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Supporting Information for

Transition-Metal-Free Borylation of Propargylic Alcohols: Structurally Variable Synthesis in Ionic Liquid Medium

Sangepu Bhavanarushi[+], Yin Xu[+], Imran Khan, Zhibin Luo, Bin Liu*, and Jimin Xie*

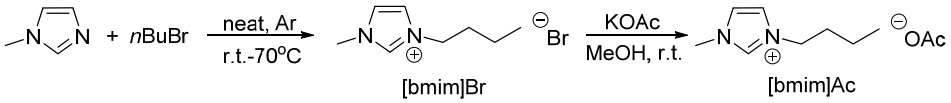
School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, China

E-mail: liub@ujs.edu.cn; xiejm@ujs.edu.cn

General date: NMR spectra were recorded on a Brucker-400 MHz spectrometer. HRMS (Bio TOF Q) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. The solvents were used directly without any purification.

Materials: All starting materials were purchased from Energy Chemical, Alfa and Aldrich and used directly.

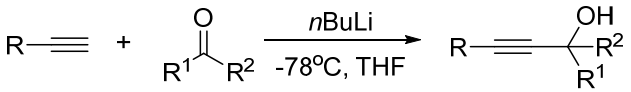
Preparation of ionic liquid:



N-methyl imidazole (41.06 g, 0.5 mol) and *n*-bromobutane (55.54 g, 0.6 mol) were added into the flamed dried flask under argon atmosphere. The reaction mixture was firstly stirred at room temperature for 1h and followed by heating slowly to 70 ºC for another 24 h. After completed and cooled to room temperature, the mixture was washed thrice with ethyl acetate (30 mL×3) to remove excess *n*-bromobutane. Then the product was drained at room temperature under vacuum for 2 h and dried continuously at 50 ºC under vacuum for another 6 h. Finally, the white waxy solid [bmim]Br was obtained in nearly quantitative yield.

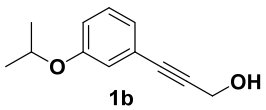
The above synthesized [bmim]Br (11.0 g, 0.05 mol) was added into the solution of KOAc (5.88 g, 0.06 mol) in MeOH (25 mL) under argon atmosphere. The mixture was then stirred vigorously for 24 h at room temperature and then filtrated to remove off the produced white solid salt NaBr. KOAc (0.98 g, 0.01 mol) was introduced into the reaction mixture and stirred for 6 h at room temperature again. This process was repeated for 3-4 times until no NaBr produced. Then MeOH was removed under vacuum at 45°C and Et_2O (10 mL) was added into the residue to separate KOAc out. The volatile solvent was removed at 45°C under vacuum for 1 h and further dryness under vacuum for another 6 h to afford colorless oil [bmim]Ac with 93% yield (9.2g). ^{1}H NMR (400 MHz, DMSO-*d*6): δ 9.80 (s, 1H), 7.83-7.82 (m, 1H), 7.76-7.75 (m, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 1.79-1.72 (m, 2H), 1.55 (s, 3H), 1.25-1.21 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

General Procedures for the Preparation of Propargylic Alcohols 1b-1n:



To a stirring solution of alkyne (5 mmol) in THF (5 mL) was added dropwise *n*BuLi (1.0 M in THF, 5.5 mL) at -78 °C. Aldehyde or ketone (6 mmol, 180 mg) was added portion wise after 0.5 h. The solution was warmed to room temperature after 1.0 h. The reaction was monitored by TLC till the consumption of the starting material. the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (20 mL) and extracted with ethyl acetate three times (20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The crude material was purified by a flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to obtain the propargylic alcohols **1b-1n**.

3-(3-isopropoxyphenyl)prop-2-yn-1-ol (1b):

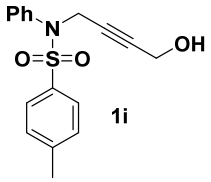


1b

Yield: 89%; light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 1H), 7.03 – 6.95 (m, 2H), 6.88 – 6.84 (m, 1H), 4.56 – 4.47 (m, 1H), 4.49 (s, 2H) 1.92 (br, 1H), 1.33 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.76, 129.55, 124.15, 123.61, 118.67, 117.15, 87.01,

85.84, 70.22, 51.75, 22.11. **IR (KBr)** ν 3419, 2978, 2933, 1738, 1575, 1486, 1373, 1289. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{12}H_{15}O_2^+$, 191.1067, Found 191.1069.

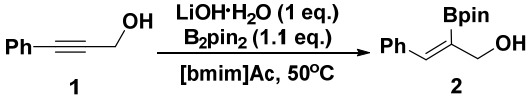
N-(4-hydroxybut-2-yn-1-yl)-4-methyl-N-phenylbenzenesulfonamide (1i):



Yield: 78%; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.33 – 7.29 (m, 3H), 7.25 – 7.21 (m, 4H), 4.45 (t, *J* = 1.9 Hz, 2H), 4.09 (s, 2H), 2.41 (s, 3H), 1.57 (br, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.86, 139.75, 135.89, 129.34, 129.17, 128.43, 128.26, 128.23, 83.89, 80.33, 51.07, 41.55, 21.68. **IR (KBr)** ν 3430, 2982, 2930, 2868, 1733, 1595, 1495, 1245. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{17}H_{18}NO_3S^+$, 316.1002, Found 316.0998.

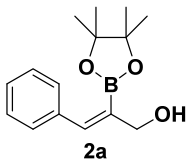
Substrates **1a**, **1m**, **1f**, **1n**, **1o** are commercially available. Spectral data of substrates **1c**[1], **1d**[2], **1e**[3], **1g**[4], **1h**[5], **1j**[6], **1k**[7], **1l**[8] was in accordance with the literature.

General procedure for the preparation of 2a-2o:



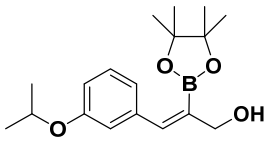
To a heterogeneous solution of 3-Phenyl-2-propyn-1-ol (26 mg, 0.2 mmol), Bis(pinacolato)diboron (56 mg, 0.22 mmol) in [bmim]Ac (0.5 mL) was added lithium hydroxide monohydrate (8.5 mg, 0.2 mmol) in one portion at room temperature. The flask was evacuated and filled with argon. The reaction mixture was stirred at 50 ºC for 4 h. After the reaction was completed, 2,3-dimethylbutane-2,3-diol (24 mg, 0.2 mmol), $MgSO_4$ (24 mg, 0.2 mmol) in DCE (0.5 mL) were added to the reaction mixture and stirred at 50 ºC for another 4 h to convert small amount of hydrolyzed boronic acid back into boronic ester. The mixture was then directly subjected to a flash column chromatography on silica gel to afford product **2a** as colorless oil (44 mg, 85 % yield).

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



Yield: 85%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.31 – 7.25 (m, 3H), 7.10 (s, 1H), 4.36 (d, *J* = 1.4 Hz, 2H), 1.74 (br, 1H), 1.28 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ142.09, 137.91, 128.77, 128.04, 127.90, 83.98, 68.87, 24.86. **IR (KBr)** ν 2956, 2922, 2851, 1406, 1308, 1254. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{15}H_{21}BO_3Na^+$, 283.1476, Found 283.1477.

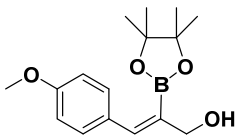
(*E*)-3-(3-isopropoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (2b):



2b

Yield: 76%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.62 – 4.52 (m, 1H), 4.37 (d, *J* = 1.0 Hz, 2H), 1.34 (d, *J* = 6.1 Hz, 6H), 1.31 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.67, 141.83, 139.17, 128.85, 121.14, 116.29, 115.34, 83.84, 69.83, 68.76, 24.72, 22.14. **IR (KBr)** ν 3423, 2977, 2927, 1577, 1382, 1309, 1260. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{18}H_{27}BO_4Na^+$, 341.1895, Found 341.1896.

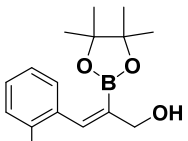
(*E*)-3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (2c):



2c

Yield: 67%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.06 (s, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.35 (s, 2H), 3.83 (s, 3H), 1.99 (br, 1H), 1.32 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.44, 142.26, 130.38, 130.15, 113.31, 83.75, 69.07, 55.25, 24.74. **IR (KBr)** ν 3420, 2978, 2930, 1607, 1511, 1303, 1246. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{16}H_{23}BO_4Na^+$, 313.1582, Found 313.1590.

(*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(o-tolyl)prop-2-en-1-ol (2d):

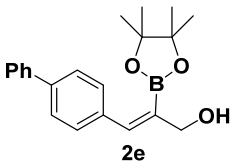


2d

Yield: 77%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.22 – 7.09 (m, 4H), 4.40 (d, *J* = 1.4 Hz, 2H), 2.33 (s, 3H), 1.89 (s, 1H), 1.24 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

140.64, 137.23, 136.05, 128.95, 127.79, 125.13, 83.66, 68.26, 24.62, 19.93. **IR (KBr)** ν 3413, 2927, 1628, 1309, 1251. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{16}H_{23}BO_3Na^+$, 297.1632, Found 297.1640.

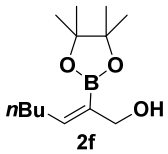
(*E*)-3-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-ol (2e):



2e

Yield: 90%; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.58 – 7.51 (m, 4H), 7.47 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.16 (s, 1H), 4.41 (d, *J* = 1.2 Hz, 2H), 1.92 (br, 1H), 1.34 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.54, 140.82, 140.53, 136.76, 129.16, 128.77, 127.32 , 127.01, 126.62, 83.91, 68.79, 24.75. **IR (KBr)** ν 3339, 2924, 1625, 1308, 1247. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{21}H_{25}BO_3Na^+$, 359.1789, Found 359.1791.

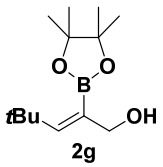
(*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-en-1-ol (2f):



2f

Yield: 67%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.41 (t, *J* = 6.1 Hz, 1H), 4.30 (d, *J* = 6.1 Hz, 2H), 2.15 (t, *J* = 6.9 Hz, 2H), 1.33 – 1.29 (m, 4H), 1.28 (s, 12H), 0.90 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.07, 83.34, 59.57, 32.35, 28.63, 24.70, 22.53, 14.02. **IR (KBr)** ν 3418, 2928, 2858, 1633, 1459, 1372, 1308. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{13}H_{25}BO_3Na^+$, 263.1789, Found 263.1787.

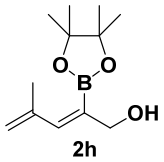
(*E*)-4,4-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-ol (2g):



2g

Yield: 65%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.01 (t, *J* = 5.3 Hz, 1H), 4.47 (d, *J* = 5.3 Hz, 2H), 1.28 (s, 12H), 1.17 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.46, 83.25, 61.29, 35.49, 30.97, 24.64. **IR (KBr)** ν 3401, 2927, 2357, 1458, 1339, 1297. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{13}H_{25}BO_3Na^+$, 263.1789, Found 263.1793.

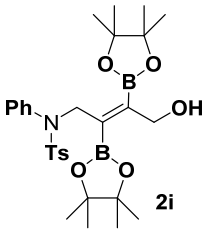
(*E*)-4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-2,4-dien-1-ol (2h):



2h

Yield: 78%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 5.03 (d, *J* = 9.5 Hz, 2H), 4.26 (s, 2H), 1.95 (s, 3H), 1.32 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.73, 118.34, 83.88, 68.98, 24.75, 21.02. **IR (KBr)** ν 3422, 2980, 2930, 2356, 1599, 1371, 1305, 1253. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{12}H_{21}BO_3Na^+$, 247.1476, Found 247.1484.

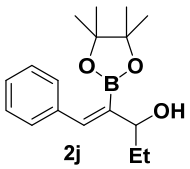
(*E*)-N-(4-hydroxy-2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (2i):



2i

Yield: 44%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.29 – 7.21 (m, 4H), 4.48 (t, *J* = 1.9 Hz, 2H), 4.12 (t, *J* = 1.9 Hz, 2H), 2.78 (s, 1H), 2.44 (s, 3H), 1.26 (s, 24H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.70, 139.64, 135.82, 129.21, 129.04, 128.31, 128.11, 83.81, 75.05, 50.90, 41.43, 24.85, 21.54. **IR (KBr)** ν 3392, 2954, 2919, 2849, 2356, 1463, 1348. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{29}H_{42}B_2NO_7S^+$, 570.2863, Found 570.2864.

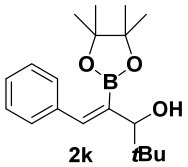
(*E*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-ol (2j):



2j Et

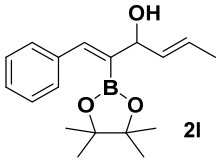
Yield: 86%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.26 (dt, *J* = 6.3, 2.6 Hz, 1H), 7.03 (s, 1H), 4.19 (t, *J* = 6.7 Hz, 1H), 2.21 (s, 1H), 1.76 – 1.69 (m, 2H), 1.29 (d, *J* = 3.0 Hz, 12H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.37, 138.07, 128.38, 127.91, 127.53, 83.85, 79.98, 30.48, 24.77, 24.76, 10.40. **IR (KBr)** ν 3448, 2974, 2927, 2340, 1627, 1459, 1379, 1304, 1248. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{17}H_{25}BO_3Na^+$, 311.1789, Found 311.1793.

(*E*)-4,4-dimethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-ol (2k):



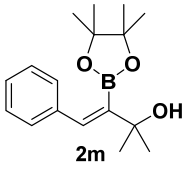
Yield: 70%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.32 – 7.25 (m, 3H), 7.08 (s, 1H), 4.03 (d, *J* = 0.8 Hz, 1H), 1.25 (d, *J* = 1.5 Hz, 9H), 1.00 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.21, 138.20, 128.52, 127.78, 127.38, 86.27, 83.88, 36.36, 26.39, 24.87. **IR (KBr)** ν 2975, 2868, 2356, 1372, 1302, 1247. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{19}H_{29}BO_3Na^+$, 339.2102, Found 339.2110.

(*1E,4E*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,4-dien-3-ol (2l):



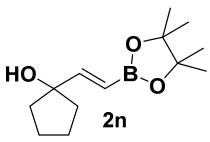
Yield: 83%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.33-7.23 (m, 3H), 7.08 (s, 1H), 5.72 (m, 2H), 4.78(d, J=5.1Hz, 1H), 2.42 (s, 1H), 1.76 – 1.72 (m, 3H), 1.28 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.37, 138.01, 133.15, 128.44, 127.88, 127.58, 126.98, 83.87, 78.20, 24.80, 24.68, 17.71. **IR (KBr)** ν 3423, 2921, 2851, 1721, 1456, 1374, 1261. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{18}H_{25}BO_3Na^+$, 323.1789, Found 323.1799.

(*E*)-2-methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (2m):



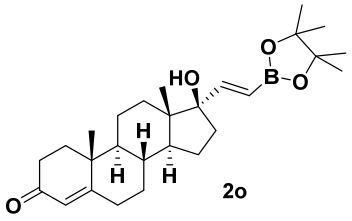
Yield: 56%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.05 (s, 1H), 2.18 (s, 1H), 1.50 (s, 6H), 1.27 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.74, 135.37, 128.16, 127.95, 127.21, 83.89, 74.09, 31.52, 30.25, 24.86. **IR (KBr)** ν 3460, 2978, 2932, 1385, 1302, 1245. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{17}H_{26}BO_3^+$, 289.1970, Found 289.1975.

(*E*)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclopentan-1-ol (2n):



Yield: 66%; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 18.1 Hz, 1H), 5.71 (d, *J* = 18.1 Hz, 1H), 1.96 – 1.83 (m, 2H), 1.80 – 1.62 (m, 6H), 1.50 (s, 1H), 1.29 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.64, 83.24, 82.92, 40.37, 24.78, 24.01. **IR (KBr)** ν 2960, 2924, 2853, 2362, 2332, 1637, 1457, 1351. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{13}H_{23}BO_3Na^+$, 261.1632, Found 261.1633.

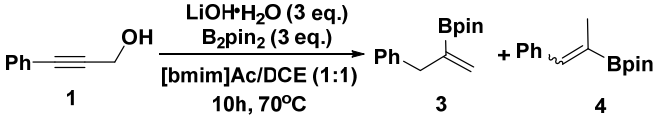
(8R,9S,10R,13S,14S,17R)-17-hydroxy-10,13-dimethyl-17-(1-(4,4,5,5-tetramethyl-1,3,2 dioxaborolan-2-yl)vinyl)-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H cyclopenta[a]phenanthren-3(2H)-one (2o):



2o

Yield: 57%; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.07 (d, *J* = 2.5 Hz, 1H), 5.73 (s, 1H), 5.57 (d, *J* = 2.4 Hz, 1H), 2.44-2.25 (m, 4H), 2.07 – 1.86 (m, 4H), 1.72 – 1.49 (m, 7H), 1.29 (s, 12H), 1.20 (s, 3H), 1.19 – 1.18 (m, 1H), 0.99 (s, 3H), 0.94 – 0.81 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.55, 129.73, 123.79, 87.00, 84.11, 53.25, 48.15, 46.60, 38.61, 36.36, 35.70, 34.44, 33.96, 32.88, 32.61, 31.66, 24.87, 24.48, 23.50, 20.79, 17.40, 14.58. **IR (KBr)** ν 2958, 2927, 2853, 2357, 2333, 1675, 1458, 1298. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{27}H_{41}BO_4Na^+$, 463.2990, Found 463.2996.

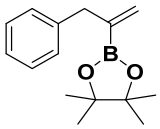
General procedure for the preparation of 3a-3g:



1 **3** **4**

To a homogeneous solution of 3-phenyl-2-propyn-1-ol (26 mg, 0.2 mmol), bis(pinacolato)diboron (152 mg, 0.6 mmol) in DCE/[bmim]Ac (1:1, 1 mL) was added lithium hydroxide monohydrate (25 mg, 0.6 mmol) in one portion at room temperature. The flask was evacuated and filled with argon. The reaction mixture was stirred at 70 °C for 10 h. After the reaction was completed, 2,3-dimethylbutane-2,3-diol (24 mg, 0.2 mmol), $MgSO_4$ (24 mg, 0.2 mmol) were added to the reaction mixture and stirred at 50 °C for another 4 h. The mixture was then directly subjected to a flash column chromatography on silica gel to afford products **3a/4a** as colorless oil (38 mg, 77 % yield, **3a**:**4a** = 3:1).

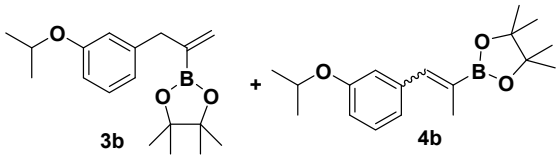
4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (3a) (major):



3a

Yield: 77% (**3a:4a =** 3:1); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.41 – 7.32 (m, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.14 (m, 2H), 5.84 (d, *J* = 3.2 Hz, 1H), 5.53 (s, 1H), 3.49 (s, 1H), 1.22 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ140.84, 129.94, 129.27, 128.22, 125.81, 83.62, 41.52, 24.81. **IR (KBr)** ν 2978, 2927, 1437, 1369, 1312, 1261. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{15}H_{21}BO_2Na^+$, 267.1527, Found 267.1532.

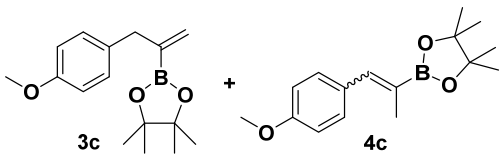
[2-(3-(3-isopropoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b) + 2-(1-(3-isopropoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (4b):



3b + 4b

Yield: 63% (**3b:4b =** 1.7:1); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) (**3b**) δ 7.24 – 7.12 (m, 1H), 6.98 – 6.88 (m, 1H), 6.81 – 6.68 (m, 2H), 5.83 (d, *J* = 3.2 Hz, 1H), 5.54 (d, *J* = 1.4 Hz, 1H), 4.59 – 4.47 (m, 1H), 3.44 (s, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 1.22 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) Mixed signals of isomers were observed. See attached ^{13}C NMR chart. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{18}H_{27}BO_3Na^+$, 325.1945, Found 325.1935.

