Supplementary Information

Photoinduced C(sp^3)–H Borylation of Alkanes Mediated by Copper(II) Chloride

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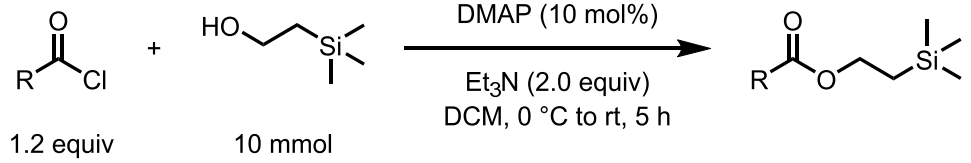
1. General Information

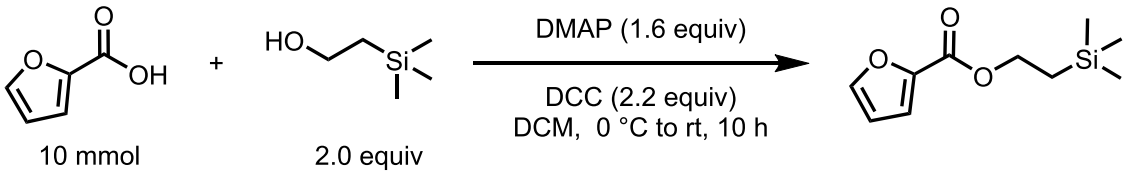
Unless otherwise noted, all solvents and reagents were used as received from commercial sources. Anhydrous MeCN was distilled over calcium hydride under nitrogen. Bis(catecholato)diboron (B_2cat_2) [98%, CAS: 13826-27-2] was purchased from Dalian Allychem Co., Ltd. Anhydrous $CuCl_2$ [98%, CAS: 7447-39-4], $FeCl_3$ [98%, CAS: 7705-08-0], $CuBr_2$ [98%, CAS: 7789-45-9], $Cu(OTf)_2$ [98%, CAS: 34946-82-2], $Cu(OAc)_2$ [98%, CAS: 142-71-2] were purchased from Adamas and used as received. B-chlorocatecholborane (ClBcat) [97%, CAS: 55718-76-8] was purchased from Sigma-Aldrich and used as received. The LED light source used for the reaction was purchased from Taobao (https://shop366082864.taobao.com/, manufacture: Zhongshan Gaodeng Lighting). ^{1}H NMR, ^{13}C NMR, ^{11}B NMR spectra were recorded on a Bruker Advance 400 or 600 spectrometer at the ambient temperature in $CDCl_3$ or MeCN-d_3. Chemical shifts (δ) are reported in parts per million (ppm) using tetramethylsilane (TMS) as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = triplet of doublets, m = multiplet). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration, Chemical shifts were referenced to the signal of residual proton solvent peak: $CDCl_3$ at δ 7.26 ppm. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm), Chemical shifts were referenced to residual solvent peak: $CDCl_3$ at δ 77.16 ppm. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2010 Pro series GC system equipped with a flame-ionization detector and an Agilent HP-1 (30 m × 0.32 mm ID × 0.25 μm df) column or a Shimadzu SH-1701 (30 m × 0.32 mm ID × 0.25 μm df) column using mesitylene as an internal standard, added during reaction workup. GC–MS analyses were performed on Thermo Scientific AS 3000 Series GC–MS System. Infrared spectra were recorded on a PerkinElmer Frontier FTIR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a Thermo Scientific Q Exactive GC Orbitrap GC–MS/MS System using electron ionization (EI) or a Thermo Scientific Liquid Chromatography & Electrostatic Field Orbitrap Mass Spectrometer using atmospheric pressure chemical ionization (APCI). Analytical TLC was done on precoated silica gel plates. Organic solutions were concentrated under reduced pressure on an IKA rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200–300 mesh).

2. General Procedures

2.1 Synthesis of Silane Raw Materials

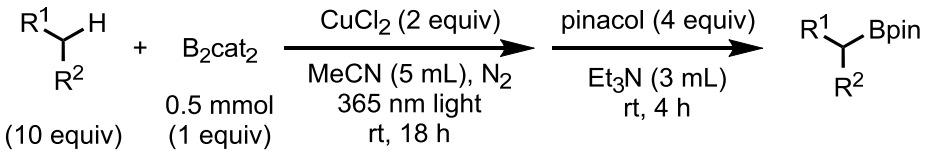


General Procedure A: To a 100 mL oven-dried flask equipped with a magnetic stir bar was charged with 2-(trimethylsilyl) ethane-1-ol (10.0 mmol, 1.0 equiv), Et_3N (10.0 mmol, 2.0 equiv) and DMAP (0.50 mmol, 10 mol%), anhydrous CH_2Cl_2 (30 mL). After cooling the reaction mixture to 0 ℃, acyl chloride (12.0 mmol, 1.2 equiv) was slowly added to the solution. The mixture was stirred at rt for 5 hours. After completion, the reaction mixture was quenched with water and extracted with DCM (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give the corresponding product.



General Procedure B: To a 100 ml oven-dried flask equipped with a magnetic stir bar was charged with 2-(trimethylsilyl) ethane-1-ol (20 mmol, 2 equiv), 2-furoic acid (10.0 mmol, 1.0 equiv), DMAP (16.0 mmol, 1.6 equiv) and anhydrous CH_2Cl_2 (30 mL). After cooling to 0 ℃, *N*,*N*'-dicyclohexylcarbodiimide (DCC, 22 mmol, 2.2 equiv) was slowly added to the solution and the mixture was stirred at 0 ℃ for 1 hour and then at rt for 10 hours. After removing the sediment, the filtrate was diluted with CH_2Cl_2 (40 mL) and water (40 mL). After separating the organic layer, the water layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give the corresponding product.

2.2 C(sp^3)–H Borylation of Alkanes and Silane



General Procedure C: To an oven-dried 25 mL Schlenk tube charged with a stir bar was added B_2cat_2 (119 mg, 0.5 mmol, 1.0 equiv) and $CuCl_2$ (134 mg, 1.0 mmol, 2.0 equiv). The vessel was evacuated and filled with nitrogen (three cycles). Anhydrous MeCN (5 mL) was then added followed by the alkane (5.0 mmol, 10 equiv) under a nitrogen atmosphere. The reaction mixture was irradiated with 365 nm (2 × 40 W) for 18 hours. A clip fan was placed over the vials to cool down the reaction system. After completion, pinacol (236 mg, 2.0 mmol, 4.0 equiv) and Et_3N (3 mL) were added and the reaction mixture was stirred for additional 4 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography.

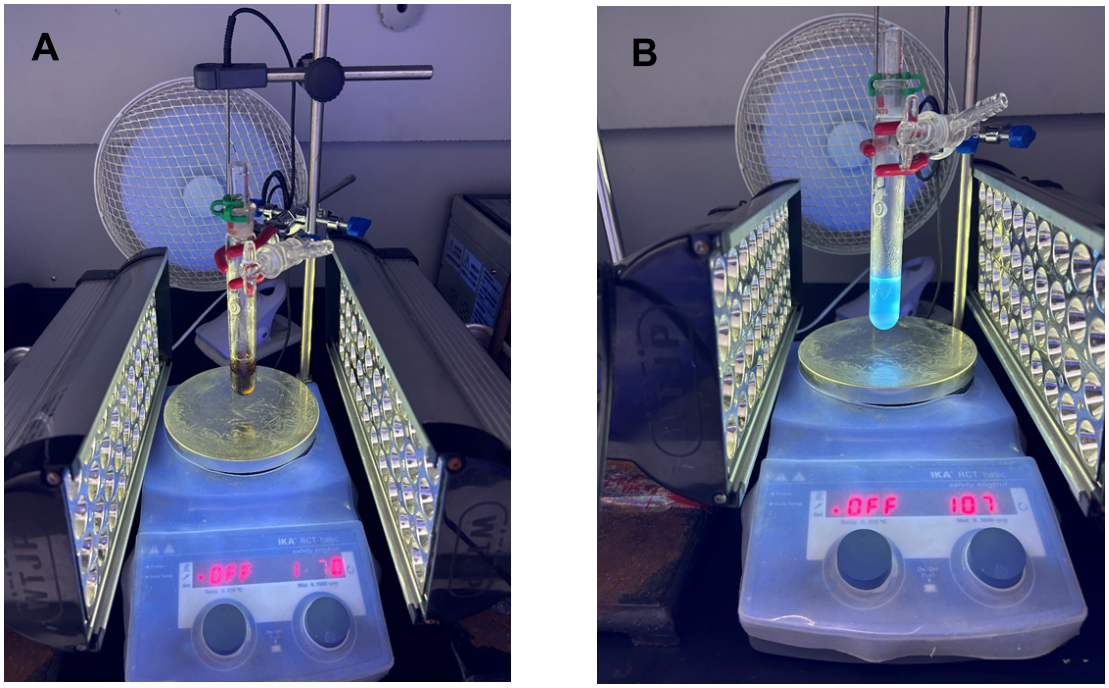
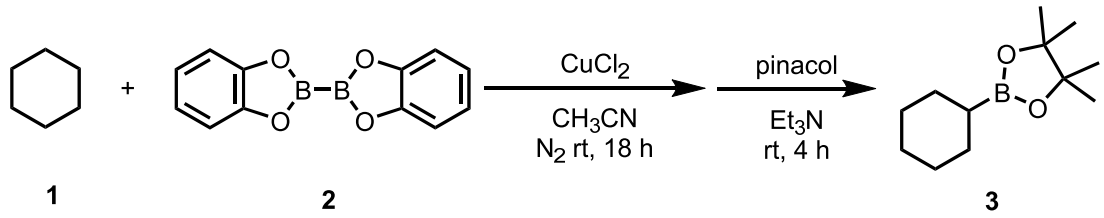


Figure S1. The set-up for the reaction. (A) Initial state; (B) The reaction state after 2 h.

2.3 Reaction Optimizations

Table S1 Screening of wavelength of light[a]

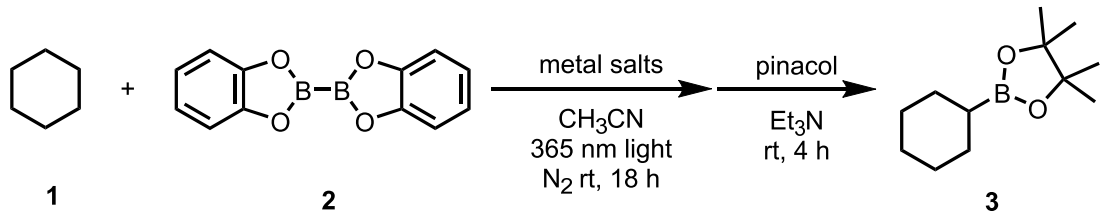


1 **2** **3**

Entry	Wavelength of light	Yield (%)[b]
1	395 nm	45
2	456 nm	12
3	365 nm	81
4	w/o light	N.R.

[a] Reaction conditions: **1** cyclohexane, **1** (5 mmol, 10 equiv), B_2cat_2, **2** (0.5 mmol, 1 equiv), $CuCl_2$ (1 mmol, 2 equiv), MeCN (5 mL), LED light, rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

Table S2 Screening of metal salts[a]

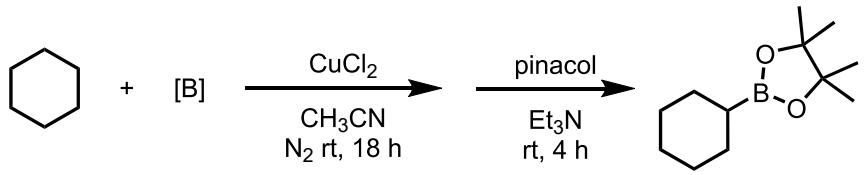


1 **2** **3**

Entry	Metal salts	Yield (%)[b]
1	$Cu(OTf)_2$	N.R.
2	$CuBr_2$	Trace
3	$Cu(OAc)_2$	N.R.
4	$FeCl_3$	36
5	$CrCl_3·6H_2O$	N.R.
6	$CuCl_2·2H_2O$	N.R.

[a] Reaction conditions: **1** cyclohexane, **1** (5 mmol, 10 equiv), B_2cat_2, **2** (0.5 mmol, 1 equiv), metal salts (1 mmol, 2 equiv), MeCN (5 mL), 365 nm LEDs (2 × 40 W), rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

Table S3 Screening of boron reagents[a]

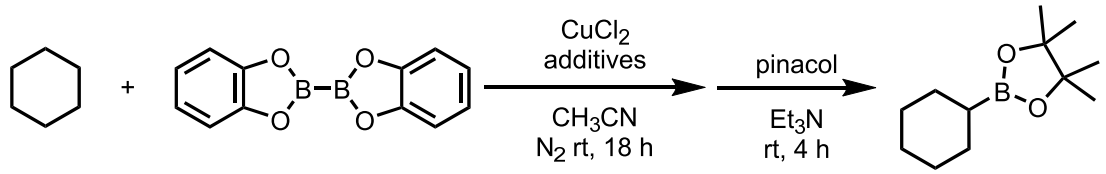


1 3

Entry	Boron reagents [B]	Yield (%)[b]
1	B_2pin_2	Trace
2	B_2nep_2	Trace
3	HBpin	N.R.
4	NHC-BH_3	N.R.

[a] Reaction conditions: **1** cyclohexane, **1** (5 mmol, 10 equiv), boron reagents (0.5 mmol, 1 equiv), $CuCl_2$ (1 mmol, 2 equiv), MeCN (5 mL), 365 nm LEDs (2 × 40 W), rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

Table S4 Screening of acids and bases additives[a]

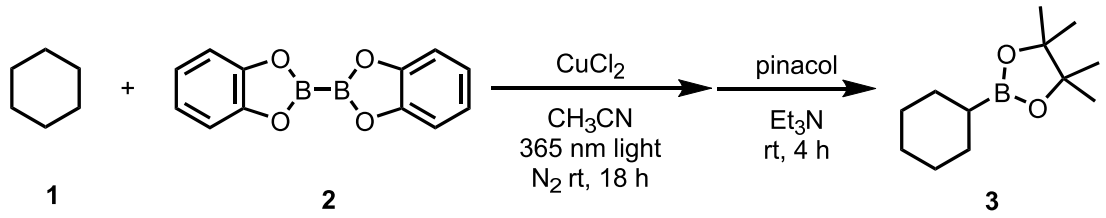


1 2 3

Entry	Additives	Yield (%)[b]
1	$NaHCO_3$	N.R.
2	K_2HPO_4	N.R.
3	Na_2CO_3	N.R.
4	HCl	62
5	CH_3COOH	Trace
6	CF_3COOH	Trace

[a] Reaction conditions: cyclohexane, **1** (5 mmol, 10 equiv), B_2cat_2, **2** (0.5 mmol, 1 equiv), $CuCl_2$ (1 mmol, 2 equiv), additives (1 mmol, 2 equiv), MeCN (5 mL), 365 nm LEDs (2 × 40 W), rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

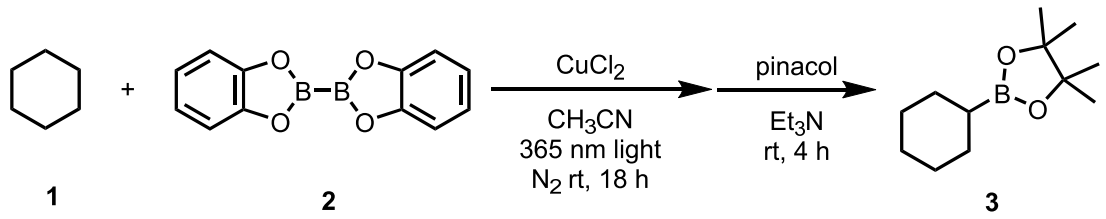
Table S5 Screening of equivalents of $CuCl_2$[a]



Entry	$CuCl_2$ (x equiv)	Yield (%)[b]
1	0.2 equiv	25
2	0.5 equiv	32
3	1.0 equiv	45
4	2.0 equiv	81
5	3.0 equiv	85

[a] Reaction conditions: cyclohexane, **1** (5 mmol, 10 equiv), B_2cat_2, **2** (0.5 mmol, 1 equiv), $CuCl_2$ (x equiv), additives (1 mmol, 2 equiv), MeCN (5 mL), 365 nm LEDs (2 × 40 W), rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

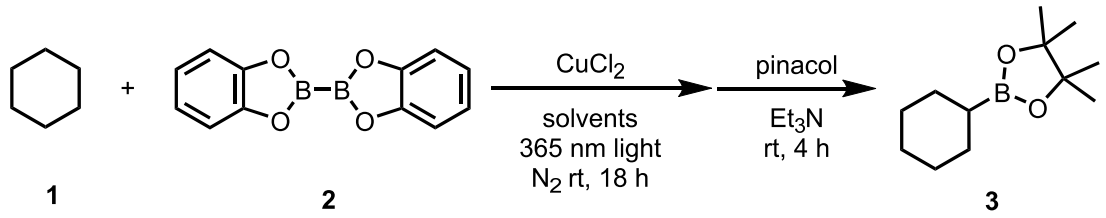
Table S6 Screening of equivalents of cyclohexane[a]



Entry	**1** (x equiv)	Yield (%)[b]
1	20 equiv	92
2	10 equiv	81
3	5 equiv	28
4	2 equiv	Trace

[a] Reaction conditions: cyclohexane, **1** (x equiv), B_2cat_2, **2** (0.5 mmol, 1 equiv), $CuCl_2$ (1 mmol, 2 equiv), additives (1 mmol, 2 equiv), MeCN (5 mL), 365 nm LEDs (2 × 40 W), rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

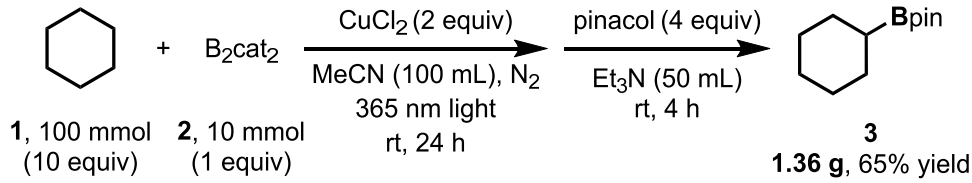
Table S7 Screening of solvents[a]



Entry	Solvents	Yield (%)[b]
1	CH_3CN	81(70)
2	MeOH	N.R.
3	Acetone	17
4	NMP	N.R.
5	CH_2Cl_2	Trace
6	EA	N.R.
7	Toluene	N.R.
8	DMF	N.R.
9	DMAc	N.R.
10	DMSO	N.R.
11	THF	Trace
12	1,4-Dioxane	N.R.
13	MTBE	N.R.

[a] Reaction conditions: cyclohexane, **1** (5 mmol, equiv), B_2cat_2, **2** (0.5 mmol, 1 equiv), $CuCl_2$ (1 mmol, 2 equiv), additives (1 mmol, 2 equiv), MeCN (5 mL), 365 nm LEDs (2 × 40 W), rt, nitrogen atmosphere, 18 h, then pinacol (2 mmol, 4 equiv), Et_3N (3 mL), rt, 4 h. [b] Yields were measured by GC using mesitylene as an internal standard.

2.4 Gram-Scale Synthesis



To an oven-dried 250 mL Schlenk tube with a stir bar was added B_2cat_2 (2.38 g, 10 mmol, 1.0 equiv) and $CuCl_2$ (2.69 g, 20 mmol, 2.0 equiv). The vessel was evacuated and filled with nitrogen (three cycles). Anhydrous MeCN (100 mL) was then added followed by the cyclohexane (8.42 g, 100.0 mmol, 10 equiv) under a nitrogen atmosphere. The reaction mixture was irradiated with 365 nm (2 × 40 W) for 24 hours. After completion, pinacol (4.73 g, 40.0 mmol, 4.0 equiv) and Et_3N (50 mL) were added and the reaction mixture was stirred for additional 4 hours. Then, the reaction was quenched with water (40 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; 50:1 to 30:1 PE: EA) to give the desired cyclohexyl boronic acid pinacol ester (1.36 g, 65%).

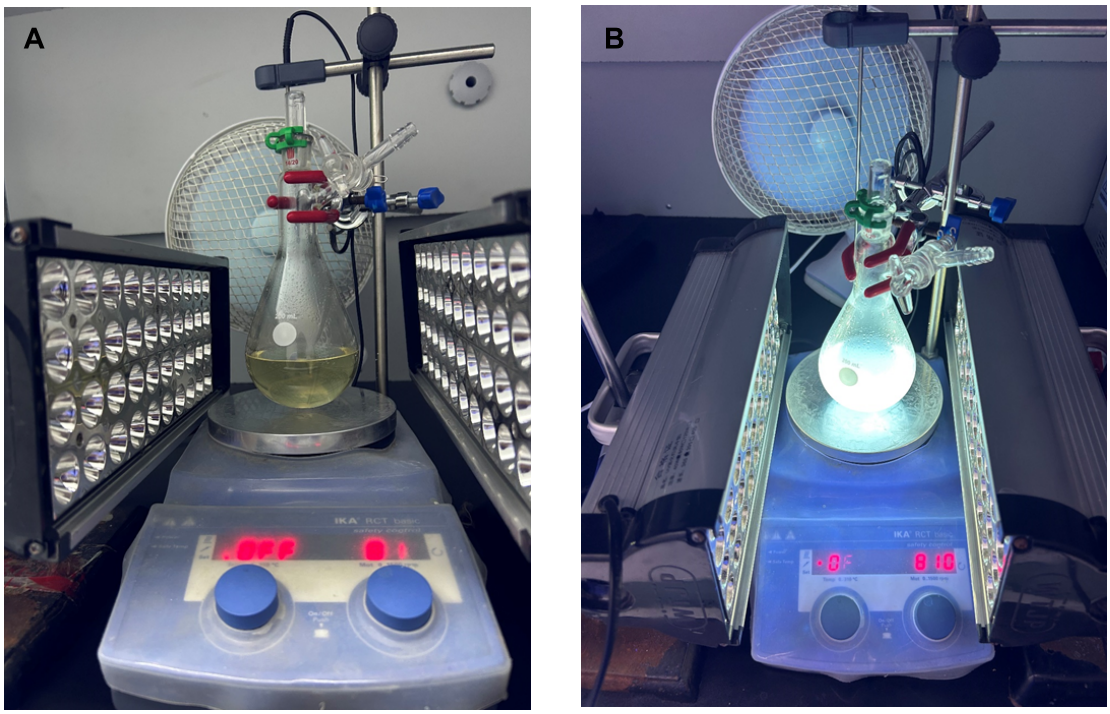
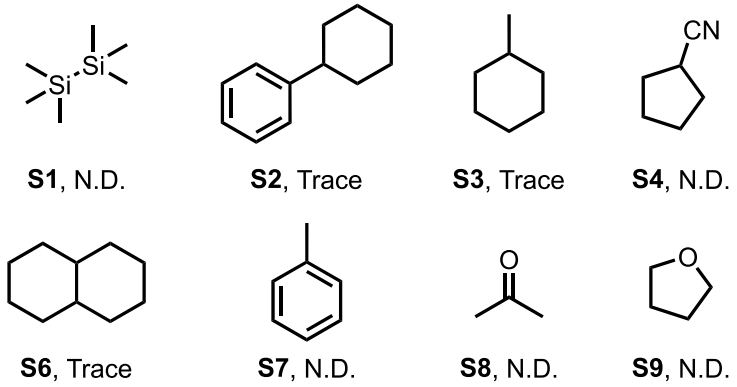


Figure S2. The set-up for a gram-scale synthesis of product **3**. (A) Initial state; (B) The reaction processing.

2.5 Unsuccessful or Low Yielding Substrates



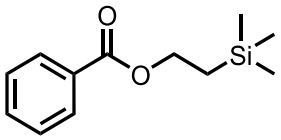
S1, N.D. **S2**, Trace **S3**, Trace **S4**, N.D.

S6, Trace **S7**, N.D. **S8**, N.D. **S9**, N.D.

Figure S3. Unsuccessful or low yielding substrates.

3. Characterization Data

3.1 Characterization Data for ester Data of Silanes Raw Materials



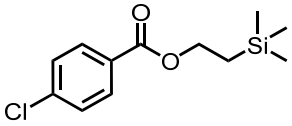
2-(Trimethylsilyl)ethyl benzoate (S10)

Prepared according to **General Procedure A** on 10.0 mmol scale. The crude residue was purified by flash column chromatography (SiO_2; 10:1 PE: EA) to afford 2-(trimethylsilyl)ethyl benzoate (1.67 g, 75%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.48 – 4.36 (m, 2H), 1.18 – 1.09 (m, 2H), 0.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 132.8, 130.8, 129.6, 128.4, 63.3, 17.6, −1.3.

All data matched that reported in the literature.[1]



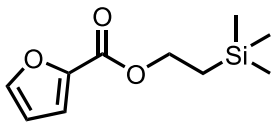
2-(Trimethylsilyl)ethyl 4-chlorobenzoate (S11)

Prepared according to **General Procedure A** on 10.0 mmol scale. The crude residue was purified by flash column chromatography (SiO_2; 10:1 PE: EA) to afford 2-(trimethylsilyl)ethyl 4-chlorobenzoate (1.82 g, 71%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 4.45 – 4.38 (m, 2H), 1.16 – 1.08 (m, 2H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 139.3, 131.0, 129.3, 128.8, 63.7, 17.6, −1.3.

All data matched that reported in the literature.[2]



2-(Trimethylsilyl)ethyl furan-2-carboxylate (S12)

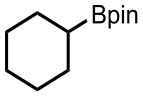
Prepared according to **General Procedure B** on 10.0 mmol scale. The crude residue was purified by flash column chromatography (SiO2; 10:1 PE: EA) to afford 2-(trimethylsilyl)ethyl furan-2-carboxylate (1.70 g, 80%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.14 (s, 1H), 6.51 – 6.45 (m, 1H), 4.41 (s, 2H), 1.17 – 1.05 (m, 2H), 0.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.2, 145.2, 117.6, 111.8, 63.4, 17.6, −1.4.

All data matched that reported in the literature.[3]

3.2 Characterization Data of Borylation Products



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

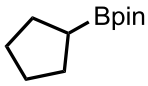
Cyclohexane (421 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 30:1 PE: EA) to afford boronic ester **3** (73.5 mg, 70%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.68 – 1.51 (m, 5H), 1.37 – 1.23 (m, 5H), 1.21 (s, 12H), 1.10 – 0.96 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 28.1, 27.3, 26.9, 24.9.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.0.

All data matched that reported in the literature.[3]



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

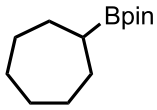
Cyclopentane (350 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **4** (66.2 mg, 68%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 – 1.68 (m, 2H), 1.64 – 1.36 (m, 6H), 1.23 (s, 12H), 1.20 – 1.10 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 28.6, 27.0, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.7.

All data matched that reported in the literature.[3]



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

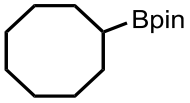
Cycloheptane (491 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **5** (54.9 mg, 49%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.80 – 1.63 (m, 4H), 1.60 – 1.37 (m, 8H), 1.23 (s, 12H), 1.08 – 1.01 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.9, 29.8, 29.1, 28.5, 24.9.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.4.

All data matched that reported in the literature.[3]



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

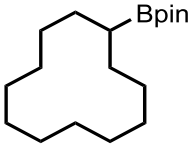
Cyclooctane (561 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **6** (56.4 mg, 47%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 – 1.30 (m, 14H), 1.23 (s, 12H), 1.12 – 1.07 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 27.7, 27.1, 27.0, 26.8, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6.

All data matched that reported in the literature.[3]



2-Cyclododecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)

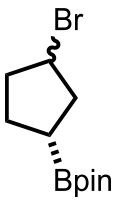
Cyclododecane (842 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **7** (65.9 mg, 45%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 1.50 – 1.22 (m, 22H), 1.21 (s, 12H), 1.05 – 1.00 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.9, 25.0, 24.9, 24.4, 24.2, 23.61, 23.57, 23.5.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6.

All data matched that reported in the literature.[4]



2-(3-Bromocyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

Bromocyclopentane (745 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **8** (31.6 mg, 23%) as a colorless oil. The d.r. 5:1 was determined by ^{1}H NMR analysis.

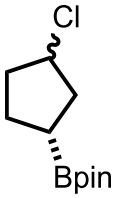
^{1}H NMR (600 MHz, $CDCl_3$) δ [4.53 (tt, *J* = 5.7, 2.9 Hz, 0.84H), 4.07 (dd, *J* = 14.9, 6.7 Hz, 0.17H)], 2.36 – 1.95 (m, 5H), 1.86 – 1.72 (m, 1H), 1.63 (dtt, *J* = 13.6, 8.8, 5.1 Hz, 1H), [1.25 (s, 2H), 1.24 (s, 10H)].

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.3, 55.4, 40.4, 38.4, 25.9, 24.9.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2.

FTIR (neat, cm^{-1}) ν_{max} 2975, 2925, 1378, 1314, 1213, 1141, 856.

HRMS (EI/M^+) *m/z* calcd. for $C_{11}H_{20}B^{79}BrO_2^+$: 274.07397, found $[M]^+$: 274.07324.



2-(3-Chlorocyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)

Chlorcyclopentan (523 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **9** (62.7 mg, 54%) as a colorless oil. The d.r. 1.8:1 was determined by ^{1}H NMR analysis.

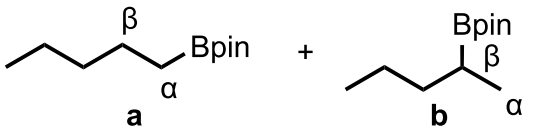
^{1}H NMR (600 MHz, $CDCl_3$) δ [4.44 (tt, *J* = 5.6, 2.8 Hz, 0.64H), 4.30 (p, *J* = 5.8 Hz, 0.36H)], 2.27 (ddd, *J* = 14.0, 9.5, 6.0 Hz, 0.35H), 2.10 – 1.86 (m, 2.36H), 1.97 – 1.86 (m, 2.49H), 1.84 – 1.76 (m, 0.44), 1.72 (q, *J* = 9.3 Hz, 0.63H), 1.65 – 1.56 (m, 0.82H), [1.24 (s, 4.2H), 1.23 (s, 7.8H).

^{13}C NMR (151 MHz, $CDCl_3$) δ [83.4, 83.3], [63.3, 61.9], [39.6, 39.5], [37.9, 37.7], [25.7, 25.4], [24.9, 24.8].

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3.

FTIR (neat, cm^{-1}) ν_{max} 2975, 2936, 1378, 1315, 1142, 971, 856.

HRMS (EI/M^+) *m/z* calcd. for $C_{11}H_{20}B^{35}ClO_2^+$: 230.12449, found $[M]^+$: 230.12374.



4,4,5,5-Tetramethyl-2-pentyl-1,3,2-dioxaborolane (a) and 4,4,5,5-tetramethyl-2-(pentan-2-yl)-1,3,2-dioxaborolane (b) (10)

Pentane (361 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **10** (39.5 mg, 40%) as a colorless oil. The α:β = 1.5:1 was determined by ^{1}H NMR (the pinacol methyl peaks). The data of major product **a** matched those reported previously.[5]

(a) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 – 1.25 (m, 5H), 1.23 (s, 12H), 0.97 – 0.90 (m, 1H), 0.87 (td, *J* = 7.1, 6.5, 2.8 Hz, 3H), 0.75 (t, *J* = 7.8 Hz, 2H).

(a) ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 34.8, 25.0, 23.8, 22.6, 14.2.

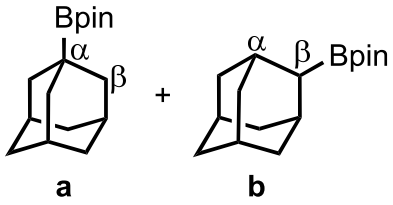
(b) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 – 1.32 (m, 5H), 1.29 – 1.25 (m, 5H), 1.23 (s, 12H), 1.00 (m, 1H).

(b) ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 35.6, 24.9, 24.1, 22.2, 14.5.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3.

FTIR (neat, cm^{-1}) ν_{max} 2959, 2926, 1370, 1314, 1143, 1013, 796.

HRMS (EI/$[M\text{-}CH_3]^+$) *m/z* calcd. for $C_{10}H_{20}BO_2^+$: 183.15508, found $[M\text{-}CH_3]^+$: 183.15490.



