Supporting Information for

Boron-Templated Dimerization of Allylic Alcohols to Form Protected 1,3-Diols via Acid Catalysis.

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General Information

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. Solvents were dried by J. C. Meyer's Solvent Purification System. Reactions requiring a moisture or oxygen-free environment were done in a nitrogen atmosphere glove box (Innovative Technology, PreLab HE system, double glove box). Flash chromatography was performed with Sorbtech silica gel (0.040-0.063µm grade). Analytical thin-layer chromatography was done with 0.25 mm coated commercial silica gel plates (Merck KGaA, DC silicagel 60 F_{254}). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on an Inova 300 (300 MHz), Inova-500 (500 MHz) or Bruker (500MHz) spectrometer. Chemical shifts are reported in delta (δ) units relative to the ^{2}H signal of the $CDCl_3$ solvent. Carbon-13 and Boron-11 nuclear magnetic resonance (^{13}C-NMR and ^{11}B-NMR) data were acquired on an Inova 500 at 125 MHz. Signals are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), qd (quartet of doublets), brs (broad singlet), m (multiplet). Coupling constants are reported in hertz (Hz). Chemical shifts are reported in ppm relative to the center line of a triplet at 77.23 ppm for chloroform-d for ^{13}C-NMR or the singlet at 0 ppm for $BF_3 \cdot O(Et)_2$ for ^{11}B-NMR. Infrared (IR) data were recorded as films on sodium chloride plates on a Thermo Scientific Nicolet IR 100 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Chiral HPLC analyses were performed on a Thermo Separation Products Spectra Series P-100 or 200 and UV100 using Chiralcel ® columns. Optical rotations were measured on a Jasco P-2000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated. Mass spectral data were obtained using ESI techniques (Agilent, 6210 TOF).

General Synthesis of Allylic Alcohols

Alcohols were prepared from aldehyde starting material, using a Horner Wadsworth Emmons reaction followed by a DIBAL reduction. An example is shown below.

To a dry flask with dry THF (25 mL) and sodium hydroxide 60% in mineral oil (17.8 mmol) Triethyl phosphonoacetate (17.8 mmol) was added dropwise. After stirring for one hour, 4-ethyl benzaldehyde (17 mmol) was added. The reaction proceeded overnight. After workup with aqueous $NaHCO_3$, product was purified by column chromatography with 15% ethyl acetate in hexanes as the eluent.

To a flame dried flask with dry DCM (15 mL) and ethyl (*E*)-3-(4-ethylphenyl)acrylate (4 mmol), DIBAL (8.1 mmol) was added dropwise at -78 C. The reaction was allowed to return to room temperature and continued for 2 h. After quenching with water, the product was extracted with ethyl acetate, the organics were dried over Na_2SO_4, the solvent was removed, and the product was purified by column chromatography on silica gel with 25% ethyl acetate in hexanes as the eluent.

Additional Optimization Studies:

Cat. (mol%)	Ligand	Solvent	T (°C)	Time (h)	Yield	D.R.
$Cu(OTf)_2$ (10)	Dppf (10)	Toluene	60	16	42	-
$Cu(OTf)_2$ (10)	-	Toluene	60	16	24	-
$Cu(OTf)_2$ (10)	PPh3	Toluene	60	16	43	-
$Cu(OTf)_2$ (10)	PPh3	DCE	60	16	54	-
$Cu(OTf)_2$ (10)	pcy3	Toluene	60	16	25	-
$Cu(OTf)_2$ (10)	bipy	Toluene	60	16	43	-
$Cu(OTf)_2$ (10)	bipy	DCE	60	16	47	-
$Cu(OTf)_2$ (10)	BINAP	Toluene	60	16	55	-
$Cu(OTf)_2$ (10)	BINAP	Dioxane	60	16	10	-
$Cu(OTf)_2$ (10)	BINAP	THF	60	16	15	-
$CuCl_2$(10)	dppf	Toluene	60	16	-	-
$Cu(OAC)_2$(10)	dppf	Toluene	60	16	-	-
TfOH (10)	-	Toluene	r.t	12	95	10 to 1
TfOH (10)	-	DCE	r.t	12	95	10 to 1
TfOH (5)	-	DCE	r.t	12	30	10 to 1
TfOH (10)	-	Toluene	60	12	90	10 to 1

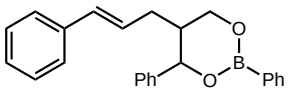
Control Studies:

To control for a hydronium effect 4 angstrom molecular sieves were added to soak up the water and reduce the potential hydronium effect. Additional studies were performed with substoichiometric phenyl boronic acid to determine the importance of equal equivalence and the acidifying effect of the phenyl boronic acid. Yields were reported based off of the phenyl boronic acid starting material. No reduction in yield was seen to indicate a controlling hydronium effect.

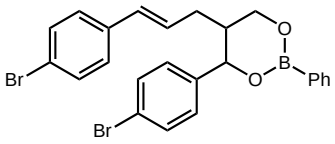
$PhB(OH)_2$ eq	Molecular Sieves	Yield
1	no	95%
0.5	no	96%
0.25	no	98%
1	yes	95%

Synthesis of dioxaborinanes via boron templated catalysis

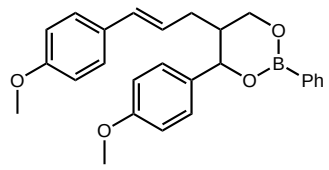
General Procedure:
In a flame dried flask, allylic alcohol (2 mmol) and phenyl boronic acid (1 mmol) were stirred in toluene (1 mL) for 10 minutes. Triflic acid (0.1 mmol) was added dropwise and the reaction was allowed to proceed for 12 h. At the conclusion of the reaction, the mixture was filtered through a plug of silica gel in a pipet and rinsed through with CH_2Cl_2, the solvent was removed, and the product was loaded directly onto a column of silica gel and eluted with mixtures of ethyl acetate or CH_2Cl_2 and hexanes with 1% triethylamine to deactivate the silica gel. The diastereoselectivity of each transformation was determined by integration of the peaks near 5-5.5 ppm corresponding to the benzylic proton of the dioxaborinane ring.



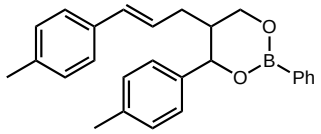
5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane (2a): Synthesized according to the general procedure using cinnamyl alcohol (1.5 g, 11.18 mmol), phenyl boronic acid (0.682 g, 5.59 mmol) and triflic acid (83.8 mg). The reaction was purified by flash chromatography with 70% DCM 30% hexanes as the eluent, 1% triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a clear oil (1.9 g, 96 % yield, 14:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.88 (d, *J*=7.0, 2H); 7.50-7.21 (m, 13H); 6.41 (d, *J*=15.9 Hz, 1H); 6.09 (td, *J*=15.7 Hz, 6.7Hz, 1H); 5.00 (d, *J*=7.3 Hz, 1H); 4.21 (dd, *J*=10.7, 3.1 Hz, 1H); 3.99 (dd, *J*=11.8, 8.0 Hz,1H); 2.39-2.32 (m, 1H); 2.24-2.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4 ; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.0; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed to gather MS data: HRMS(EI) calculated for $C_{18}H_{21}O_2$, [M+H]+; 269.1542, found 269.1545



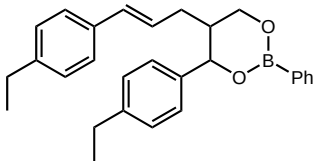
(E)-4-(4-bromophenyl)-5-(3-(4-bromophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2b): Synthesized according to the general procedure using 4-bromo cinnamyl alcohol (170.4 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 70% DCM 30% hexanes as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a brown oil (204 mg, 56%, 14:1 DR). R_f: 0.7 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.52-7.38 (m, 5H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.10-6.00 (m, 1H), 4.96 (d, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 11.7, 3.3 Hz, 1H), 4.02-3.96 (m, 1H), 2.36-2.28 (m, 1H), 2.25-2.13 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 140.3, 135.9, 134.0, 131.7, 131.6, 131.0, 128.4, 128.2, 127.7, 127.6, 126.9, 122.0, 121.1, 69.9, 64.5, 43.0, 32.3; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53; IR (film) νmax 3025, 2920, 1900, 1599, 1311, 1259, 641; HRMS(EI) calculated for $C_{24}H_{21}BBr_2O_2Na$, [M+Na] 534.9873, found 534.9871.



(E)-4-(4-methoxyphenyl)-5-(3-(4-methoxyphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2c): Synthesized according to the general procedure using 4-methoxy cinnamyl alcohol (131.4 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a yellow oil (153.6 mg, 96 %, 10:1 DR). R_f: 0.6 in DCM; ^{1}H NMR (500MHz, $CDCl_3$), δ 7.88 (d, *J*=7.7Hz, 2H); 7.49-7.44 (m, 1H); 7.41-7.36 (m, 2H); 7.31 (d, *J*=8.4 Hz, 2H); 7.28-7.23 (m, 2H) 6.96 (d, *J*=8.4 Hz, 2H); 6.86 (d, *J*=8.4 Hz, 2H); 6.36 (d, *J*=15.5 Hz, 1H); 5.92 (dt, *J*=15.4 Hz, 7.9, 1H); 4.93 (d, *J*=8.5 Hz, 1H); 4.23 (dd, *J*=4.1, 11.88 Hz, 1H); 3.98 (dd, *J*=8.5, 11.2 Hz, 1H); 3.85 (s, 3H); 3.82 (s, 3H); 2.32-2.27 (m, 1H); 2.18-2.10 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 159.4, 159.0, 134.1, 134.0, 133.6, 131.8, 130.8, 130.0, 127.8, 127.7, 127.6, 127.3, 127.2, 127.1, 127.1, 124.2, 114.0, 113.9, 113.8, 77.7.7, 65.0, 55.3, 55.3, 46.1, 43.4, 32.3; ^{11}B NMR (160 MHz, $CDCl_3$) δ 27.53; IR (film) νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed to gather MS data HRMS(EI) calculated for $C_{20}H_{24}O_4Na$, [M+Na]+; 351.1567, found 351.1570.

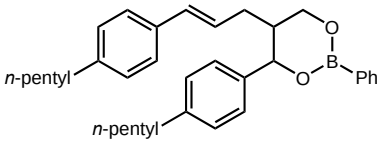


(E)-2-phenyl-4-(p-tolyl)-5-(3-(p-tolyl)allyl)-1,3,2-dioxaborinane (2d): Synthesized according to the general procedure using 4-methyl cinnamyl alcohol (59.2 mg, 0.4 mmol), phenyl boronic acid (24.4 mg, 0.2 mmol) and triflic acid (0.2 uL, .02 mmol). The reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a yellow oil (59.2 mg, 90.5 %, 9:1 DR). R_f: 0.8 in DCM; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 15.5 Hz, 1H), 6.02 (dt, *J* = 8.8, 15.7 Hz, 1H), 4.96 (d, *J* = 7.0 Hz, 1H), 4.23 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.00-3.97 (m, 1H), 2.41 (s, 3H), 2.36 (s, 3H), 2.21-2.14 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 138.5, 137.7, 137.1, 134.4, 134.1, 134.0, 132.3, 130.8, 129.3, 129.2, 129.2, 127.6, 126.5, 126.0, 125.4, 77.9, 64.7, 43.3, 32.4, 21.2; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53; IR (film)νmax 3023, 2920, 1901, 1600, 1312, 1260; Boron removed HRMS(EI) calculated for $C_{20}H_{24}O_2Na$, [M+Na]+; 319.1669, found 319.1671.

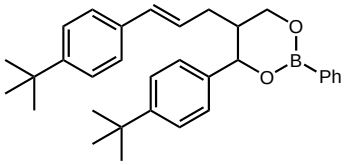


(*E*)-4-(4-ethylphenyl)-5-(3-(4-ethylphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2e): Synthesized according to the general procedure using 4-ethylcinnamyl alcohol (129.8 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The

reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and partial hydrolysis of the boronic ester. The product was isolated as a yellow oil (157 mg, 95 %, 11:1 DR). R_f: 0.1 in 1:1 DCM:hexanes ^{1}H NMR (500MHz, $CDCl_3$), δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 15.5 Hz, 1H), 6.02 (dt, *J*=8.8, 15.7 Hz, 1H), 4.96 (d, *J* = 7 Hz, 1H), 4.23 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.00-3.97 (m, 1H), 2.69 (q, *J* = 7.6 2H), 2.64 (q, *J* = 7.6, 2H) 2.39-2.32 (m, 1H), 2.24-2.16 (m, 2H), 1.28 (t, *J* =7.5, 3H), 1.24 (t, J = 7.6, 3H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 138.5, 137.7, 137.1, 134.4, 134.1, 134.0, 132.3, 130.8, 129.3, 129.2, 129.2, 127.6, 126.5, 126.0, 125.4, 77.9, 64.7, 43.2, 32.4, 21.2, 21.2 ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated For $C_{22}H_{28}O_2Na$, [M+Na]+; 347.1982, found 347.1980 .

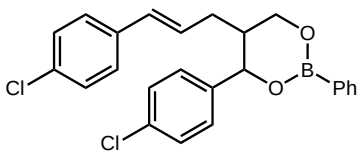


(E)-4-(4-pentylphenyl)-5-(3-(4-pentylphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2f): Synthesized according to the general procedure using 4-pentyl cinnamyl alcohol (163.4 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a yellow oil (120.6 mg, 61%, 10:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.48-7.11 (m, 11H), 6.37 (d, *J* = 15.5 Hz, 1H), 6.04-5.98 (m, 1H), 4.96 (d, *J* = 7.0 Hz, 1H), 4.21 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.97 (dd, *J* = 11.0, 7.5 Hz, 1H), 2.65- 2.57 (m, 4H), 2.35-2.30 (m, 1H), 2.20-2.15 (m, 2H), 1.66-1.58 (m, 4H), 1.36-1.32 (m, 8H), 0.93-0.89 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 142.8, 142.2, 138.6, 134.6, 134.0, 132.3, 130.8, 128.6, 128.5, 127.6, 126.4, 126.2, 126.0, 125.9, 125.7, 125.4, 125.4, 77.9, 64.7, 43.2, 35.7, 35.6, 32.4, 31.6, 31.5, 31.4, 31.3, 31.2, 31.1, 29.7, 22.6, 22.6, 14.1, 14.0; ^{11}B NMR (160 MHz, $CDCl_3$), δ 25.39; IR (film)νmax 3050, 3023, 2930, 2857, 1701, 1605, 1312, 1144; HRMS(EI) calculated for $C_{34}H_{44}BO_2$, [M+H]+; 495.3434 found 495.3432.

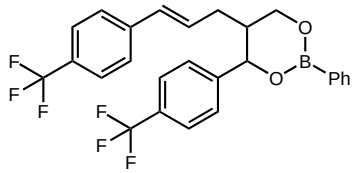


(E)-4-(4-(tert-butyl)phenyl)-5-(3-(4-(tert-butyl)phenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2g): Synthesized according to the general procedure using 4-tert butyl cinnamyl alcohol (152.2 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a light yellow solid (87.7 mg, 47%, 11:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; Melting point 86-112 °C; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.47-7.23 (m, 11H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.03-5.97 (m, 1H), 4.96 (d, *J* = 7.0Hz, 1H), 4.20 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.96 (dd, *J* = 11.5, 8.0 Hz, 1H), 2.37-2.31 (m, 1H), 2.21-2.14 (m, 2H), 1.34 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 150.9, 150.4, 138.4, 134.4,

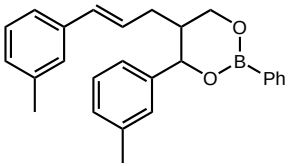
134.0, 132.1, 130.8, 127.6, 126.2, 125.8, 125.5, 125.4, 77.9, 69.9, 64.8, 43.2, 34.6, 34.5, 32.5, 31.4, 31.3; ^{11}B NMR (160 MHz, $CDCl_3$), δ 26.65; IR (film)νmax 3026, 2962, 2903, 2868, 1714, 1601, 1314, 1268, 1143; Boron removed for MS. HRMS(EI) calculated for $C_{26}H_{36}O_2Na$, [M+Na]+; 403.2608, found 403.2609.



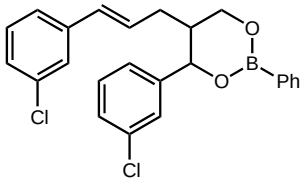
(*E*)-4-(4-chlorophenyl)-5-(3-(4-chlorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2h)
Synthesized according to the general procedure using 4-chloro cinnamyl alcohol (134.89 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol), triflic acid (0.4 uL, .04 mmol) and DCE (.4 mL) at 45 ^{o}C. The reaction was purified by flash chromatography with 50% DCM 50% hexanes as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a light-yellow oil (131 mg, 77%, 8:1 DR). R_f: 0.7 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.4Hz, 2H), 7.52-7.38 (m, 5H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.10-6.00 (m, 1H), 4.96 (d, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 11.7, 3.3 Hz, 1H), 4.02-3.96 (m, 1H), 2.36-2.28 (m, 1H), 2.25-2.13 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 140.3, 135.9, 134.0, 131.7, 131.6, 131.0, 128.3, 128.2, 127.7, 127.6, 126.9, 122.0, 121.1, 69.9, 64.5, 43.0, 32.3; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53; IR (film) νmax 3025, 2920, 1900, 1599, 1311, 1259, 641; boron removed for MS. HRMS(EI) calculated for $C_{18}H_{19}Cl_2O_2$, [M+H]+; 337.0757, found 337.0761



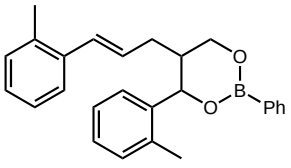
(E)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-5-(3-(4-(trifluoromethyl)phenyl)allyl)-1,3,2-dioxaborinane (2i):
Synthesized according to the general procedure using 4-trifluoro methyl cinnamyl alcohol (161.7 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a yellow oil (33.3 mg, 17%, 10:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.92-7.87 (m, 2H), 7.71 (d, *J*=8.2 Hz, 2H); 7.61-7.47 (m, 6H); 7.45-7.37 (m, 4H); 6.52-6.40 (m, 1H); 6.16 (dt, *J* = 7.0 Hz, 15.63, 1H); 5.07 (d, *J* = 7.3 Hz, 1H); 4.22 (dd, *J* = 4.1, 12.2 Hz, 1H); 4.07-3.98 (m, 1H); 2.45-2.19 (m, 3H); ^{13}C NMR (75.436 MHz, $CDCl_3$), δ 145.27, 140.29, 134.02, 131.66, 131.13, 130.64, 130.20, 129.12, 128.78, 127.74, 126.93, 126.26, 125.98, 125.64 (J=3.79, 7.38), 125.54 (J=3.66, 7.31), 64.40, 42.98, 32.34; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.41; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated for $C_{20}H_{19}F_6O_2$, [M+H]+; 405.1284, found: 405.1286.



(*E*)-2-phenyl-4-(*m*-tolyl)-5-(3-(*m*-tolyl)allyl)-1,3,2-dioxaborinane (2j):
Synthesized according to the general procedure using 3-methyl cinnamyl alcohol (118.6 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM as the eluent, 1% Triethyl amine was added to neutralize the eluent and prevent partial hydrolysis of the boronic ester. The product was isolated as a clear oil (125 g, 82%, 10:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 4H), 7.14 (d, *J* = 8 Hz, 2H), 6.38 (d, *J* = 15.5 Hz, 1H), 6.02 (dt, *J* = 8.8, 15.7Hz, 1H), 4.96 (d, *J* = 7 Hz, 1H), 4.23 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.00-3.97 (m, 1H), 2.41 (s, 3H), 2.36 (s, 3H), 2.21-2.14 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 138.5, 137.7, 137.1, 134.4, 134.1, 134.0, 132.3, 130.8, 129.3, 129.2, 129.2, 127.6, 126.5, 126.0, 125.4, 77.9, 64.7, 43.2, 32.4, 21.2; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53; IR (film)νmax 3023, 2920, 1901, 1600, 1312, 1260; Boron removed for MS. HRMS(EI) calculated for $C_{20}H_{24}O_2Na$, [M+Na]+; 319.1669, found 319.1669.

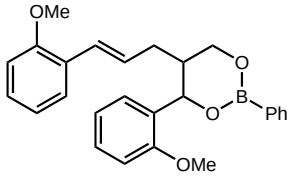


(*E*)-4-(3-chlorophenyl)-5-(3-(3-chlorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2k)
Synthesized according to the general procedure using 3-chloro cinnamyl alcohol (134.89 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol), triflic acid (0.4 uL, .04 mmol), and DCE (.4 mL) at 45 ^{o}C. The reaction was purified by flash chromatography with 50% DCM 50% hexanes and 1% triethylamine. The product was isolated as a light-yellow oil (101.5 mg, 60%, 10:1 DR). R_f: 0.7 in DCM; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.52-7.38 (m, 5H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.10-6.00 (m, 1H), 4.96 (d, *J* = 6.9 Hz, 1H), 4.21 (dd, *J* = 11.7, 3.3 Hz, 1H), 4.02-3.96 (m, 1H), 2.36-2.28 (m, 1H), 2.25-2.13 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 140.33, 135.86, 133.98, 131.68, 131.61, 131.01, 128.35, 128.25, 127.69, 127.59, 126.92, 121.98, 121.13, 69.89, 64.53, 43.04, 32.27; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53; IR (film) νmax 3025, 2920, 1900, 1599, 1311, 1259, 641; Boron removed for MS. HRMS(EI) calculated for $C_{18}H_{19}Cl_2O_2$, [M+H]+; 337.0757, found 337.0760

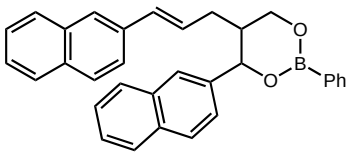


(*E*)-2-phenyl-4-(*o*-tolyl)-5-(3-(*o*-tolyl)allyl)-1,3,2-dioxaborinane (2l):
Synthesized according to the general procedure using 2-methyl cinnamyl alcohol (118.6 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The

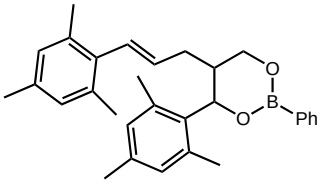
reaction was purified by flash chromatography with 100% DCM and 1% triethylamine. The product was isolated as a clear liquid (149.2 mg, 97.6%, 11:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.97 (d, *J* = 7.0 Hz, 2H); 7.58-7.18 (m, 11H); 6.71 (d, *J* = 16.1 Hz, 1H); 6.06 (dt, *J* = 7.0 Hz, 15.64, 1H); 5.40-5.33 (m, 1H); 4.32 (dd, *J* = 4.2, 11.98 Hz, 1H); 4.06 (dd, *J* = 6.6, 11.38 Hz, 1H); 2.49 (s, 3H); 2.468-2.265 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 139.4, 136.4, 135.1, 134.9, 134.1, 130.9, 130.8, 130.7, 130.3, 128.0, 127.7, 127.7, 127.3, 126.4, 126.2, 126.1, 125.6, 64.1, 41.8, 33.0, 20.0, 19.6; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53 ; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated for $C_{20}H_{24}O_2Na$, [M+Na]+; 319.1669, found 319.1670.



