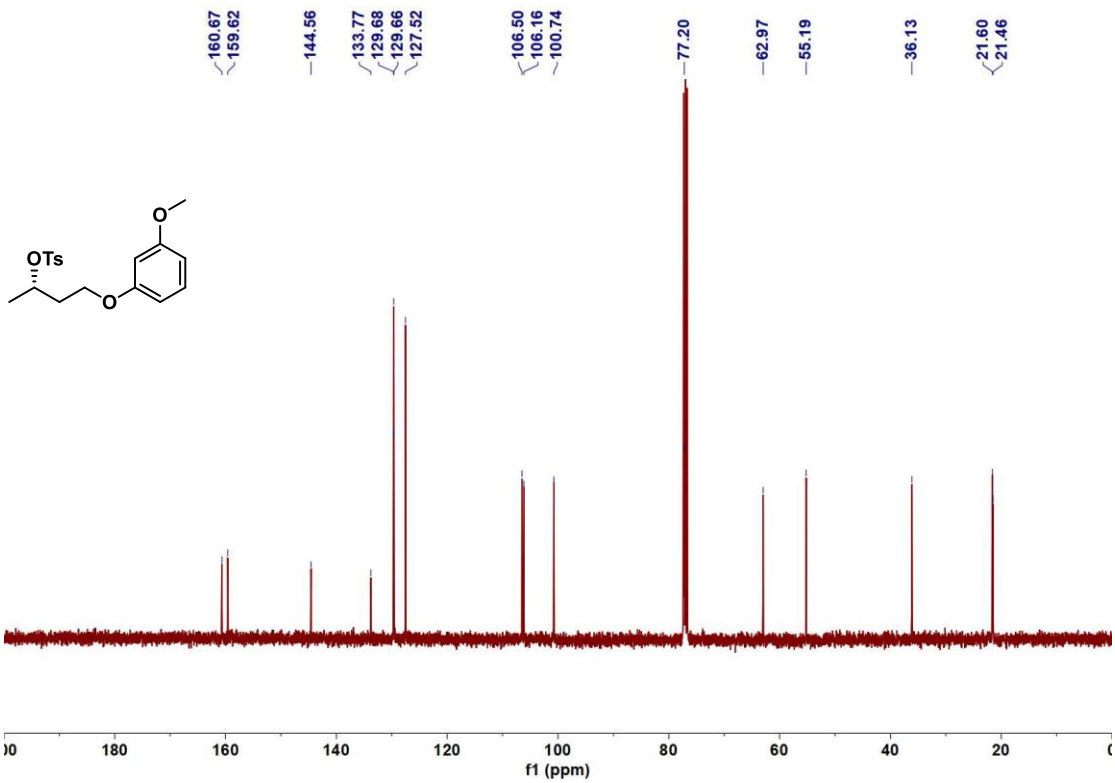


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of (*S*)-4-(3-methoxyphenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

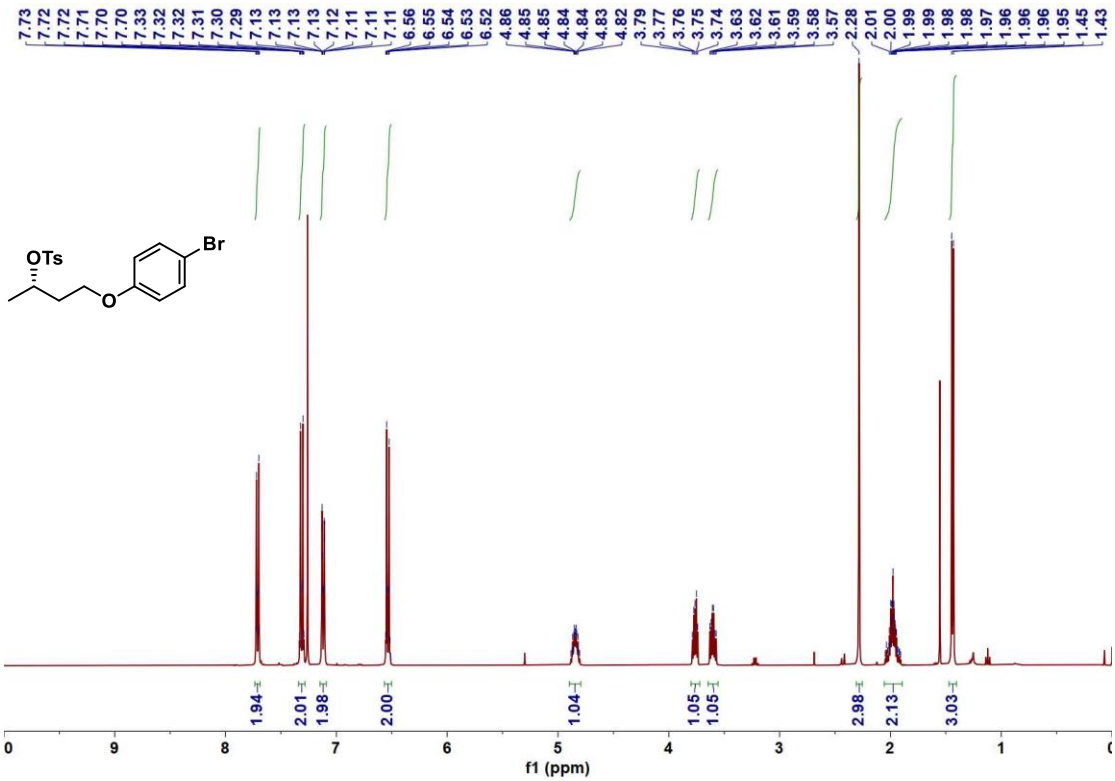


Figure S86. ^{1}H NMR spectrum of (*S*)-4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

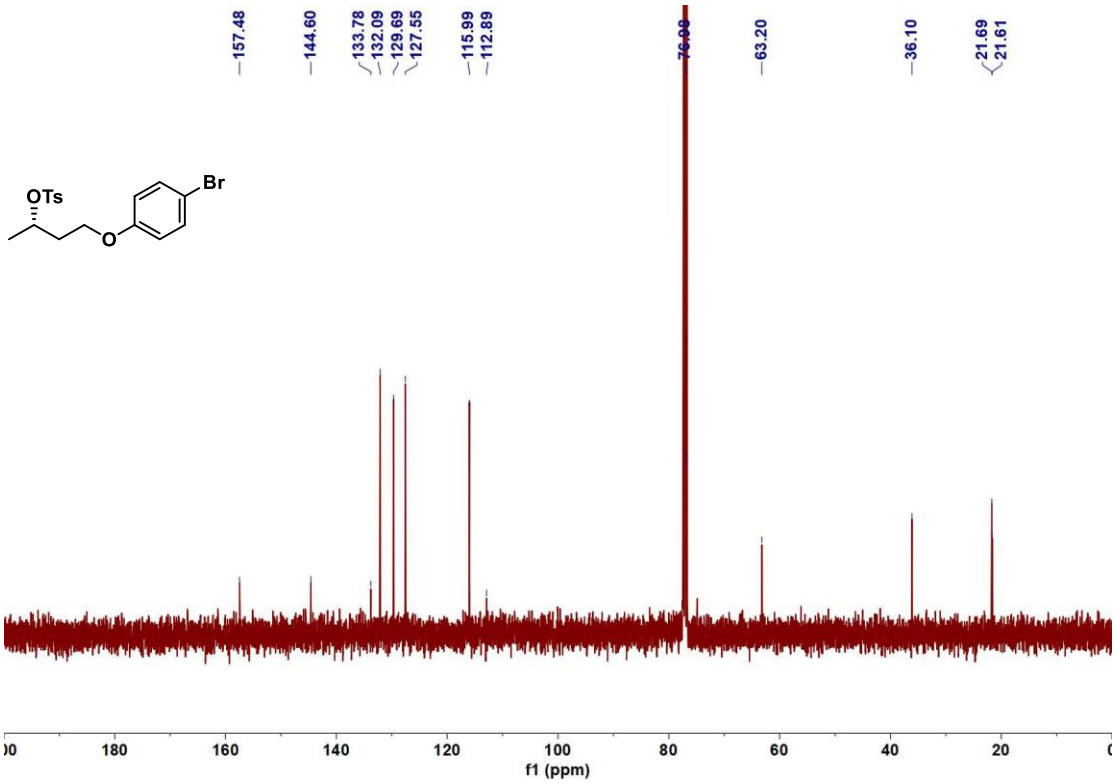


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum of (*S*)-4-(4-bromophenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

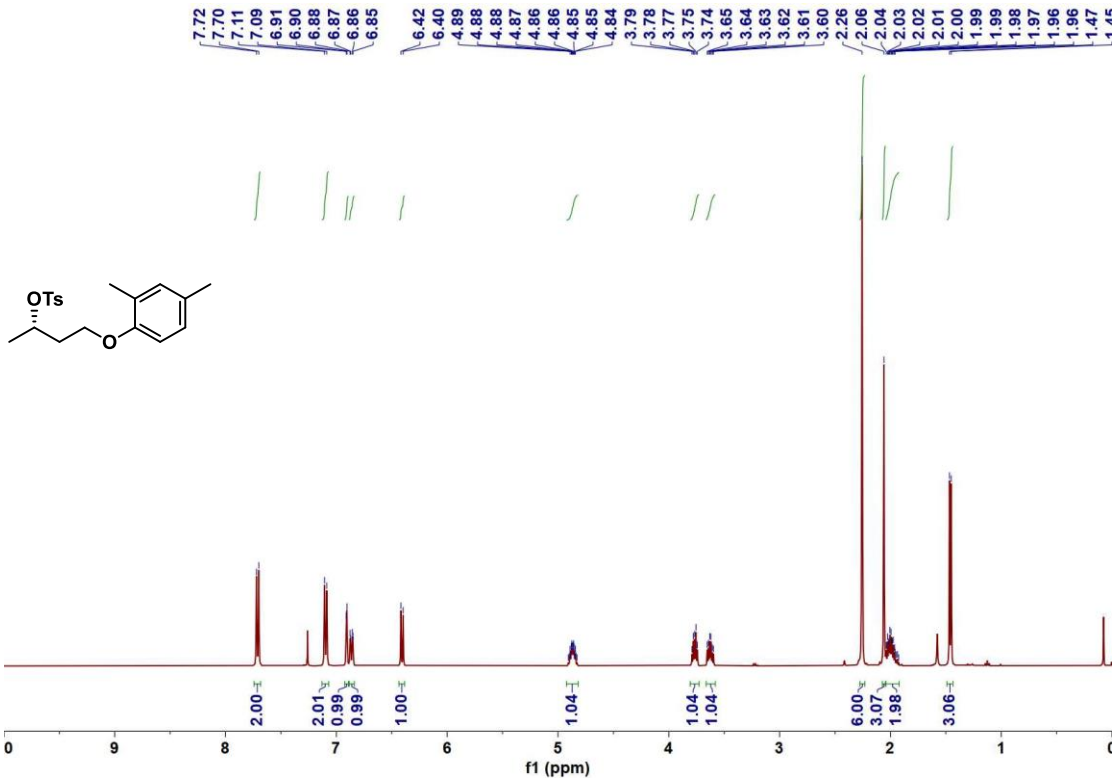


Figure S88. ^{1}H NMR spectrum of (*S*)-4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

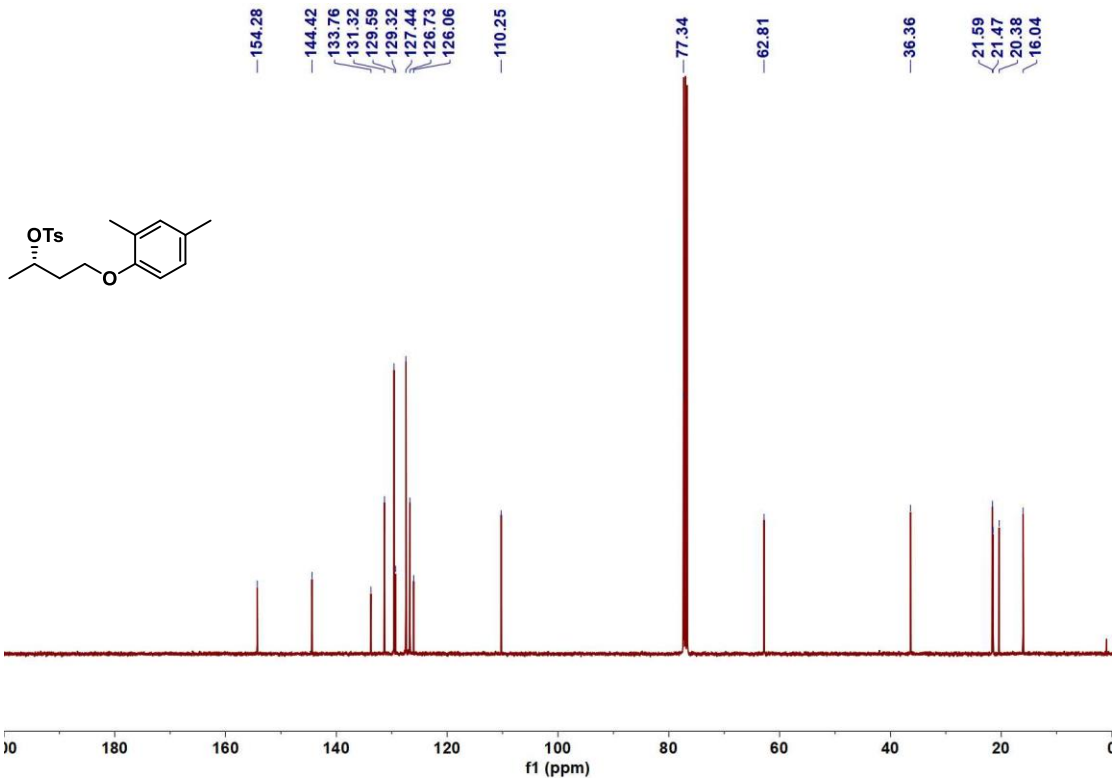


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of (*S*)-4-(2,4-dimethylphenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

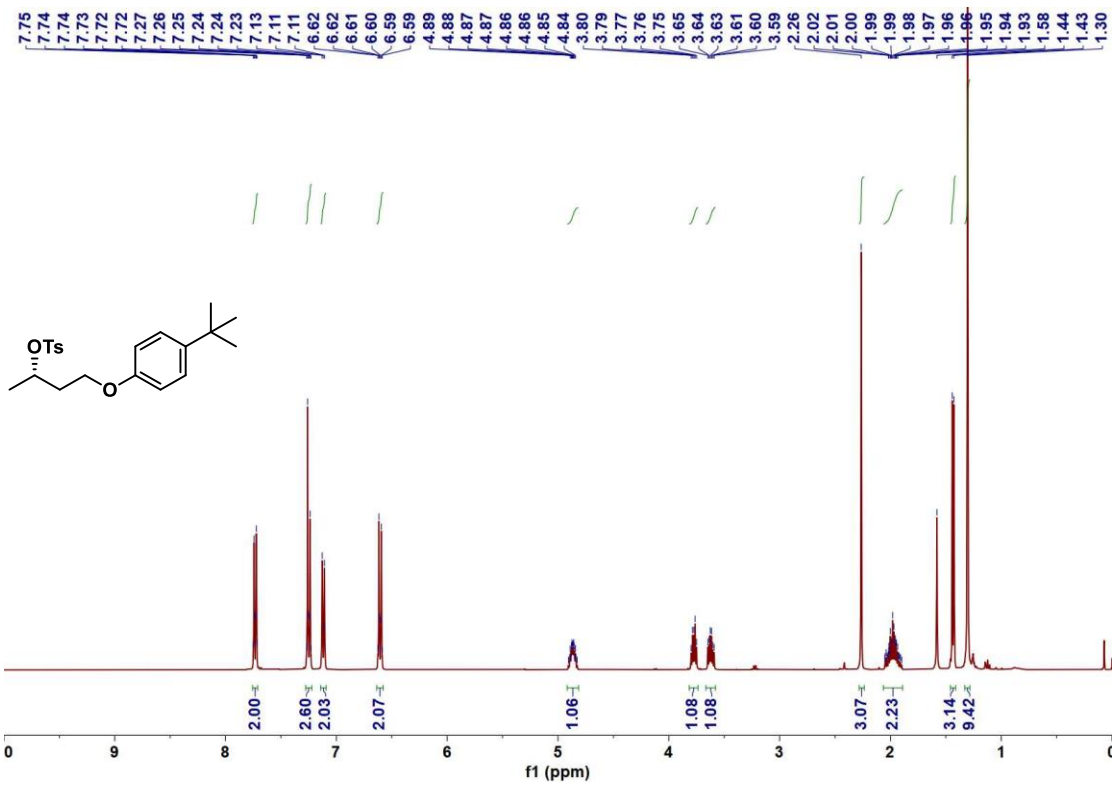


Figure S90. ^{1}H NMR spectrum of (*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

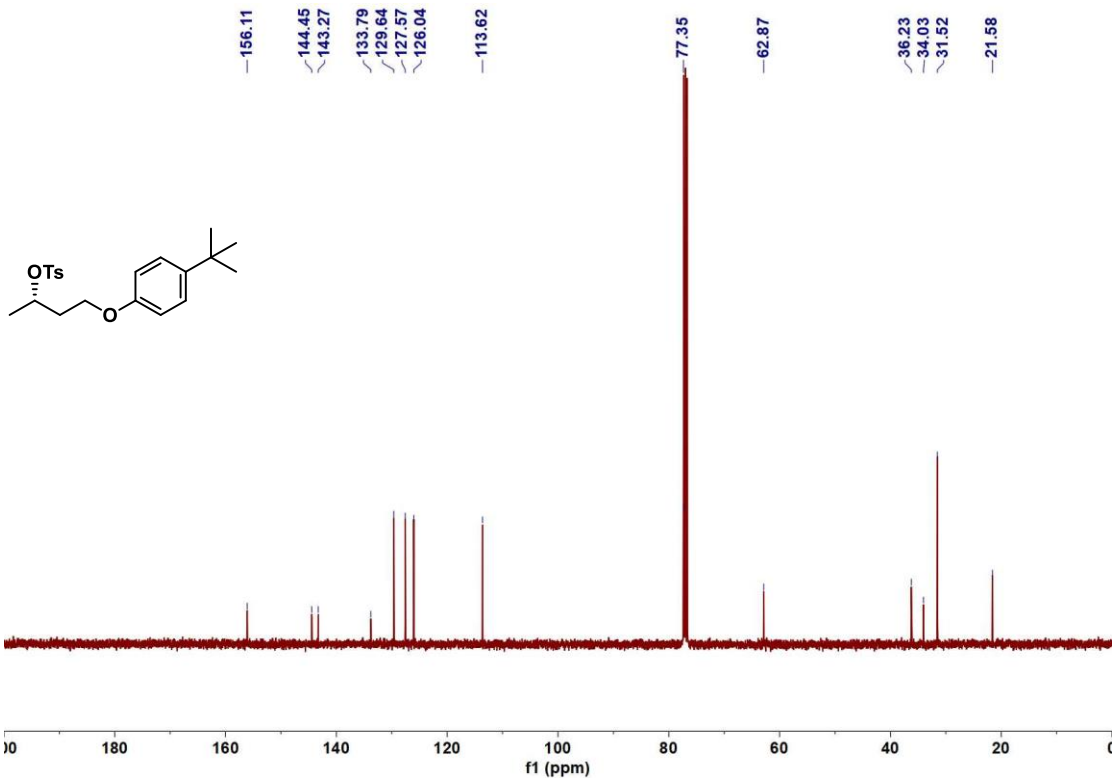


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of (*S*)-4-(4-(tert-butyl)phenoxy)butan-2-yl 4-methylbenzenesulfonate in $CDCl_3$ at 298K

13. NMR spectra of borylation products

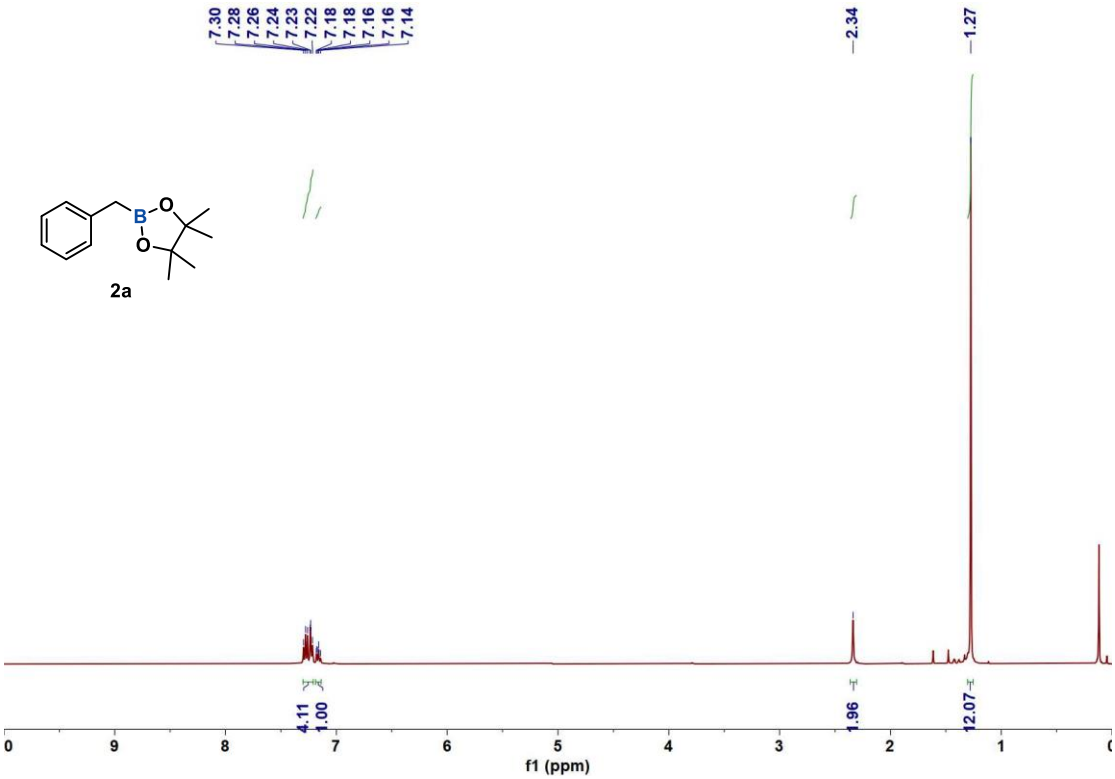


Figure S92. ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 298K

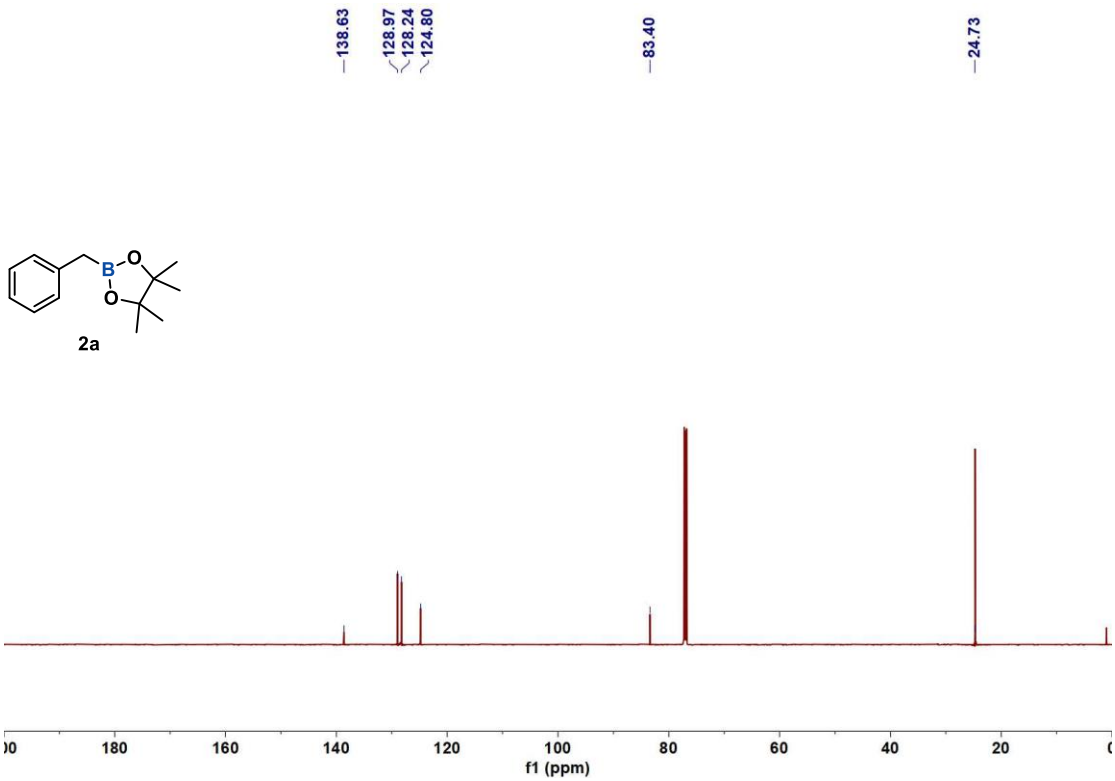


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$ at 298K

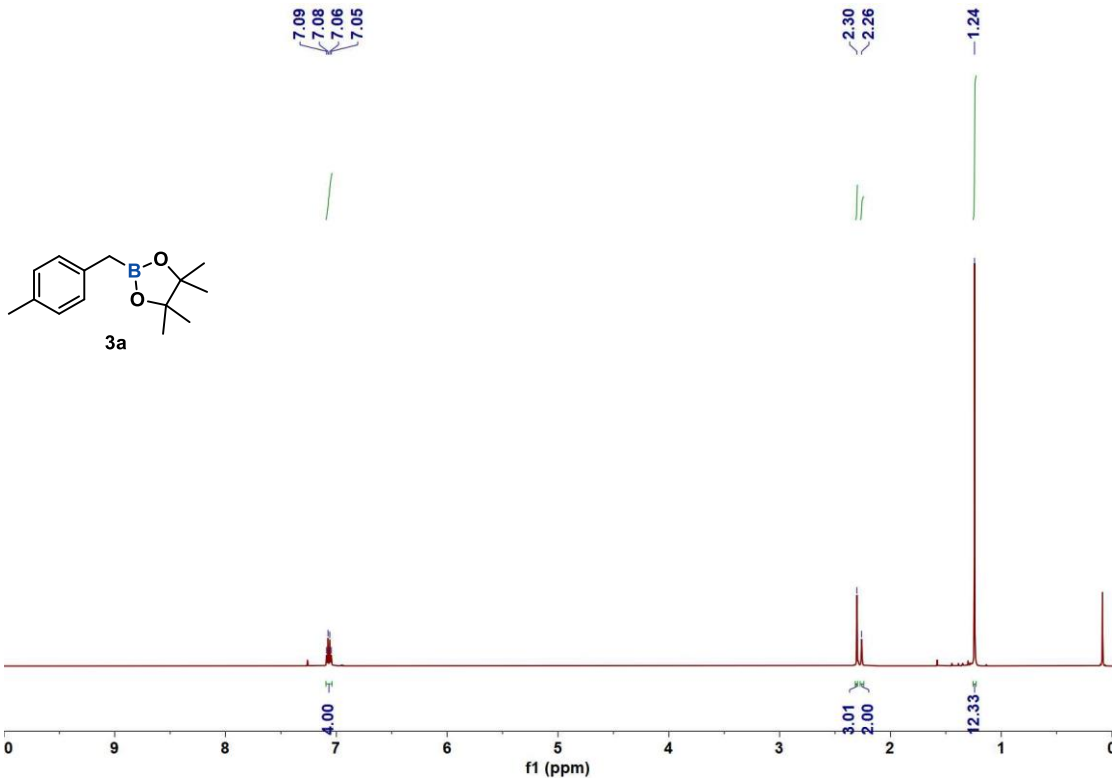


Figure S94. ^{1}H NMR spectrum of **3a** in $CDCl_3$ at 298K

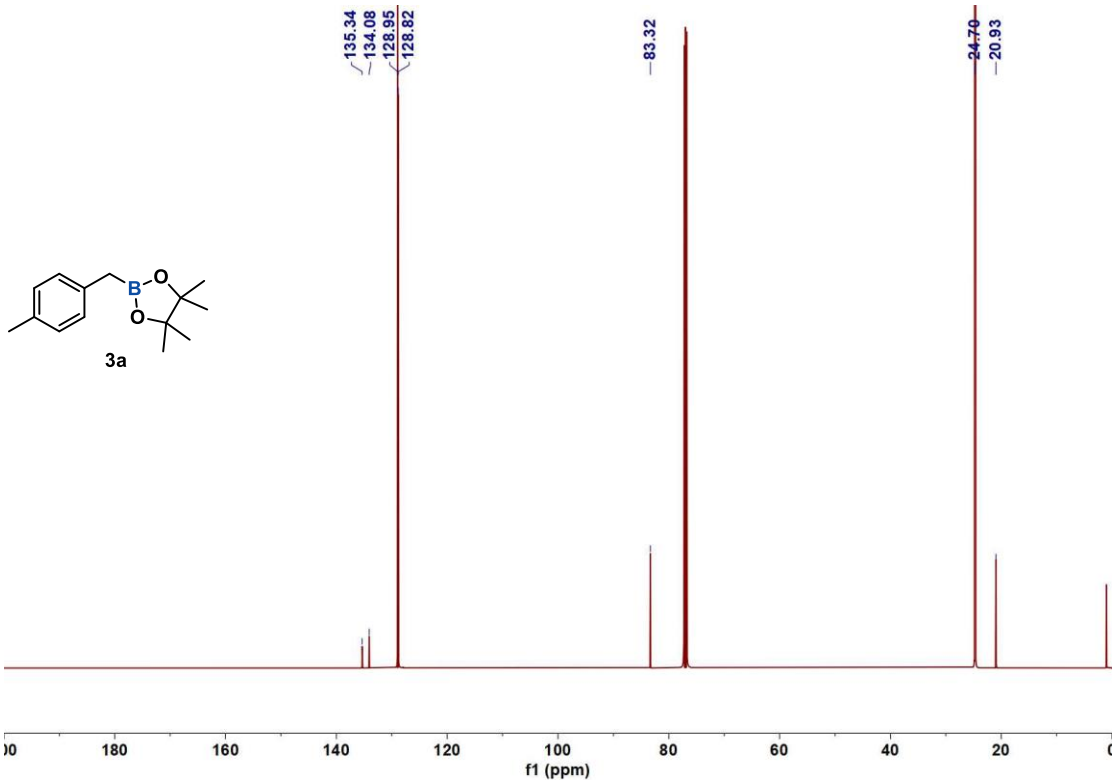


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$ at 298K

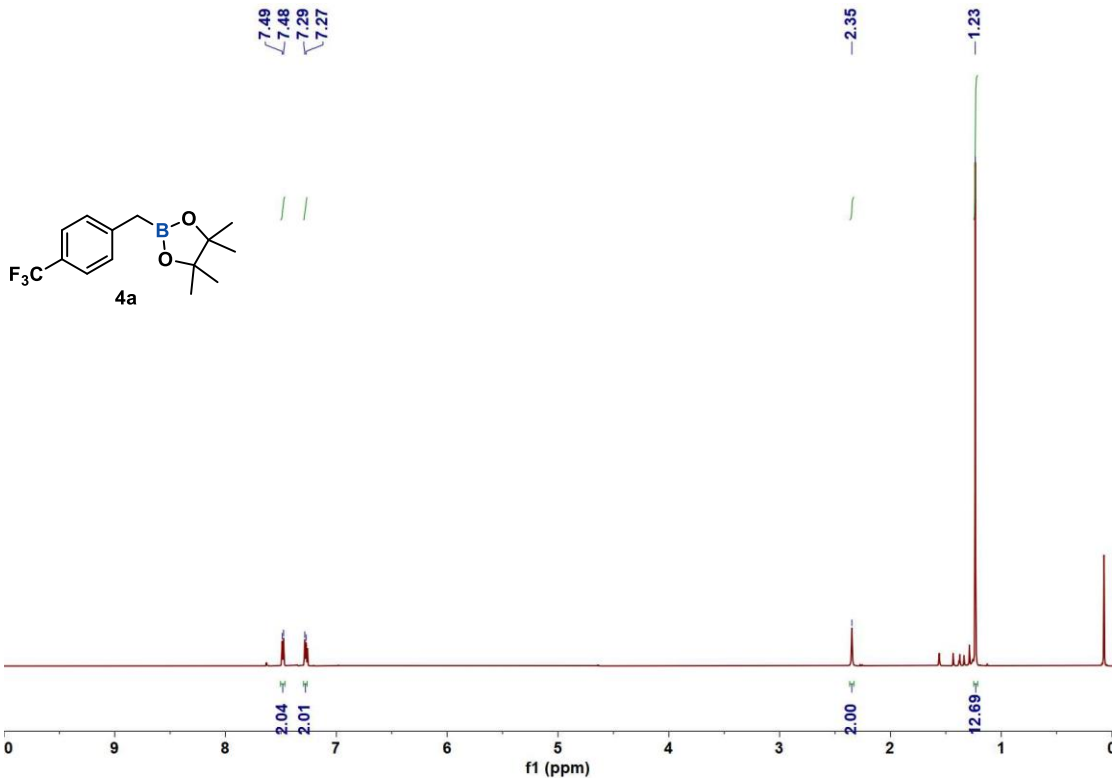


Figure S96. ^{1}H NMR spectrum of **4a** in $CDCl_3$ at 298K

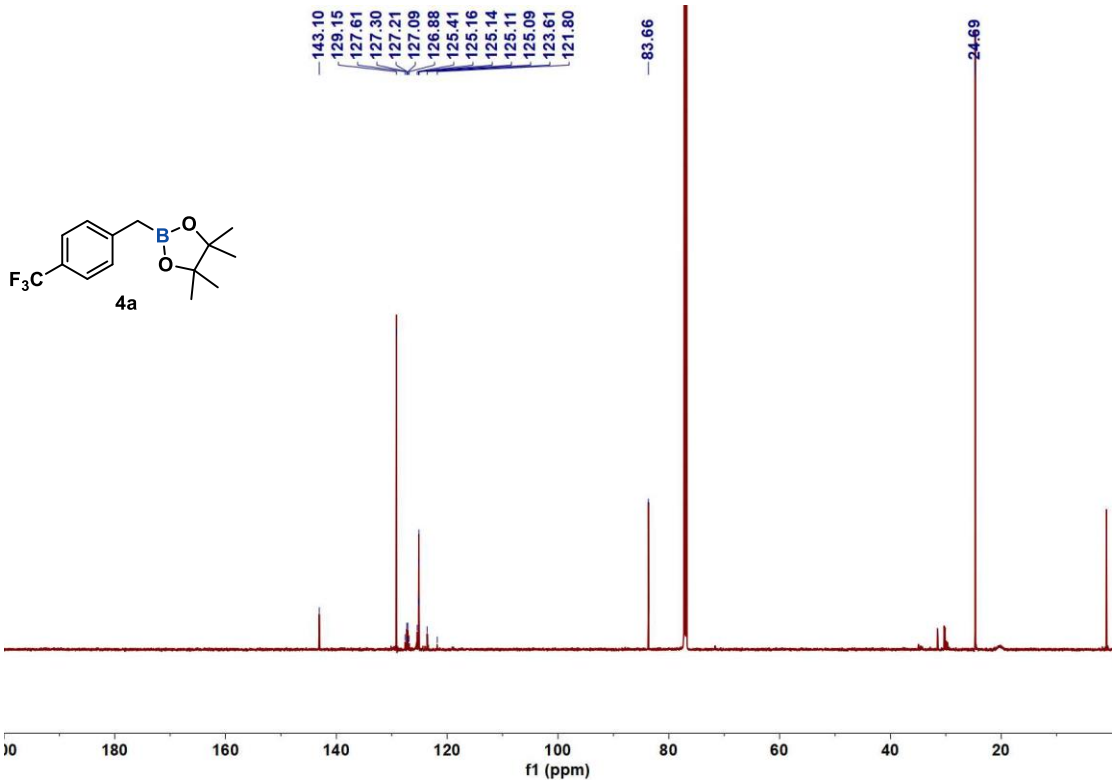


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$ at 298K

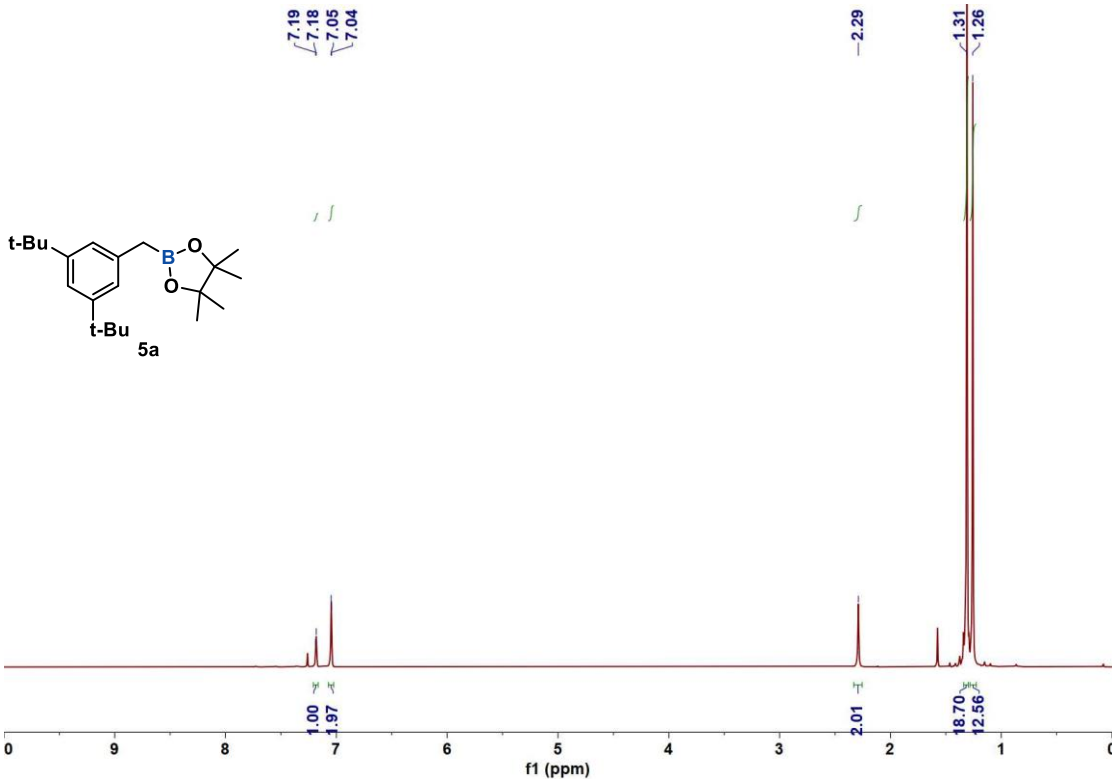


Figure S98. ^{1}H NMR spectrum of **5a** in $CDCl_3$ at 298K

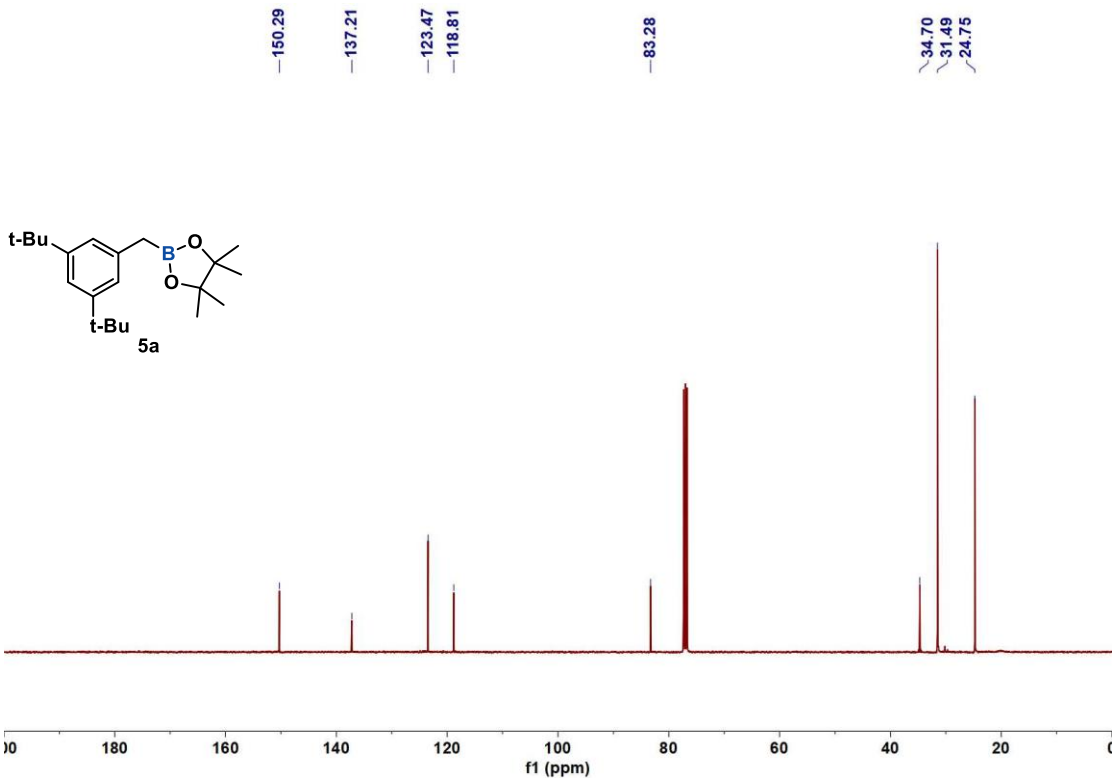


Figure S99. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ at 298K

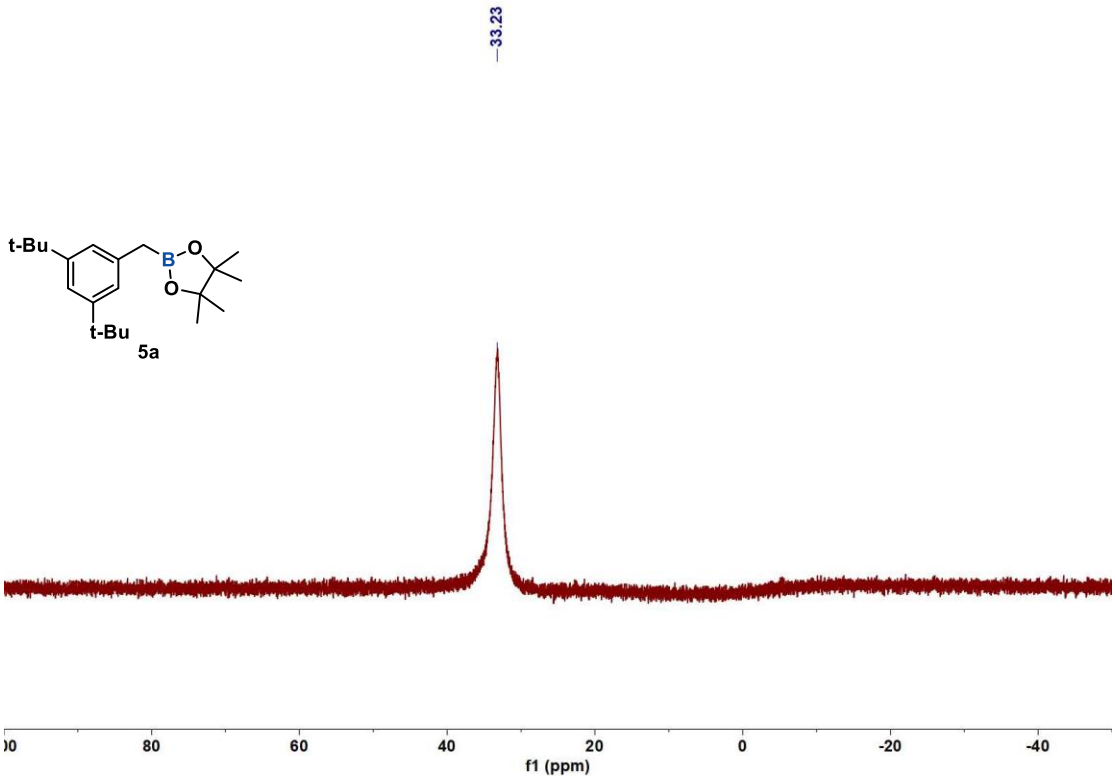


Figure S100. $^{11}B\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ at 298K