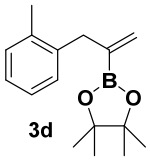
2-(3-(4-methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c) + 2-(1-(4-methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c):



3c + 4c

Yield: 52% (**3c:4c =** 1:1.5); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): **(3c)** δ 7.13 – 7.08 (m, 2H), 6.83 – 6.78 (m, 2H), 5.80 (d, *J* = 3.3 Hz, 1H), 5.50 (s, 1H), 3.78 (s, 3H), 3.42 (s, 2H), 1.21 (s, 12H); (*cis* **4c**) δ 7.39 – 7.34 (m, 2H), 7.18 (s, 1H), 6.91 – 6.86 (m, 2H), 3.82 (s, 3H), 2.00 (d, *J* = 1.7 Hz, 3H), 1.31 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$): **(3c)** δ 157.87, 132.92, 130.19, 129.57, 113.67, 83.60, 55.37, 40.61, 24.84; (*cis* **4c**) δ 158.80, 142.10, 131.08, 130.90, 113.62, 83.54, 55.36, 24.99, 16.06. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{16}H_{23}BO_3Na^+$, 297.1632, Found 297.1624.

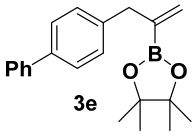
4,4,5,5-tetramethyl-2-(3-(o-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3d) (major):



3d

Yield: 72% (**3d:4d =** 6:1); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 4H), 5.92 – 5.73 (m, 1H), 5.31 (s, 1H), 3.46 (t, *J* = 1.5 Hz, 2H), 2.25 (s, 3H), 1.25 (s, 12H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.68, 136.84, 130.14, 130.06, 129.75, 126.13, 125.79, 83.65, 38.31, 24.87, 19.55. **IR (KBr)** ν 2978, 2926, 1619, 1423, 1370, 1310, 1272. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{16}H_{24}BO_2^+$, 259.1864, Found 259.1872.

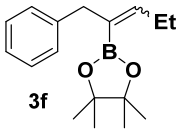
2-(3-([1,1'-biphenyl]-4-yl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e) (major):



3e

Yield: 55% (**3e:4e =** 5:1); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 7.46 – 7.40 (m, 2H), 7.36 – 7.26 (m, 3H), 5.88 (s, 1H), 5.60 (s, 1H), 3.54 (s, 2H), 1.24 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.36, 140.04, 138.74, 130.10, 129.67, 128.81, 127.11, 127.07, 126.99, 83.68, 41.15, 24.84. **IR (KBr)** ν 2979, 2927, 2852, 1616, 1486, 1366, 1317. **HRMS (ESI)** m/z : $(MNa)^+$ Calc. for: $C_{21}H_{25}BO_2Na^+$, 343.1840, Found 343.1828.

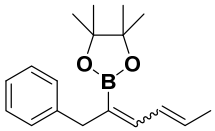
(*E/Z*)-4,4,5,5-tetramethyl-2-(1-phenylpent-2-en-2-yl)-1,3,2-dioxaborolane (3f):



3f

Yield: 66% (*E/Z* =1:1.3); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): (*cis* **3f**) δ 7.24–7.20 (m, 4H), 7.14–7.12 (m, 1H), 6.41 (t, *J* = 7.0 Hz, 1H), 3.51 (s, 2H), 2.23 (p, *J* = 7.5 Hz, 2H), 1.20 (s, 12H), 1.00 (t, *J* = 7.6 Hz, 3H); (*trans* **3f**) δ 7.24 – 7.19 (m, 4H), 7.16 – 7.12 (m, 1H), 6.05 (t, *J* = 7.4 Hz, 1H), 3.43 (s, 2H), 2.34 (p, *J* = 7.5 Hz, 2H), 1.15 (s, 12H), 0.99 (t, *J* = 7.6 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$): (*cis* **3f**) δ 148.84, 142.09, 128.70, 128.15, 125.44, 83.31, 34.28, 24.79, 22.32, 13.64; (*trans* **3f**) δ 148.64, 142.01, 129.12, 128.11, 125.63, 83.04, 42.92, 24.79, 24.70, 14.74. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{17}H_{26}BO_2^+$, 273.2020, Found 273.2039.

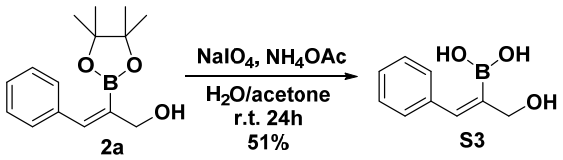
4,4,5,5-tetramethyl-2-(1-phenylhexa-2,4-dien-2-yl)-1,3,2-dioxaborolane (3g):



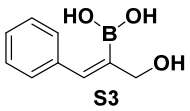
3g

Yield: 72% (*E/Z* =1:1); Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) Mixed signals of isomers were observed. See attached ^{1}H NMR chart; **^{13}C NMR** (100 MHz, $CDCl_3$) Mixed signals of isomers were observed. See attached ^{13}C NMR chart. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{18}H_{26}BO_2^+$, 285.2020, Found 285.2008.

Preparation of S3 for XRD:



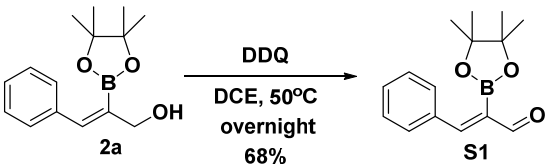
(*E*)-(3-hydroxy-1-phenylprop-1-en-2-yl)boronic acid (S3):



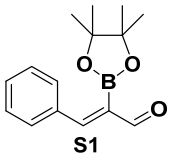
S3

To acetone/water (2/1) solution (0.5 mL) was added **2a** (52 mg, 0.2 mmol). $NaIO_4$ (129 mg, 0.6 mmol) and NH_4OAc (47 mg, 0.6 mmol) were sequentially added to the solution and the mixture was stirred at room temperature for 24h. Once completed (monitored by TLC), the reaction was treated with water and extracted with EtOAc. Organic layers were combined, washed with brine, dried over Na_2SO_4, and filtered. Solvents were removed under reduced pressure and the crude product was recrystallized from pentane/EtOAc to afford **S3** as colorless crystal (18 mg, 51%). **^{1}H NMR** (400 MHz, DMSO-*d*6) δ 7.92 (s, 2H), 7.38 – 7.31 (m, 2H), 7.32 – 7.25 (m, 2H), 7.20 – 7.13 (m, 1H), 6.63 (s, 1H), 4.74 (s, 1H), 4.18 (d, *J* = 3.1 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-*d*6) δ 138.80, 129.98, 128.14, 127.24, 126.36, 65.45. **IR (KBr)** ν 3541, 2925, 2854, 1675, 1460, 1378, 1299. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_9H_{11}BO_3Na^+$, 201.0693, Found 201.0705.

Derivatization of 2a:

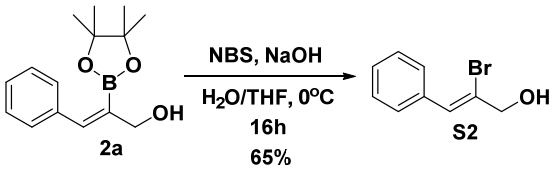


(*E*)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylaldehyde (S1):

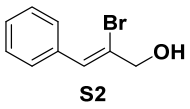


S1

To a solution of **2a** (52 mg, 0.2 mmol) in THF (1 mL) was added DDQ (68 mg, 0.3 mmol). The mixture was stirred at 50 ºC overnight. After the reaction was finished, the reaction was quenched with saturated aqueous $NaHSO_3$ and extracted with EtOAc. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford product **S1** as light yellow solid (35 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.73 (s, 1H), 7.64 – 7.57 (m, 2H), 7.43 – 7.38 (m, 3H), 1.37 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.68, 160.17, 135.75, 130.86, 129.50, 128.83, 84.83, 24.97. **IR (KBr)** ν 3420, 2973, 2360, 1667, 1320, 1260. **HRMS (ESI)** m/z : $(MH)^+$ Calc. for: $C_{15}H_{20}BO_3^+$, 295.1500, Found 295.1503.



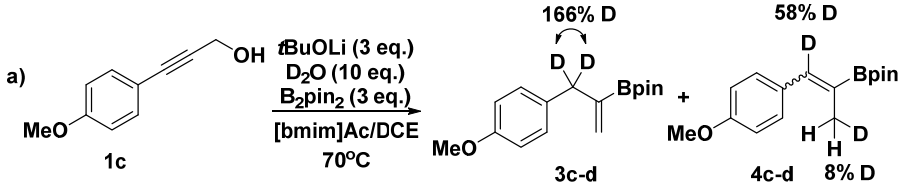
(Z)-2-bromo-3-phenylprop-2-en-1-ol (S2):



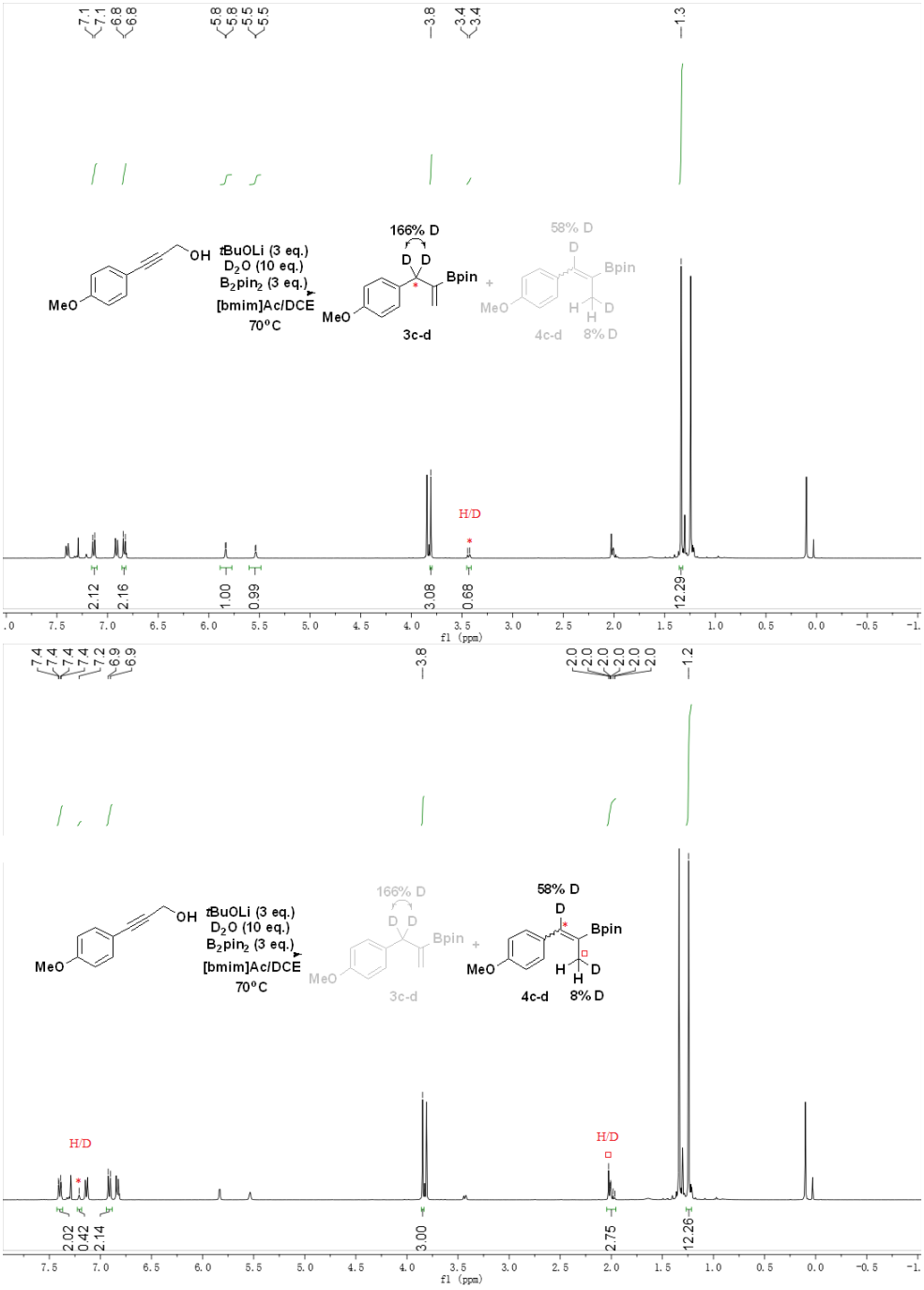
S2

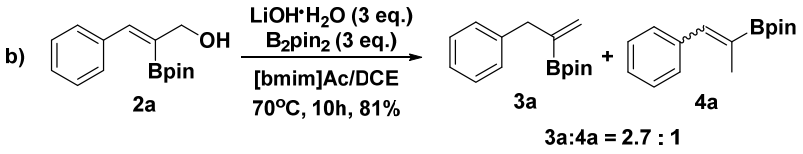
To a solution of **2a** (52 mg, 0.2 mmol) in THF (1 mL) was added aqueous NaOH (3M, 0.3 mL) followed by N-bromosuccinimide (71mg, 0.4 mmol). The mixture was stirred at 0 ºC for 16h. After the reaction was finished, the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford product **S2** as light yellow oil (28 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.39-7.32 (m, 3H), 7.09 (s, 1H), 4.42 (s, 2H), 2.14 (br , 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.4, 129.4, 128.6, 128.3, 125.7, 69.8. The spectral data was in accordance with the literature.[9]

Control Experiments



To a homogeneous solution of **1c** (32.4 mg, 0.2 mmol), bis(pinacolato)diboron (152 mg, 0.6 mmol) in DCE/[bmim]Ac (1:1, 1 mL) was added *t*BuOLi (48 mg, 0.6 mmol) and D_2O (40 mg, 2 mmol) at room temperature. The flask was evacuated and filled with argon. The reaction mixture was stirred at 70 ºC for 24 h. After the reaction was completed, the mixture was then directly subjected to a flash column chromatography on silica gel to afford products **3c-d/4c-d** for NMR study.





To a homogeneous solution of **2a** (32 mg, 0.2 mmol), bis(pinacolato)diboron (152 mg, 0.6 mmol) in DCE/[bmim]Ac (1:1, 1 mL) was added lithium hydroxide monohydrate (25 mg, 0.6 mmol) in one portion at room temperature. The flask was evacuated and filled with argon. The reaction mixture was stirred at 70 °C for 10 h. After the reaction was completed, 2,3-dimethylbutane-2,3-diol (24 mg, 0.2 mmol), $MgSO_4$ (24 mg, 0.2 mmol) were added to the reaction mixture and stirred at 50 °C for another 4 h. The mixture was then directly subjected to a flash column chromatography on silica gel to afford products **3a**/**4a** as colorless oil (39 mg, 81 % yield, **3a**:**4a** = 2.7:1). The **3a**/**4a** ratio is close to the outcome from standard condition of **1a** (**3a**:**4a** = 3:1) which indicated both **3a** and **4a** were highly possible generated from **2a**.

^{11}B NMR Spectra of ionic liquids with B_2pin_2:

To better understand the interaction between ionic liquids and diboron, three samples were prepared as shown below to study the ^{11}B NMR. As shown in **Figure 1**, the only new peak shown at 20 ppm in three spectra could be attributed to $[RO\text{-}B_2pin_2]^-$ species wherein RO^- refers to hydroxyl ion or acetate ion. No NHC·diboron complex observed in all the cases.[10]

Sample 1: [bmim]Ac (150 mg) and B_2pin_2 (25 mg, 0.1 mmol) in $CDCl_3$ (0.6 mL)

Sample 2: [bmim]Ac (150 mg), B_2pin_2 (25 mg, 0.1 mmol) and $LiOH·H_2O$ (17 mg, 0.4 mmol) in $CDCl_3$ (0.6 mL)

Sample 3: [TBA]Ac (150 mg) and B_2pin_2 (25 mg, 0.1 mmol) in $CDCl_3$ (0.6 mL)

BminAc

Sample Name:

Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:

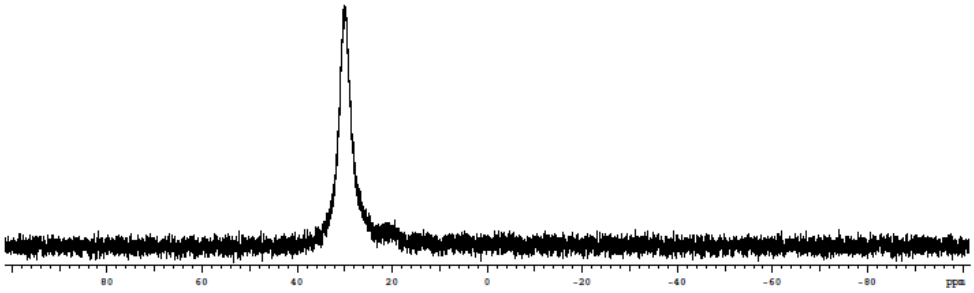
Sample directory:

FidFile: BminAc-B

Pulse Sequence: s2pul
Solvent: cdcl3
Data collected on: Nov 29 2018

30.039

[bmim]Ac + B_2pin_2



BminAc+LiOH

Sample Name:

Data Collected on:
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Archive directory:

Sample directory:

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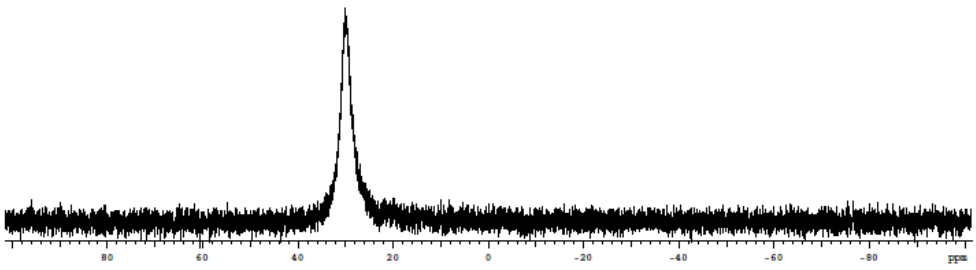
Pulse Sequence: s2pul
Solvent: cdcl3
Data collected on: Nov 29 2018

30.061

[bmim]Ac + B_2pin_2 + LiOH•H_2O



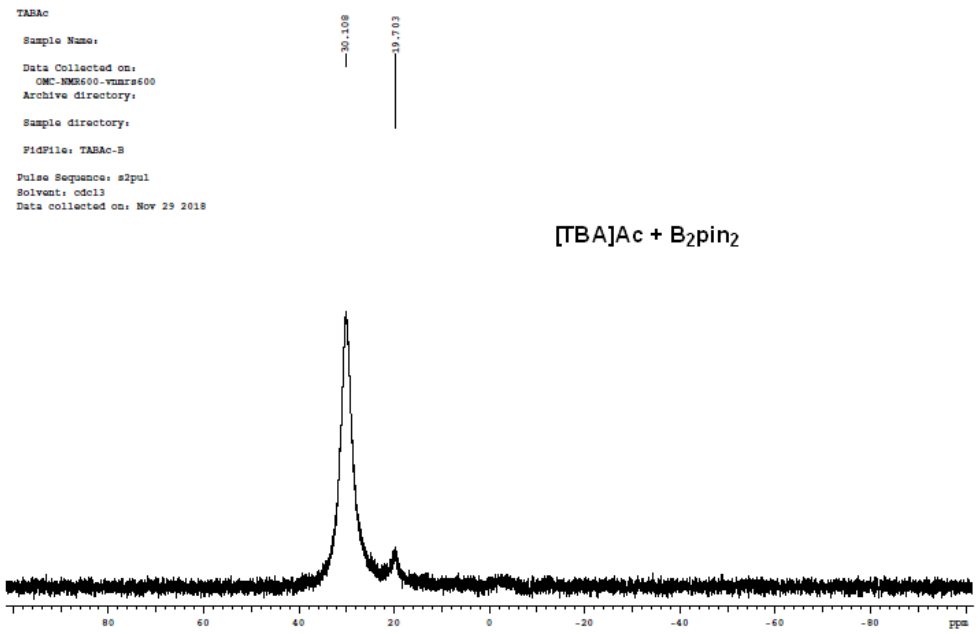


Figure 1. ^{11}B NMR Spectra of ionic liquids with B_2pin_2 in $CDCl_3$ at 25°C

References:

