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## 1. General information.

### General considerations.

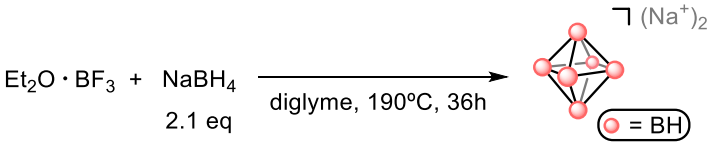
Reactions were performed using standard schlenk line or glovebox techniques under a $N_2$ atmosphere. Anhydrous MeCN, THF, $Et_2O$, DCM were used from a Solvent Purification System (SPS) are used for reactions. Solvents used in the glovebox are from the SPS and were stored in a glovebox over activated 3Å molecular sieves. $K_3PO_4$ was purchased from Sigma-Aldrich. Tetrabutylammonium hydroxide (55 wt % in $H_2O$) was purchased from Oakwood Chemical. Tetrabutylammonium bromide ($NBu_4Br$) was purchased from Acros Organics, deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. $MePh_3PBr$ was purchased from Oakwood Chemical, Lot No. A0356673. $BF_3{\bullet}Et_2O$ was purchased from Sigma-Aldrich, Lot No. SHBH4070V. $NaBH_4$ was purchased from Strem Chemicals, Inc. All other reagents were purchased from commercial vendors and used without further purification.

### Instrumentations.

$^1H$, $^{13}C\{^1H\}$, and $^{11}B$, $^{11}B\{^1H\}$, $^{31}P\{^1H\}$, $^{19}F$ and $^{77}Se$ NMR spectra were recorded on a Bruker AV500, a Bruker AV400 or a Bruker DRX 500 spectrometer. MestReNova (Version 12.0.4-22023) software was used to process the NMR data. $^1H$ and $^{13}C$ 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). $^{11}B$ spectra were referenced to $BF_3{\cdot}Et_2O$ as an external standard in a capillary in a $CDCl_3$-filled NMR tube immediately prior to collecting $^{11}B$ spectra of the reported compounds. $^{31}P\{^1H\}$ spectra were referenced to $H_3PO_4$ as an external standard in a capillary in a $CDCl_3$-filled NMR tube immediately prior to collecting $^{31}P$ spectra of the reported compounds. $^{77}Se$ spectra were referenced to $(PhSe)_2$ as an external standard (δ 463 ppm) in a capillary in a $CDCl_3$-filled NMR tube immediately prior to collecting $^{77}Se$ spectra. Microwave reactions were performed using a CEM Discover SP microwave synthesis reactor. The reactions were conducted in glass 10 mL microwave reactor vials purchased from CEM with silicone /PTFE caps equipped with a stir bar. Mass spectrometry data were acquired using a Q Exactive™ or Waters LCT Premier mass spectrometer by direct injection. Agilent High-resolution Mass spectrometry was used collect mass data for final alkyl boronic ester products. X-ray Photoelectron Spectroscopy (XPS) measurements were conducted using an AXIS Ultra DLD instrument (Kratos Analytical Inc., Chestnut Ridge, NY, USA). All XPS spectra were measured using a monochromatic Al Kα X-ray source (10 mA for both survey and high-resolution scans, 15 kV) with a 300 × 700 nm oval spot size. The pressure of the analyzer chamber was maintained below $4\times10^{-9}$ Torr during the measurement. Spectra were collected with 20 eV for high-resolution spectra of B 1s using a 300 ms dwell time and 30 scans. All XPS peaks were charge referenced to the adventitious carbon 1s signal at 284.6 eV. Cyclic voltammetry (CV) was performed on substituted clusters using a CH Instruments Model 600D potentiostat with a glassy carbon disc working electrode, platinum wire counter electrode, and Ag/AgCl wire reference in a saturated solution of KCl in $CH_3CN$. $CH_3CN$ solutions were degassed for 10 minutes by sparging with dry nitrogen gas. All experiments were conducted in a 0.1M $[NnBu_4][PF_6]/CH_3CN$ solution with 0.5 mM analyte concentrations and were performed under constant flow of dry nitrogen gas. Ferrocene was used as an internal standard.

**2. Preparation of hexaborate anions 7, 8 and 9.**

**Synthesis of $Na_2B_6H_6$ (7) (Modified from Kabbani)**[1]




A 1 L round bottom, 3-neck flask was charged with 30 g (793 mmol) of $NaBH_4$ in a $N_2$ glovebox. The reaction flask was then transferred out and a reflux condenser connected to a $N_2$ Schlenk line was attached. 400 mL of dry diglyme (stored over 3Å molecular sieves) were added to the reaction flask with stirring. **Caution:** heating $NaBH_4$ in diglyme can result in the formation of $B_2H_6$ so during the initial heating step, the nitrogen is allowed to flow out of the flask through an acetone trap. The reaction mixture is then heated in an oil bath at 60 ºC for 30 minutes. At this point, the acetone trap can be removed and a silicon oil bubbler attached to the Schlenk line is sufficient to prevent any overpressure. Holding the oil bath at 60 ºC, $BF_3$•$Et_2O$ (48 mL, 374 mmol based on $BF_3$, diluted with 50 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 $BF_3$•$Et_2O$ was complete, the reaction mixture was heated to 100 ºC for 1 hr. and then heated to 190 ºC for 40 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 40 ºC before being filtered and washed with an additional 50 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, rather than completely drying the mixture, but this tends to result in some loss of $Na_2B_6H_6$. 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 under vacuum and gave 9.1 g $Na_2B_6H_6$ (0.0779 mol, 80 %). The yield was based on chemical equation below using $BF_3$•$Et_2O$ as the limiting reagent[1]:

$$5\ NaBH_4 + 4\ BF_3{\bullet}Et_2O \longrightarrow 3\ NaBF_4 + Na_2B_6H_6 + 7\ H_2 + 4\ Et_2O$$

**$^{11}$B NMR ($CDCl_3$, 128 MHz)** δ -13.93 (d, *J* = 119.8 Hz). **$^{11}$B{$^1$H} NMR ($CDCl_3$, 128 MHz)** δ -13.98 (s)

Additional notes: Residual $NaBF_4$ can be removed by dissolving the $Na_2B_6H_6$ in water followed by treatment with KCl and filtration through celite. It is likely that very small amount of residual borates remains and these can be removed by precipitation of $B_6H_6^{2-}$ with organic cations such as $NBu_4^+$ or $MePPh_3^+$.

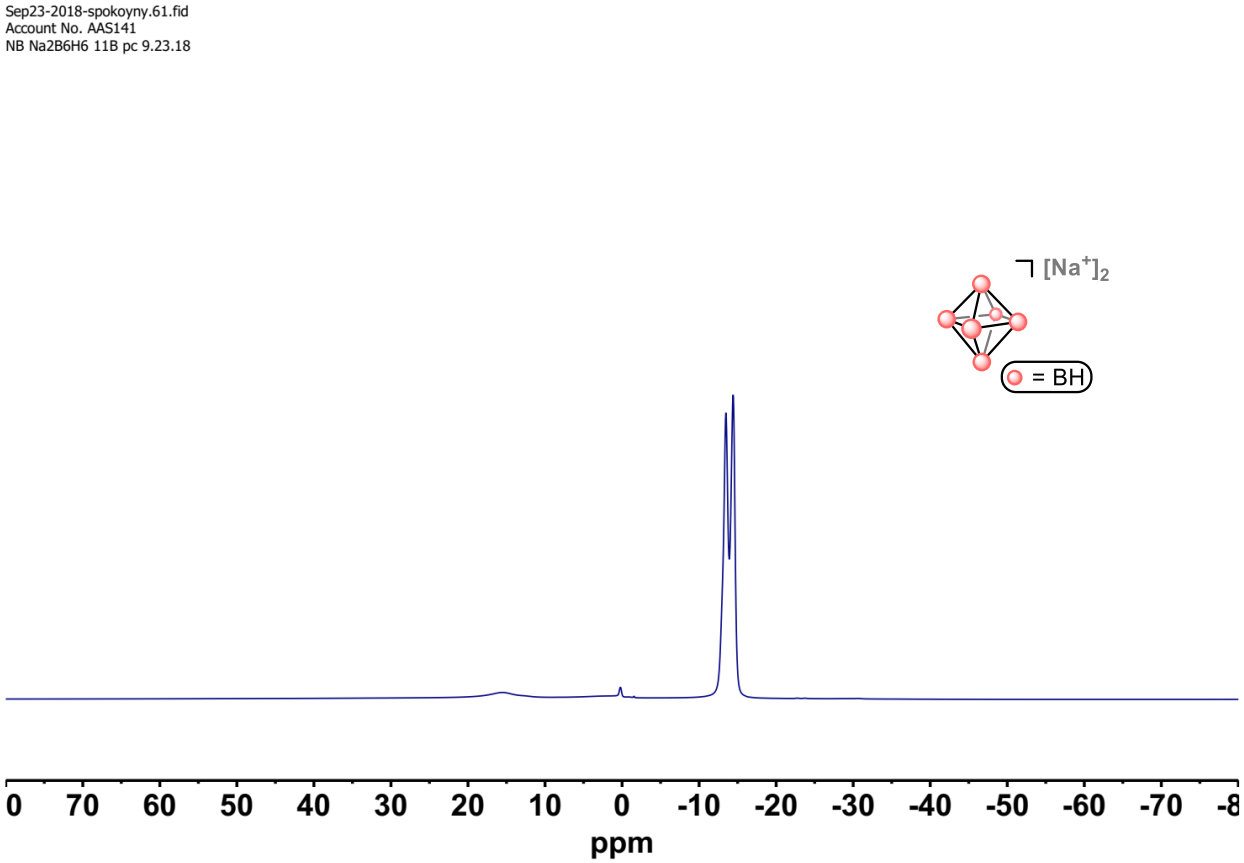



**Fig. S1.** $^{11}B$ NMR spectrum of **7** in $D_2O$ at 298K.

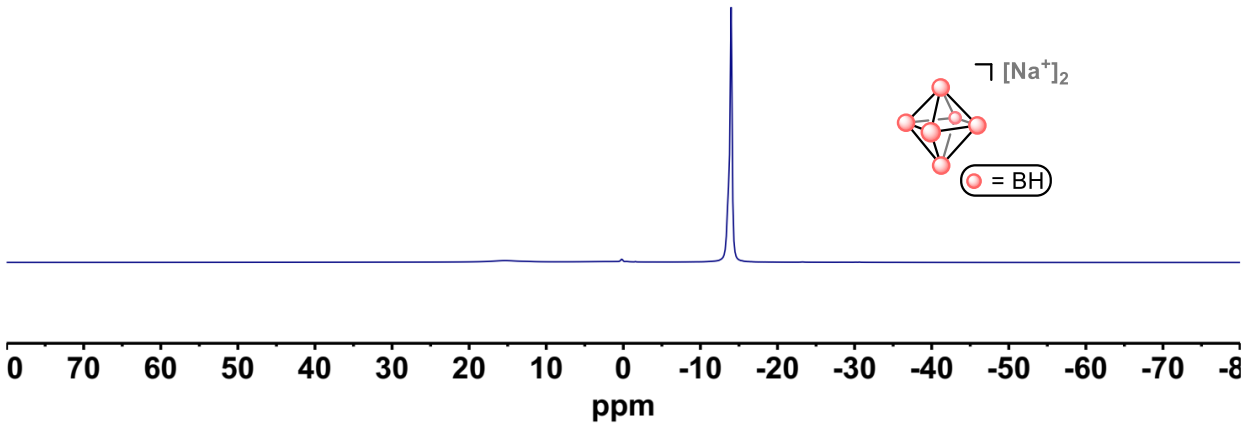
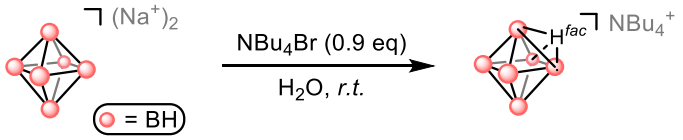



**Fig. S2.** $^{11}B\{^1H\}$ NMR spectrum of **7** in $D_2O$ at 298K.

**Synthesis of [NBu$_4$][B$_6$H$_6$H$^{fac}$] (8).**




The synthesis of [NBu$_4$][B$_6$H$_6$H$^{fac}$] has been reported before (*32*). A 200 mL round flask was charged with Na$_2$B$_6$H$_6$ (2.33 g, 20 mmol) and H$_2$O (15 mL). Under stirring, an aqueous solution of NBu$_4$Br (6.12 g, 19 mmol) in 20 mL of H$_2$O 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$_2$O (3 × 10 mL), then the white solid was dried under vacuum to remove residual water. Recrystallization from hot EtOH/MeOH (1:1, v/v) gave white crystals (2.8 g, 45%).
**$^1$H NMR (CDCl$_3$, 400 MHz)** δ 3.32-3.10 (m, 8H), 1.70-1.55 (m, 8H), 1.44 (hd, *J* = 7.3, 1.7 Hz, 8H), 1.00 (td, *J* = 7.3, 1.8 Hz, 12H), -5.30 (s, 1H, facial proton). **$^{11}$B NMR (CDCl$_3$, 128 MHz)** δ -13.45 (d, *J* = 143.9 Hz, 6B). **$^{11}$B{$^1$H} NMR (CDCl$_3$, 400 MHz)** δ -13.45 (s).

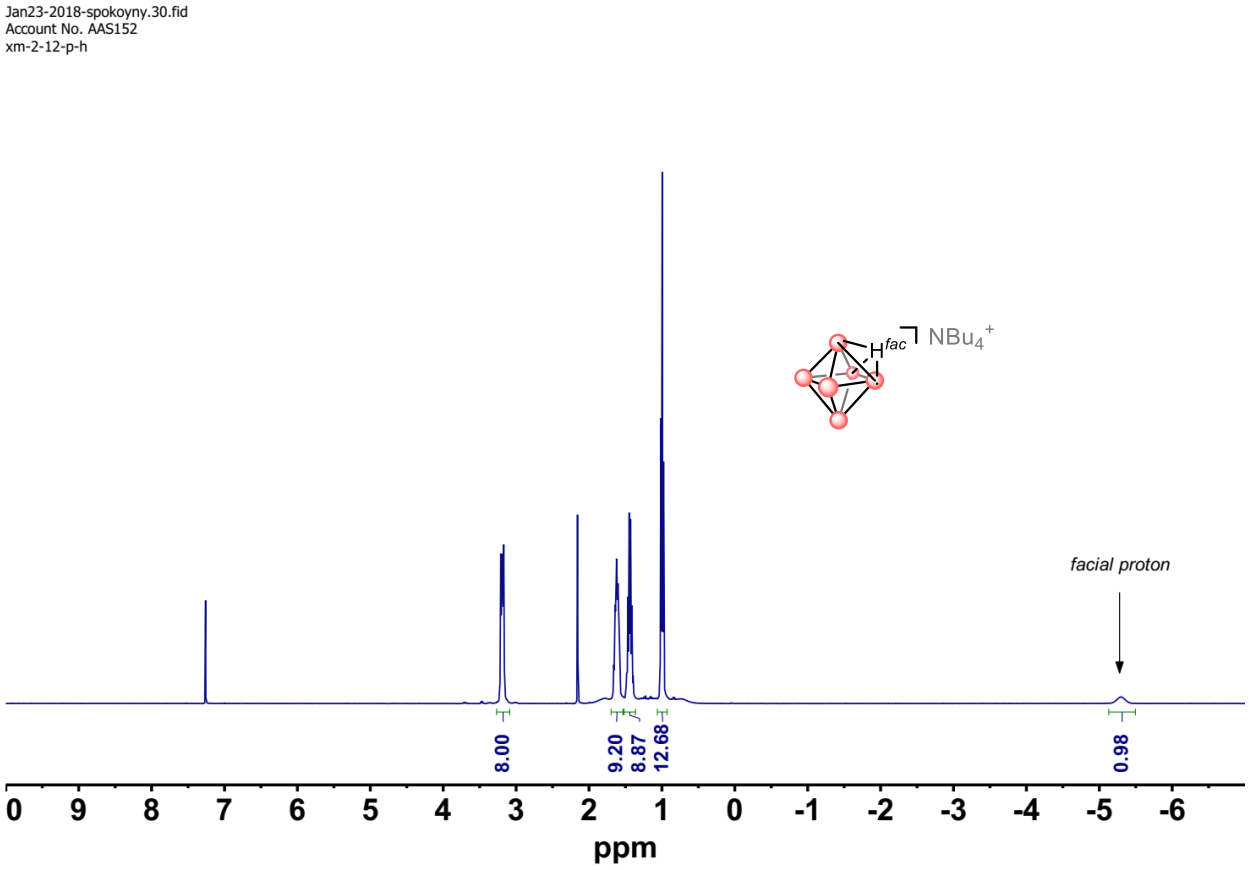



**Fig. S3.** $^1$H NMR spectrum of **8** in CDCl$_3$ at 298K.

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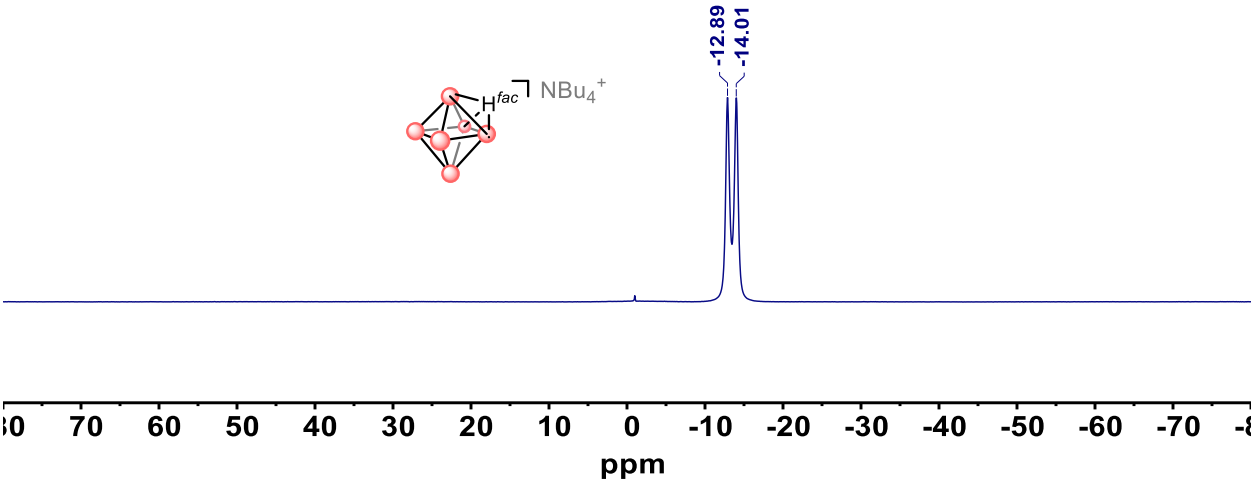



**Fig. S4.** $^{11}B$ NMR spectrum of **8** in $CDCl_3$ at 298K.

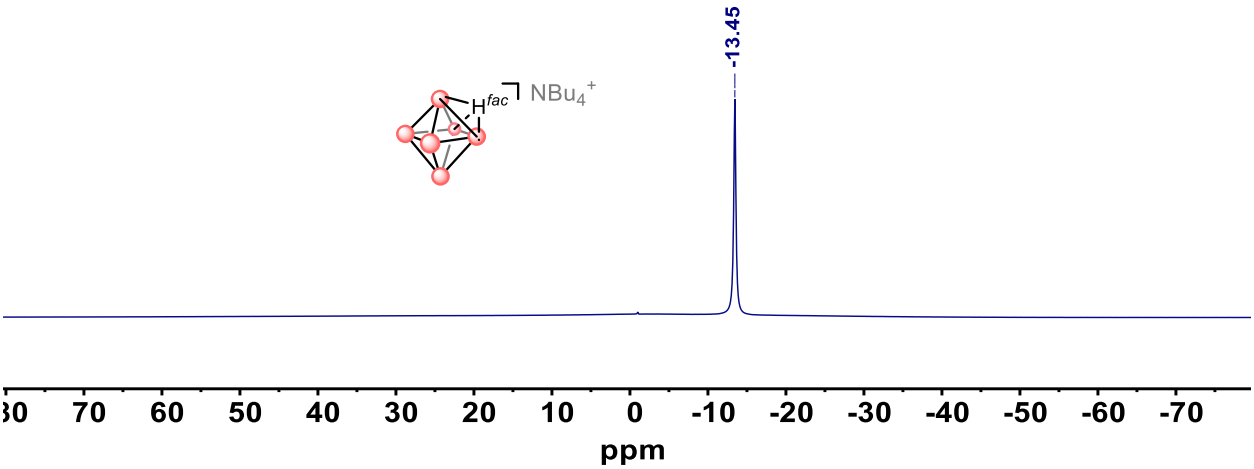
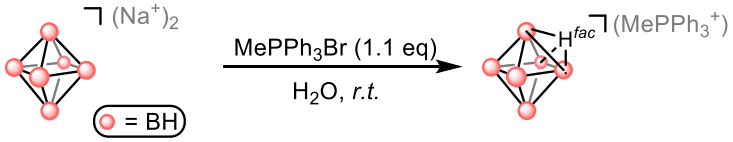



**Fig. S5.** $^{11}B\{^1H\}$ NMR spectrum of **8** in $CDCl_3$ at 298K.

**Synthesis of $[MePPh_3][B_6H_6H^{fac}]$(9)**




A 200 mL round flask was charged with $Na_2B_6H_6$ (1.16 g, 10 mmol) and $H_2O$ (10 mL). Under stirring, an aqueous solution of $MePPh_3Br$ (4.23 g, 11 mmol, 1.1 eq) in 20 mL of $H_2O$ was added. A large amount of white precipitate formed immediately. The reaction mixture was stirred for another three hours. The white precipitate was collected by filtration and washed with $H_2O$ (3 × 10 mL), then the white solids were dried under vacuum to remove residual water. Recrystallization from hot EtOH/MeOH (1:1, v/v) gave white crystal (1.4 g, 40%). Crystals suitable for single crystal X-ray diffraction studies are obtained by slow evaporation of concentrated MeCN solution of **9**.
**$^1$H NMR ($CD_2Cl_2$, 500 MHz)** δ 7.94-7.84 (m, 3H), 7.73 (td, *J* = 7.8, 3.4 Hz, 6H), 7.67-7.58 (m, 6H), 2.83 (d, *J* = 13.2 Hz, 3H), -5.47 (s, 1H, facial proton). **$^{11}$B NMR ($CD_2Cl_2$, 161 MHz)** δ -11.95 (d, *J* = 142.4 Hz). **$^{11}$B{$^1$H} NMR ($CD_2Cl_2$, 161 MHz)** δ -11.97 (s). **$^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 203 MHz)** δ 19.70 (s). **$^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 500 MHz)** δ 135.41 (d, *J* = 3.1 Hz), 132.89 (d, *J* = 10.8 Hz), 130.46 (d, *J* = 13.0 Hz), 118.31 (d, *J* = 89.2 Hz), 10.13 (d, *J* = 58.7 Hz).

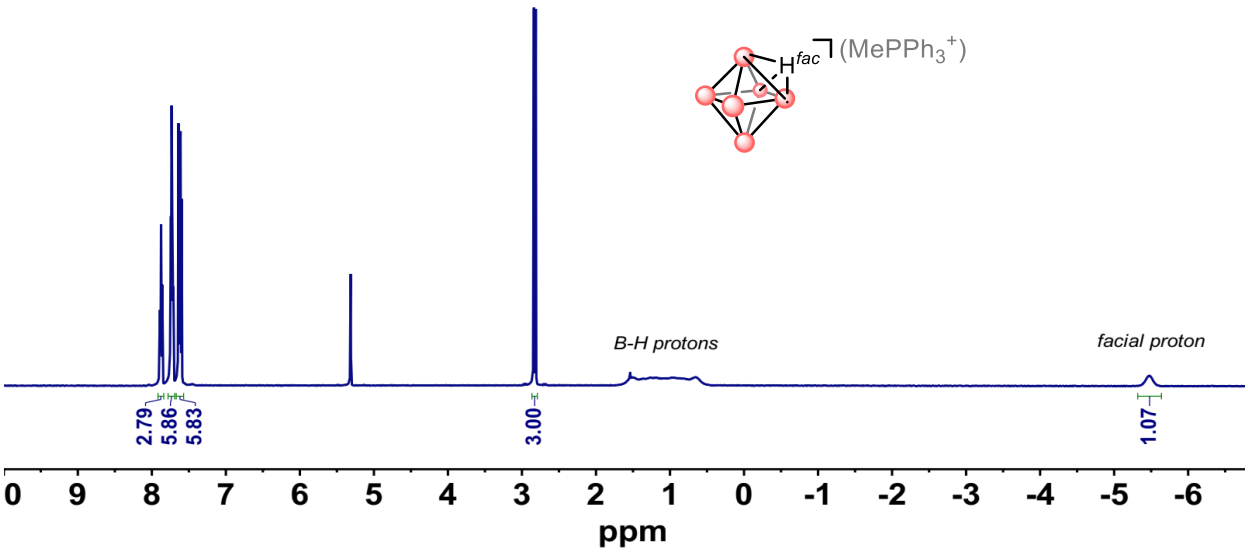



**Fig. S6.** $^1$H NMR spectrum of **9** in $CD_2Cl_2$ at 298K.

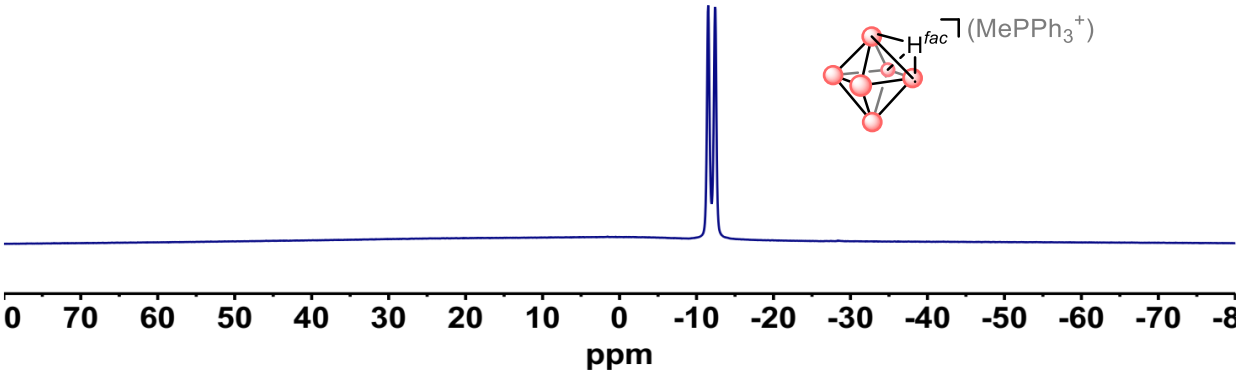



**Fig. S7.** $^{11}B$ NMR spectrum of **9** in $CD_2Cl_2$ at 298K.

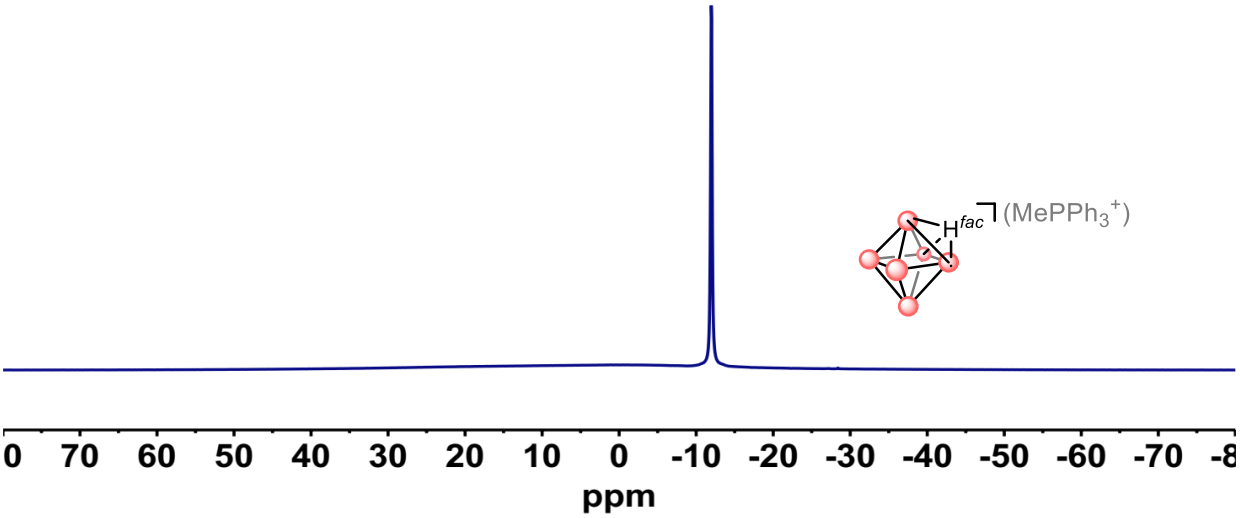



**Fig. S8.** $^{11}B\{^1H\}$ NMR spectrum of **9** in $CD_2Cl_2$ at 298K.

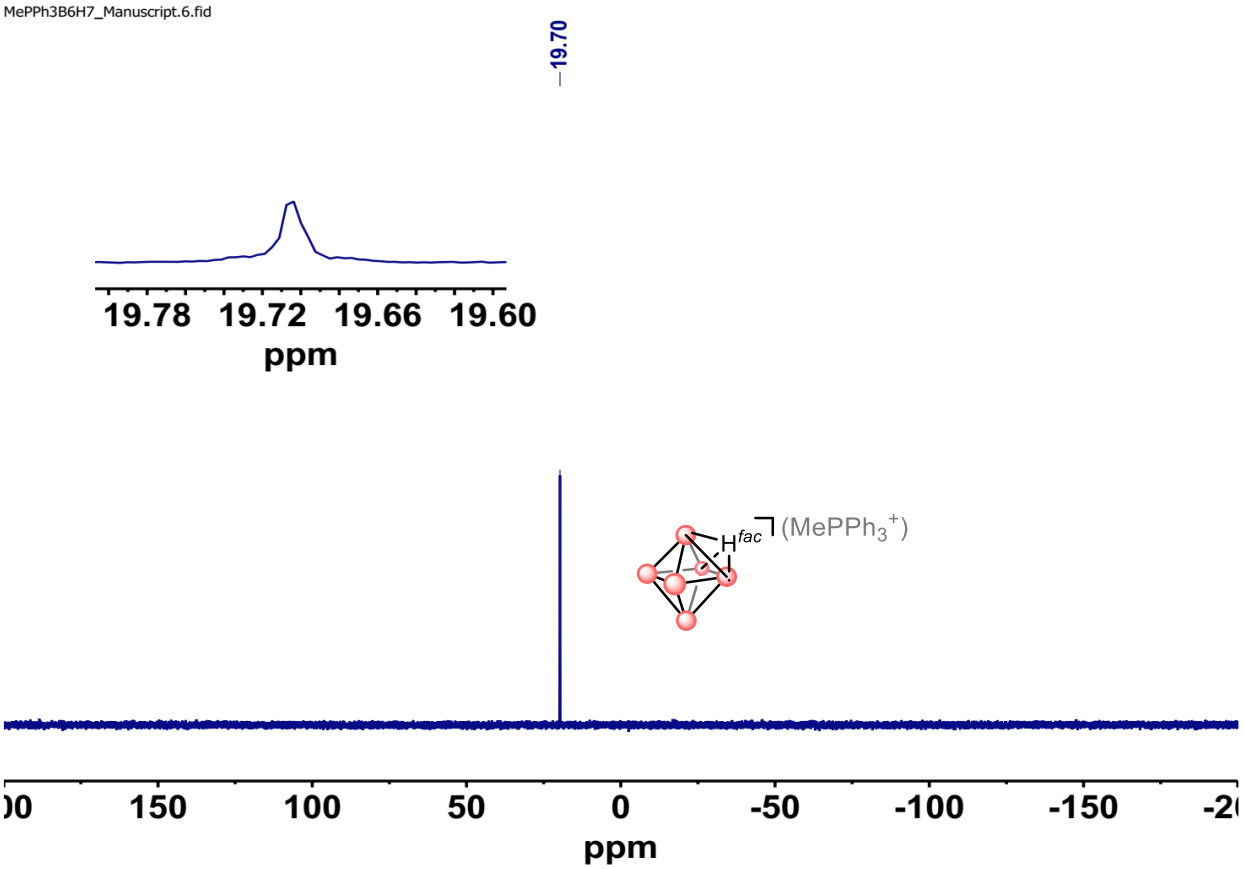



**Fig. S9.** $^{31}P\{^{1}H\}$ NMR spectrum of **9** in $CD_2Cl_2$ at 298K.

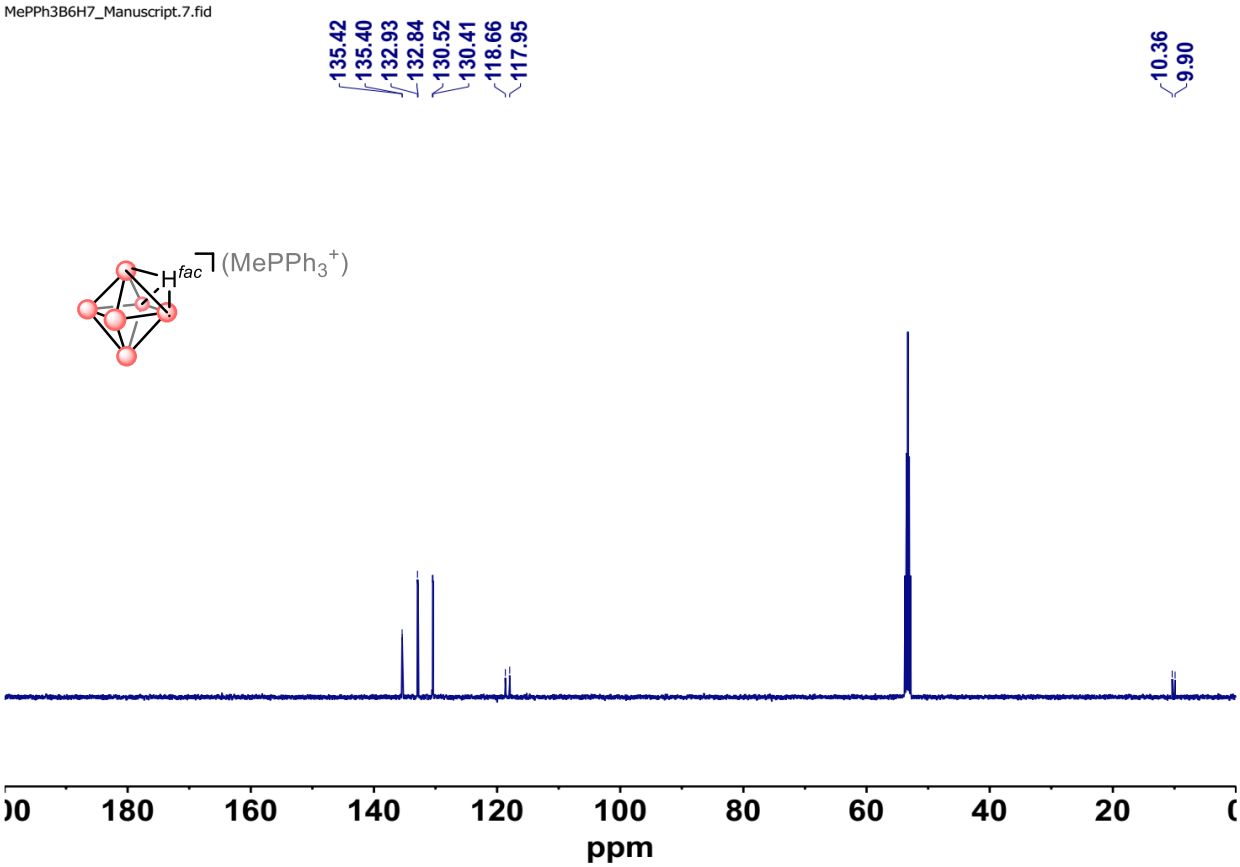


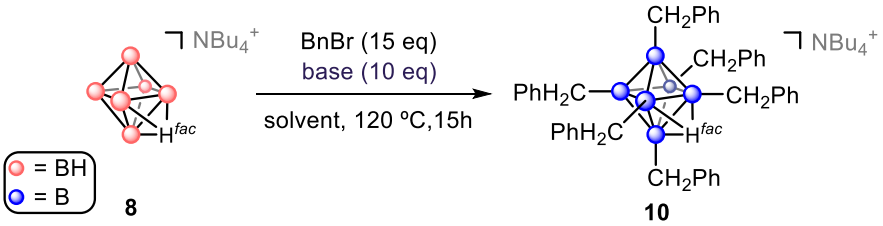

**Fig. S10.** $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CD_2Cl_2$ at 298K.

### 3. Optimization of reaction conditions for peralkylation of hexaborate anions.

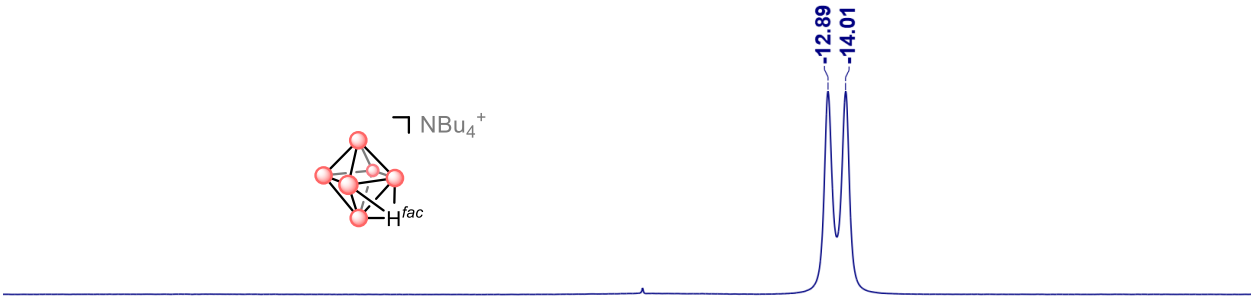
#### General procedures for optimization of reaction conditions

In a glovebox, a 10 mL glass tube was charged with a stir bar, $[NBu_4][B_6H_6H^{fac}]$ (32 mg, 0.1 mmol) and $K_3PO_4$ (1 mmol, 10 eq), then the solvent (0.5 mL) was added and stirred for 2 min. Benzyl bromide (0.18 mL, 1.5 mmol, 15 eq) was added via a syringe, the glass tube was sealed with screw cap, wrapped with electrical tape and transferred out of the glovebox. The reaction tube was heated in an oil bath at 120 °C for 15 hours. The reaction mixture was cooled to room temperature and diluted with MeCN (2 mL). $^{11}B$ NMR spectroscopy was used to determine the ratio of **10**/**8**.

**Table S1.** Optimization of perbenzylation of hexaborate $[NBu_4][B_6H_6H^{fac}]$.




| entry | base | solvent | **10**/**8** ratio | conversion (%) |
|---|---|---|---|---|
| 1 | DIEA | DMF | 10/1 | 90 |
| 2 | *t*-BuOK | DMF | -- | >95 |
| 3 | $Cs_2CO_3$ | DMF | -- | >95 |
| 4 | DIEA | 1,4-Dioxane | 5/1 | 83 |
| 5 | $Cs_2CO_3$ | 1,4-Dioxane | 9/1 | 90 |
| 6 | $Cs_2CO_3$ | DMAc | 2/1 | 66 |
| 7 | DIEA | DMAc | 3/1 | 75 |
| 8 | *t*-BuOK | MeCN | -- | >95 |
| 9 | $Cs_2CO_3$ | MeCN | 2.5/1 | 70 |
| 10 | $K_3PO_4$ | MeCN | >20/1 | >95 |



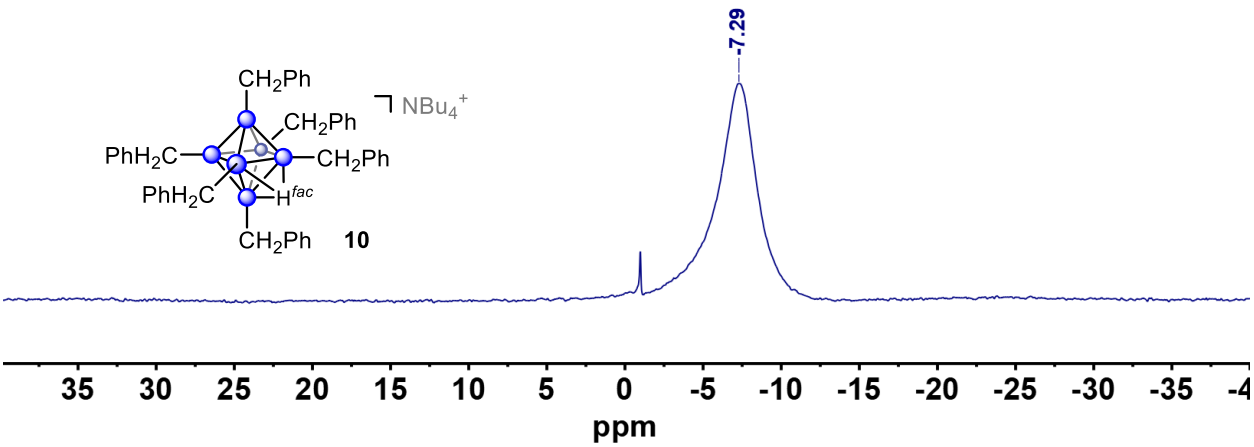



**Fig. S11.** $^{11}$B NMR spectra of substrate **8** and reaction mixture under condition (**Table S1**, entry 10) after 15 hours. The $^{11}$B NMR spectra were measured in $CH_3CN$ at 298K.

**General procedure for the synthesis of perbenzylated hexaborates 10 and 11.**

In the glovebox, a 10 mL glass tube was charged with a stir bar, $[NBu_4][B_6H_6H^{fac}]$ (63 mg, 0.2 mmol) and $K_3PO_4$ (426 mg, 2 mmol, 10 eq), then MeCN (1.0 mL) was added and stirred for 2 min. Benzyl bromide (3.0 mmol, 15 eq) was added via a syringe, the glass tube was sealed with a screw cap, wrapped with electrical tape and transferred out of the glovebox. The reaction tube was heated at 120 °C for 15 hours. The reaction mixture was cooled to room temperature and diluted with MeCN (2 mL). Solids were filtered off and the $^{11}$B NMR spectrum of the filtrate was used to confirm the conversion of **8**. The solvent was removed under vacuum. The light orange oil obtained was washed with hexanes (3 × 5 mL). Then ethanol (0.1 mL) was added and the orange oil solidified immediately. The light orange solid was dissolved in a minimum amount of boiling ethanol and then slowly cooled to room temperature which gave light orange crystals **10** (104 mg, 69%). **$^1$H NMR ($CD_2Cl_2$, 400 MHz)** δ 7.04 (t, *J* = 7.6 Hz, 12H), 6.93-6.84 (m, 6H), 6.82-6.76 (m, 12H), 2.55-2.43 (m, 8H), 1.80 (s, 12H), 1.32-1.14 (m, 16H), 1.00 (t, *J* = 7.1 Hz, 12H), -3.54 (s, 1H, facial proton). **$^{11}$B NMR ($CD_2Cl_2$, 128 MHz)** δ -6.18 (s). The NMR spectra are consistent with our previous report[2].

The **11** was obtained following the same procedure, recrystallization gave light orange crystals **11** (182 mg, 70%). **$^1$H NMR ($CD_2Cl_2$, 400 MHz)** δ 7.16 (d, *J* = 8.3 Hz, 12H), 6.56 (d, *J* = 8.4 Hz, 12H), 2.73-2.63 (m, 8H), 1.74 (s, 12H), 1.41-1.27 (m, 16H), 1.02 (t, *J* = 1H, 6.9 Hz, 12H), -3.75 (s, 1H, facial proton). **$^{11}$B NMR ($CD_2Cl_2$, 128 MHz)** δ -7.56 (s). The NMR spectra are consistent with our previous report[2].

**The synthesis attempt for perpropylated hexaborates 12.**

In the glovebox, a 10 mL glass tube was charged with a stir bar, $[NBu_4][B_6H_6H^{fac}]$ (63 mg, 0.2 mmol) and $K_3PO_4$ (425 mg, 2 mmol, 10 eq), then MeCN (1.0 mL) was added and stirred for 2 min. Propyl iodide (0.29 mL, 3.0 mmol, 15 eq) was added via a syringe, the glass tube was sealed with a screw cap, wrapped with electrical tape and transferred out of the glovebox. The reaction tube was heated at 120 °C for 15 hours. The reaction mixture was cooled to room temperature and diluted with MeCN (2 mL). The solids were filtered off and the $^{11}$B NMR spectrum of the filtrate was used to confirm full substitution of **8**. Further purifications including adding ethanol and hexanes did not precipitate any solids. Internal standard (1,3,5-trimethoxybenzene) was added to quantify the yield of the **12** (<5% $^1$H NMR yield). The solids obtained after filtration could be dissolved in $H_2O$ (5 mL), the $^{11}$B NMR spectrum showed one doublet suggesting the presence of $[B_6H_6H^{fac}]^-$.

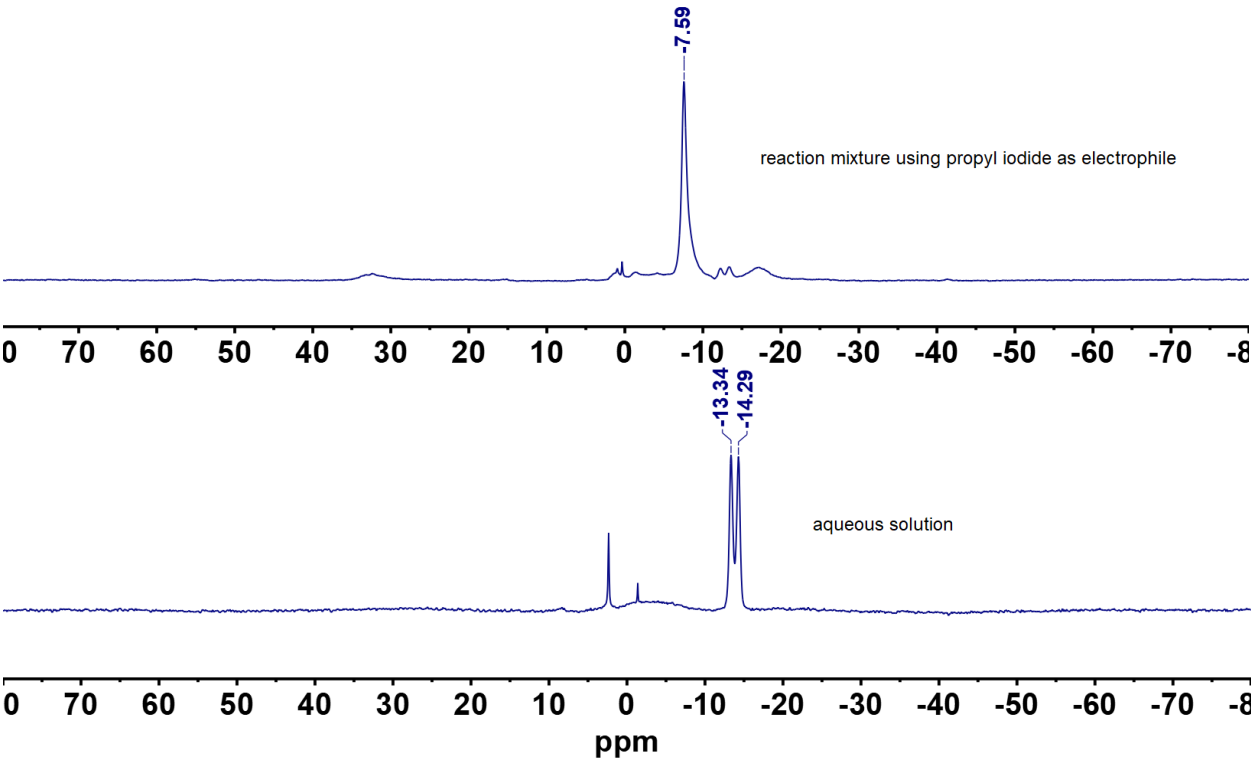



**Fig. S12.** $^{11}$B NMR spectra of reaction mixture after treating **8** with propyl iodide using standard conditions and aqueous solution of solids obtained from filtration.

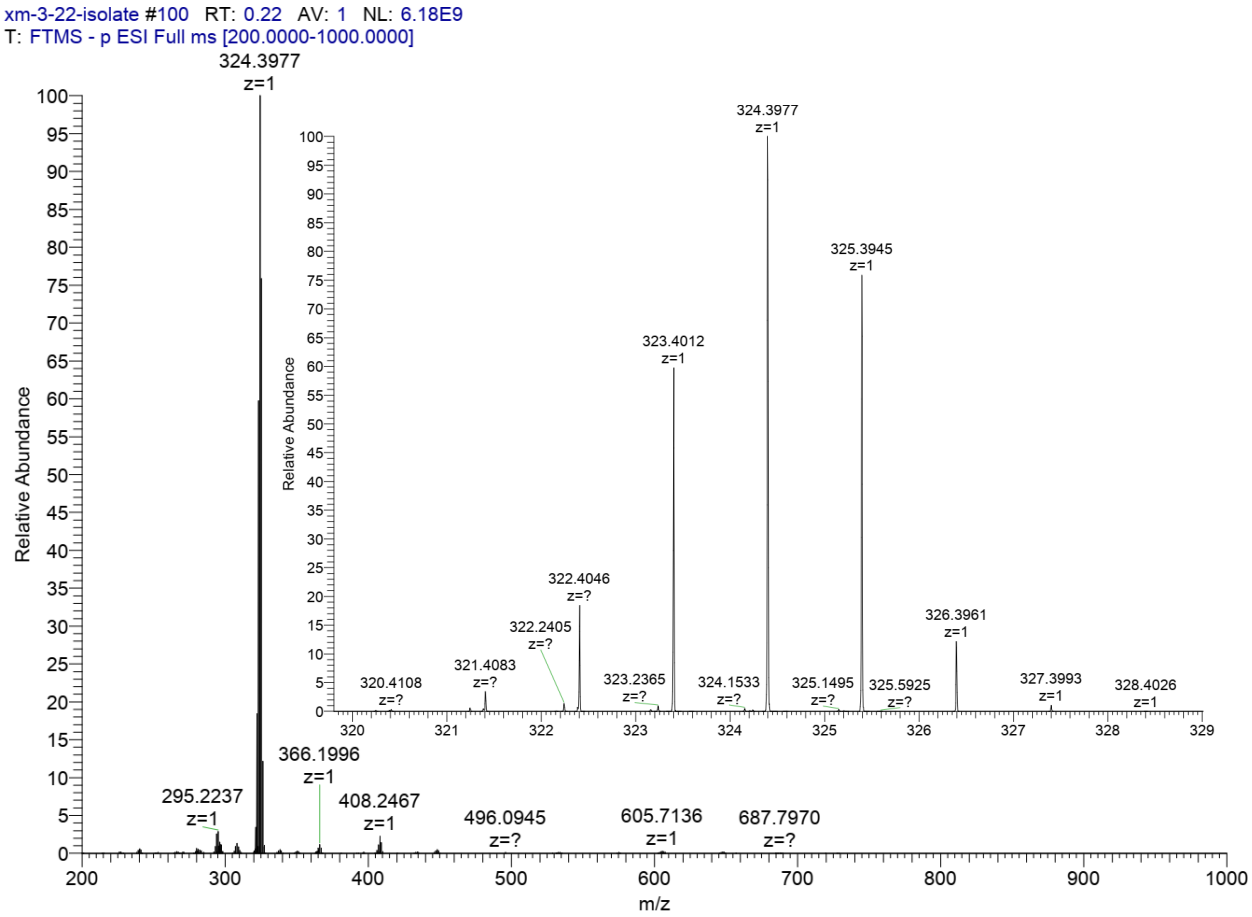



**Fig. S13.** ESI-MS(-) of reaction mixture containing **12**.

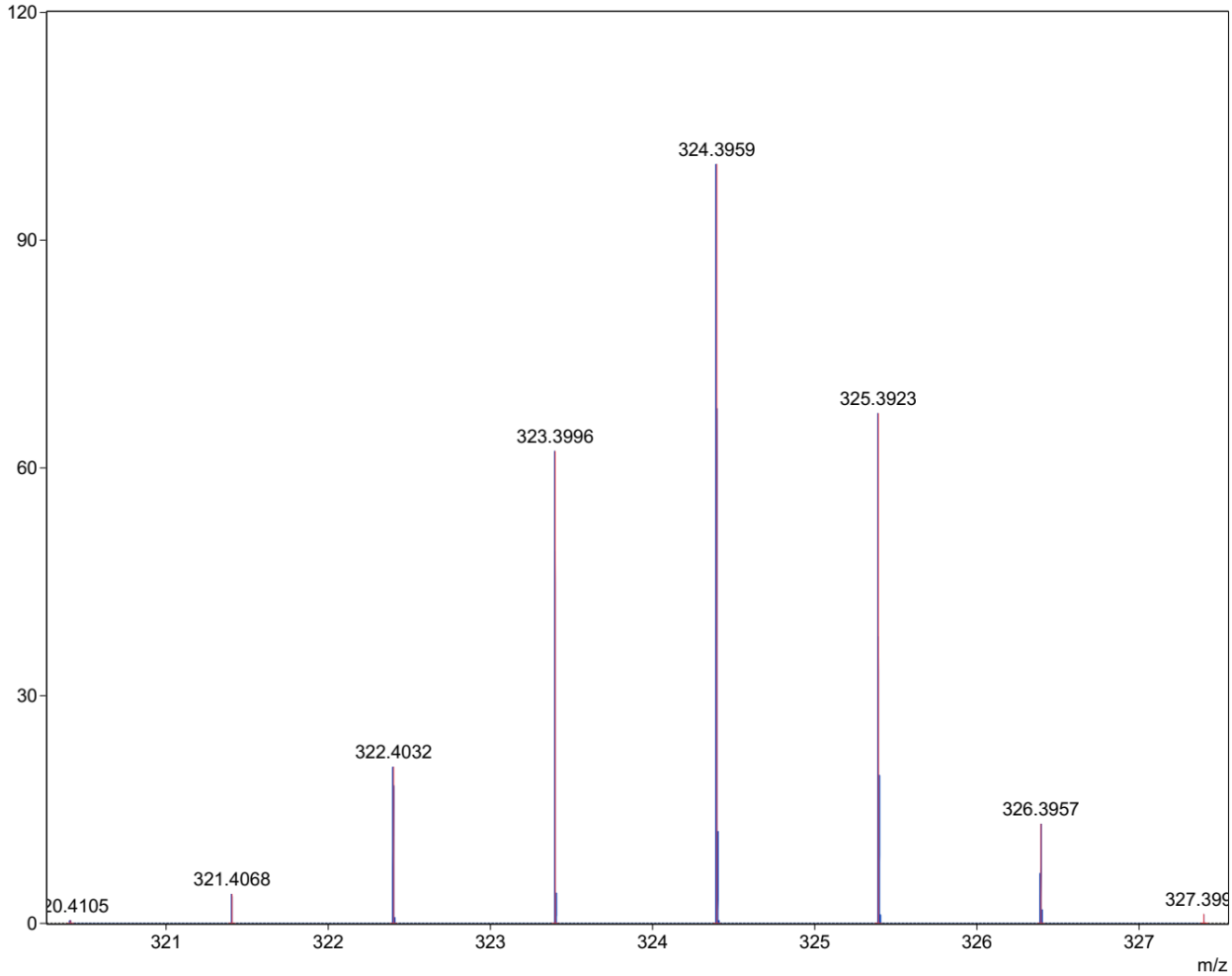
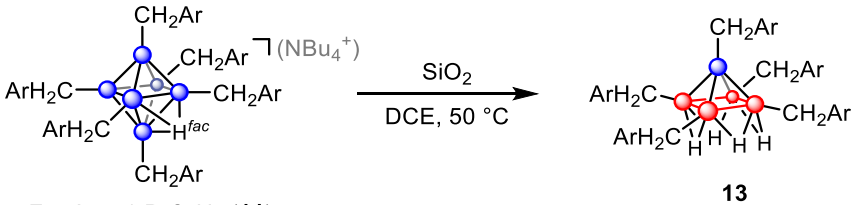



**Fig. S14.** *Simulated* ESI-MS(-) of **12**.

**4. Deconstruction studies of perbenzylated hexaborate anions.**

**Partial deconstruction in the presence of silica gel to produce 13.**




For Ar = 4-$BrC_6H_4$ (**11**)

**13**

$[NBu_4]B_6((CH_2\text{-}4\text{-}Br\text{-}C_6H_4)_6(H^{fac}))$ (**11**) (198mg, 0.149 mmol) was charged to a round bottom with 10mL 1,2-dichloroethane. 1g of $SiO_2$ was added and resulting mixture was heated to 50 ˚C overnight. Reaction progress was monitored by $^{11}B$ NMR spectroscopy. Sequential additions of $SiO_2$ (Silicycle SiliaFlash G-60, 70-230 Mesh, 9g in total) and solvent (25mL in total) were necessary until the starting material was fully consumed. The resulting mixture was filtered, and the filtrate was charged with charcoal and stirred overnight. The mixture was again filtered and the filtrate was dried *in vacuo*. The pale yellow residue was subjected to silica gel chromatography (3:1 hexanes/dichloromethane as eluent) and the desired product **13** was obtained as a white powder (11mg). **$^1$H NMR ($CDCl_3$, 500 MHz)** δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 8H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 8.3 Hz, 8H), 2.15 (s, 2H), 2.00 (s, 8H), -0.84 (s, 4H, bridging H). **$^{13}$C NMR ($CDCl_3$, 126 MHz)** δ 144.57, 141.32, 131.70, 131.27, 130.05, 129.64, 118.76, 117.63, 17.49. **$^{11}$B NMR ($CDCl_3$, 161 MHz)** δ -4.77 (s, 4B), -40.08 (s, 1B).
ESI-MS(-) for $[M-H]^-$: calculated: 906.8932. measured: 906.6887.

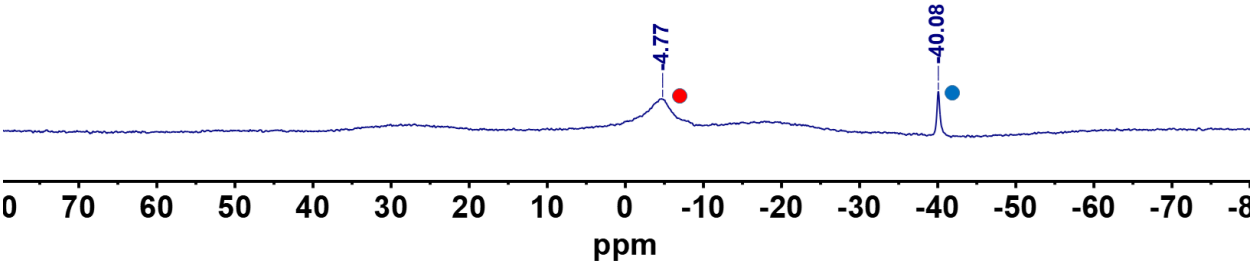



**Fig. S15.** $^{11}$B NMR spectrum of reaction mixture after treating **11** with silica gel.

JCA-IV-222_iso.3.fid

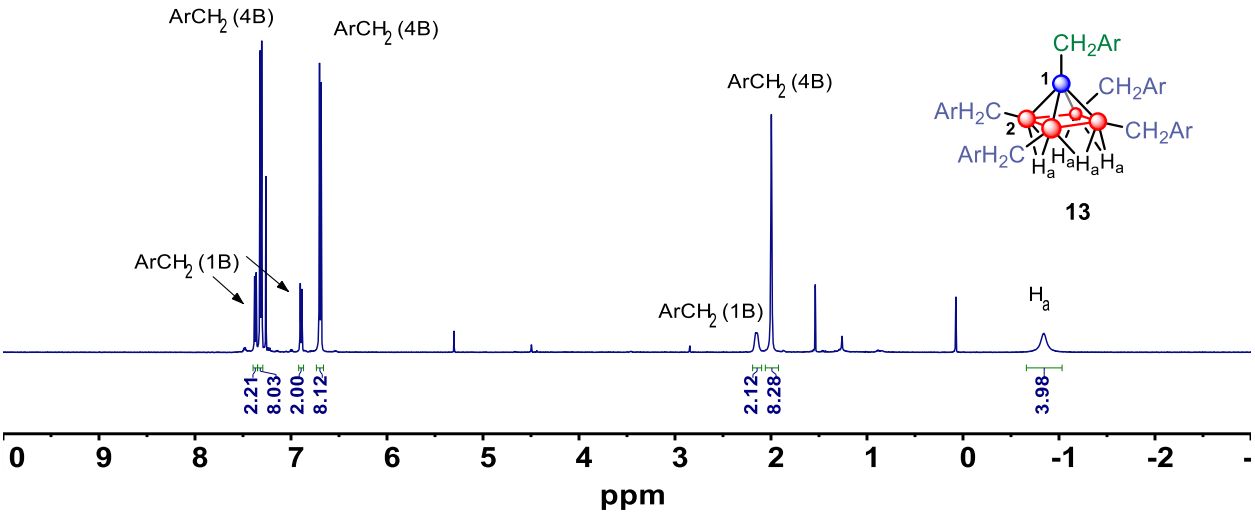



**Fig. S16.** $^{1}$H NMR spectrum of **13** in $CDCl_3$ at 298K.

JCA-IV-222_iso.2.fid

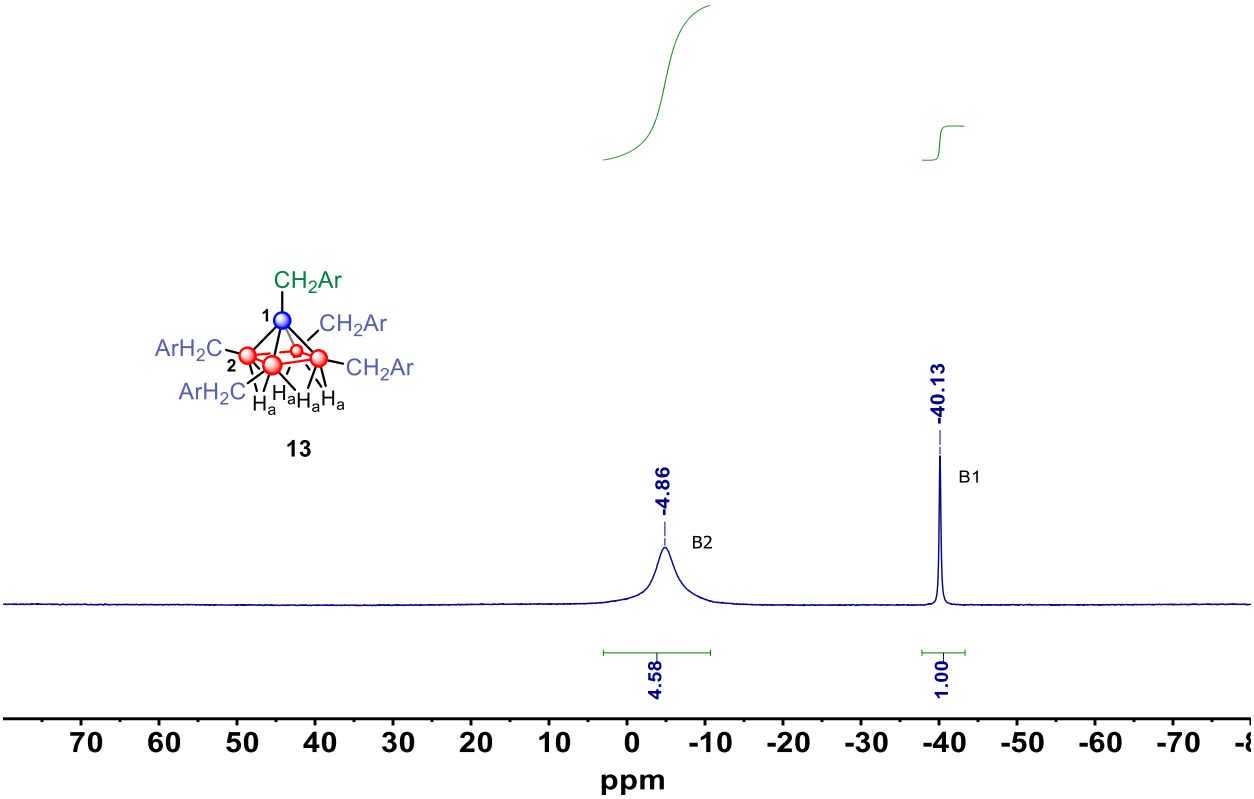



**Fig. S17.** $^{11}B$ NMR spectrum of **13** in $CDCl_3$ at 298K.

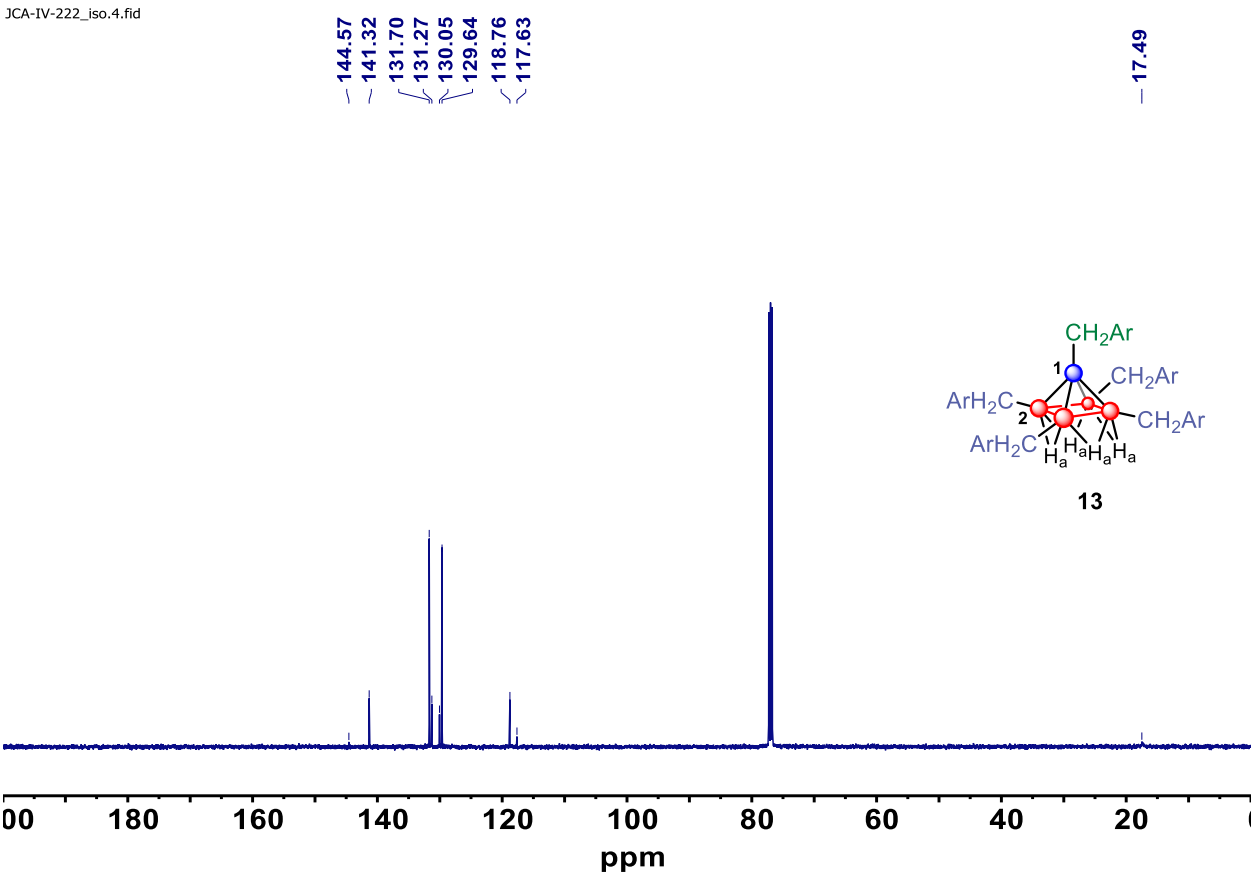



**Fig. S18.** $^{13}C\{^{1}H\}$ NMR spectrum of **13** in $CDCl_3$ at 298K.

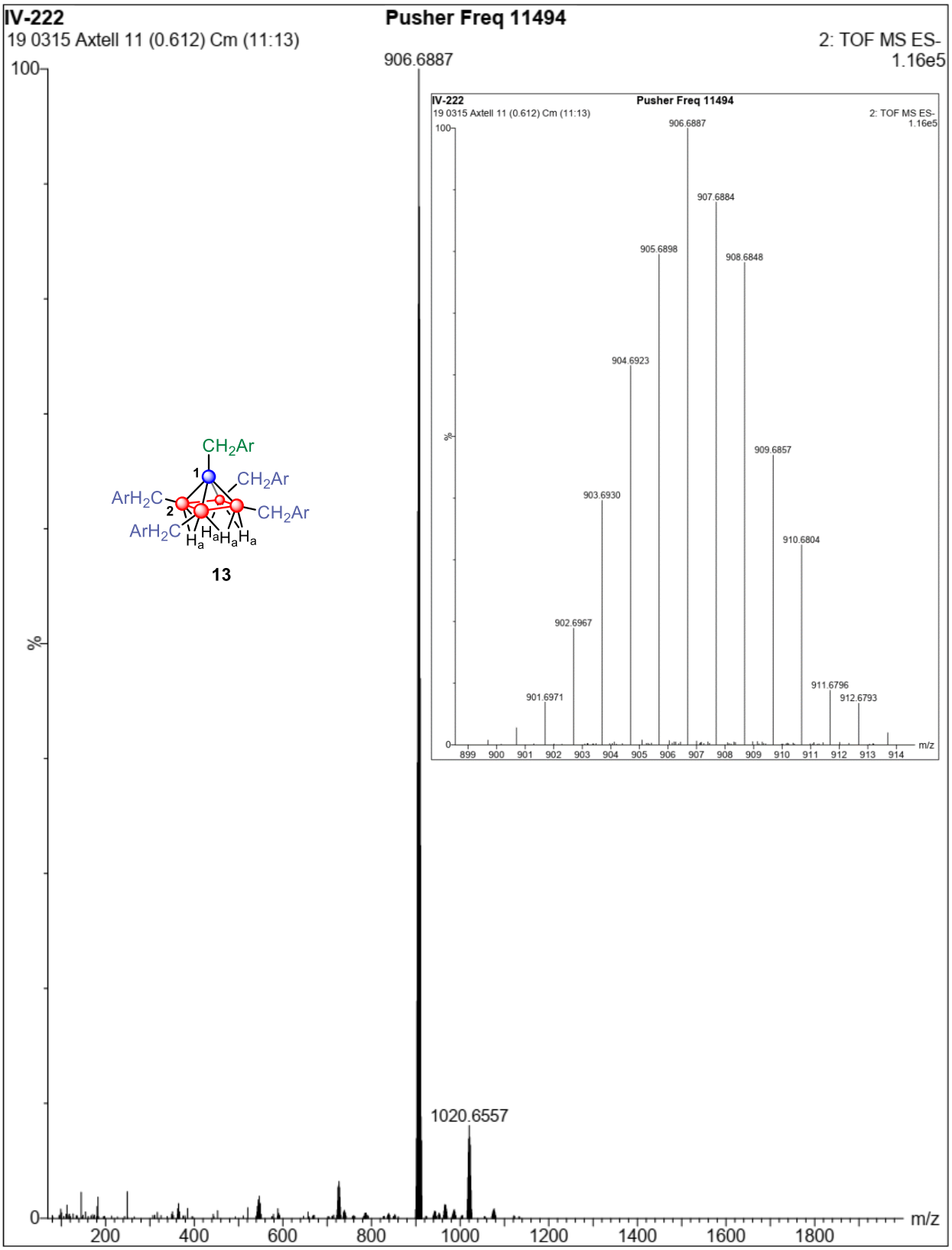



**Fig. S19.** ESI-MS(-) of **13**.

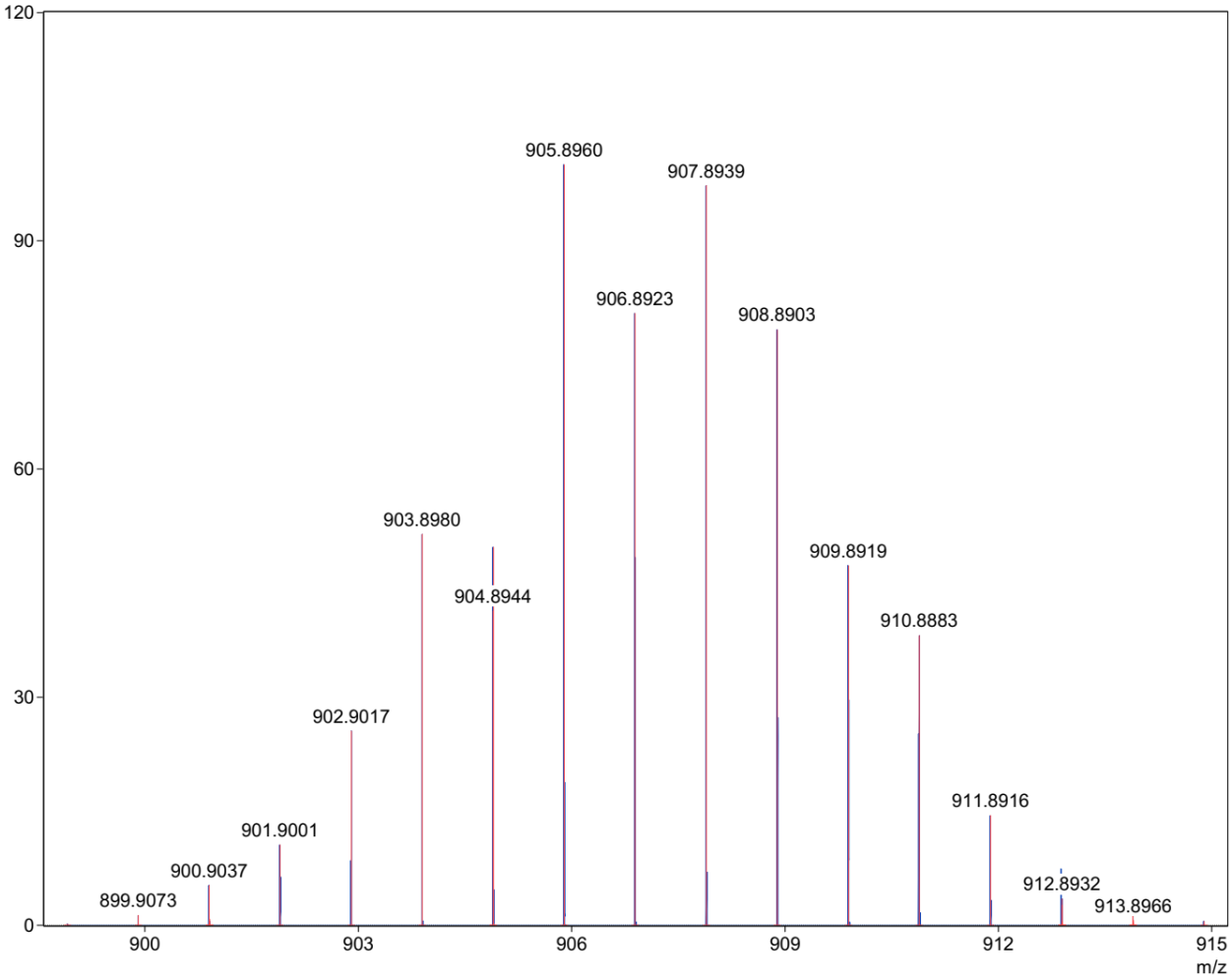
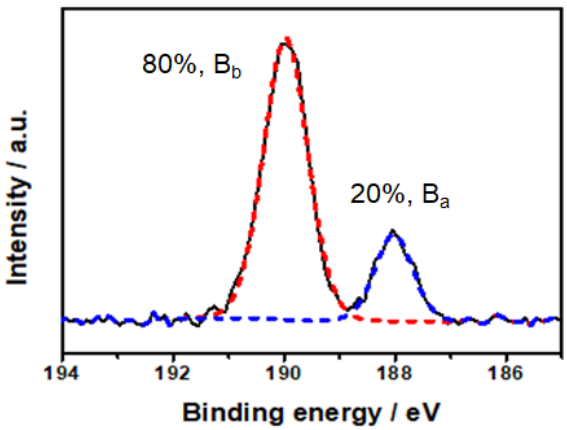
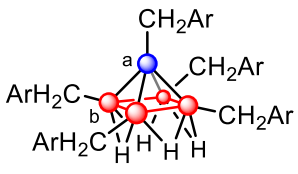



**Fig. S20.** *Simulated* ESI-MS(-) of **13**.

**XPS studies of 13.**

The Boron 1s XPS region consists of two peaks (4:1 ratio), the peak marked in red (190.0 eV) corresponds to $B_b$ and peak marked in blue (188.0 eV) corresponds to $B_a$.




**13**

**Fig. S21.** Boron 1s XPS region for **13**.

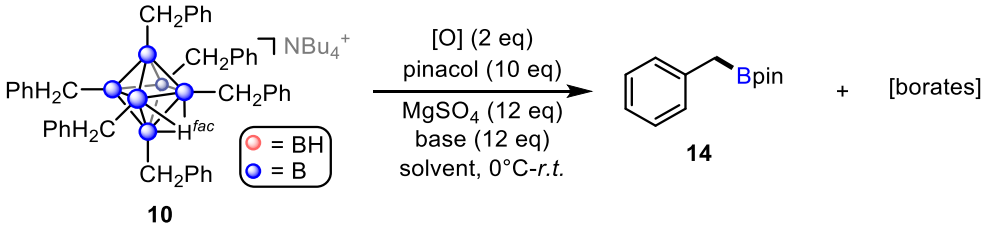
**Deconstruction studies in the presence of external oxidants.**

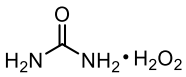
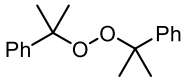
**General reaction conditions**

A 20 mL scintillation vial was charged with **10** (38 mg, 0.05 mmol) and pinacol (60 mg, 0.5 mmol). Anhydrous THF (1.0 mL) and anhydrous $MgSO_4$ (73 mg, 12 eq) were added. Under stirring, the oxidant (0.1 mmol, 2 equiv) was added. The reaction mixture was stirred for 12 hours. Then the reaction mixture was filtered through celite and the $^{11}B$ NMR spectrum of the filtrate was used to determine the ratio of **14**/**10**/borates and deconstruction progress. Isolated yields were obtained for entries 6 and 7 to quantify the efficiency of the deconstruction process. To isolate the product **14** and **15**, the filtrates from entry 6 and 7 were concentrated under vacuum. Column separation (hexanes/EtOAc = 15:1) gave products. For **14**: **$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.34-7.07 (m, 5H), 2.31 (s, 2H), 1.25 (s, 12H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)** δ 33.15 (s). CAS registry No. 87100-28-5.

