

## Supporting Information

### Electrochemical hydroboration of carbonyl compounds

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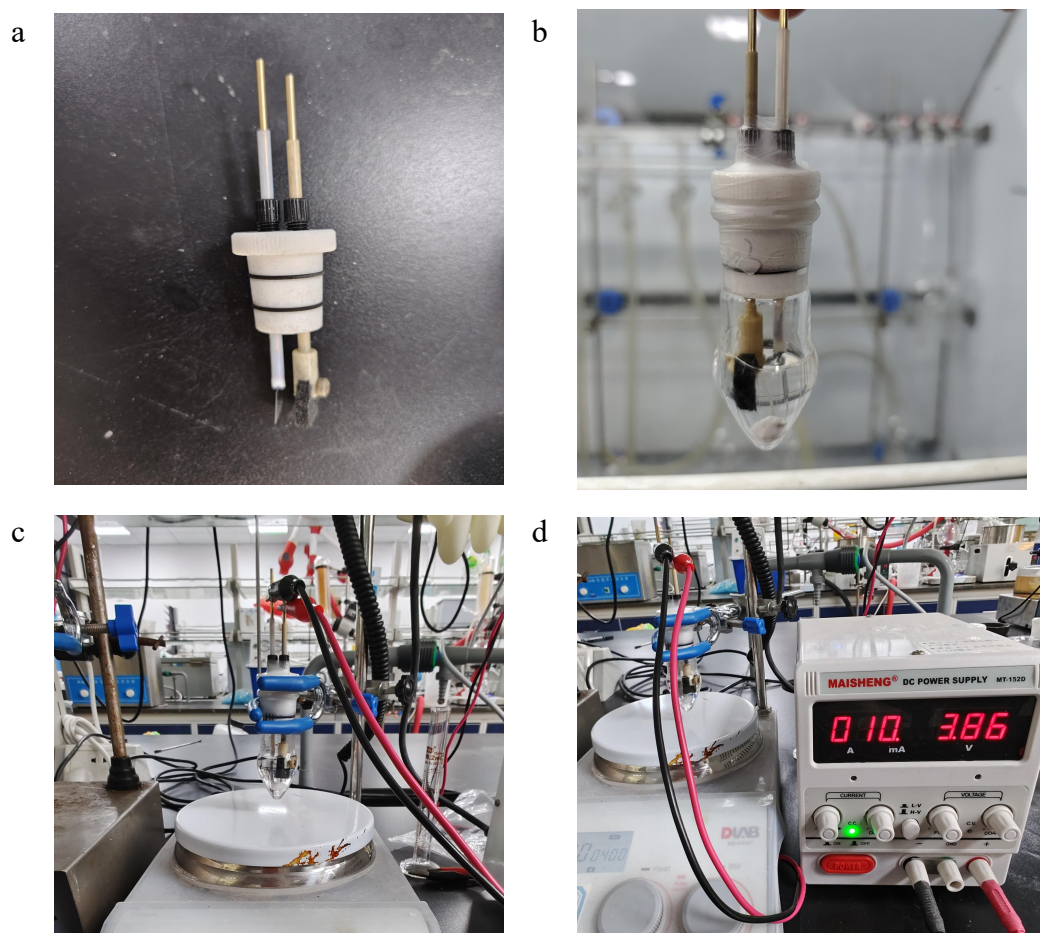
References

## EXPERIMENTAL SECTION

**General Information.** All air-sensitive manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}$  NMR spectra were recorded at 25 °C on Bruker Avance III 600 MHz spectrometer in deuterated solvents and chemical shifts were referenced to  $\text{CDCl}_3$  as an internal standard. DBpin was synthesized by literature procedure.<sup>1-3</sup> All reagents were used without further purification.

**General Procedure for Aldehyde Hydroboration with HBpin.** In a 5 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar, aldehydes (0.5 mmol), HBpin (79.8  $\mu\text{L}$ , 0.55 mmol),  $\text{Et}_4\text{NBF}_4$  (108.5 mg, 0.5 mmol) and MeCN (3 mL) were added, respectively. The flask was equipped with graphite felt electrode ( $10\times 10\times 3\text{ mm}^3$ ) as the anode and platinum plate ( $10\times 10\times 0.10\text{ mm}^3$ ) as the cathode. The mixture was stirred for 3 h under a continuous current of 5 mA at room temperature. The progress of the reaction was monitored by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy which indicated the completion of the reaction by the disappearance of aldehyde (RCHO) proton and appearance of a new  $\text{CH}_2$  resonance.

**General Procedure for Ketone Hydroboration with HBpin.** In a 5 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar, ketones (0.5 mmol), HBpin (108.8  $\mu\text{L}$ , 0.75 mmol),  $\text{Et}_4\text{NBF}_4$  (108.5 mg, 0.5 mmol) and MeCN (3 mL) were added, respectively. The flask was equipped with graphite felt electrode ( $10\times 10\times 3\text{ mm}^3$ ) as the anode and platinum plate ( $10\times 10\times 0.10\text{ mm}^3$ ) as the cathode. The mixture was stirred for 3 h under a continuous current of 10 mA at room temperature. Then the mixture was extracted with ethyl acetate, the combined organic phases were washed with brine, dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After the solvent were removed in vacuum, the pure alcohol product was obtained by flash column chromatography on silica gel with ethyl acetate/petroleum ether as eluents.



**Figure S1.** Set-up diagrams of undivided cell electrolysis.

**Gram-scale Hydroboration of Benzophenone.** In a 5 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar, benzophenone (1.82 g, 10 mmol), HBpin (2.2 mL, 15 mmol), Et<sub>4</sub>NBF<sub>4</sub> (2.17 g, 10 mmol) and MeCN (15 mL) were added, respectively. The flask was equipped with graphite felt electrode (15×15×3 mm<sup>3</sup>) as the anode and platinum plate (15×15×0.10 mm<sup>3</sup>) as the cathode. The mixture was stirred for 6 h under a continuous current of 10 mA at room temperature. Then the mixture was extracted with ethyl acetate, the combined organic phases were washed with brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The pure alcohol product **4o** (1.40 g, 7.6 mmol, 76% yield) was obtained by flash column chromatography on silica gel with ethyl acetate/petroleum ether as eluents.

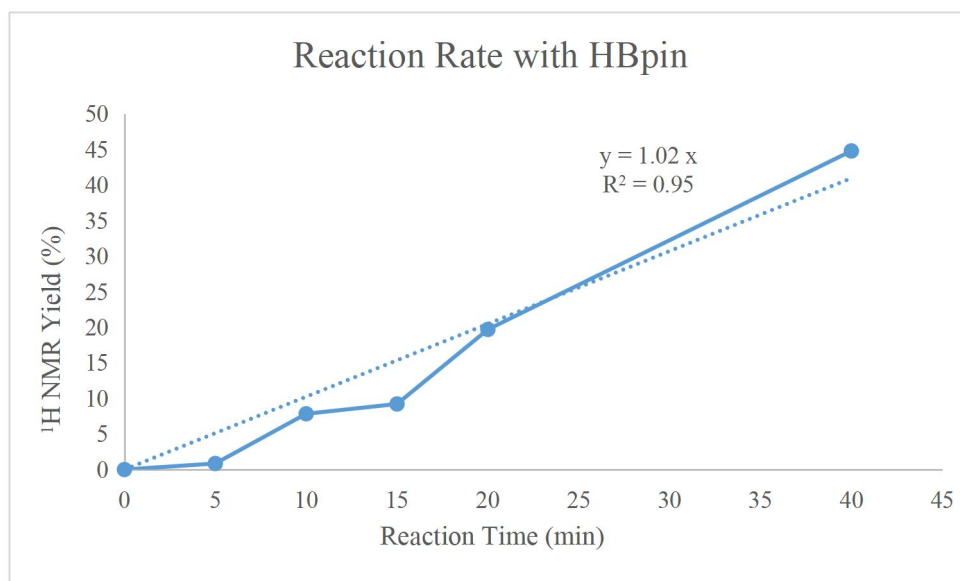
**Deuterium-labelling Experiment in CD<sub>3</sub>CN.** In a 5 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar, acetophenone (58.2  $\mu$ L, 0.5 mmol), HBpin (108.8  $\mu$ L, 0.75 mmol), Et<sub>4</sub>NBF<sub>4</sub> (108.5 mg, 0.5 mmol) and CD<sub>3</sub>CN (3 mL) were added. The flask was equipped with graphite felt electrode (10 $\times$ 10 $\times$ 3 mm<sup>3</sup>) as the anode and platinum plate (10 $\times$ 10 $\times$ 0.10 mm<sup>3</sup>) as the cathode. The mixture was stirred for 3 h under a continuous current of 10 mA at room temperature. The ratio of mixed products *d*-**4a** and **4a** were monitored by <sup>1</sup>H NMR spectroscopy.

**Deuterium-labelling Experiment in DBpin.** In a 5 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar, acetophenone (58.2  $\mu$ L, 0.5 mmol), DBpin (560  $\mu$ L, 1.33 M solution in anhydrous THF, 0.75 mmol), Et<sub>4</sub>NBF<sub>4</sub> (108.5 mg, 0.5 mmol) and MeCN (3 mL) were added. The flask was equipped with graphite felt electrode (10 $\times$ 10 $\times$ 3 mm<sup>3</sup>) as the anode and platinum plate (10 $\times$ 10 $\times$ 0.10 mm<sup>3</sup>) as the cathode. The mixture was stirred for 3 h under a continuous current of 10 mA at room temperature. The ratio of mixed products *d*-**4a** and **4a** were monitored by <sup>1</sup>H NMR spectroscopy.

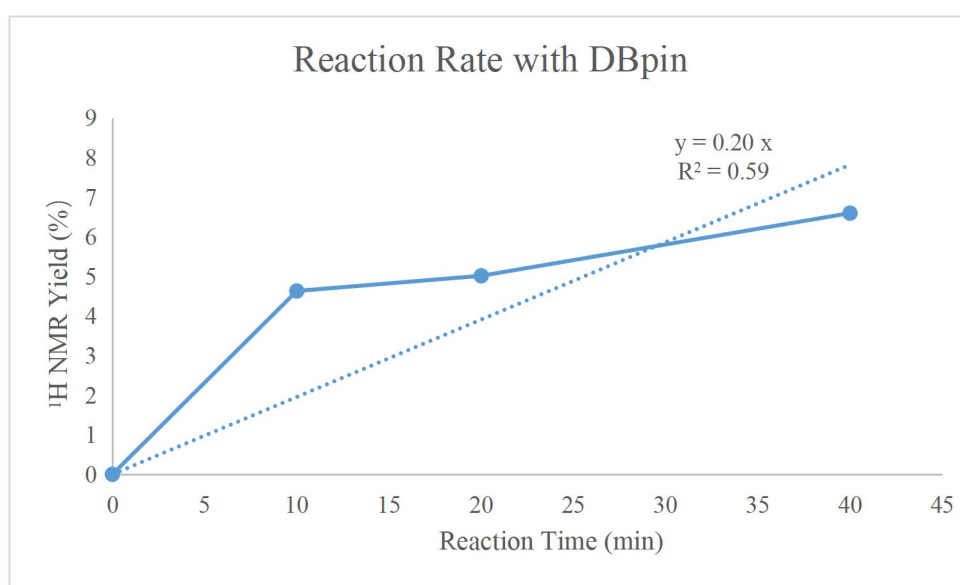
**Kinetic Isotope Effect (KIE) Experiment.** In a 5 mL, oven-dried, round-bottomed flask equipped with a magnetic stir bar, acetophenone (58.2  $\mu$ L, 0.5 mmol), DBpin (560  $\mu$ L, 1.33 M solution in anhydrous THF, 0.75 mmol) or HBpin (108.8  $\mu$ L, 0.75 mmol), Et<sub>4</sub>NBF<sub>4</sub> (108.5 mg, 0.5 mmol) and MeCN (3 mL) were added. The flask was equipped with graphite felt electrode (10 $\times$ 10 $\times$ 3 mm<sup>3</sup>) as the anode and platinum plate (10 $\times$ 10 $\times$ 0.10 mm<sup>3</sup>) as the cathode. Then the mixture was extracted with ethyl acetate, the combined organic phases were washed with brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>.

HBpin: 5 reactions were set up and stopped at 5 min, 10 min, 15 min, 20 min, 40 min, respectively.

DBpin: 3 reactions were set up and stopped at 10 min, 20 min, 40 min, respectively. The reaction yields were determined by <sup>1</sup>H NMR using dimethylsulfoxide as an internal standard.



The coefficient of the linear trend curve corresponds to the reaction rate  $k_H = 1.02$



The coefficient of the linear trend curve corresponds to the reaction rate  $k_D = 0.20$

With the method, the  $KIE = k_H/k_D = 5.1$ .

**Radical Inhibition Experiment with 1,1-diphenylethylene, TEMPO or BHT.** In a 25 mL, over-dried, three-necked, round-bottomed flask equipped with a magnetic stir bar, acetophenone (58.2  $\mu$ L, 0.5 mmol), HBpin (108.8  $\mu$ L, 0.75 mmol), Et<sub>4</sub>NBF<sub>4</sub> (108.5 mg, 0.5 mmol), CH<sub>3</sub>CN (3 mL) and 1,1-diphenylethylene (132  $\mu$ L, 0.75 mmol), TEMPO (117 mg, 0.75 mmol) or BHT (165mg, 0.75 mmol) were added, respectively. The flask was equipped with graphite felt electrode (10 $\times$ 10 $\times$ 3 mm<sup>3</sup>) as the anode and

platinum plate ( $10 \times 10 \times 0.10 \text{ mm}^3$ ) as the cathode. The mixtures were stirred for 3 h under a continuous current of 10 mA at room temperature. The yield of **4a** and **5** were determined by  $^1\text{H}$  spectroscopy.

**Procedures for Cyclic Voltammetry (CV).** Cyclic voltammetry experiments were conducted in a 25 mL three-electrode cell equipped with a glassy Carbon working electrode, a Ag/AgCl reference electrode and a platinum wire counter electrode, and the reference electrode was submerged in a saturated aqueous KCl solution, at  $100 \text{ mV S}^{-1}$  scan rate: background ( $\text{Et}_4\text{NBF}_4$ , 0.1 M in MeCN) and the potential range was 0-5 V; HBpin (0.1 M in MeCN) and the potential range was -5-5 V; acetophenone (0.1 M in MeCN) and the potential range was 0-5 V; the mixture of acetophenone (0.1 M in MeCN) and HBpin (0.1 M in MeCN) and the potential range was -3.5-3.5 V. The current was reported in mA and potential was reported in V.

**Spectroscopic Data for Products of 2, 4 and 5.** *2-(benzyloxy)pinacolborane (2a)*.<sup>4</sup> Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33-7.25 (m, 5H), 4.92 (s, 2H), 1.26 (s, 12H).  $^{11}\text{B}$  NMR (193 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.35.

*2-(2-fluorobenzyloxy)pinacolborane (2b)*.<sup>4</sup> Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44-7.42 (m, 1H), 7.27-7.25 (m, 1H), 7.14-7.11 (m, 1H), 7.03-7.00 (m, 1H), 4.99 (s, 2H), 1.27 (s, 12H).  $^{11}\text{B}$  NMR (193 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.35.

*2-(3-fluorobenzyloxy)pinacolborane (2c)*.<sup>4</sup> Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32-7.31 (m, 1H), 7.10-7.06 (m, 2H), 6.97-6.95 (m, 1H), 4.90 (s, 2H), 1.26 (s, 12H).  $^{11}\text{B}$  NMR (193 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.33.

*2-(4-fluorobenzyloxy)pinacolborane (2d)*.<sup>4</sup> Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24-7.22 (m, 2H), 6.94-6.91 (m, 2H), 4.79 (s, 2H), 1.17 (s, 12H).  $^{11}\text{B}$  NMR (193 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.28.

*2-(2-chlorobenzyloxy)pinacolborane (2e)*.<sup>4</sup> Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 (m, 1H), 7.31 (m, 1H), 7.28-7.20 (m, 2H), 5.01 (s, 2H), 1.28 (s, 12H).  $^{11}\text{B}$  NMR (193 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.38.

*2-(3-chlorobenzyloxy)pinacolborane (2f)*.<sup>4</sup> Yellow oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$

7.20 (s, 1H), 7.16-7.12 (m, 3H), 4.81 (s, 2H), 1.19 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 24.47.

*2-(4-chlorobenzyloxy)pinacolborane (2g)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.25-7.22 (m, 4H), 4.86 (s, 2H), 1.25 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 24.35.

*2-(4-nitrophenyl) pinacolborane (2h)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.10 (d, *J* = 6.0 Hz, 2H), 7.43 (d, *J* = 6.0 Hz, 2H), 4.94 (s, 2H), 1.18 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.34.

*2-((4-methylbenzyl)oxy)pinacolborane (2i)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.19 (d, *J* = 6.0 Hz, 2H), 7.10 (d, *J* = 6.0 Hz, 2H), 4.83 (s, 2H), 2.29 (s, 3H), 1.22 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.33.

*2-(4-methoxybenzyloxy)pinacolborane (2j)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 6.0 Hz, 2H), 7.19 (m, 2H), 4.81 (s, 2H), 3.16 (s, 3H), 1.19 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.36.

*N,N-dimethyl-4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-aniline (2k)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.18 (d, *J* = 12 Hz, 2H), 6.68 (d, *J* = 12 Hz, 2H), 4.75 (s, 2H), 2.91 (s, 6H), 1.24 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 24.47.

*4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenyl acetate (2l)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 6.0 Hz, 2H), 6.98 (d, *J* = 6.0 Hz, 2H), 4.82 (s, 2H), 2.21 (s, 3H), 1.18 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.08.

*N-(4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenyl)acetamide (2m)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.77 (s, 1H), 7.59 (d, *J* = 6.0 Hz, 2H), 7.19 (d, *J* = 6.0 Hz, 2H), 4.82 (s, 2H), 2.13 (s, 3H), 1.25 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.02.

*2-(cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.38-7.23 (m, 5H), 6.62 (d, *J* = 18 Hz, 1H), 6.30-6.27 (m, 1H), 4.53 (d, *J* = 6.0 Hz, 2H), 1.25 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.18.

*2-(cyclohexylmethoxy)pinacolborane (2o)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.54 (d, *J* = 6.0 Hz, 2H), 1.61-1.59 (m, 6H), 1.55-1.53 (m, 1H), 1.14 (s, 12H),

1.04-1.02 (m, 2H), 0.84-0.79 (m, 2H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.01.

*4,4,5,5-tetramethyl-2-(pentyloxy)-1,3,2-dioxaborolane (2p)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.70 (t, *J* = 6.0 Hz, 2H), 1.44 (m, 2H), 1.19 (m, 2H), 1.17 (s, 12H), 0.77 (m, 3H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 21.98.

*2-(4-chlorobutoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.70 (t, *J* = 6.0 Hz, 2H), 1.44 (m, 2H), 1.19 (m, 2H), 1.17 (s, 12H), 0.77 (m, 2H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 21.97.

*4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)pyridine (2r)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.38 (m, 2H), 7.17 (m, 2H), 4.75 (s, 2H), 1.05 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.23.

*2-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)pyridine (2s)*.<sup>4</sup> Yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.63-8.60 (m, 1H), 7.98-7.96 (m, 1H), 7.74-7.72 (m, 1H), 7.50-7.48 (m, 1H), 5.08 (s, 2H), 1.23 (s, 12H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>): δ 22.32.

*1-phenylethan-1-ol (4a)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.36-7.24 (m, 5H), 4.87 (q, *J* = 6.0 Hz, 1H), 2.05 (s, 1H), 1.48 (d, *J* = 6.0 Hz, 3H).

*1-(2-fluorophenyl)ethan-1-ol (4b)*.<sup>4</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.49-7.46 (m, 1H), 7.25-7.21 (m, 1H), 7.25-7.21 (m, 1H), 7.02-6.99 (m, 1H), 5.20 (q, *J* = 6.0 Hz, 1H), 2.07 (s, 1H), 1.51 (d, *J* = 6.0 Hz, 3H).

*1-(3-fluorophenyl)ethan-1-ol (4c)*.<sup>4</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.29-7.25 (m, 1H), 7.18-7.10 (m, 1H), 6.95-6.91 (m, 2H), 4.86 (q, *J* = 6.0 Hz, 1H), 2.33 (s, 1H), 1.46 (d, *J* = 6.0 Hz, 3H).

*1-(4-fluorophenyl)ethan-1-ol (4d)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.33-7.31 (m, 2H), 7.11-7.09 (m, 2H), 4.86 (q, *J* = 6.0 Hz, 1H), 2.71 (s, 1H), 1.46 (d, *J* = 6.0 Hz, 3H).

*1-(4-chlorophenyl)ethan-1-ol (4e)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.31-7.30 (m, 2H), 7.12-7.10 (m, 2H), 4.87 (q, *J* = 6.0 Hz, 1H), 1.47 (d, *J* = 6.0 Hz, 3H).

*1-(2-bromophenyl)ethan-1-ol (4f)*.<sup>4</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.59-7.58 (m, 1H), 7.51-7.50 (m, 1H), 7.35-7.32 (m, 1H), 7.13-7.10 (m, 1H), 5.23 (q,



$J = 6.0$  Hz, 1H), 2.05 (s, 1H) 1.48 (d,  $J = 6.0$  Hz, 3H).

*1-(4-bromophenyl)ethan-1-ol (4g)*.<sup>4</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.46-7.44 (d,  $J = 12$  Hz, 2H), 7.23-7.21 (d,  $J = 12$  Hz, 2H), 4.83 (q,  $J = 6.0$  Hz, 1H), 2.13 (s, 1H) 1.45-1.44 (d,  $J = 6.0$  Hz, 3H).