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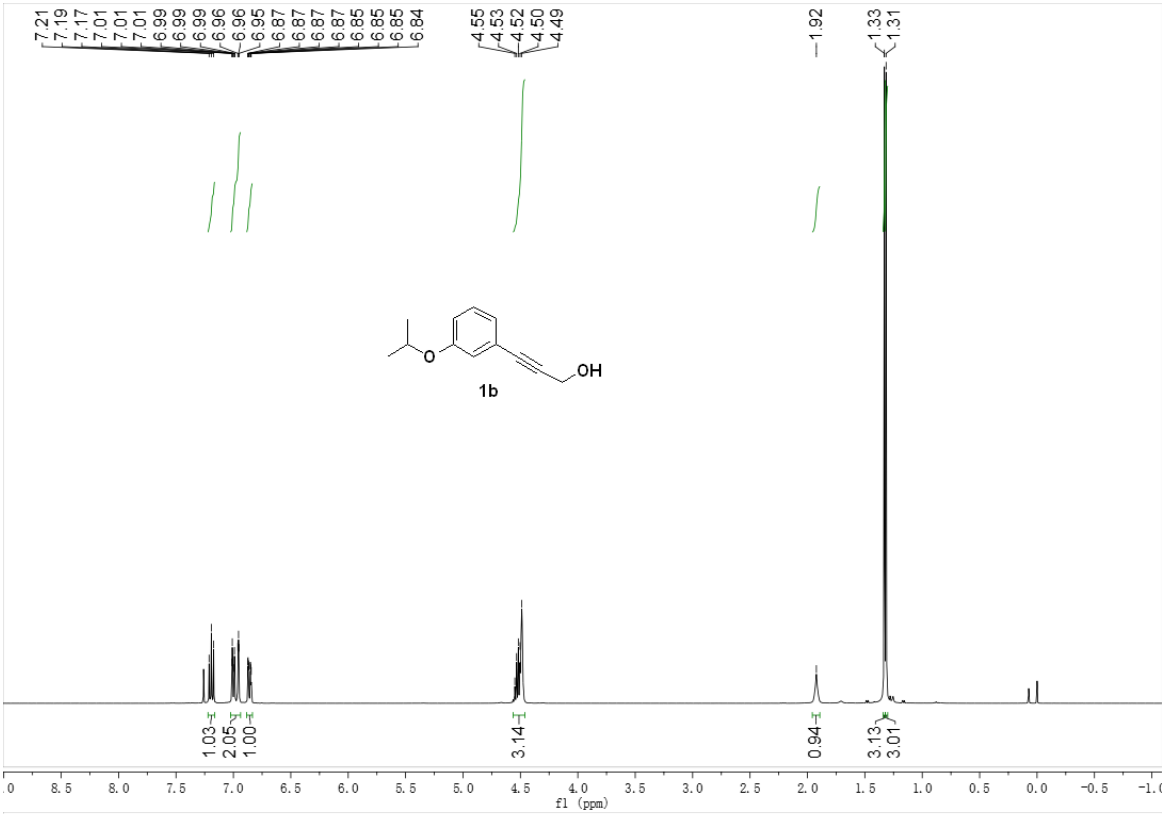
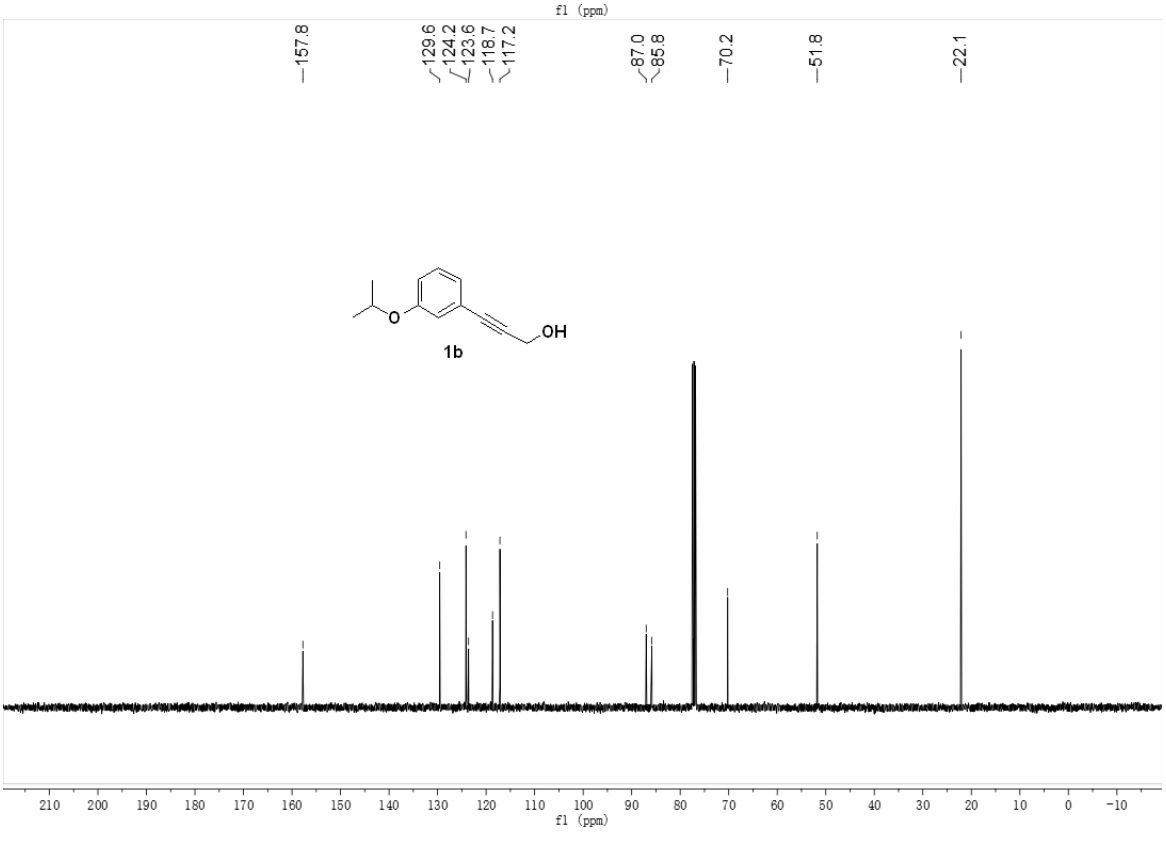
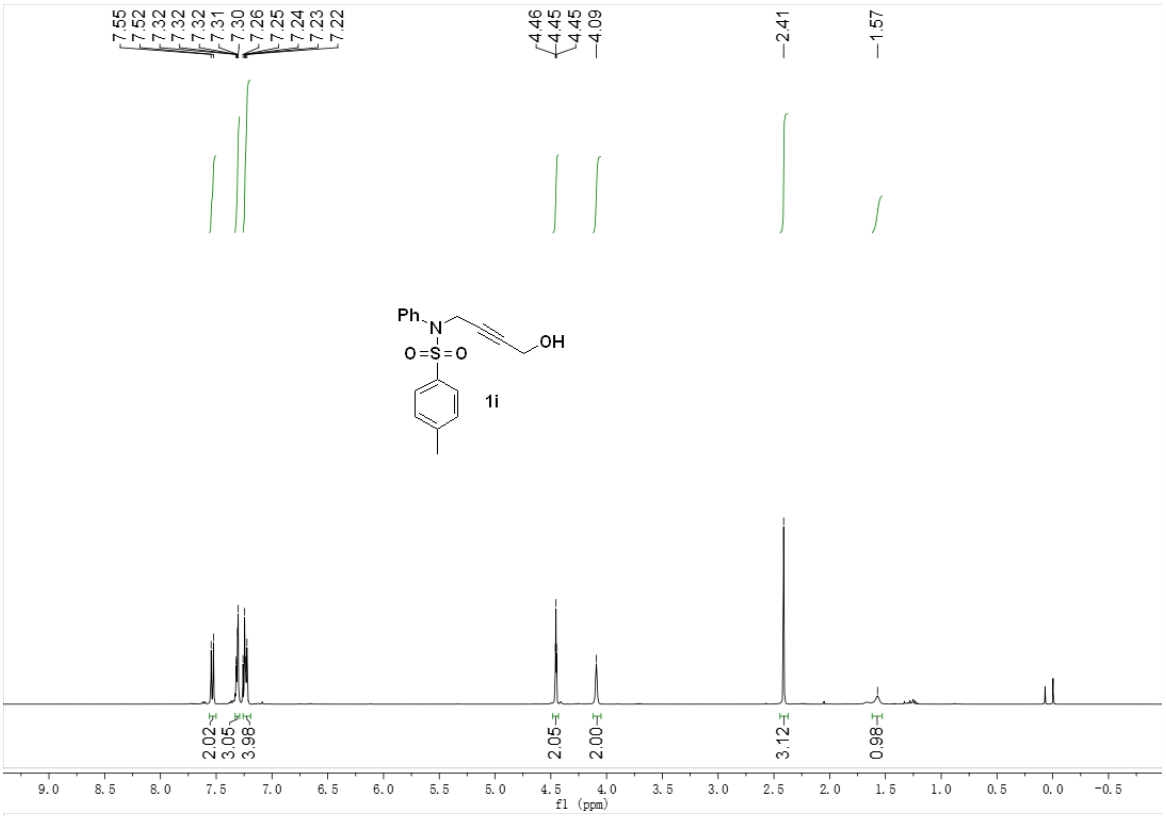
Spectra Data



