Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

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1. General information

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. All solvents (CH_2Cl_2, toluene and THF) were dried and purified following standard procedures. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by staining with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^{1}H NMR spectra were reported in δ ppm referenced to an internal $SiMe_4$ standard. The abbreviations s, brs, d, t, q and m stand for the resonance multiplicity singlet, broad singlet, doublet, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

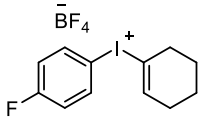
2. Preparation of substrates

All of the required non-commercially available iodonium salts were prepared following reported protocols. Substrates **1a-1f** [1]; Substrates **1g-1m** [2]. Unless otherwise noted, iodonium salts were stored in brown vials in the freezer at -18 °C for months.

[1] Angewandte Chemie International Edition, 2010, 49, 4092-4095.

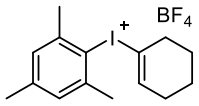
[2] Org. Lett. 2018, 20, 8061−8063.

Cyclohex-1-en-1-yl(4-fluorophenyl)iodonium tetrafluoroborate



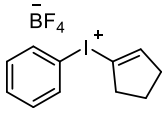
White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 – 7.89 (m, 2H), 7.24 – 7.17 (m, 2H), 7.07 – 7.00 (m, 1H), 2.63 – 2.61 (m, 2H), 2.48 – 2.45 (m, 2H), 1.85 – 1.81 (m, 2H), 1.76 – 1.62 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4 (d, *J* = 256.8 Hz), 147.8, 138.6 (d, *J* = 9.1 Hz), 120.2 (d, *J* = 23.1 Hz), 117.9 (d, *J* = 22.0 Hz), 101.64, 34.3, 30.3, 25.7, 20.2; HRMS (ES^+) exact mass calculated for $[M\text{-}BF_4]^+$ $C_{12}H_{13}FI^+$ requires ***m/z*** 303.0040, found ***m/z*** 303.0045.

Cyclohex-1-en-1-yl(mesityl)iodonium tetrafluoroborate



Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (s, 2H), 6.85 – 6.49 (m, 1H), 2.57 (s, 6H), 2.45 – 2.43 (m, 2H), 2.40 – 2.35 (m, 2H), 2.34 (s, 3H), 1.83 – 1.74 (m, 2H), 1.69 – 1.64 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 144.2, 143.2, 130.6, 117.9, 115.2, 33.5, 29.9, 27.2, 25.6, 21.1, 20.4; HRMS (ES^+) exact mass calculated for $[M\text{-}BF_4]^+$ $C_{15}H_{20}I^+$ requires ***m/z*** 327.0604, found ***m/z*** 327.0607.

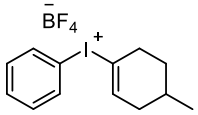
Cyclopent-1-en-1-yl(phenyl)iodonium tetrafluoroborate (1b)



White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.47 (m, 2H), 6.94 (t, *J* = 2.4 Hz, 1H), 2.72 – 2.65 (m, 4H), 2.12 – 1.84 (m, 2H); ^{13}C NMR (151

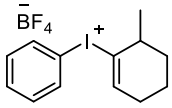
MHz, $CDCl_3$) δ 150.6, 135.7, 132.8, 132.4, 109.8, 109.0, 37.9, 33.9, 23.2; HRMS (ES^+) exact mass calculated for $[M\text{-}BF_4]^+$ $C_{11}H_{12}I^+$ requires ***m/z*** 270.9978, found ***m/z*** 270.9974.

(4-Methylcyclohex-1-en-1-yl)(phenyl)iodonium tetrafluoroborate (1c)



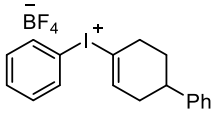
White solid; ^1H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.07 – 6.89 (m, 1H), 2.74 – 2.60 (m, 2H), 2.59 – 2.35 (m, 1H), 2.13 – 2.08 (m, 1H), 1.81 – 1.78 (m, 2H), 1.53 – 1.47 (m, 1H), 0.92 (d, J = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 135.8, 132.9, 132.5, 119.3, 108.5, 37.9, 34.2, 33.4, 26.5, 20.8; HRMS (ES^+) exact mass calculated for $[M\text{-}BF_4]^+$ $C_{13}H_{16}I^+$ requires ***m/z*** 299.0291, found ***m/z*** 299.0296.

(6-Methylcyclohex-1-en-1-yl)(phenyl)iodonium tetrafluoroborate (1d)



White solid; It was used directly in the next reaction without NMR characterization because of its poor stability.

Phenyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)iodonium tetrafluoroborate (1f)



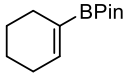
White solid; ^1H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.21 (t, *J* = 6.9 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 3H), 3.02 – 2.49 (m, 5H), 2.04 – 201 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 144.0, 135.7, 132.7, 132.4, 128.8, 126.9, 126.8, 119.9, 110.2, 37.8, 37.2, 34.6, 32.5; HRMS (ES^+) exact mass calculated for $[M\text{-}BF_4]^+$ $C_{13}H_{16}I^+$ requires ***m/z*** 361.0448, found ***m/z*** 316.0446.

3. General procedures for the boronation of iodonium salts

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged sequentially with CuI (0.02 mmol, 10 mol %), PPh_3 (0.02 mmol, 10 mol %), $(BPin)_2$ (0.2 mmol, 1.0 equiv) and *t*-BuOLi (0.40 mmol, 2.0 equiv). The tube was placed under vacuum and backfilled with N_2 (3 times). THF (2 mL) was added, and the resulting suspension was then cooled to 0 ℃. A solution of iodonium salts (0.3mmol, 1.5 equiv) in THF (2 mL) was added dropwise. The resulting suspension was stirred vigorously at this temperature for 30 min, the crude product was finally purified by flash column chromatography on silica gel.

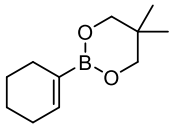
(**The carbon directly attached to the boron atom was not detected due to quadrupolar broadening**)

2-(Cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3aa)



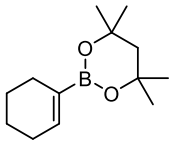
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 – 6.36 (m, 1H), 2.10 – 2.05 (m, 4H), 1.59 – 1.56 (m, 4H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 83.1, 26.7, 26.2, 24.9, 22.6, 22.3; HRMS (ES^+) exact mass calculated for ($C_{12}H_{22}BO_2$) $[M+H]^+$ requires ***m/z*** 209.1707, found ***m/z*** 209.1701.

2-(Cyclohex-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (3ab)



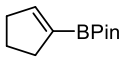
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 – 6.33 (m, 1H), 3.62 (s, 4H), 2.08 – 2.04 (m, 4H), 1.59 – 1.56 (m, 4H), 0.96 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 72.2, 31.8, 26.7, 25.9, 22.9, 22.5, 22.0; HRMS (ES^+) exact mass calculated for ($C_{11}H_{20}BO_2$) $[M+H]^+$ requires ***m/z*** 195.1551, found ***m/z*** 195.1557.

2-(Cyclohex-1-en-1-yl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (3ac)



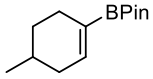
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 – 6.35 (m, 1H), 2.09 – 2.06 (m, 4H), 1.80 (d, J = 2.4 Hz, 2H), 1.59 – 1.55 (m, 4H), 1.33 (d, J = 2.5 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 70.3, 49.1, 32.0, 26.7, 26.0, 23.0, 22.6; HRMS (ES^+) exact mass calculated for ($C_{13}H_{24}BO_2$) $[M+H]^+$ requires ***m/z*** 223.1864, found ***m/z*** 223.1869.

2-(Cyclopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba)



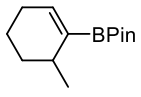
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (t, J = 2.2 Hz, 1H), 2.46 – 2.36 (m, 4H), 1.82 (p, J = 7.6 Hz, 2H), 1.27 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 83.2, 34.9, 34.7, 24.9, 24.1; HRMS (ES^+) exact mass calculated for ($C_{11}H_{20}BO_2$) $[M+H]^+$ requires ***m/z*** 195.1551, found ***m/z*** 195.1557.

4,4,5,5-Tetramethyl-2-(4-methylcyclohex-1-en-1-yl)-1,3,2-dioxaborolane (3ca)



Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 – 6.42 (m, 1H), 2.30 – 1.93 (m, 3H), 1.82 – 1.49 (m, 4H), 1.25 (s, 12H), 0.93 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 83.1, 35.4, 31.0, 28.2, 26.5, 25.0, 24.9, 22.2; HRMS (ES^+) exact mass calculated for ($C_{13}H_{24}BO_2$) $[M+H]^+$ requires ***m/z*** 223.1864, found ***m/z*** 223.1867.

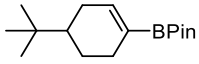
4,4,5,5-Tetramethyl-2-(6-methylcyclohex-1-en-1-yl)-1,3,2-dioxaborolane (3da)



Colorless liquid;

HRMS (ES^+) exact mass calculated for ($C_{13}H_{24}BO_2$) $[M+H]^+$ requires ***m/z*** 223.1864, found ***m/z*** 223.1868.

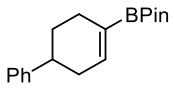
2-(4-(Tert-butyl)cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ea)



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 – 6.31 (m, 1H), 2.37 – 2.20 (m, 1H), 2.17 – 1.95 (m, 2H), 1.91 – 1.73 (m, 2H), 1.24 (s, 13H), 1.11 – 0.99 (m, 1H), 0.84 (s, 9H); ^{13}C NMR (101 MHz,

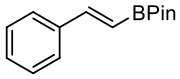
$CDCl_3$) δ 143.5, 83.1, 43.8, 32.3, 28.5, 27.9, 27.2, 24.9 (d, *J* = 5.2 Hz), 24.0; HRMS (ES^+) exact mass calculated for ($C_{16}H_{30}BO_2$) $[M+H]^+$ requires ***m/z*** 265.2333, found ***m/z*** 265.2337.

4,4,5,5-Tetramethyl-2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (3fa)



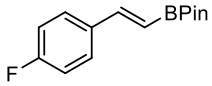
Colorless liquid; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.24 – 7.15 (m, 3H), 6.67 – 6.66 (m, 1H), 2.91 – 2.70 (m, 1H), 2.49 – 2.10 (m, 4H), 2.02 – 1.87 (m, 1H), 1.80 – 1.62 (m, 1H), 1.28 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 142.4, 128.5, 127.0, 126.1, 83.3, 39.9, 35.0, 29.9, 27.2, 25.0 (d, *J* = 3.4 Hz); HRMS (ES^+) exact mass calculated for ($C_{18}H_{26}BO_2$) $[M+H]^+$ requires ***m/z*** 285.2020, found ***m/z*** 285.2024.

4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (3ga)



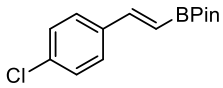
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.32 (d, *J* = 18.4 Hz, 1H), 7.28 – 7.15 (m, 3H), 6.09 (d, *J* = 18.4 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 137.6, 129.0, 128.7, 127.2, 83.5, 24.9; HRMS (ES^+) exact mass calculated for ($C_{14}H_{20}BO_2$) $[M+H]^+$ requires ***m/z*** 231.1551, found ***m/z*** 231.1557.

2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ha)



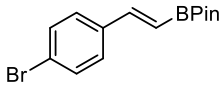
White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 248.6 Hz), 148.3, 133.9 (d, *J* = 3.3 Hz), 128.8 (d, *J* = 8.2 Hz), 115.7 (d, *J* = 21.7 Hz), 83.5, 24.9; HRMS (ES^+) exact mass calculated for ($C_{14}H_{19}BFO_2$) $[M+H]^+$ requires ***m/z*** 249.1457, found ***m/z*** 249.1452.

2-(4-Chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ia)



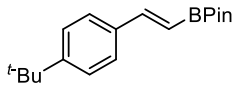
White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.07 (m, 3H), 6.03 (d, *J* = 18.4 Hz, 1H), 1.21 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 136.1, 134.7, 128.9, 128.4, 83.6, 24.9; HRMS (ES^+) exact mass calculated for ($C_{14}H_{19}BClO_2$) $[M+H]^+$ requires ***m/z*** 265.1161, found ***m/z*** 265.1167.

2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ja)



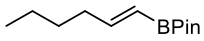
White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.14 (m, 3H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 136.5, 131.9, 128.6, 123.0, 83.6, 24.9; HRMS (ES^+) exact mass calculated for ($C_{14}H_{19}BBrO_2$) $[M+H]^+$ requires m/z 309.0656, found m/z 309.0659.

2-(4-(Tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ka)



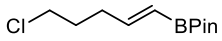
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.25 (m, 3H), 6.04 (d, *J* = 18.4 Hz, 1H), 1.23, 1.23 (s, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 149.5, 134.9, 126.9, 125.6, 83.4, 34.8, 31.4, 24.9; HRMS (ES^+) exact mass calculated for ($C_{18}H_{28}BO_2$) $[M+H]^+$ requires ***m/z*** 287.2177, found ***m/z*** 287.2179.