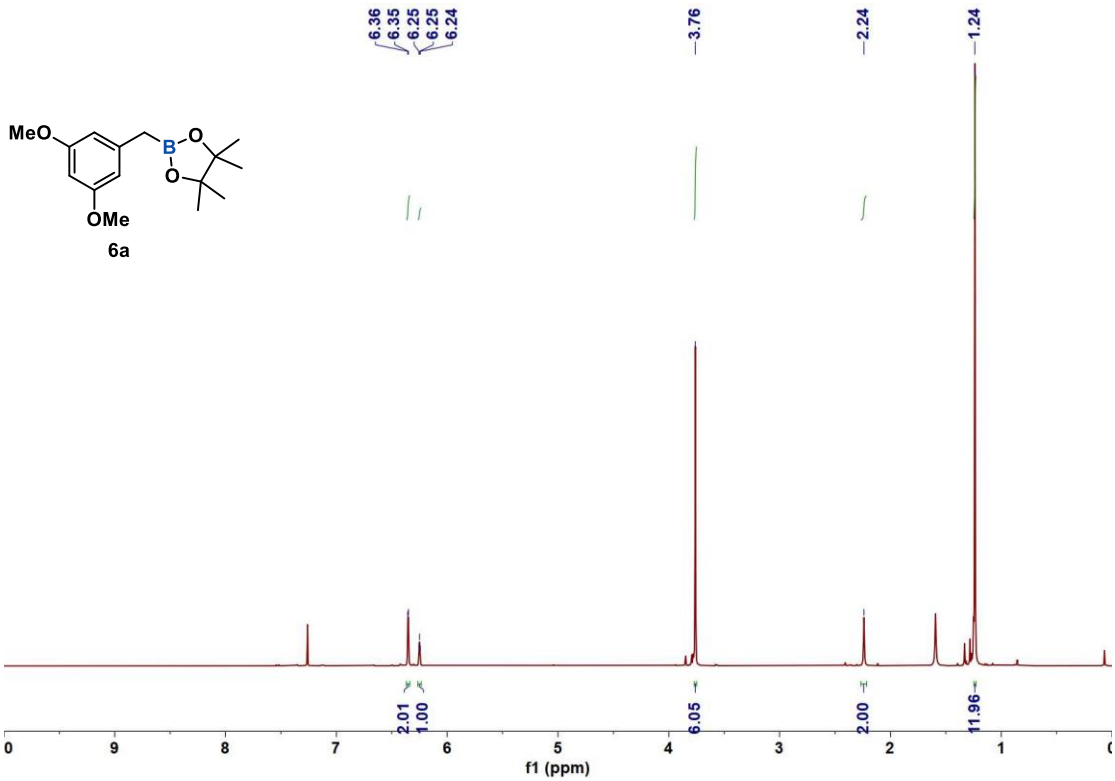


Figure S101. ^{1}H NMR spectrum of **6a** in $CDCl_3$ at 298K

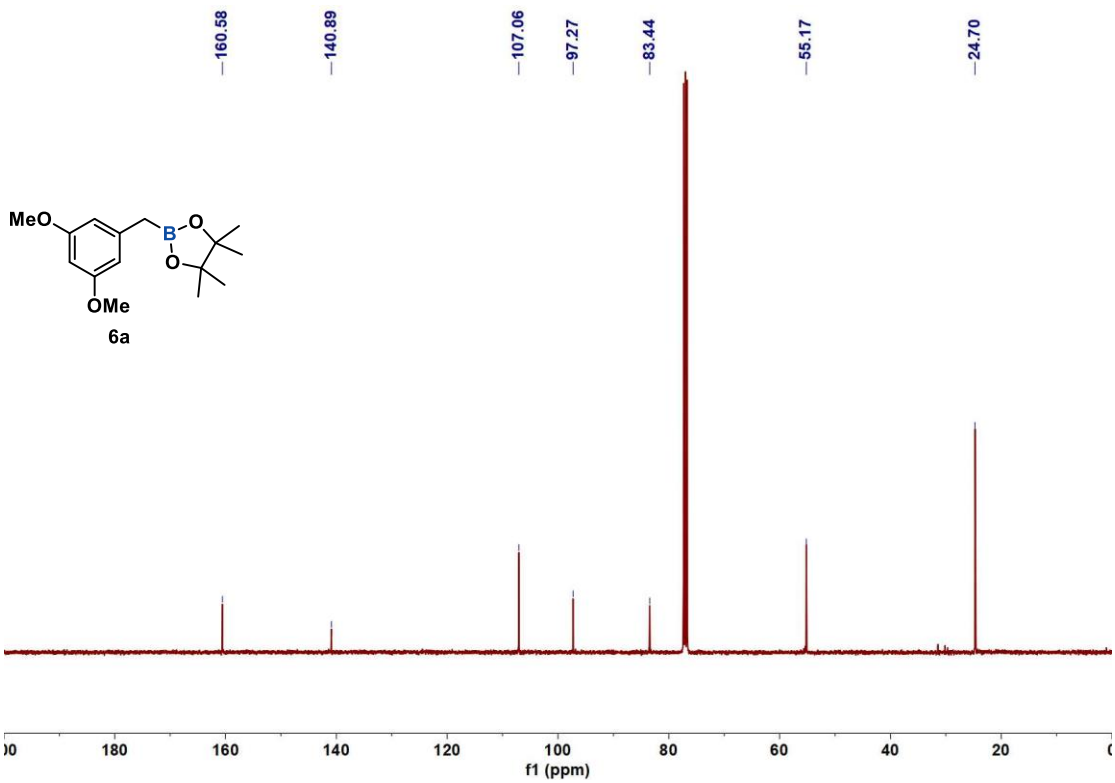


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$ at 298K

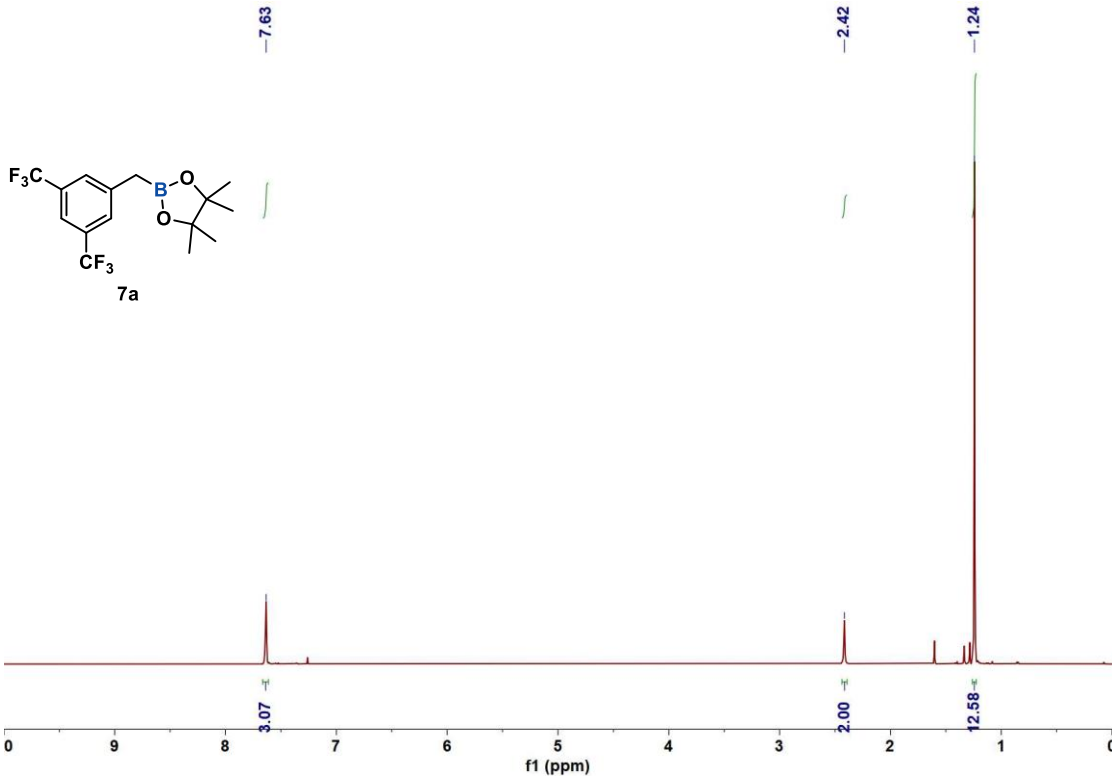


Figure S103. ^{1}H NMR spectrum of **7a** in $CDCl_3$ at 298K

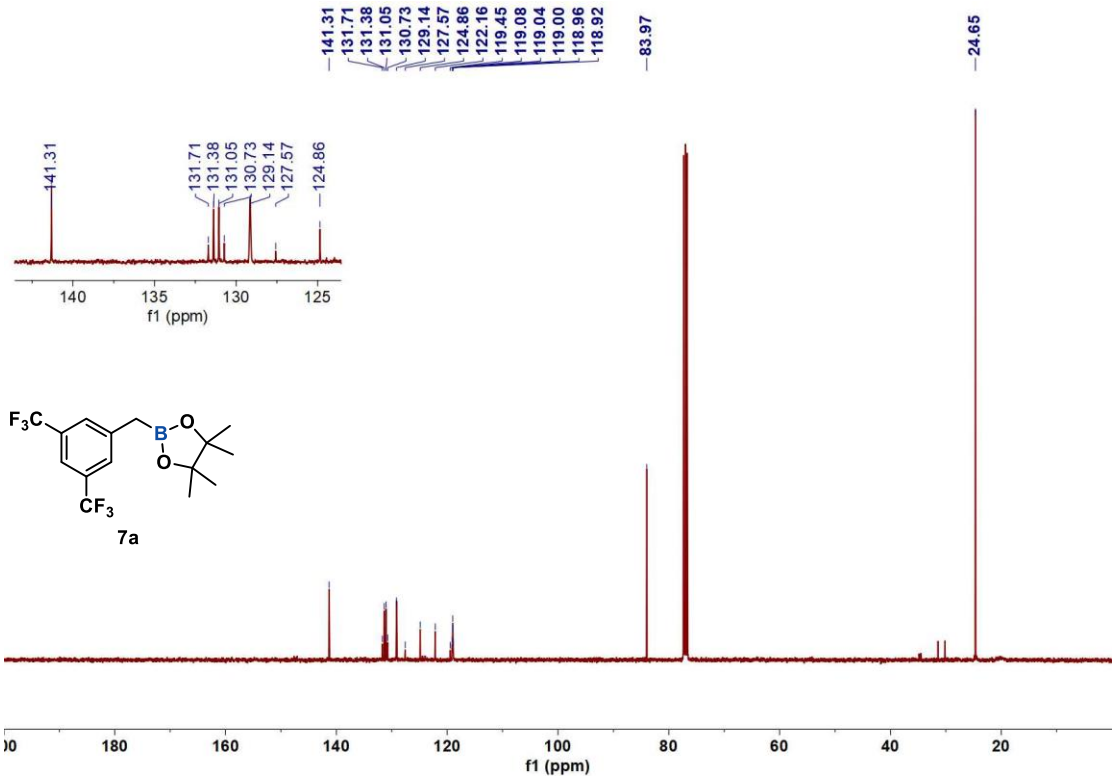


Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$ at 298K

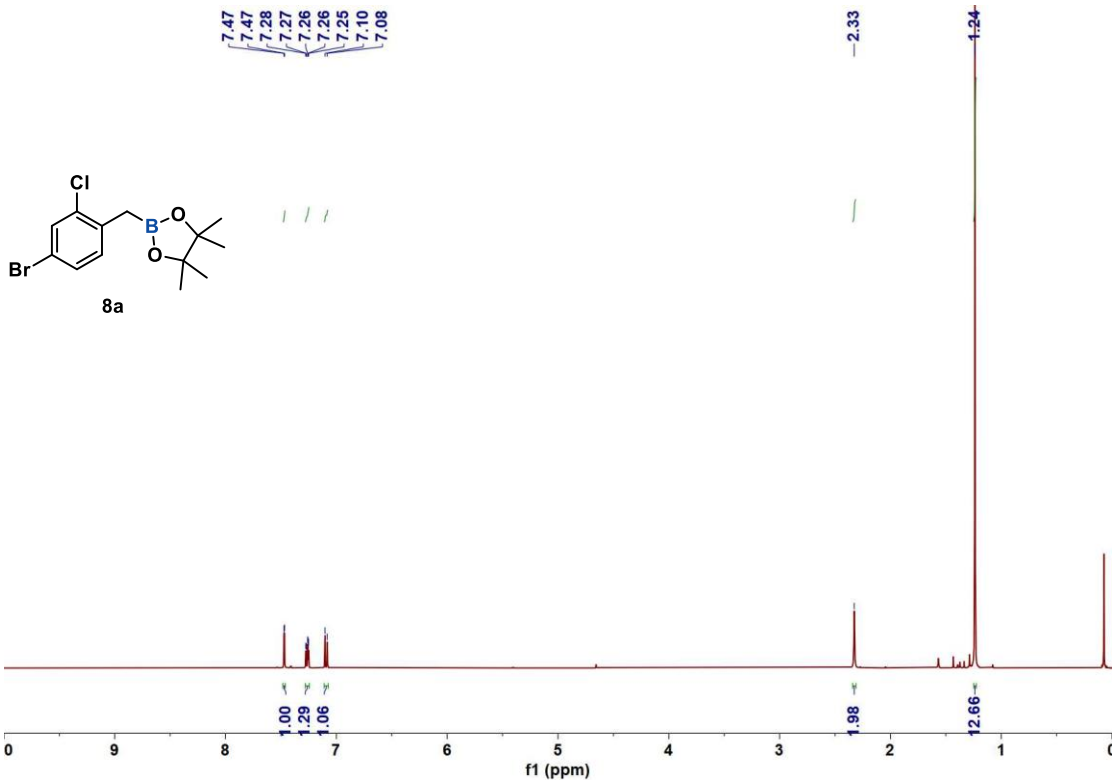


Figure S105. ^{1}H NMR spectrum of **8a** in $CDCl_3$ at 298K

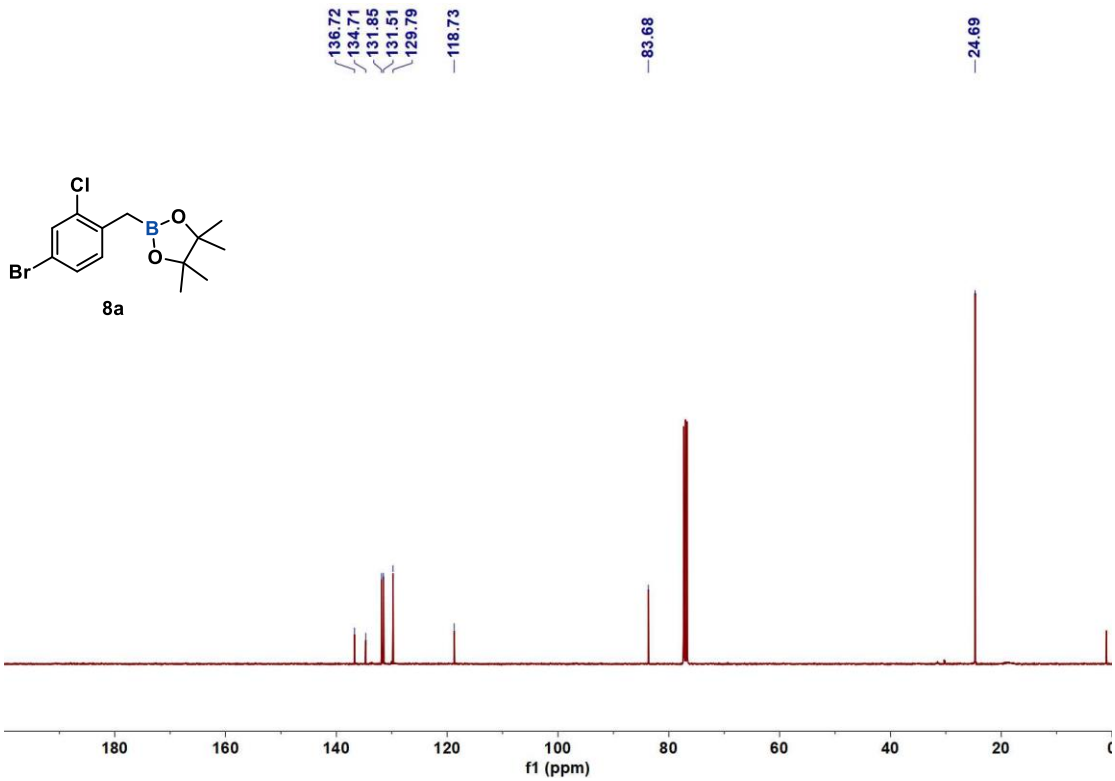


Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum of **8a** in $CDCl_3$ at 298K

