Water-Assisted Diboron Activation: Efficient Synthesis of Alkyl 1,2-bis(boronates) and 1,1,2-tris(boronates)

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I. General Information

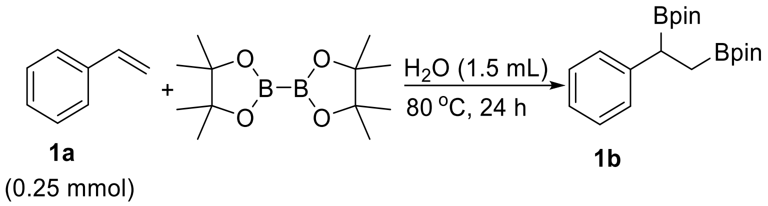
Unless otherwise noted all the reactions are performed in nitrogen filled KIYON glove box or using standard Schlenk technique. All reagents were purchased from Avra, BLDpharm, SDFCL or Aldrich and were used as received. B_2pin_2 and B_2neop_2 were obtained as a gift from AllyChem Co. Ltd. $CDCl_3$ and D_2O were purchased from Cambridge Isotope Laboratories and were dried using molecular sieves and deoxygenated using the freeze pump-thaw method. Commercially available, pre-coated TLC sheets ALUGRAM® Xtra Sil G/UV254 was purchased from MACHEREY-NAGEL GmbH & Co. The removal of solvent was performed on a rotary evaporator in vacuum at a maximum temperature of 40 ˚C. All NMR spectra were recorded at ambient temperature using a Bruker Avance 500 NMR spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{11}B, 160 MHz) or Bruker Avance 400 NMR spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{11}B, 128 MHz). ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm), whereas ^{13}C NMR spectra are reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm). ^{11}B NMR signals were quoted relative to $BF_3 \cdot Et_2O$. All ^{11}B and ^{13}C NMR spectra were broad-band ^{1}H decoupled. GC-MS data were acquired using SHIMADZU GC-MS QP 2010SE system. High resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument.

II. Optimization of the Reaction Conditions for the Alkene Diboration

Experimental Procedures for Examples Described in Table 1.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, B_2pin_2 (1.5 equiv.: 0.37 mmol, 95 mg; 2 equiv.: 0.25 mmol, 127 mg), styrene (**1a**, 26 mg, 0.25 mmol) and H_2O (1-1.5 mL) were added. The reaction mixture was stirred at given temperature and time. Et_2O (10 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR ($CDCl_3$) spectroscopy using nitromethane as an internal standard.

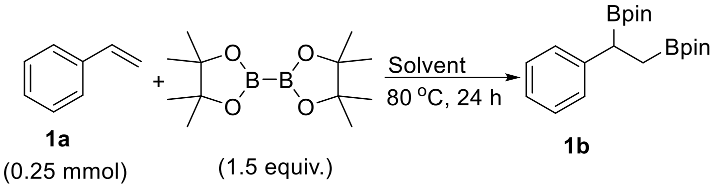
Table S1. Optimization of reaction conditions.[a]



Entry	Solvent (1.5 mL)	B_2pin_2 (equiv.)	Time (h)	Temp. (°C)	Yield[b] (%) **1b**
1	H_2O	2.0	24	RT	78
2	H_2O	2.0	24	50	97
3	H_2O	2.0	24	80	>99
4	H_2O	2.0	24	100	>99
5	H_2O	0.5	24	80	70
6	H_2O	1.0	24	80	95
7	H_2O	1.5	24	80	>99
8	H_2O	1.5	1	80	55
9	H_2O	1.5	6	80	96
10	H_2O	1.5	9	80	>99
11	H_2O	1.5	12	80	>99

[a] Reaction conditions: **1a** (0.25 mmol, 1 equiv.), B_2pin_2, H_2O (1.5 mL) for 24 h unless otherwise stated.
[b] Yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard.

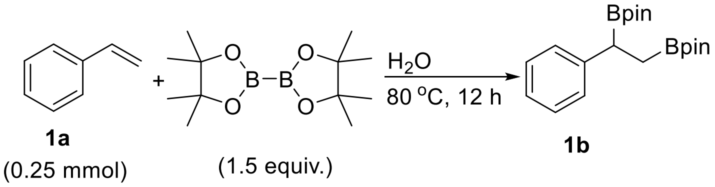
Table S2. Control experiments for the diboration of styrene (**1b**).[a]



Entry	H_2O (mL)	B_2pin_2 (equiv.)	Time (h)	Temp. (°C)	Yield[b] (%) **1b**
1	0.5	1.5	12	80	99
2	1	1.5	12	80	99
3	1.5	1.5	12	80	>99
4	2	1.5	12	80	>99
5[c]	0.5	1.5	12	80	93
6[d]	1.5	1.5	12	80	93
7[e]	1.5	1.5	12	80	>99
8[f]	1.5	1.5	12	80	98

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), B_2pin_2 (1.5 equiv.), distilled H_2O at 80 °C unless otherwise stated. [b]Yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard. [c]Reaction was performed using D_2O. [d]Reaction was performed in air using Milli-Q H_2O. [e]Reaction was performed using degassed Milli-Q H_2O. [f]Reaction was performed using tap H_2O.

Table S3. Screening of B_2pin_2 obtained from various vendors for the diboration of styrene (**1a**).[a]



Entry	B_2pin_2 (1.5 equiv.)	Time (h)	Temp. (°C)	Yield[b] (%) **1b**
1	AllyChem (99% purity)	12	80	>99
2	TCI (>99% purity)	12	80	>99
3	Hyma (98% purity)	12	80	>99
4[c]	AllyChem (99% purity)	12	80	>99

[a]Reaction conditions: **1a** (0.25 mmol, 1 equiv.), B_2pin_2 (1.5 equiv.), HPLC H_2O (1.5 mL) at 80 °C unless otherwise stated. [b]Yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard. [c]Reaction was performed using sublimed B_2pin_2.

III. Substrate Scope of Alkenes Diboration Reaction

Experimental Procedures for Examples Described in Table 2.

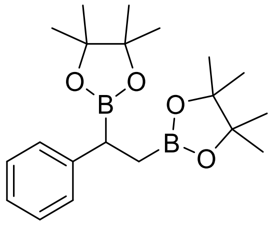
General Procedure A. In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, B_2pin_2 (1.5 equiv.: 0.37 mmol, 95 mg), styrene (**1a**, 26 mg, 0.25 mmol) and H_2O (1.5 mL) were added. The reaction mixture was stirred at 80 ºC temperature for 12 h. Et_2O (10 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (5 mL) was added. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR ($CDCl_3$) spectroscopy using nitromethane as an internal standard.

General Procedure B. In a 25 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkene (1 mmol), B_2pin_2 (1.5 equiv., 1.5 mmol, 381 mg), and H_2O (4 mL) were added and the reaction mixture was stirred vigorously at 80 ºC for 12 h. Et_2O (20 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (15 mL) was added. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated in vacuum, and the residue was purified by column chromatography.

Gram Scale Reaction C.

In a 50 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (10 mmol; 1.04 g), B_2pin_2 (1.5 equiv., 15 mmol, 3.81 g), and H_2O (15 mL) were added and the reaction mixture was stirred vigorously at 80 ºC for 12 h. Et_2O (50 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (30 mL) was added. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 30 mL). The combined organics were dried (Na_2SO_4) and concentrated in vacuum, and the residue was purified by column chromatography to give 2,2'-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1b**) in 86% isolated yield (3.08 g).

2,2'-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1b)

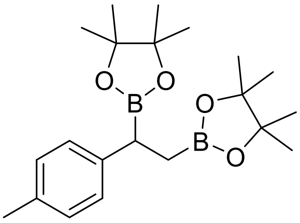


Following general procedure B, a colourless viscous liquid in 90% yield (322 mg) from styrene (**1a**, 104 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22-7.20 (m, 4H), 7.10-7.07 (m, 1H), 2.52 (dd, *J* = 11.0, 5.5 Hz, 1H), 1.38 (d, *J* = 4.5 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.17 (s, 6H), 1.13 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.5, 128.2, 128.0, 125.0, 83.3, 83.1, 25.1, 25.04, 24.8, 24.6, 14.4 (Br). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.9. GC-MS: m/z: 358 (M^+).

HRMS (ESI) calcd. for $C_{20}H_{36}NB_2O_4$ $[M+NH_4]^+$: 376.2830; found $[M+NH_4]^+$: 376.2865.

These spectroscopic data match those previously reported.[1]

2,2'-(1-(*p*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b)



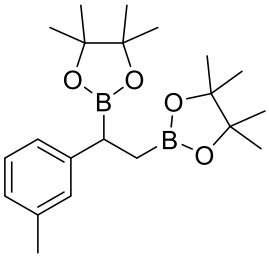
Following general procedure B, white solid (m.p. 78-79 °C) in 90% yield (335 mg) from 4-methyl styrene (**2a**, 118 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.48 (dd, *J* = 11.0, 5.0 Hz, 1H), 2.28 (s, 3H), 1.37 (dd, *J* = 16, 10.5 Hz, 1H), 1.22 (s, 12H), 1.20 (s, 6H), 1.18 (s, 6H), 1.09 (dd, *J* = 16, 6 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, ppm): δ 142.4, 134.2, 129.0, 127.8, 83.2, 83.0, 25.85(br) 25.0, 24.8, 24.7, 24.6, 21.0, 14.8 (br). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ 33.5. GC-MS: m/z: 372 (M^+).

HRMS (ESI) calcd. for $C_{21}H_{38}NB_2O_4$ $[M+NH_4]^+$: 390.2987; found $[M+NH_4]^+$: 390.2954.

These spectroscopic data match those previously reported.[1]

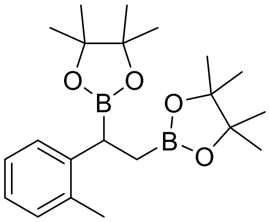
2,2'-(1-(*m*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b)



Following general procedure B, a colorless liquid in 80% yield (298 mg) from 2-methyl-2-vinylbenzene (**3a**, 118 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 7.2 Hz, 1H), 7.08 (dd, J=13.0, 6.7 Hz, 2H), 7.00 (t, *J* = 6.8 Hz, 1H), 2.69 (dd, *J* = 10.1, 6.0 Hz, 1H), 2.33 (s, 3H), 1.36 (dd, *J* = 15.9, 10.5 Hz, 1H), 1.18 (s, 12H), 1.18 (s, 6H), 1.17 (s, 6H), 1.08 (dd, *J* = 15.9, 5.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 143.9, 135.8, 130.0, 127.6, 126.0, 124.9, 83.2, 83.1, 25.0, 24.8, 24.7, 24.6, 23.4 (br), 20.2, 13.9 (br). ^{11}B NMR (160 MHz, $CDCl_3$): δ 32.8. GC-MS: m/z: 372 (M^+).
HRMS (ESI) calcd. for $C_{21}H_{35}B_2O_4$ $[M+H]^+$: 373.2721; found $[M+H]^+$: 373.2621.

These spectroscopic data match those previously reported.[2]

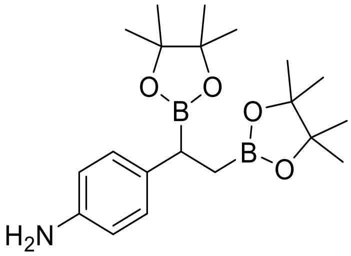
2,2'-(1-(*o*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4b)



Following general procedure B, a colorless liquid in 90% yield (335 mg) from 1-methyl-2-vinylbenzene (**4a**, 118 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 7.0Hz, 1H), 2.48 (dd, *J* = 11.0, 5.5 Hz, 1H), 2.29 (s, 3H), 1.36 (dd, *J* = 16, 11.0 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.18 (s, 6H), 1.10 (dd, *J* = 16.0, 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.3, 137.5, 128.2, 128.0, 125.7, 12.9, 83.2, 83.0, 25.0, 24.7, 24.6, 24.5, 21.5. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.6. GC-MS: calcd. for $C_{21}H_{34}B_2O_4$ $(M)^+$: 372; found: m/z: 372 (M^+).

These spectroscopic data match those previously reported.[3,4]

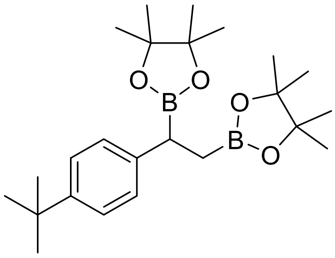
4-(1,2-Bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (5b)



Following general procedure B, yellowish liquid in 86% yield (321 mg) from 4-vinylaniline (**5a**, 173mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. Multiple attempts were made to purify **5b**; however, it tends to decompose during the column chromatography process, and the best-acquired data has been incorporated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 8.2 Hz, 2H), 4.10 (br, 2H), 2.36 (dd, *J* = 10.9, 5.7 Hz, 1H), 1.27 (dd, *J* = 16, 10.5 Hz, 1H), 1.16 (s, 12H), 1.14 (s, 6H), 1.13 (s, 6H), 1.10 (dd, *J* = 16, 6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.2, 135.6, 128.6, 115.5, 83.5, 83.0, 82.98, 82.92, 25.0, 24.9, 24.8, 24.7, 24.6, 24.5, 24.0, 21.5 (br), 14.5 (br). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.7. GC-MS: m/z: 373 (M^+). HRMS (ESI) calcd. for $C_{20}H_{33}B_2NKO_4$ $[M+K]^+$: 412.2233; found $[M+K]^+$: 412.2152.

These spectroscopic data match those previously reported.[2]

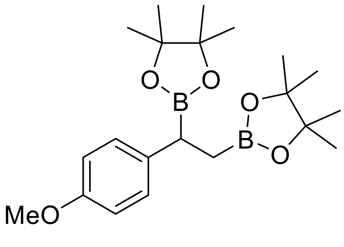
2,2'-(1-(4-Terterybutylphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6b)



Following general procedure B, a white solid (m.p. 75-76 °C) in 69 % yield (286 mg) from 1-(tert-butyl)-4-vinylbenzene (**6a**, 118 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 2.39 (dd, *J* = 11.0, 5.5 Hz, 1H), 1.26 (d, *J* = 4.8 Hz, 1H), 1.19 (s, 9H), 1.17 (s, 6H), 1.11 (s, 12H), 1.10 (s, 6H), 1.00 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 142.1, 127.5, 125.0, 83.2, 82.9, 34.2, 31.4, 25.9 (br), 25.0, 24.9, 24.8, 24.7, 24.5, 14.5 (br).^{11}B NMR (160 MHz, $CDCl_3$) δ 34.9(br).
GC-MS: calcd. for $C_{24}H_{40}B_2O_4$ $(M)^+$: 414; found: m/z: 414 (M^+).

These spectroscopic data match those previously reported.[3]

2,2'-(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7b)

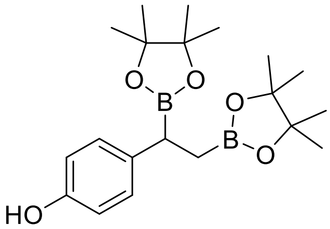


Following general procedure B, colorless oil in 80% yield (310 mg) from 1-methoxy-4-vinylbenzene (**7a**, 134 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 2.46 (dd, *J* = 15.8, 5.7 Hz, 1H), 1.33 (dd, *J* = 9.7, 6.1Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.18 (s, 6H), 1.08 (dd, *J* = 15.8, 5.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 157.1, 137.4, 128.7, 113.6, 83.1, 82.9, 55.0, 25.0, 24.7, 24.6, 24.5, 25.4, 14.7 (br). ^{11}B NMR (126 MHz, $CDCl_3$): δ 33.8.

GC-MS: calcd. for $C_{21}H_{34}B_2O_5$ $(M)^+$: 388; found: 388 (M^+).

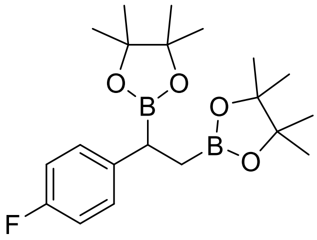
These spectroscopic data match those previously reported.[5]

4-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenol (8b)



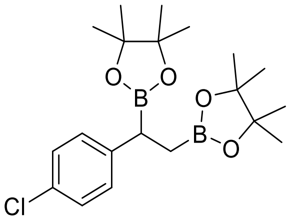
Following general procedure B, colorless oil in 64% yield (239 mg) from 4-vinylphenol (**8a**, 120 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 80:20% Hex/EtOAc. Multiple attempts were made to purify **8b**; however, they tend to decompose during the column chromatography process, and the best-acquired data has been incorporated. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.02 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.9 Hz, 2H), 4.85 (br, 1H), 2.42 (dd, *J* = 10.2, 6.0 Hz, 1H), 1.36 (m, 1H), 1.22 (s, 12H), 1.17 (s, 12H), 1.04 (m, 1H). ^{11}B NMR (126 MHz, CDCl$_3$): δ 33.6. GC-MS: m/z: 374 (M$^+$).
HRMS (ESI) calcd. for $C_{20}H_{33}B_2O_5$ [M+H]$^+$: 375.2514; found [M+H]$^+$: 375.2518.
These spectroscopic data match those previously reported.[4b]

2,2'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9b)



Following general procedure B, a yellowish liquid in 91% yield (342 mg) from 1-fluoro-4-vinylbenzene (**9a**, 122 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.16 (dd, *J* = 7.4, 5.7 Hz, 1H), 6.90 (t, *J* = 8.4 Hz, 1H), 2.50 (dd, *J* = 9.9, 6.0 Hz, 1H), 1.31 (d, *J* = 10.4 Hz, 1H), 1.18 (d, *J* = 9.0 Hz, 12H), 1.09 (dd, *J* = 16.0, 5.9 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 160.9 (d, *J* = 243.6 Hz), 141.0 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 20.9 Hz), 83.4, 83.2, 25.4 (br), 25.0, 24.8, 24.7, 24.6, 14.8 (br) ^{11}B NMR (128 MHz, CDCl$_3$): δ 33.7.
GC-MS: calcd. for $C_{20}H_{31}B_2O_4F$ (M)$^+$: 376; found: m/z: 376 (M$^+$).
These spectroscopic data match those previously reported.[1]

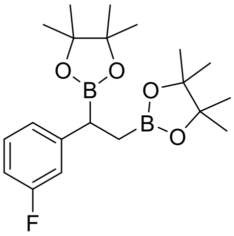
2,2'-(1-(4-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10b)



Following general procedure B, a white solid in 87% yield (341 mg) from 1-chloro-4-vinylbenzene (**10a**, 138 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (dd, *J* = 19.8, 8.3 Hz, 1H), 2.42 (dd, *J* = 10.2, 5.7 Hz, 1H), 1.27 (dd, *J* = 15.8, 10.7 Hz, 1H), 1.15 – 1.08 (m, 6H), 1.01 (dd, *J* = 15.9, 5.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.0, 130.7, 129.4, 128.3, 83.5, 83.3, 25.1, 24.8, 24.6, 14.1 (br). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.8. GC-MS: calcd. for $C_{20}H_{31}B_2O_4Cl$ $(M)^+$: 392; found: m/z: 392 (M^+).

These spectroscopic data match those previously reported.[3]

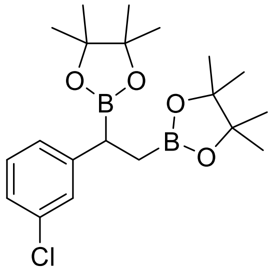
2,2'-(1-(3-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (11b)



Following general procedure B, a yellowish liquid in 89% yield (335 mg) from 1-fluoro-3-vinylbenzene (**11a**, 122 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 14.3, 7.8 Hz, 1H), 6.96 (dd, *J* = 24.0, 9.0 Hz, 2H), 6.78 (t, *J* = 7.0 Hz, 1H), 2.53 (dd, *J* = 10.0, 6.0 Hz, 1H), 1.34 (dd, *J* = 15.8, 10.8 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.18 (s, 6H), 1.10 (dd, *J* = 15.8, 5.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 163.0 (d, *J* = 244.7 Hz), 148.3 (d, *J* = 7.2 Hz), 129.5 (d, *J* = 8.4 Hz), 123.7 (d, *J* = 2.5 Hz), 114.8 (d, *J* = 21.0 Hz), 111.9 (d, *J* = 21.2 Hz), 83.5, 83.3, 29.8, 26.1 (br), 25.1, 24.8, 24.6, 14.2 (br). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.8. GC-MS: m/z: 376 (M^+). HRMS (ESI) calcd. for $C_{20}H_{32}B_2FO_4$ $[M+H]^+$: 377.2471; found $[M+H]^+$: 377.2349.

These spectroscopic data match those previously reported.[2]

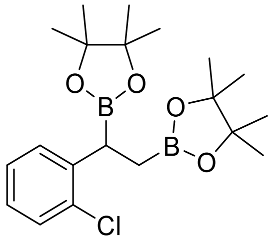
2,2'-(1-(3-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12b)



Following general procedure B, a yellowish liquid in 90% yield (353 mg) from 1-chloro-3-vinylbenzene (**12a**, 138 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.16-7.13 (m, 1H), 7.06-7.03 (m, 1H), 2.90 (dd, *J* = 10.0, 7.0 Hz, 1H), 1.38 (dd, *J* = 16.0, 10.0 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.19 (s, 6H) 1.12 (dd, *J* = 16.0, 7.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.7, 133.9, 129.7, 129.3, 126.8, 126.4, 83.5, 83.2, 25.0, 25.0, 24.9, 24.8, 24.7, 13.1 (br). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.7. GC-MS: m/z: 392 (M^+). HRMS (ESI) calcd. for $C_{20}H_{32}B_2ClO_4$ $[M+H]^+$: 393.2175; found $[M+H]^+$: 393.2119.

These spectroscopic data match those previously reported.[2]

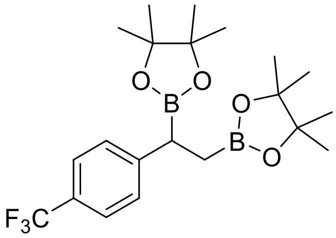
2,2'-(1-(2-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13b)



Following general procedure B, a yellowish liquid in 55% yield (215 mg) from 1-chloro-2-vinylbenzene (**13a**, 138 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21-7.19 (m, 2H), 7.09-7.05 (m, 1H), 6.99-6.95 (m, 1H), 2.82 (dd, *J* = 10.0, 7.0 Hz, 1H), 1.32 (dd, *J* = 16.0, 10.0 Hz, 1H), 1.14 (s, 12H), 1.12 (s, 6H), 1.12 (s, 6H), 1.04 (dd, *J* = 16.0, 7.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.4, 133.9, 129.7, 129.3, 126.8, 126.4, 83.6, 83.2, 25.1, 25.0, 24.9, 24.8, 24.7, 13.2 (br). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.4. GC-MS: calcd. for $C_{20}H_{31}B_2ClO_4$ $(M)^+$: 392; found: 392 (M^+).

These spectroscopic data match those previously reported.[3]

2,2'-(1-(4-Triflorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (14b)

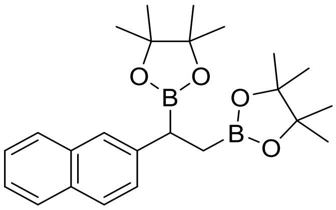


Following general procedure B, a colorless liquid in 45% yield (192 mg) from 1-(trifluoromethyl)-4-vinylbenzene (**14a**, 172 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.51 (dd, *J* = 10.5, 5.8 Hz, 1H), 1.30 (dd, *J* = 16.5, 5.8 Hz, 1H), 1.12-1.10 (m, 24H), 0.80 (dd, *J* = 13.3, 6.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.8 (d, *J* = 2.5 Hz), 128.3, 127.2 (q, *J* = 32 Hz), 124.9 (q, *J* = 272 Hz), 125.0 (q, *J* = 4 Hz), 83.5, 83.2, 26.7 (br), 24.9, 24.6, 24.6, 24.5, 14.1 (br). ^{11}B NMR (128 MHz, $CDCl_3$): 33.8.

GC-MS: calcd. for $C_{21}H_{31}B_2O_4F_3$ $(M)^+$: 426; found: m/z: 426 (M^+).

These spectroscopic data match those previously reported.[4]

2,2’-(1-(Naphthalen-2-yl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (15b)

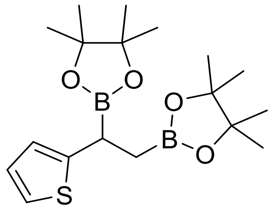


Following general procedure B, a white solid (m.p. 145-146 °C) in 70% yield (286 mg) from 2-vinylnaphthalene (**15a**, 154 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 95:5% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.69 (m, 3H), 7.65 (s, 1H), 7.43–7.33 (m, 3H), 2.71 (dd, *J* = 10.6, 5.6 Hz, 1H), 1.49 (dd, *J* = 15.8, 11.0 Hz, 1H), 1.20 (s, 12H), 1.20 (s, 6H), 1.18 (s, 6H), 0.85 (dd, *J* = 21.0, 9.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.1, 133.9, 131.7, 127.5, 127.5, 127.4, 125.5, 124.6, 83.3, 83.1, 25.0, 24.7, 24.7, 24.5. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.2.

GC-MS: calcd. for $C_{24}H_{34}B_2O_4$ $(M)^+$: 408; found: m/z: 408 (M^+).

These spectroscopic data match those previously reported.[1]

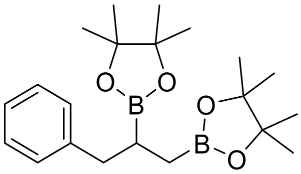
2,2’-(1-(Thiophen-2-yl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (16b)



Following general procedure B, a colorless liquid in 92% yield (335 mg) from 2-vinylthiophene (**16a**, 110 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.03 (d, *J* = 5.1 Hz, 1H), 6.87 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.80 (d, *J* = 3.2 Hz, 1H), 2.81 (dd, *J* = 10.7, 5.4 Hz, 1H), 1.38 (dd, *J* = 16.0, 10.8 Hz, 1H), 1.22-1.21 (m, 24H), 1.11 (dd, *J* = 15.8, 8.6 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 149.1, 126.7, 123.1, 122.3, 83.6, 83.3, 25.1, 24.9, 24.8, 24.7, 15.34 (br). ^{11}B NMR (128 MHz, CDCl$_3$): 33.5. GC-MS: m/z: 364 (M$^+$). HRMS (ESI) calcd. for $C_{18}H_{31}B_2O_4S$ [M+H]$^+$: 365.2129; found [M+H]$^+$: 365.2136.

These spectroscopic data match those previously reported.[2]

2,2’-(3-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (17b)

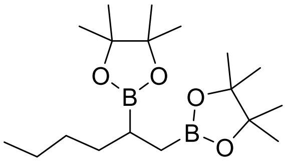


Following general procedure B, a white solid in 80 % yield (298 mg) from allylbenzene (**17a**, 118 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, CDCl$_3$): 7.20-7.15 (m, 4H), 7.09 (t, *J* = 6.65 Hz, 1H), 2.77 (dd, *J* = 13.4, 7.5 Hz, 1H), 2.58 (dd, *J* = 13.4, 8.3 Hz, 1H), 1.47-1.41 (m 1H), 1.19 (s, 12H), 1.15 (s, 6H), 1.13 (s, 6H), 0.82 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 142.4, 129.2, 128.0, 125.5, 83.0, 82.9, 39.6, 25.1, 25.0, 24.9, 24.87, 24.8, 20.6 (br), 12.1 (br). ^{11}B NMR: δ = 34.3 (br).

GC-MS: m/z: calcd. for $C_{21}H_{34}B_2O_4$ (M)$^+$: 372; found: 372 (M$^+$).

These spectroscopic data match those previously reported.[3]

2,2’-(Hexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (18b)

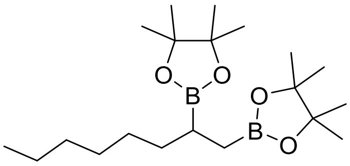


Following general procedure B, a colorless liquid in 89% yield (301 mg) from hex-1-ene (**18a**, 84 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.17-1.99 (m, 1H), 1.42-1.36 (m, 2H), 1.24-1.06 (m, 4H), 1.05-1.02 (m, 24H), 0.92-0.90 (m, 3H), 0.67-0.61 (m, 1H), 0.58-0.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.2, 82.5, 33.2, 30.9, 24.8, 24.7, 24.6, 24.4, 22.7, 18.1 (br), 13.9, 12.5 (br). ^{11}B NMR: δ = 30.5 (br).

GC-MS: calcd. for $C_{18}H_{36}B_2O_4$ $(M)^+$: 338; found: m/z: 338 (M^+).

These spectroscopic data match those previously reported.[4]

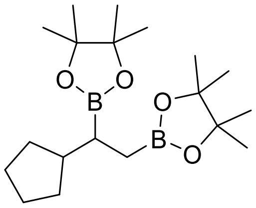
2,2'-(Octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (19b)



Following general procedure B, a colorless liquid in 88% yield (322 mg) from 1-octene (**19a**, 122 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.41 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.27 (m, 8H), 1.19 (m, 24H), 1.10–1.07 (m, 2H), 0.83 (t, *J* = 6.5 Hz, 3H), 0.77 (d, *J* = 5.6 Hz, 1H), 0.74 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 82.8, 82.7, 33.8, 31.8, 29.5, 28.8, 24.9, 24.8, 24.8, 24.7, 22.6, 18.4 (br), 14.1, 12.7 (br). ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.3 (br). GC-MS: calcd. for $C_{20}H_{40}B_2O_4$ $(M)^+$: 366; found m/z: 366 (M^+).

These spectroscopic data match those previously reported.[6]

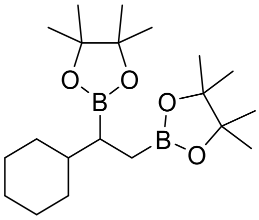
2,2’-(1-Cyclopentylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (20b)



Following general procedure B, a colourless viscus liquid in 92% yield (322 mg) from vinyl cyclopentane (**20a**, 96 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55-1.46 (m, 4H), 1.28-1.17 (m, 4H), 0.96 (s, 12H) 0.94 (s, 12H), 0.76-0.63 (m, 2H), 0.57-0.52 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 82.8, 82.7, 43.8, 31.8, 31.7, 25.5, 25.3, 24.9, 24.8, 24.7, 23.9 (br), 19.1, 11.6 (br). ^{11}B NMR: δ = 33.1 (br). GC-MS: m/z: 350 (M^+). HRMS (ESI) calcd. for $C_{19}H_{36}B_2O_4Na$ $[M+Na]^+$: 373.2697; found $[M+Na]^+$: 373.2692.

These spectroscopic data match those previously reported.[2]

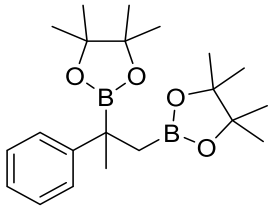
2,2'-(1-Cyclohexylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (21b)



Following general procedure B, a colourless viscus liquid in 90% yield (328 mg) from vinylcyclohexane (**21a**, 110 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66-1.58 (m, 4H), 1.34–1.24 (m, 4H), 1.21–1.05 (m, 24H), 1.09-0.97 (m, 2H), 0.90–0.80 (m, 2H), 0.75 (dd, J = 15.7, 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 82.8, 82.7, 41.5, 32.1, 32.0, 26.9, 26.9, 26.8, 25.0, 24.9, 24.9, 24.8, 24.7, 9.2 (br). ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.9 (br). GC-MS: calcd. for $C_{20}H_{38}B_2O_4$ $(M)^+$: 364; found m/z: 364 (M^+).

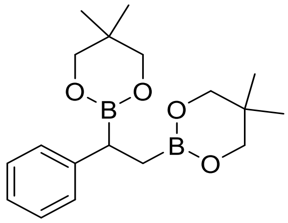
These spectroscopic data match those previously reported.[6]

2,2'-(2-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (22b)



Following general procedure B, a colourless liquid in 71% yield (264 mg) from prop-1-en-2-ylbenzene (**22a**, 118 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.3, Hz, 1H), 1.49 (d, *J* = 15.6 Hz, 1H), 1.42 (s,3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.19 (s, 6H), 1.14 (1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 129.9, 126.5, 124.9, 83.4, 83.1, 27.4 (br), 25.2, 24.8, 24.8, 24.7, 24.5, 22.2 (br). ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.72. GC-MS: calcd. for $C_{21}H_{34}B_2O_4$ $(M)^+$: 372; found m/z: 372 (M^+).
These spectroscopic data match those previously reported.[5]

2,2'-(1-Phenylethane-1,2-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane) (23b)



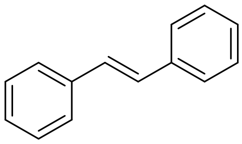
Following general procedure B using B_2neop_2 in place of B_2pin_2 as boron reagent, a colourless liquid in 89% yield (375 mg) from styrene (**1a**, 104 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 98:2% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-7.09 (m, 4H), 6.96 (t, *J* = 7.0 Hz, 1H), 3.48-3.42 (m, 8H), 2.31 (dd, *J* = 12.0, 5.0 Hz, 1H), 1.24 (dd, *J* = 16.0, 12.0 Hz, 1H), 0.91 (dd, *J* = 16.0, 5.0 Hz, 1H), 0.80 (12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.7, 127.8, 127.6, 124.3, 71.9, 71.8, 29.7 (br), 21.6, 21.6, 17.5 (br). ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3 (br).

GC-MS: calcd. for $C_{18}H_{28}B_2O_4$ $(M)^+$: 330; found: m/z: 330 (M^+).

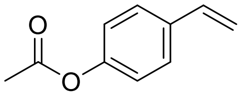
These spectroscopic data match those previously reported.[6]

List of Unsuccessful Substrates

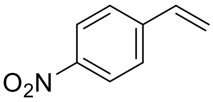
A complete list of unsuccessful alkene substrates for the water assisted diboration reaction.



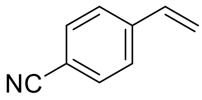
Yield : 0%



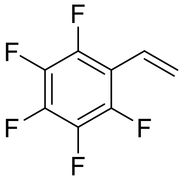
Yield : 0%



Yield : 0%



Yield : 0%



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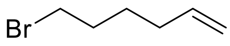

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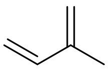
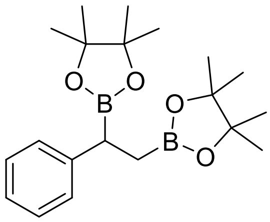


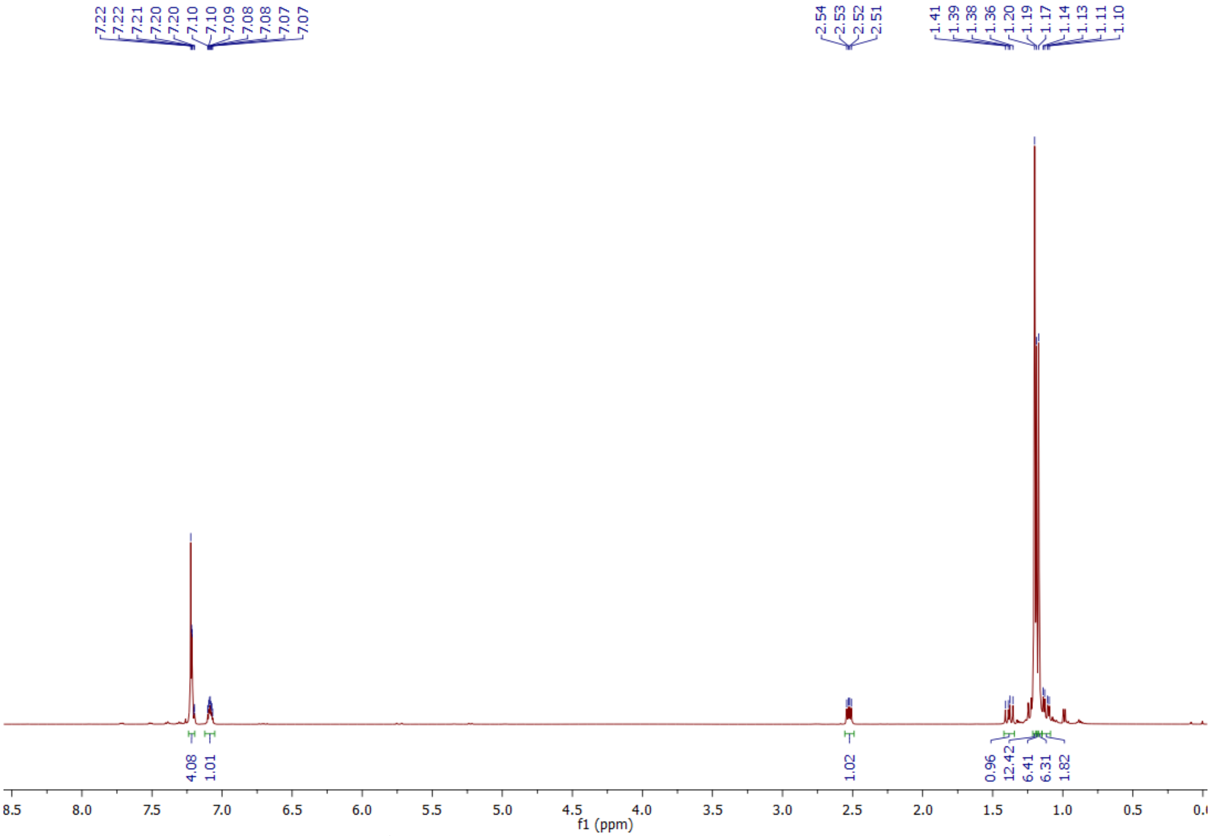
Yield : Mixture

IV. NMR Spectra of Alkene Diboration Products

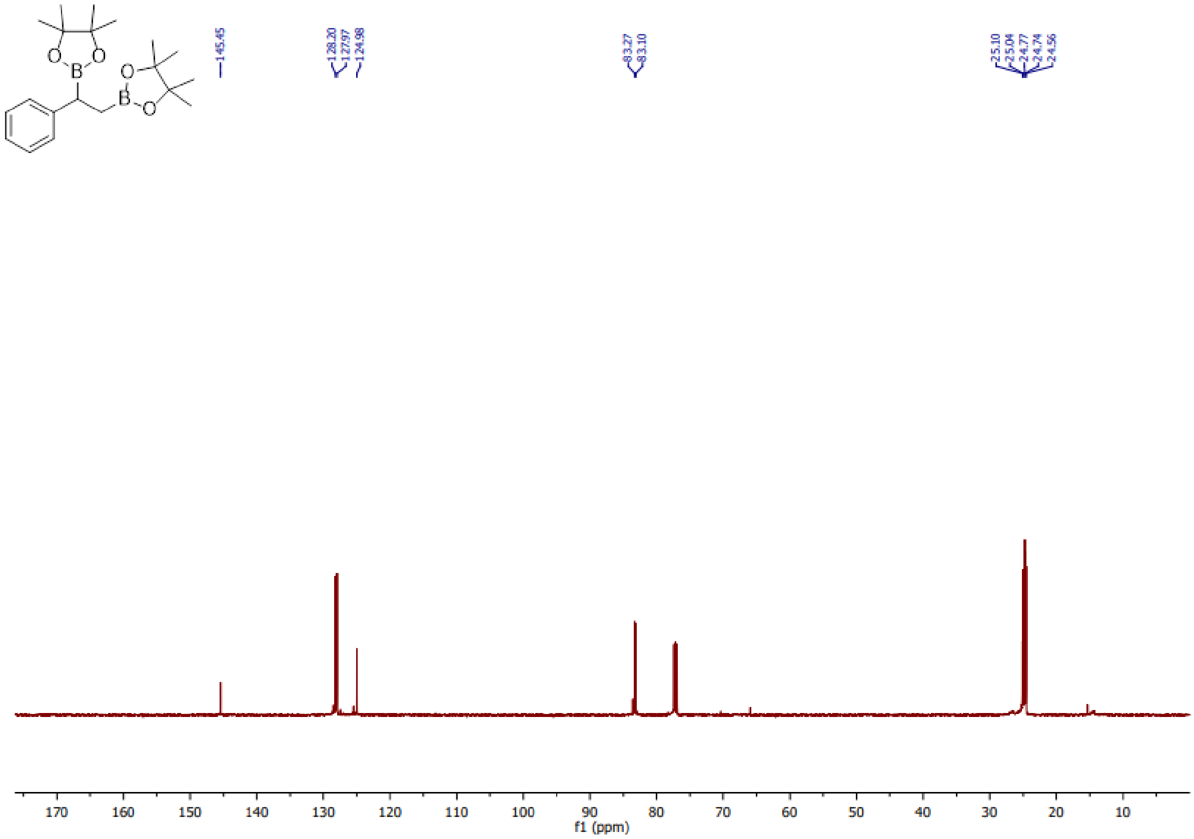
Note: Resonances denoted by (#) corresponds to solvent/grease. Resonance at δ = 1.56 ppm corresponds to H_2O and peak at δ = 0.07 corresponds to silicone grease.