For **15**: **$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.23 (s, 2H), 1.23 (s, 12H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)** δ 33.13 (s). CAS registry No. 477841-90-0.

**Table S2** Deconstruction perbenzylated of hexaborate **10**




| entry | oxidant | solvent | base | **14**/**10**/borate ratio | yield (**14**, %) |
|---|---|---|---|---|---|
| 1 |  | THF | -- | 0/93/7 | -- |
| 2 |  | THF | -- | 0/100/0 | -- |
| 3 | $Na_2CO_3$•1/2 $H_2O_2$ | THF | -- | 0/100/0 | -- |
| 4 | $CuSO_4$•$5H_2O$ | THF | -- | 0/100/0 | -- |
| 5 | $K_3Fe(CN)_6$ | THF | -- | 0/100/0 | -- |
| 6 | TCNQ | THF | -- | 17/0/1 | 47 |
| 7 | TCNQ | MeCN | -- | 10/0/1 | 42 |
| 8 | TCNQ | MeCN | $K_2CO_3$ | 0/100/0 | -- |
| 9 | TCNQ | THF | $K_2CO_3$ | 1/3/0 | -- |

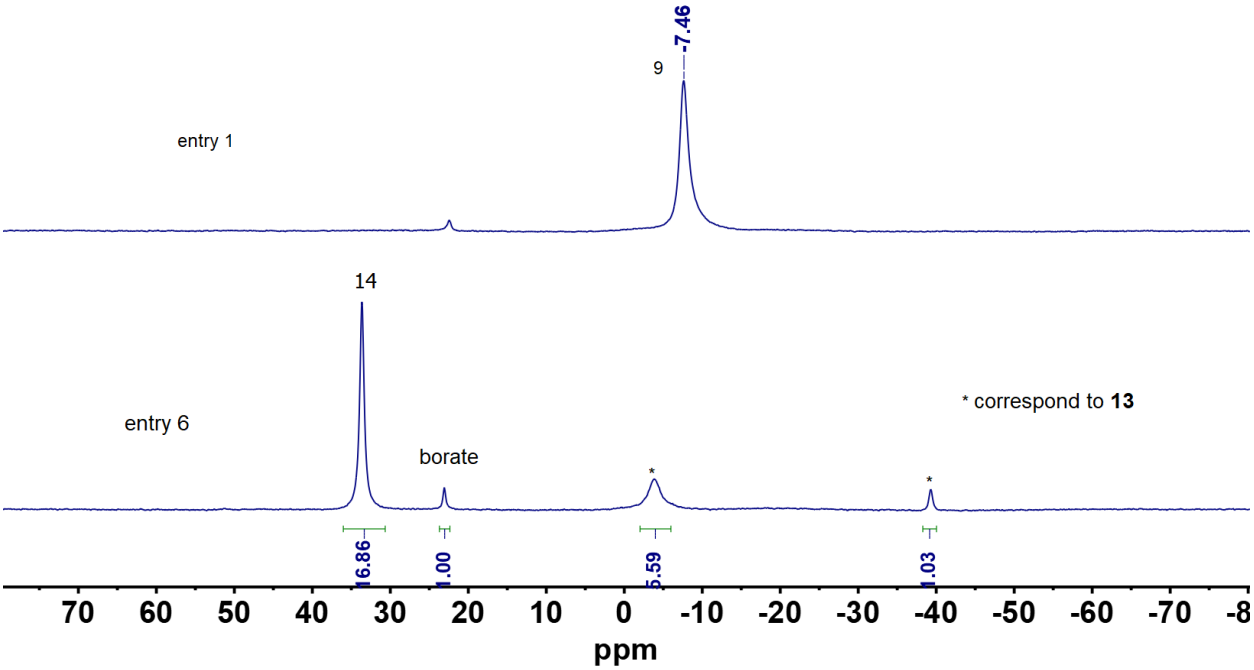
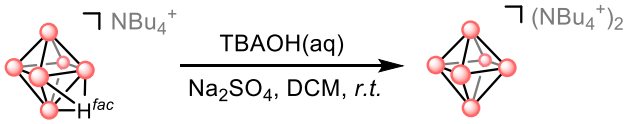



**Fig. S22.** Representative $^{11}B$ NMR spectra of reaction mixture after deconstruction of **10**.

**5. Synthesis of hexaborate dianion 16 and 17.**

Synthesis of *closo*-hexaborate dianion $[NBu_4]_2[B_6H_6]$ (**16**):




The $[NBu_4][B_6H_6H^{fac}]$ (628 mg, 2 mmol) was added to a 20 mL scintillation vial, then a stir bar and 6 mL of dry DCM from the SPS were added. Under stirring, TBAOH solution (1.0 mL, 2 mmol, 55% w/w in water) was added dropwise. Dry $Na_2SO_4$ (14 g, stored in oven at 120 °C) was added in ten portions over 5 min. After addition, the mixture was kept stirring for 3 hours. The solids were filtered off and the solvent was removed under reduced pressure. Further drying on a lyophilizer to remove residual water gave off-white solid **15** (944 mg, 85%). **$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 3.39 (m, 8H, $NBu_4$), 1.63 (m, 8H, $NBu_4$), 1.44 (sextet, *J* = 7.4 Hz, 8H, $NBu_4$), 0.95 (triplet, *J* = 7.4 Hz, 12H, $NBu_4$). 0.23-1.83 (br, 6H, B–H). Facial proton $H^{fac}$ is not observed. **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ -13.51 (d, *J* = 120.2 Hz). **$^{11}$B{$^1$H} NMR ($CDCl_3$, 128 MHz)**: δ -13.52.

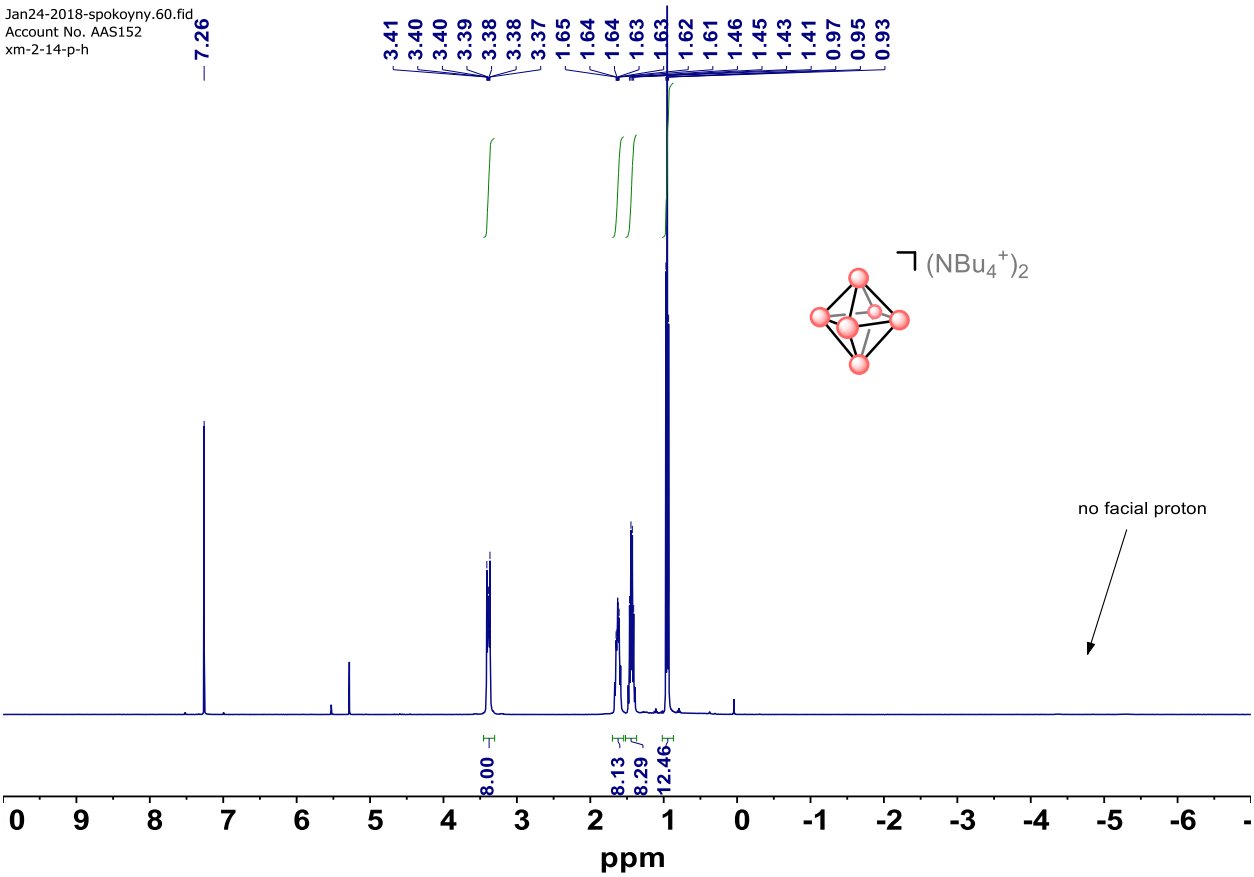



**Fig. S23.** $^1$H NMR spectrum of **16** in $CDCl_3$ at 298K.

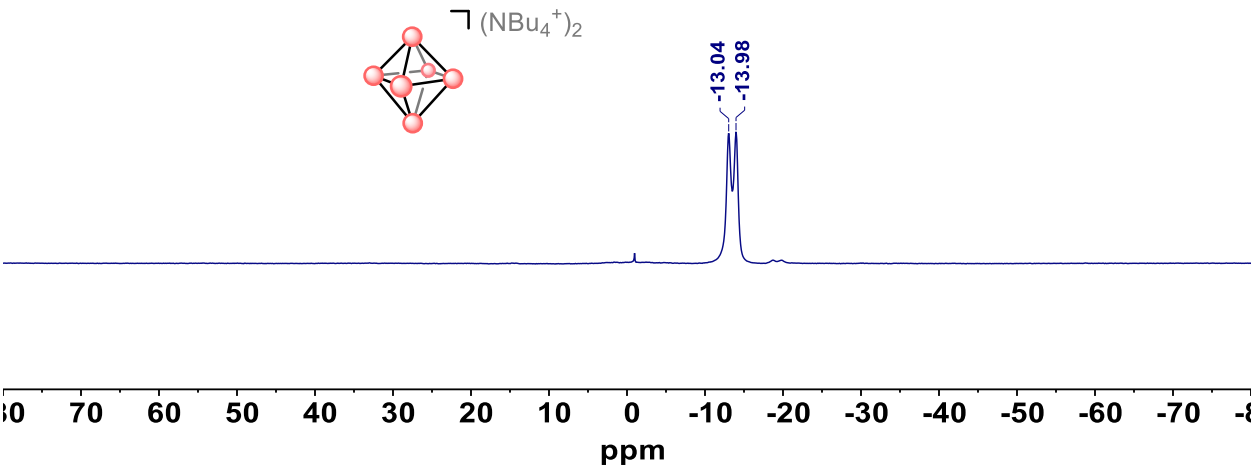



**Fig. S24.** $^{11}B$ NMR spectrum of **16** in $CDCl_3$ at 298K.

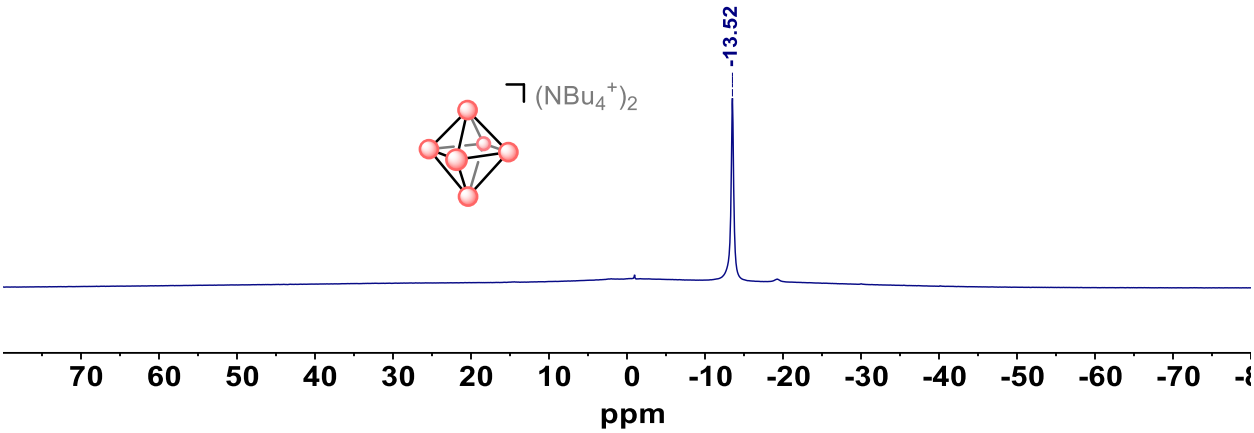
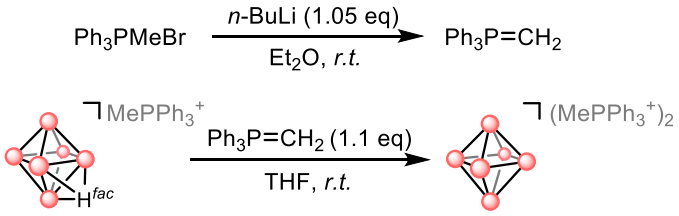



**Fig. S25.** $^{11}B\{^1H\}$ NMR spectrum of **16** in $CDCl_3$ at 298K.

**Synthesis of *closo*-hexaborate dianion $[Ph_3MeP]_2[B_6H_6]$ (17):**




$MePPh_3Br$ (1.78 g, 5 mmol) was suspended in a 25 mL round flask with 6 mL of $Et_2O$ in a $N_2$ filled glovebox, then *n*-BuLi (2.2 mL, 2.5 M in hexanes) was added dropwise via syringe. The suspension became an orange solution and was kept stirring overnight. The solution was filtered through celite and solvent was removed *in vacuo* in the glovebox to give orange yellow solid phosphorane (0.85 g, 62%). In a 20 mL scintillation vial, the $[Ph_3MeP][B_6H_6H^{fac}]$ was dissolved in 3 mL of dry THF in glovebox. Under stirring, $Ph_3P=CH_2$ dissolved in 3 mL of dry THF was added to the $[Ph_3MeP][B_6H_6H^{fac}]$ solution and large amount of yellow solids precipitated out. The yellow solids were collected after stirring overnight and washed with THF (2 mL×3), the solids were further dried *in vacuo* to yield the product **16** (1.39 g, 89%). Crystals suitable for single crystal X-ray diffraction studies are obtained by diffusing $Et_2O$ into a concentrated MeCN solution of **17**.

**$^1$H NMR ($CD_2Cl_2$, 500 MHz,)**: δ 7.85-7.73 (m, 9H), 7.71-7.62 (m, 6H), 3.35 (d, *J* = 13 Hz, 3H), 0.10-1.24 (br, 6H, B–H). **$^{11}$B NMR ($CD_2Cl_2$, 160 MHz)**: δ -10.95 (d, *J* = 119.3 Hz). **$^{13}$C NMR ($CD_2Cl_2$,126 MHz)** δ 134.52 (d, *J* = 3.1 Hz), 133.37 (d, *J* = 10.9 Hz), 130.03 (d, *J* = 12.9 Hz), 119.51 (d, *J* = 88.3 Hz), 10.72 (d, *J* = 55.9 Hz). **$^{11}$B{$^1$H} NMR ($CD_2Cl_2$, 160 MHz)**: δ -10.97. **$^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 202 MHz)**: δ 20.76.

JCA-IV-231_iso.5.fid

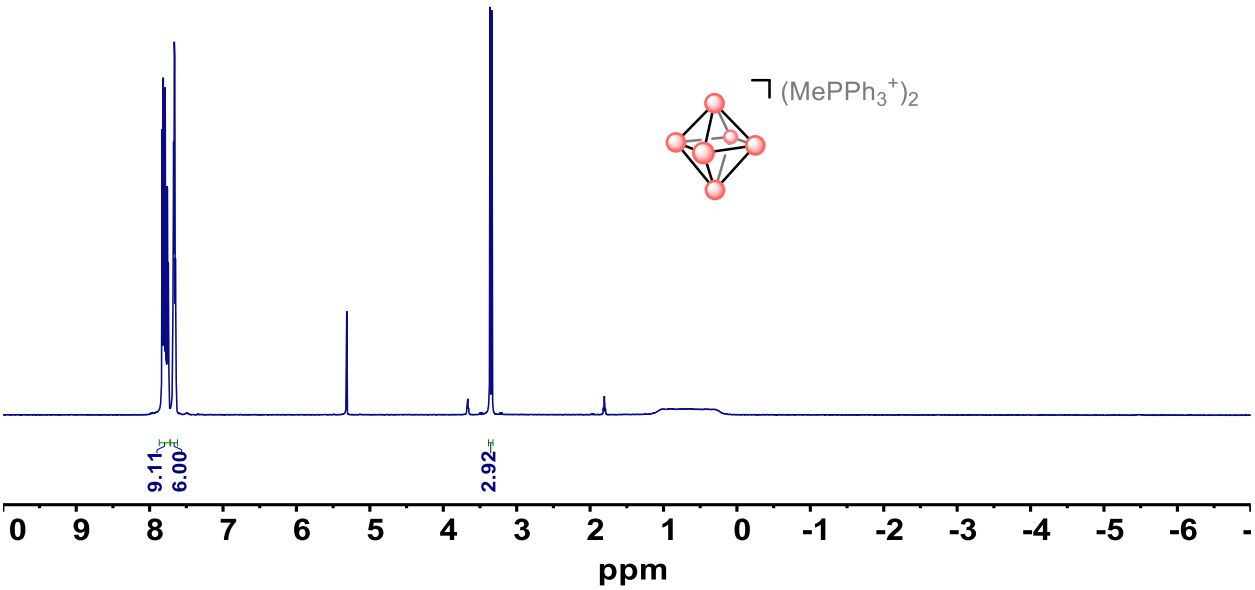



**Fig. S26.** $^{1}$H NMR spectrum of **17** in $CD_2Cl_2$ at 298K.

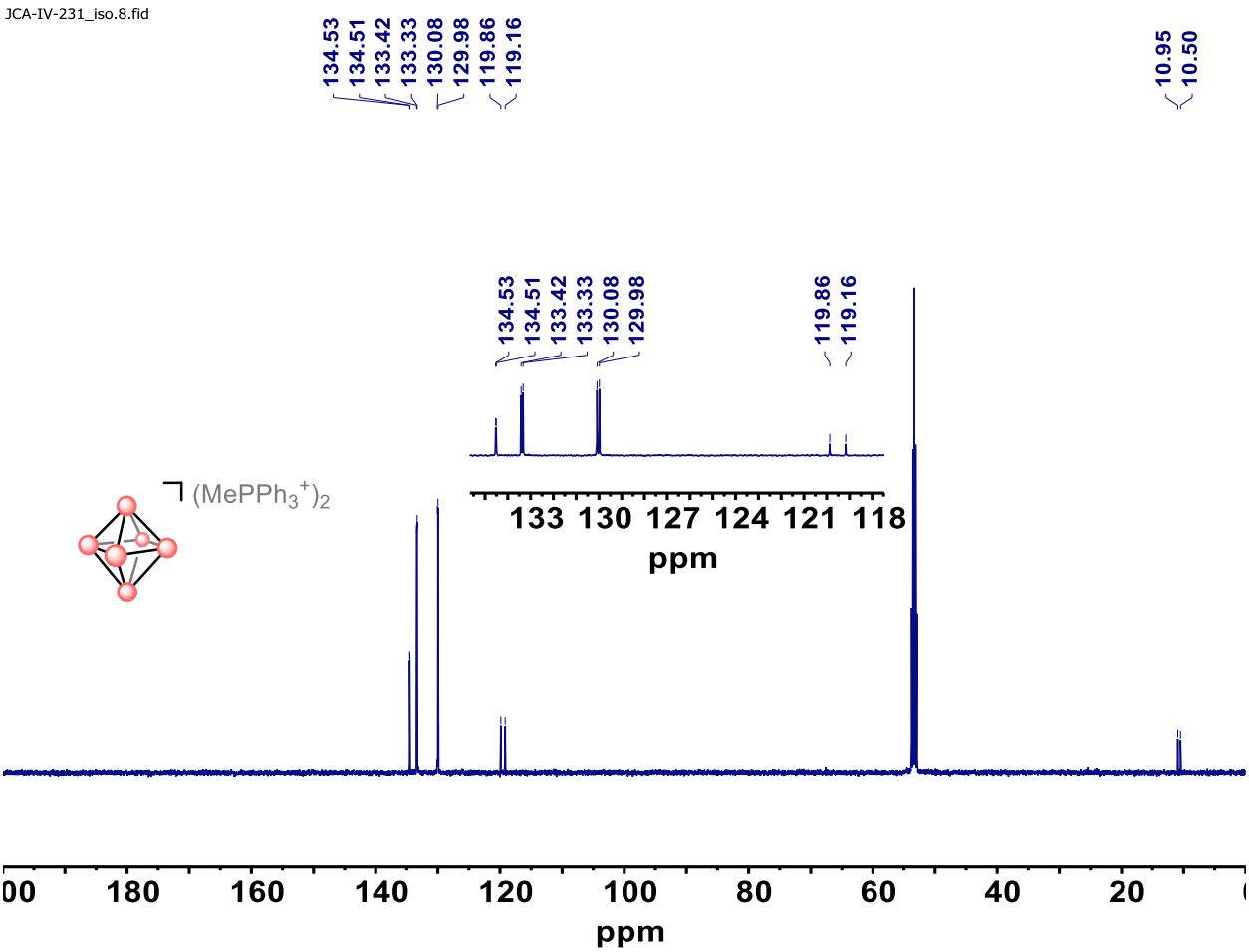



**Fig. S27.** $^{13}C\{^{1}H\}$ NMR spectrum of **17** in $CD_2Cl_2$ at 298K.

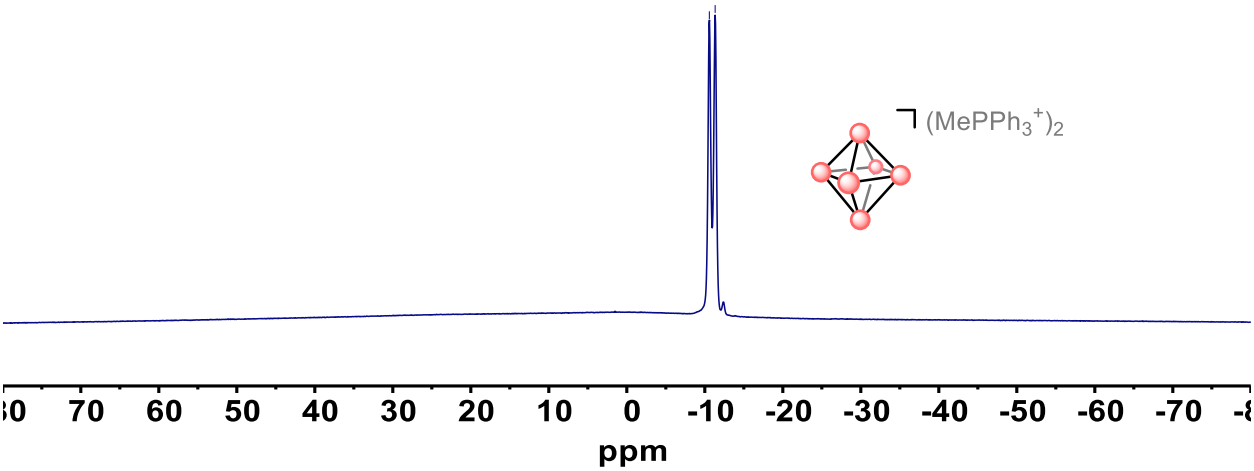



**Fig. S28.** $^{11}B$ NMR spectrum of **17** in $CD_2Cl_2$ at 298K.

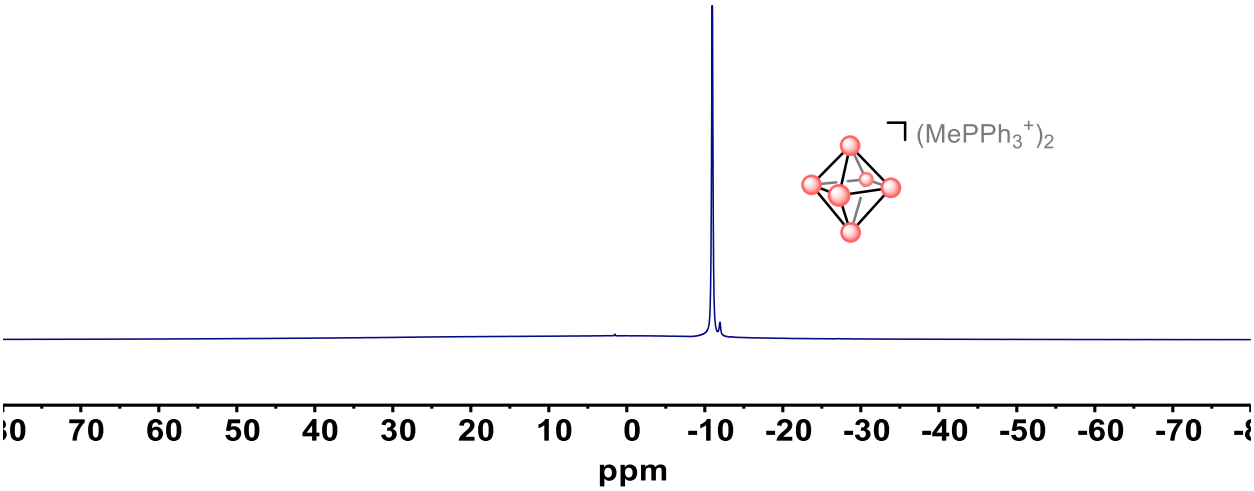



**Fig. S29.** $^{11}B\{^{1}H\}$ NMR spectrum of **17** in $CD_2Cl_2$ at 298K.

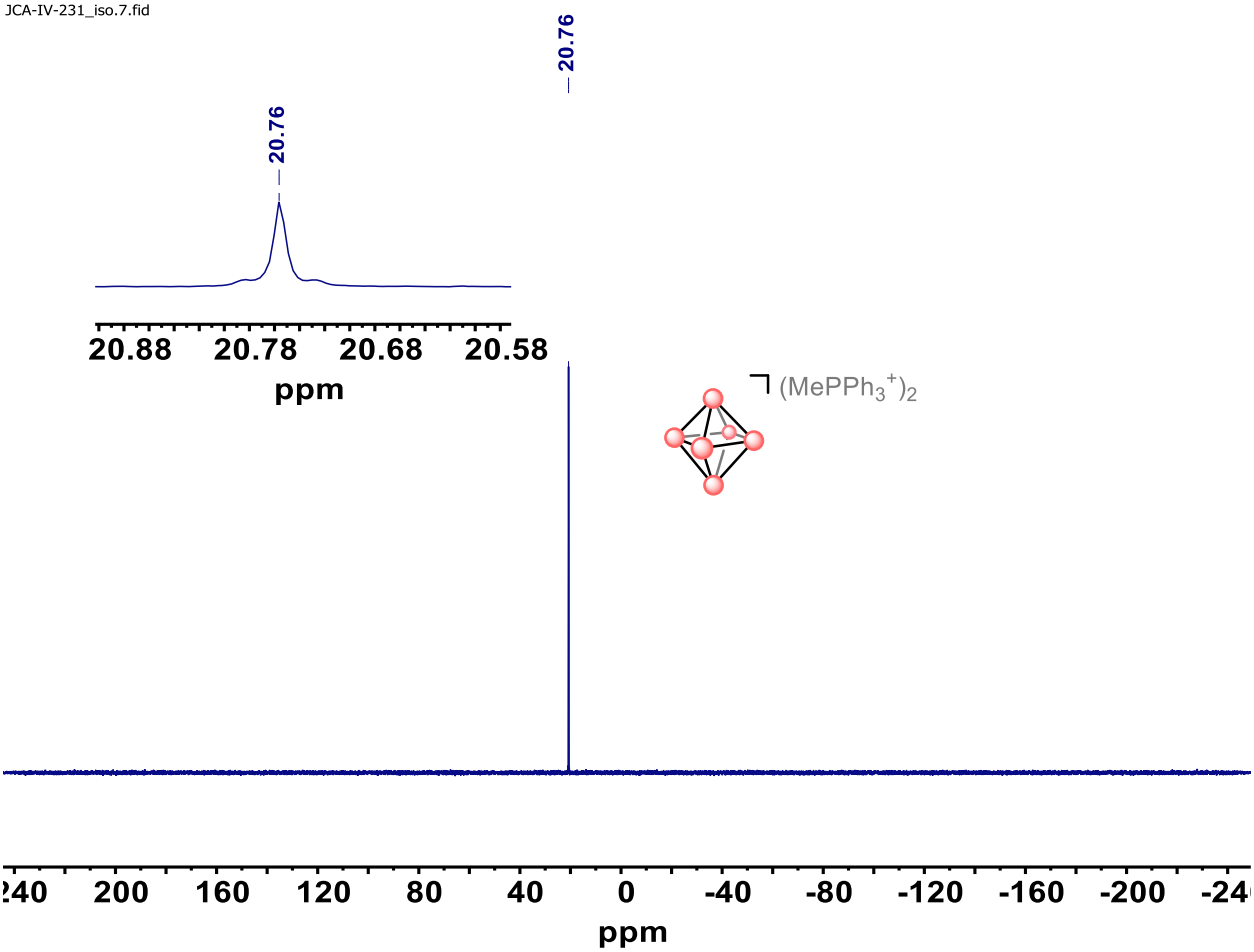
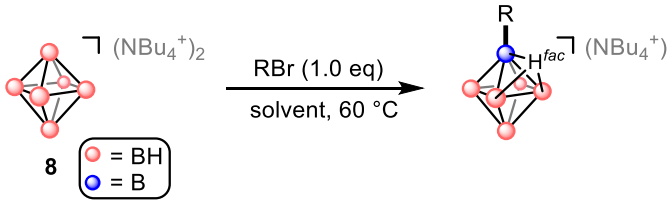



**Fig. S30.** $^{31}P\{^{1}H\}$ NMR spectrum of **17** in $CD_2Cl_2$ at 298K.

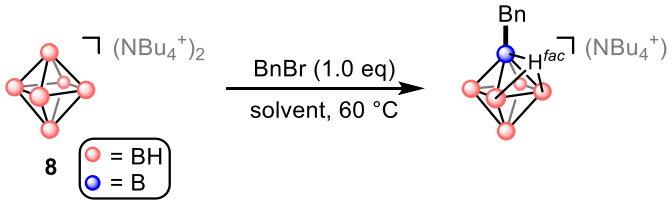
**6. Monosubstitution and subsequent deconstruction studies.**

**General reaction conditions for solvent screening.**

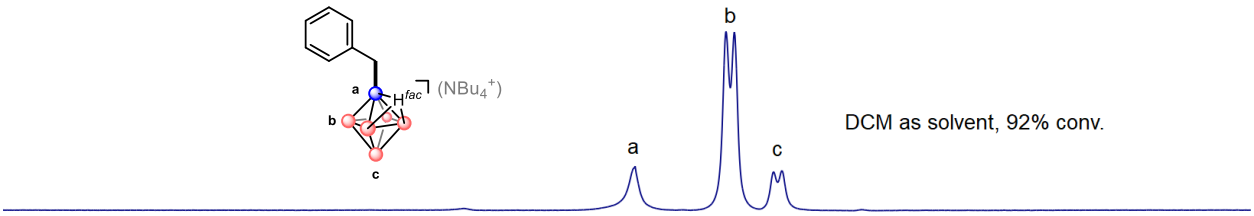


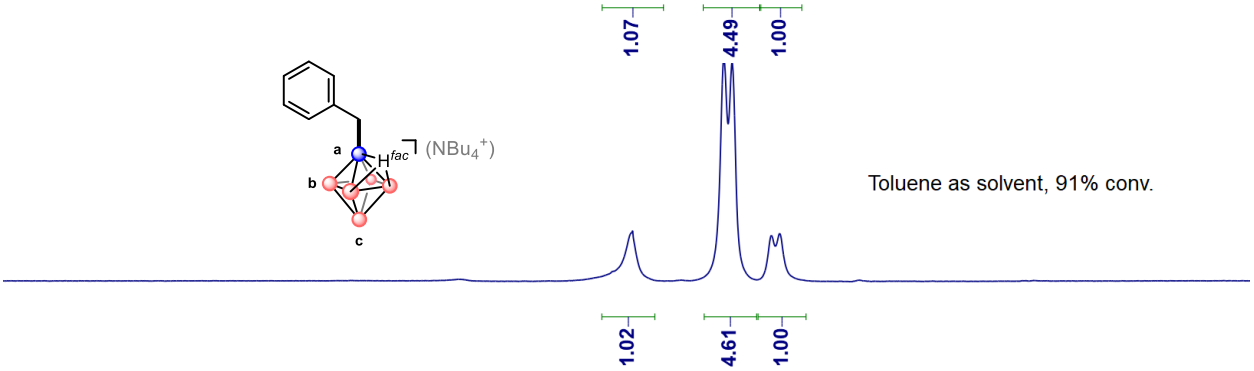

In a nitrogen filled glove box, the hexaborate dianion **16** $TBA_2[B_6H_6]_2$ (56 mg, 0.1 mmol) and a stir bar were added to a 10 mL glass tube with a screw cap. Dry solvent (1 mL) was added and stirred for 1 min. Then, alkyl bromide (0.1 mmol) was added via 25 µL micro-syringe. The glass tube was sealed, wrapped with electrical tape and transferred out of the glove box. The mixture was stirred in an oil bath at 60 °C for 12 hours. The colorless solution was cooled down and diluted with $CH_3CN$ or THF, from $^{11}B$ NMR the conversion could be determined.

*The assignment of boron signals is shown here. The signal c corresponds to boron atom $B_c$ of substituted cluster, unreacted hexaborate anion signal overlapped with signal b corresponds to equatorial boron $B_b$. We do not observe any degradation of hexaborate dianions during substitution step based on $^{11}B$ NMR spectroscopy. Thus the ratio of substituted cluster/hexaborate can be calculated. The ratio of cluster/hexaborate = 1/{(4.49-1×4)/6}=1/0.085, the conversion = 1/(1+0.085) = 92%.*




*Solvents screening:*



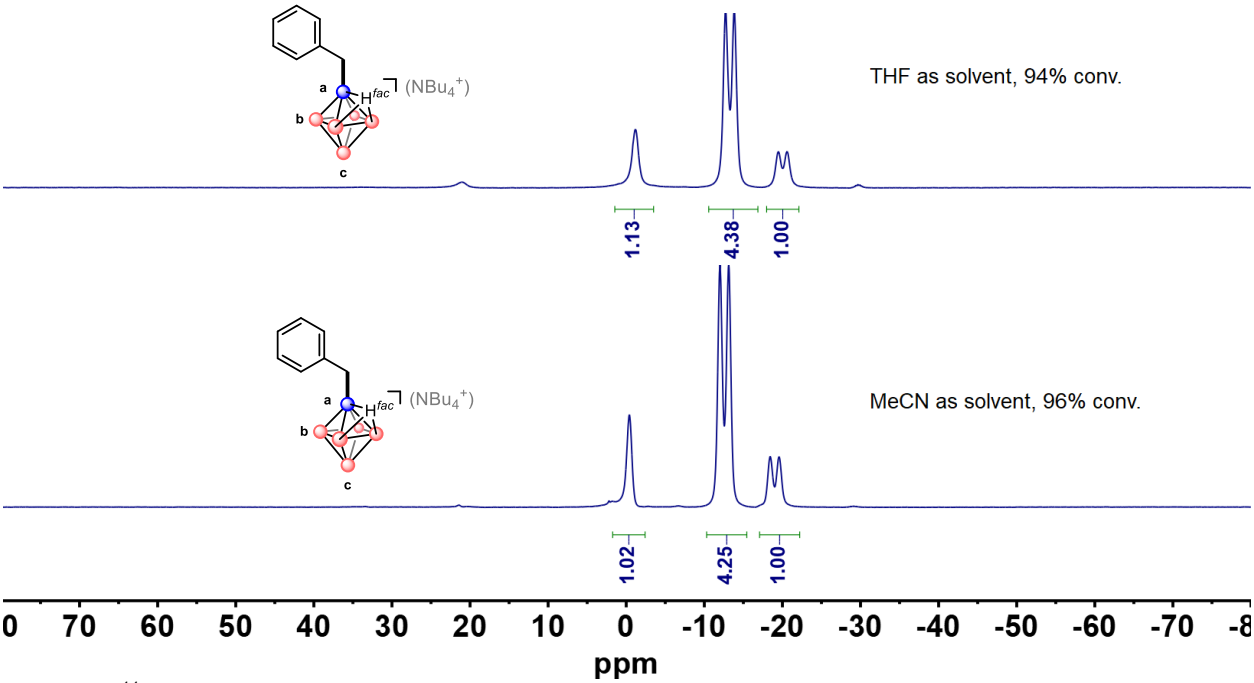
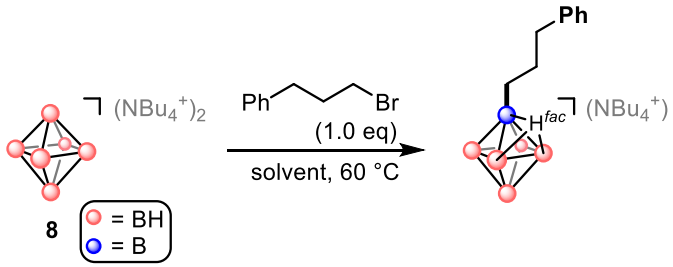
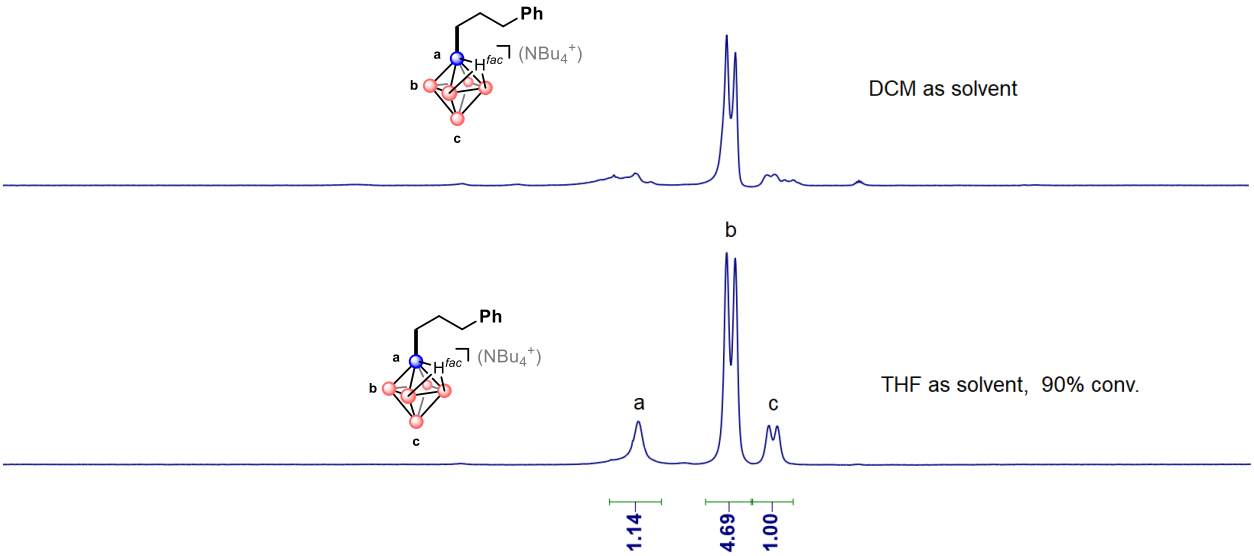



**Fig. S31.** $^{11}$B NMR spectra of solvent screening for monosubstitution with benzyl bromide.




*Solvents screening:*



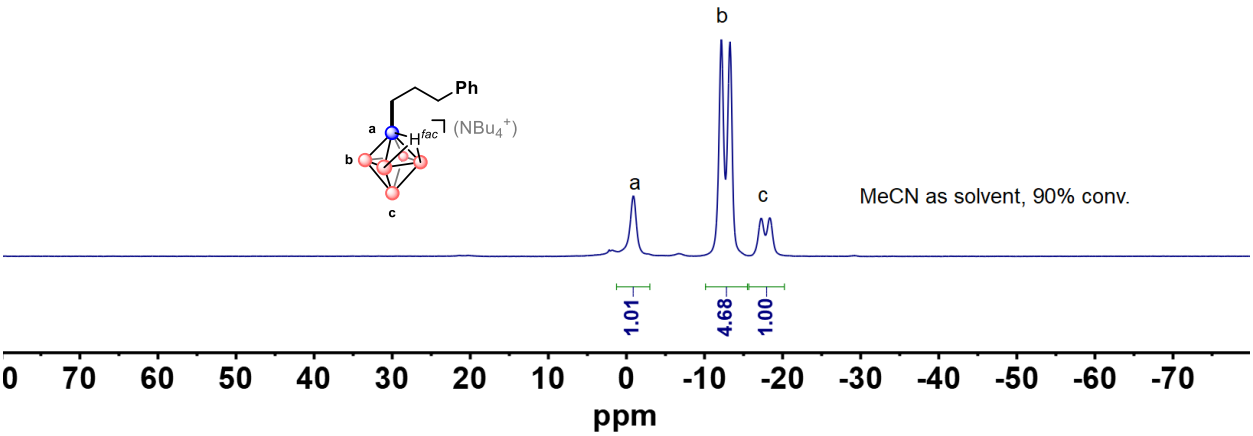
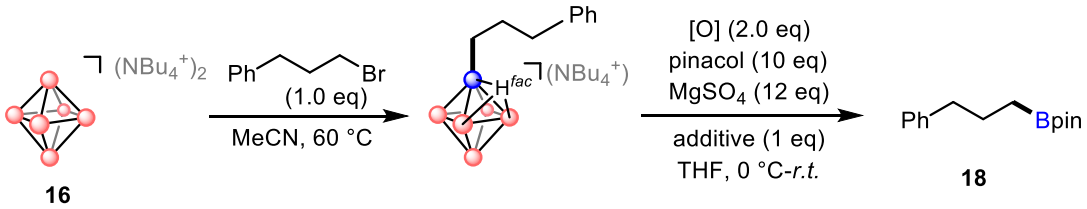



**Fig. S32.** $^{11}$B NMR spectra of solvent screening for monosubstitution with phenyl propyl bromide.

**General reaction conditions for deconstruction studies.**

The reaction mixture using hexaborate dianion **16** $TBA_2[B_6H_6]_2$ (56 mg, 0.1 mmol) and phenyl propyl bromide (15 µL, 0.1 mmol) was obtained using MeCN (1.0 mL) as a solvent following the above procedure. $^{11}$B NMR spectroscopy was used to determine the conversion (90%). The solvent was removed and the resulting colorless oil was washed with hexanes (5 mL) and residual solvent was removed under vacuum. Then the oil was dissolved in THF (1.0 mL), pinacol (100 mg, 10 eq) and $MgSO_4$ (144 mg, 12 eq) were added and cooled down to 0 °C. Under stirring, oxidant (0.2 mmol) was added and the cooling bath was removed. The mixture was stirred for another 12 hours. The resulting light brown yellow mixture was filtered through celite and the solvent was removed under vacuum. 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) was added as an internal standard to determine the $^1$H NMR yield.

**Table S3.** Deconstruction studies of alkyl substituted hexaborate using different oxidants and additives.



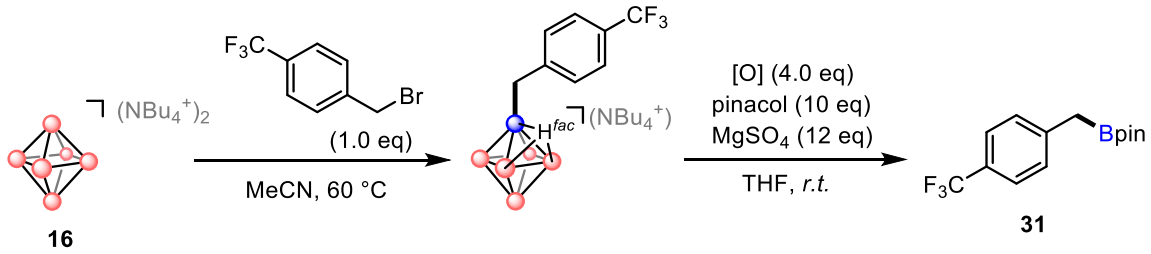

| entry | oxidant | additive | yield (%)* |
|---|---|---|---|
| 1 | TCNQ | -- | 61 |
| 2 | TCNQ | $Sc(OTf)_3$ | 59 |
| 3 | TCNQ | $Zn(OTf)_2$ | 60 |
| 4 | $NOBF_4$ | -- | 61 |
| 5 | $CeSO_4{\bullet}H_2SO_4$ | -- | 28 |
| 6 | $(NH_4)_2Ce(NO_3)_6$ | -- | 44 |

*$^1$H NMR (1,3,5-trimethoxybenzene as internal standard) yield over two steps

The reaction mixture using hexaborate dianion **16** $TBA_2[B_6H_6]_2$ (56 mg, 0.1 mmol) and 4-trifluoromethyl benzyl bromide (24 mg, 0.1 mmol) was obtained using MeCN (1.0 mL) as a solvent at room temperature. $^{11}$B NMR spectroscopy was used to determine the conversion (89%). The solvent was removed and the resulting colorless oil was washed with hexanes (5 mL) and residual solvent was removed under vacuum. Then the oil was dissolved in THF (1.0 mL), pinacol (100 mg, 10 eq) and $MgSO_4$ (144 mg, 12 eq) were

added. Under stirring, oxidant (0.4 mmol) was added. The mixture was stirred for another 12 hours. The resulting light brown yellow mixture was filtered through celite and the solvent was removed under vacuum. 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as $^1$H NMR internal standard was added to determine the $^1$H NMR yield over two steps.

**Table S4.** Deconstruction studies of 4-$CF_3$ benzyl substituted hexaborate using different oxidants.

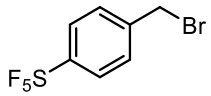



| entry | oxidant | additive | yield (%)* |
|---|---|---|---|
| 1 | TCNQ | -- | 63 |
| 2 | $NOBF_4$ | -- | 66 |

*$^1$H NMR (1,3,5-trimethoxybenzene as internal standard) yield over two steps.

**7. Preparation of electrophiles.**

Most of the benzyl bromides and alkyl bromides used in the substrate table are commercially available and were used as received.




Procedure: 4-$SF_5$-toluene (975uL, 1.37 mmol), AIBN (18mg, 0.110 mmol), NBS (245mg, 1.37 mmol) were charged to a Schlenk flask with 10mL of $C_2H_4Cl_2$. The resulting mixture was degassed and backfilled twice with $N_2$ and subsequently placed in an oil bath heated to 80˚C. The mixture was allowed to stir for 24 hours, after which the resulting solution was allowed to cool and the solvent was removed *in vacuo*. The resulting residue was charged with diethyl ether and the solid was filtered away through Celite. The filtrate was dried *in vacuo* and subjected to silica gel chromatography with a hexanes eluent. Fractions containing the desired product, as judged by NMR spectroscopy, were combined and the solvent was removed to give the desired white solid (327 mg, 80%).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 4.48 (s, 2H). **$^{13}$C NMR ($CDCl_3$, 126 MHz)** δ 153.40 (p, *J* = 17.4 Hz), 141.53, 129.21, 126.41 (p, *J* = 4.7 Hz), 30.96. **$^{19}$F NMR ($CDCl_3$, 376 MHz)** δ 83.97 (p, *J* = 149 Hz, 1F), 63.02 (s, 2F), 62.62 (s, 2F).

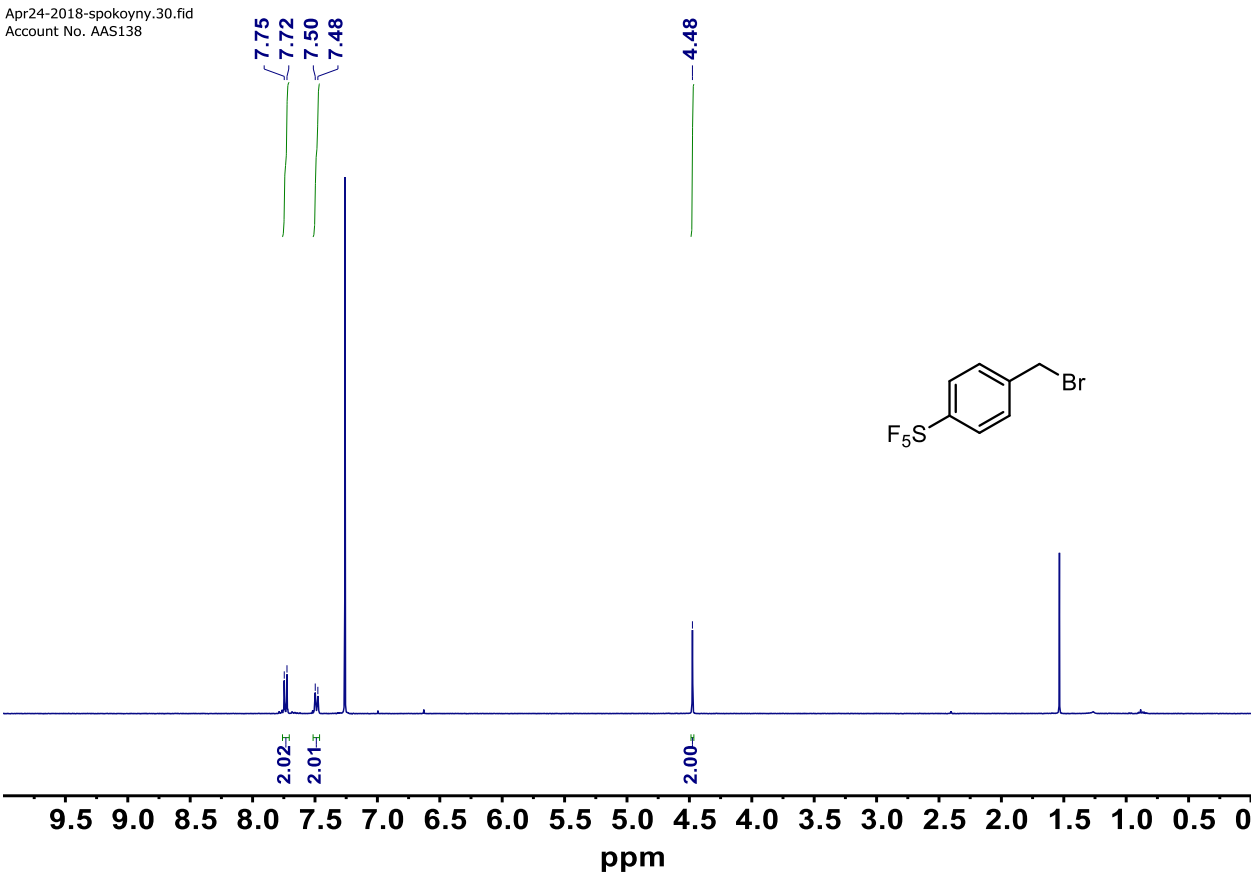



**Fig. S33.** $^{1}$H NMR spectrum of (4-(bromomethyl)phenyl)pentafluoro-λ6-sulfane in $CDCl_3$ at 298K.

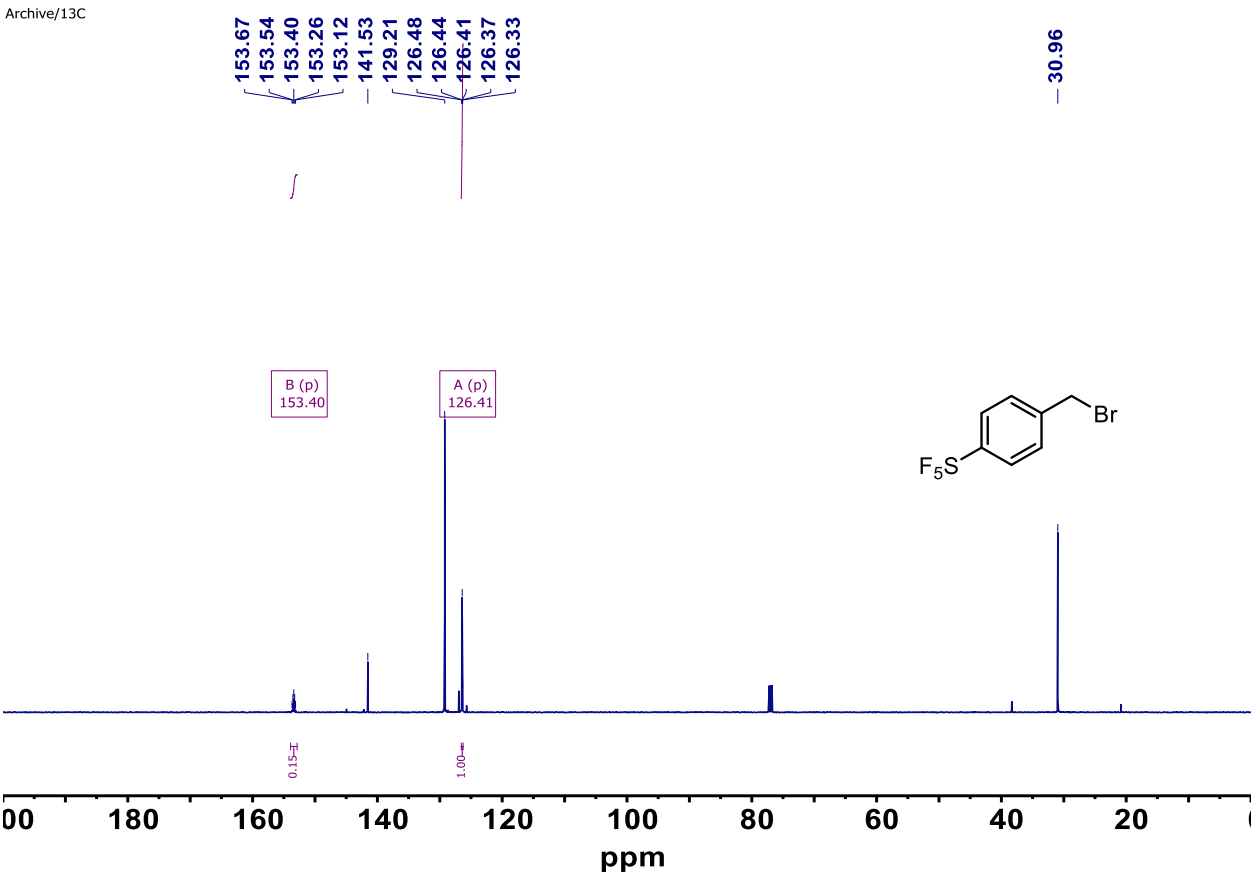



**Fig. S34.** $^{13}C\{^{1}H\}$ NMR spectrum of (4-(bromomethyl)phenyl)pentafluoro-λ6-sulfane in $CDCl_3$ at 298K.

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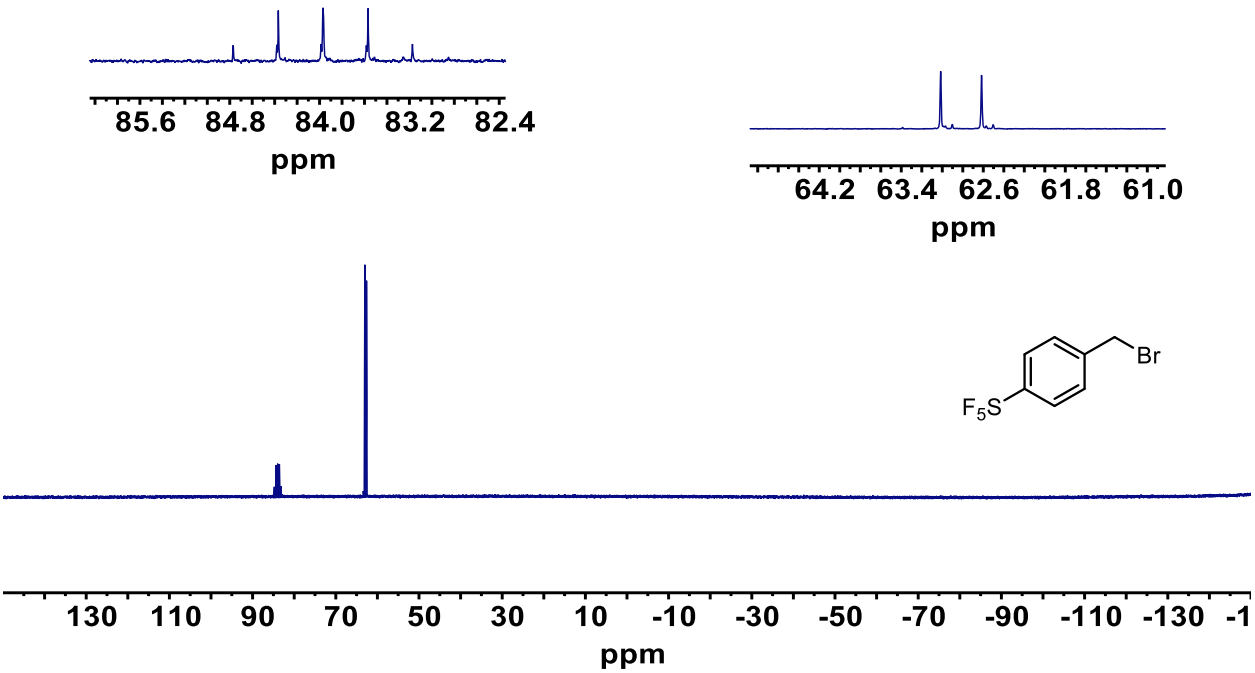
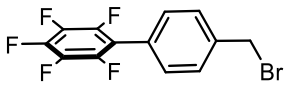
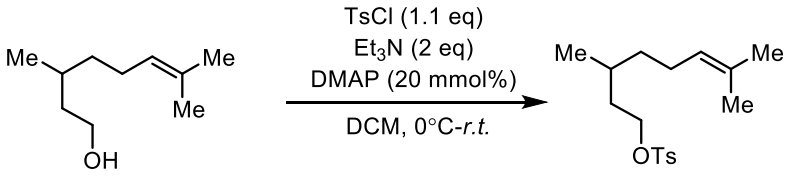



**Fig. S35.** $^{19}F$ NMR spectrum of (4-(bromomethyl)phenyl)pentafluoro-λ6-sulfane in $CDCl_3$ at 298K.

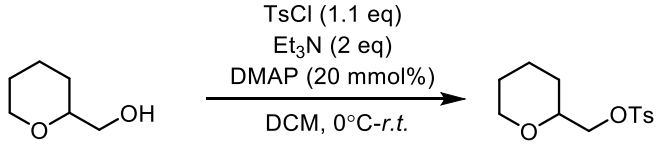



The synthesis of 4'-(bromomethyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl has been reported by our group recently[3] and was used as an electrophile in this nucleophilic borylation procedure.

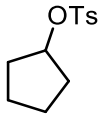



The 3,7-dimethyloct-6-en-1-ol (1.56 g, 10 mmol) and a stir bar were added to a 100 mL round flask, then DCM (20 mL), $Et_3N$ (2.6 mL, 20 mmol, 2 eq) and DMAP (0.18 g, 1.5 mmol, 0.2 eq) were added. The mixture was stirred for 5 min and cooled to 0 °C, then TsCl (2.1 g, 11 mmol, 1.1 eq) was added. After addition, the ice bath was removed and the mixture was kept stirring for 12 hours. The full consumption of the starting alcohol was confirmed by TLC. Water (20 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layers were combined and dried over $Na_2SO_4$ and concentrated under vacuum. Column chromatography gave a colorless oil (1.8 g, 58%).

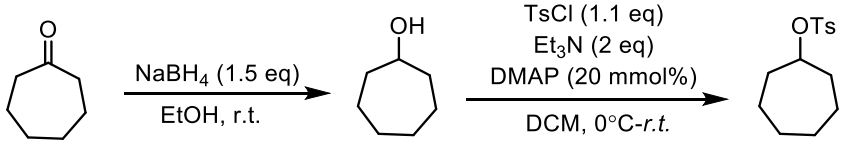
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.32 (m, 2H), 5.02 (dddd, *J* = 7.1, 5.7, 2.9, 1.4 Hz, 1H), 4.12-4.01 (m, 2H), 2.45 (s, 3H), 1.99-1.79 (m, 2H), 1.73-1.63 (m, 4H), 1.57 (s, 3H), 1.54-1.37 (m, 2H), 1.24 (m, 1H), 1.10 (m, 1H), 0.81 (d, *J* = 6.5 Hz, 3H). **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ 144.60, 133.24, 131.44, 129.77, 127.86, 124.29, 69.02, 36.68, 35.63, 28.84, 25.66, 25.23, 21.60, 19.01, 17.59. The NMR spectra are consistent with literature report[4]. CAS registry No. 41144-01-8




The (tetrahydro-2H-pyran-2-yl)methanol (0.58 g, 5 mmol) and a stir bar were added to a 100 mL round flask, then DCM (15 mL), $Et_3N$ (1.3 mL, 10 mmol, 2 eq) and DMAP (0.1 g, 0.75 mmol, 0.2 eq) were added. The mixture was stirred for 5 min and cooled to 0 °C, then TsCl (1.05 g, 5.5 mmol, 1.1 eq) was added. After addition, the ice bath was removed and the mixture was kept stirring for 12 hours. The full consumption of the starting alcohol was confirmed by TLC. Water (20 mL) was added to the mixture and extracted with DCM (10 mL×3), the organic layer was combined and dried over $Na_2SO_4$ and concentrated under vacuum. Column chromatography gave a white solid (1.1 g, 80%).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36-7.30 (m, 2H), 3.99-3.86 (m, 3H), 3.52 (dtd, *J* = 12.4, 5.2, 2.1 Hz, 1H), 3.36 (td, *J* = 11.3, 3.2 Hz, 1H), 2.43 (s, 3H), 1.87-1.78 (m, 1H), 1.59-1.38 (m, 4H), 1.32-1.17 (m, 1H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 144.67, 133.01, 129.73, 127.94, 74.87, 72.50, 68.28, 27.55, 25.49, 22.70, 21.59. The NMR spectra are consistent with literature report[5]. CAS registry No. 75434-63-8

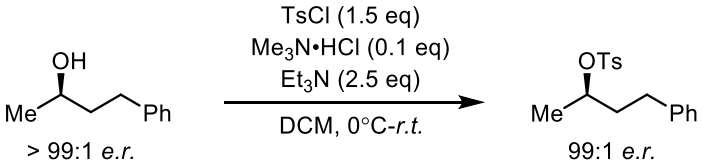



Cyclopentyl 4-methylbenzenesulfonate was prepared using the same procedure mentioned above. Cyclopentanol (0.86 g, 10 mmol), $Et_3N$ (2.6 mL, 20 mmol, 2 eq), DMAP (0.18 g, 1.5 mmol, 0.2 eq) and TsCl (2.1 g, 11 mmol, 1.1 eq) were used. Column chromatography gave a colorless oil (0.8 g, 33%).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.76 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.33-7.28 (m, 2H), 5.04-4.77 (m, 1H), 2.42 (s, 3H), 1.84-1.65 (m, 6H), 1.58-1.45 (m, 2H). **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)** δ 144.32, 134.42, 129.66, 127.55, 85.44, 32.99, 22.98, 21.49. The NMR spectra are consistent with literature report[6]. CAS registry No. 3558-06-3.




Cycloheptanone (3.36g, 30 mmol), a stir bar and EtOH (40 mL) were added to 100 mL round flask, under stirring, the $NaBH_4$ (1.7 g, 45 mmol) was added in several portions and stirred overnight. The reaction mixture was diluted with water (40 mL) and the EtOH was removed under reduced pressure. The aqueous solution was extracted with $Et_2O$ (15 mL×3) and dried over $NaSO_4$. The $Et_2O$ was reduced under reduced pressure and 3.0 g crude cycloheptanol. The crude cycloheptanol (1.1 g, ~10 mmol) was subjected to the tosylation reaction conditions mentioned above. Cycloheptyl 4-methylbenzenesulfonate (2.1 g, 80%) was obtained after column separation.

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.81-7.76 (m, 2H), 7.35-7.29 (m, 2H), 4.66 (tt, *J* = 7.7, 4.7 Hz, 1H), 2.44 (s, 3H), 1.91-1.69 (m, 4H), 1.67-1.56 (m, 2H), 1.55-1.45 (m, 4H), 1.40-1.26 (m, 2H). **$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 144.24, 134.71, 129.67, 127.58, 84.43, 34.51, 28.05, 22.16, 21.58. The NMR spectra are consistent with literature report[7]. CAS registry No. 957-29-9




The literature procedure[8] was used to prepare chiral electrophile (*R*)-4-phenylbutan-2-yl 4-methylbenzenesulfonate. TsCl (0.5 g, 2.6 mmol, 1.5 eq) and $Me_3N^{\bullet}HCl$ (19 mg, 0.2 mmol, 0.1 eq) were added to a 50 mL round flask and DCM (4 mL) was added. Then the solution was cooled to 0 °C. Under stirring, $Et_3N$ (0.7 mL, 5 mmol, 2.5 eq) was added dropwise. The chiral alcohol (0.3 g, 2 mmol) was dissolved in 3 mL of DCM and added to the stirring solution. The resulting solution was then stirred for 1 hour at 0 °C. The complete conversion was observed by TLC ($R_f$ = 0.6, hexanes/EtOAc = 5:1). Dimethyldiaminopropane (400 mg, 2 eq) was added and cold bath was removed. Then water (20 mL) was added and extracted with DCM (5 mL×3) and the organic layer was washed with 1 M HCl, saturated $NaHCO_3$, brine and dried over $Na_2SO_4$. The DCM was removed under reduced pressure. Column separation gave the product as a colorless oil (0.56 g, 92%, 99:1 *e.r.*).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.83-7.77 (m, 2H), 7.35-7.31 (m, 2H), 7.25 (m, 2H), 7.20-7.13 (m, 1H), 7.06 (m, 2H), 4.65 (dqd, *J* = 7.4, 6.3, 4.9 Hz, 1H), 2.61 (ddd, *J* = 13.8, 10.1, 6.0 Hz, 1H), 2.50 (ddd, *J* = 14.0, 10.0, 6.0 Hz, 1H), 2.45 (s, 3H), 1.94 (dddd, *J* = 14.2, 10.0, 7.3, 6.0 Hz, 1H), 1.81 (dddd, *J* = 14.2, 10.1, 6.0, 5.0 Hz, 1H), 1.31 (d, *J* = 6.3 Hz, 3H). **$^{13}$C{$^1$H} NMR** (**$CDCl_3$, 101 MHz**) δ 144.47, 140.80, 134.50, 129.74, 128.41, 128.24, 127.70, 126.02, 79.84, 38.12, 31.13, 21.60, 20.82. The NMR spectra are consistent with literature report (*38*).
Chiral HPLC conditions: OJ column (10% *i*-PrOH/hexanes, flow rate 1.0 mL/min, 20 °C); retention time for chiral compound (**Fig. S37**): $t_1$ = 17.9 min (major), $t_2$ = 21.8 min (minor).

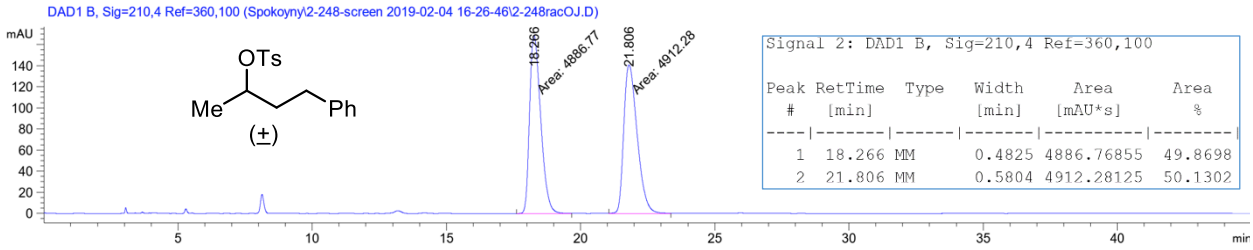



**Fig. S36.** HPLC trace of standard racemic sample.

Synthesized chiral sample (99:1 *e.r.*):

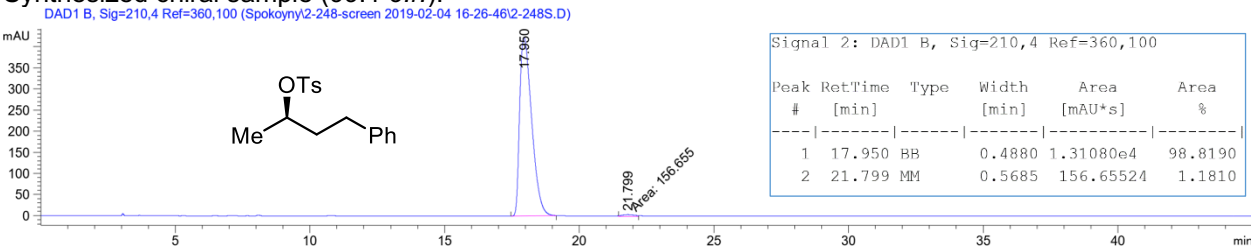
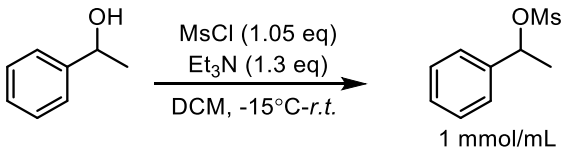
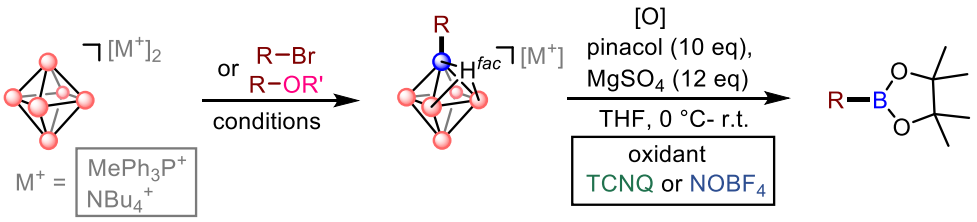



**Fig. S37.** HPLC trace of synthesized chiral sample (99:1 *e.r.*).




The literature procedure[9] was used to prepare the 1-phenylethyl methanesulfonate solution in DCM. The benzylic alcohol (365 mg, 3 mmol), $NEt_3$ (0.54 mL, 3.9 mmol), and $CH_2Cl_2$ (2.5 mL) were added to a 20 mL scintillation vial. Under a nitrogen atmosphere, the vial was cooled to –15 °C and stirred for 5 min, and then mesyl chloride (0.24 mL, 3.08 mmol) was added in one portion via syringe, which resulted in the precipitation of a white solid. The mixture was stirred at –15 °C for 30 min, and then the solid was filtered off using a syringe filter. The total volume of solution was measured (3 mL) and the vial containing the solution was sealed and transferred to glovebox freezer for storage (-35 °C).

**8. Substitutions of dianions, deconstruction procedures and characterization data.**



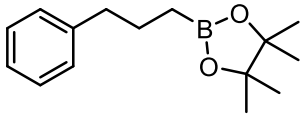

**Method A** (*alkyl bromides using TCNQ as oxidant*): In a nitrogen-filled glove box, the hexaborate dianion (0.4 mmol) and a stir bar were added to a 10 mL glass tube with a screw cap. Dry $CH_3CN$ (2 mL) was added and stirred for 1 min until the dianion was fully dissolved. Alkyl bromide (0.4 mmol) was added via 25 µL micro-syringe (used a spatula in the case of solid alkyl bromides). The glass tube was sealed, wrapped with electrical tape and transferred out of the glove box. The mixture was stirred in an oil bath at 60 °C for 12 hours. The colorless solution was cooled down and diluted with $CH_3CN$, from $^{11}B$ NMR the conversion could be determined. The solvent was removed *in vacuo* and resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under reduced pressure, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transferred to a 20 mL scintillation vial, pinacol (400 mg, 4 mmol) and a stir bar were added. Dry $MgSO_4$ (576 mg) was added and the mixture was stirred for 3 min before cooling to 0 °C. TCNQ (160 mg, 0.8 mmol) was added in four portions over 2 min. The ice bath was removed and a dark green mixture formed gradually. The mixture was kept stirring for 12 hours and color changed to light yellow-brown. The solvent was removed under reduced pressure and the residual solids were extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

**Method B** (*benzyl bromides using TCNQ as oxidant*): In a nitrogen-filled glove box, the hexaborate dianion (0.4 mmol) and a stir bar were added to a 10 mL glass tube with a screw cap. Dry $CH_3CN$ (2 mL) was added and stirred for 1 min until the dianion was fully dissolved. benzyl bromide or substituted benzyl bromide (0.4 mmol) was added via 25 µL micro-syringe (used a spatula in the case of solid benzyl bromides). The glass tube was sealed, wrapped with electrical tape and transferred out of the glove box. The mixture was stirrred at r.t. for 12 hours. The colorless solution was diluted with $CH_3CN$, from $^{11}B$ NMR the conversion could be determined. The solvent was removed *in vacuo* and the resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under vacuum, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transferred to a 20 mL scintillation vial, pinacol (400 mg, 4 mmol) and a stir bar were added. Dry $MgSO_4$ (576 mg) was added and the mixture was stirred for 3 min and TCNQ (160 mg, 0.8 mmol) was added at 0 °C in four portions over 2 min at room temp. After the addition, the cold bath was removed the reaction mixture was kept stirring for 12 hours and solvent was removed under reduced pressure. The residue was extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation to give benzyl boronic ester products.

**Method C** (*alkyl bromides using $NOBF_4$ as oxidant*): In a nitrogen-filled glove box, the hexaborate dianion (0.4 mmol) and a stir bar were added to a 10 mL glass tube with a screw. Dry $CH_3CN$ (2 mL) was added and stirred for 1 min until the dianion was fully dissolved. Alkyl bromides (0.4 mmol) were added via 25 µL micro-syringe (used a spatula in the case of solid alkyl bromides). The glass tube was sealed, wrapped with electrical tape and transferred out of the glove box. The mixture was stirred at 60 °C for 12 hours. The resulting colorless solution was cooled down and diluted with $CH_3CN$. From $^{11}B$ NMR the conversion could be determined. The solvent was removed *in vacuo* and resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under vacuum, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transferred to a 20 mL scintillation vial, pinacol (400 mg, 4 mmol) and a stir bar were added. Dry $MgSO_4$ (576 mg) was added and the mixture was stirred for 3 min and $NOBF_4$ (117 mg, 1.0 mmol) was added in four portions over 2 min at room temp (gas evolution is observed! >=20 mL reaction vial recommended). The mixture was kept stirring for 12 hours and solvent was removed under reduced pressure. The residue was extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation to give alkyl boronic ester products.

**Method D** (*benzyl bromides using $NOBF_4$ as oxidant*): In a nitrogen-filled glove box, the hexaborate dianion (0.4 mmol) and a stir bar were added to a 10 mL glass tube with a screw. Dry $CH_3CN$ (2 mL) was added and stirred for 1 min until the dianion was fully dissolved. Benzyl bromides (0.4 mmol) were added via 25 μL micro-syringe (used spatula in the case of solids). The glass tube was sealed, wrapped with electrical tape and transferred out of the glove box. The mixture was stirred at r.t. for 12 hours. The resulting colorless solution was cooled down and diluted with $CH_3CN$. From $^{11}B$ NMR the conversion could be determined. The solvent was removed *in vacuo* and the resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under vacuum, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transferred to a 20 mL scintillation vial, pinacol (400 mg, 4 mmol) and a stir bar were added. Dry $MgSO_4$ (576 mg) was added and the mixture was stirred for 3 min and $NOBF_4$ (184 mg, 1.6 mmol) was added in four portions over 2 min at room temp (gas evolution is observed! >=20 mL reaction vial recommended). The mixture was kept stirring for 12 hours and solvent was removed under reduced pressure. The residue was extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation to give the benzyl boronic ester products.

**Method E** (*alkyl pseudohalides using TCNQ as oxidant*): In a nitrogen-filled glove box, the hexaborate dianion (0.6 or 0.8 mmol) and a stir bar were added to a 10 mL microwave tube. Dry $CH_3CN$ (0.5 mL) was added and stirred for 1 min until the dianion was fully dissolved. Pseudohalides (0.4 mmol) were added via 25 μL micro-syringe (used a spatula in the case of solids). The microwave tube was sealed and transferred out of the glove box. The mixture was stirred in a microwave reactor at 140 °C for 5 hours. The light orange solution was diluted with $CH_3CN$, from $^{11}B$ NMR the conversion could be determined. The solvent was removed *in vacuo* and the resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under vacuum, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transferred to a 20 mL scintillation vial, pinacol (400 mg, 4 mmol) and a stir bar were added. Dry $MgSO_4$ (576 mg) was added and the mixture was stirred for 3 min and TCNQ (160 mg, 0.8 mmol) was added in four portions over 2 min at 0 °C. The cold bath was then removed. Upon warming up to room temperature, the vial was heated at 40 °C oil bath for 6 hours. The solvent was removed under reduced pressure and the residue was extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.