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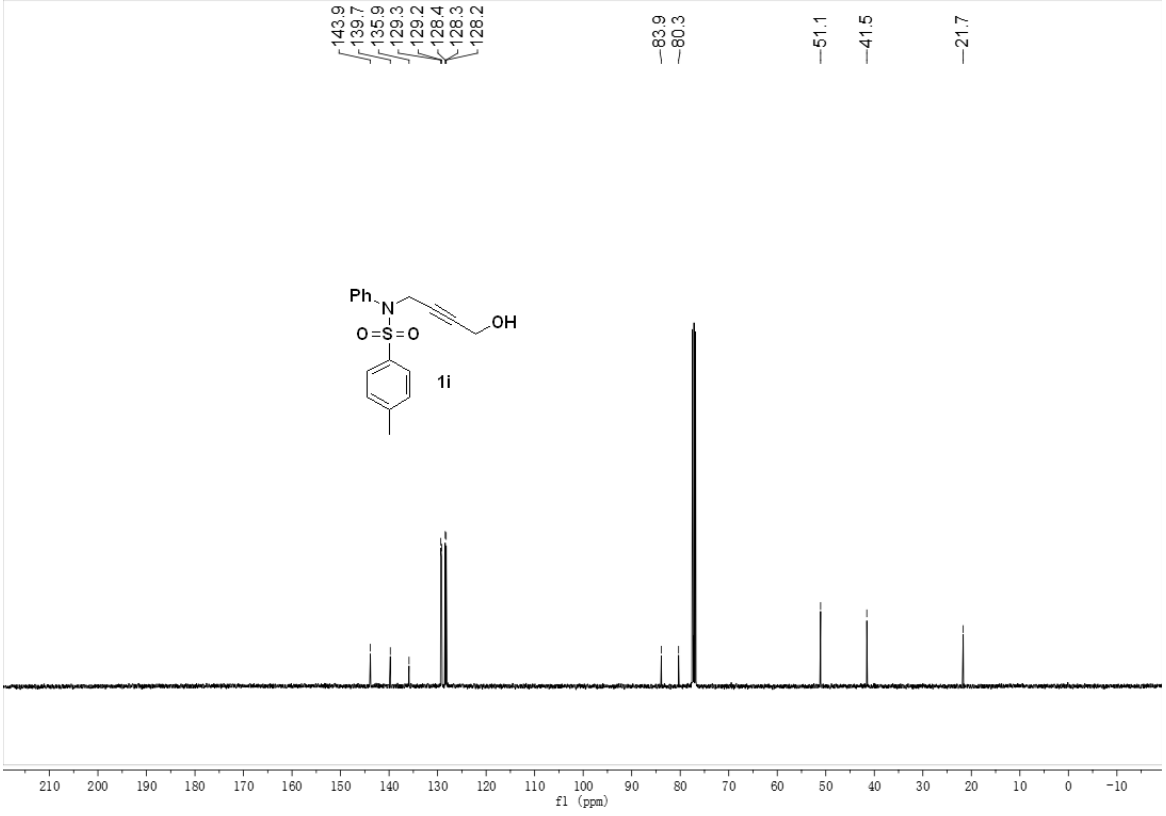
4.45
4.45
4.09
2.41
1.57
Ph
N
O=S=O
OH
1i
2.02
3.05
3.98
2.05
2.00
3.12
0.98
f1 (ppm)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N
O=S=O
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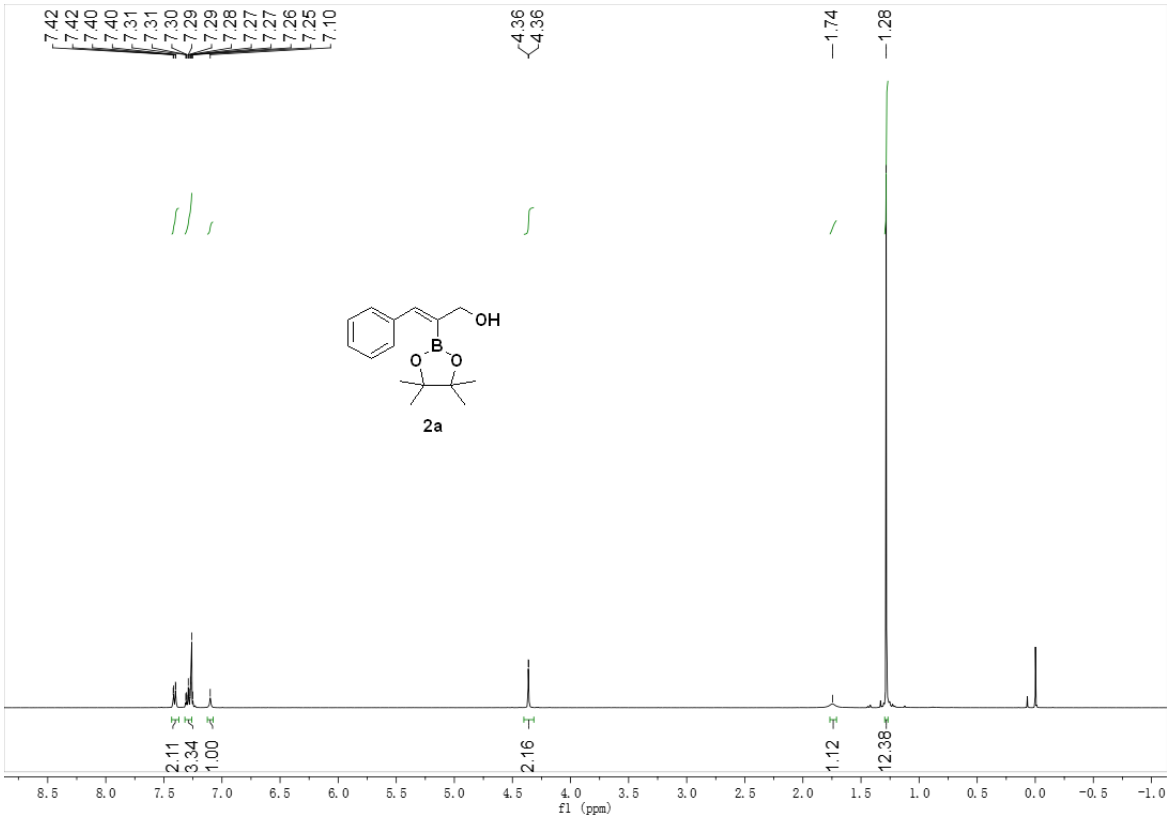
1i
f1 (ppm)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7.25
7.10
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4.36
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B
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O
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2.16
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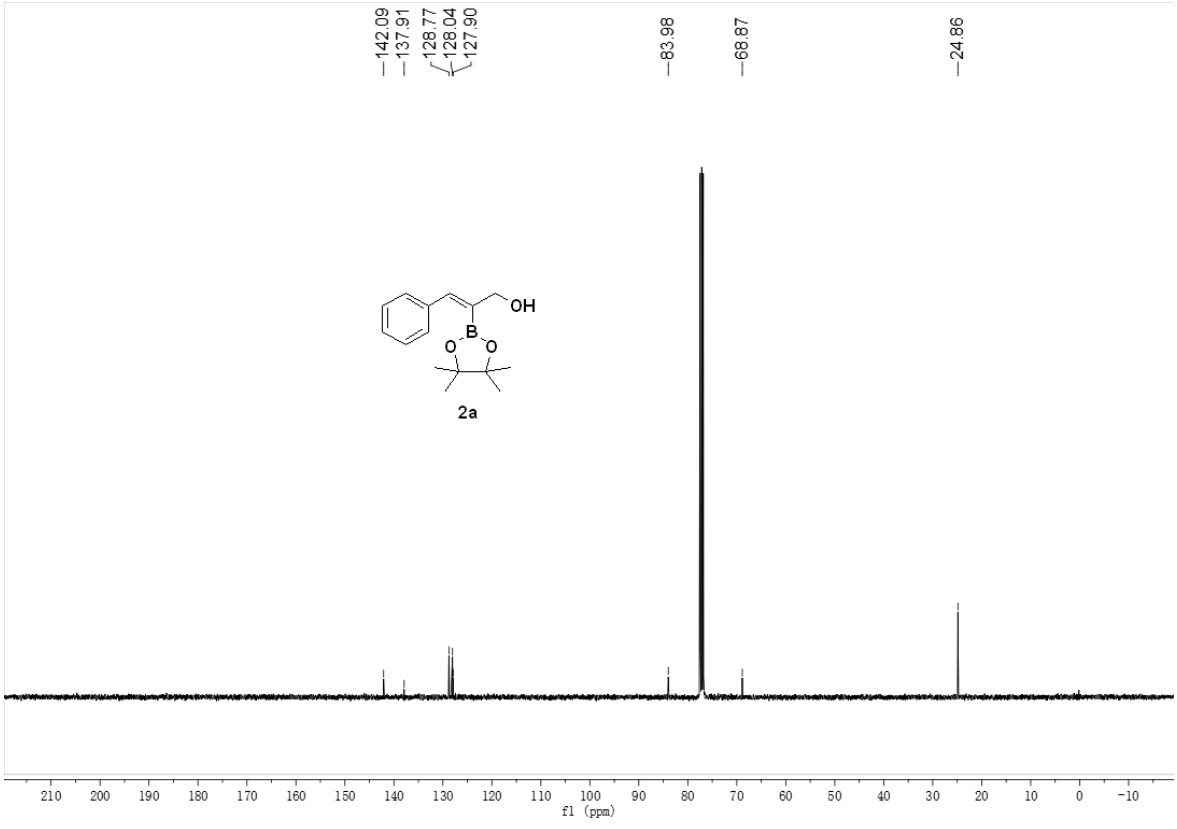
12.38
f1 (ppm)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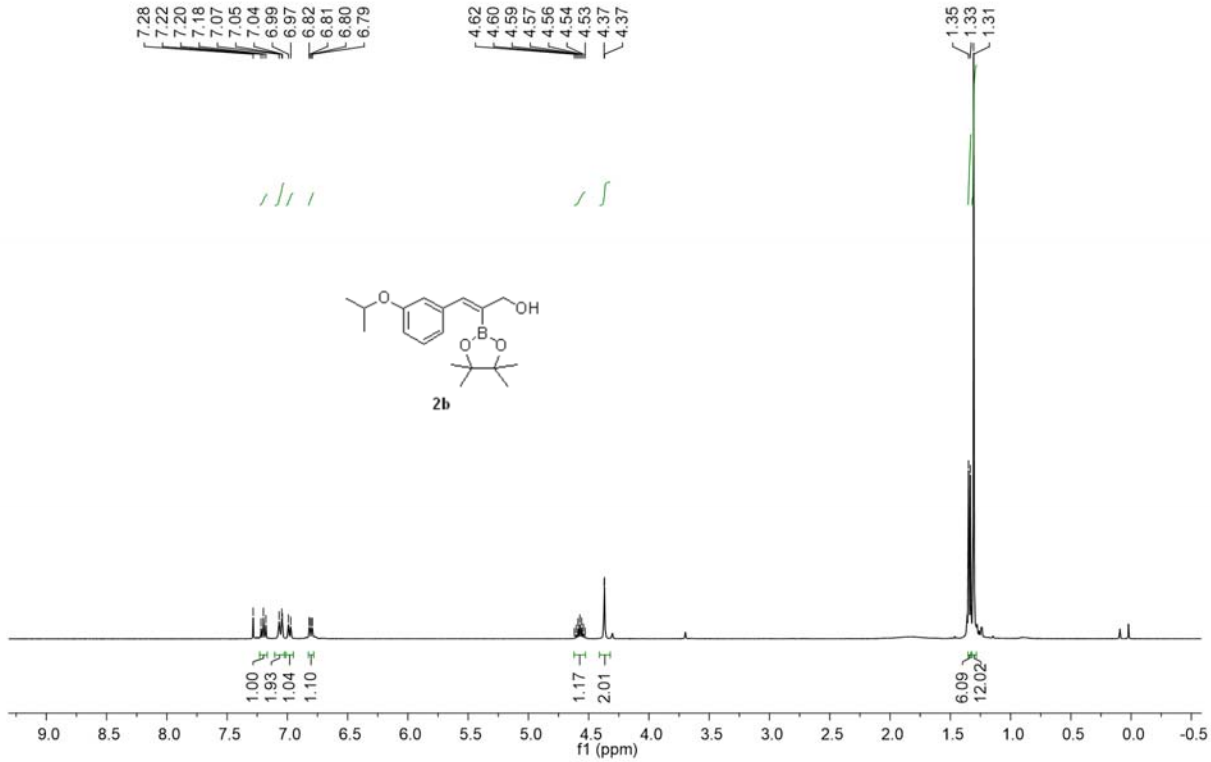
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4.60
4.59
4.57
4.56
4.54
4.53
4.37
4.37
1.35
1.33
1.31
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B
O
O
2b
1.00
1.93
1.04
1.10
1.17
2.01
6.09
12.02
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8.5
8.0