2-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (a) and 2-((1*r*,3r,5*r*,7*r*)-adamantan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (b) (11)

Adamantane (681 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **11** (47.2 mg, 36%) as a white solid. The α:β = 3:1 was determined by ^{1}H NMR (the pinacol methyl peaks).

(a) ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.87 – 1.82 (m, 3H), 1.81 – 1.71 (m, 12 H), 1.20 (s, 12H).

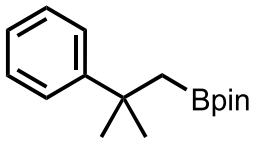
(a) ^{13}C NMR (151 MHz, $CDCl_3$) δ 82.7, 38.1, 37.6, 27.7, 24.8.

(b) ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.05 (br, 2H), 1.91 – 1.86 (m, 1H), 1.81 – 1.71 (m, 11 H), 1.36 (br, 1H), 1.25 (s, 12H).

(b) ^{13}C NMR (151 MHz, $CDCl_3$) 82.9, 39.4, 37.8, 36.4, 29.5, 28.4, 28.2, 25.0.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.6.

The data of products **a** and **b** matched that reported in the literature.[6]



4,4,5,5-Tetramethyl-2-(2-methyl-2-phenylpropyl)-1,3,2-dioxaborolane (12)

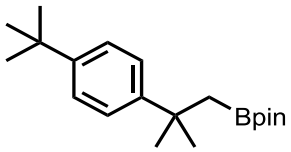
tert-Butylbenzene (671 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **12** (34.8 mg, 27%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.5 Hz, 2H), 7.23 (t, J = 3.9 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H), 1.39 (s, 6H), 1.23 (s, 2H), 1.07 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 128.0, 125.6, 125.4, 82.9, 36.4, 31.5, 24.8.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.1.

All data matched that reported in the literature.[6]



2-(2-(4-(*tert*-Butyl)phenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)

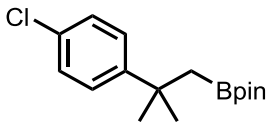
1,4-Di-*tert*-butylbenzene (952 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **13** (49.0 mg, 31%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 1.42 (s, 6H), 1.30 (s, 9H), 1.23 (s, 2H), 1.08 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 148.0, 125.3, 124.8, 82.8, 36.0, 34.3, 31.5, 31.4, 24.8.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.1.

All data matched that reported in the literature.[3]



2-(2-(4-Chlorophenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(14)

1-*tert*-Butyl-4-chlorobenzene (843 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **14** (67.9 mg, 46%) as a colorless oil.

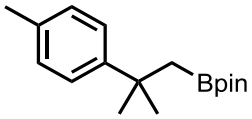
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (d, J = 8.6 Hz, 2H), 7.25 – 7.20 (d, J = 8.6 Hz, 2H), 1.39 (s, 6H), 1.22 (s, 2H), 1.10 (s, 12H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 131.1, 128.0, 127.2, 83.0, 36.2, 31.5, 24.8.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.0.

FTIR (neat, cm^{-1}) ν_{max} 2961, 2925, 1355, 1323, 1142, 1012, 825.

HRMS (EI/M^+) *m/z* calcd. for $C_{16}H_{24}B^{35}ClO_2^+$: 294.15579, found $[M]^+$: 294.15480.



4,4,5,5-Tetramethyl-2-(2-methyl-2-(*p*-tolyl)propyl)-1,3,2-dioxaborolane (15)

4-*tert*-Butyltoluene (741 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **15** (58.7 mg, 43%) as a colorless oil.

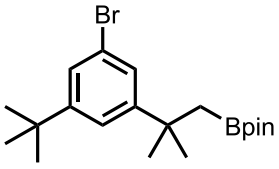
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 2.31 (s, 3H), 1.42 (s, 6H), 1.25 (s, 2H), 1.13 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 134.7, 128.6, 125.5, 82.8, 36.1, 31.4, 24.9, 21.0.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.2.

FTIR (neat, cm^{-1}) ν_{max} 2961, 2925, 1699, 1607, 1355, 1142, 970, 816.

HRMS (EI/M^+) *m/z* calcd. for $C_{17}H_{27}BO_2^+$: 274.21041, found $[M]^+$: 274.20991.



2-(2-(3-Bromo-5-(*tert*-butyl)phenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

3,5-Di-*tert*-butylbromobenzene (1.35 g, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **16** (69.1 mg, 35%) as a colorless oil.

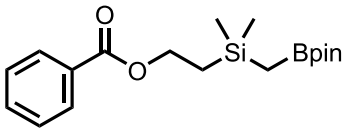
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.33 (s, 1H), 7.29 (s, 1H), 1.39 (s, 6H), 1.29 (s, 9H), 1.23 (s, 2H), 1.10 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 152.8, 126.2, 125.6, 122.1, 121.6, 82.9, 36.7, 35.1, 31.4, 29.9, 24.8.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.1.

FTIR (neat, cm^{-1}) ν_{max} 2956, 2920, 1354, 1320, 1140, 862, 802, 704.

HRMS (APCI/$[M+H]^+$) *m/z* calcd. for $C_{20}H_{33}O_2B^{79}Br^+$: 395.17515, found $[M+H]^+$: 395.17638.



2-(Dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silyl)ethyl benzoate (17)

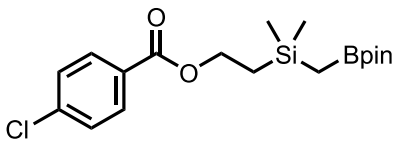
2-(Trimethylsilyl)ethyl benzoate (**S1**) (1.11 g, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **17** (54.8 mg, 31%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.52 – 4.37 (m, 2H), 1.24 (s, 12H), 1.21 – 1.15 (m, 2H), 0.16 (s, 2H), 0.13 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 132.8, 130.9, 129.6, 128.4, 83.0, 63.3, 25.1, 17.9, −1.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.7.

All data matched that reported in the literature.[3]



2-(Dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silyl)ethyl 4-chlorobenzoate (18)

2-(Trimethylsilyl)ethyl 4-chlorobenzoate (**S2**) (1.28 g, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **18** (47.5 mg, 25%) as a colorless oil.

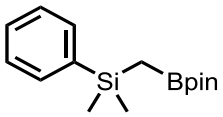
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 4.48 – 4.39 (m, 2H), 1.24 (s, 12H), 1.20 – 1.14 (m, 2H), 0.16 (s, 2H), 0.13 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 139.2, 131.1, 129.3, 128.8, 83.1, 63.6, 25.1, 17.9, −1.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.5.

FTIR (neat, cm^{-1}) ν_{max} 2954, 2929, 1718, 1295, 1271, 1115, 838, 761.

HRMS [EI/(M-H)$^+$] *m/z* calcd. for $C_{18}H_{27}B^{35}ClO_4Si^+$: 381.14547, found [M-H]$^+$: 381.14497.



Dimethyl(phenyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silane (19)

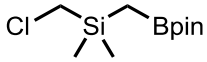
Trimethylphenylsilane (752 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **19** (35.1 mg, 25%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.48 (m, 2H), 7.42 – 7.26 (m, 3H), 1.18 (s, 12H), 0.36 (s, 2H), 0.33 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 133.6, 128.9, 127.8, 83.0, 25.0, −0.7.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.8.

All data matched that reported in the literature.[3]



(Chloromethyl)dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silane (20)

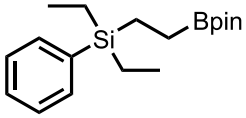
Chloromethyltrimethylsilane (613 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **20** (48.6 mg, 39%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 2H), 1.23 (s, 12H), 0.19 (s, 2H), 0.17 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.1, 31.7, 25.1, −2.7.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.6.

All data matched that reported in the literature.[7]



Diethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (21)

Triethylphenylsilane (770 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **21** (36.6 mg, 23%) as a colorless oil.

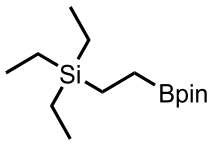
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.39 – 7.29 (m, 3H), 1.23 (s, 12H), 0.95 (m, 6H), 0.89 – 0.70 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 128.8, 127.7, 83.1, 25.0, 7.6, 4.6, 3.4, 1.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.3.

FTIR (neat, cm^{-1}) ν_{max} 2955, 2925, 1358, 1144, 1109, 721, 700.

HRMS (EI/$[M\text{-}CH_3]^+$) *m/z* calcd. for $C_{17}H_{28}BO_2Si^+$: 303.19461, found $[M\text{-}CH_3]^+$: 303.19422.



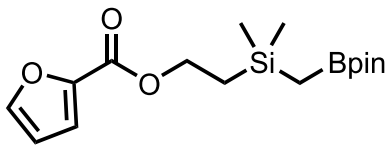
Triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (22)

Tetraethyl silane (722 mg, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column chromatography (SiO_2; 50:1 PE: EA) to afford boronic ester **22** (48.5 mg, 36%) as a colorless oil. The r.r. = 10: 1 was determined by ^{1}H NMR, and the NMR spectra of the major product matched those reported previously.[8]

Major product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.23 (s, 12H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.75 – 0.65 (m, 2H), 0.48 (q, *J* = 7.9 Hz, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 24.9, 7.6, 4.0, 3.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.4.



2-(Dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silyl)ethyl furan-2-carboxylate (23)

2-(Trimethylsilyl)ethyl furan-2-carboxylate **S3** (1.06 g, 5.0 mmol) was borylated according to **General Procedure C**. The crude reside was purified by flash column

chromatography (SiO_2; 30:1 PE: EA) to afford boronic ester **23** (27.6 mg, 17%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.15 (d, *J* = 3.3 Hz, 1H), 6.57 – 6.40 (m, 1H), 4.49 – 4.34 (m, 2H), 1.23 (s, 12H), 1.19 – 1.10 (m, 2H), 0.15 (s, 2H), 0.12 (s, 6H).

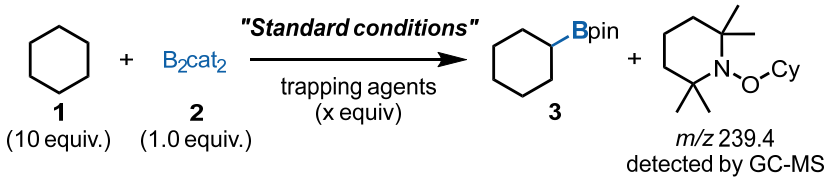
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.2, 145.3, 117.6, 111.9, 83.1, 63.4, 25.1, 17.9, −1.0.

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.6.

All data matched that reported in the literature.[3]

4. Mechanistic Experiments

4.1 Radical trapping experiments



Entry	Trapping agents (x equiv)	GC-MS yield of **3** (%)
1	TEMPO (1 equiv)	36
2	TEMPO (2 equiv)	19
3	TEMPO (3 equiv)	0
4	BHT (1 equiv)	20
5	BHT (2 equiv)	Trace
6	BHT (3 equiv)	0

To an oven dried 25 mL Schlenk tube with a stir bar was added B_2cat_2 (119 mg, 0.5 mmol, 1.0 equiv), $CuCl_2$ (134 mg, 1.0 mmol, 2.0 equiv) and trapping agents (TEMPO and BHT, 1–3 equiv). The vessel was evacuated and filled with nitrogen (three cycles). Anhydrous MeCN (5 mL) was then added followed by the cyclohexane (421 mg, 5.0 mmol, 10 equiv.) under a nitrogen atmosphere. The reaction mixture was irradiated with 365 nm light for 18 hours. After irradiation, pinacol (236 mg, 2.0 mmol, 4.0 equiv.) and Et_3N (3 mL) was added and stirred for another for 4 hours. The reaction mixture was transferred into a vial containing EtOAc (15 mL), H_2O (20 mL). After vigorously shaking and allowing the two layers to separate, take the top organic phase carefully for GC−MS analysis. The yields of **3** in the reaction with different equivalent of trapping agents were determined by GC−MS.

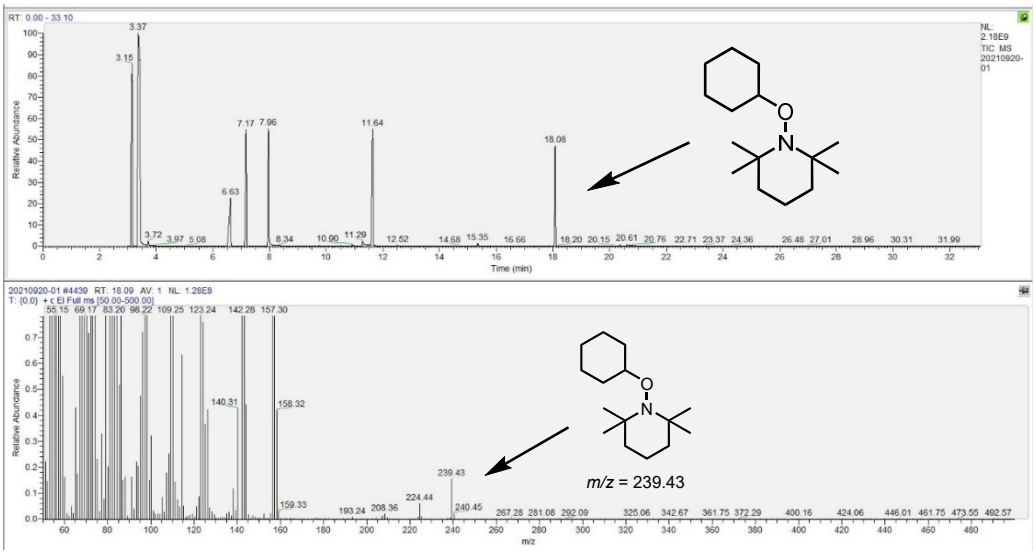


Figure S4. GC−MS spectrum of the cyclohexyl–TEMPO adduct.

4.2 NMR studies

To an oven-dried 10 mL vial equipped with a stir bar was added the B_2cat_2 (23.8 mg, 0.1 mmol, 1.0 equiv) and $CuCl_2$ (26.9 mg, 0.2 mmol, 2.0 equiv). The vessel was evacuated and filled with nitrogen (three cycles) and MeCN-d_3 (1 mL) was then added followed by the cyclohexane (84.2 mg, 1.0 mmol, 10 equiv.) under a nitrogen atmosphere. The reaction mixture was irradiated with 365 nm light (2 × 40 W) for 12 hours. Irradiation was stopped and a sample (0.6 mL) was removed for NMR analysis. ClBcat should have a characteristic ^{11}B NMR chemical shift at ~28.4 ppm.[9] However, due to the trace amount of water in MeCN-d_3, ClBcat can easily hydrolysis to HOBcat (a signal at ~22.5 ppm in ^{11}B NMR) (Figure S5). To verify this result, we conducted a control ^{11}B NMR experiment and a ^{1}H NMR analysis (Figure S6) of the ClBcat, which was purchased from Sigam-Aldrich. Indeed, a signal at ~22.6 ppm for HOBcat was observed in ^{11}B NMR, and ^{1}H NMR analysis of ClBcat also confirmed the *in situ* formation HOBcat due to trace water in MeCN-d_3, similar to those reported previously by Aggarwal and Noble.[3]

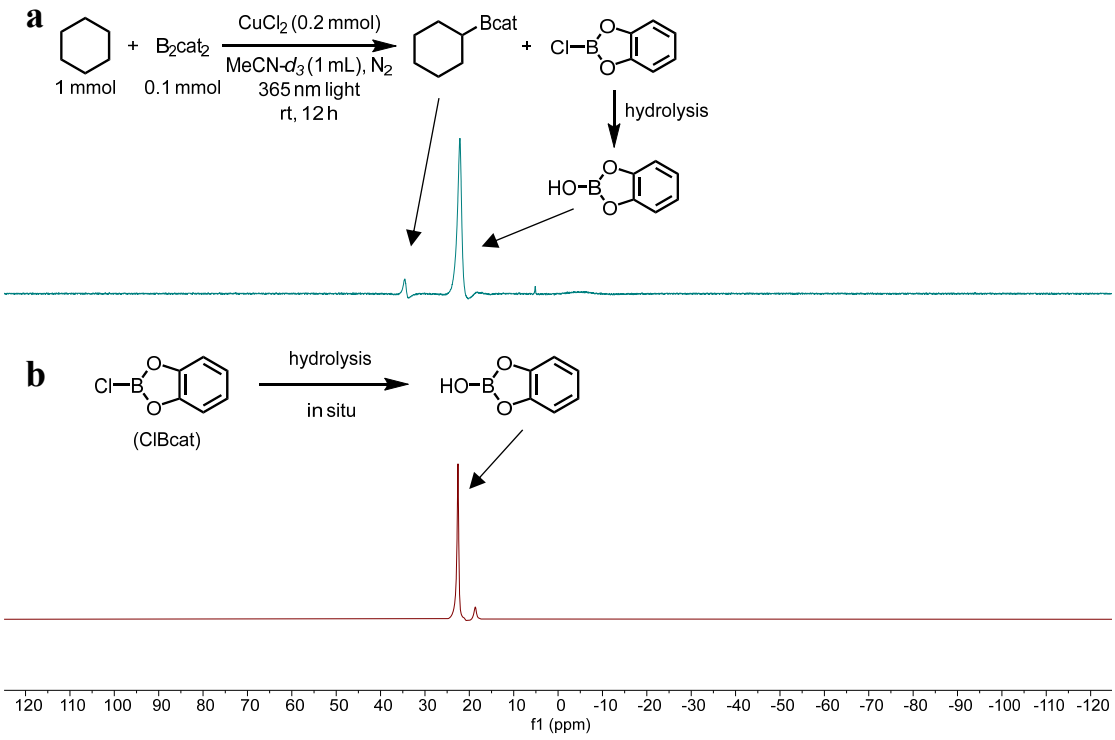


Figure S5. Stacked ^{11}B NMR spectra showing the formation of HOBCat from ClBCat in MeCN-d_3. a Reaction mixture. b pure ClBcat sample in MeCN-d_3.

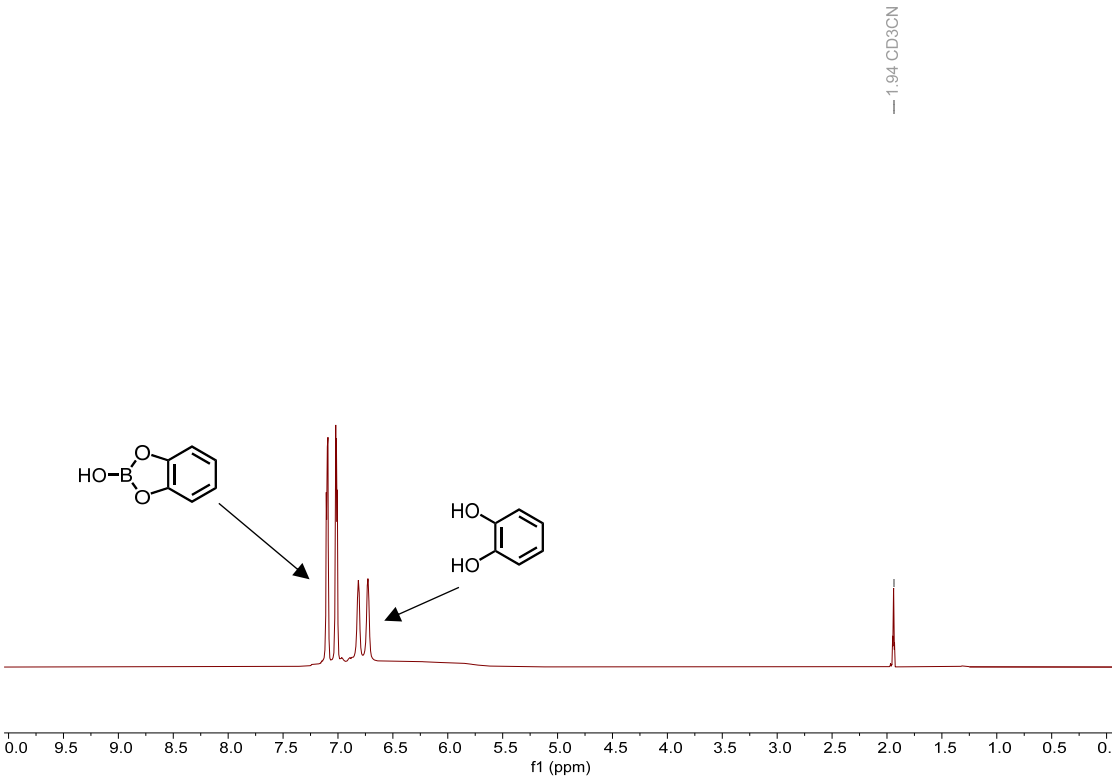


Figure S6. ^{1}H NMR spectra showing the formation of HOBCat from ClBCat in MeCN-d_3.

4.3 GC−MS Analysis of the Model Reaction

To an oven-dried 25 mL Schlenk tube with a stir bar was added B_2cat_2 (119 mg, 0.5 mmol, 1.0 equiv), $CuCl_2$ (134 mg, 1.0 mmol, 2.0 equiv). The vessel was evacuated and filled with nitrogen (three cycles). Anhydrous MeCN (5 mL) was then added followed by the cyclohexane (421 mg, 5.0 mmol, 10 equiv.) under a nitrogen atmosphere. The reaction mixture was irradiated with 365 nm light (2 × 40 W) for 12 hours. After irradiation, the reaction mixture was diluted by EtOAc and determined by GC−MS. It was found that cyclohexyl chloride (t_R = 7 min, *m/z* = 118) can be detected by GC−MS analysis.

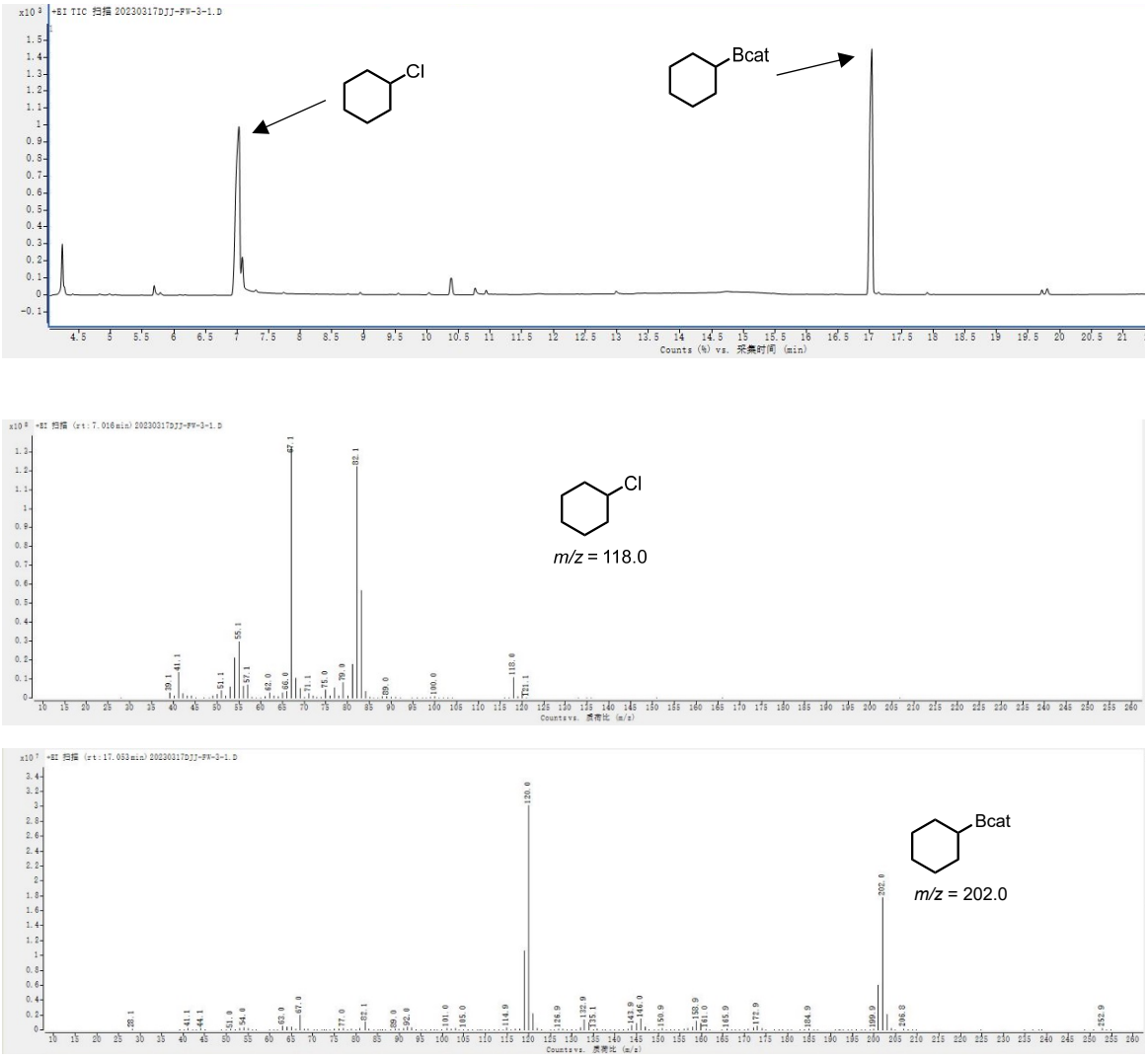
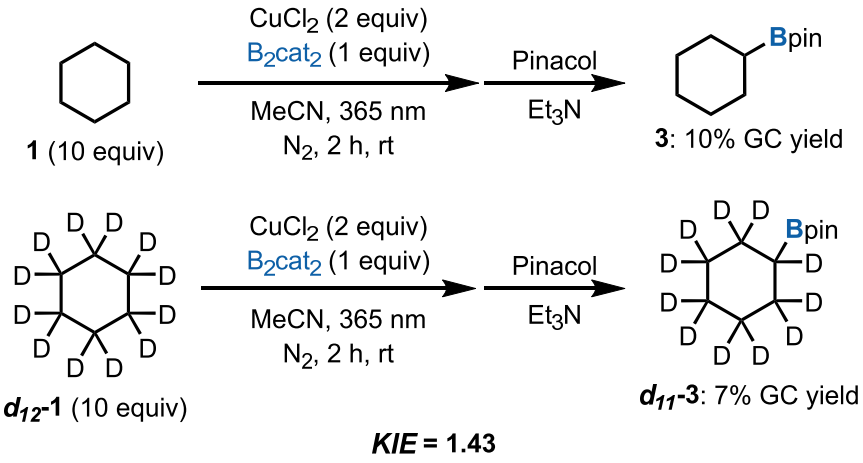


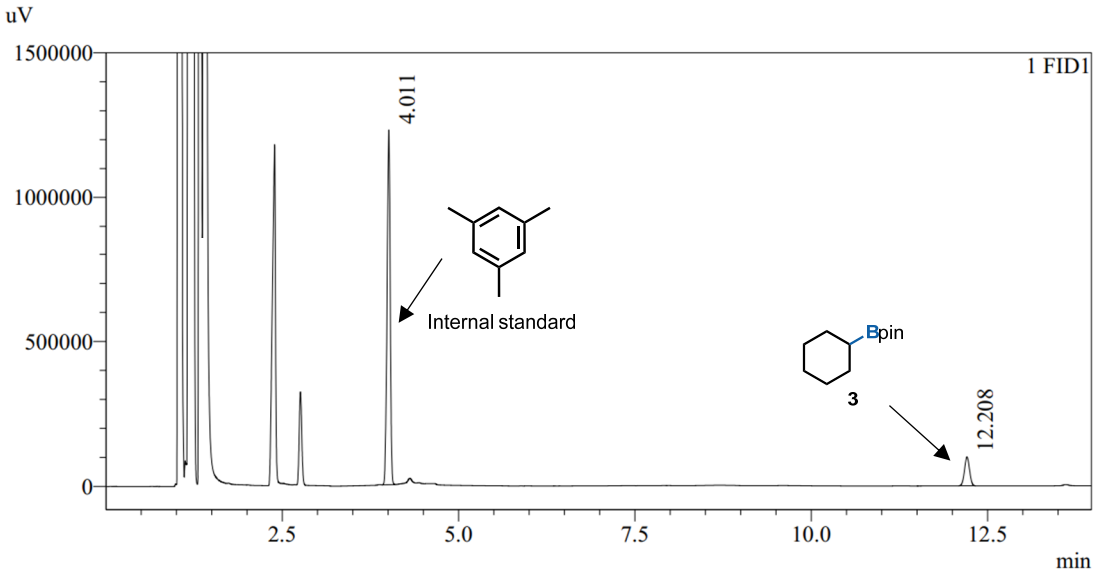
Figure S7. GC−MS analysis of the model reaction.

4.4 Parallel Kinetic Isotope Effect



B_2cat_2 (119 mg, 0.5 mmol, 1.0 equiv), $CuCl_2$ (134 mg, 1.0 mmol, 2.0 equiv) were added into two oven-dried 25 mL Schlenk tubes with stir bars, respectively. The vessels were evacuated and filled with nitrogen (three cycles). Under a nitrogen atmosphere, cyclohexane (421 mg, 5.0 mmol, 10 equiv.) and cyclohexane-d_{12} (482 mg, 5.0 mmol, 10 equiv) were added respectively and anhydrous MeCN (5 mL) was then added. The two reaction mixtures were irradiated with 365 nm light (2 × 40 W) for 2 hours to keep the reaction under a low conversion. After irradiation, pinacol (236 mg, 2.0 mmol, 4.0 equiv) and Et_3N (3 mL) was added and stirring was continued for 3 hours. Mesitylene (60 mg, 0.5 mmol) was added to the reaction mixture as an internal standard, respectively. The two reaction mixtures were quenched with water and extracted with EtOAc. These two reactions were analyzed by GC using an Agilent HP-1 (30 m × 0.32 mm ID × 0.25 μm df) column under the following conditions: initial column temperature, 60 °C; initial hold time, 1 min, rate of temperature ramp 1, 5 °C/min, temperature 150 °C; hold time, 1 min; rate of temperature ramp 2, 20 °C/min; final temperature 230 °C; injection temperature, 250 °C; detection temperature, 250 °C. The effluent was combusted in an H_2/air flame and detected using a flame ionization detector (FID). Response factor of the products compared to the mesitylene internal standard was 1.342. The yields of cyclohexane borate **3** and deuterated cyclohexane borate ***d*$_{11}$-3** were 10% and 7%, respectively. The ratio of **3** to ***d*$_{11}$-3** was measured as K_H/K_D = 1.43.

〈色谱图〉



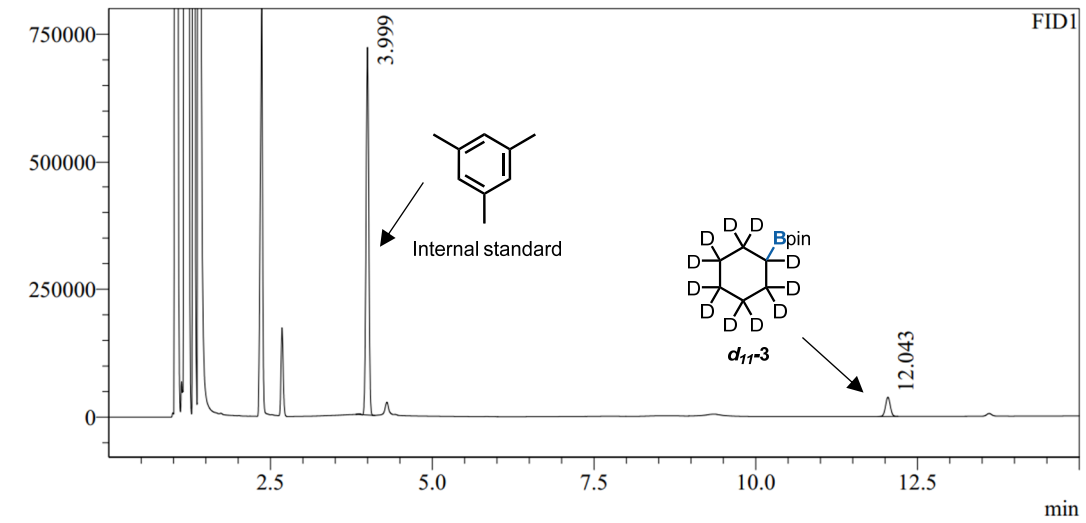
〈峰表〉

FID1

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.011	3768996	1224109	88.575		M	
2	12.208	486133	98291	11.425		M	
总计		4255129	1322400				

Figure S8. GC yield determination for the conversion of **1** to **3**.