2-(Hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3la)



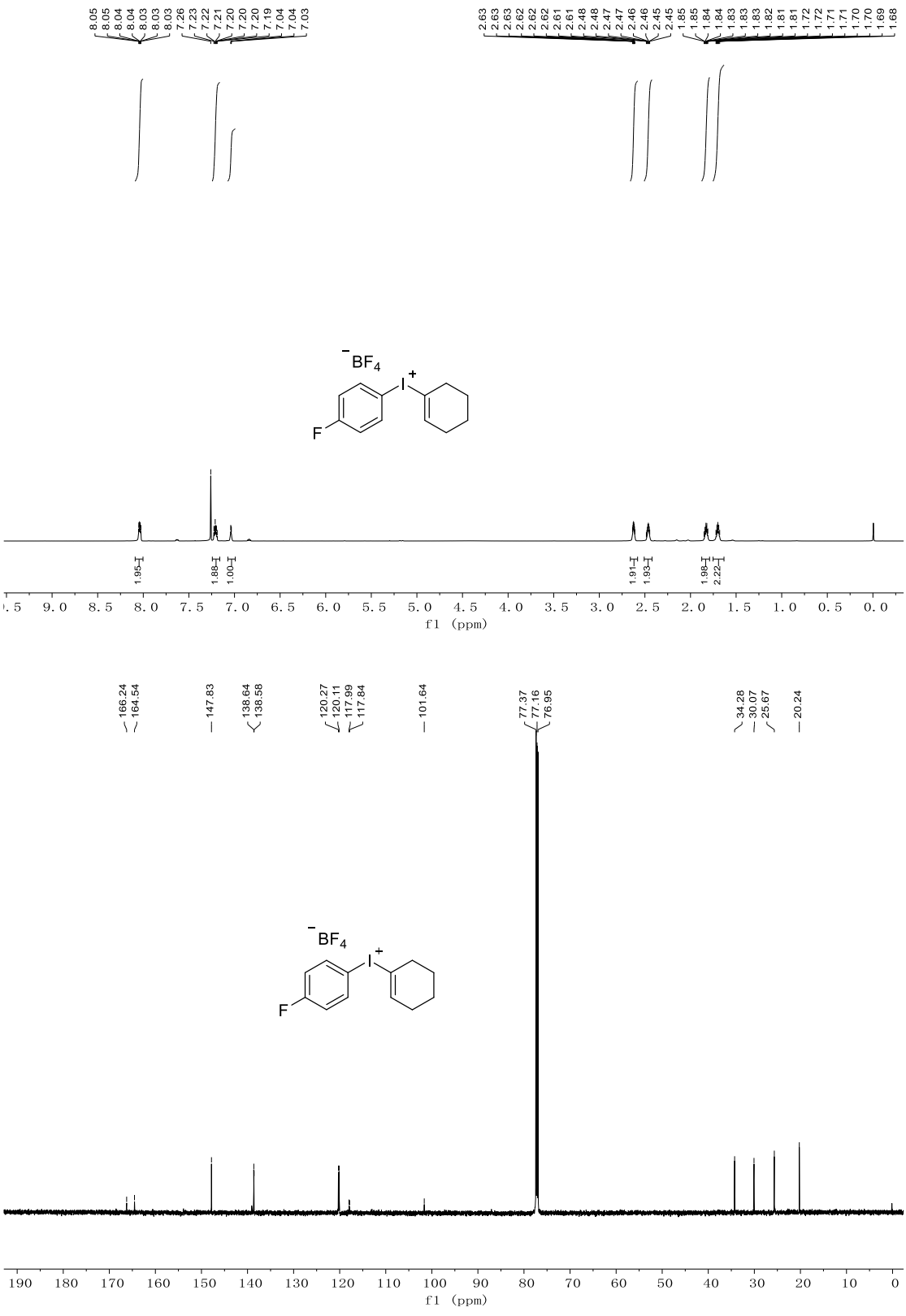
Colorless liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.60 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.39 (d, *J* = 18.0 Hz, 1H), 2.25 – 1.98 (m, 2H), 1.51 – 1.11 (m, 16H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 83.0, 35.6, 30.5, 24.9, 22.4, 14.0; HRMS (ES^+) exact mass calculated for ($C_{12}H_{24}BO_2$) $[M+H]^+$ requires ***m/z*** 211.1864, found ***m/z*** 211.1869.

2-(5-Chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ma)

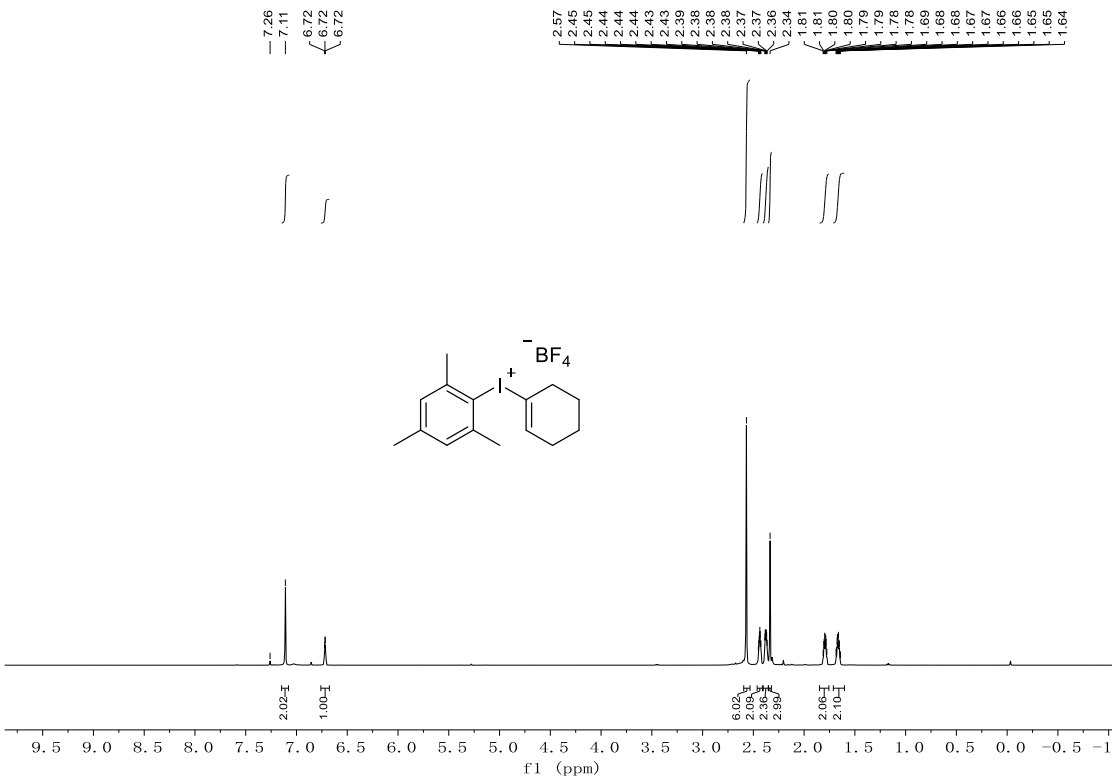


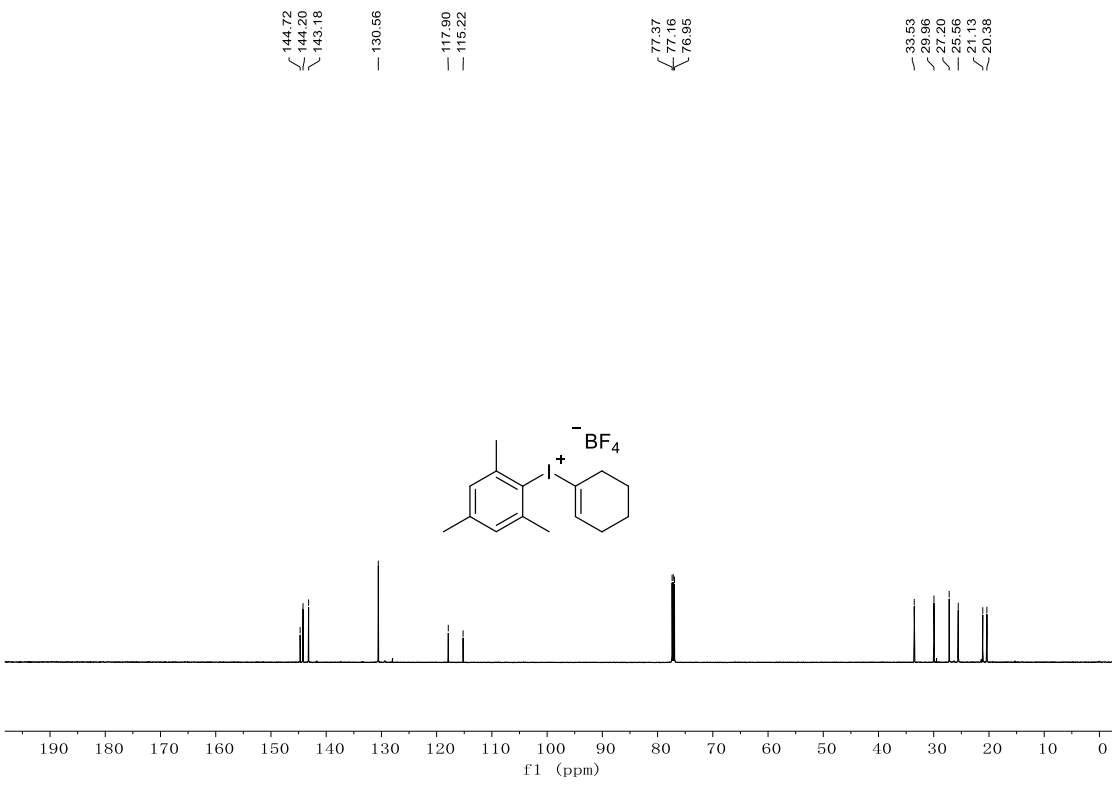
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.47 (d, *J* = 18.0 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.89 (p, *J* = 6.9 Hz, 2H), 1.25 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 83.3, 44.4, 32.8, 31.1, 24.9; HRMS (ES^+) exact mass calculated for ($C_{11}H_{21}BClO_2$) $[M+H]^+$ requires ***m/z*** 231.1318, found ***m/z*** 231.1326.

Cyclohex-1-en-1-yl(4-fluorophenyl)iodonium tetrafluoroborate

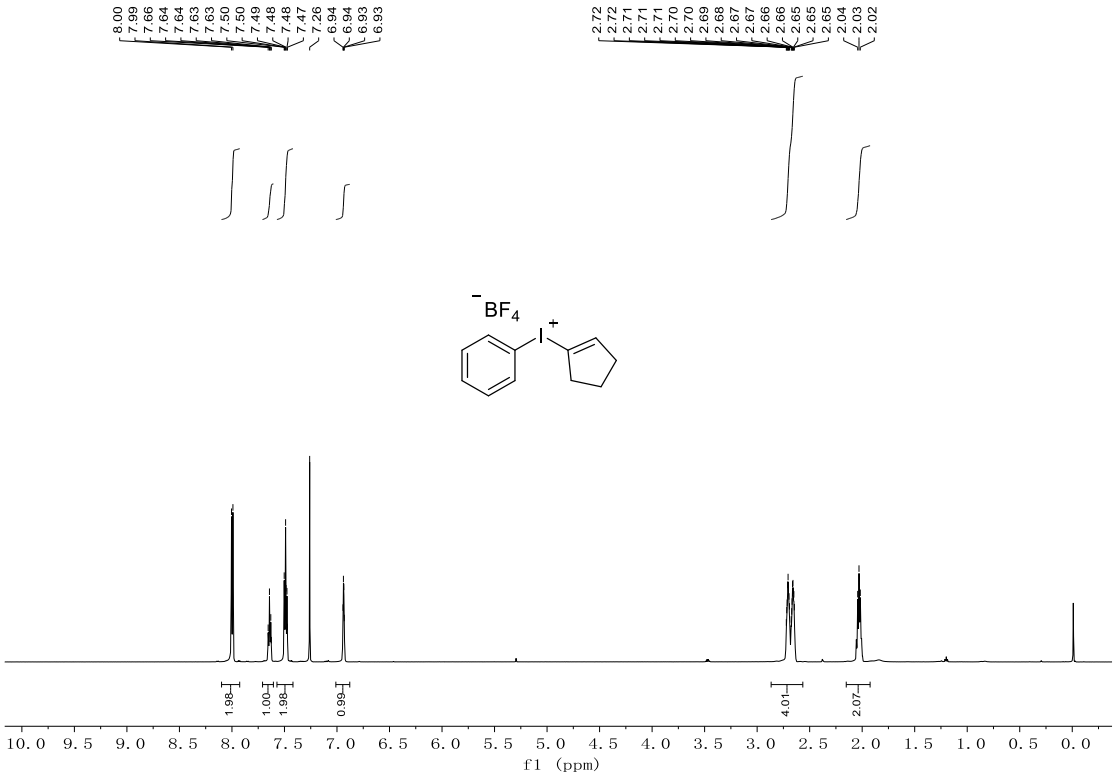


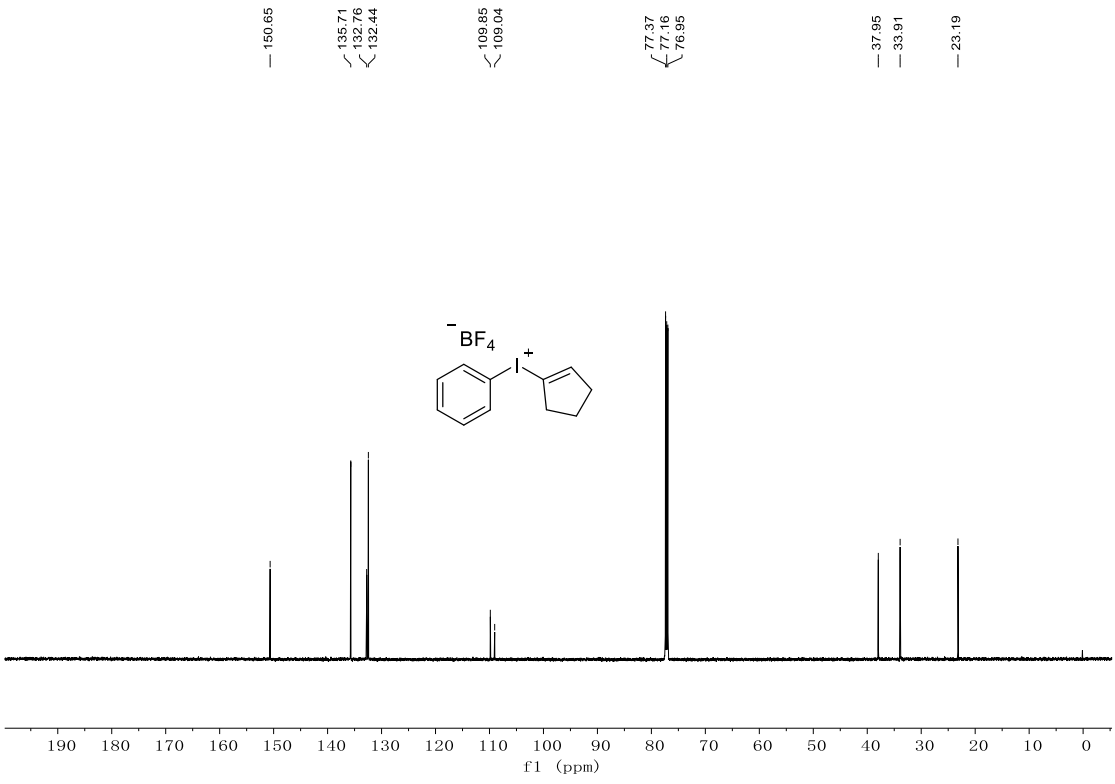
Cyclohex-1-en-1-yl(mesityl)iodonium tetrafluoroborate