2,2’-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1b)



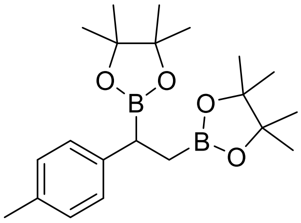


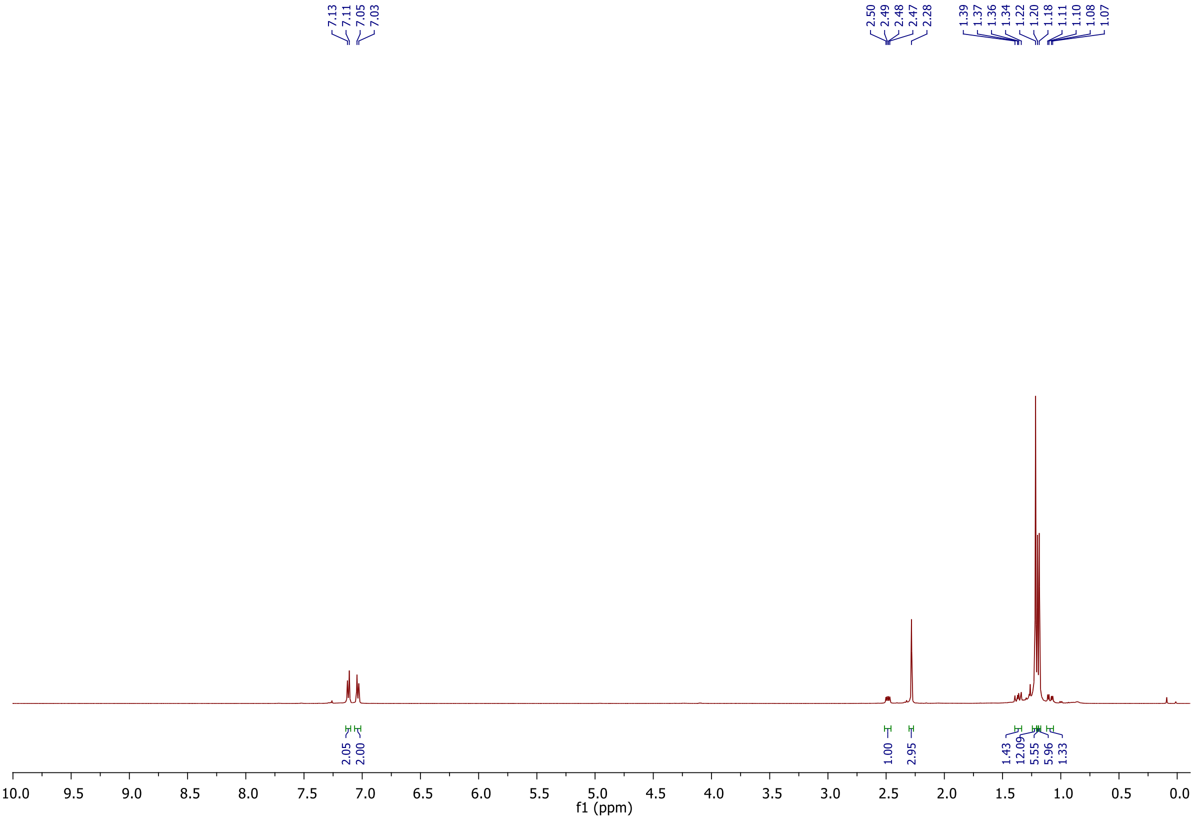
^{1}H NMR of **1b** (500 MHz, $CDCl_3$)



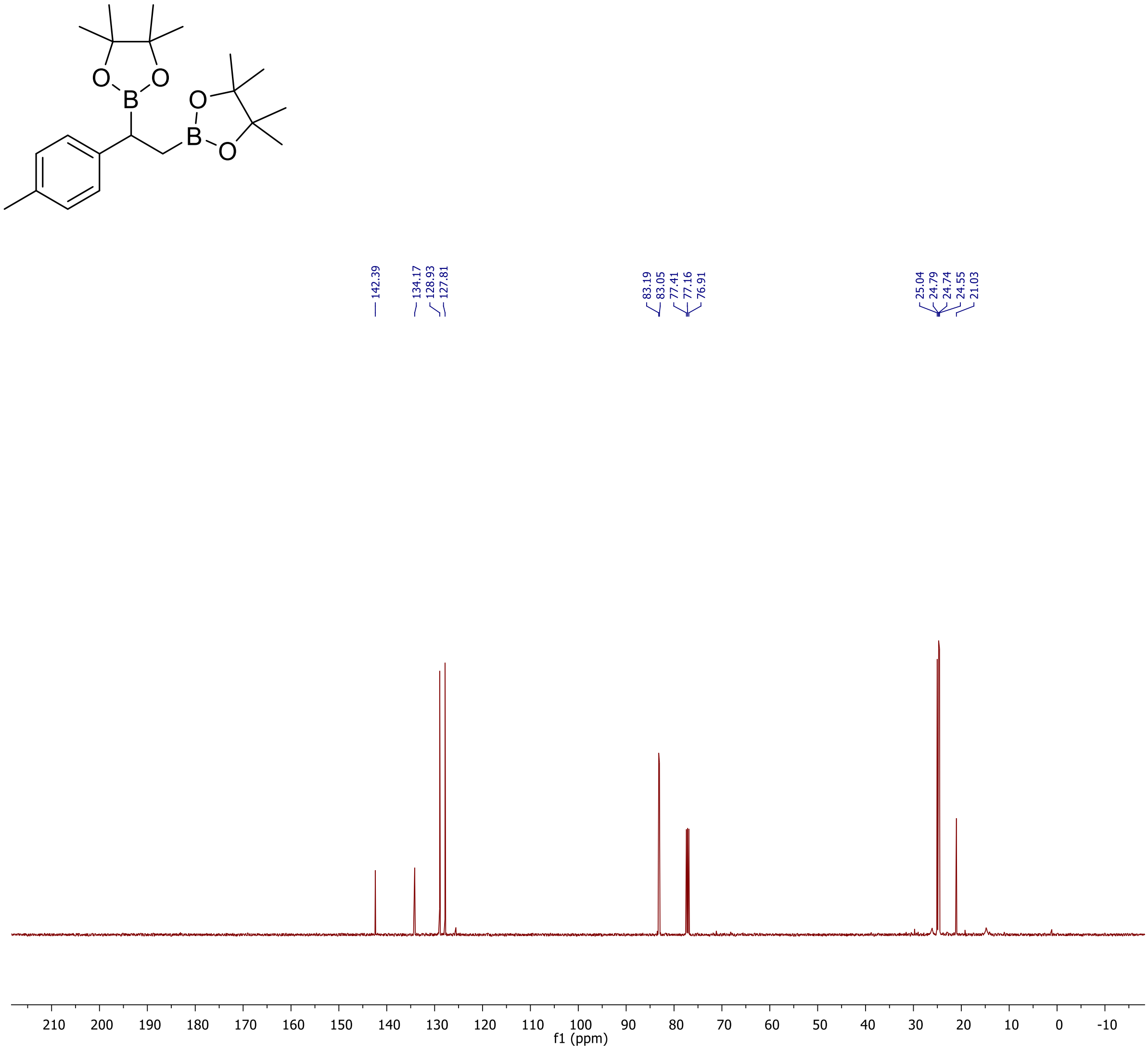
^{13}C{^{1}H} NMR of **1b** (126 MHz, $CDCl_3$)

2,2'-(1-(*p*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b)



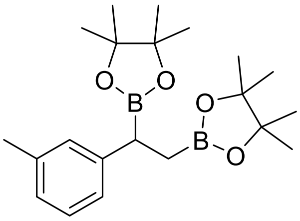


^{1}H NMR of **2b** (500 MHz, $CDCl_3$)

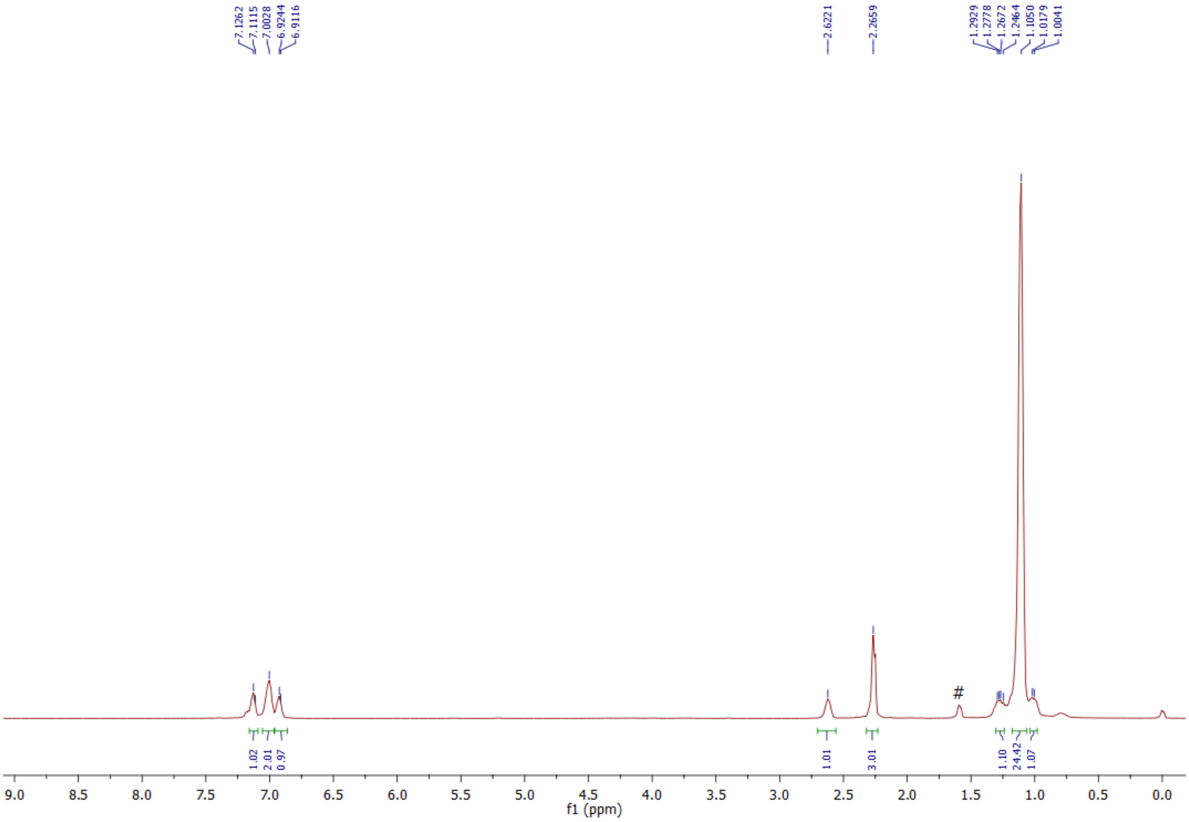


$^{13}C\{^{1}H\}$ NMR of **2b** (126 MHz, $CDCl_3$)

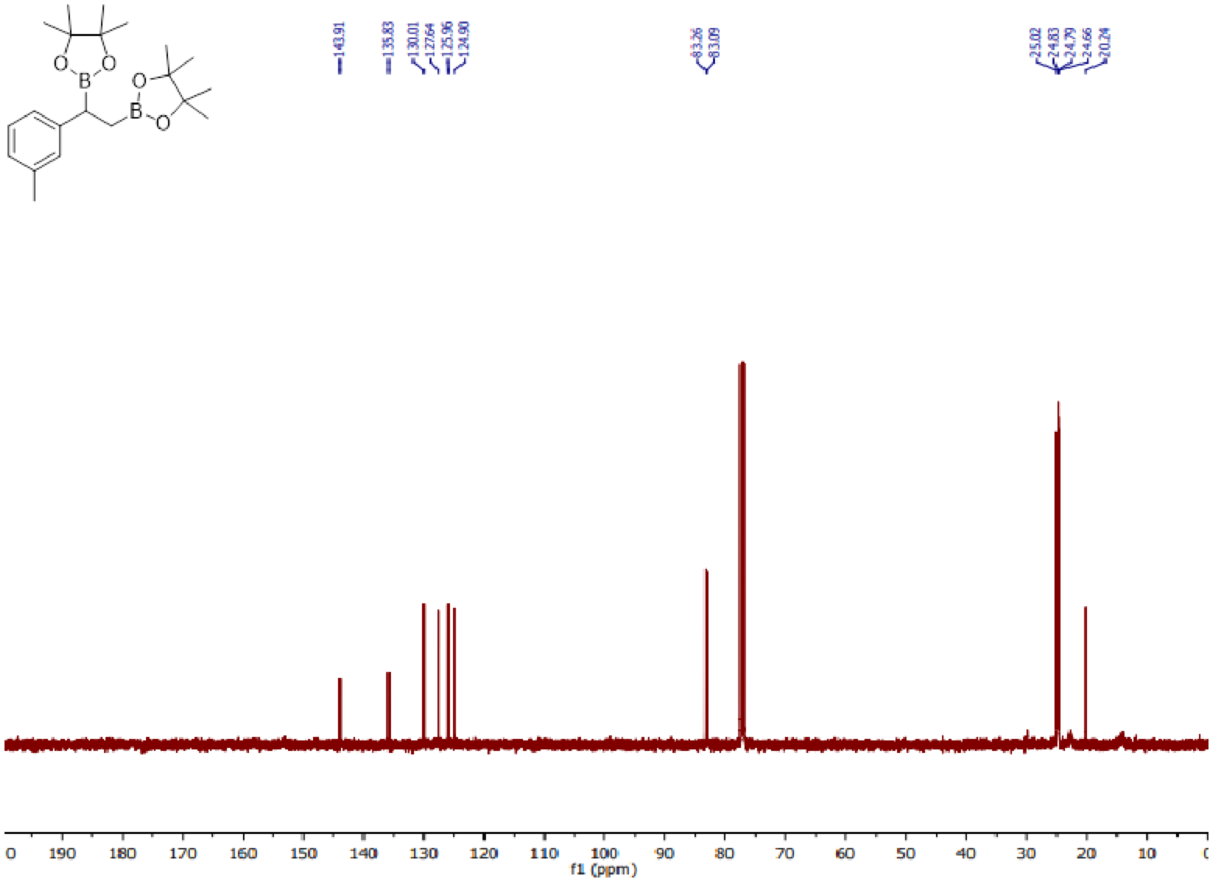
2,2'-(1-(*m*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b)



(#) Peak at δ = 1.56 ppm corresponds to H_2O

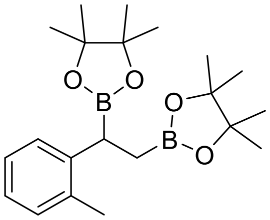


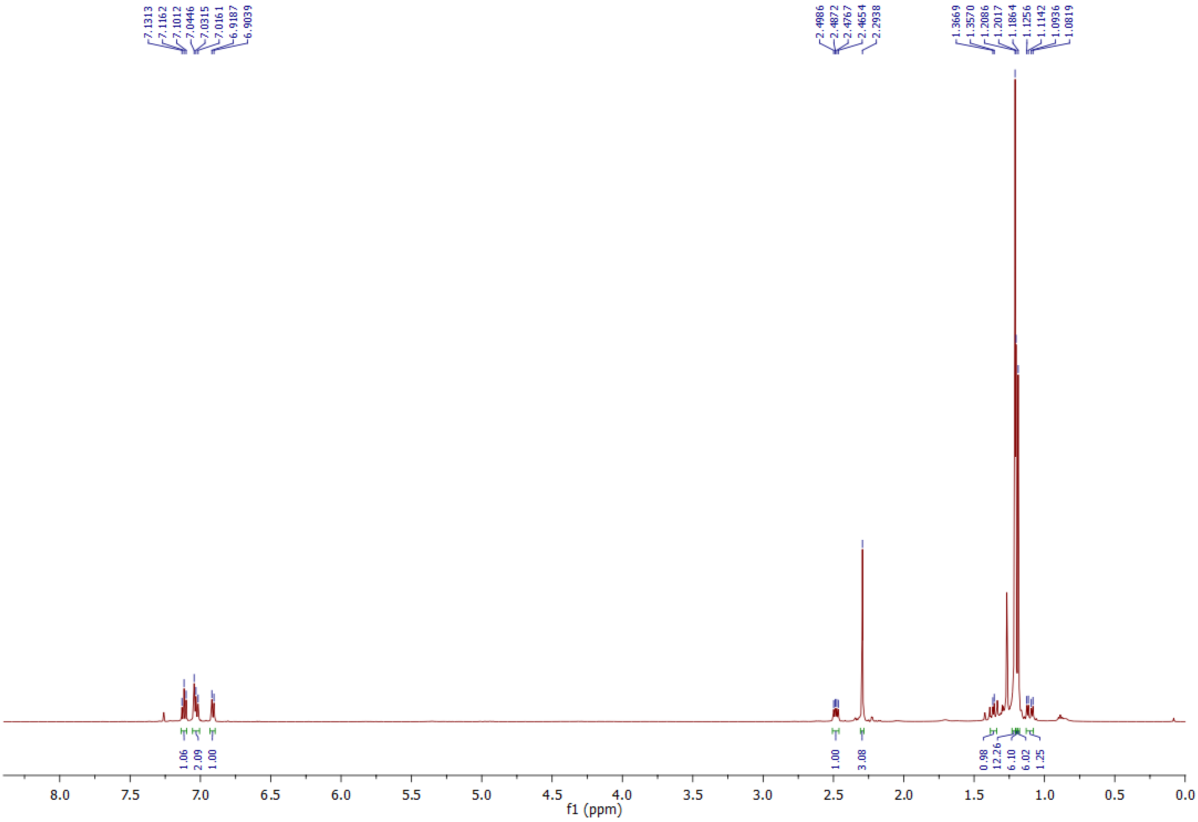
^{1}H NMR of **3b** (500 MHz, $CDCl_3$)



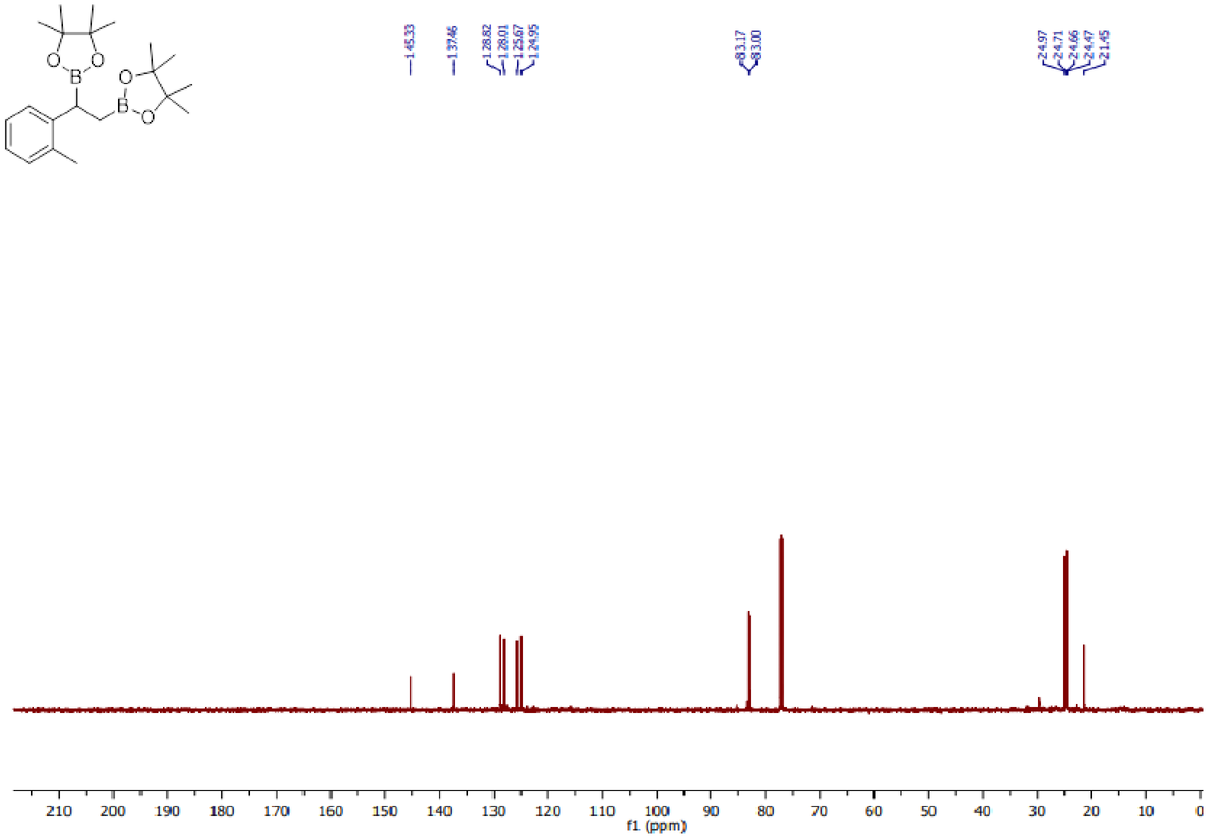
$^{13}C\{^1H\}$ NMR of **3b** (126 MHz, $CDCl_3$)

2,2'-(1-(*o*-Tolyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4b)



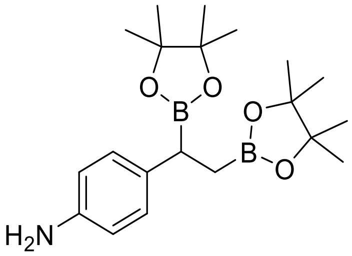


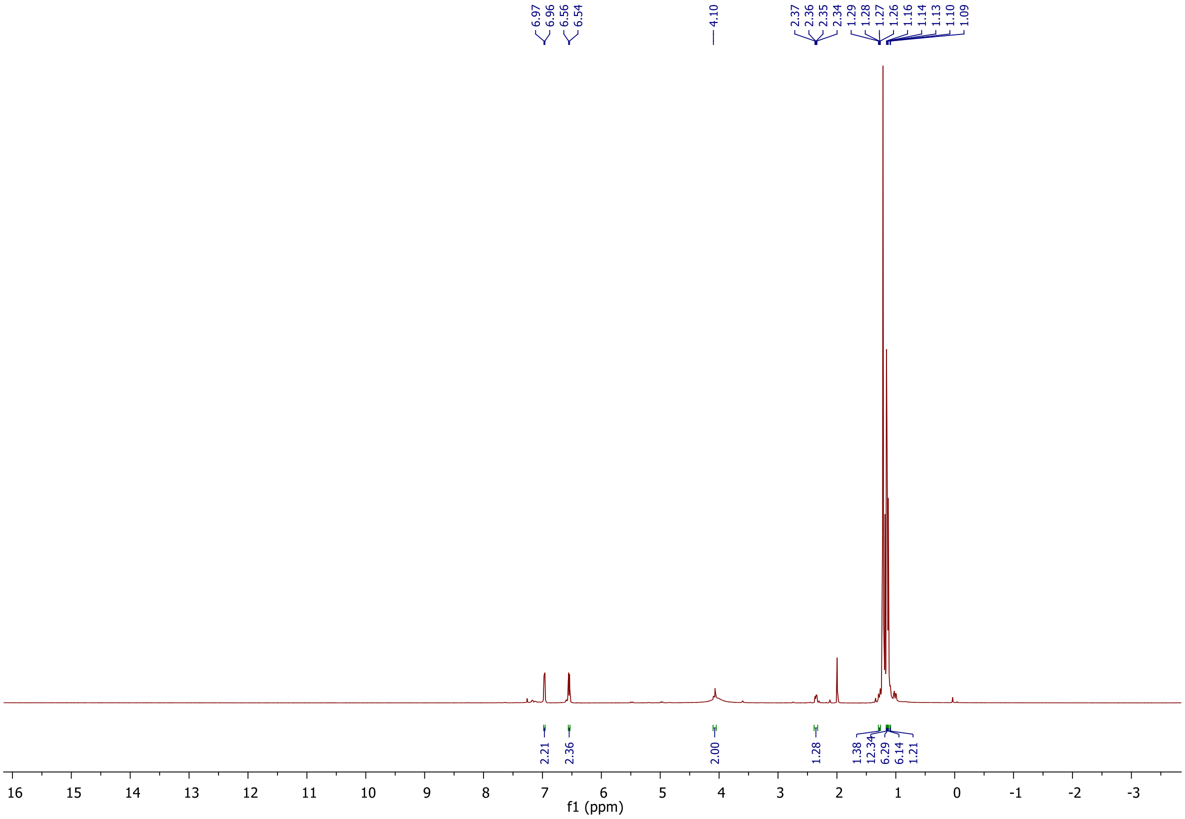
^{1}H NMR of **4b** (500 MHz, $CDCl_3$)



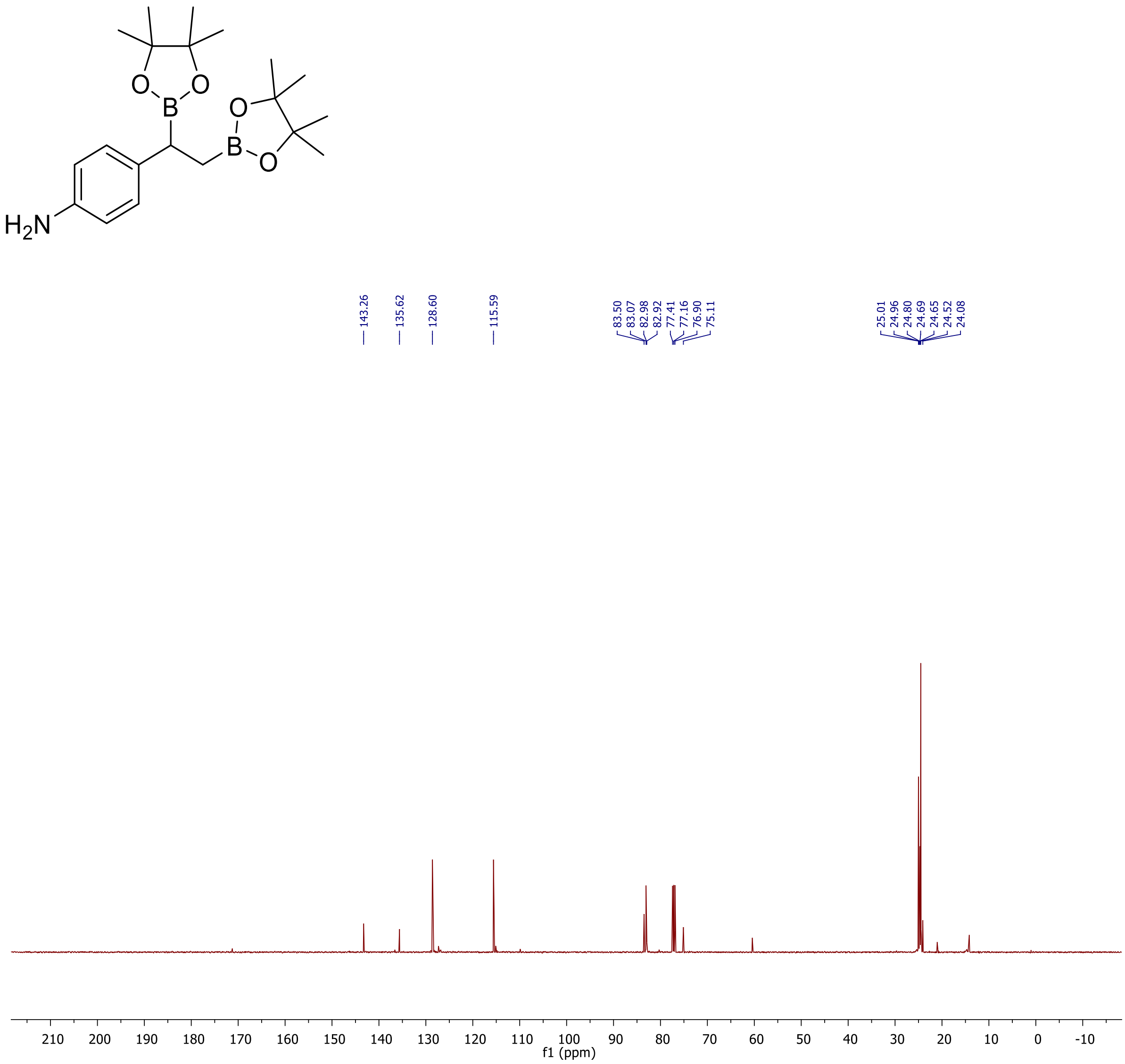
$^{13}C\{^{1}H\}$ NMR of **4b** (126 MHz, $CDCl_3$)

4-(1,2-Bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (5b)



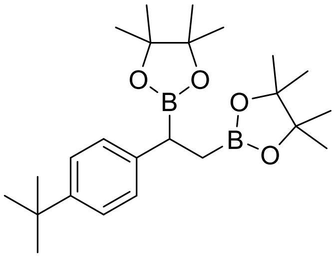


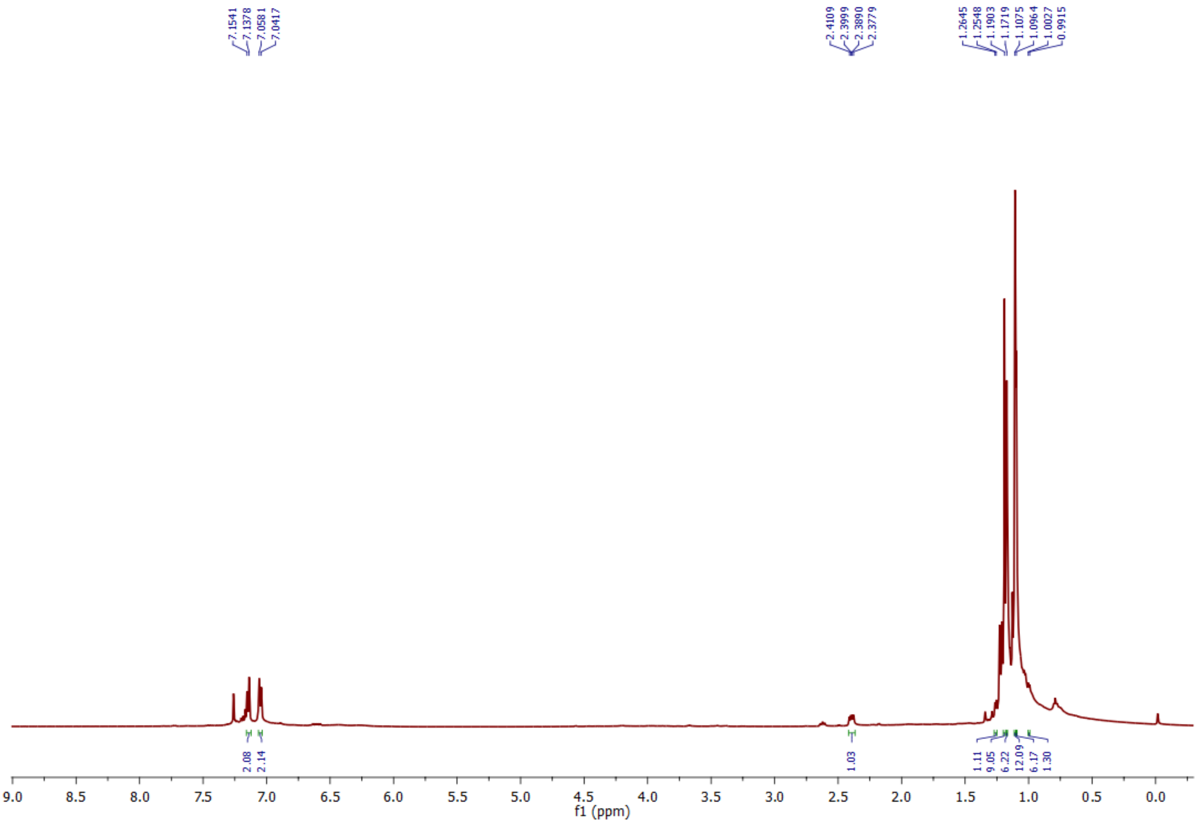
^{1}H NMR of **5b** (500 MHz, CDCl$_3$)



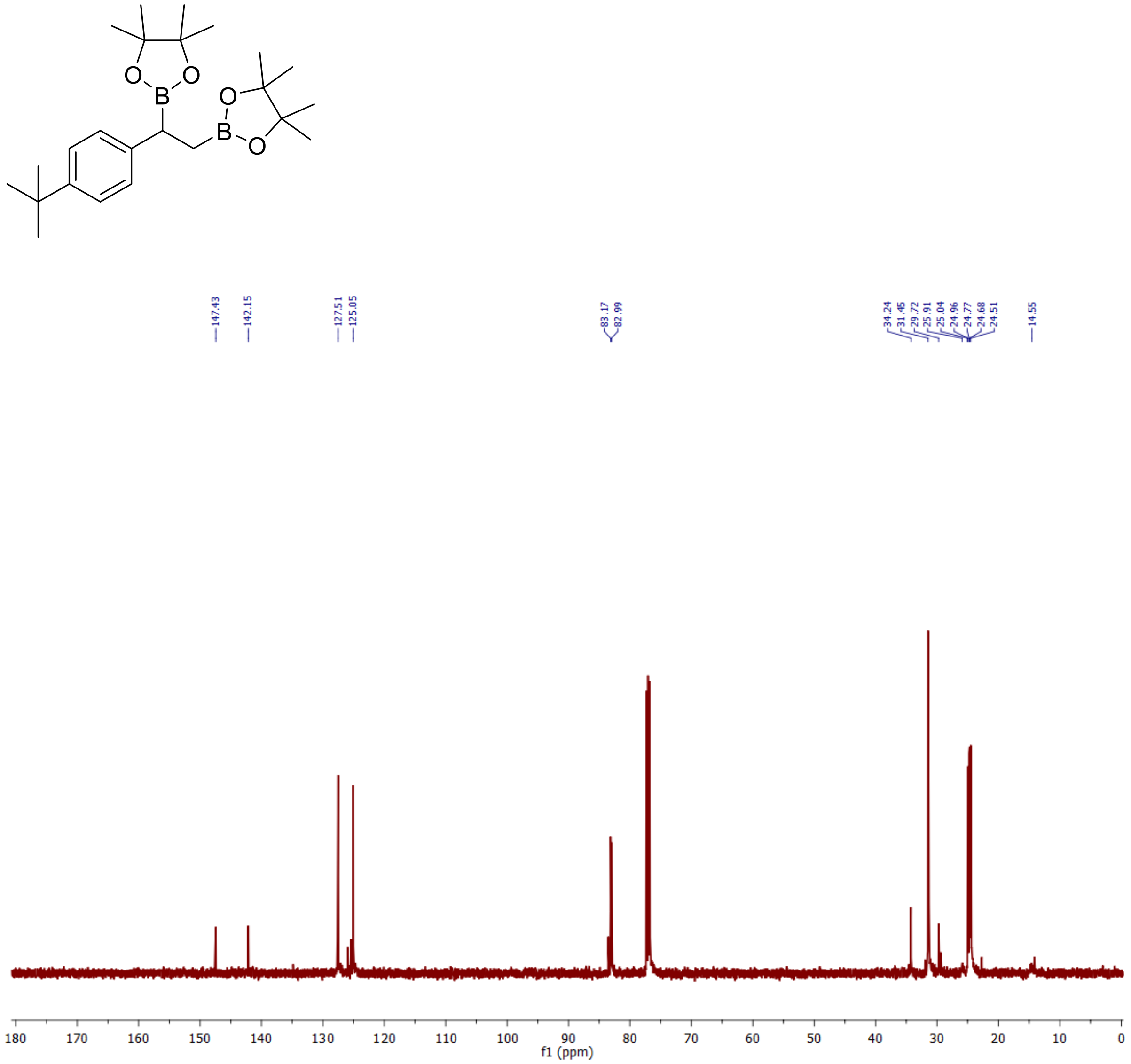
$^{13}C\{^{1}H\}$ NMR of **5b** (126 MHz, $CDCl_3$)

2,2'-(1-(4-Terterybutylphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6b)



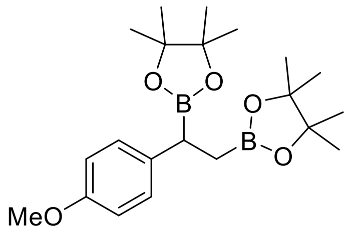


^{1}H NMR of **6b** (500 MHz, $CDCl_3$)

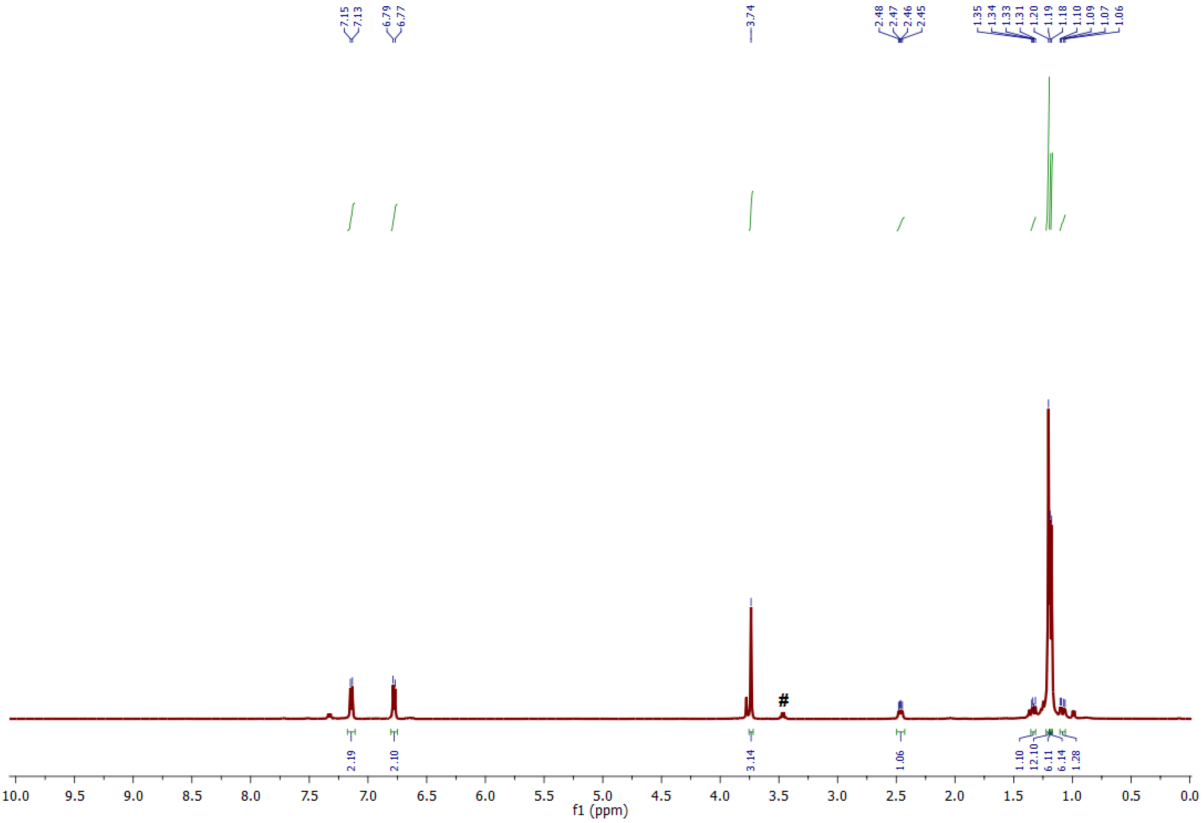


^{13}C{^{1}H} NMR of **6b** (126 MHz, CDCl$_3$)

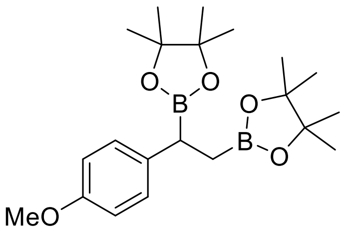
2,2'-(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7b)

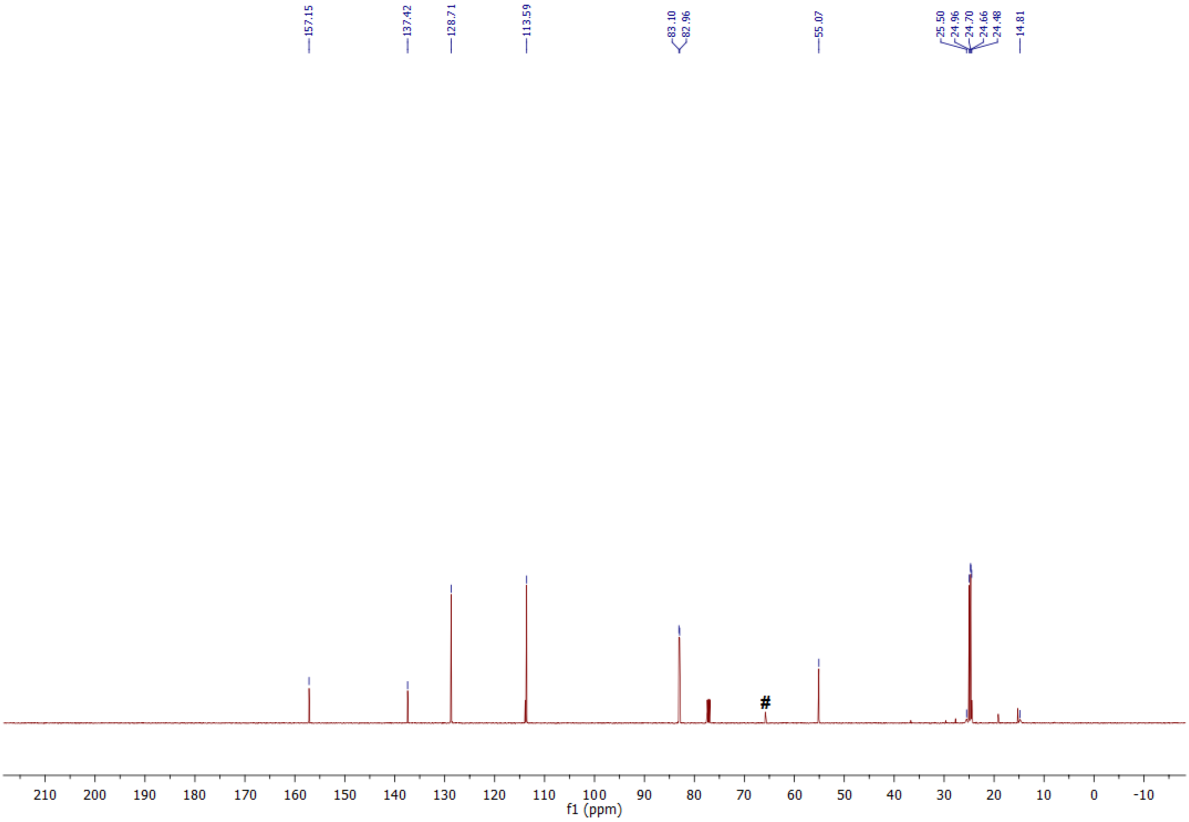


(#) Peak at δ = 3.48 ppm corresponds to Et_2O.



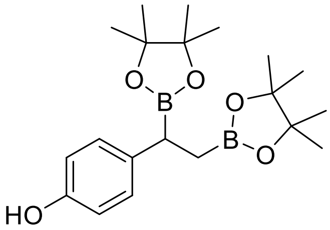
^{1}H NMR of **7b** (500 MHz, $CDCl_3$)



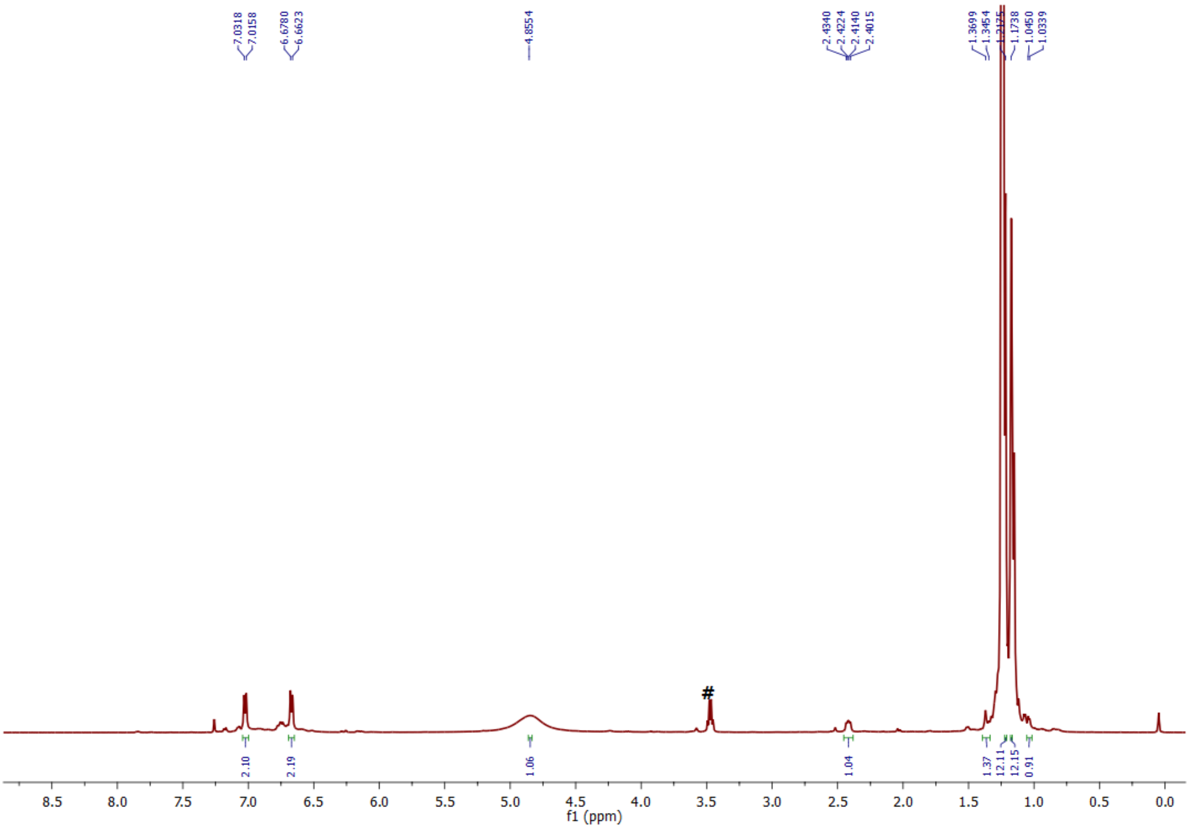


^{13}C{^{1}H} NMR of **7b** (126 MHz, CDCl$_3$)

4-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenol (8b)

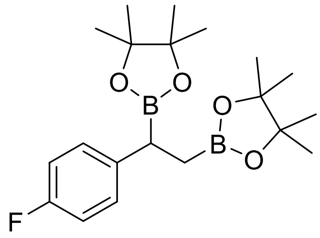


(#) Peak at δ = 3.48 ppm corresponds to Et_2O.