〈色谱图〉



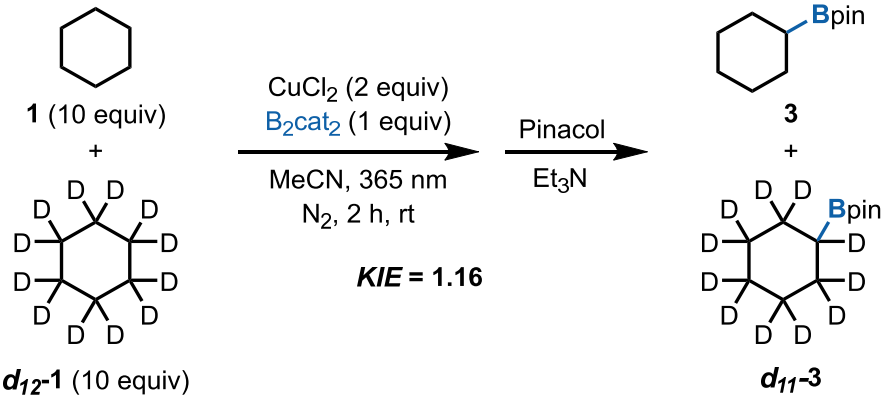
〈峰表〉

FID1

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	3.999	2116067	717342	91.718		M	
2	12.043	191089	37494	8.282		M	
总计		2307157	754836				

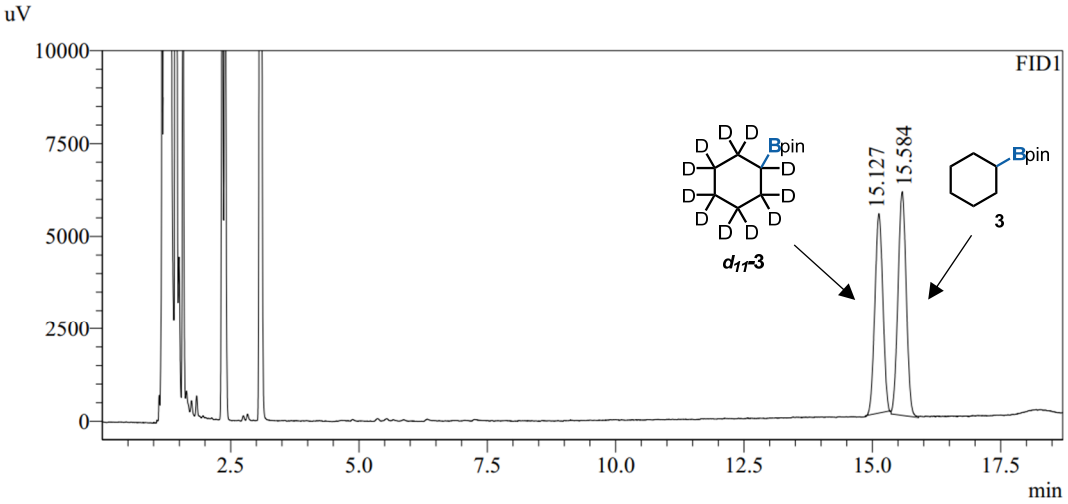
Figure S9. GC yield determination for the conversion of ***d*$_{12}$-1** to ***d*$_{11}$-3**.

4.5 Intermolecular Kinetic Isotope Effect



To an oven dried 25 mL Schlenk tube with a stir bar was added B_2cat_2 (59 mg, 0.25 mmol, 1.0 equiv) and $CuCl_2$ (67 mg, 0.5 mmol, 2.0 equiv). The vessel was evacuated and filled with nitrogen (three cycles). Anhydrous MeCN (2.5 mL) was then added followed by the cyclohexane (**1**, 210 mg, 2.5 mmol, 10 equiv) and cyclohexane-d_{12} (***d*$_{12}$-1**, 241 mg, 2.5 mmol, 10 equiv) under a nitrogen atmosphere. The reaction mixture was irradiated with 365 nm light (2 × 40 W) for 2 hours to keep the reaction under a low conversion. After irradiation, pinacol (118 mg, 1.0 mmol, 4.0 equiv) and Et_3N (1.5 mL) was added and stirring was continued for 3 hours. The reaction mixture was quenched with water and extracted with EtOAc. The mixture was analyzed by GC using a Shimadzu SH-1701 (30 m × 0.32 mm ID × 0.25 μm df) column under the following conditions: initial column temperature, 80 °C; initial hold time, 0 min, rate of temperature ramp, 1 °C/min, final temperature 110 °C; hold time, 1 min; injection temperature, 250 °C; detection temperature, 250 °C. The effluent was combusted in an H_2/air flame and detected using a flame ionization detector (FID). The ratio of cyclohexane borate **3** (t_R = 15.548 min) to deuterated cyclohexane borate ***d*$_{11}$-3** (t_R = 15.127 min) was measured as K_H/K_D = 1.16.

〈色谱图〉



〈峰表〉

FID1

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	15.127	58479	5398	46.288		M	
2	15.584	67858	6047	53.712		M	
总计		126337	11445				

Figure S10. GC analysis of the intermolecular competition reaction.

5. References

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5. (a) M. Pang, C. Wu, X. Zhuang, F. Zhang, M. Su, Q. Tong, C.-H. Tong and W. Wang, *Organometallics*, 2018, **37**, 1462–1467; (b) X.-F. Zhou, Y.-D. Wu, J.-J. Dai, Y.-J. Li, Y., Huang and H.-J. Xu, *RSC Adv.*, 2015, **5**, 46672–46676.
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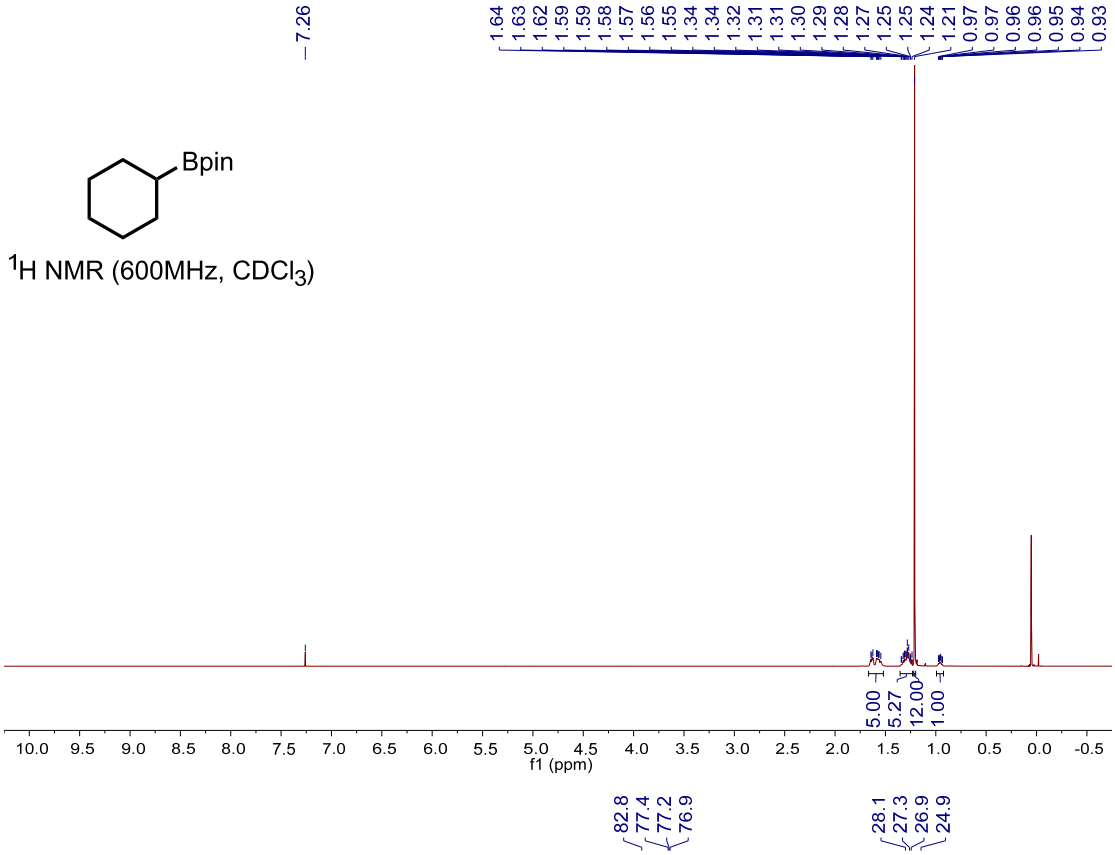
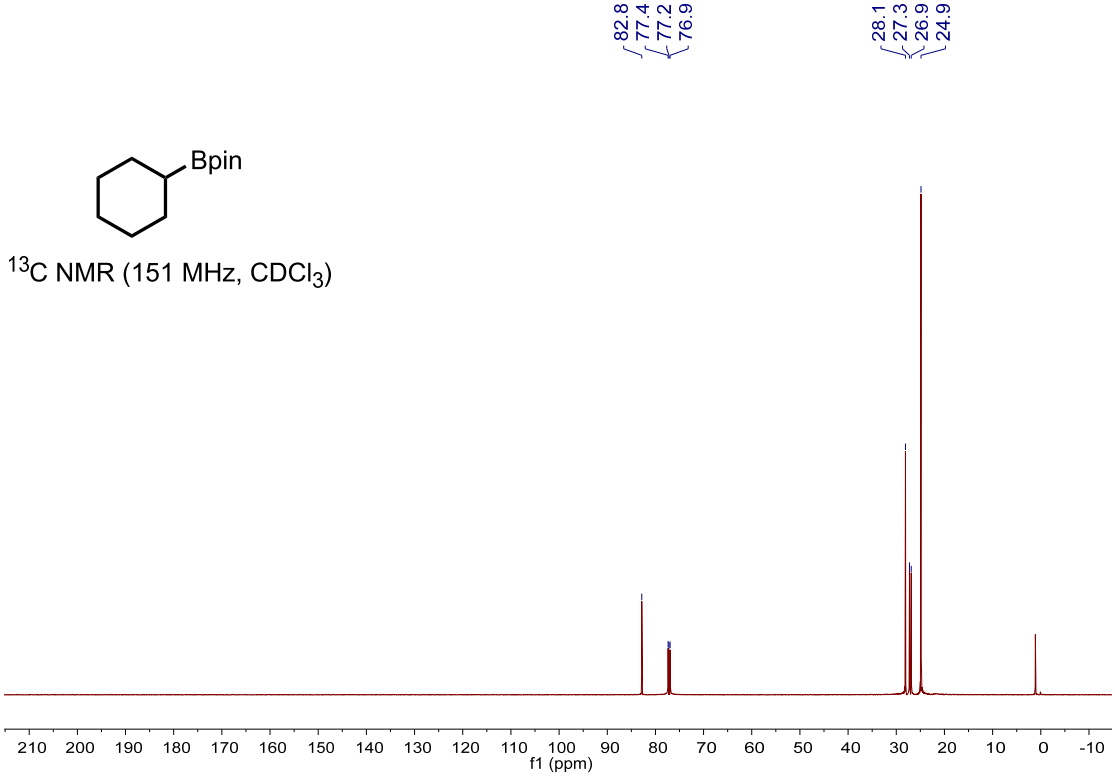
6. Copies of NMR and HRMS Spectra

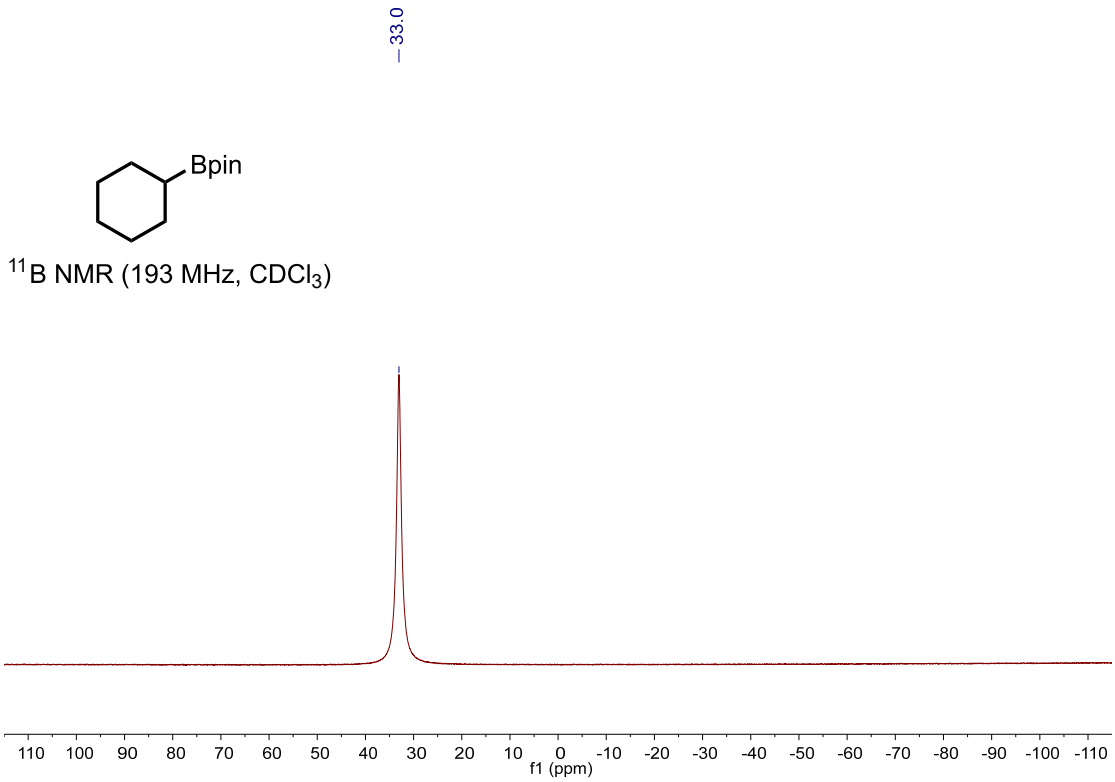
2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)



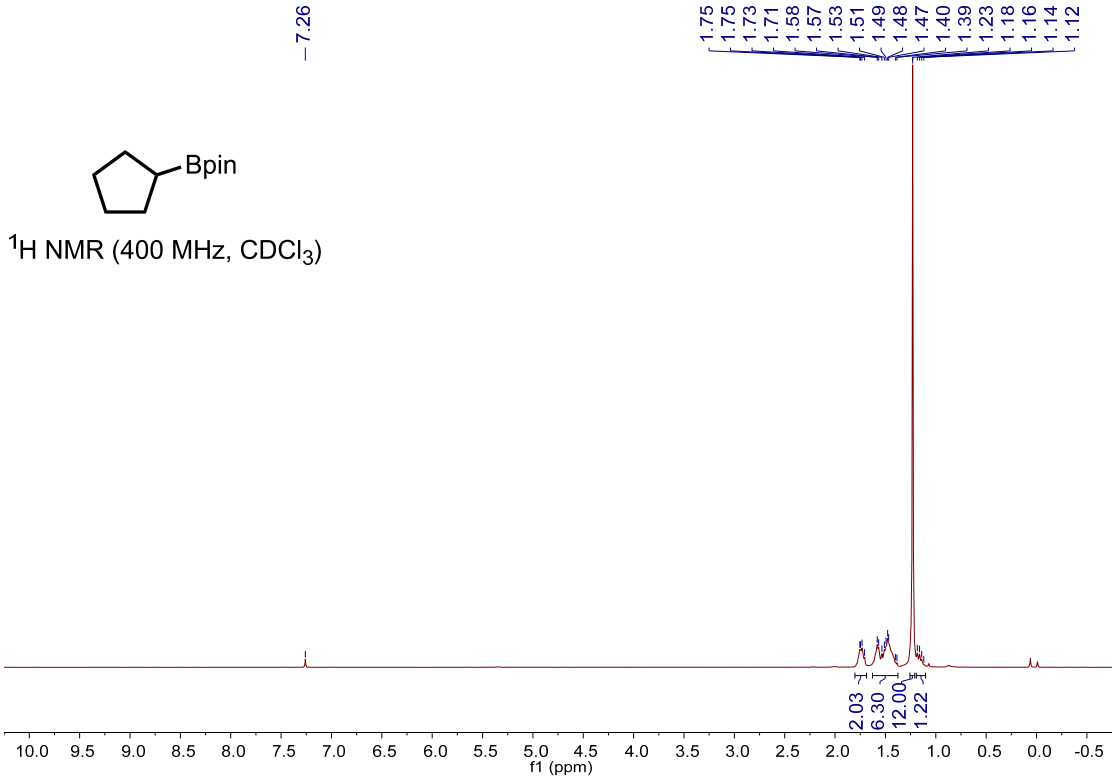
^{1}H NMR (600MHz, $CDCl_3$)



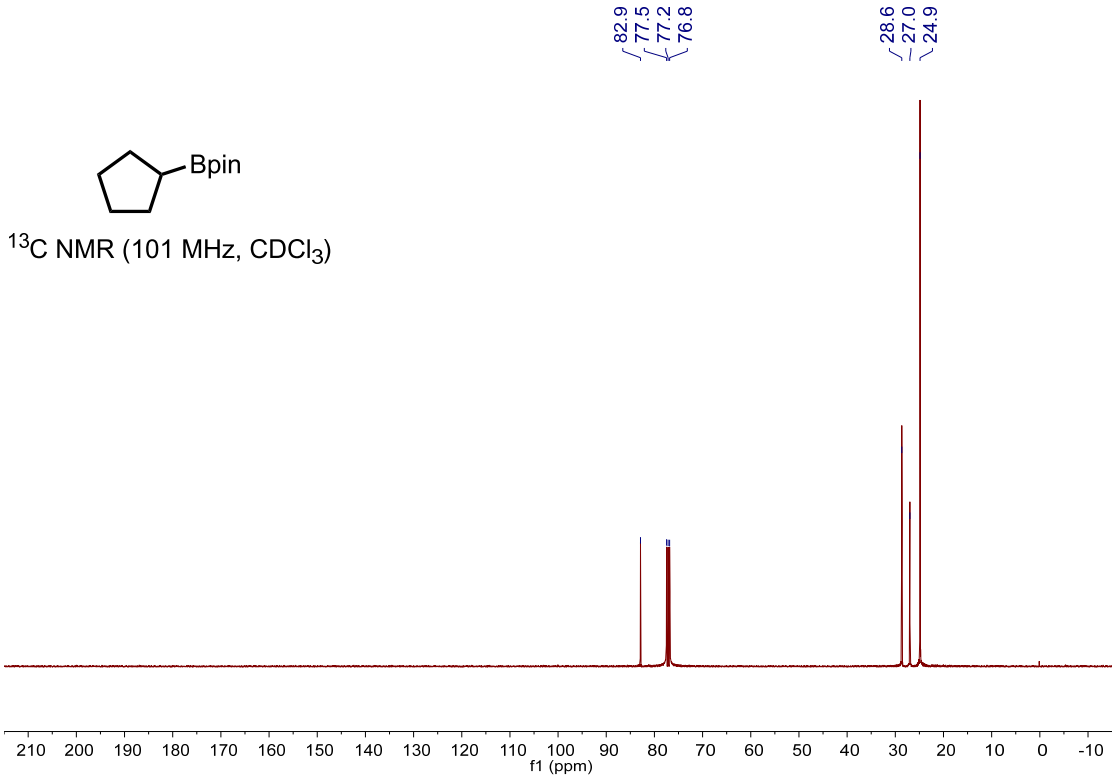
^{13}C NMR (151 MHz, $CDCl_3$)


33.0
Bpin
11B NMR (193 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

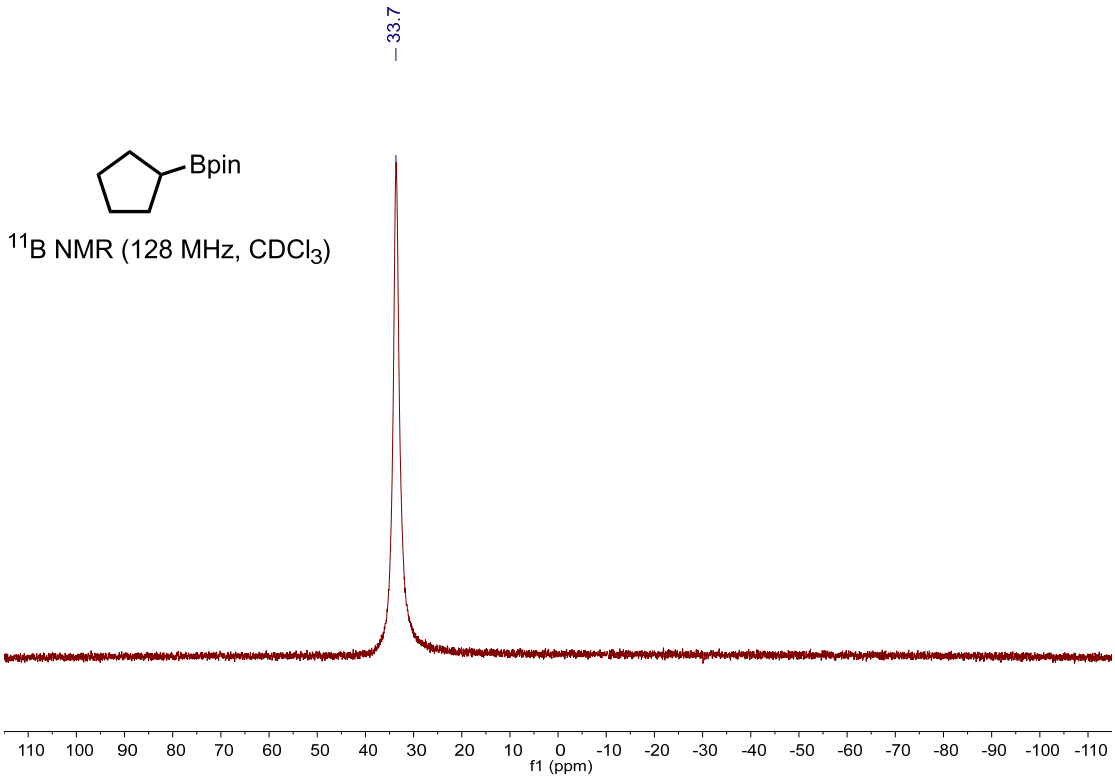
2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)



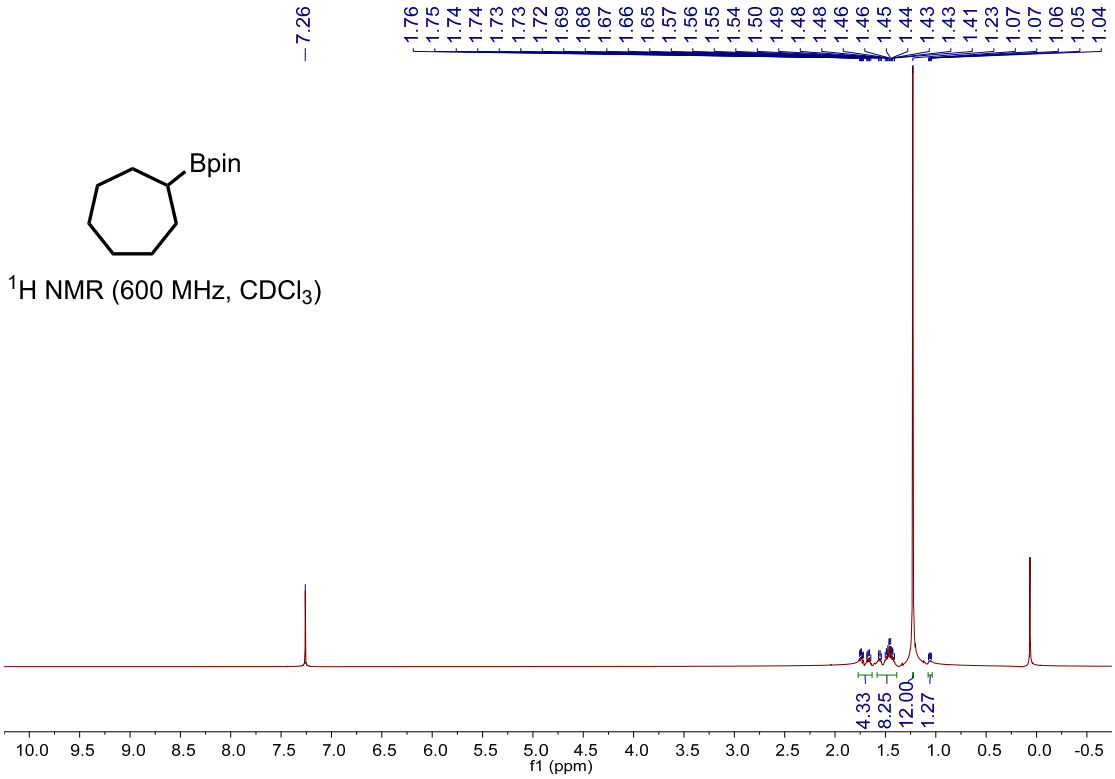
^{1}H NMR (400 MHz, $CDCl_3$)



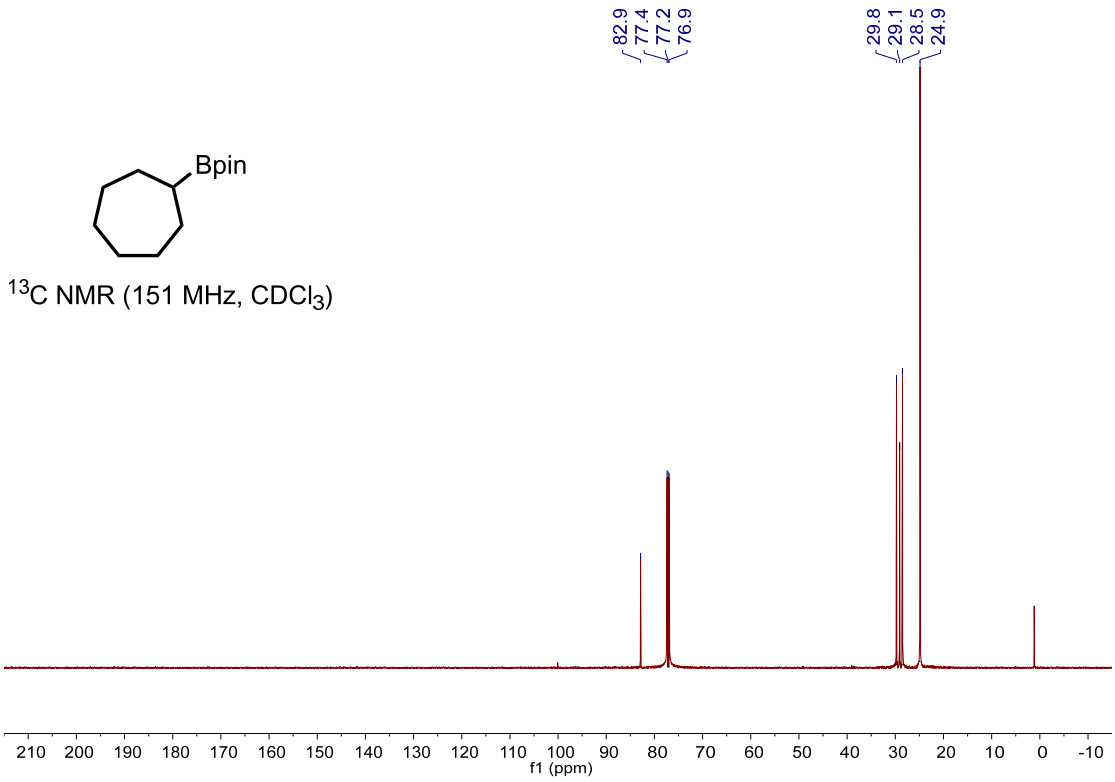
^{13}C NMR (101 MHz, $CDCl_3$)


33.7
Bpin
^{11}B NMR (128 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

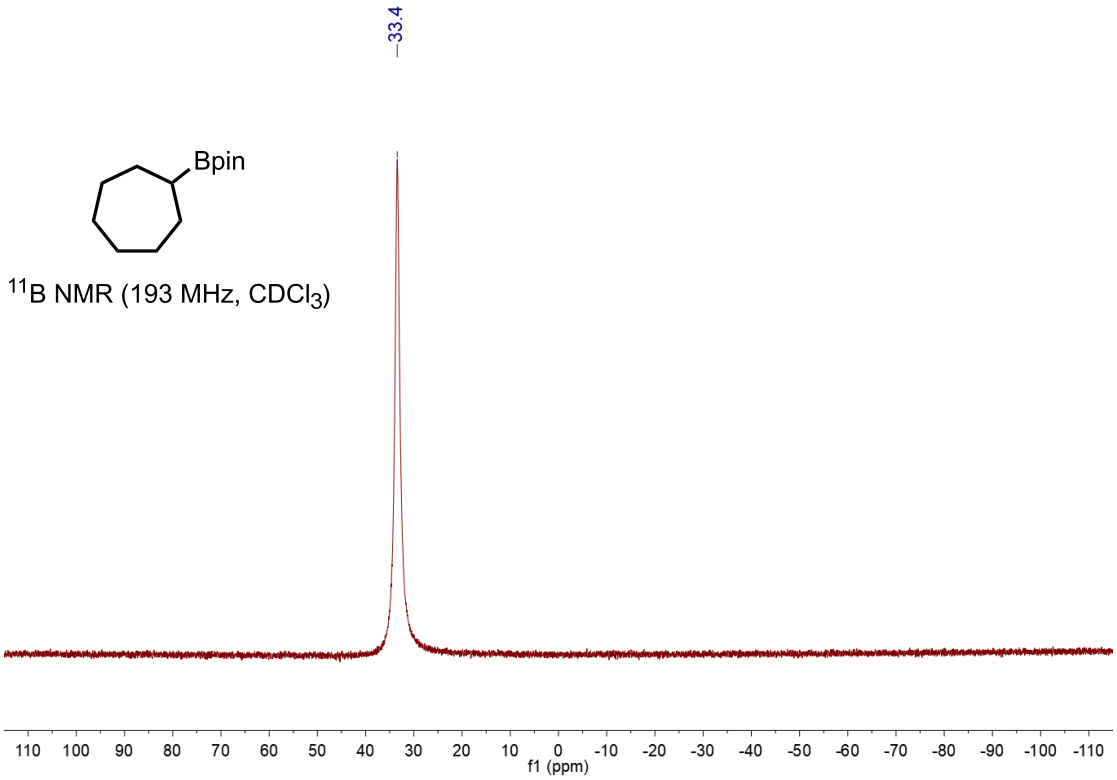
2-Cycloheptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)



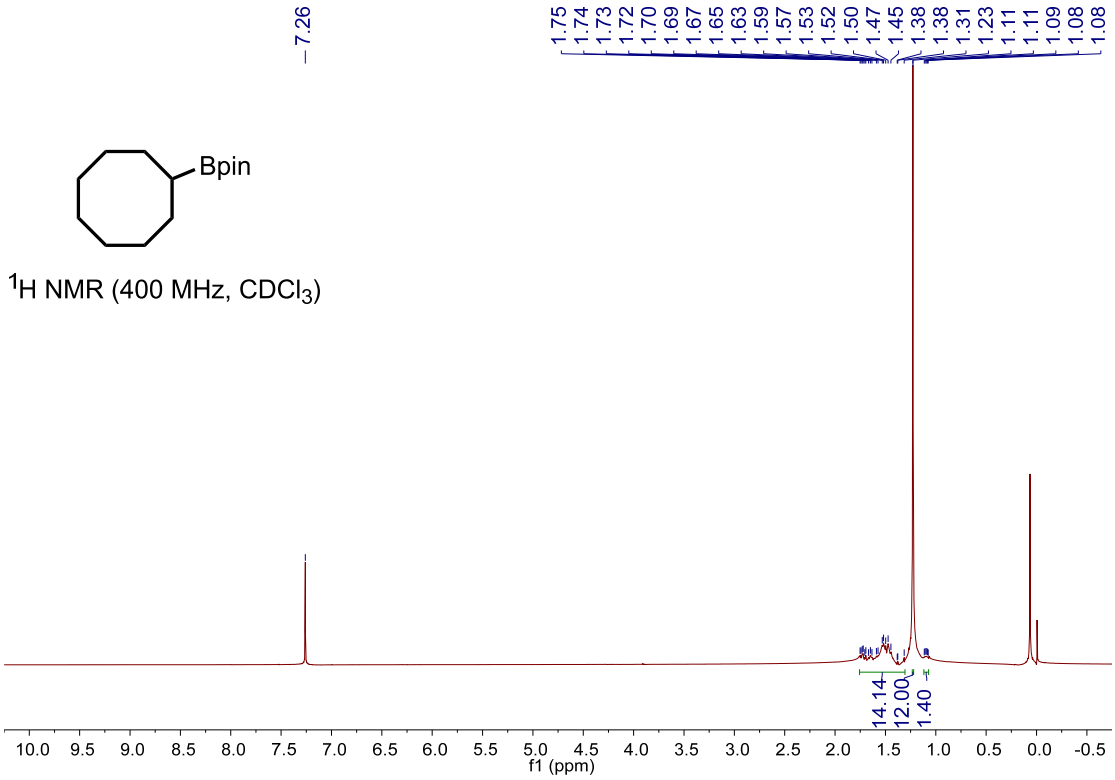
^{1}H NMR (600 MHz, $CDCl_3$)