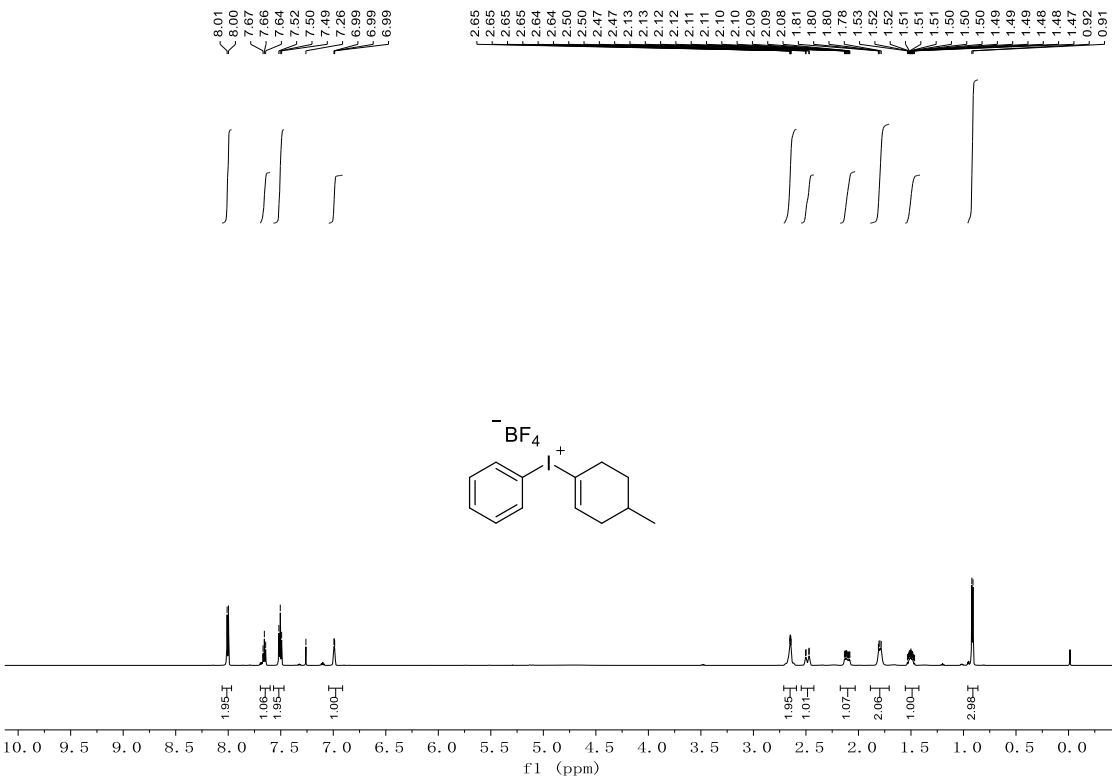


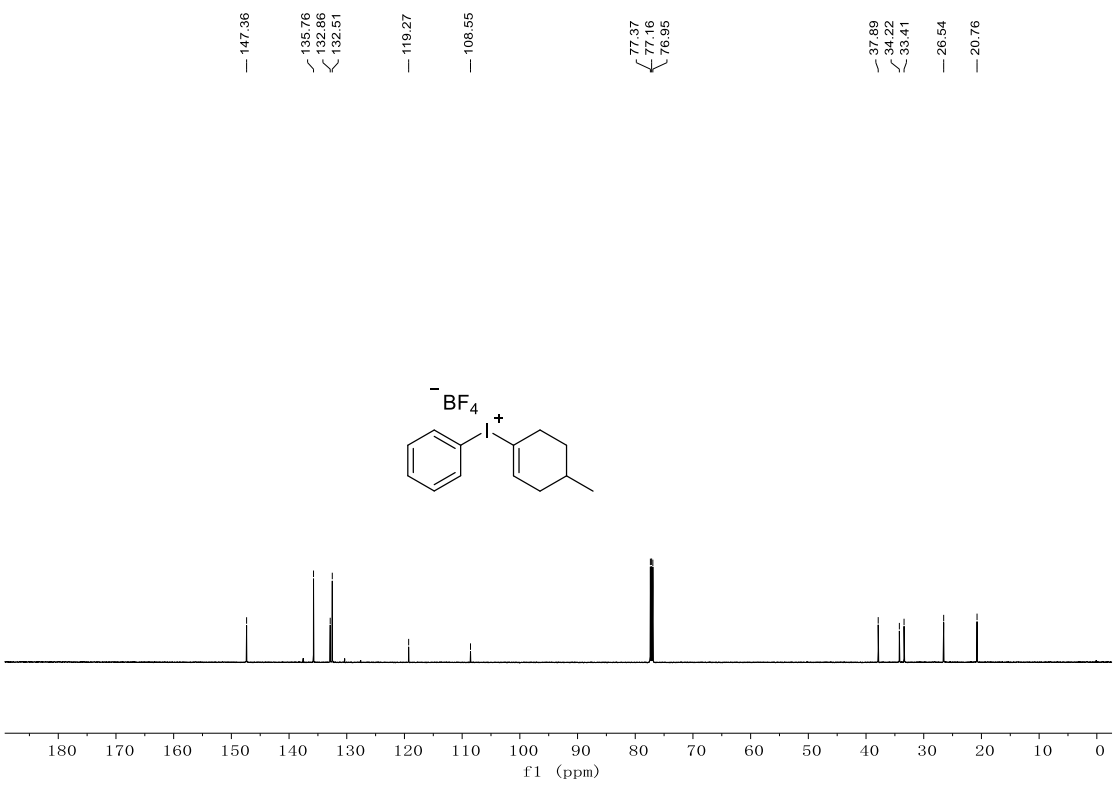
Cyclopent-1-en-1-yl(phenyl)iodonium tetrafluoroborate (1b)



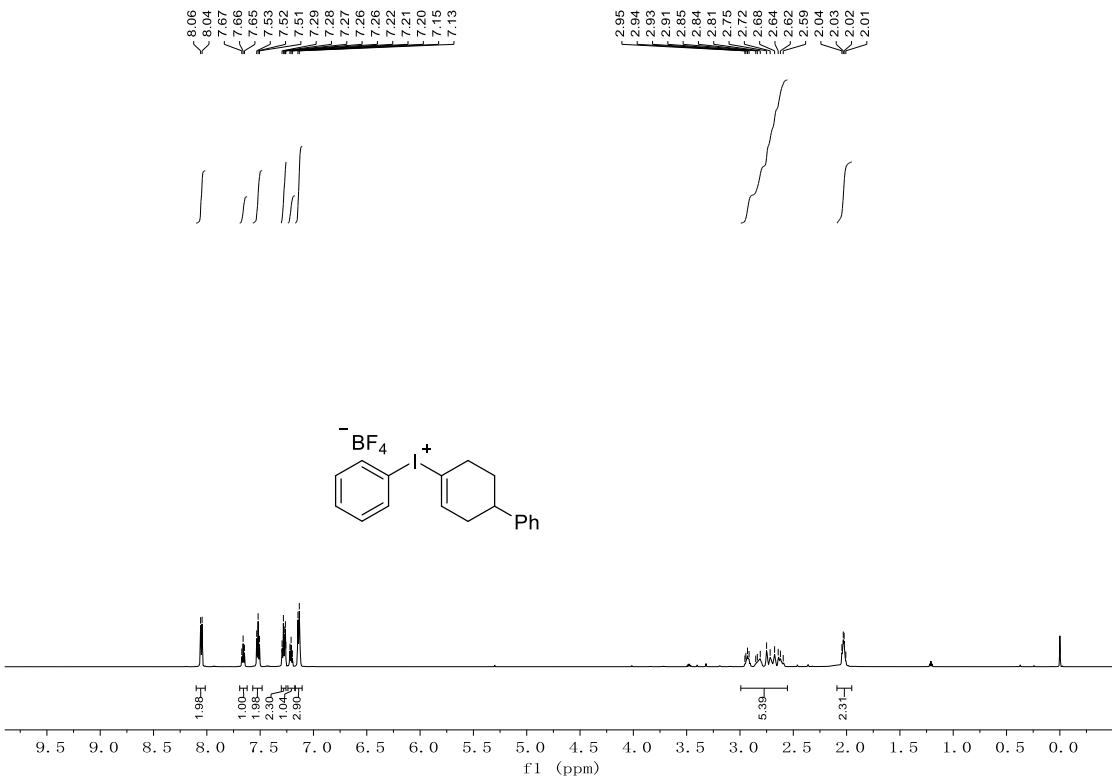


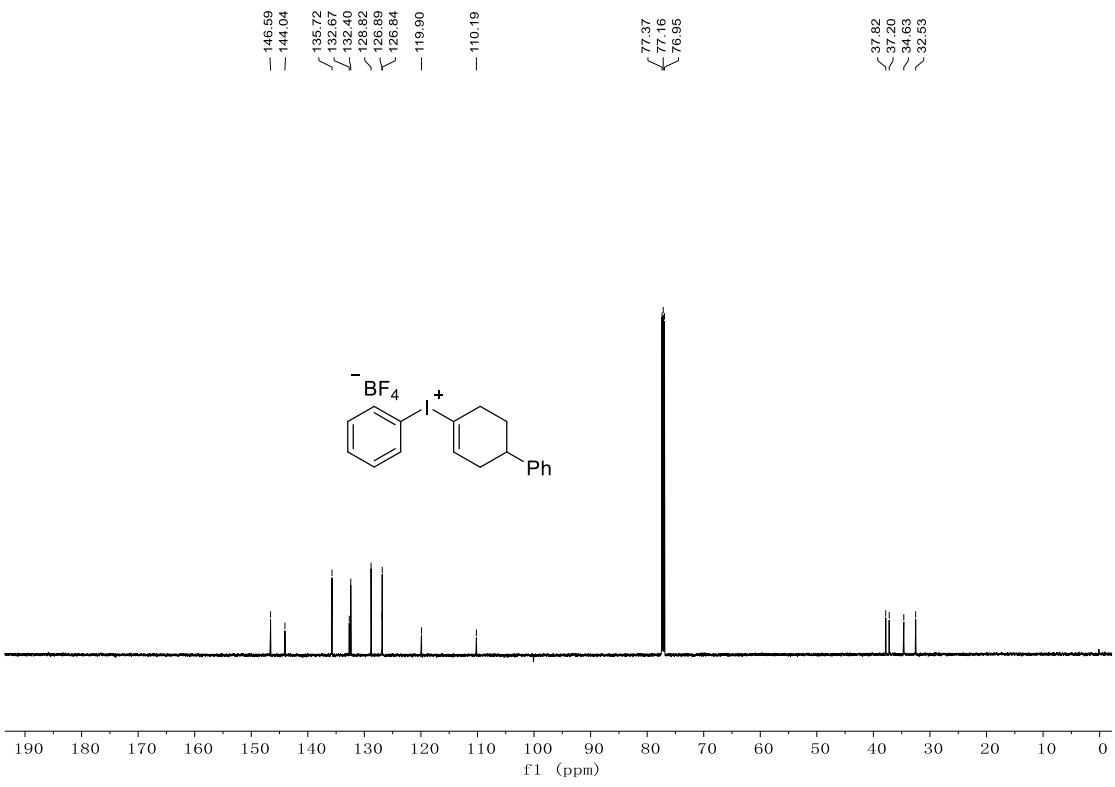
(4-Methylcyclohex-1-en-1-yl)(phenyl)iodonium tetrafluoroborate (1c)