*1-(4-nitrophenyl)ethan-1-ol (4h)*.<sup>5</sup> Yellowish oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (d,  $J = 12$  Hz, 1H), 7.55 (d,  $J = 6.0$  Hz, 1H), 5.02 (q,  $J = 6.0$  Hz, 1H), 2.15 (s, 1H), 1.53 (d,  $J = 6.0$  Hz, 3H).

*1-(4-(trifluoromethyl)phenyl)ethan-1-ol (4i)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d,  $J = 6.0$  Hz, 2H), 7.49 (d,  $J = 6.0$  Hz, 2H), 4.97 (q,  $J = 6.0$  Hz, 1H), 1.95 (s, 1H), 1.51 (d,  $J = 6.0$  Hz, 3H).

*1-(o-tolyl)ethan-1-ol (4j)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d,  $J = 6.0$  Hz, 2H), 7.24-7.21 (m, 1H), 7.18-7.10 (m, 2H), 2.34 (s, 3H), 1.47 (d,  $J = 6.0$  Hz, 3H).

*1-(p-tolyl)ethan-1-ol (4k)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.27-7.26 (m, 2H), 7.16 (d,  $J = 6.0$  Hz, 2H), 4.86 (q,  $J = 6.0$  Hz, 1H), 2.34 (s, 3H) 1.76 (s, 1H), 1.49 (d,  $J = 6.0$  Hz, 3H).

*1-(4-methoxyphenyl)ethan-1-ol (4l)*.<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (d,  $J = 6.0$  Hz, 2H), 6.89 (d,  $J = 6.0$  Hz, 2H), 4.86 (q,  $J = 6.0$  Hz, 1H), 3.81 (s, 3H), 1.49 (d,  $J = 6.0$  Hz, 3H).

*1-(naphthalen-2-yl)ethan-1-ol (4m)*.<sup>5</sup> White solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.85-7.81 (m, 4H), 7.52-7.46 (m, 3H), 5.08 (q,  $J = 6.0$  Hz, 1H), 1.90 (s, 1H), 1.57 (d,  $J = 6.0$  Hz, 3H).

*2-methyl-1-phenylpropan-1-ol (4n)*.<sup>4</sup> Colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.50-7.48 (m, 2H), 7.31-7.29 (m, 2H), 7.18-7.15 (m, 1H), 2.28-2.22 (m, 1H), 1.20 (s, 12H), 1.09 (d,  $J = 6.0$  Hz, 3H), 0.65 (d,  $J = 6.0$  Hz, 3H), <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>):  $\delta$  22.02.

*diphenylmethanol (4o)*.<sup>5</sup> White solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.39-7.35 (m, 4H), 7.35-7.33 (m, 4H), 7.27-7.25 (m, 2H), 5.86 (s, 1H), 2.22 (s, 1H).

*(2-fluorophenyl)(phenyl)methanol (4p)*.<sup>5</sup> White solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.50-7.47 (m, 1H), 7.38-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.26-7.21 (m, 2H),

7.14-7.11 (m, 1H), 7.01-6.98 (m, 1H), 6.11 (s, 1H), 2.41 (s, 1H).

*1-(pyridin-4-yl)ethan-1-ol (4q)*.<sup>6</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.15-8.13 (m, 2 H), 7.51-7.49 (m, 2 H), 5.00-4.96 (q, *J* = 6.5 Hz, 1 H), 2.69 (s, 1 H), 1.49-1.47 (dd, *J* = 6.5 and 4.5 Hz, 3 H).

*1-cyclohexylethan-1-ol (4r)*.<sup>6</sup> Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.88-3.84 (m, 1H), 1.79-1.74 (m, 1H), 1.73-1.69 (m, 2H), 1.67-1.65 (m, 4H), 1.60-1.56 (m, 4H), 1.19 (s, 12H), 1.09-1.07(d, *J* = 6.0 Hz, 3H). <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>) δ 21.94.

*Cyclohexanol (4s)*.<sup>6</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.60 (br, 1 H), 1.88 (m, 2 H), 1.75-1.68 (m, 2 H), 1.54-1.50(m, 1 H), 1.26 (m, 4 H), 1.16 (m, 1 H).

*2-(2,6-di-tert-butyl-4-methylphenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)*.

Green oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.02(s, 2H), 2.27 (s, 3H), 1.40 (s, 18H), 1.27 (s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 149.1, 140.6, 131.5, 126.4, 83.6, 35.2, 31.7, 30.4, 25.2, 21.4. <sup>11</sup>B NMR (193 MHz, CDCl<sub>3</sub>) δ 21.20.

NMR spectra of hydroboration products (**o**: residual MeCN; **x**: residual Et<sub>4</sub>NBF<sub>4</sub>)

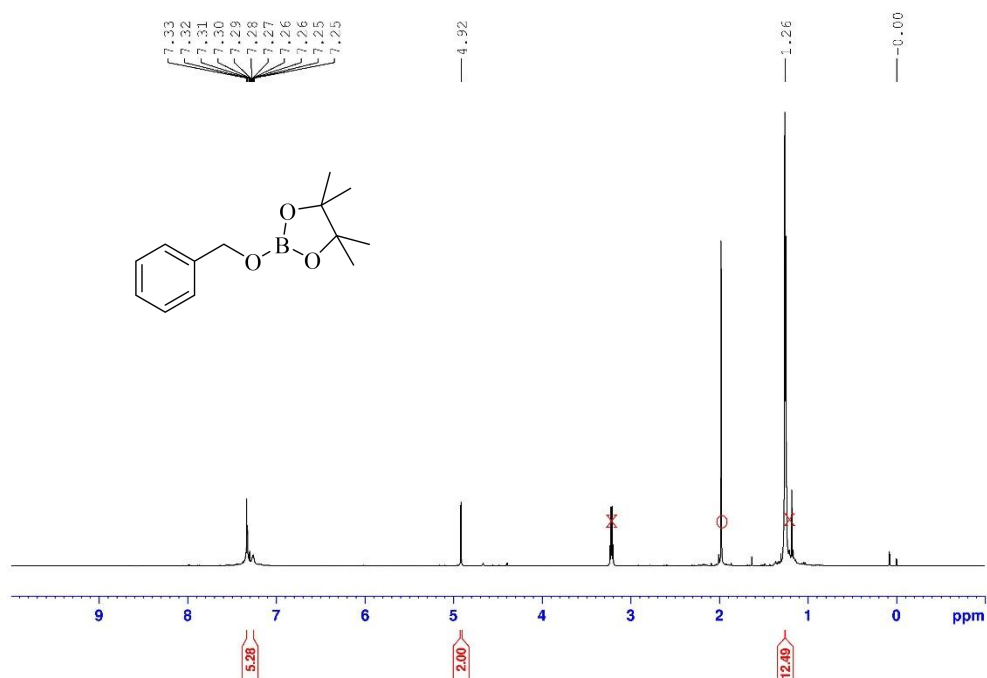


Figure S2. <sup>1</sup>H NMR spectrum of 2a in CDCl<sub>3</sub>.

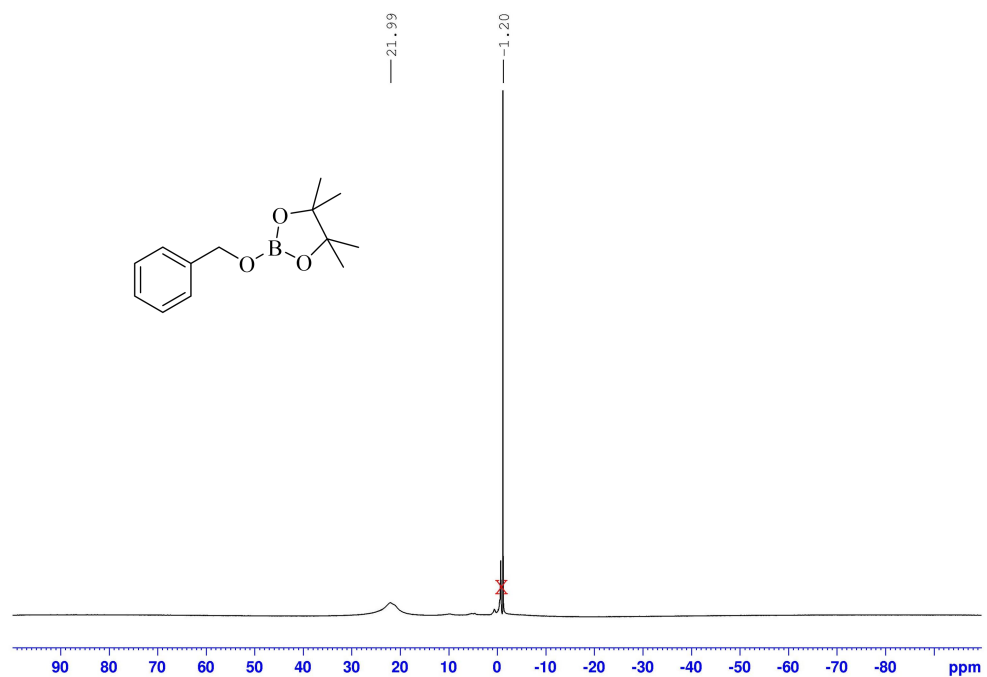
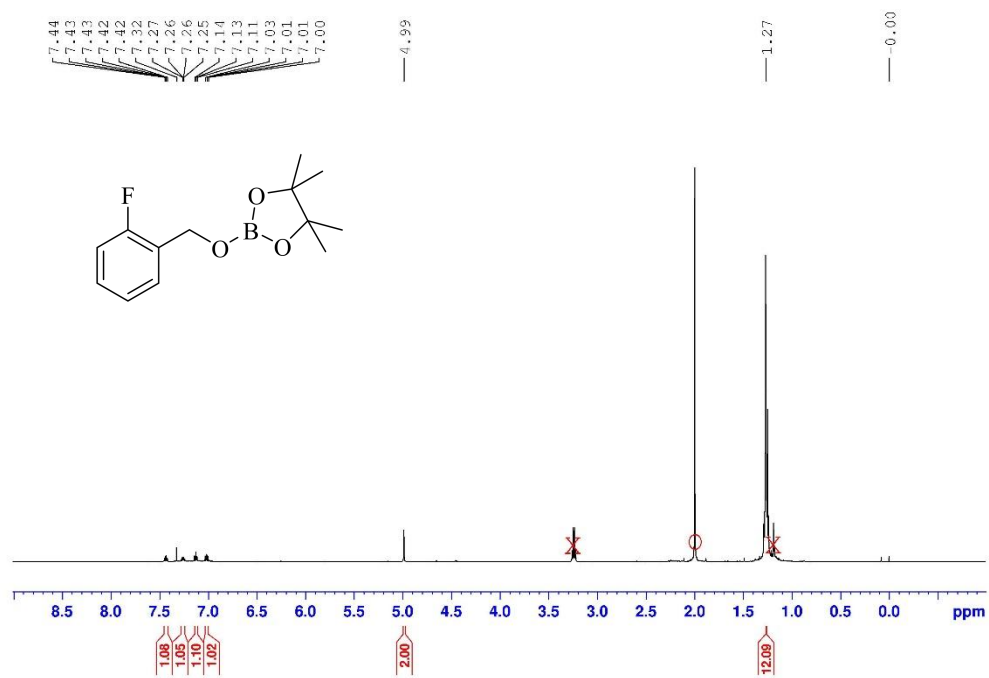
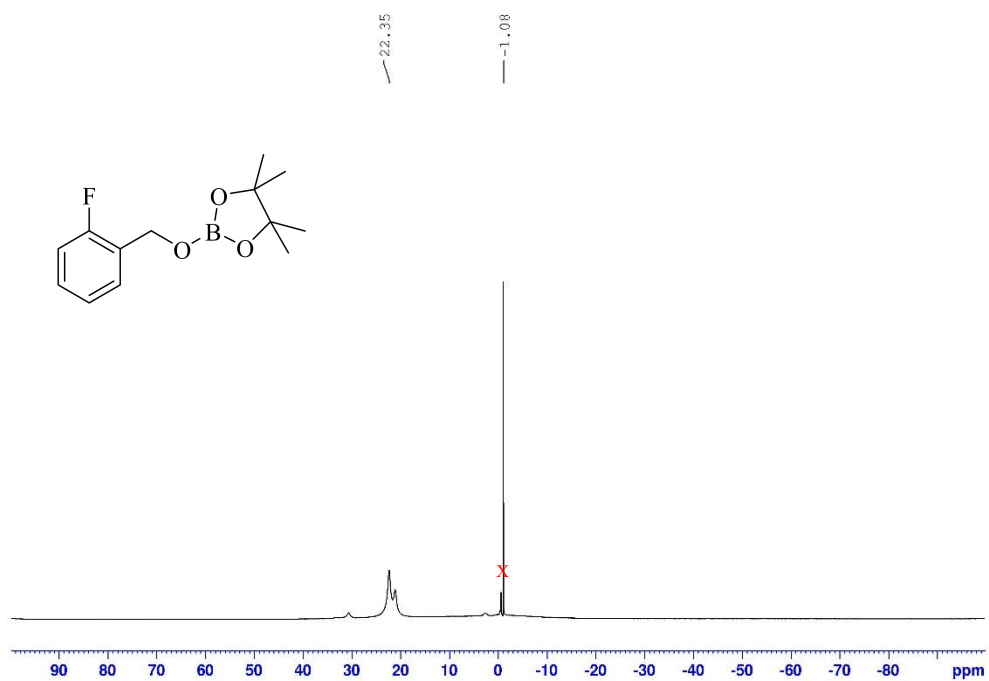


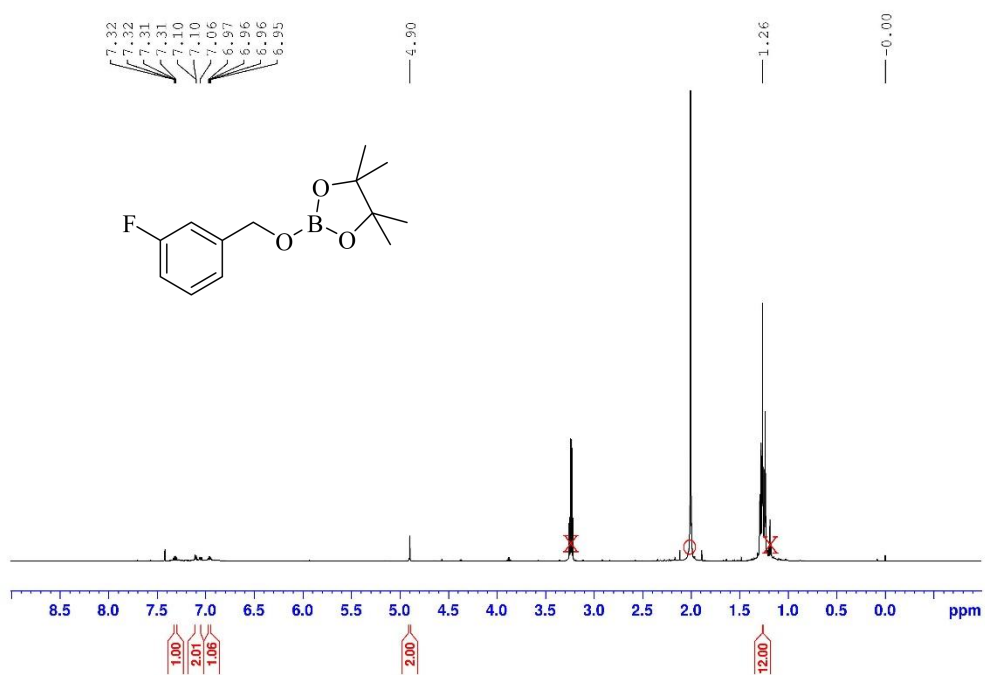
Figure S3. <sup>11</sup>B NMR spectrum of 2a in CDCl<sub>3</sub>.



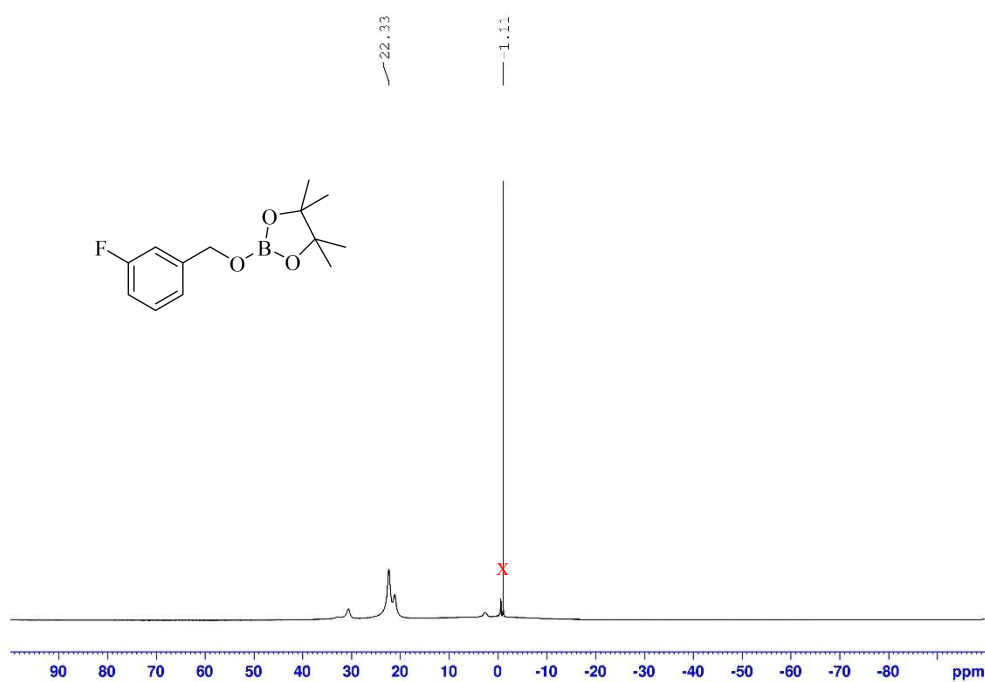
**Figure S4.** <sup>1</sup>H NMR spectrum of 2b in CDCl<sub>3</sub>.



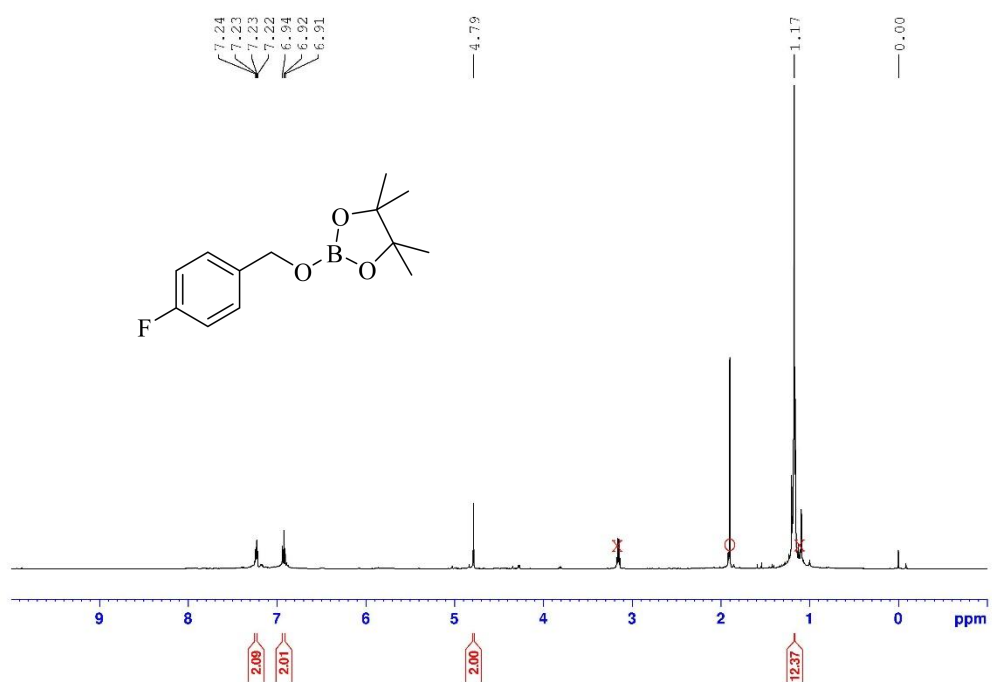
**Figure S5.** <sup>11</sup>B NMR spectrum of 2b in CDCl<sub>3</sub>.