4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**18**)
**Method A** and **method C** are applied. Phenyl propyl bromide (61.6 μL, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. **For method A**, the $^{11}B$ NMR after substitution step:

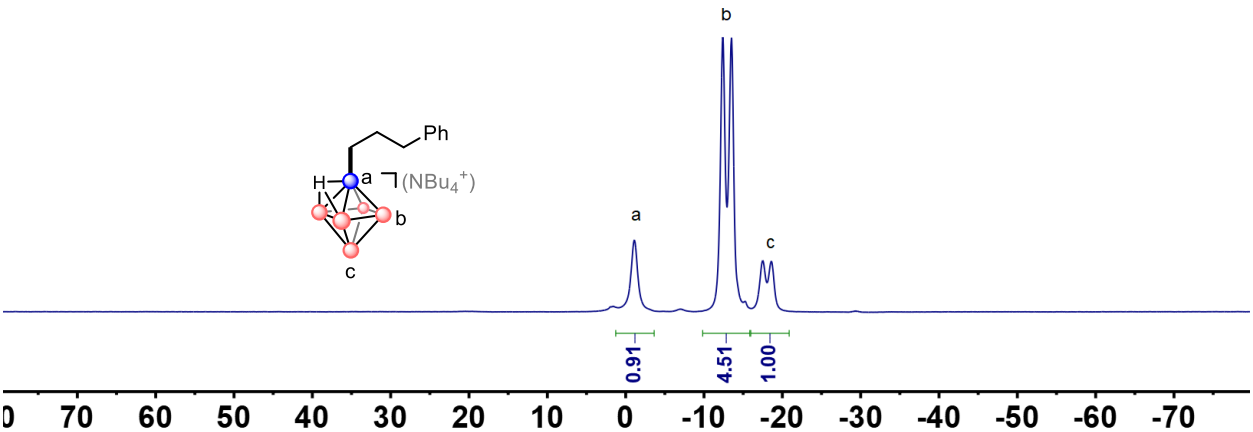



**Fig. S38.** $^{11}B$ NMR spectrum after substitution step with phenyl propyl bromide.

*The assignment of boron signals is shown here. The signal c corresponds to boron atom $B_c$ of substituted cluster, unreacted hexaborate anion signal overlapped with signal b corresponds to equatorial boron $B_b$. The ratio of substituted cluster/hexaborate = 1/{(4.49-1×4)/6}=1/0.085, the conversion = 1/(1+0.085) = 92%.*

**For method C**, $^{11}$B NMR after substitution step (90% conversion):

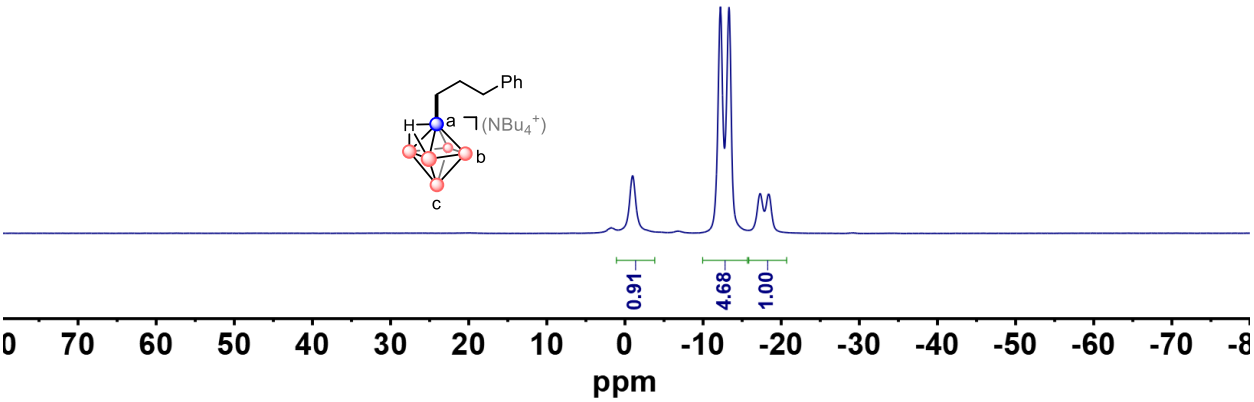
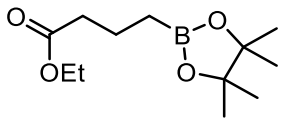



**Fig. S39.** $^{11}$B NMR spectrum after substitution step with phenyl propyl bromide (method C).

The title compound was purified by flash column chromatography (silica gel, 20:1 to 15:1 hexanes/ EtOAc) to give a colorless oil. $R_f$ = 0.78 (silica gel, hexanes/EtOAc = 10:1).

For method A, 68 mg (67%) of product was obtained. For method C, 72 mg (73%) of product was obtained.

**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.30-7.23 (m, 2H), 7.21-7.14 (m, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.74 (pent, *J* = 7.8 Hz, 2H), 1.25 (s, 12H, -$CH_3$), 0.84 (t, *J* = 7.9 Hz, 2H, -$CH_2$-Bpin). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 34.09. **$^{13}$C{$^1$H} NMR ($CDCl_3$,101 MHz)**: δ 142.67, 128.52, 128.13, 125.53, 82.89, 38.56, 26.07, 24.80. 10.80 (B-$CH_2$, br). The NMR spectra are consistent with the literature report[10]. CAS registry No. 329685-40-7.




ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (**19**).

**Method A** is applied. Ethyl 4-bromobutanoate (57.2 μL, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (87% conversion):

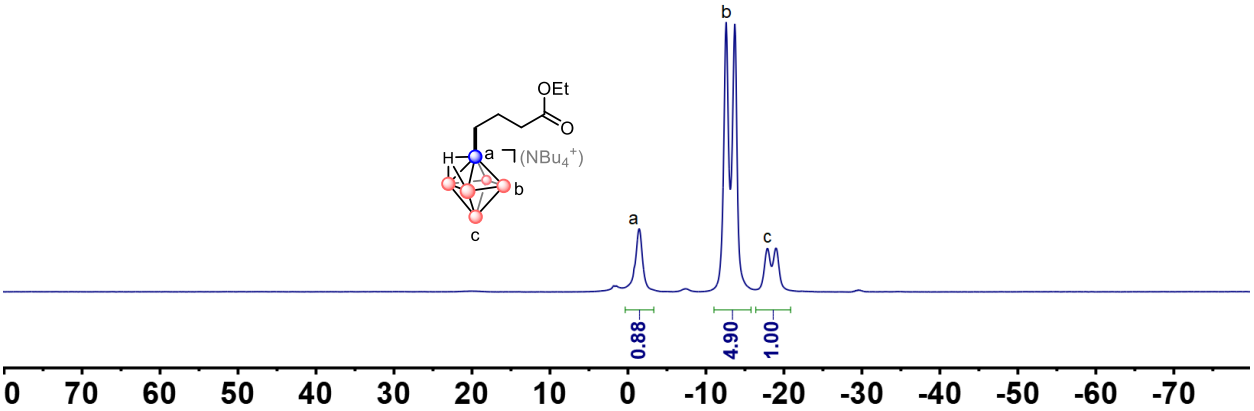
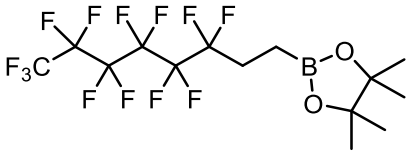



**Fig. S40.** $^{11}$B NMR spectrum after substitution step with Ethyl 4-bromobutanoate.

The title compound was purified by flash column chromatography (silica gel, 6:1 to 5:1 hexanes/DCM, then 12:1 hexanes/EtOAc) to give a colorless oil (59 mg, 60%). $R_f$ = 0.54 (silica gel, hexanes/EtOAc = 4:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 4.09 (q, *J* = 7.1 Hz, 2H, -$OCH_2$-), 2.29 (t, *J* = 7.7 Hz, 2H, -$CH_2CO$-), 1.72 (q, *J* = 7.8 Hz, 2H, -$CH_2$-), 1.23 (t, *J* = 7.2 Hz, 3H, -$CH_3$), 0.79 (t, *J* = 7.8 Hz, 2H, -$CH_2$-). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 33.84. **$^{13}$C{$^1$H} NMR ($CDCl_3$,101 MHz)**: δ 173.65, 83.00, 60.03, 36.56, 24.77, 19.61, 14.22. The carbon directly attached to boron is not observed due to quadrupolar relaxation.
HRMS *m/z* [M-Me]$^+$: calculated: 227.1449, found: 227.1436.
The NMR spectra are consistent with the literature report[10]. CAS registry No. 1392140-97-4



4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3,2-dioxaborolane (**20**)
**Method A** is applied. 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (379.2 mg, 0.8 mmol) and $[Ph_3MeP]_2[B_6H_6]_2$ (250 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (89% conversion):

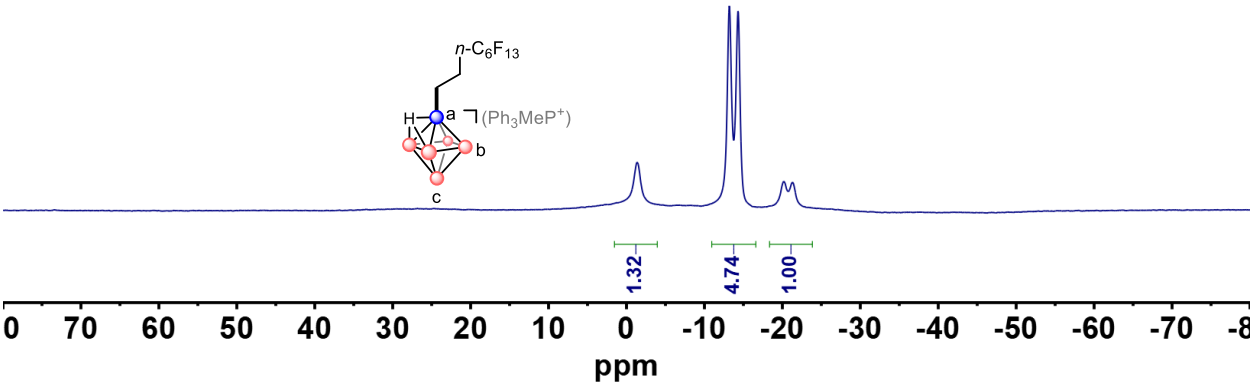
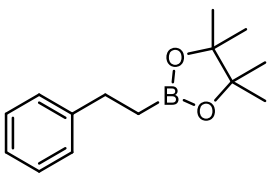



**Fig. S41.** $^{11}$B NMR spectrum after substitution step with 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane.

The title compound was purified by flash column chromatography (silica gel, 20:1 hexanes/EtOAc) to give a colorless oil (85 mg, 45%). $R_f$ = 0.56 (silica gel, hexanes/EtOAc = 15:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 2.28-2.10 (m, 2H), 1.25 (s, 12H, -$CH_3$), 1.07-0.99 (m, 2H, -$CH_2$-B). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 33.53. **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)** δ 83.63, 25.73 (t, *J* = 25.7 Hz, -$CF_2\underline{C}H_2$), 24.74. all other carbons attached to fluorine are not assigned[11]. **$^{19}$F NMR ($CDCl_3$, 376 MHz)** -80.83 (t, J = 10 Hz, 3F), -116.09 (dddt, *J* = 18.8, 14.3, 9.0, 4.5 Hz, 2F), -121.95 (p, *J* = 14.4 Hz, 2F), -122.87 (tdt, *J* = 19.6, 14.6, 6.9 Hz, 2F), -123.42 – -123.68 (m, 2F), -125.98 – -126.47 (m, 2F).
HRMS *m/z* [M-Me]$^+$: calculated: 459.0796, found: 459.0792.
The NMR spectra are consistent with the literature report[11].



4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**21**)
**Method A** is applied. (2-bromoethyl)benzene (74 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ are used for substitution step. The $^{11}B$ NMR after substitution step (83% conversion):

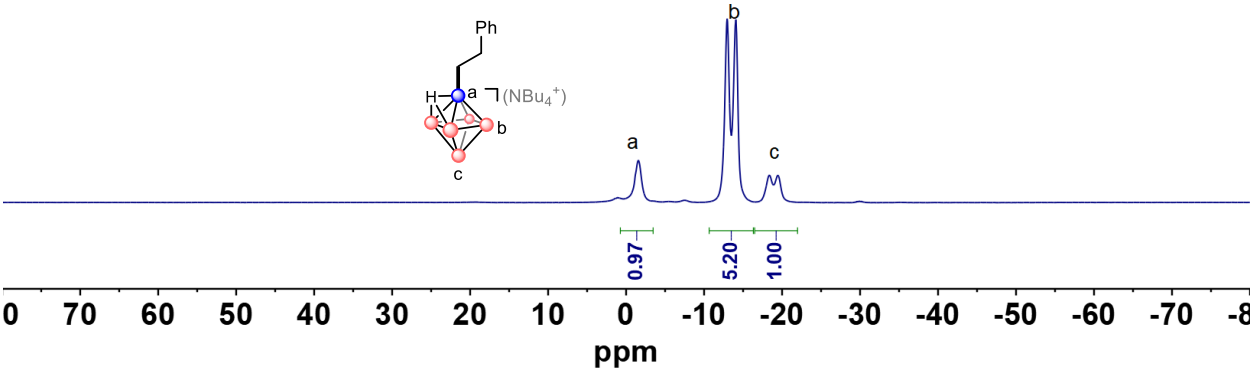
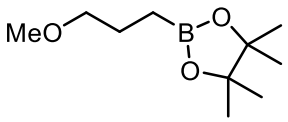



**Fig. S42.** $^{11}B$ NMR spectrum after substitution step with (2-bromoethyl)benzene.

The title compound was purified by flash column chromatography (silica gel, 7:1 to 5:1 hexanes/DCM) to give a colorless oil (49 mg, 53%). $R_f$ = 0.61 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 7.30 – 7.20 (m, 1H), 7.19 – 7.13 (m, 4H), 2.83 – 2.69 (m, 2H), 1.23 (s, 12H), 1.16 (t, *J* = 7.8 Hz, 2H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 33.91. **$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz)** δ 144.38, 128.14, 127.96, 125.45, 83.05, 29.92, 24.77. The carbon directly attached to boron is not observed due to quadrupolar relaxation.
HRMS *m/z* $[M]^+$: calculated: 232.1635, found: 232.1619
The NMR spectra are consistent with the literature report[12]. CAS registry No. 165904-22-3




2-(3-methoxypropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**22**)
**Method A** and **method C** are applied. 1-bromo-3-methoxypropane (45.2 μL, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step.
For **method A**, the $^{11}B$ NMR after substitution step (87% conversion):

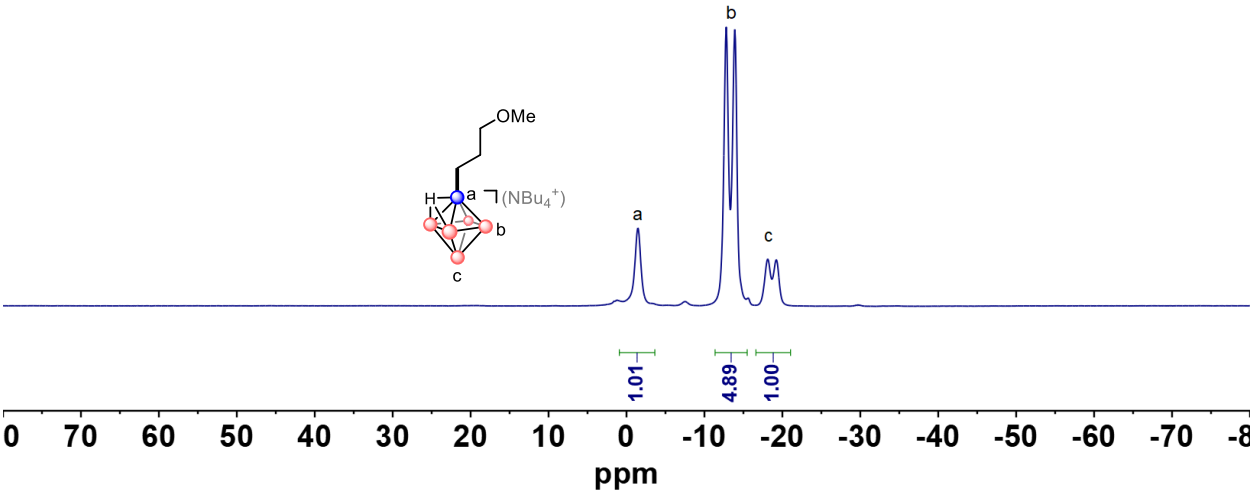



**Fig. S43.** $^{11}B$ NMR spectrum after substitution step with 1-bromo-3-methoxypropane.

For **method C**, the $^{11}$B NMR after substitution step (87% conversion):

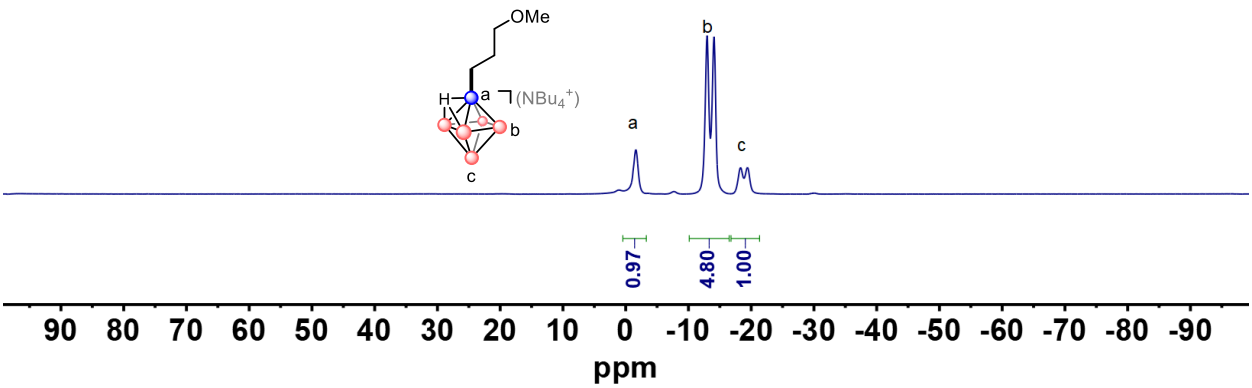
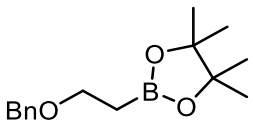



**Fig. S44.** $^{11}$B NMR spectrum after substitution step with 1-bromo-3-methoxypropane (method C).

The title compound was purified by flash column chromatography (silica gel, 15:1 to 12:1 hexanes/ EtOAc) to give a colorless oil. $R_f$ = 0.35 (silica gel, hexanes/EtOAc = 10:1).
For method A, 39 mg (50%) of product was obtained. For method C, 42 mg (52%) of product was obtained. **$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 3.34 (t, *J* = 6.7 Hz, 2H, -$CH_2$-), 3.31 (s, 3H, -$OCH_3$), 1.68 (pent, *J* = 7.1 Hz, 2H, -$CH_2$-), 1.23 (s, 12H, -$CH_3$), 0.78 (t, *J* = 7.7 Hz, 2H, -$CH_2$-). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 33.96. **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ 82.92, 74.57, 58.38, 24.78, 23.98. The carbon directly attached to boron is not observed due to quadrupolar relaxation.
HRMS *m/z* [M-Me]$^+$: calculated: 185.1344, found: 185.1332. CAS registry No. 667917-13-7




2-(2-(benzyloxy)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23**)
**Method A** is applied. ((2-bromoethoxy)methyl)benzene (86 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step.
The $^{11}$B NMR after substitution step (75% conversion):

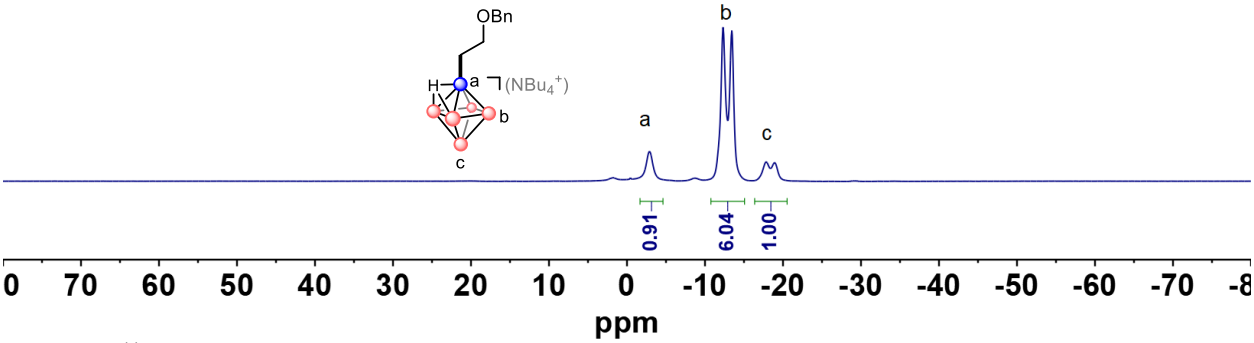
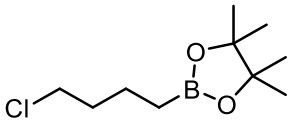



**Fig. S45.** $^{11}$B NMR spectrum after substitution step with ((2-bromoethoxy)methyl)benzene.
The title compound was purified by flash column chromatography (silica gel, 10:1 hexanes/ EtOAc) to give a colorless oil (32 mg, 32%). $R_f$ = 0.28 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 1H NMR (400 MHz, Chloroform-d) δ 7.30-7.23 (m, 1H), 7.21-7.16 (m, 4H), 4.43 (s, 2H, $PhCH_2$–O–), 3.56 (t, *J* = 7.9 Hz, 2H, O–$CH_2$–), 1.17-1.16 (m, 14H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 33.57. **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ $^1$H NMR (101 MHz, $CDCl_3$) δ 138.80, 128.24, 127.58, 127.32, 83.14, 72.54, 67.04, 24.79. The carbon directly attached to boron is not observed due to quadrupolar relaxation.

HRMS *m/z* $[M]^+$: calculated: 262.1740, found: 262.1722.




2-(4-chlorobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**)

**Method A** is applied. *For the substitution step, the reaction was stirred at r.t. instead of 60 °C.* 1-bromo-4-chlorobutane (69 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}B$ NMR after substitution step (79% conversion):

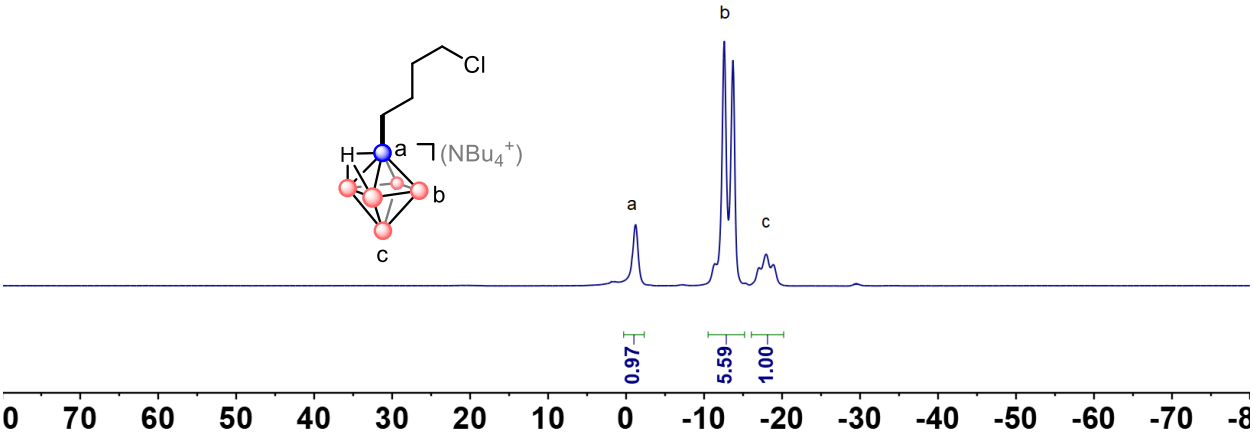
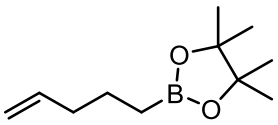



**Fig. S46.** $^{11}B$ NMR spectrum after substitution step with 1-bromo-4-chlorobutane.

The title compound was purified by flash column chromatography (silica gel, 15:1 hexanes/ EtOAc) to give a colorless oil (33 mg, 37%). $R_f$ = 0.76 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 3.52 (t, *J* = 6.8 Hz, 2H), 1.78 (pent, *J* = 7.0 Hz, 2H), 1.54 (pent, *J* = 7.8 Hz, 2H), 1.24 (s, 12H), 0.79 (t, *J* = 7.9 Hz, 2H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 33.95. **$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz)**: δ 83.02, 44.84, 35.09, 24.80, 21.39. The carbon directly attached to boron is not observed due to quadrupolar relaxation.
HRMS *m/z* $[M\text{-}Me]^+$: calculated: 203.1005, found: 203.1000.
The NMR spectra are consistent with the literature report[12].




4,4,5,5-tetramethyl-2-(pent-4-en-1-yl)-1,3,2-dioxaborolane (**25**)
**Method A** is applied. 5-bromopent-1-ene (30 mg, 0.2 mmol) and $TBA_2[B_6H_6]_2$ (112 mg, 0.2 mmol) are used for substitution step. The $^{11}B$ NMR after substitution step (96% conversion):

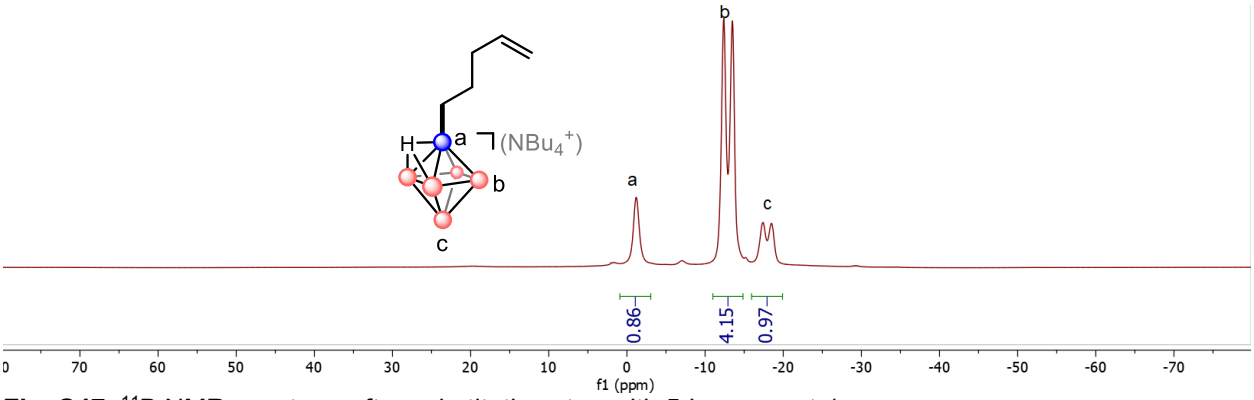
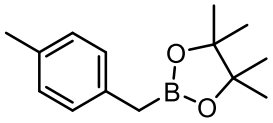



**Fig. S47.** $^{11}$B NMR spectrum after substitution step with 5-bromopent-1-ene.

The title compound was purified by flash column chromatography (silica gel, 20:1 hexanes/ EtOAc) to give a colorless oil (21 mg, 54%).
**$^{1}$H NMR (CDCl$_3$, 400 MHz)**: δ 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, =CH-), 5.03-4.89 (m, 2H, CH$_2$=), 2.13-1.98 (m, 2H), 1.51 (pent, *J* = 7.9, 2H), 1.24 (s, 12H), 0.79 (t, *J* = 7.9 Hz, 2H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 34.13. **$^{13}$C{$^{1}$H} NMR (CDCl$_3$, 101 MHz)** δ 138.94, 114.45, 82.89, 36.36, 24.81, 23.38. The carbon directly attached to boron is not observed due to quadrupolar relaxation.
HRMS *m/z* [M-Me]$^+$: calculated: 181.1394, found: 181.1388.




4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (**27**)
**Method B** is used. 4-methyl benzyl bromide (74 mg, 0.4 mmol) and TBA$_2$[B$_6$H$_6$]$_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (94% conversion):

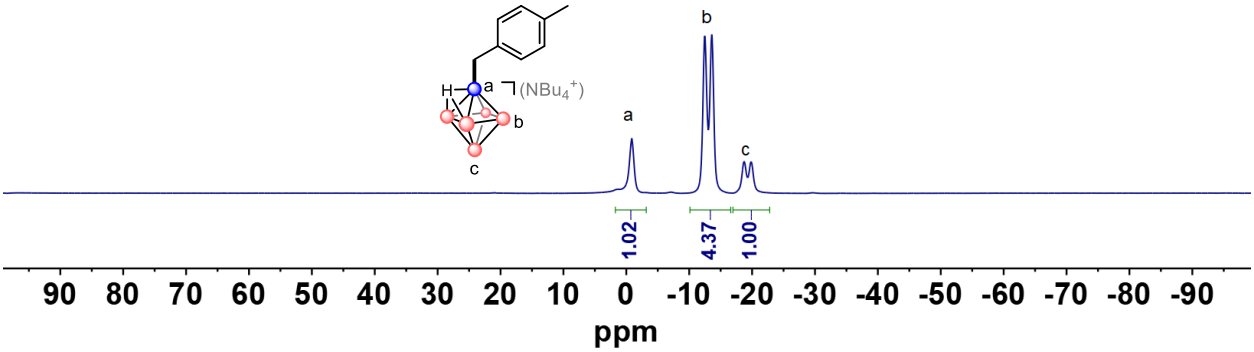
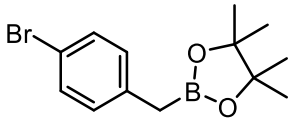



**Fig. S48.** $^{11}$B NMR spectrum after substitution step with 4-methyl benzyl bromide.

The title compound was purified by flash column chromatography (silica gel, 20:1 hexanes/ EtOAc) to give a colorless oil (47 mg, 50%). R$_f$ = 0.73 (silica gel, hexanes/EtOAc = 8:1).
**$^{1}$H NMR (CDCl$_3$, 400 MHz)**: δ 7.11-7.03 (m, 4H), 2.30 (s, 3H), 2.26 (s, 2H), 1.24 (s, 12H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 33.16. **$^{13}$C{$^{1}$H} NMR (CDCl$_3$, 101 MHz)** δ 135.34, 134.06, 128.94, 128.82, 83.31, 24.70, 20.92. The carbon directly attached to boron is not observed due to quadrupolar relaxation. The NMR spectra are consistent with the literature report[13]. CAS registry No. 356570-52-0
HRMS *m/z* [M]$^+$: calculated: 232.1635, found: 232.1626.




2-(4-bromobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**)
**Method D** is used. 1-bromo-4-(bromomethyl)benzene (100 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}B$ NMR after substitution step (86% conversion):

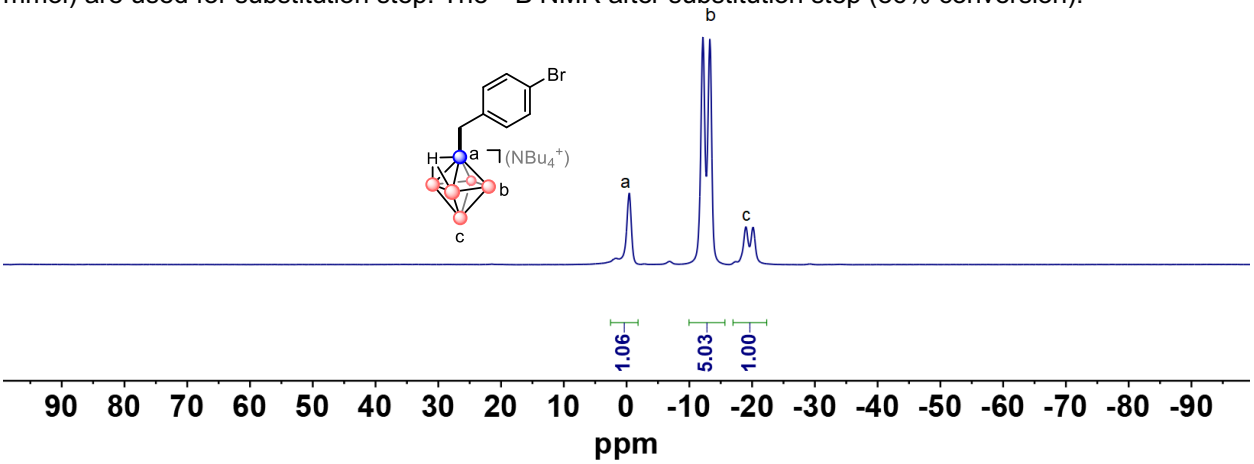
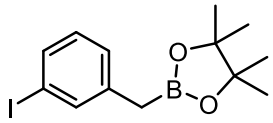



**Fig. S49.** $^{11}B$ NMR spectrum after substitution step with 1-bromo-4-(bromomethyl)benzene.
The title compound was purified by flash column chromatography (silica gel, 20:1 hexanes/ EtOAc) to give a colorless oil (52 mg, 44%). $R_f$ = 0.60 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.39-7.31 (m, 2H), 7.09-7.01 (m, 2H), 2.23 (s, 2H), 1.23 (s, 12H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 32.88. **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ 137.68, 131.22, 130.71, 118.54, 83.54, 24.69. The carbon directly attached to boron is not observed due to quadrupolar relaxation. The NMR spectra are consistent with the literature report[13]. CAS registry No. 477841-90-0.
HRMS *m/z* $[M]^+$: calculated: 296.0583, found: 296.0561.




2-(3-iodobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**)
**Method B** is used. 1-(bromomethyl)-3-iodobenzene (119 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}B$ NMR after substitution step (92% conversion):

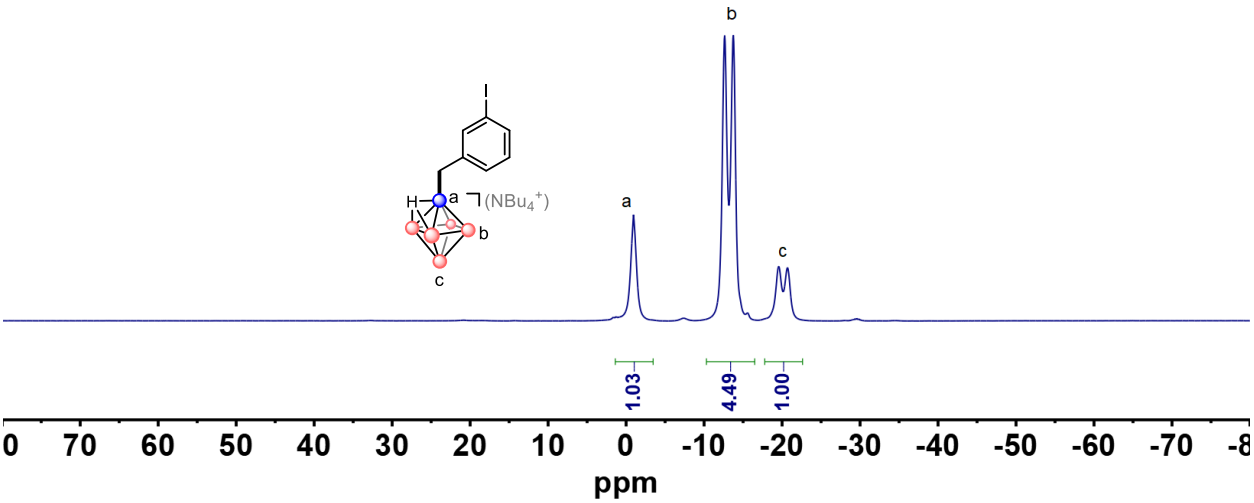
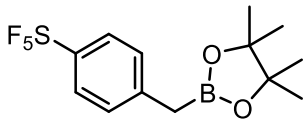



**Fig. S50.** $^{11}$B NMR spectrum after substitution step with 1-(bromomethyl)-3-iodobenzene.

The title compound was purified by flash column chromatography (silica gel, 20:1 hexanes/ EtOAc) to give a colorless oil (81 mg, 59%). $R_f$ = 0.72 (silica gel, hexanes/EtOAc = 8:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 7.55 (t, *J* = 1.8 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.14 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 2.23 (s, 2H), 1.23 (s, 12H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 32.86. **$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz)**: δ 141.17, 137.88, 133.92, 129.88, 128.24, 94.41, 83.57, 24.68. The carbon directly attached to boron is not observed due to quadrupolar relaxation. The NMR spectra are consistent with the literature report[14]. CAS registry No. 1800284-53-0.
HRMS *m/z* [M]$^+$: calculated: 344.0445, found: 344.0433.




4,4,5,5-tetramethyl-2-(4-(pentafluoro-λ$^6$-sulfaneyl)benzyl)-1,3,2-dioxaborolane (**29**)
**Method D** is used. (4-(bromomethyl)phenyl)pentafluoro-λ$^6$-sulfane (119 mg, 0.4 mmol) and TBA$_2$[B$_6$H$_6$]$_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (86% conversion):

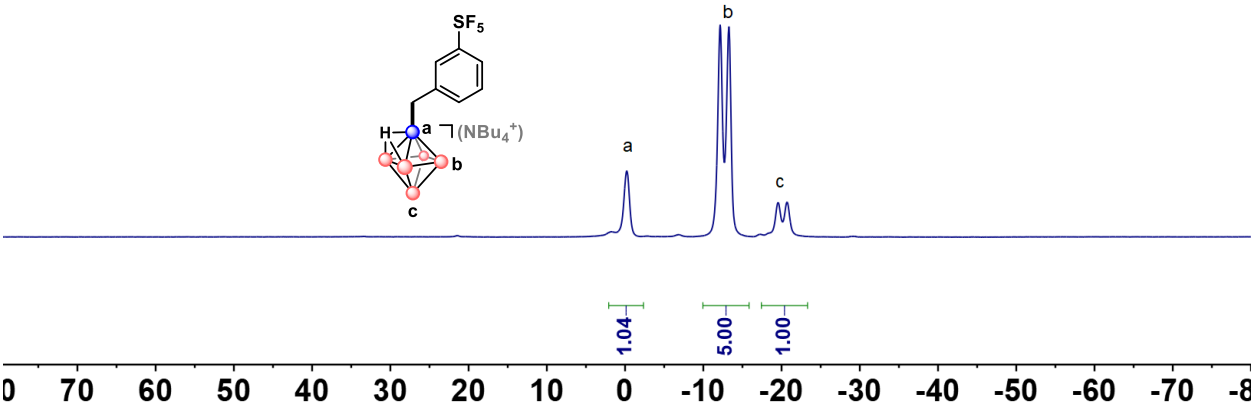
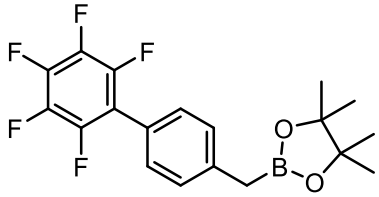



**Fig. S51.** $^{11}$B NMR spectrum after substitution step with (4-(bromomethyl)phenyl) pentafluoro-λ$^6$-sulfane.

The title compound was purified by flash column chromatography (silica gel, 15:1 to 12:1 hexanes/ EtOAc) to give a colorless oil (32 mg, 23%). $R_f$ = 0.42 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.71-7.53 (m, 2H), 7.27-7.21 (m, 2H), 2.33 (s, 2H), 1.24 (s, 12H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 32.86. **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ 143.17, 129.03, 125.85 (d, *J* = 4.17 Hz), 125.80 (d, *J* = 5.1 Hz), 83.77, 24.71. The carbon directly attached to boron was not observed due to quadrupolar relaxation. **$^{19}$F NMR (376 MHz, $CDCl_3$)** δ 85.76 (pent, *J* = 152.2 Hz), 63.50, 63.11.
HRMS *m/z* $[M]^+$: calculated: 344.1041, found: 344.1030.




4,4,5,5-tetramethyl-2-((2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)methyl)-1,3,2-dioxaborolane (**30**)
**Method B** is used. 4'-(bromomethyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (135 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (93% conversion):

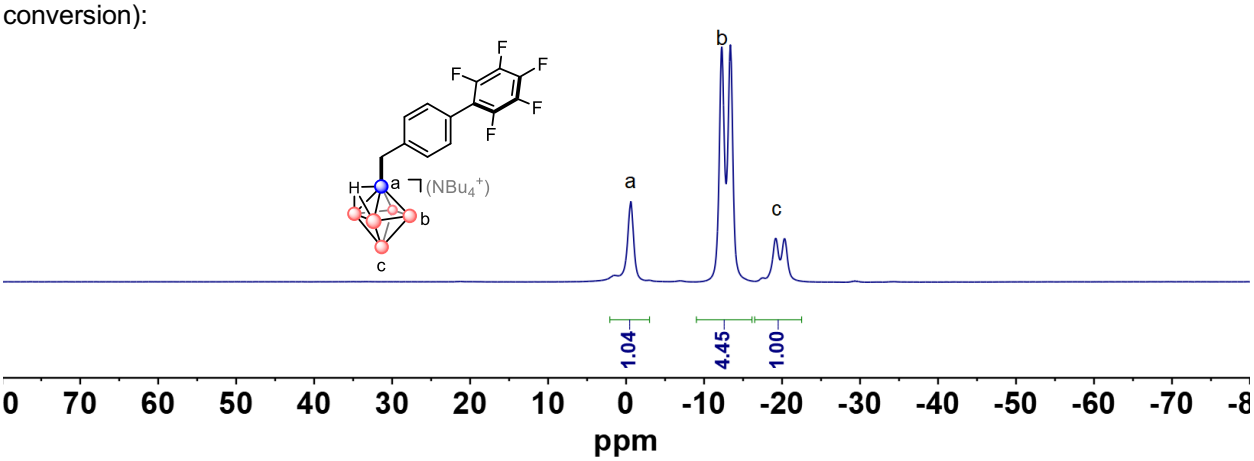
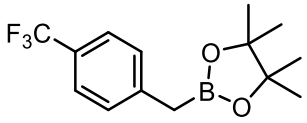



**Fig. S52.** $^{11}$B NMR spectrum after substitution step with 4'-(bromomethyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl.
The title compound was purified by flash column chromatography (silica gel, 15:1 hexanes/ EtOAc) to give a colorless oil (78 mg, 51%). $R_f$ = 0.67 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.33-7.27 (m, 4H), 2.36 (s, 2H), 1.26 (s, 12H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 33.03. **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ 145.41, 142.91, 140.30, 138.86, 136.35, 129.98, 129.36, 122.80, 83.61, 24.72. The carbon directly attached to boron was not observed due to quadrupolar relaxation. **$^{19}$F NMR ($CDCl_3$, 376 MHz)** δ -143.31 (dd, *J* = 23.0, 8.2 Hz, 2F), -156.42 (t, *J* = 20.9 Hz, 1F), -161.28 – -163.45 (m, 2F).
HRMS *m/z* $[M]^+$: calculated: 384.1320, found: 384.1291.




4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (**31**)
**Method D** is used. 1-(bromomethyl)-4-(trifluoromethyl)benzene (96 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (92% conversion):

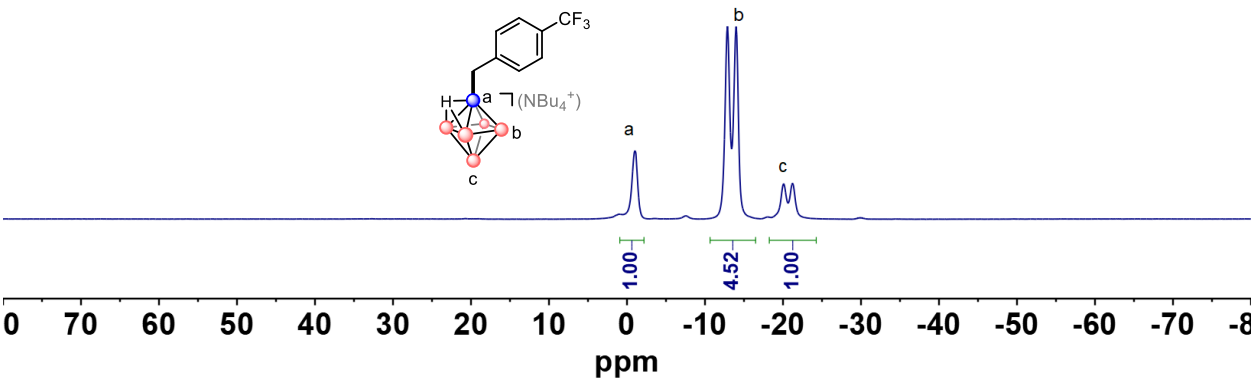
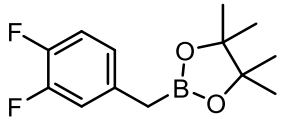



**Fig. S53.** $^{11}$B NMR spectrum after substitution step with 1-(bromomethyl)-4-(trifluoromethyl)benzene.

The title compound was purified by flash column chromatography (silica gel, 12:1 hexanes/DCM to 20:1 hexanes/ EtOAc) to give a colorless oil (56 mg, 49%). $R_f$ = 0.45 (silica gel, hexanes/EtOAc = 10:1). **$^{1}$H NMR (CDCl$_3$, 400 MHz)**: δ 7.53-7.45 (m, 2H), 7.32-7.26 (m, 2H), 2.35 (s, 2H), 1.23 (s, 12H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 32.88. **$^{13}$C{$^{1}$H} NMR (CDCl$_3$, 101 MHz)**: δ 143.12, 129.16, 127.21 (q, *J* = 32 Hz), 125.12 (q, *J* = 3.88 Hz), 124.52 (q, *J* = 271.1 Hz, $\underline{C}F_3$), 83.67, 24.69. The carbon directly attached to boron was not observed due to quadrupolar relaxation. **$^{19}$F NMR (CDCl$_3$, 376 MHz)** δ -62.18 (s, $C\underline{F}_3$). The NMR spectra are consistent with the literature report[14]. CAS registry No. 475250-46-5
HRMS *m/z* [M]$^+$: calculated: 286.1352, found: 286.1322.




2-(3,4-difluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**32**)
**Method D** is used. 4-(bromomethyl)-1,2-difluorobenzene (83 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (225 mg, 0.4 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (93% conversion):

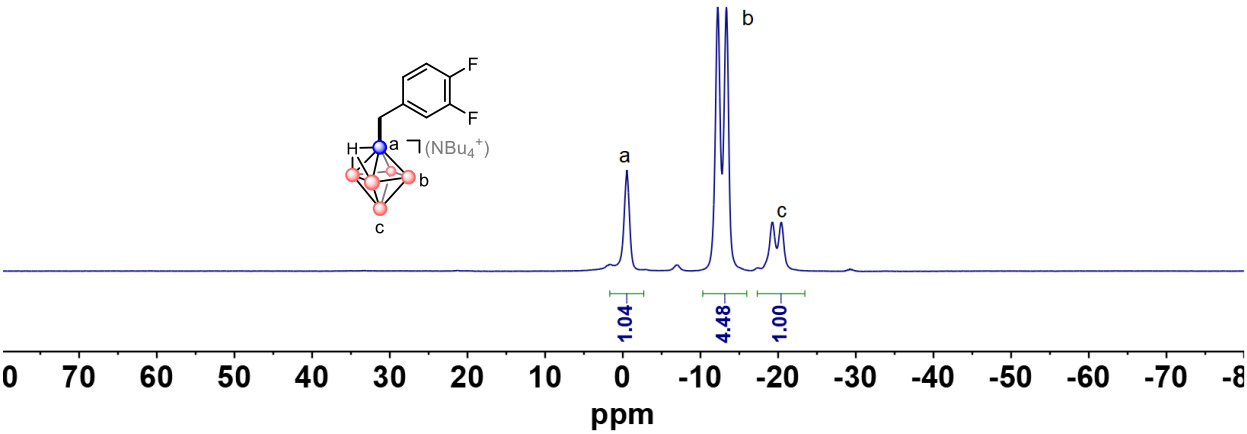
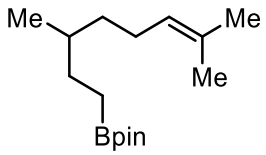



**Fig. S54.** $^{11}$B NMR spectrum after substitution step with 4-(bromomethyl)-1,2-difluorobenzene.

The title compound was purified by flash column chromatography (silica gel, 7:1 hexanes/DCM to 12:1 hexanes/ EtOAc) to give a colorless oil (54 mg, 52%). $R_f$ = 0.41 (silica gel, hexanes/EtOAc = 10:1). **$^{1}$H NMR (CDCl$_3$, 400 MHz)**: δ 7.05-6.94 (m, 2H), 6.89-6.81 (m, 1H), 2.24 (s, 2H), 1.23 (s, 12H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 32.87 (s). **$^{13}$C NMR (CDCl$_3$, 101 MHz)**: δ 124.70 (d, *J* = 3.5 Hz), 124.64 (d, *J* = 3.5 Hz), 117.62 (d, *J* = 17.7 Hz), 116.71 (d, *J* = 16.9 Hz), 83.65, 24.70. The carbon directly attached to boron was not observed due to quadrupolar relaxation. **$^{19}$F NMR (CDCl$_3$, 376 MHz)** δ -138.95 (ddd, *J* = 20.8, 11.7, 8.2 Hz), -143.97 (dddd, *J* = 22.0, 11.3, 7.7, 4.3 Hz).
HRMS *m/z* [M]$^+$: calculated: 254.1290, found: 254.1259




2-(3,7-dimethyloct-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**33**)
**Method A** is used. 3,7-dimethyloct-6-en-1-yl 4-methylbenzenesulfonate (124.2 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (292 mg, 0.52 mmol, 1.3 equiv) are used for substitution step. The mixture is heated to 100 °C instead of 60 °C The $^{11}B$ NMR after substitution step (83% conversion):

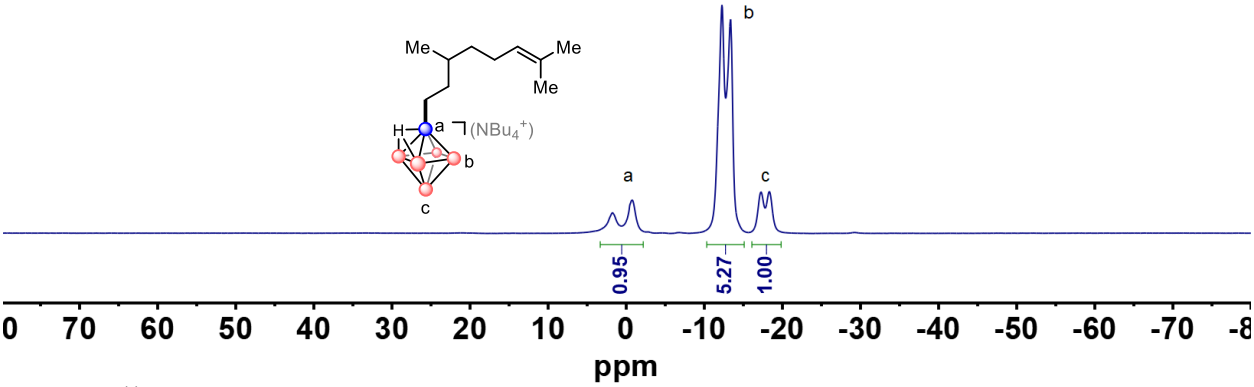
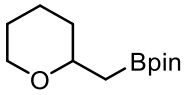



**Fig. S55.** $^{11}B$ NMR spectrum after substitution step with 3,7-dimethyloct-6-en-1-yl 4-methylbenzenesulfonate.

The title compound was purified by flash column chromatography (silica gel, 15:1 hexanes/EtOAc) to give a colorless oil (63 mg, 59%). $R_f$ = 0.79 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 5.09 (ddq, *J* = 8.6, 5.6, 1.4 Hz, 1H), 2.06-1.85 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.47-1.28 (m, 3H), 1.23 (s, 12H), 1.14-1.05 (m, 1H), 0.96-0.88 (m, 1H), 0.84 (d, J = 6.4, 3H), 0.74 (ddd, *J* = 13.9, 10.0, 6.0 Hz, 2H). **$^{11}B$ NMR ($CDCl_3$, 128 MHz)**: δ 34.30 (s). **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz)**: δ 130.80, 125.11, 82.78, 36.69, 34.52, 30.88, 25.67, 25.56, 24.79, 19.06, 17.58. The carbon directly attached to boron was not observed due to quadrupolar relaxation.
HRMS *m/z* $[M]^+$: calculated: 266.2417, found: 266.2397.




4,4,5,5-tetramethyl-2-((tetrahydro-2H-pyran-2-yl)methyl)-1,3,2-dioxaborolane (**34**)
**Method E** is used. (tetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate (108 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (334 mg, 0.6 mmol, 1.5 equiv) are used for substitution step. The mixture is heated to 140 °C using microwave reactor. The $^{11}B$ NMR after substitution step (83% conversion):

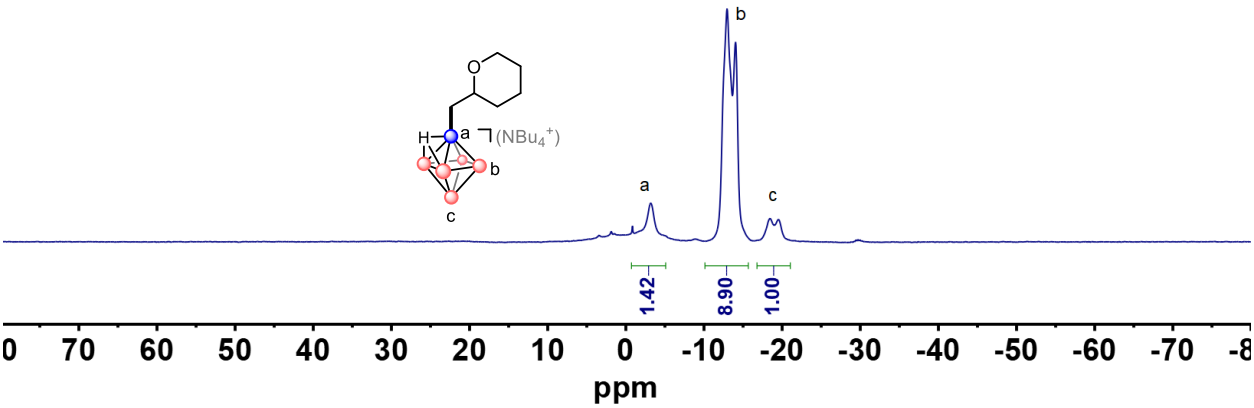
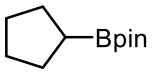



**Fig. S56.** $^{11}$B NMR spectrum after substitution step with (tetrahydro-2H-pyran-2-yl)methyl 4-methylbenzenesulfonate.

The title compound was purified by flash column chromatography (silica gel, 10:1 hexanes/EtOAc) to give a colorless oil (34 mg, 32%). $R_f$ = 0.54 (silica gel, hexanes/EtOAc = 5:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 3.93 (ddt, *J* = 11.4, 3.8, 1.8 Hz, 1H), 3.55-3.38 (m, 2H), 1.83-1.61 (m, 4H), 1.58-1.37 (m, 3H), 1.24 (s, 12H), 0.92-0.81 (m, 1H). **$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 33.30 (s). **$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz)**: δ 83.07, 75.52, 68.44, 33.80, 25.89, 24.70, 23.76. The carbon directly attached to boron was not observed due to quadrupolar relaxation.
HRMS *m/z* [M-Me]$^+$: calculated: 211.1500, found: 211.1505.




2-cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**35**)
**Method E** is used. cyclopentyl 4-methylbenzenesulfonate (97 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (444 mg, 0.8 mmol, 2.0 equiv) are used for substitution step. The mixture is heated to 140 °C using microwave reactor. The $^{11}$B NMR after substitution step (85% conversion):

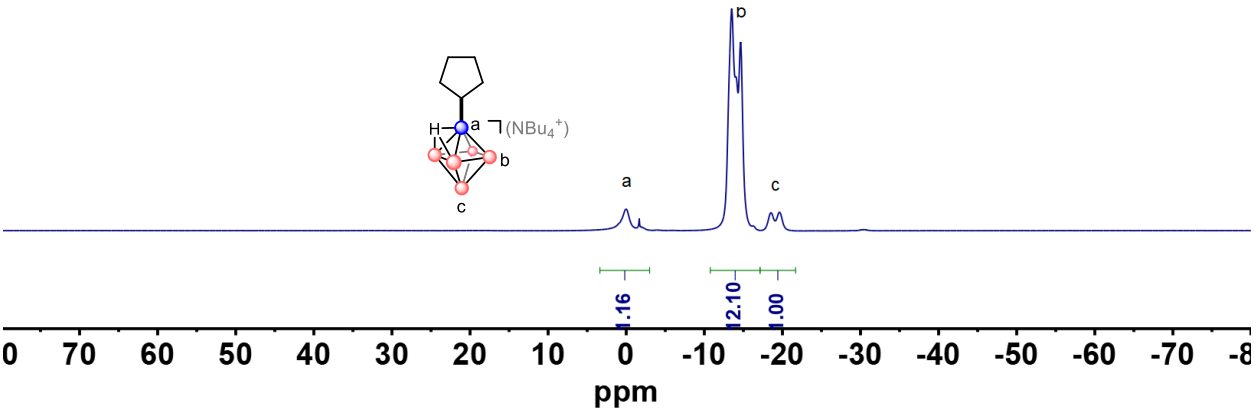
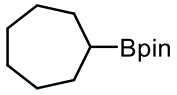



**Fig. S57.** $^{11}$B NMR spectrum after substitution step with cyclopentyl 4-methylbenzenesulfonate.

The title compound was purified by flash column chromatography (silica gel, 18:1 to 15:1 hexanes/EtOAc) to give a colorless oil (33 mg, 42%). $R_f$ = 0.82 (silica gel, hexanes/EtOAc = 8:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 1.80-1.69 (m, 2H), 1.63-1.40 (m, 6H), 1.23 (s, 12H), 1.20 – 1.12 (m, 1H).
**$^{11}$B NMR (CDCl$_3$, 128 MHz)**: δ 34.65 (s). **$^{13}$C{$^1$H} NMR (CDCl$_3$, 101 MHz)**: δ 82.74, 28.48, 26.81, 24.70. The carbon directly attached to boron was not observed due to quadrupolar relaxation. Spectroscopic data matches that reported in the literature[15]. CAS registry No. 66217-55-8.

HRMS *m/z* $[M\text{-}Me]^+$: calculated: 181.1394, found: 181.1388.




2-cycloheptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**36**)
**Method E** is used. cycloheptyl 4-methylbenzenesulfonate (107 mg, 0.4 mmol) and $TBA_2[B_6H_6]_2$ (440 mg, 0.8 mmol, 2.0 equiv) are used for substitution step. The mixture is heated to 140 °C using microwave reactor. The $^{11}B$ NMR after substitution step (98% conversion):

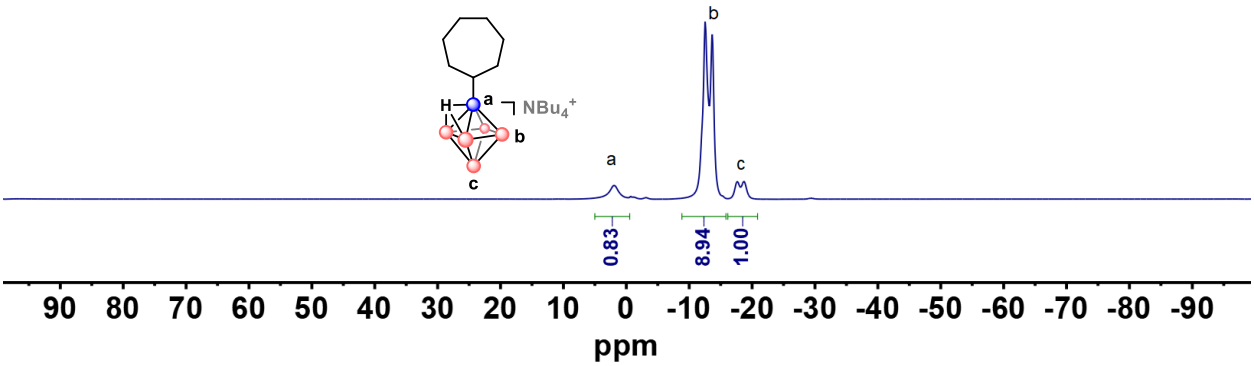
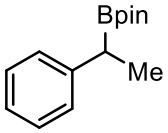



**Fig. S58.** $^{11}B$ NMR spectrum after substitution step with cycloheptyl 4-methylbenzenesulfonate.

The title compound was purified by flash column chromatography (silica gel, 18:1 to 16:1 to 15:1 hexanes/EtOAc) to give a colorless oil (37 mg, 40%). $R_f$ = 0.86 (silica gel, hexanes/EtOAc = 8:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 1.80-1.61 (m, 4H), 1.59-1.37 (m, 8H), 1.22 (s, 12H), 1.06 (m, 1H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 34.43 (s). **$^{13}$C{$^1$H} NMR ($CDCl_3$, 101 MHz)**: δ 82.71, 29.58, 28.93, 28.32, 24.69. The carbon directly attached to boron was not observed due to quadrupolar relaxation. Spectroscopic data matches that reported in the literature[15]. CAS registry No. 931583-43-6.
HRMS *m/z* $[M\text{-}Me]^+$: calculated: 209.1707, found: 209.1702.




4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**38**)
**Method A** is used. 1-phenylethyl methanesulfonate (0.4 mL, DCM solution, 1 mmol/mL), $TBA_2[B_6H_6]_2$ (220 mg, 0.4 mmol, 1.0 equiv) are used for substitution step. The mixture is heated to 60 °C. The $^{11}B$ NMR after substitution step (58% conversion):

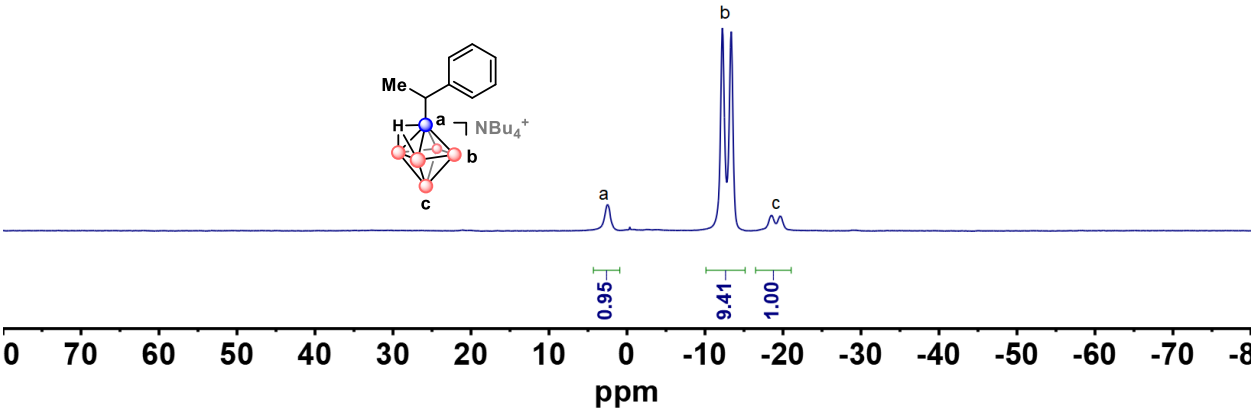
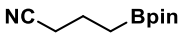



**Fig. S59.** $^{11}$B NMR spectrum after substitution step with 1-phenylethyl methanesulfonate solution.

The title compound was purified by flash column chromatography (silica gel, 18:1 to 16:1 hexanes/EtOAc) to give a colorless oil (39 mg, 42%). $R_f$ = 0.76 (silica gel, hexanes/EtOAc = 8:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 7.31-7.21 (m, 4H), 7.17-7.09 (m, 1H), 2.44 (q, *J* = 7.5 Hz, 1H), 1.33 (s, 12H). The NMR data are consistent with literature report[13]. CAS registry No. 174090-36-9

**Additional substrates:**




4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile
**Method A** is used. 4-bromobutanenitrile (30 mg, 0.2 mmol) and $TBA_2[B_6H_6]_2$ (111 mg, 0.2 mmol) are used for substitution step. The $^{11}$B NMR after substitution step (74% conversion):

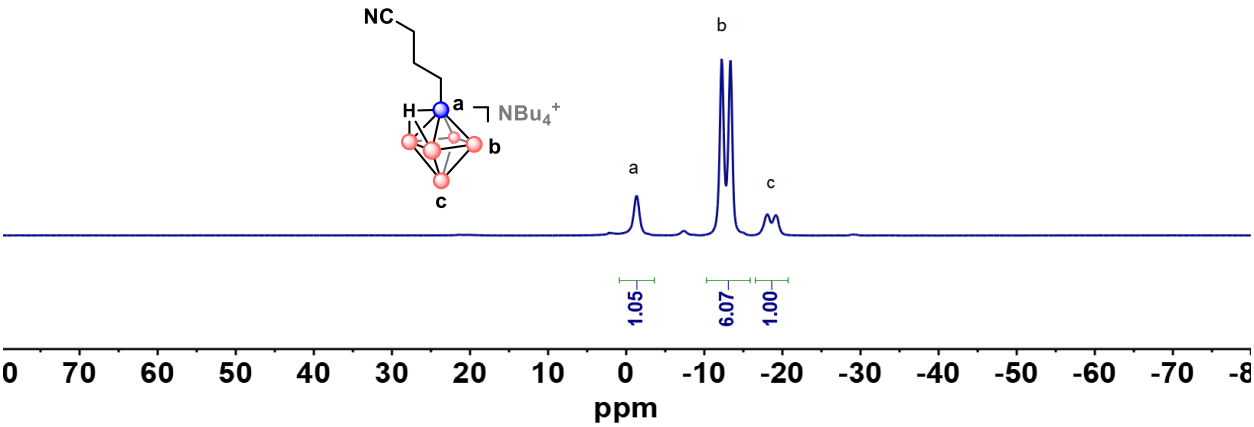
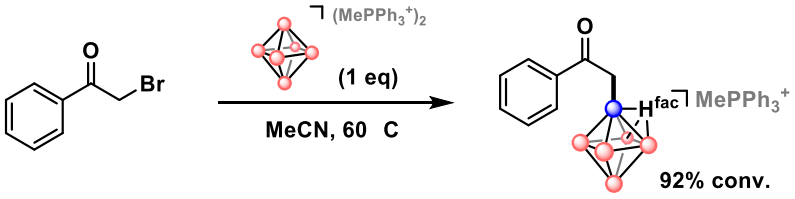



**Fig. S60.** $^{11}$B NMR spectrum after substitution step with 4-bromobutanenitrile.

The title compound was purified by flash column chromatography (silica gel, 15:1 to 12:1 hexanes/EtOAc) to give a colorless oil (24 mg, 60%). $R_f$ = 0.52 (silica gel, hexanes/EtOAc = 6:1).
**$^1$H NMR (CDCl$_3$, 400 MHz)**: δ 2.36 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.72 (m, 2H), 1.24 (s, 12H), 0.99 – 0.88 (m, 2H). **$^{13}$C NMR (CDCl$_3$, 101 MHz)** δ 129.49, 83.38, 25.03, 24.82, 20.40. **$^{11}$B NMR (CDCl$_3$,128 MHz)** δ 33.56 (s). The NMR data are consistent with literature report[16]. CAS registry No. 238088-16-9




**Method A** is used. 2-bromo-1-phenylethan-1-one (30 mg, 0.15 mmol) and $(MePPh_3)_2[B_6H_6]$ (94 mg, 0.15 mmol) are used for substitution step. From $^{11}B$ NMR spectrum, no borates (containing B-O bond) were observed. The $^{11}B$ NMR after substitution step (92% conversion):

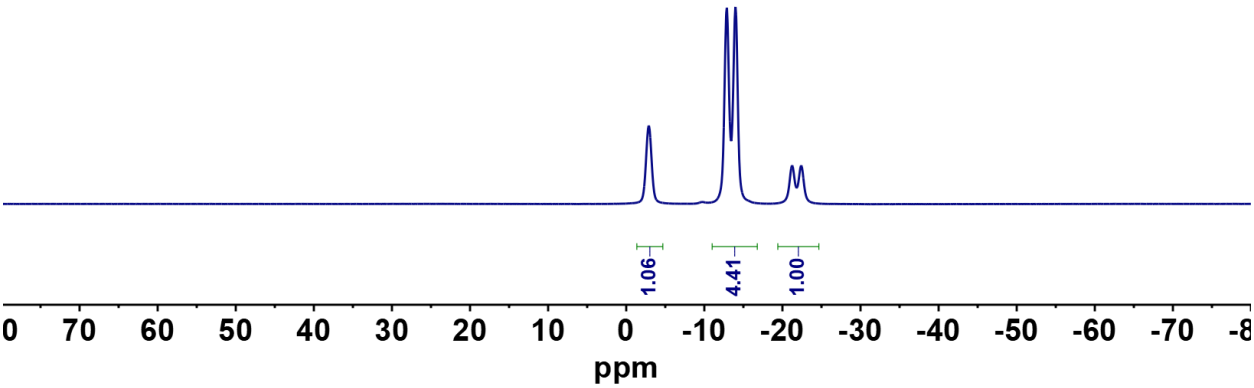



**Fig. S61.** $^{11}B$ NMR spectrum after substitution step with 2-bromo-1-phenylethan-1-one.

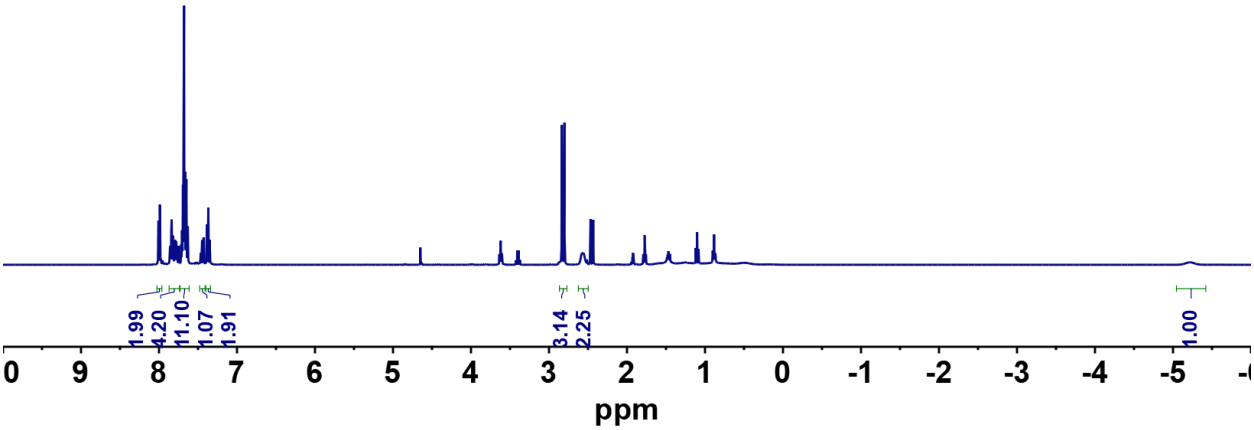



**Fig. S62.** $^{1}H$ NMR spectrum of crude mixture after substitution step with 2-bromo-1-phenylethan-1-one in $CD_3CN$ at 298K.

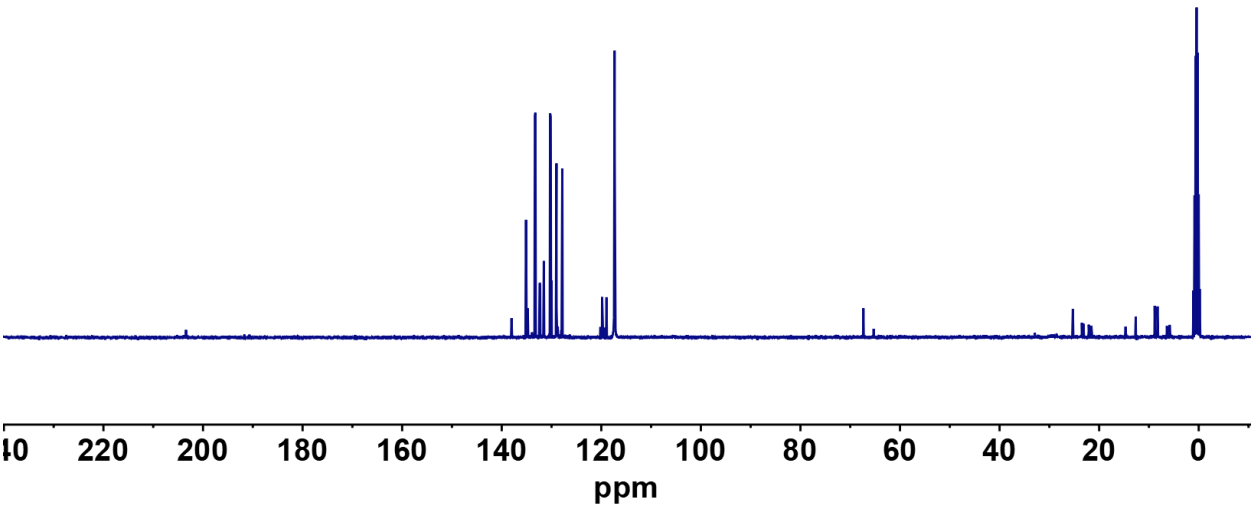



**Fig. S63.** $^{13}C$ NMR spectrum of crude mixture after substitution step with 2-bromo-1-phenylethan-1-one in $CD_3CN$ at 298K.

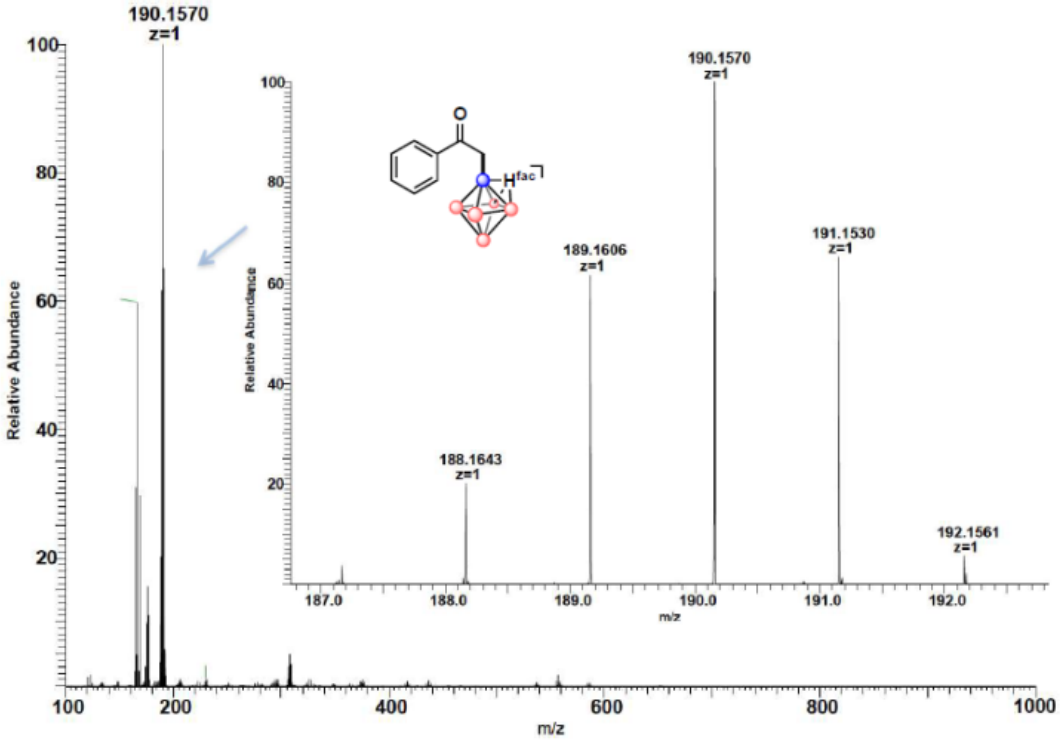



**Fig. S64.** ESI-MS(-) of crude mixture after substitution step with 2-bromo-1-phenylethan-1-one.

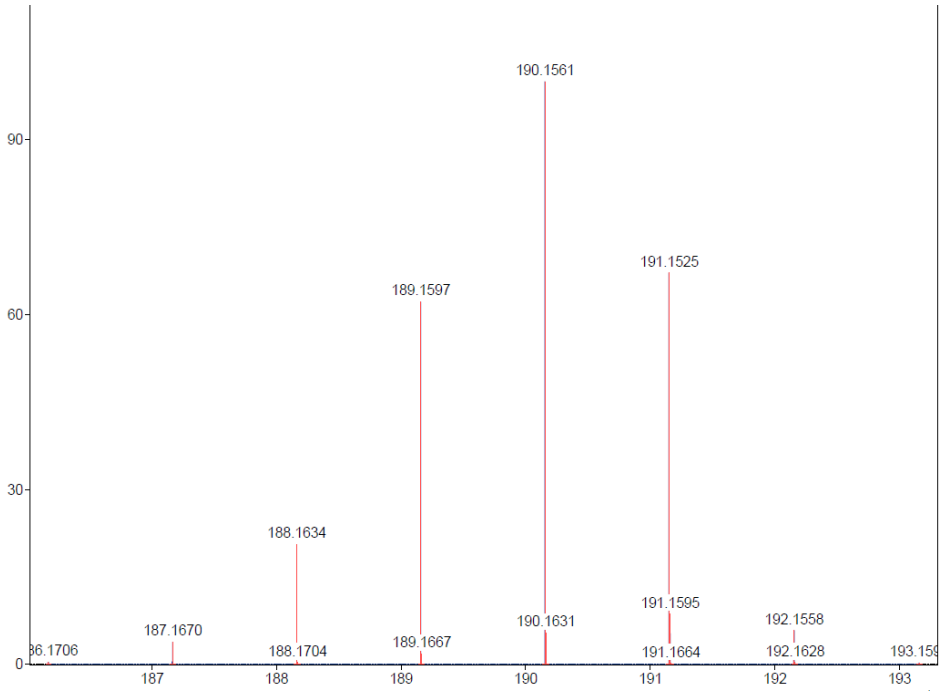
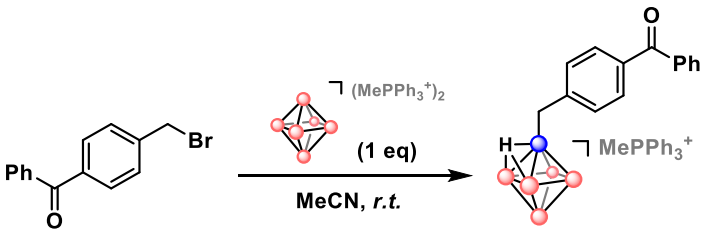



**Fig. S65.** *Simulated* ESI-MS(-) of the substituted cluster.




**Method B** is used. (4-(bromomethyl)phenyl)(phenyl)methanone (55.1 mg, 0.2 mmol) and $(MePPh_3)_2[B_6H_6]$ (126 mg, 0.2 mmol) are used for substitution step. The $^{11}B$ NMR after substitution step (97% conversion):

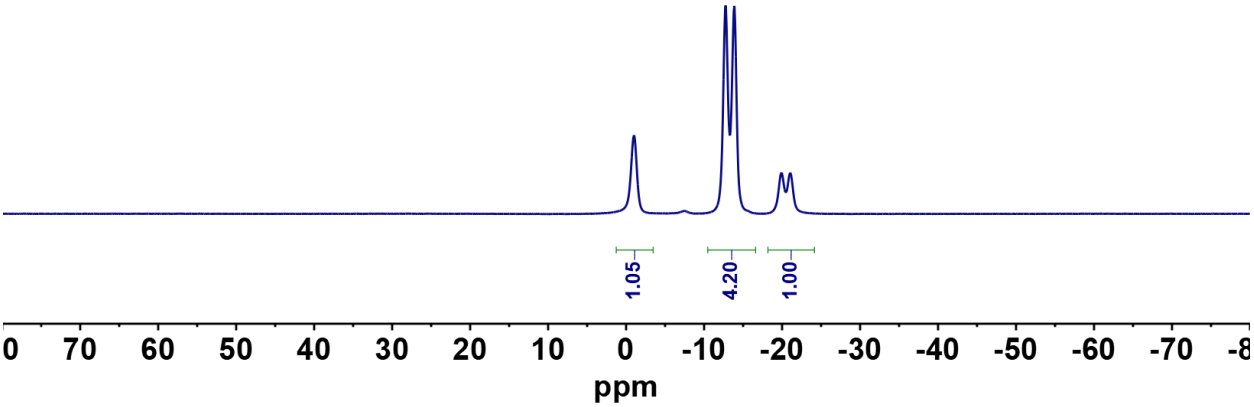



**Fig. S66.** $^{11}B$ NMR spectrum after substitution step with (4-(bromomethyl)phenyl)(phenyl)methanone.

After the oxidative deconstruction of the substituted cluster, the reaction mixture was purified by flash column chromatography (silica gel, 15:1 to 11:1 hexanes/EtOAc) to give a colorless oil (37 mg). $R_f$ = 0.56 (silica gel, hexanes/EtOAc = 6:1). The oil is a mixture of the final alkyl-Bpin (15% yield) and 4-

methylbenzophenone (68% yield) over two steps as an inseparable mixture on silica gel. A possible protodeboronation reaction took place during the oxidative deconstruction step to produce the 4-methylbenzophenone.

