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Supporting Information

Electrochemical Hydroboration of Alkynes

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General Informations

Reactions were performed with ElectraSyn® 2.0 package from IKA© device. Flash chromatographies were performed with silica gel (0.040-0.060 nm). Analytical thin layer chromatographies were performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm) and/or chemical staining with a *p*-anisaldehyde solution. NMR spectra were recorded on a Brucker DXP 300 instrument at 300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F and 96 MHz for ^{11}B in $CDCl_3$ or benzene-d^6 at room temperature unless otherwise stated. Chemical shifts (δ) were quoted in parts per million (ppm) relative to the residual peak of $CHCl_3$ (δ_H = 7.26 ppm and δ_C = 77.16 ppm) and benzene (δ_H = 7.16 ppm and δ_C = 128.06 ppm). Spectra are reported as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets q = quartet and m = multiplet), integration and coupling constant. High-resolution mass spectra (HRMS) were recorded on Waters LCT Premier and IR spectra were recorded on a PerkinElmer Spectrum 100. Melting point were measured with the Stuart SMP3 device in open capillaries.

Solvents

Methanol 99.9% extra-dry AcroSeal™ was used for reactions. Technical grade solvents for extraction and purification (cyclohexane, dichloromethane, *n*-pentane, ethyl acetate, diethyl ether and petroleum ether) were used without purification.

Reagents

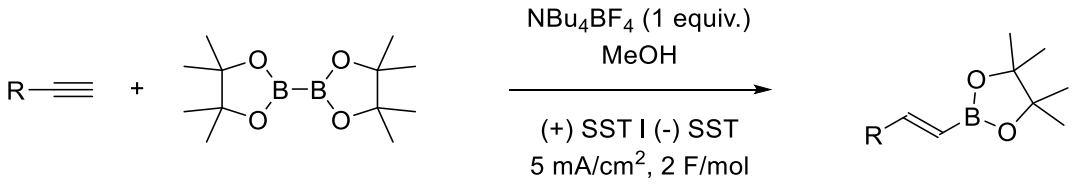
All reagents were commercials and used as received except compounds below.

(4-ethynylphenyl)methanol and 2-ethynylnaphthalene were prepared according to the literature.[1]

(R)-2,5,7,8-tetramethyl-6-(prop-2-yn-1-yloxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane was prepared according to the literature.[2]

2-(4-ethynylphenyl)-2-methyl-1,3-dioxolane was prepared according to the literature.[1,3]

Boronate Formation



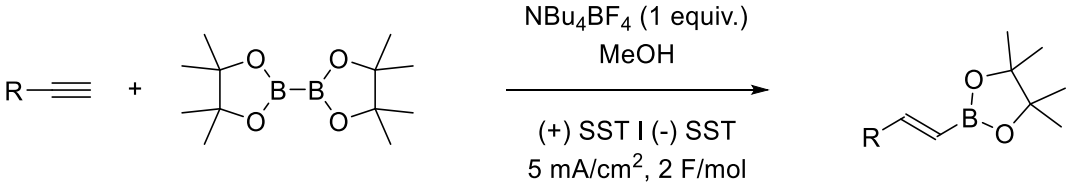
General procedure A

In a 5 mL IKA© vial were added the alkyne derivative (0.2 mmol, 1 equiv.), B_2Pin_2 (102 mg, 0.4 mmol, 2 equiv.) and NBu_4BF_4 (66 mg, 0.2 mmol, 1 equiv.) in anhydrous MeOH (4 mL). The reaction mixture was stirred under air before starting the IKA ElectraSyn© device ((+) SST, (-) SST, 5 mA/cm^2, 2 F/mol, 64 min). Then, HCl 1 M (2 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Then, the residue was purified by flash chromatography. *[SST=Stainless Steel]*

General procedure B

In a 5 mL IKA© vial were added the alkyne derivative (0.2 mmol, 1 equiv.), B_2Pin_2 (102 mg, 0.4 mmol, 2 equiv.), K_2CO_3 (28 mg, 0.2 mmol, 1 equiv.) and NBu_4BF_4 (66 mg, 0.2 mmol, 1 equiv.) in anhydrous MeOH (4 mL). The reaction mixture was stirred under air before starting the IKA ElectraSyn© device ((+) SST, (-) SST, 5 mA/cm^2, 2.5 F/mol, 100 min). Then, HCl 1 M (2 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Then, the residue was purified by flash chromatography. *[SST=Stainless Steel]*

Products purification and characterization



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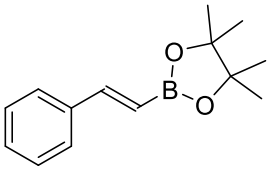
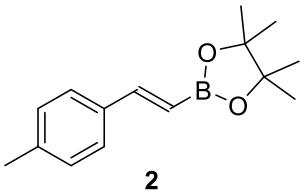
(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (1)



1

Prepared following the general procedure **A** in duplicate and combined prior to purification. **Yield:** 84% (77.1 mg, 0.34 mmol). Flash column chromatography: pentane/EtOAc: 98:2; Pale yellow oil; **R_f:** 0.66 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.50-7.48 (m, 2H), 7.40 (d, *J* = 19.0 Hz, 1H), 7.34-7.29 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.7, 137.6, 129.0, 128.7, 127.2, 83.5, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.8; **IR (neat, cm^{-1}):** ν 2978, 2927, 1623, 1350, 1321, 1209, 1142, 747; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{20}BO_2$: 231.1556, found: 231.1560 (+ 1.7 ppm). The data were consistent with those reported in the literature.[4]

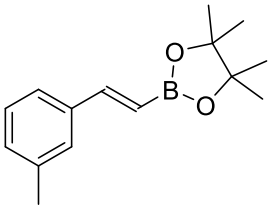
(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2)



2

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 85% (83.4 mg, 0.34 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow amorphous solid; **R_f:** 0.63 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.41-7.35 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.12 (d, *J* = 18.5 Hz, 1H), 2.35 (s, 3H), 1.32 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.6, 139.1, 134.9, 129.4, 127.1, 83.4, 24.9, 21.5. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.5; **IR (neat, cm^{-1}):** ν 2978, 2921, 1626, 1346, 1324, 1139, 798, 493; **HRMS (EI$^+$):** calcd for [MS] $C_{15}H_{21}BO_2$: 244.16346, found: 244.16391 (-1.8 ppm). The data were consistent with those reported in the literature.[4]

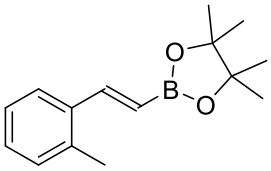
(*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (3)



3

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 91% (88.5 mg, 0.36 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow amorphous solid; **R_f:** 0.68 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 18.4 Hz, 1H), 7.31 (m, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.17 (d, *J* = 18.4 Hz, 1H), 2.35 (s, 3H), 1.32 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.8, 138.2, 137.5, 129.8, 128.6, 127.9, 124.3, 83.4, 24.9, 21.5. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.9; **IR (neat, cm^{-1}):** ν 2978, 2927, 1624, 1343, 1321, 1141, 849, 776, 645; **HRMS (EI$^+$):** calcd for [MS] $C_{15}H_{21}BO_2$: 244.16346, found: 244.16383 (+ 1.5 ppm). The data were consistent with those reported in the literature.[5]

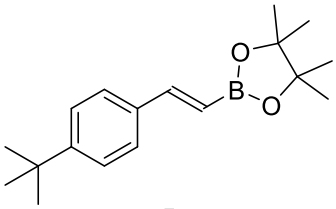
(*E*)-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane (4)



4

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 73% (71 mg, 0.29 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow amorphous solid; **R_f:** 0.69 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 18.2 Hz, 1H), 7.59-7.56 (m, 1H), 7.21-7.16 (m, 3H), 6.11 (d, *J* = 18.2 Hz, 1H), 2.44 (s, 3H), 1.33 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 147.2, 136.8, 136.4, 130.5, 128.7, 126.2, 125.9, 83.4, 24.9, 19.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.0; **IR (neat, cm^{-1}):** ν 2979, 2928, 1618, 1347, 1328, 1141, 762; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{15}H_{22}BO_2$: 245.1713, found: 245.1703 (- 4.1 ppm). The data were consistent with those reported in the literature.[6]

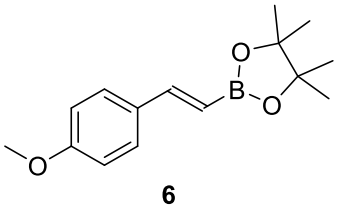
(*E*)-2-(4-(*tert*-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)



5

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 82% (94.3 mg, 0.33 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow solid; **Mp:** 77-78 °C (pentane/EtOAc); **R_f:** 0.68 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.45-7.35 (m, 5H), 6.12 (d, *J* = 18.4 Hz, 1H), 1.31 (app s, 21H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 152.3, 149.5, 134.9, 127.0, 125.6, 83.4, 34.8, 31.4, 25.0. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.8; **IR (neat, cm^{-1}):** ν 2963, 2927, 2870, 1624, 1346, 1323, 1141, 813, 558; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{18}H_{28}BO_2$: 287.2182, found: 287.2175 (- 2.4 ppm). The data were consistent with those reported in the literature.[4]

(*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)

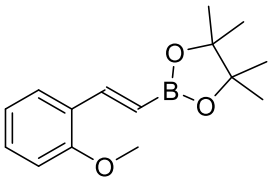


6

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 75% (75.2 mg, 0.30 mmol). Flash column chromatography: pentane/EtOAc: 98:2; Yellow amorphous solid; **R_f:** 0.64 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.45-7.32 (m, 3H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.02 (d, *J* = 18.4 Hz, 1H), 3.79 (s, 3H), 1.30 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 160.4, 149.2, 130.5, 128.6, 114.0, 83.3, 55.3, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.8; **IR (neat, cm^{-1}):** ν 2980, 2927, 1624, 1510, 1353, 1322, 1250, 1212, 1136, 805; **HRMS (API$^+$):** calcd for

[M+H]$^+$ $C_{15}H_{22}BO_3$: 261.1662, found: 261.1668 (+ 2.3 ppm). The data were consistent with those reported in the literature.[4]

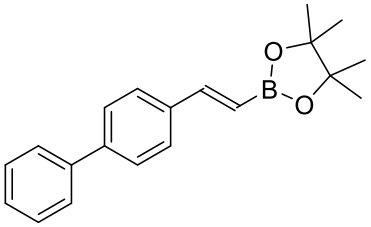
(*E*)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)



7

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 70% (72.4 mg, 0.28 mmol). Flash column chromatography: pentane/EtOAc: 95:5; Yellow amorphous solid; **R_f:** 0.37 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 18.6 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.26 (td, *J* = 7.8, 1.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.19 (d, *J* = 18.6 Hz, 1H), 3.84 (s, 3H), 1.31 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 157.4, 144.2, 130.1, 127.1, 126.6, 120.6, 110.9, 83.3, 55.4, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.8; **IR (neat, cm^{-1}):** ν 2979, 2932, 1617, 1488, 1346, 1322, 1242, 1123, 1141, 1123, 848, 750, 730; **HRMS (API$^+$):** calcd for [M+H]$^+$ $C_{15}H_{22}BO_3$: 261.1662, found: 261.1655 (- 2.7 ppm).

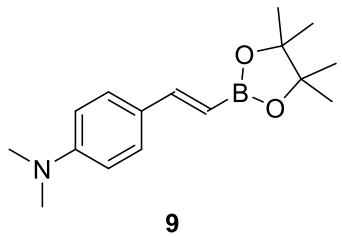
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)



8

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 42% (51.5 mg, 0.17 mmol). Flash column chromatography: pentane/EtOAc: 30:1; White solid; **Mp:** 104-105 °C (pentane/EtOAc); **R_f:** 0.41 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.63-7.59 (m, 6H), 7.50-7.47 (m, 1H), 7.45-7.43 (m, 2H), 7.38-7.33 (m, 1H), 6.23 (d, *J* = 18.4 Hz, 1H), 1.34 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.1, 141.7, 140.7, 136.6, 128.9, 127.6, 127.6, 127.4, 127.1, 83.5, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.1; **IR (neat, cm^{-1}):** ν 3029, 2976, 2925, 2856, 1620, 1349, 1325, 1139, 1001, 818, 762, 699, 503; **HRMS (EI$^+$):** calcd for [MS] $C_{20}H_{23}BO_2$: 306.1791, found: 306.1784 (- 2.4 ppm). The data were consistent with those reported in the literature.[4]

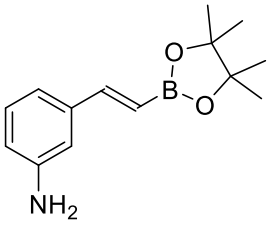
(*E*)-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (9)



9

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 92% (100.2 mg, 0.37 mmol). Flash column chromatography: pentane/EtOAc: 30:1; Brown solid; **Mp:** 97-98 °C (pentane/EtOAc); **R_f:** 0.48 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 18.8 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 5.92 (d, *J* = 18.3 Hz, 1H), 2.98 (s, 6H), 1.31 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 151.1, 149.9, 128.5, 126.0, 112.1, 83.1, 40.4, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.1; **IR (neat, cm^{-1}):** ν 2977, 2927, 1601, 1522, 1351, 1321, 1137, 800, 510; **HRMS (ESI$^+$):** calcd for [M+H]$^+$ $C_{16}H_{25}BNO_2$: 274.1978, found: 274.1987 (+ 3.3 ppm). The data were consistent with those reported in the literature.[4]

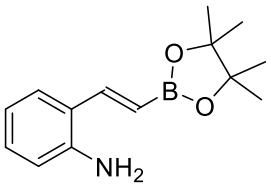
(*E*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (10)



10

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 68% (66.5 mg, 0.27 mmol). Flash column chromatography: pentane/EtOAc: 9:1; Yellow oil; **R_f:** 0.45 (petroleum ether/EtOAc: 7:3); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.29 (d, *J* = 18.5 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.78 (s, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 6.08 (d, *J* = 18.4 Hz, 1H), 3.71-3.44 (m, 2H), 1.29 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.9, 146.6, 138.6, 129.5, 118.0, 116.0, 113.5, 83.4, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.9; **IR (neat, cm^{-1}):** ν 3377, 2981, 2933, 1735, 1623, 1350, 1321, 1141, 849, 775; **HRMS (ESI$^+$):** calcd for $[M+H]^+$ $C_{14}H_{21}BNO_2$: 246.1665, found: 246.1666 (+ 0.4 ppm). The data were consistent with those reported in the literature.[7]

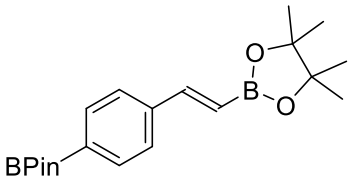
(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (11)



11

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 43% (42.4 mg, 0.17 mmol). Flash column chromatography: pentane/EtOAc: 87:13; Yellow oil; **R_f:** 0.33 (petroleum ether/EtOAc: 8:2); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 18.3 Hz, 1H), 7.42 (d, *J* = 7.70 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 18.2 Hz, 1H), 3.97 (s_{brd}, 2H), 1.32 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 144.9, 144.6, 129.9, 127.5, 123.6, 118.9, 116.4, 83.4, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 31.0; **IR (neat, cm^{-1}):** ν 3348, 2977, 2925, 2855, 1613, 1569, 1452, 1349, 1313, 1139, 849, 748; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{21}BNO_2$: 246.1665 found: 246.1670 (+ 2.0 ppm).

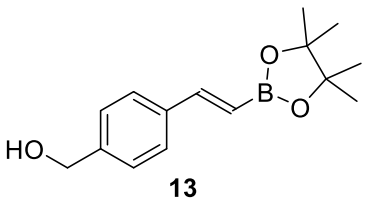
(*E*)-4,4,5,5-tetramethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)-1,3,2-dioxaborolane (12)



12

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 56% (80.0 mg, 0.22 mmol). Flash column chromatography: pentane/EtOAc: 97:3; White solid; **Mp:** 203-204 °C (pentane/EtOAc); **R_f:** 0.64 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 18.5 Hz, 1H), 6.23 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H), 1.30 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.5, 140.1, 135.1, 126.4, 83.9, 83.5, 25.0, 24.9. The carbons bearing the boron derivatives were not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 31.8; **IR (neat, cm^{-1}):** ν 2980, 2925, 2854, 1623, 1348, 1326, 1139, 813, 638; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{20}H_{31}B_2O_4$: 357.2408, found: 357.2425 (+ 4.8 ppm). The data were consistent with those reported in the literature.[4]

(*E*)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanol (13)

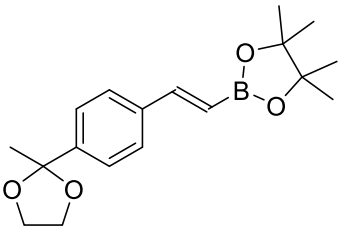


13

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 67% (70 mg, 0.27 mmol). Flash column chromatography: pentane/EtOAc: 8:2; White solid; **Mp:** 84-85 °C (pentane/EtOAc); **R_f:** 0.2 (petroleum ether/EtOAc: 8:2); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 18.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.10 (d, *J* = 18.4 Hz, 1H), 4.62 (s, 2H), 2.64 (s_{brd}, 1H), 1.29 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.2, 141.9, 136.8, 127.3, 127.2, 83.5, 64.8, 24.8. The carbon bearing boron was not

observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.4; **IR (neat, cm^{-1}):** ν 3442, 2978, 2928, 2874, 1622, 1380, 1371, 1347, 1321, 1213, 1138, 968, 997, 844, 801, 490; **HRMS (API$^+$):** calcd for $[M+H-H_2O]^+$ $C_{15}H_{20}BO_2$: 243.1556, found: 243.1562 (+ 2.5 ppm).

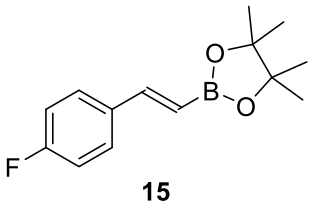
(*E*)-4,4,5,5-tetramethyl-2-(4-(2-methyl-1,3-dioxolan-2-yl)styryl)-1,3,2-dioxaborolane (14)



14

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 67% (84.9 mg, 0.27 mmol). Flash column chromatography: pentane/EtOAc: 9:1; White solid; **Mp:** 106-107 °C (pentane/EtOAc); **R_f:** 0.40 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.43-7.43 (m, 4H), 7.36 (d, *J* = 18.5 Hz, 1H), 6.14 (d, *J* = 18.4 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 2H), 3.73 (t, *J* = 6.7 Hz, 2H), 1.62 (s, 3H), 1.29 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.1, 144.1, 137.1, 127.0, 125.6, 108.7, 83.4, 64.5, 27.5, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.8; **IR (neat, cm^{-1}):** ν 2977, 2929, 2853, 1622, 1370, 1345, 1328, 1197, 1142, 1124, 1033, 848, 812, 578; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{18}H_{26}BO_4$: 317.1924, found: 317.1933 (+ 2.8 ppm). The data were consistent with those reported in the literature.[4]

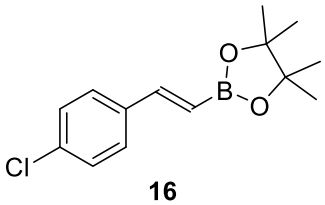
(*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)



15

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 80% (79.4 mg, 0.32 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow amorphous solid; **R_f:** 0.58 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.48-7.43 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.04-6.99 (m, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.3 (d, J_{C-F} = 249 Hz), 148.3, 133.8 (d, J_{C-F} = 3 Hz), 128.8 (d, J_{C-F} = 8 Hz), 115.7 (d, J_{C-F} = 22 Hz), 83.5, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.8; **^{19}F NMR (282 MHz, $CDCl_3$):** δ -112.3; **IR (neat, cm^{-1}):** ν 2978, 2927, 1623, 1600, 1507, 1349, 1324, 1209, 1223, 1141, 811; **HRMS (EI$^+$):** calcd for [MS] $C_{14}H_{18}BFO_2$: 248.1384, found: 248.1386 (+ 0.9 ppm). The data were consistent with those reported in the literature.[4]

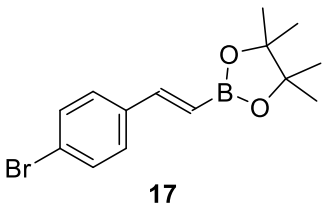
(*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)



16

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 88% (93.2 mg, 0.35 mmol). Flash column chromatography: pentane/EtOAc: 40:1; White solid; **Mp:** 88-89 °C (pentane/EtOAc); **R_f:** 0.72 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.36-7.28 (m, 3H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.30 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.1, 136.0, 134.7, 128.9, 128.3, 83.6, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **IR (neat, cm^{-1}):** ν 2976, 2930, 1625, 1347, 1321, 1140, 802; **HRMS (EI$^+$):** calcd for [MS] $C_{14}H_{18}BClO_2$: 266.10589, found: 266.10620 (+ 1.2 ppm). The data were consistent with those reported in the literature.[5]

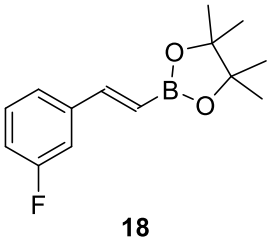
(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)



17

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 68% (83.3 mg, 0.27 mmol). Flash column chromatography: pentane/EtOAc: 99:1; Yellow solid; **Mp:** 88-89 °C (pentane/EtOAc); **R_f:** 0.73 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.46-7.44 (d, *J* = 8.3 Hz, 2H), 7.35-7.28 (m, 3H), 6.14 (d, *J* = 18.4 Hz, 1H), 1.30 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.2, 136.5, 131.9, 128.6, 123.0, 83.6, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **IR (neat, cm^{-1}):** ν 2974, 2928, 1625, 1344, 1320, 1260, 799, 486; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{19}BBrO_2$: 309.0661, found: 309.0648 (- 4.2 ppm). The data were consistent with those reported in the literature.[11]

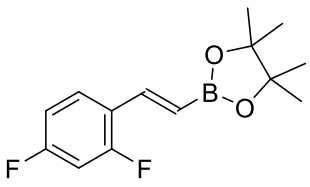
(*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)



18

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 61% (60.1 mg, 0.24 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Pale yellow oil; **R_f:** 0.49 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.28 (d, *J* = 18.6 Hz, 1H), 7.23-7.16 (m, 2H), 7.12-7.09 (m, 1H), 6.94-6.89 (m, 1H), 6.10 (d, *J* = 18.4 Hz, 1H), 1.25 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.2 (d, $J_{C\text{-}F}$ = 246 Hz), 148.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 140.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 130.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 123.1 (d, $J_{C\text{-}F}$ = 2.7 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz), 113.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 83.6, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.0; **^{19}F NMR (282 MHz, $CDCl_3$):** δ -113.5; **IR (neat, cm^{-1}):** ν 2979, 2930, 1627, 1582, 1346, 1325, 1244, 1140, 849, 779; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{19}BFO_2$: 249.1462, found: 249.1467 (+ 2.0 ppm). The data were consistent with those reported in the literature.[8]

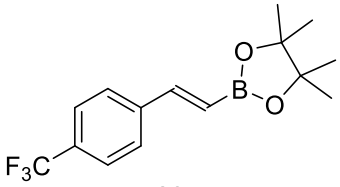
(*E*)-2-(2,4-difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19)



19

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 76% (80.3 mg, 0.30 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow oil; **R_f:** 0.63 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.56-7.46 (m, 2H), 6.86-6.74 (m, 2H), 6.14 (d, *J* = 18.6 Hz, 1H), 1.29 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.2 (dd, $^1J_{C\text{-}F}$ = 251 Hz, $^3J_{C\text{-}F}$ = 12 Hz), 160.9 (dd, $^1J_{C\text{-}F}$ = 254 Hz, $^3J_{C\text{-}F}$ = 12 Hz), 140.4 (dd, $^1J_{C\text{-}F}$ = 3 Hz, $^3J_{C\text{-}F}$ = 1 Hz), 128.5 (dd, $^1J_{C\text{-}F}$ = 10 Hz, $^3J_{C\text{-}F}$ = 5 Hz), 122.0 (dd, $^1J_{C\text{-}F}$ = 12 Hz, $^3J_{C\text{-}F}$ = 4 Hz), 111.7 (dd, $^1J_{C\text{-}F}$ = 22 Hz, $^3J_{C\text{-}F}$ = 4 Hz), 104.2 (t, $J_{C\text{-}F}$ = 26 Hz), 83.6, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **^{19}F NMR (282 MHz, $CDCl_3$):** δ -109.0 (d, $^4J_{F\text{-}F}$ = 8 Hz), -113.4 (d, $^4J_{F\text{-}F}$ = 8 Hz); **IR (neat, cm^{-1}):** ν 2981, 2933, 1627, 1500, 1349, 1327, 1138, 967, 848; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{18}BF_2O_2$: 267.1368, found: 267.1370 (+ 0.7 ppm). The data were consistent with those reported in the literature.[9]

(*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (20)

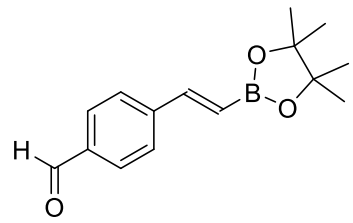


20

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 79% (94.3 mg, 0.32 mmol). Flash column chromatography: pentane/EtOAc: 40:1; Yellow amorphous solid; **R_f:** 0.61 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.60-7.54 (m, 4H), 7.40 (d, *J* = 18.4 Hz, 1H), 6.26 (d, *J* = 18.4 Hz, 1H),1.31 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):**

δ 147.8, 140.9, 130.6 (q, $J_{C\text{-}F}$ = 32 Hz), 127.3, 125.7 (q, $J_{C\text{-}F}$ = 4 Hz), 124.2 (q, $J_{C\text{-}F}$ = 272 Hz), 83.7, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **^{19}F NMR (282 MHz, $CDCl_3$):** δ -62.6; **IR (neat, cm^{-1}):** ν 2980, 2927, 1628, 1614, 1321, 1105, 1066, 814; **HRMS (EI$^+$):** calcd for [MS] $C_{15}H_{18}BF_3O_2$: 298.13519, found: 298.13409 (- 3.7ppm). The data were consistent with those reported in the literature.[5]

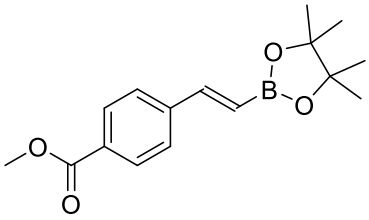
(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzaldehyde (21)



21

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 51% (52.1 mg, 0.20 mmol). Flash column chromatography: pentane/EtOAc: 92:8; White solid; **Mp:** 96-97 °C (pentane/EtOAc); **R_f:** 0.34 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.99 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 18.5 Hz, 1H), 6.31 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 191.8, 147.9, 143.3, 136.4, 130.2, 127.6, 83.8, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.9; **IR (neat, cm^{-1}):** ν 3976, 2928, 1686, 1623, 1370,1348, 1327, 1139, 1124, 845, 804, 493; **HRMS (API$^+$):** calcd for $[M+H+ACN]^+$ $C_{17}H_{23}BNO_3$: 300.1771, found: 300.1776 (+ 1.7 ppm).

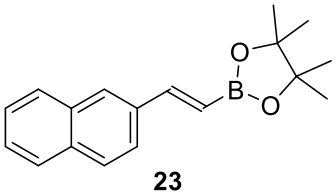
Methyl (*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (22)



22

Prepared following to general procedure **A** using a charge of 2.5 F/mol. The reaction was run in duplicate and combined prior to purification. **Yield:** 60% (69.2 mg, 0.24 mmol). Flash column chromatography: pentane/EtOAc: 94:6; White solid; **Mp:** 111-112 °C (pentane/EtOAc); **R_f:** 0.46 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 18.5 Hz, 1H), 6.26 (d, *J* = 18.4 Hz, 1H), 3.89 (s, 3H), 1.30 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.9, 148.2, 141.8, 130.2, 130.0, 127.0, 83.7, 52.2, 24.9. The carbon bearing boron was not observed. **^{11}B (96 MHz, $CDCl_3$):** δ 29.7; **IR (neat, cm^{-1}):** ν 2975, 2939, 1714, 1628, 1350, 1320, 1275, 1146, 1111, 759; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{16}H_{22}BO_4$: 289.1611, found: 289.1605 (- 2.1 ppm). The data were consistent with those reported in the literature.[6]

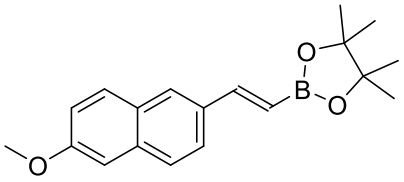
(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (23)



23

Prepared following to general procedure **A** using a charge of 2.5 F/mol. The reaction was run in duplicate and combined prior to purification **Yield:** 65% (72.8 mg, 0.26 mmol). Flash column chromatography: pentane/EtOAc: 98:2; Yellow solid; **Mp:** 70-71 °C (pentane/EtOAc); **R_f:** 0.53 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.86-7.80 (m, 4H), 7.74-7.71 (m, 1H), 7.60 (d, *J* = 18.4 Hz, 1H), 7.49-7.46 (m, 2H), 6.32 (d, *J* = 18.4 Hz, 1H), 1.35 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.6, 135.1, 133.8, 133.5, 128.5, 128.4, 128.1, 127.8, 126.5, 126.4, 123.5, 83.5, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.6; **IR (neat, cm^{-1}):** ν 3058, 2925, 2854, 1620, 1366, 1327, 1141, 812, 475; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{18}H_{22}BO_2$: 281.1713, found: 281.1724 (+ 3.9 ppm). The data were consistent with those reported in the literature.[10]

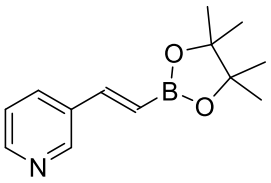
(*E*)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24)



24

Prepared following to general procedure **A** using a charge of 2.5 F/mol. The reaction was run in duplicate and combined prior to purification. **Yield:** 84% (104.4 mg, 0.34 mmol). Flash column chromatography: pentane/EtOAc: 25:1; White solid; **Mp:** 140-141 °C (pentane/EtOAc); **R_f:** 0.43 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.78 (s, 1H), 7.74-7.68 (m, 3H), 7.56 (d, *J* = 18.4 Hz, 1H), 7.15-7.10 (m, 2H), 6.25 (d, *J* = 18.4 Hz, 1H), 3.90 (s, 3H), 1.34 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 158.3, 149.8, 135.1, 133.0, 130.0, 128.9, 128.0, 127.2, 124.1, 119.1, 105.9, 83.4, 55.4, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.4; **IR (neat, cm^{-1}):** ν 2975, 2926, 2855, 1619, 1392, 1355, 1328, 1259, 1202, 1142, 841, 813, 632, 472; **HRMS (API$^+$)**: calcd for $[M+H]^+$ $C_{19}H_{24}BO_3$: 311.1819, found: 311.1826 (+ 2.2 ppm).

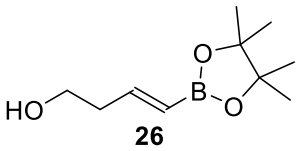
(*E*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (25)



25

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 63% (58.3 mg, 0.25 mmol). Flash column chromatography: cyclohexane/EtOAc: 9:1; White solid; **Mp:** 53-55 °C (pentane/EtOAc); **R_f:** 0.63 (petroleum ether/EtOAc: 7:3); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.69 (s, 1H), 8.52 (m, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 18.5 Hz, 1H), 7.28 (t, *J* = 6.2 Hz, 1H), 6.25 (d, *J* = 18.5 Hz, 1H), 1.32 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.8, 149.2, 145.8, 133.3, 133.1, 123.7, 83.7, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.8; **IR (neat, cm^{-1}):** ν 2979, 2928, 1627, 1417, 1352, 1329, 1141, 796, 645; **HRMS (ESI$^+$):** calcd for $[M+H]^+$ $C_{13}H_{19}BNO_2$: 232.1509, found: 232.1514 (+ 2.2 ppm). The data were consistent with those reported in the literature.[11]

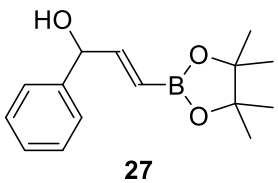
(*E*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (26)



26

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 51% (40.3 mg, 0.20 mmol). Flash column chromatography: pentane/EtOAc: 8:2; Colourless oil; **R_f:** 0.40 (petroleum ether/EtOAc: 8:2); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.58 (dt, *J* = 18.0, 6.6 Hz, 1H), 5.53 (d, *J* = 18.0 Hz, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.44-2.38 (m, 2H), 1.72 (s_{brd}, 1H), 1.24 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 150.2, 83.3, 61.3, 39.2, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **IR (neat, cm^{-1}):** ν 3429, 2978, 2931, 1639, 1358, 1317, 1142, 969, 849; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{10}H_{20}BO_3$: 199.1506, found: 199.1515 (+ 4.5 ppm). The data were consistent with those reported in the literature.[8]

(*E*)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (27)

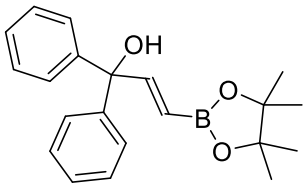


27

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 65% (67.2 mg, 0.26 mmol). Flash column chromatography: pentane/EtOAc: 85:15; Colorless amorphous solid; **R_f:** 0.13 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.37-7.29 (m, 5H), 6.77 (dd, *J* = 18.0, 5.3 Hz, 1H), 5.75 (dd, *J* = 18.0, 1.0 Hz, 1H), 5.24 (d, *J* = 4.8 Hz, 1H), 2.41 (s, 1H), 1.27 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 153.9, 142.1, 128.6, 127.9, 126.6, 83.5, 76.2, 24.9, 24.8. The carbon

bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.4; **IR (neat, cm^{-1}):** ν 3445, 2976, 2870, 1632, 1396, 1358, 1331, 1141, 992, 847, 766, 706, 657, 544; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{15}H_{22}BO_3$: 261.1662, found: 261.1670 (+ 3.1 ppm). The data were consistent with those reported in the literature.[12]

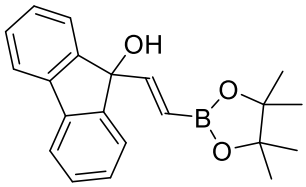
(*E*)-1,1-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (28)



28

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 63% (84.8 mg, 0.25 mmol). Flash column chromatography: pentane/EtOAc: 9:1; White solid; **Mp:** 121-122 °C (pentane/EtOAc); **R_f:** 0.23 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, C_6D_6):** δ 7.56 (d, *J* = 17.9 Hz, 1H), 7.41 (d, *J* = 7.0 Hz, 4H), 7.03 (dd, *J* = 15.8, 8.1 Hz, 6H), 6.17 (d, *J* = 17.9 Hz, 1H), 2.34 (s, 1H), 1.03 (s, 12H); **^{13}C NMR (75 MHz, C_6D_6):** δ 157.6, 146.3, 128.4, 127.5, 127.3, 83.3, 80.1, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.4; **IR (neat, cm^{-1}):** ν 3481, 2981, 1637, 1351, 1321, 1141, 849, 698, 658; **HRMS (API$^+$):** calcd for $[M+H-H_2O]^+$ $C_{21}H_{24}BO_2$: 319.1869, found: 319.1842 (- 8.5 ppm). The data were consistent with those reported in the literature.[12]

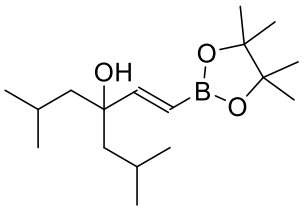
(*E*)-9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-9H-fluoren-9-ol (29)



29

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 82% (109.8 mg, 0.33 mmol). Flash column chromatography: pentane/EtOAc: 85:15; Yellow amorphous solid; **R_f:** 0.45 (petroleum ether/EtOAc: 8:2); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.38-7.27 (m, 4H), 6.63 (d, *J* = 18.0 Hz, 1H), 5.96 (d, *J* = 18.0 Hz, 1H), 2.59 (s, 1H), 1.21 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 152.9, 147.7, 139.7, 129.2, 128.1, 124.8, 120.1, 83.3, 83.2 24.8. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.4; **IR (neat, cm^{-1}):** ν 3376, 3064, 2978, 2933, 2244, 1636, 1346, 1142, 732; **HRMS (API$^+$):** calcd for $[M+H-H_2O]^+$ $C_{21}H_{22}BO_2$: 317.1713, found: 317.1723 (+ 3.2 ppm). The data were consistent with those reported in the literature.[12]

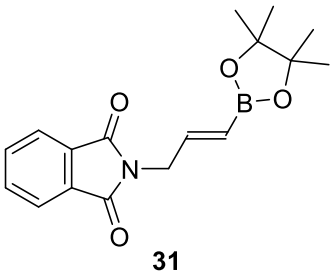
(*E*)-2,8-dimethyl-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)nonan-5-ol (30)



30

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 57% (67.2 mg, 0.23 mmol). Flash column chromatography: pentane/EtOAc: 9:1; White amorphous solid; **R_f:** 0.26 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.58 (d, *J* = 18.2 Hz, 1H), 5.58 (d, *J* = 18.2 Hz, 1H), 1.72-1.63 (m, 2H), 1.43-1.39 (m, 4H), 1.24 (s, 12H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.85 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 159.5, 83.2, 50.4, 25.1, 24.9, 24.7, 24.0. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.8; **IR (neat, cm^{-1}):** ν 3503, 2979, 2952, 2869, 1638, 1349, 1278, 1143, 1123, 849; **HRMS (API$^+$):** calcd for $[M+H-H_2O]^+$ $C_{17}H_{32}BO_2$: 279.2495, found: 279.2501 (+ 2.1 ppm).

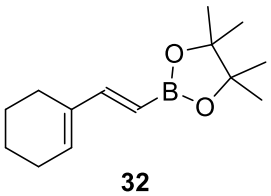
(*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione (31)



31

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 52% (65.2 mg, 0.21 mmol). Flash column chromatography: pentane/EtOAc: 88:12; Colourless oil; **R_f:** 0.39 (petroleum ether/EtOAc: 8:2); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.82-7.79 (m, 2H), 7.69-7.66 (m, 2H), 6.55 (dt, *J* = 18.0, 4.5 Hz, 1H), 5.43 (d, *J* = 18.0 Hz, 1H), 4.33 (dd, *J* = 4.4, 1.6 Hz, 2H), 1.18 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 167.9, 145.3, 134.1, 132.1, 123.4, 83.4, 41.1, 24.8. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.2; **IR (neat, cm^{-1}):** ν 3474, 2979, 2929, 1773, 1711, 1645, 1389, 1360, 1322, 1141, 953, 848, 713, 529; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{17}H_{21}BNO_4$: 314.1564, found: 314.1568 (+ 1.3 ppm).

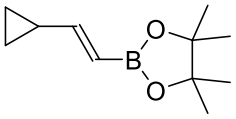
(*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32)



32

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 81% (75.8 mg, 0.32 mmol). Flash column chromatography: pentane/EtOAc: 98:2; Colourless oil; **R_f:** 0.55 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.00 (d, *J* = 18.3 Hz, 1H), 5.94 (app s, 1H), 5.40 (d, *J* = 18.2 Hz, 1H), 2.13-2.12 (m, 4H), 1.64-1.56 (m, 4H), 1.25 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 153.3, 137.2, 134.3, 83.1, 26.2, 24.8, 23.8, 22.5, 22.4. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.0; **IR (neat, cm^{-1}):** ν 2978, 2928, 2860, 1607, 1341, 1334, 1319, 1143, 970, 850, 771; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{24}BO_2$: 235.1869, found: 235.1873 (+ 1.7 ppm). The data were consistent with those reported in the literature.[11]

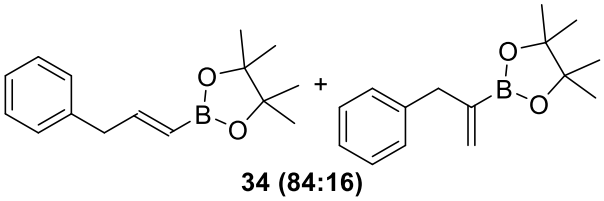
(*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33)



33

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 39% (30.4 mg, 0.16 mmol). Flash column chromatography: Cyclohexane/EtOAc: 99:1; Colourless oil; **R_f:** 0.83 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.07 (dd, *J* = 17.8, 9.3 Hz, 1H), 5.49 (d, *J* = 17.8 Hz, 1H), 1.59-1.47 (m, 1H), 1.25 (s, 12H), 0.83-0.77 (m, 2H), 0.56-0.51 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 158.7, 83.1, 24.9, 17.2, 8.0. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.4; **IR (neat, cm^{-1}):** ν 2979, 2930, 1633, 1380, 1326, 1313, 1297, 1139, 970, 947, 845, 653; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{11}H_{20}BO_2$: 195.1556, found: 195.1547 (- 4.6 ppm). The data were consistent with those reported in the literature.[11]

(*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane & 4,4,5,5-tetra methyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (34)



34 (84:16)

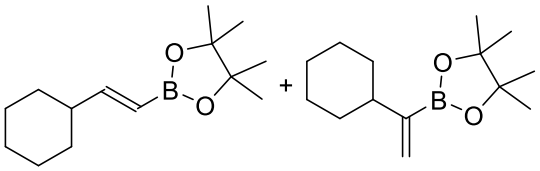
Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 55% (53.2 mg, 0.22 mmol). Flash column chromatography: pentane/EtOAc: 97:3; Colorless oil; **R_f:** 0.56 (petroleum ether/EtOAc: 9:1);

MAJOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.32-7.22 (m, 3H), 7.20- 7.17 (m, 2H), 6.78 (dd, *J* = 17.8, 6.3 Hz, 1H), 5.46 (d, *J* = 17.8 Hz, 1H), 3.49 (d, *J* = 5.3 Hz, 2H), 1.26 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ152.6, 139.2, 129.0, 128.5, 126.3, 83.2, 42.4, 24.9. The carbon bearing

boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **IR (neat, cm^{-1}):** ν 3028, 2978, 2929, 1636, 1359, 1319, 1141, 970, 851, 698; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{15}H_{22}BO_2$: 245.1713, found: 245.1711 (- 0.8 ppm). The data were consistent with those reported in the literature.[5]

MINOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.32-7.22 (m, 3H), 7.20- 7.17 (m, 2H), 5.85 (app s, 1H), 5.54 (app s, 1H), 3.49 (d, *J* = 5.2 Hz, 2H), 1.22 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 140.8, 129.9, 129.3, 128.2, 125.8, 83.6, 41.5, 24.8. The carbon bearing boron was not observed.

(*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(1-cyclohexyl vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)



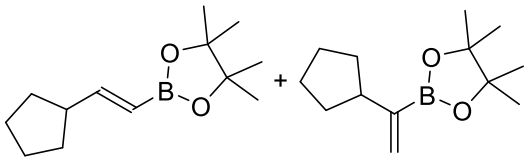
35 (89:11)

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 58% (54.9 mg, 0.23 mmol, ratio 88:12). Flash column chromatography: pentane/EtOAc: 99:1; Colourless oil; **R_f:** 0.78 (petroleum ether/EtOAc: 9:1);

MAJOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.56 (dd, *J* = 18.2, 6.1 Hz, 1H), 5.35 (d, *J* = 18.2 Hz, 1H), 2.02-1.99 (m, 1H), 1.73-1.61 (m, 6H), 1.25 (s, 12H), 1.19-1.02 (m, 4H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 160.0, 83.1, 43.4, 32.0, 26.3, 26.1, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.7; **IR (neat, cm^{-1}):** ν 2978, 2924, 2852, 1635, 1370, 1348, 1319, 1144, 970, 850; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{14}H_{26}BO_2$: 237.2026, found: 237.2022 (- 1.7 ppm). The data were consistent with those reported in the literature.[11]

MINOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.68 (app s, 1H), 5.53 (app s, 1H), 2.02-1.99 (m, 1H), 1.73-1.61 (m, 6H), 1.25 (s, 12H), 1.19-1.02 (m, 4H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 126.0, 83.3, 42.9, 32.6, 26.8, 26.4, 24.8. The carbon bearing boron was not observed.

(*E*)-2-(2-cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(1-cyclopentyl vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)



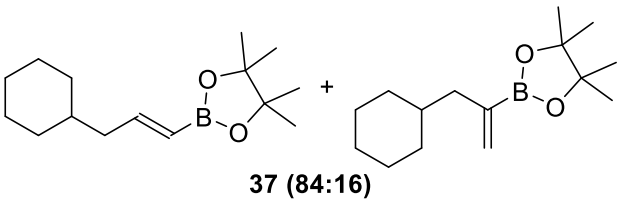
36 (96:4)

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 41% (36.6 mg, 0.16 mmol, ratio 96:4). Flash column chromatography: pentane/EtOAc: 99:1; Colourless oil; **R_f:** 0.79 (petroleum ether/EtOAc: 9:1);

MAJOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.60 (dd, *J* = 17.9, 7.2 Hz, 1H), 5.39 (d, *J* = 17.9 Hz, 1H), 2.57-2.44 (m, 1H), 1.78-1.76 (m, 2H), 1.64-1.55 (m, 4H), 1.39-1.33 (m, 2H), 1.26 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 159.1, 83.1, 46.3, 32.5, 25.4, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.8; **IR (neat, cm^{-1}):** ν 2978, 2953, 2869, 1635, 1367, 1317, 1143, 970, 849; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{13}H_{24}BO_2$: 223.1869, found: 223.1880 (+ 4.9 ppm). The data were consistent with those reported in the literature.[11]

MINOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.69 (app s, 1H), 5.58 (app s, 1H), 2.57-2.44 (m, 1H), 1.78-1.76 (m, 2H), 1.64-1.55 (m, 4H), 1.39-1.33 (m, 2H), 1.26 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 126.2, 83.3, 45.7, 32.2, 25.2, 24.9. The carbon bearing boron was not observed.

(*E*)-2-(3-cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(3-cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37)



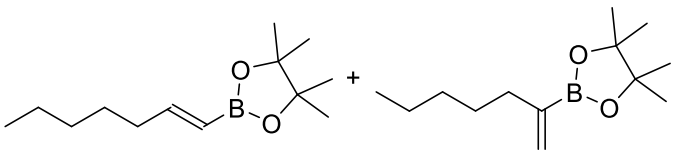
37 (84:16)

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 56% (56.0 mg, 0.22 mmol, ratio 89:11). Flash column chromatography: pentane/EtOAc: 99:1; Colourless oil; **R_f:** 0.78 (petroleum ether/EtOAc: 9:1);

MAJOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.59 (dt, *J* = 17.7, 6.7 Hz, 1H), 5.39 (d, *J* = 17.6 Hz, 1H), 2.04 (t, *J* = 6.7 Hz, 2H), 1.71-1.64 (m, 4H), 1.38-1.33 (m, 1H), 1.26 (s, 12H), 1.18-1.04 (m, 4H), 0.93-0.82 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 153.7, 83.1, 44.3, 37.3, 33.3, 26.6, 26.4, 24.9. The carbon bearing boron was not observed. **^{11}B (96 MHz, $CDCl_3$):** δ 30.1; **IR (neat, cm^{-1}):** ν 2978, 2922, 2852, 1638, 1360, 1316, 1144, 971, 850; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{15}H_{28}BO_2$: 251.2182, found: 251.2176 (- 2.4 ppm). The data were consistent with those reported in the literature.[11]

MINOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.77 (app s, 1H), 5.54 (app s, 1H), 2.04 (t, *J* = 6.7 Hz, 2H), 1.71-1.64 (m, 4H), 1.38-1.33 (m, 1H), 1.26 (s, 12H), 1.18-1.04 (m, 4H), 0.93-0.82 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 130.1, 83.4, 43.4, 37.8, 29.8, 26.8, 26.5, 24.8. The carbon bearing boron was not observed.

