Supporting Information

$AgSbF_6$-Catalyzed *anti*-Markovnikov Hydroboration of Terminal Alkynes

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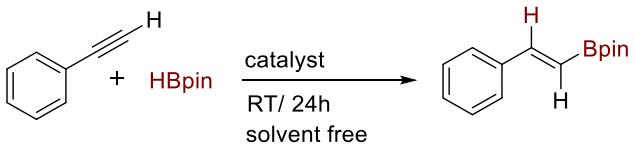
General experimental information: *Caution: organic azides might be explosive!* So, care must be taken when handling organic azides.

All reactions were performed under an argon atmosphere using MBraun glove box or Schlenk techniques. NMR spectra were recorded on Bruker 400 and 500 MHz FT-NMR spectrometer at room temperature. All ^{1}H and ^{13}C NMR spectra were referenced internally to solvent signals. ^{11}B NMR spectra were referenced externally to $BF_3 \cdot Et_2O$ in $CDCl_3$ (δ = 0 ppm), ^{19}F NMR spectra were referenced to α,α,α-trifluorotoluene (0.05% in $CDCl_3$; δ = –63.73 ppm), and ^{31}P NMR spectra were referenced externally to H_3PO_4 (85% in H_2O; δ = 0 ppm). ^{11}B NMR spectra taken in normal NMR tube were processed with a backward linear prediction algorithm to eliminate the broad ^{11}B background signal around 0 ppm from the NMR tube.[1a-c] Electron spray ionization (ESI) mass spectra were recorded with an Agilent 6545A Q-TOF mass spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K. Crystallographic details for the compound ***E*-4** are given in Table S2. Crystallographic data for compound ***E*-4** has been deposited to the Cambridge Crystallographic Data Center (CCDC-1863300). $AgSbF_6$ and HBpin were purchased from Sigma Aldrich and Alfa Aesar, respectively. All the other required chemicals purchased from commercial sources and used as it is without further purification. The starting materials 2-ethynyl anisole, 4-ethynylbenzotrifluoride, methyl 4-ethynylbenzoate, 2-ethynyl naphthalene, 6-methoxy 1-ethynylnaphthalene, 1-ethynyl naphthalene, 9-ethynylphenanthrene, 1,4-diethynyl benzene, 1,3,5-triethynyl benzene, 4-ethynylstyrene, 4-ethynyl acetophenone and phenylacetylene-D were synthesized according to the literature procedures.[1d-k]

Table S1. Optimization of hydroboration reaction of phenyl acetylene[a]



Entry	Catalyst	Mol%	Yield (%)[b]
1	[Ru(*p*-cymene)Cl_2]$_2$	0.1	ND[c]
2[d]	[Ru(*p*-cymene)Cl_2]$_2$	0.1	81
3	$AgSbF_6$	0.4	68
4	$AgSbF_6$	1	92
5	AgOTf	1	74

6	$AgBF_4$	1	68
7	$AgPF_6$	1	76
8	Ag_2O	1	69
9[e]	$AgSbF_6$	1	ND[c]

[a]Reaction condition: phenylacetylene (1 mmol), pinacolborane (1.1 mmol). [b]all are isolated yields and the product configuration is determined by ^{1}H NMR analysis. [c]No borylated product was observed; ND: Not Detected. [d]0.4 mol% $AgSbF_6$ was also used. [e]Bis(pinacolato)diboron instead of HBpin and 0.5 mL toluene were used.

General procedure for hydroboration of terminal alkynes: $AgSbF_6$ (3.4-6.8 mg, 1-2 mol%) was placed in a Schlenk tube and pinacolborane (1.1 or 2.0 mmol per alkyne function) were added inside the glove box. Outside the glove box, alkyne (1.0 mmol) and toluene (0.5 mL, in the case of solid substrate) were added to the reaction mixture under argon. The Schlenk tube was closed and allowed to stir at room temperature for 24 or 48 hours under inert atmosphere. The products were isolated by column chromatography over silica gel using ethyl acetate-hexane mixture as eluent.

Analytical data for the hydroborated products:

*(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Table 2, compound **E-1**)*[2]: Prepared from phenylacetylene (0.10 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.211 g, 0.92 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.0 Hz, 2H), 7.44 (d, J = 18.4 Hz, 1H), 7.35–7.28 (m, 3H), 6.21 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 137.6, 129.0, 128.7, 127.2, 83.5, 25.0 ppm.^{11}B NMR (160 MHz, $CDCl_3$) δ 30.18 ppm.

*(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-2**)*[2]: Prepared from 4-ethynyltoluene (0.12 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.217 g, 0.89 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 3H), 7.14 (d, J = 7.9 Hz, 2H), 6.11 (d, J = 18.5 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 139.1, 134.9, 129.4, 127.2, 83.4, 24.9, 21.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.17 ppm.

*(E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-3**)*[4]: Prepared from 3-ethynyltoluene (0.12 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.211 g, 0.86 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 18.4 Hz, 1H), 7.30 (s, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.15 (d, J = 18.4 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 138.2, 137.6, 129.8, 128.6, 127.9, 124.4, 83.4, 24.9, 21.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.06 ppm.

*(E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-4**)*[2]: Prepared from 4-*tert*-butylphenylacetylene (0.16 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.232 g, 0.81 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.41–7.35 (m, 3H), 6.13 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 149.5, 134.9, 127.0, 125.7, 83.4, 31.4, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.23 ppm. HRMS (ESI): calcd. for $C_{18}H_{27}BO_2$ ($[M-H]^+$) : 285. 2140, found: 285.2137.

*(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Table 2, compound **E-5**)*[2]: Prepared from 4-ethynyl-α,α,α-trifluorotoluene (0.17 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow solid (0.204 g, 0.68 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 7.40 (d, J = 18.5 Hz, 1H), 6.26 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 140.9, 130.6 (d, J = 33.0 Hz), 127.6, 127.3, 125.7 (q, J = 3.7 Hz), 83.8, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.19 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}BO_2F_3$ ($[M-H]^+$) : 297. 1388, found: 297.1377.

*Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (Table 2, compound **E-6**)*[2]: Prepared from methyl 4-ethynylbenzoate (0.16 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.216 g, 0.75 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 18.4 Hz, 1H), 6.27 (d, J = 18.4 Hz, 1H), 3.90 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.3, 141.9, 130.0, 127.0, 83.7, 52.2, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.15 ppm. HRMS (ESI): calcd. for $C_{16}H_{21}BO_4$ ($[M-H]^+$): 287. 1569, found: 287.1584.

*(E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-7**)*[4]: Prepared from 1-ethynyl-4-fluorobenzene (0.12 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow solid (0.204 g, 0.82 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 7.35 (d, J = 18.4 Hz, 1H), 7.02 (t, J = 8.6 Hz, 2H), 6.07 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 248.6 Hz), 148.3, 133.83, 128.8 (d, J = 8.3 Hz), 115.7 (d, J = 21.7 Hz), 83.5, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.11 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.37 ppm. HRMS (ESI): calcd. for $C_{14}H_{18}BO_2F$ ($[M-H]^+$): 247.1420, found: 247.1431.

*(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-8**)*[2]: Prepared from 4-ethynylanisole (0.13 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.214 g, 0.82 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 18.4 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.01 (d, J = 18.4 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 149.2, 130.5, 128.6, 114.1, 83.3, 55.4, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.37 ppm.

*(E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-9**)*[5]: Prepared from 2-ethynylanisole (0.13 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.144 g, 0.56 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 18.7 Hz, 1H), 7.54 (d, J= 6.8 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.18 (d, J = 18.6 Hz, 1H), 3.82 (s, 3H), 1.29 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 144.2, 130.1, 127.1, 126.6, 120.6, 111.0, 83.3, 55.4, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.26 ppm. HRMS (ESI): calcd. for $C_{15}H_{21}BO_3$ ($[M-H]^+$): 259.1620, found: 259.1618.

*(E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-10**)*[7]: Prepared from 1-ethynyl-3,5-dimethoxybenzene (0.16 g, 1.0 mmol) and pinacolborane (0.26 g, 2.0mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.264 g, 0.91 mmol, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 18.4 Hz, 1H), 6.56 (d, J = 2.3 Hz, 2H), 6.32 (t, J = 2.2 Hz, 1H), 6.05 (d, J = 18.4 Hz, 1H), 3.68 (s, 6H), 1.21 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 149.5, 139.6, 105.1, 101.4,

83.5, 55.4, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.18 ppm. HRMS (ESI): calcd. for $C_{16}H_{23}BO_4$ ([M-H]$^+$): 289.1726, found: 289.1726.

*(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-11**)*[5]: Prepared from 2-ethynyl-naphthalene (0.15 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.253 g, 0.90 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 4H), 7.71 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 18.4 Hz, 1H), 7.48–7.46 (m, 2H), 6.31 (d, J = 18.4 Hz, 1H), 1.35 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 135.1, 133.9, 133.6, 128.5, 128.4, 128.1, 127.8, 126.5, 126.4, 123.5, 83.5, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.17 ppm. HRMS (ESI): calcd. for $C_{18}H_{21}BO_2$ ([M-H]$^+$): 279. 1679, found: 279.1662.

*(E)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-12**)*[8]: Prepared from 2-ethynyl-6-methoxynaphthalene (0.18 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a white solid (0.286 g, 0.92 mmol, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.68–7.67 (m, 2H), 7.53 (d, J = 18.4 Hz, 1H), 7.13 (dd, J = 8.8, 2.5 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H), 6.22 (d, J = 18.4 Hz, 1H), 3.91 (s, 3H), 1.33 (s, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 149.8, 135.2, 133.2, 130.1, 129.0, 128.0, 127.2, 124.2, 119.2, 106.1, 83.5, 55.5, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.70 ppm. HRMS (ESI): calcd. For $C_{19}H_{23}BO_3$ ([M-H]$^+$): 309.1777, found: 309.1784.

*(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-13**)*[6]: Prepared from 1-ethynylnaphthalene (0.15 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.182 g, 0.65 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33–8.29 (m, 2H), 7.86 (dd, J = 15.6, 8.0 Hz, 2H), 7.80 (d, J = 7.2 Hz, 1H), 7.55–7.50 (m, 3H), 6.36 (d, J = 18.1 Hz, 1H), 1.39 (s, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 135.4, 133.7, 131.2, 129.1, 128.6, 126.2, 125.9, 125.6, 124.1, 123.8, 83.5, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.17 ppm. HRMS (ESI): calcd. for $C_{18}H_{21}BO_2$ ([M-H]$^+$): 279.1679, found: 279.1662.

*(E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-14**)*: Prepared from 9-ethynylphenanthrene (0.20 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated

as a pale yellow liquid (0.212 g, 0.64 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.0 Hz, 1H), 8.65 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 18.1 Hz, 1H), 7.97 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.70–7.57 (m, 5H), 6.37 (d, J = 18.0 Hz, 1H), 1.38 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 134.7, 131.8, 130.8, 130.5, 130.4, 129.2, 127.0, 126.9, 126.8, 126.7, 125.5, 124.8, 123.2, 122.6, 83.6, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.82 ppm. HRMS (ESI): calcd. for $C_{22}H_{23}BO_2$ ([M-H]$^+$): 329.1827, found: 329.1826.

*(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-15**)*[2]: Prepared from 3-ethynylthiophene (0.11 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.203 g, 0.86 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 18.4 Hz, 1H), 7.31–7.28 (m, 2H), 7.27–7.25 (m, 1H), 5.94 (d, J = 18.3 Hz, 1H), 1.30 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.4, 126.2, 125.2, 125.0, 83.4, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.15 ppm. HRMS (ESI): calcd. for$C_{12}H_{17}BO_2S$ ([M-H]$^+$): 235.1079, found : 235.1078.

*4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-2-yl)-1,3,2-dioxaborolane and (E)-4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (Table 2, compound **E-16**)*[9]: Prepared from phenyl propargylether (0.13 g, 1.0 mmol) and pinacolborane (0.26 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.146 g, 0.56 mmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, α+β), 6.94–6.89 (m, α+β), 6.76 (dt, J = 18.2, 4.4 Hz, β), 6.03–6.00 (m, α), 5.83 (dt, J = 18.1, 1.8 Hz, β), 4.64 (t, J = 1.8 Hz, α), 4.61 (dd, J = 4.4, 1.8 Hz, β), 1.28 (s, α), 1.27 (s, β) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 158.5, 147.3, 129.9, 129.4, 129.3, 120.8, 120.6, 115.0, 114.7, 83.7, 83.4, 69.2, 24.8 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.71 ppm. HRMS (ESI): calcd. for $C_{15}H_{21}BO_3$ ([M-H]$^+$): 259.1620, found: 259.1623.

*(E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate (Table 2, compound **E-17**) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate*[3,9]: Prepared from propargyl benzoate (0.16 g, 1.0 mmol) and pinacolborane (0.26 g, 2.0 mmol). After purification by column chromatography, the compound was isolated as acolourless liquid (0.191 g, 0.66 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.2 Hz, α+β), 7.56 (t, J = 7.4 Hz, α+β), 7.45–7.41 (m, α+β), 6.73 (dt, J = 18.1 Hz and 4.4 Hz, β), 5.97 (d, J = 18.9 Hz, α), 5.80 (d, J = 18.1

Hz, β), 4.95 (s, α), 4.91 (d, *J* = 4.4 Hz, β), 1.27 (s, 12H, α+β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 146.1, 133.2, 129.8, 128.7, 128.5, 127.1, 83.6, 65.9, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.61 ppm. HRMS (ESI): calcd. for $C_{16}H_{21}BO_4$ ($[M-H]^+$): 287.1569, found: 287.1578.

*(E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-18**)*[3]: Prepared from 1-hexyne (0.08 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.166 g, 0.79 mmol, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.42 (d, *J* = 18.0 Hz, 1H), 2.17–2.13 (m, 2H), 1.41–1.39 (m, 2H), 1.32–1.31 (m, 2H), 1.26 (s, 12H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 83.1, 35.6, 30.5, 24.9, 22.4, 14.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.85 ppm.

*(E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-19**)*[3]: Prepared from 1-decyne (0.14 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.182 g, 0.68 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (dt, *J* = 17.7, 6.3 Hz, 1H), 5.42 (d, *J* = 18.0 Hz, 1H), 2.14 (dd, *J* = 13.3, 6.4 Hz, 2H), 1.41 (s, 2H), 1.26 (s, 22H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 83.1, 36.0, 32.0, 29.6, 29.4, 28.4, 24.9, 22.8, 14.2 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.67 ppm. HRMS (ESI): calcd. for $C_{16}H_{31}BO_2$ ($[M-H]^+$): 265.2453, found: 265.2452.

*1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2, compound **E-20**)*[10]: Prepared from 1,4-diethynylbenzene (0.13 g, 1.0 mmol) and pinacolborane (0.28 g, 2.2 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.173 g, 0.45 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H), 7.37 (d, *J* = 18.4 Hz, 2H), 6.18 (d, *J* = 18.4 Hz, 2H), 1.31 (s, 24H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.6, 138.1, 132.5, 127.5, 127.0, 83.5, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.12 ppm. HRMS (ESI): calcd. for $C_{22}H_{32}B_2O_4$ ($[M-2H]^+$): 380.2559, found: 380.2547.

*1,3,5-tris((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2, compound **E-21**)*[11]: Prepared from 1,3,5-triethynylbenzene (0.15 g, 1.0 mmol) and pinacolborane (0.42 g, 3.3 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.416 g, 0.78 mmol, 78%). ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.53 (s, 3H), 7.32 (d, J = 18.4 Hz, 3H), 6.17 (d, J = 18.4 Hz, 3H), 1.31 (s, 36H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 138.2, 130.9, 126.4, 122.9, 83.6, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.08 ppm. HRMS (ESI): calcd. for $C_{30}H_{45}B_3O_6$ ($[M-3H]^+$): 531.3604, found: 531.3632.

*(E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (Scheme 2, compound **E-22**)*[4]: Prepared from 4-ethynylstyrene (0.13 g, 1.0 mmol) and pinacolborane (0.14 g, 1.1 mmol). After purification by column chromatography, the compound was isolated as a colourless liquid (0.184 g, 0.72 mmol, 72%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.2 Hz, 2H), 7.39 (t, J = 8.8 Hz, 3H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 6.17 (d, J = 18.5 Hz, 1H), 5.76 (dd, J = 17.6, 0.6 Hz, 1H), 5.26 (dd, J = 10.9, 0.6 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 138.3, 137.1, 136.5, 127.4, 126.6, 114.4, 83.5, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.16 ppm.

*(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (Scheme 2, compound **E-23**)*[6]: Prepared from 4-ethynylbenzonitrile (0.13 g, 1.0 mmol) and pinacolborane (0.26 g, 2.0 mmol) in 1:1 solvent mixture of THF and toluene. After purification by column chromatography, the compound was isolated as a pale yellow liquid (0.123 g, 0.48 mmol, 48%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J= 8.4 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 18.4 Hz, 1H), 6.27 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 141.9, 132.6, 127.6, 118.9, 112.2, 83.9, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.13 ppm.

Analytical data for the derivatization of compound *E*-1:

*(E)-(2-iodovinyl)benzene (Scheme 3, compound **1a**)*[12]: To a solution of compound ***E*-1** (0.12 g, 0.5 mmol) in THF (5 mL) were added a 3.0 M solution of NaOH (60 mg, 1.5 mmol). After 10 minutes I_2 (0.25 g, 1.0 mmol) was added to the reaction mixture and stirred for 20 minutes at room temperature. The reaction mixture was diluted with dichloromethane and then the organic phase was washed with a saturated solution of $Na_2S_2O_3$ then with brine. The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The crude residue was dissolved in dichloromethane, purified by column chromatography and was isolated as a colourless liquid (90 mg, 0.39 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 14.9 Hz, 1H), 7.33–7.29 (m, 5H), 6.84 (d, J = 14.9 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 137.8, 128.8, 128.5, 126.1, 76.8 ppm.

*(E)-(2-azidovinyl)benzene (Scheme 3, compound **1b**)*[13]: In a 10 mL round bottom flask sodium azide (81 mg, 1.25 mmol), $CuSO_4.5H_2O$ (0.125 g, 0.5 mmol), ***E*-1** (0.12 g, 0.5 mmol) were dissolved in MeOH (4 mL) and the reaction mixture was stirred for 4 h at room temperature. All volatile solvents were removed under reduced pressure. The crude residue was dissolved in dichloromethane, purified by column chromatography and was isolated as a colourless liquid (44 mg, 0.30 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 4H), 7.22 (m, 1H), 6.61 (d, J = 13.8 Hz, 1H), 6.28 (d, J = 13.8 Hz, 1H) ppm.^{13}C NMR (126 MHz, $CDCl_3$) δ 128.9, 127.5, 126.9, 126.0, 120.0 ppm.

*(E)-(2-bromovinyl)benzene (Scheme 3, compound **1c**)*[14]: $AgSbF_6$ (1.7 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (70 mg, 0.55 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (51 mg, 0.5 mmol) was added to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. To the solution of crude reaction mixture were added sodium bromide (0.13 g, 1.25 mmol), $CuSO_4.5H_2O$ (0.125 g, 0.5 mmol) in MeOH (4 mL) and the reaction mixture was stirred for 12 h at room temperature. All volatile solvents were removed under reduced pressure. The crude residue was dissolved in dichloromethane, purified by column chromatography and was isolated as a colourless liquid (68 mg, 0.37 mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.25 (m, 5H), 7.07 (d, J = 14.0 Hz, 1H), 6.73 (d, J = 14.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3, 136.1, 128.9, 128.4, 126.3, 106.7 ppm.

*(E)-(2-chlorovinyl)benzene (Scheme 3, compound **1d**)*[15]: $AgSbF_6$ (1.7 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (70 mg, 0.55 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (51 mg, 0.5 mmol) was added to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. To the solution of crude reaction mixture were added THF (2 mL), H_2O (0.5 mL) and $CuCl_2$ (0.134 g, 1 mmol) were added. After 16 h at 70 ºC, the resulting mixture was extracted with EtOAc (10 mL) and the organic layer was dried over $MgSO_4$. After filtration and evaporation of all volatiles, the residue was purified by column chromatography and was isolated as a white solid (53 mg, 0.38 mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 5H), 6.84 (d, J = 13.7 Hz, 1H), 6.65 (d, J = 13.6 Hz, 1H) ppm.^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 133.5, 128.9, 128.3, 126.3, 118.9 ppm.

*(E)-(2-(allyloxy)vinyl)benzene (Scheme 3, compound **1e**)*[16]: $AgSbF_6$ (1.7 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (70 mg, 0.55 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (51 mg, 0.5 mmol) was added to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. To a solution of crude reaction mixture were added allyl alcohol (3 mL), triethylamine (0.20 g, 2.0 mmol) and $Cu(OAc)_2$ (0.182 g, 1.0 mmol). The reaction was capped and stirred for 16 h at room temperature. The reaction mixture was diluted with dichloromethane (20 mL) and washed with water, brine, and dried over anhydrous $MgSO_4$. The volatiles were removed under reduced pressure. The crude residue was dissolved in dichloromethane, purified by column chromatography to get the compound as a colourless liquid (65 mg, 0.41 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26 (m, 4H), 7.18 (t, J = 6.9 Hz, 1H), 7.03 (d, J = 12.9 Hz, 1H), 6.04 (ddd, J = 22.5, 10.7, 5.4 Hz, 1H), 5.94 (d, J = 12.9 Hz, 1H), 5.43 (d, J = 17.2 Hz, 1H), 5.32 (d, J = 10.5 Hz, 1H), 4.41 (d, J = 5.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 136.4, 133.3, 128.7, 125.8, 125.2, 118.0, 106.8, 70.9 ppm.

*(E)-1-styryl-4-(trifluoromethyl)benzene (Scheme 3, compound **1f**)*[17]: $AgSbF_6$ (1.7 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (70 mg, 0.55 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (51 mg, 0.5 mmol) was added to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. To a solution of crude reaction mixture were added $Pd(PPh_3)_4$ (29 mg, 5 mol%), 1-bromo-benzotrifluoride (0.17 g, 0.8 mmol), and NaOH (40 mg, 1.0 mmol). The tube was sealed

and purged with argon before the addition of 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 16 h. After the reaction was complete, the reaction mixture was concentrated under vacuum. The crude residue was dissolved in dichloromethane, purified by column chromatography and was isolated as a white solid (96 mg, 0.39 mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 18.5, 8.4 Hz, 1H), 7.61 (s, 3H), 7.54 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.32–7.29 (m, 1H), 7.16 (dd, J = 38.5, 16.3 Hz, 2H) ppm.^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 136.8, 131.4, 129.0, 128.5, 127.8, 127.3, 126.9, 126.7, 125.8 (q, J = 3.8 Hz) ppm.

(1E, 3E)-1,4-diphenylbuta-1,3-diene (Scheme 3, compound **24***)*[19]: To an oven-dried Schlenk tube was added $Pd(PPh_3)_4$ (29 mg, 5 mol%.), ***E*-1** (0.12 g, 0.5 mmol), **1a** (0.18 g, 0.8 mmol), and NaOH (40 mg, 1.0 mmol). The tube was sealed and purged with argon before the addition of 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 16 h. After the reaction was complete, the reaction mixture was concentrated under vacuum. The crude residue was dissolved in dichloromethane, purified by column chromatography and was isolated as a white solid (76 mg, 0.37 mmol, 74%). Along with the desired *E*,*E*-diene one more compound (one of the other possible isomers) was also present in <10%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.9 Hz, 4H), 7.34 (t, J = 7.5 Hz, 4H), 7.26–7.24 (m, 2H), 6.97 (d, J = 11.9 Hz, 2H), 6.68 (d, J = 12.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.0, 129.4, 128.8, 127.7, 126.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{14}$ ($[M]^+$): 206.1096, found: 206.1096.

(E)-1-(3,5-dimethoxystyryl)-2,4-dimethoxybenzene (Scheme 4, compound ***E*-25***)*[18]: To an oven-dried schlenk tube was added $Pd(PPh_3)_4$ (29 mg, 5 mol%.), ***E*-10 (**0.15 g, 0.5 mmol), 1-iodo-2,4-dimethoxybenzene (0.20 g, 0.8 mmol), and NaOH (40 mg, 1.0 mmol). The tube was sealed and purged with argon before the addition of 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 °C for 16 h. After the reaction was complete, the reaction mixture was concentrated under vacuum. The crude residue was dissolved in dichloromethane, purified by column chromatography and was isolated as a colourless liquid (98 mg, 0.326 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 16.4 Hz, 1H), 6.96 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 2.2 Hz, 2H), 6.53 (dd, J = 8.5, 2.3 Hz, 1H), 6.48 (d, J = 2.3 Hz, 1H), 6.38 (t, J = 2.2 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.7, 158.2, 140.5, 132.0, 127.5, 127.0, 123.9, 119.4, 105.1, 104.5, 99.5, 98.6, 55.6, 55.4 ppm. HRMS (ESI): calcd. for $C_{18}H_{21}O_4$ ($[M]^+$): 300.1362, found: 300.1374.

Control experiments:

Procedure for chemoselective hydroboration of phenylacetylene: $AgSbF_6$ (3.4 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (0.14 g, 1.1 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (0.10 g, 1.0 mmol) and styrene (0.10 g, 1 mmol) were added under argon to the reaction mixture. The schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. The reaction mixture was diluted with dichloromethane and mixture was subjected to column chromatography over silica gel using ethyl acetate-hexane mixture as eluent. The compound, (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (***E*-1**), was isolated as a pale yellow liquid (0.186 g, 0.81 mmol, 81%). Spectral data are in agreement with the compound ***E*-1**. 79% of styrene was also recovered.

Procedure for Mercury dropping test: $AgSbF_6$ (3.4 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (0.14 g, 1.1 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (0.10 g, 1.0 mmol) and mercury (0.40 g, 2 mmol) were added under argon to the reaction mixture. The schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. After the reaction, mercury drop was separated out and the reaction mixture was diluted with dichloromethane and the mixture was subjected to column chromatography over silica gel using ethyl acetate-hexane mixture as eluent. The compound, (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane ***E*-1**, was isolated as a pale yellow liquid (0.205 g, 0.89 mmol, 89%). Spectral data are in agreement with the compound ***E*-1**.

Procedure for hydroboration of phenylacetylene-D_1: $AgSbF_6$ (3.4 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (0.14 g, 1.1 mmol) were added inside the glove box. Outside the glove box, phenylacetylene-D_1 (0.10 g, 1.0 mmol) was added under argon to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. The reaction mixture was diluted with dichloromethane, and the mixture was subjected to column chromatography over silica gel using ethyl acetate-hexane mixture as eluent. The compound, (*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-*D*)-1,3,2-dioxaborolane, was isolated as a pale yellow liquid (0.141 g, 0.61 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 2H), 7.40 (br, 1H), 7.35–7.29 (m, 3H), 1.32 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 137.6, 129.0, 128.7, 127.2, 83.5, 24.9 ppm. Spectral data are in agreement with the reported literature.[20]

Radical scavenger experiments: $AgSbF_6$ (3.4 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (0.14 g, 1.1 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (0.10 g, 1.0 mmol) and radical scavenger (0.5 mmol to 3 mmol) were added to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. The reaction mixture was diluted with dichloromethane and after analysing with TLC, the mixture was subjected to column chromatography over silica gel using ethyl acetate-hexane mixture as eluent.

In situ NMR monitoring experiment: $AgSbF_6$ (20 mg, 0.06 mmol) was placed in a Young NMR tube and pinacolborane (22 mg, 0.17 mmol) were added inside the glove box. During the pinacolborane addition the liberation of gas were observed. Subsequently benzene-d_6/ toluene-d_8 was added and the tube was closed with PTFE stopper. The mixture was immediately monitored using multinuclear NMR analysis.

In situ NMR monitoring of intermediate trapping experiment with $P(OMe)_3$: $AgSbF_6$ (3.4 mg, 1 mol%) was placed in a Schlenk tube and pinacolborane (0.14 g, 1.1 mmol) were added inside the glove box. Outside the glove box, phenylacetylene (0.10 g, 1.0 mmol) and $P(OMe)_3$ (1.86 g, 15 mmol) were added to the reaction mixture. The Schlenk tube was closed under argon and allowed to stir at room temperature for 24 hours. After the reaction, all the volatiles were removed in vacuo, $CDCl_3$ was added to the residue and NMR spectra were recorded.

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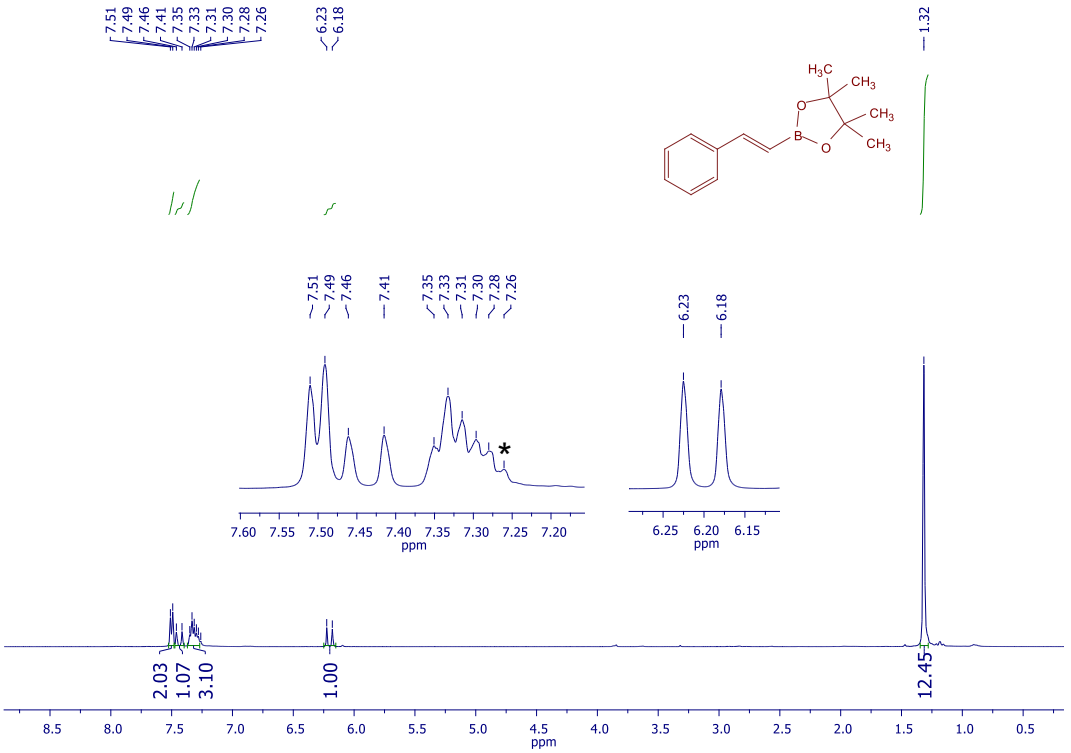
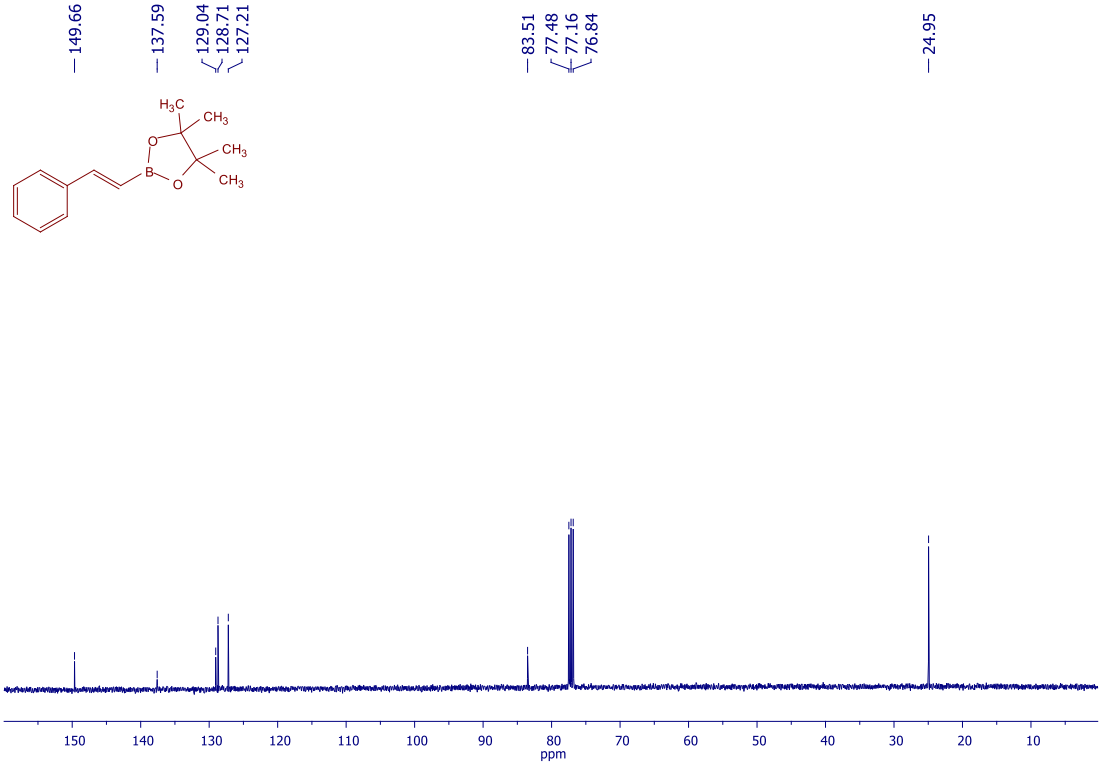
Table S2: Crystal data and refinement parameters for the compound *E*-4

Identification code	Compound ***E*-4**
Chemical formula	$C_{18}H_{27}BO_2$
Formula weight	286.21 g/mol
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal size	0.10 x 0.22 x 0.25 mm
Crystal habit	colourless rectangular
Crystal system	monoclinic
Space group	*P* 1 21/n 1
Unit cell dimensions	a = 9.4277(7) Å α = 90°
	b = 16.8208(17) Å β = 95.868(3)°
	c = 33.332(3) Å γ = 90°
Volume	5258.1(8) $Å^3$
Z	12
Density (calculated)	1.085 g/cm^3
Absorption coefficient	0.067 mm^{-1}
F(000)	1872
Theta range for data collection	1.36 to 25.00°
Reflections collected	28583
Independent reflections	9239 [R(int) = 0.0561]
Absorption correction	multi-scan
Max. and min. transmission	0.9930 and 0.9830
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	9239 / 0 / 590
Goodness-of-fit on F^2	1.064
Final R indices	0.1203, 0.3141
[I > 2σ(I)]	
R indices (all data)	0.1746, 0.3471
Extinction coefficient	0.0006(3)
Largest diff. peak and hole	0.787 and -0.392 $eÅ^{-3}$
R.M.S. deviation from mean	0.077 $eÅ^{-3}$

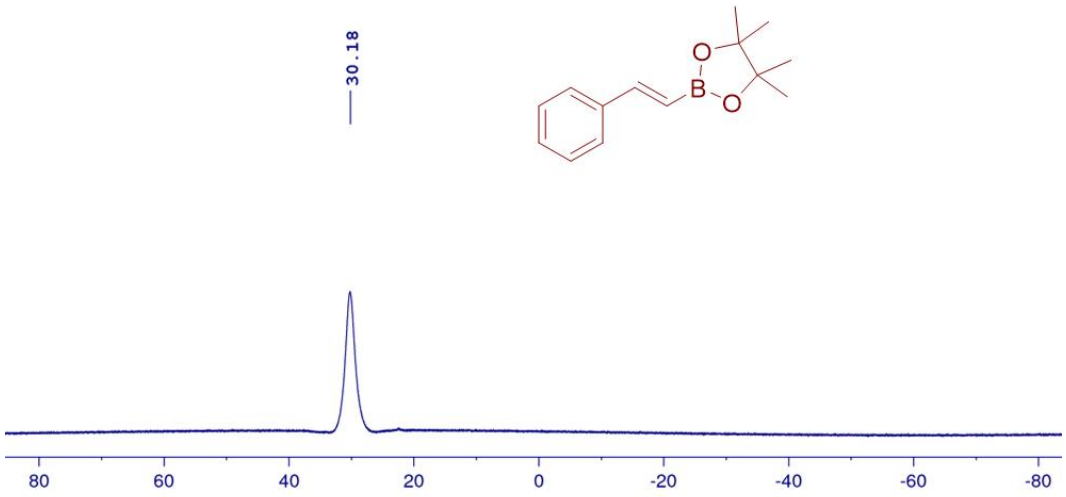
NMR spectra of hydroborated compounds in $CDCl_3$:



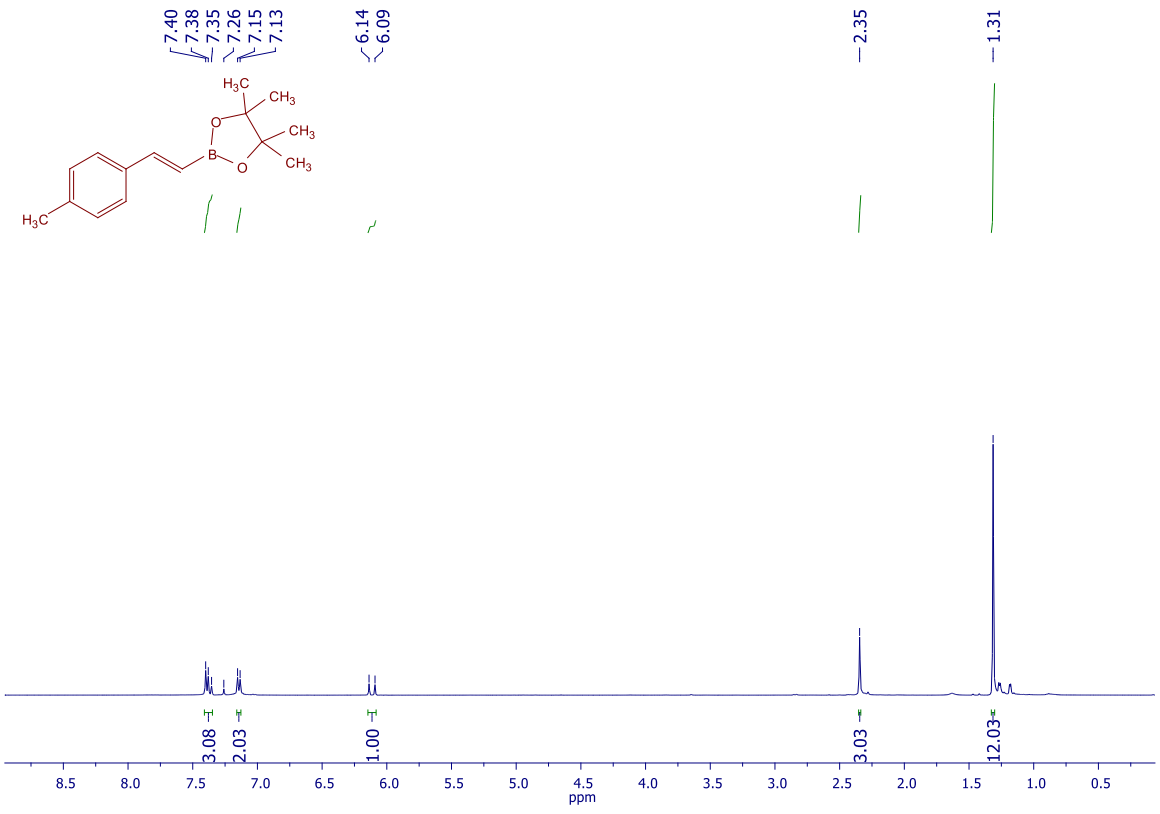
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Table 2, compound **E-1**) in $CDCl_3$ (*)*



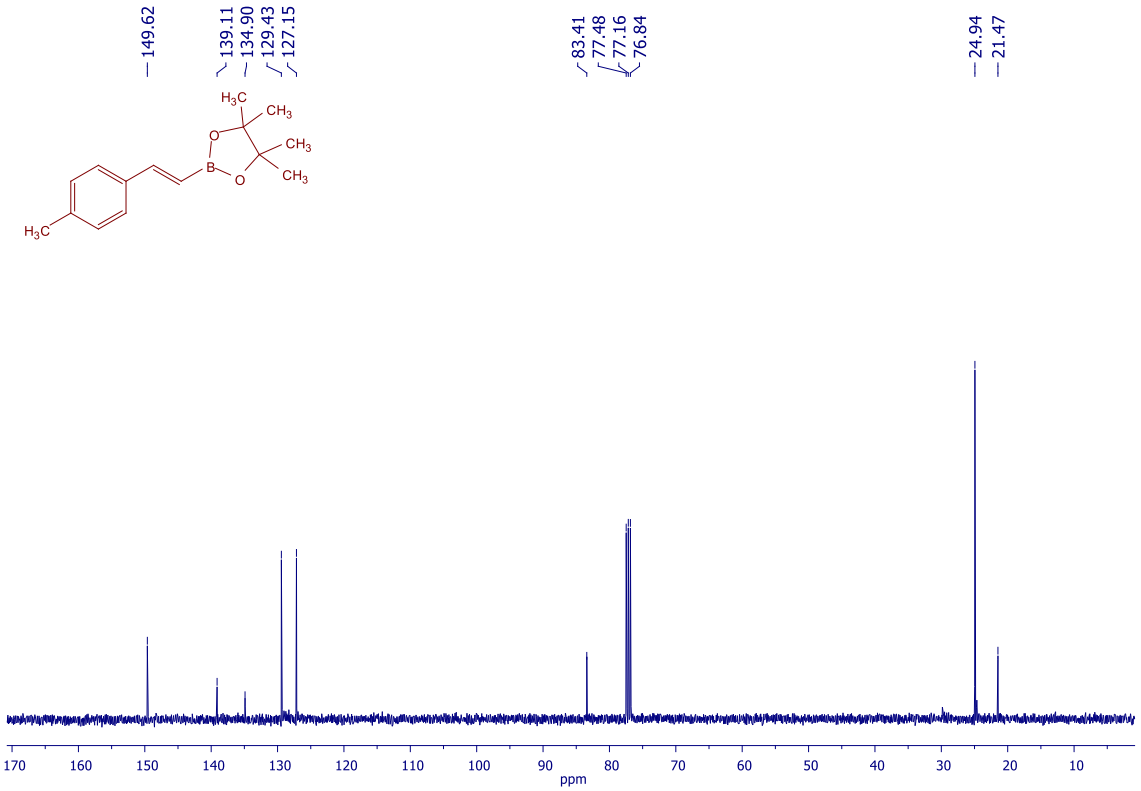
*[13]C NMR of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Table 2, compound **E-1**)*



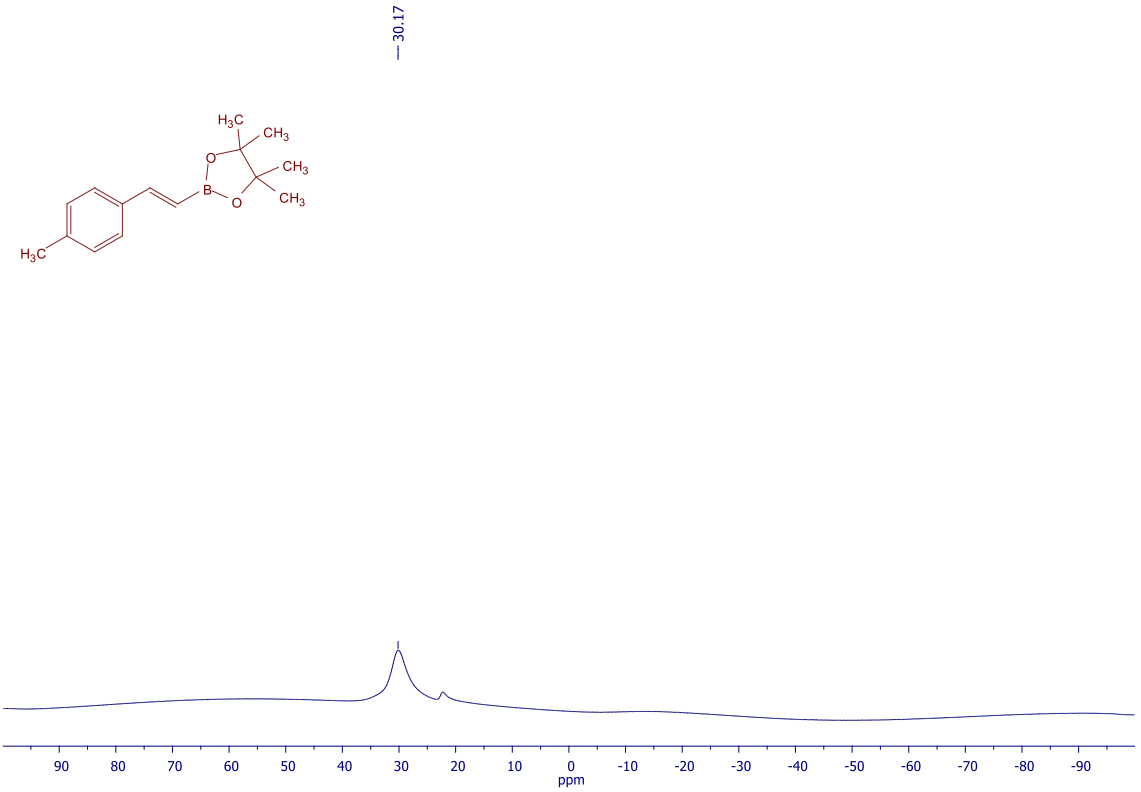
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Table 2, compound **E-1**)*



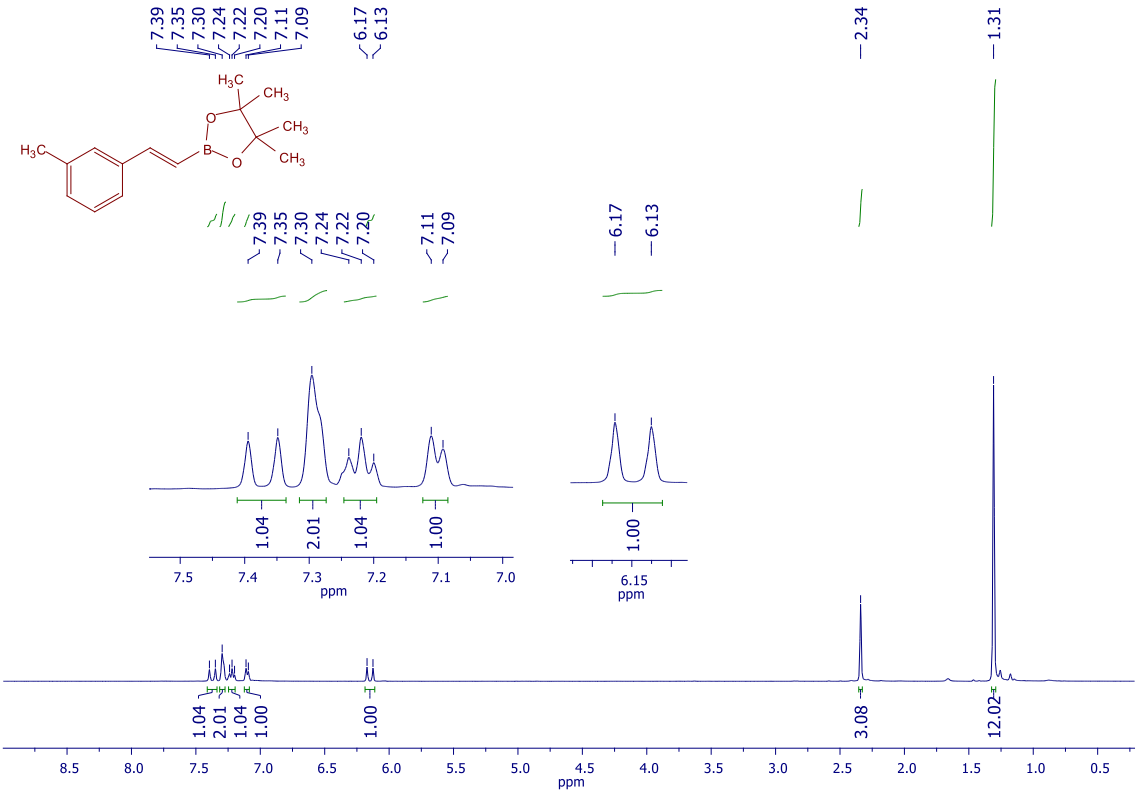
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-2**)*



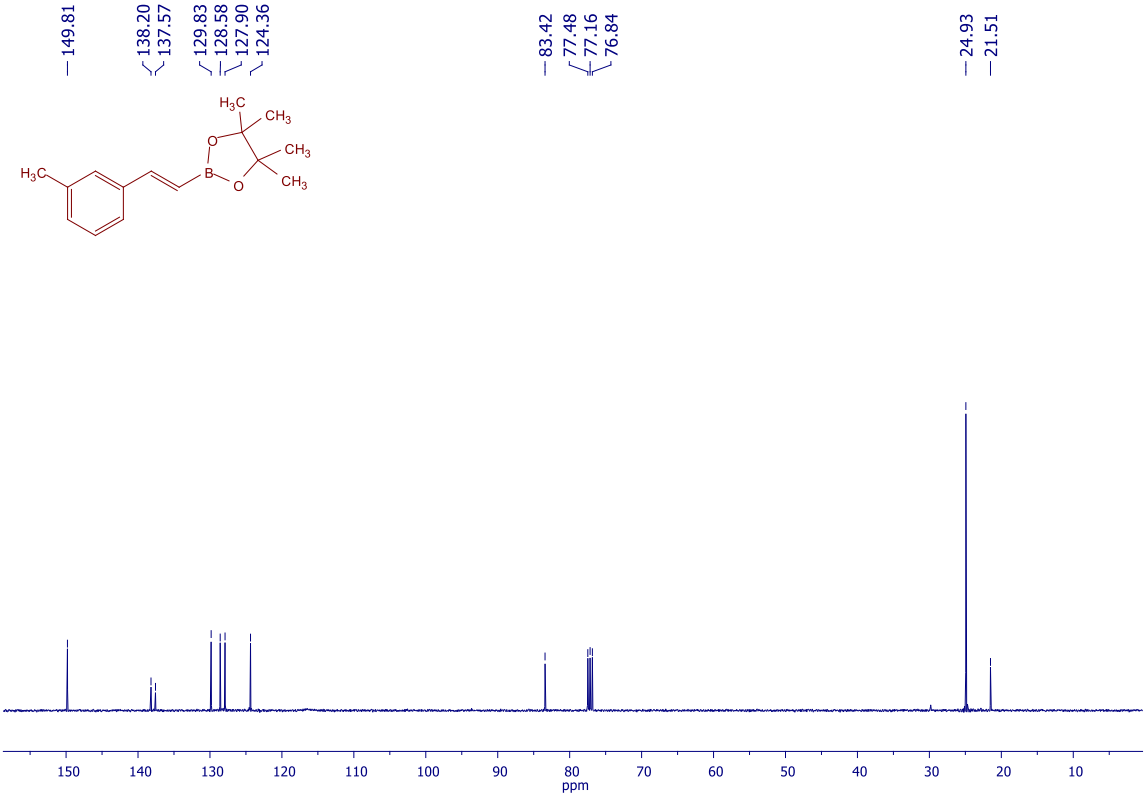
*^{13}C NMR of (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-2**)*



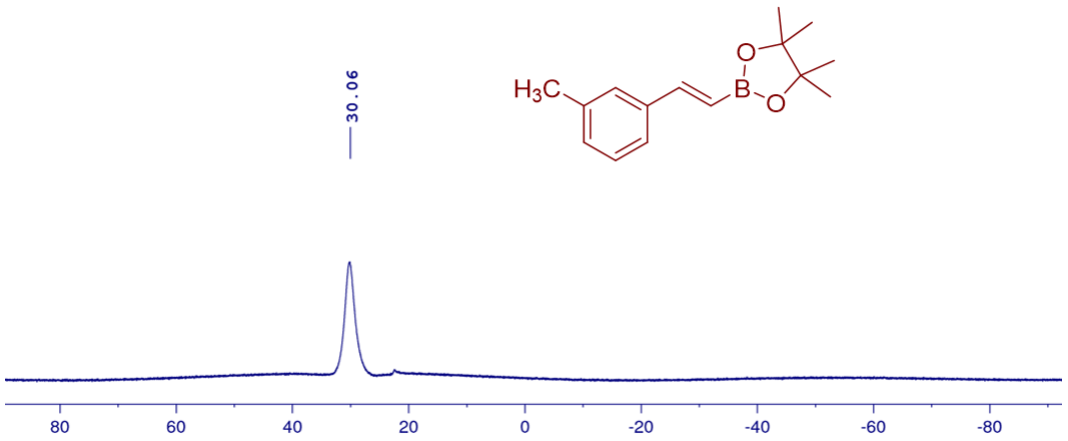
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-2**)*



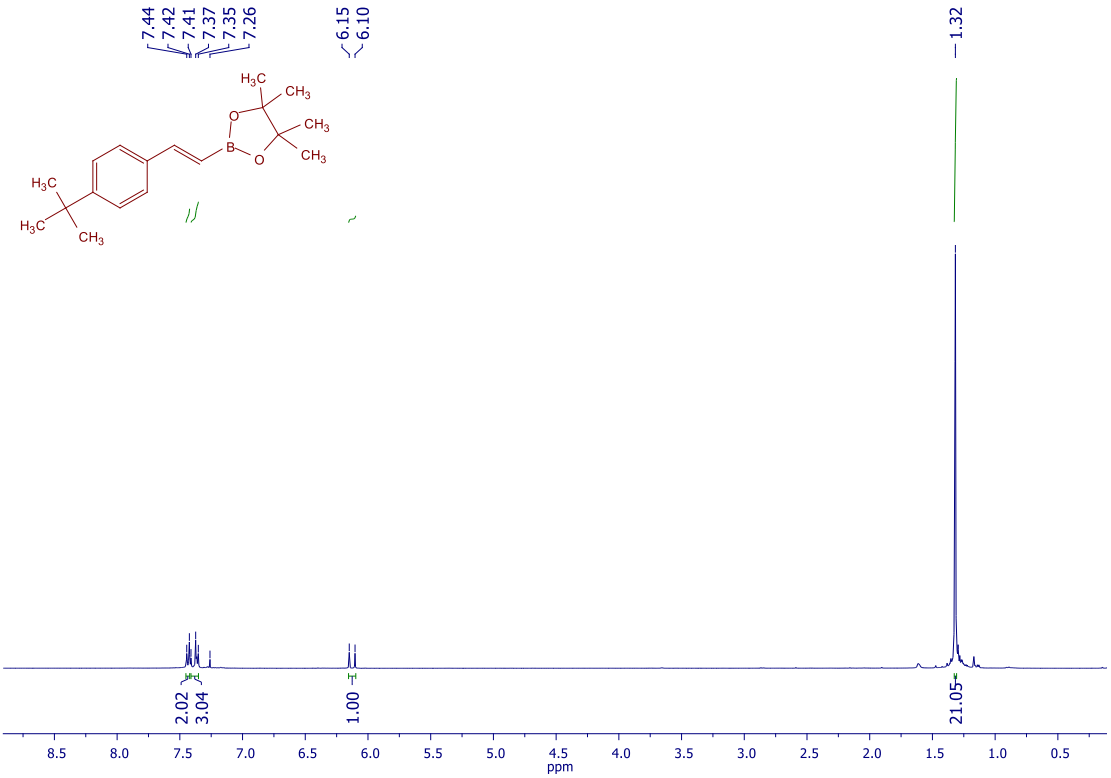
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-3**)*



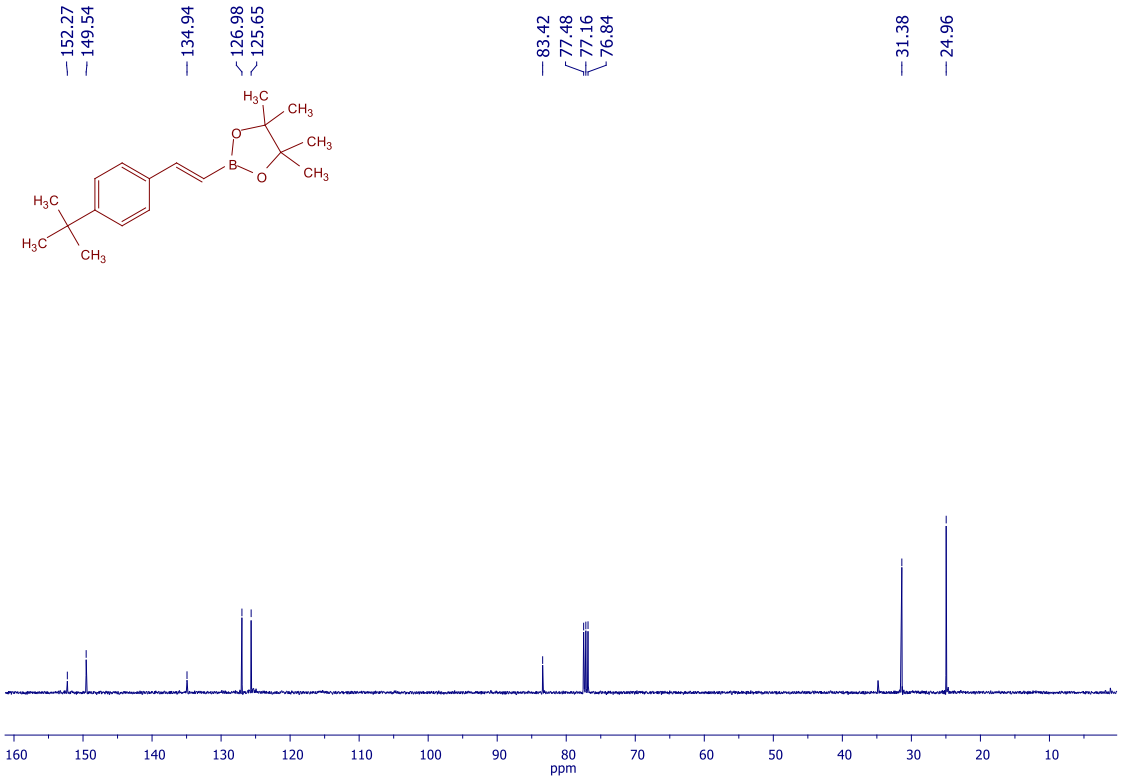
*^{13}C NMR of (E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-3**)*



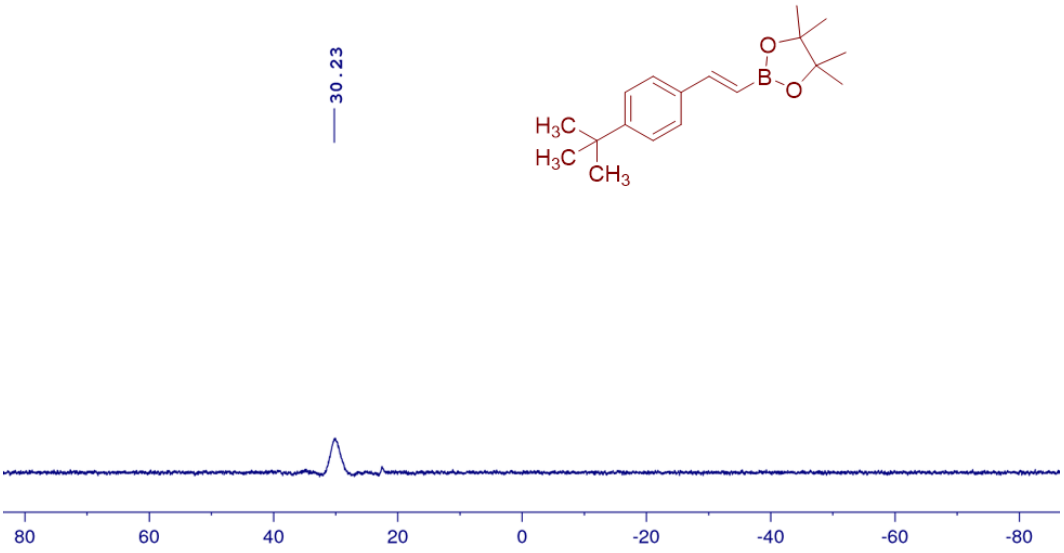
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Table 2, compound **E-3**)*



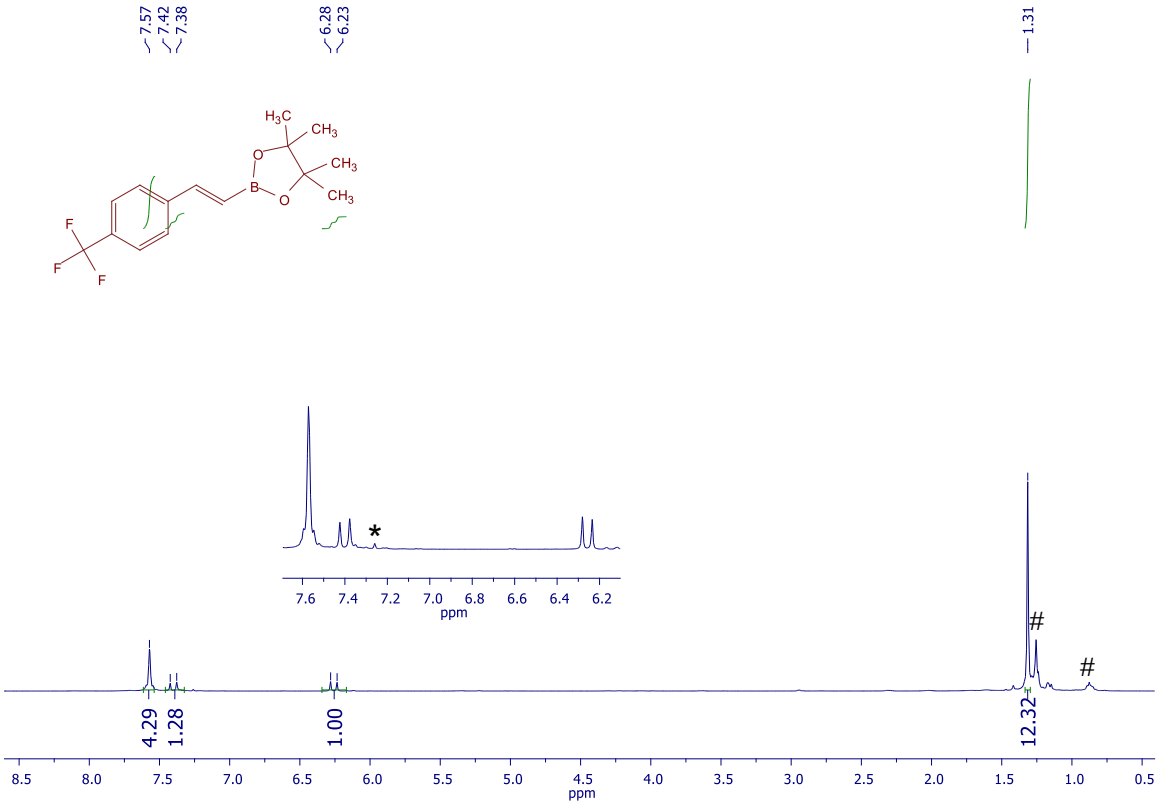
*[1]H NMR of (E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-4**)*



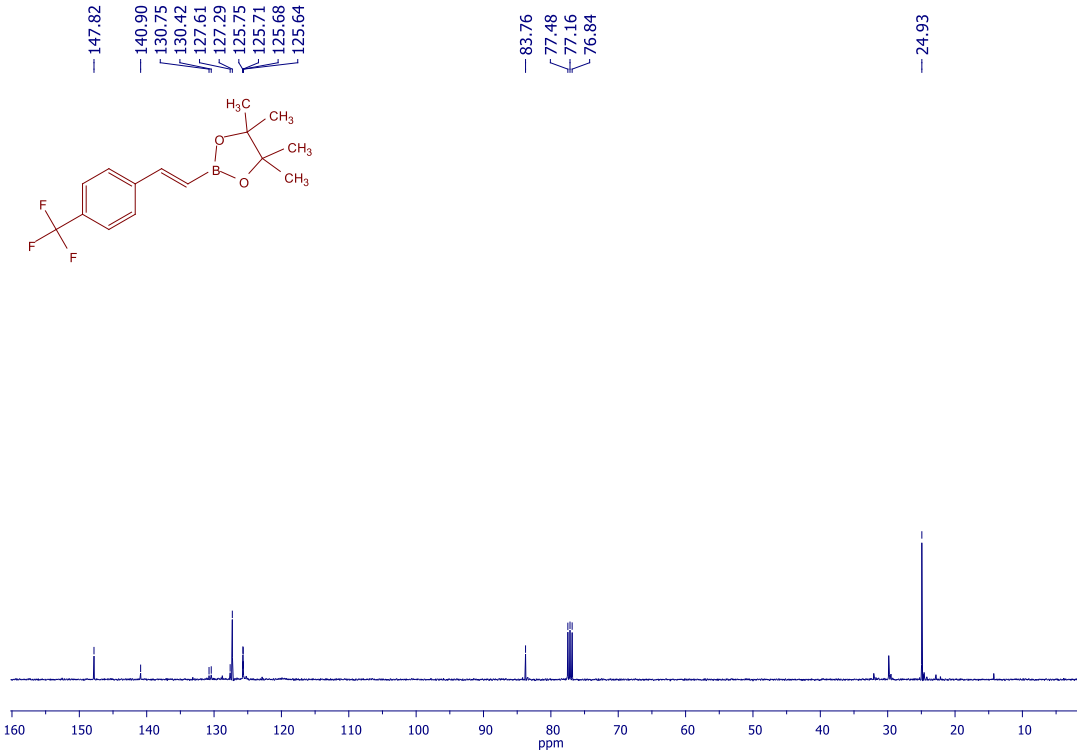
*^{13}C NMR of (E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-4**)*



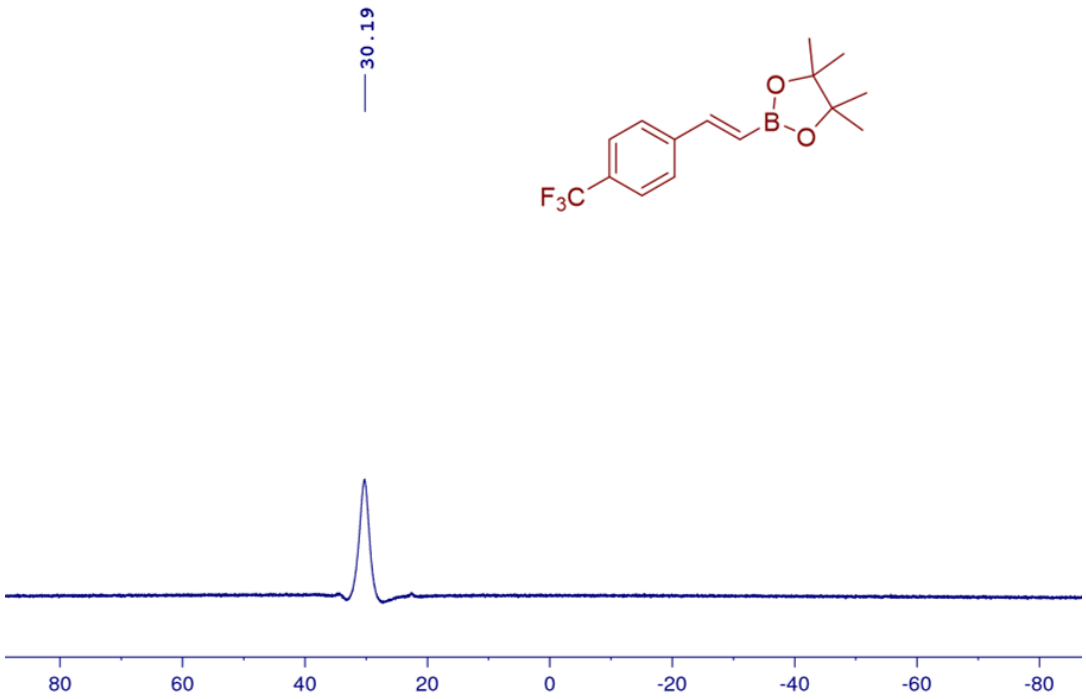
*^{11}B NMR of (E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-4**)*



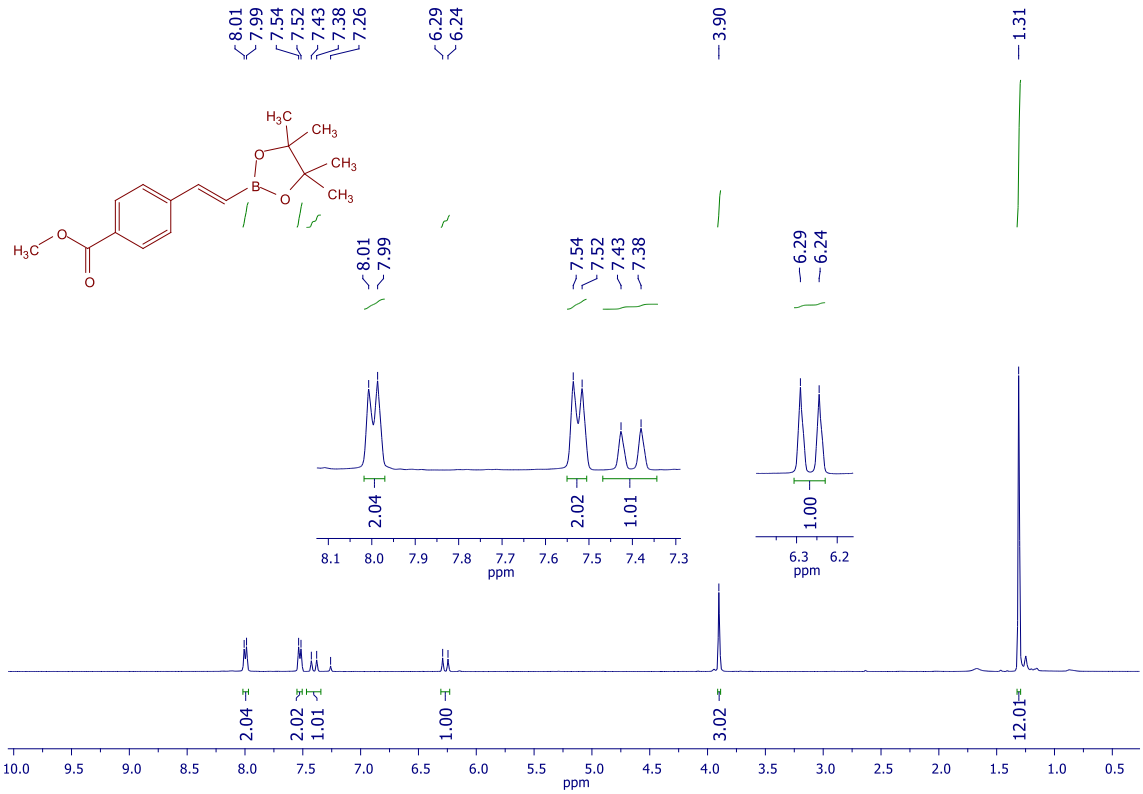
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Table 2,compound **E-5**) in $CDCl_3$ (*). # indicates the impurity of grease.*



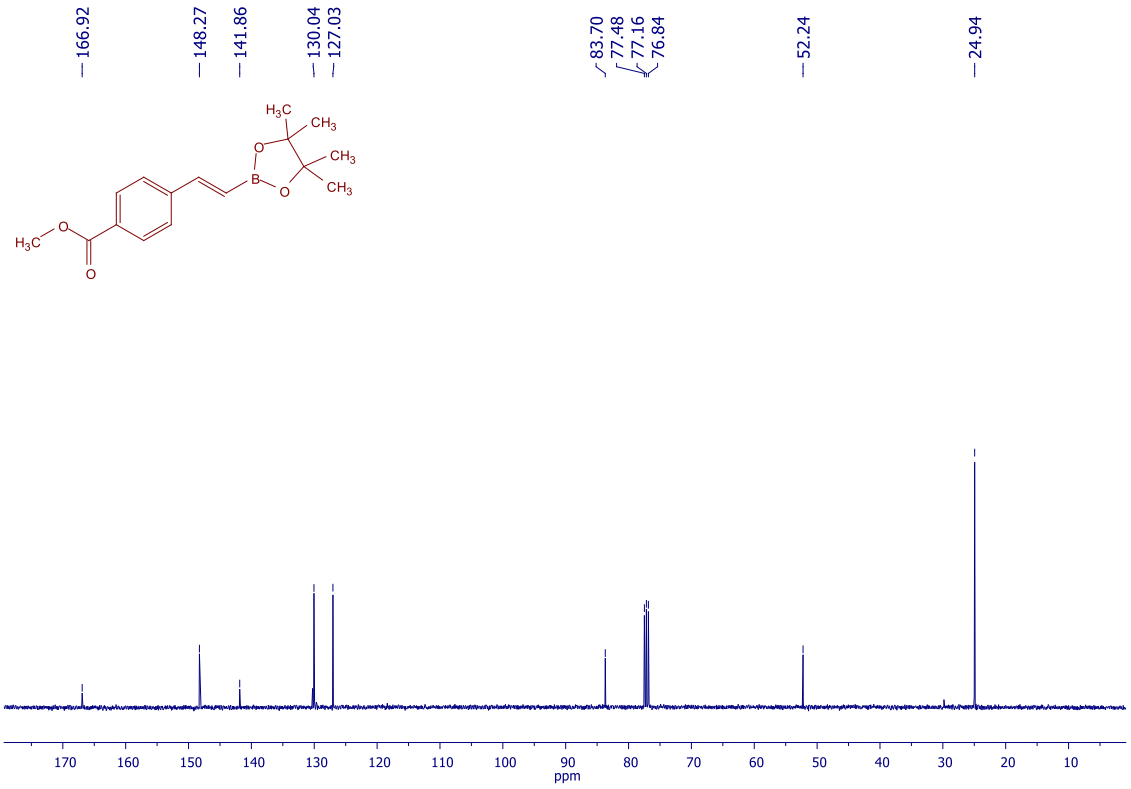
*^{13}C NMR of (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Table 2, compound **E-5**)*