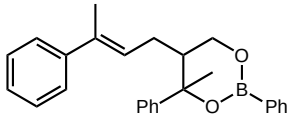
(*E*)-4-(2-methoxyphenyl)-5-(3-(2-methoxyphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2m): Synthesized according to the general procedure using 2-methoxy cinnamyl alcohol (131.4 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM and 1% triethylamine. The product was isolated as yellow oil (89.5 mg, 54%, 8:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.88 (d, *J* = 7.7 Hz, 2H); 7.49-7.44 (m, 1H); 7.41-7.36 (m, 2H); 7.31 (d, *J* = 8.4Hz, 2H); 7.28-7.23 (m, 2H) 6.96 (d, *J* = 8.4 Hz, 2H); 6.86 (d, *J* = 8.4 Hz, 2H); 6.36 (d, *J* = 15.5 Hz, 1H); 5.92 (dt, *J* = 7.8, 15.40 Hz, 1H); 4.93 (d, *J* = 8.5 Hz, 1H); 4.23 (dd, *J* = 4.1, 11.88 Hz, 1H); 3.98 (dd, *J* = 8.5, 11.2 Hz, 1H); 3.85 (s, 3H); 3.82 (s, 3H); 2.32-2.27 (m, 1H); 2.18-2.10 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 159.4, 159.0, 134.0, 134.0, 133.5, 131.8, 130.8, 130.0, 127.8, 127.7, 127.6, 127.3, 127.2, 127.1, 127.1, 124.2, 114.0, 113.9, 113.8, 77.7.7, 64.9, 55.3, 55.3, 46.1, 43.4, 32.4; ^{11}B NMR (160 MHz, $CDCl_3$) δ 27.53; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for HRMS(EI) calculated for $C_{20}H_{24}O_2Na$, [M+Na]+; 351.1567, found 351.1570.



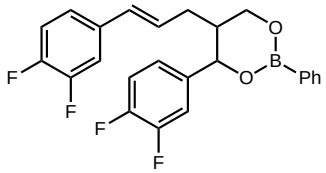
(E)-4-(naphthalen-2-yl)-5-(3-(naphthalen-2-yl)allyl)-2-phenyl-1,3,2-dioxaborinane (2n): Synthesized according to the general procedure using 3-(naphthalen-2-yl)prop-2-en-1-ol alcohol (147.4 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM and 1% triethylamine. The product was isolated as a yellow oil (96.3 mg, 53%). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500MHz, $CDCl_3$), δ 7.88 (d, *J* = 7.0 Hz, 2H); 7.50-7.21 (m, 17H); 6.41 (d, *J* = 15.9 Hz, 1H); 6.09 (dt, *J* = 15.7, 6.7 Hz, 1H); 5.00 (d, *J* = 7.3 Hz, 1H); 4.21 (dd, *J* = 10.7, 3.1 Hz, 1H); 3.99 (dd, *J* = 11.8, 8.0 Hz, 1H); 2.39-2.32 (m, 1H); 2.24-2.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; HRMS(EI) calcd. for $C_{32}H_{28}BO_2$, [M+H]+; 455.2177, found 455.2175.



(*E/Z*)-4-mesityl-5-(3-mesitylallyl)-2-phenyl-1,3,2-dioxaborinane (2o):
Synthesized according to the general procedure using (*E*)-3-mesitylprop-2-en-1-ol (141.0 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM and 1% triethylamine. The product was isolated as a yellow oil as a mixture of cis and trans isomers. (144.4 g, 82%, 8:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.98 (d, *J* = 7.0 Hz, 2H); 7.58-7.18 (m, 5H); 6.71 (d, *J* = 16.1 Hz, 1H); 6.06 (dt, *J* = 15.6, 7.1Hz, 1H); 5.40-5.33 (m, 1H); 4.32 (dd, *J* = 12.0, 4.2Hz, 1H); 4.06 (dd, *J* = 11.4, 6.6Hz, 1H); 2.49 (s, 3H); 2.47-2.26 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 139.4, 136.4, 135.1, 134.9, 134.1, 130.9, 130.8, 130.7, 130.3, 128.0, 127.7, 127.7, 127.3, 126.4, 126.2, 126.1, 125.6, 64.1, 41.8, 33.0, 19.9, 19.6; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.53 ; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated For $C_{24}H_{32}O_2Na$, [M+Na]+; 375.2295, found 375.2293

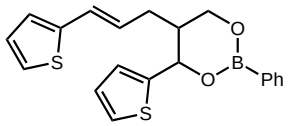


(*E*)-4-methyl-2,4-diphenyl-5-(3-phenylbut-2-en-1-yl)-1,3,2-dioxaborinane (2p):
Synthesized according to the general procedure using (*E*)-3-phenylbut-2-en-1-ol alcohol (118.6 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM and 1% triethylamine. The product was isolated as a clear oil (61.2 mg, 40%). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.95 (d, *J* = 7.0 Hz, 2H); 7.51-7.23 (m, 13H); 6.71 (d, *J* = 16.1 Hz, 1H); 6.06 (dt, *J* = 15.64, 7.0 Hz, 1H); 5.71-5.65 (m, 1H); 4.04-3.95 (m, *J* = 4.2, 11.98 Hz, 2H); 2.44-2.38 (m, 1H), 2.29-2.23 (m, 2H), 1.96 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 146.72, 143.58, 137.04, 134.04, 130.80, 128.36, 128.23, 127.70, 127.14, 126.83, 125.64, 125.26, 125.15, 63.01, 46.61, 25.75, 15.97; ^{11}B NMR (160 MHz, $CDCl_3$), δ ; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated For $C_{20}H_{24}O_2Na$, [M+Na]+; 319.1669, found 319.1668.

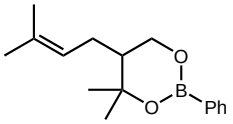


(E)-4-(3,4-difluorophenyl)-5-(3-(3,4-difluorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane (2q):
Synthesized according to the general procedure using (*E*)-3-(3,4-difluorophenyl)prop-2-en-1-ol (141 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM and 1% triethylamine. The product was isolated as a clear oil (44.3 mg, 26%, 10:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.87 (d, *J* = 7.0 Hz, 2H), 7.47-7.23 (m, 9H), 6.33

(d, *J* = 6.0 Hz, 1H), 6.05-5.95 (m, 1H), 4.95 (d, *J* = 7.0 Hz, 1H), 4.21 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.99 (dd, *J* = 11.5, 8.0 Hz, 1H), 2.37-2.25 (m, 1H), 2.22-2.14 (m, 2H);^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261 Boron removed for MS. HRMS(EI) calculated for $C_{18}H_{16}F_4O_2Na$, [M+Na]+; 363.0979, found 363.0980.

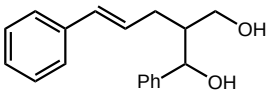


(E)-2-phenyl-4-(thiophen-2-yl)-5-(3-(thiophen-2-yl)allyl)-1,3,2-dioxaborinane (2r):
Synthesized according to the general procedure using (*E*)-3-(thiophen-2-yl)prop-2-en-1-ol (141 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 100% DCM and 1% triethylamine.
The product was isolated as a yellowish oil (90.8 mg, 62%, 8:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.86 (d, *J* = 7.0 Hz, 2H), 7.47-7.23 (m, 4H), 7.2-6.8 (m, 5H) 6.33 (d, *J* = 6.0 Hz, 1H), 6.05-5.95 (m, 1H), 5.21 (d, *J* = 7.0 Hz, 1H), 4.21 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.99 (dd, *J* = 11.5, 8.0 Hz, 1H), 2.37-2.25 (m, 1H), 2.22-2.14 (m, 2H);^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4 ; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated for $C_{14}H_{16}O_2S_2Na$, [M+Na]+; 303.0484, found 303.0485.



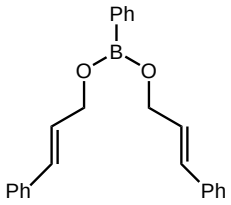
4,4-dimethyl-5-(3-methylbut-2-en-1-yl)-2-phenyl-1,3,2-dioxaborinane (2s):
Synthesized according to the general procedure using 3-methylbut-2-en-1-ol (68.9 mg, 0.8 mmol), phenyl boronic acid (48.8 mg, 0.4 mmol) and triflic acid (0.4 uL, .04 mmol). The reaction was purified by flash chromatography with 70% DCM 30% hexanes and 1% triethylamine. The product was isolated as an oil (87.8 mg, 85%, 8:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.84 (dd, *J* = 8.1, 1.7 Hz, 2H); 7.51-7.33 (m, 3H); 5.23-5.14 (m, 1H); 4.13 (dd, *J* = 11.6, 4.3 Hz, 1H); 3.95-3.77 (m, 1H); 2.40-2.33 (m, 1H); 2.22-2.13 (m, 1H); 1.93-1.88 (m, 1H); 1.77 (s, 3H); 1.67 (s, 3H); 1.48 (s, 3H); 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 133.7, 133.5, 130.4, 129.1, 128.2, 127.5, 121.8, 73.9, 63.1, 48.6, 33.9, 29.3, 26.4, 25.8, 23.8, 17.8; ^{11}B NMR (160 MHz, $CDCl_3$), δ 25.6; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed for MS. HRMS(EI) calculated for $C_{10}H_{20}O_2Na$, [M+Na]+; 195.1356, found 195.1351.

Derivatization Studies



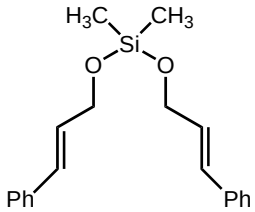
2-cinnamyl-1-phenylpropane-1,3-diol (3)
In a vial 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane (0.4 mmol, 141.7mg) and sodium hydroxide (2 mmol, 80mg) in a 1:1 solution of THF:H_2O (8 mL) was stirred at 60 °C for 20 h.

The product was then extracted from the mixture with DCM, and the combined organics were dried over sodium sulphate. The product was isolated as an oil (107.3 mg, 100%). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.50-7.21 (m, 10 H); 6.41 (d, *J*=15.9 Hz, 1H); 6.09 (dt, *J* = 15.7, 6.7 Hz, 1H); 5.00 (d, *J* =7.3, 1H); 4.21 (dd, *J*=10.73, 3.12 Hz, 1H); 3.99 (dd, *J* = 11.77, 7.96 Hz, 1H); 2.393-2.320 (m, 1H); 2.245-2.163 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4 ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; HRMS(EI) calculated for $C_{18}H_{21}O_2$, [M+H]+; 268.1463, found 268.1725



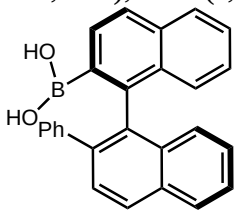
Dicinnamyl phenylboronate (4)

In a dry vial cinnamyl alcohol (0.8 mmol, 107.4 mg) and phenyl boronic acid (0.4 mmol, 48.8 mg) were stirred in toluene (0.4 mL) for 10 min at room temperature. The product was achieved in quantitative yield and used for the following reaction. The product was isolated as a clear oil (141.7 mg, >99%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.85 (d, *J* = 7.2 Hz, 1 H); δ 7.68 (d, *J* = 5.9 Hz, 1 H); δ 7.43-7.17 (m, 15 H); δ 6.67-6.57 (m, 2 H); δ 6.38-6.26 (m, 2 H); δ 4.71 (d, 4 H) ^{13}C NMR (126 MHz, $CDCl_3$), δ 137.0, 134.8, 133.6, 131.5, 130.7, 130.1, 128.7, 128.1, 128.0, 127.7, 126.6; HRMS(EI) calculated for $C_{24}H_{24}BO_2$, [M+H]+ 355.1864, found 355.1861



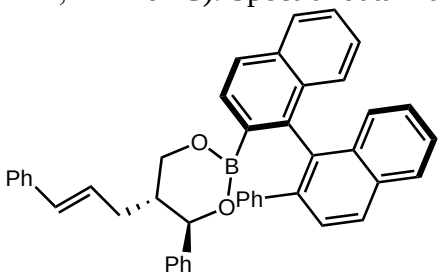
bis(cinnamyloxy)dimethylsilane (5)

In a dry vial, cinnamyl alcohol (7.5 mmol, 1.026 g) and triethylamine (7.8 mmol, 1.1 mL) were stirred for 5 minutes at room temperature in dichloromethane (8mL). Dimethyldichlorosilane (3.7 mmol, 0.45 mL) was added slowly and the reaction was stirred for 4 hours at room temperature. The solution was concentrated, washed with pentane, and filtered. The reaction was purified by flash chromatography with 5% methanol in dichloromethane. The product was isolated as an oil (817 mg, 68%). Characterization matched literature by Fleming, (*Tet. Lett.* **1992**, *33*, 1013-1016). ^{1}H NMR (500 MHz, CDCl3): δ = 7.38 (d, *J* = 8.5 Hz, 4 H), 7.31 (t, *J* = 8.0 Hz, 4 H), 7.25-7.23 (m, 2 H), 6.63-6.59 (m, 2 H), 6.36-6.29 (m, 2 H), 4.45- 4.44 (dd, *J* = 1.5, 5.5 Hz, 3 H), 4.43-4.41 (dd, *J* = 1.5, 5.5 Hz, 1 H), 0.26 (s, 4 H), 0.20 (s, 2 H).



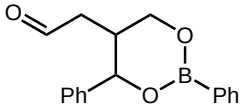
(2'-phenyl-[1,1'-binaphthalen]-2-yl)boronic acid (6)

Prepared following the procedure by Hisashi (*Synthesis*, **2017**, *49*, 175–180). A mixture of 1,1′-binaphthyl-2,2′-diboronic acid (3, 171 mg, 0.5 mmol, 1 equiv), $Pd(PPh_3)_4$ (14.4 mg, 2.5 mol%), $Ba(OH)_2 \cdot 8H_2O$ (315.5 mg, 1 mmol, 2 equiv), and iodobenzene (56 μL, 0.5 mmol, 1 equiv) in THF (5 mL) and water (1 mL) was heated at 60 °C for 14 h. The mixture was then allowed to cool down to r.t. The residue was extracted with CH_2Cl_2, washed with brine and dried (Na_2SO_4). After filtration and removal of solvent, the crude product was purified by column chromatography (hexane/EtOAc 4:1) to afford the product (136 mg, 73%) as a white solid. The enantiomeric excess of **6** was determined to be 96.4 percent ee by HPLC (Hexanes/iPrOH 80:20, flow rate = 1.0 mL/min, λ = 254 nm, T = 20 °C). Spectral data matched reported literature.



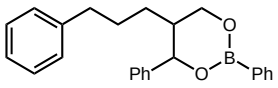
(4*R*,5*R*)-5-cinnamyl-4-phenyl-2-((*R*)-2'-phenyl-[1,1'-binaphthalen]-2-yl)-1,3,2-dioxaborinane (7)

In a flame dried vial cinnamyl alcohol (0.748 mmol, 100 mg) and 2'-phenyl-[1,1'-binaphthalen]-2-yl)boronic acid (0.374 mmol, 140 mg) were stirred in toluene (0.4 mL) at room temperature for 10 min. Triflic acid (0.0374 mmol, 5.6 mg) was added and the reaction continued for 8 h. The reaction was purified by flash chromatography with 70% DCM 30% hexanes and 1% triethylamine. The product was isolated as an oil. (162.2 mg, 71.4%, 1.2:1 DR) ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.92 (d, *J*=7.0 Hz, 1H); 7.50-7.21 (m, 23H); 6.41 (d, *J*=15.9 Hz, 1H); 6.09 (td, *J*=15.7, 6.7 Hz, 1H); 5.00 (d, *J*=7.3 Hz, 1H); 4.21 (dd, *J*=10.7, 3.1 Hz, 1H); 3.99 (dd, *J*=11.8, 7.9 Hz, 1H); 2.39-2.32 (m, 1H); 2.24-2.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4 ; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; HRMS(EI) calculated $C_{44}H_{35}BnaO_2^+$, $[M+Na]^+$; 629.2622, found 629.2619



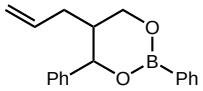
2-(2,4-diphenyl-1,3,2-dioxaborinan-5-yl)acetaldehyde (8)

In a dry vial 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane (0.28 mmol, 100 mg) and 2.5% wt Osmium tetroxide (0.0043 mmol) were dissolved in 0.6 mL THF:H_2O 3:1 solution. Sodium periodate (0.56 mmol, 120 mg) was added slowly and the reaction proceeded stirring at room temperature for two hours. The reaction was quenched with sodium bicarbonate, extracted with CH_2Cl_2 and then purified by flash chromatography. The product was isolated as an oil (77 mg, 98.2%, 14:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.62 (s, 1H), δ 7.91 (d, *J* = 7.0 Hz, 2H), 7.47-7.30 (m, 10H), 5.01 (d, *J* = 7.2 Hz, 1H), 4.20 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.95-3.90 (m, 1H), 2.73-2.68 (m, 1H), 2.66-2.46 (m, 2H) ; ^{13}C NMR (126 MHz, $CDCl_3$), δ 199.5, 140.7, 134.2, 131.1, 128.8, 128.3, 127.6, 126.4, 64.2, 43.0, 37.6; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1700, 1312, 1261; HRMS(EI) calculated. for $C_{17}H_{17}O_3B$, [M+H]+; 280.1271, found 280.1702



2,4-diphenyl-5-(3-phenylpropyl)-1,3,2-dioxaborinane (9)

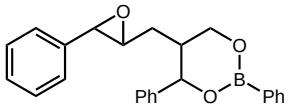
In a flame dried vial with 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane (0.4235 mmol, 150 mg) and 10% palladium on carbon (20 mg) were stirred in methanol (4 mL) for 7 h while H_2 gas was bubbled through. Product was purified by column chromatography. The product was isolated as an oil (137.9 mg, 91%, 14:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.88 (d, *J*=7.0 Hz, 2H); 7.50-7.21 (m, 15H); 4.93 (d, J=7.29 Hz, 1H); 4.21 (dd, *J*=10.73, 3.12 Hz, 1H); 3.99 (dd, *J*=11.8, 8.0 Hz, 1H); 2.39-2.32 (m, 2H); 2.24-2.16 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.6, 127.3, 126.5, 126.4, 126.1, 77.9, 64.5, 43.2, 32.4; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; Boron removed HRMS(EI) calculated for $C_{24}H_{25}BO_2$, [M+H]+; 356.1948, found 356.1760



5-allyl-2,4-diphenyl-1,3,2-dioxaborinane (10)

In a flame dry vile with 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane (2a) (.28 mmol) and Hoveyda Grubbs 2nd generation catalyst (0.02 mmol) in DCE (10 mL) Ethylene gas was bubbled through via a balloon and syringe. After 48 h crude product was purified by column chromatography with 1:1 DCM:hexanes as the eluent. The product was isolated as an oil (56.4 mg, 72%, 14:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.89 (d, *J*=7.0 Hz, 2H); 7.50-7.34 (m, 8H); 5.78-5.68 (m, 1H); 5.12-5.05 (m, 2 H); 4.96 (d, *J*=7.4 Hz, 1H); 4.18 (dd, *J*=11.9, 4.0 Hz, 1H); 3.96-3.91 (m, 1H); 2.25-2.18 (m, 1H); 2.15-2.00 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 134.7, 134.0, 130.9, 128.5, 127.9, 127.6, 126.5, 117.5, 77.9, 64.6, 42.6, 33.1; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261;

HRMS(EI) calculated. for $C_{18}H_{19}BO_2$, [M+H]+; 278.1478, found 278.2058.



2,4-diphenyl-5-((3-phenyloxiran-2-yl)methyl)-1,3,2-dioxaborinane (11)

Dimethyldioxirane (DMDO) was prepared following the procedure in Org. Synth. 2013, 90, 350-357. In a vial with 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane (100 mg, 0.2823 mmol) and DMDO (0.3105 mmol) in 10 mL acetone was stirred for 16 h at room temperature. Solvent was removed under reduced pressure and purified by chromatography with 70:30 DCM hexane as the eluent. Product was purified as a 1:1 ratio of diastereomers. The product was isolated as an oil (73.6 mg, 71.4%, 14:1 DR). R_f: 0.1 in 1:1 DCM:hexanes; ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.89 (d, J=7.0 Hz, 2H); 7.50-7.18 (m, 15H); 5.00 (dd, J=7.3 Hz, 1H); 4.43-4.26 (m, 1H); 4.07 (d, J=44.6 Hz, 1H); 2.92-2.85 (m, 1H); 2.38-2.29 (m, 1H); 1.95-1.81 (m, 1H); 1.71-1.44(m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 141.4, 137.1, 134.0, 134.0, 132.6, 130.8, 128.5, 128.5, 128.0, 127.7, 126.6, 126.4, 125.5, 125.4, 78.2, 77.9, 65.2, 64.3, 61.0, 60.5, 59.2, 58.2, 42.1, 40.8, 31.7; ^{11}B NMR (160 MHz, $CDCl_3$), δ 27.04; IR (film)νmax 3057, 3027, 2903, 1950, 1600, 1312, 1261; δ ;

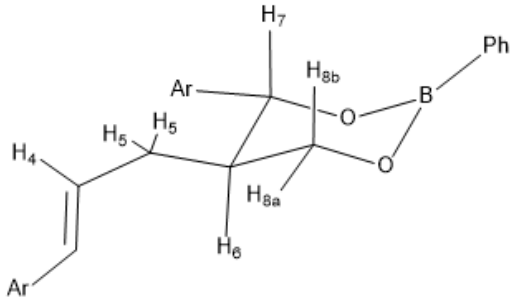
IR (film)νmax 3057, 3027, 2903, 1950, 1312, 1261; HRMS(EI) calculated. for $C_{24}H_{23}O_3B$, [M+H]+; 370.1740, found 370.3520

NOE Studies

NOE studies were performed on (**tertbutyl substrate with Boron**) to confirm the trans stereochemistry of our two substituents. Table **X** shows the relative intensities of the peaks for hydrogens in question. From the below table, we can see that H_7 sees H_{8b} but cannot see H_{8a}, and H_6 can see H_{8a} but not H_{8b}. Although we have these results, the intensities do not exactly match expected ratios for a molecule in a chair conformation. However, through process of elimination we know that it cannot be any other arrangement. If H_7 was equatorial, it would not be able to see H_{8a} or H_{8b} so it must be axial. Similarly, if H_6 was equatorial it would have to see H_{8b} much more strongly than it currently does. The odd intensity ratios in our NOE experiments are due to the boron distorting the ring as it strains to move towards a 120° bond angle. The J-coupling values also help to prove this. 1,2 diaxial hydrogens (H_6 and H_7, and H_6 and H_{8b}) should have coupling values between 8-13 Hz, but here $J_{7,6}$ = 7.0 Hz and $J_{8b,6}$ = 8.0 Hz which are a little low due to the distorted chair shape. Although the coupling between an axial and equatorial hydrogen in a 1,2 relationship is about right ($J_{8a,6}$ = 3.7 Hz), the relationship between geminal hydrogens is also a little lower than what would be expected ($J_{8a,8b}$ = 11.5 Hz). We can further confirm the trans nature of our substrates by comparing the NOE studies of (**tertbutyl substrate)** with the crystal structure taken of (**cinnamyl derivative**) where the ring substituents come off trans and the bond angle of boron is 123.3°. Thus, we can infer that all of our substrates contain the same stereochemistry.