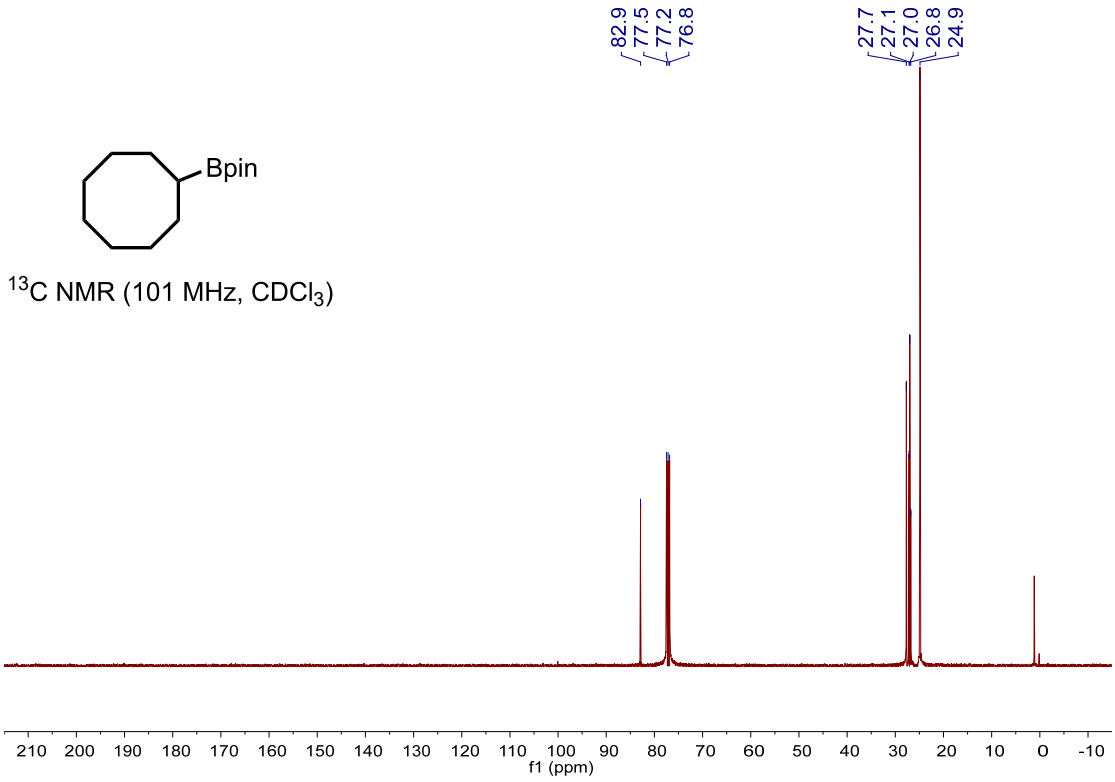
^{13}C NMR (151 MHz, $CDCl_3$)


33.4
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

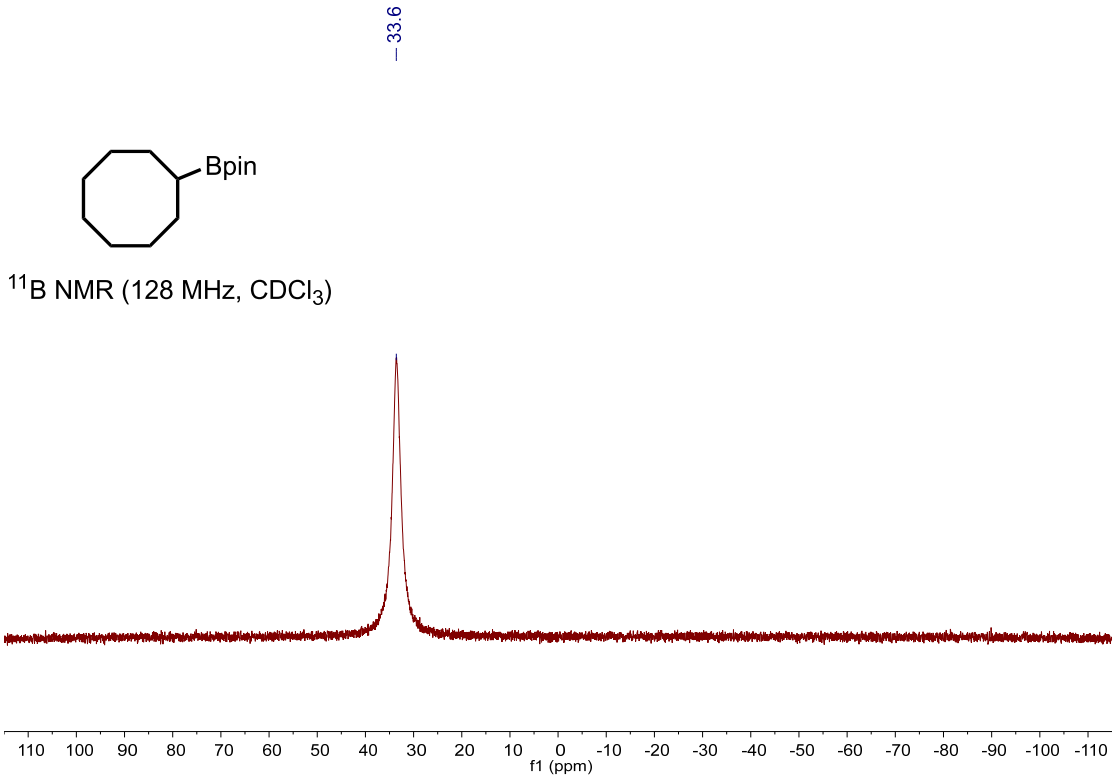
2-Cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



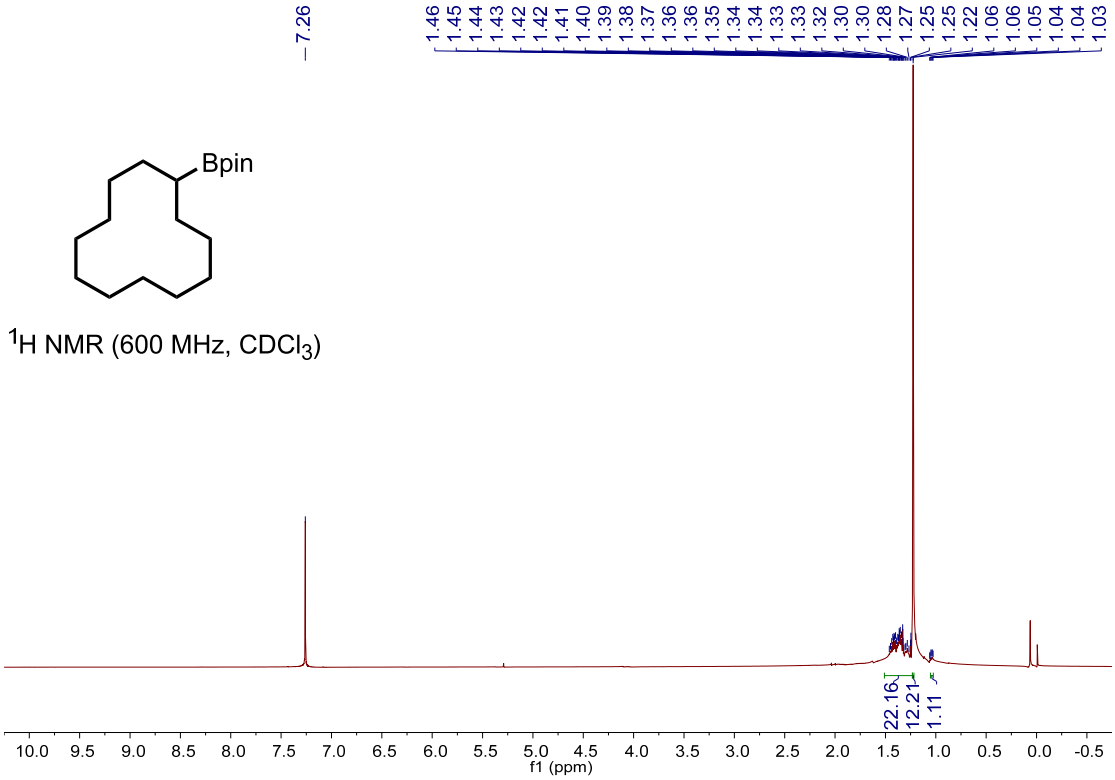
^{1}H NMR (400 MHz, $CDCl_3$)



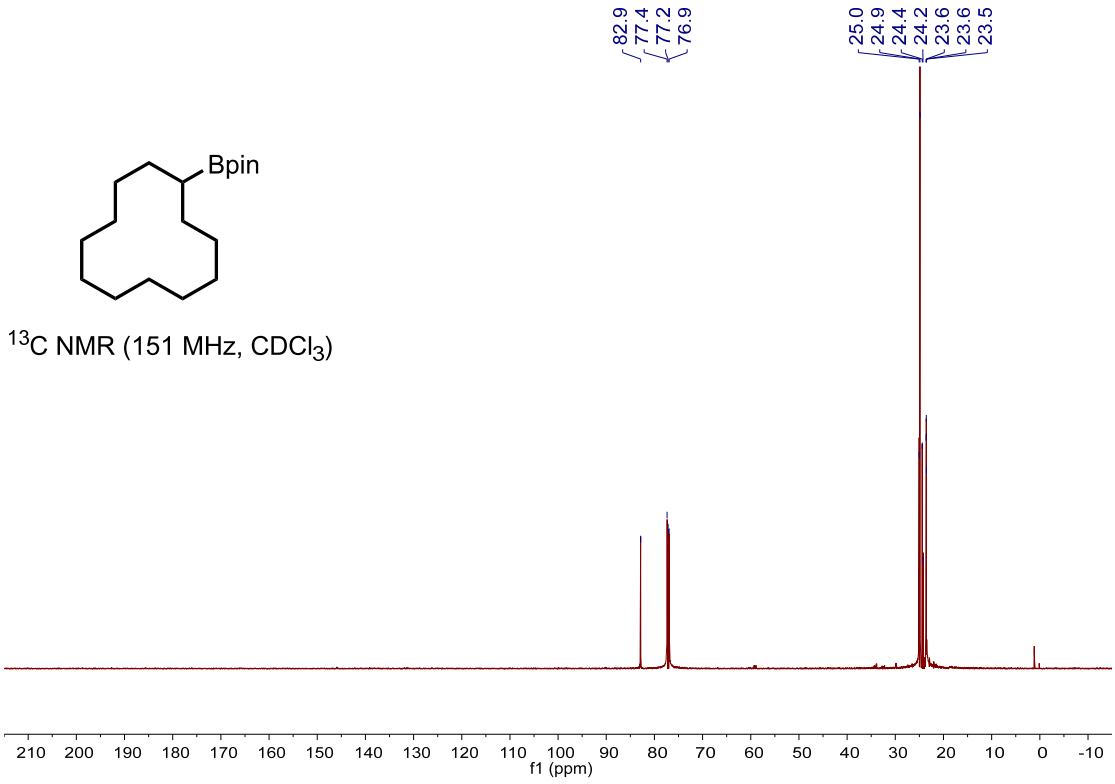
^{13}C NMR (101 MHz, $CDCl_3$)


33.6
Bpin
^{11}B NMR (128 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

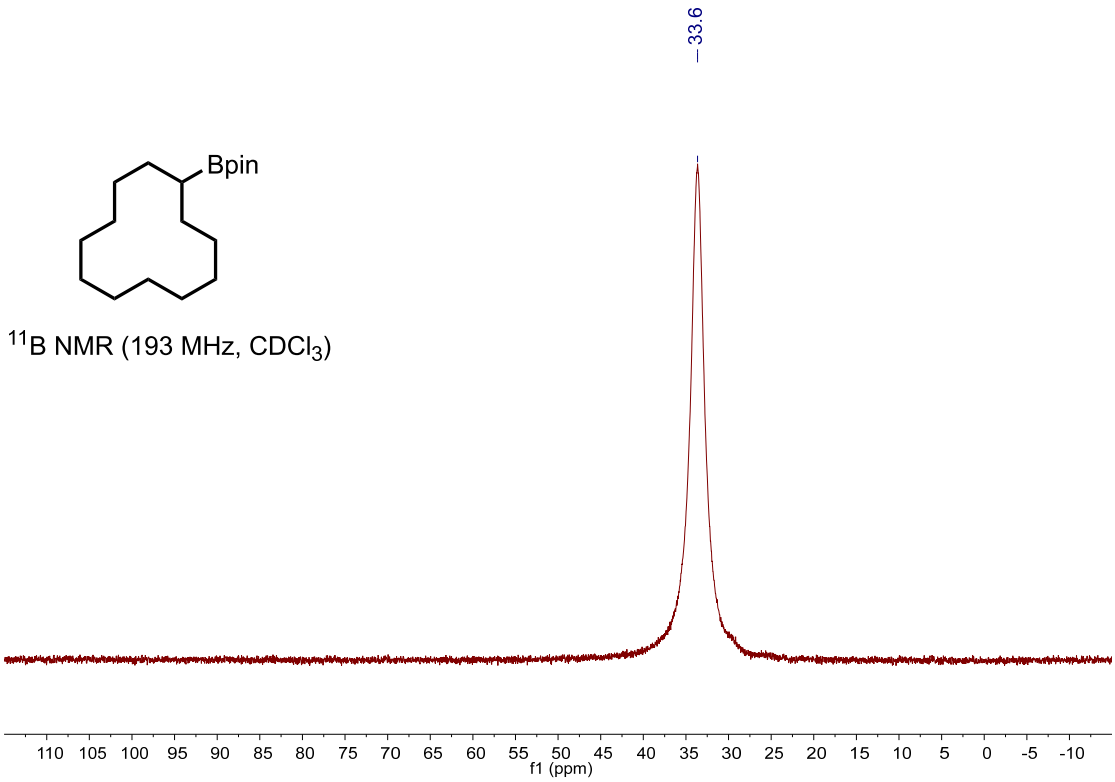
2-Cyclododecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)



^{1}H NMR (600 MHz, $CDCl_3$)

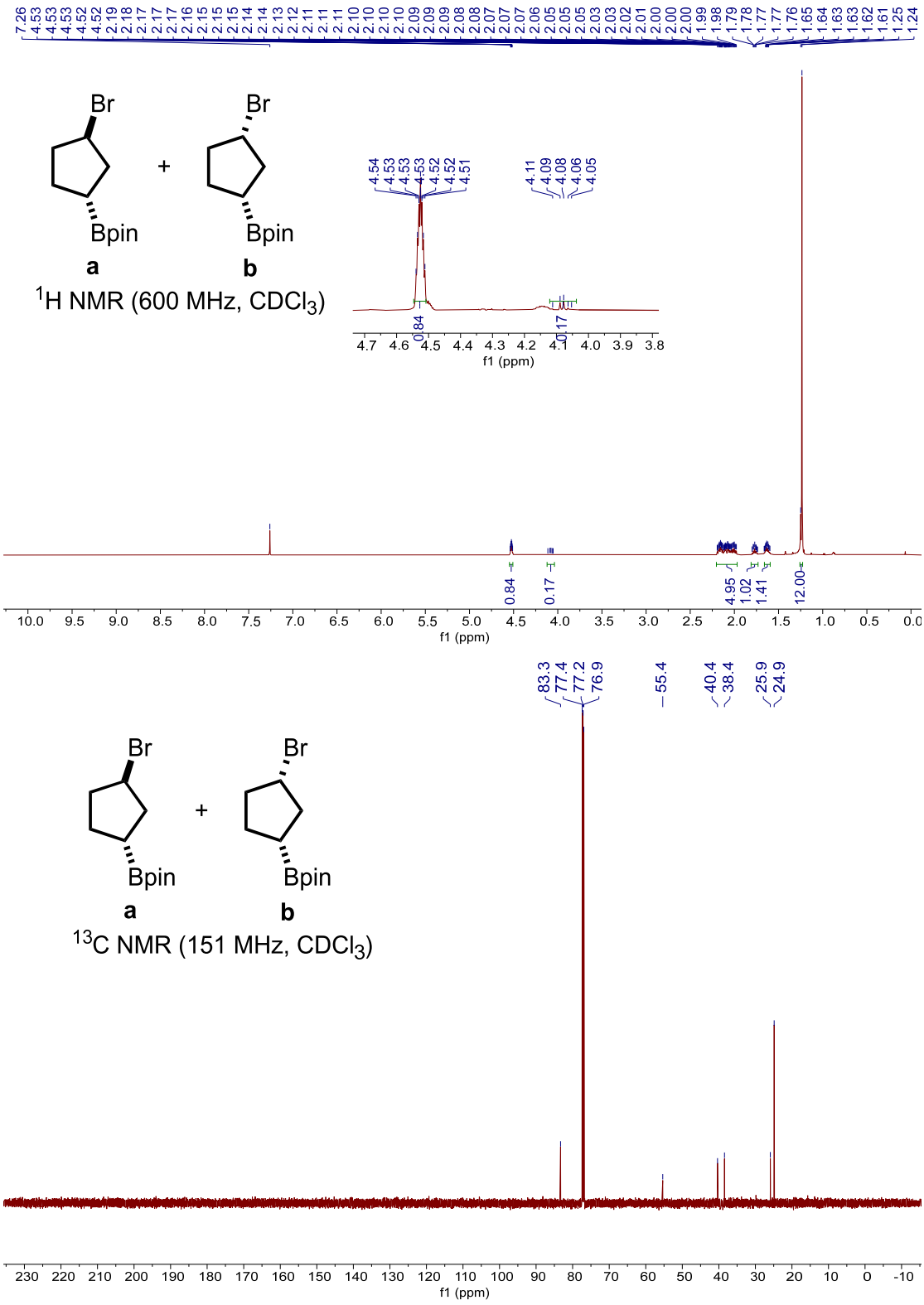


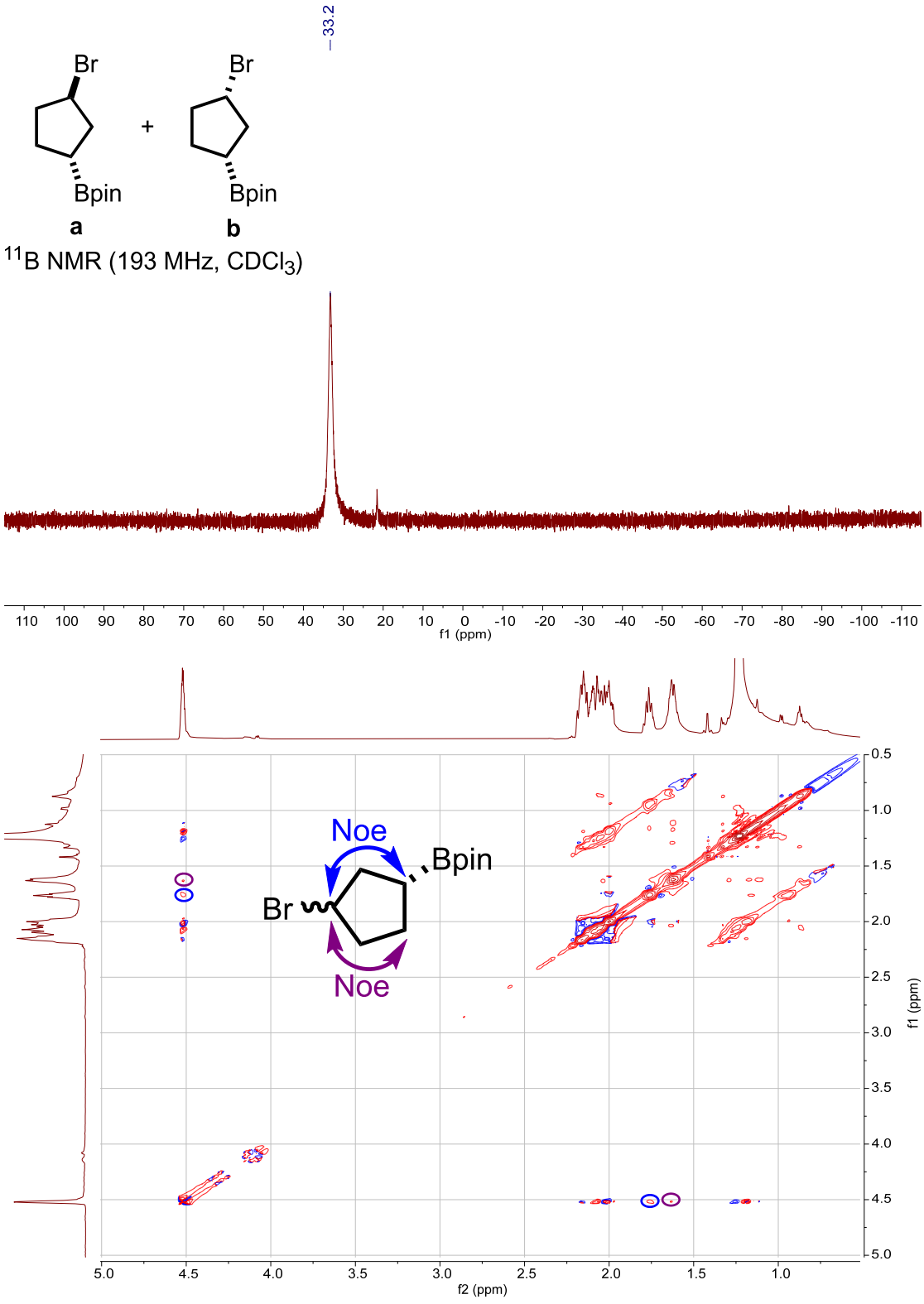
^{13}C NMR (151 MHz, $CDCl_3$)

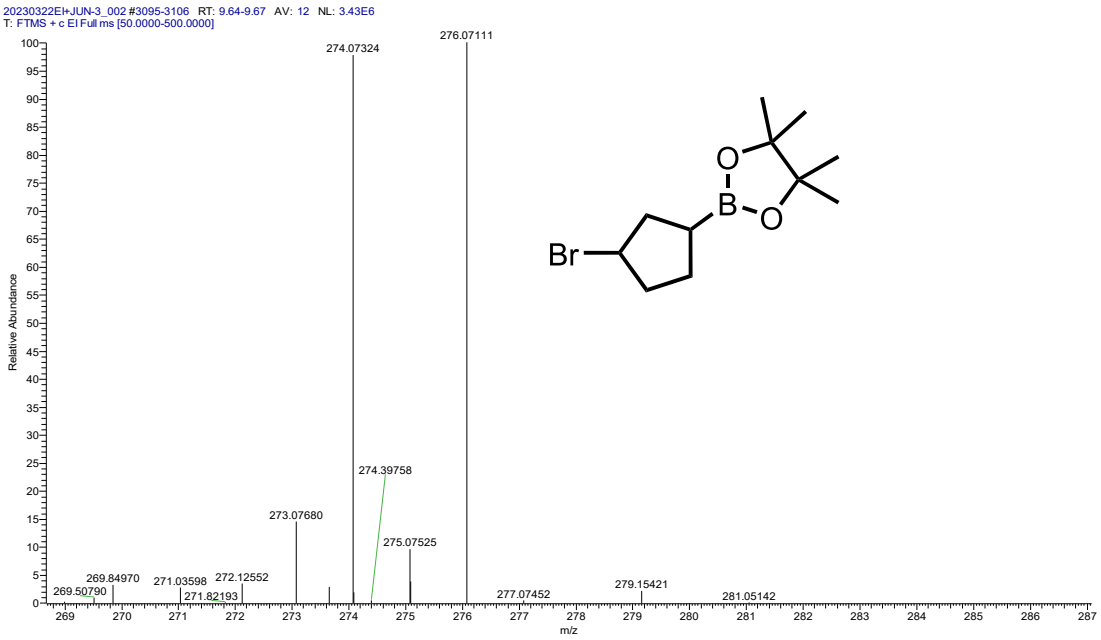


^{11}B NMR (193 MHz, $CDCl_3$)

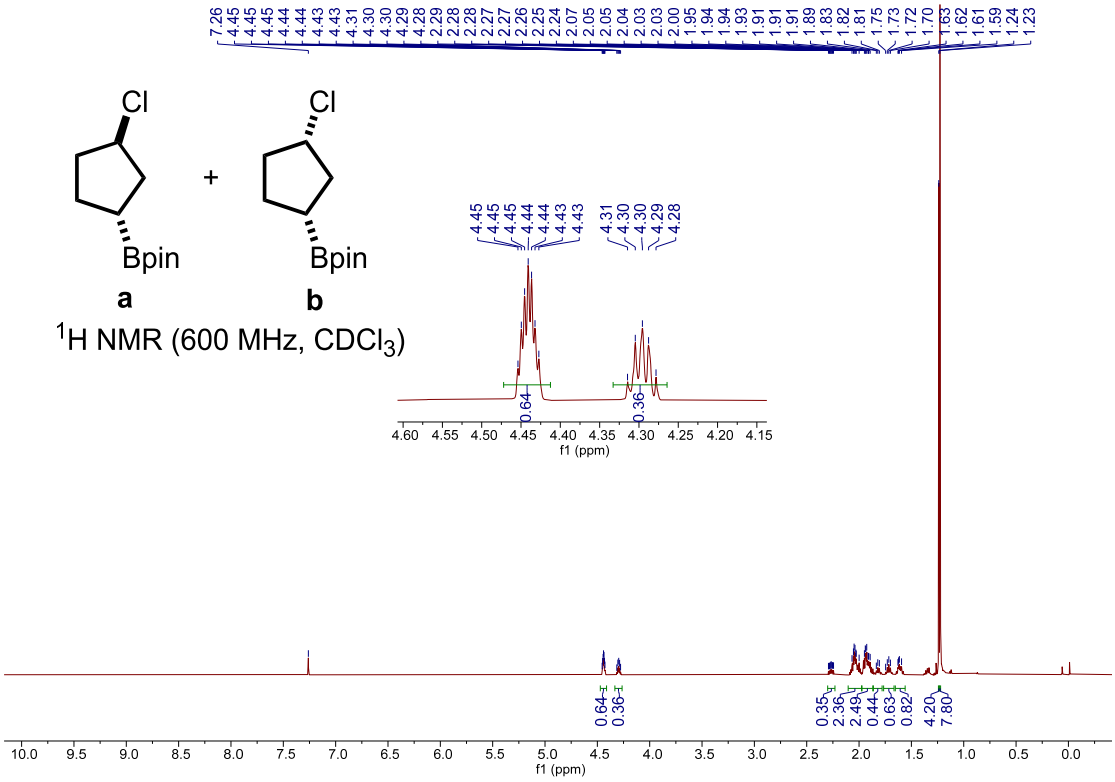
2-(3-Bromocyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

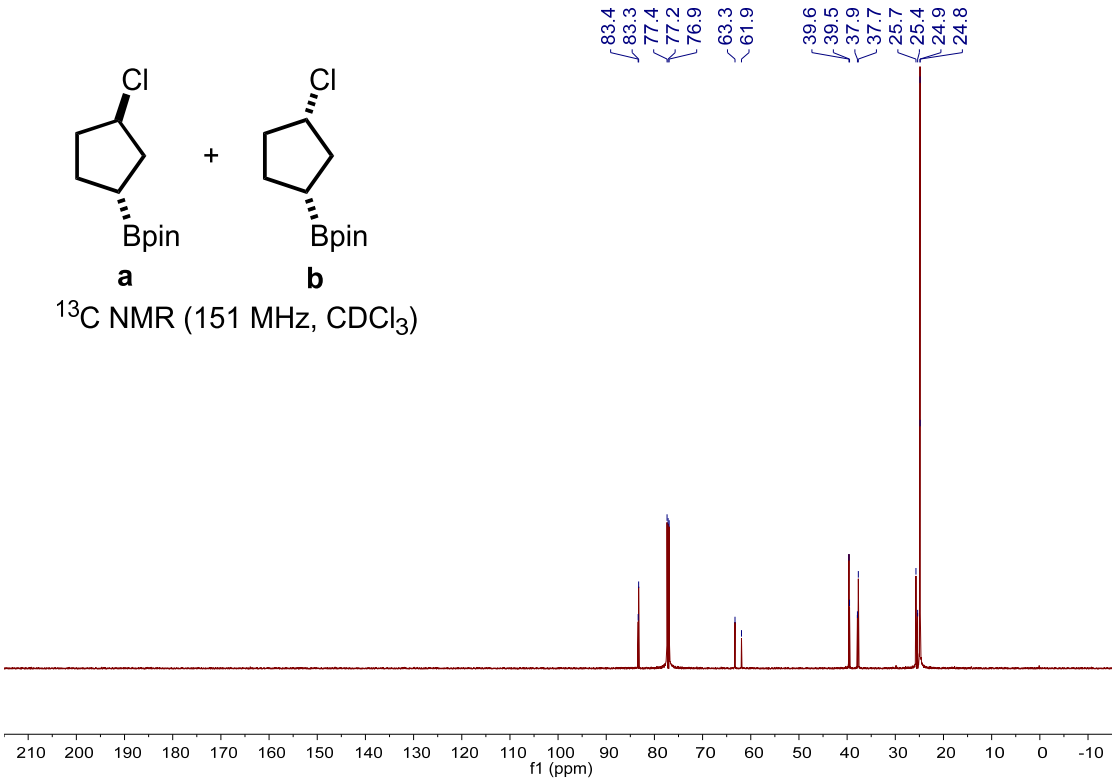


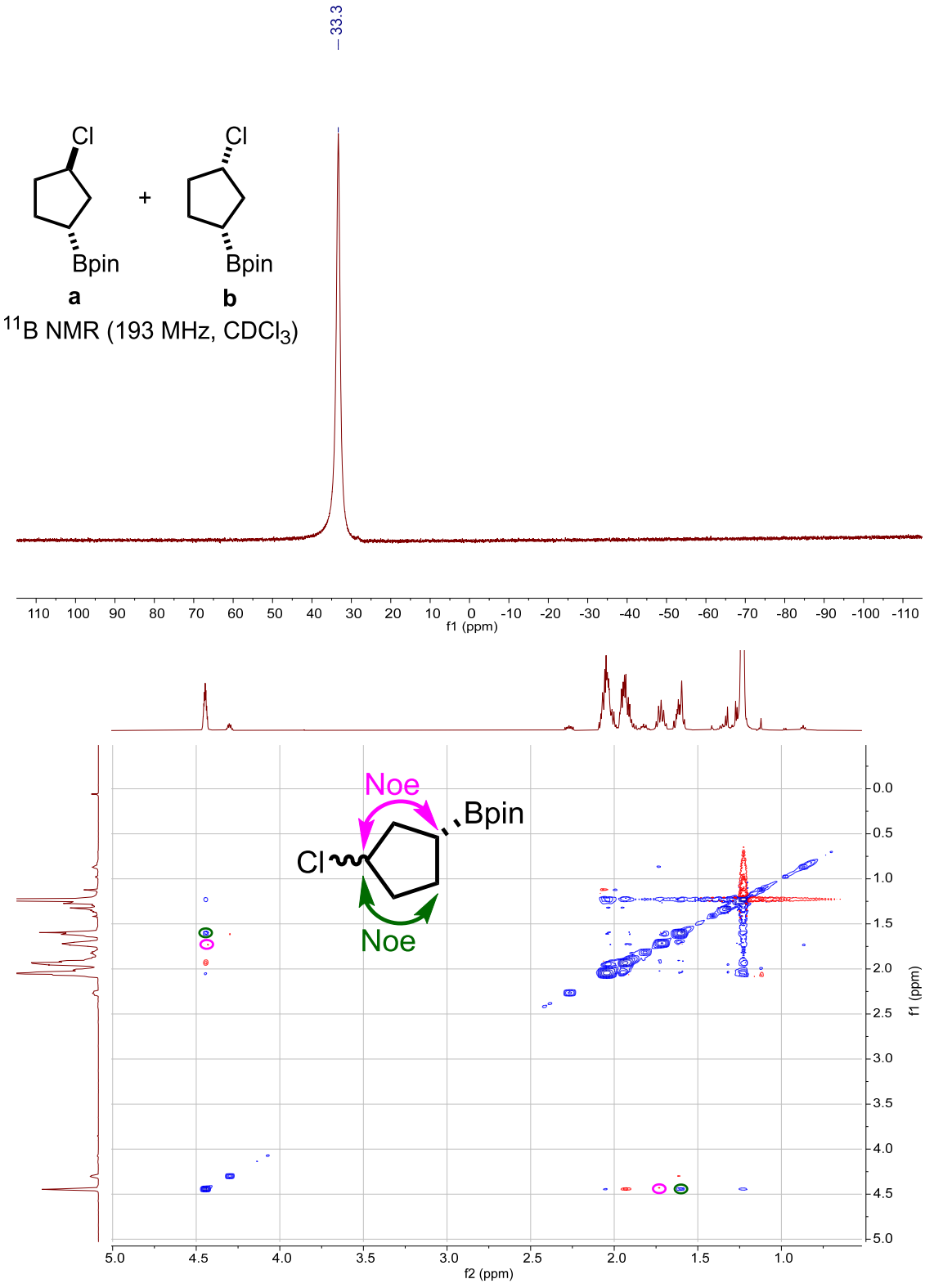

33.2
Br
Bpin
a
+
Br
Bpin
b
11B NMR (193 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)
Noe
Bpin
Br
Noe
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)