**$^{1}$H NMR ($CDCl_3$, 400 MHz)**: δ 7.78 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.62 – 7.54 (m, 1H), 7.47 (ddd, *J* = 8.2, 6.4, 1.4 Hz, 2H), 7.32 – 7.23 (m, 2H), 2.44 (s, 2.3H), 2.38 (s, 0.29H), 1.24 (s, 2H). **$^{13}$C NMR ($CDCl_3$, 101 MHz)**: signals corresponding to 4-methylbenzophenone: δ 196.53, 143.25, 137.99, 134.91, 132.17, 130.33, 129.95, 128.99, 128.23, 21.67. Signals corresponding to alkyl-Bpin: δ 196.52, 144.52, 138.11, 134.34, 132.05, 130.44, 128.89, 128.18, 126.58, 83.70, 24.74. $^{11}$B NMR ($CDCl_3$,128 MHz) δ 33.08 (s). HRMS *m/z* $[M]^+$: calculated: 322.1740, found: 322.1727 (alkyl-Bpin).

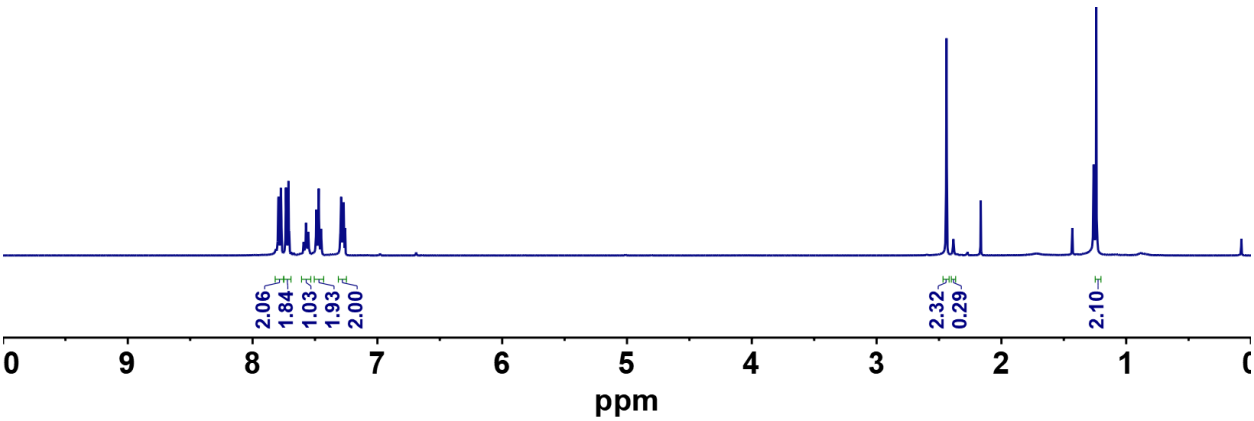



**Fig. S67.** $^{1}$H NMR spectrum of the mixture of alkyl-Bpin and 4-methylbenzophenone in $CDCl_3$ at 298 K.

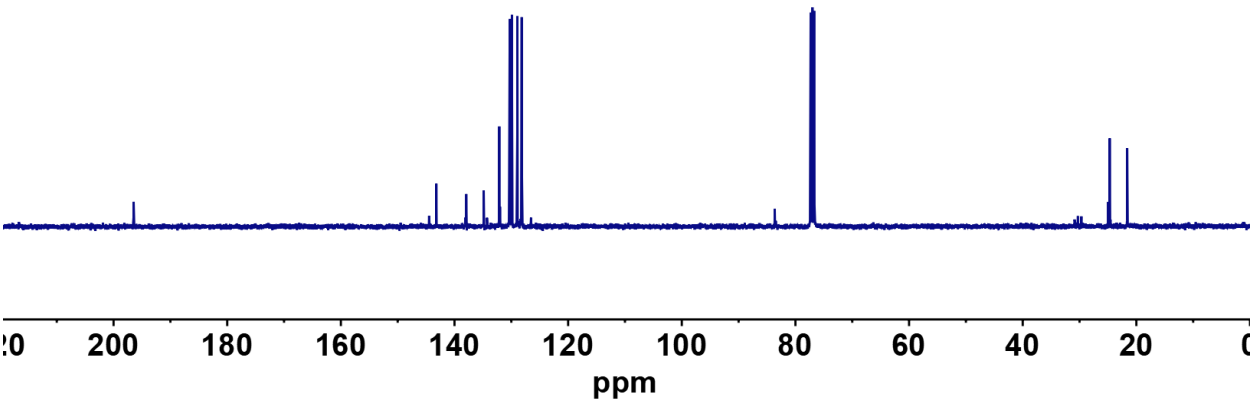



**Fig. S68.** $^{13}$C NMR spectrum of the mixture of alkyl-Bpin and 4-methylbenzophenone in $CDCl_3$ at 298 K.

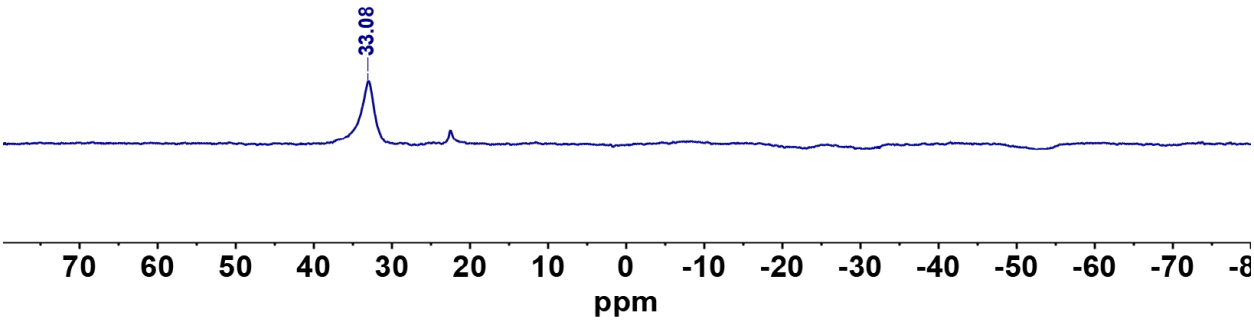
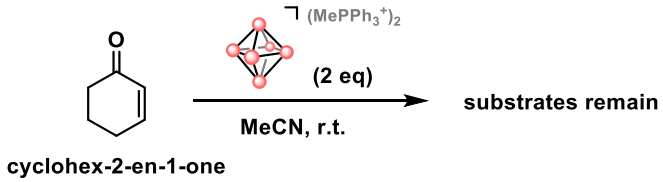


**Fig. S69.** $^{11}B$ NMR spectrum in $CDCl_3$ at 298 K.




**Method A** is used. Cyclohex-2-en-1-one (10 mg, 0.1 mmol) and $(MePPh_3)_2[B_6H_6]$ (130 mg, 0.2 mmol) are combined in acetonitrile and stirred at room temperature for four hours. We did not observe any change in the $^{11}B$ NMR spectrum of the reaction solution.

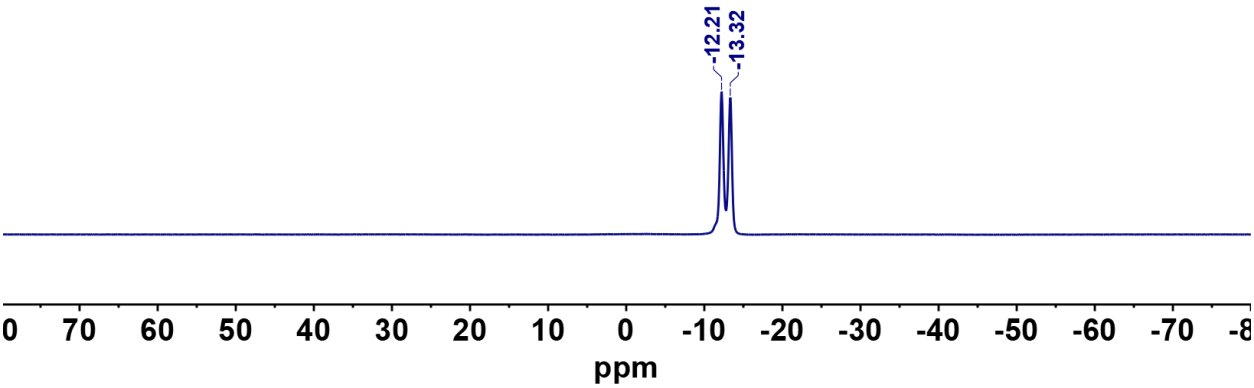
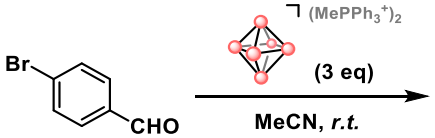



**Fig. S70.** $^{11}B$ NMR spectrum of reaction mixture after fours of stirring.




4-bromobenzaldehyde (9 mg, 0.05 mmol) and $(MePPh_3)_2[B_6H_6]$ (97 mg, 0.15 mmol, 3 equiv) are combined in deuterated acetonitrile and stirred at room temperature for four hours. We did not observe any change in the $^{11}B$ NMR spectrum of the reaction solution.

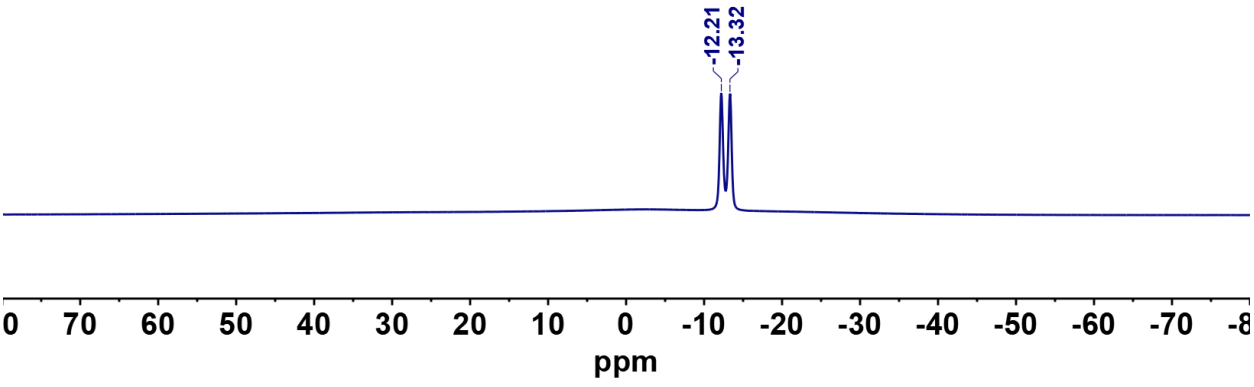
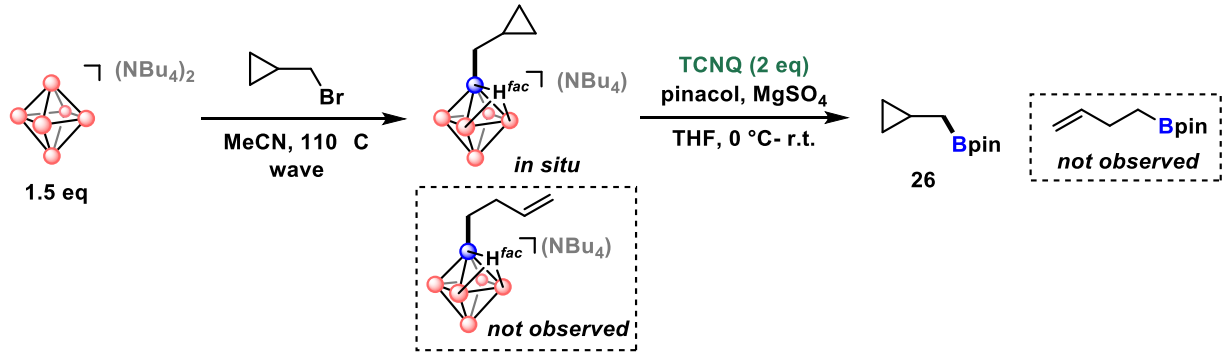


**Fig. S71.** $^{11}$B NMR spectrum of crude reaction mixture after stirring for four hours.

**9. Mechanistic studies using radical clock substrate and chiral electrophile.**




**Method E** was used. In a nitrogen filled glove box, the hexaborate dianion (334 mg, 0.6 mmol) and a stir bar were added to a 10 mL microwave tube. Dry $CH_3CN$ (0.5 mL) was added and stirred for 1 min until the dianion was fully dissolved. (bromomethyl)cyclopropane (39 µL, 0.4 mmol) was added via 25 µL micro-syringe. The microwave tube was sealed and transferred out of the glove box. The mixture was stirred in the microwave reactor at 110 °C for 6 hours. The light orange solution was concentrated and then diluted with $CD_3CN$, from the $^1$H NMR spectrum of the crude reaction mixture, no ring-opened substitution was observed. Only the cyclopropyl substituent is observed. From $^{11}$B NMR the conversion could be determined (98%).

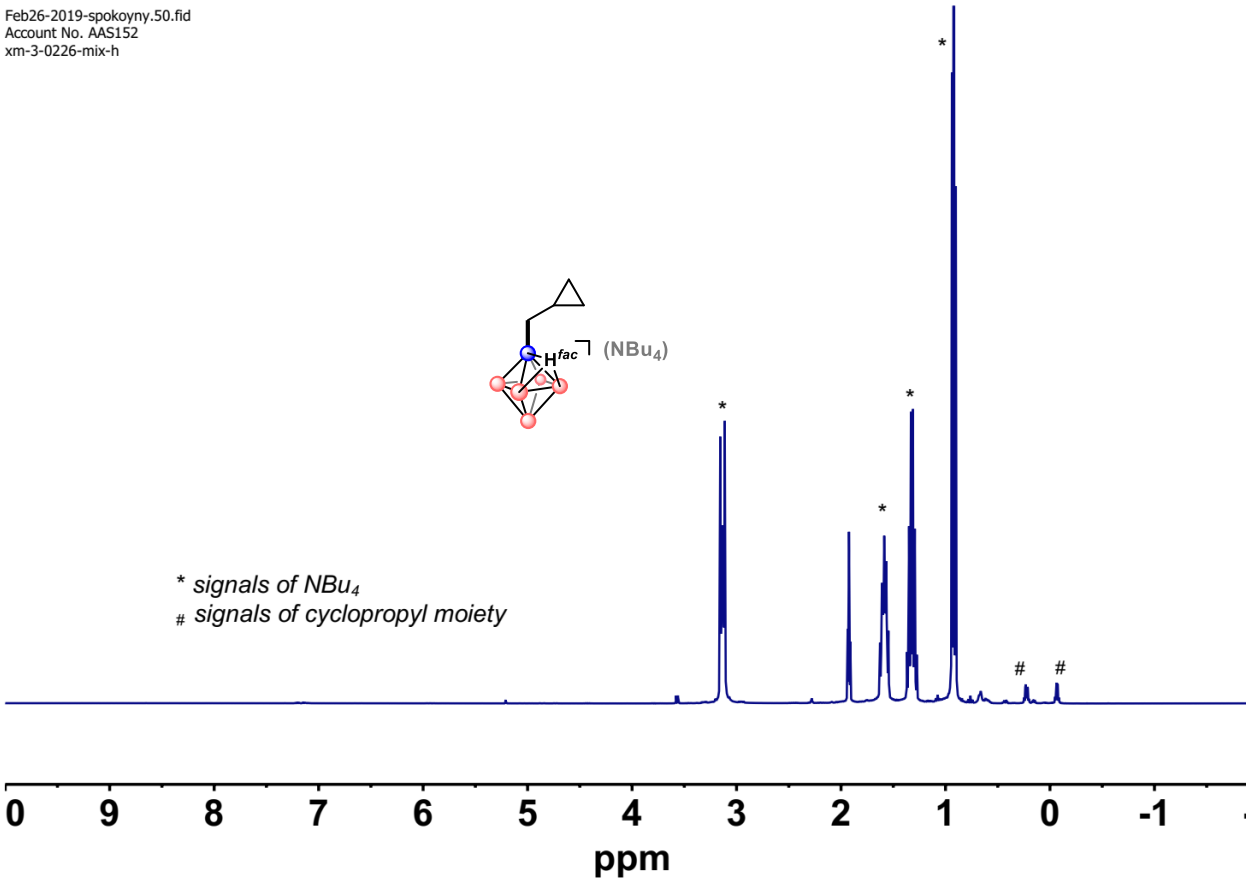


**Fig. S74.** $^{1}$H NMR spectrum of reaction mixture using (bromomethyl)cyclopropane in $CD_3CN$ at 298K.

The solvent was removed *in vacuo* and the resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under vacuum, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transferred to a 20 mL scintillation vial, pinacol (400 mg, 4 mmol), and a stir bar were added. Dry $MgSO_4$ (576 mg) was added and the mixture was stirred for 3 min and TCNQ (160 mg, 0.8 mmol) was added in four portions over 2 min at 0 °C. The cold bath was then removed. Upon warming up to room temperature, the vial was heated at 40 °C in an oil bath for 6 hours. The solvent was removed under reduced pressure and the residue was extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation to give the alkyl boronic ester products.

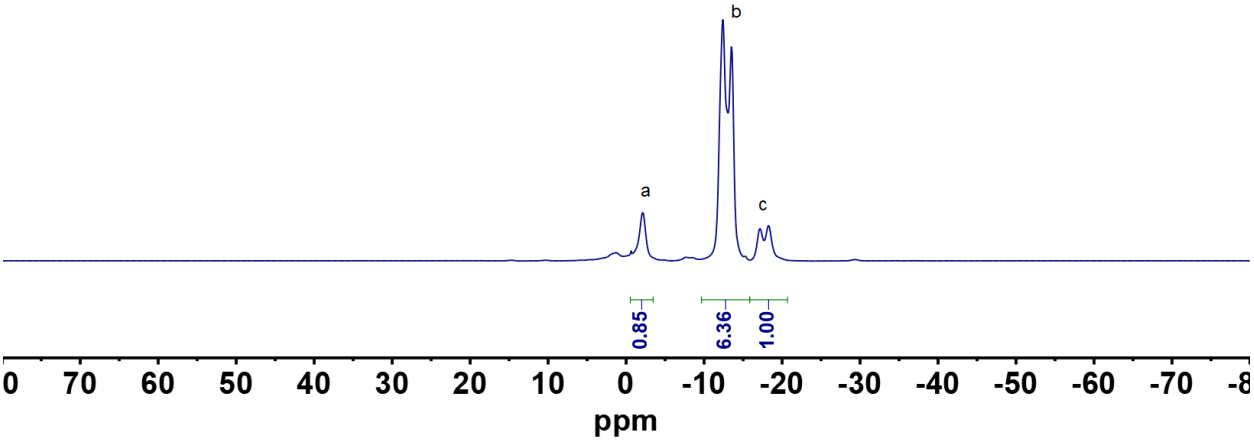
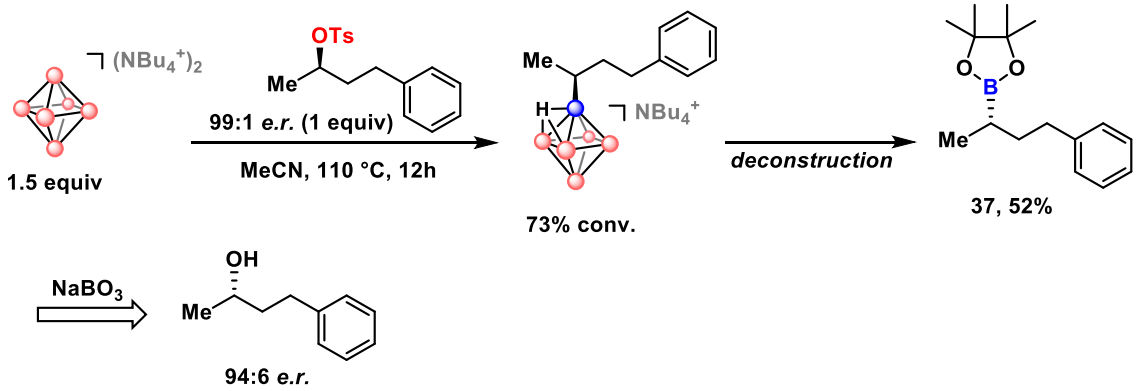



**Fig. S75.** $^{11}$B NMR spectrum after substitution step with (bromomethyl)cyclopropane.

The title compound **26** was purified by flash column chromatography (silica gel, 18:1 to 15:1 hexanes/EtOAc) to give a colorless oil (38 mg, 51%). $R_f$ = 0.84 (silica gel, hexanes/EtOAc = 6:1). **$^{1}$H NMR ($CDCl_3$, 400 MHz)**: δ 1.25 (s, 12H), 0.76 – 0.67 (m, 1H), 0.45-0.36 (m, 2H), 0.03– -0.05 (m, 2H). **$^{11}$B NMR ($CDCl_3$, 128 MHz)**: δ 33.66 (s). **$^{13}$C{$^{1}$H} NMR ($CDCl_3$, 101 MHz)**: δ 82.94, 24.78, 5.91, 5.70. The carbon directly attached to boron was not observed due to quadrupolar relaxation.
HRMS *m/z* $[M\text{-}Me]^+$: calculated: 167.1238, found: 167.1236.

**Substitution/deconstruction sequence using chiral electrophile:**




**Method A** is used. In a nitrogen filled glove box, the hexaborate dianion $TBA_2B_6H_6$ (167 mg, 0.3 mmol) and a stir bar were added to a 10 mL glass tube with a screw cap. Dry $CH_3CN$ (1 mL) was added and stirred for 1 min until the dianion was fully dissolved. (R)-4-phenylbutan-2-yl 4-methylbenzenesulfonate (61 mg, 0.2 mmol) was added. The glass tube was sealed, wrapped with electrical tape and transferred

out of the glove box. The mixture was stirred in an oil bath at 90 °C for 12 hours. The colorless solution was cooled down and diluted with $CH_3CN$, from $^{11}B$ NMR the conversion could be determined as 70%.

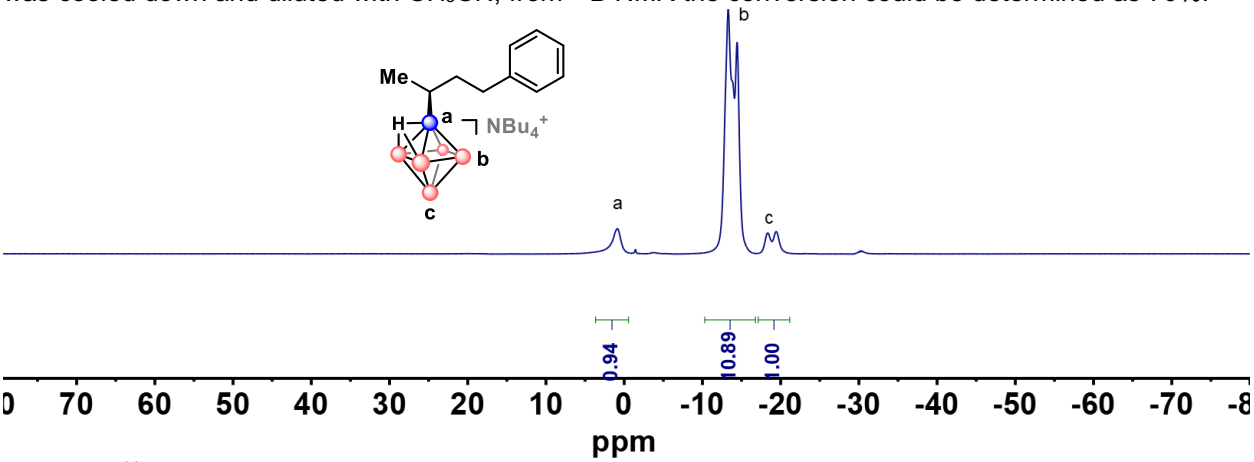
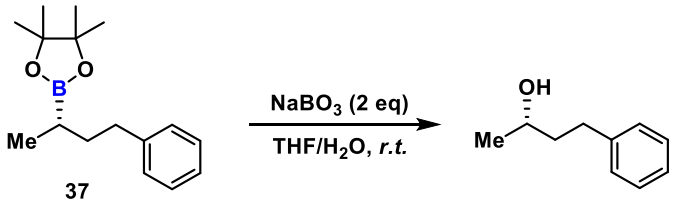



**Fig. S76.** $^{11}B$ NMR spectrum after substitution step with (R)-4-phenylbutan-2-yl 4-methylbenzenesulfonate.

The solvent was removed *in vacuo* and the resulting oil was washed with $Et_2O$ (1 mL×3). Upon further drying under reduced pressure, the crude product of the substituted cluster was dissolved in 2 mL of dry THF and transfer to a 20 mL scintillation vial, pinacol (200 mg, 2 mmol) and a stir bar were added. Dry $MgSO_4$ (289 mg) was added and the mixture was stirred for 3 min before cooling to 0 °C. TCNQ (80 mg, 0.4 mmol) was added in four portions over 2 min. The ice bath was removed and a dark green mixture formed gradually. The mixture was kept stirring for 12 hours and color changed to light yellow-brown. The solvent was removed under reduced pressure and the residual solids were extracted with hexanes/ethyl acetate (10 mL, 4:1 v/v). The extract was concentrated and subjected to column separation (20:1 to 18:1 hexanes/EtOAc) to give the product **37** in 52% yield. $R_f$ = 0.78 (silica gel, hexanes/EtOAc = 10:1).
**$^1$H NMR ($CDCl_3$, 400 MHz)**: δ 7.32-7.24 (m, 2H), 7.22-7.14 (m, 3H), 2.66-2.59 (m, 2H), 1.85-1.74 (m, 1H), 1.25 (s, 12H), 1.12-0.99 (m, 4H). **$^{11}B$ NMR ($CDCl_3$, 128 MHz)**: δ 34.49 (s). **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz)**: δ 143.08, 128.42, 128.18, 125.49, 82.88, 35.30, 35.27, 24.78, 24.73, 15.39. The carbon directly attached to boron was not observed due to quadrupolar relaxation.
HRMS *m/z* $[M]^+$: calculated: 260.1948, found: 260.1918.

**Determination of absolute stereochemistry and *e.r.* value of 37.**




The *e.r.* of **37** was measured after oxidation by $NaBO_3$ using the procedure reported in the literature[17]. **37** (26 mg, 0.1 mmol) was dissolved in THF (1.0 mL) and transferred to 20 mL vial, then $NaBO_3$ (50 mg, 0.2 mmol) and $H_2O$ (1 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 (10:1 to 8:1 hexanes/EtOAc) gave a colorless oil (13 mg, 87%, 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, 20 °C); retention time for compound (**Fig. S65**): $t_1$ = 7.3 min (minor), $t_2$ = 9.4 min (major).

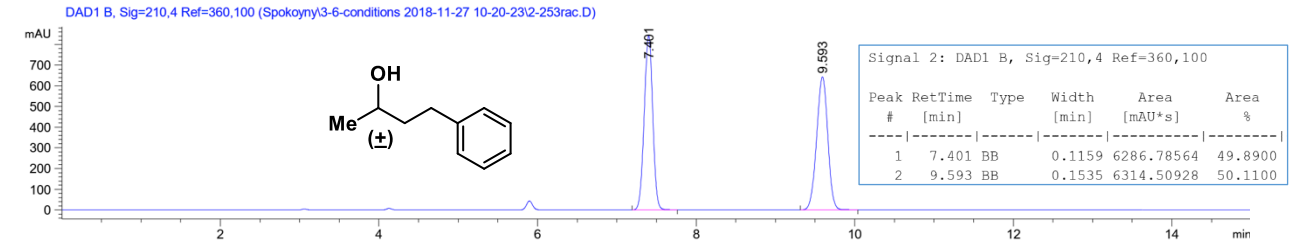



**Fig. S77.** HPLC trace of standard racemic alcohol.

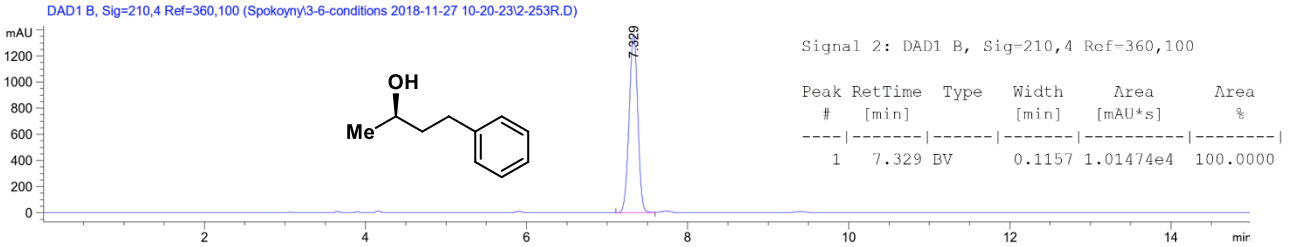



**Fig. S78.** HPLC trace of standard (*R*)-4-phenylbutan-2-ol sample.

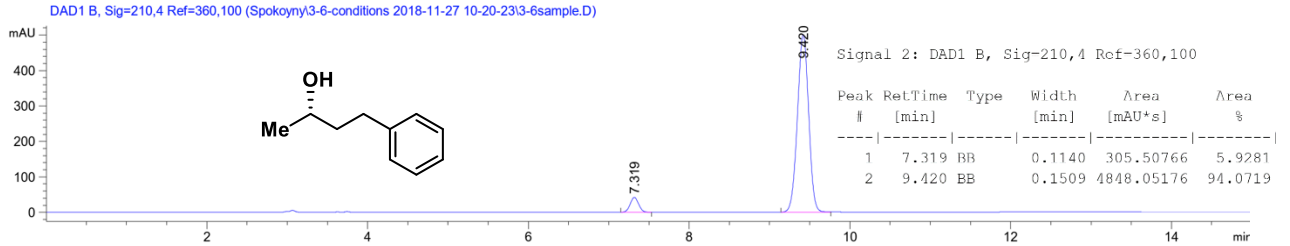
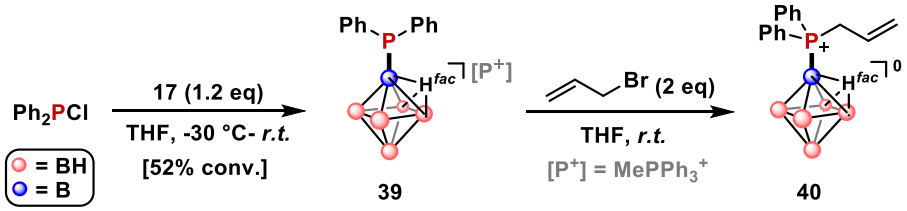



**Fig. S79.** HPLC trace of purified sample from oxidation of **37** (94:6 *e.r.*).

**10. Synthesis of B-heteroatom bond forming products 39-43.**

**Synthesis of B–P bond containing zwitterion compound 40.**




$[MePPh_3]_2[B_6H_6]$ (**17**) (79 mg, 0.12 mmol, 1.2 eq) and a stir bar were added to a 20 mL scintillation vial in the glovebox. Then THF (1 mL) was added and the vial was kept in a -30 °C freezer in the glove box for 20 min. In a separate 4 mL scintillation vial, the $Ph_2PCl$ (23 mg, 0.1 mmol) was added and THF (1 mL) was added. The THF solution of $Ph_2PCl$ was kept in the freezer in the glove box for 20 min. Then both vials were taken out the freezer and the cold THF solution of $Ph_2PCl$ was added dropwise to the stirring suspension of $[MePPh_3]_2[B_6H_6]$ ($[MePPh_3]_2[B_6H_6]$ dianion is not very soluble in THF at r.t.) and warmed up gradually in the glovebox. The bright yellow suspension slowly turned light yellow over the course of three hours. The resulting pale yellow to white suspension was filtered through a syringe filter (25 mm, 0.45 µm pore size) and concentrated under vacuum. The conversion of the reaction was determined by $^{11}B$ NMR spectroscopy of the solution (60% conversion). The resulting light yellow powder was washed with $Et_2O$ (3 mL×3) and dried under vacuum again to obtain a yellowish powder containing both **39** and hexaborate starting material. The $^{31}P\{^1H\}$ show a broad peak at -5 ppm indicating a quadruple relaxation caused by a boron nucleus.

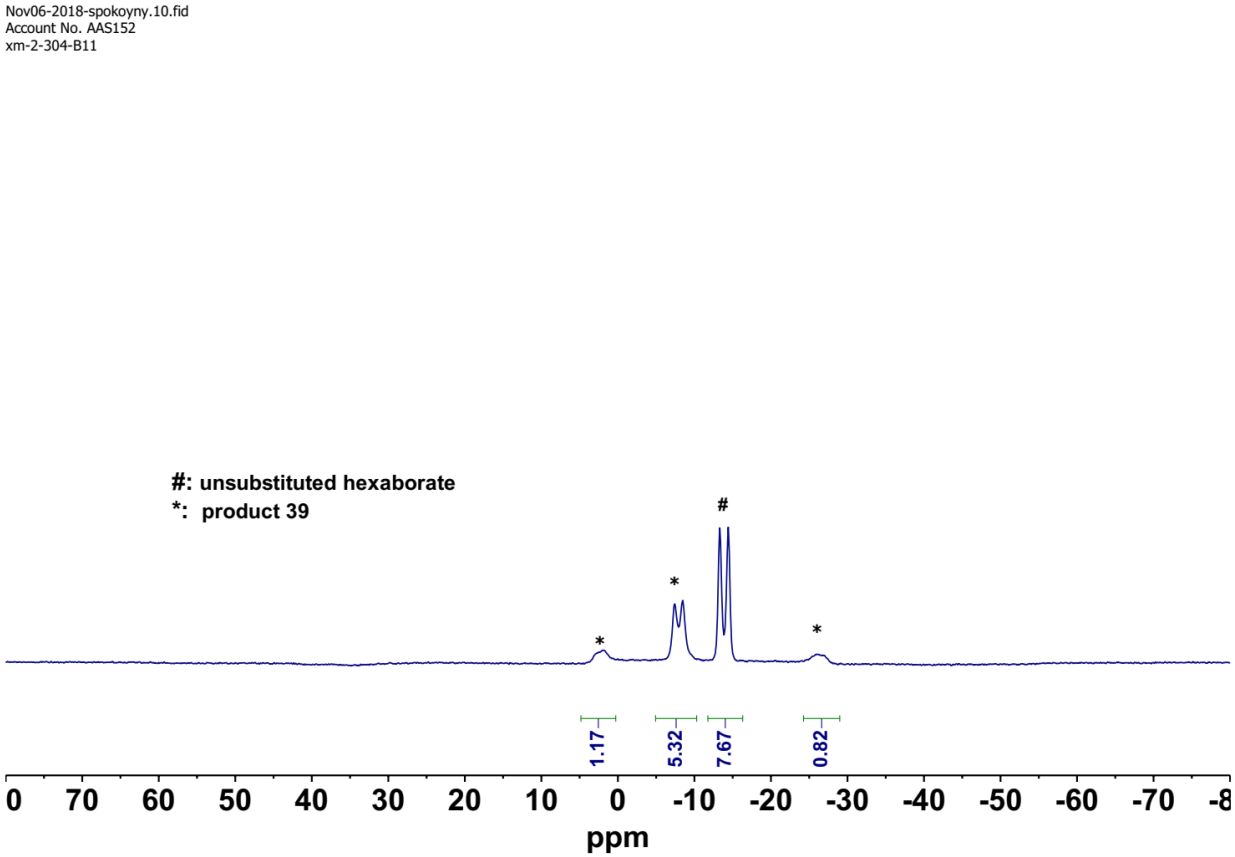



**Fig. S80.** $^{11}B$ NMR spectrum of reaction mixture containing **39** in $CH_3CN$ at 298K.

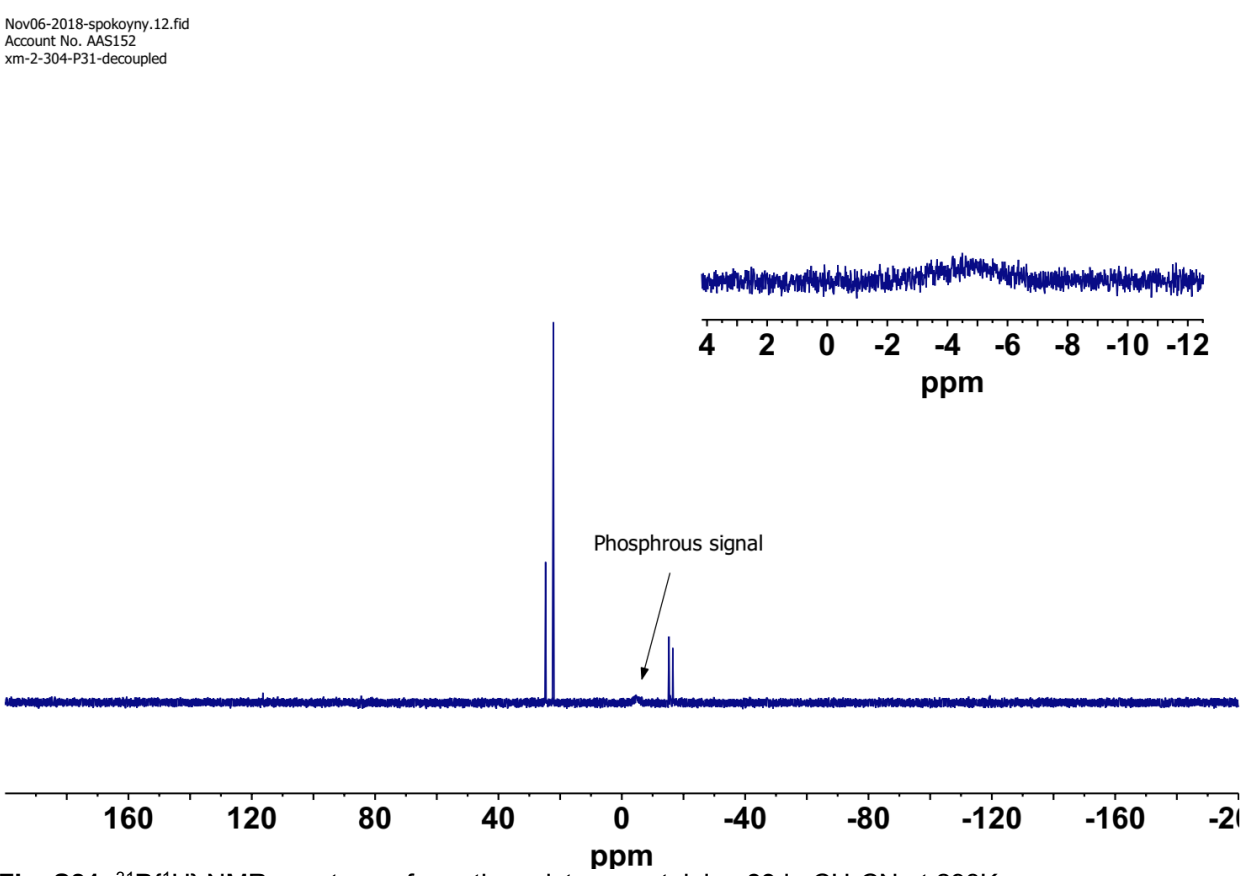



**Fig. S81.** $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture containing **39** in $CH_3CN$ at 298K.

The obtained yellow powder from the previous step was dissolved in THF (1 mL) in the glovebox and under stirring, allyl bromide (12 mg, 0.1 mmol) was added. The color of the solution slowly changed from light yellow to colorless and salt precipitate formed over the course of 3 hours. The solution was left stirring overnight and the solids were filtered off via syringe filter. The solution was concentrated under vacuum and pentane/$Et_2O$ (4:1 v/v, total 5 mL) was added to the mixture to precipitate out $PPh_3MeBr$ and unreacted hexaborate. The solids were filtered off using a syringe filter and the colorless solution was concentrated to give a colorless oil. The oil was extracted with pentane/$Et_2O$ (6:1 v/v, total 3.5 mL) and the extract was concentrated to obtain the compound **40** (10 mg, 65% yield for the second step).
**$^{1}$H NMR ($CDCl_3$, 400 MHz)**: δ $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.72 (m, 4H), 7.61 – 7.55 (m, 2H), 7.55 – 7.47 (m, 4H), 5.95 – 5.79 (m, 1H), 5.20 (ddq, *J* = 10.1, 3.9, 1.1 Hz, 1H), 5.10 (ddq, *J* = 16.9, 4.9, 1.3 Hz, 1H), 3.25 (dd, *J* = 14.2, 7.4 Hz, 2H), -4.49 (s, 1H, $H^{fac}$).
**$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 203 MHz)** δ -3.00 (multiplet, *J* [$^{31}$P-$^{11}$B(I=3/2)] = 176 Hz).
**$^{11}$B NMR** (**$CDCl_3$, 128 MHz**) δ -7.24 (d, *J* = 161.8 Hz), -10.75 (d, *J* = 156.9 Hz), -17.06 (d, $^{1}J_{P\text{-}B}$ = 175.1 Hz). **$^{11}B\{^{1}H\}$ NMR** (**$CDCl_3$, 128 MHz**) δ -7.13 (s, 1B), -10.68 (s, 4B), -17.02 (d, $^{1}J_{P\text{-}B}$ = 174.8 Hz, 1B).
**$^{13}C\{^{1}H\}$ NMR** (**$CDCl_3$, 126 MHz**) δ 132.93 (d, *J* = 9.5 Hz), 132.41 (d, *J* = 2.9 Hz), 129.13 (d, *J* = 11.5 Hz), 126.25 (d, *J* = 7.2 Hz), 124.81 (d, *J* = 70.3 Hz), 122.48 (d, *J* = 12.1 Hz), 32.33 (d, *J* = 44.8 Hz).
ESI-MS(-) for $[M\text{-}H]^-$: calculated: 296.1897. measured: 296.1901

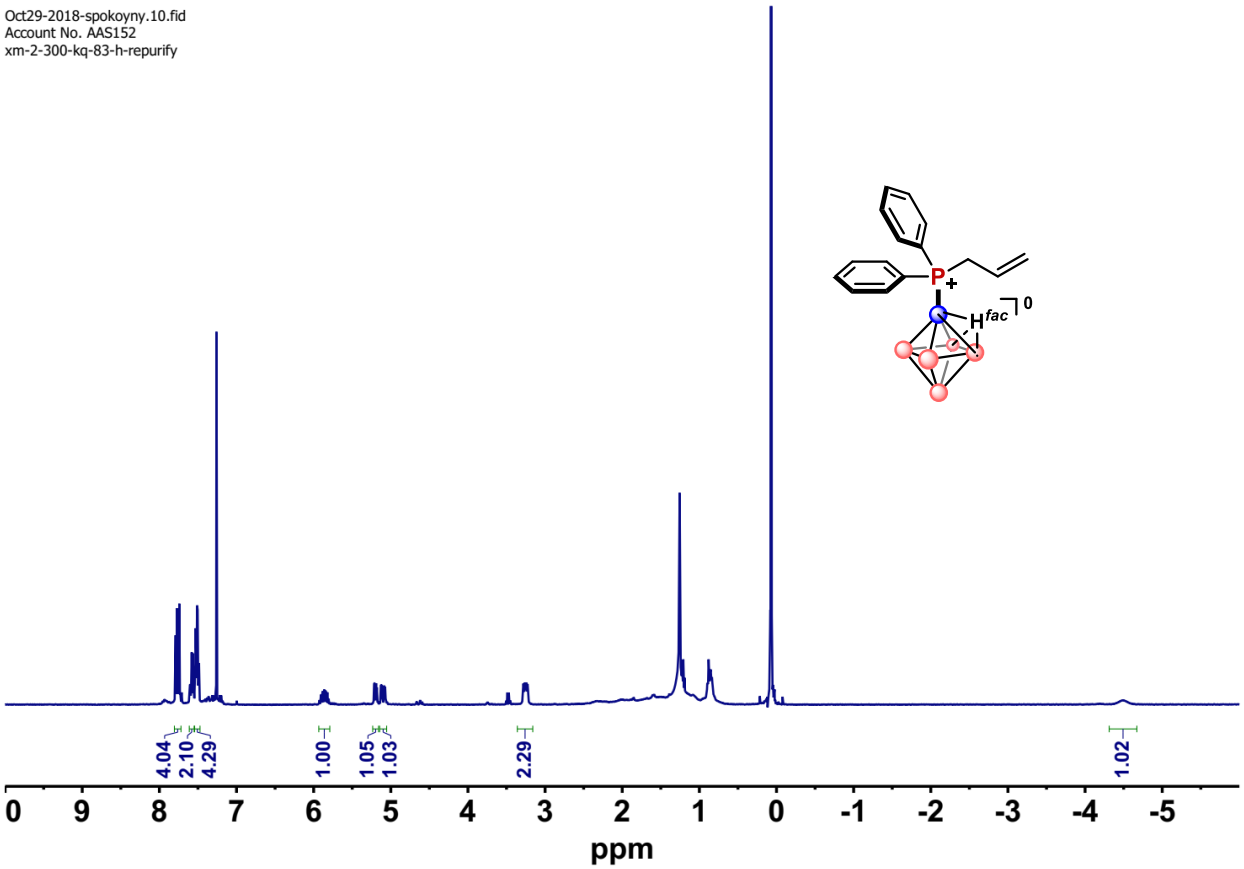



**Fig. S82.** $^{1}$H NMR spectrum of **40** in $CDCl_3$ at 298K.

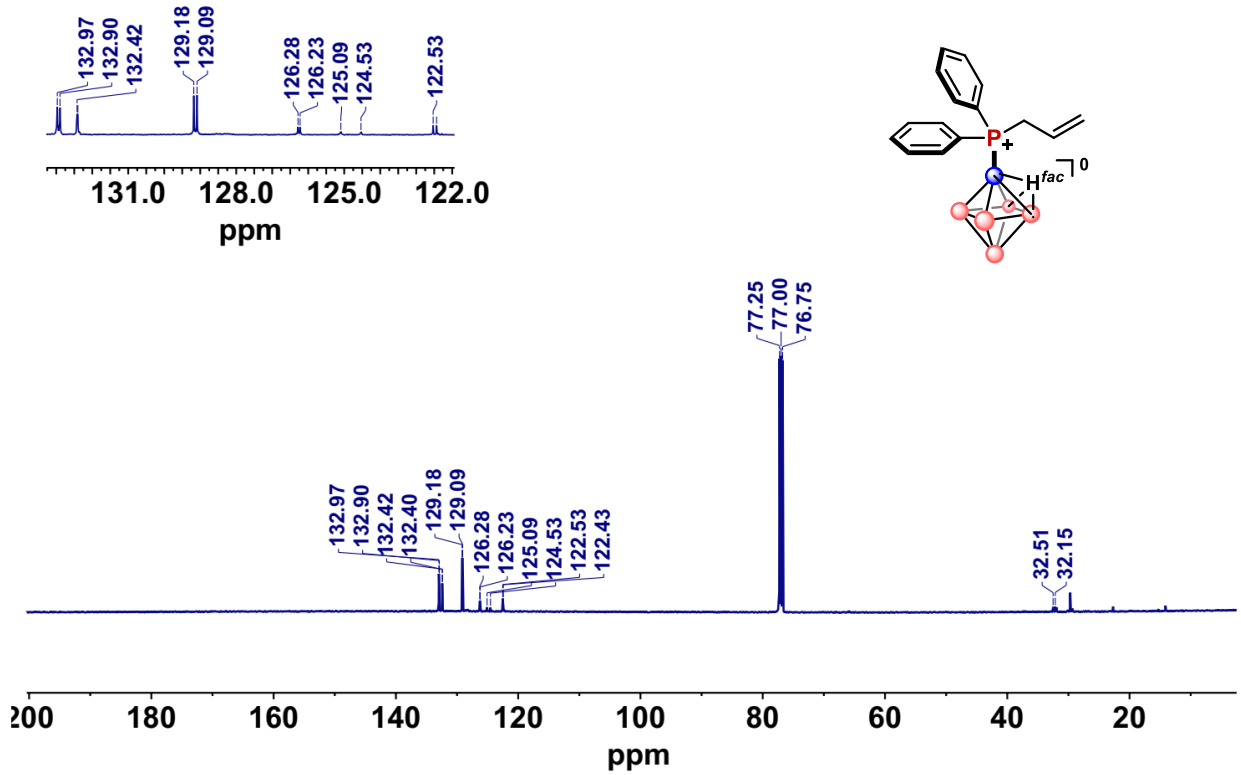



**Fig. S83.** $^{13}C\{^{1}H\}$ NMR spectrum of **40** in $CDCl_3$ at 298K.

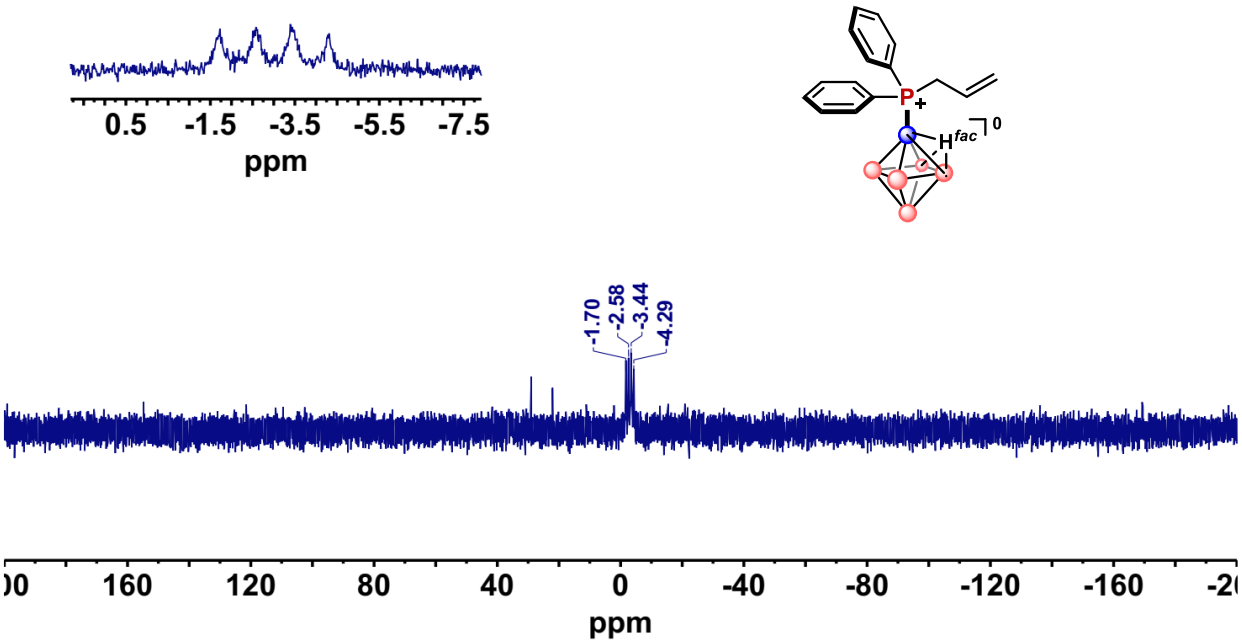



**Fig. S84.** $^{31}P\{^{1}H\}$ NMR spectrum of **40** in $CDCl_3$ at 298K.

Oct29-2018-spokoyny.11.fid
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xm-2-300-kq-83-B11-repurify

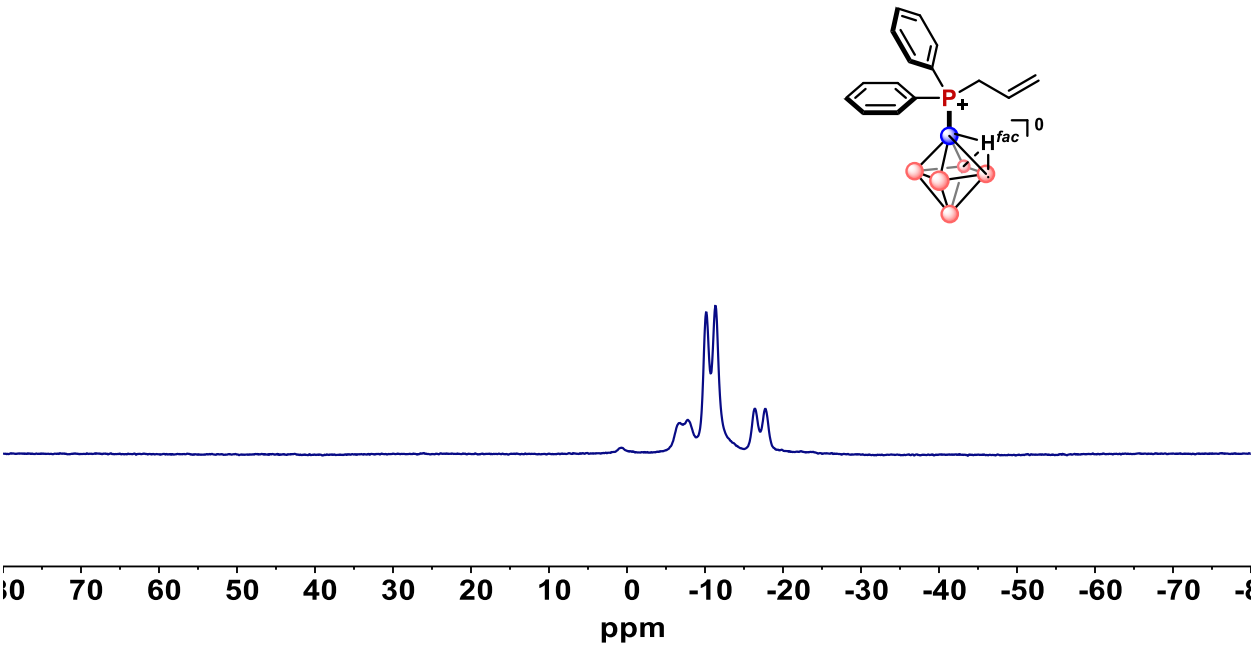


**Fig. S85.** $^{11}B$ NMR spectrum of **40** in $CDCl_3$ at 298K.

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xm-2-KQ-83-B11-decoupled

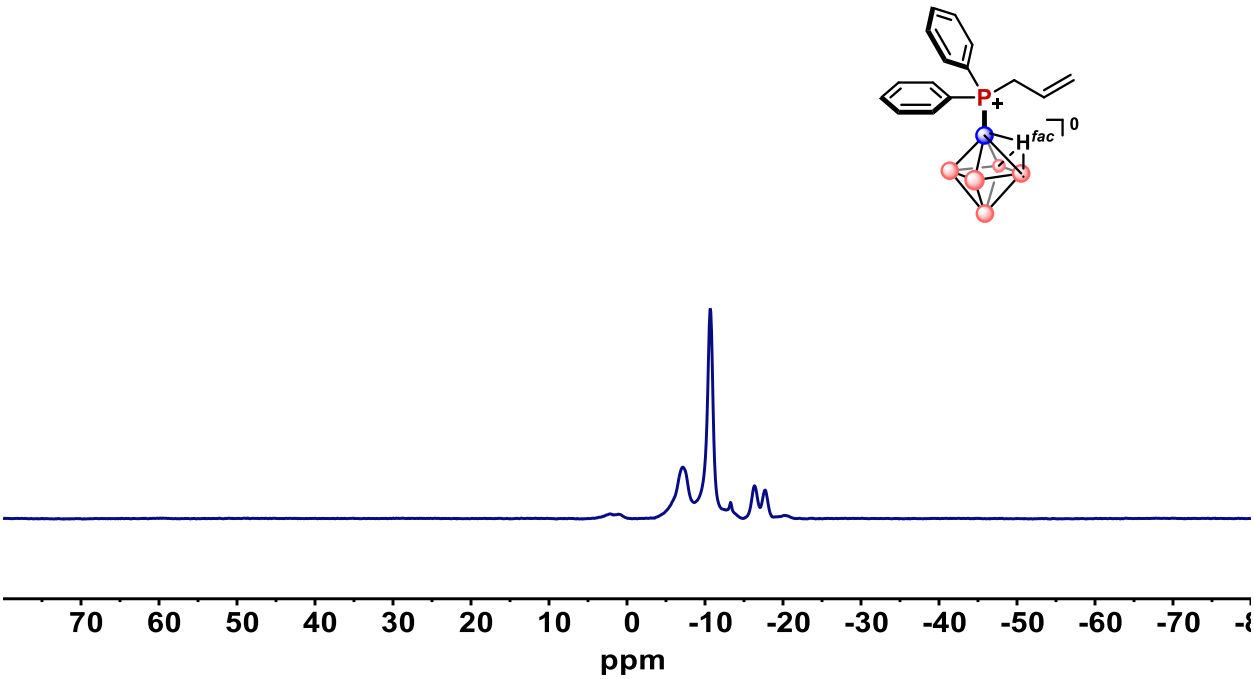



**Fig. S86.** $^{11}B\{^{1}H\}$ NMR spectrum of **40** in $CDCl_3$ at 298K.

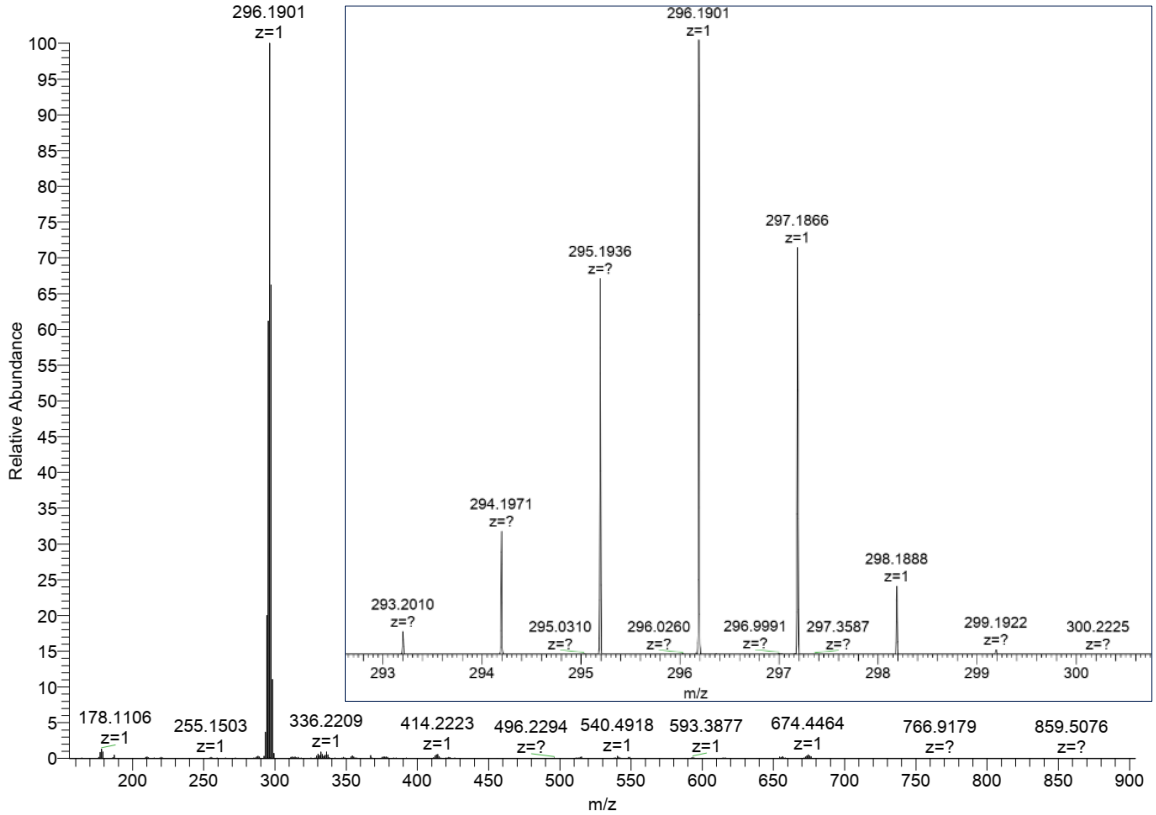



**Fig. S87.** ESI-MS(-) of [**40**-H$^+$]$^-$

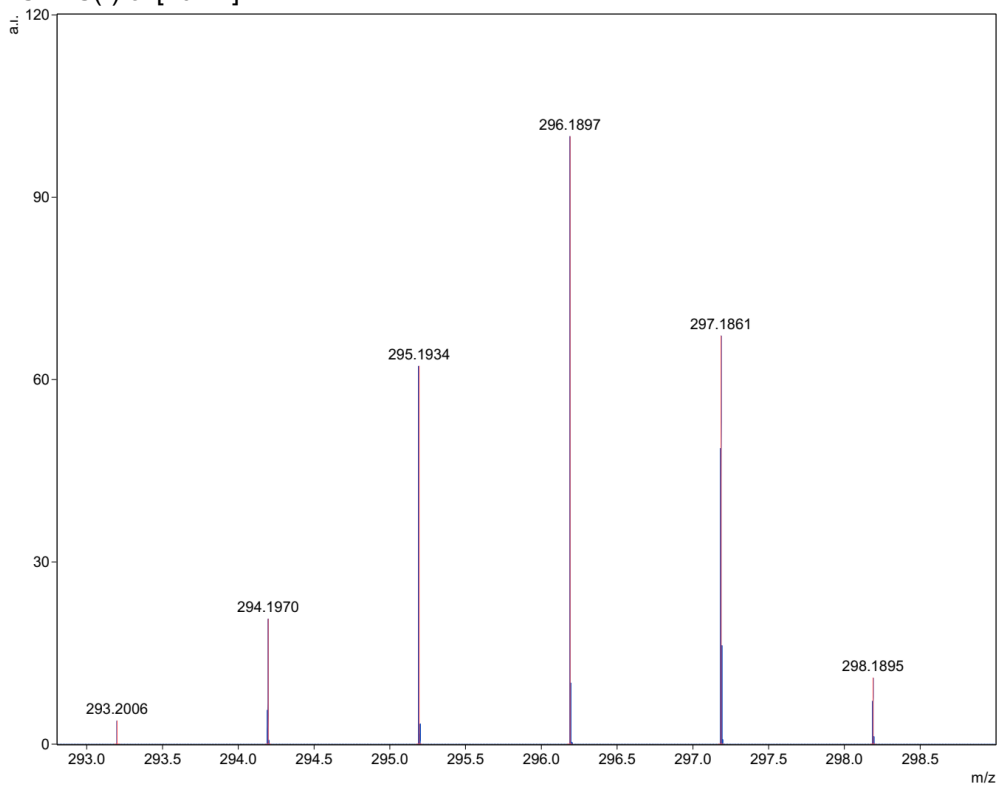
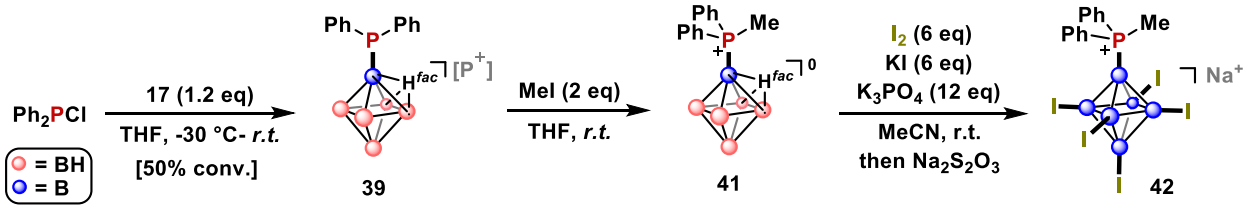



**Fig. S88.** *Simulated* ESI-MS(-) of [**40**-H$^+$]$^-$**.**

**Synthesis of B–P bond containing penta-iodo hexaborate compound 42.**




$[MePPh_3]_2[B_6H_6]$ (**17**) (159 mg, 0.24 mmol, 1.2 eq) and a stir bar were added to a 20 mL scintillation vial in the glovebox. Then THF (1 mL) was added and the vial was kept in a -30 °C freezer in the glove box for 20 min. In a separate 4 mL scintillation vial, the $Ph_2PCl$ (45 mg, 0.2 mmol) was added and THF (1 mL) was added. The THF solution of $Ph_2PCl$ was kept in the freezer in the glove box for 20 min. Then both vials were taken out the freezer and the cold THF solution of $Ph_2PCl$ was added dropwise to the stirring suspension of $[MePPh_3]_2[B_6H_6]$ ($[MePPh_3]_2[B_6H_6]$ dianion is not very soluble in THF at r.t.) and warmed up gradually in the glovebox. The bright yellow suspension slowly turned light yellow over the course of three hours. The resulting pale yellow to white suspension was filtered through a syringe filter (25 mm, 0.45 µm pore size) and concentrated under vacuum. The conversion of the reaction was determined by $^{11}B$ NMR spectra of the solution (50% conversion). The resulting light yellow powder was washed with $Et_2O$ (3 mL×3) and dried under vacuum again to obtain a yellowish powder containing both **39** and hexaborate starting material.

The obtained yellow powder from the previous step was dissolved in THF (1 mL) in the glovebox and under stirring, Methyl iodide (16 mg, 0.1 mmol) was added. The color of the solution slowly changed from light yellow to colorless and salt precipitate formed over the course of 1 hour. The solution was left stirring overnight and the solids were filtered off via syringe filter. The solution was concentrated under vacuum and pentane/$Et_2O$ (4:1 v/v, total 5 mL) was added to the mixture to precipitate out $PPh_3MeBr$ and unreacted hexaborate. The solids were filtered off using a syringe filter and the colorless solution was concentrated to give a colorless oil. The oil was extracted with pentane/$Et_2O$ (6:1 v/v, total 3.5 mL) and the extract was concentrated to obtain the compound **41** (~13 mg, contains small amount of impurities). The obtained **41** was used for per-iodination without further purification.

**$^1$H NMR ($CD_2Cl_2$, 400 MHz)** δ 7.80-7.71 (m, 4H), 7.65-7.57 (m, 2H), 7.52 (dddd, *J* = 8.4, 5.8, 2.9, 1.6 Hz, 4H), 2.10 (dd, *J* = 12.0 Hz, 3H), -4.58 (s, 1H). **$^{11}$B NMR ($CD_2Cl_2$,128 MHz)** δ -8.13 (d, *J* = 163.5 Hz, 1B), -10.94 (d, *J* = 156.2 Hz, 4B), -15.87 (d, *J* = 175.4 Hz, 1B). **$^{11}$B{$^1$H} NMR ($CD_2Cl_2$,128 MHz)** δ -8.10 (s, 1B), -10.98 (s, 4B), -15.86 (d, *J* = 175.3 Hz, 1B). **$^{31}$P{$^1$H} NMR ($CD_2Cl_2$,162 MHz)** δ -7.86 (multiplet, *J* [$^{31}$P-$^{11}$B(I=3/2)] = 171 Hz).

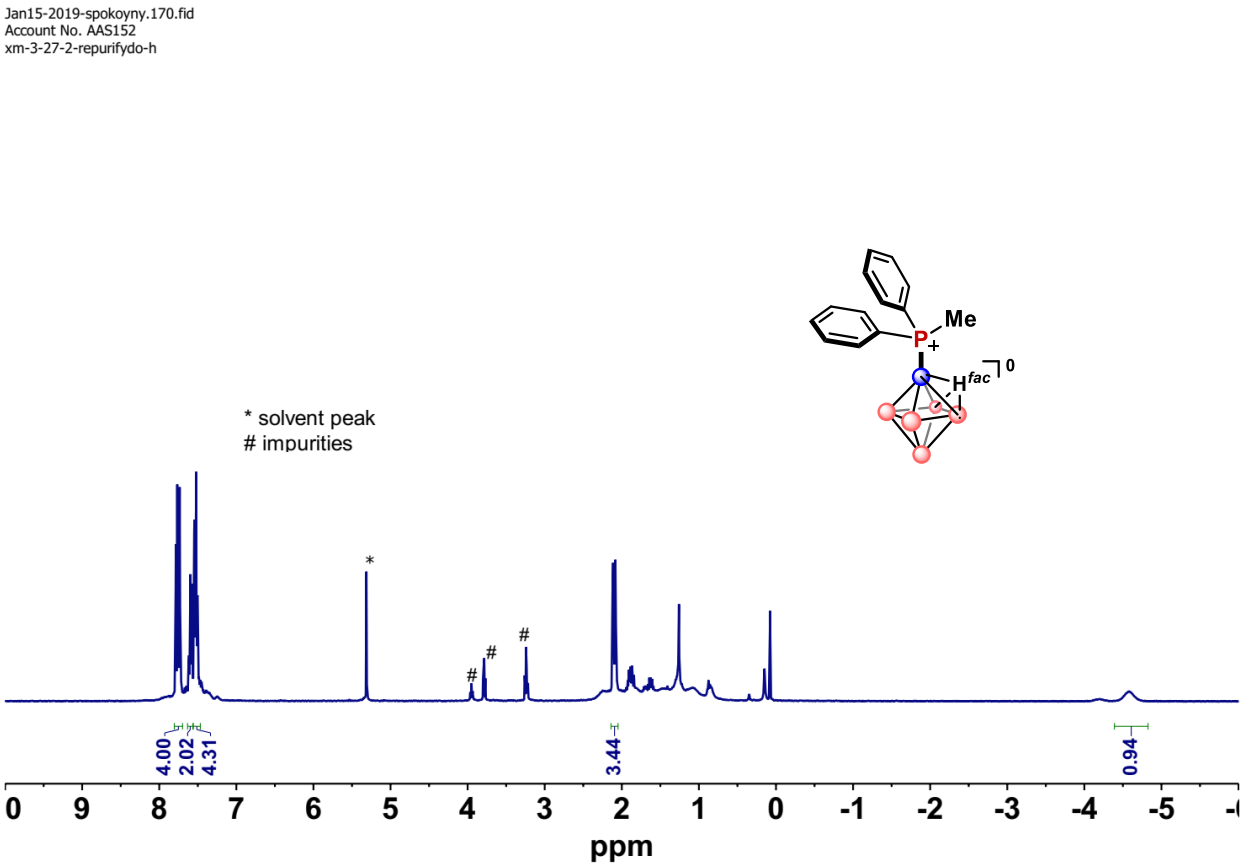



**Fig. S89.** $^{1}H$ NMR spectrum of **41** in $CD_2Cl_2$ at 298K.

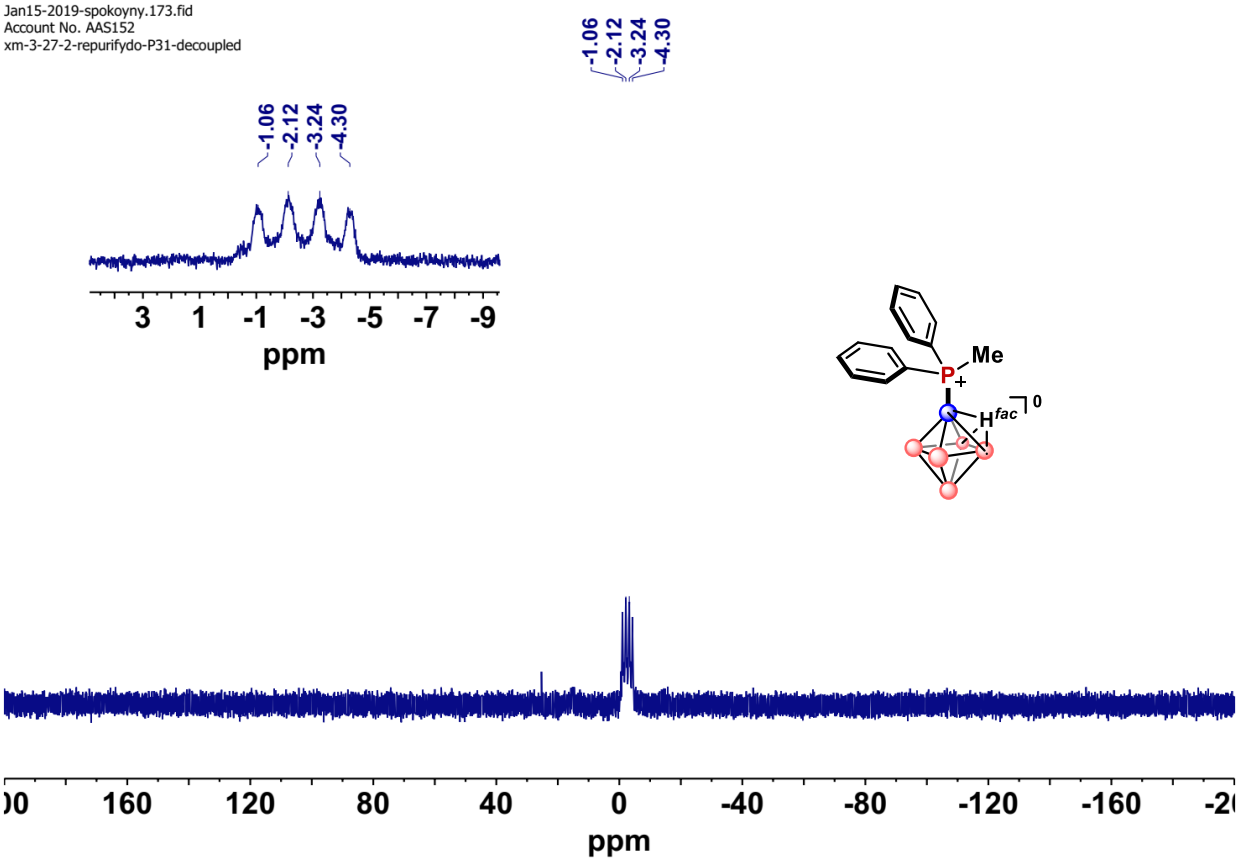



**Fig. S90.** $^{31}P\{^{1}H\}$ NMR spectrum of **41** in $CD_2Cl_2$ at 298K.

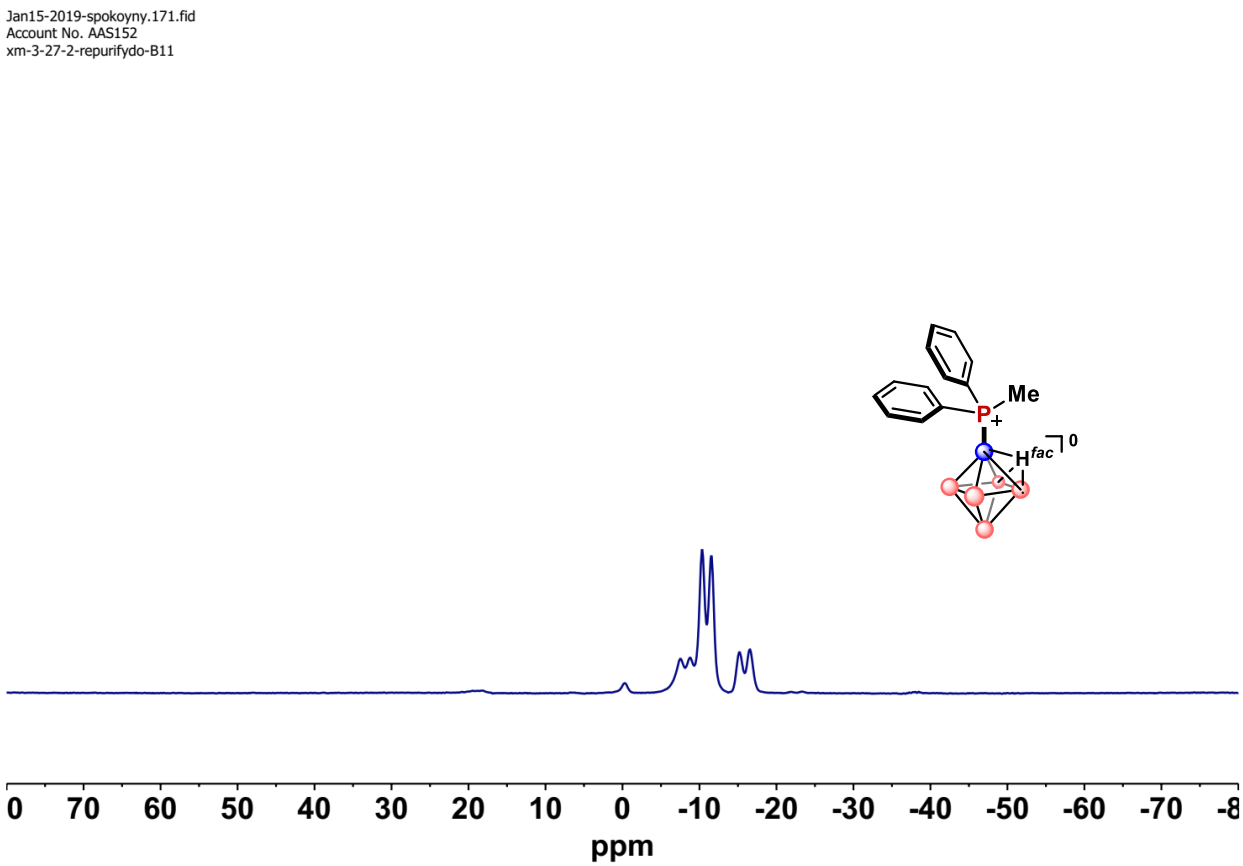



**Fig. S91.** $^{11}B$ NMR spectrum of **41** in $CD_2Cl_2$ at 298K.

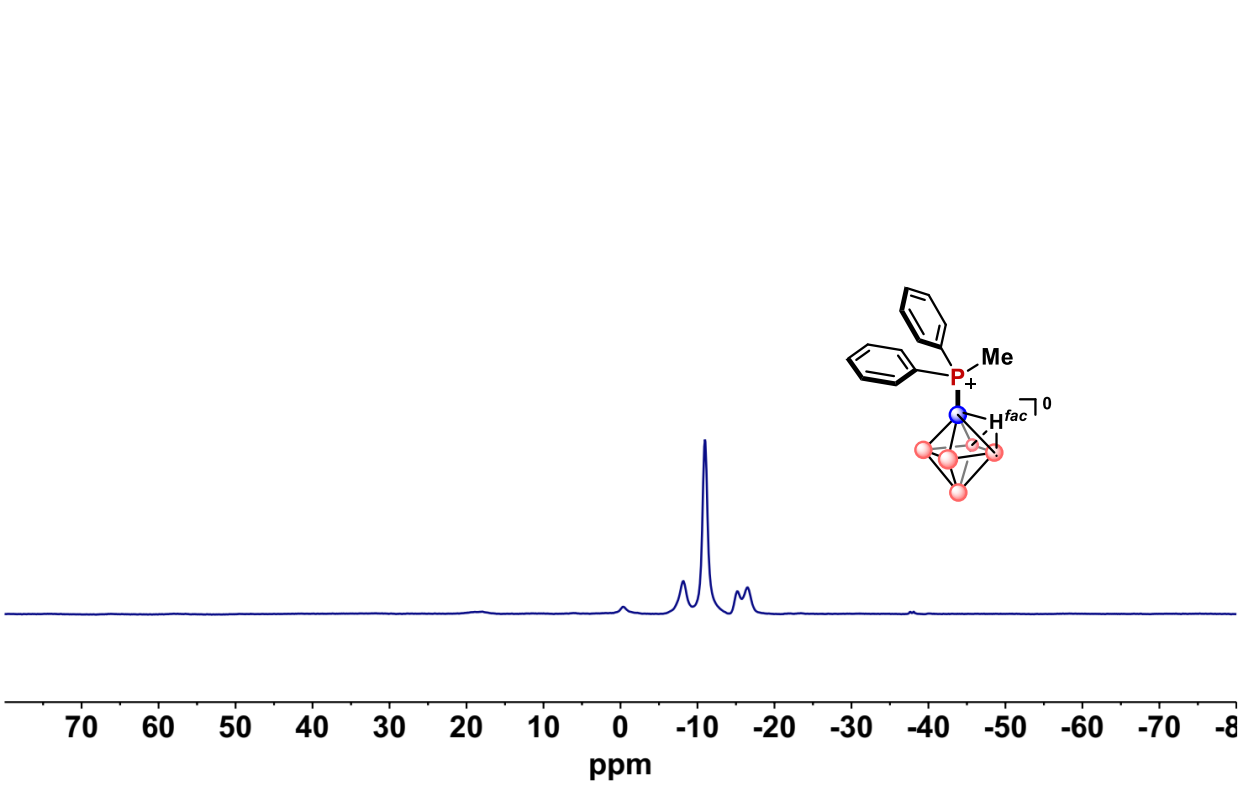



**Fig. S92.** $^{11}B\{^1H\}$ NMR spectrum of **41** in $CD_2Cl_2$ at 298K.

In the glovebox, **41** (13 mg, ~0.05 mmol) obtained from the previous step was dissolved in MeCN (1.0 mL) in a 20 mL scintillation vial, KI (51 mg, 0.3 mmol, 6 eq), $K_3PO_4$ (127 mg, 0.6 mmol, 12 eq) and a stir bar were added to the vial. Under stirring, $I_2$ (76 mg, 0.3 mmol, 6 eq) was added at room temperature and the mixture turned dark red. The mixture was kept stirring overnight and then transferred out of the glovebox. Saturated $Na_2S_2O_3$ solution was added to quench residual $I_2$. The resulting colorless mixture was extracted with $Et_2O$ (3 mL×3), Dried over $Na_2SO_4$ and concentrated under vacuum to give 42 as white powder (19 mg). The resulting white powder was transferred to a 20 mL scintillation vial, dissolved in a minimum amount of DCM (~0.5 mL), layered with $Et_2O$ (3 mL) and sealed with a screw cap and stored at ambient temperature. Single crystals of **42** grown over the course of two days were suitable for single crystal X-ray diffraction studies.