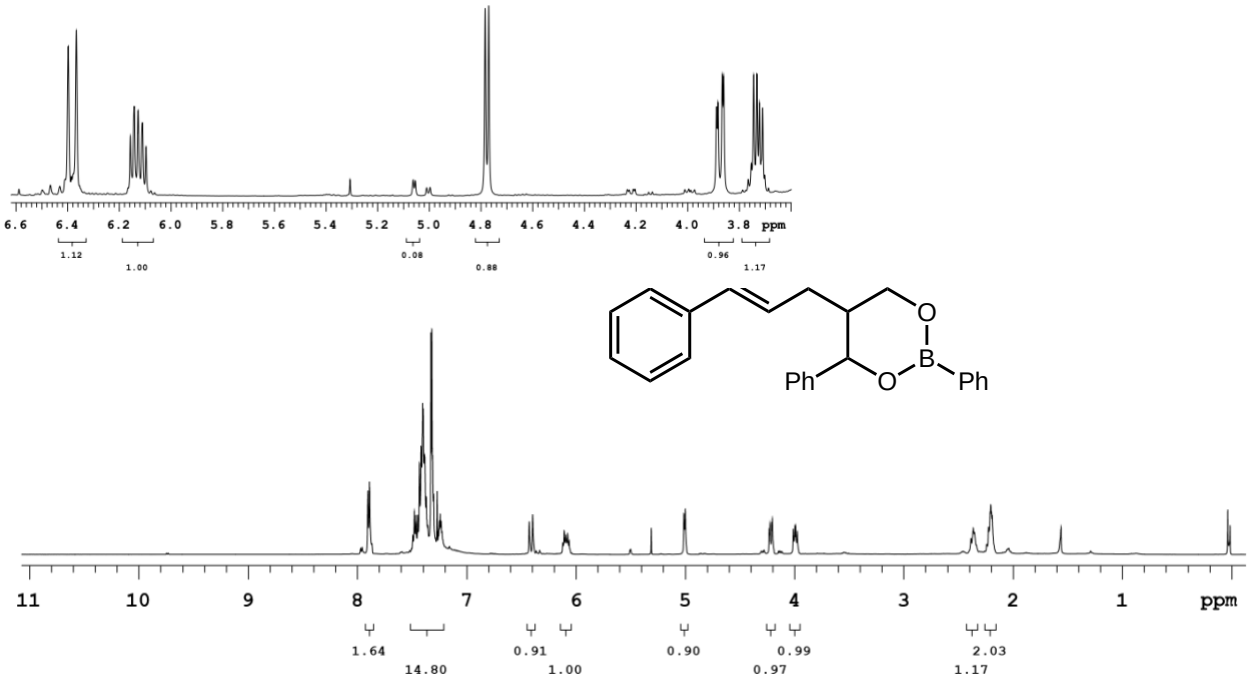
Table **X**. How strongly different hydrogens see each other in (**tbu substrate**) by NOE experiments.

	H_4	H_5	H_6	H_7	H_{8a}	H_{8b}
H_6	2.2%	3.6%	-	2.1%	1.2%	no
H_7	0.6%	2.5%	1.4%	-	no	1.5%
H_{8a}	no	4%	no	no	-	20%
H_{8b}	0.7%	3.0%	0.4%	2.4%	19%	-

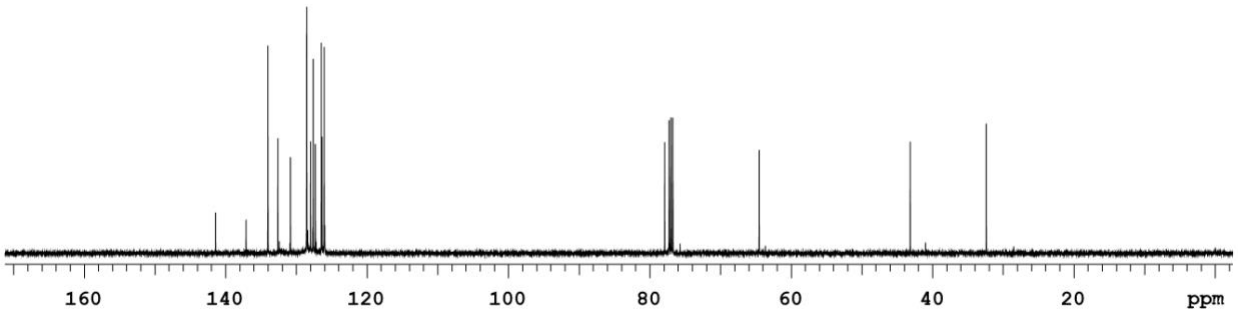


NMR Data

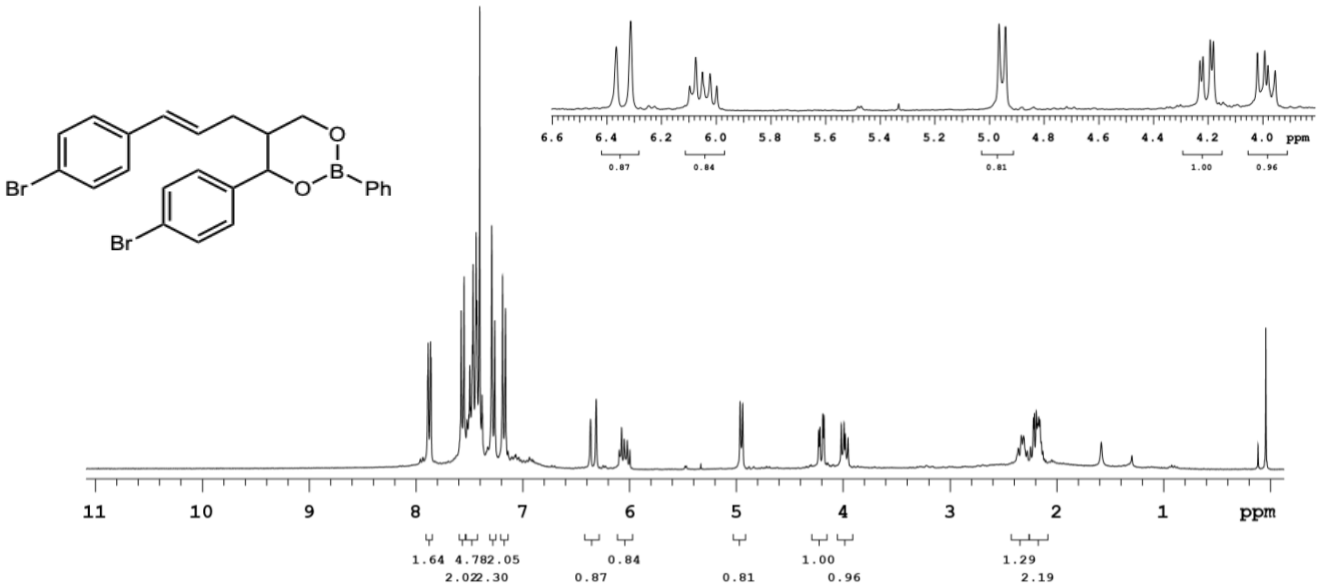
2a. 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane ^{1}H NMR



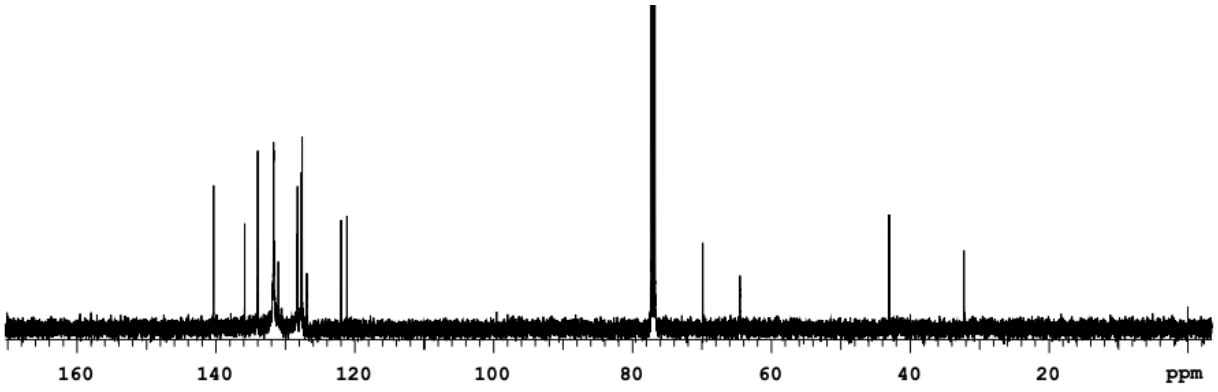
2a. 5-cinnamyl-2,4-diphenyl-1,3,2-dioxaborinane ^{13}C NMR



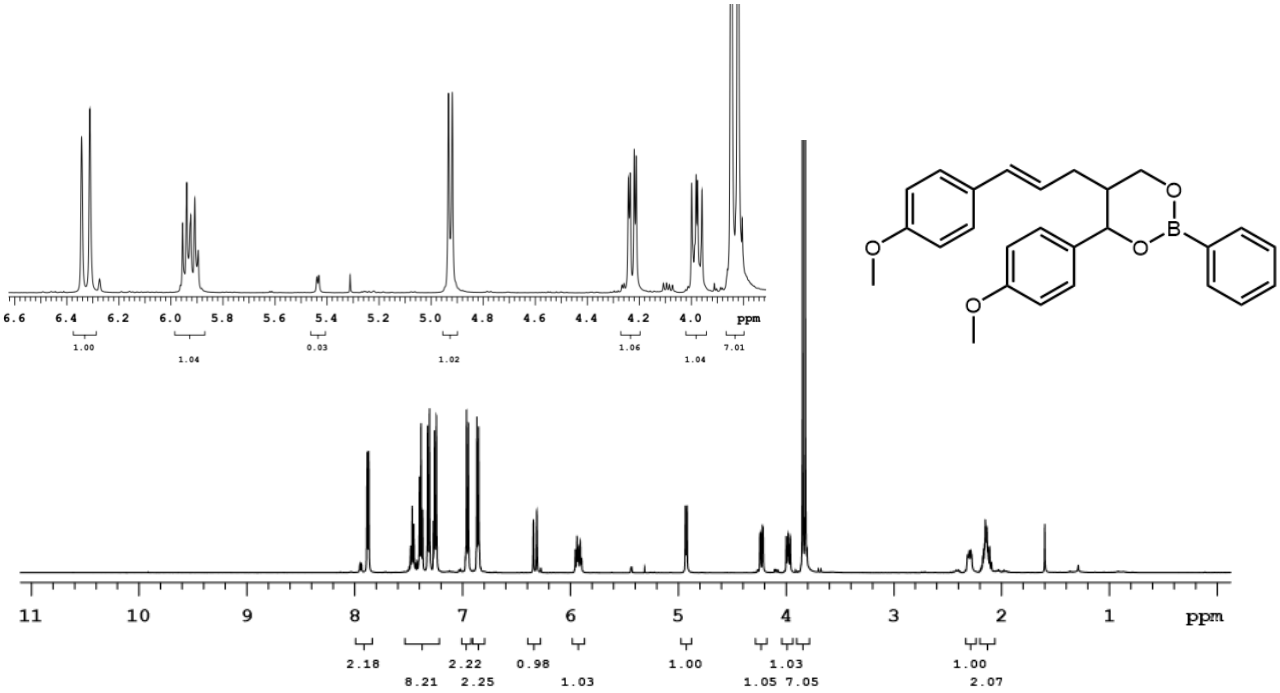
2b. (E)-4-(4-bromophenyl)-5-(3-(4-bromophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{1}$H NMR



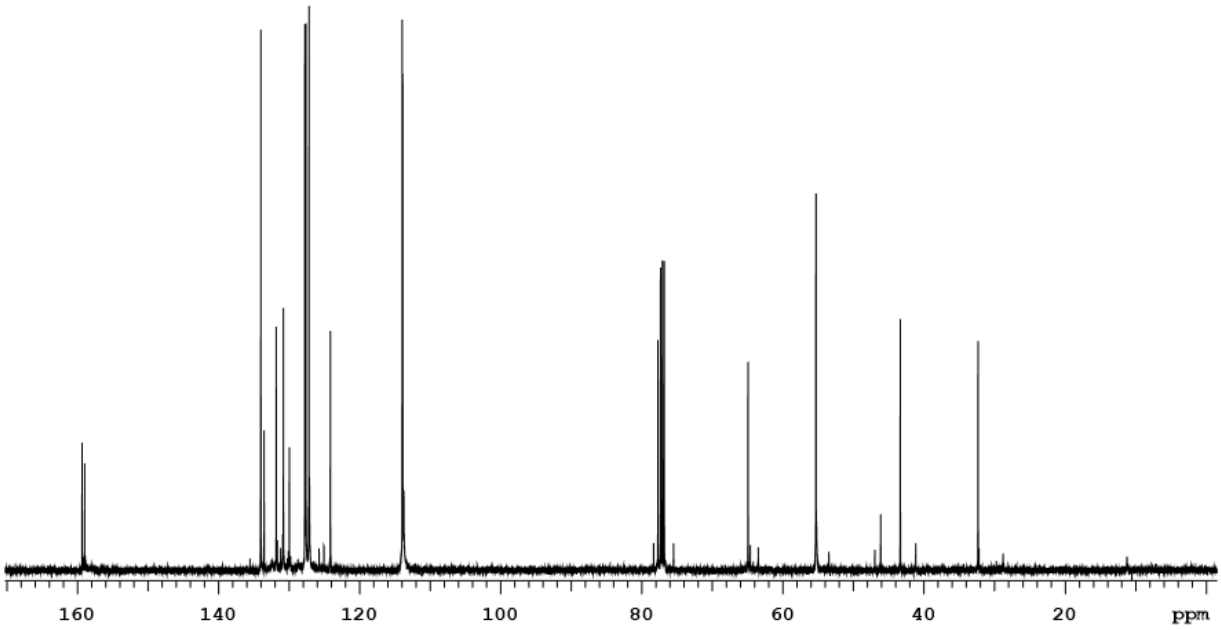
2b. (E)-4-(4-bromophenyl)-5-(3-(4-bromophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{13}$C NMR



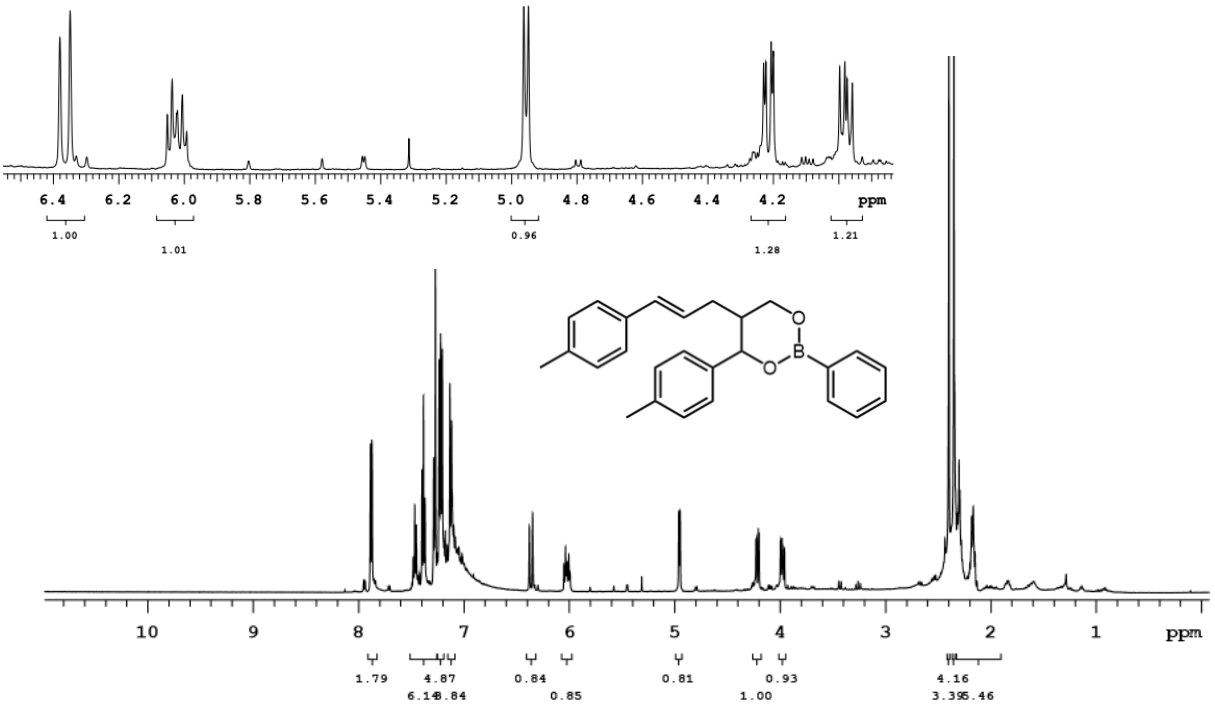
2c. (E)-4-(4-methoxyphenyl)-5-(3-(4-methoxyphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane ^{1}H NMR



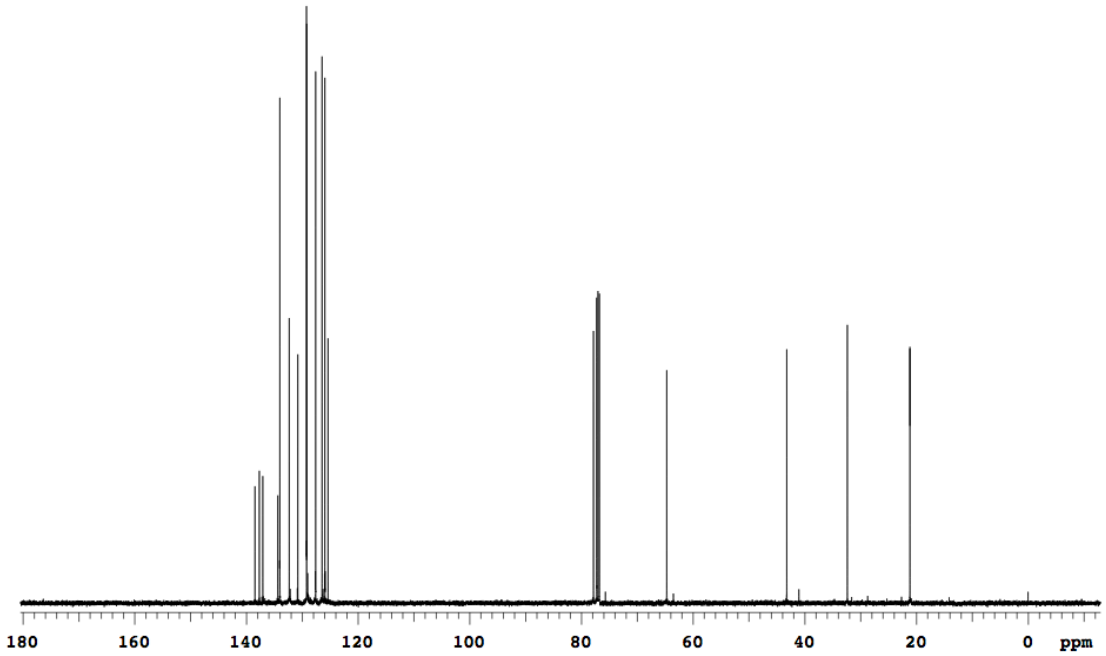
2c. (E)-4-(4-methoxyphenyl)-5-(3-(4-methoxyphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane ^{13}C NMR



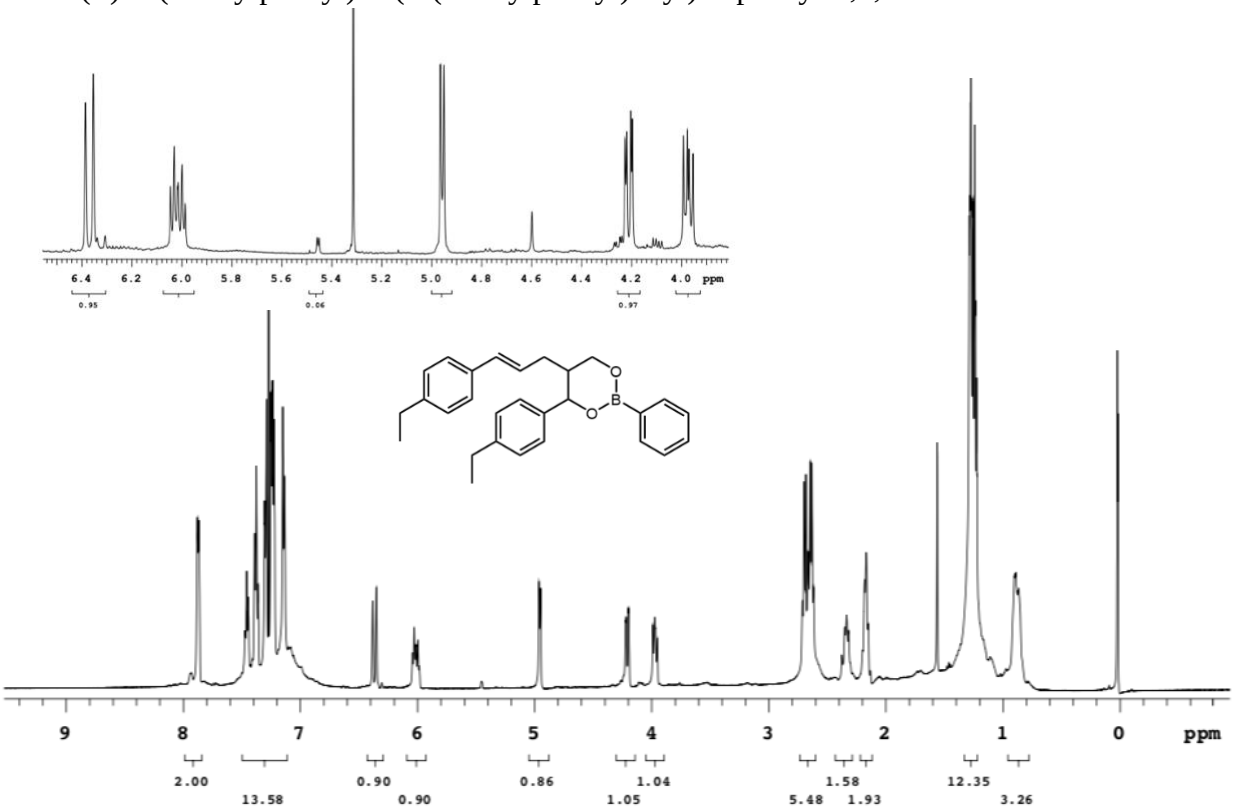
2d. (E)-2-phenyl-4-(p-tolyl)-5-(3-(p-tolyl)allyl)-1,3,2-dioxaborinane ^{1}H NMR