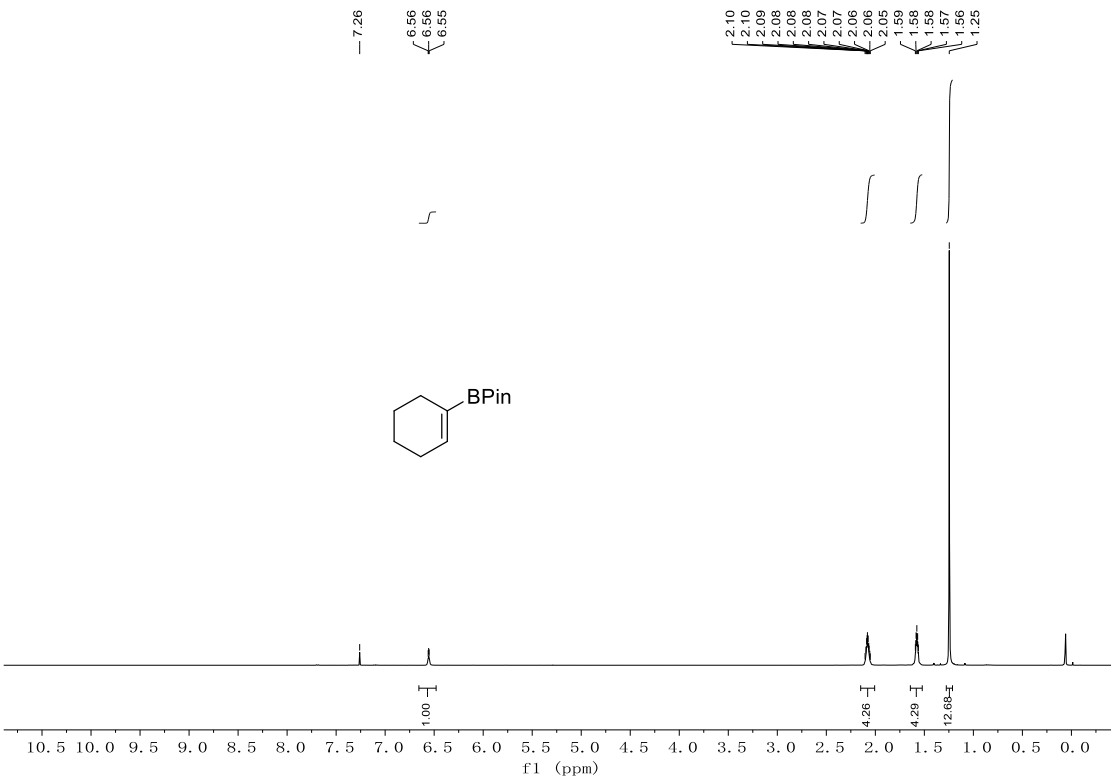


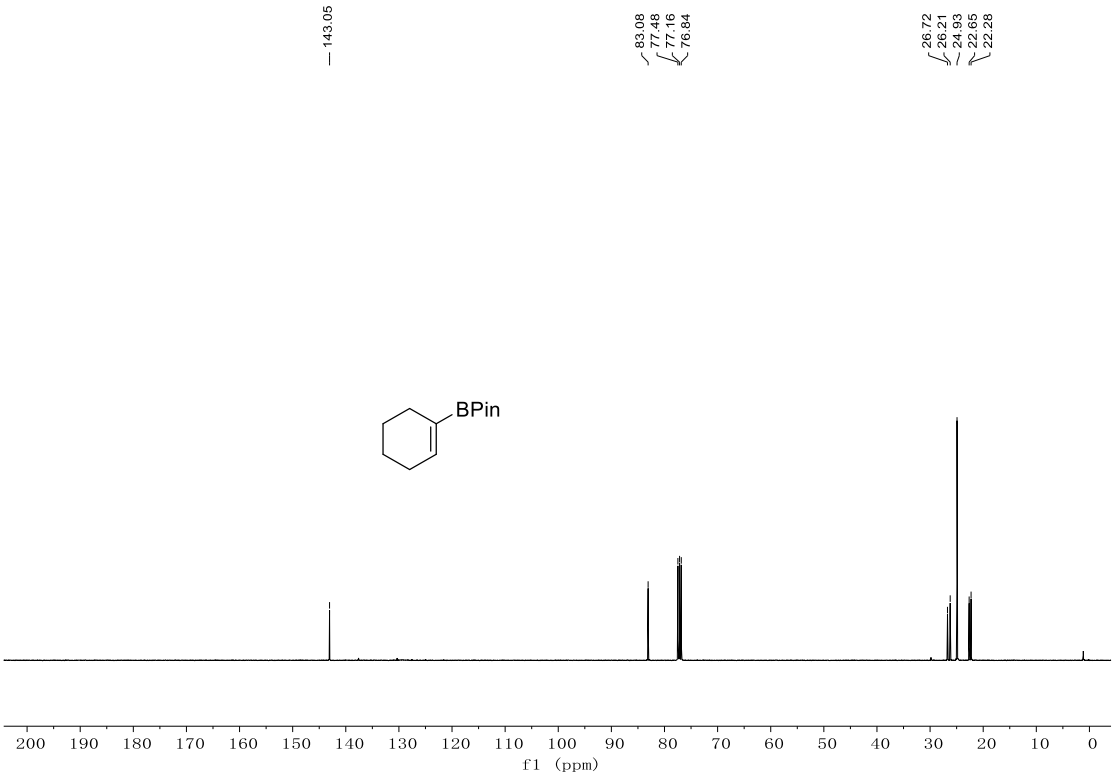
Phenyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)iodonium tetrafluoroborate (1f)



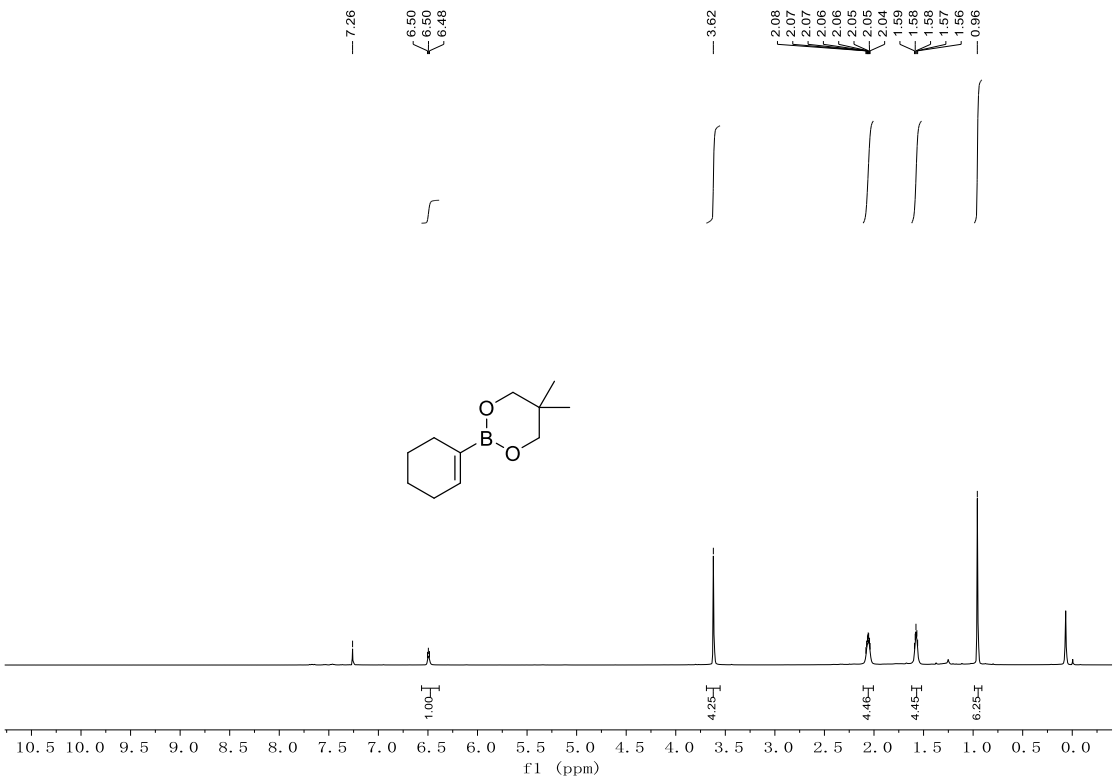


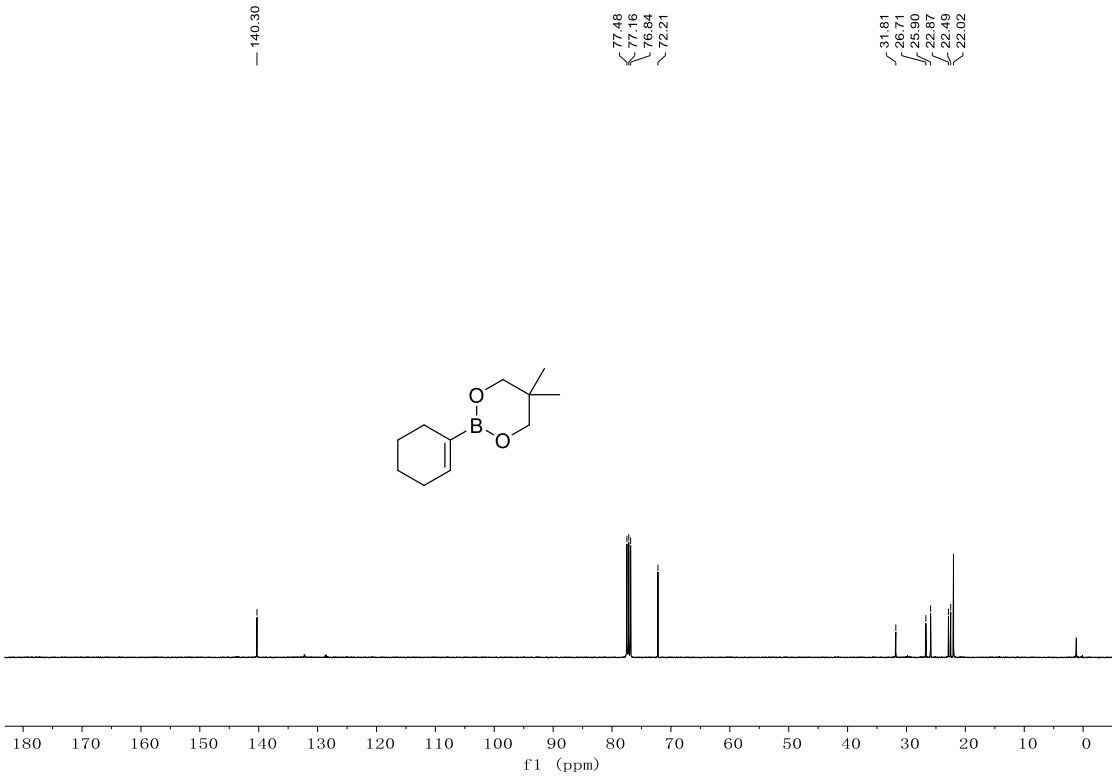
2-(Cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3aa)



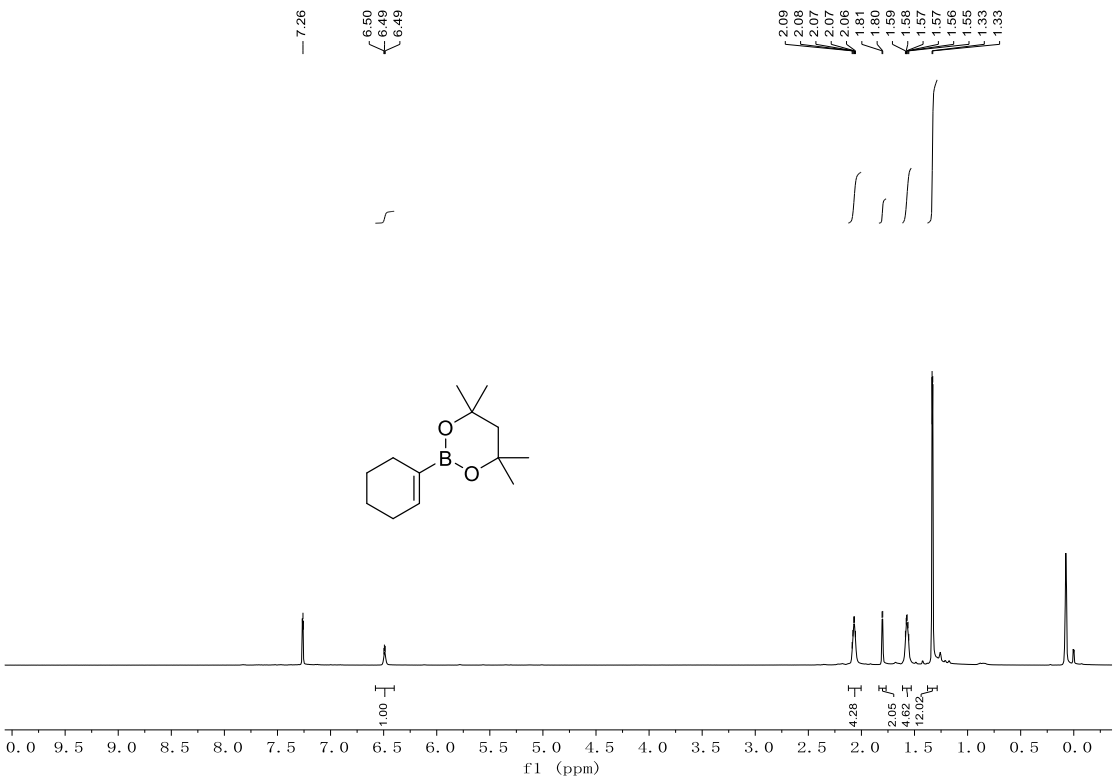


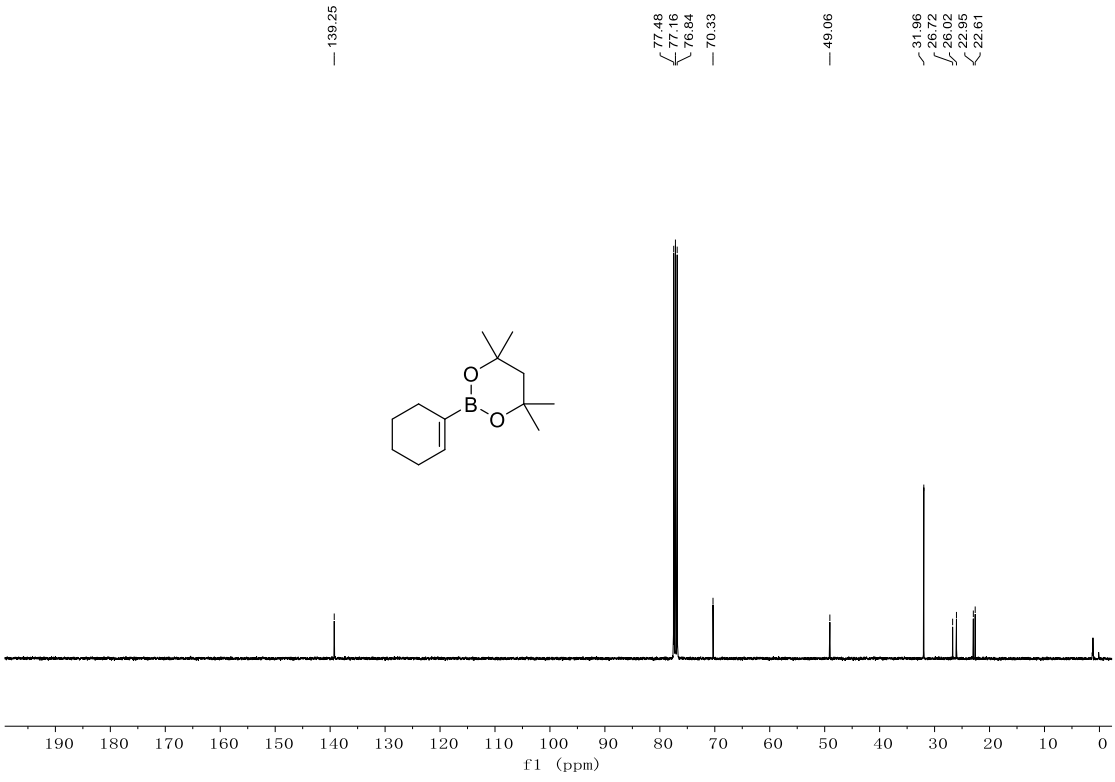
2-(Cyclohex-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (3ab)