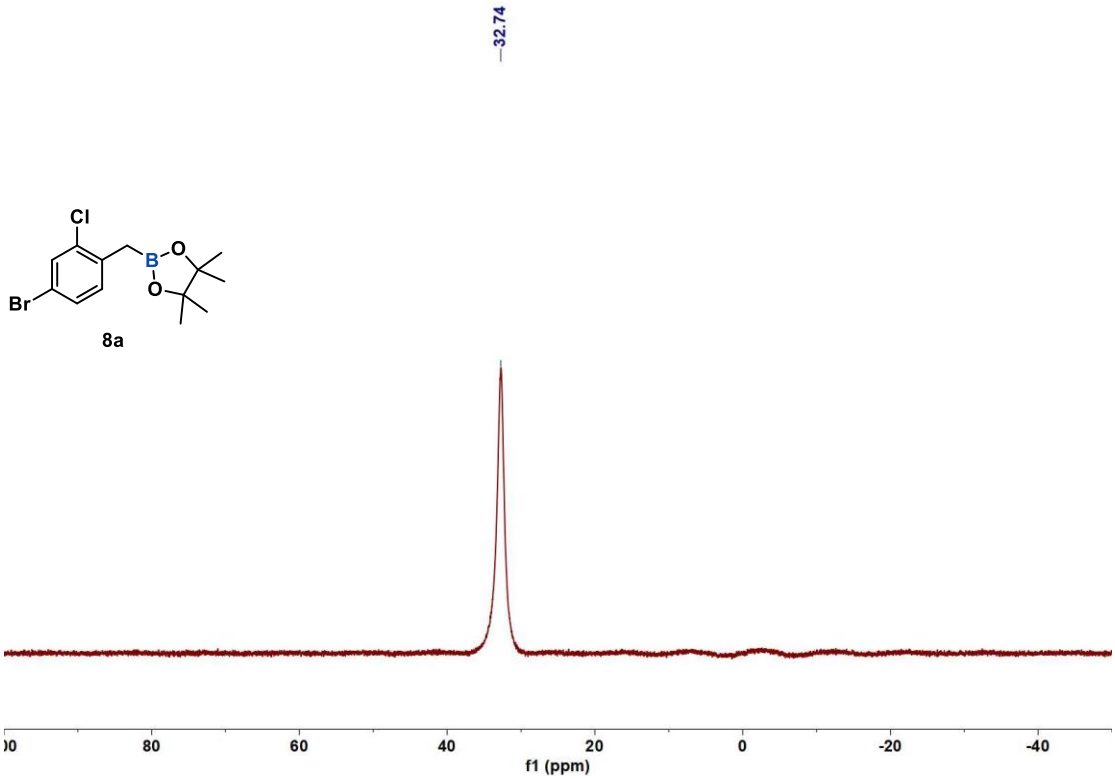


Figure S107. $^{11}B\{^{1}H\}$ NMR spectrum of **8a** in $CDCl_3$ at 298K

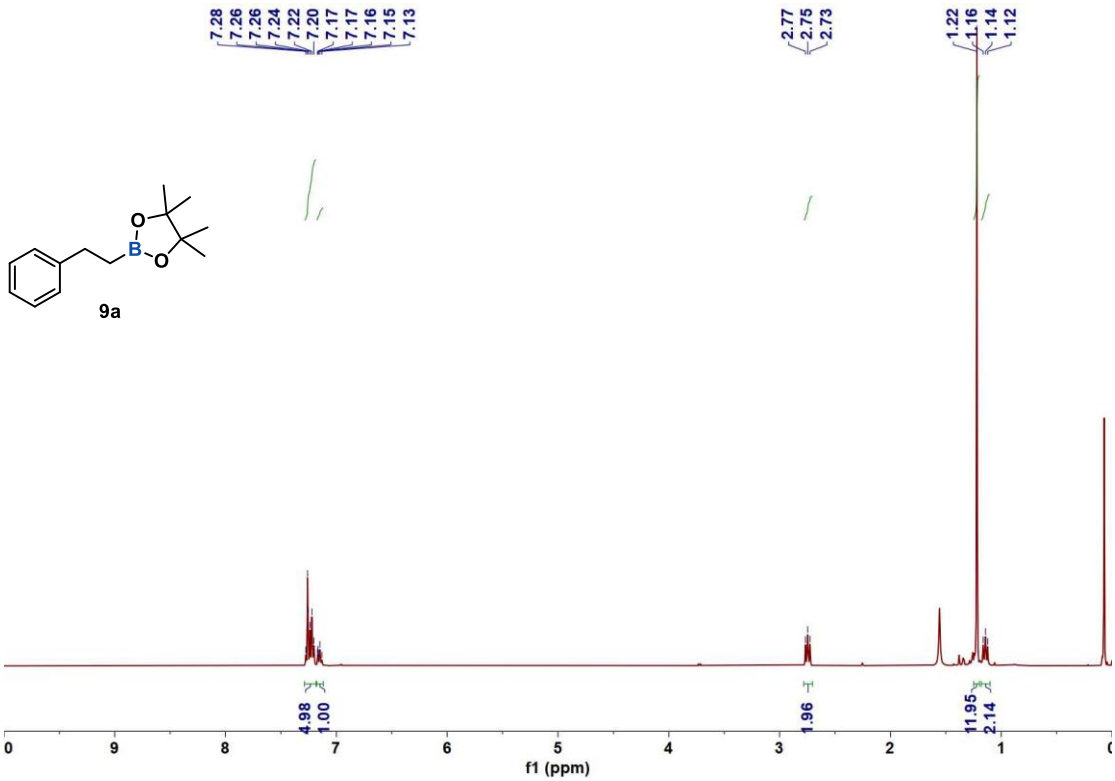


Figure S108. ^{1}H NMR spectrum of **9a** in $CDCl_3$ at 298K

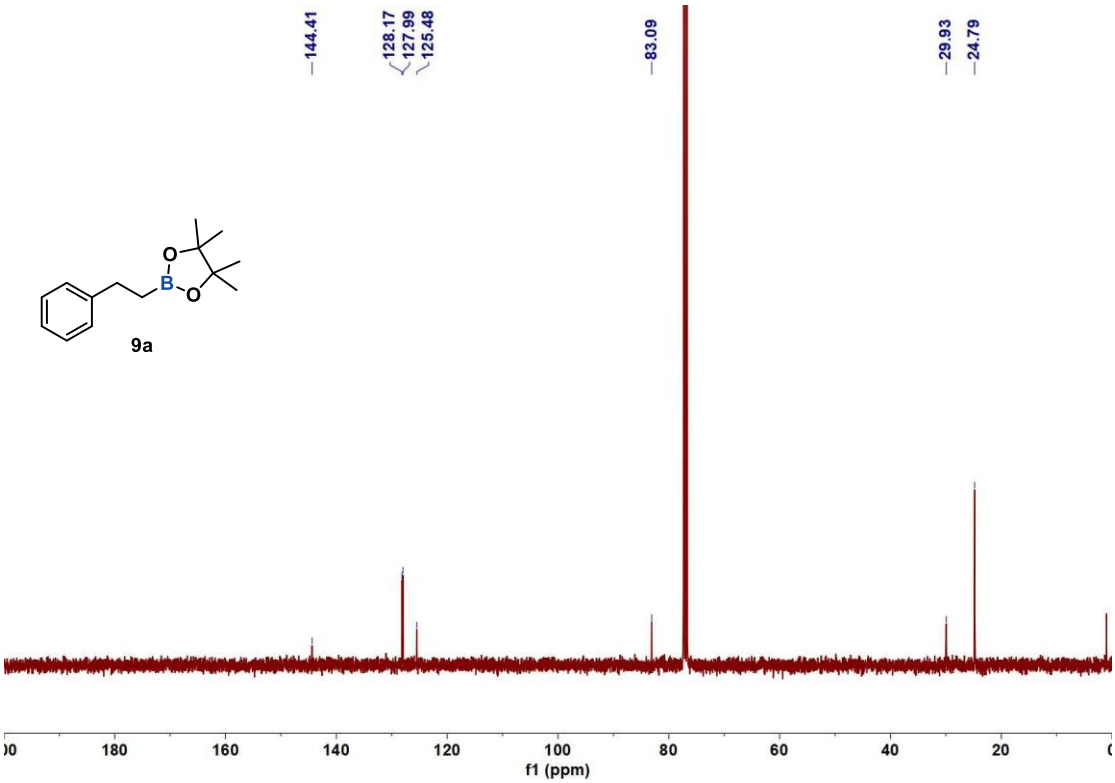


Figure S109. $^{13}C\{^{1}H\}$ NMR spectrum of **9a** in $CDCl_3$ at 298K

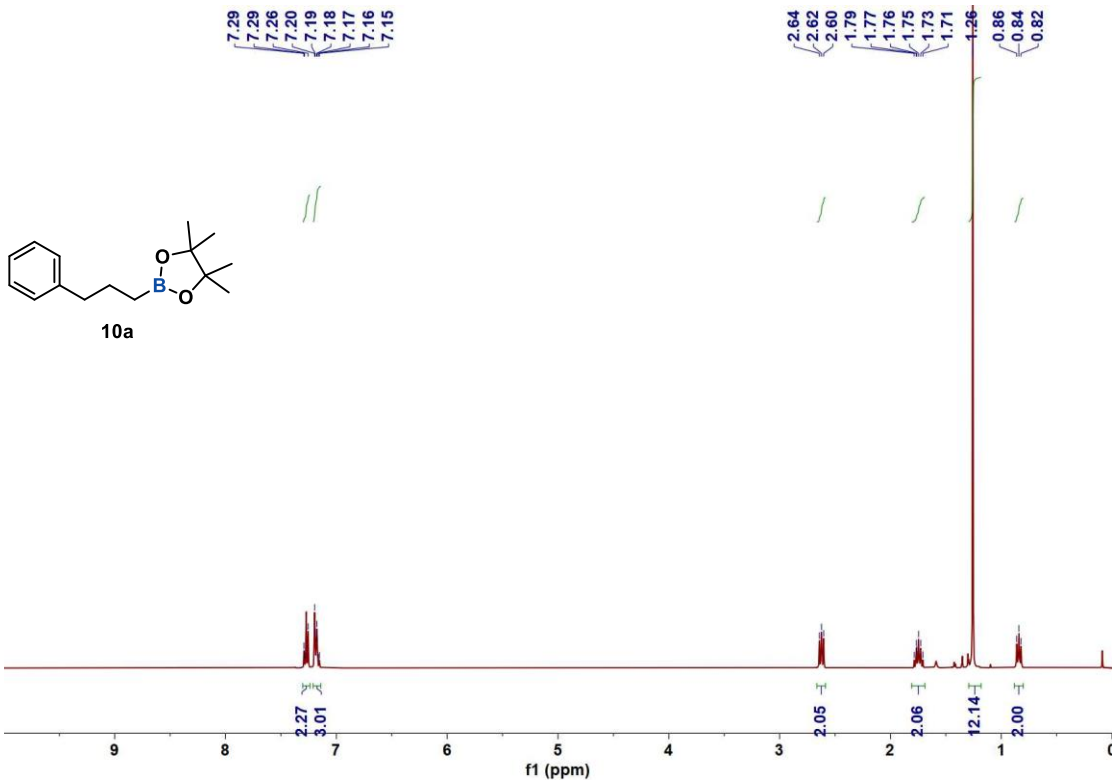


Figure S110. ^{1}H NMR spectrum of **10a** in $CDCl_3$ at 298K

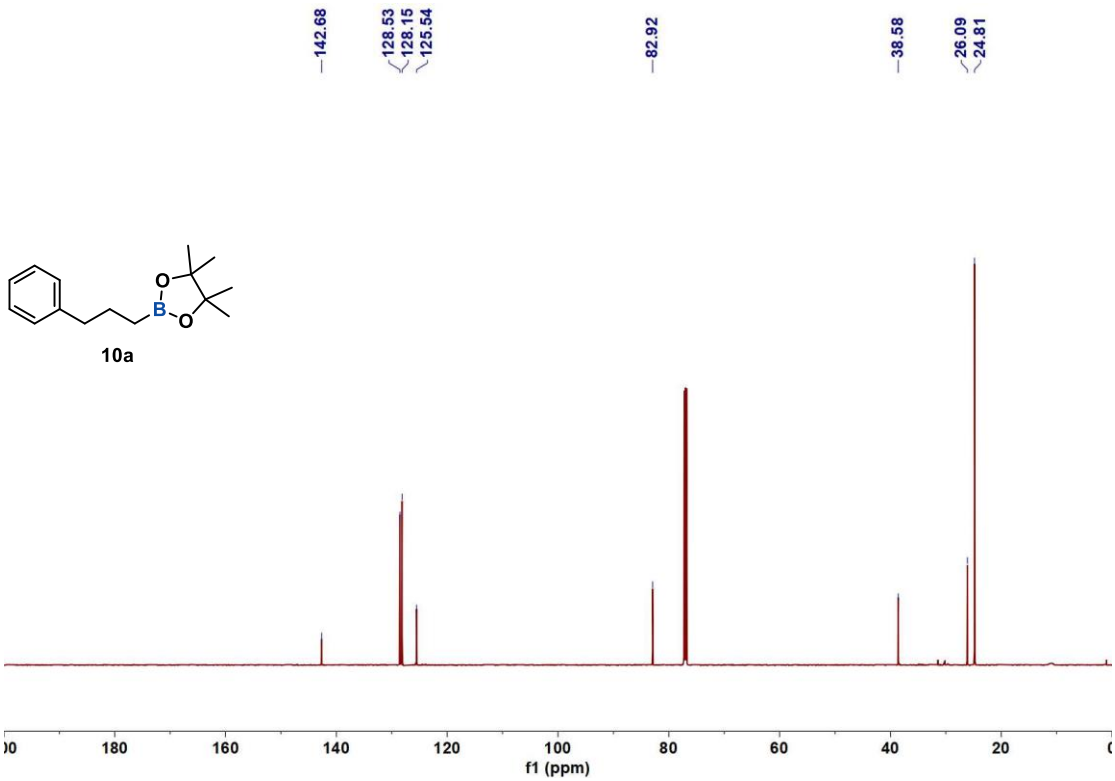


Figure S111. $^{13}C\{^{1}H\}$ NMR spectrum of **10a** in $CDCl_3$ at 298K

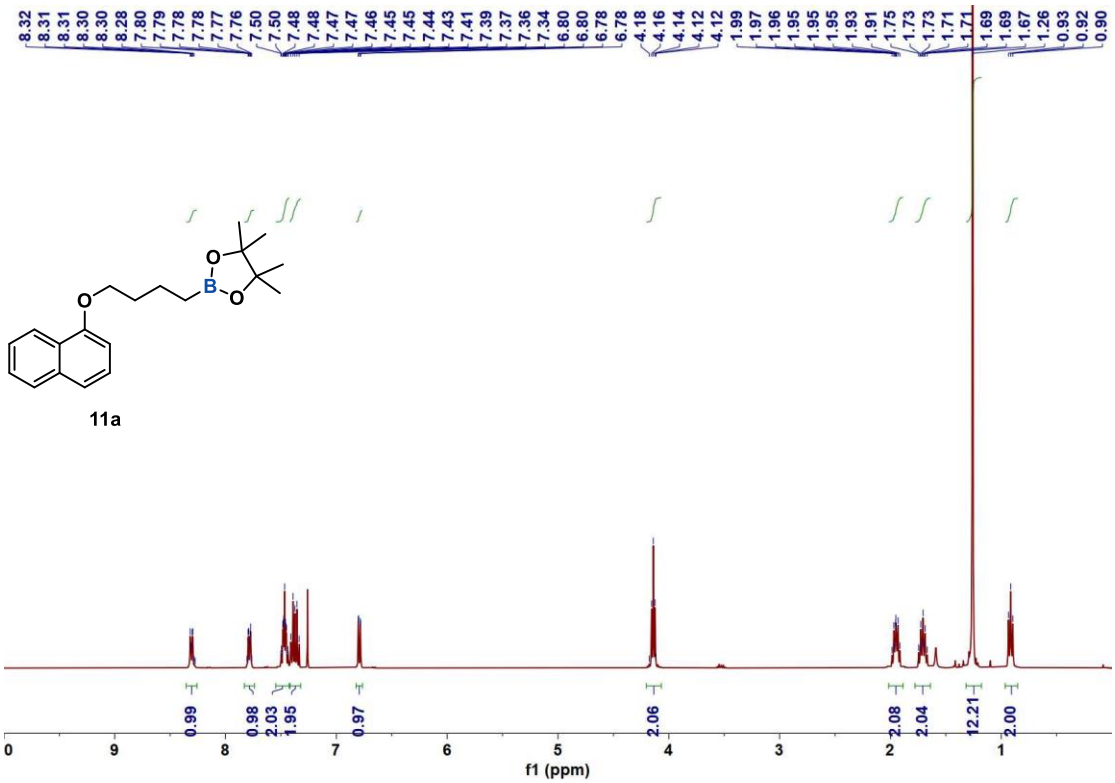


Figure S112. ^{1}H NMR spectrum of **11a** in $CDCl_3$ at 298K

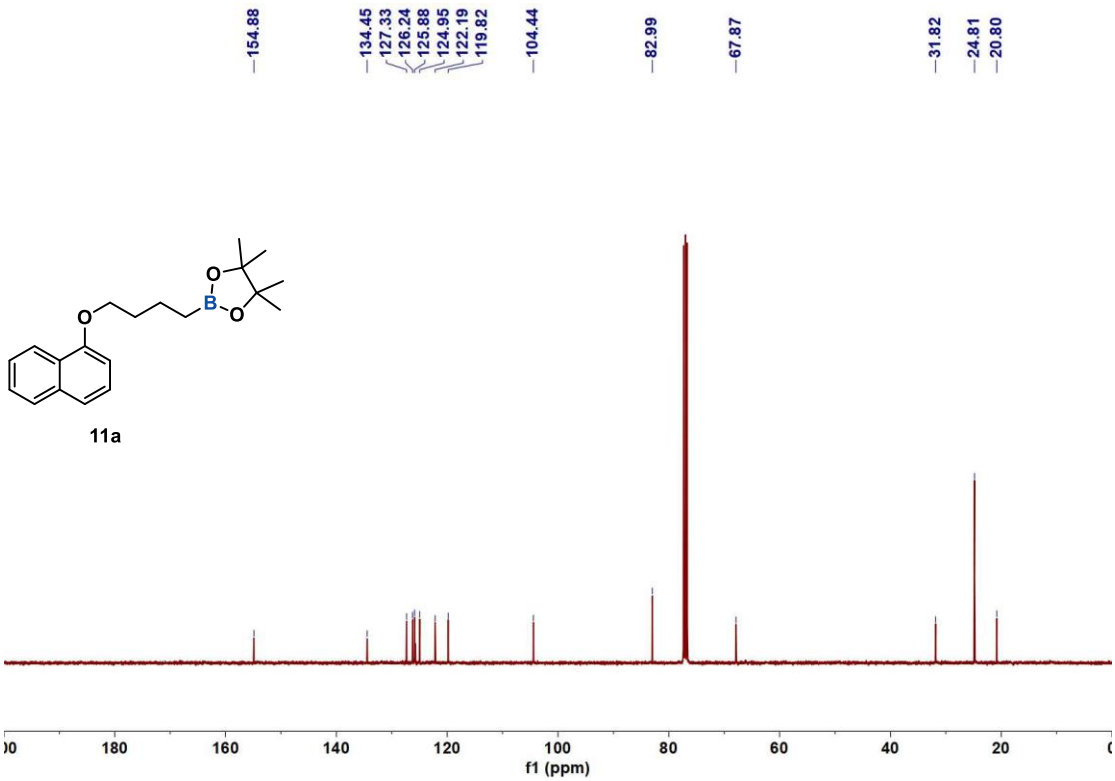


Figure S113. $^{13}C\{^{1}H\}$ NMR spectrum of **11a** in $CDCl_3$ at 298K

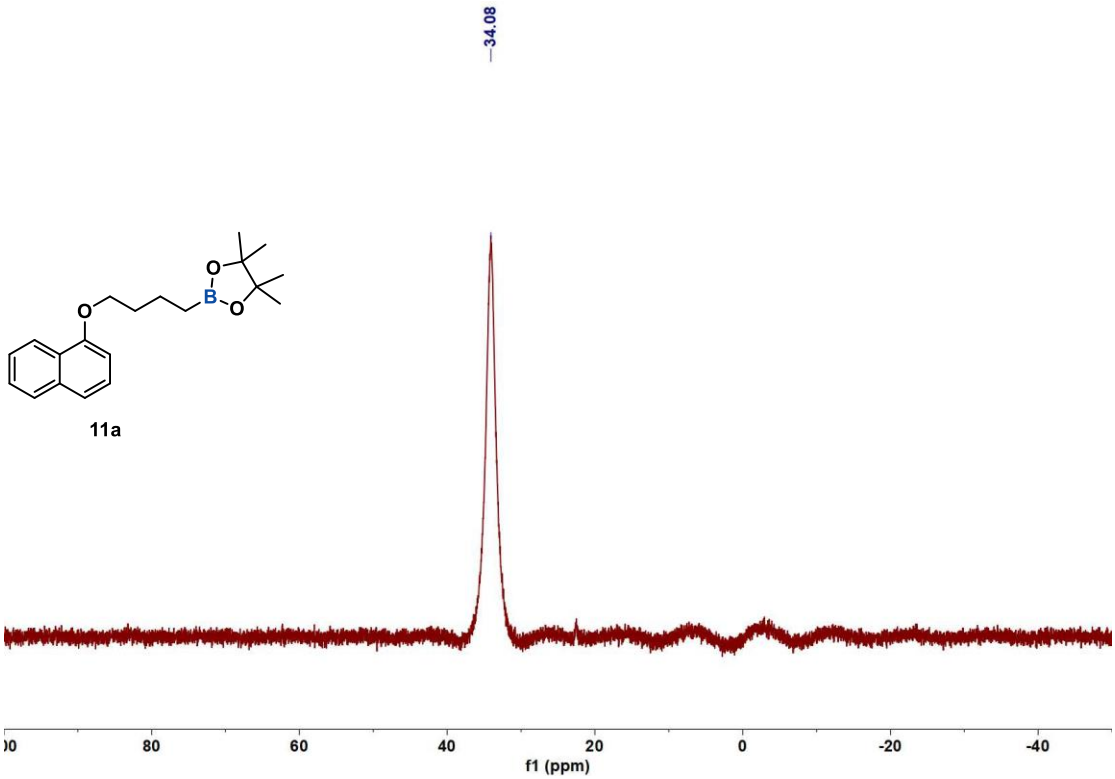


Figure S114. $^{11}B\{^{1}H\}$ NMR spectrum of **11a** in $CDCl_3$ at 298K

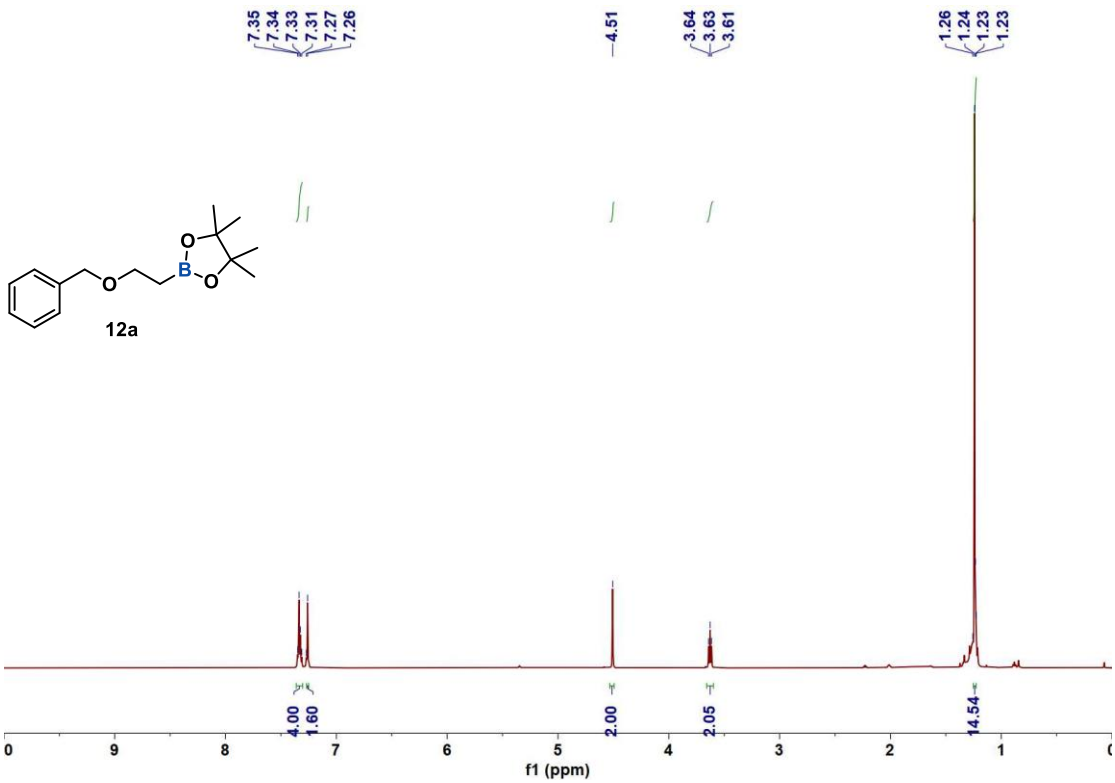


Figure S115. ^{1}H NMR spectrum of **12a** in $CDCl_3$ at 298K

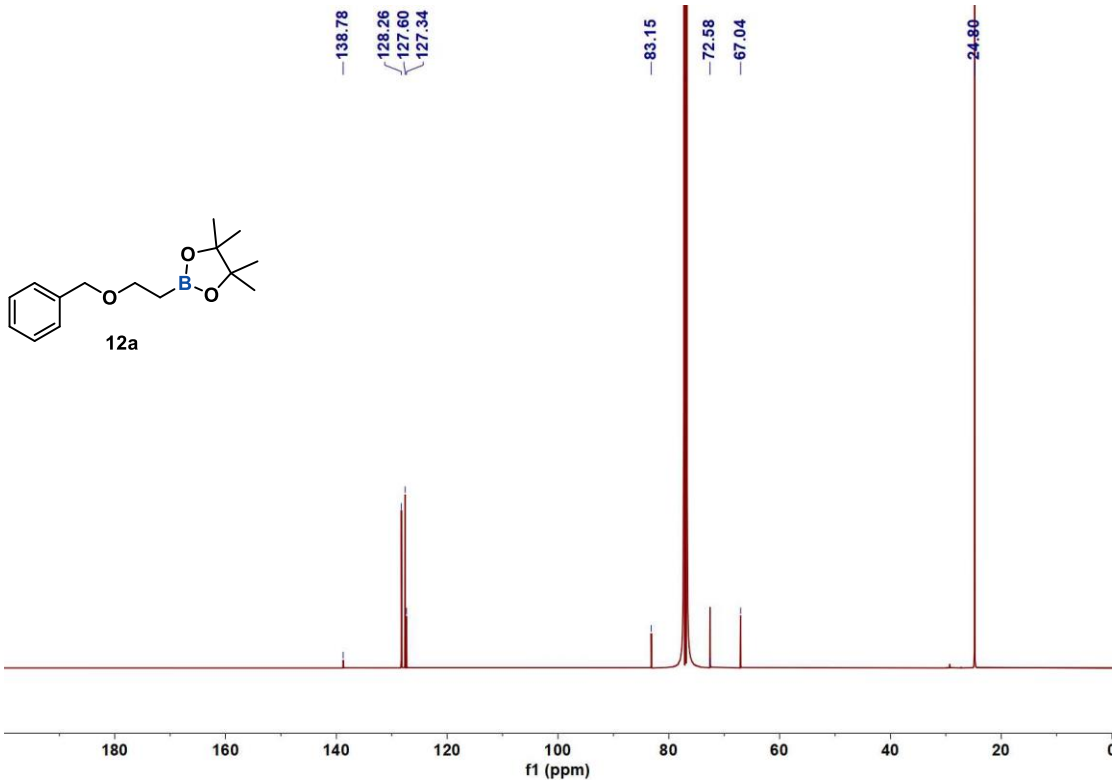


Figure S116. $^{13}C\{^{1}H\}$ NMR spectrum of **12a** in $CDCl_3$ at 298K

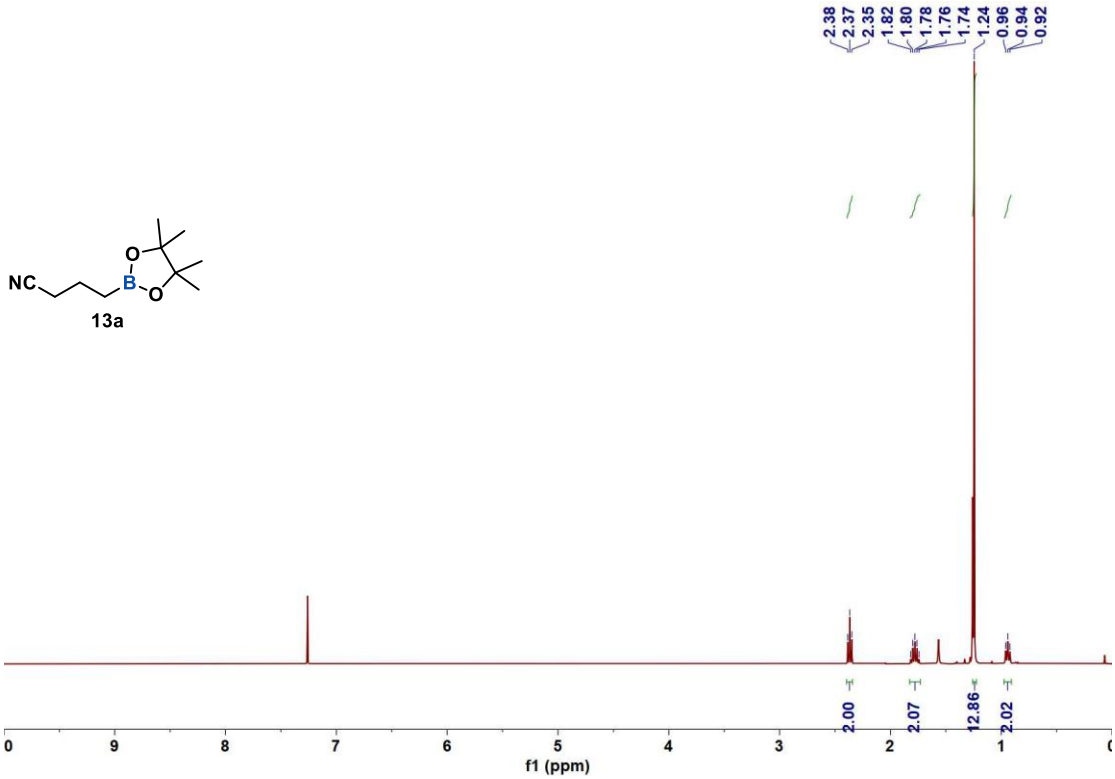


Figure S117. ^{1}H NMR spectrum of **13a** in $CDCl_3$ at 298K

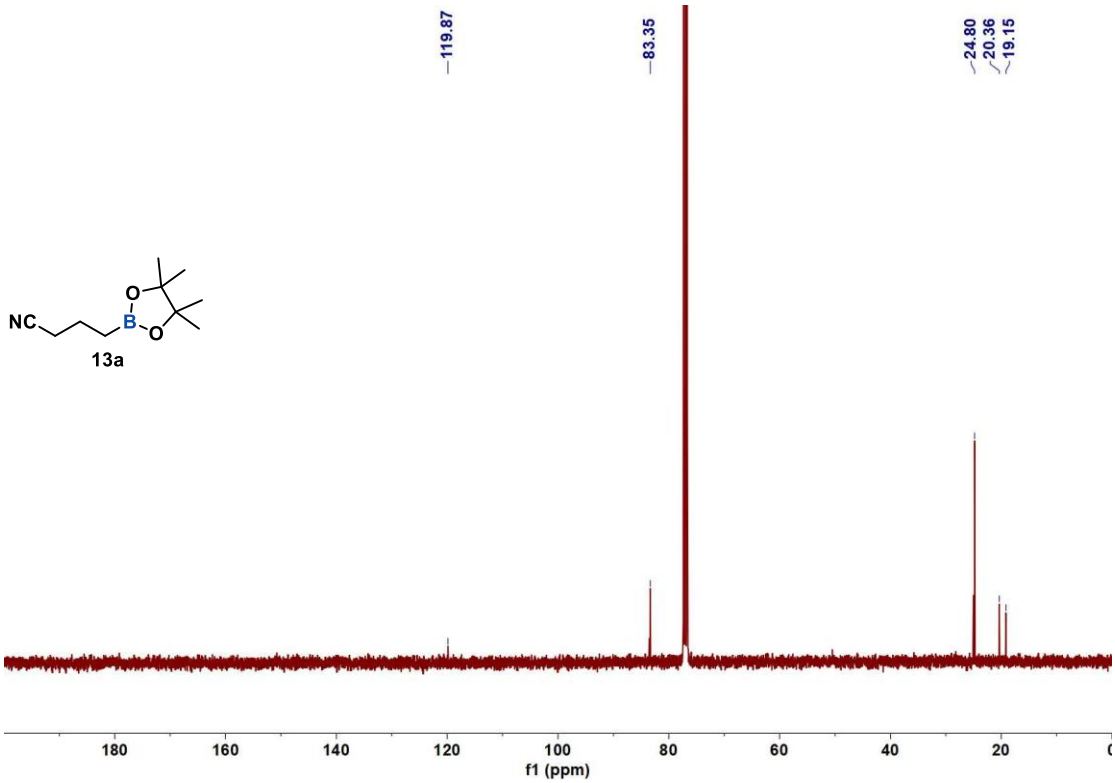


Figure S118. $^{13}C\{^{1}H\}$ NMR spectrum of **13a** in $CDCl_3$ at 298K

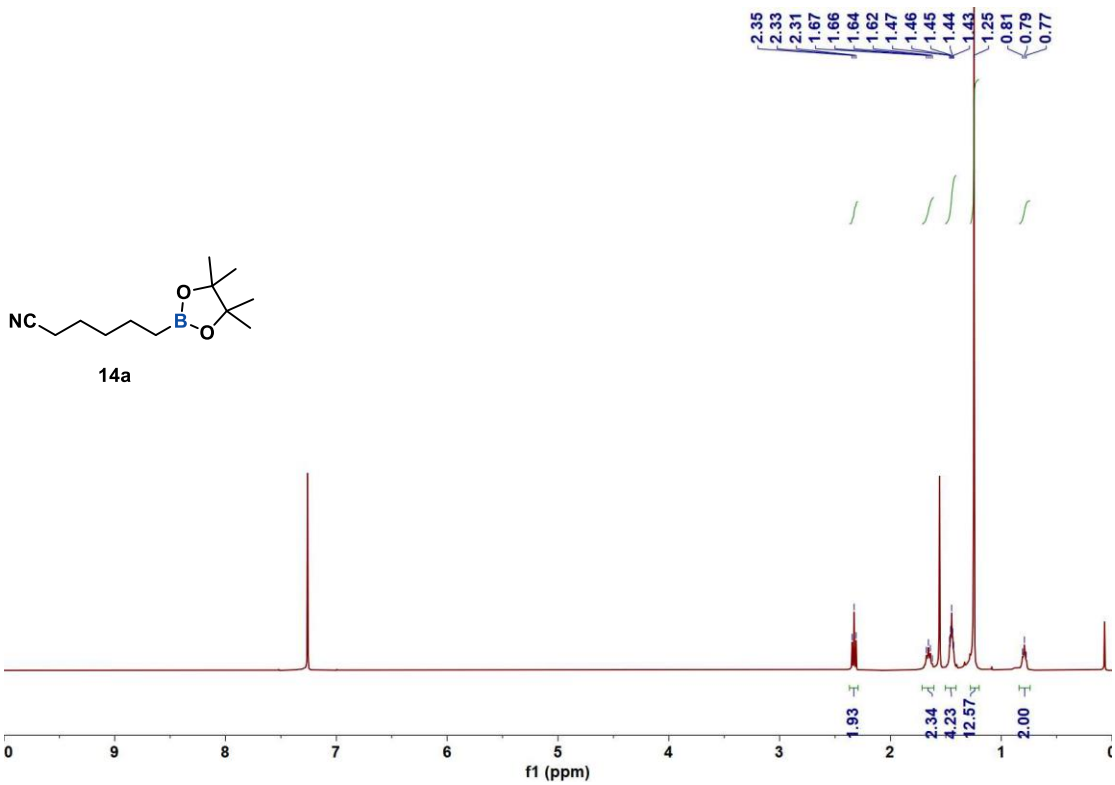


Figure S119. ^{1}H NMR spectrum of **14a** in $CDCl_3$ at 298K

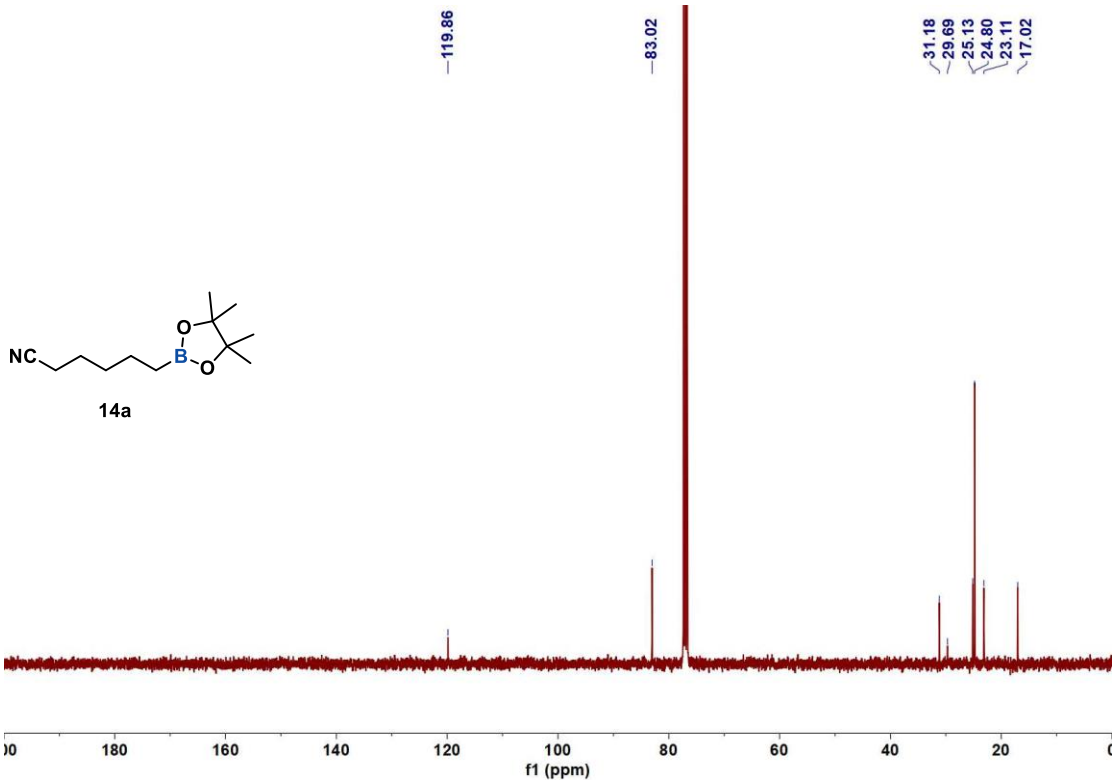


Figure S120. $^{13}C\{^{1}H\}$ NMR spectrum of **14a** in $CDCl_3$ at 298K

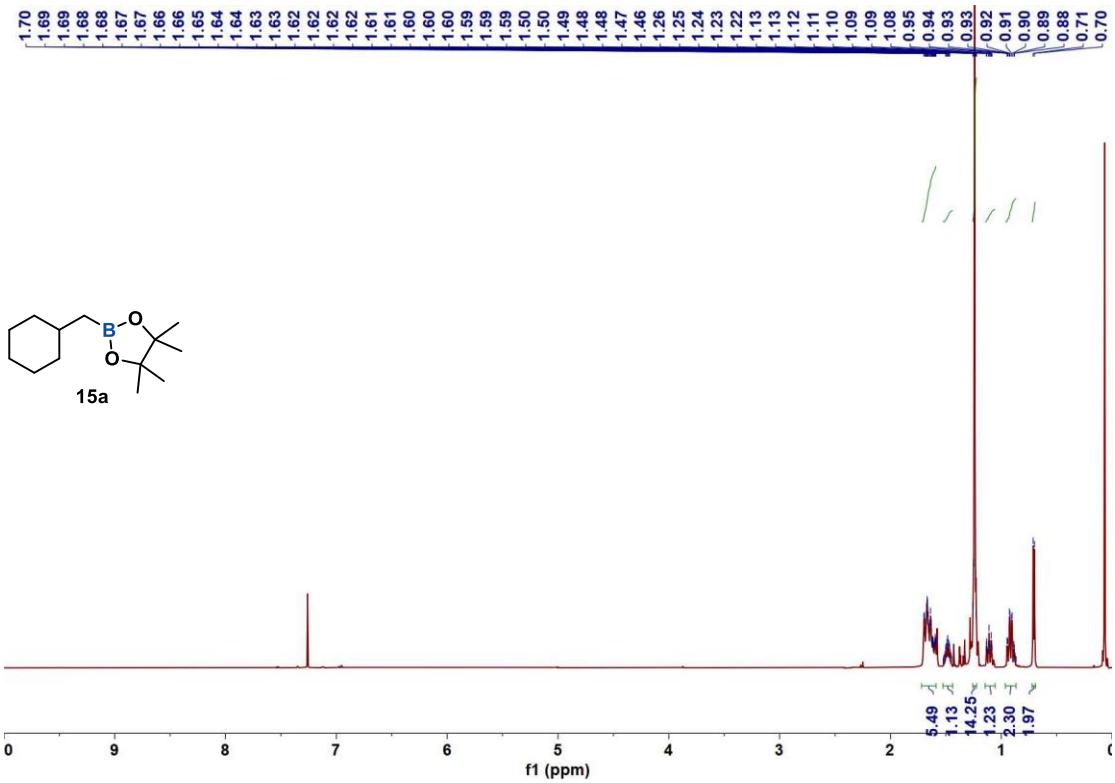


Figure S121. ^{1}H NMR spectrum of **15a** in $CDCl_3$ at 298K

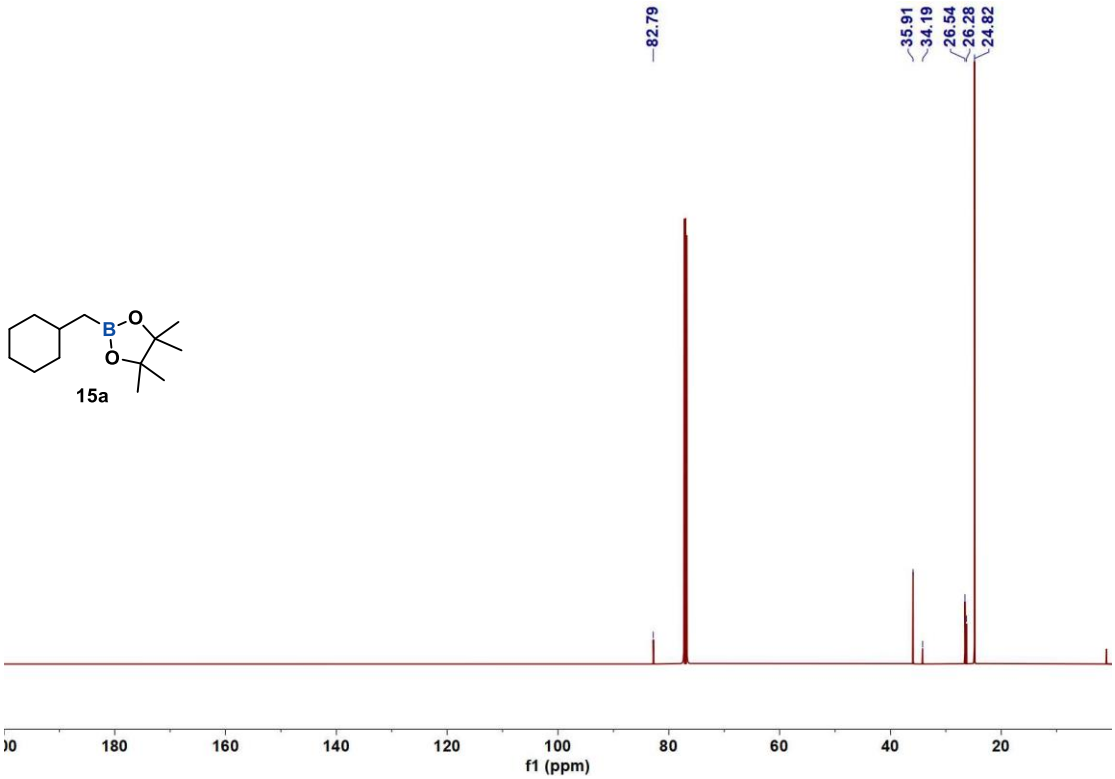


Figure S122. $^{13}C\{^{1}H\}$ NMR spectrum of **15a** in $CDCl_3$ at 298K

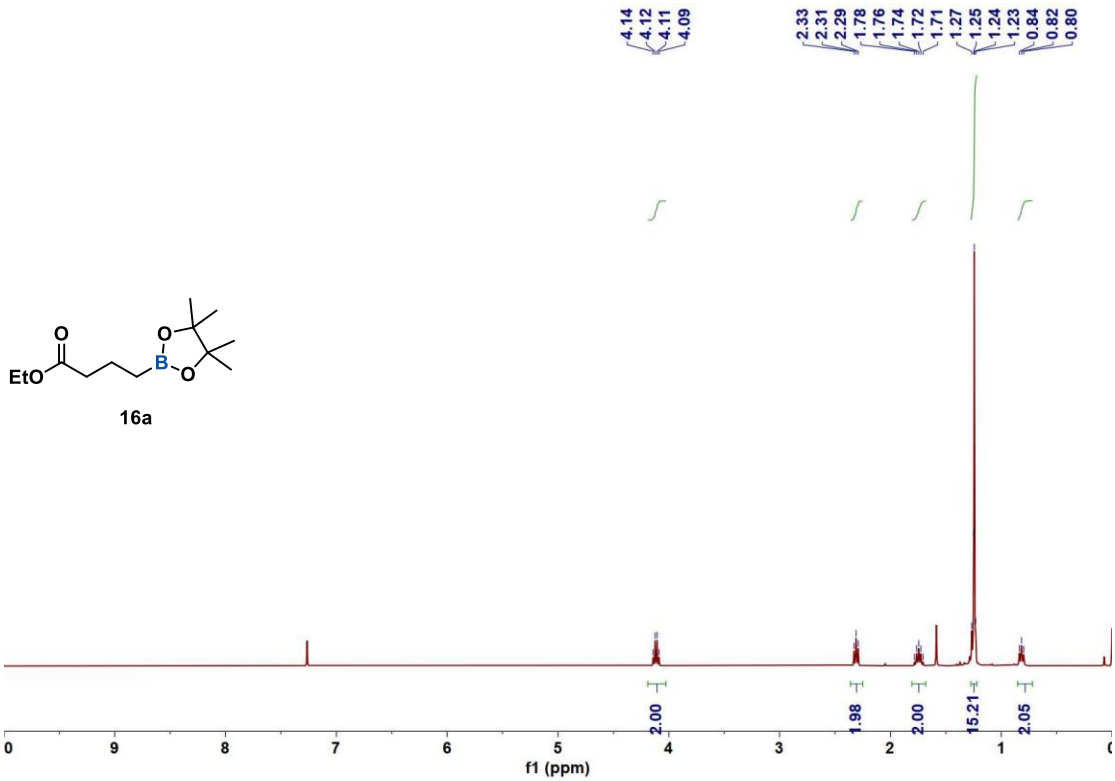


Figure S123. ^{1}H NMR spectrum of **16a** in $CDCl_3$ at 298K

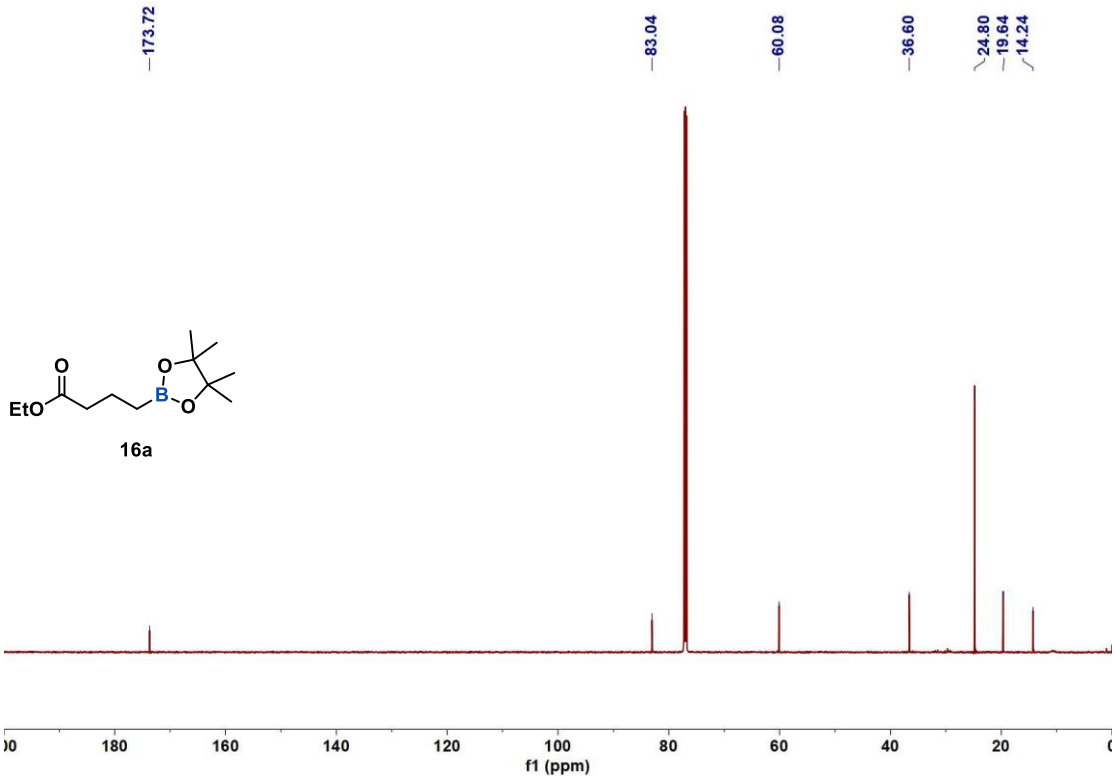


Figure S124. $^{13}C\{^{1}H\}$ NMR spectrum of **16a** in $CDCl_3$ at 298K

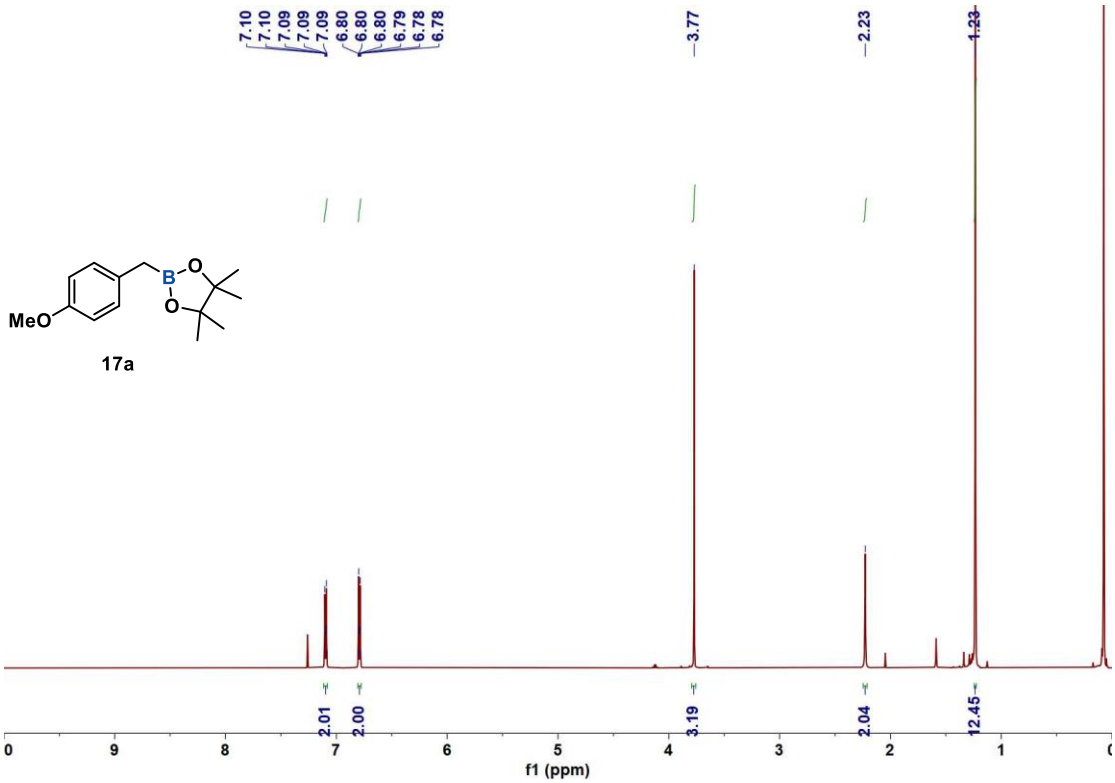


Figure S125. ^{1}H NMR spectrum of **17a** in $CDCl_3$ at 298K

