Supplementary Information

Selective electrocatalytic hydroboration of aryl alkenes

Yahui Zhang,[a] Xiangyu Zhao,[c] Ce Bi,[a,b] Wenqi Lu,[a] Mengyuan Song,[a] Dongdong Wang[a] and Guangyan Qing*[a,b]

[a]Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, P. R. China.

[b]College of Chemistry and Chemical Engineering, Wuhan Textile University, 1 Sunshine Road, Wuhan 430200, P. R. China.

[c]Sixth Laboratory, Sinopec Dalian (Fushun) Research Institute of Petroleum and Petrochemicals, 96 Nankai Road, Dalian 116045, P. R. China.

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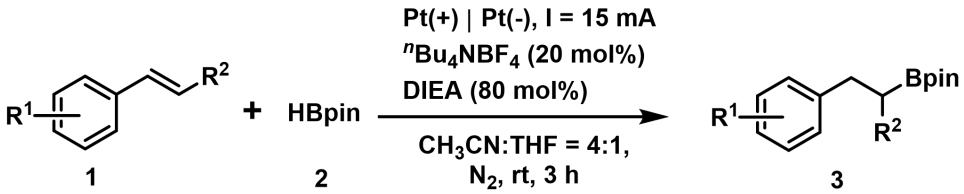
I. General Information

Materials. All manipulations were carried out under argon atmosphere by using standard Schlenk techniques and Mikrouna argon-filled glove box. All solvents were dried and distilled over appropriate drying agents under argon. Various alkenes (aladdin), pinacolborane (HBpin, Aldrich), $^{n}Bu_4NBF_4$ (aladdin), NaO^{t}Bu (aladdin), 2,2',6,6'-tetramethyl-1-piperidinyloxy (TEMPO, aladdin), galvinoxyl free radical (Aldrich), d_8-styrene (Aldrich), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, aladdin), triethylamine (Et_3N, aladdin), *N*,*N*-diisopropylethylamine (DIEA, aladdin), $NaBD_4$ (Heowns), pinacol (Heowns), allyl bromide (Allyl-Br, aladdin) and $NaBO_3 \bullet 4H_2O$ (Energy Chemical) were obtained from commercial suppliers and used without further purification. THF-d_8 and CD_3CN were purchased from Alfa Aesar and used with dried with 4Å molecular sieve. DBpin was prepared according to literature procedures.[1-2]

Instruments. Instrument for electrolysis was dual display potentiostat (CHI760E) (Shanghai Chenhua). The anode and cathode electrodes were all platinum electrodes (15 mm × 15 mm × 0.3 mm), which were purchased from Shanghai Vietnamese Magnetic Electronics. Gas chromatographic (GC) analyses were performed on an Agilent GC-8860 gas chromatography instrument with a FID detector and naphthalene was added as internal standard. Hydrogen detection experiments were recorded on a SHIMADZU GC-2014 gas chromatography instrument. ^{1}H, ^{2}D, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker 400 M Ultra Shield spectrometer. Chemical shifts (δ) were given in parts per million relative to $CDCl_3$ (7.26 ppm for ^{1}H; 77.16 ppm for ^{13}C). ESI-HRMS data were recorded on a HPLC/Q-Tof mass spectrometer. EPR spectra were recorded at room temperature on a JEOL JES-FE3AX spectrometer. Infrared spectra were recorded on a NICOLET iS50 ATR spectrometer. Molecular structure of compound **7t** was obtained on a Brüker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

II. Experimental Procedures and Analytical Data



General procedures for alkene hydroboration with pinacolborane (HBpin) (3a–3h). In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, alkenes (1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h, and the set-up diagrams are shown in Figure S1a–1c. After the solution of the crude products were concentrated in vacuum, the pure products (**3a**–**3h**) were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.

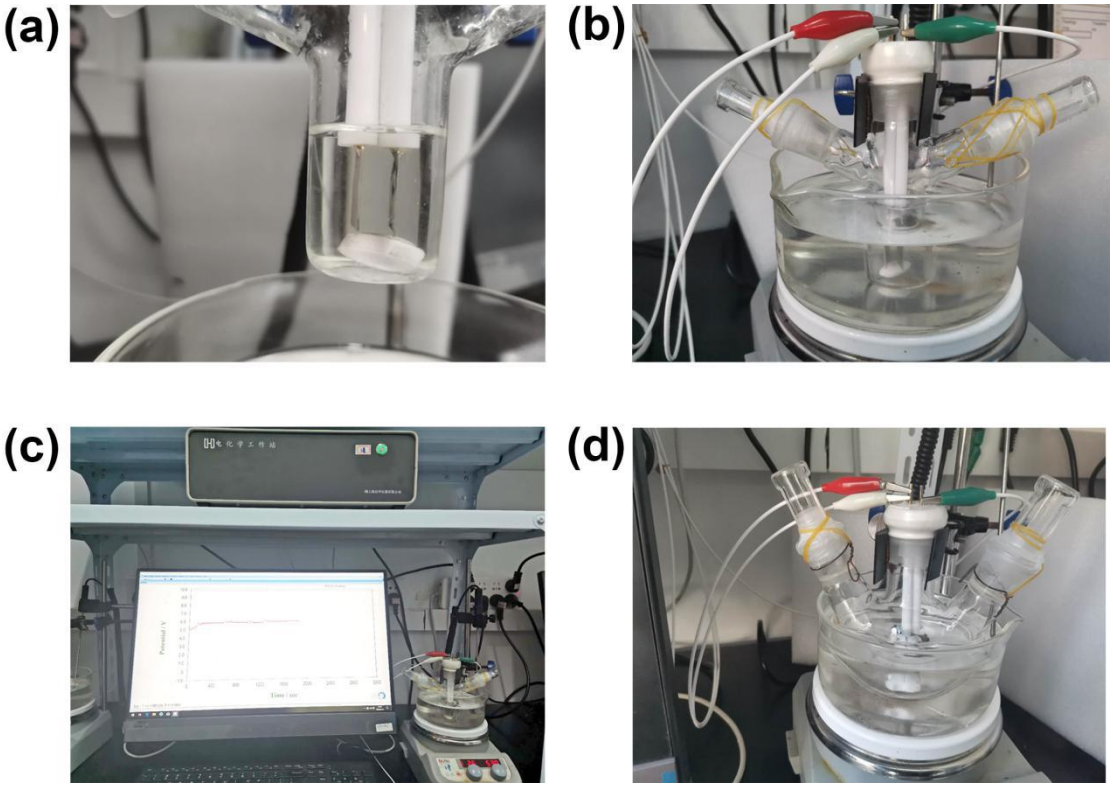


Figure S1. (a, b, c) Set-up diagrams of undivided cell electrolysis. (d) Device for gram scale synthesis.

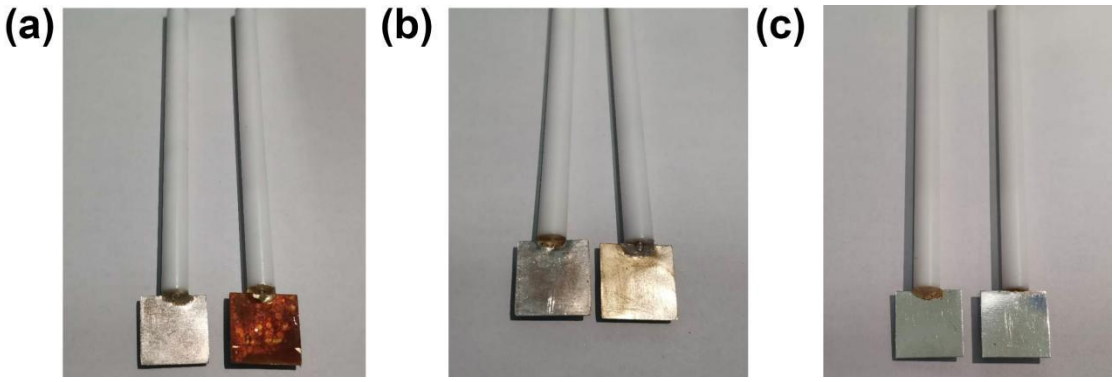
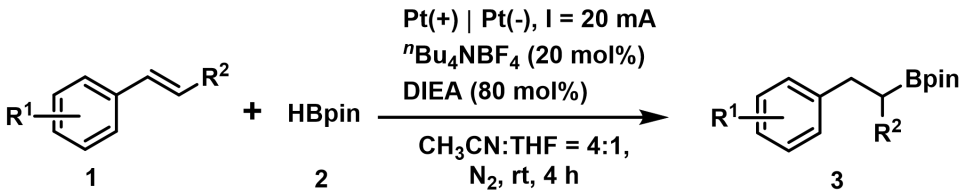
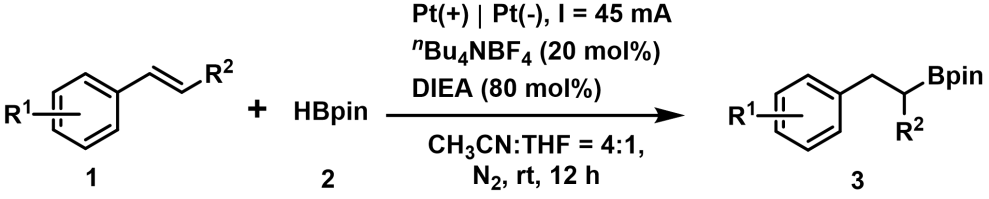


Figure S2. Varying degrees of attachment of unknown yellow compounds on the anode surface after the electrolyzed reaction between styrene and HBpin under different conditions. (a) In the absence of THF and DIEA. (b) In the absence of DIEA. (c) Under the standard conditions. The cathode is in the left and the anode is on the right.

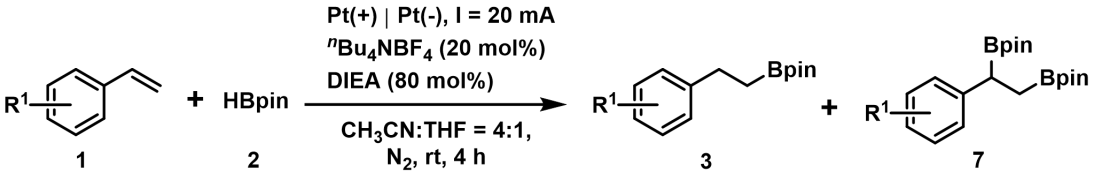


General procedures for alkene hydroboration with HBpin (3i–3r). In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, alkenes (1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 20 mA constant current under room temperature for 4 h, and the set-up diagrams are shown in Figure S1a–1c. After the solution of the crude products were concentrated in vacuum, the pure products (**3i**–**3r**) were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.

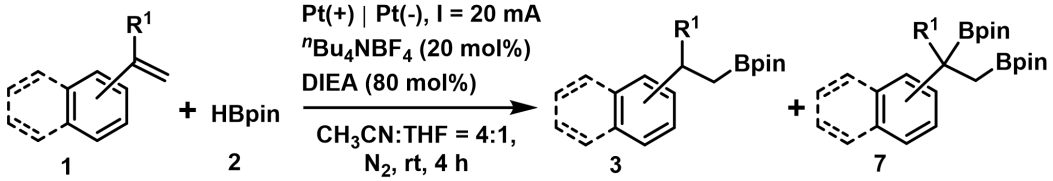


General procedures for gram scale synthesis (3a, 3b, 3d, 3e, 3g and 3h). In an

over-dried undivided three-neck flask (250 mL) equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, alkenes (10 mmol), HBpin (1.6 mL, 11 mmol), DIEA (1.32 mL, 8 mmol), $^{n}Bu_4NBF_4$ (658 mg, 2 mmol), CH_3CN (80 mL) and THF (20 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 45 mA constant current under room temperature for 12 h, and the set-up diagram is shown in Figure S1d. After the solution of the crude products were concentrated in vacuum, the pure products were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



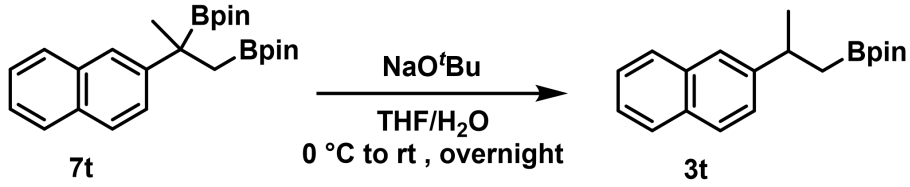
General procedures for alkene diborylation with HBpin (7a, 7b and 7g). In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, alkenes (1.0 mmol), HBpin (1280 μL, 8.8 mmol), DIEA (132 μL, 0.8 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 20 mA constant current under room temperature for 4 h, and the set-up diagrams are shown in Figure S1a-1c. After the solution of the crude products were concentrated in vacuum, the pure products were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



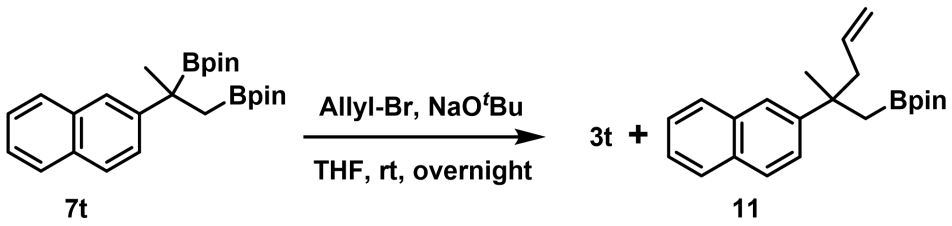
General procedures for alkene diborylation with HBpin (7r–7t). In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, alkenes (1.0 mmol), HBpin (640 μL, 4.4 mmol), DIEA (132 μL, 0.8 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF

(2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 20 mA constant current under room temperature for 4 h, and the set-up diagrams are shown in Figure S1a–1c. After the solution of the crude products were concentrated in vacuum, the pure products (**7r**–**7t**) were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.

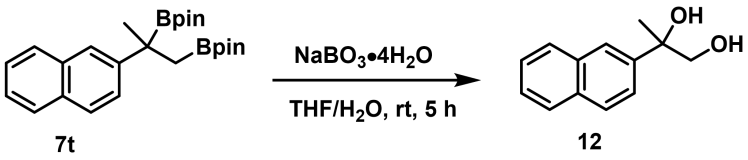
General procedures for the transformations of diboronate ester 7t.



A Schlenk tube (10 mL) equipped with a magnetic stir bar was added with diboronate ester **7t** (84 mg, 0.20 mmol), NaO^{t}Bu (19 mg, 0.20 mmol) and THF (1.0 mL) at 0 °C, followed by three drops of water. The resulting solution was warming to room temperature overnight. Then the mixture was diluted with CH_2Cl_2, dried with anhydrous Na_2SO_4 and filtered with diatomite. After the solution was concentrated in vacuum, the pure product **3t** (36 mg, 0.12 mmol, 61% yield) was obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



In an argon-filled glove-box, a Schlenk tube (10 mL) equipped with a magnetic stir bar was added with diboronate ester **7t** (84 mg, 0.20 mmol), NaO^{t}Bu (192 mg, 2.00 mmol), Allyl-Br (86 μL, 1.00 mmol) and anhydrous THF (1.0 mL) at room temperature, then the mixture was stirred overnight. Then the mixture was diluted with CH_2Cl_2 and filtered with diatomite. After the solution was concentrated in vacuum, the pure product **3t** (17 mg, 0.06 mmol, 29% yield) and **11** (30 mg, 0.09 mmol, 45% yield) were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



A Schlenk tube (10 mL) equipped with a magnetic stir bar was added with diboronate ester **7t** (127 mg, 0.30 mmol), $NaBO_3 \bullet 4H_2O$ (370 mg, 2.40 mmol), THF (3.0 mL) and H_2O (3.0 mL) at room temperature, then the resulting solution was stirred for 5 h and quenched with saturated $Na_2S_2O_3$ aqueous solution. Then the mixture was extracted with CH_2Cl_2, dried with anhydrous Na_2SO_4 and filtered with diatomite. After the solution was concentrated in vacuum, the pure product **12** (57 mg, 0.28 mmol, 94% yield) was obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.

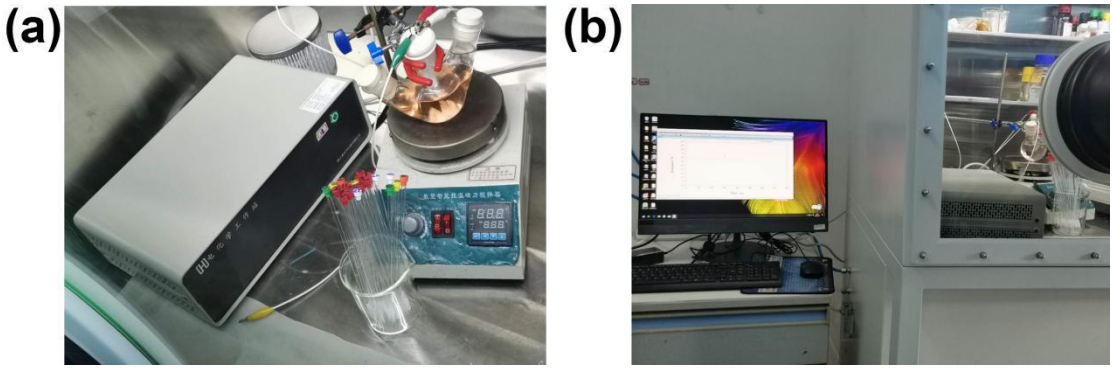
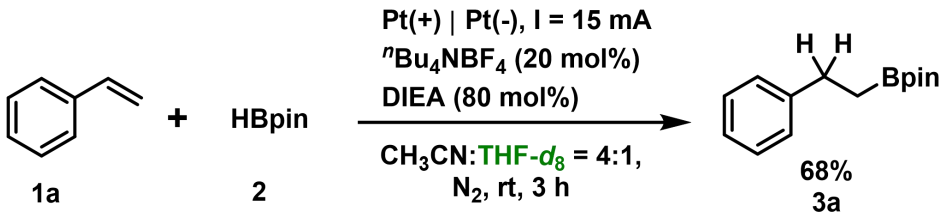
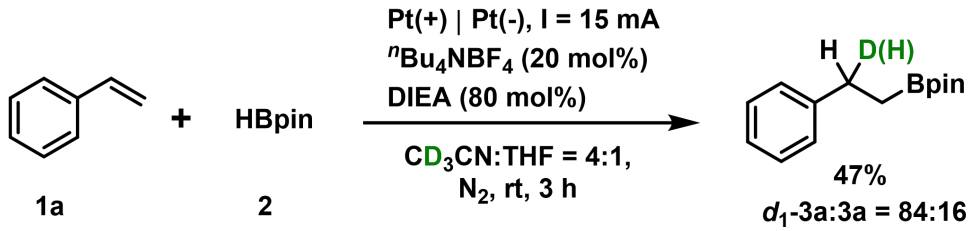


Figure S3. (a, b) Set-up diagrams for *in situ* ^{1}H NMR experiments.

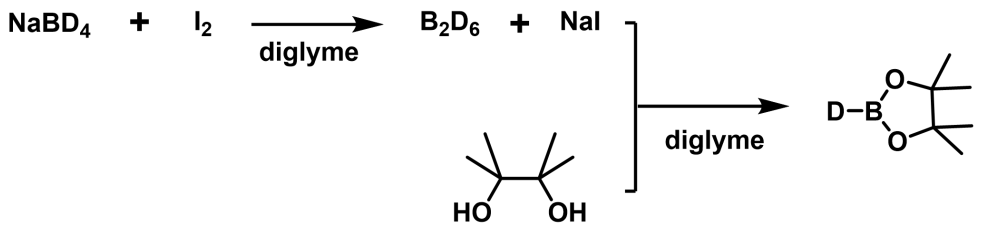
***In situ* ^{1}H NMR experiments to monitor the electrochemical reaction between styrene and HBpin**. In an over-dried undivided three-neck flask (250 mL) equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (1.14 mL, 10 mmol), HBpin (11 mmol or 88 mmol), DIEA (1.32 mL, 8 mmol), $^n Bu_4NBF_4$ (658 mg, 2 mmol), CH_3CN (80 mL) and THF (20 mL) were added in an argon-filled glove box. Then the reaction mixture was stirred and electrolyzed at a 45 mA constant current under room temperature for 12 h, and the set-up diagram is shown in Figure S3. The ^{1}H NMR spectra were collected every 0.5 h. The test samples were made up of 0.3 mL original samples and 0.2 mL CD_3CN, and the sample collection was completed in the glove box.



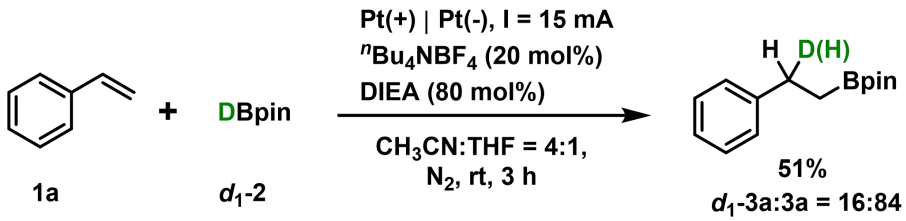
Deuterium-labelling experiment in THF-d_8. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), ^{n}Bu$_4$NBF$_4$ (65.8 mg, 0.2 mmol), CH$_3$CN (8 mL) and THF-d_8 (2 mL) were added under argon atmosphere. Then the mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. After the solution of the crude product was concentrated in vacuum, the pure product **3a** was obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



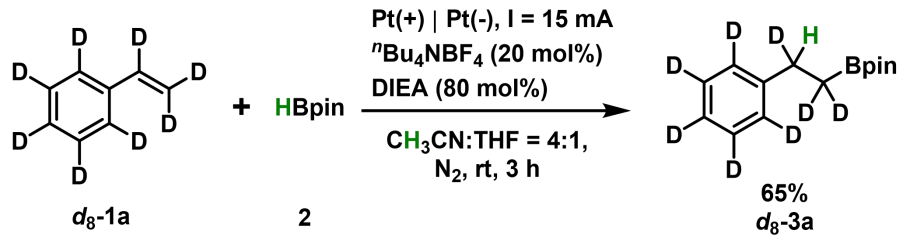
Deuterium-labelling experiment in CD$_3$CN. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), ^{n}Bu$_4$NBF$_4$ (65.8 mg, 0.2 mmol), CD$_3$CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. After the solution of the crude products were concentrated in vacuum, the mixed products ***d*$_1$-3a** and **3a** were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



Preparation of DBpin. The procedures were conducted the literature method.[1-2] A suspension solution of $NaBD_4$ (0.5 g, 12.2 mmol) in diglyme (10 mL) was added to the Schlenk tube equipped with a magnetic stir bar in an argon atmosphere. Then the above tube was connected to the second Schlenk tube with the cooled solution (0 °C) of pinacol (0.48 g, 4.08 mmol) in absolute THF (5 mL) *via* a plastic cannula, and the cannula submersed in THF solution. Iodine (1.55 g, 6.11 mmol) was dissolved in diglyme (6 mL) and the solution was slowly added to the $NaBD_4$ suspension over 1 h with a syringe. At the end of the addition of iodine, stream of N_2 was pass through the THF solution for about 2 h to remove the excess unreacted B_2D_6 at room temperature. ^1H NMR data confirmed that the transformation of pinacol was completed. The 3.0 mL of THF solution was considered to be concentrated at 1.36 M DBpin.



Deuterium-labelling experiment with DBpin. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), DBpin (0.8 mL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), $^nBu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (1.4 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. After the solution of the crude products were concentrated in vacuum, the mixed products ***d*₁-3a** and **3a** were obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.



d_8-1a 2 d_8-3a

Deuterium-labelling experiment with d_8-styrene. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, d_8-styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), ^{n}Bu$_4$NBF$_4$ (65.8 mg, 0.2 mmol), CH$_3$CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. After the solution of the crude product was concentrated in vacuum, the pure product ***d*$_8$-3a** was obtained by flash chromatography on silica gel using petroleum and ethyl acetate as eluent.

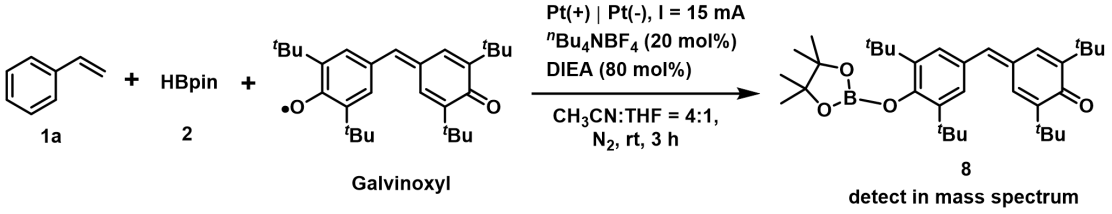
H$_2$ detection experiment under the standard conditions. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), ^{n}Bu$_4$NBF$_4$ (65.8 mg, 0.2 mmol), CH$_3$CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. A large number of tiny bubbles were observed during electrolysis and the release rate (mL·min^{-1}) of gas with time was analyzed by SHIMADZU GC-2014 gas chromatography instrument.

H$_2$ detection experiment to monitor the electrochemical reaction in the absence of styrene and HBpin. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, DIEA (132 μL, 0.8 mmol), ^{n}Bu$_4$NBF$_4$ (65.8 mg, 0.2 mmol), CH$_3$CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. The release rate (mL·min^{-1}) of gas during the electrochemical reaction with time was analyzed by SHIMADZU GC-2014 gas chromatography instrument.

H_2 detection experiment to monitor the electrochemical reaction in the absence of styrene, HBpin, DIEA and THF. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol) and CH_3CN (8 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. The release rate ($mL \cdot min^{-1}$) of gas during the electrochemical reaction with time was analyzed by SHIMADZU GC-2014 gas chromatography instrument.

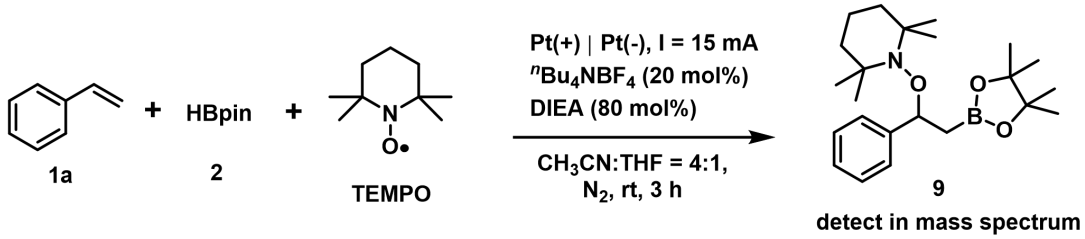
H_2 detection experiment to monitor the electrochemical reaction in the absence of DIEA. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. The release rate ($mL \cdot min^{-1}$) of gas during electrolysis with time was analyzed by SHIMADZU GC-2014 gas chromatography instrument.

H_2 detection experiment to monitor the electrochemical reaction in the absence of styrene, HBpin and DIEA. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h. The release rate ($mL \cdot min^{-1}$) of gas during the electrochemical reaction with time was analyzed by SHIMADZU GC-2014 gas chromatography instrument.



Radical inhibition experiment with galvinoxyl radical. In an over-dried undivided

three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), galvinoxyl radical (422 mg, 1.0 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h, and the yield of product **3a** was determined by gas chromatography analysis. The adduct **8** of galvinoxyl radical and boron radical was determined by mass spectrometry.



Radical inhibition experiment with 2,2',6,6'-tetramethyl-1-piperidinyloxy (TEMPO). In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then different equivalents (0.25, 0.50, 0.75 or 1.0 mmol) of TEMPO were added to this system, respectively. The reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature for 3 h, and the yield of product **3a** was determined by gas chromatography analysis. The adduct **9** of carbon radical at the benzyl site with TEMPO was determined by mass spectrometry.

The radical inhibition experiment using 2-vinylphthalene as substrate was similar to the above method. The adducts of boron radical (namely compound **13**) and carbon radical (namely compound **14**) at the benzyl site with TEMPO were determined by gas chromatography-mass spectrometry and mass spectrometry, respectively.

Procedures for cyclic voltammetry (CV) in CH_3CN. Cyclic voltammetry experiments were conducted in a 10 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. The CV experiments were performed in CH_3CN (10 mL) with $^nBu_4NBF_4$ (32.9 mg, 0.1 mmol). The scan rate was 100 $mV \cdot S^{-1}$ and the potential range was 0-5 V. The current was reported in mA and potential were reported in V against $Fc^{+/0}$ redox couple.

Procedures for cyclic voltammetry (CV) of DIEA in CH_3CN. Cyclic voltammetry experiments were conducted in a 10 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. The CV experiments were performed in CH_3CN (10 mL) containing $^nBu_4NBF_4$ (32.9 mg, 0.1 mmol) and DIEA (16.5 μL, 0.1 mmol). The scan rate was 100 $mV \cdot S^{-1}$ and the potential range was 0-5 V. The current was reported in mA and potential were reported in V against $Fc^{+/0}$ redox couple.

Procedures for cyclic voltammetry (CV) of HBpin in CH_3CN. Cyclic voltammetry experiments were conducted in a 10 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. The CV experiments were performed in CH_3CN (10 mL) containing $^nBu_4NBF_4$ (32.9 mg, 0.1 mmol) and HBpin (14.5 μL, 0.1 mmol). The scan rate was 100 $mV \cdot S^{-1}$ and the potential range was 0-5 V. The current was reported in mA and potential were reported in V against $Fc^{+/0}$ redox couple.

EPR experiment under the standard conditions. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), DMPO (113 mg, 1.0 mmol), $^nBu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature. After 30 min, the solution was taken out and injected into a capillary tube with one end closed, then the solution was analyzed by EPR spectrometer at room temperature. Only one type of racial had been trapped by

DMPO: DMPO–H: g =2.0071, A_N = 14.74 G, A_H = 19.74 G.

EPR experiment to monitor the electrochemical reaction in the absence of HBPin. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, styrene (114 μL, 1.0 mmol), DIEA (132 μL, 0.8 mmol), DMPO (113 mg, 1.0 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature. After 30 min, the solution was taken out and injected into a capillary tube with one end closed, then the solution was analyzed by EPR spectrometer at room temperature. Two type of radicals had been trapped by DMPO: DMPO–H and DMPO–CH_2CN (**10**, g = 2.0052, A_N = 14.47 G, A_H = 20.82 G).

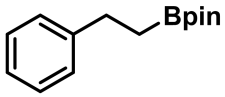
EPR experiment to monitor the electrochemical reaction in the absence of styrene. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, HBpin (160 μL, 1.1 mmol), DIEA (132 μL, 0.8 mmol), DMPO (113 mg, 1.0 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature. After 30 min, the solution was taken out and injected into a capillary tube with one end closed, then the solution was analyzed by EPR spectrometer at room temperature. Only DMPO–H was detected.

EPR experiment to monitor the electrochemical reaction in the absence of styrene and HBpin. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, DIEA (132 μL, 0.8 mmol), DMPO (113 mg, 1.0 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature. After 30 min, the solution was taken out and injected into a capillary tube with one end closed, the the solution was analyzed by EPR spectrometer at room temperature. Two type of radicals had been trapped by DMPO: DMPO–H and **10**.

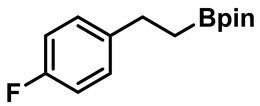
EPR experiment to monitor the electrochemical reaction in the absence of

styrene, HBpin and DIEA. In an over-dried undivided three-neck flask equipped with two platinum electrodes (15 mm × 15 mm × 0.3 mm) as both anode and cathode, DMPO (113 mg, 1.0 mmol), $^{n}Bu_4NBF_4$ (65.8 mg, 0.2 mmol), CH_3CN (8 mL) and THF (2 mL) were added under argon atmosphere. Then the reaction mixture was stirred and electrolyzed at a 15 mA constant current under room temperature. After 30 min, the solution was taken out and injected into a capillary tube with one end closed, then the solution was analyzed by EPR spectrometer at room temperature. Two type of radicals had been trapped by DMPO: DMPO–H and **10**. The reduction state of the corresponding adduct **10** was detected by mass spectrometry.

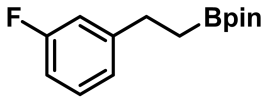
III. Spectroscopic Data of Products



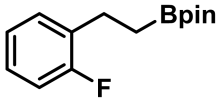
4,4',5,5'-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (3a)[3]: Colorless oil was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.19-7.24 (m, 4H), 7.12-7.15 (m, 1H), 2.74 (t, J = 8.0 Hz, 2H), 1.20 (s, 12H), 1.13 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.02.



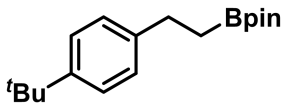
2-(4-Fluorophenethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3b)[3]: Colorless oil was obtained in 69% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.14-7.17 (m, 2H), 6.91-6.95 (m, 2H), 2.71 (t, J = 8.0 Hz, 2H), 1.21 (s, 12H), 1.11 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.4 (d, J = 241.0 Hz), 140.1 (d, J = 3.0 Hz), 129.5 (d, J = 8.0 Hz), 115.0 (d, J = 21.0 Hz), 83.3, 29.3, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.61. ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ − 118.37.



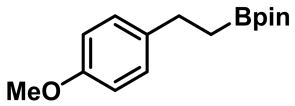
2-(3-Fluorophenethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3c)[4]: Colorless oil was obtained in 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.17-7.22 (m, 1H), 6.97-6.99 (m, 1H), 6.91-6.94 (m, 1H), 6.81-6.85 (m, 1H), 2.75 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.13 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 164.2 (d, J = 243.0 Hz), 147.1 (d, J = 7.0 Hz), 129.6 (d, J = 8.0 Hz), 123.8 (d, J = 2.0 Hz), 115.1 (d, J = 21.0 Hz), 112.5 (d, J = 21.0 Hz), 83.3, 29.8, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.77. ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ − 114.20.



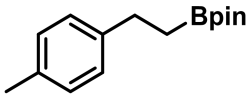
4,4',5,5'-Tetramethyl-2-(2-fluorophenylethyl)-1,3,2-dioxaborolane (3d)[5]: Colorless oil was obtained in 66% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21-7.25 (m, 1H), 7.10-7.16 (m, 1H), 7.01-7.05 (m, 1H), 6.95-7.00 (m, 1H), 2.78 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.15 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.4 (d, J = 243.0 Hz), 131.3 (d, J = 16.0 Hz), 130.2 (d, J = 6.0 Hz), 127.3 (d, J = 8.0 Hz), 123.9 (d, J = 3.0 Hz), 115.2 (d, J = 22.0 Hz), 83.2, 24.9, 23.3 (d, J = 2.0 Hz). ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.77. ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ − 118.78.



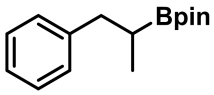
2-(4-(Tert-Butyl)phenethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3e)[5]: Colorless oil was obtained in 74% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28-7.30 (m, 2H), 7.14-7.16 (m, 2H), 2.72 (t, J = 8.0 Hz, 2H), 1.30 (s, 9H), 1.22 (s, 12H), 1.14 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.4, 141.5, 127.7, 125.2, 83.2, 34.5, 31.6, 29.5, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.91.



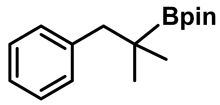
2-(4-Methoxyphenethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3f)[3]: Colorless oil was obtained in 69% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.14 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 3.78 (s, 3H), 2.69 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.12 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.8, 136.7, 129.0, 113.7, 83.2, 55.4, 29.2, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.79.



4,4',5,5'-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (3g)[3]: Colorless oil was obtained in 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.09 (q, J = 8.0 Hz, 4H), 2.73 (t, J = 8.0 Hz, 2H), 2.32 (s, 3H), 1.25 (s, 12H), 1.14 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.5, 134.9, 129.0. 128.0, 83.2, 29.6, 24.9, 21.1. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.09.

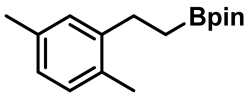


4,4',5,5'-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (3h)[3]: Colorless oil was obtained in 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.13-7.24 (m, 5H), 2.81 (dd, J = 8.0, 12.0 Hz, 1H), 2.55 (dd, J = 8.0, 12.0 Hz, 1H), 1.33-1.38 (m, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.97 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.5, 129.0, 128.1, 125.7, 83.1, 39.1, 24.8, 15.3. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.31.

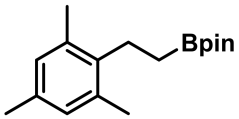


4,4',5,5'-Tetramethyl-2-(2-methyl-1-phenylpropan-2-yl)-1,3,2-dioxaborolane (3i)[6]: Colorless oil was obtained in 57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.14-7.23 (m, 5H), 2.62 (s, 2H), 1.22 (s, 12H), 0.95 (s, 6H). ^{13}C NMR (100 MHz,

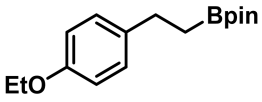
$CDCl_3$, ppm): δ 140.6, 130.3, 127.8, 125.8, 83.2, 46.5, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.60.



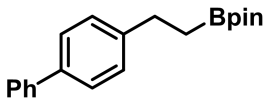
2-(2,5-Dimethylphenethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3j)[5]: Colorless oil was obtained in 70% isolated yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.03 (d, J = 8.0 Hz, 2H), 6.90-6.91 (m, 1H), 2.70 (t, J = 8.0 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 1.26 (s, 12H), 1.11 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.4, 135.2, 132.6, 130.0, 129.1, 126.4, 83.2, 27.3, 24.9, 21.1, 18.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.03.



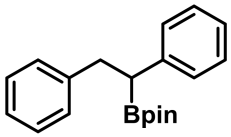
4,4',5,5'-Tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (3k)[4]: Pale yellow solid was obtained in 67% isolated yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.82 (s, 2H), 2.68 (t, J = 8.0 Hz, 2H), 2.30 (s, 6H), 2.25 (s, 3H), 1.28 (s, 12H), 0.96 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.6, 135.8, 134.8, 128.9, 83.2, 25.0, 23.4, 20.9, 19.8. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.84.



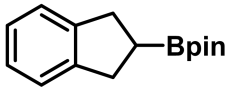
2-(4-Ethoxyphenethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3l): Colourless oil was obtained in 61% isolated yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.11 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.99 (q, J = 6.8 Hz, 2H), 2.70 (t, J = 8.0 Hz, 2H), 1.39 (t, J = 6.8 Hz, 3H), 1.22 (s, 12H), 1.13 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.0, 136.5, 128.9, 114.3, 83.0, 63.4, 29.1, 24.9, 15.0. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.03. FT-IR (ATR): 3031, 2978, 2927, 2871, 1612, 1511, 1370, 1319, 1239, 1143, 1049, 967, 850, 804, 521. ESI-HRMS (*m/z*): cacld. for [**3l** + H]$^+$: 276.2006; found: 276.2006.



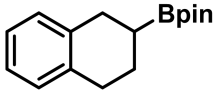
(2-([1,1'-Biphenyl]-4-yl)ethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3m)[4]: White solid was obtained in 57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.58-7.60 (m, 2H), 7.51-7.54 (m, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.30-7.35 (m, 3H), 2.81 (t, J = 8.0 Hz, 2H), 1.25 (s, 12H), 1.20 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 143.7, 141.4, 138.6, 128.8, 128.6, 127.1, 127.1, 127.0, 83.3, 29.7, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.01.



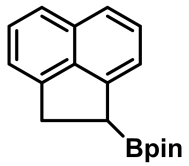
(1,2-Diphenylethyl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3n)[5]: Colorless oil was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.12-7.25 (m, 10H), 3.12-3.18 (m, 1H), 2.94-2.99 (m, 1H), 2.66-2.70 (m, 1H), 1.11 (s, 6H), 1.10 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.7, 141.9, 129.0, 128.5, 128.5, 128.2, 125.9, 125.5, 83.5, 39.0, 24.7, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.08.



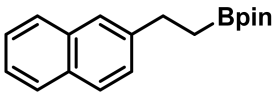
(2,3-Dihydro-1H-inden-2-yl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3o)[3]: Colorless oil was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21-7.23 (m, 2H), 7.11-7.13 (m, 2H), 2.95-3.11 (m, 4H), 1.84-1.94 (m, 1H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.5, 126.0, 124.3, 83.4, 35.3, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.56.



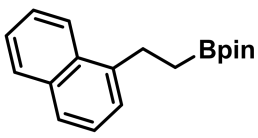
4,4',5,5'-Tetramethyl-2-(1,2,3,4-tetrahydro-2-naphthalenyl)-1,3,2-dioxaborolane (3p)[3]: Colorless oil was obtained in 64% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.09 (s, 4H), 2.75-2.92 (m, 4H), 2.04-2.07 (m, 1H), 1.64-1.74 (m, 1H), 1.35-1.41 (m, 1H), 1.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.4, 136.9, 129.0, 128.9, 125.3, 83.0, 30.6, 29.7, 24.8, 24.7, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.08.



(1,2-Dihydroacenaphthylen-1-yl)-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (3q)[7]: Pale yellow oil was obtained in 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56-7.60 (m, 2H), 7.42-7.46 (m, 2H), 7.34-7.35 (m, 1H), 7.28-7.30 (m, 1H), 3.55 (d, J = 6.4 Hz, 2H), 3.30 (t, J = 6.8 Hz, 1H), 1.27 (d, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.5, 146.5, 139.2, 131.9, 128.0, 127.8, 122.2, 121.8, 119.2, 119.0, 83.8, 33.2, 25.1, 24.7, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.34.

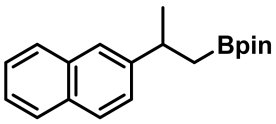


4,4',5,5'-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (3r)[8]: Colourless oil was obtained in 6% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.74-7.80 (m, 3H), 7.45-7.65 (m, 1H), 7.36-7.45 (m, 3H), 2.92 (t, J = 8 Hz, 2H), 1.24 (m, 2H), 1.22 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.1, 133.8, 132.1, 127.8, 127.7, 127.6, 127.4, 125.9, 125.8, 125.0, 83.3, 30.4, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.79.

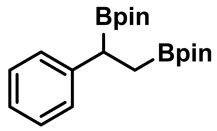


4,4',5,5'-Tetramethyl-2-(2-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (3s)[3]:

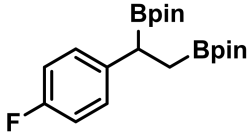
Colourless oil was obtained in 3% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.13 (d, J =8.4 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.56-7.73 (m, 1H), 7.42-7.48 (m, 2H), 3.27 (t, J = 8.0 Hz, 2H), 1.35 (t, J = 8.0 Hz, 2H), 1.28 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.5, 133.9, 131.9, 128.8, 126.4, 125.7, 125.7, 125.4, 125.1, 124.1, 83.2, 27.1, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.08.



4,4',5,5'-Tetramethyl-2-(2-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (3t)[3]: Colourless oil was obtained in 2% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.76-7.79 (m, 3H), 7.67 (s, 1H), 7.39-7.46 (m, 3H), 3.20-3.26 (m, 1H), 1.39 (d, J = 6.8 Hz, 3H), 1.27-1.29 (m, 2H), 1.16 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.8, 133.7, 132.2, 127.9, 127.7, 127.7, 126.0, 125.8, 125.1, 124.5, 83.1, 36.0, 24.9, 24.9, 24.8. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.03.

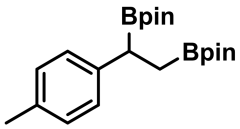


2,2'-(1-Phenylethane-1,2-diyl)bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolane) (7a)[9]: Colourless oil was obtained in 41% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22 (d, J = 4.4 Hz, 4H), 7.07-7.11 (m, 1H), 2.51 (dd, J = 5.6, 10.8 Hz, 1H), 1.38 (dd, J = 11.2, 14.8 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.17 (s, 6H), 1.13 (dd, J = 6.0, 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.5, 128.3, 128.0, 125.0, 83.3, 83.2, 25.1, 24.8, 24.8, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.03.

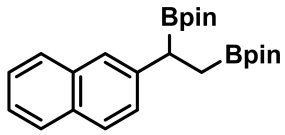


2,2'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolane) (7b)[10]: Colourless oil was obtained in 43% isolated yield. ^{1}H NMR (400 MHz,

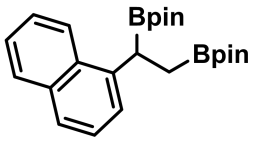
$CDCl_3$, ppm): δ 7.15-7.18 (m, 2H), 6.88-6.92 (m, 1H), 2.50 (dd, J = 6.0, 10.4 Hz, 1H), 1.32 (dd, J = 10.8, 17.2 Hz, 1H), 1.19 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 1.07 (dd, J = 10.0, 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.1 (d, J =240.4 Hz), 141.1 (d, J = 3.0 Hz), 129.3 (d, J = 7.6 Hz), 115.0 (d, J = 20.8 Hz), 83.4, 83.2, 25.1, 24.8, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.70.



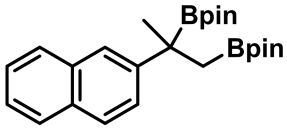
2,2'-(1-p-Tolylethane-1,2-diyl)bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolane) (7g)[9]: White solid was obtained in 20% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.11 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 2.47 (dd, J = 5.2, 10.8 Hz, 1H), 2.28 (s, 3H), 1.33-1.37 (m, 1H), 1.21 (s, 12H), 1.20 (s, 6H), 1.18 (s, 6H), 1.06-1.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.4, 134.2, 129.0, 127.9, 83.3, 83.1, 25.1, 24.8, 24.8, 24.6, 21.1. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.78.



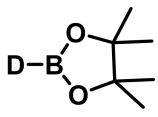
2,2'-(1-(naphthalen-2-yl)ethane-1,2-diyl)bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolane) (7r): White solid was obtained in 71% isolated yield, m.p. 145-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70-7.77 (m, 3H), 7.65 (s, 1H), 7.34-7.42 (m, 3H), 2.69 (dd, J = 6.0, 11.2 Hz, 1H), 1.23-1.24 (m, 2H), 1.20 (s, 12H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.0, 133.8, 131.7, 128.0, 127.4, 127.2, 126.6, 125.6, 124.9, 123.9, 83.5, 83.2, 25.3, 24.9, 24.8, 24.7, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.04. FT-IR (ATR): 3052, 2977, 2930, 1469, 1369, 1389, 1271, 1139, 969, 845, 761, 675, 477. ESI-HRMS (*m/z*): cacld. for [**7r** + H]$^+$: 407.2789; found: 407.2794.



2,2'-(1-(naphthalen-1-yl)ethane-1,2-diyl)bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolane) (7s): Colourless oil was obtained in 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.17-8.19 (m, 1H), 7.80-7.82 (m, 1H), 7.63-7.65 (m, 1H), 7.38-7.46 (m, 4H), 3.22 (dd, J = 6.0, 10.0 Hz, 1H), 1.24-1.25 (m, 2H), 1.21 (s, 6H), 1.20 (s, 12H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.2, 134.1, 132.1, 128.7, 125.9, 125.9, 125.3, 125.2, 125.0, 124.7, 83.5, 83.2, 25.1, 24.8, 24.8, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.78. FT-IR (ATR): 3062, 2978, 2931, 1736, 1509, 1447, 1453, 1329, 1143, 981, 850, 779, 673. ESI-HRMS (*m/z*): cacld. for [**7s** + H]$^{+}$: 407.2789; found: 407.2772.

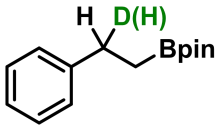


2,2'-(2-(naphthalen-2-yl)propane-1,2-diyl)bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolane) (7t): White solid was obtained in 88% isolated yield, m.p. 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.72-7.79 (m, 4H), 7.59-7.61 (m, 1H), 7.36-7.43 (m, 2H), 1.51 (s, 3H), 1.26-1.27 (m, 2H), 1.22 (s, 12H), 1.21 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.0, 133.8, 131.7, 128.0, 127.4, 127.2, 126.6, 125.6, 125.0, 124.0, 83.5, 83.2, 25.2, 24.9, 24.8, 24.7, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 34.24. FT-IR (ATR): 3055, 2976, 2929, 1476, 1380, 1312, 1139, 1112, 970, 859, 747, 475. ESI-HRMS (*m/z*): cacld. for [**7t** + H]$^{+}$: 421.2945; found: 421.2929.



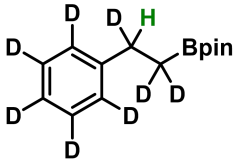
***d*$_1$-pinacolborane (DBPin)[1-2]:** DBpin was obtained of 1.36 M in THF**.** ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.19 (s, 12H). ^{2}D NMR (62 MHz, $CDCl_3$, ppm): δ 2.86-4.50 (br). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 83.1, 24.8. ^{11}B NMR (128 MHz, $CDCl_3$,

ppm): δ 28.08.

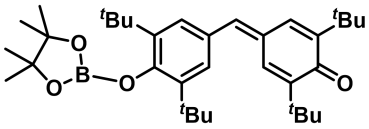


monodeuterium boronic ester d_1-3a:3a = 84:16: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.24-7.25 (m, 2H), 7.20-7.21 (m, 2H), 7.13-7.15 (m, 1H), 2.71-2.76 (m, 1.16H), 1.21 (s, 12H), 1.13-1.14 (m, 2H). ^{2}D NMR (62 MHz, $CHCl_3$, ppm): δ 2.74. ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.5, 128.3, 128.1, 125.6, 83.2, 29.8, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.71.

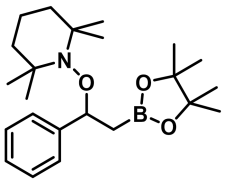
monodeuterium boronic ester d_1-3a:3a = 16:84: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21-7.25 (m, 4H), 7.13-7.17 (m, 1H), 2.76 (t, J = 8.0 Hz, 1.84H), 1.22 (s, 12H), 1.15 (t, J = 8.0 Hz, 2H). ^{2}D NMR (62 MHz, $CDCl_3$, ppm): δ 2.88 (d, J = 4.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.6, 128.3, 128.1, 125.6, 83.2, 30.0, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.91.



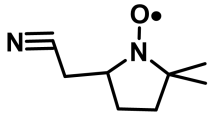
mono-proteo boronic ester d_8-3a: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.72 (s, 1H), 1.22 (s, 12H). ^{2}D NMR (62 MHz, $CHCl_3$, ppm): δ 7.20-7.30 (m, 5D), 2.74 (s, 1D), 1.12 (s, 2D). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.3, 128.0, 127.8, 127.5, 125.1, 83.2, 29.5, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.91.



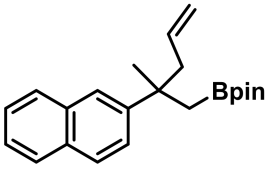
8: ESI-HRMS (*m/z*): cacld. for [**8** + H]$^+$: 548.4146; found: 548.4141.



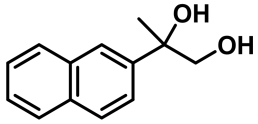
9: ESI-HRMS (*m/z*): cacld. for [**9** + H]$^+$: 387.3054; found: 387.3053.



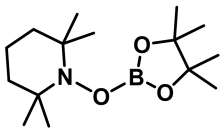
10: ESI-HRMS (*m/z*): cacld. for [**10** + 2H]$^+$: 155.1179; found: 155.1182.



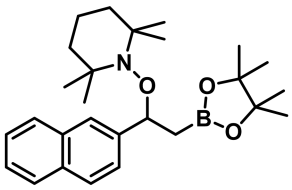
4,4',5,5'-tetramethyl-2-(2-methyl-2-(naphthalen-2-yl)pent-4-en-1-yl)-1,3,2-dioxaborolane (11): Colourless liquid was obtained in 45% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.72-7.79 (m, 4H), 7.54-7.57 (m, 1H), 7.39-7.45 (m, 2H), 5.47-5.58 (m, 1H), 4.90-4.99 (m, 2H), 2.47-2.63 (m, 2H), 1.53 (s, 3H), 1.25-1.28 (m, 2H), 1.05 (s, 6H), 1.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.9, 135.8, 133.4, 131.8, 128.1, 127.5, 127.4, 125.7, 125.4, 125.2, 124.4, 117.1, 82.9, 49.5, 39.6, 27.1, 24.8, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 33.17. FT-IR (ATR): 3058, 2976, 2925, 2855, 1734, 1355, 1325, 1143, 969, 848, 816, 746. ESI-HRMS (*m/z*): cacld. for [**11** + H]$^+$: 336.2370; found: 336.2375.