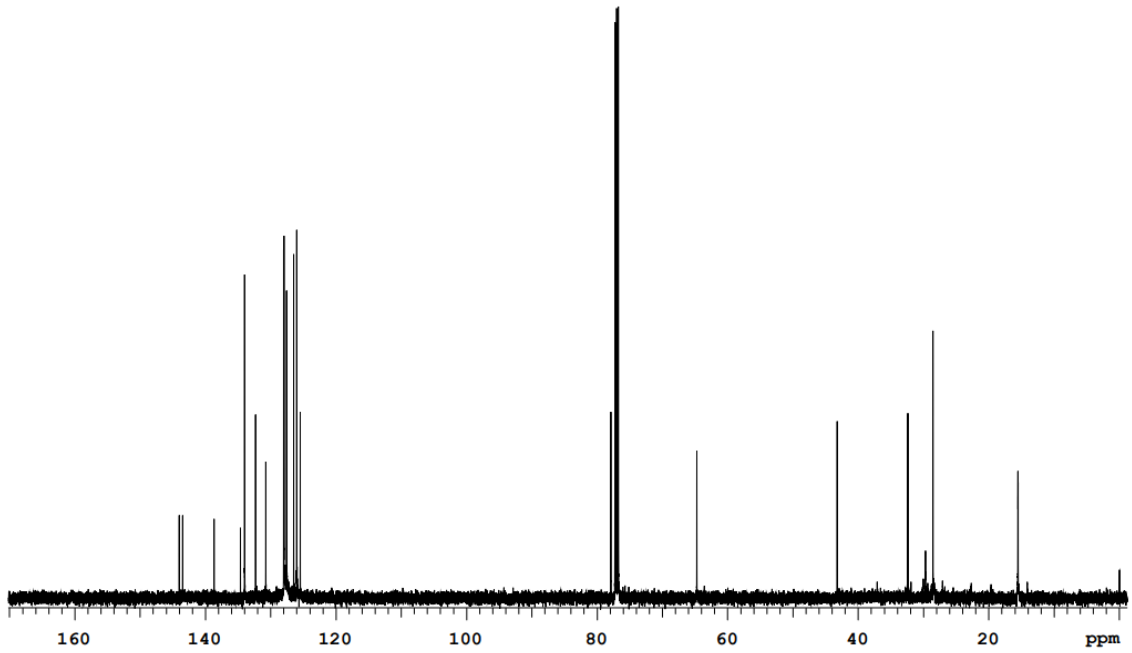
2d. (E)-2-phenyl-4-(p-tolyl)-5-(3-(p-tolyl)allyl)-1,3,2-dioxaborinane ^{13}C NMR



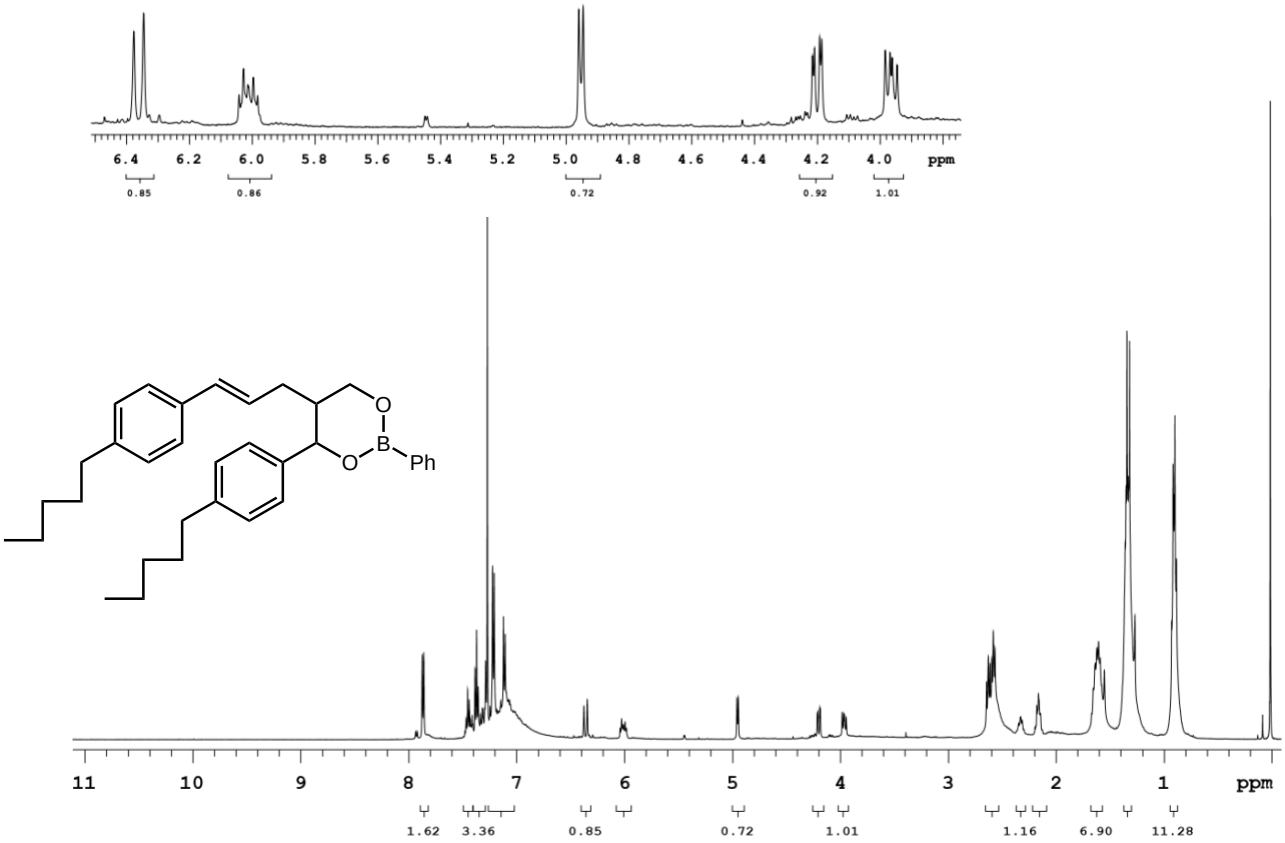
2e. (*E*)-4-(4-ethylphenyl)-5-(3-(4-ethylphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{1}$H NMR



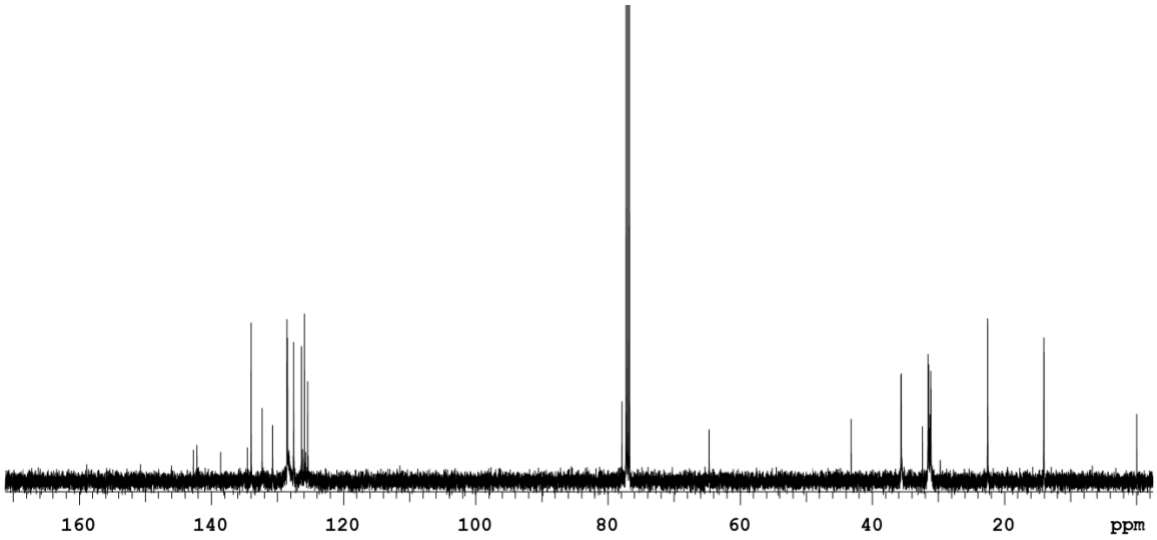
2e. (*E*)-4-(4-ethylphenyl)-5-(3-(4-ethylphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{13}$C NMR



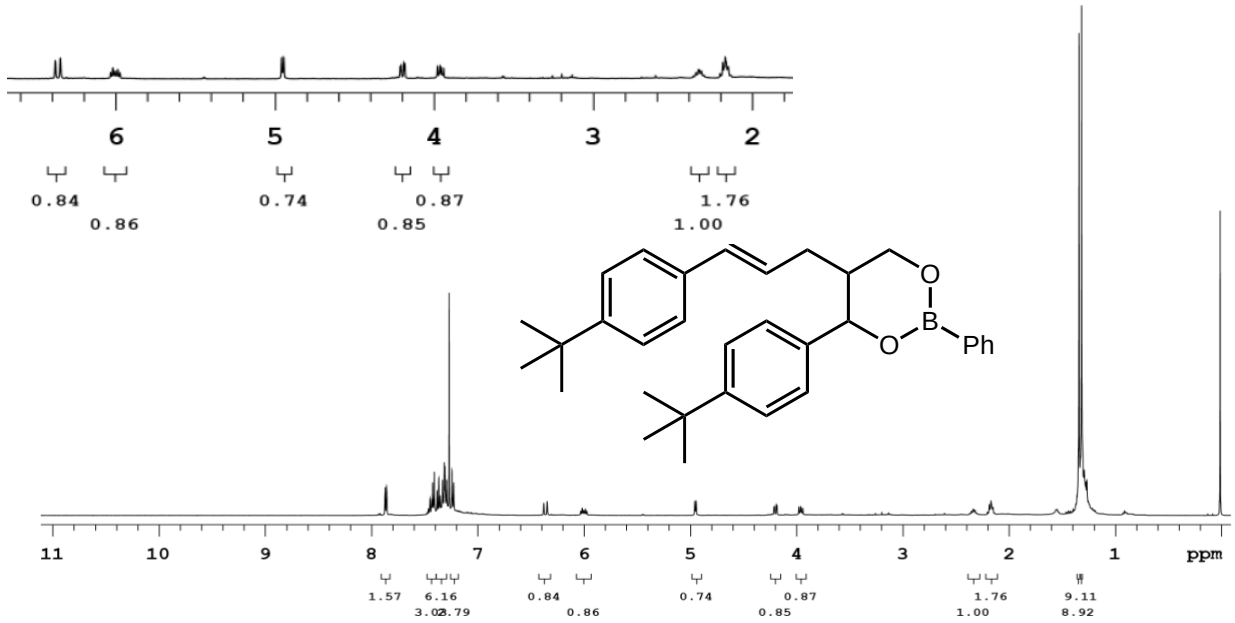
2f. (E)-4-(4-pentylphenyl)-5-(3-(4-pentylphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{1}$H NMR



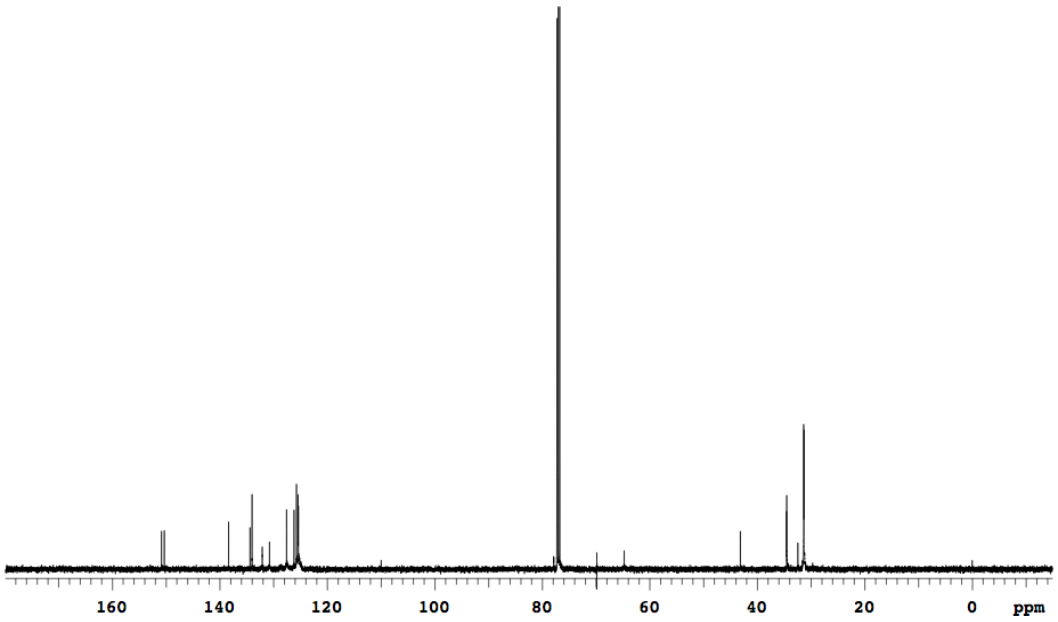
2f. (E)-4-(4-pentylphenyl)-5-(3-(4-pentylphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{13}$C NMR



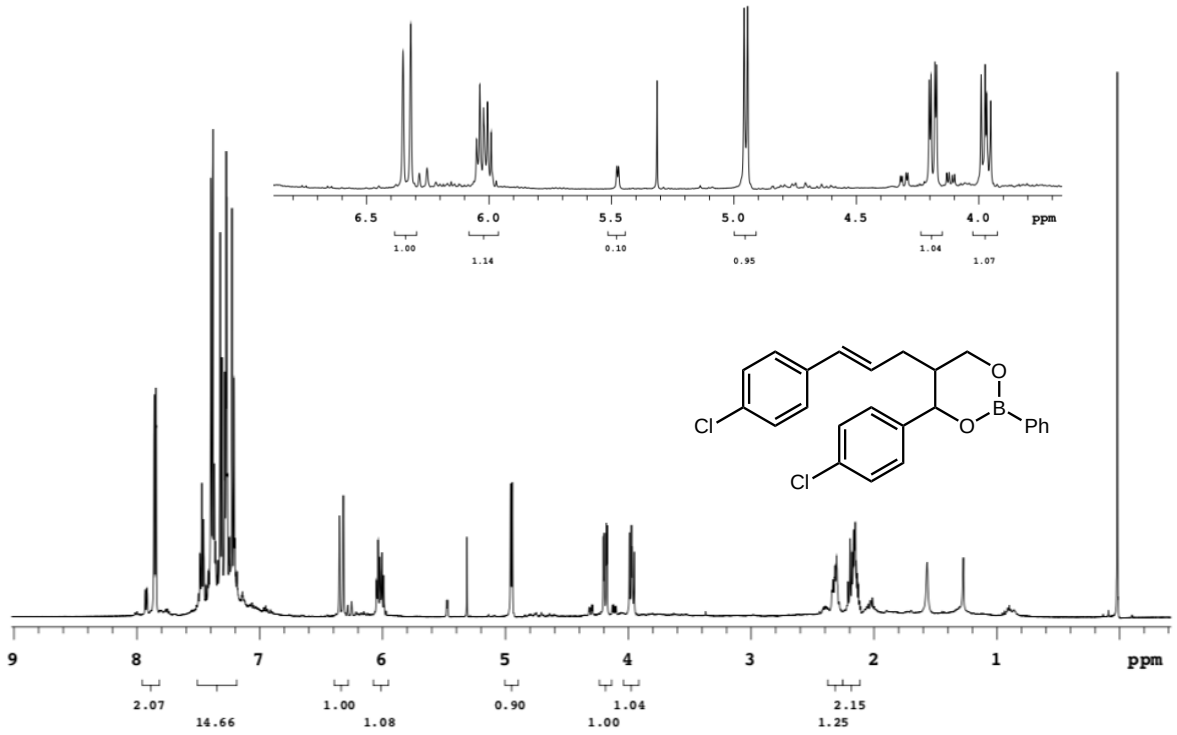
2g. (E)-4-(4-(tert-butyl)phenyl)-5-(3-(4-(tert-butyl)phenyl)allyl)-2-phenyl-1,3,2-dioxaborinane
$_{1}$H NMR



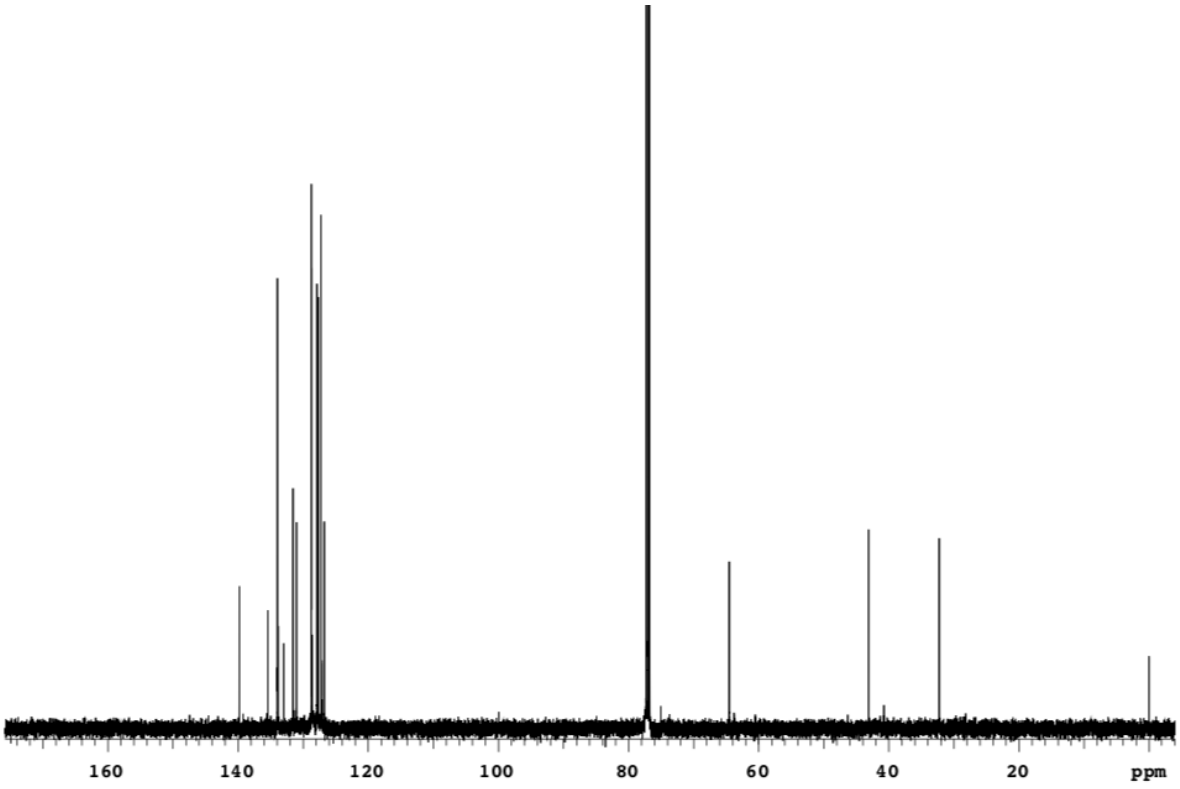
2g. (E)-4-(4-(tert-butyl)phenyl)-5-(3-(4-(tert-butyl)phenyl)allyl)-2-phenyl-1,3,2-dioxaborinane
$_{13}$C NMR



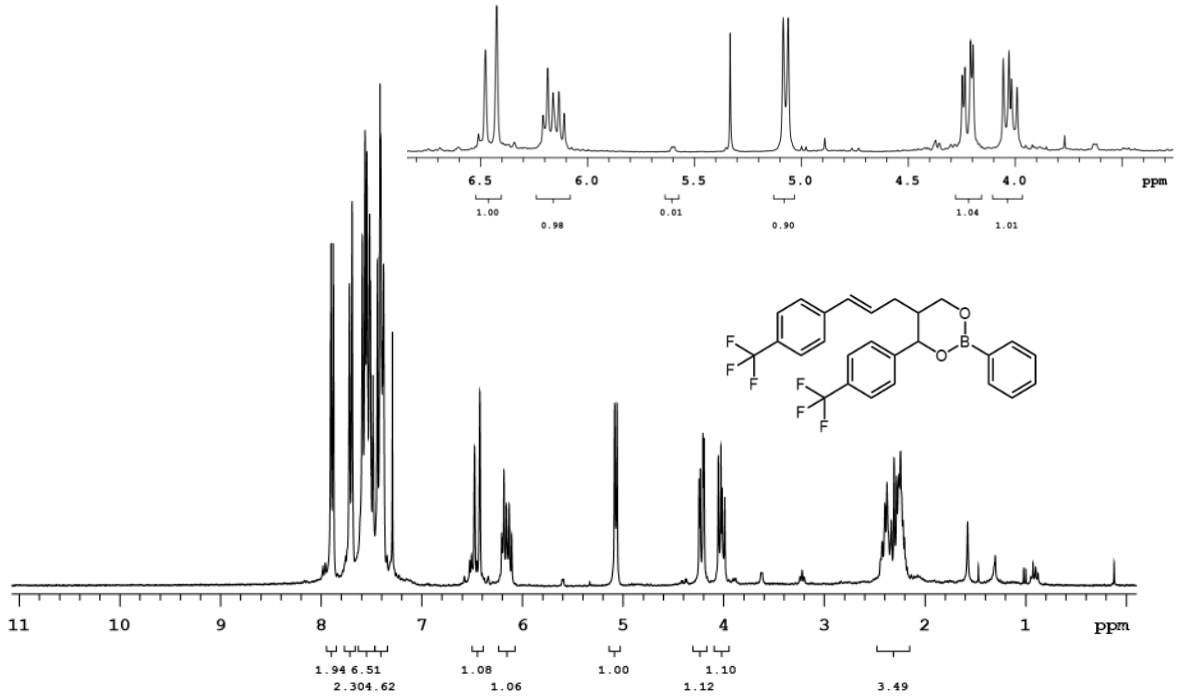
2h (*E*)-4-(4-chlorophenyl)-5-(3-(4-chlorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{1}$H NMR