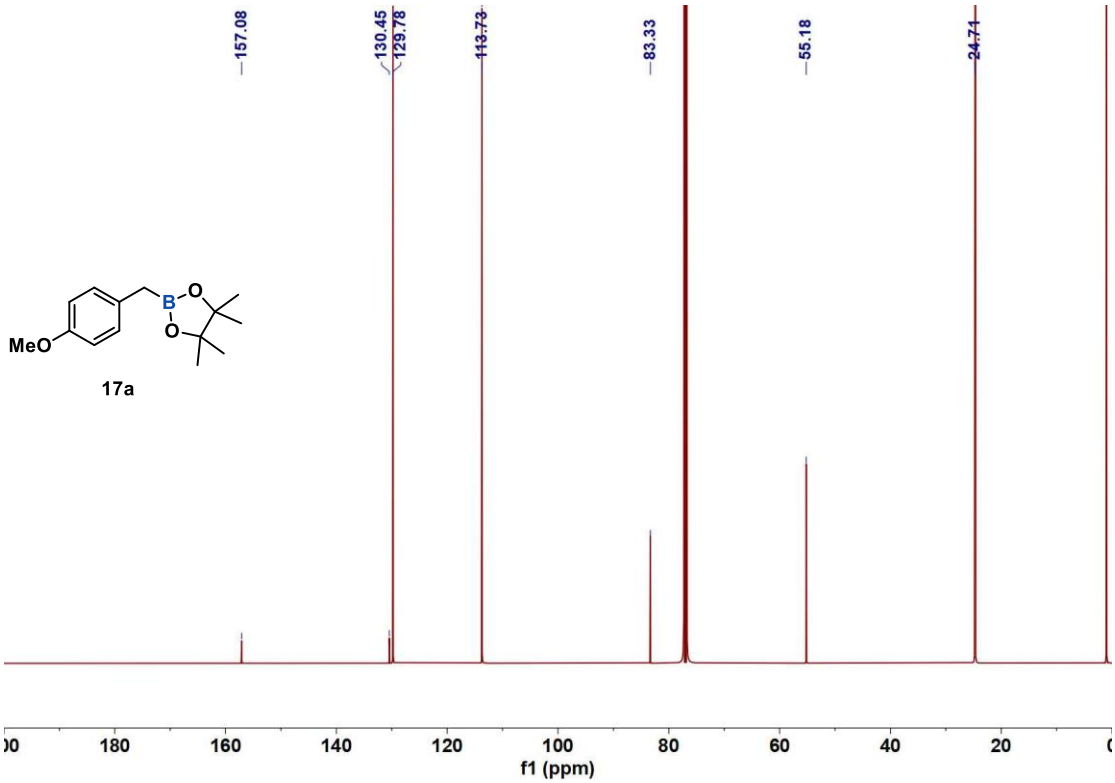


Figure S126. $^{13}C\{^{1}H\}$ NMR spectrum of **17a** in $CDCl_3$ at 298K

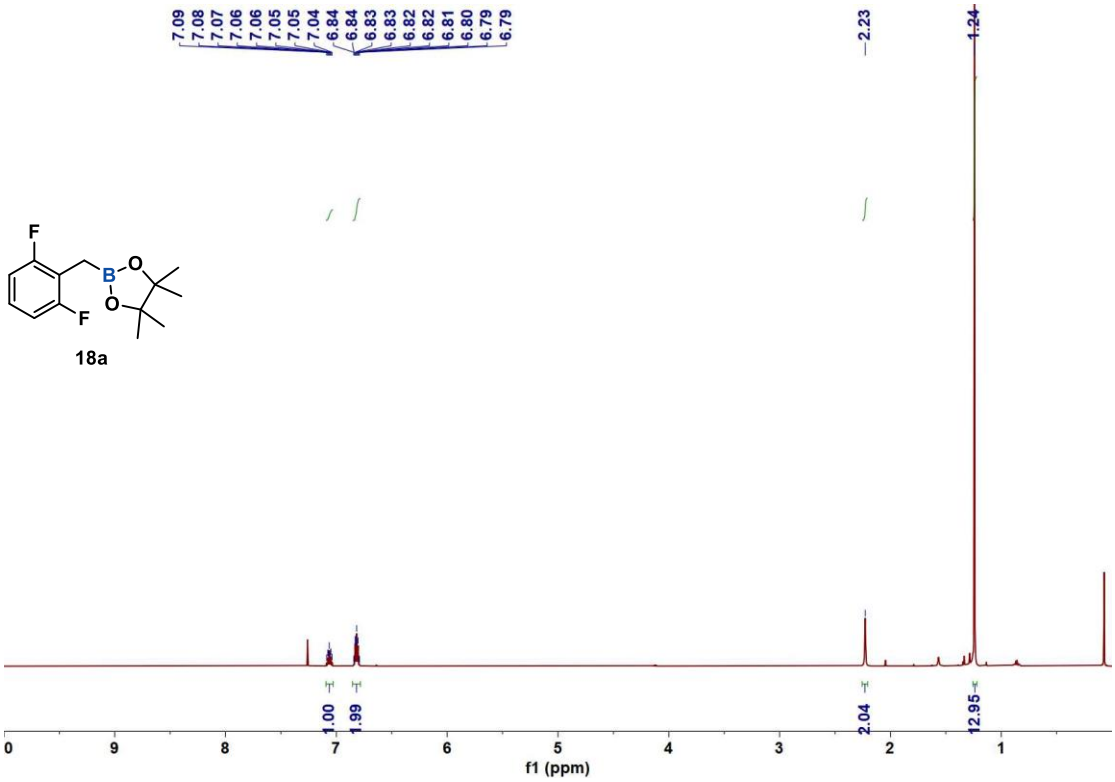


Figure S127. ^{1}H NMR spectrum of **18a** in $CDCl_3$ at 298K

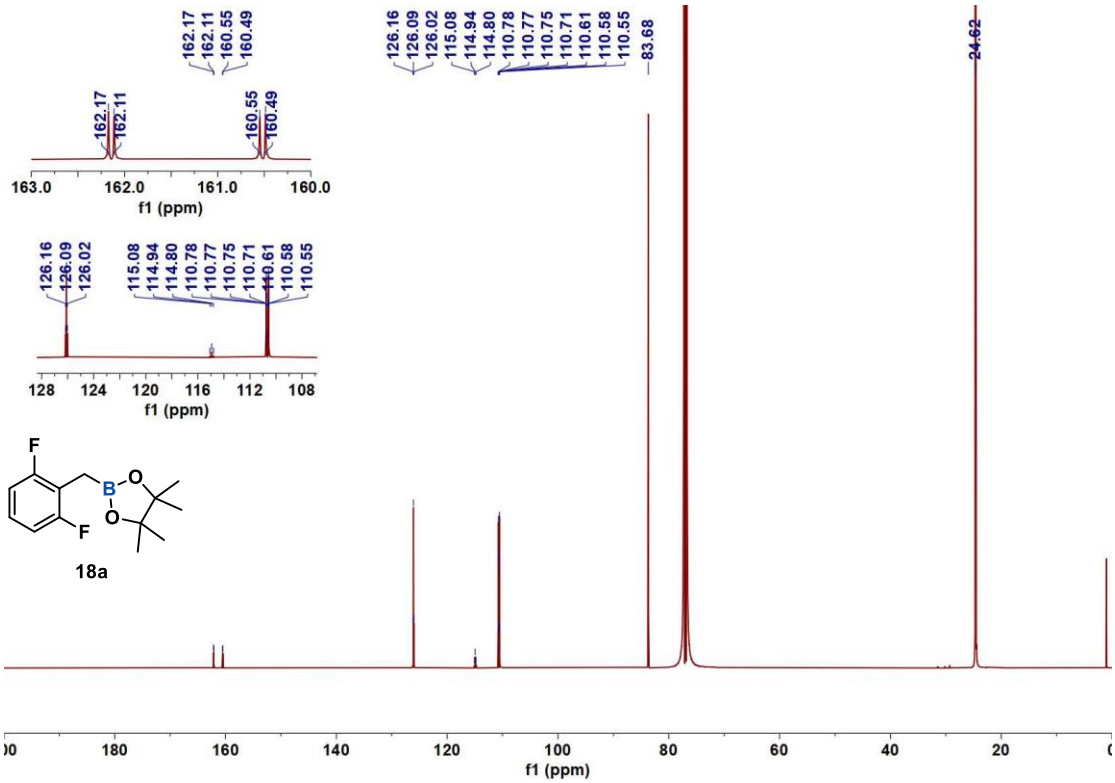


Figure S128. $^{13}C\{^{1}H\}$ NMR spectrum of **18a** in $CDCl_3$ at 298K

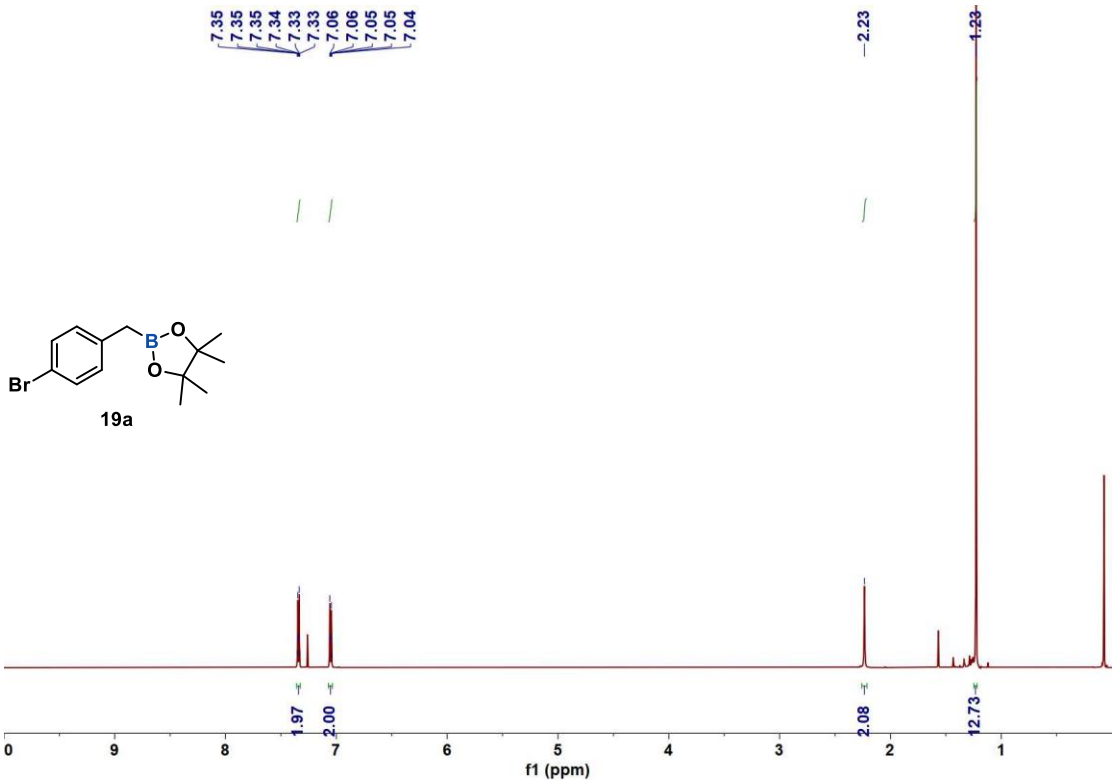


Figure S129. ^{1}H NMR spectrum of **19a** in $CDCl_3$ at 298K

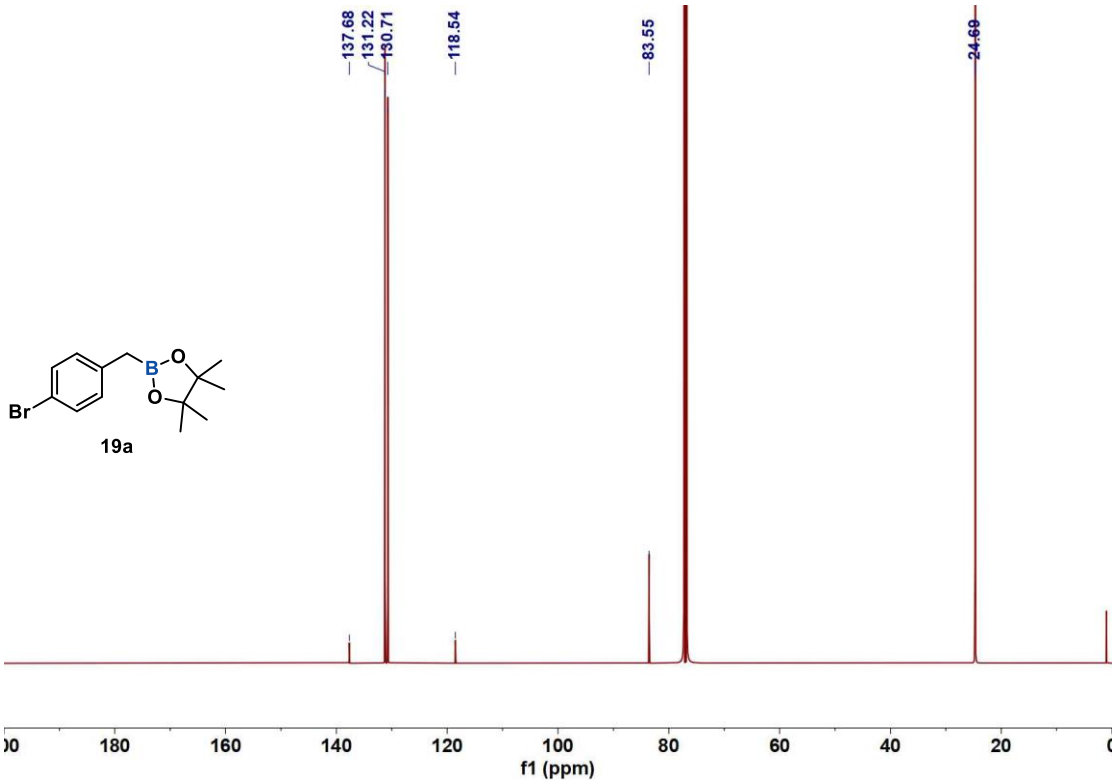


Figure S130. $^{13}C\{^{1}H\}$ NMR spectrum of **19a** in $CDCl_3$ at 298K

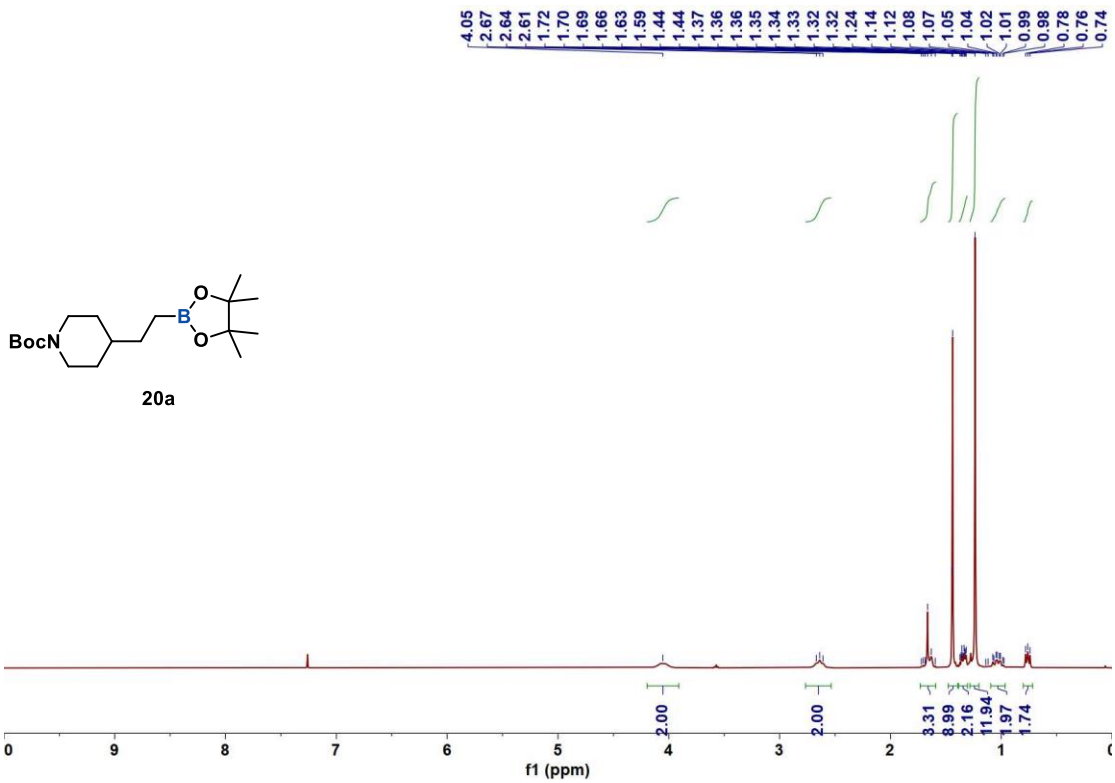


Figure S131. ^{1}H NMR spectrum of **20a** in $CDCl_3$ at 298K

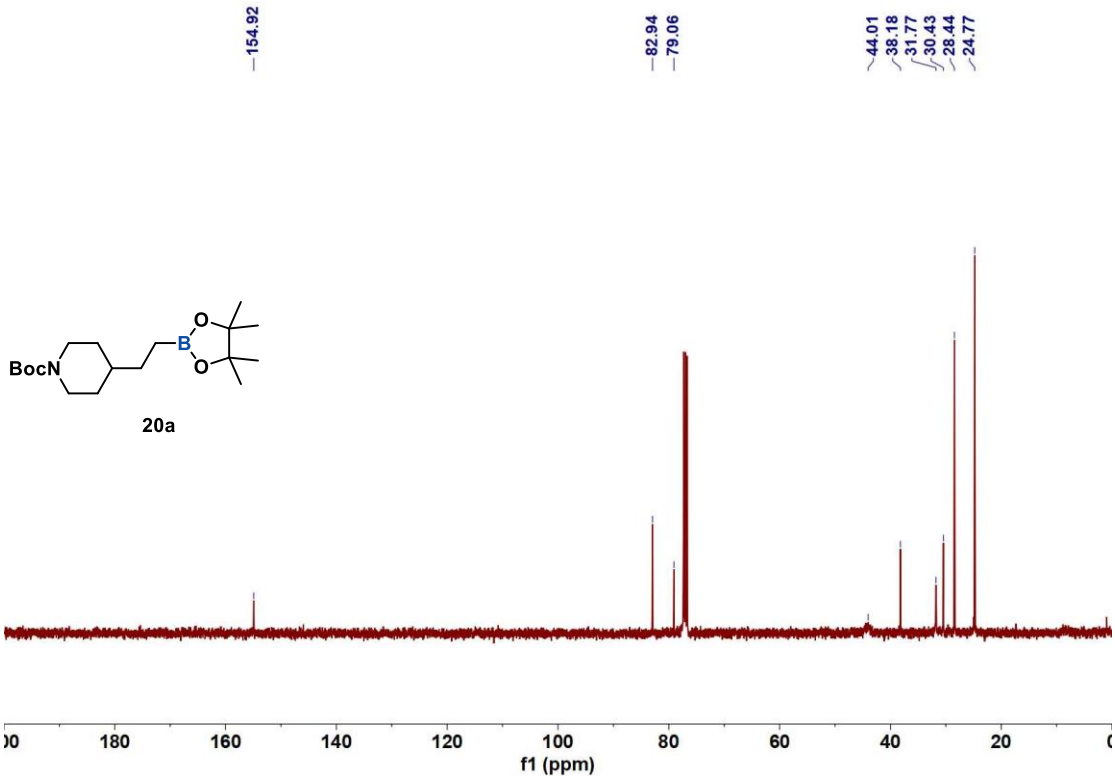


Figure S132. $^{13}C\{^{1}H\}$ NMR spectrum of **20a** in $CDCl_3$ at 298K

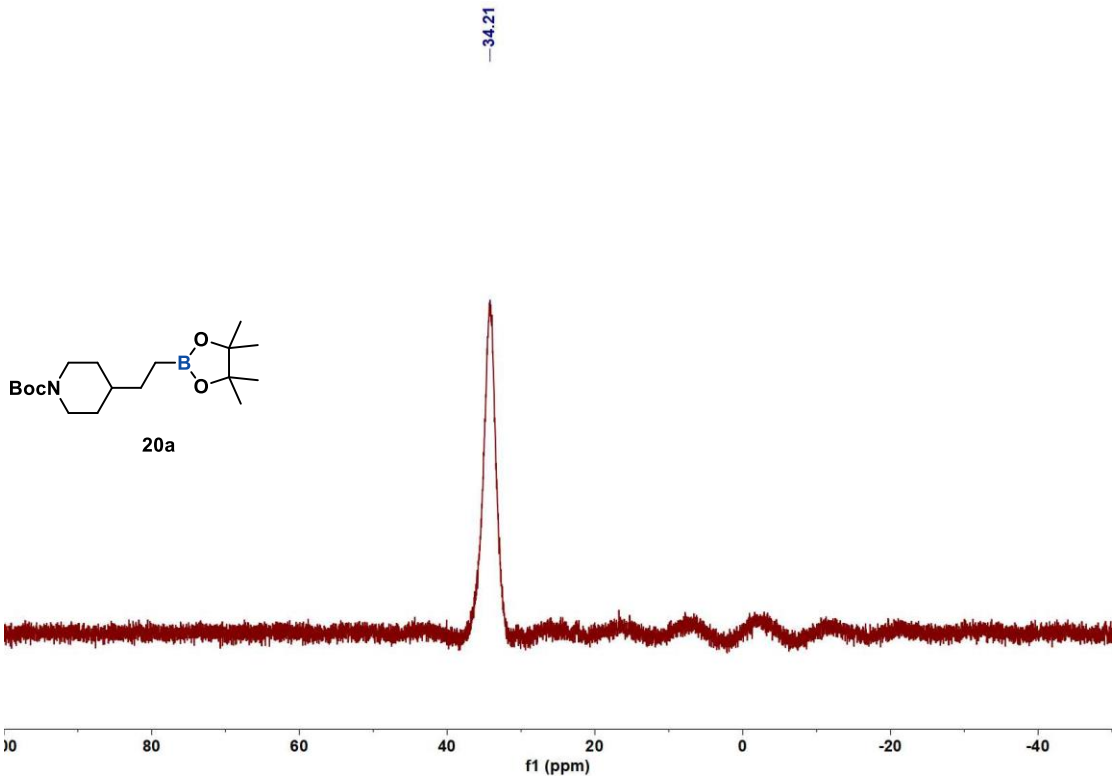


Figure S133. $^{11}B\{^{1}H\}$ NMR spectrum of **20a** in $CDCl_3$ at 298K

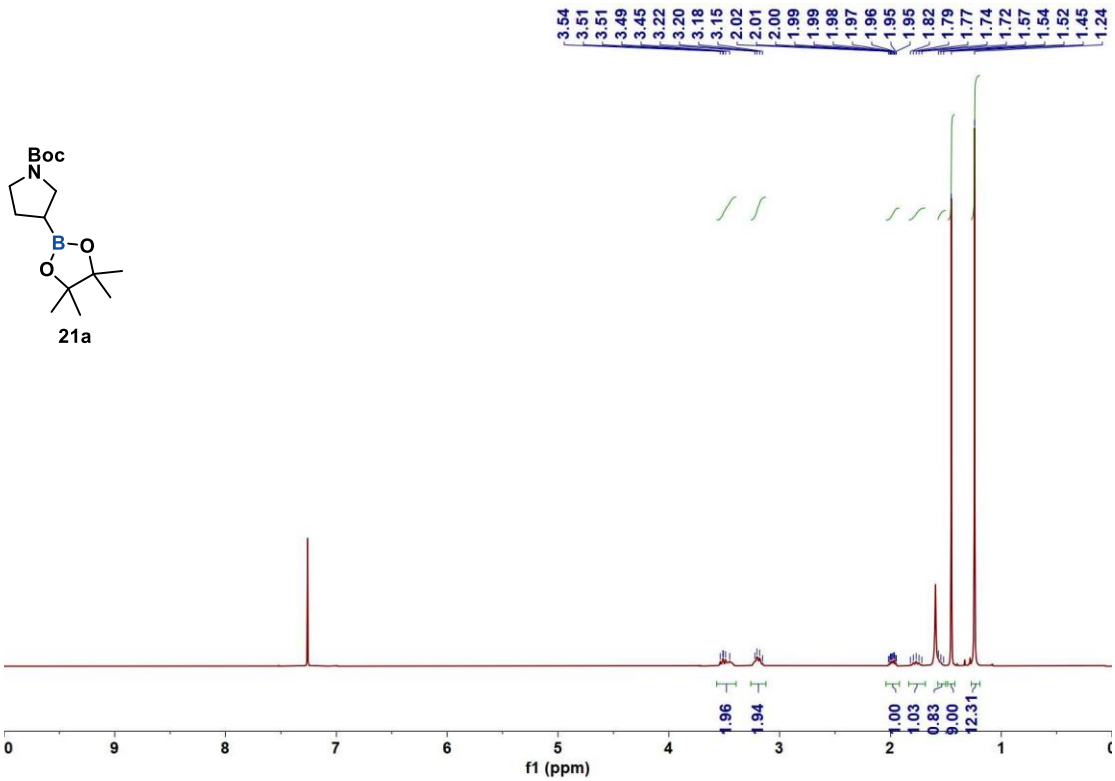


Figure S134. ^{1}H NMR spectrum of **21a** in $CDCl_3$ at 298K

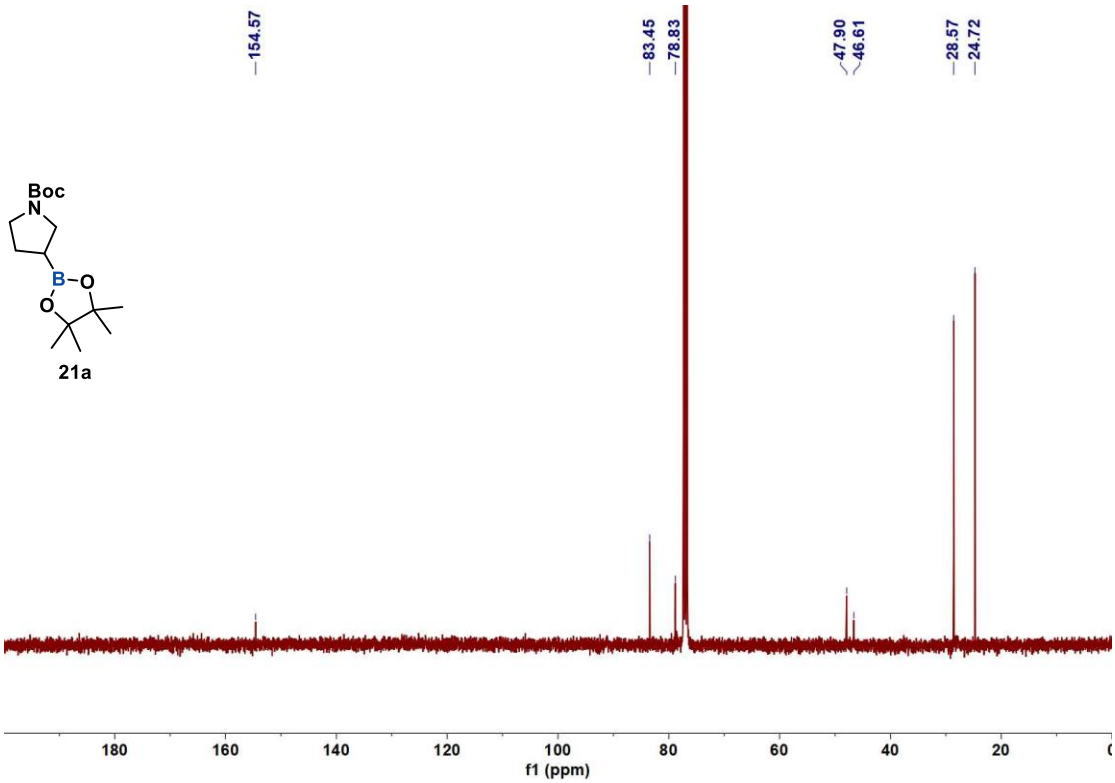


Figure S135. $^{13}C\{^{1}H\}$ NMR spectrum of **21a** in $CDCl_3$ at 298K

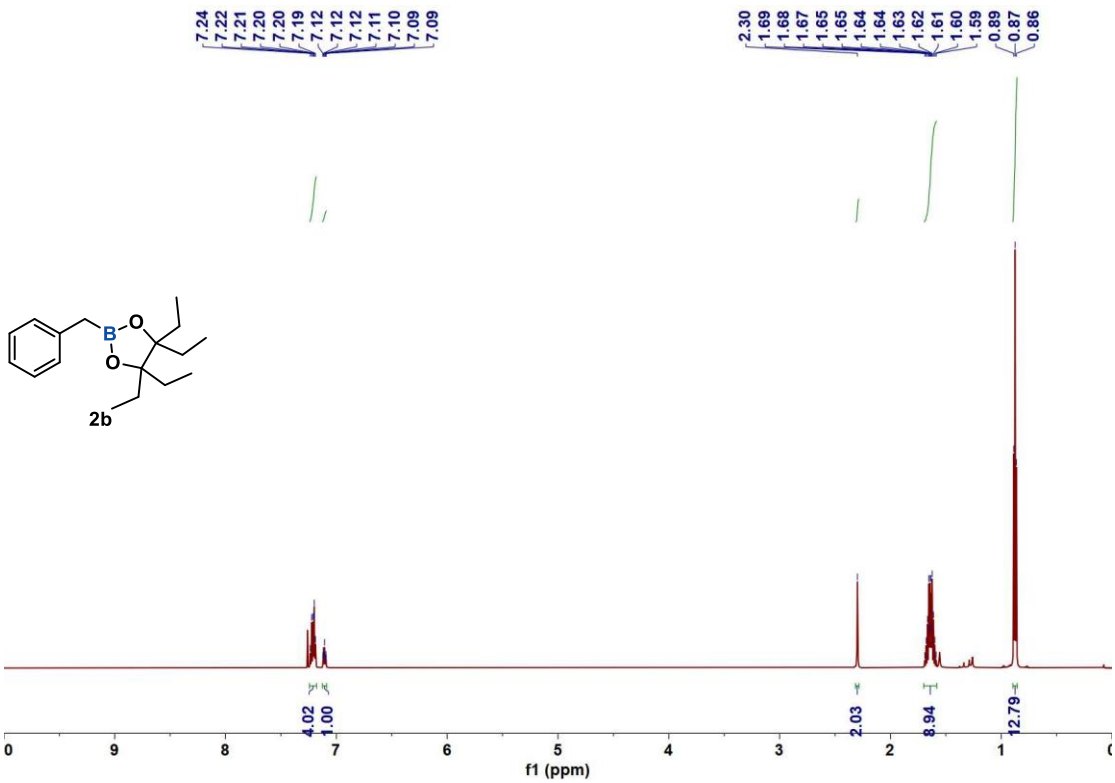


Figure S136. ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 298K

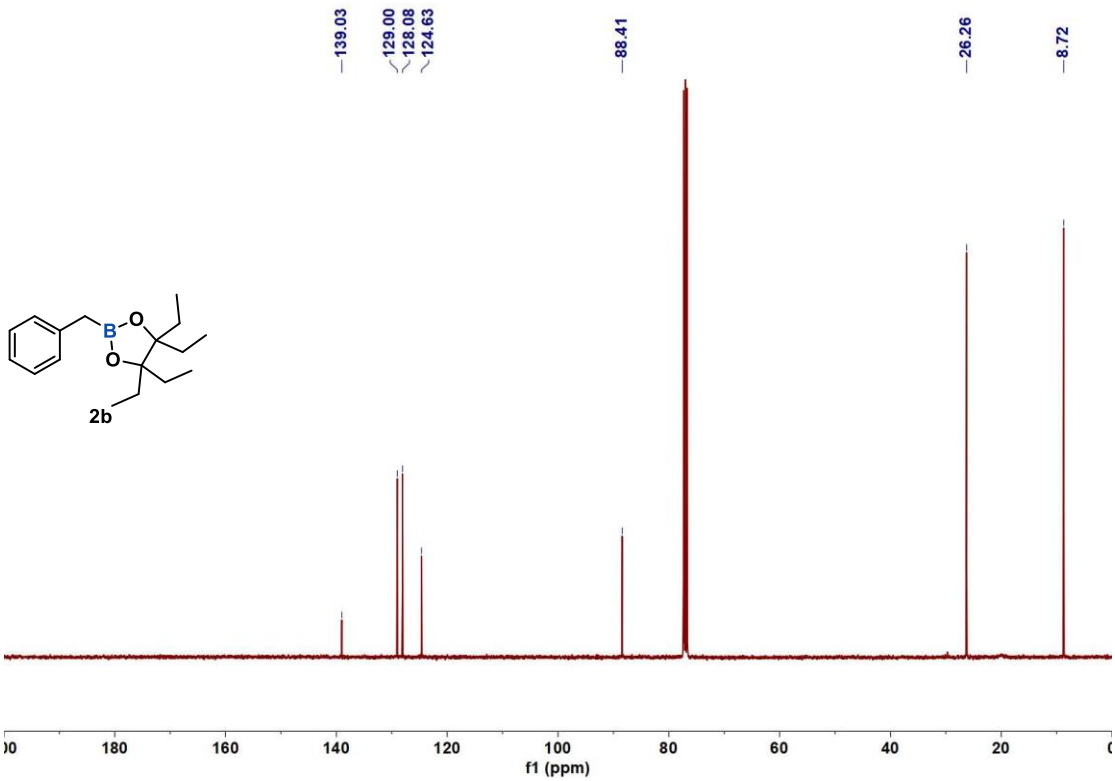


Figure S137. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$ at 298K

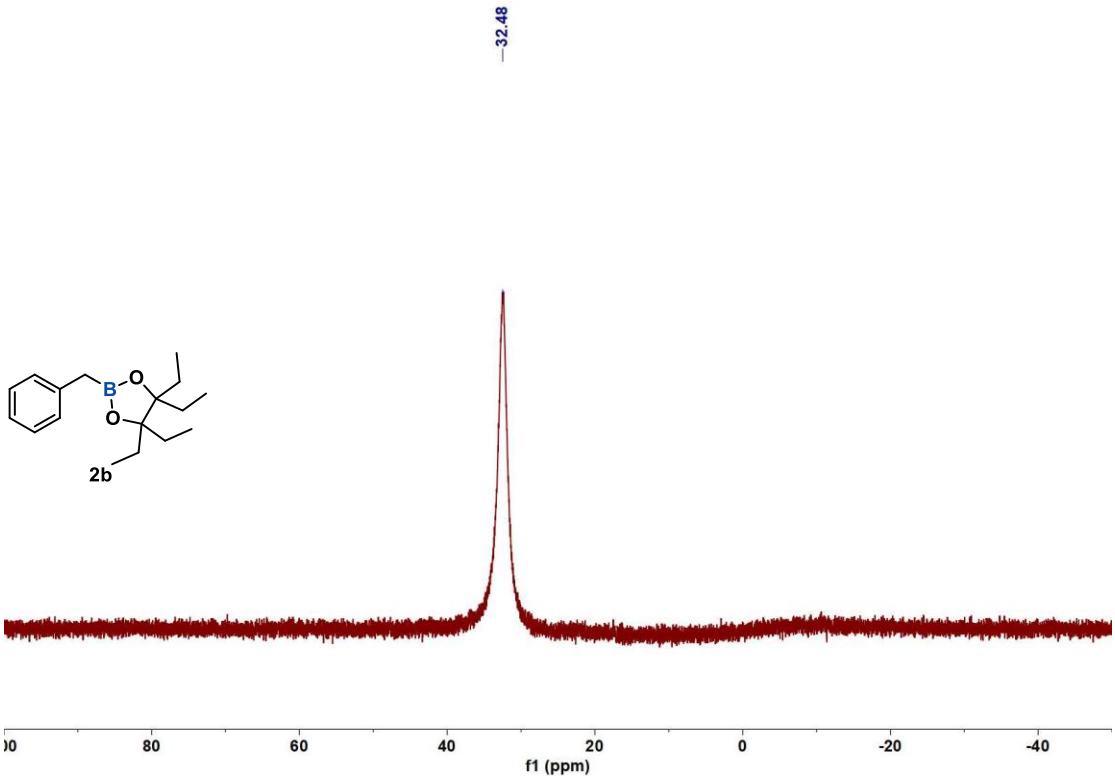


Figure S138. $^{11}B\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$ at 298K

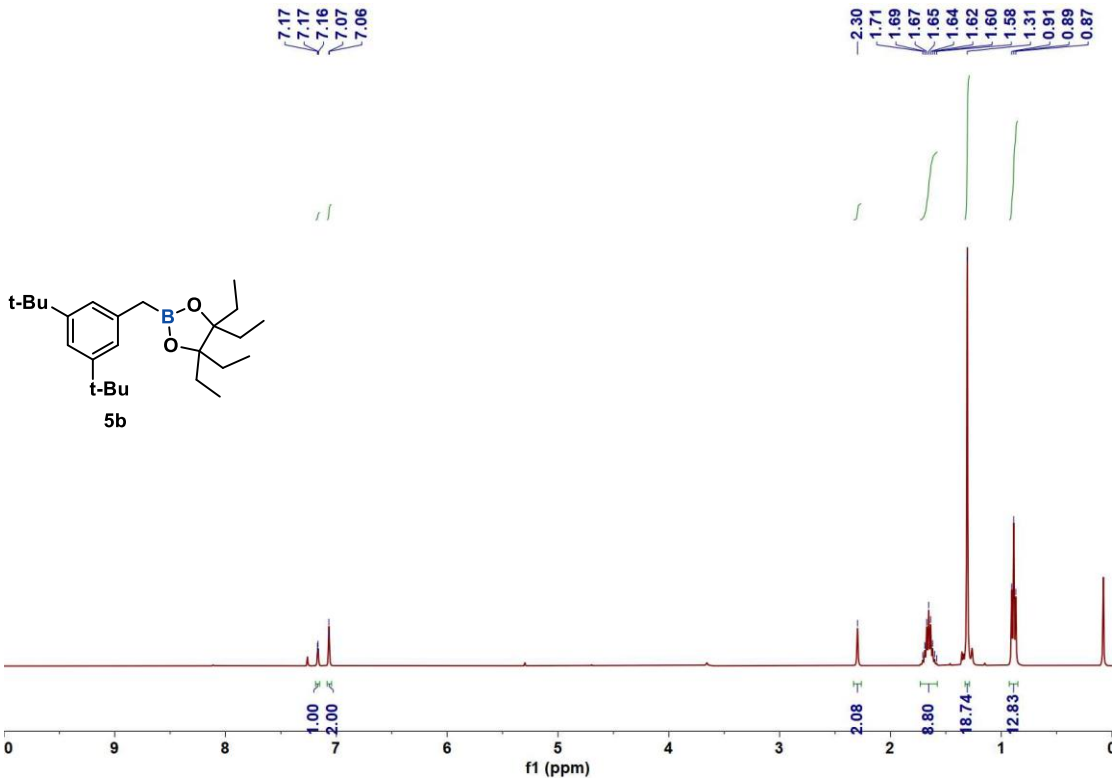


Figure S139. ^{1}H NMR spectrum of **5b** in $CDCl_3$ at 298K

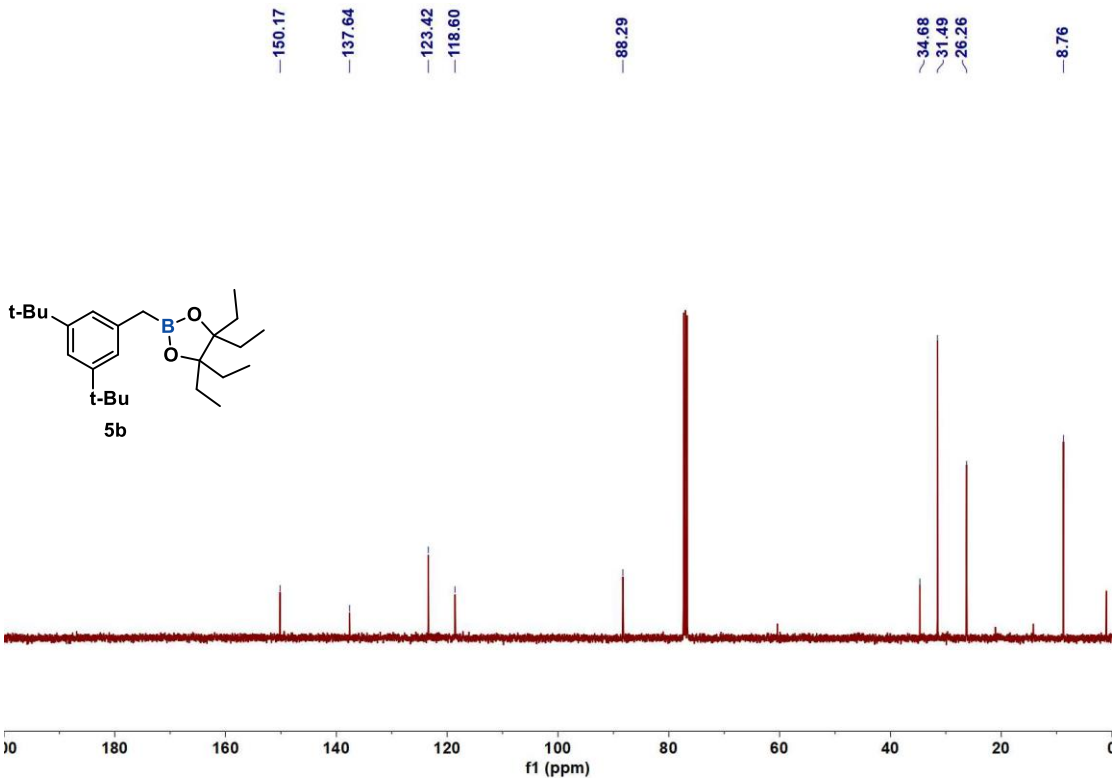


Figure S140. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$ at 298K

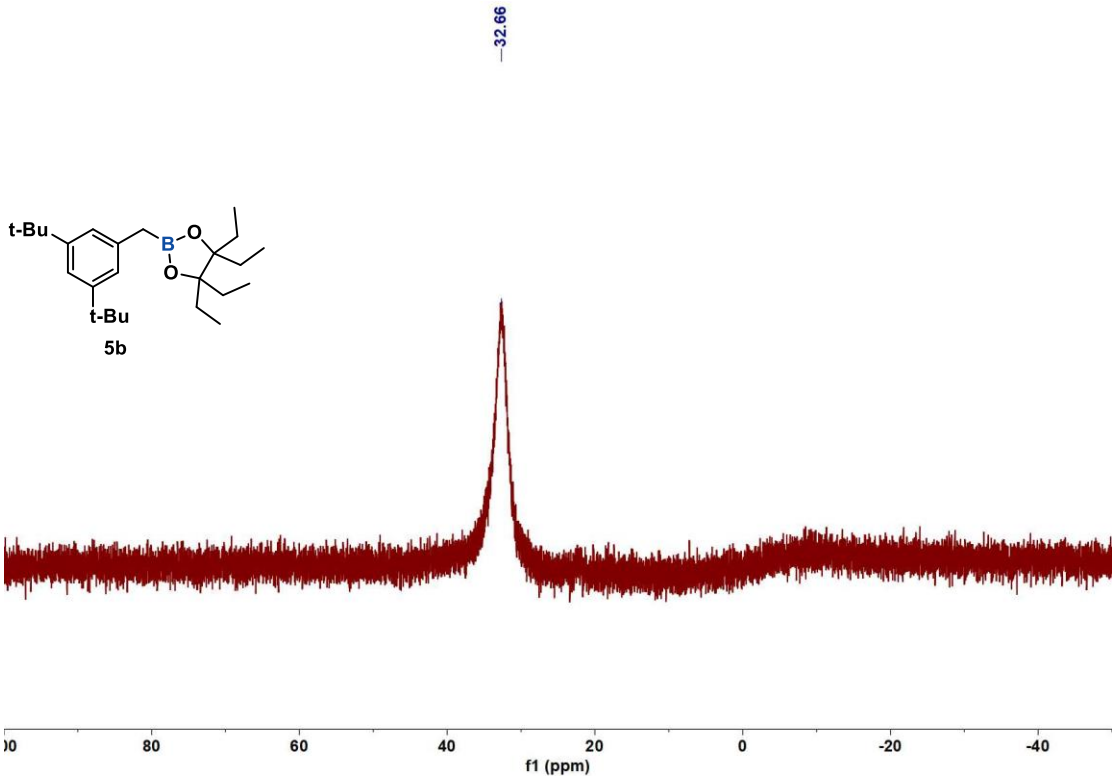


Figure S141. $^{11}B\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$ at 298K

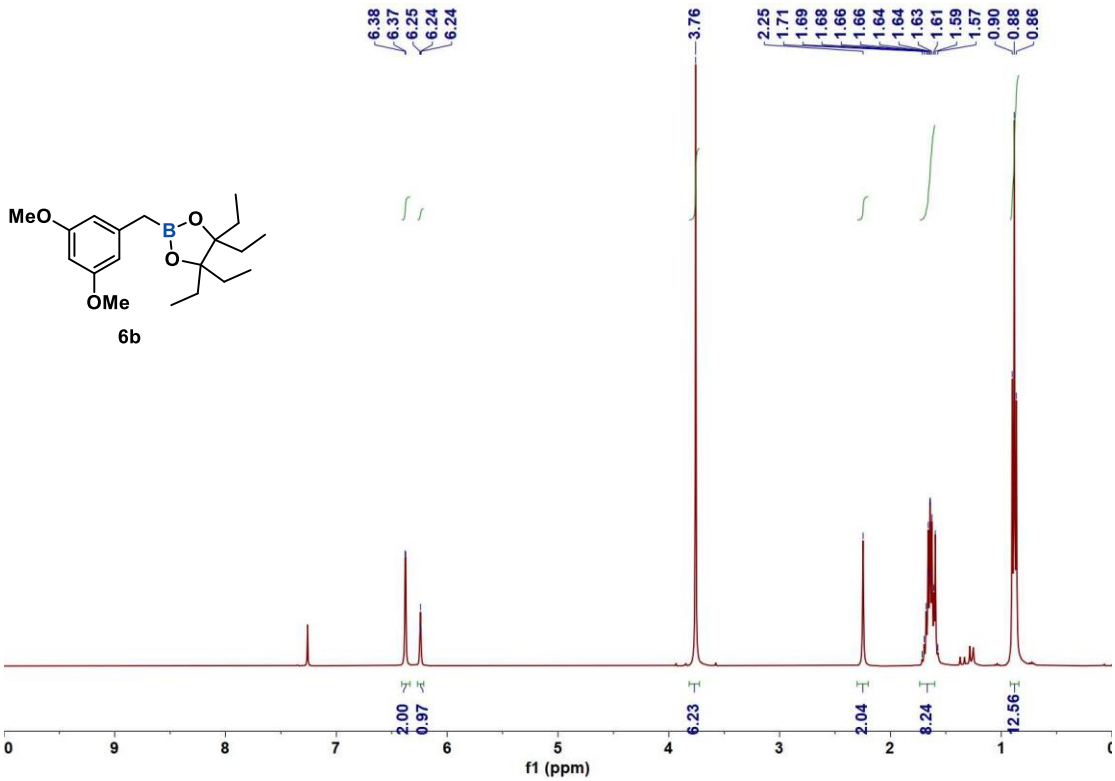


Figure S142. ^{1}H NMR spectrum of **6b** in $CDCl_3$ at 298K

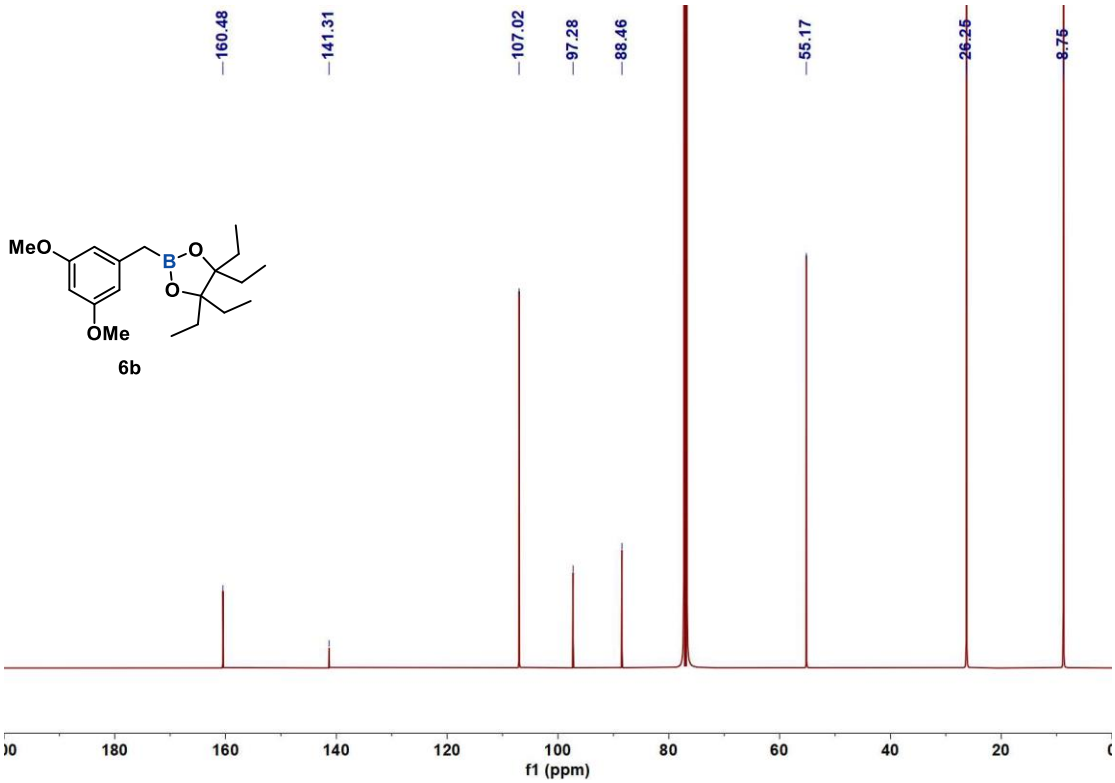


Figure S143. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** in $CDCl_3$ at 298K