2-(naphthalen-2-yl)propane-1,2-diol (12)[11]: White solid was obtained in 94% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93 (s, 1H), 7.82-7.85 (m, 3H), 7.46-7.51 (m, 3H), 3.85-3.88 (m, 1H), 3.67-3.69 (m, 1H), 2.93 (br, 1H), 2.17 (br, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.4, 133.3, 132.6, 128.3, 128.3, 127.6, 126.4, 126.1, 124.1, 123.5, 75.1, 71.0, 26.1.



13: GC-MS (*m/z*): cacld. for [**13**]$^+$: 282.2355; found: 282.2385.



14: ESI-HRMS (*m/z*): cacld. for [**14** + H]$^+$: 437.3210; found: 437.3218.

IV. References

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V. Gas Spectra

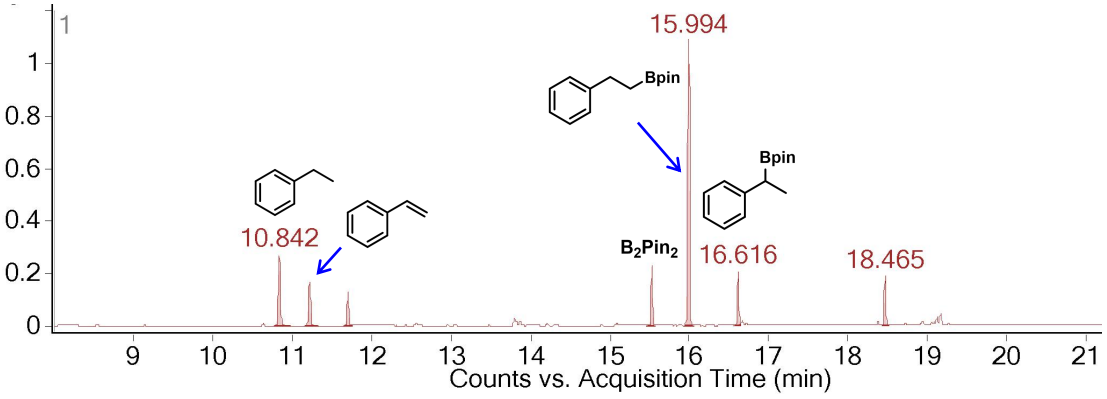


Figure S4. GC–MS spectrum of the hydroboration reaction between styrene and HBpin in the CH_3CN/THF mixture under the standard conditions.

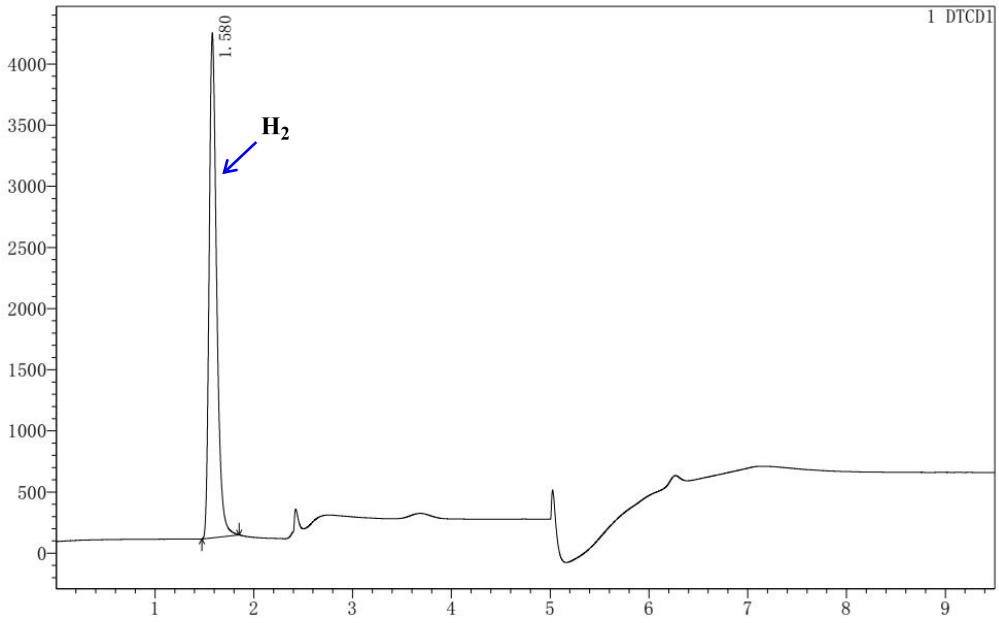
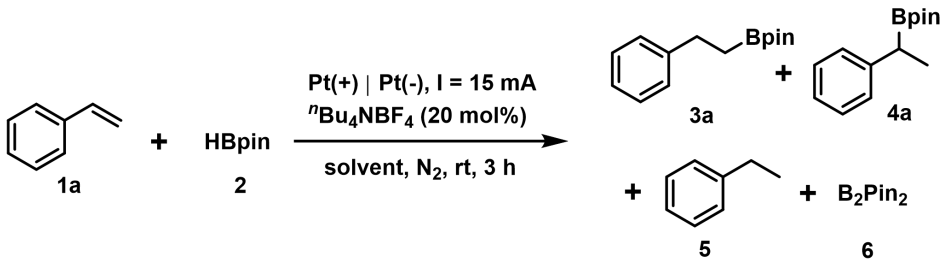


Figure S5. GC spectrum of gases produced in the hydroboration reaction between styrene and HBpin in the CH_3CN/THF mixture under the standard conditions.

VI. Electrochemical Conditions Screening

Table S1. Screening of solvent[a]



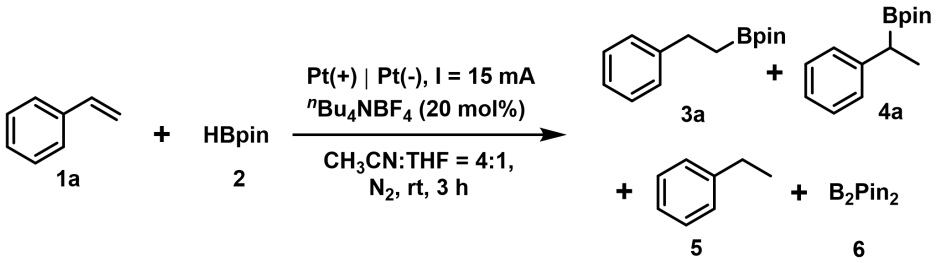
Entry	Solvent	Yield of 3a (%)[b]	3a/4a/5/6[c]
1	CH_3CN:THF = 7:3	49	59:8:21:12
2	**CH_3CN:THF = 4:1**	**56**	**62:9:17:12**
3	CH_3CN:THF = 9:1	43	57:9:24:10
4	CH_3CN:THF = 9.5:0.5	49	60:6:20:14
5	CH_3CN:Et_2O = 4:1	45	77:0:13:10
6	CH_3CN:1,4-dioxane = 4:1	48	62:0:28:10

[a]Reaction conditions: **1a** (1.0 mmol), **2** (1.1 mmol), ^{n}Bu$_4$NBF$_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=15 mA, solvent, the total volume of the solvent is 10 mL, N_2, rt, 3 h.

[b]The yields of **3a** were determined by gas chromatography (GC) analysis using naphthalene as internal standard.

[c]The selectivity are determined by gas chromatography (GC) analysis.

Table S2. Screening of electrode and temperature[a]



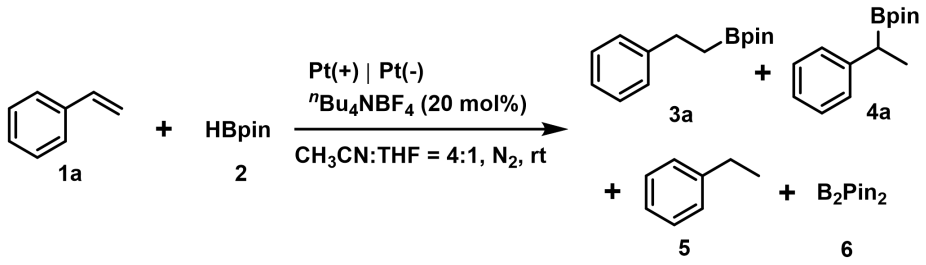
Entry	Variation from the standard conditions	Yield of 3a(%)[b]	3a/4a/5/6[c]
1	C(+) | Pt(−), 40 °C	20	59:0:36:5
2	Pt(+) | Ni(−), 40 °C	40	56:27:9:8
3	C(+) | Pt(−)	31	63:0:30:7
4	Pt(+) | Ni(−)	51	57:9:24:10
5	60 °C	38	59:6:27:8
6	40 °C	42	60:8:22:10
7	**none**	**56**	**62:9:17:12**
8	0 °C	53	61:10:17:12

[a]Reaction conditions: **1a** (1.0 mmol), **2** (1.1 mmol), $^{n}Bu_4NBF_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=15 mA, CH_3CN:THF=4:1 (*v*/*v*), the total volume of the solvent is 10 mL, N_2, rt, 3 h.

[b]The yields of **3a** were determined by gas chromatography (GC) analysis using naphthalene as internal standard.

[c]The selectivity are determined by gas chromatography (GC) analysis.

Table S3. Screening of time, current and electrolyte[a]



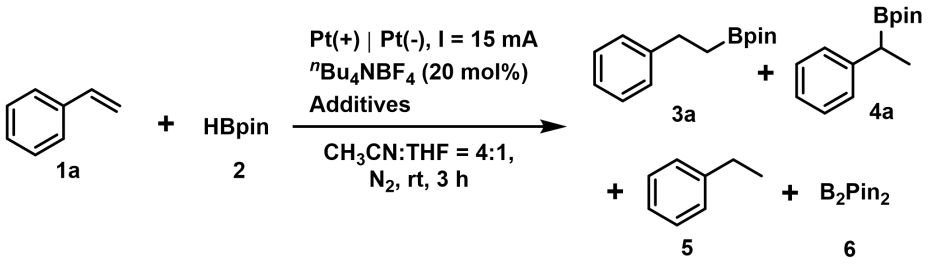
Entry	Variation from the standard conditions	Yield of 3a (%)[b]	3a/4a/5/6[c]
1	2 h	39	59:9:23:9
2	4 h	55	68:7:10:15
3	10 mA	37	68:8:8:16
4	13 mA	49	65:9:14:12
5	**none**	**56**	**67:7:15:11**
6	20 mA	51	57:8:25:10
7	30 mA	53	55:14:27:4
8	0.5 eq. ^{n}Bu$_4$NBF$_4$	51	58:10:20:12

[a]Reaction conditions: **1a** (1.0 mmol), **2** (1.1 mmol), ^{n}Bu$_4$NBF$_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=15 mA, CH$_3$CN:THF=4:1 (*v*/*v*), the total volume of the solvent is 10 mL, N$_2$, rt, 3 h.

[b]The yields of **3a** were determined by gas chromatography (GC) analysis using naphthalene as internal standard.

[c]The selectivity are determined by gas chromatography (GC) analysis.

Table S4. Screening of additives[a]



Entry	Additives	Yield of 3a (%)[b]	3a/4a/5/6[c]
1[a]	Et_3N (1.1 eq.)	44	65:10:23:2
2[c]	Et_3N (1.1 eq.)	51	75:10:13:2
3[a]	DIEA (1.1 eq.)	60	73:10:13:4
4[c]	DIEA (1.1 eq.)	67	76:11:12:1
5[c]	DIEA (0.9 eq.)	71	76:7:14:3
6[c]	**DIEA (0.8 eq.)**	**72**	**82:5:11:2**
7[c]	DIEA (0.65 eq.)	69	79:7:11:3
8[c]	DIEA (0.55 eq.)	70	81:5:12:2
9[c]	DIEA (0.4 eq.)	67	74:7:15:4
10[c]	DIEA (0.25 eq.)	63	69:7:19:5

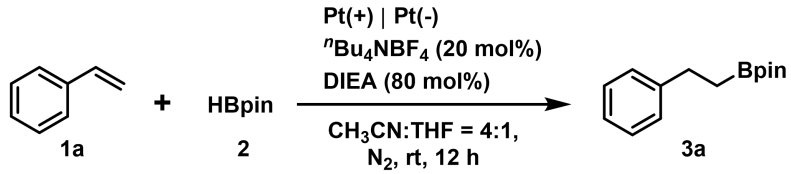
[a]Reaction conditions: **1a** (1.0 mmol), **2** (1.1 mmol), ^{n}Bu$_4$NBF$_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=15 mA, additives, CH_3CN (10 mL), N_2, rt, 3 h.

[b]The yields of **3a** were determined by gas chromatography (GC) analysis using naphthalene as internal standard.

[c]Reaction conditions: **1a** (1.0 mmol), **2** (1.1 mmol), ^{n}Bu$_4$NBF$_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=15 mA, additives, CH_3CN:THF=4:1 (*v*/*v*), the total volume of the solvent is 10 mL, N_2, rt, 3 h.

[c]The selectivity are determined by gas chromatography (GC) analysis.

Table S5. Screening of current in gram-scale experiments[a]

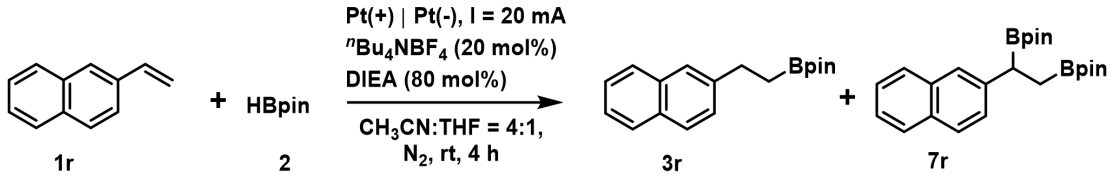


Entry	Current	Yield of 3a (%)[b]
1	15 mA	31
2	30 mA	46
3	**45 mA**	**61**

[a]Reaction conditions: **1a** (10 mmol), **2** (11 mmol), DIEA (80 mol%), $^{n}Bu_4NBF_4$ (20 mol%), Pt(+)|Pt(−), constant current, CH_3CN:THF=4:1 (*v/v)*, the total volume of the solvent is 100 mL, N_2, rt, 12 h.

[b]Isolated yields are shown.

Table S6. Screening of the molar ratio of 2-vinylphthalene to HBpin to prepare diboronate ester **7r**[a]

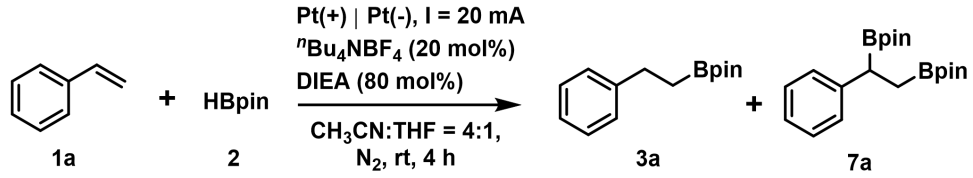


Entry	1r:2 (mol:mol)	3r:7r[b]
1	1:1.1	65:35
2	1:2.2	38:61
3	1:3.3	14:86
4	1:4.4	9:91

[a]Reaction conditions: **1r** (1.0 mmol), **2**, DIEA (80 mol%), $^{n}Bu_4NBF_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=20 mA, CH_3CN:THF=4:1 (*v/v)*, the total volume of the solvent is 10 mL, N_2, rt, 4 h.

[b]The yield ratios of **3r** to **7r** were determined by the peak area ratios of gas chromatography (GC).

Table S7. Screening of the molar ratio of styrene to HBpin to prepare diboronate ester **7a**[a]



Entry	1a:2 (mol:mol)	3a:7a[b]
1	1:4.4	65:35
2	1:6.6	53:47
3	1:8.8	40:60
4	1:10.0	40:60

[a]Reaction conditions: **1a** (1.0 mmol), **2**, DIEA (80 mol%), $^{n}Bu_4NBF_4$ (20 mol%), Pt(+)|Pt(−), constant current (I)=20 mA, CH_3CN:THF=4:1 (*v/v)*, the total volume of the solvent is 10 mL, N_2, rt, 4 h.

[b]The yield ratios of **3a** to **7a** were determined by the peak area ratios of gas chromatography (GC).

VII. Crystal Information

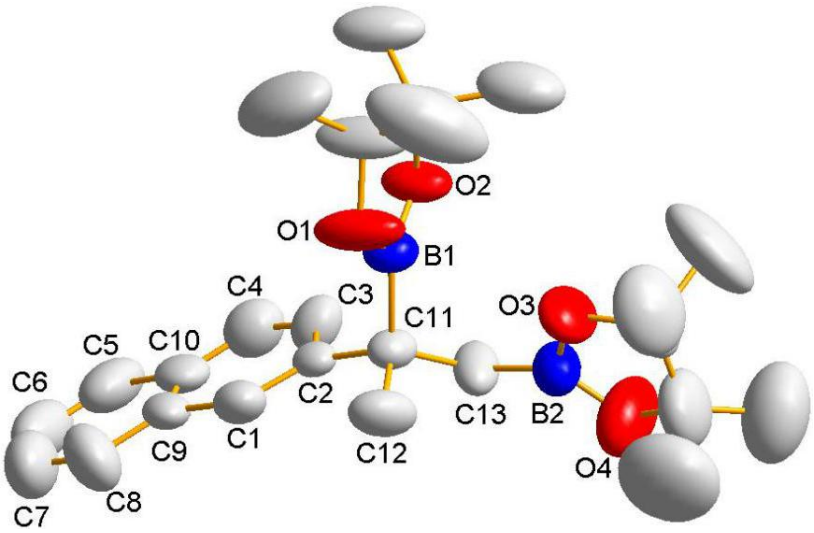


Figure S6. ORTEP diagram of compound **7t**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms on carbons are omitted for the sake of clarity.

Table S8. Crystal data and structural refinement for compound **7t**

Compound	**7t**
Formula	$C_{25}H_{36}B_2O_4$
Formula weight	422.16
Crystal dimensions (mm^3)	0.26 × 0.25 × 0.25
Crystal system	monoclinic
Space group	'P 21/n'
a (Å)	6.5462(6)
b (Å)	27.280(2)
c (Å)	14.4106(12)
α (°)	90.00
β (°)	90.549(3)
γ (°)	90.00
Volume ($Å^3$)	2573.4(4)
Z	4
T (K)	293(2)
D_{calcd} (g cm^{-3})	1.090
μ (mm^{-1})	0.070
F (000)	912
No. of rflns. collected	21174
No. of indep. rflns. /R_{int}	3893 / 0.0551
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	2526
Data / restraints / parameters	3893 / 103 / 308
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.1499 / 0.3733
R_1 / wR_2 (all data)	0.1952 / 0.3965
GOF (on F^2)	1.001
Largest diff. peak and hole (e $Å^{-3}$)	0.974 / −0.359
CCDC No.	2022111

Table S9. Selected bond distances and angles for **7t**

Distances (Å)			
B1–O1	1.319(8)	B2–O3	1.355(9)
B1–O2	1.347(8)	B2–O4	1.320(9)
B1–C11	1.588(8)	B2–C13	1.585(11)
Angles (°)			
C2–C11–B1	107.1(5)	C12–C11–B1	109.4(5)
C13–C11–B1	111.0(5)	C11–C13–B2	111.3(6)

VIII. NMR Spectra

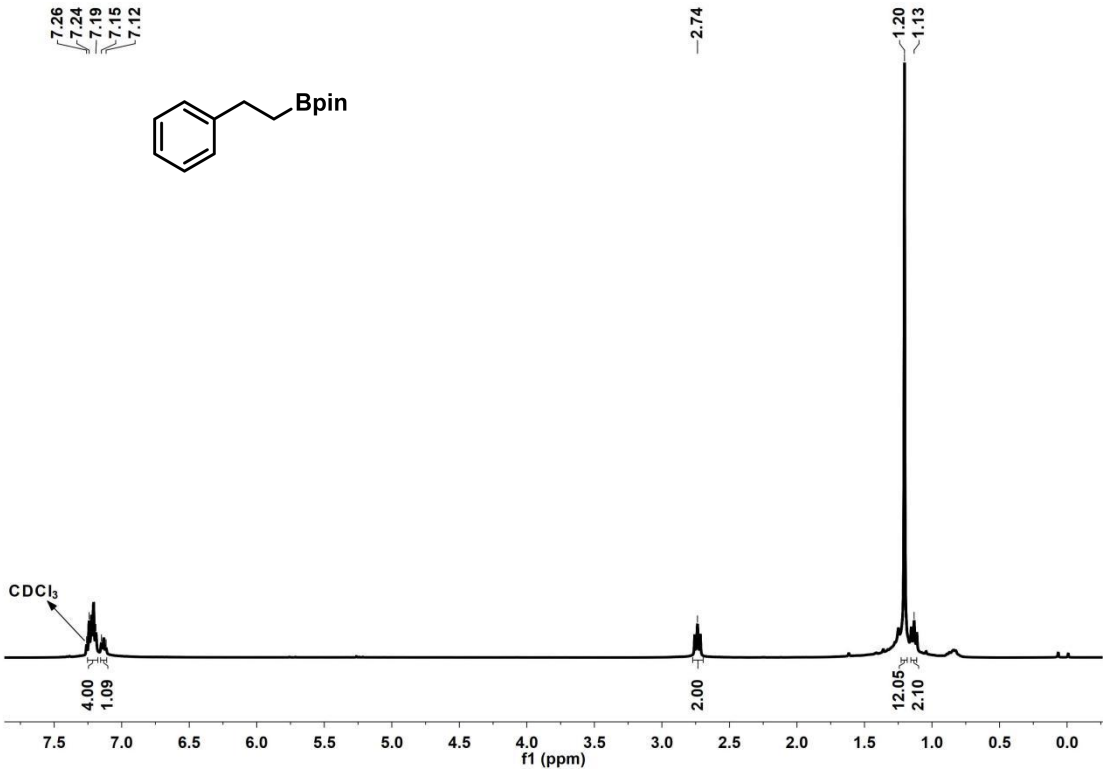


Figure S7. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

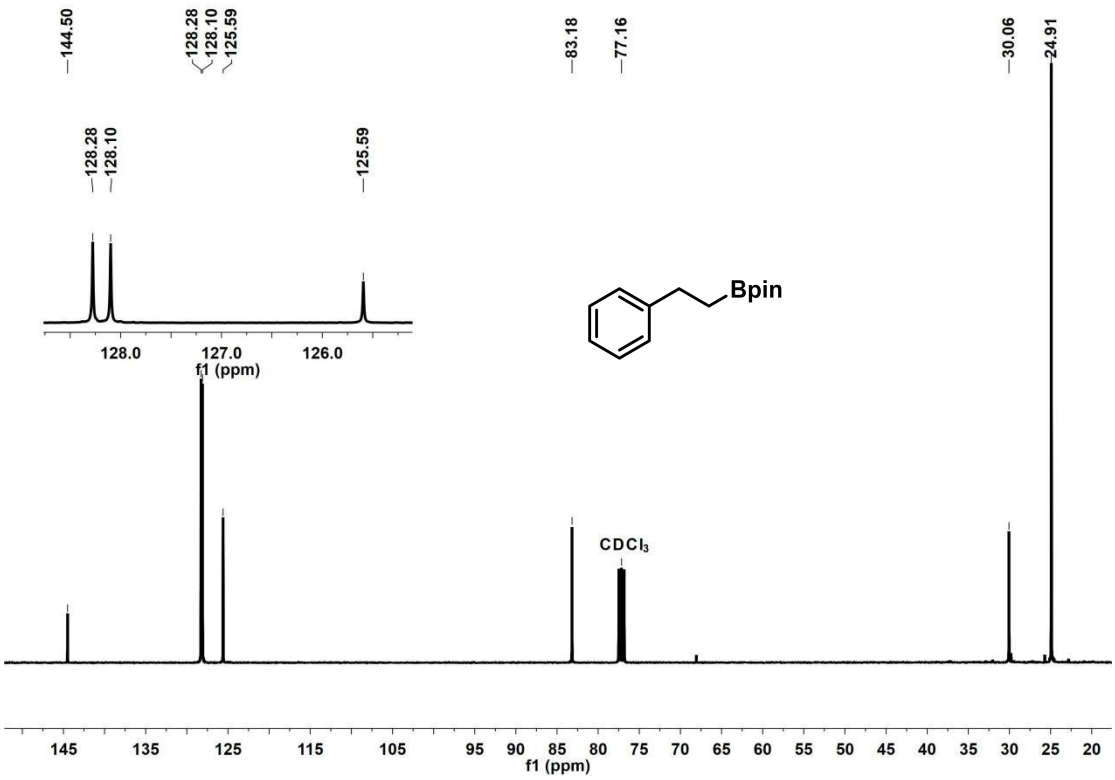


Figure S8. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

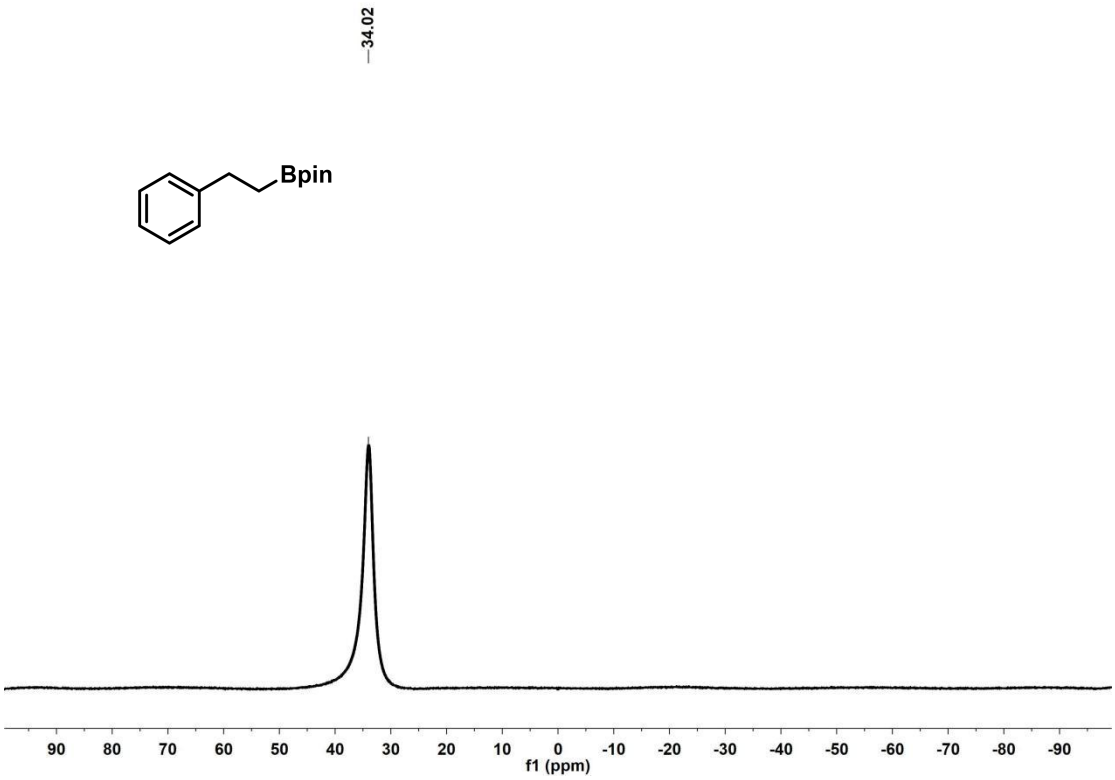


Figure S9. ^{11}B NMR spectrum of **3a** in $CDCl_3$.

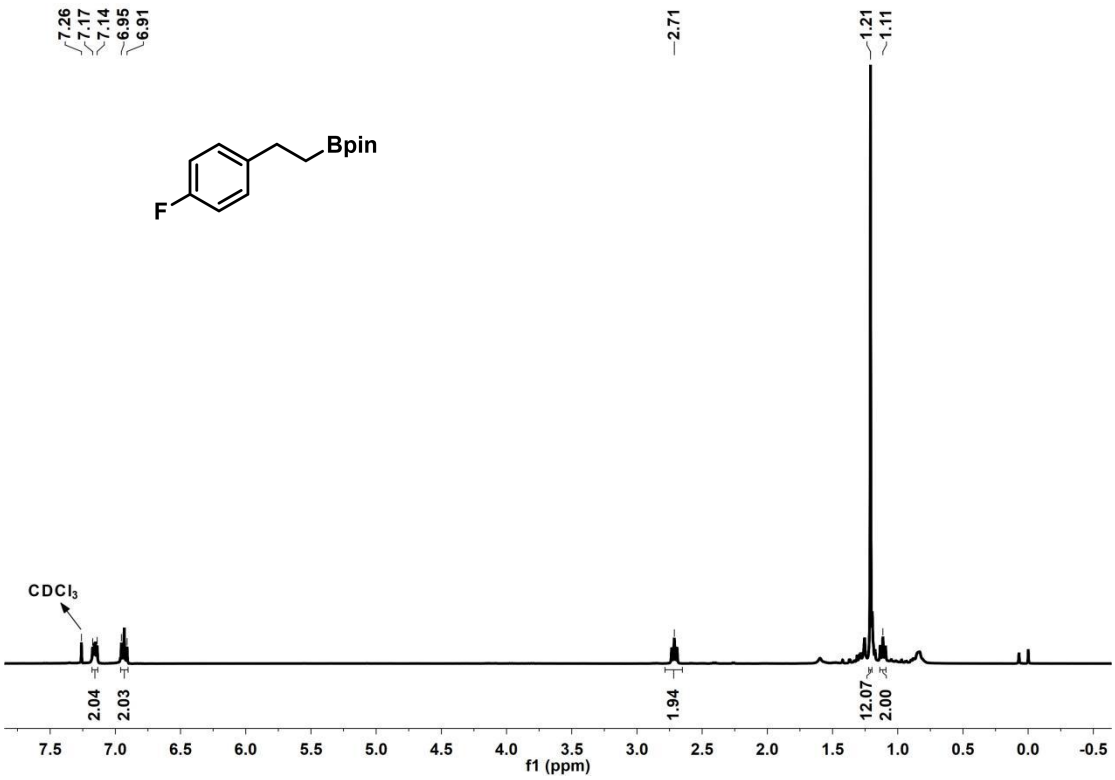


Figure S10. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

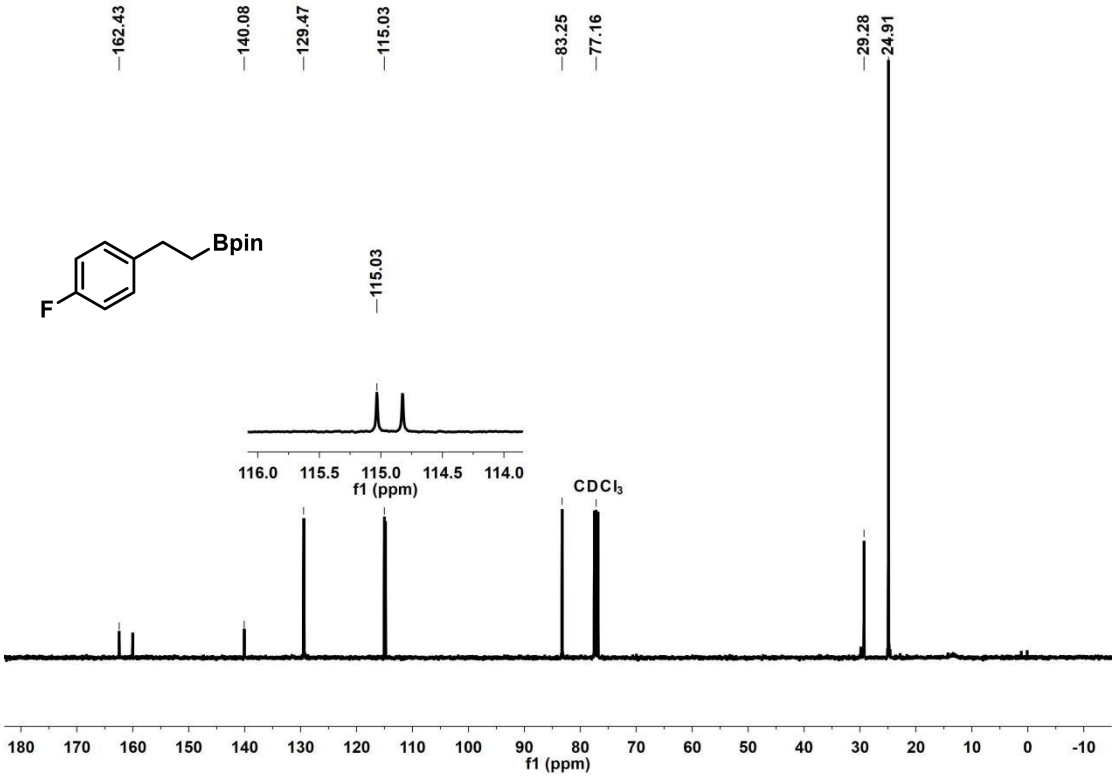


Figure S11. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

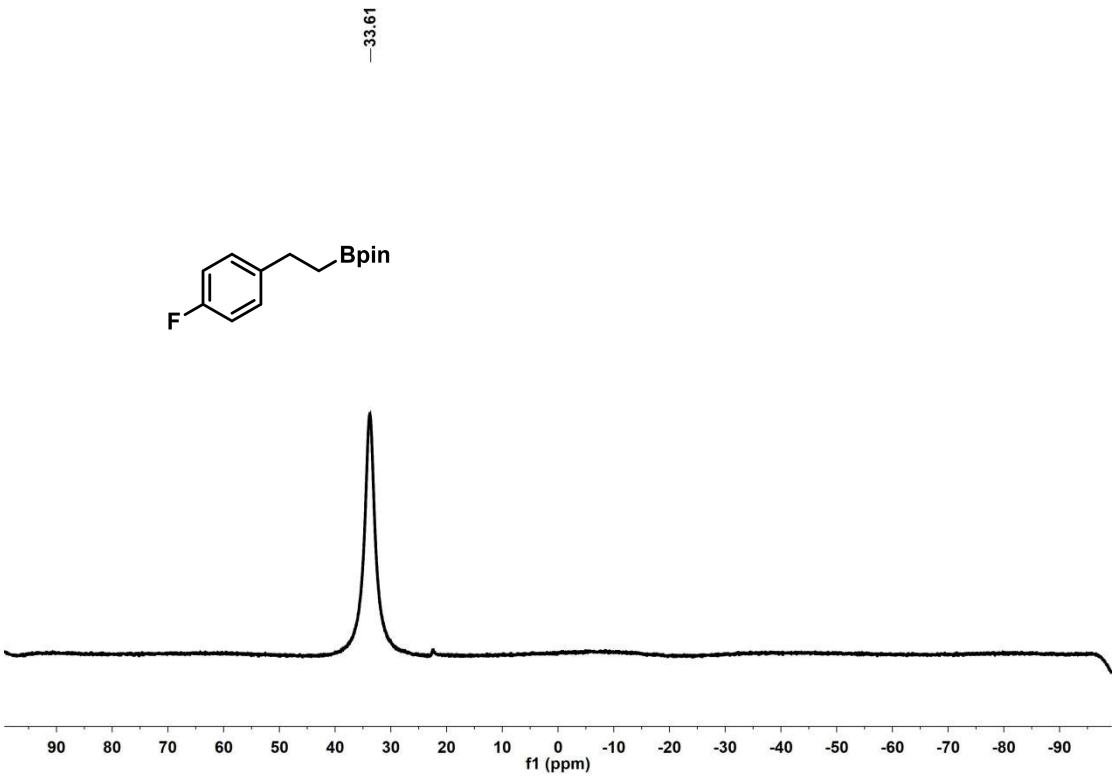


Figure S12. ^{11}B NMR spectrum of **3b** in $CDCl_3$.

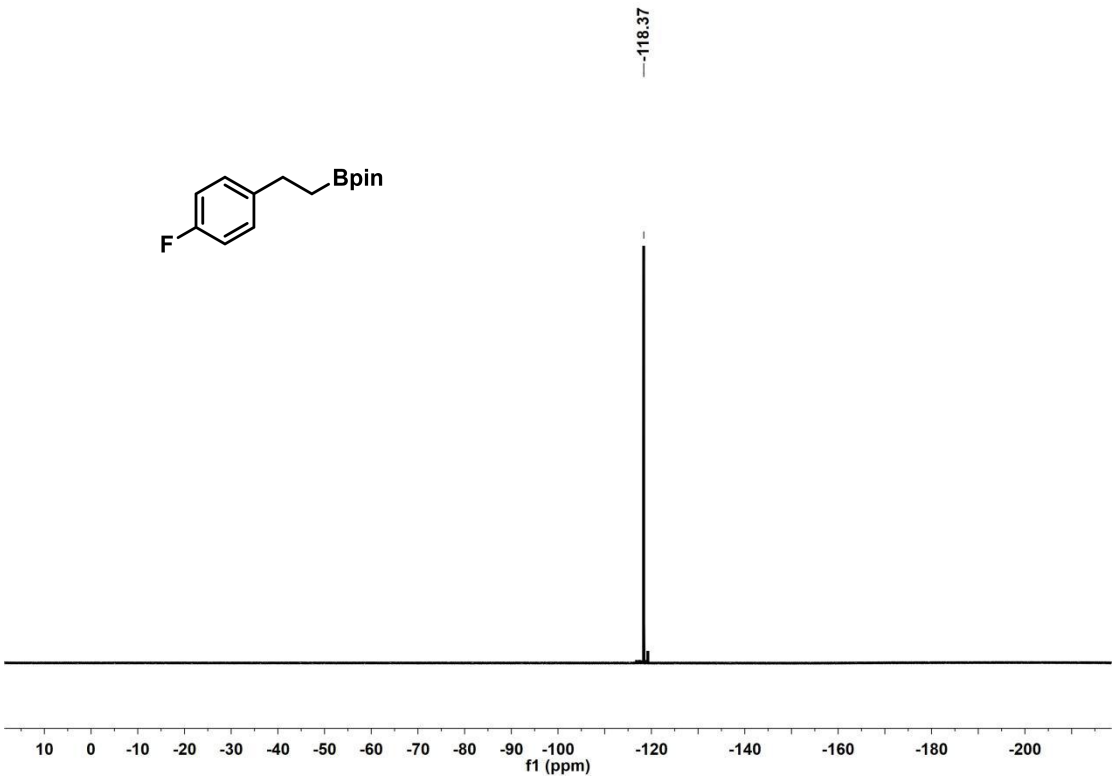


Figure S13. ^{19}F NMR spectrum of **3b** in $CDCl_3$.

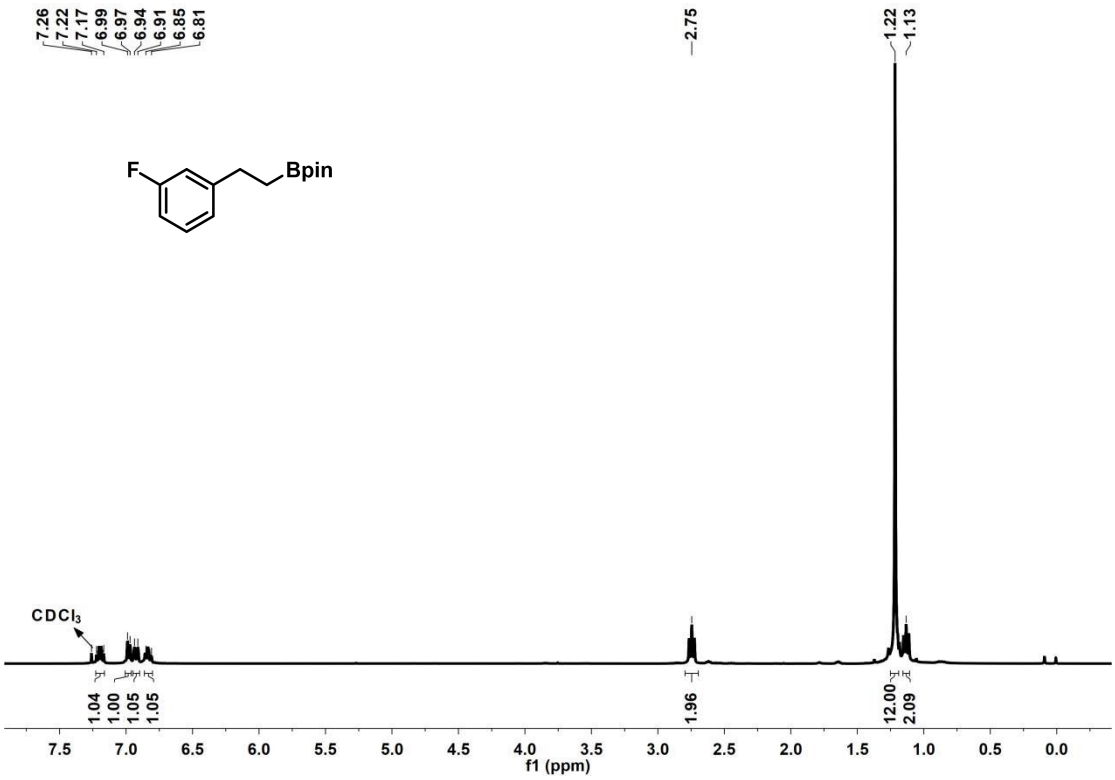


Figure S14. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

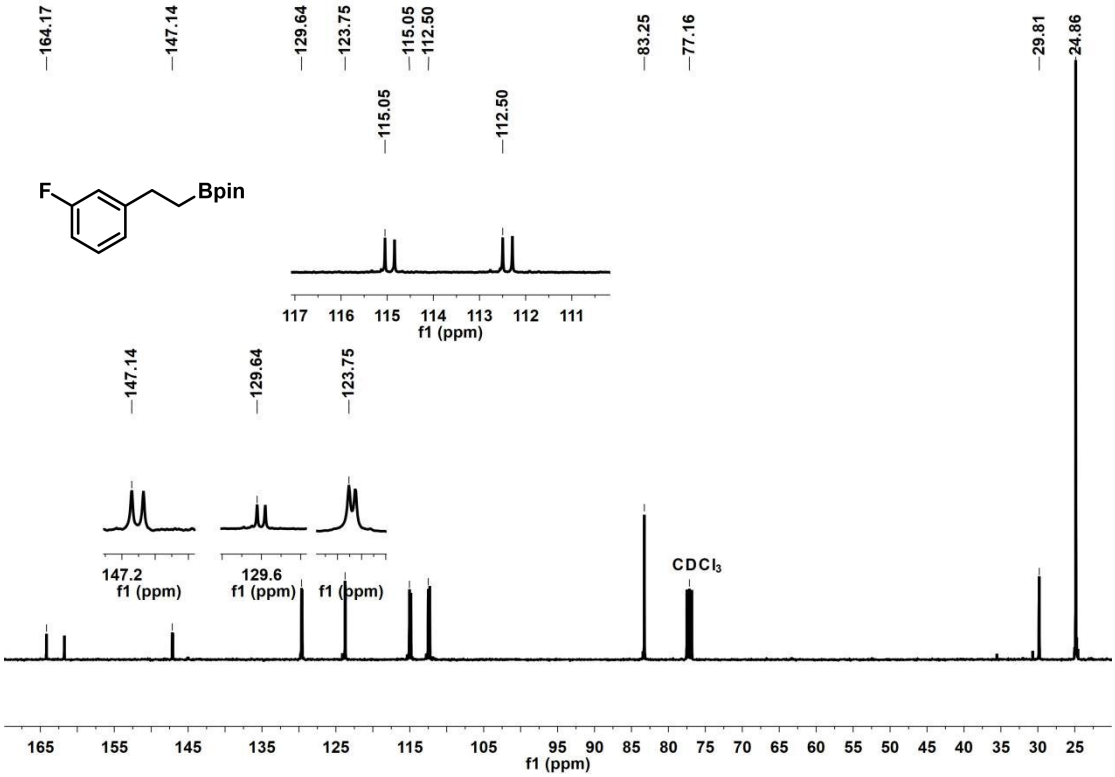


Figure S15. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

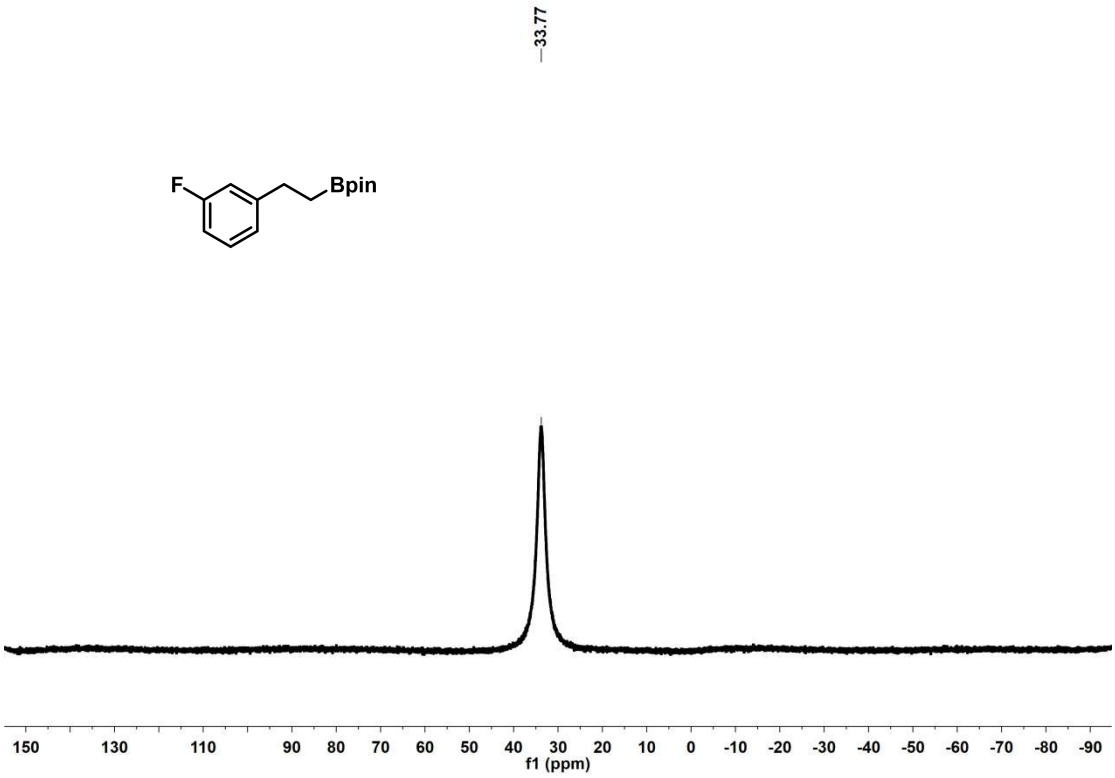


Figure S16. ^{11}B NMR spectrum of **3c** in $CDCl_3$.

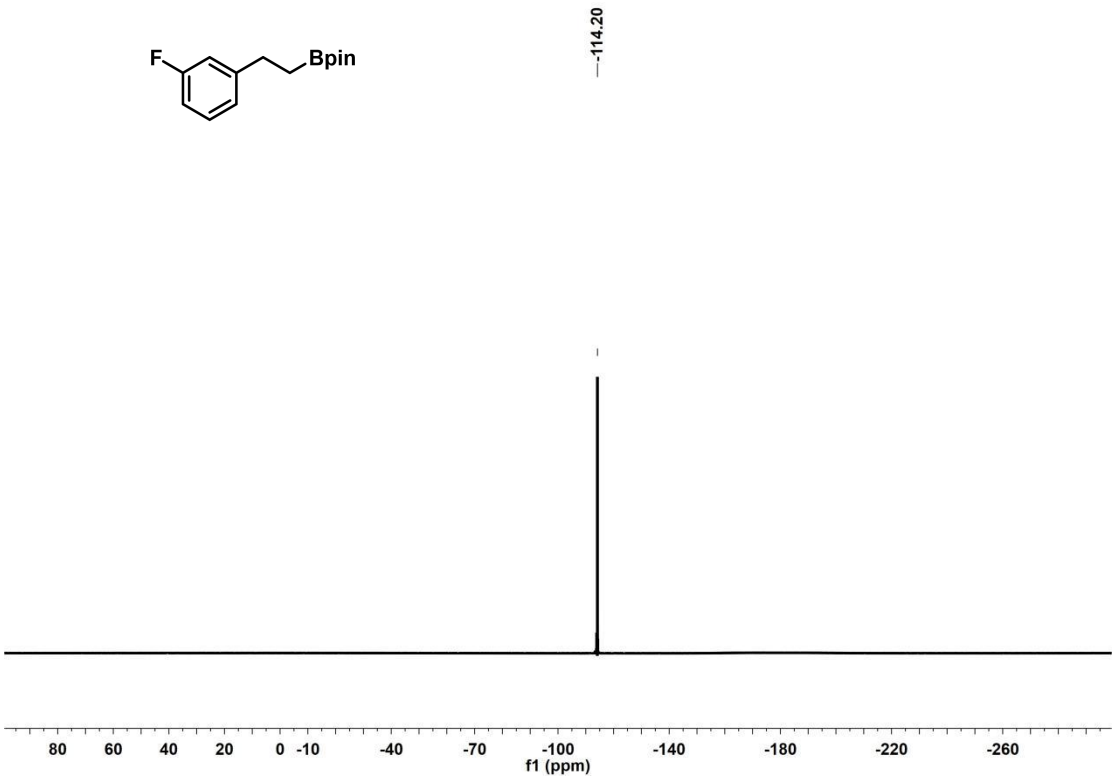


Figure S17. ^{19}F NMR spectrum of **3c** in $CDCl_3$.