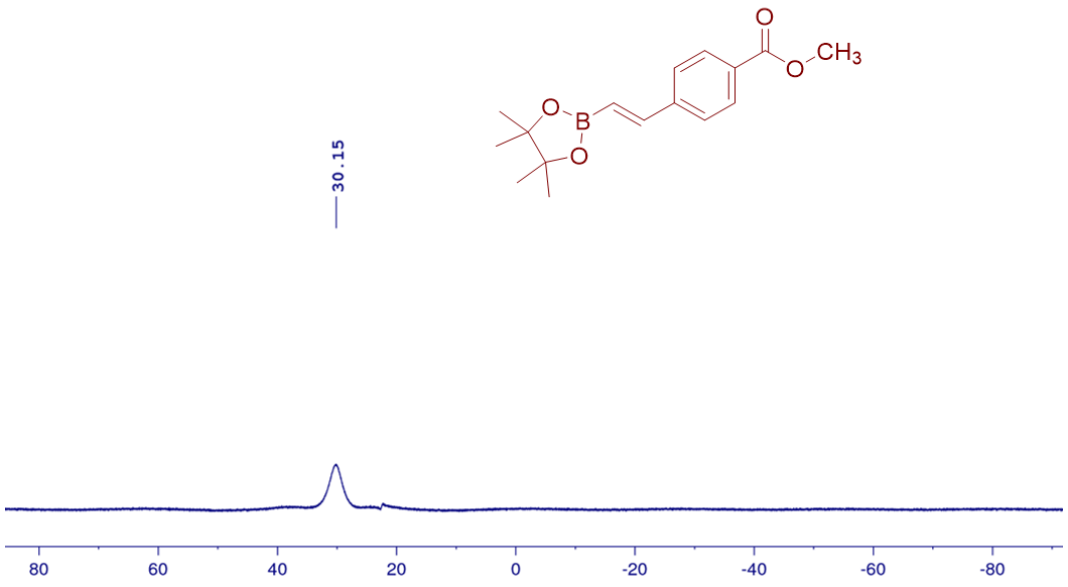
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Table 2, compound **E-5**)*



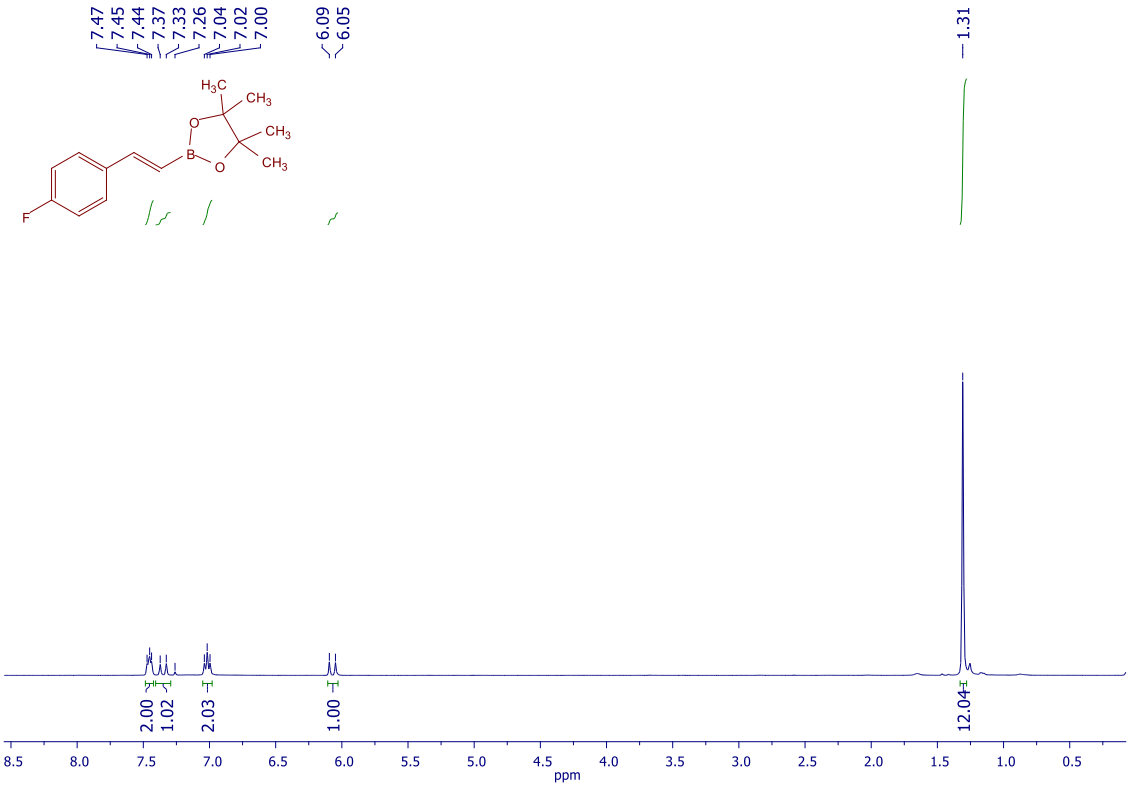
*[1]H NMR of Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (Table 2,compound **E-6**)*



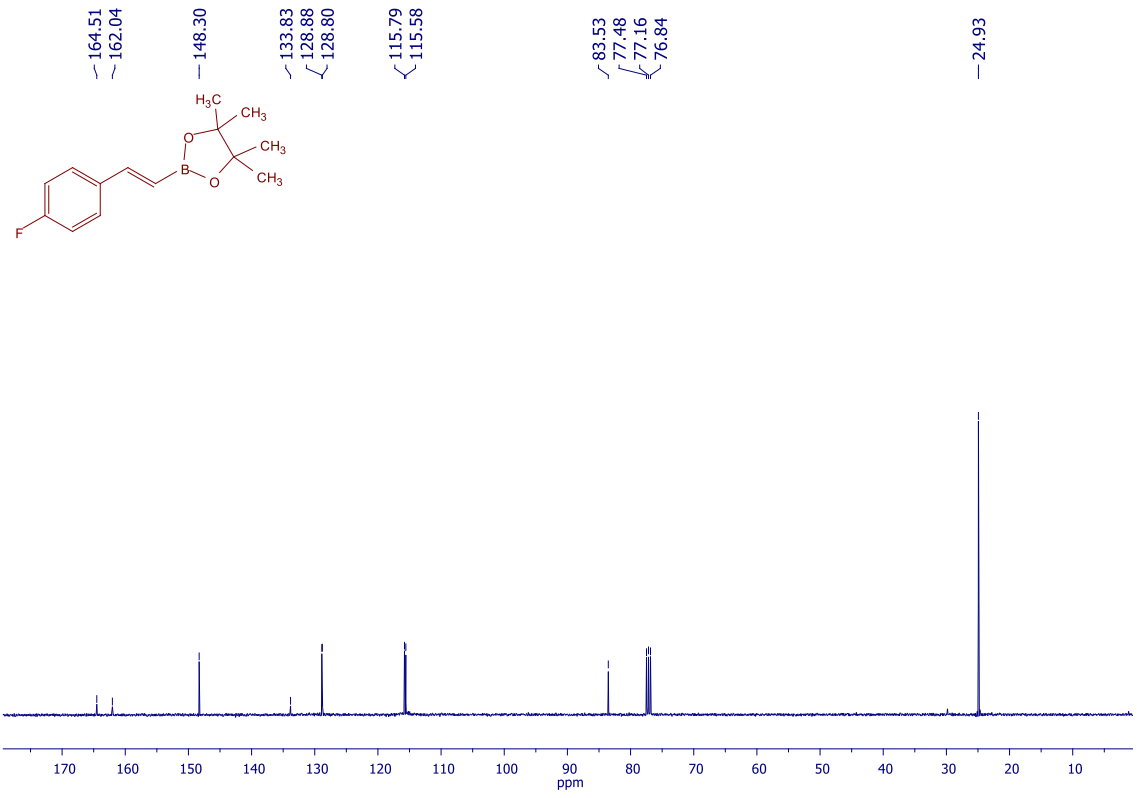
*^{13}C NMR of Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (Table 2,compound **E-6**)*



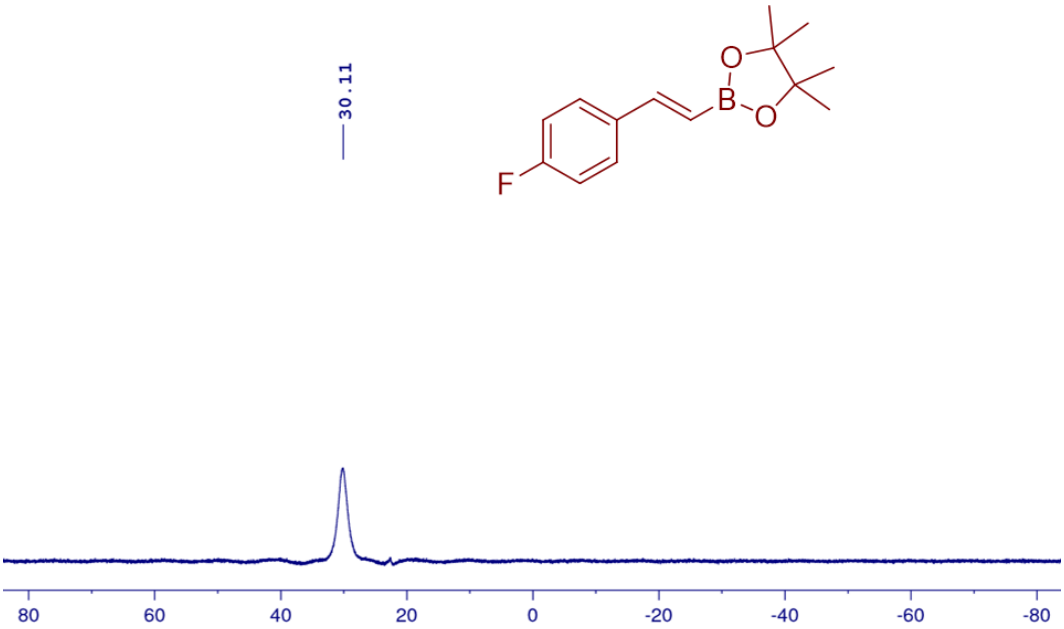
*^{11}B NMR of Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (Table 2,compound **E-6**)*



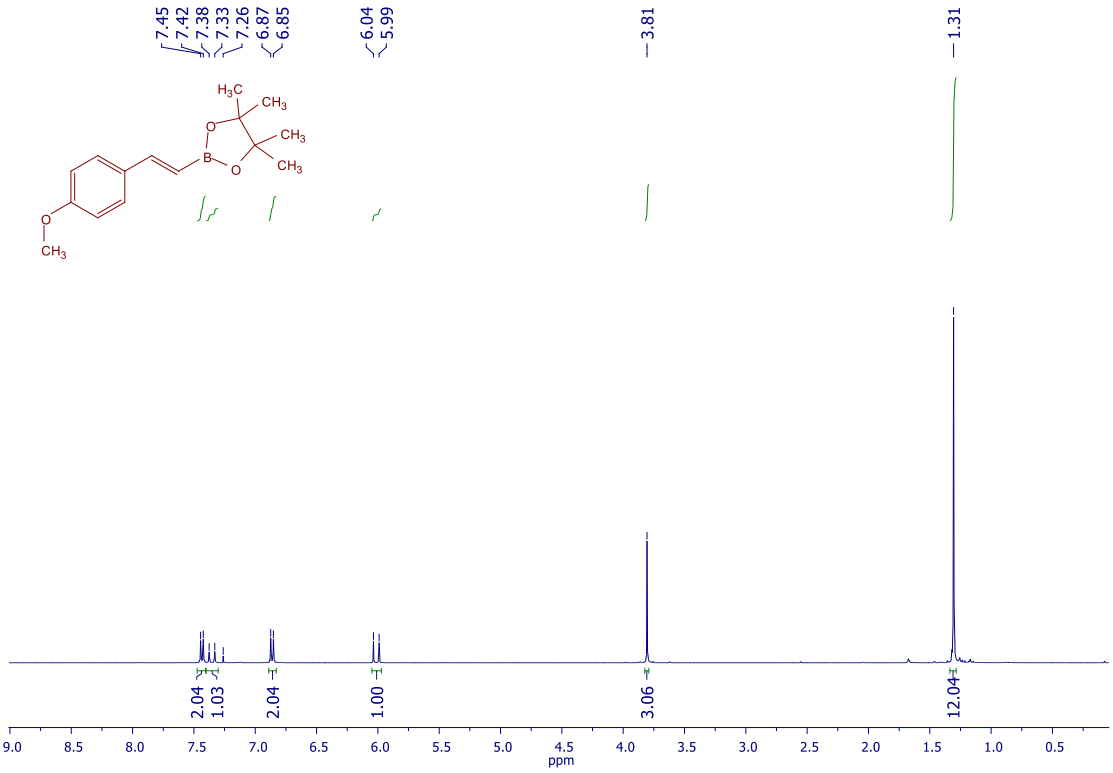
*[1]H NMR of (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-7**)*



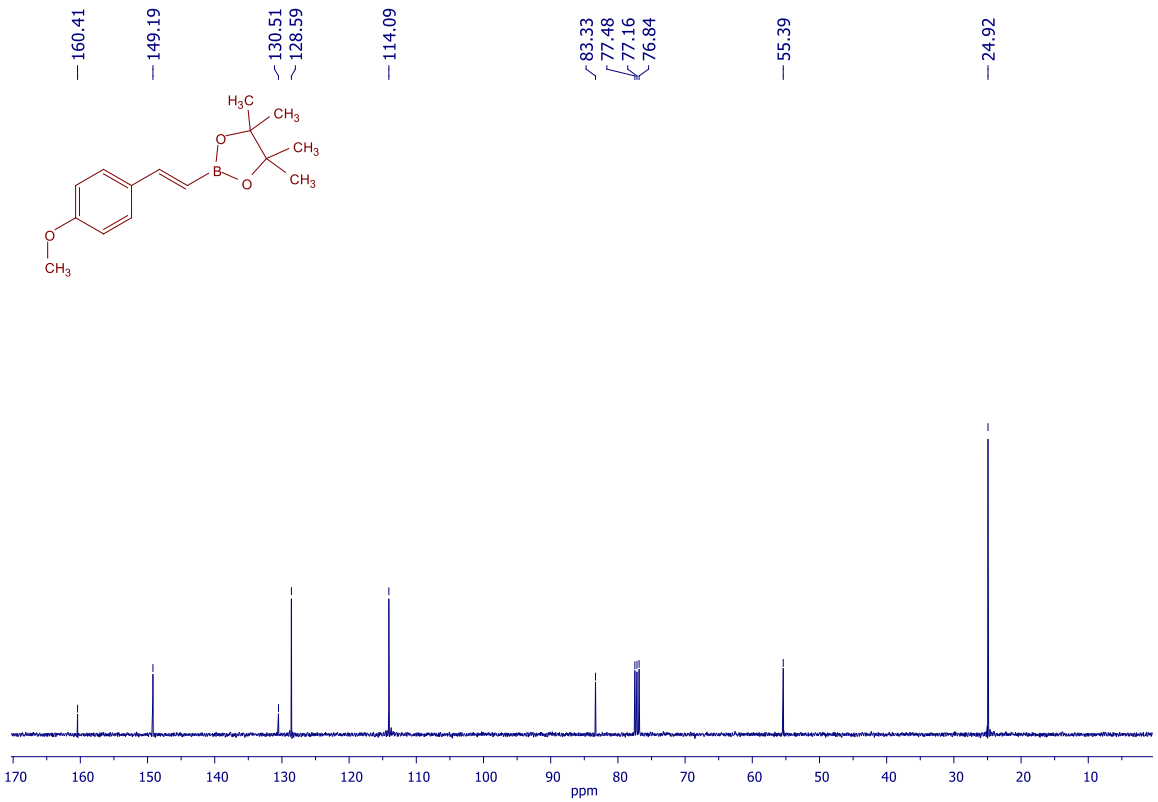
*[13]C NMR of (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-7**)*



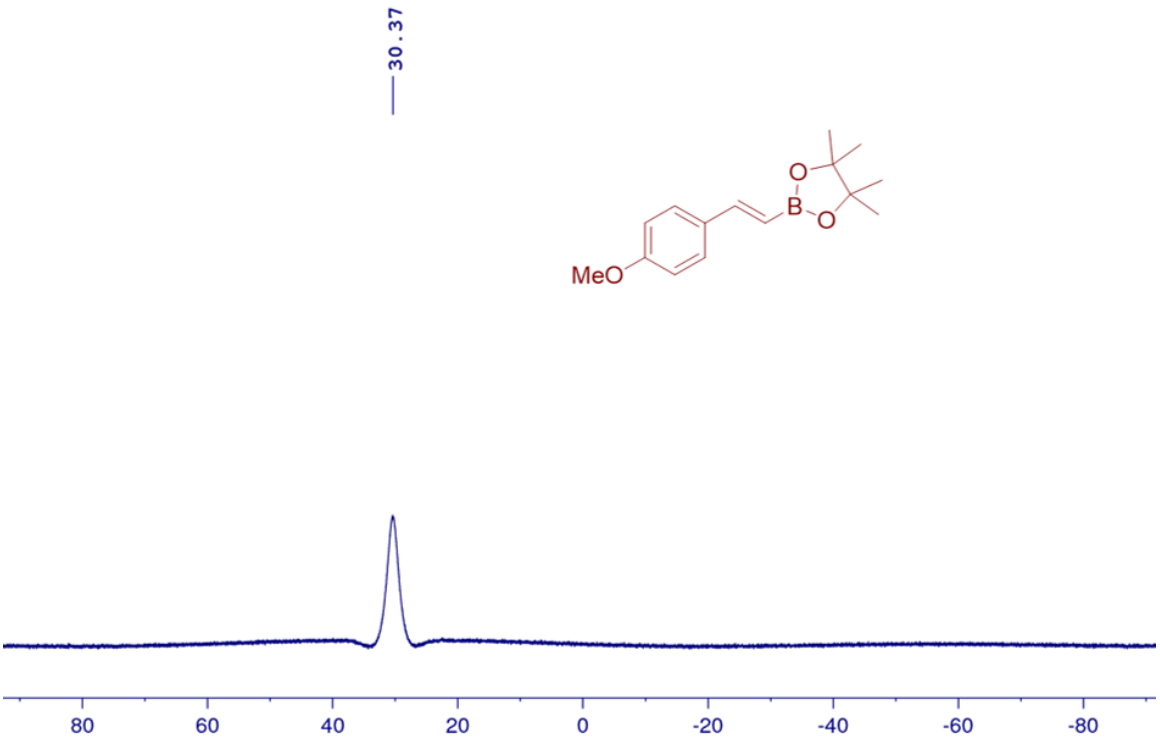
*[11]B NMR of (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-7**)*



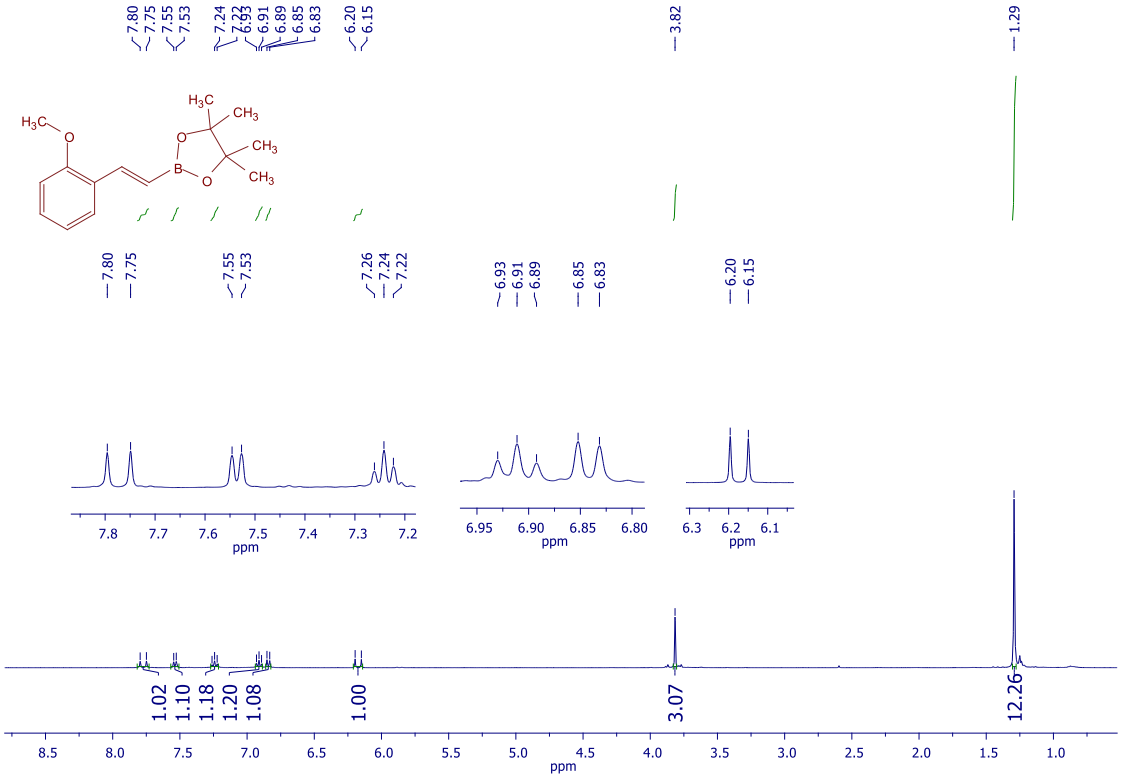
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-(4-methoxystyryl)-1,3,2-dioxaborolane (Table 2, compound **E-8**)*



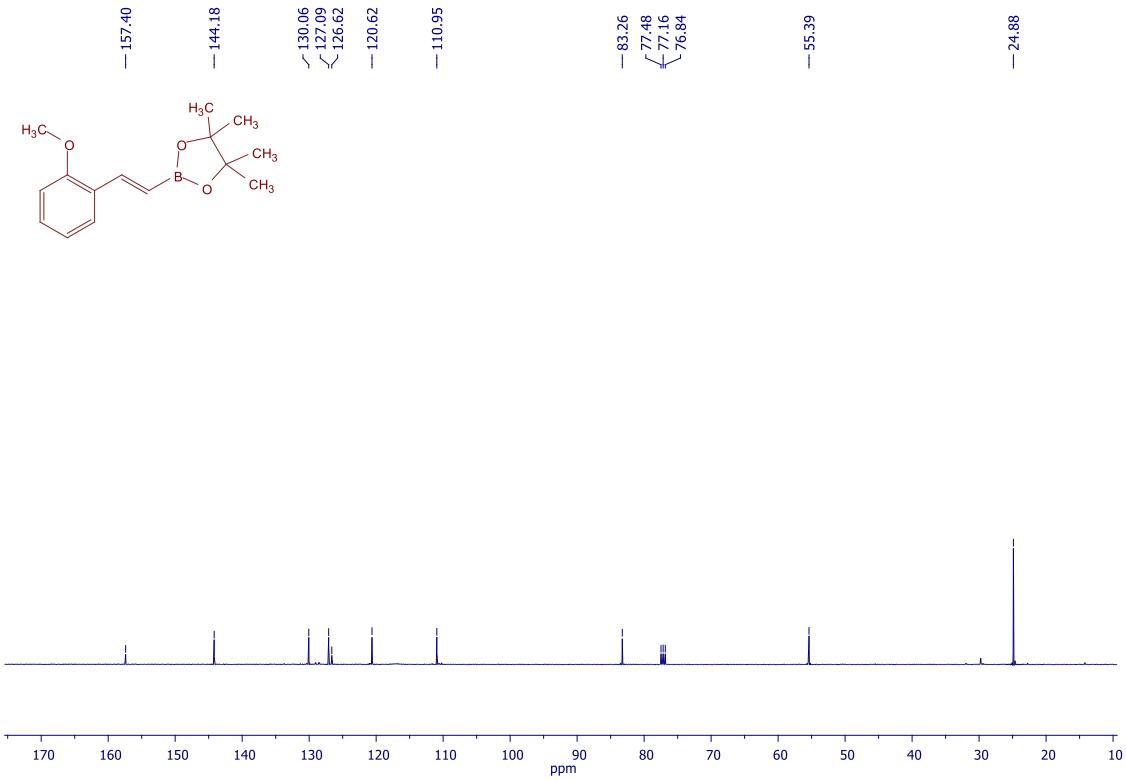
*^{13}C NMR of (E)-4,4,5,5-tetramethyl-2-(4-methoxystyryl)-1,3,2-dioxaborolane (Table 2, compound **E-8**)*



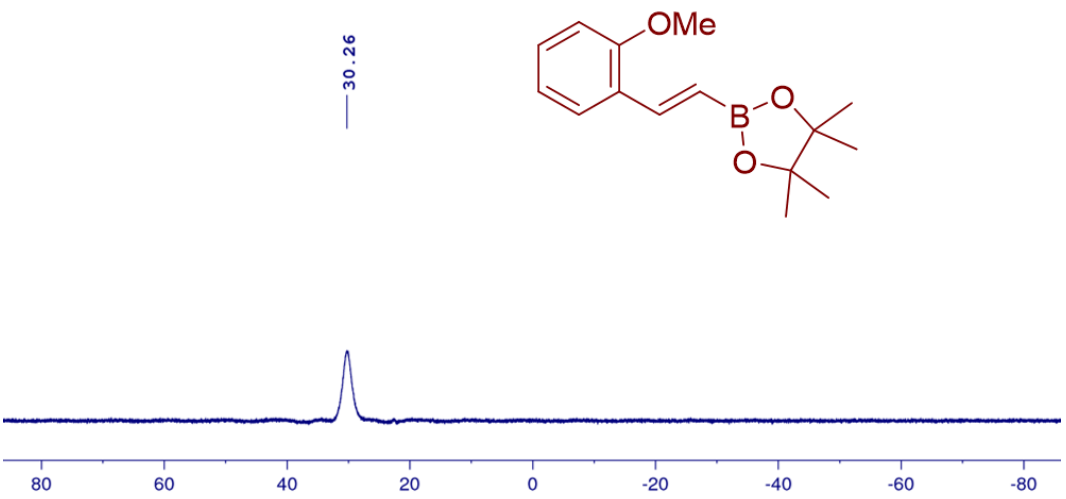
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(4-methoxystyryl)-1,3,2-dioxaborolane (Table 2, compound **E-8**)*



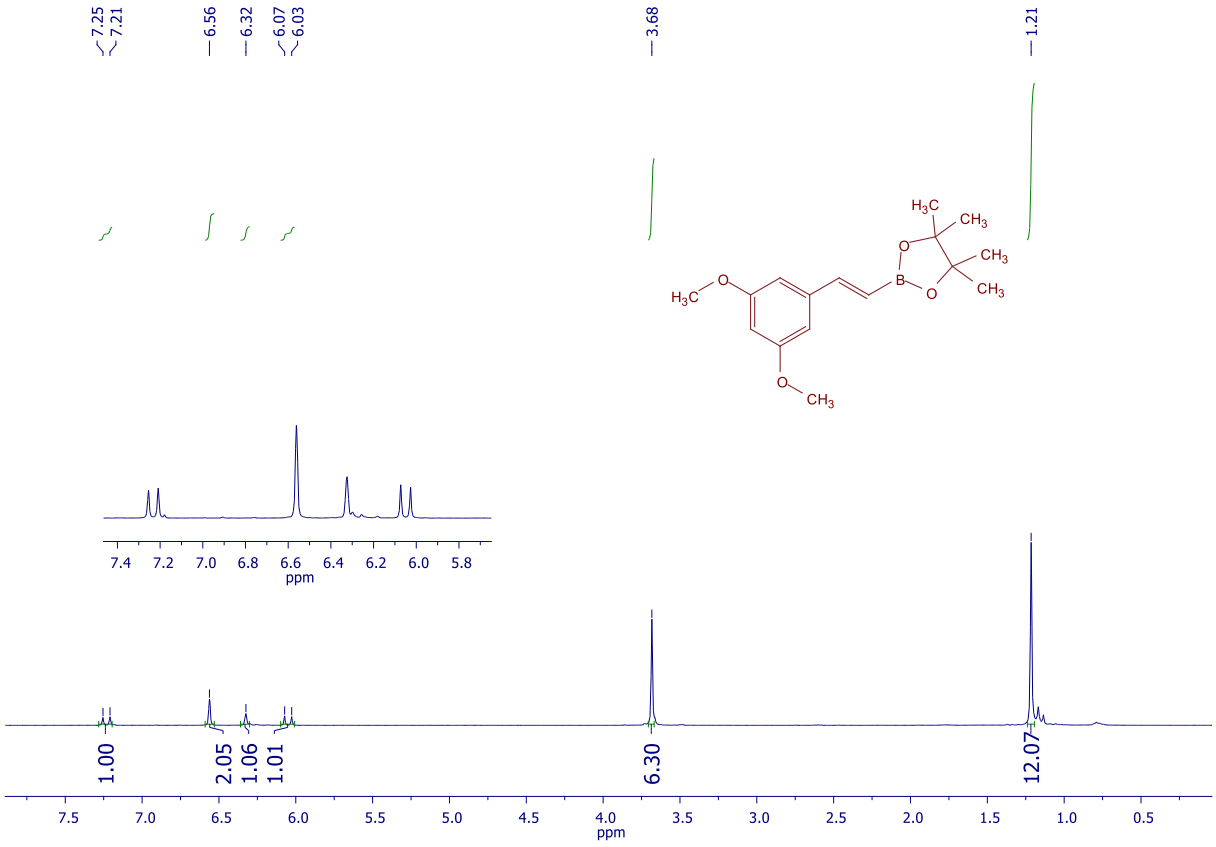
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(2-methoxystyryl)-1,3,2-dioxaborolane (Table 2, compound **E-9**)*



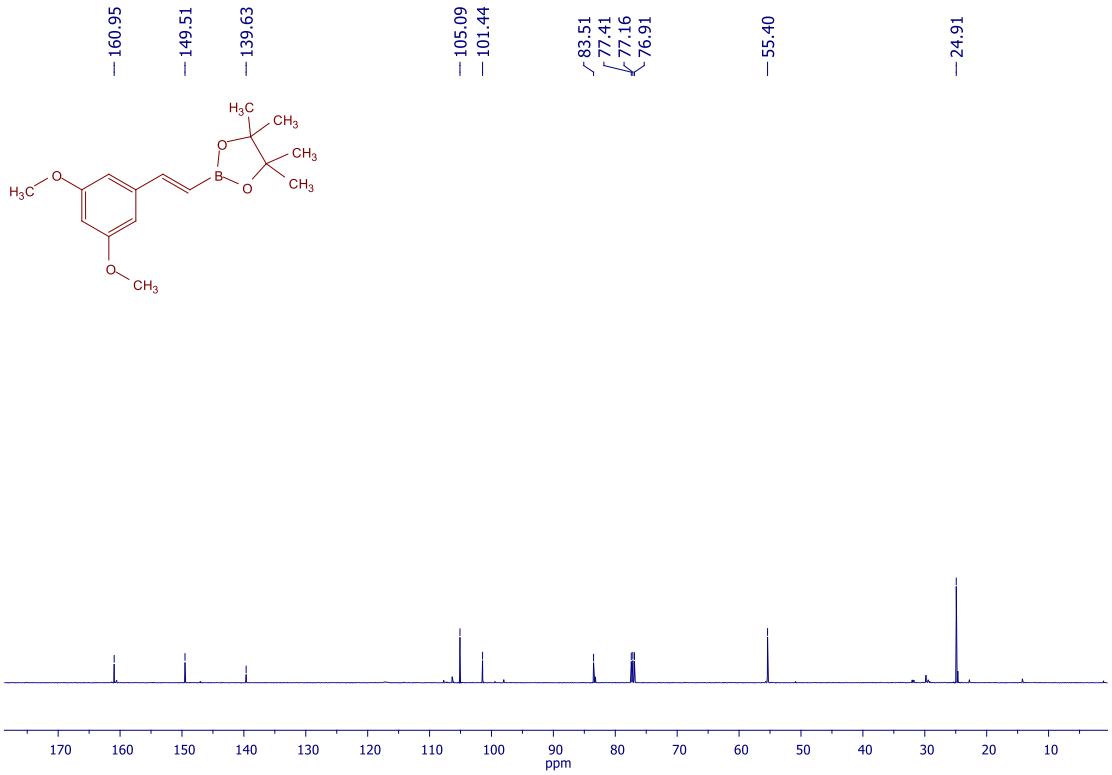
*^{13}C NMR of (E)-4,4,5,5-tetramethyl-2-(2-methoxystyryl)-1,3,2-dioxaborolane (Table 2, compound **E-9**)*



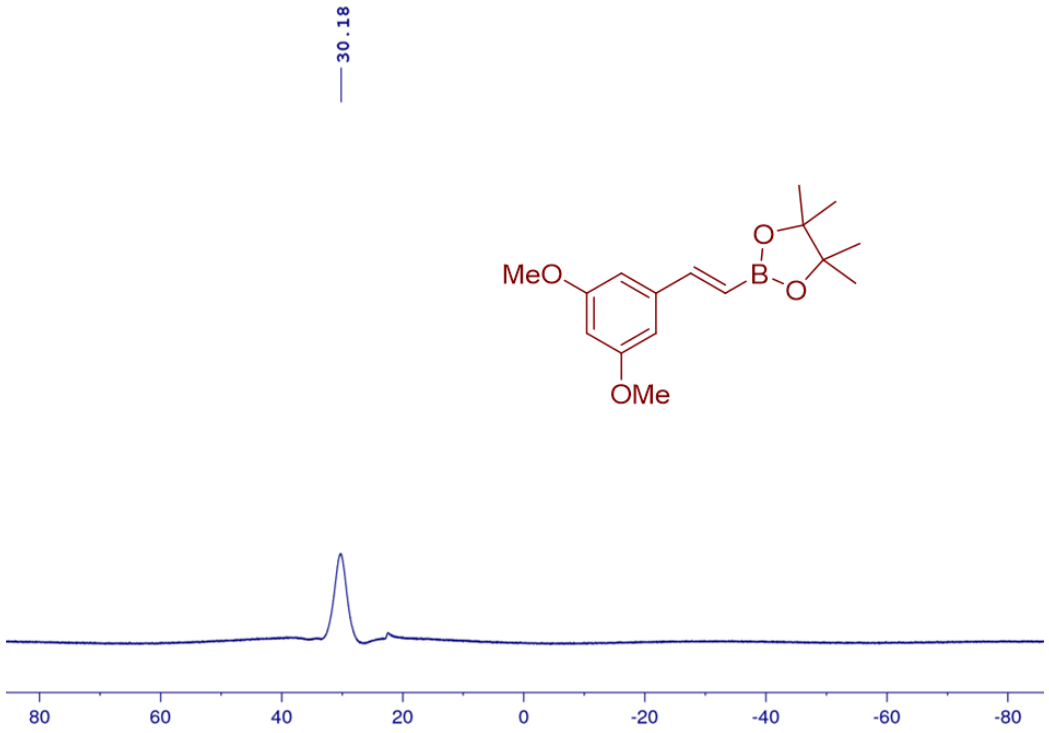
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(2-methoxystyryl)-1,3,2-dioxaborolane (Table 2, compound **E-9**)*