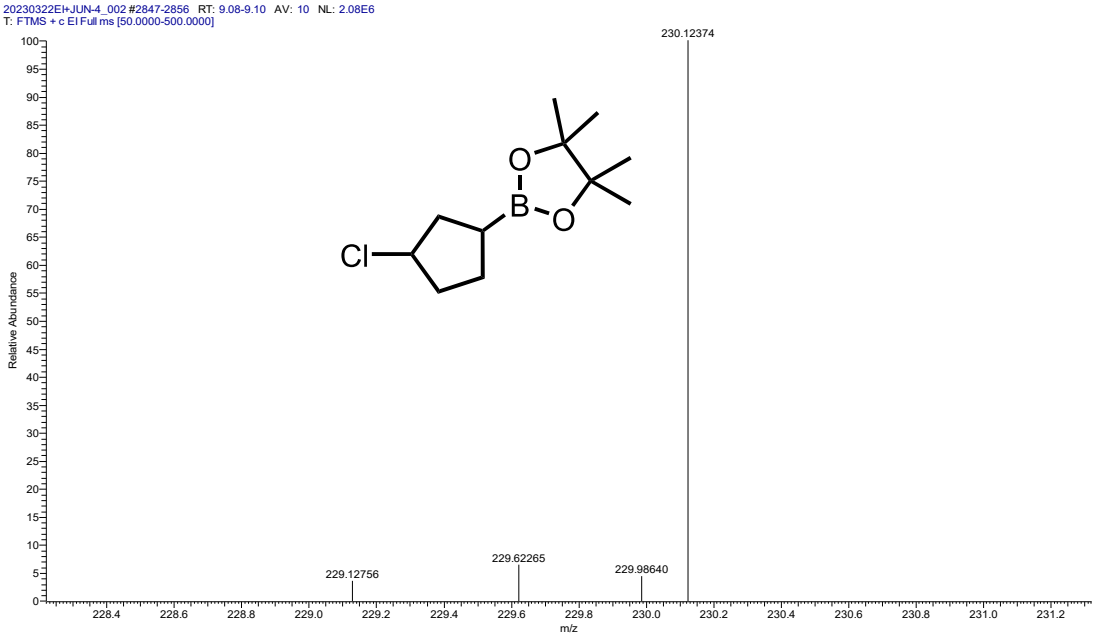

20230322EI+JUN-3_002 #3095-3106 RT: 9.64-9.67 AV: 12 NL: 3.43E6
T: FTMS + c EI Full ms [50.0000-500.0000]
Relative Abundance
m/z
276.07111
274.07324
274.39758
273.07680
275.07525
269.84970
271.03598
272.12552
269.50790
271.82193
277.07452
279.15421
281.05142
O
B
O
Br

2-(3-Chlorocyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)

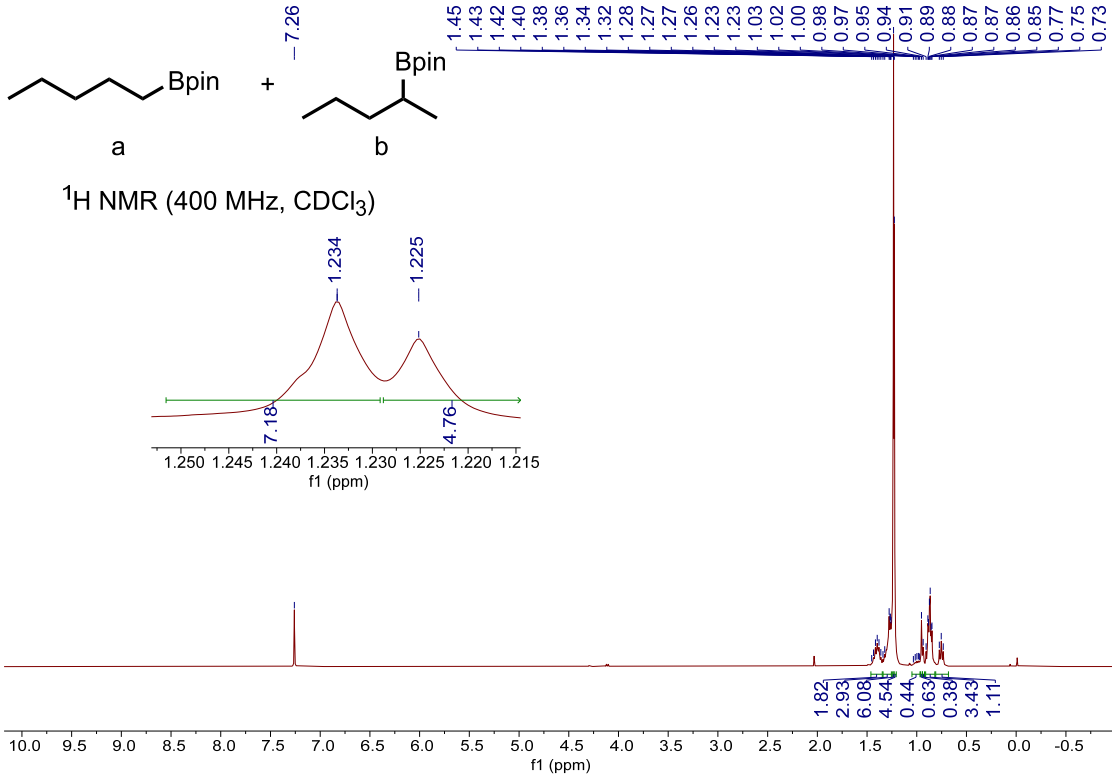


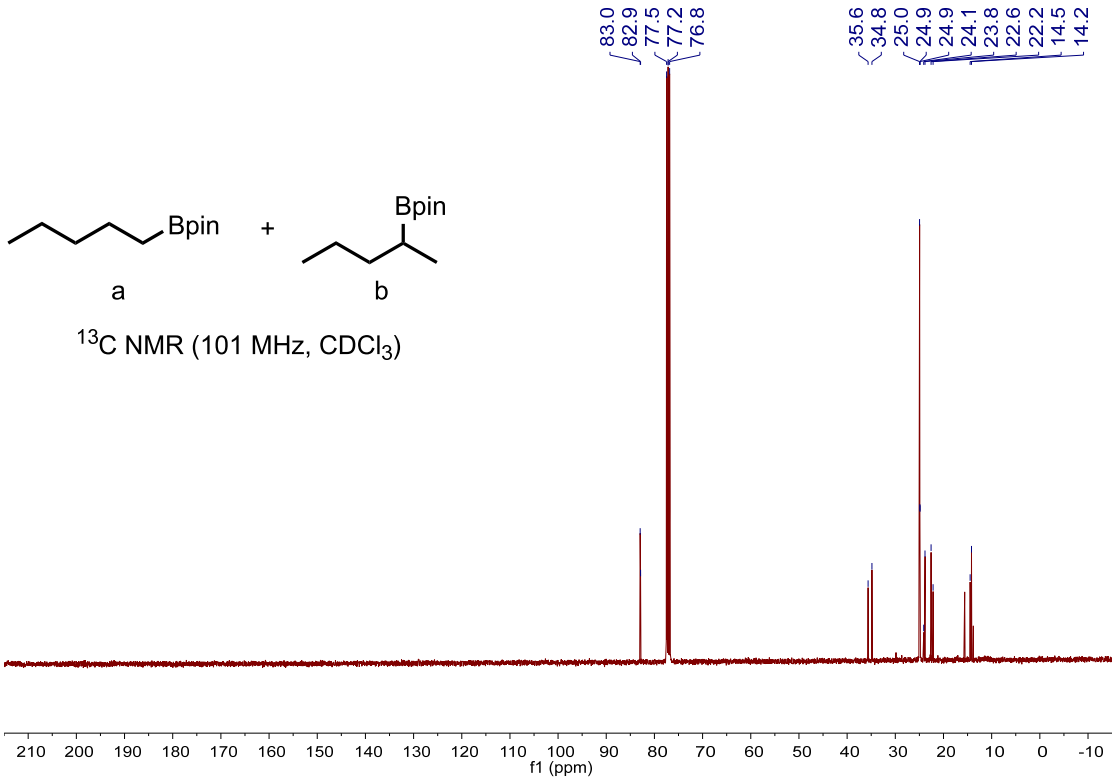


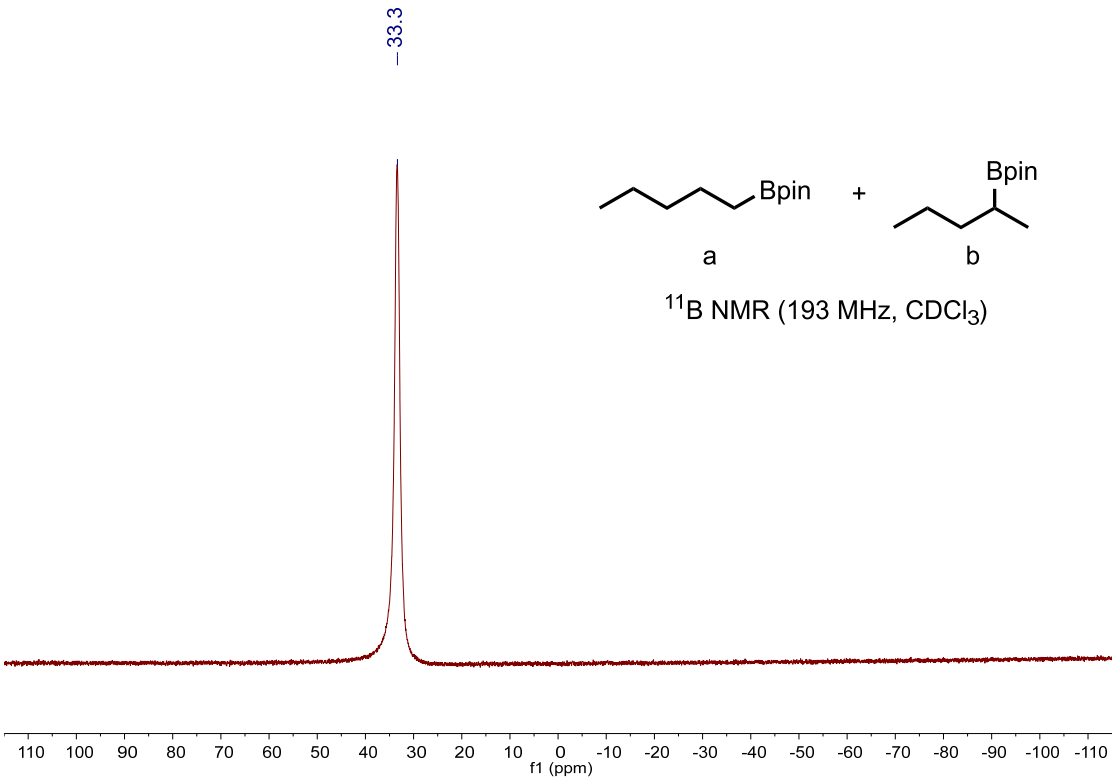

33.3
Cl
Bpin
a
Cl
Bpin
b
+
^{11}B NMR (193 MHz, $CDCl_3$)
f1 (ppm)
Noe
Bpin
Cl
Noe
f2 (ppm)
f1 (ppm)

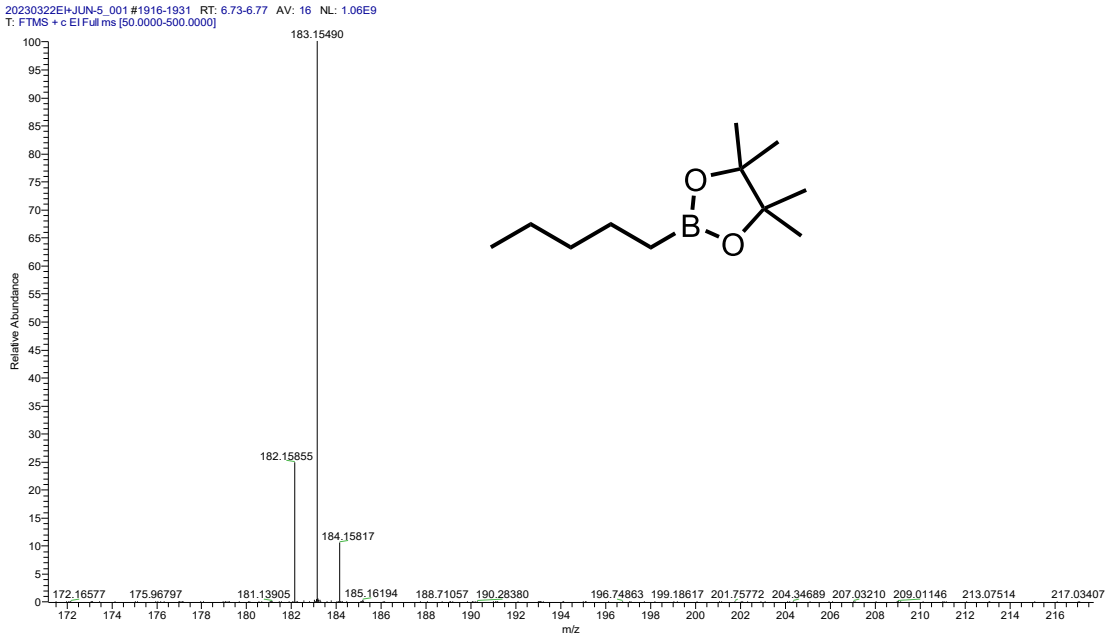

20230322EI+JUN-4_002 #2847-2856 RT: 9.08-9.10 AV: 10 NL: 2.08E6
T: FTMS + c EI Full ms [50.0000-500.0000]
230.12374
229.62265
229.98640
229.12756
Relative Abundance
m/z
O
B
O
Cl

4,4,5,5-Tetramethyl-2-pentyl-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-(pentan-2-yl)-1,3,2-dioxaborolane (10)

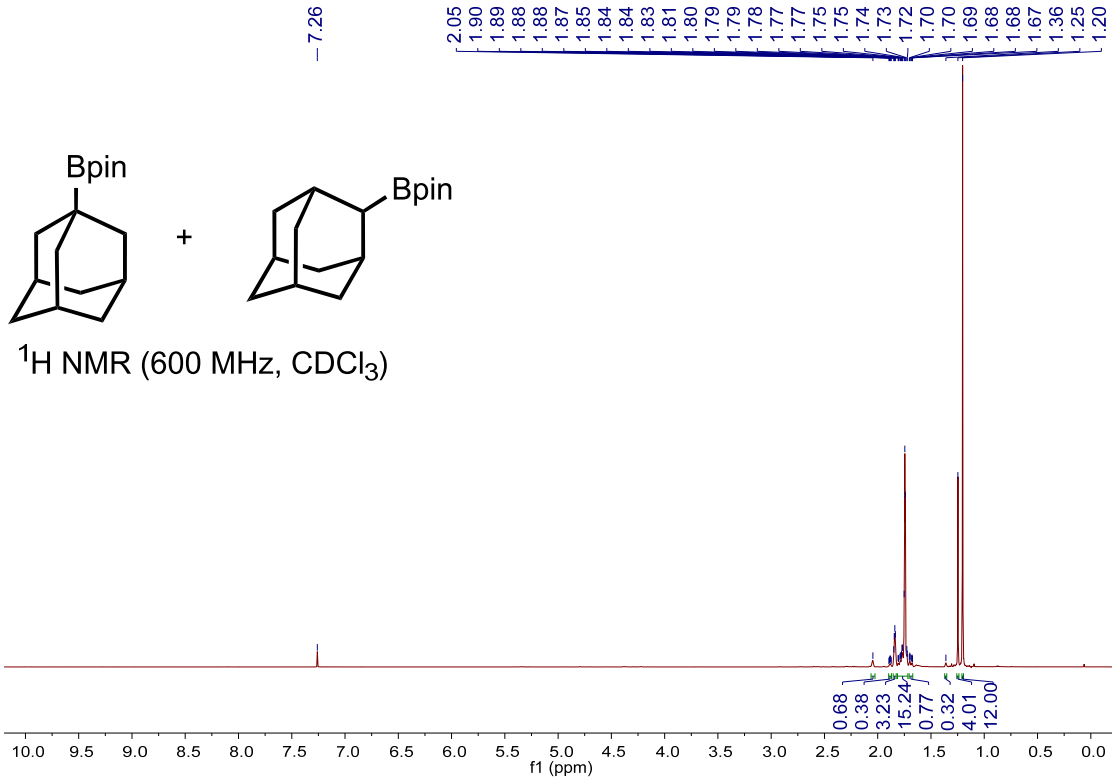


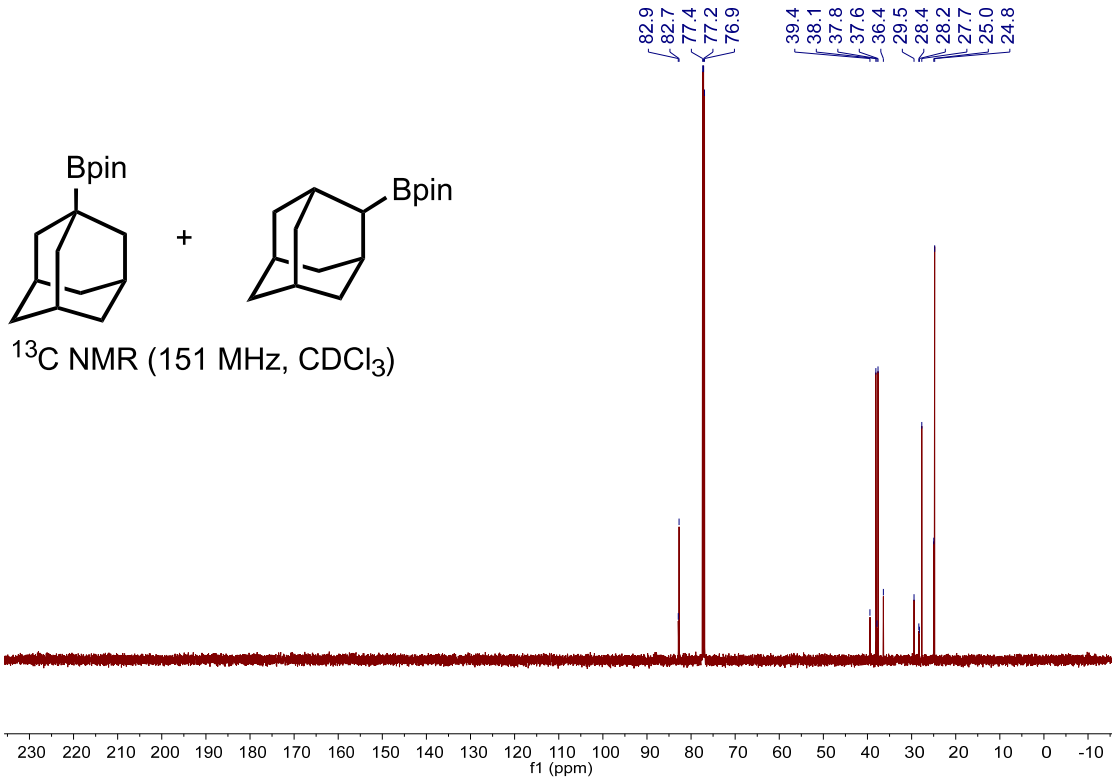


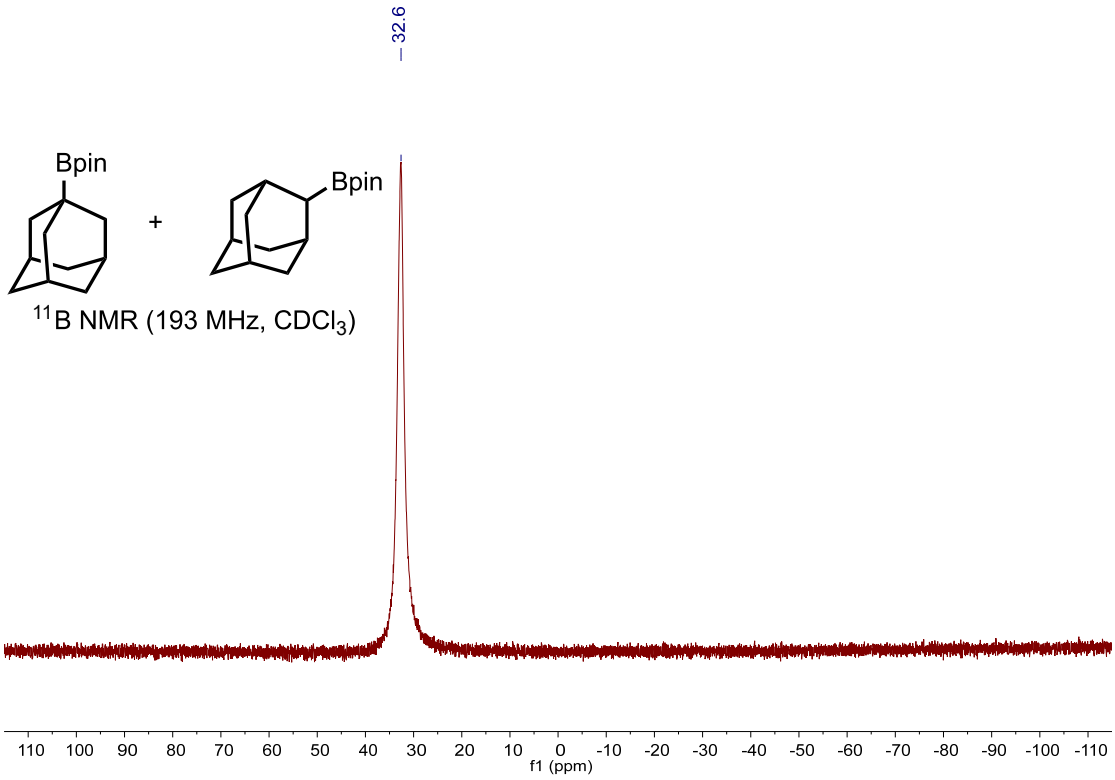

33.3
Bpin
+
Bpin
a
b
^{11}B NMR (193 MHz, CDCl$_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


20230322EI+JUN-5_001 #1916-1931 RT: 6.73-6.77 AV: 16 NL: 1.06E9
T: FTMS + c EI Full ms [50.0000-500.0000]
183.15490
182.15855
184.15817
172.16577
175.96797
181.13905
185.16194
188.71057
190.28380
196.74863
199.18617
201.75772
204.34689
207.03210
209.01146
213.07514
217.03407
Relative Abundance
m/z
O
B
O

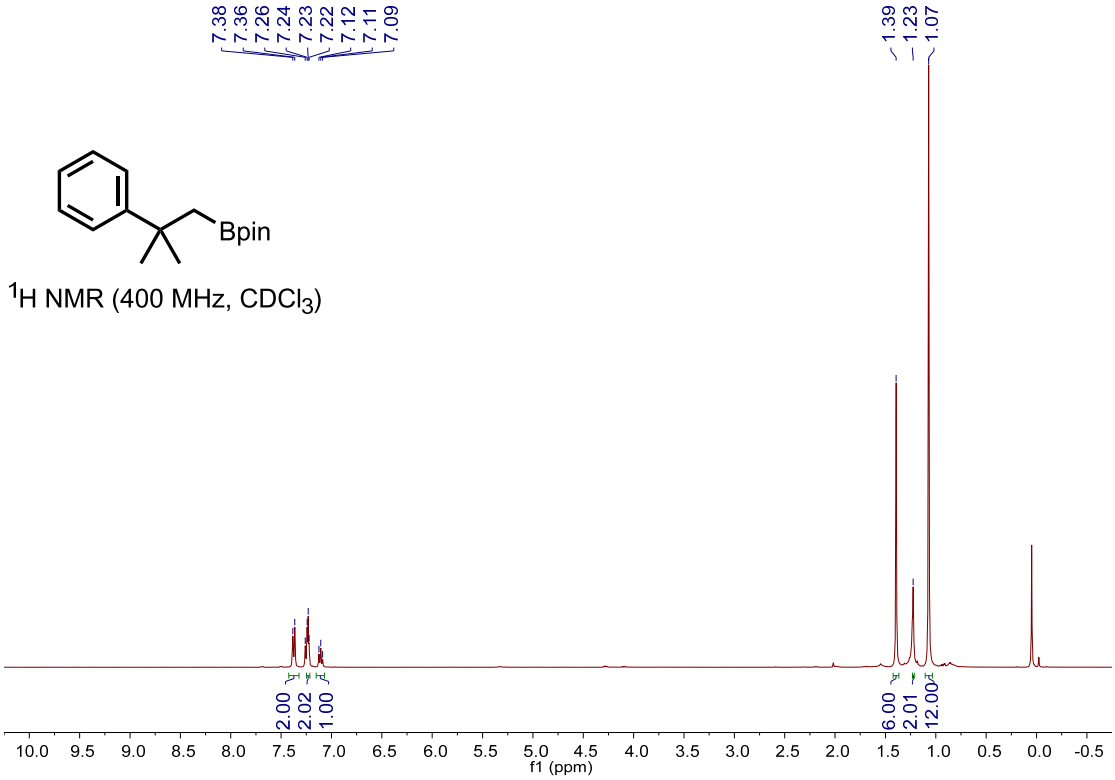
2-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(a) and 2-((1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(b) (11)



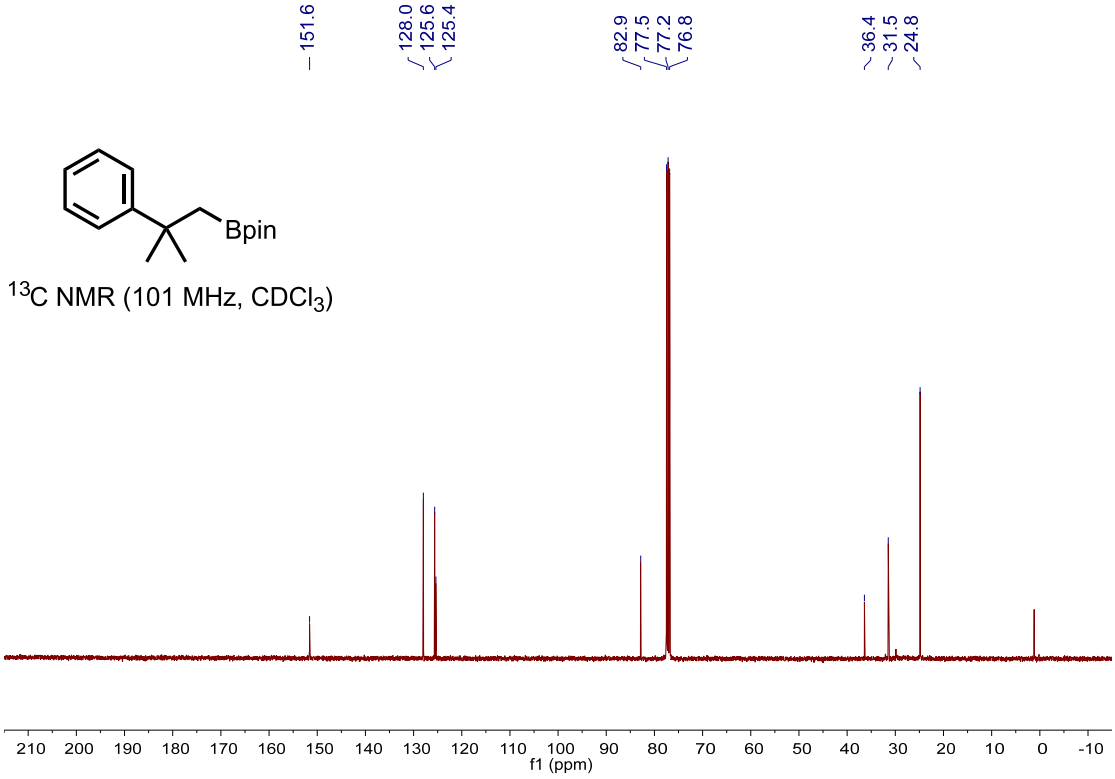



32.6
Bpin
+
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

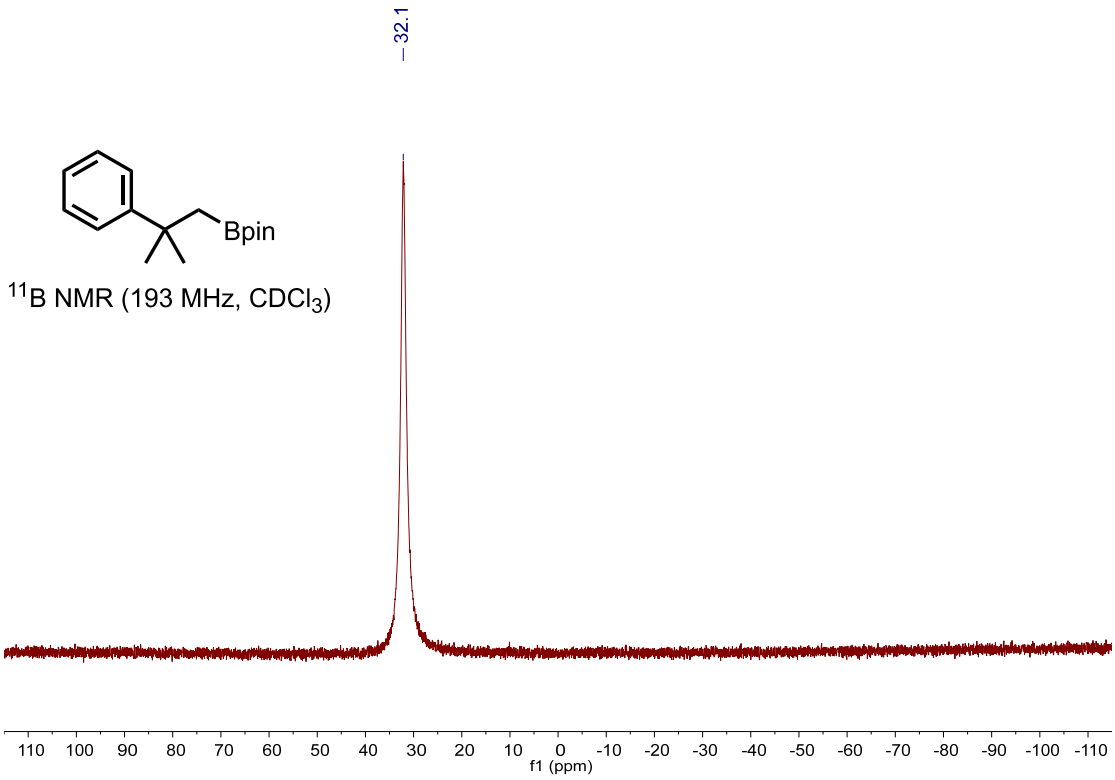
4,4,5,5-Tetramethyl-2-(2-methyl-2-phenylpropyl)-1,3,2-dioxaborolane (12)