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7.0
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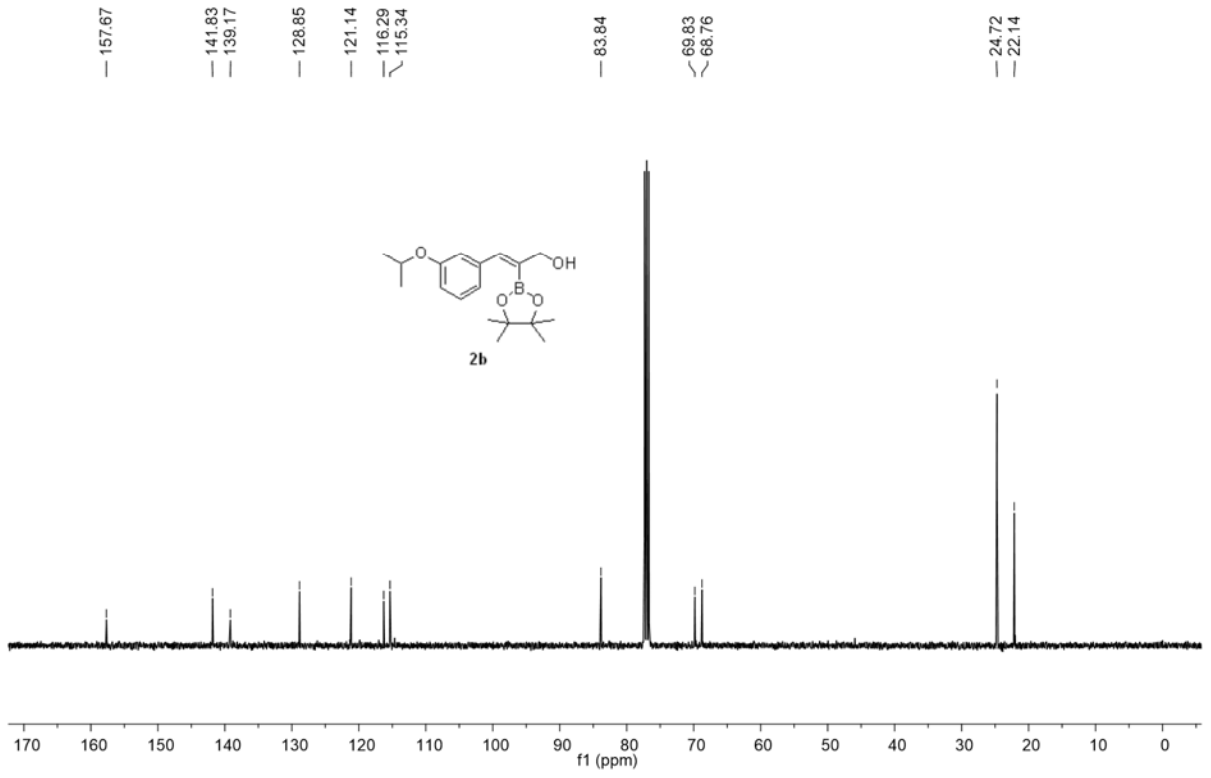
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B
O
O
2b
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10
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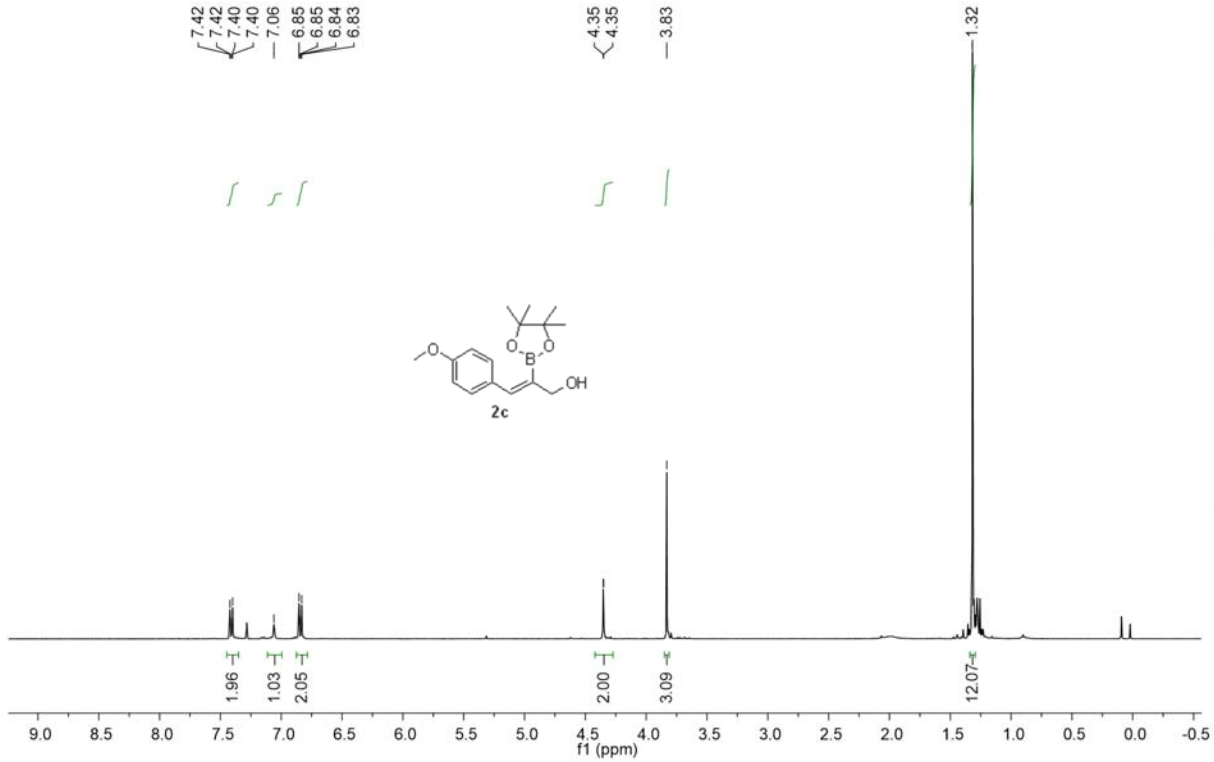
f1 (ppm)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2.00
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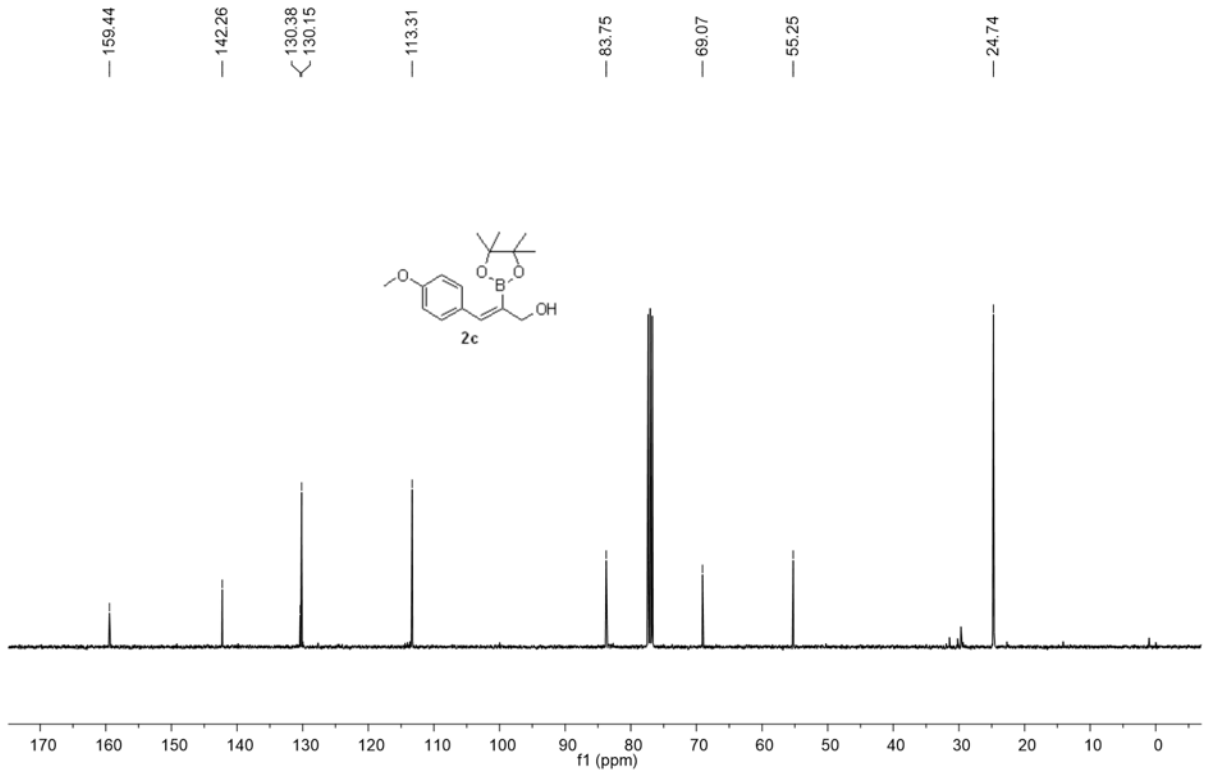
f1 (ppm)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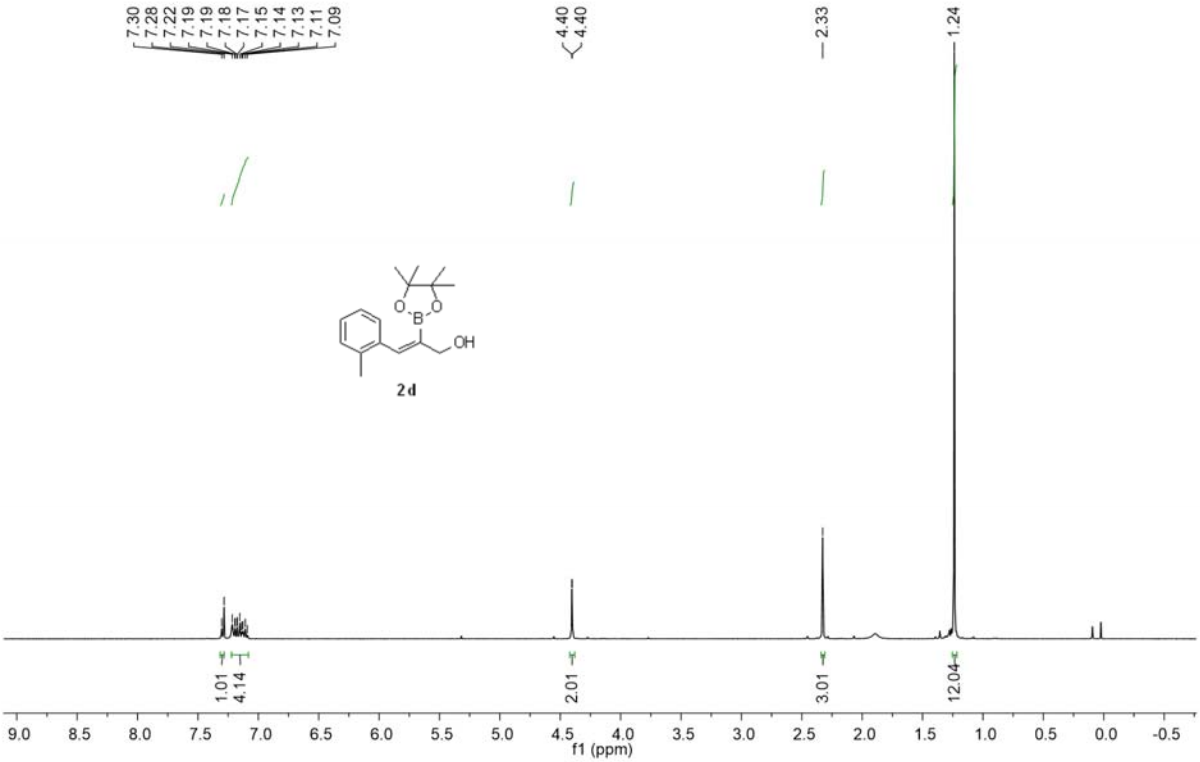
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4.40
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1.24
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4.14
2.01
3.01
12.04
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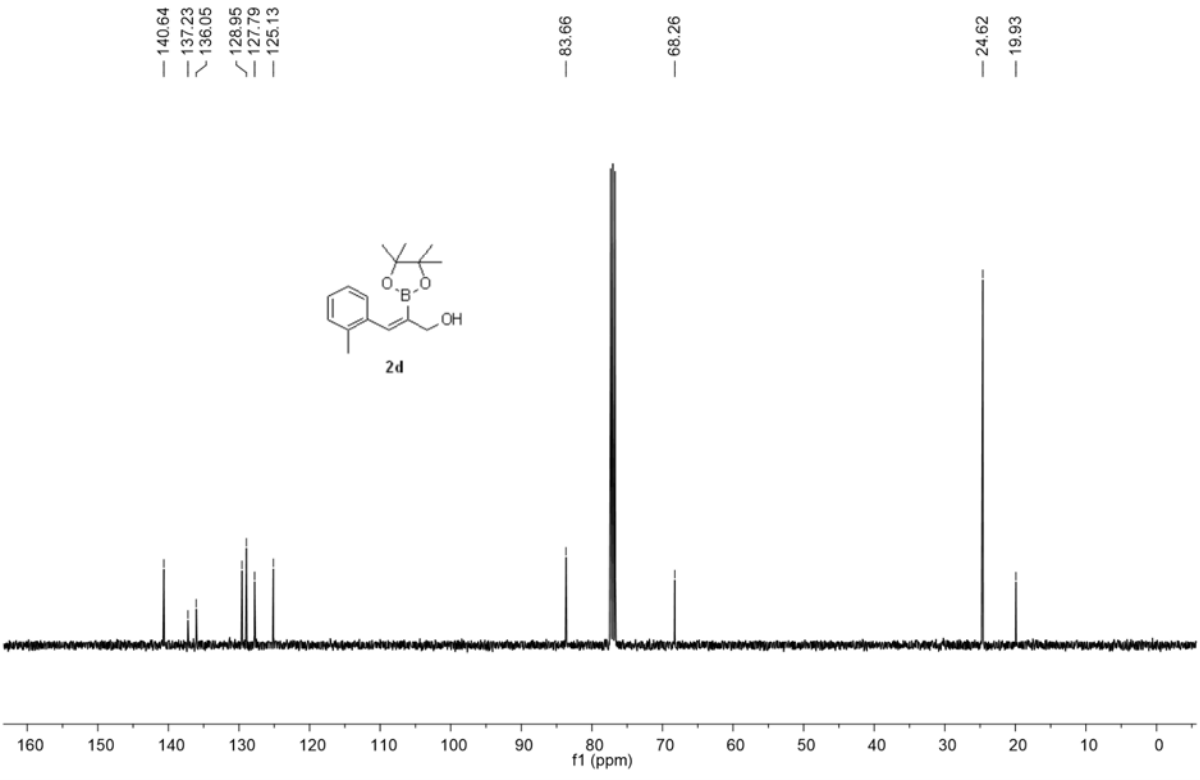
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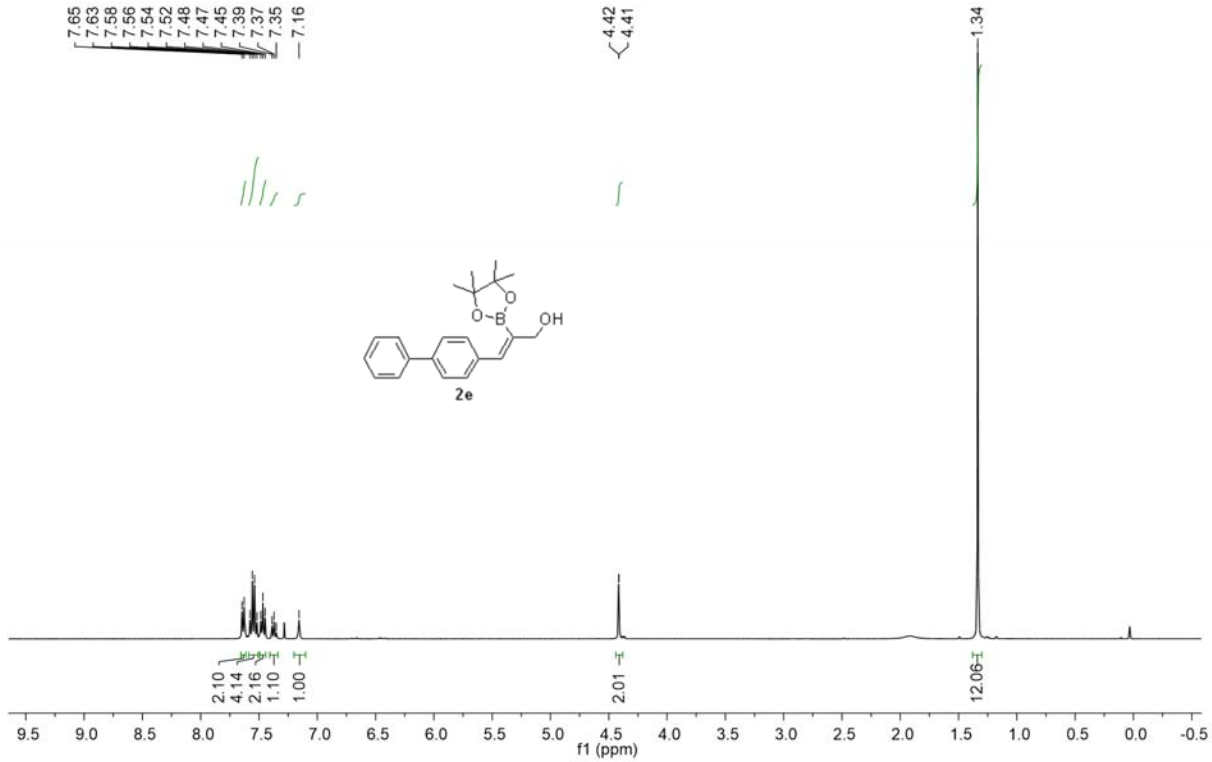
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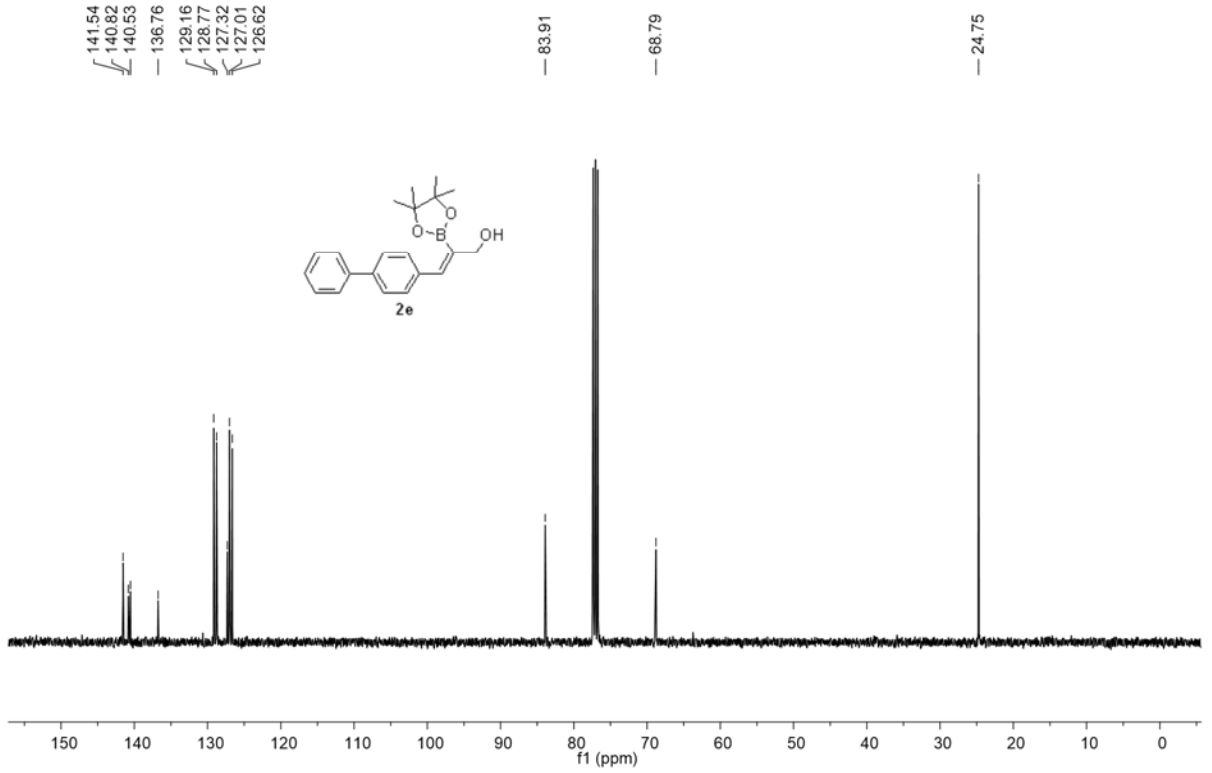