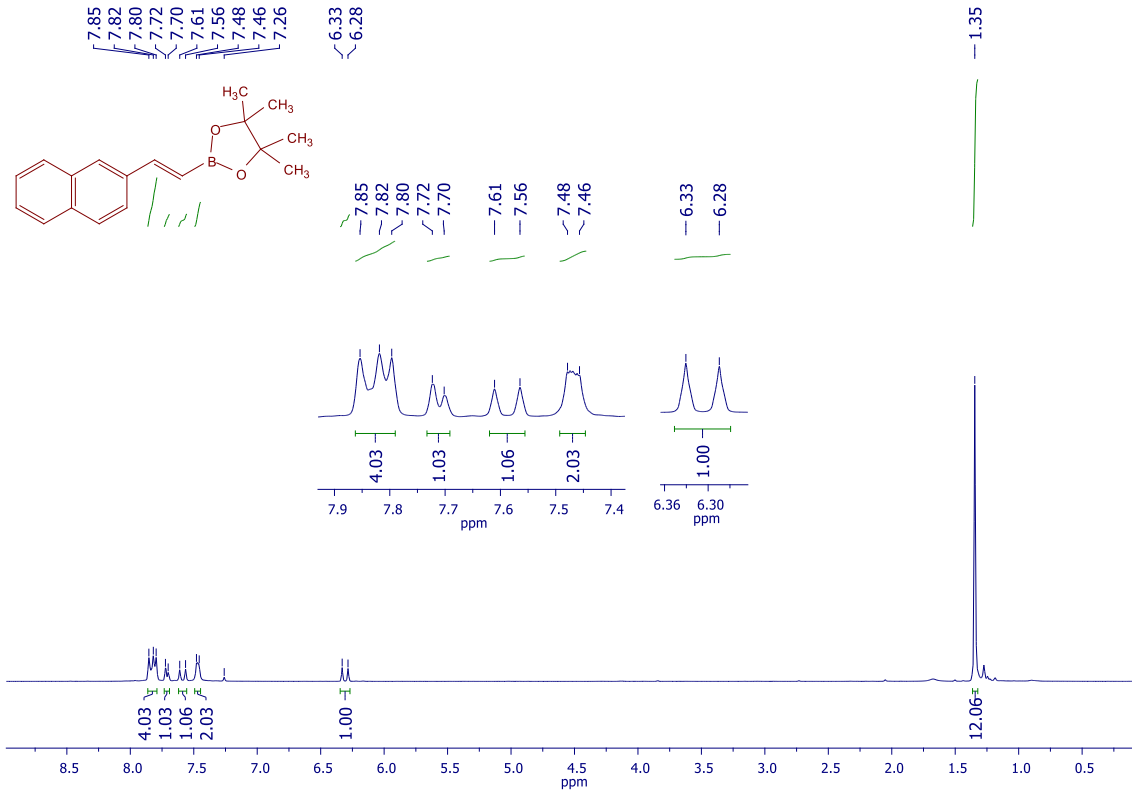
*^{1}H NMR of (E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-10**)*



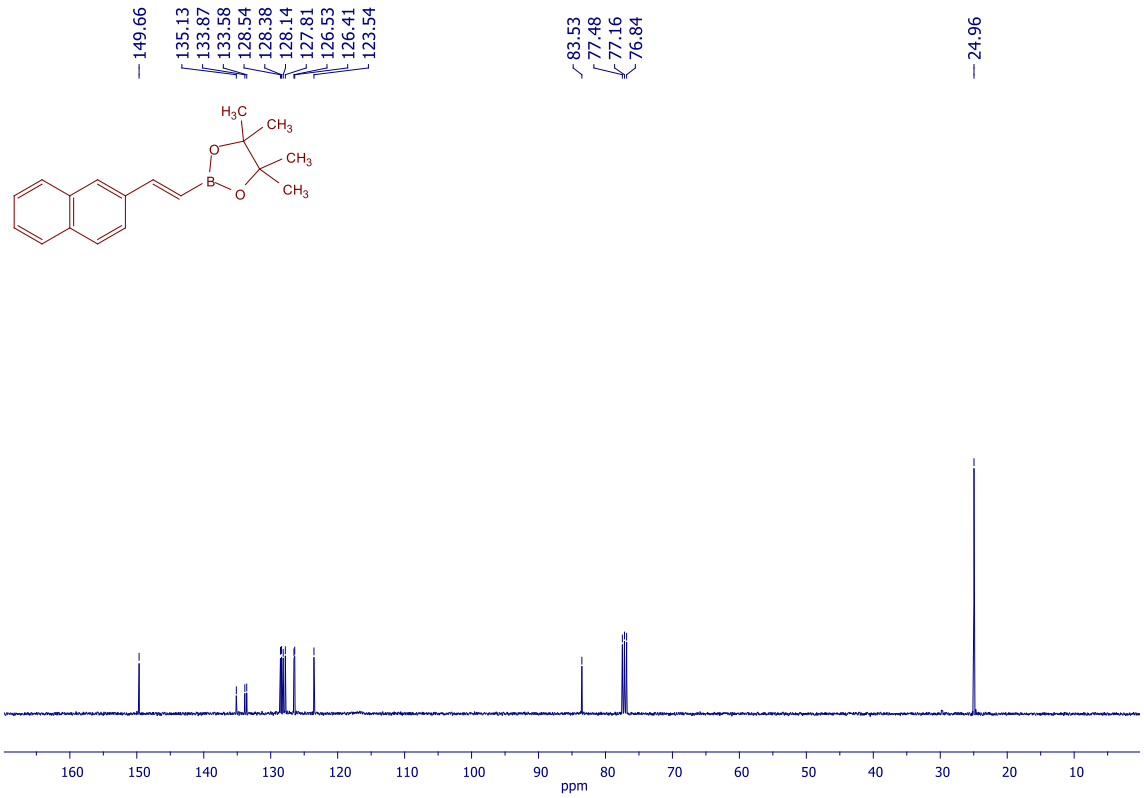
*^{13}C NMR of (E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-10**)*



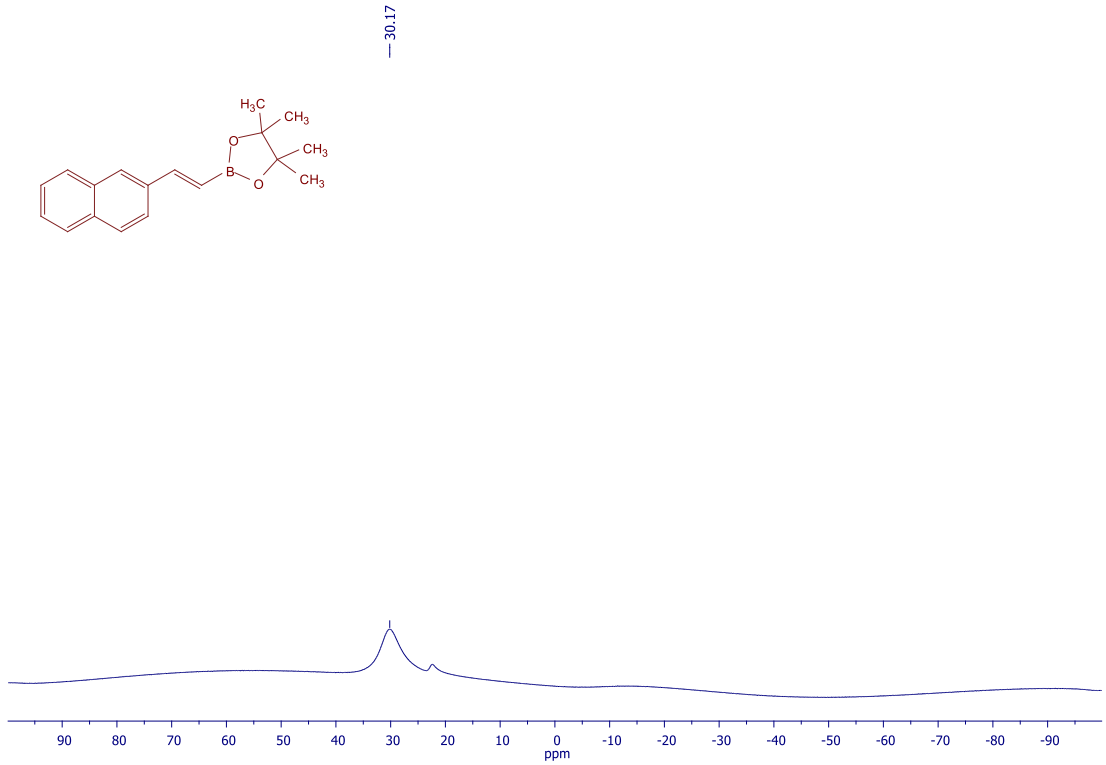
*^{11}B NMR of (E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-10**)*



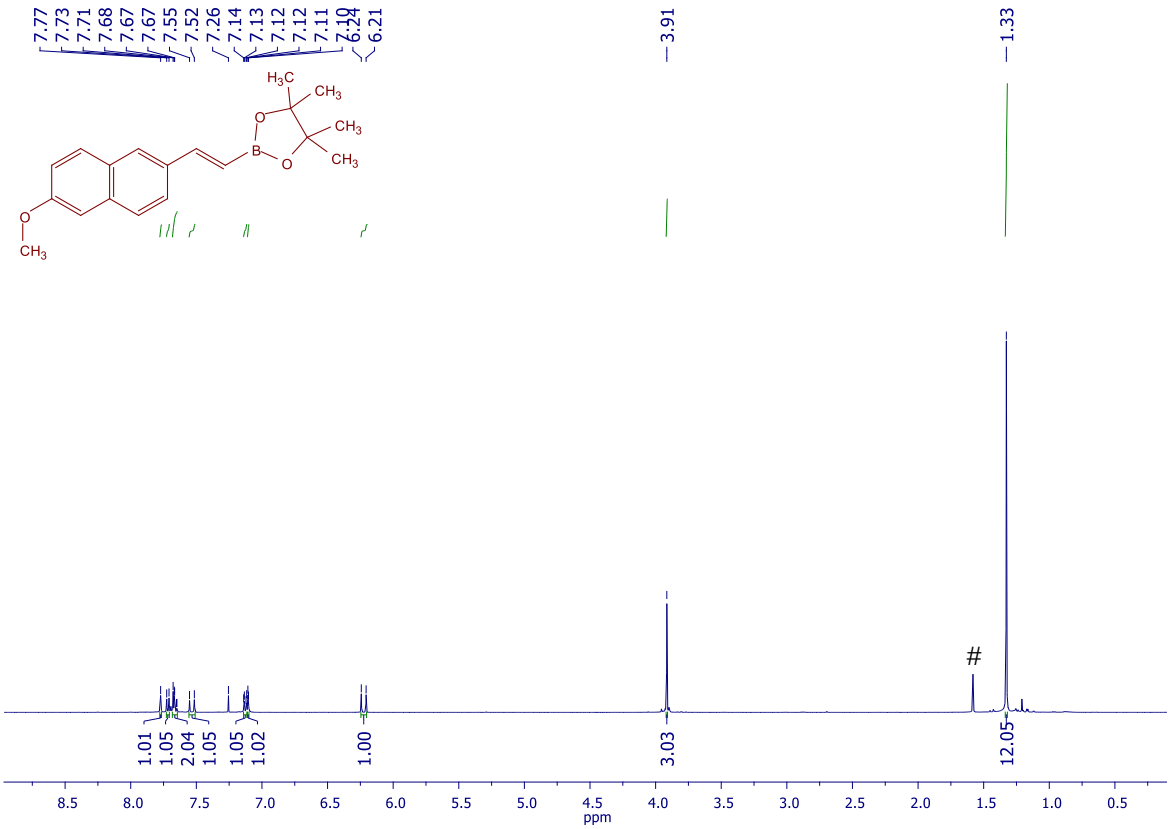
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Table 2,compound **E-11**)*



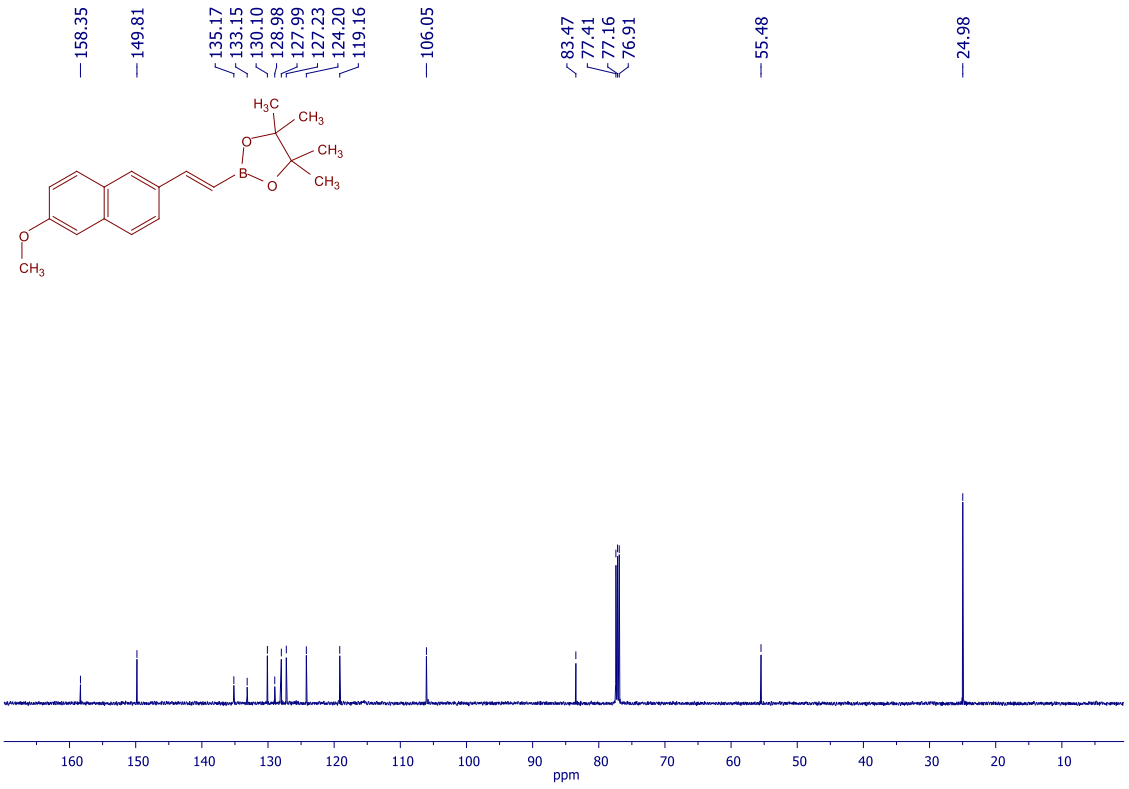
*[13]C NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Table 2,compound **E-11**)*



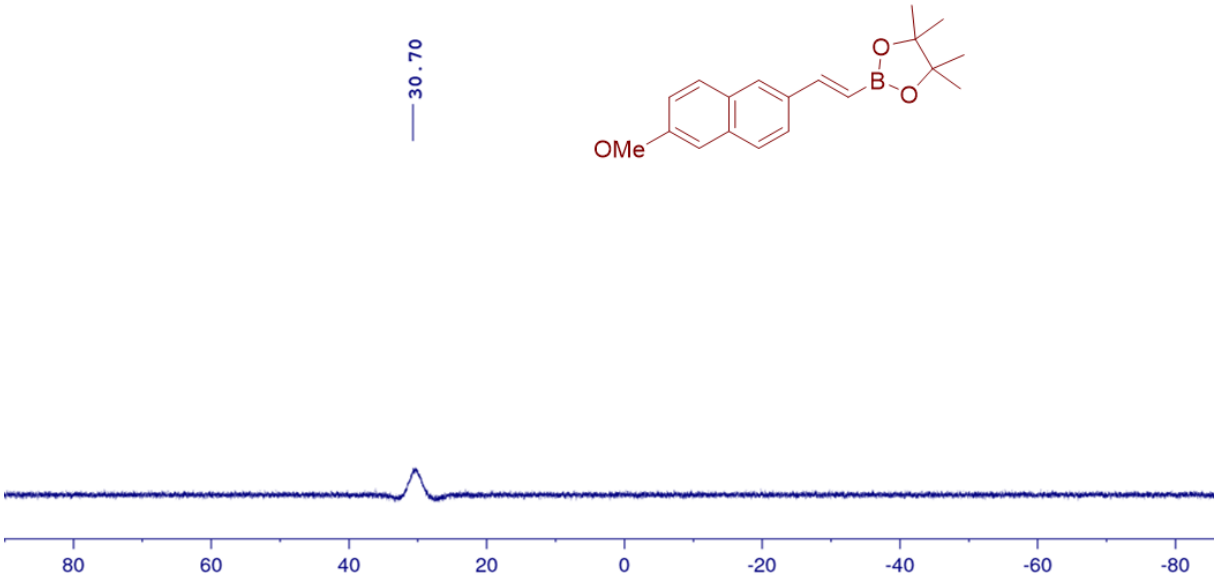
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Table 2,compound **E-11**)*



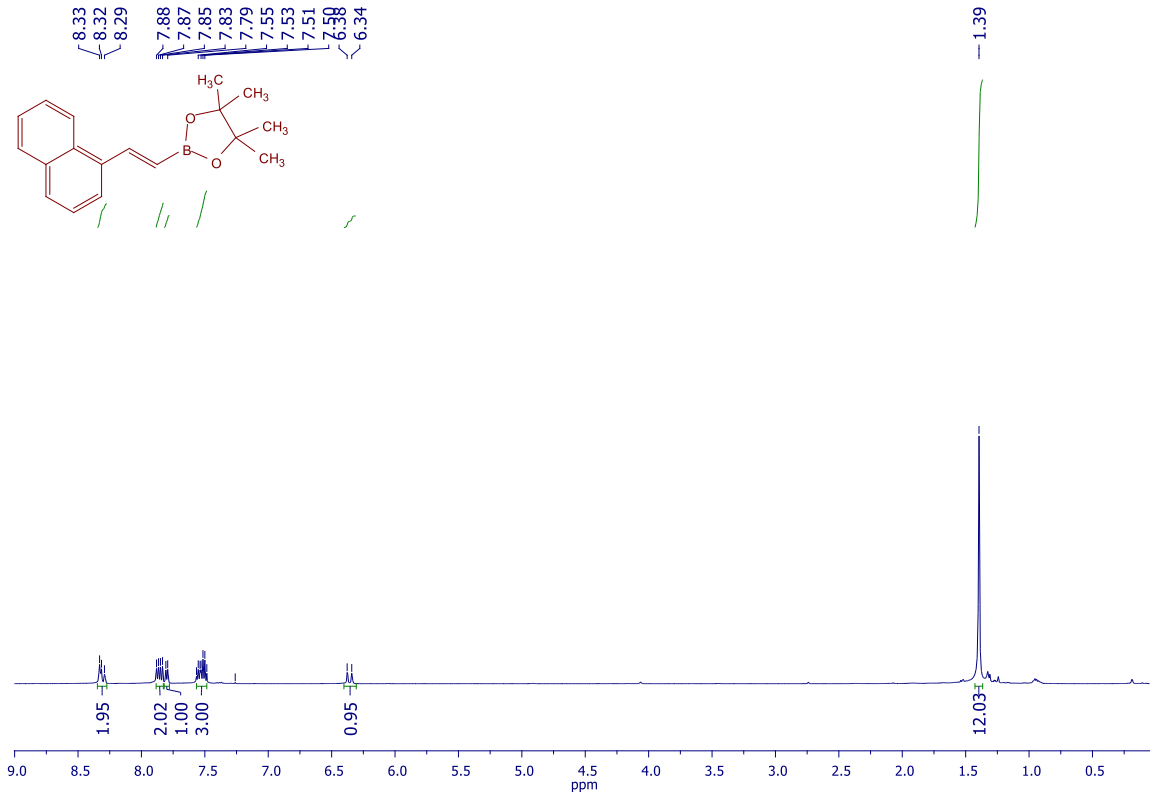
*[1]H NMR of (E)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2,compound **E-12**). # indicates solvent impurity of H_2O in $CDCl_3$.*



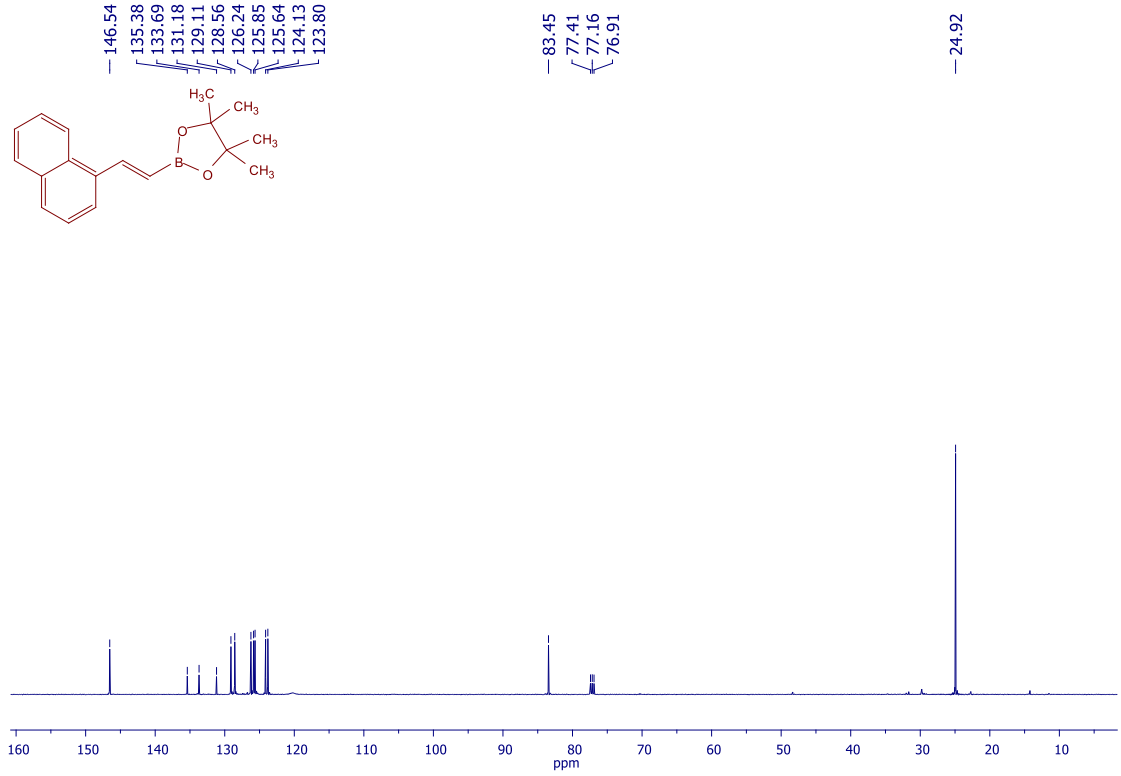
*^{13}C NMR of (E)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2,compound **E-12**)*



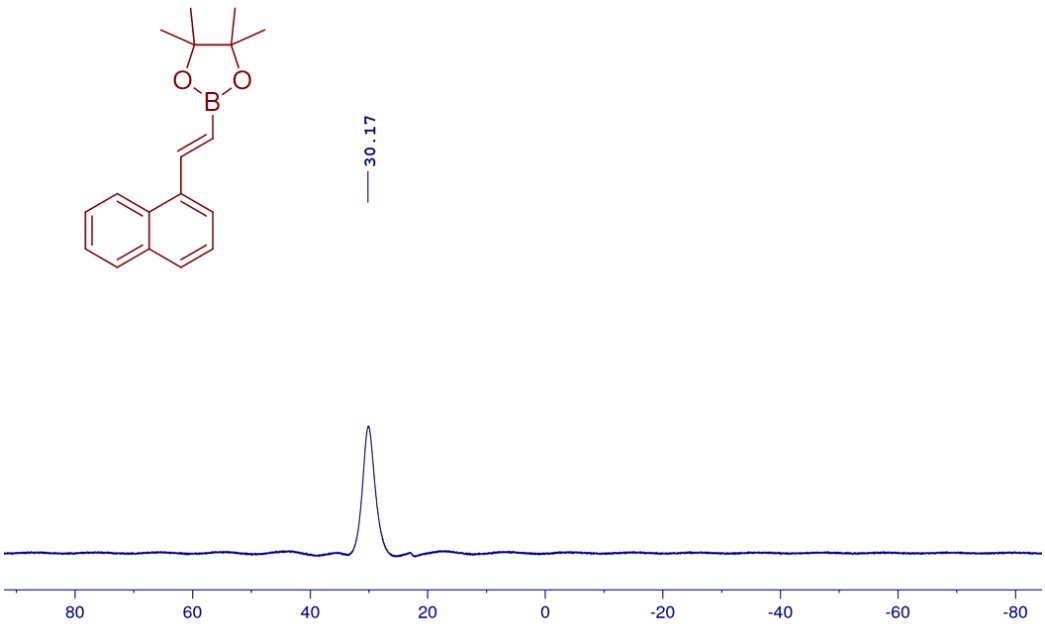
*^{11}B NMR of (E)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2,compound **E-12**)*



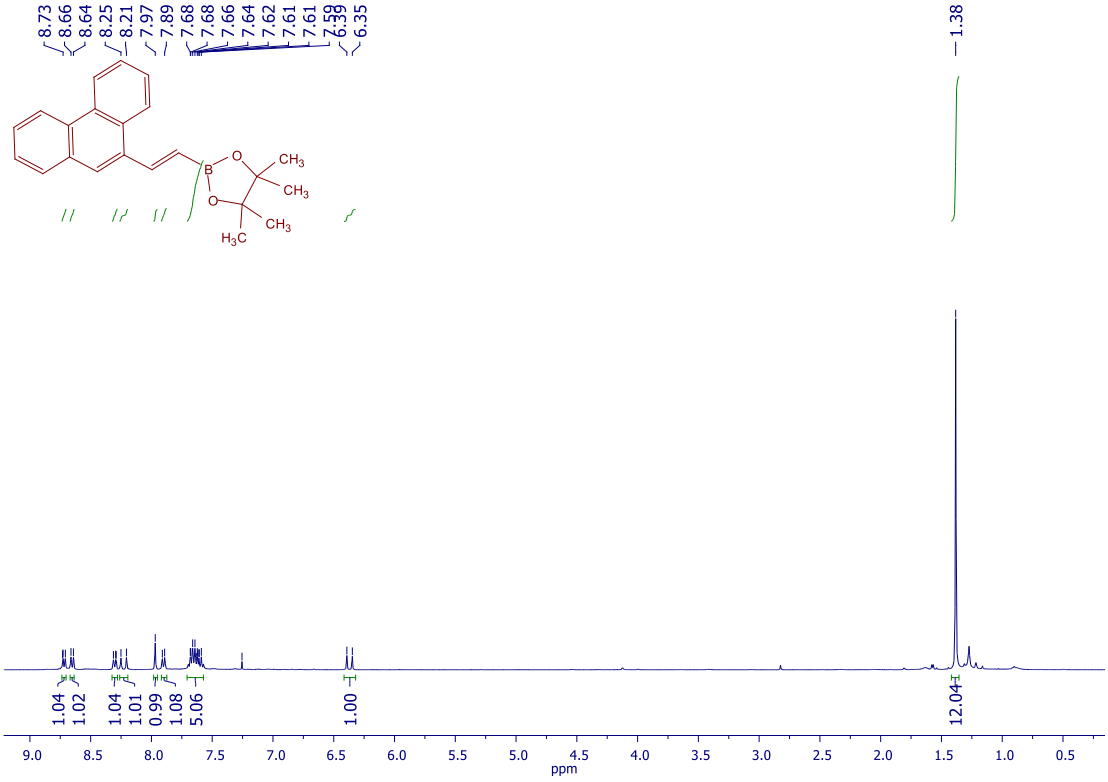
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-13**)*



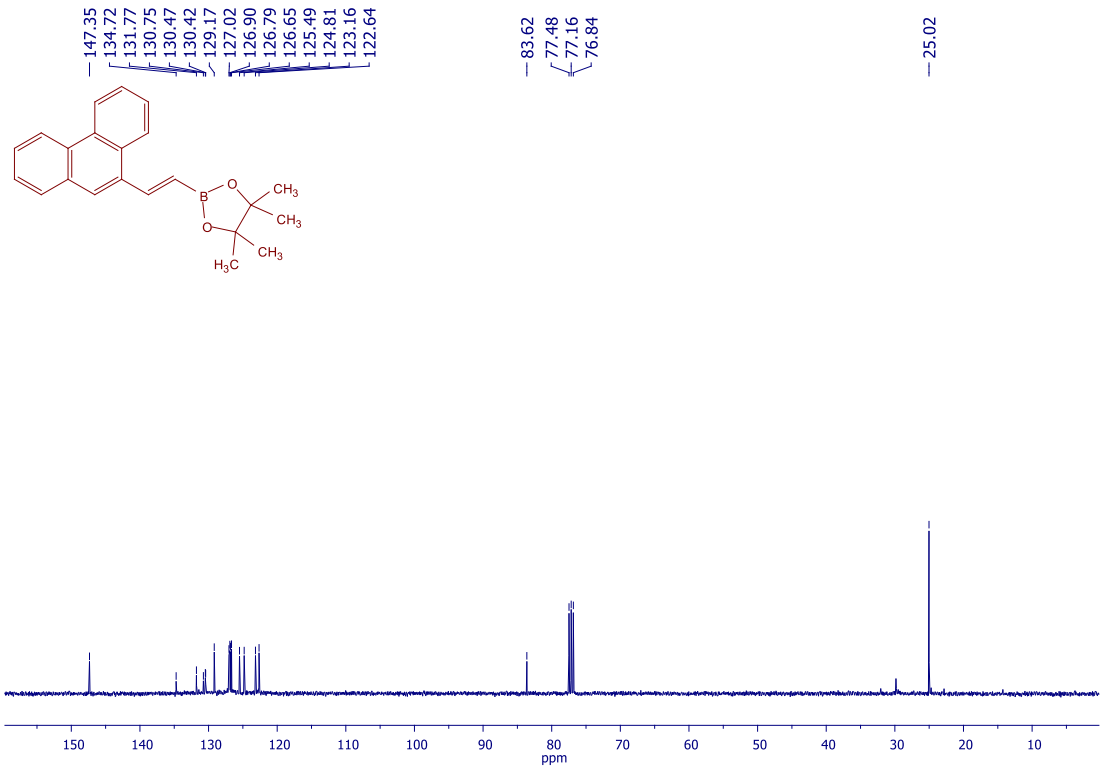
*[13]C NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-13**)*



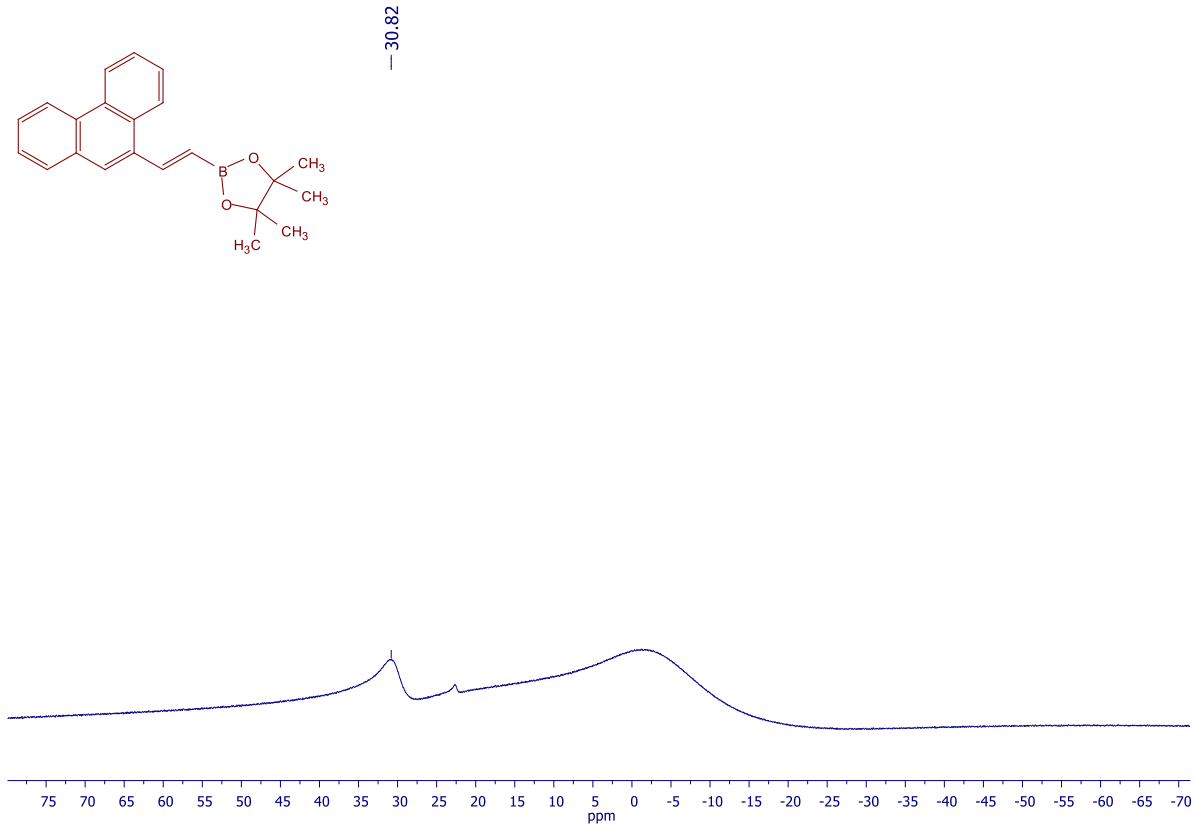
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-13**)*



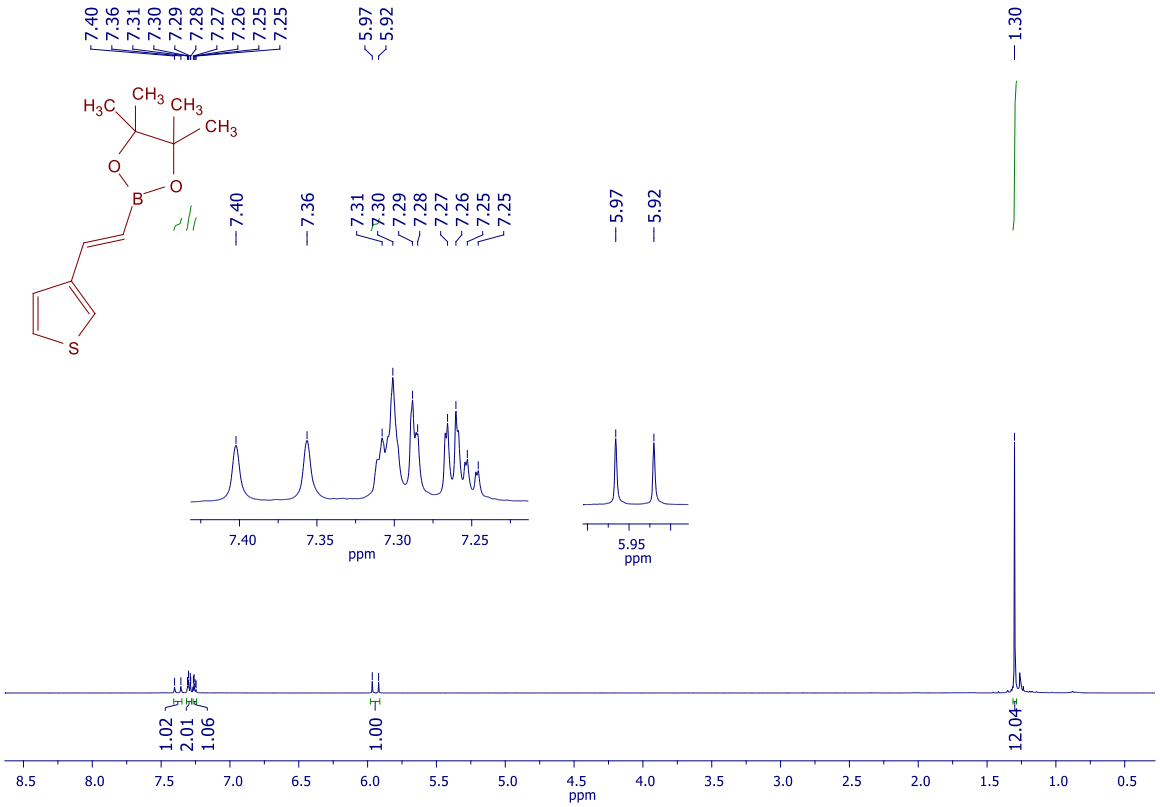
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (Table 2,compound **E-14**)*