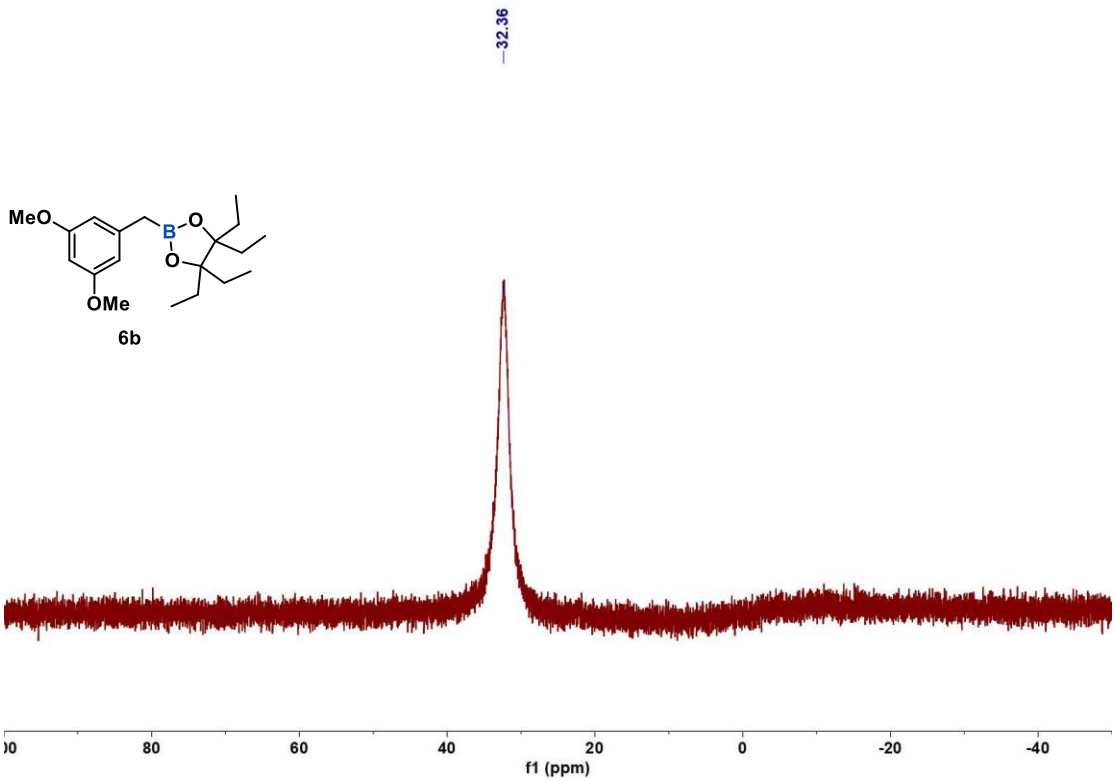


Figure S144. $^{11}B\{^{1}H\}$ NMR spectrum of **6b** in $CDCl_3$ at 298K

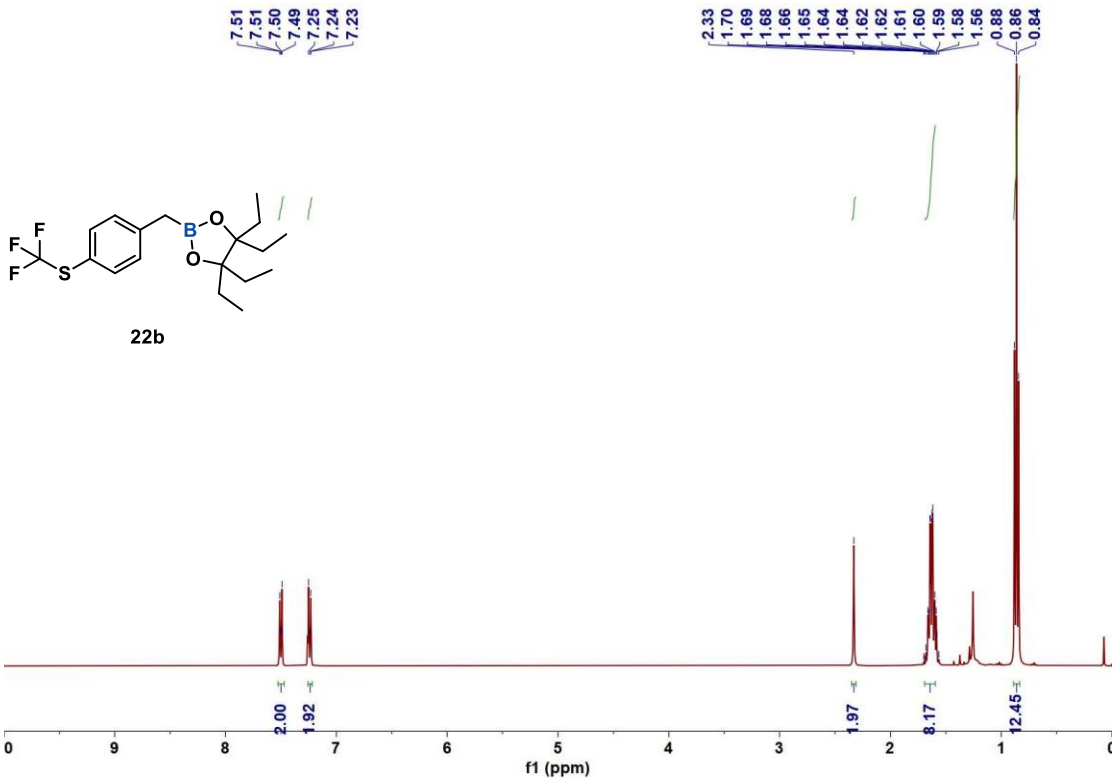


Figure S145. ^{1}H NMR spectrum of **22b** in $CDCl_3$ at 298K

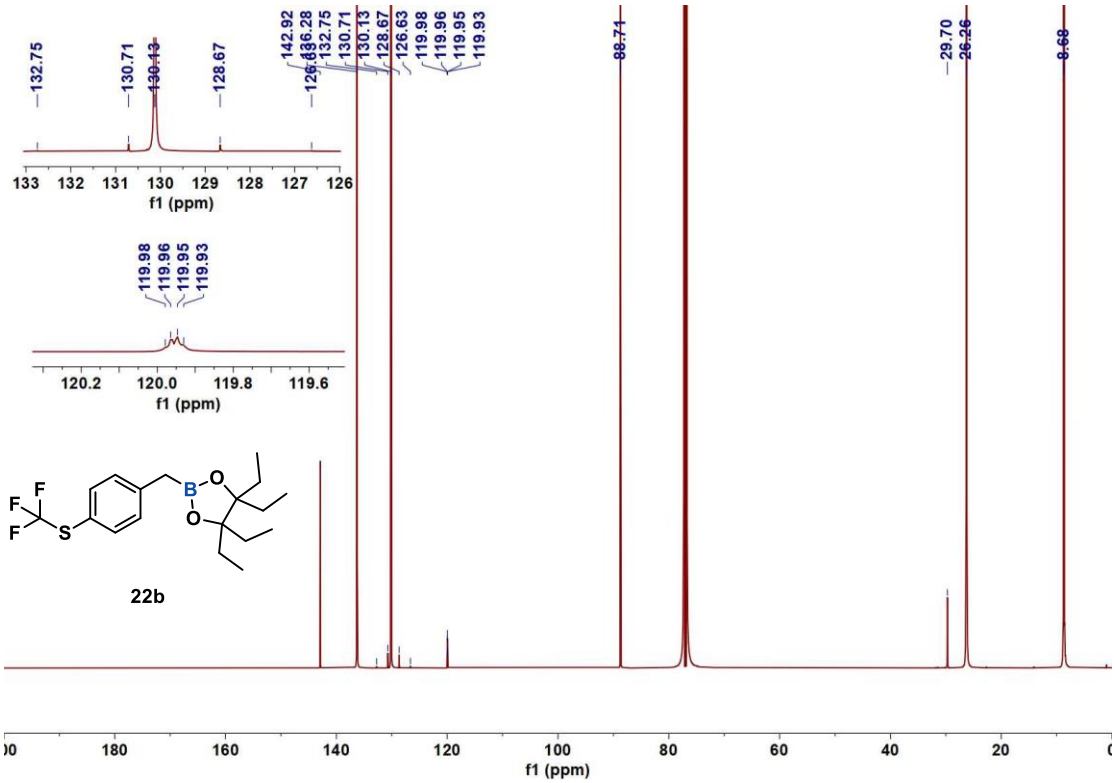


Figure S146. $^{13}C\{^{1}H\}$ NMR spectrum of **22b** in $CDCl_3$ at 298K

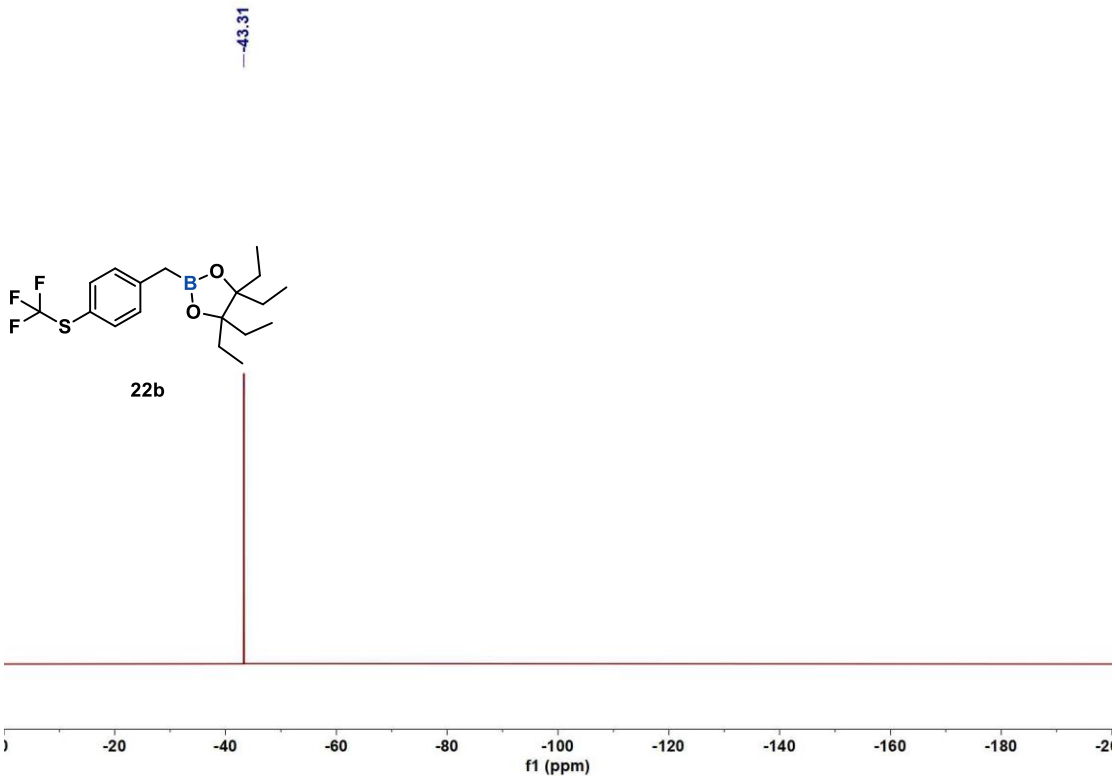


Figure S147. $^{19}F\{^{1}H\}$ NMR spectrum of **22b** in $CDCl_3$ at 298K

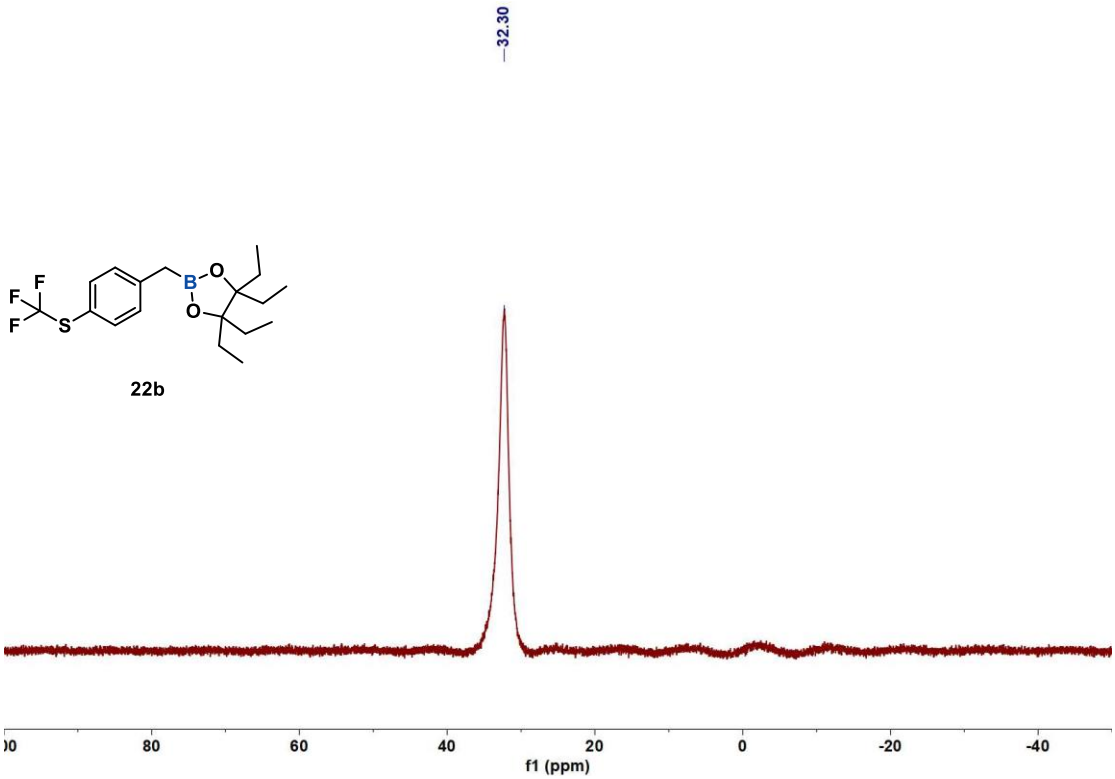


Figure S148. $^{11}B\{^{1}H\}$ NMR spectrum of **22b** in $CDCl_3$ at 298K

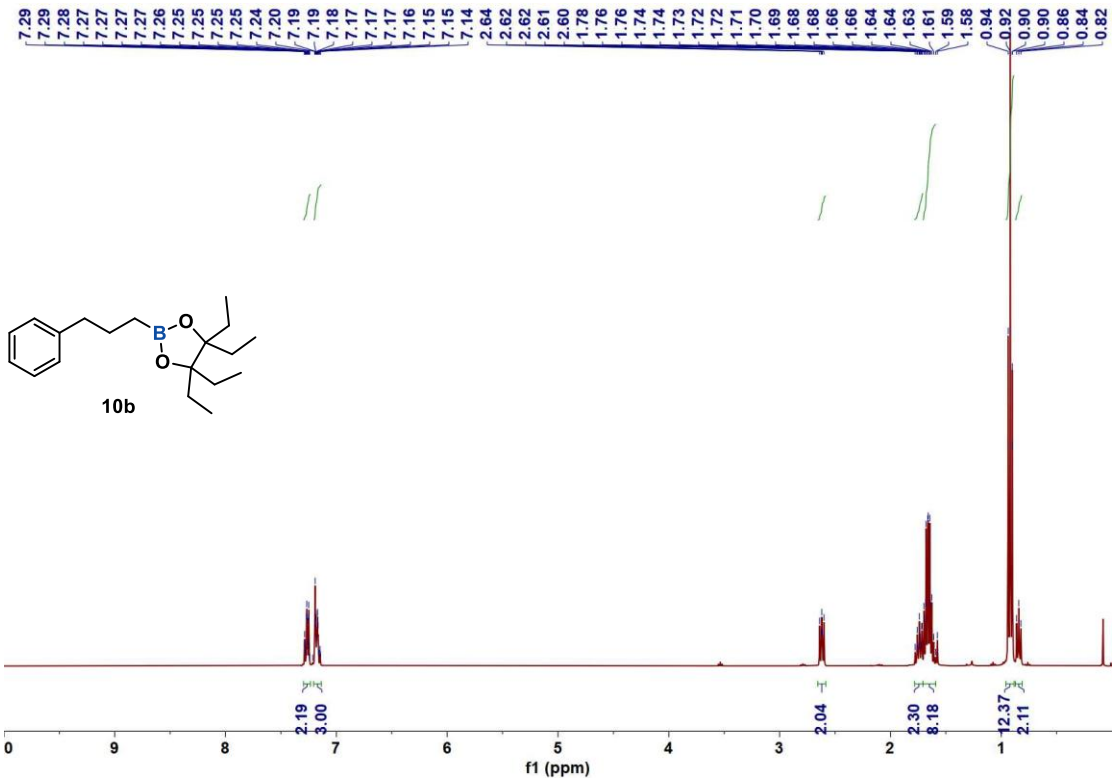


Figure S149. ^{1}H NMR spectrum of **10b** in $CDCl_3$ at 298K

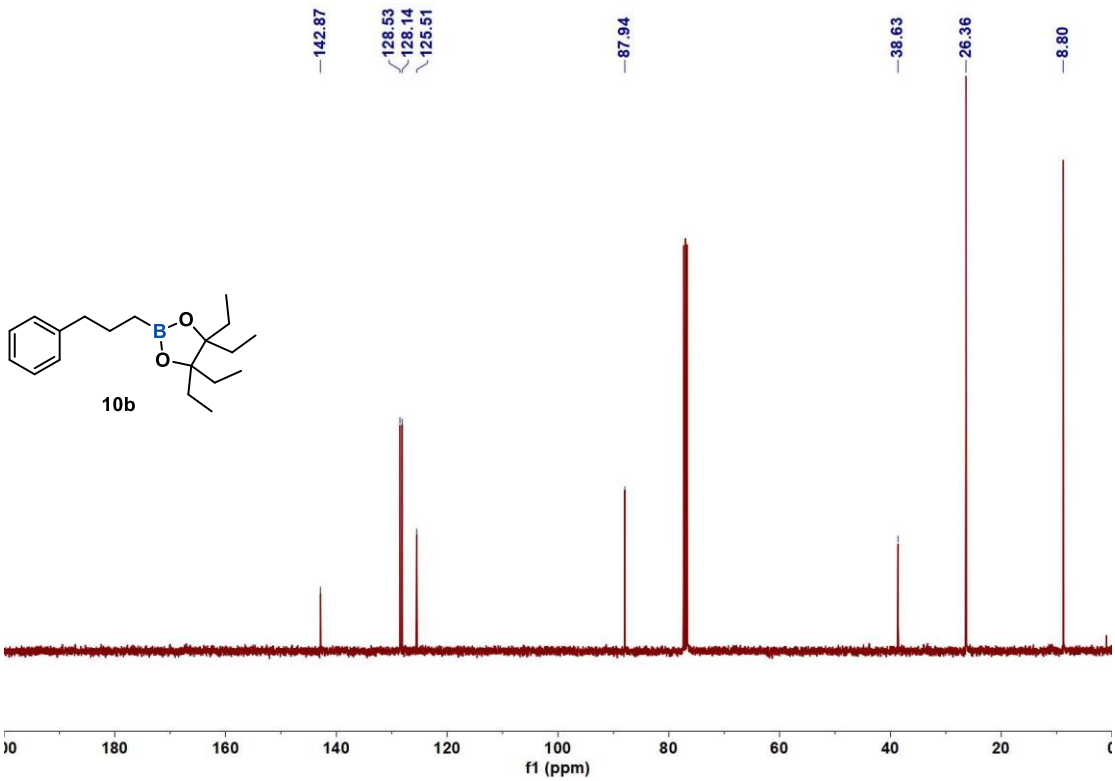


Figure S150. $^{13}C\{^{1}H\}$ NMR spectrum of **10b** in $CDCl_3$ at 298K

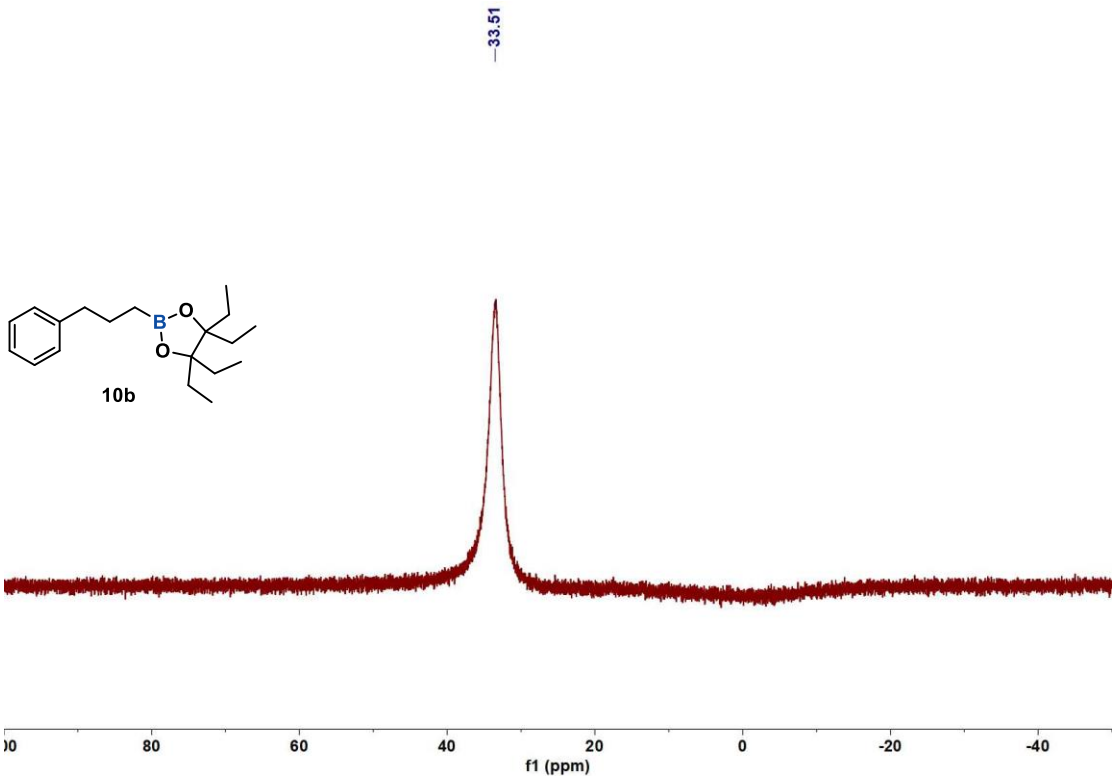


Figure S151. $^{11}B\{^{1}H\}$ NMR spectrum of **10b** in $CDCl_3$ at 298K

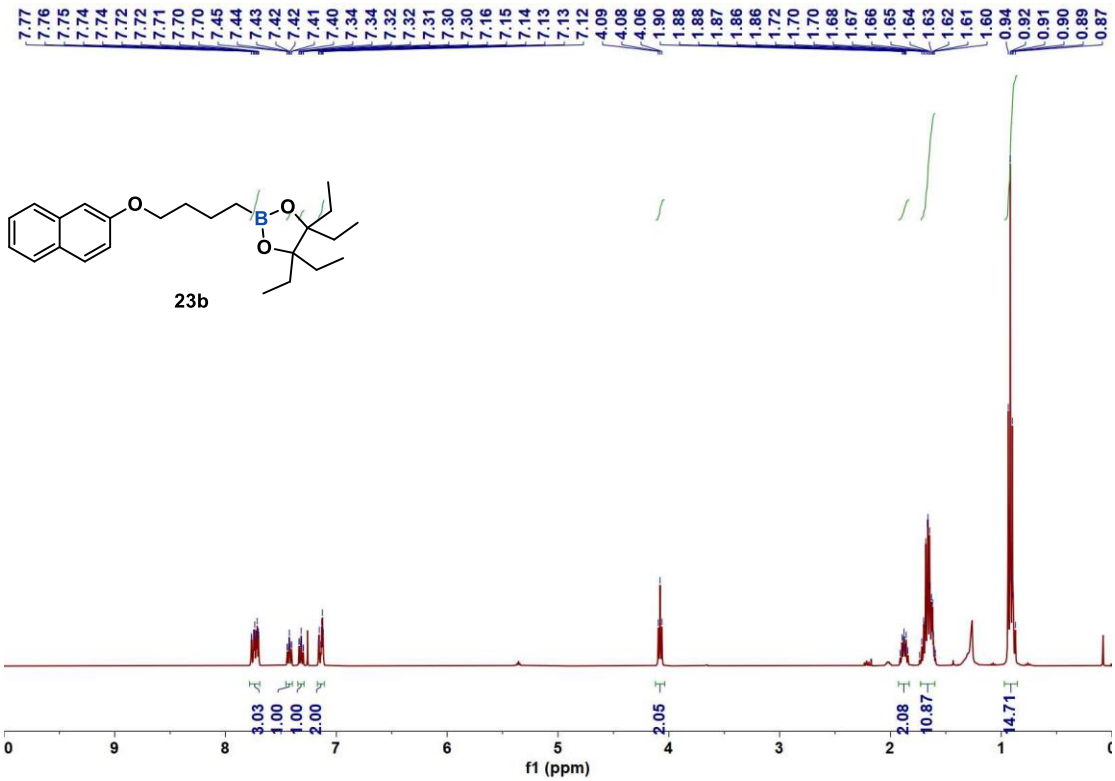


Figure S152. ^{1}H NMR spectrum of **23b** in $CDCl_3$ at 298K

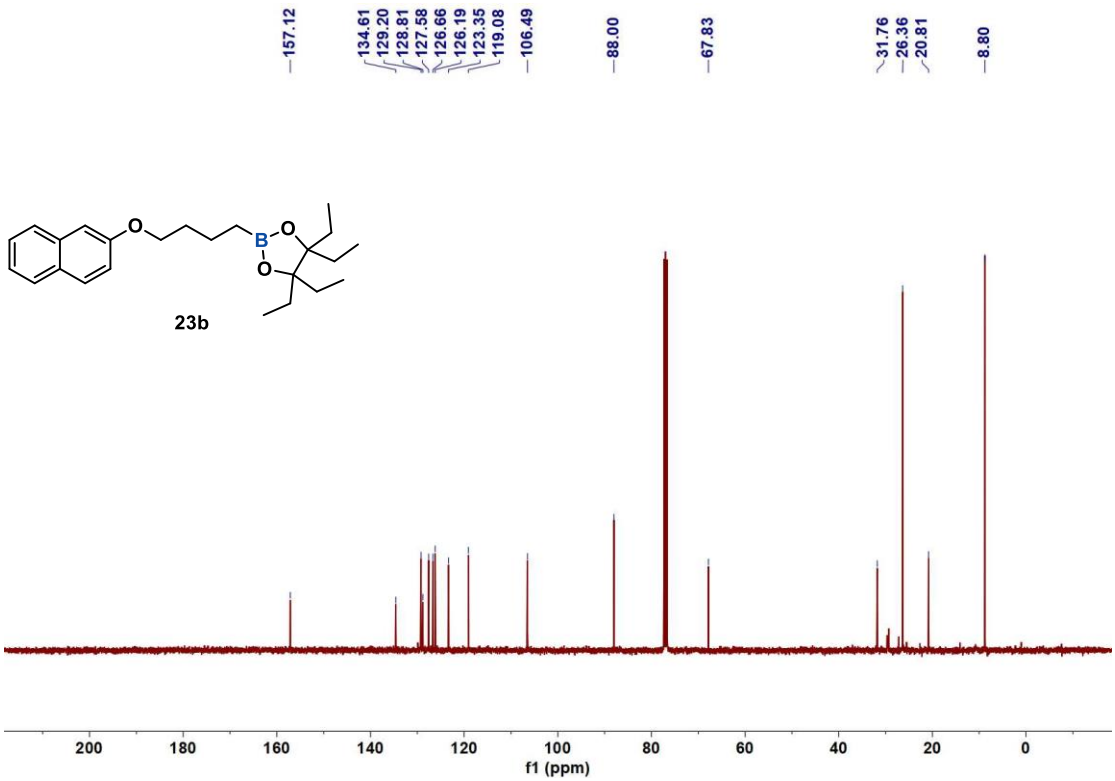


Figure S153. $^{13}C\{^{1}H\}$ NMR spectrum of **23b** in $CDCl_3$ at 298K

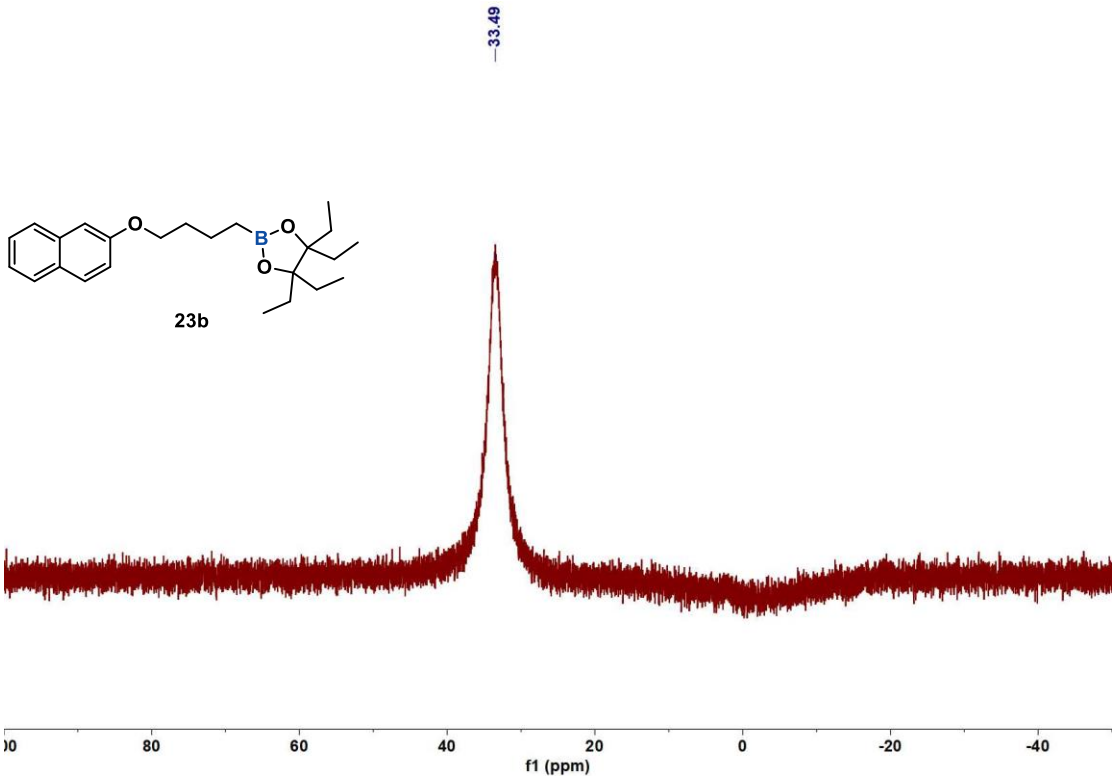


Figure S154. $^{11}B\{^{1}H\}$ NMR spectrum of **23b** in $CDCl_3$ at 298K

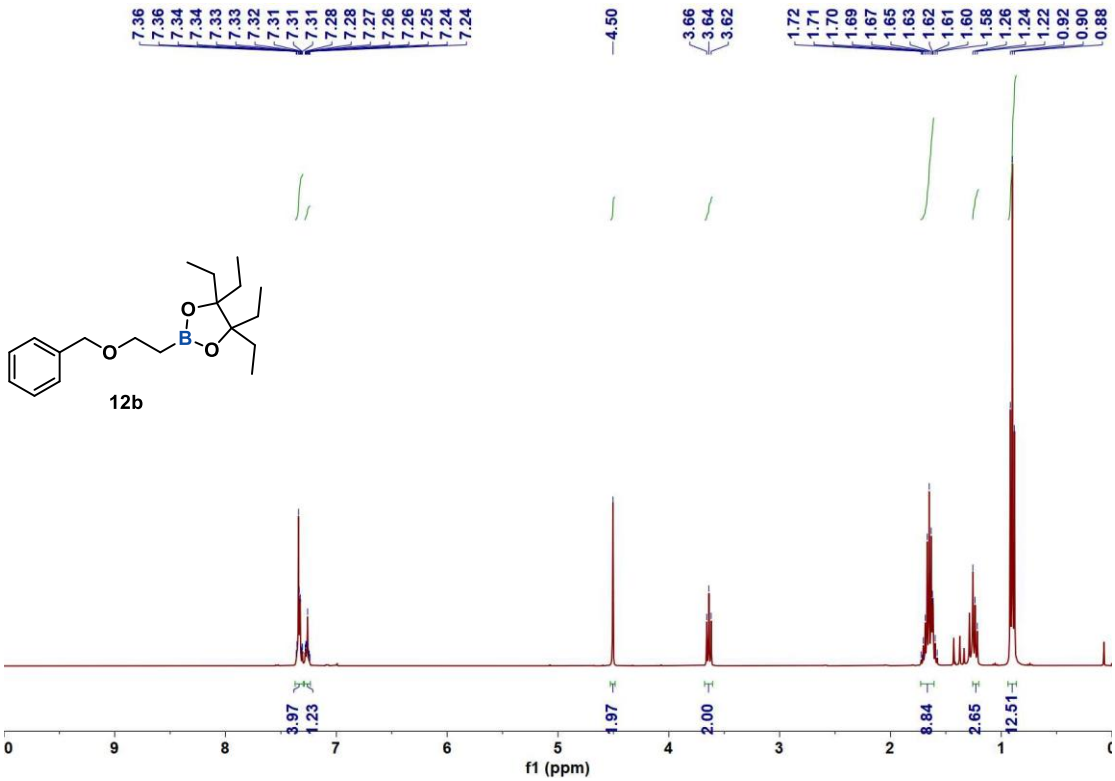


Figure S155. ^{1}H NMR spectrum of **12b** in $CDCl_3$ at 298K

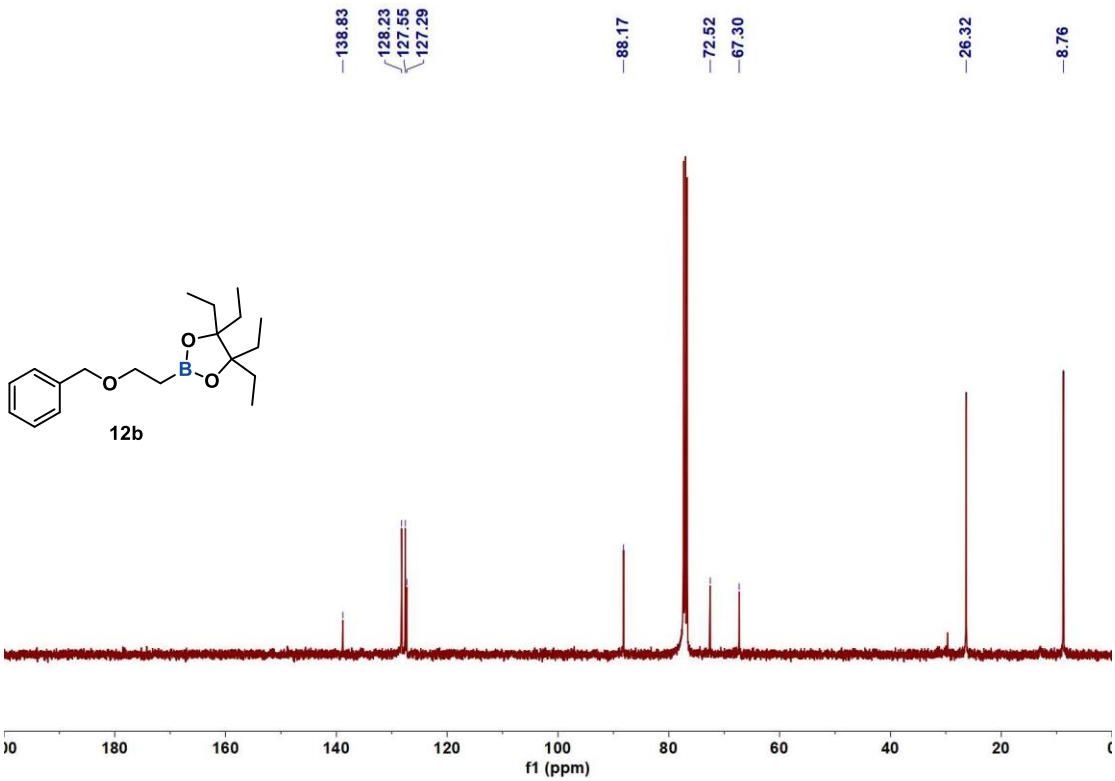


Figure S156. $^{13}C\{^{1}H\}$ NMR spectrum of **12b** in $CDCl_3$ at 298K

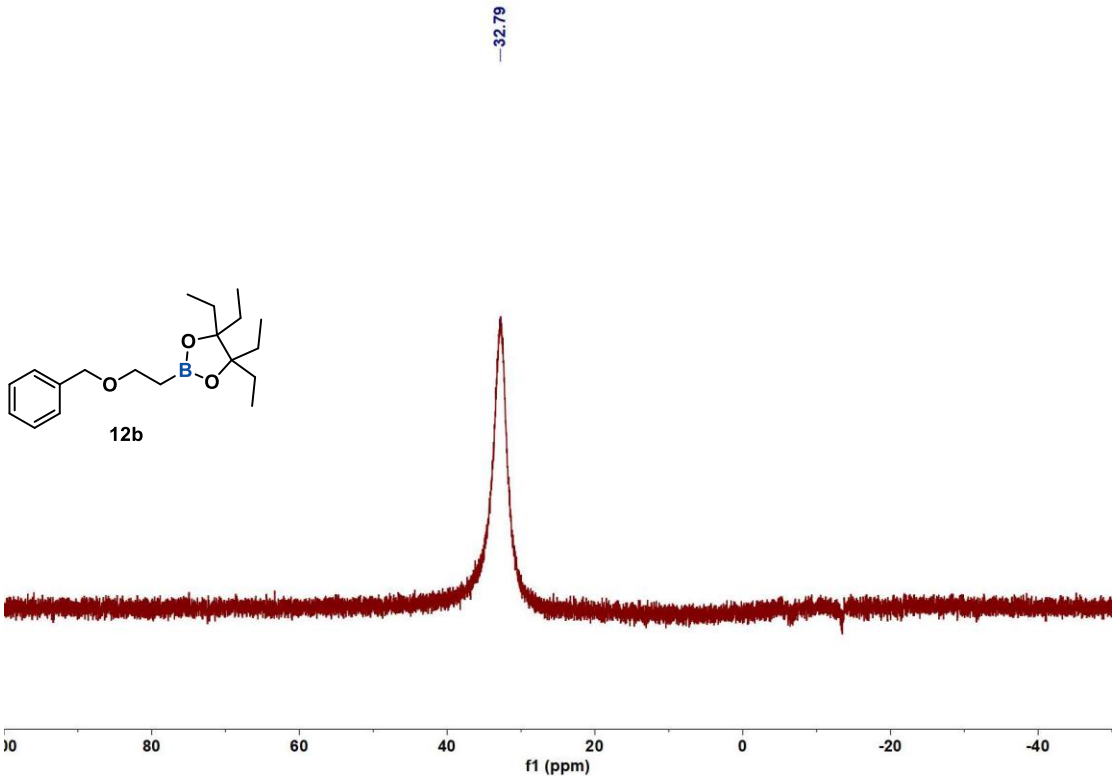


Figure S157. $^{11}B\{^{1}H\}$ NMR spectrum of **12b** in $CDCl_3$ at 298K

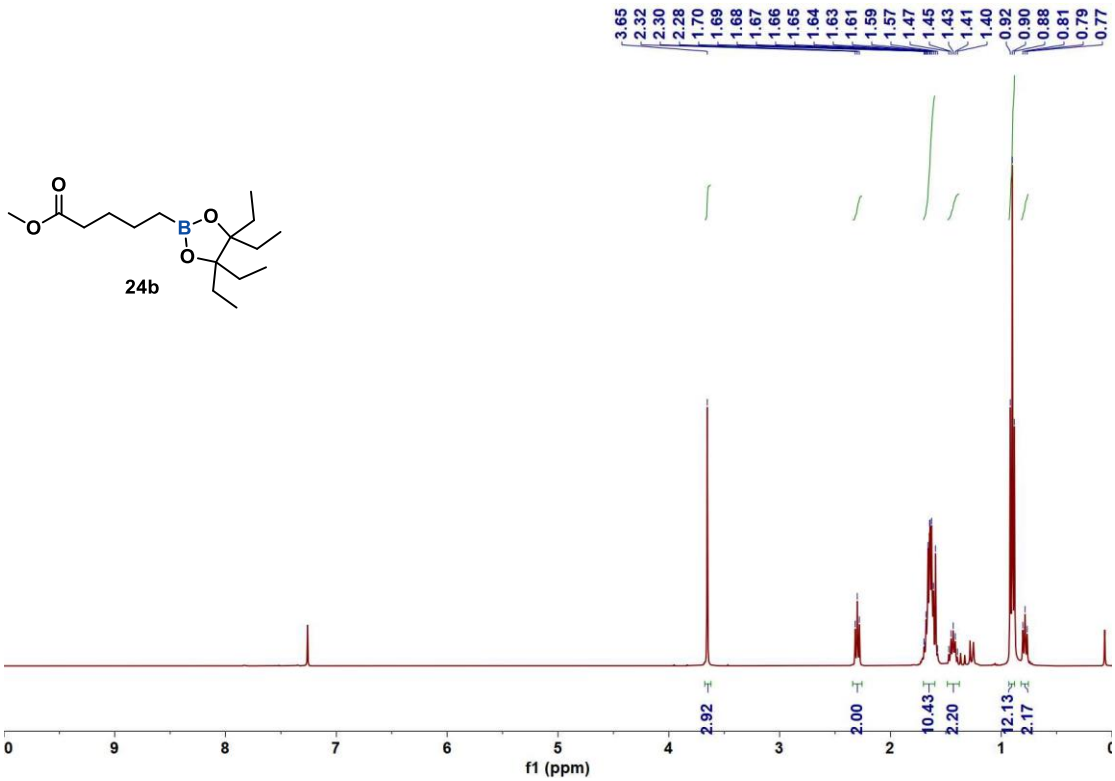


Figure S158. ^{1}H NMR spectrum of **24b** in $CDCl_3$ at 298K

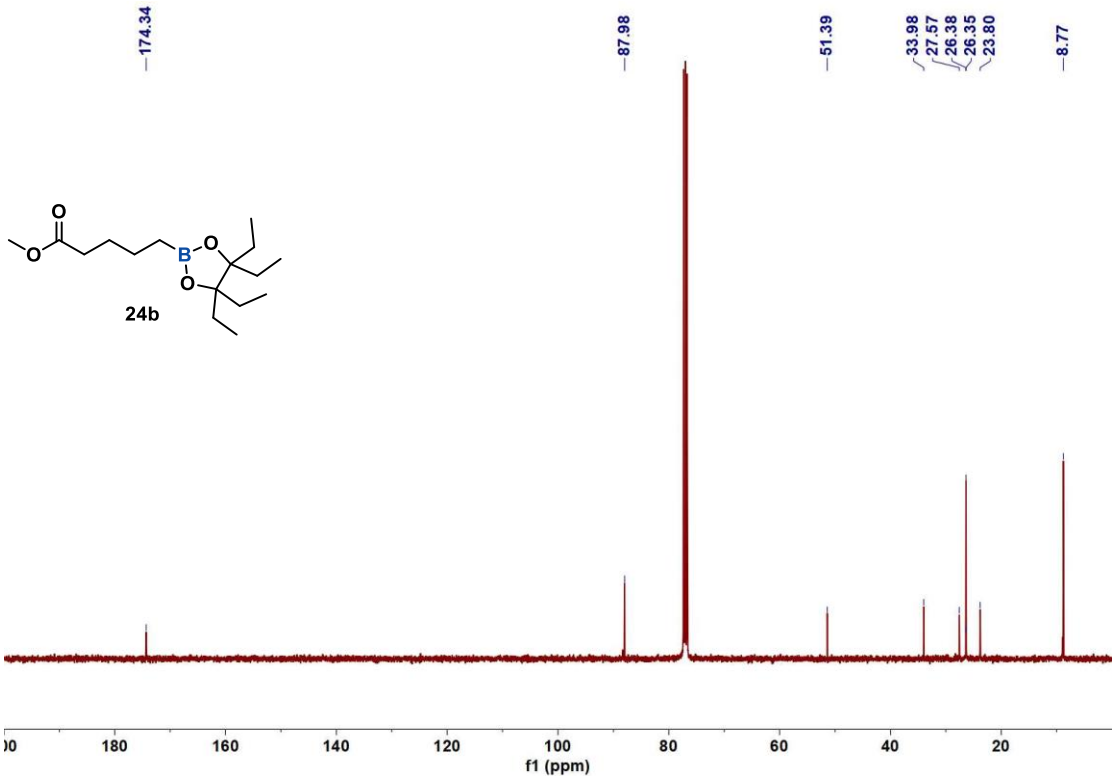


Figure S159. $^{13}C\{^{1}H\}$ NMR spectrum of **24b** in $CDCl_3$ at 298K

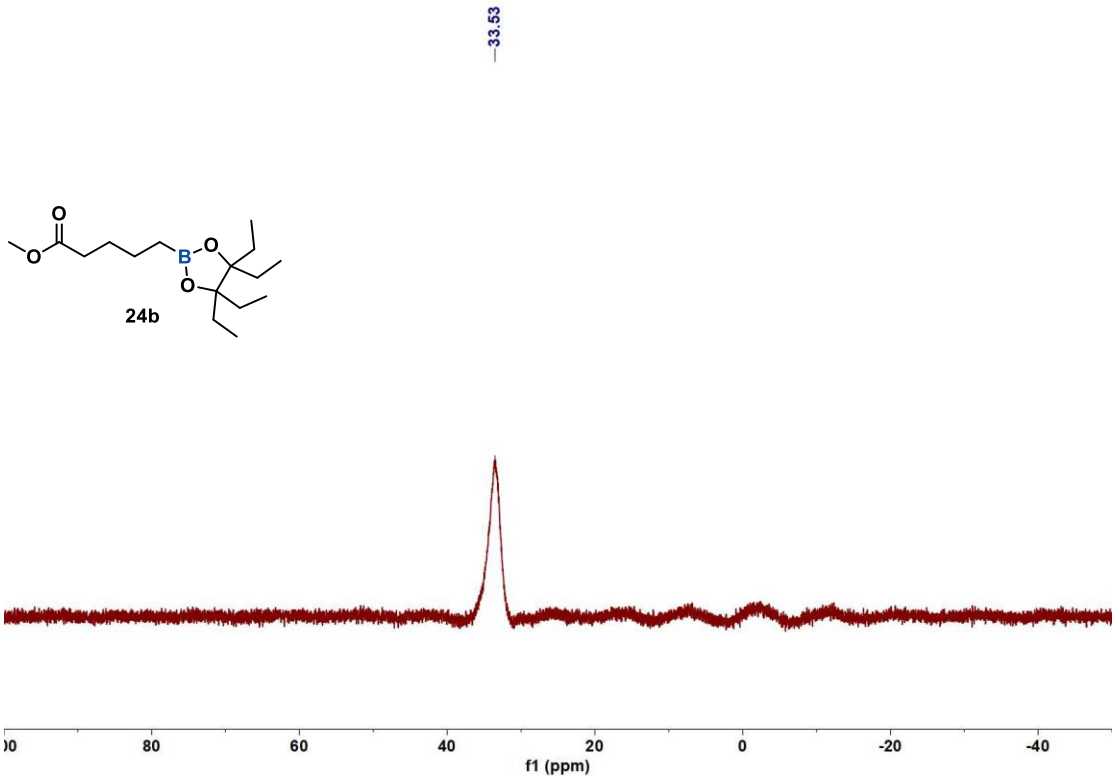


Figure S160. $^{11}B\{^{1}H\}$ NMR spectrum of **24b** in $CDCl_3$ at 298K

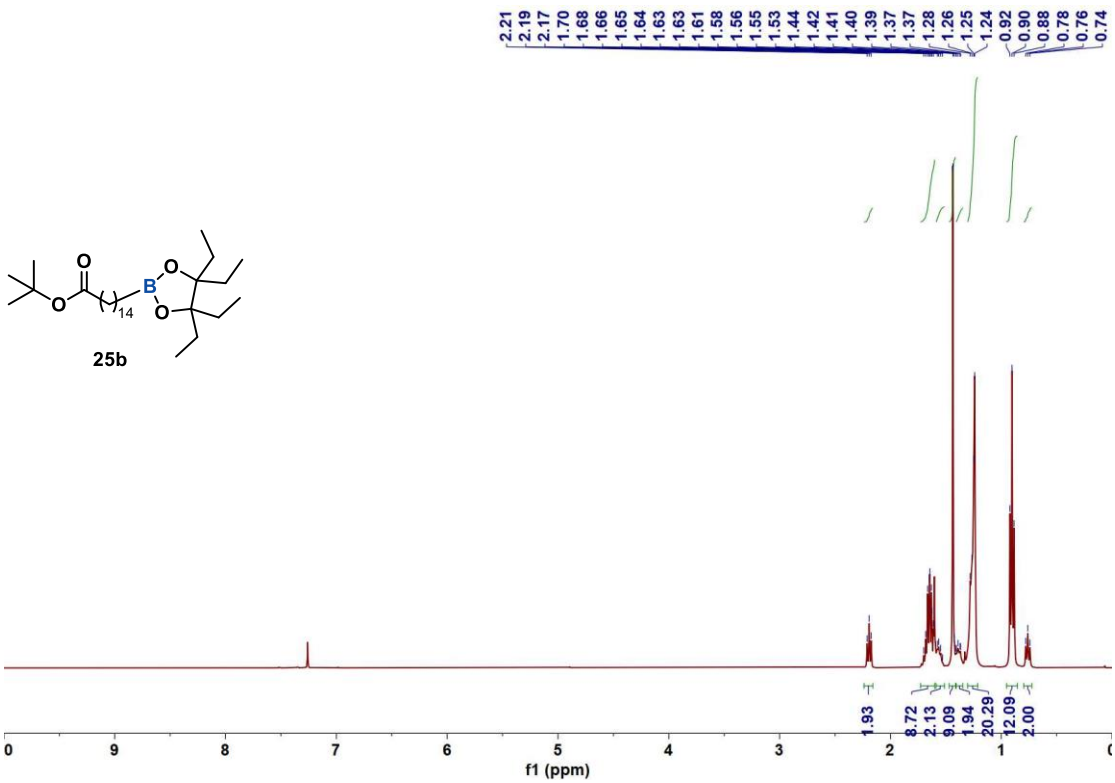


Figure S161. ^{1}H NMR spectrum of **25b** in $CDCl_3$ at 298K