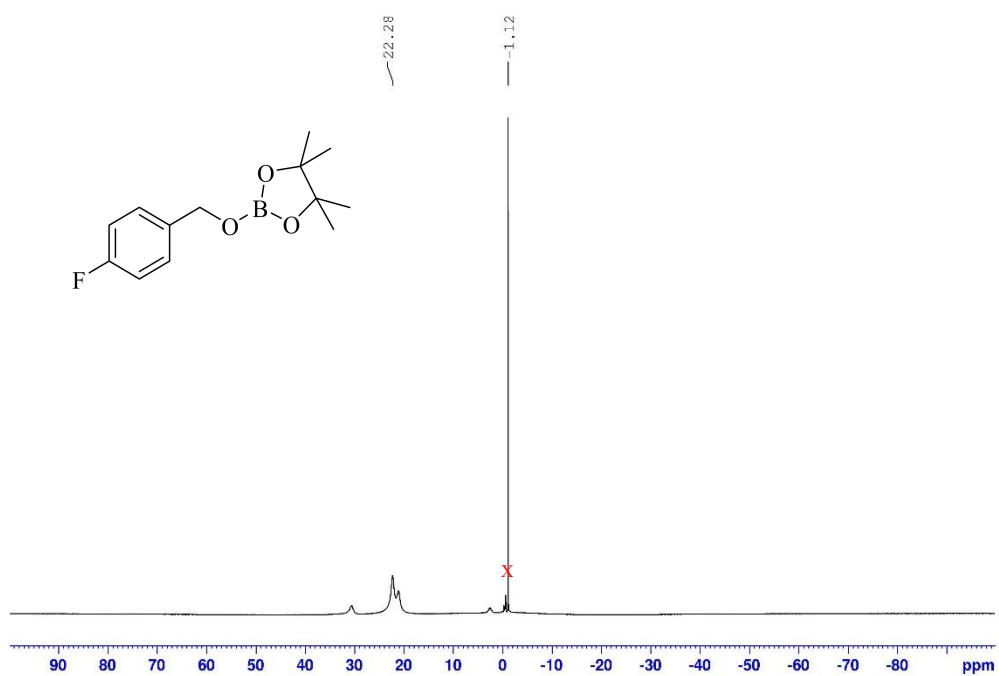
**Figure S6.** <sup>1</sup>H NMR spectrum of 2c in CDCl<sub>3</sub>.



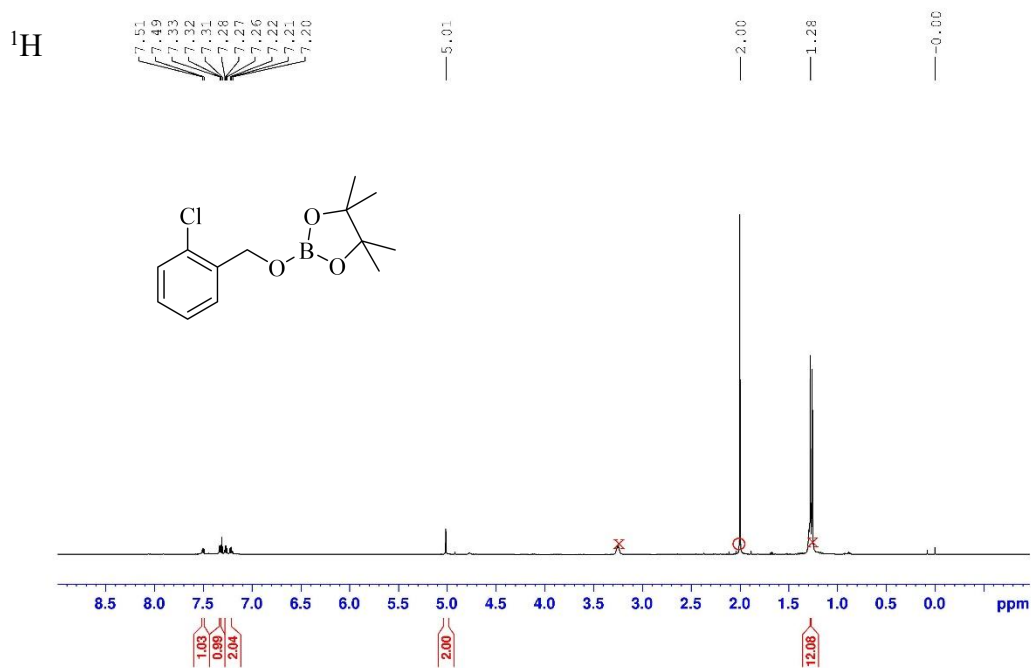
**Figure S7.** <sup>11</sup>B NMR spectrum of 2c in CDCl<sub>3</sub>.



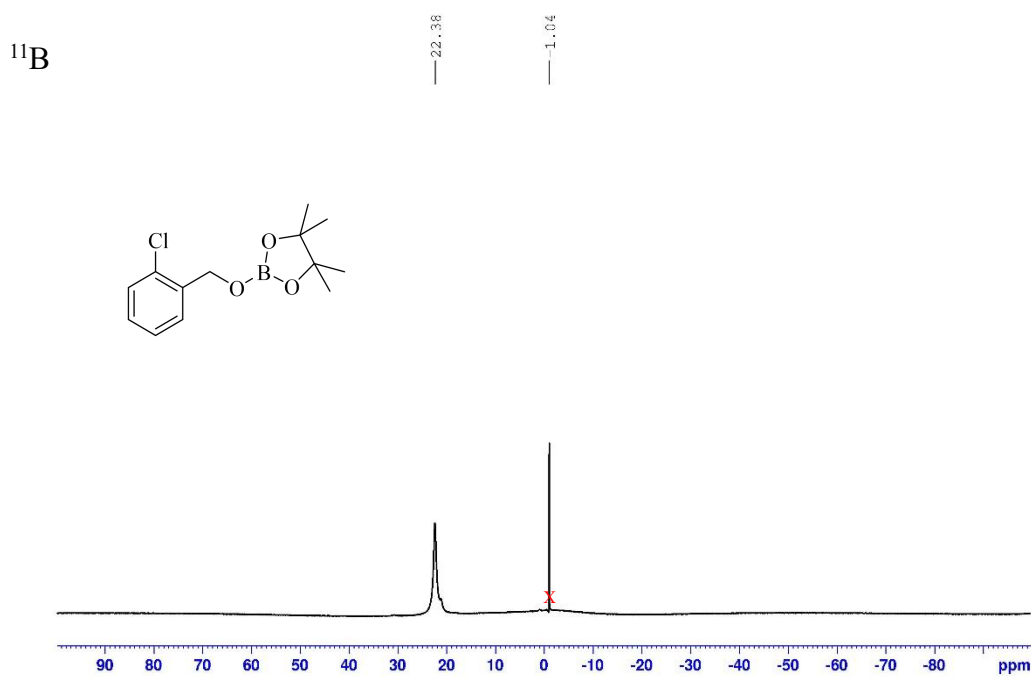
**Figure S8.** <sup>1</sup>H NMR spectrum of 2d in CDCl<sub>3</sub>.



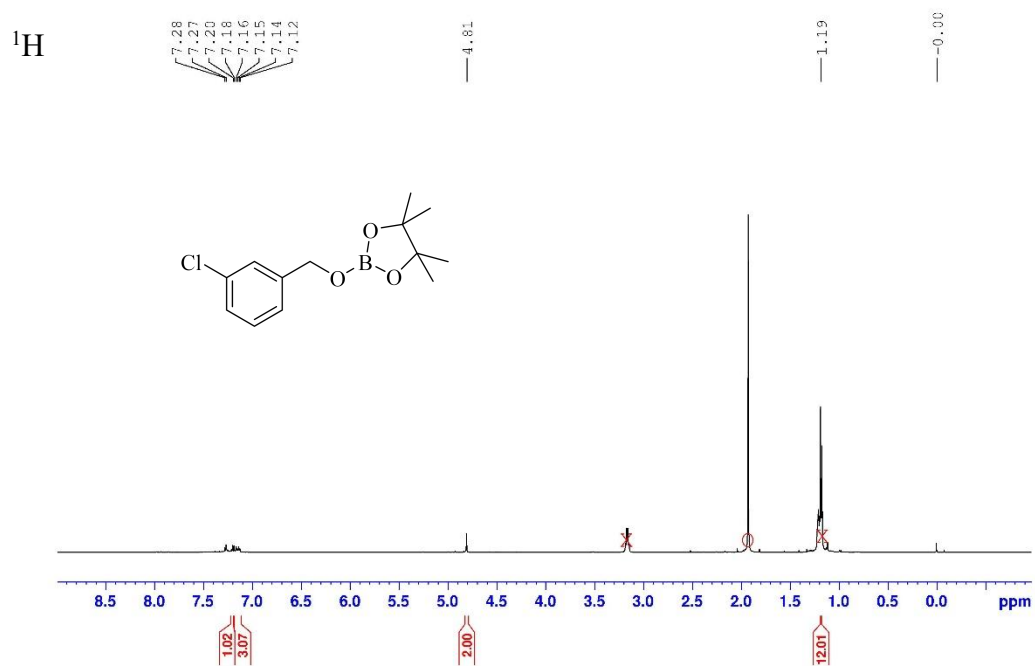
**Figure S9.** <sup>11</sup>B NMR spectrum of 2d in CDCl<sub>3</sub>.



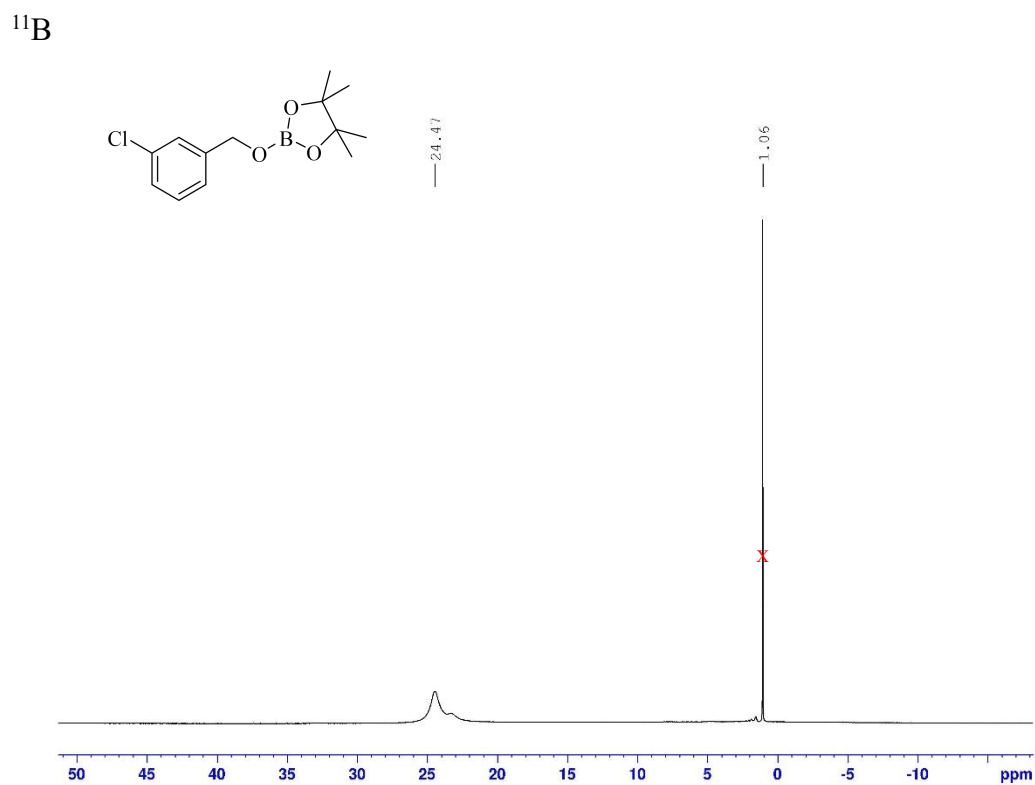
**Figure S10.**  $^1\text{H}$  NMR spectrum of 2e in  $\text{CDCl}_3$ .



**Figure S11.**  $^{11}\text{B}$  NMR spectrum of 2e in  $\text{CDCl}_3$ .



**Figure S12.**  $^1\text{H}$  NMR spectrum of 2f in  $\text{CDCl}_3$ .



**Figure S13.**  $^{11}\text{B}$  NMR spectrum of 2f in  $\text{CDCl}_3$ .



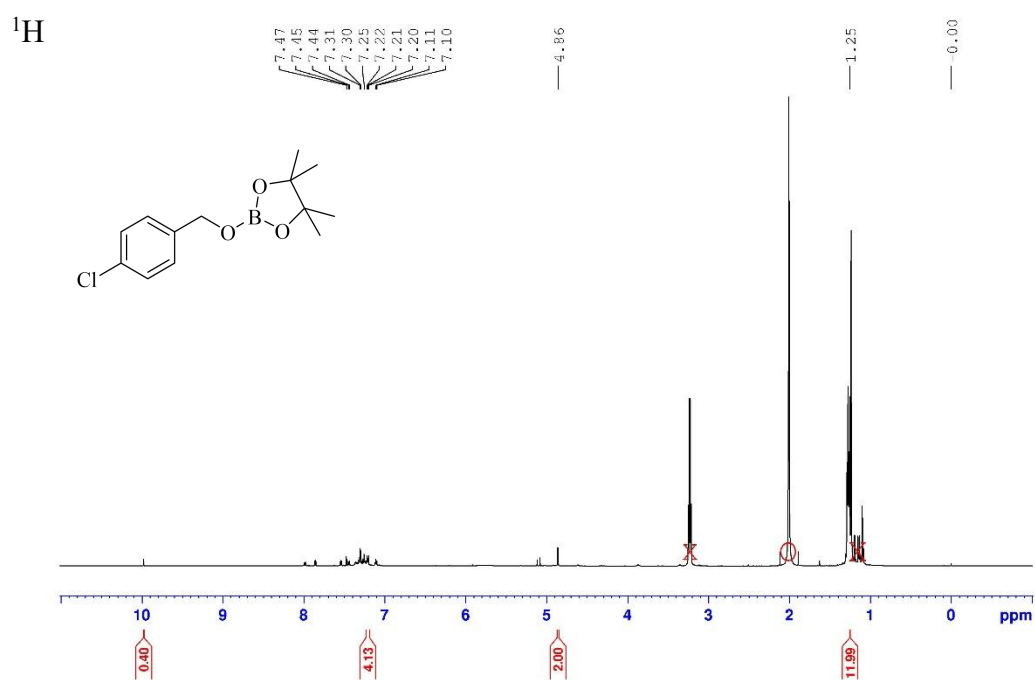


Figure S14. <sup>11</sup>B NMR spectrum of 2g in CDCl<sub>3</sub>.

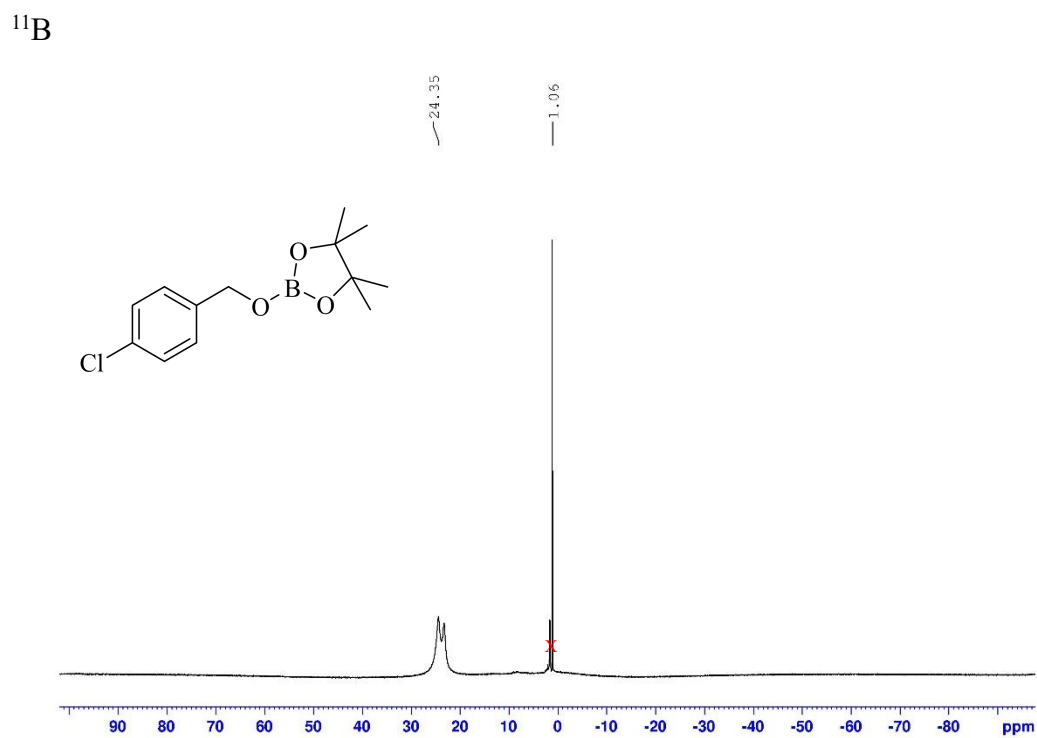


Figure S14. <sup>11</sup>B NMR spectrum of 2g in CDCl<sub>3</sub>.

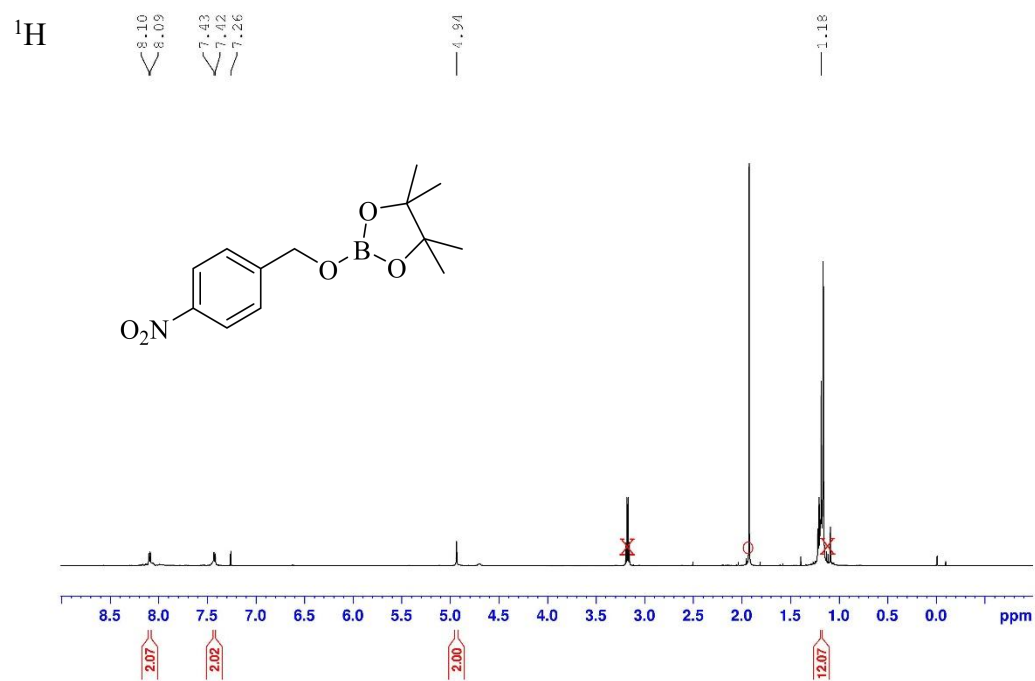


Figure S15. <sup>1</sup>H NMR spectrum of 2h in CDCl<sub>3</sub>.