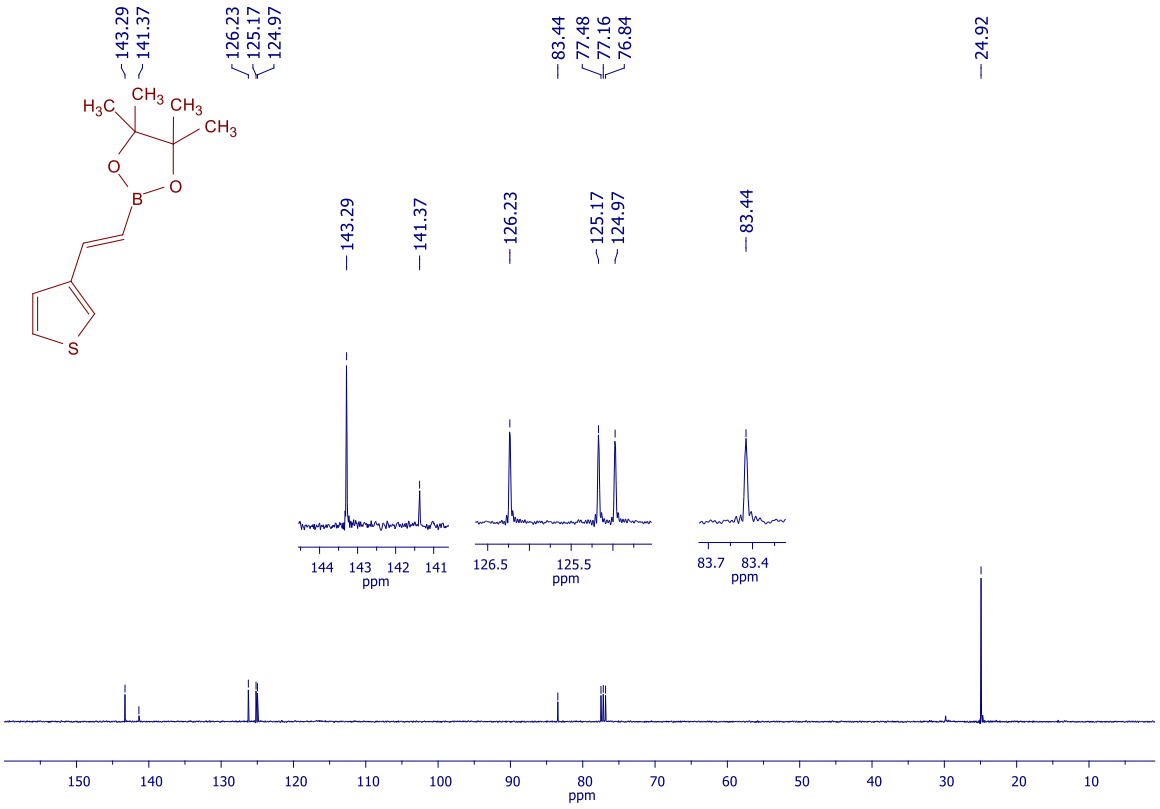
*[13]C NMR of (E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (Table 2,compound **E-14**)*



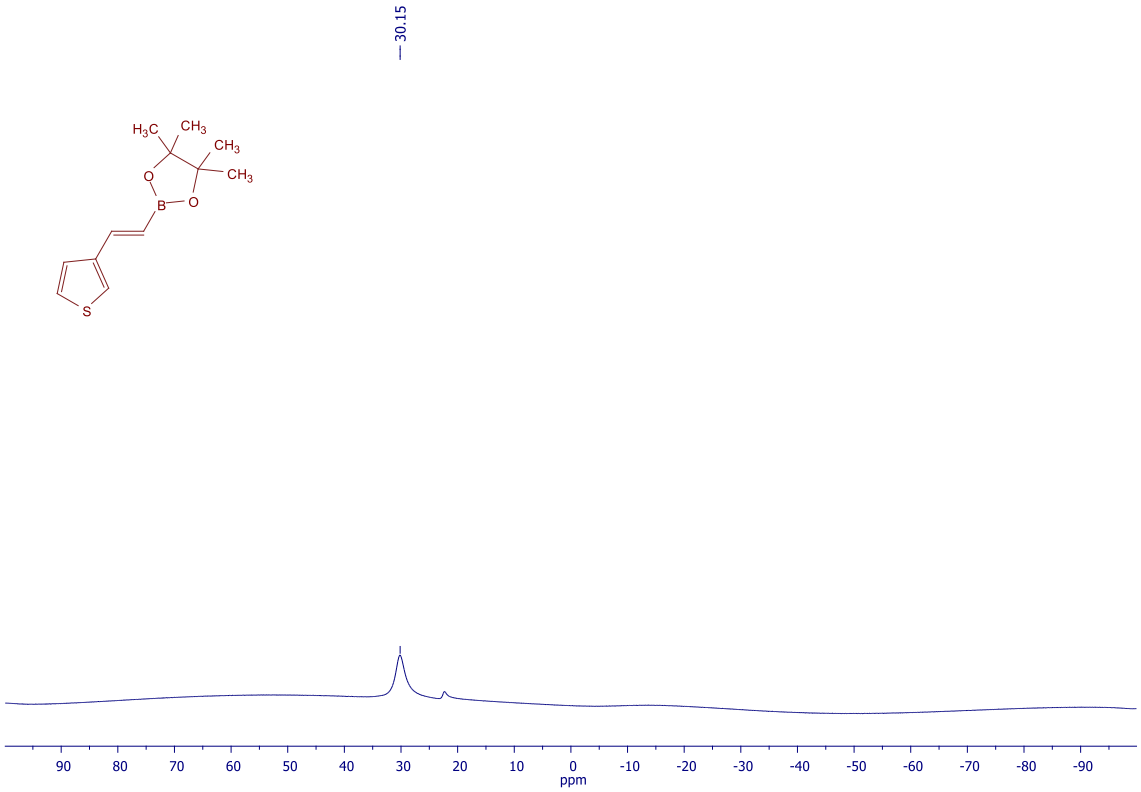
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (Table 2,compound **E-14**)*



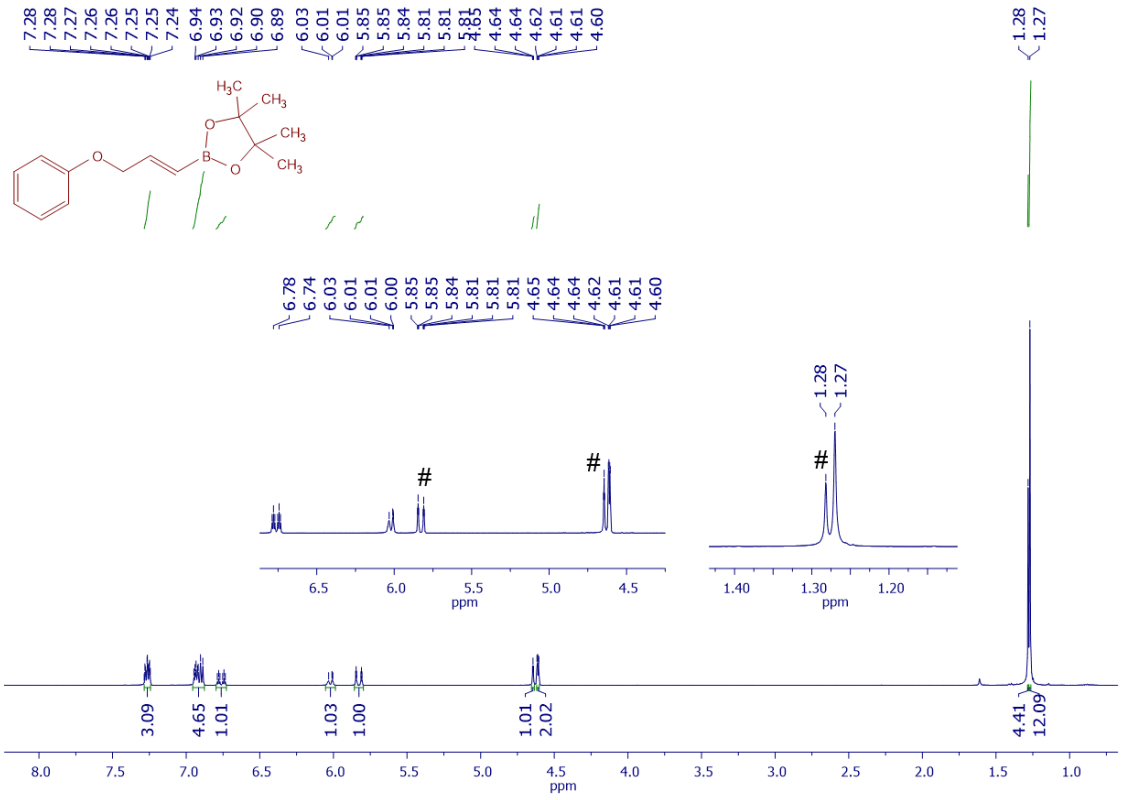
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-15**)*



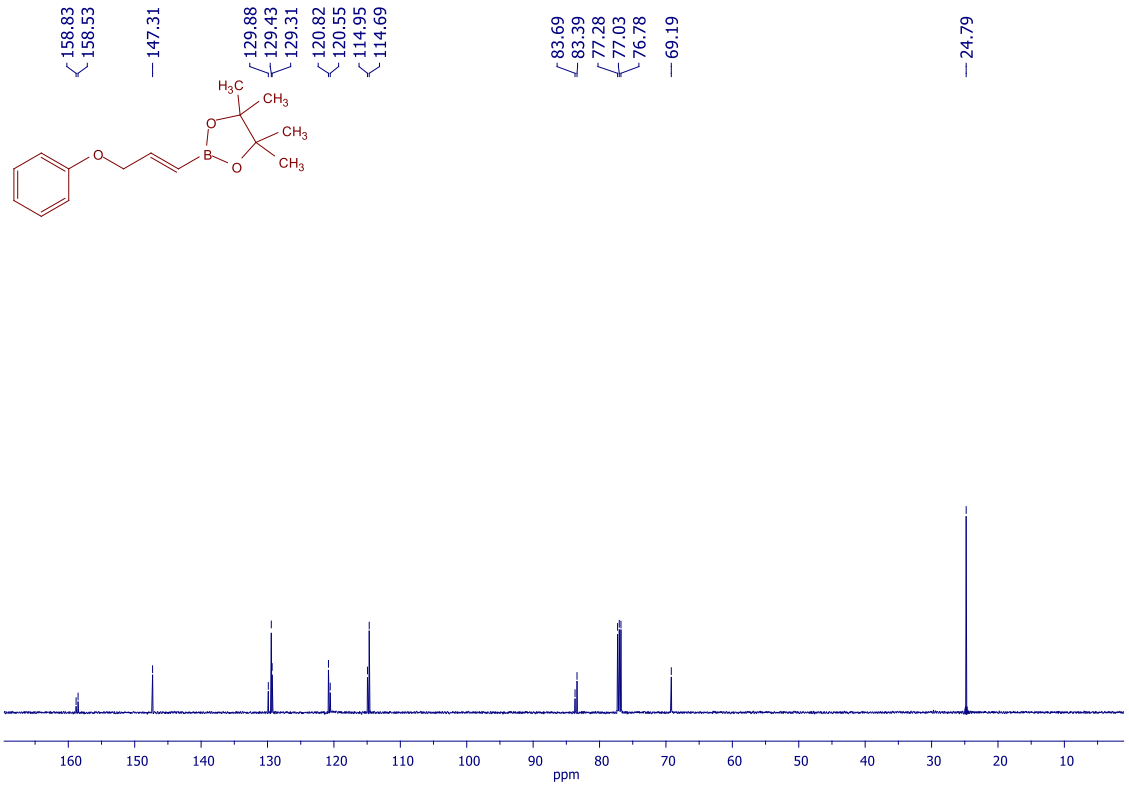
*[13]C NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-15**)*



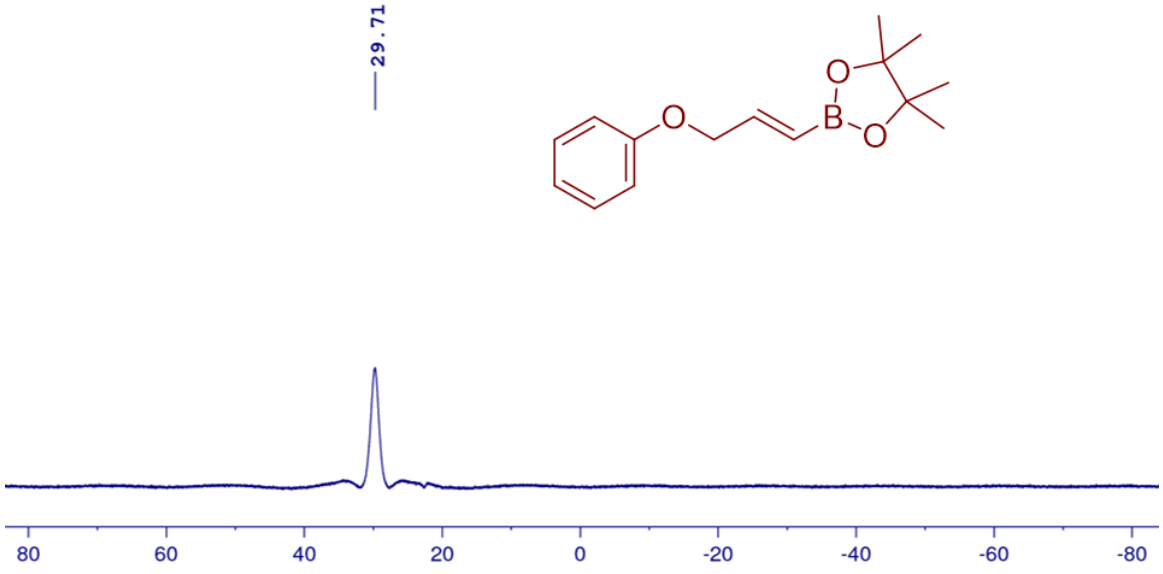
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Table 2, compound **E-15**)*



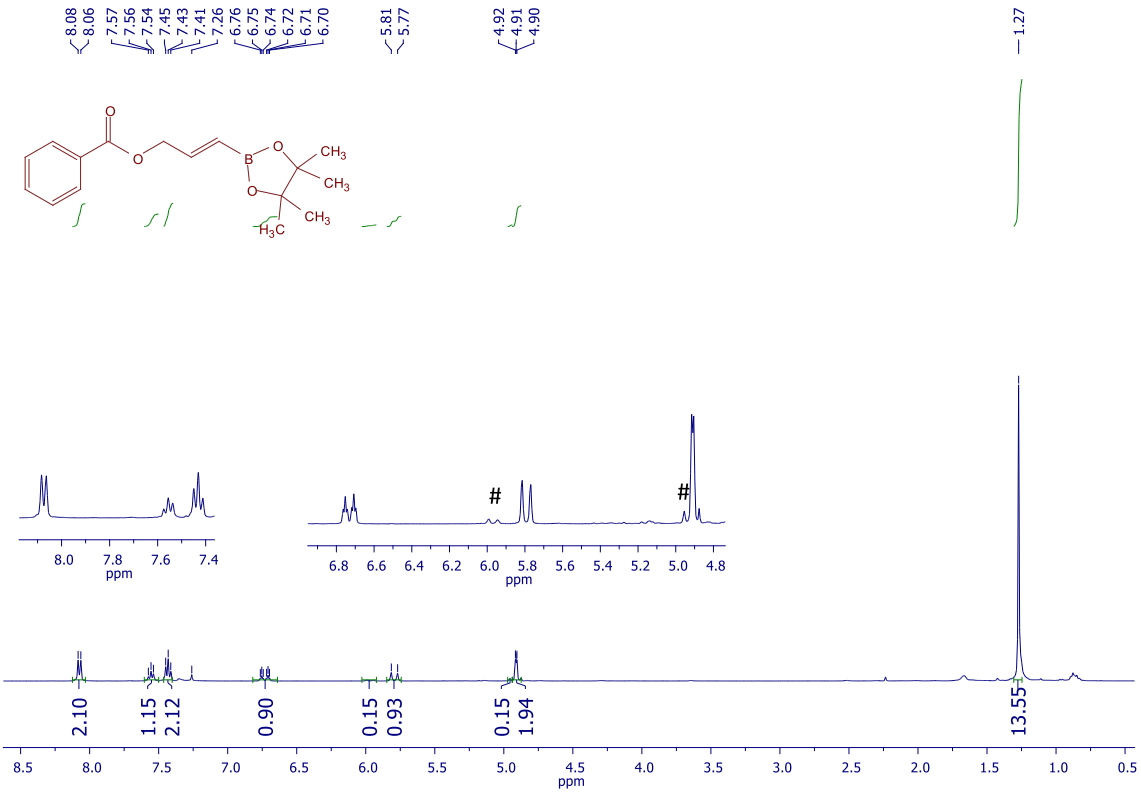
*[1]H NMR of 4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-2-yl)-1,3,2-dioxaborolane and (E)-4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (Table 2, **E-16**).* It is a mixture of the *α- (corresponding peaks are denoted by #)* and *β*-isomer in 27:73 ratio.[9]



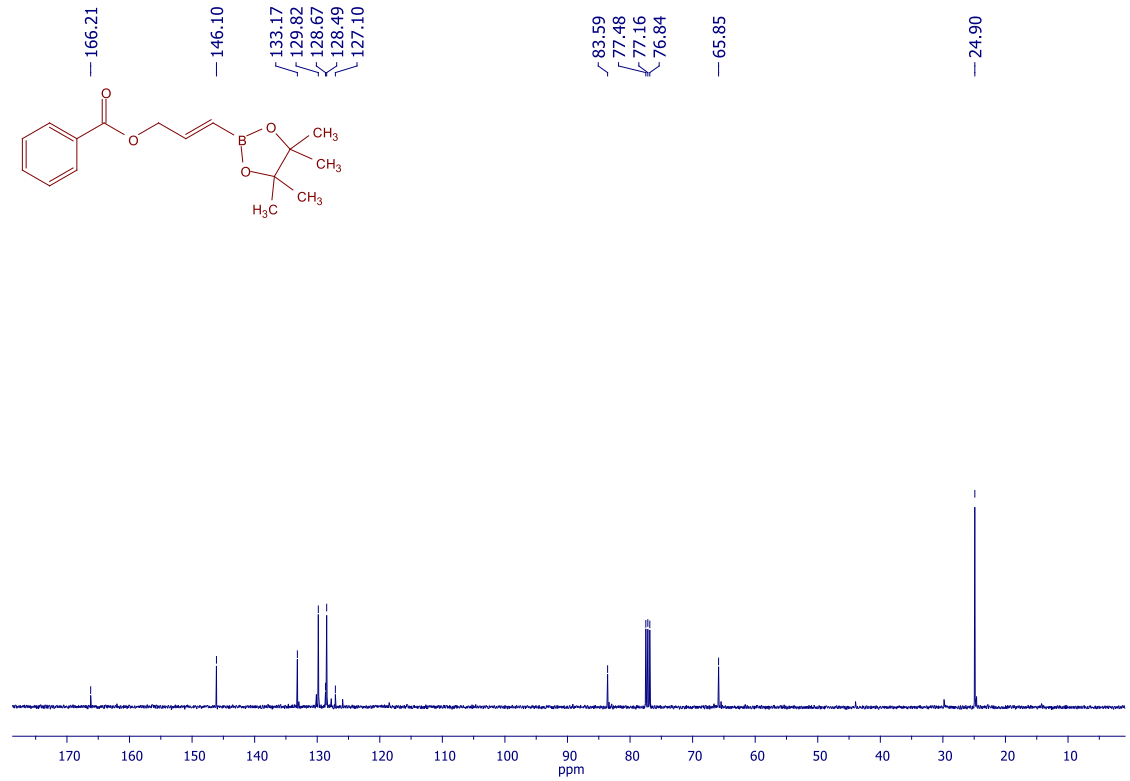
*^{13}C NMR of 4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-2-yl)-1,3,2-dioxaborolane and (E)-4,4,5,5-tetramethyl-2- (3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (Table 2, **E-16**)*



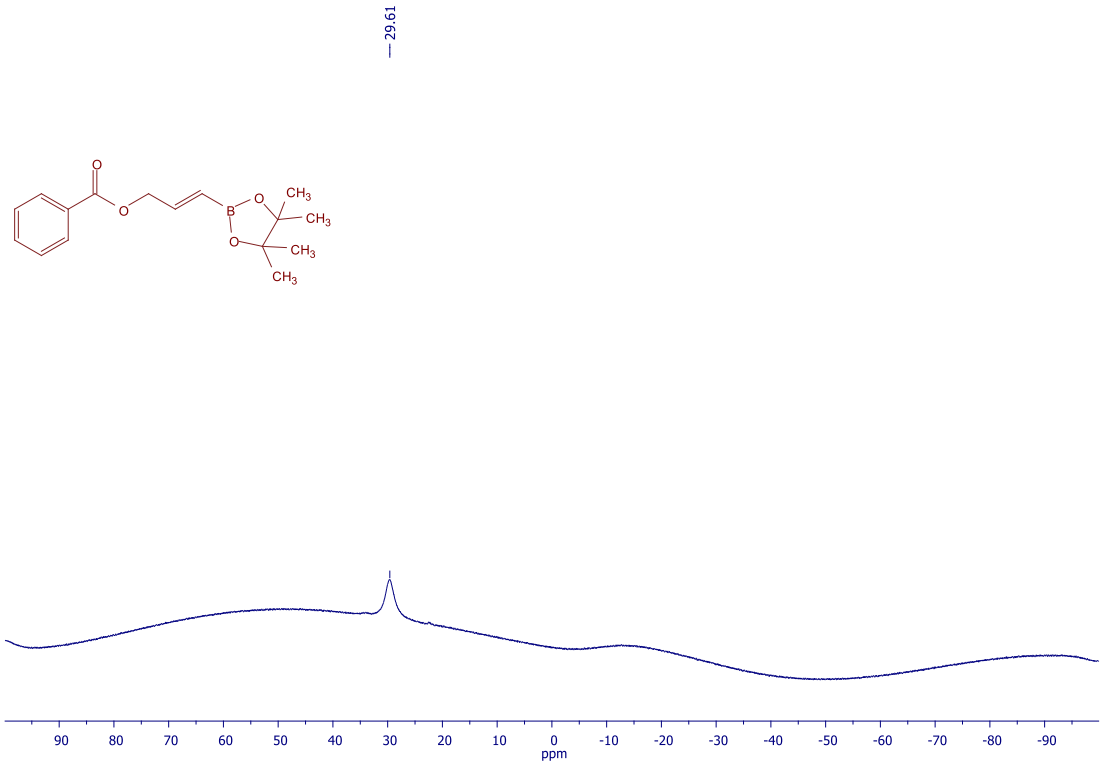
*^{1}H NMR of 4,4,5,5-tetramethyl-2-(3-phenoxyprop-1-en-2-yl)-1,3,2-dioxaborolane and (E)-4,4,5,5-tetramethyl-2- (3-phenoxyprop-1-en-1-yl)-1,3,2-dioxaborolane (Table 2, **E-16**)*



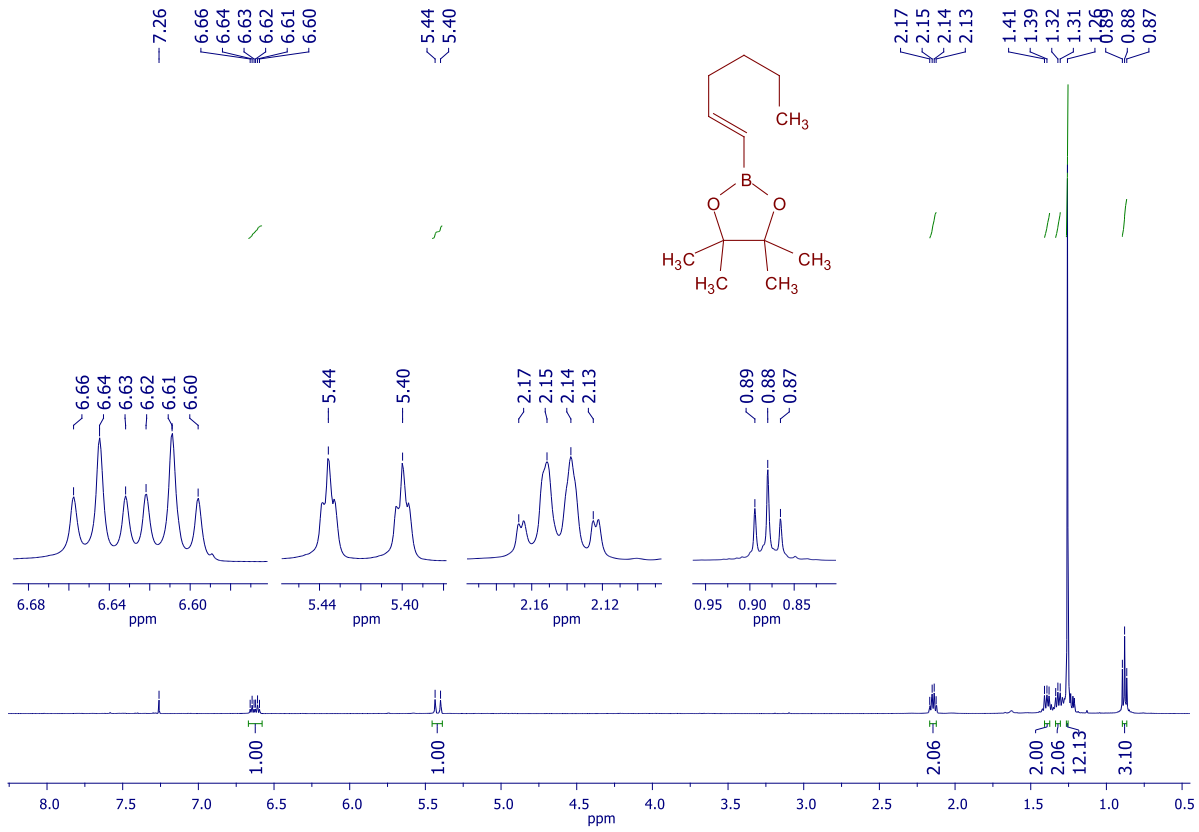
*[1]H NMR of (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate (Table 2, compound **E-17**). It is a mixture of the α-(corresponding peaks are marked by #) and β-isomer in 7:93 ratio.[3]*



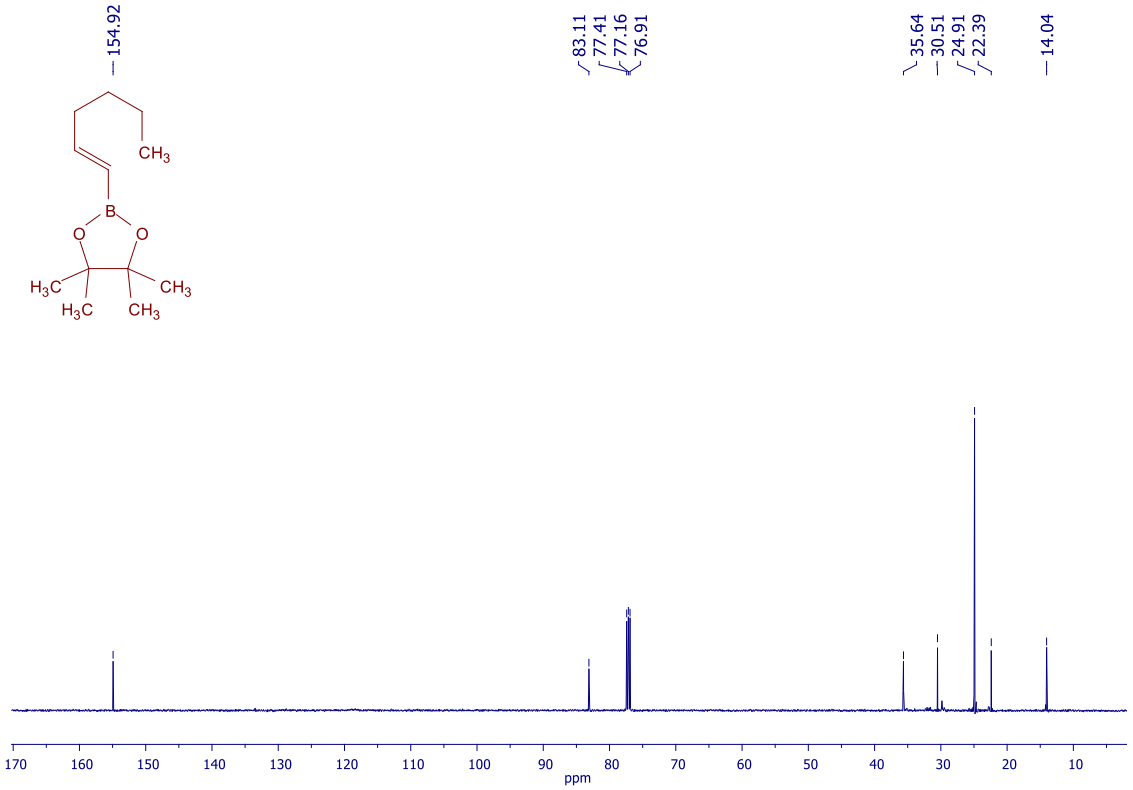
*[13]C NMR of (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate (Table 2, compound **E-17**)*



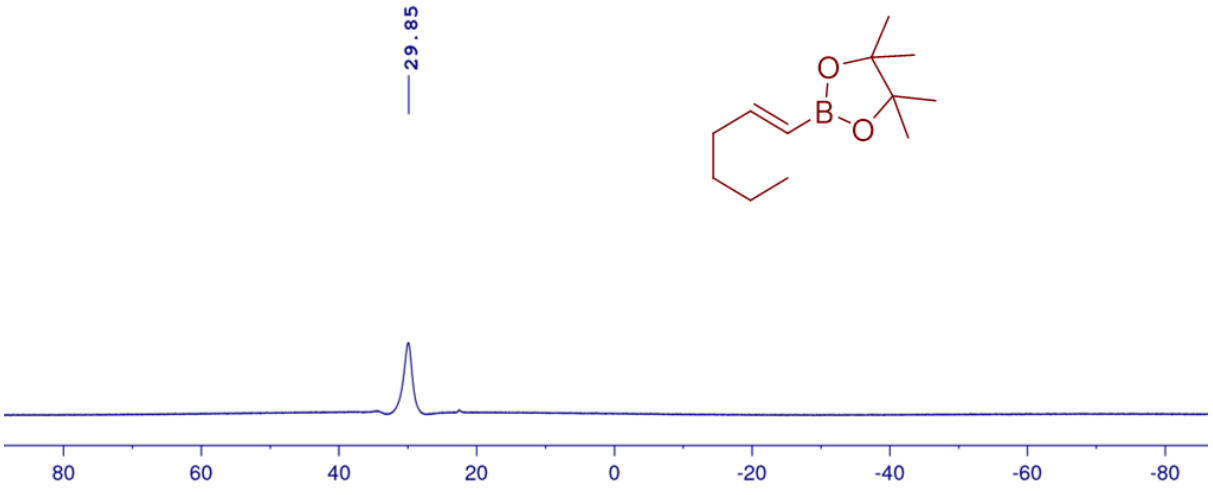
*^{13}B NMR of (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl benzoate (Table 2, compound **E-17**).*



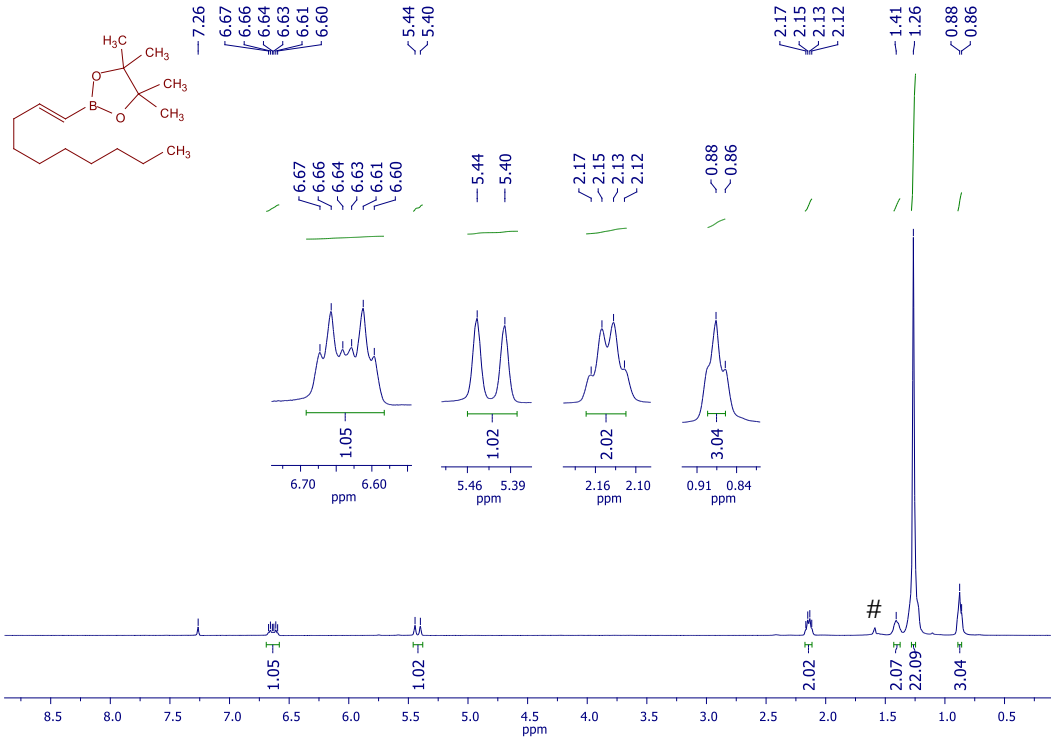
*^{1}H NMR of (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-18**)*



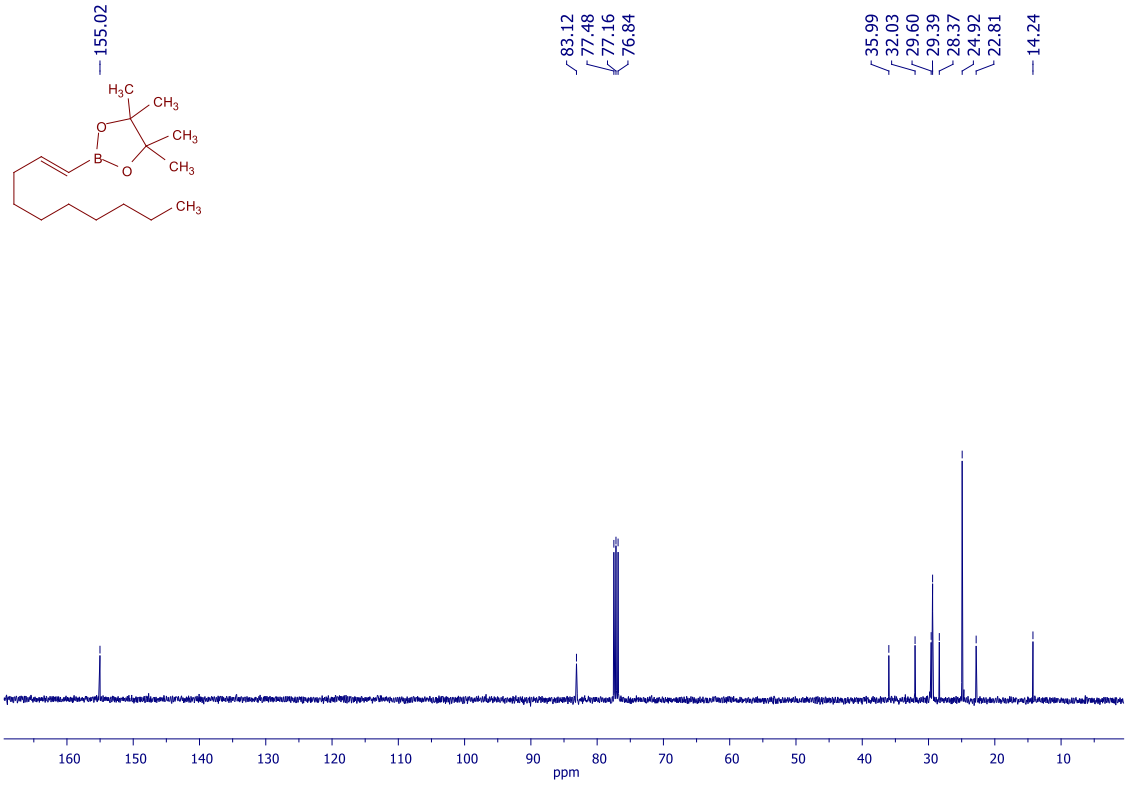
*^{13}C NMR of (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-18**)*