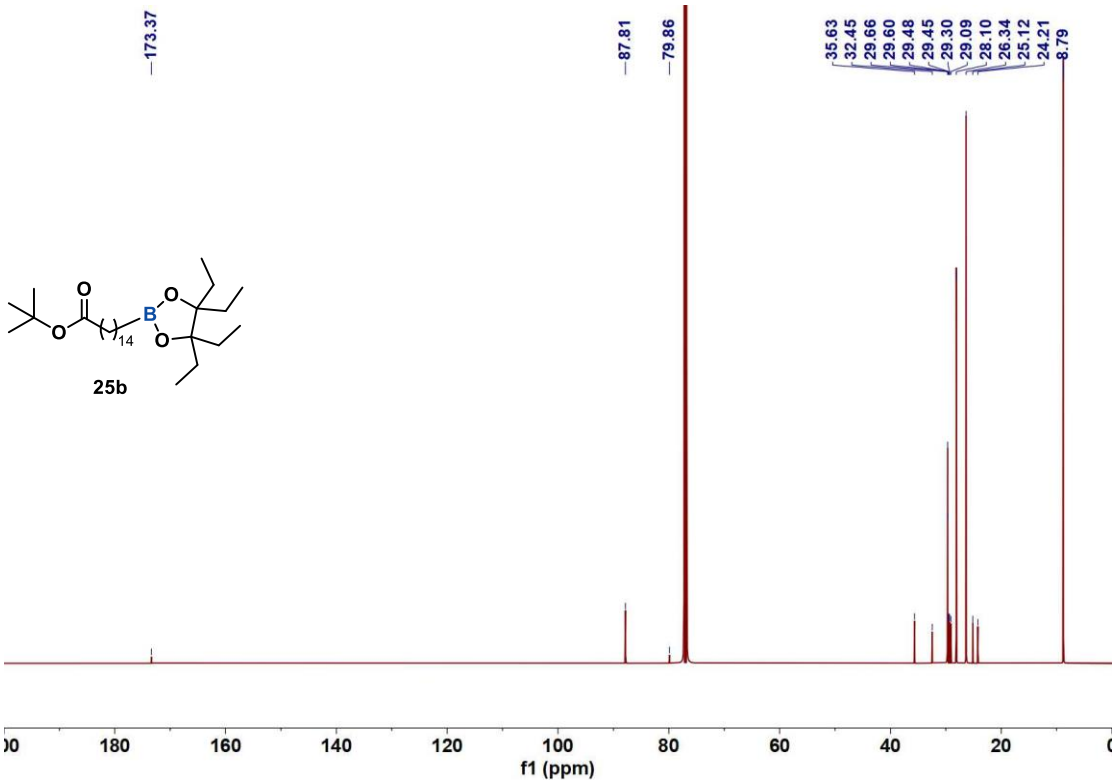


Figure S162. $^{13}C\{^{1}H\}$ NMR spectrum of **25b** in $CDCl_3$ at 298K

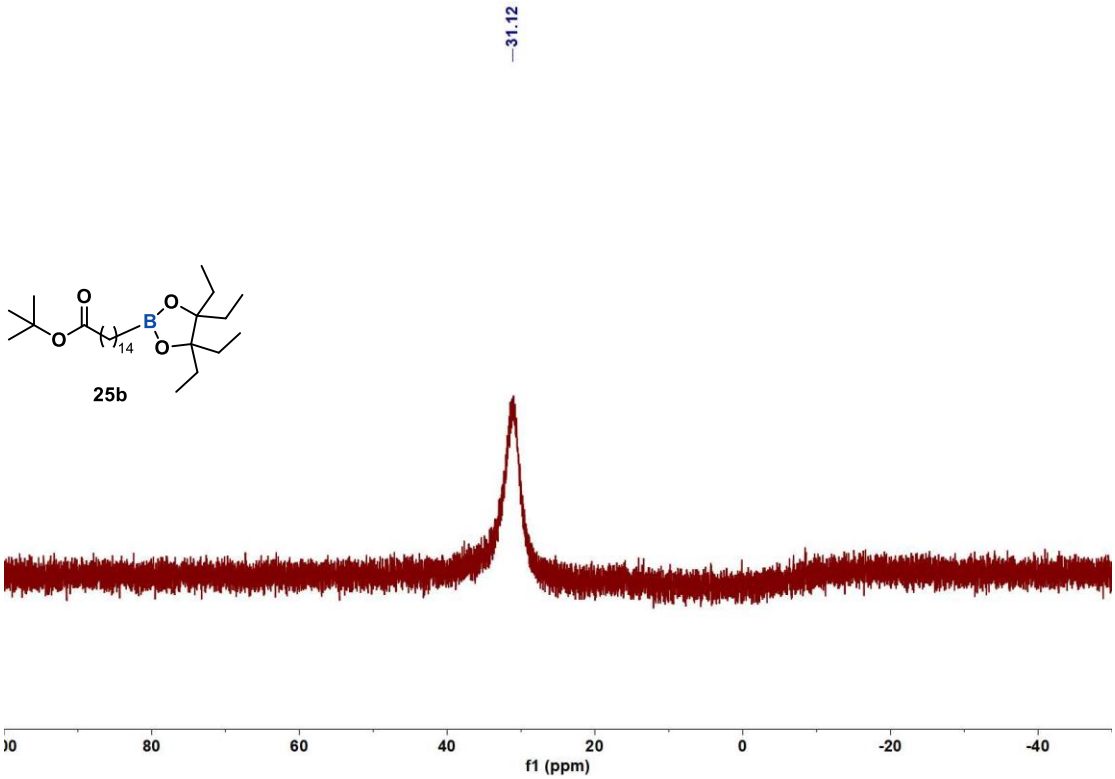


Figure S163. $^{11}B\{^{1}H\}$ NMR spectrum of **25b** in $CDCl_3$ at 298K

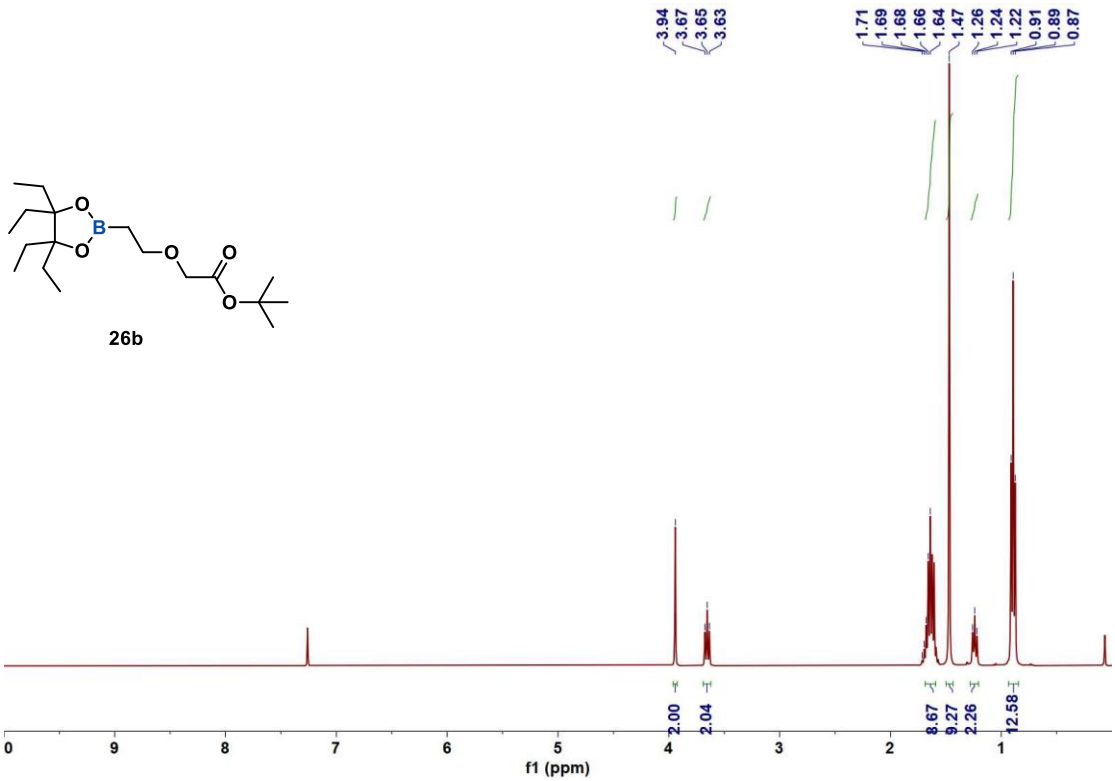


Figure S164. ^{1}H NMR spectrum of **26b** in $CDCl_3$ at 298K

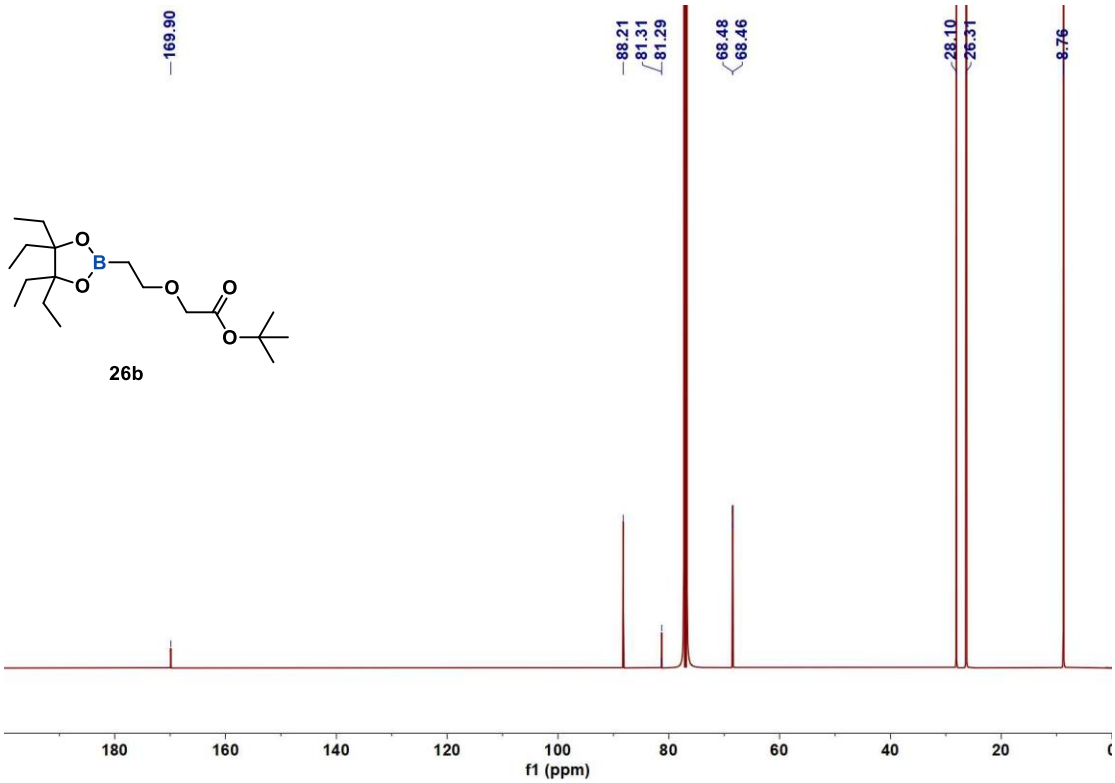


Figure S165. $^{13}C\{^{1}H\}$ NMR spectrum of **26b** in $CDCl_3$ at 298K

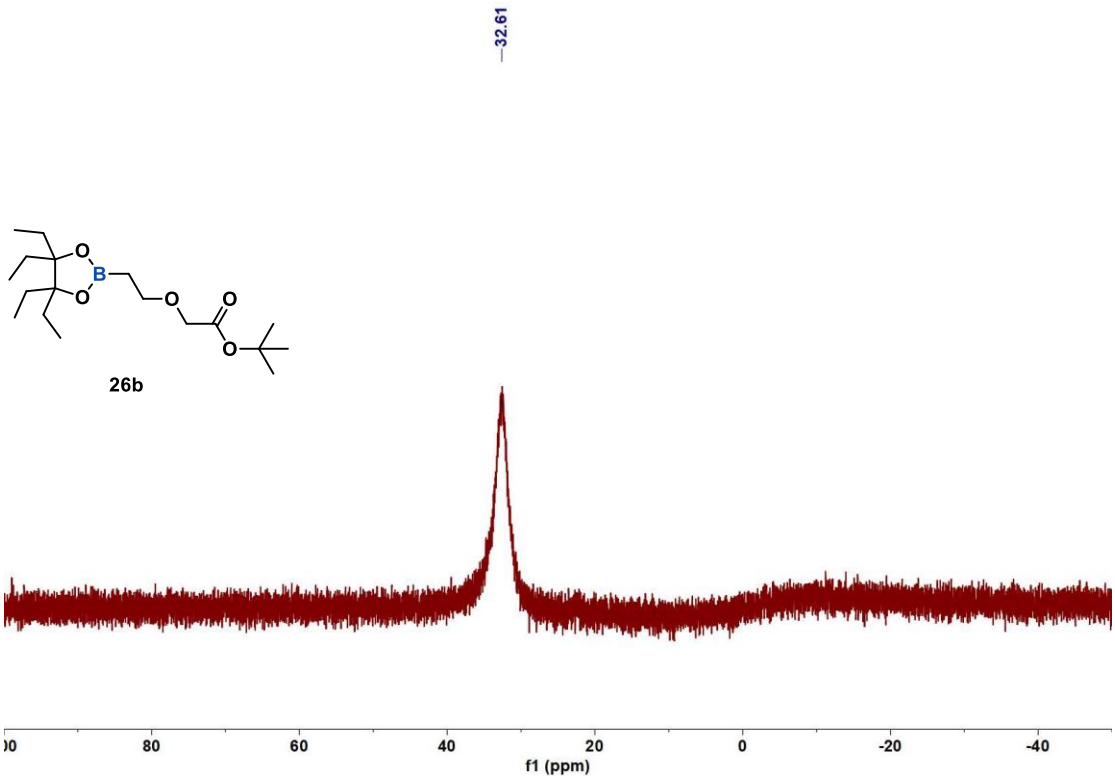


Figure S166. $^{11}B\{^{1}H\}$ NMR spectrum of **26b** in $CDCl_3$ at 298K

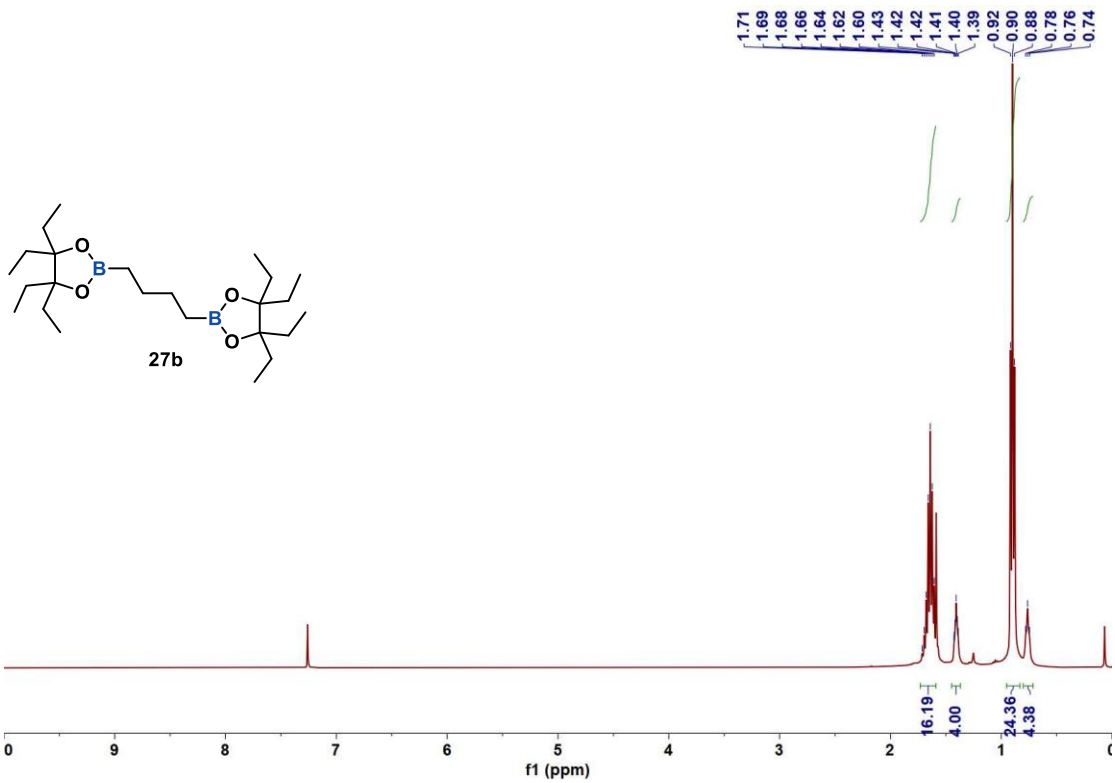


Figure S167. ^{1}H NMR spectrum of **27b** in $CDCl_3$ at 298K

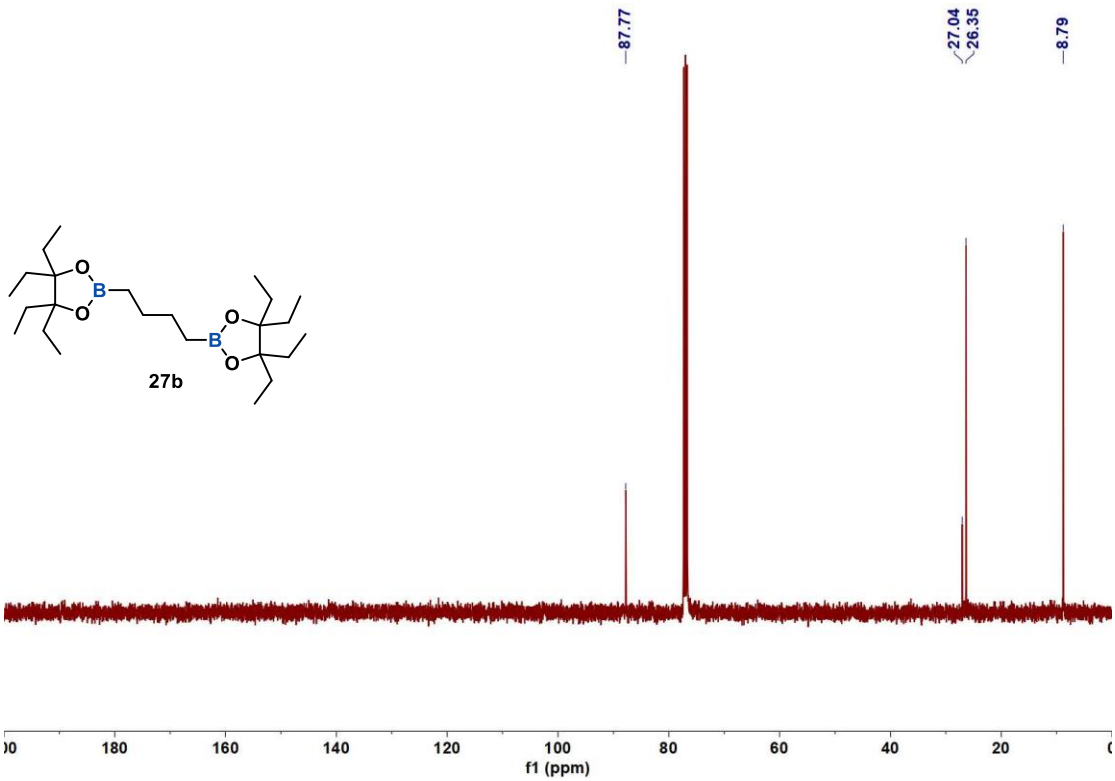


Figure S168. $^{13}C\{^{1}H\}$ NMR spectrum of **27b** in $CDCl_3$ at 298K

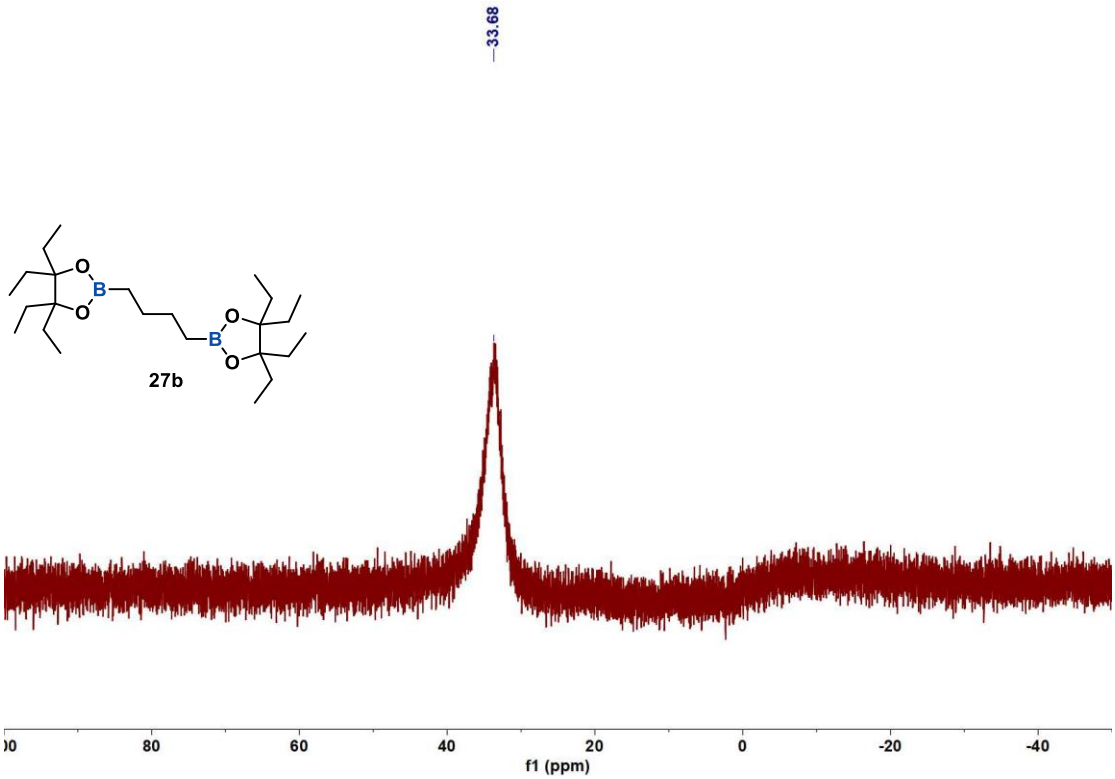


Figure S169. $^{11}B\{^{1}H\}$ NMR spectrum of **27b** in $CDCl_3$ at 298K

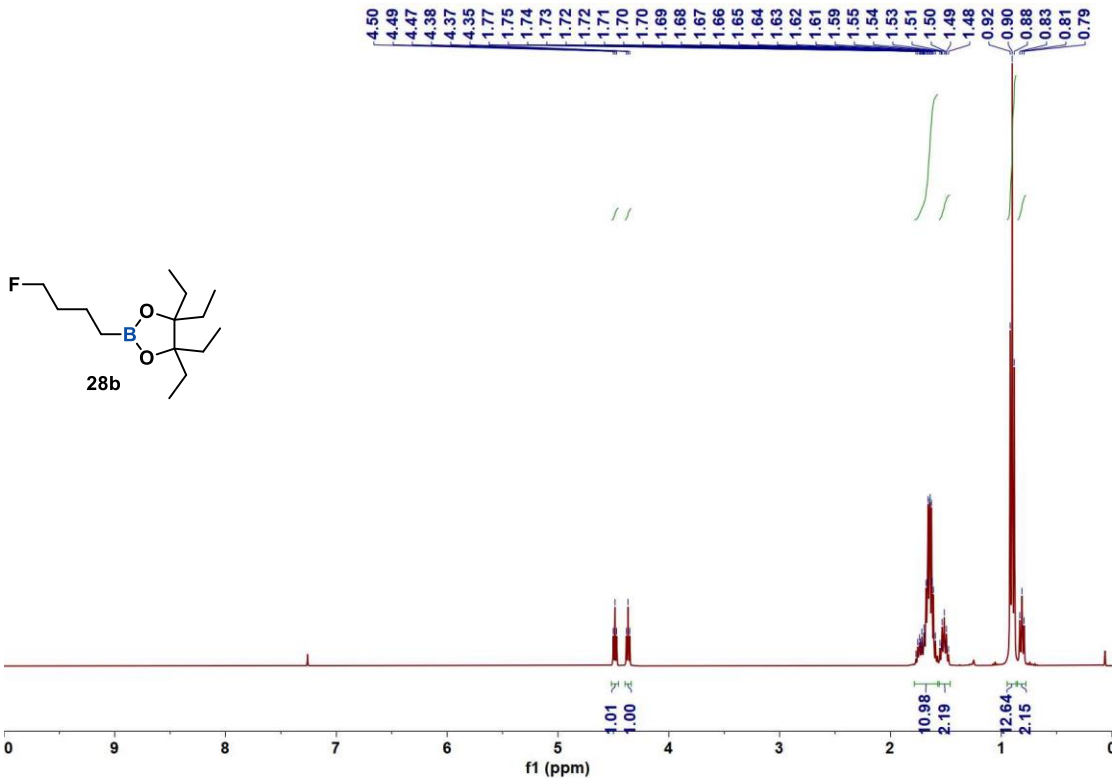


Figure S170. ^{1}H NMR spectrum of **28b** in $CDCl_3$ at 298K

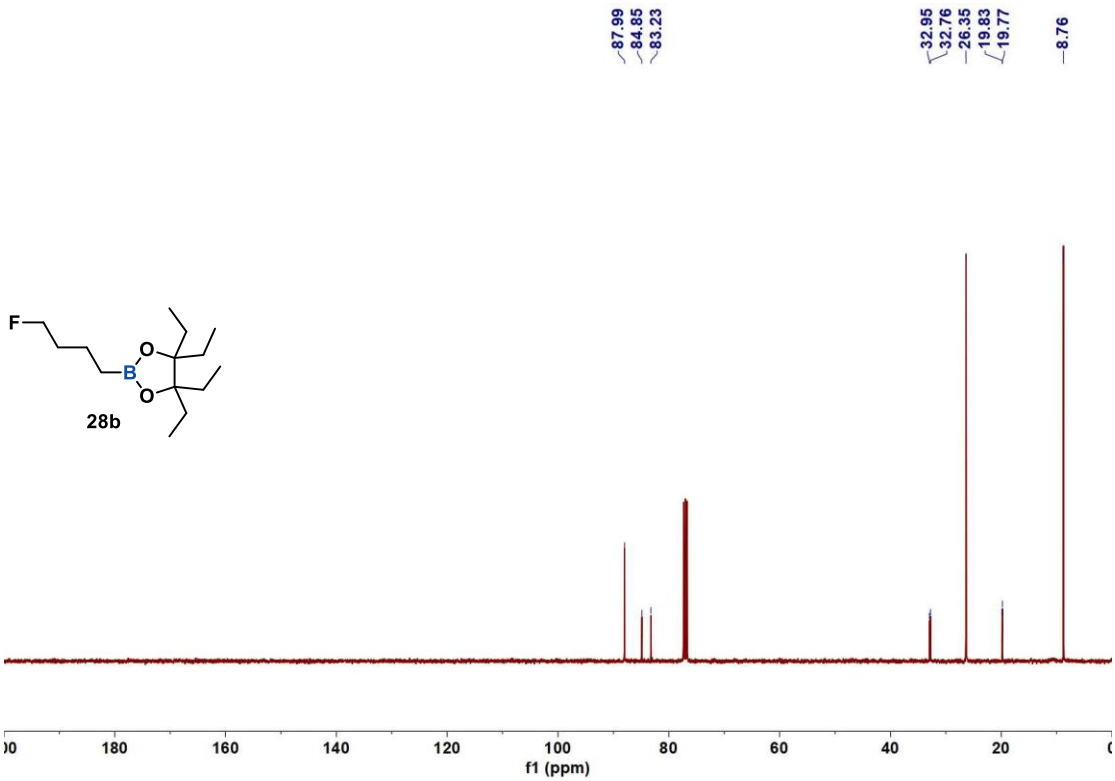


Figure S171. $^{13}C\{^{1}H\}$ NMR spectrum of **28b** in $CDCl_3$ at 298K

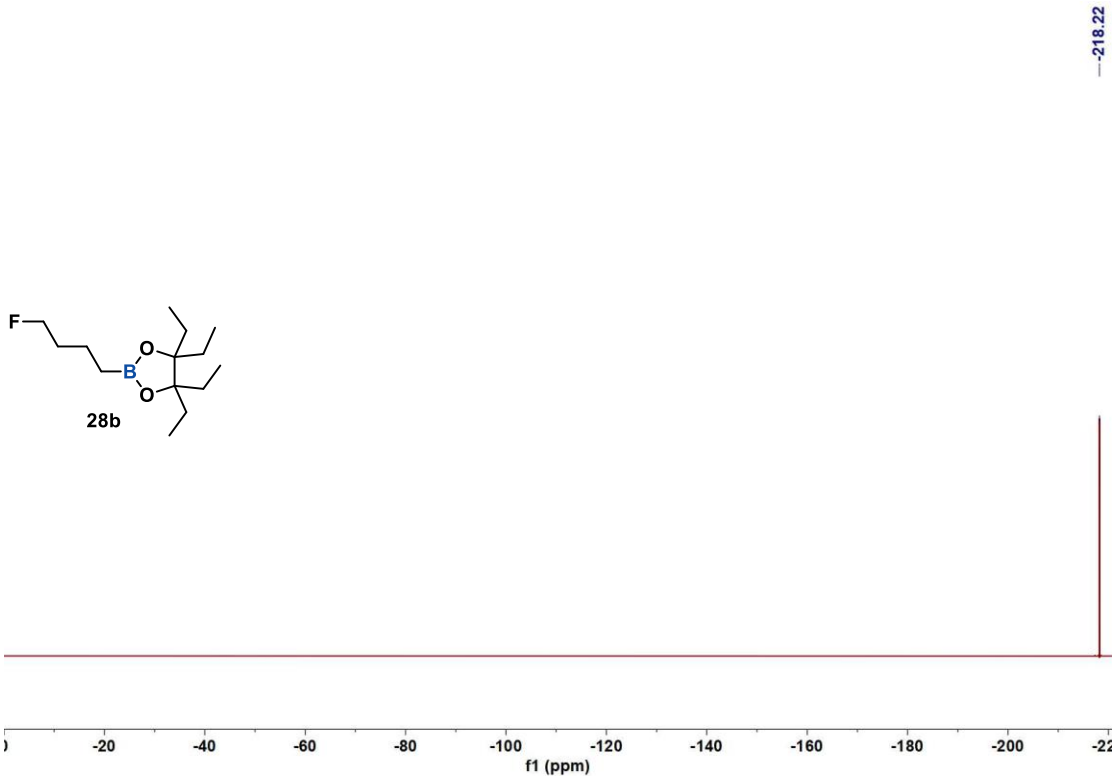


Figure S172. $^{19}F\{^{1}H\}$ NMR spectrum of **28b** in $CDCl_3$ at 298K

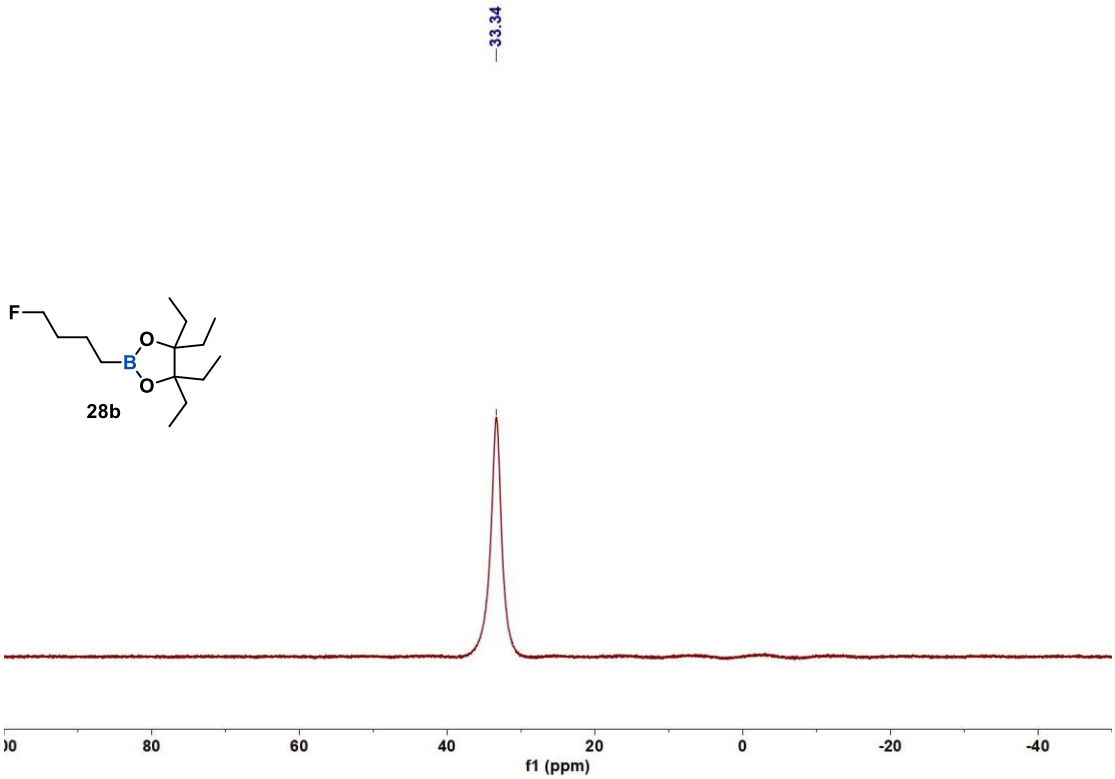


Figure S173. $^{11}B\{^{1}H\}$ NMR spectrum of **28b** in $CDCl_3$ at 298K

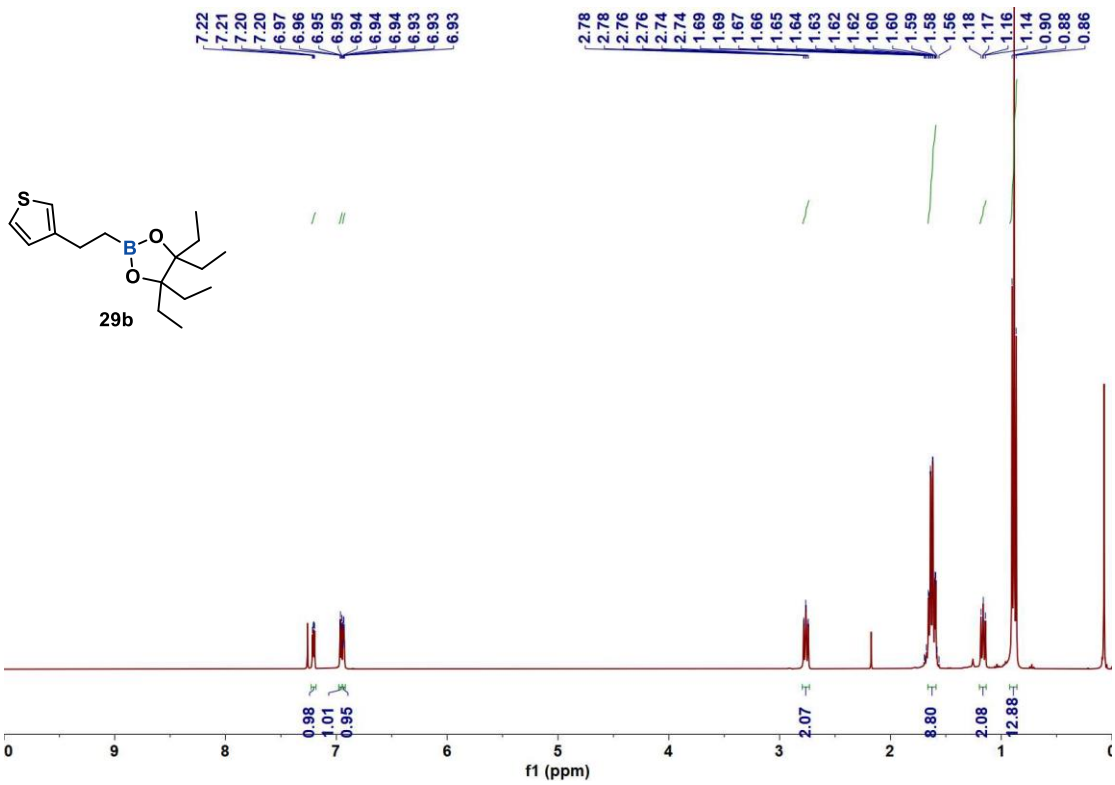


Figure S174. ^{1}H NMR spectrum of **29b** in $CDCl_3$ at 298K

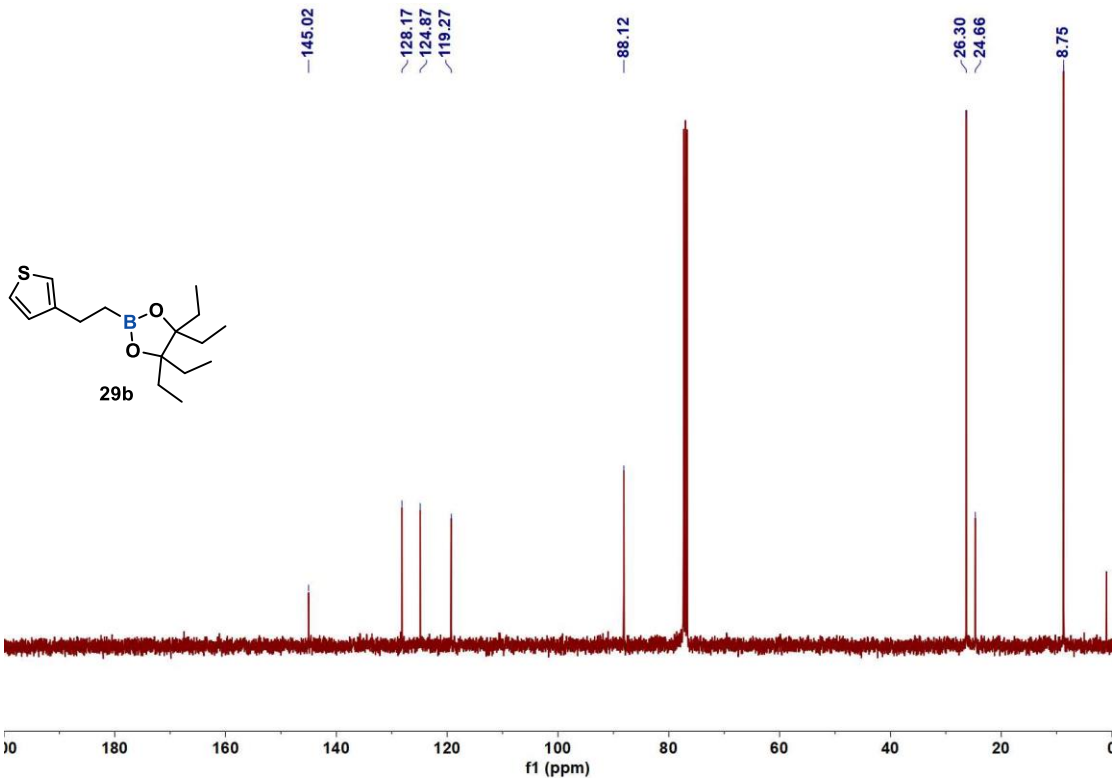


Figure S175. $^{13}C\{^{1}H\}$ NMR spectrum of **29b** in $CDCl_3$ at 298K

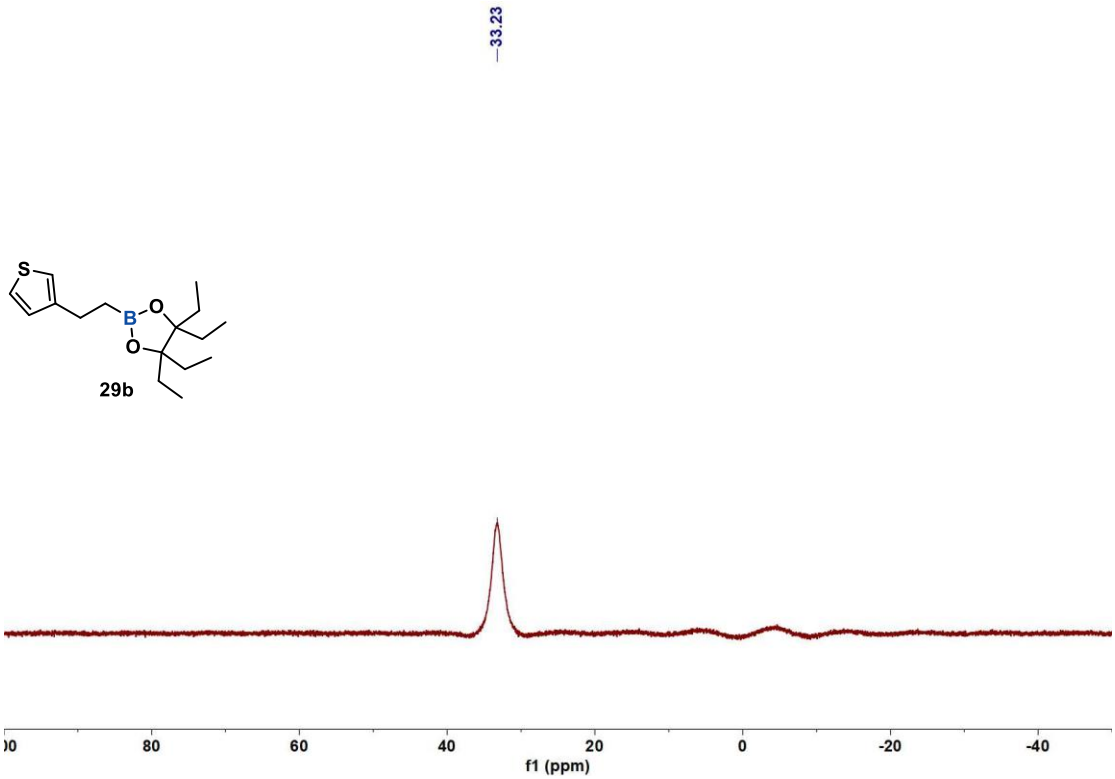


Figure S176. $^{11}B\{^{1}H\}$ NMR spectrum of **29b** in $CDCl_3$ at 298K

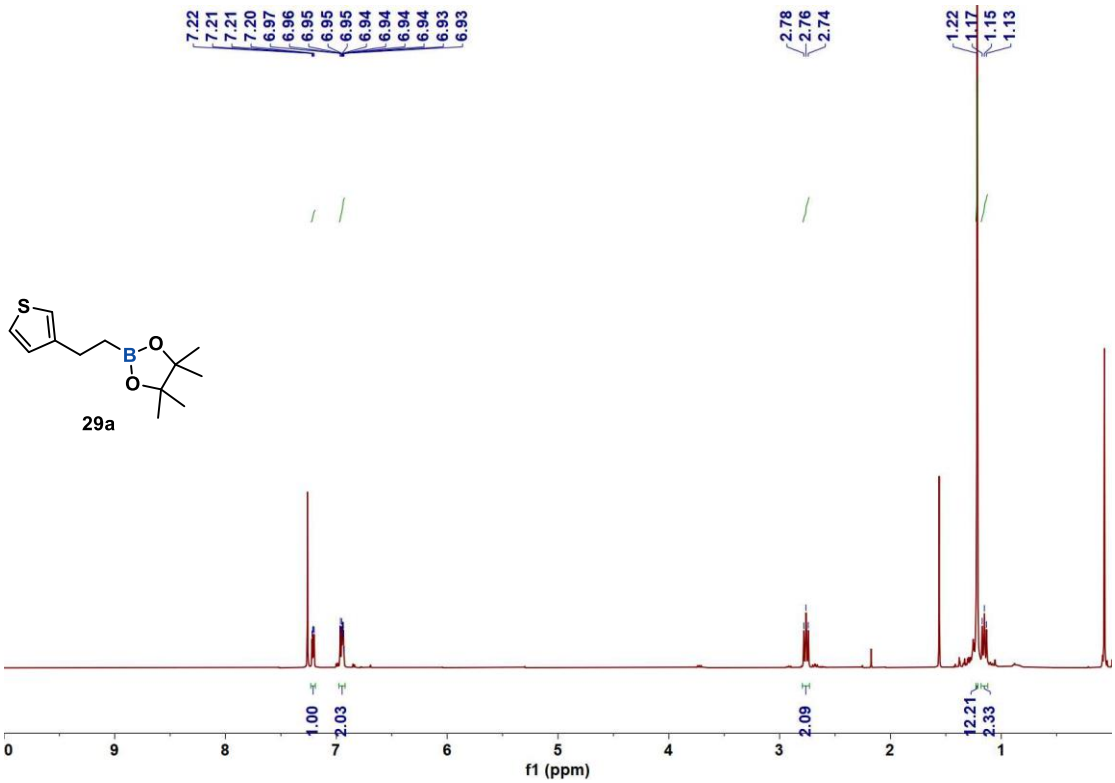


Figure S177. ^{1}H NMR spectrum of **29a** in $CDCl_3$ at 298K

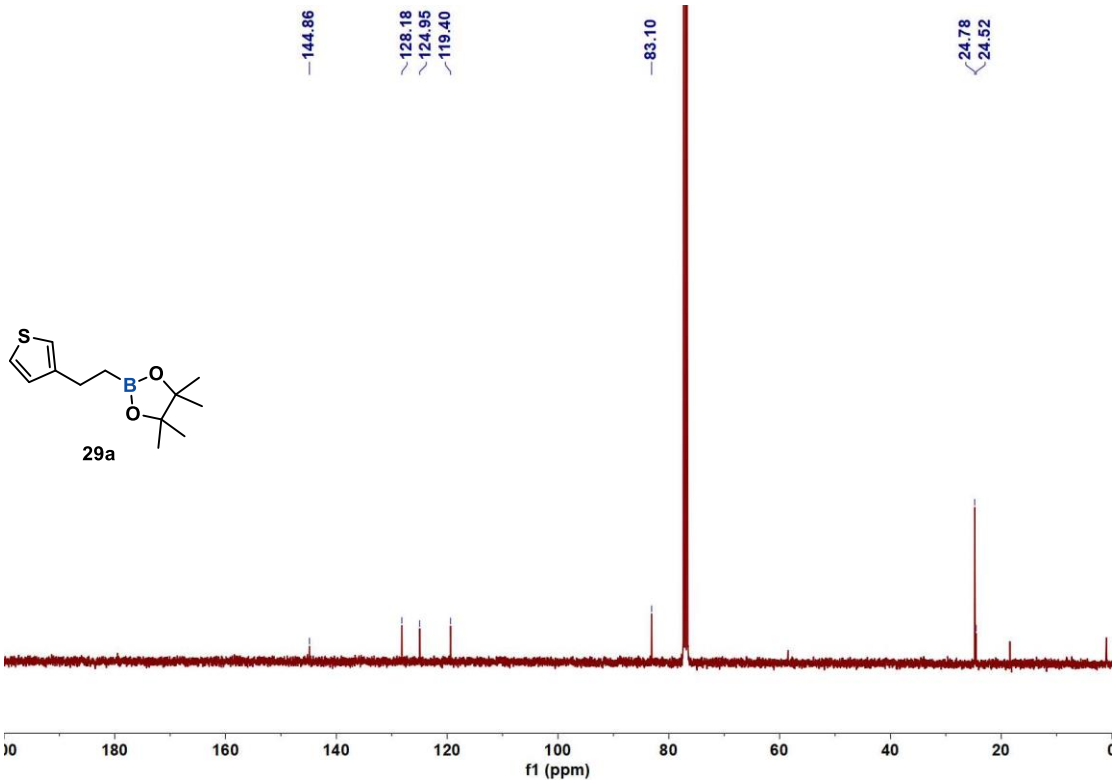


Figure S178. $^{13}C\{^{1}H\}$ NMR spectrum of **29a** in $CDCl_3$ at 298K

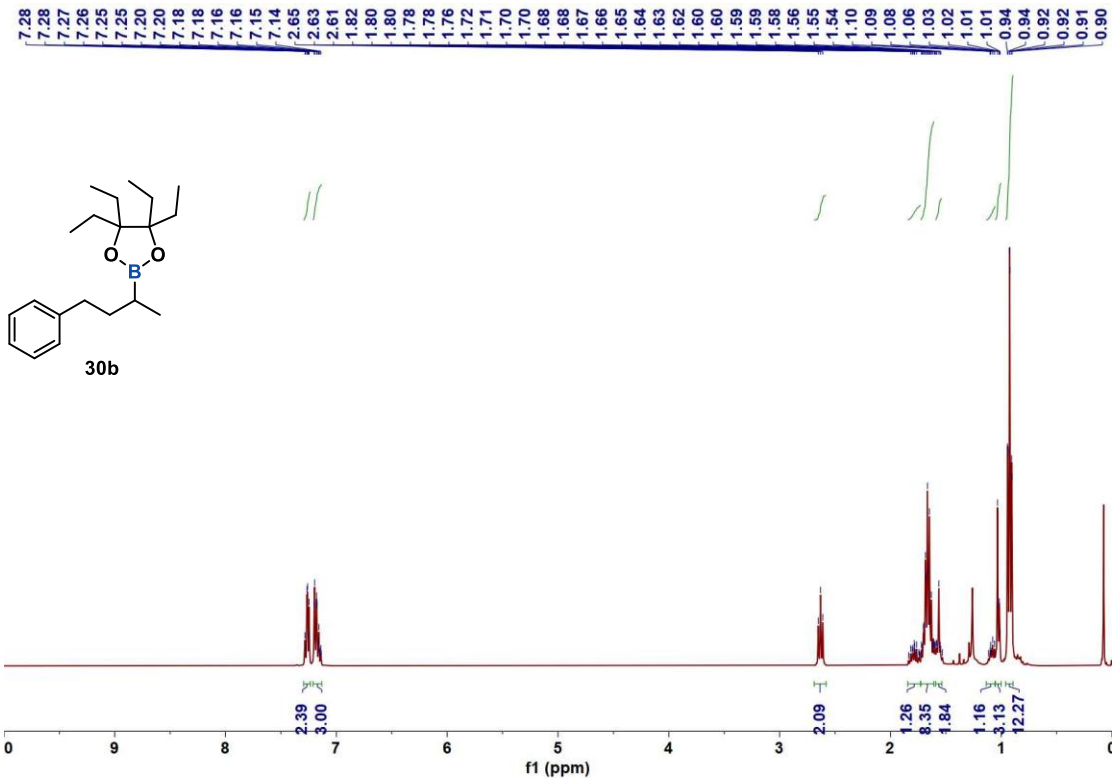