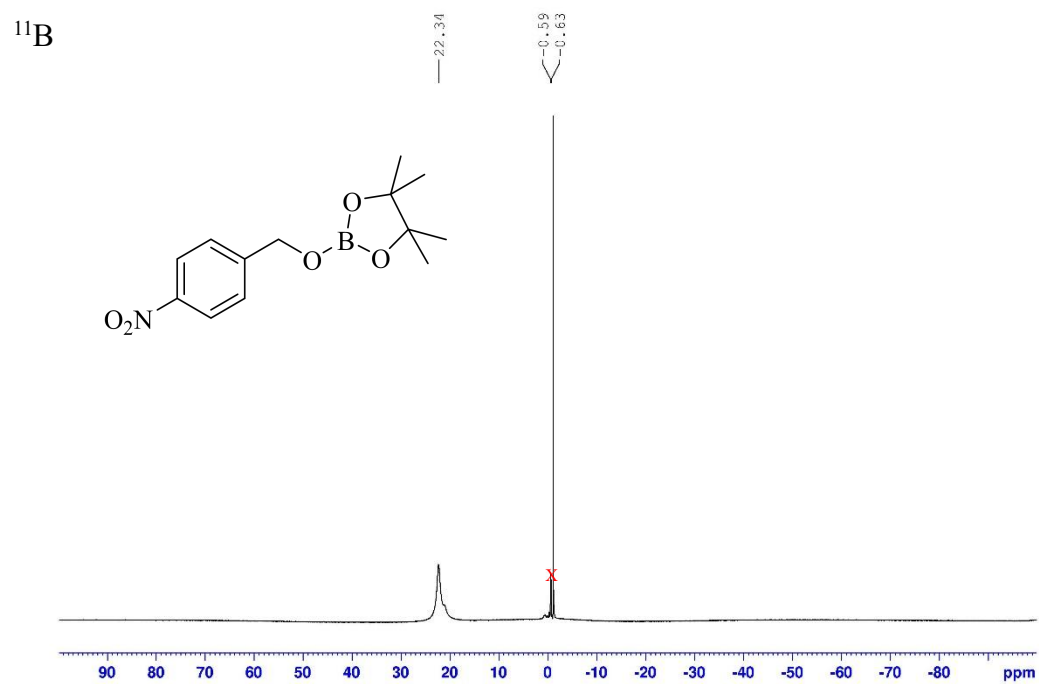
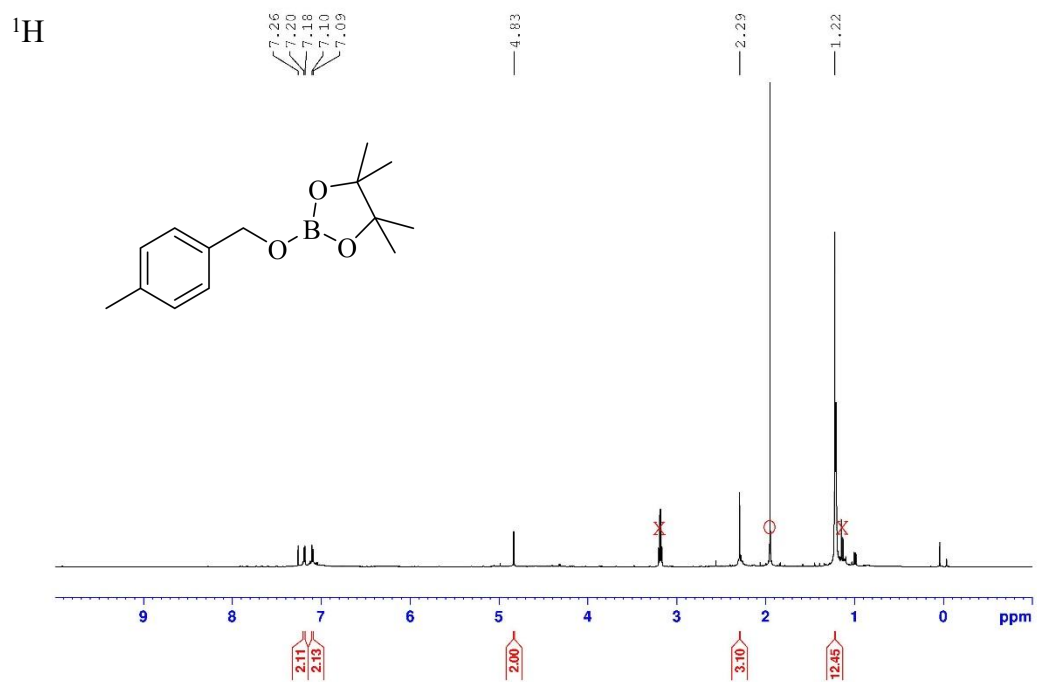
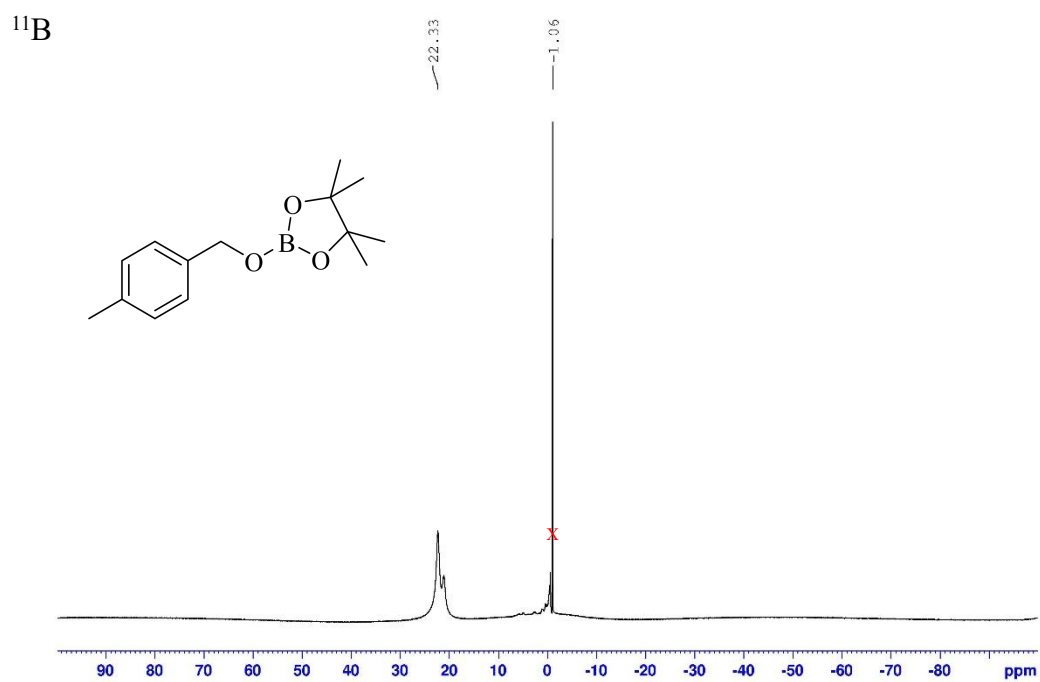


Figure S15. <sup>1</sup>H NMR spectrum of 2h in CDCl<sub>3</sub>.



**Figure S17.** <sup>1</sup>H NMR spectrum of 2i in CDCl<sub>3</sub>.



**Figure S18.** <sup>11</sup>B NMR spectrum of 2i in CDCl<sub>3</sub>.

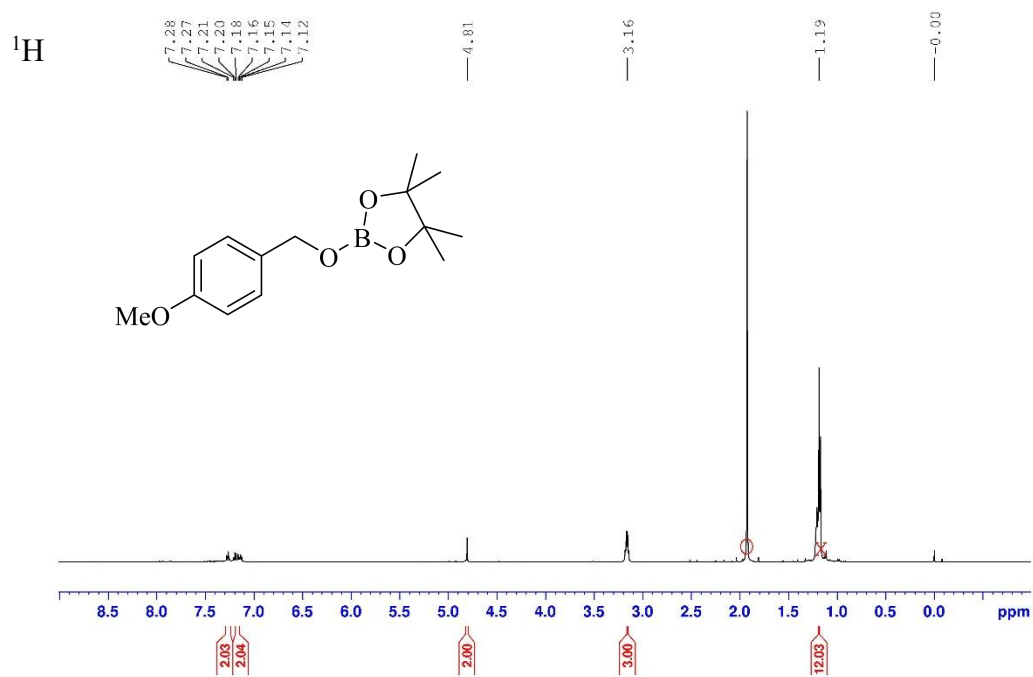


Figure S19. <sup>1</sup>H NMR spectrum of 2j in CDCl<sub>3</sub>.

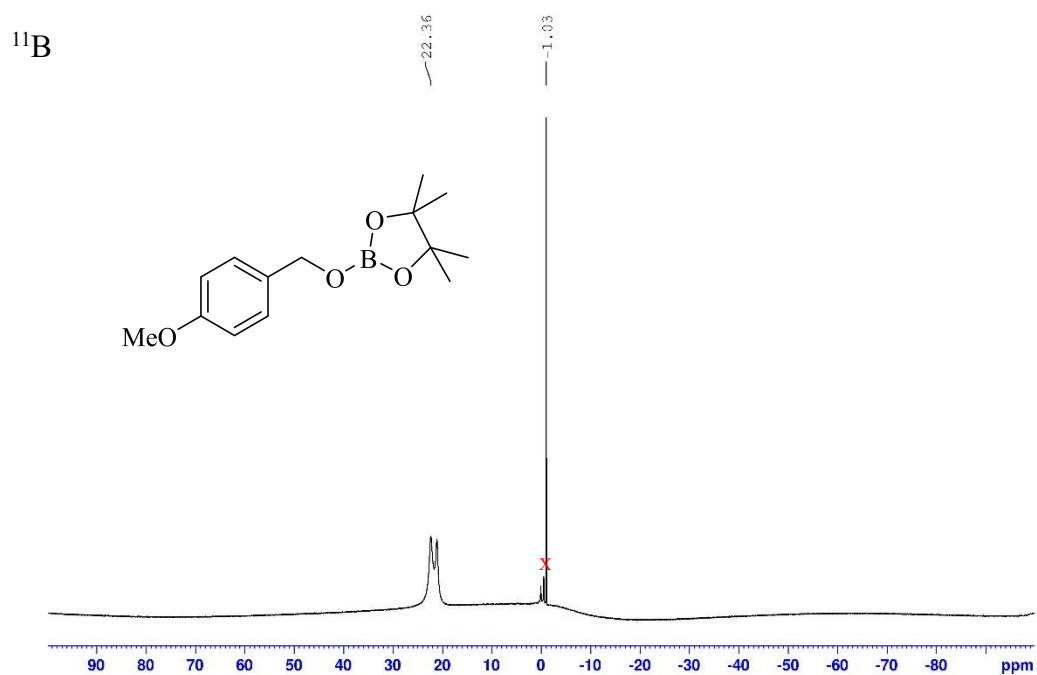
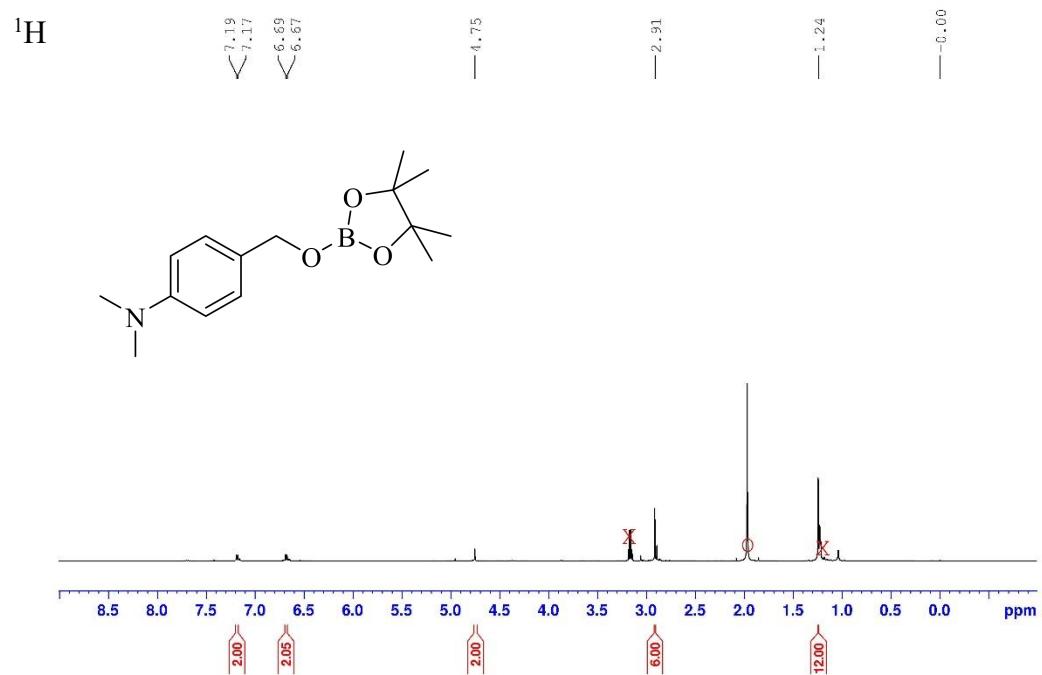
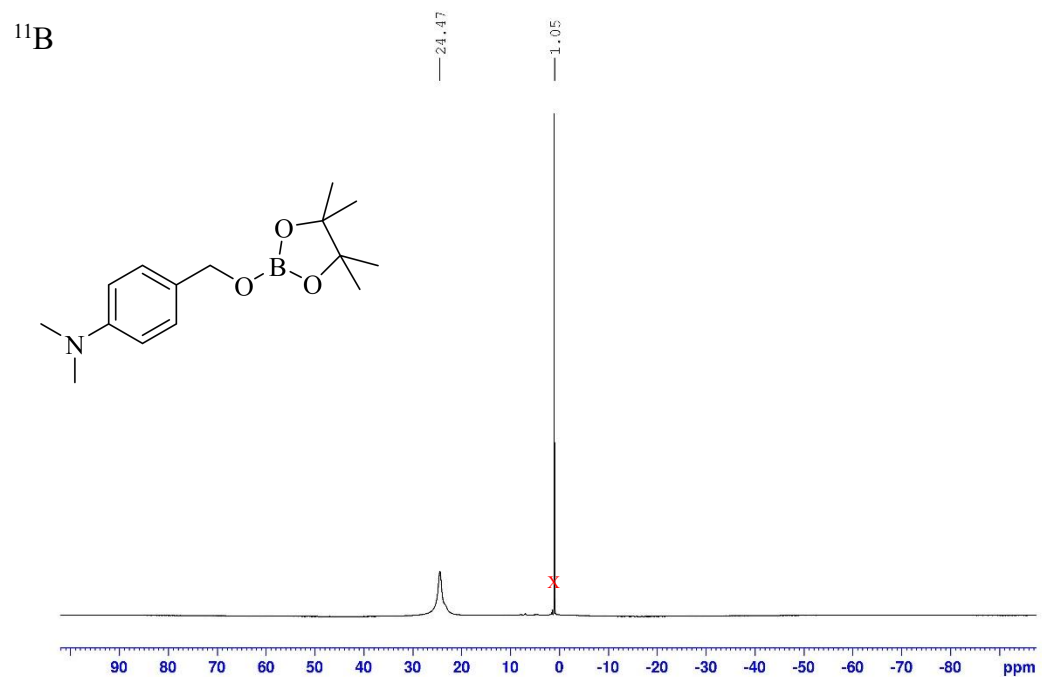


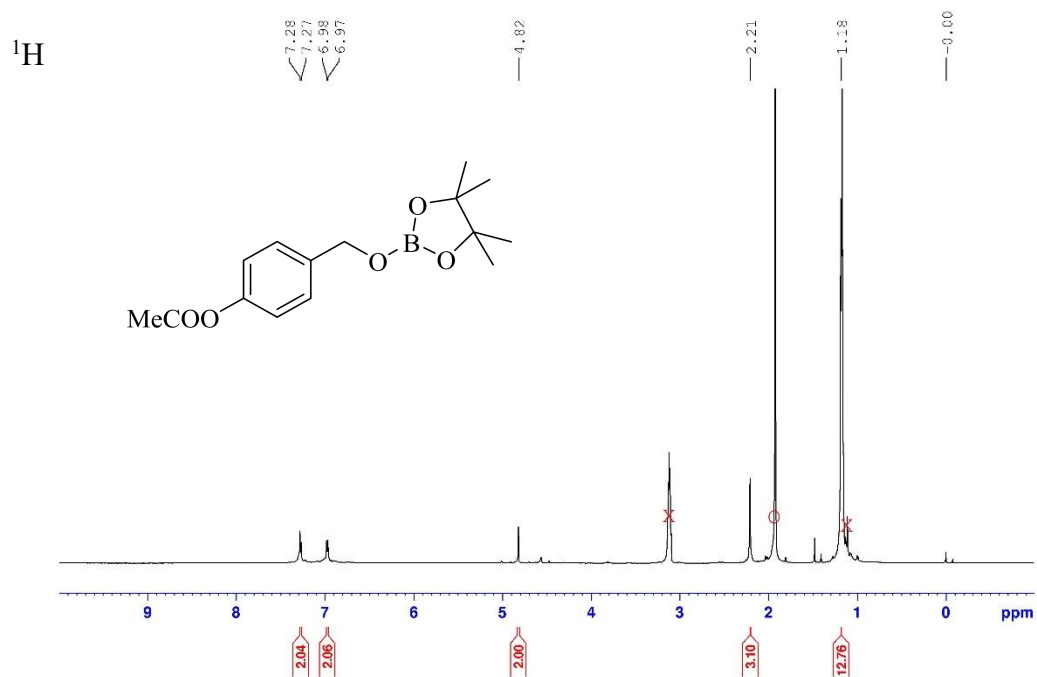
Figure S20. <sup>11</sup>B NMR spectrum of 2j in CDCl<sub>3</sub>.



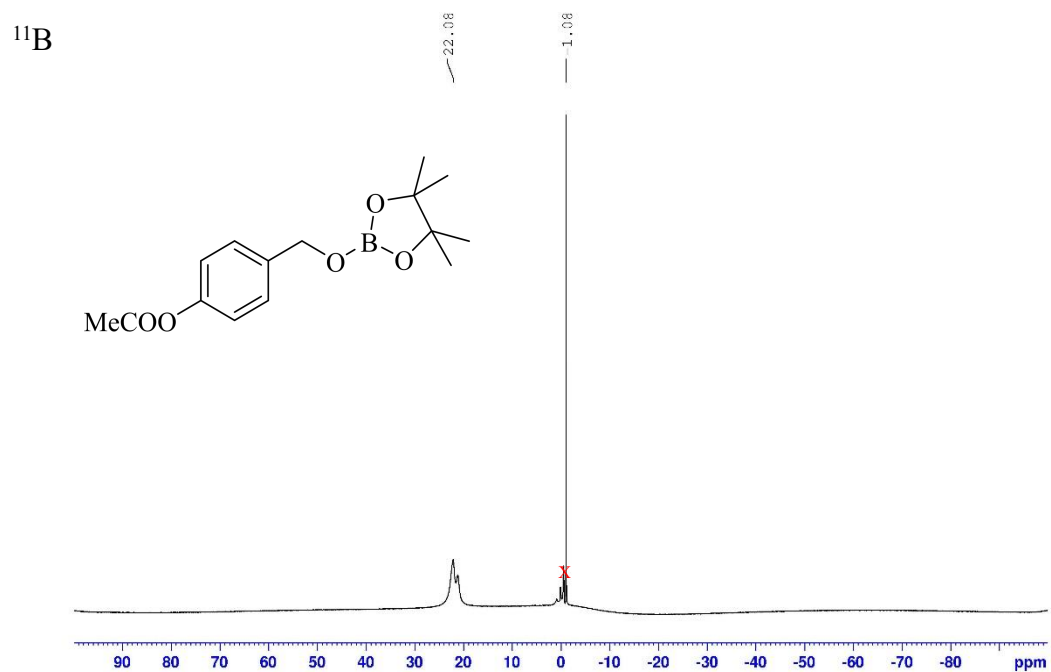
**Figure S21.**  $^1\text{H}$  NMR spectrum of 2k in  $\text{CDCl}_3$ .



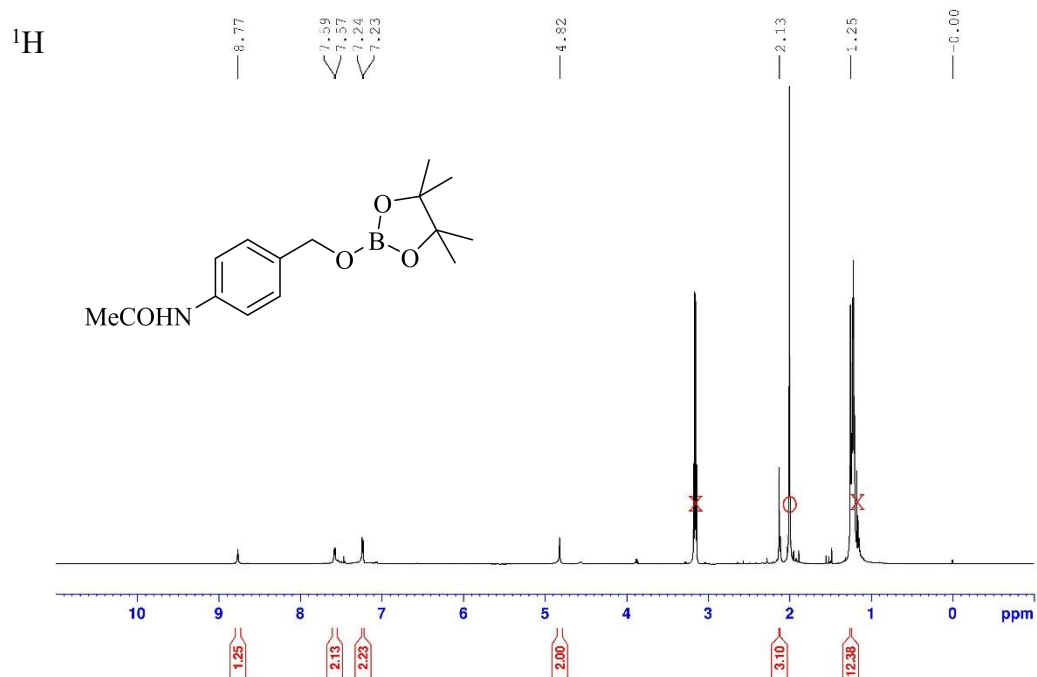
**Figure S22.**  $^{11}\text{B}$  NMR spectrum of 2k in  $\text{CDCl}_3$ .