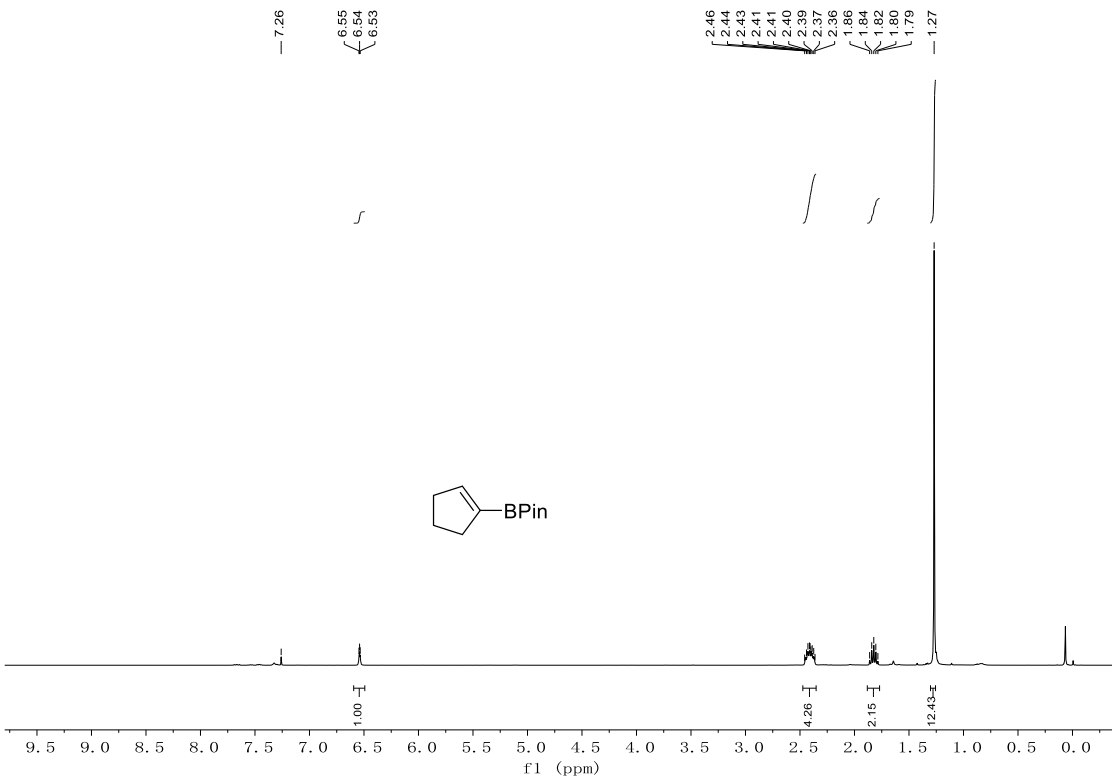


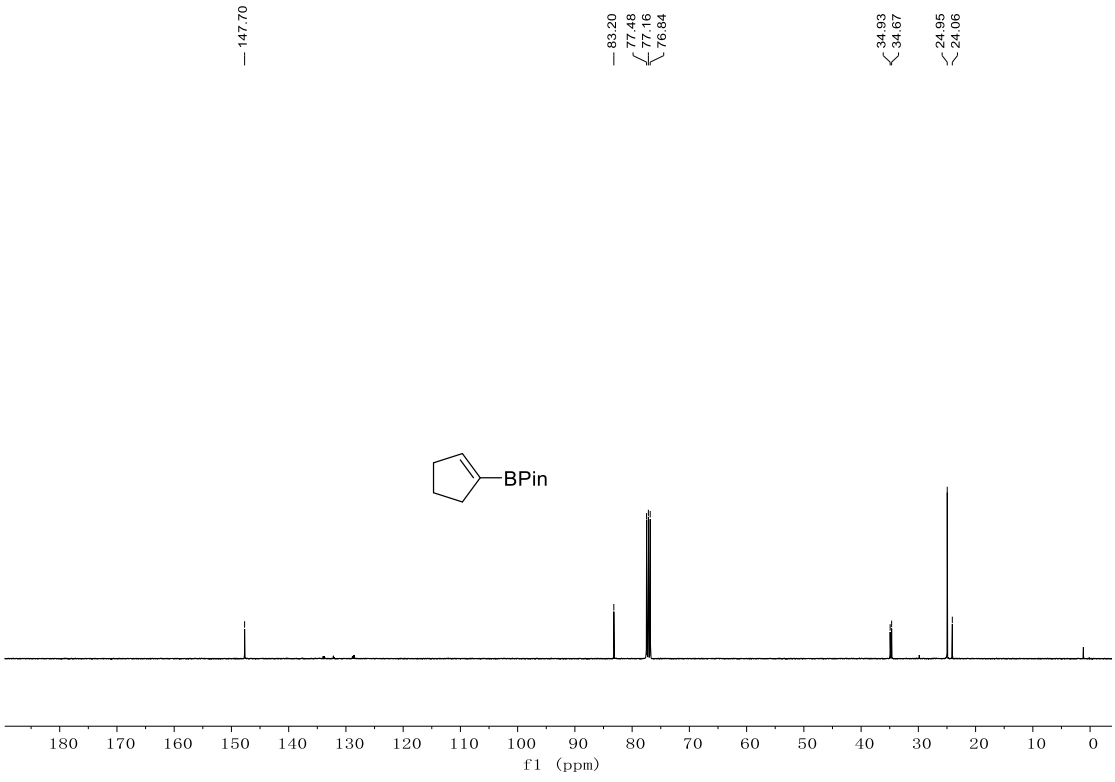
2-(Cyclohex-1-en-1-yl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (3ac)



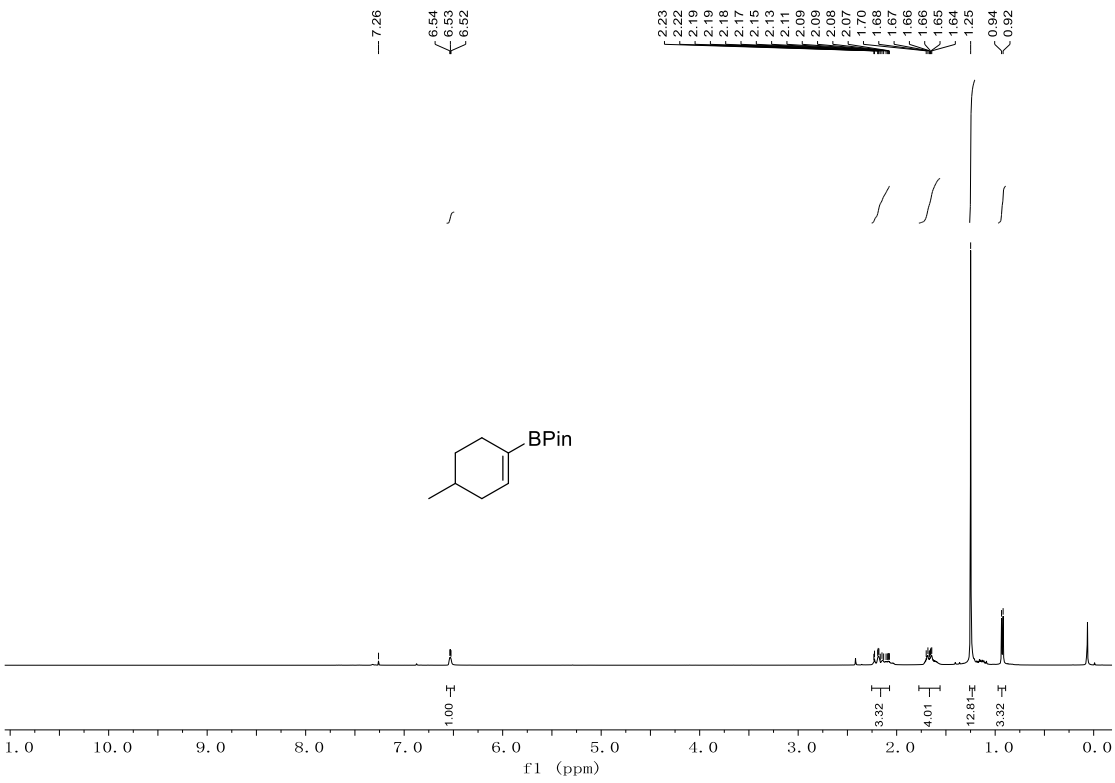


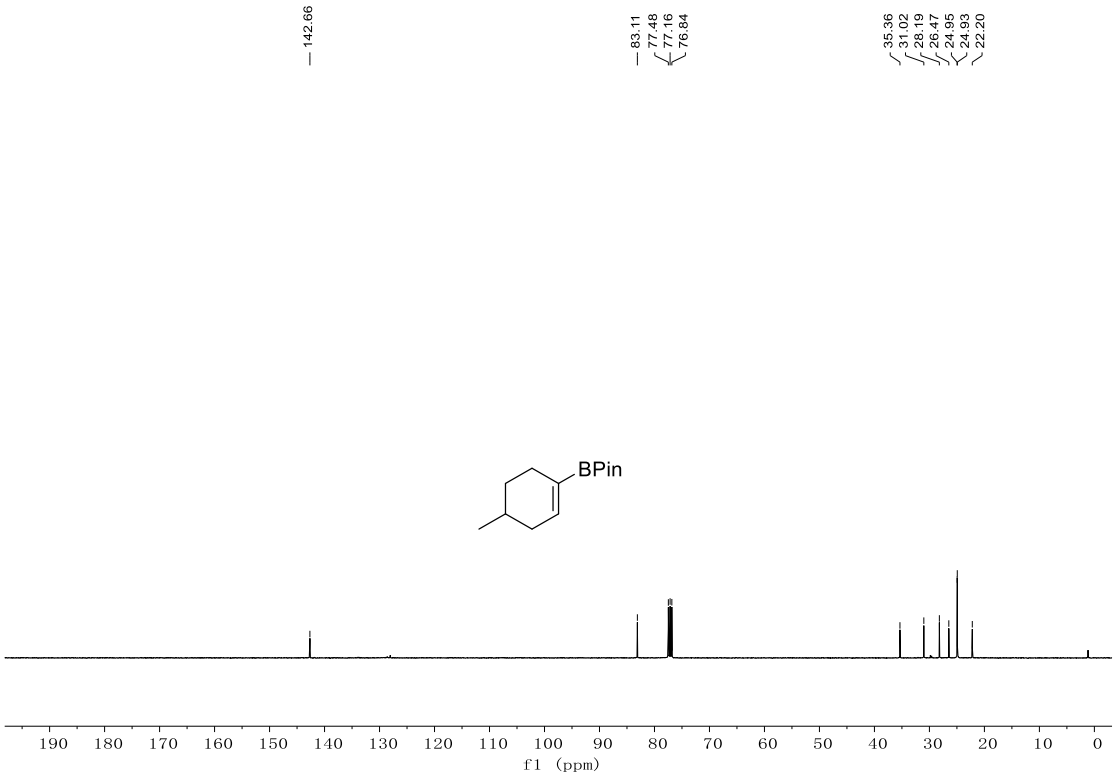
2-(Cyclopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba)