(*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(hept-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)



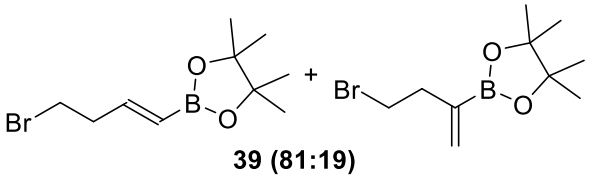
38 (81:19)

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 46% (41.1 mg, 0.18 mmol, ratio 81:19). Flash column chromatography: pentane/EtOAc: 98:2; Colourless oil; **R_f:** 0.80 (petroleum ether/EtOAc: 9:1);

MAJOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.62 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.41 (d, *J* = 18.0 Hz, 1H), 2.13 (dd, *J* = 13.3, 6.4 Hz, 2H), 1.42-1.29 (m, 6H), 1.25 (s, 12H), 0.88-0.84 (m, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 155.0, 83.1, 35.9, 31.5, 28.0, 24.9, 22.7, 14.1. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.6; **IR (neat, cm^{-1}):** ν 2978, 2959, 2927, 2858, 1638, 1360, 1316, 1143, 972, 850; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{13}H_{26}BO_2$: 225.2026, found: 225.2025 (- 0.4 ppm). The data were consistent with those reported in the literature.[13]

MINOR: **^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.72 (app s, 1H), 5.57 (app s, 1H), 2.13 (dd, *J* = 13.3, 6.4 Hz, 2H), 1.42-1.29 (m, 6H), 1.25 (s, 12H), 0.88-0.84 (m, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 128.8, 83.4, 35.4, 31.6, 29.0, 24.9, 22.7, 14.2. The carbon bearing boron was not observed. The data were consistent with those reported in the literature.[14]

(*E*)-2-(4-bromobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(4-bromobut-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)

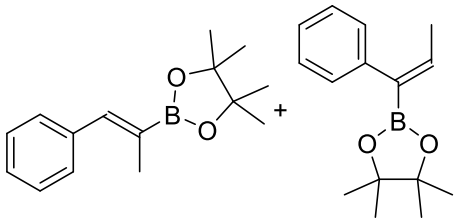


39 (81:19)

Prepared following to general procedure **A** in duplicate and combined prior to purification.
MAJOR: **Yield:** 33% (33.9 mg, 0.13 mmol). Flash column chromatography: pentane /EtOAc: 98:2; Colourless oil; **R_f:** 0.57

(petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.54 (dt, *J* = 18.0, 6.3 Hz, 1H), 5.53 (d, *J* = 18.0 Hz, 1H), 3.42 (t, *J* = 7.2 Hz, 2H), 2.75-2.68 (m, 2H), 1.26 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 149.7, 83.4, 38.9, 30.9, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.0; **IR (neat, cm^{-1}):** ν 2976, 2924, 2855, 1638, 1361, 1324, 1141, 847; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{10}H_{19}BBrO_2$: 261.0661, found: 261.0670 (+ 3.4 ppm). The data were consistent with those reported in the literature.[15]
MINOR: **Yield:** 18% (18.5 mg, 0.07 mmol). Flash column chromatography: pentane/EtOAc: 99:1; Colourless oil; **R_f:** 0.63 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.92 (app s, 1H), 5.71 (app s, 1H), 3.50 (t, *J* = 7.4 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 1.26 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 132.5, 83.8, 39.1, 32.9, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 30.3; **IR (neat, cm^{-1}):** ν 2978, 2926, 2855, 1369, 1311, 1141; **HRMS (EI$^+$):** calcd for [MS] $C_{10}H_{18}BBrO_2$: 260.0583, found: 260.0582 (- 0.4 ppm).

(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane & (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (40)

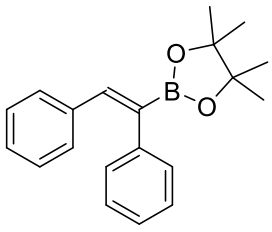


40 (70:30)

Prepared following to general procedure **B**. **Yield:** 49% (24 mg, 0.10 mmol, ratio 70:30). Flash column chromatography: pentane/EtOAc: 98:2; Colourless oil; **R_f:** 0.67 (petroleum ether/EtOAc: 9:1);

MAJOR: **^{1}H NMR (300 MHz, C_6D_6):** δ 7.75 (s, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.14-7.08 (m, 2H), 7.06-6.99 (m, 1H), 2.20 (d, *J* = 0.9 Hz, 3H), 1.12 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 142.5, 138.0, 129.5, 128.1, 127.2, 83.6, 25.0, 16.0. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 31.2; **IR (neat, cm^{-1}):** ν 2978, 2930, 2865, 1616, 1367, 1337, 1307, 1144, 1103, 751, 699, 667; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{15}H_{22}BO_2$: 245.1713, found: 245.1722 (+ 3.7 ppm).
MINOR: **^{1}H NMR (300 MHz, C_6D_6):** δ 7.37-7.33 (m, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.14-7.08 (m, 2H), 7.06-6.99 (m, 1H), 2.67 (d, *J* = 7.0 Hz, 3H), 1.06 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 142.8, 139.9, 129.2, 127.8, 126.0, 83.5, 24.8, 16.1. The carbon bearing boron was not observed.

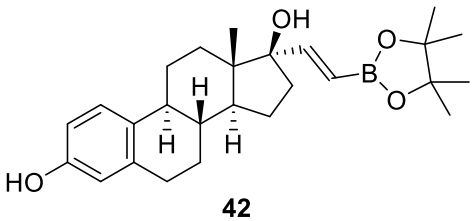
(*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (41)



41

Prepared following to general procedure **B**. **Yield:** 58% (35.8 mg, 0.12 mmol). Flash column chromatography: pentane/EtOAc: 98:2; Colourless oil; **R_f:** 0.67 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, C_6D_6):** δ 7.89 (s, 1H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.23-7.19 (m, 4H), 7.09-7.06 (m, 1H), 6.94-6.92 (m, 3H), 1.12 (s, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 143.4, 140.5, 137.0, 130.0, 128.9, 128.3, 127.9, 127.7, 126.3, 83.8, 24.9. The carbon bearing boron was not observed. **^{11}B NMR (96 MHz, $CDCl_3$):** δ 29.9; **IR (neat, cm^{-1}):** ν 3053, 2988, 2929, 1606, 1377, 1342, 1318, 1140, 694, 683, 481; **HRMS (API$^+$):** calcd for $[M+H]^+$ $C_{20}H_{24}BO_2$: 307.1869, found: 307.1877 (+ 2.6 ppm).

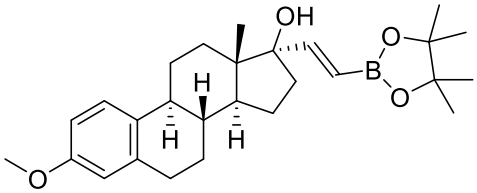
(8*R*,9*S*,13*S*,14*S*,17*R*)-13-methyl-17-((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (42)



42

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 66% (111.4 mg, 0.26 mmol). Flash column chromatography: pentane/EtOAc: 74:26; White solid; **Mp:** 243-244 °C (pentane/EtOAc); **R_f:** 0.25 (petroleum ether/EtOAc: 7:3); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.58 (s, 1H), 6.97-6.91 (m, 2H), 6.59 (d, *J* = 10.5 Hz, 2H), 5.69 (d, *J* = 18.3 Hz, 1H), 2.81-2.62 (m, 2H), 2.00-1.66 (m, 6H), 1.35 (s, 12H), 1.28-1.10 (m, 8H), 0.85 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 158.9, 154.3, 138.4, 132.4, 125.9, 115.5, 112.9, 112.1, 85.1, 84.1, 49.2, 47.2, 42.2, 38.8, 37.2, 32.3, 29.7, 27.2, 25.7, 25.0, 24.7, 23.4, 14.2; **^{11}B NMR (96 MHz, $CDCl_3$):** δ 23.4; **IR (neat, cm^{-1}):** ν 3372, 2974, 2924, 2866, 1626, 1382, 1348, 1137, 1004, 852; **HRMS (API$^+$):** calcd for $[M+H-H_2O]^+$ $C_{26}H_{36}BO_3$: 407.2758, found: 407.2767 (+ 2.2 ppm).

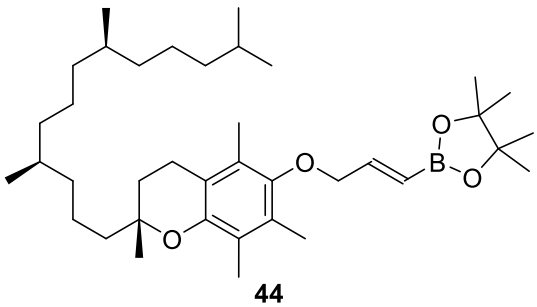
(8*R*,9*S*,13*S*,14*S*,17*R*)-3-methoxy-13-methyl-17-((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxa borolan-2-yl)vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (43)



43

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 37% (65.2 mg, 0.15 mmol). Flash column chromatography: pentane/EtOAc: 8:2; White solid; **Mp:** 165-166 °C (pentane/EtOAc); **R_f:** 0.27 (petroleum ether/EtOAc: 8:2); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 18.2 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 5.61 (d, *J* = 18.2 Hz, 1H), 3.77 (s, 3H), 2.86-2.83 (m, 2H), 2.31-2.24 (m, 1H), 2.19-2.11 (m, 1H), 2.05-1.97 (m, 1H), 1.90-1.83 (m, 2H), 1.77-1.68 (m, 2H), 1.60-1.56 (m, 2H), 1.52-1.48 (m, 2H), 1.45-1.42 (m, 1H), 1.40-1.40 (m, 1H), 1.35-1.34 (m, 1H), 1.29 (s, 12H), 0.94 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 157.5, 157.4, 138.0, 132.7, 126.4, 115.1, 113.8, 111.5, 85.0, 83.4, 55.2, 49.2, 47.2, 43.6, 39.5, 36.4, 32.5, 29.9, 27.4, 26.3, 24.9, 24.9, 23.5, 14.3; **^{11}B NMR (96 MHz, $CDCl_3$):** δ 31.5; **IR (neat, cm^{-1}):** ν 3498, 2974, 2915, 2873, 1630, 1499, 1348, 1143, 994; 970, 849, 658; **HRMS (API$^+$):** calcd for $[M+H-H_2O]^+$ $C_{27}H_{38}BO_3$: 421.2914, found: 421.2912 (- 0.5 ppm).

4,4,5,5-tetramethyl-2-((*E*)-3-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl) chroman-6-yl)oxy)prop-1-en-1-yl)-1,3,2-dioxaborolane (44)



44

Prepared following to general procedure **A** in duplicate and combined prior to purification. **Yield:** 27% (64.7 mg, 0.11 mmol). Flash column chromatography: pentane/EtOAc: 98:2; Colourless oil; **R_f:** 0.77 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.82 (dt, *J* = 4.4, 18.2 Hz, 1H), 5.92 (d, *J* = 18.1 Hz, 1H), 4.26-4.24 (m, 2H), 2.58-2.54 (m, 2H), 2.15 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.81-1.74 (m, 3H), 1.60 (s, 3H), 1.54-1.46 (m, 5H), 1.42-1.36 (m, 5H), 1.29 (s, 12H), 1.16-1.04 (m, 10H), 0.88-0.83 (m, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.7, 148.3, 148.0, 128.0, 126.0, 123.0, 117.6, 83.4, 74.9, 74.3, 40.2; 39.5, 37.6, 37.6, 37.4, 32.9, 32.8, 31.4, 28.1, 25.2, 24.9, 24.6, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 12.9, 12.0, 11.9. The carbon bearing boron was not observed. **^{11}B NMR**

(96 MHz, $CDCl_3$): δ 31.6; **IR (neat, cm^{-1}):** ν 2926, 2868, 1645, 1458, 1367, 1346, 1321, 1257, 1144, 1091, 736; **HRMS (ESI^+):** calcd for $[M+H]^+$ $C_{38}H_{66}BO_4$: 597.5054, found: 597.5073 (+ 3.2 ppm).

Scale Up

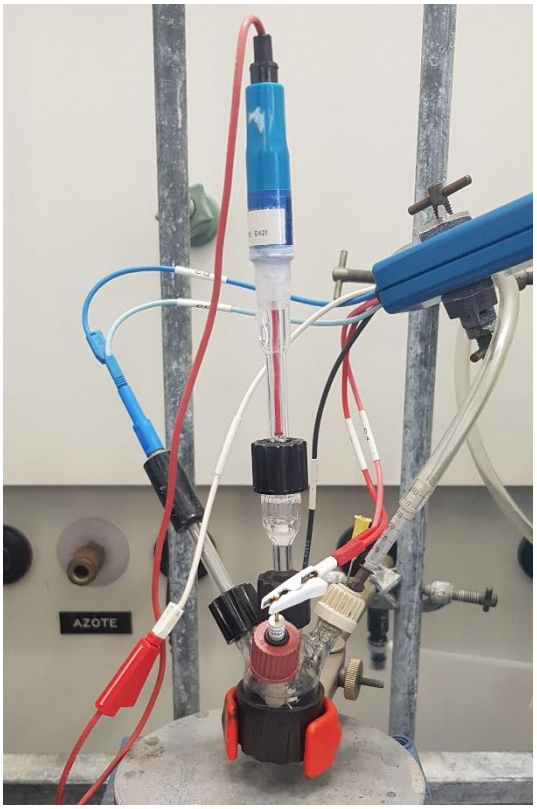
In a 10 mL IKA© vial were added the 4-ethynylanisole (52 µL, 0.4 mmol, 1 equiv.), B_2Pin_2 (204 mg, 0.8 mmol, 2 equiv.) and NBu_4BF_4 (132 mg, 0.4 mmol, 1 equiv.) in anhydrous MeOH (8 mL). The reaction mixture was stirred under air before starting the IKA ElectraSyn© device ((+)SST, (-)SST, 5 mA/cm^2, 2 F/mol, 128 min). Then, HCl 1 M (4 mL) was added and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Then, the residue was purified by flash chromatography (pentane/EtOAc: 98:2) to obtain a pale-yellow oil with 71% yield (73.5 mg, 0.28 mmol).

In a 20 mL IKA© vial were added the 4-ethynylanisole (104 µL, 0.8 mmol, 1 equiv.), B_2Pin_2 (406 mg, 1.6 mmol, 2 equiv.) and NBu_4BF_4 (263 mg, 0.8 mmol, 1 equiv.) in anhydrous MeOH (16 mL). The reaction mixture was stirred under air before starting the IKA ElectraSyn© device ((+)SST, (-)SST, 5 mA/cm^2, 2 F/mol, 256 min). Then, HCl 1 M (8 mL) was added and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Then, the residue was purified by flash chromatography (pentane/EtOAc: 98:2) to obtain a pale-yellow oil with 51% yield (106.6 mg, 0.41 mmol).

Mechanistic studies

Cyclic voltammetry Measurements

CV measurements were done under Argon (Ar) with Gold (Au) as the working electrode, Platinum (Pt) as the counter electrode and Saturated calomel electrode (Hg_2Cl_2) as the reference at 200 $mV.s^{-1}$ in a 0.1 M solution of NBu_4BF_4 in anhydrous MeOH (13 mL).



Picture 1: Home-made cell for cyclic voltammetry

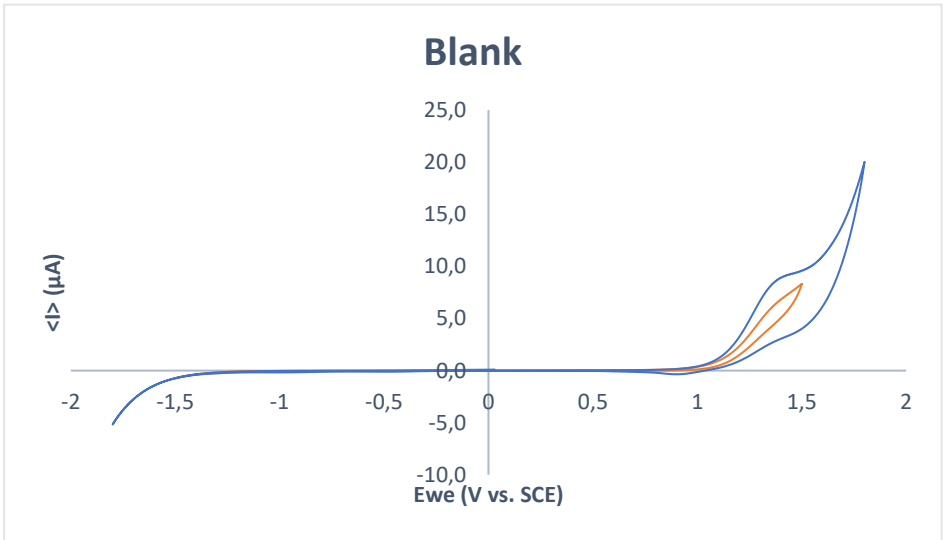


Figure 1: Blank - Anydrous MeOH, NBu_4BF_4 0.1M
1.8 V to -1.8 V in oxidation (blue), 1.5 V to -1.5 V in oxidation (orange)

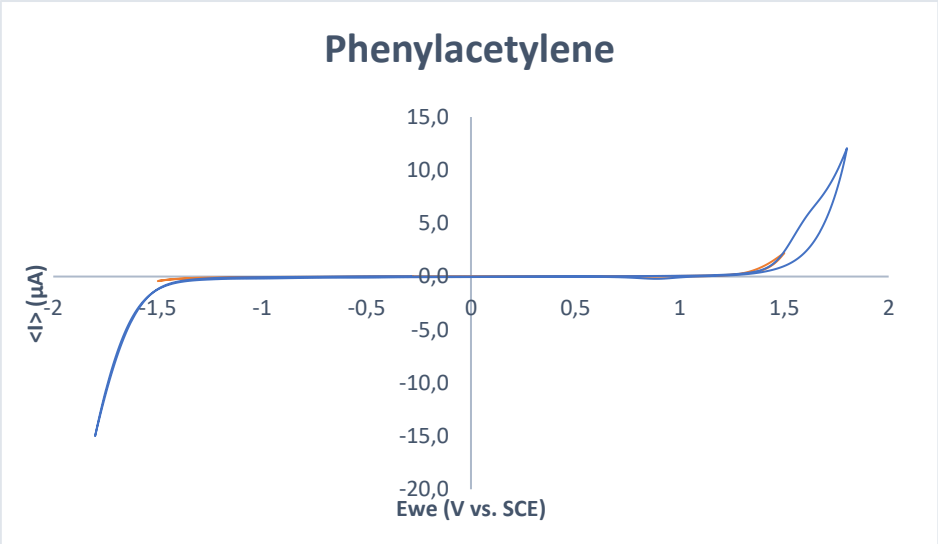


Figure 2: Phenylacetylene 2.3.10^{-2} M
1.8 V to -1.8 V in oxidation (blue), 1.5 V to -1.5 V in oxidation (orange)

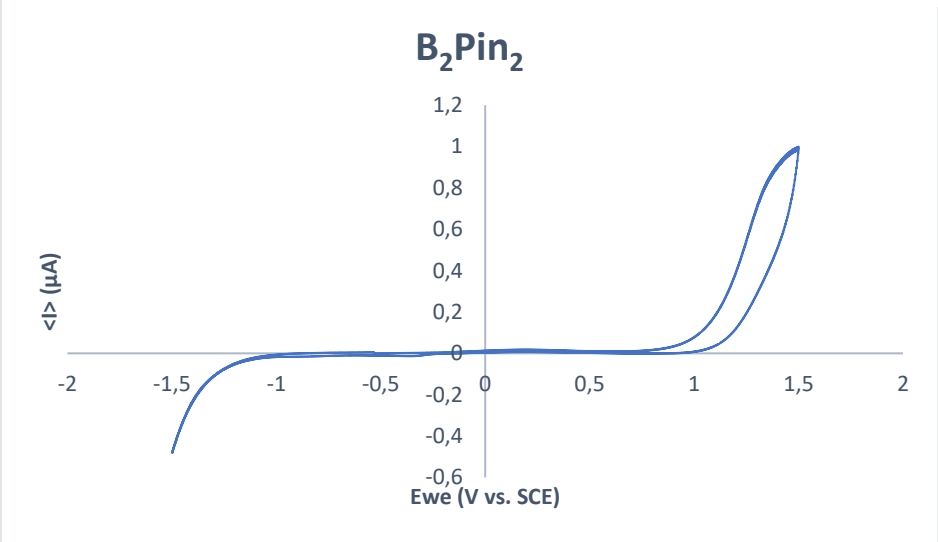


Figure 3: B_2Pin_2 2.3.10^{-2} M
1.5 V to -1.5 V in oxidation

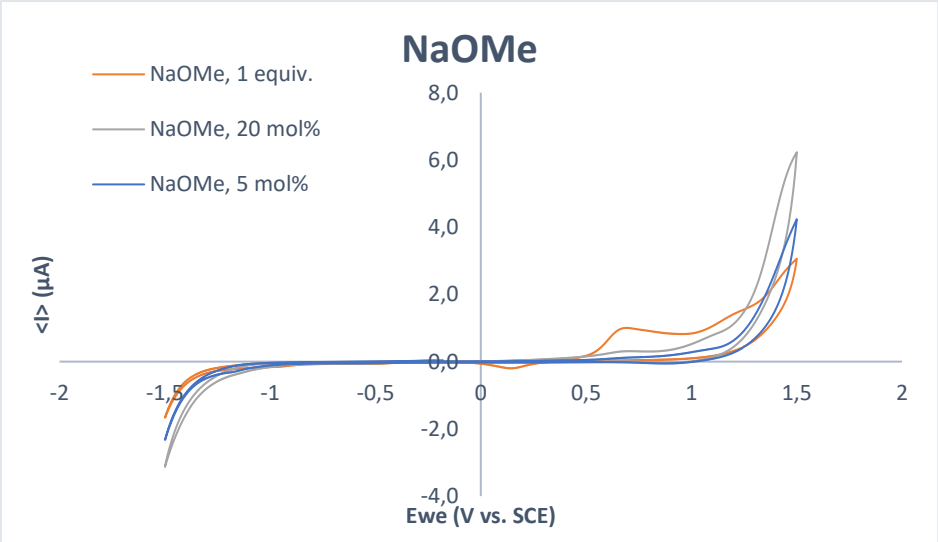


Figure 4: NaOMe, 2.3.10^{-2} M (Red), 4.7.10^{-3} M (Green), 1.5.10^{-3} M (Blue)
1.5 V to -1.5 V in oxidation
oxidation wave: 0.6V

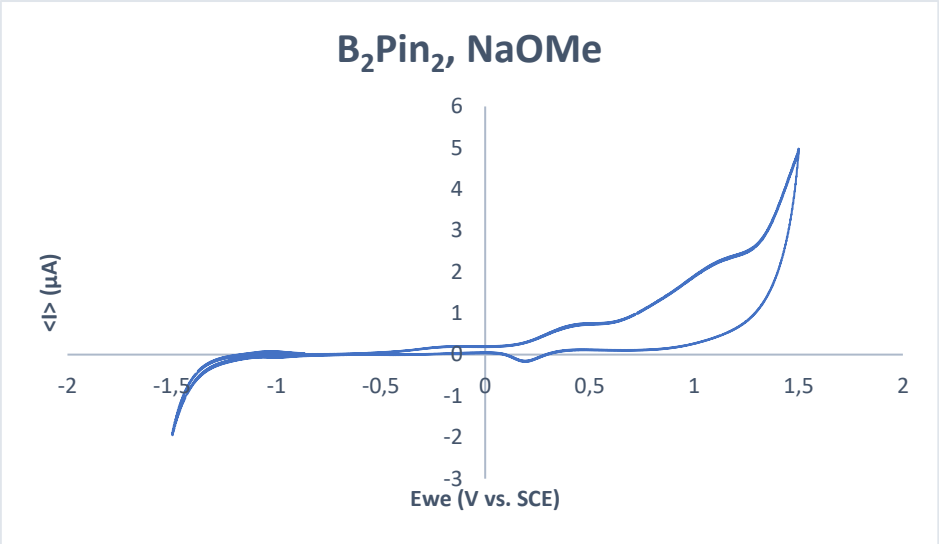


Figure 5: B_2Pin_2 2.3.10^{-2} M, NaOMe, 2.3.10^{-2} M
1.5 V to -1.5 V in oxidation
oxidation wave: 1.2V

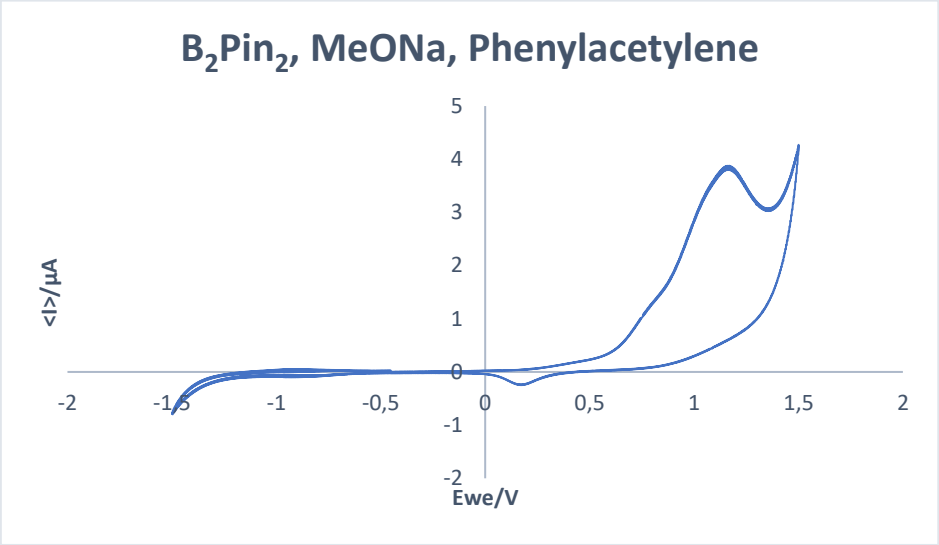
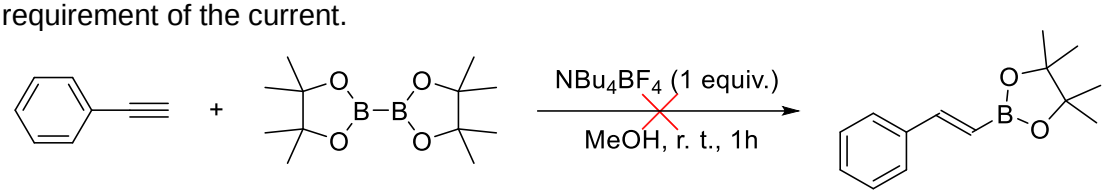


Figure 6: B_2Pin_2 2.3.10^{-2} M, NaOMe 2.3.10^{-2} M, phenylacetylene 2.3.10^{-2} M
1.5 V to -1.5 V in oxidation
oxidation wave: 1.2V

For the CV measurements of the phenylacetylene and the B_2Pin_2, no oxidation or reduction wave was observed.

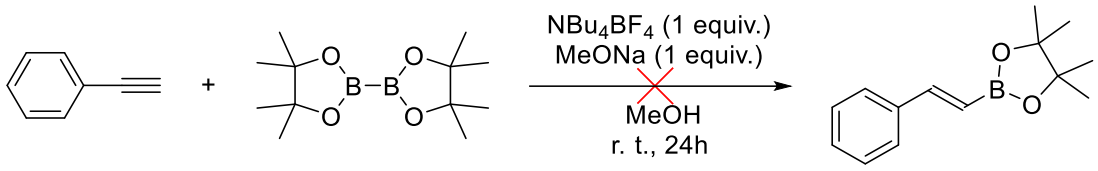
Control Experiments

Following the procedure **A** except the current, these reactions below were started to confirm the requirement of the current.



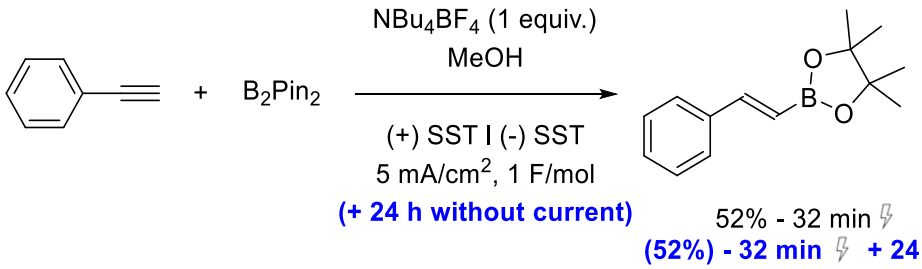
n. r.

In a 5 mL IKA© vial were added the alkyne derivative (0.2 mmol, 1 equiv.), B_2Pin_2 (102 mg, 0.4 mmol, 2 equiv.), NaOMe (11 mg, 0.2 mmol, 1 equiv.) and NBu_4BF_4 (66 mg, 0.2 mmol, 1 equiv.) in anhydrous MeOH (4 mL). The reaction mixture was stirred under air for 24 h. Then, HCl 1 M (2 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure.



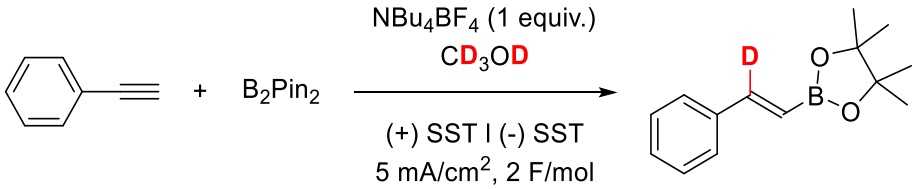
n. r.

Following the procedure **A** except the charge, these reactions below were started to confirm the requirement of electrochemistry and to know if metals of Stainless Steel play a role in the reaction.

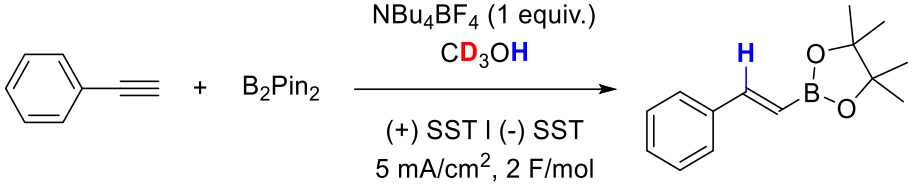


No change of ^{1}H-NMR yield was observed after leaving the same reaction <u>for 24 h under stirring</u> with the electrodes and without current.

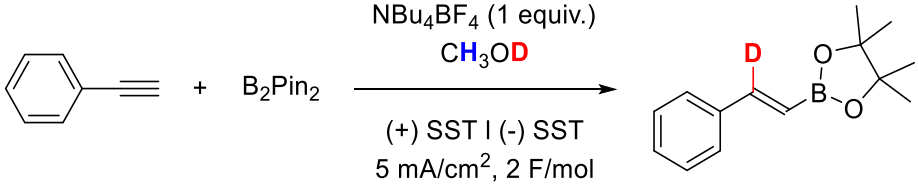
Deuteration experiments



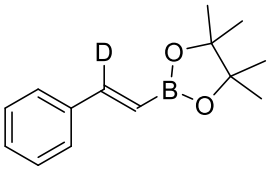
42% isolated yield



63% isolated yield



47% isolated yield



[D]-1

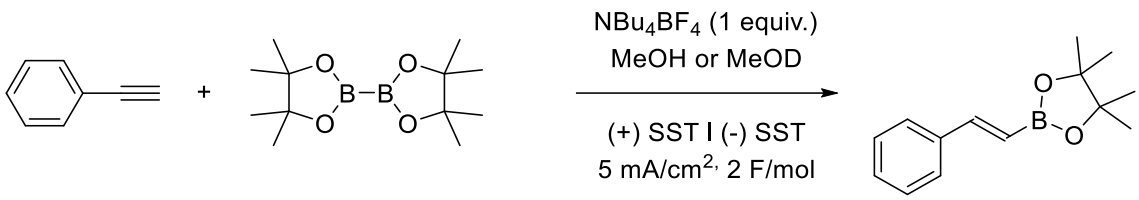
Prepared following to the procedure **A** with methanol-d_4. **Yield:** 42% (19.4 mg, 0.08 mmol). Flash chromatography: pentane/EtOAc: 98:2; Pale yellow oil; **R_f:** 0.66 (petroleum ether/EtOAc: 9:1); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.51-7.48 (m, 2H), 7.34-7.31 (m, 3H), 6.17 (s, 1H), 1.32 (s, 12H).

To conclude, the formation of the product **[D]-1** shows that the H atom comes from the bond O-H from the methanol. Moreover, as a significant decrease of the reaction yield was observed, a KIE measurement was driven.

Kinetic Isotope Effect (KIE)

Two different methods of the KIE measurement were done to compare the effect of the overpotential of D on the cathode.

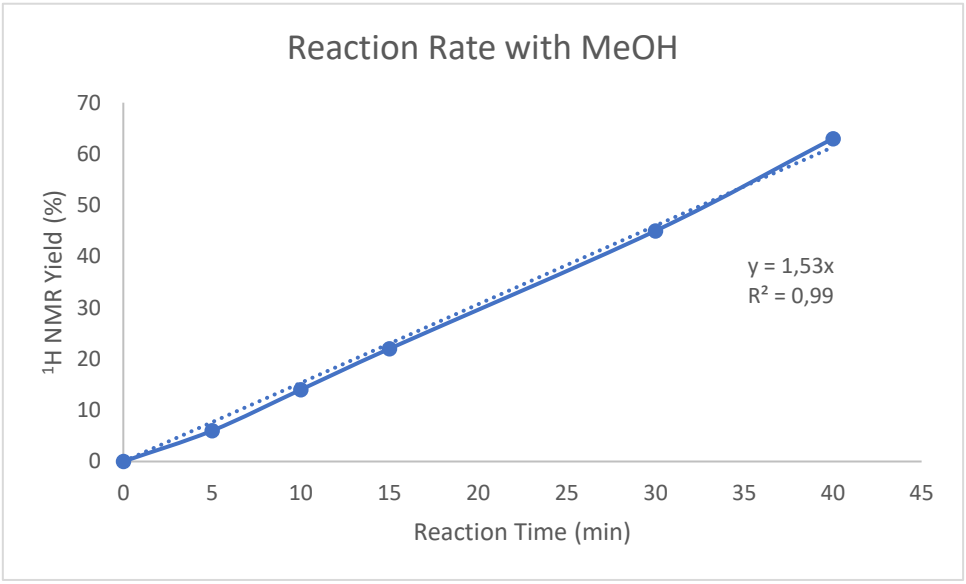
1rst method:



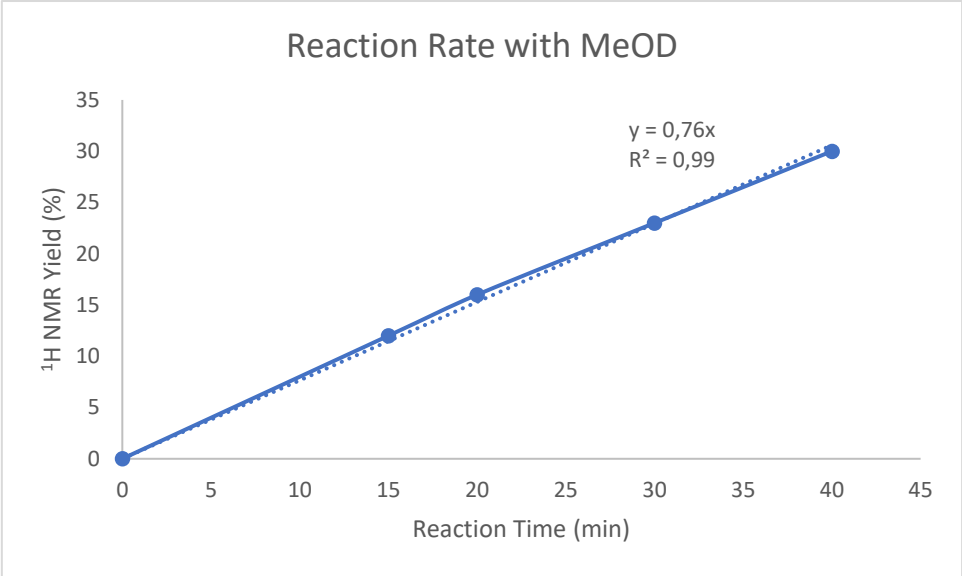
In a 5 mL IKA© vial were added phenylacetylene (22 µL, 0.2 mmol, 1 equiv.), B_2Pin_2 (102 mg, 0.4 mmol, 2 equiv.) and NBu_4BF_4 (66 mg, 0.2 mmol, 1 equiv.) in anhydrous MeOH or MeOD (4 mL). The reaction mixture was stirred under air before starting the IKA ElectraSyn© device ((+)SST, (-)SST, 5 mA/cm^2, 2 F/mol). Then, HCl 1 M (2 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

MeOH: 5 reactions were set up and stopped at 5 min, 10 min, 15 min, 30 min and 40 min, respectively.
The reaction yields were determined by ^{1}H NMR using *N,N*-dimethylformamide as an internal standard.

MeOD: 4 reactions were set up and stopped at 15 min, 20 min, 30 min and 40 min, respectively.
The reaction yields were determined by ^{1}H NMR using *N,N*-dimethylformamide as an internal standard.



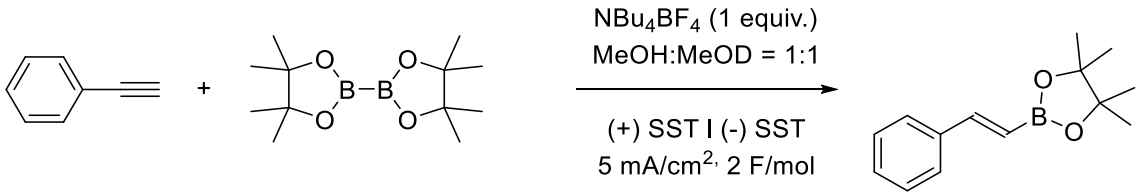
The coefficient of the linear trend curve corresponds to the reaction rate **k_H = 1.53**



The coefficient of the linear trend curve corresponds to the reaction rate $\mathbf{k_D = 0.76}$

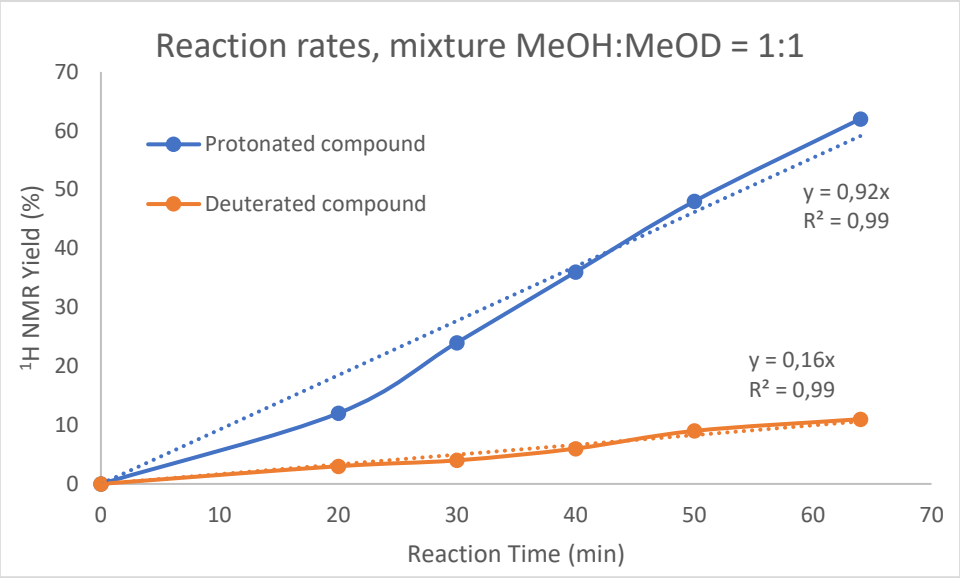
With the 1rst method, the $\mathbf{KIE = k_H/k_D = 2.01.}$

2nd method:



In a 5 mL IKA© vial were added phenylacetylene (22 µL, 0.2 mmol, 1 equiv.), B_2Pin_2 (102 mg, 0.4 mmol, 2 equiv.) and NBu_4BF_4 (66 mg, 0.2 mmol, 1 equiv.) in anhydrous mixture of MeOH:MeOD = 1:1 (4 mL). The reaction mixture was stirred under air before starting the IKA ElectraSyn© device ((+)SST, (-)SST, 5 mA/cm^2, 2 F/mol). Then, HCl 1 M (2 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with a NH_4Cl saturated aqueous solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

5 reactions were set up and stopped at 20 min, 30 min, 40 min, 50 min and 64 min respectively. The reaction yields were determined by ^{1}H NMR using *N,N*-dimethylformamide as an internal standard.



With the 2nd method, the **KIE = k_H/k_D = 5.75.**

Sensitivity assessment

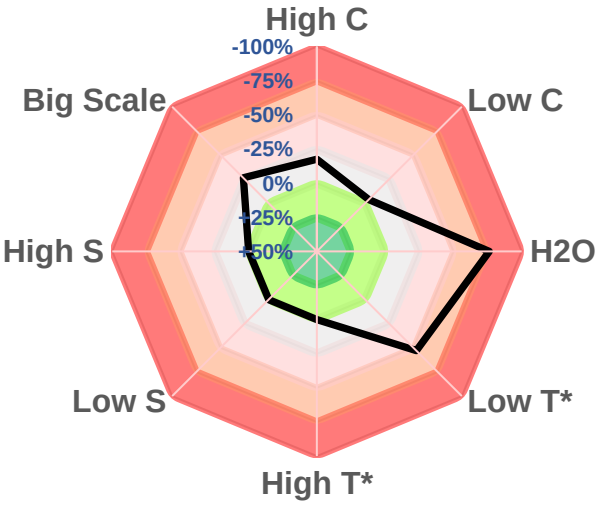
Following the procedure **A.** NMR Yields were determined by ^{1}H NMR using *N,N*-dimethylformamide and triphenylmethane as an internal standards.

Sensitivity assessment was performed in analogy with the literature[16] and adapted for electrochemistry.

#	EXPERIMENT	n (mmol)	V (mL)	C (Mol/L)	SET UP
1	Low C	0.18[1]	4	0.045	
2	High C	0.22[1]	4	0.055	
3	High H_2O	0.2	4	0.05	+ 40 µL H_2O
4	Low T	0.4	8	0.05	10°C
5	High T	0.4	8	0.05	32°C
6	Low S	0.15	3	0.05	S = 1.28 cm^2
7	High S	0.25	5	0.05	S = 3.32 cm^2
8	Control 1	0.2	4	0.05	
9	Control 2	0.4	8	0.05	
10	Big Scale	0.8	16	0.05	

[1]Volume cannot be changed with IKA Eletrasyn device otherwise the contact surface of the electrode changes.

#	EXPERIMENT	^{1}H NMR YIELD (%)	DEVIATION VALUES (%)
1	Low C	77	-3.8
2	High C	66	-17.5
3	High H2O	19	-76.3
4	Low T$^{\neq}$	33	-52.9
5	High T$^{\neq}$	70	0
6	Low S	80	0
7	High S	80	0
8	Control1	80	-
9	Control2$^{\neq}$	70	-
10	Big Scale	59	-26.3



For the control of the temperature, a home-made cell was designed, see bellow (Picture 2).

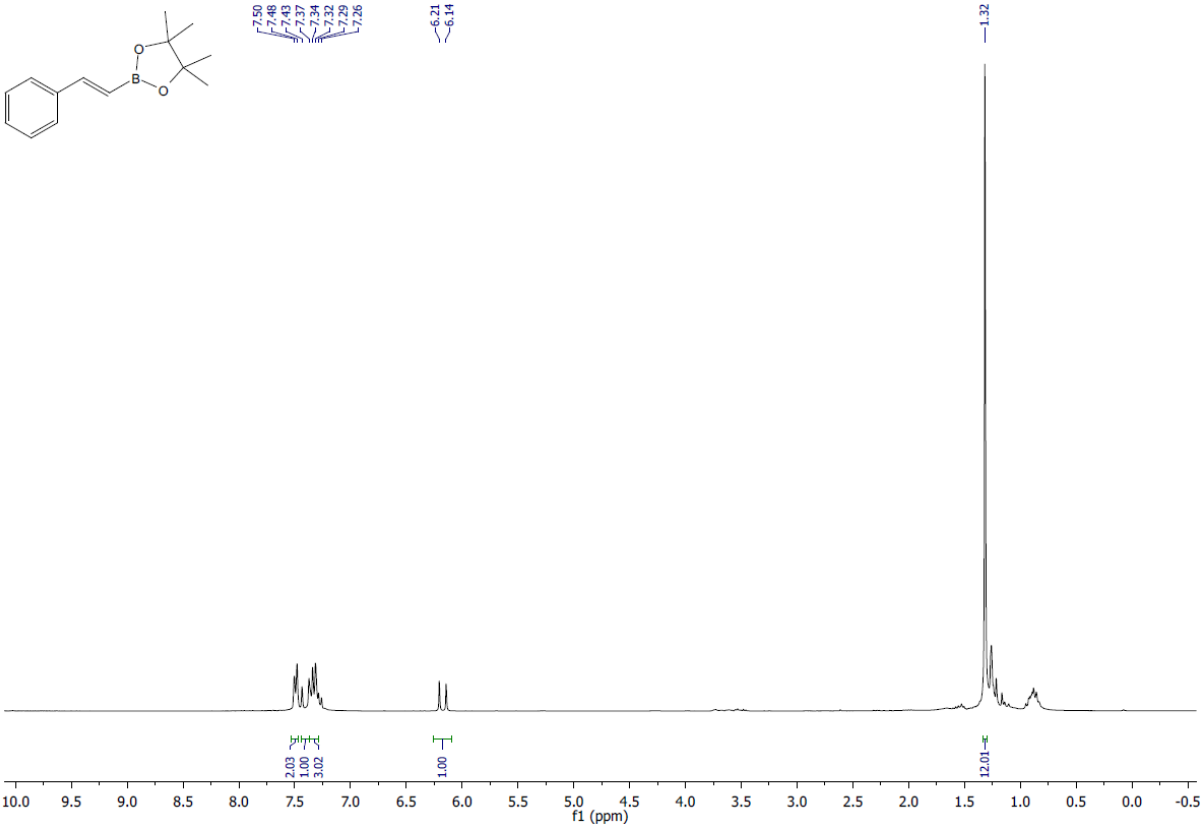
Picture 2: Home-made cell to control the temperature.

To conclude, the reaction is sensible to water and low temperature.