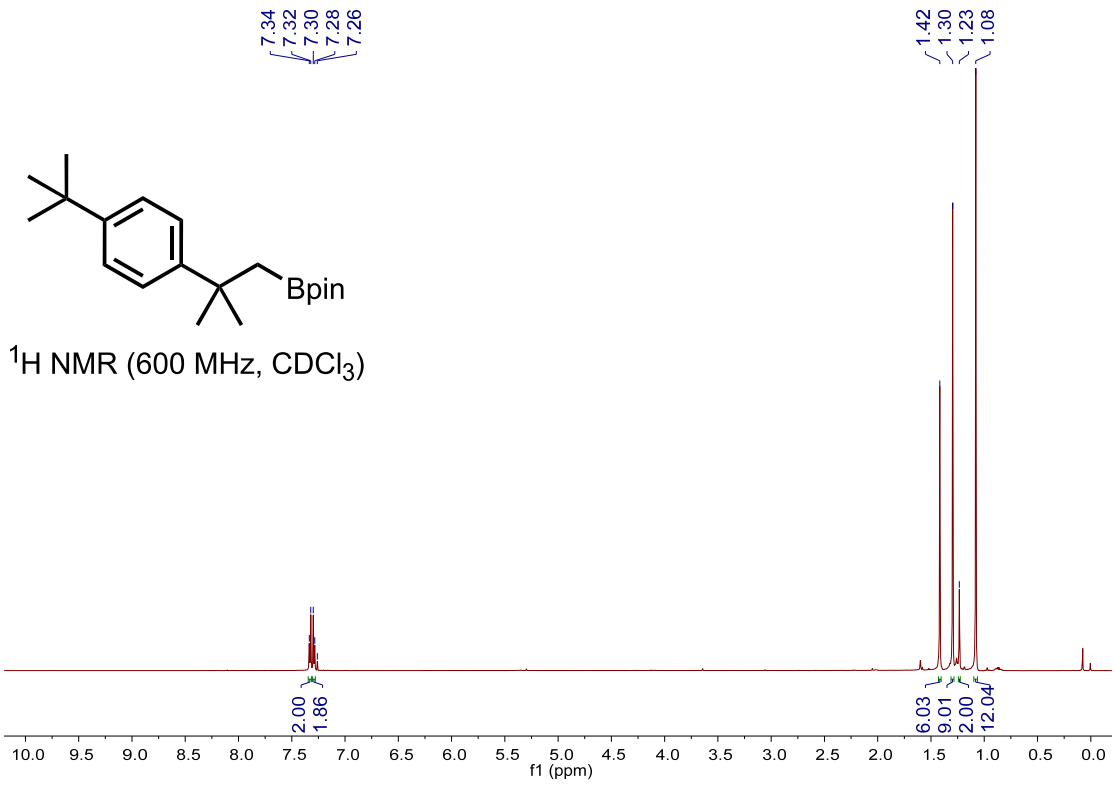
^{1}H NMR (400 MHz, $CDCl_3$)



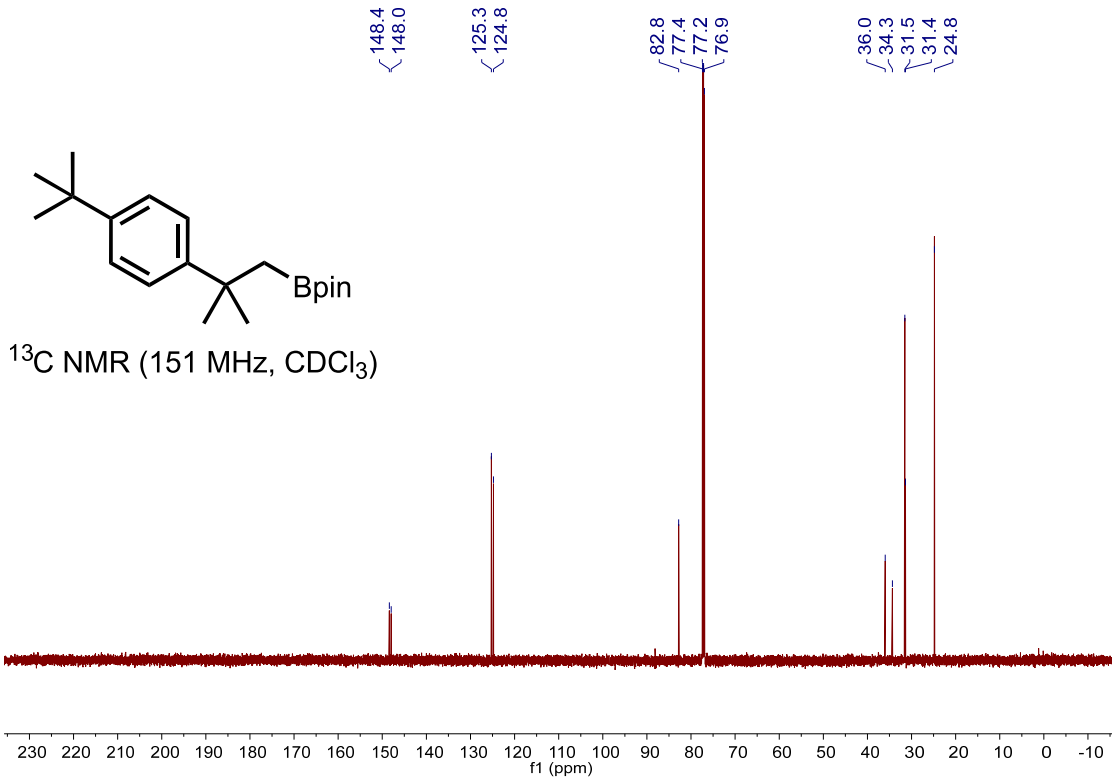
^{13}C NMR (101 MHz, $CDCl_3$)


32.1
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

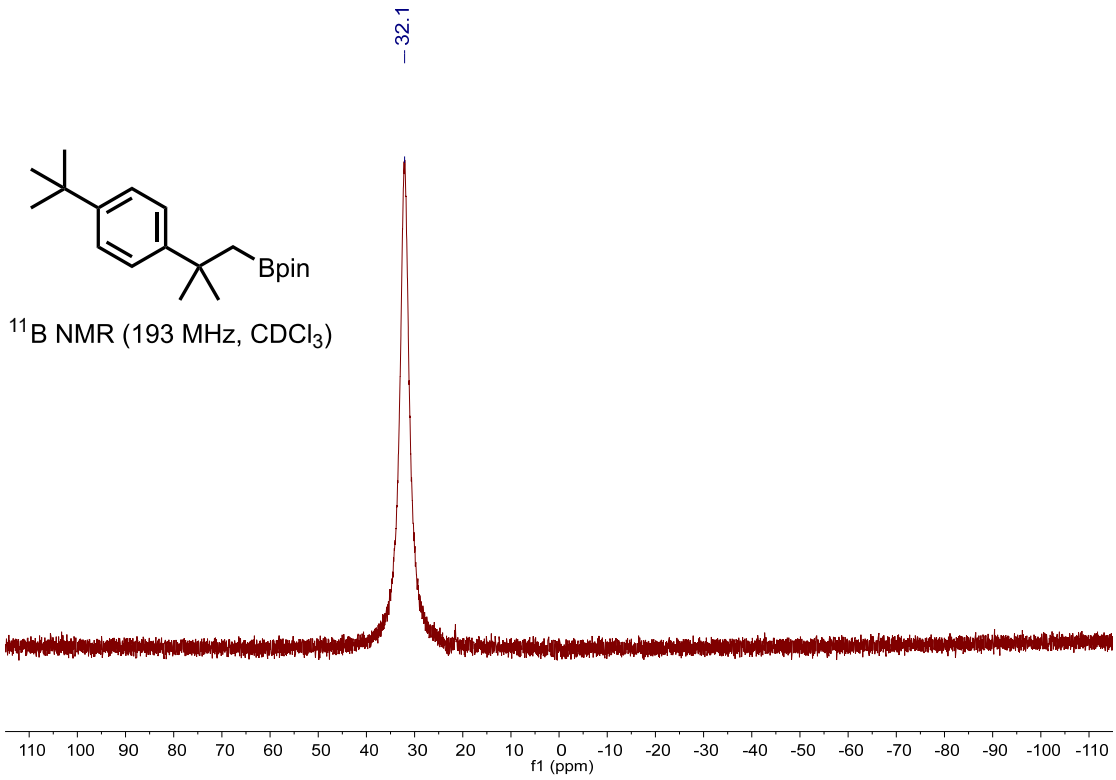
2-(2-(4-(*tert*-Butyl)phenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)



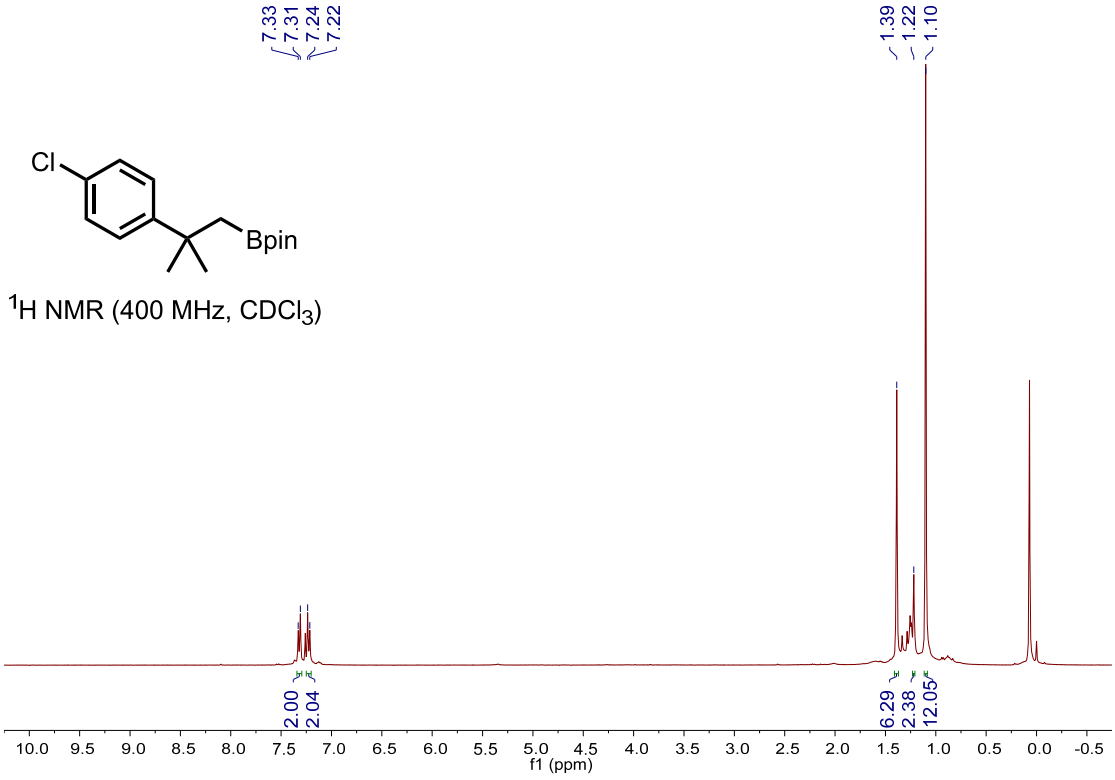
^{1}H NMR (600 MHz, $CDCl_3$)



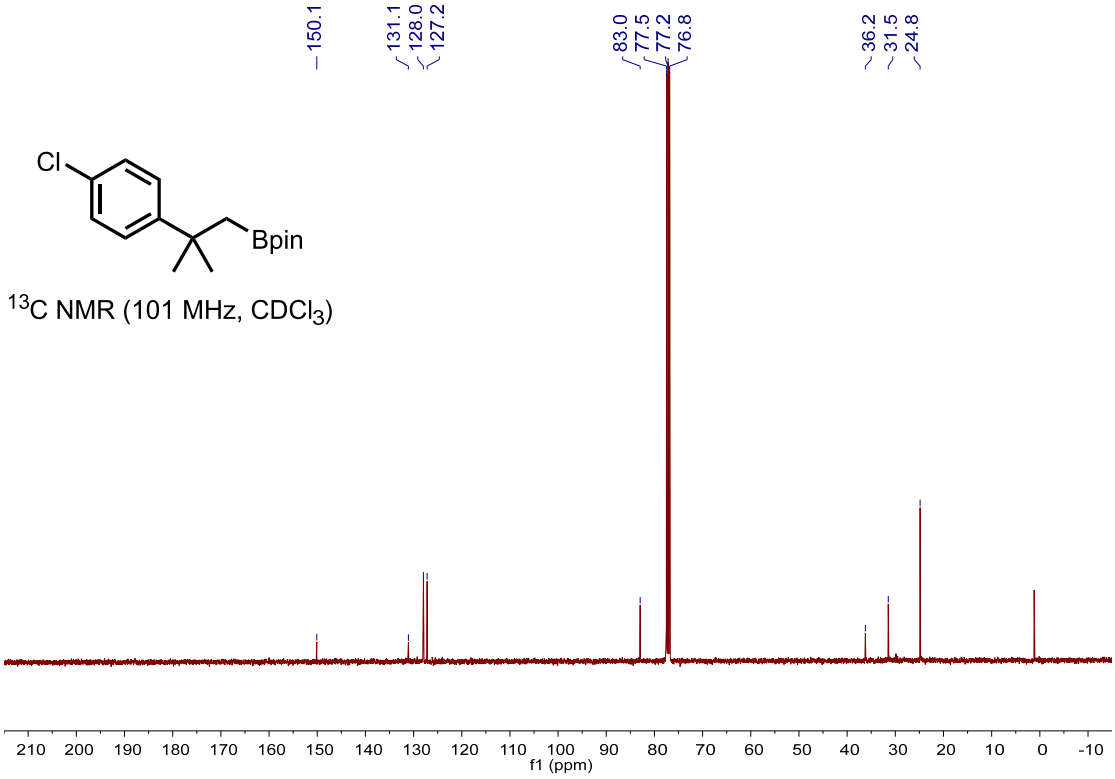
^{13}C NMR (151 MHz, $CDCl_3$)


32.1
Bpin
11B NMR (193 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

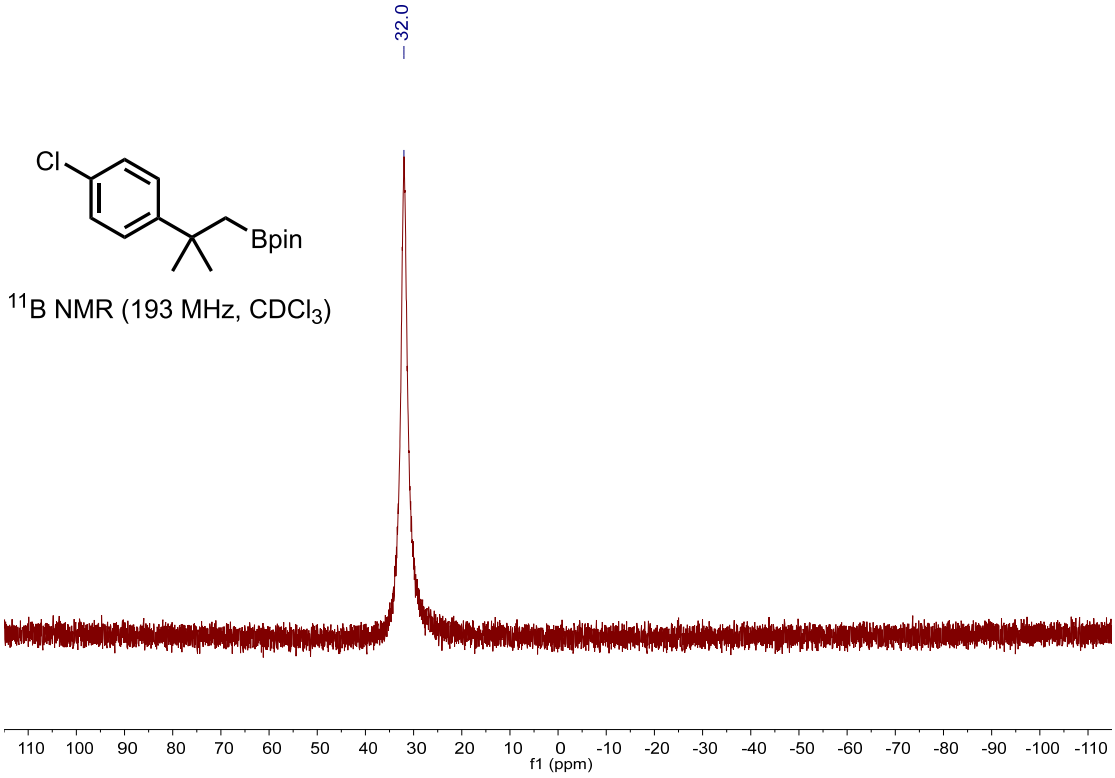
2-(2-(4-Chlorophenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)

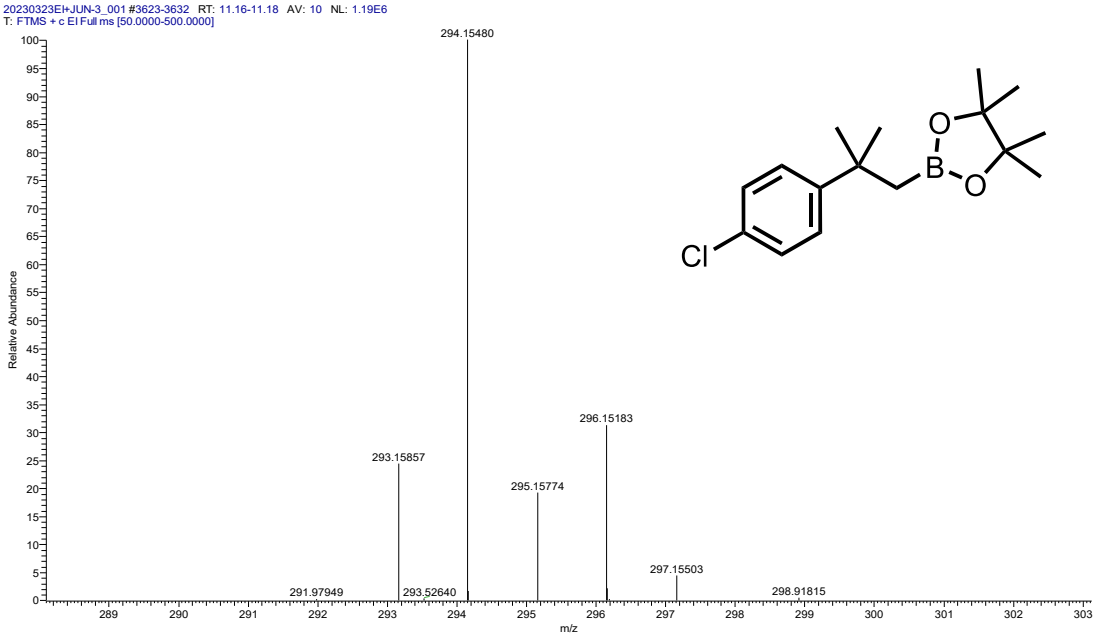


^{1}H NMR (400 MHz, $CDCl_3$)

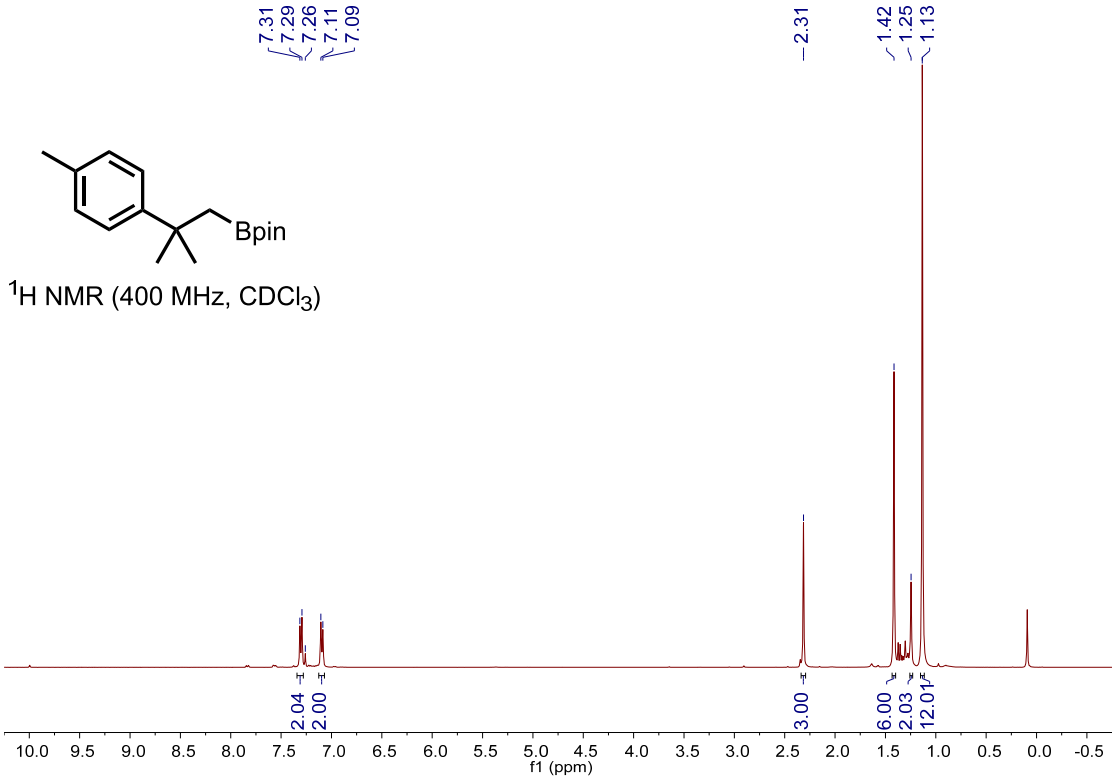


^{13}C NMR (101 MHz, $CDCl_3$)

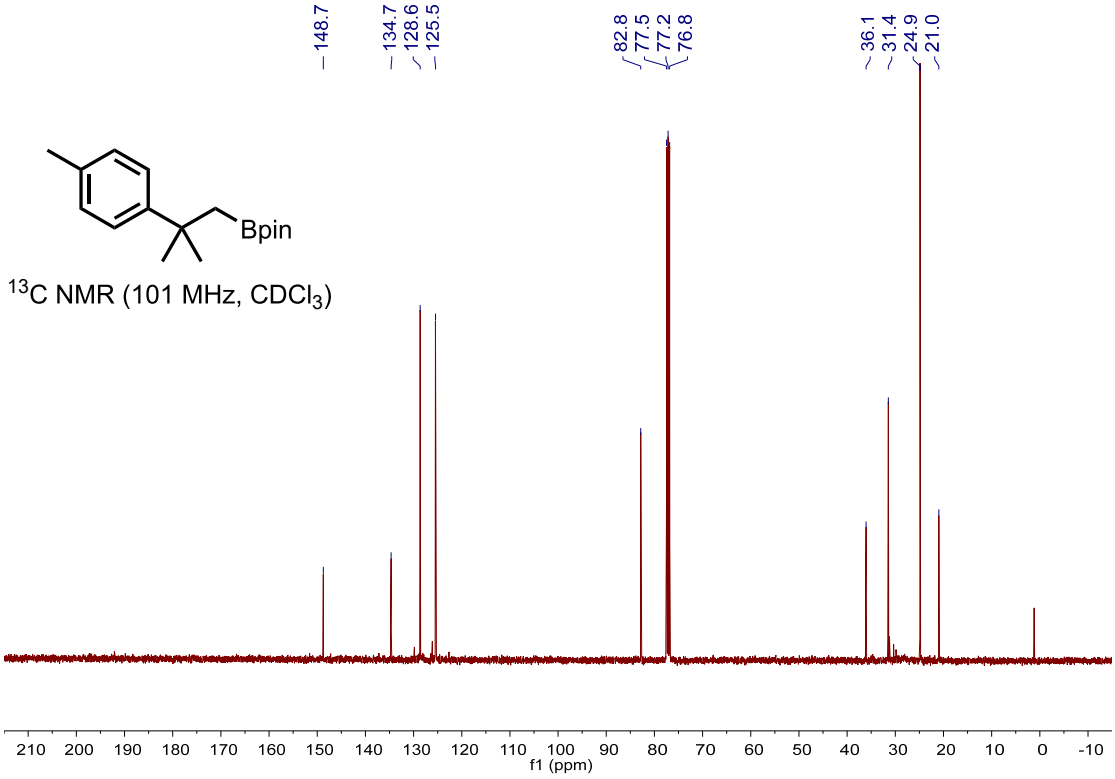

32.0
Cl
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


20230323EI+JUN-3_001 #3623-3632 RT: 11.16-11.18 AV: 10 NL: 1.19E6
T: FTMS + c EI Full ms [50.0000-500.0000]
294.15480
296.15183
293.15857
295.15774
297.15503
291.97949
293.52640
298.91815
Relative Abundance
m/z
Cl
O
B
O

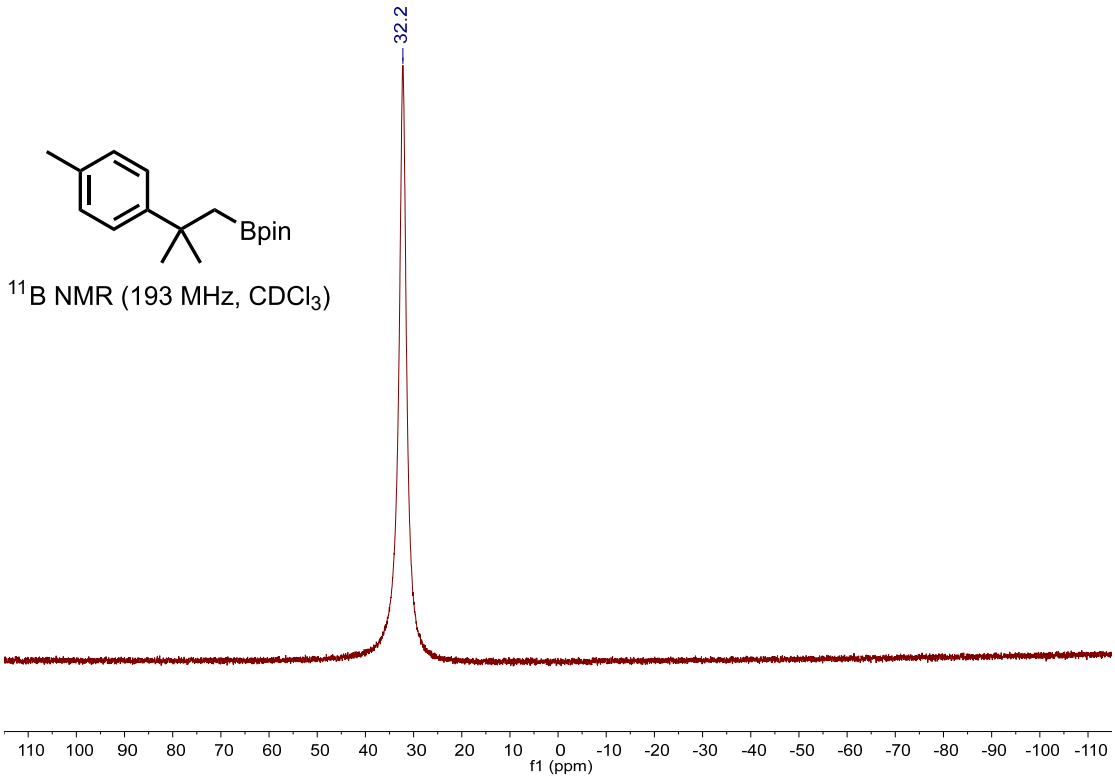
4,4,5,5-Tetramethyl-2-(2-methyl-2-(p-tolyl)propyl)-1,3,2-dioxaborolane (15)

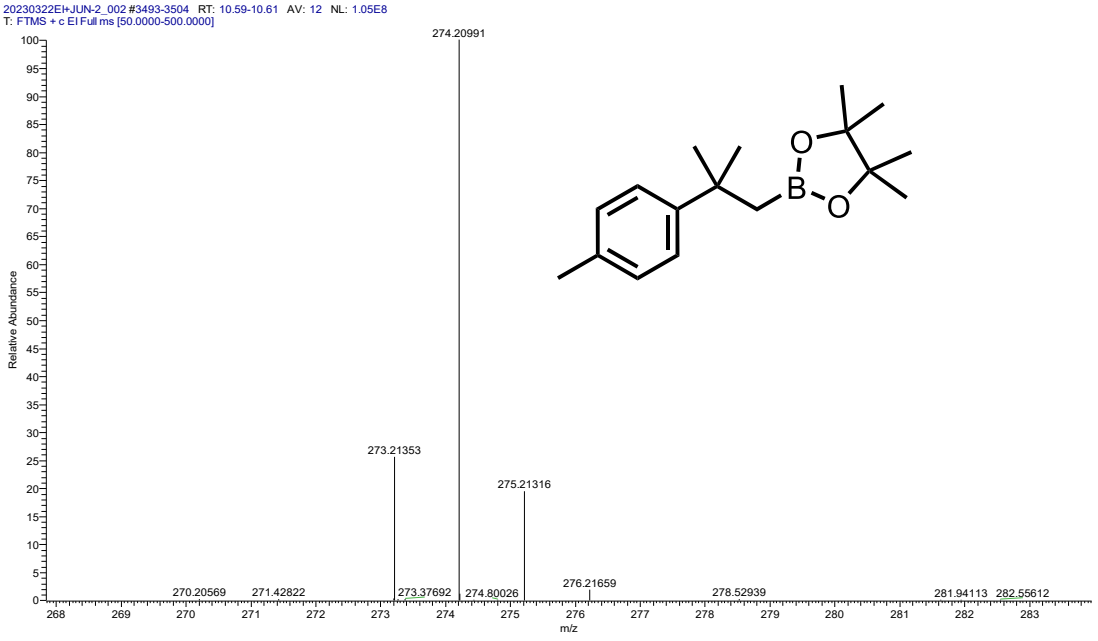


^{1}H NMR (400 MHz, $CDCl_3$)

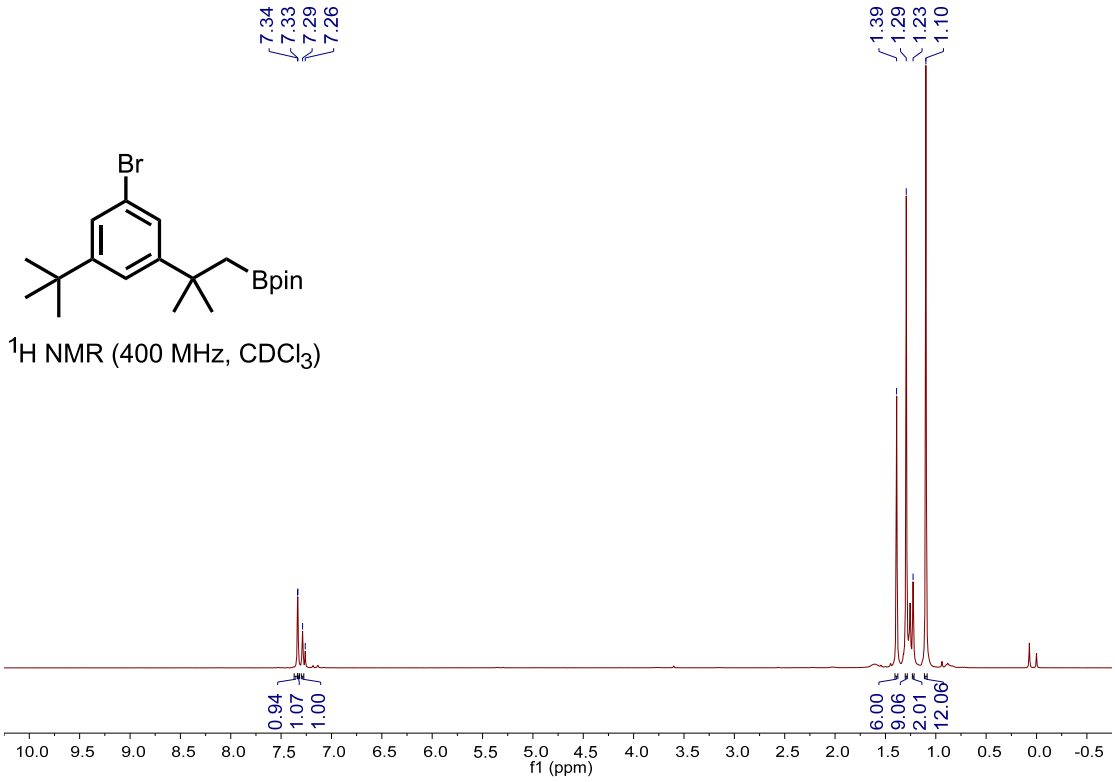


^{13}C NMR (101 MHz, $CDCl_3$)