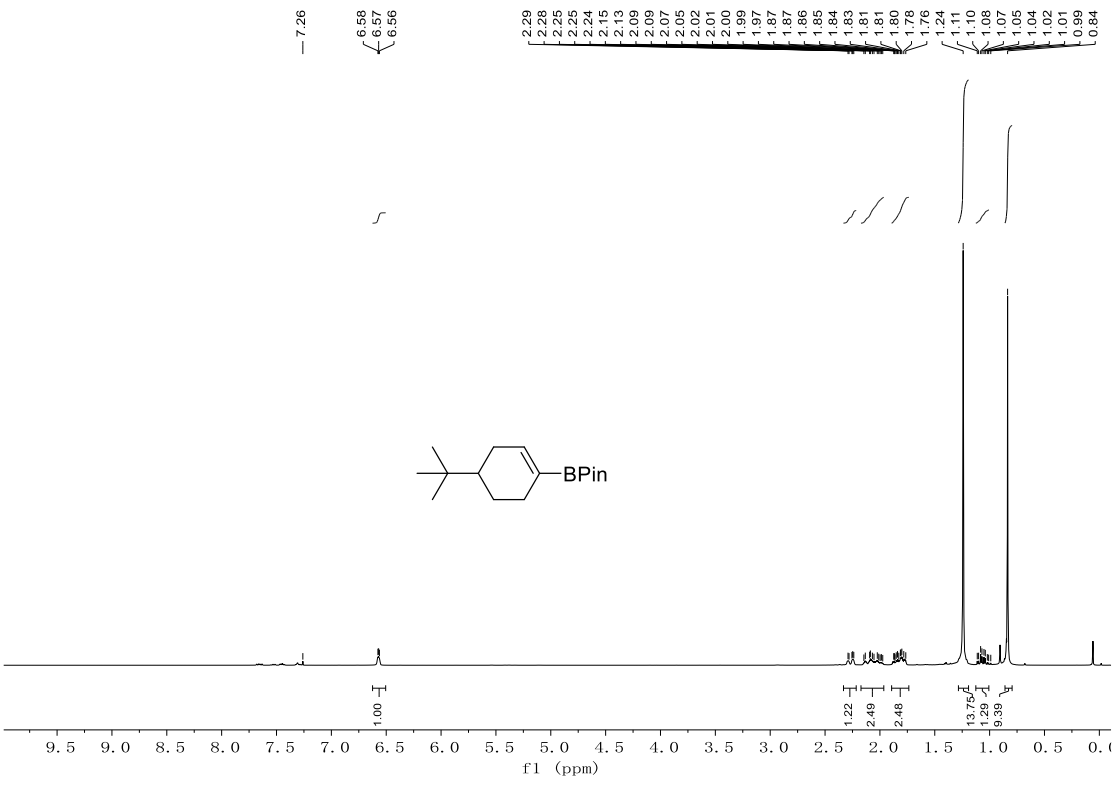


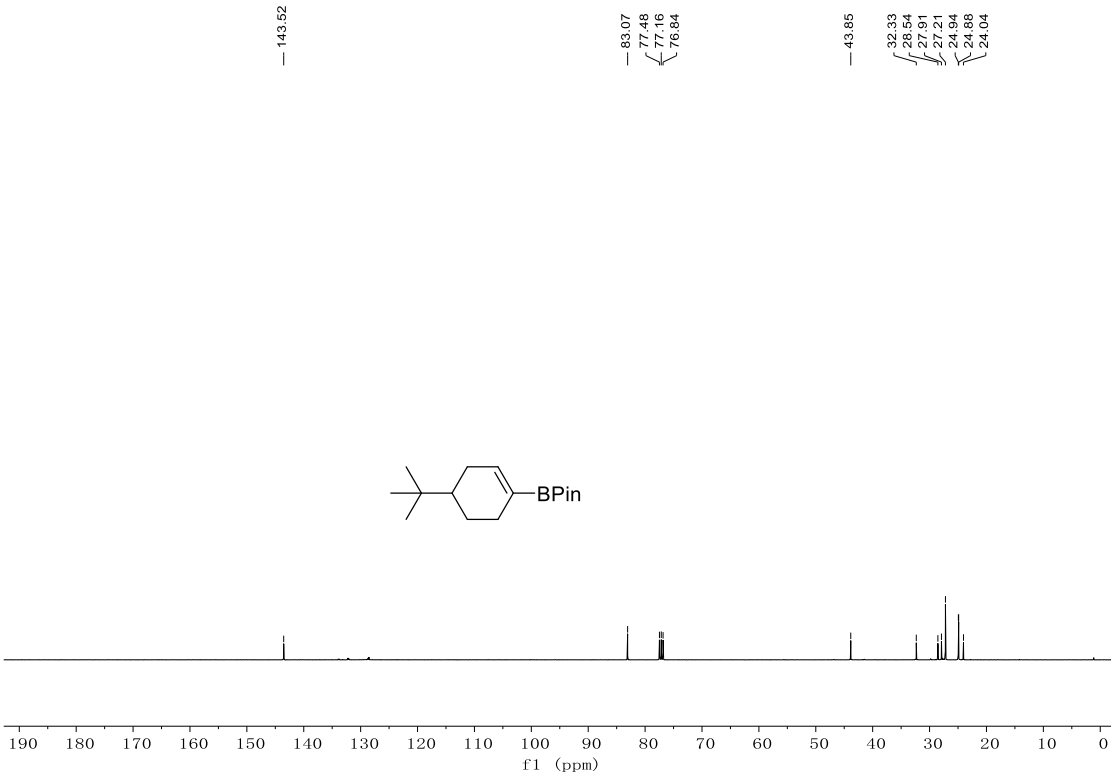
4,4,5,5-Tetramethyl-2-(4-methylcyclohex-1-en-1-yl)-1,3,2-dioxaborolane (3ca)



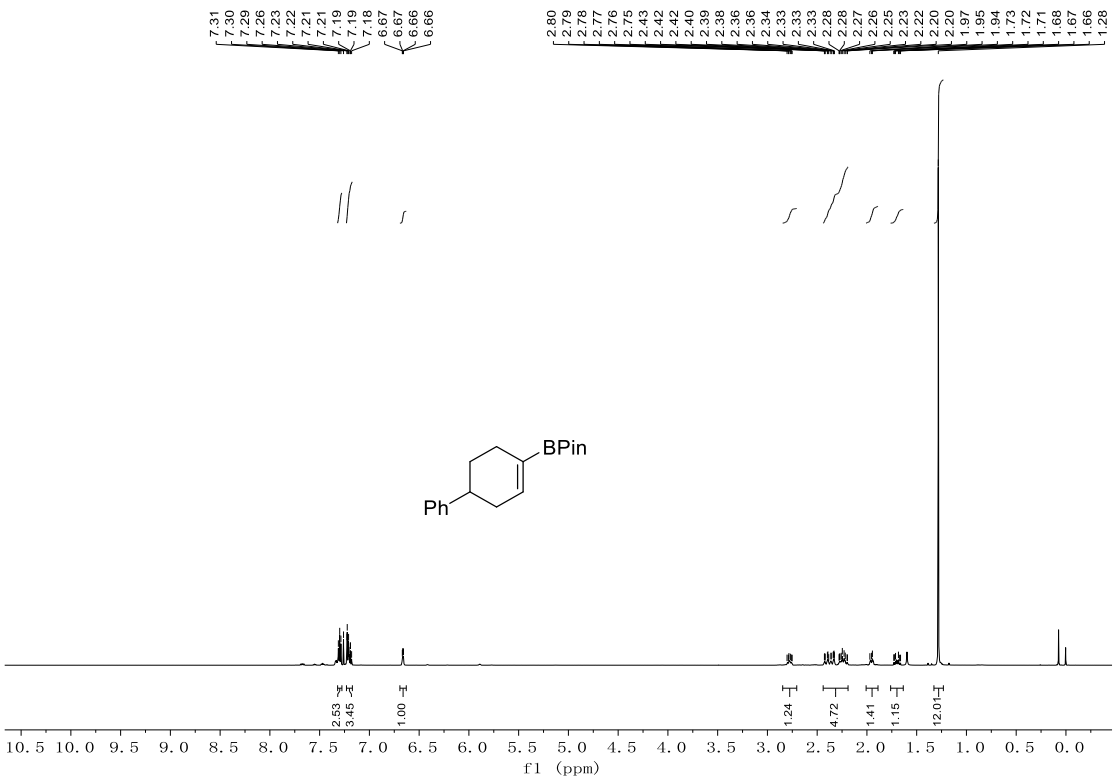


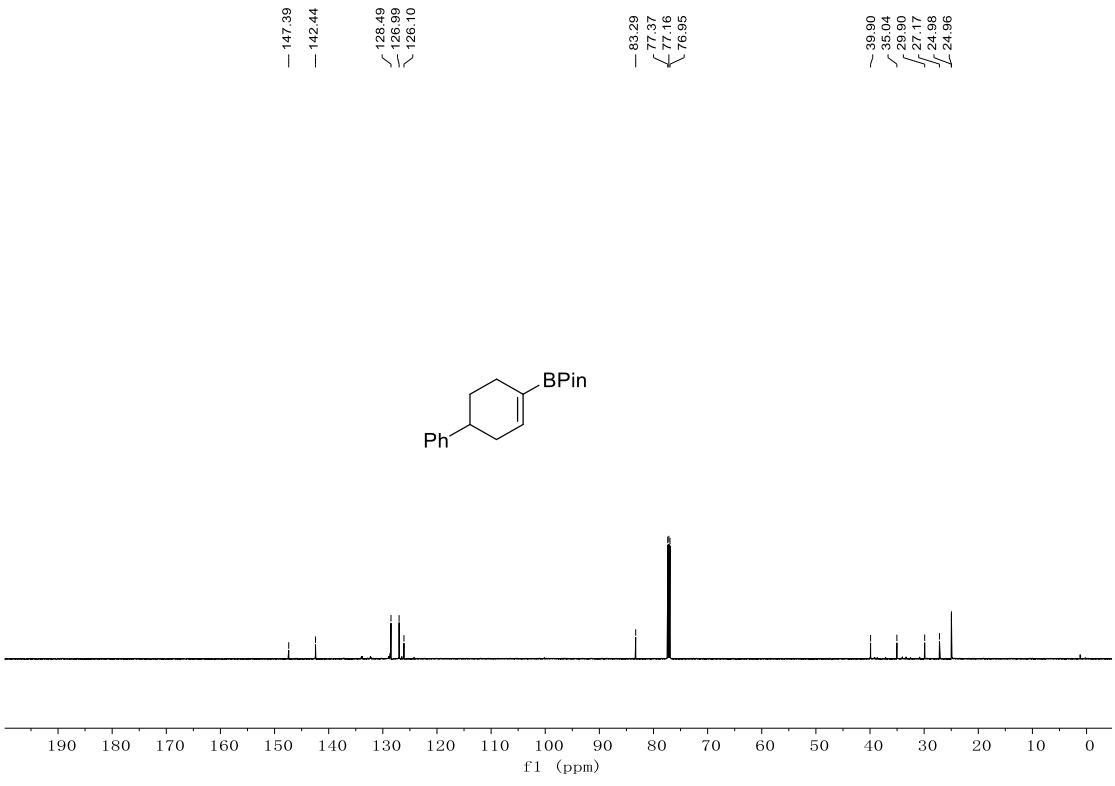
2-(4-(Tert-butyl)cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ea)



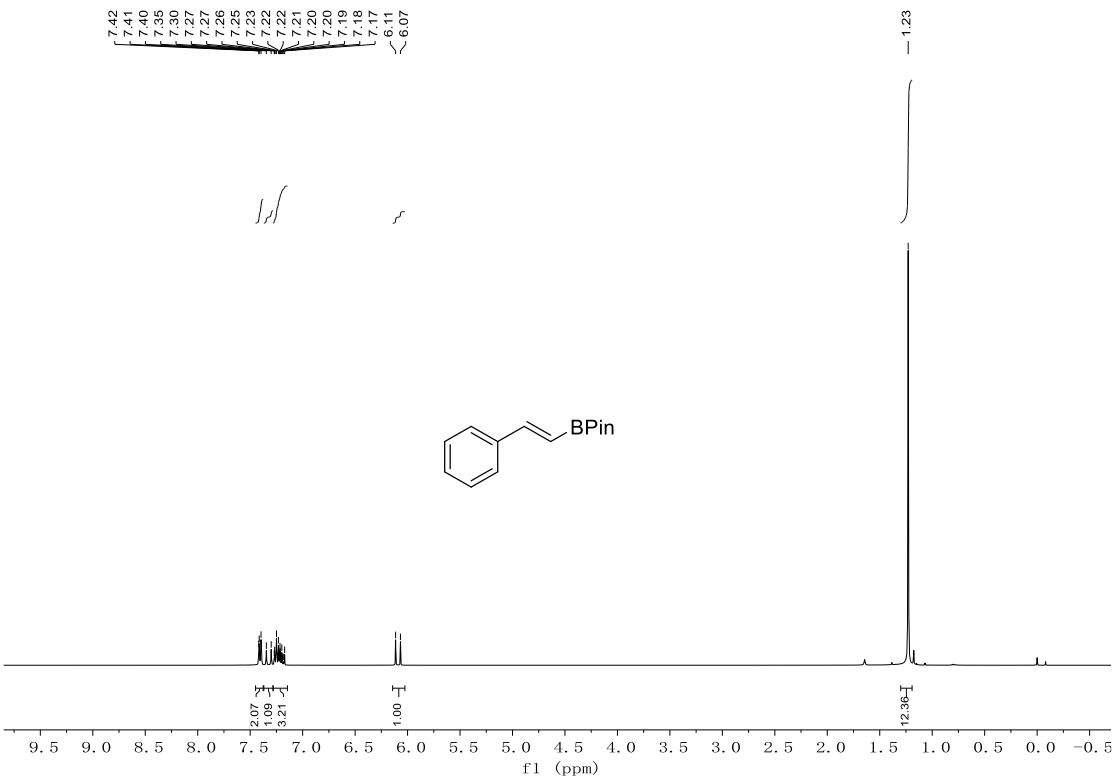


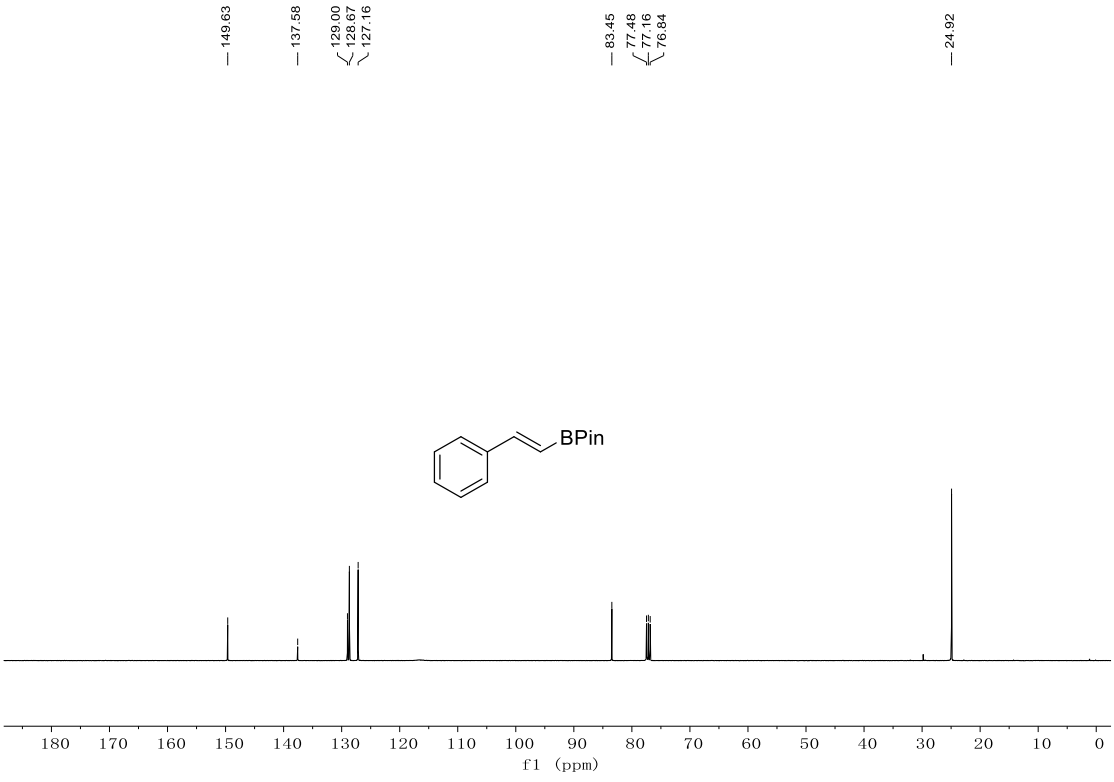
4,4,5,5-Tetramethyl-2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (3fa)