Figure S179. ^{1}H NMR spectrum of **30b** in $CDCl_3$ at 298K

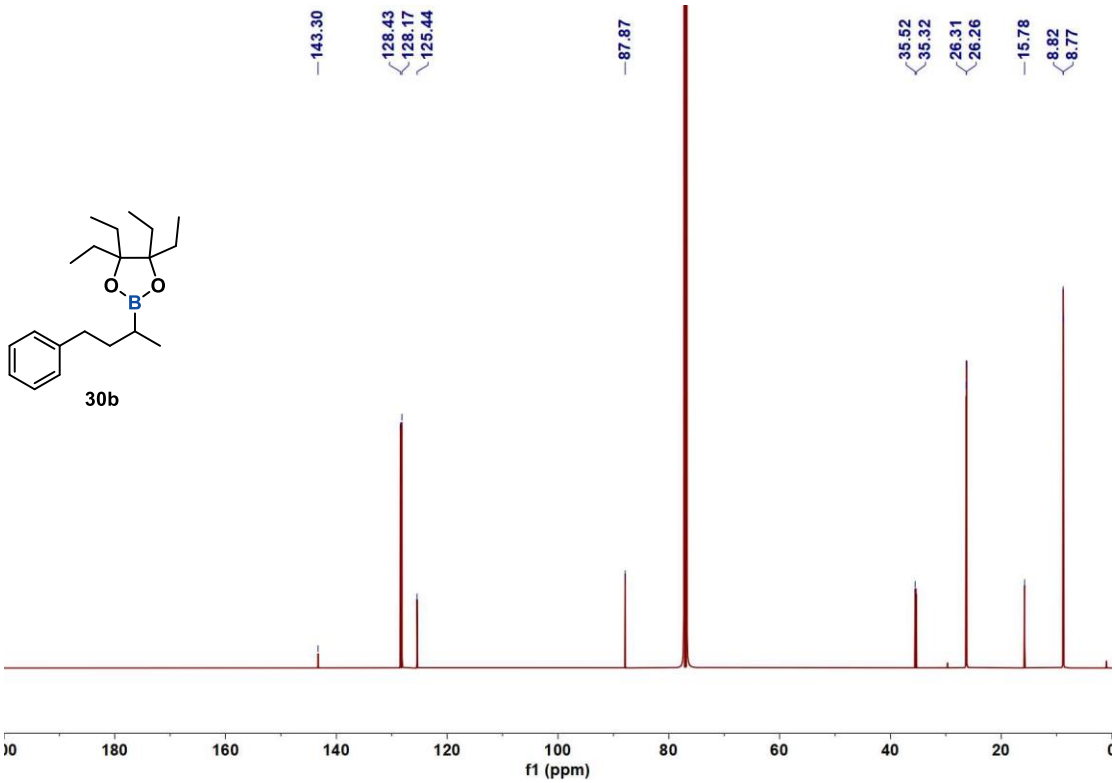


Figure S180. $^{13}C\{^{1}H\}$ NMR spectrum of **30b** in $CDCl_3$ at 298K

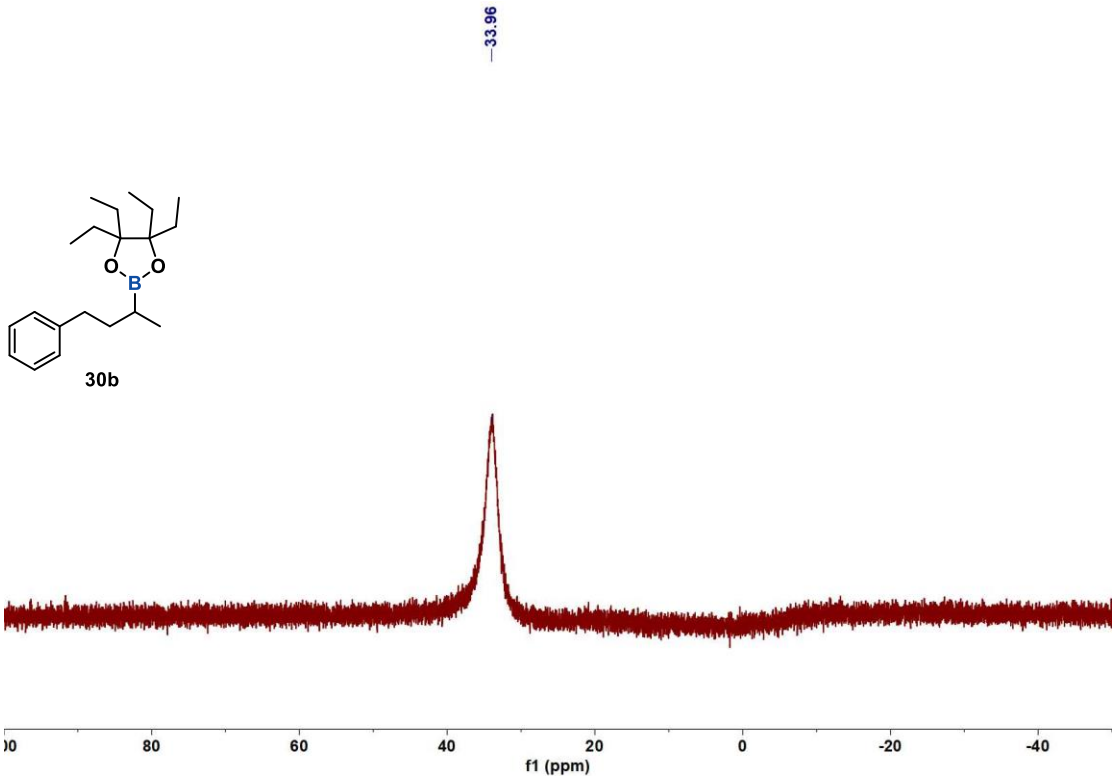


Figure S181. $^{11}B\{^{1}H\}$ NMR spectrum of **30b** in $CDCl_3$ at 298K

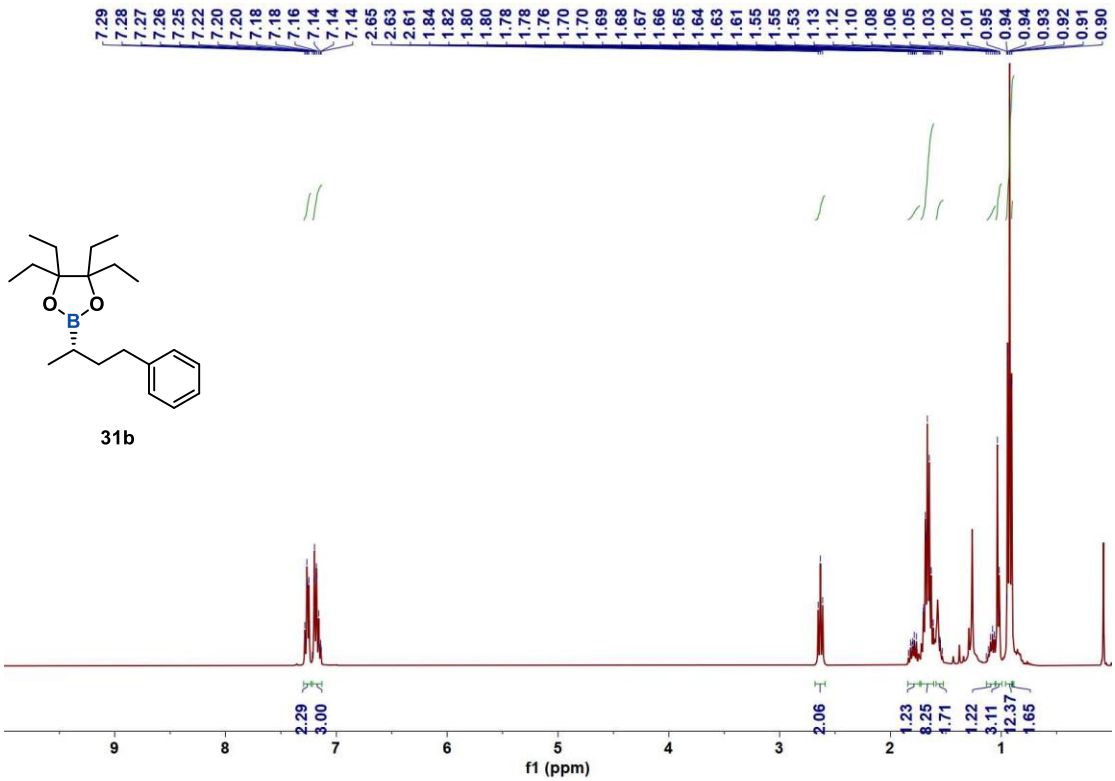


Figure S182. ^{1}H NMR spectrum of **31b** in $CDCl_3$ at 298K

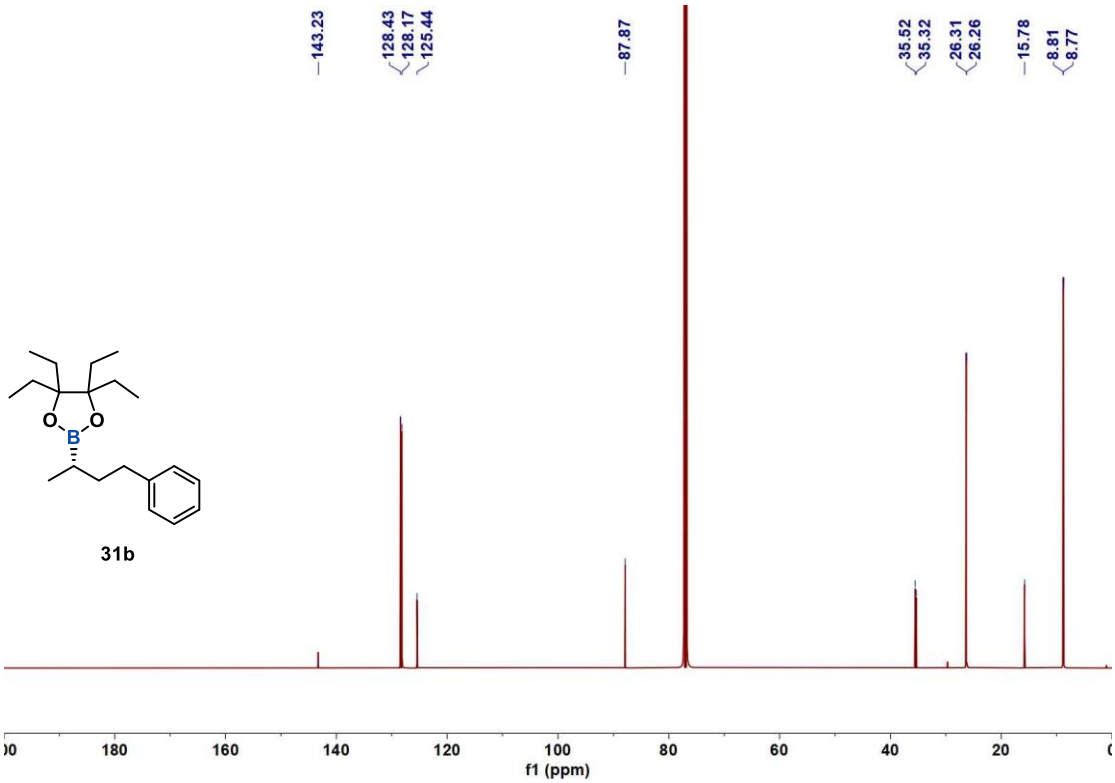


Figure S183. $^{13}C\{^{1}H\}$ NMR spectrum of **31b** in $CDCl_3$ at 298K

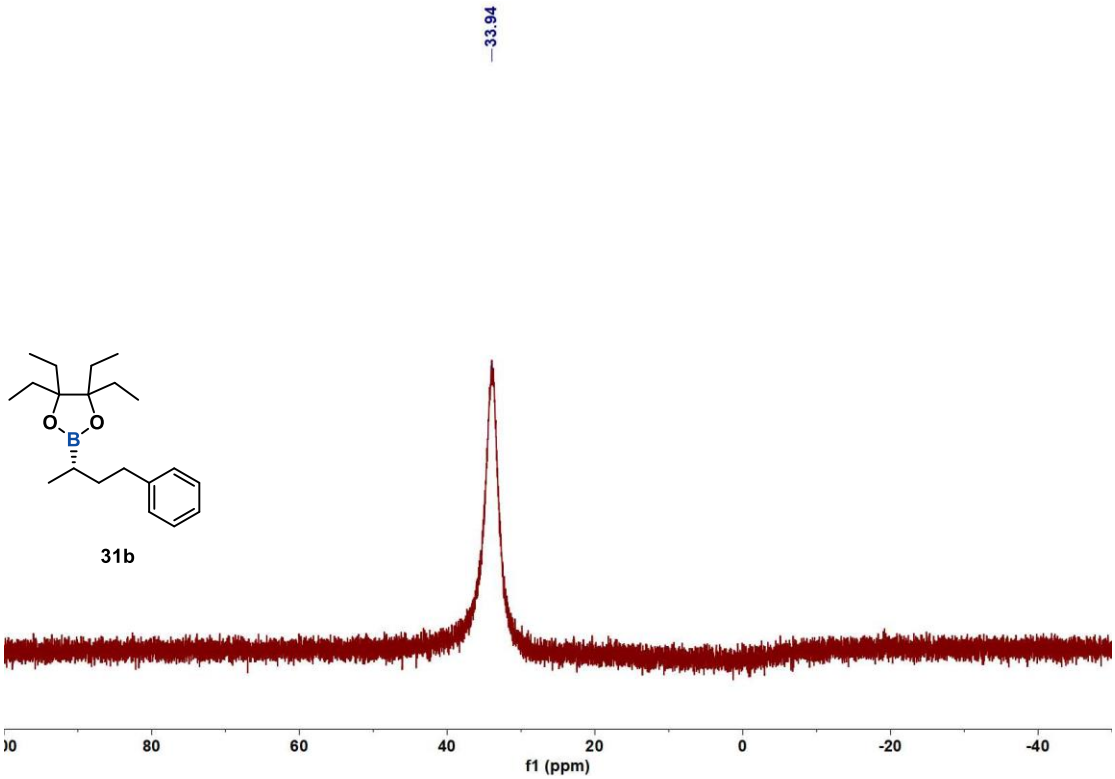


Figure S184. $^{11}B\{^{1}H\}$ NMR spectrum of **31b** in $CDCl_3$ at 298K

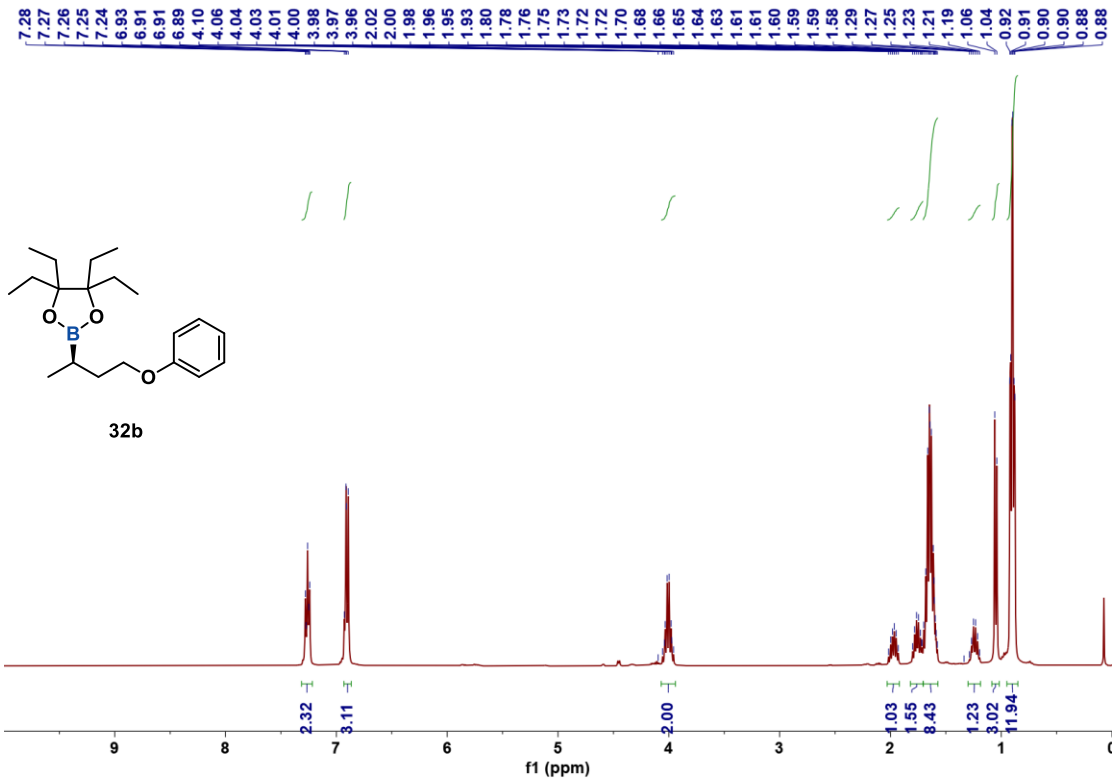


Figure S185. ^{1}H NMR spectrum of **32b** in $CDCl_3$ at 298K

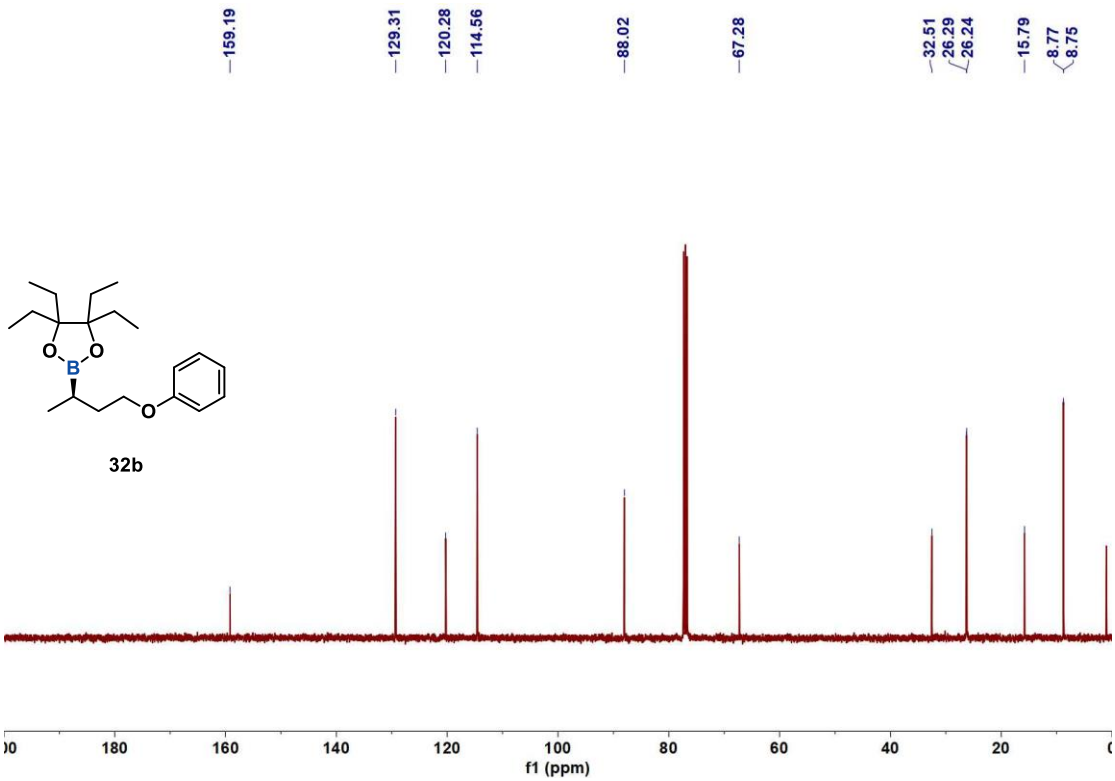


Figure S186. $^{13}C\{^{1}H\}$ NMR spectrum of **32b** in $CDCl_3$ at 298K

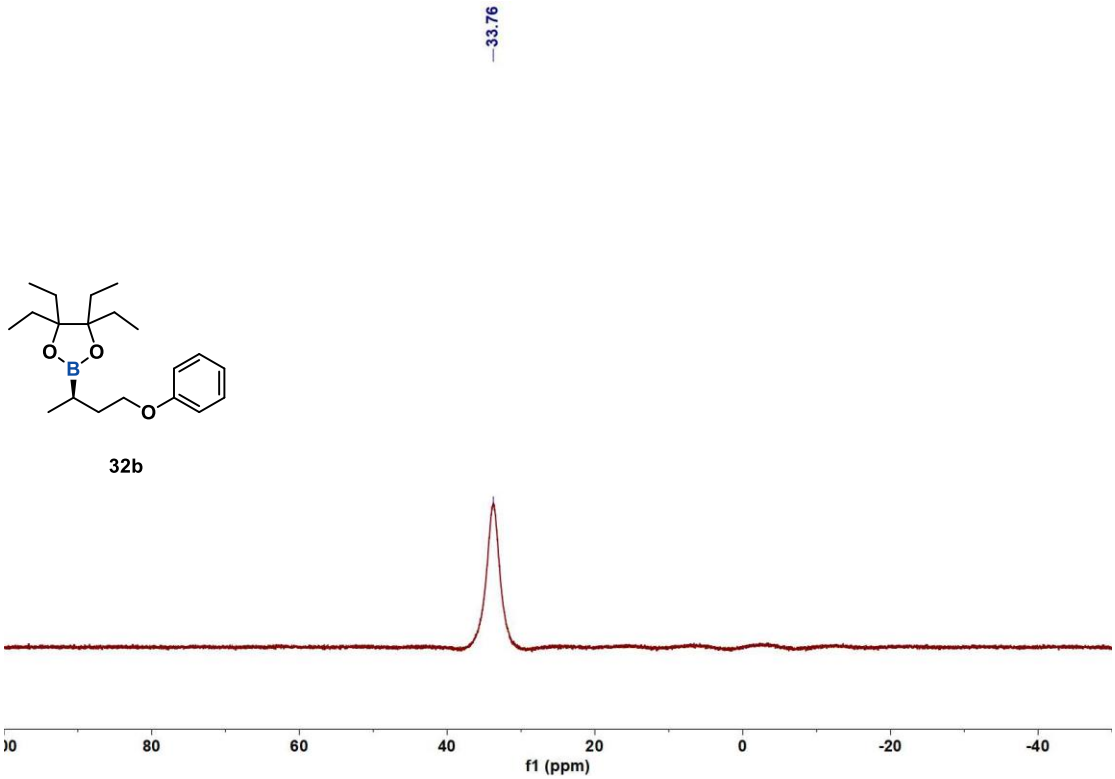


Figure S187. $^{11}B\{^{1}H\}$ NMR spectrum of **32b** in $CDCl_3$ at 298K

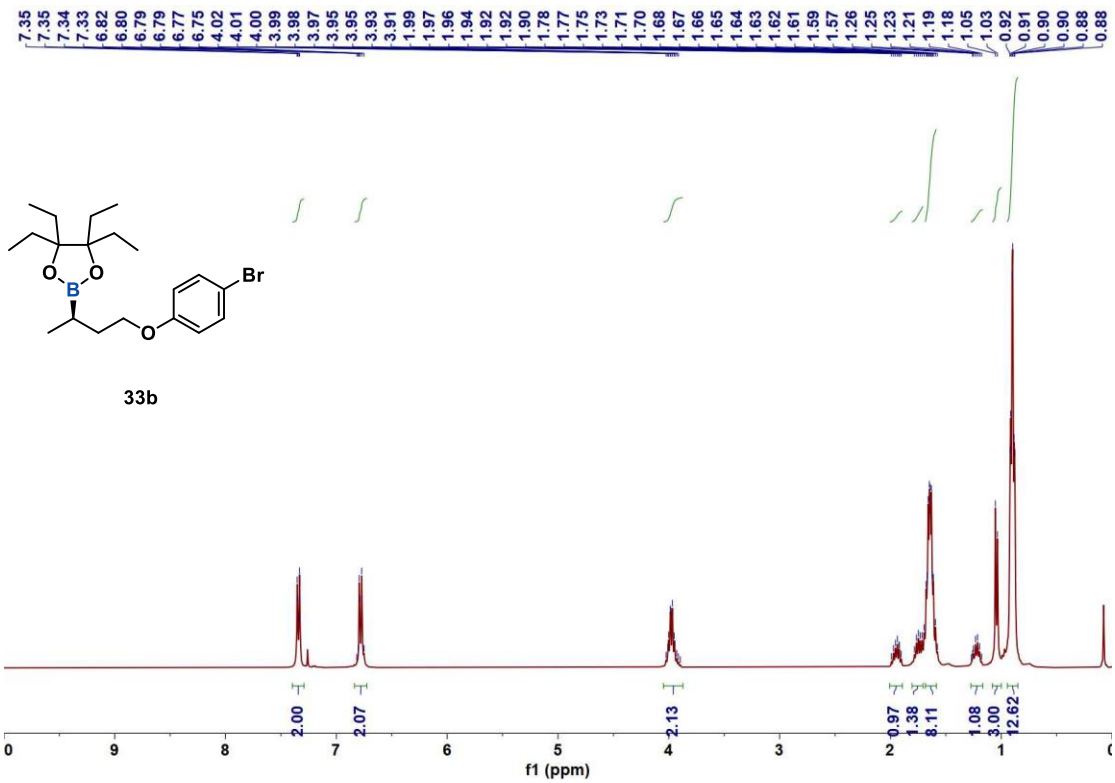


Figure S188. ^{1}H NMR spectrum of **33b** in $CDCl_3$ at 298K

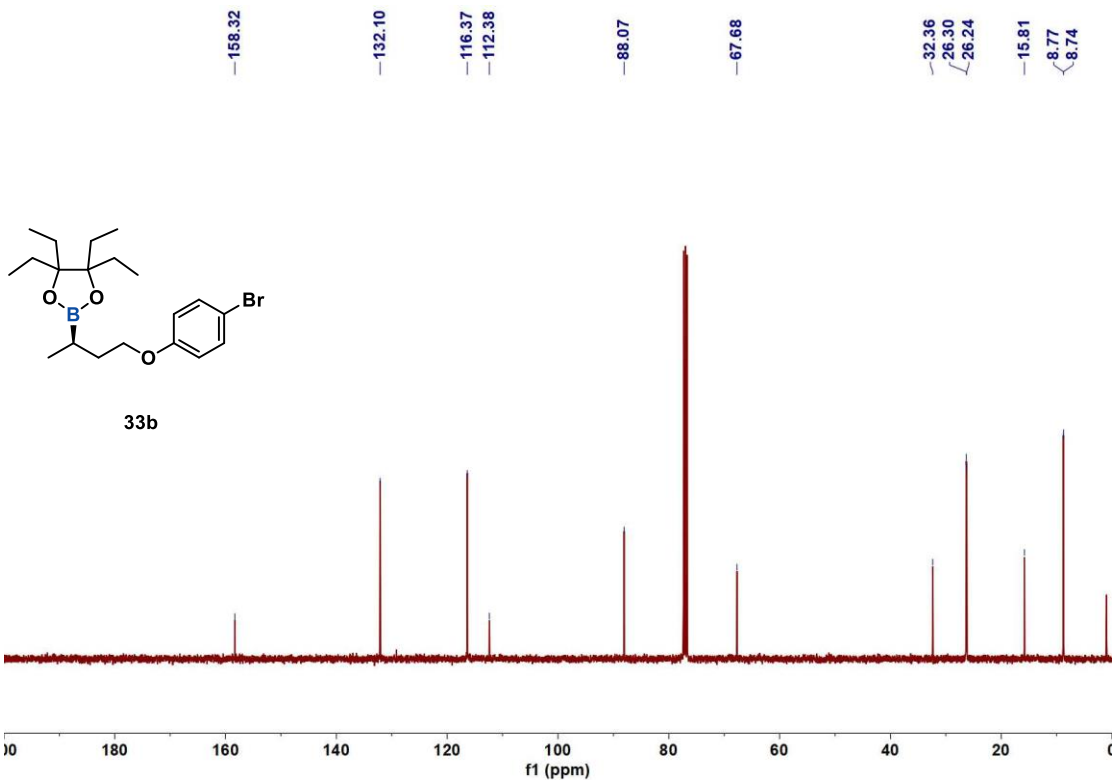


Figure S189. $^{13}C\{^{1}H\}$ NMR spectrum of **33b** in $CDCl_3$ at 298K

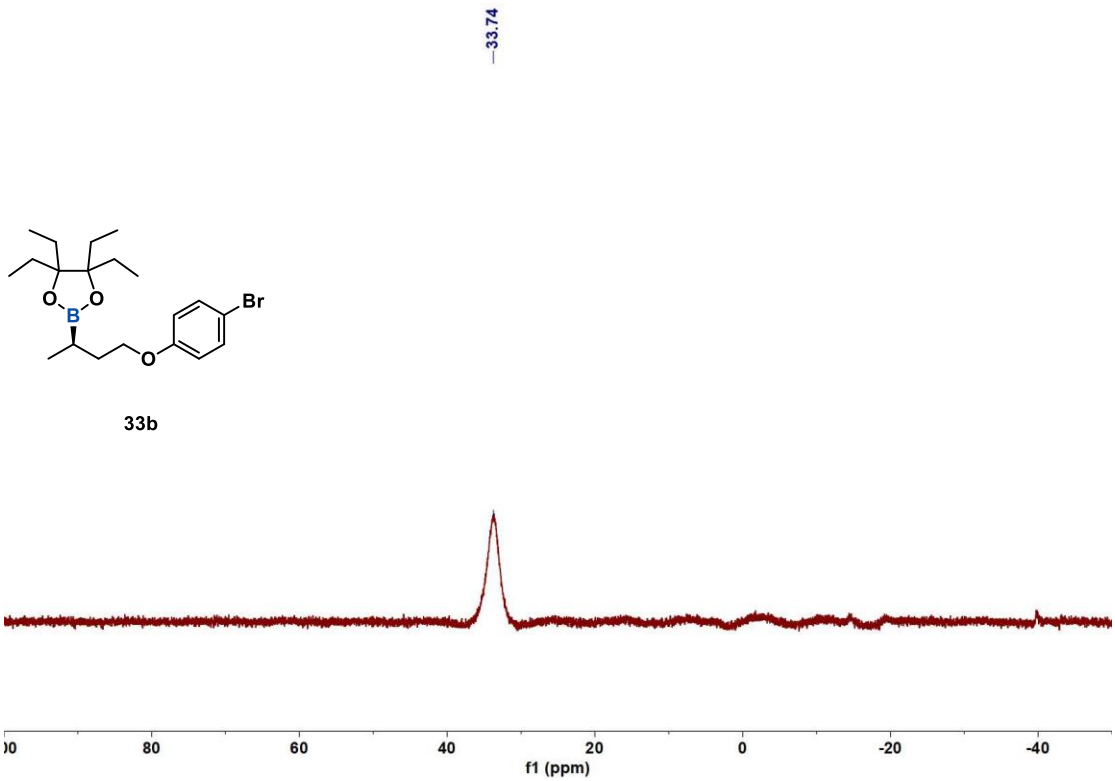


Figure S190. $^{11}B\{^{1}H\}$ NMR spectrum of **33b** in $CDCl_3$ at 298K

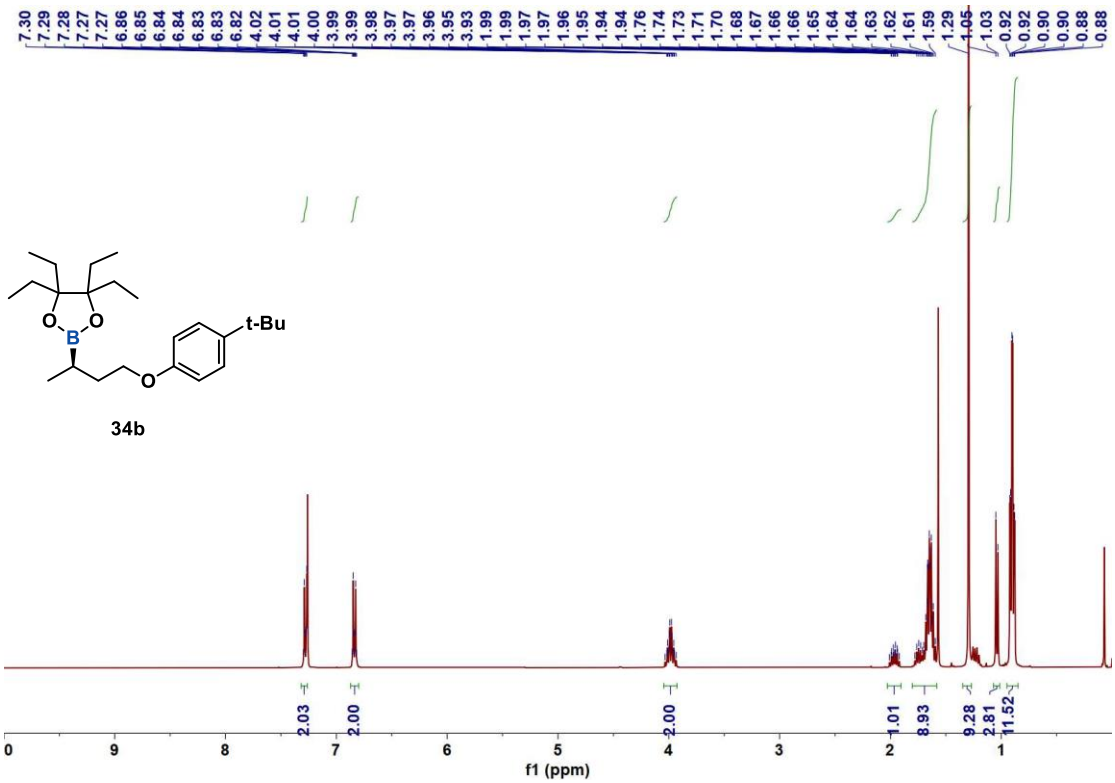


Figure S191. ^{1}H NMR spectrum of **34b** in $CDCl_3$ at 298K

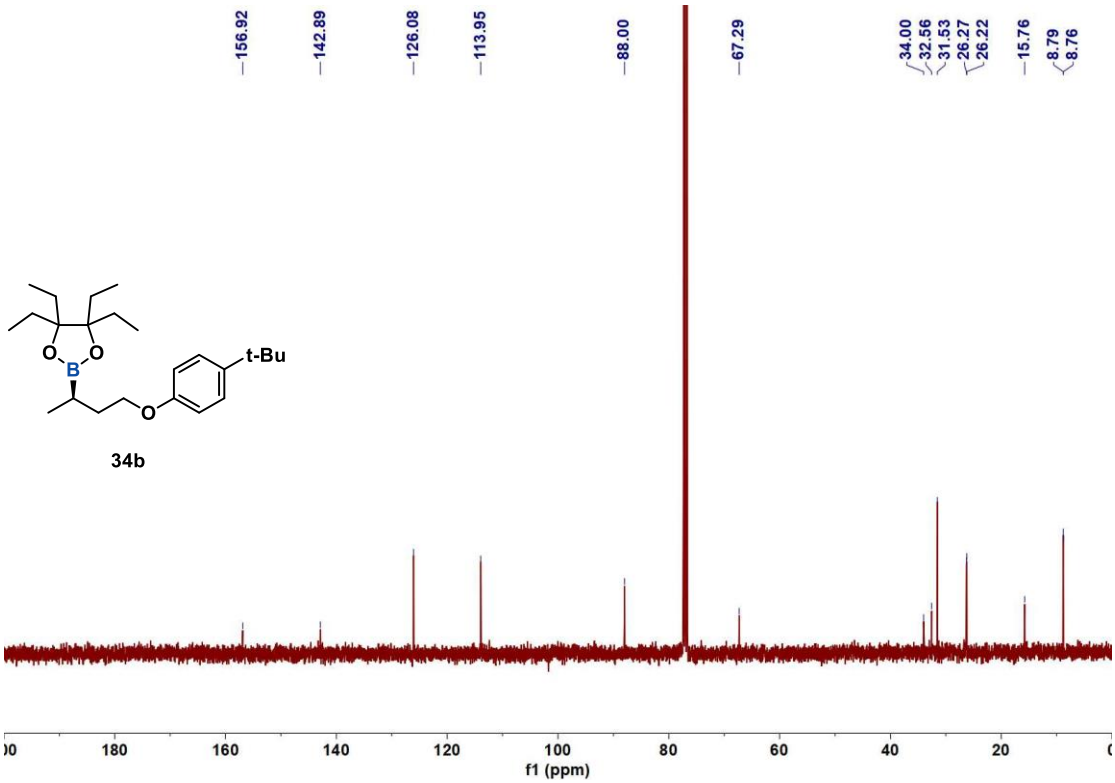


Figure S192. $^{13}C\{^{1}H\}$ NMR spectrum of **34b** in $CDCl_3$ at 298K

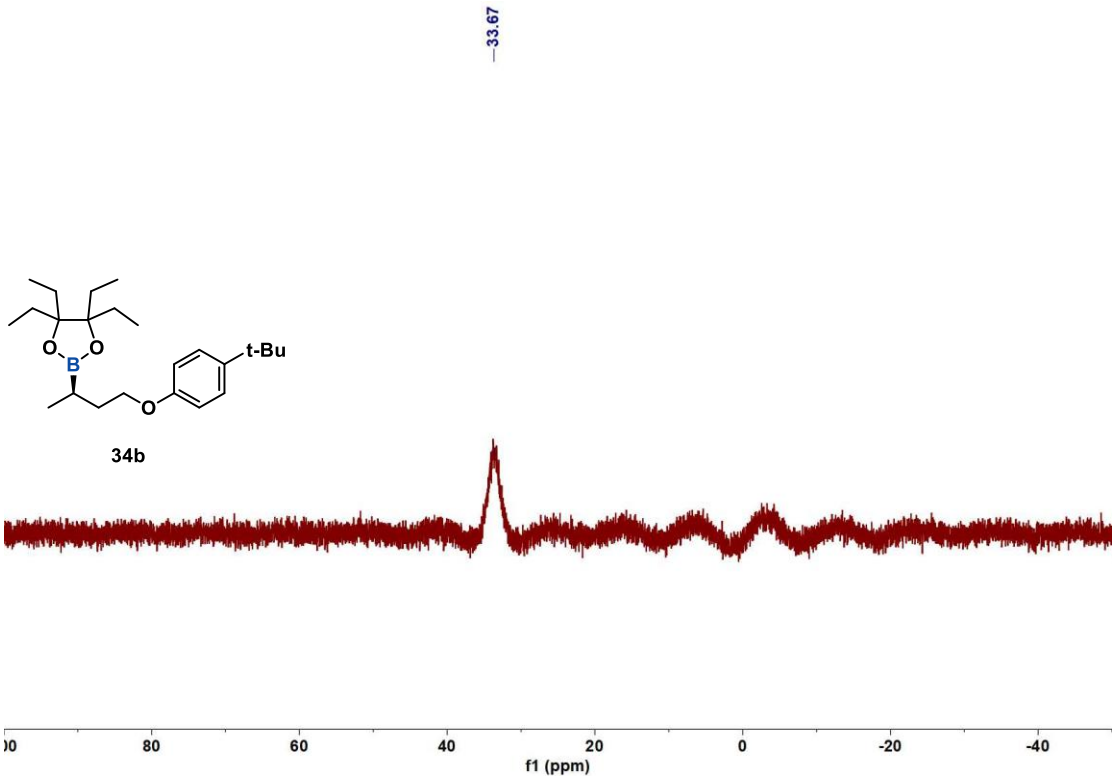


Figure S193. $^{11}B\{^{1}H\}$ NMR spectrum of **34b** in $CDCl_3$ at 298K

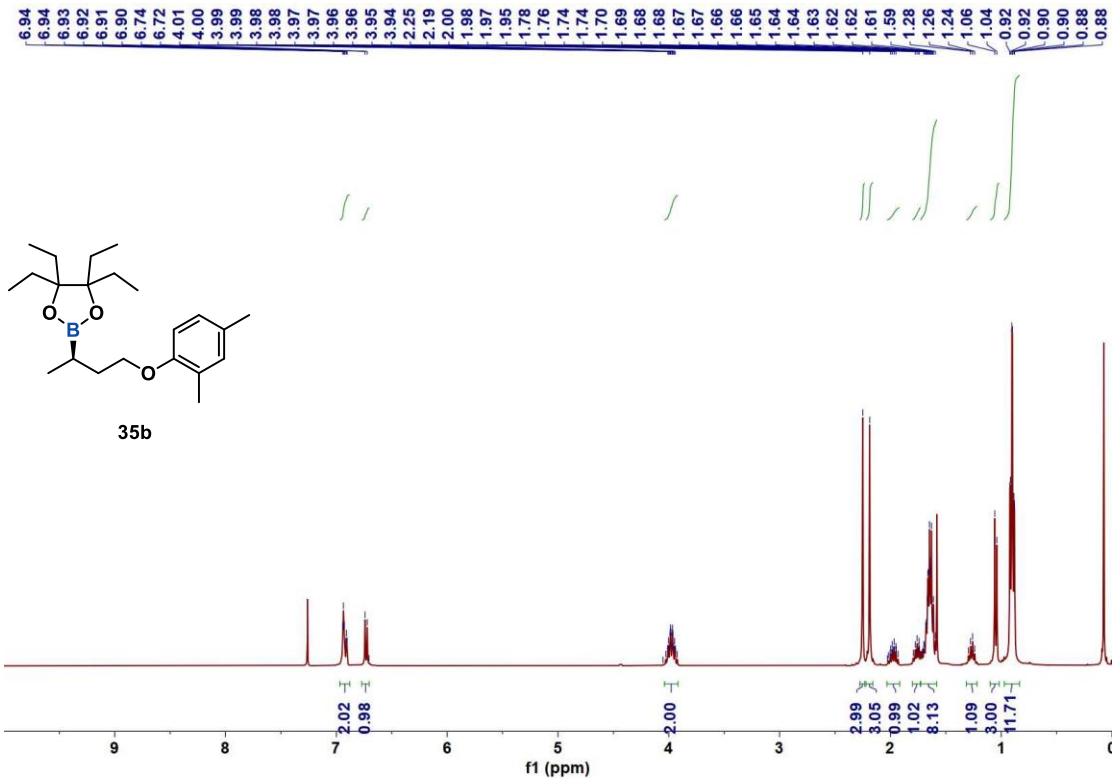


Figure S194. ^{1}H NMR spectrum of **35b** in $CDCl_3$ at 298K

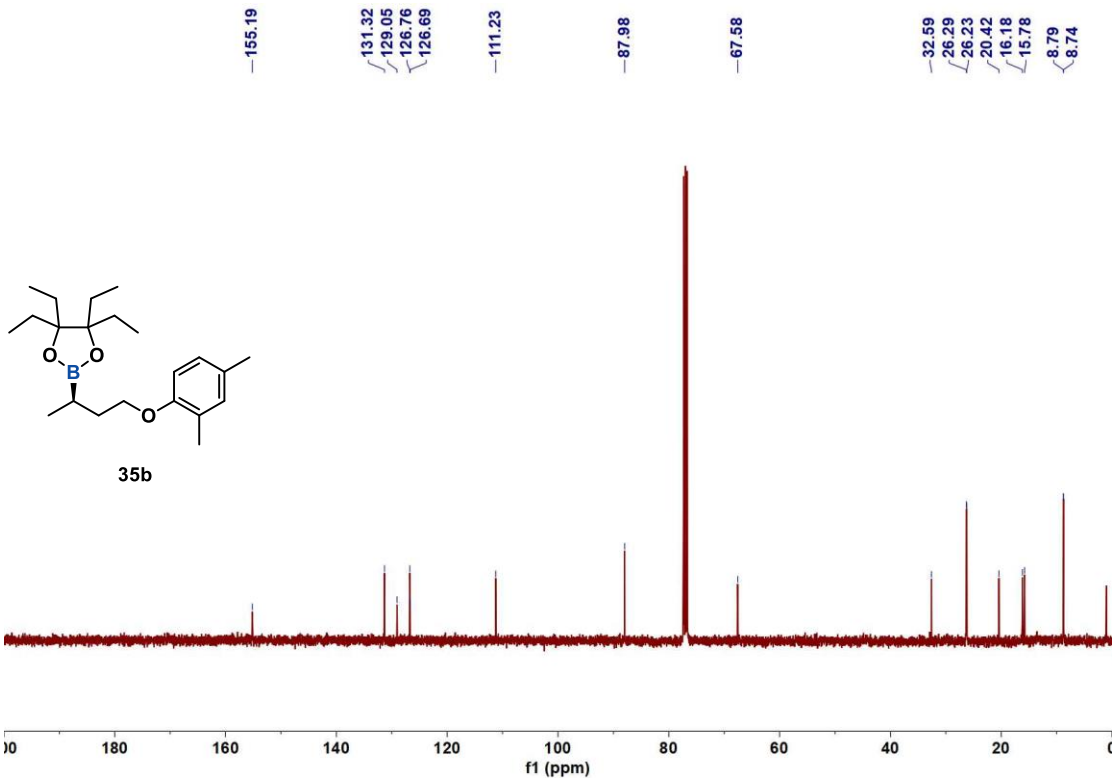


Figure S195. $^{13}C\{^{1}H\}$ NMR spectrum of **35b** in $CDCl_3$ at 298K

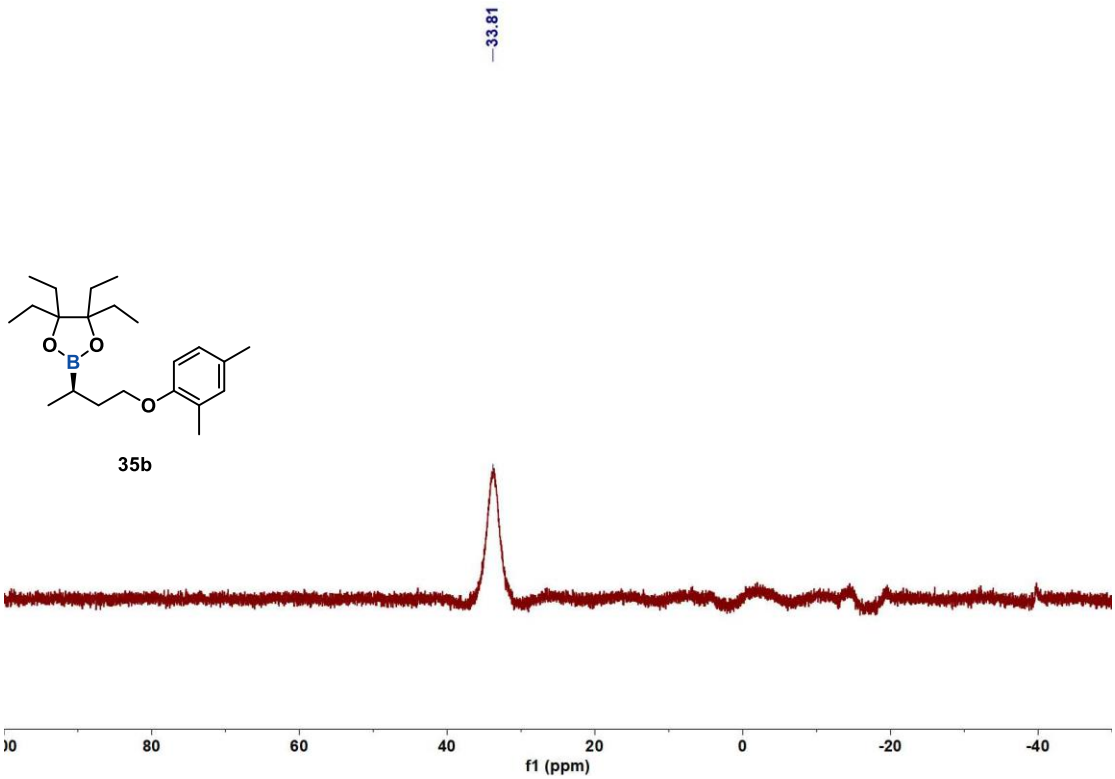


Figure S196. $^{11}B\{^{1}H\}$ NMR spectrum of **35b** in $CDCl_3$ at 298K

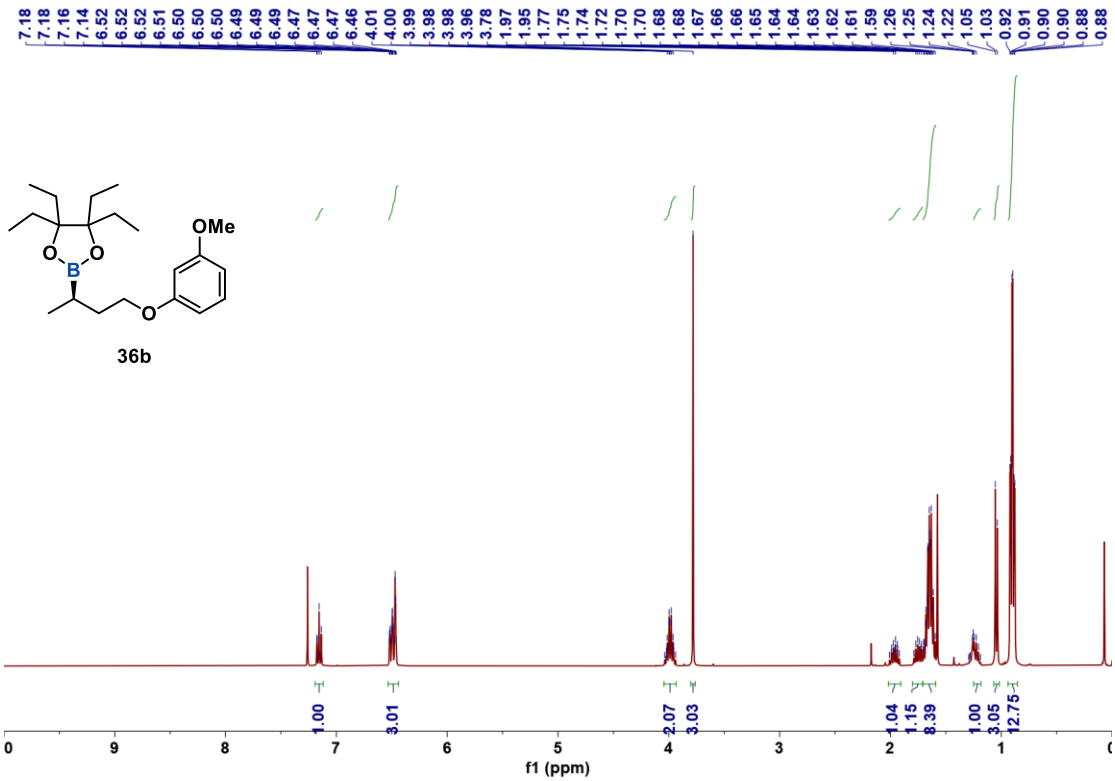