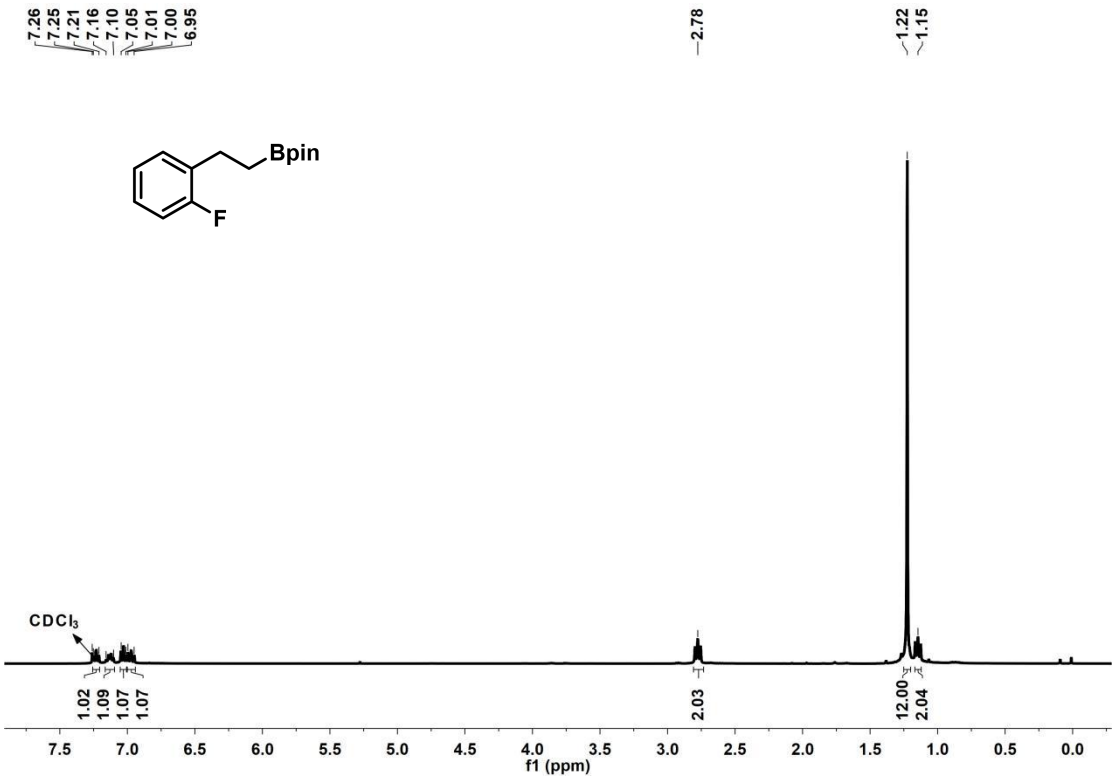


Figure S18. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

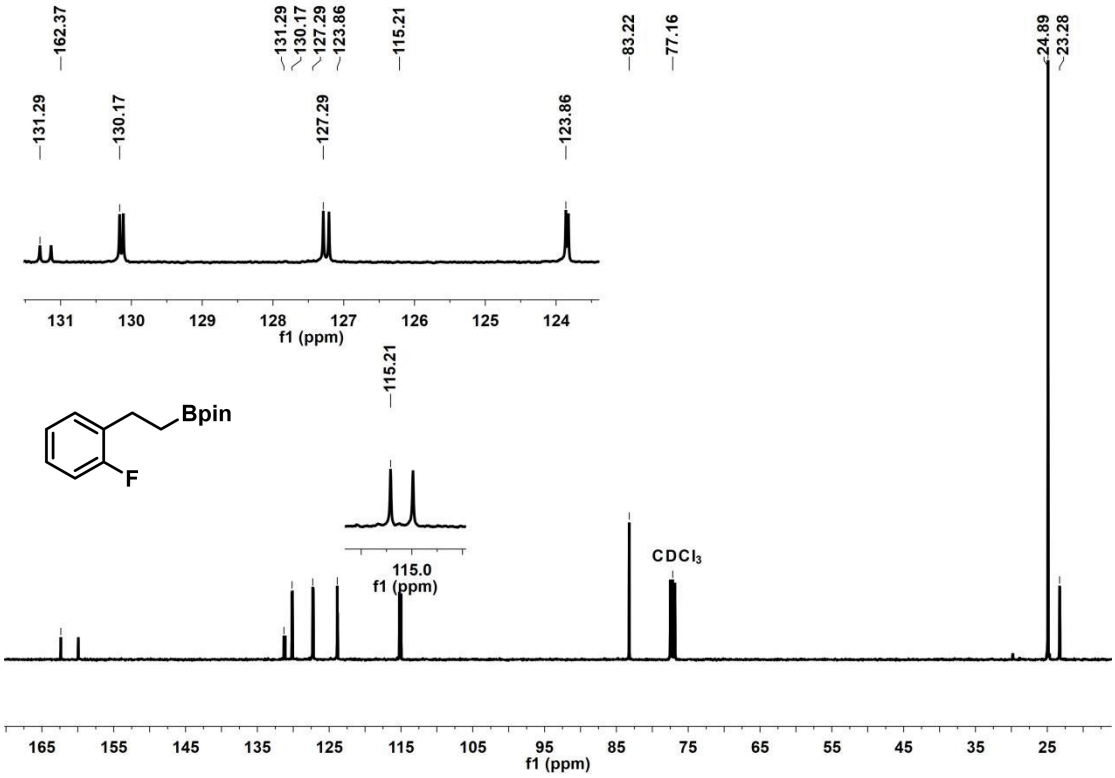


Figure S19. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

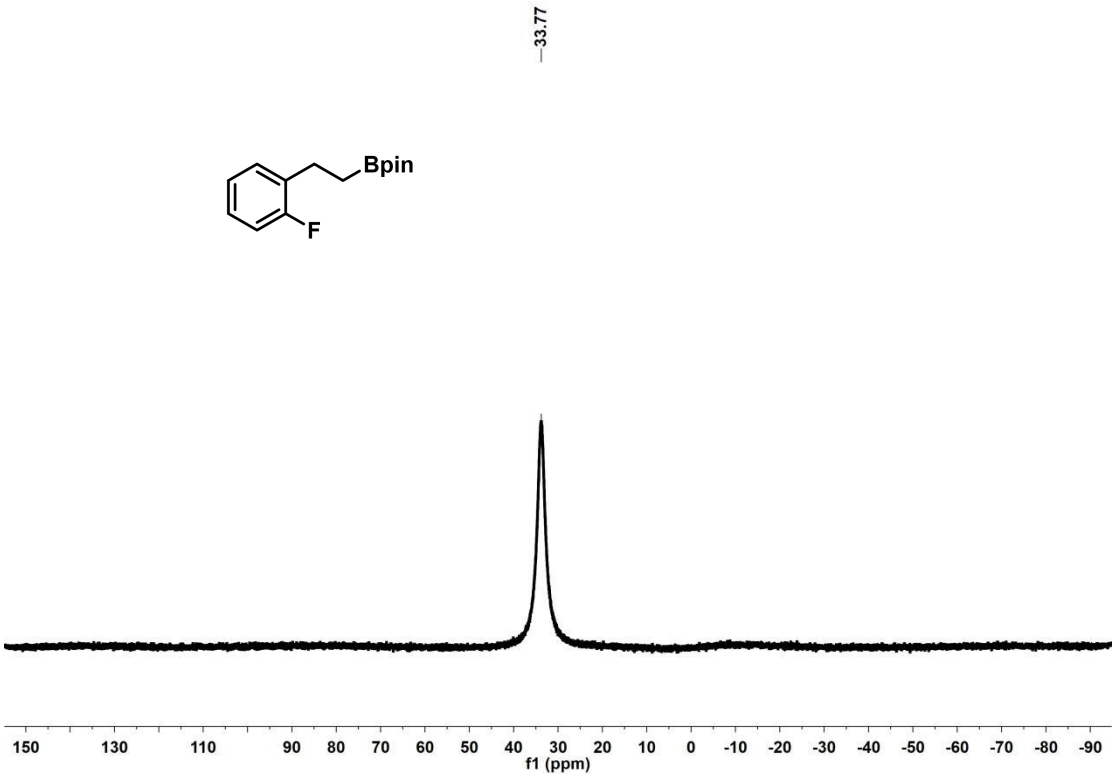


Figure S20. ^{11}B NMR spectrum of **3d** in $CDCl_3$.

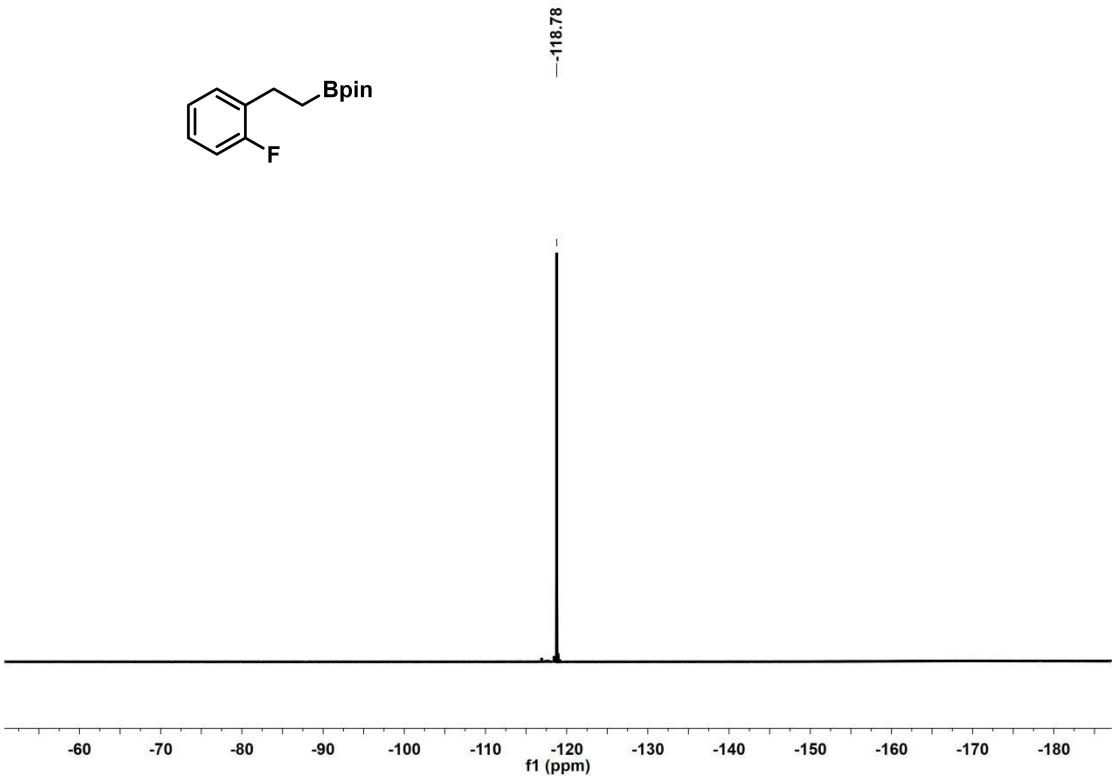


Figure S21. ^{19}F NMR spectrum of **3d** in $CDCl_3$.

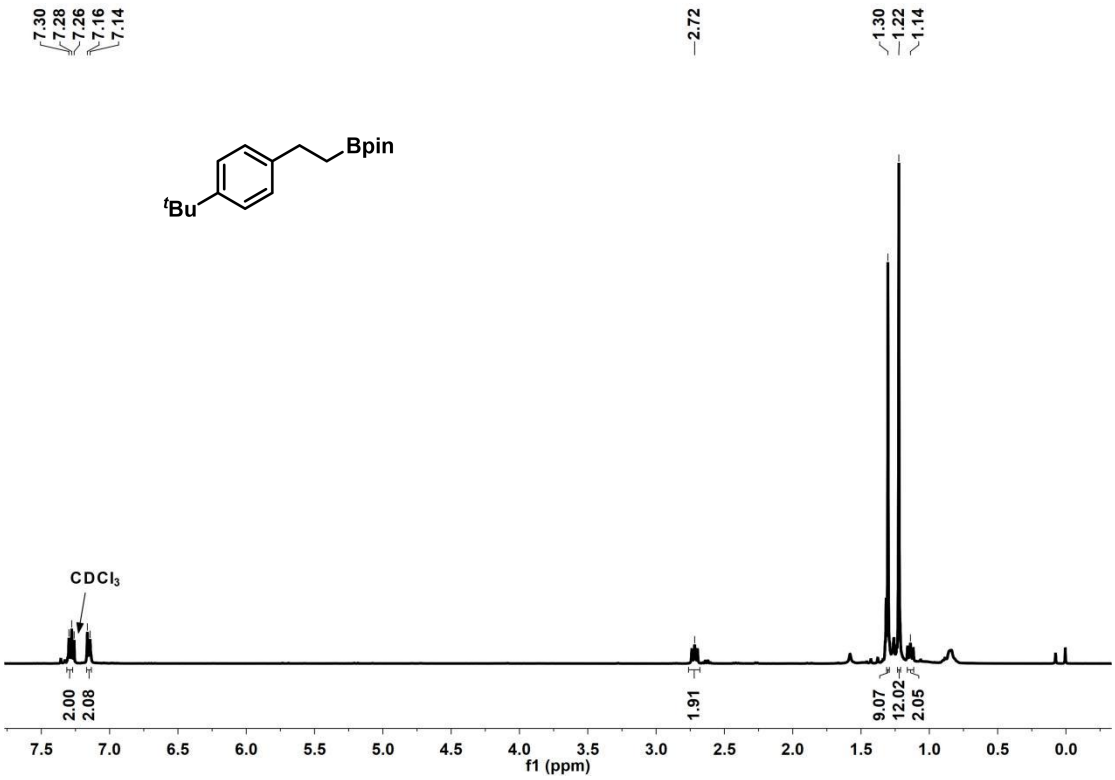


Figure S22. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

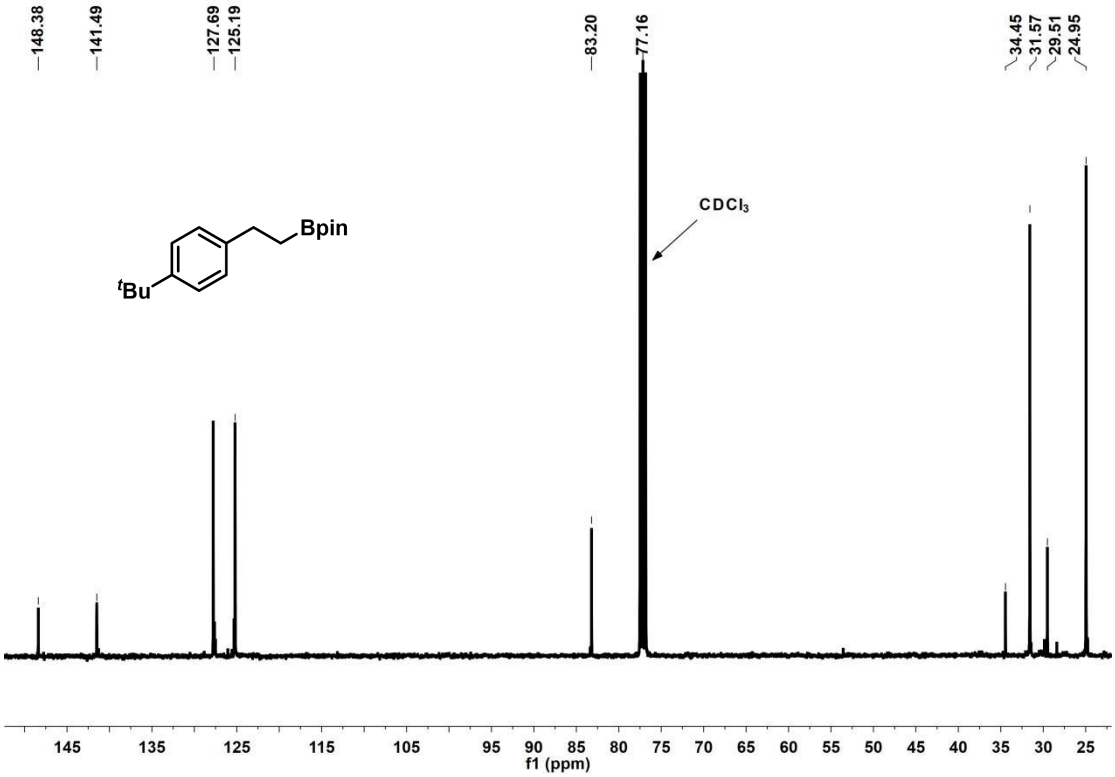


Figure S23. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

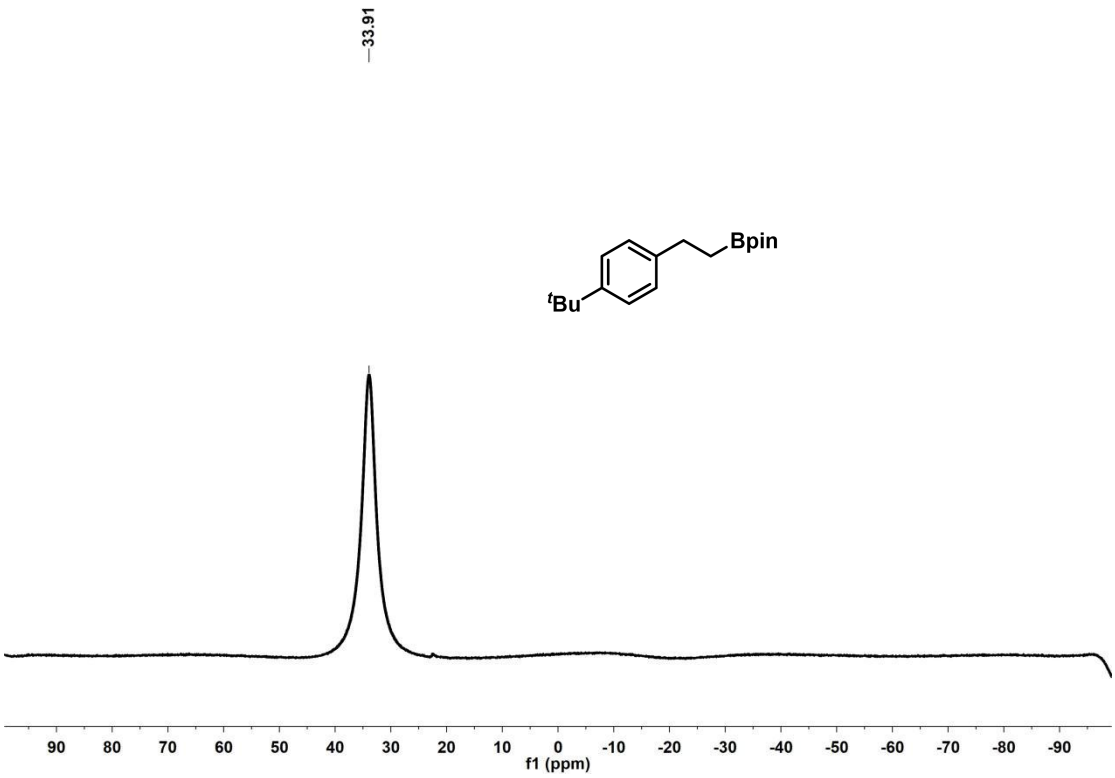


Figure S24. ^{11}B NMR spectrum of **3e** in $CDCl_3$.

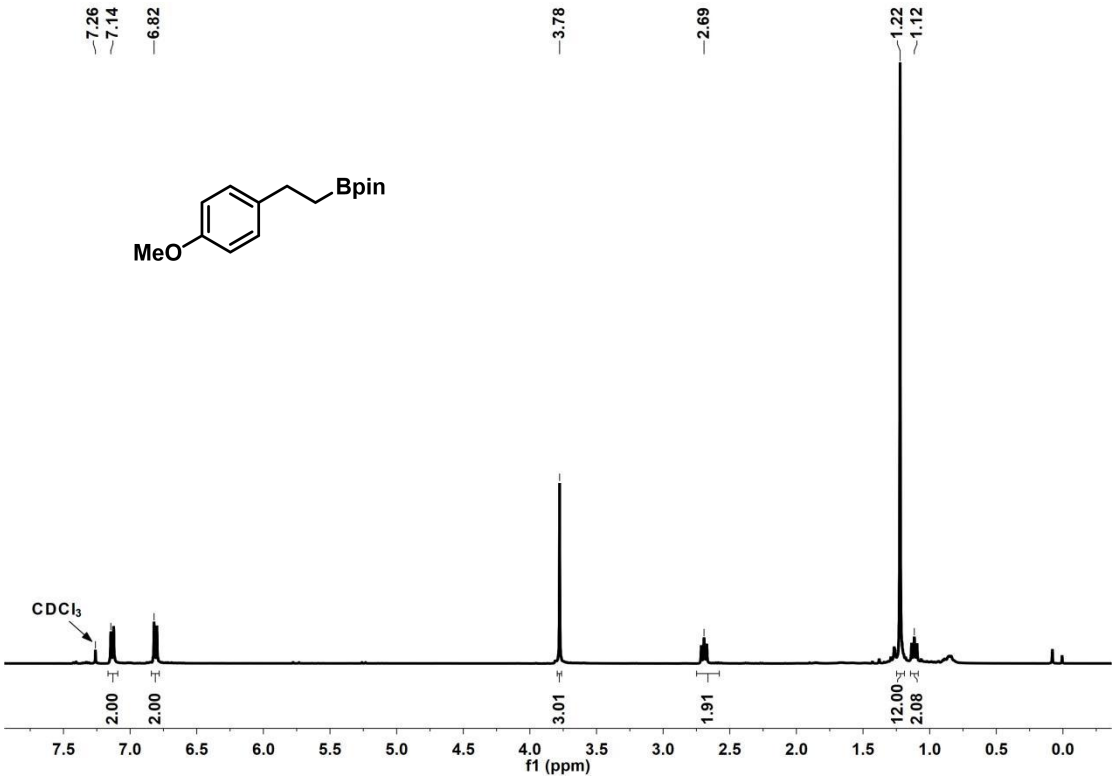


Figure S25. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

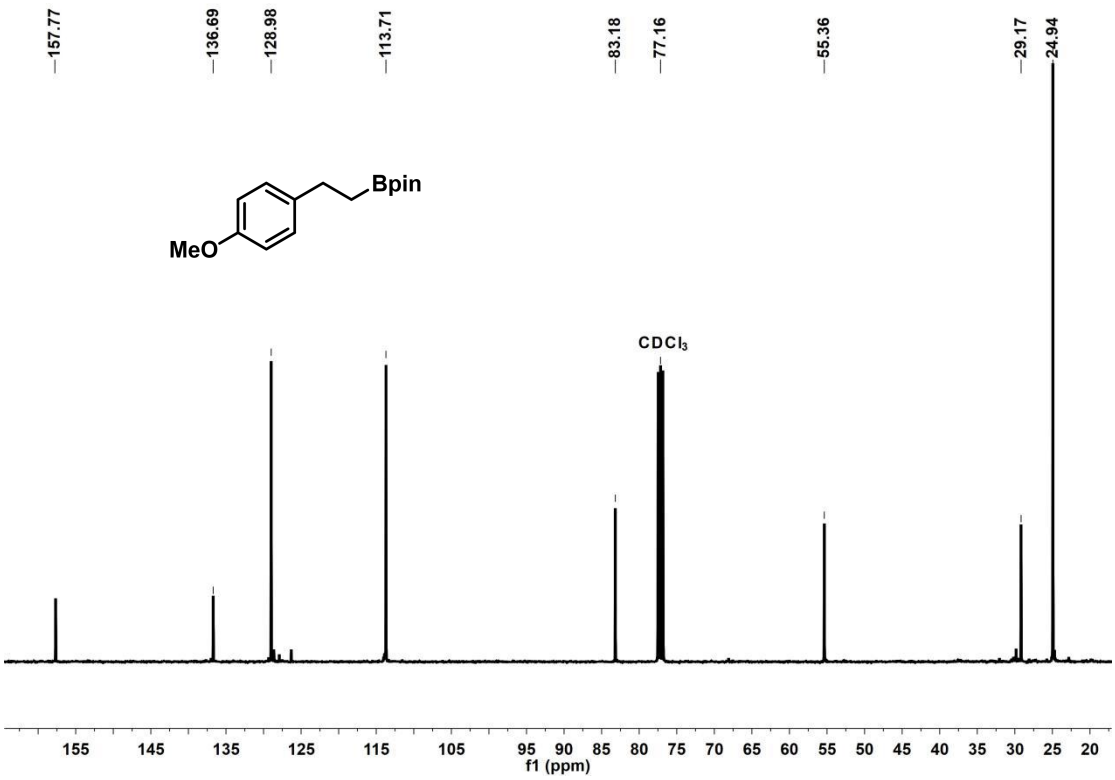


Figure S26. ^{13}C NMR spectrum of **3f** in $CDCl_3$.

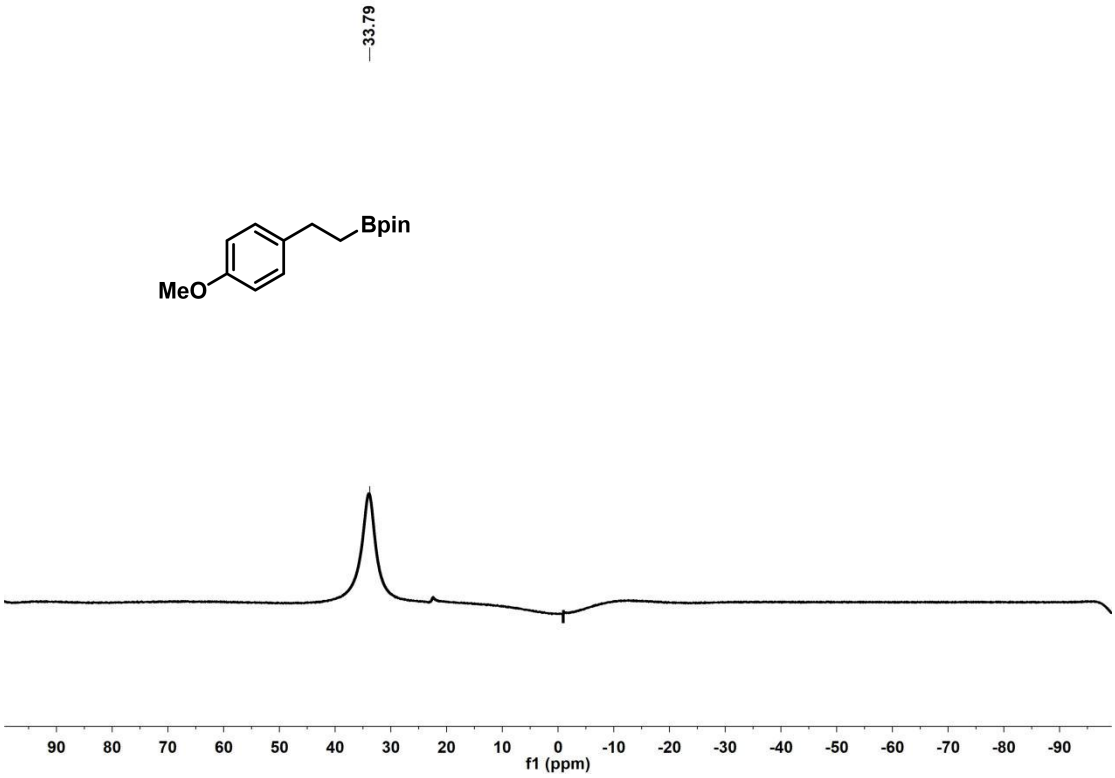


Figure S27. ^{11}B NMR spectrum of **3f** in $CDCl_3$.

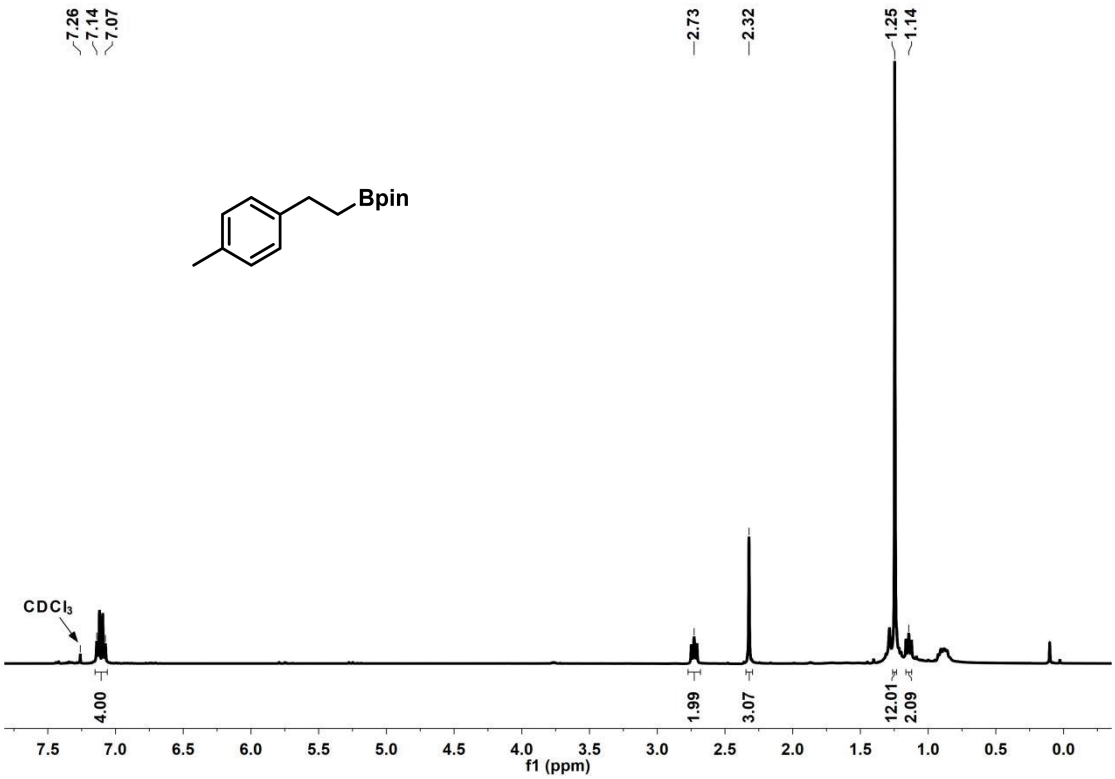


Figure S28. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

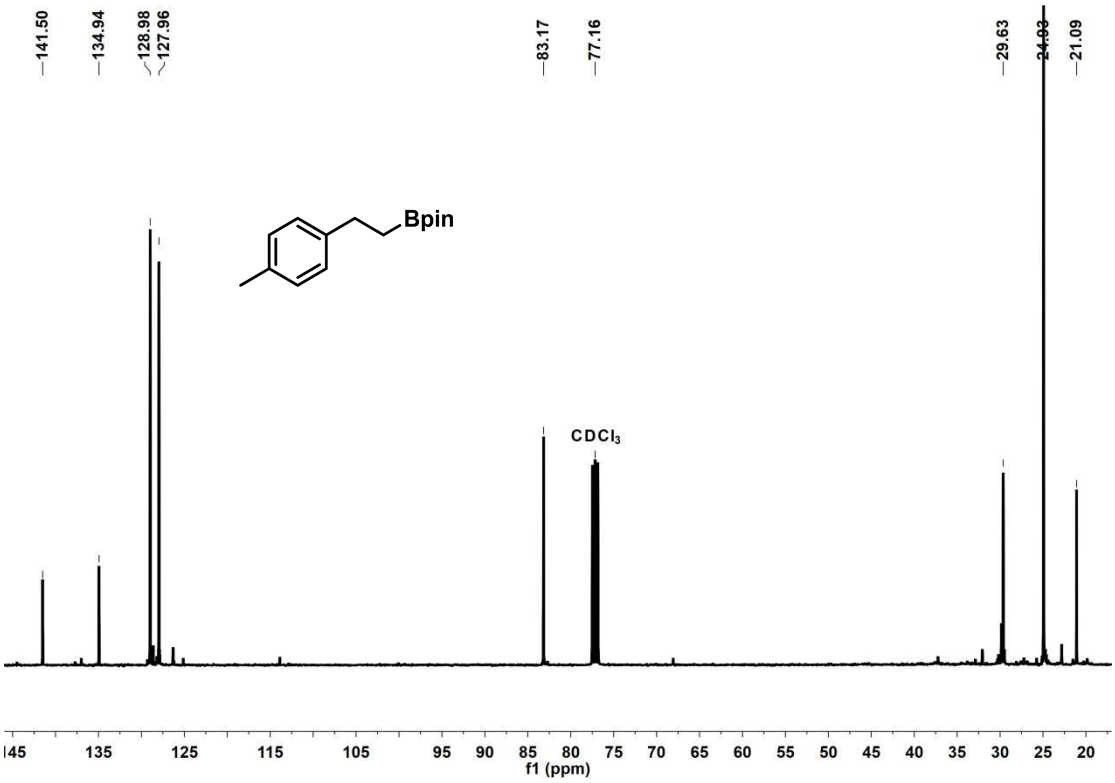


Figure S29. ^{13}C NMR spectrum of **3g** in $CDCl_3$.

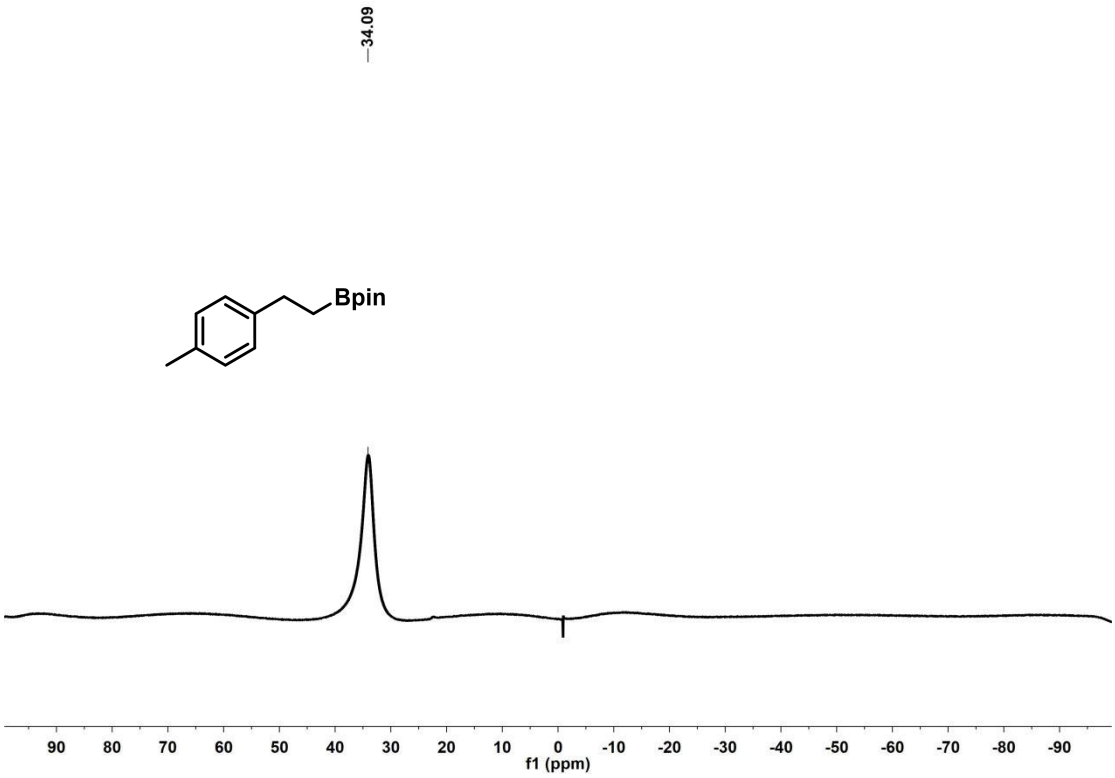


Figure S30. ^{11}B NMR spectrum of **3g** in $CDCl_3$.

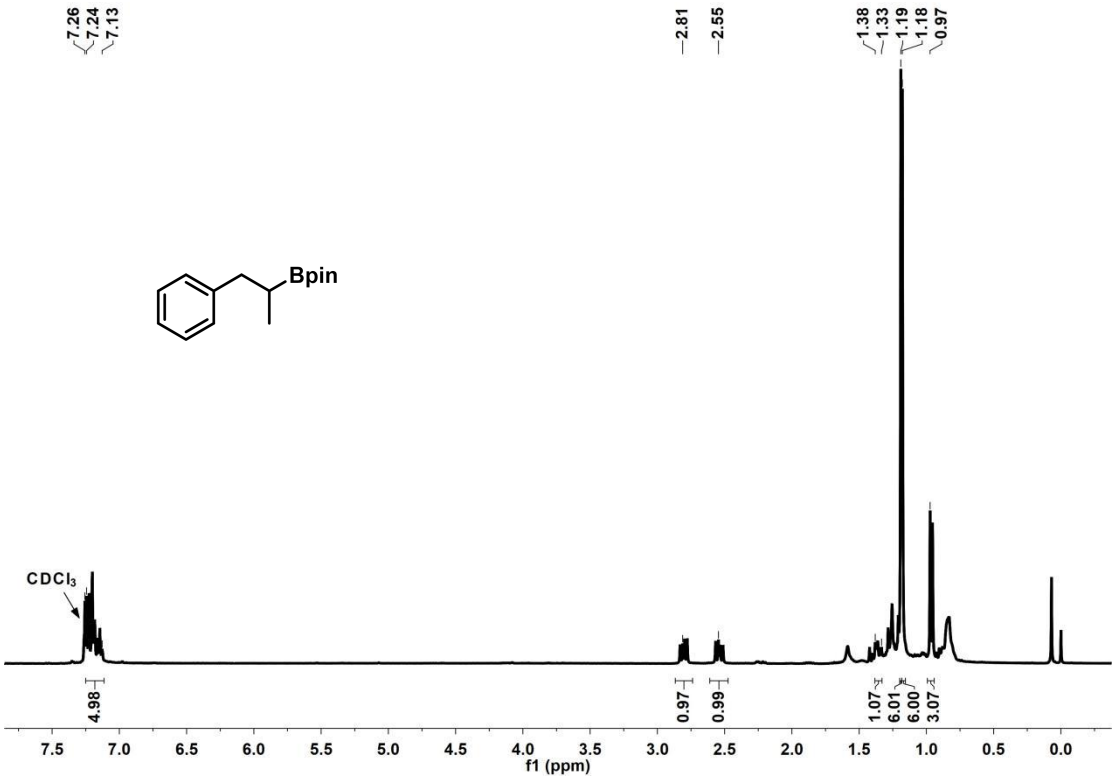


Figure S31. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

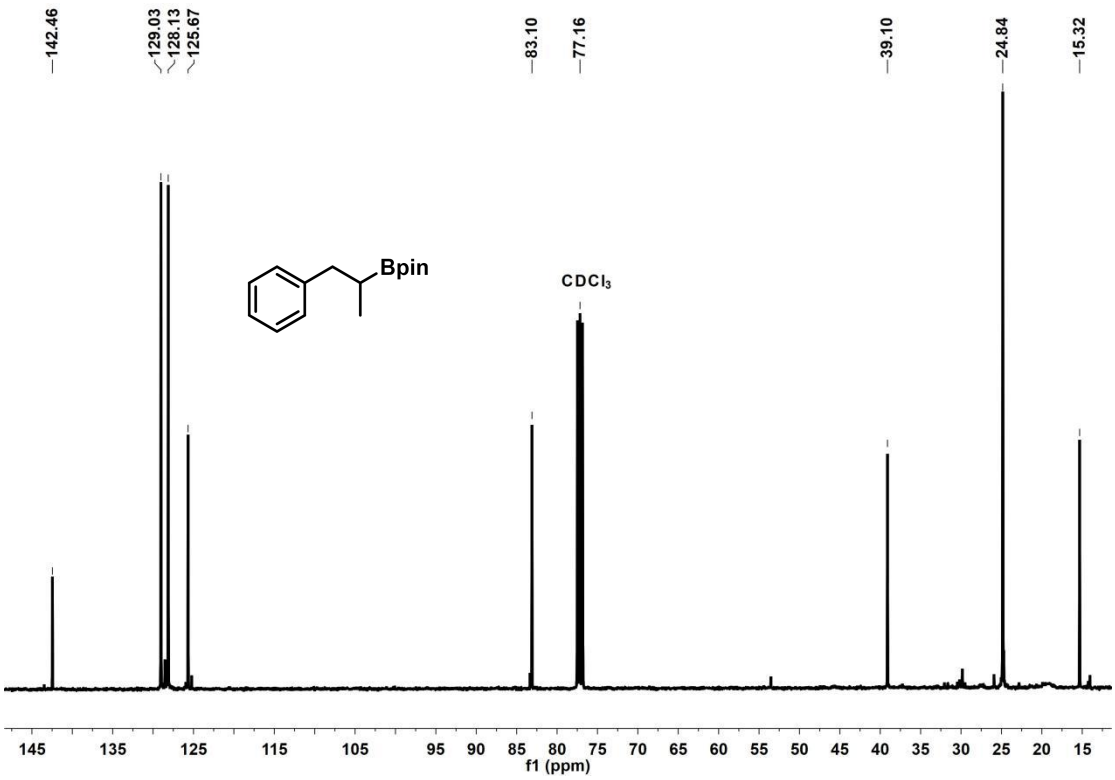


Figure S32. ^{13}C NMR spectrum of **3h** in $CDCl_3$.

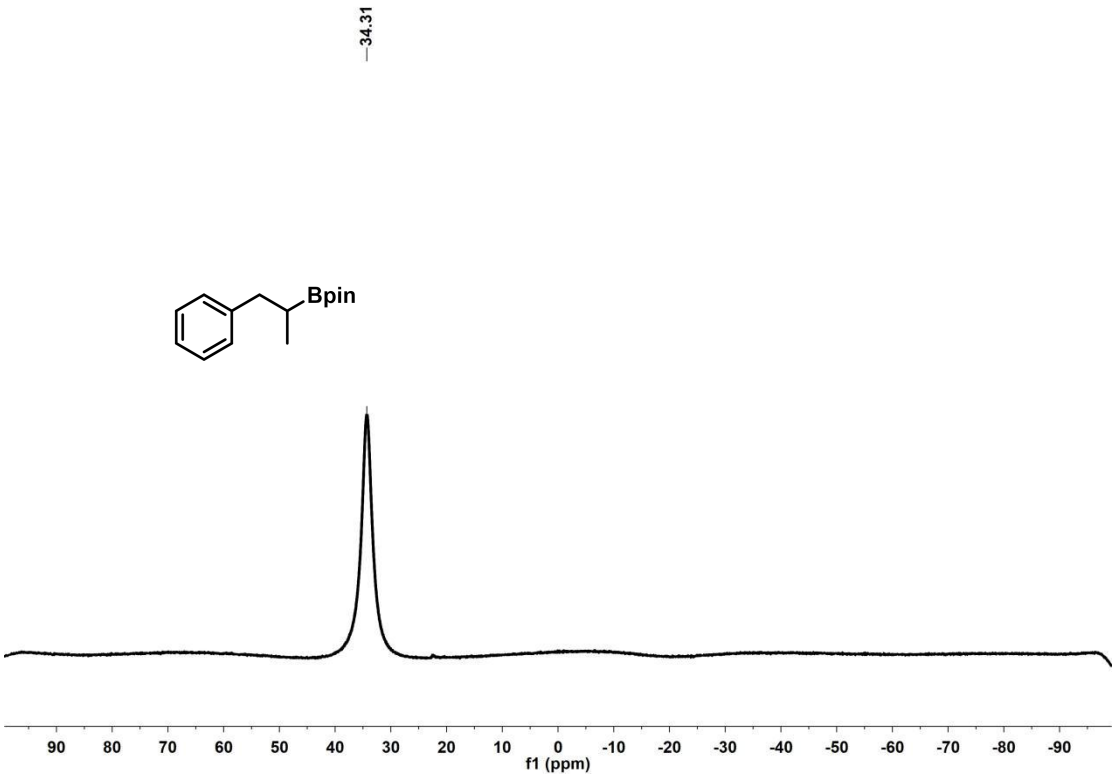


Figure S33. ^{11}B NMR spectrum of **3h** in $CDCl_3$.

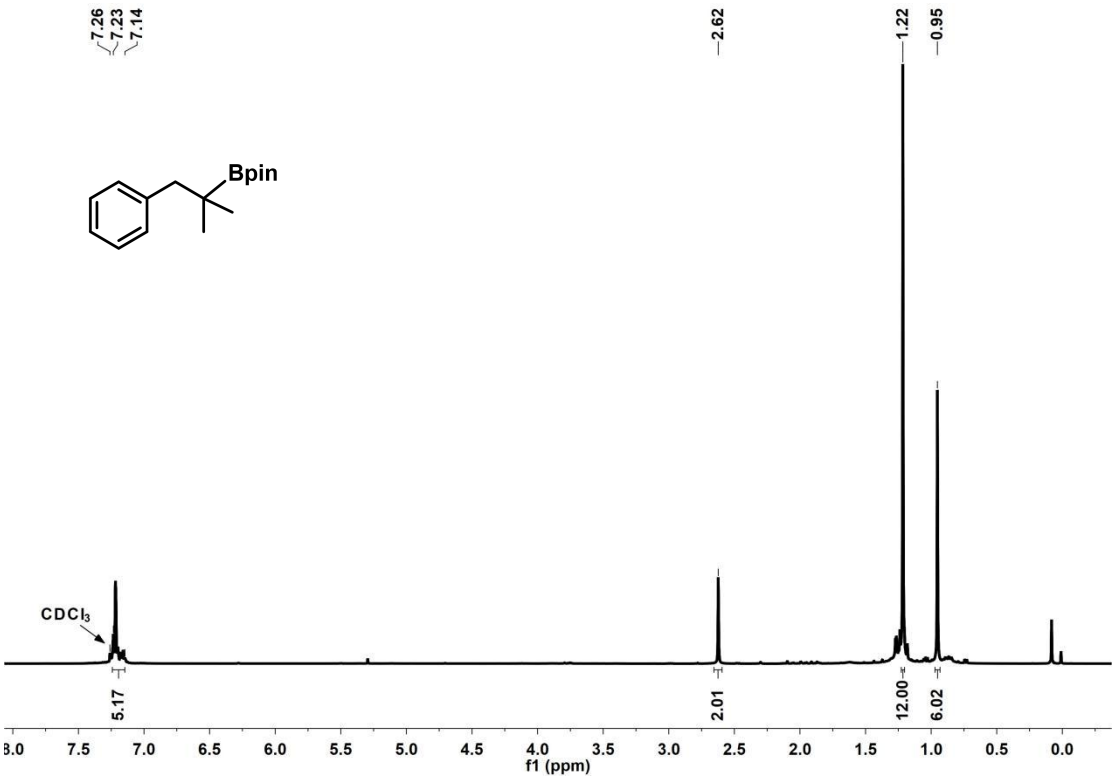


Figure S34. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

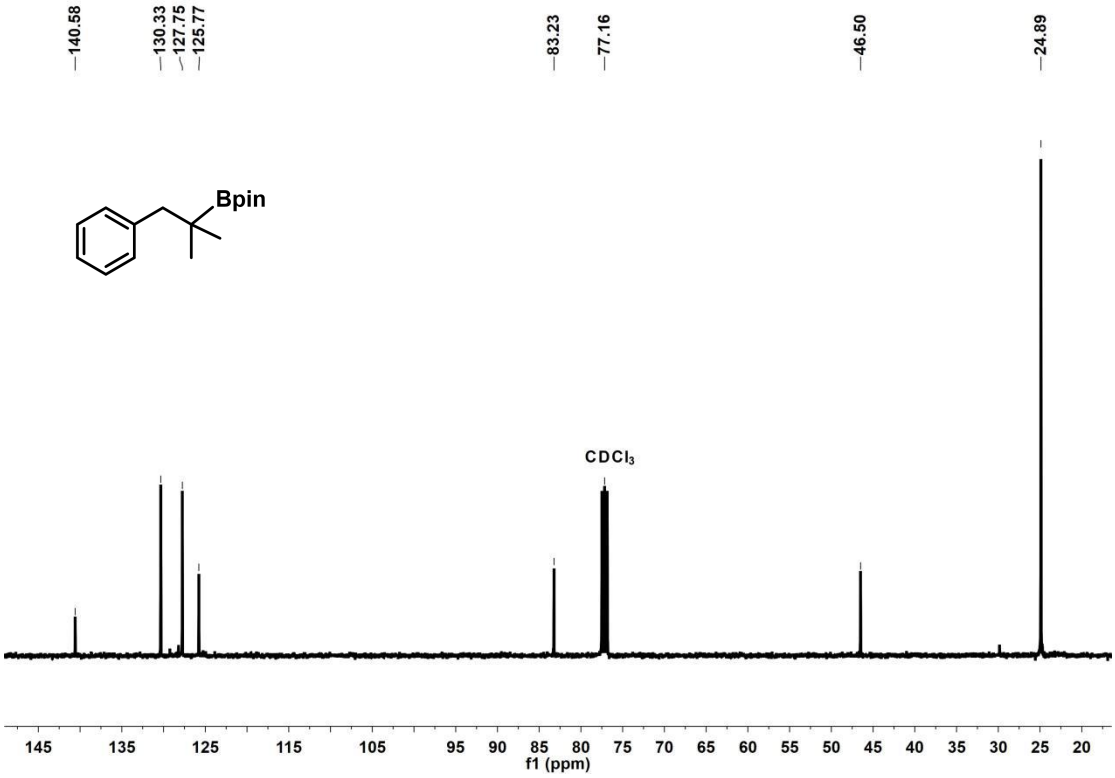


Figure S35. ^{13}C NMR spectrum of **3i** in $CDCl_3$.

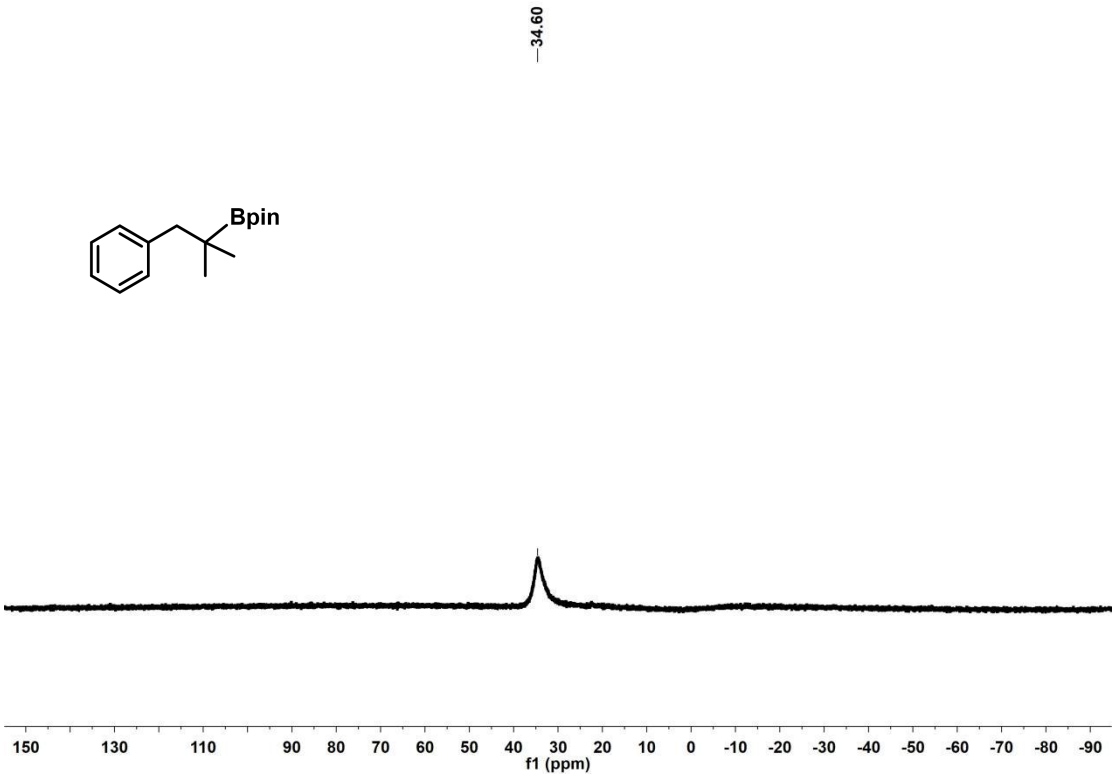


Figure S36. ^{11}B NMR spectrum of **3i** in $CDCl_3$.

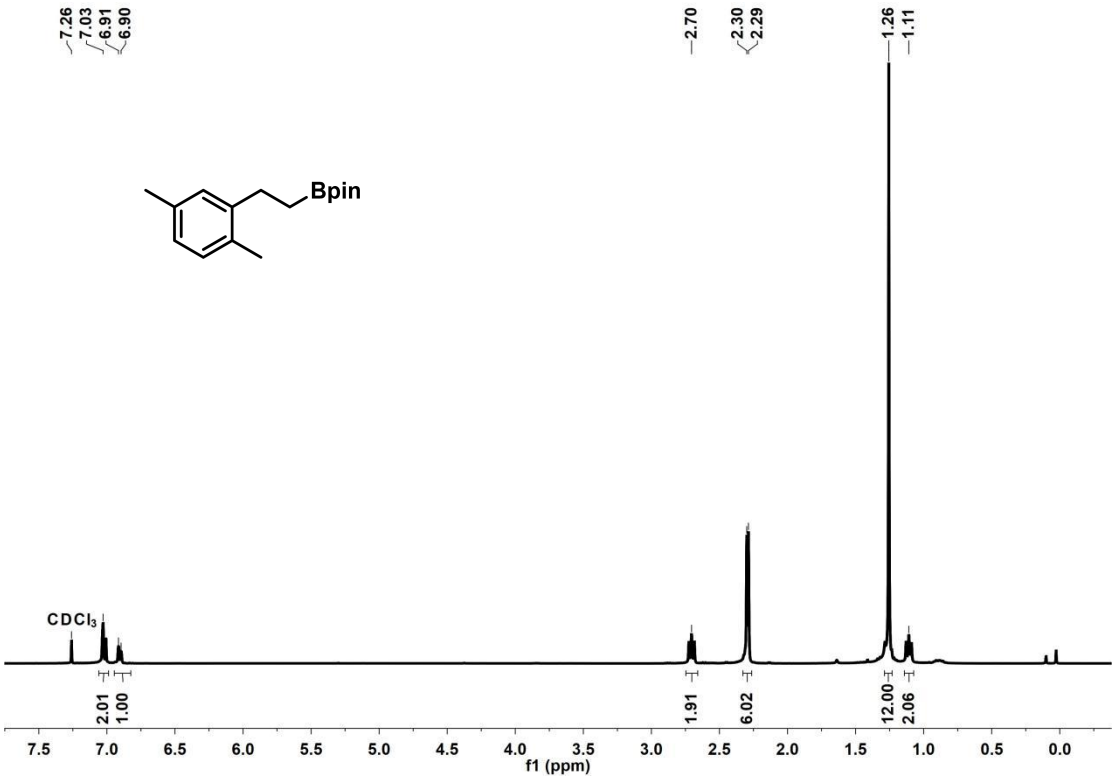


Figure S37. ^{1}H NMR spectrum of **3j** in $CDCl_3$.