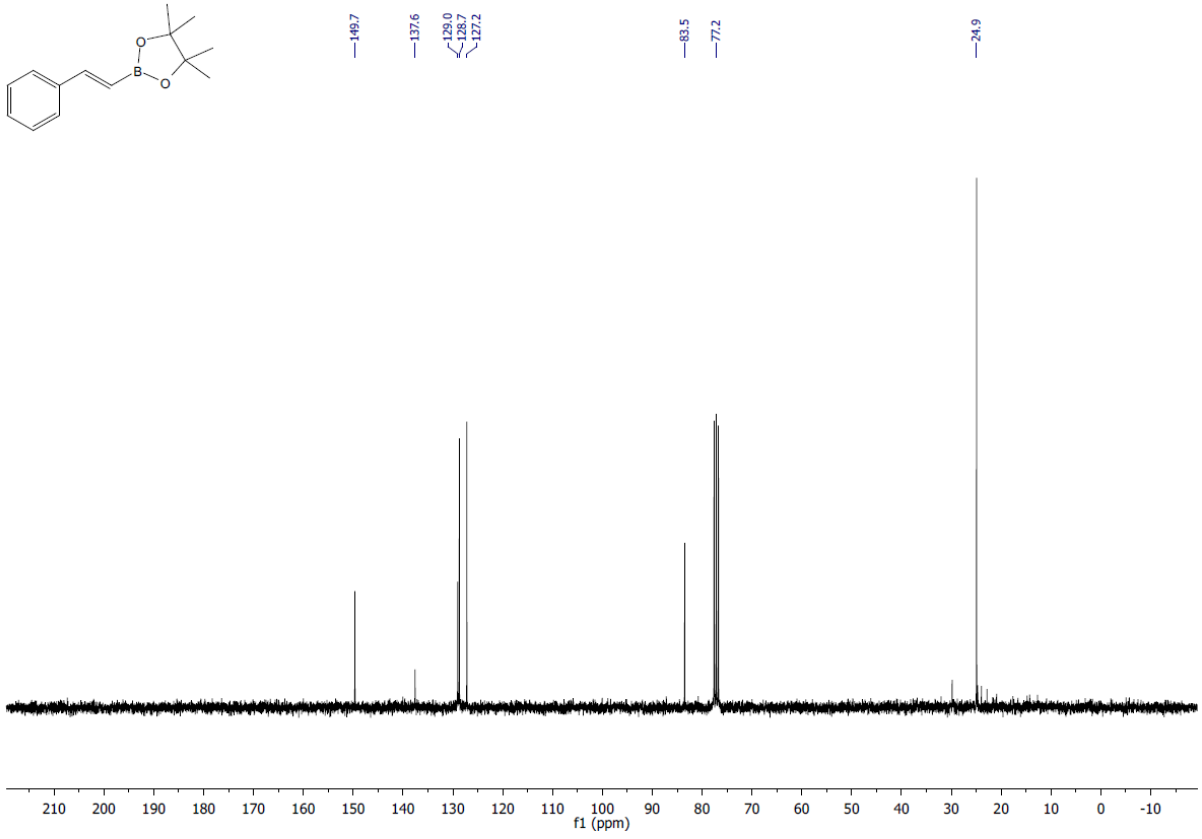
NMR-Spectra of Key Compounds

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (1)

^{1}H NMR (300 MHz, $CDCl_3$)

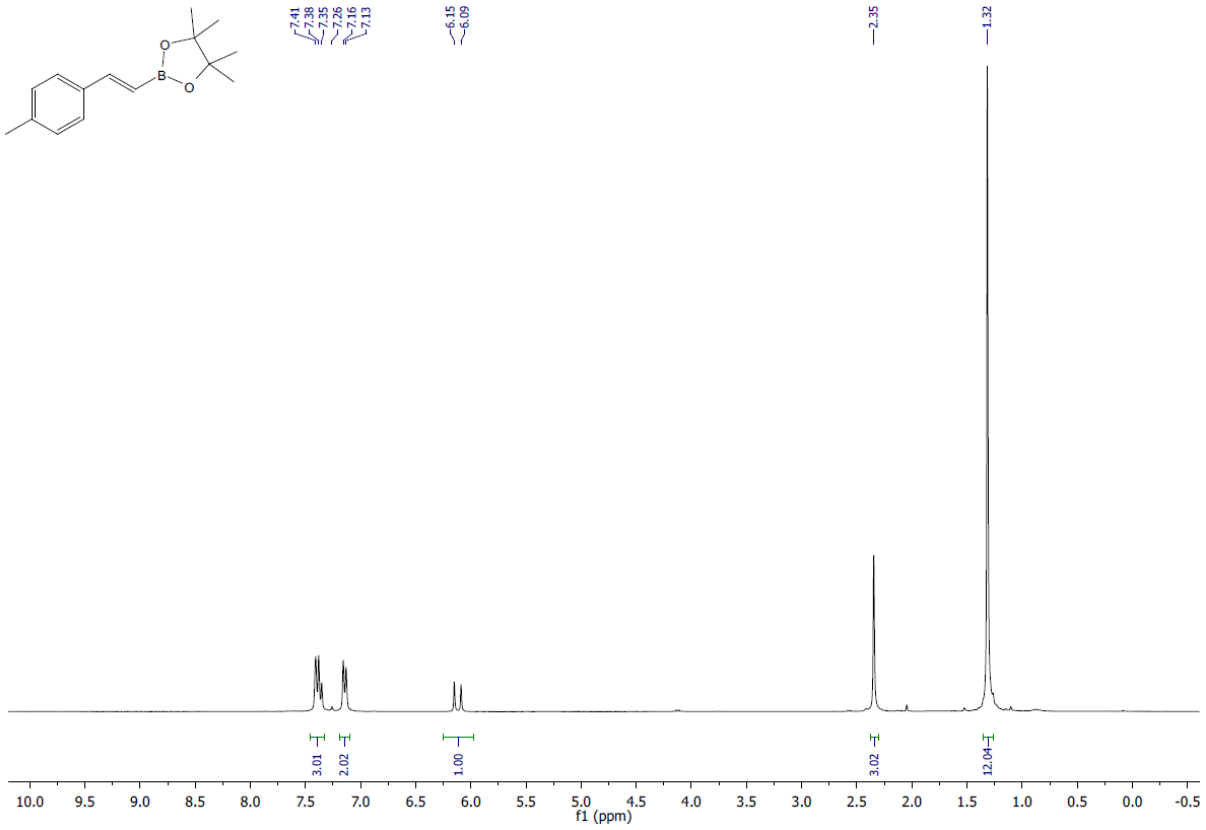


^{13}C NMR (75 MHz, $CDCl_3$)

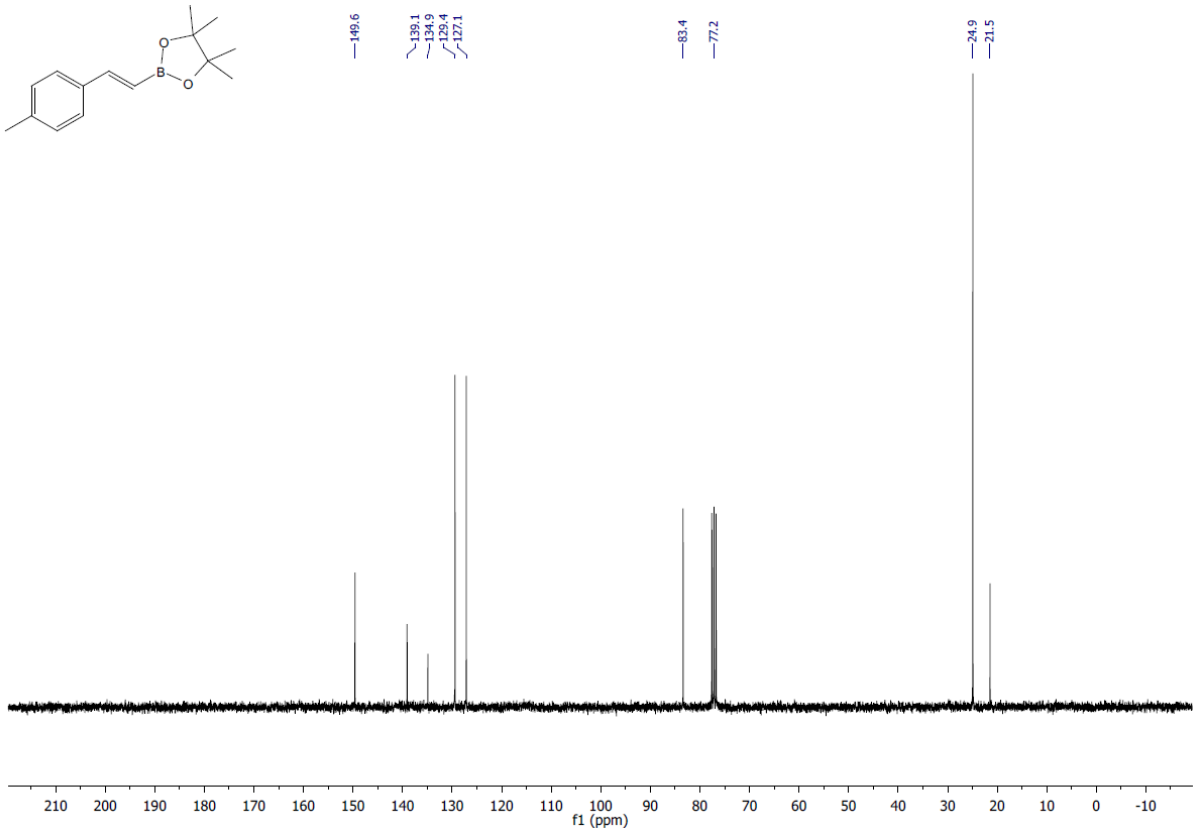


(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2)

^{1}H NMR (300 MHz, $CDCl_3$)

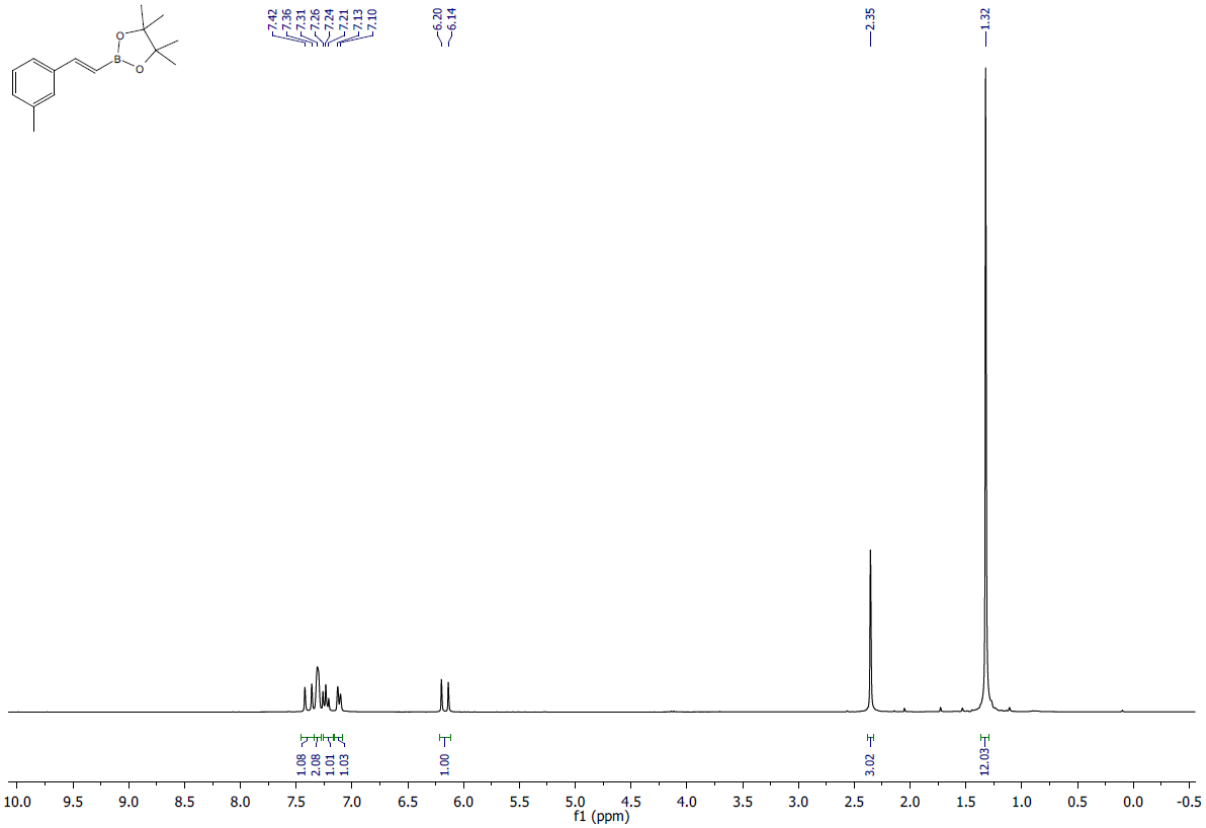


^{13}C NMR (75 MHz, $CDCl_3$)

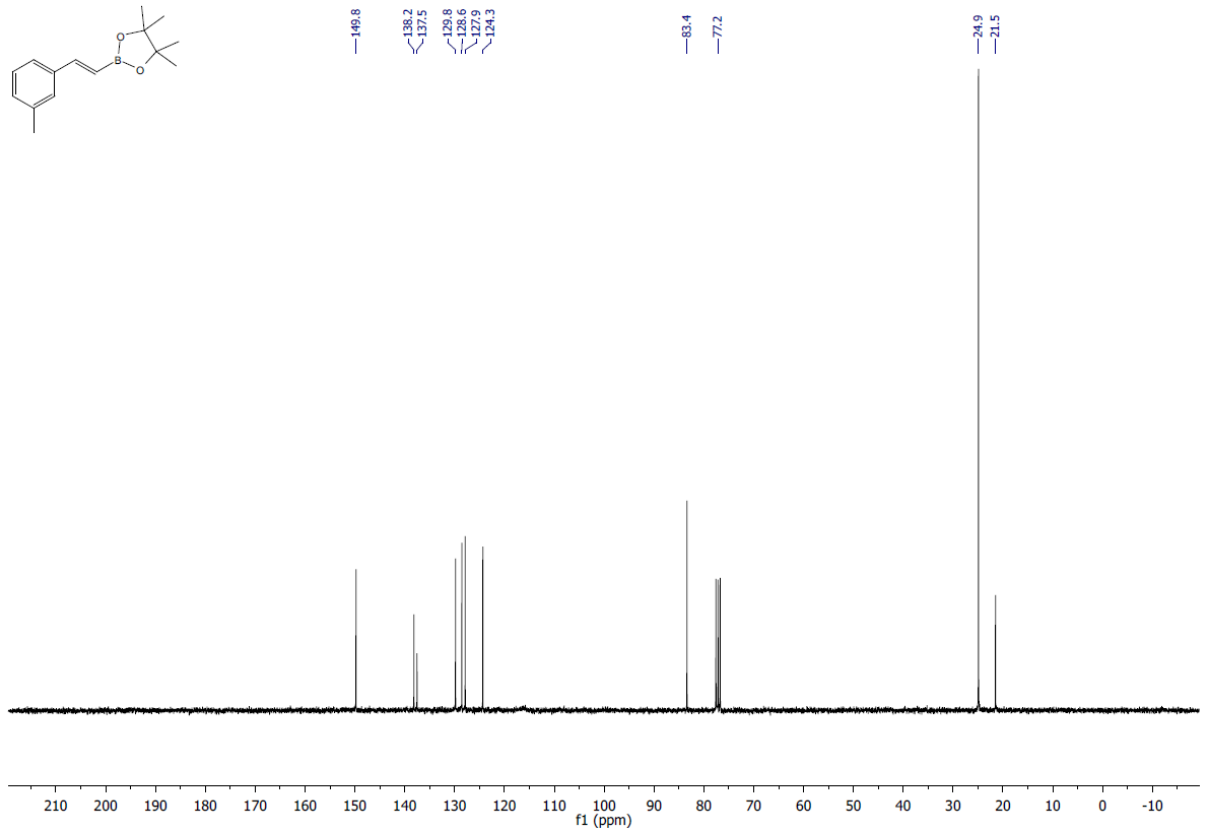


(*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (3)

^{1}H NMR (300 MHz, $CDCl_3$)

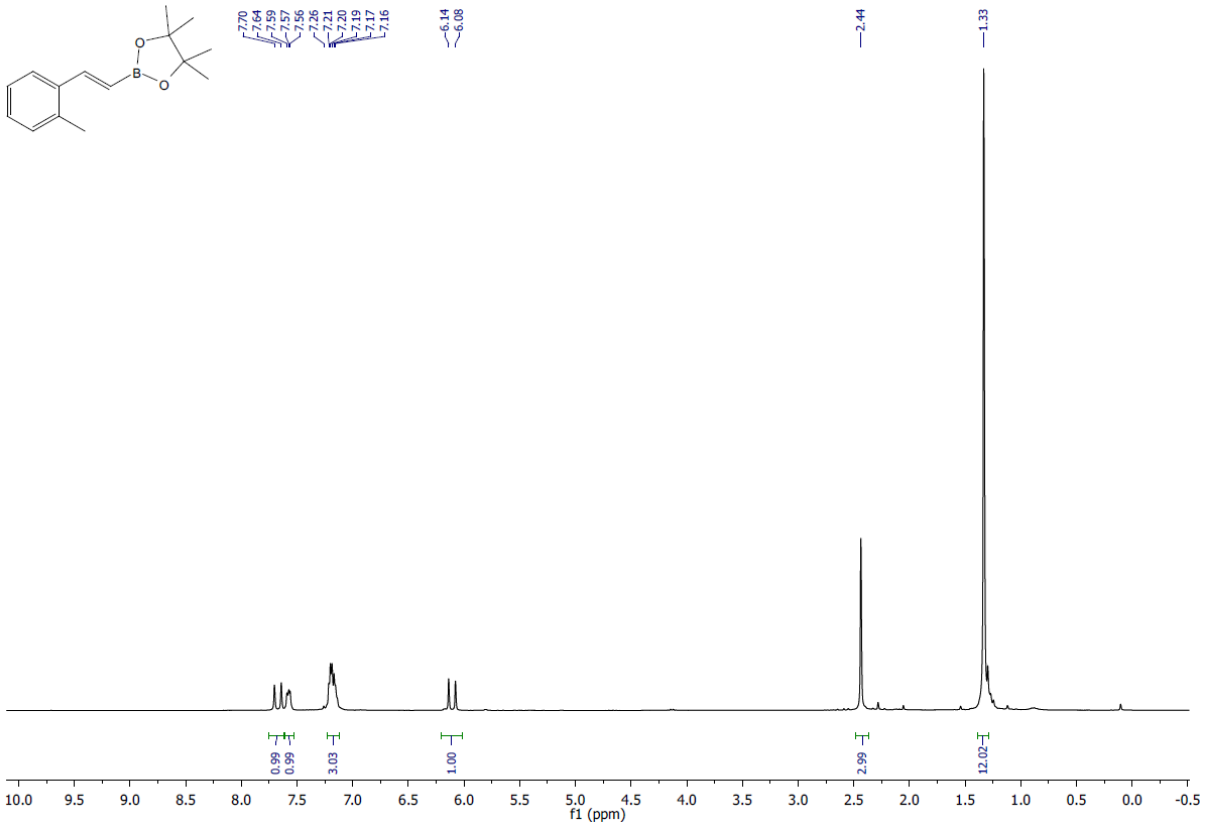


^{13}C NMR (75 MHz, $CDCl_3$)

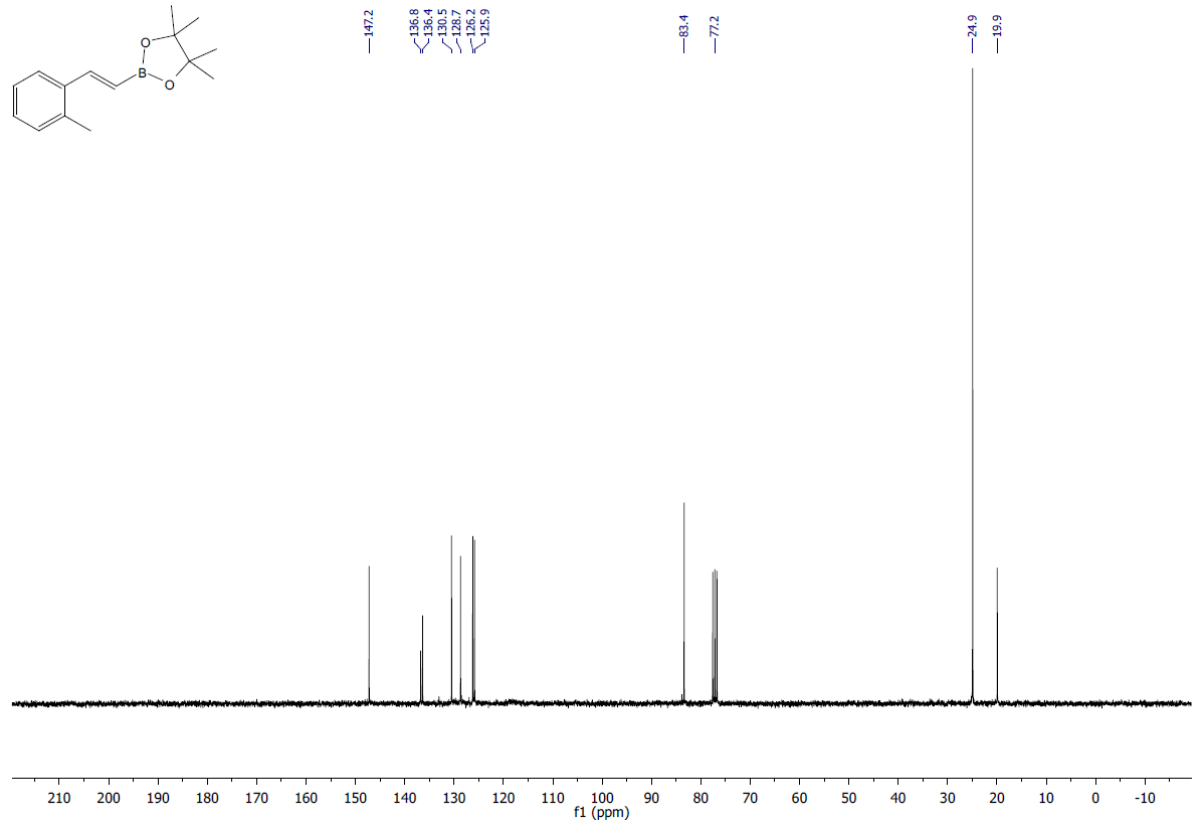


(*E*)-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane (4)

^{1}H NMR (300 MHz, $CDCl_3$)

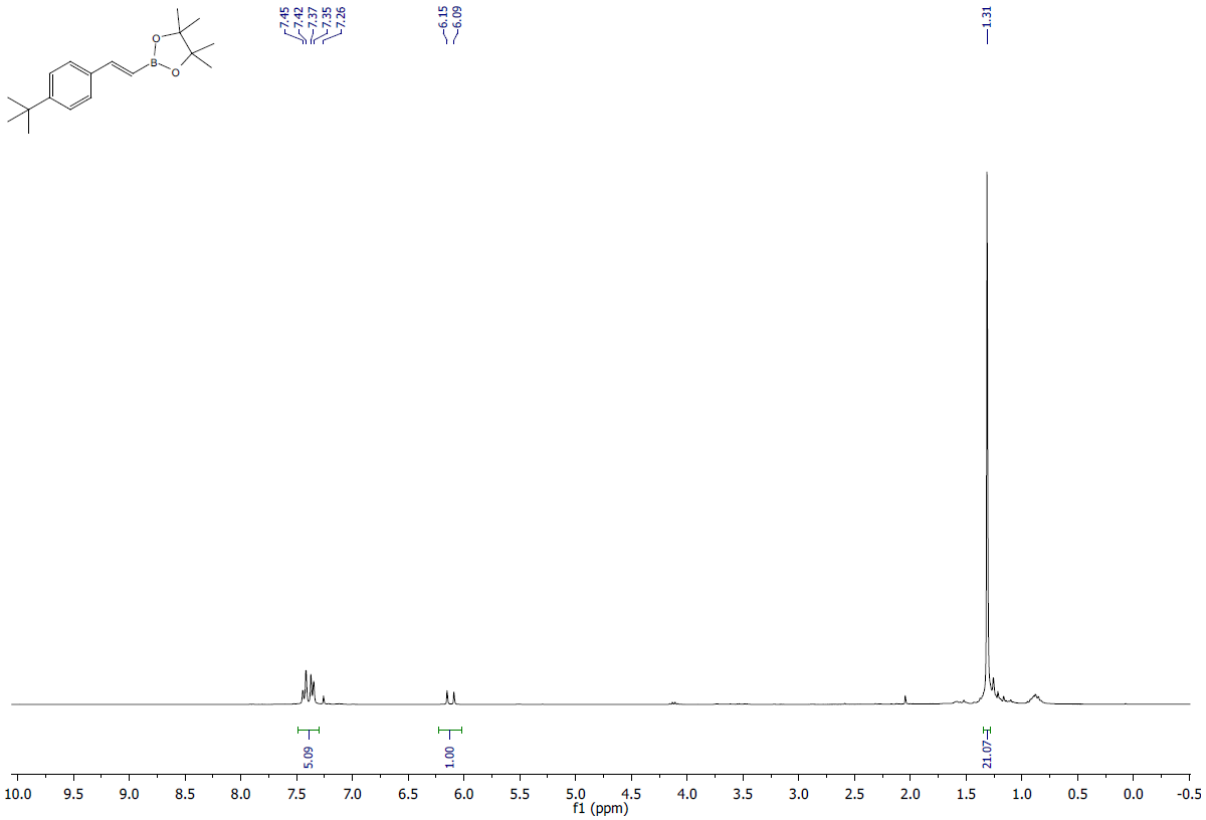


^{13}C NMR (75 MHz, $CDCl_3$)

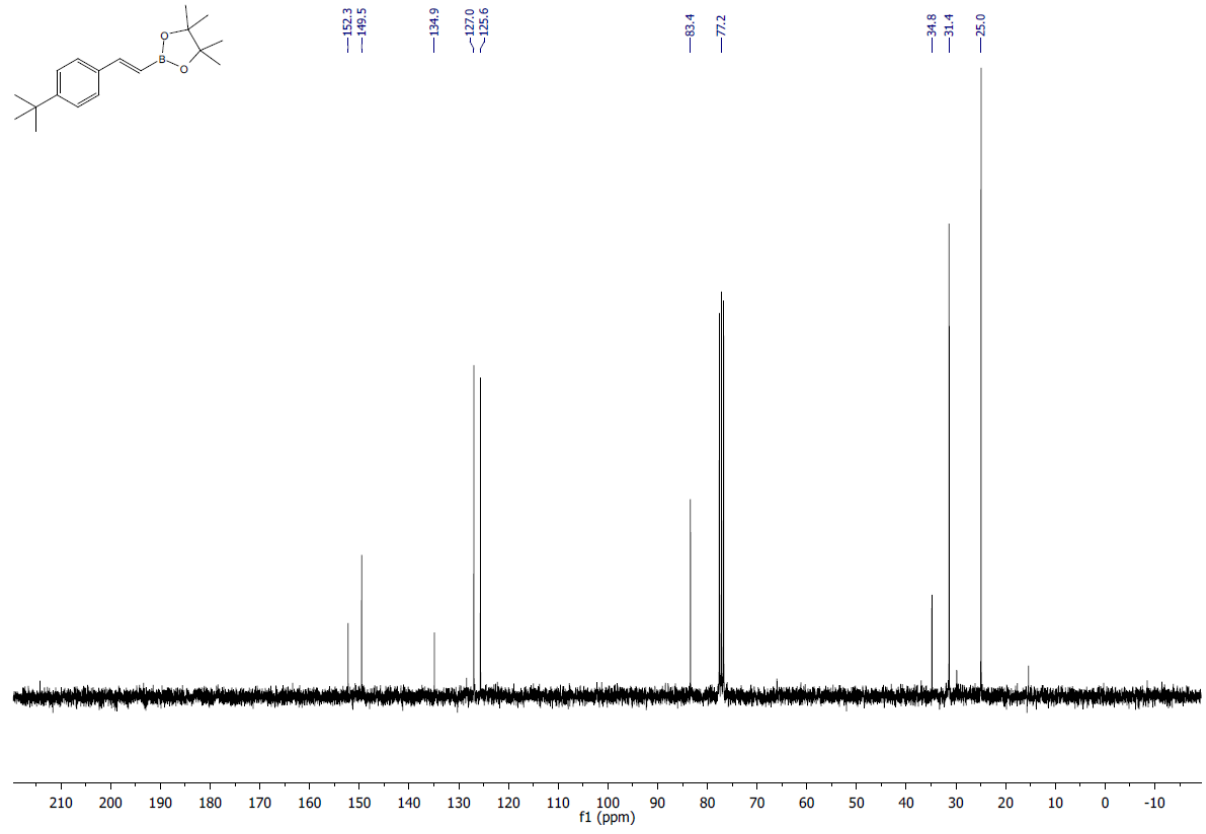


(*E*)-2-(4-(*tert*-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

^{1}H NMR (300 MHz, $CDCl_3$)

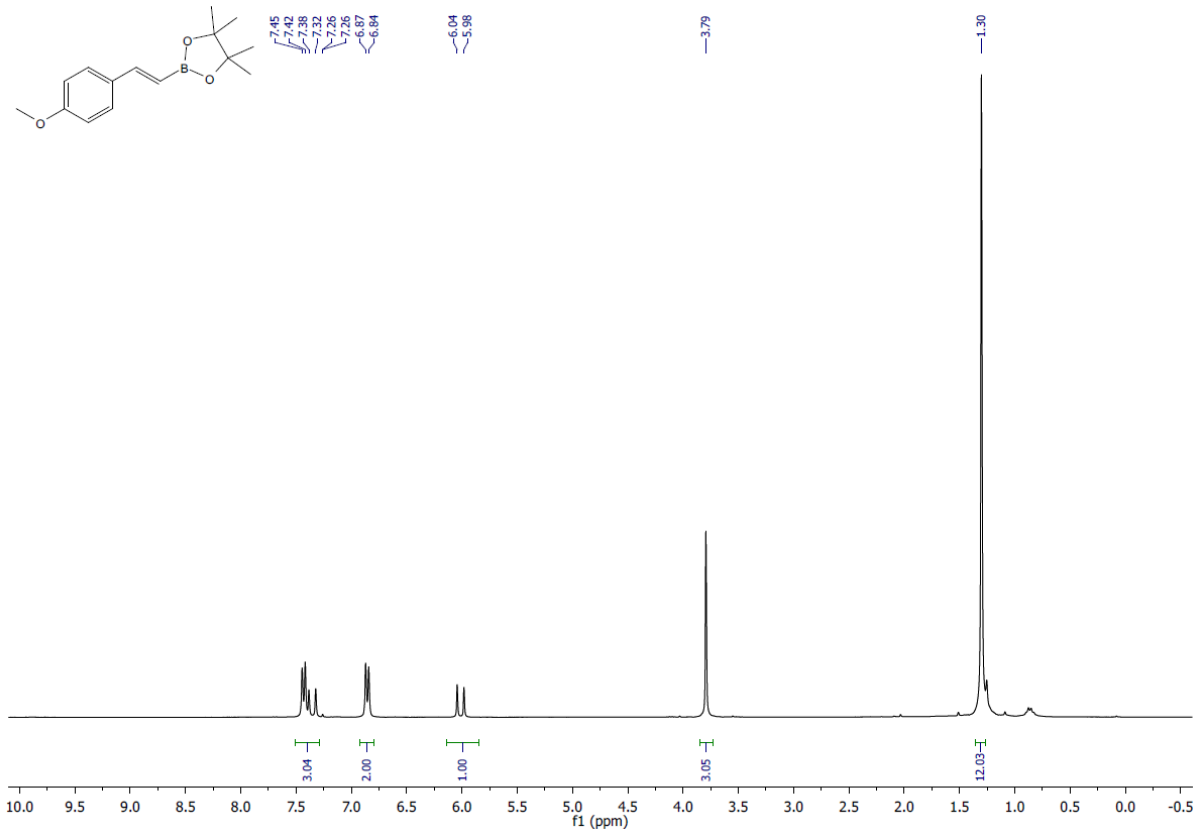


^{13}C NMR (75 MHz, $CDCl_3$)

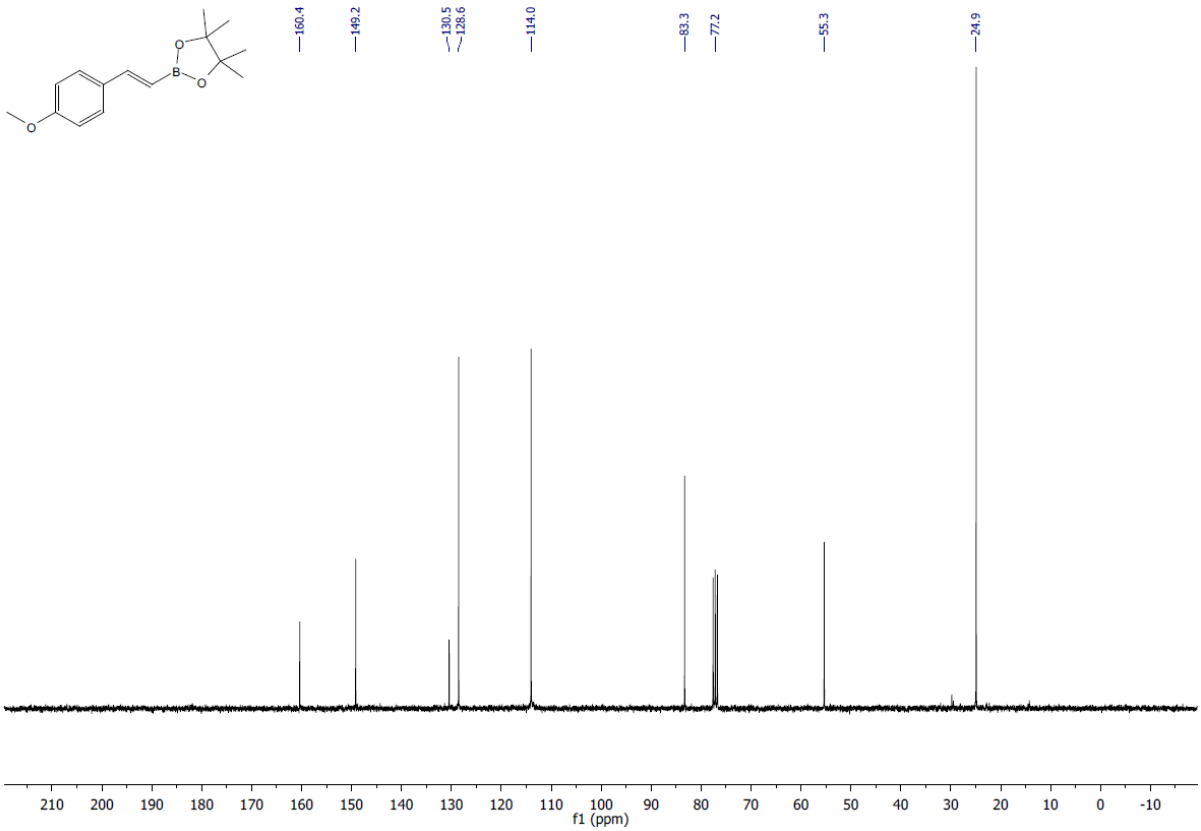


(*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)

^{1}H NMR (300 MHz, $CDCl_3$)

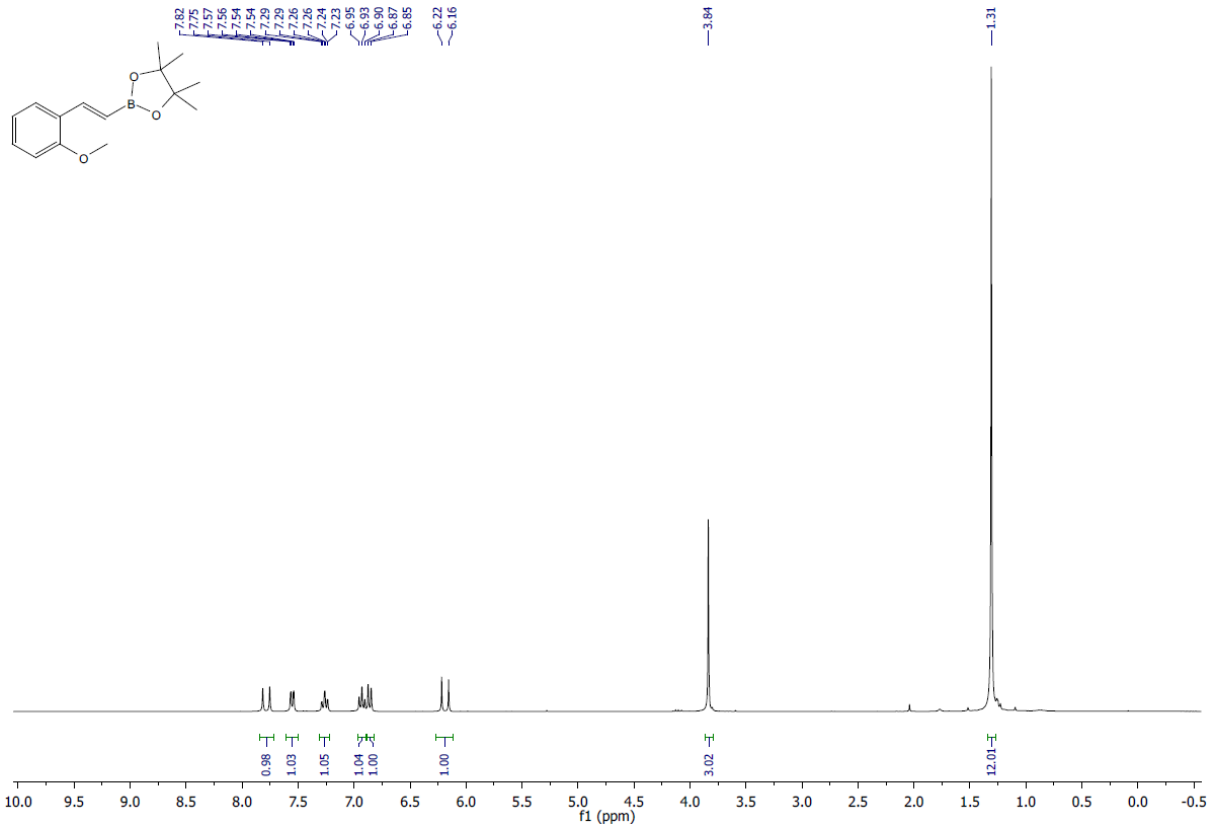


^{13}C NMR (75 MHz, $CDCl_3$)

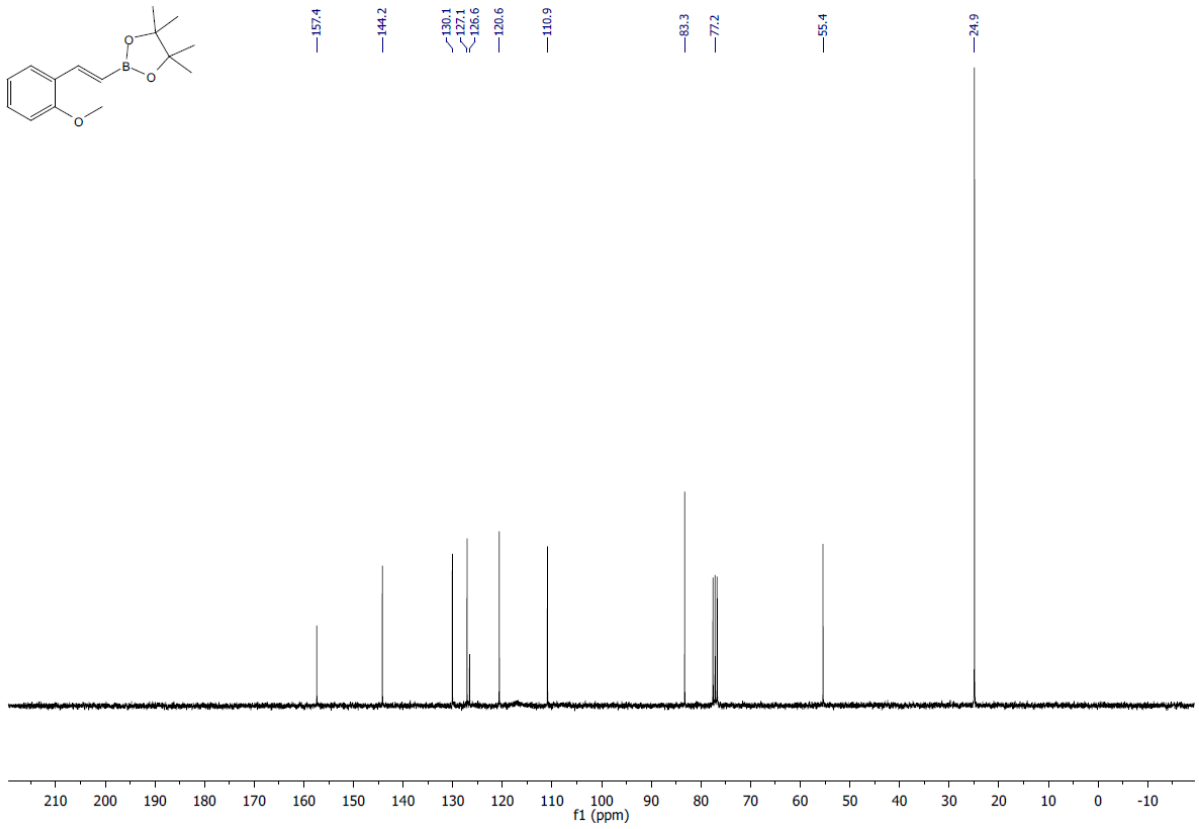


(*E*)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)

^{1}H NMR (300 MHz, $CDCl_3$)

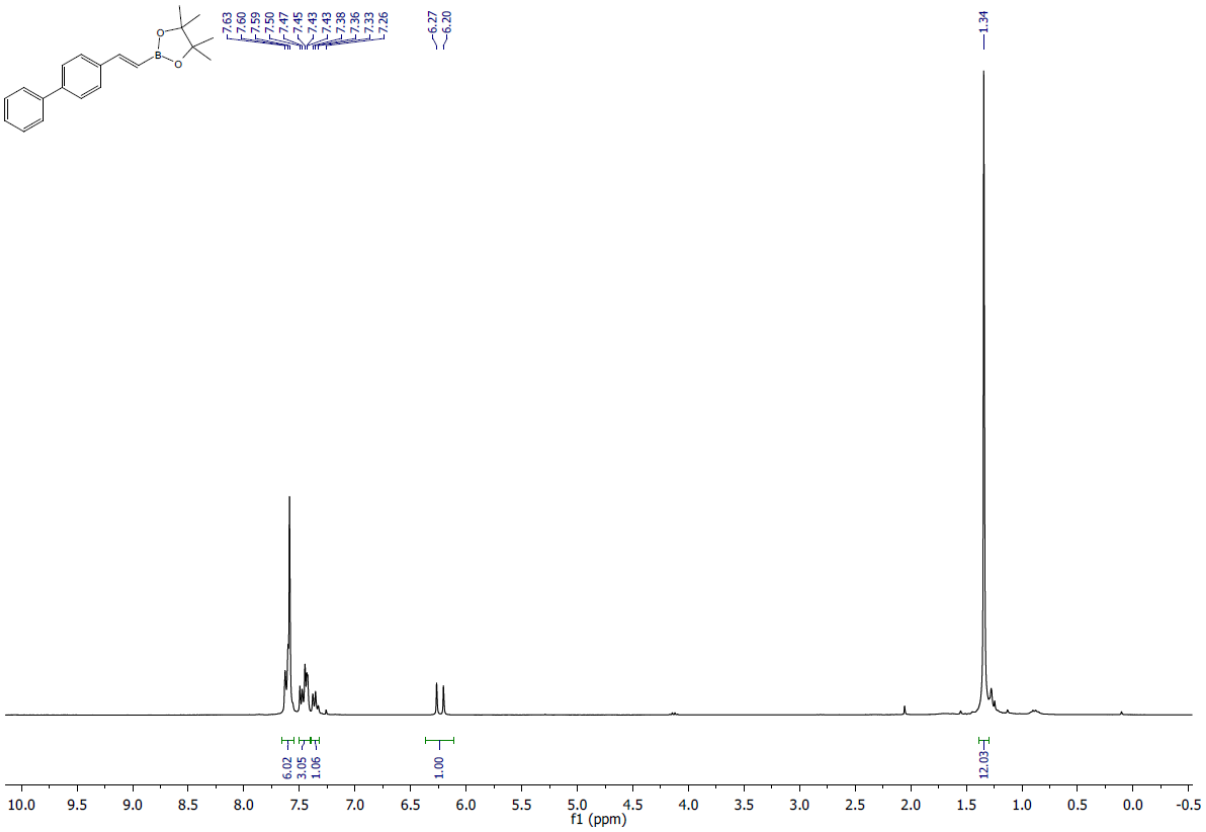


^{13}C NMR (75 MHz, $CDCl_3$)

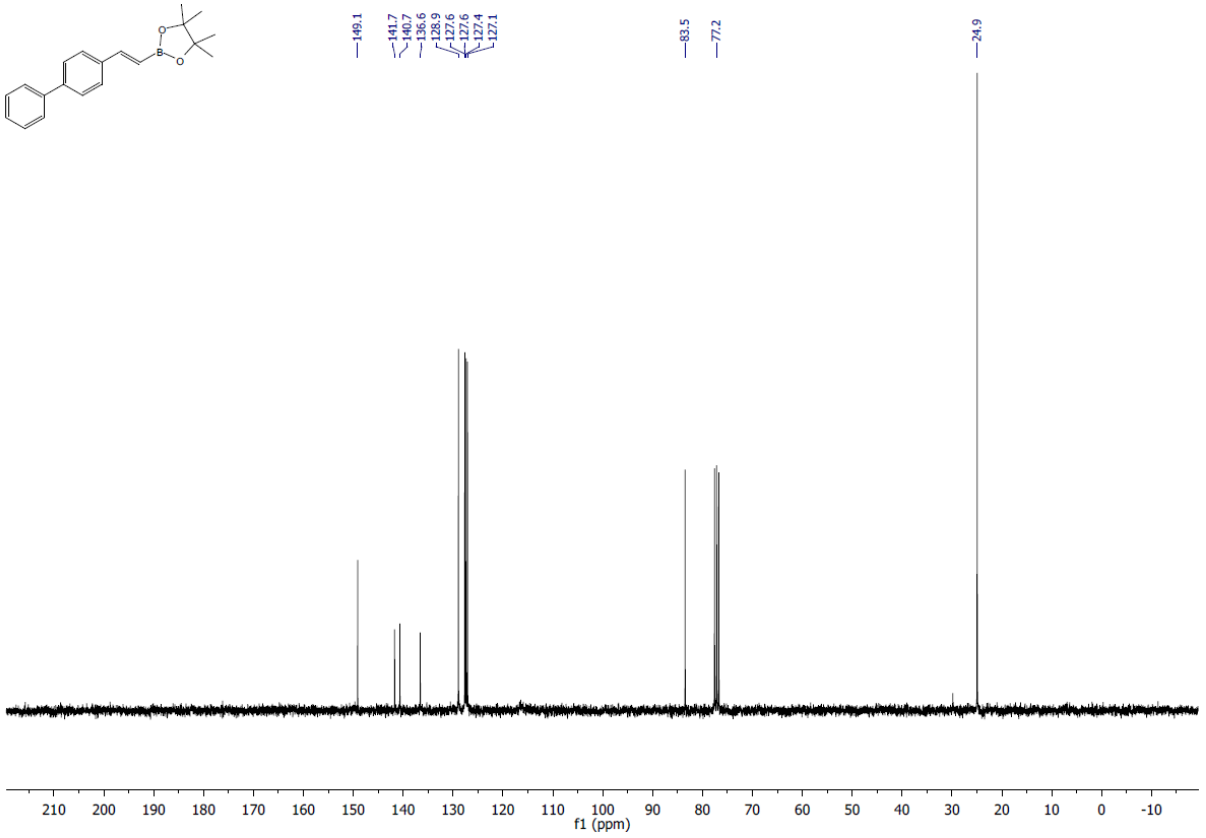


(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

^{1}H NMR (300 MHz, $CDCl_3$)