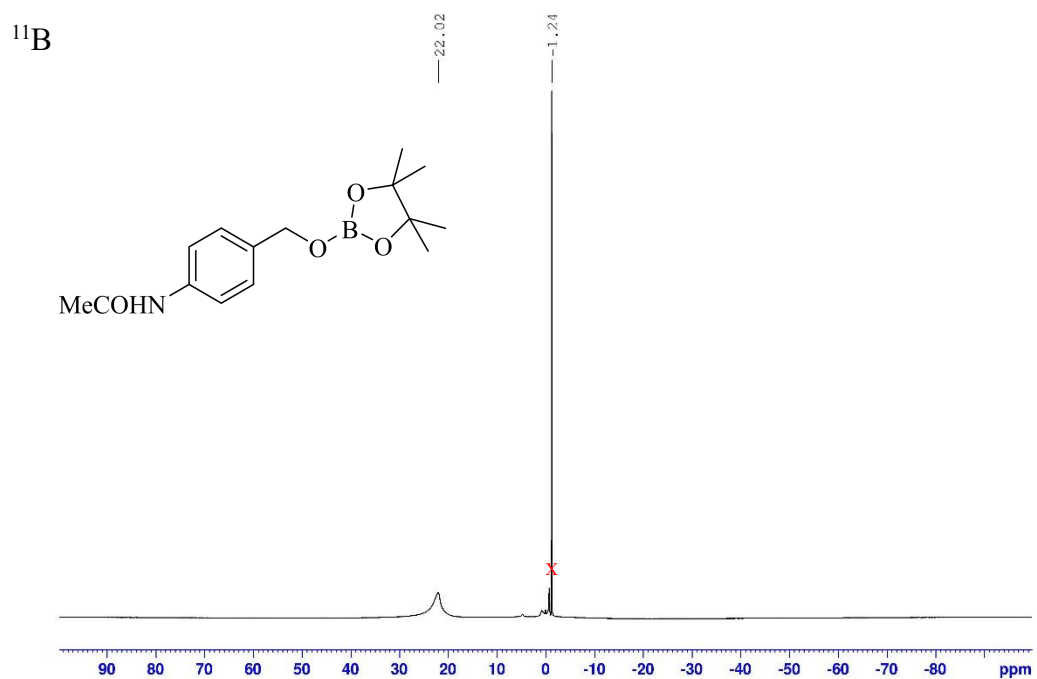
**Figure S23.** <sup>1</sup>H NMR spectrum of 21 in CDCl<sub>3</sub>.



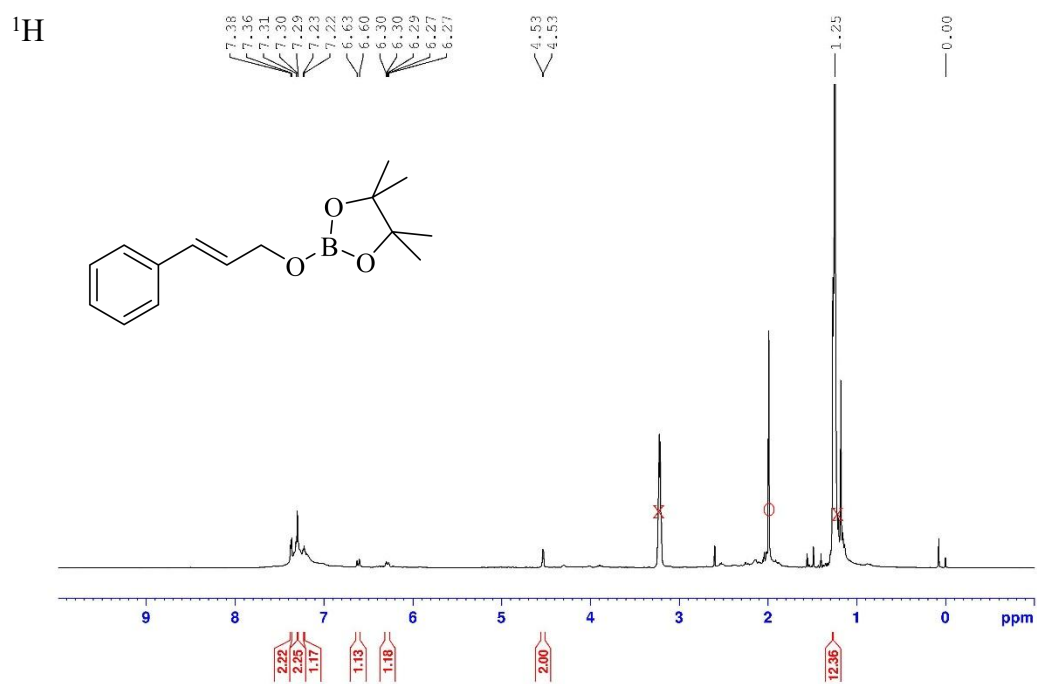
**Figure S24.** <sup>11</sup>B NMR spectrum of 21 in CDCl<sub>3</sub>.



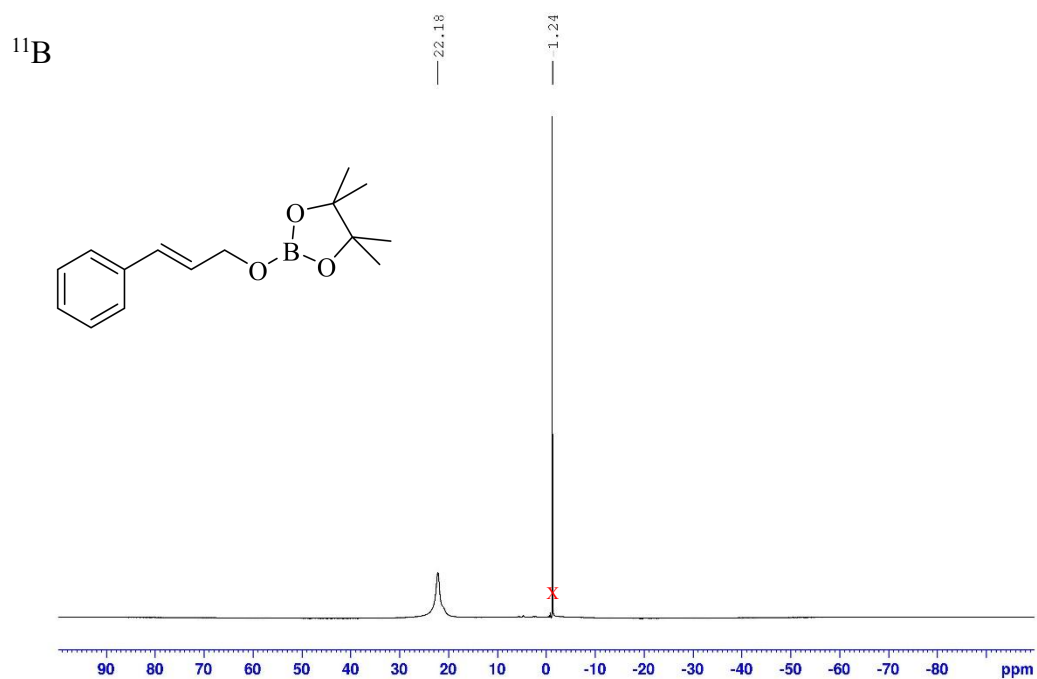
**Figure S25.**  $^1\text{H}$  NMR spectrum of 2m in  $\text{CDCl}_3$ .



**Figure S26.**  $^{11}\text{B}$  NMR spectrum of 2m in  $\text{CDCl}_3$ .

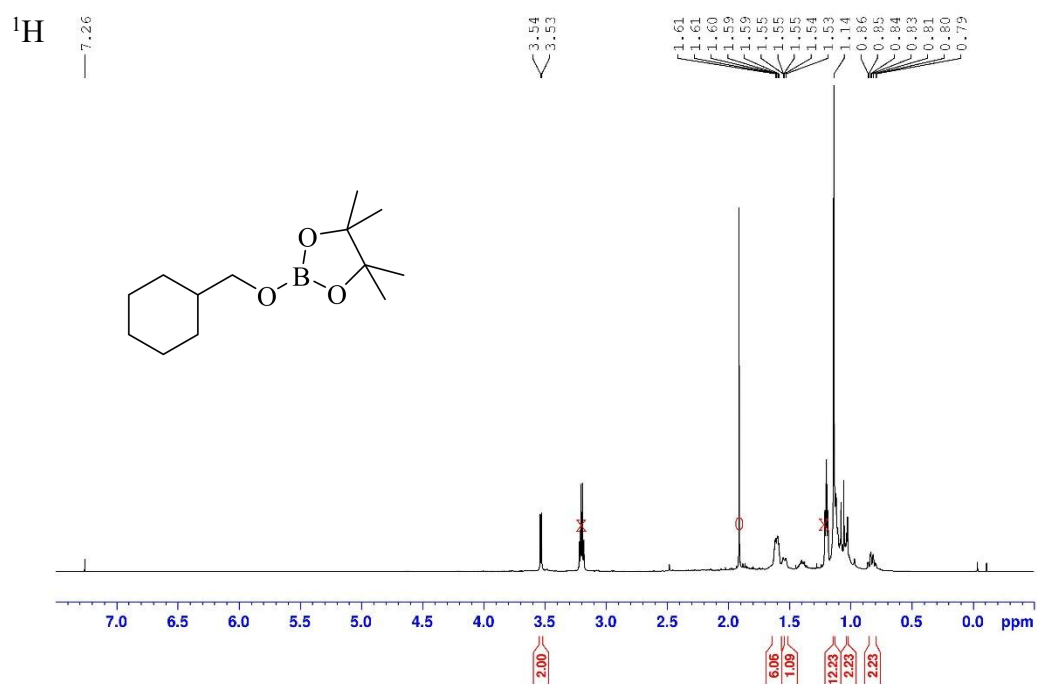


**Figure S27.**  $^1\text{H}$  NMR spectrum of **2n** in  $\text{CDCl}_3$ .

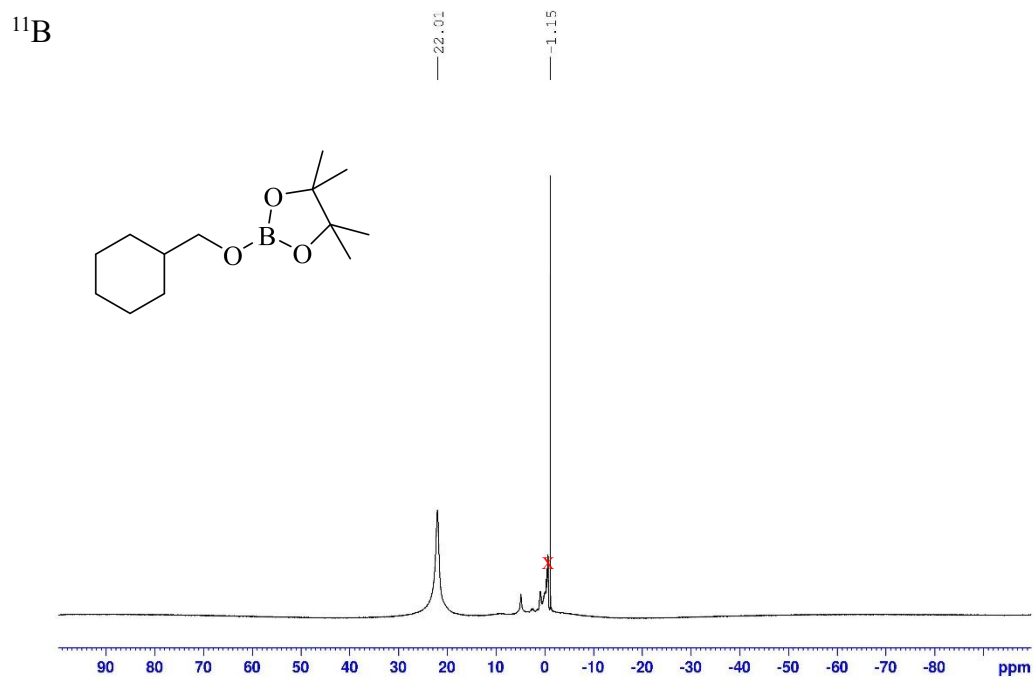


**Figure S28.**  $^{11}\text{B}$  NMR spectrum of **2n** in  $\text{CDCl}_3$ .



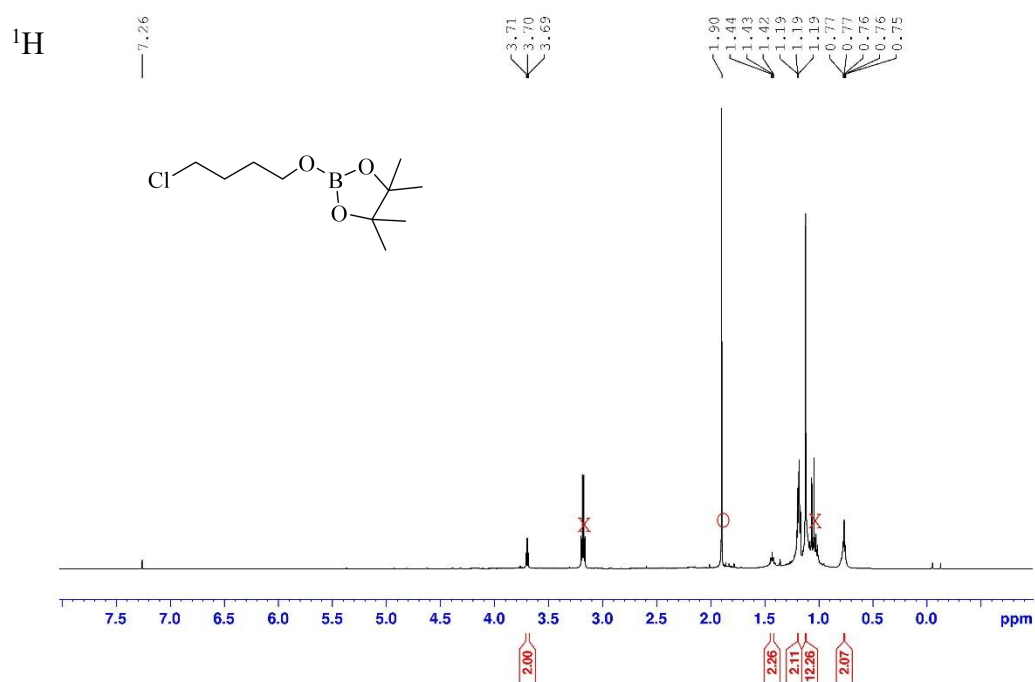


**Figure S29.** <sup>1</sup>H NMR spectrum of 2o in CDCl<sub>3</sub>.

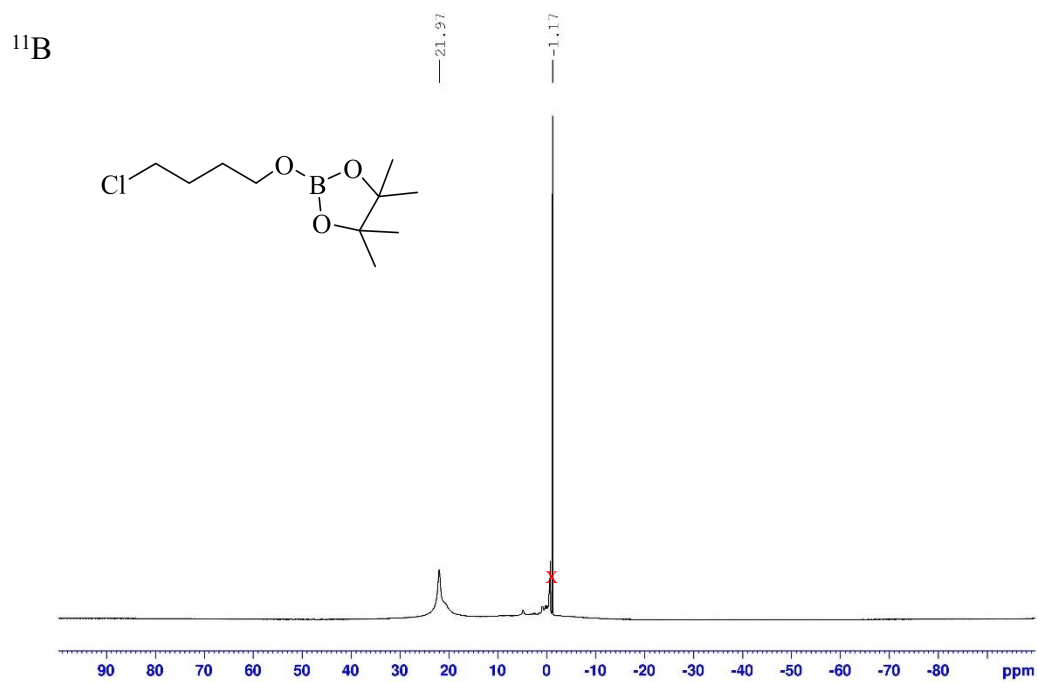


**Figure S30.** <sup>11</sup>B NMR spectrum of 2o in CDCl<sub>3</sub>.

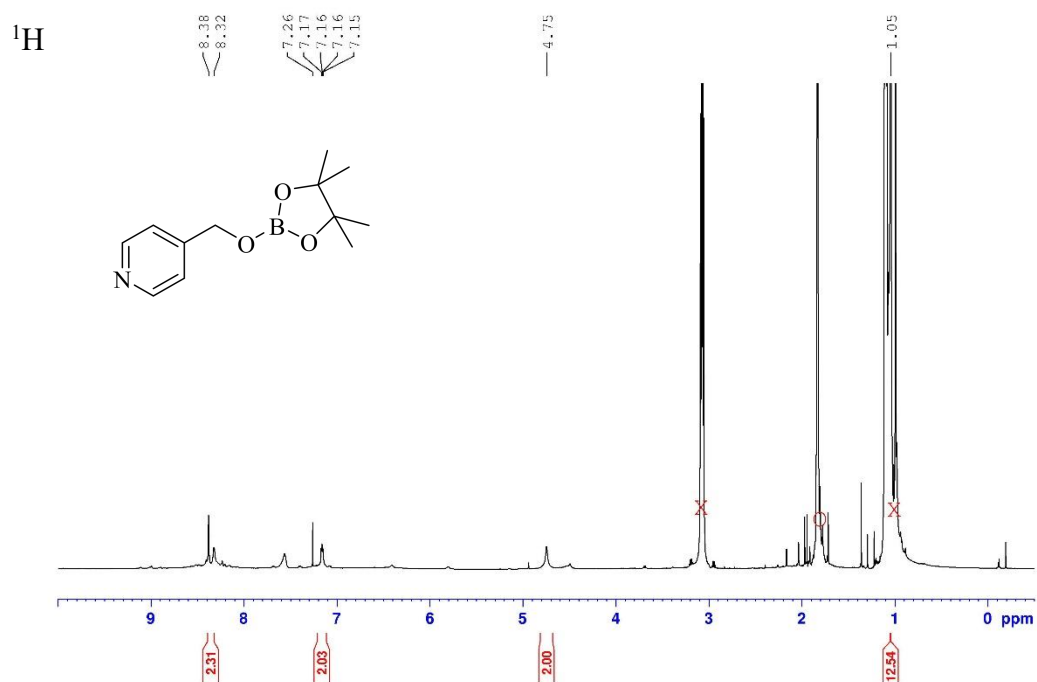




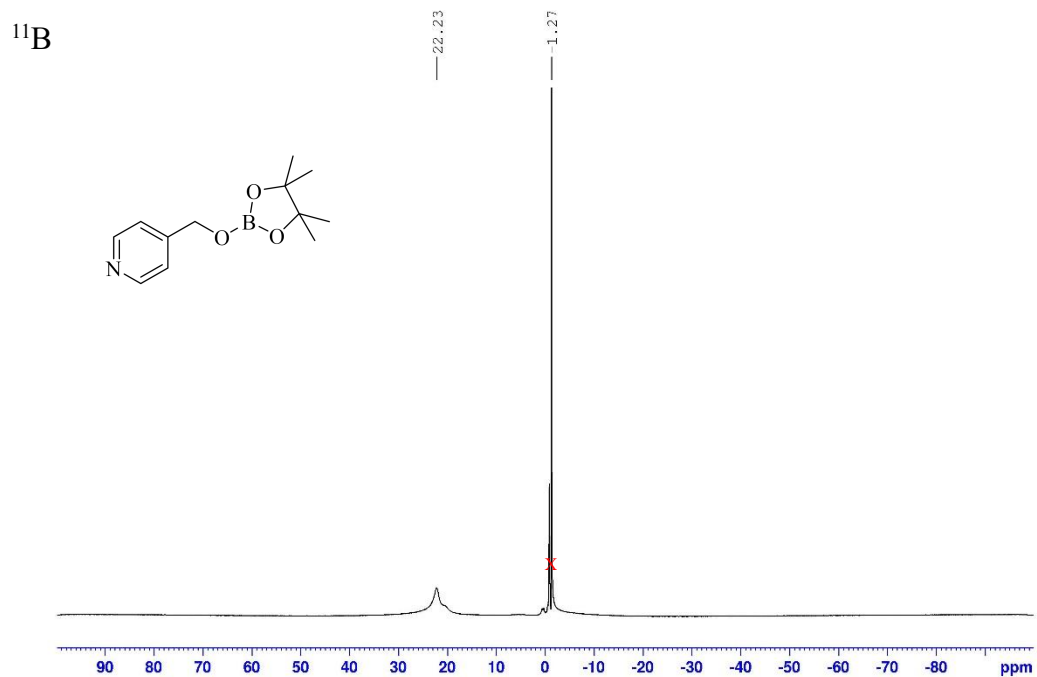
**Figure S33.** <sup>1</sup>H NMR spectrum of 2q in CDCl<sub>3</sub>.