**$^1$H NMR ($CD_2Cl_2$, 400 MHz)**: δ 7.82-7.68 (m, 4H), 7.62-7.49 (m, 6H), 2.20 (d, *J* = 12.2 Hz, 2.5H), 2.14 (d, *J* = 12.0 Hz, 0.5H). **$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 162 MHz)** δ 1.50 – -3.75 (broad peak). **$^{11}B\{^1H\}$ NMR ($CD_2Cl_2$, 128 MHz)** δ -13.85 (s, 1B), -21.66 (s, 1B), -23.27 (s, 4B). **$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$ ,101 MHz)** δ 132.89 (d, *J* = 11.0 Hz), 132.29 (d, *J* = 2.7 Hz), 129.09 (d, *J* = 11.9 Hz), 125.36 (s, 0H), 125.00 (d, *J* = 75.5 Hz), 36.42 (d, *J* = 50.0 Hz)

ESI-MS(-) for $[M]^-$: calculated: 899.6573. measured: 899.6580

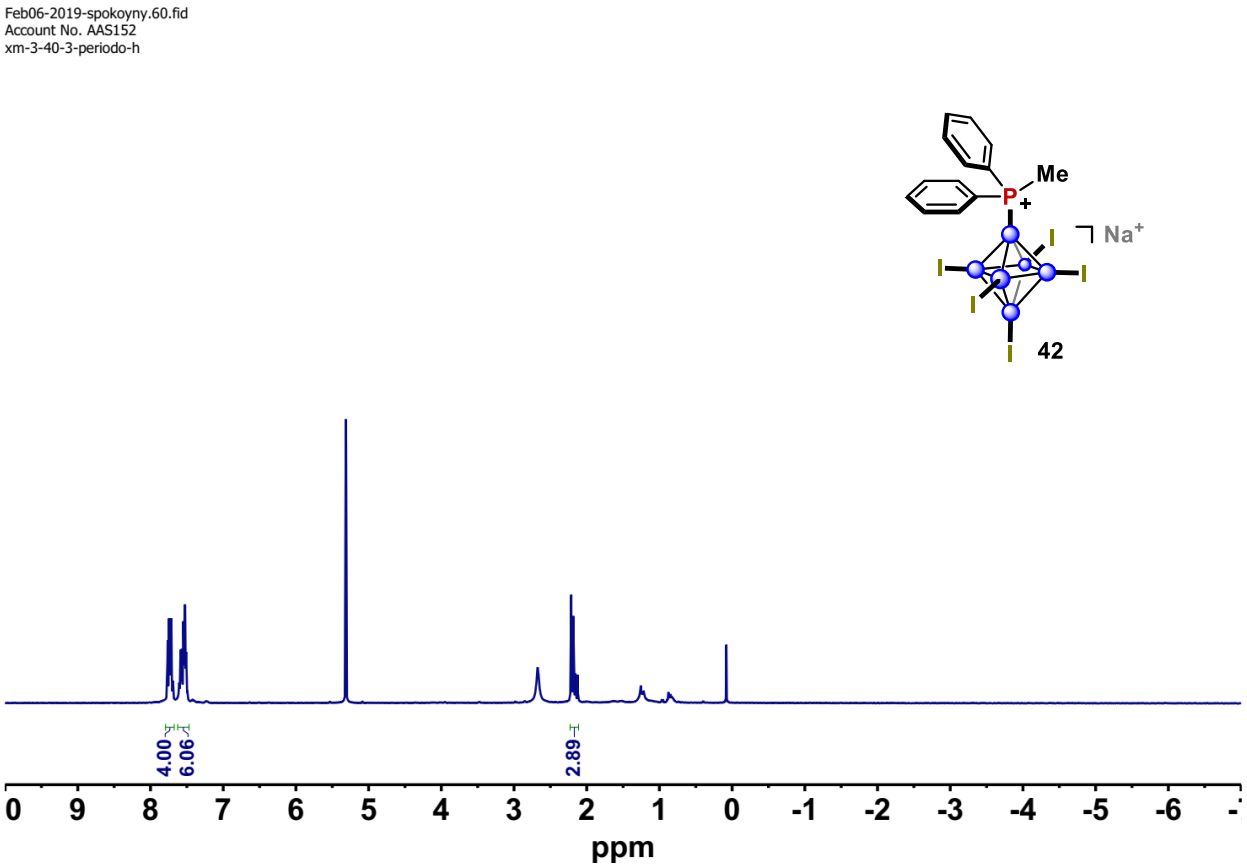



**Fig. S93.** $^{1}$H NMR spectrum of **42** in $CD_2Cl_2$ at 298K.

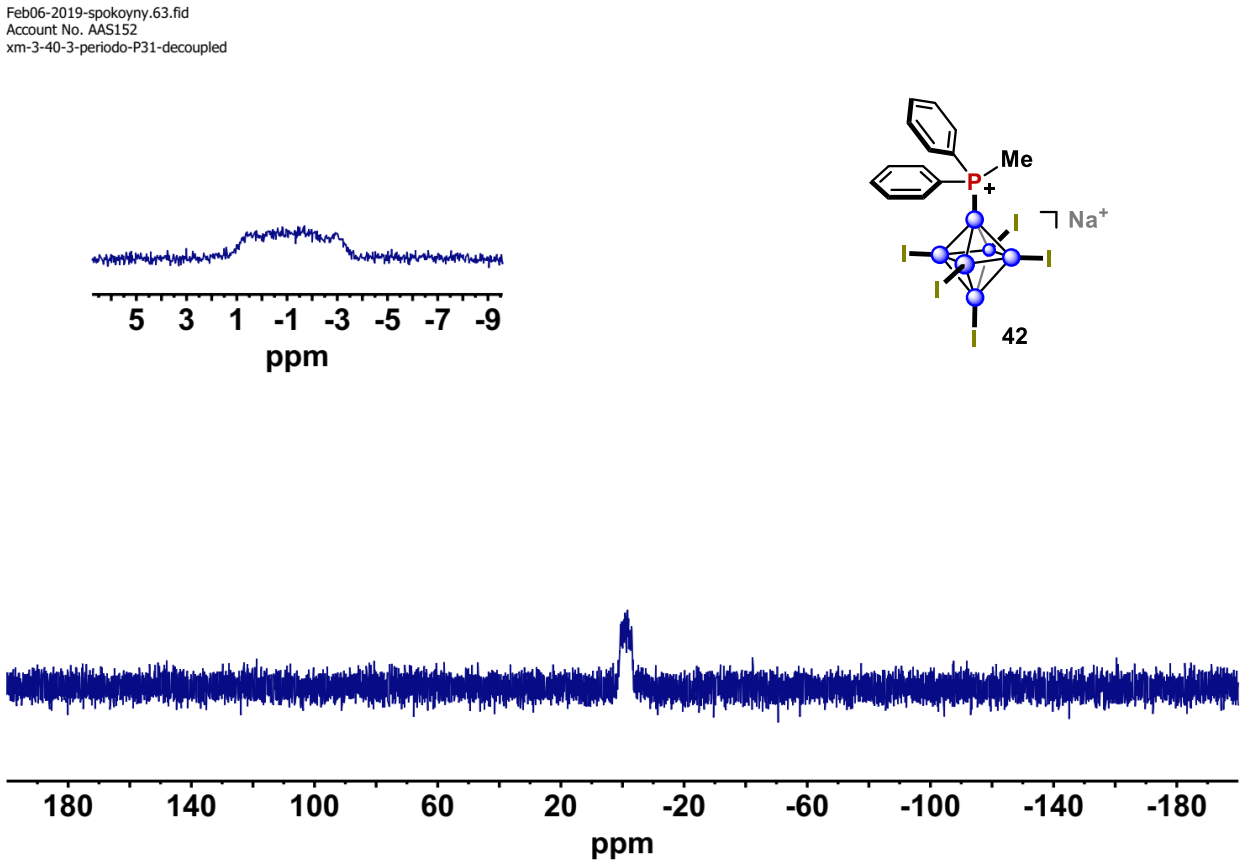



**Fig. S94.** $^{31}P\{^{1}H\}$ NMR spectrum of **42** in $CD_2Cl_2$ at 298K.

XM-3-40-3_purified_CD2Cl2.4.fid

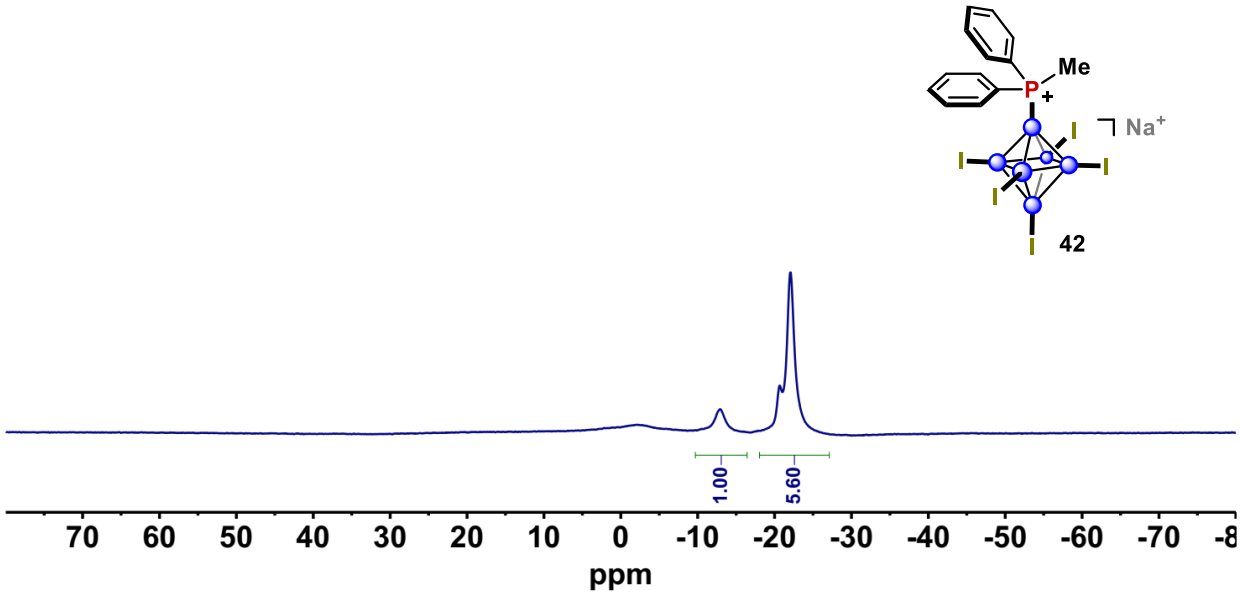



**Fig. S95.** $^{11}B\{^{1}H\}$ NMR spectrum of **42** in $CD_2Cl_2$ at 298K.

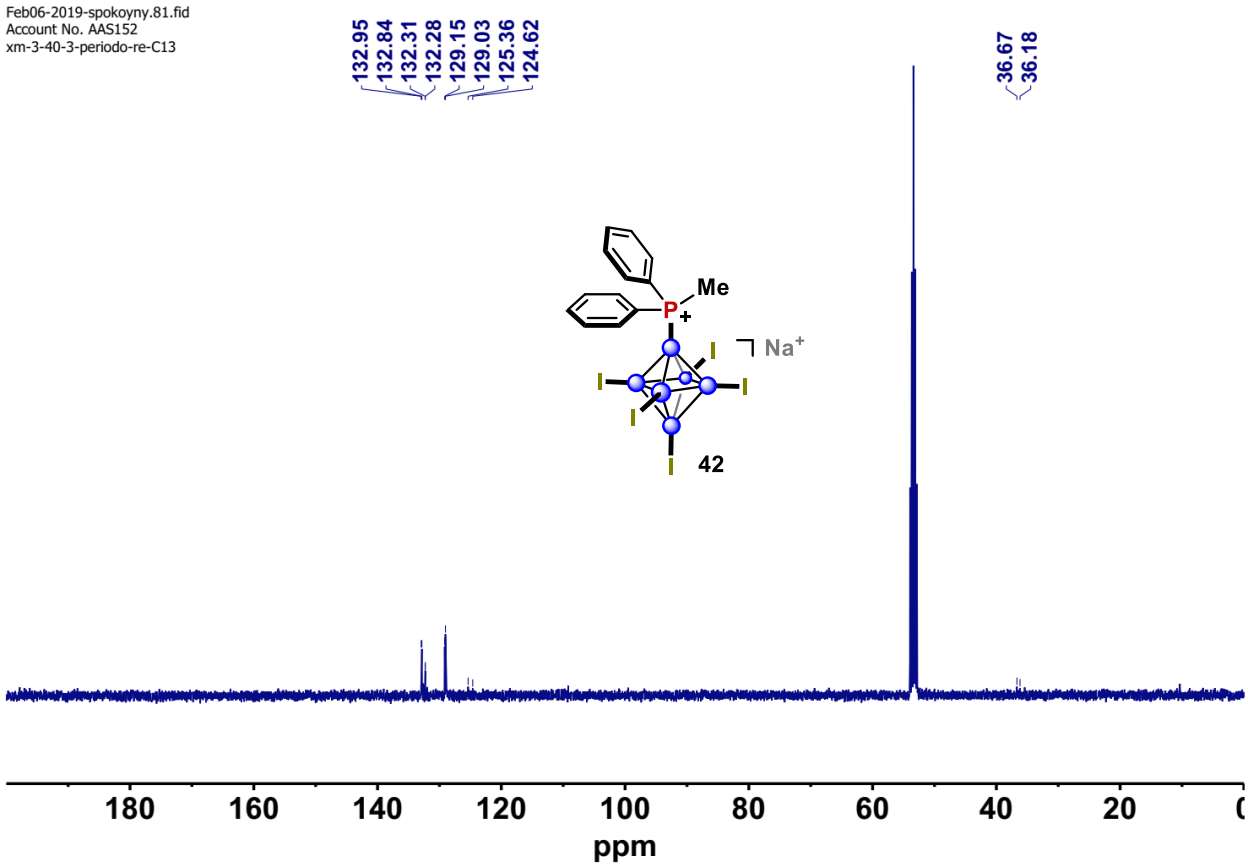



**Fig. S96.** $^{13}C\{^{1}H\}$ NMR spectrum of **42** in $CD_2Cl_2$ at 298K.

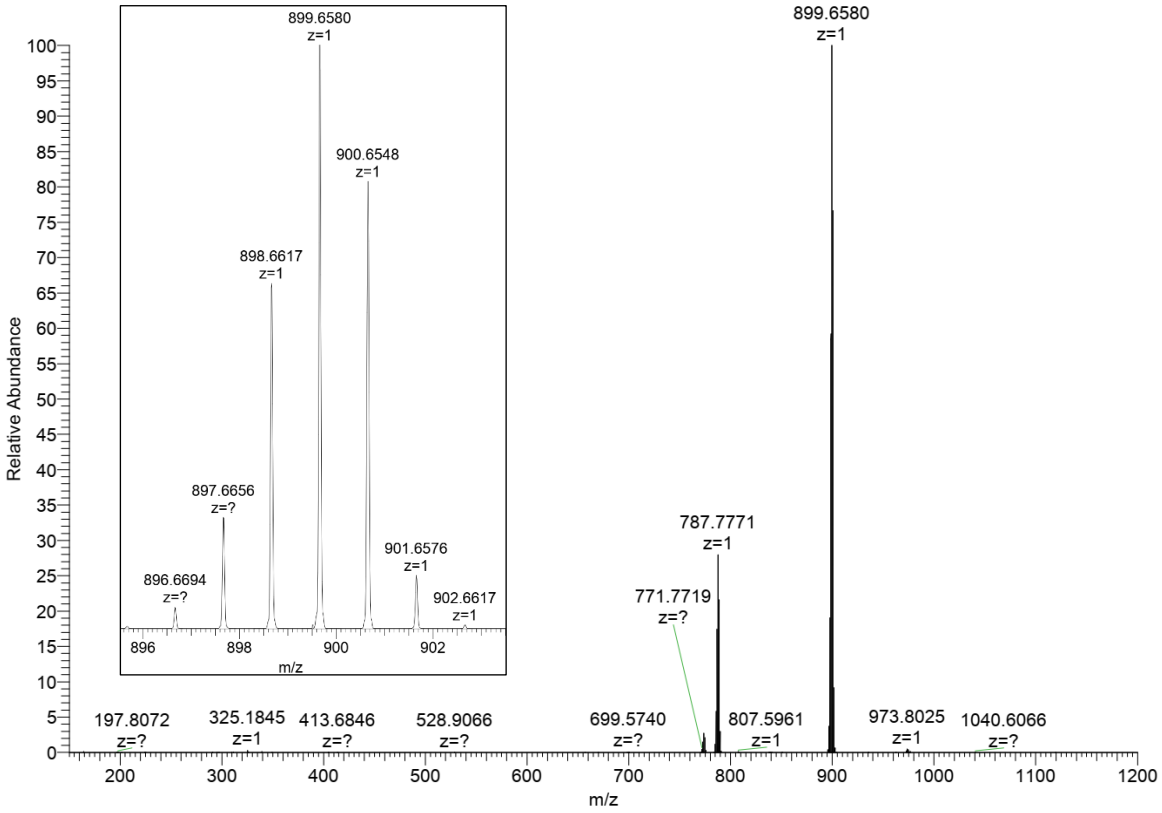



**Fig. S97.** ESI-MS(-) of [**42**]$^-$

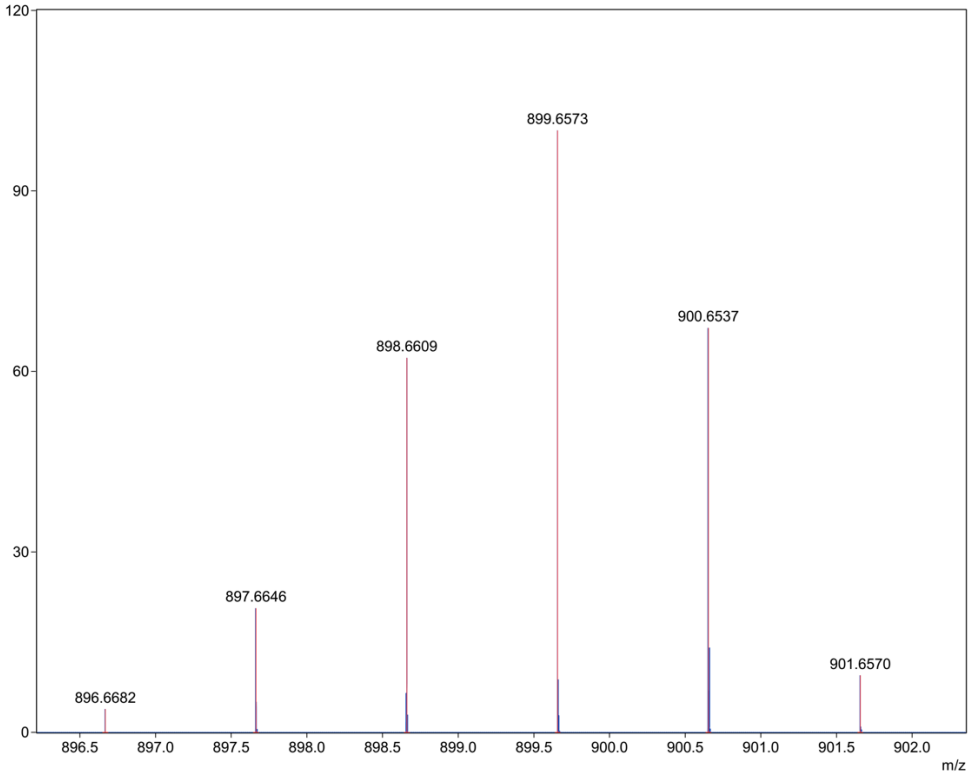
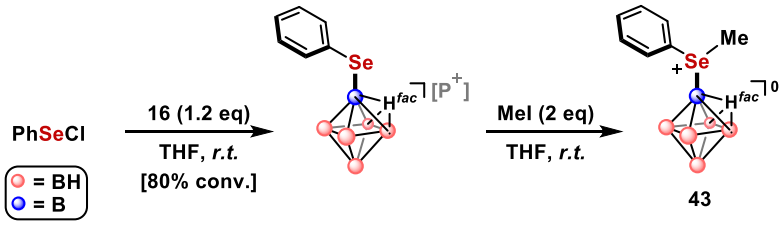



**Fig. S98.** *Simulated* ESI-MS(-) of [**42**]$^-$**.**

**Synthesis of B–Se bond containing compound 43.**




$[MePPh_3]_2[B_6H_6]$ (**17**) (158 mg, 0.24 mmol, 1.2 eq) and a stir bar were added to a 20 mL scintillation vial in the glovebox. Then THF (1 mL) was added. In a separate 4 mL scintillation vial, the PhSeCl (39 mg, 0.2 mmol) was added and THF (1 mL) was added to dissolve the dark red crystals. The THF solution of PhSeCl was added dropwise to the stirring suspension of $[MePPh_3]_2[B_6H_6]$ ($[MePPh_3]_2[B_6H_6]$ dianion is not very soluble in THF at r.t.). The bright yellow suspension slowly turned colorless over the course of three hours. The resulting white suspension was filtered through a syringe filter (25 mm, 0.45 μm pore size) and concentrated *in vacuo*. The conversion of the reaction was determined by $^{11}B$ NMR spectroscopy of the solution (78% conversion). The resulting pale yellow to white solid was washed with $Et_2O$ (3 mL×3) and dried under vacuum. Then the solid was dissolved in THF (1 mL) in the glovebox and under stirring, methyl iodide (29 mg, 0.2 mmol) was added. The color of the solution quickly changed from light yellow to colorless and salt precipitate formed over the course of 30 min. The solution was left stirring overnight and the solids were filtered off via syringe filter. The solution was concentrated under vacuum and pentane/$Et_2O$ (5:1 v/v, total 5 mL) was added to the mixture to precipitate out $PPh_3MeBr$ and unreacted hexaborate. The solids were filtered off using a syringe filter and the colorless solution was concentrated to give a colorless oil. The oil was extracted with pentane/$Et_2O$ (7:1 v/v, total 4.0 mL) and the extract was concentrated to obtain the compound **43** (16 mg, 33% yield over two steps).

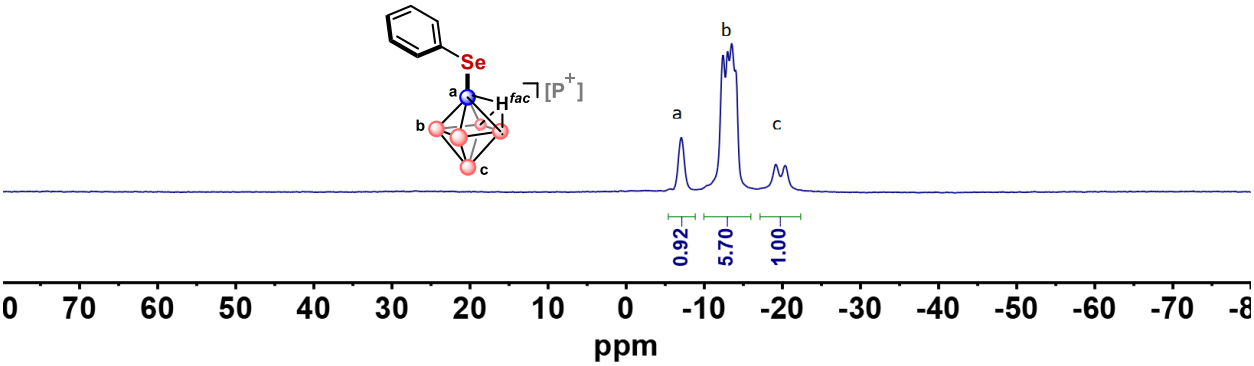



**Fig. S99.** $^{11}B$ NMR of Reaction mixture after substitution step using PhSeCl as electrophile.

**$^1$H NMR ($CDCl_3$, 400 MHz)** δ 7.91-7.81 (m, 2H), 7.61-7.45 (m, 3H), 2.72 (s, 3H), -4.57 (s, 1H, facial proton). **$^{11}$B NMR ($CDCl_3$, 128 MHz)** δ -10.06 (s, 1B), -12.39 (d, *J* = 160.1 Hz, 4B), -15.42 (d, *J* = 166.7 Hz, 1B). **$^{11}$B{$^1$H} NMR ($CDCl_3$, 128 MHz)** δ -10.05 (s, 1B), -12.40 (s, 4B), -15.40 (s, 1B). **$^{13}$C NMR ($CDCl_3$, 101 MHz, $CDCl_3$)** δ 131.66, 130.98, 130.48, 127.18, 25.98. **$^{77}$Se NMR ($CDCl_3$, 95 MHz,)** δ 205.31 (s). ESI-MS(-) for $[M-H]^-$: calculated: 242.0777. measured: 242.0777

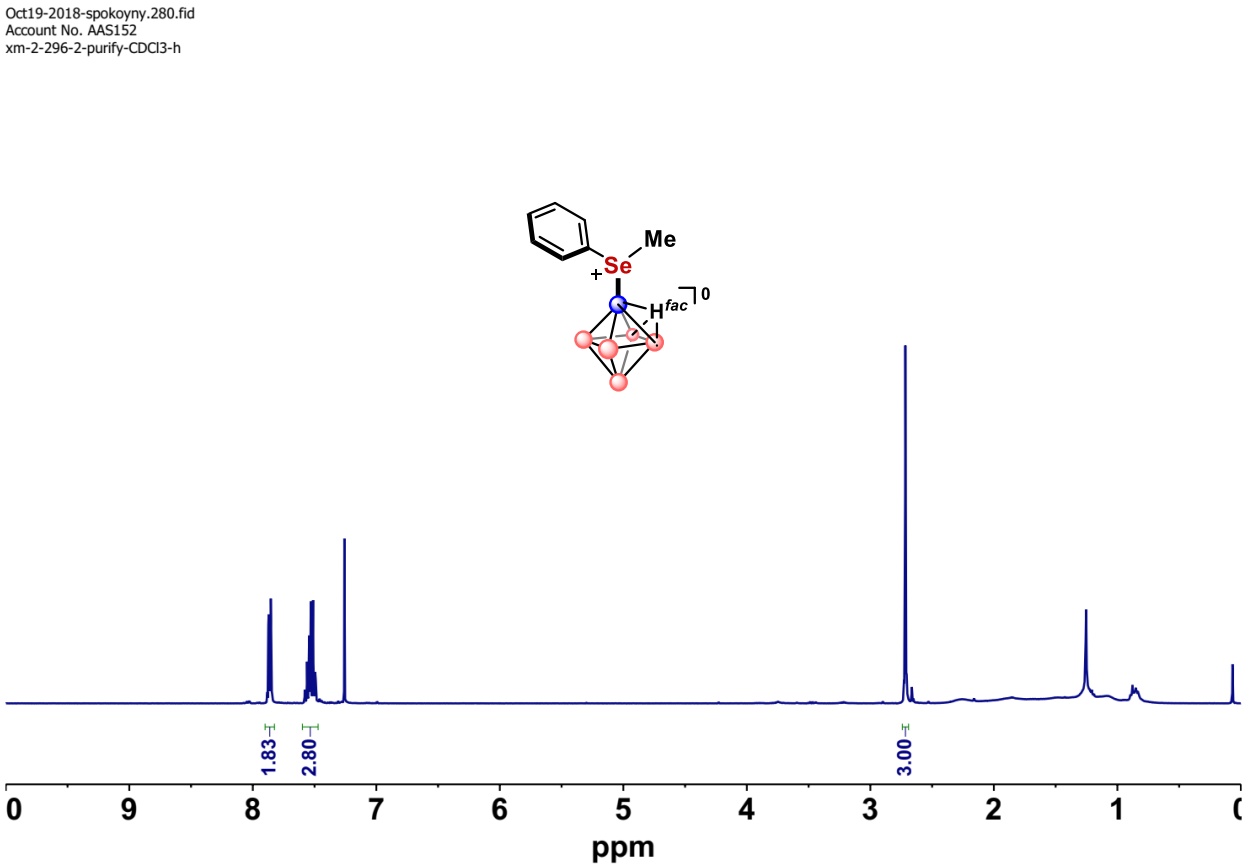



**Fig. S100.** $^{1}$H NMR spectrum of **43** in $CDCl_3$ at 298K.

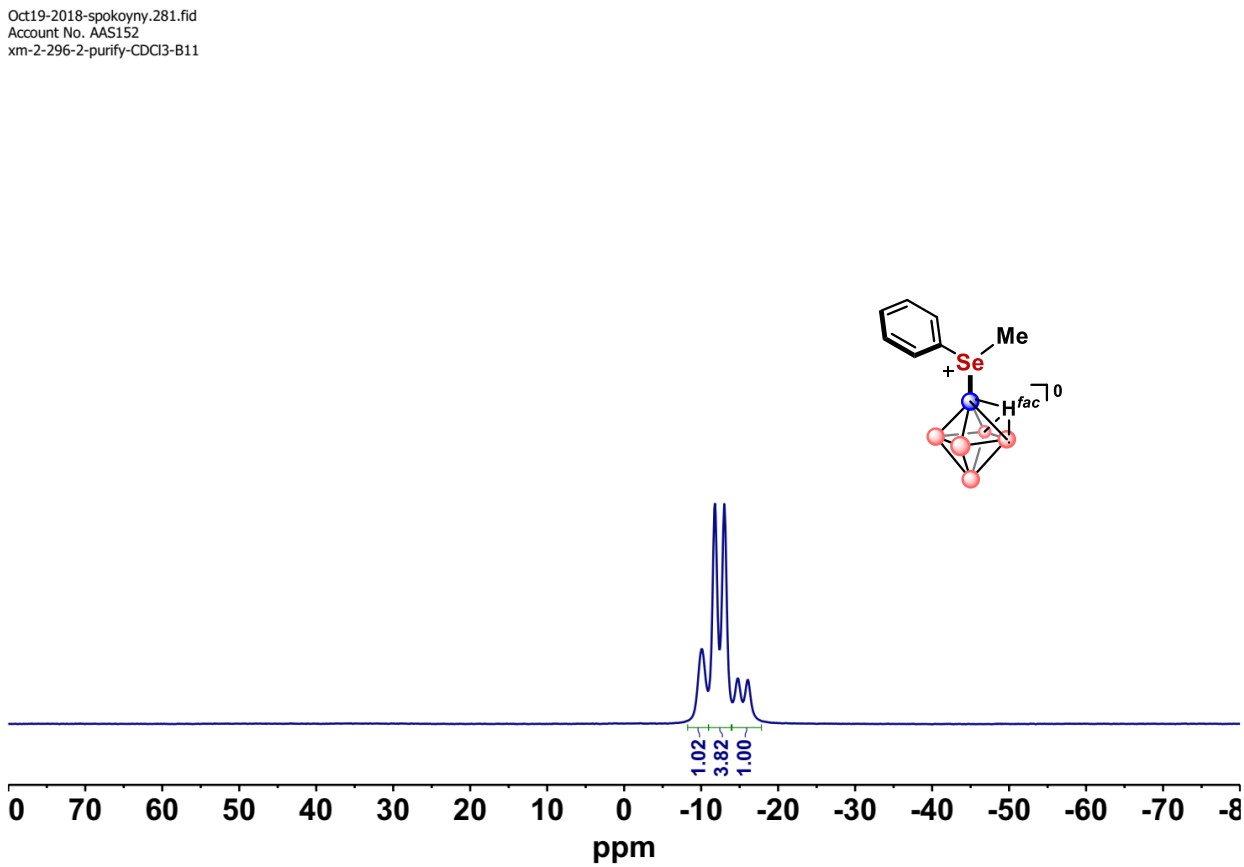



**Fig. S101.** $^{11}B$ NMR spectrum of **43** in $CDCl_3$ at 298K.

Oct19-2018-spokoyny.282.fid
Account No. AAS152
xm-2-296-2-purify-CDCl3-B11-decoupled

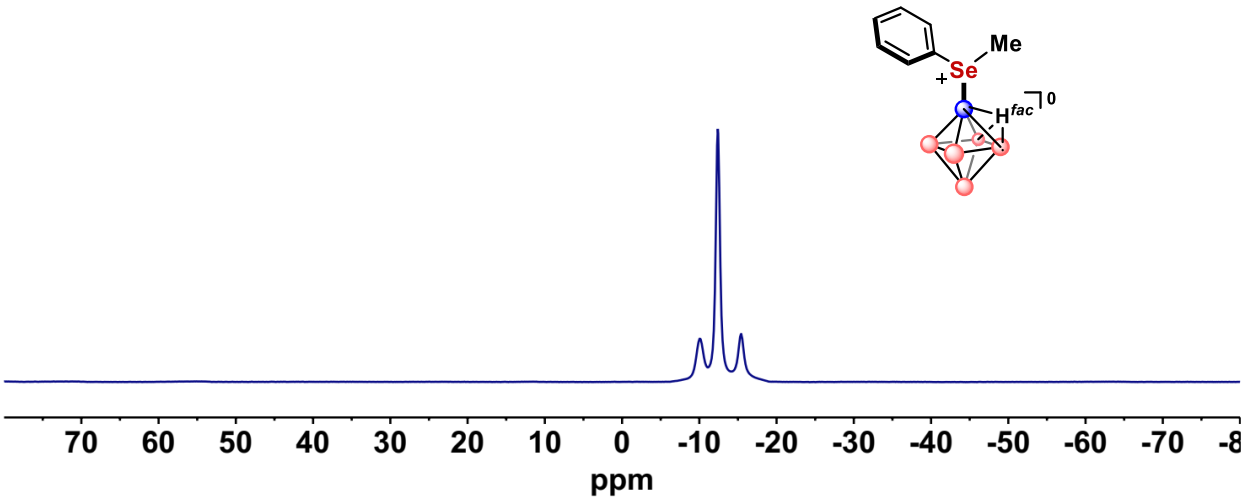



**Fig. S102.** $^{11}B\{^{1}H\}$ NMR spectrum of **43** in $CDCl_3$ at 298K.

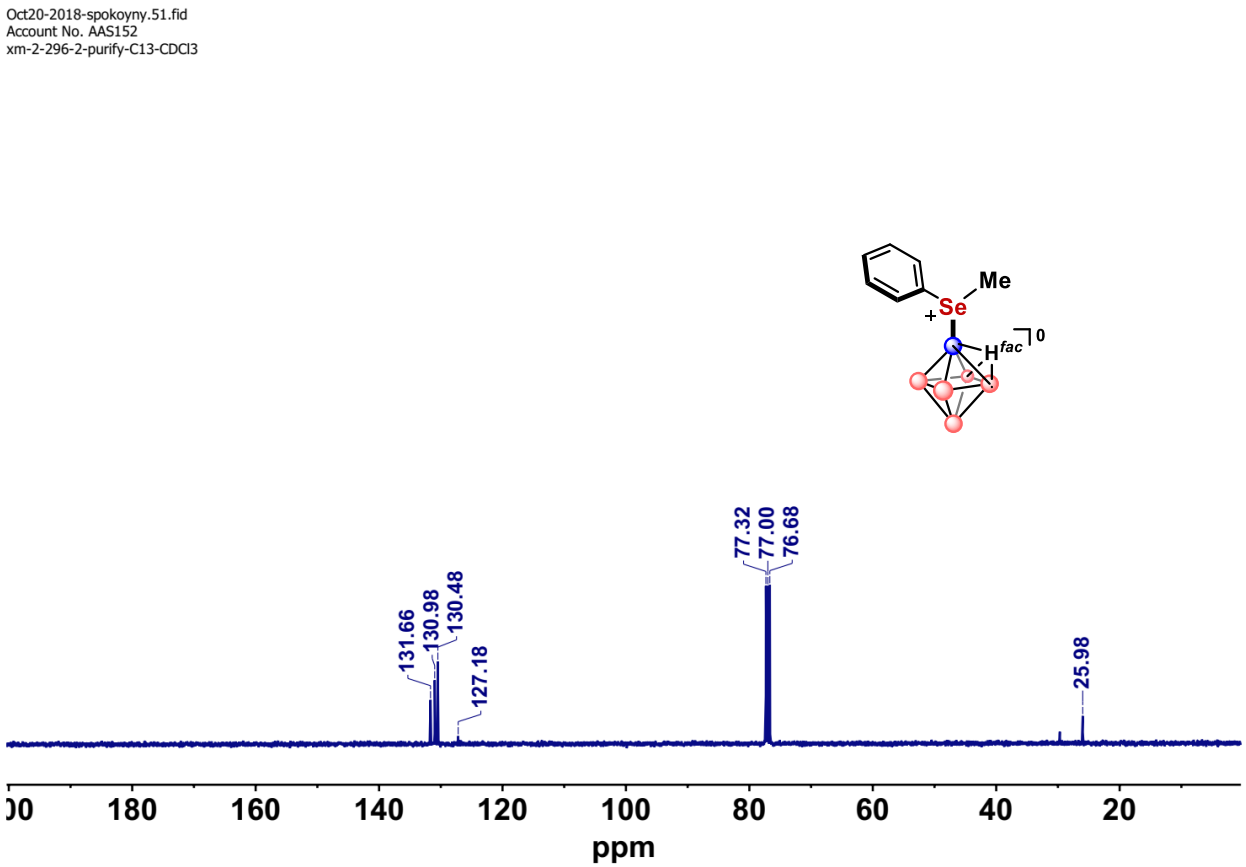



**Fig. S103.** $^{13}C\{^{1}H\}$ NMR spectrum of **43** in $CDCl_3$ at 298K.

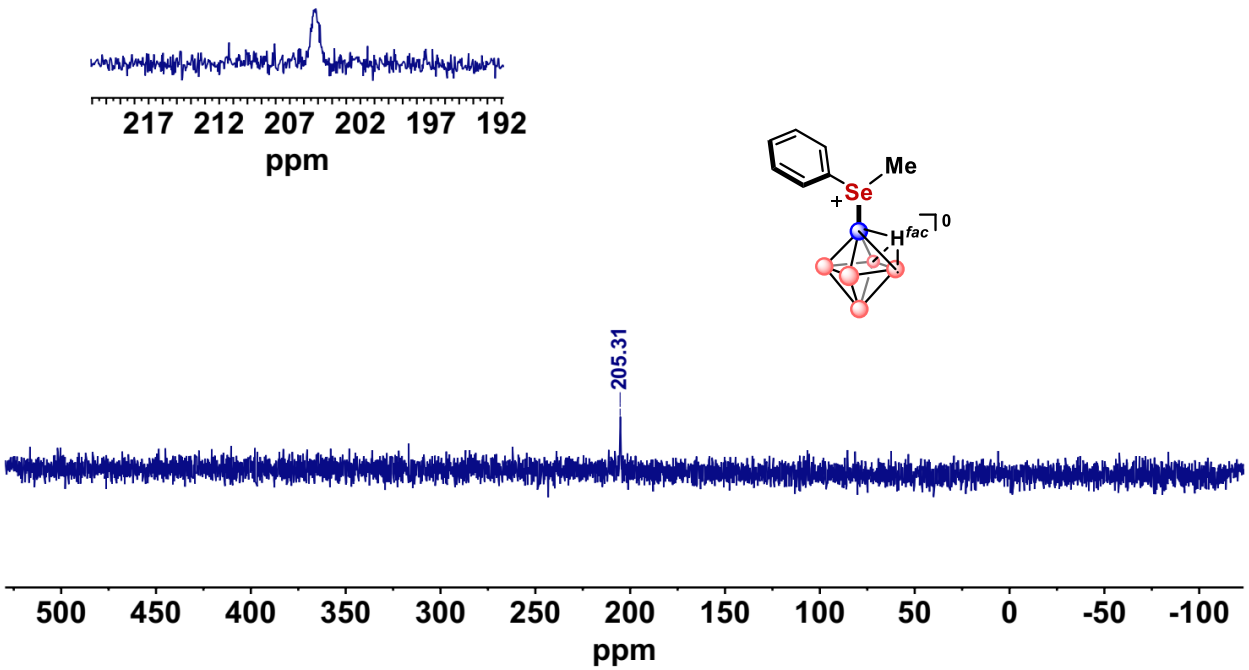



**Fig. S104.** $^{77}$Se NMR spectrum of **43** in $CDCl_3$ at 298K.

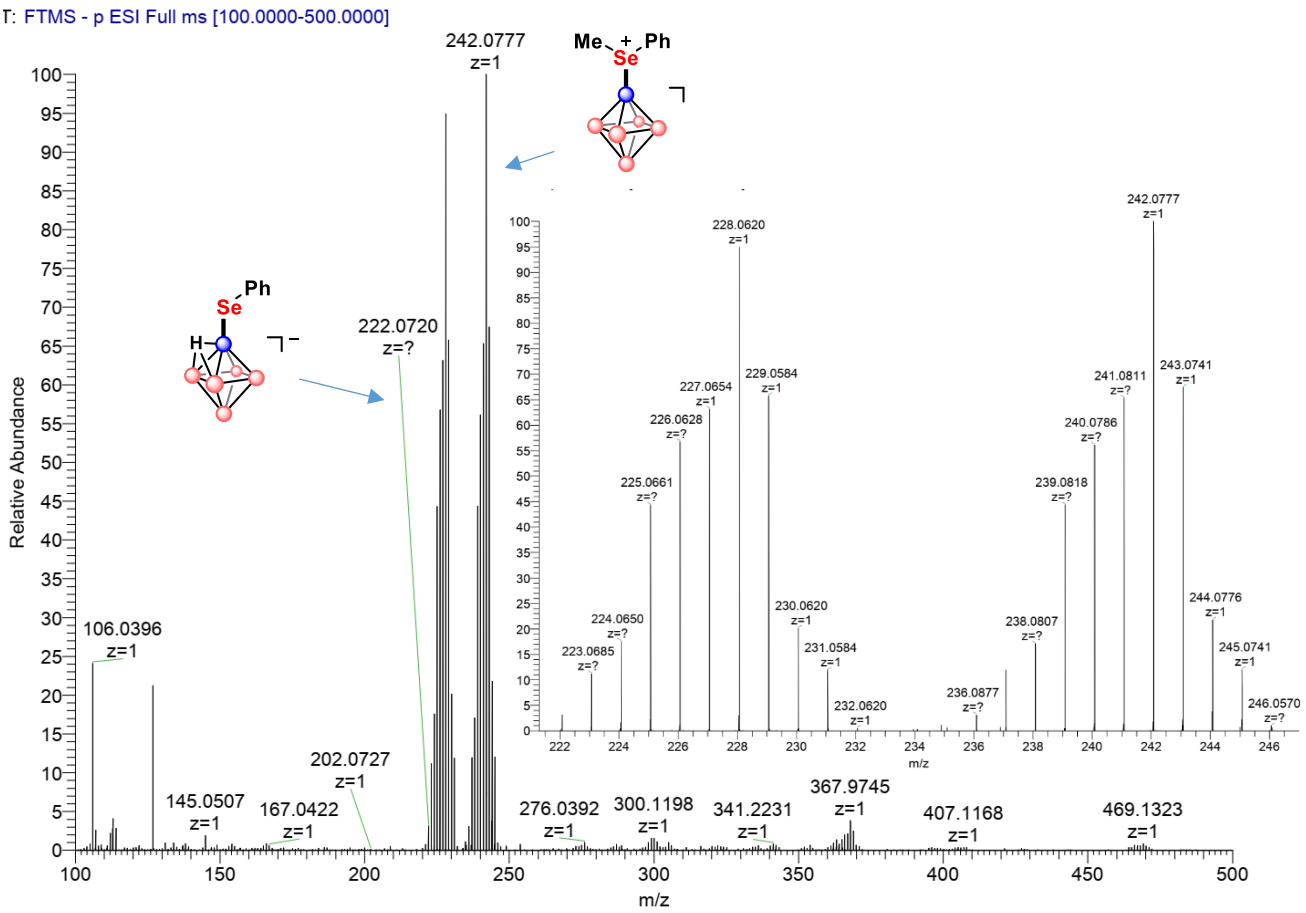



**Fig. S105.** ESI-MS(-) of [**43**-Me]$^-$ and [**43**-H]$^-$.

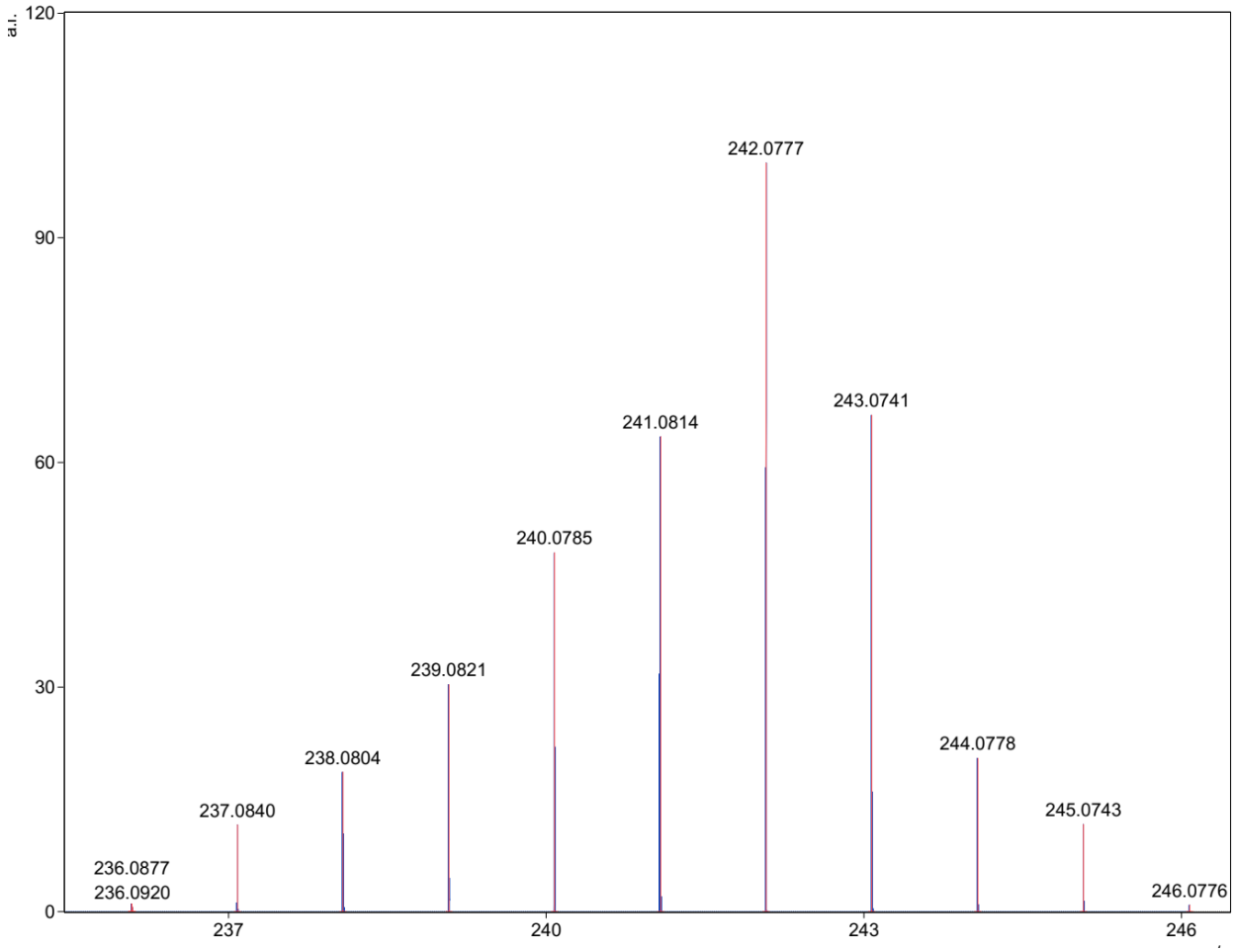



**Fig. S106.** *Simulated* ESI-MS(-) of [**43**-H]$^-$.

## 11.Crystallographic Characterization of 9, 13, 17 and 42.

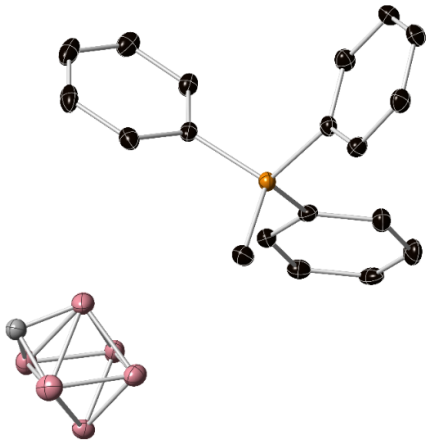


**Fig. S107.** Solid-state structure of **9**.

Solid structure of **9** with thermal ellipsoid rendered at the 50% probability level, hydrogen atoms (except the facial proton in grey) are omitted for clarity.

**Table S5**. Crystallographic data and structure refinement for **9**.

| | |
|---|---|
| Identification code | JCA-IV-048-B |
| Empirical formula | C19 H25 B6 P |
| Formula weight | 349.22 |
| Temperature | 100.0 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 21.616(7) Å α = 90°. |
| | b = 13.391(5) Å β = 109.711(11)°. |
| | c = 14.997(6) Å γ = 90°. |
| Volume | 4087(3) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.135 $Mg/m^3$ |
| Absorption coefficient | 0.134 $mm^{-1}$ |
| F(000) | 1472 |
| Crystal size | 0.3 × 0.3 × 0.05 $mm^3$ |
| Theta range for data collection | 1.001 to 26.485°. |
| Index ranges | -27≤h≤21, -16≤k≤16, -18≤l≤18 |
| Reflections collected | 27419 |
| Independent reflections | 8419 [*R*(int) = 0.0436] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7454 and 0.6990 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 8419 / 0 / 527 |
| Goodness-of-fit on $F^2$ | 0.985 |
| Final R indices [I > 2σ(I)] | R1 = 0.0428, wR2 = 0.0936 |
| R indices (all data) | R1 = 0.0676, wR2 = 0.1066 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.354 and -0.289 $e.Å^{-3}$ |

**Table S6**. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 8747(1) | 8235(1) | 3829(1) | 16(1) |
| P(1') | 6249(1) | 11853(1) | 197(1) | 16(1) |
| C(1) | 9524(1) | 8784(2) | 3962(1) | 23(1) |
| C(1') | 5510(1) | 11292(1) | -567(1) | 22(1) |
| C(2) | 8860(1) | 6927(1) | 4046(1) | 17(1) |
| C(2') | 6109(1) | 13147(1) | 370(1) | 17(1) |
| C(3) | 9095(1) | 6565(1) | 4970(1) | 20(1) |
| C(3') | 6311(1) | 13569(2) | 1268(1) | 24(1) |
| C(4) | 9247(1) | 5565(1) | 5129(1) | 22(1) |
| C(4') | 6215(1) | 14580(2) | 1368(1) | 28(1) |
| C(5) | 9170(1) | 4930(1) | 4373(1) | 24(1) |
| C(5') | 5925(1) | 15165(2) | 581(1) | 27(1) |
| C(6) | 8940(1) | 5285(2) | 3456(1) | 27(1) |
| C(6') | 5719(1) | 14746(1) | -316(1) | 24(1) |
| C(7) | 8782(1) | 6281(1) | 3285(1) | 23(1) |
| C(7') | 5811(1) | 13739(1) | -428(1) | 22(1) |
| C(8) | 8187(1) | 8428(1) | 2652(1) | 18(1) |
| C(8') | 6872(1) | 11773(1) | -341(1) | 16(1) |
| C(9) | 7525(1) | 8192(1) | 2452(1) | 22(1) |
| C(9') | 7344(1) | 12516(1) | -178(1) | 24(1) |
| C(10) | 7082(1) | 8386(2) | 1564(1) | 24(1) |
| C(10') | 7841(1) | 12432(2) | -559(1) | 25(1) |
| C(11) | 7289(1) | 8826(2) | 878(1) | 25(1) |
| C(11') | 7865(1) | 11614(1) | -1108(1) | 23(1) |
| C(12) | 7942(1) | 9047(2) | 1068(1) | 24(1) |
| C(12') | 7401(1) | 10868(2) | -1260(1) | 25(1) |
| C(13) | 8396(1) | 8839(1) | 1952(1) | 21(1) |
| C(13') | 6901(1) | 10942(1) | -882(1) | 21(1) |
| C(14) | 8423(1) | 8806(1) | 4665(1) | 18(1) |
| C(14') | 6517(1) | 11219(1) | 1308(1) | 17(1) |
| C(15) | 7932(1) | 8331(1) | 4916(1) | 21(1) |
| C(15') | 7182(1) | 11212(1) | 1856(1) | 21(1) |
| C(16) | 7667(1) | 8805(2) | 5530(1) | 26(1) |
| C(16') | 7382(1) | 10770(2) | 2740(1) | 26(1) |
| C(17) | 7896(1) | 9731(2) | 5898(1) | 30(1) |
| C(17') | 6925(1) | 10329(2) | 3080(1) | 29(1) |
| C(18) | 8386(1) | 10195(2) | 5662(1) | 28(1) |
| C(18') | 6268(1) | 10330(2) | 2536(1) | 29(1) |
| C(19) | 8650(1) | 9740(1) | 5038(1) | 23(1) |
| C(19') | 6060(1) | 10777(1) | 1655(1) | 23(1) |
| B(1) | 10640(1) | 7703(2) | 6537(2) | 25(1) |
| B(1') | 5514(1) | 6158(2) | 2889(2) | 23(1) |
| B(2) | 10941(1) | 8588(2) | 7368(2) | 31(1) |
| B(2') | 5766(1) | 7168(2) | 2405(2) | 24(1) |
| B(3) | 10644(1) | 7832(2) | 8187(2) | 27(1) |
| B(3') | 5196(1) | 7278(2) | 3043(2) | 27(1) |
| B(4) | 11163(1) | 7378(2) | 7641(2) | 21(1) |
| B(4') | 6308(1) | 6589(2) | 3359(1) | 20(1) |
| B(5) | 10071(1) | 8171(2) | 6986(2) | 30(1) |
| B(5') | 6064(1) | 7738(2) | 3576(2) | 28(1) |
| B(6) | 10362(1) | 6996(2) | 7287(2) | 24(1) |
| B(6') | 5776(1) | 6666(2) | 3995(2) | 24(1) |

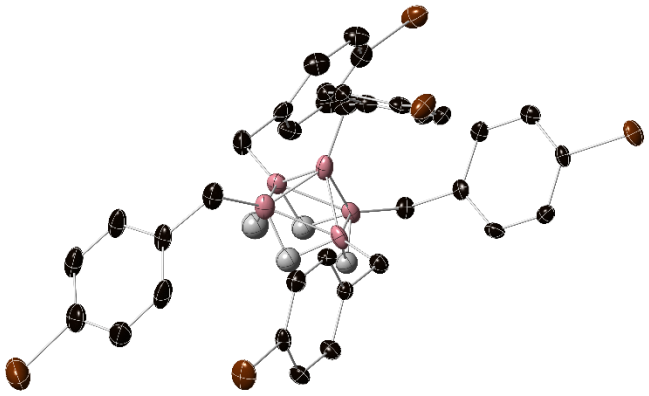


**Fig. S108.** Solid-state structure of **13.**

Solid structure of **13** with thermal ellipsoid rendered at the 50% probability level, hydrogen atoms (except the bridging proton in grey) are omitted for clarity.

**Table S8**. Crystallographic data and structure refinement for **13**.

| | |
|---|---|
| Identification code | JCA-III-226 |
| Empirical formula | C35 H34 B5 Br5 |
| Formula weight | 908.22 |
| Temperature | 100.0 K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 8.8059(16) Å α = 97.390(5)°. |
| | b = 11.348(2) Å β = 94.678(7)°. |
| | c = 21.316(4) Å γ = 100.323(8)°. |
| Volume | 2066.3(6) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.460 $Mg/m^3$ |
| Absorption coefficient | 4.884 $mm^{-1}$ |
| F(000) | 888 |
| Crystal size | 0.28 × 0.26 × 0.24 $mm^3$ |
| Theta range for data collection | 2.650 to 25.000°. |
| Index ranges | -10≤h≤8, -13≤k≤13, -24≤l≤25 |
| Reflections collected | 17618 |
| Independent reflections | 7279 [R(int) = 0.0333] |
| Completeness to theta = 25.000° | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.5624 and 0.3989 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7279 / 0 / 422 |
| Goodness-of-fit on $F^2$ | 1.055 |
| Final R indices [I>2σ(I)] | R1 = 0.0374, wR2 = 0.0879 |
| R indices (all data) | R1 = 0.0557, wR2 = 0.0937 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.841 and -0.761 $e.Å^{-3}$ |
| SQUEEZE | Found: 91e/uc. Calc. for two toluene, 100e/uc |

**Table S9**. Atomic coordinates (× $10^4$) and equivalent isotropic displacement parameters (Å$^2$× $10^3$) for **13**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(3) | 2239(1) | 2273(1) | -935(1) | 27(1) |
| Br(2) | 2524(1) | 10116(1) | 175(1) | 34(1) |
| Br(4) | 3455(1) | 102(1) | 4379(1) | 36(1) |
| Br(1) | 7854(1) | 933(1) | 1626(1) | 33(1) |
| Br(5) | 1622(1) | 6507(1) | 6032(1) | 58(1) |
| C(19) | 1795(4) | 3334(3) | -229(2) | 17(1) |
| C(4) | 5875(5) | 2475(4) | 1202(2) | 25(1) |
| C(12) | 2795(5) | 9509(4) | 961(2) | 26(1) |
| C(26) | 3030(5) | 1022(3) | 3717(2) | 20(1) |
| C(18) | 2543(4) | 4533(3) | -123(2) | 20(1) |
| C(17) | 2208(4) | 5300(3) | 385(2) | 19(1) |
| C(7) | 6903(4) | 4327(4) | 2209(2) | 22(1) |
| C(1) | 5043(5) | 5598(4) | 1811(2) | 28(1) |
| C(8) | 3425(5) | 8114(4) | 2722(2) | 28(1) |
| C(22) | 2009(5) | 2935(3) | 2174(2) | 21(1) |
| C(5) | 7001(4) | 2369(4) | 1673(2) | 21(1) |
| C(21) | 383(4) | 3670(3) | 664(2) | 19(1) |
| C(3) | 5261(5) | 3516(4) | 1248(2) | 25(1) |
| C(20) | 706(4) | 2884(3) | 158(2) | 19(1) |
| C(6) | 7535(4) | 3289(4) | 2174(2) | 20(1) |
| C(25) | 4203(5) | 1463(4) | 3376(2) | 22(1) |
| C(24) | 3861(5) | 2085(4) | 2877(2) | 22(1) |
| C(2) | 5751(5) | 4461(4) | 1748(2) | 22(1) |
| C(16) | 1124(4) | 4881(3) | 786(2) | 16(1) |
| C(15) | 772(5) | 5720(4) | 1344(2) | 21(1) |
| C(9) | 3212(5) | 8629(3) | 2114(2) | 24(1) |
| C(10) | 4210(5) | 8484(4) | 1644(2) | 29(1) |
| B(2) | 2859(6) | 6675(4) | 2624(2) | 22(1) |
| B(4) | 2237(6) | 4341(4) | 2364(2) | 22(1) |
| B(5) | 3460(6) | 5444(4) | 2993(2) | 25(1) |
| C(29) | 4709(5) | 5412(4) | 3570(2) | 29(1) |
| C(32) | 2465(6) | 4963(4) | 4998(2) | 40(1) |
| C(30) | 4070(5) | 5655(4) | 4200(2) | 25(1) |
| C(13) | 1787(5) | 9671(4) | 1411(2) | 28(1) |
| B(1) | 3560(6) | 5535(4) | 2209(2) | 23(1) |
| C(14) | 2003(5) | 9230(4) | 1988(2) | 27(1) |
| C(33) | 2662(6) | 6148(4) | 5297(2) | 36(1) |
| C(11) | 4003(5) | 8907(4) | 1066(2) | 25(1) |
| C(28) | 1212(5) | 1809(4) | 3079(2) | 22(1) |
| C(23) | 2369(4) | 2261(3) | 2719(2) | 17(1) |
| C(34) | 3576(6) | 7079(4) | 5066(2) | 36(1) |
| C(35) | 4258(6) | 6820(4) | 4524(2) | 32(1) |
| C(31) | 3170(6) | 4737(4) | 4456(2) | 36(1) |
| C(27) | 1531(5) | 1178(4) | 3581(2) | 26(1) |
| B(3) | 1675(5) | 5596(4) | 1993(2) | 20(1) |

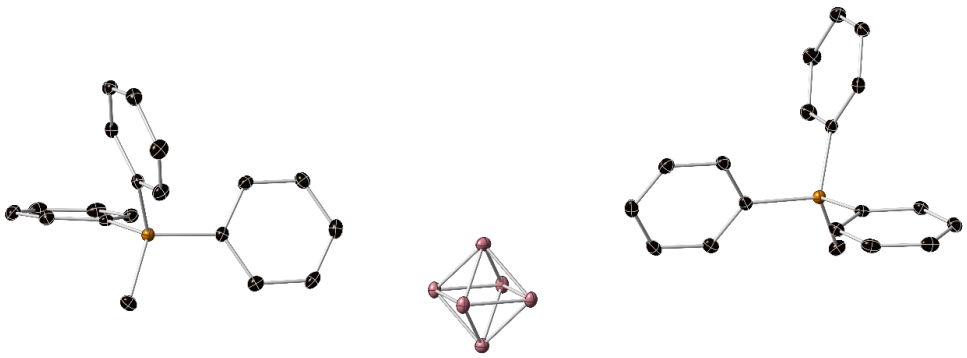


**Fig. S109.** Solid-state structure of **17.**

Solid structure of **17** with thermal ellipsoid rendered at the 50% probability level, hydrogens are omitted for clarity.

**Table S11**. Crystallographic data and structure refinement for **17**.

| | |
|---|---|
| Identification code | JCA-IV-063 |
| Empirical formula | C38 H42 B6 P2 |
| Formula weight | 625.51 |
| Temperature | 100.0 K |
| Wavelength | 1.54178 Å |
| Crystal system | Monoclinic |
| Space group | C 2/c |
| Unit cell dimensions | a = 26.672(2) Å α = 90°. |
| | b = 9.1609(6) Å β = 132.497(3)°. |
| | c = 18.891(3) Å γ = 90°. |
| Volume | 3403.4(6) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.221 $Mg/m^3$ |
| Absorption coefficient | 1.346 $mm^{-1}$ |
| F(000) | 1320 |
| Crystal size | 0.3 × 0.28 × 0.26 $mm^3$ |
| Theta range for data collection | 4.497 to 68.247°. |
| Index ranges | -26≤h≤31, -11≤k≤10, -22≤l≤22 |
| Reflections collected | 12289 |
| Independent reflections | 3055 [*R*(int) = 0.0327] |
| Completeness to theta = 67.679° | 98.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7531 and 0.6875 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3055 / 0 / 222 |
| Goodness-of-fit on $F^2$ | 1.039 |
| Final R indices [I>2σ(I)] | R1 = 0.0333, wR2 = 0.0873 |
| R indices (all data) | R1 = 0.0363, wR2 = 0.0897 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.446 and -0.271 $e.Å^{-3}$ |

**Table S12**. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **17**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 8508(1) | 4567(1) | 8277(1) | 12(1) |
| C(1) | 9036(1) | 3004(2) | 8640(1) | 17(1) |
| C(2) | 8228(1) | 4577(1) | 8917(1) | 13(1) |
| C(3) | 7542(1) | 4392(2) | 8435(1) | 16(1) |
| C(4) | 7353(1) | 4248(2) | 8961(1) | 19(1) |
| C(5) | 7844(1) | 4276(2) | 9958(1) | 20(1) |
| C(6) | 8523(1) | 4492(2) | 10437(1) | 18(1) |
| C(7) | 8718(1) | 4646(2) | 9920(1) | 16(1) |
| C(8) | 8972(1) | 6196(2) | 8512(1) | 14(1) |
| C(9) | 8958(1) | 7422(2) | 8935(1) | 15(1) |
| C(10) | 9273(1) | 8702(2) | 9017(1) | 17(1) |
| C(11) | 9594(1) | 8772(2) | 8669(1) | 20(1) |
| C(12) | 9621(1) | 7535(2) | 8268(1) | 23(1) |
| C(13) | 9315(1) | 6242(2) | 8188(1) | 20(1) |
| C(14) | 7778(1) | 4493(2) | 7012(1) | 14(1) |
| C(15) | 7645(1) | 3293(2) | 6449(1) | 16(1) |
| C(16) | 7071(1) | 3308(2) | 5472(1) | 18(1) |
| C(17) | 6635(1) | 4494(2) | 5057(1) | 18(1) |
| C(18) | 6770(1) | 5690(2) | 5617(1) | 18(1) |
| C(19) | 7340(1) | 5694(2) | 6592(1) | 16(1) |
| B(1) | 5000 | 3827(2) | 2500 | 16(1) |
| B(2) | 5177(1) | 2496(2) | 3289(1) | 14(1) |
| B(3) | 5000 | 1159(2) | 2500 | 15(1) |
| B(4) | 4404(1) | 2493(2) | 2115(1) | 15(1) |

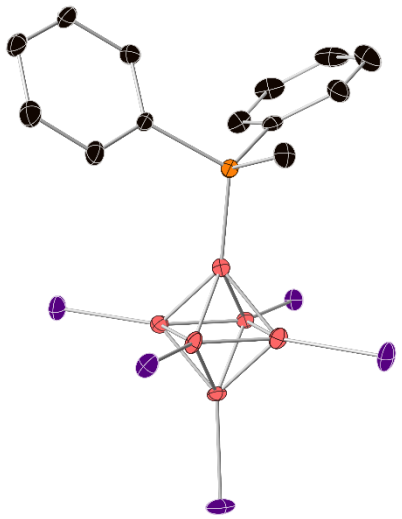


**Fig. S110**. Solid-state structure of **42**.
Solid structure of **42** with thermal ellipsoids rendered at the 50% probability level, hydrogen atoms and cation $[Na(H_2O)_5]^+$ are omitted for clarity. To some degree all I-atom sites (primarily I(6)) contain some small amount of lighter halogen, but that even for I(6) the B-I distance is only 0.01Å shorter than the average of the other four and the thermal ellipsoid for I(6) is equal to the average of the other four. Why this effect is most prominent for I(6) is unknown.

**Table S14**. Crystallographic data and structure refinement for **42**.

| | |
|---|---|
| Identification code | XM-3-27-2 |
| Empirical formula | C13 H23 B6 I5 Na O5 P |
| Formula weight | 1012.63 |
| Temperature | 100.0 K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 8.2411(5) Å α = 99.2250(10)°. |
| | b = 10.1687(6) Å β = 102.3640(10)°. |
| | c = 18.8673(12) Å γ = 104.3460(10)°. |
| Volume | 1457.75(15) $Å^3$ |
| Z | 2 |
| Density (calculated) | 2.307 $Mg/m^3$ |
| Absorption coefficient | 5.425 $mm^{-1}$ |
| F(000) | 924 |
| Crystal size | 0.28 × 0.26 × 0.24 $mm^3$ |
| Theta range for data collection | 1.134 to 28.373°. |
| Index ranges | -11≤h≤11, -13≤k≤13, -25≤l≤21 |
| Reflections collected | 21082 |
| Independent reflections | 7279 [*R*(int) = 0.0671] |
| Completeness to theta = 25.242° | 99.8 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.5949 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7279 / 0 / 285 |
| Goodness-of-fit on $F^2$ | 1.054 |

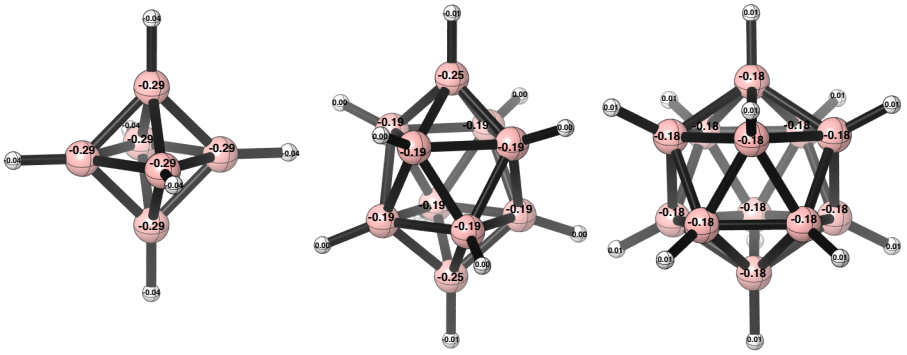
| | |
|---|---|
| Final R indices [I>2σ(I)] | R1 = 0.0478, wR2 = 0.1360 |
| R indices (all data) | R1 = 0.0512, wR2 = 0.1395 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 2.148 and -2.663 e.Å$^{-3}$ |

**Table S15**. Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for **42**. U(eq) is defined as one third of the trace of the orthogonalized U$^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 1678(1) | 5009(1) | 5844(1) | 22(1) |
| I(2) | 5280(1) | 3007(1) | 7313(1) | 15(1) |
| I(3) | 7510(1) | 7114(1) | 6429(1) | 22(1) |
| I(4) | 7852(1) | 7501(1) | 9099(1) | 21(1) |
| I(5) | 4005(1) | 9315(1) | 7531(1) | 16(1) |
| P(1) | 1989(2) | 5334(1) | 8302(1) | 10(1) |
| C(1) | 5(7) | 5523(6) | 7776(3) | 17(1) |
| C(2) | 2385(6) | 6382(6) | 9223(3) | 13(1) |
| C(3) | 2048(7) | 5800(6) | 9814(3) | 18(1) |
| C(4) | 2202(8) | 6665(7) | 10486(3) | 24(1) |
| C(5) | 2659(7) | 8094(7) | 10576(3) | 24(1) |
| C(6) | 3017(7) | 8677(6) | 9991(3) | 22(1) |
| C(7) | 2904(7) | 7830(6) | 9318(3) | 18(1) |
| C(8) | 1612(7) | 3554(6) | 8376(3) | 14(1) |
| C(9) | 2937(7) | 3161(6) | 8810(3) | 20(1) |
| C(10) | 2668(8) | 1787(7) | 8883(4) | 24(1) |
| C(11) | 1090(9) | 800(7) | 8524(4) | 28(1) |
| C(12) | -216(9) | 1166(6) | 8074(4) | 27(1) |
| C(13) | 30(7) | 2551(6) | 8005(3) | 20(1) |
| B(1) | 3721(7) | 5885(6) | 7818(3) | 11(1) |
| B(2) | 4504(8) | 7331(6) | 7501(3) | 13(1) |
| B(3) | 3634(7) | 5767(6) | 6898(3) | 13(1) |
| B(4) | 5004(7) | 5073(6) | 7425(3) | 12(1) |
| B(5) | 5816(7) | 6542(6) | 7126(3) | 11(1) |
| B(6) | 5927(7) | 6677(6) | 8054(3) | 12(1) |
| Na(1) | -2610(3) | 884(3) | 5253(1) | 27(1) |
| O(1) | -3593(7) | 2966(6) | 5530(3) | 39(1) |
| O(2) | -4735(6) | -340(5) | 5807(3) | 27(1) |
| O(3) | -2555(6) | -1422(5) | 4727(2) | 27(1) |
| O(4) | -773(6) | 1598(5) | 4470(2) | 26(1) |
| O(5) | 137(7) | 977(6) | 6191(3) | 36(1) |

## 12. Computational details.

Quantum mechanical calculations were performed with Gaussian 09[18]. The geometry of each boron cluster was optimized in the gas phase using the B3LYP functional[19-22] with the 6-31+G(d) basis set with Grimme's D3 empirical dispersion[23]. We derived the atomic charges using the Hirshfeld population analysis[24]. Frontier molecular orbitals were calculated using population analysis.