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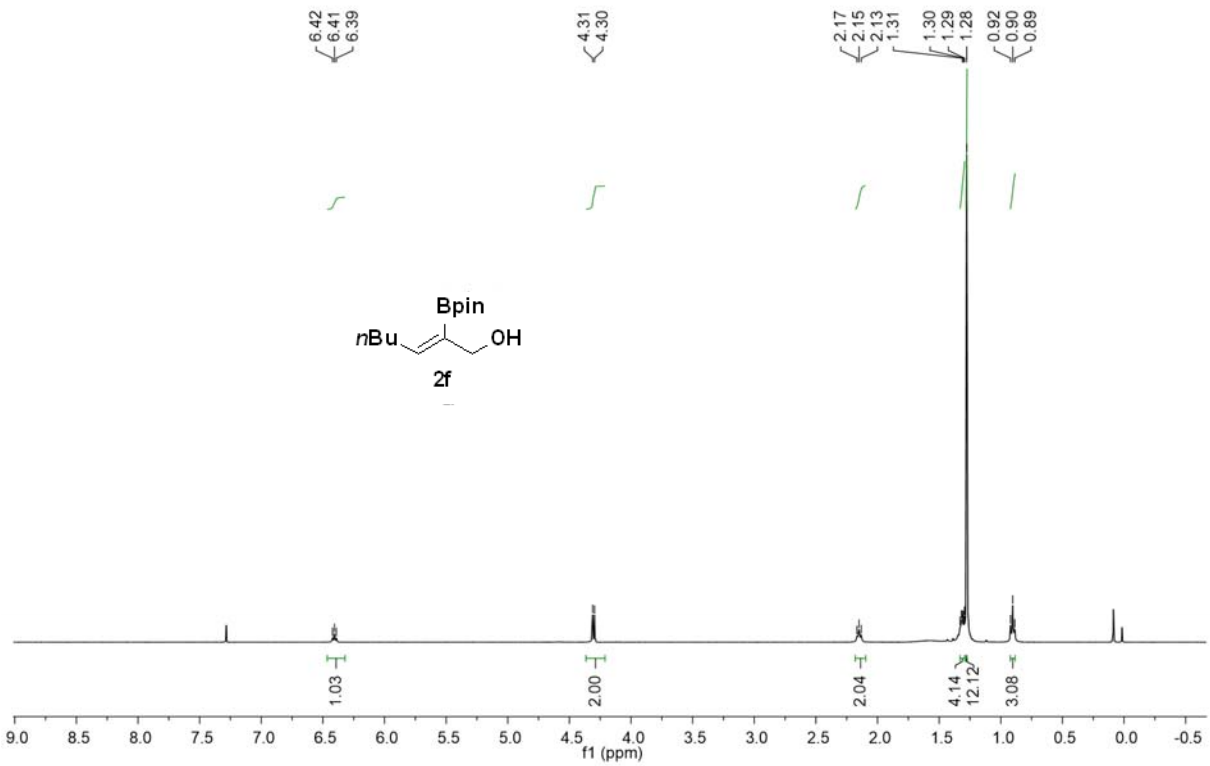
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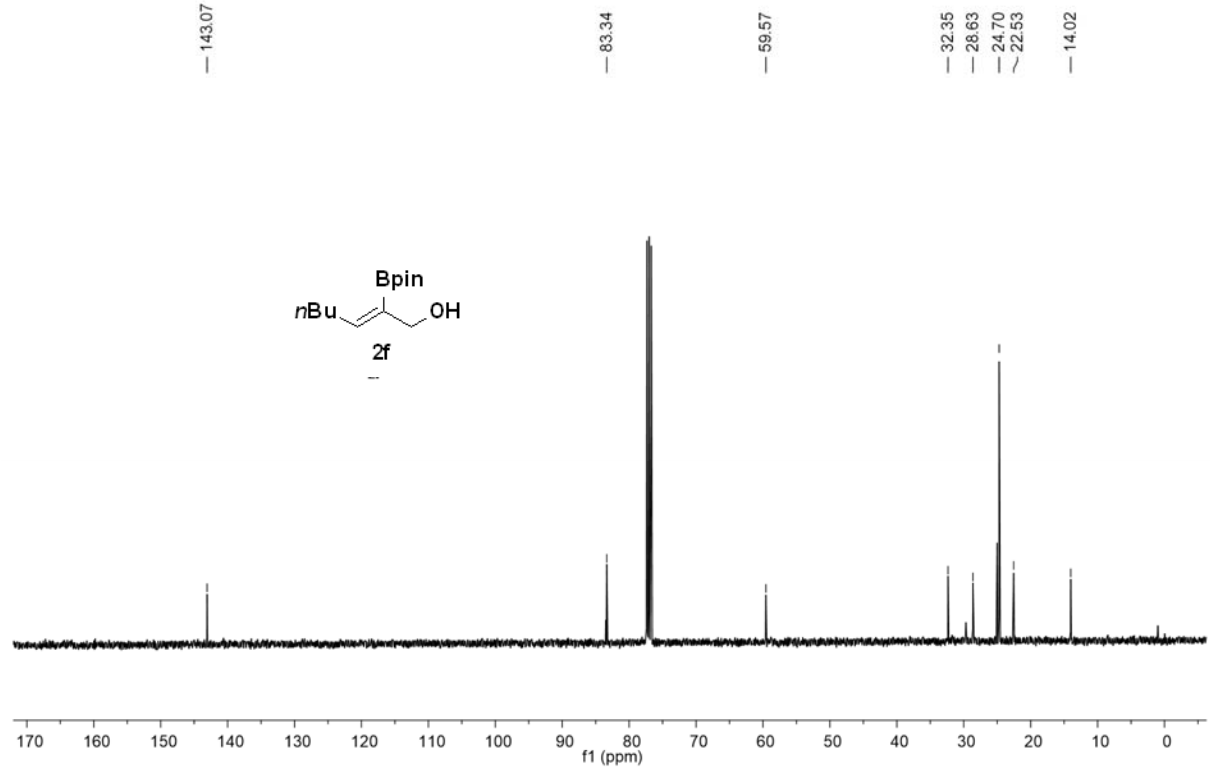
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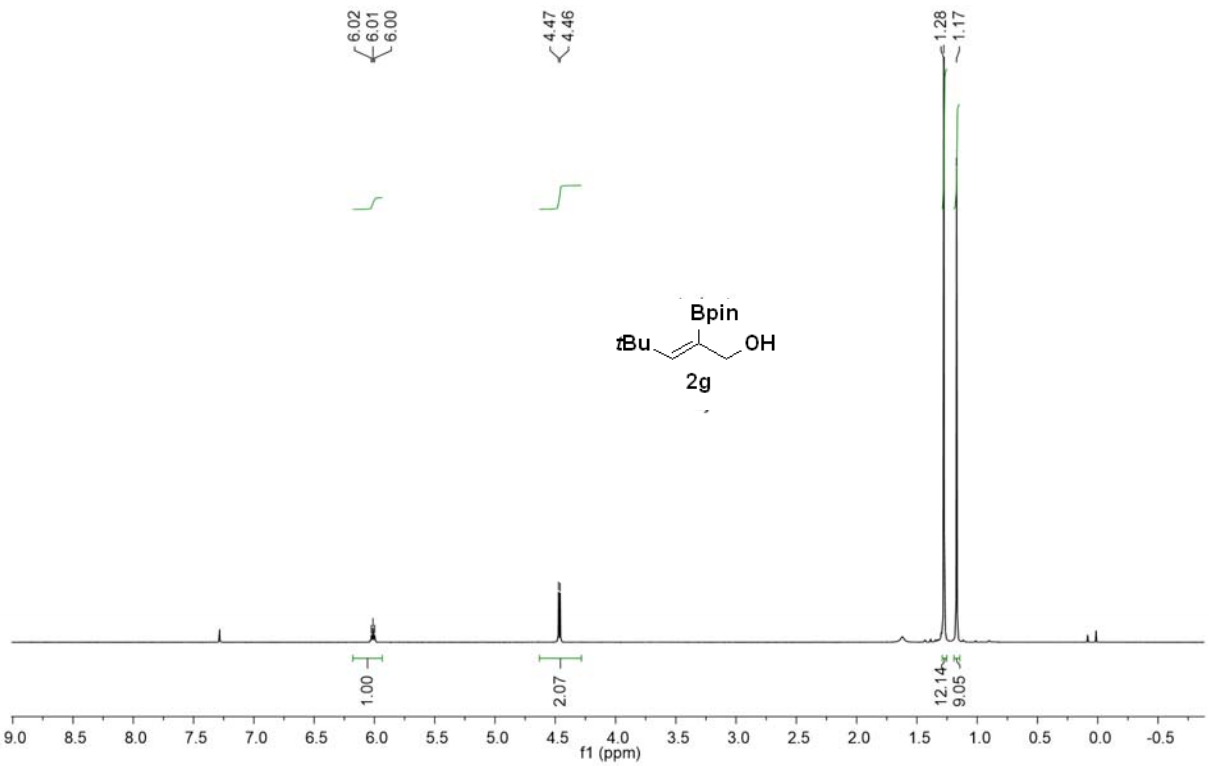
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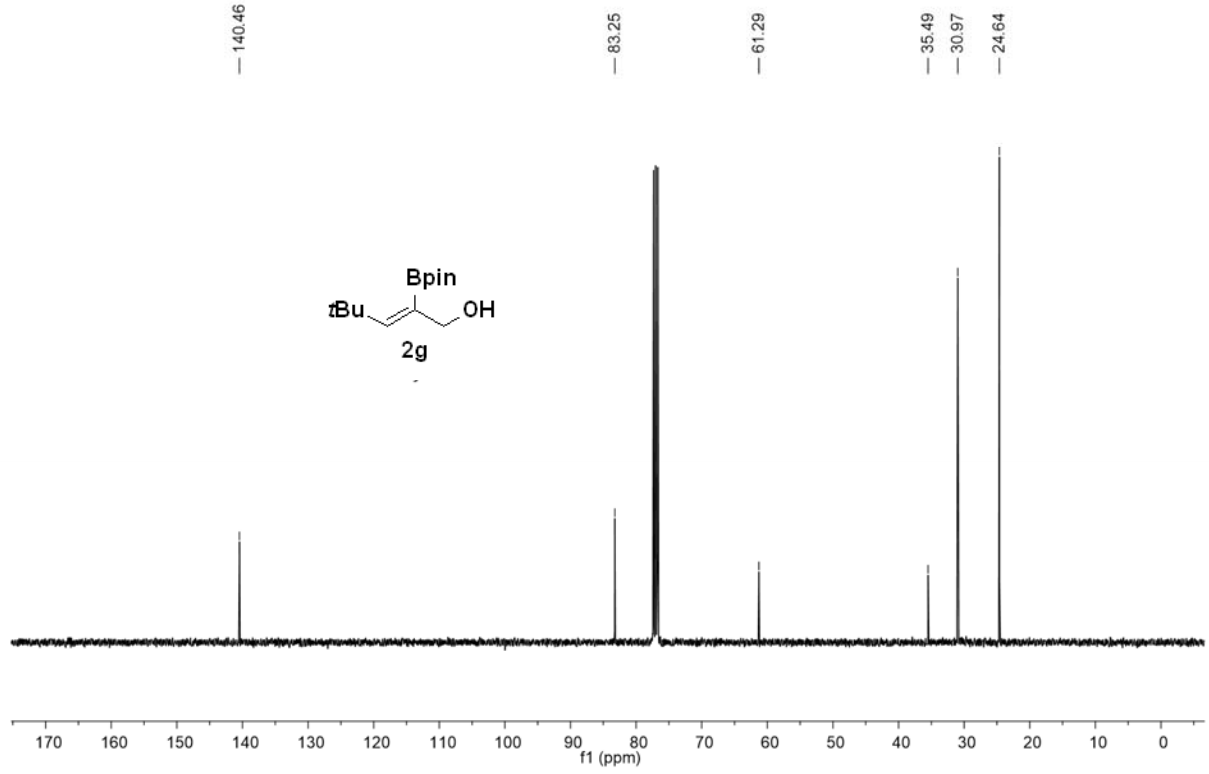
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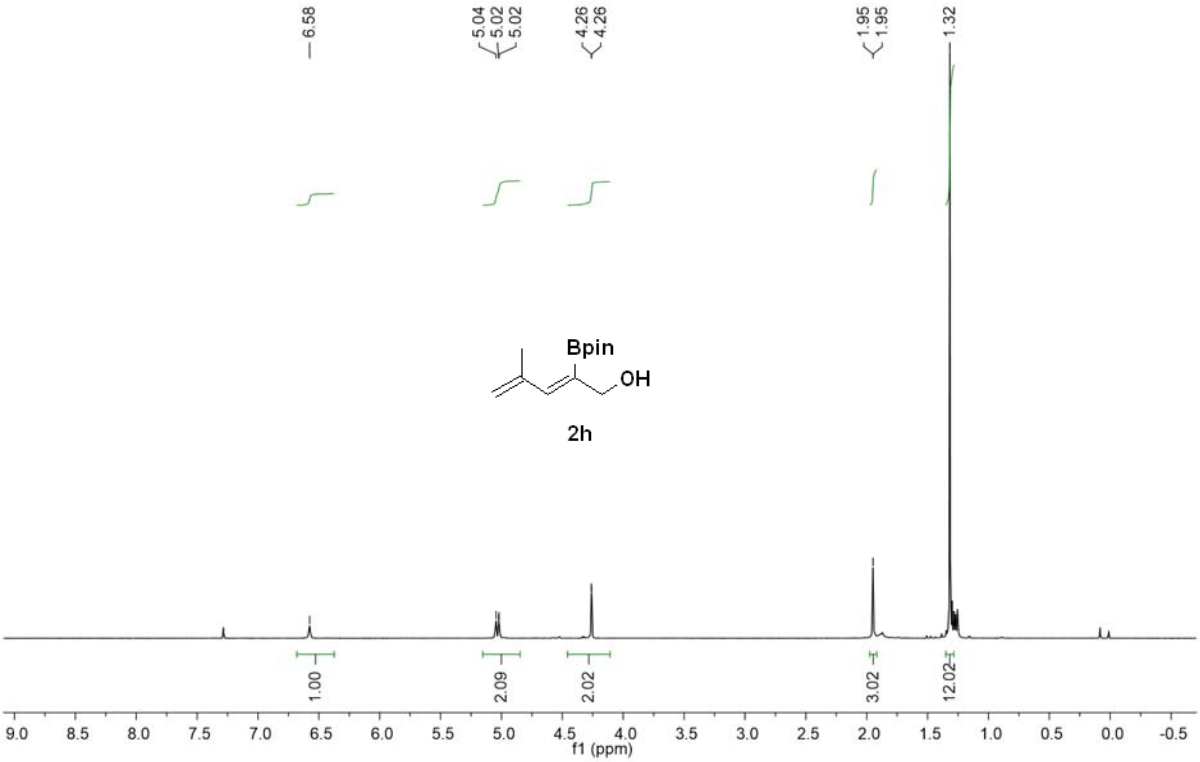
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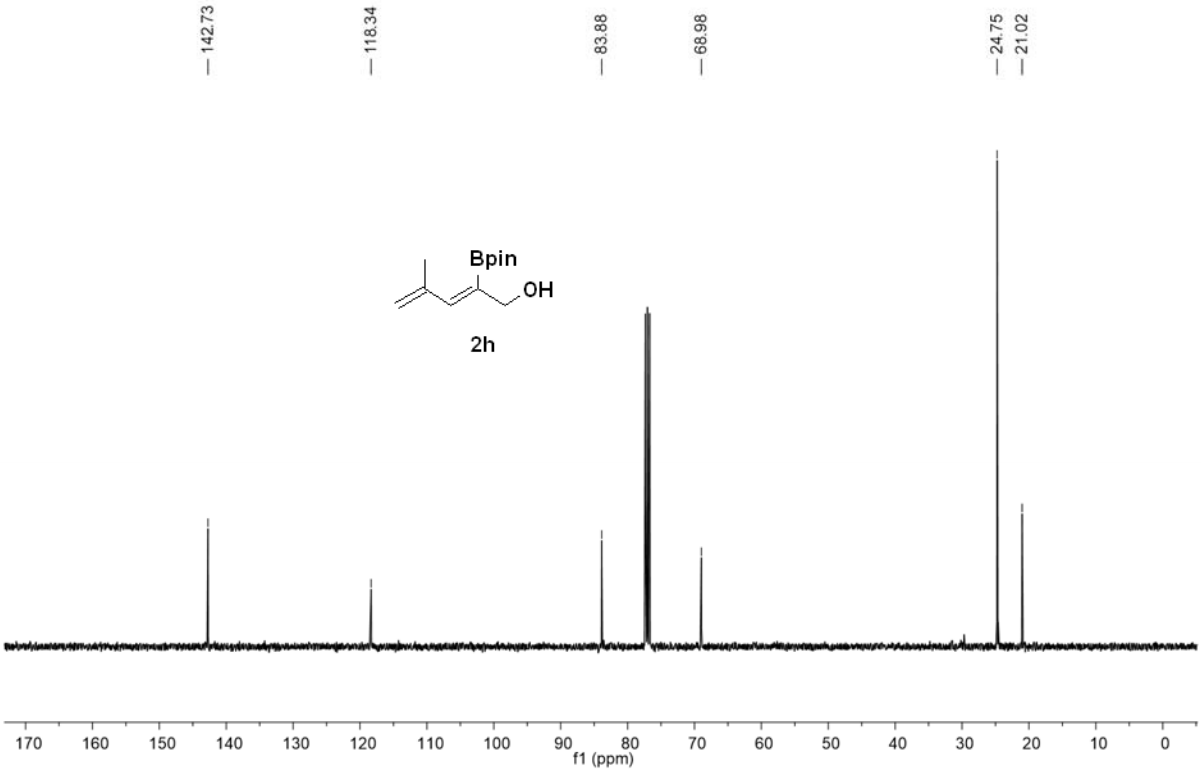
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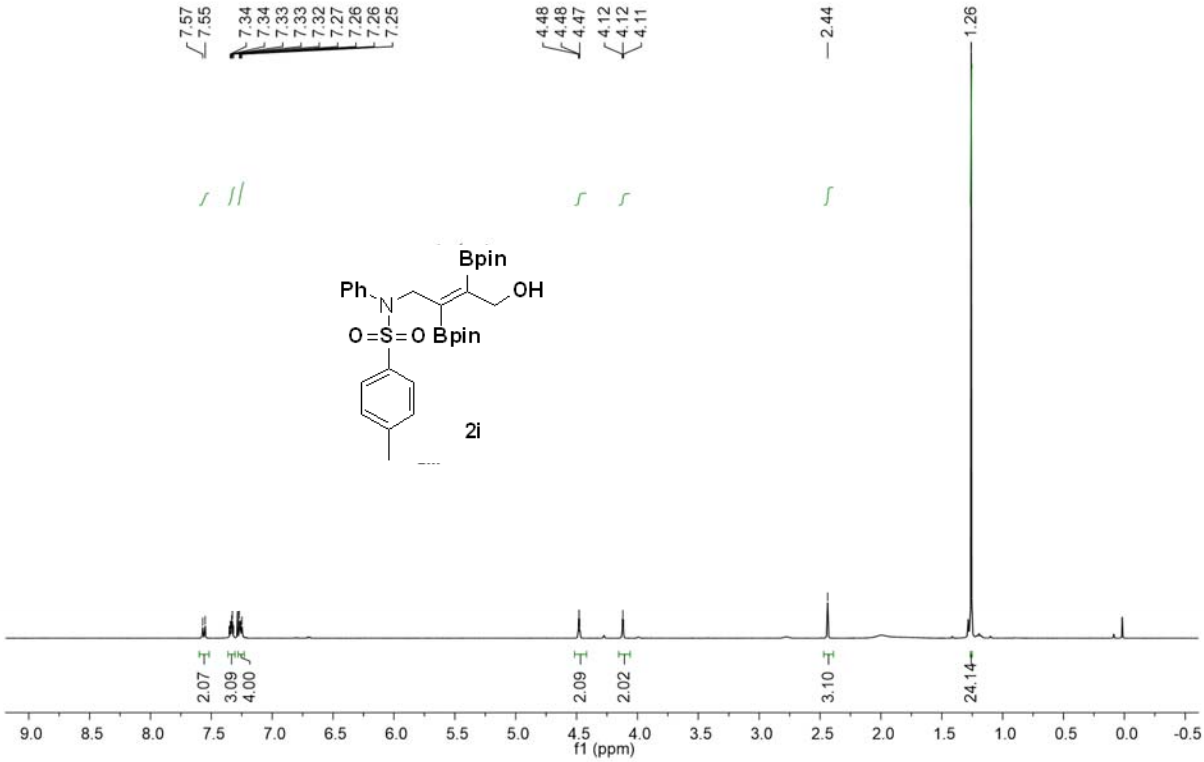
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4.12
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Ph
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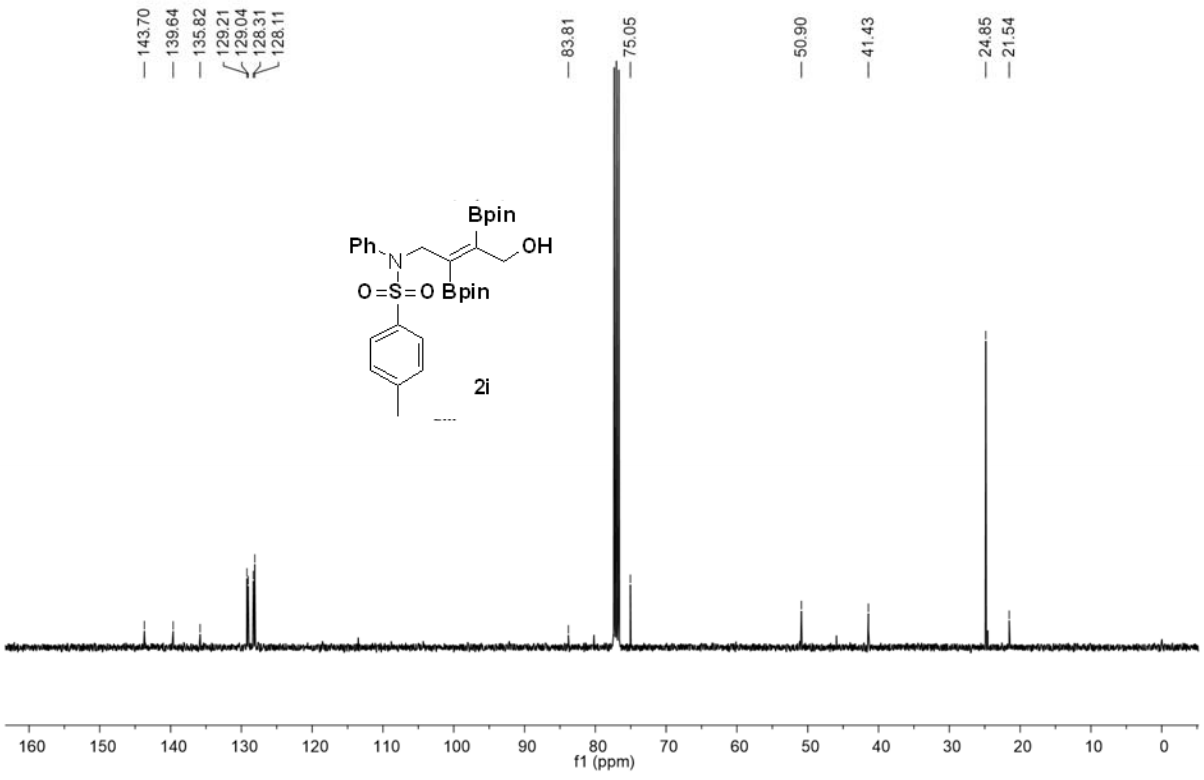
f1 (ppm)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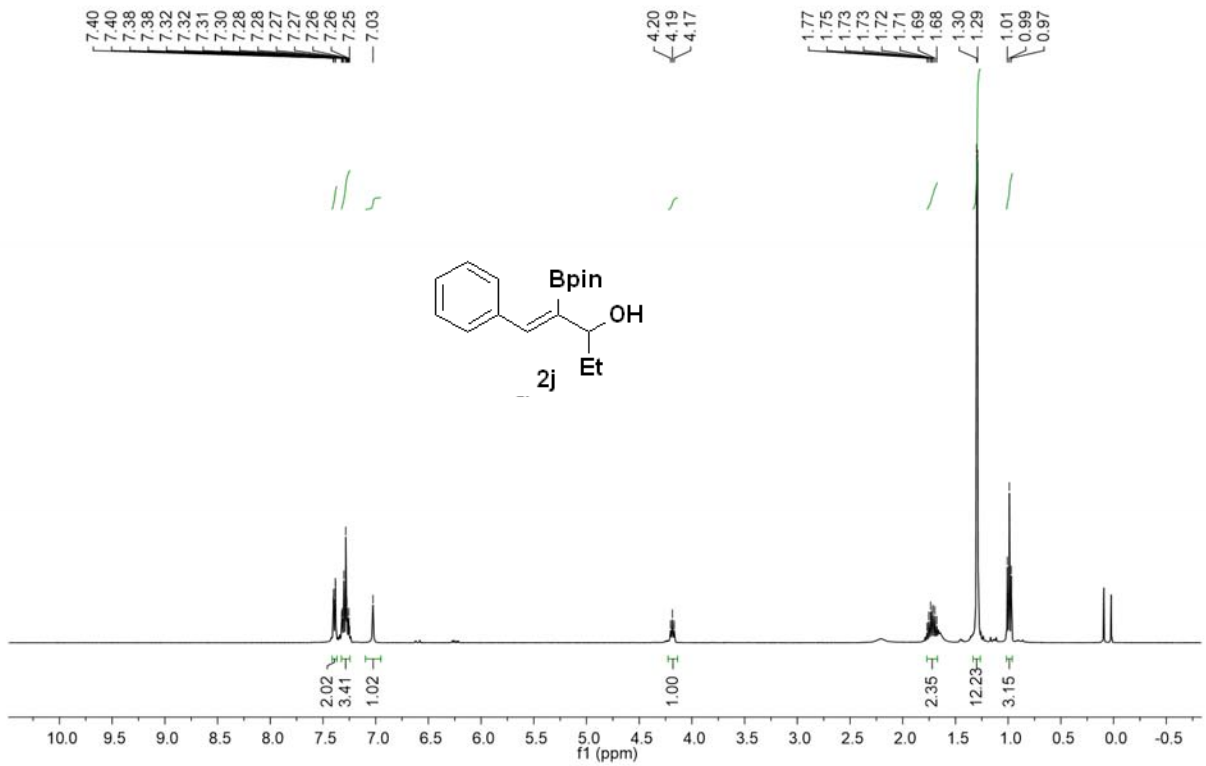
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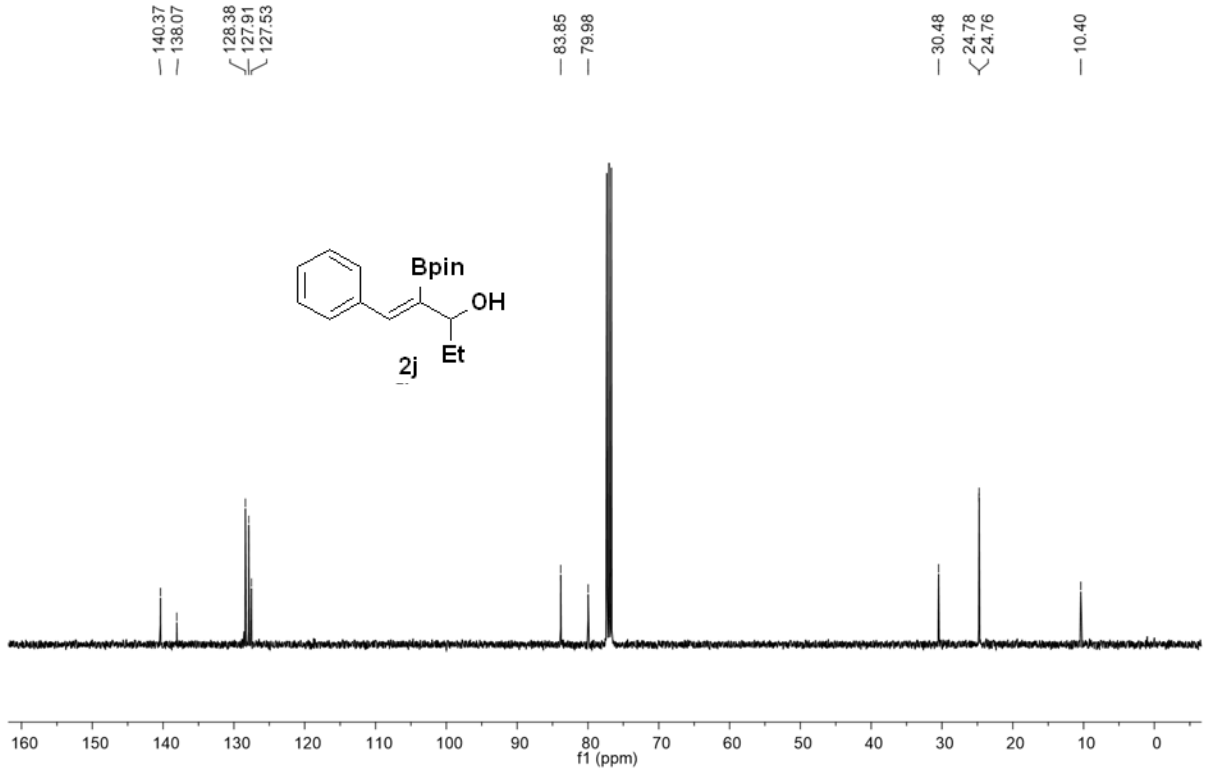
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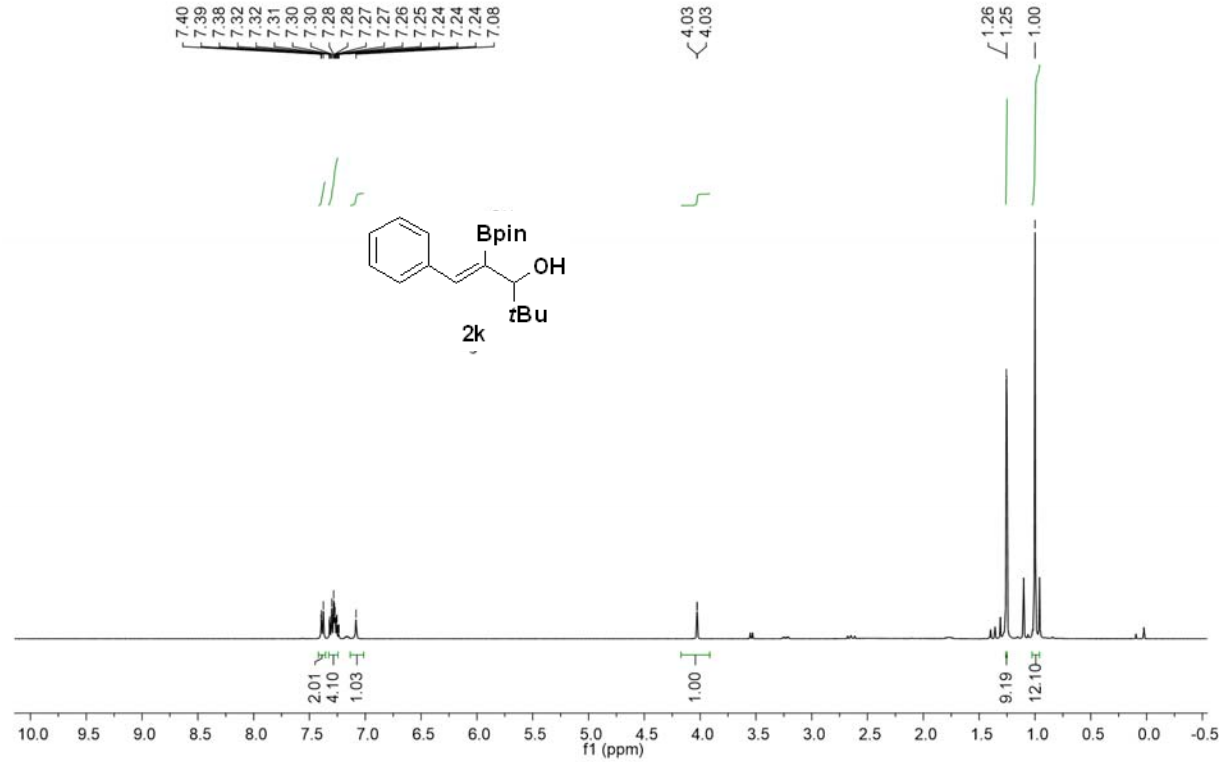