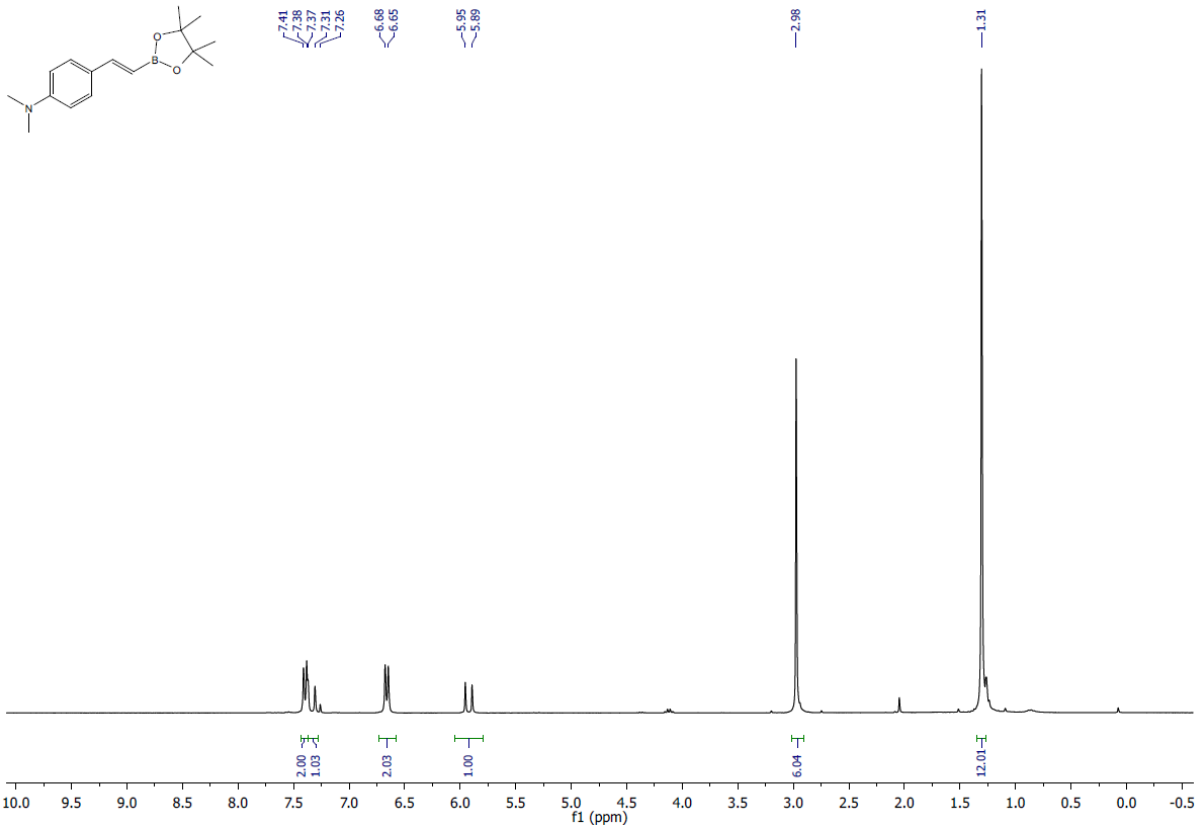


^{13}C NMR (75 MHz, $CDCl_3$)

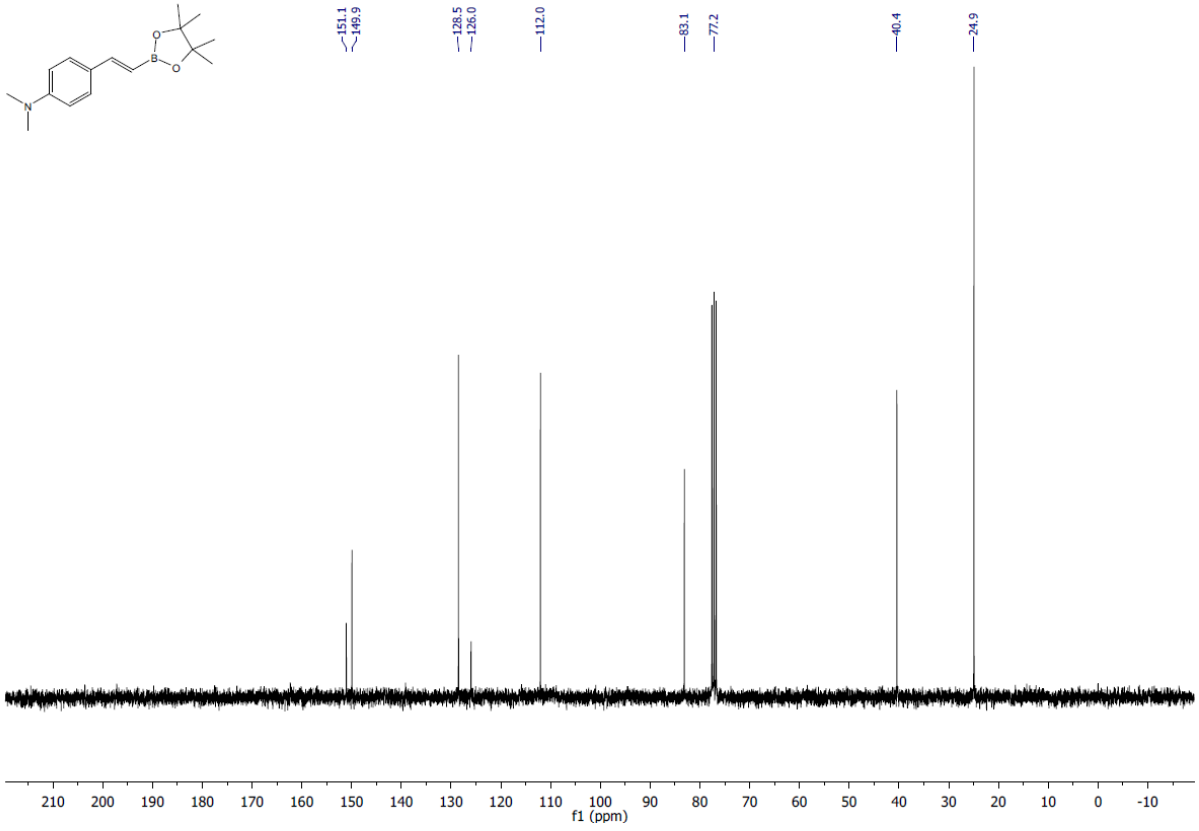


(*E*)-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (9)

^{1}H NMR (300 MHz, $CDCl_3$)

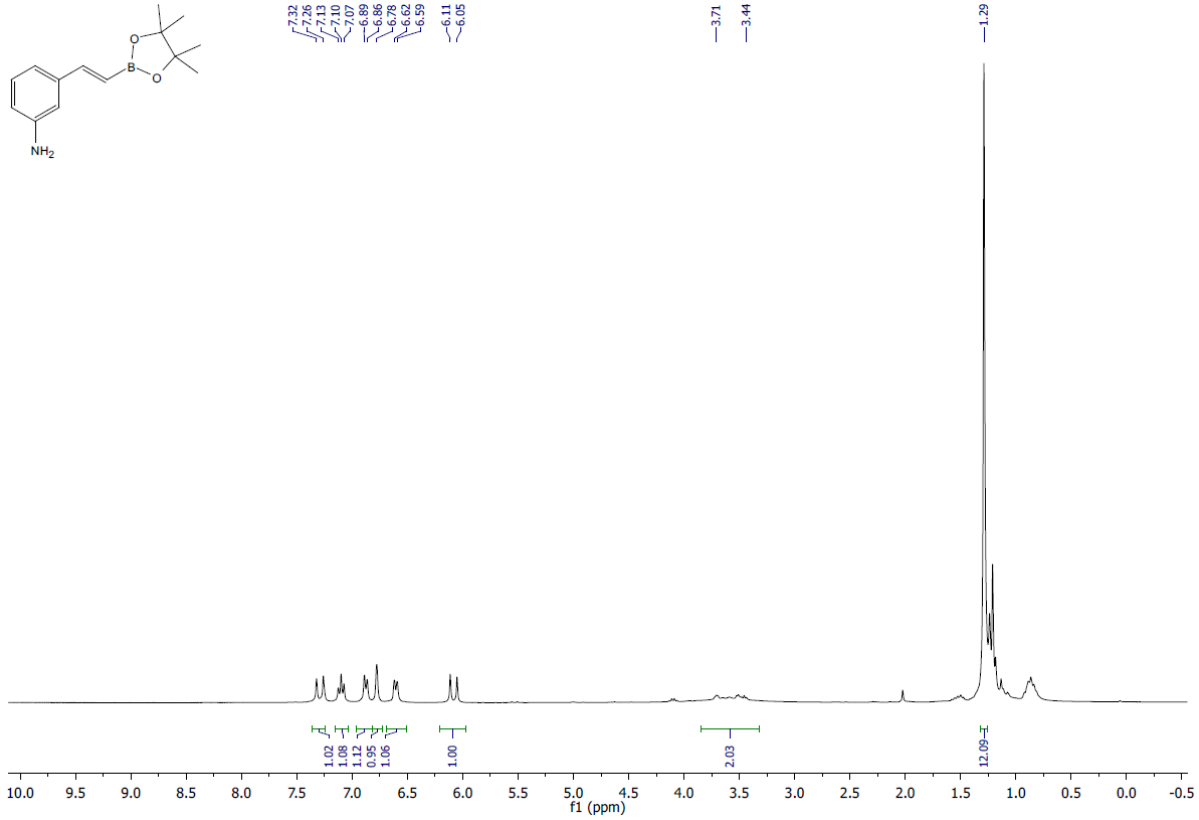


^{13}C NMR (75 MHz, $CDCl_3$)

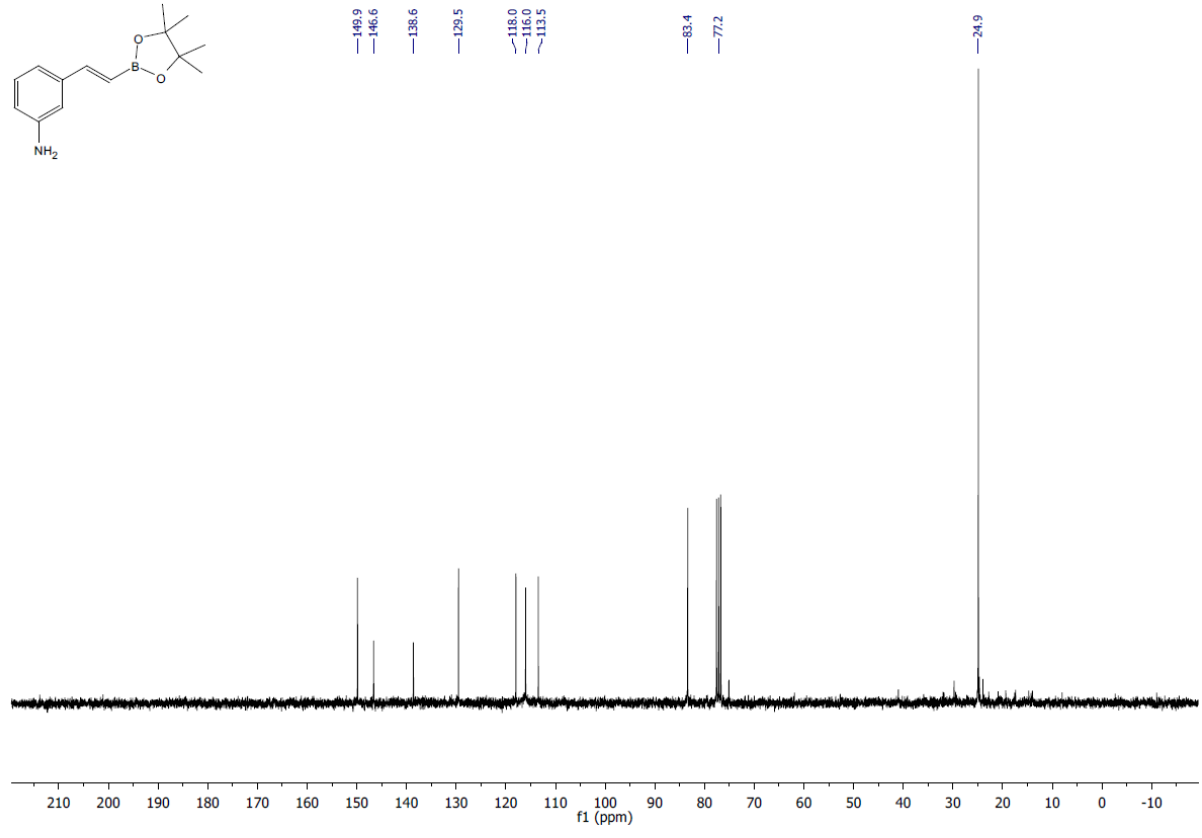


(*E*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (10)

^{1}H NMR (300 MHz, $CDCl_3$)

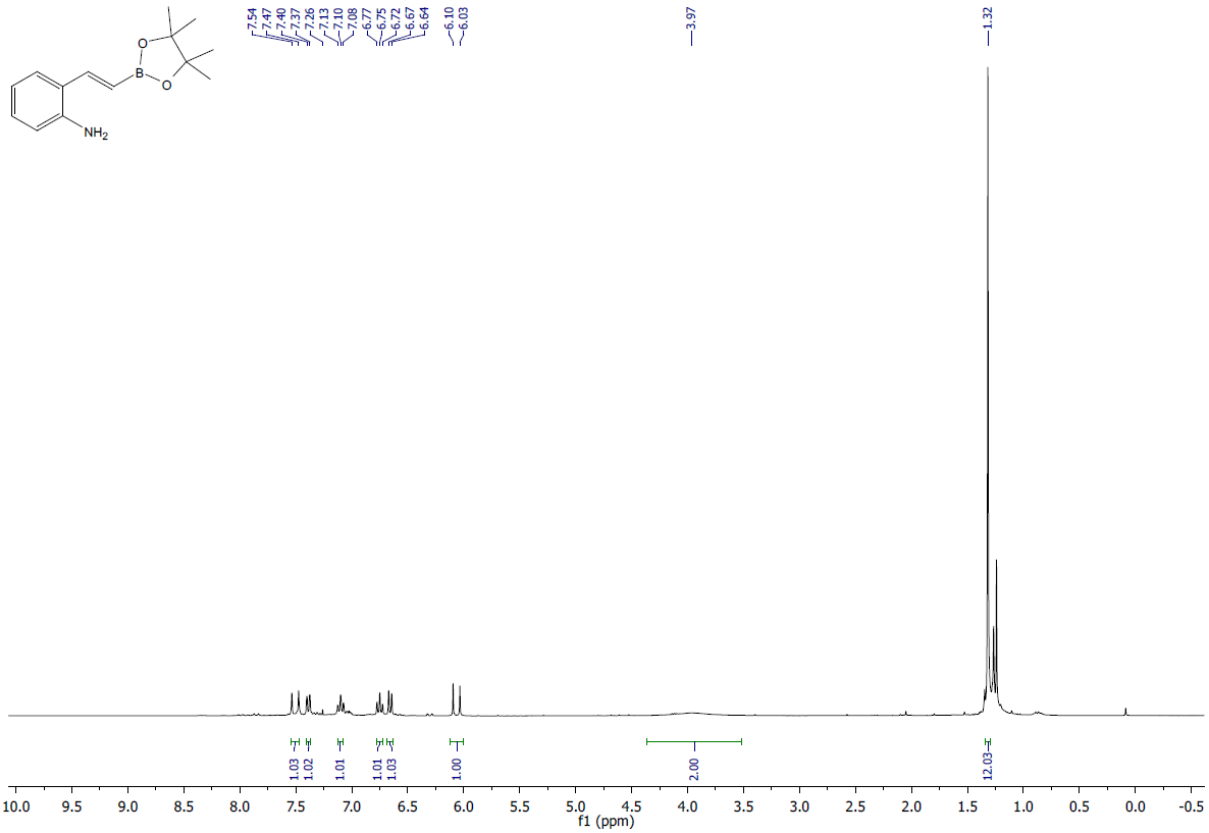


^{13}C NMR (75 MHz, $CDCl_3$)

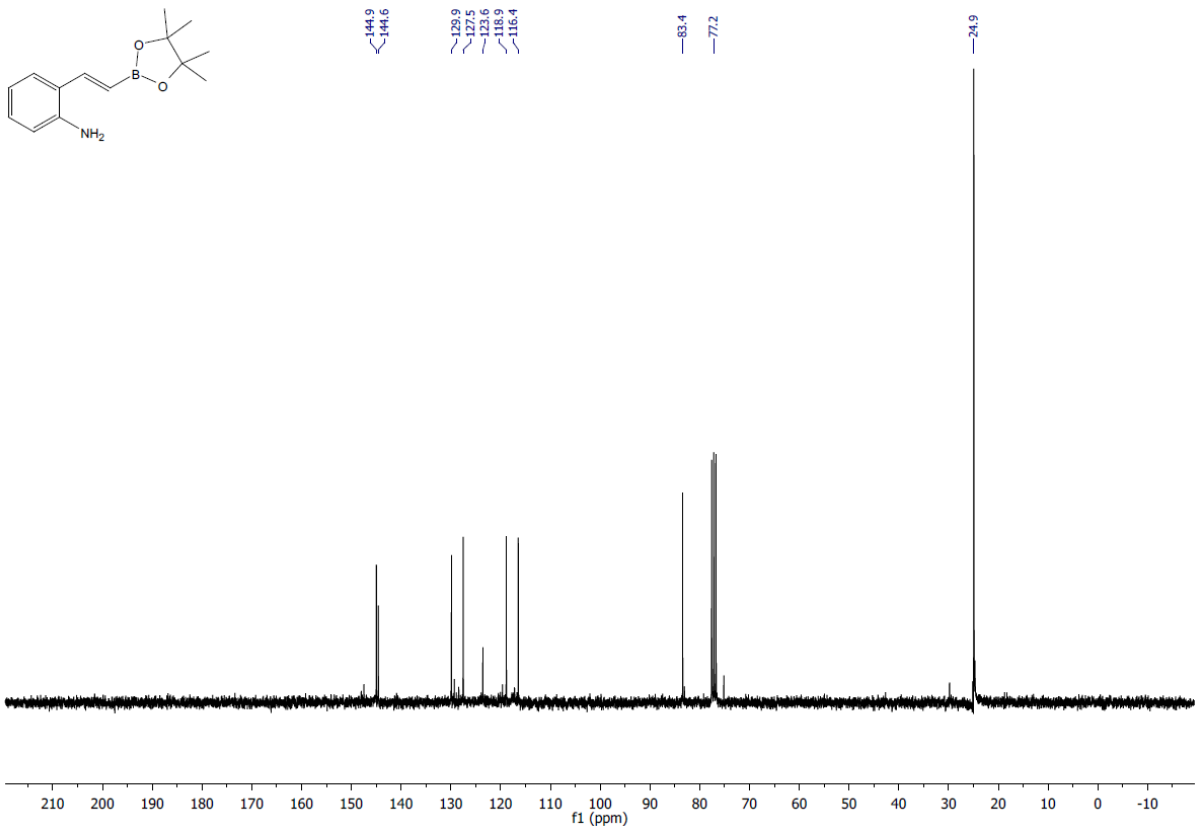


(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (11)

^{1}H NMR (300 MHz, $CDCl_3$)

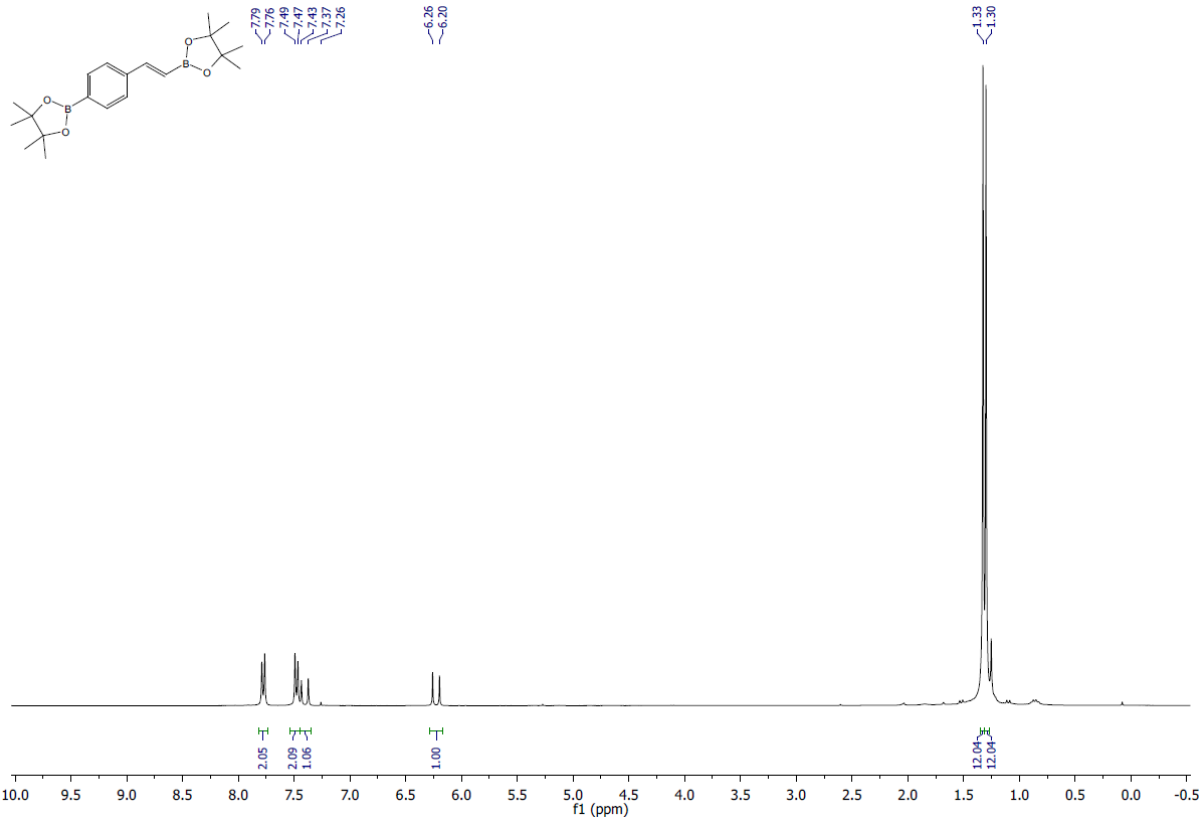


^{13}C NMR (75 MHz, $CDCl_3$)

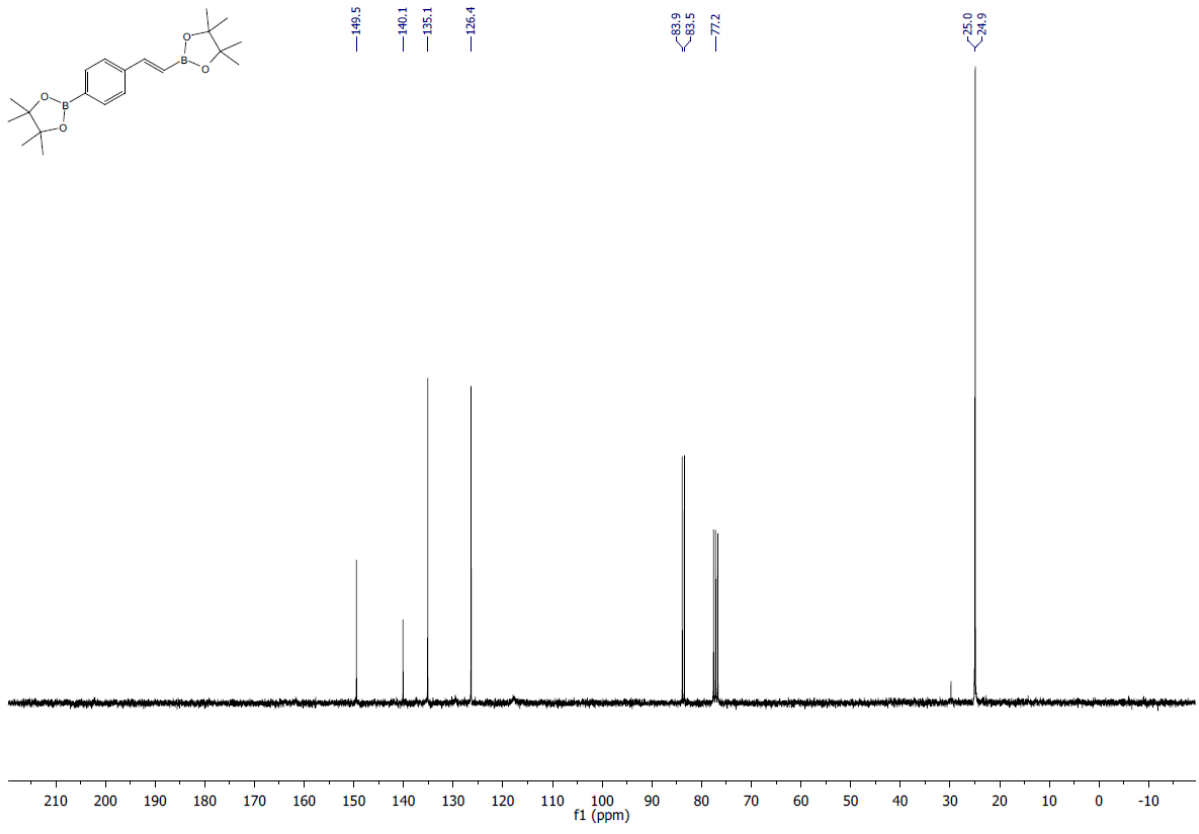


(*E*)-4,4,5,5-tetramethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)-1,3,2-dioxaborolane (12):

^{1}H NMR (300 MHz, $CDCl_3$)

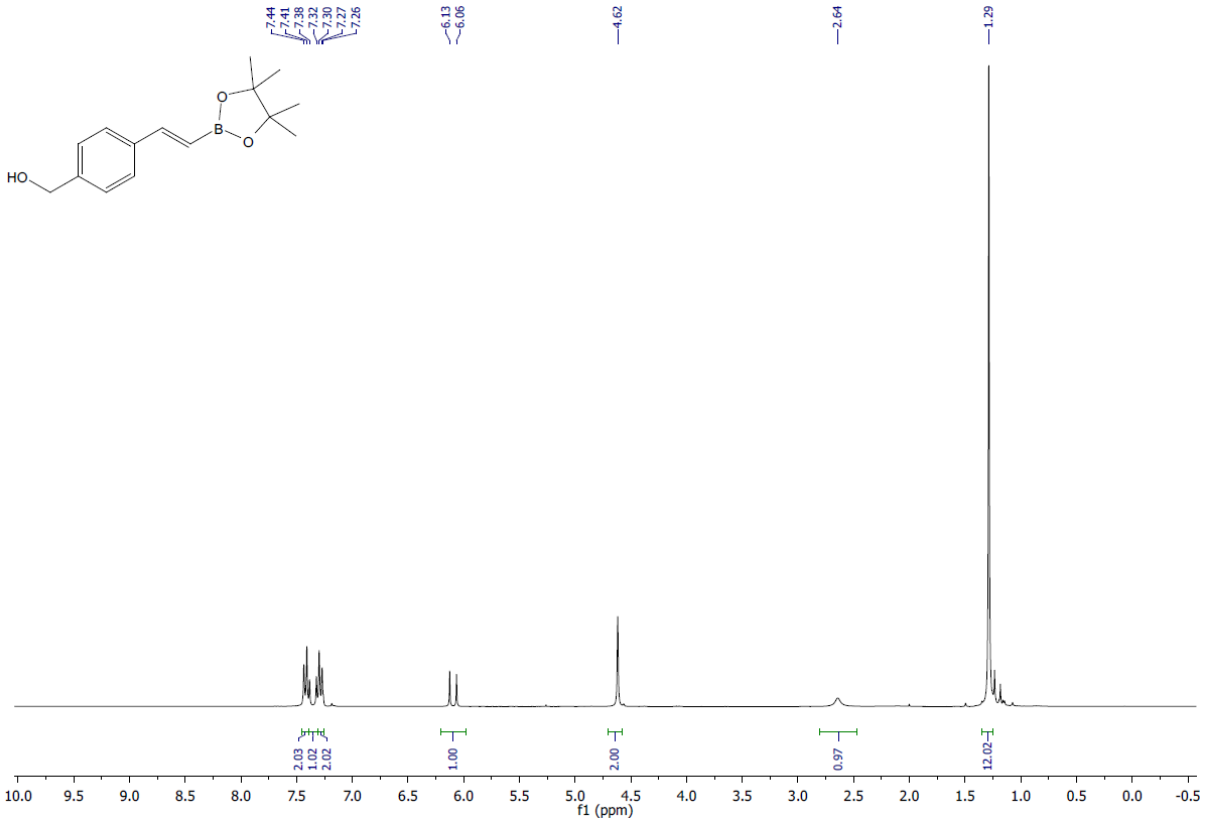


^{13}C NMR (75 MHz, $CDCl_3$)

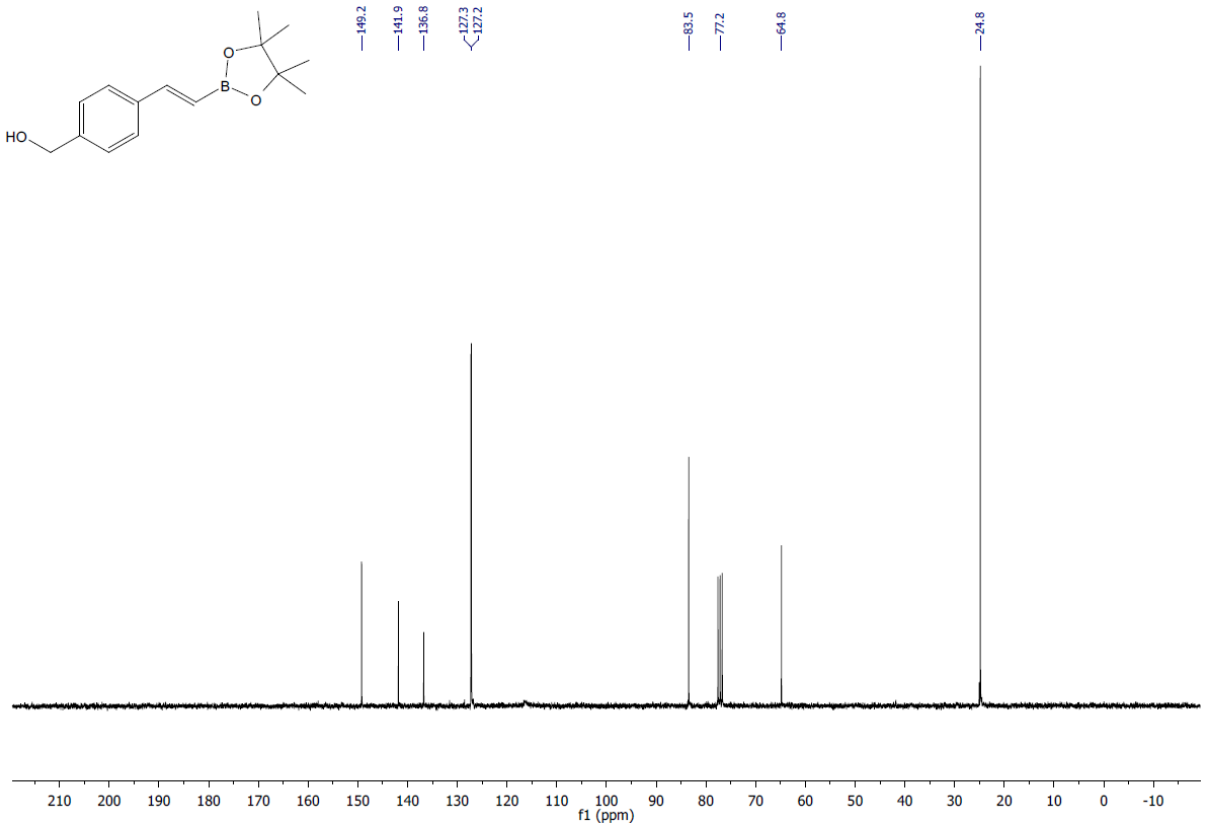


(*E*)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanol (13):

^{1}H NMR (300 MHz, $CDCl_3$)

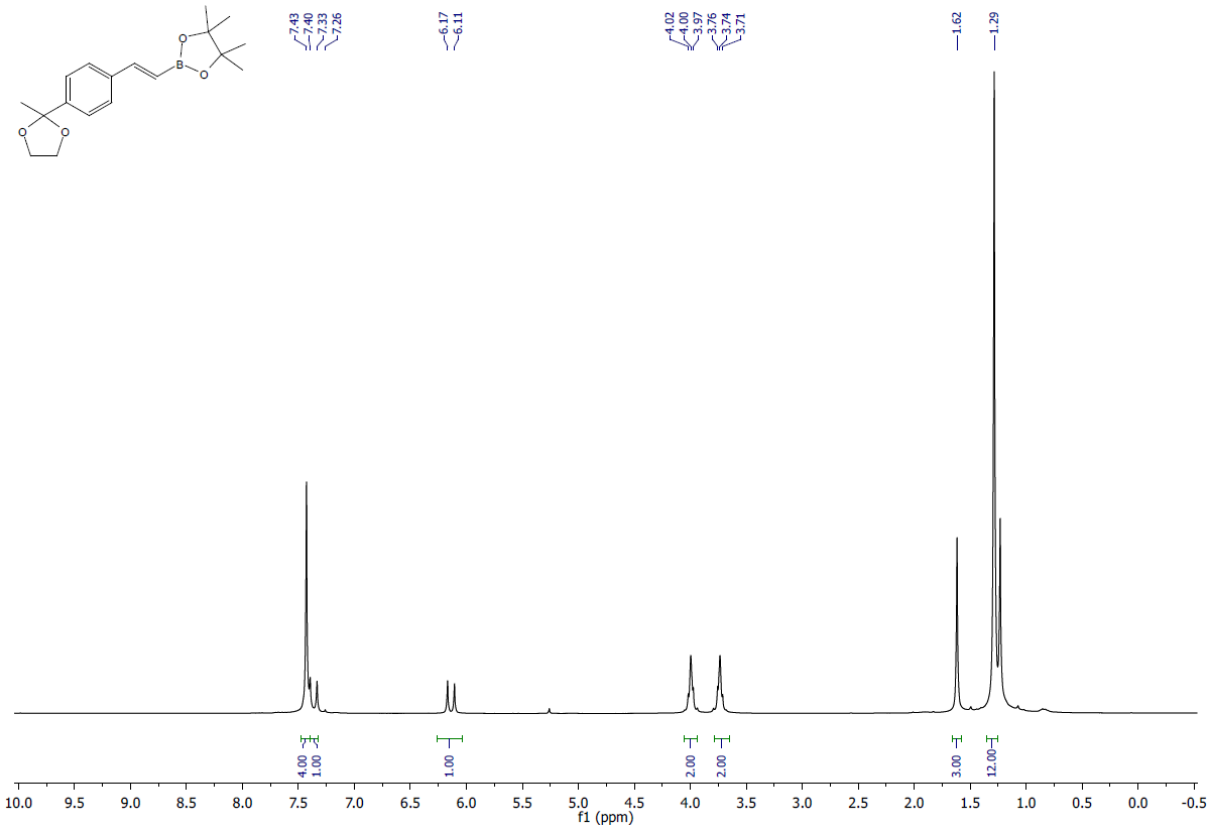


^{13}C NMR (75 MHz, $CDCl_3$)

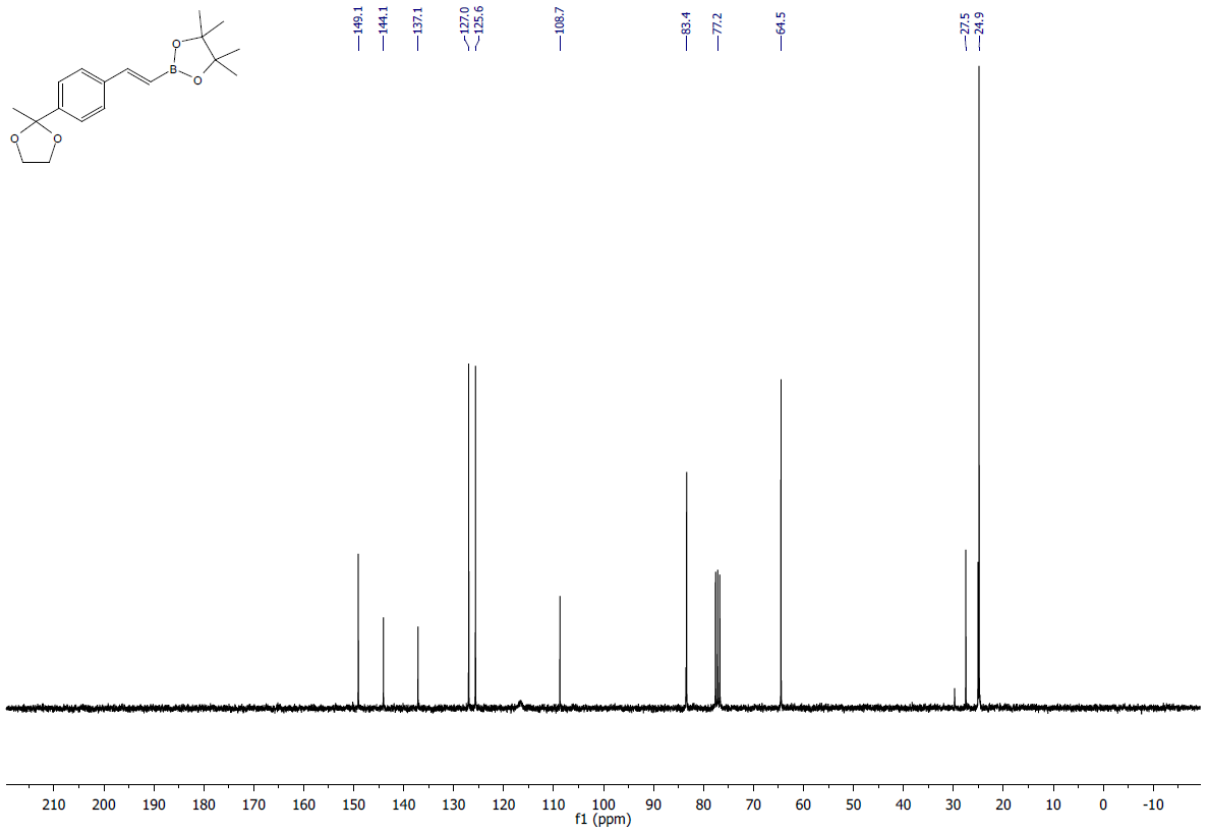


(*E*)-4,4,5,5-tetramethyl-2-(4-(2-methyl-1,3-dioxolan-2-yl)styryl)-1,3,2-dioxaborolane (14)

^{1}H NMR (300 MHz, $CDCl_3$)

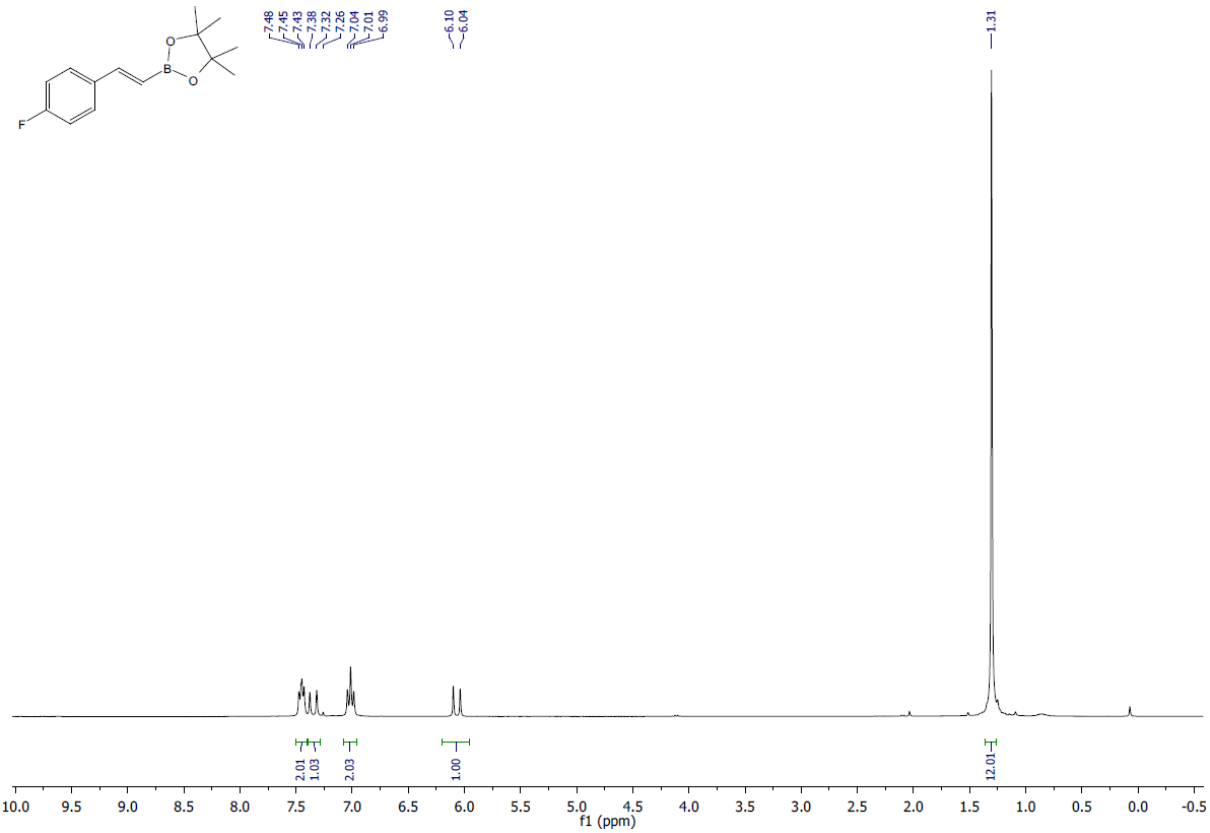


^{13}C NMR (75 MHz, $CDCl_3$)

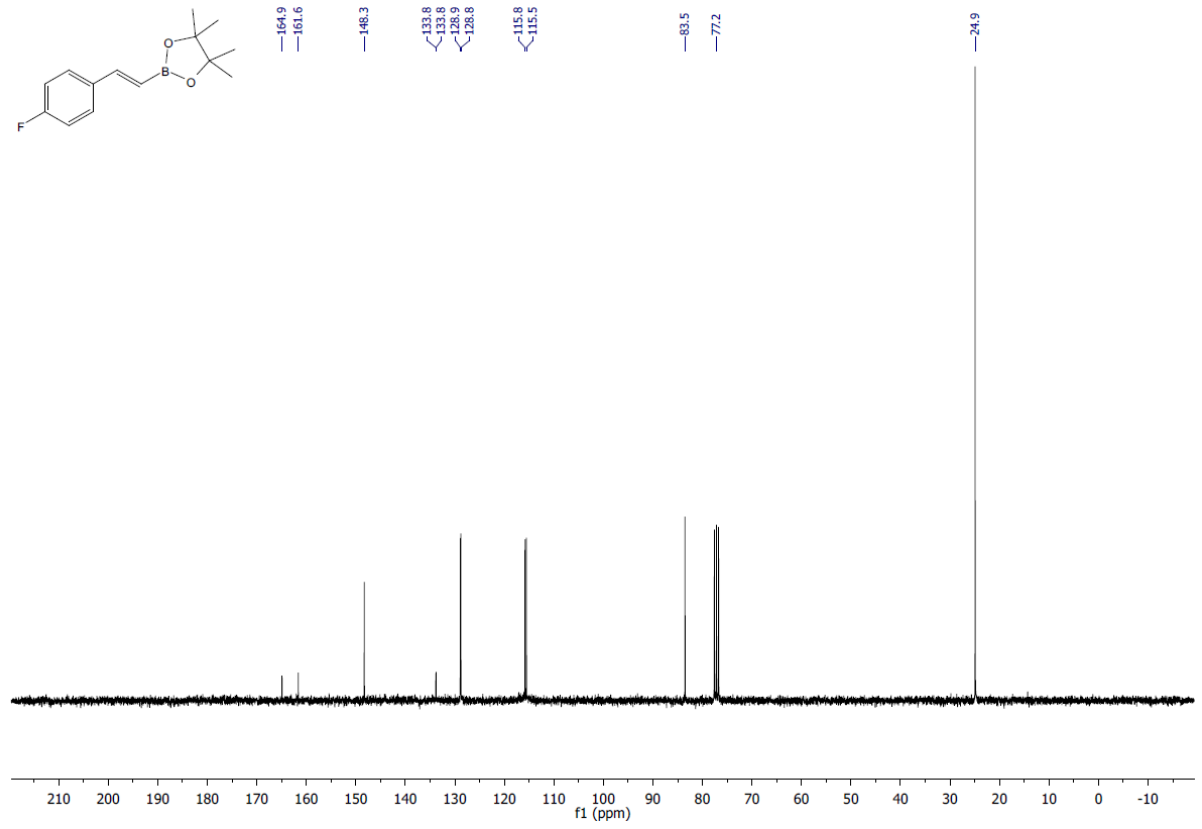


(*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)

^{1}H NMR (300 MHz, $CDCl_3$)

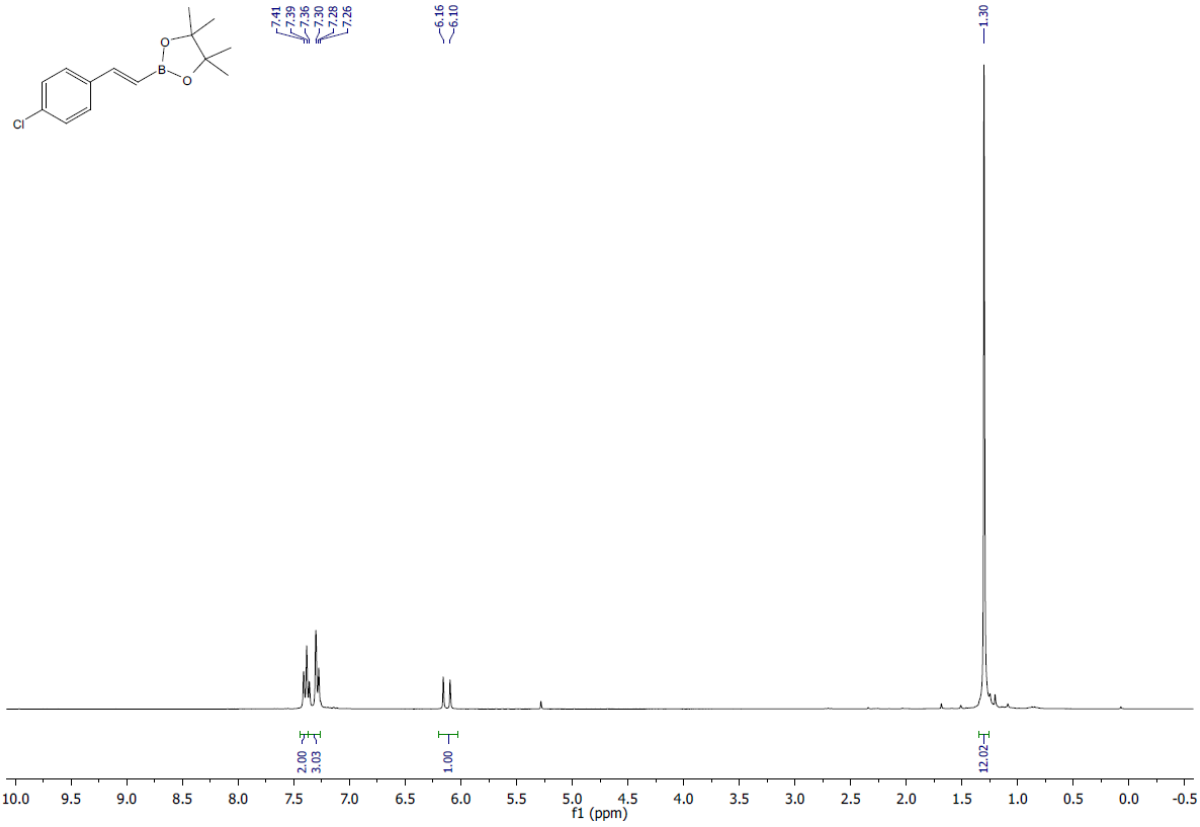


^{13}C NMR (75 MHz, $CDCl_3$)