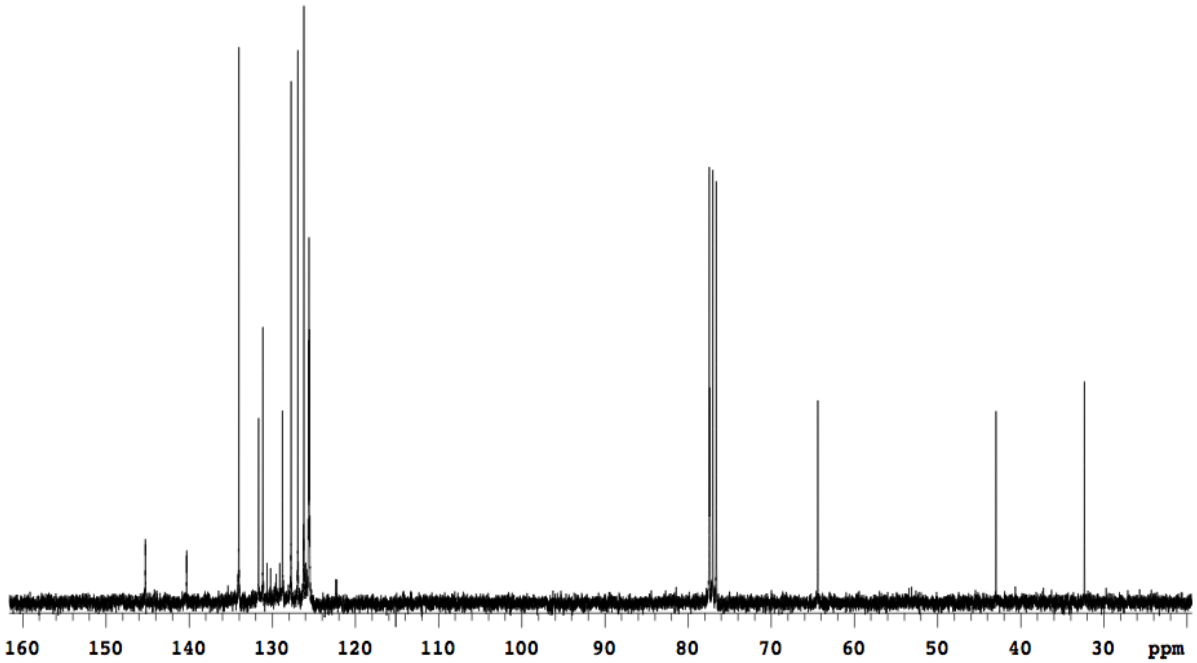
2h (*E*)-4-(4-chlorophenyl)-5-(3-(4-chlorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{13}$C NMR



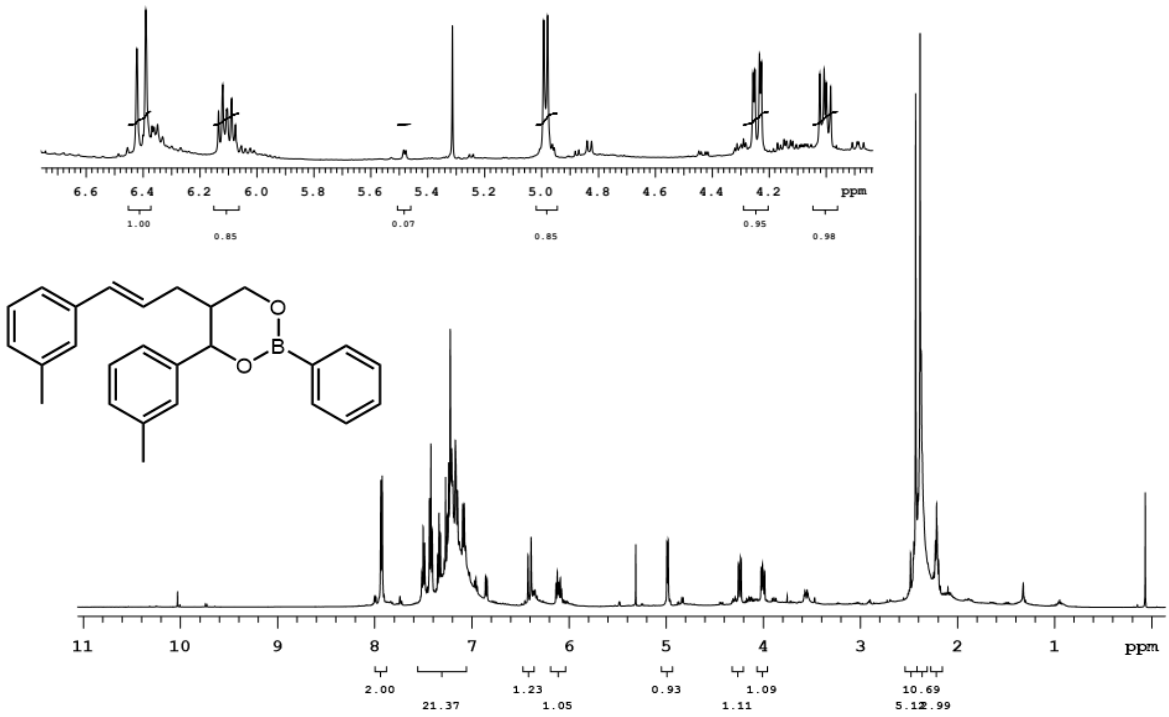
2i. (E)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-5-(3-(4-(trifluoromethyl)phenyl)allyl)-1,3,2-dioxaborinane $_{1}$H NMR



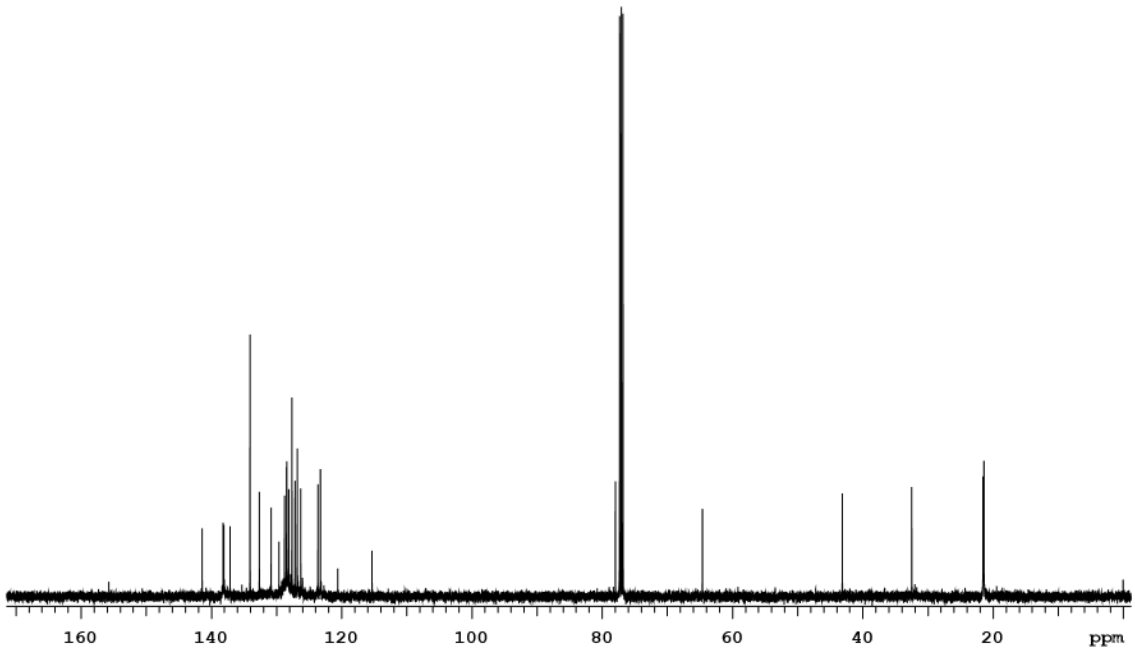
2i. (E)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-5-(3-(4-(trifluoromethyl)phenyl)allyl)-1,3,2-dioxaborinane $_{13}$C NMR



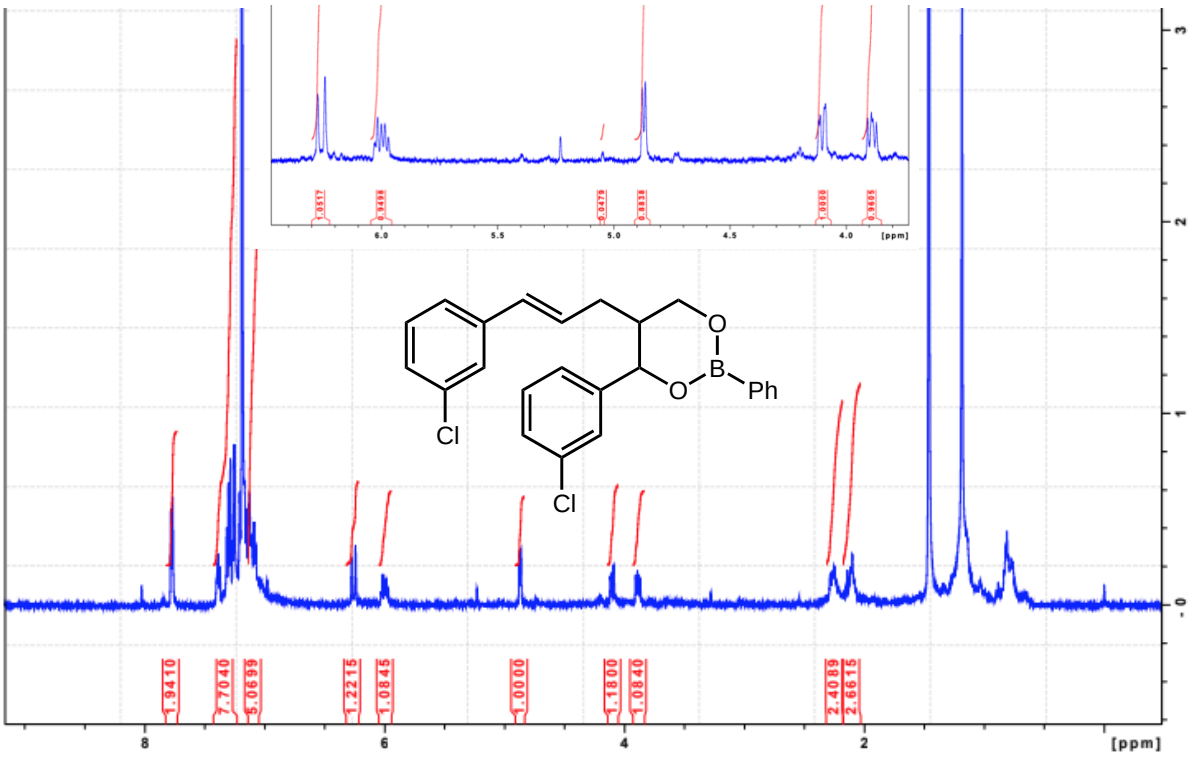
2j. (*E*)-2-phenyl-4-(*m*-tolyl)-5-(3-(*m*-tolyl)allyl)-1,3,2-dioxaborinane ^{1}H NMR



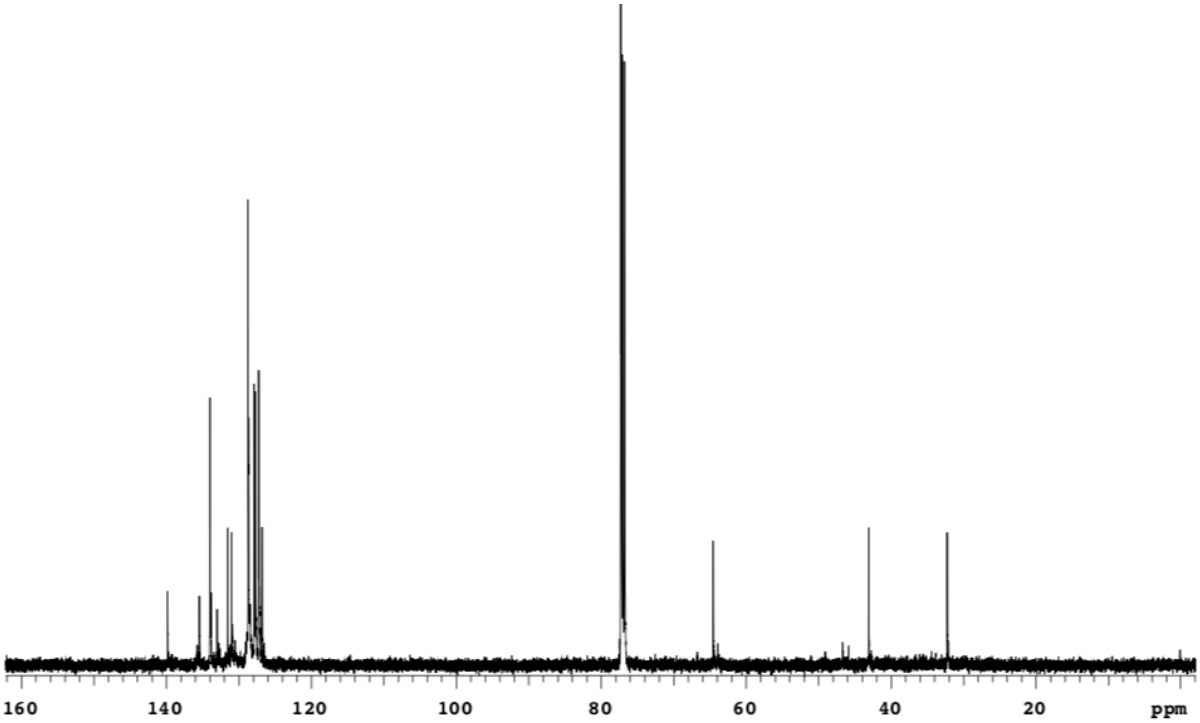
2j. (*E*)-2-phenyl-4-(*m*-tolyl)-5-(3-(*m*-tolyl)allyl)-1,3,2-dioxaborinane ^{13}C NMR



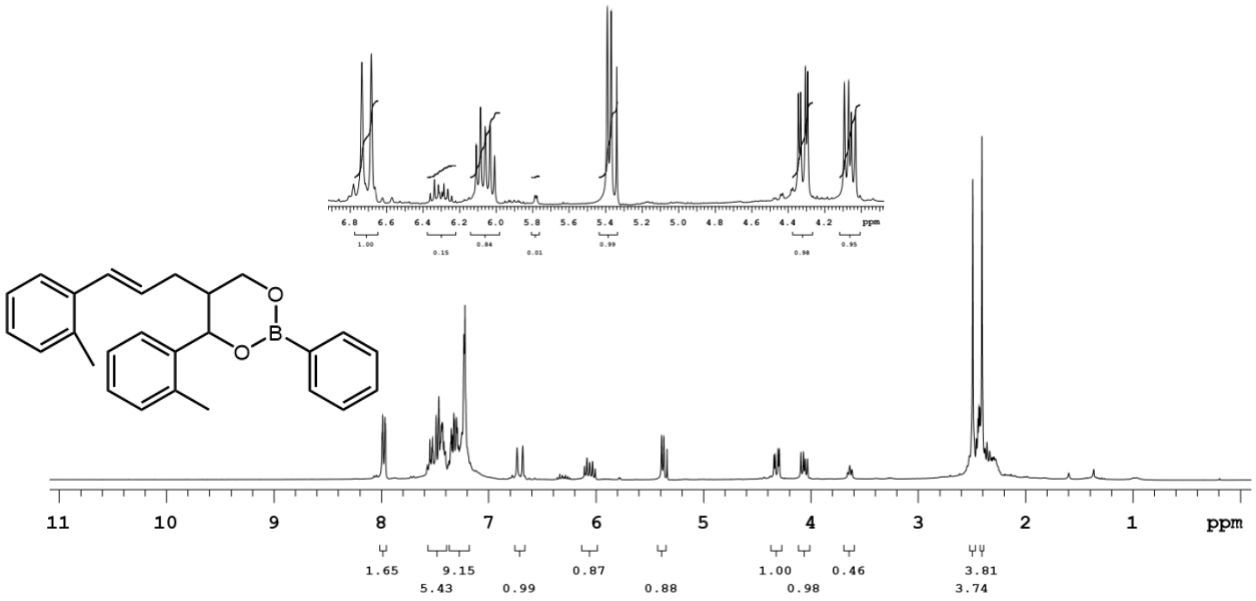
2k. (*E*)-4-(3-chlorophenyl)-5-(3-(3-chlorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{1}$H NMR



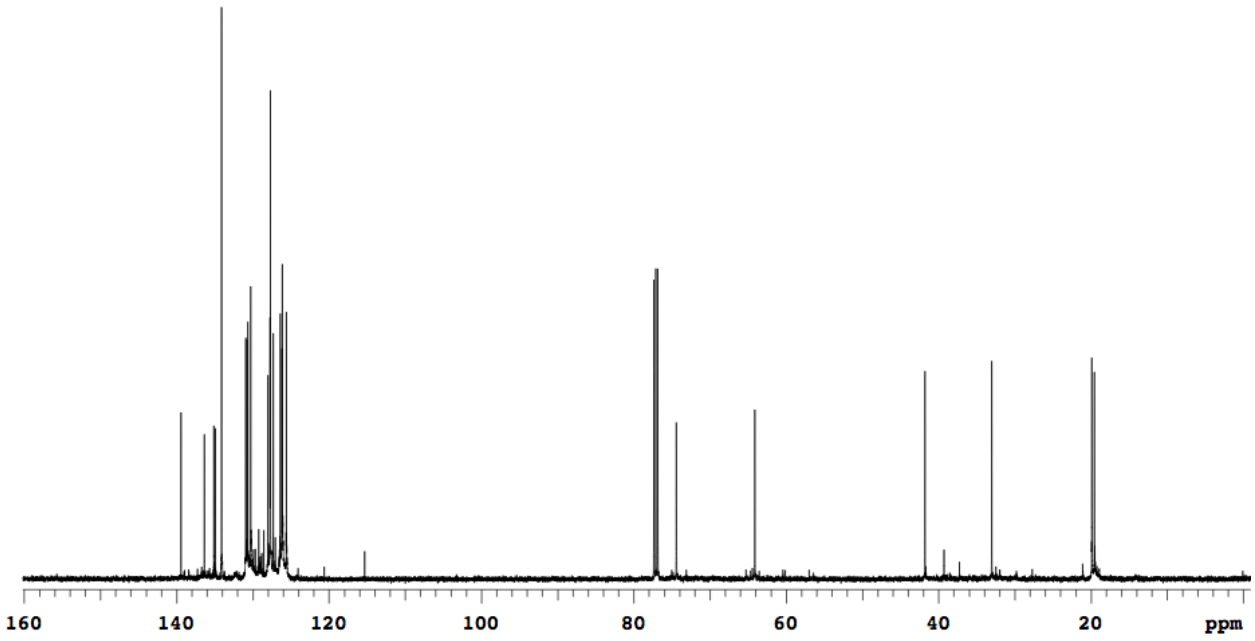
2k. (*E*)-4-(3-chlorophenyl)-5-(3-(3-chlorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane $_{13}$C NMR



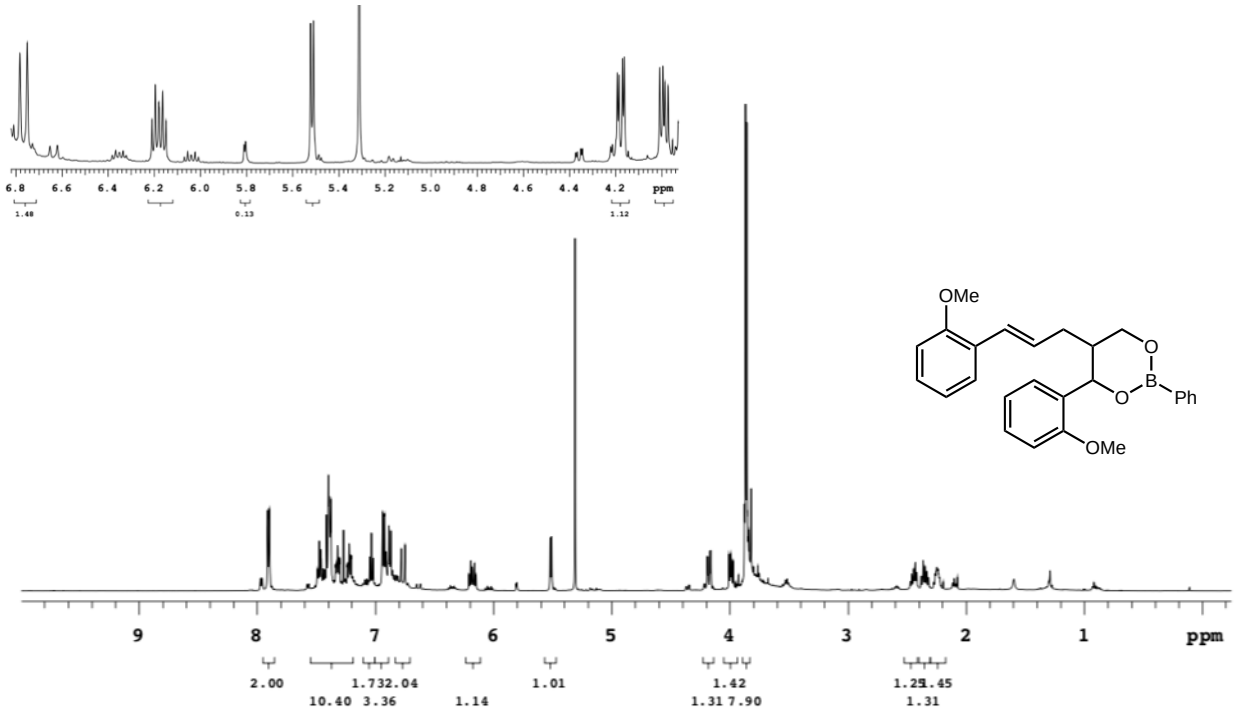
2l. (*E*)-2-phenyl-4-(*o*-tolyl)-5-(3-(*o*-tolyl)allyl)-1,3,2-dioxaborinane $_{1}$H NMR



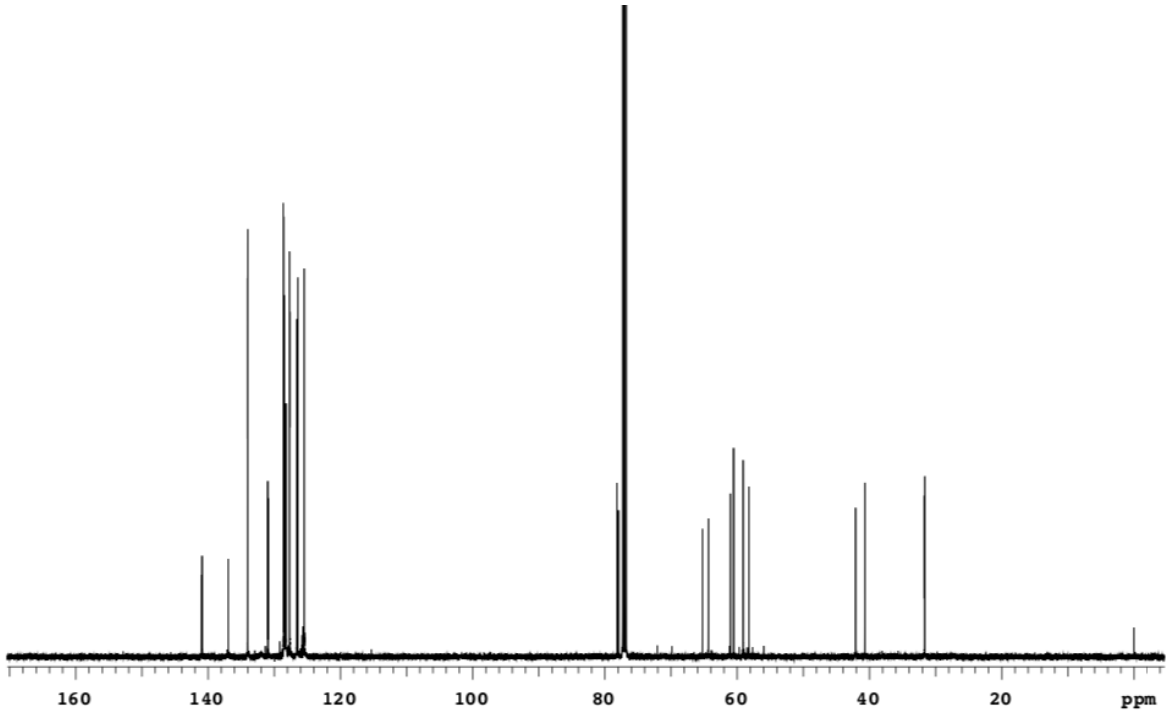
2l. (*E*)-2-phenyl-4-(*o*-tolyl)-5-(3-(*o*-tolyl)allyl)-1,3,2-dioxaborinane $_{13}$C NMR