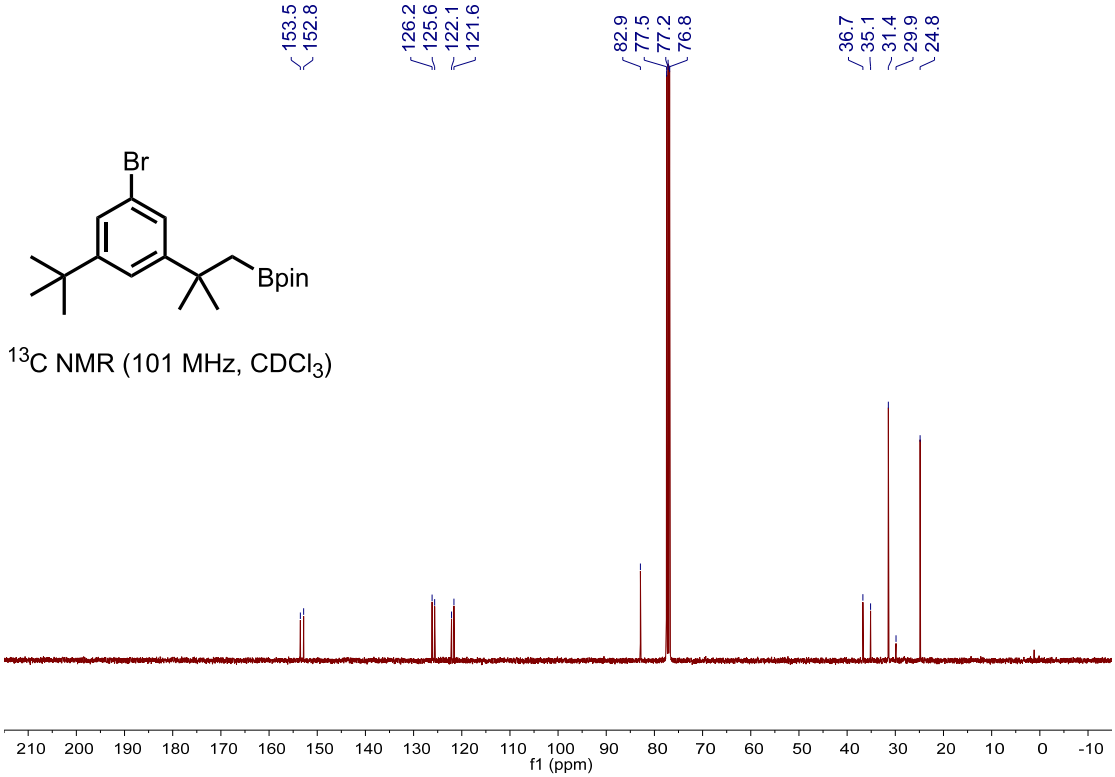

32.2
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


20230322EI+JUN-2_002 #3493-3504 RT: 10.59-10.61 AV: 12 NL: 1.05E8
T: FTMS + c EI Full ms [50.0000-500.0000]
274.20991
273.21353
275.21316
276.21659
270.20569
271.42822
273.37692
274.80026
278.52939
281.94113
282.55612
Relative Abundance
m/z
O
B
O

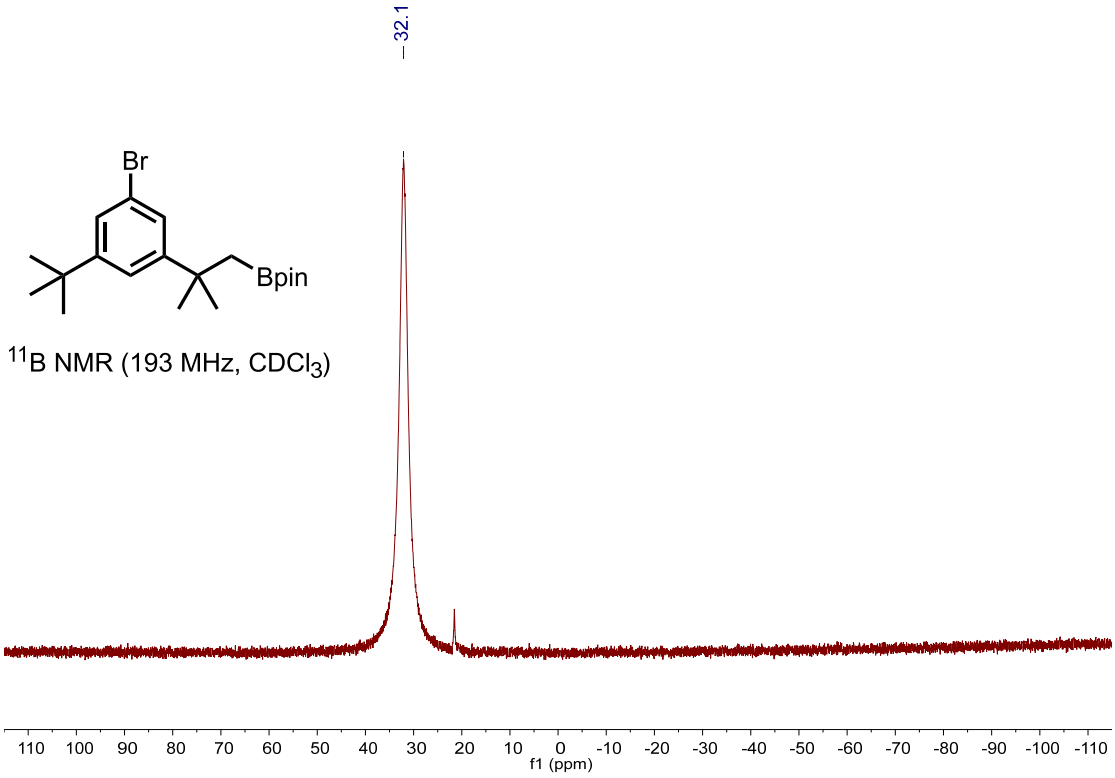
2-(2-(3-Bromo-5-(*tert*-butyl)phenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

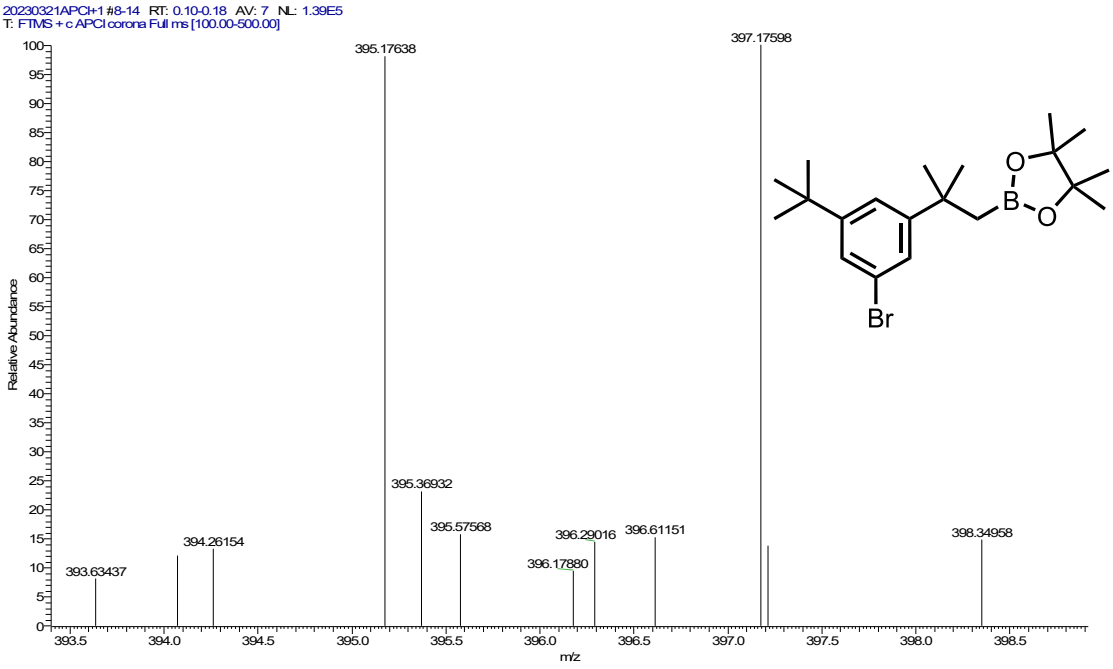


^{1}H NMR (400 MHz, $CDCl_3$)

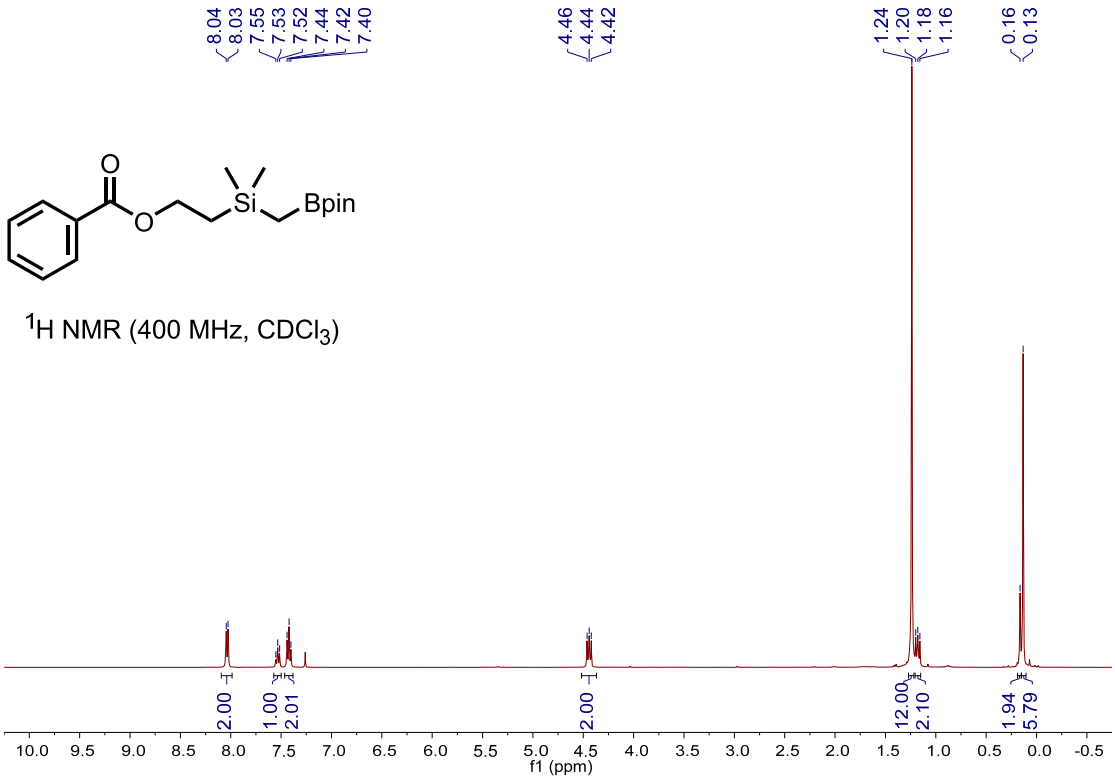


^{13}C NMR (101 MHz, $CDCl_3$)

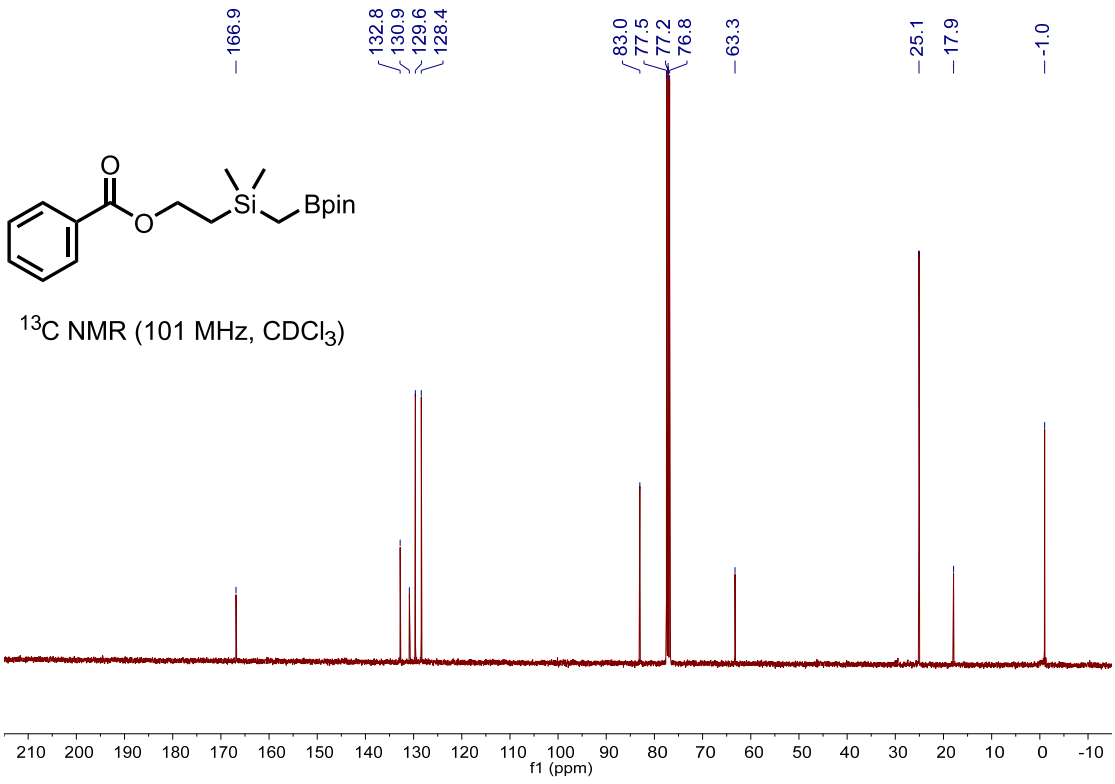

32.1
Br
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


20230321APCI+1 #8-14 RT: 0.10-0.18 AV: 7 NL: 1.39E5
T: FTMS + c APCI corona Full ms [100.00-500.00]
395.17638
397.17598
395.36932
395.57568
396.29016
396.61151
396.17880
394.26154
393.63437
398.34958
Relative Abundance
m/z
O
B
O
Br

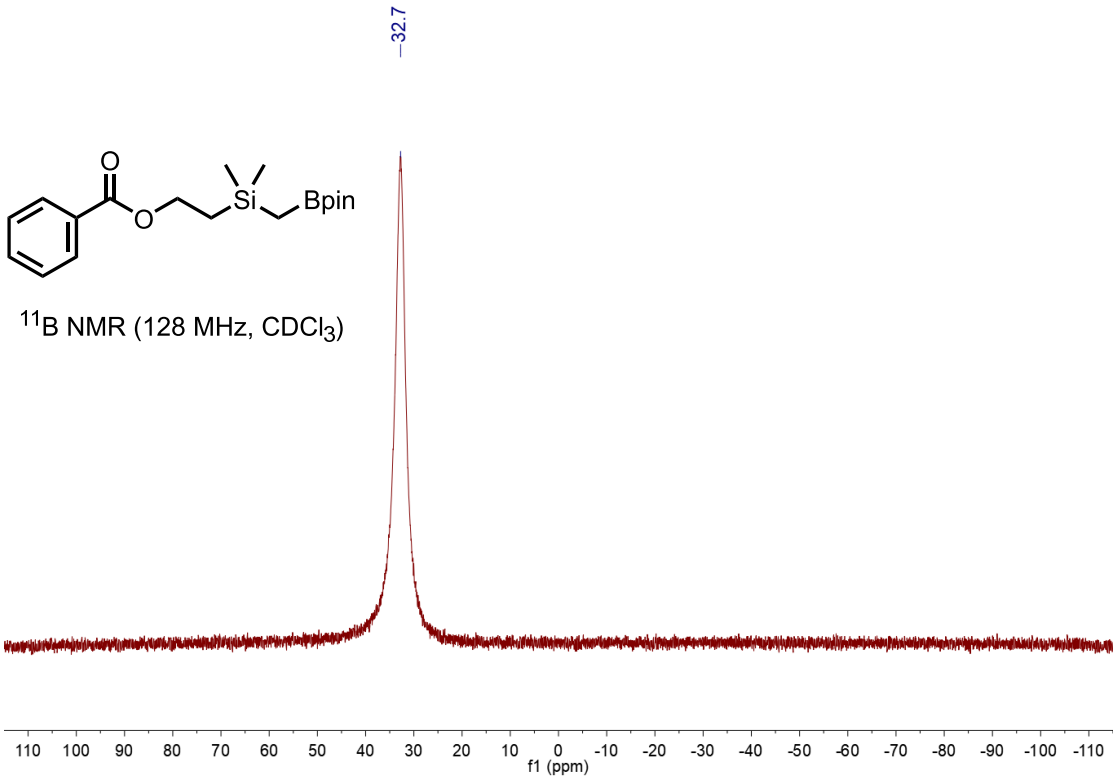
2-(Dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silyl)ethyl benzoate (17)



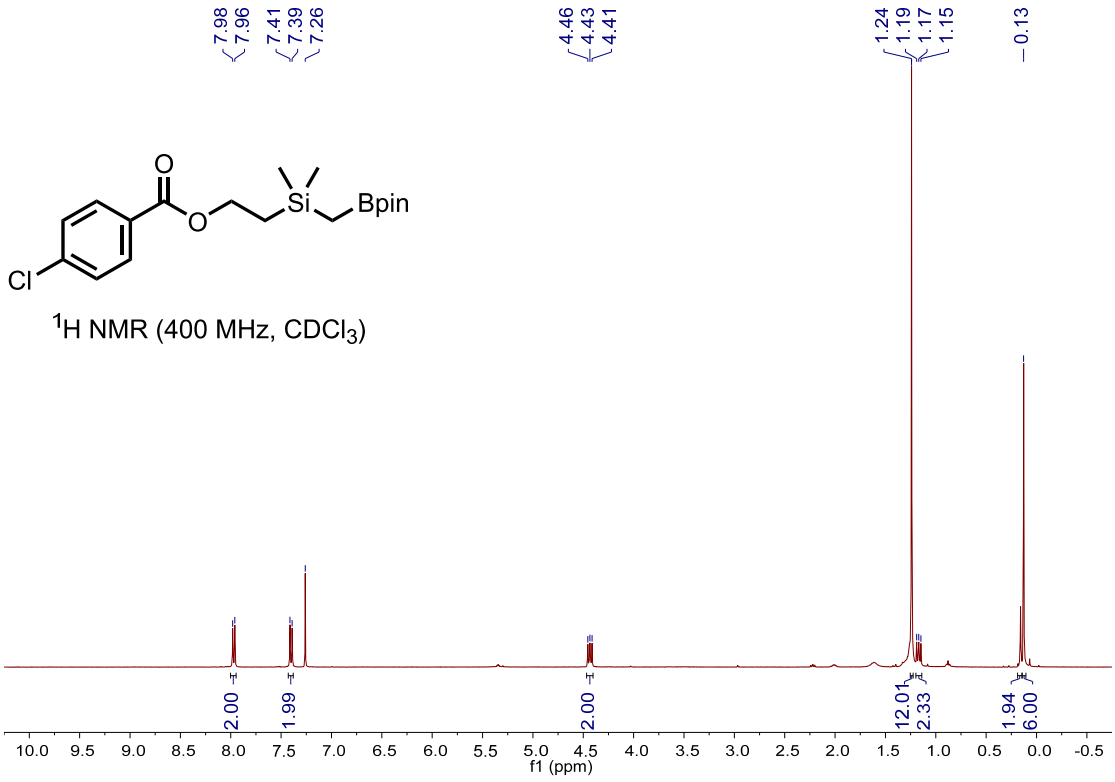
^{1}H NMR (400 MHz, $CDCl_3$)



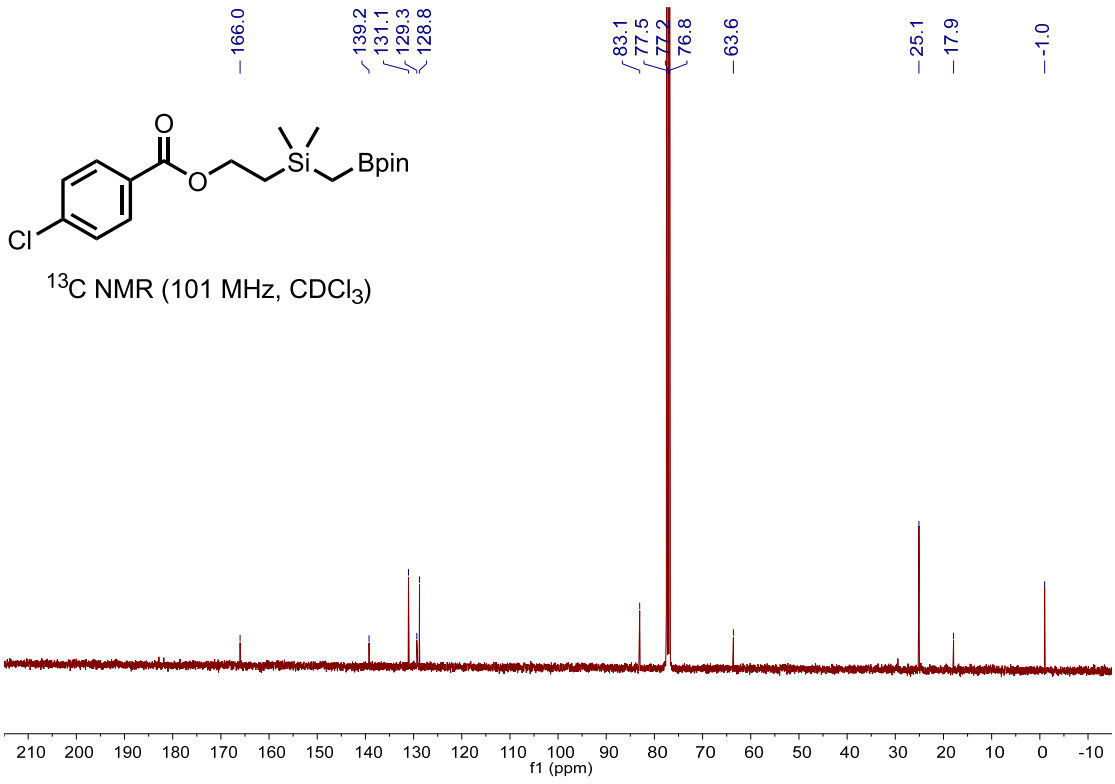
^{13}C NMR (101 MHz, $CDCl_3$)


32.7
O
O
Si
Bpin
^{11}B NMR (128 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

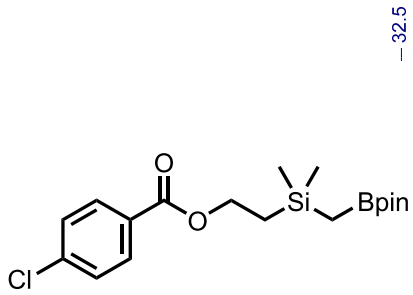
2-(Dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silyl)ethyl 4-chlorobenzoate (18)



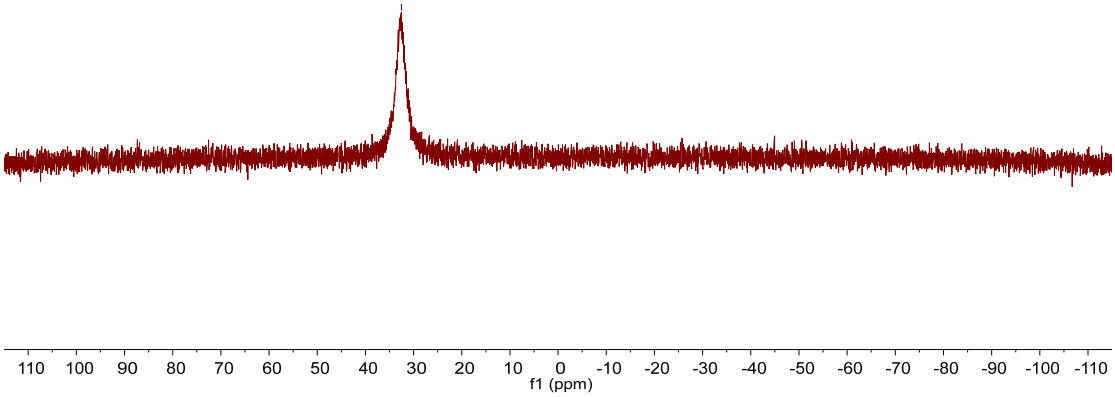
^{1}H NMR (400 MHz, $CDCl_3$)

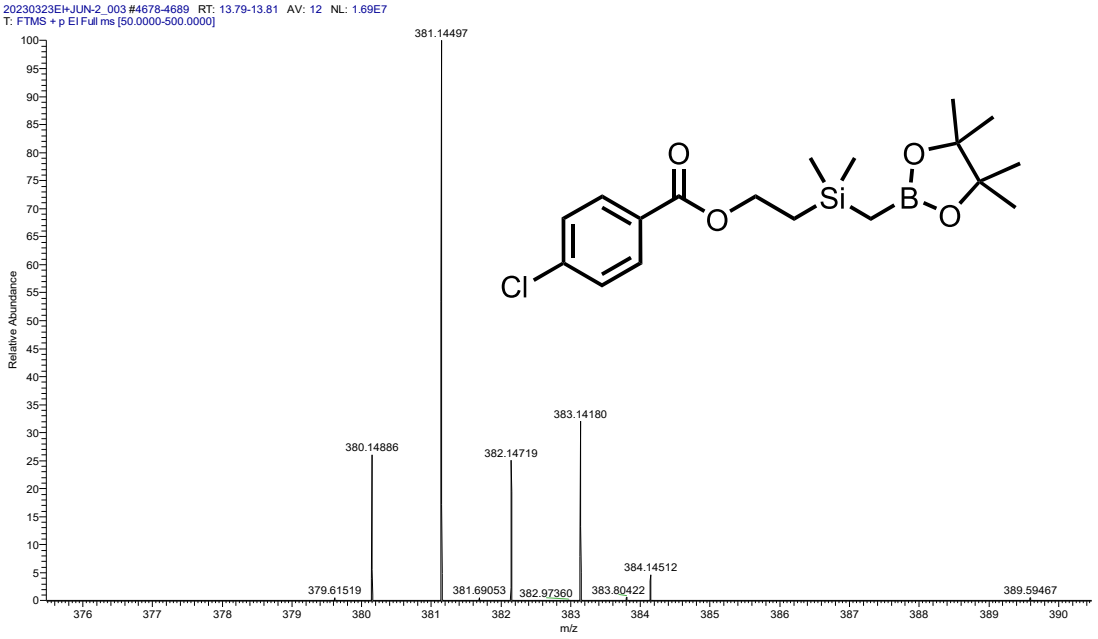


^{13}C NMR (101 MHz, $CDCl_3$)

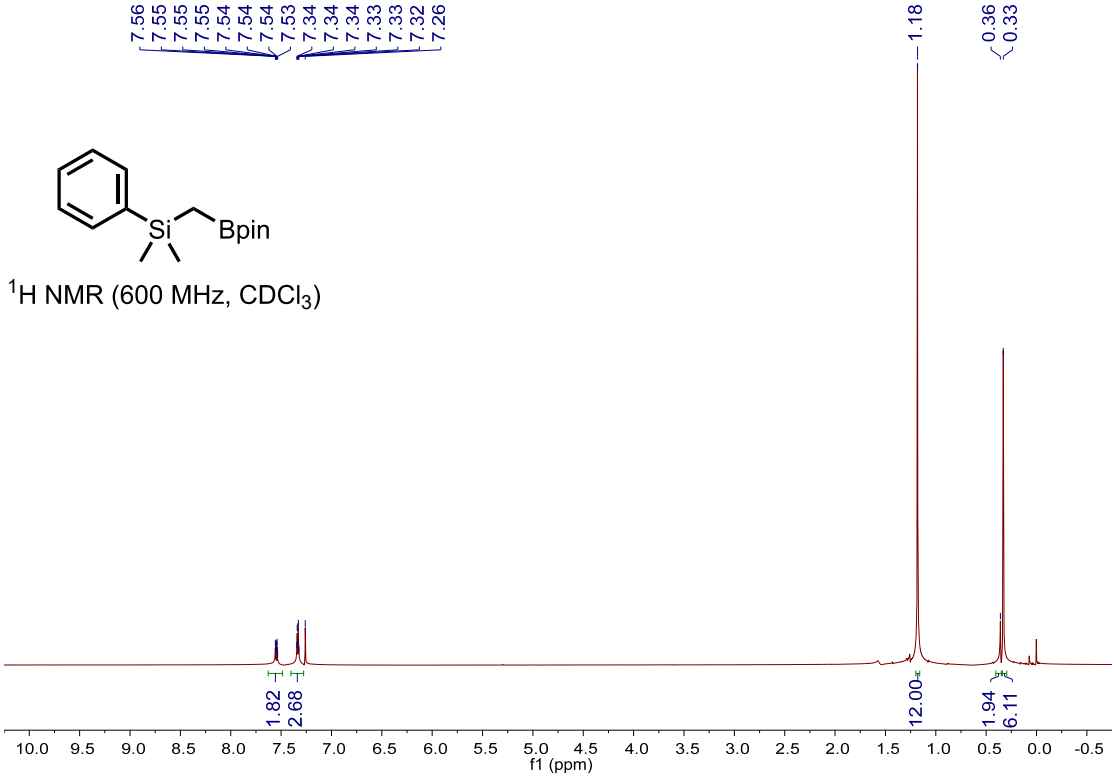


^{11}B NMR (128 MHz, $CDCl_3$)