**Figure S34.** <sup>11</sup>B NMR spectrum of 2q in CDCl<sub>3</sub>.



**Figure S35.**  $^1\text{H}$  NMR spectrum of 2r in  $\text{CDCl}_3$ .



**Figure S36.**  $^{11}\text{B}$  NMR spectrum of 2r in  $\text{CDCl}_3$ .

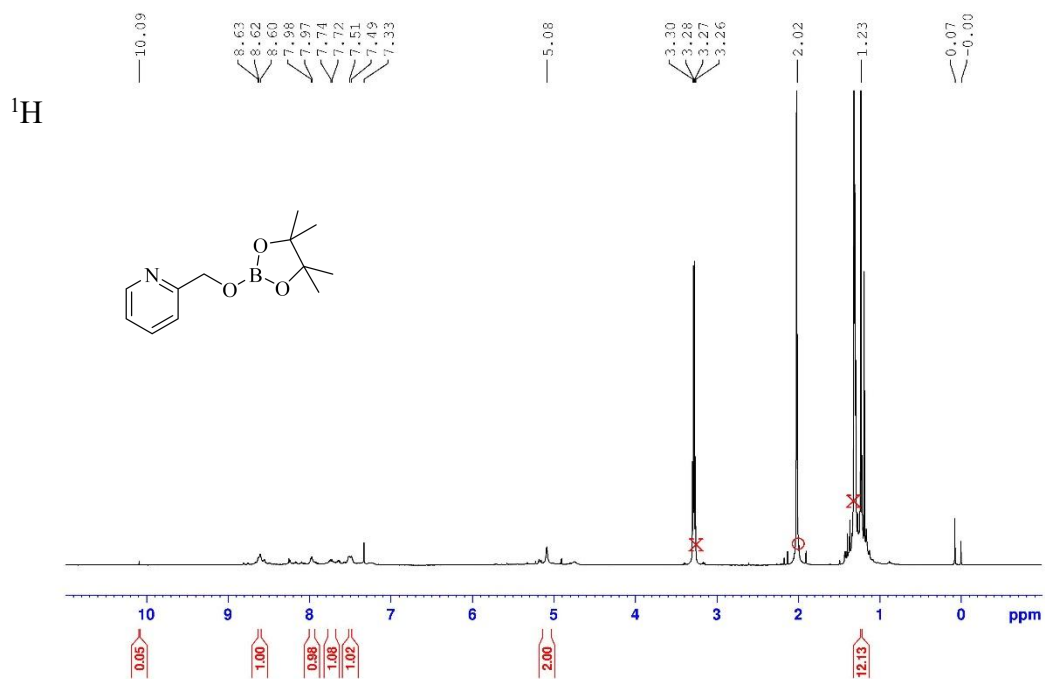


Figure S37. <sup>1</sup>H NMR spectrum of 2s in CDCl<sub>3</sub>.

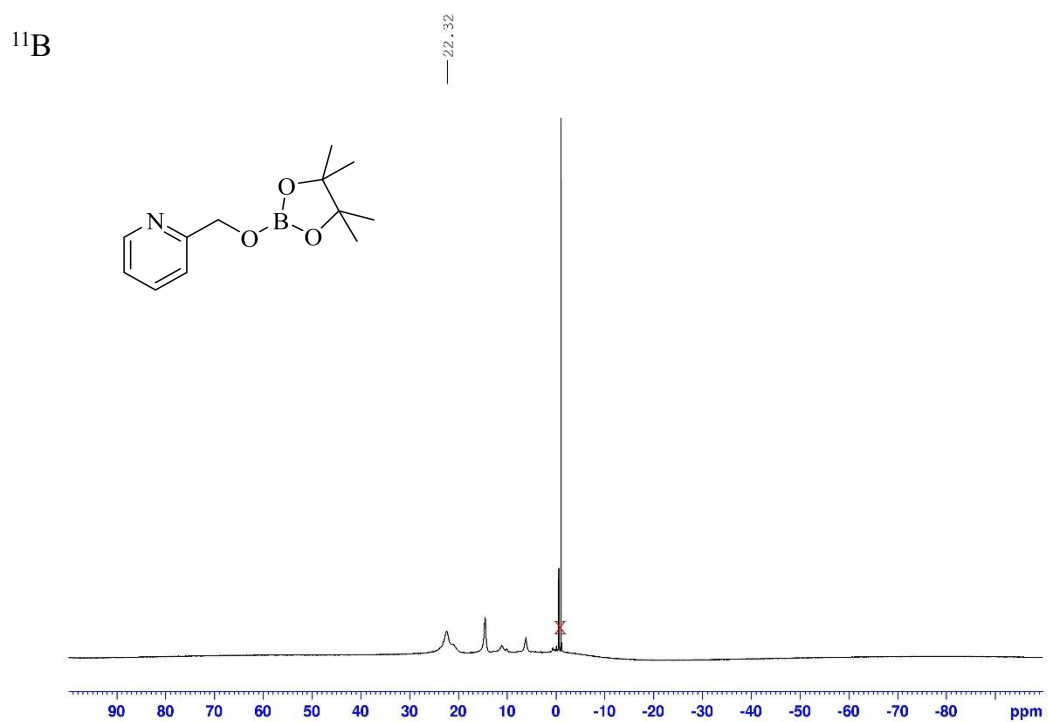


Figure S38. <sup>11</sup>B NMR spectrum of 2s in CDCl<sub>3</sub>.

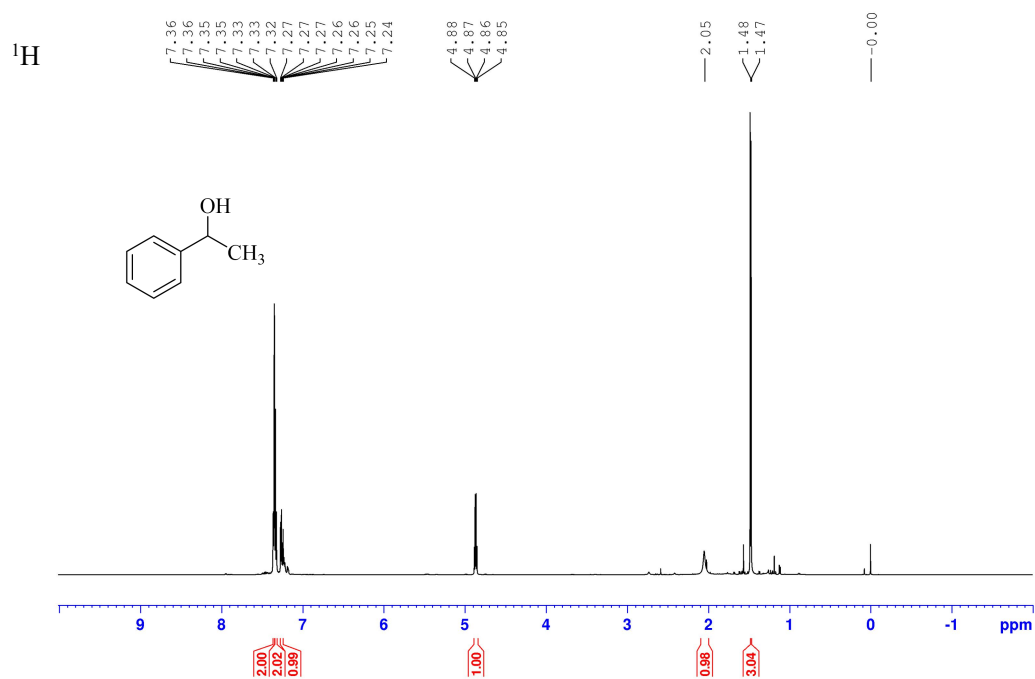


Figure S39. <sup>1</sup>H NMR spectrum of 4a in CDCl<sub>3</sub>.

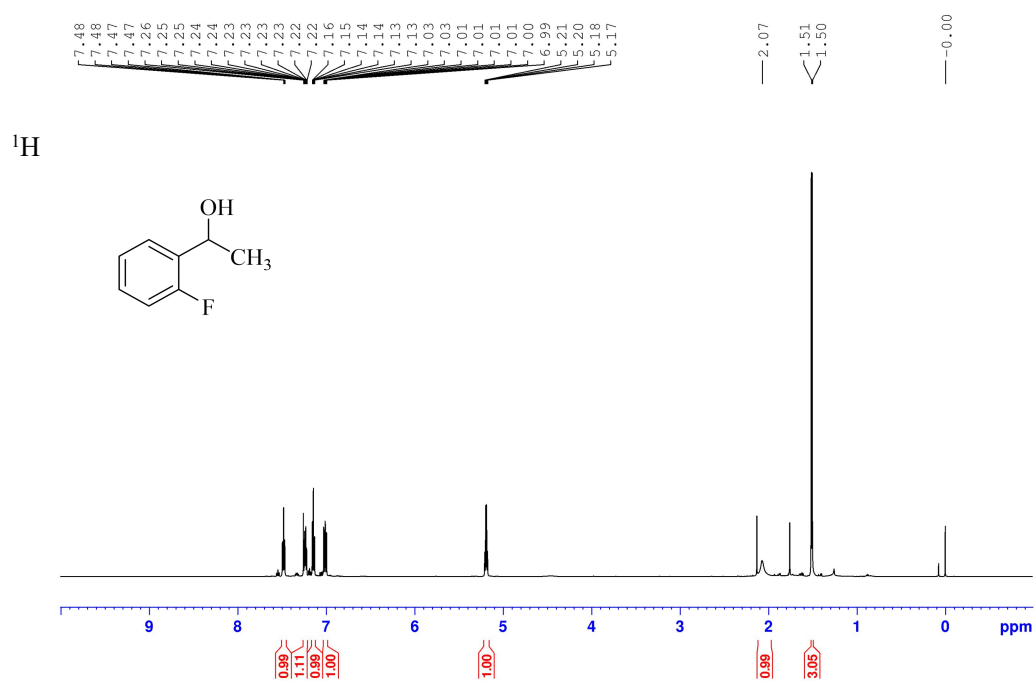


Figure S40. <sup>1</sup>H NMR spectrum of 4b in CDCl<sub>3</sub>.

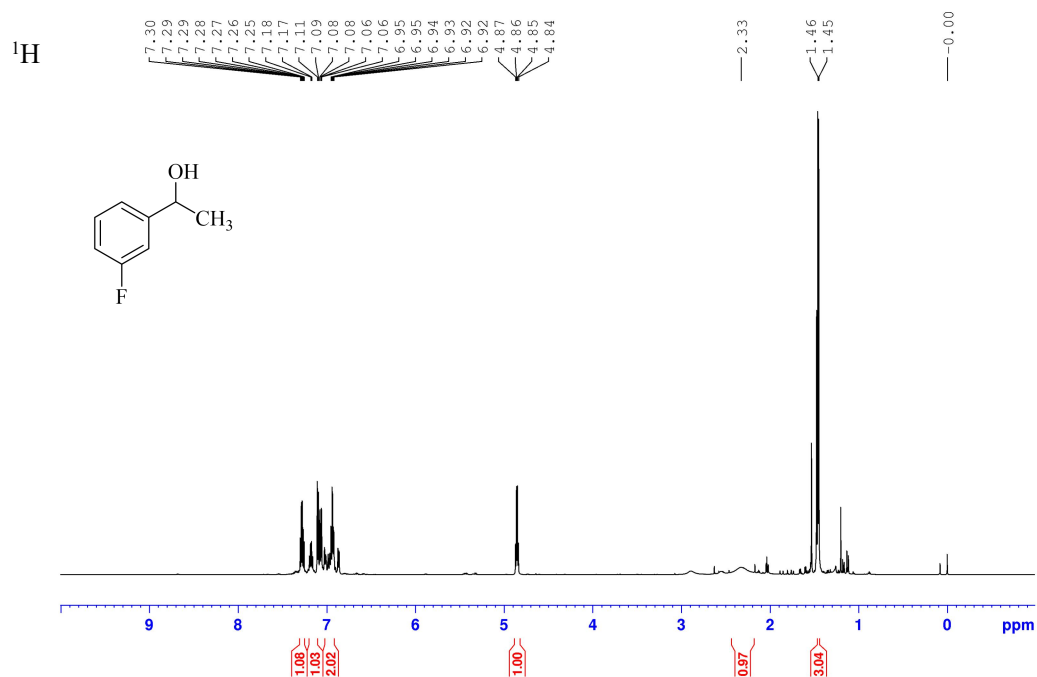


Figure S41. <sup>1</sup>H NMR spectrum of 4c in CDCl<sub>3</sub>.

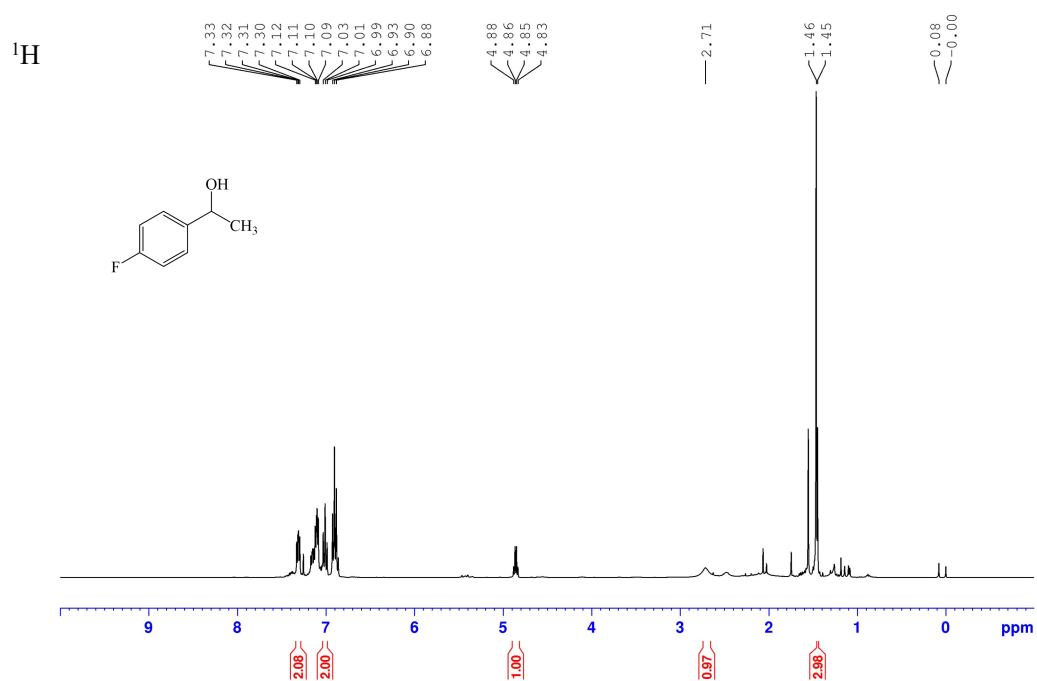


Figure S42. <sup>1</sup>H NMR spectrum of 4d in CDCl<sub>3</sub>.

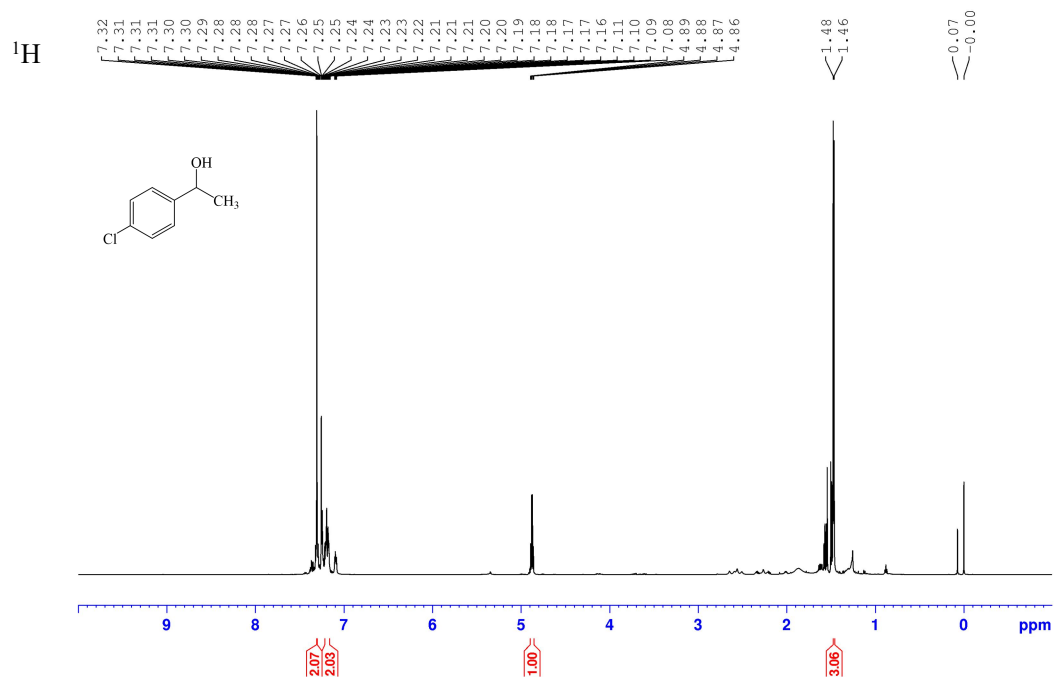


Figure S43. <sup>1</sup>H NMR spectrum of 4e in CDCl<sub>3</sub>.

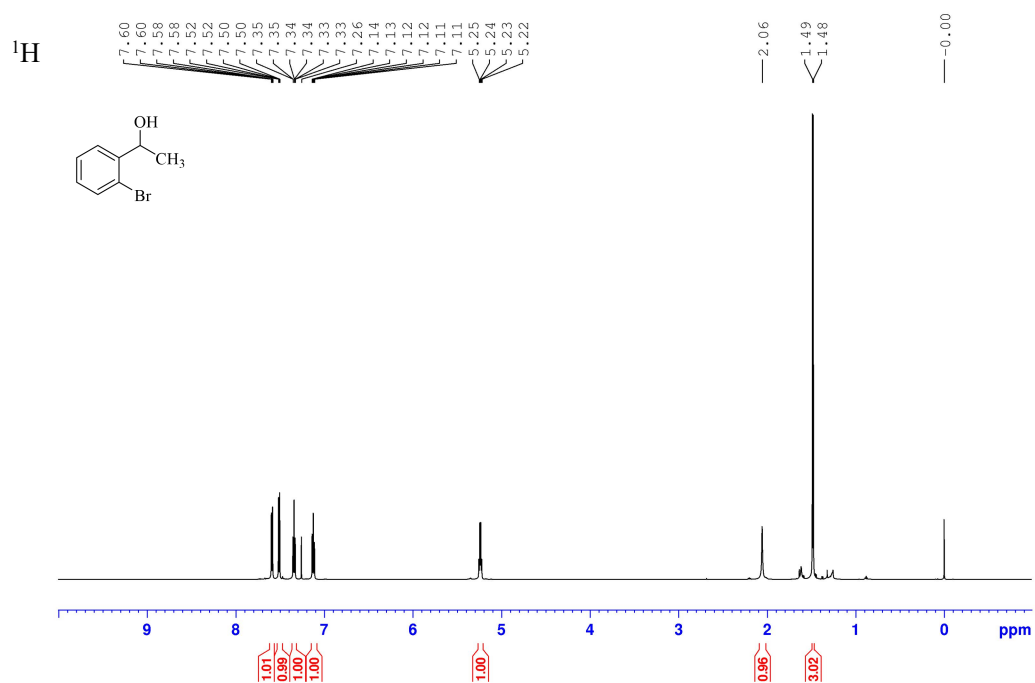


Figure S44. <sup>1</sup>H NMR spectrum of 4f in CDCl<sub>3</sub>.



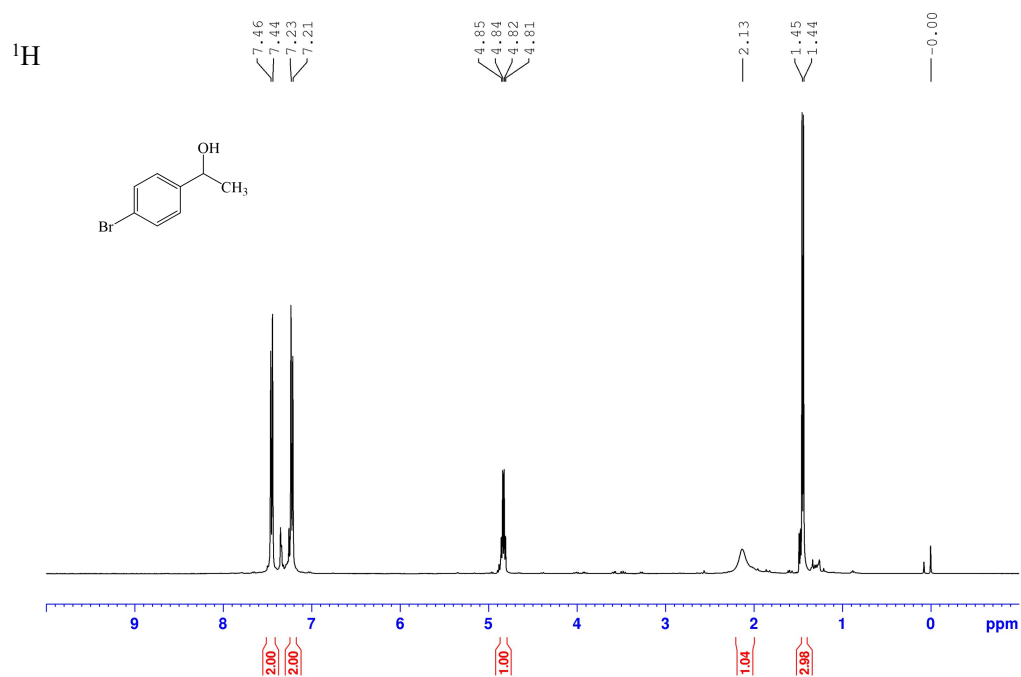


Figure S45.  $^1\text{H}$  NMR spectrum of 4g in  $\text{CDCl}_3$ .