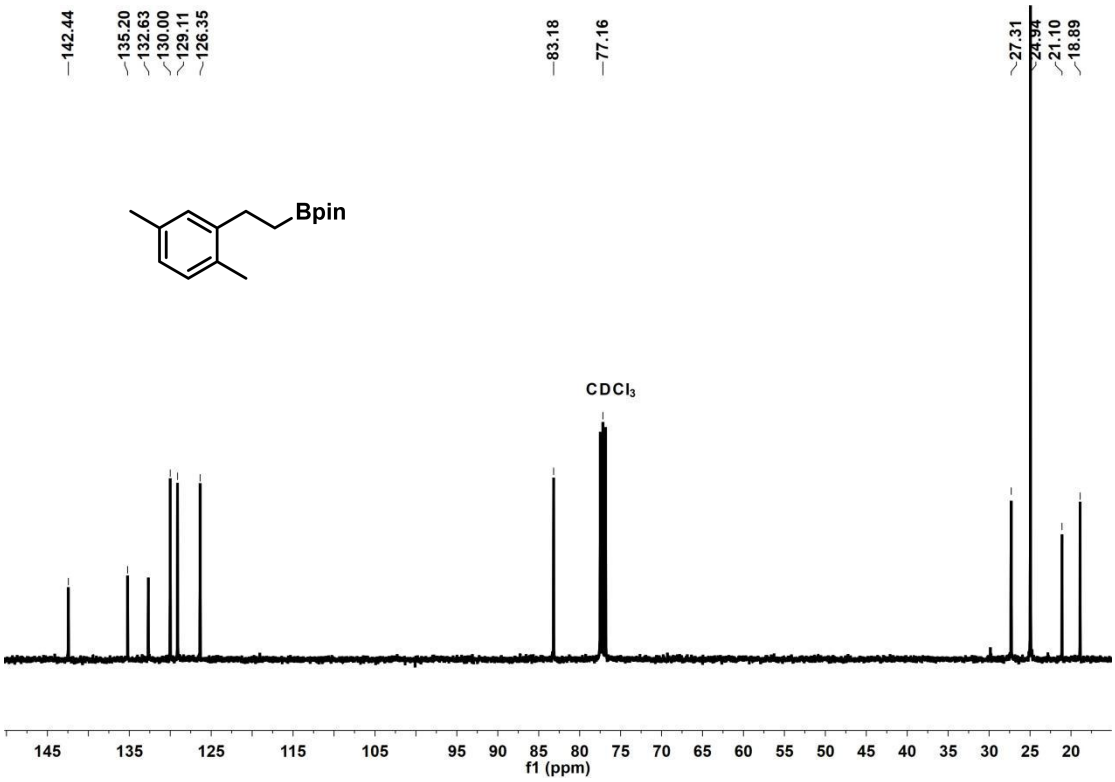


Figure S38. ^{13}C NMR spectrum of **3j** in $CDCl_3$.

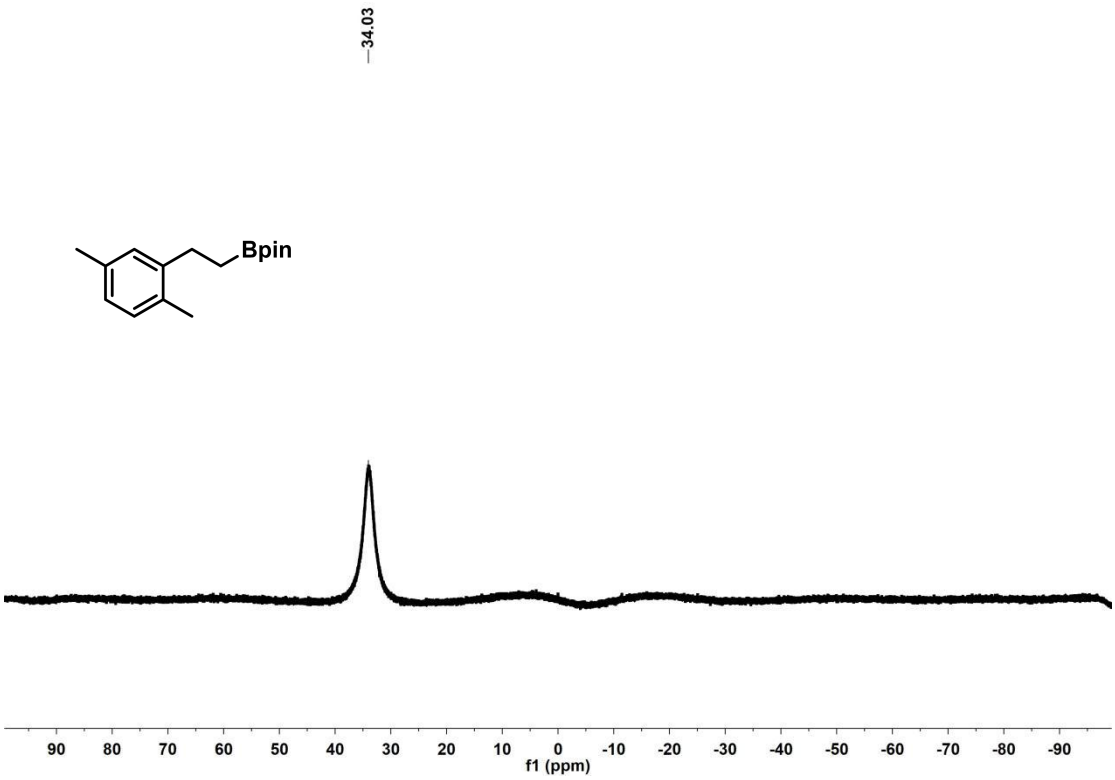


Figure S39. ^{11}B NMR spectrum of **3j** in $CDCl_3$.

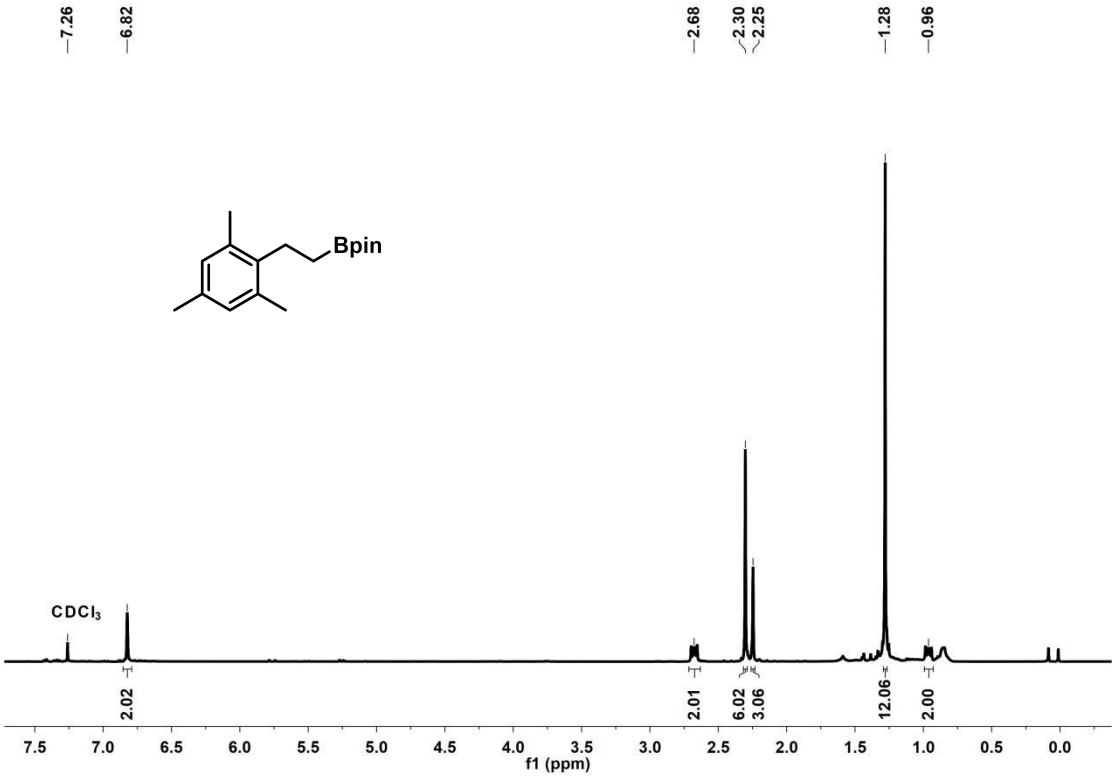


Figure S40. ^{1}H NMR spectrum of **3k** in $CDCl_3$.

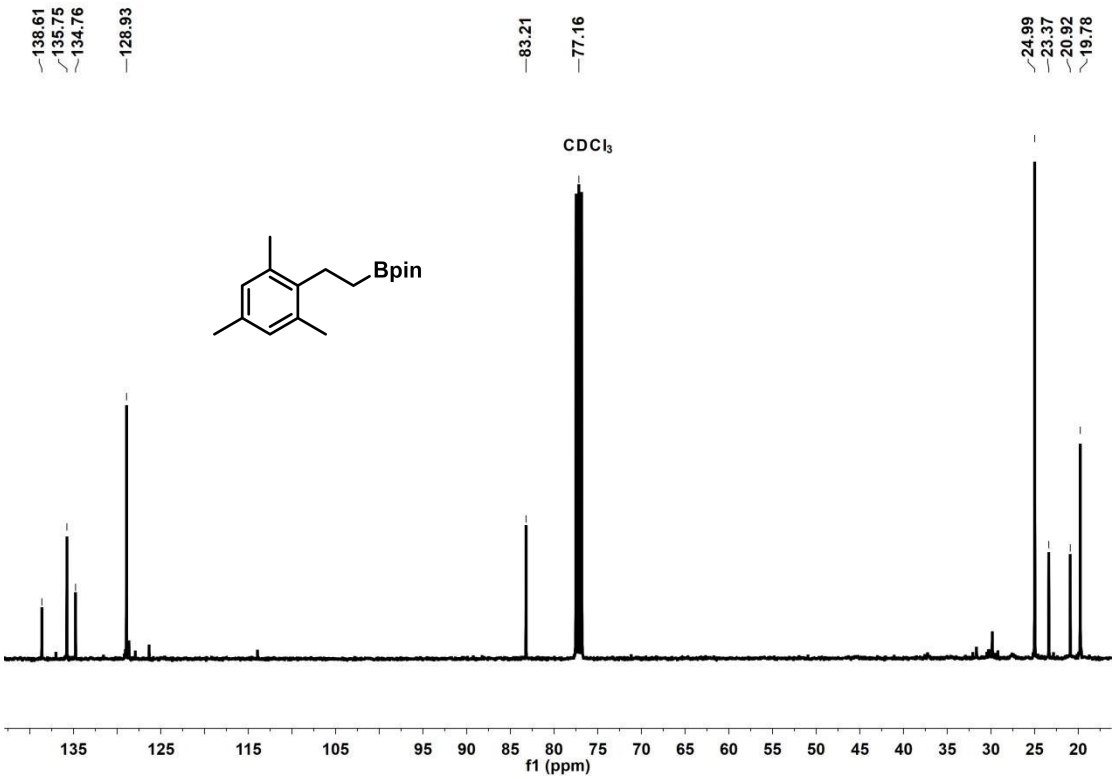


Figure S41. ^{13}C NMR spectrum of **3k** in $CDCl_3$.

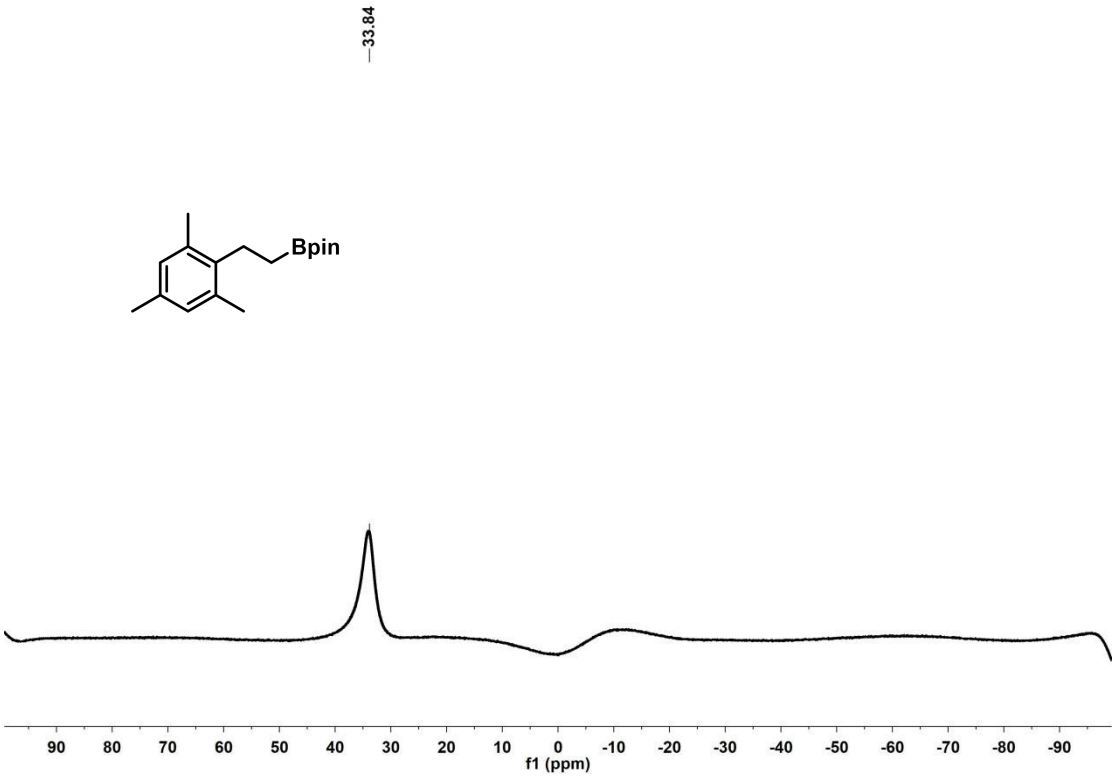


Figure S42. ^{11}B NMR spectrum of **3k** in $CDCl_3$.

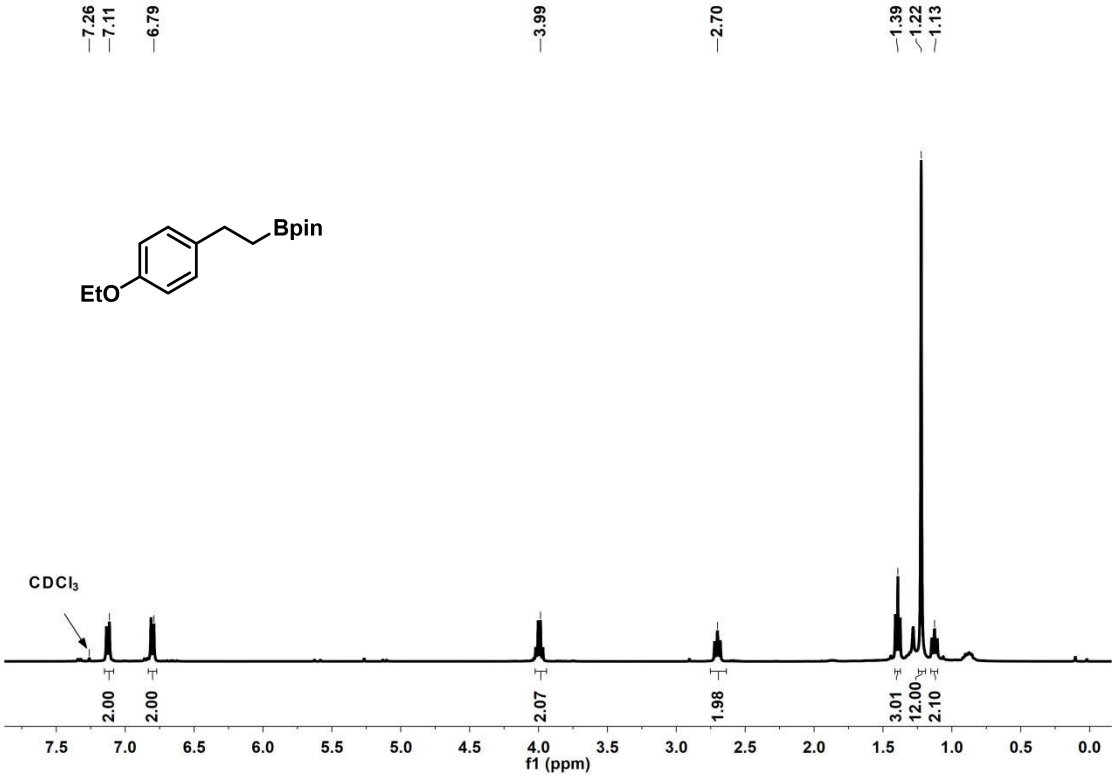


Figure S43. ^{1}H NMR spectrum of **3l** in $CDCl_3$.

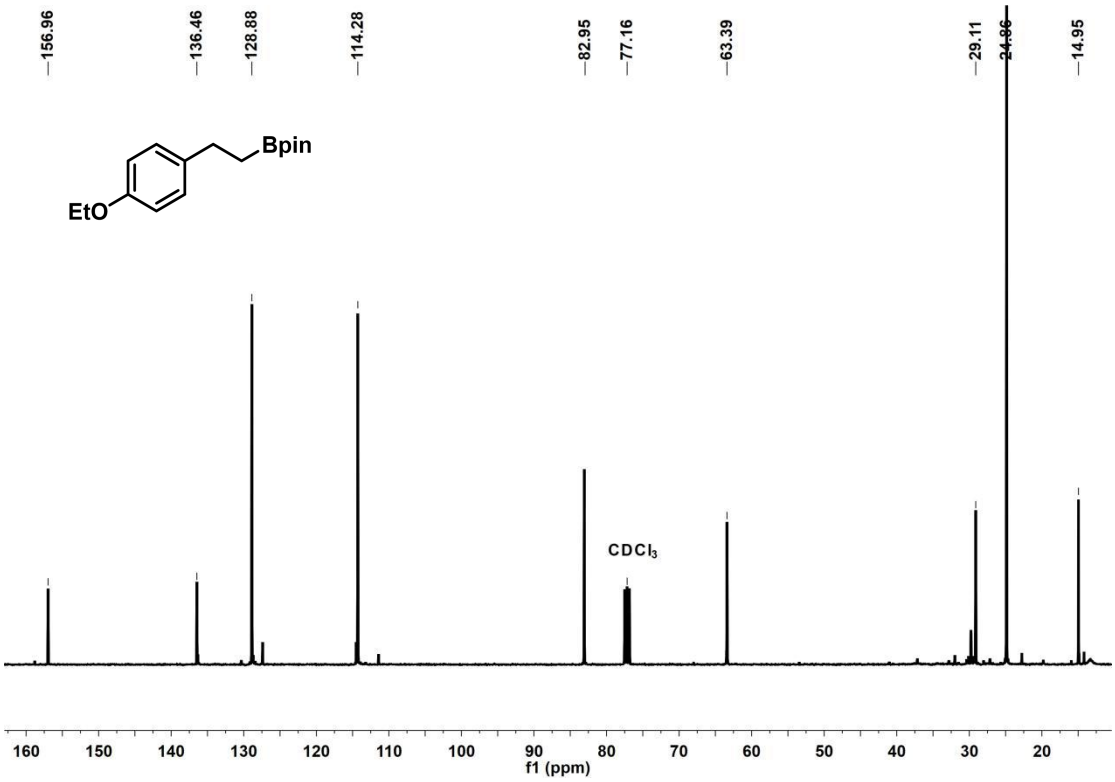


Figure S44. ^{13}C NMR spectrum of **3l** in $CDCl_3$.

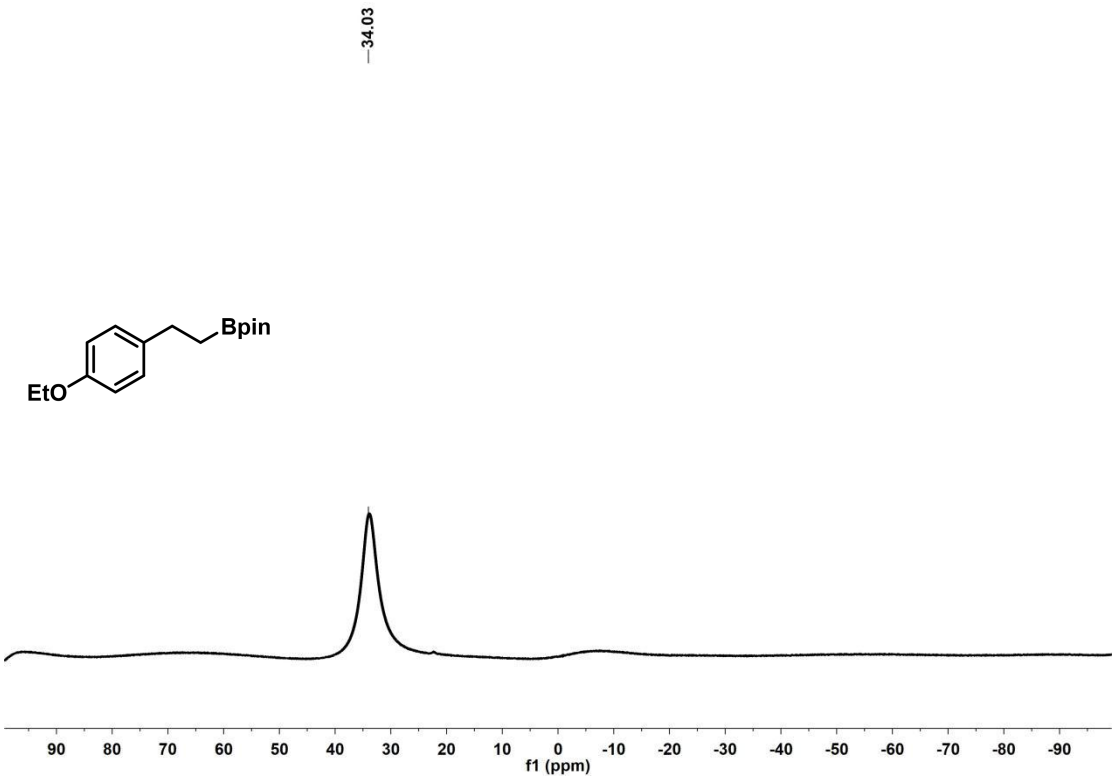


Figure S45. ^{11}B NMR spectrum of **3l** in $CDCl_3$.

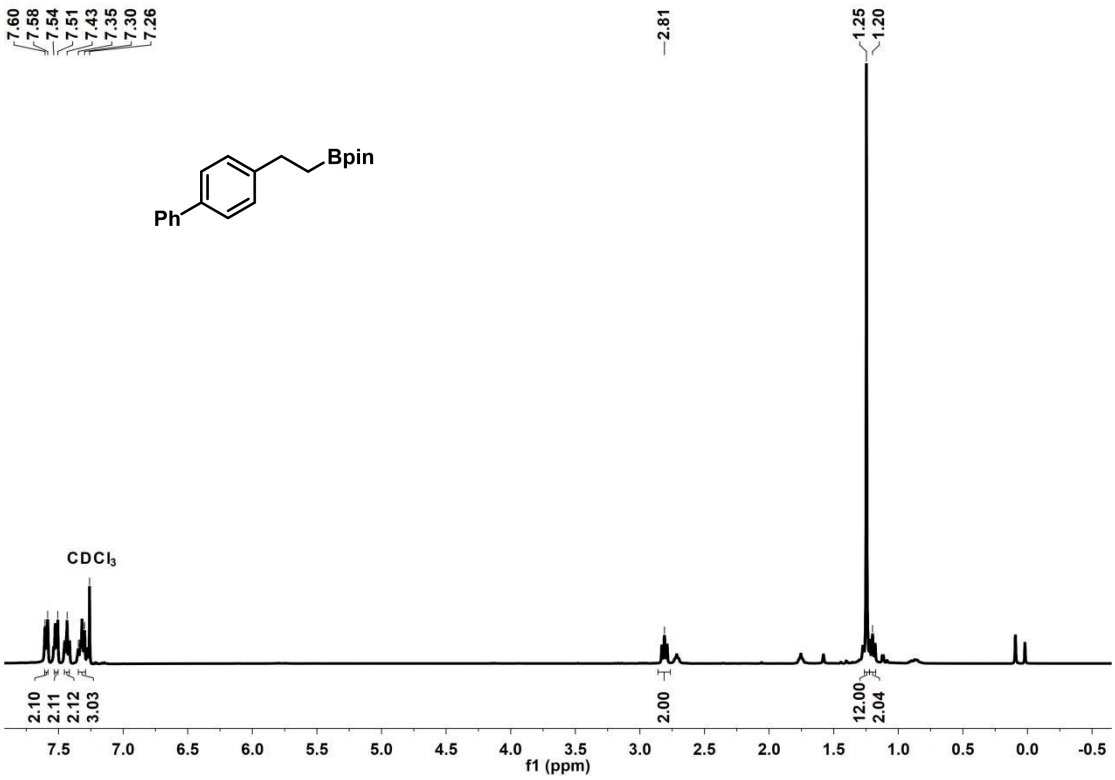


Figure S46. ^{1}H NMR spectrum of **3m** in $CDCl_3$.

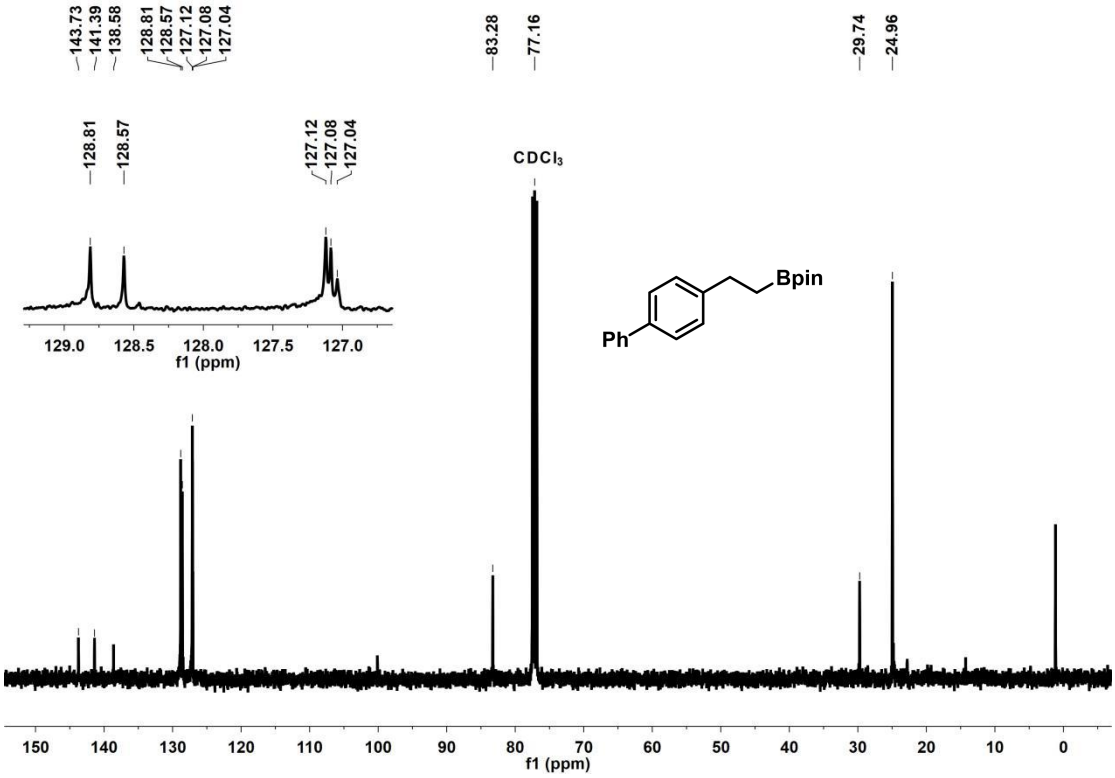


Figure S47. ^{13}C NMR spectrum of **3m** in $CDCl_3$.

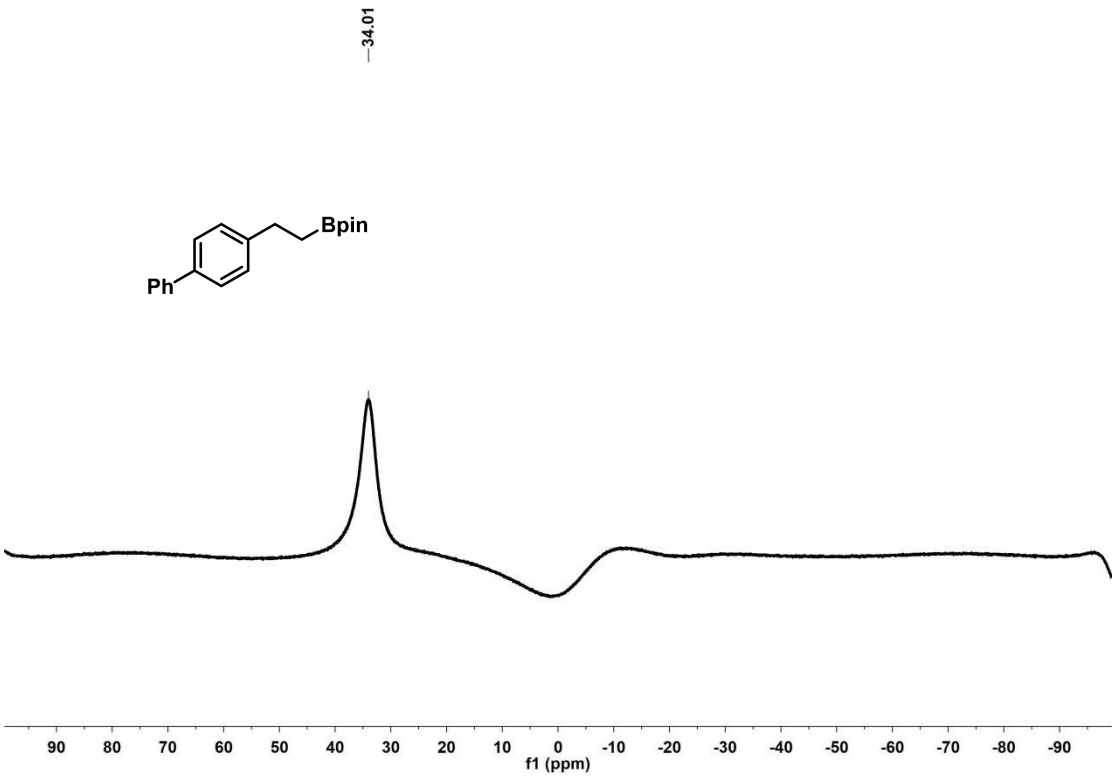


Figure S48. ^{11}B NMR spectrum of **3m** in $CDCl_3$.

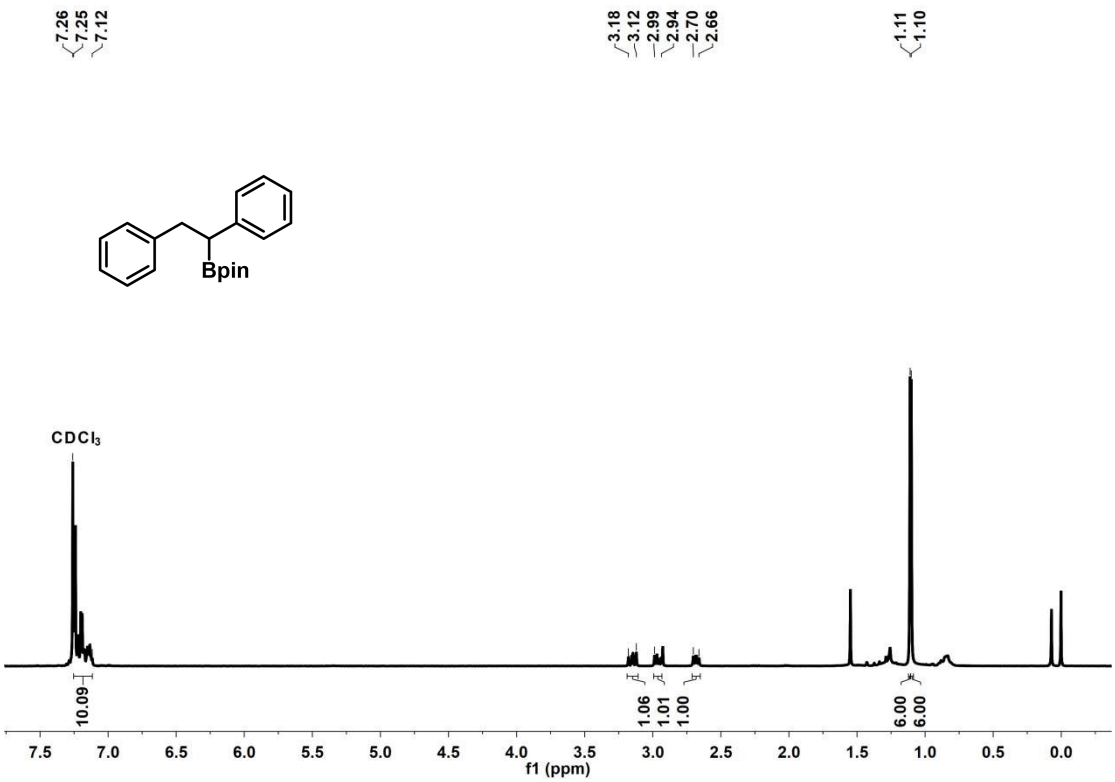


Figure S49. ^{1}H NMR spectrum of **3n** in $CDCl_3$.

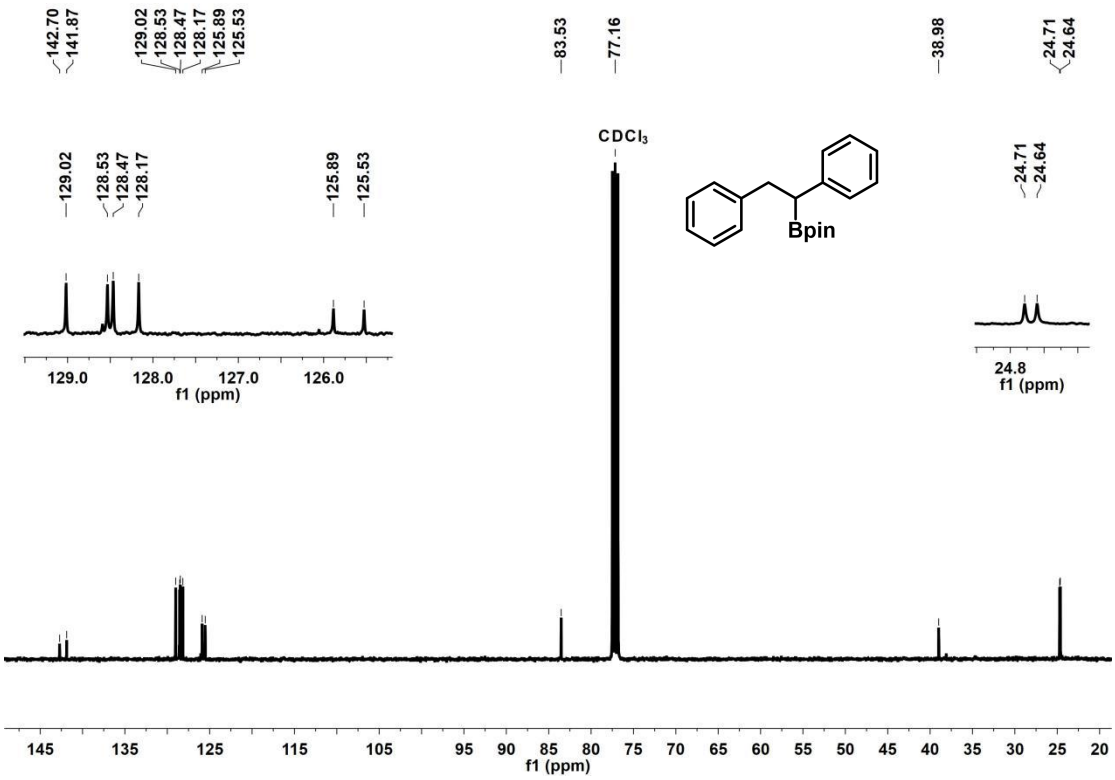


Figure S50. ^{13}C NMR spectrum of **3n** in $CDCl_3$.

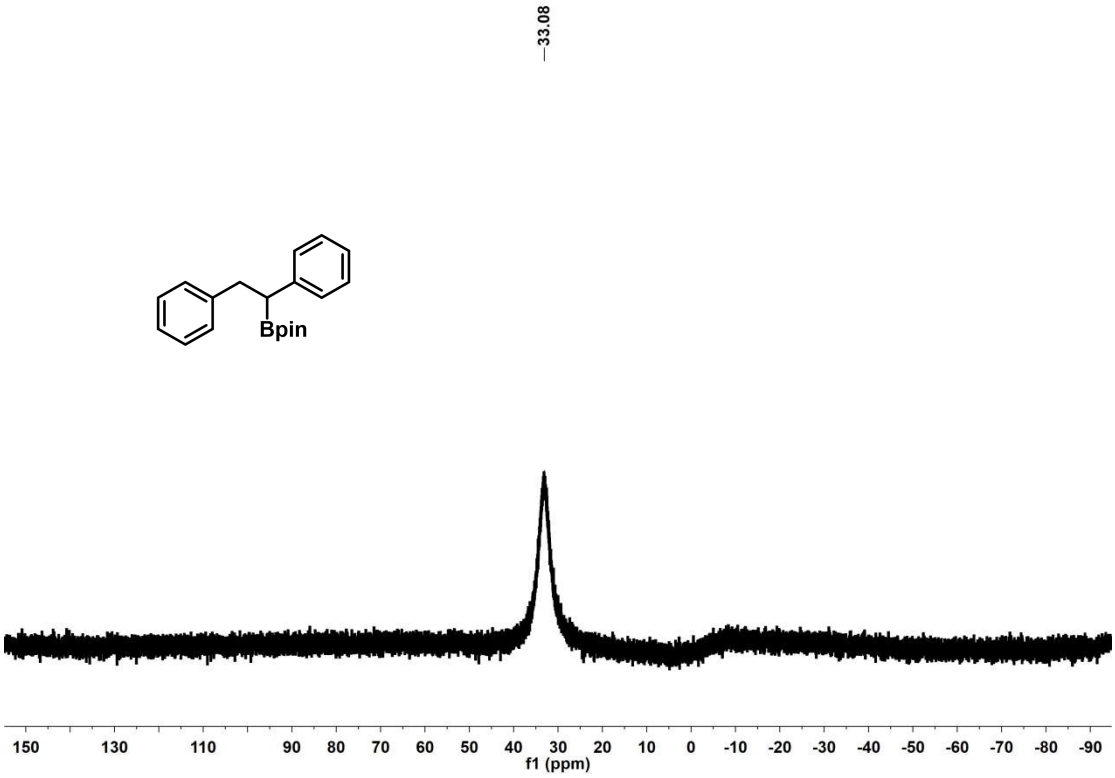


Figure S51. ^{11}B NMR spectrum of **3n** in $CDCl_3$.

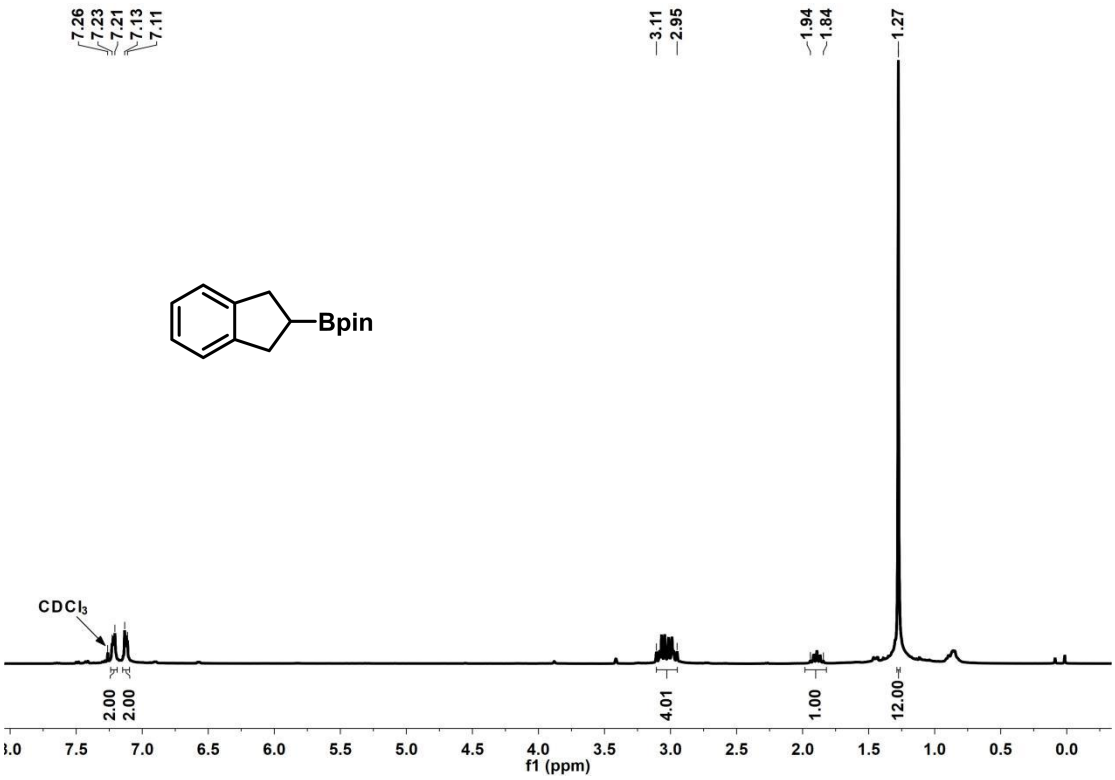


Figure S52. ^{1}H NMR spectrum of **3o** in $CDCl_3$.

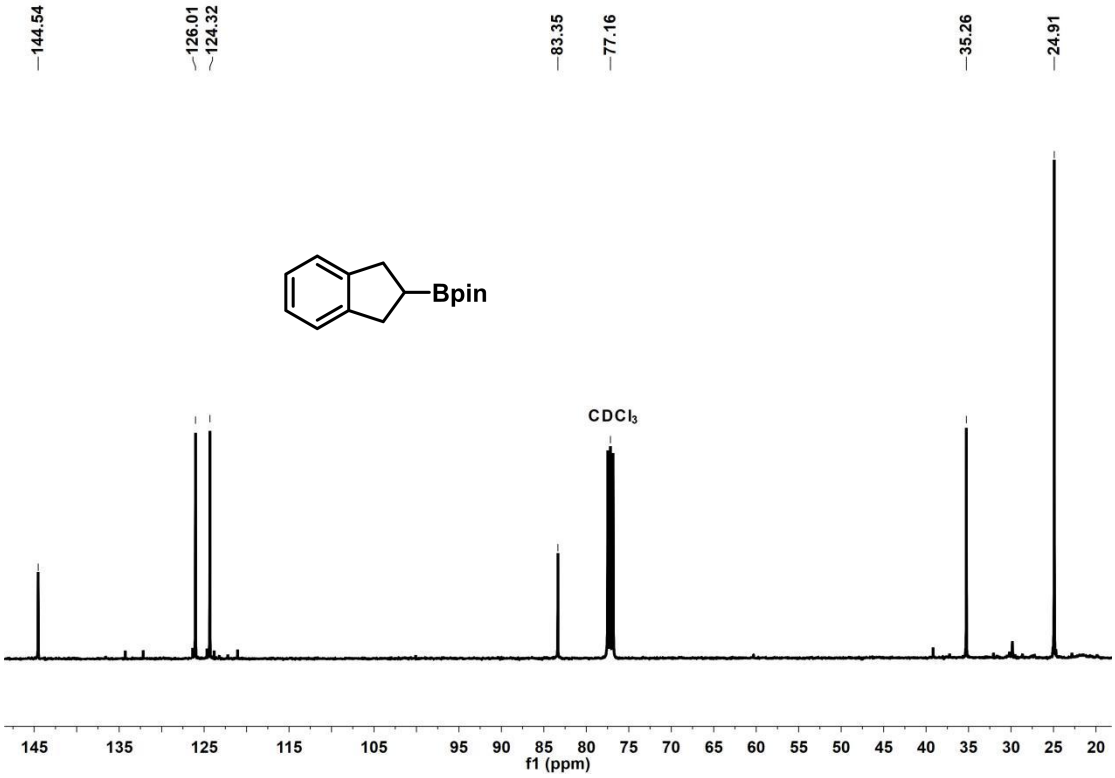


Figure S53. ^{13}C NMR spectrum of **3o** in $CDCl_3$.

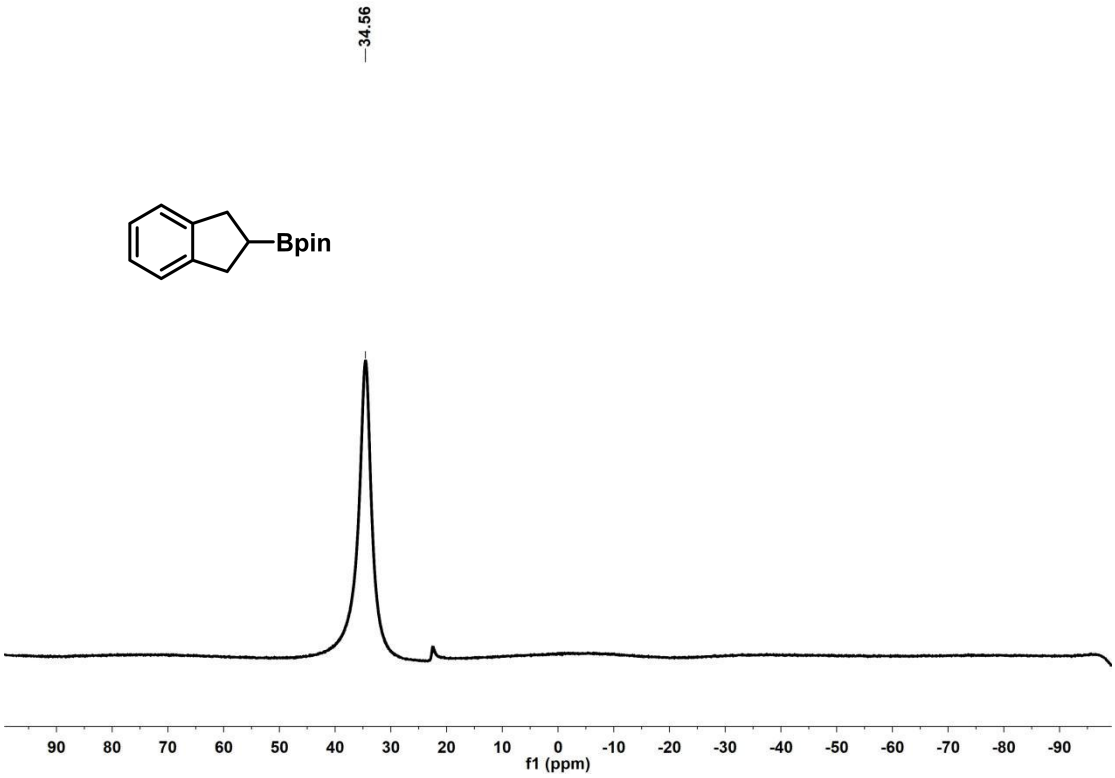


Figure S54. ^{11}B NMR spectrum of **3o** in $CDCl_3$.

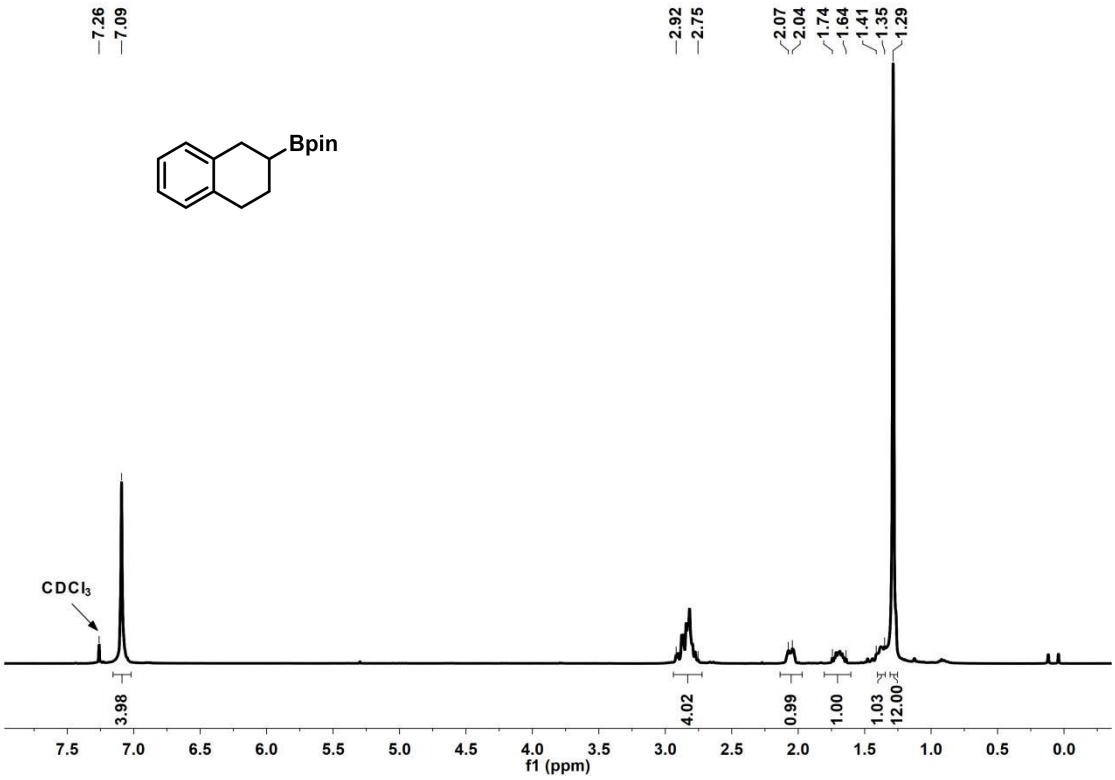


Figure S55. ^{1}H NMR spectrum of **3p** in $CDCl_3$.