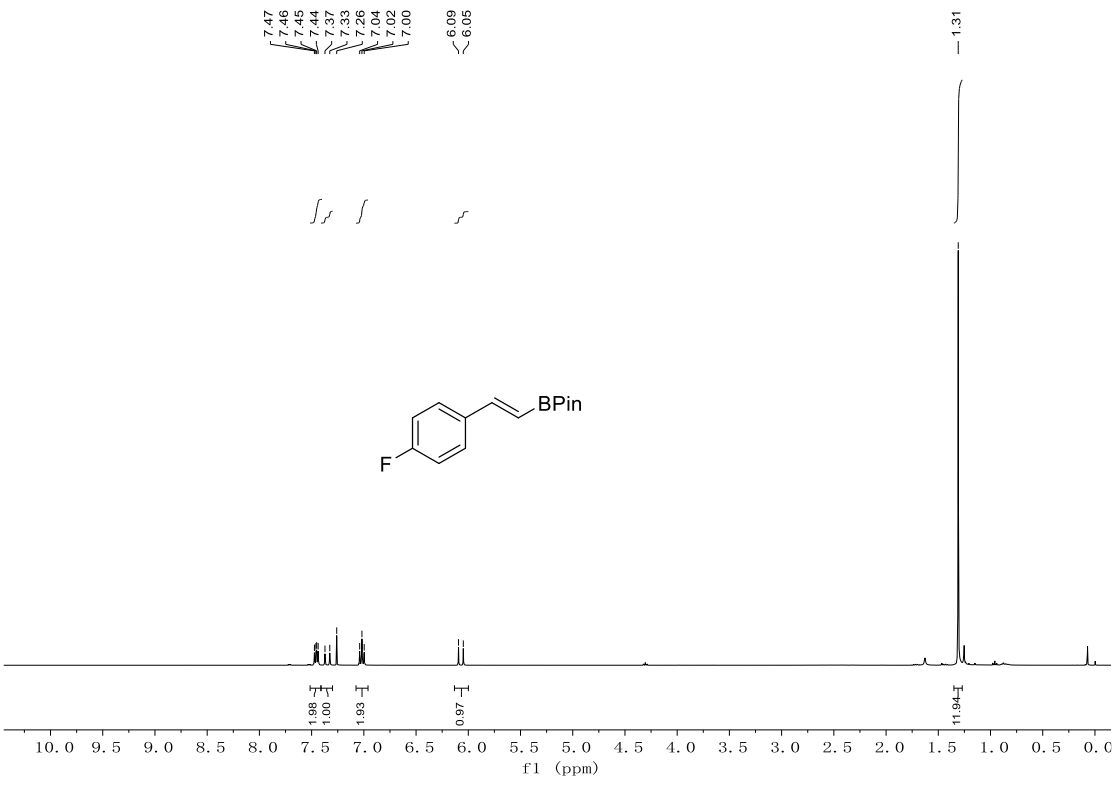


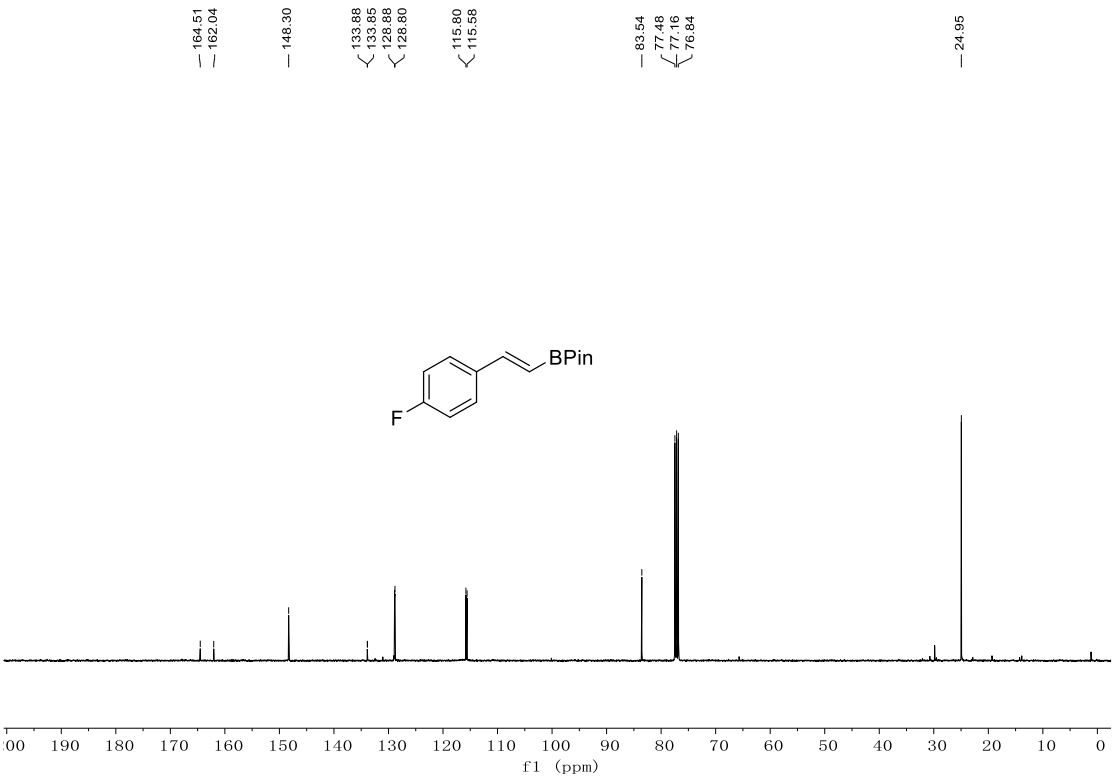
4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (3ga)



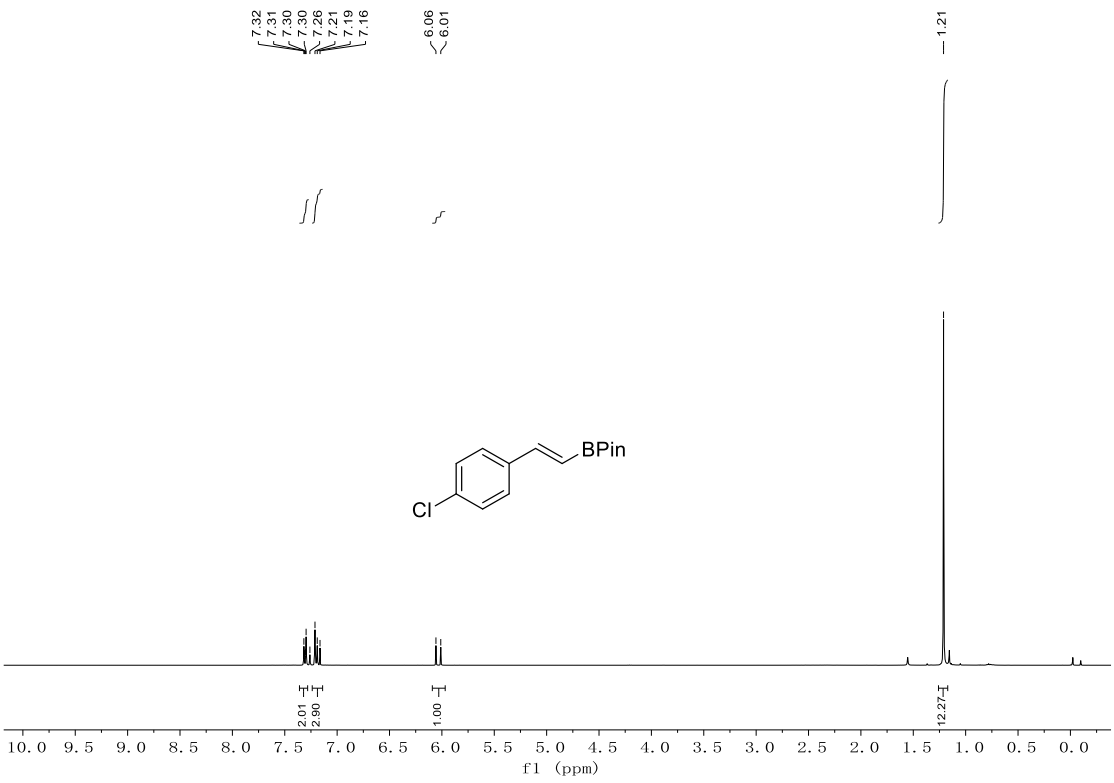


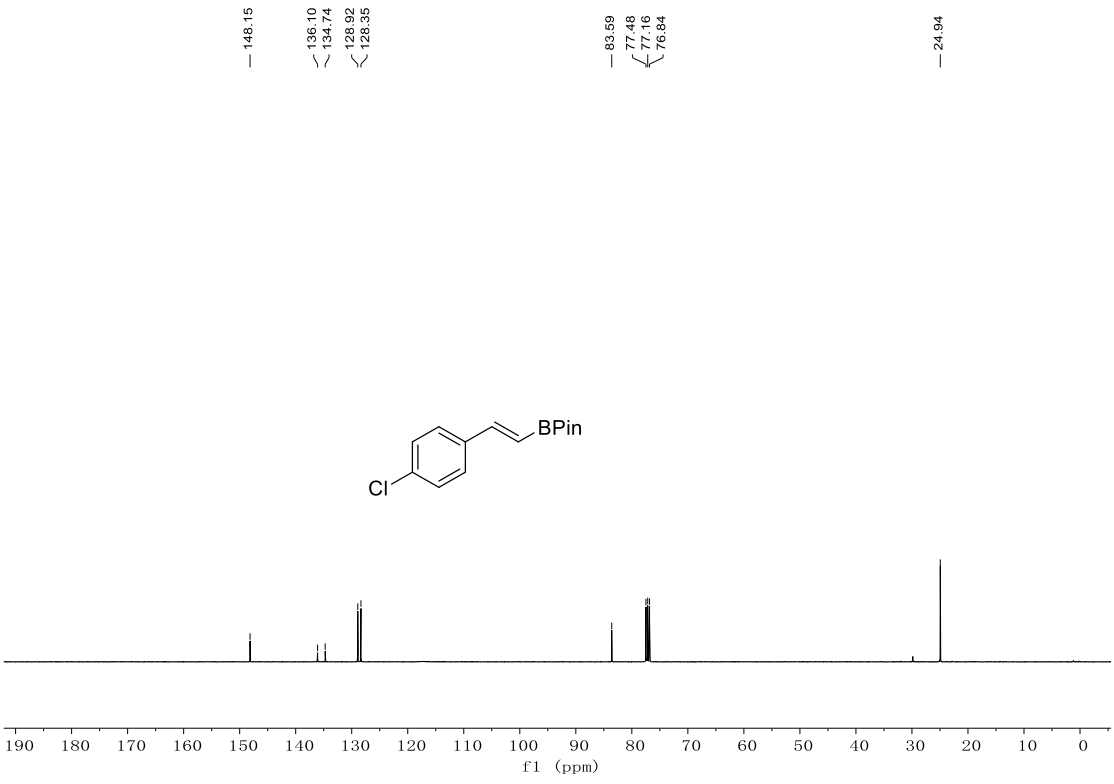
2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ha)