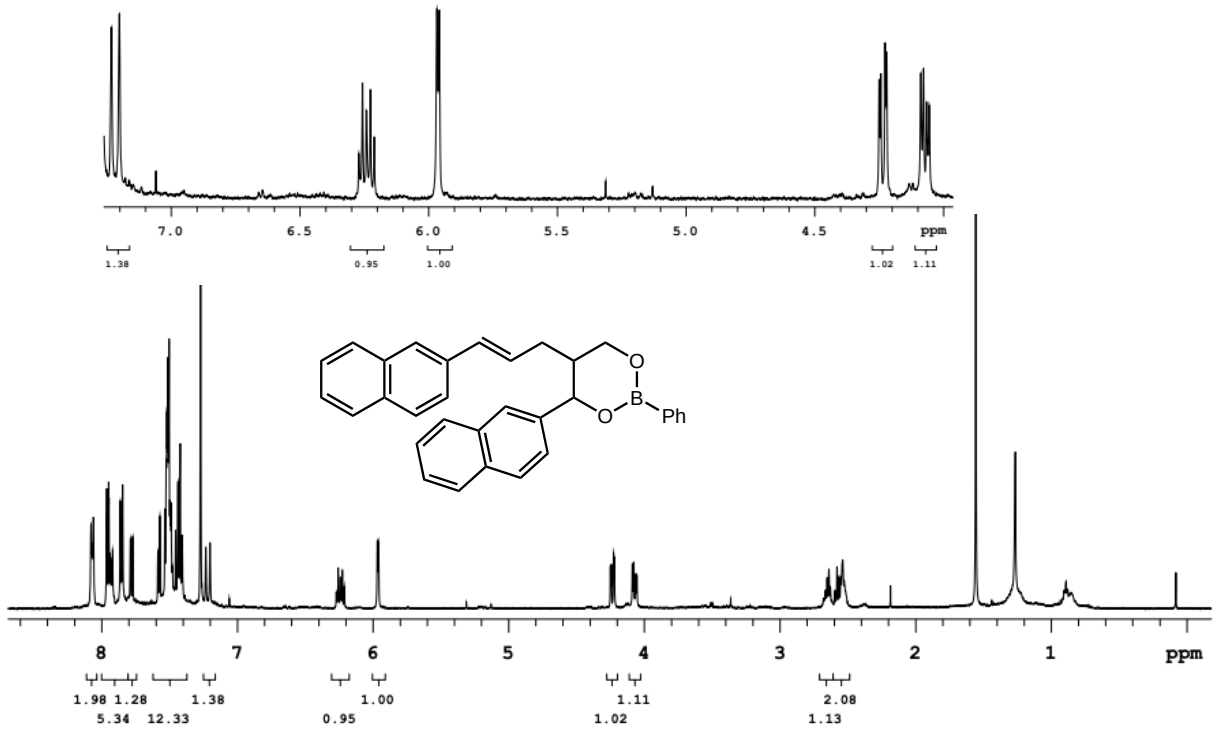
2m. (*E*)-4-(2-methoxyphenyl)-5-(3-(2-methoxyphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane ^{1}H NMR



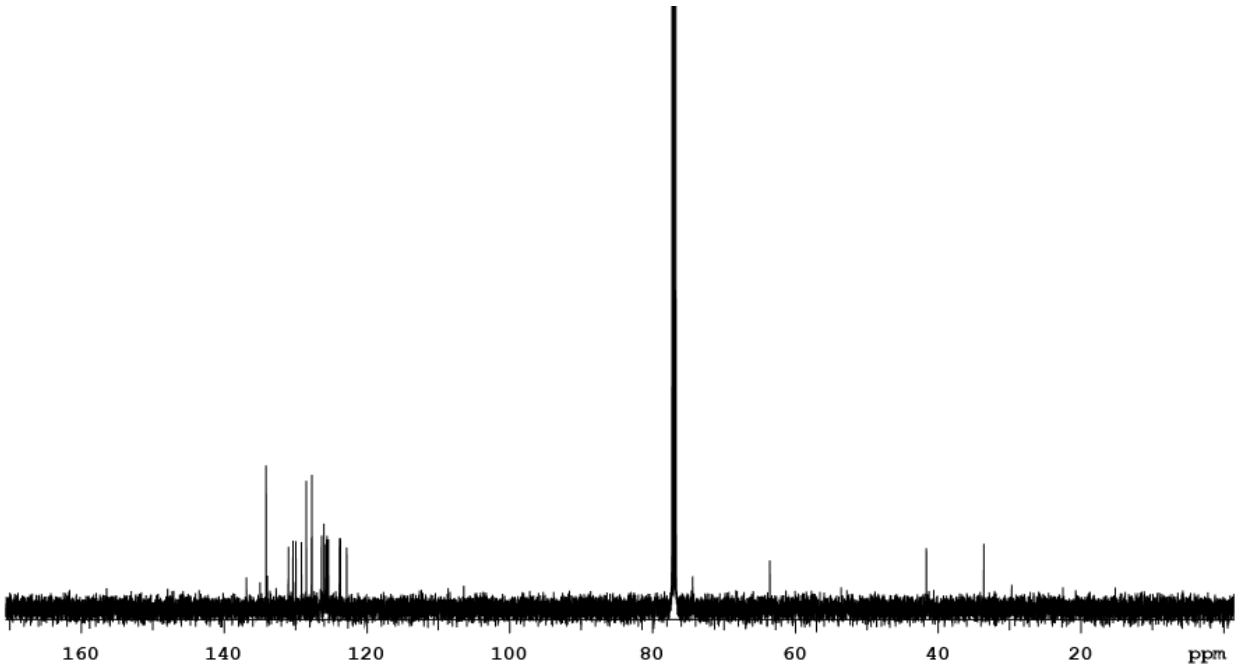
2m. (*E*)-4-(2-methoxyphenyl)-5-(3-(2-methoxyphenyl)allyl)-2-phenyl-1,3,2-dioxaborinane ^{13}C NMR



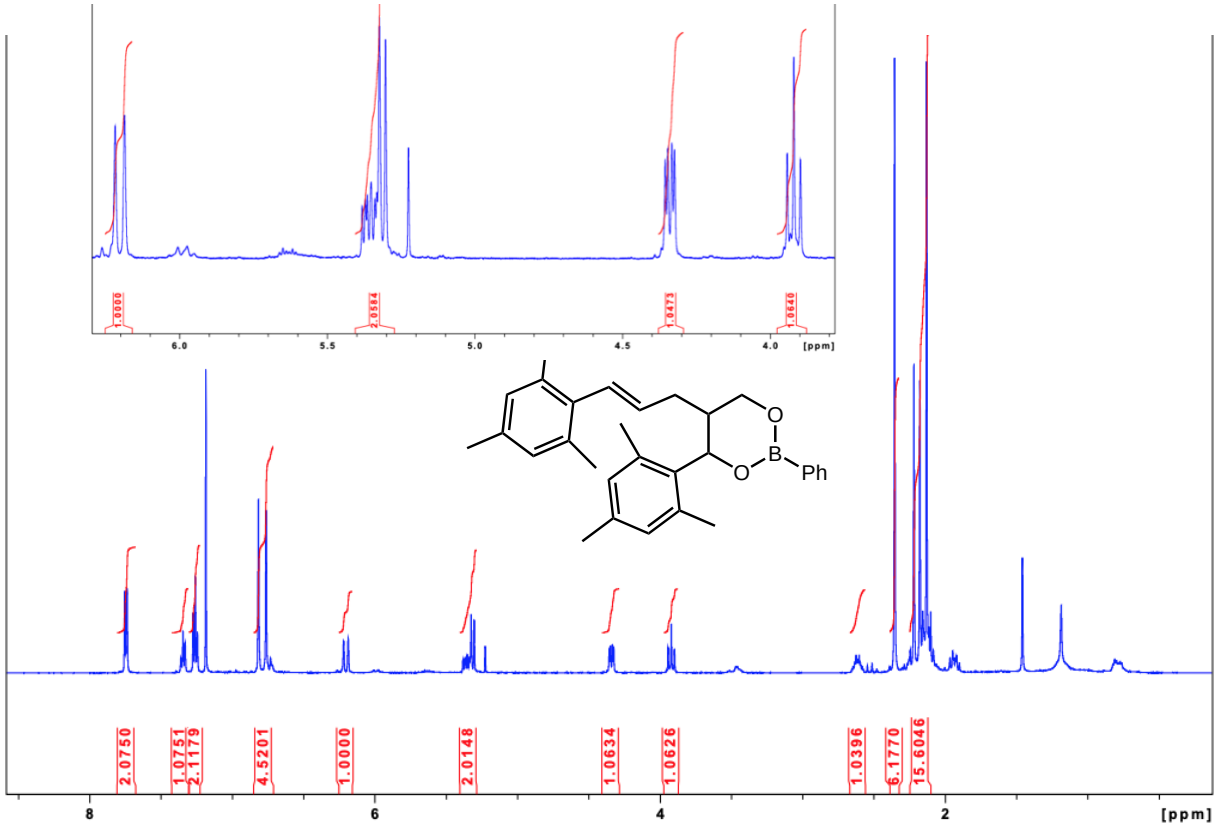
2n. (E)-1-(naphthalen-1-yl)-2-(3-(naphthalen-1-yl)allyl)propane-1,3-diol ^{1}H NMR



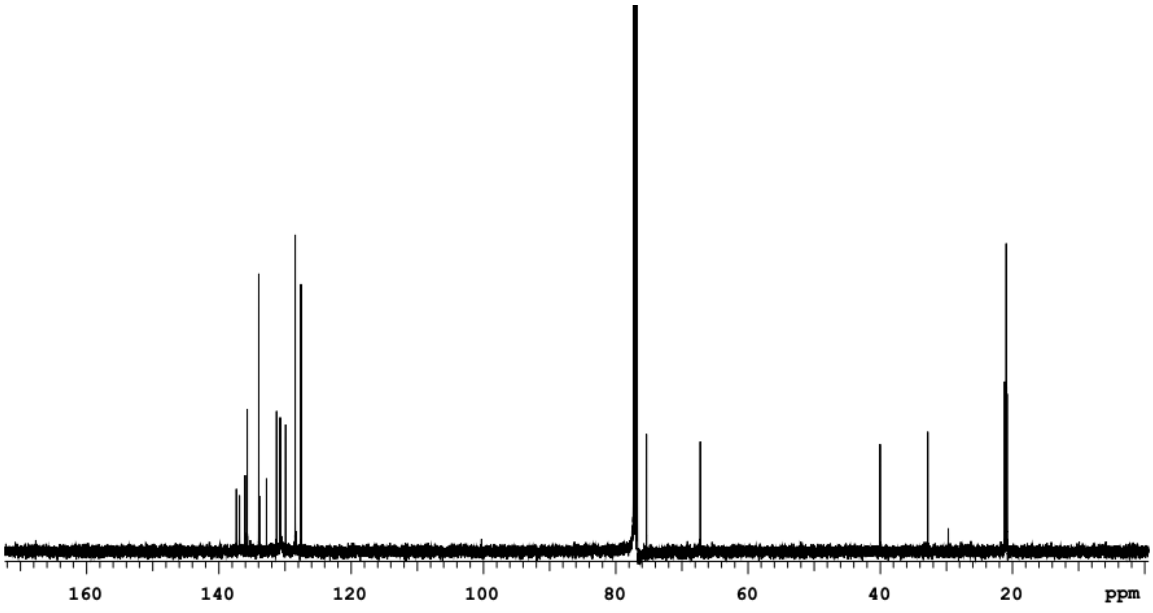
2n. (E)-1-(naphthalen-1-yl)-2-(3-(naphthalen-1-yl)allyl)propane-1,3-diol ^{13}C NMR



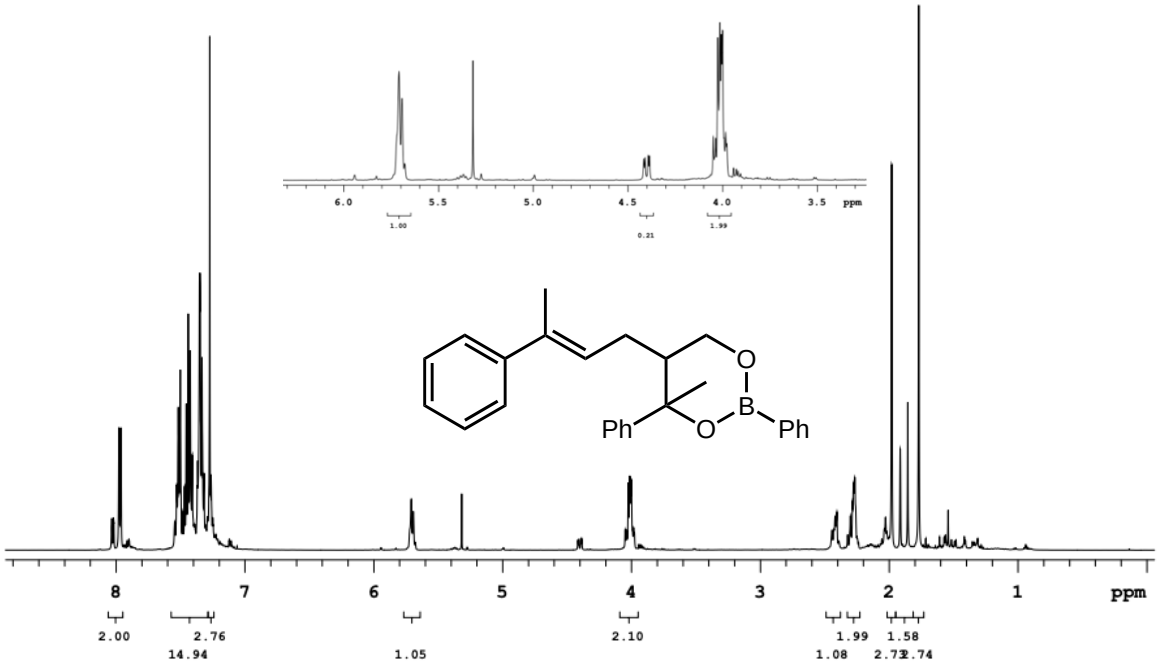
2o. (*E*)-4-(4-(*tert*-butyl)phenyl)-5-(3-(4-(*tert*-butyl)phenyl)allyl)-2-phenyl-1,3,2-dioxaborinane
$_{1}$H NMR



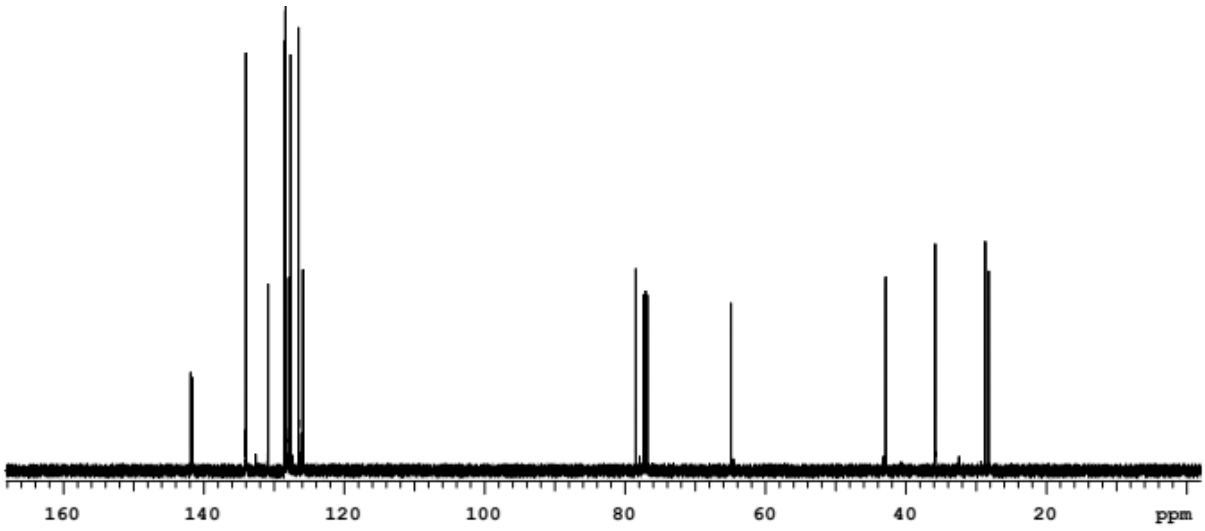
2o. (*E*)-4-(4-(*tert*-butyl)phenyl)-5-(3-(4-(*tert*-butyl)phenyl)allyl)-2-phenyl-1,3,2-dioxaborinane
$_{13}$C NMR



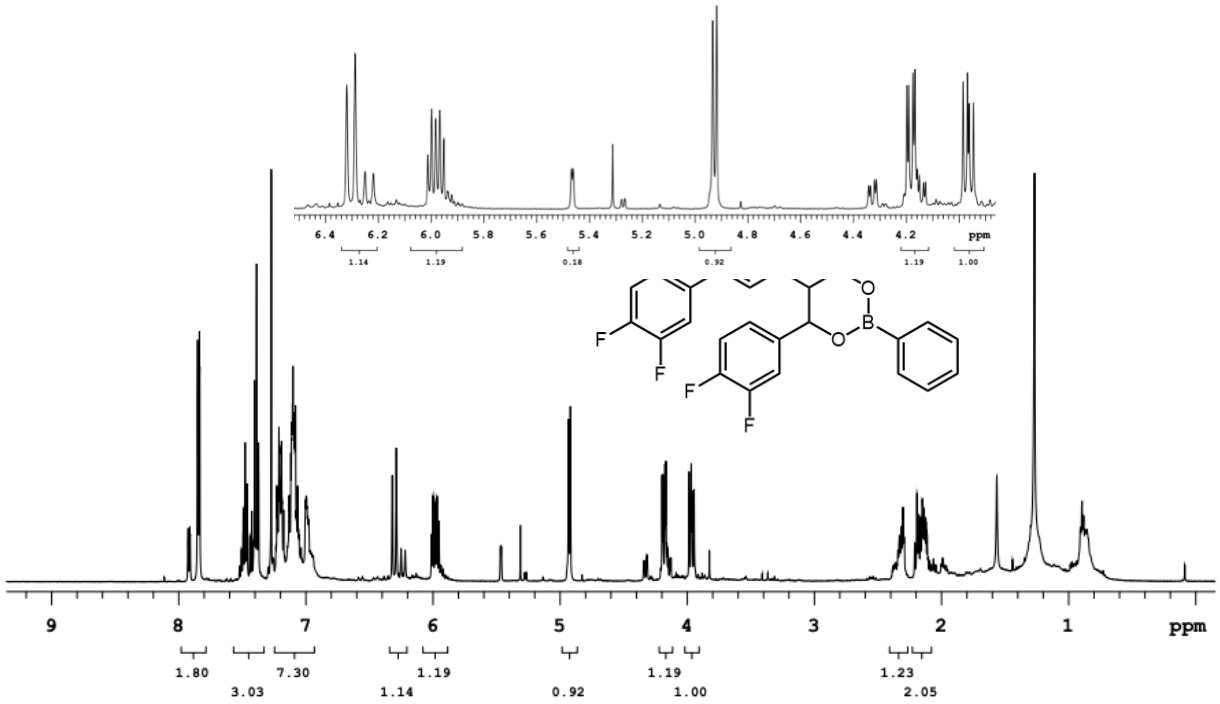
2p. (E)-3-phenyl-2-(3-phenylbut-2-en-1-yl)butane-1,3-diol ^{1}H NMR



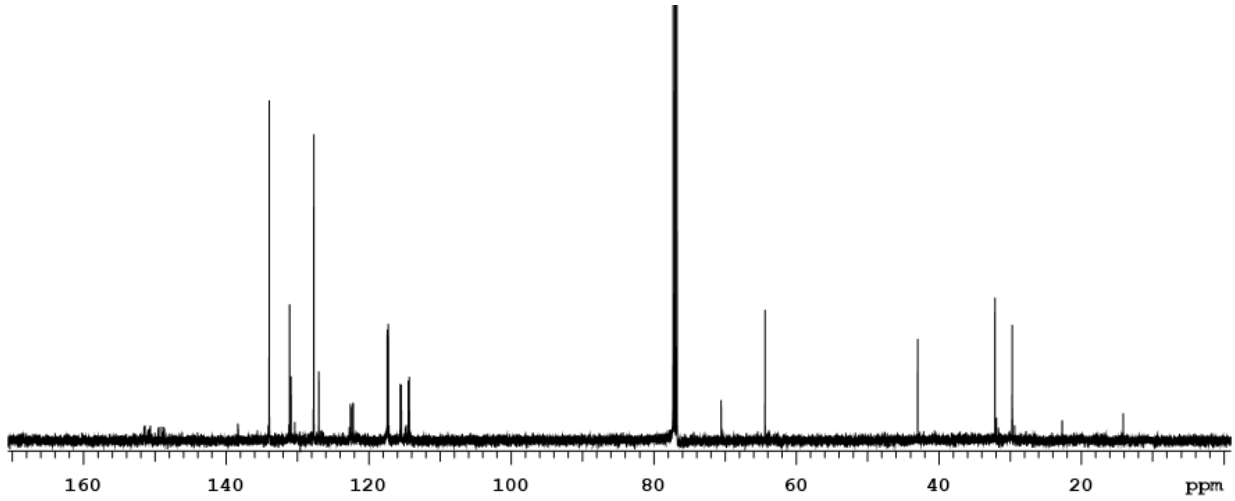
2p. (E)-3-phenyl-2-(3-phenylbut-2-en-1-yl)butane-1,3-diol ^{13}C NMR