$B_6H_6^{2-}$ $B_{10}H_{10}^{2-}$ $B_{12}H_{12}^{2-}$

**Fig. S111.** Calculated Hirshfeld charges of boron clusters: $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$.

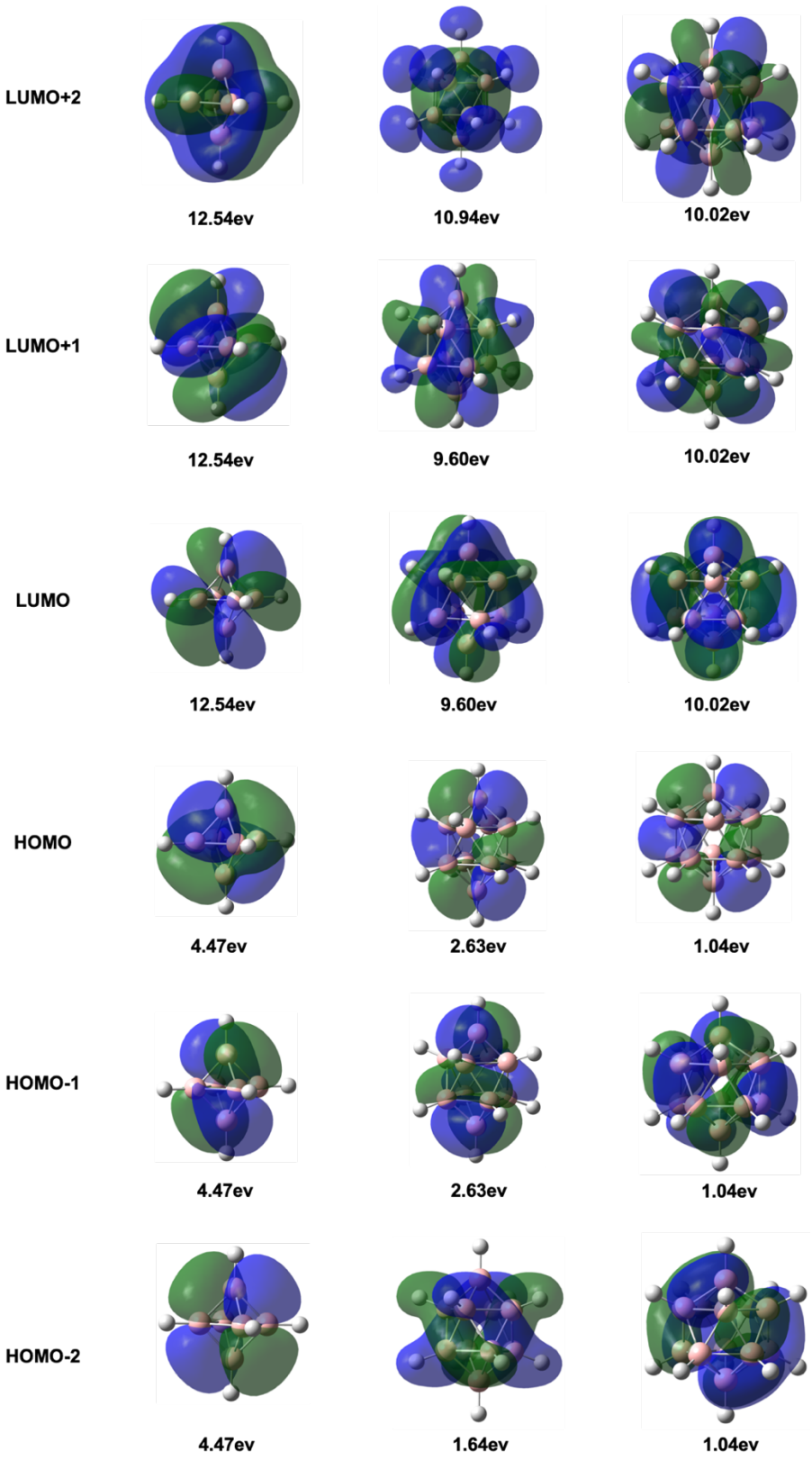



**Fig. S112.** Frontier molecular orbitals (FMOs) for $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$.

**Table S17.** Cartesian coordinates, energies, and vibrational frequencies.

**$B_6H_6^{2-}$**

| | | | |
|---|---|---|---|
| B | -1.05300900 | 0.54800700 | 0.32113400 |
| B | -0.63484500 | -0.90935200 | -0.53116800 |
| B | 0.00069100 | -0.62057300 | 1.06148500 |
| B | 0.63495100 | 0.90924100 | 0.53105400 |
| B | 1.05300600 | -0.54788200 | -0.32107300 |
| B | -0.00082900 | 0.62054200 | -1.06141900 |
| H | 0.00209400 | -1.23691100 | 2.11471800 |
| H | -2.09832900 | 1.09111200 | 0.63988900 |
| H | -1.26569300 | -1.81135300 | -1.05809700 |
| H | 2.09829800 | -1.09099700 | -0.63995500 |
| H | 1.26566000 | 1.81132700 | 1.05803800 |
| H | -0.00185000 | 1.23690300 | -2.11465600 |

**$B_{10}H_{10}^{2-}$**

| | | | |
|---|---|---|---|
| B | 1.86282200 | 0.00040200 | -0.00013400 |
| B | -1.86285300 | 0.00010300 | 0.00003800 |
| B | 0.76342700 | -0.65037300 | -1.12915400 |
| B | -0.76279800 | -0.33863300 | 1.25837200 |
| B | -0.76327800 | 0.33884400 | -1.25853300 |
| B | 0.76344800 | 0.65040800 | 1.12933200 |
| B | 0.76324300 | -1.12930500 | 0.65040500 |
| B | -0.76321500 | -1.25871000 | -0.33807700 |
| B | -0.76309100 | 1.25852300 | 0.33820700 |
| B | 0.76212200 | 1.12911700 | -0.65050900 |
| H | 3.07181300 | 0.00045000 | 0.00006900 |
| H | -3.07161700 | -0.00143100 | 0.00020600 |
| H | 1.16864800 | -1.22088000 | -2.11906200 |
| H | -1.16920600 | -0.63451400 | 2.36165800 |
| H | -1.16849400 | 0.63477600 | -2.36214300 |
| H | 1.16814700 | 1.22148000 | 2.11909000 |
| H | 1.16945500 | -2.11924100 | 1.22026500 |
| H | -1.16842100 | -2.36212600 | -0.63495200 |
| H | -1.16910500 | 2.36151300 | 0.63627100 |
| H | 1.16964800 | 2.11809800 | -1.22113000 |

**$B_{12}H_{12}^{2-}$**

| | | | |
|---|---|---|---|
| B | -1.51512600 | -0.64251100 | -0.43452300 |
| B | 0.01540400 | -1.45342000 | -0.88576700 |
| B | -0.49821800 | -1.40125000 | 0.82792800 |
| B | 0.49824800 | 1.40130800 | -0.82792300 |
| B | -0.42859800 | 0.10580800 | -1.64349000 |
| B | -1.25959500 | 0.19018600 | 1.12855900 |
| B | 1.21648800 | -1.12145100 | 0.39865400 |
| B | -1.21646800 | 1.12132500 | -0.39872100 |
| B | 1.25949700 | -0.19023200 | -1.12854000 |
| B | -0.01552200 | 1.45333400 | 0.88561600 |
| B | 1.51505900 | 0.64242100 | 0.43433200 |
| B | 0.42865700 | -0.10571900 | 1.64336500 |
| H | -0.85112900 | -2.39677000 | 1.41619800 |
| H | 0.85140800 | 2.39710700 | -1.41562100 |
| H | -2.08105400 | 1.91753100 | -0.68200400 |
| H | 2.15414600 | -0.32439300 | -1.93053500 |
| H | -0.73346200 | 0.18015100 | -2.81102200 |

| | | | |
|---|---|---|---|
| H | -2.59129300 | -1.09933700 | -0.74234600 |
| H | 0.02757500 | -2.48572500 | -1.51479200 |
| H | -2.15366700 | 0.32469500 | 1.93105400 |
| H | 2.08126300 | -1.91712500 | 0.68262200 |
| H | -0.02709400 | 2.48539300 | 1.51507600 |
| H | 2.59091300 | 1.09951400 | 0.74289900 |
| H | 0.73325800 | -0.18004200 | 2.81102200 |

**Table S18.** Geometry optimizations with frequency calculations.

| Structures | ZPVE | TCE | TCH | TCG | Egas | Hgas | Ggas |
|---|---|---|---|---|---|---|---|
| $B_6H_6^{2-}$ | 0.133881 | 0.141309 | 0.142253 | 0.103795 | -254.69186 | -254.54961 | -254.58807 |
| $B_{10}H_{10}^{2-}$ | 0.074897 | 0.080273 | 0.081217 | 0.047539 | -152.70511 | -152.6239 | -152.65757 |
| $B_{12}H_{12}^{2-}$ | 0.166107 | 0.174021 | 0.174965 | 0.135262 | -305.74262 | -305.56765 | -305.60736 |

ZPVE = zero-point vibrational energy; TCE = thermal correction to energy; TCH = thermal correction to enthalpy; TCG = thermal correction to Gibbs free energy.