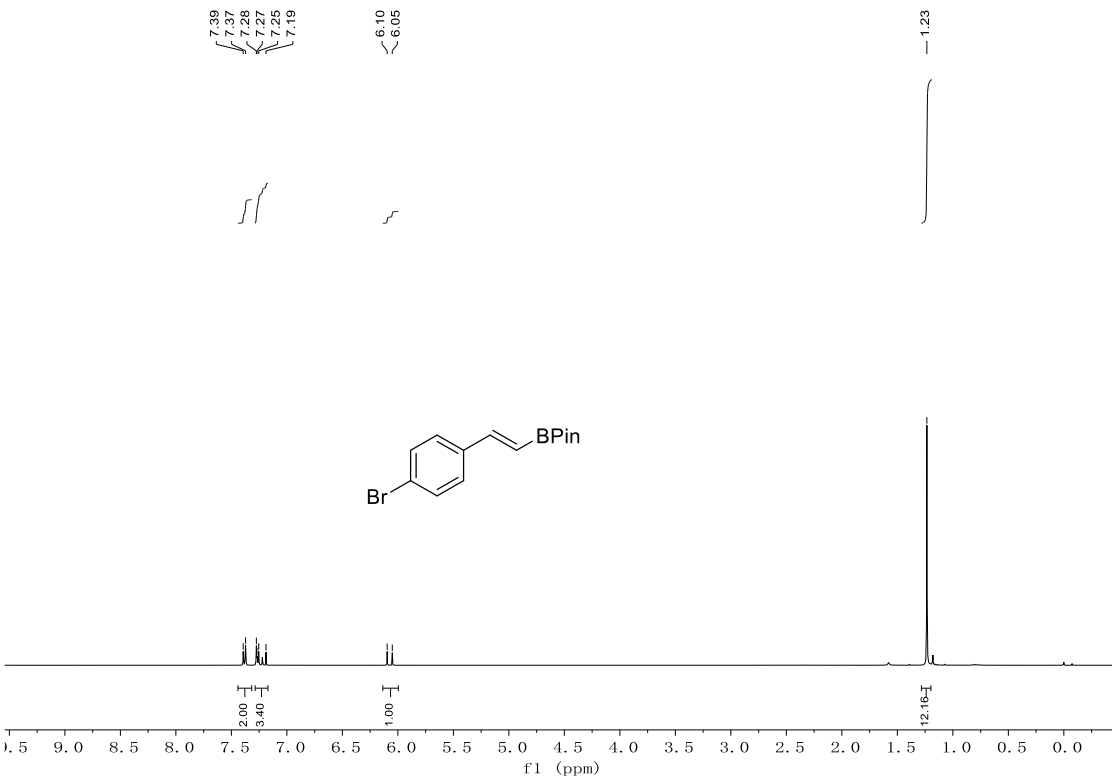


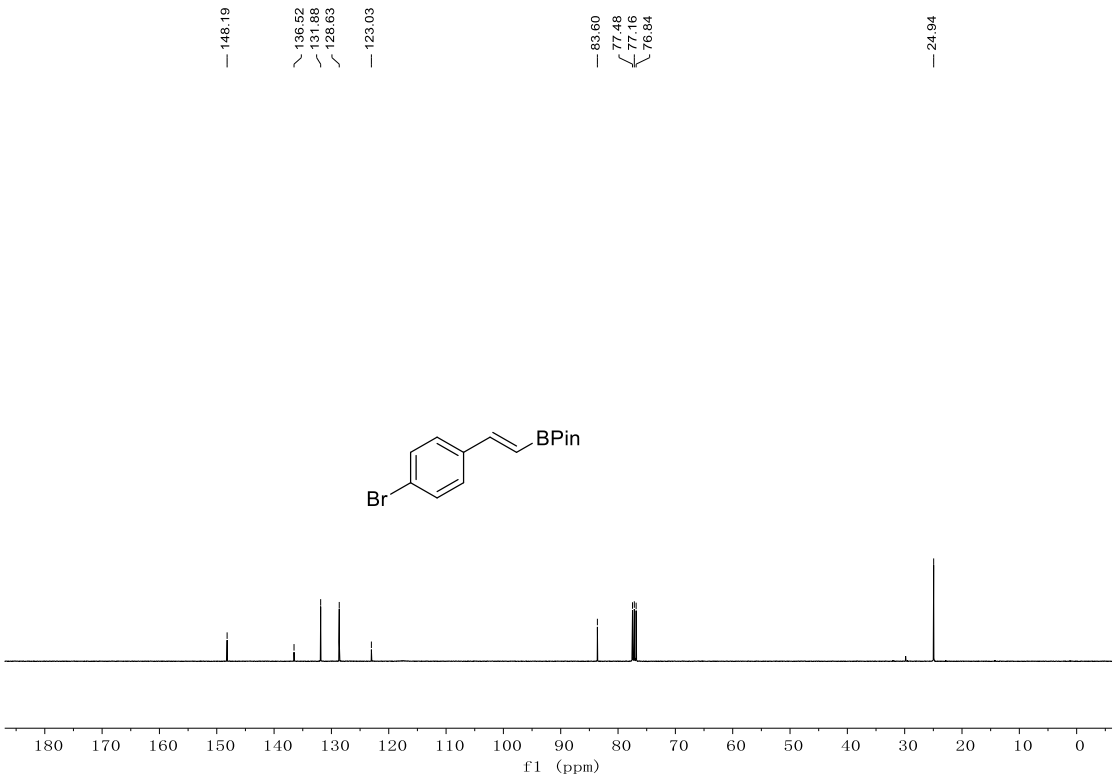
2-(4-Chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ia)



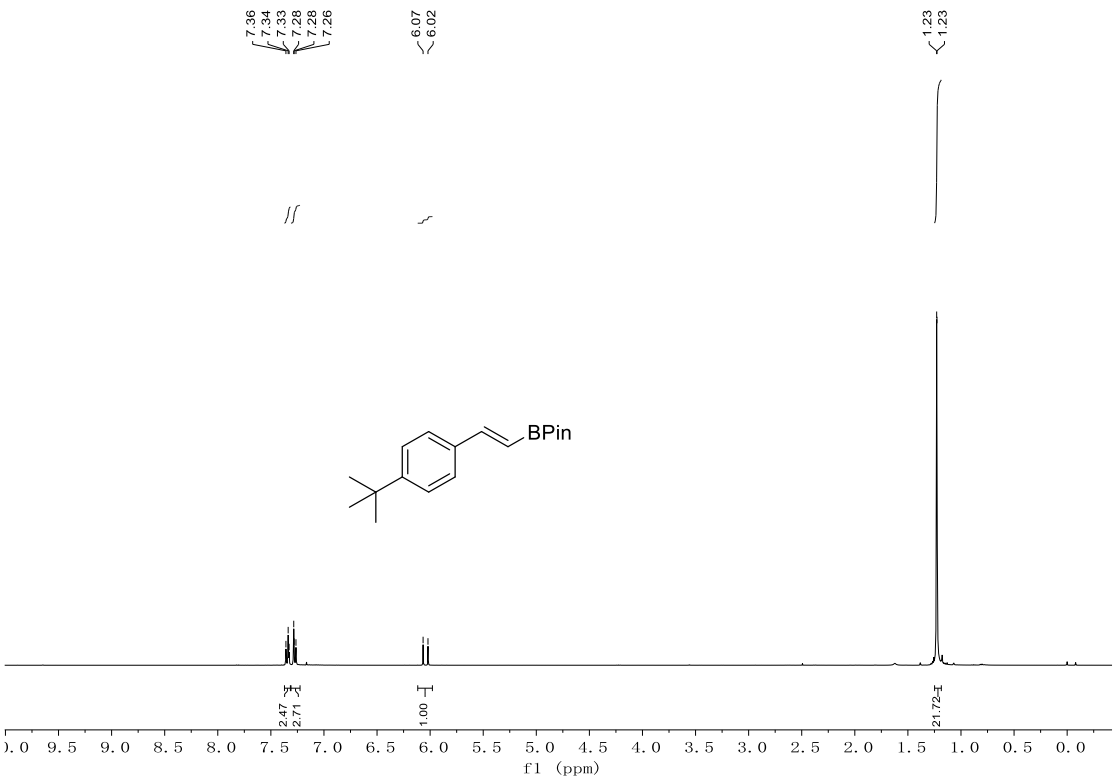


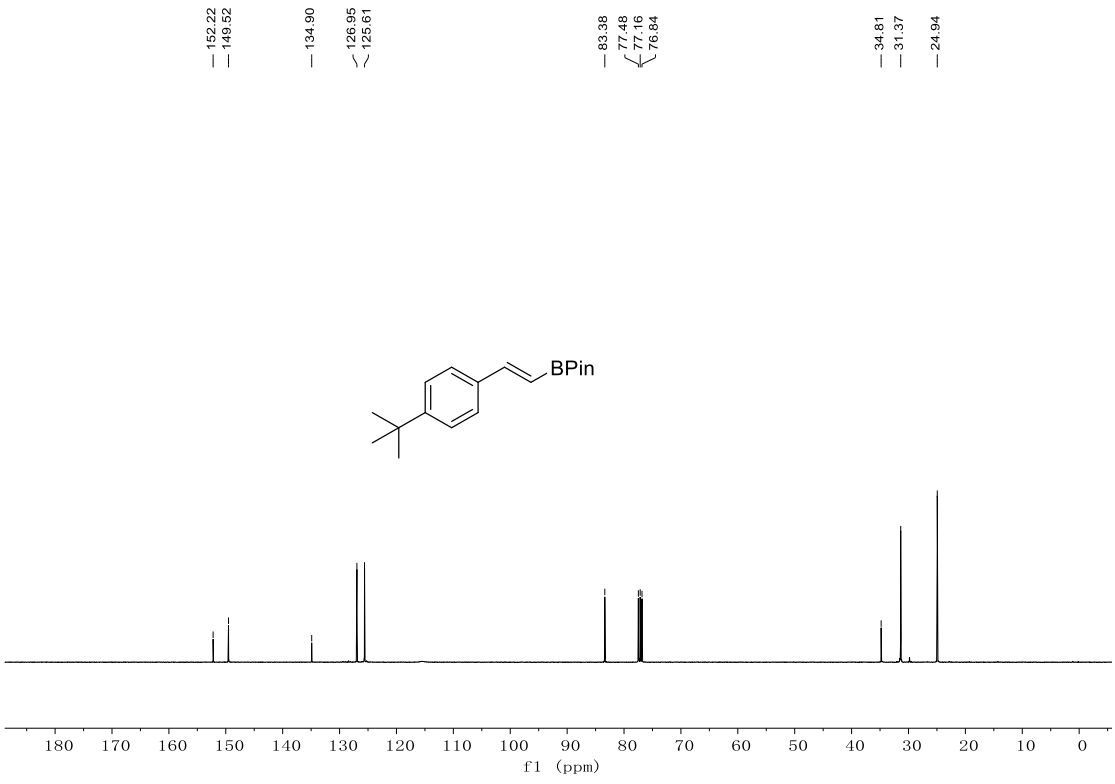
2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ja)



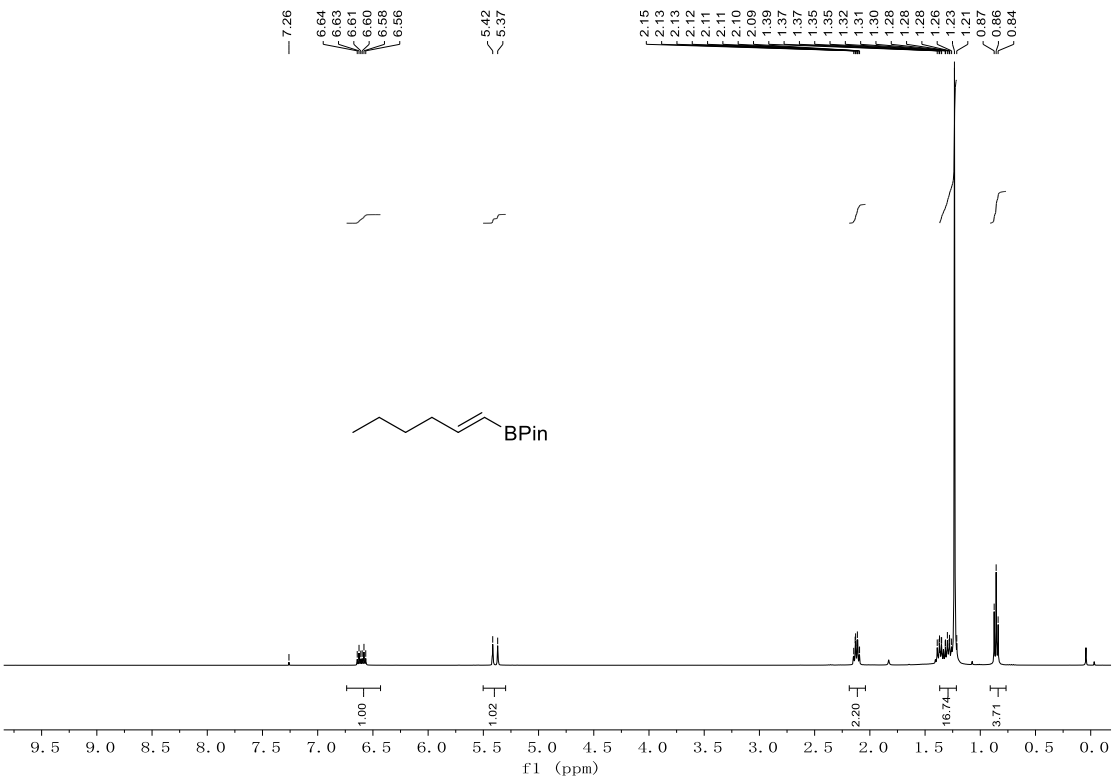


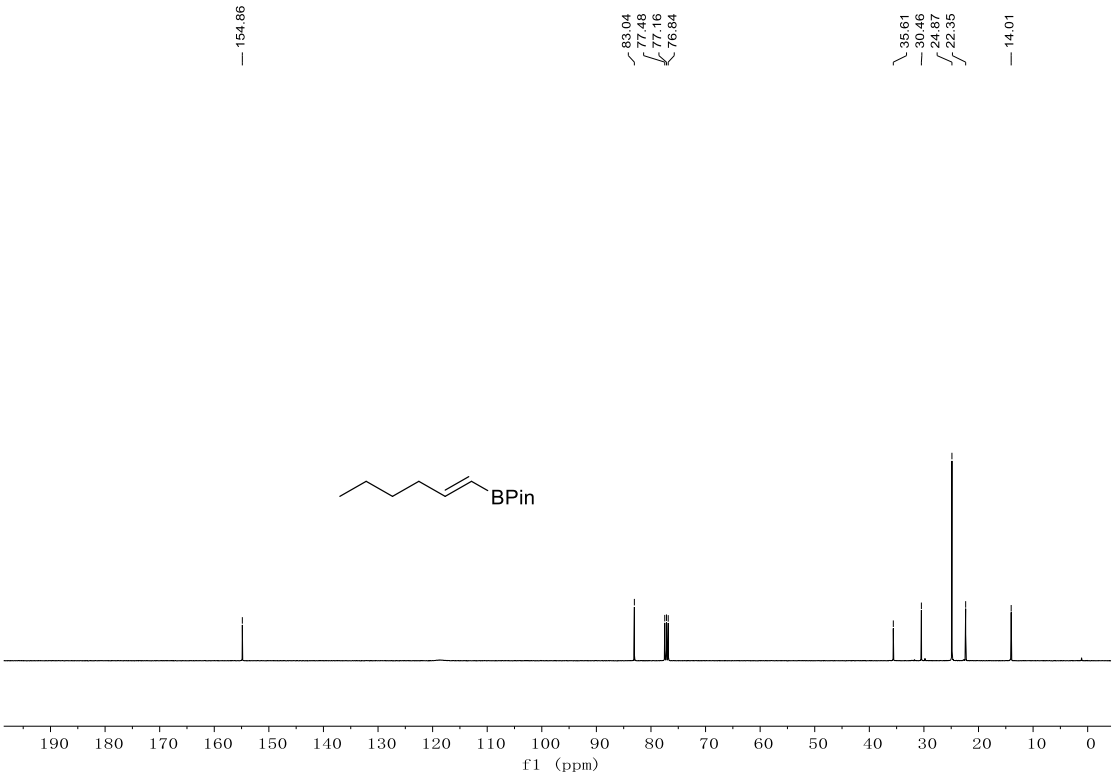
2-(4-(Tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ka)





2-(Hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3la)





2-(5-Chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ma)