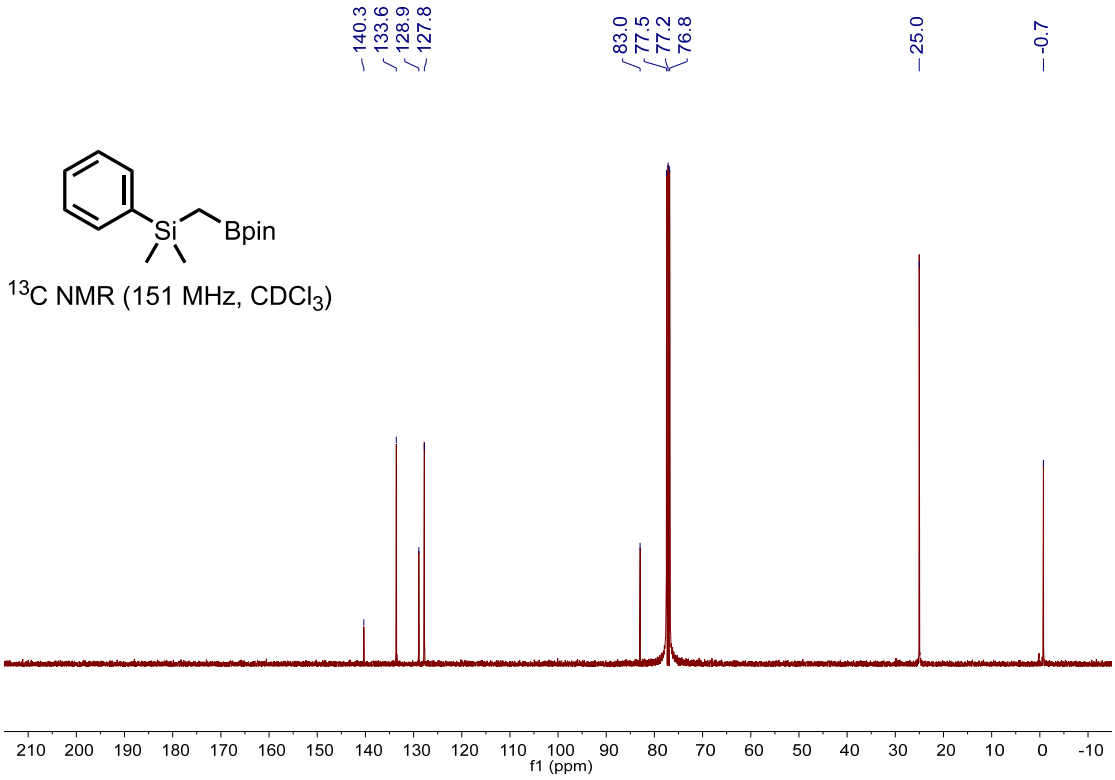




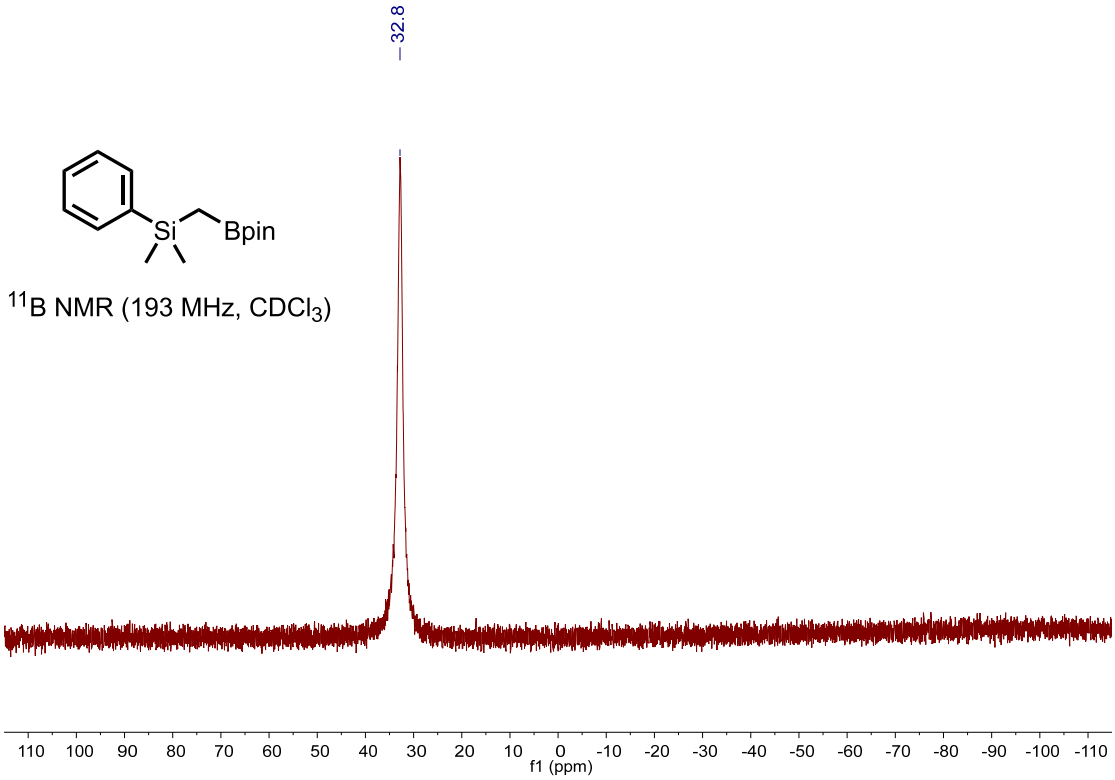
Dimethyl(phenyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silane (19)



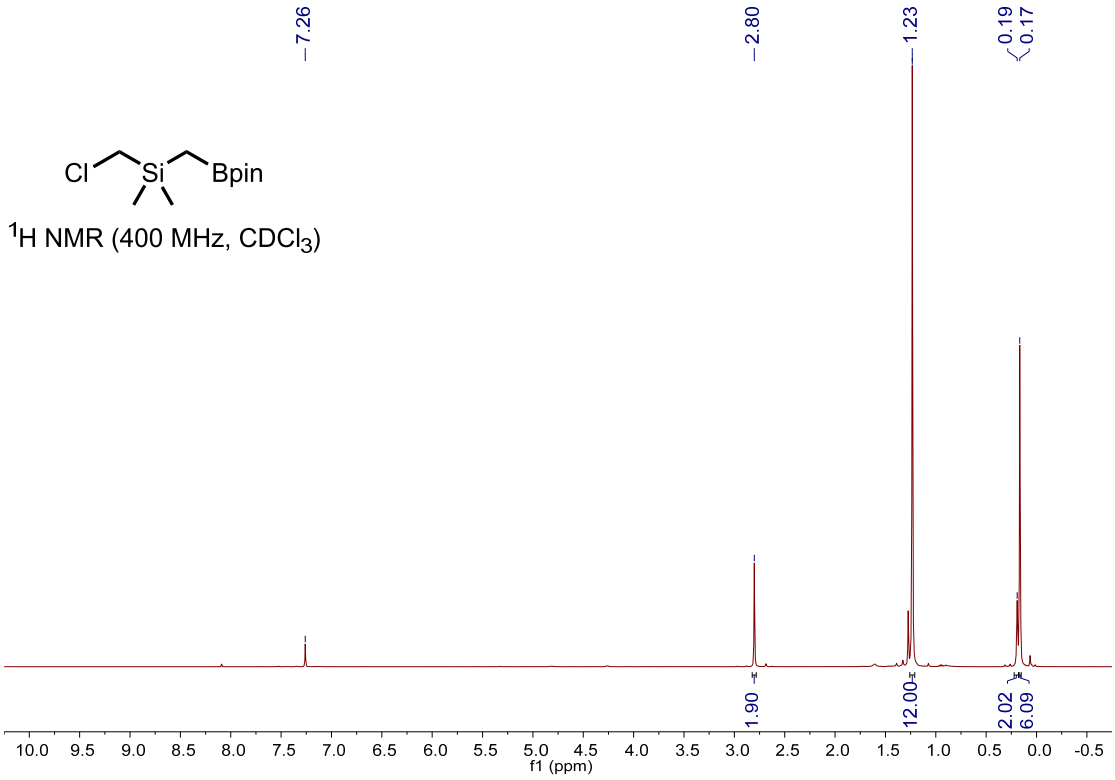
^{1}H NMR (600 MHz, $CDCl_3$)

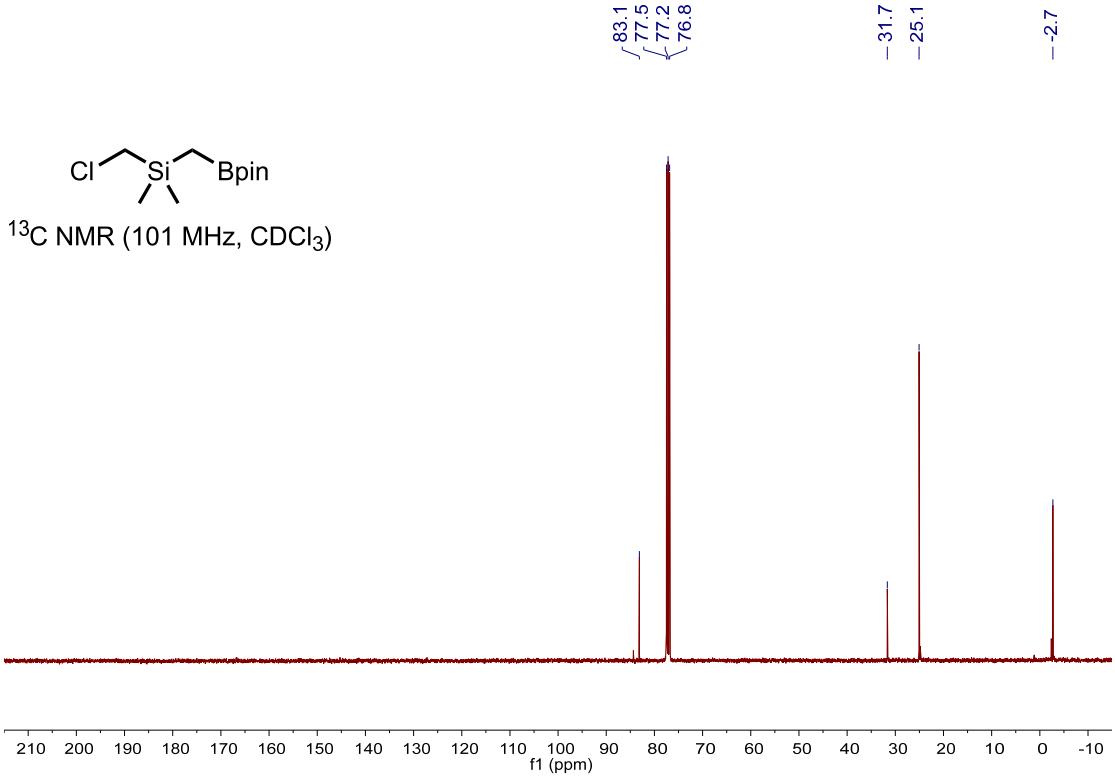


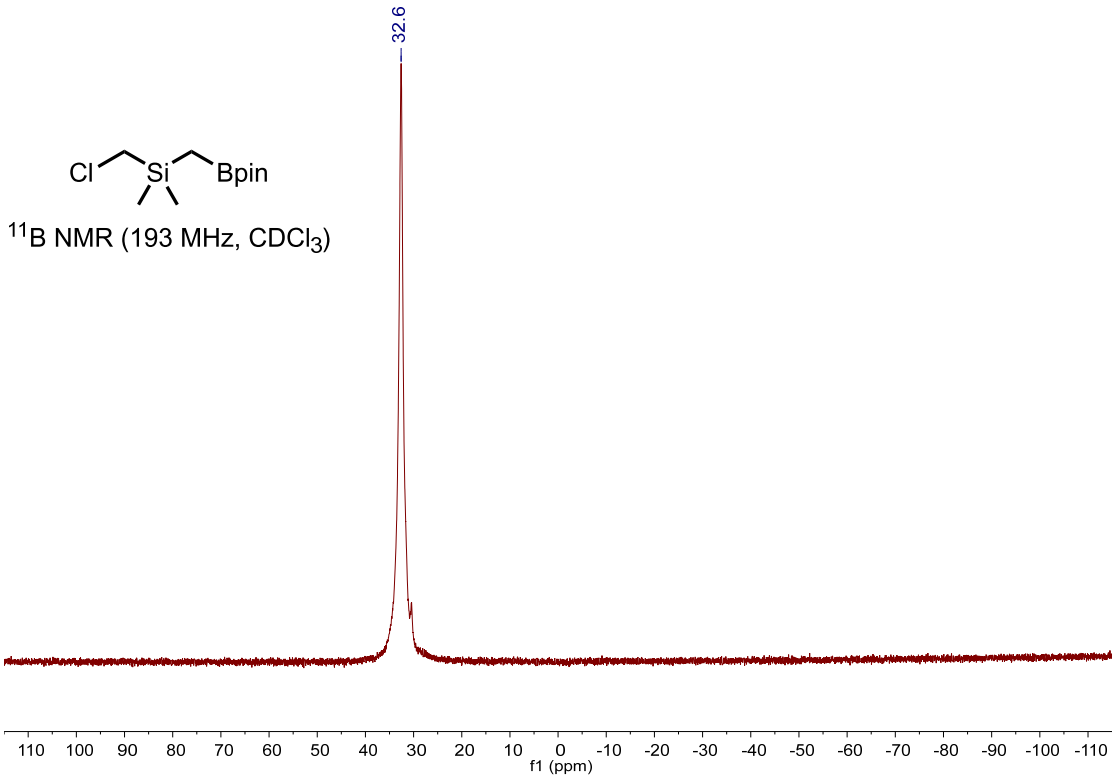
^{13}C NMR (151 MHz, $CDCl_3$)


32.8
Si
Bpin
11B NMR (193 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

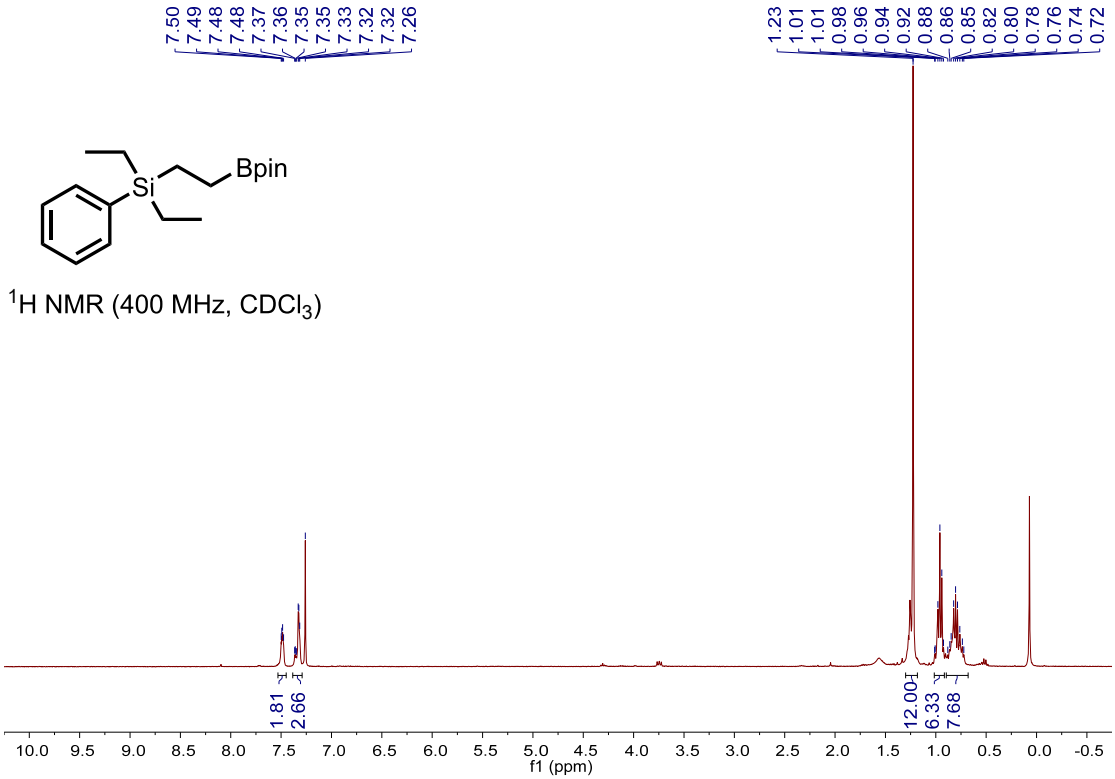
(Chloromethyl)dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silane (20)



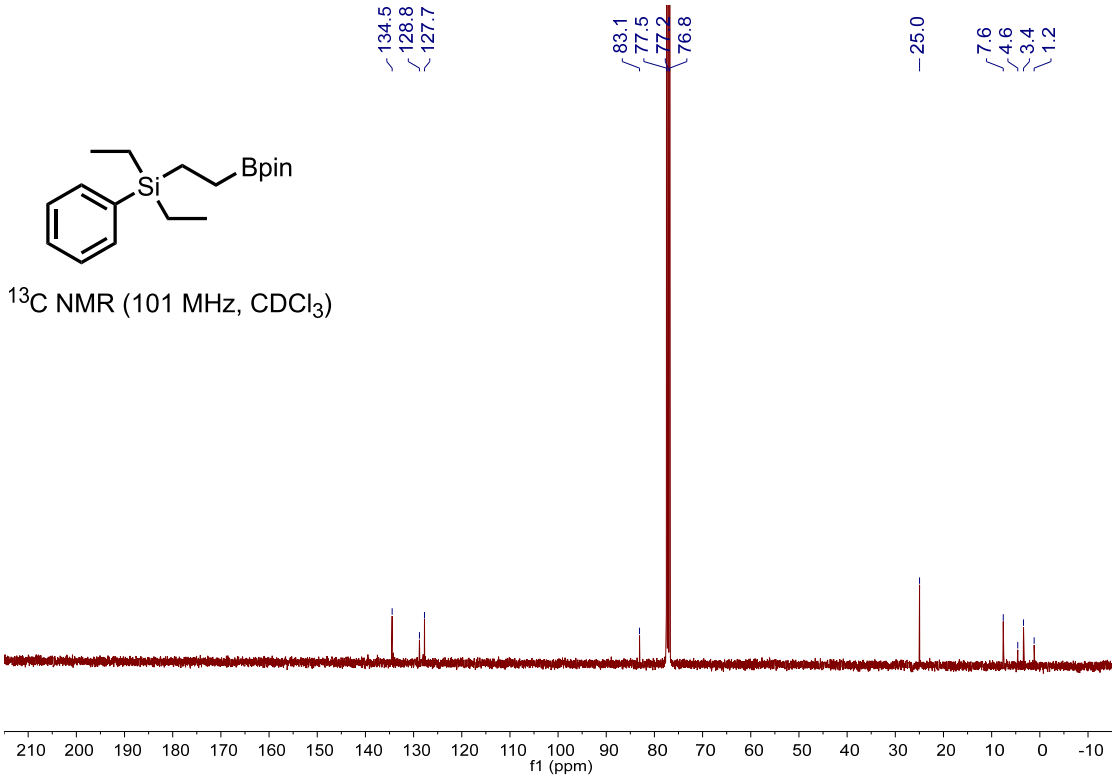



32.6
Cl
Si
Bpin
^{11}B NMR (193 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

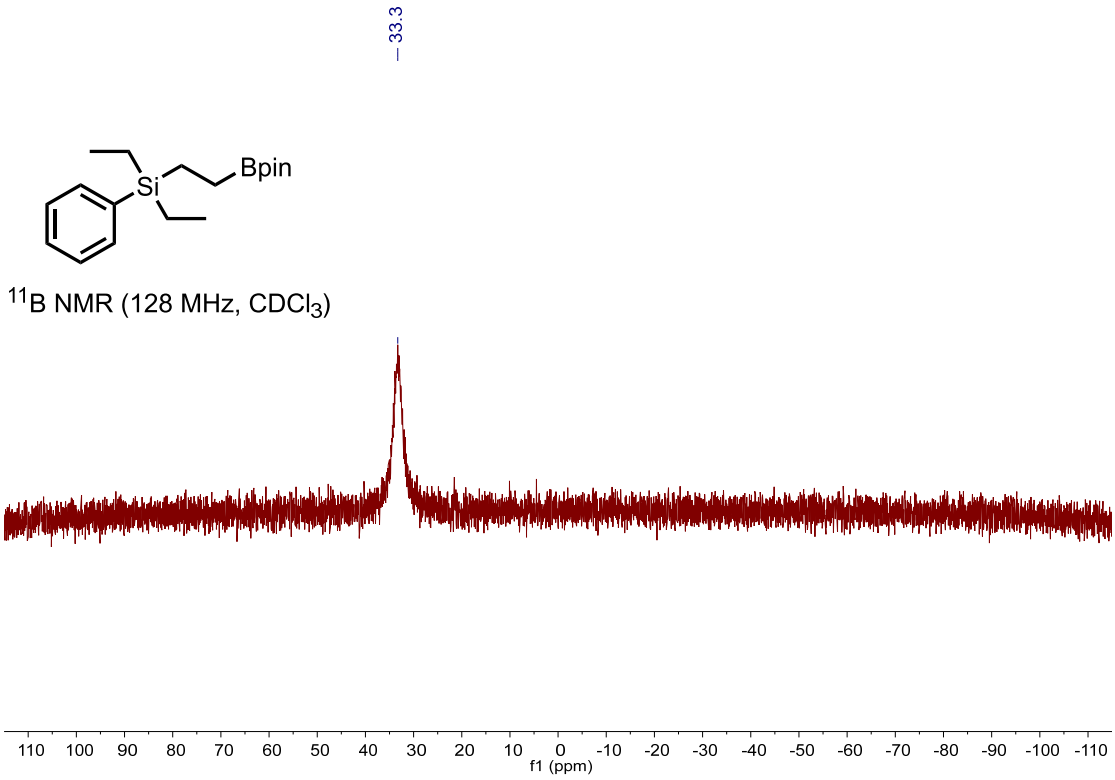
Diethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (21)

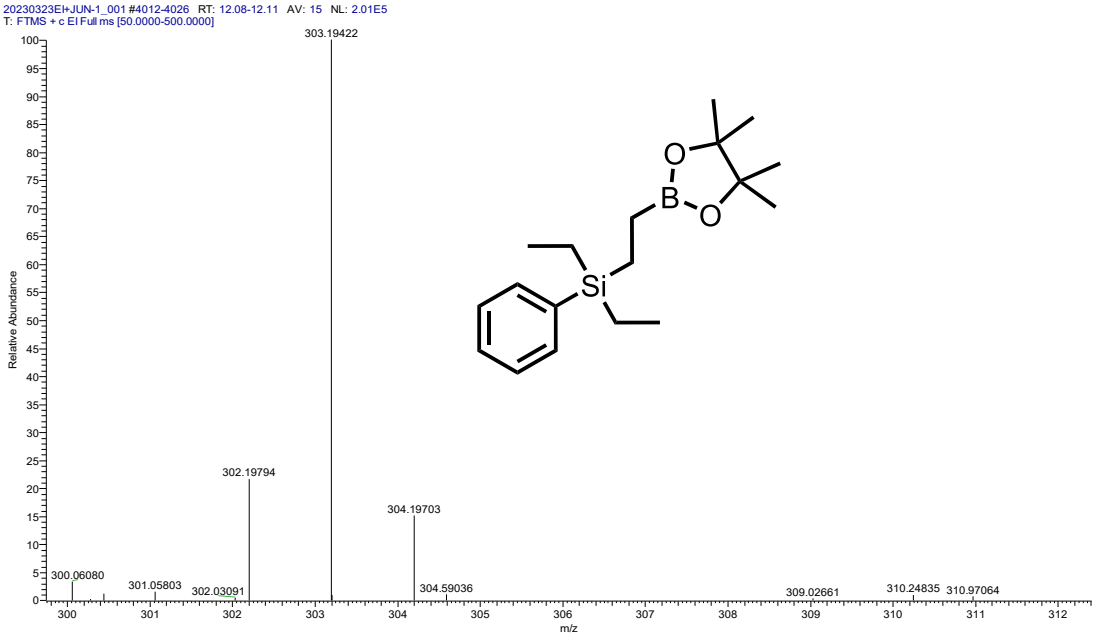


^{1}H NMR (400 MHz, $CDCl_3$)

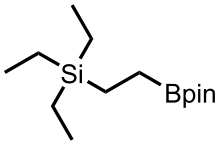


^{13}C NMR (101 MHz, $CDCl_3$)

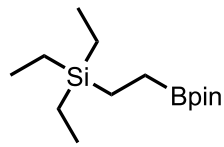

33.3
Si
Bpin
^{11}B NMR (128 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


20230323EI+JUN-1_001 #4012-4026 RT: 12.08-12.11 AV: 15 NL: 2.01E5
T: FTMS + c EI Full ms [50.0000-500.0000]
303.19422
302.19794
304.19703
300.06080
301.05803
302.03091
304.59036
309.02661
310.24835
310.97064
Relative Abundance
m/z
O
B
O
Si

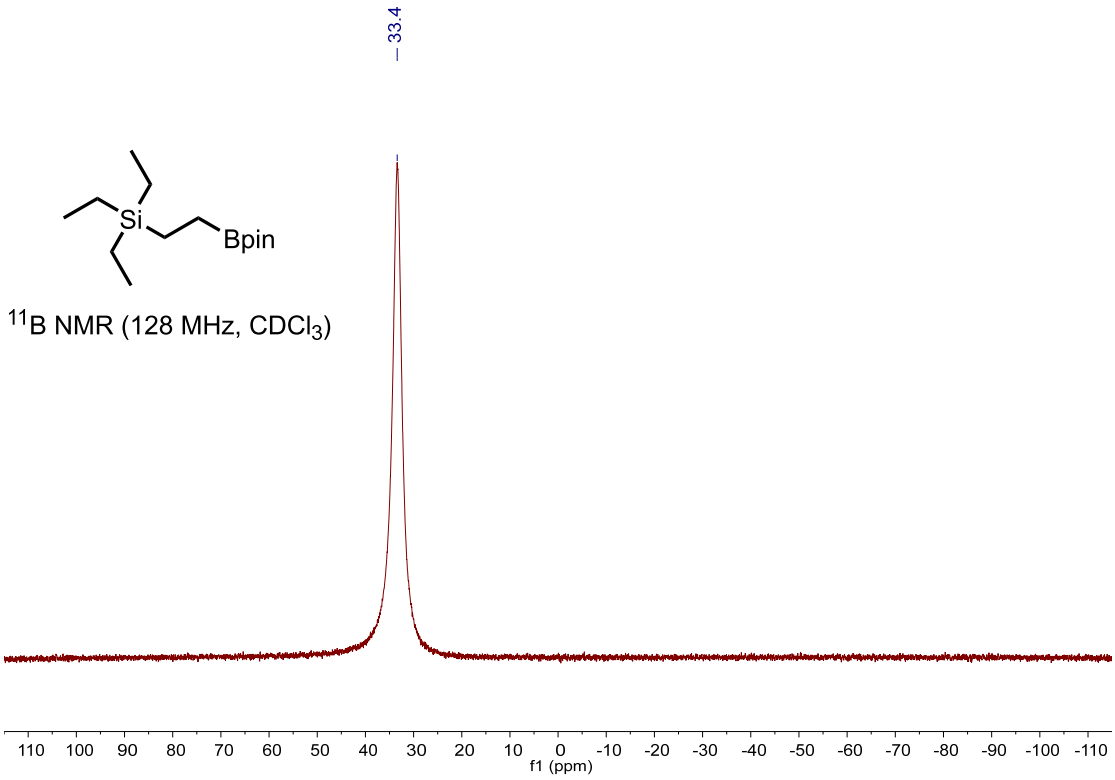
Triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (22)



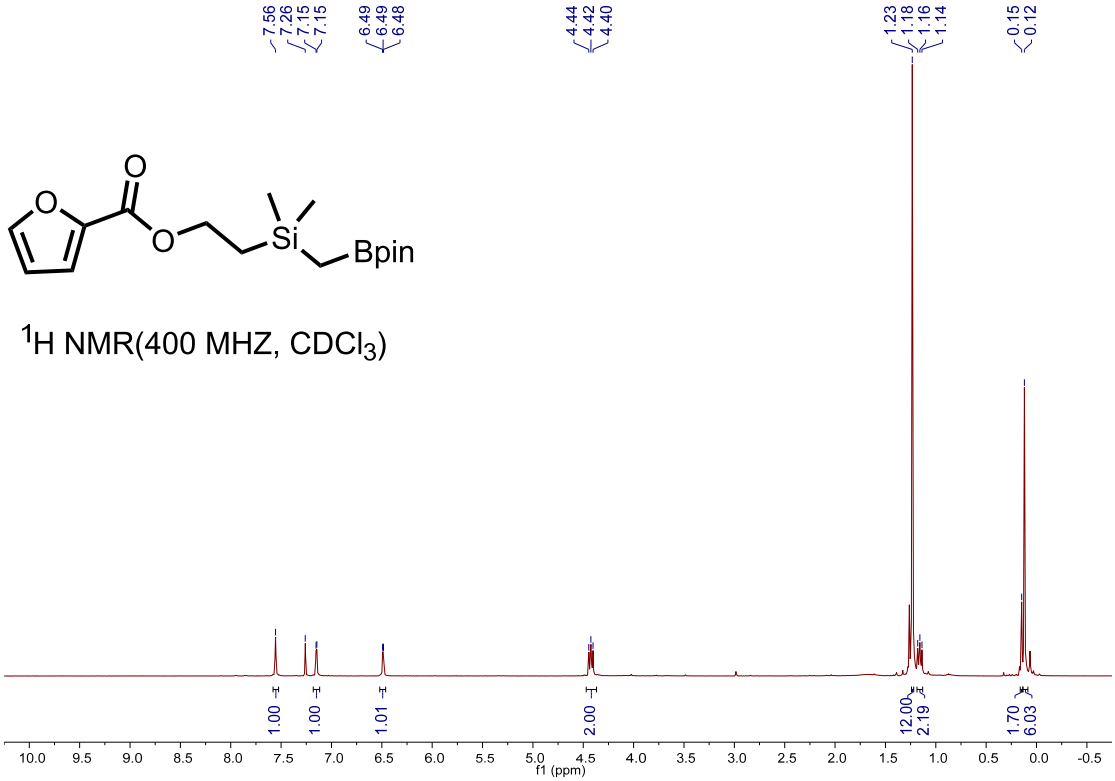
^{1}H NMR (400 MHz, $CDCl_3$)

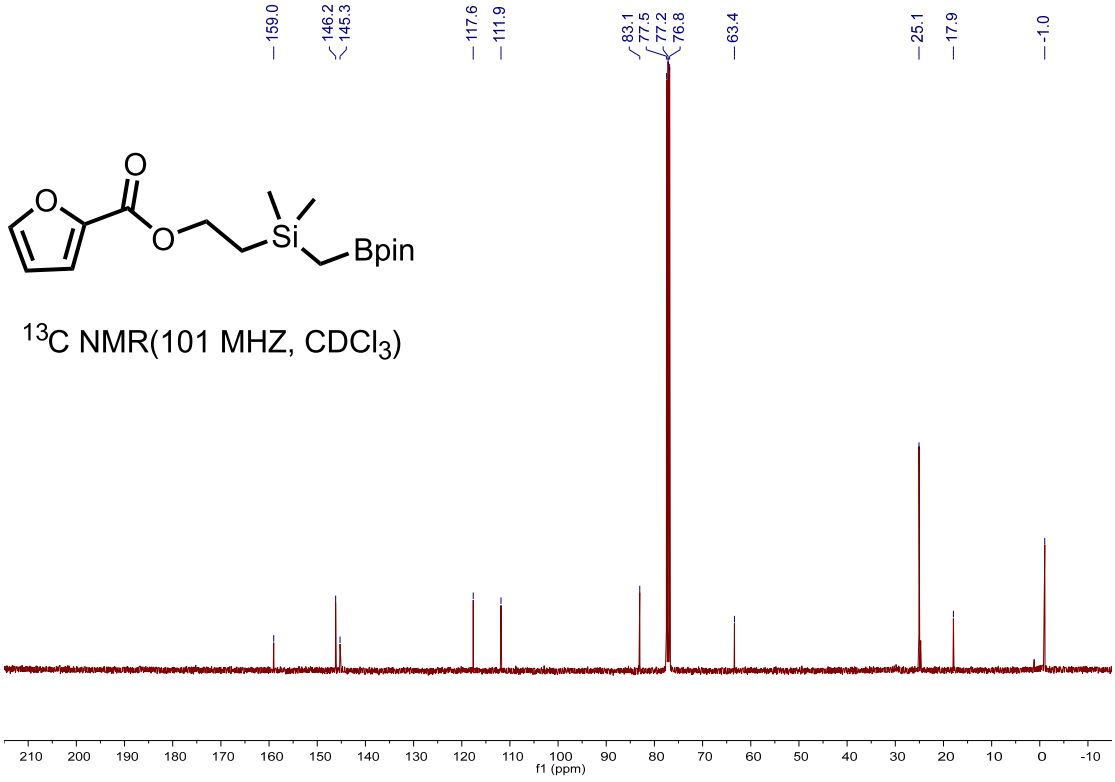


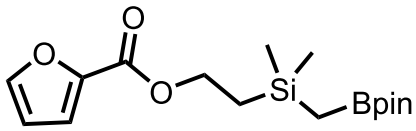
^{13}C NMR (101 MHz, $CDCl_3$)


33.4
Si
Bpin
^{11}B NMR (128 MHz, $CDCl_3$)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

2-(Dimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)silyl)ethyl furan-2-carboxylate (23)







^{11}B NMR(193 MHZ, $CDCl_3$)