Figure S197. ^{1}H NMR spectrum of **36b** in $CDCl_3$ at 298K

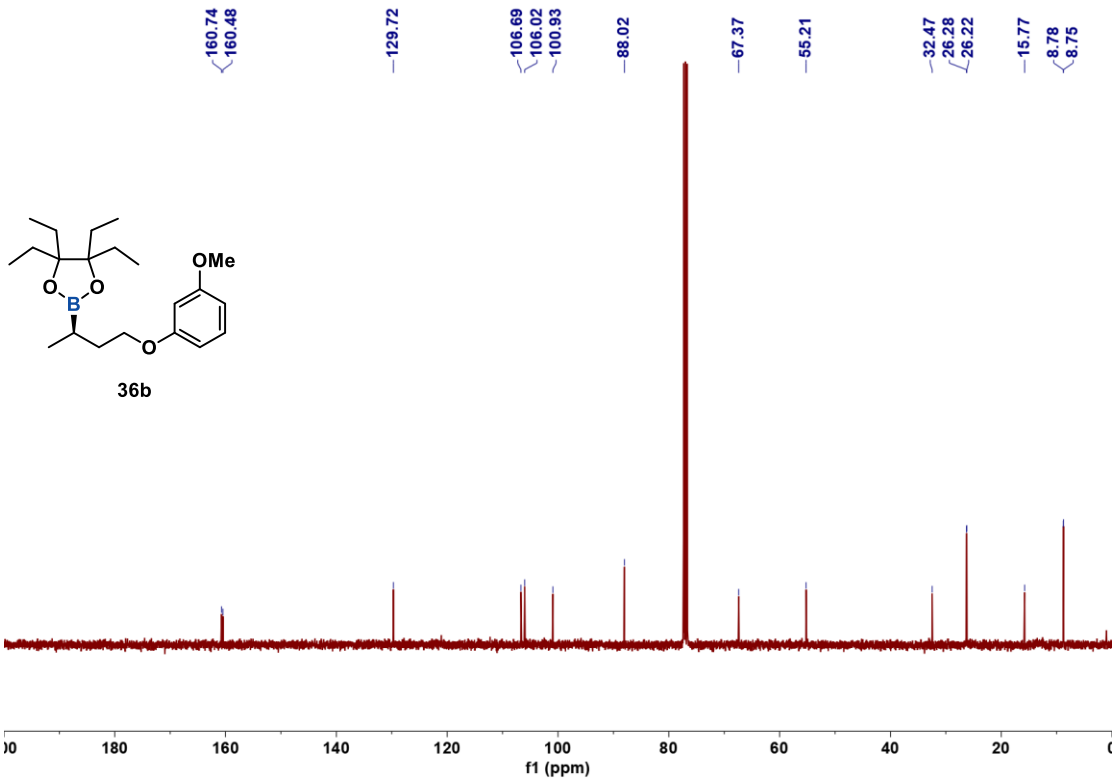


Figure S198. $^{13}C\{^{1}H\}$ NMR spectrum of **36b** in $CDCl_3$ at 298K

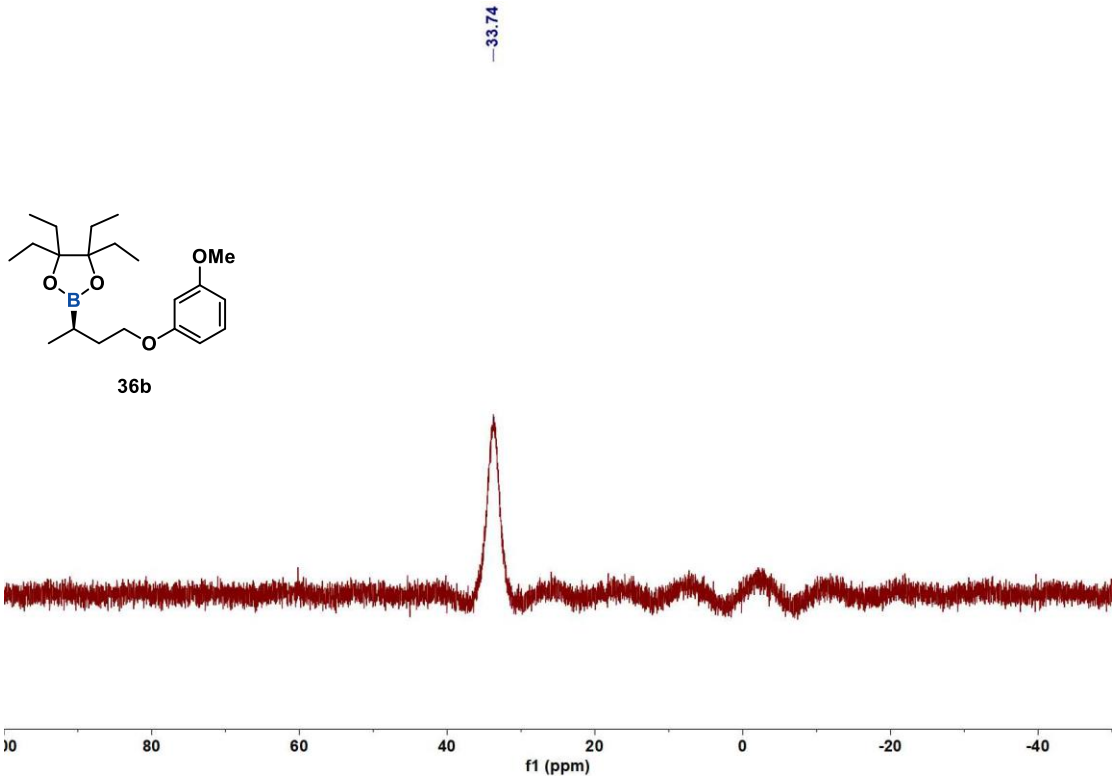


Figure S199. $^{11}B\{^{1}H\}$ NMR spectrum of **36b** in $CDCl_3$ at 298K

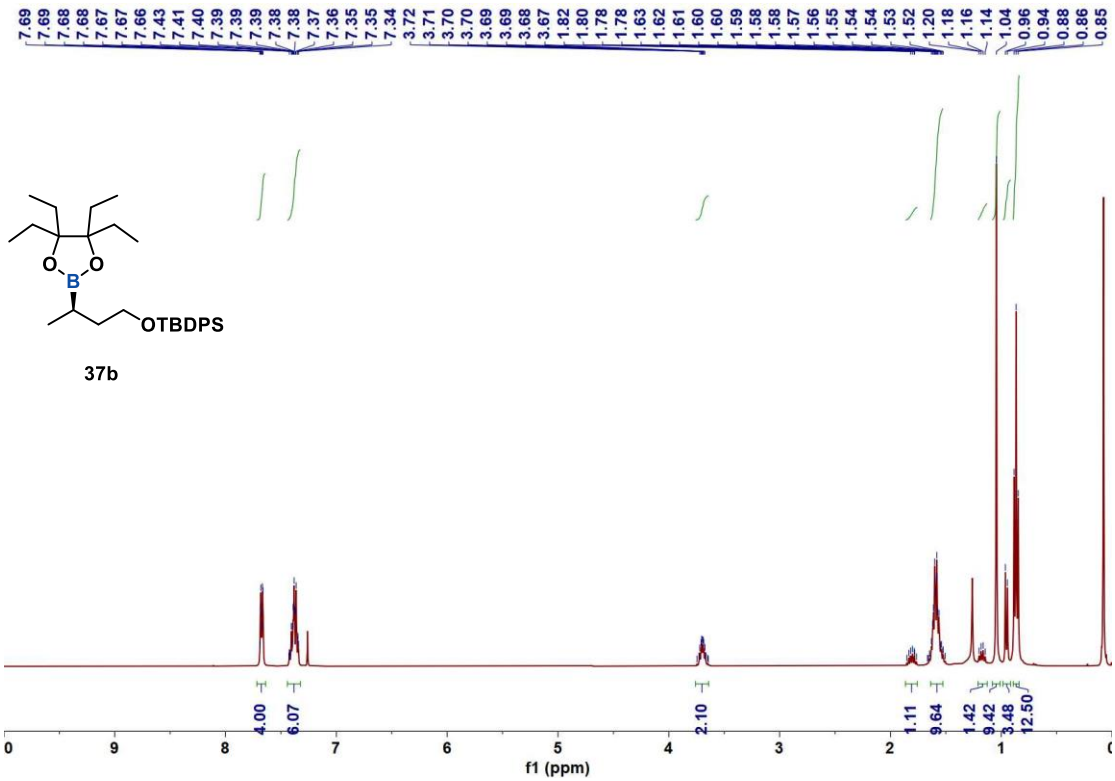


Figure S200. ^{1}H NMR spectrum of **37b** in $CDCl_3$ at 298K

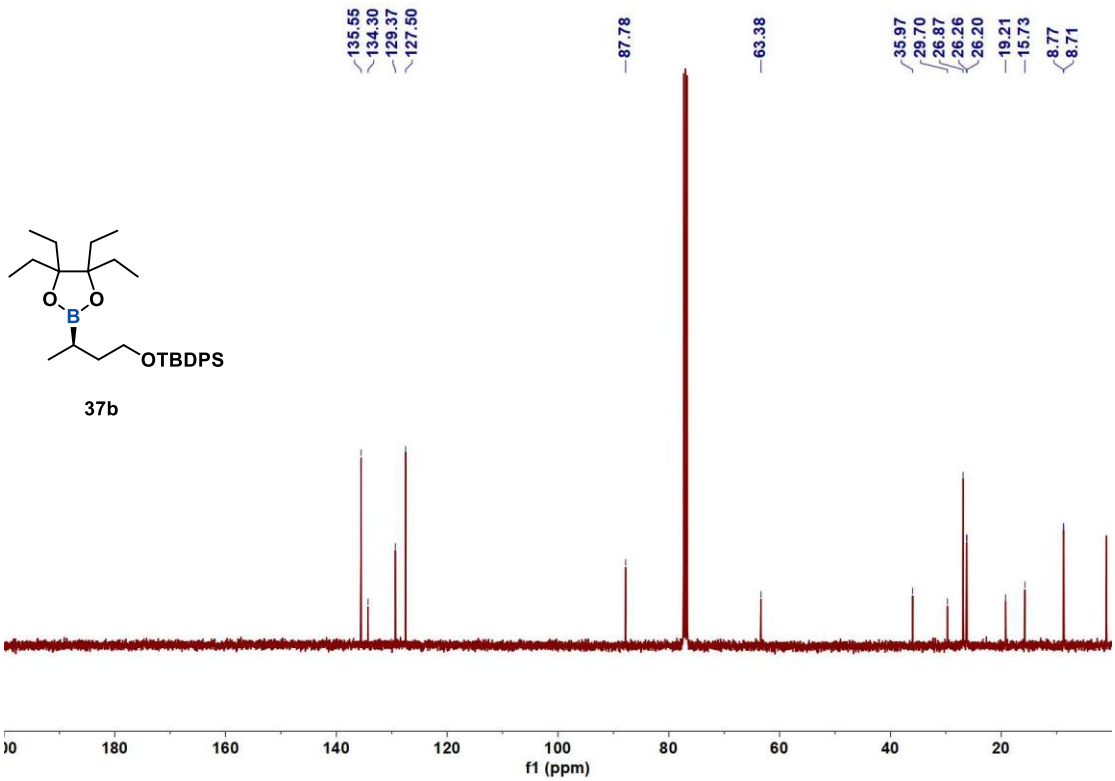


Figure S201. $^{13}C\{^{1}H\}$ NMR spectrum of **37b** in $CDCl_3$ at 298K

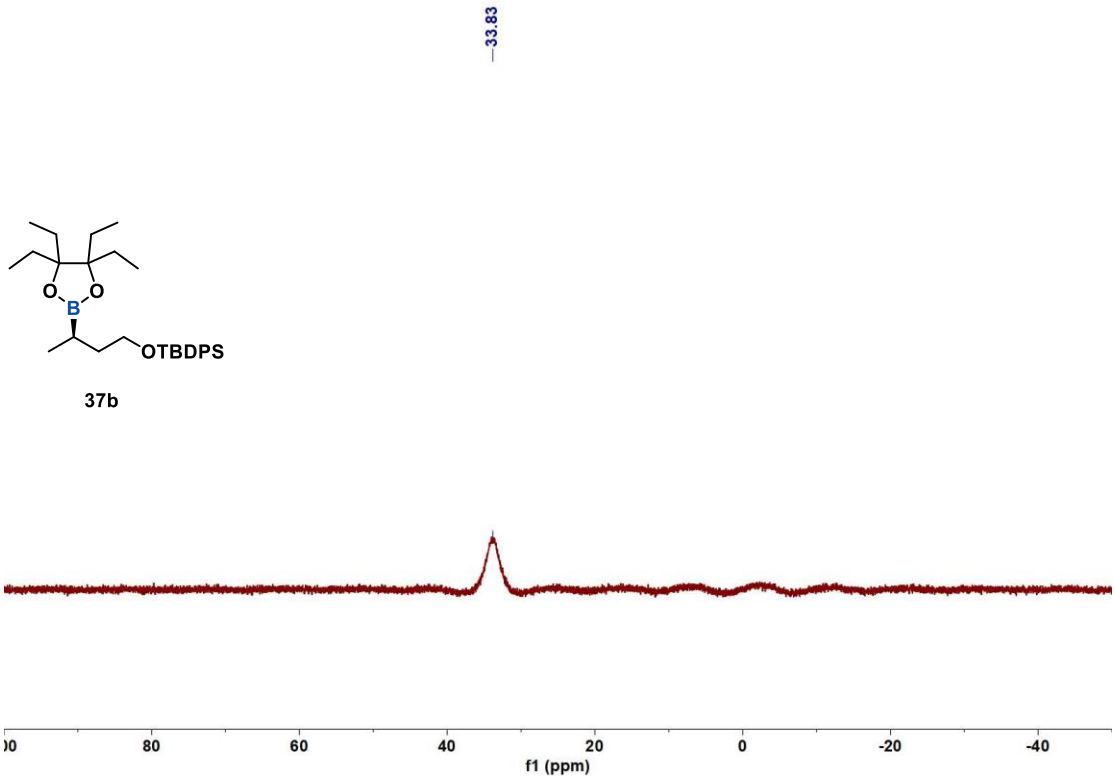


Figure S202. $^{11}B\{^{1}H\}$ NMR spectrum of **37b** in $CDCl_3$ at 298K

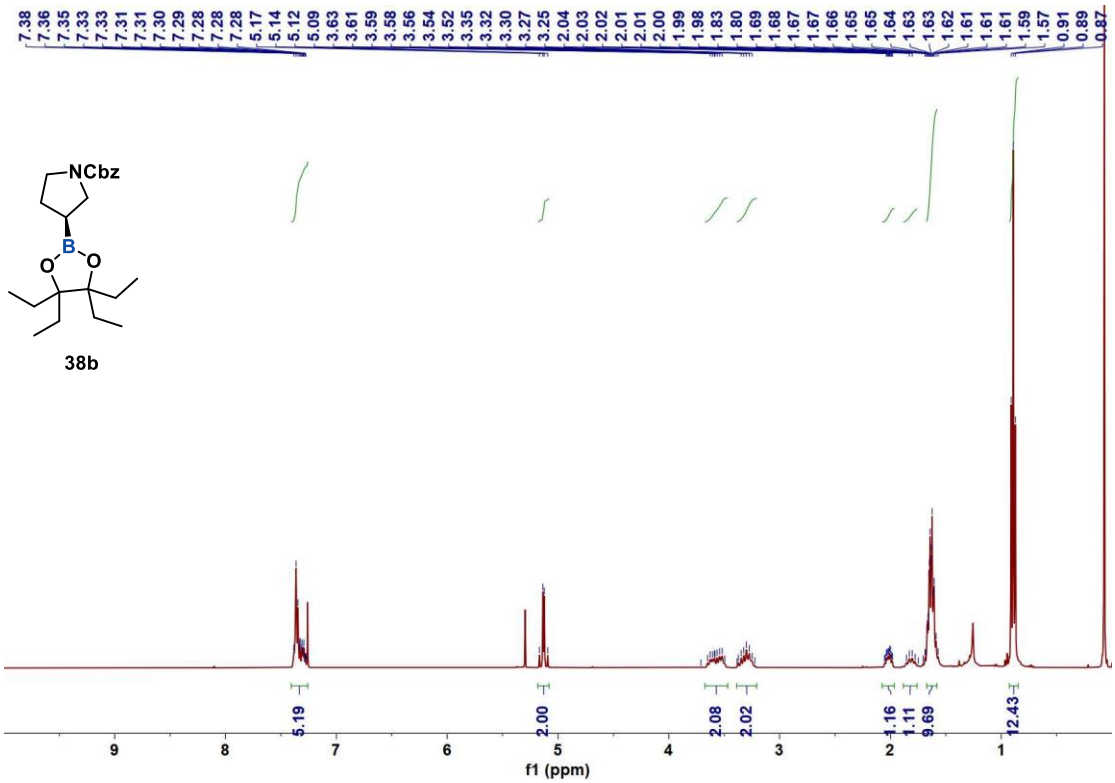


Figure S203. ^{1}H NMR spectrum of **38b** in $CDCl_3$ at 298K

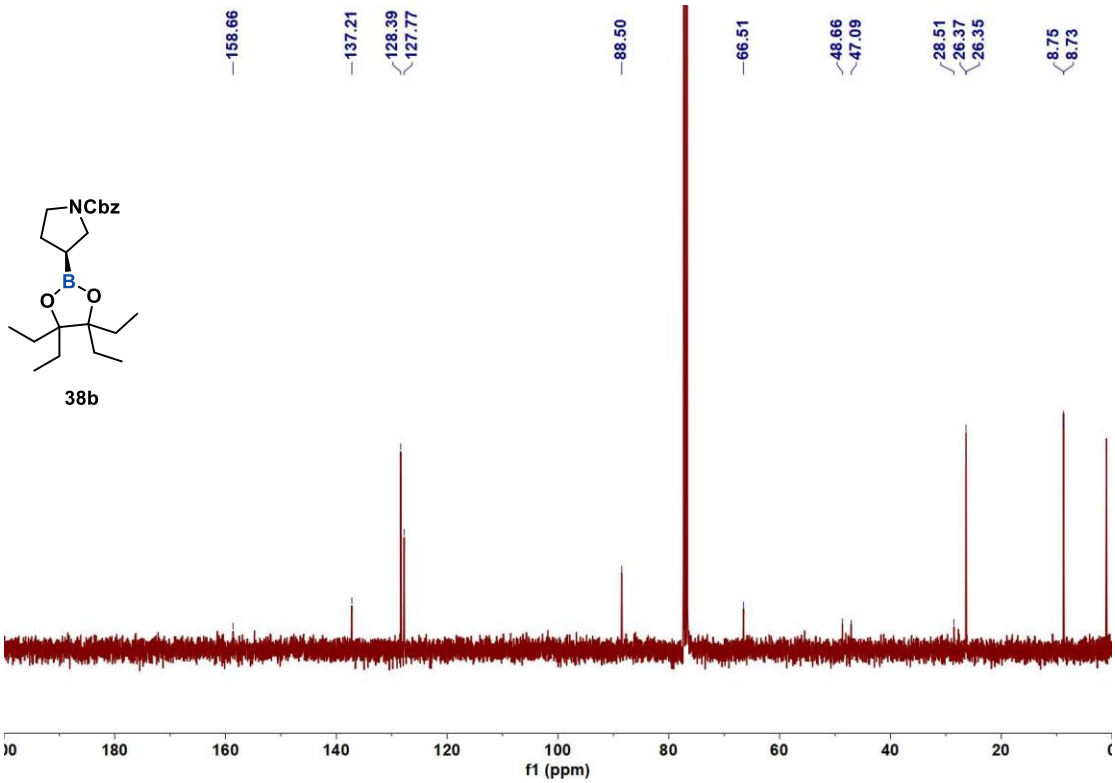


Figure S204. $^{13}C\{^{1}H\}$ NMR spectrum of **38b** in $CDCl_3$ at 298K

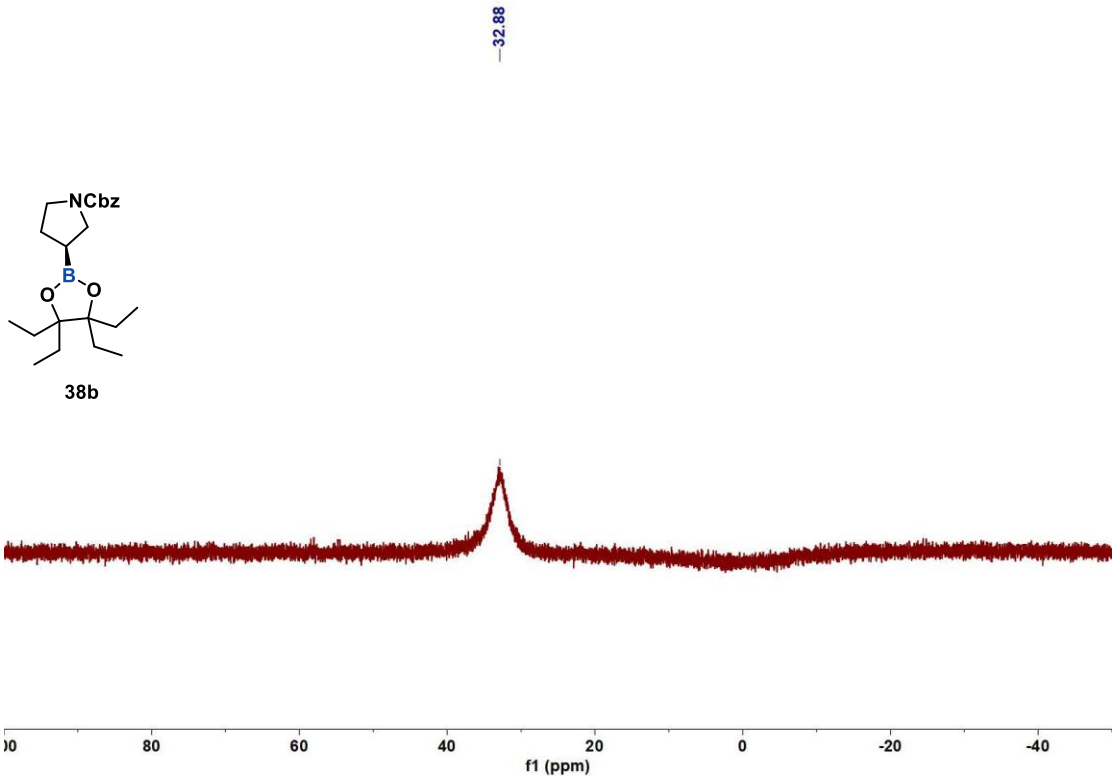


Figure S205. $^{11}B\{^{1}H\}$ NMR spectrum of **38b** in $CDCl_3$ at 298K

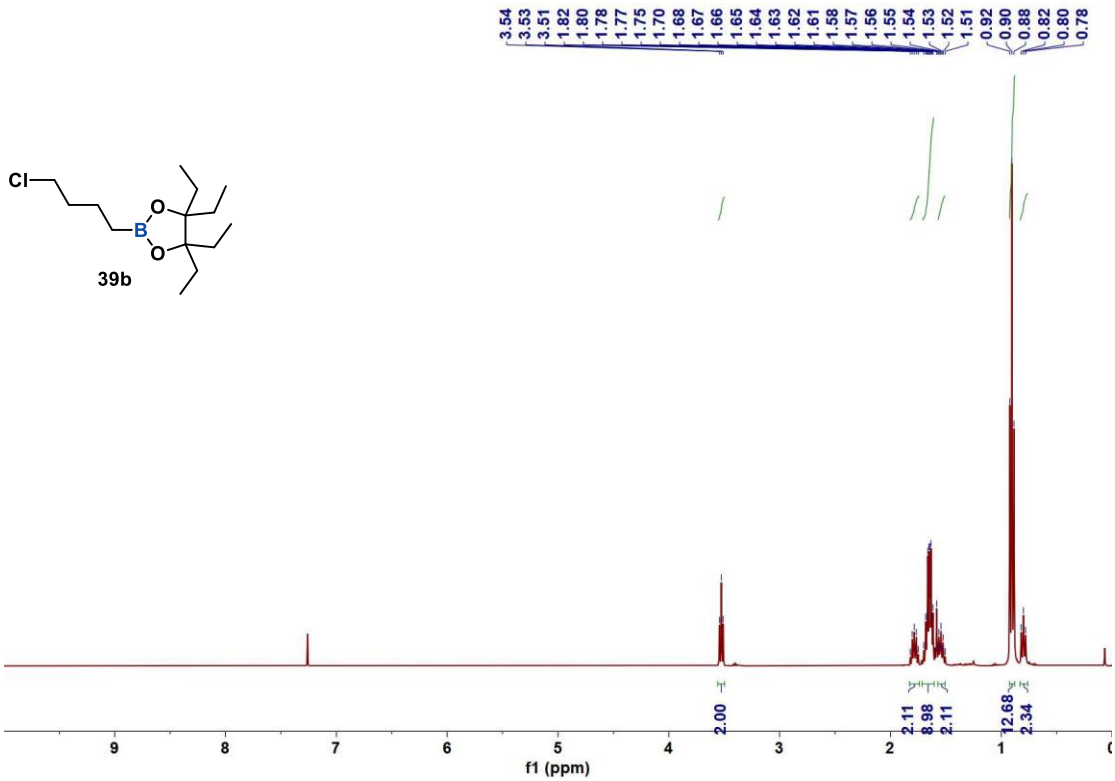


Figure S206. ^{1}H NMR spectrum of **39b** in $CDCl_3$ at 298K

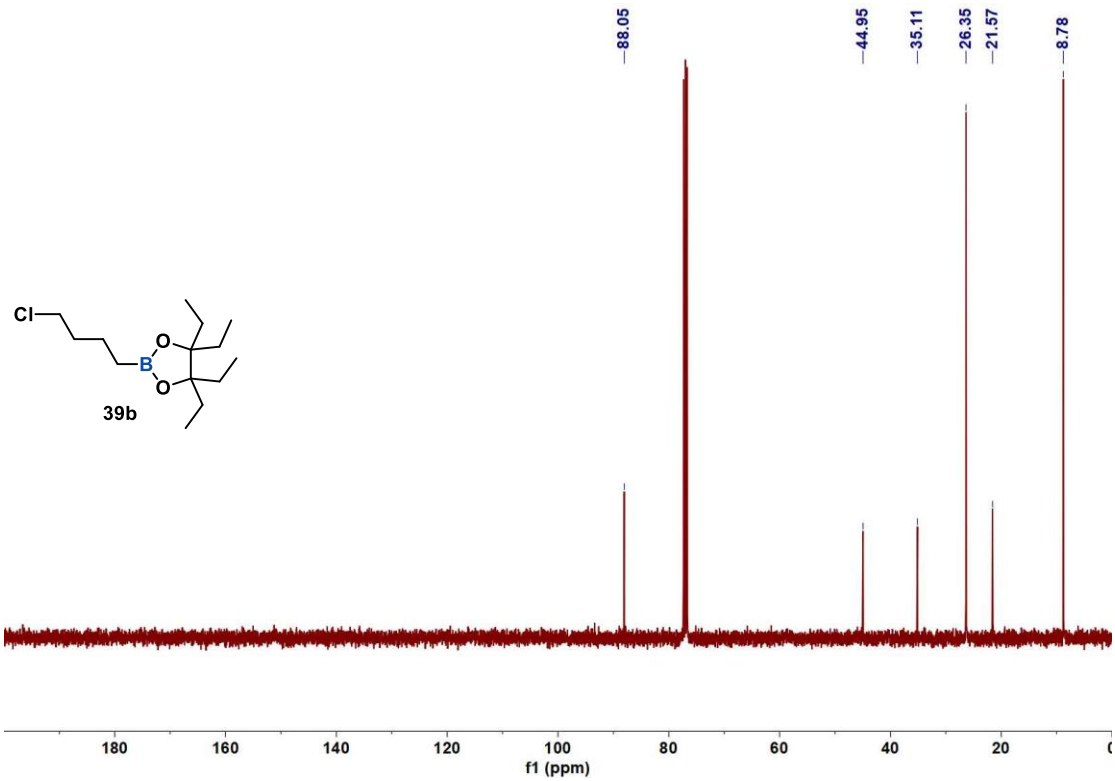


Figure S207. $^{13}C\{^{1}H\}$ NMR spectrum of **39b** in $CDCl_3$ at 298K

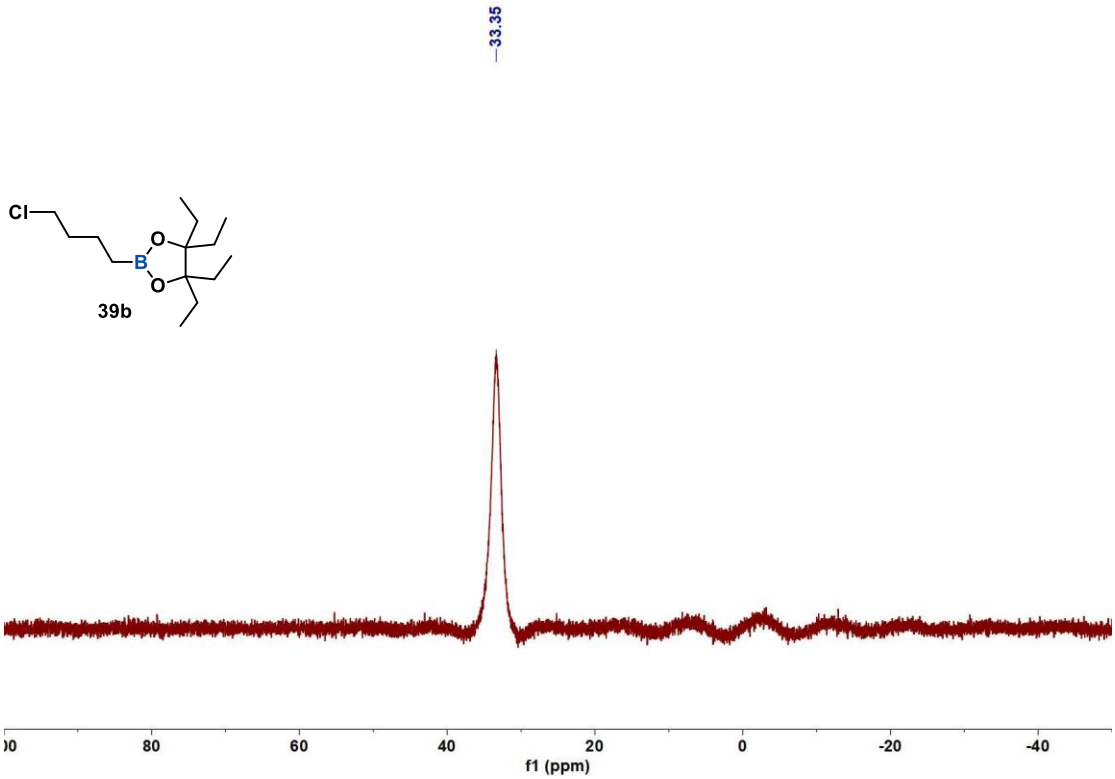
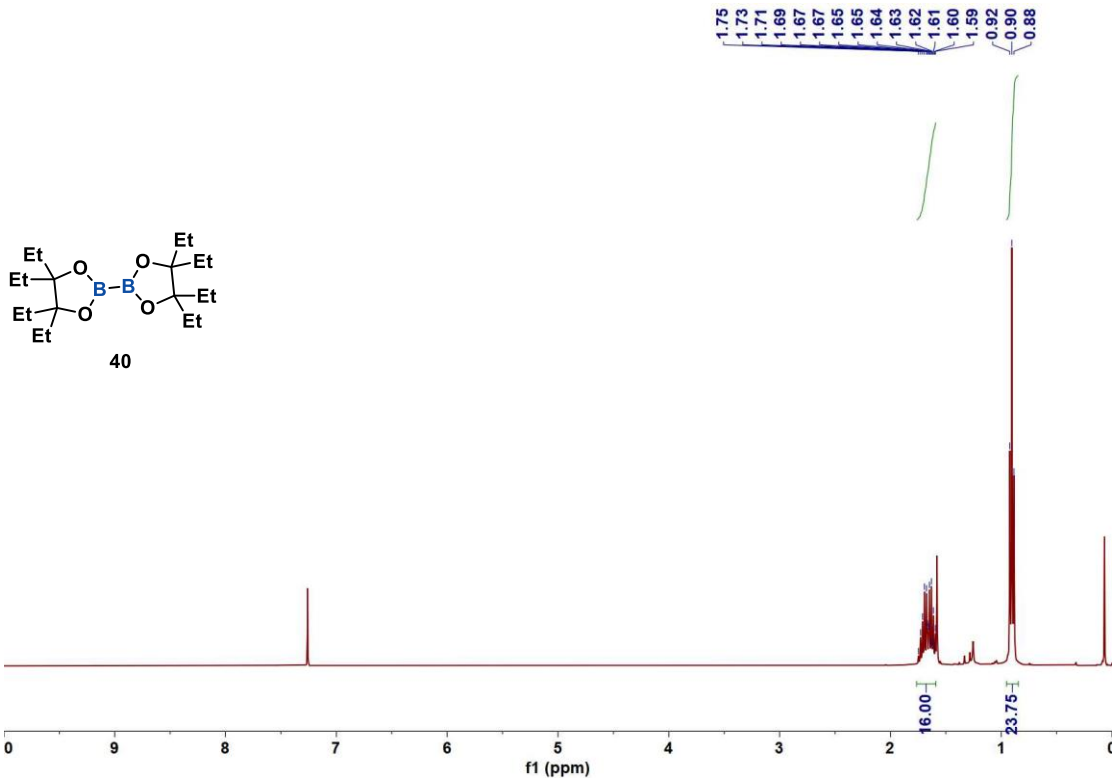


Figure S208. $^{11}B\{^{1}H\}$ NMR spectrum of **39b** in $CDCl_3$ at 298K



40

Figure S209. ^{1}H NMR spectrum of **40** in $CDCl_3$ at 298K

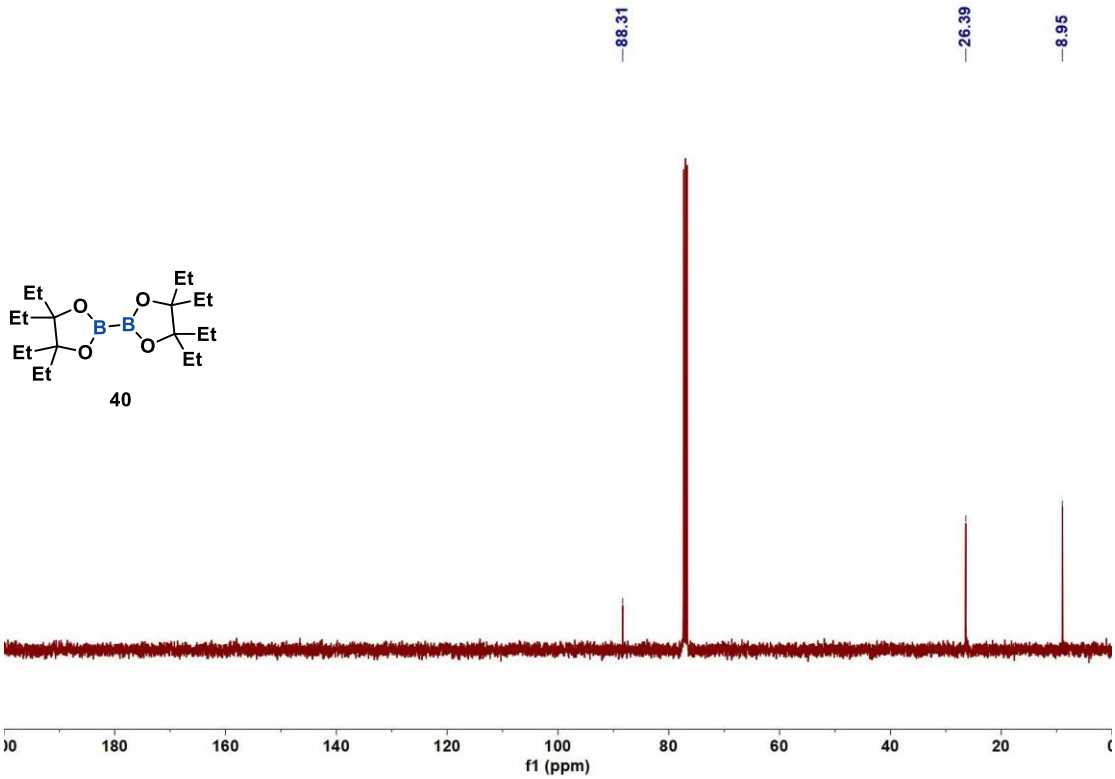


Figure S210. $^{13}C\{^{1}H\}$ NMR spectrum of **40** in $CDCl_3$ at 298K

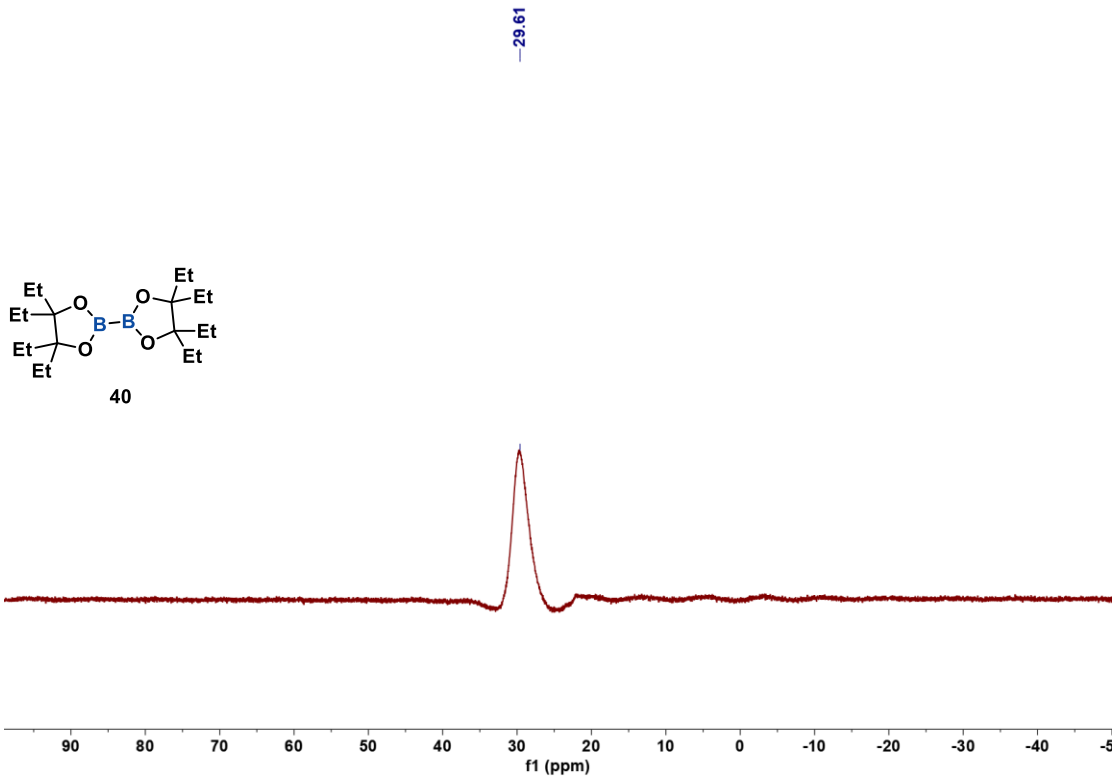


Figure S211. $^{11}B\{^{1}H\}$ NMR spectrum of **40** in $CDCl_3$ at 298K

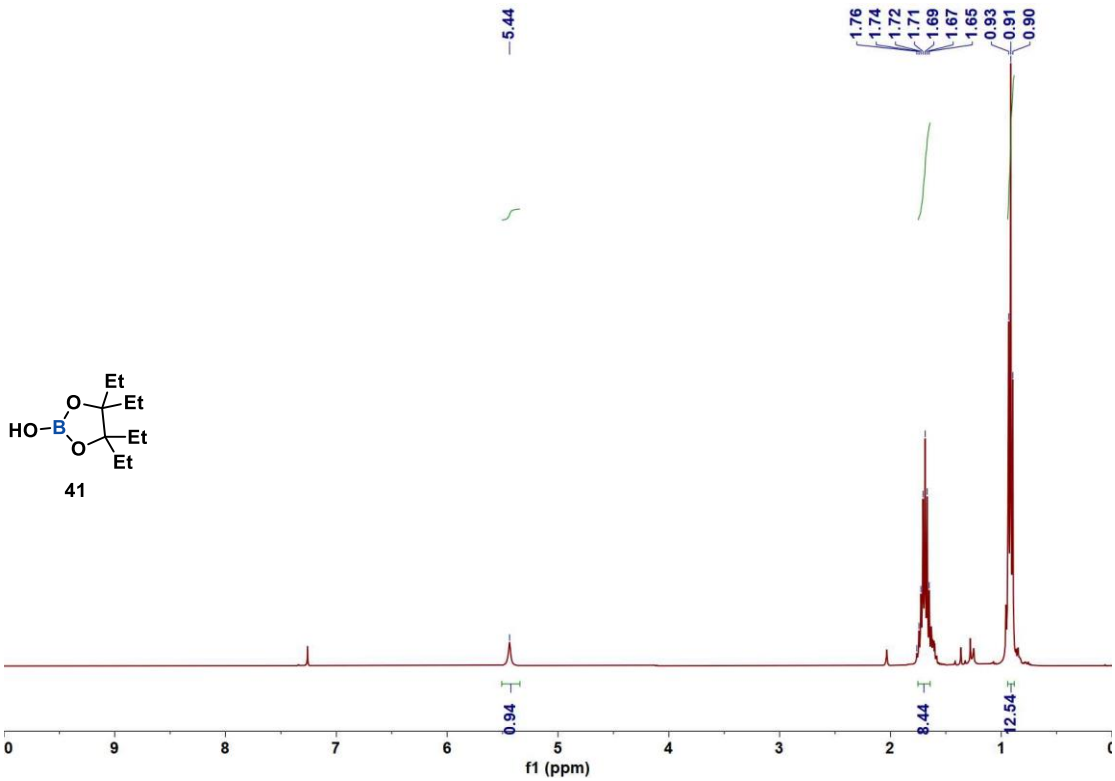


Figure S212. ^{1}H NMR spectrum of **41** in $CDCl_3$ at 298K

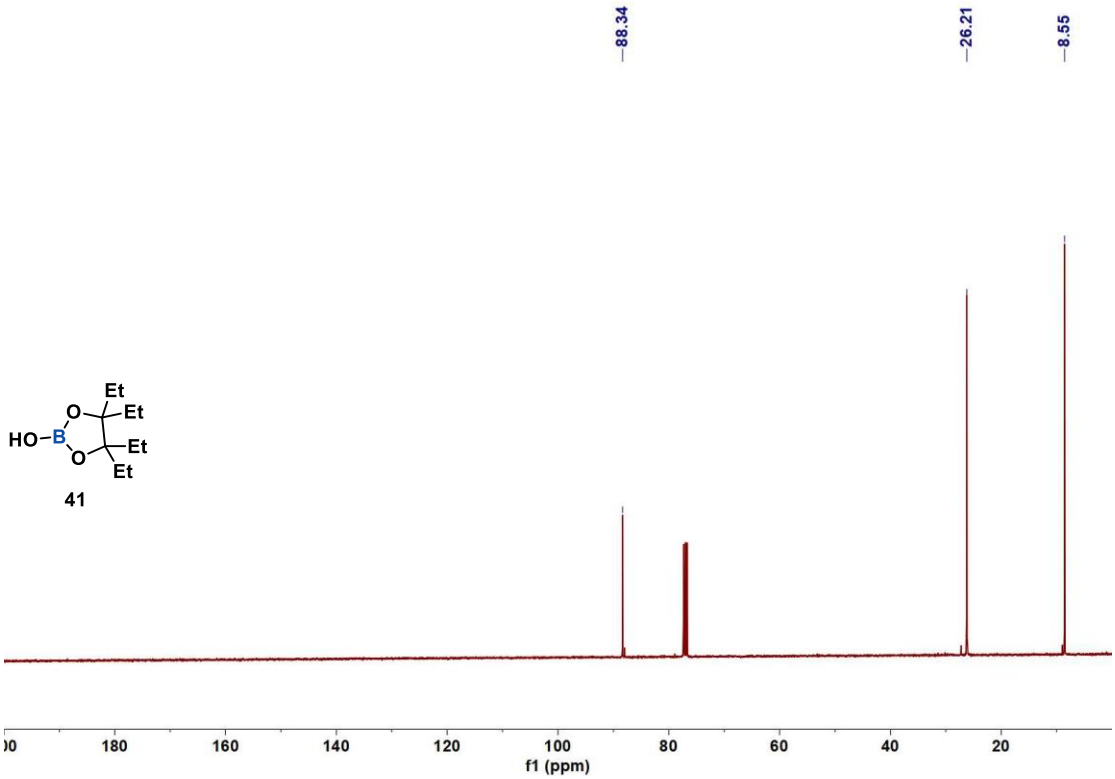


Figure S213. $^{13}C\{^{1}H\}$ NMR spectrum of **41** in $CDCl_3$ at 298K

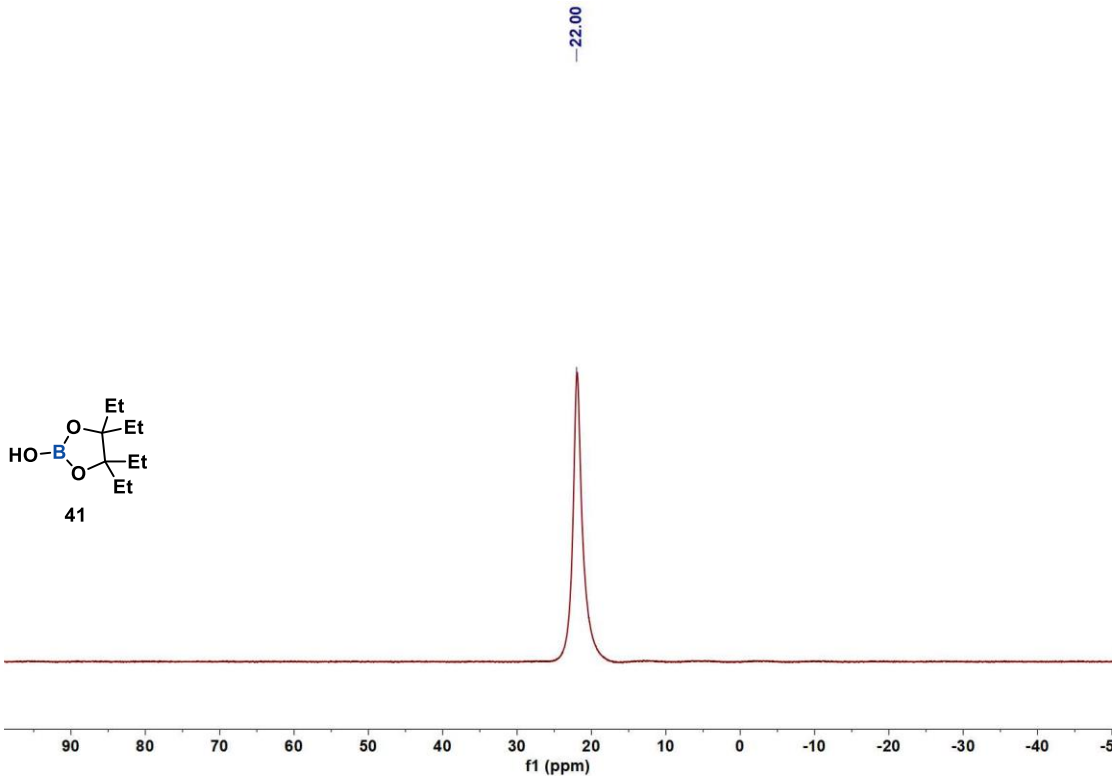


Figure S214. $^{11}B\{^{1}H\}$ NMR spectrum of **41** in $CDCl_3$ at 298K