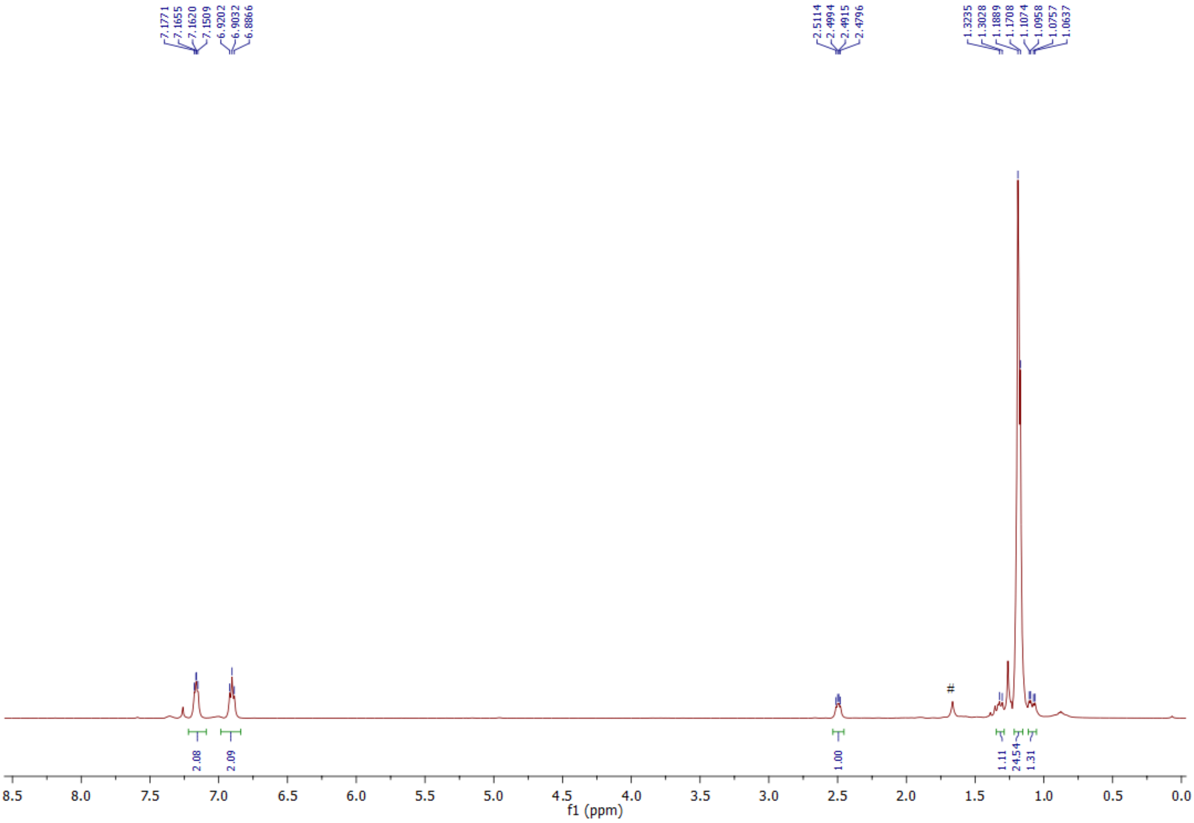


^{1}H NMR of **8b** (500 MHz, $CDCl_3$)

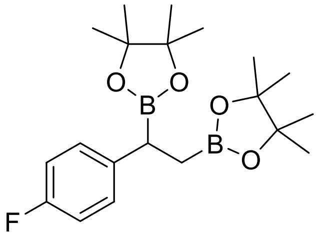
2,2'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9b)

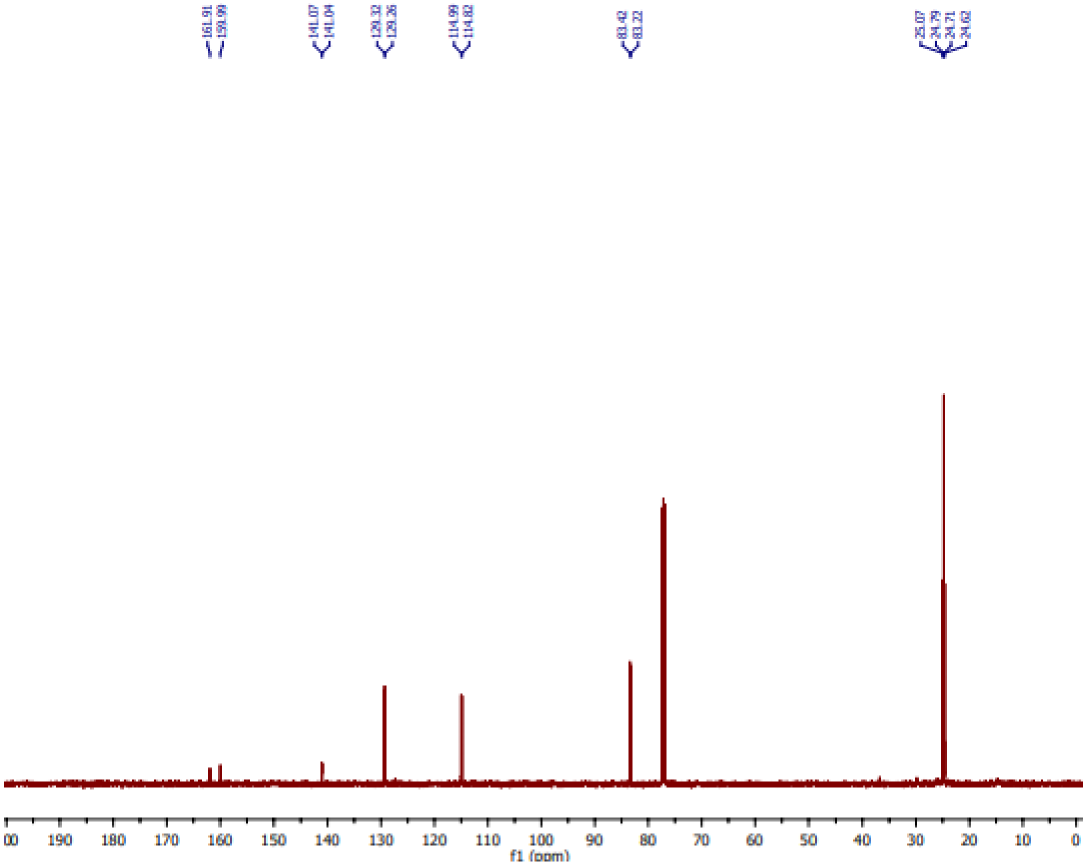


(#) Peak at δ = 1.56 ppm corresponds to H_2O



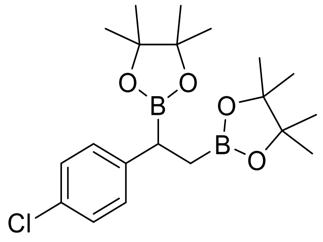
^{1}H NMR of **9b** (500 MHz, $CDCl_3$)



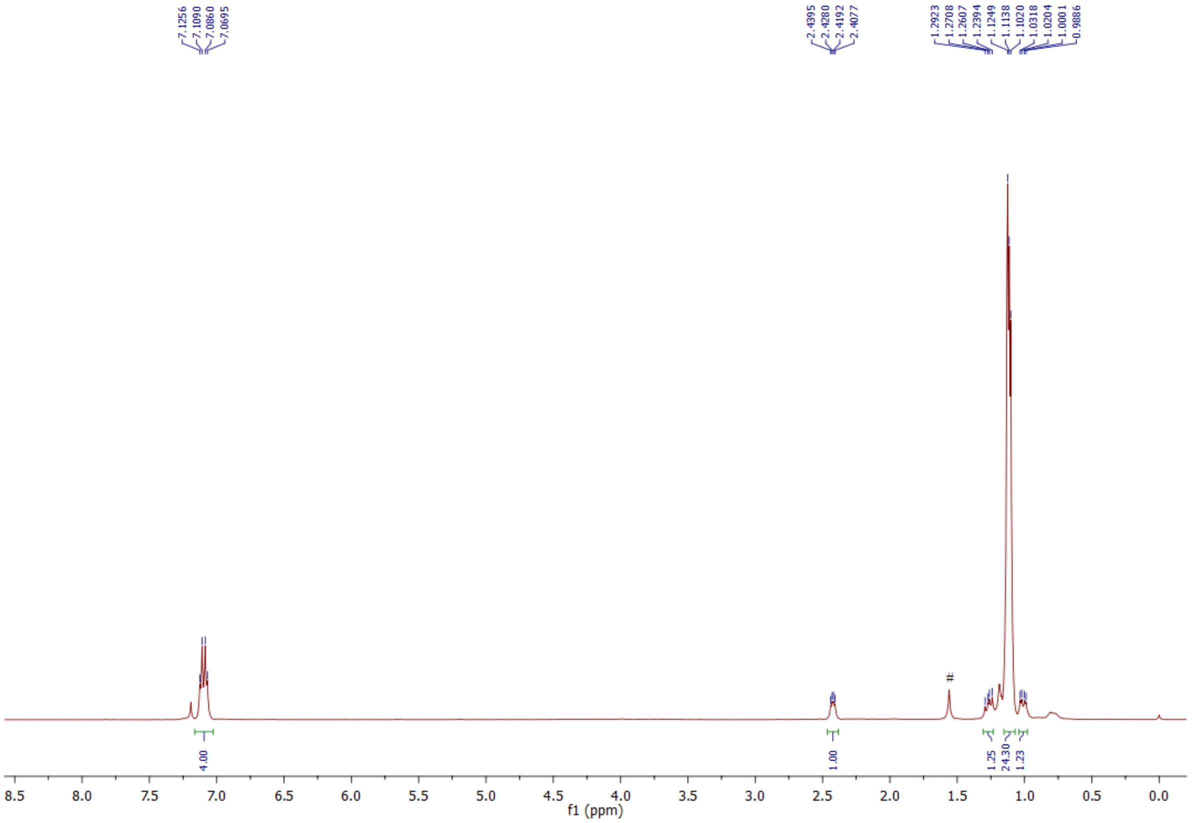


$^{13}C\{^1H\}$ NMR of **9b** (126 MHz, $CDCl_3$)

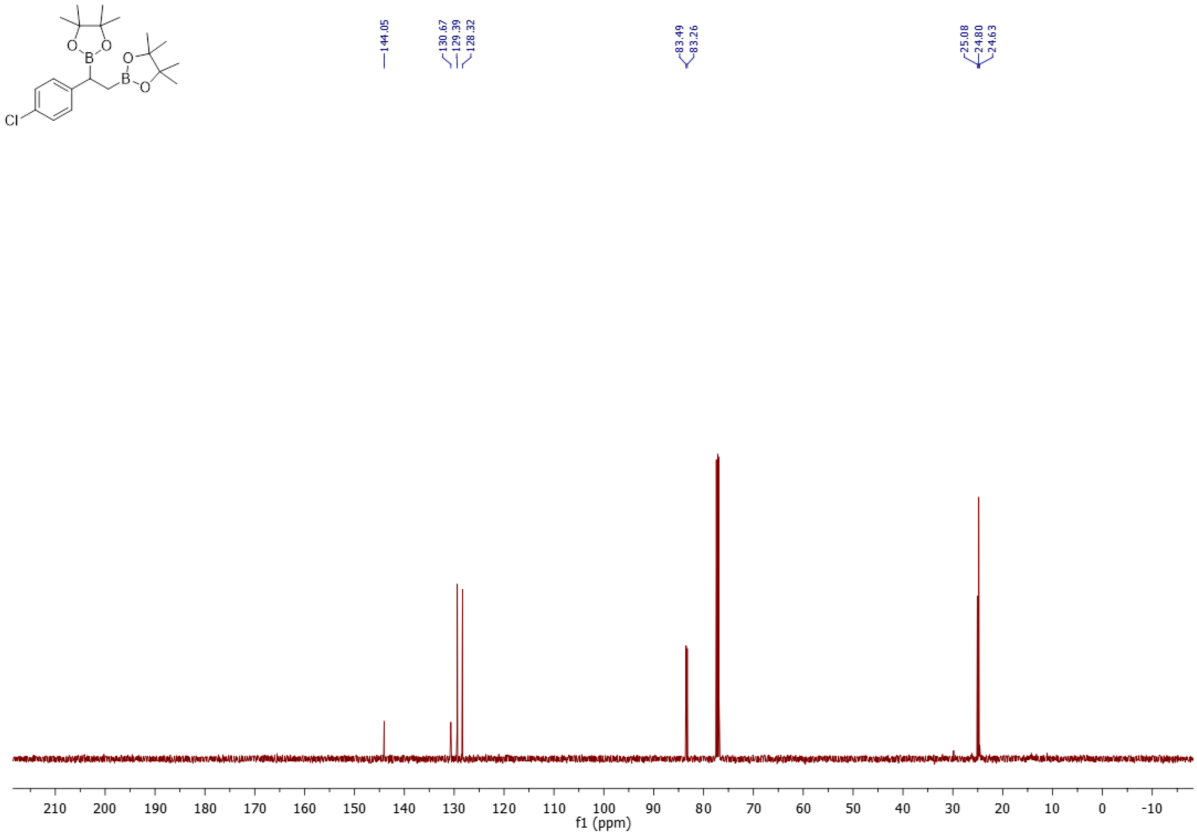
2,2'-(1-(4-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10b)



(#) Peak at δ = 1.56 ppm corresponds to H_2O

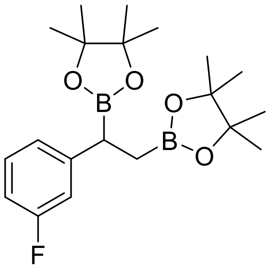


^{1}H NMR of **10b** (500 MHz, $CDCl_3$)

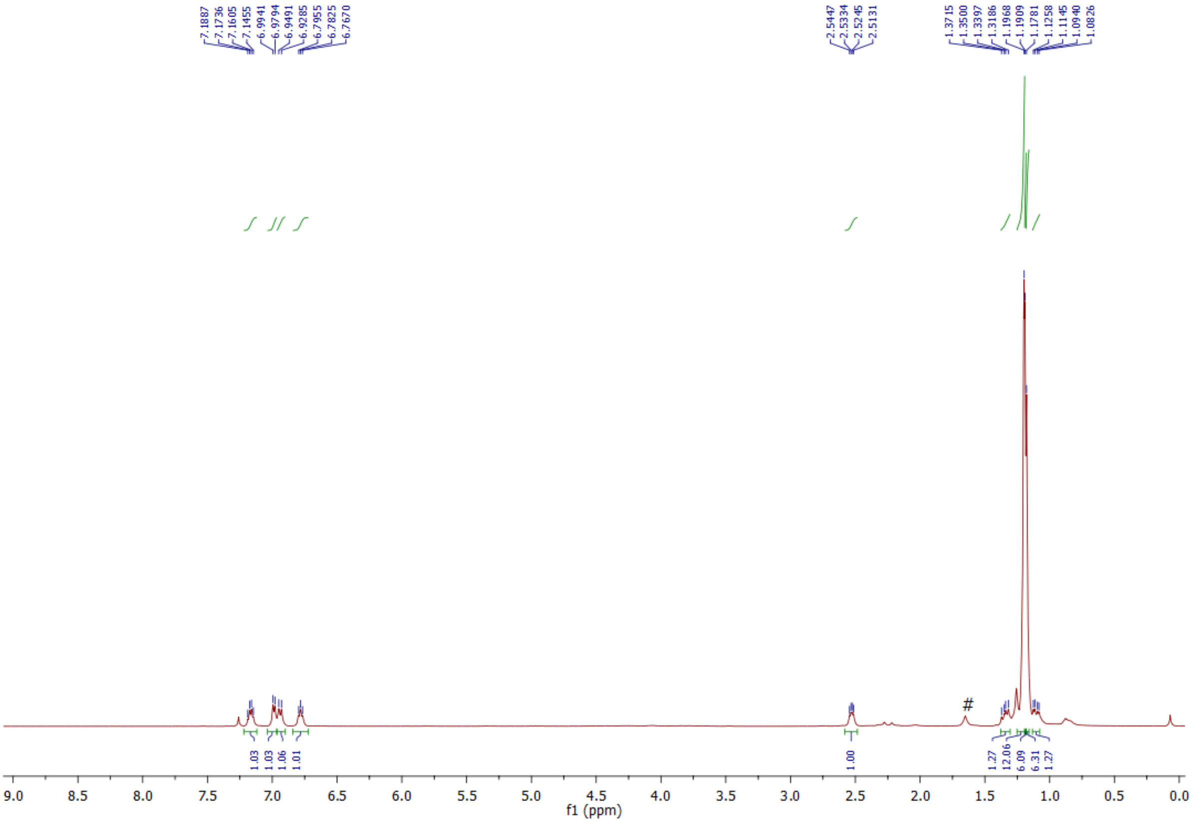


$^{13}C\{^{1}H\}$ NMR of **10b** (126 MHz, $CDCl_3$)

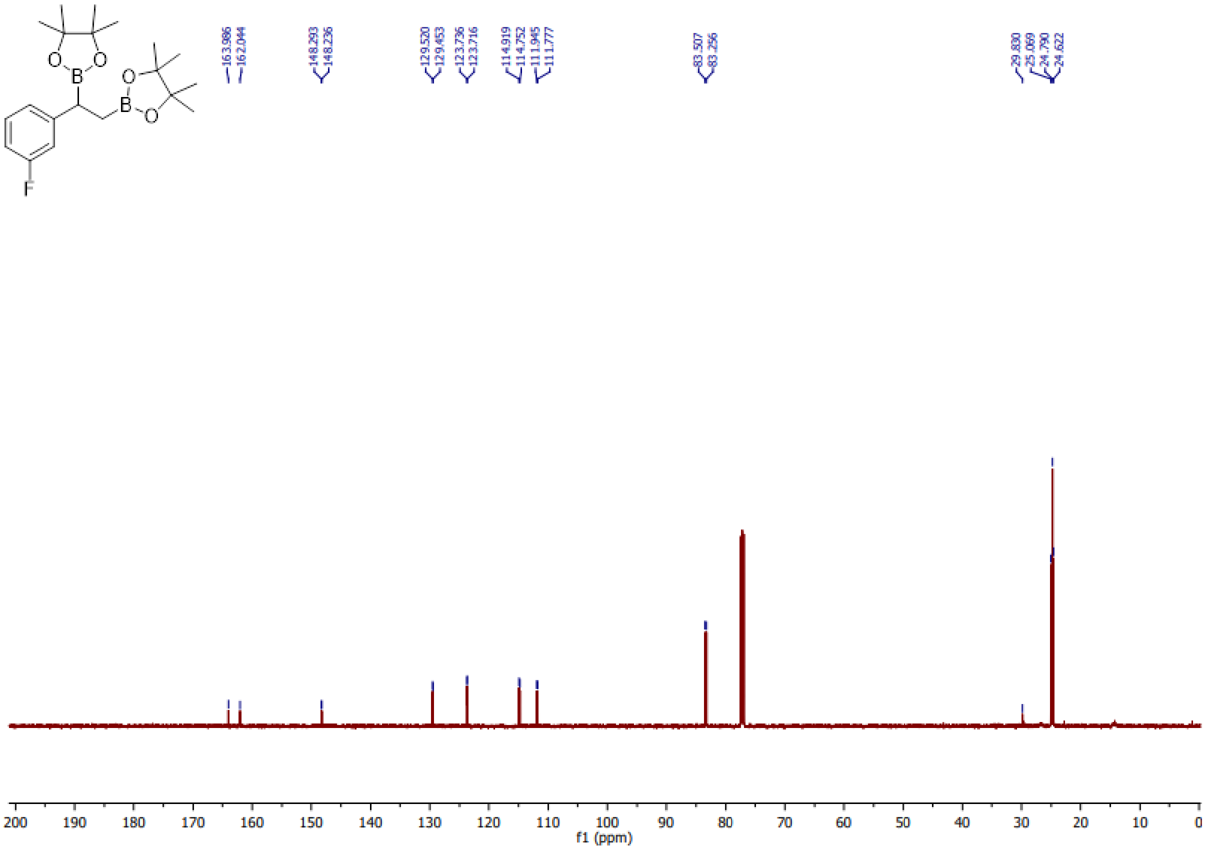
2,2'-(1-(3-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (11b)



(#) Peak at δ = 1.56 ppm corresponds to H_2O

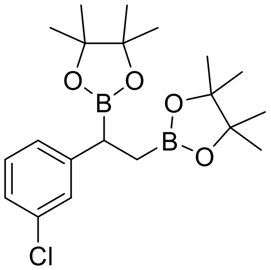


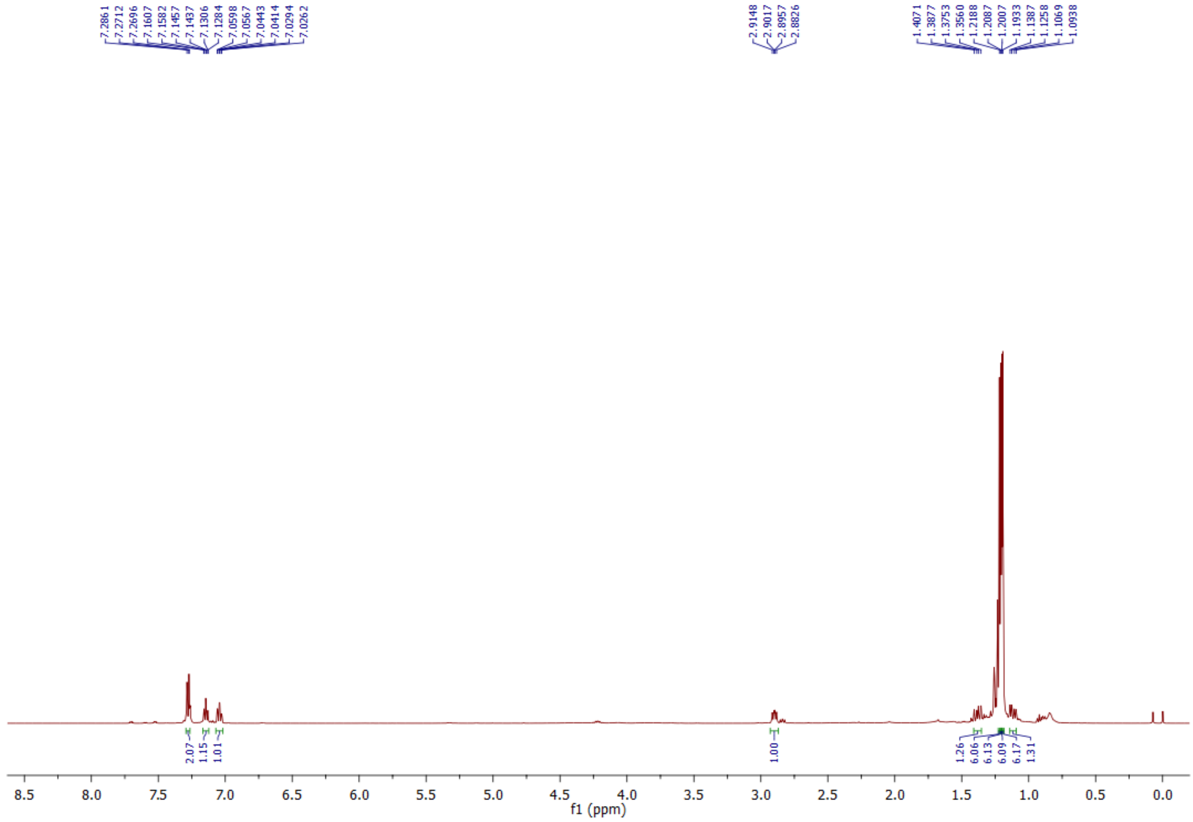
^{1}H NMR of **11b** (500 MHz, $CDCl_3$)



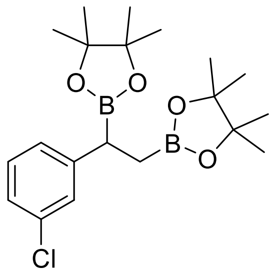
$^{13}C\{^1H\}$ NMR of **11b** (126 MHz, $CDCl_3$)

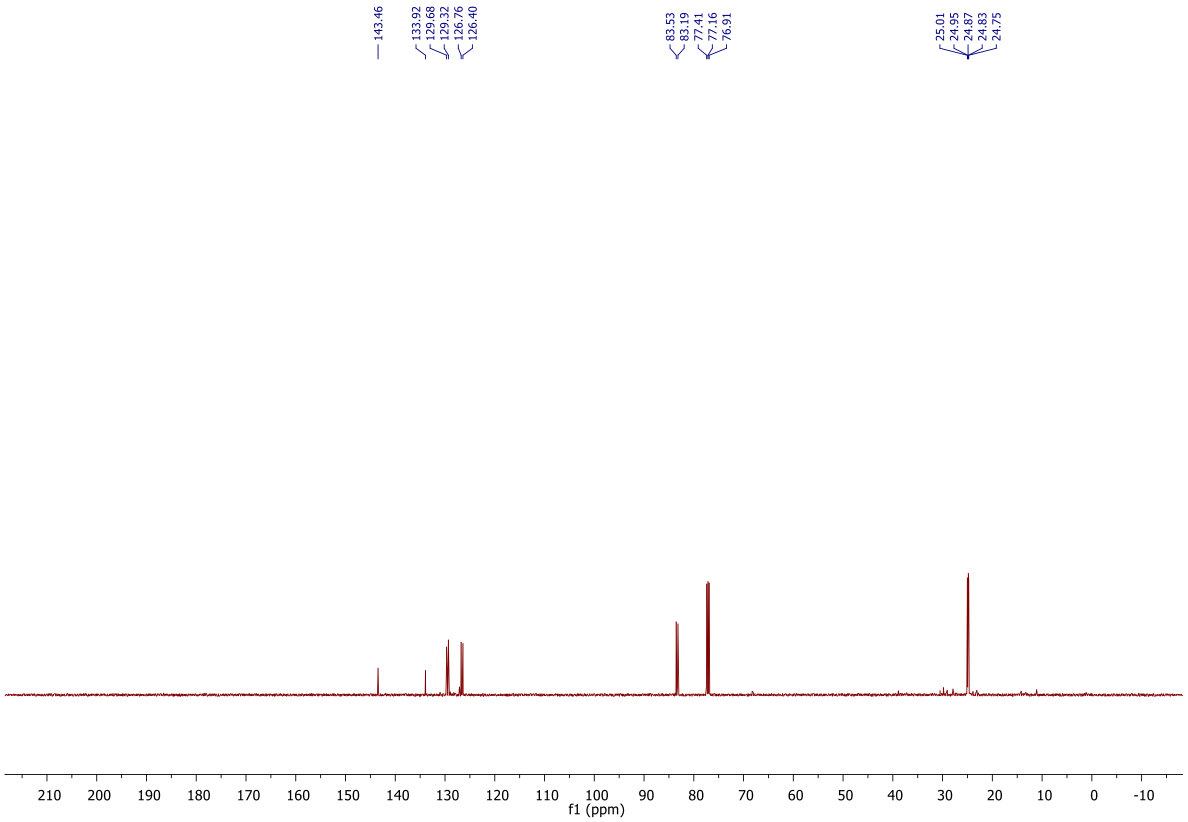
2,2'-(1-(3-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12b)





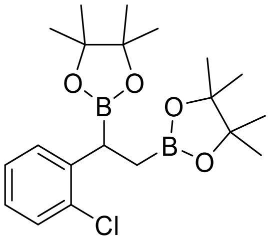
^{1}H NMR of **12b** (500 MHz, $CDCl_3$)

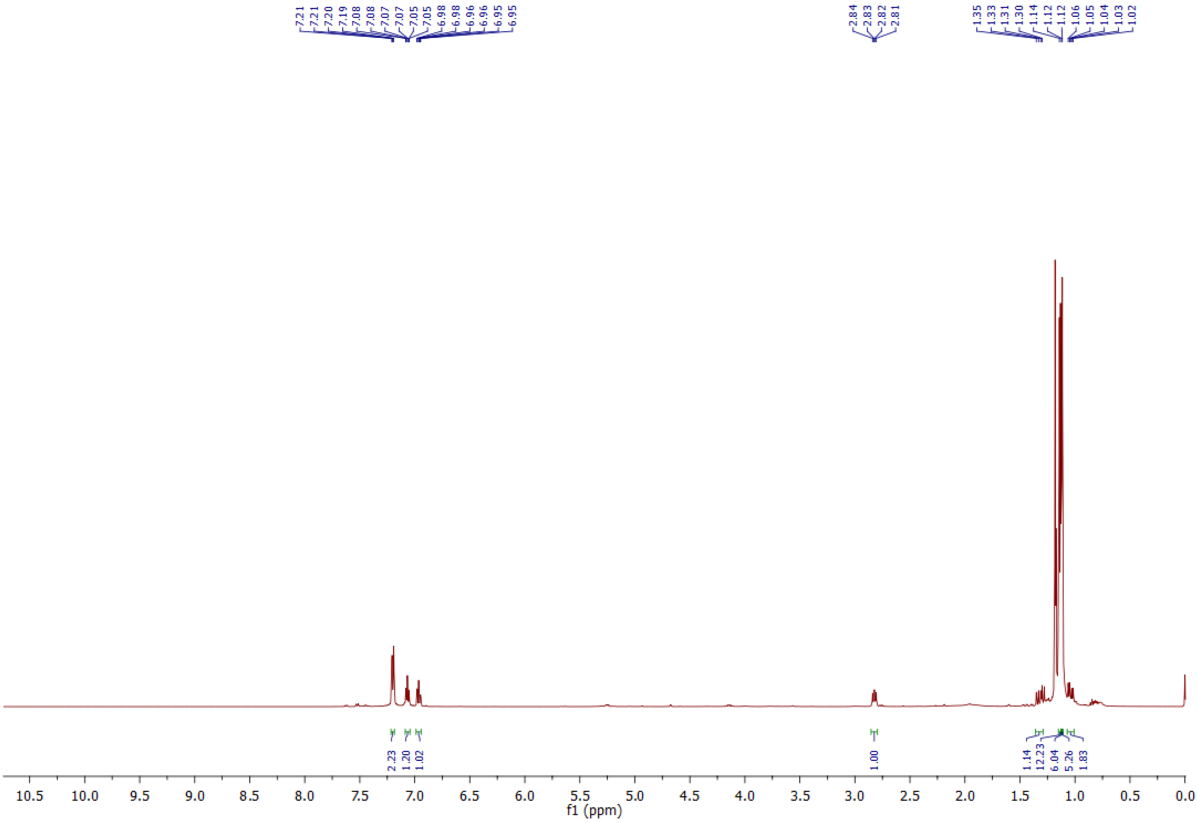




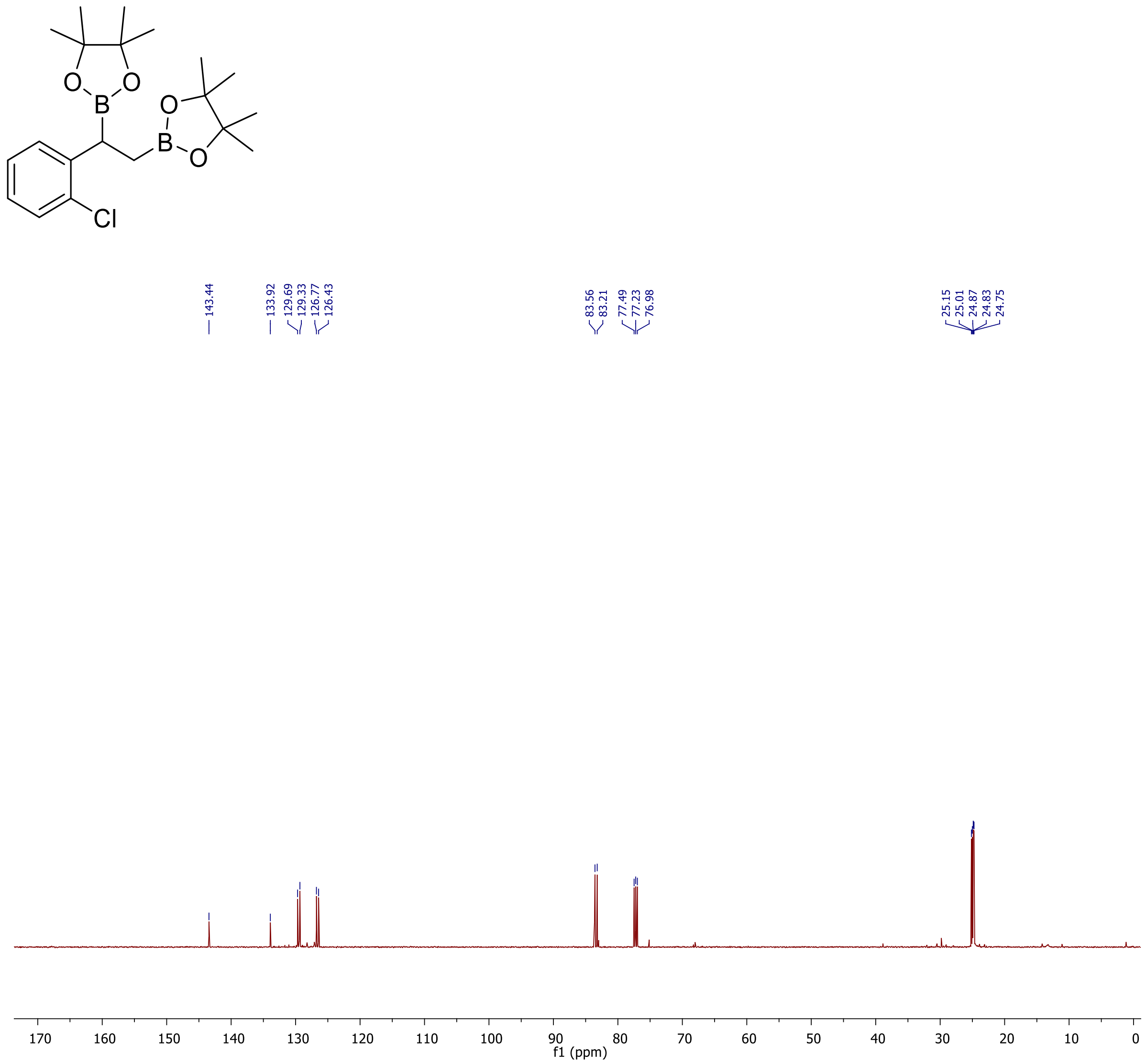
$^{13}C\{^{1}H\}$ NMR of **12b** (126 MHz, $CDCl_3$)

2,2'-(1-(2-Chlorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13b)



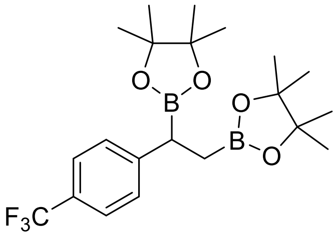


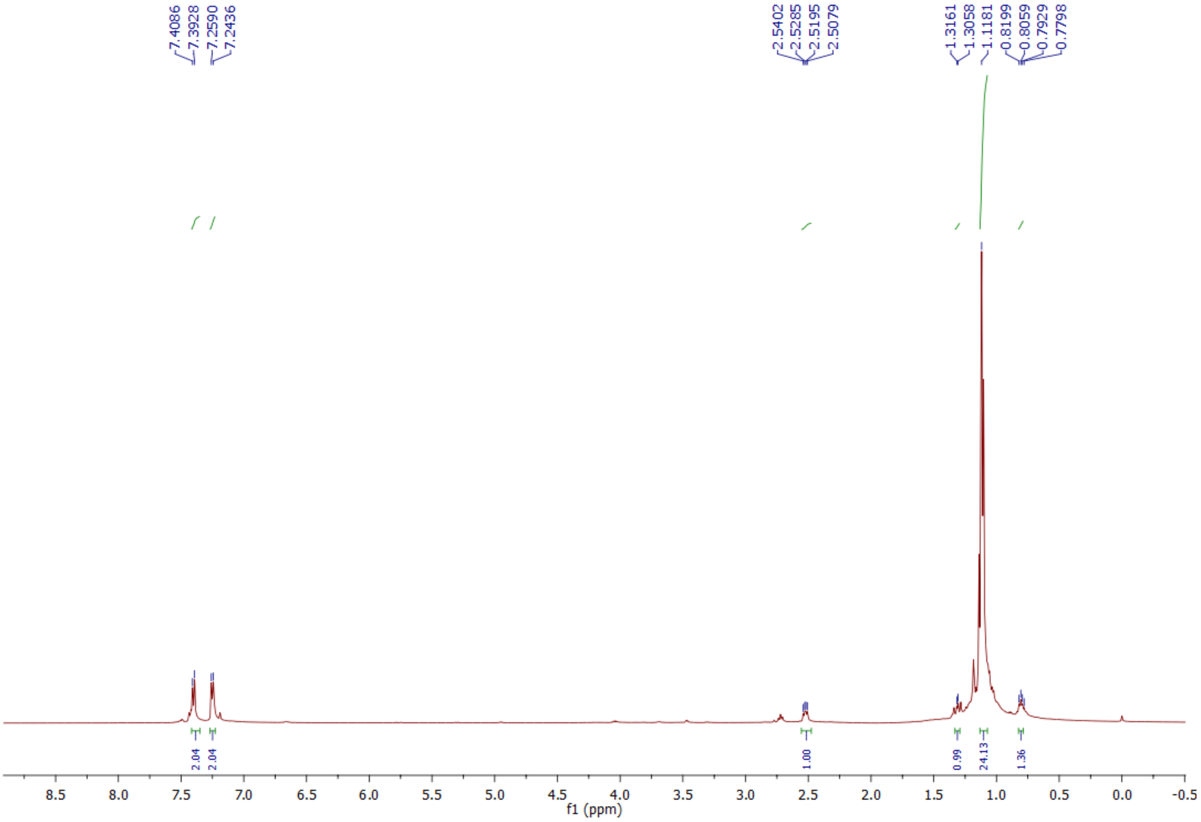
^{1}H NMR of **13b** (500 MHz, $CDCl_3$)



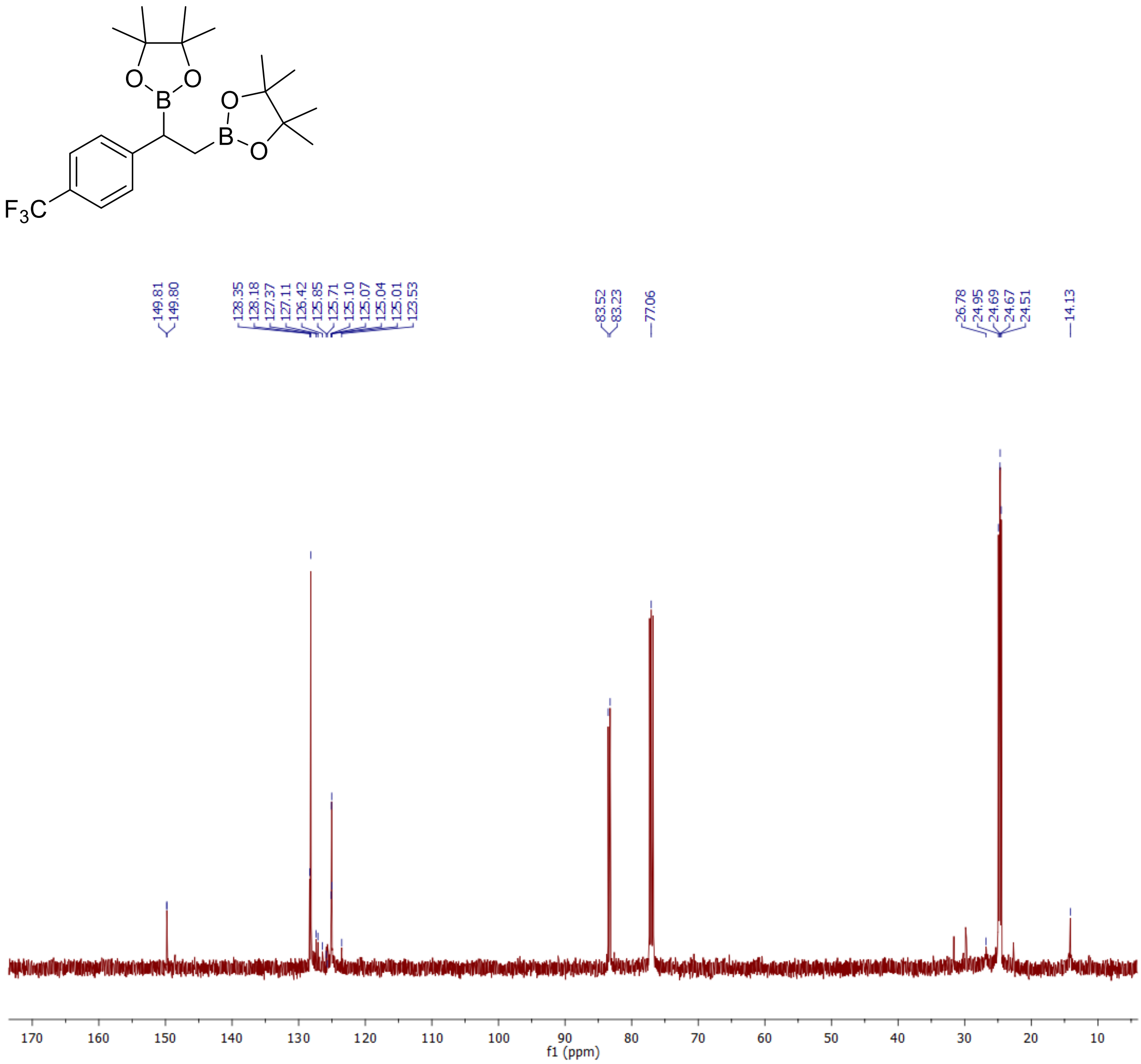
$^{13}C\{^{1}H\}$ NMR of **13b** (126 MHz, $CDCl_3$)

2,2'-(1-(4-Triflorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (14b)



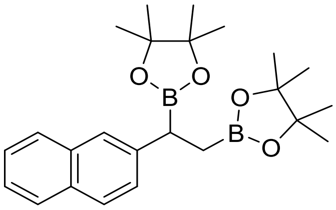


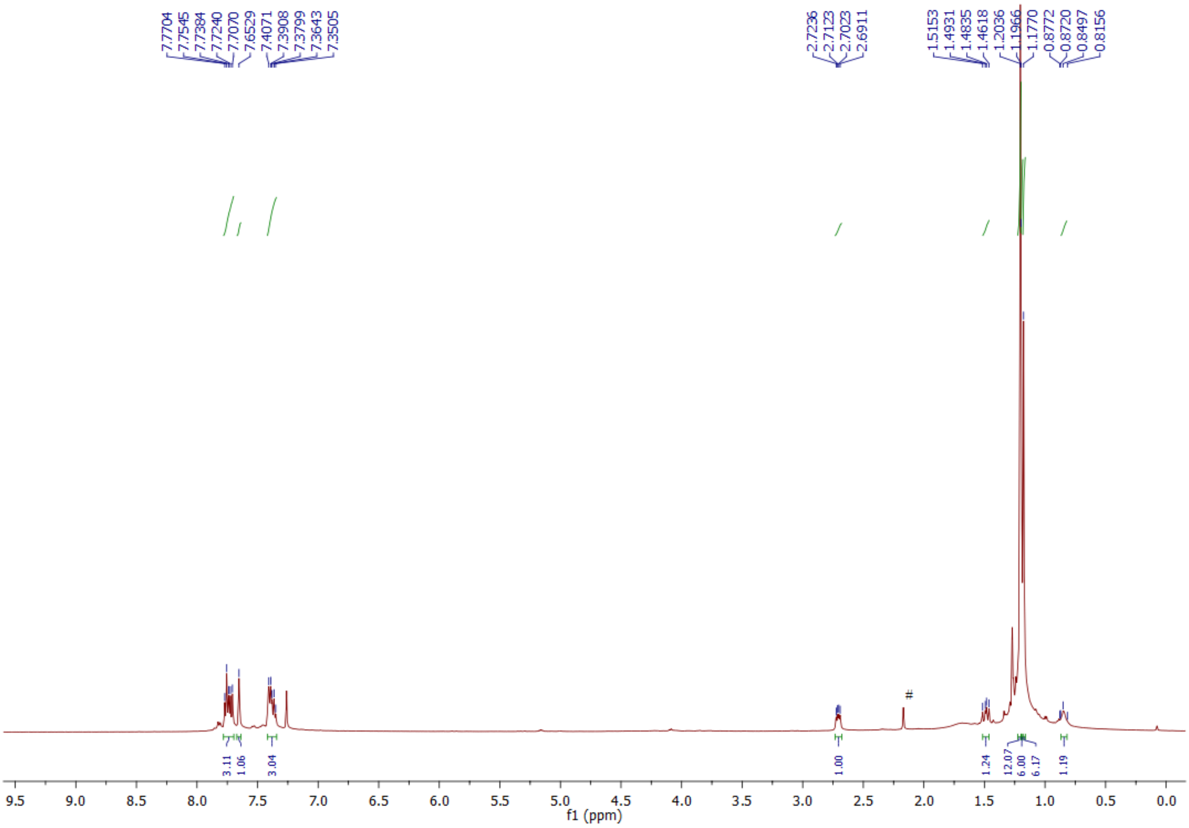
^{1}H NMR of **14b** (500 MHz, $CDCl_3$)



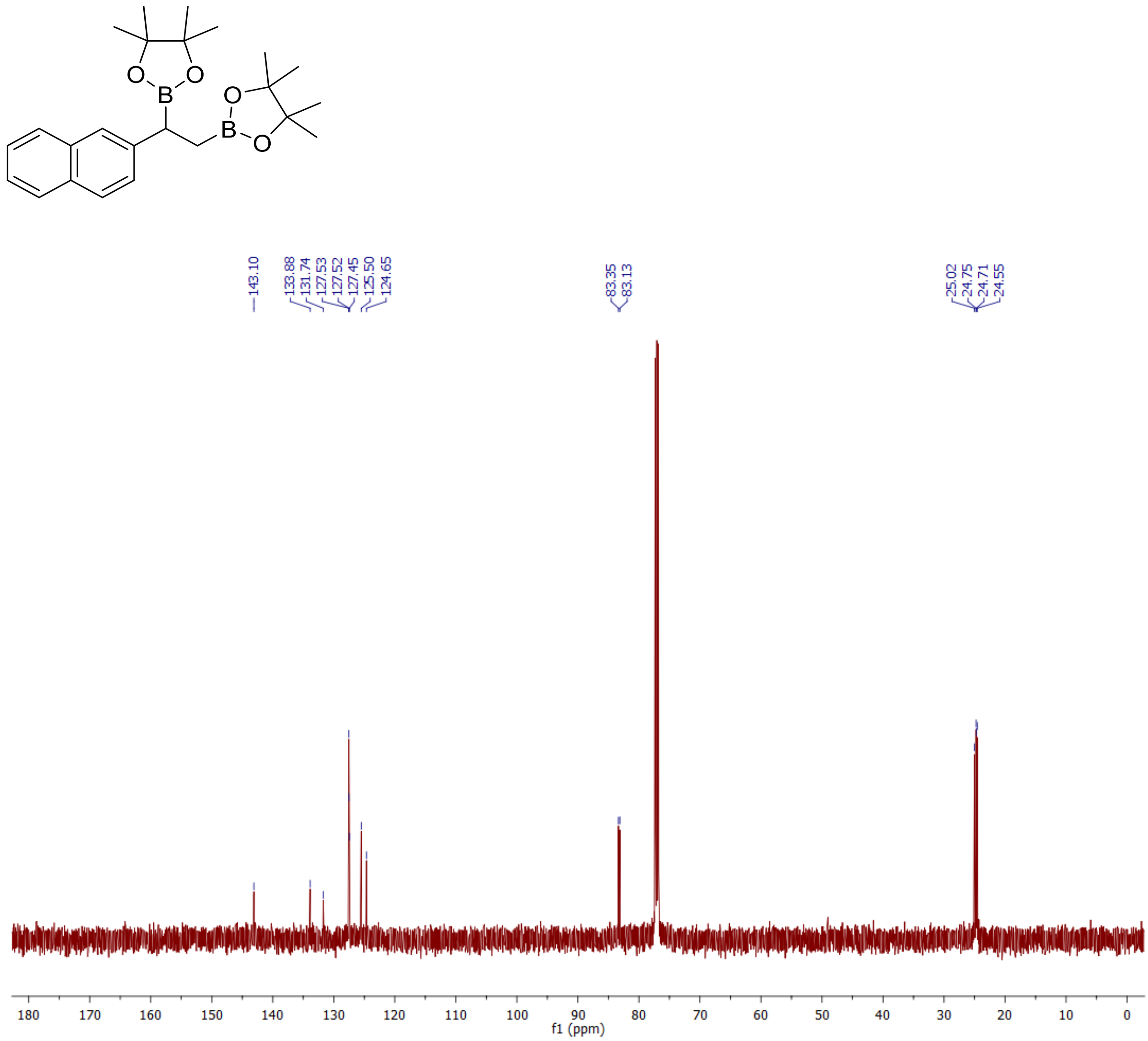
$^{13}C\{^{1}H\}$ NMR of **14b** (126 MHz, $CDCl_3$)

2,2’-(1-(Naphthalen-2-yl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (15b)



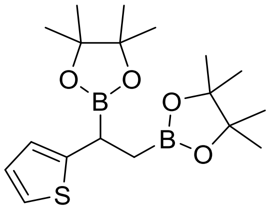


^{1}H NMR of **15b** (500 MHz, $CDCl_3$)

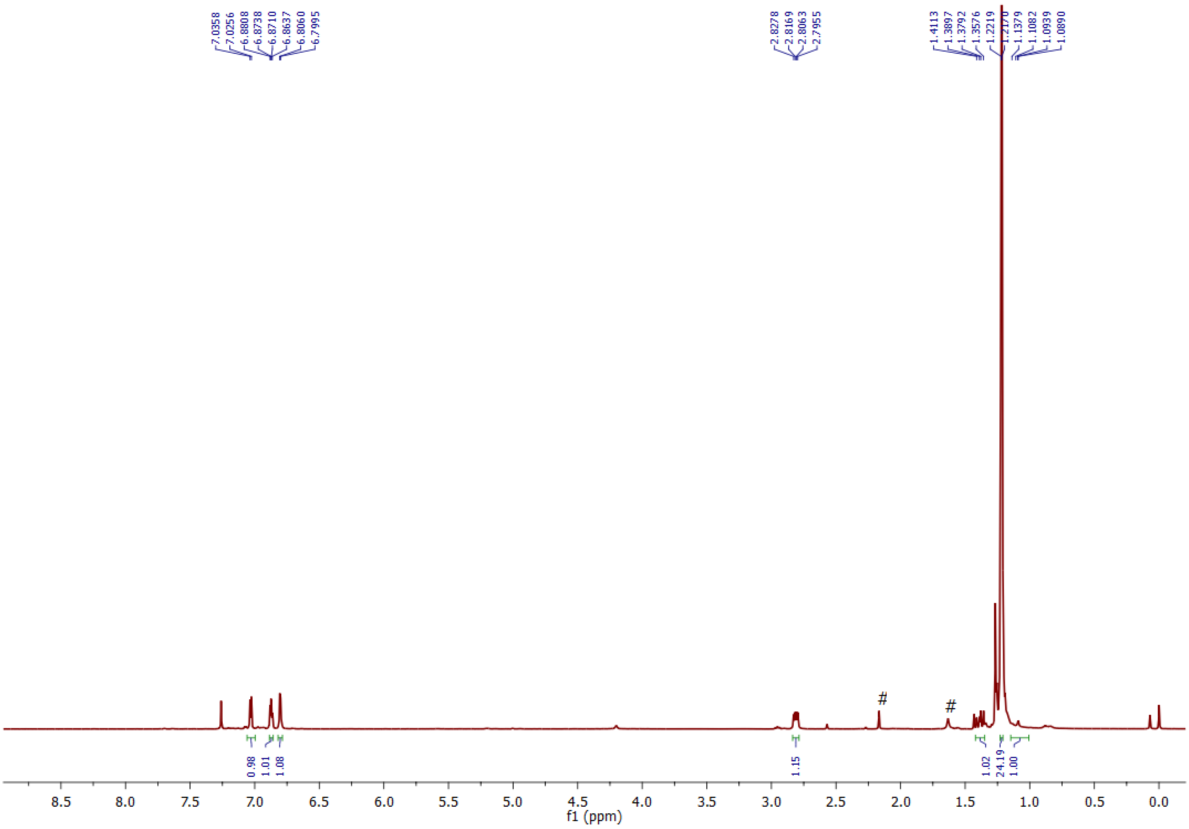


$^{13}C\{^{1}H\}$ NMR of **15b** (126 MHz, $CDCl_3$)

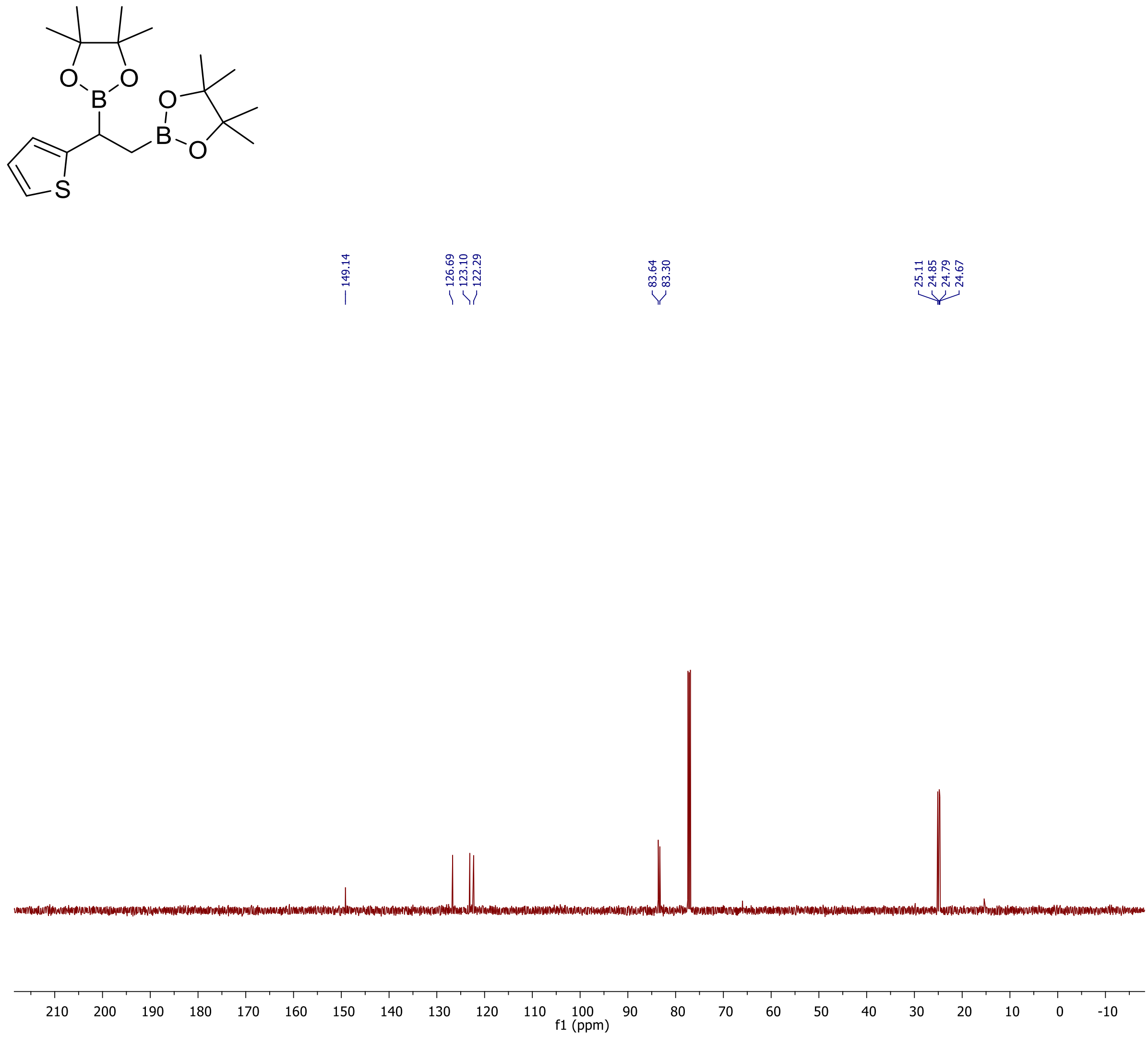
2,2’-(1-(Thiophen-2-yl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (16b)



(#) Peak at δ = 1.56 ppm corresponds to H_2O and at δ = 2.16 ppm corresponds to acetone.