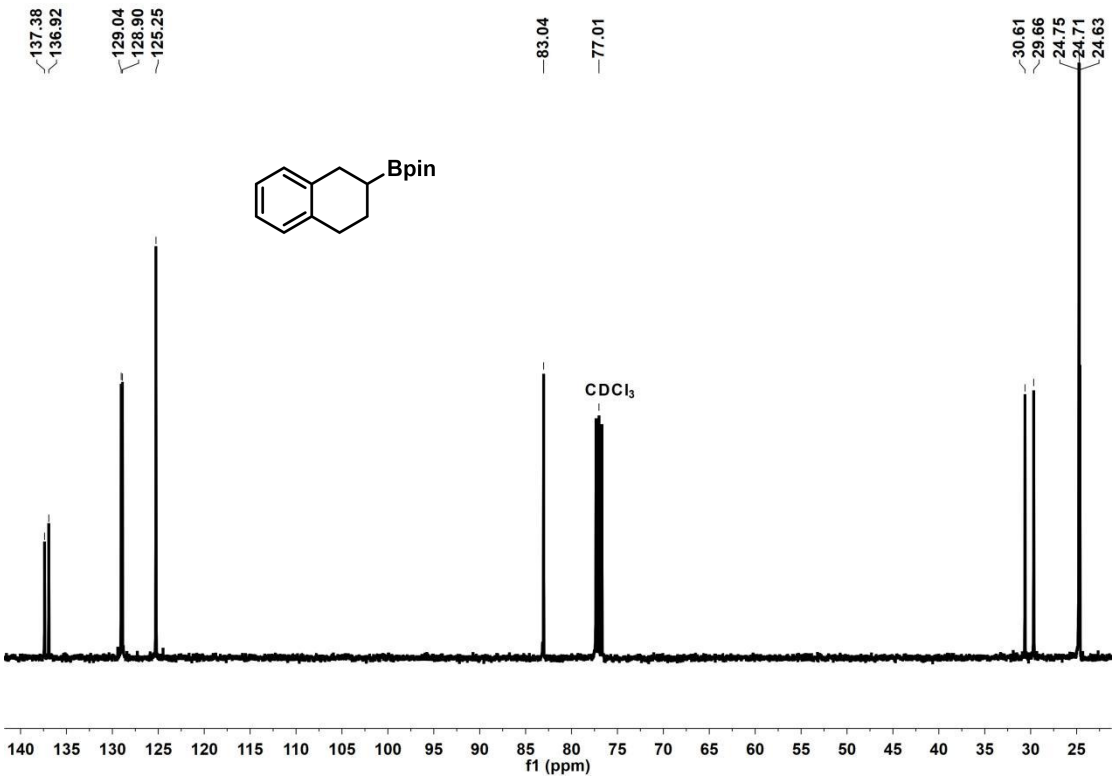


Figure S56. ^{13}C NMR spectrum of **3p** in $CDCl_3$.

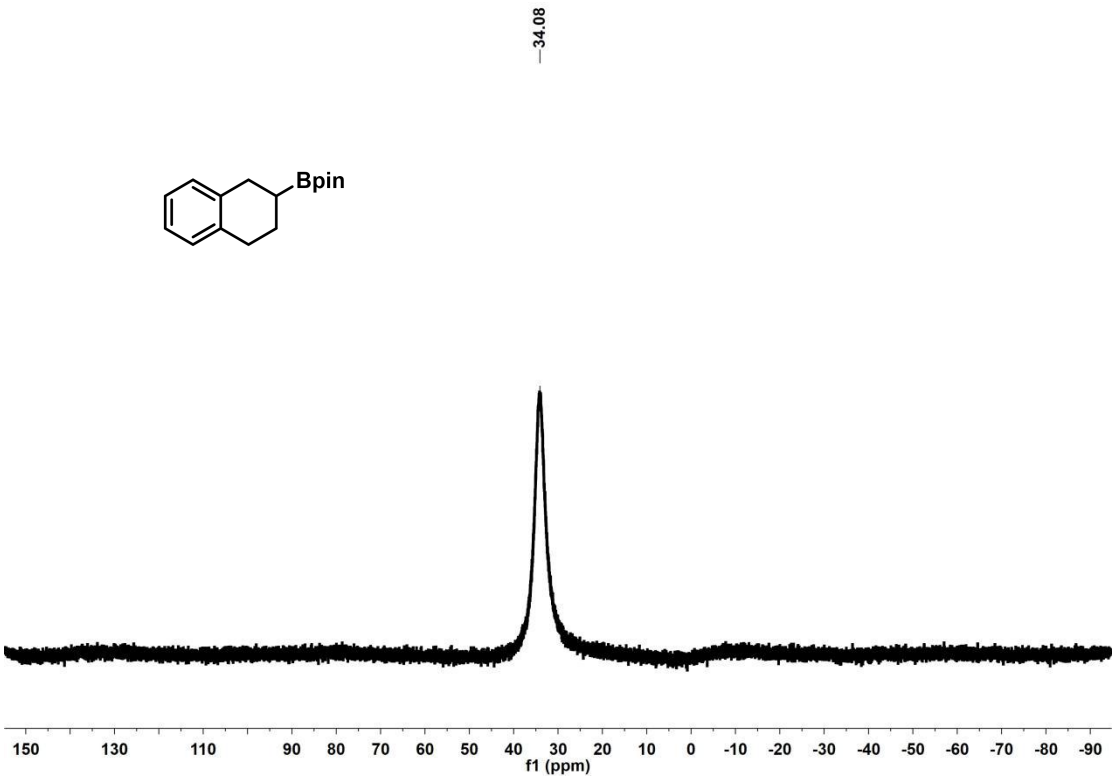


Figure S57. ^{11}B NMR spectrum of **3p** in $CDCl_3$.

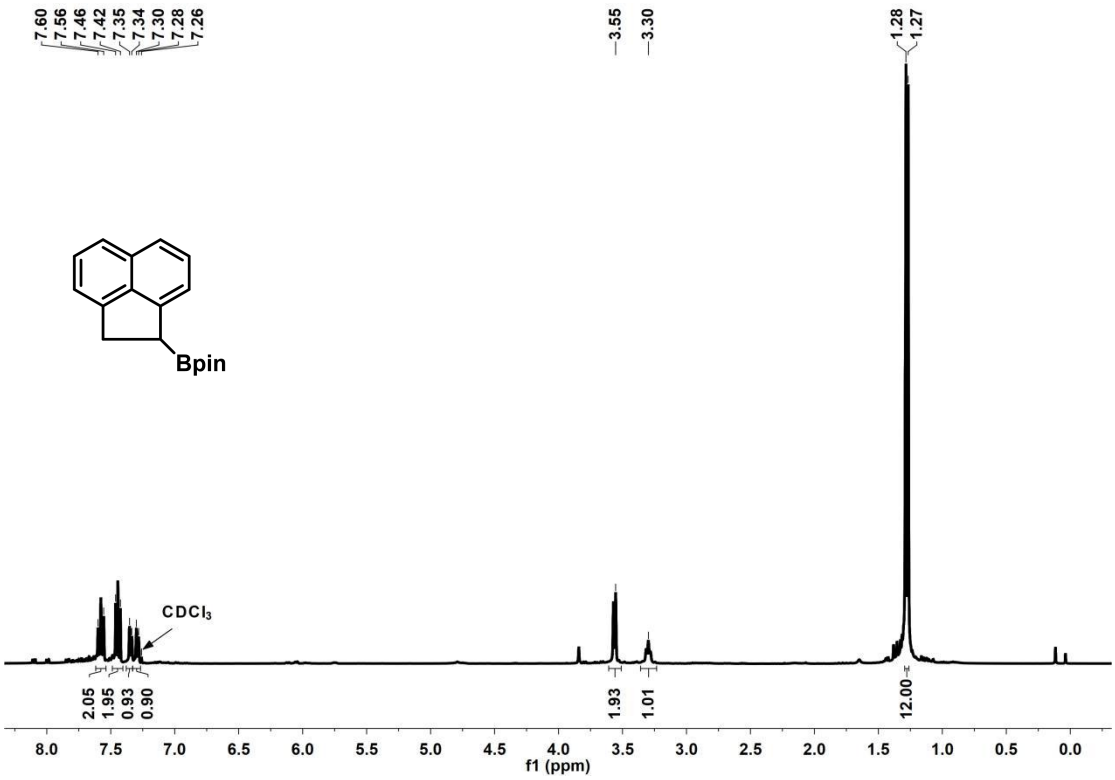


Figure S58. ^{1}H NMR spectrum of **3q** in $CDCl_3$.

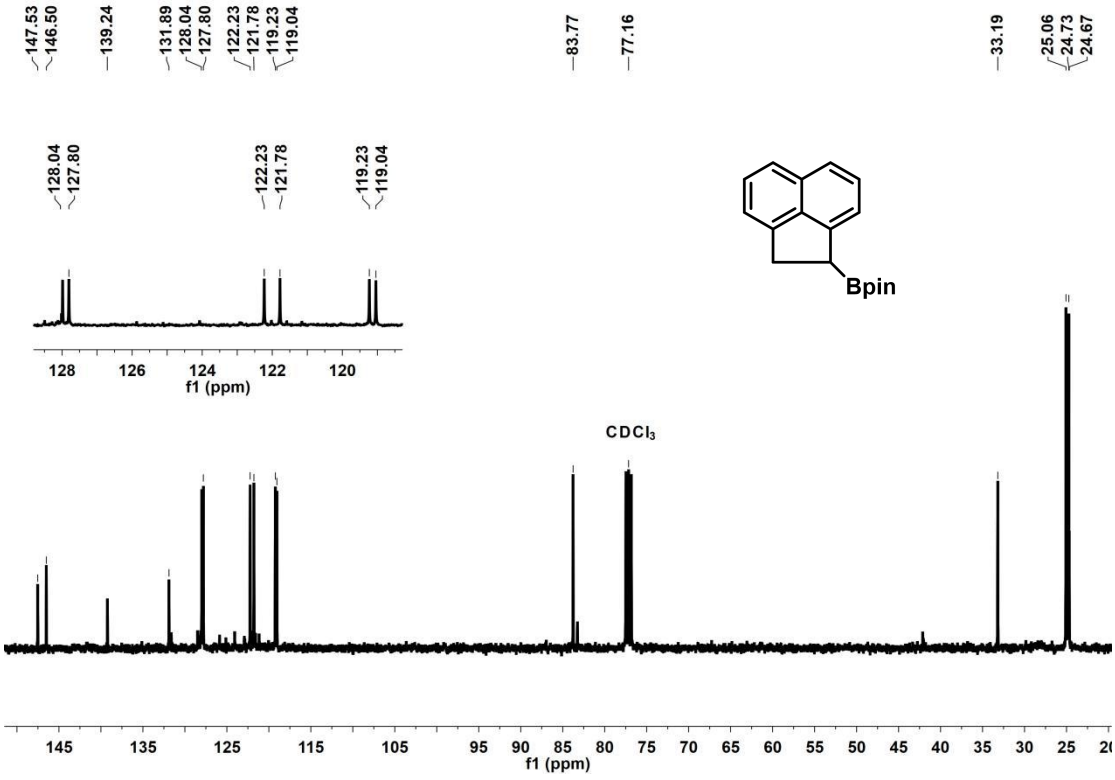


Figure S59. ^{13}C NMR spectrum of **3q** in $CDCl_3$.

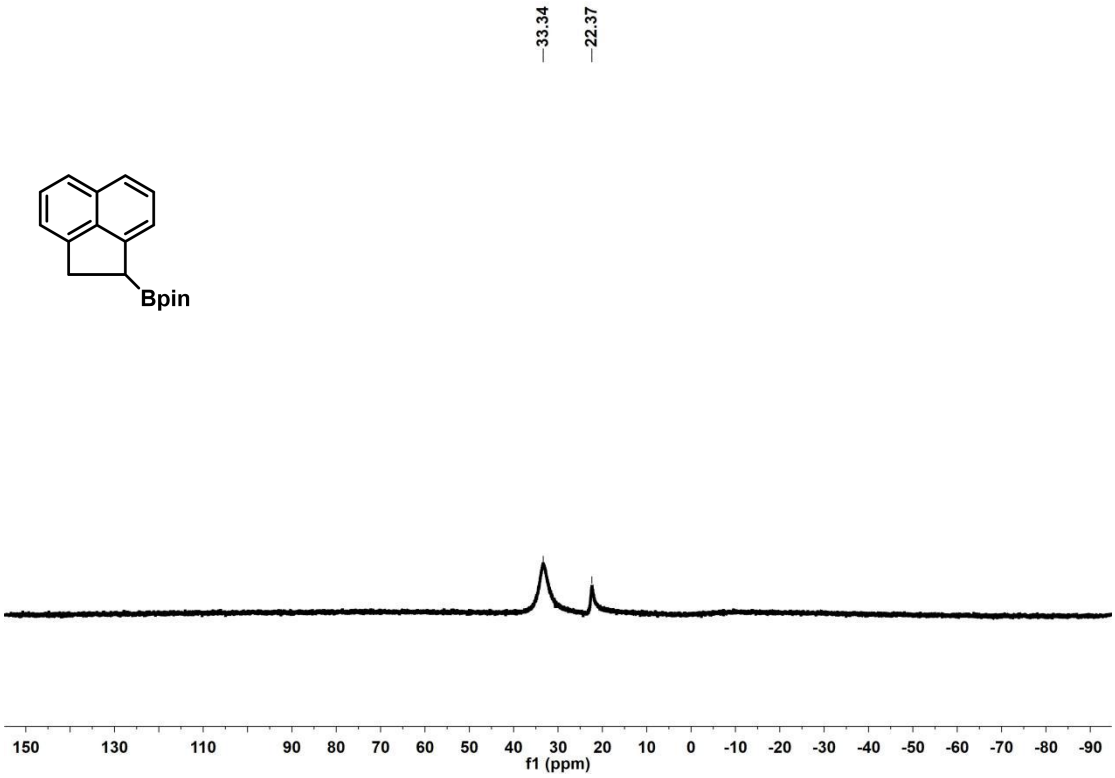


Figure S60. ^{11}B NMR spectrum of **3q** in $CDCl_3$.

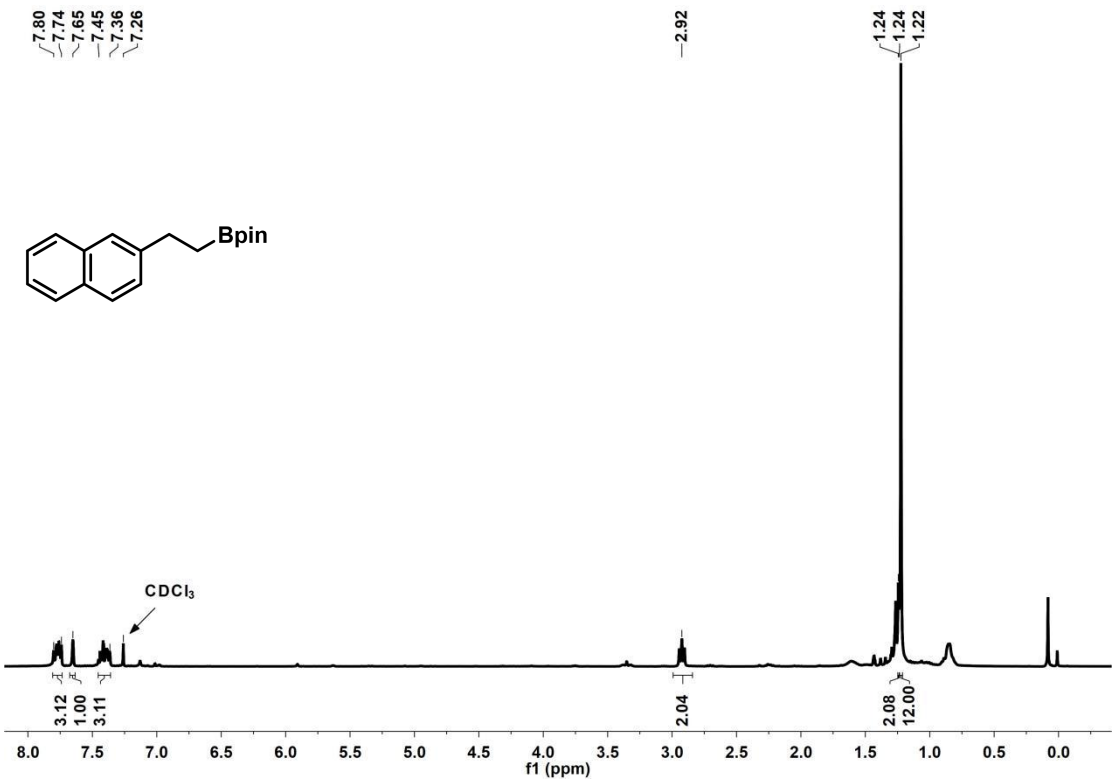


Figure S61. ^{1}H NMR spectrum of **3r** in $CDCl_3$.

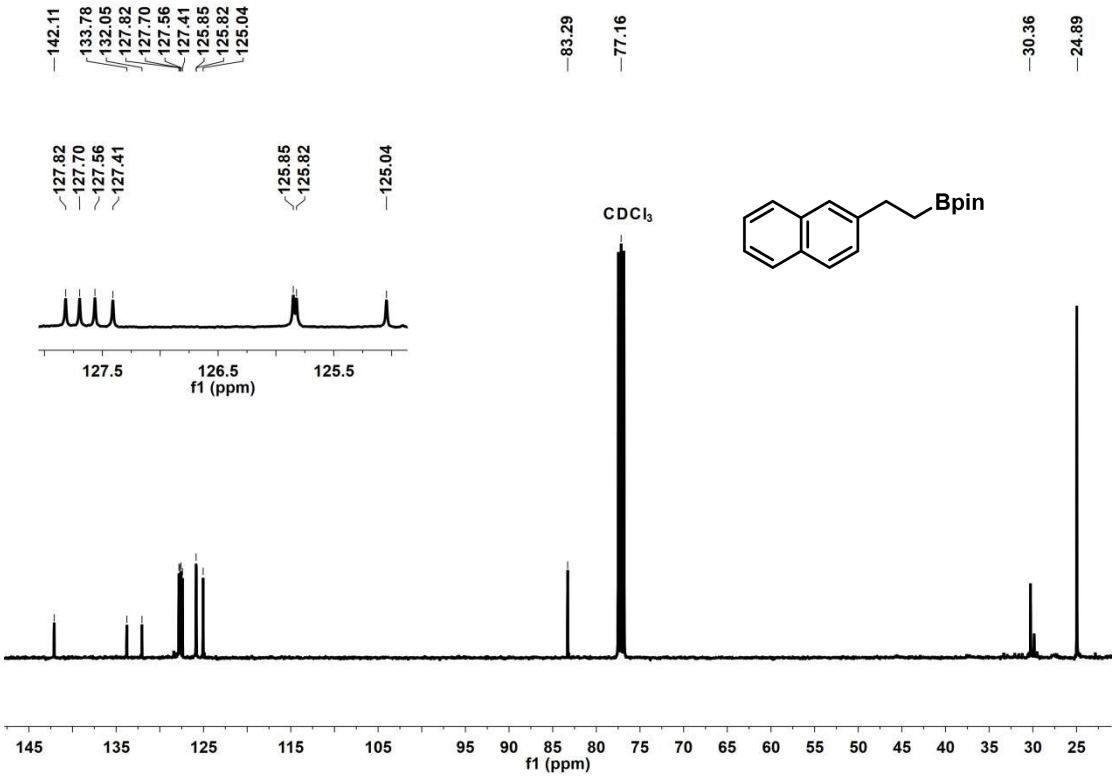


Figure S62. ^{13}C NMR spectrum of **3r** in $CDCl_3$.

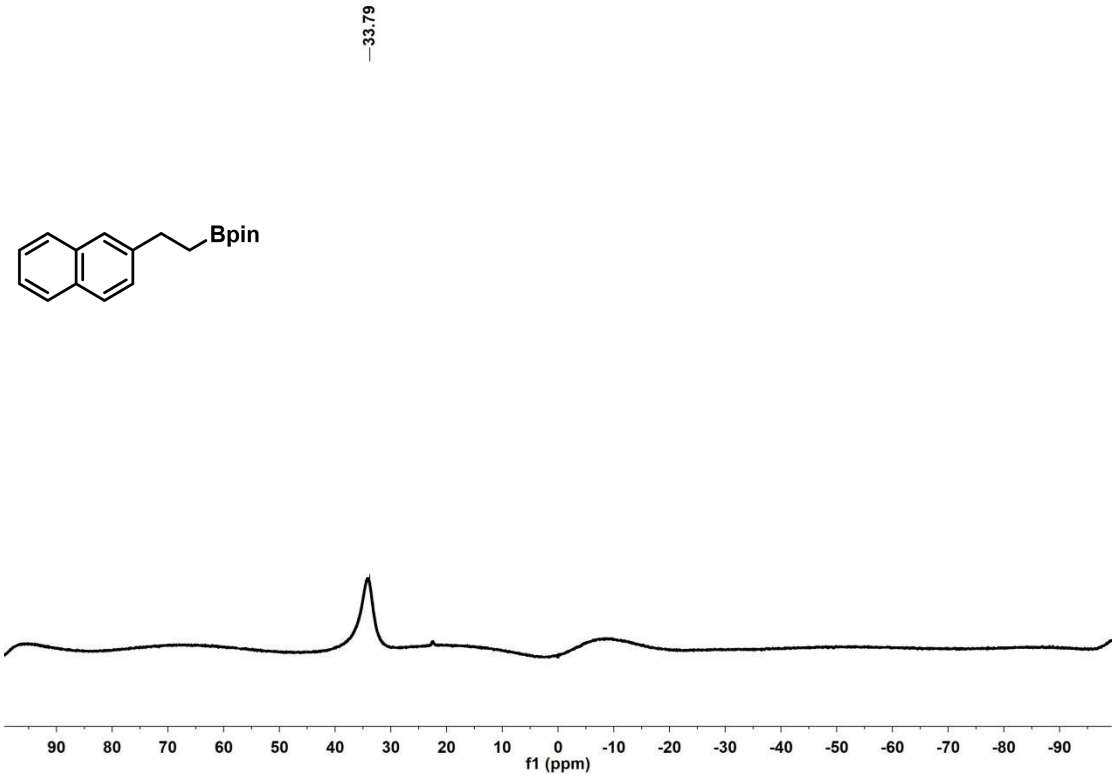


Figure S63. ^{11}B NMR spectrum of **3r** in $CDCl_3$.

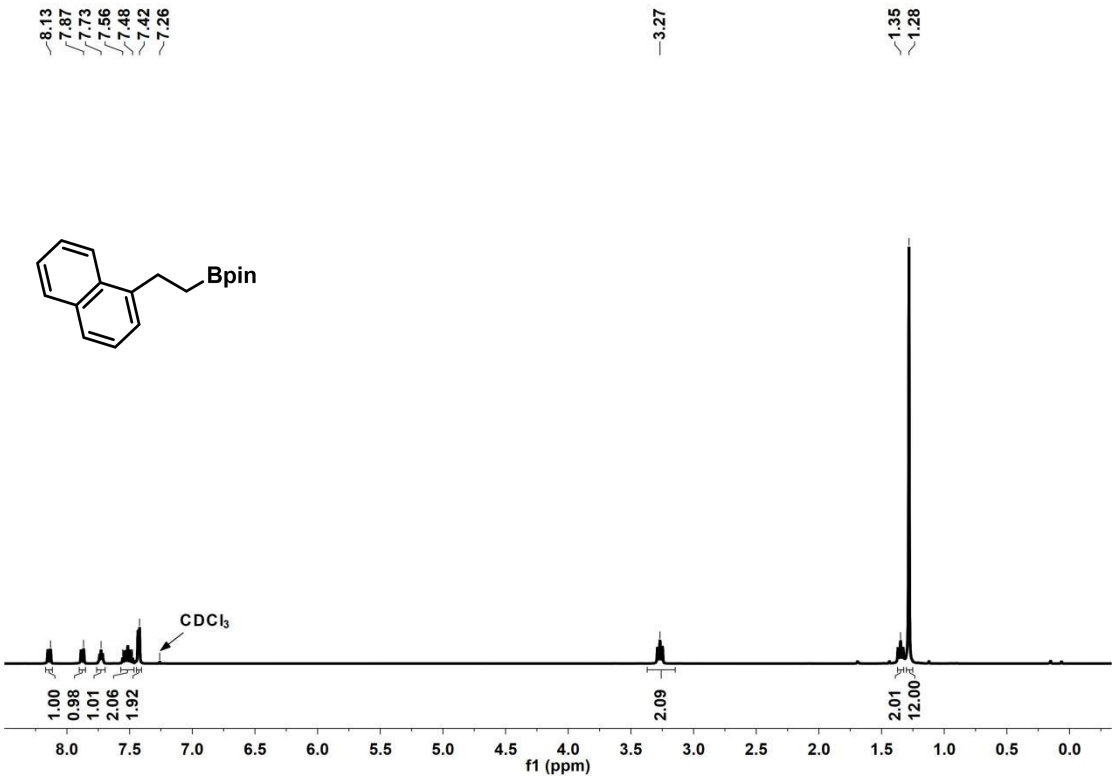


Figure S64. ^{1}H NMR spectrum of **3s** in $CDCl_3$.

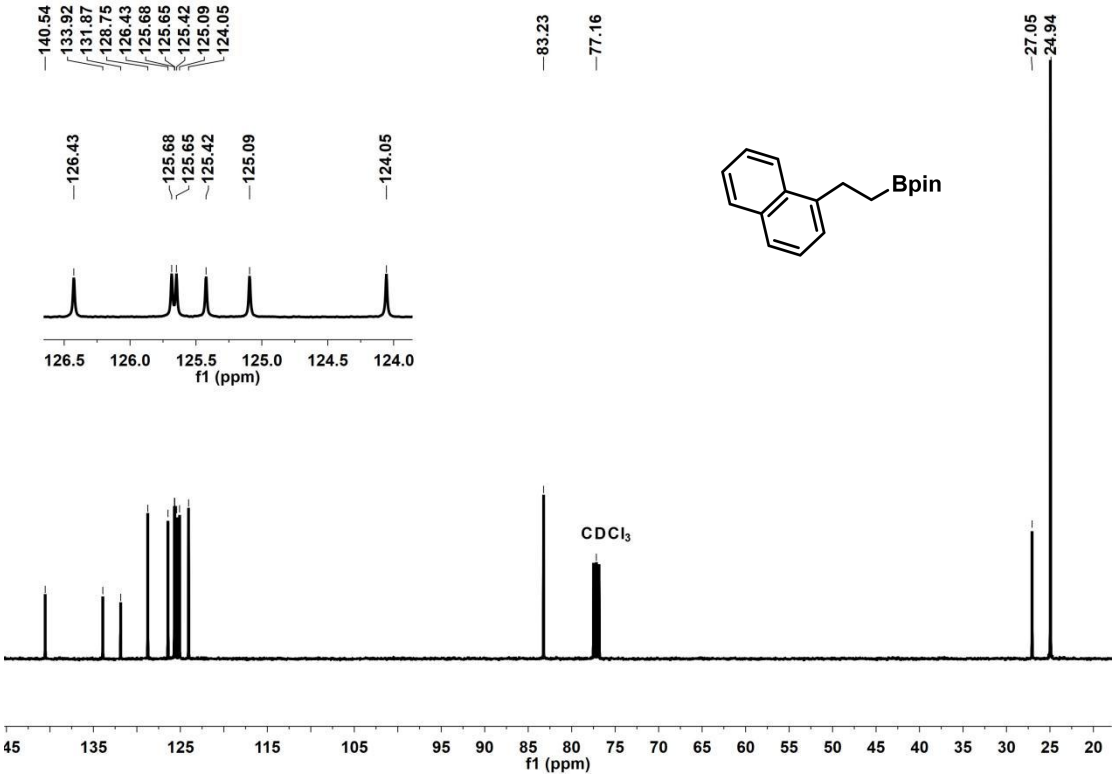


Figure S65. ^{13}C NMR spectrum of **3s** in $CDCl_3$.

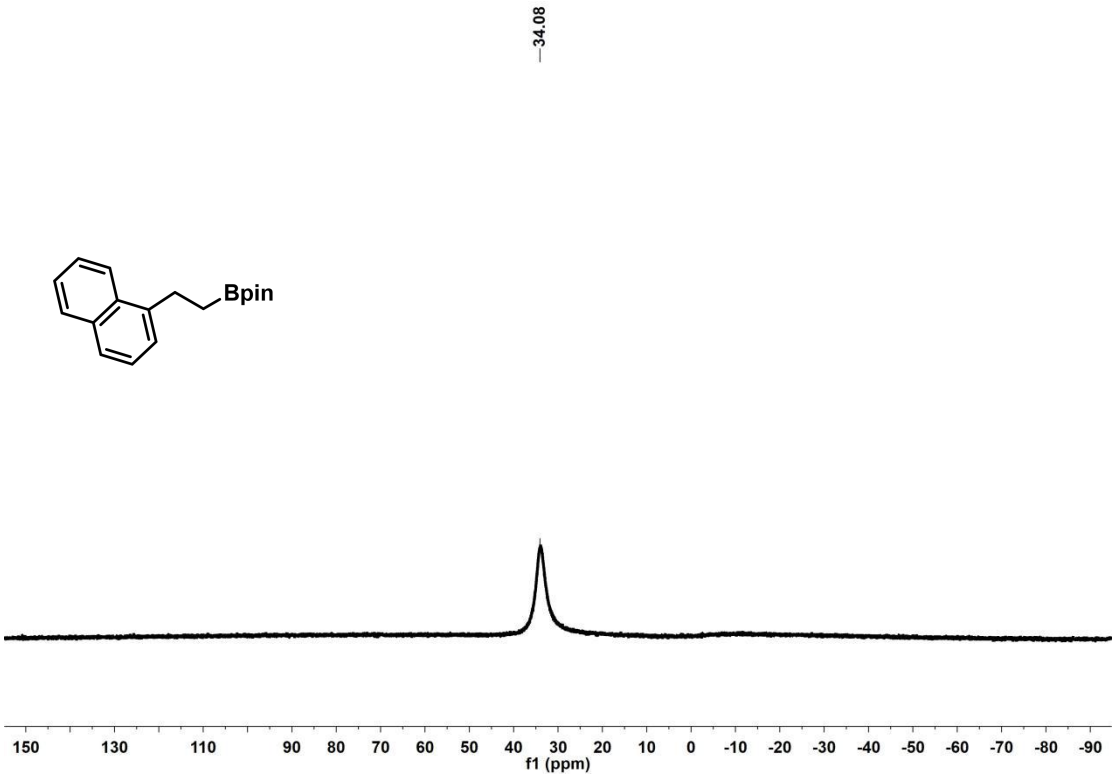


Figure S66. ^{11}B NMR spectrum of **3s** in $CDCl_3$.

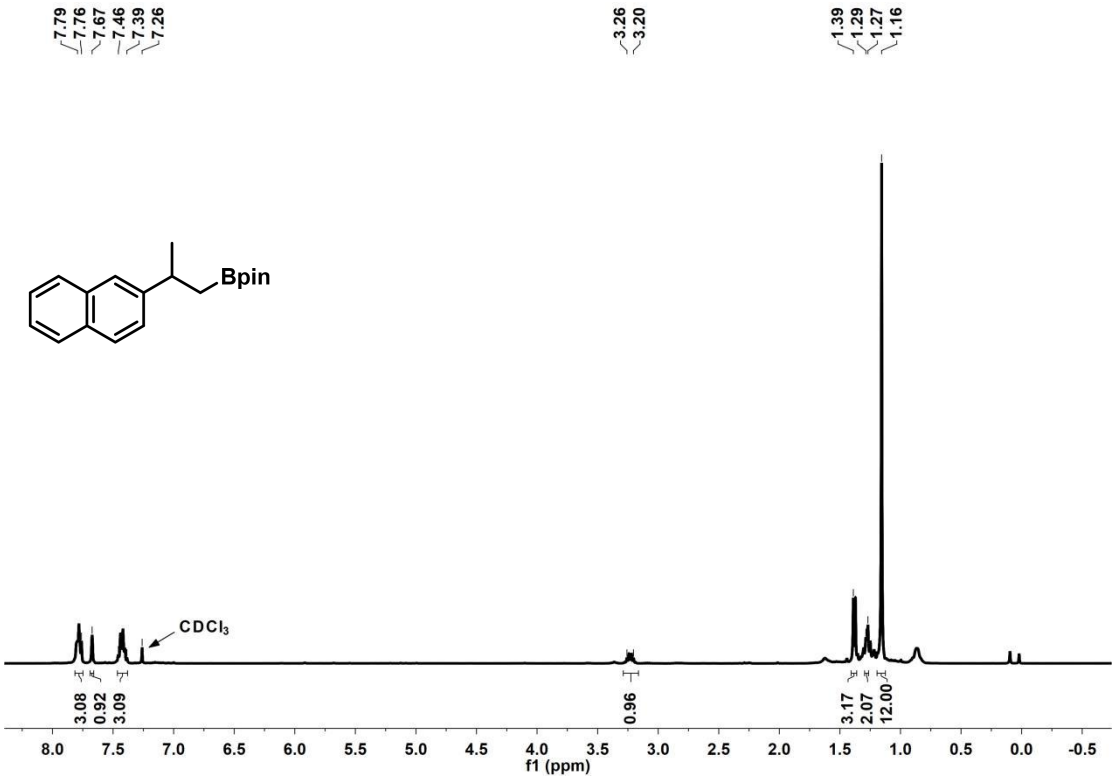


Figure S67. ^{1}H NMR spectrum of **3t** in $CDCl_3$.

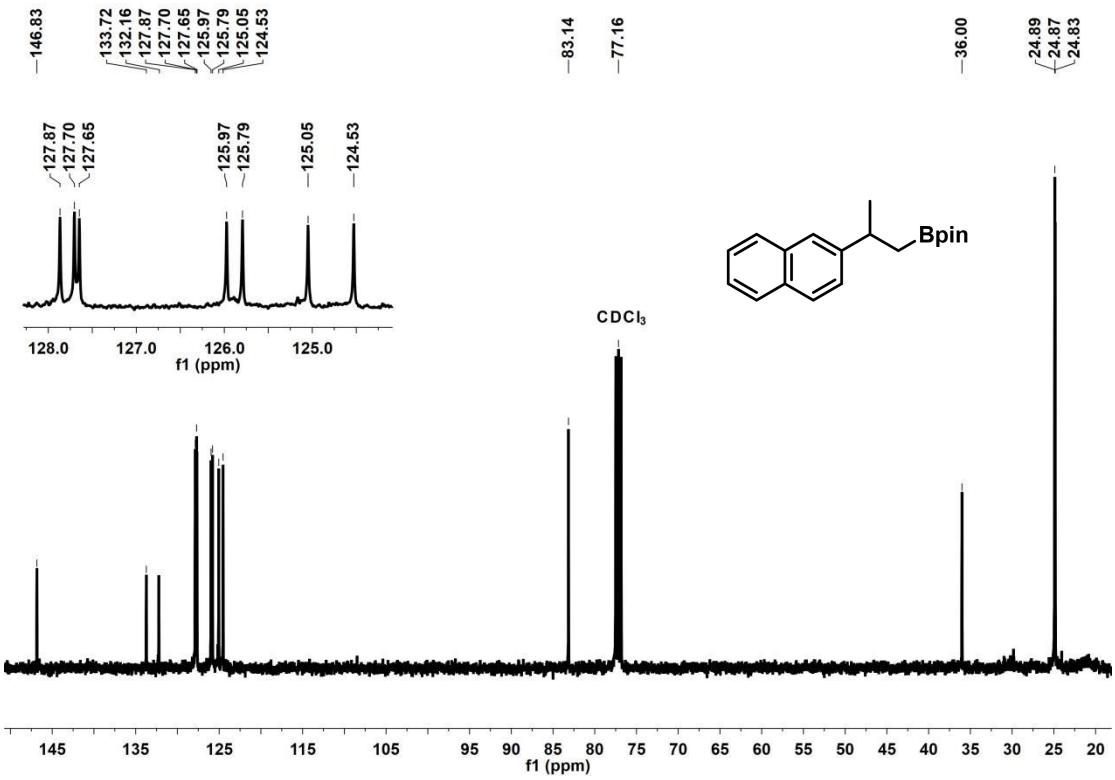


Figure S68. ^{13}C NMR spectrum of **3t** in $CDCl_3$.

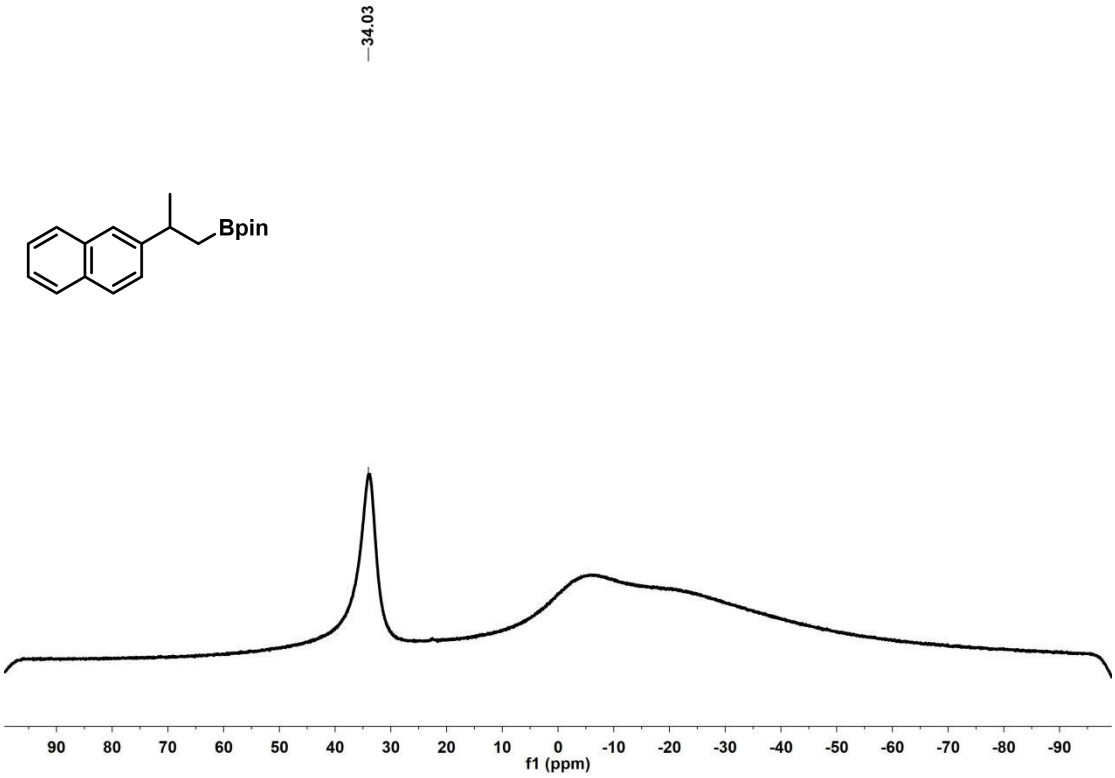


Figure S69. ^{11}B NMR spectrum of **3t** in $CDCl_3$.

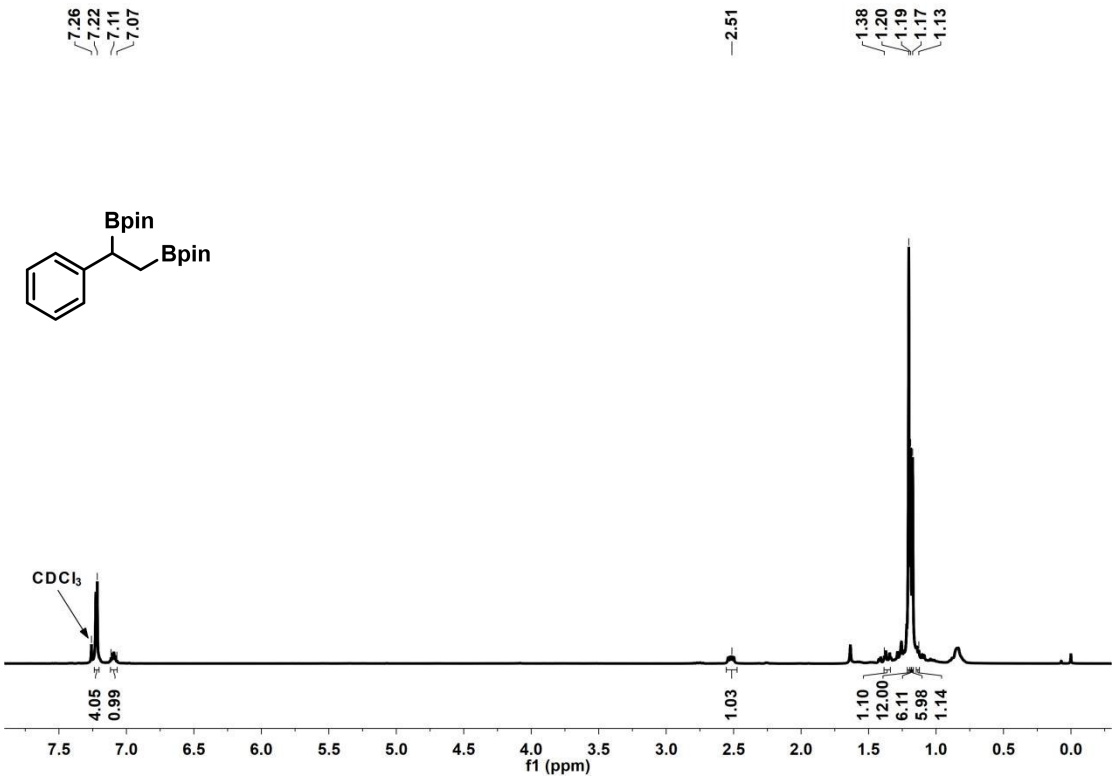


Figure S70. ^{1}H NMR spectrum of **7a** in $CDCl_3$.

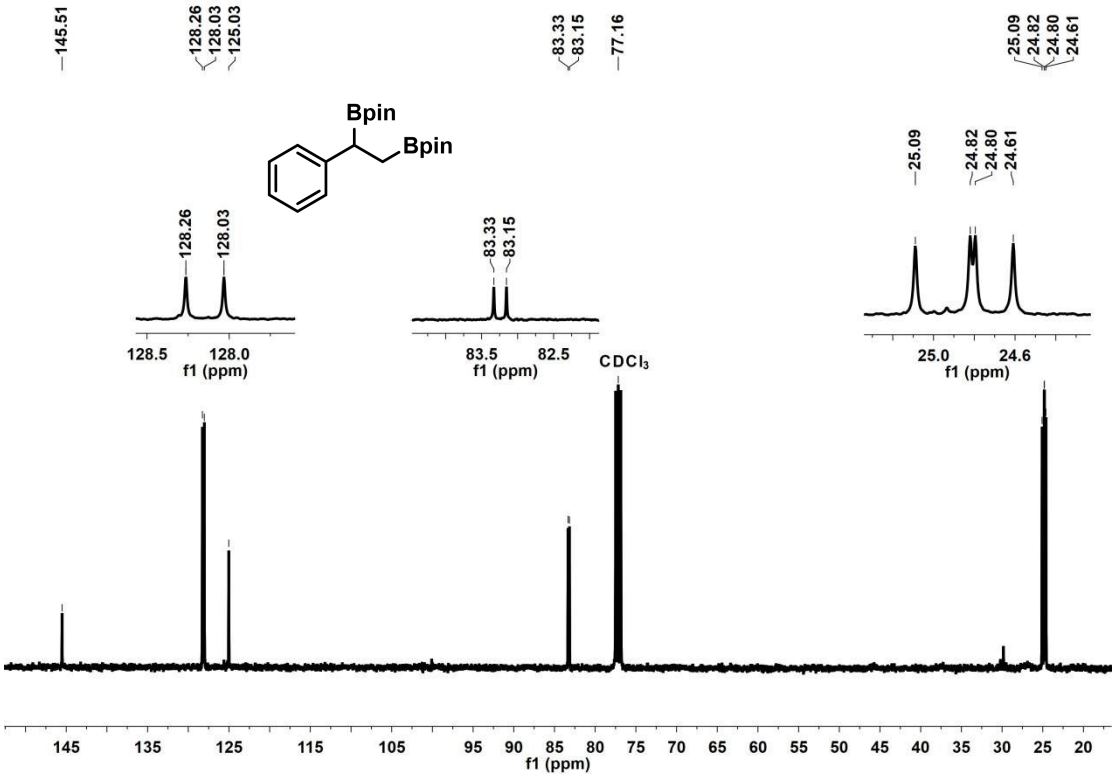


Figure S71. ^{13}C NMR spectrum of **7a** in $CDCl_3$.

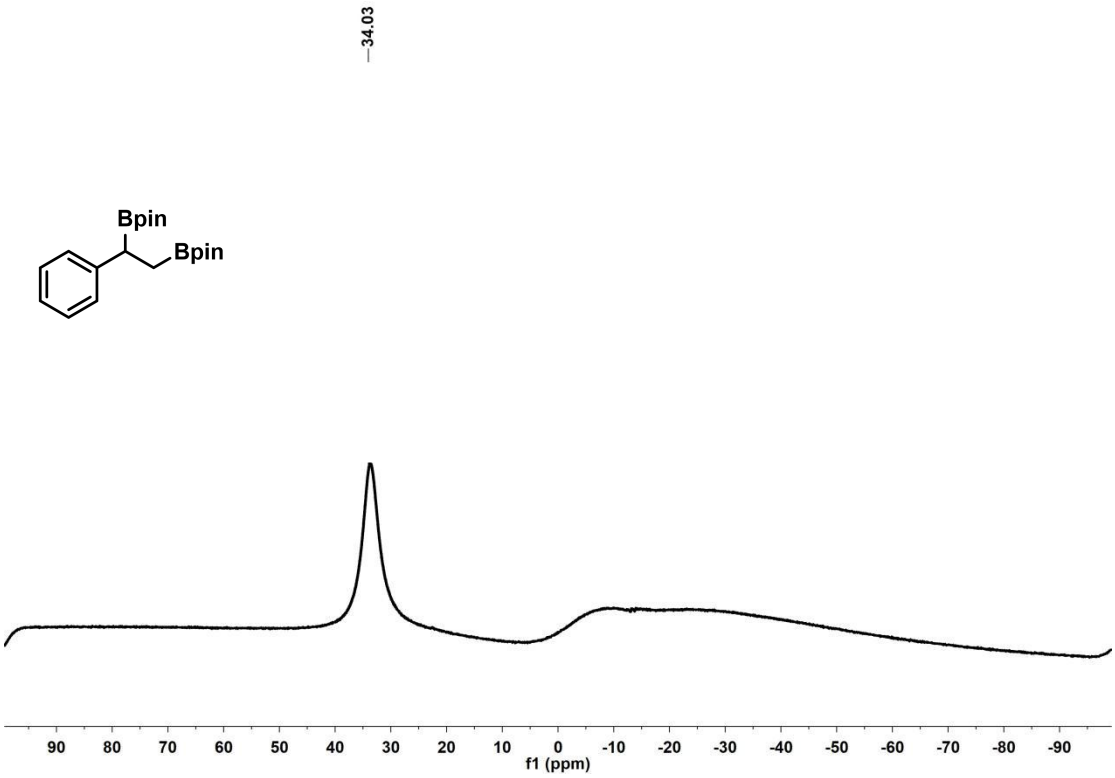


Figure S72. ^{11}B NMR spectrum of **7a** in $CDCl_3$.

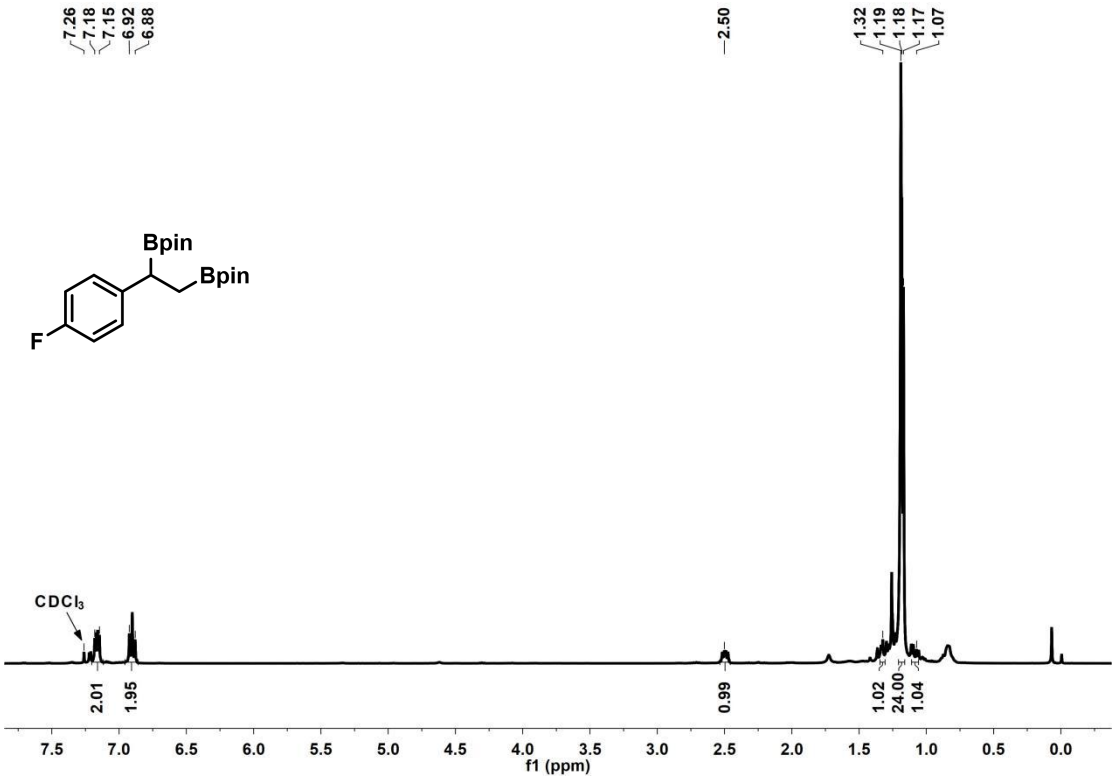


Figure S73. ^{1}H NMR spectrum of **7b** in $CDCl_3$.

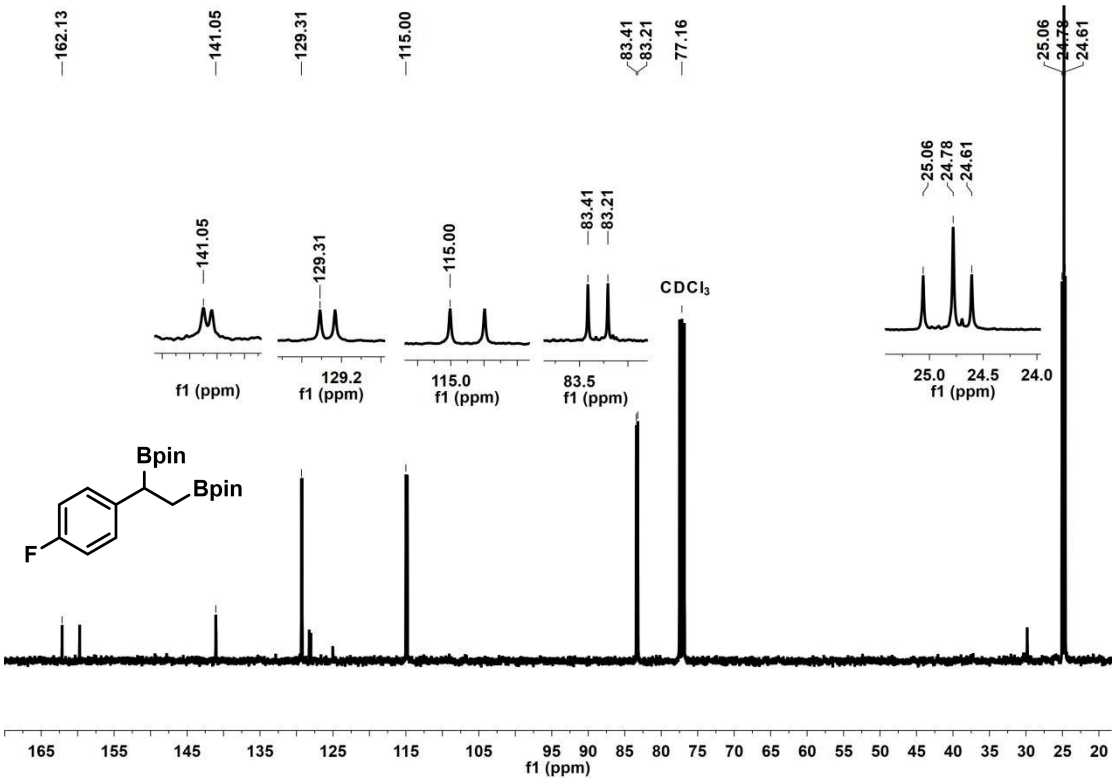


Figure S74. ^{13}C NMR spectrum of **7b** in $CDCl_3$.