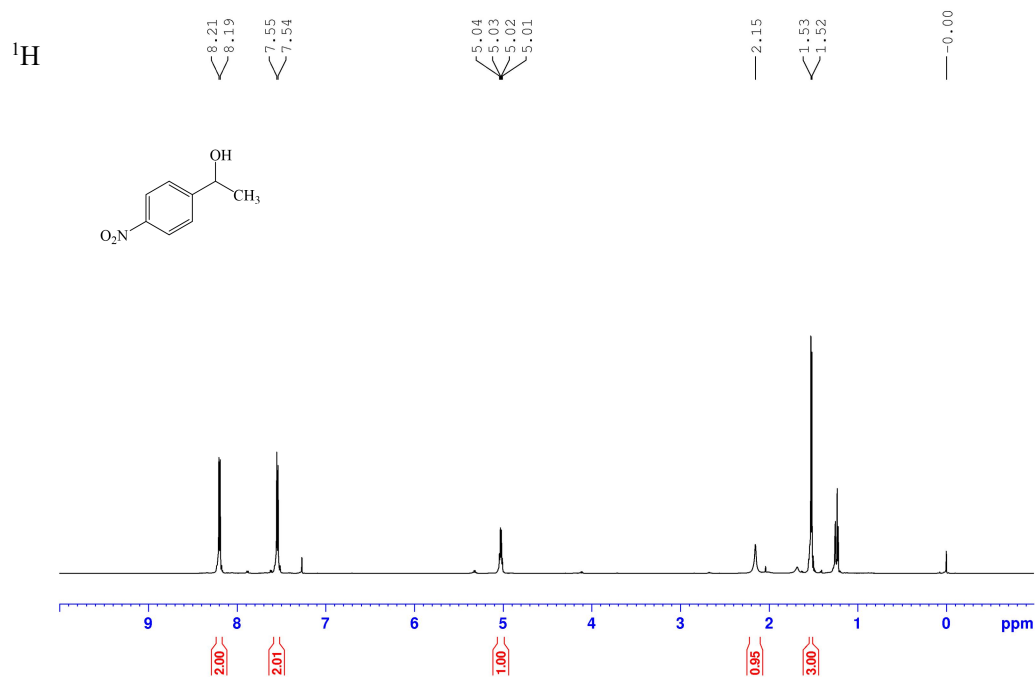


Figure S46.  $^1\text{H}$  NMR spectrum of 4h in  $\text{CDCl}_3$ .

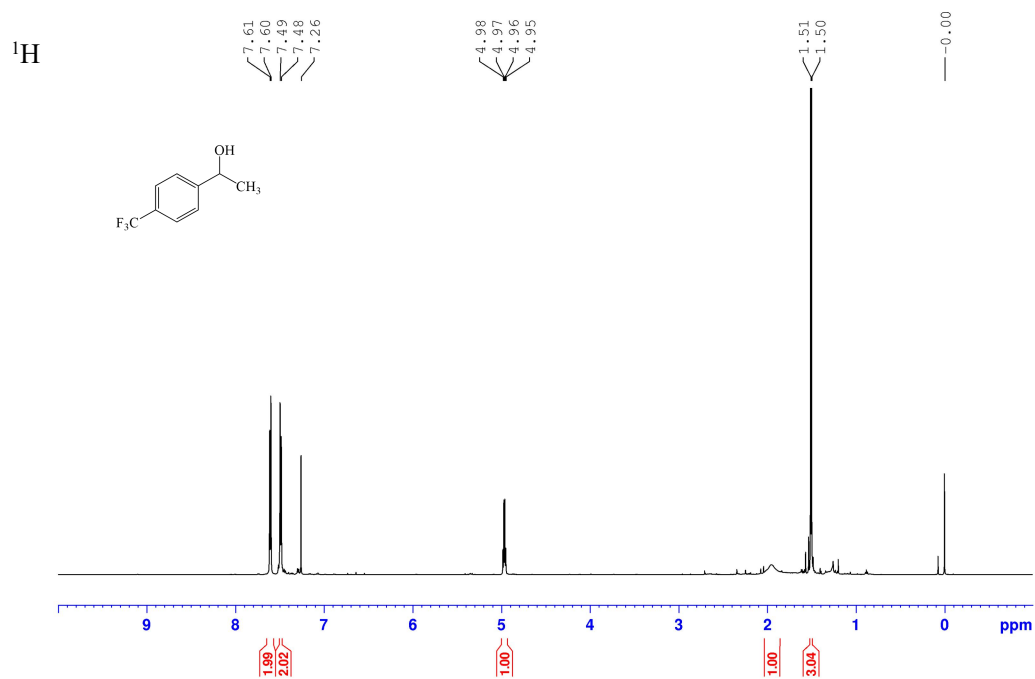


Figure S47. <sup>1</sup>H NMR spectrum of 4i in CDCl<sub>3</sub>.

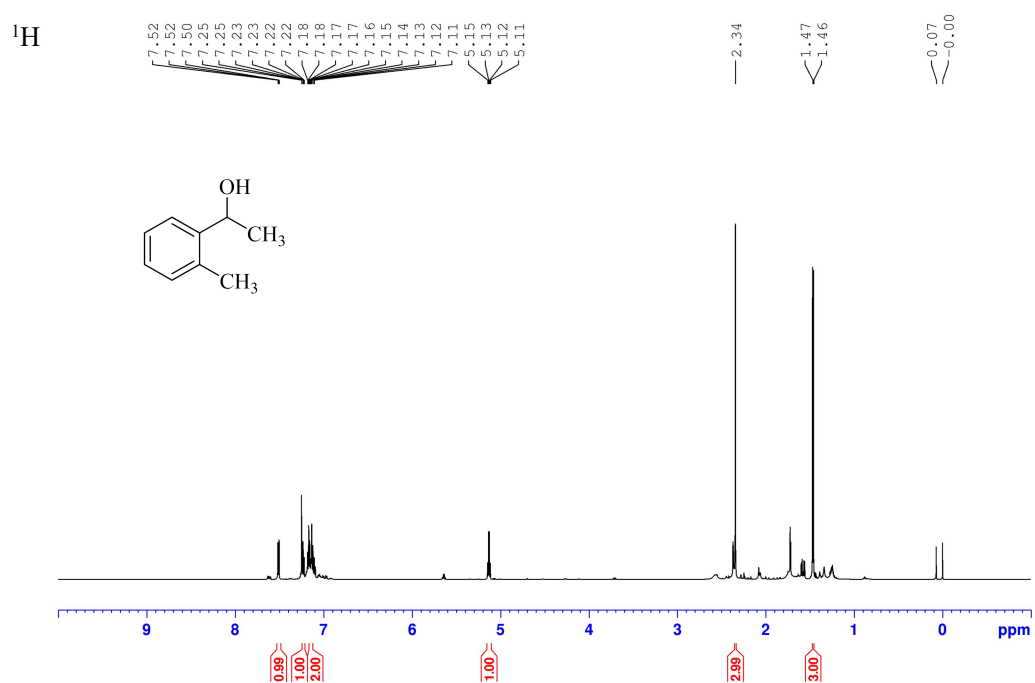


Figure S48. <sup>1</sup>H NMR spectrum of 4j in CDCl<sub>3</sub>.

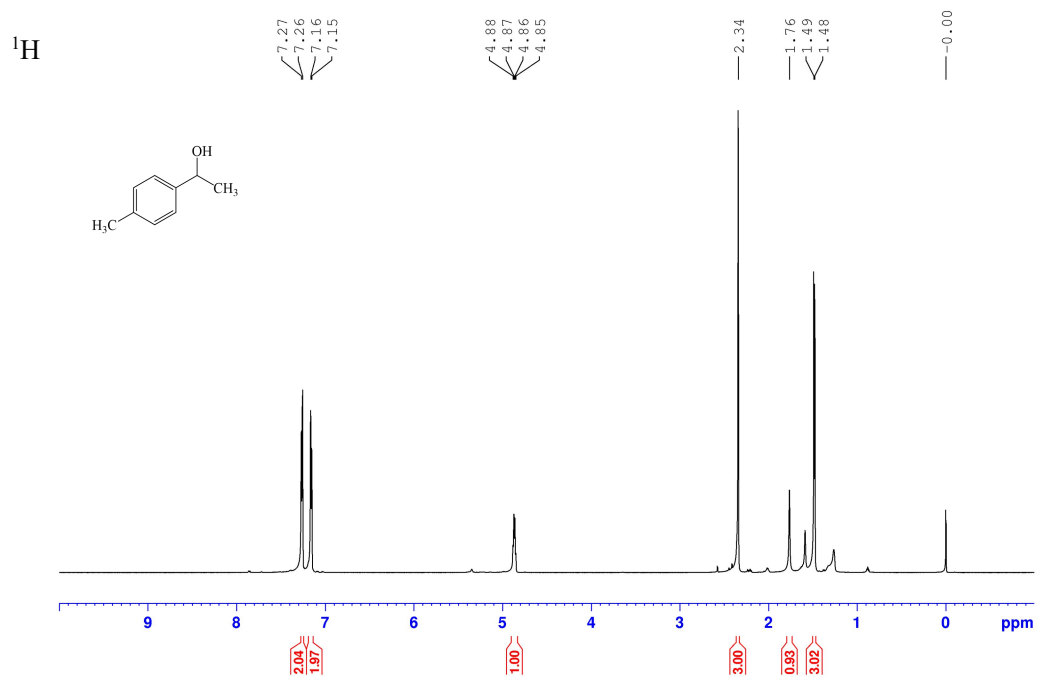


Figure S49. <sup>1</sup>H NMR spectrum of 4k in CDCl<sub>3</sub>.

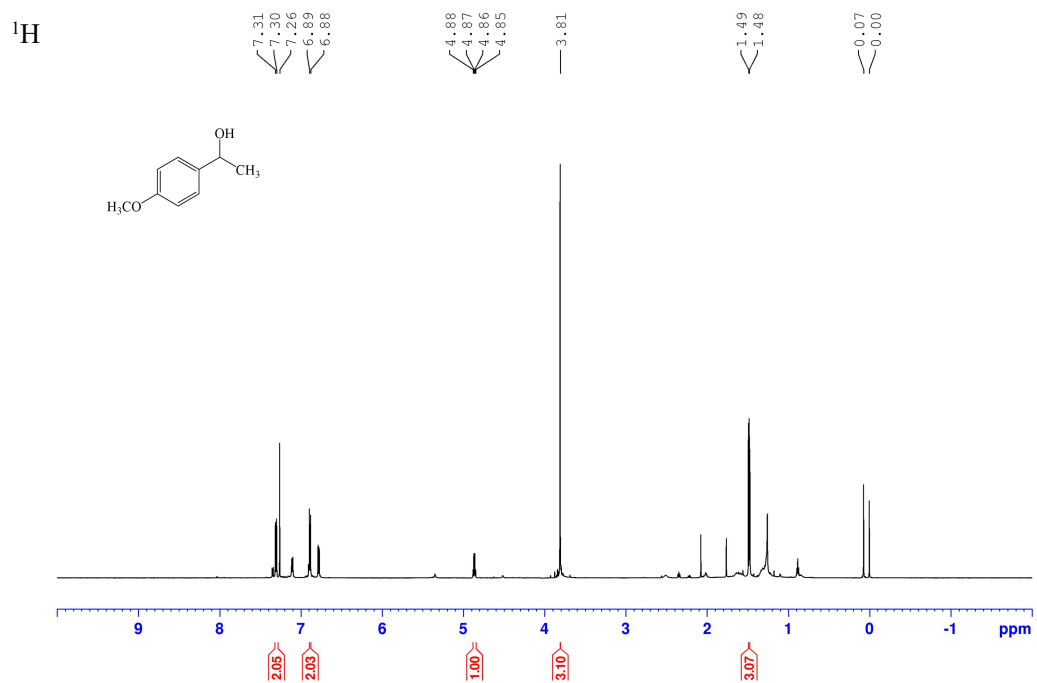


Figure S50. <sup>1</sup>H NMR spectrum of 4l in CDCl<sub>3</sub>.

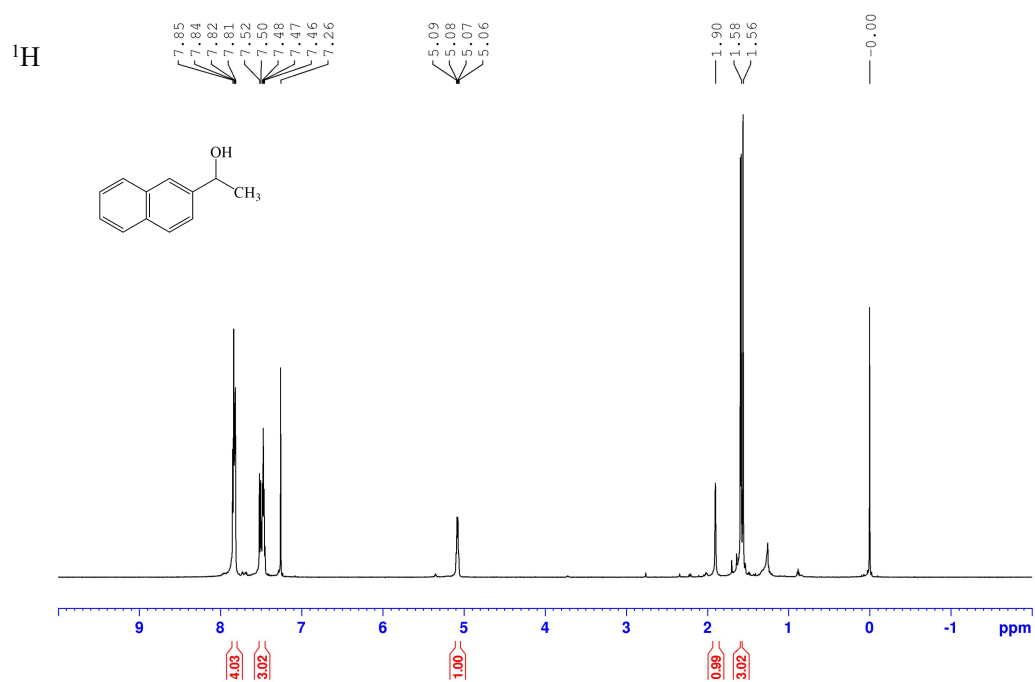


Figure S51. <sup>1</sup>H NMR spectrum of 4m in CDCl<sub>3</sub>.

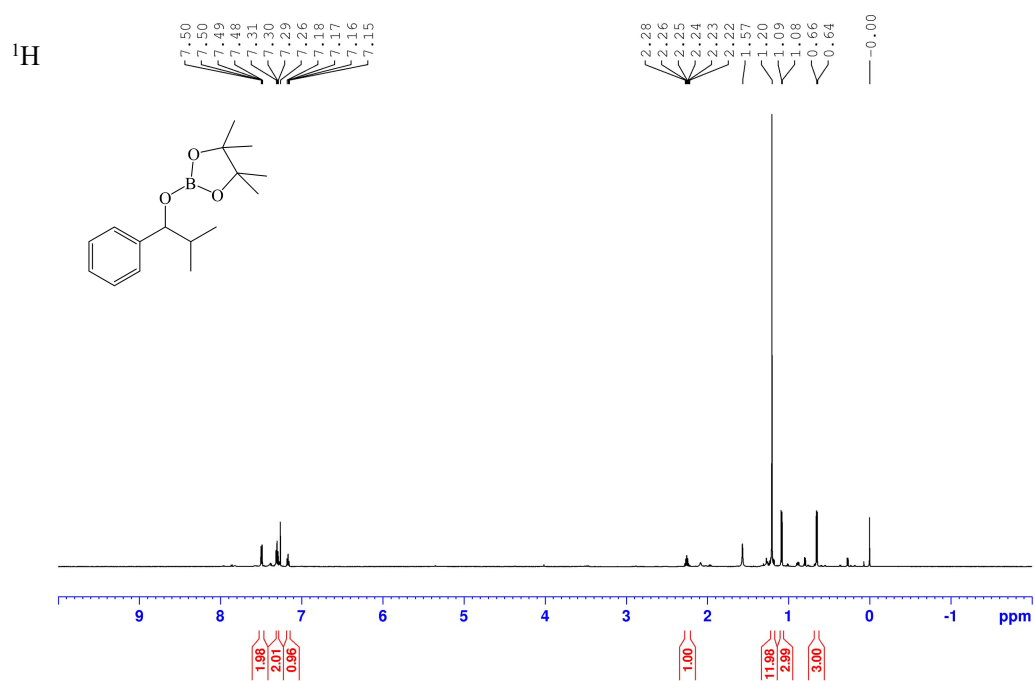


Figure S52. <sup>1</sup>H NMR spectrum of 4n in CDCl<sub>3</sub>.

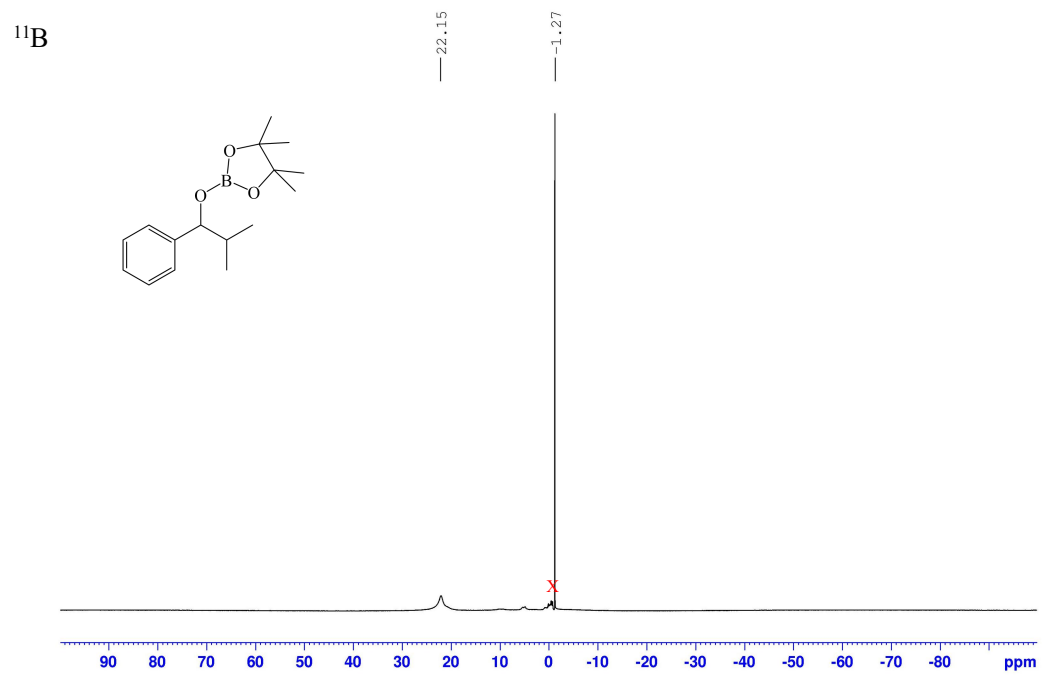


Figure S53. <sup>11</sup>B NMR spectrum of 4n in CDCl<sub>3</sub>.

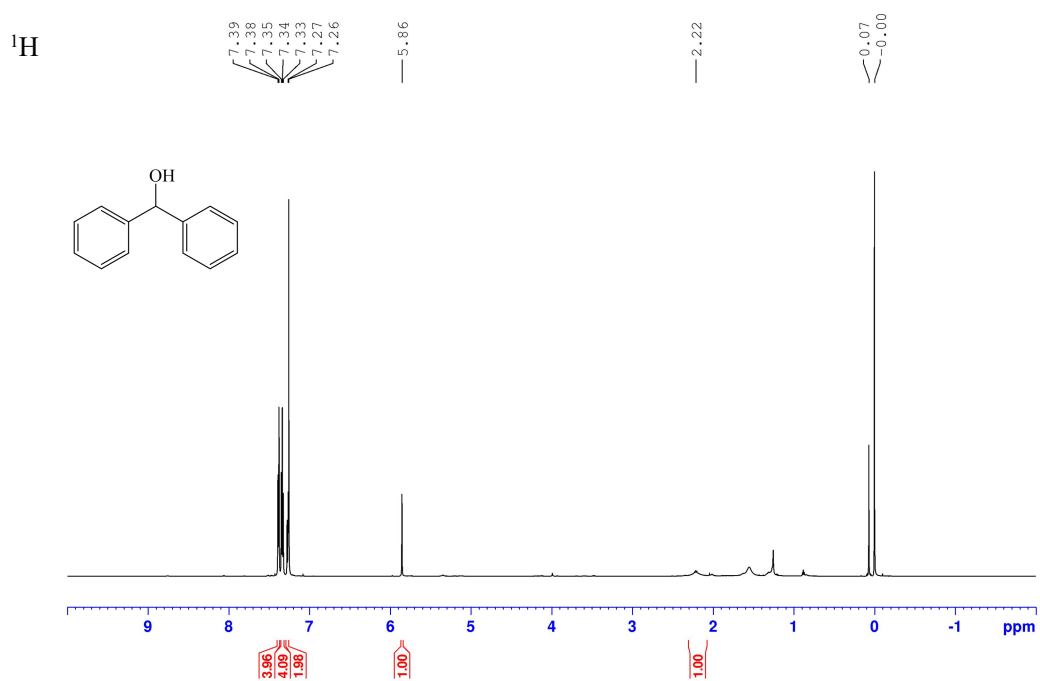


Figure S54. <sup>1</sup>H NMR spectrum of 4o in CDCl<sub>3</sub>.