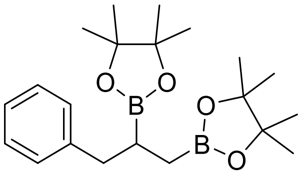


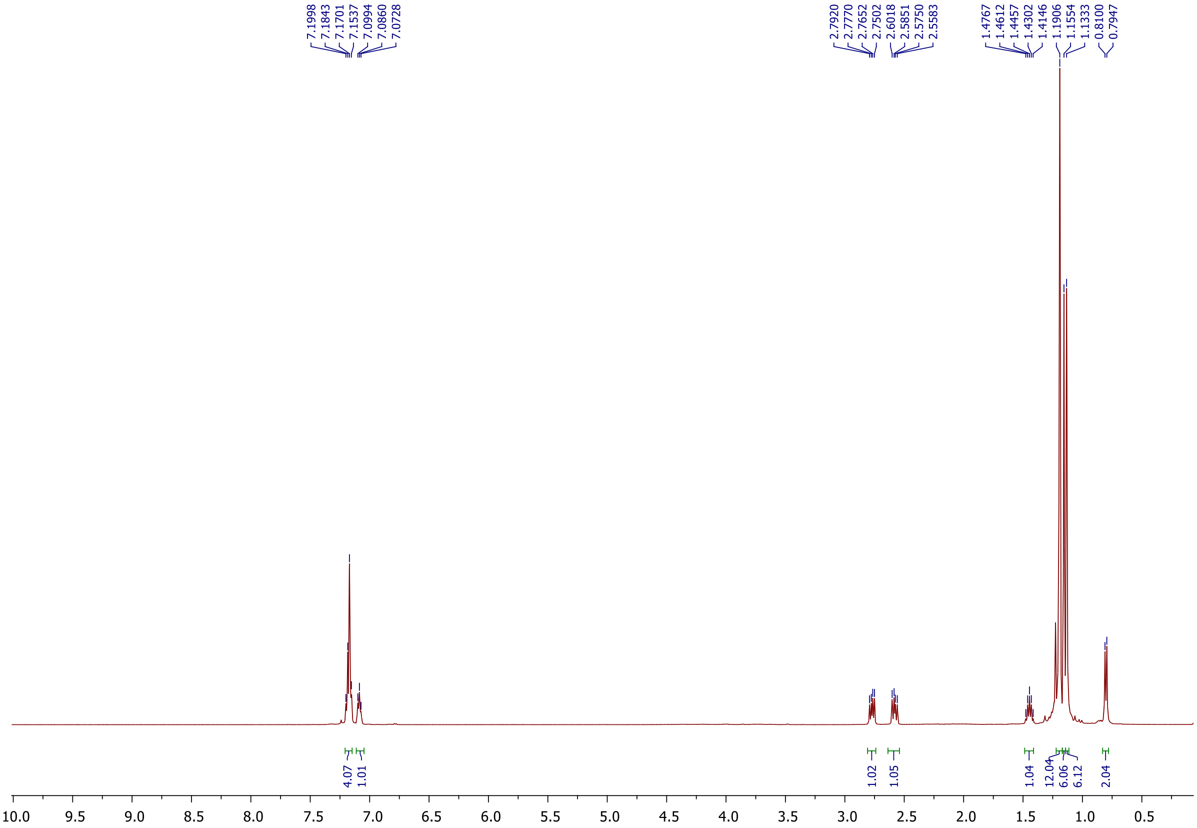
^1H NMR of **16b** (500 MHz, $CDCl_3$)



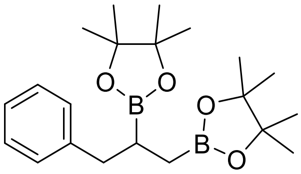
$^{13}C\{^{1}H\}$ NMR of **16b** (126 MHz, $CDCl_3$)

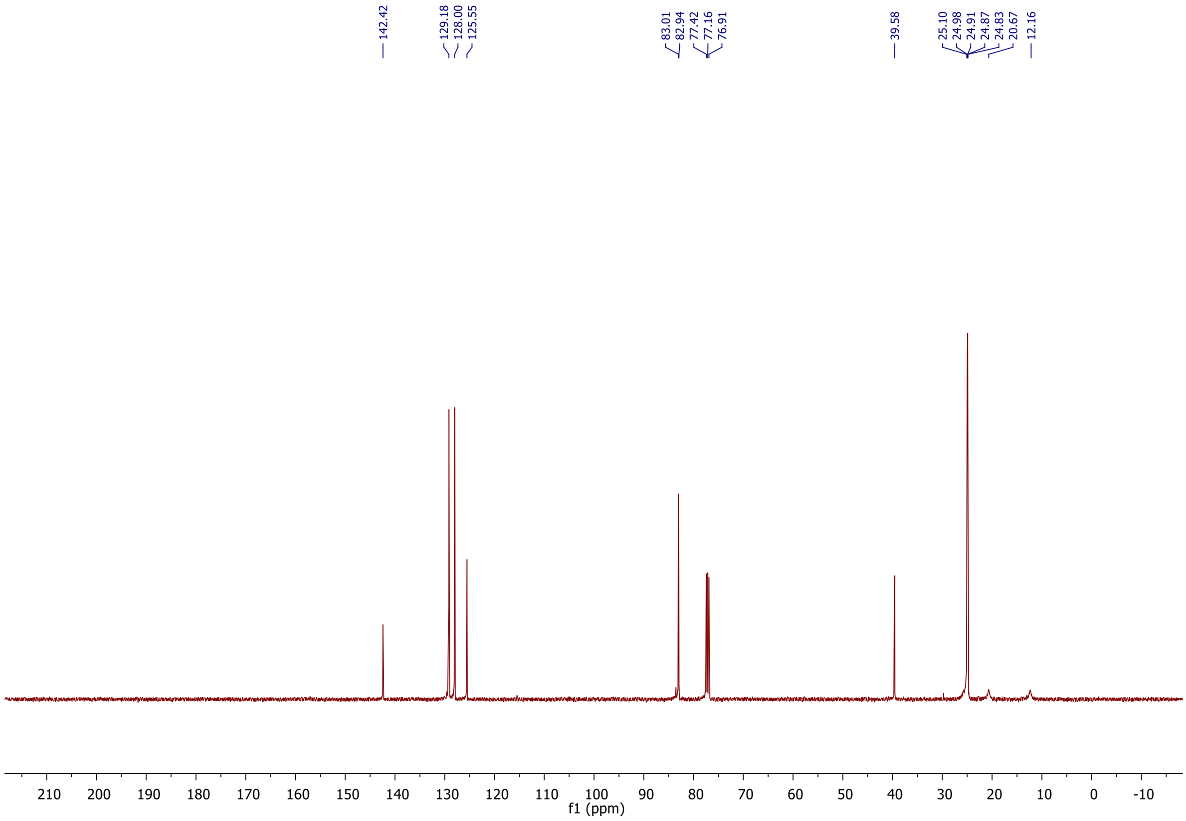
2,2’-(3-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (17b)





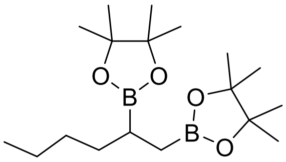
^{1}H NMR of **17b** (500 MHz, $CDCl_3$)

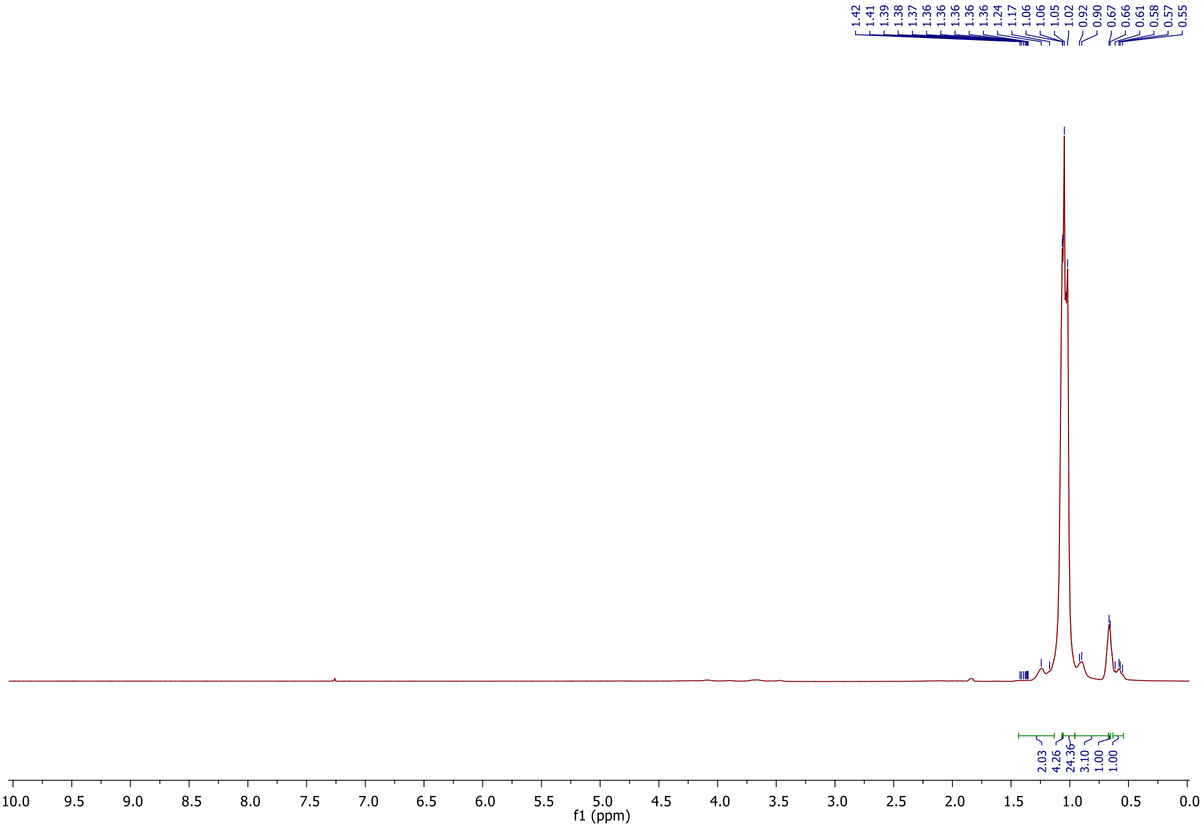




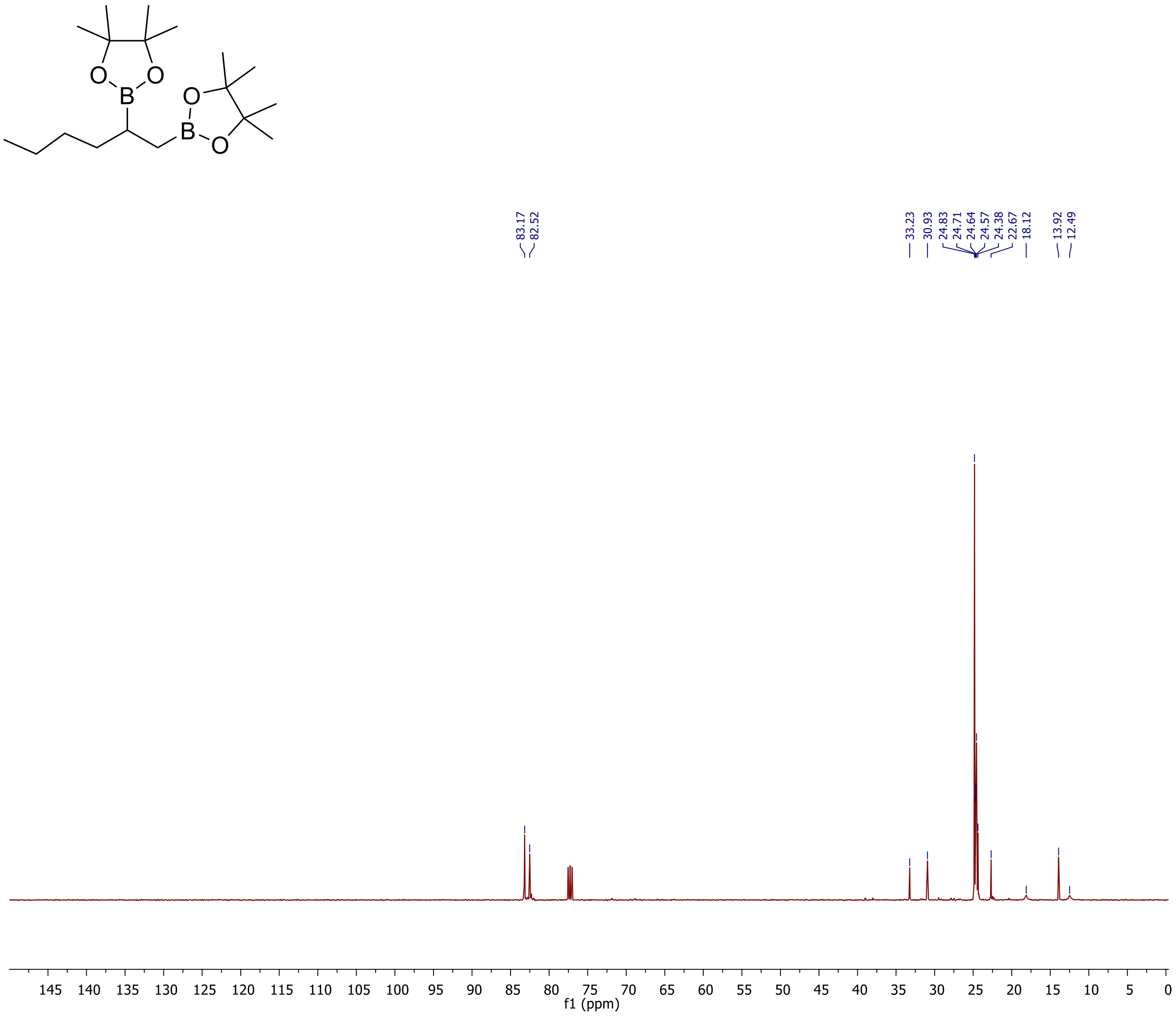
$^{13}C\{^{1}H\}$ NMR of **17b** (126 MHz, $CDCl_3$)

2,2’-(Hexane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (18b)



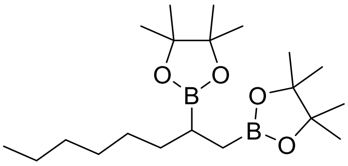


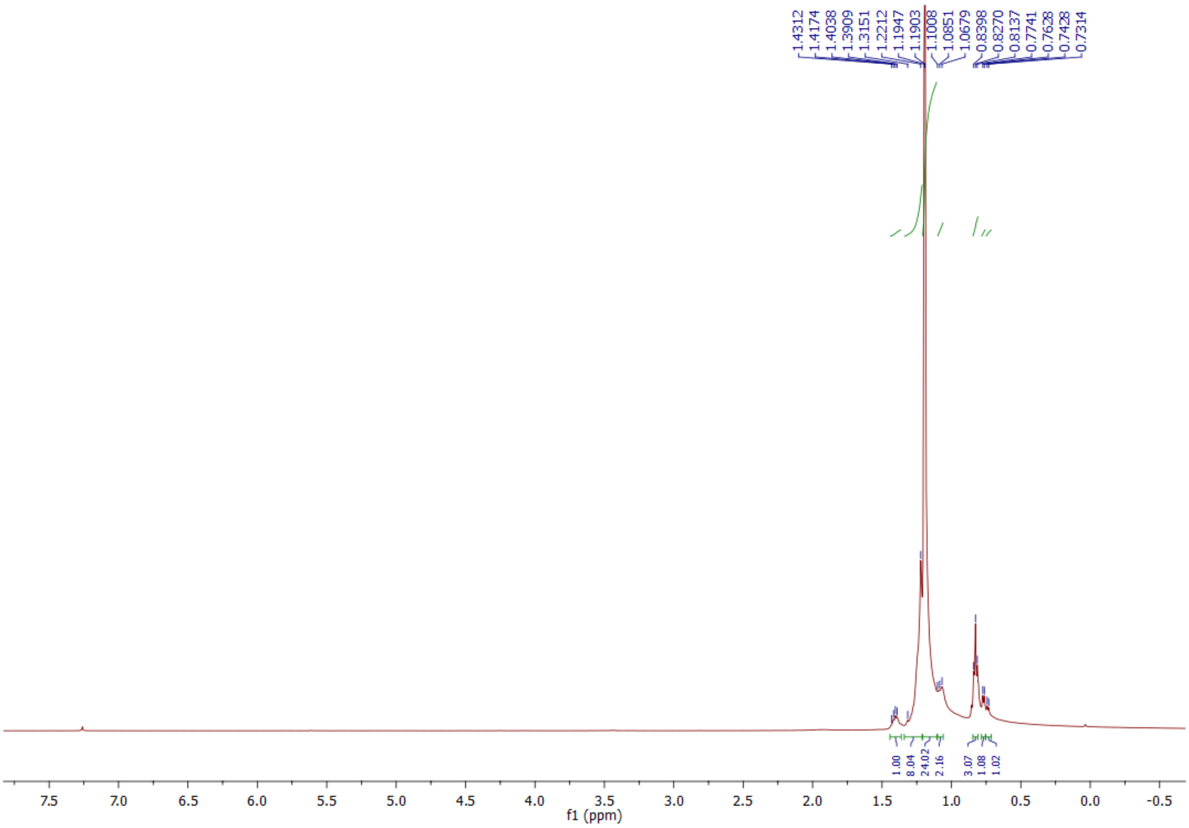
^{1}H NMR of **18b** (500 MHz, CDCl$_3$)



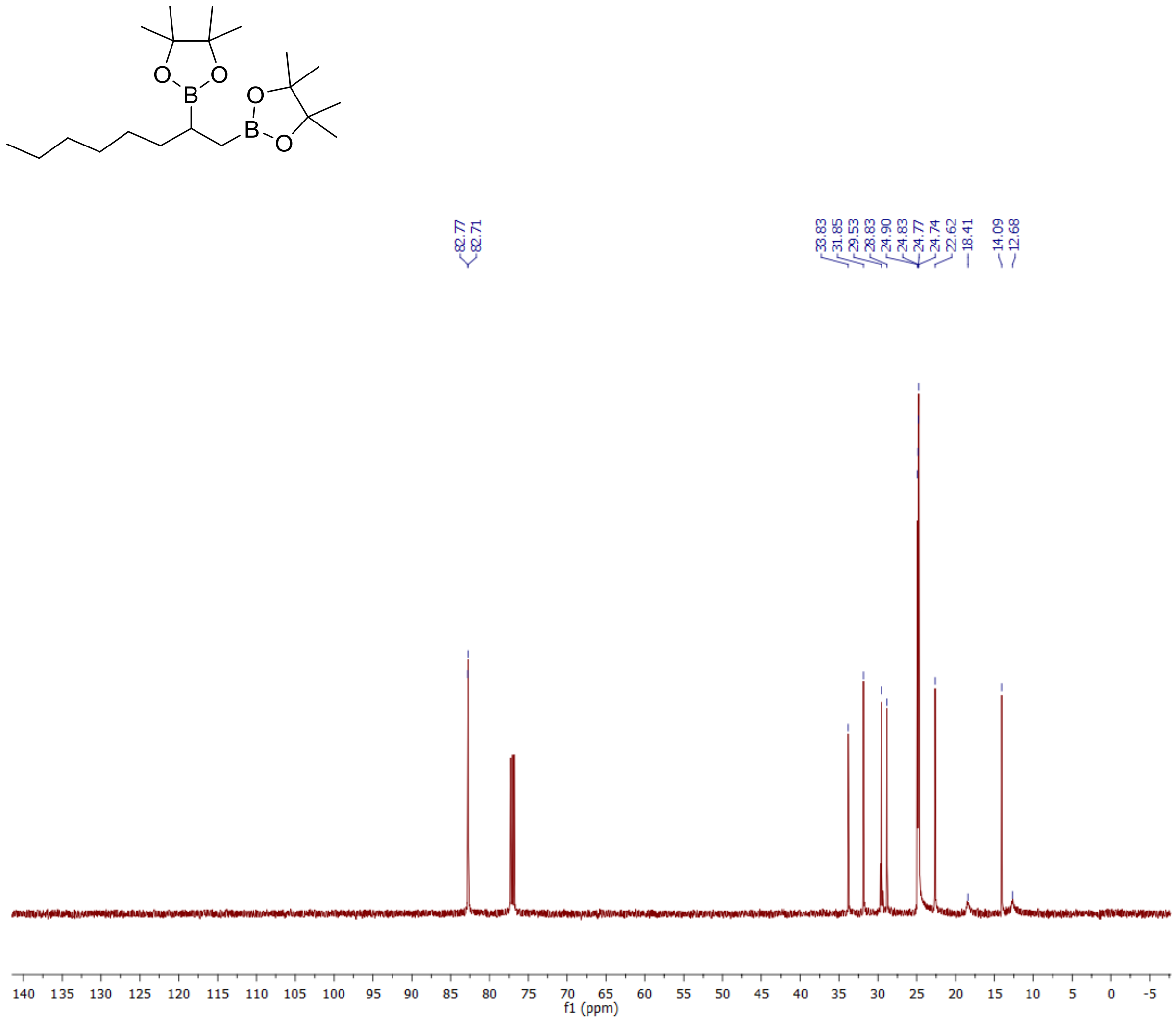
$^{13}C\{^1H\}$ NMR of **18b** (126 MHz, $CDCl_3$)

2,2'-(Octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (19b)



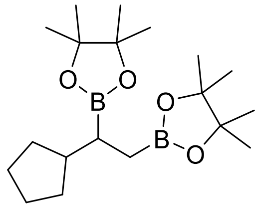


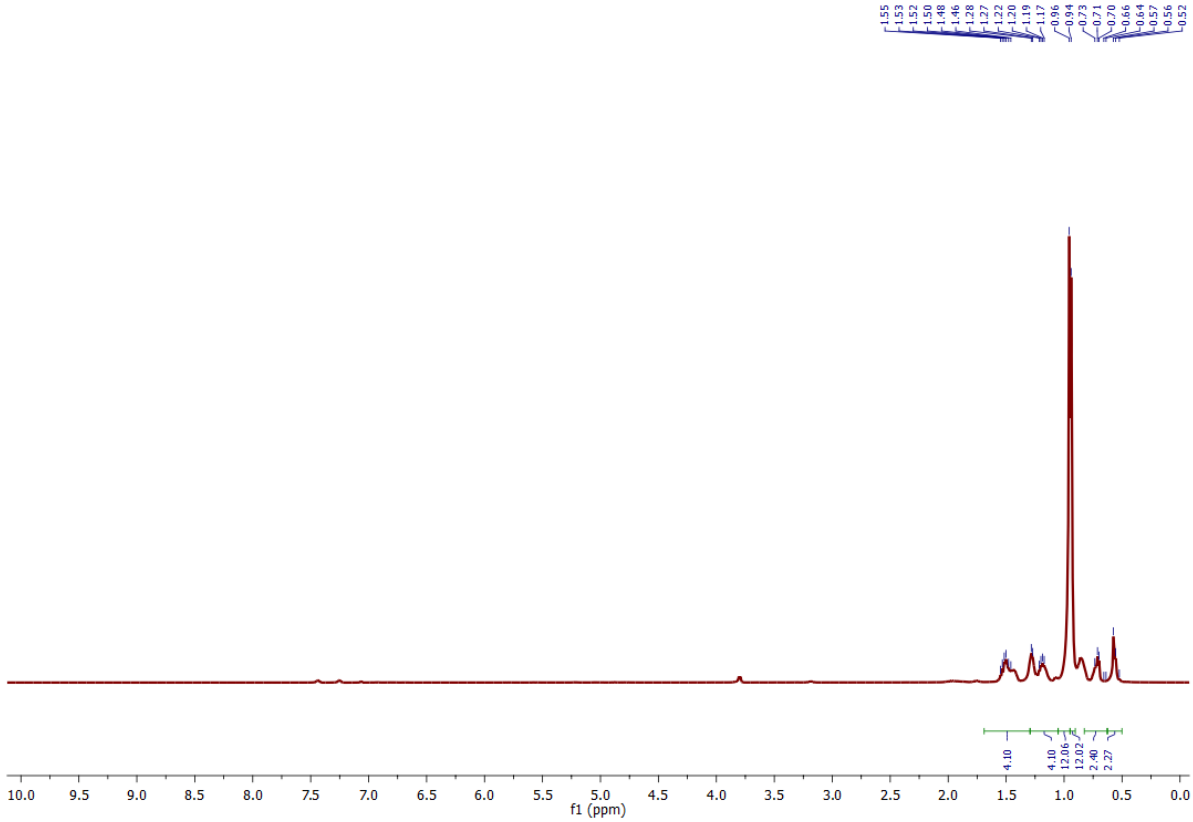
^{1}H NMR of **19b** (500 MHz, $CDCl_3$)



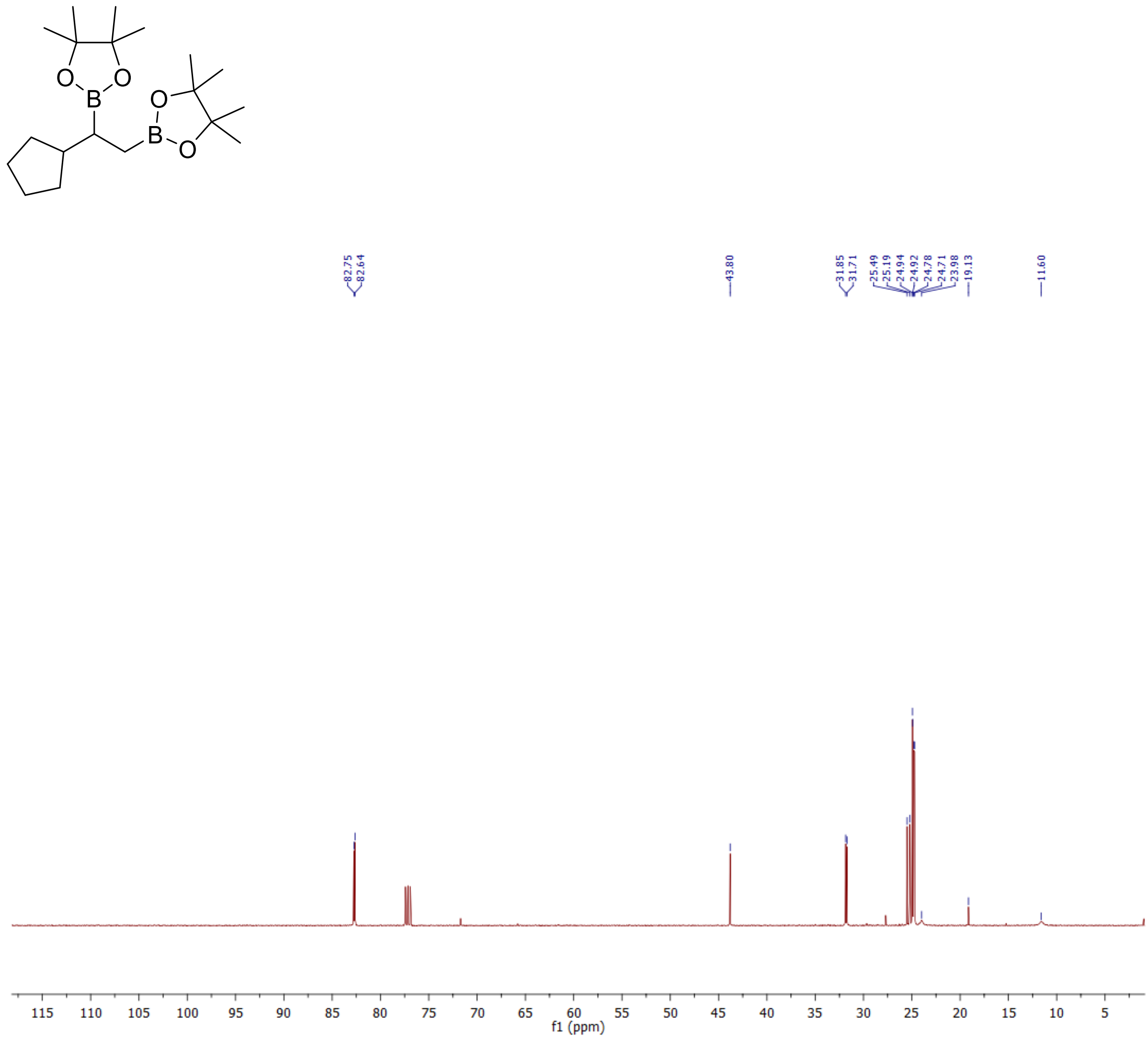
$^{13}C\{^{1}H\}$ NMR of **19b** (126 MHz, $CDCl_3$)

2,2’-(1-Cyclopentylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (20b)



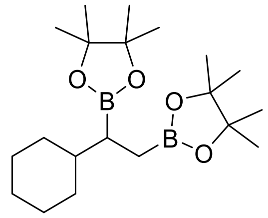


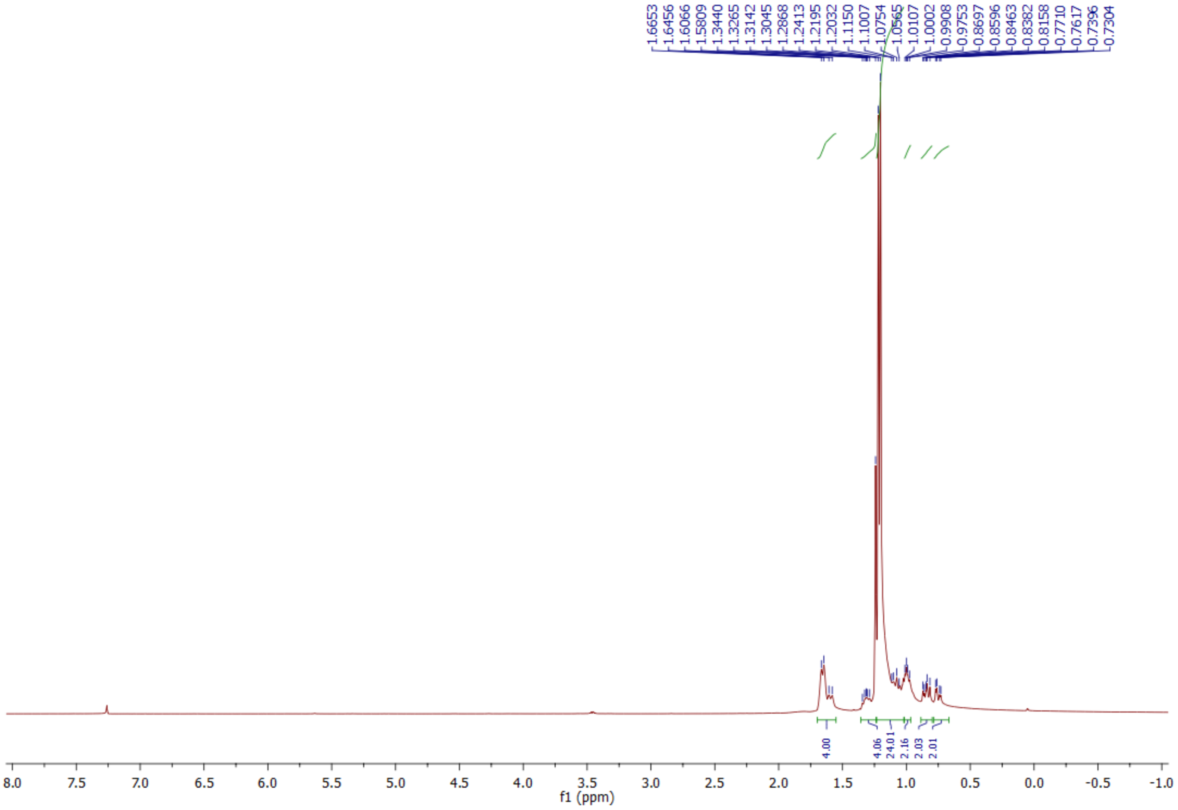
^{1}H NMR of **20b** (500 MHz, $CDCl_3$)



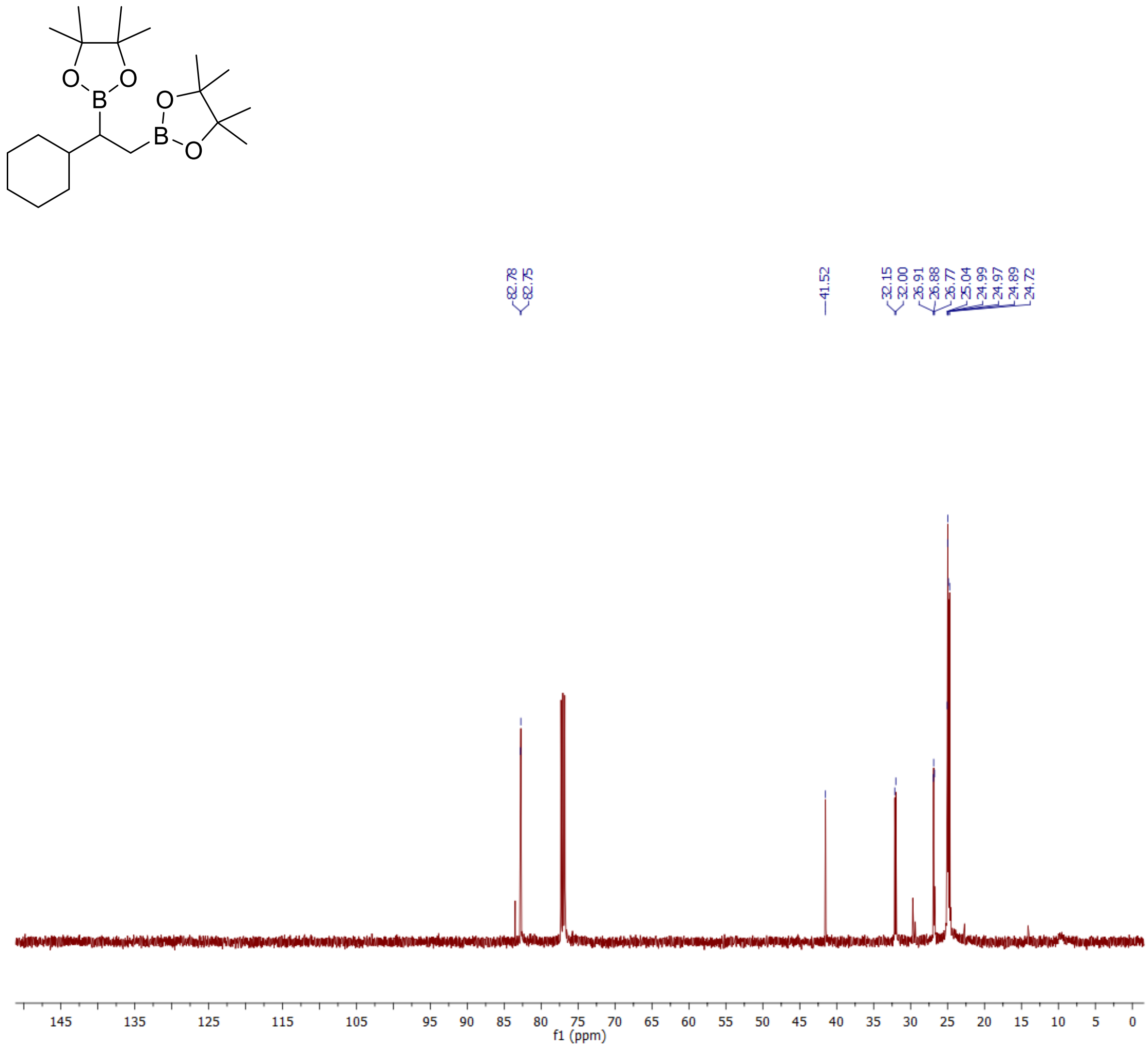
$^{13}C\{^1H\}$ NMR of **20b** (126 MHz, $CDCl_3$)

2,2'-(1-Cyclohexylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (21b)



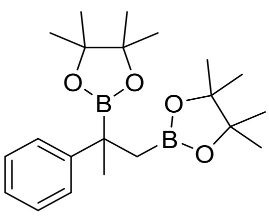


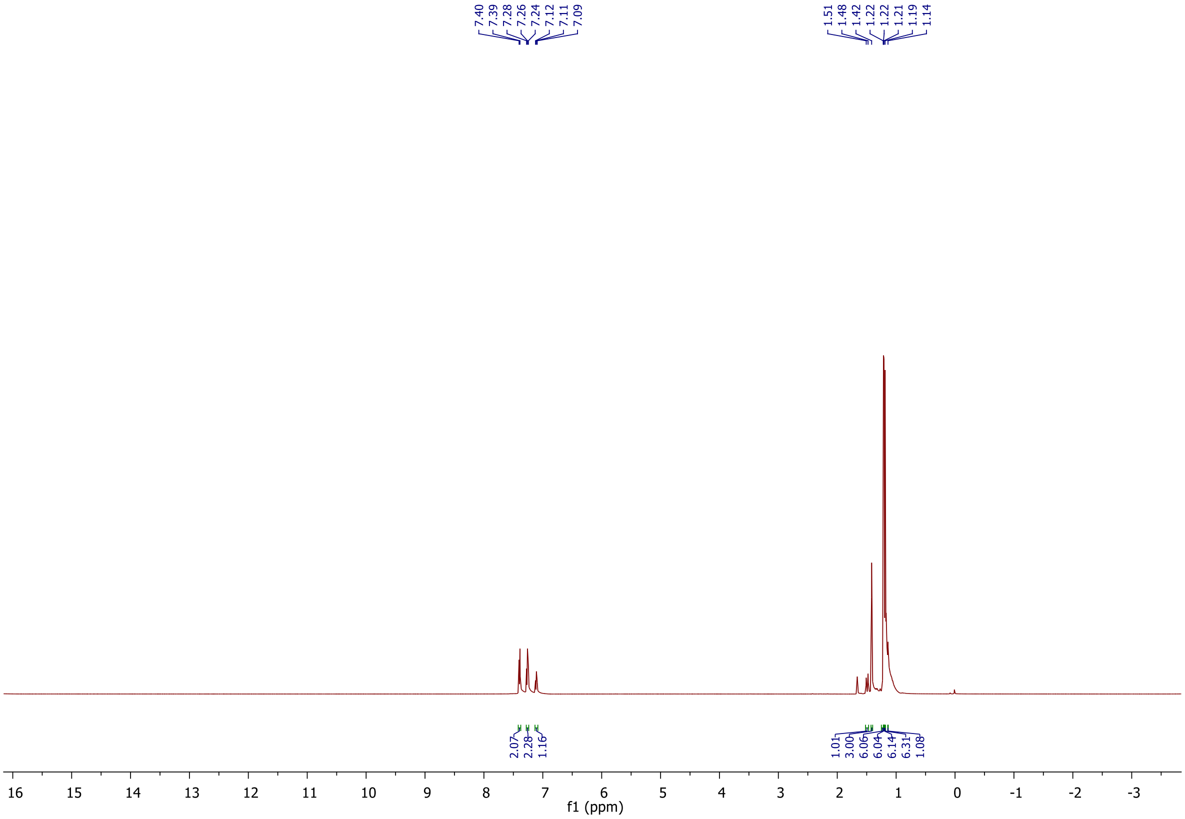
^{1}H NMR of **21b** (500 MHz, $CDCl_3$)



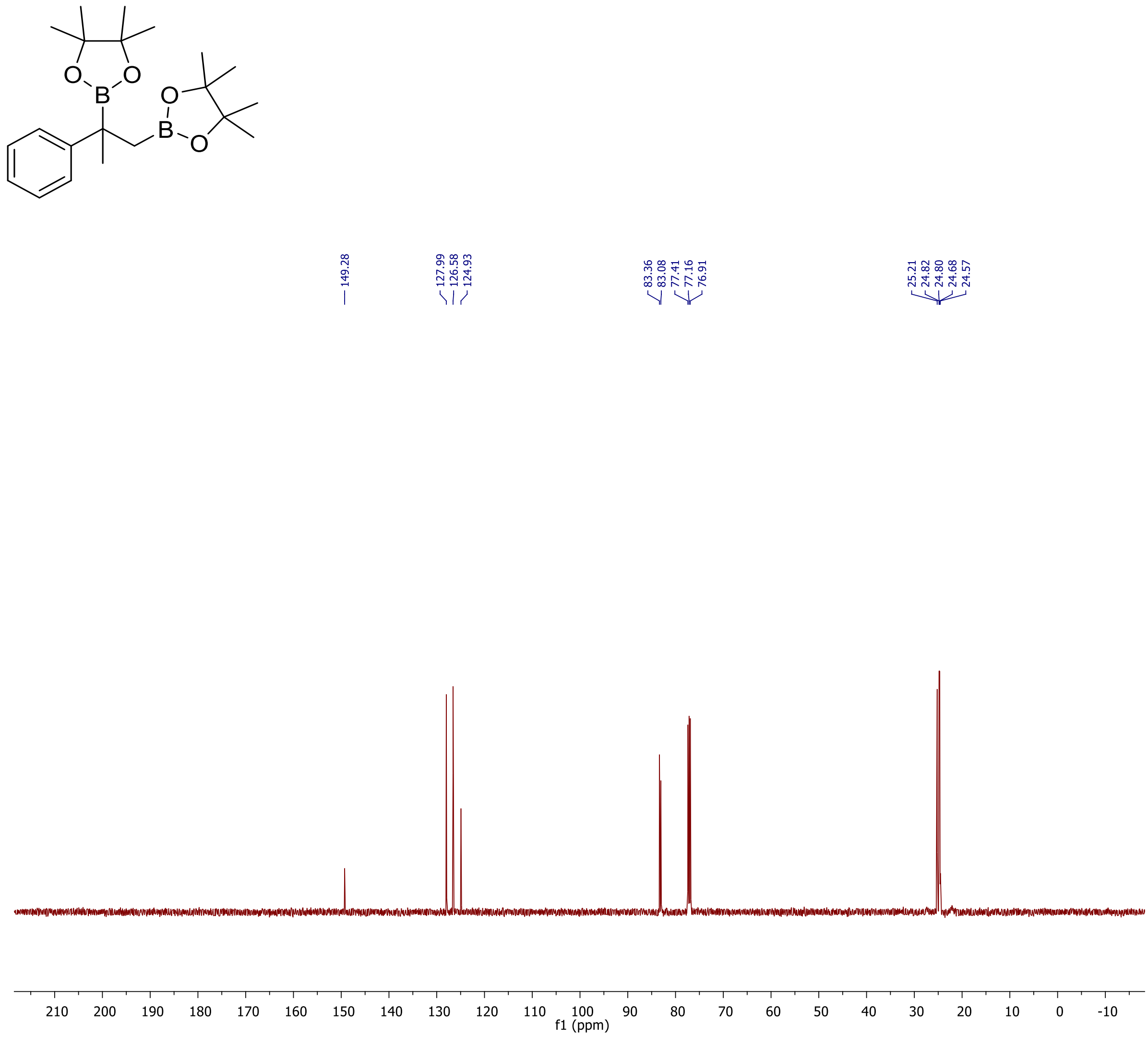
$^{13}C\{^{1}H\}$ NMR of **21b** (126 MHz, $CDCl_3$)

2,2'-(2-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (22b)