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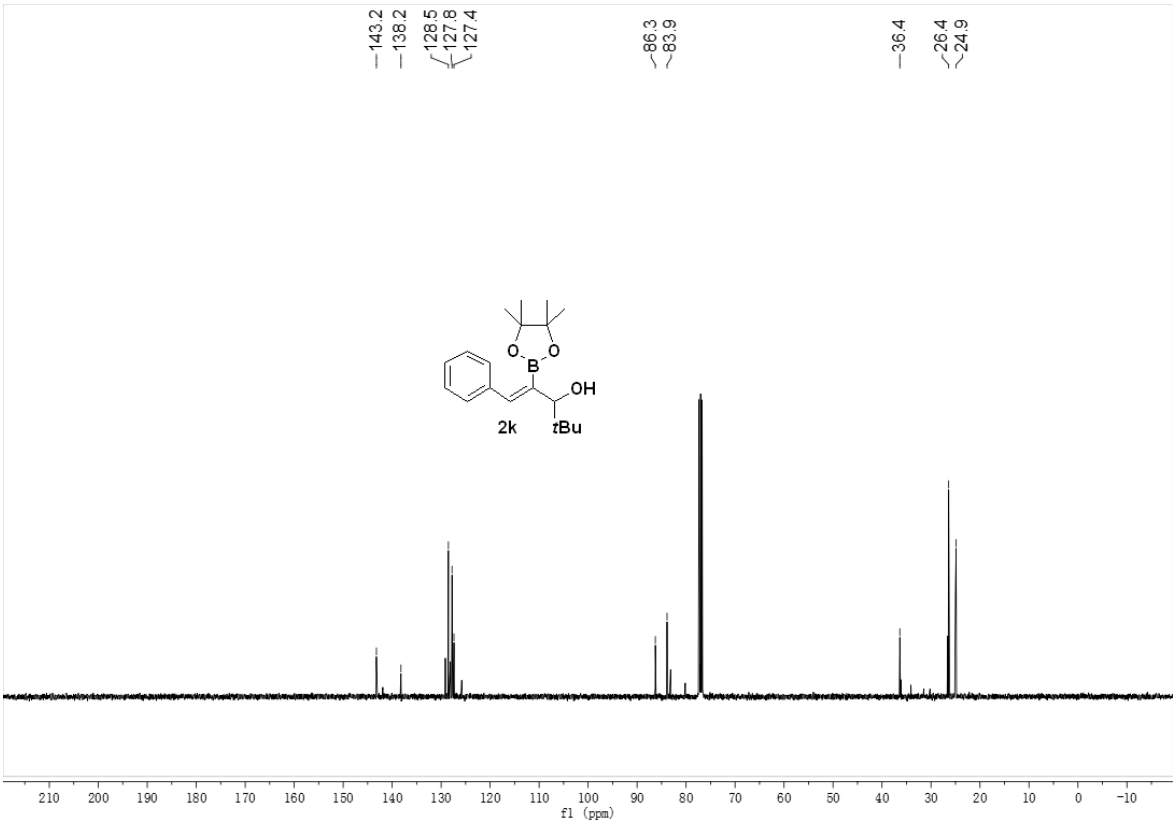
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tBu
210
200
190
180
170
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30
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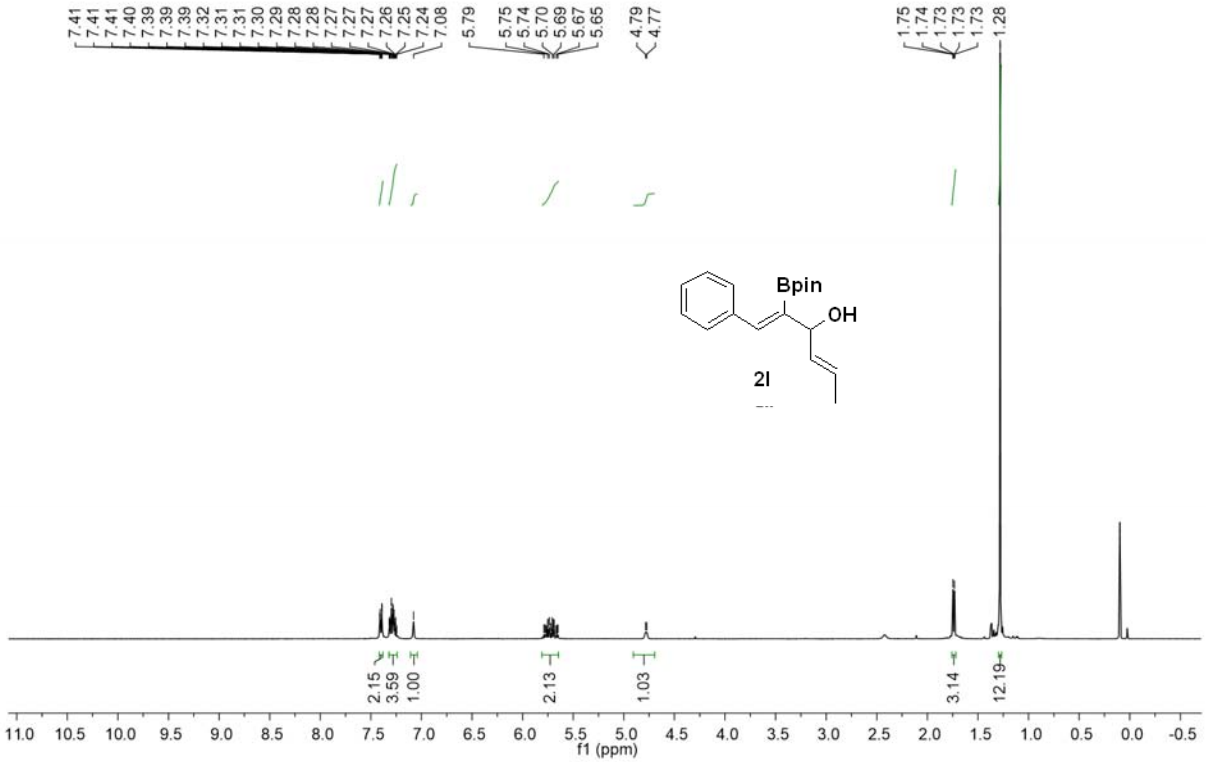
f1 (ppm)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1.00
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1.03
3.14
12.19
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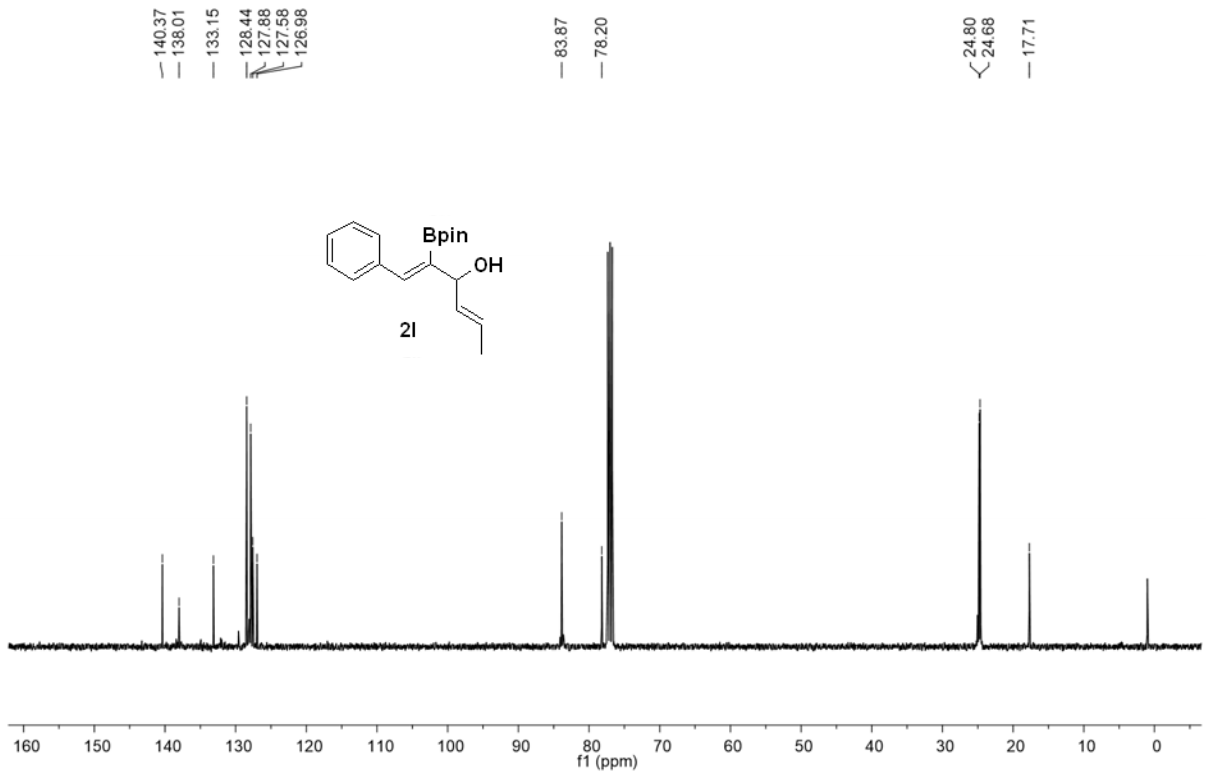
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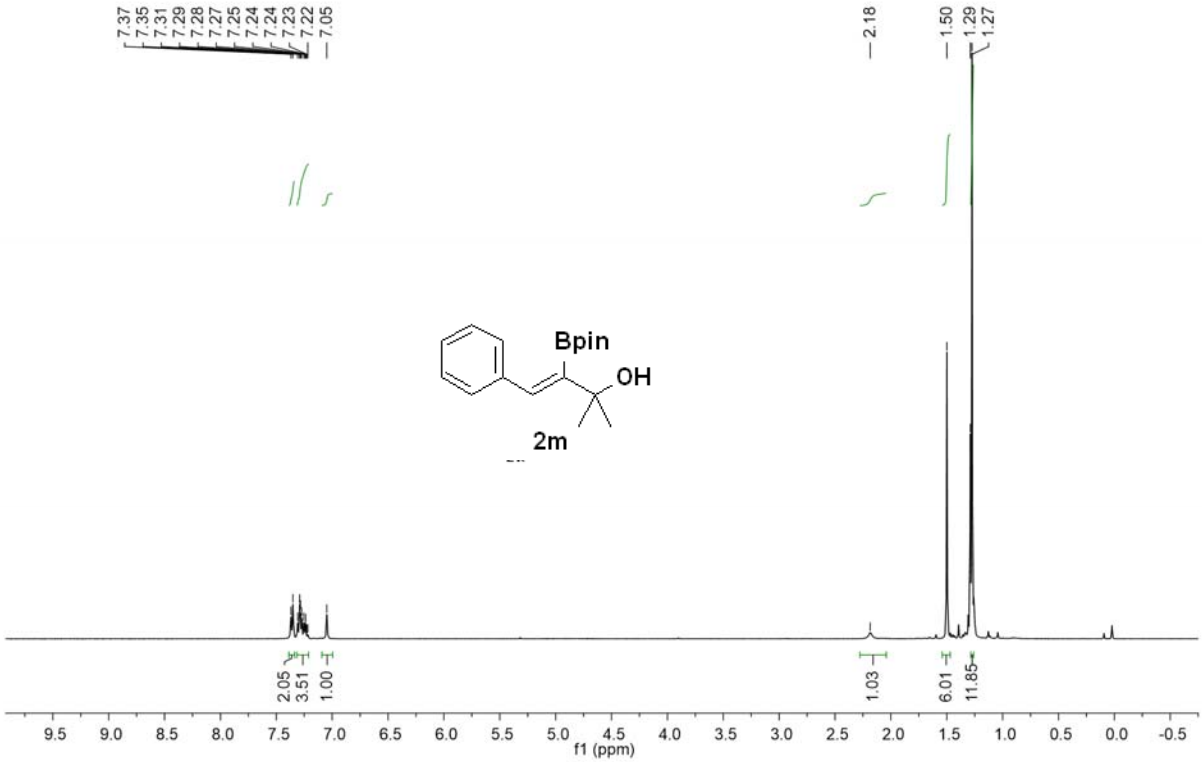
2l
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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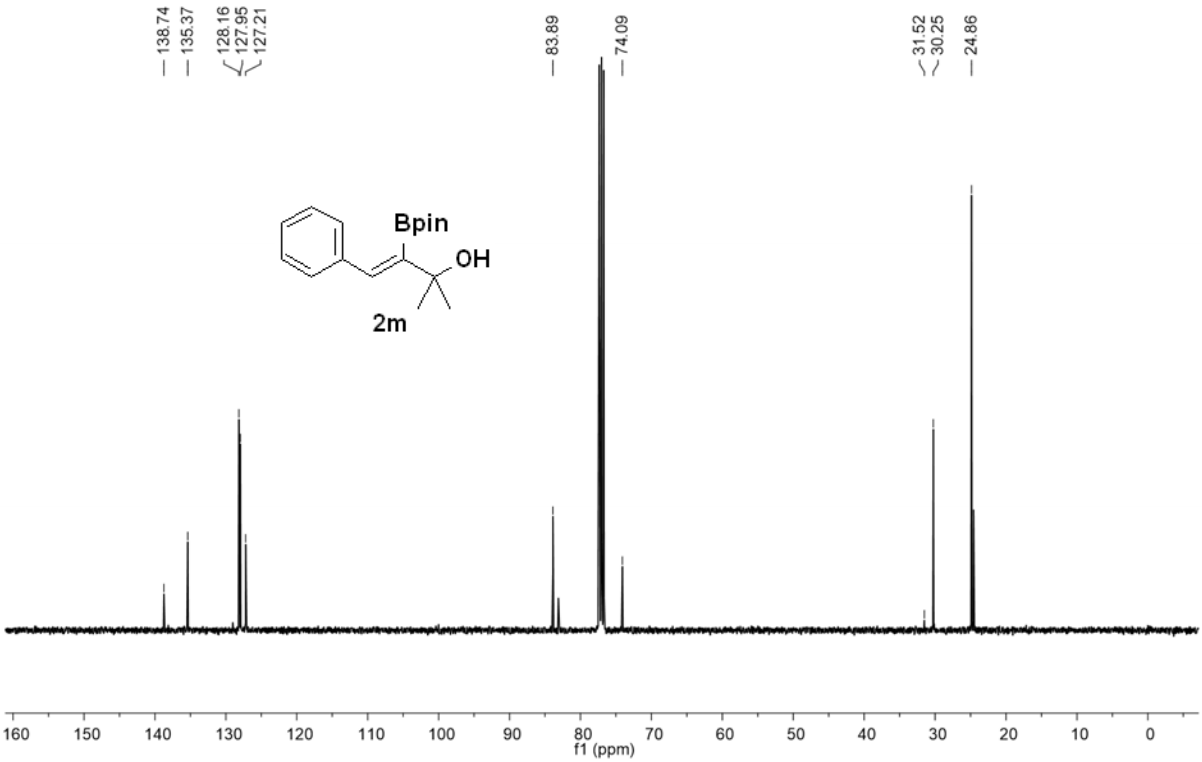
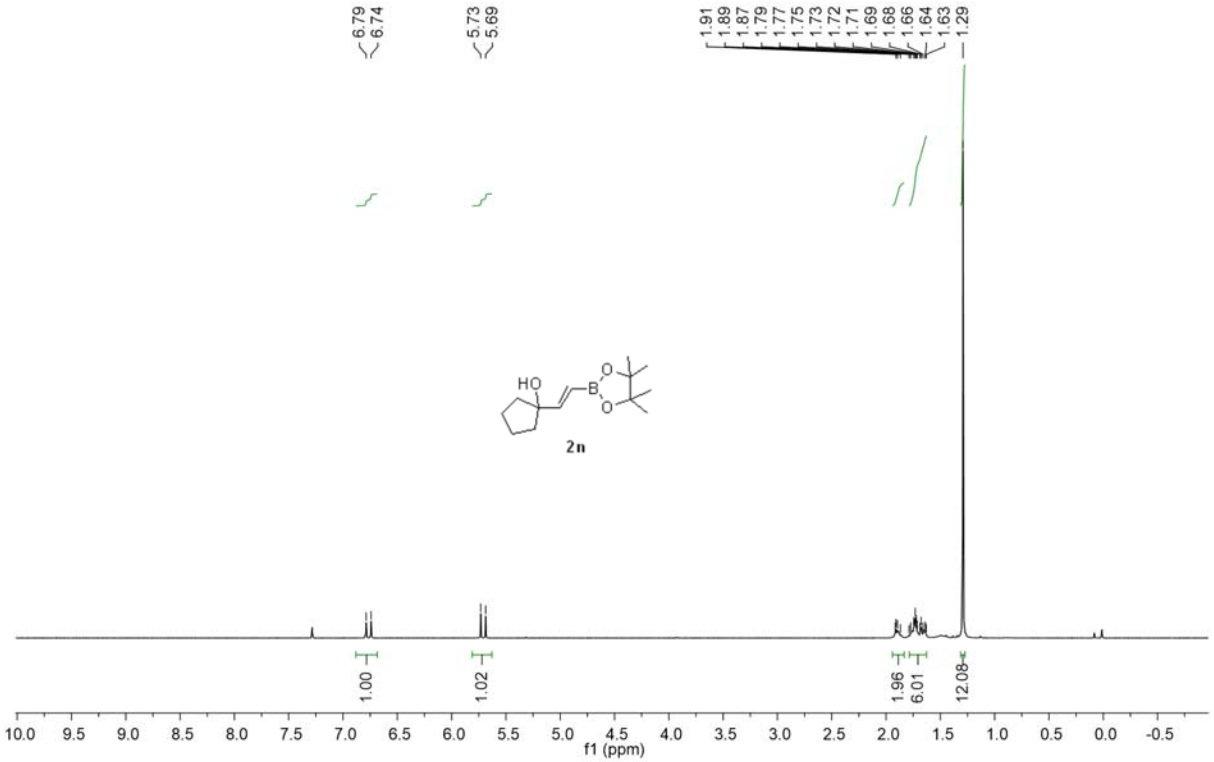
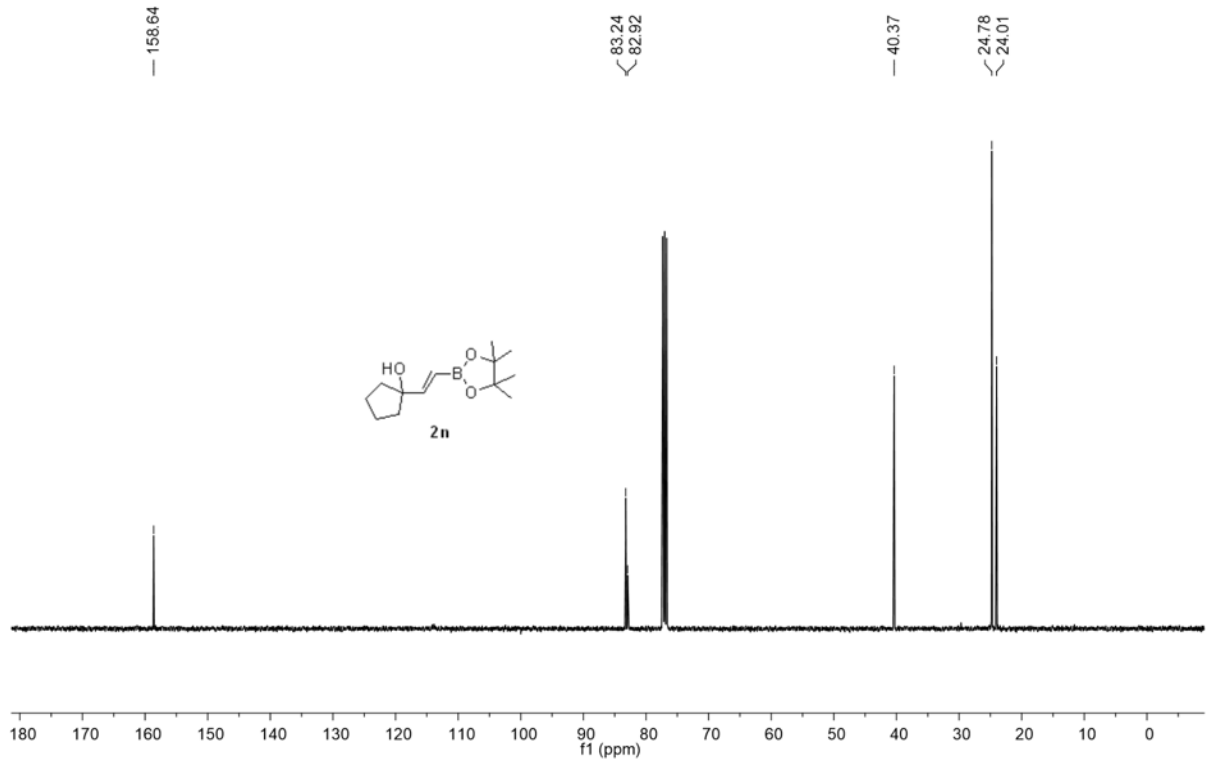
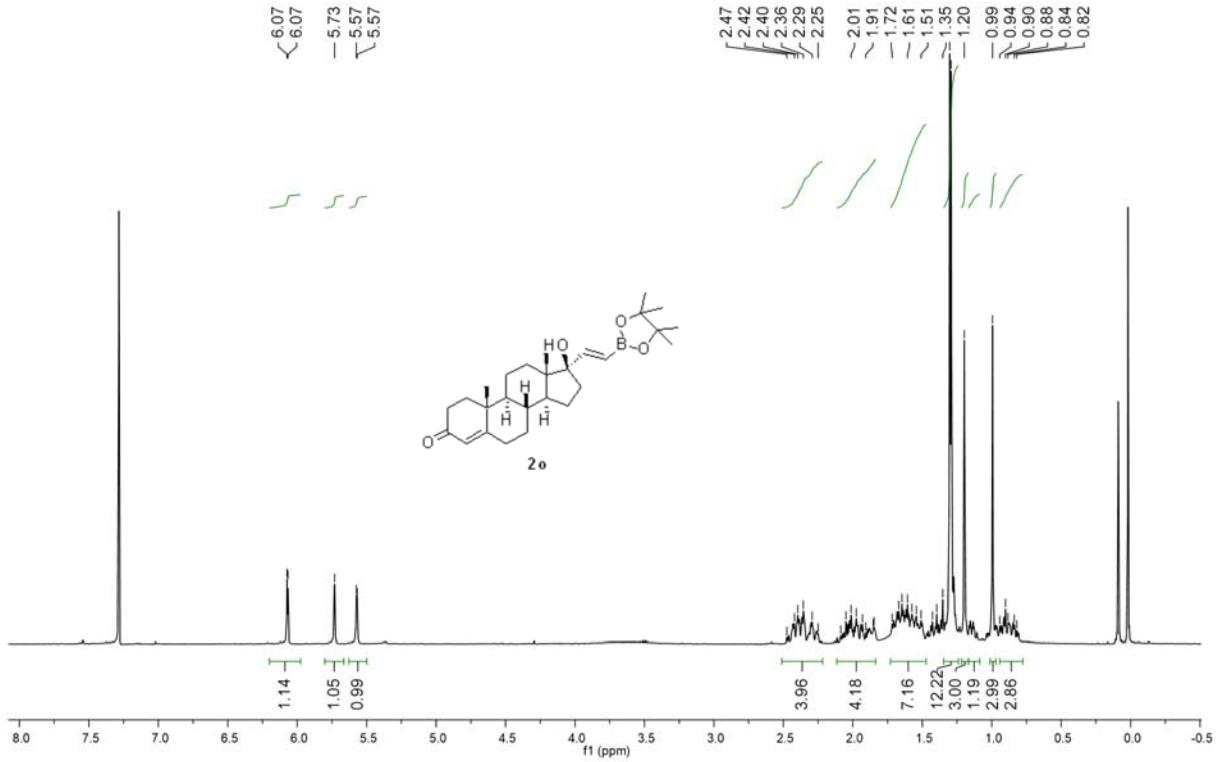
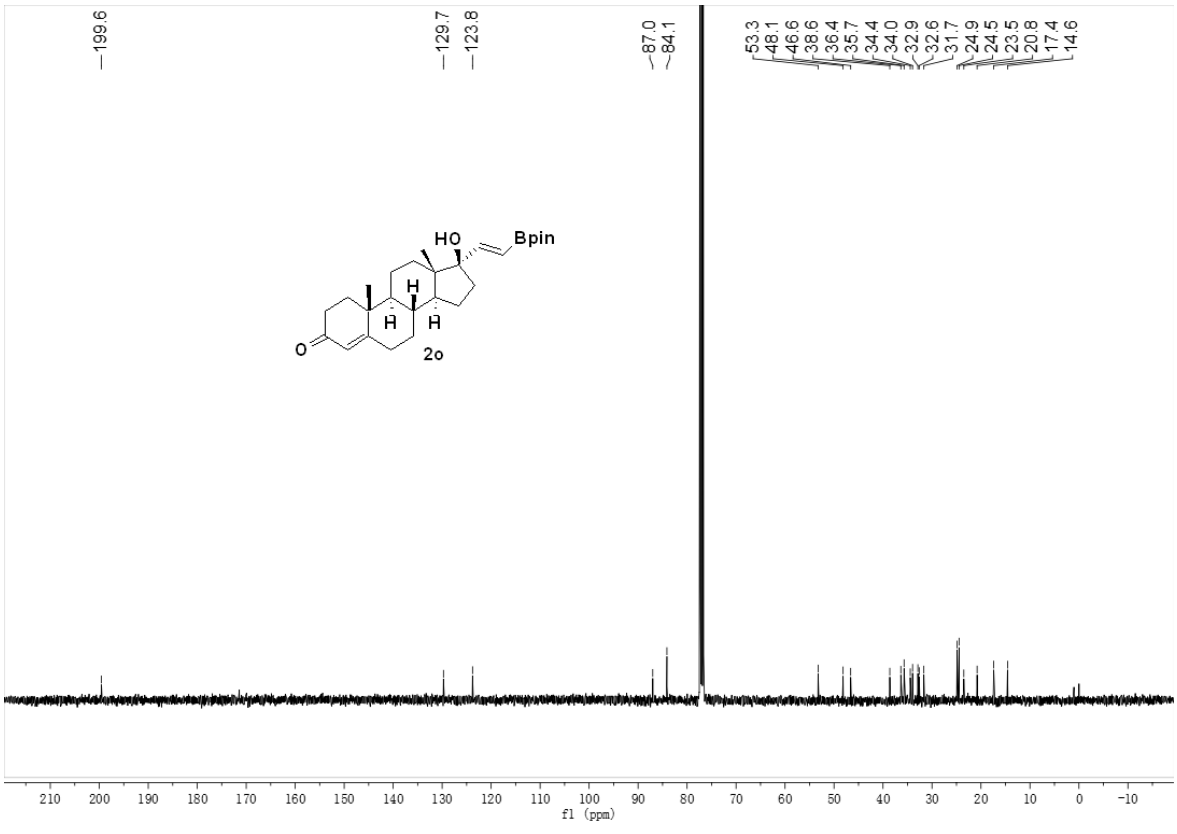
7.35
7.31
7.29
7.28
7.27
7.25
7.24
7.24
7.23
7.22
7.05
2.18
1.50
1.29
1.27
Bpin
OH
2m
2.05
3.51
1.00
1.03
6.01
11.85
f1 (ppm)