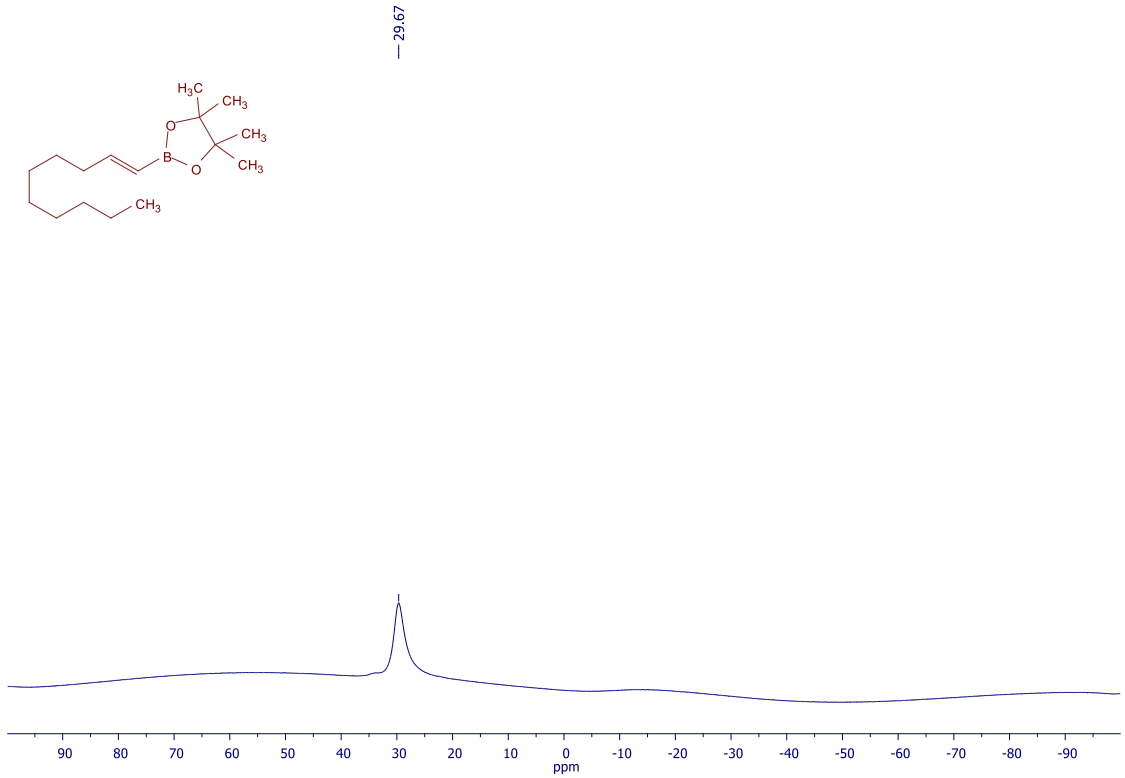
*^{11}B NMR of (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-18**)*



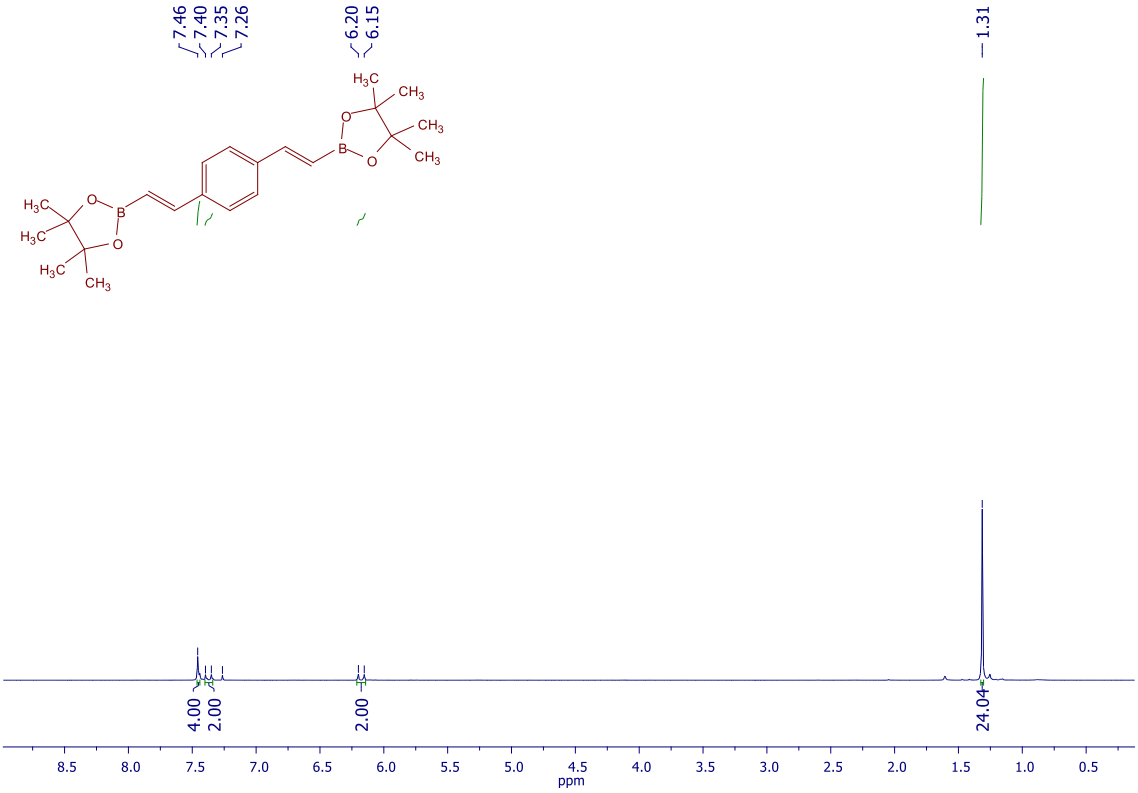
*^{1}H NMR of (E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-19**). # indicates solvent impurity of H_2O in $CDCl_3$.*



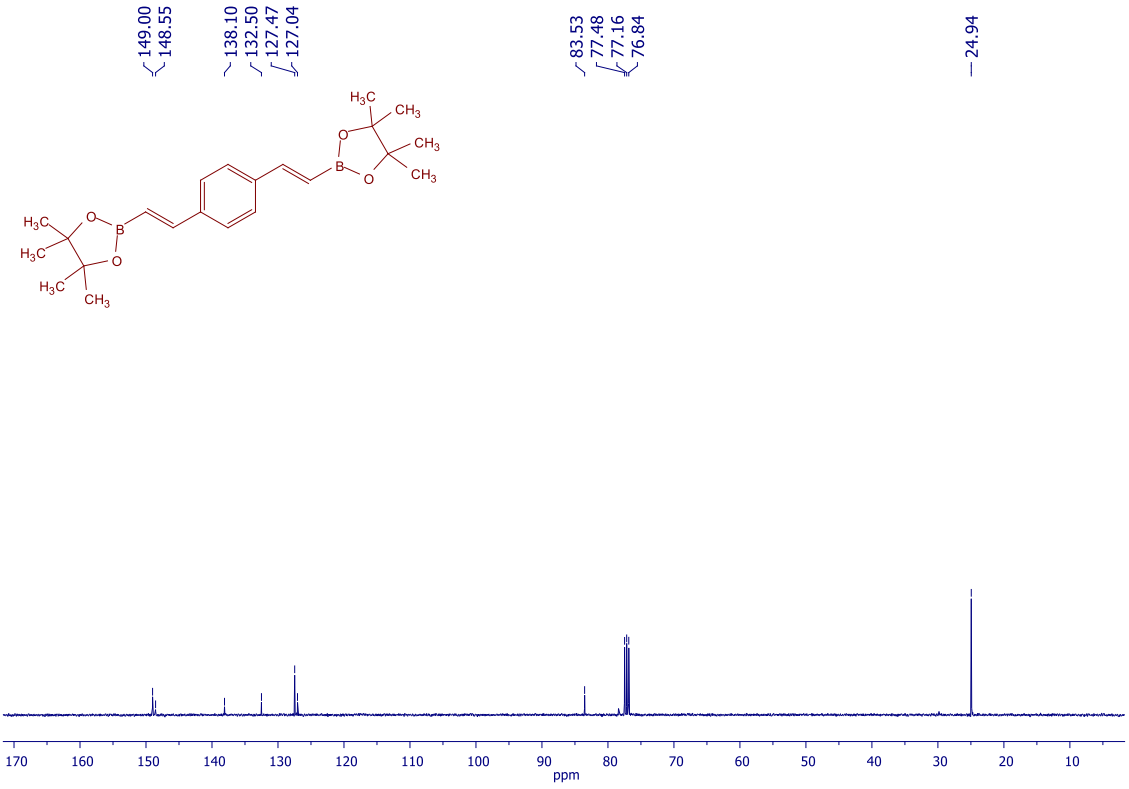
*^{13}C NMR of (E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-19**)*



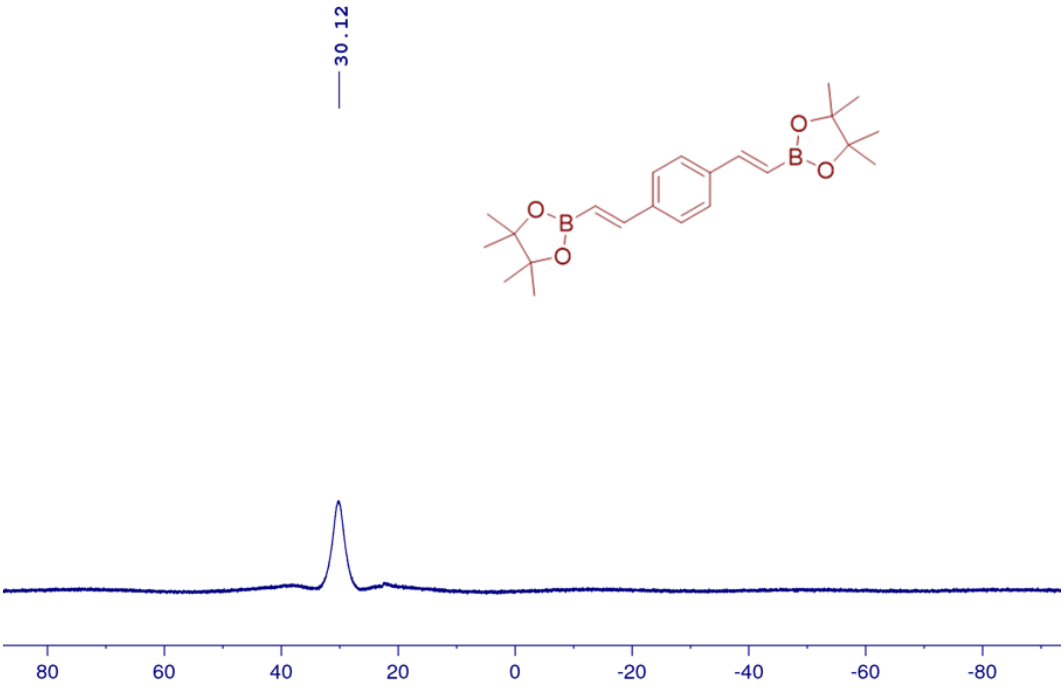
*^{11}B NMR of (E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, compound **E-19**)*



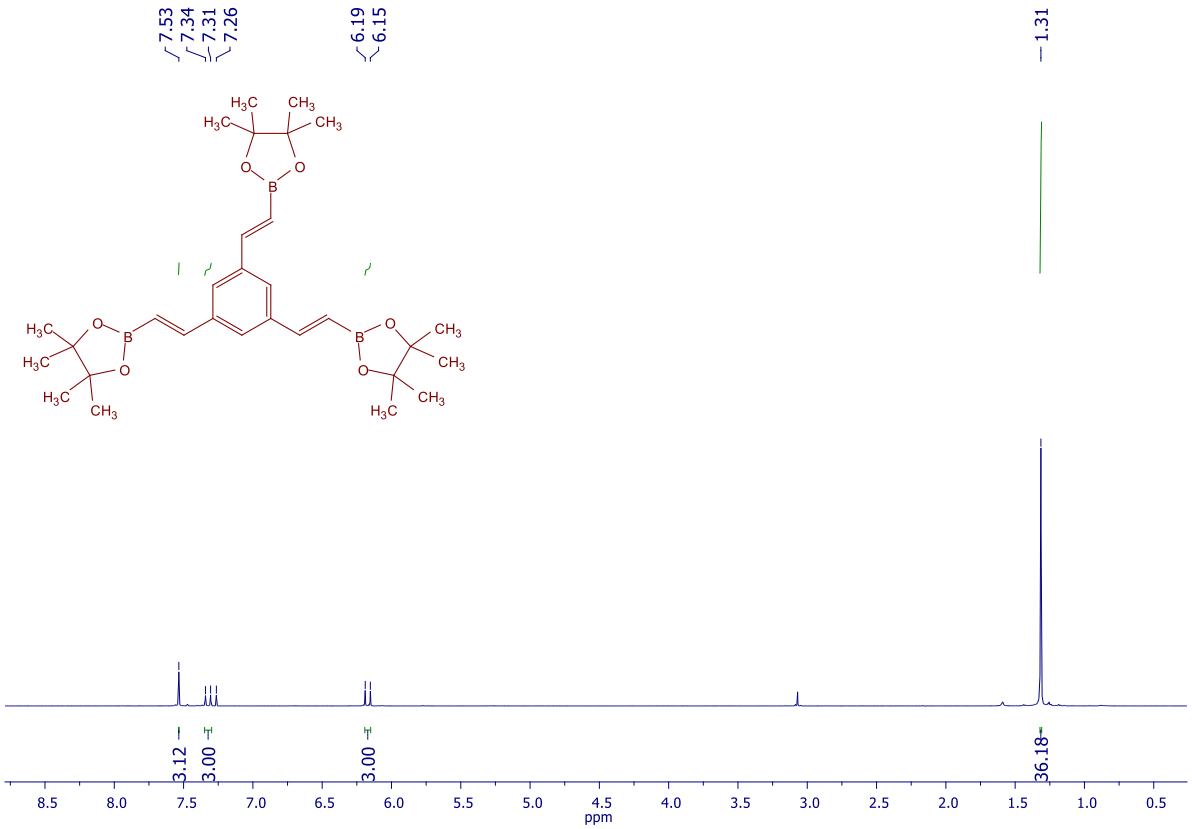
*^{1}H NMR of 1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2, compound **E-20**)*



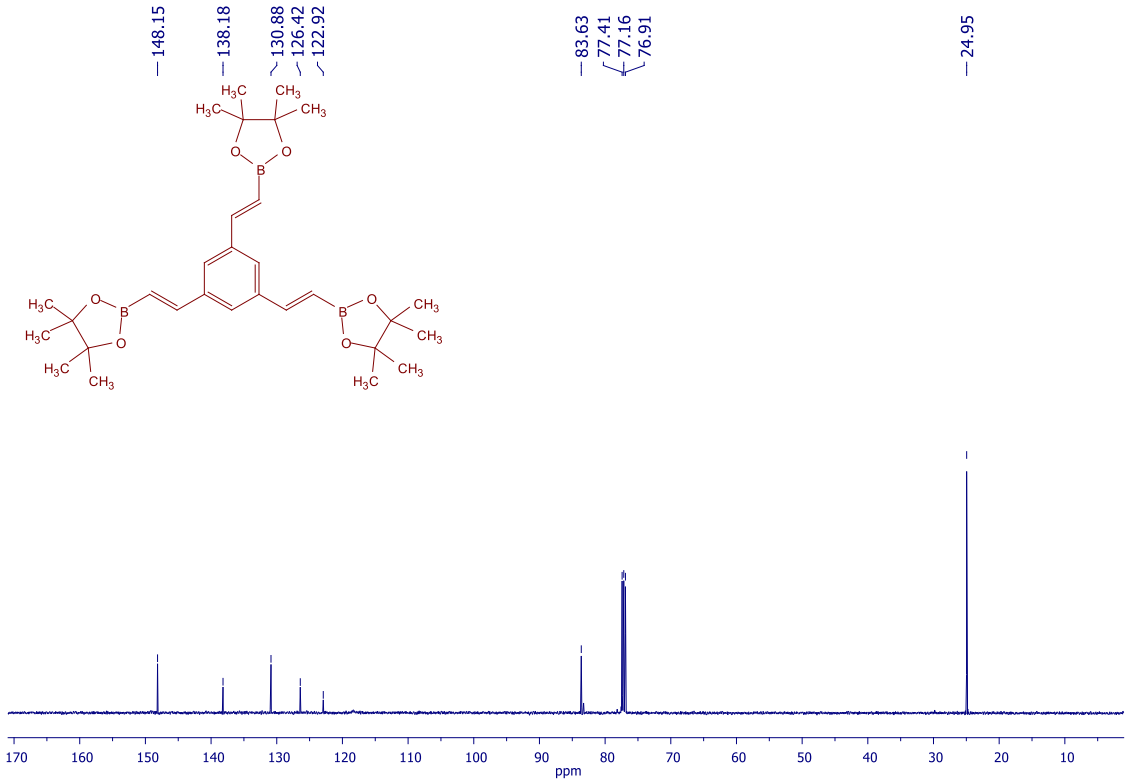
*^{13}C NMR of 1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2, compound **E-20**)*



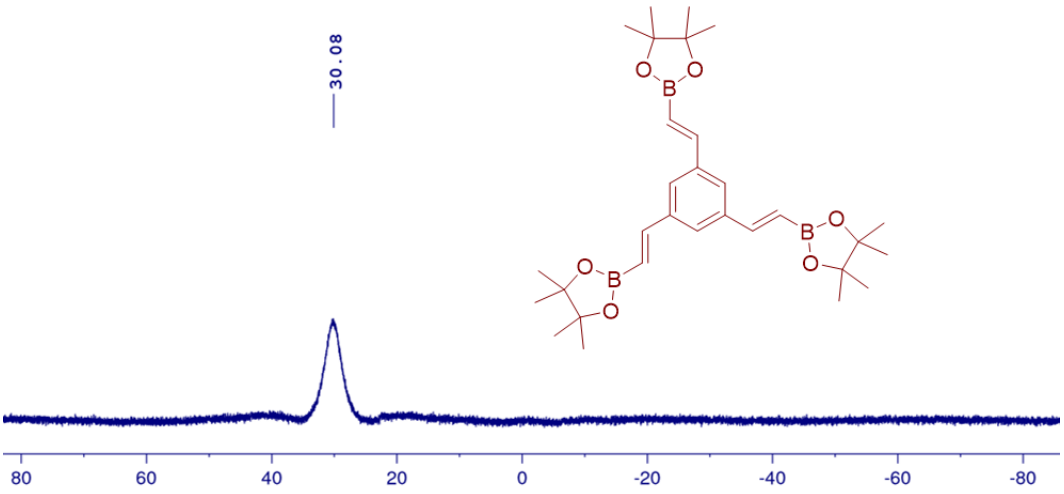
*^{11}B NMR of 1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2, compound **E-20**)*



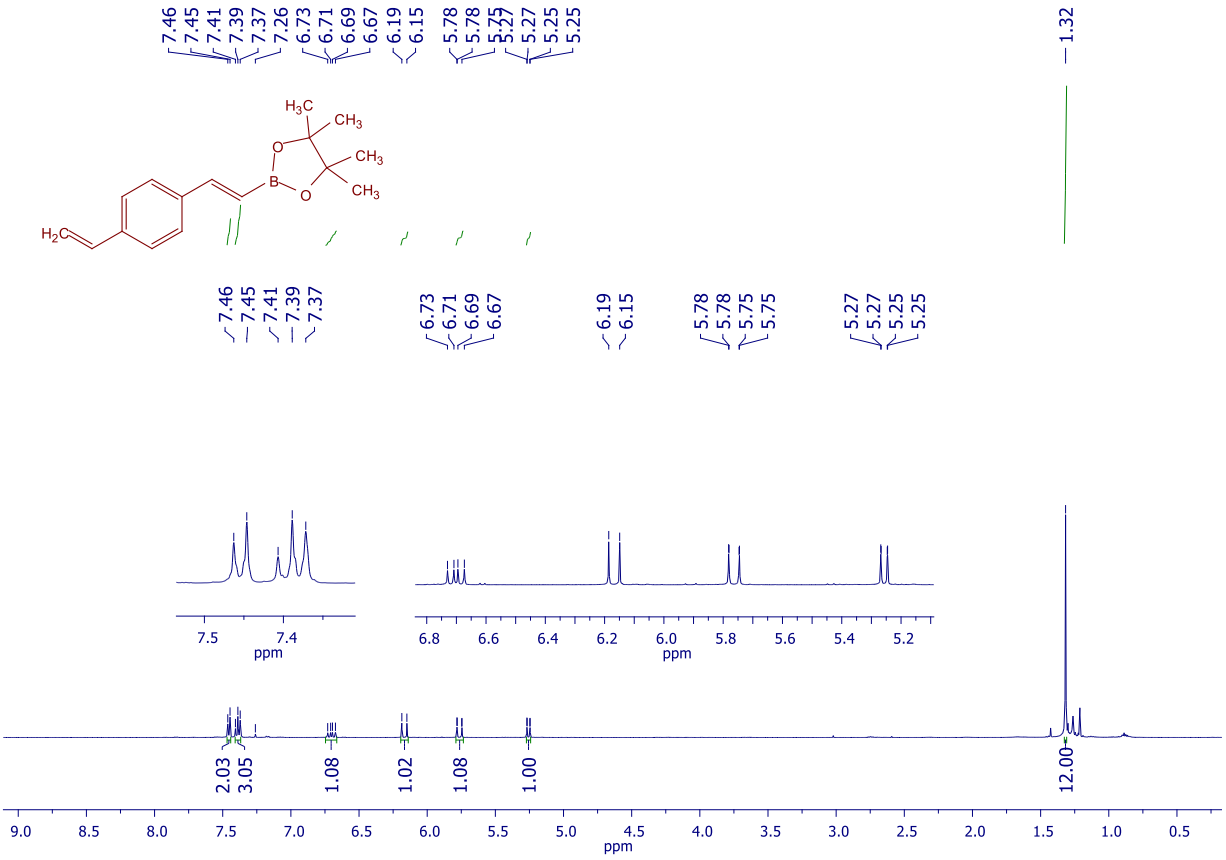
*[1]H NMR of 1,3,5-tris((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2,compound **E-21**)*



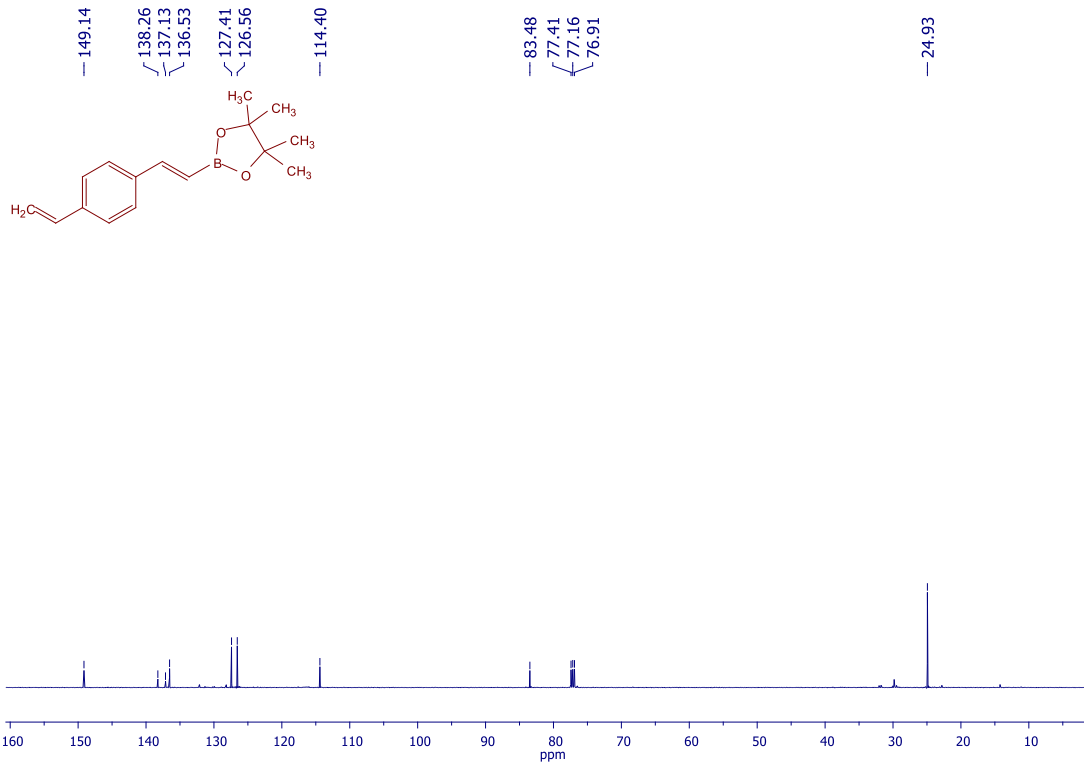
*[13]C NMR of1,3,5-tris((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2,compound **E-21**)*



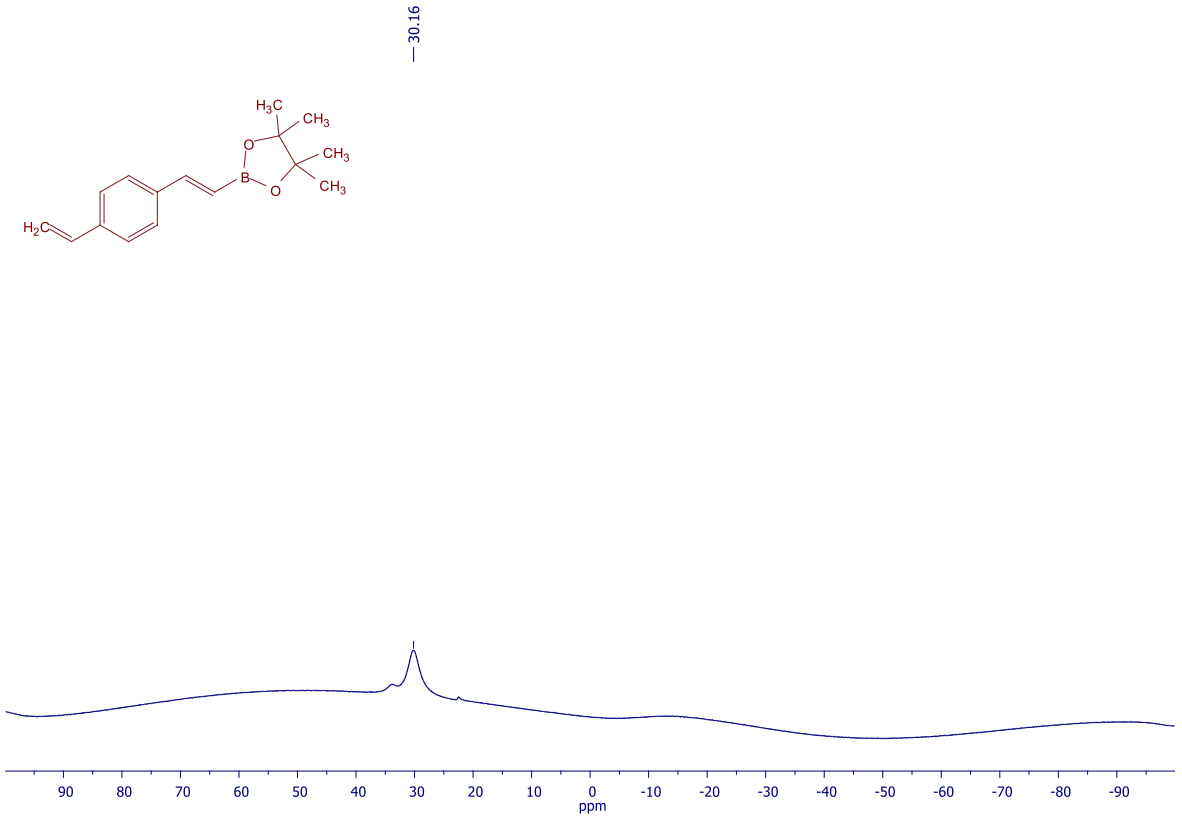
*^{11}B NMR of 1,3,5-tris((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Table 2,compound **E-21**)*



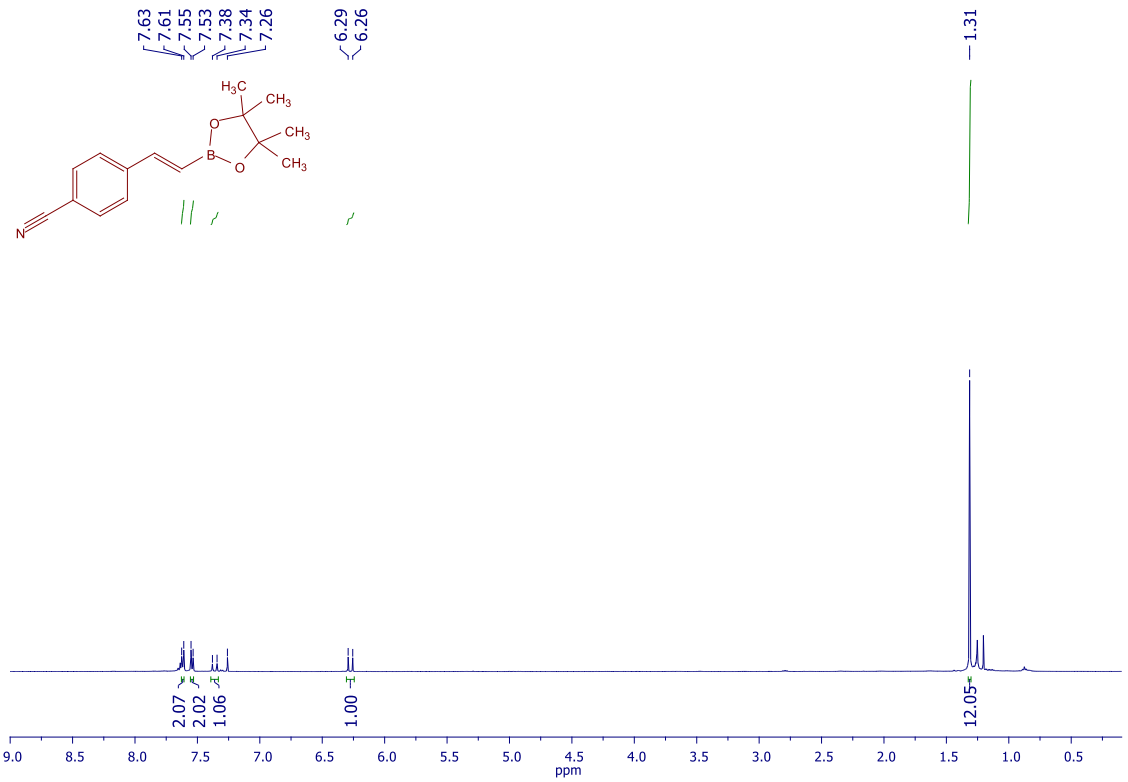
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (Scheme 2, compound **E-22**)*



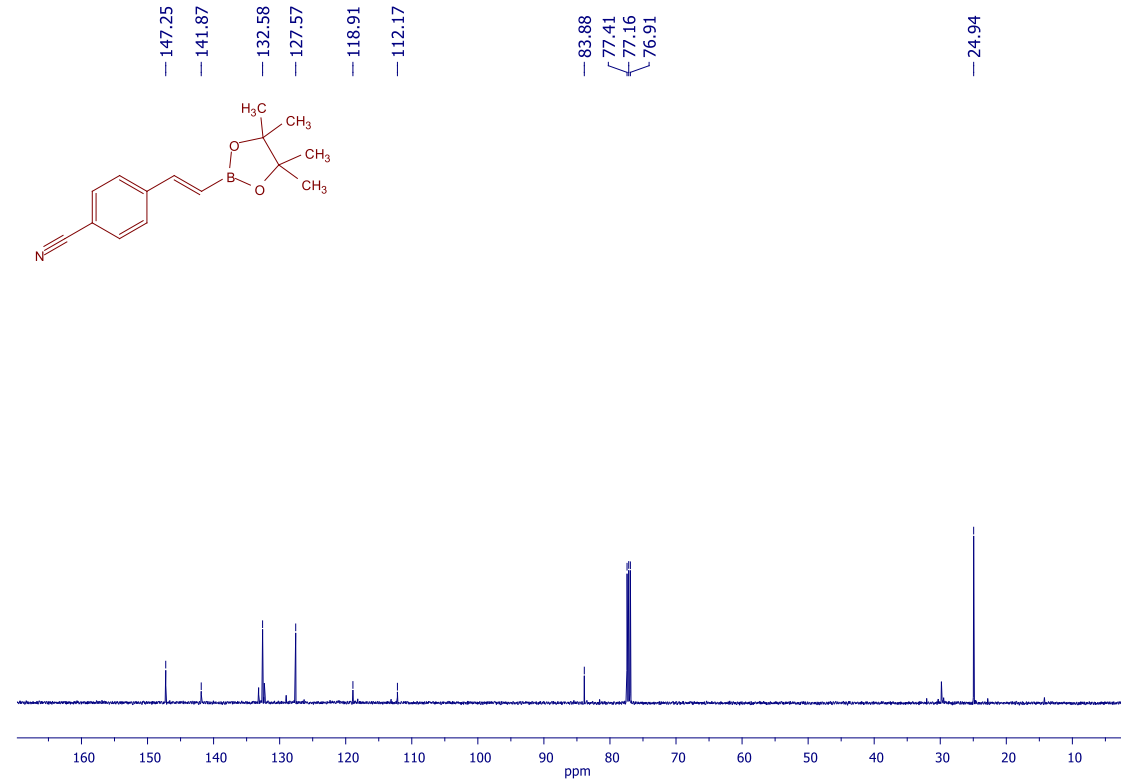
*^{13}C NMR of (E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (Scheme 2, compound **E-22**)*



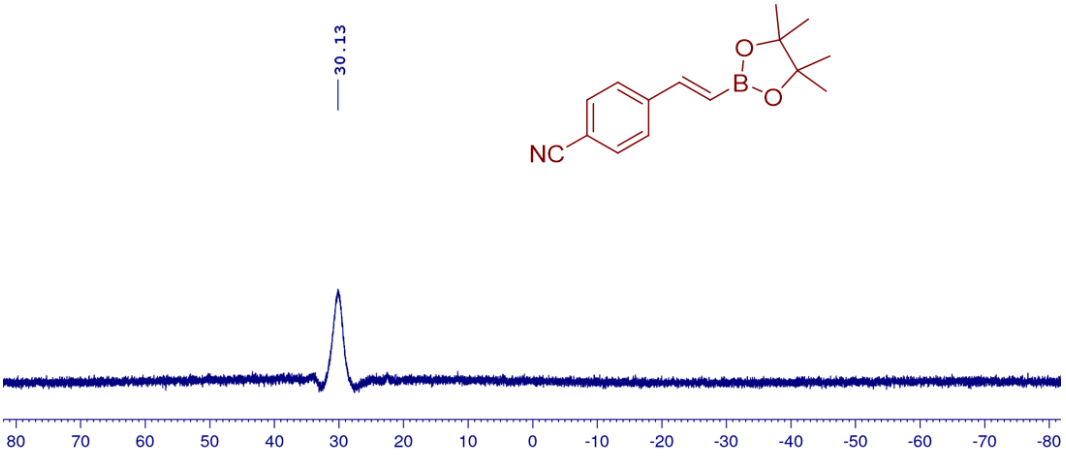
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (Scheme 2, compound **E-22**)*



*[1]H NMR of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (Scheme 2, compound **E-23**)*