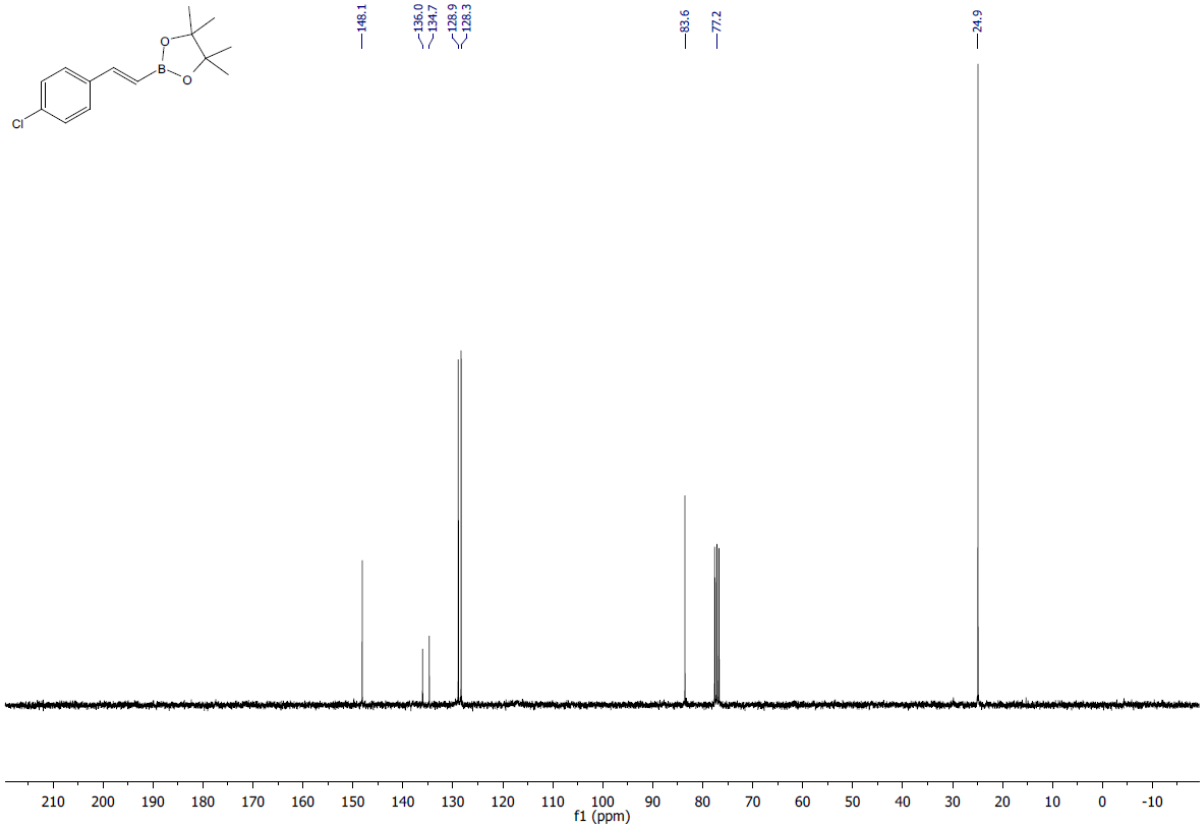


(*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

^{1}H NMR (300 MHz, $CDCl_3$)

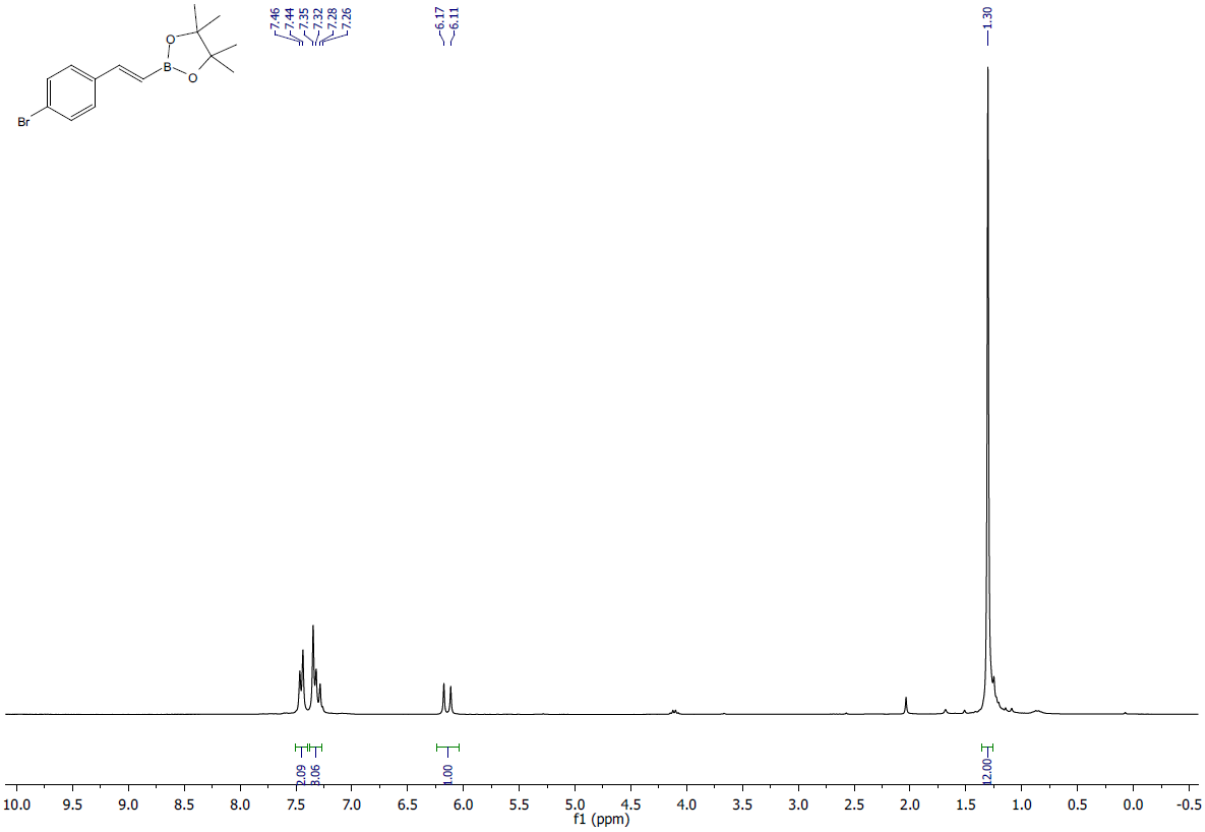


^{13}C NMR (75 MHz, $CDCl_3$)

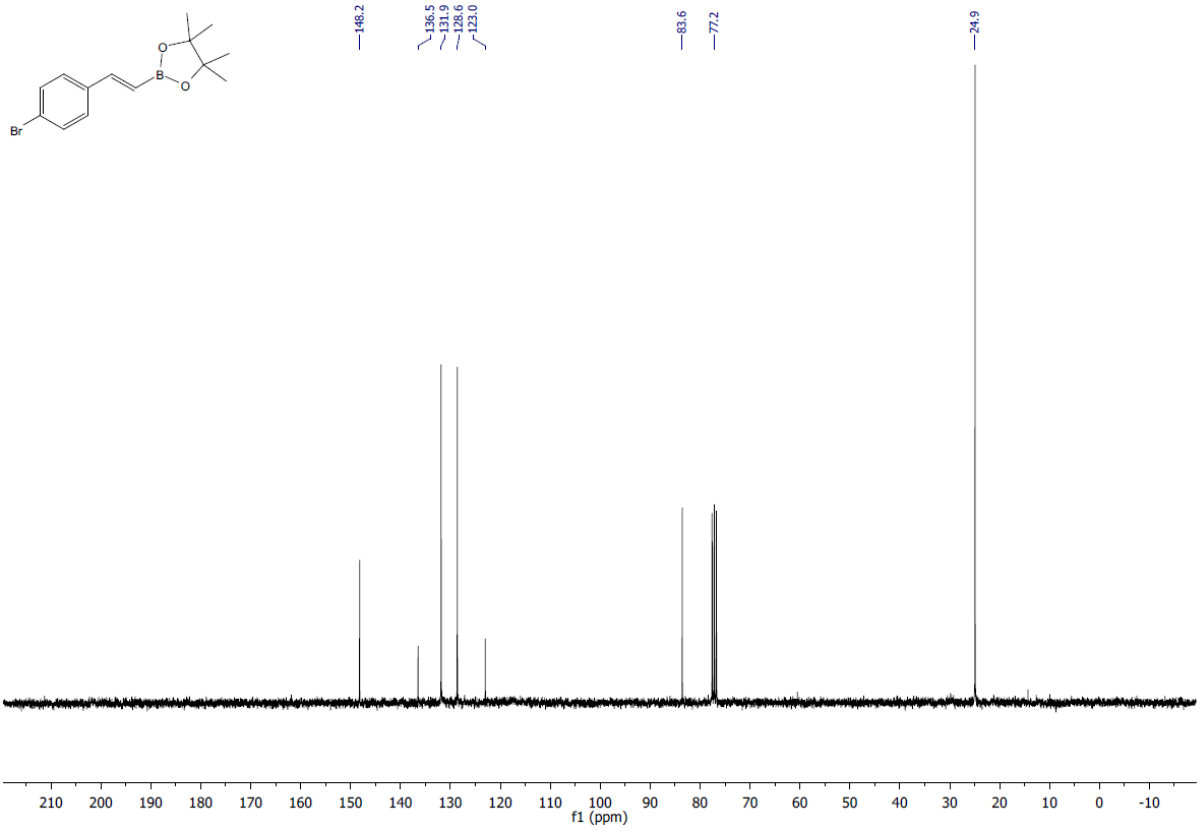


(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)

^{1}H NMR (300 MHz, $CDCl_3$)

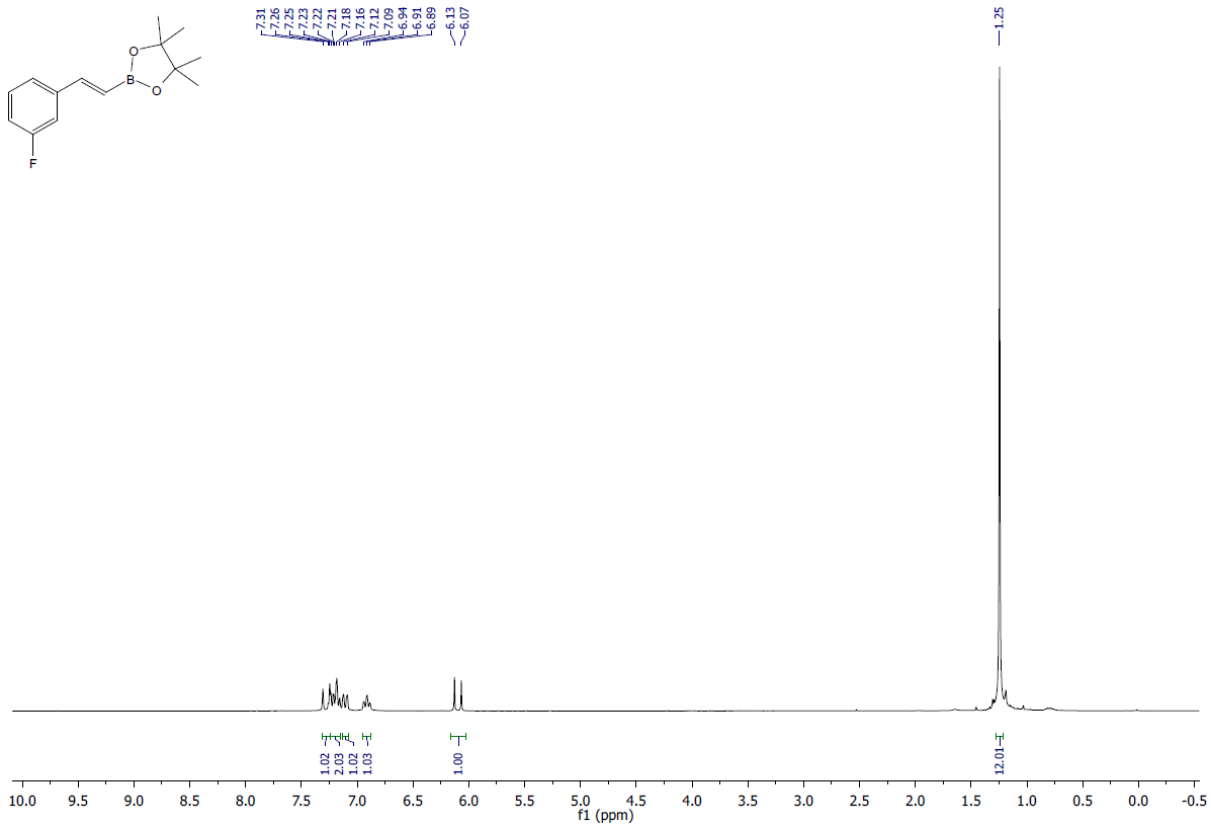


^{13}C NMR (75 MHz, $CDCl_3$)

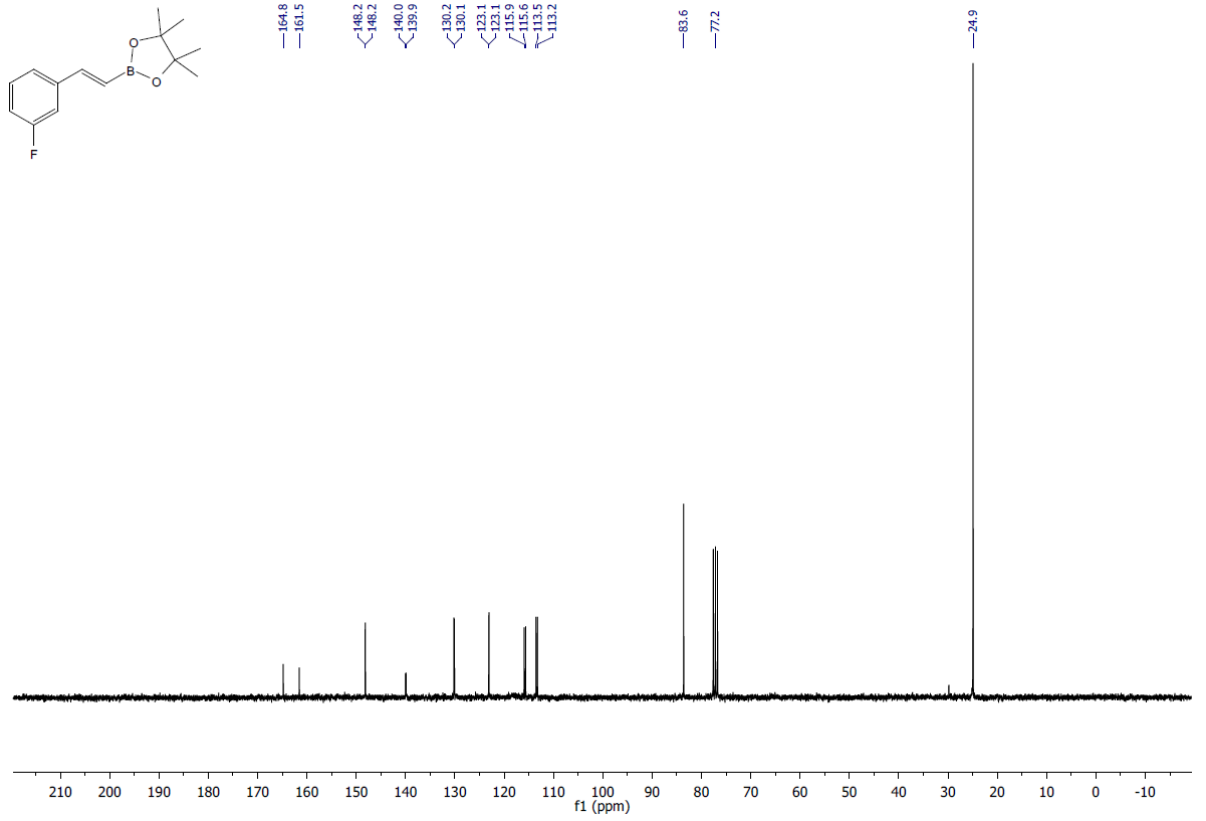


(*E*)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)

^{1}H NMR (300 MHz, $CDCl_3$)

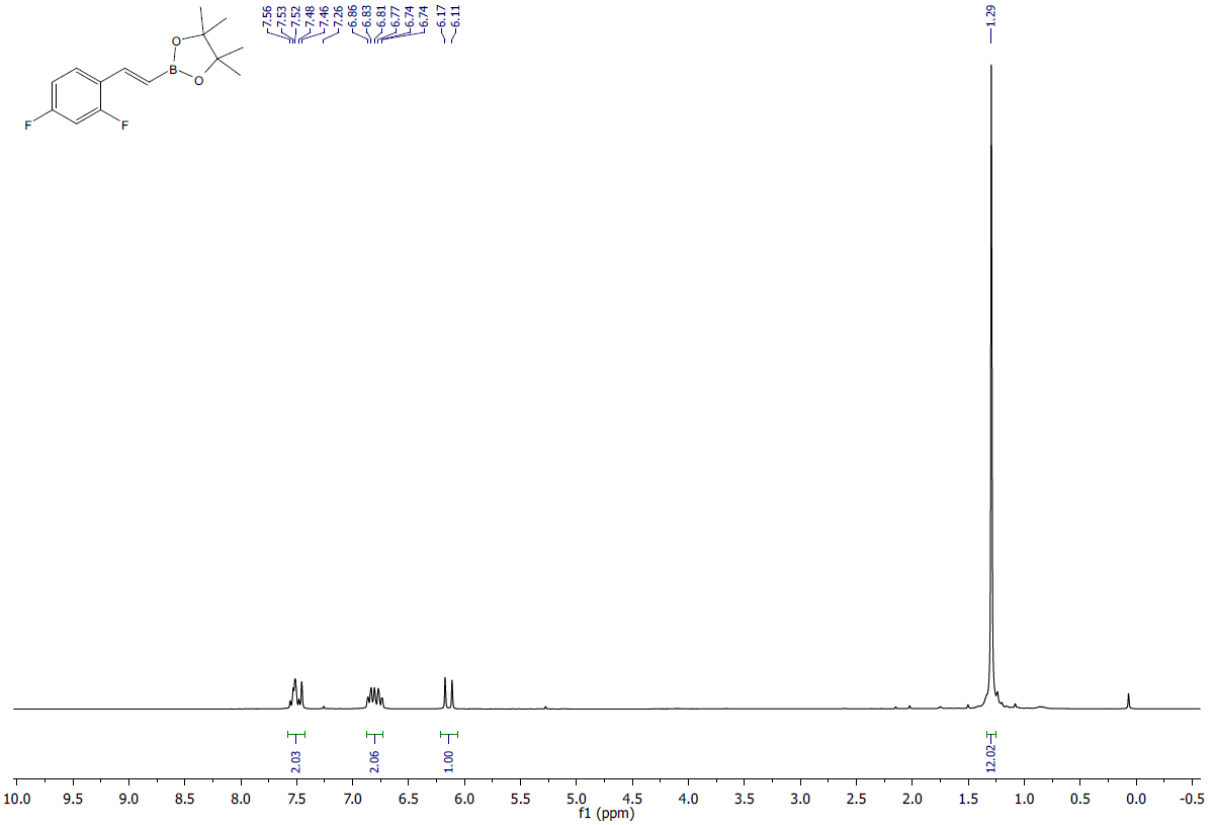


^{13}C NMR (75 MHz, $CDCl_3$)

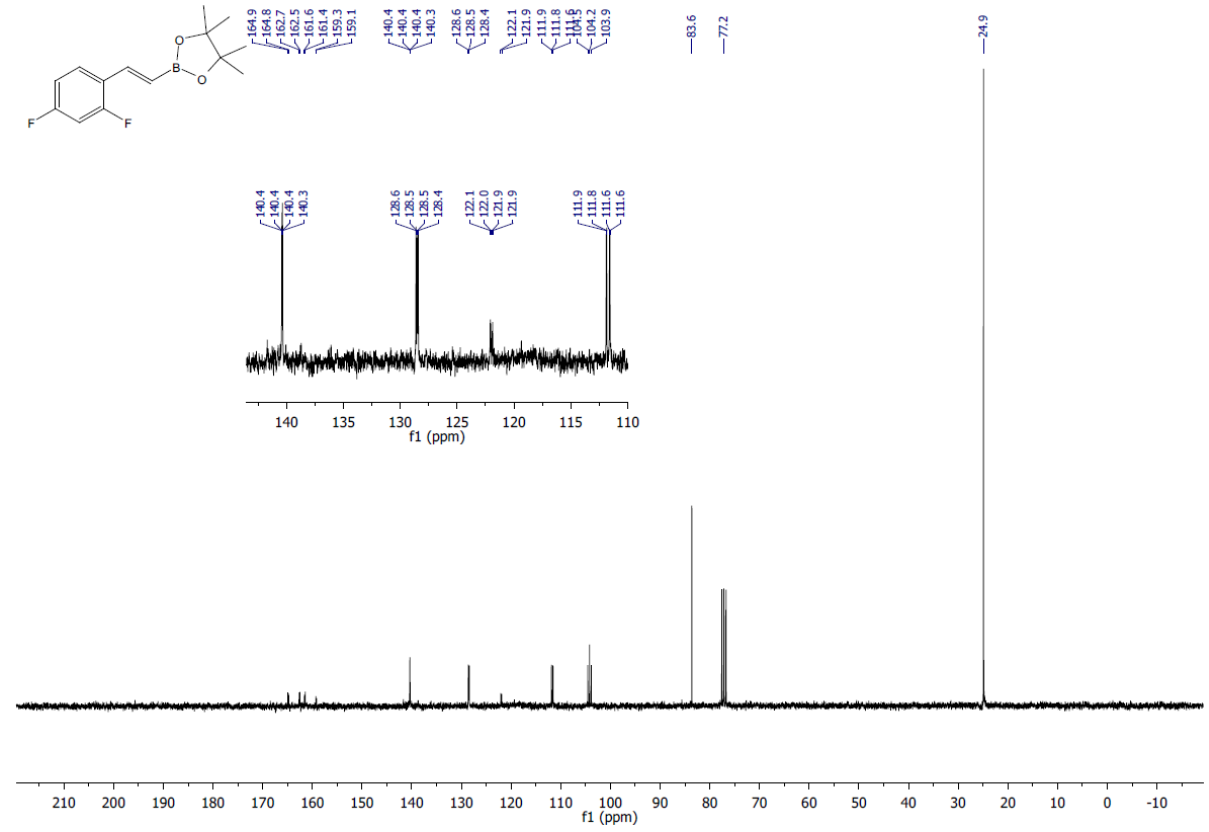


(*E*)-2-(2,4-difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19)

^{1}H NMR (300 MHz, $CDCl_3$)

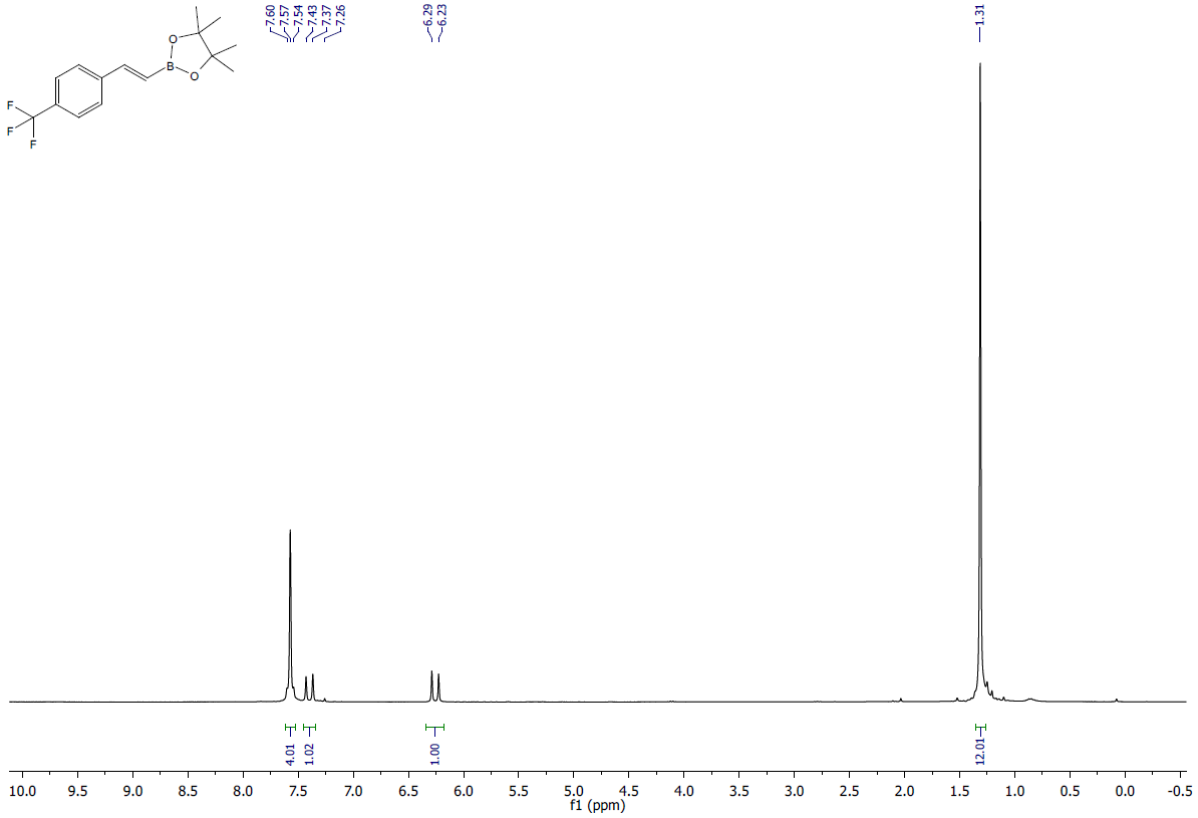


^{13}C NMR (75 MHz, $CDCl_3$)

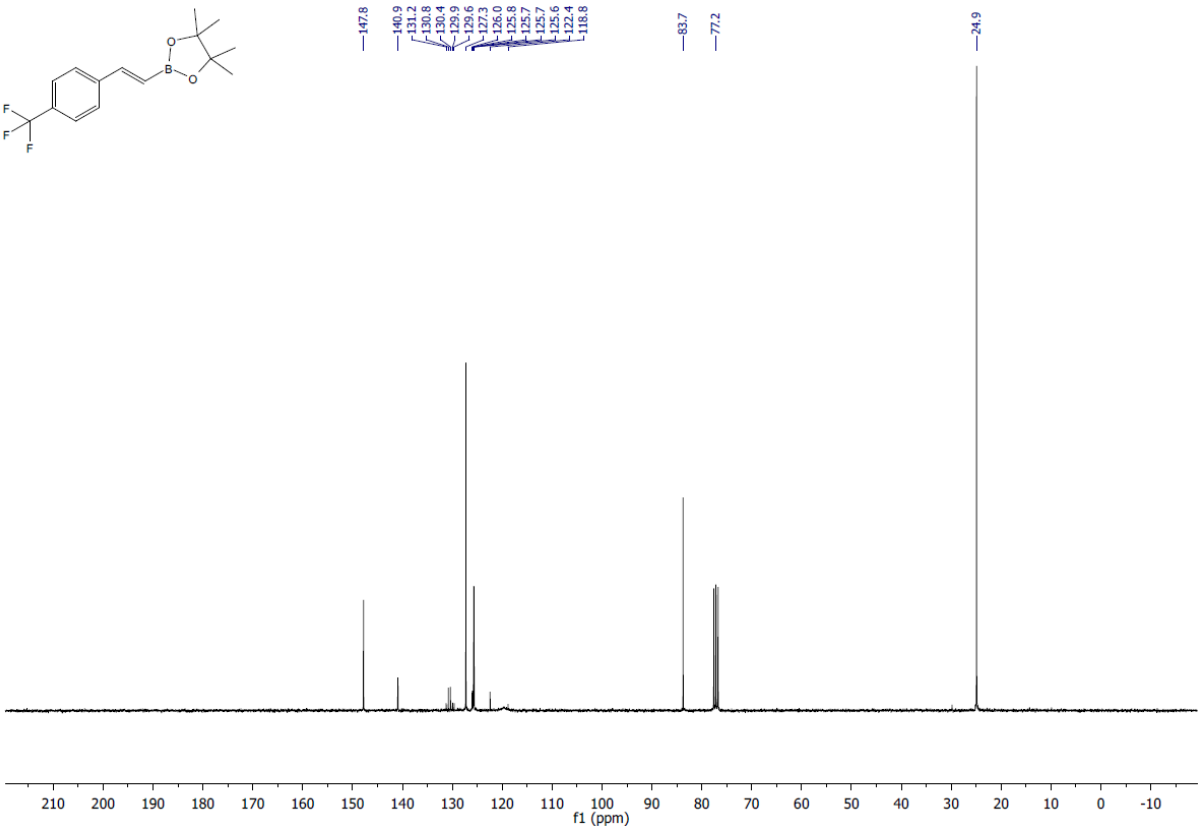


(*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (20)

^{1}H NMR (300 MHz, $CDCl_3$)

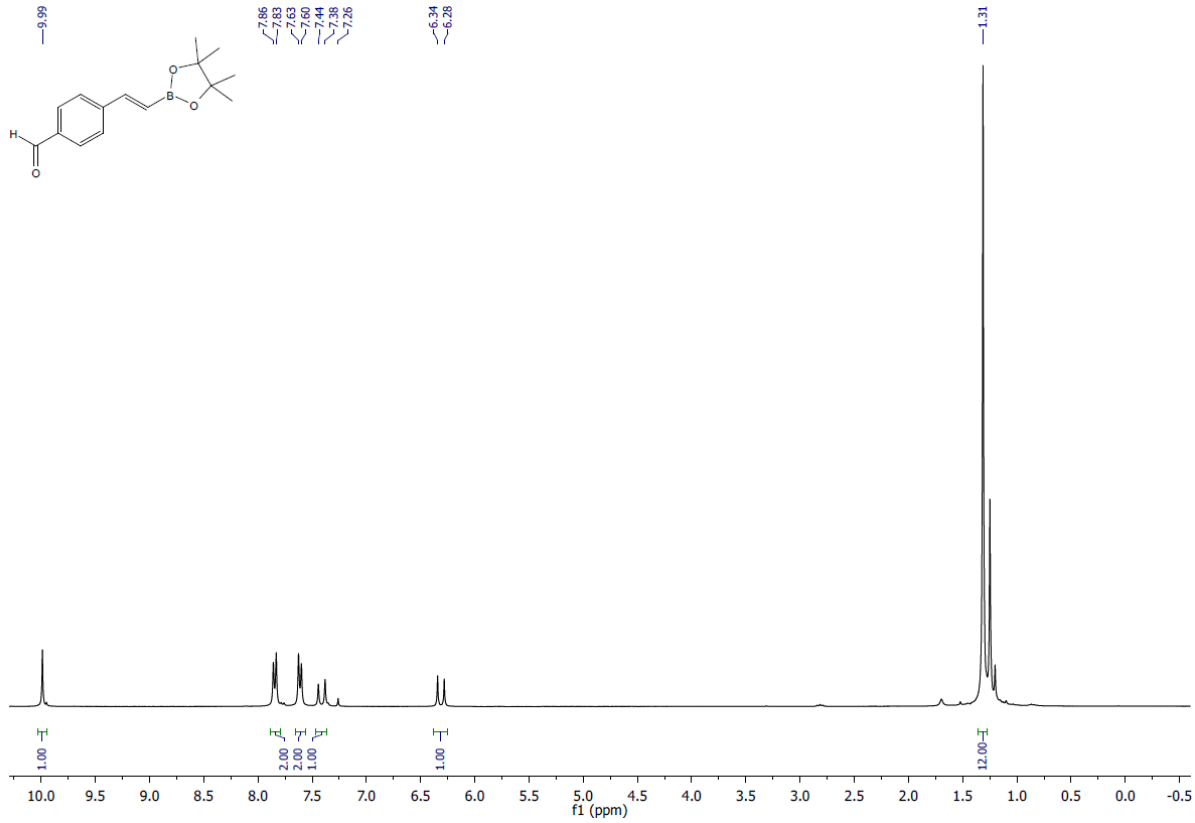


^{13}C NMR (75 MHz, $CDCl_3$)

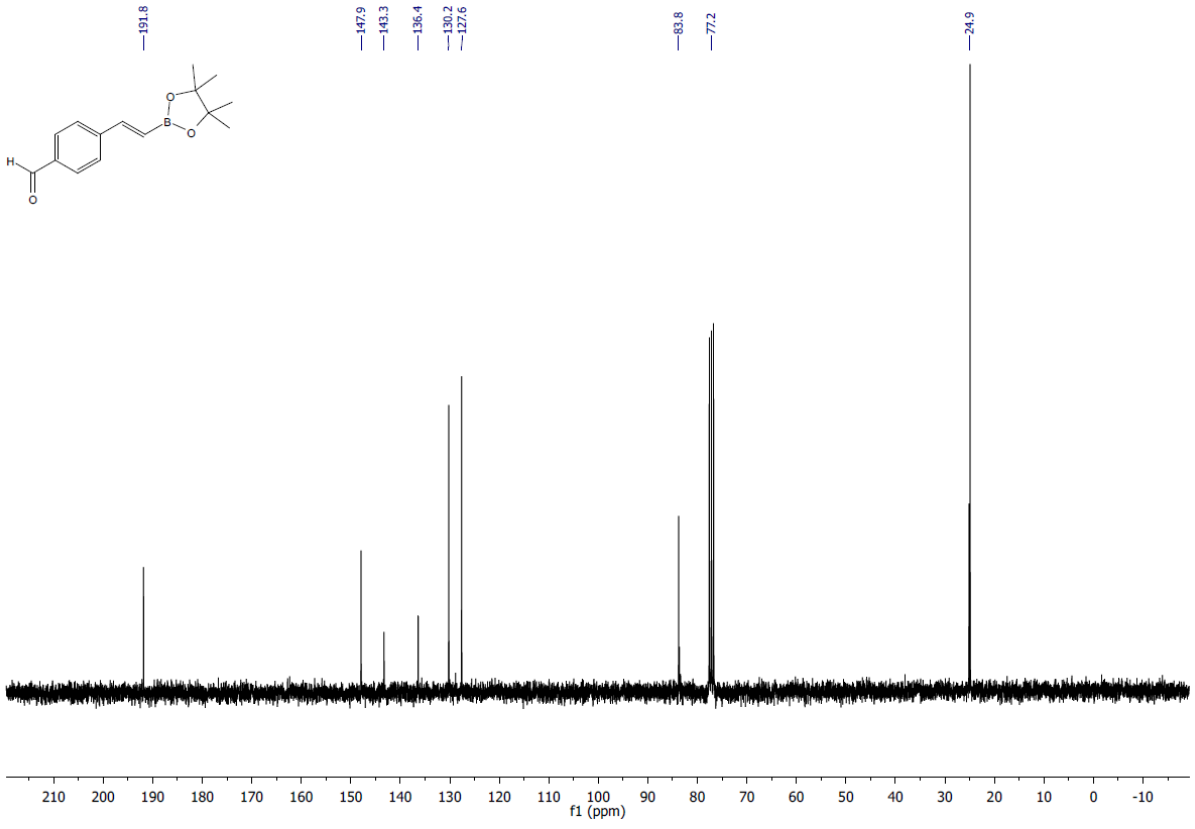


(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzaldehyde (21)

^{1}H NMR (300 MHz, $CDCl_3$)

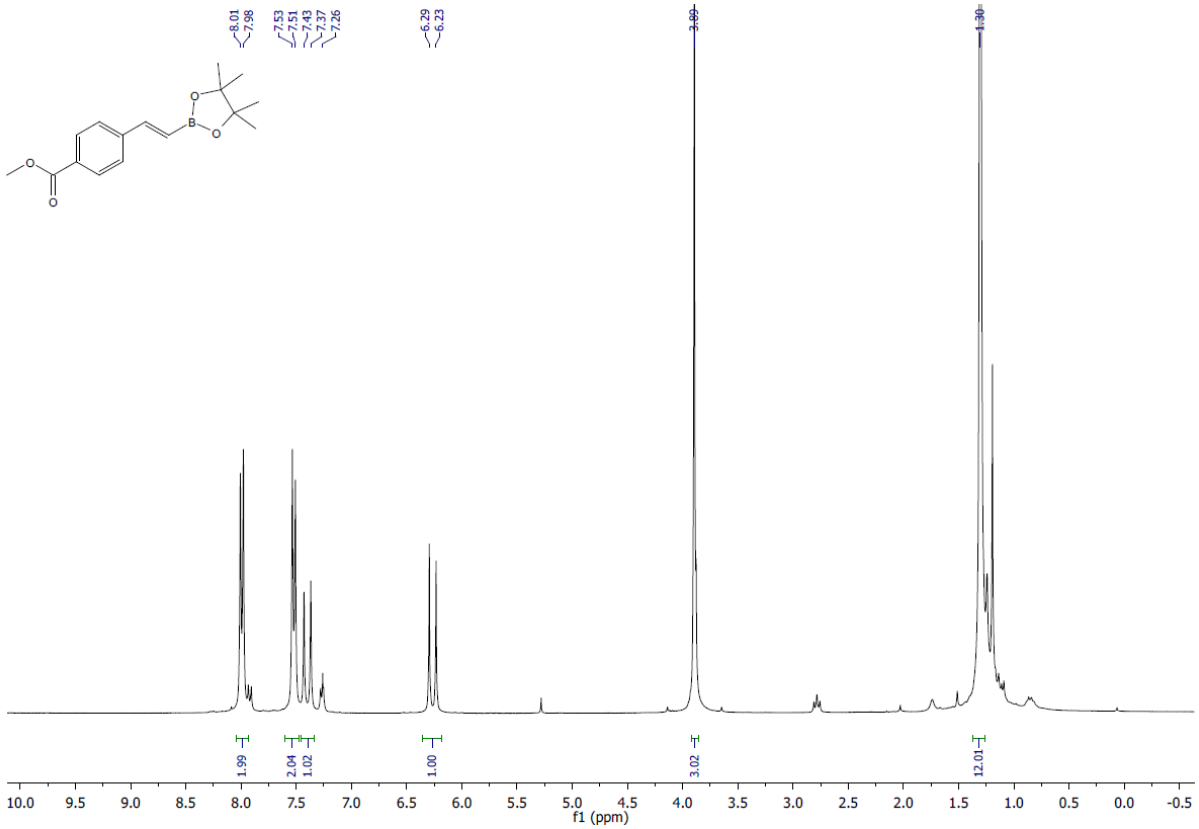


^{13}C NMR (75 MHz, $CDCl_3$)

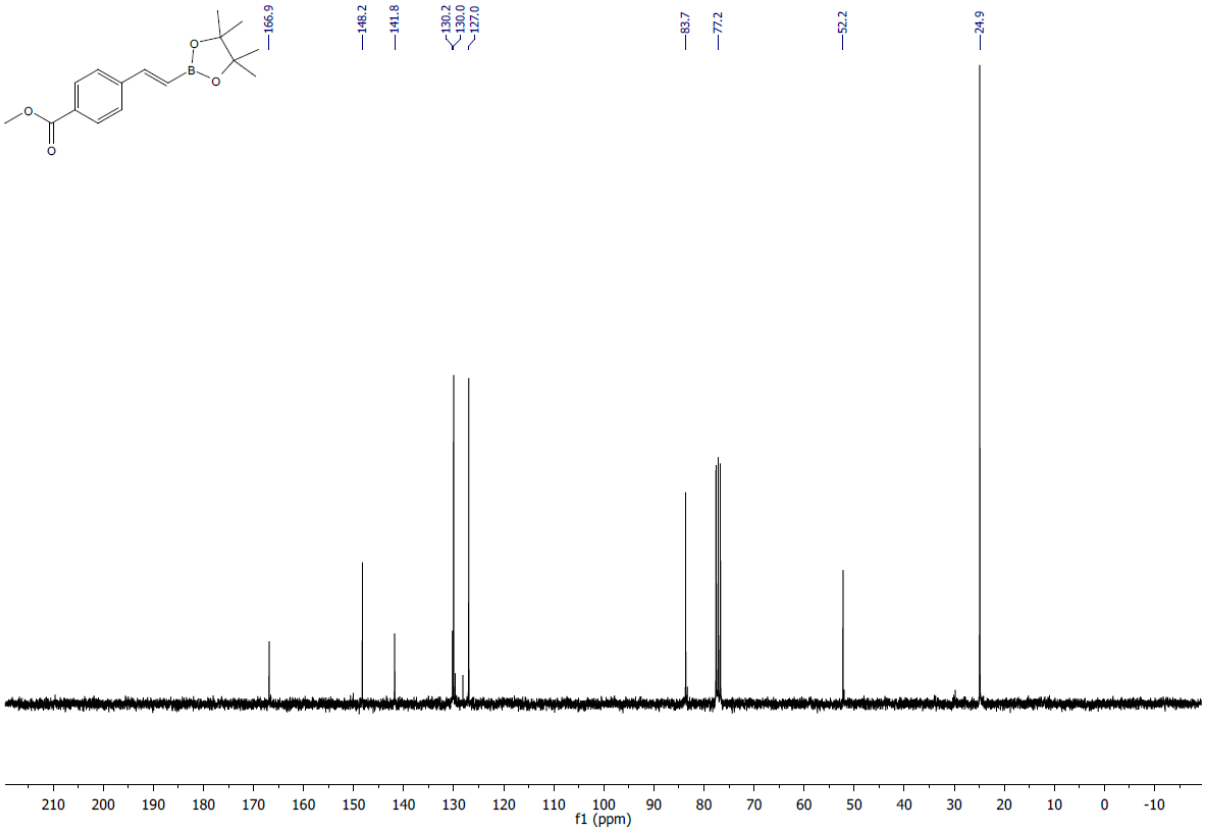


Methyl (*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (22)

^{1}H NMR (300 MHz, $CDCl_3$)

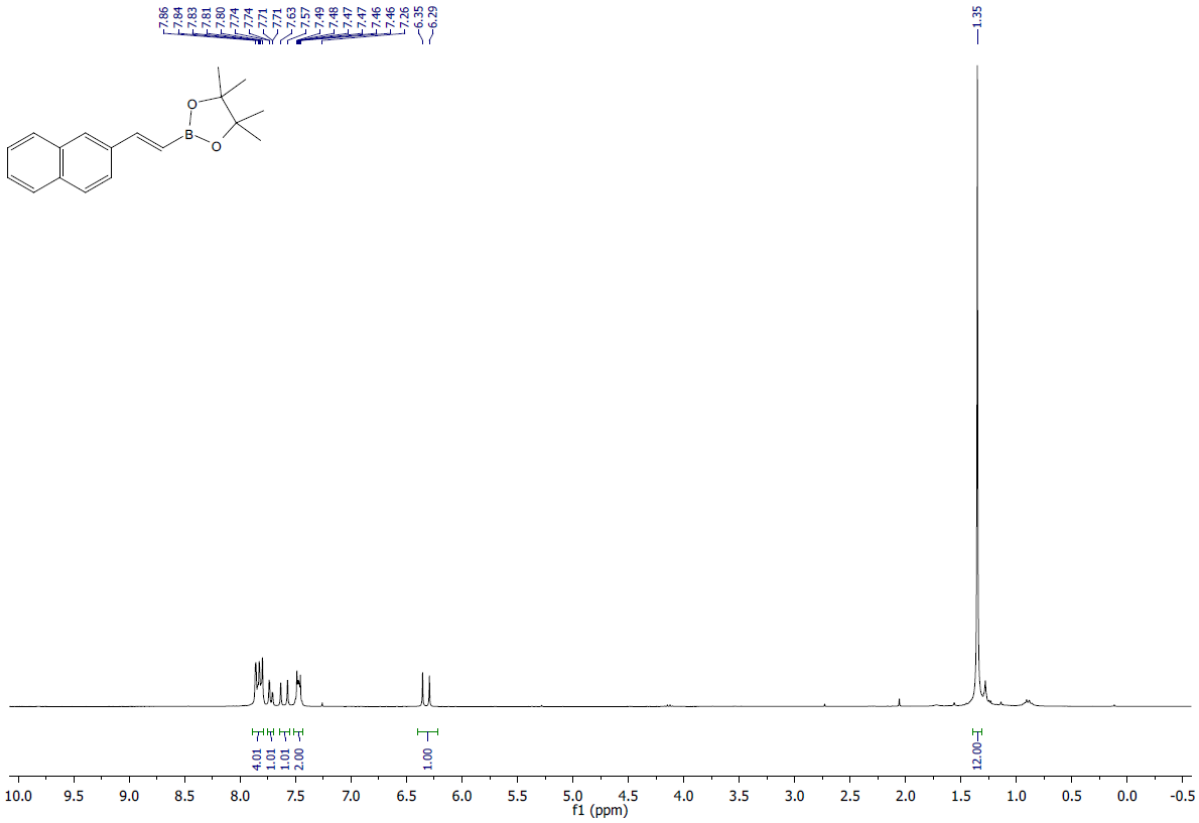


^{13}C NMR (75 MHz, $CDCl_3$)

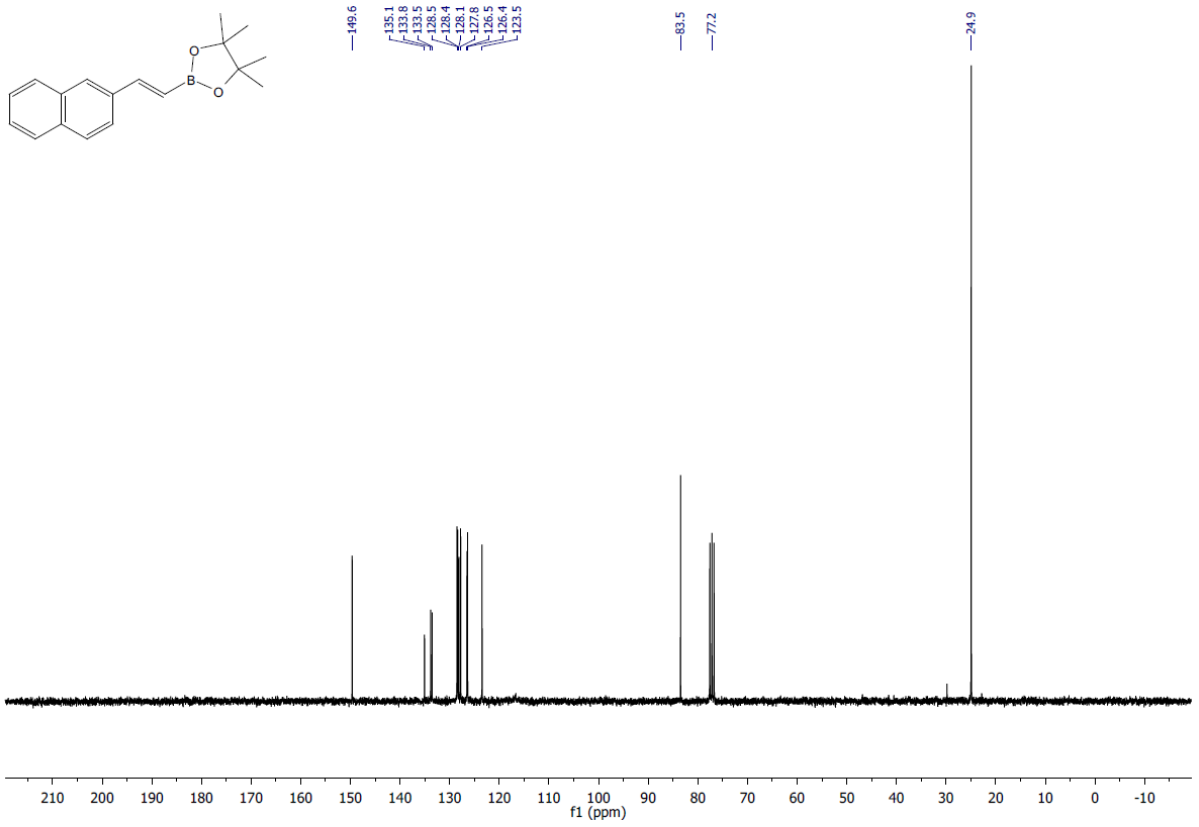


(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (23)