**References and Notes**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## NMR spectra of borylation products

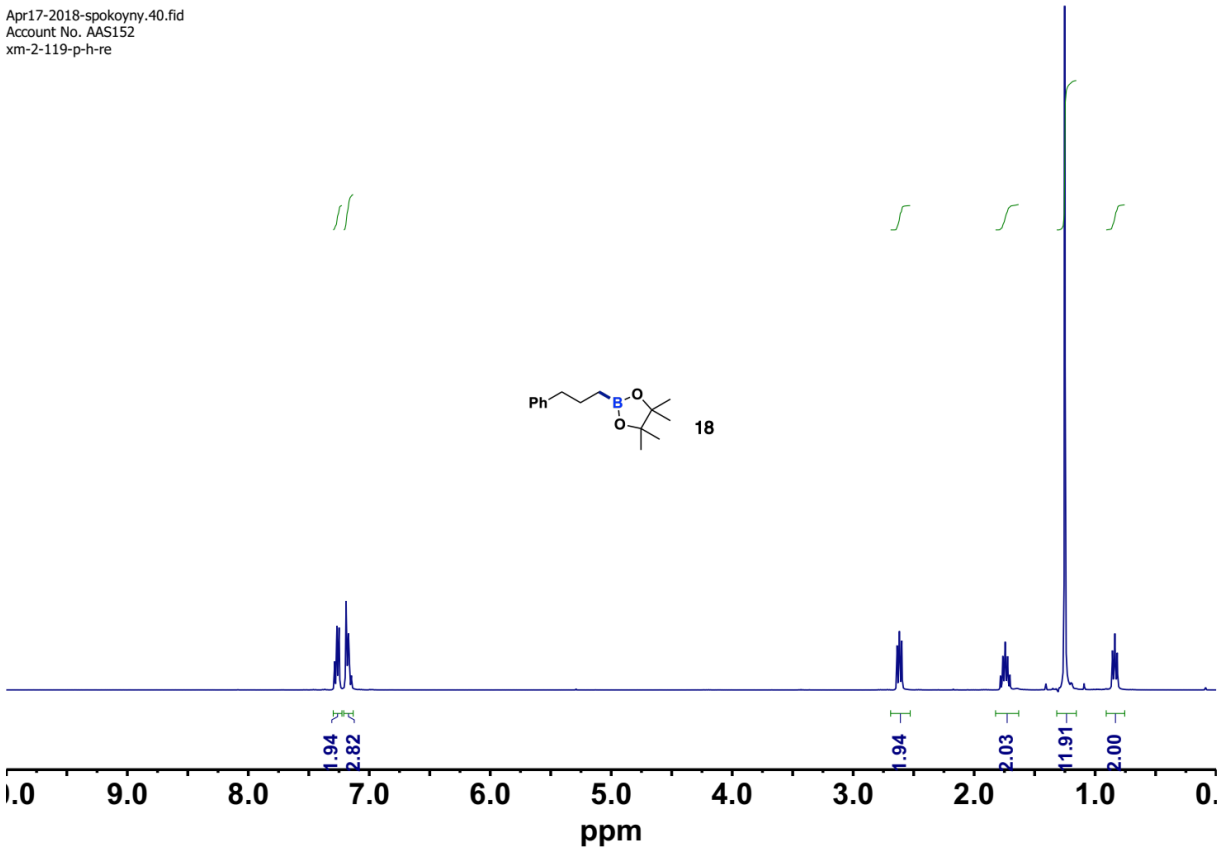


**Fig. S113.** $^{1}H$ NMR spectrum of **18** in $CDCl_3$ at 298K.

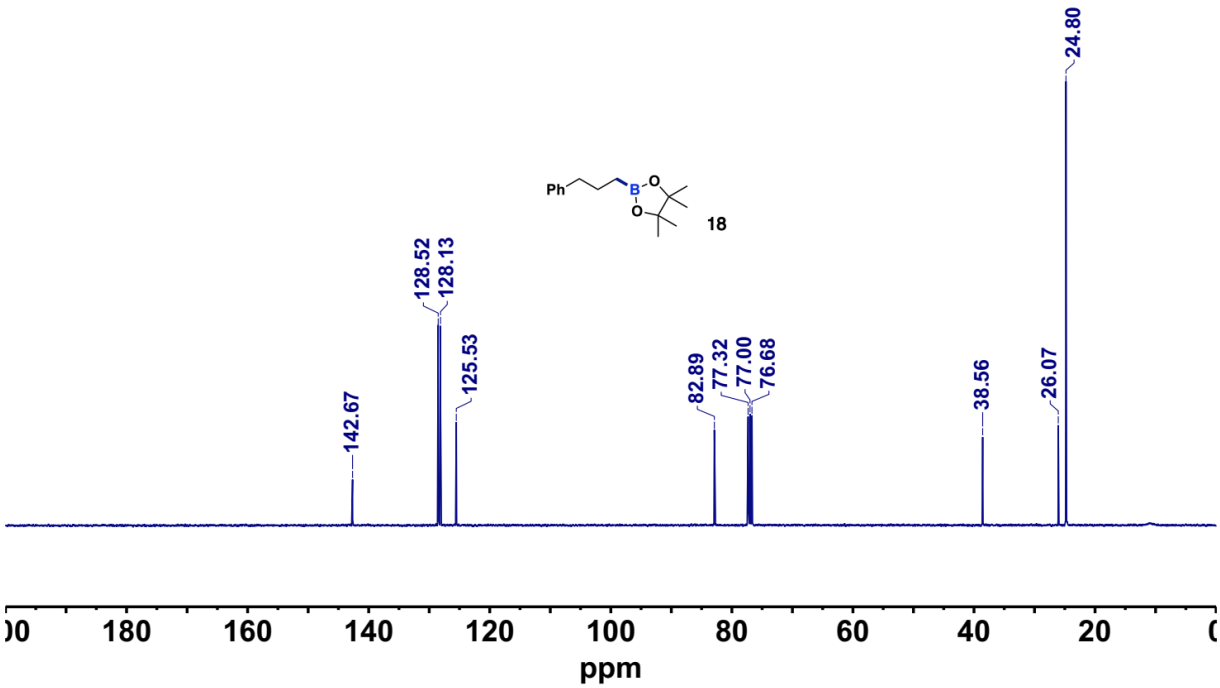


**Fig. S114.** $^{13}C\{^{1}H\}$ NMR spectrum of **18** in $CDCl_3$ at 298K.

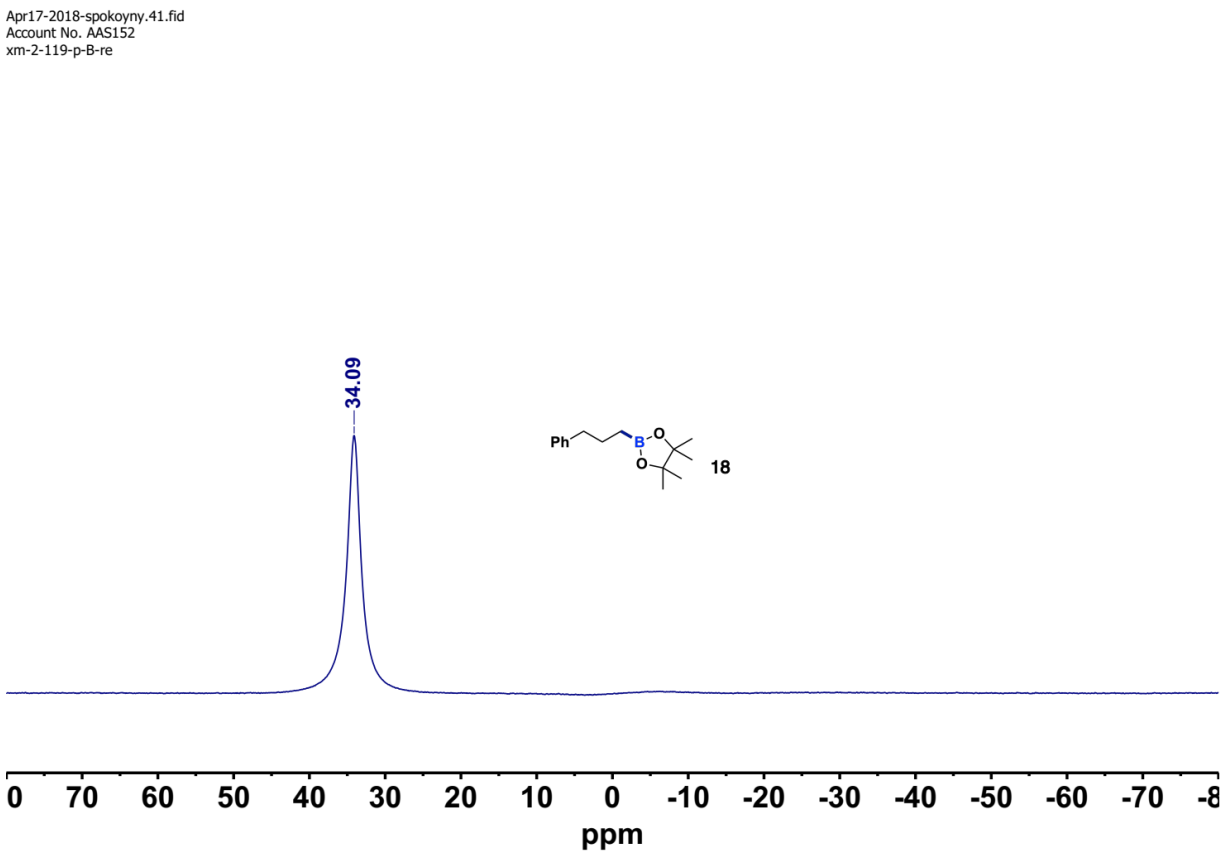


**Fig. S115.** $^{11}B$ NMR spectrum of **18** in $CDCl_3$ at 298K.

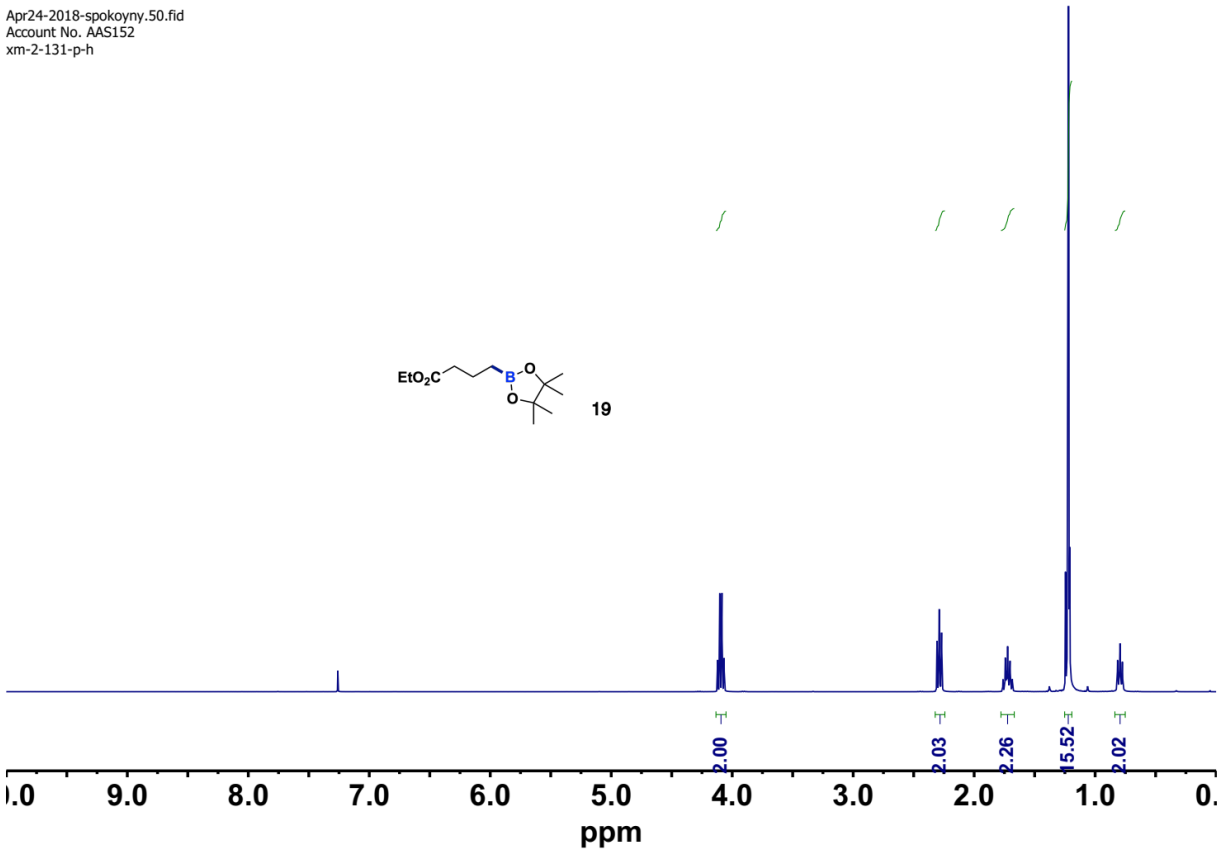


**Fig. S116**. $^{1}H$ NMR spectrum of **19** in $CDCl_3$ at 298K.

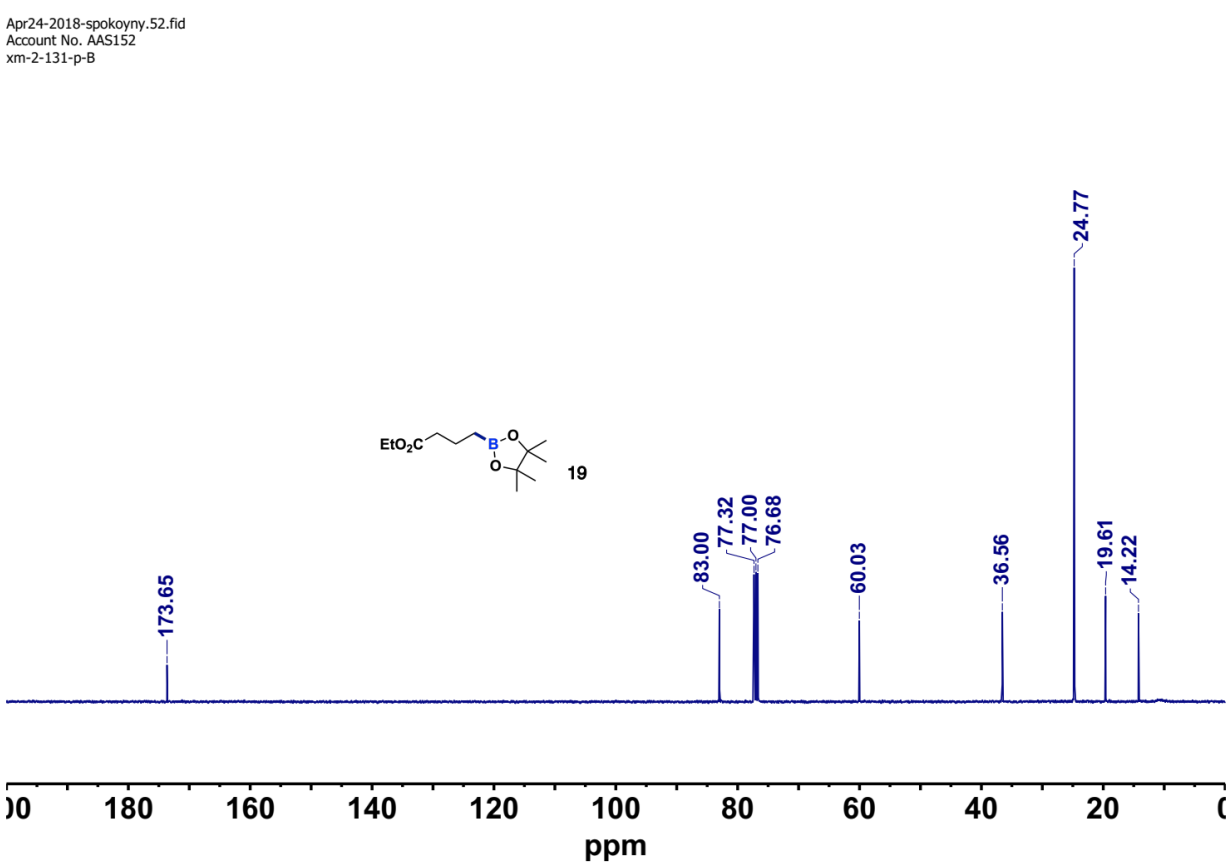


**Fig. S117.** $^{13}C\{^{1}H\}$ NMR spectrum of **19** in $CDCl_3$ at 298K.

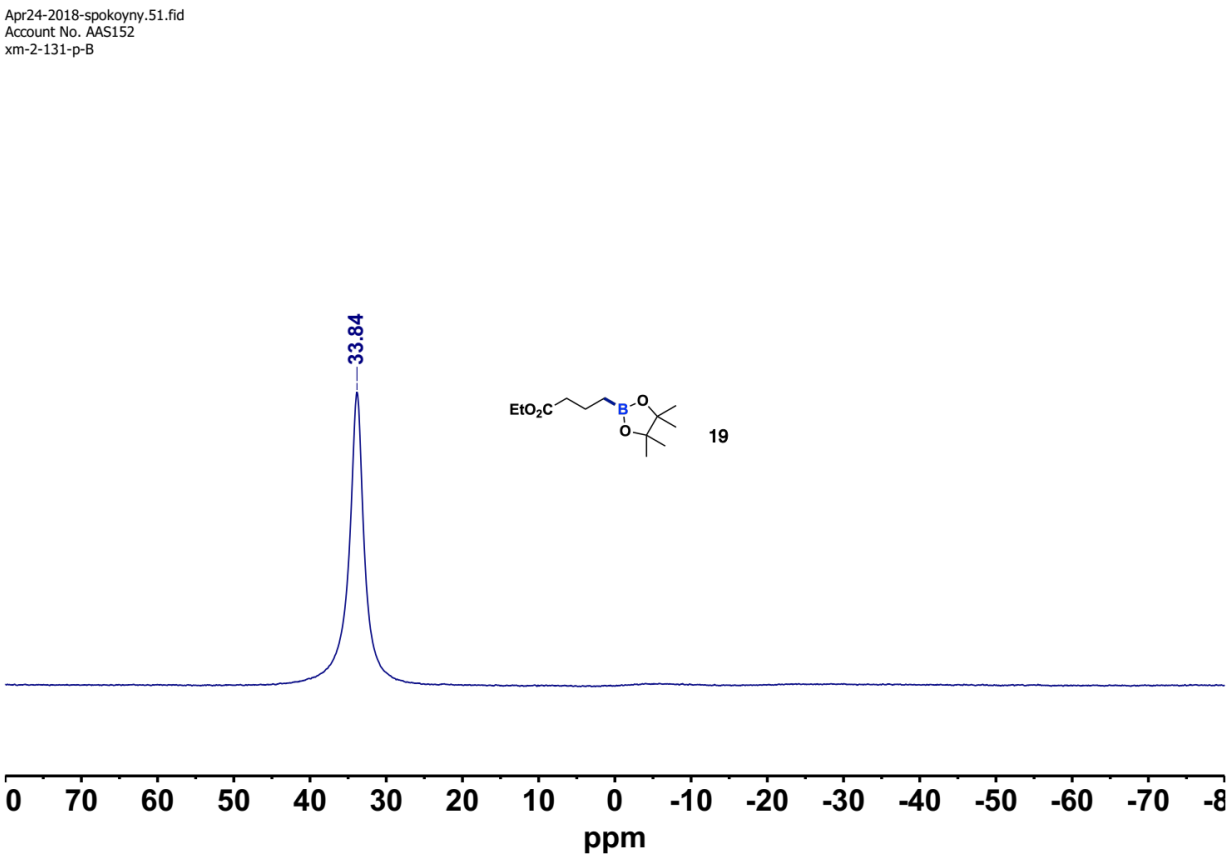


**Fig. S118**. $^{11}B$ NMR spectrum of **19** in $CDCl_3$ at 298K.

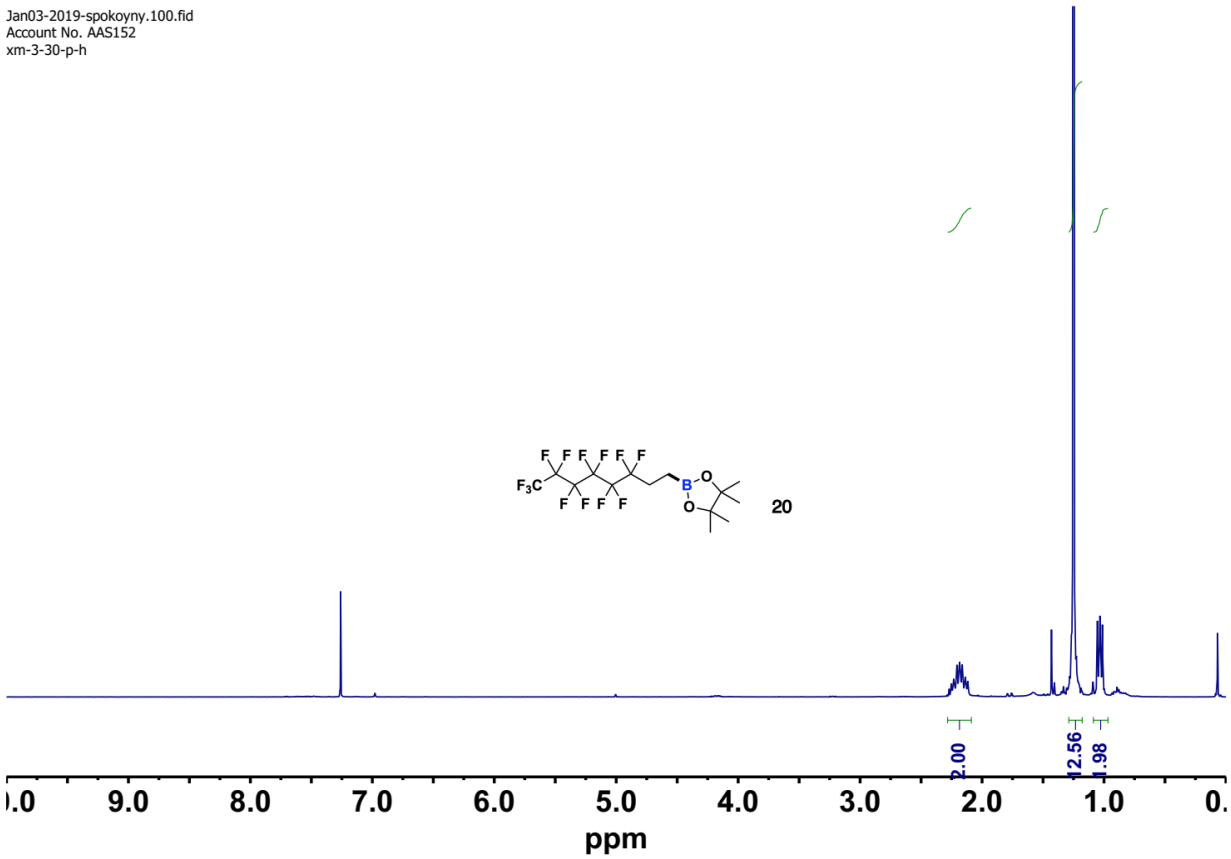


**Fig. S119**. $^{1}H$ NMR spectrum of **20** in $CDCl_3$ at 298K.

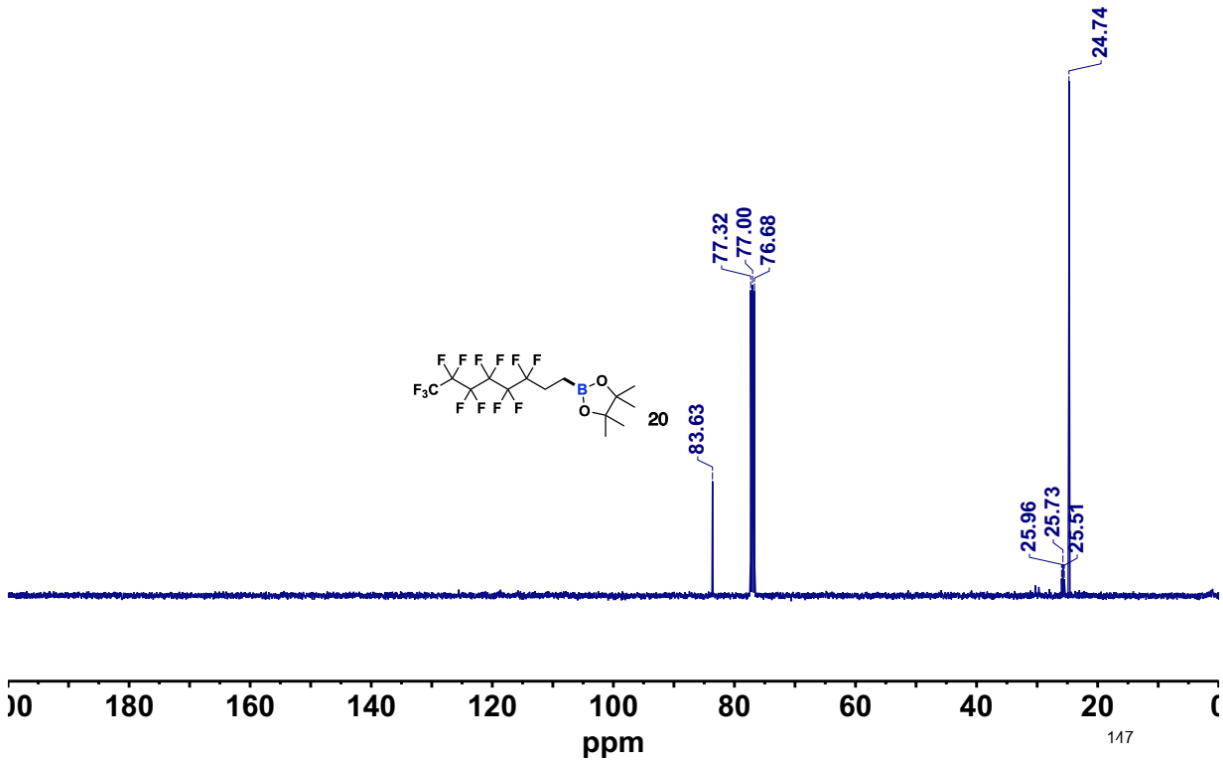


**Fig. S120**. $^{13}C\{^{1}H\}$ NMR spectrum of **20** in $CDCl_3$ at 298K.

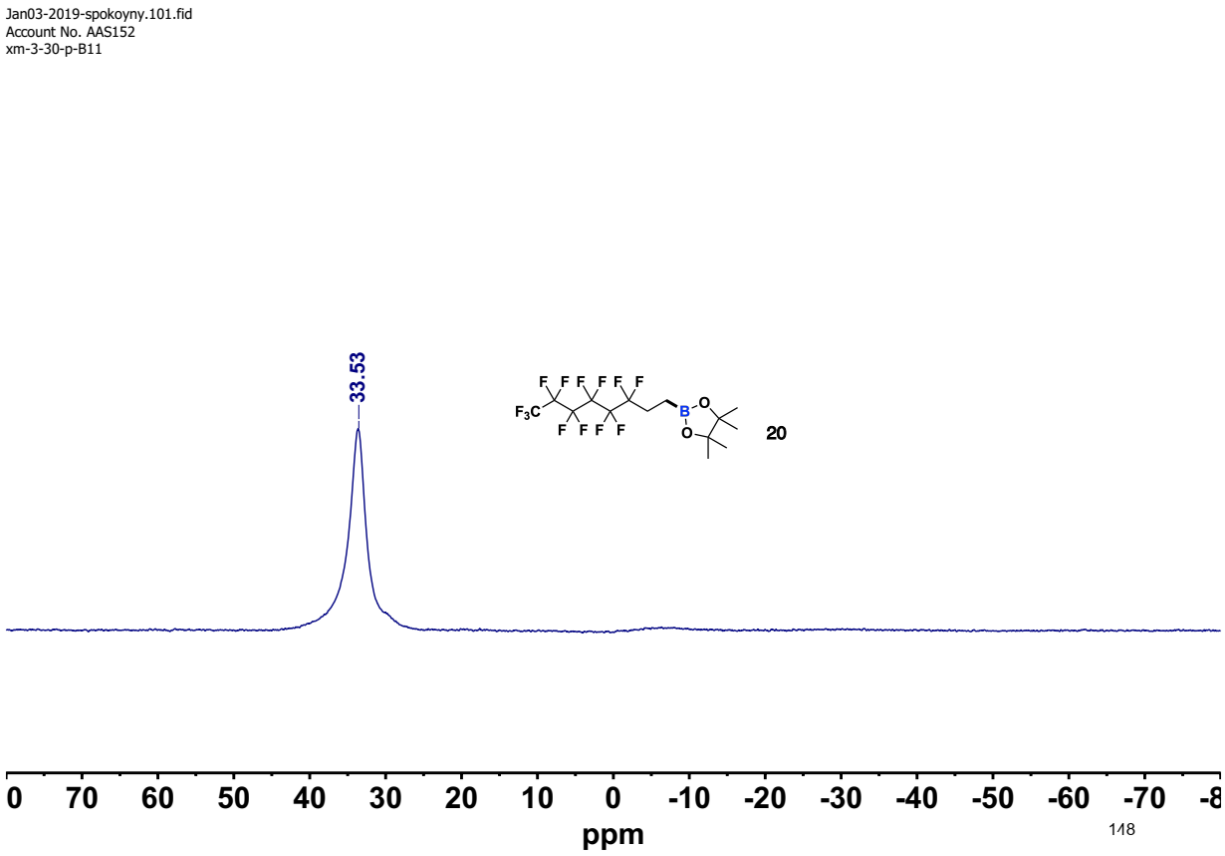


**Fig. S121**. $^{11}B$ NMR spectrum of **20** in $CDCl_3$ at 298K.

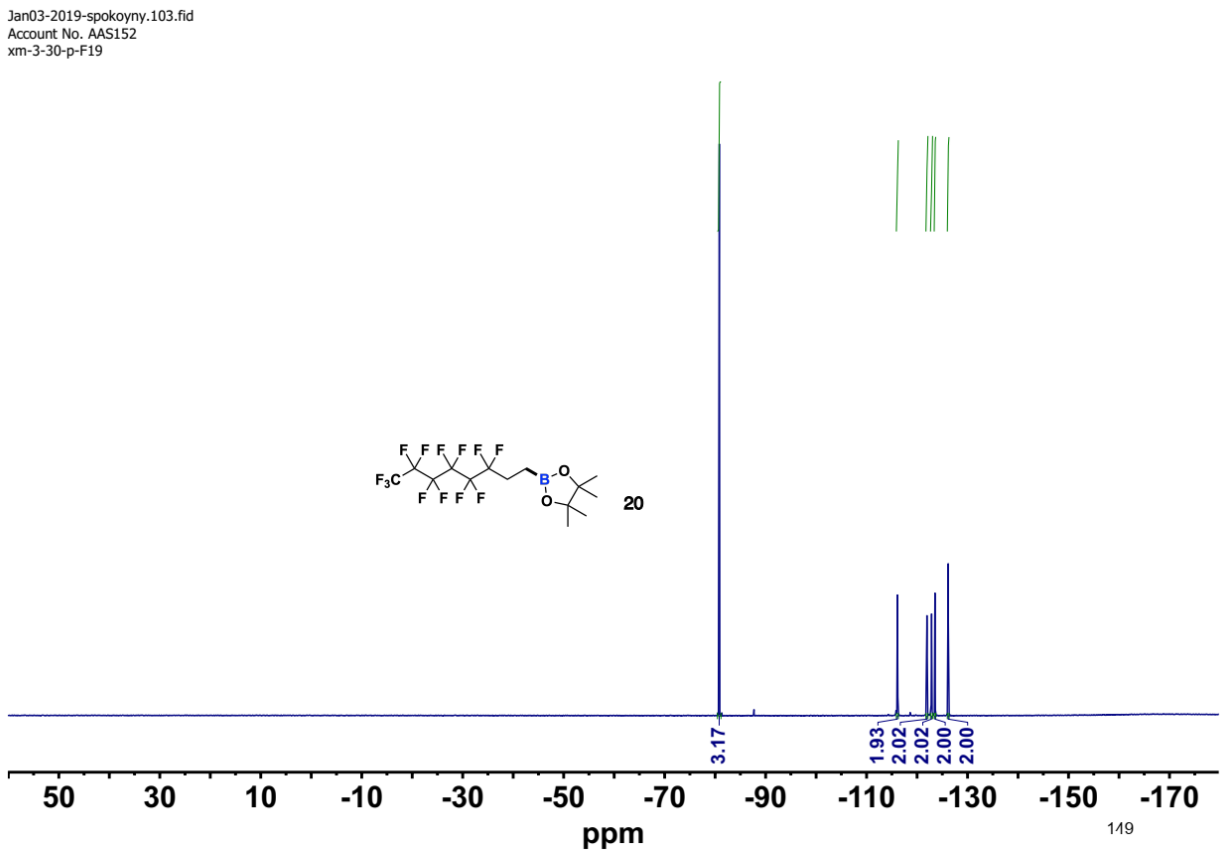


**Fig. S122**. $^{19}F$ NMR spectrum of **20** in $CDCl_3$ at 298K.

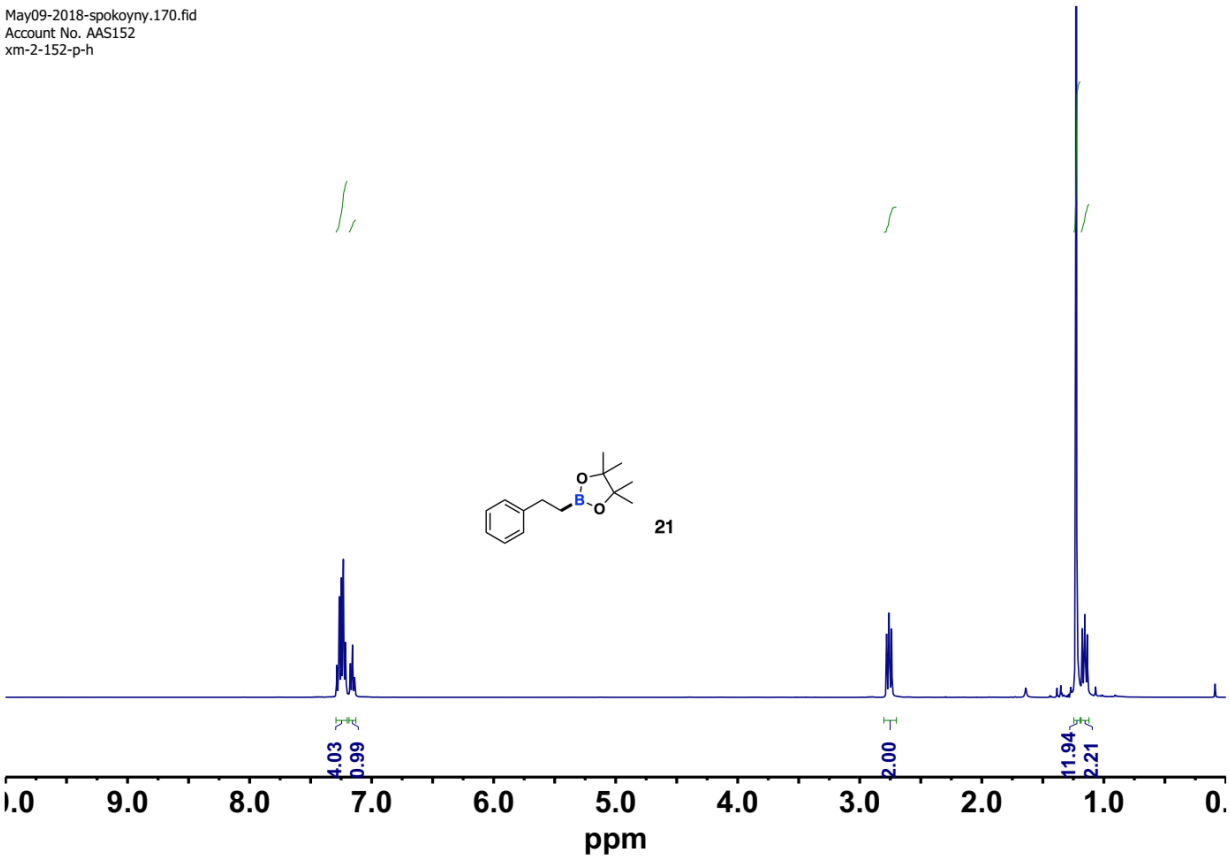


**Fig. S123**. $^{1}H$ NMR spectrum of **21** in $CDCl_3$ at 298K.

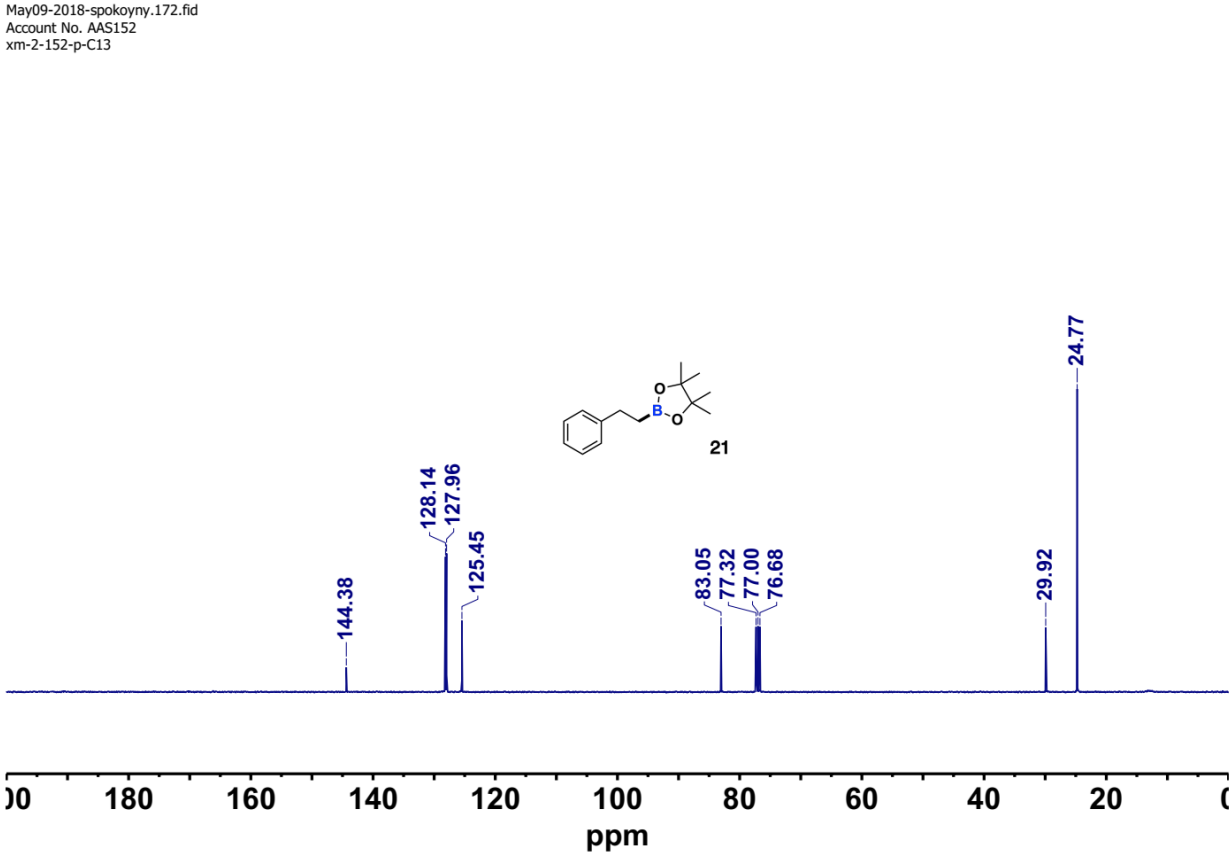


**Fig. S124**. $^{13}C\{^{1}H\}$ NMR spectrum of **21** in $CDCl_3$ at 298K.

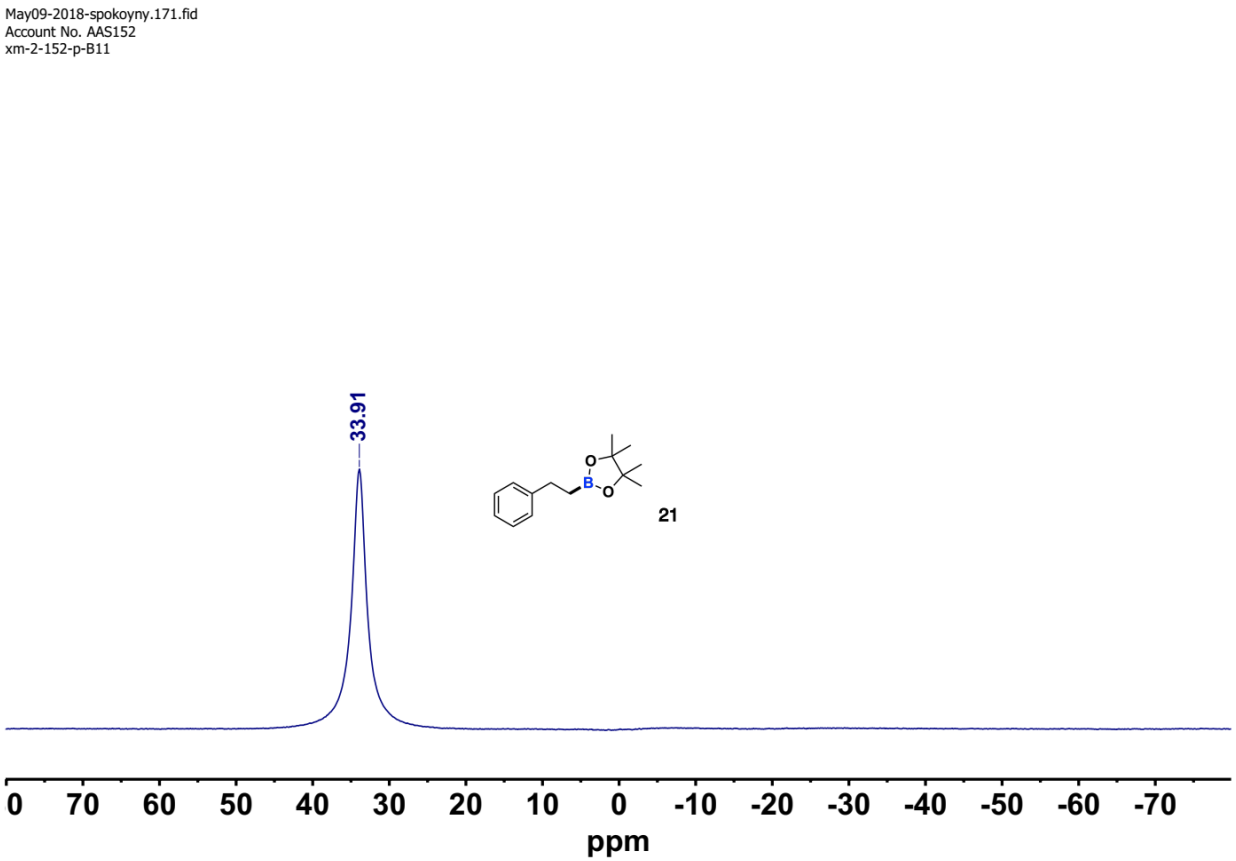


**Fig. S125**. $^{11}B$ NMR spectrum of **21** in $CDCl_3$ at 298K.

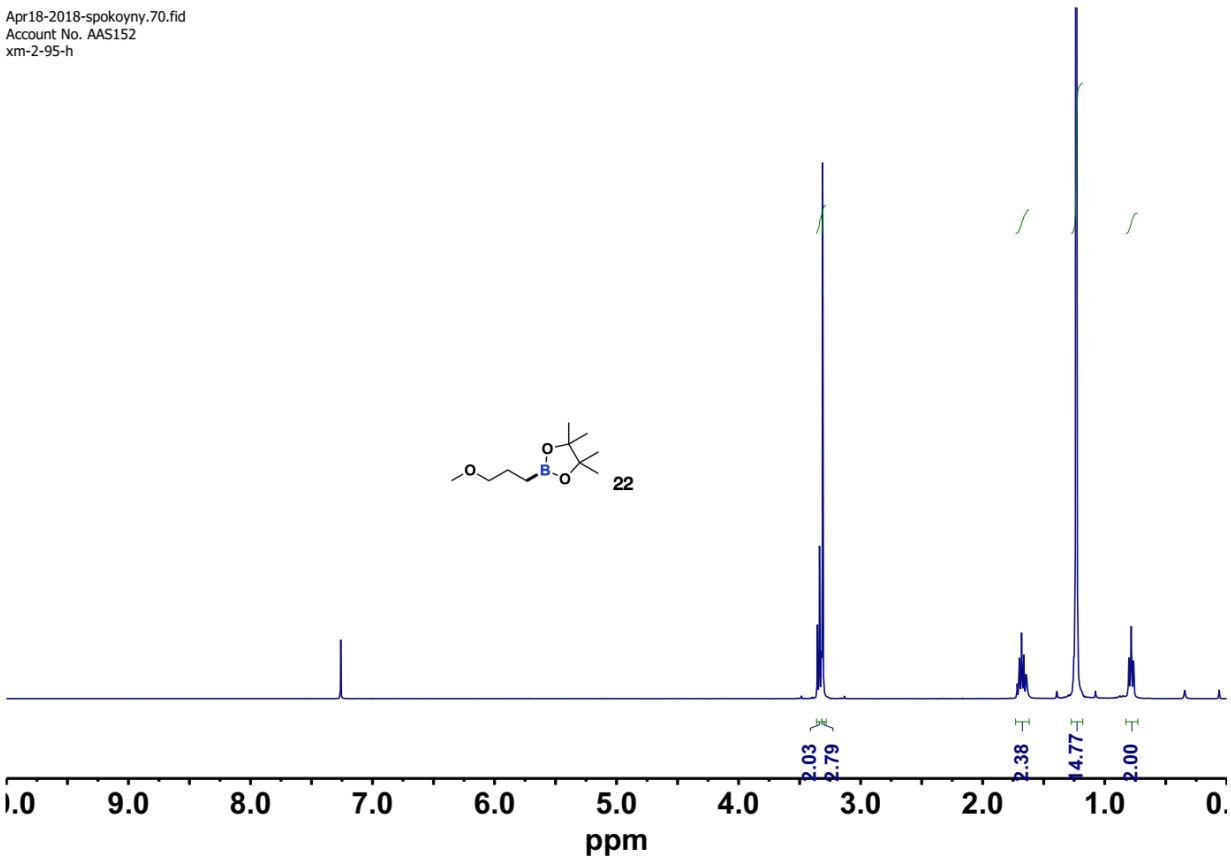


**Fig. S126**. $^{1}H$ NMR spectrum of **22** in $CDCl_3$ at 298K.

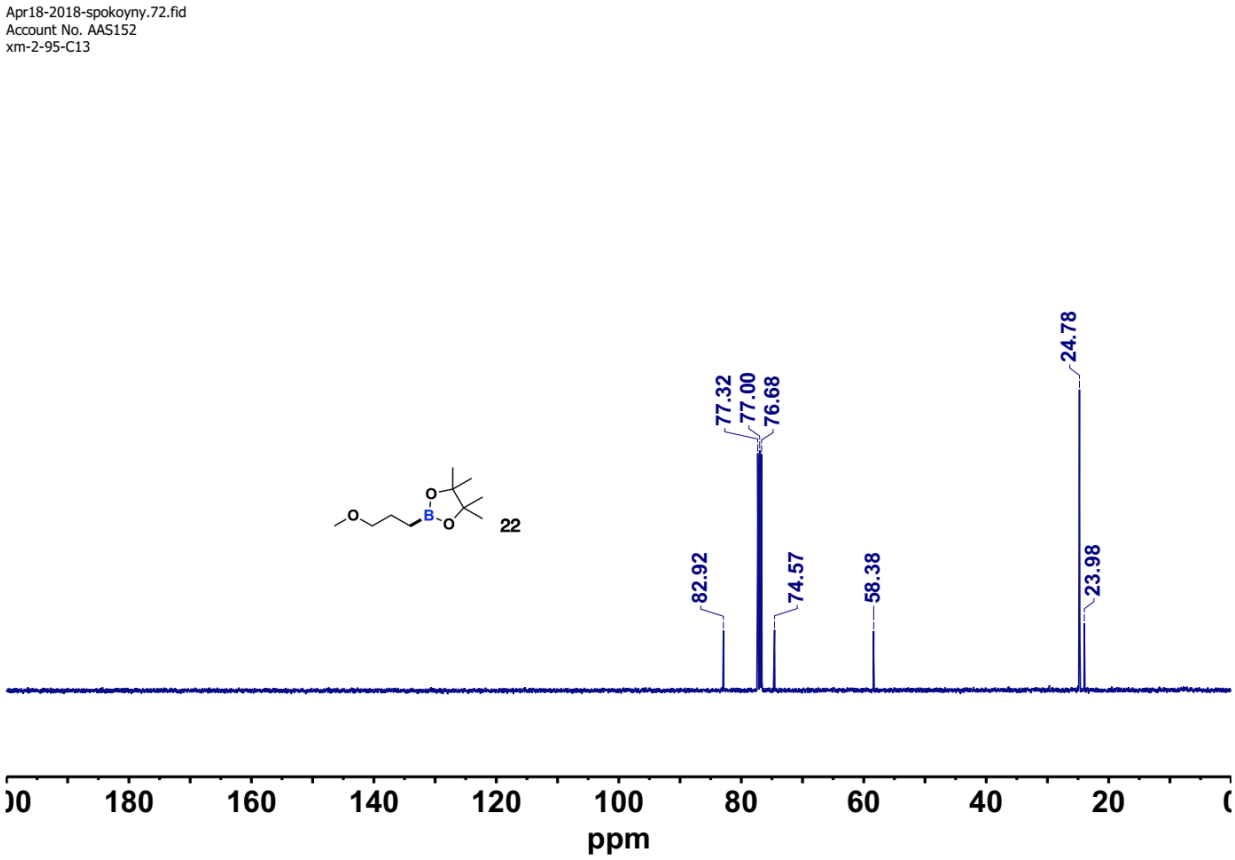


**Fig. S127**. $^{13}C\{^{1}H\}$ NMR spectrum of **22** in $CDCl_3$ at 298K.

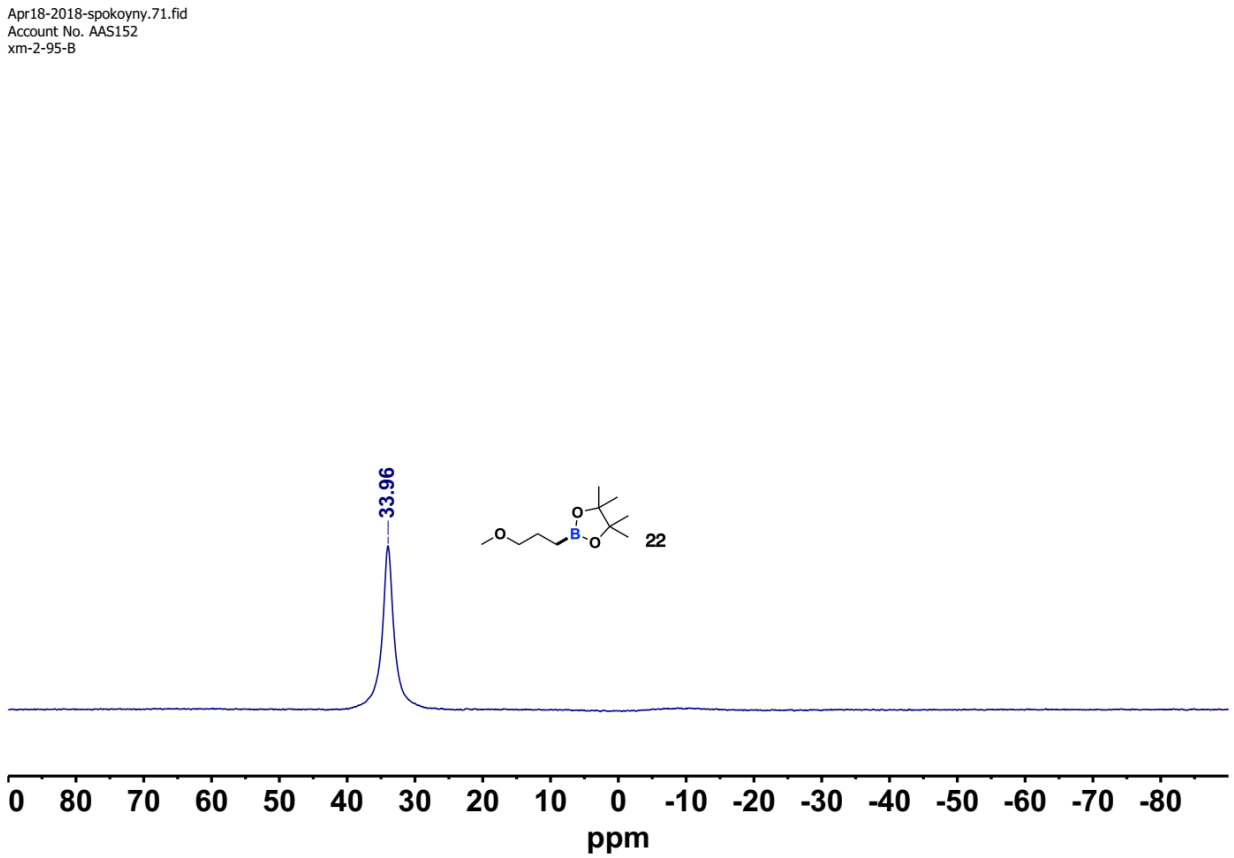


**Fig. S128**. $^{11}B$ NMR spectrum of **22** in $CDCl_3$ at 298K.

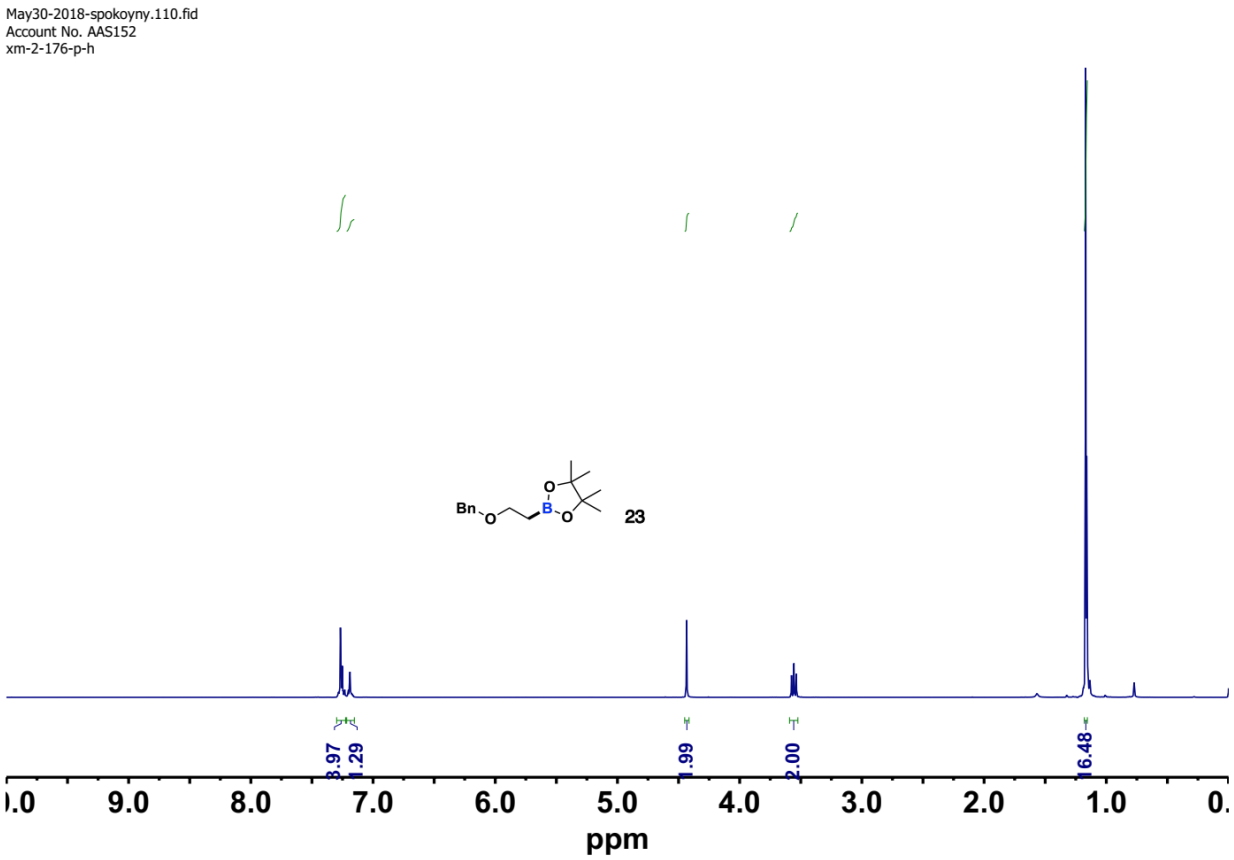


**Fig. S129**. $^{1}H$ NMR spectrum of **23** in $CDCl_3$ at 298K.

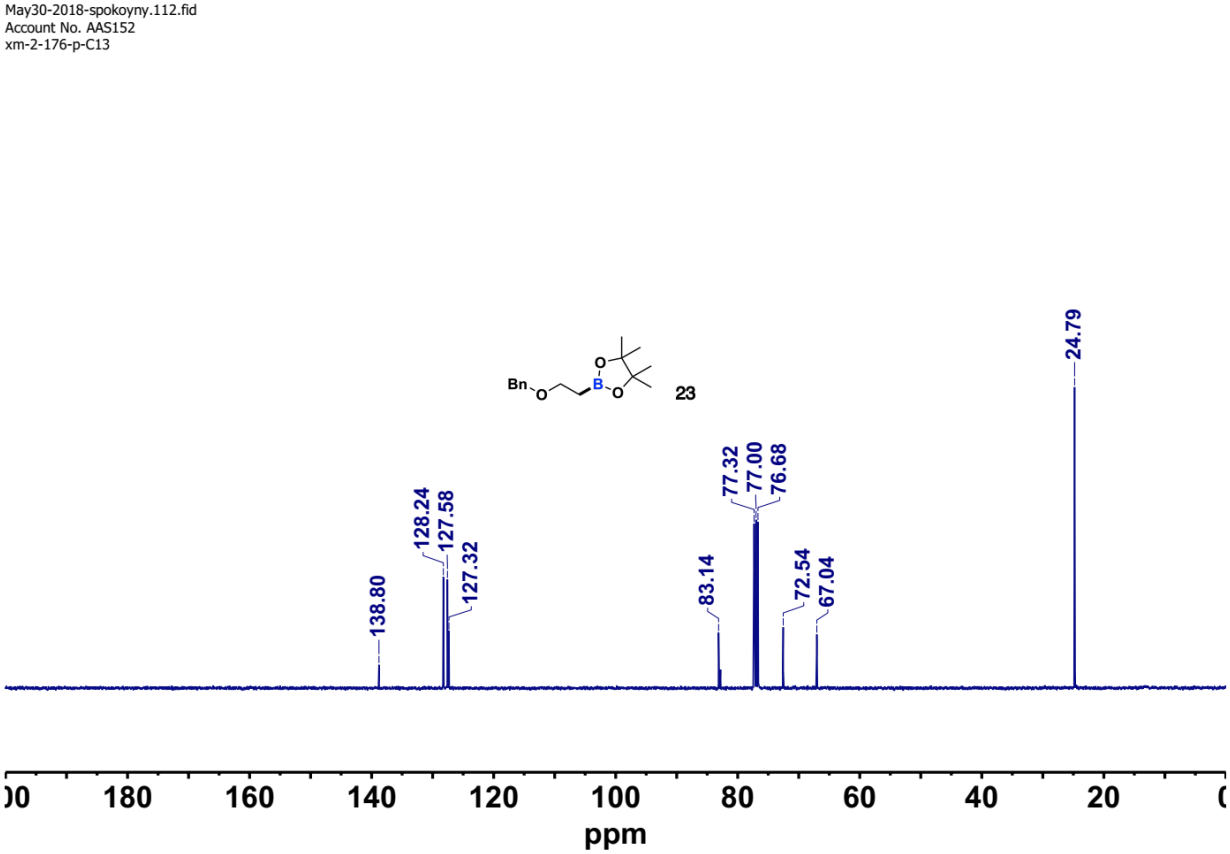


**Fig. S130**. $^{13}C\{^{1}H\}$ NMR spectrum of **23** in $CDCl_3$ at 298K.

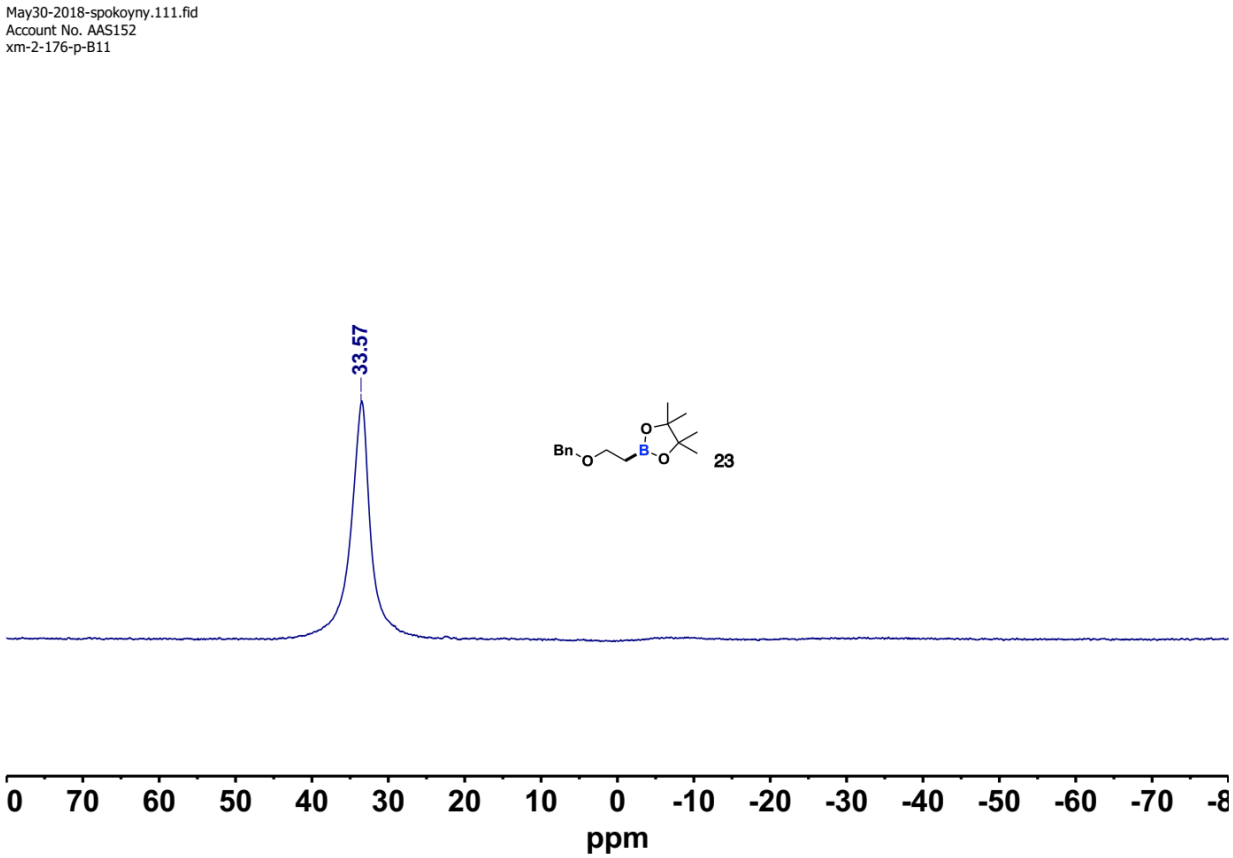


**Fig. S131**. $^{11}B$ NMR spectrum of **23** in $CDCl_3$ at 298K.

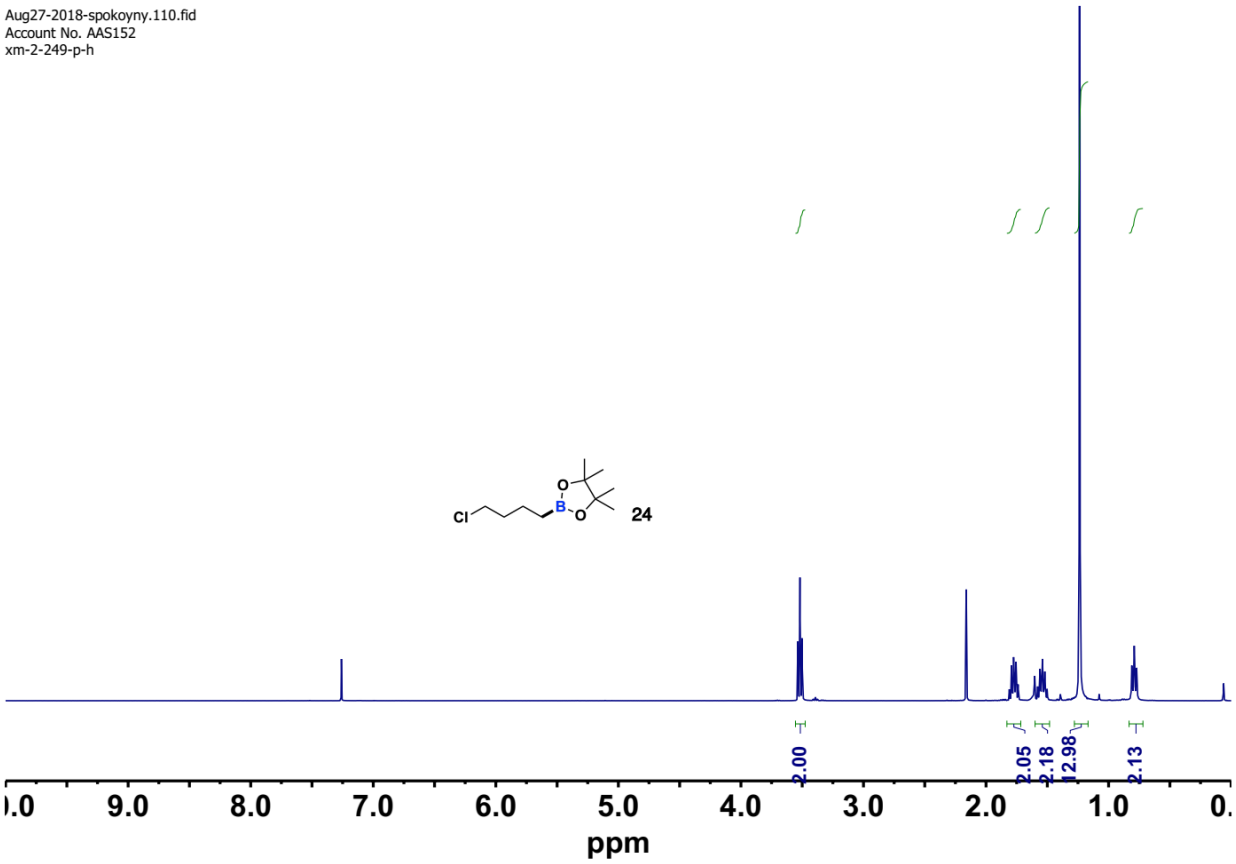


**Fig. S132**. $^{1}H$ NMR spectrum of **24** in $CDCl_3$ at 298K.

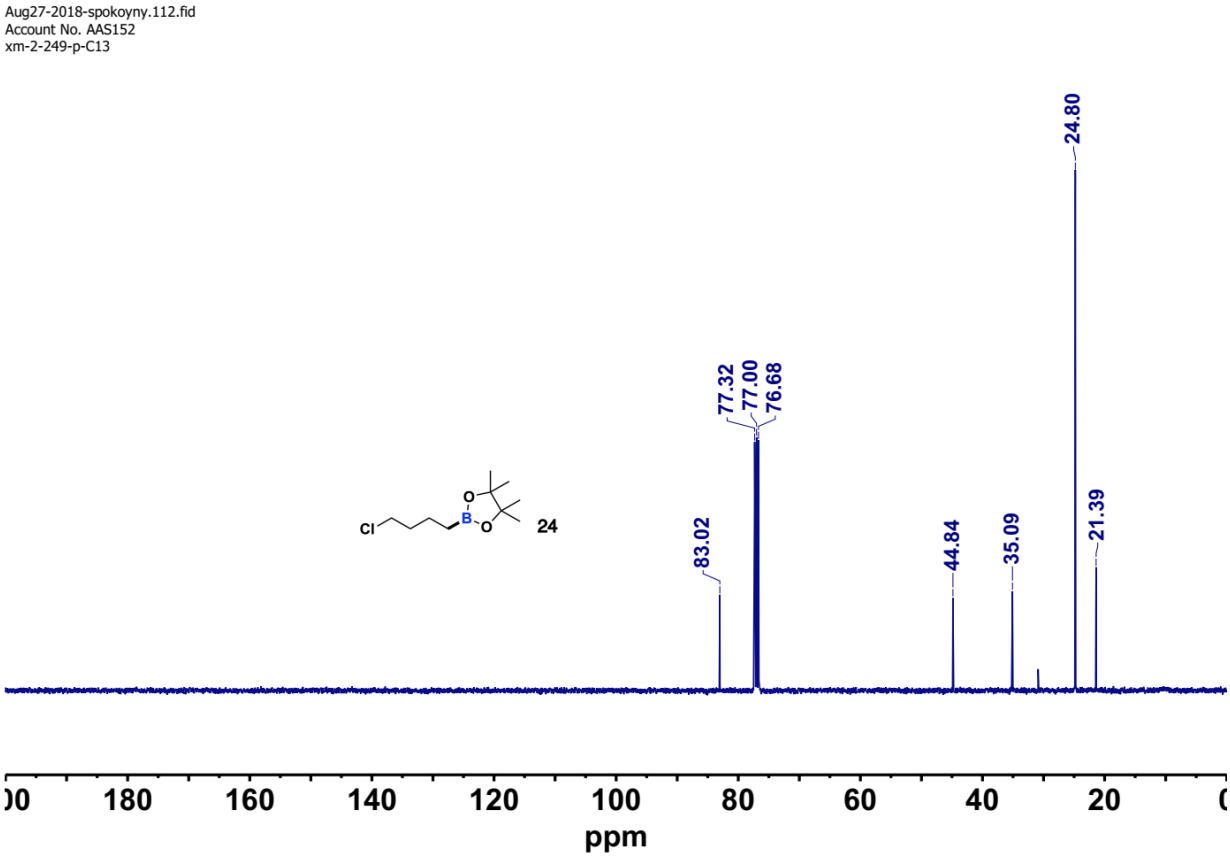


**Fig. S133**. $^{13}C$ NMR spectrum of **24** in $CDCl_3$ at 298K.

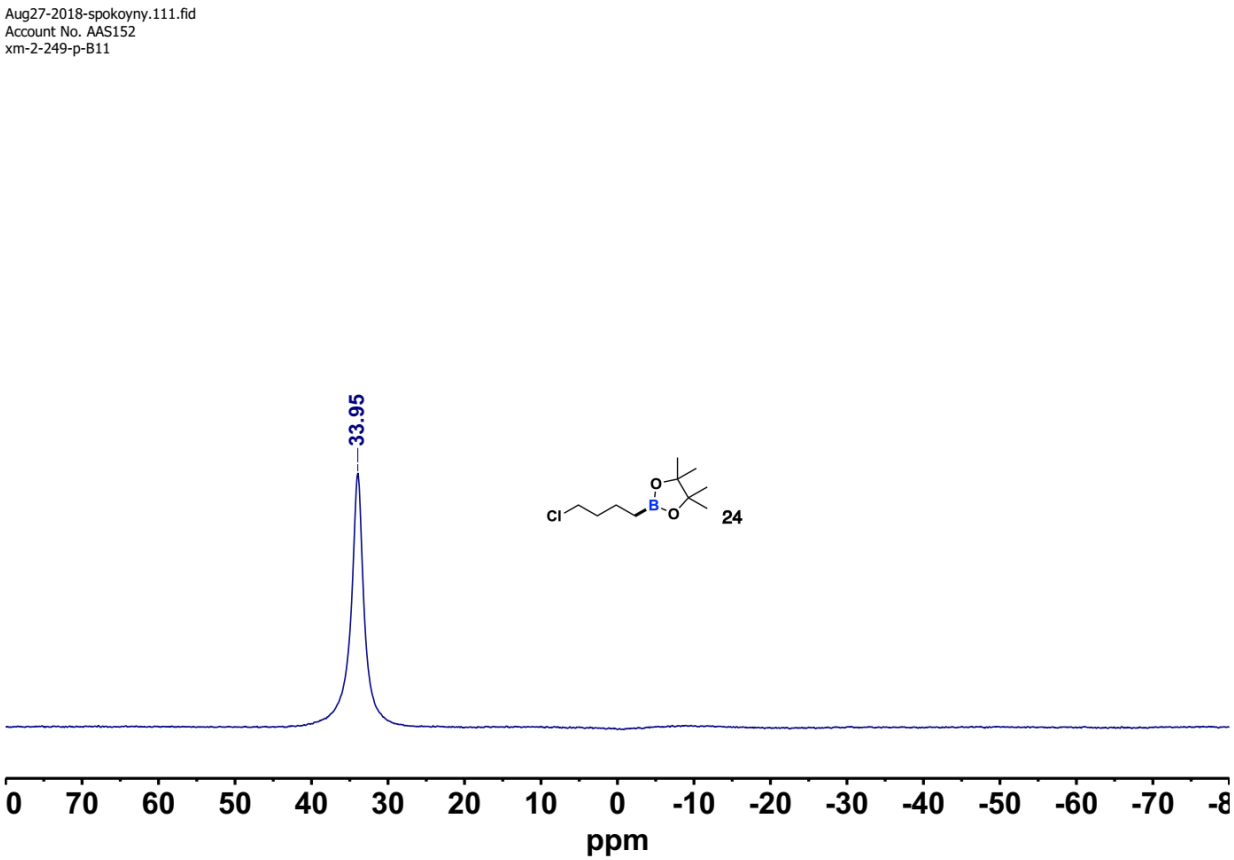


**Fig. S134**. $^{11}B$ NMR spectrum of **24** in $CDCl_3$ at 298K.

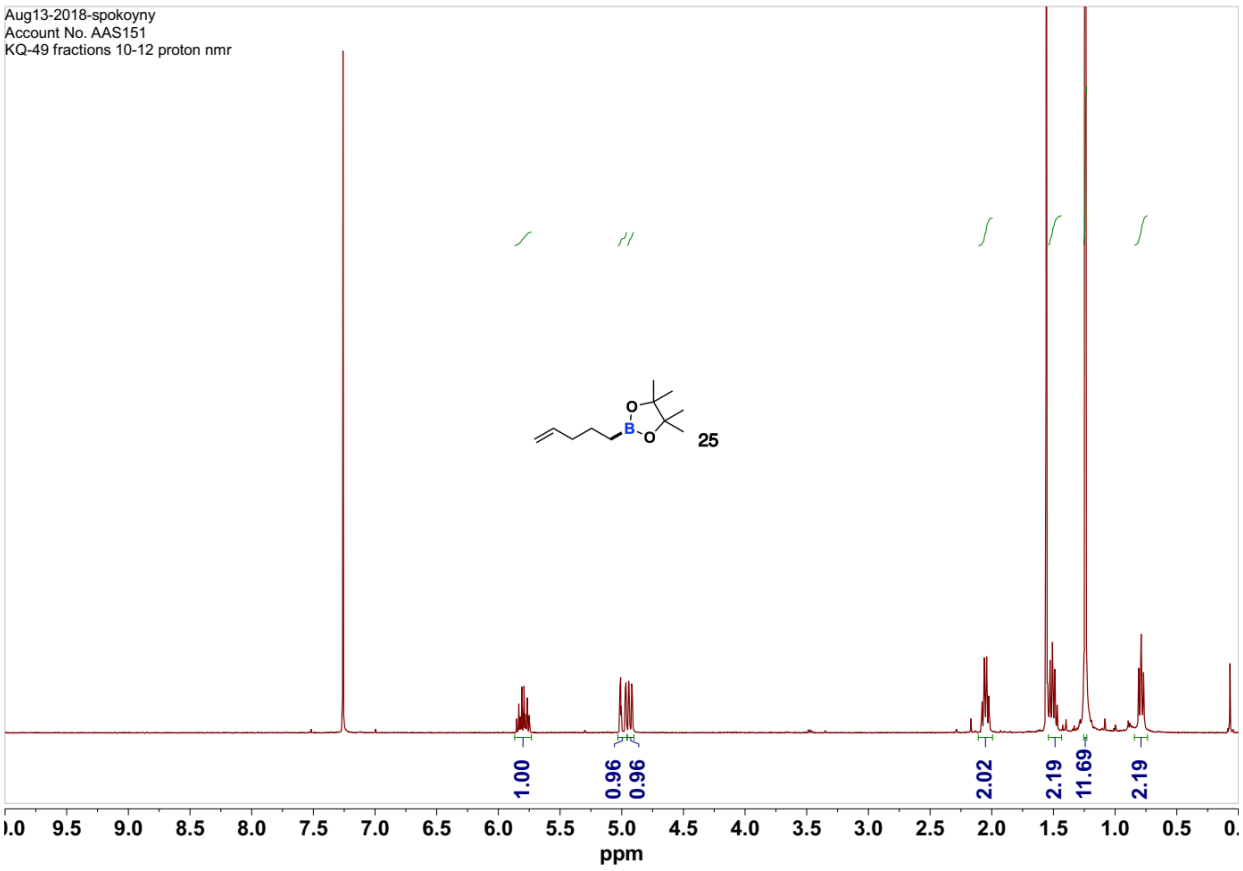


**Fig. S135**. $^{1}H$ NMR spectrum of **25** in $CDCl_3$ at 298K.

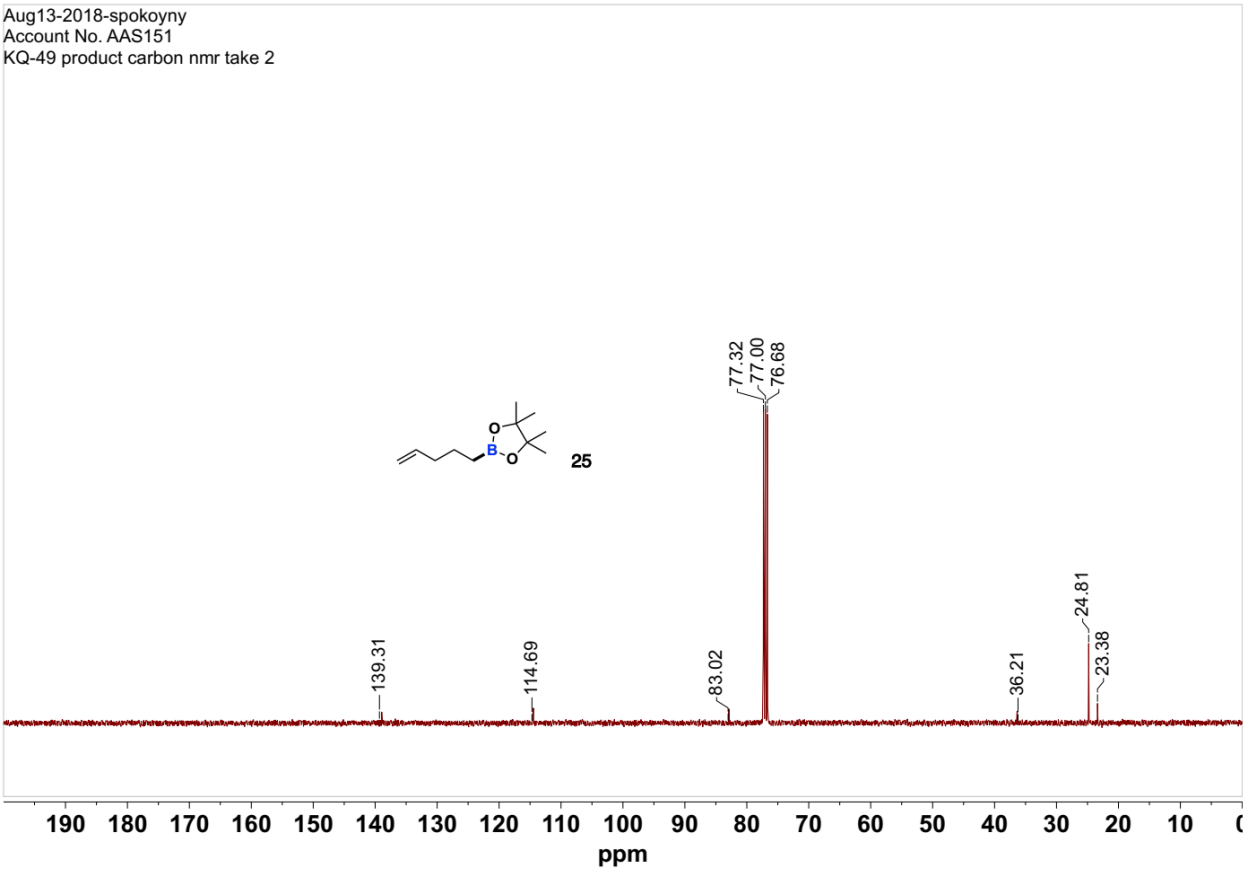


**Fig. S136**. $^{13}C\{^{1}H\}$ NMR spectrum of **25** in $CDCl_3$ at 298K.

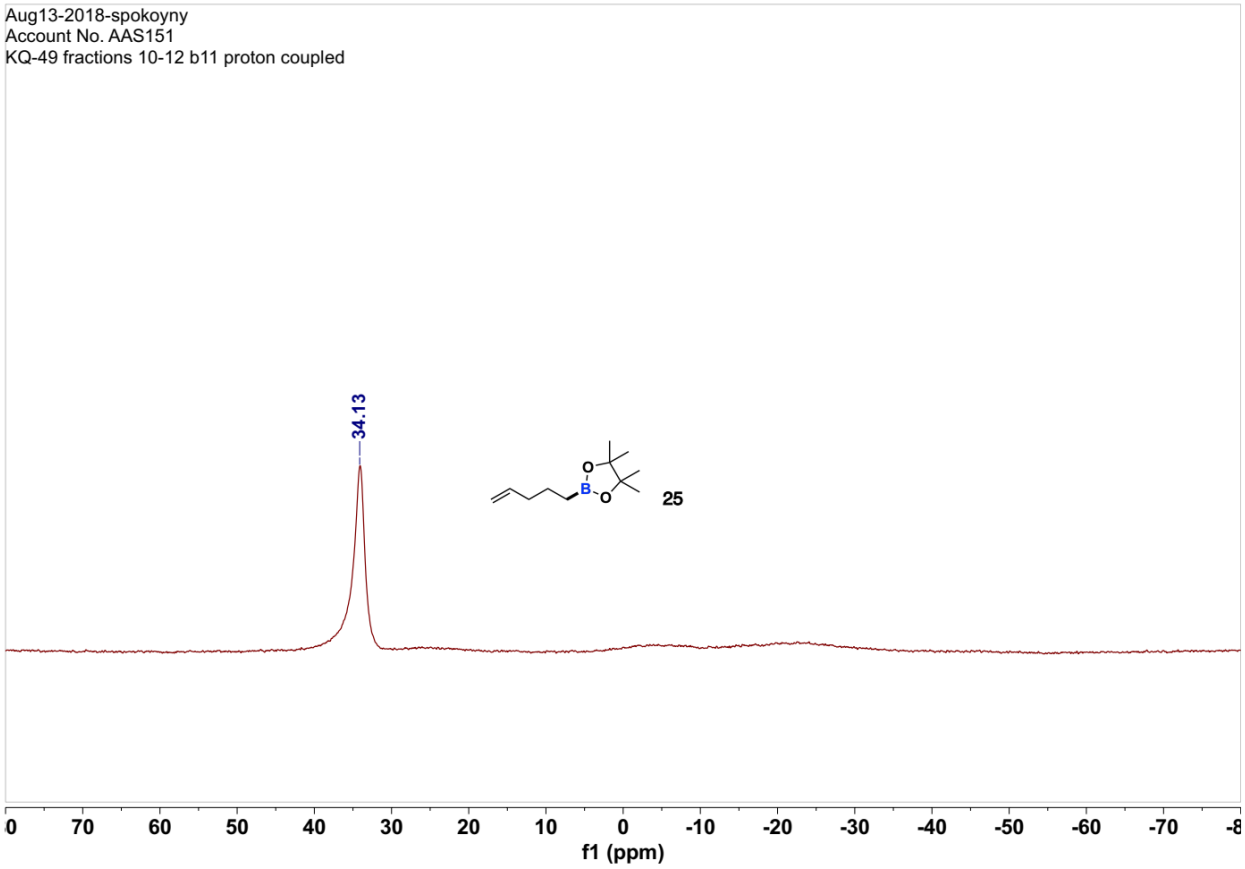


**Fig. S137**. $^{11}B$ NMR spectrum of **25** in $CDCl_3$ at 298K.

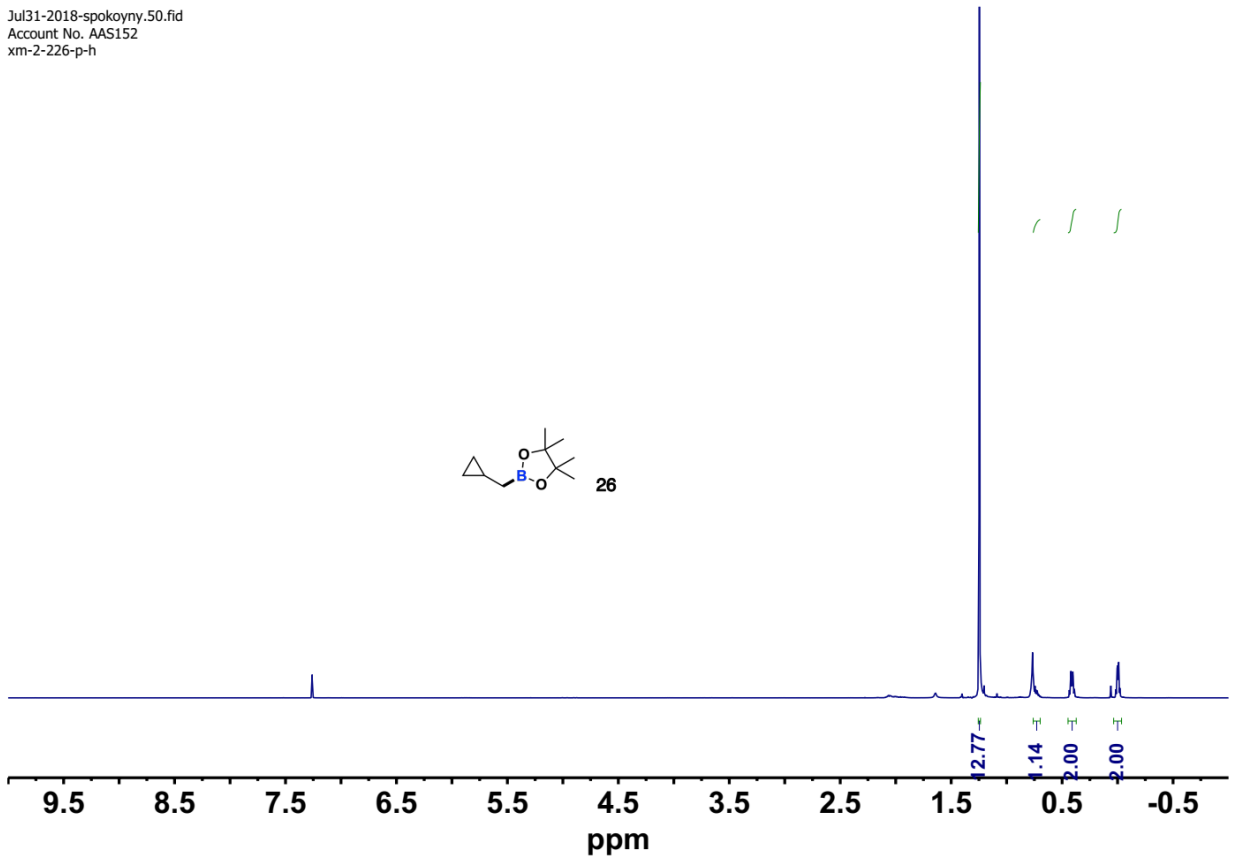


**Fig. S138**. $^{1}H$ NMR spectrum of **26** in $CDCl_3$ at 298K.

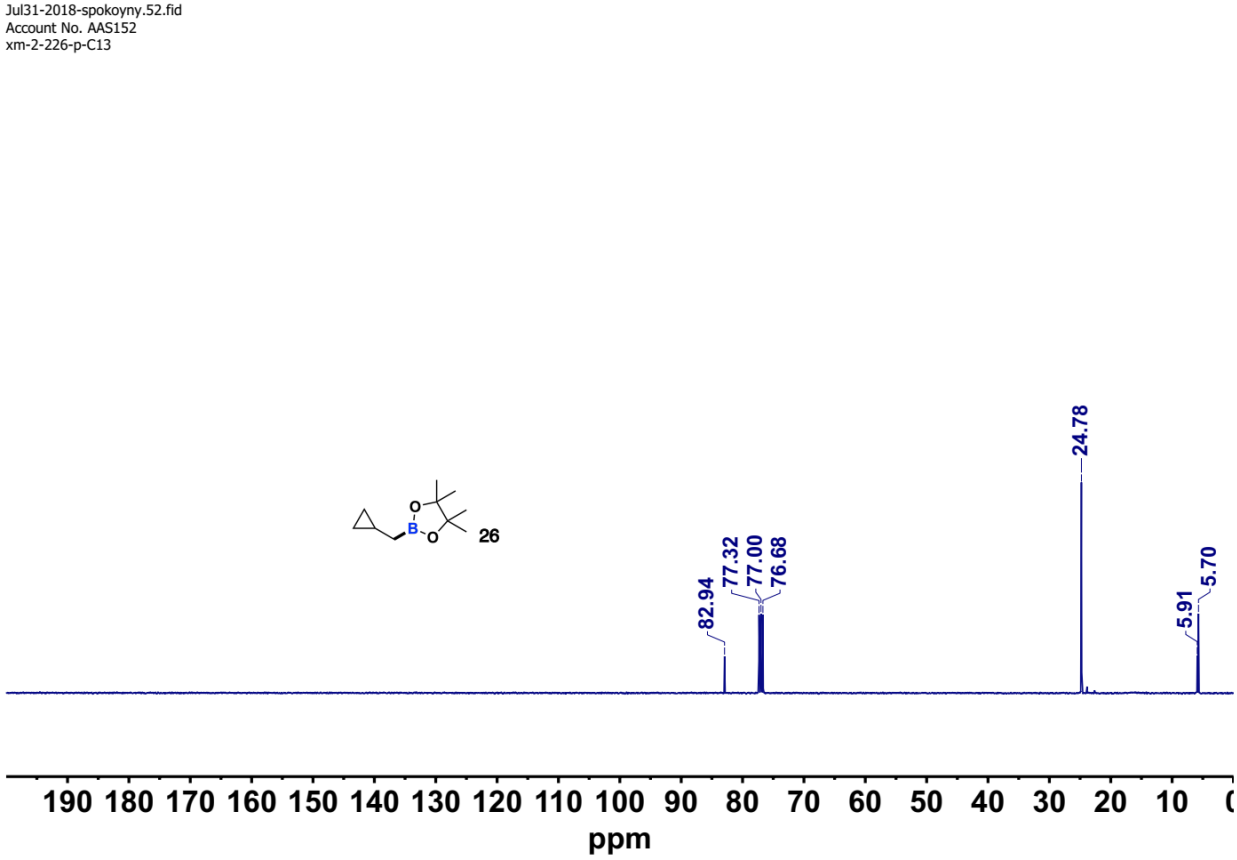


**Fig. S139**. $^{13}C\{^{1}H\}$ NMR spectrum of **26** in $CDCl_3$ at 298K.

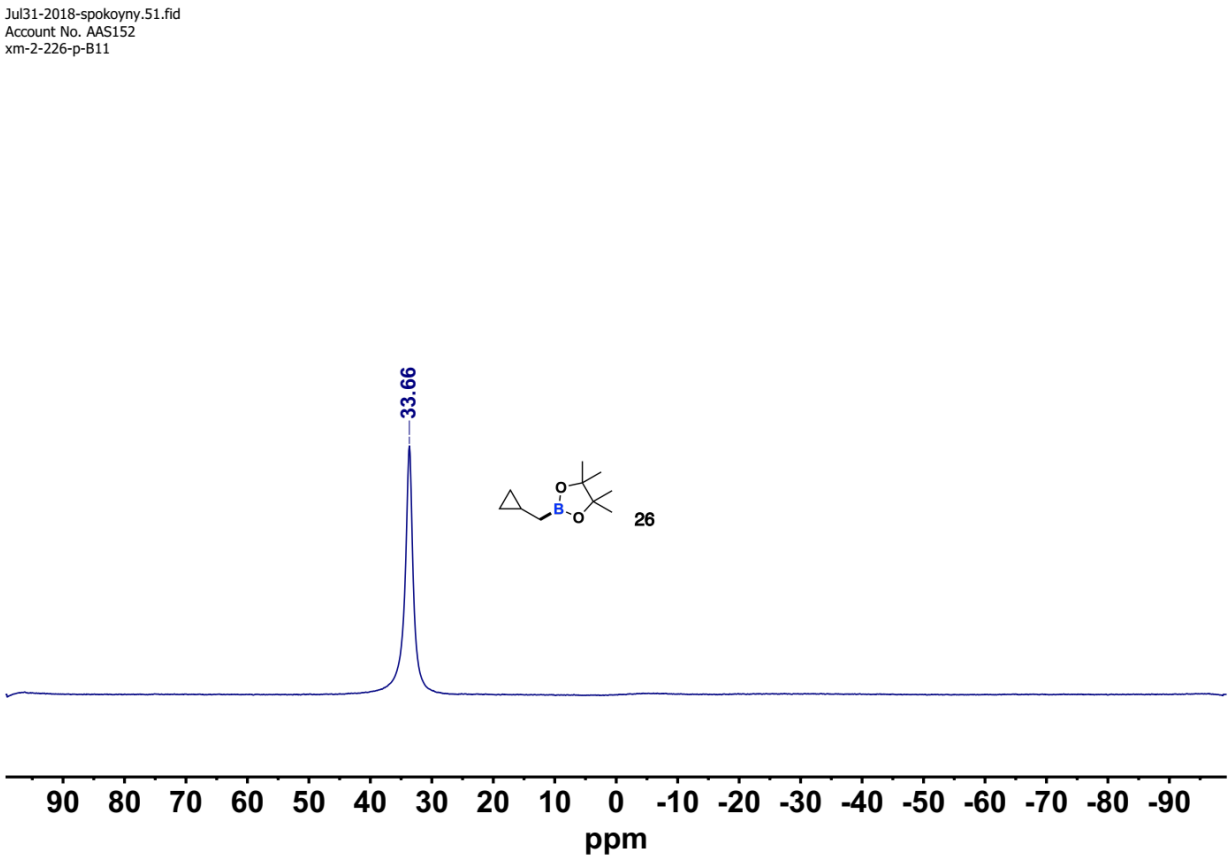


**Fig. S140**. $^{11}B$ NMR spectrum of **26** in $CDCl_3$ at 298K.

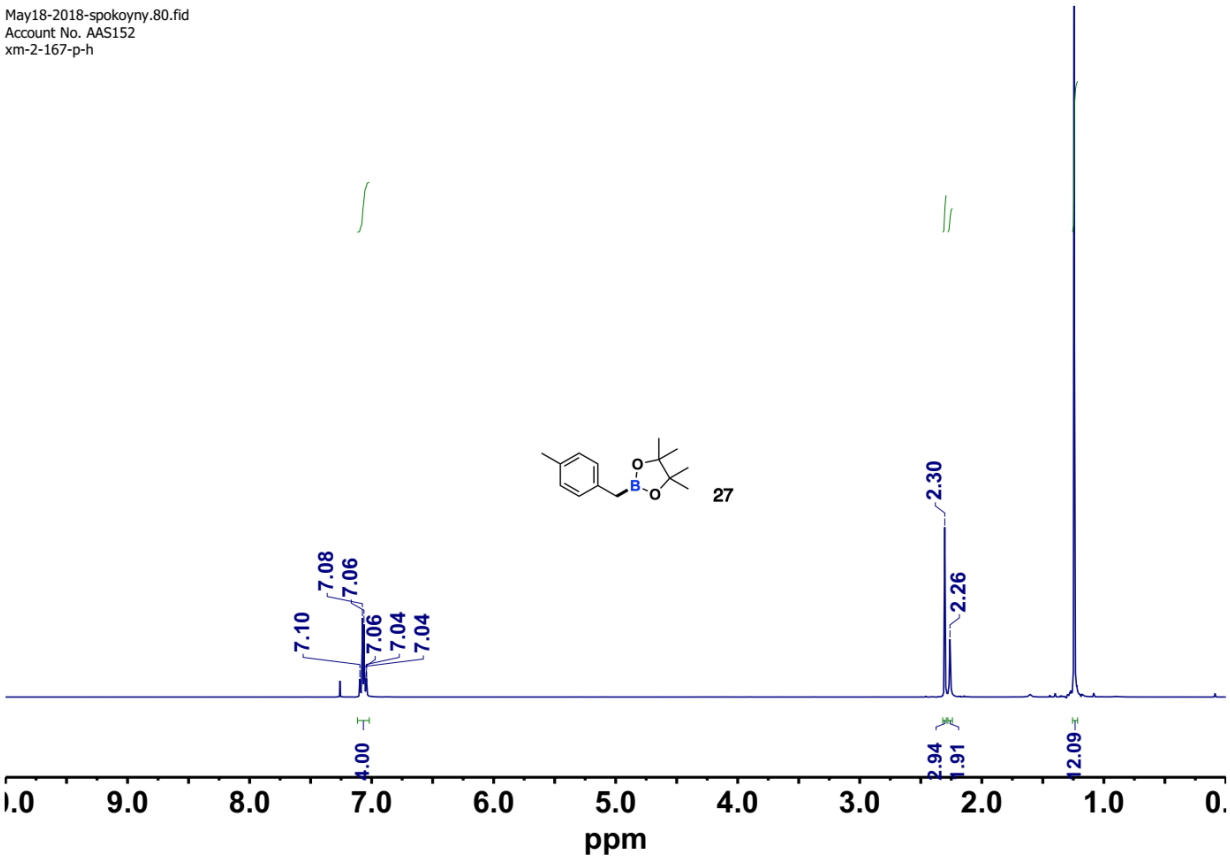


**Fig. S141**. $^{1}H$ NMR spectrum of **27** in $CDCl_3$ at 298K.

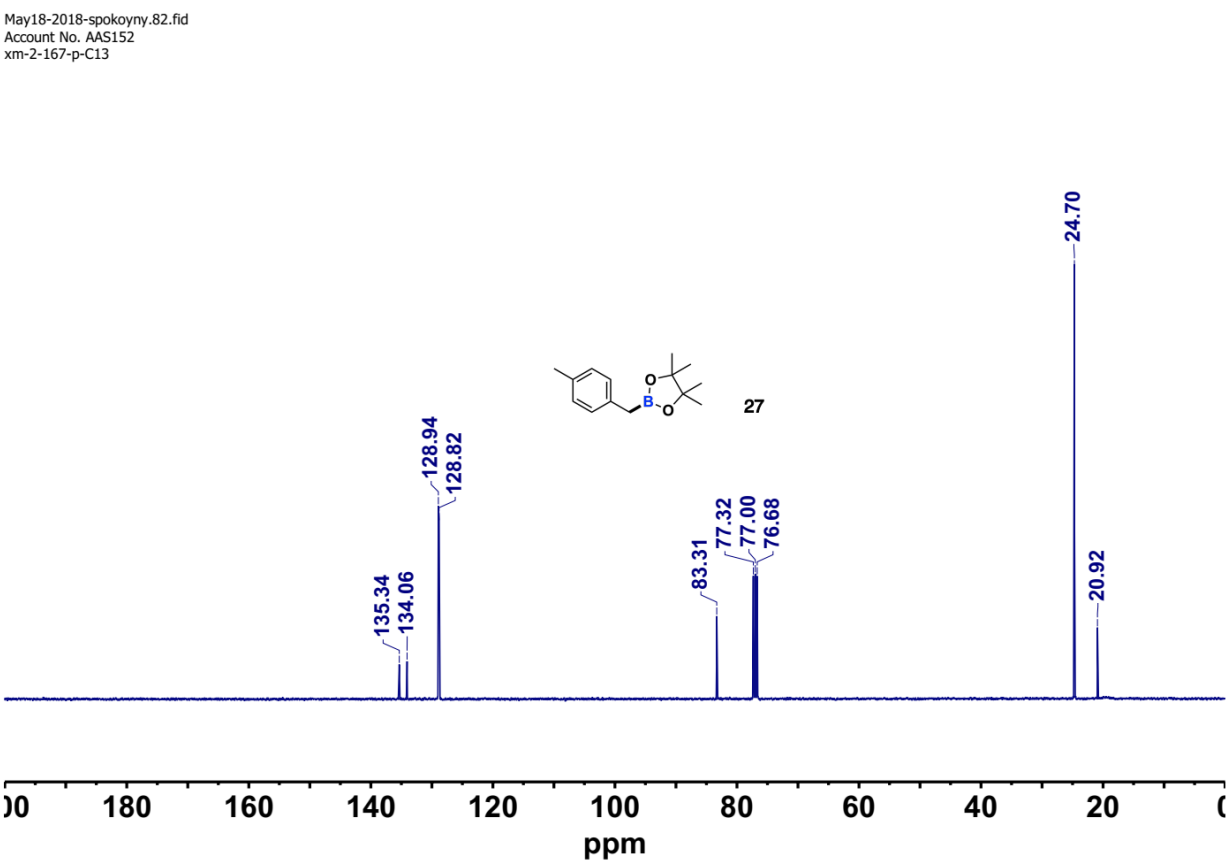


**Fig. S142**. $^{13}C\{^{1}H\}$ NMR spectrum of **27** in $CDCl_3$ at 298K.

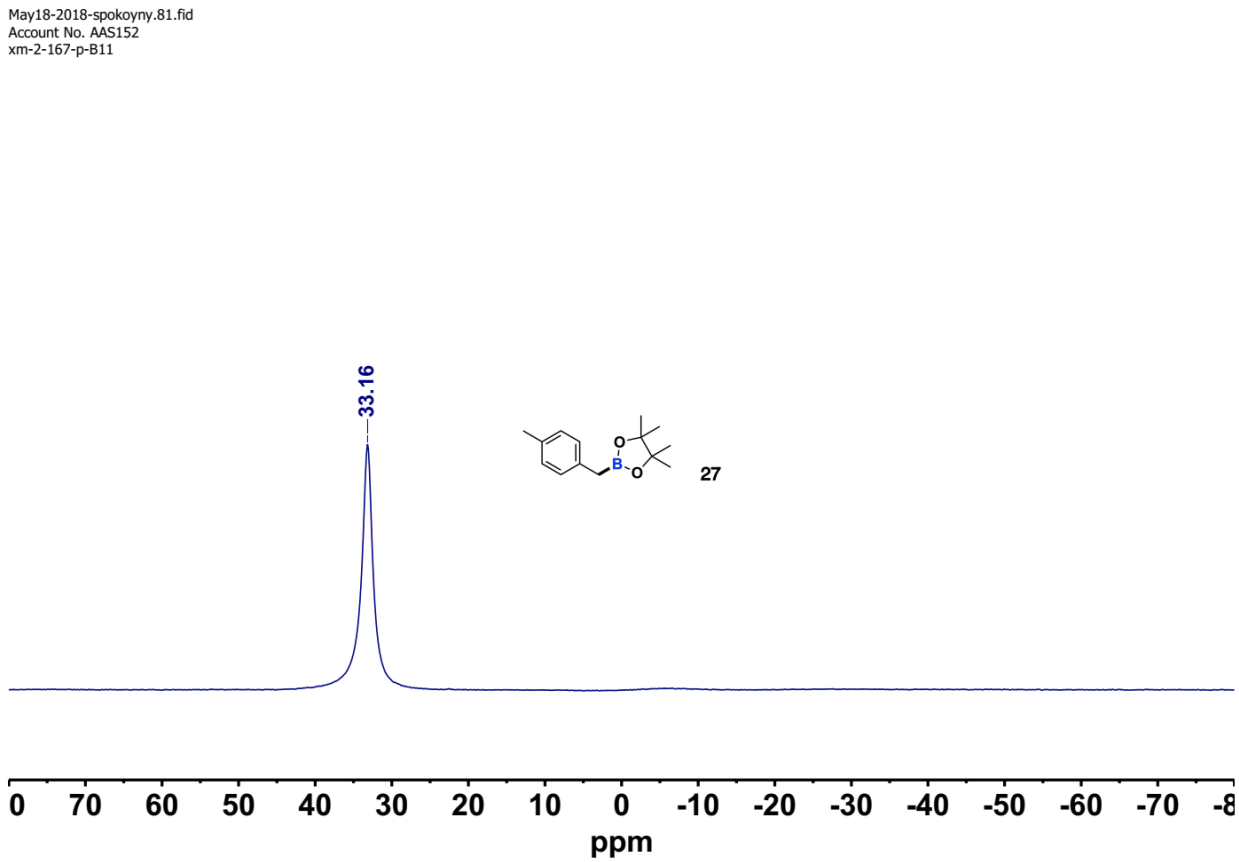


**Fig. S143**. $^{11}B$ NMR spectrum of **27** in $CDCl_3$ at 298K.

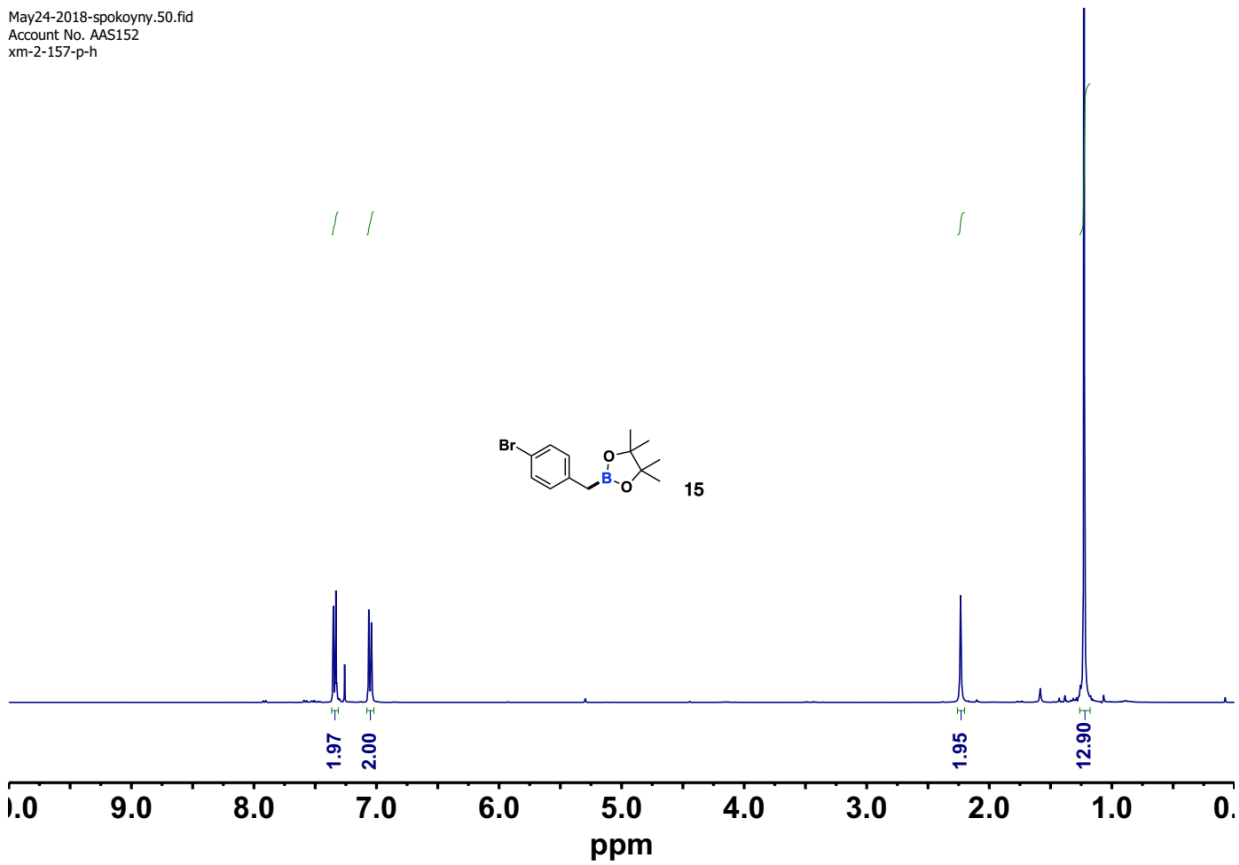


**Fig. S144**. $^{1}H$ NMR spectrum of **15** in $CDCl_3$ at 298K.

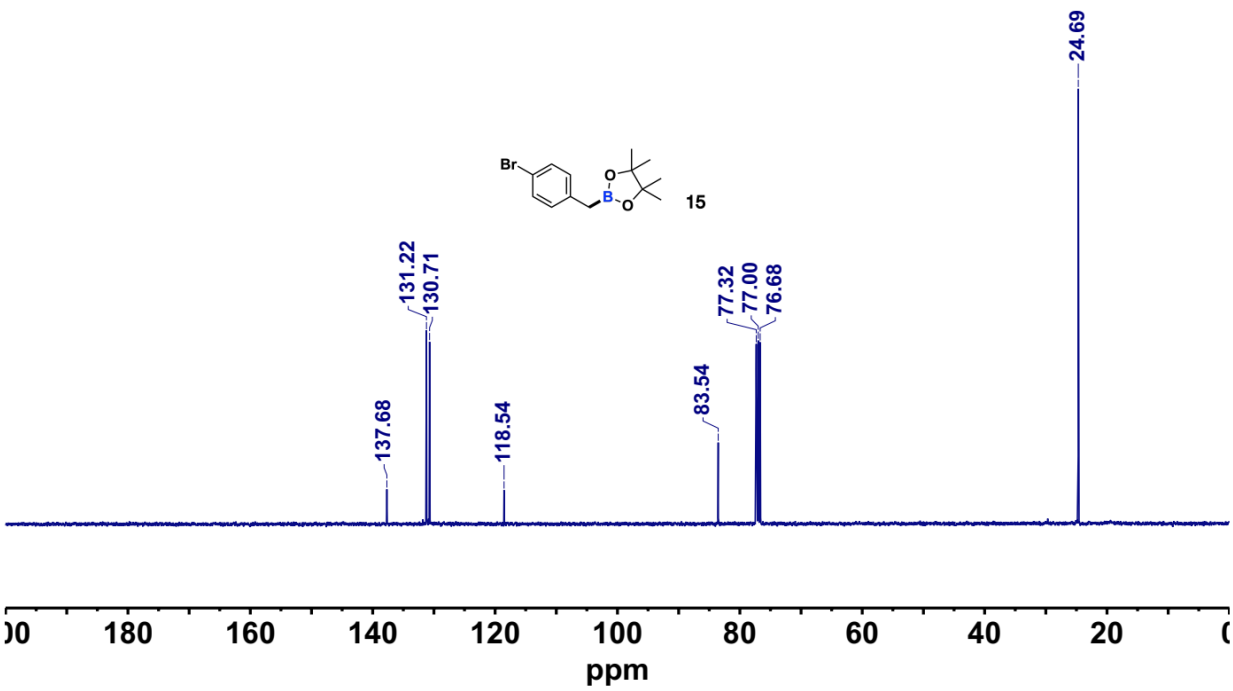


**Fig. S145**. $^{13}C\{^{1}H\}$ NMR spectrum of **15** in $CDCl_3$ at 298K.

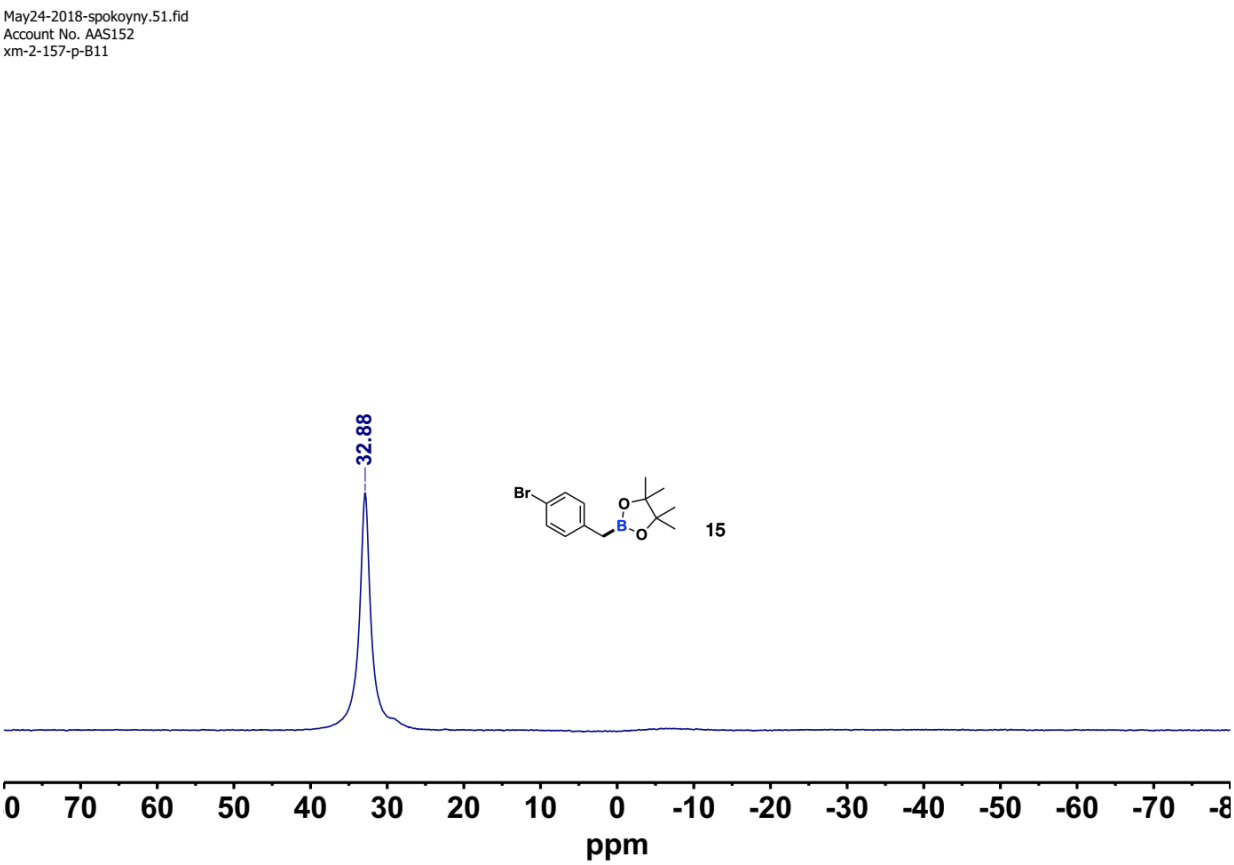


**Fig. S146**. $^{11}B$ NMR spectrum of **15** in $CDCl_3$ at 298K.

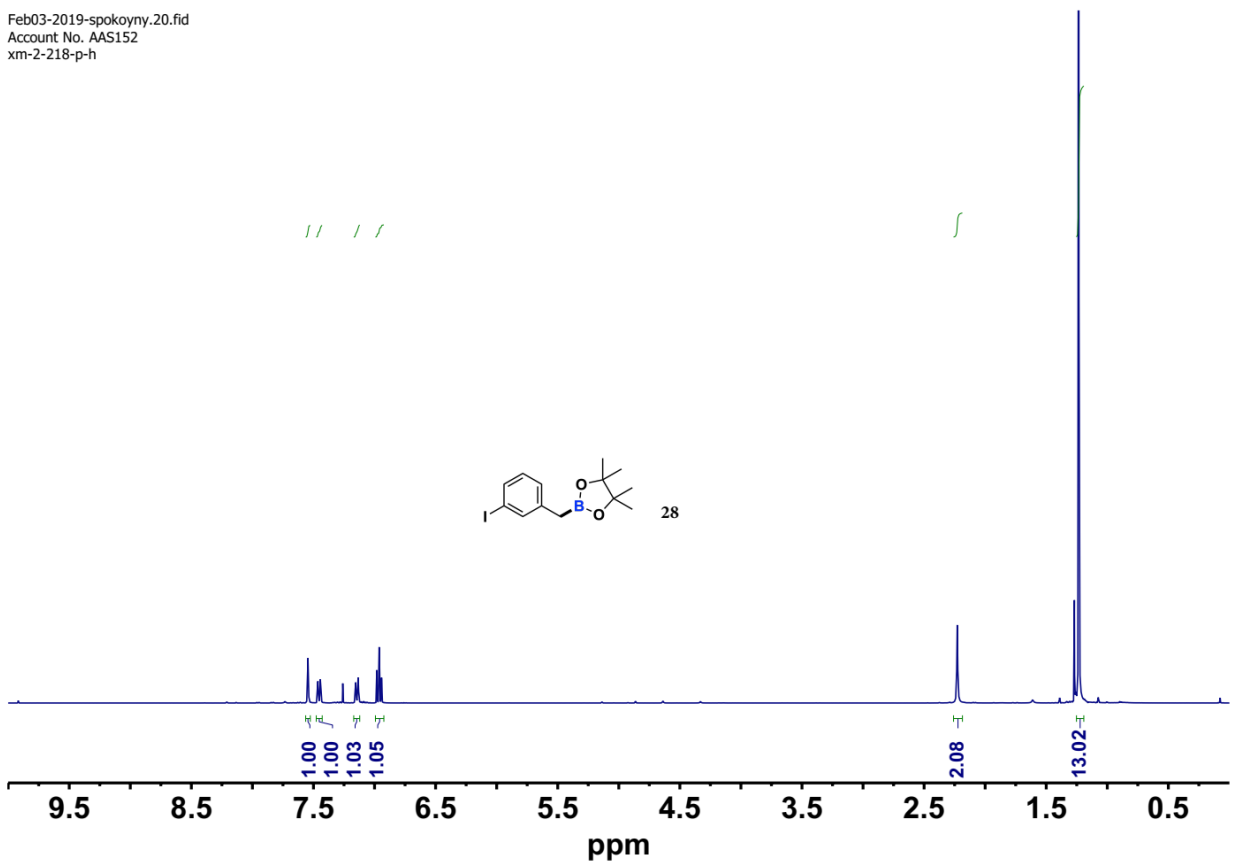


**Fig. S147**. $^{1}H$ NMR spectrum of **28** in $CDCl_3$ at 298K.

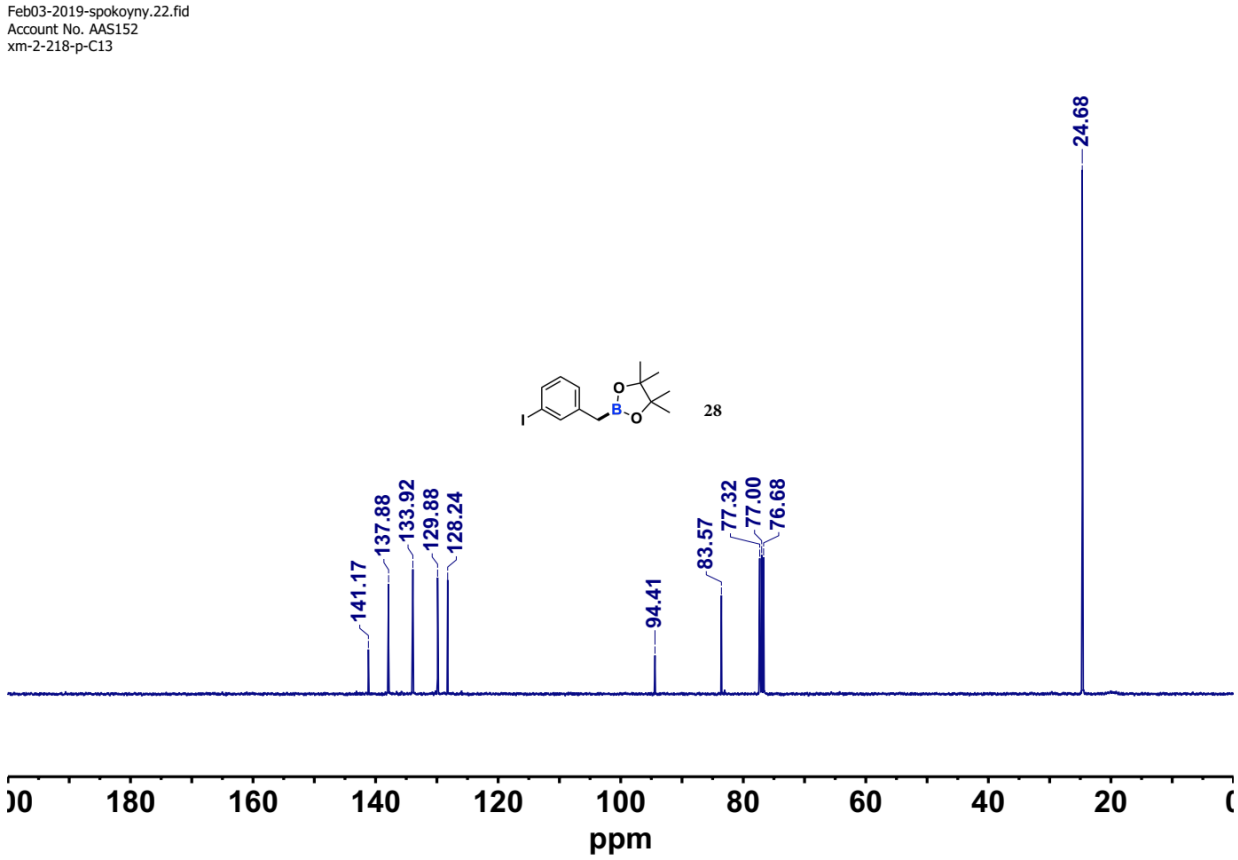


**Fig. S148**. $^{13}C\{^{1}H\}$ NMR spectrum of **28** in $CDCl_3$ at 298K.

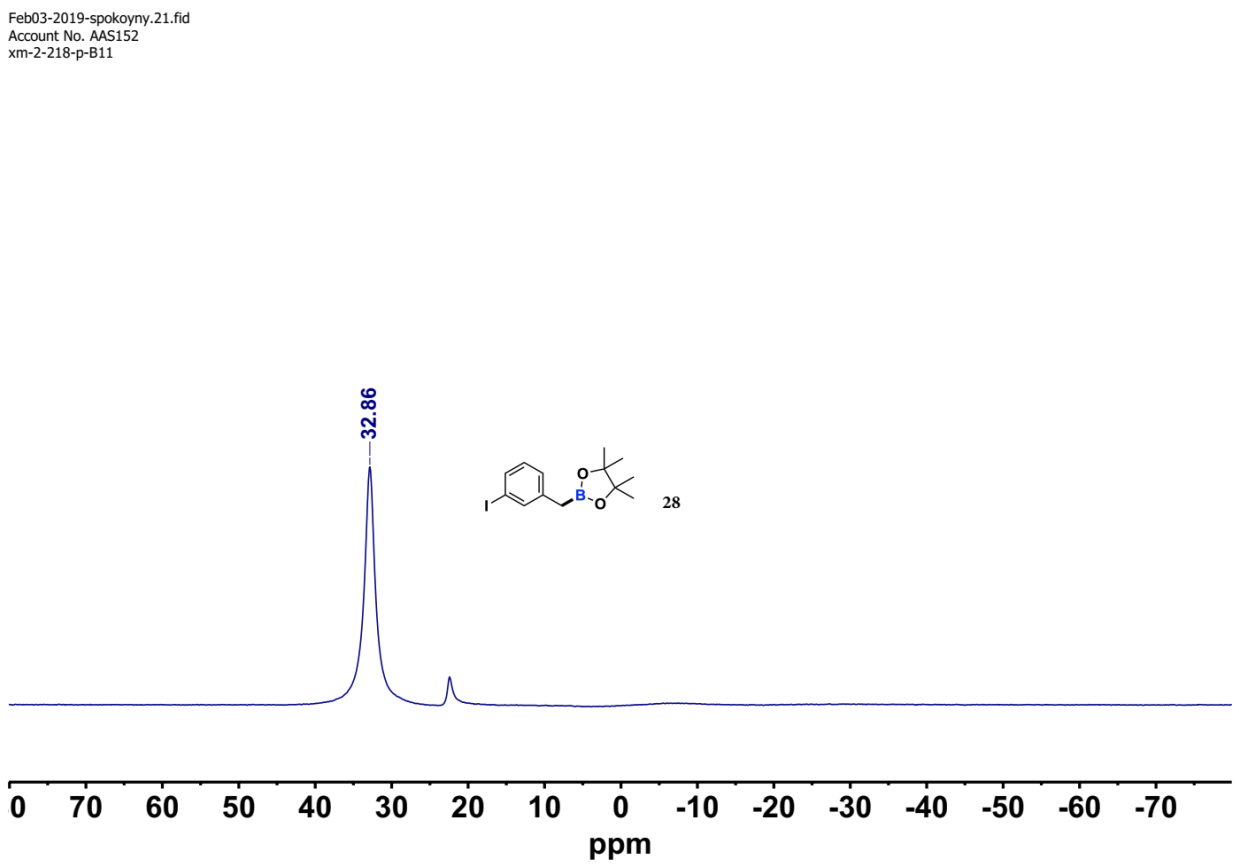


**Fig. S149**. $^{11}B$ NMR spectrum of **28** in $CDCl_3$ at 298K.

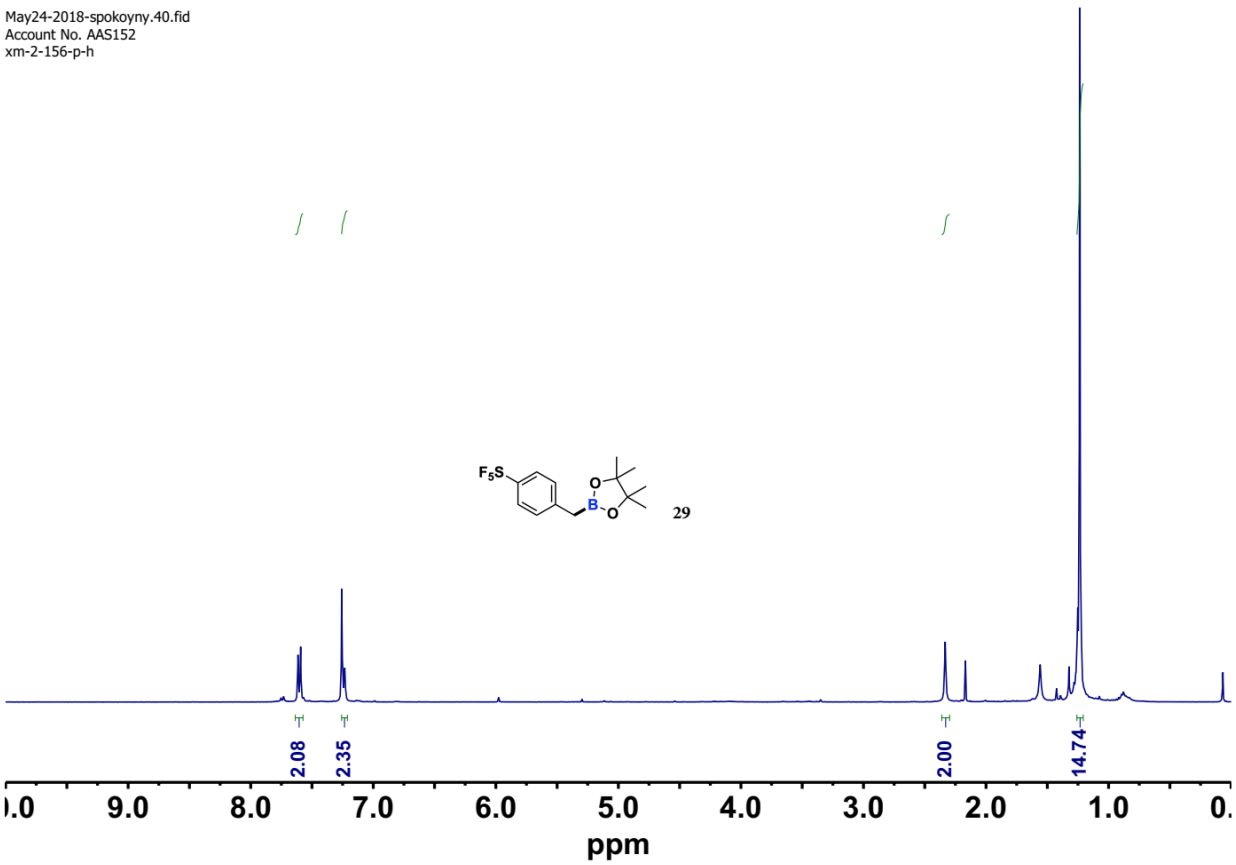


**Fig. S150**. $^{1}$H NMR spectrum of **29** in $CDCl_3$ at 298K.

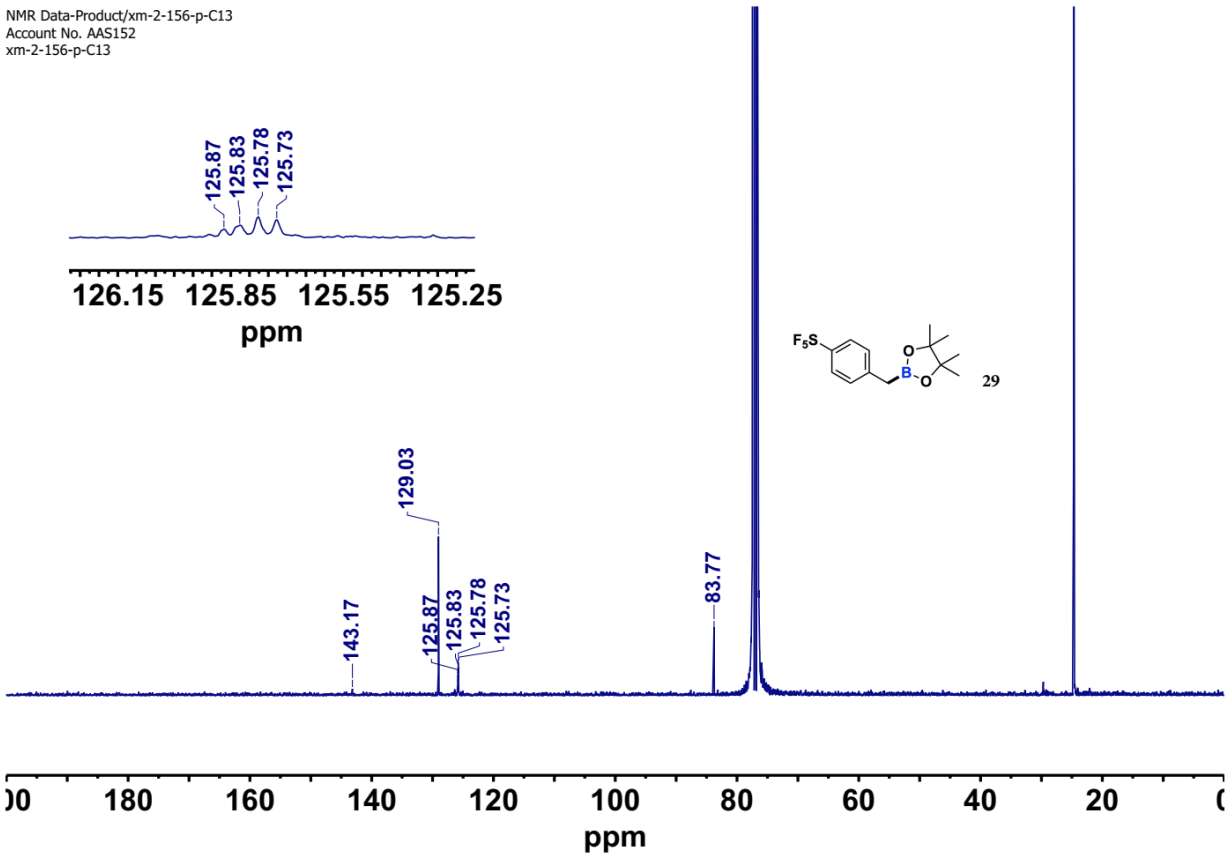


**Fig. S151**. $^{13}C$ NMR spectrum of **29** in $CDCl_3$ at 298K.

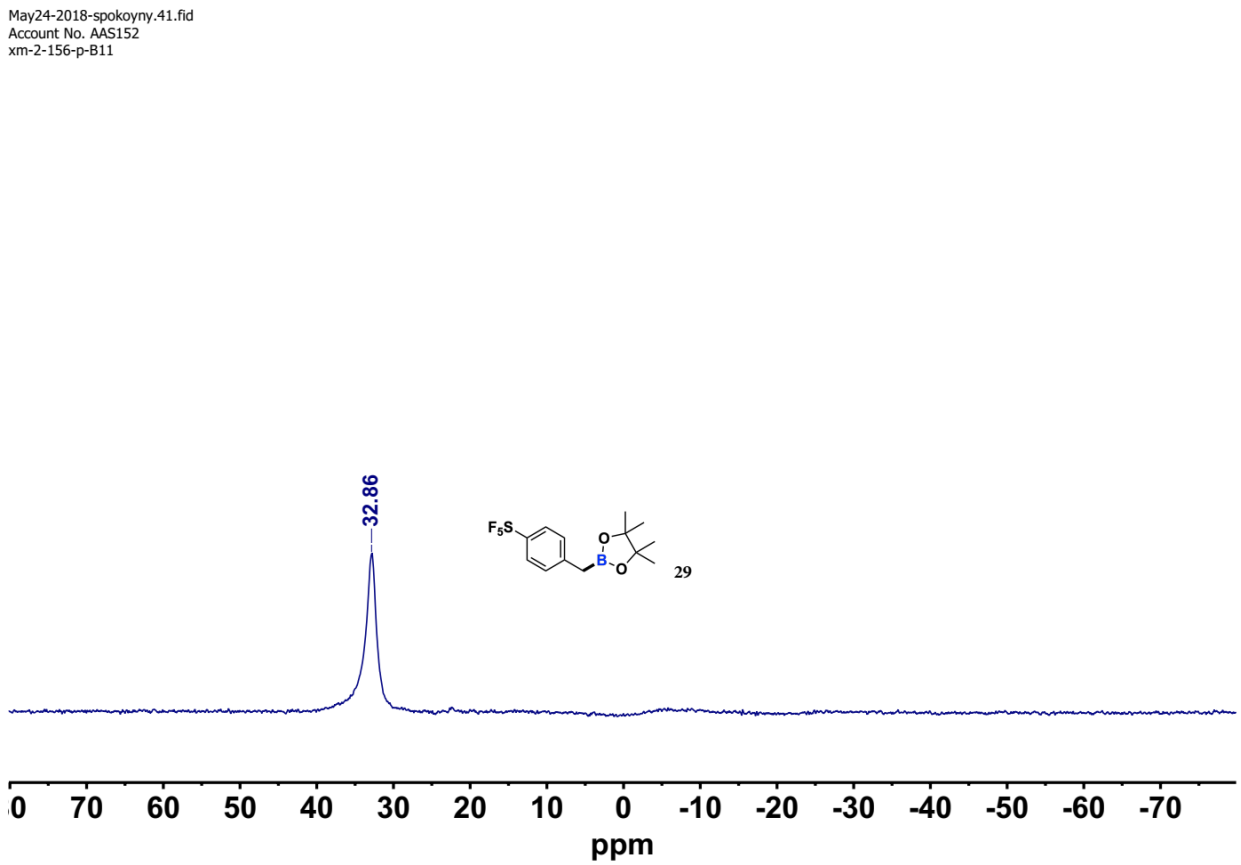


**Fig. S152**. $^{11}B$ NMR spectrum of **29** in $CDCl_3$ at 298K.

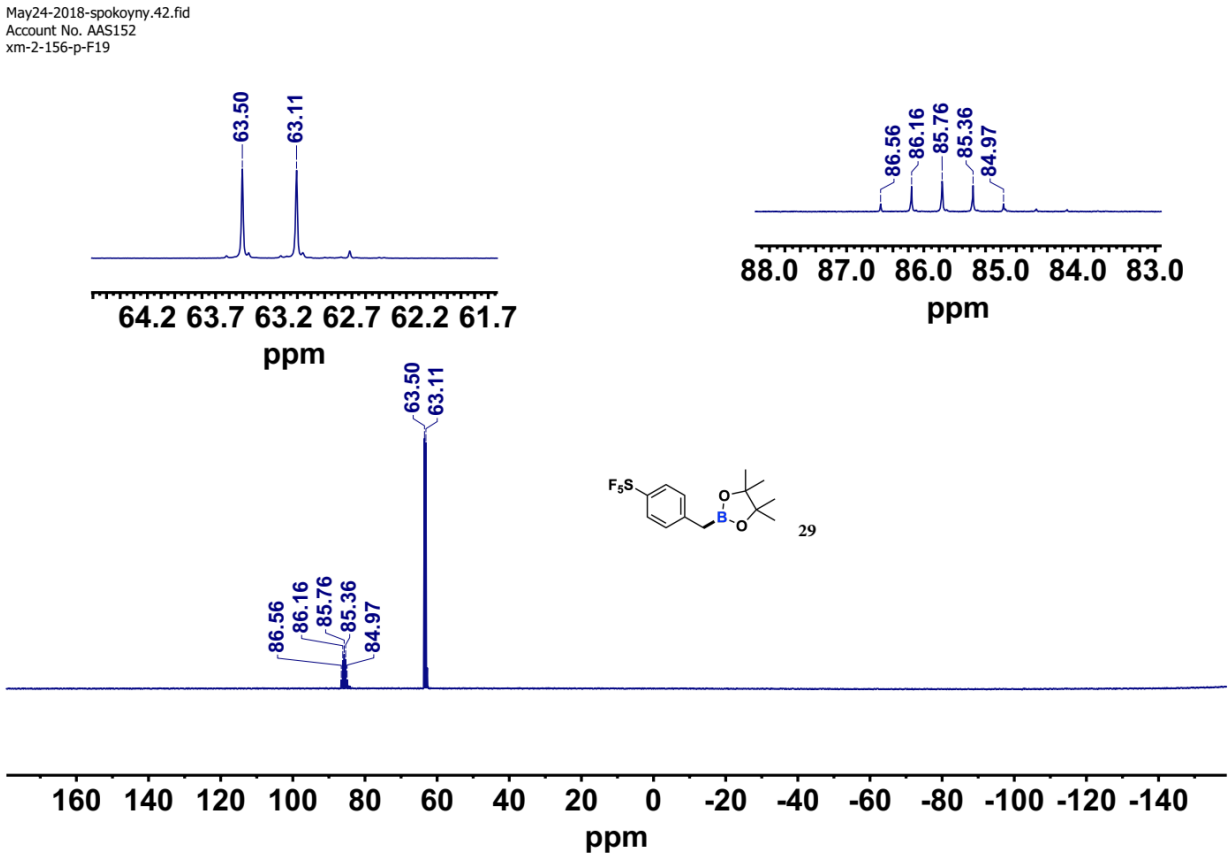


**Fig. S153**. $^{19}F$ NMR spectrum of **29** in $CDCl_3$ at 298K.

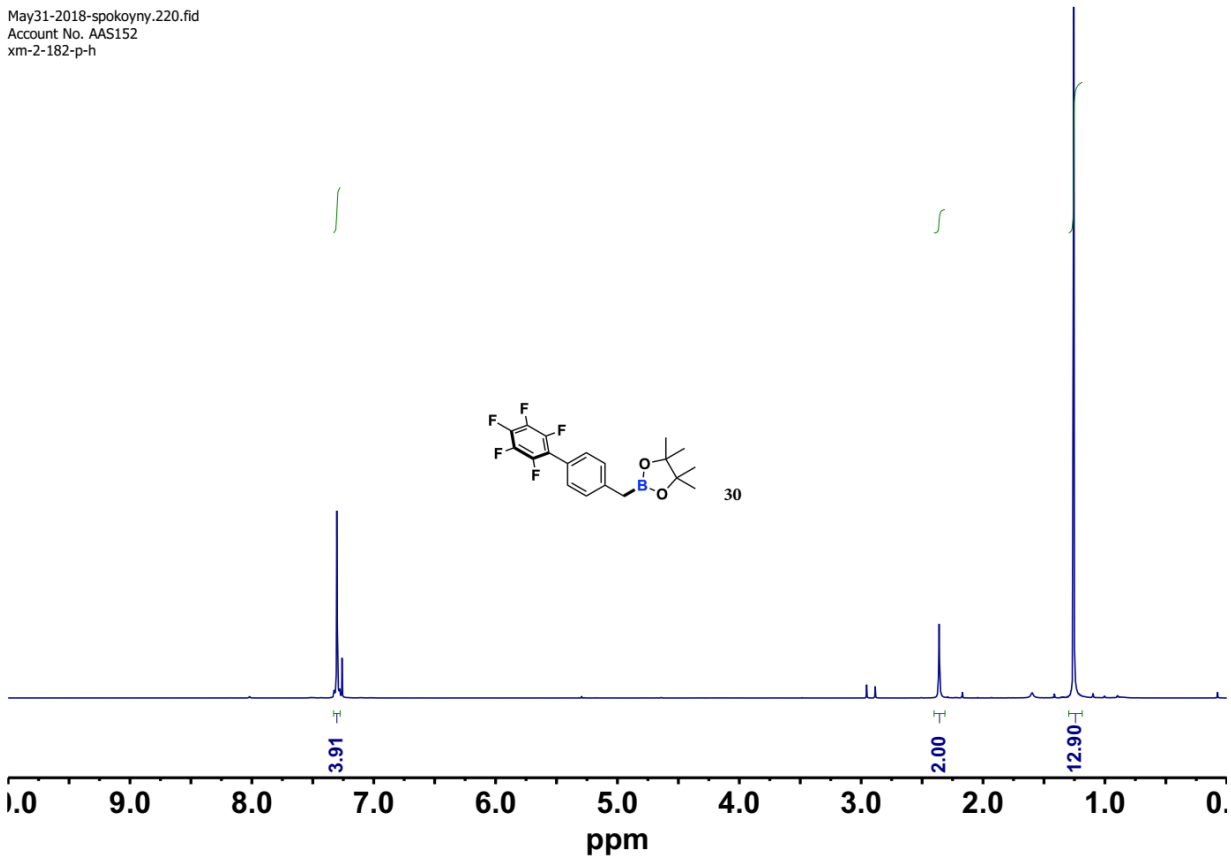


**Fig. S154**. $^{1}H$ NMR spectrum of **30** in $CDCl_3$ at 298K.

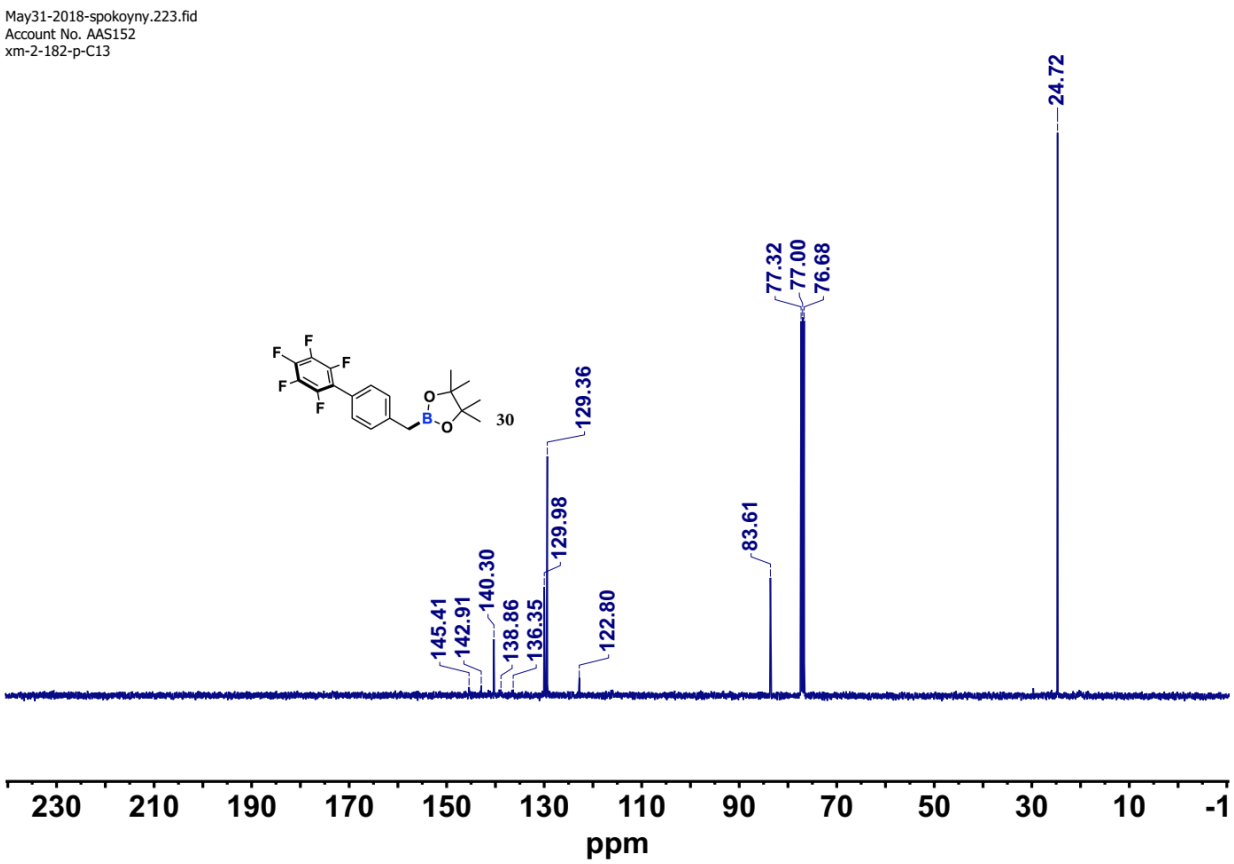


**Fig. S155**. $^{13}C\{^{1}H\}$ NMR spectrum of **30** in $CDCl_3$ at 298K.

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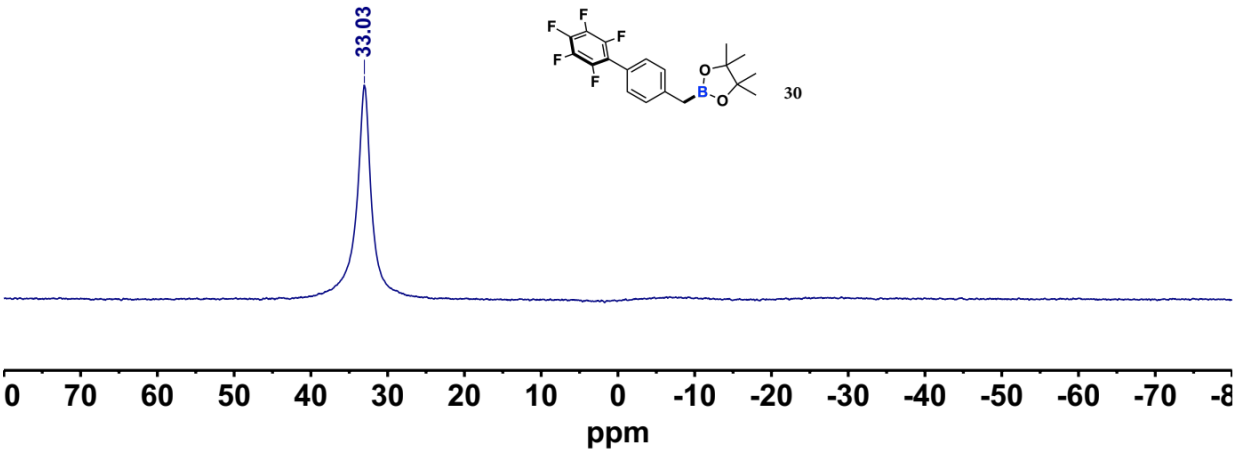