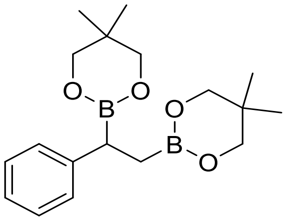


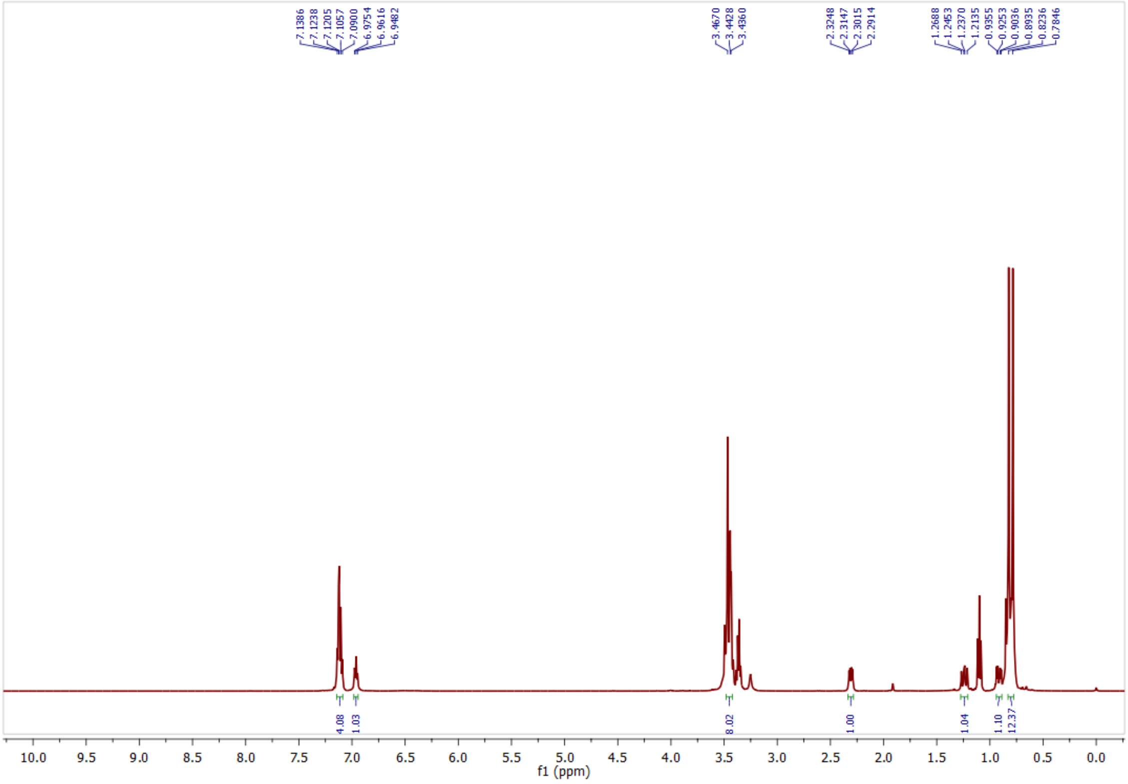
^{1}H NMR of **22b** (500 MHz, $CDCl_3$)



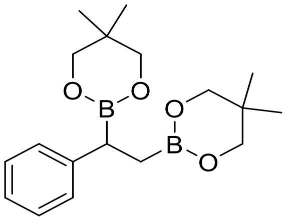
$^{13}C\{^{1}H\}$ NMR of **22b** (126 MHz, $CDCl_3$)

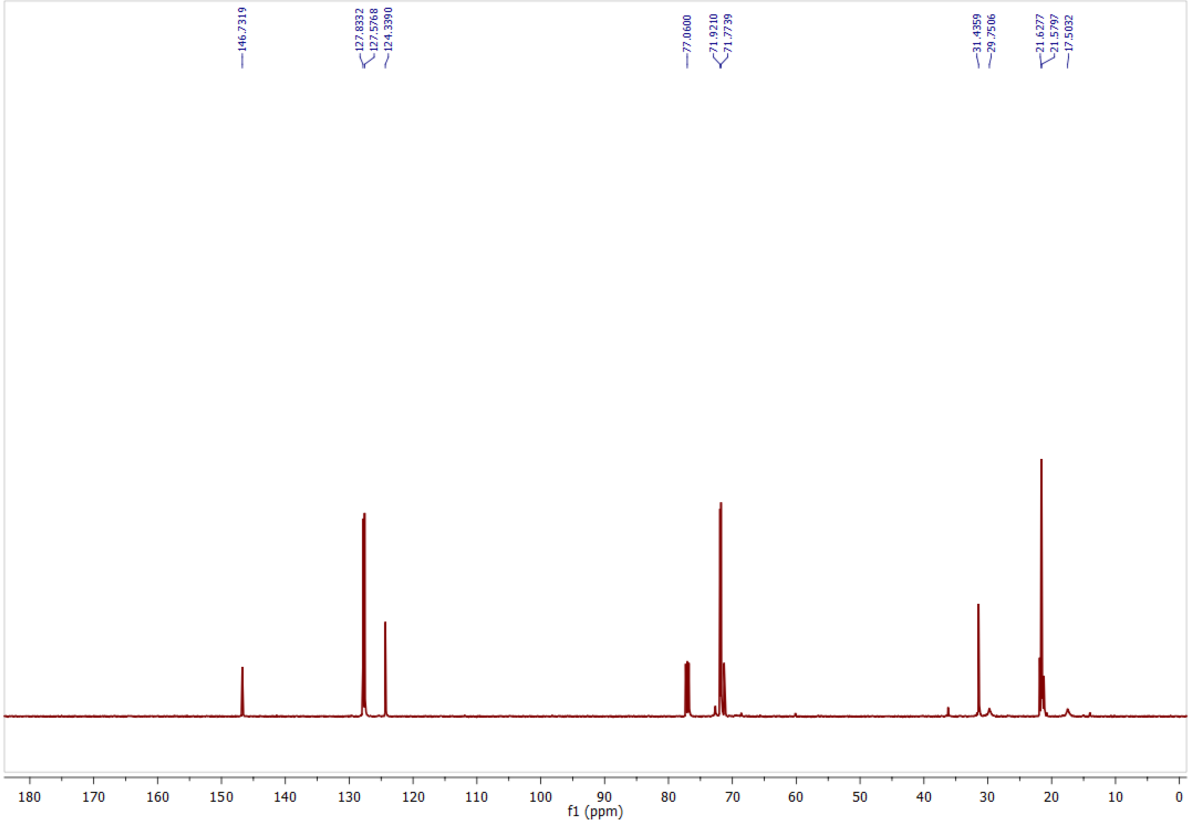
2,2'-(1-Phenylethane-1,2-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane) (23b)





^{1}H NMR of **23b** (500 MHz, CDCl$_3$)





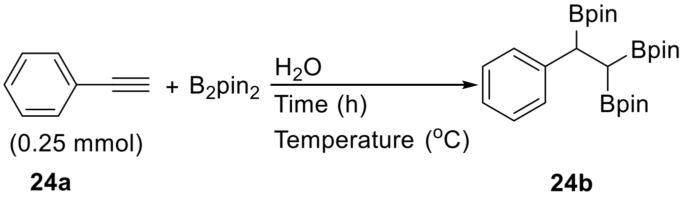
^{13}C{^{1}H} NMR of **23b** (126 MHz, CDCl$_3$)

V. Optimization and Substrate Scope of Alkynes Triboration Reaction

Experimental Procedure for Examples Described in Table 3.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, B_2pin_2 (2 equiv.: 0.5 mmol, 127 mg; 3 equiv.: 0.75 mmol, 190 mg), phenylacetylene (**24a**, 26 mg, 0.25 mmol) and H_2O (1.5-2.0 mL) were added. The reaction mixture was stirred at given temperature and time. Et_2O (10 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (5 mL) was added. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4) and concentrated. In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^1H NMR ($CDCl_3$) spectroscopy using nitromethane as an internal standard.

Table S4. Optimization of reaction conditions for 1,1,2-triboration of phenylacetylene (**24a**).[a]



Entry	H_2O (mL)	B_2pin_2 (equiv.)	Time (h)	Temp. (°C)	Yield **24b** (%)[b]
1	0.5	2.0	24	100	24
2	1.0	2.0	24	100	48
3	1.5	2.0	24	100	52
4	2.0	2.0	24	100	53
5[c]	-	2.0	24	100	0
6	1.5	2.0	24	120	82
7	1.5	3.0	24	120	82

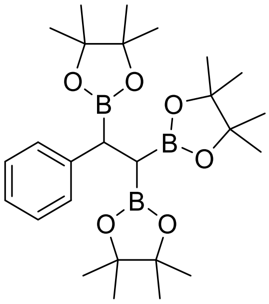
[a]Reaction conditions: **24a** (0.25 mmol, 1 equiv.), B_2pin_2, and HPLC grade H_2O. [b]Yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard. [c]Reaction was performed in the absence of water.

Experimental Procedure for Examples Described in Table 4.

General Procedure D. In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkyne (0.25 mmol), B_2pin_2 (2 equiv., 0.5 mmol, 127 mg), and H_2O (1.5 mL) were added and the reaction mixture was stirred vigorously at 120 ºC for 24 h. Et_2O (10 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (5 mL) was added. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4). In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^{1}H NMR ($CDCl_3$) spectroscopy using nitromethane as an internal standard.

General Procedure E. In a 15 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkyne (1 mmol), B_2pin_2 (2 equiv., 2.0 mmol, 508 mg), and H_2O (4 mL) were added and the reaction mixture was stirred vigorously at 120 ºC for 24 h. Et_2O (20 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (15 mL) was added. The layers were separated and the organic layer was 10 washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 10 mL). The combined organics were dried (Na_2SO_4) and concentrated in vacuum, and the residue was purified by column chromatography.

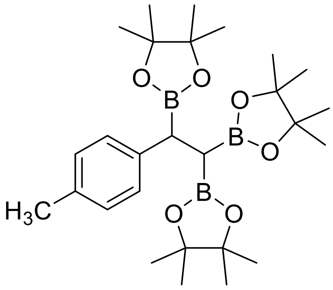
2,2',2''-(2-Phenylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (24b)



Following general procedure E, white solid in 74% yield (358 mg) from phenylacetylene (**24a**, 102 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.13 (m, 4H), 7.04-6.99 (m, 1H), 2.65 (d, *J* = 13.0 Hz, 1H), 1.43 (d, *J* = 13.0 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.14 (s, 6H), 1.12 (s, 6H), 0.93 (s, 6H), 0.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 128.5, 127.8, 124.7, 83.1, 83.0, 82.6, 24.8, 24.7, 24.4, 24.3, 24.2. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.2 (br). GC-MS: calcd. for $C_{26}H_{43}B_3O_6$ $(M)^+$: 484; found: m/z: 484 (M^+).

These spectroscopic data match those previously reported.[7]

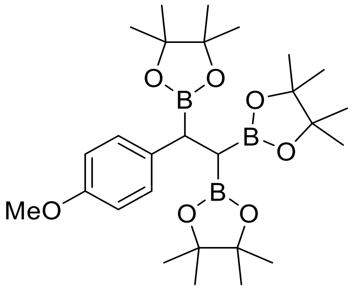
2,2',2''-(2-(p-Tolyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (25b)



The reaction was performed following the general procedure E, white solid in 72% yield (358 mg) from 1-ethynyl-4-methylbenzene (**25a**, 116 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 2.61 (d, *J* = 12.7 Hz, 1H), 2.23 (s, 3H), 1.38 (d, *J* = 12.6 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.14 (s, 6H), 1.12 (s, 6H), 0.94 (s, 6H), 0.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 133.8, 128.5, 128.3, 83.0, 82.9, 82.6, 24.9, 24.8, 24.6, 24.4, 24.3, 24.2, 21.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.0 (br). GC-MS: calcd. for $C_{27}H_{45}B_3O_6$ $(M)^+$: 498; found: m/z: 498 (M^+).

These spectroscopic data match those previously reported.[8]

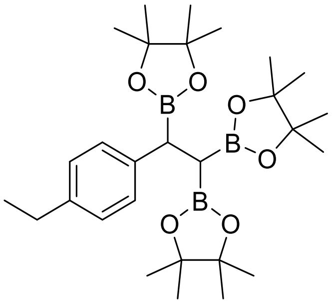
2,2',2''-(2-(4-Methoxyphenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (26b)



Following general procedure E, white solid in 42% yield (216 mg) from 1-ethynyl-4-methoxybenzene (**26a**, 132 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 2.59 (d, *J* = 12.7 Hz, 1H), 1.36 (d, *J* = 12.6 Hz, 1H), 1.22 (s, 6H), 1.20 (s, 6H), 1.13 (s, 6H), 1.11 (s, 6H), 0.94 (s, 6H), 0.93 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.0, 137.5, 129.3, 113.3, 83.0, 82.9, 82.6, 55.2, 27.2(br), 24.9, 24.7, 24.5, 24.4, 24.3. 14.0 (br).^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.2 (br). GC-MS: calcd. for $C_{27}H_{45}B_3O_7$ $(M)^+$: 514; found: m/z: 514 (M^+).

These spectroscopic data match those previously reported.[9]

2,2',2''-(2-(4-Ethylphenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (27b)

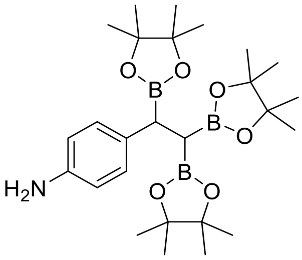


Following general procedure E, white solid in 62% yield (317 mg) from 1-ethyl-4-ethynylbenzene (**27a**, 130 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 2.61 (d, *J* = 12.7Hz, 1H), 2.52 (dd, *J* = 15.2,7.6 Hz, 2H), 1.40 (d, *J* = 12.6 Hz, 1H), 1.26-1.22 (m, 15H), 1.14 (s, 6H), 1.12 (s, 6H), 0.92 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 140.5, 128.5, 127.4, 83.0, 83.0, 82.6, 28.5, 24.9, 24.8, 24.7, 24.4, 24.3, 24.2, 15.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.0 (br). GC-MS:

m/z: 512 (M^+). HRMS (ESI) calcd. for $C_{28}H_{47}B_3O_6Na$ $[M+Na]^+$: 535.3550; found $[M+Na]^+$: 535.3378.

These spectroscopic data match those previously reported.[2]

4-(1,2,2-*tris*(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (28b)

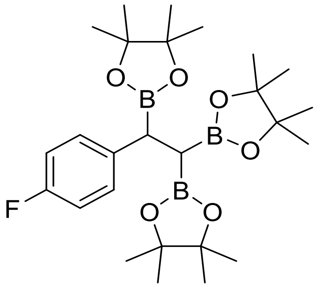


Following general procedure E, a yellowish liquid 69% yield (344 mg) from 4-ethynylaniline (**28a**, 117 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. Multiple attempts were made to purify **28b**; however, it tends to decompose during the column chromatography process, and the best-acquired data has been incorporated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.92 (d, *J* = 7.5 Hz, 2H), 6.46 (d, *J* = 7.6 Hz, 2H), 4.24 (br, 2H), 2.49-2.46 (m, 1H), 1.30-1.28 (m, 1H), 1.15 (s, 6H), 1.14 (s, 6H), 1.06 (s, 6H), 1.05 (s, 6H), 0.89 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 135.4, 129.1, 115.3, 82.8, 82.8, 82.5, 27.0 (br), 24.7, 24.6, 24.5, 24.4, 24.3, 24.1, 13.6 (br). ^{11}B NMR (160 MHz, $CDCl_3$): δ 34.7 (br). GC-MS: m/z: 499 (M^+).

HRMS (ESI) calcd. for $C_{26}H_{45}B_3NO_6$ $[M+H]^+$: 500.3526; found $[M+H]^+$: 500.3556.

These spectroscopic data match those previously reported.[2]

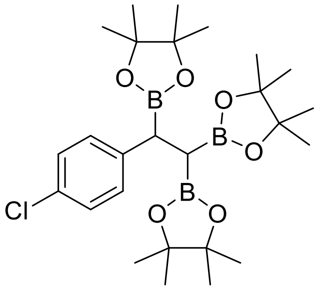
2,2',2''-(2-(4-Fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (29b)



Following general procedure E, a white solid in 68% yield (341 mg) from 1-ethynyl-4-fluorobenzene (**29a**, 120 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 6.85 (t, *J* = 17.5 Hz, 2H), 2.64 (d, *J* = 12.7 Hz, 1H), 1.30 (d, *J* = 2.8 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H), 1.14 (s, 6H), 1.12 (s, 6H), 0.96 (s, 6H), 0.93 (s, 6H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.8 (d, *J* = 241.8 Hz), 141.0 (d, *J* = 2.8 Hz), 129.7 (d, *J* = 7.7 Hz), 114.5 (d, *J* = 21.0 Hz), 83.2, 83.1, 82.7, 24.9, 24.8, 24.7, 24.5, 24.4, 24.3. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 34.2 (br). GC-MS: calcd. for $C_{26}H_{42}B_3O_6F$ (M)$^+$: 502; found: m/z: 502 (M$^+$).

These spectroscopic data match those previously reported.[9]

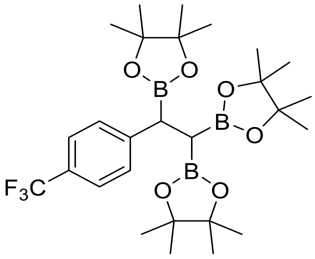
2,2',2''-(2-(4-Chlorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (30b)



Following general procedure E, a white solid in 56% yield (290 mg) from 1-chloro-4-ethynylbenzene (**30a**, 136 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.10 (m, 4H), 2.64 (d, *J* = 13.0 Hz 1H) 1.38 (d, *J* = 13.0 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.13 (s, 6H), 1.12 (s, 6H), 0.97 (s, 6H), 0.93 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.0, 130.3, 129.8, 127.9, 83.2, 83.1, 82.8, 27.7 (br), 24.9, 24.8, 24.7, 24.5, 24.4, 24.3, 13.7 (br).^{11}B NMR (160 MHz, $CDCl_3$): δ = 34.3 (br). GC-MS: m/z: 518 (M$^+$). HRMS (ESI) calcd. for $C_{26}H_{42}B_3ClNaO_6$ [M+Na]$^+$: 541.2847; found [M+Na]$^+$: 541.2693.

These spectroscopic data match those previously reported.[2]

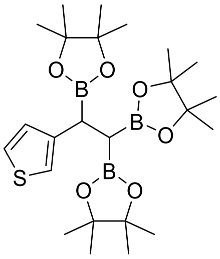
2,2',2''-(2-(4-(Trifluoromethyl)phenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (31b)



Following general procedure E, colorless oil in 34% yield (188 mg) from 1-ethynyl-4-(trifluoromethyl) benzene (**31a**, 170 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. A careful analysis of the crude reaction mixture of **31a** revealed the formation of diboration and hydroboration byproducts along with **31b**. **31b**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.68 (d, *J* = 13.0 Hz, 1H), 1.38 (d, *J* = 13.0 Hz, 1H), 1.17 (s, 6H), 1.16 (s, 6H), 1.08 (s, 6H), 1.06 (s, 6H), 0.88 (s, 6H), 0.83 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 149.0, 127.7 (d, *J* = 8.0 Hz), 126.2 (d, *J* = 2.0 Hz), 125.9, 123.7 (q, *J* = 4.0 Hz), 82.4, 82.3, 81.9, 27.5, 23.9, 23.8. 23.6, 23.4, 23.3, 23.2. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening. ^{11}B NMR (160 MHz, CDCl$_3$): δ = 34.5 (br). GC-MS: calcd. for $C_{27}H_{42}B_3O_6F_3$ (M)$^+$: 552; found: m/z: 552 (M$^+$).

These spectroscopic data match those previously reported.[10]

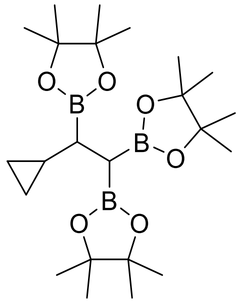
2,2',2''-(2-(Thiophen-3-yl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (32b)



Following general procedure E, colorless oil in 30% yield (147 mg) from 3-ethynylthiophene (**32a**, 108 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. A careful analysis of the crude reaction mixture of **32a** revealed the formation of diboration and hydroboration byproducts along with **32b**. Further, performing the reaction for shorter and longer time did not improve the outcome of the reactions. **32b**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.10-7.06 (m, 1H), 6.94 (dd, *J* = 0.95, 0.95 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 2.80 (d, *J* = 12.5 Hz, 1H), 1.36 (d, *J* = 12.3 Hz, 1H) 1.21 (s, 6H), 1.20 (s, 6H), 1.14 (s, 6H), 1.13 (s, 6H), 1.01 (s, 6H), 0.99 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.4, 128.6, 124.1, 119.2, 83.1, 83.1, 82.7, 24.9, 24.8, 24.6, 24.5, 24.4, 24.3, 23.4 (br). ^{11}B NMR (160 MHz, $CDCl_3$): δ = 33.8 (br). GC-MS: calcd. for $C_{24}H_{41}B_3O_6S$ $(M)^+$: 490; found: m/z: 490 (M^+).

These spectroscopic data match those previously reported.[7]

2,2',2''-(2-Cyclopropylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (33b)

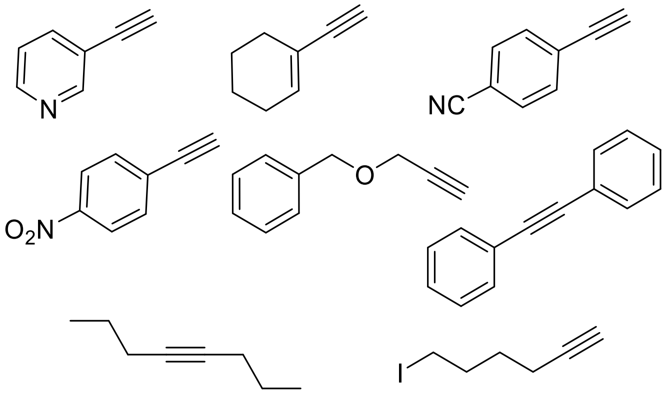


Following general procedure E, colorless oil in 45% yield (202 mg) from ethynylcyclopropane (**33a**, 66 mg, 1 mmol) was obtained by column chromatography (silica gel 60-120 mesh) using eluent: 92:8% Hex/EtOAc. ^1H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 24H), 1.17 (s, 12H), 0.90 (d, J = 7.3 Hz, 1H), 0.65 (d, J = 5.1 Hz, 2H), 0.31 (d, J = 2.4 Hz, 2H), 0.18 (d, J = 9.0 Hz, 1H), 0.09 (d, J = 8.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 82.8, 82.6, 82.6, 25.0, 24.9, 24.8, 24.6, 24.6, 14.9, 12.2 (br), 6.1, 4.2. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 34.3 (br). GC-MS: calcd. for $C_{23}H_{43}B_3O_6$ $(M)^+$: 448; found: m/z: 448 (M^+).

These spectroscopic data match those previously reported.[7]

List of Unsuccessful Alkyne Substrates

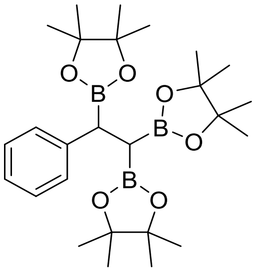
A complete list of unsuccessful alkyne substrates for the water-mediated triboration reactions. Not a trace of desired products was observed by GC-MS analysis.



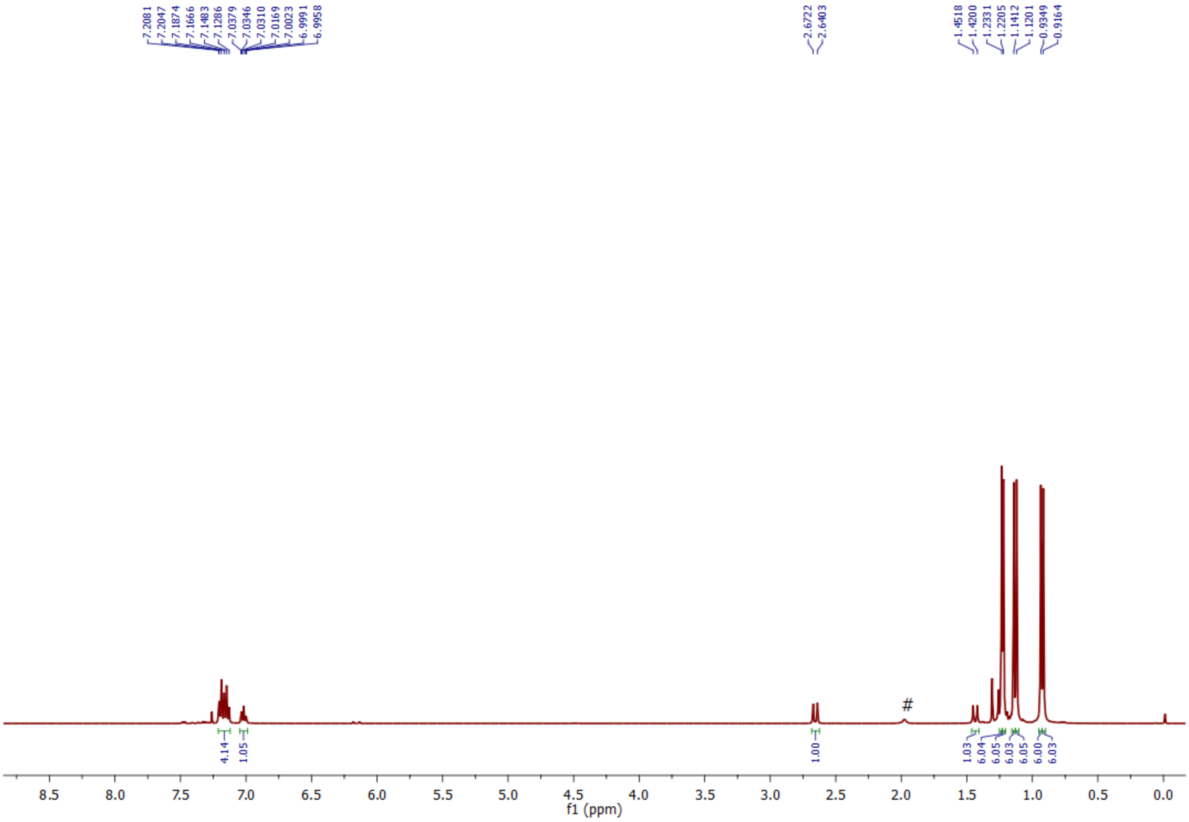
VI. NMR Spectra of 1,1,2-Trisborylalkanes

Note**:** Resonances denoted by (#) corresponds to solvent/grease and (*) for starting material.

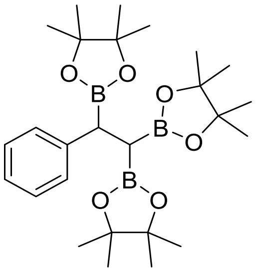
2,2’,2’’-(2-Phenylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (24b)

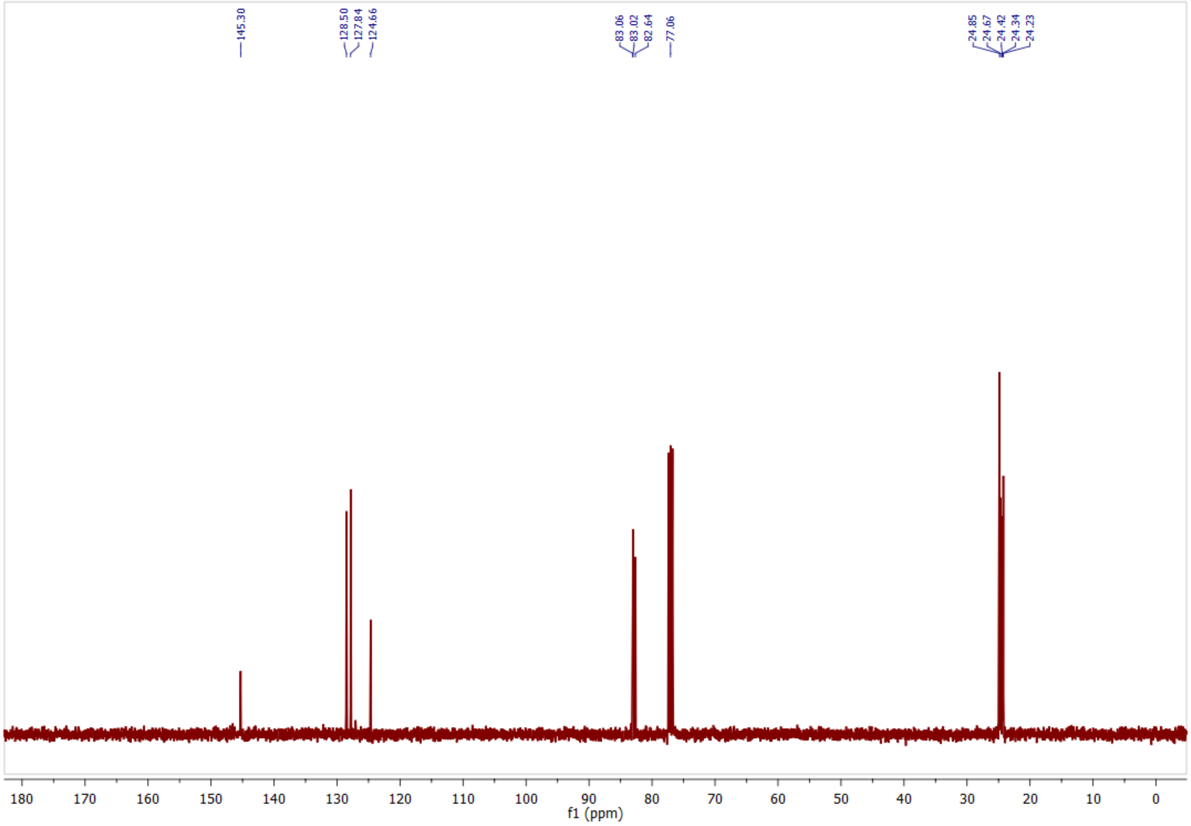


(#) Peak at δ = 2.17 ppm corresponds to acetone



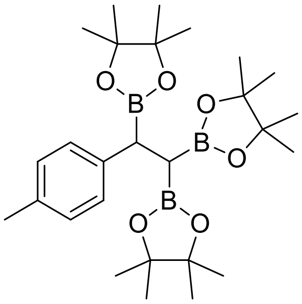
^{1}H NMR of **24b** (400 MHz, $CDCl_3$)



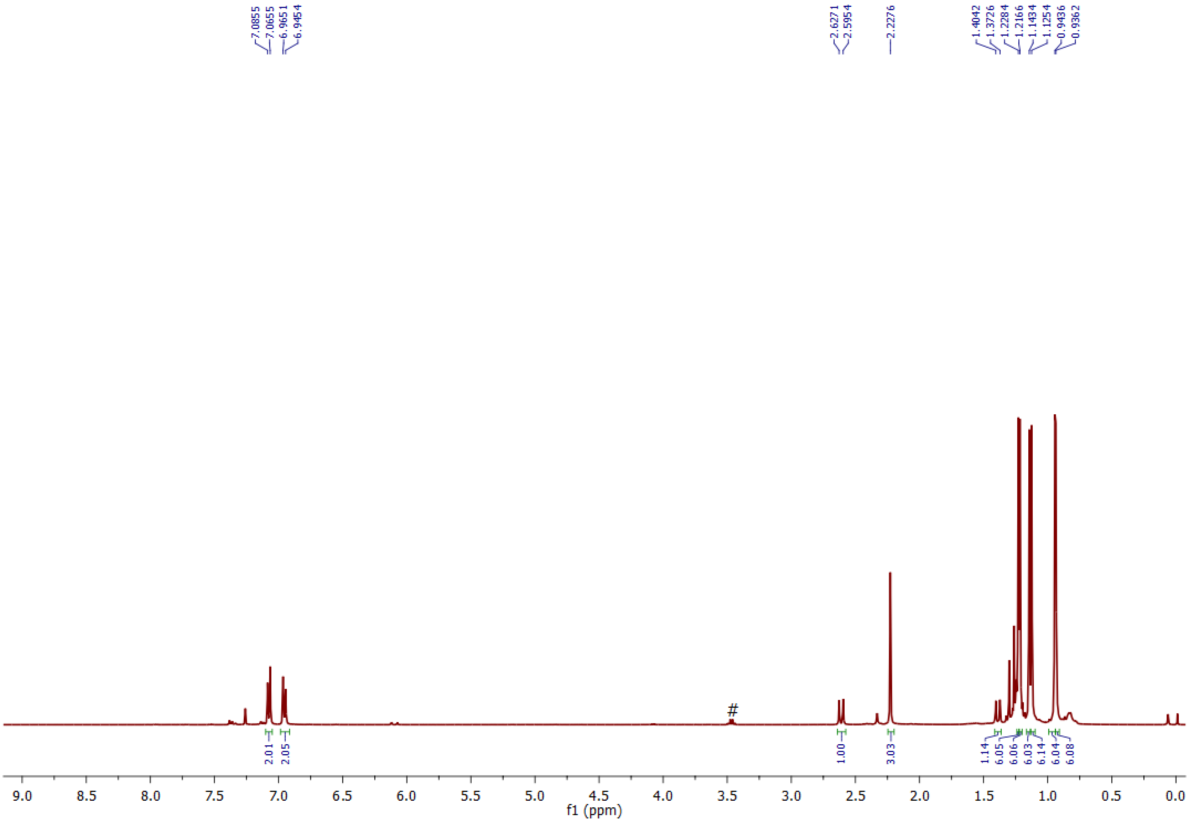


^{13}C NMR of **24b** (100 MHz, CDCl$_3$)

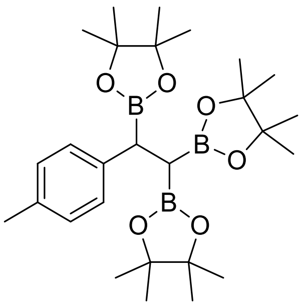
2,2’,2’’-(2-(p-Tolyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (25b)

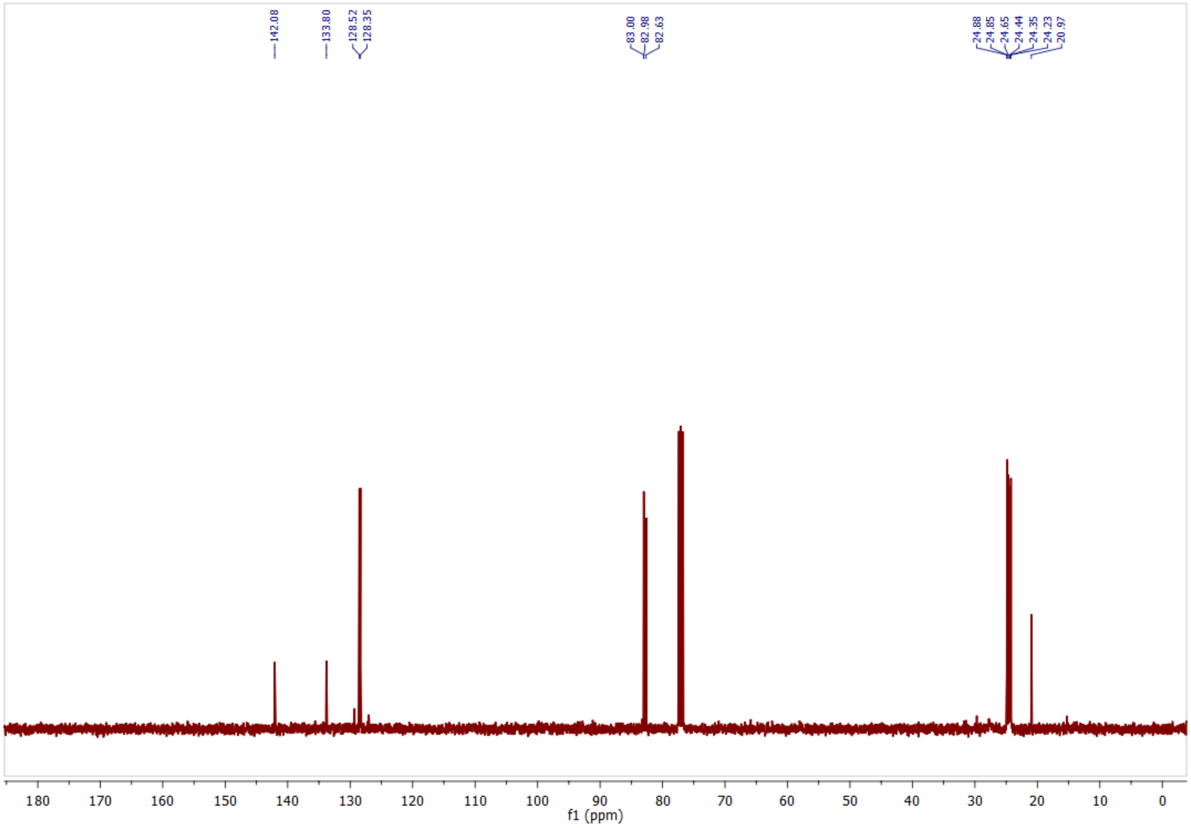


(#) Peak at δ = 3.48 ppm corresponds to Et_2O



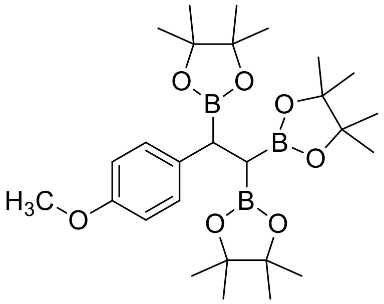
^{1}H NMR of **25b** (400 MHz, $CDCl_3$)

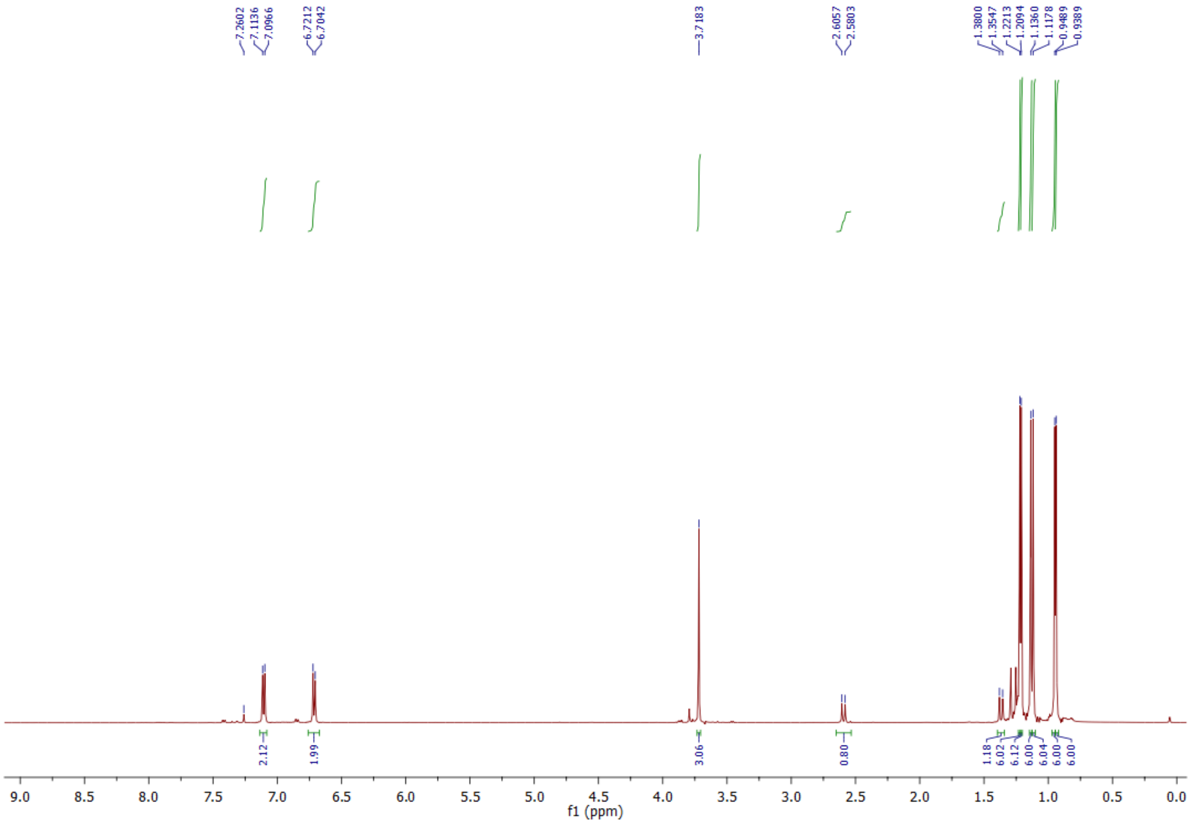




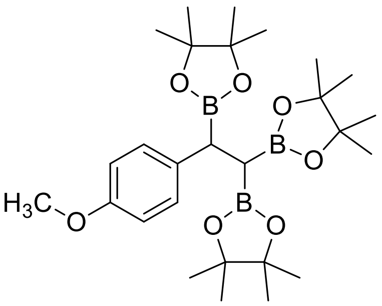
^{13}C NMR of **25b** (100 MHz, $CDCl_3$)

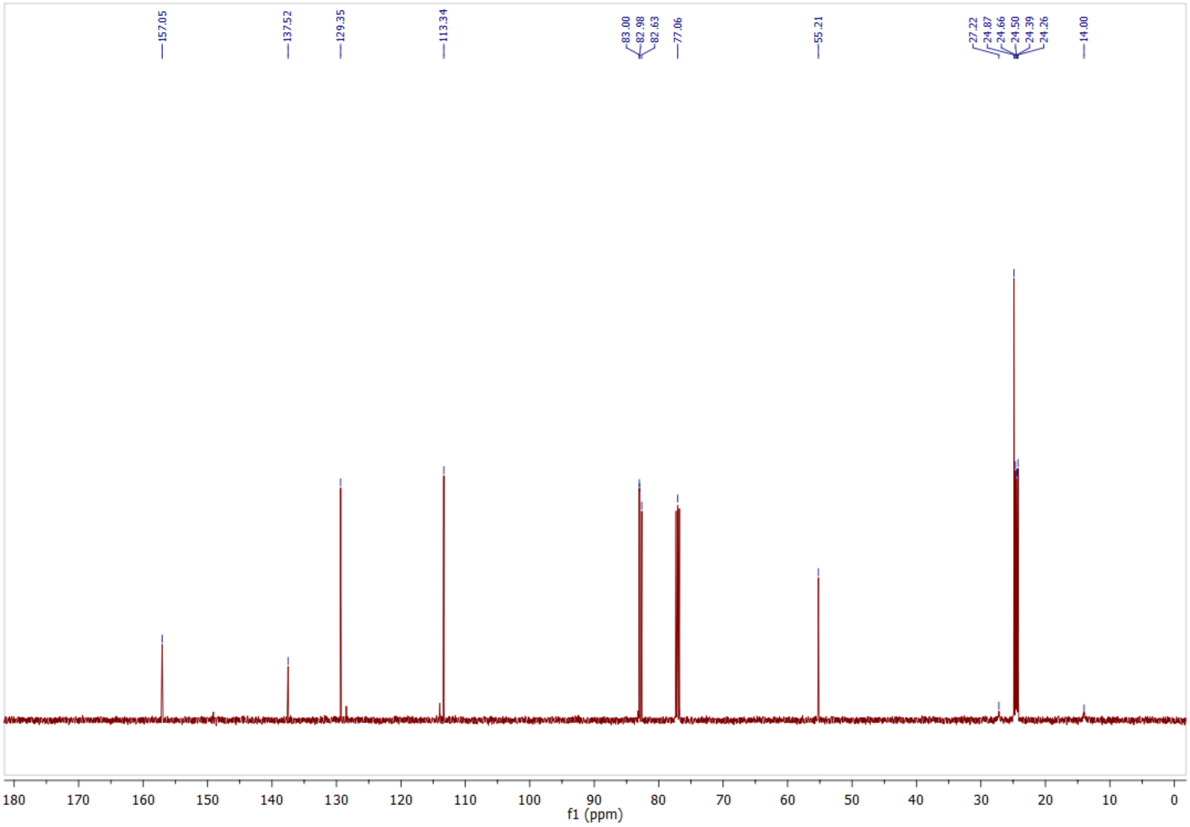
2,2',2''-(2-(4-Methoxyphenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (26b)





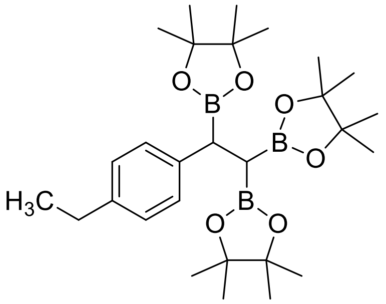
^{1}H NMR of **26b** (500 MHz, CDCl$_3$)

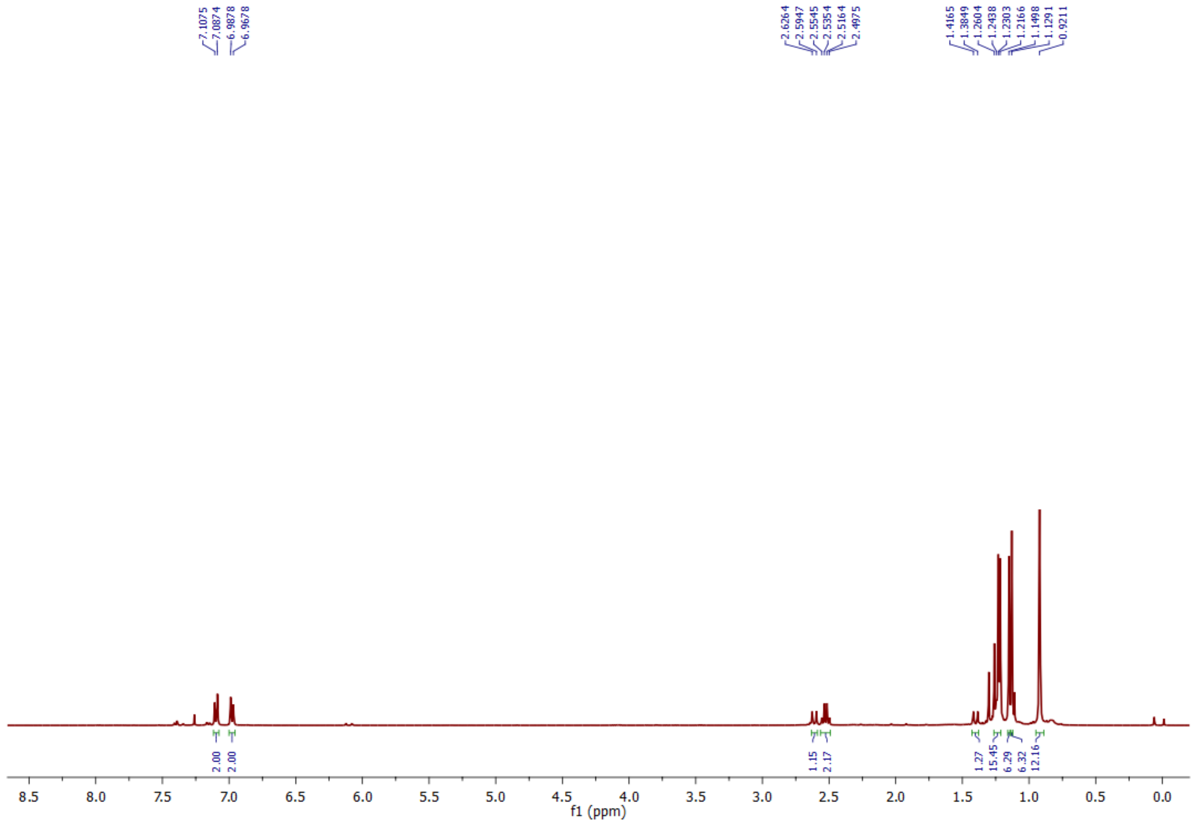




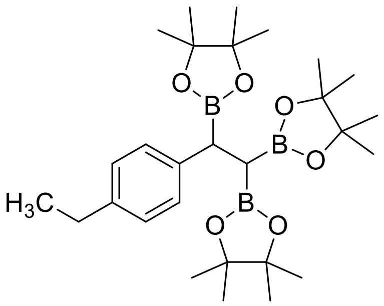
^{13}C NMR of **26b** (126 MHz, $CDCl_3$)