^{1}H NMR (300 MHz, $CDCl_3$)

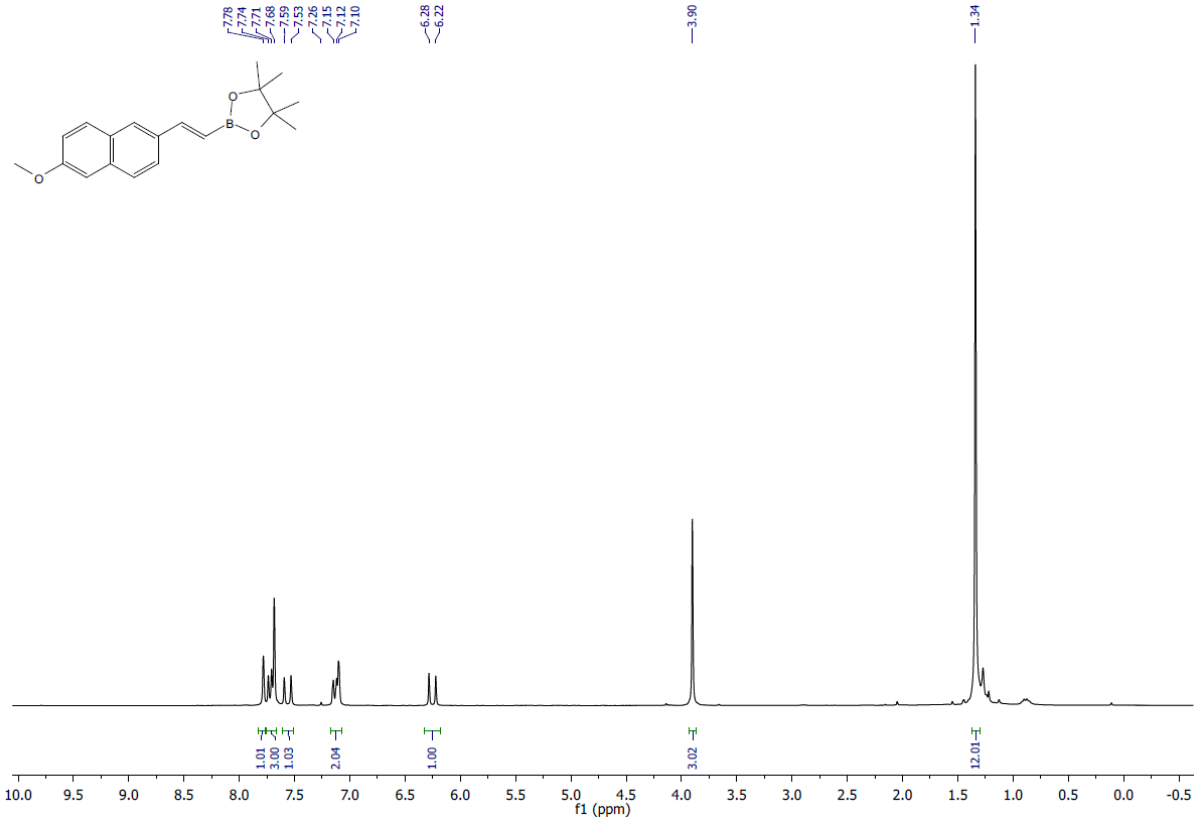


^{13}C NMR (75 MHz, $CDCl_3$)

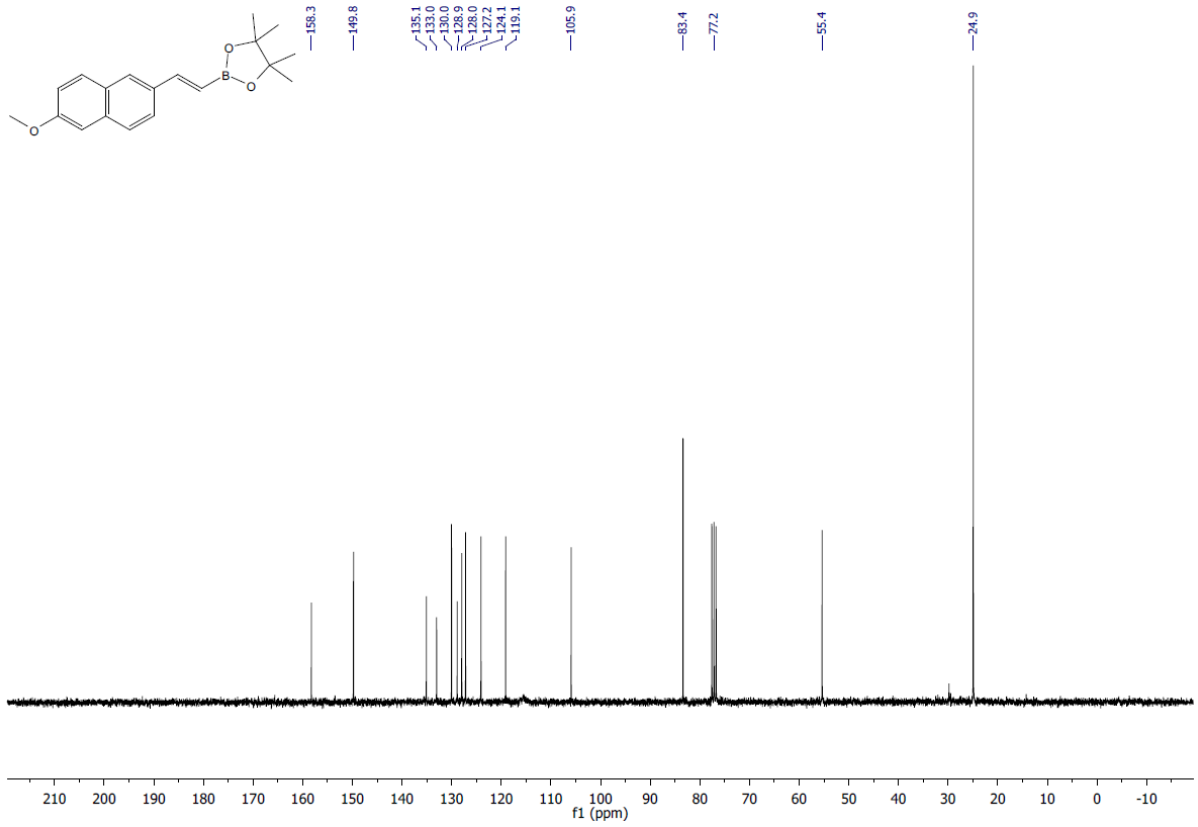


(*E*)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24)

^{1}H NMR (300 MHz, $CDCl_3$)

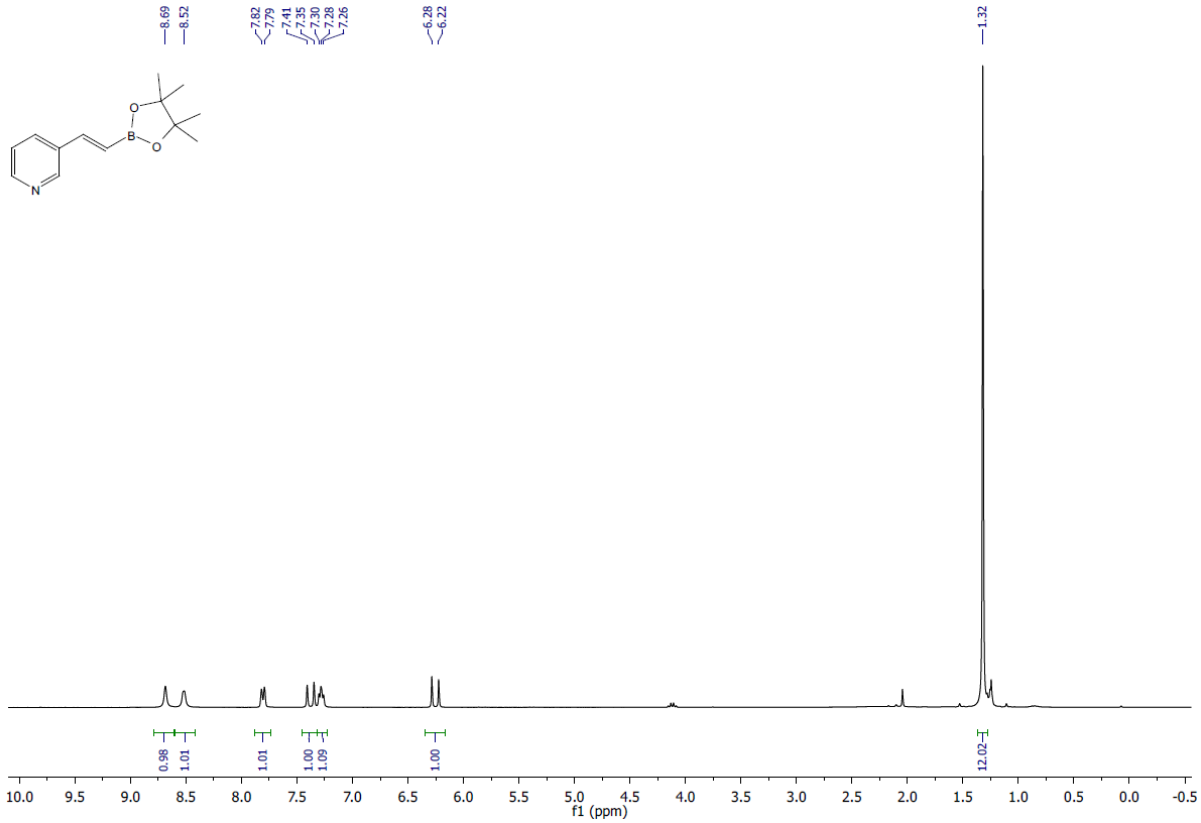


^{13}C NMR (75 MHz, $CDCl_3$)

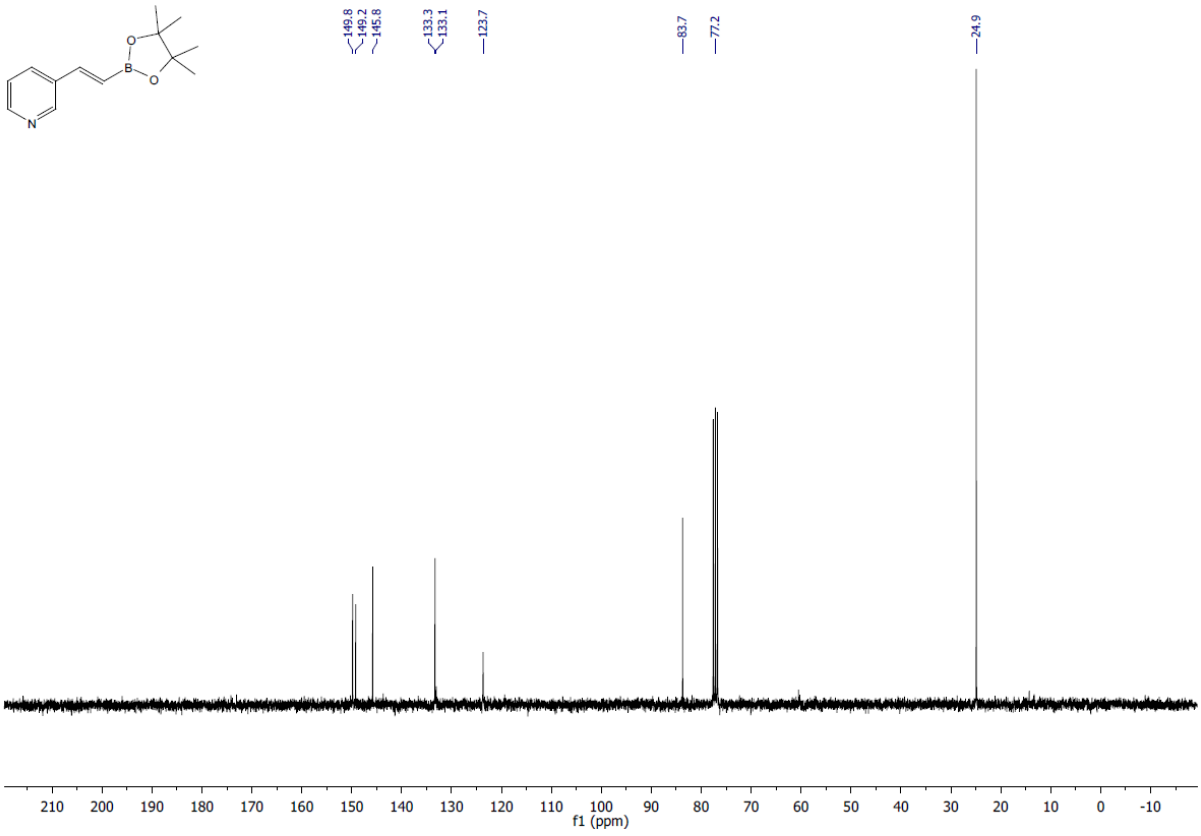


(*E*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (25)

^{1}H NMR (300 MHz, $CDCl_3$)

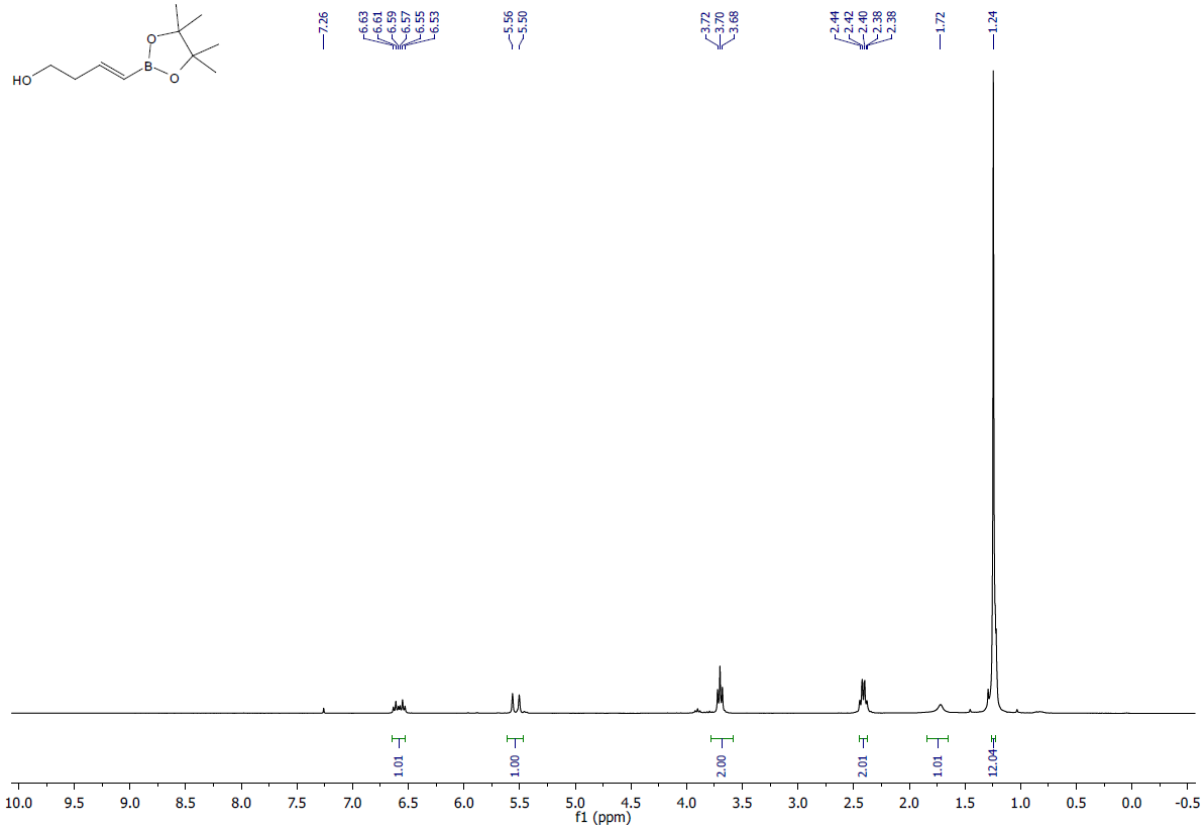


^{13}C NMR (75 MHz, $CDCl_3$)

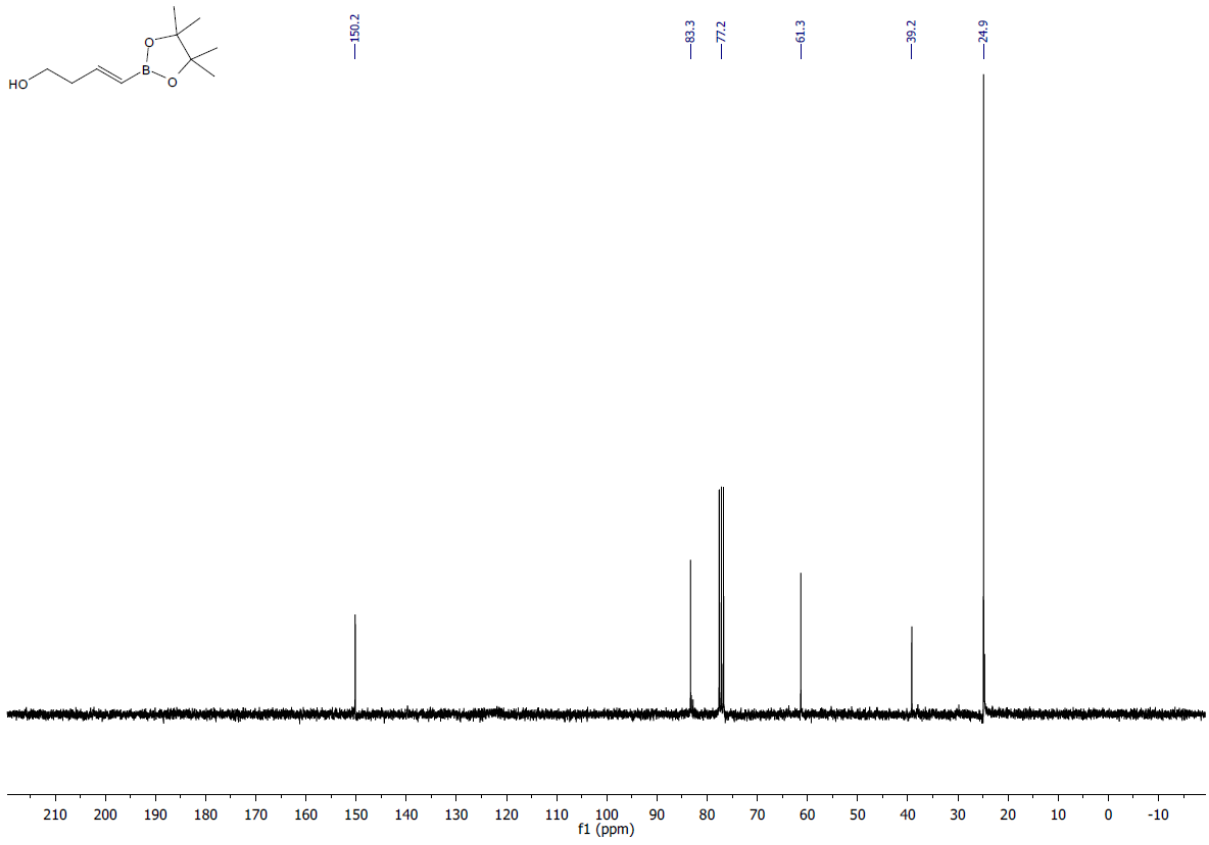


(*E*)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol (26)

^{1}H NMR (300 MHz, $CDCl_3$)

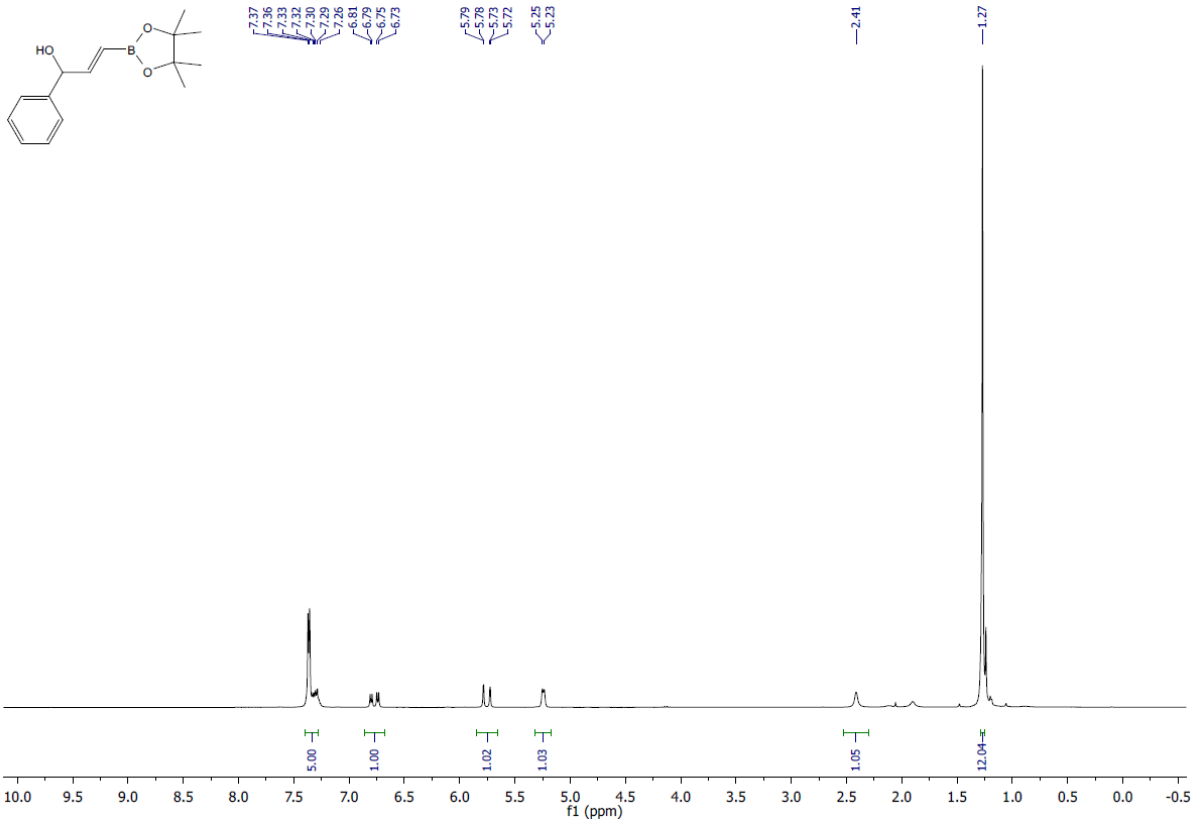


^{13}C NMR (75 MHz, $CDCl_3$)

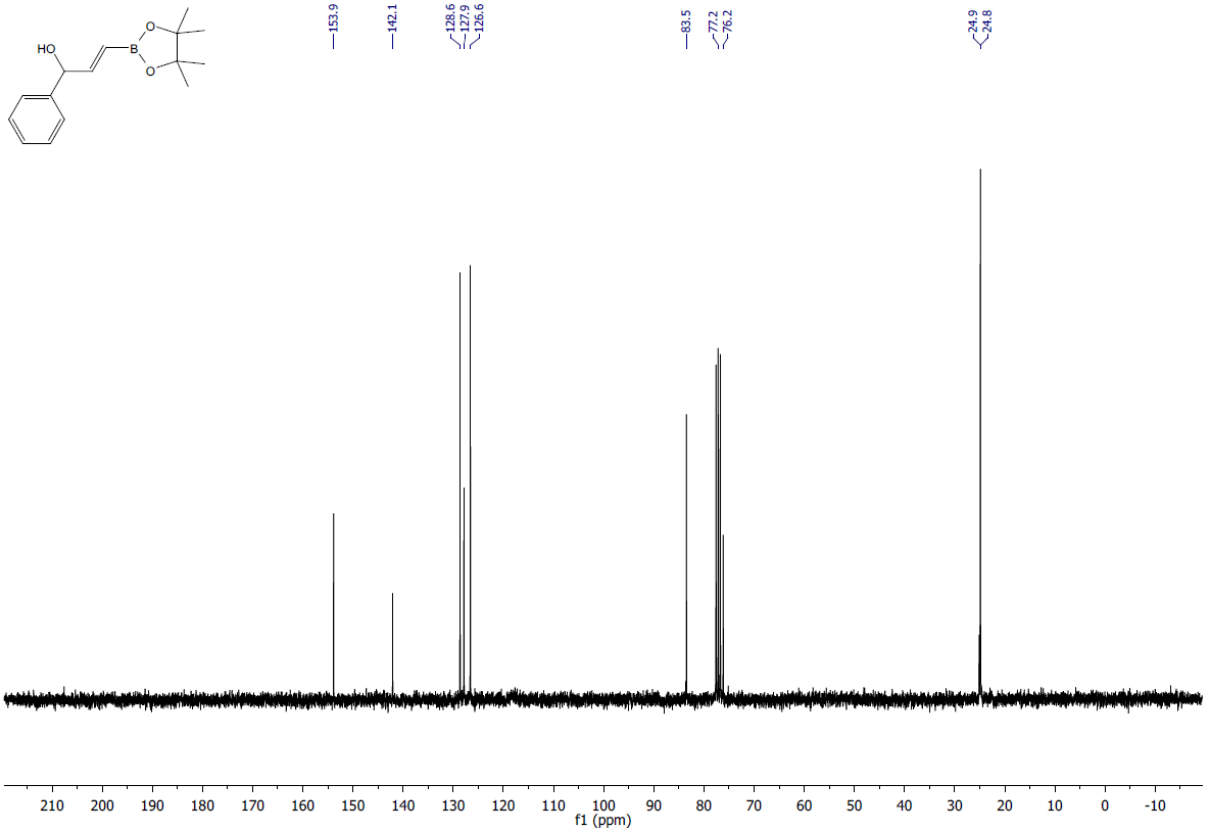


(*E*)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (27)

^{1}H NMR (300 MHz, $CDCl_3$)

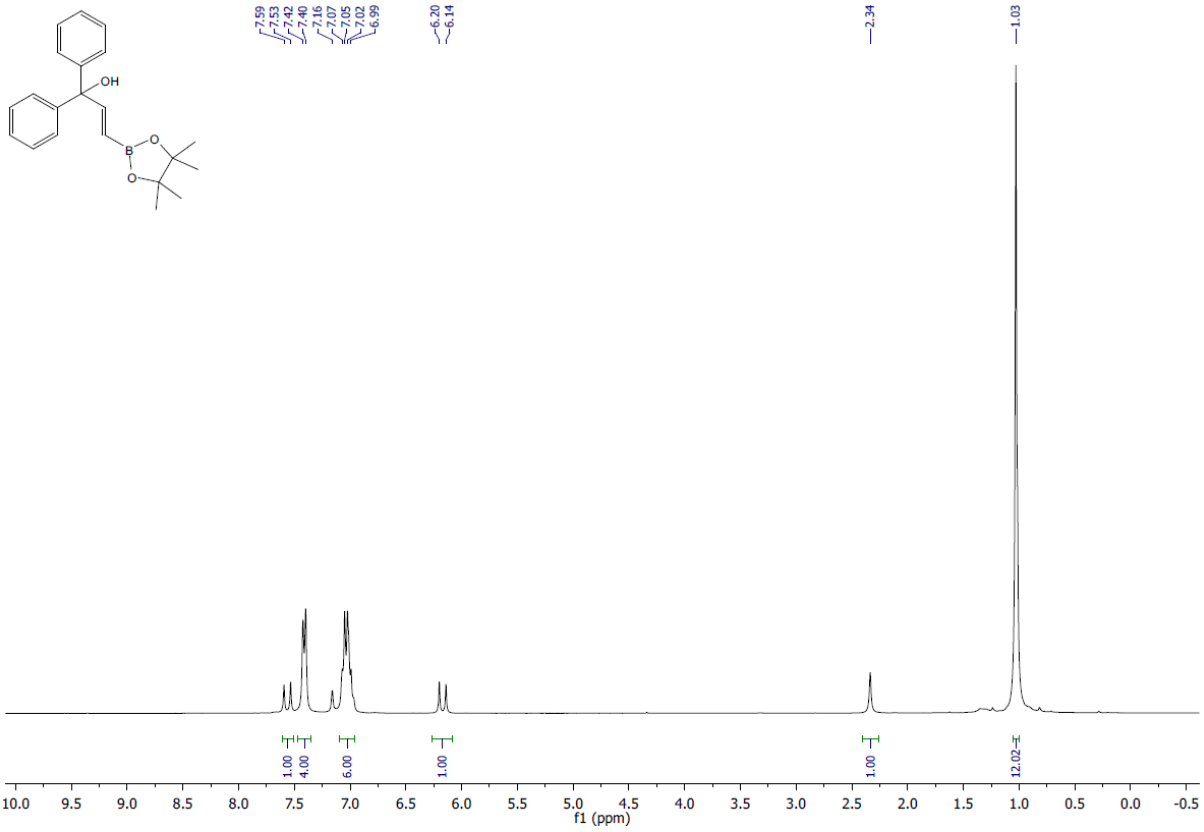


^{13}C NMR (75 MHz, $CDCl_3$)

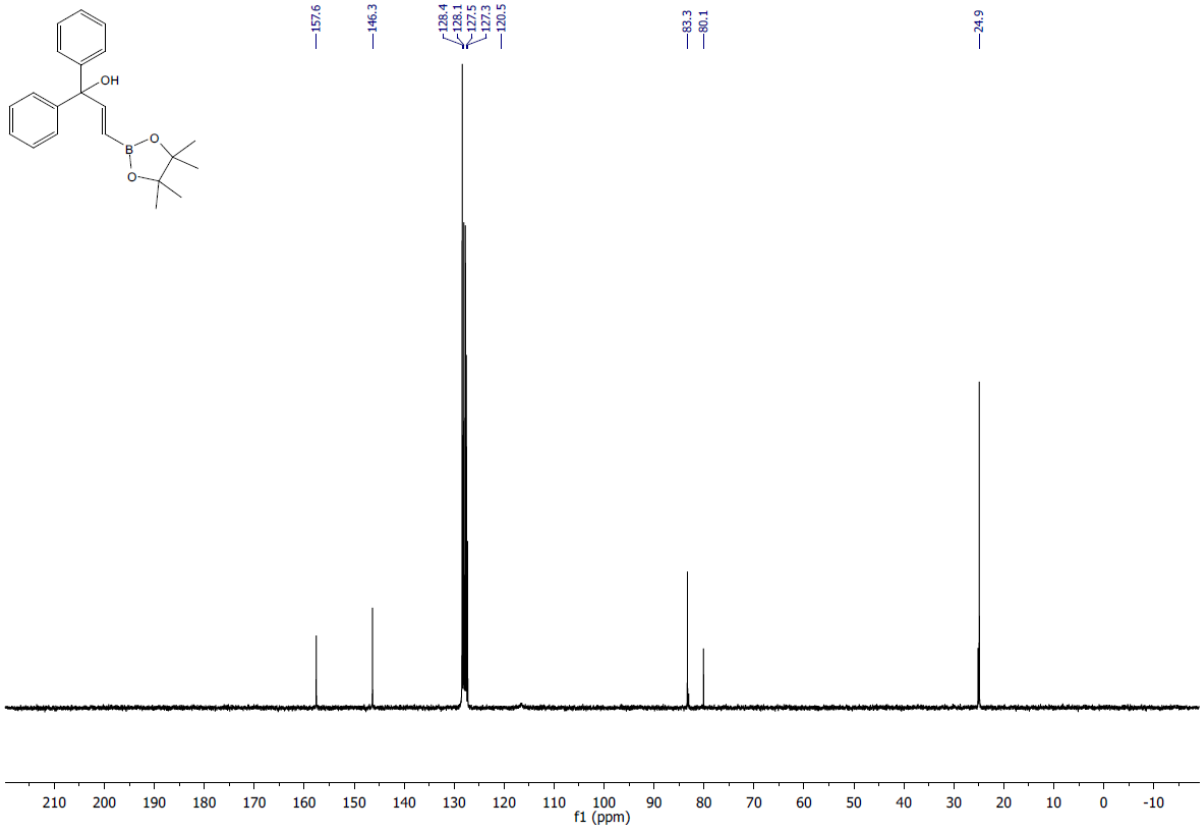


(*E*)-1,1-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (28)

^{1}H NMR (300 MHz, C_6D_6)

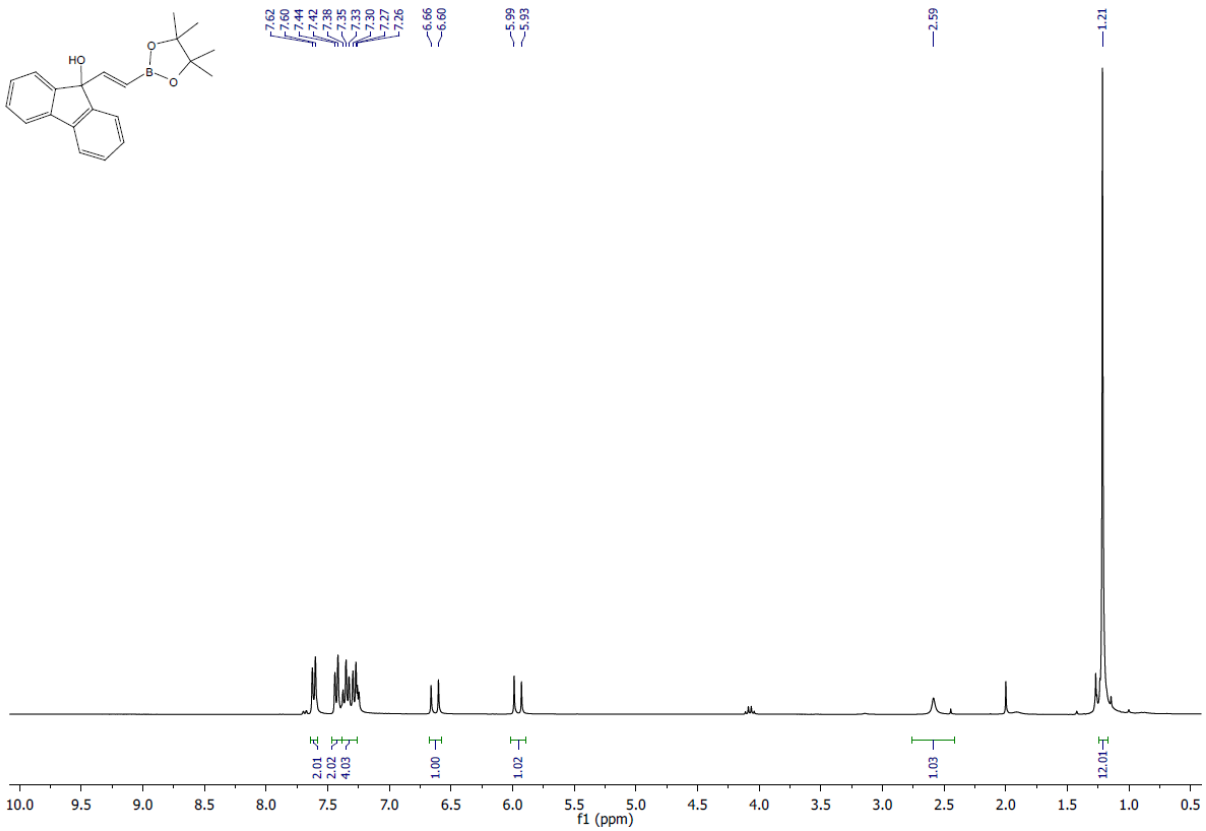


^{13}C NMR (75 MHz, C_6D_6)

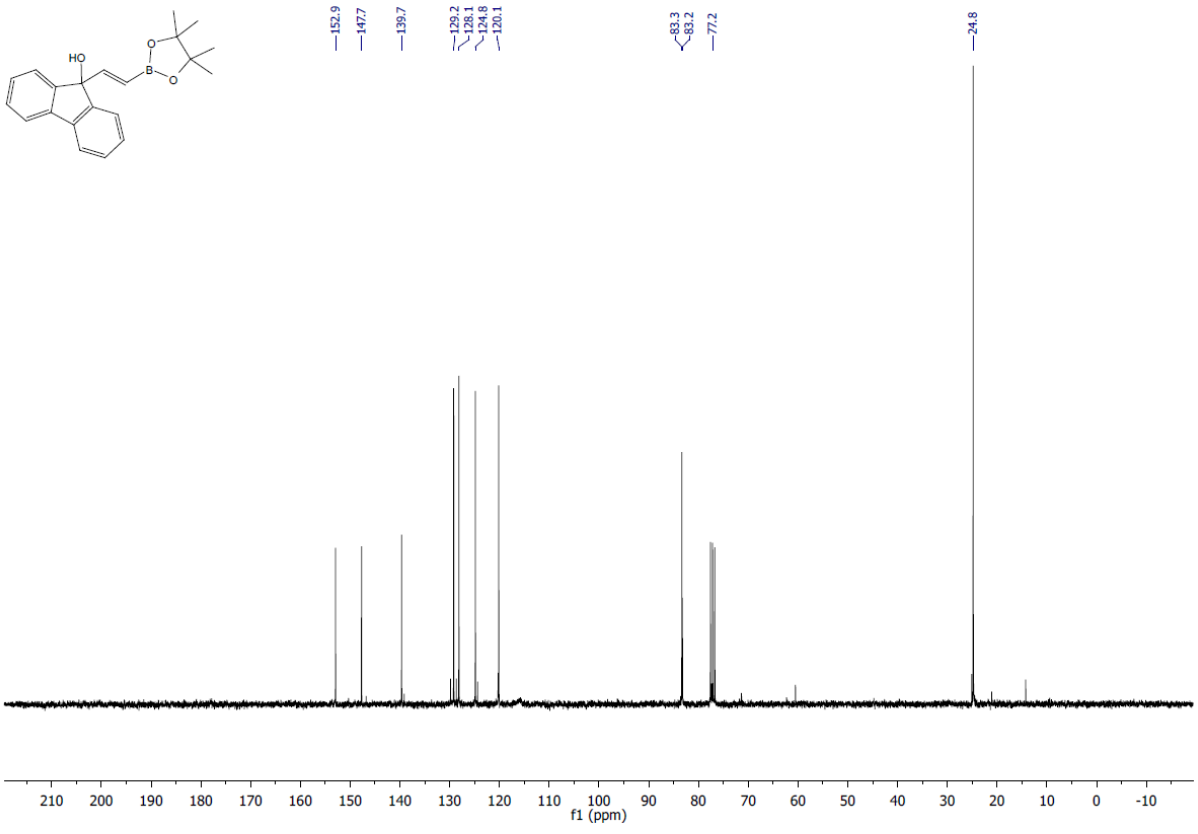


(*E*)-9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-9H-fluoren-9-ol (29)

^{1}H NMR (300 MHz, $CDCl_3$)

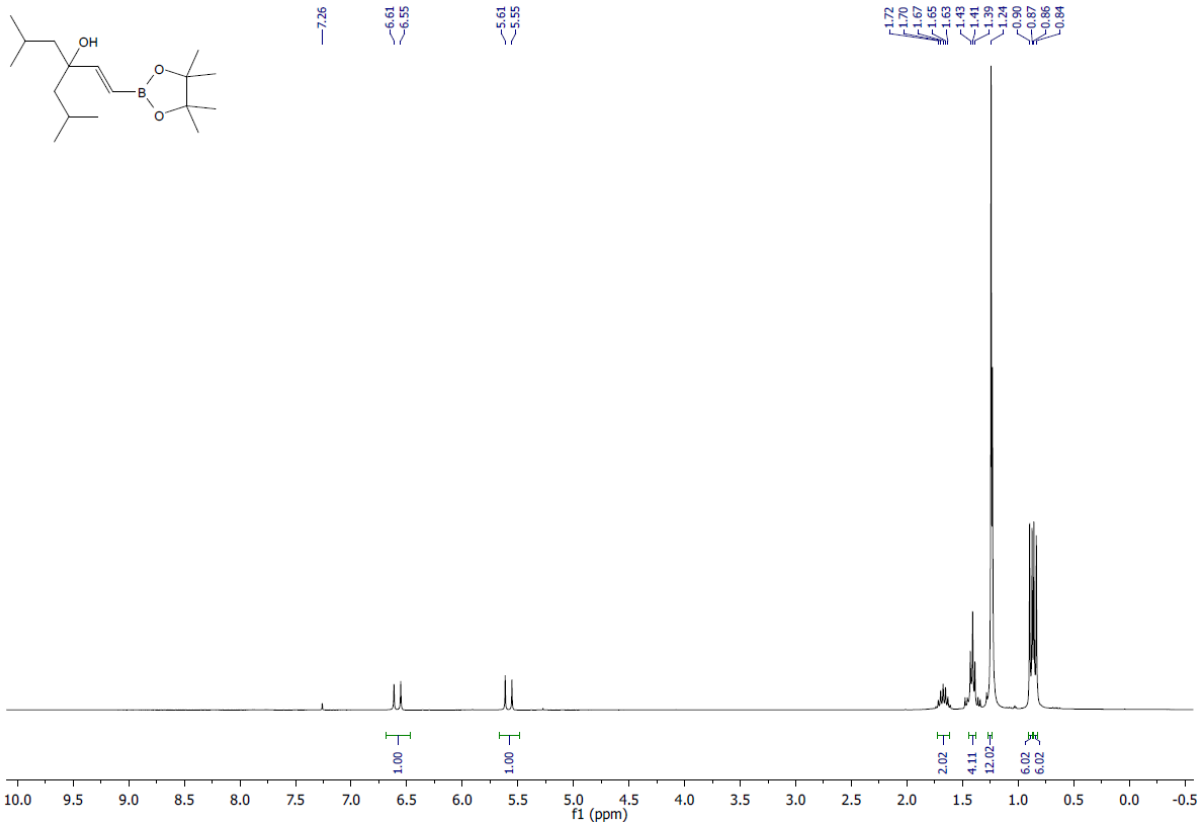


^{13}C NMR (75 MHz, $CDCl_3$)

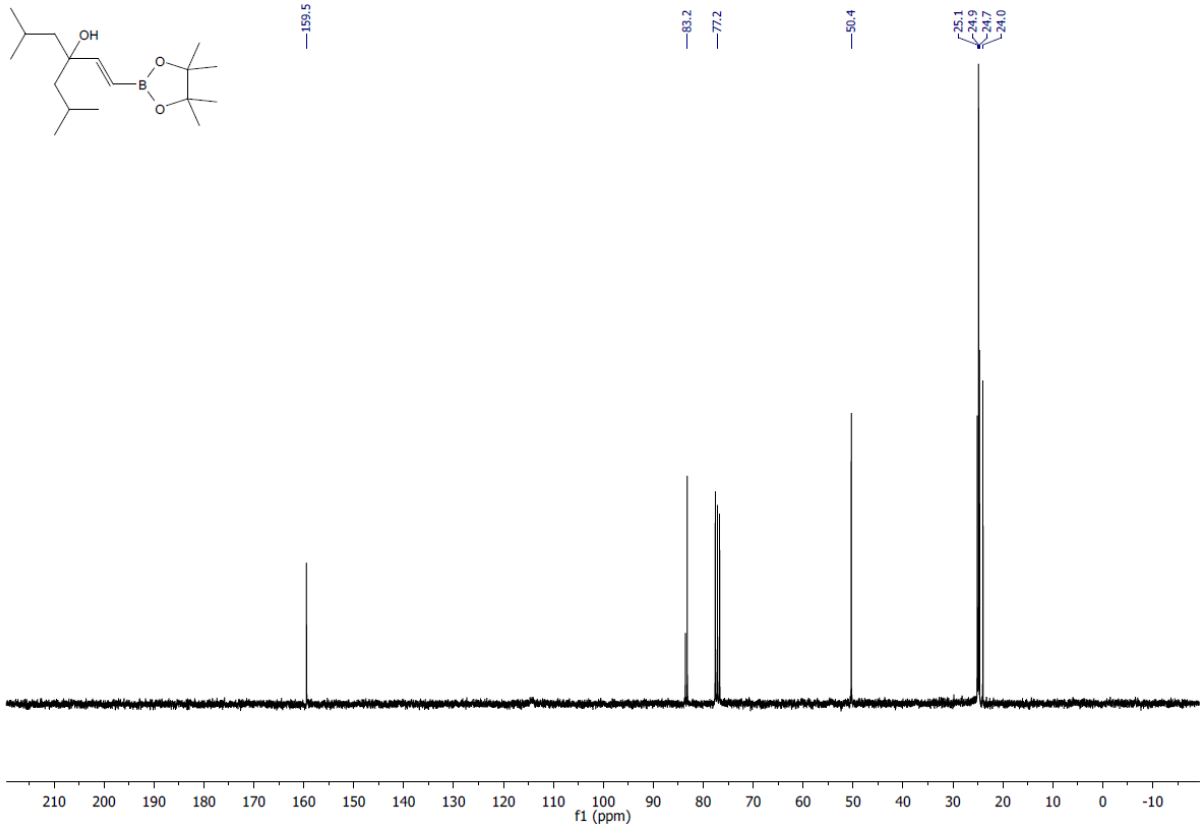


(*E*)-2,8-dimethyl-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)nonan-5-ol (30)

^{1}H NMR (300 MHz, $CDCl_3$)