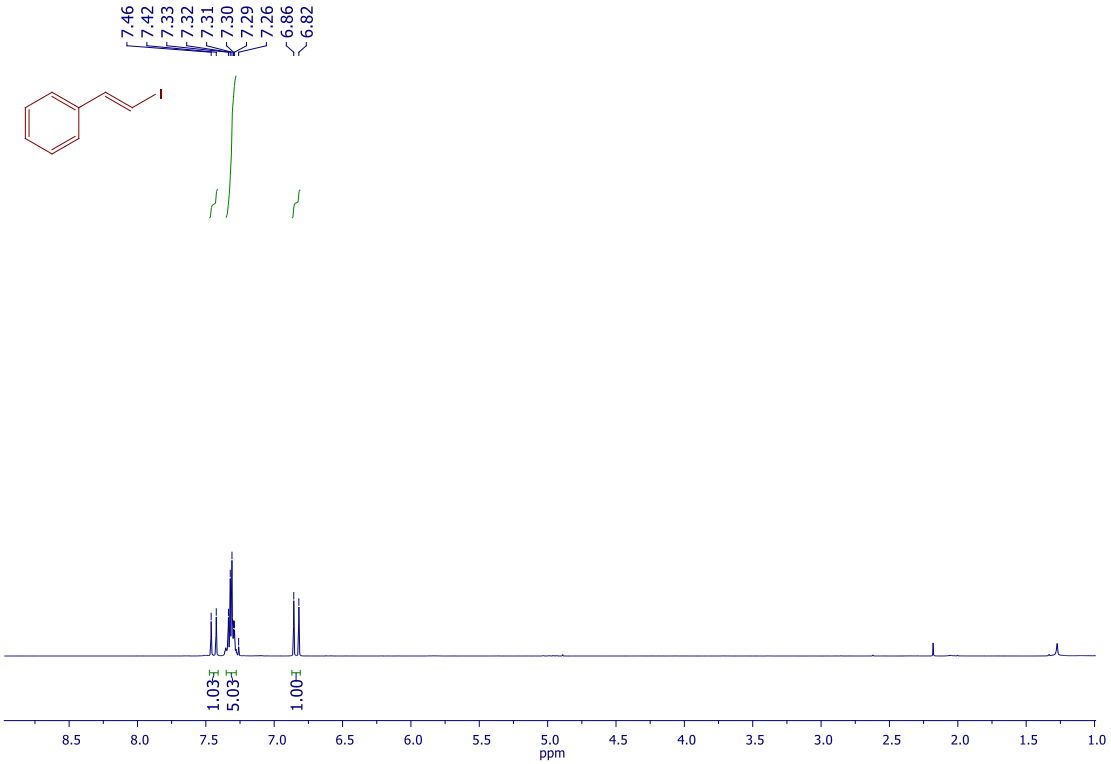


*[13]C NMR of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (Scheme 2, compound **E-23**)*

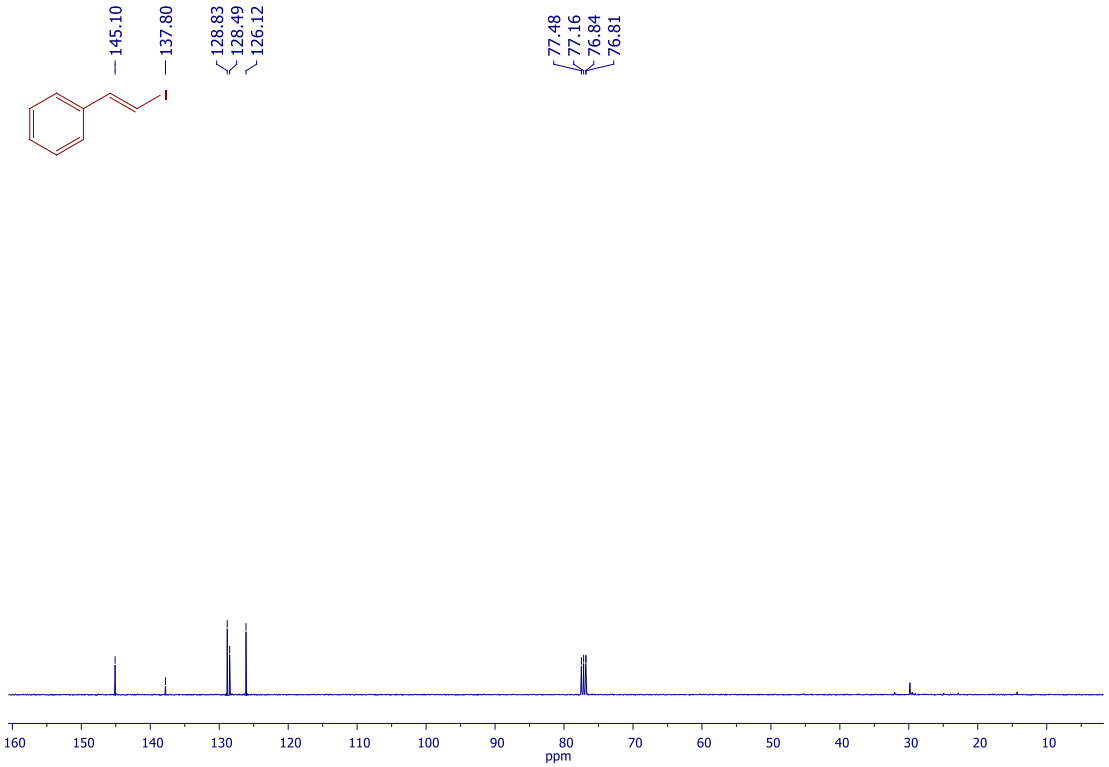


*[11]B NMR of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (Scheme 2, compound **E-23**)*

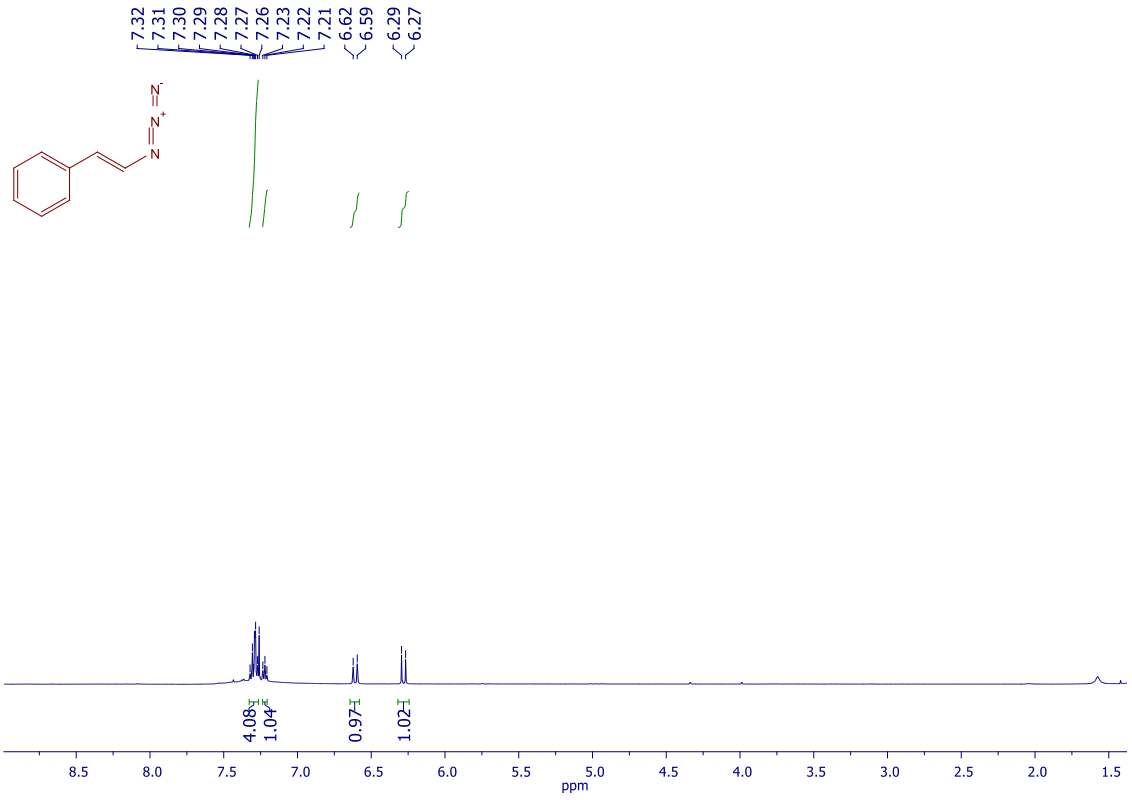
NMR spectra in $CDCl_3$ for derivatization of compound *E*-1:



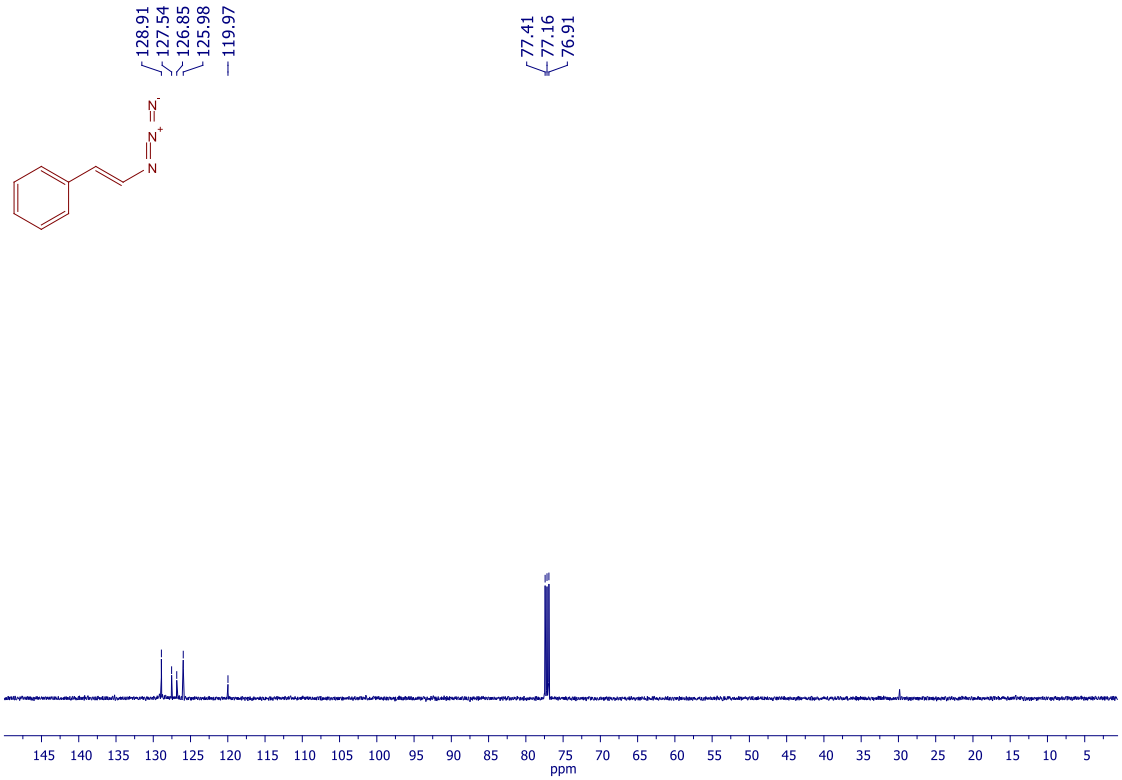
*[1]H NMR of (E)-(2-iodovinyl)benzene (Scheme 3, compound **1a**)*



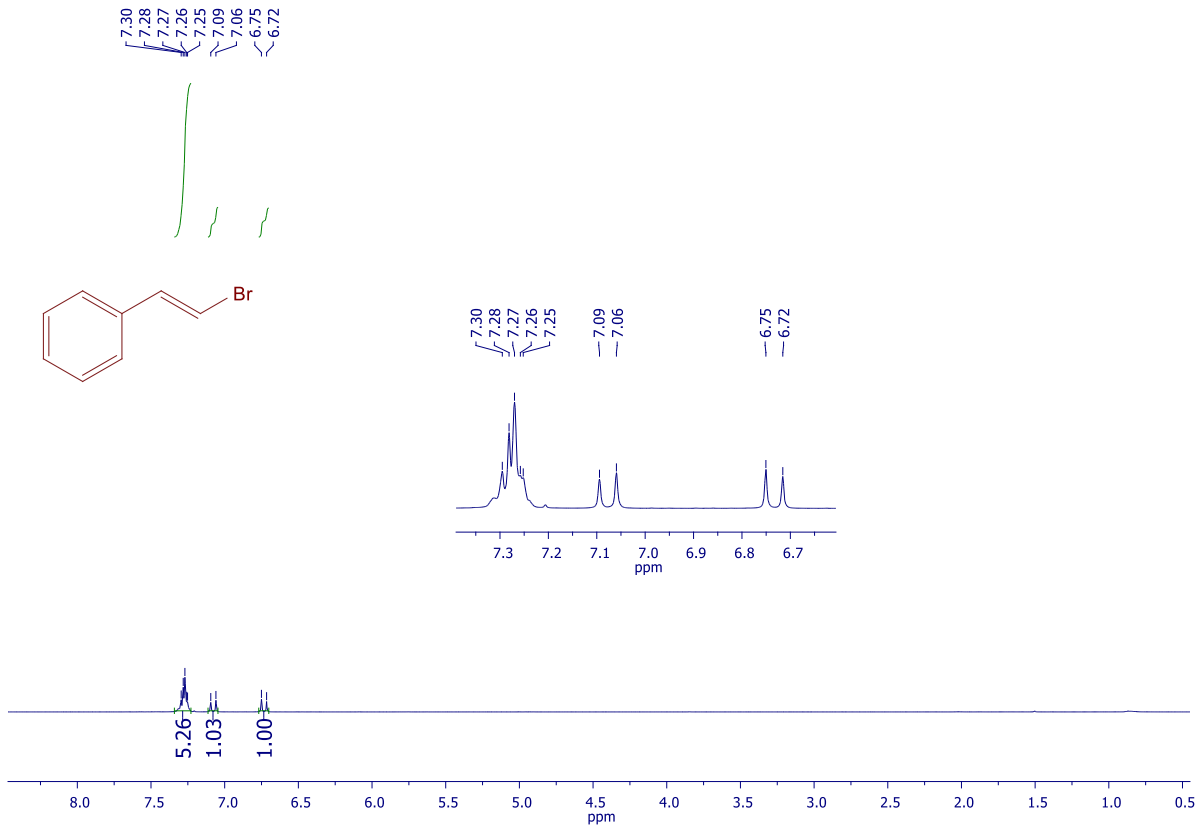
*^{13}C NMR of (E)-(2-iodovinyl)benzene (Scheme 3, compound **1a**)*



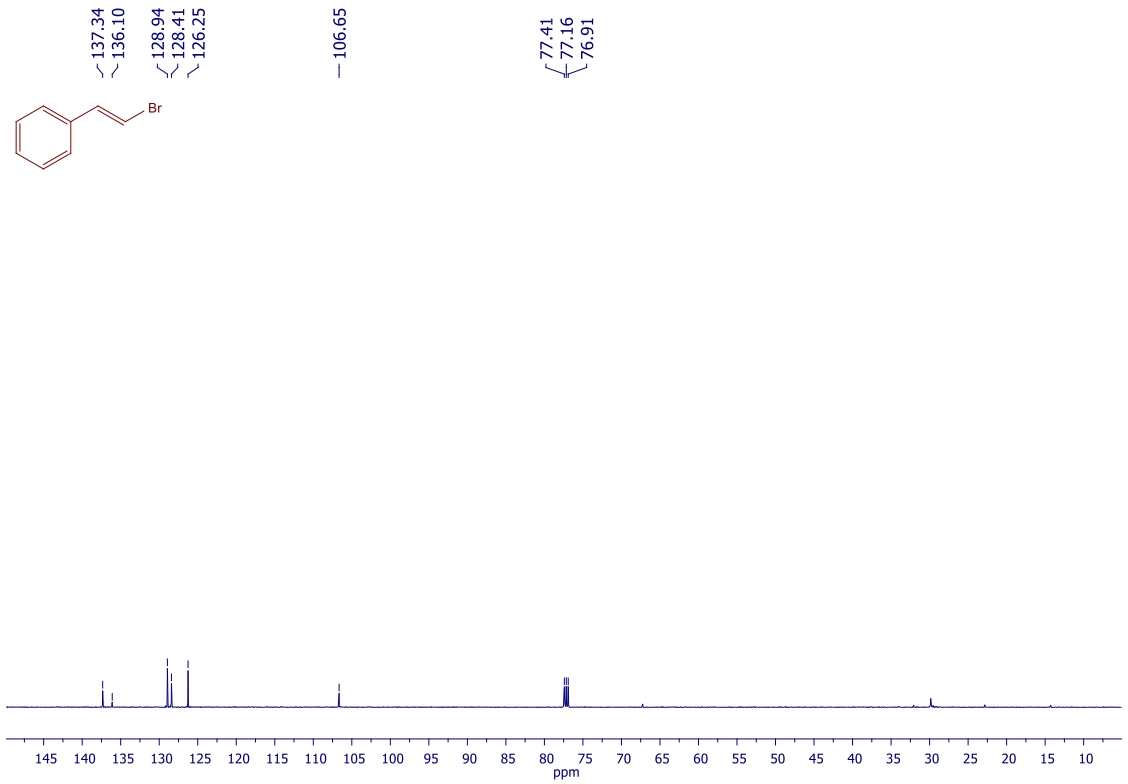
*^{1}H NMR of (E)-(2-azidovinyl)benzene (Scheme 3, compound **1b**)*



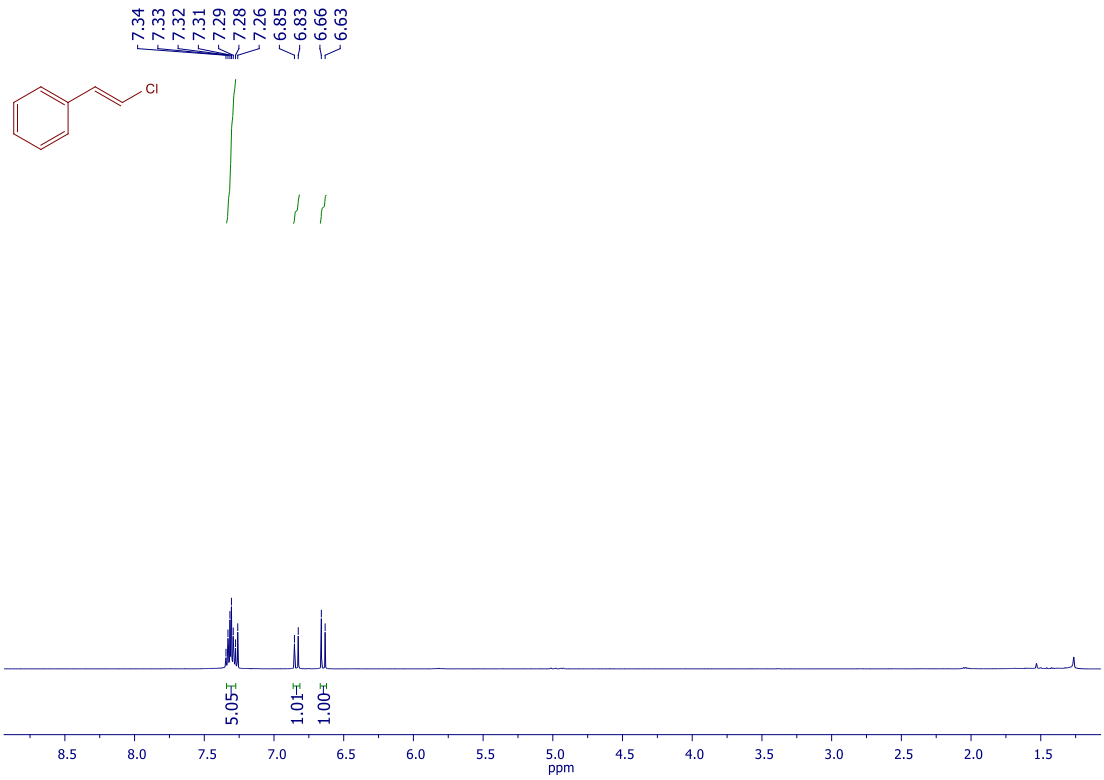
*[13]C NMR of (E)-(2-azidovinyl)benzene (Scheme 3, compound **1b**)*



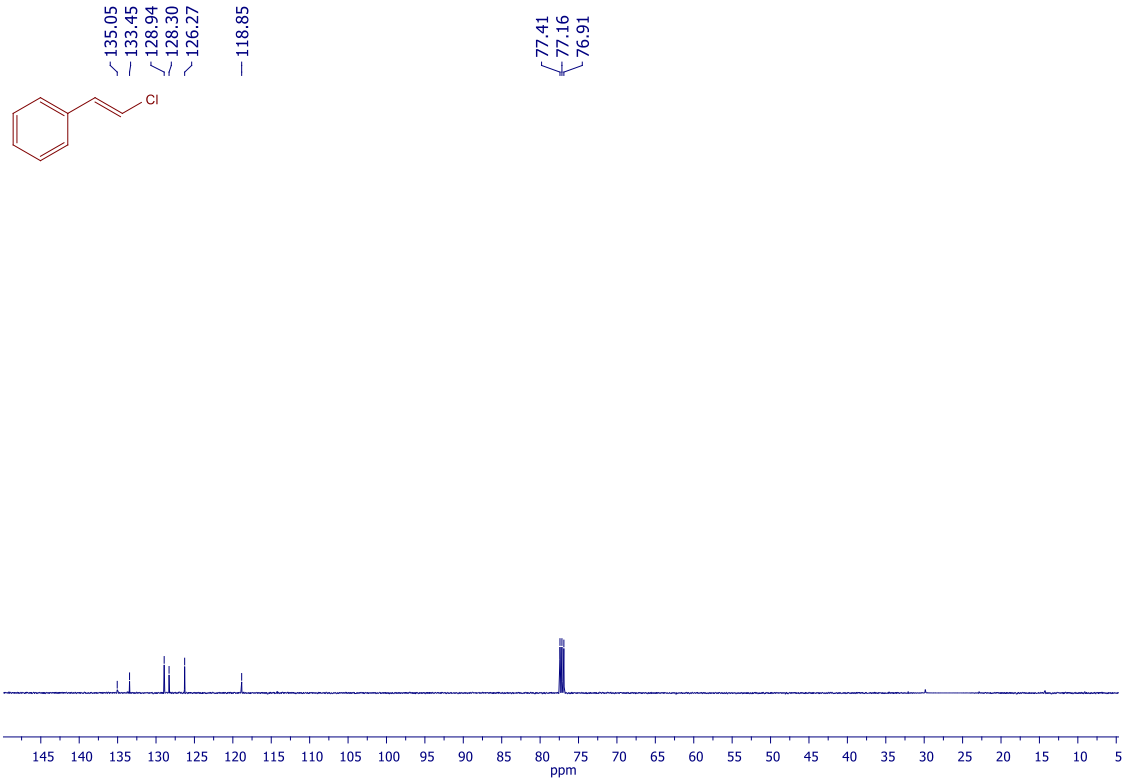
*[1]H NMR of (E)-(2-bromovinyl)benzene (Scheme 3, compound **1c**)*



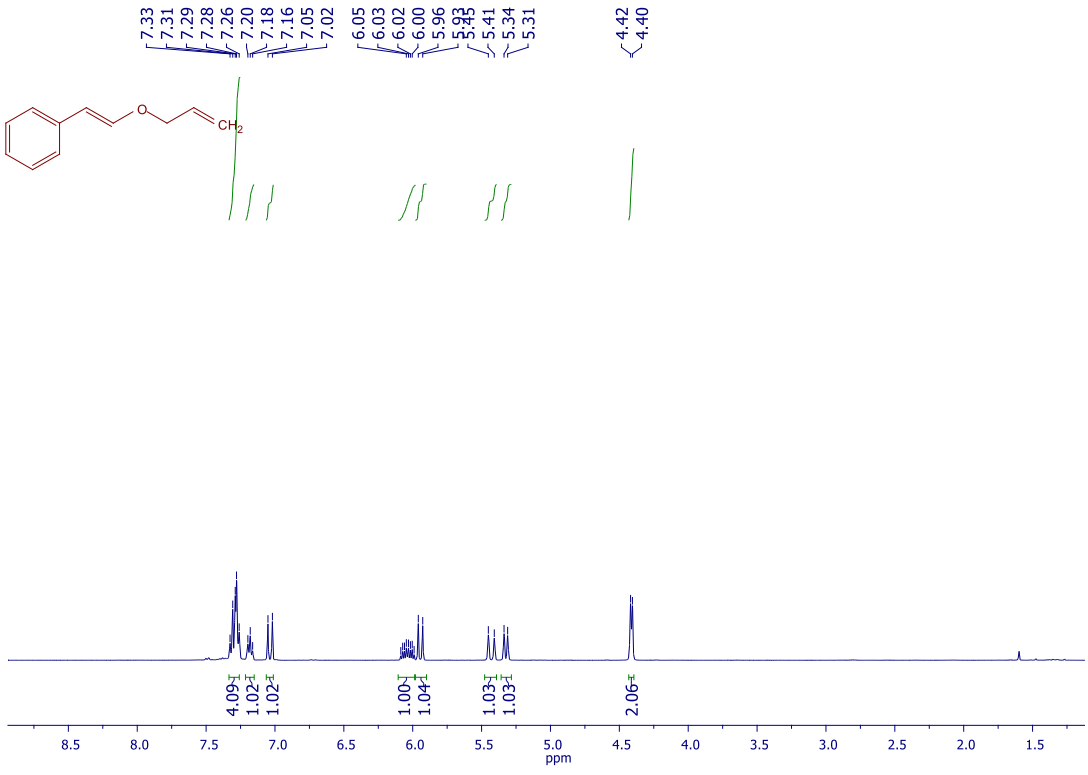
*^{13}C NMR of (E)-(2-bromovinyl)benzene (Scheme 3, compound **1c**)*



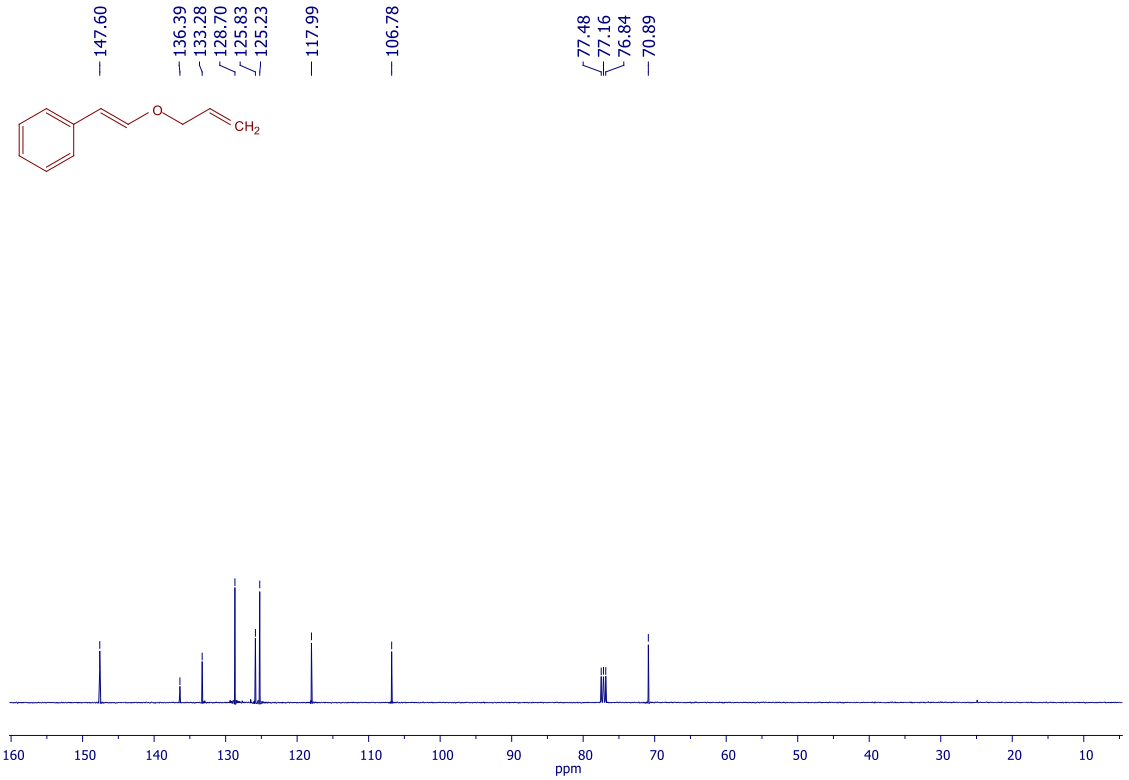
*^{1}H NMR of (E)-(2-chlorovinyl)benzene (Scheme 3, compound **1d**)*



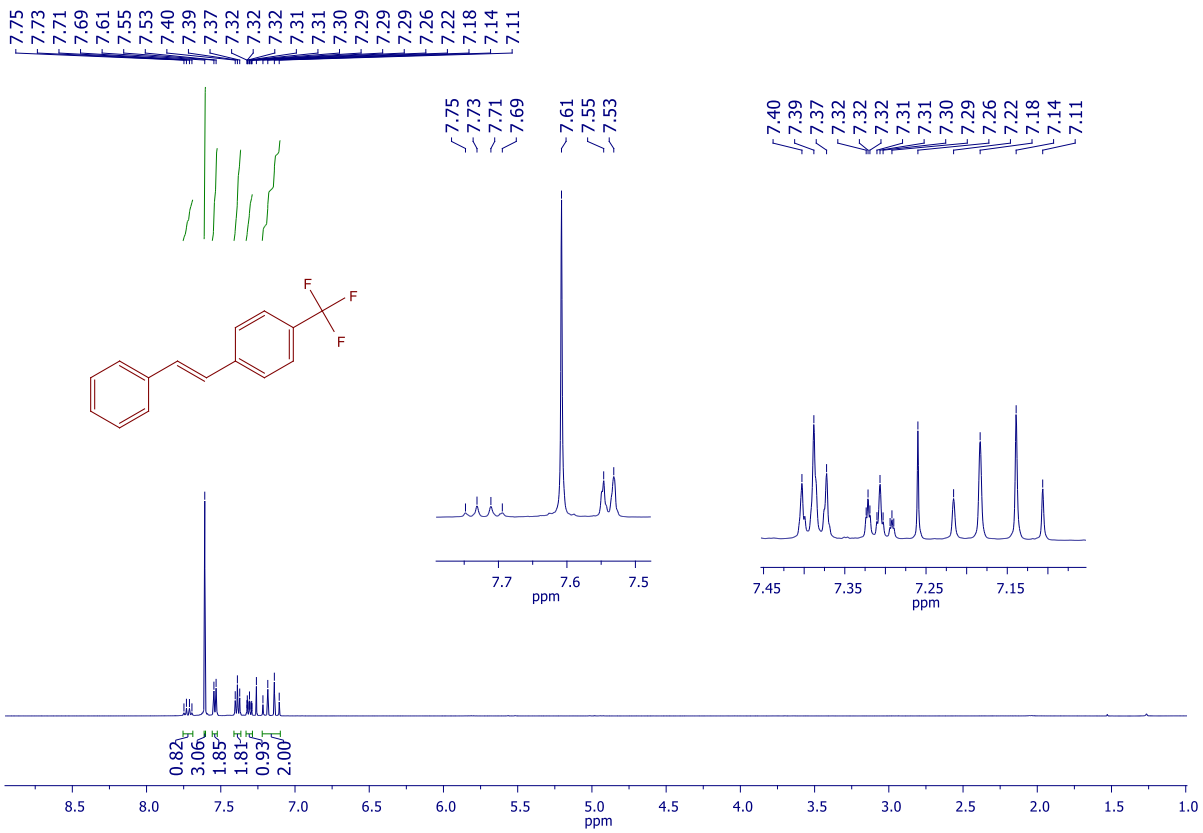
*[13]C NMR of (E)-(2-chlorovinyl)benzene (Scheme 3, compound **1d**)*



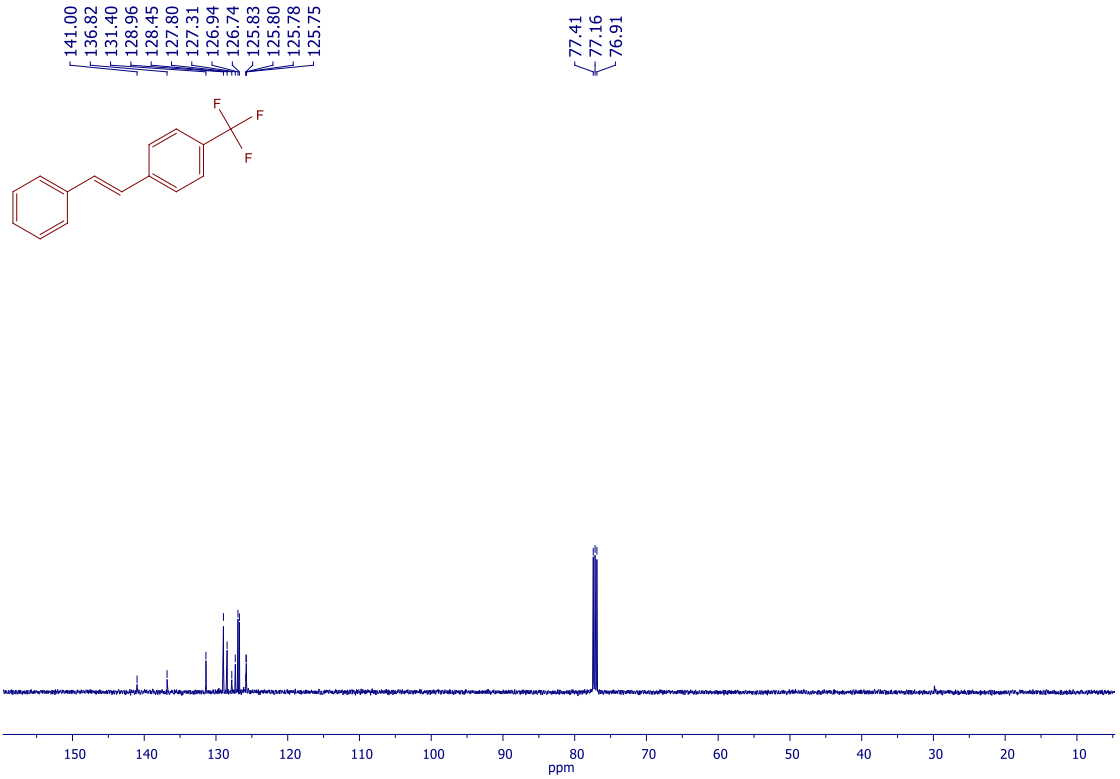
*[1]H NMR of (E)-(2-(allyloxy)vinyl)benzene (Scheme 3, compound **1e**)*