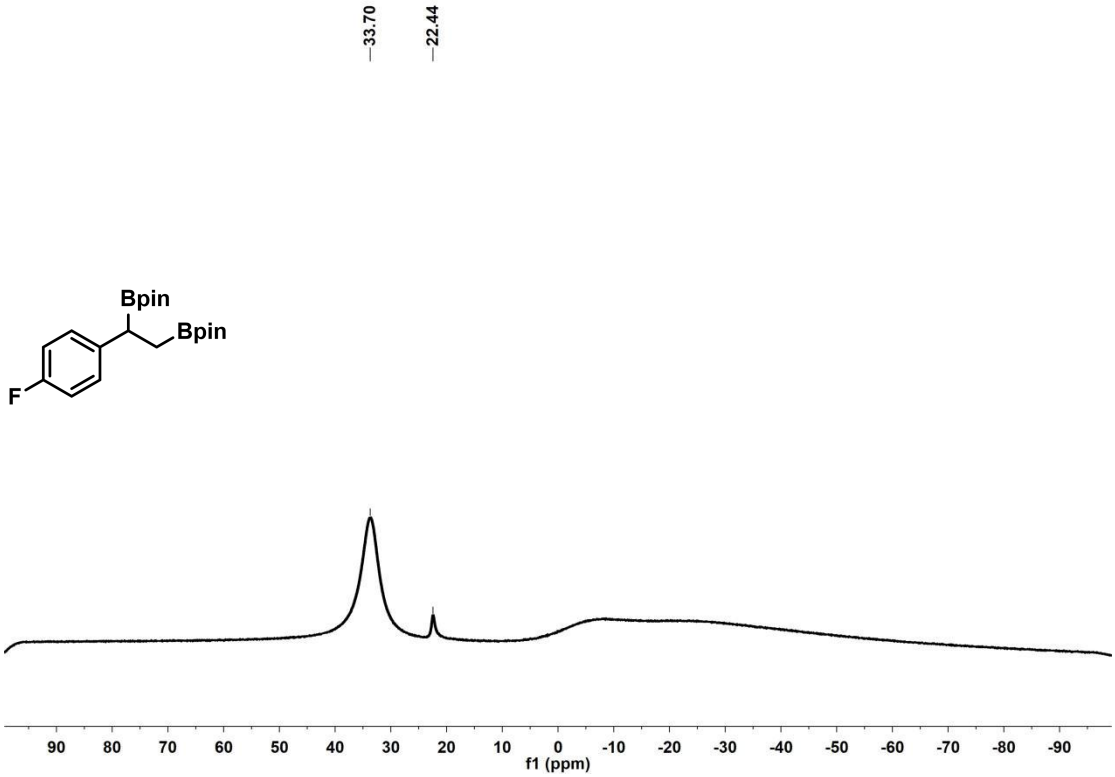


Figure S75. ^{11}B NMR spectrum of **7b** in $CDCl_3$.

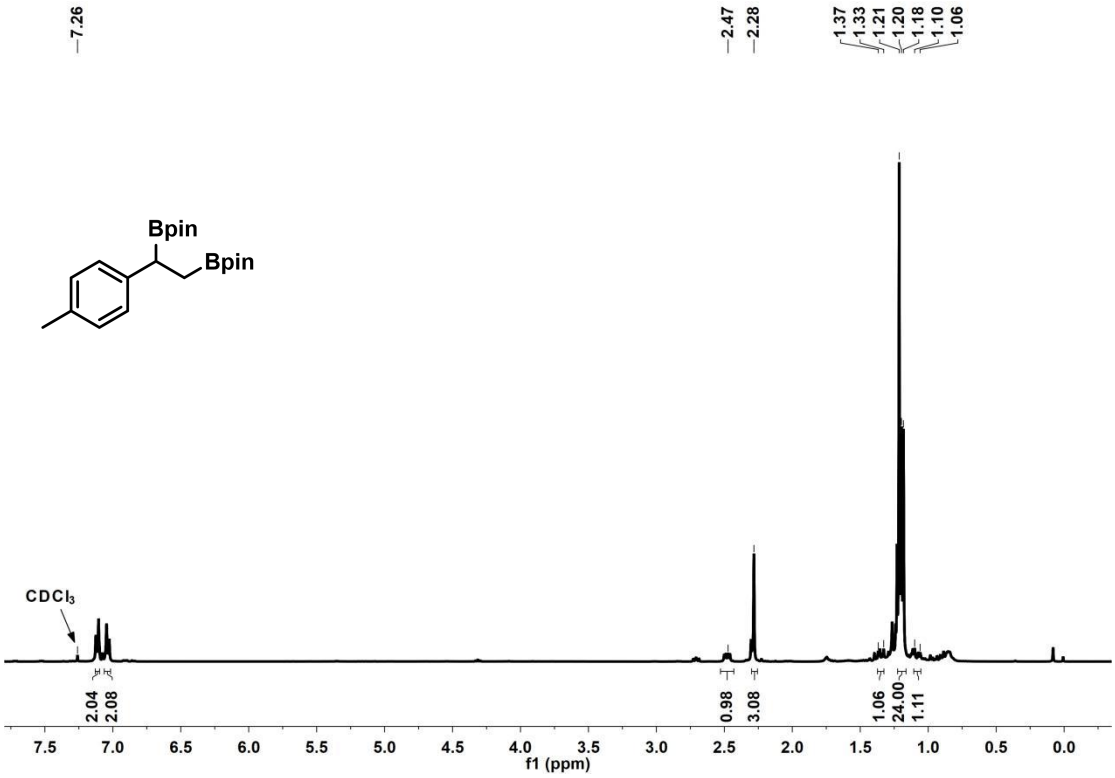


Figure S76. ^{1}H NMR spectrum of **7g** in $CDCl_3$.

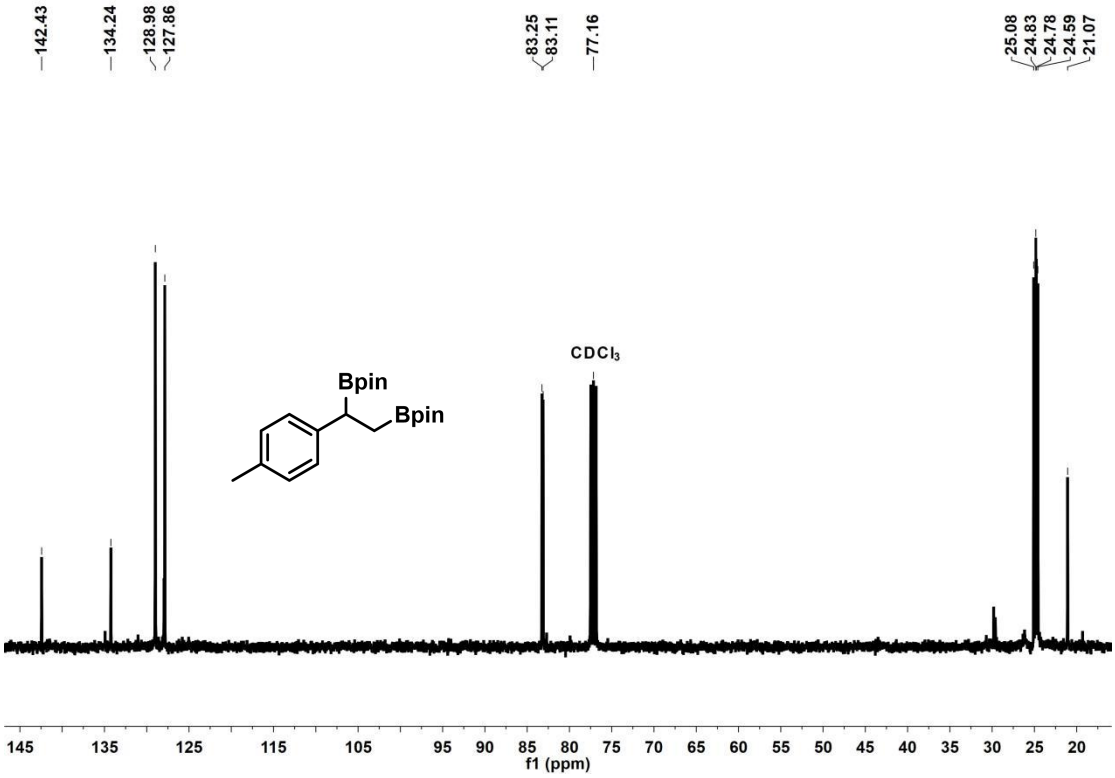


Figure S77. ^{13}C NMR spectrum of **7g** in $CDCl_3$.

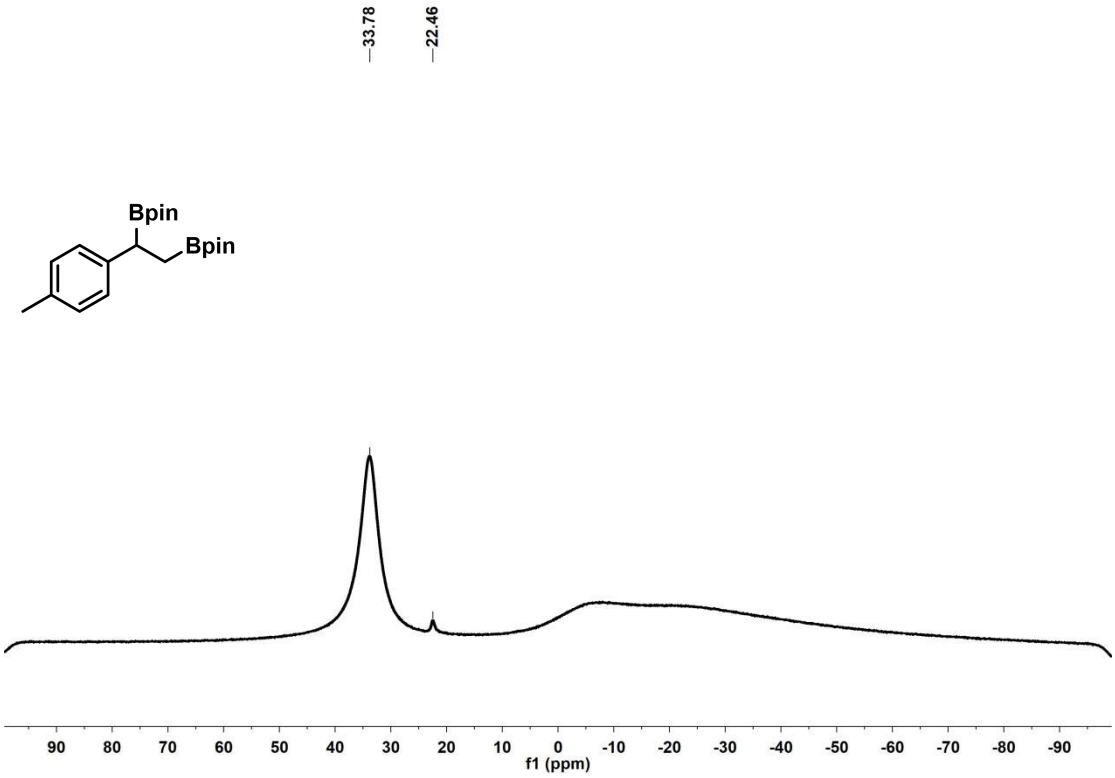


Figure S78. ^{11}B NMR spectrum of **7g** in $CDCl_3$.

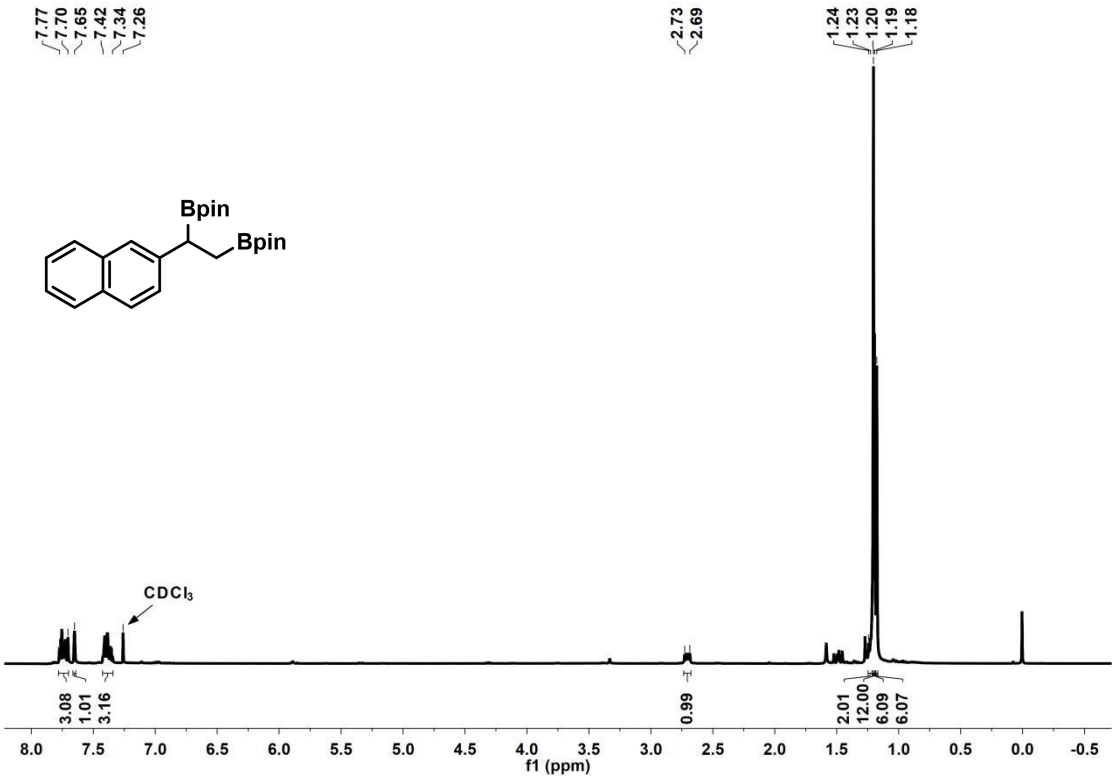


Figure S79. ^{1}H NMR spectrum of **7r** in $CDCl_3$.

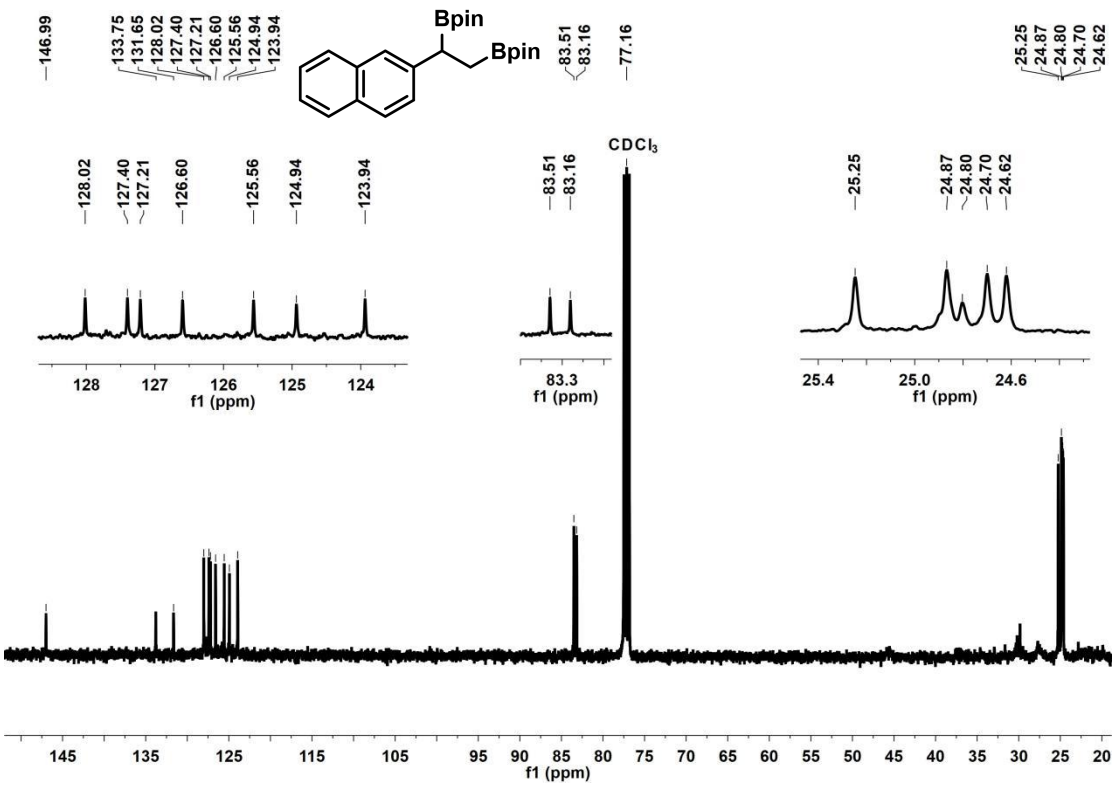


Figure S80. ^{13}C NMR spectrum of **7r** in $CDCl_3$.

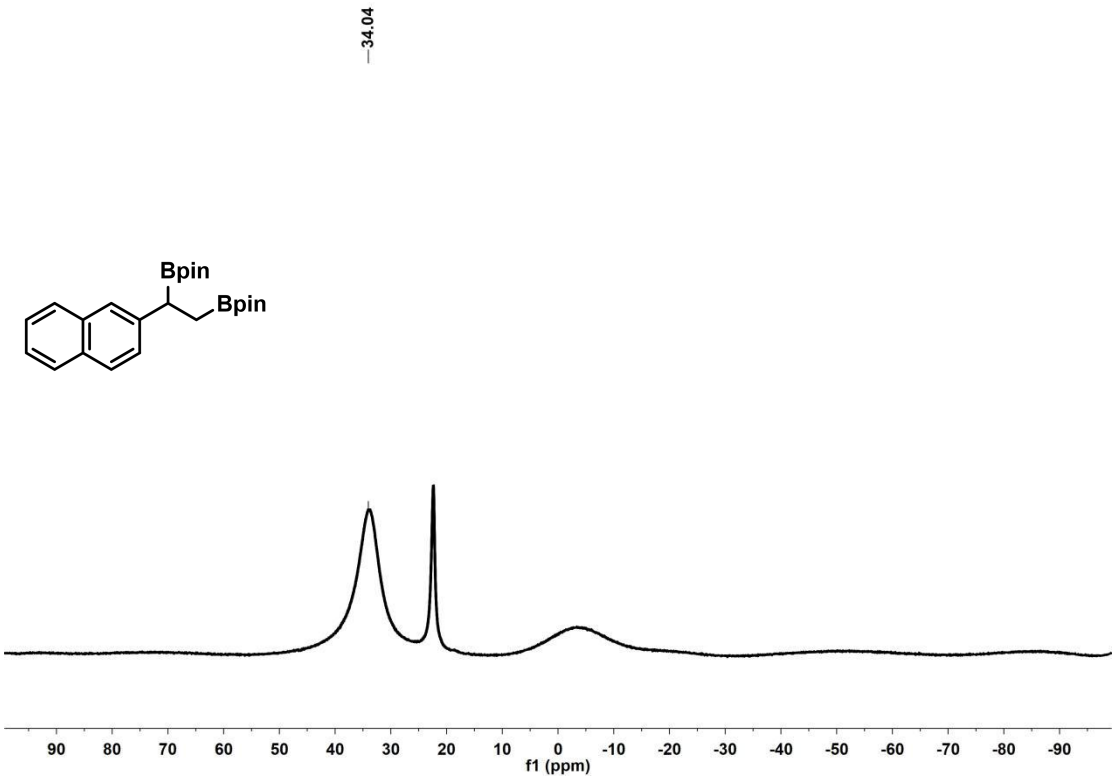


Figure S81. ^{11}B NMR spectrum of **7r** in $CDCl_3$.

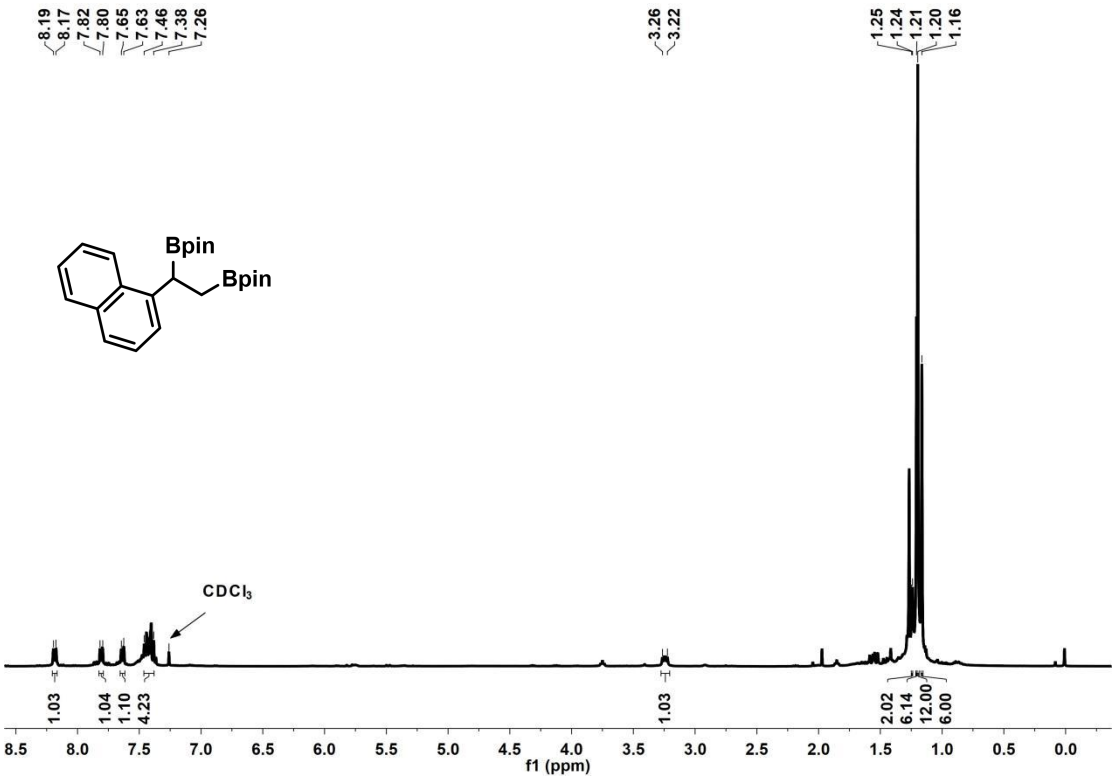


Figure S82. ^{1}H NMR spectrum of **7s** in $CDCl_3$.

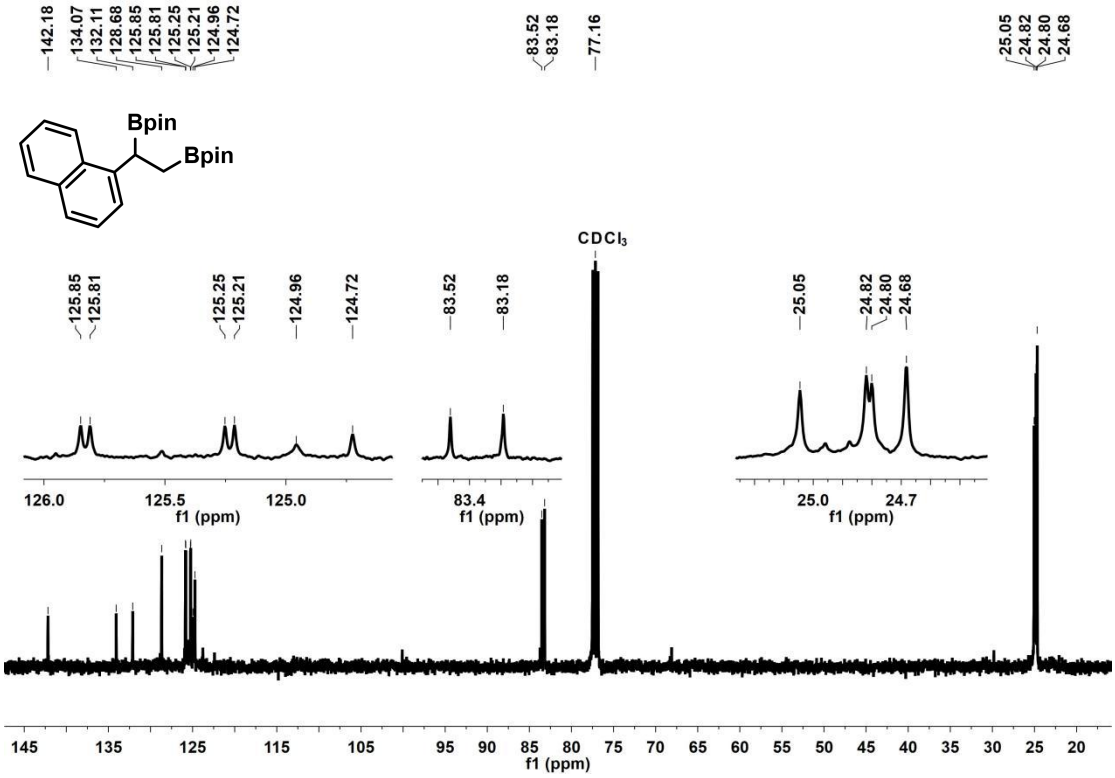


Figure S83. ^{13}C NMR spectrum of **7s** in $CDCl_3$.

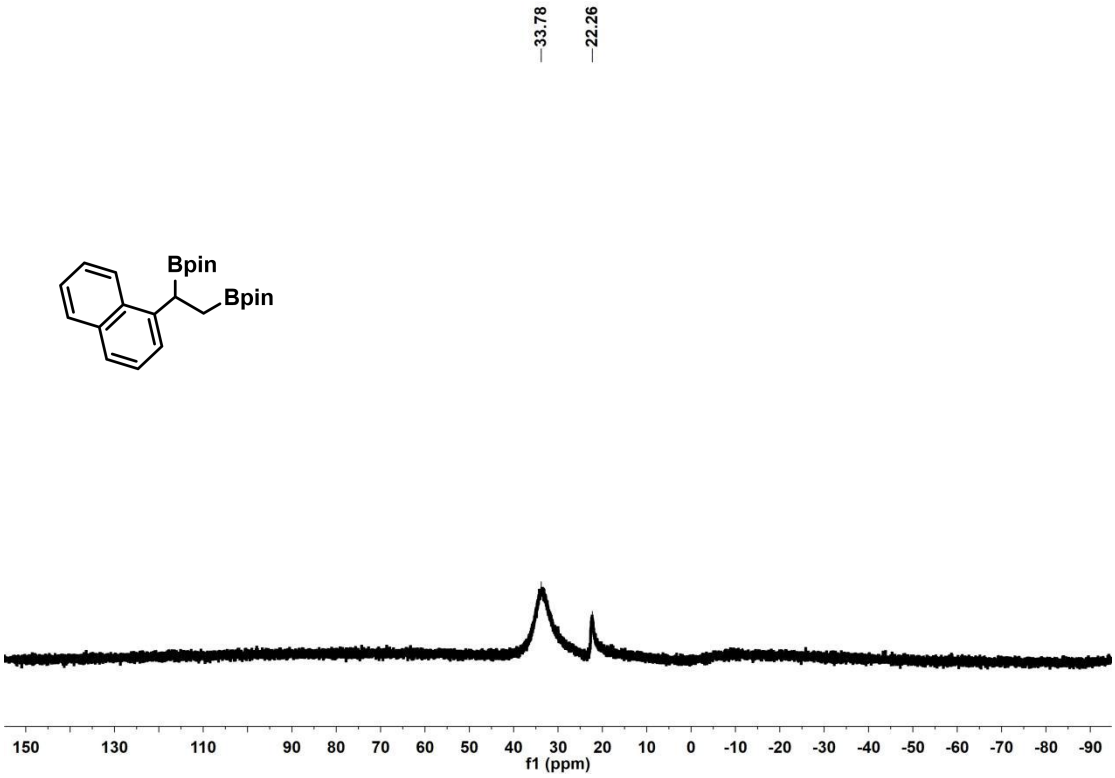


Figure S84. ^{11}B NMR spectrum of **7s** in $CDCl_3$.

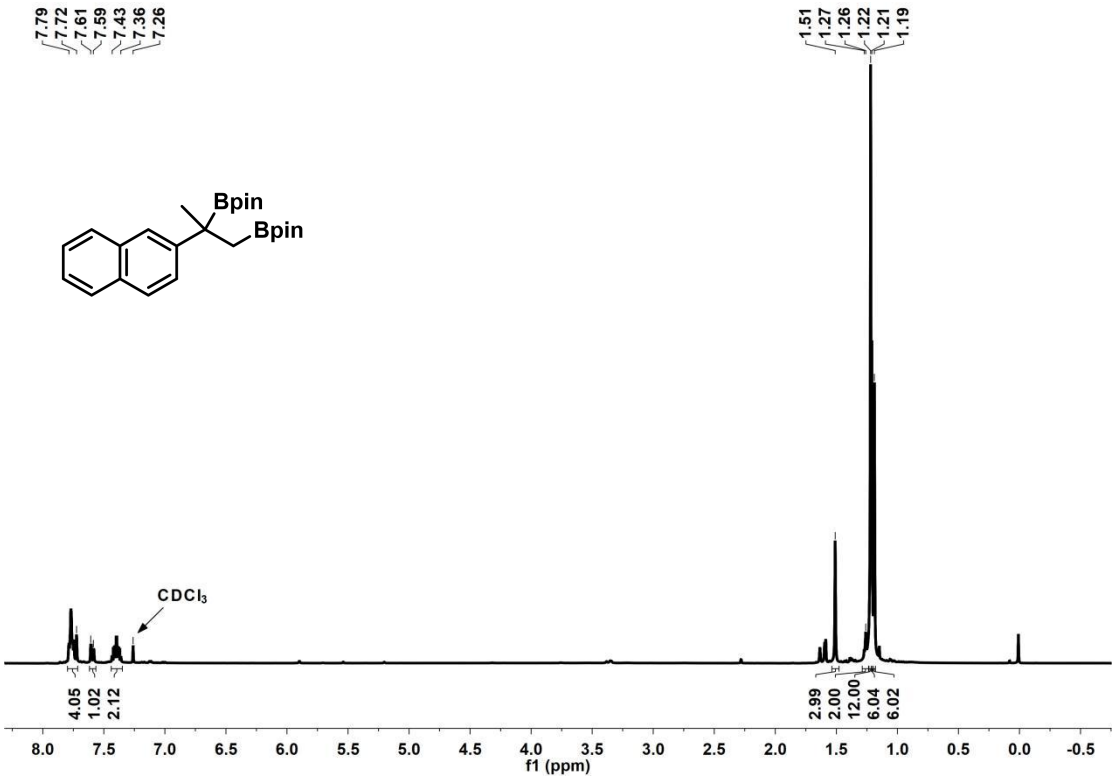


Figure S85. ^{1}H NMR spectrum of **7t** in $CDCl_3$.

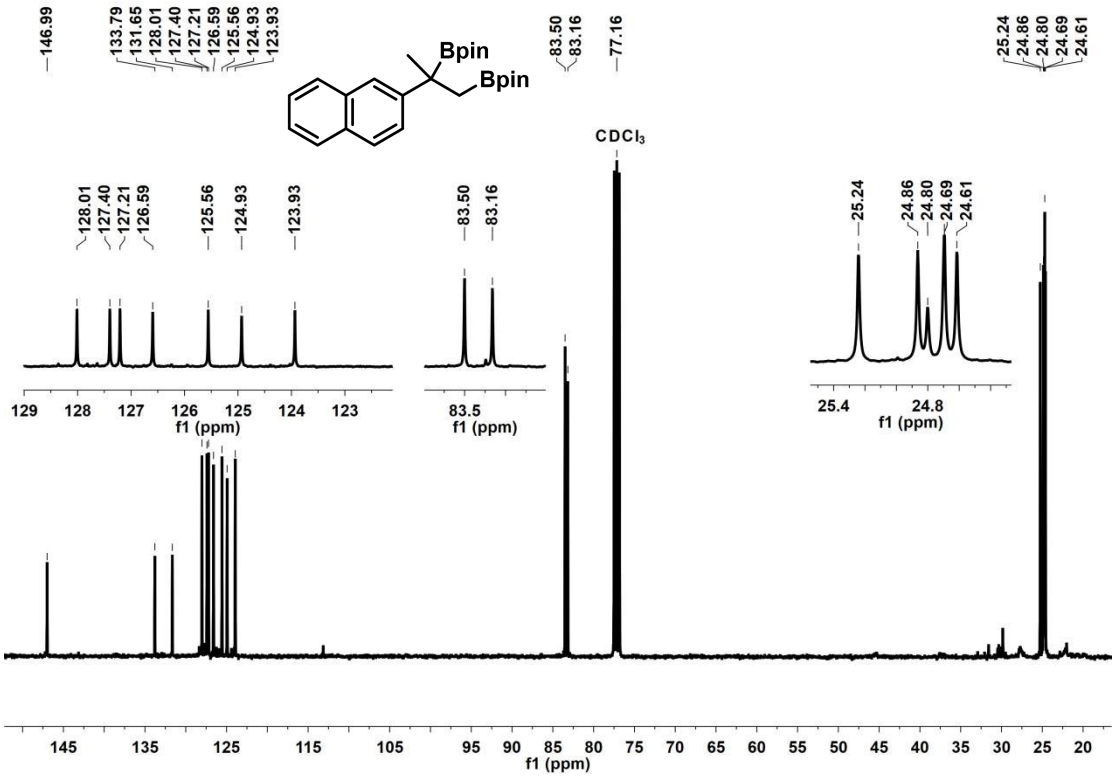


Figure S86. ^{13}C NMR spectrum of **7t** in $CDCl_3$.

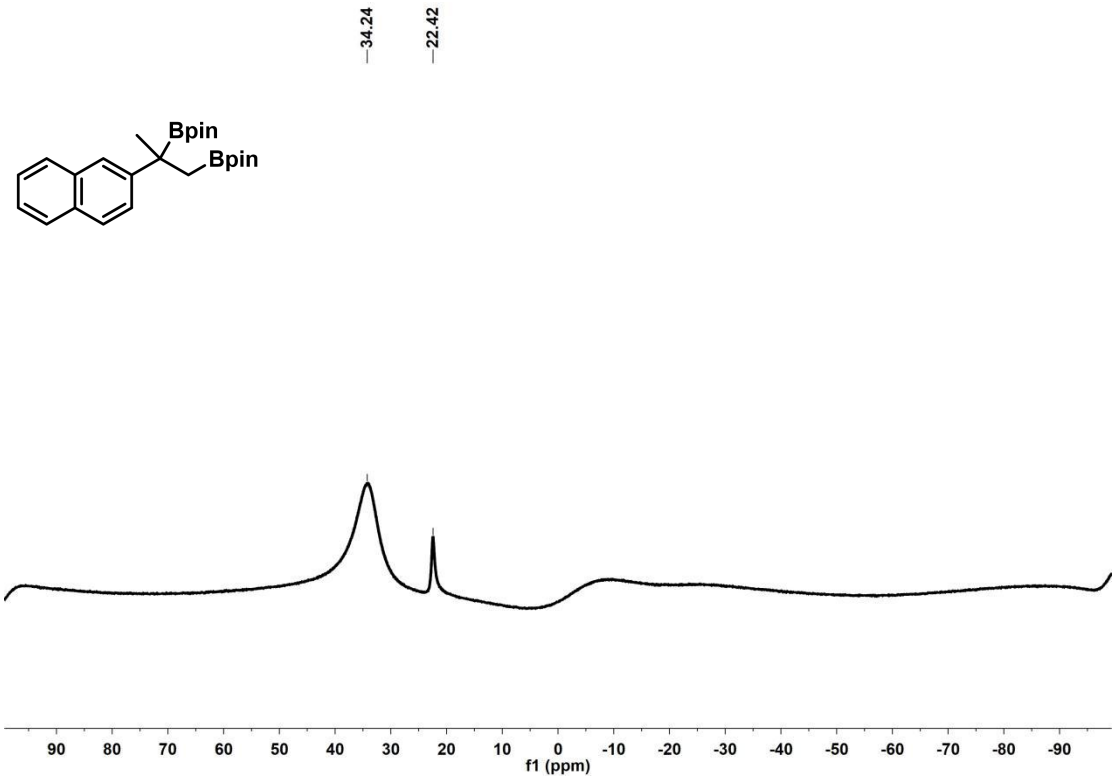


Figure S87. ^{11}B NMR spectrum of **7t** in $CDCl_3$.

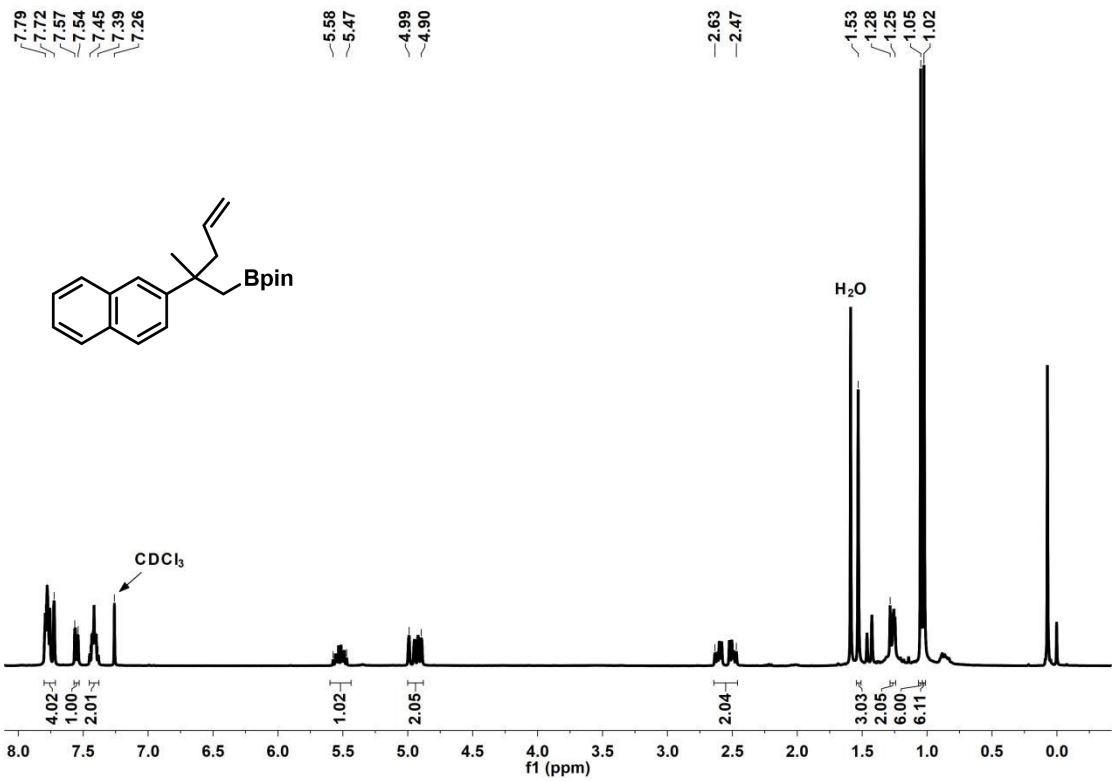


Figure S88. ^{1}H NMR spectrum of **11** in $CDCl_3$.

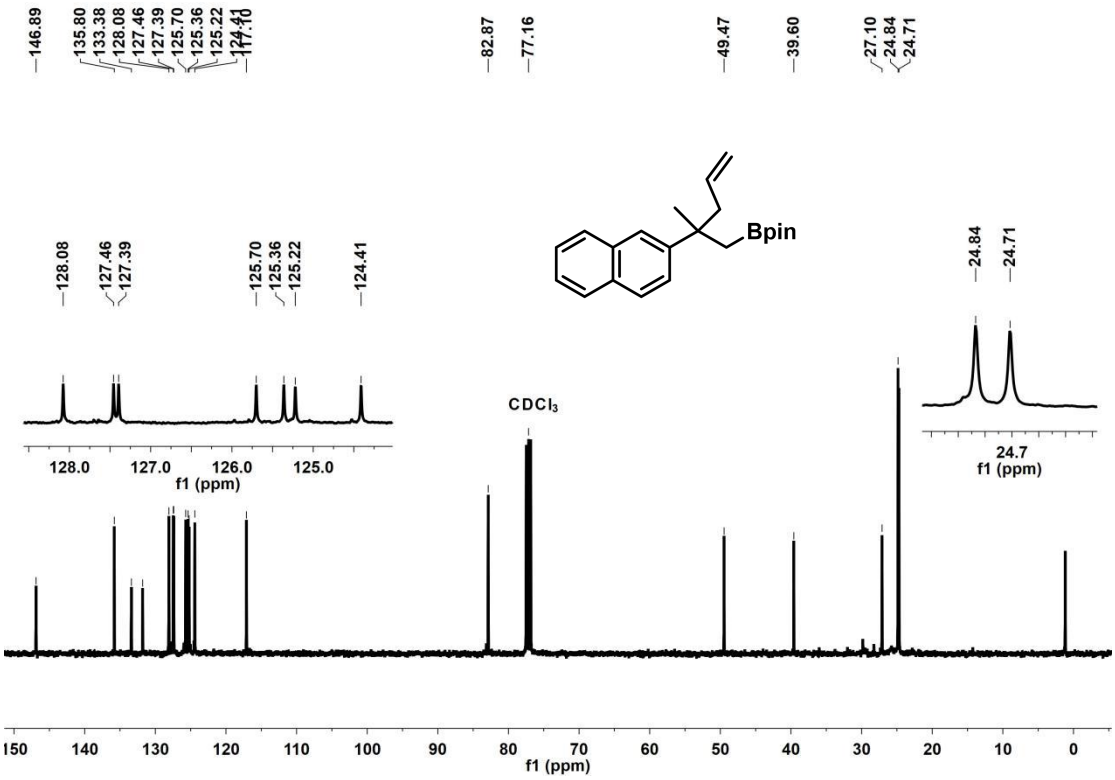
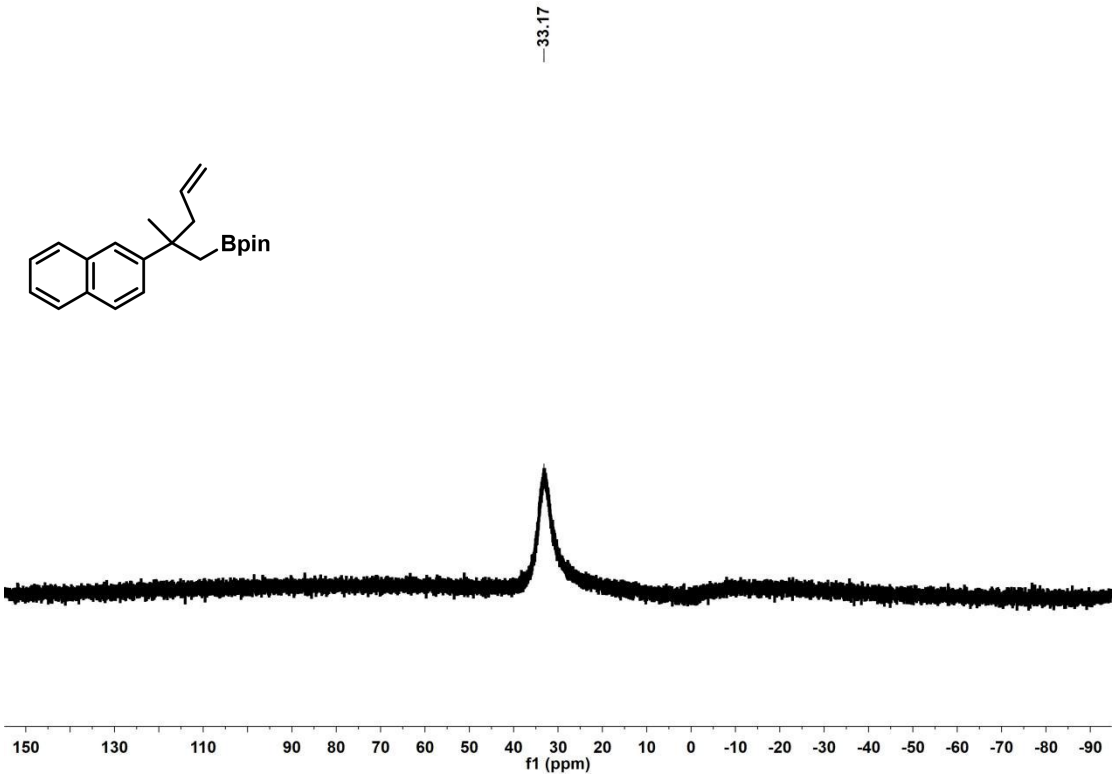


Figure S89. ^{13}C NMR spectrum of **11** in $CDCl_3$.



SFigure S90. ^{11}B NMR spectrum of **11** in $CDCl_3$.

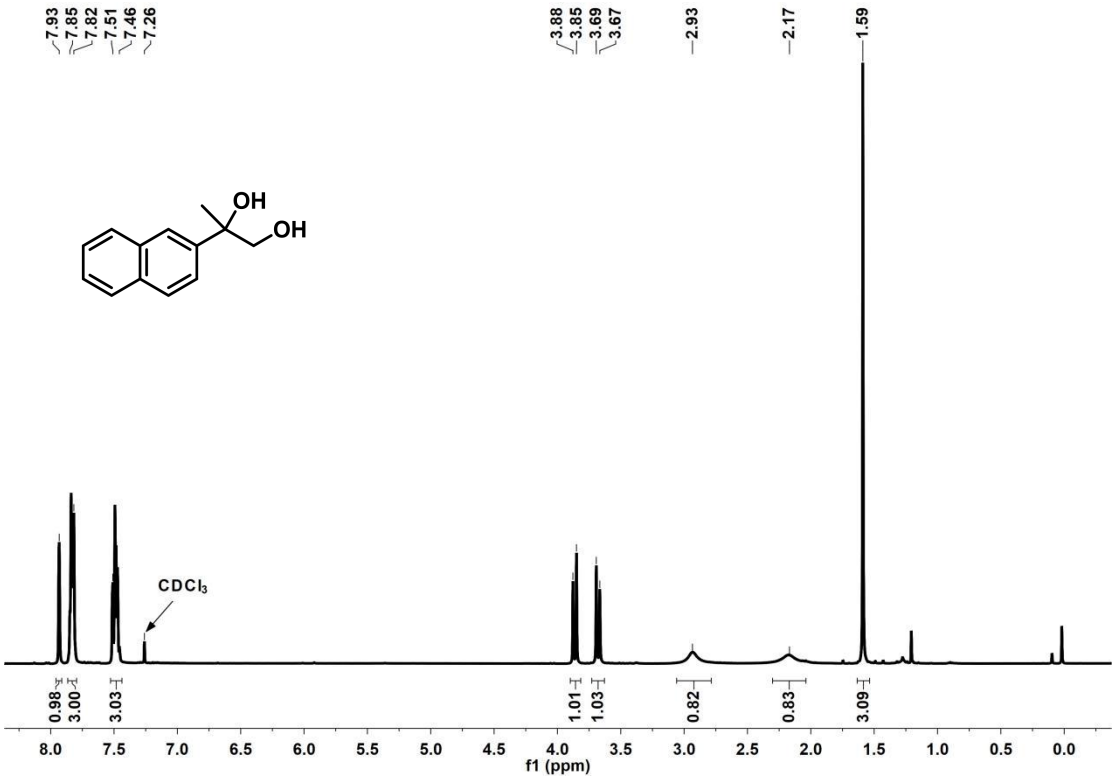


Figure S91. ^{1}H NMR spectrum of **12** in $CDCl_3$.

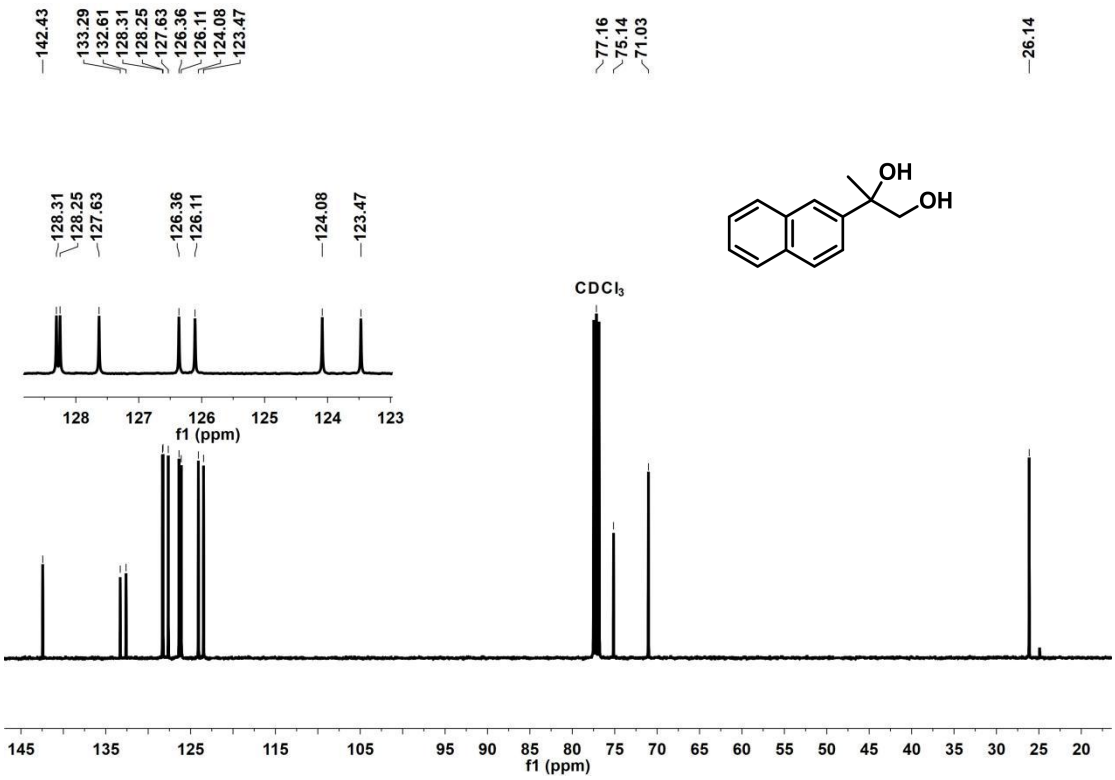


Figure S92. ^{13}C NMR spectrum of **12** in $CDCl_3$.