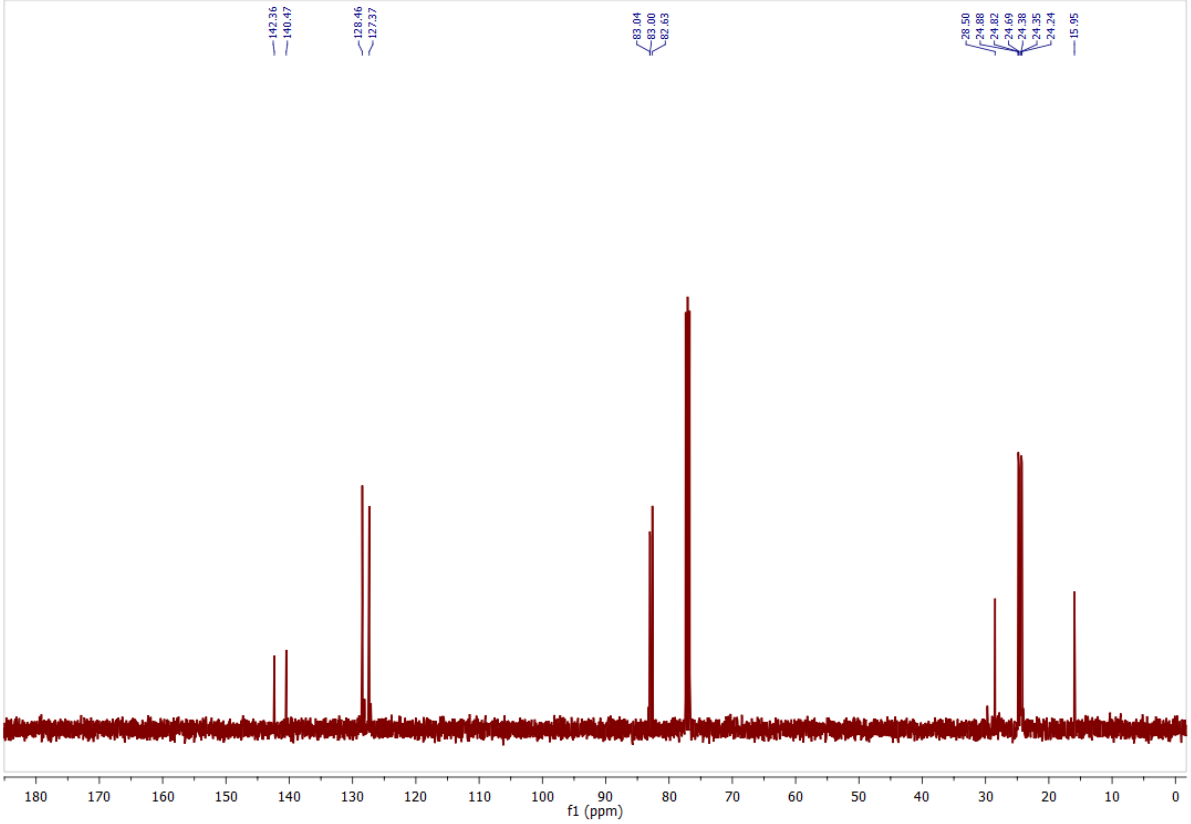
2,2’,2’’-(2-(4-Ethylphenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (27b)





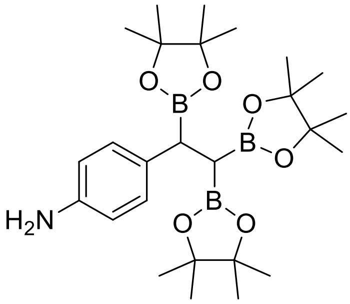
^{1}H NMR of **27b** (400 MHz, CDCl$_3$)

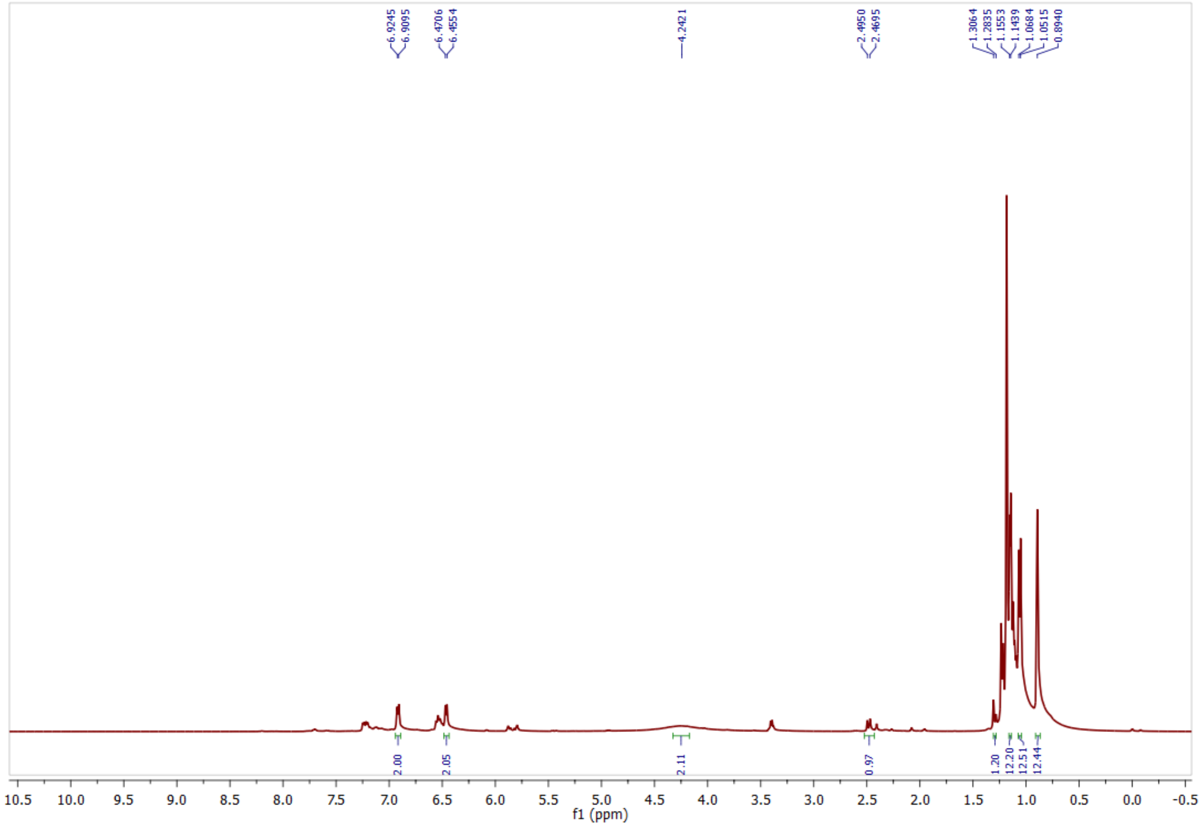




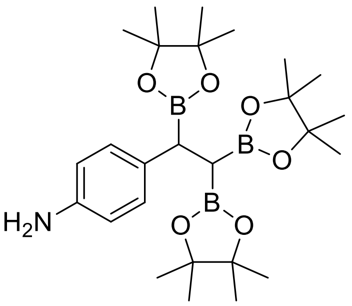
^{13}C NMR of **27b** (100 MHz, $CDCl_3$)

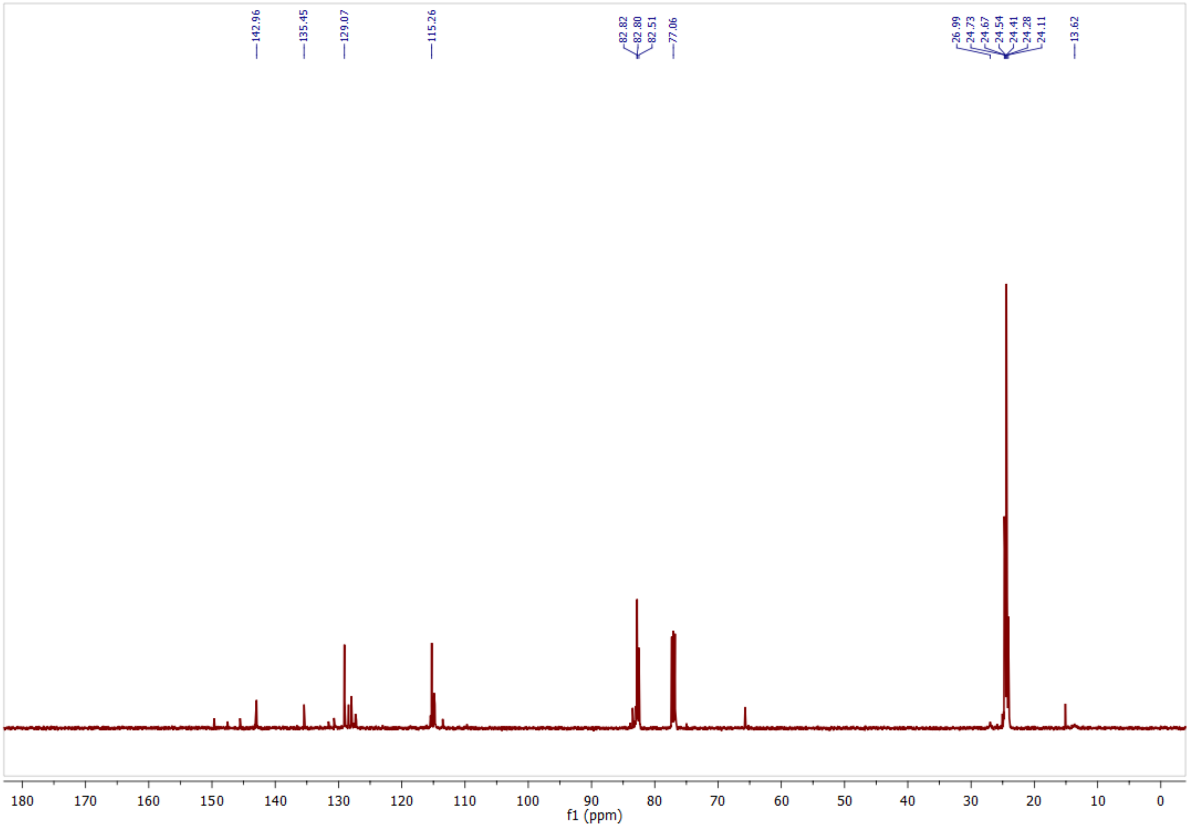
4-(1,2,2-*tris*(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (28b)



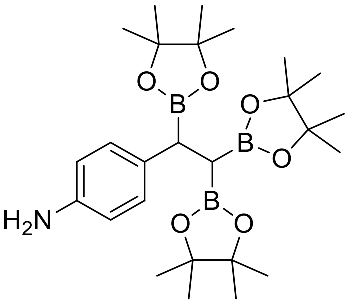


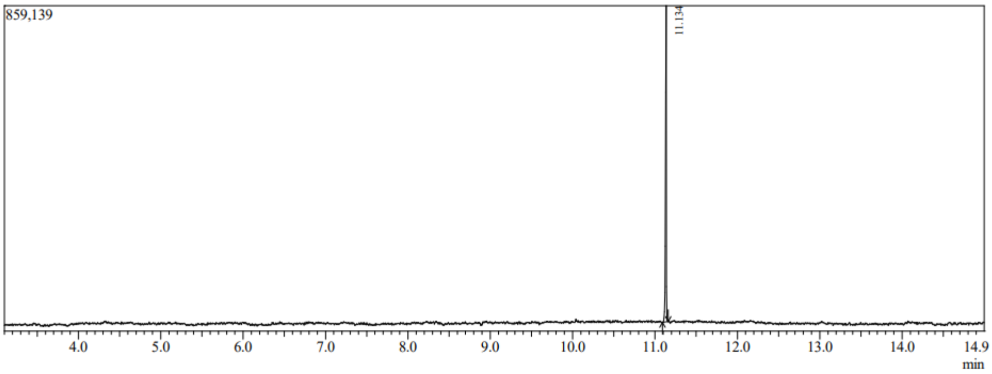
^{1}H NMR of **28b** (500 MHz, $CDCl_3$)





^{13}C NMR of **28b** (126 MHz, $CDCl_3$)





Peak Report TIC

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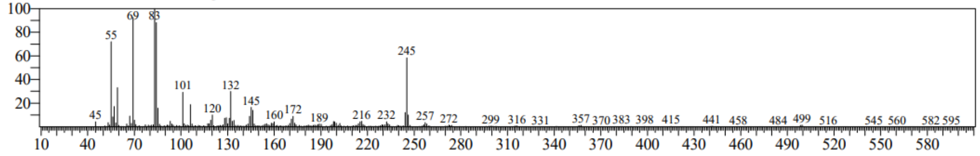
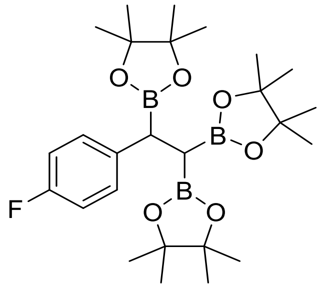
				559453	100.00	834343	100.00			

Line#:1 R.Time:11.135(Scan#:1608) MassPeaks:409
RawMode:Averaged 11.130-11.140(1607-1609) BasePeak:83.10(54742)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

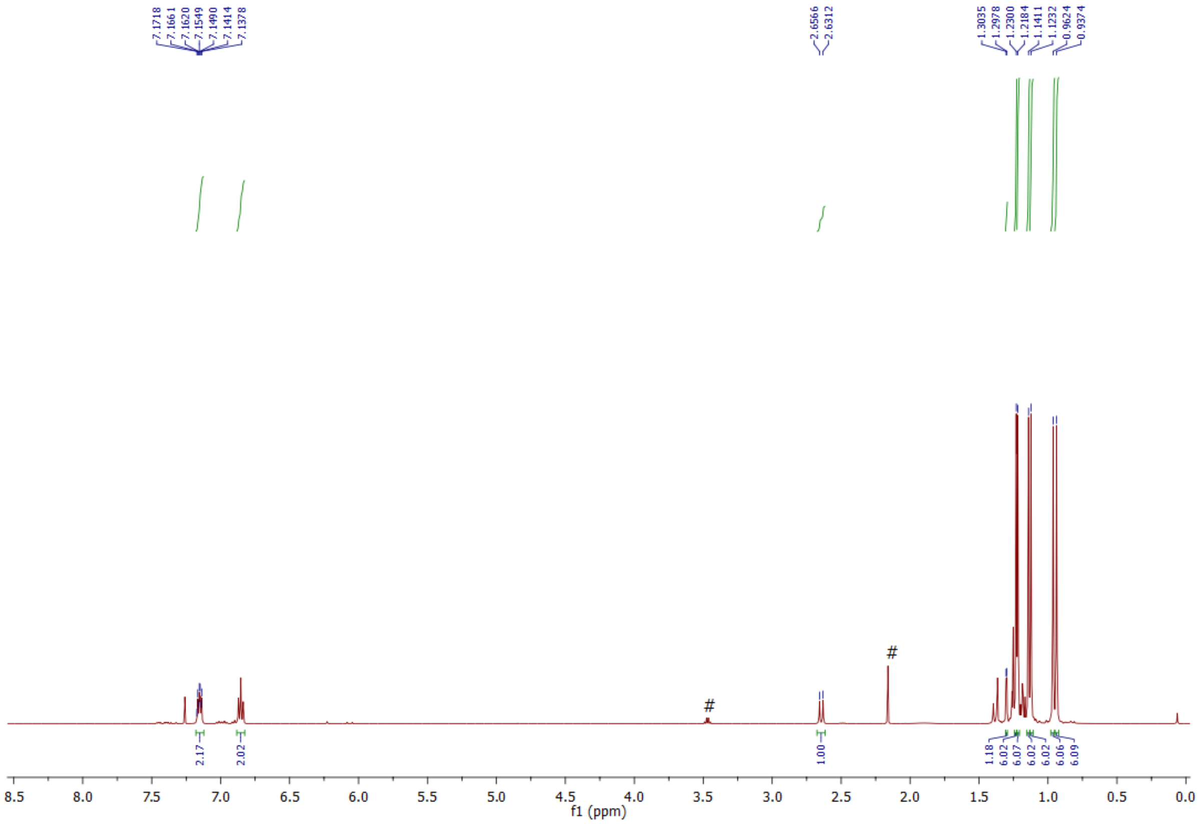


GC-MS of **28b**

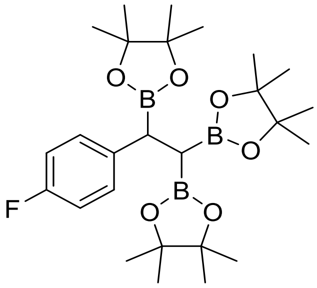
2,2',2''-(2-(4-Fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (29b)

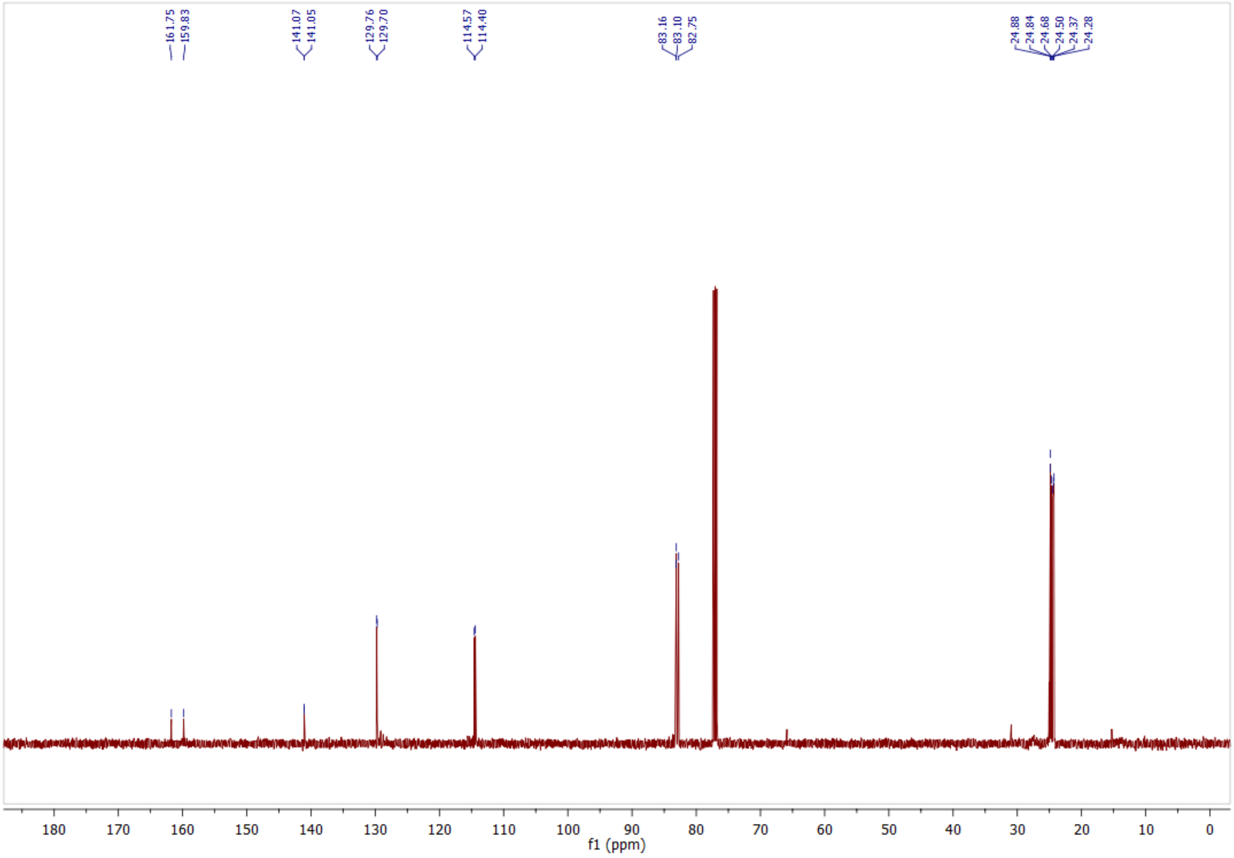


(#) Peak at δ = 2.17 & 3.48 ppm corresponds to acetone and Et_2O, respectively.



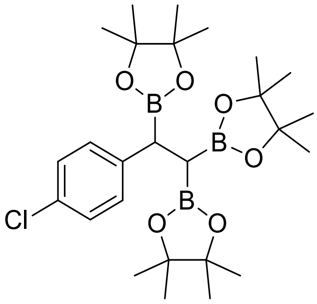
^{1}H NMR of **29b** (500 MHz, $CDCl_3$)



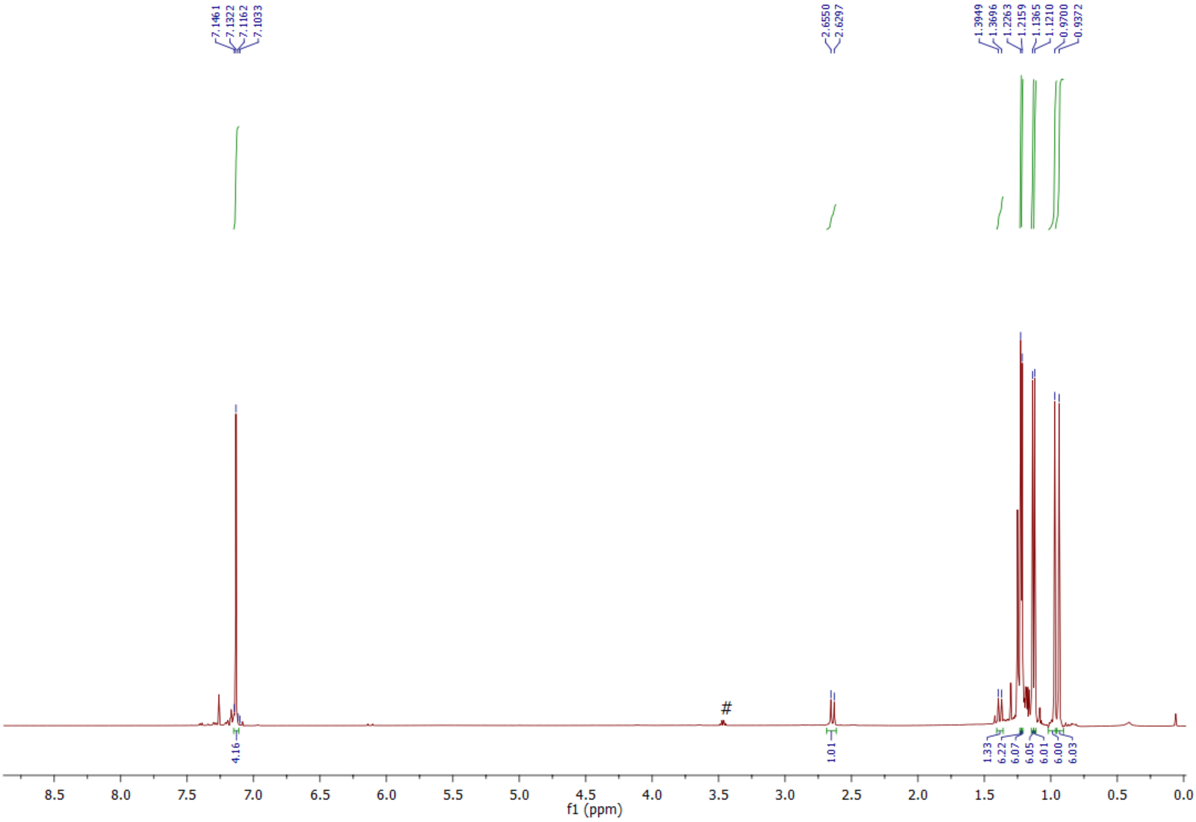


^{13}C{^{1}H} NMR of **29b** (126 MHz, CDCl$_3$)

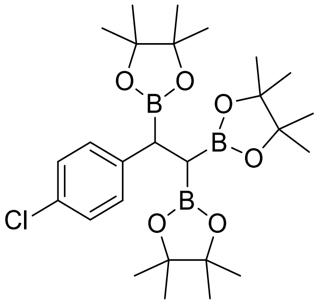
2,2’,2’’-(2-(4-Chlorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (30b)

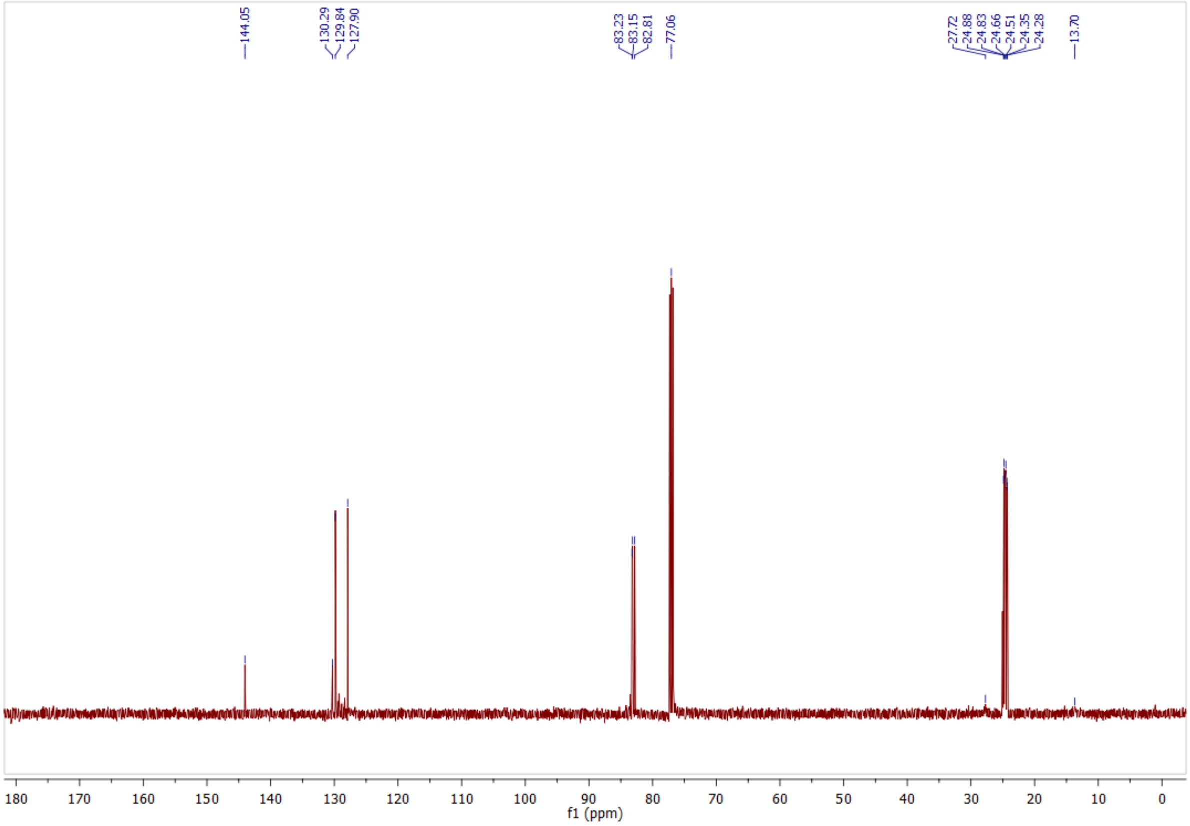


(#) Peak at δ = 3.48 ppm corresponds to Et_2O.



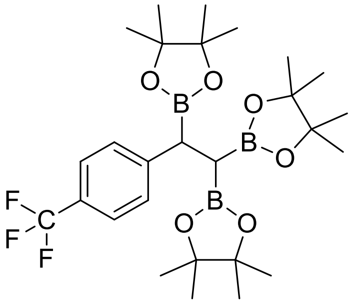
^{1}H NMR of **30b** (500 MHz, $CDCl_3$)



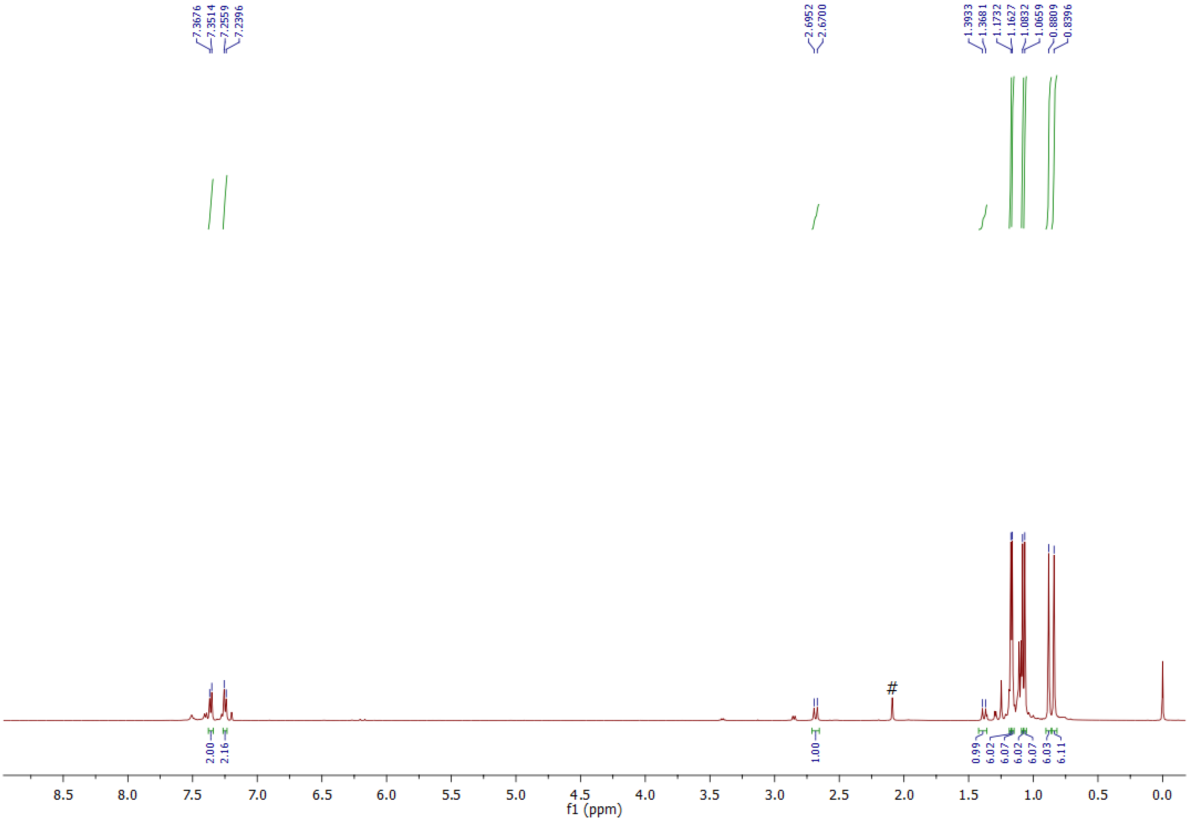


^{13}C NMR of **30b** (126 MHz, CDCl$_3$)

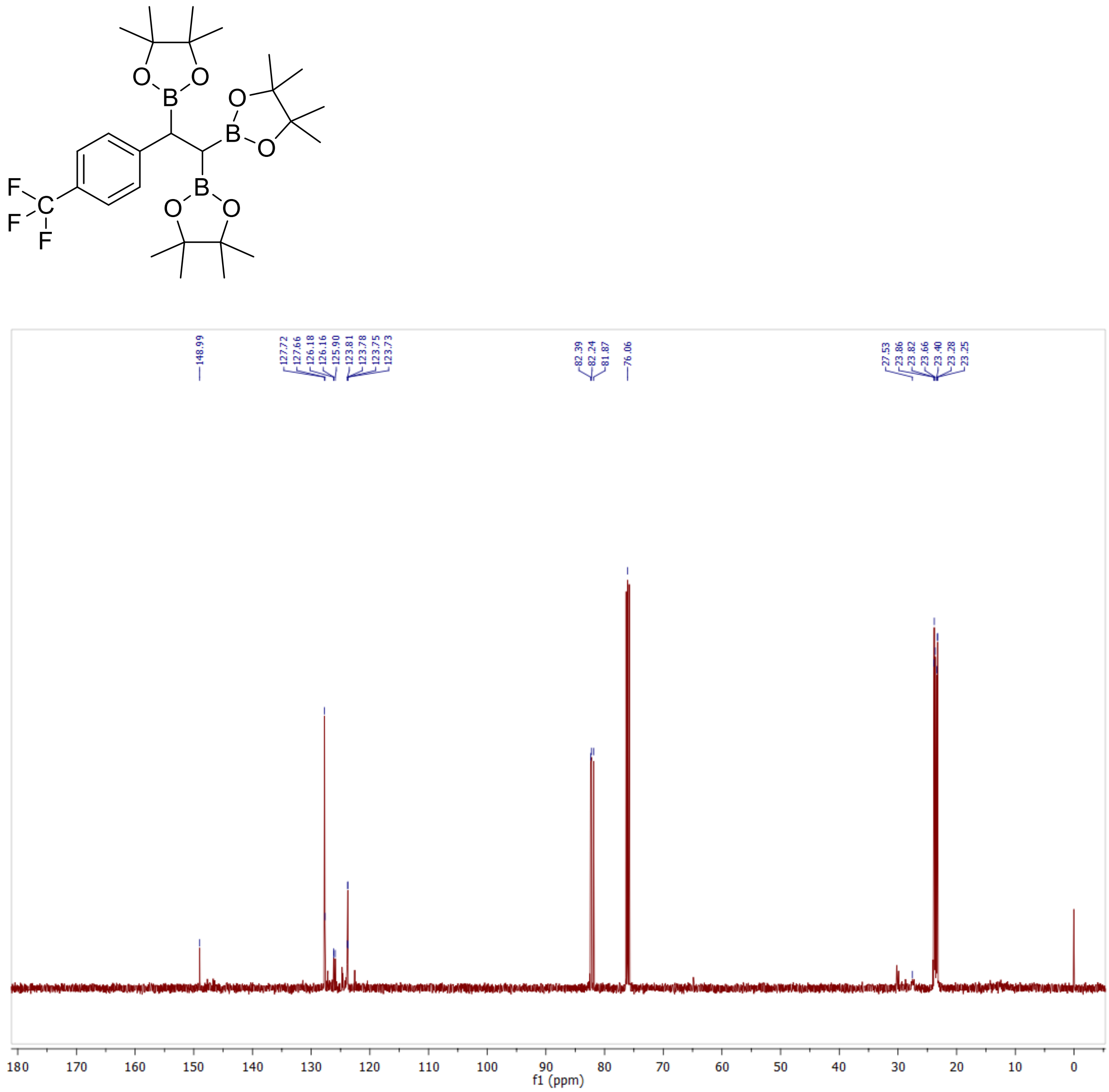
2,2’,2’’-(2-(4-(Trifluoromethyl)phenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (31b)



(#) Peak at δ = 2.17 ppm corresponds to acetone

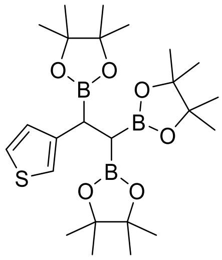


^{1}H NMR of **31b** (500 MHz, CDCl$_3$)

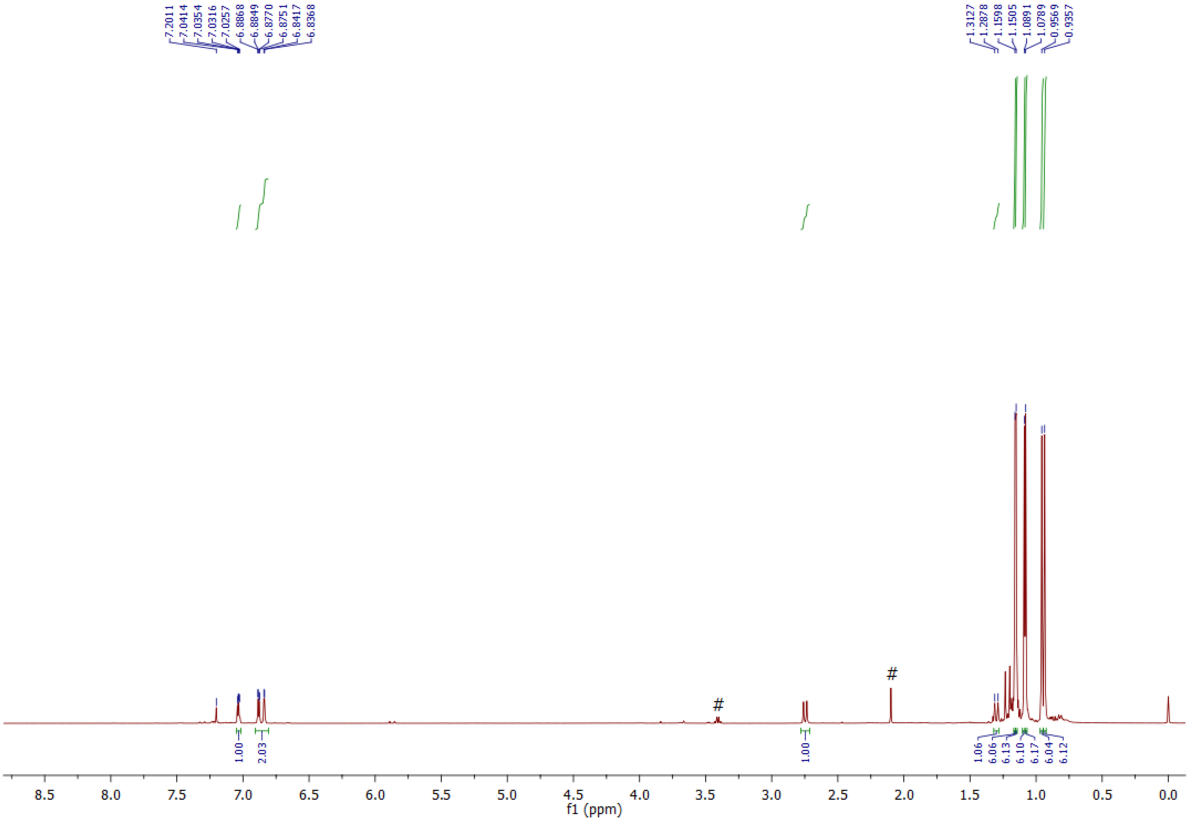


^{13}C NMR of **31b** (126 MHz, $CDCl_3$)

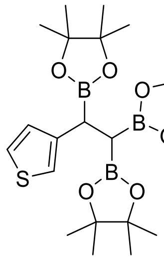
2,2',2''-(2-(Thiophen-3-yl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (32b)

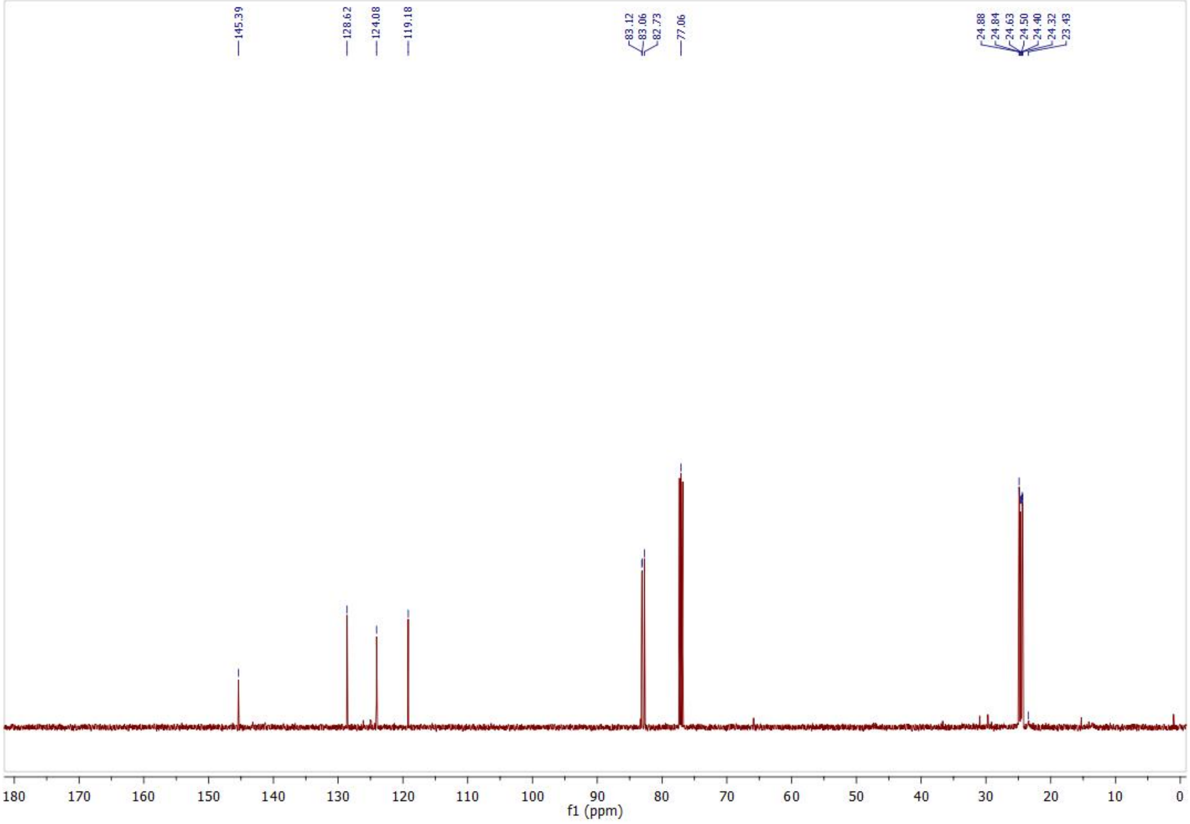


(#) Peak at δ = 2.17 & 3.48 ppm corresponds to acetone and Et_2O, respectively.