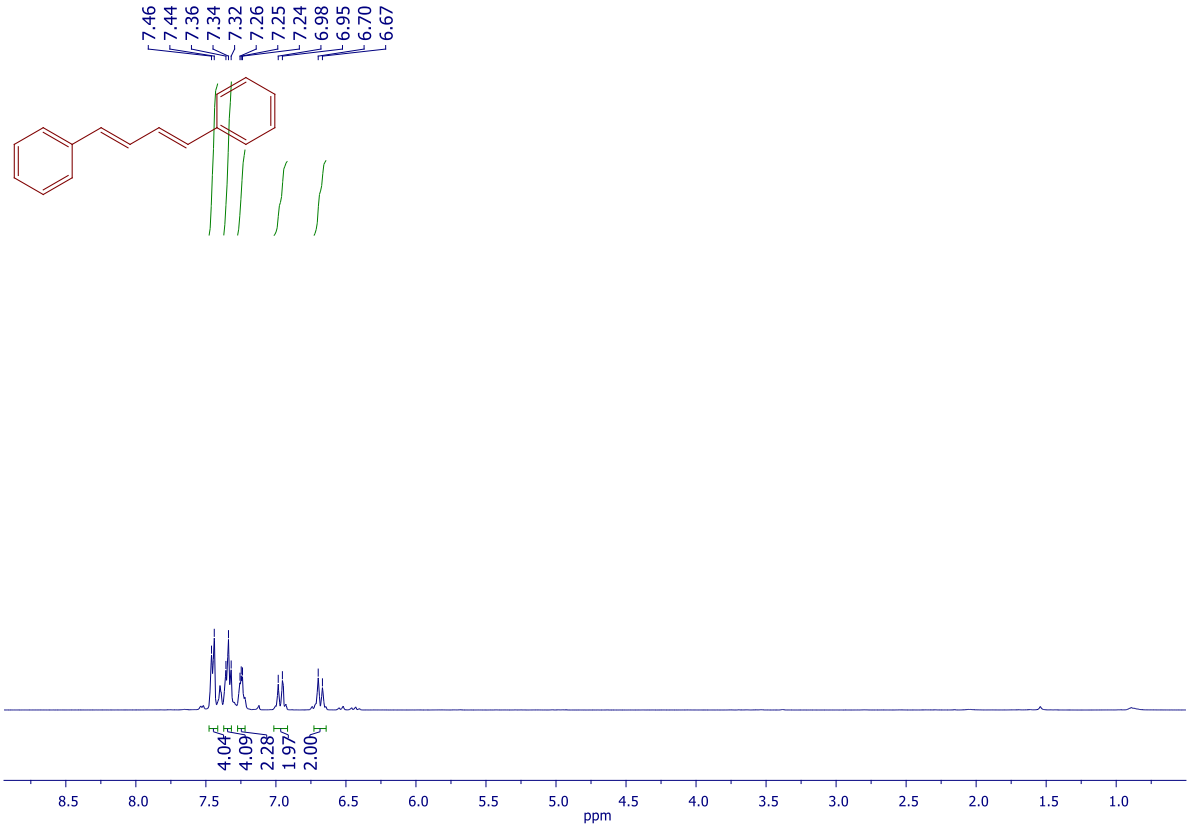
*[13]C NMR of (E)-(2-(allyloxy)vinyl)benzene (Scheme 3, compound **1e**)*



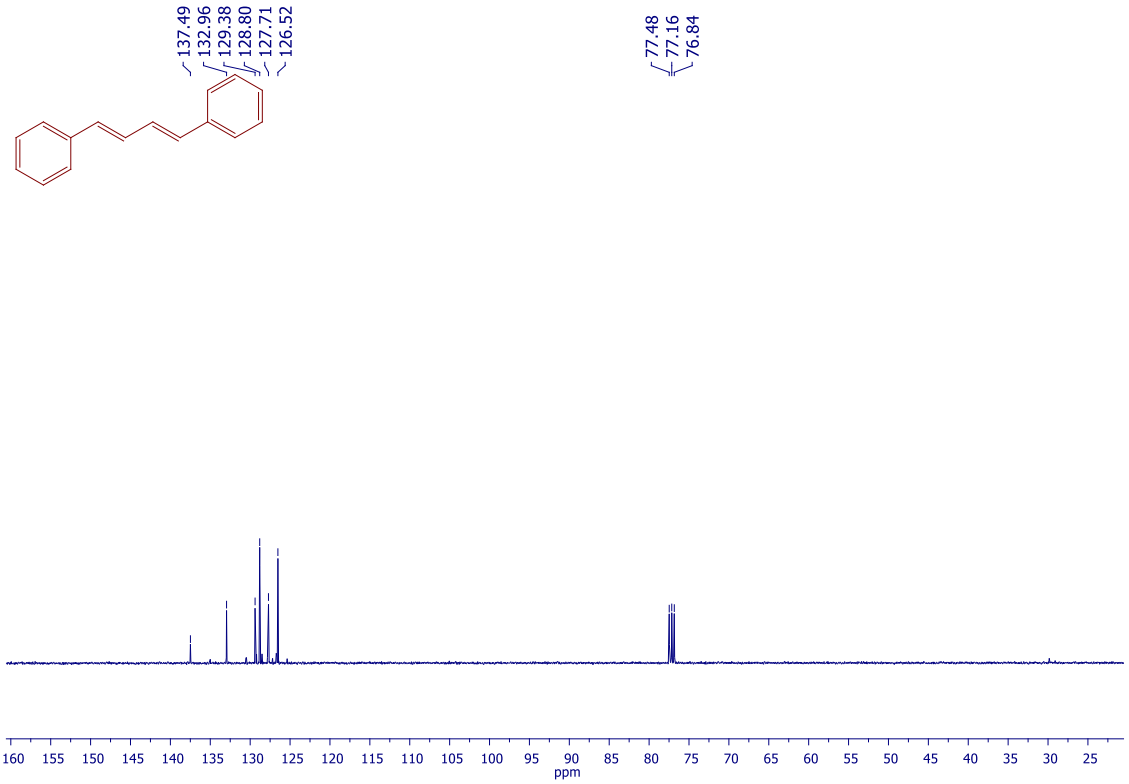
*[1]H NMR of (E)-1-styryl-4-(trifluoromethyl)benzene (Scheme 3, compound **1f**)*



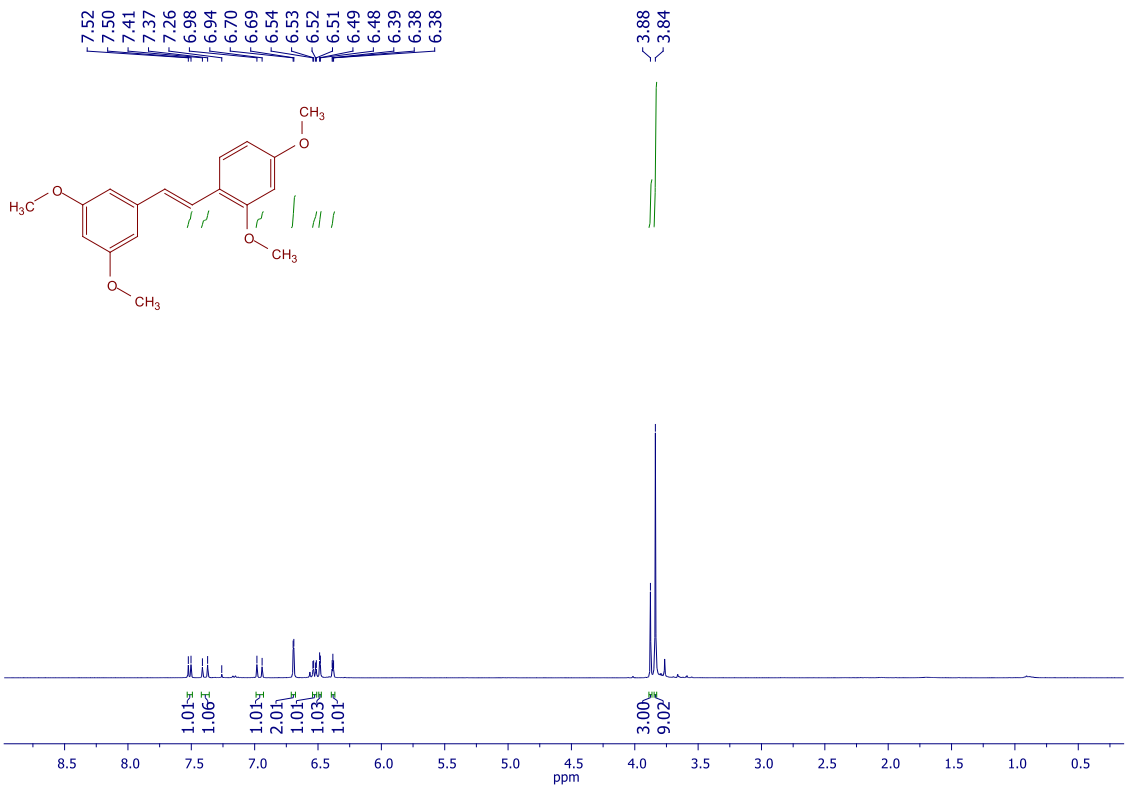
*^{13}C NMR of (E)-1-styryl-4-(trifluoromethyl)benzene (Scheme 3, compound **1f**)*



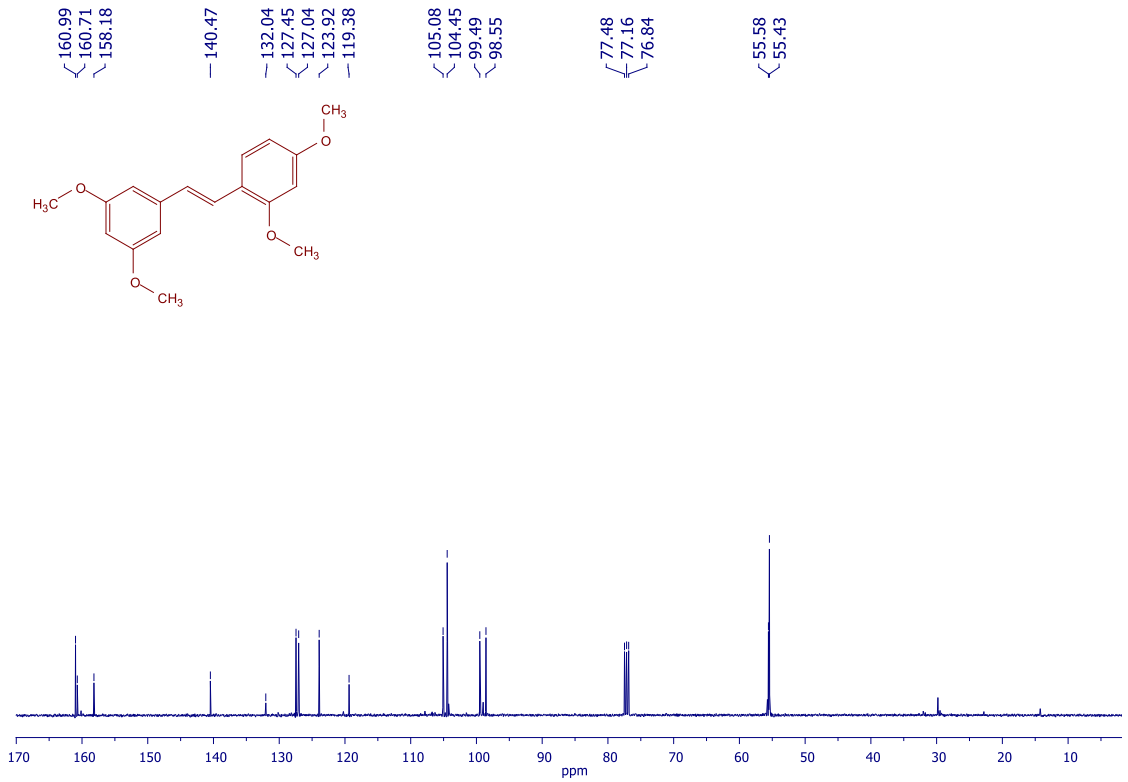
*^{1}H NMR of (1E,3E)-1,4-diphenylbuta-1,3-diene (Scheme 3, compound **24**)*



*^{13}C NMR of (1E,3E)-1,4-diphenylbuta-1,3-diene (Scheme 3, compound **24**)*

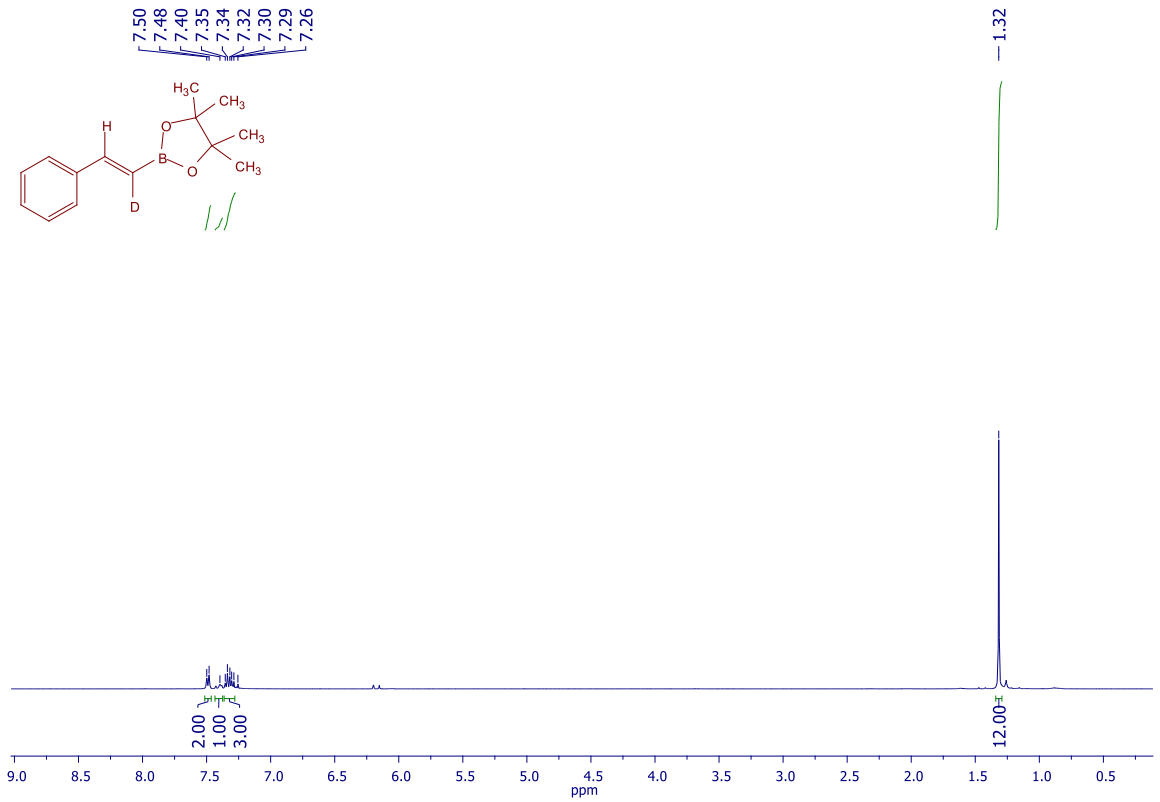


*^{1}H NMR of (E)-1-(3,5-dimethoxystyryl)-2,4-dimethoxybenzene (Scheme 4, compound **E-25**)*

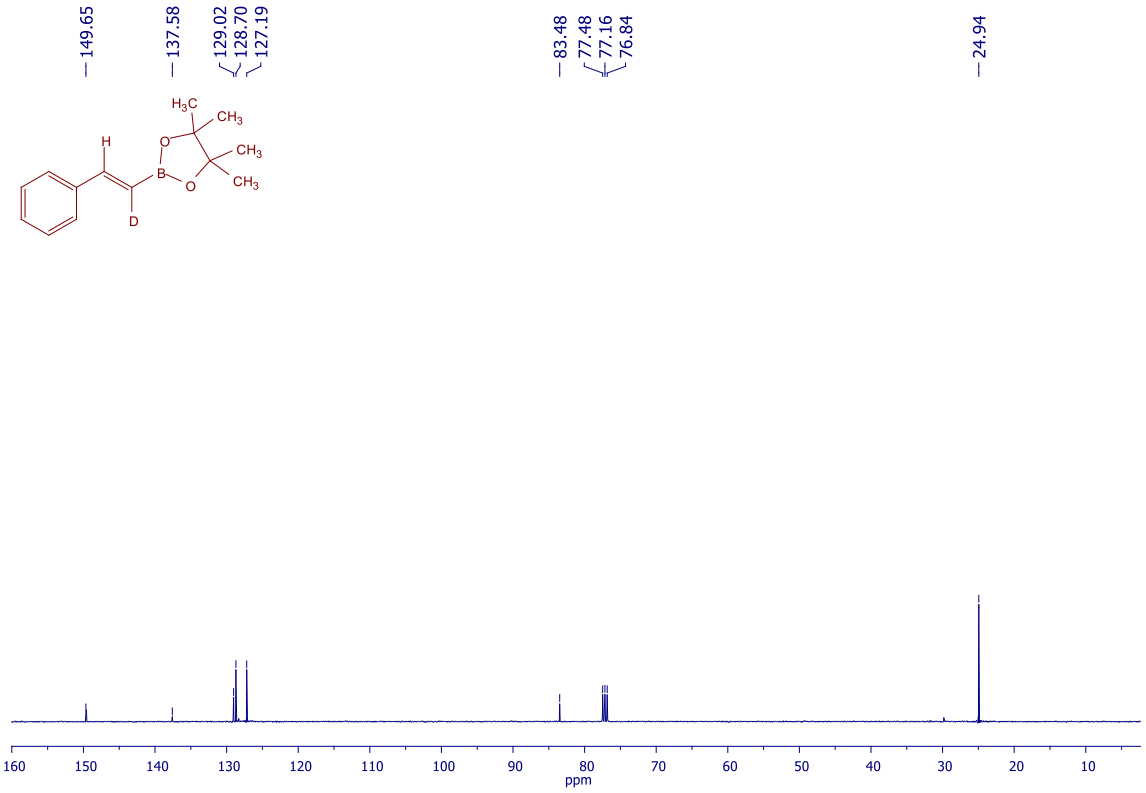


*[13]C NMR of (E)-1-(3,5-dimethoxystyryl)-2,4-dimethoxybenzene (Scheme 4, compound **E-25**)*

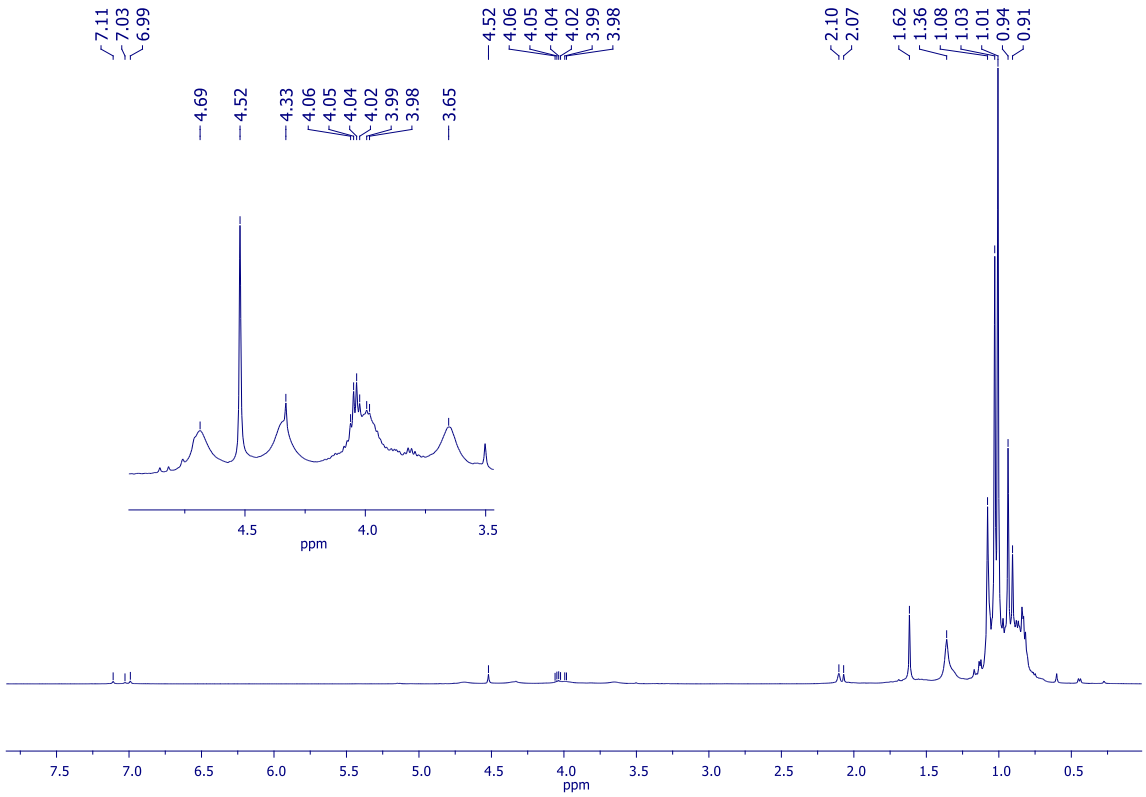
Spectra of controlled experiments:



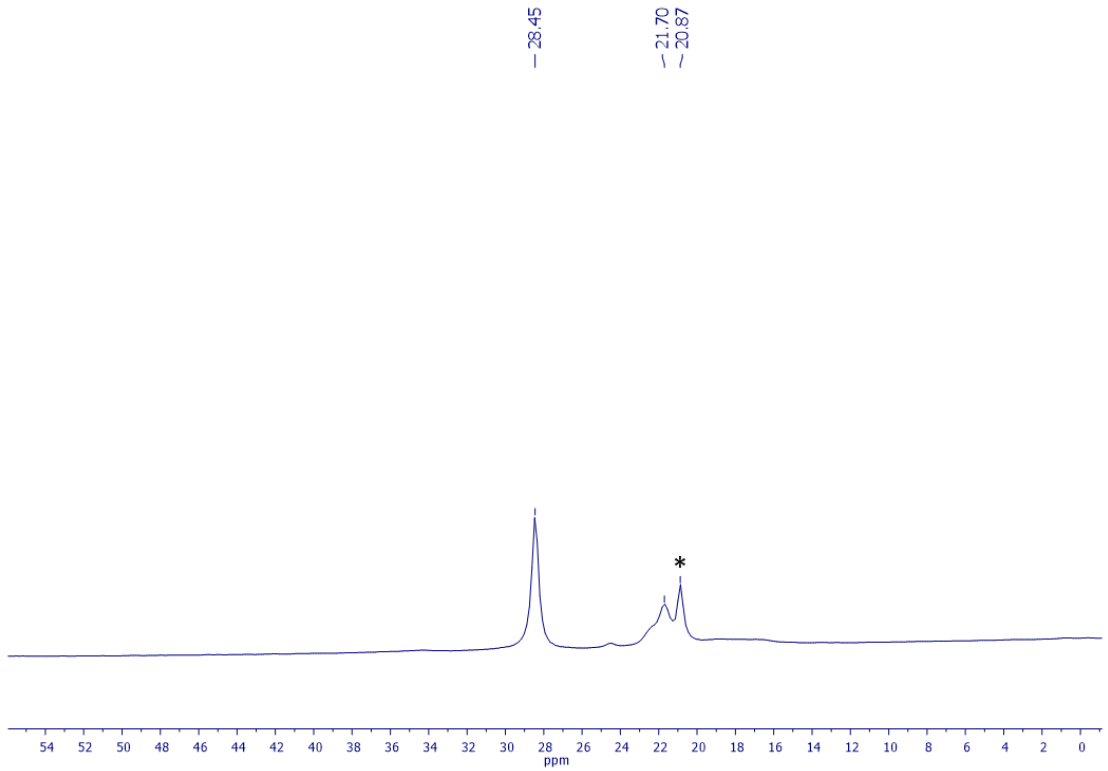
[1]H NMR of (*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-*D*)-1,3,2-dioxaborolane



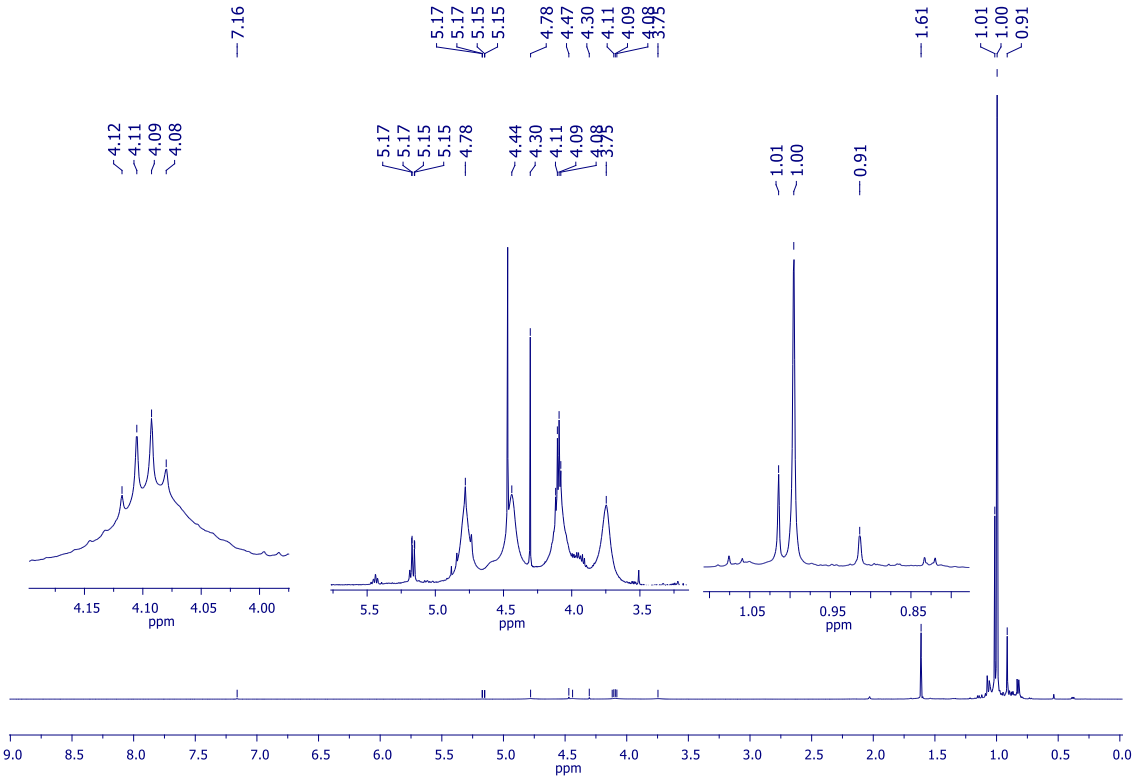
^{13}C NMR of (*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-*D*)-1,3,2-dioxaborolane



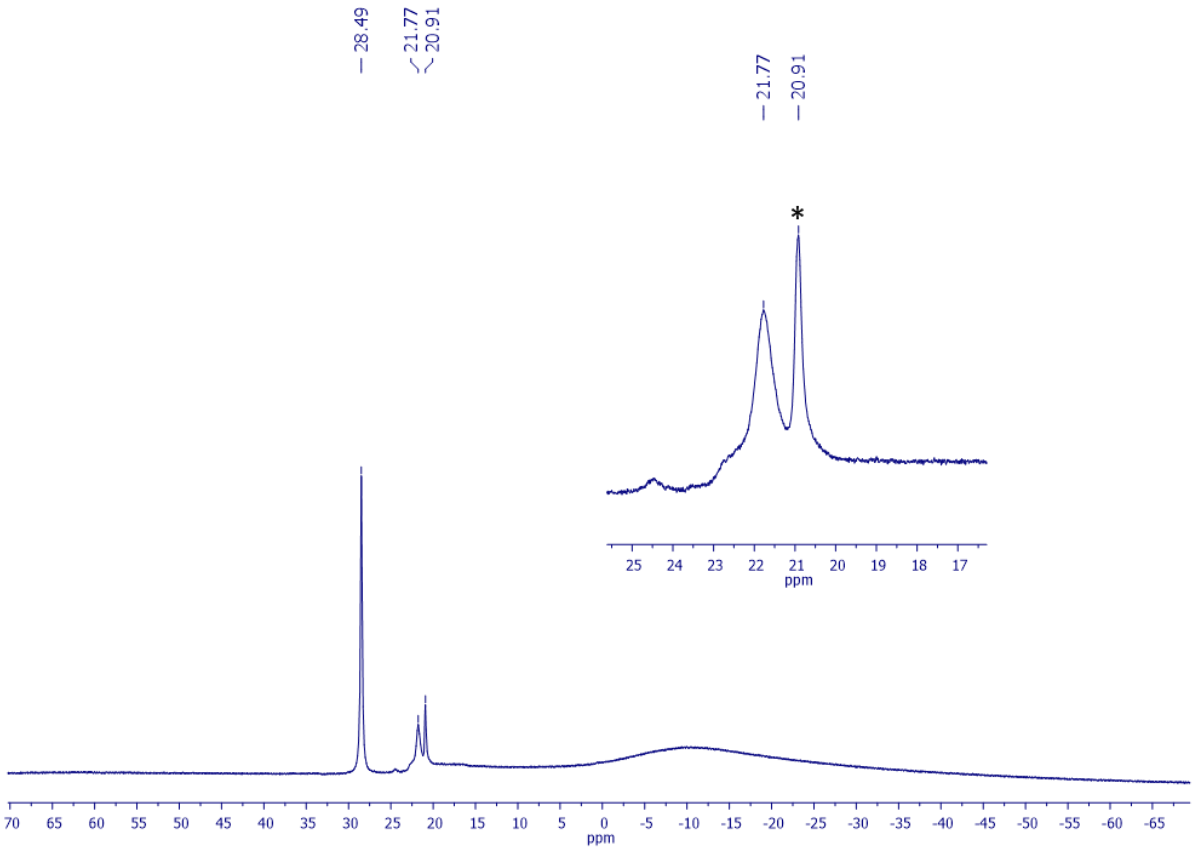
^{1}H NMR of the reaction mixture of $AgSbF_6$ and HBpin in toluene-d_8



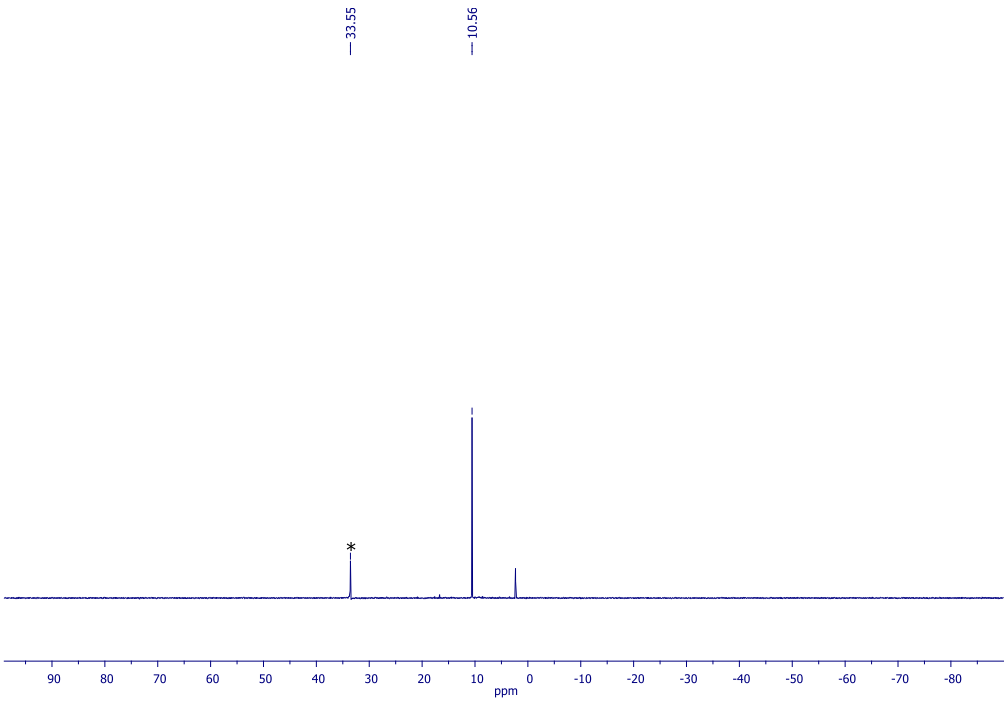
^{11}B NMR of the reaction mixture of $AgSbF_6$ and HBpin in toluene-d_8 (indicates the decomposition product B_2pin_3)*



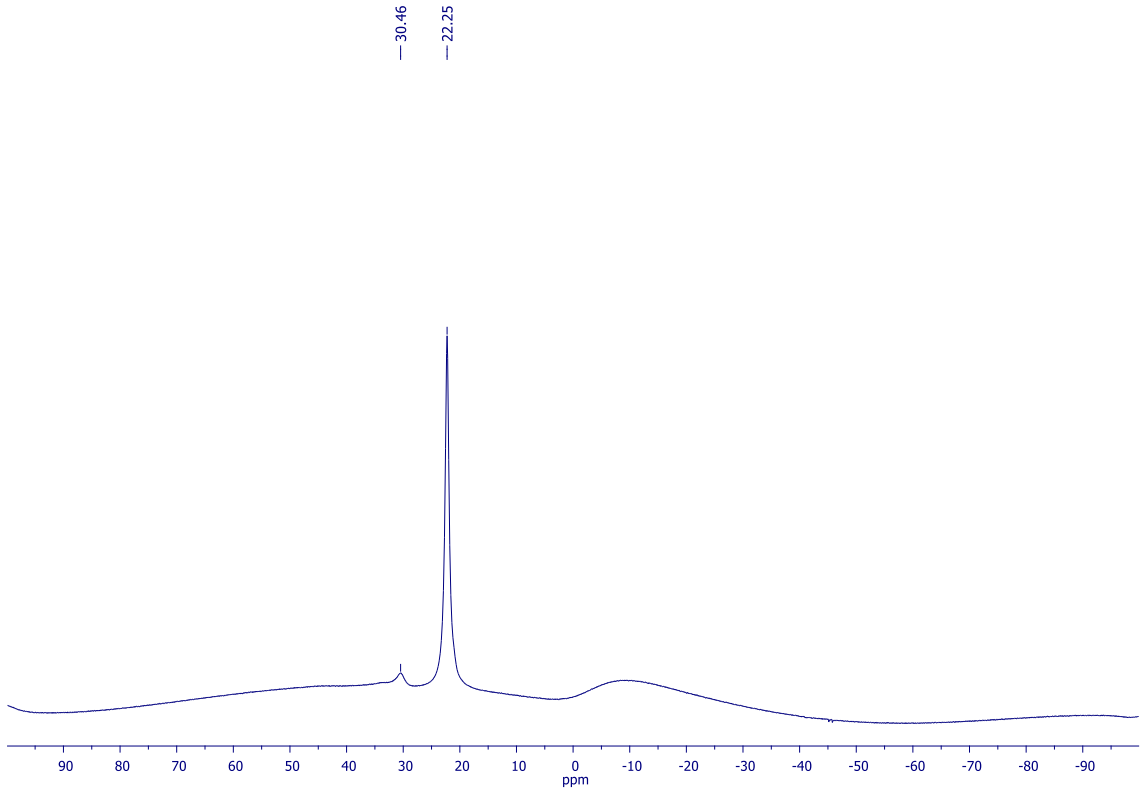
^{1}H NMR of the reaction mixture of $AgSbF_6$ and HBpin in benzene-d_6



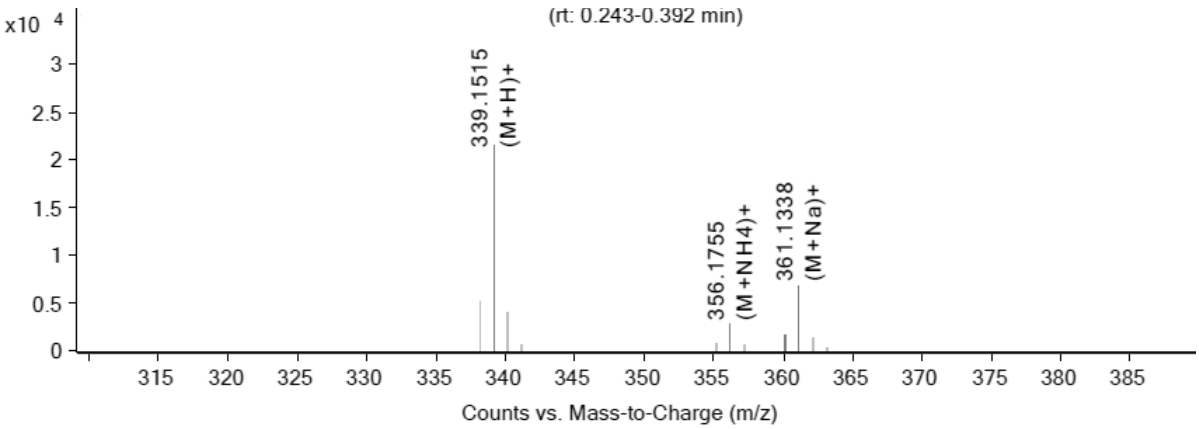
^{11}B NMR of the reaction mixture of $AgSbF_6$ and HBpin in benzene-d_6 (indicates the decomposition product B_2pin_3)*



^{31}P NMR of the reaction mixture of standard phenyl acetylene hydroboration reaction in presence of excess $P(OMe)_3$ in $CDCl_3$. * indicates the impurity of $(O=)P(OMe)_3$



^{11}B NMR of the reaction mixture of standard phenyl acetylene hydroboration reaction in presence of excess $P(OMe)_3$ in $CDCl_3$



Portion of the ESI mass spectrum of the reaction mixture of standard phenyl acetylene hydroboration reaction in presence of excess $P(OMe)_3$. M corresponds to the styrenyl radical (scheme 6, a) trapped with $(O=)P(OMe)_2$.