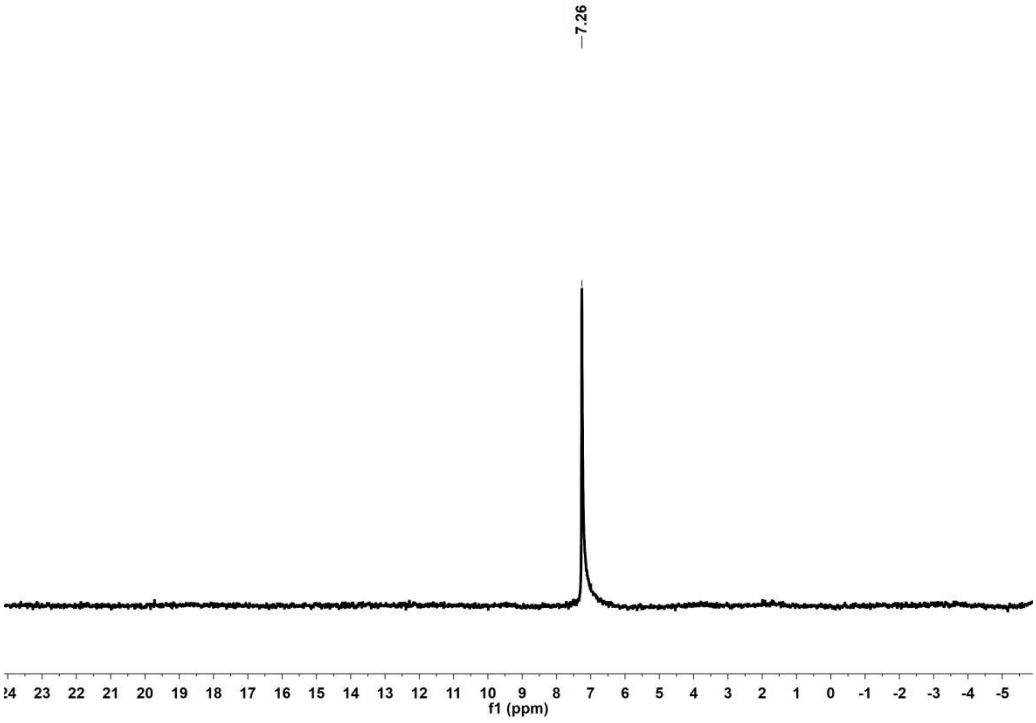


Figure S93. ^{2}D NMR spectrum ($CDCl_3$) of deuterium-labelling experiment in THF-d_8. No deuterium product was detected.

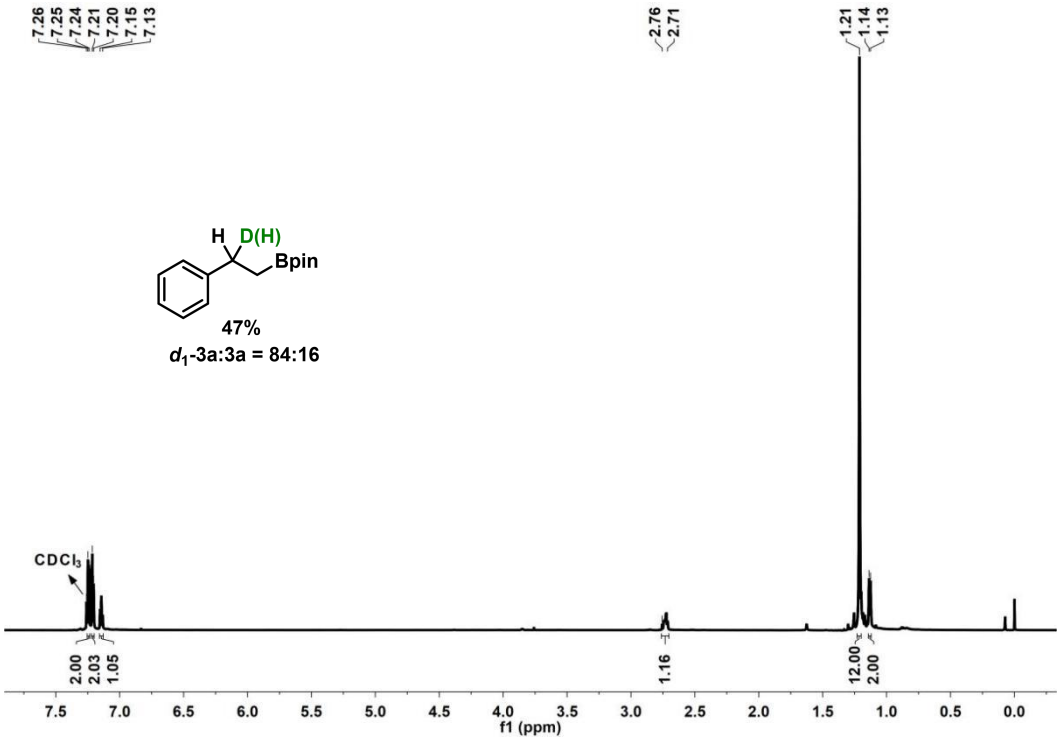


Figure S94. [1]H NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 84:16 in $CDCl_3$. The deuterium-labelling experiment was conducted in CD_3CN solvent.

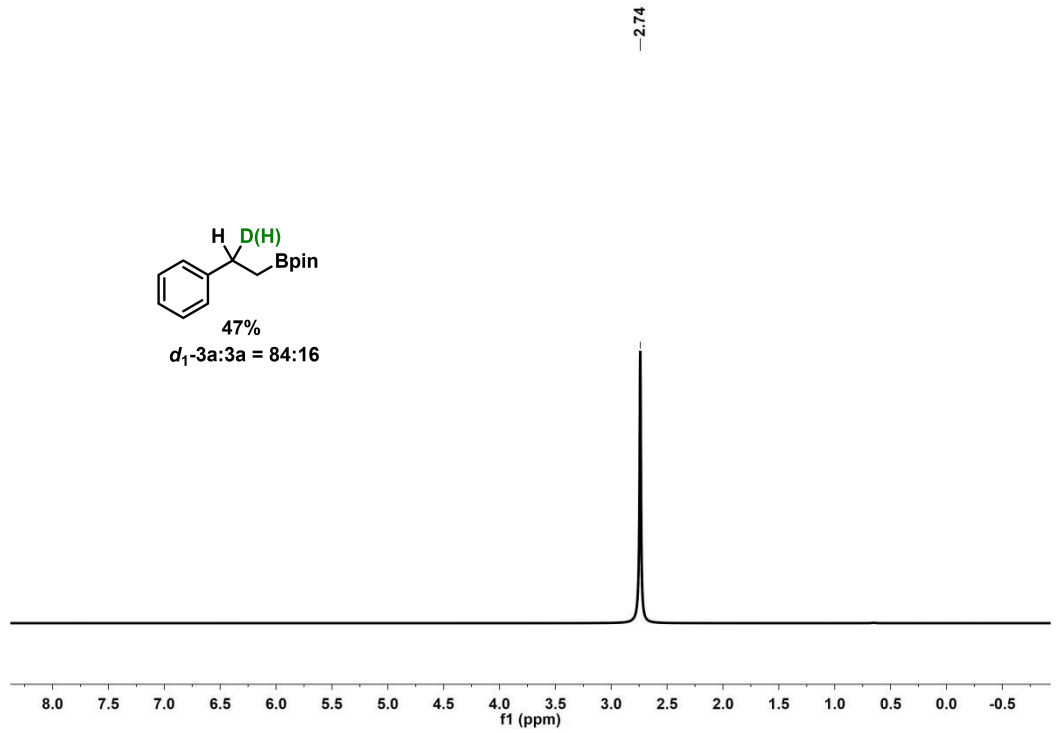


Figure S95. [2]D NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 84:16 in $CHCl_3$. The deuterium-labelling experiment was conducted in CD_3CN solvent.

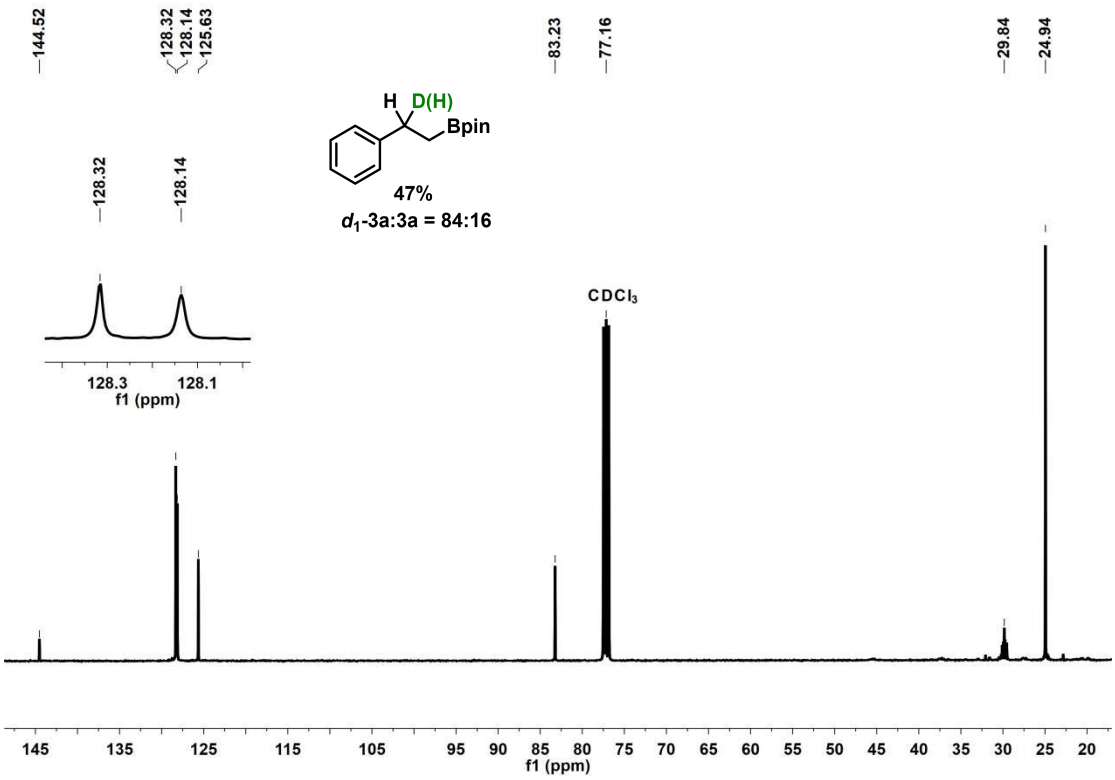


Figure S96. ^{13}C NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 84:16 in $CDCl_3$. The deuterium-labelling experiment was conducted in CD_3CN solvent.

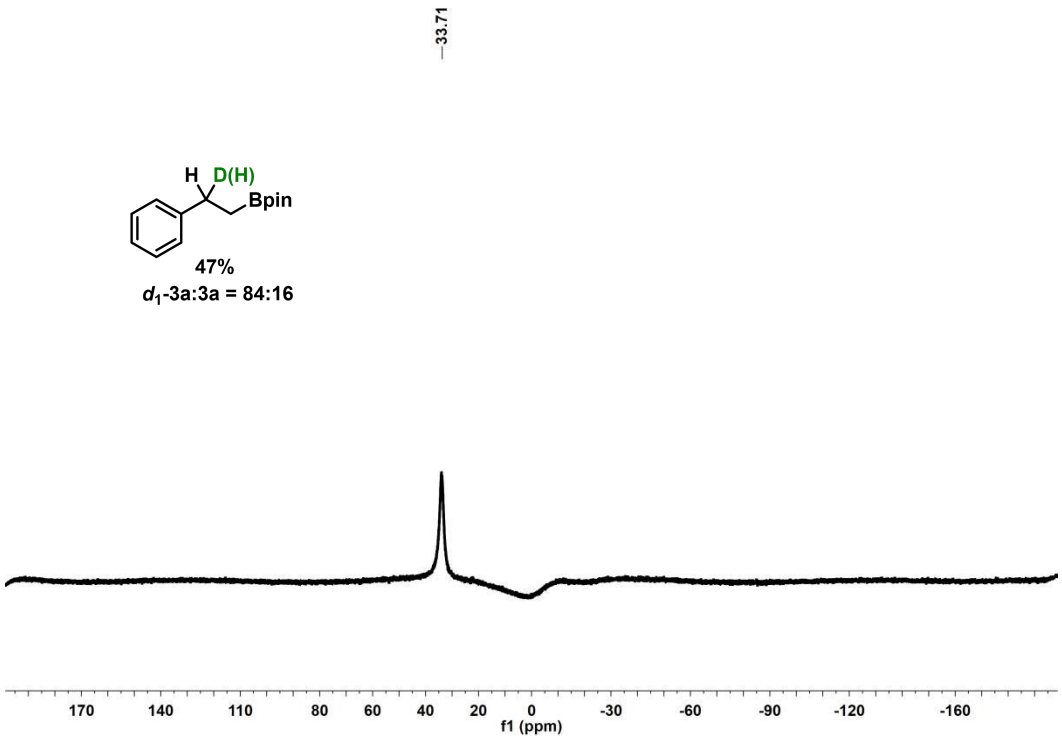


Figure S97. ^{11}B NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 84:16 in $CDCl_3$. The deuterium-labelling experiment was conducted in CD_3CN solvent.

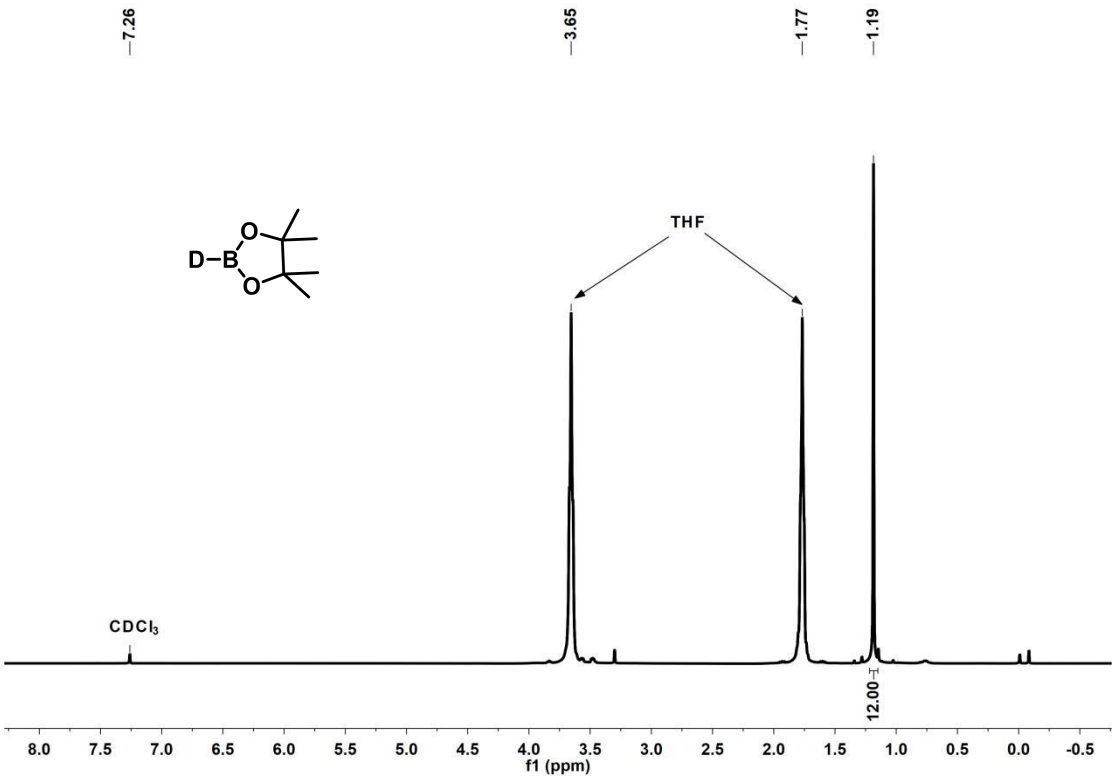


Figure S98. ^{1}H NMR spectrum of DBpin in $CDCl_3$.

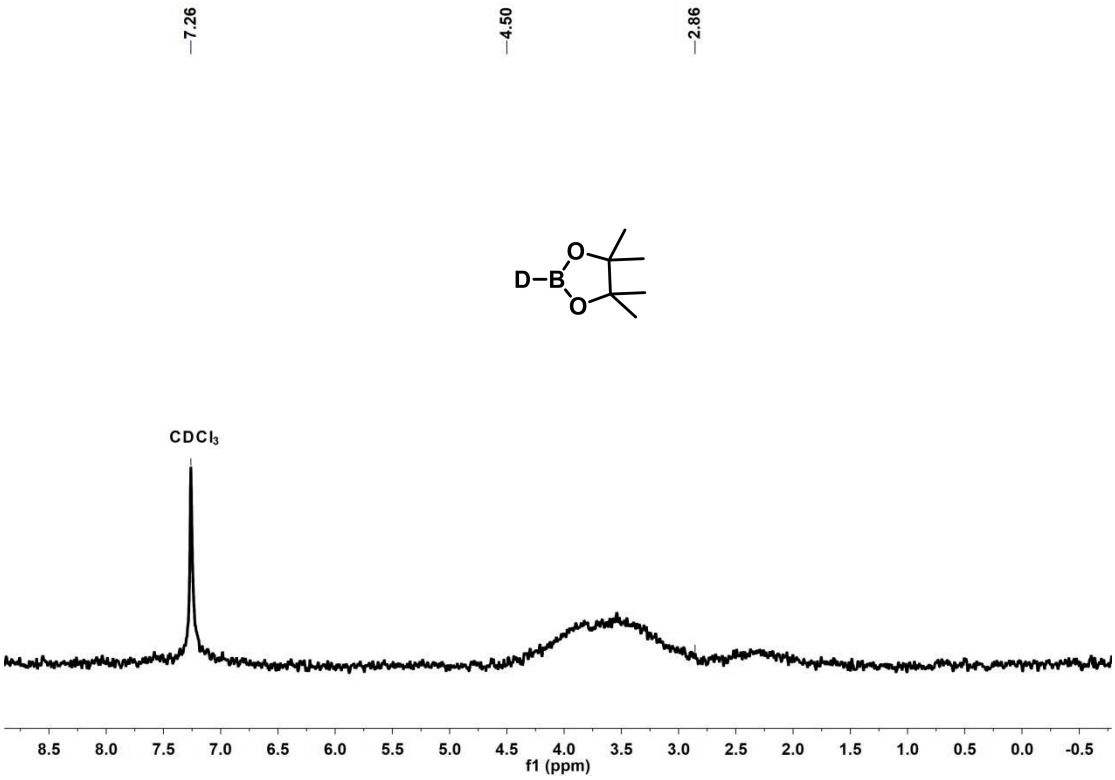


Figure S99. ^{2}D NMR spectrum of DBpin in $CDCl_3$.

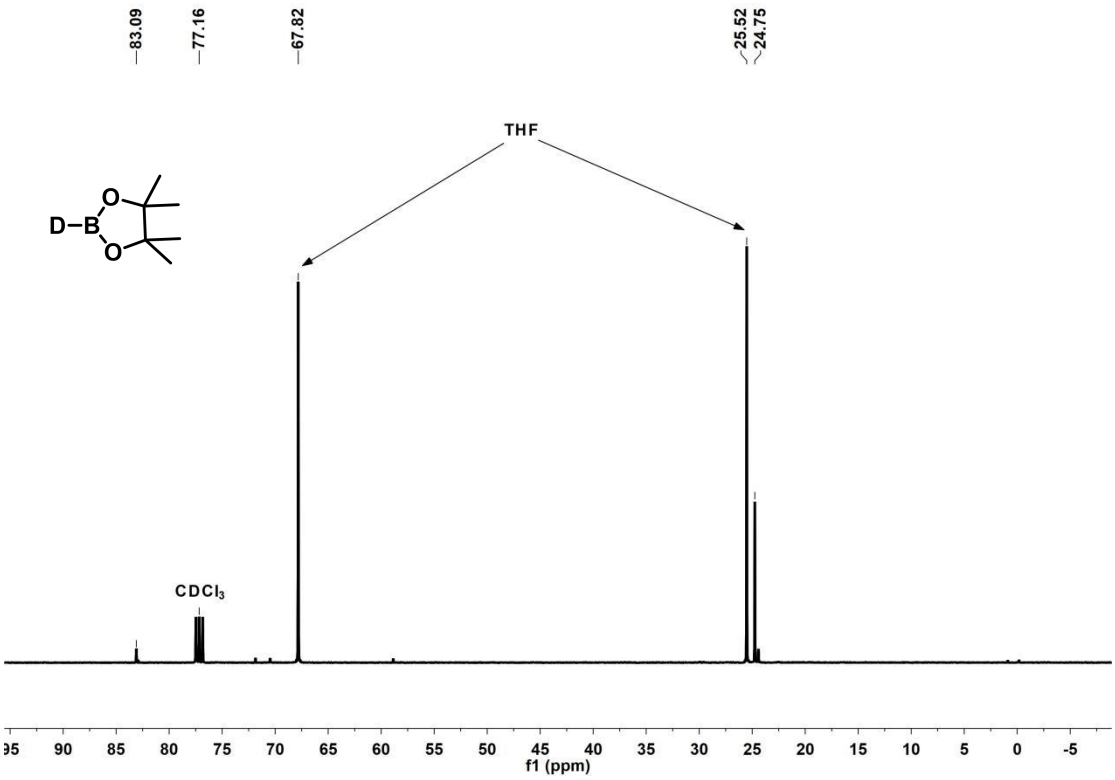


Figure S100. ^{13}C NMR spectrum of DBpin in $CDCl_3$.

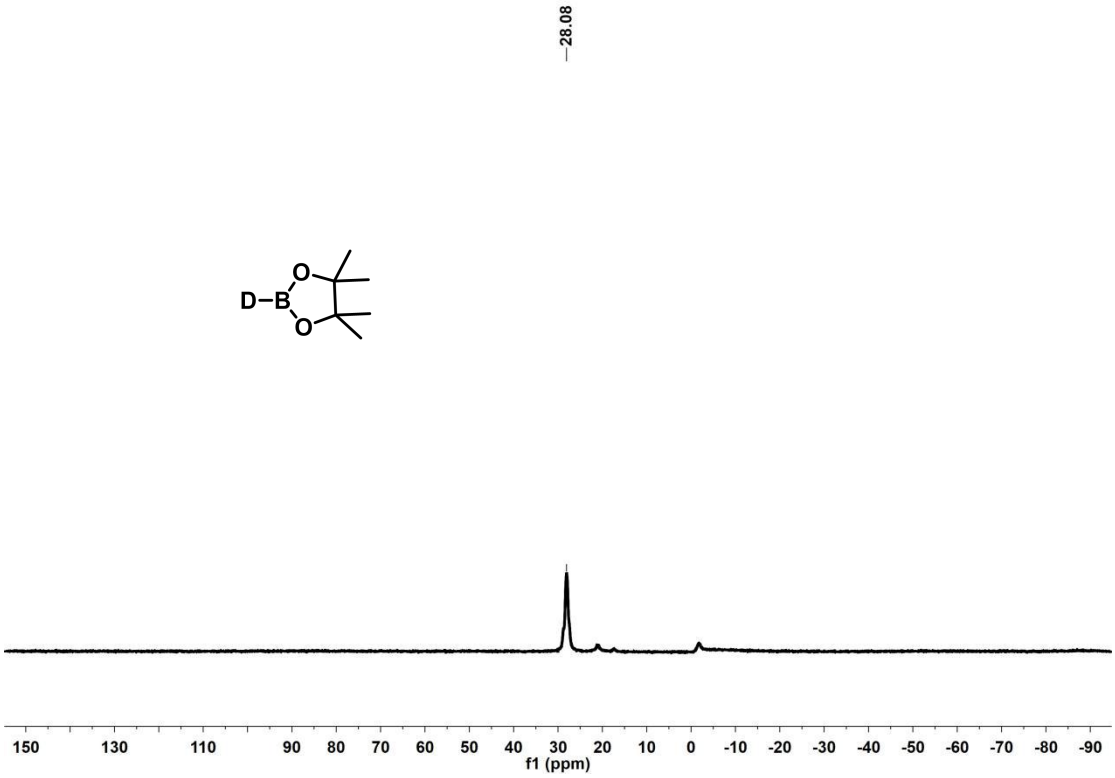


Figure S101. ^{11}B NMR spectrum of DBpin in $CDCl_3$.

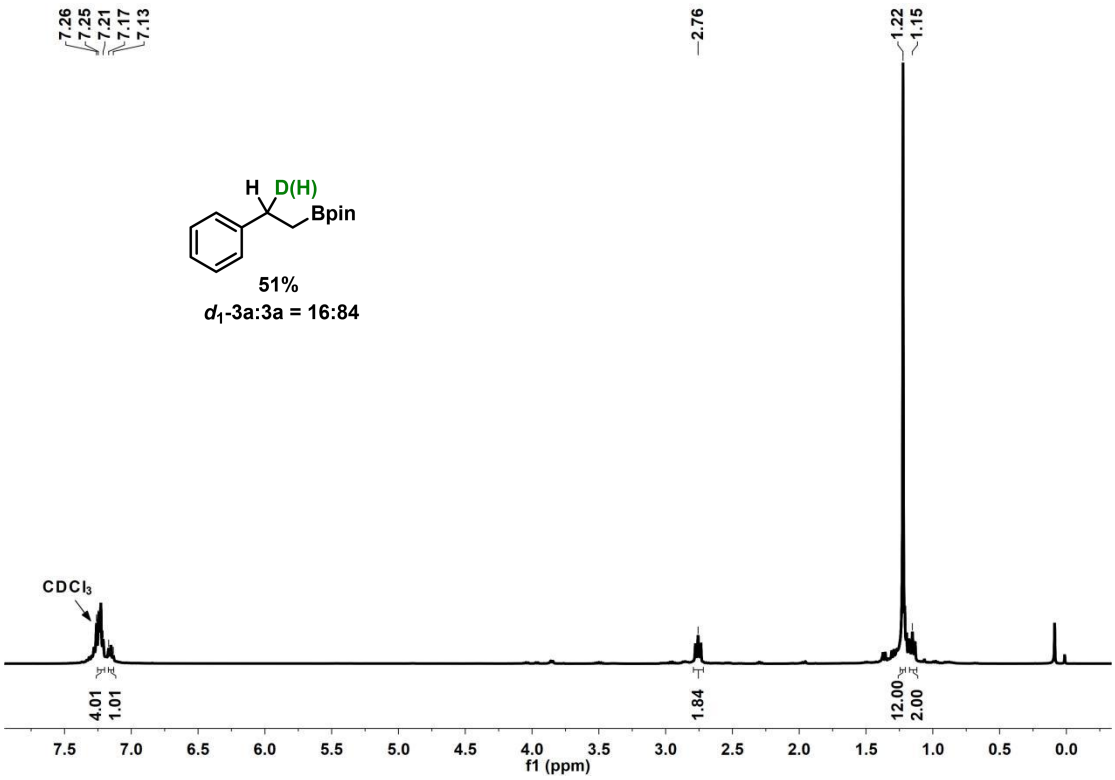


Figure S102. ^{1}H NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 16:84 in $CDCl_3$. The deuterium-labelling experiment was conducted with DBpin as substrate.

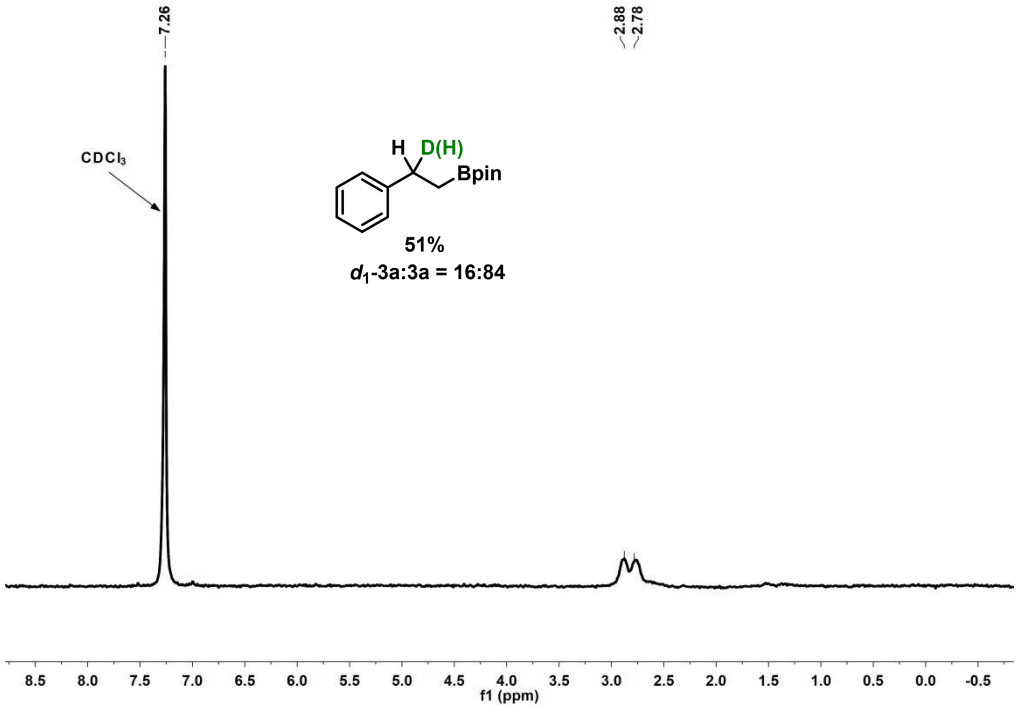


Figure S103. ^{2}D NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 16:84 in $CDCl_3$. The deuterium-labelling experiment was conducted with DBpin as substrate.

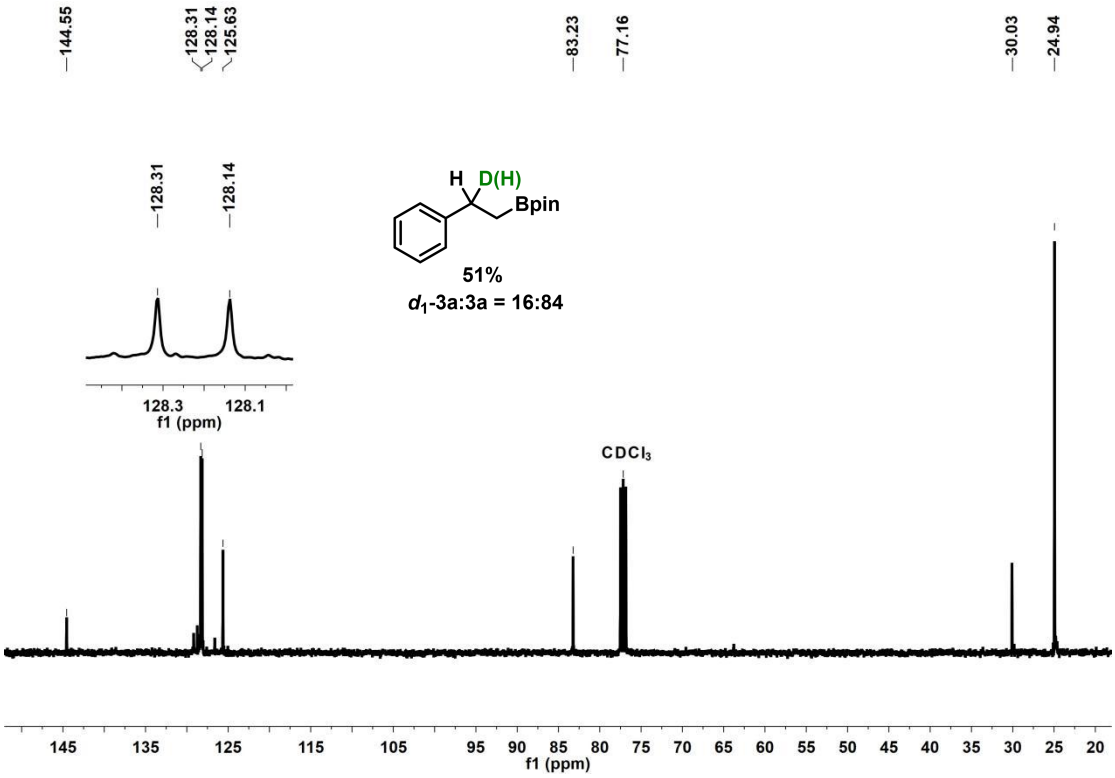


Figure S104. ^{13}C NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 16:84 in $CDCl_3$. The deuterium-labelling experiment was conducted with DBpin as substrate.

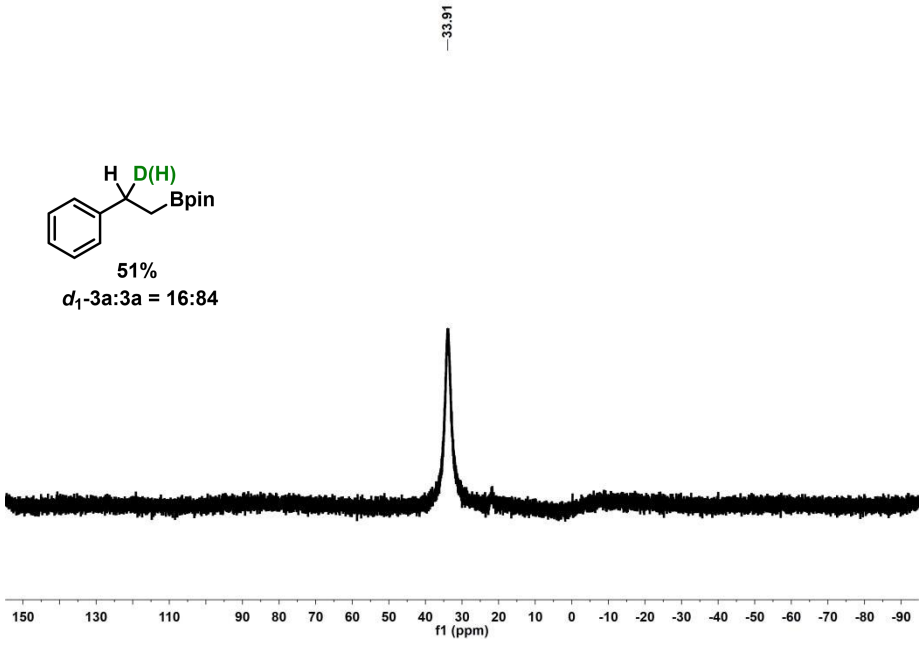


Figure S105. ^{11}B NMR spectrum of the mixture of d_1-**3a** and **3a** in a ratio of 16:84 in $CDCl_3$. The deuterium-labelling experiment was conducted with DBpin as substrate.

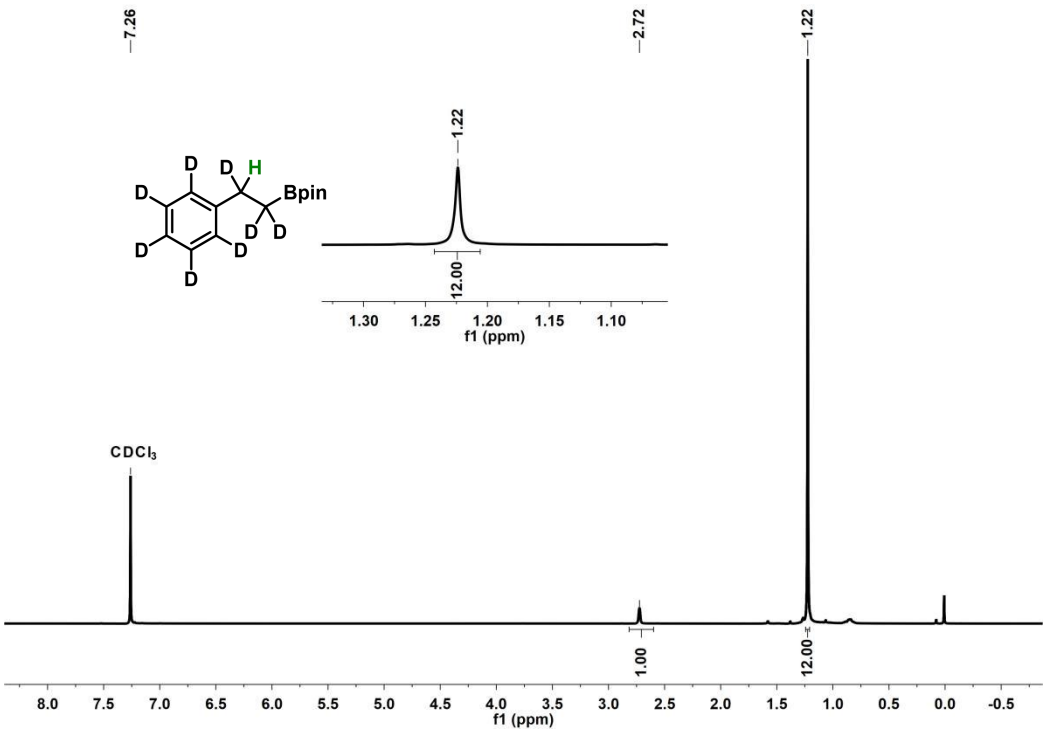


Figure S106. ^{1}H NMR spectrum of d_8-**3a** in $CDCl_3$. The deuterium-labelling experiment was conducted with d_8-styrene as substrate.

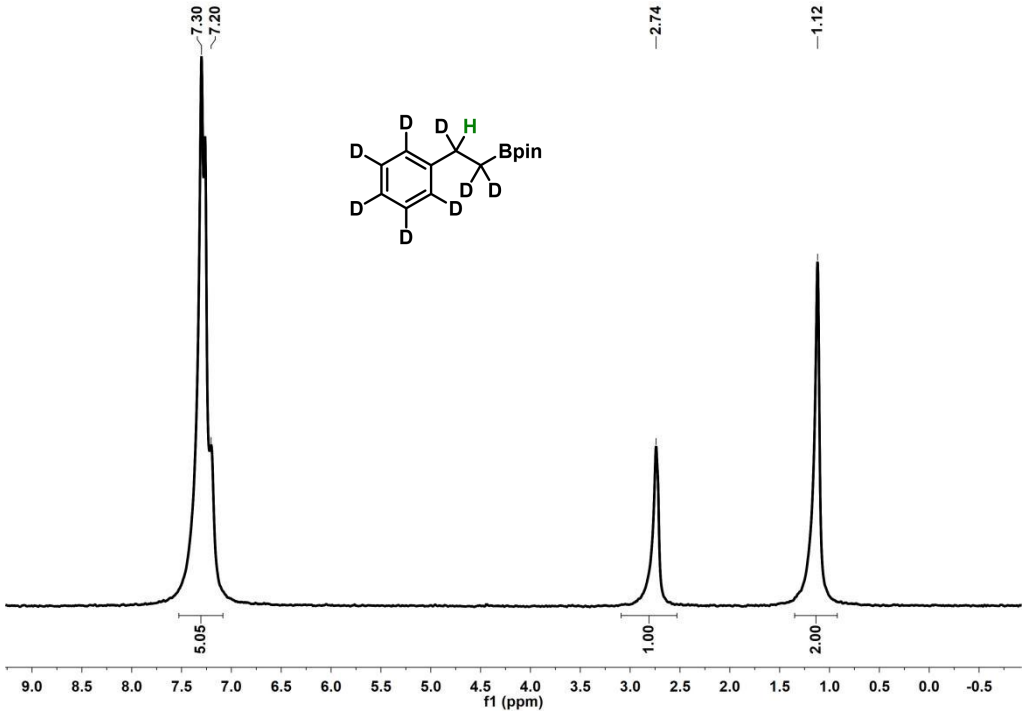


Figure S107. ^{2}D NMR spectrum of d_8-**3a** in $CHCl_3$. The deuterium-labelling experiment was conducted with d_8-styrene as substrate.

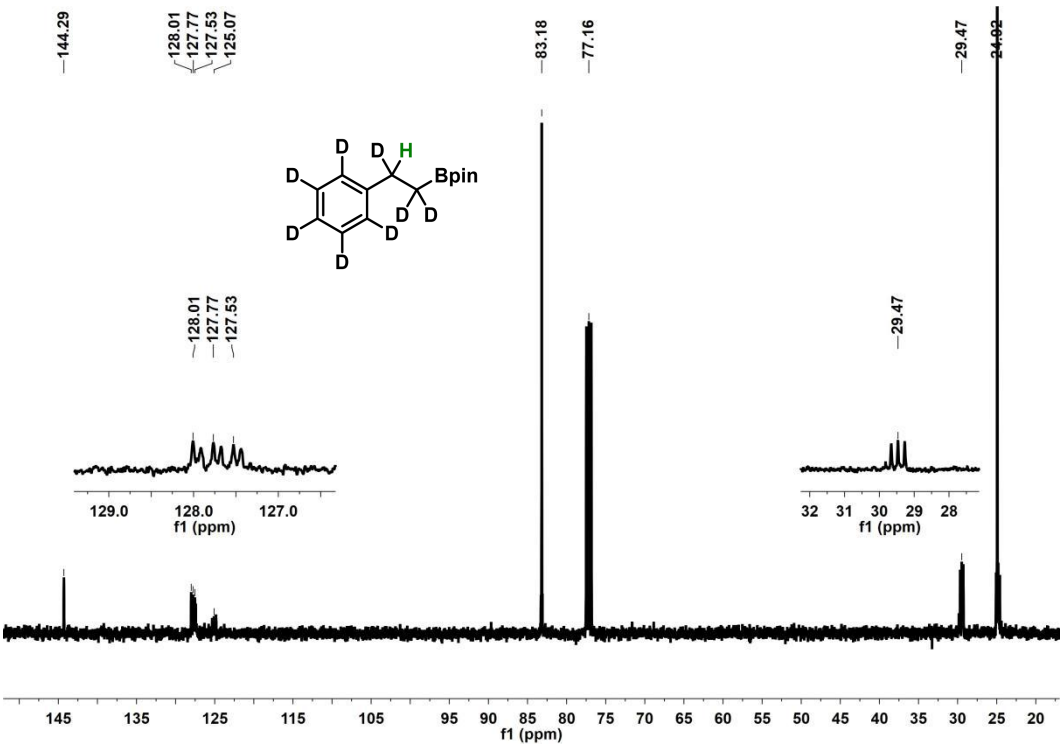


Figure S108. ^{13}C NMR spectrum of d_8-**3a** in $CDCl_3$. The deuterium-labelling experiment was conducted with d_8-styrene as substrate.

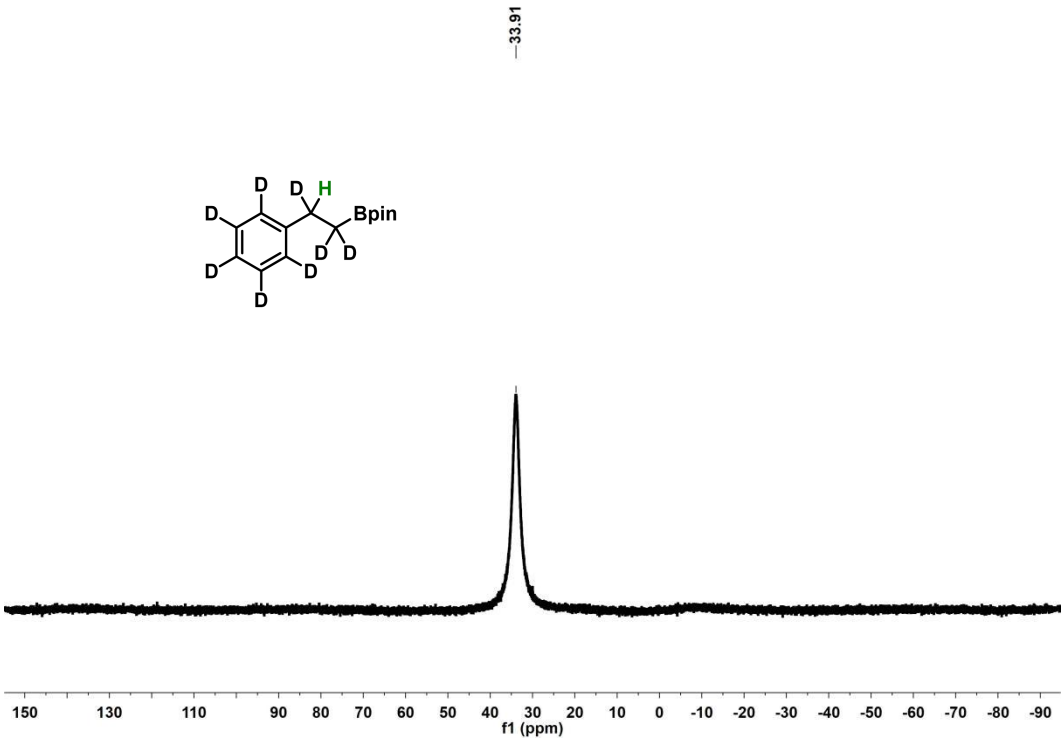
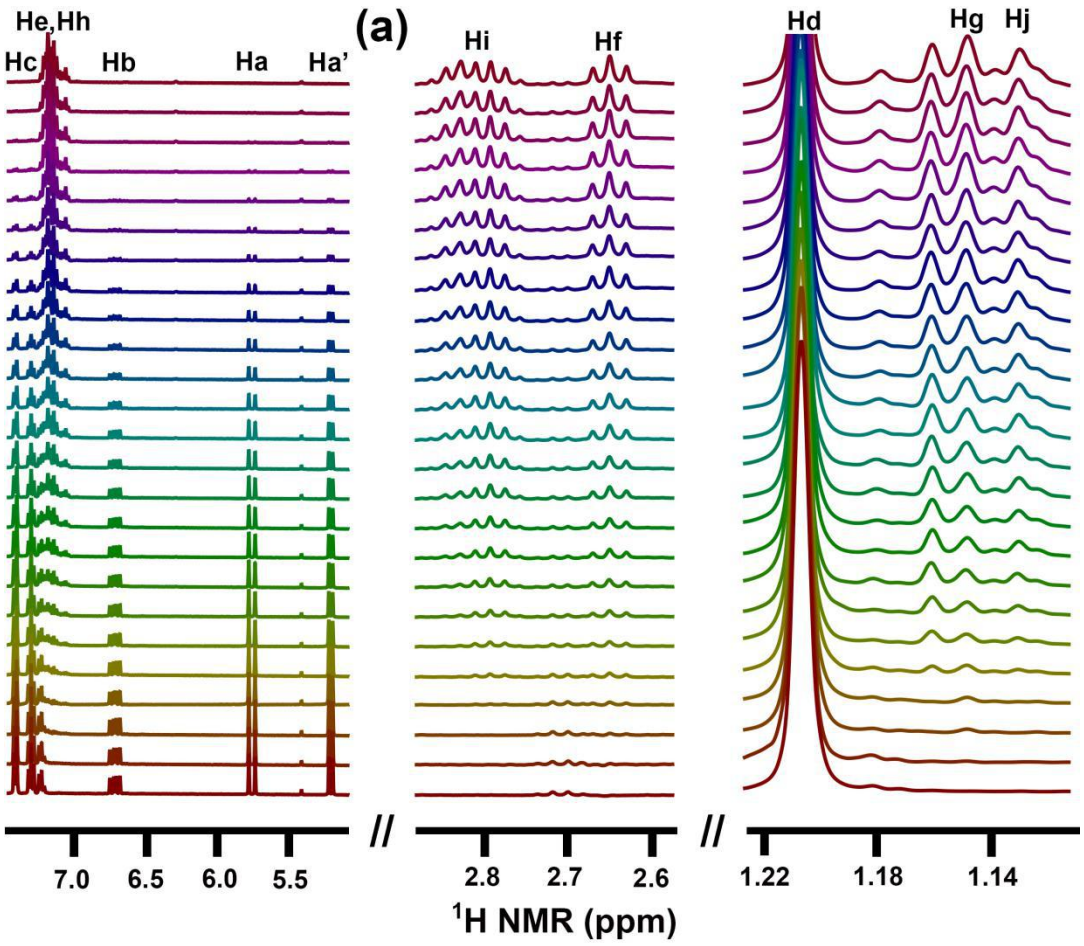
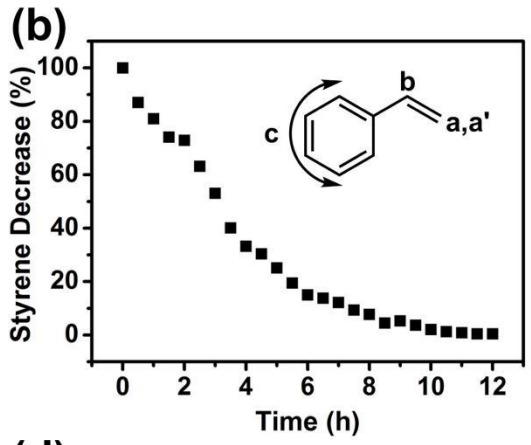
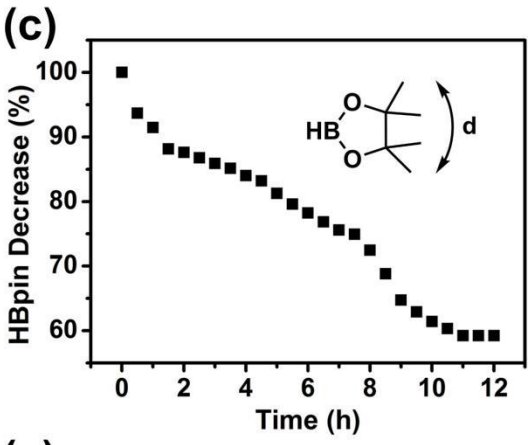
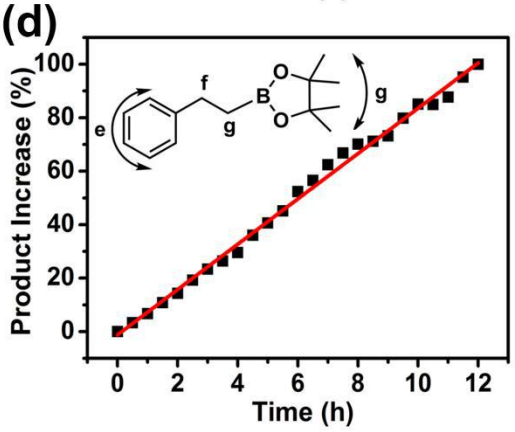


Figure S109. ^{11}B NMR spectrum of d_8-**3a** in $CDCl_3$. The deuterium-labelling experiment was conducted with d_8-styrene as substrate.


(a)
He,Hh
Hc
Hb
Ha
Ha'
Hi
Hf
Hd
Hg
Hj
7.0
6.5
6.0
5.5
2.8
2.7
2.6
1.22
1.18
1.14
^{1}H NMR (ppm)


(b)
Styrene Decrease (%)
Time (h)
c
b
a,a'


(c)
HBpin Decrease (%)
Time (h)
HB
O
O
d


(d)
Product Increase (%)
Time (h)
e
f
g
B
O
O
g

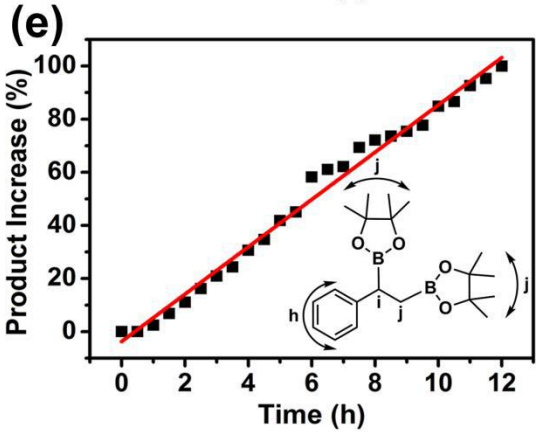

(e)
Product Increase (%)
Time (h)
j
B
O
O
h
i
j
B
O
O
j

Figure S110. *In situ* ^{1}H NMR data of electrochemical hydroboration of styrene (10 mmol) with HBpin (88 mmol). **a** ^{1}H NMR spectra were collected every 0.5 h. The test samples were made up of 0.3 mL original samples and 0.2 mL CD_3CN. Total volume of the reaction solution was 100 mL. **b** Decreased trend of styrene under electrolysis, determined by the *in situ* ^{1}H NMR data. Initial peak area of CH group at the benzyl site of styrene was defined as 100%. **c** Decreased trend of HBpin under electrolysis, determined by the *in situ* ^{1}H NMR data. Initial peak area of CH_3 group of HBpin was defined as 100%. **d** Increased trend of product **3a** under electrolysis, determined by the *in situ* ^{1}H NMR data. Final peak area of CH_2 at the benzyl site of **3a** was defined as 100%. **e** Increased trend of product **7a** under electrolysis, determined by the *in situ* ^{1}H NMR data. Final peak area of CH at the benzyl site of **7a** was defined as 100%.