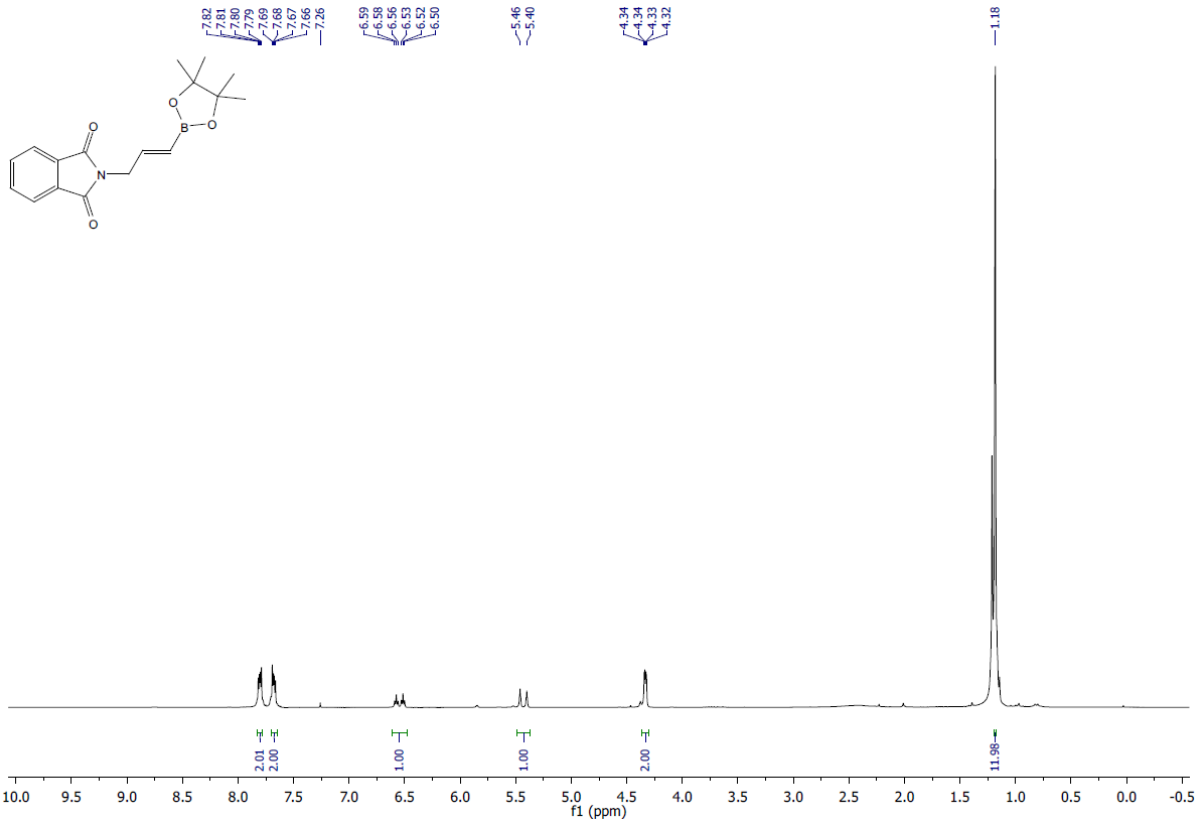


^{13}C NMR (75 MHz, $CDCl_3$)

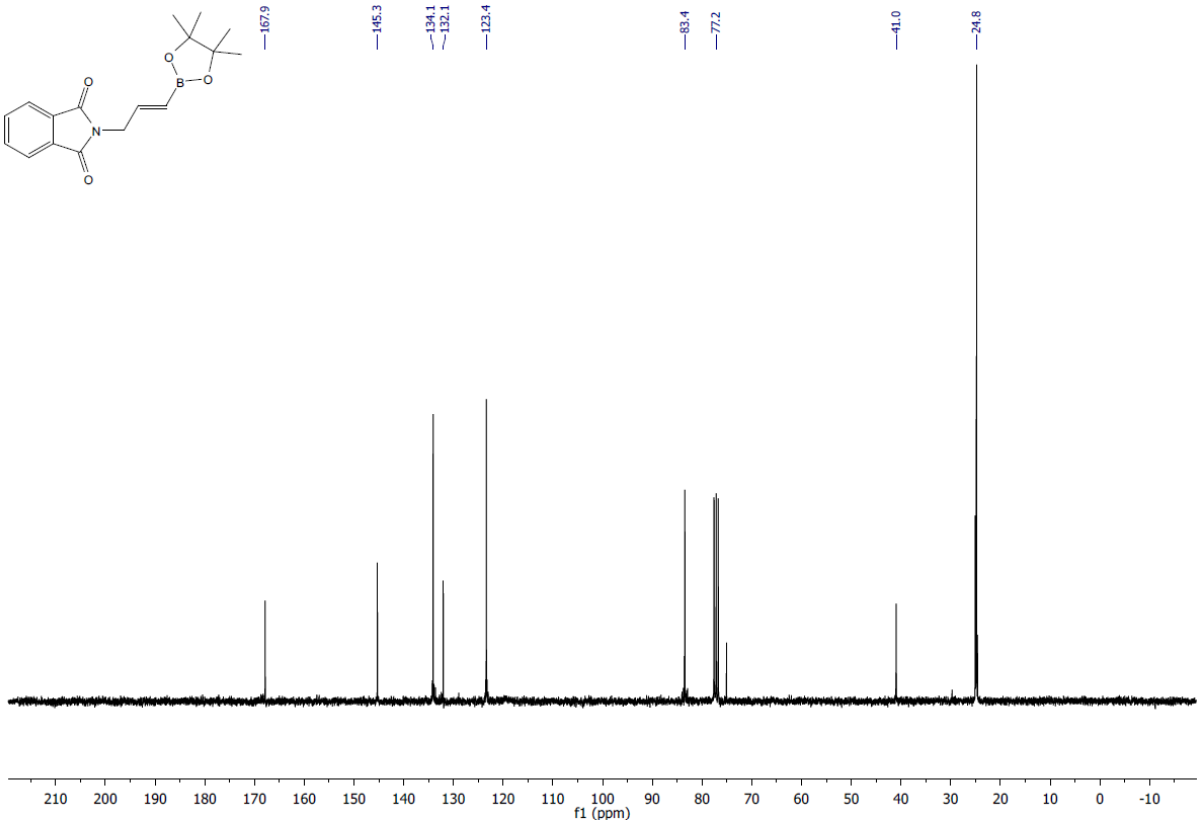


(*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione (31)

^{1}H NMR (300 MHz, $CDCl_3$)

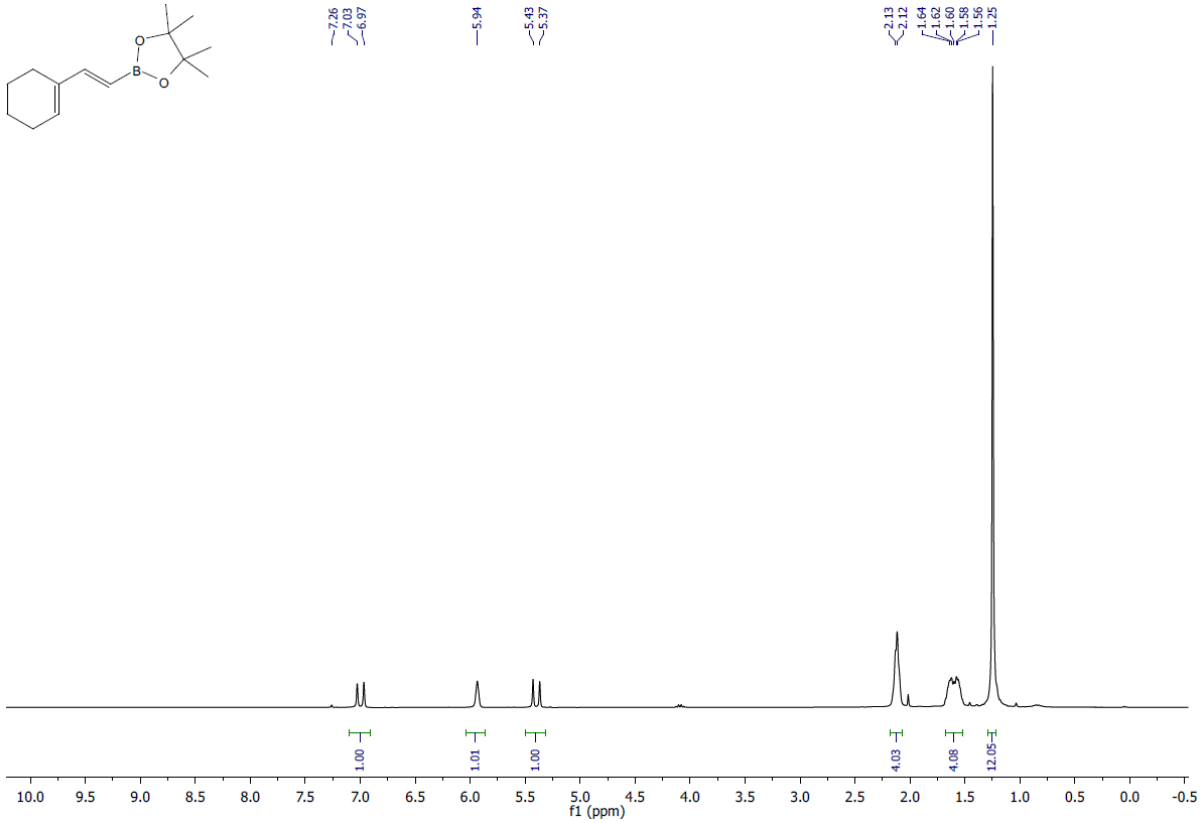


^{13}C NMR (75 MHz, $CDCl_3$)

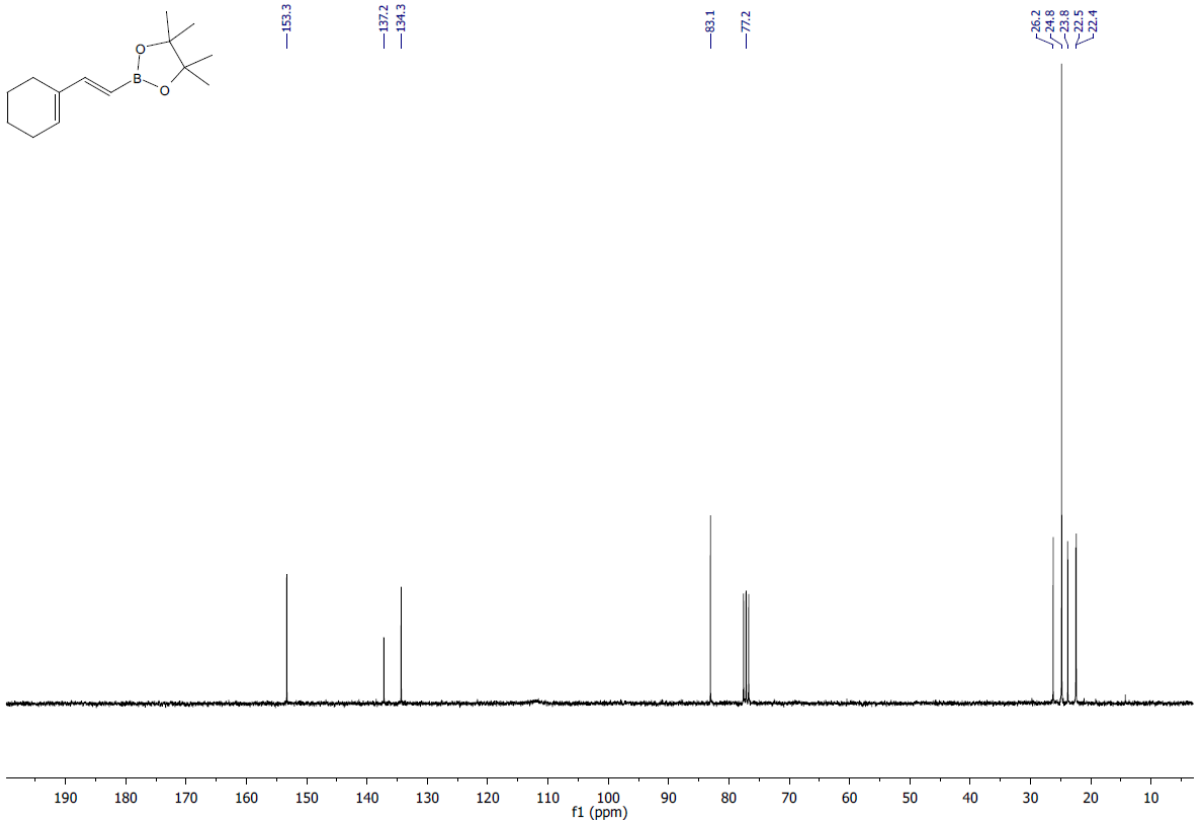


(*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32)

^{1}H NMR (300 MHz, $CDCl_3$)

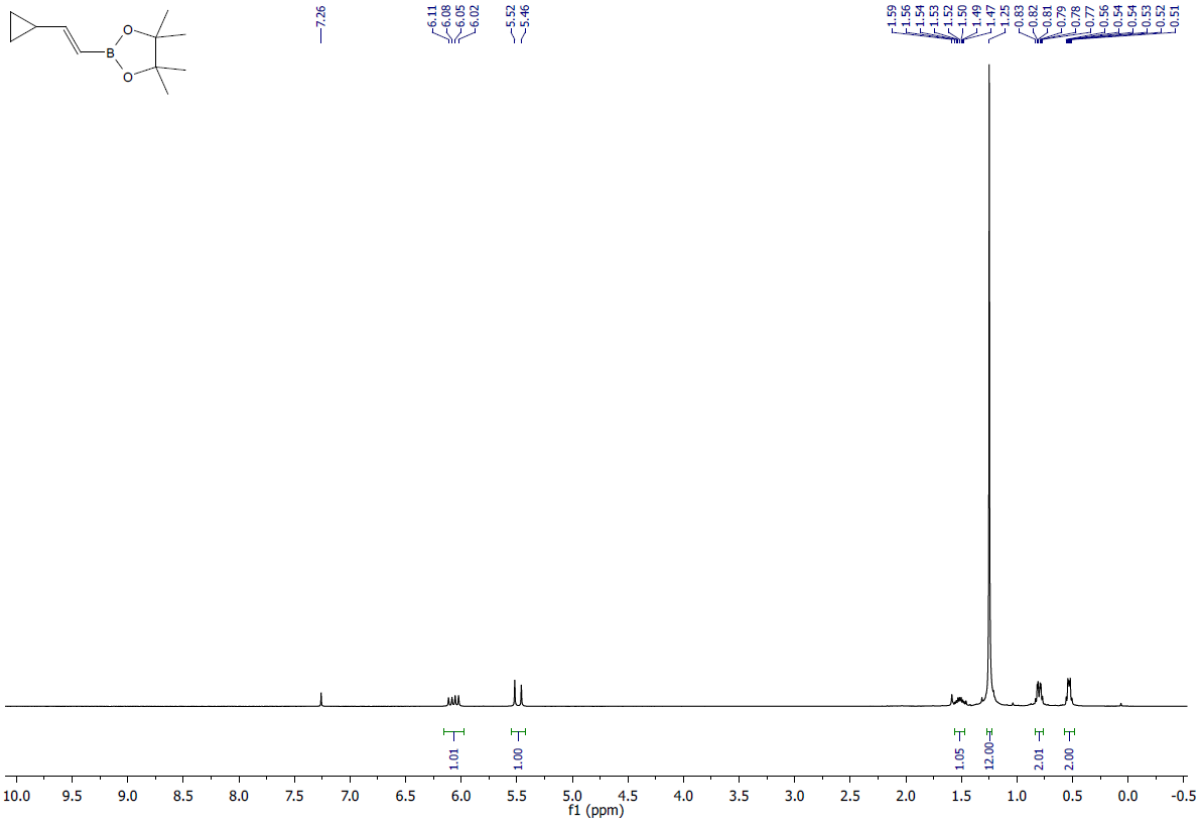


^{13}C NMR (75 MHz, $CDCl_3$)

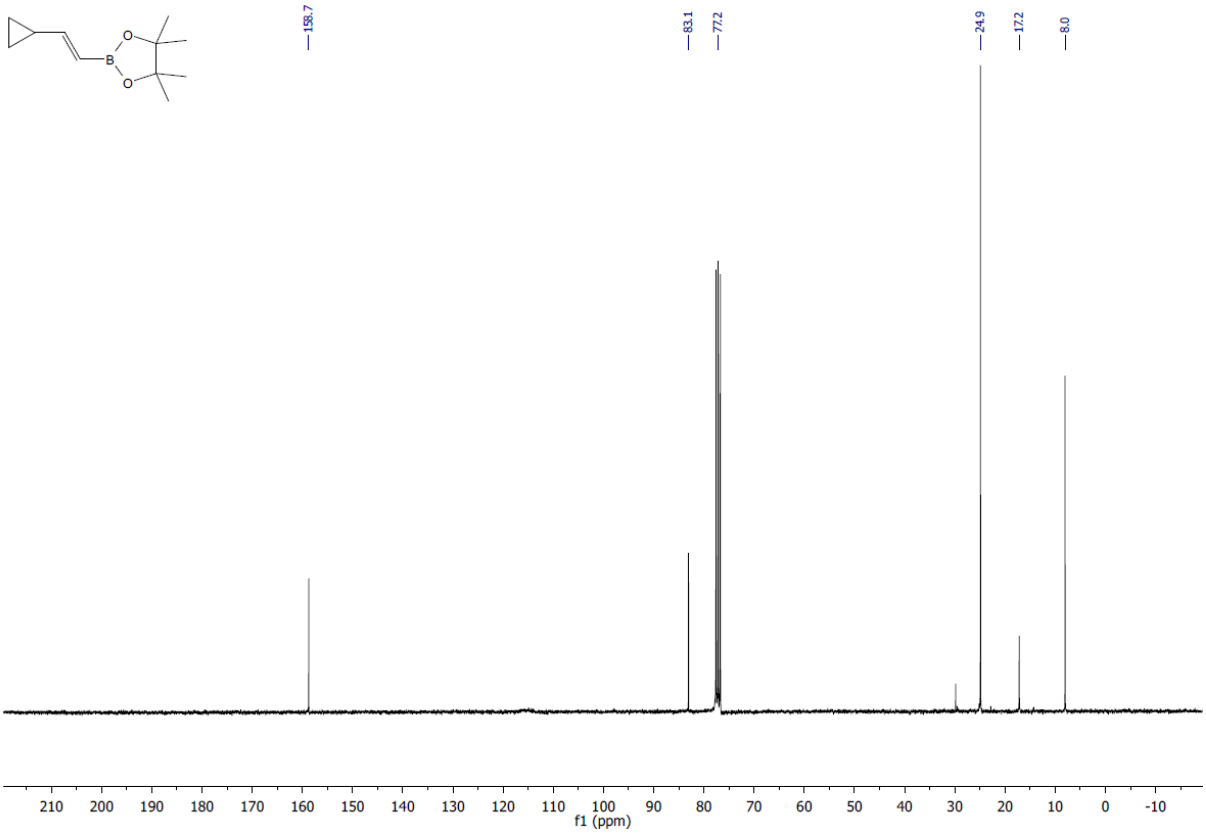


(*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33)

^{1}H NMR (300 MHz, $CDCl_3$)

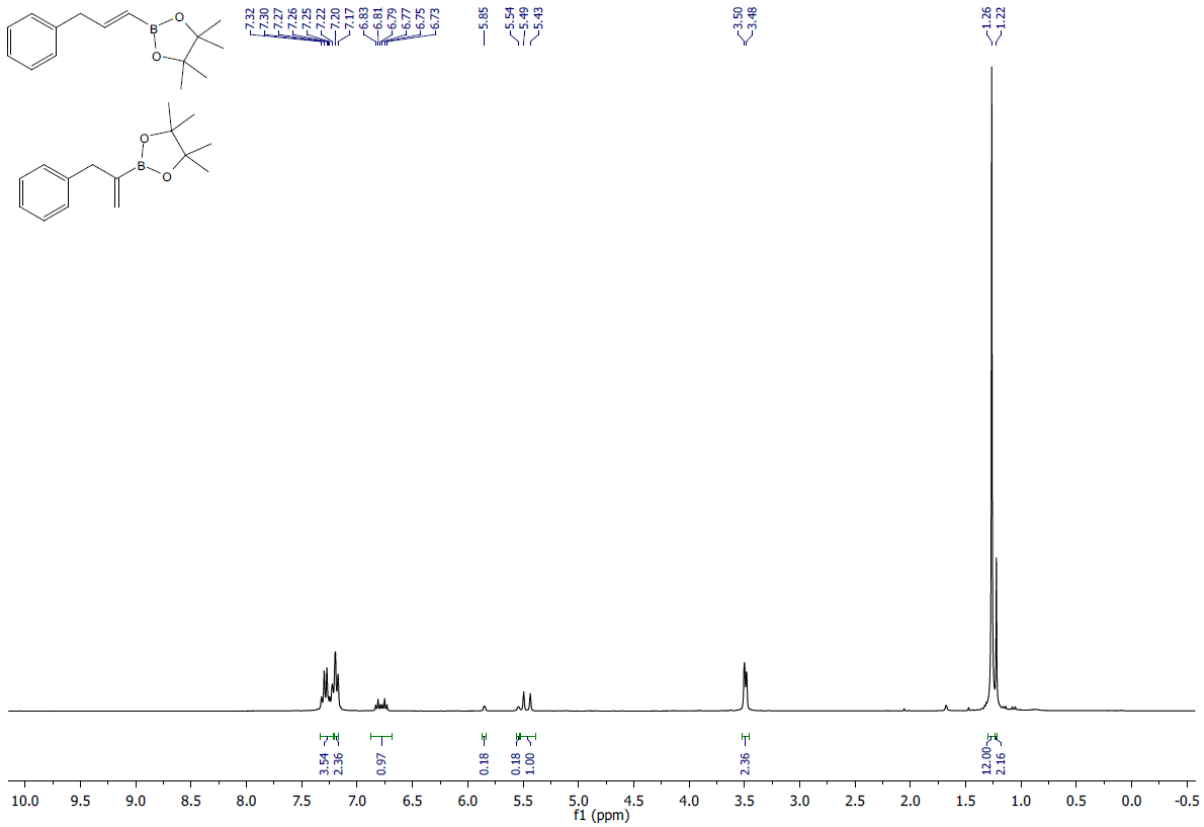


^{13}C NMR (75 MHz, $CDCl_3$)

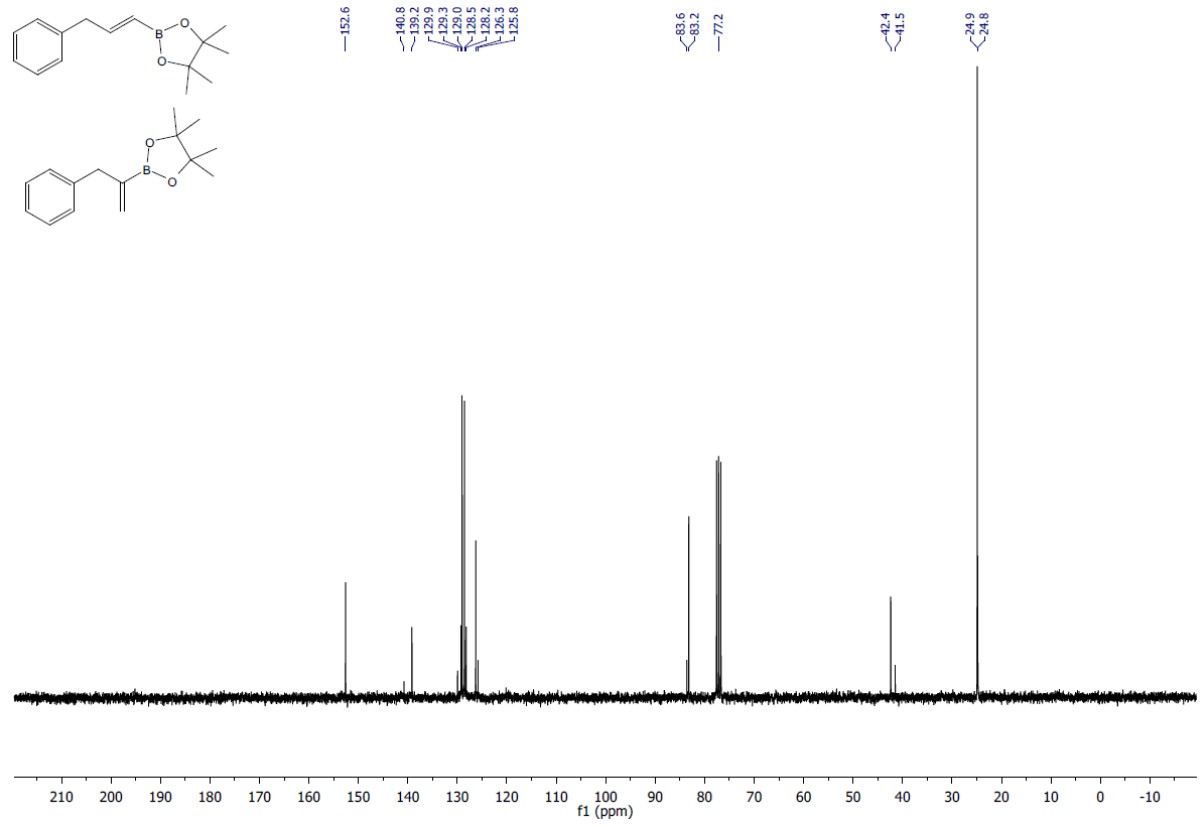


(*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane & 4,4,5,5-tetra methyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (34)

^{1}H NMR (300 MHz, $CDCl_3$)

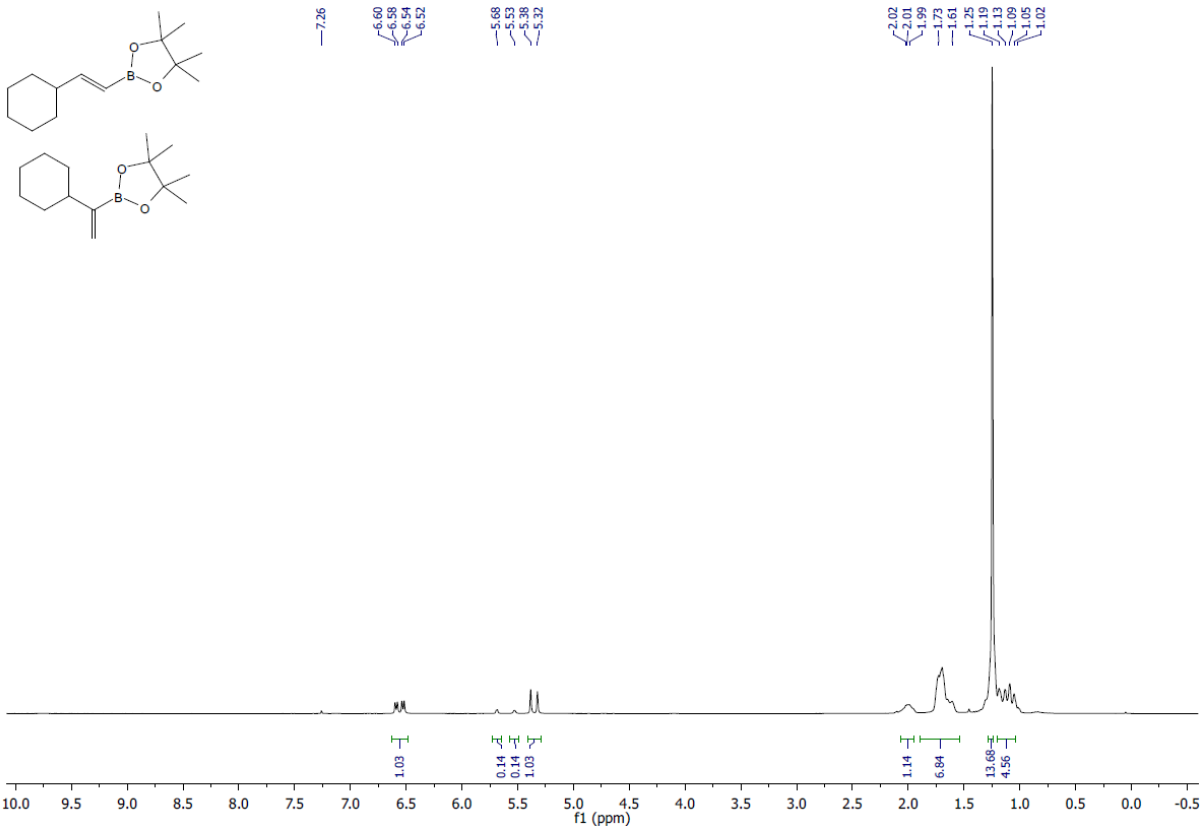


^{13}C NMR (75 MHz, $CDCl_3$)

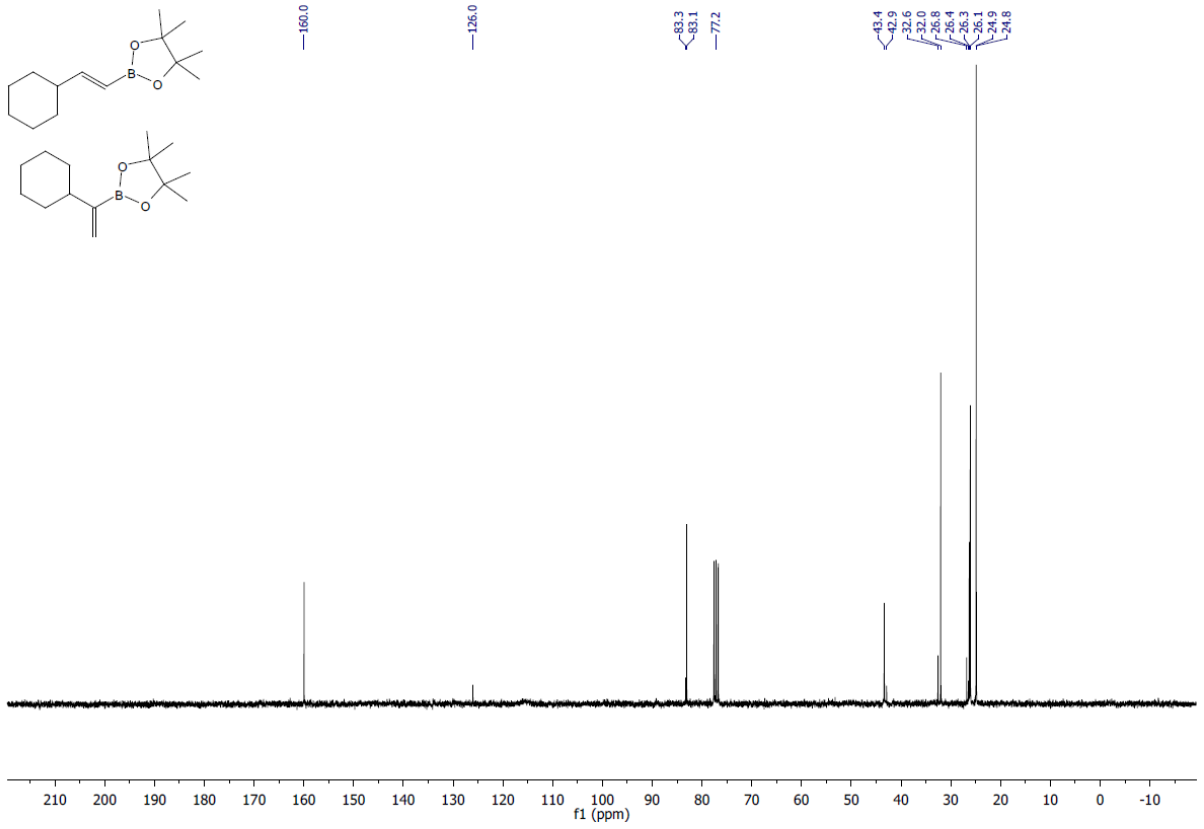


(*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(1-cyclohexyl vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)

^{1}H NMR (300 MHz, $CDCl_3$)

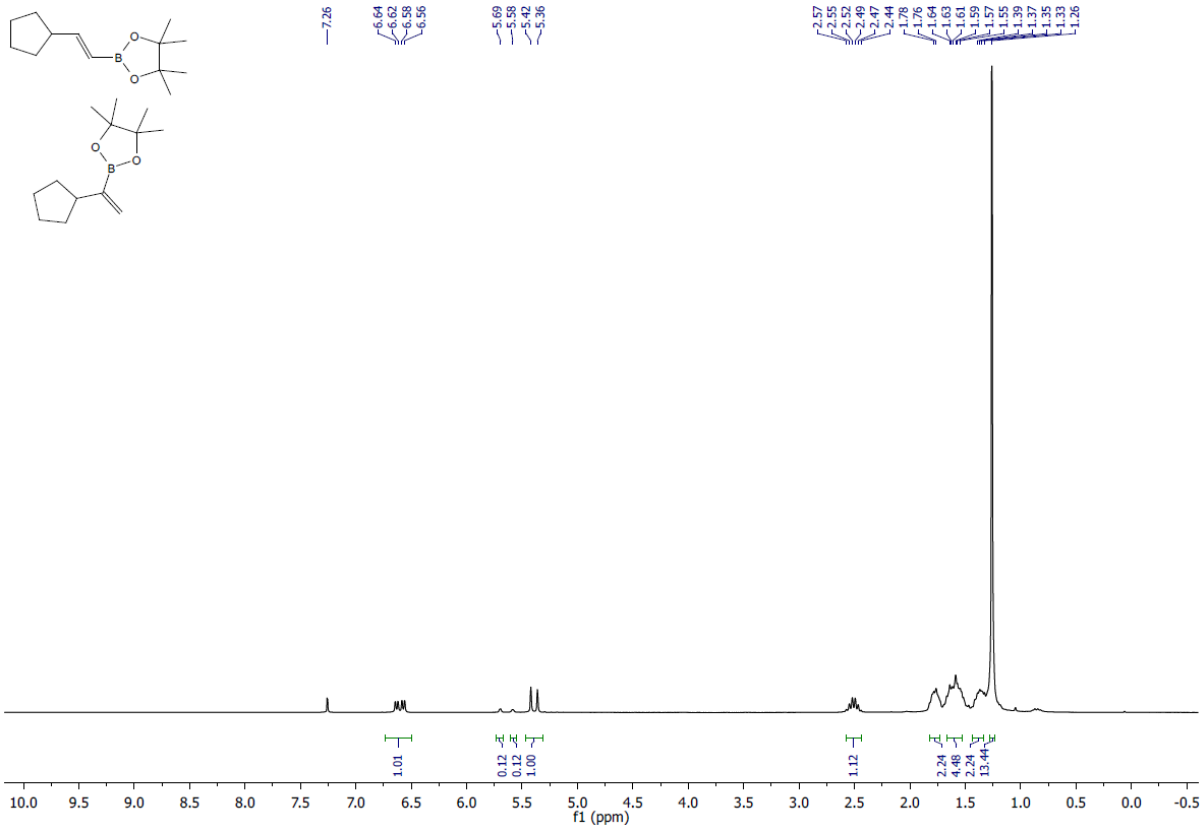


^{13}C NMR (75 MHz, $CDCl_3$)

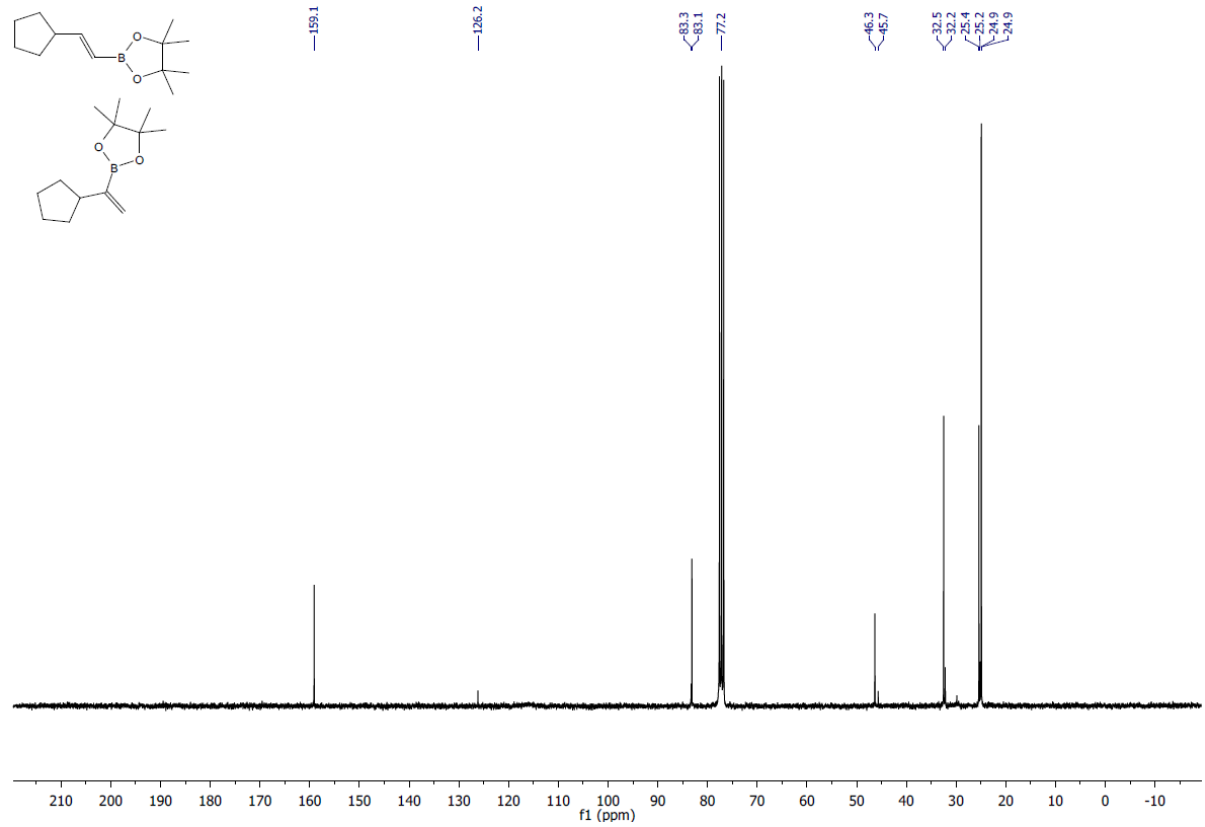


(*E*)-2-(2-cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(1-cyclopentyl vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)

^{1}H NMR (300 MHz, $CDCl_3$)

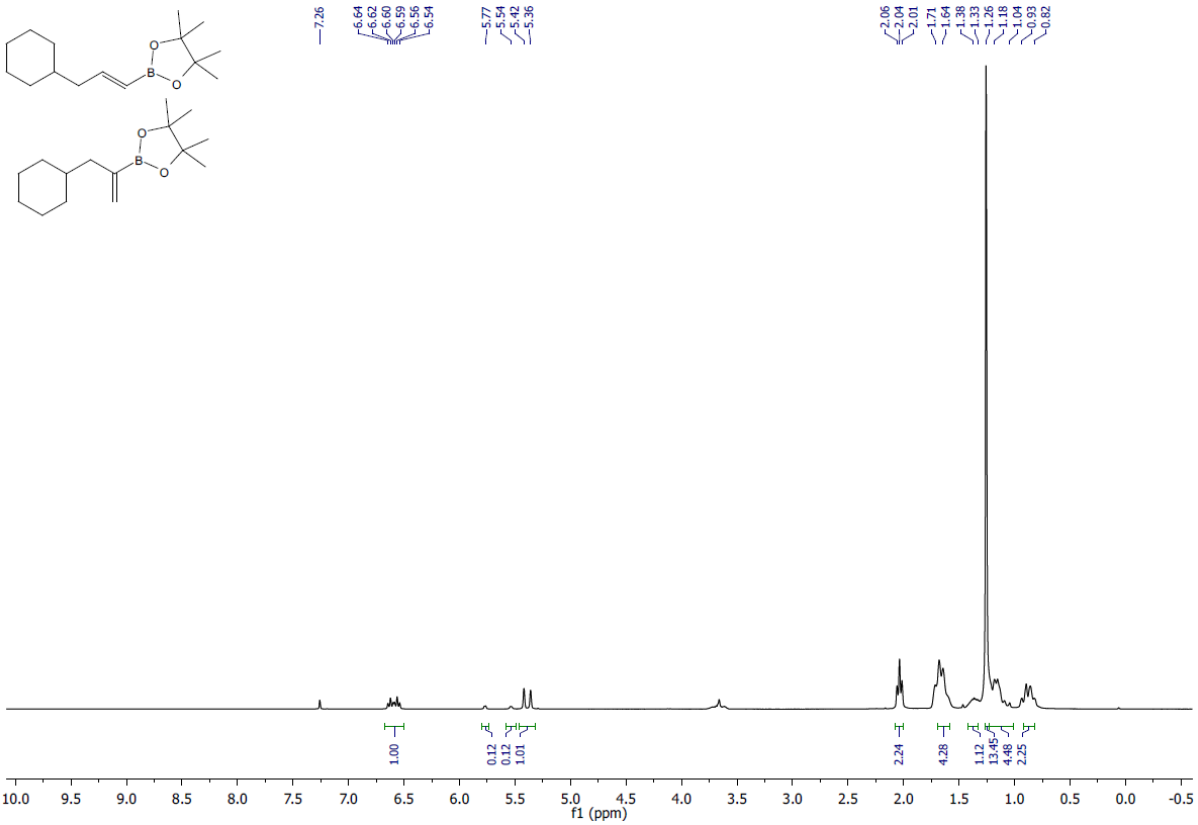


^{13}C NMR (75 MHz, $CDCl_3$)

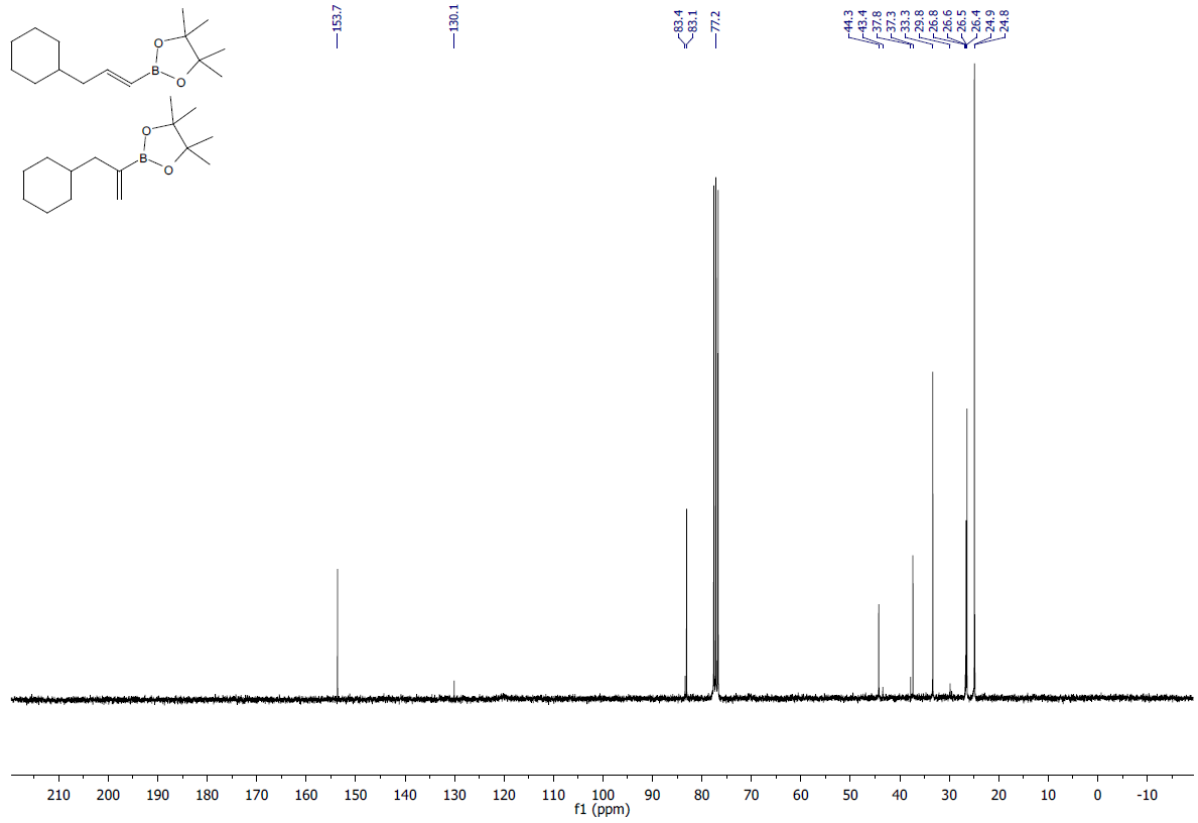


(*E*)-2-(3-cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(3-cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (37)

^{1}H NMR (300 MHz, $CDCl_3$)

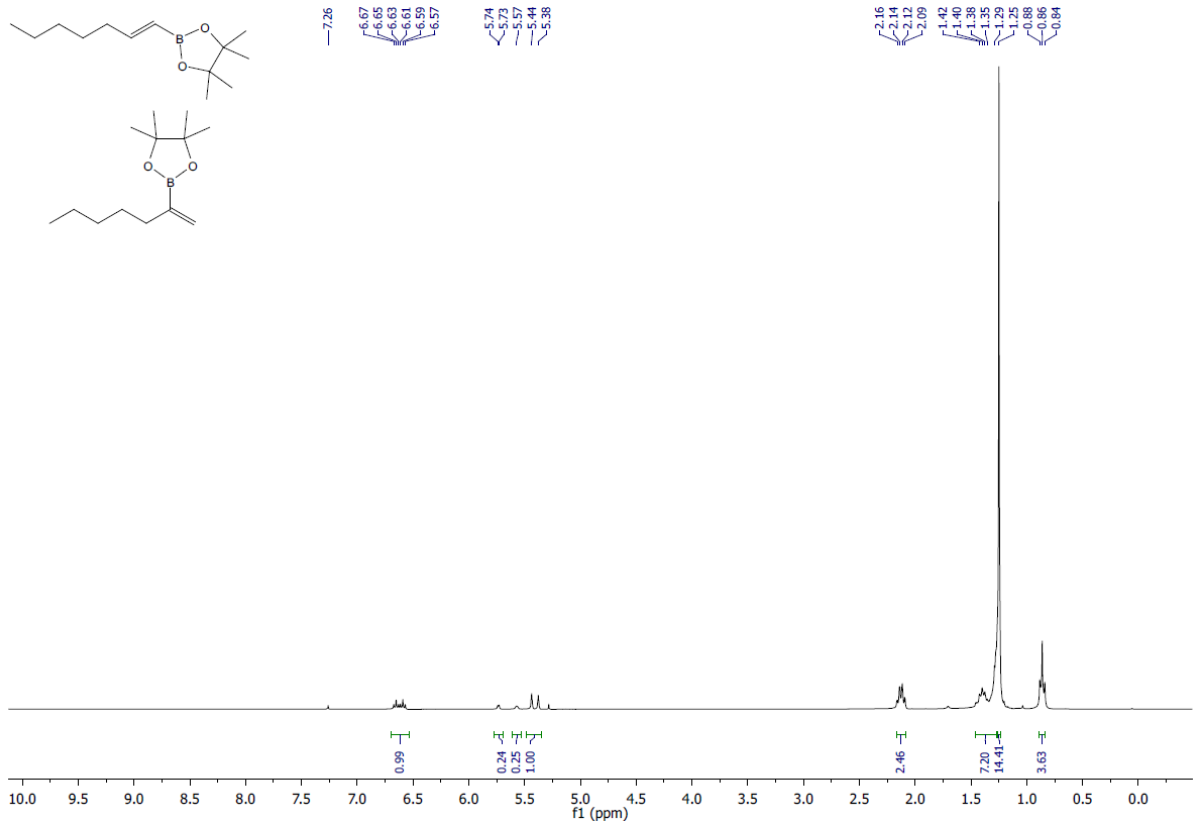


^{13}C NMR (75 MHz, $CDCl_3$)