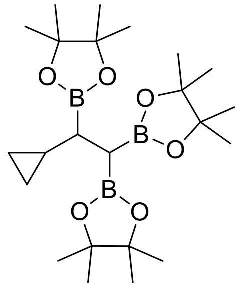
^{1}H NMR of **32b** (500 MHz, $CDCl_3$)

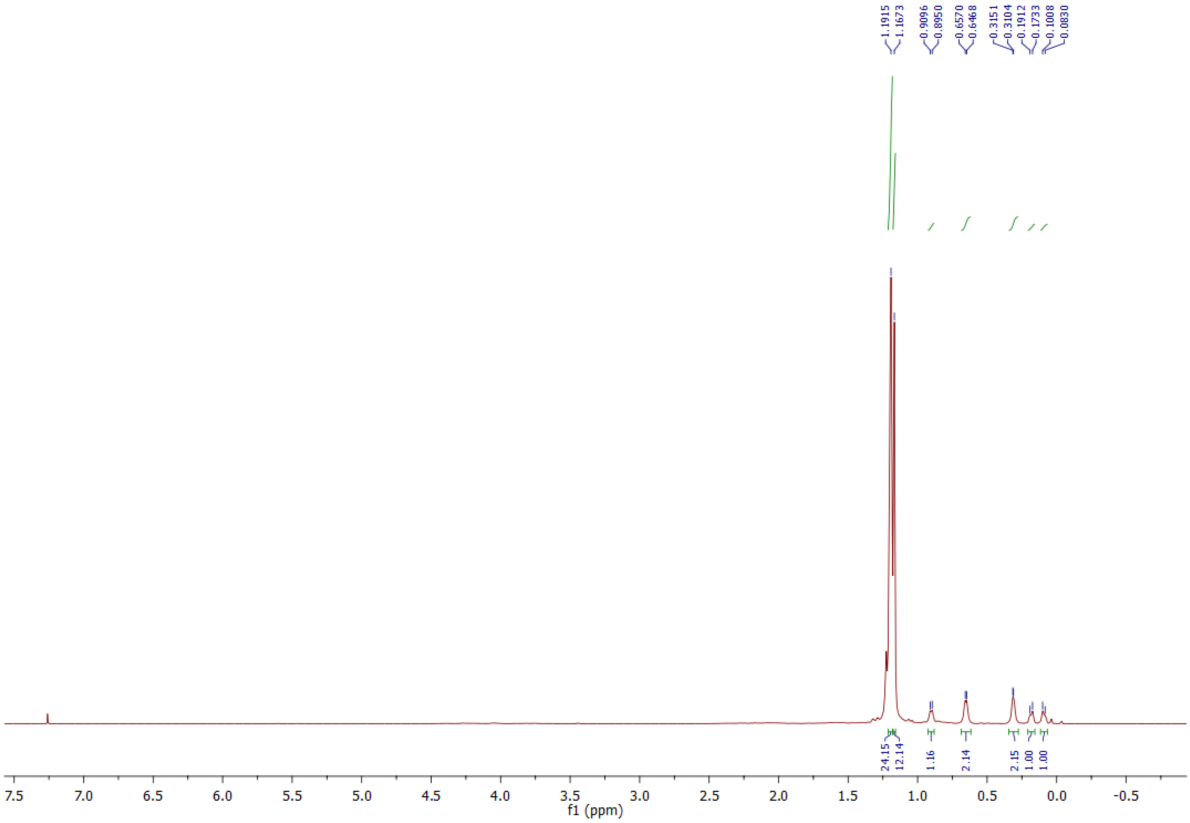




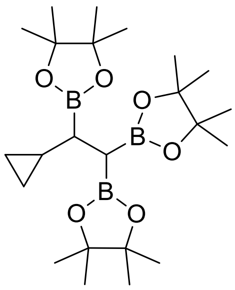
^{13}C NMR of **32b** (126 MHz, $CDCl_3$)

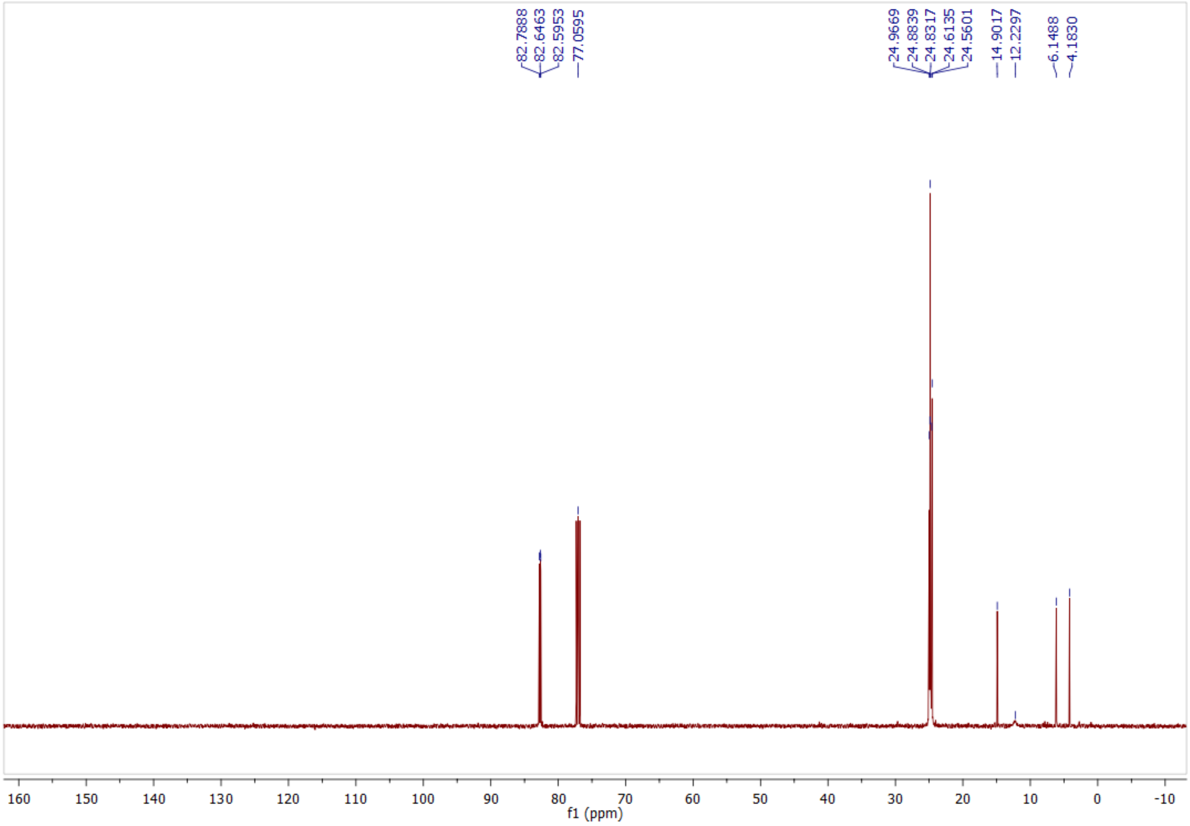
2,2’,2’’-(2-Cyclopropylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (33b)





^{1}H NMR of **33b** (500 MHz, $CDCl_3$)

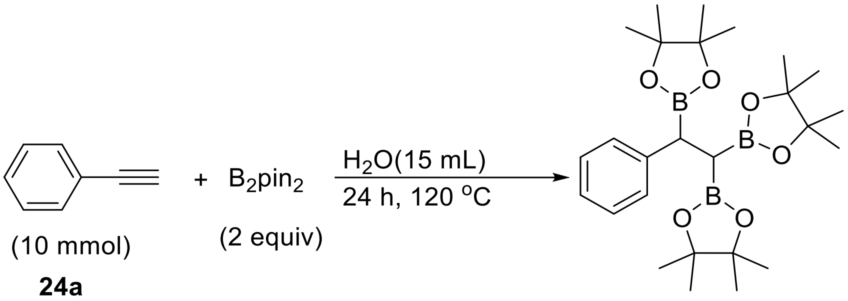




^{13}C NMR of **33b** (126 MHz, CDCl$_3$)

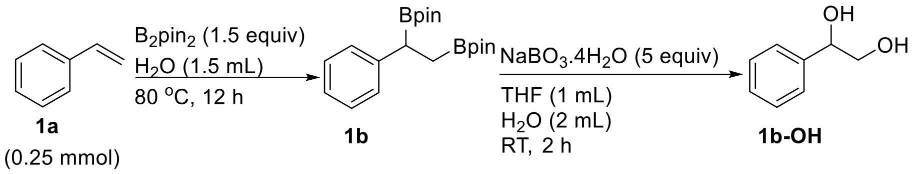
VII. Synthetic Application

a) Gram Scale Reaction. In a 50 mL thick-walled reaction tube equipped with a magnetic stirring bar, phenyl acetylene (**24a**, 10 mmol; 1.02 g), B_2pin_2 (2.0 equiv., 20 mmol, 5.08 g), and H_2O (15 mL) were added and the reaction mixture was stirred vigorously at 120 ºC for 24 h. Et_2O (50 mL) was added to the crude reaction mixture which was then transferred to a separatory funnel followed by H_2O (30 mL) was added. The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 30 mL). The combined organics were dried (Na_2SO_4) and concentrated in vacuum, and the residue was purified by column chromatography to give 2,2',2''-(2-phenylethane-1,1,2-triyl)*tris*(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**24b**) in 76% isolated yield (3.68 g).



24b = 82% (^{1}H NMR yield)
76% (3.68 g, isolated yield)

b)

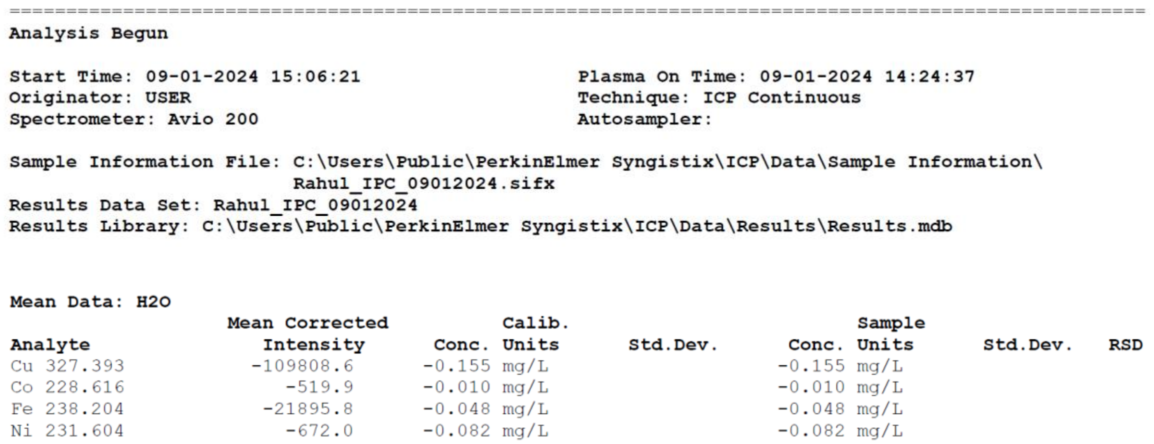


To a solution of **1b** (90 mg, 0.25 mmol) generated *in situ* from styrene in THF (1 mL) and H_2O (2 mL) were added with $NaBO_3{\cdot}4H_2O$ (5 equiv). The mixture was stirred at room temperature for 2 h. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum to give product **1b-OH** as colourless oil (31 mg, 89%). The corresponding alcohol was identified by GC-MS analysis. GC-MS: M/Z: 138 (M^+).

VIII. Mechanistic investigations

Control Experiments:

a) ICP-OES (inductively coupled plasma-optical emission spectrometry) analysis of HPLC grade water.



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====================================================================================================
Analysis Begun

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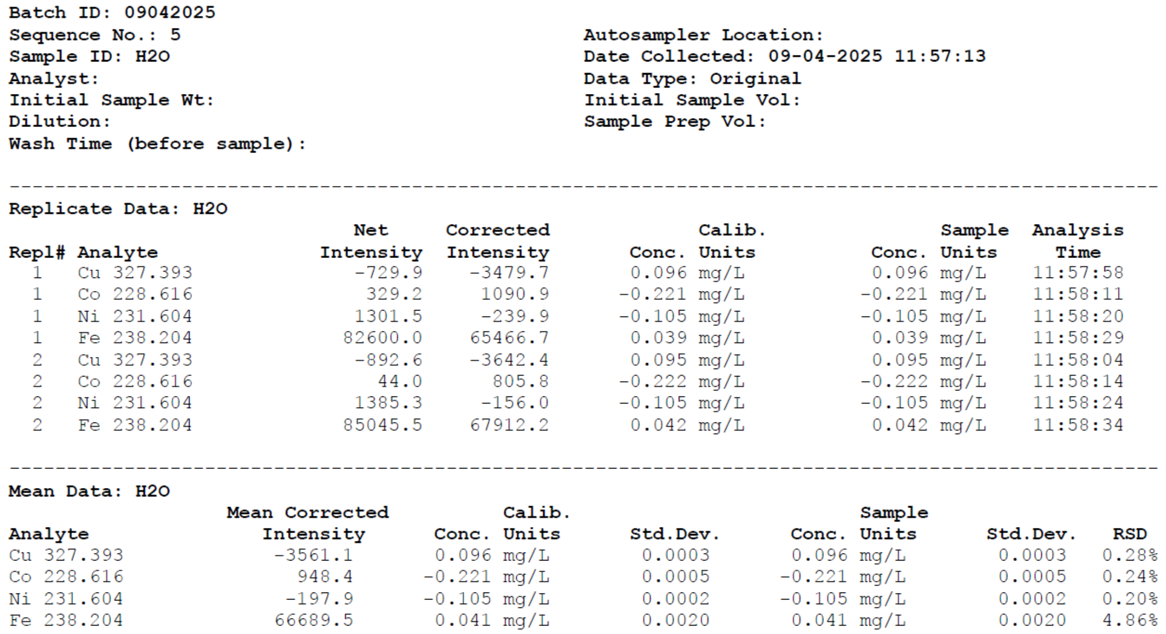
Originator: USER                                  Technique: ICP Continuous
Spectrometer: Avio 200                            Autosampler:

Sample Information File: C:\Users\Public\PerkinElmer Syngistix\ICP\Data\Sample Information\
                         Rahul_IPC_09012024.sifx
Results Data Set: Rahul_IPC_09012024
Results Library: C:\Users\Public\PerkinElmer Syngistix\ICP\Data\Results\Results.mdb


Mean Data: H2O
                   Mean Corrected           Calib.                         Sample
Analyte               Intensity       Conc. Units     Std.Dev.       Conc. Units      Std.Dev.     RSD
Cu 327.393            -109808.6      -0.155 mg/L                    -0.155 mg/L
Co 228.616               -519.9      -0.010 mg/L                    -0.010 mg/L
Fe 238.204             -21895.8      -0.048 mg/L                    -0.048 mg/L
Ni 231.604               -672.0      -0.082 mg/L                    -0.082 mg/L
```

Repeated ICP-OES analysis result of HPLC grade H_2O.



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Sequence No.: 5                                   Autosampler Location:
Sample ID: H2O                                    Date Collected: 09-04-2025 11:57:13
Analyst:                                          Data Type: Original
Initial Sample Wt:                                Initial Sample Vol:
Dilution:                                         Sample Prep Vol:
Wash Time (before sample):

-----------------------------------------------------------------------------------------------------
Replicate Data: H2O
                              Net     Corrected              Calib.                Sample  Analysis
Repl# Analyte               Intensity  Intensity        Conc. Units          Conc. Units     Time
  1   Cu 327.393               -729.9    -3479.7        0.096 mg/L           0.096 mg/L   11:57:58
  1   Co 228.616                329.2     1090.9       -0.221 mg/L          -0.221 mg/L   11:58:11
  1   Ni 231.604               1301.5     -239.9       -0.105 mg/L          -0.105 mg/L   11:58:20
  1   Fe 238.204              82600.0    65466.7        0.039 mg/L           0.039 mg/L   11:58:29
  2   Cu 327.393               -892.6    -3642.4        0.095 mg/L           0.095 mg/L   11:58:04
  2   Co 228.616                 44.0      805.8       -0.222 mg/L          -0.222 mg/L   11:58:14
  2   Ni 231.604               1385.3     -156.0       -0.105 mg/L          -0.105 mg/L   11:58:24
  2   Fe 238.204              85045.5    67912.2        0.042 mg/L           0.042 mg/L   11:58:34

-----------------------------------------------------------------------------------------------------
Mean Data: H2O
                   Mean Corrected           Calib.                         Sample
Analyte               Intensity       Conc. Units     Std.Dev.       Conc. Units      Std.Dev.     RSD
Cu 327.393              -3561.1       0.096 mg/L        0.0003       0.096 mg/L         0.0003   0.28%
Co 228.616                948.4      -0.221 mg/L        0.0005      -0.221 mg/L         0.0005   0.24%
Ni 231.604               -197.9      -0.105 mg/L        0.0002      -0.105 mg/L         0.0002   0.20%
Fe 238.204              66689.5       0.041 mg/L        0.0020       0.041 mg/L         0.0020   4.86%
```
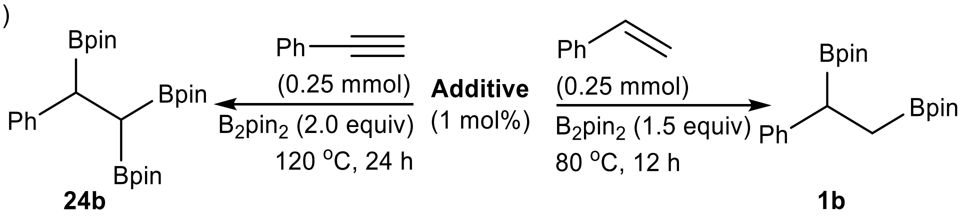

b) Effects of transition metal as additives:

i)



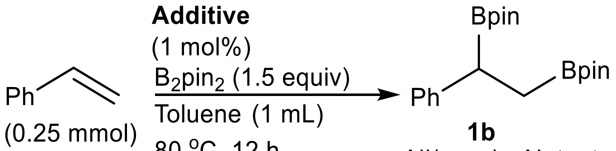
24b

1b

$Mn(acac)_2•4H_2O$: not observed
$FeCl_3$: not observed
$Co(acac)_2$: not observed
CuI: not observed
$Zn(NO_3)_2•6H_2O$: not observed

$Mn(acac)_2•4H_2O$: not observed
$FeCl_3$: not observed
$Co(acac)_2$: not observed
CuI: not observed
$Zn(NO_3)_2•6H_2O$: not observed

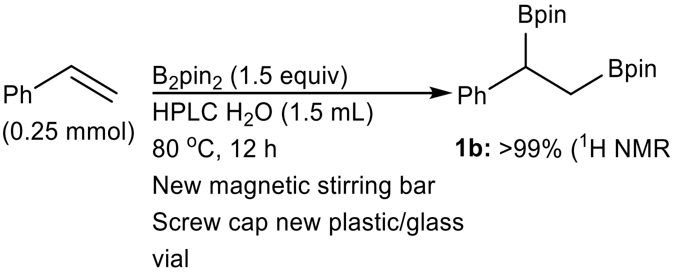
ii)



1b

$Ni(acac)_2$: Not a trace of **1b** was observed
(trace of hydroboration product was observed)
$Fe(acac)_2$: Not a trace of **1b** was observed
$Co(acac)_2$: Not a trace of **1b** was observed
(trace of hydroboration product was observed)
CuCl: Not a trace of **1b** was observed

iii)



1b: >99% (^{1}H NMR yield)

To eliminate if this di- and tri-boration reactions are mediated by trace metals, many transition-metals were examined in the absence of water.

i) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene or phenylacetylene (**1a** or **24a**, 0.25 mmol), B_2pin_2 (1.5 equiv or 2.0 equiv), and transition metal precursor (1 mol%) were added. The reaction mixture was stirred at indicated time and temperature. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The reaction mixture was analysed by ^{1}H NMR spectroscopy ($CDCl_3$) and GC-MS.

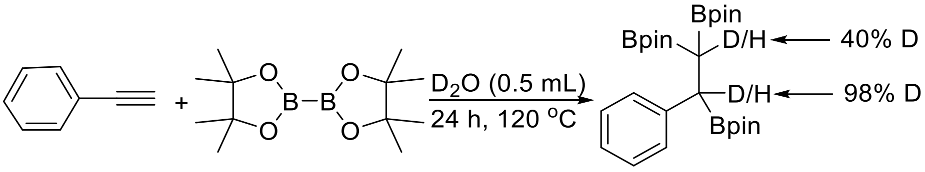
ii) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol), B_2pin_2 (1.5 equiv), transition metal precursor (1 mol%) and toluene (1 mL) were added. The reaction mixture was stirred at 80 °C for 12 h. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The reaction mixture was analysed by ^{1}H NMR spectroscopy ($CDCl_3$) and GC-MS. However, not a trace of desired diboration product was observed by GC-MS.

When the reaction was performed in the presence of CuCl as an additive (~1 mg, 4 mol%) in toluene solvent (1 mL) did not provide trace of desired diboration product. When $Ni(acac)_2$ and $Co(acac)_2$ were used in toluene solvent, a trace of hydroboration product was observed by GC-MS analysis.

In addition, reactions were performed in the presence of CuCl as an additive (~1 mg, 4 mol%) in acetonitrile (1 mL) as well as DMF solvent (1 mL). In both the solvents CuCl (4 mol%) was quite soluble. Both the reactions were carried out in the absence of water. In both the cases no product formation was observed by GC-MS analysis.

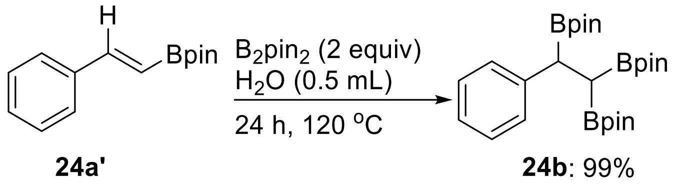
iii) In a 10 mL screw cap **new** plastic/glass vial equipped with a **new** magnetic stirring bar styrene (**1a**, 0.25 mmol), B_2pin_2 (1.5 equiv), and H_2O (1.5 mL) were added. The reaction mixture was stirred at 80 °C for 12 h. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The reaction mixture was analysed by ^{1}H NMR spectroscopy ($CDCl_3$) and GC-MS.

c) Isotope Labelling Experiment.



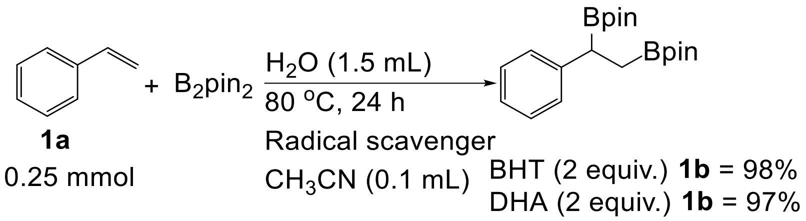
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, phenylacetylene (**24a**, 0.25 mmol; 26 mg), B_2pin_2 (2.0 equiv, 0.5 mmol, 127 mg), and D_2O (0.5 mL) were added and the reaction was stirred vigorously at 120 °C temperature for 24 h. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of celite. The solvent was removed in vacuo, and obtained product was determined by GC-MS and ^{1}H NMR spectroscopy ($CDCl_3$).

d) Transformation of vinylboronate ester to 1,1,2-tris(boronate) ester.



In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrylboronate ester (0.125 mmol), B_2pin_2 (2.0 equiv, 0.25 mmol, 64 mg), and H_2O (0.5 mL) were added and reaction mixture was stirred vigorously at 120 °C 24 h. The crude reaction mixture was dissolved in ethyl acetate (5 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The product yield was determined from GC-MS analysis and ^{1}H NMR spectroscopy ($CDCl_3$).

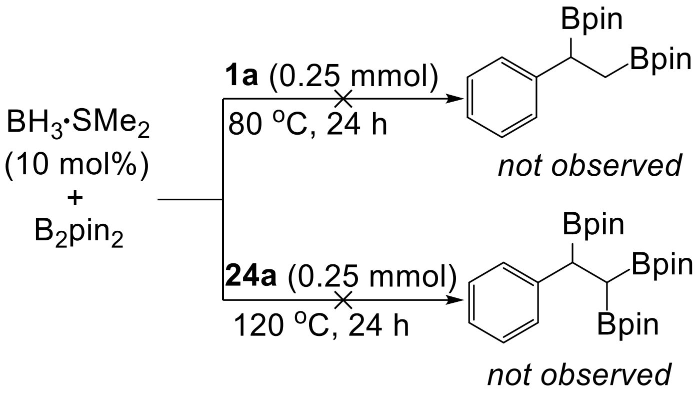
e) Radical scavenger experiments:



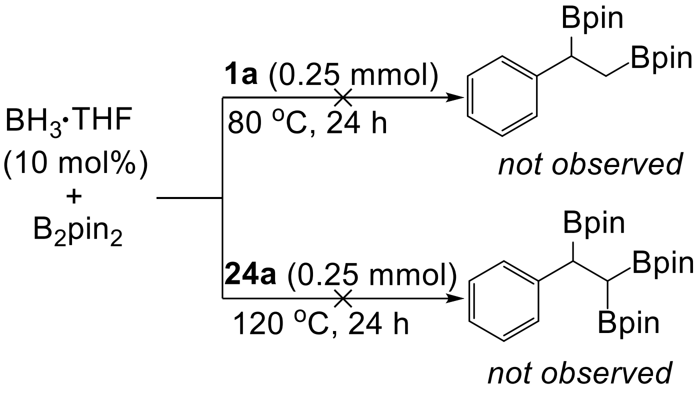
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol), B_2pin_2 (1.5 equiv), radical scavenger (2 equiv.), CH_3CN (0.1 mL)* and H_2O (1.5 mL) were added. The reaction mixture was stirred at 80 °C for 12 h. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The reaction mixture was analysed by ^{1}H NMR spectroscopy and GC-MS.

*CH_3CN was added to the reaction mixture to improve the solubility of the radical scavenger.

f) Experimental procedure for BH_3 catalyzed di- and triboration:



In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene or phenylacetylene (**1a** or **24a**, 0.25 mmol), B_2pin_2 (1.5 equiv or 2.0 equiv), and $BH_3{\cdot}SMe_2$ (2 mg, 2 µL, 10 mol%) were added. The reaction mixture was stirred at indicated time and temperature. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The reaction mixture was analysed by ^1H NMR spectroscopy and GC-MS. After careful analysis of the crude reaction mixture of styrene (**1a**) by GC-MS and ^1H NMR spectroscopy, the formation of a small amount of hydroboration product was observed. In the phenylacetylene reaction mixture, only the starting substrate and B_2pin_2 were observed by GC-MS analysis.

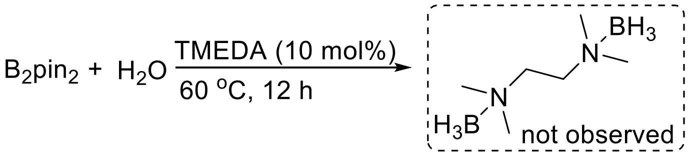


In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene or phenylacetylene (**1a** or **24a**, 0.25 mmol), B_2pin_2 (1.5 equiv or 2.0 equiv), and $BH_3{\cdot}THF$ (2 mg, 25 µL, 10 mol%) were added. The reaction mixture was stirred at indicated time and temperature. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum, and nitromethane was added as an internal standard. The reaction mixture was analysed by ^1H NMR spectroscopy ($CDCl_3$)

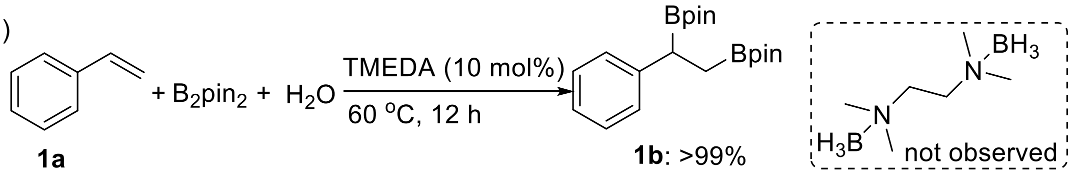
and GC-MS. After careful analysis of the crude reaction mixture of styrene (**1a**) by GC-MS and ^{1}H NMR spectroscopy, the formation of hydroboration product was observed. Only the starting substrate and B_2pin_2 were observed in the phenylacetylene (**24a**) reaction mixture confirm by GC-MS analysis.

g) Experimental procedure for: i) Reaction of B_2pin_2 with H_2O in the presence of TMEDA. ii) Reaction of 1a with B_2pin_2 in H_2O in the presence of TMEDA.

i)



ii)



i) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, B_2pin_2 (0.25 mmol, 64 mg), H_2O (0.5 mL) and tetramethylethylenediamine (TMEDA, 10 mol%) were added. The reaction mixture was stirred at 60 °C for 12 h. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^{11}B NMR spectroscopy and GC-MS.

The reaction of B_2pin_2 with H_2O in the presence of TMEDA at 60 °C showed no evidence for the formation of BH_3 *via* ^{11}B NMR spectroscopy.

The reaction of B_2pin_2 with TMEDA in water in the absence of substrate leads to decomposition of the B_2pin_2, presumably assisted by the TMEDA acting as a base to form hydroxide.

In Figure S1, the peak at δ 22.3 ppm in the boron NMR spectrum could be due to B-O species, such as pinB-OH, pinB-O-Bpin, $B(OH)_3$, etc.

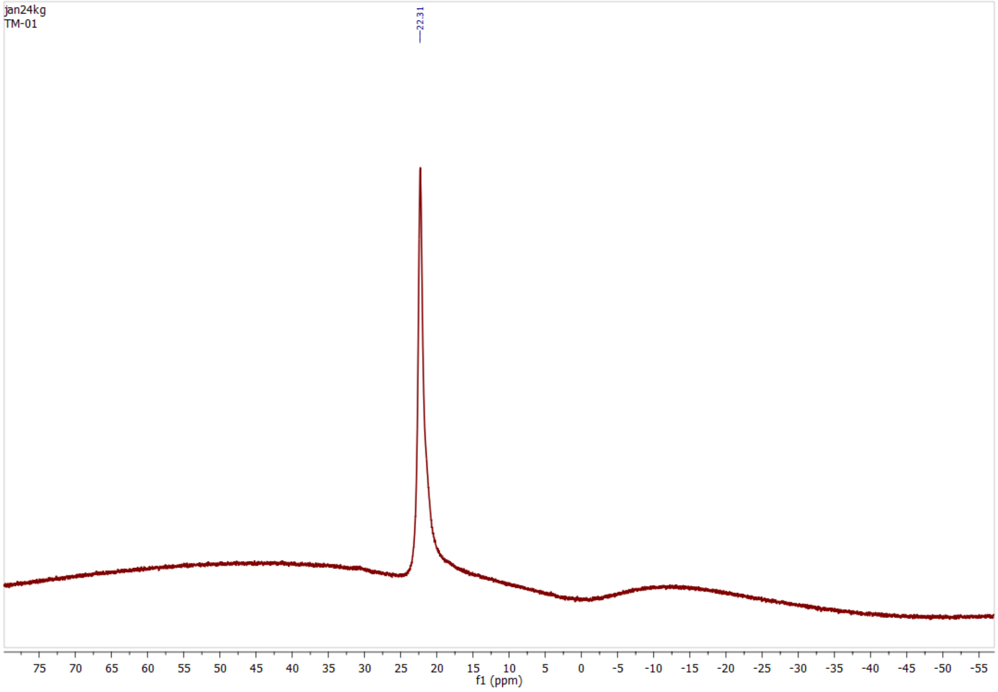


Figure S1. ^{11}B NMR (160 MHz, $CDCl_3$) of the crude mixture of B_2pin_2 and H_2O in the presence of TMEDA (10 mol%).

ii) In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), B_2pin_2 (1.5 equiv., 0.38 mmol, 97 mg), H_2O (1.5 mL) and tetramethylethylenediamine (TMEDA, 10 mol%) were added. The reaction mixture was stirred at 60 °C for 12 h. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^{11}B NMR spectroscopy and GC-MS.

GC-MS and ^{1}H NMR spectroscopy confirmed the formation of desired diboration product in >99% yield. In addition, no resonance was observed related to the formation of the TMEDA·$(BH_3)_2$ complex by ^{11}B NMR spectroscopy. These experimental results demonstrated that under our reaction conditions H_2O cannot act as an activating agent to facilitate the formation of borane from B_2pin_2, exclude the possibility of any hidden catalyst.

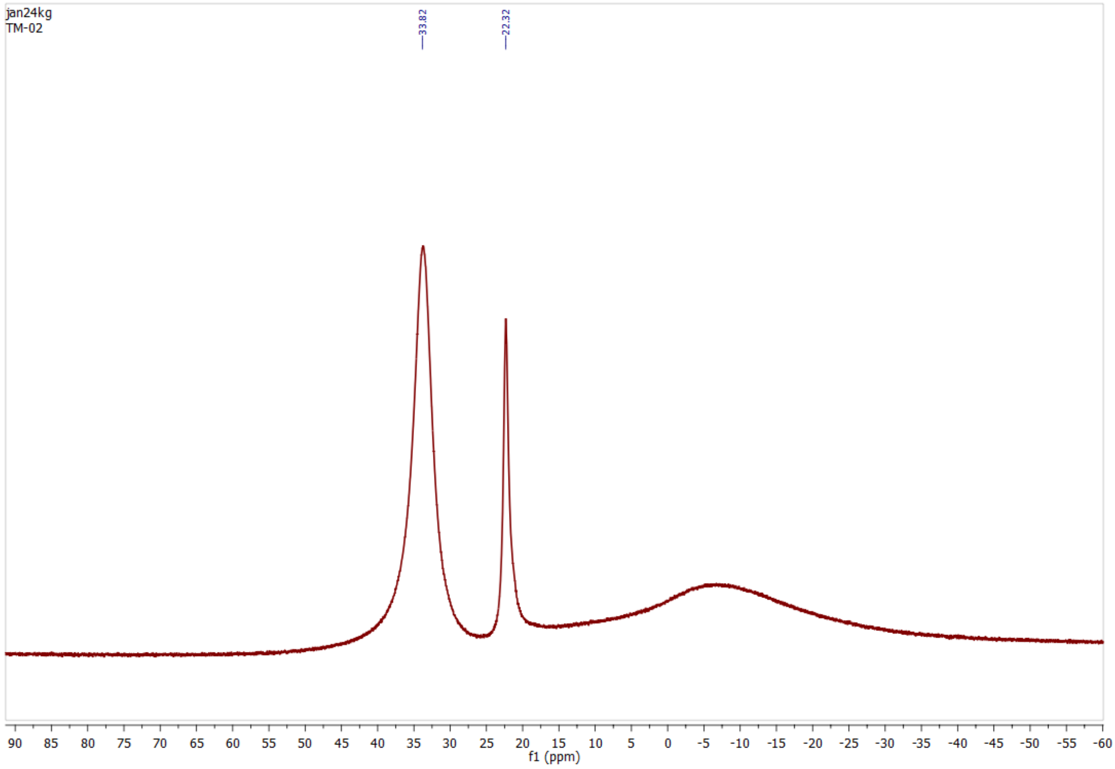
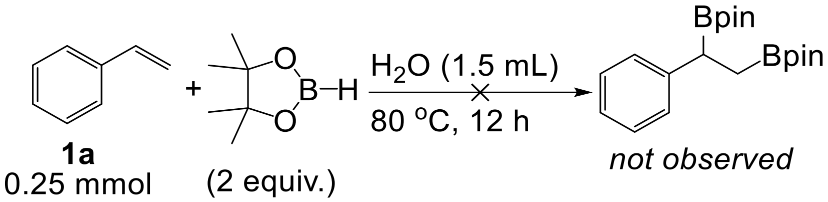


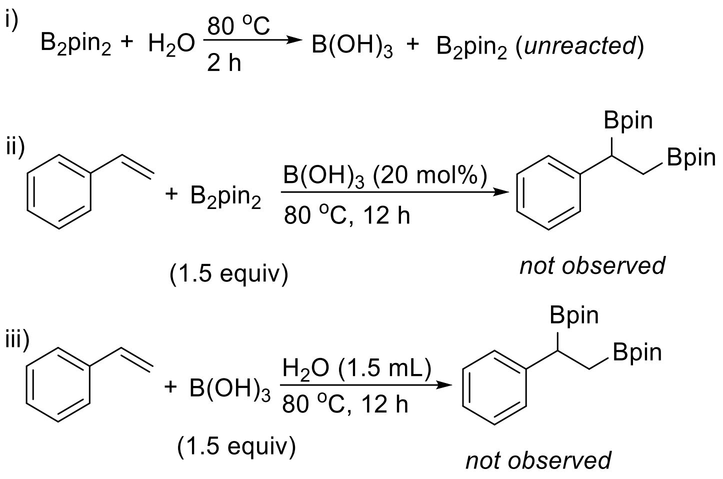
Figure S2. ^{11}B NMR (160 MHz, $CDCl_3$) of the crude mixture of styrene (**1a**), B_2pin_2 and H_2O in the presence of TMEDA (10 mol%).

h) Diboration of styrene (1a) with HBpin:



In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26.03 mg), HBpin (2.0 equiv, 64 mg, 0.5 mmol), and H_2O (1.5 mL) were added and reaction mixture was kept under stirring for 12 h at 80 °C. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^{1}H NMR spectroscopy and GC-MS.

i) Reaction in the presence of $B(OH)_3$:



i) In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, B_2pin_2 (0.25 mmol, 64 mg), and H_2O (0.5 mL) were added and reaction mixture was kept under stirring for 2 h/24 h at 80 °C. The crude reaction mixture was analysed by ^{11}B NMR spectroscopy.

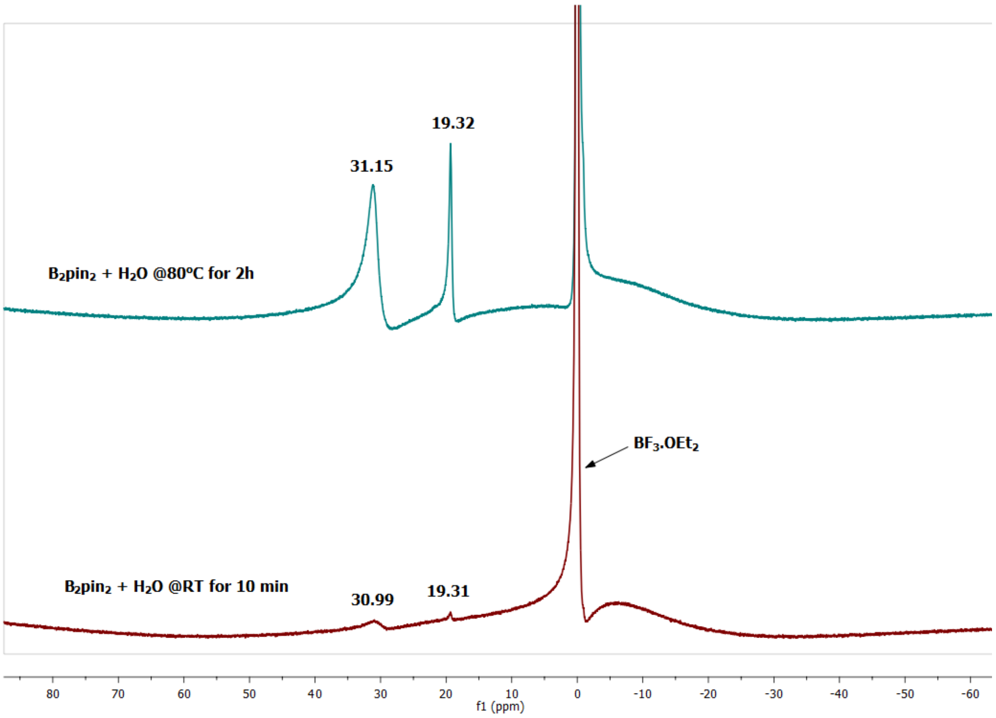


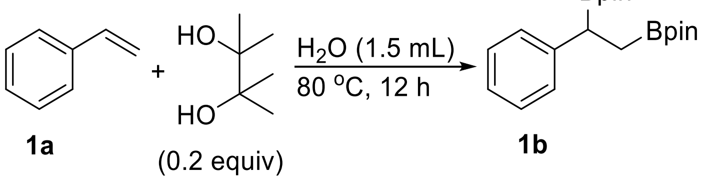
Figure S3. ^{11}B NMR (160 MHz, $CDCl_3$) of reaction mixture of B_2pin_2 and H_2O.

Investigation of the reaction mixture of B_2pin_2 and H_2O at room temperature by ^{11}B NMR spectroscopy showed resonance at δ 30.99 ppm and at δ 19.31 ppm (Figure S3, bottom). The downfield resonance is probably due to unreacted B_2pin_2, or due to hydrolysis of B_2pin_2 to BBA or pinB-$B(OH)_2$. The upfield resonance is probably due to the decomposition product $B(OH)_3$, pinB-OH or pinB-O-Bpin. Further, stirring the reaction mixture of B_2pin_2 and H_2O at 80 °C for 2 h showed resonance at δ 31.15 ppm and at δ 19.32 ppm (Figure S3, top). There is slight downfield shift in the B_2pin_2 resonance, probably due to weak interaction between diboron and water molecules. Also, it is possible that the resonance at δ 31.15 ppm might be not only due to B_2pin_2 but also overlaps with BBA.

ii) In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), B_2pin_2 (1.5 equiv, 95 mg, 0.37 mmol), $B(OH)_3$ (20 mol%, 0.05 mmol, 3 mg), and H_2O (1.5 mL) were added and reaction mixture was kept under stirring for 12 h at 80 °C. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^{1}H NMR spectroscopy and GC-MS.

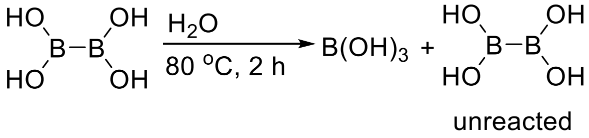
iii) In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), $B(OH)_3$ (1.5 equiv, 0.375 mmol, 23 mg), and H_2O (1.5 mL) were added and reaction mixture was kept under stirring for 12 h at 80 °C. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^{1}H NMR spectroscopy and GC-MS.

j) Reaction in the presence of pinacol:



In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), B_2pin_2 (1.5 equiv, 95 mg, 0.37 mmol), pinacol (20 mol%, 0.05 mmol, 6 mg), and H_2O (1.5 mL) were added and reaction mixture was kept under stirring at 80 °C. After regular interval, crude reaction mixture was analysed by GC-MS analysis after work-up process. After 12 h, crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^1H NMR spectroscopy and GC-MS. No desired product was observed after 1 h and only 5% **1b** was formed after 12 h.

k) Reaction of BBA with H_2O.



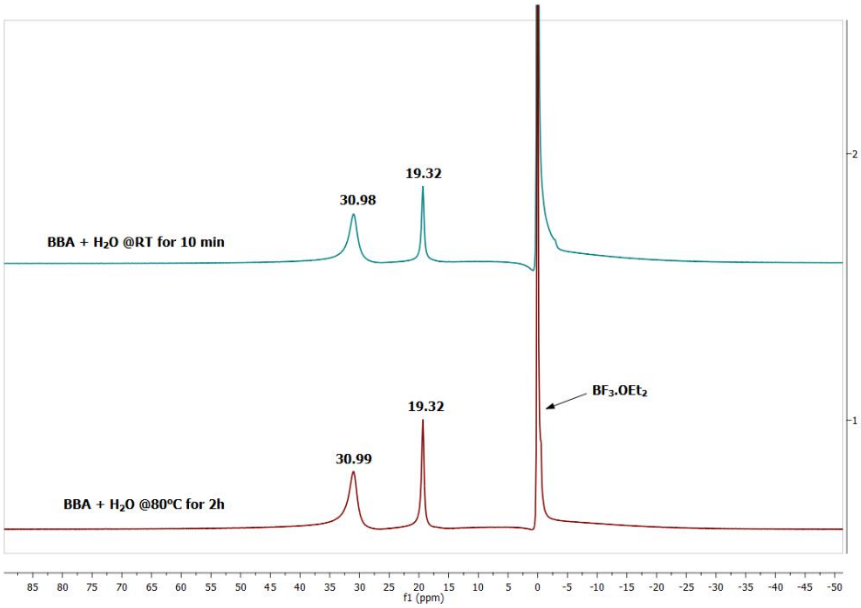


Figure S4. ^{11}B NMR (160 MHz, $CDCl_3$) of reaction mixture of BBA and H_2O.

In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, BBA (0.25 mmol, 23 mg), and H_2O (0.5 mL) were added and reaction mixture was kept under stirring for 2 h at 80 °C. The crude reaction mixture was analysed by ^{11}B NMR spectroscopy.

Investigation of the reaction mixture of BBA and H_2O at room temperature by ^{11}B NMR spectroscopy showed resonance at δ 30.98 ppm and at δ 19.32 ppm (Figure S4, top). The downfield resonance is due to BBA and the upfield due to $B(OH)_3$. Further, stirring the reaction mixture of BBA and H_2O at 80 °C for 2 h showed resonance at δ 30.99 ppm and at δ 19.32 ppm (Figure S4, bottom). There is no shift in the BBA resonance.

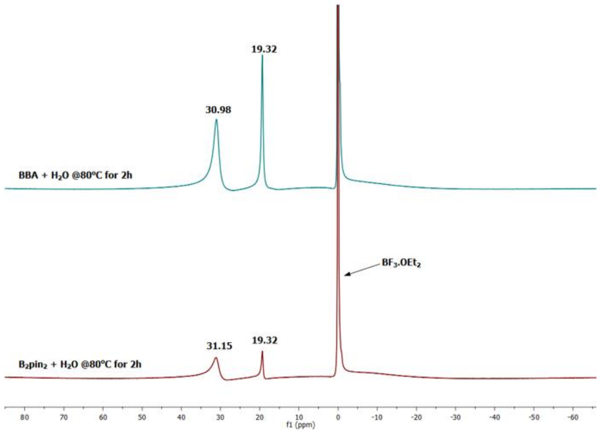
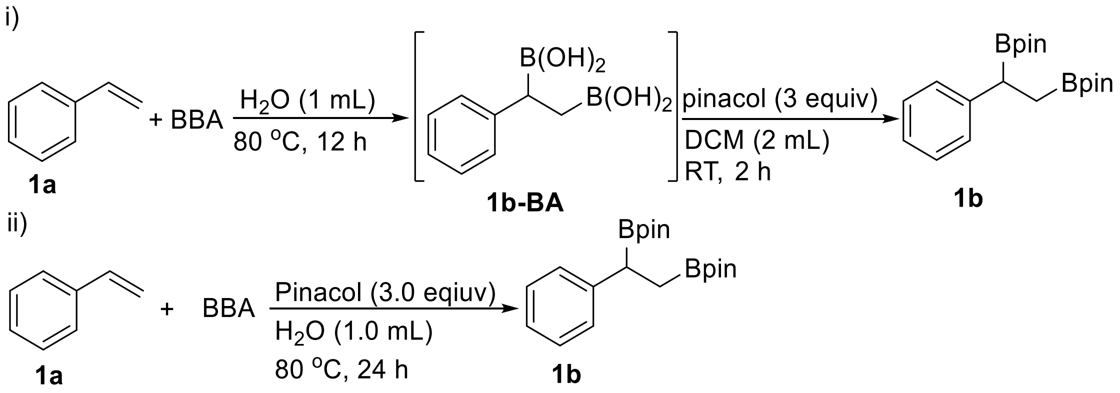


Figure S5. ^{11}B NMR spectra of B_2pin_2 and BBA hydrolysis.

l) Diboration of alkene using BBA.

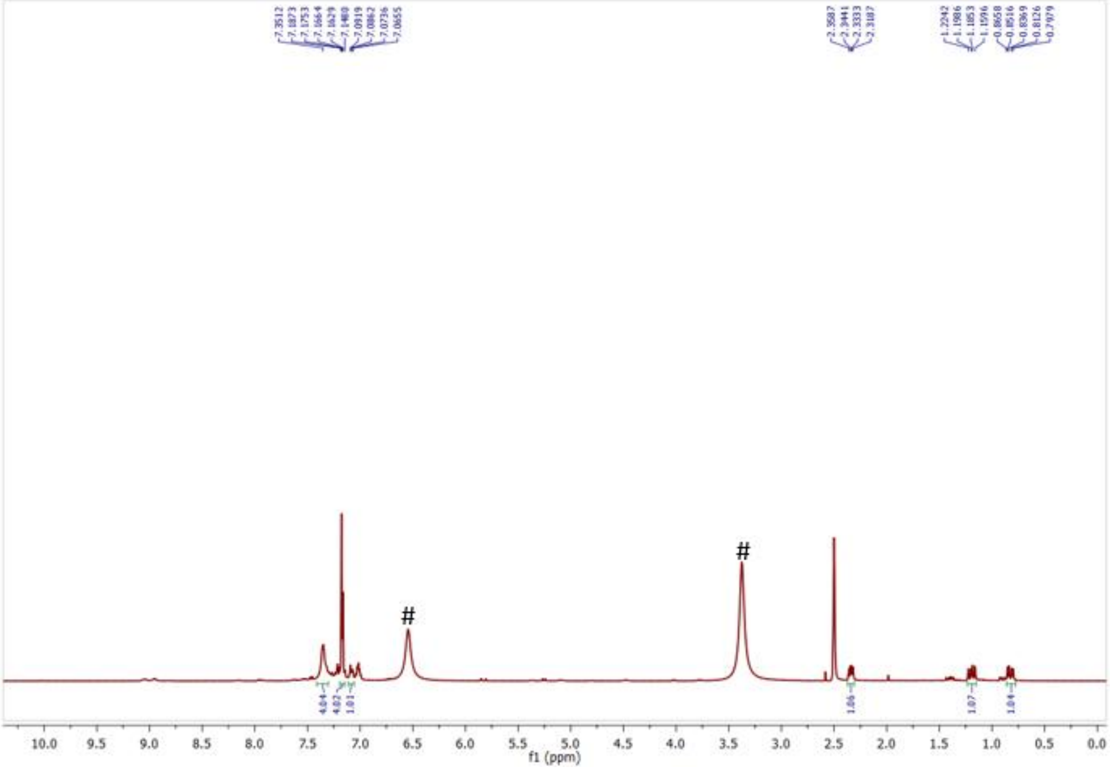


i) In a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), BBA (1.5 equiv, 34 mg, 0.37 mmol), and H_2O (1.5 mL) were added and reaction mixture was kept under stirring for 12 h at 80 °C. The crude reaction was transferred to a separatory funnel followed by the addition of EtOAc (5 mL) and then aq HCl (5 mL of a 1 M solution). The layers were separated, and the water layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. To the crude mixture was added CH_2Cl_2 (2 mL) and pinacol (89 mg, 0.75 mmol, 3 equiv). The reaction was stirred for 2 h. The crude mixture was transferred to a separatory funnel followed by the addition of H_2O (5 mL). The layers were separated, and the water layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The reaction mixture was analysed by ^1H and ^{13}C NMR spectroscopy and GC-MS.