IX. Cyclic Voltammogram

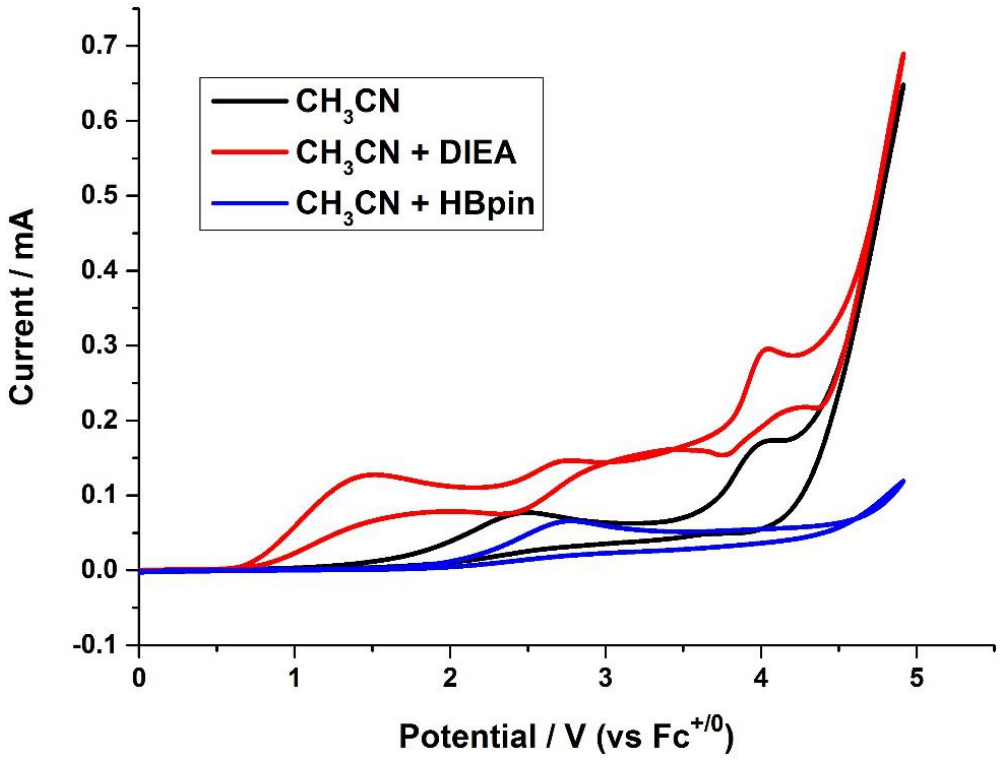


Figure S111. Cyclic voltammogram of DIEA (10 mM) and HBpin (10 mM) in ^{n}Bu$_4$NBF$_4$/CH$_3$CN at room temperature.

X. EPR Spectra

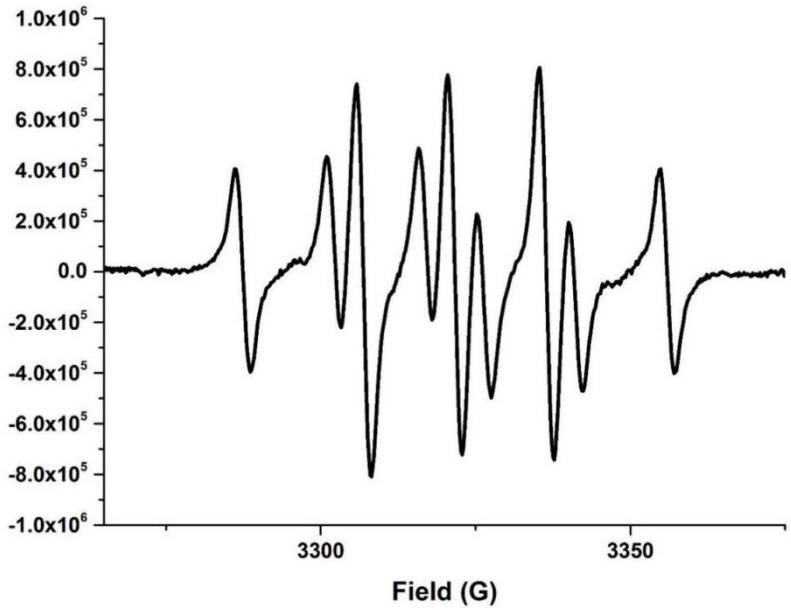


Figure S112. EPR spectrum under the standard conditions. Standard conditions: styrene (1.0 mmol), HBpin (1.1 mmol), $^{n}Bu_4NBF_4$ (20 mol%), DIEA (0.8 mmol), DMPO (1.0 mmol), Pt(+)|Pt(−), constant current (I) = 15 mA, CH_3CN:THF = 4:1 (*v/v*), the total volume of the solvent is 10 mL, N_2, rt, 0.5 h. One type of radical had been trapped by DMPO: DMPO–H.

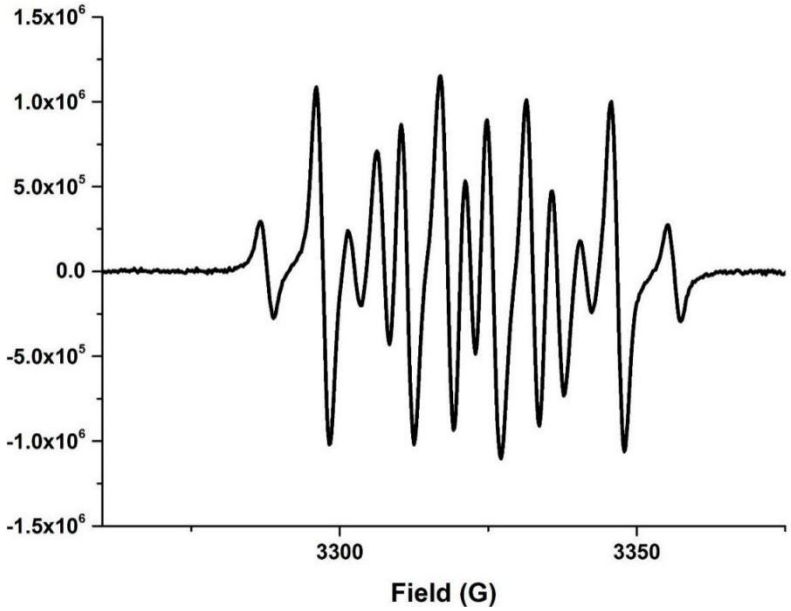


Figure S113. EPR spectrum to monitor the electrochemical reaction in the absence of HBPin. Two type of radicals had been trapped by DMPO: DMPO–H and DMPO–CH_2CN (**10**).

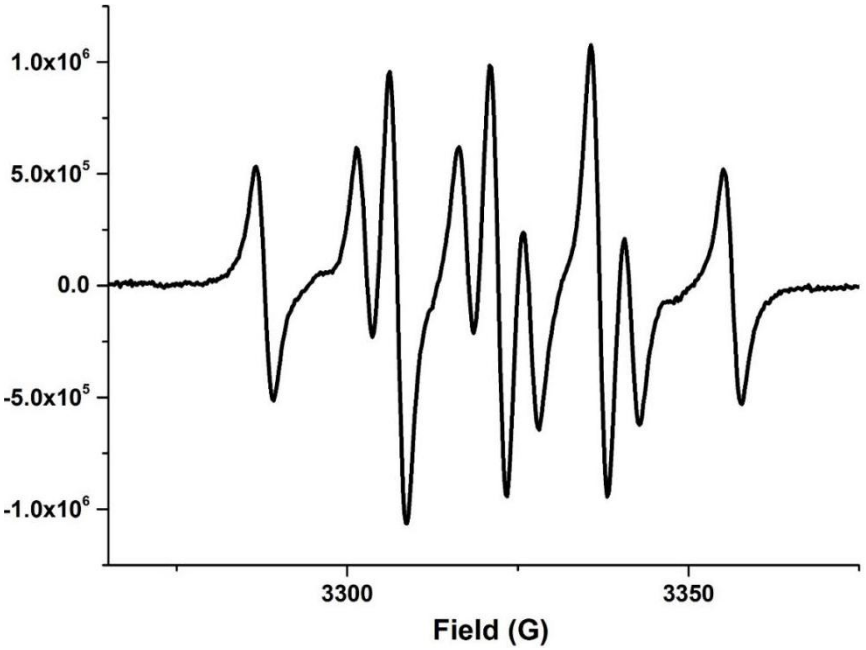


Figure S114. EPR spectrum to monitor the electrochemical reaction in the absence of styrene. One type of radical had been trapped by DMPO: DMPO–H.

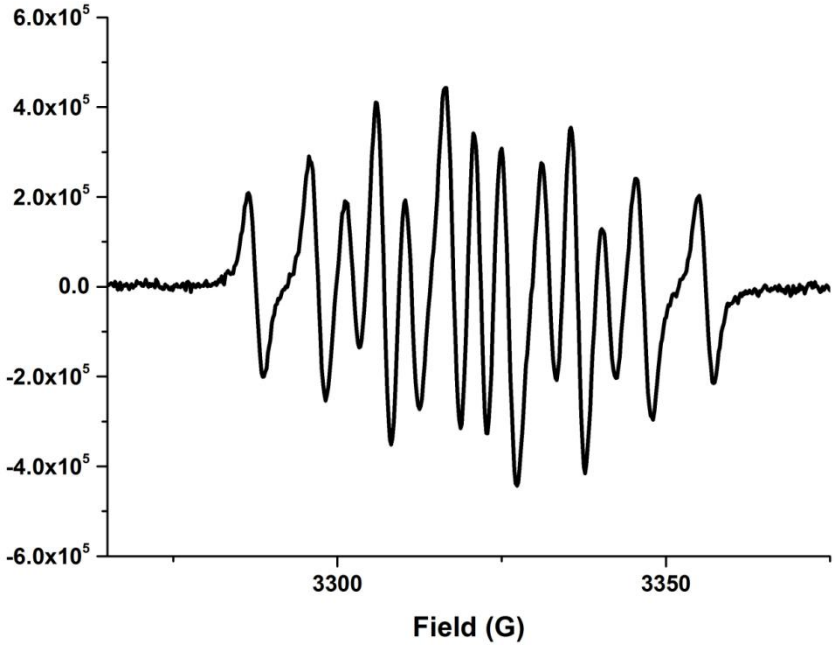


Figure S115. EPR spectrum to monitor the electrochemical reaction in the absence of styrene and HBpin. Two type of radicals had been trapped by DMPO: DMPO–H and DMPO–CH_2CN (**10**).

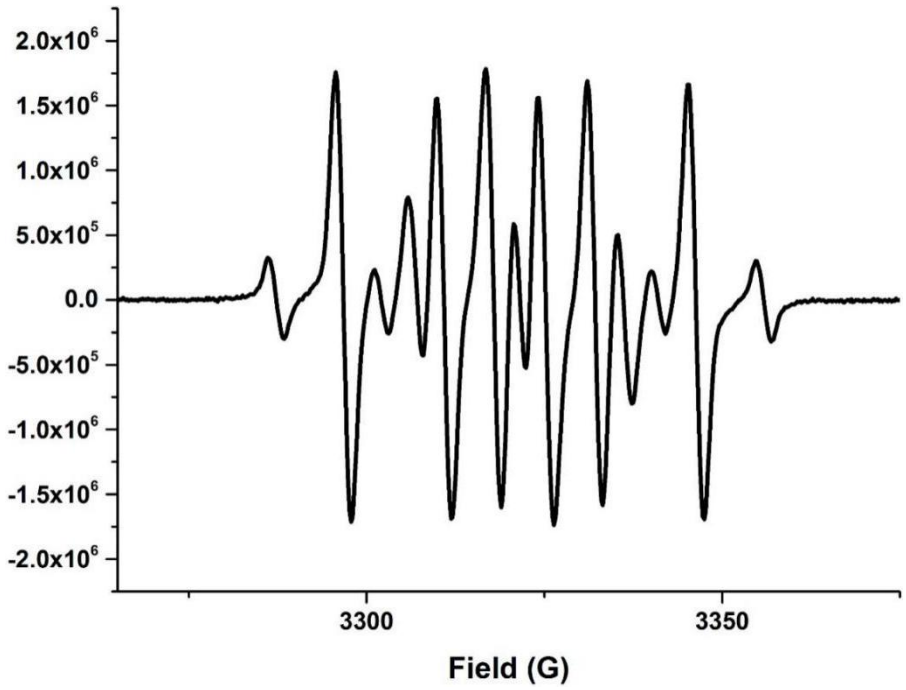


Figure S116. EPR spectrum to monitor the electrochemical reaction in the absence of styrene, HBpin and DIEA. Two type of radicals had been trapped by DMPO: DMPO–H and DMPO–CH_2CN (**10**).

XI. Mass Spectra

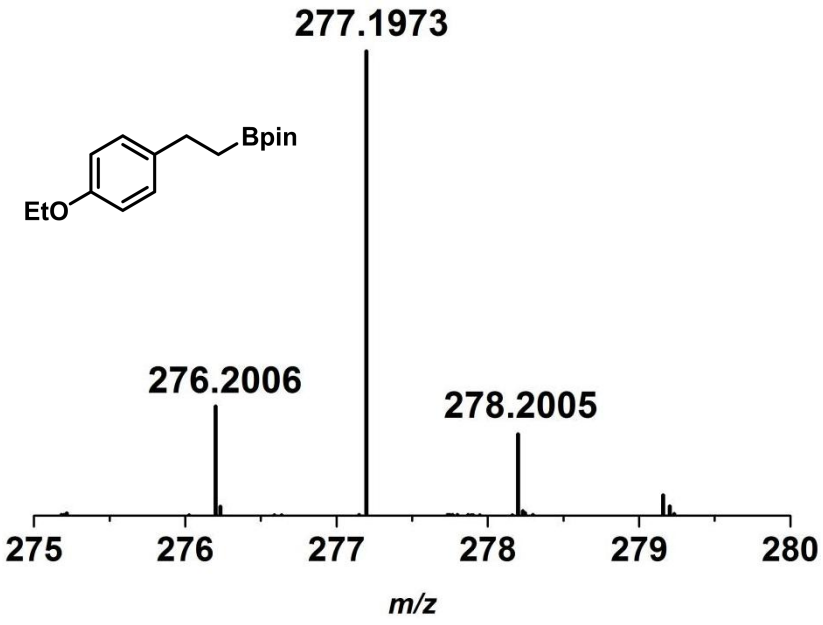


Figure S117. ESI-HRMS spectrum of **3l** in CH_3CN.

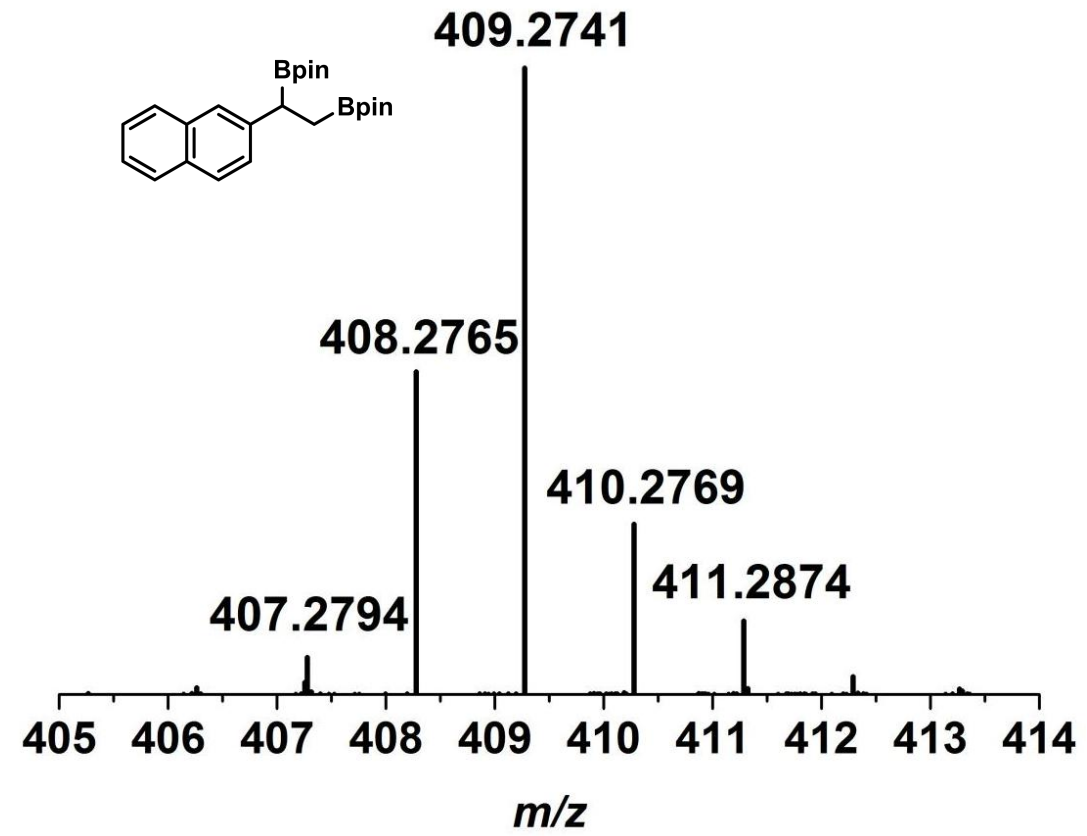


Figure S118. ESI-HRMS spectrum of **7r** in CH_3CN.

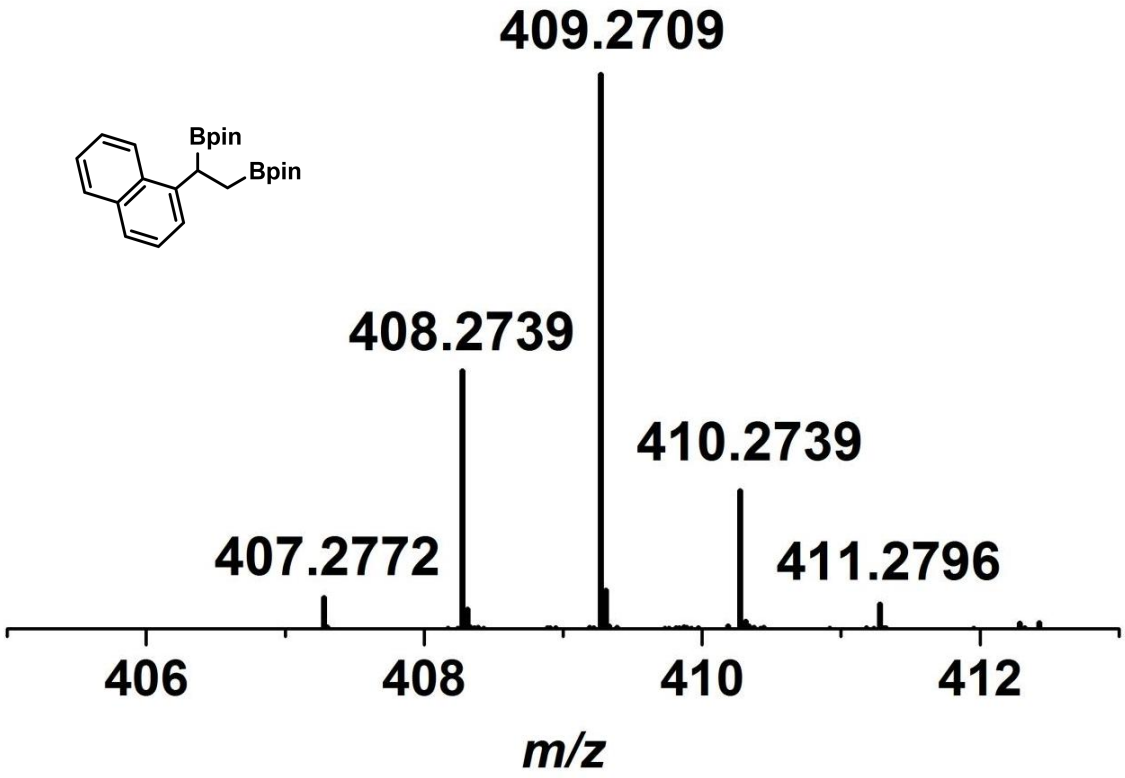


Figure S119. ESI-HRMS spectrum of **7s** in CH_3CN.

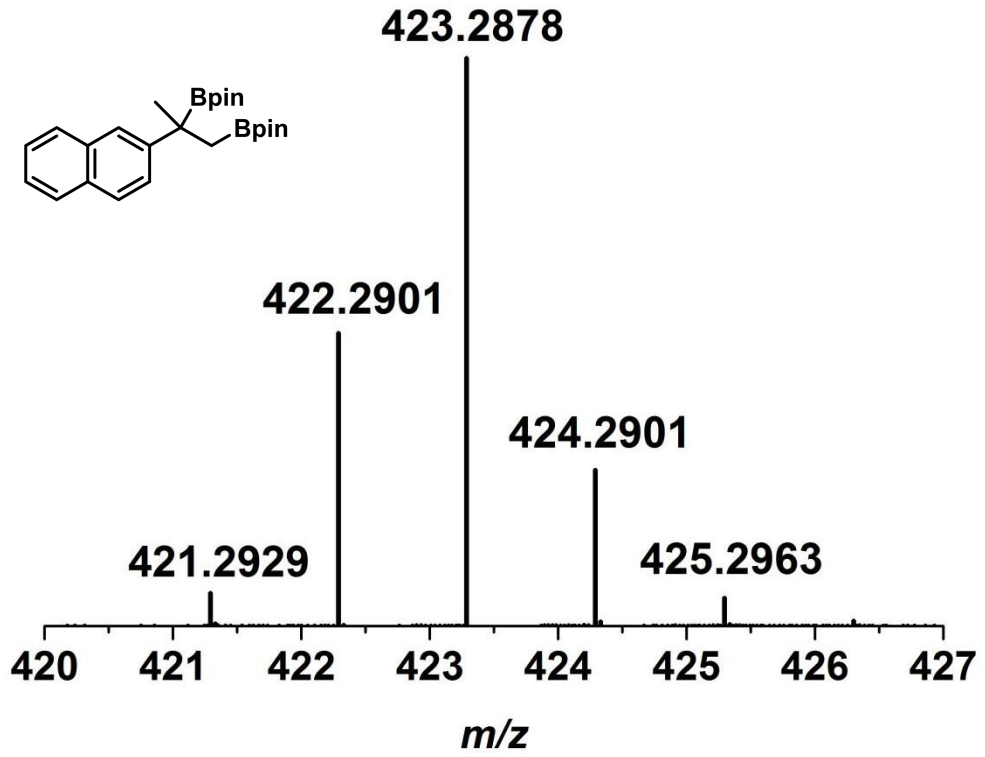


Figure S120. ESI-HRMS spectrum of **7t** in CH_3CN.

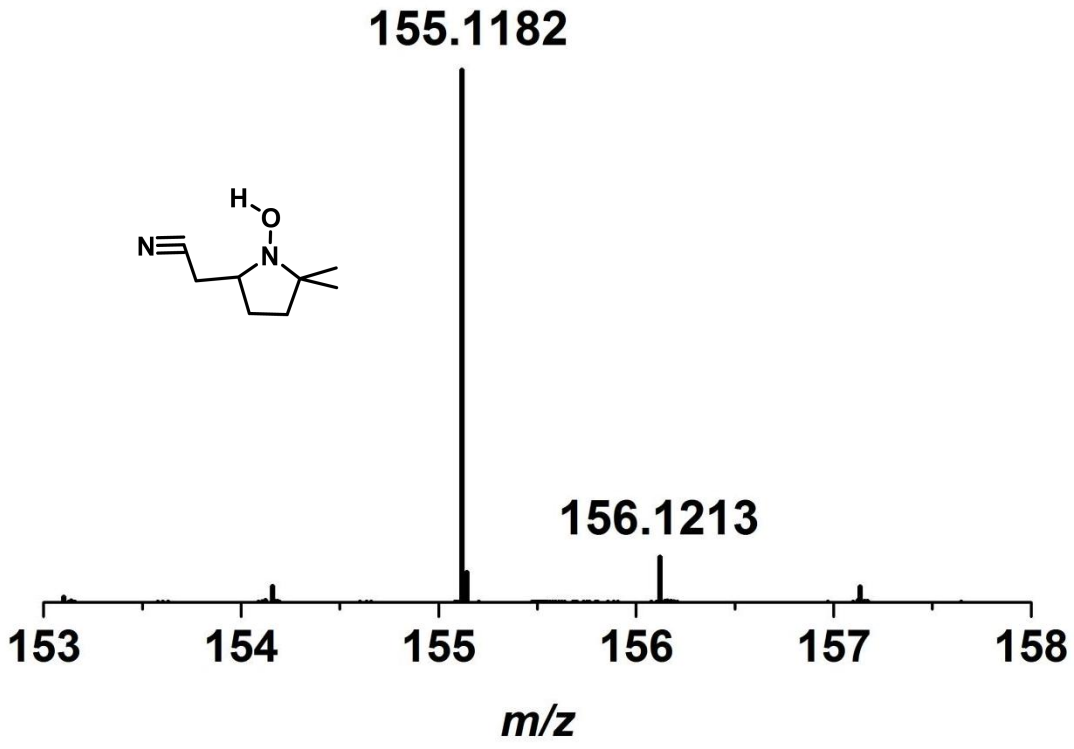


Figure S121. ESI-HRMS spectrum of reduction state of the corresponding adduct DMPO–CH_2CN (**10**) in CH_3CN/THF mixture.

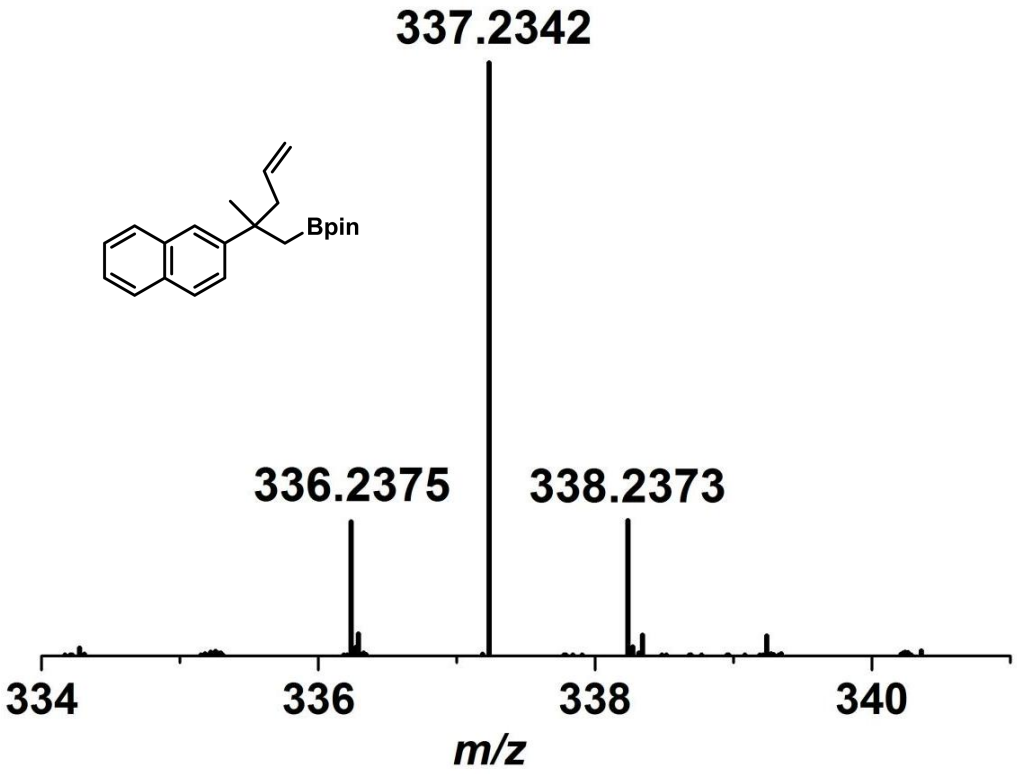


Figure S122. ESI-HRMS spectrum of **11** in CH_3CN.

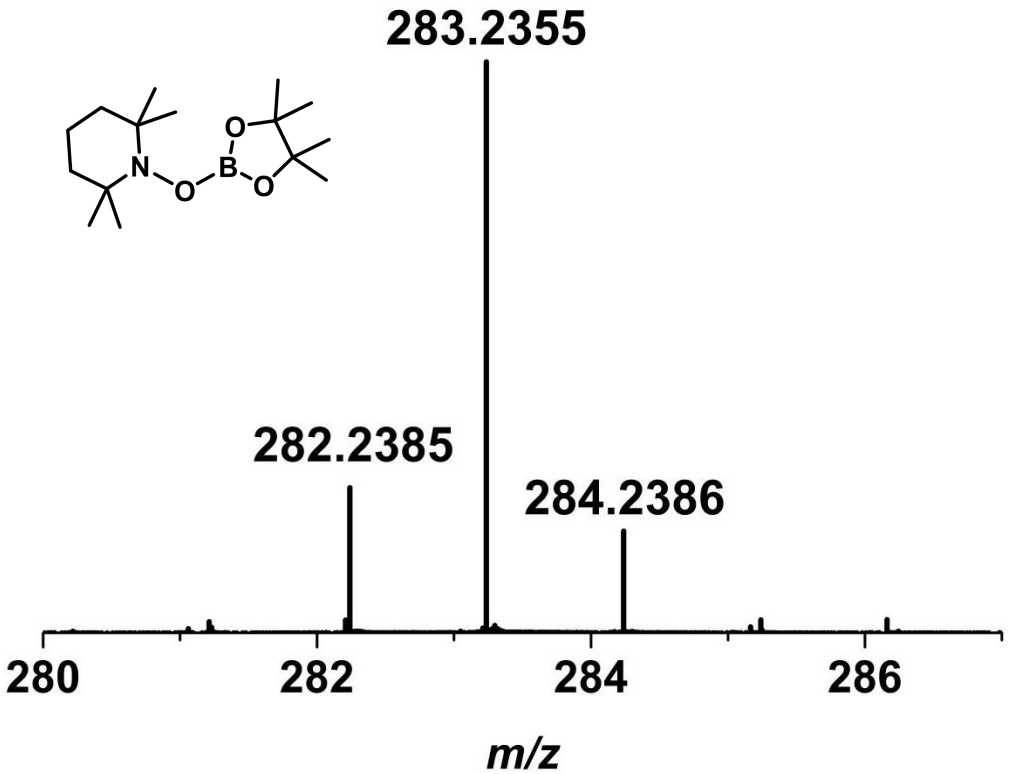


Figure S123. GC-MS spectrum of **13** in CH_3CN.

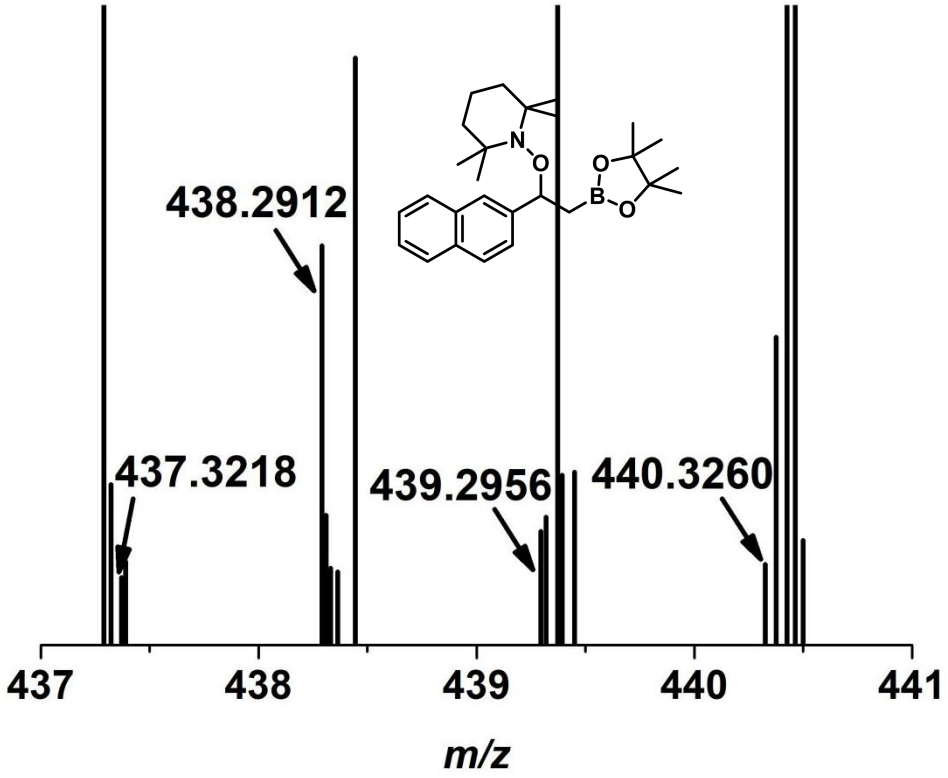


Figure S124. ESI-HRMS spectrum of **14** in CH_3CN.

XII. FT-IR (ATR) Spectra

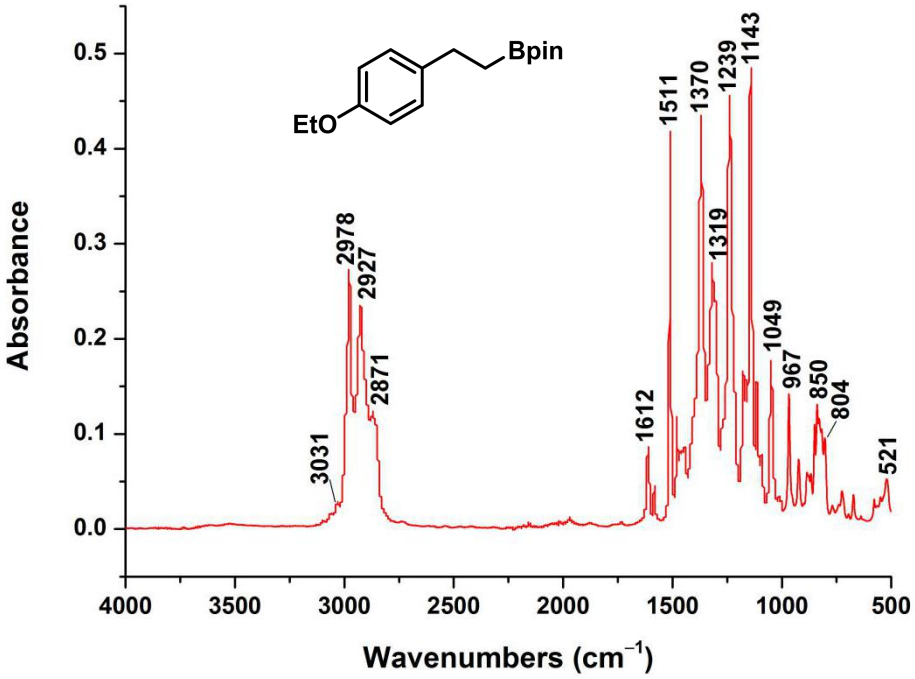


Figure S125. FT-IR (ATR) spectrum of **3l**.

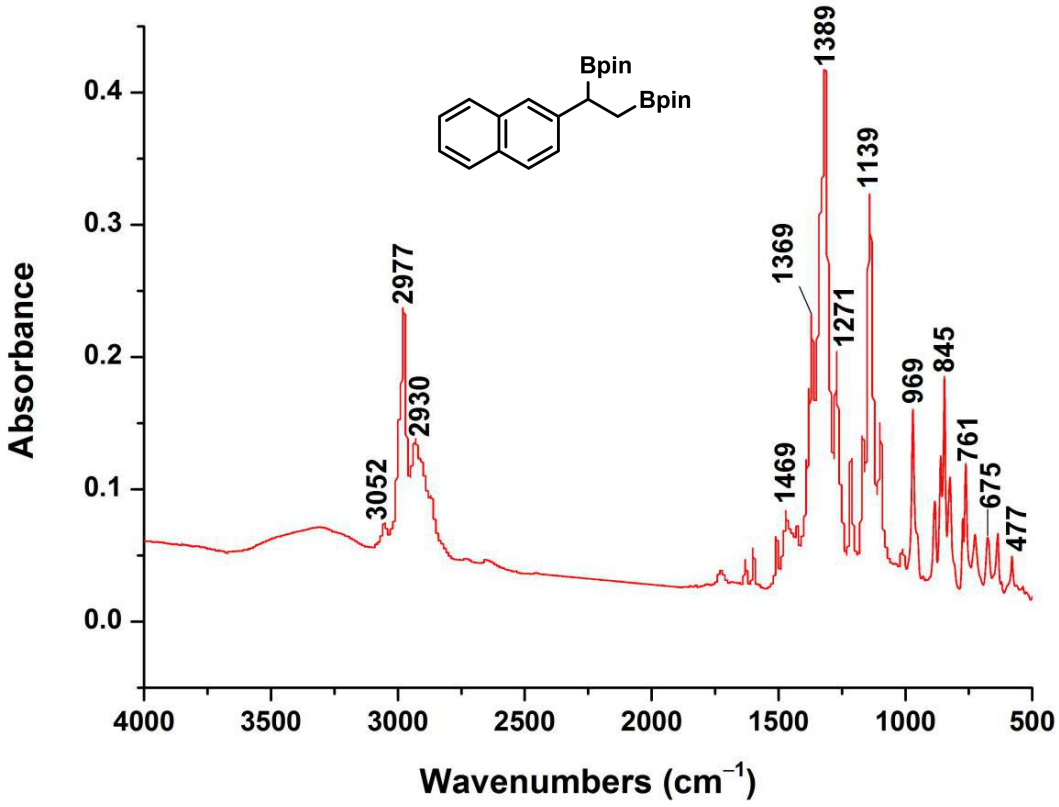


Figure S126. FT-IR (ATR) spectrum of **7r**.

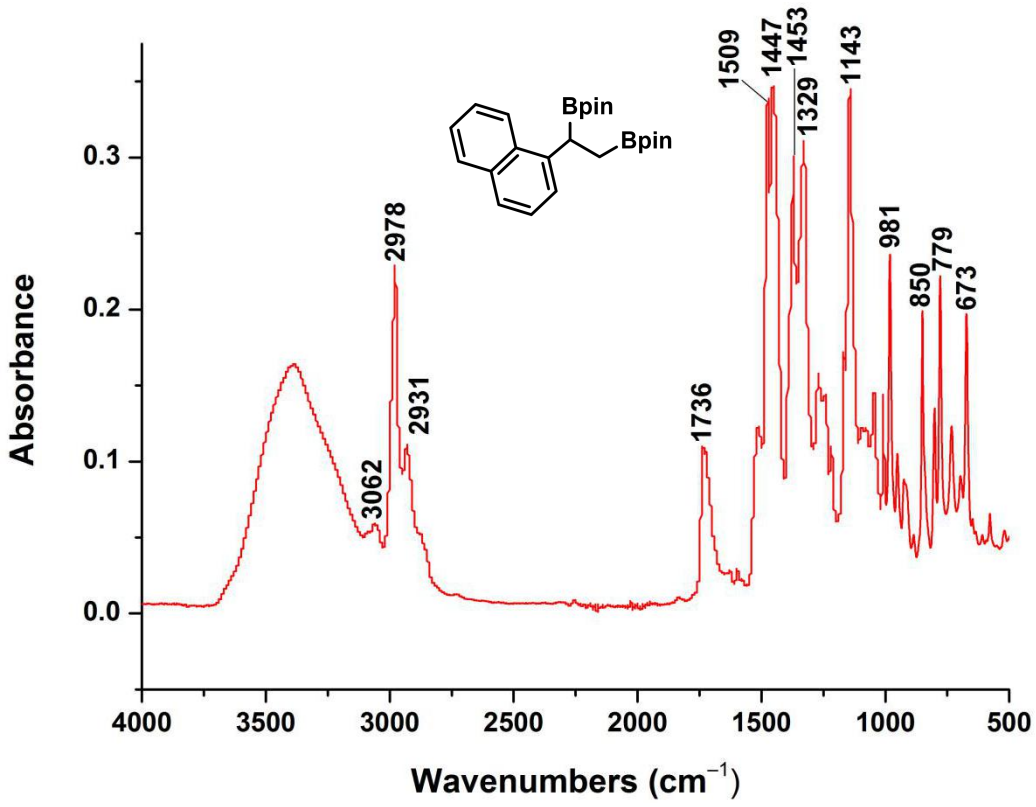


Figure S127. FT-IR (ATR) spectrum of **7s**.

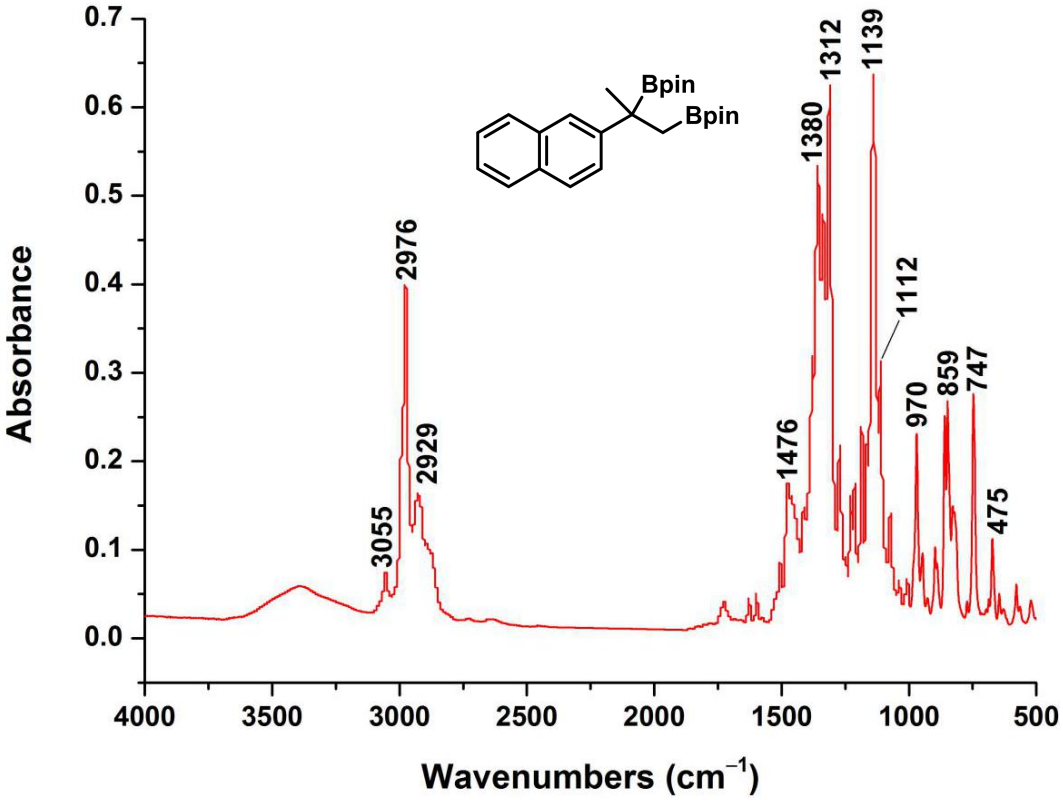


Figure S128. FT-IR (ATR) spectrum of **7t**.

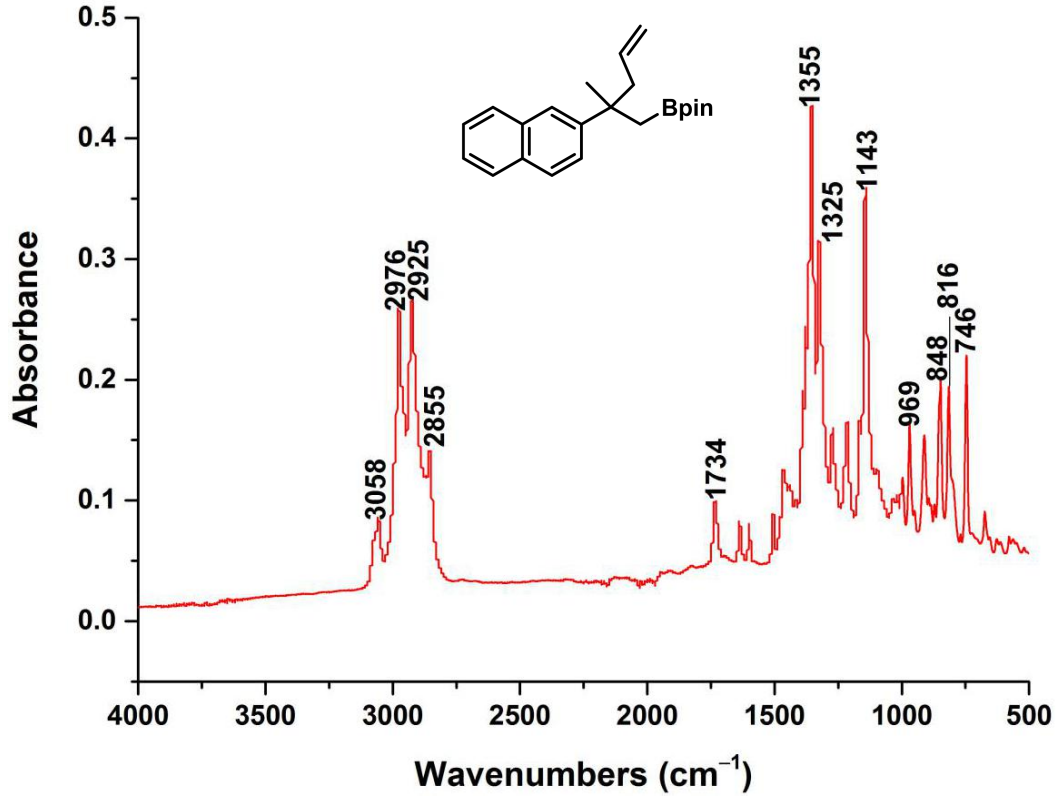


Figure S129. FT-IR (ATR) spectrum of **11**.

XIII. Proposed Electrochemical Cycle in the Absence of DIEA

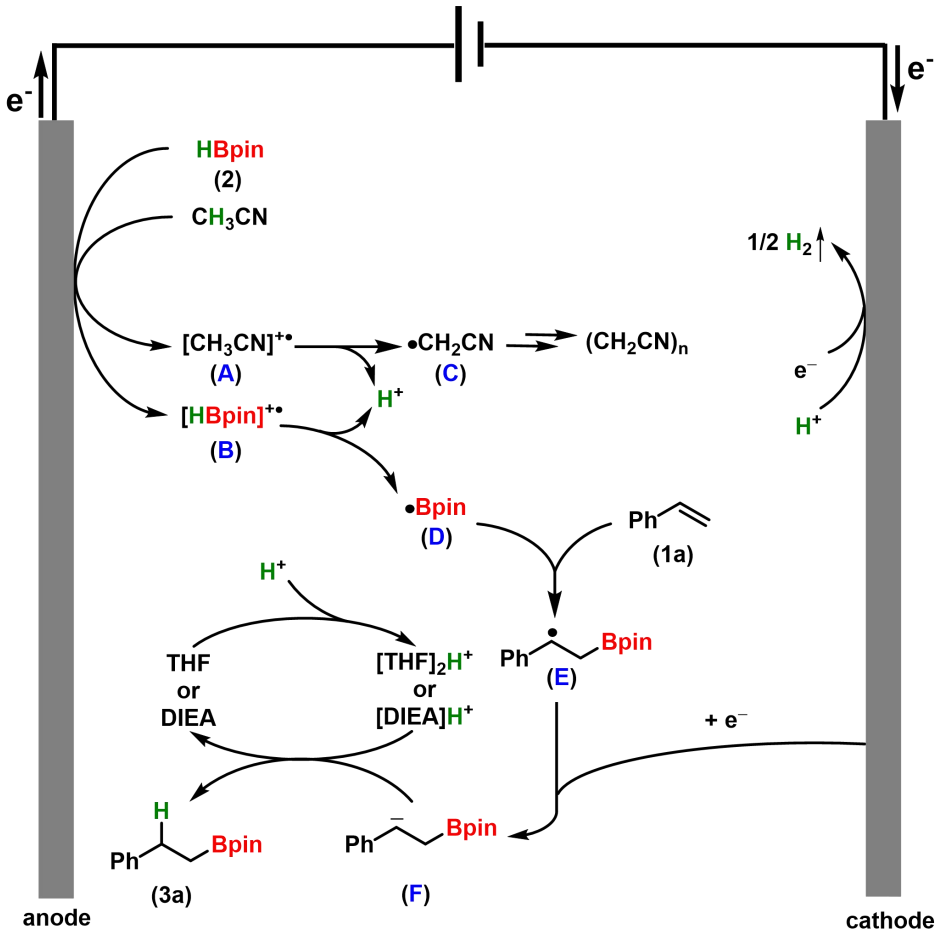


Figure S130. A possible mechanism of electrochemical hydroboration with styrene as substrate in the absence of DIEA.

XIV. Proposed Electrochemical Cycle for Diboration

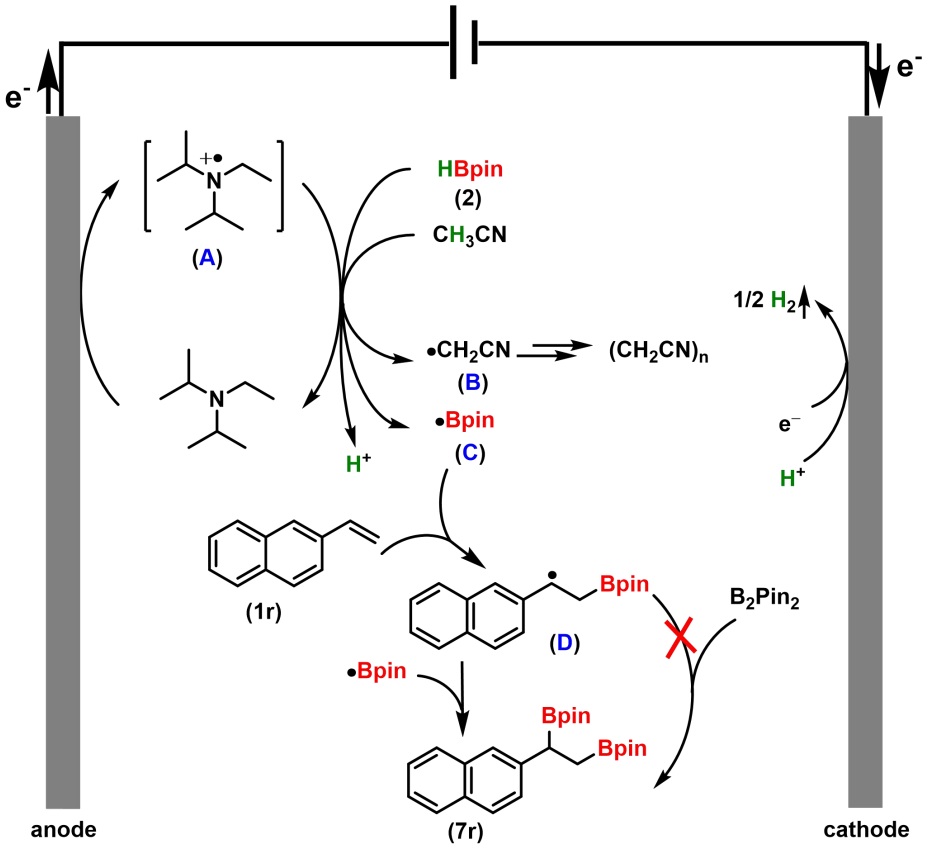


Figure S131. A possible mechanism of electrochemical hydroboration with 2-vinylphthalene as substrate.

Using $^{n}Bu_4NBF_4$ (20 mol%) as the supporting electrolyte and CH_3CN:THF (*v*:*v* = 4:1) as the mixed solvent, with the addition of 0.8 equivalent of DIEA, and 15 mA constant current at room temperature for 3 h under inert atmosphere, both hydroboration product (**3r**) and diboronate ester (**7r**) were detected with 1.0 equivalent of 2-vinylphthalene and 1.1 equivalents of HBpin as substrates (Scheme 1 in manuscript). The yield of product **7r** did not increase when additional 3.3 equivalents of B_2Pin_2 were added to this system. In addition, no diboronate esters **7r** was observed when B_2Pin_2 as the only source of boron. These results indicated that the formation of diboronate ester was not associated with B_2Pin_2 and hydroboration product could not transfer to diboronate ester in the presence of HBpin or B_2Pin_2.