**Fig. S156**. $^{11}B$ NMR spectrum of **30** in $CDCl_3$ at 298K.

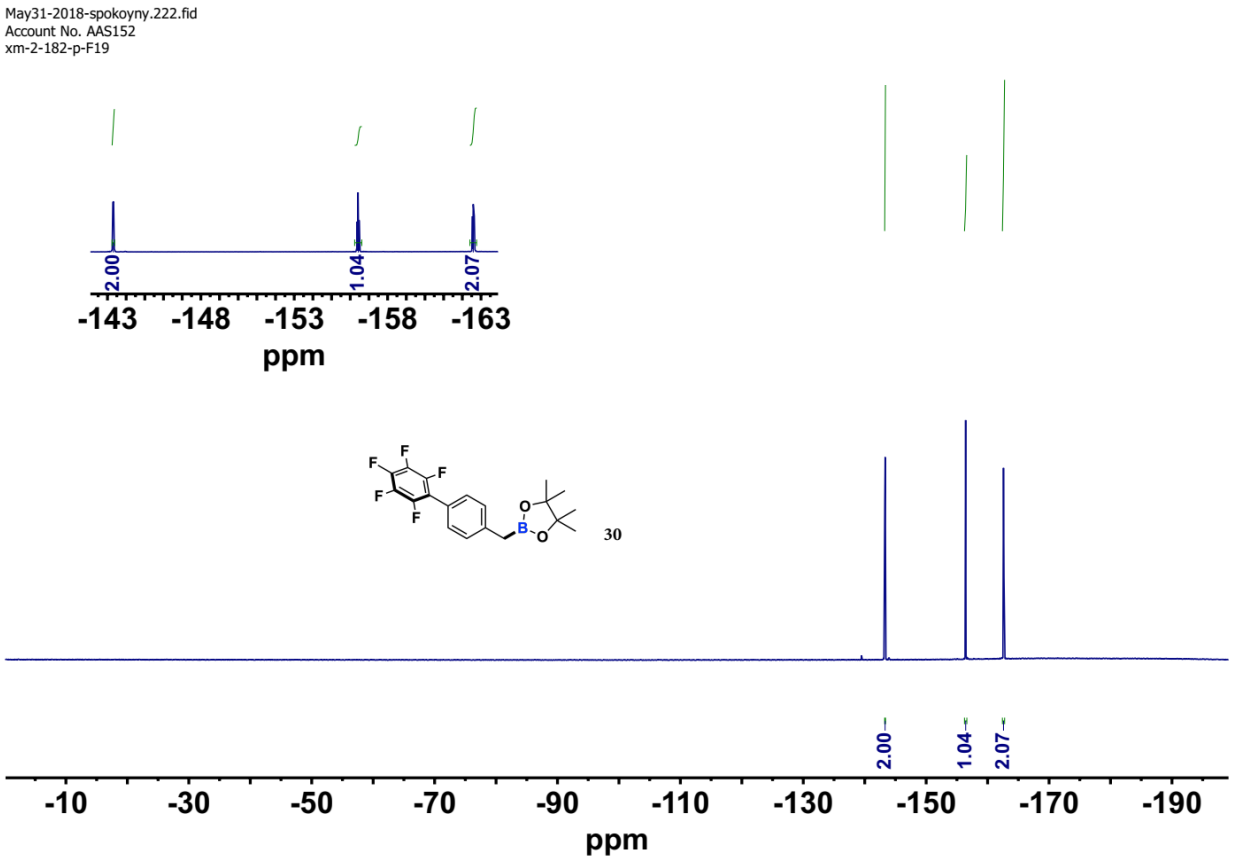


**Fig. S157**. $^{19}F$ NMR spectrum of **30** in $CDCl_3$ at 298K.

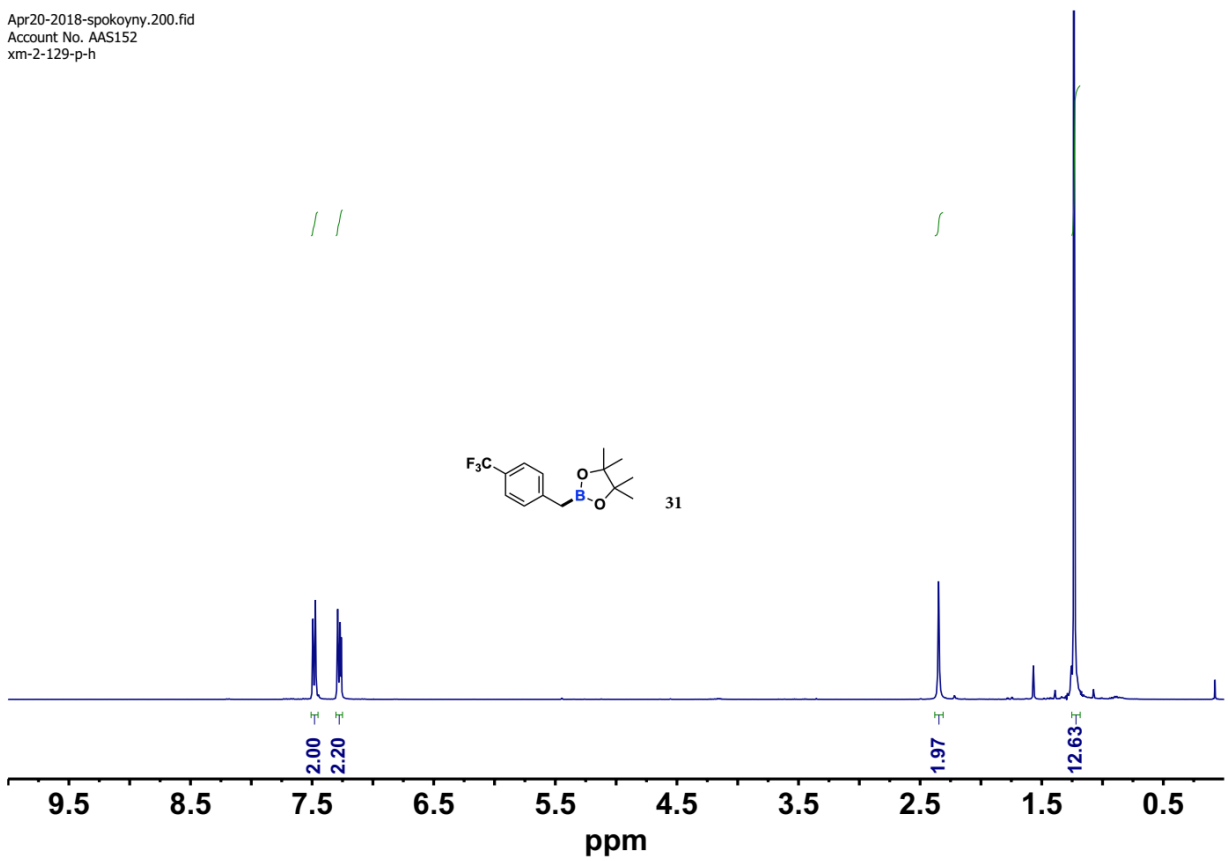


**Fig. S158**. $^{1}$H NMR spectrum of **31** in $CDCl_3$ at 298K.

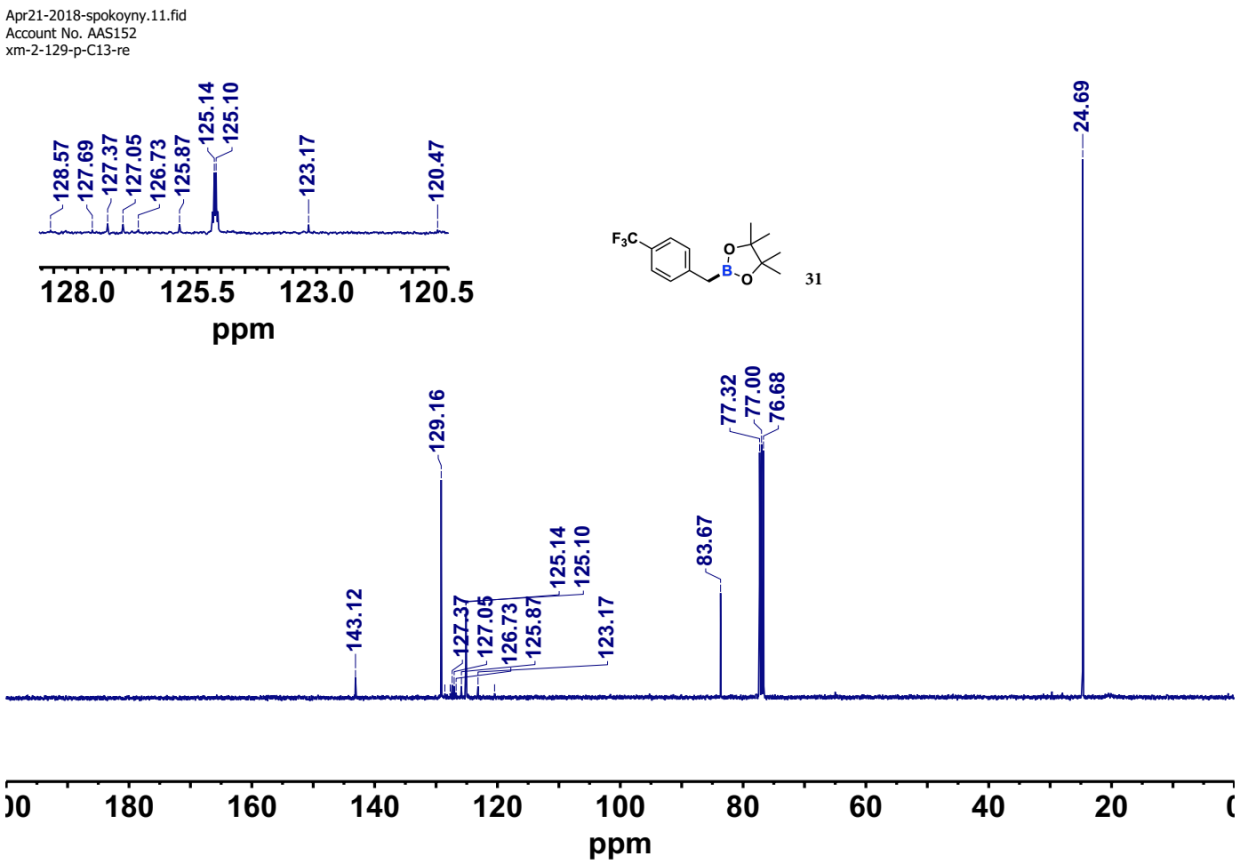


**Fig. S159**. $^{13}C\{^{1}H\}$ NMR spectrum of **31** in $CDCl_3$ at 298K.

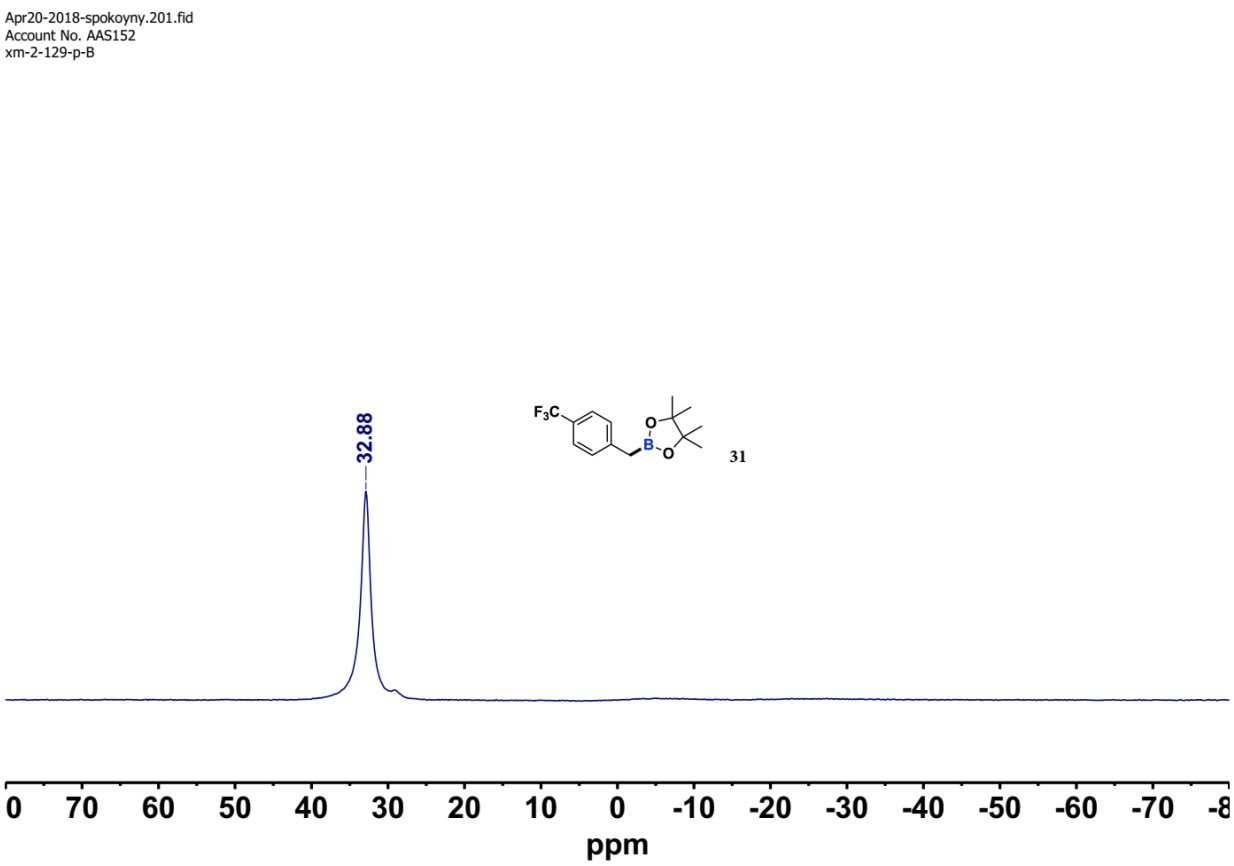


**Fig. S160**. $^{11}B$ NMR spectrum of **31** in $CDCl_3$ at 298K.

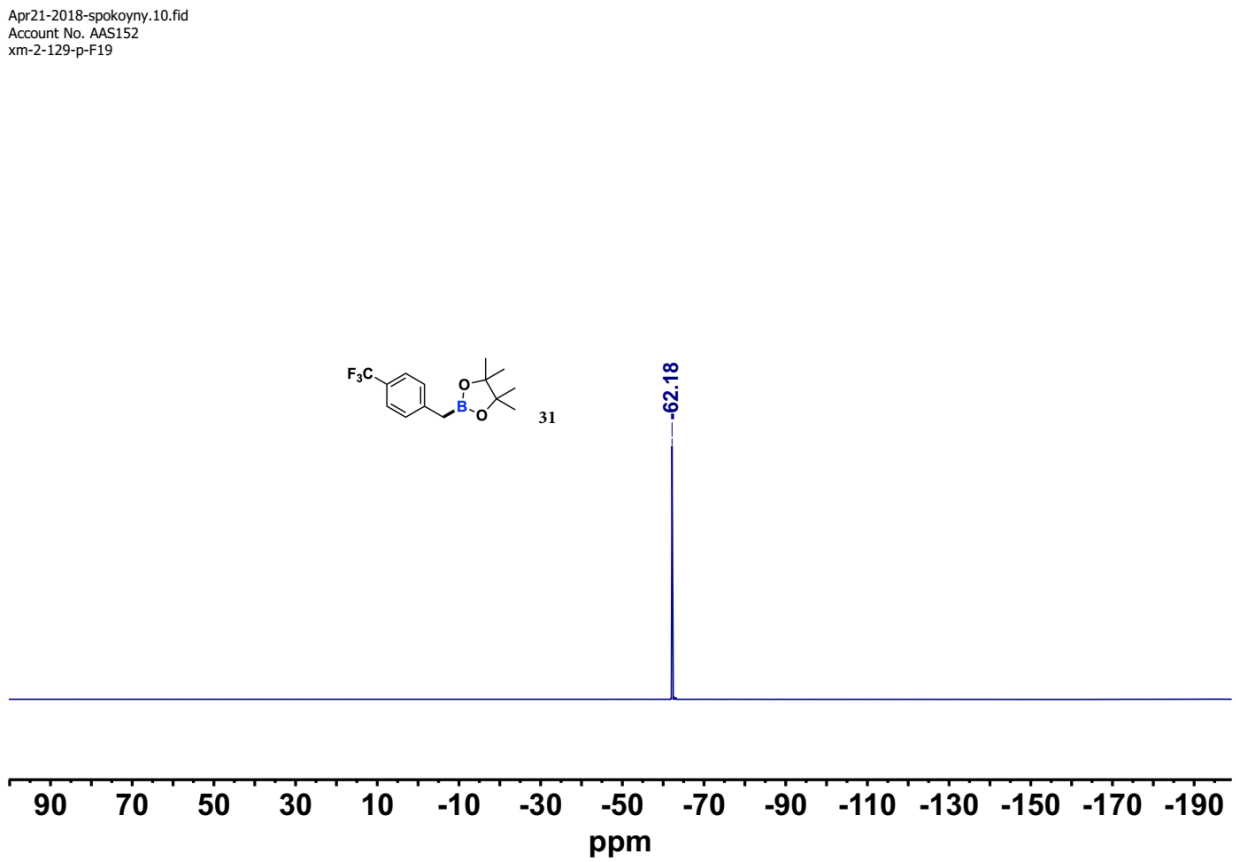


**Fig. S161**. $^{19}F$ NMR spectrum of **31** in $CDCl_3$ at 298K.

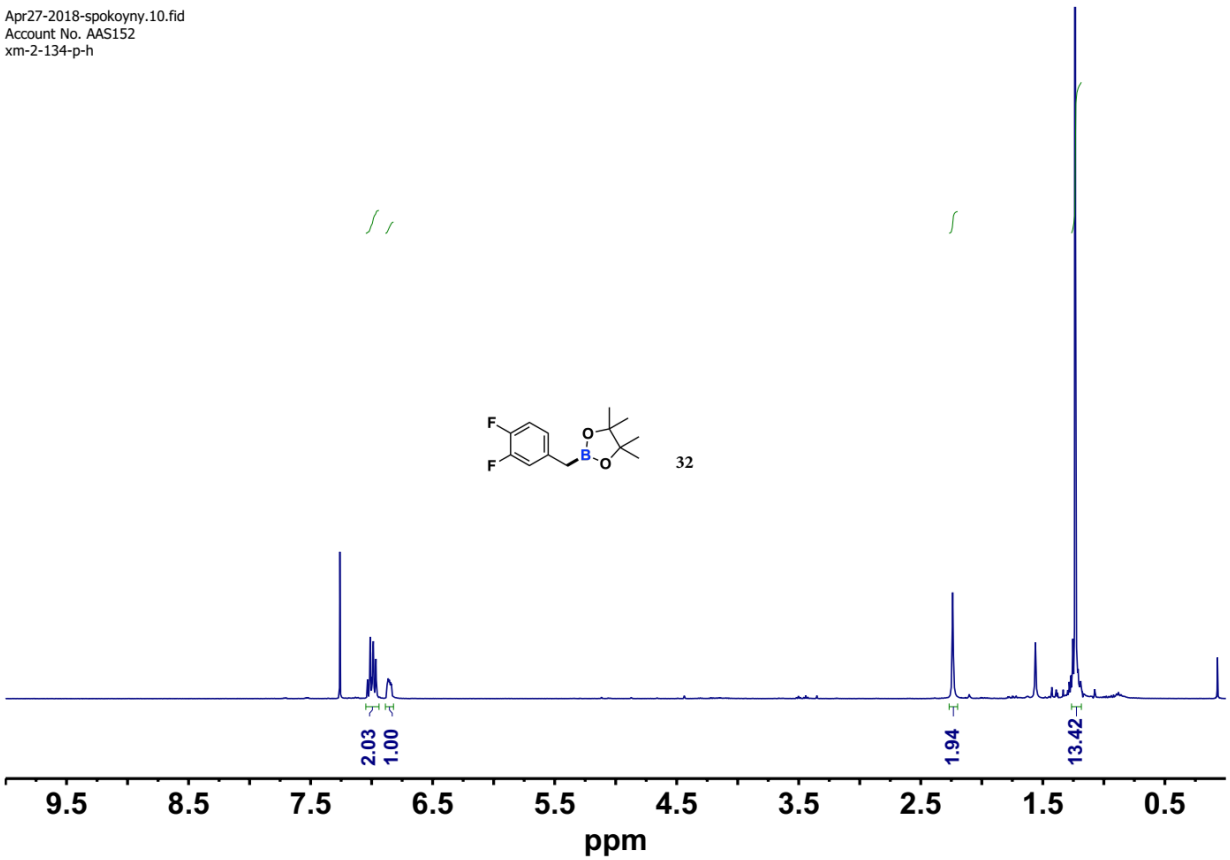


**Fig. S162**. $^{1}H$ NMR spectrum of **32** in $CDCl_3$ at 298K.

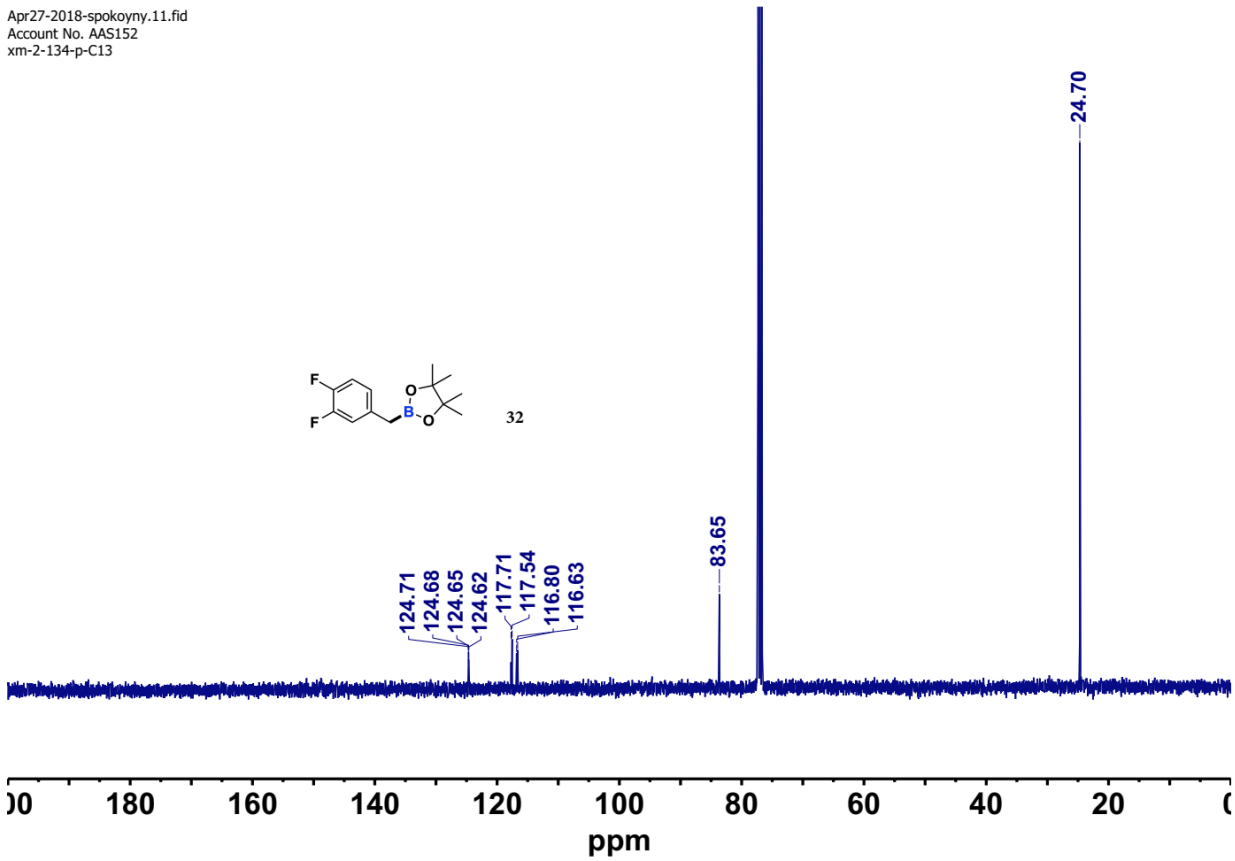


**Fig. S163**. $^{13}C\{^{1}H\}$ NMR spectrum of **32** in $CDCl_3$ at 298K.

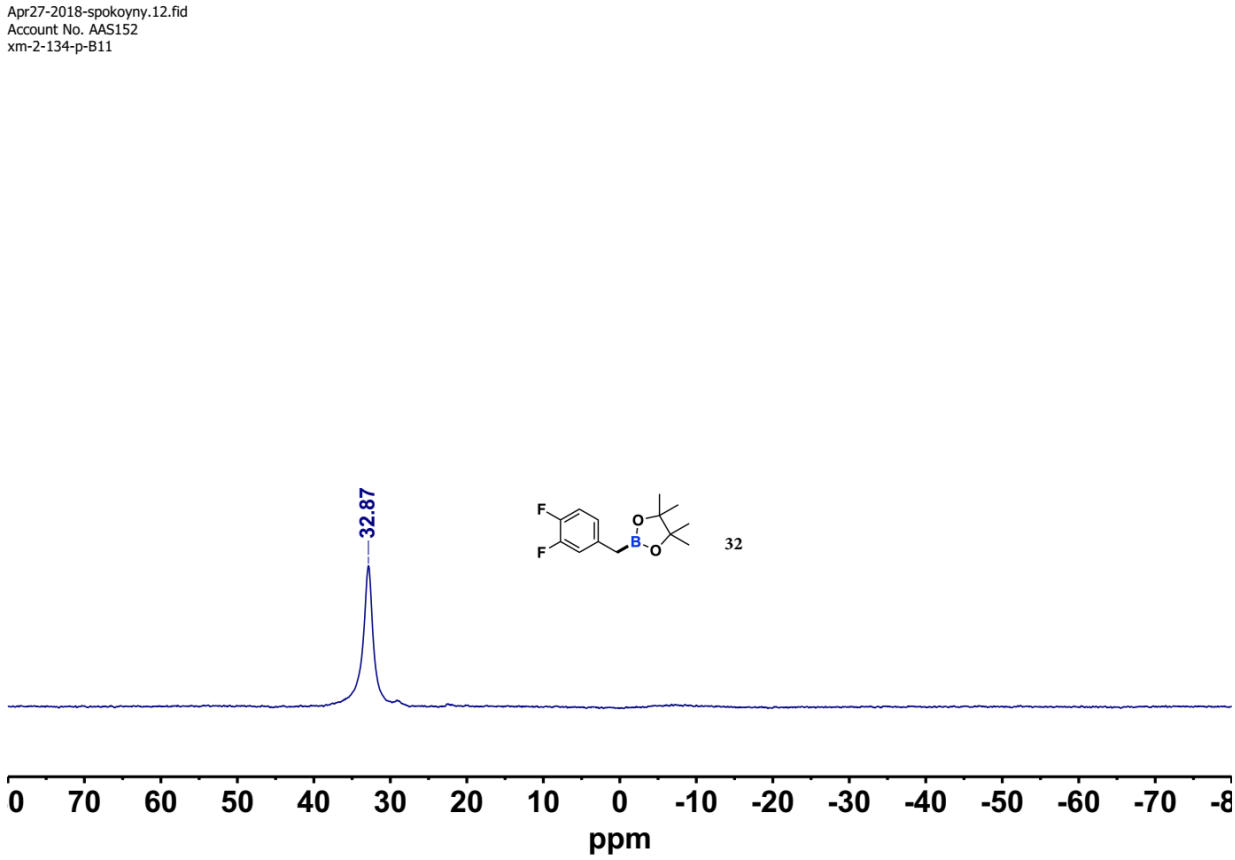


**Fig. S164**. $^{11}B$ NMR spectrum of **32** in $CDCl_3$ at 298K.

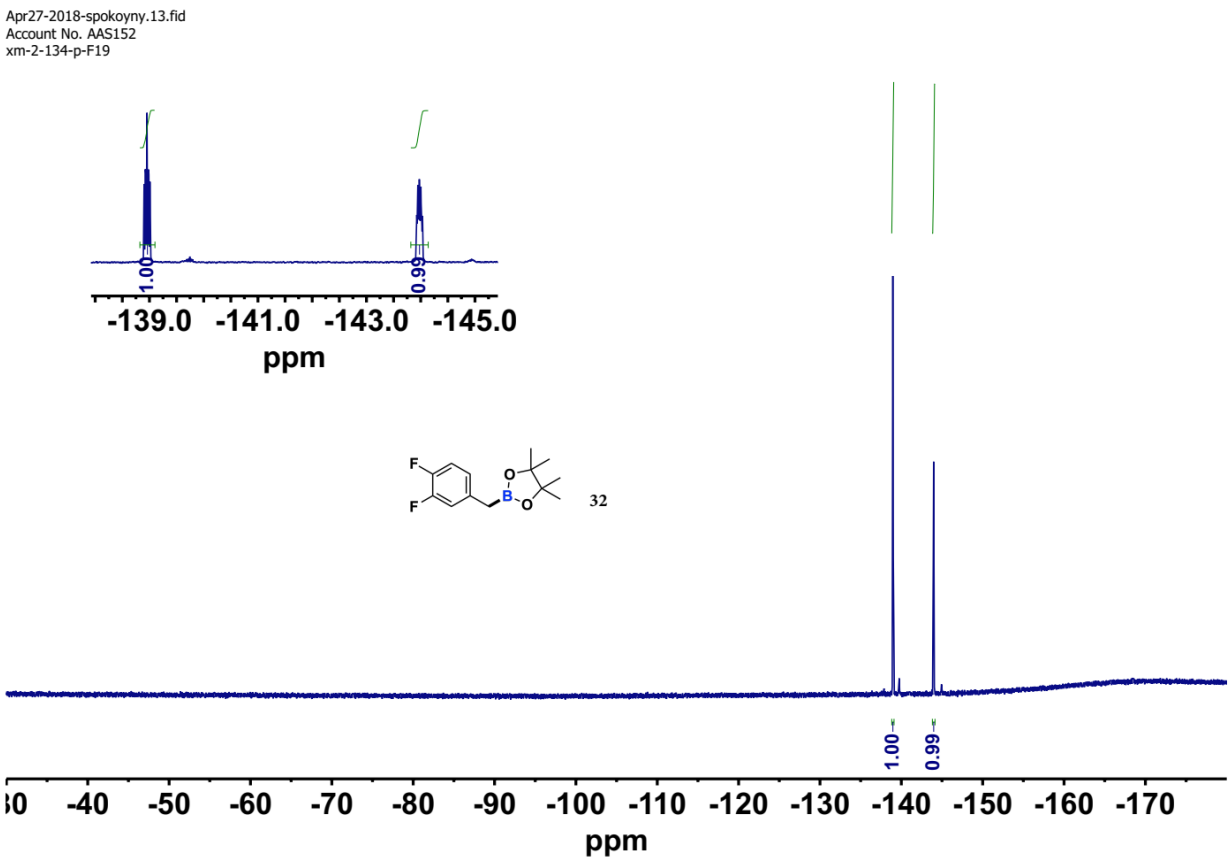


**Fig. S165**. $^{19}F$ NMR spectrum of **32** in $CDCl_3$ at 298K.

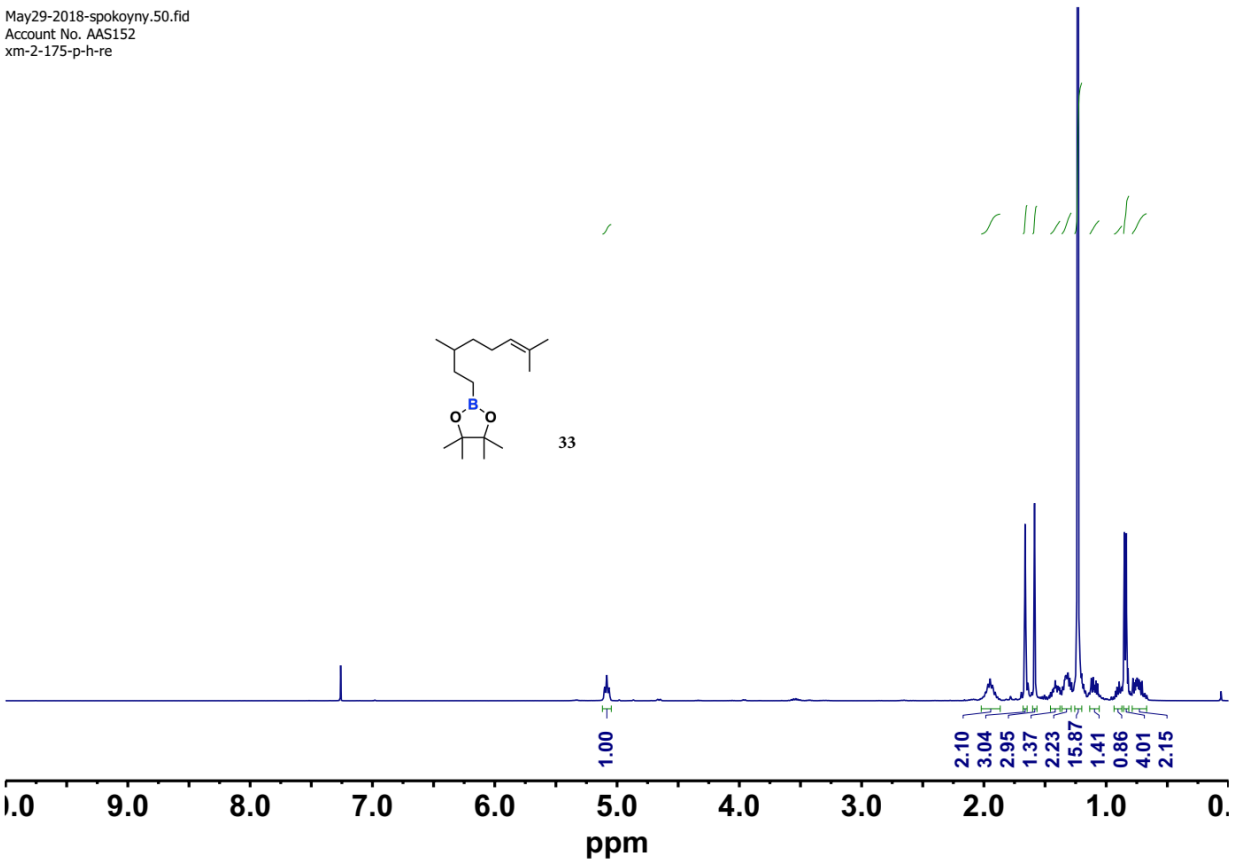


**Fig. S166**. $^{1}H$ NMR spectrum of **33** in $CDCl_3$ at 298K.

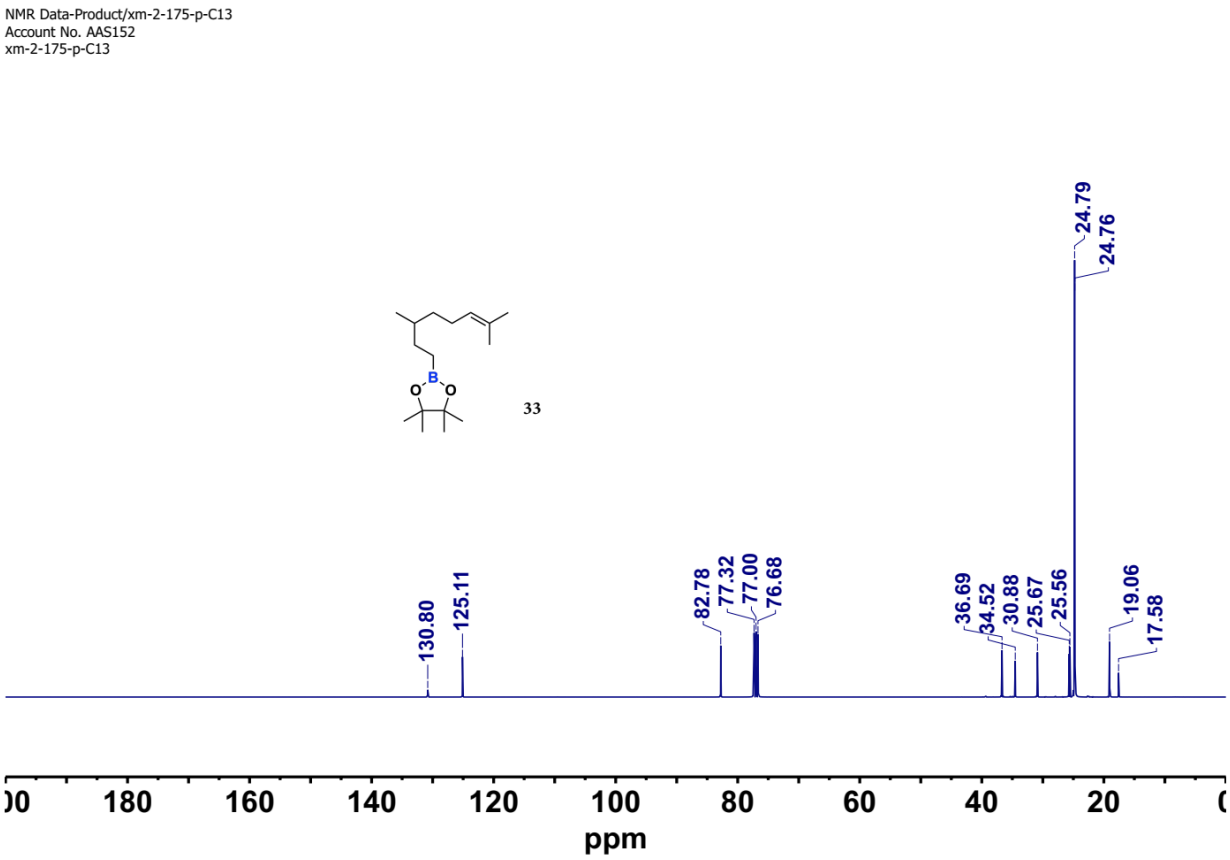


**Fig. S167**. $^{13}C\{^{1}H\}$ NMR spectrum of **33** in $CDCl_3$ at 298K.

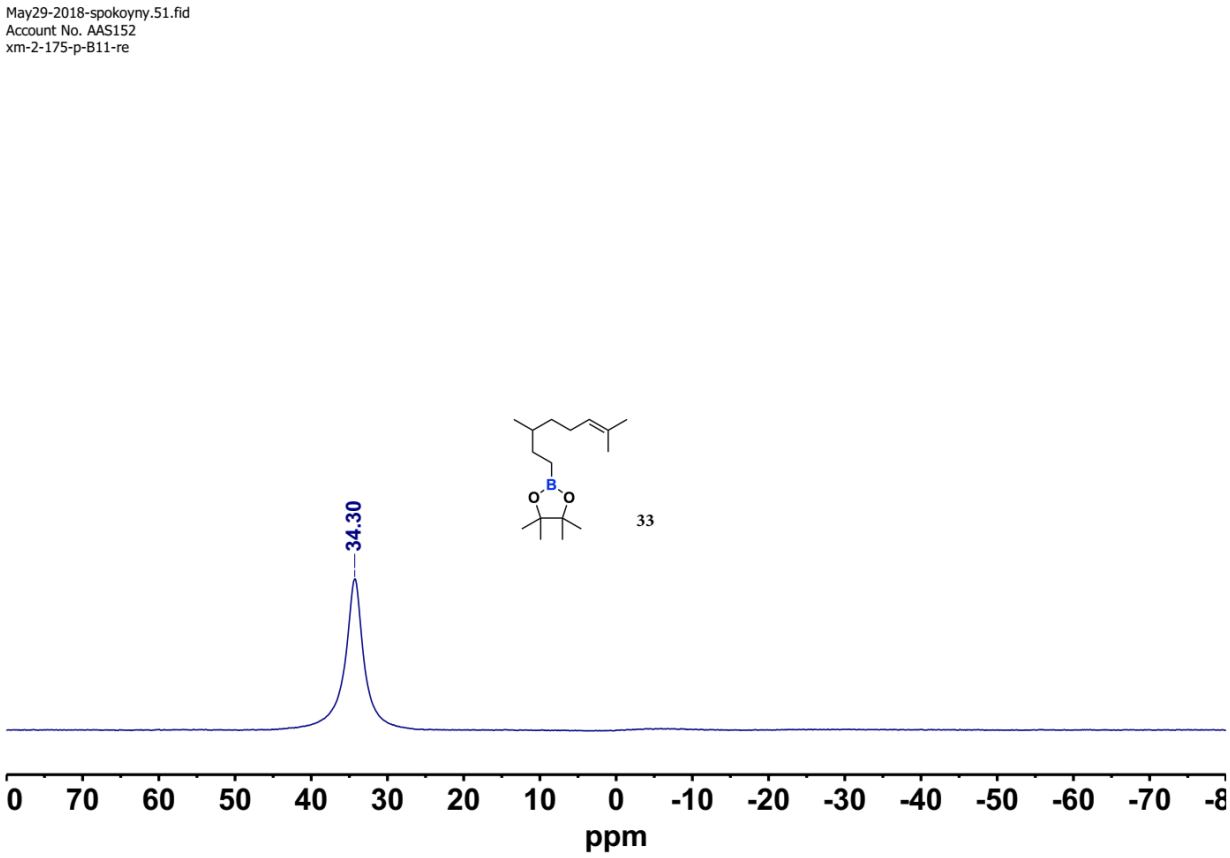


**Fig. S168**. $^{11}B$ NMR spectrum of **33** in $CDCl_3$ at 298K.

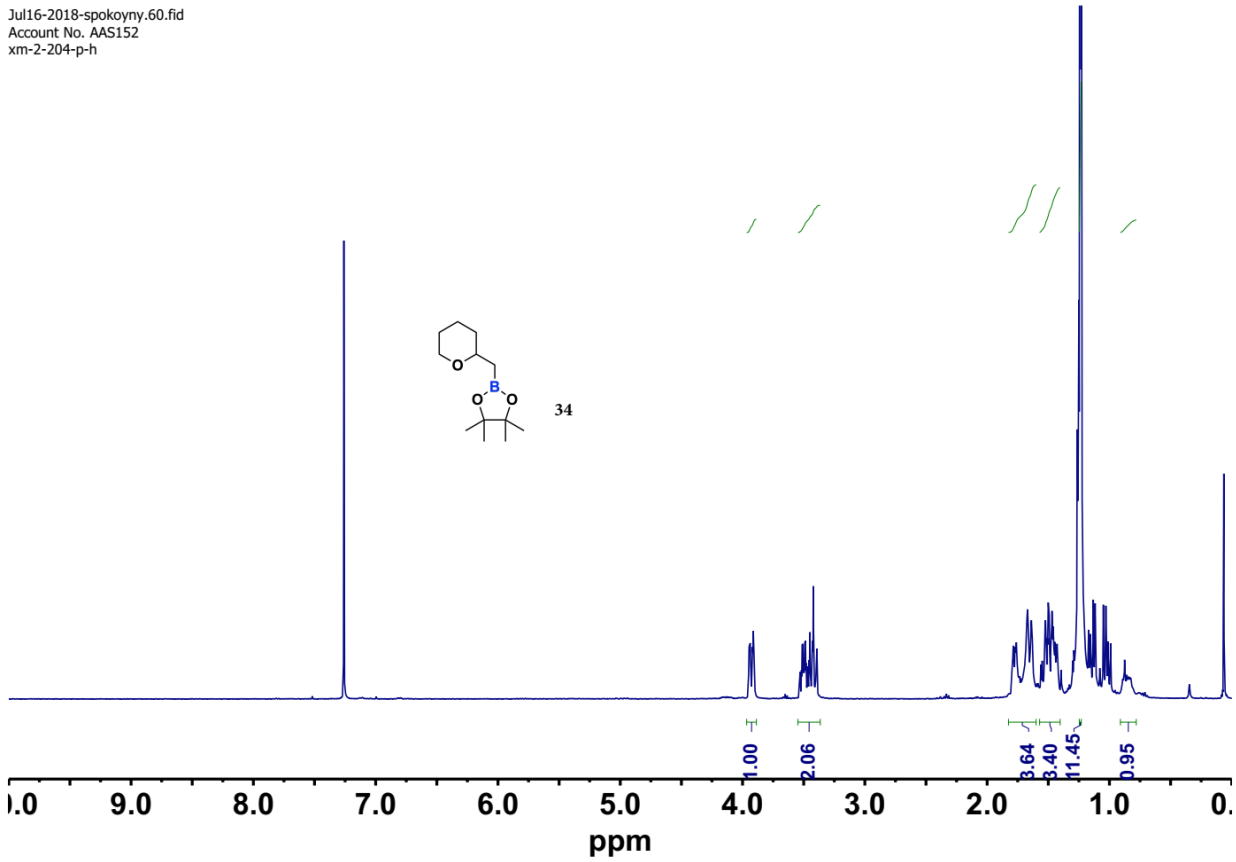


**Fig. S169**. $^{1}H$ NMR spectrum of **34** in $CDCl_3$ at 298K.

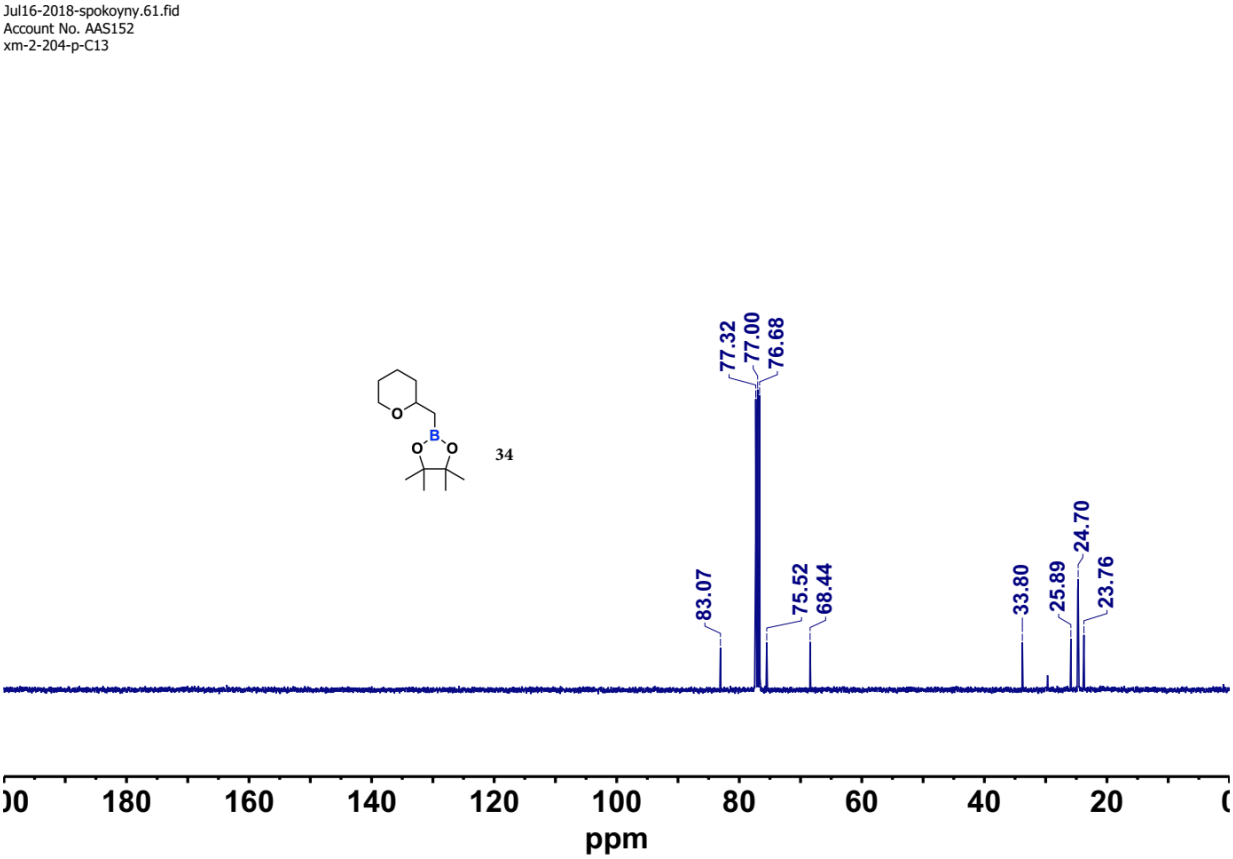


**Fig. S170**. $^{13}C\{^{1}H\}$ NMR spectrum of **34** in $CDCl_3$ at 298K.

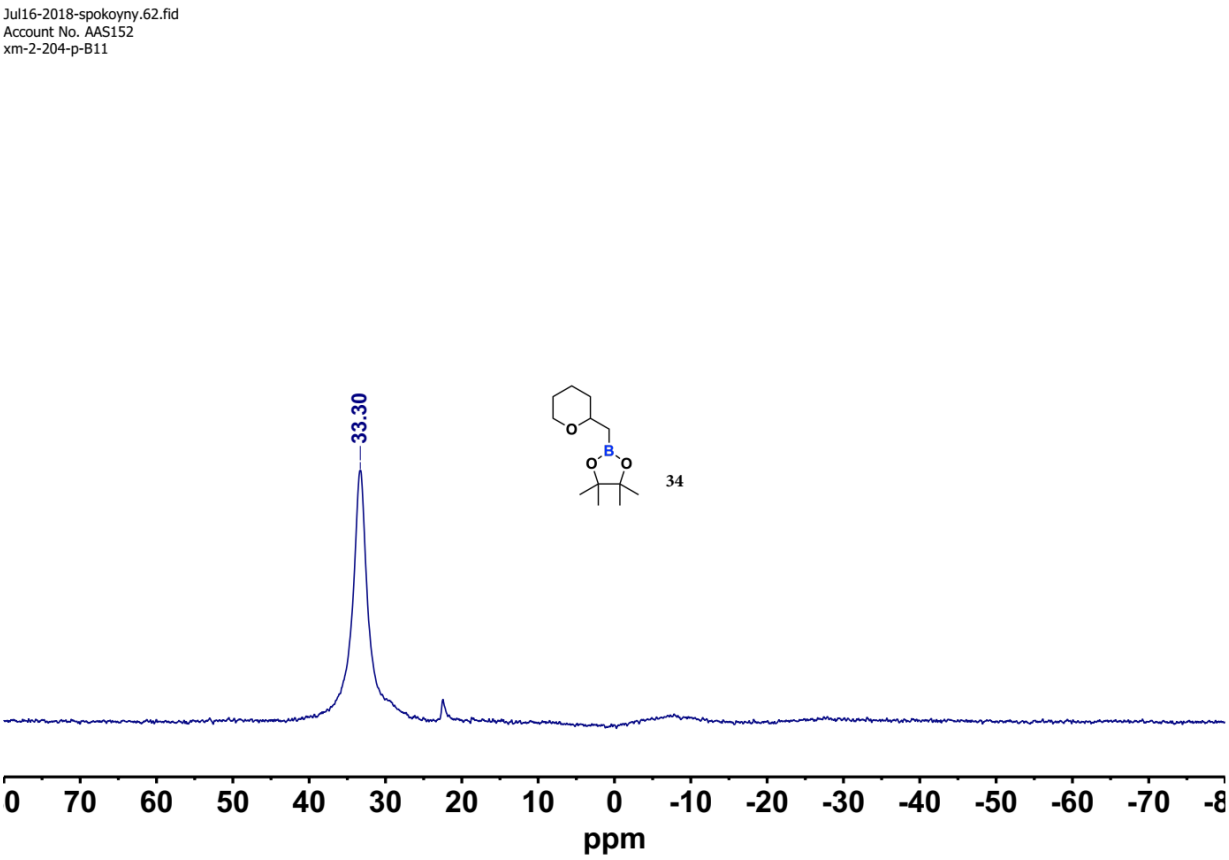


**Fig. S171**. $^{11}B$ NMR spectrum of **34** in $CDCl_3$ at 298K.

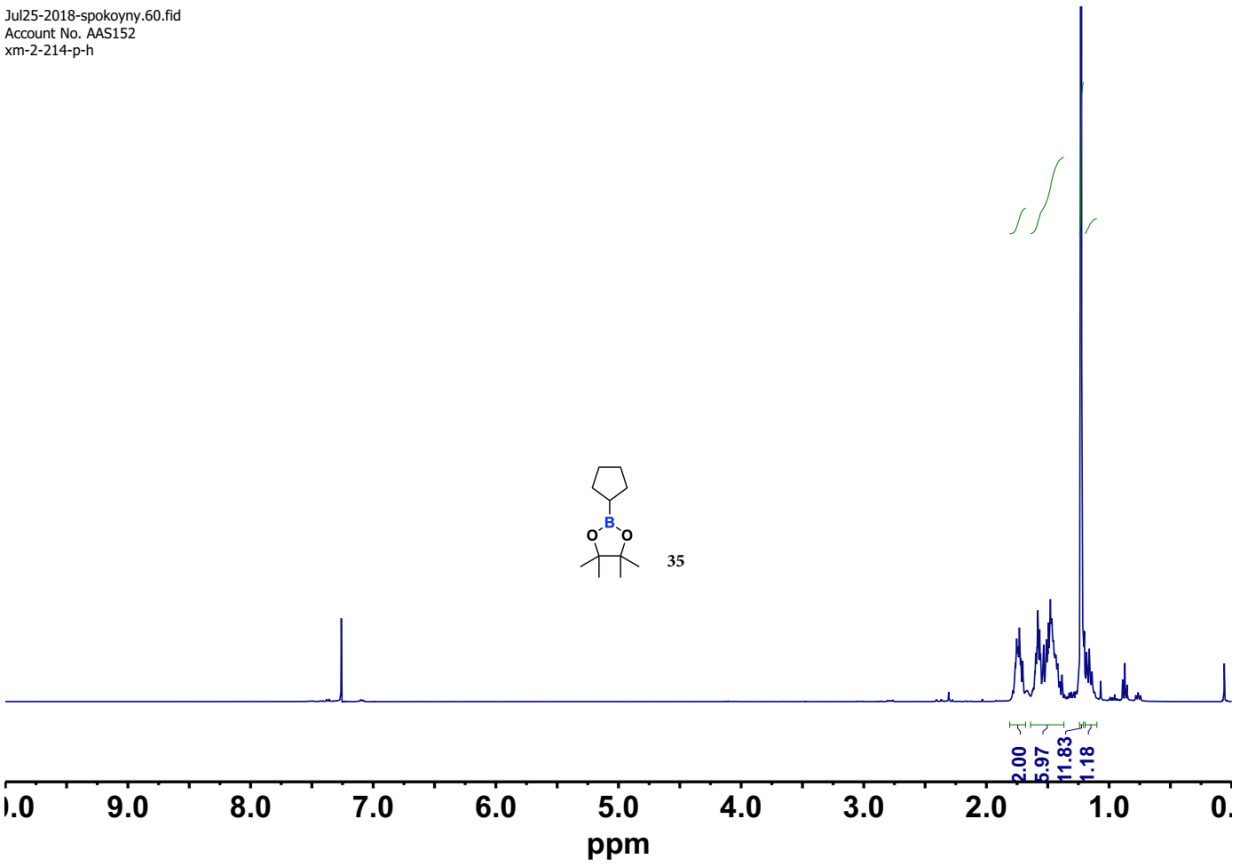


**Fig. S172**. $^{1}$H NMR spectrum of **35** in $CDCl_3$ at 298K.

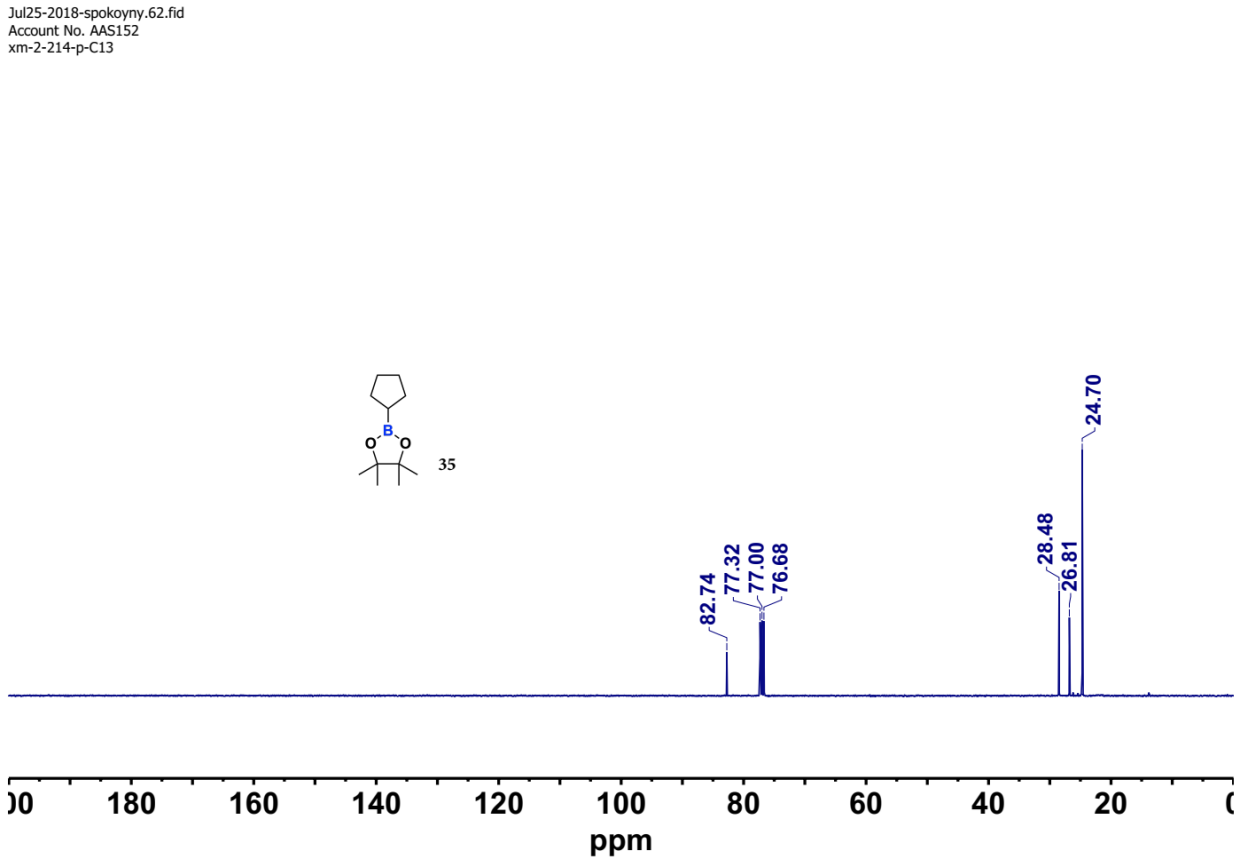


**Fig. S173**. $^{13}C\{^{1}H\}$ NMR spectrum of **35** in $CDCl_3$ at 298K.

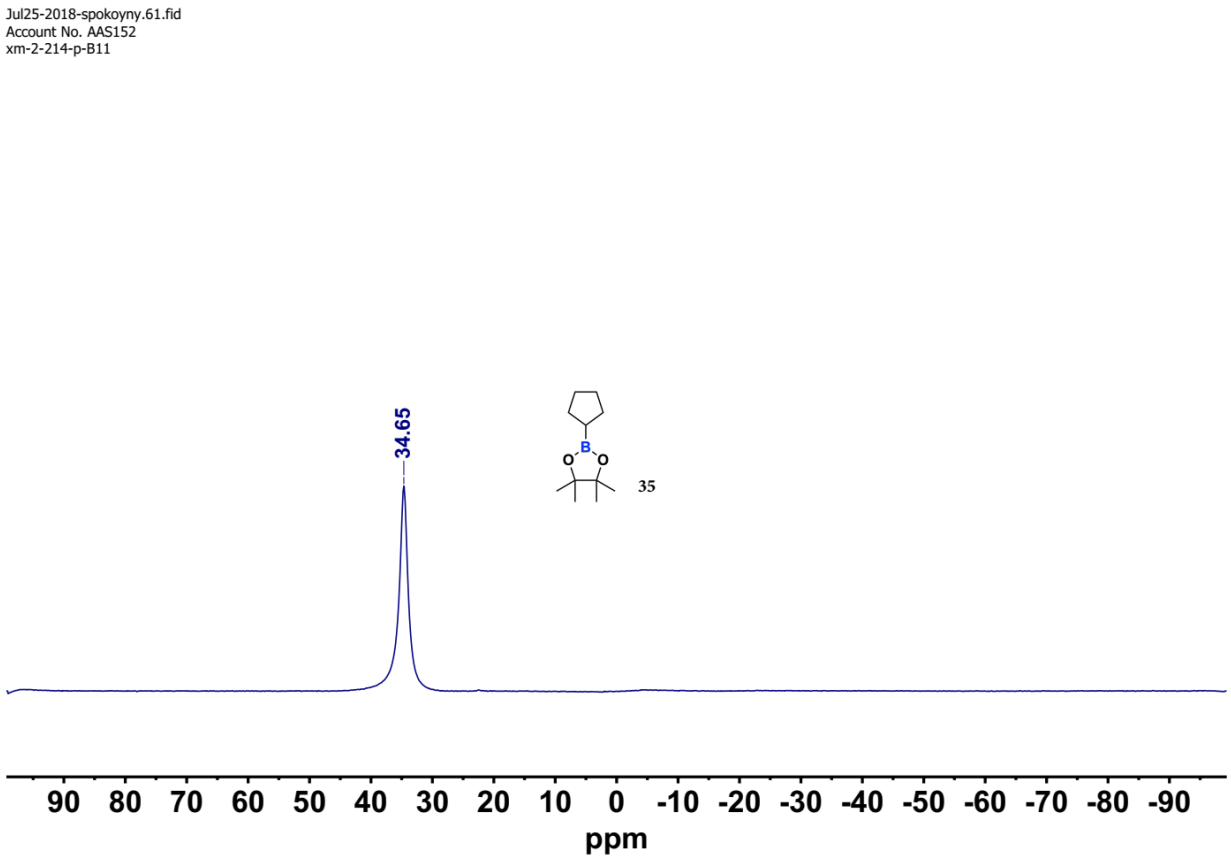


**Fig. S174**. $^{11}B$ NMR spectrum of **35** in $CDCl_3$ at 298K.

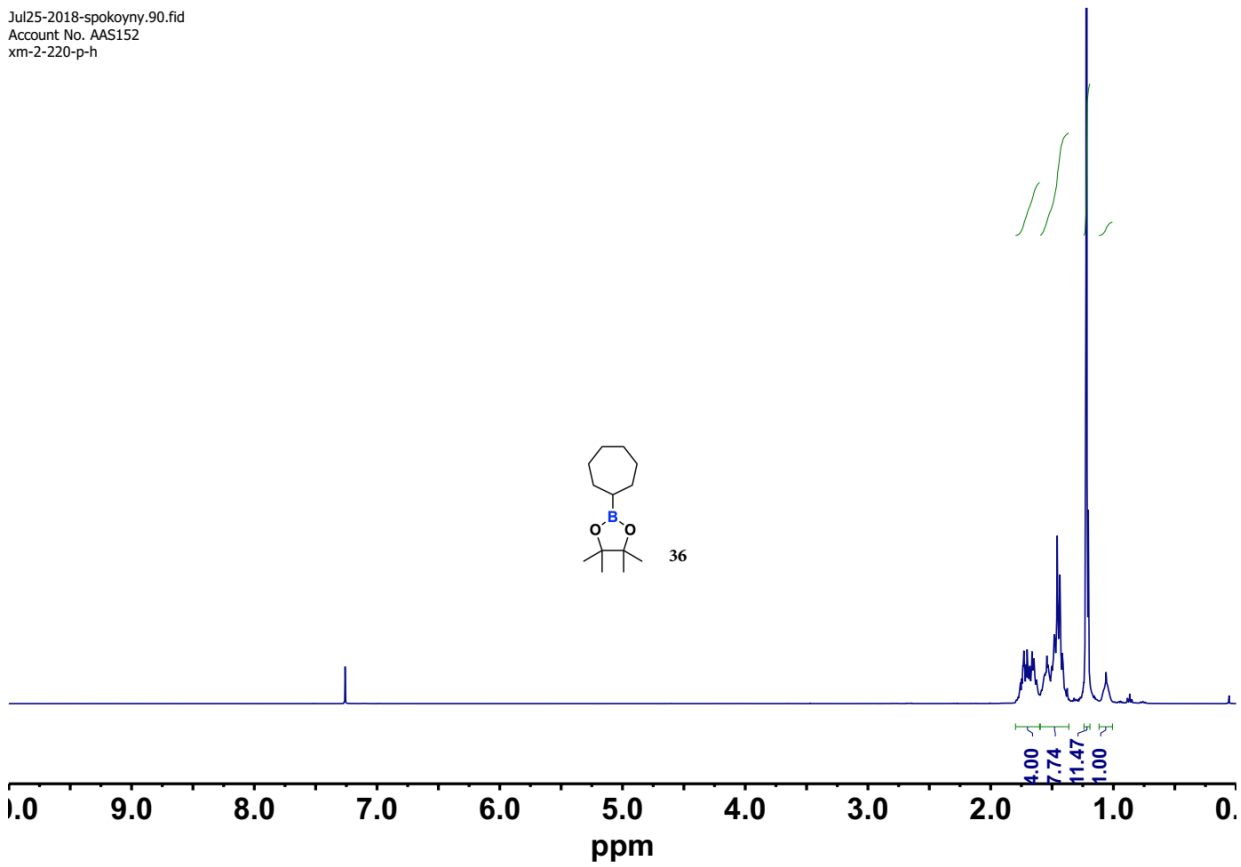


**Fig. S175**. $^{1}H$ NMR spectrum of **36** in $CDCl_3$ at 298K.

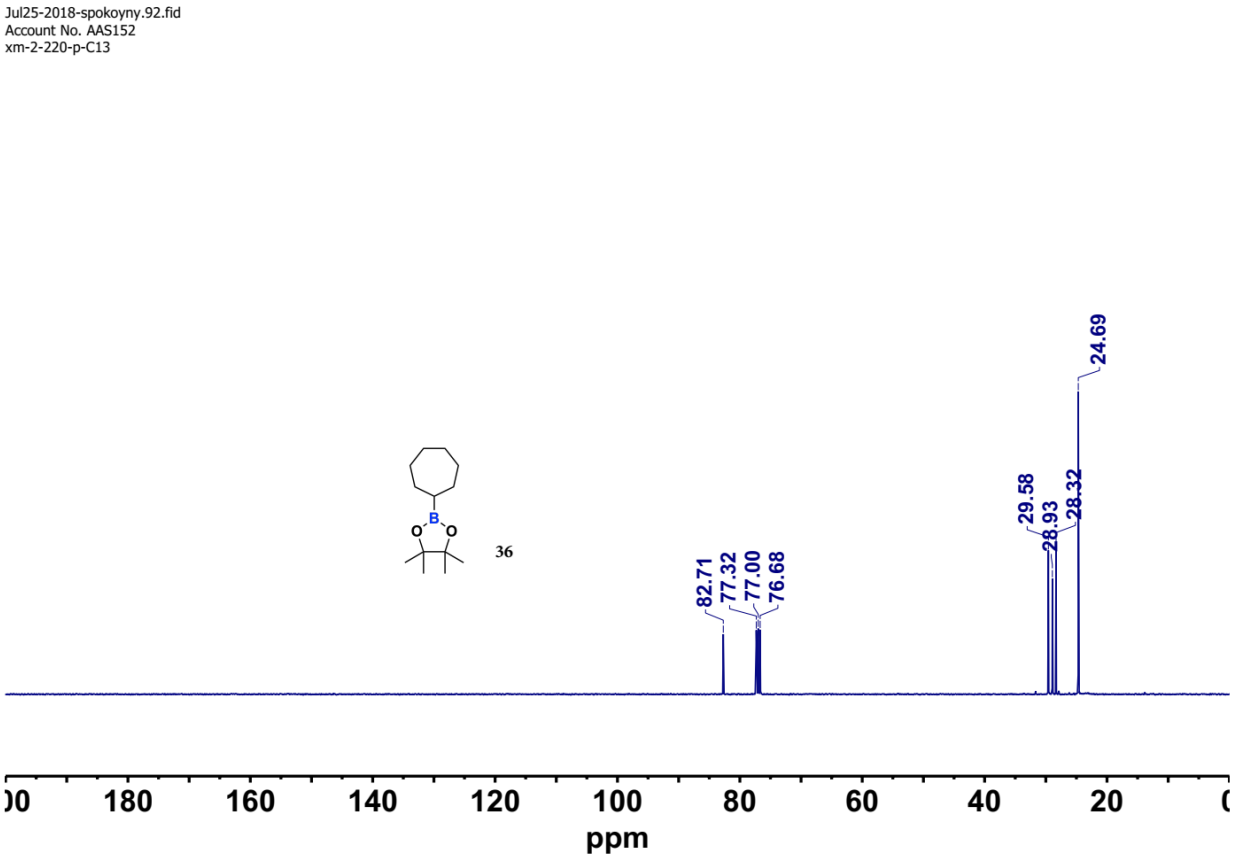


**Fig. S176**. $^{13}C\{^{1}H\}$ NMR spectrum of **36** in $CDCl_3$ at 298K.

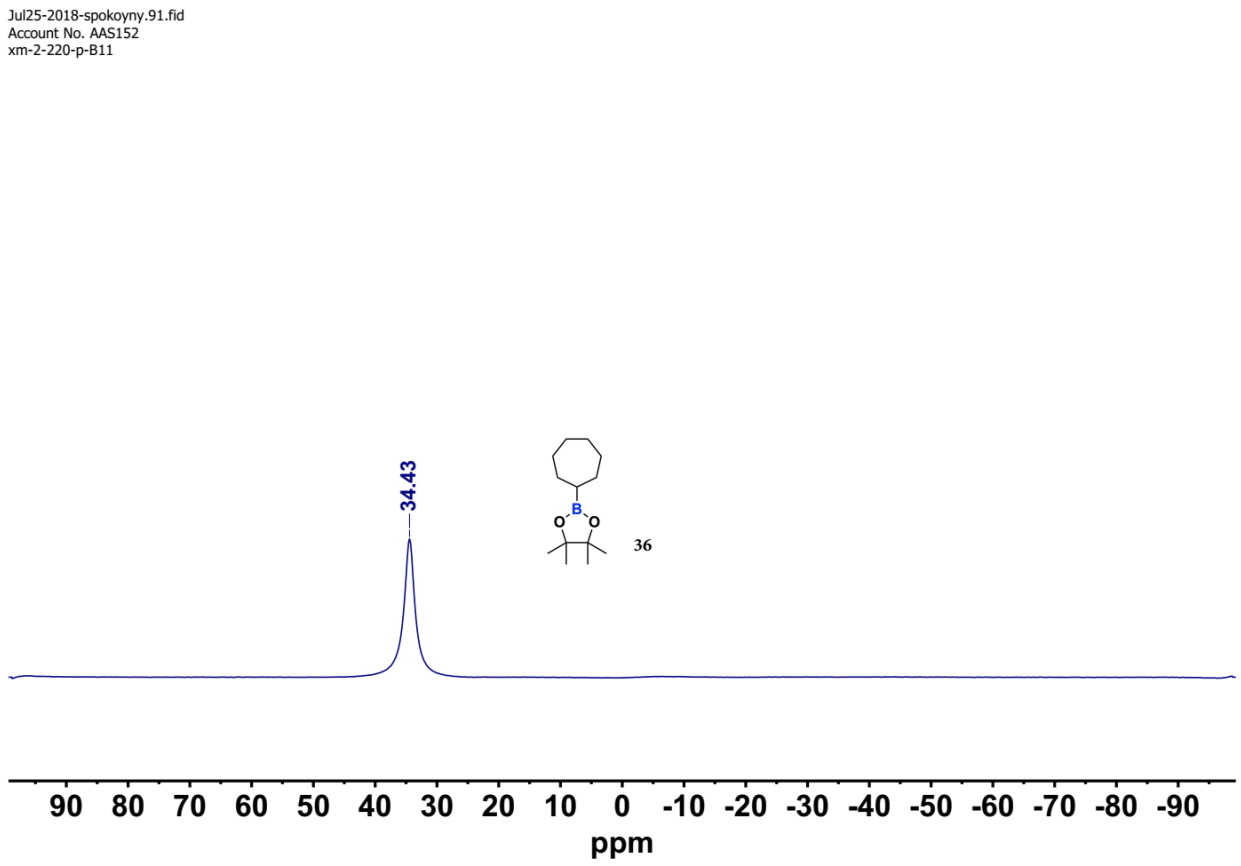


**Fig. S177**. $^{11}B$ NMR spectrum of **36** in $CDCl_3$ at 298K.

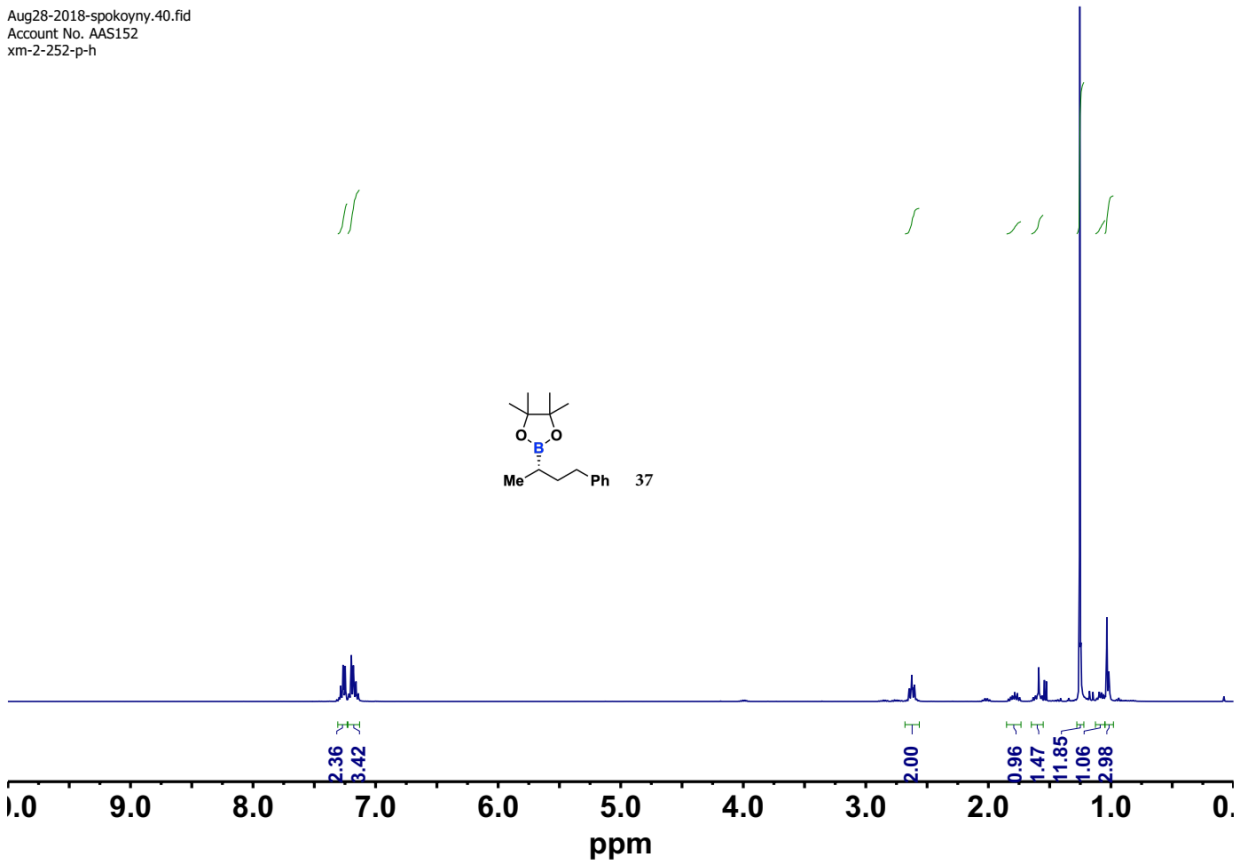


**Fig. S178**. $^{1}H$ NMR spectrum of **37** in $CDCl_3$ at 298K.

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Account No. AAS152
xm-2-252-p-C13

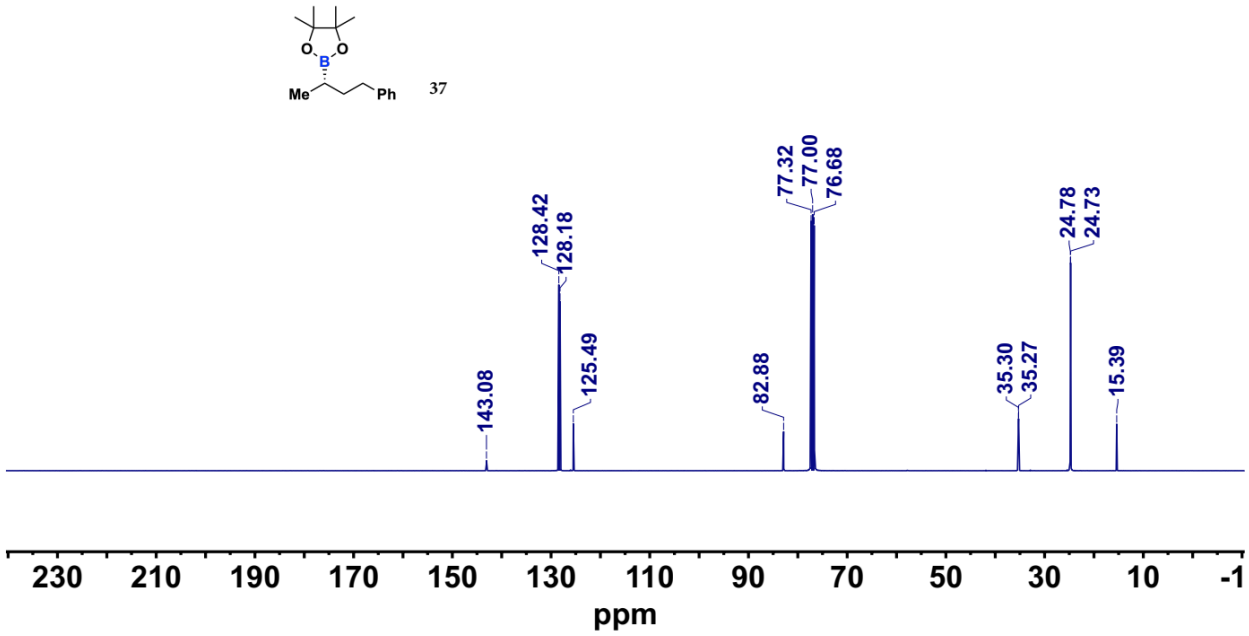


**Fig. S179**. $^{13}C\{^{1}H\}$ NMR spectrum of **37** in $CDCl_3$ at 298K.

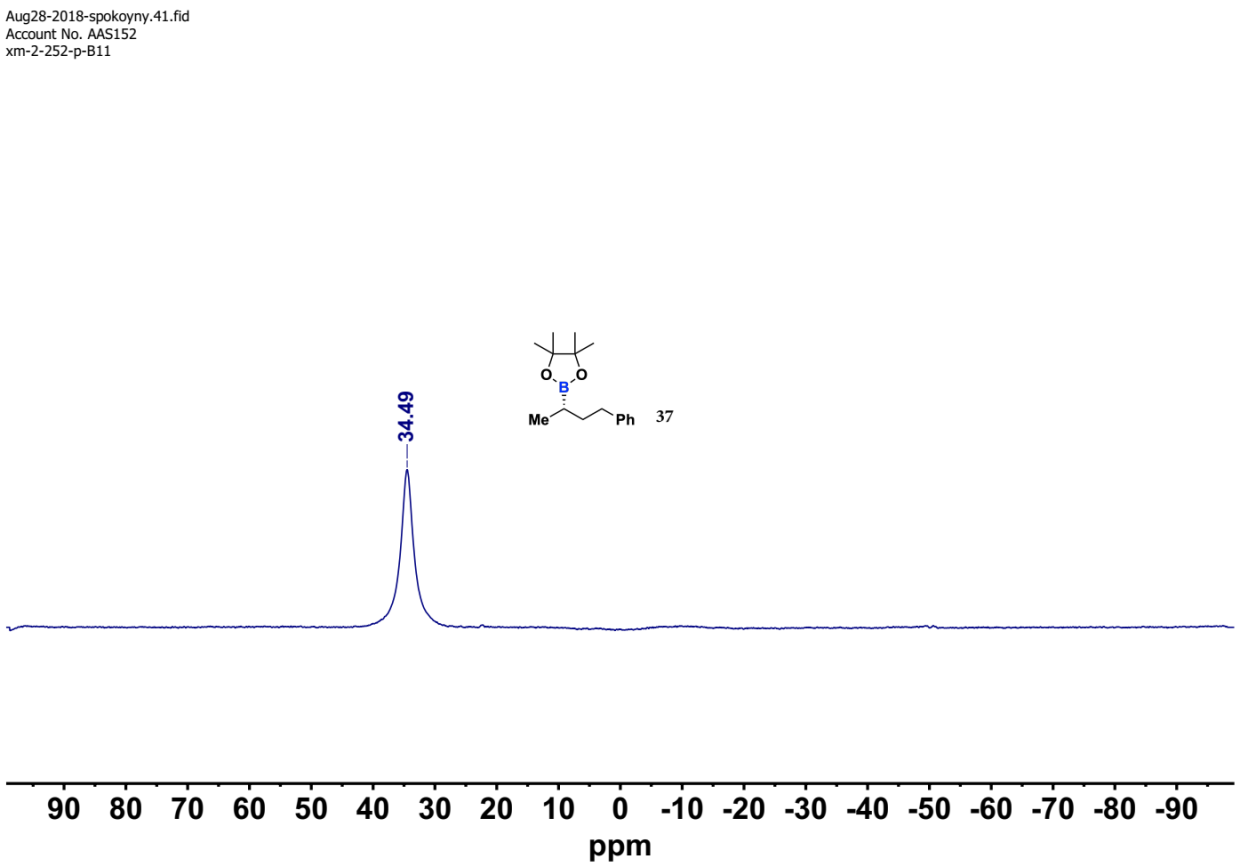


**Fig. S180**. $^{11}B$ NMR spectrum of **37** in $CDCl_3$ at 298K.