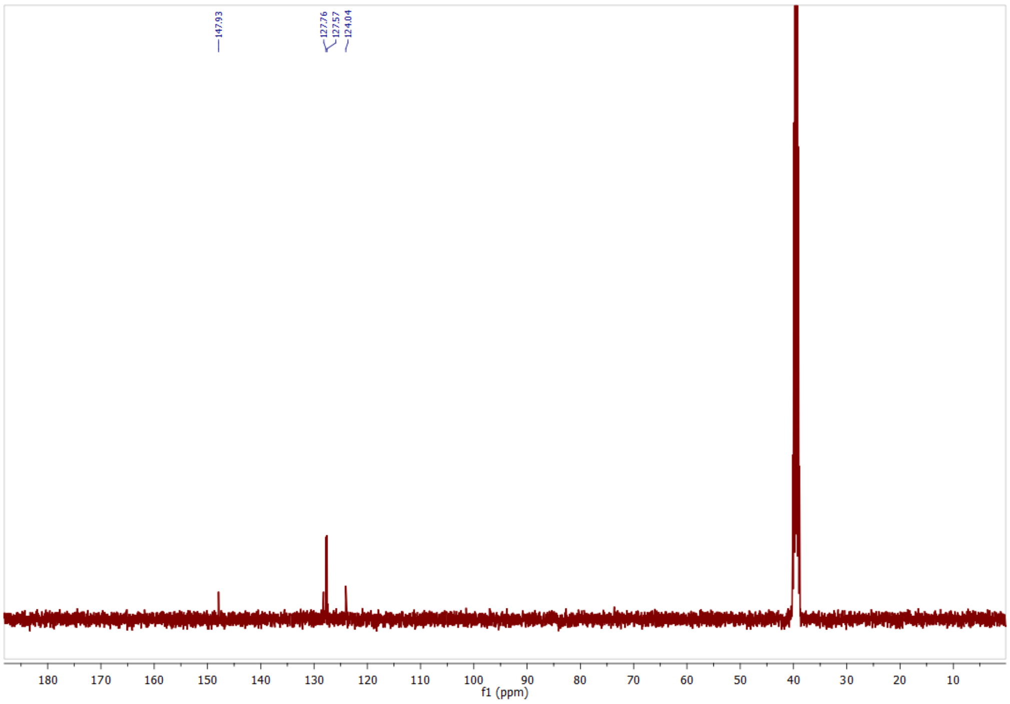
(1-Phenylethane-1,2-diyl)diboronic acid (**1b-BA**).

After the reaction stirred for 12 h at 80 °C, the crude reaction was transferred to a separatory funnel followed by the addition of EtOAc (5 mL) and then aq HCl (5 mL of a 1 M solution). The layers were separated, and the water layer was extracted with EtOAc (2 × 5 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The intermediate **1b-BA** was characterized by ^1H and ^{13}C NMR spectroscopy in DMSO-d_6 solvent.

^1H NMR (400 MHz, DMSO-d_6): δ 7.35 (br, 4H), 7.19-7.15 (m, 4H), 7.09-7.07 (m, 1H), 2.34 (dd, J = 10.0, 6.0 Hz, 1H), 1.19 (dd, J = 16.0, 10.0 Hz, 1H), 0.82 (dd, J = 16.0, 6.0 Hz, 1H) [peak at δ 6.6 due to $B(OH)_3$ and δ 3.3 due to H_2O]. ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.9, 127.8, 127.6, 124.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.



^{1}H NMR of **1b-BA** (400 MHz, DMSO-d_6)



^{13}C NMR of **1b-BA** (100 MHz, DMSO-d_6)

ii) In nitrogen atmosphere, a glass vial equipped with magnetic stirring bar, styrene (**1a**, 0.25 mmol, 26 mg), BBA (1.5 equiv, 34 mg, 0.37 mmol), pinacol (89 mg, 0.75 mmol, 3 equiv), and H_2O (1.0 mL) were added and reaction mixture was kept under stirring for 12 h at 80 °C. The crude reaction mixture was dissolved in ethyl acetate (10 mL) and passed through a plug of Celite. The solvent was removed in vacuum. The reaction mixture was analysed by ^{1}H NMR spectroscopy and GC-MS.

Experimental Procedure for Examples Described in Table 5.

General Procedure F. In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, alkene (0.25 mmol), BBA (1.5 equiv, 34 mg, 0.37 mmol), pinacol (89 mg, 0.75 mmol, 3 equiv), and H_2O (1.5 mL) were added and the reaction mixture was stirred vigorously at 80 ºC for 24 h. The crude reaction was dissolved in Et_2O (5 mL) and then transferred to a separatory funnel followed by the addition of H_2O (5 mL). The layers were separated and the organic layer was washed once with brine. The combined aqueous layers were further extracted with Et_2O (3 x 5 mL). The combined organics were dried (Na_2SO_4). In the concentrated crude reaction mixture nitromethane was added as an internal standard. The product yield was determined by ^{1}H NMR spectroscopy using nitromethane as an internal standard.

IX. Computational Studies

All calculations were performed employing a DFT method implemented in the Gaussian 16 suite of programs.[11] For geometry optimization and frequency analysis, we adopted the B3LYP functional,[12-14] in addition to including the Grimme dispersion corrections including Becke-Johnson damping (D3BJ).[15,16] The electronic configuration of all non-metal elements was described with the Ahlrichs split-valence plus single polarization basis set def2-SVP.[17] The geometries were optimized without any symmetry constraints. The free energies (ΔG), calculated at the B3LYP/def2-SVP-D3 levels are reported throughout the article unless otherwise mentioned.

i) **Water-assisted diboration of styrene with $B_2(OH)_4$.**

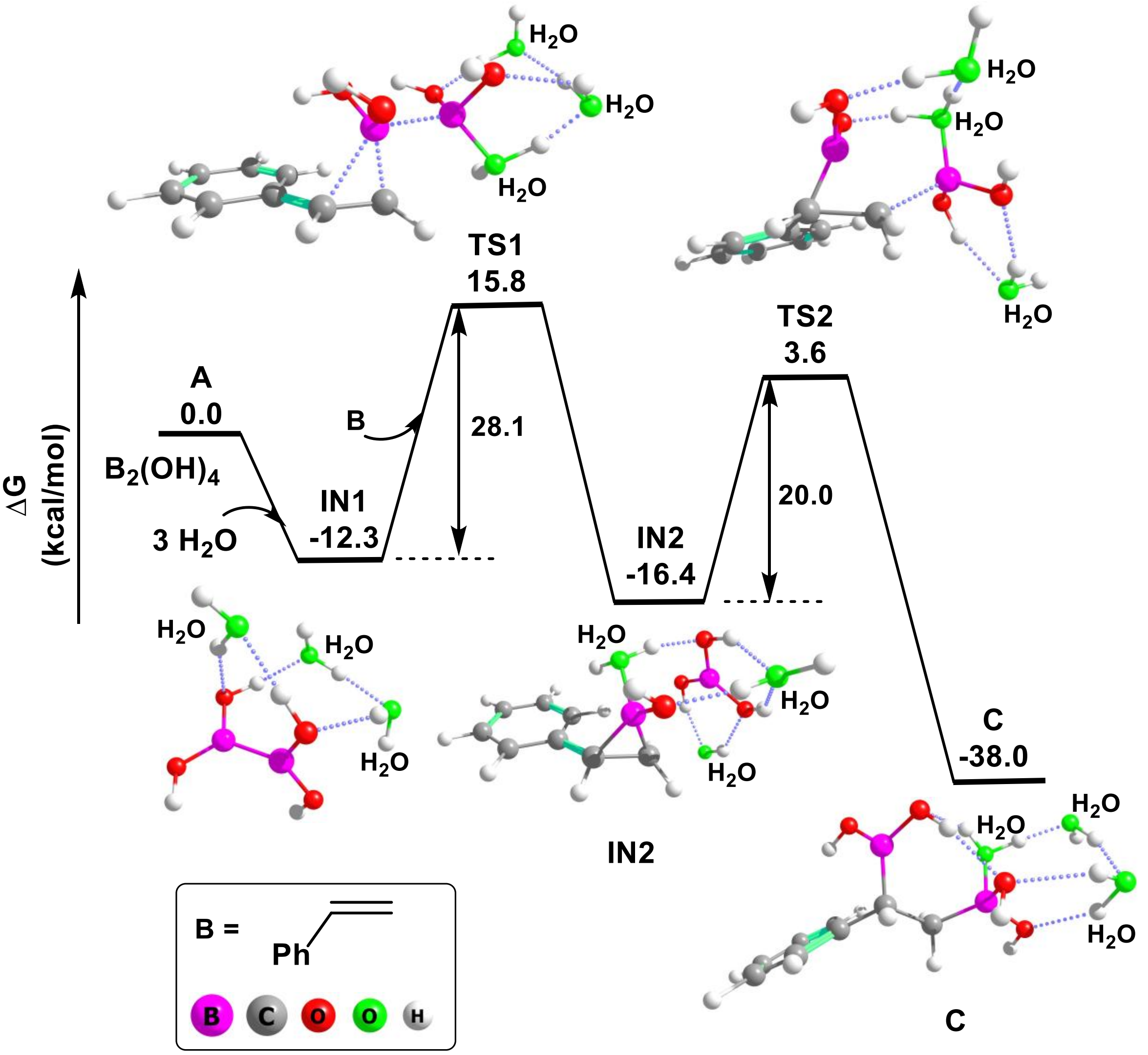
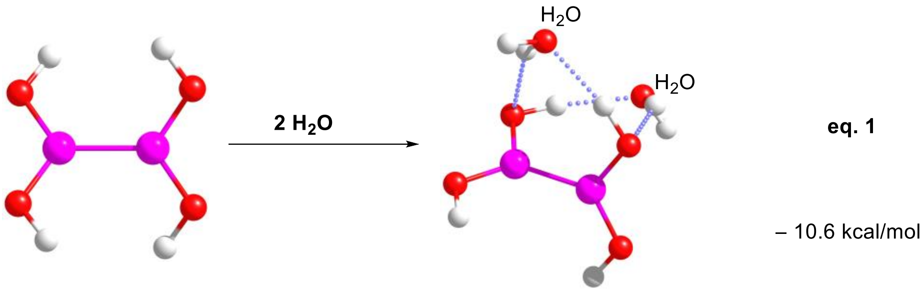
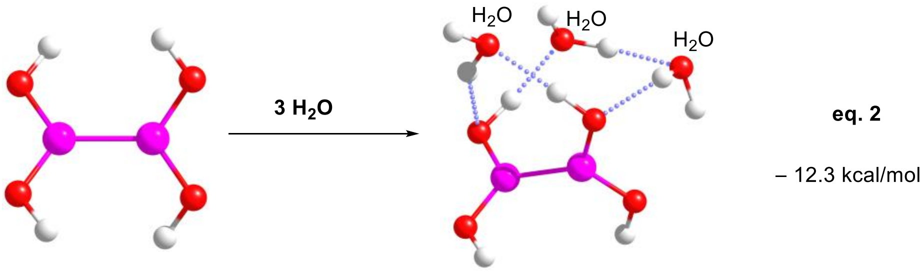


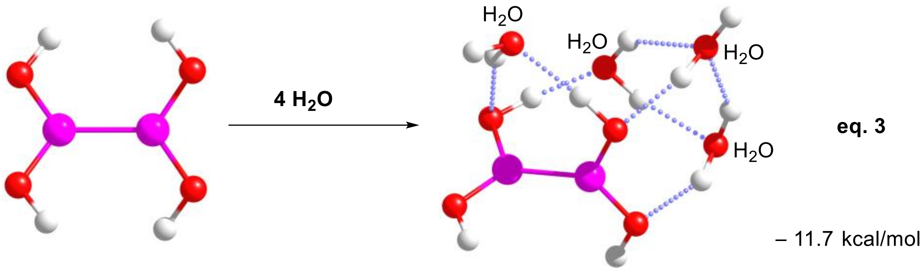
Figure S6. DFT-calculated free energy profile of water-assisted diboration of styrene with $B_2(OH)_4$. All energies are in kcal/mol. The green-colored oxygen atom represents the oxygen from a water molecule.

To shed light on the mechanism, quantum chemical calculations were performed using density functional theory (DFT) employing the Gaussian 16 suit of programs. The reaction starts by the addition of water to $B_2(OH)_4$ to generate the intermediate adduct species, **IN1** and this step is endergonic by -12.5 kcal/mol. Next, addition of styrene (**B**) leads to the formation of intermediate **IN2** through four-member transition state **TS1**, which has a barrier of 28.1 kcal/mol from **IN1**. Subsequently, another group [-$B(OH)_2$] transfer to the styrene *via* transition state **TS2**, gives the highly exergonic product complex (**C**, -38.0 kcal/mol) with water molecules. This last step is associated with the transition state barrier of 20.0 kcal/mol.

ii) **Interaction of BBA with 2, 3, and 4 water molecules**.







Interaction of 2, 3, and 4 water molecules (eq. 1-3) with $B_2(OH)_4$ showed that the formation of the adduct with three water molecules is more favourable than the formation of the two- and four-water molecules. Therefore, we have considered three water molecules for the calculation.

iii) **DFT studies using pinB-B(OH)$_2$ as active species.**

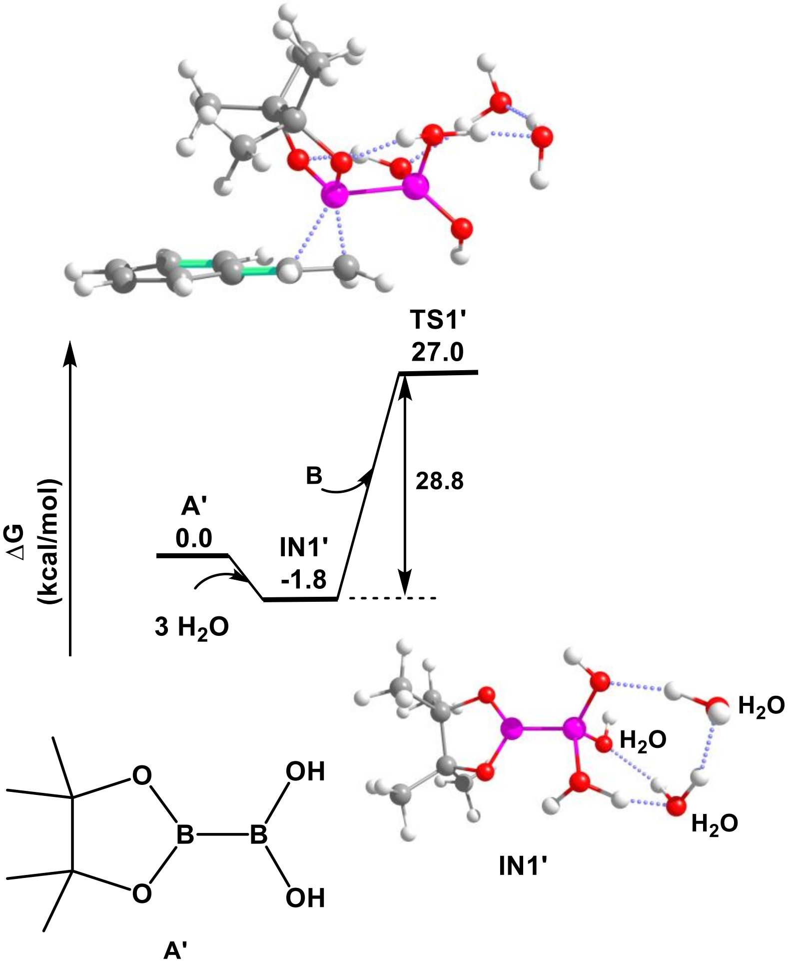


Figure S7. Free energy profile for the styrene with pinB-B(OH)$_2$ reaction. All energies are in kcal/mol.

To explore the possibility that the active species when employing B$_2$pin$_2$ is actually pinB-B(OH)$_2$, in which only one of the pinacolato groups is hydrolyzed off from one boron, DFT studies was carries out using pinB-B(OH)$_2$ as active species.

If we consider the reaction proceeding through the Bpin–B(OH)$_2$ intermediate, the formation of intermediate **IN1′** is found to be thermodynamically less favorable compared to the formation of **IN1** in the originally proposed pathway (Figure S6). Additionally, the energy barrier associated with the first step in this alternative pathway is significantly higher, making it a less likely route under the given reaction conditions.

iv) **Charge on styrene (B), IN1, and TS1.**

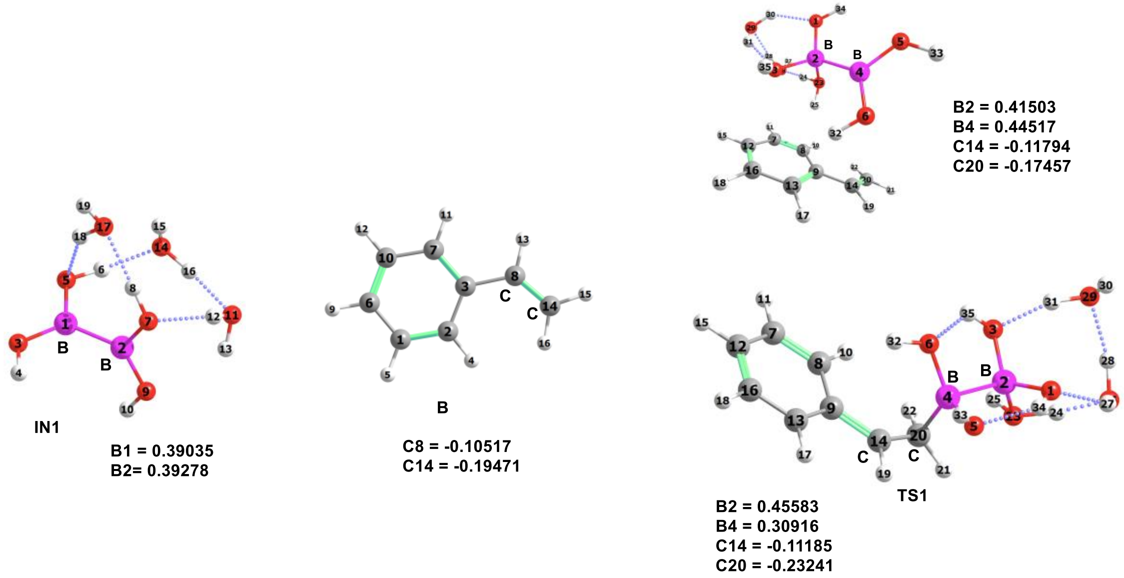


Figure S8. NBO charges for intermediate **IN1**, styrene (**B**), and the transition state **TS1**.

We calculated the NBO charges for intermediate **IN1**, styrene (**B**), and the transition state **TS1** (Figure S8). The results indicate that in **TS1**, the alkene moiety of styrene accumulates a greater negative charge compared to free styrene. Concurrently, one of the boron atoms from the B–B bond exhibits an increased positive charge.

v) **The effect of CF_3-substituation at phenyl ring.**

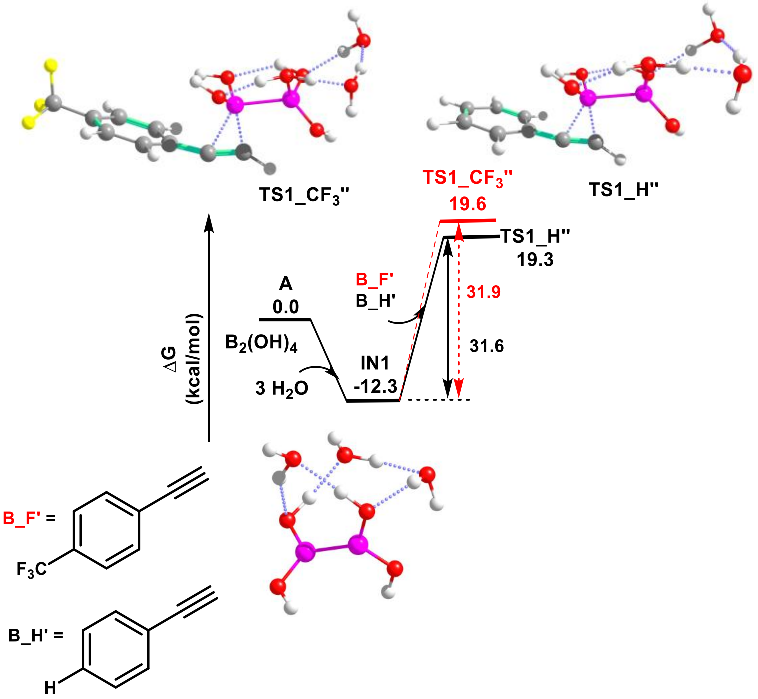


Figure S9. Free energy profile for the diboration of 1-ethynyl-4-(trifluoromethyl)benzene (**31a**) with $B_2(OH)_4$ reaction. All energies are in kcal/mol.

We have performed DFT studies to look into the effect of CF_3-substituation at phenyl ring (Figure S9). The result showed that barrier for **TS1_CF₃″** (CF$_3$-substituted transition state) is higher than phenylacetylene (**TS1_H″**). Probably, due to hight barrier the yield of **31b** is low. This result also aligns with the experimental results which demonstrate the necessity of higher temperature for the triboration of alkynes in comparison with diboration of alkenes.

In addition, careful analysis of the crude reaction mixture of **31a** revealed the formation of diboration and hydroboration products along with **31b**.

Table S5. Cartesian coordinates (Å) of the optimized structures of all intermediate and transition states at the B3LYP/Def2-SVP-D3 level of theory.

A

$B_2(OH)_4$

B	-0.899500000	0.890547000	1.541426000
B	-1.383981000	0.227307000	3.068300000
O	0.161896000	1.743265000	1.404234000
H	0.650038000	1.874948000	2.223829000
O	-1.545434000	0.606331000	0.369005000
H	-2.332547000	0.065312000	0.492055000
O	-1.736751000	-1.084879000	3.230227000
H	-1.617725000	-1.610059000	2.431864000
O	-1.446793000	0.970487000	4.215567000
H	-1.266713000	1.905418000	4.071204000

IN1

B	-0.869021000	0.903133000	1.548663000
B	-1.362356000	0.251669000	3.075533000
O	0.335012000	1.513388000	1.309150000
H	0.893791000	1.566392000	2.091749000
O	-1.663257000	0.736713000	0.449920000
H	-2.570539000	0.396202000	0.685031000
O	-1.438707000	-1.102832000	3.263667000
H	-1.274024000	-1.600778000	2.434801000
O	-1.763560000	0.987285000	4.168072000
H	-1.704848000	1.937505000	4.021126000
O	-4.152657000	-0.845556000	3.833186000
H	-3.254848000	-1.231690000	3.862538000
H	-4.010004000	-0.006850000	4.297245000
O	-3.870900000	-0.556490000	1.132989000
H	-3.487166000	-1.430372000	0.956299000
H	-4.120751000	-0.595868000	2.089714000
O	-1.385207000	-2.011029000	0.676870000
H	-1.320915000	-1.116749000	0.278007000
H	-0.783443000	-2.574489000	0.172875000

B

Styrene

C	-3.986205000	1.518964000	0.844565000
C	-2.830374000	0.978796000	0.285598000
C	-2.874207000	-0.226773000	-0.441922000
H	-1.879809000	1.499876000	0.415425000
H	-3.929281000	2.455356000	1.405113000
C	-5.217286000	0.869572000	0.691964000
C	-4.119088000	-0.866078000	-0.585670000
C	-1.682260000	-0.838632000	-1.051785000
H	-6.122030000	1.295935000	1.131640000
C	-5.278769000	-0.326404000	-0.026236000
H	-4.172614000	-1.802811000	-1.147074000
H	-6.233771000	-0.842357000	-0.152048000
H	-1.875642000	-1.776134000	-1.585879000
C	-0.423399000	-0.378411000	-1.020421000
H	0.384943000	-0.923303000	-1.513389000
H	-0.148560000	0.548178000	-0.509283000

TS1

Freq.= -307.6813

O	2.473737000	-1.774770000	0.661565000
B	1.685284000	-0.602252000	0.846466000
O	1.491557000	-0.094491000	2.173761000
B	-0.056539000	-1.213480000	0.278858000
O	0.208000000	-2.414737000	-0.468563000
O	-0.711624000	-1.315848000	1.550241000
C	-3.968263000	1.020610000	1.596860000
C	-2.750674000	0.819047000	0.947652000
C	-2.664705000	-0.004704000	-0.199294000
H	-1.852534000	1.302298000	1.335121000
H	-4.006390000	1.665219000	2.478612000
C	-5.134670000	0.405199000	1.131194000
C	-3.852909000	-0.630026000	-0.643655000
C	-1.423728000	-0.257343000	-0.911904000
H	-6.085936000	0.566070000	1.643326000
C	-5.067800000	-0.423863000	0.005830000
H	-3.810044000	-1.277561000	-1.523591000
H	-5.970531000	-0.914526000	-0.366627000
H	-1.498177000	-0.929215000	-1.769399000
C	-0.152940000	0.280217000	-0.632662000
H	0.596440000	0.271398000	-1.424701000
H	-0.084694000	1.147029000	0.029706000
O	2.477800000	0.544394000	0.112770000
H	3.538976000	0.296235000	0.300801000
H	2.277155000	1.384114000	0.552342000
O	4.684015000	-0.310158000	0.689927000
H	4.273575000	-1.190795000	0.533115000
H	4.594906000	-0.242823000	1.687751000
O	3.939508000	-0.311807000	3.231107000
H	3.974247000	-1.244892000	3.486393000
H	2.979350000	-0.181077000	3.011579000
H	-1.675104000	-1.391118000	1.522252000
H	-0.446859000	-3.096997000	-0.279023000
H	1.931031000	-2.417303000	0.163314000
H	0.639577000	-0.457894000	2.485934000

IN2

O	2.220908000	1.850798000	-2.034623000
B	1.704589000	2.133100000	-0.790608000
O	2.100401000	1.391162000	0.323179000
B	-0.067886000	-0.765335000	-0.519272000
O	0.905623000	-1.819808000	-0.553902000
O	0.047929000	-0.007947000	0.850062000
C	-3.506255000	1.814787000	0.914474000
C	-2.527351000	1.232714000	0.097537000
C	-2.624044000	-0.117330000	-0.316680000
H	-1.701249000	1.858642000	-0.250821000
H	-3.399312000	2.861646000	1.210839000
C	-4.613535000	1.078438000	1.332404000
C	-3.759583000	-0.838747000	0.112835000
C	-1.559736000	-0.796340000	-1.085443000
H	-5.378174000	1.534014000	1.965510000
C	-4.734886000	-0.254241000	0.916282000
H	-3.867459000	-1.881550000	-0.197651000

H	-5.602623000	-0.843805000	1.224723000
H	-1.888611000	-1.706660000	-1.597481000
C	-0.460796000	0.032648000	-1.798504000
H	-0.143279000	-0.377585000	-2.762847000
H	-0.624073000	1.112381000	-1.843549000
O	0.780386000	3.097202000	-0.598018000
H	0.470420000	3.449529000	-1.465081000
H	-0.779916000	0.493808000	1.020405000
O	0.354982000	3.473246000	-3.235750000
H	0.826610000	4.225238000	-3.619442000
H	1.023281000	2.759108000	-3.210862000
O	3.143943000	-0.584264000	-1.125911000
H	3.937565000	-1.129743000	-1.185935000
H	2.369754000	-1.200204000	-0.967487000
H	0.833638000	0.640955000	0.802027000
H	0.707072000	-2.533966000	0.064103000
H	2.661961000	0.977153000	-2.039817000
H	2.710116000	0.671366000	0.038326000

TS2

Freq.= -332.4078

O	2.133581000	1.058376000	-2.374951000
B	1.482060000	1.217567000	-1.122751000
O	2.348885000	0.767933000	0.043760000
B	0.132524000	-0.962238000	0.124486000
O	0.989084000	-2.125006000	-0.013861000
O	0.482077000	-0.213297000	1.314237000
C	-3.092607000	2.082897000	1.071459000
C	-2.104877000	1.353356000	0.381024000
C	-2.300691000	-0.017735000	0.066475000
H	-1.186894000	1.871499000	0.050026000
H	-2.915880000	3.147230000	1.297214000
C	-4.297130000	1.473080000	1.456007000
C	-3.526536000	-0.614117000	0.456769000
C	-1.245238000	-0.849945000	-0.583965000
H	-5.069520000	2.048077000	1.990908000
C	-4.509879000	0.118132000	1.137685000
H	-3.706564000	-1.675608000	0.217475000
H	-5.454746000	-0.373233000	1.422137000
H	-1.656540000	-1.749323000	-1.082045000
C	-0.118860000	-0.112714000	-1.433252000
H	0.195513000	-0.762731000	-2.271545000
H	-0.550515000	0.818460000	-1.840778000
O	0.892066000	2.433692000	-0.824747000
H	0.627464000	2.872683000	-1.680189000
H	-0.235509000	0.425527000	1.524124000
O	0.724103000	3.126185000	-3.466255000
H	1.402981000	3.824560000	-3.541136000
H	1.271619000	2.299090000	-3.431108000
O	3.232335000	-1.364316000	-1.078814000
H	4.007157000	-1.873020000	-0.776165000
H	2.409298000	-1.844368000	-0.716168000
H	1.661957000	0.440875000	0.785143000
H	0.482805000	-2.866117000	-0.389778000
H	2.554365000	0.178719000	-2.457645000
H	2.867540000	-0.059591000	-0.275615000

C

O	2.449130000	-0.860008000	-2.258233000
B	1.596906000	-1.254674000	-1.166063000
O	1.443707000	-2.733486000	-1.146062000
B	-0.424321000	-1.505682000	1.253998000
O	0.556750000	-2.459268000	1.394761000
O	-0.867505000	-0.928789000	2.398720000
C	-3.325804000	1.837082000	0.445959000
C	-2.156610000	1.079924000	0.328643000
C	-2.191531000	-0.247679000	-0.138480000
H	-1.197762000	1.534241000	0.592362000
H	-3.269726000	2.866196000	0.809819000
C	-4.560453000	1.284988000	0.095321000
C	-3.441861000	-0.784542000	-0.485195000
C	-0.933942000	-1.085032000	-0.206815000
H	-5.474808000	1.876066000	0.184622000
C	-4.612414000	-0.030554000	-0.373154000
H	-3.495262000	-1.814603000	-0.848925000
H	-5.571232000	-0.473990000	-0.653512000
H	-1.201490000	-2.033763000	-0.708299000
C	0.204611000	-0.433974000	-1.048630000
H	-0.189821000	-0.255608000	-2.067181000
H	0.431854000	0.569301000	-0.645861000
O	2.436559000	-0.989525000	0.164387000
H	3.418647000	-1.315854000	0.089200000
H	2.002927000	-1.456015000	0.915801000
O	4.792584000	-1.854729000	-0.119722000
H	5.388094000	-1.153571000	-0.418958000
H	4.630935000	-2.420328000	-0.937897000
O	3.987866000	-3.087898000	-2.279454000
H	3.642472000	-2.243902000	-2.639976000
H	3.163521000	-3.414986000	-1.867607000
H	-1.555122000	-0.269655000	2.226941000
H	0.779216000	-2.868422000	0.527858000
H	2.248110000	0.026808000	-2.574018000
H	0.804627000	-2.995033000	-1.821309000

$B_2(OH)_4$. $2H_2O$ (eq. 1)

B	-0.892900000	0.952575000	1.525039000
B	-0.931531000	0.094773000	3.030325000
O	0.128834000	1.732973000	1.050245000
H	0.853939000	1.820934000	1.677848000
O	-1.925314000	0.760337000	0.642811000
H	-2.658551000	0.254401000	1.061175000
O	-0.871285000	-1.275179000	2.997356000
H	-0.652647000	-1.597870000	2.093670000
O	-1.134863000	0.629479000	4.275703000
H	-1.207790000	1.589635000	4.262352000
O	-0.526714000	-1.701313000	0.307851000
H	-1.092503000	-0.946086000	0.055023000
H	0.328015000	-1.491631000	-0.093790000
O	-3.554655000	-0.881013000	2.119505000
H	-2.805499000	-1.340856000	2.545838000
H	-4.047062000	-0.506961000	2.863424000

$B_2(OH)_4$. $4H_2O$ (eq. 3)

B	-0.947591000	0.910585000	1.442579000
B	-1.242259000	-0.047723000	2.852791000
O	0.158059000	1.694370000	1.227070000
H	0.751671000	1.725280000	1.984693000
O	-1.789140000	0.777293000	0.378438000

H	-2.626061000	0.291864000	0.628261000
O	-1.007259000	-1.397709000	2.786853000
H	-0.685901000	-1.644209000	1.883847000
O	-1.746068000	0.388119000	4.062135000
H	-1.878183000	1.343106000	4.081396000
O	-4.465451000	-0.588369000	3.883583000
H	-4.274315000	-1.540011000	3.767842000
H	-3.624695000	-0.249951000	4.237535000
O	-3.854939000	-0.617701000	1.234388000
H	-3.678983000	-1.567089000	1.367215000
H	-4.215635000	-0.375779000	2.123005000
O	-0.430699000	-1.684007000	0.170039000
H	-0.951048000	-0.890924000	-0.078377000
H	0.455246000	-1.493422000	-0.168819000
O	-3.290654000	-2.868726000	2.834669000
H	-2.387378000	-2.503627000	2.975212000
H	-3.216097000	-3.827283000	2.922169000

A’

B	0.180190000	0.146512000	-0.462876000
C	1.129443000	-2.455603000	2.346762000
O	0.513968000	-1.229156000	1.871084000
B	0.587046000	-1.214180000	0.501749000
O	1.022172000	-2.409724000	-0.010271000
C	1.063432000	-3.379810000	1.069767000
C	-0.228994000	-4.194252000	0.979342000
H	-0.298387000	-4.639519000	-0.023771000
H	-0.249982000	-5.005486000	1.721650000
H	-1.113385000	-3.558602000	1.130372000
C	2.271148000	-4.286077000	0.871234000
H	2.381448000	-4.979121000	1.719587000
H	2.138596000	-4.883557000	-0.042811000
H	3.198105000	-3.708584000	0.765551000
C	2.558661000	-2.098640000	2.761250000
H	2.520494000	-1.293220000	3.509019000
H	3.079513000	-2.959797000	3.204734000
H	3.145224000	-1.738231000	1.903903000
C	0.345222000	-2.965666000	3.548479000
H	-0.722761000	-3.071420000	3.320123000
H	0.733557000	-3.940622000	3.881389000
H	0.444197000	-2.255701000	4.382856000
O	-0.198761000	1.333877000	0.091552000
H	-0.198997000	1.283360000	1.054889000
O	0.218462000	0.098443000	-1.825616000
H	0.494332000	-0.772617000	-2.135028000

IN1’

O	-2.732898000	0.374947000	-0.754177000
B	-1.816272000	-0.629445000	0.145399000
O	-2.377365000	-0.645617000	1.477944000
O	-2.054945000	-1.915557000	-0.508033000
H	-3.806795000	-1.891407000	-1.166216000
H	-1.765414000	-2.623961000	0.078773000
O	-4.543378000	-1.250336000	-1.283339000
H	-3.559116000	-0.177646000	-1.099192000
H	-4.932354000	-1.221457000	-0.368779000
O	-5.058743000	-0.928378000	1.336167000
H	-5.335930000	-0.007217000	1.438499000
H	-4.090534000	-0.896777000	1.543425000
H	-2.180439000	0.666245000	-1.499596000
H	-1.907629000	-0.050257000	2.070824000
O	-0.037365000	0.782275000	-1.257469000
C	1.388700000	0.910213000	-1.480245000
C	1.964185000	0.651815000	-0.036815000
C	1.778033000	-0.174747000	-2.487249000
C	1.682435000	2.290827000	-2.052036000
B	-0.237778000	0.013550000	-0.119739000
O	0.934843000	-0.172507000	0.566158000
C	2.063973000	1.925130000	0.806914000
C	3.284603000	-0.106721000	-0.000953000
H	2.259030000	1.642619000	1.851719000
H	2.880415000	2.578392000	0.465410000
H	1.124043000	2.495270000	0.778188000
H	4.072051000	0.453715000	-0.528646000
H	3.603519000	-0.244229000	1.042853000
H	3.191834000	-1.099801000	-0.458327000
H	1.172128000	-0.048714000	-3.396450000
H	2.840116000	-0.110748000	-2.766033000
H	1.578952000	-1.178721000	-2.085801000
H	1.262344000	3.087053000	-1.424504000
H	2.767679000	2.451573000	-2.146221000
H	1.237445000	2.379189000	-3.054451000

TS1’

O	-2.803413000	0.158515000	-0.521912000
B	-2.020399000	-1.143998000	-0.319943000
O	-1.950307000	-1.573332000	1.026678000
C	3.670341000	-1.621463000	1.394101000
C	2.549770000	-1.621840000	0.565907000
C	2.555554000	-0.933125000	-0.669046000
H	1.650671000	-2.147115000	0.888601000
H	3.634685000	-2.160706000	2.344450000
C	4.831376000	-0.932267000	1.027705000
C	3.740763000	-0.245891000	-1.023545000
C	1.406572000	-0.873748000	-1.550501000
H	5.705016000	-0.930891000	1.683472000
C	4.858180000	-0.245915000	-0.191724000
H	3.776598000	0.287312000	-1.977481000
H	5.759206000	0.292536000	-0.497109000
H	1.505087000	-0.246831000	-2.439081000
C	0.185004000	-1.589986000	-1.401498000
H	-0.430823000	-1.738266000	-2.291040000
H	0.175162000	-2.460761000	-0.736894000
O	-2.567052000	-2.090487000	-1.219681000
H	-4.588358000	-1.533870000	-1.469977000
H	-2.325009000	-2.983823000	-0.948513000
O	-5.028144000	-0.770485000	-1.052273000
H	-3.772135000	-0.045902000	-0.873412000
H	-5.082471000	-1.059350000	-0.099841000
O	-4.630010000	-1.431048000	1.527379000
H	-4.714956000	-0.640401000	2.077897000
H	-3.654910000	-1.592963000	1.503720000
H	-2.177837000	0.790726000	-1.003713000
H	-1.245091000	-1.057892000	1.463980000
O	-0.622055000	1.058959000	-1.203483000
C	-0.027250000	2.131886000	-0.434961000
C	0.165510000	1.488129000	1.009672000
C	1.290097000	2.527418000	-1.104634000

C	-0.984279000	3.320649000	-0.472867000
B	-0.246390000	-0.194386000	-0.579874000
O	0.132947000	0.072975000	0.769801000
C	-0.986649000	1.806831000	1.970326000
C	1.497598000	1.838294000	1.671037000
H	-0.854569000	1.210528000	2.885961000
H	-1.000751000	2.868154000	2.258216000
H	-1.959145000	1.546755000	1.530798000
H	1.590248000	2.924589000	1.826087000
H	1.554175000	1.345591000	2.652751000
H	2.348435000	1.485563000	1.076594000
H	1.091888000	2.766436000	-2.159905000
H	1.726398000	3.414937000	-0.624087000
H	2.029342000	1.721660000	-1.064620000
H	-1.989528000	3.054315000	-0.120339000
H	-0.608656000	4.144619000	0.151798000
H	-1.070081000	3.689377000	-1.505968000

B_H’

C	-5.526628000	-0.113253000	-1.033621000
C	-4.213875000	0.164529000	-0.655324000
C	-3.135362000	-0.287529000	-1.442401000
H	-4.006894000	0.733914000	0.252488000
H	-6.354211000	0.242453000	-0.415510000
C	-5.785530000	-0.843336000	-2.197966000
C	-3.406373000	-1.022715000	-2.614090000
C	-1.785864000	-0.004469000	-1.057384000
H	-6.815325000	-1.059329000	-2.491568000
C	-4.722133000	-1.296145000	-2.985212000
H	-2.573283000	-1.374118000	-3.225357000
H	-4.919599000	-1.866900000	-3.895558000
C	-0.641628000	0.235713000	-0.730829000
H	0.370122000	0.448205000	-0.442303000

B_F’

C	3.072206000	0.974773000	0.758500000
C	1.774956000	0.773725000	1.221050000
C	1.123801000	-0.457763000	1.007951000
H	1.252088000	1.568185000	1.755698000
H	3.574049000	1.927809000	0.932487000
C	3.739622000	-0.048594000	0.076207000
C	1.807786000	-1.481766000	0.322717000
C	-0.209214000	-0.666690000	1.483360000
C	3.104990000	-1.277141000	-0.138461000
H	1.310390000	-2.439066000	0.159693000
H	3.632372000	-2.075814000	-0.662230000
C	-1.340622000	-0.844011000	1.884603000
H	-2.341491000	-1.000081000	2.240447000
C	5.122215000	0.190722000	-0.472995000
F	5.812985000	1.066644000	0.277090000
F	5.838647000	-0.944985000	-0.535619000
F	5.076079000	0.694638000	-1.721480000

TS1_H’’

O	2.351807000	-0.676137000	0.848010000
B	1.967616000	0.123279000	-0.418504000
O	2.267004000	1.505664000	-0.312767000
B	0.027765000	0.011657000	-0.034406000
O	-0.079473000	-1.095371000	0.914325000
O	-0.224169000	1.324378000	0.481762000
C	-4.456626000	1.254783000	0.049327000
C	-3.262118000	1.093095000	-0.653241000
C	-2.627591000	-0.173011000	-0.698170000
H	-2.814056000	1.931948000	-1.188982000
H	-4.939437000	2.234923000	0.068765000
C	-5.037901000	0.175708000	0.721903000
C	-3.220418000	-1.258541000	-0.006980000
C	-1.364598000	-0.319590000	-1.317726000
H	-5.974343000	0.308203000	1.267994000
C	-4.412257000	-1.077178000	0.689340000
H	-2.728189000	-2.231671000	-0.030413000
H	-4.861631000	-1.923994000	1.214022000
C	-0.153990000	-0.377323000	-1.656554000
H	0.570458000	-0.617745000	-2.430184000
O	2.625879000	-0.506005000	-1.517995000
H	4.293675000	-1.424062000	-0.727041000
H	2.839067000	0.168661000	-2.174681000
O	4.622951000	-1.431022000	0.191716000
H	3.254443000	-1.179457000	0.711619000
H	4.910656000	-0.485833000	0.310687000
O	4.836584000	1.243527000	0.551939000
H	4.743657000	1.386690000	1.504232000
H	3.954148000	1.517731000	0.198778000
H	-1.152436000	1.491921000	0.704365000
H	-0.716869000	-0.908984000	1.616792000
H	1.528299000	-1.164552000	1.144548000
H	1.511310000	1.956587000	0.107248000

TS1_CF_3’’

O	2.318207000	-0.701236000	0.852647000
B	1.957170000	0.132383000	-0.397490000
O	2.264102000	1.509292000	-0.254042000
B	0.009759000	0.025421000	-0.049528000
O	-0.143095000	-1.084450000	0.873026000
O	-0.275182000	1.331369000	0.443311000
C	-4.447606000	1.263560000	0.036201000
C	-3.273627000	1.103020000	-0.694221000
C	-2.648258000	-0.167368000	-0.776924000
H	-2.831858000	1.948936000	-1.222744000
H	-4.928498000	2.241883000	0.085111000
C	-5.021479000	0.174874000	0.703119000
C	-3.239256000	-1.261469000	-0.093512000
C	-1.407232000	-0.315837000	-1.427585000
C	-4.410032000	-1.085794000	0.632500000
H	-2.761530000	-2.240051000	-0.148893000
H	-4.863237000	-1.934812000	1.147476000
C	-0.174440000	-0.355291000	-1.686668000
H	0.575047000	-0.584273000	-2.439242000
O	2.617160000	-0.475800000	-1.503079000
H	4.299815000	-1.441847000	-0.702439000
H	2.832513000	0.207425000	-2.150271000
O	4.589858000	-1.445813000	0.228738000
H	3.232579000	-1.198618000	0.716291000

H	4.886072000	-0.502834000	0.355955000
O	4.839835000	1.213187000	0.591556000
H	4.781689000	1.384759000	1.541844000
H	3.957546000	1.504106000	0.253256000
H	-1.182274000	1.456884000	0.760749000
H	-0.783369000	-0.902758000	1.574377000
H	1.501092000	-1.201473000	1.126769000
H	1.511672000	1.963711000	0.164810000
C	-6.254600000	0.363039000	1.542601000
F	-7.000116000	1.398225000	1.118022000
F	-7.036272000	-0.731677000	1.536553000
F	-5.944356000	0.609567000	2.833165000

X. References

1. Y. Zhang, X. Zhao, C. Bi, W. Lu, M. Song, D. Wang and G. Qing, *Green Chem.*, 2021, **23**, 1691-1699.
2. K. S. Patil, Shivakumar R, R. Kumar, M. V. Mane and S. K. Bose, *J. Org. Chem*. 2025, **90**, 4140-4148
3. S. A. Rzhevskiy, M. A. Topchiy, K. A. Lyssenko, A. N. Philippova, M. A. Belaya, A. A. Ageshina, M. V. Bermeshev, M. S. Nechaev and A. F. Asachenko, *J. Organomet. Chem*., 2020, **912**, 121140.
4. (a) A. Paptchikhine, P. Cheruku, M. Engman and P. G. Andersson, *Chem. Commun.*, 2009, 5996-5998; (b) B. Zhang, X. Xu, L. Tao, Z. Lin and W. Zhao, *ACS Catal.* 2021, **11**, 9495–9505.
5. M. Huang, J. Hu, S. Shi, A. Friedrich, J. Krebs, S. A. Westcott, U. Radius and T. B. Marder, *Chem. Eur. J.*, 2022, **28**, e202200480.
6. (a) J. Ramírez, A. M. Segarra and E. Fernández, *Tetrahedron: Asymmetry*, 2005, **16**, 1289-1294; (b) A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás and E. Fernández, *Angew. Chem. Int. Ed* 2011, **50**, 7158–7161; (c) A. Bonet, C. Sole, H. Gulyás and E. Fernández, *Org. Biomol. Chem.* 2012, **10**, 6621-6623.
7. G. Gao, J. Yan, K. Yang, F. Chen and Q. Song, *Green Chem.*, 2017, **19**, 3997–4001.
8. Z. Kuang, S. Mai, K. Yang and Q. Song, *Sci. Bull.*, 2019, **64**, 1685–1690.
9. B. Zhang, X. Xu, L. Tao, Z. Lin and W. Zhao, *ACS Catal.*, 2021, **11**, 9495–9505.
10. G. L. Gao, Z. J. Kuang and Q. L. Song, *Org. Chem. Front.*, 2018, **5**, 2249–2253.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 2016, 16, Revision C.02. Gaussian, Inc.: Wallingford CT.

12 A. Becke, *Phys. Rev. A*, 1988, **38**, 3098−3100.
13 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822−8824.
14 J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406−7406.
15 S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 2011, **32**, 1456−1465.
16 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
17 F. Weigend, R. Ahlrichs, *Phys.Chem. Chem. Phys.* 2005, **7**, 3297−3305.