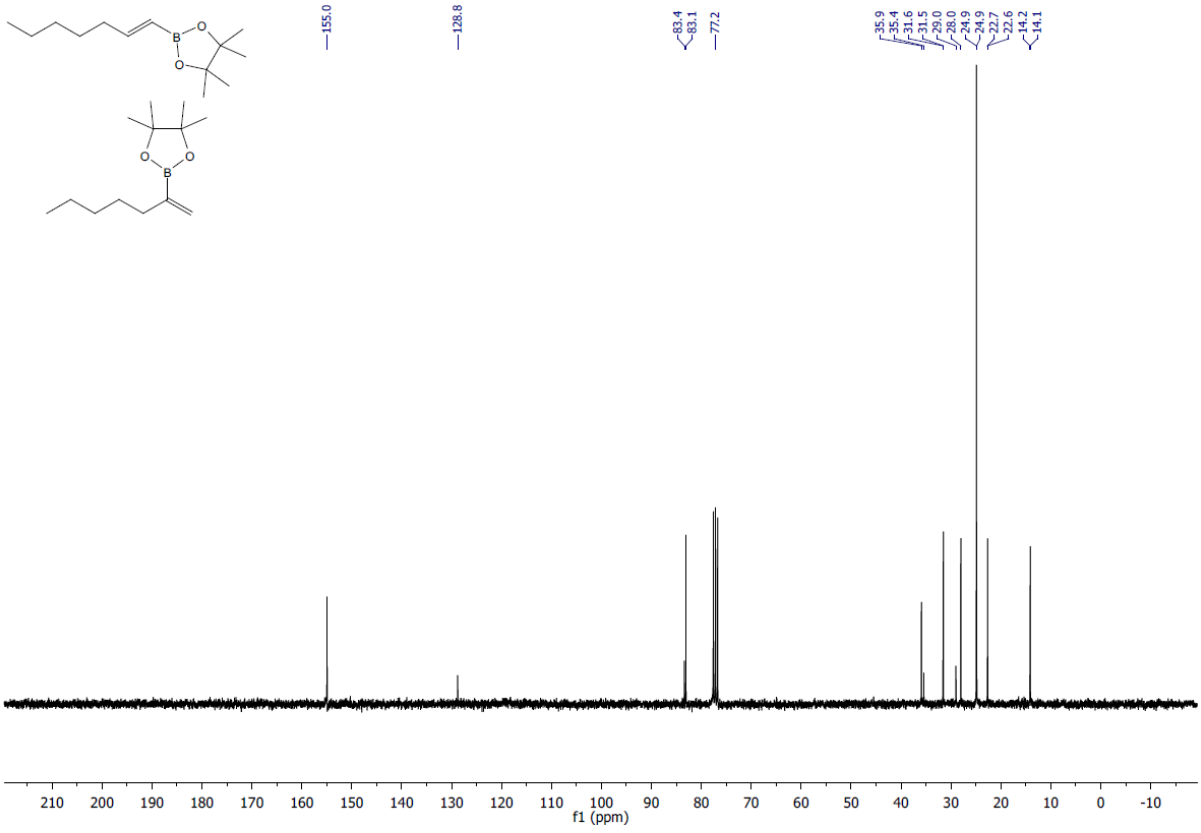


(*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane & 2-(hept-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

^{1}H NMR (300 MHz, $CDCl_3$)

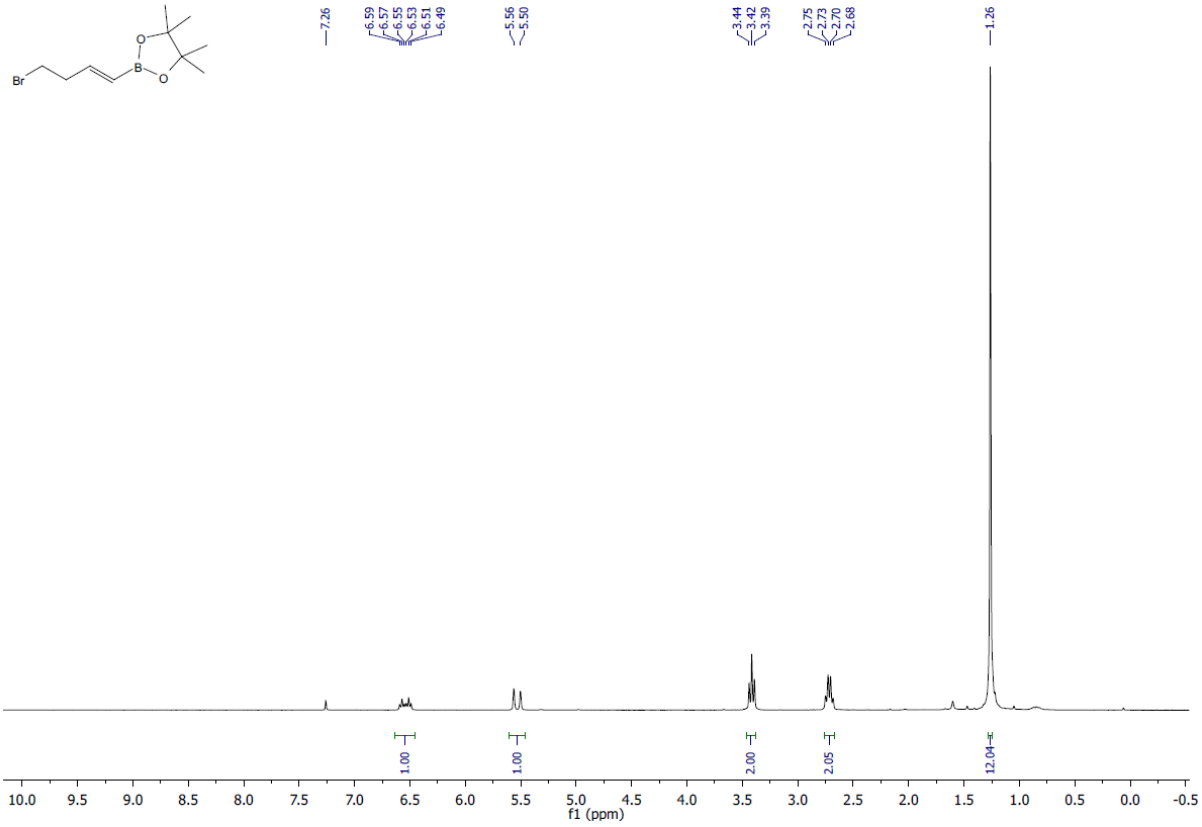


^{13}C NMR (75 MHz, $CDCl_3$)

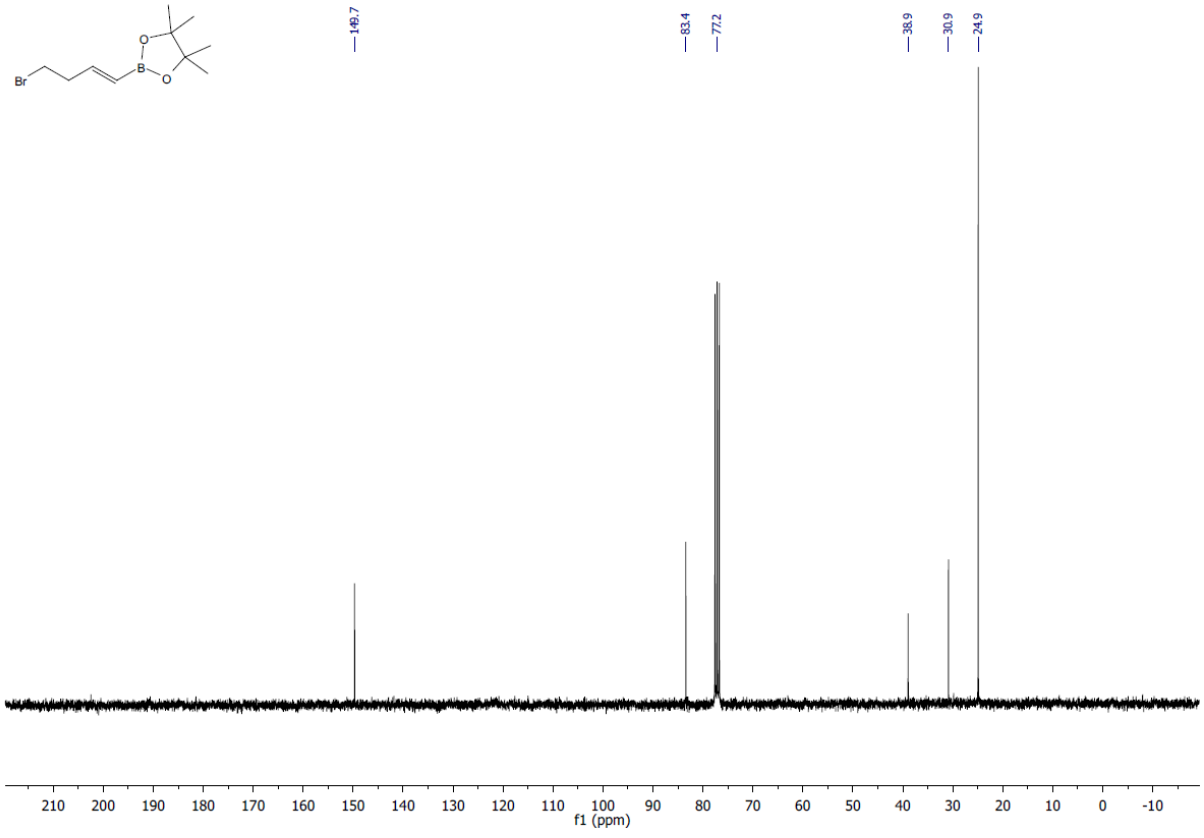


(*E*)-2-(4-bromobut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39, Major)

^{1}H NMR (300 MHz, $CDCl_3$)

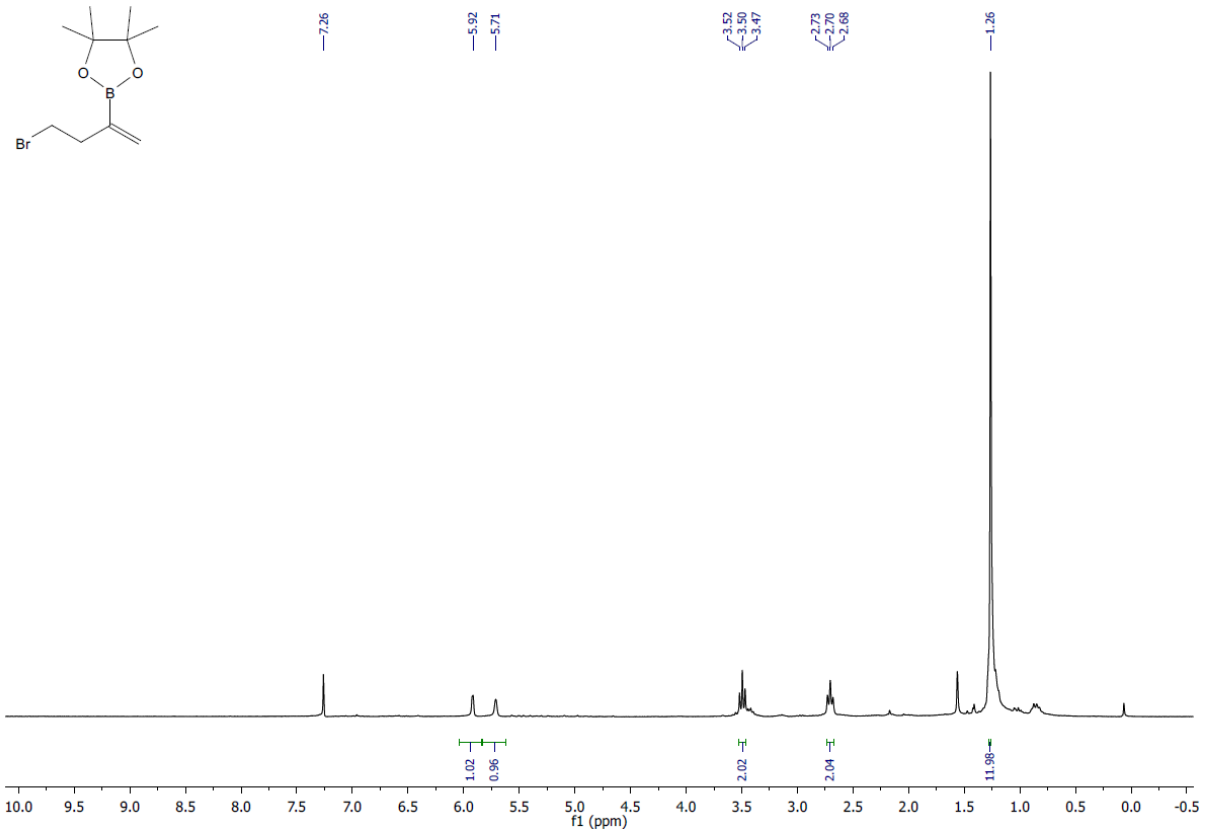


^{13}C NMR (75 MHz, $CDCl_3$)

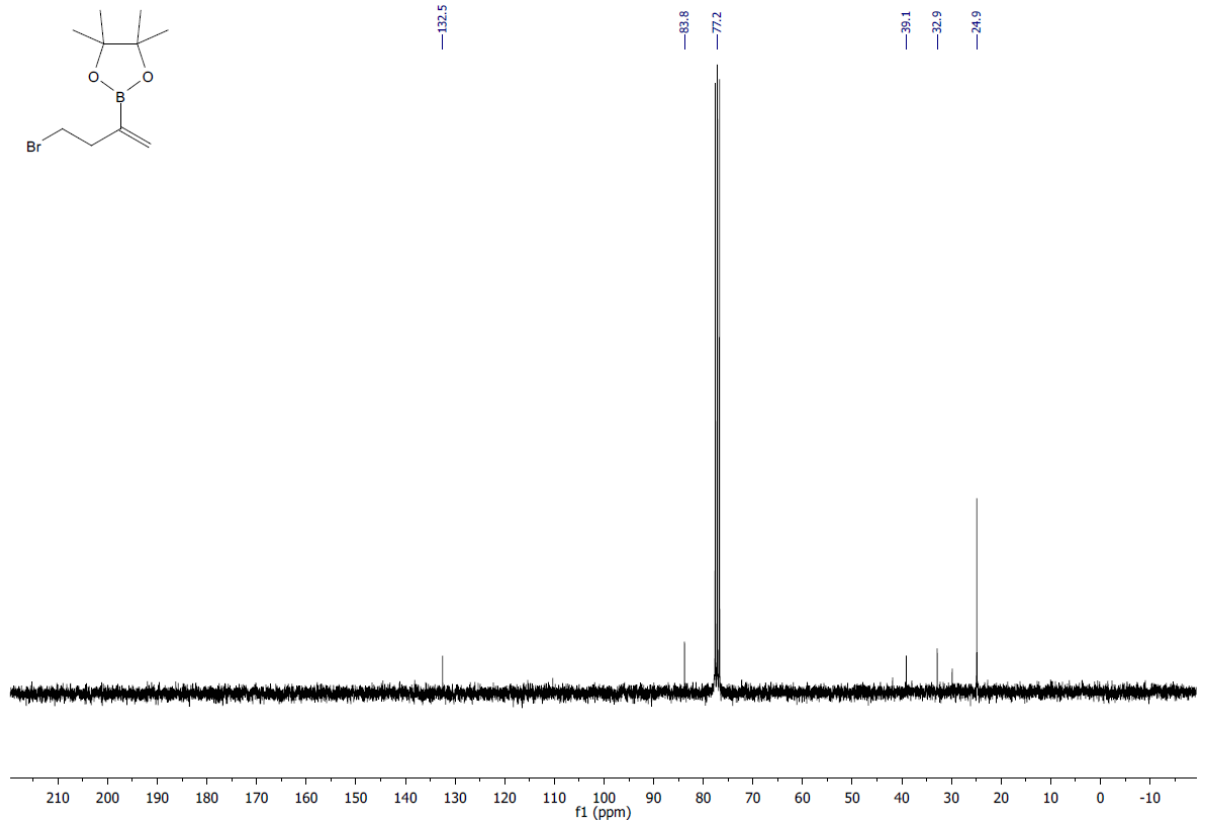


2-(4-bromobut-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39, Minor)

^{1}H NMR (300 MHz, $CDCl_3$)

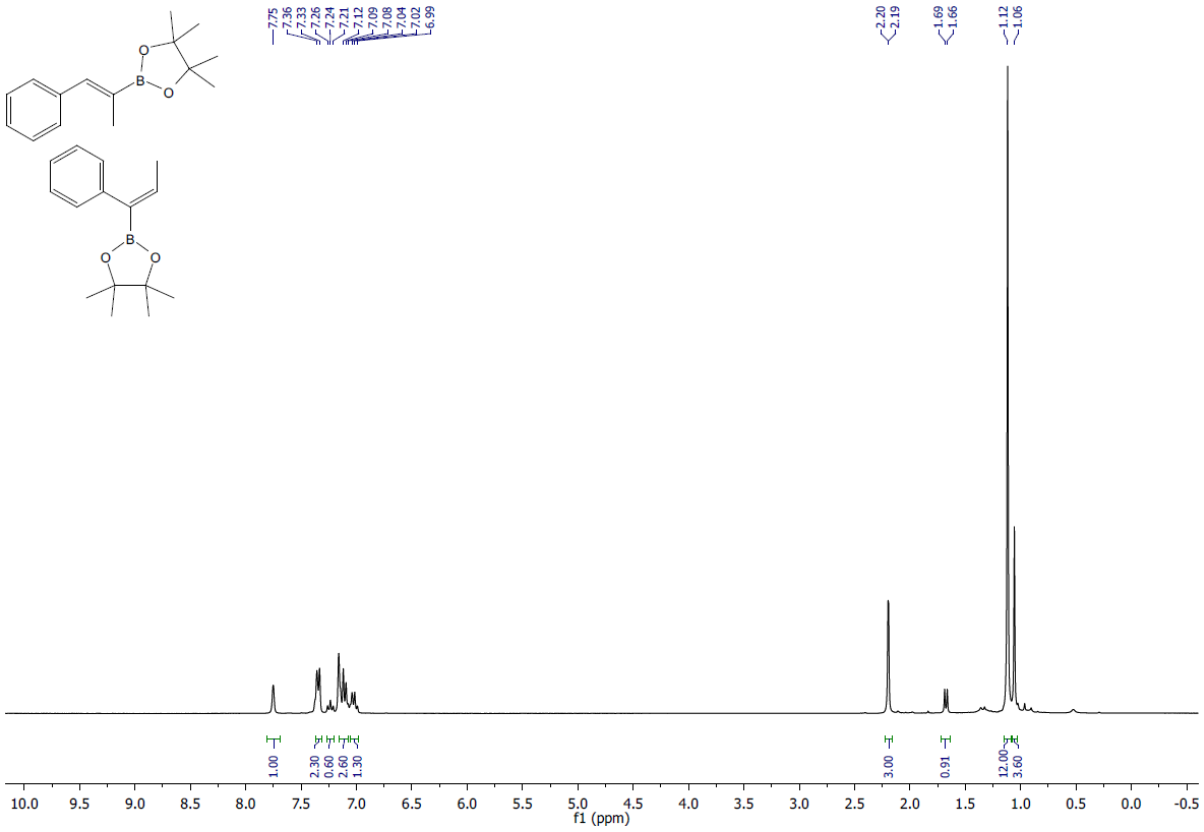


^{13}C NMR (75 MHz, $CDCl_3$)

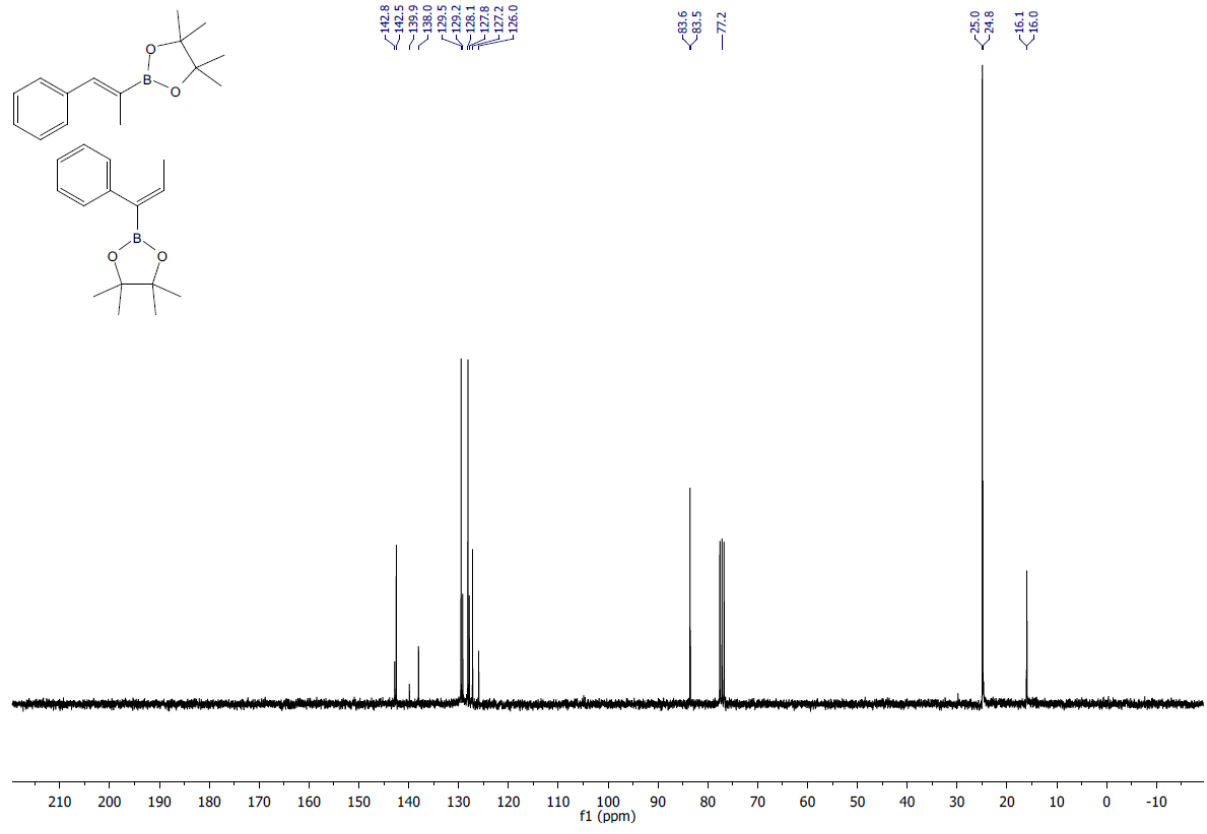


(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane & (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (40)

^{1}H NMR (300 MHz, C_6D_6)

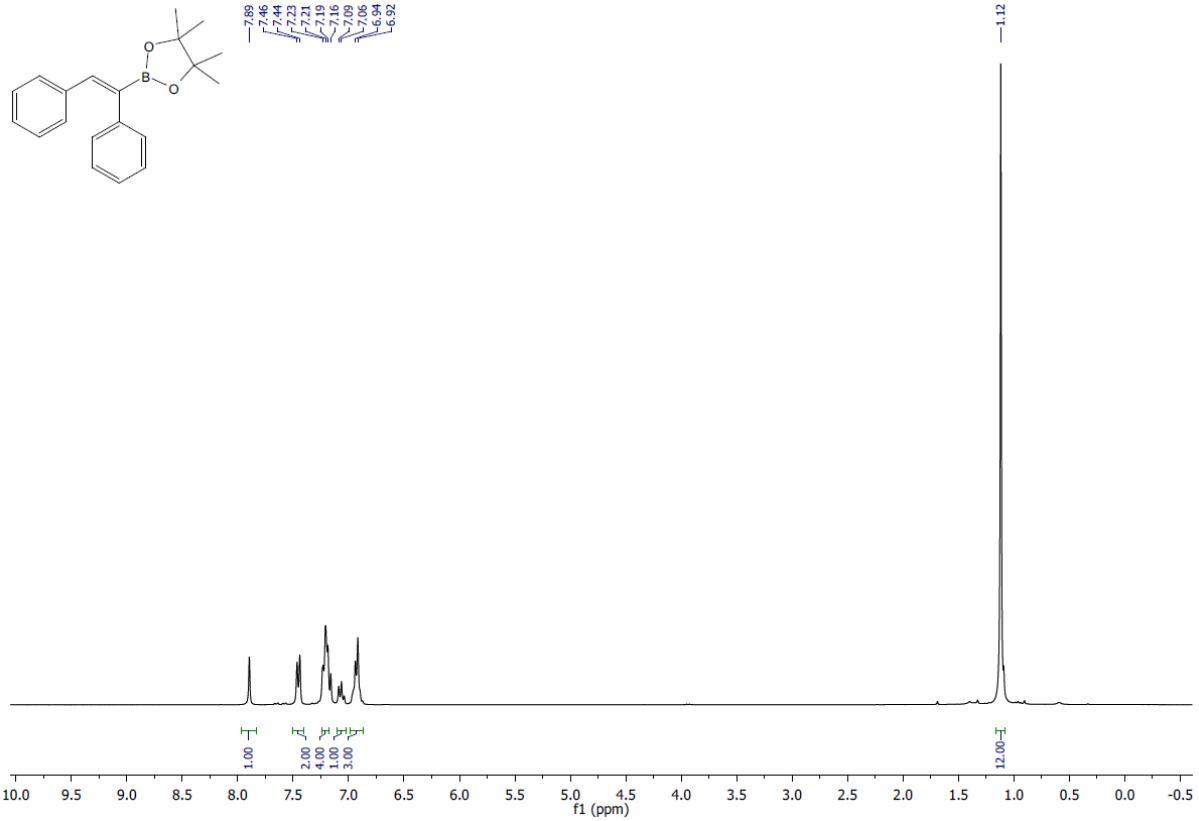


^{13}C NMR (75 MHz, $CDCl_3$)

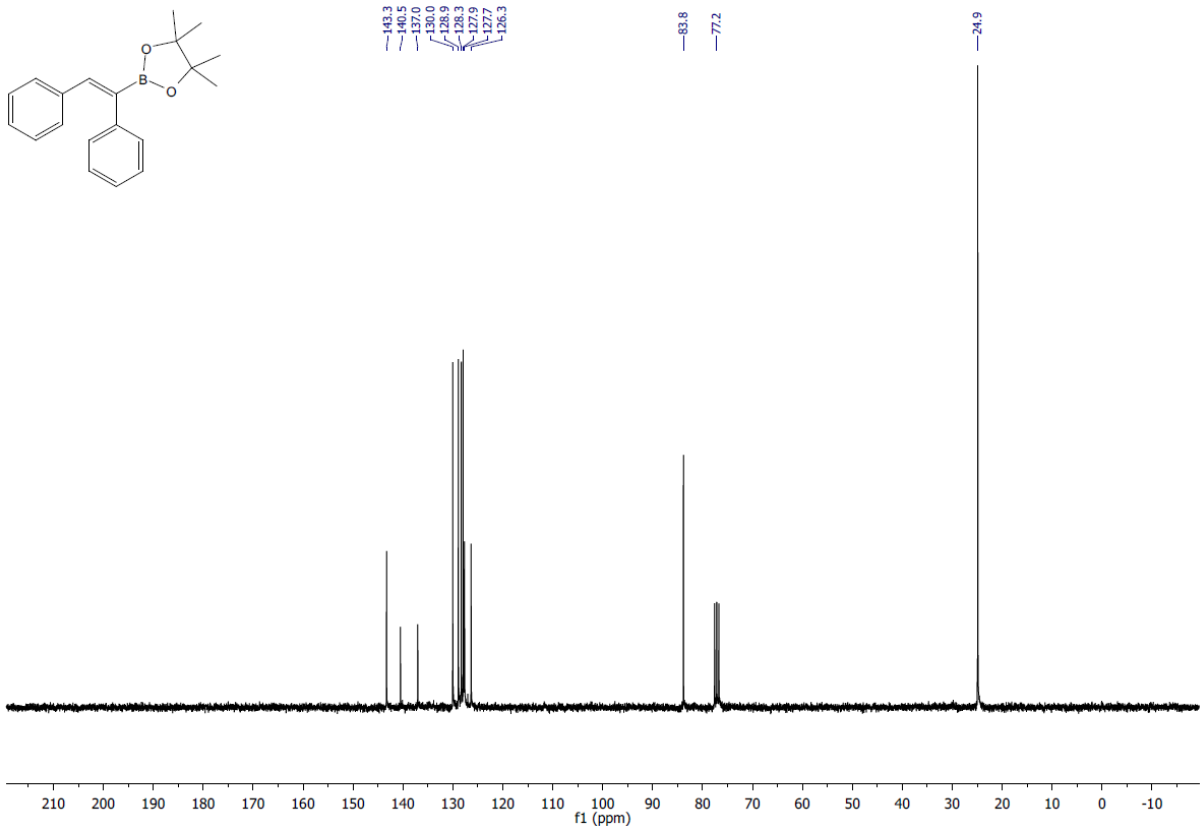


(*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (41)

^{1}H NMR (300 MHz, C_6D_6)

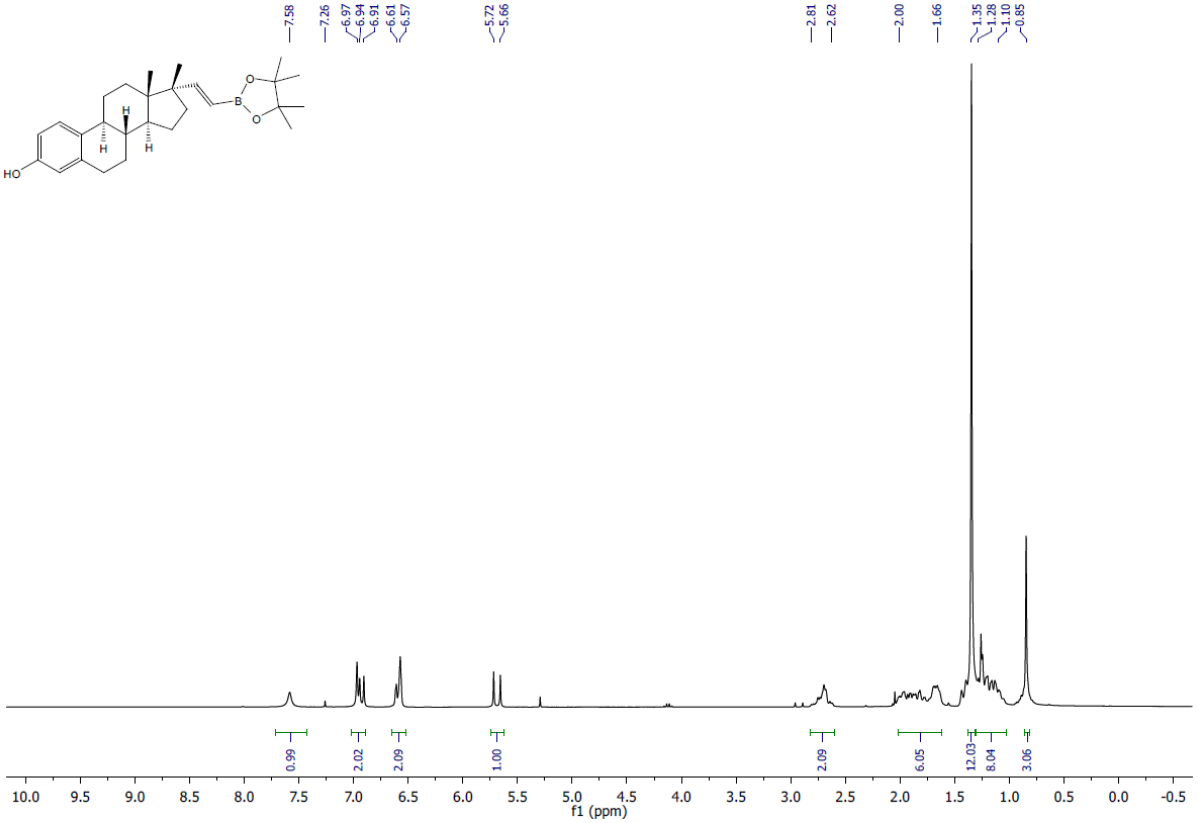


^{13}C NMR (75 MHz, $CDCl_3$)

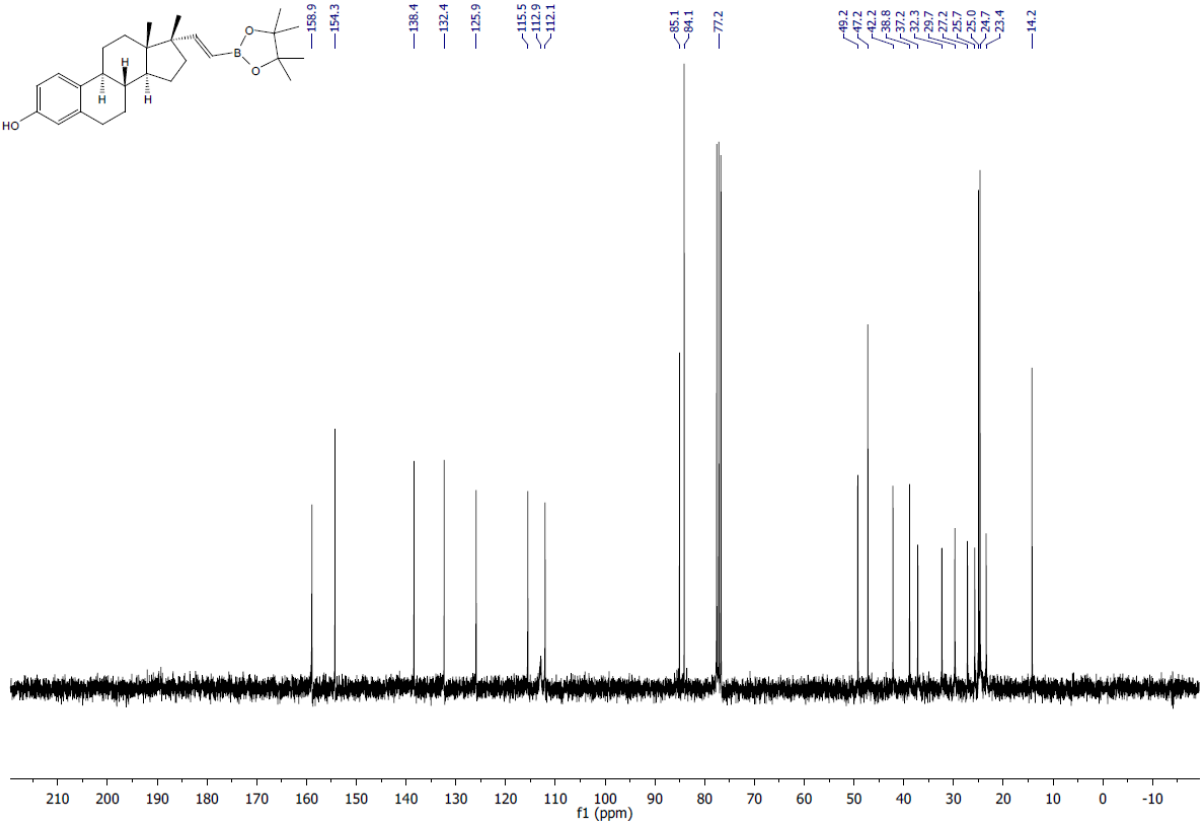


(8*R*,9*S*,13*S*,14*S*,17*R*)-13-methyl-17-((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (42)

^{1}H NMR (300 MHz, $CDCl_3$)

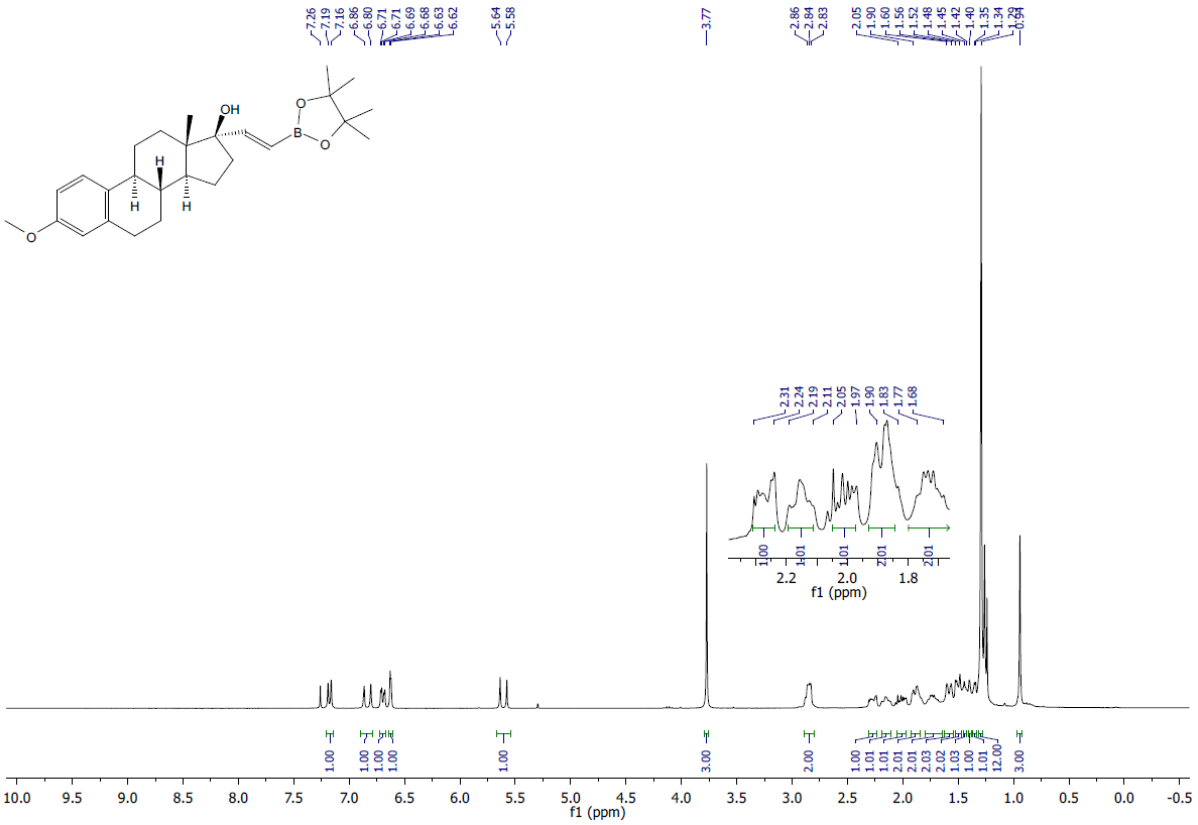


^{13}C NMR (75 MHz, $CDCl_3$)

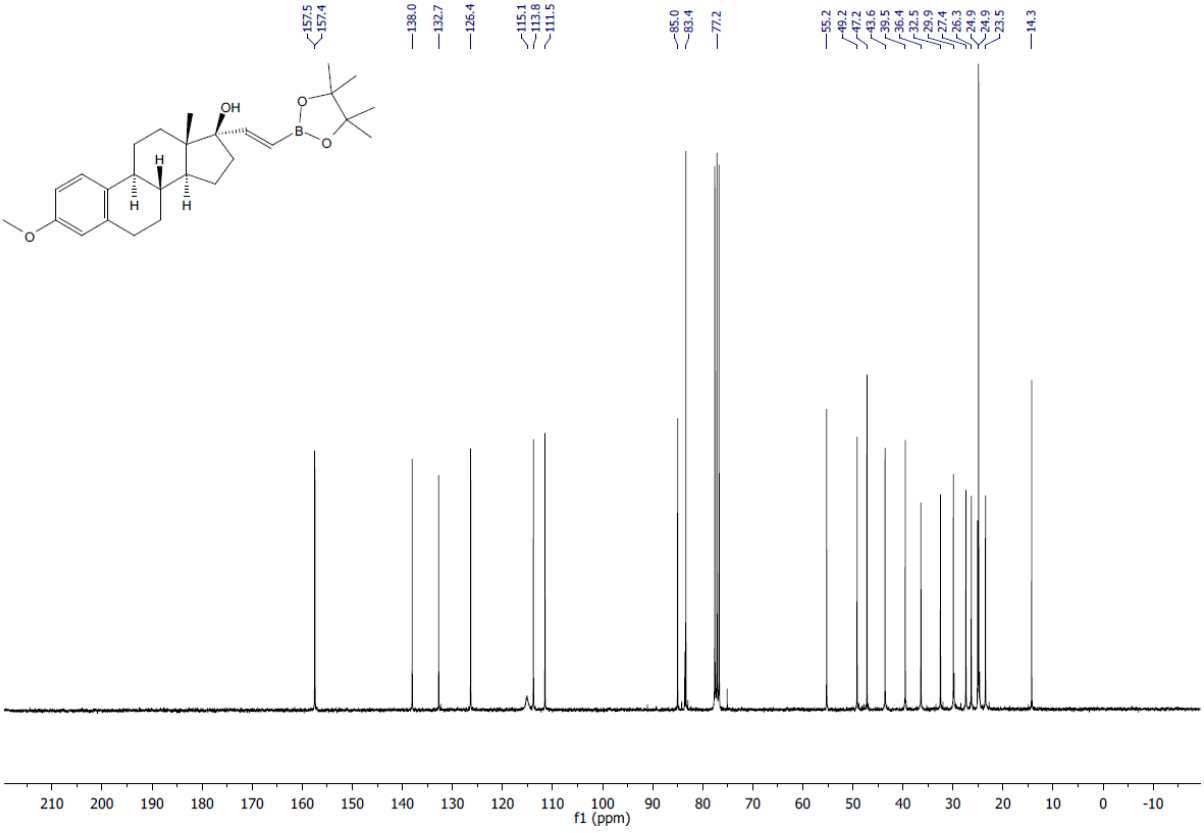


(8*R*,9*S*,13*S*,14*S*,17*R*)-3-methoxy-13-methyl-17-((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (43)

^{1}H NMR (300 MHz, $CDCl_3$)

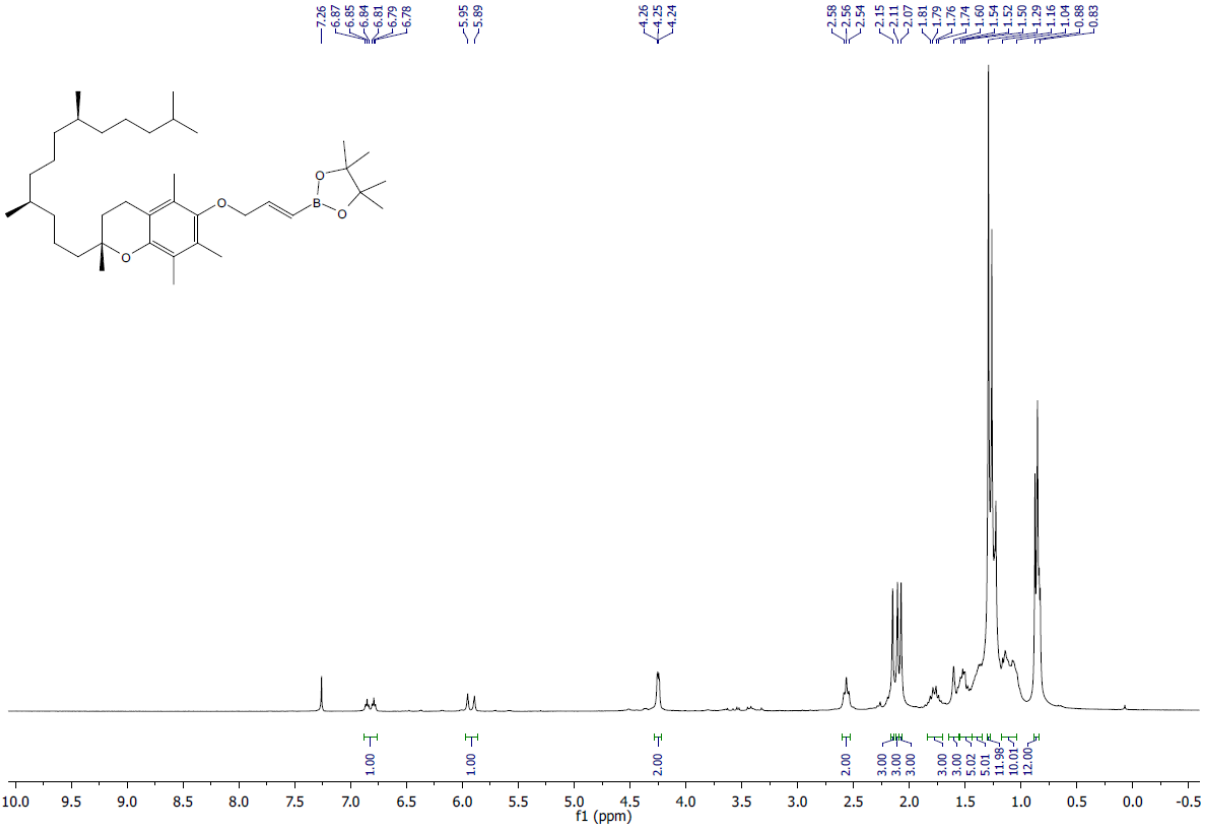


^{13}C NMR (75 MHz, $CDCl_3$)

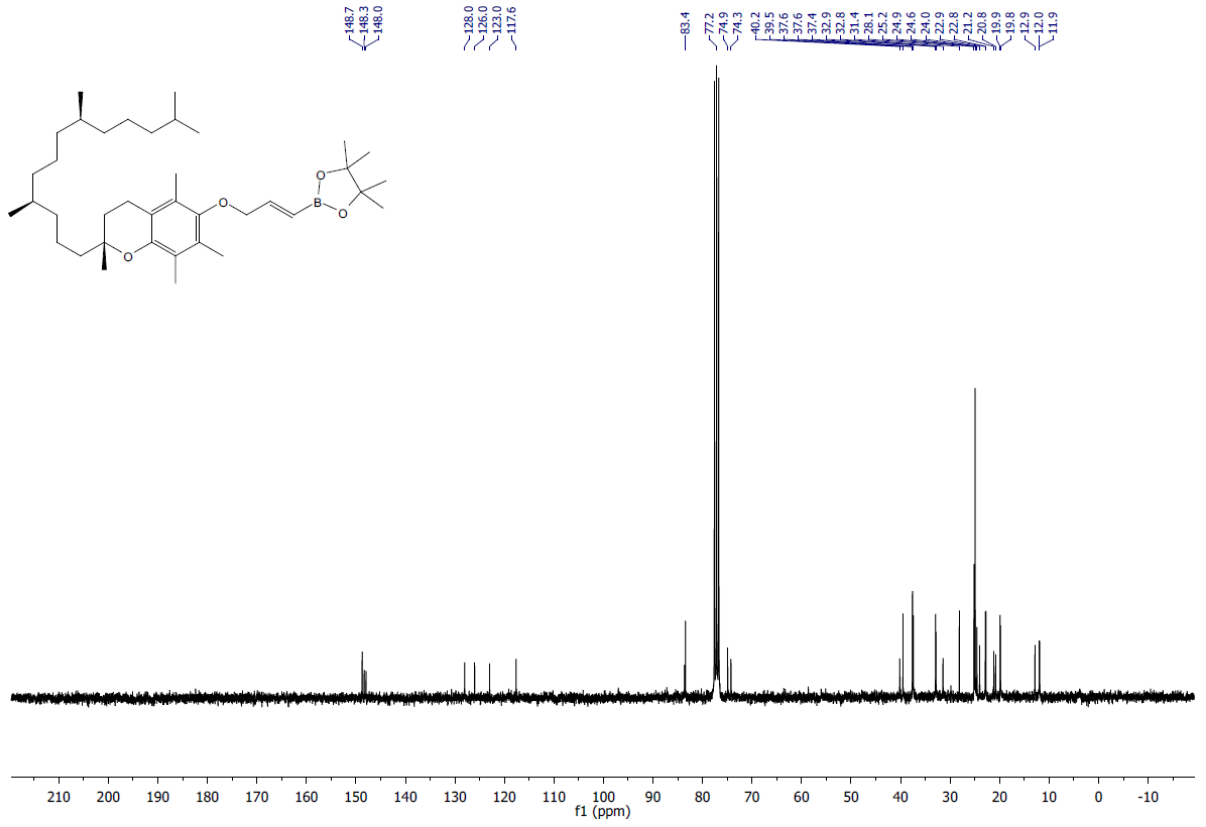


4,4,5,5-tetramethyl-2-((*E*)-3-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl) chroman-6-yl)oxy)prop-1-en-1-yl)-1,3,2-dioxaborolane (44)

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



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