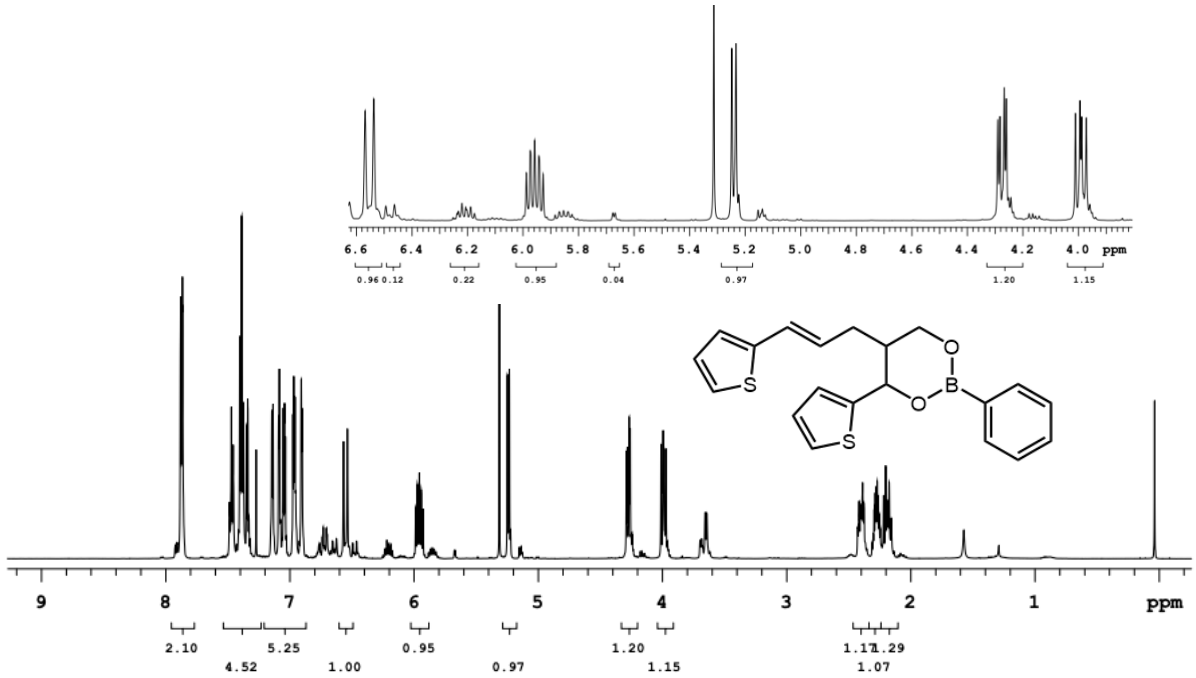
2q. (E)-4-(3,4-difluorophenyl)-5-(3-(3,4-difluorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane ^{1}H NMR



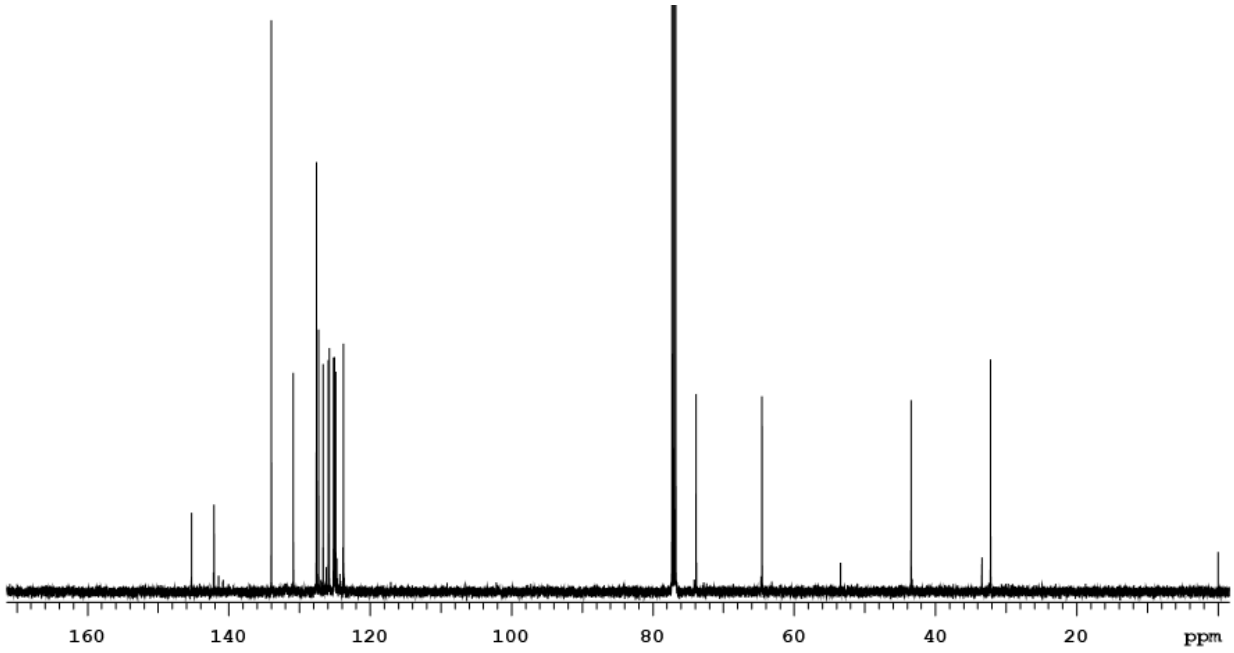
2q. (E)-4-(3,4-difluorophenyl)-5-(3-(3,4-difluorophenyl)allyl)-2-phenyl-1,3,2-dioxaborinane ^{13}C NMR



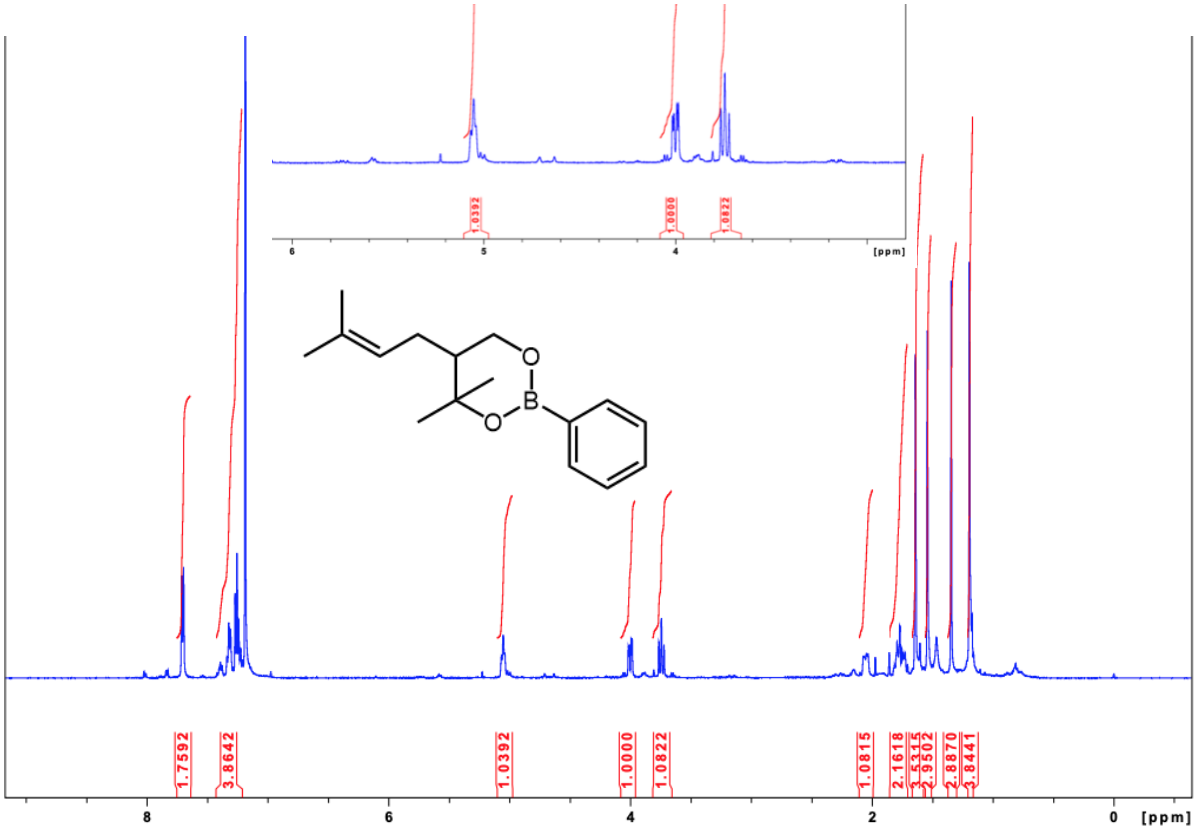
2r. (E)-2-phenyl-4-(thiophen-2-yl)-5-(3-(thiophen-2-yl)allyl)-1,3,2-dioxaborinane ^{1}H NMR



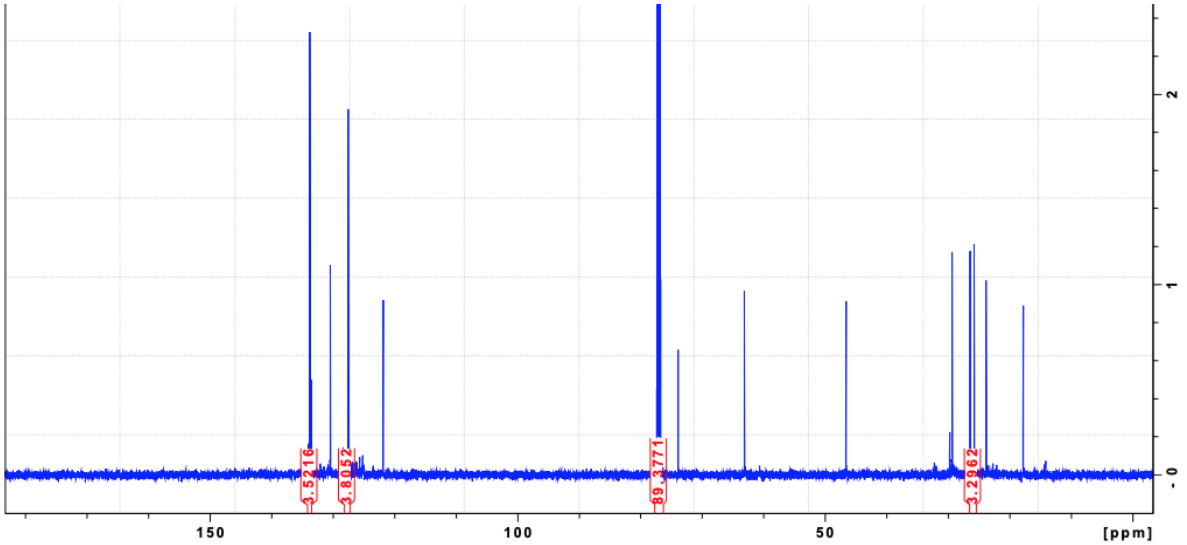
2r. (E)-2-phenyl-4-(thiophen-2-yl)-5-(3-(thiophen-2-yl)allyl)-1,3,2-dioxaborinane ^{13}C NMR



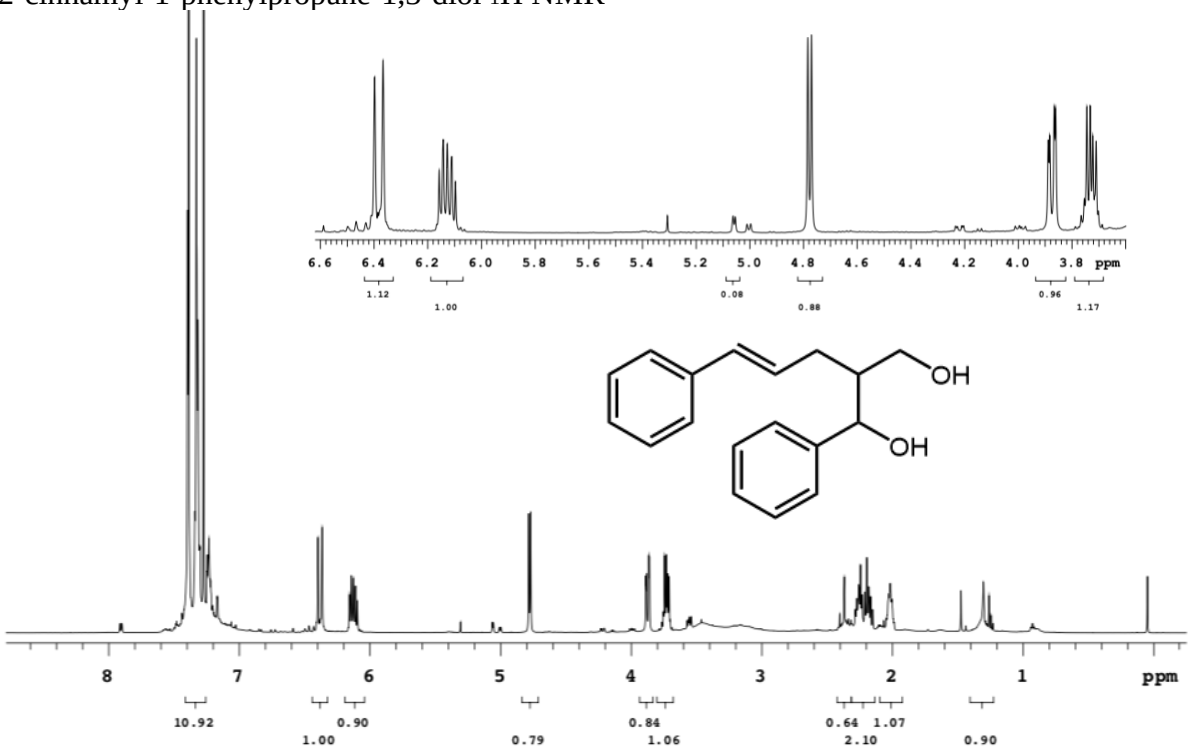
2s. 4,4-dimethyl-5-(3-methylbut-2-en-1-yl)-2-phenyl-1,3,2-dioxaborinane ^{1}H NMR



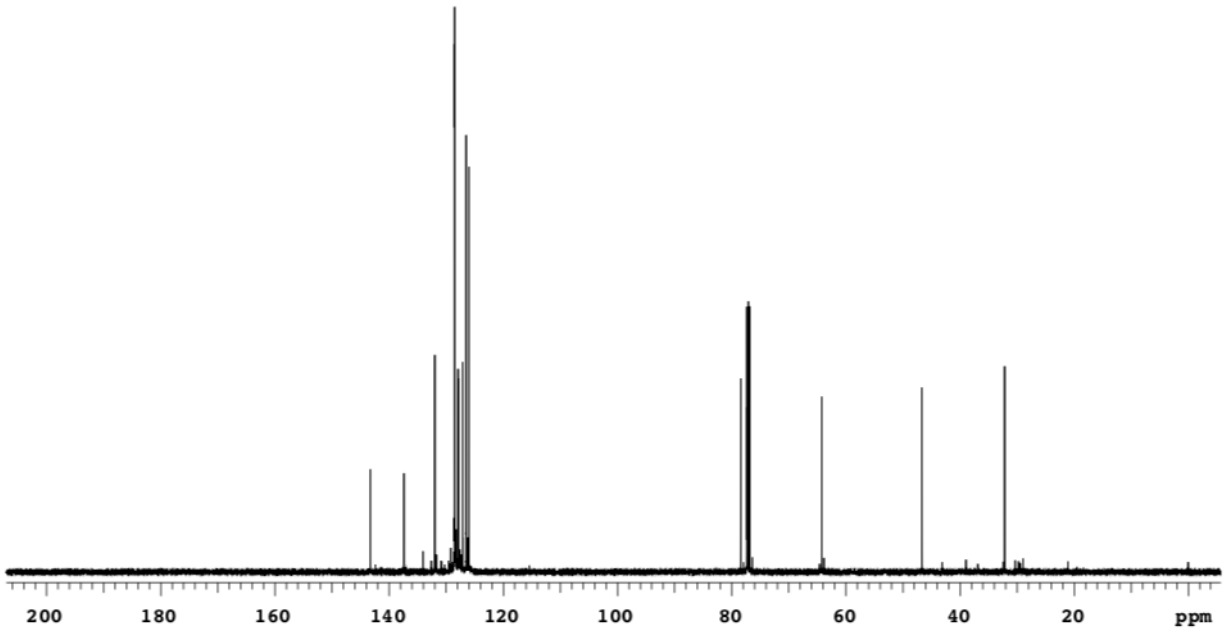
2s. 4,4-dimethyl-5-(3-methylbut-2-en-1-yl)-2-phenyl-1,3,2-dioxaborinane ^{13}C NMR



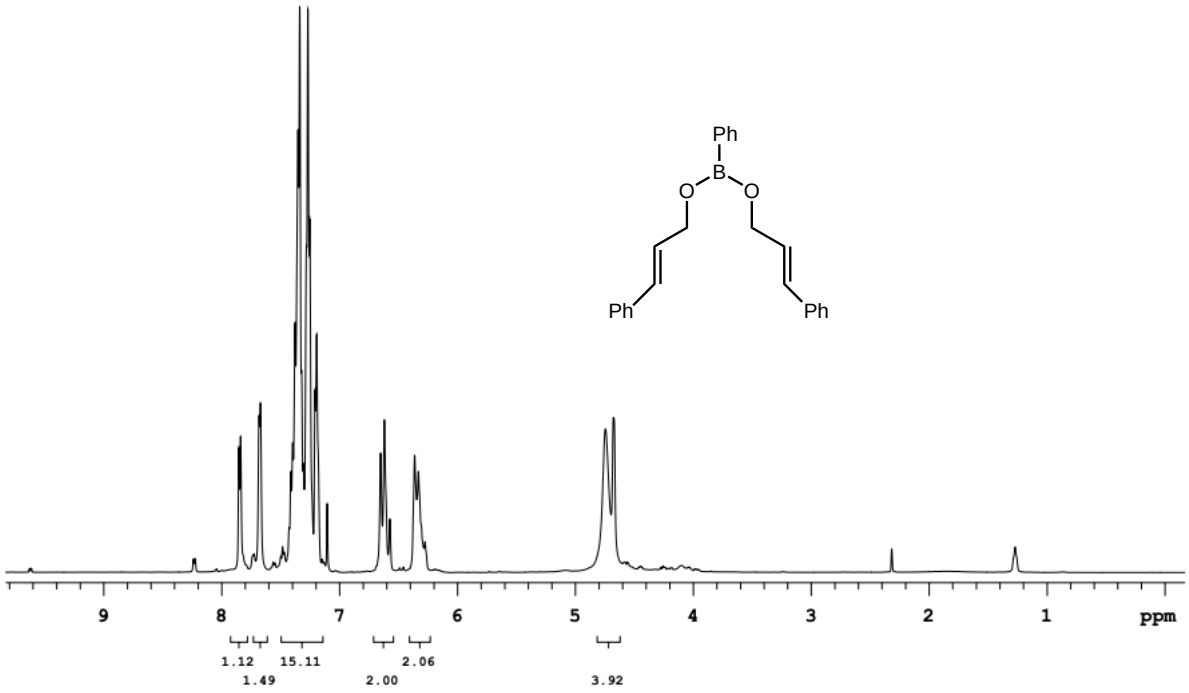
3. 2-cinnamyl-1-phenylpropane-1,3-diol $_{1}$H NMR



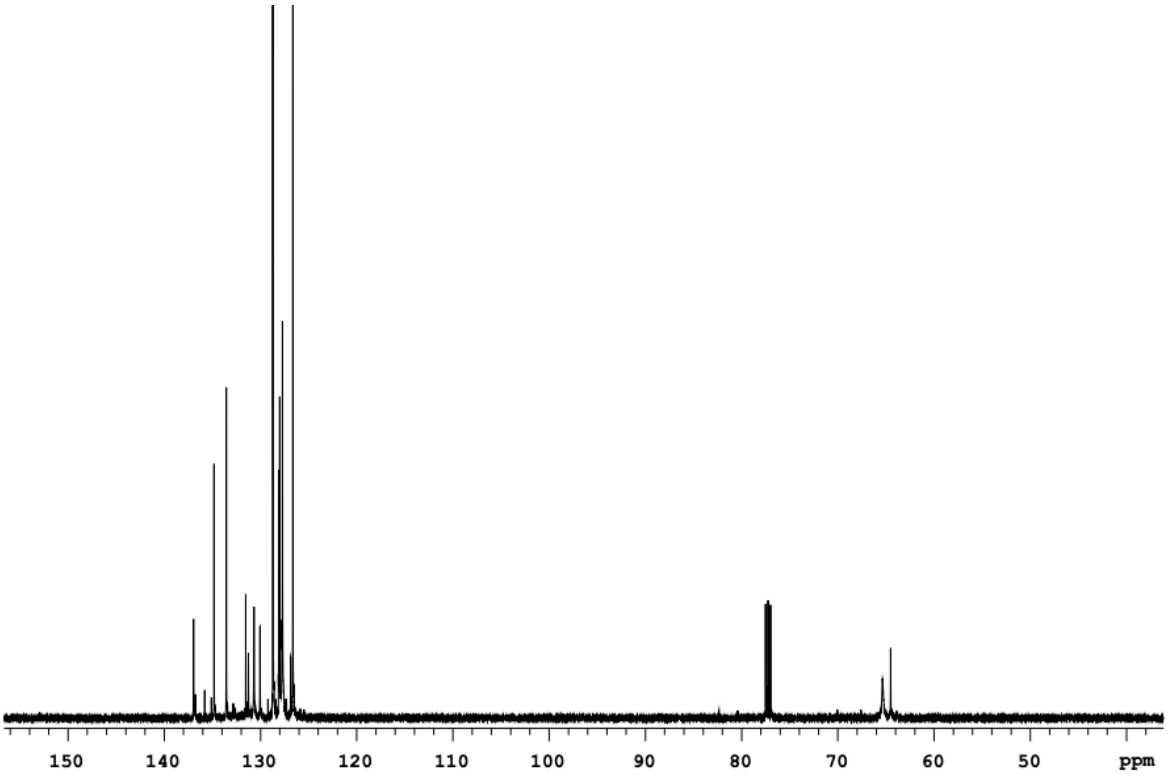
3. 2-cinnamyl-1-phenylpropane-1,3-diol $_{13}$C NMR