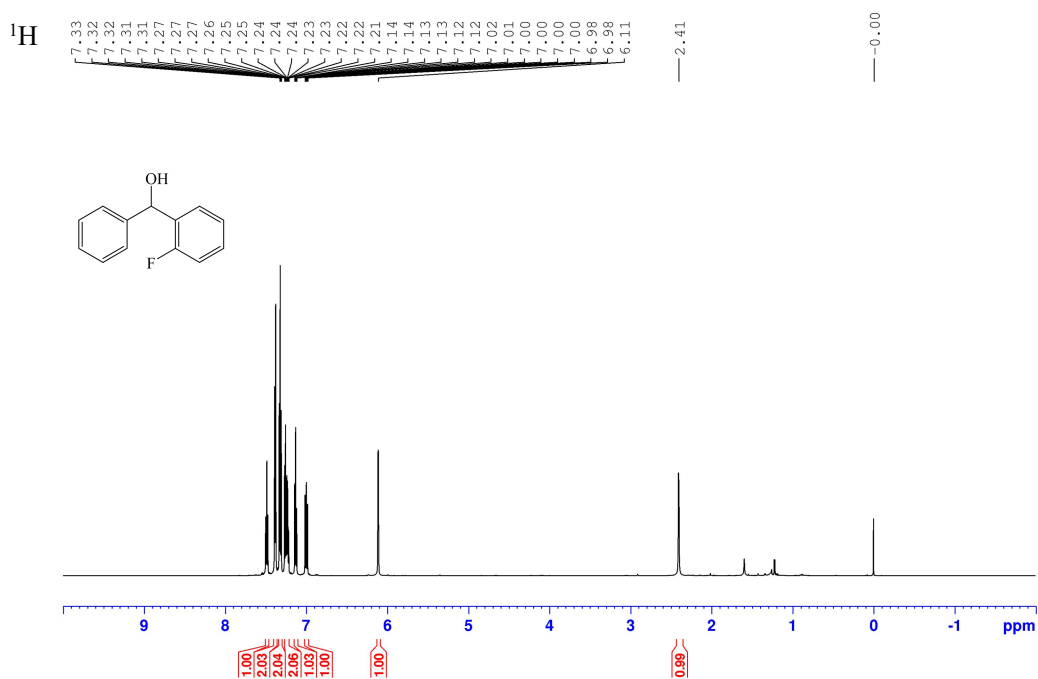


Figure S55. <sup>1</sup>H NMR spectrum of 4p in CDCl<sub>3</sub>.

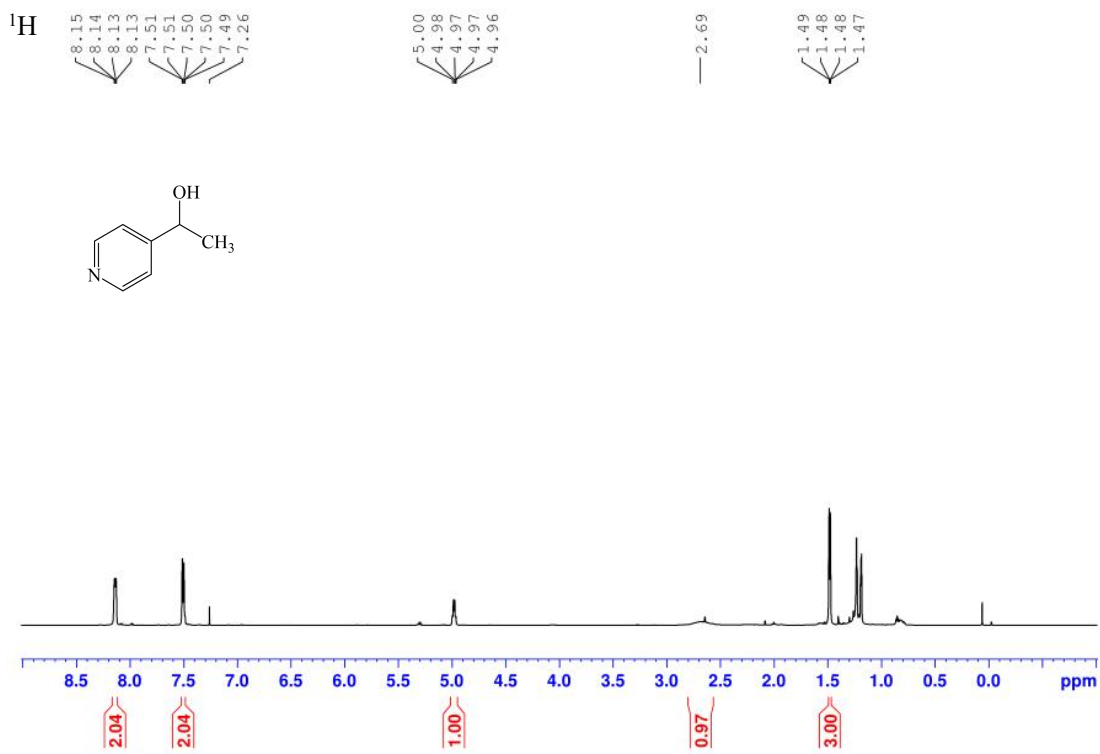
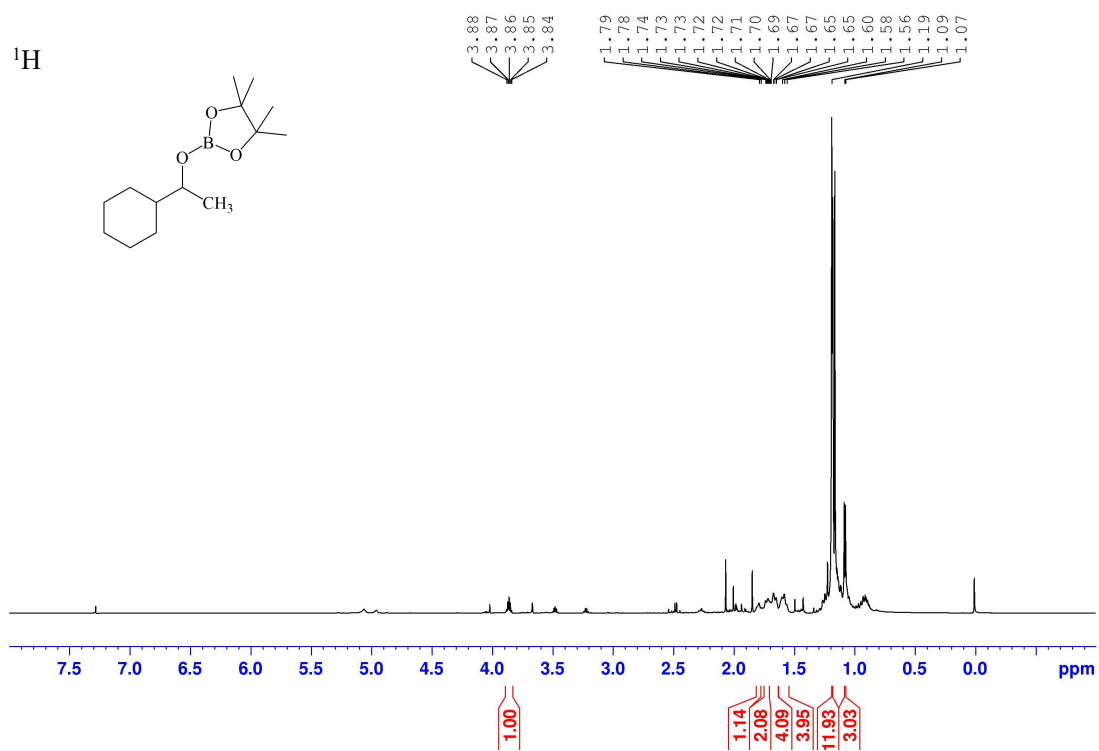
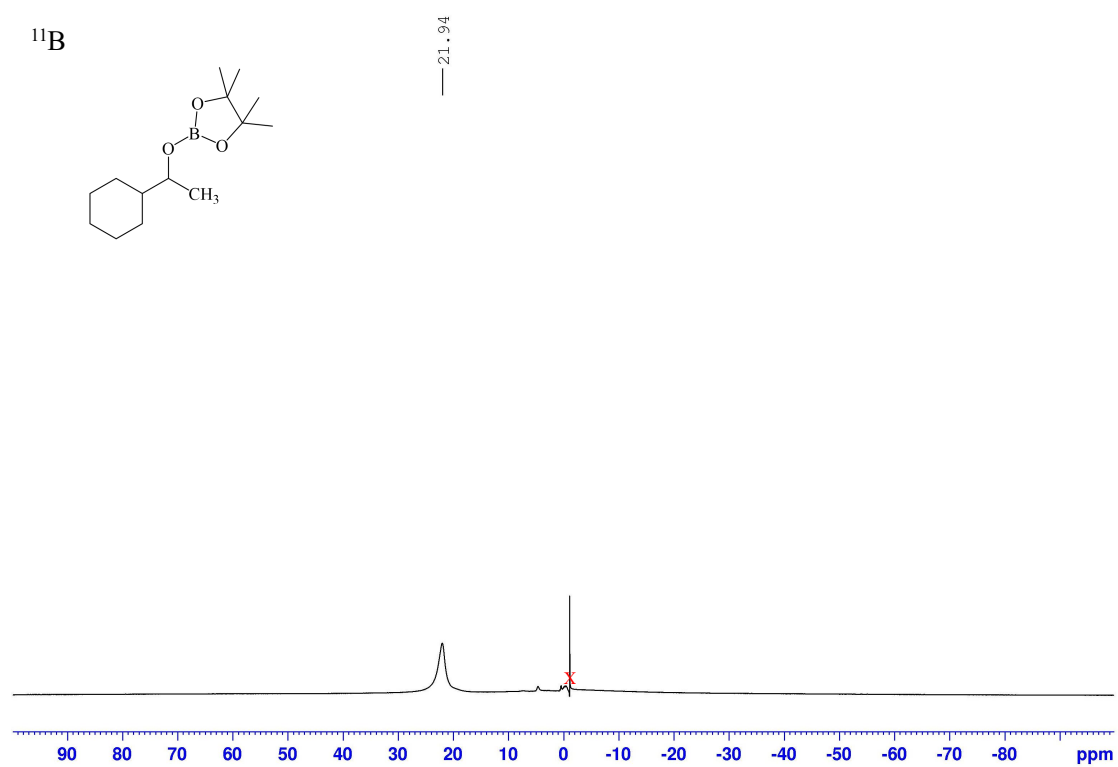


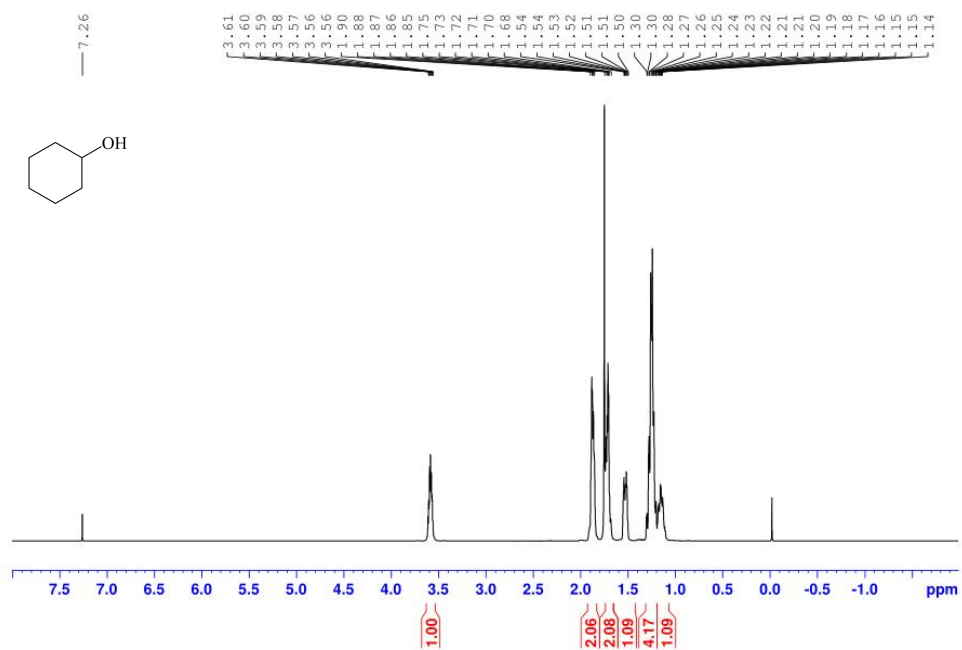
Figure S56. <sup>1</sup>H NMR spectrum of 4q in CDCl<sub>3</sub>.



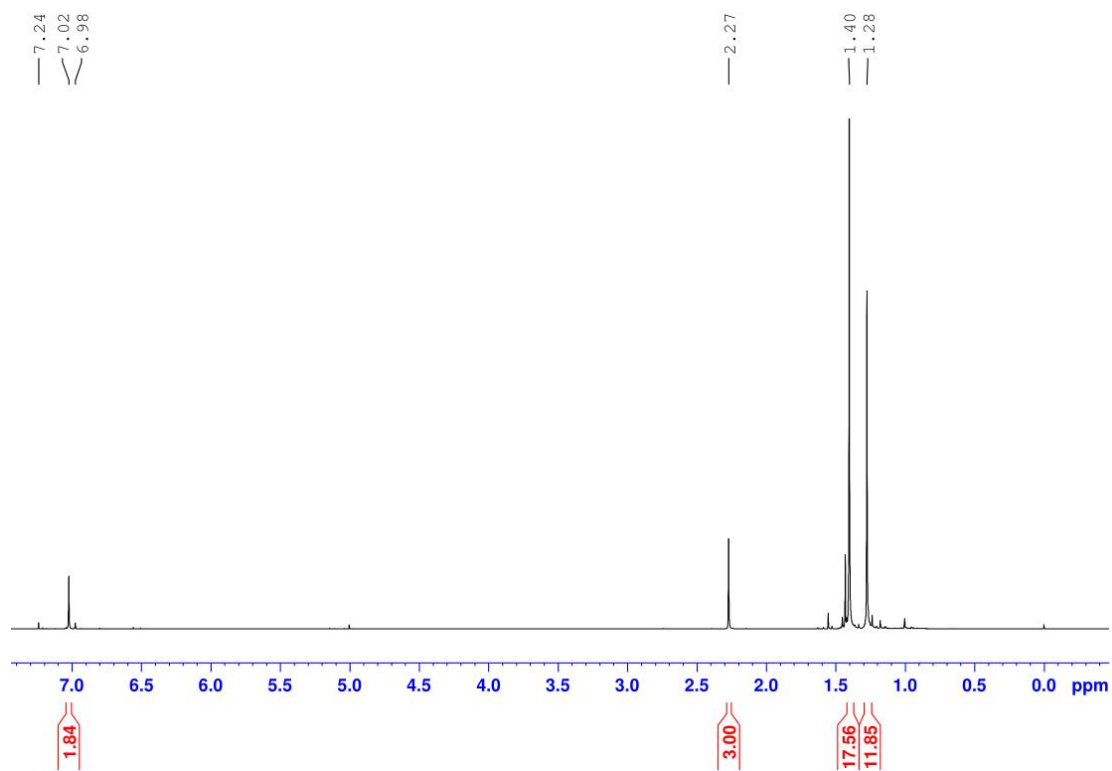
**Figure S57.** <sup>1</sup>H NMR spectrum of 4r in CDCl<sub>3</sub>.



**Figure S58.** <sup>11</sup>B NMR spectrum of 4r in CDCl<sub>3</sub>.

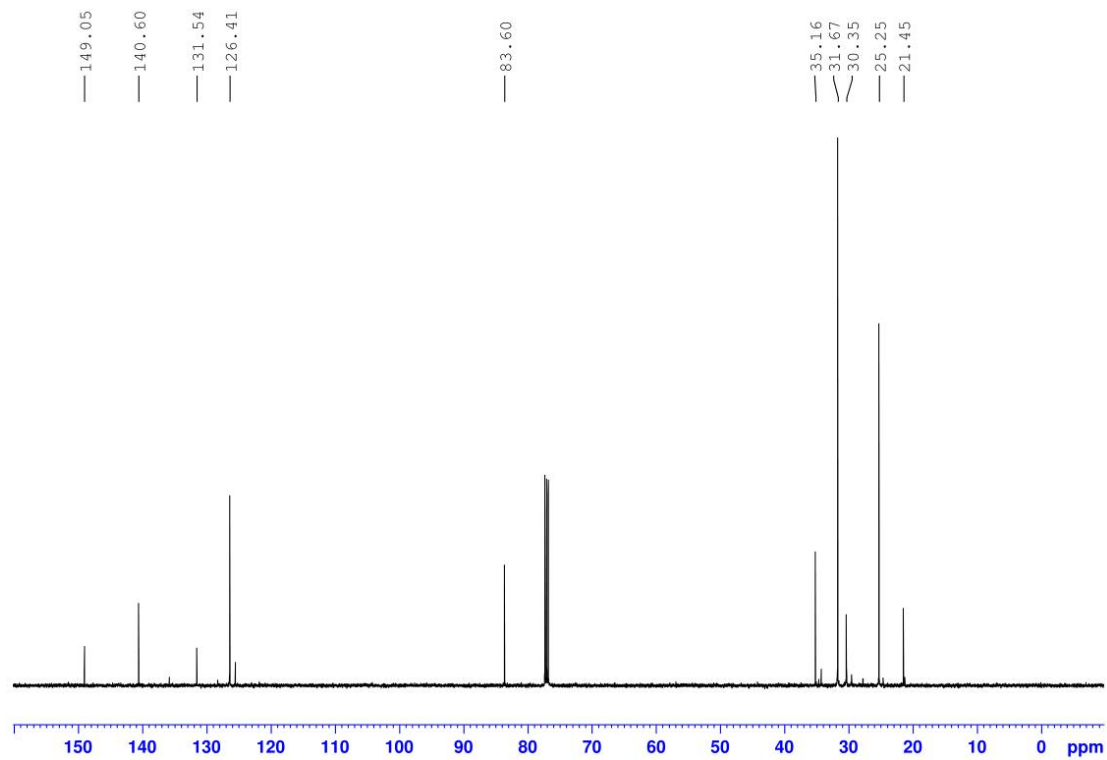


**Figure S59.** <sup>1</sup>H NMR spectrum of 4s in CDCl<sub>3</sub>.

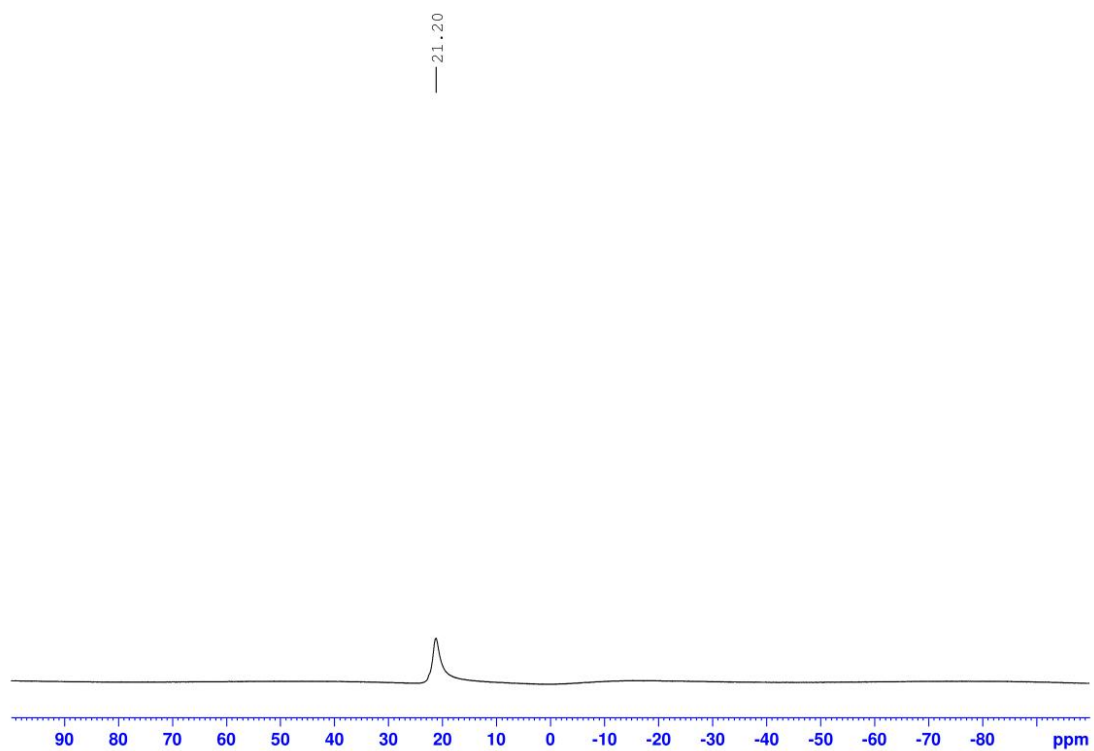


**Figure S60.** <sup>1</sup>H NMR spectrum of 5 in CDCl<sub>3</sub>.





**Figure S61.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 5 in  $\text{CDCl}_3$ .



**Figure S62.**  $^{11}\text{B}$  NMR spectrum of 5 in  $\text{CDCl}_3$ .

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