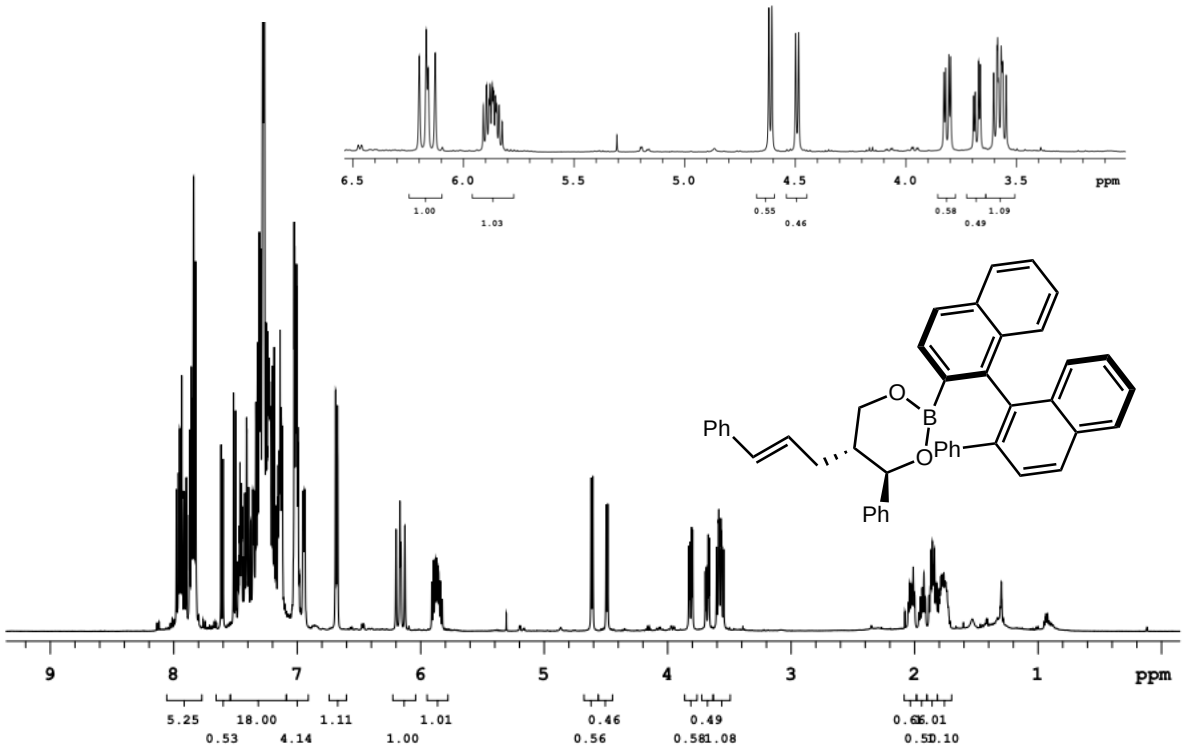
4. Dicinnamyl phenylboronate ^{1}H NMR



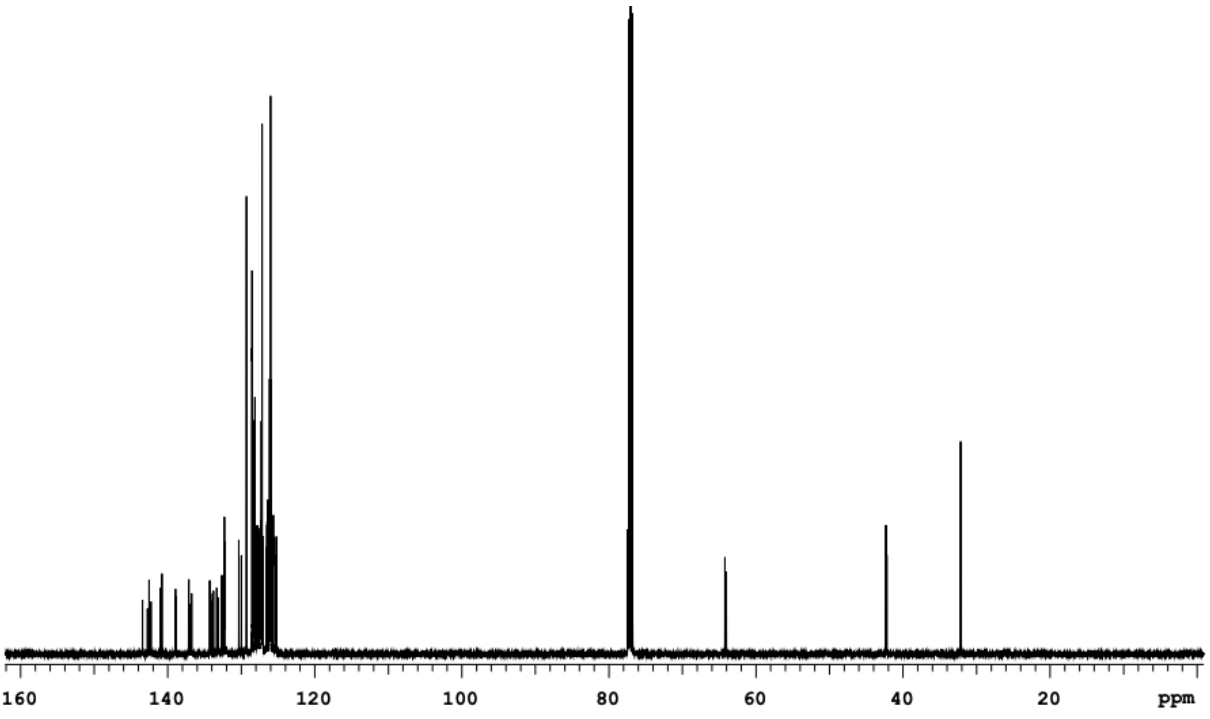
4. Dicinnamyl phenylboronate ^{13}C NMR



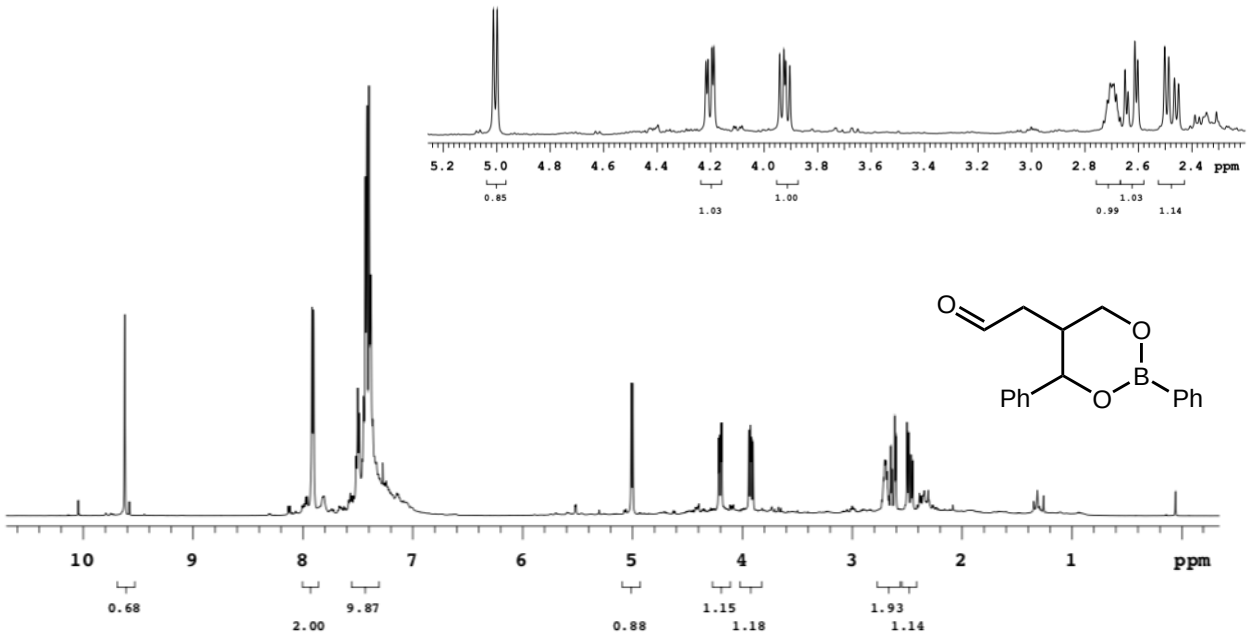
7. (4*R*,5*R*)-5-cinnamyl-4-phenyl-2-((*R*)-2'-phenyl-[1,1'-binaphthalen]-2-yl)-1,3,2-dioxaborinane
$_{1}$H NMR



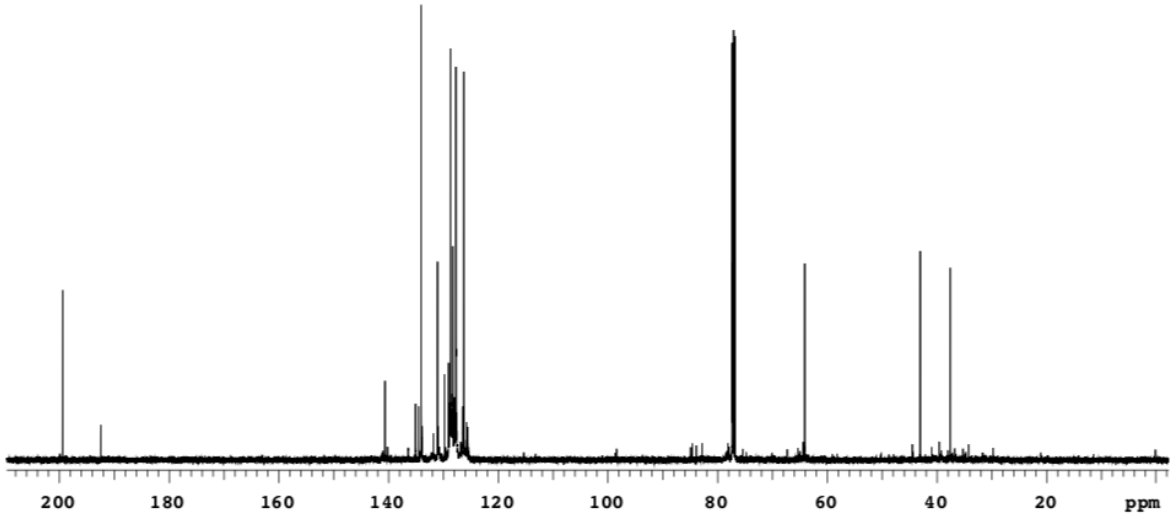
7. (4*R*,5*R*)-5-cinnamyl-4-phenyl-2-((*R*)-2'-phenyl-[1,1'-binaphthalen]-2-yl)-1,3,2-dioxaborinane
$_{13}$C NMR



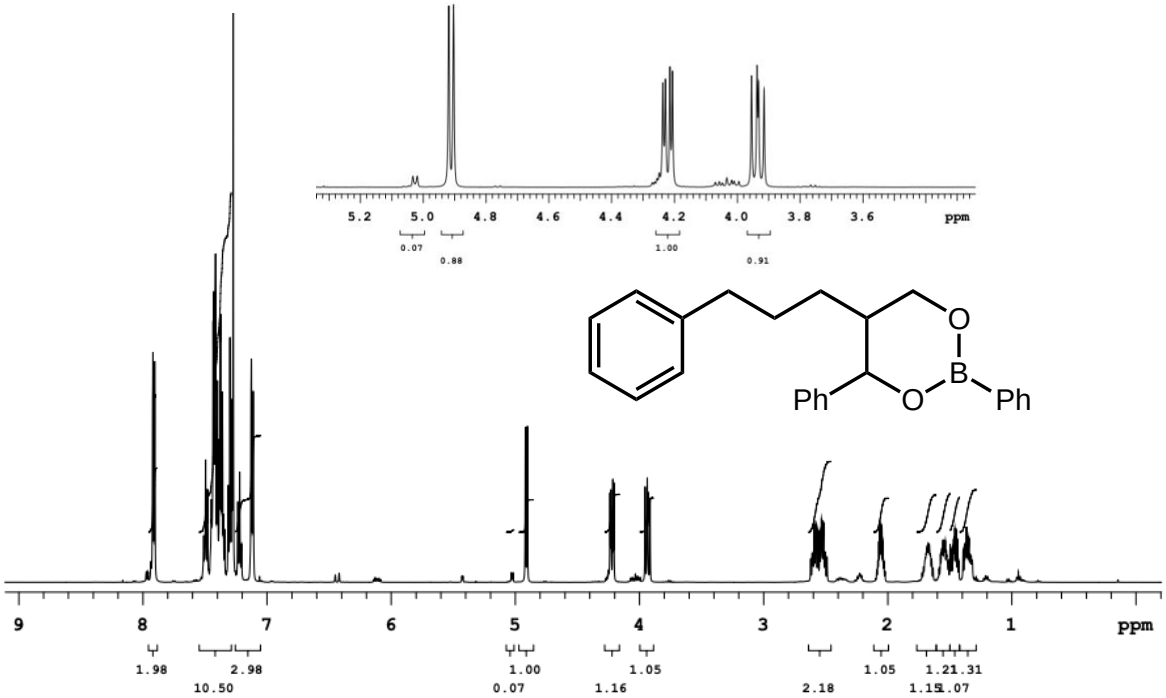
8. 2-(2,4-diphenyl-1,3,2-dioxaborinan-5-yl)acetaldehyde ^{1}H NMR



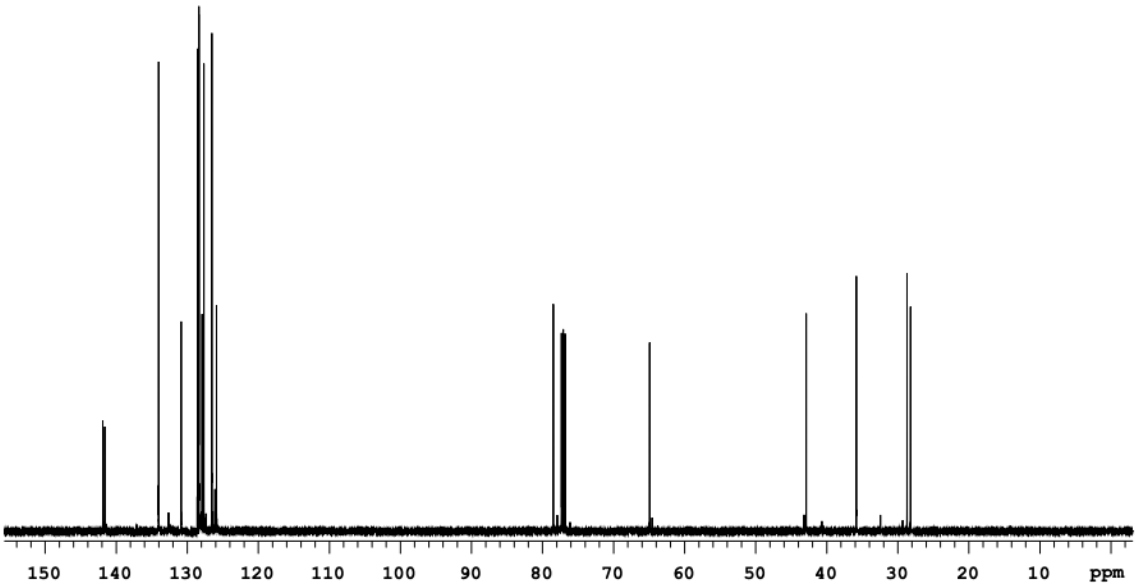
8. 2-(2,4-diphenyl-1,3,2-dioxaborinan-5-yl)acetaldehyde ^{13}C NMR



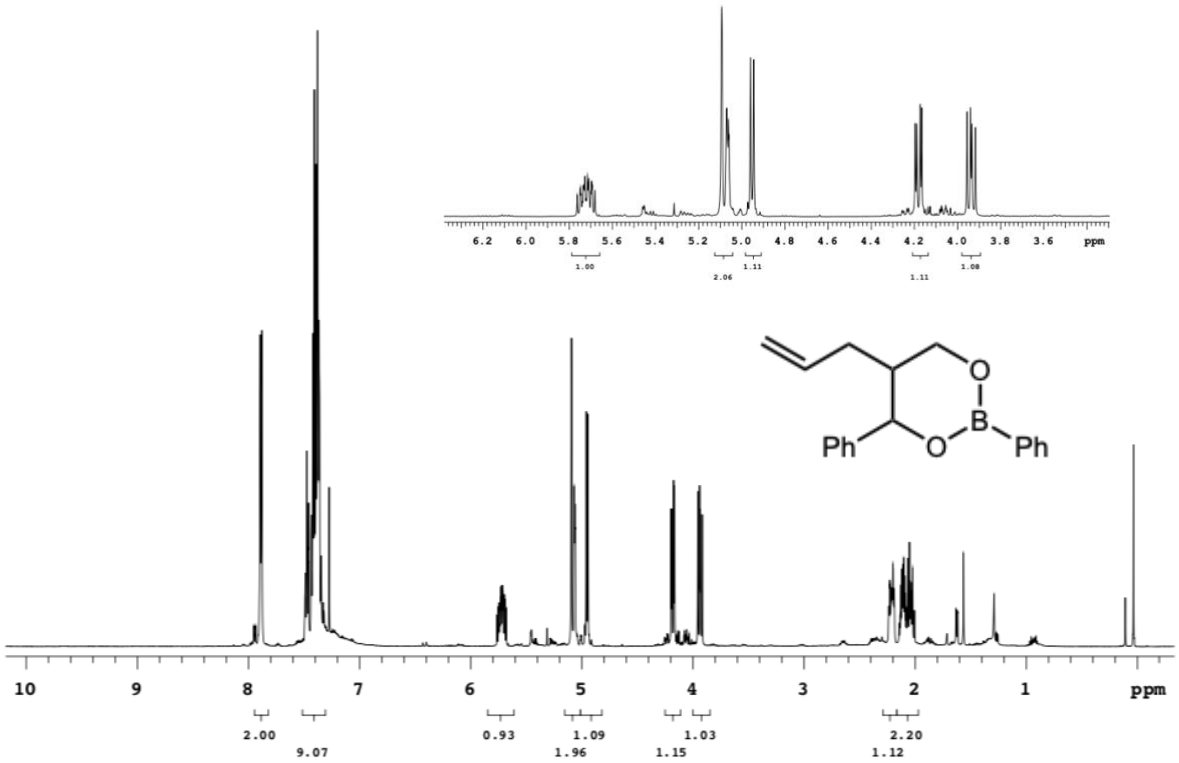
9. 2,4-diphenyl-5-(3-phenylpropyl)-1,3,2-dioxaborinane ^{1}H NMR



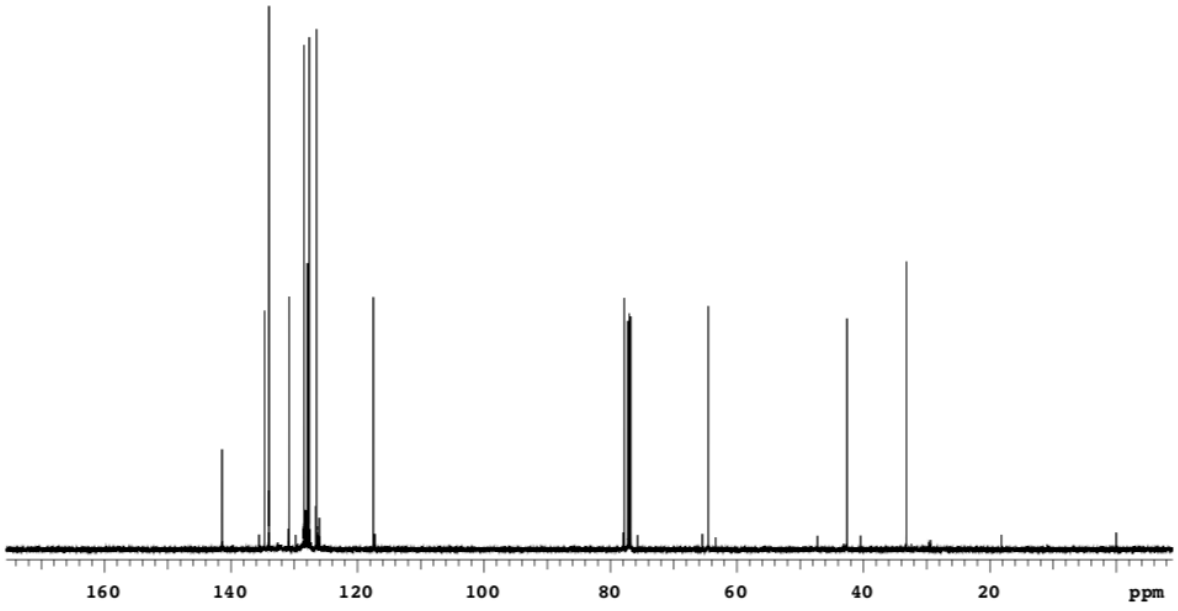
9. 2,4-diphenyl-5-(3-phenylpropyl)-1,3,2-dioxaborinane ^{13}C NMR



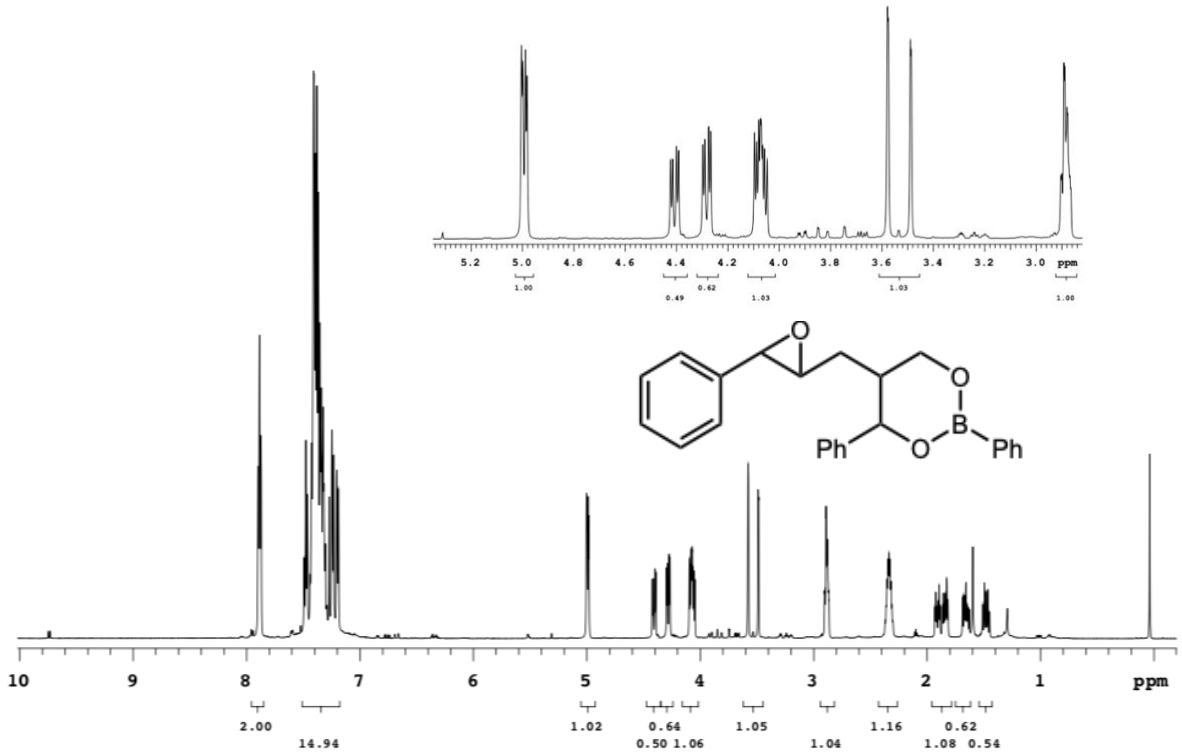
10. 5-allyl-2,4-diphenyl-1,3,2-dioxaborinane ^{1}H NMR



10. 5-allyl-2,4-diphenyl-1,3,2-dioxaborinane ^{13}C NMR



11. 2,4-diphenyl-5-((3-phenyloxiran-2-yl)methyl)-1,3,2-dioxaborinane ^{1}H NMR



11. 2,4-diphenyl-5-((3-phenyloxiran-2-yl)methyl)-1,3,2-dioxaborinane ^{13}C NMR