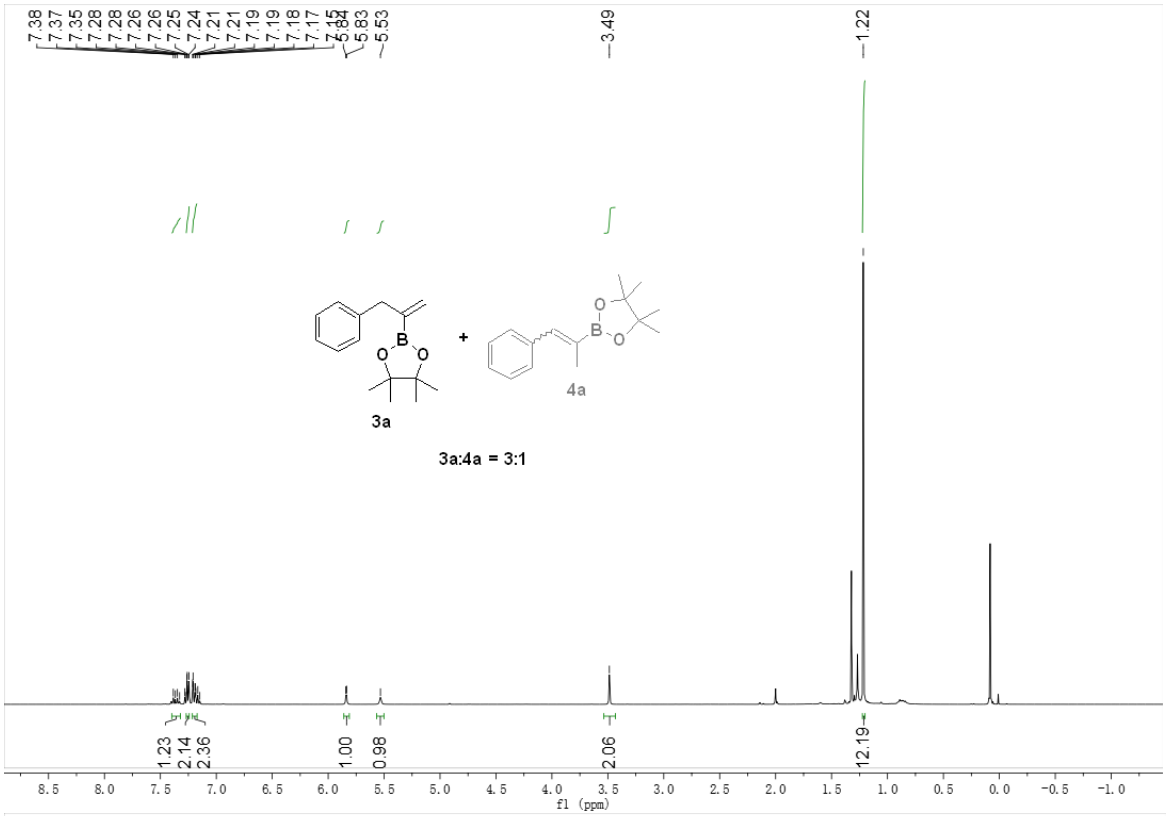

138.74
135.37
128.16
127.95
127.21
83.89
74.09
31.52
30.25
24.86
Bpin
OH
2m
f1 (ppm)

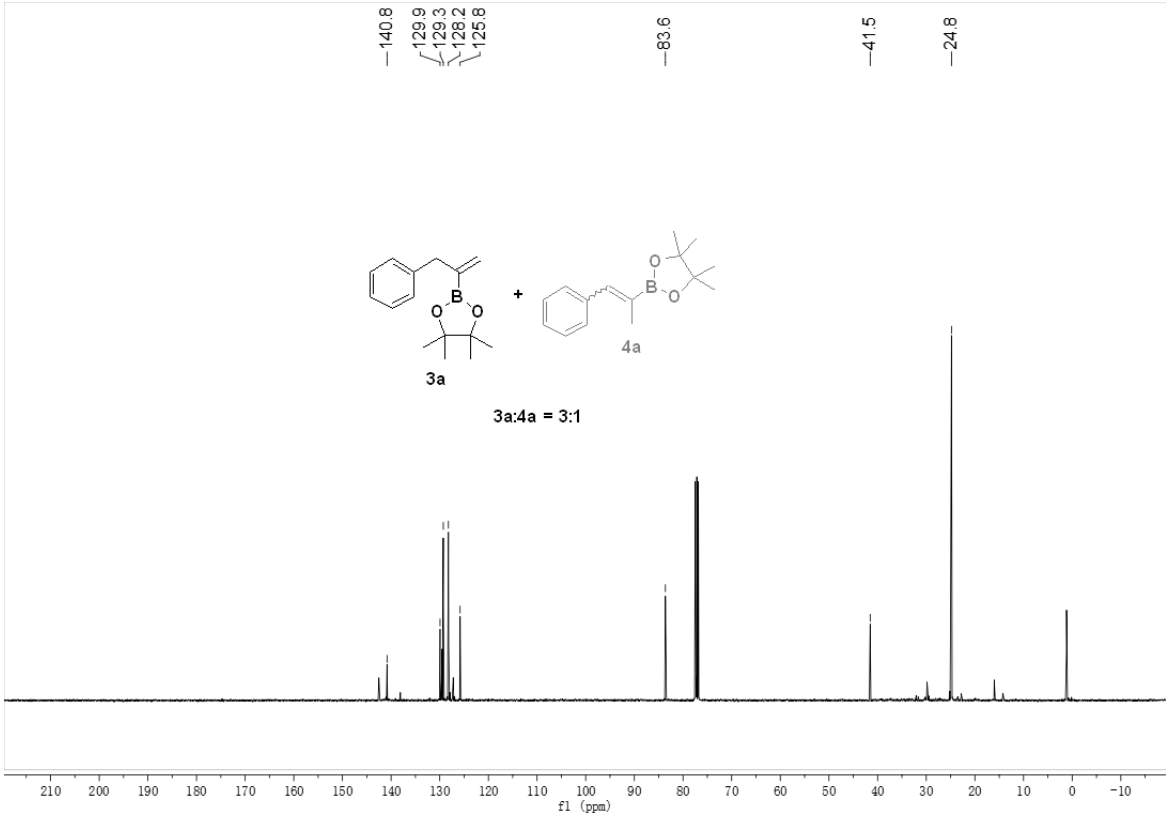

6.79
6.74
5.73
5.69
1.91
1.89
1.87
1.79
1.77
1.75
1.73
1.72
1.71
1.69
1.68
1.66
1.64
1.63
1.29
HO
B
O
O
2n
1.00
1.02
1.96
6.01
12.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

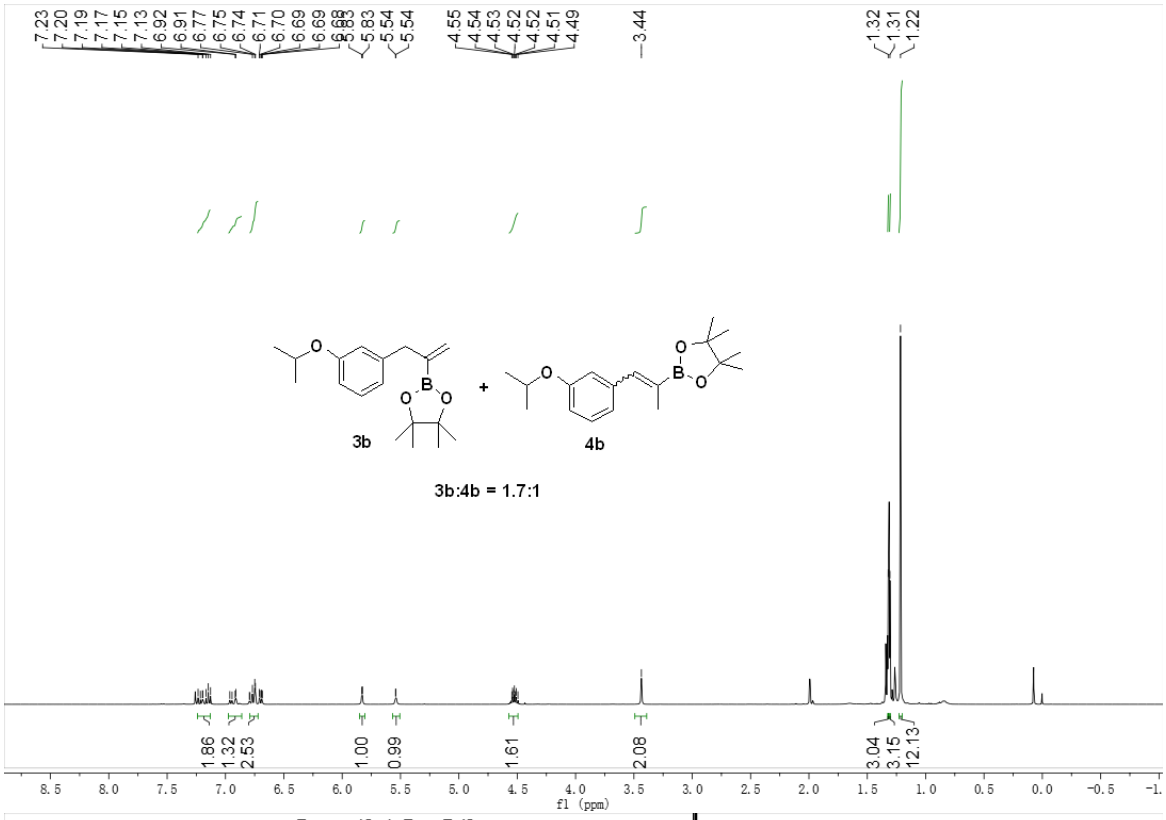

158.64
83.24
82.92
40.37
24.78
24.01
HO
B
O
O
2n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

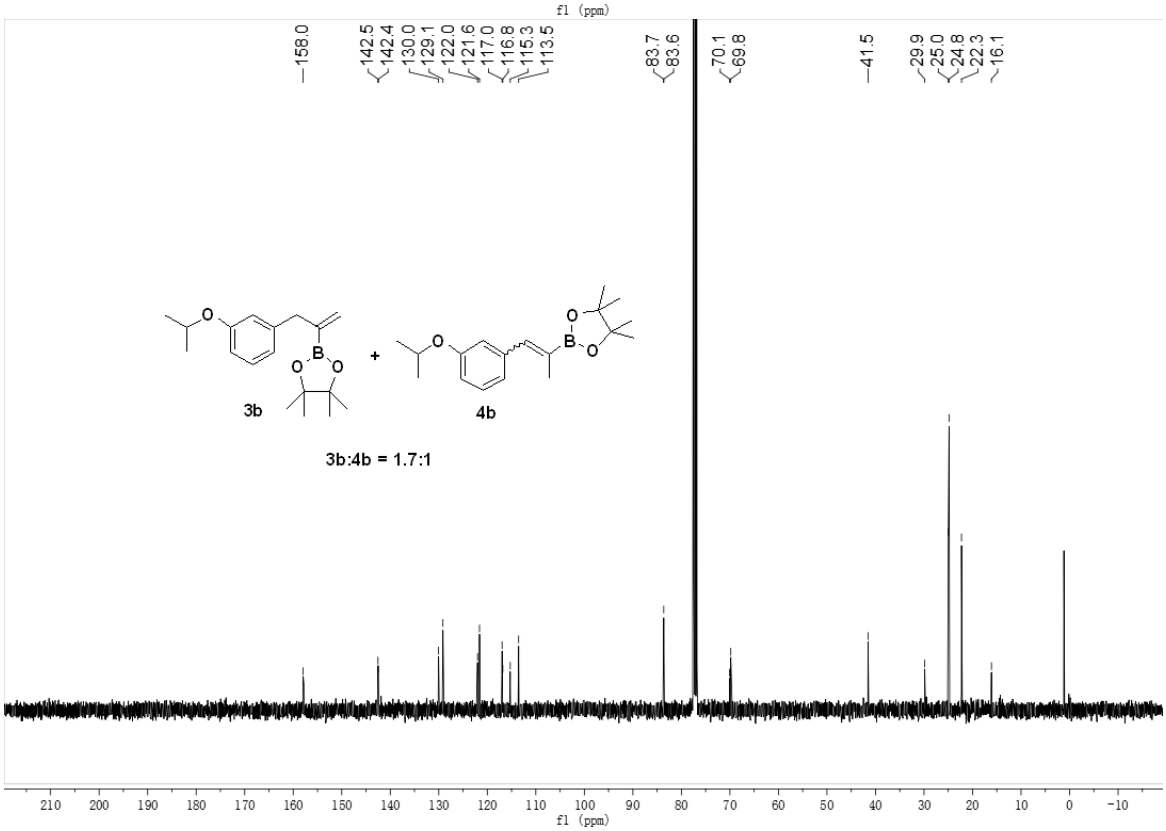

6.07
6.07
5.73
5.57
5.57
2.47
2.42
2.40
2.36
2.29
2.25
2.01
1.91
1.72
1.61
1.51
1.35
1.20
0.99
0.94
0.90
0.88
0.84
0.82
HO
B
O
O
H
H
H
O
2o
1.14
1.05
0.99
3.96
4.18
7.16
12.22
3.00
1.19
2.99
2.86
f1 (ppm)

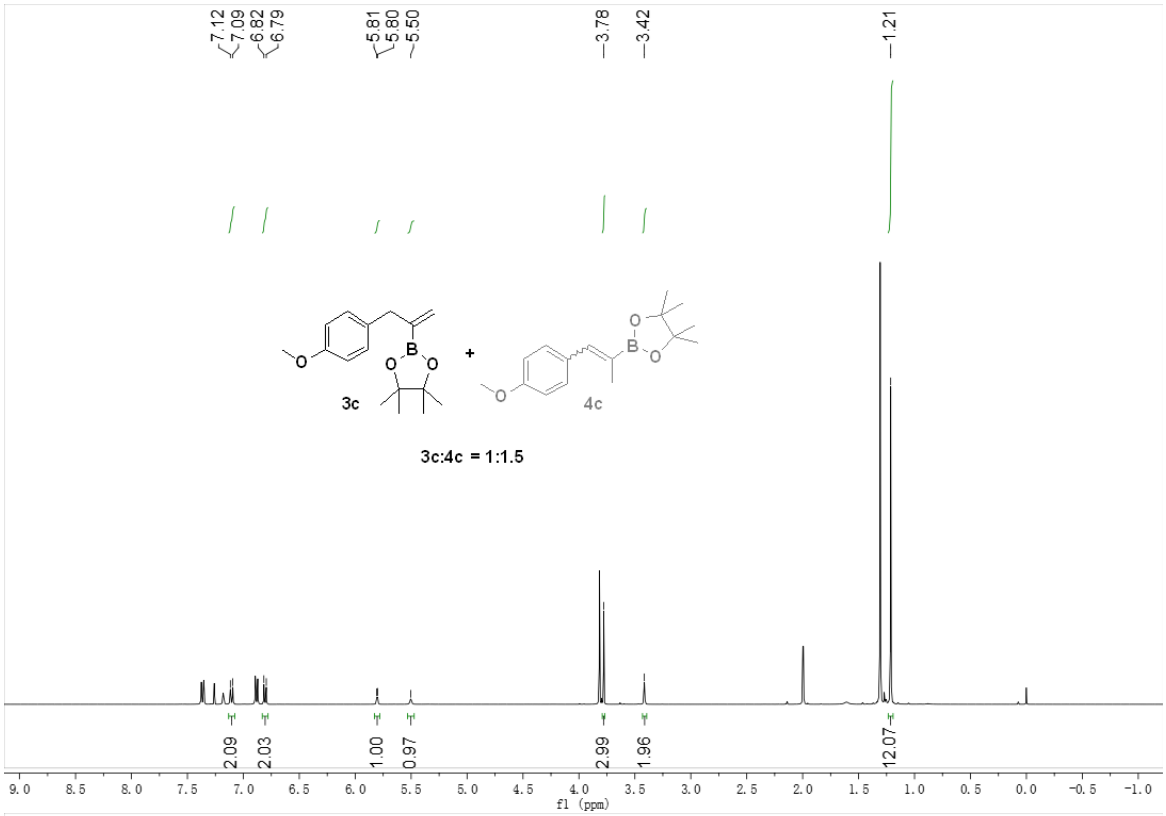

199.6
129.7
123.8
87.0
84.1
53.3
48.1
46.6
38.6
36.4
35.7
34.4
34.0
32.9
32.6
31.7
24.9
24.5
23.5
20.8
17.4
14.6
HO
Bpin
H
H
H
O
2o
f1 (ppm)

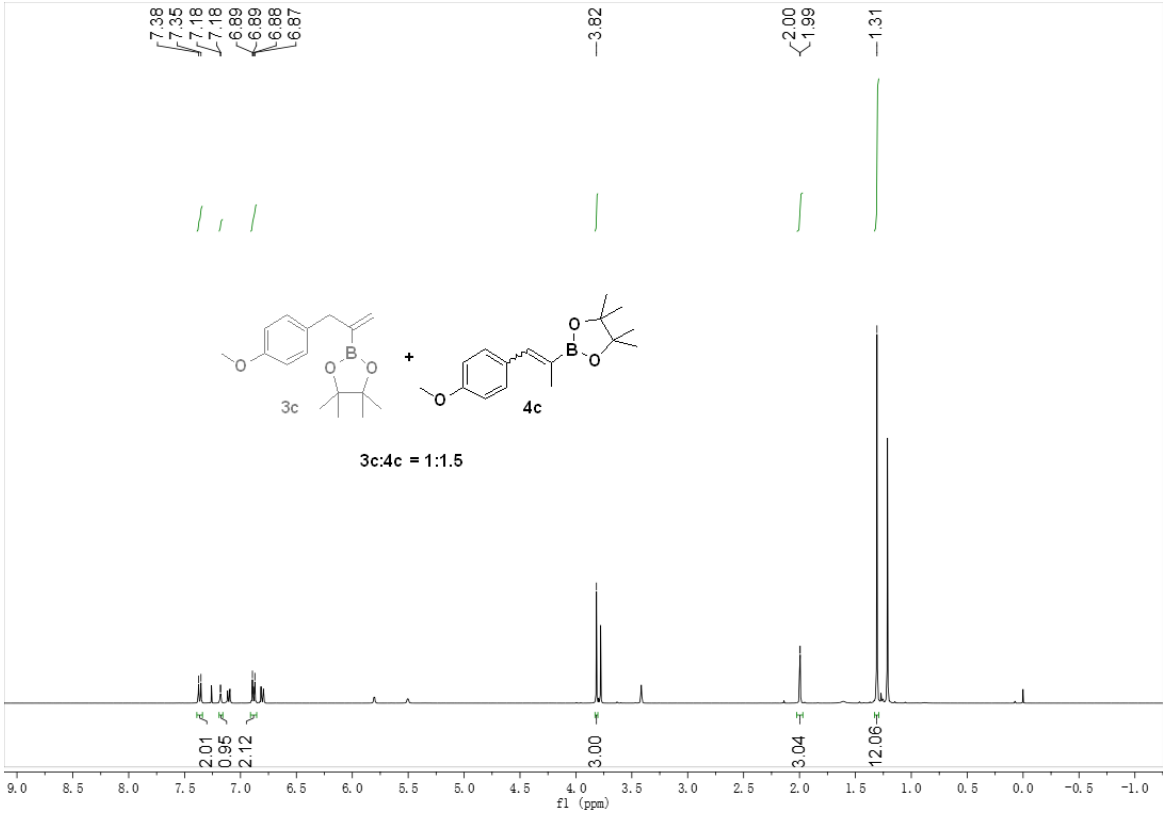

7.38
7.37
7.35
7.28
7.28
7.26
7.26
7.25
7.24
7.21
7.21
7.19
7.19
7.18
7.17
7.15
5.84
5.83
5.53
3.49
1.22
3a
4a
3a:4a = 3:1
1.23
2.14
2.36
1.00
0.98
2.06
12.19
f1 (ppm)

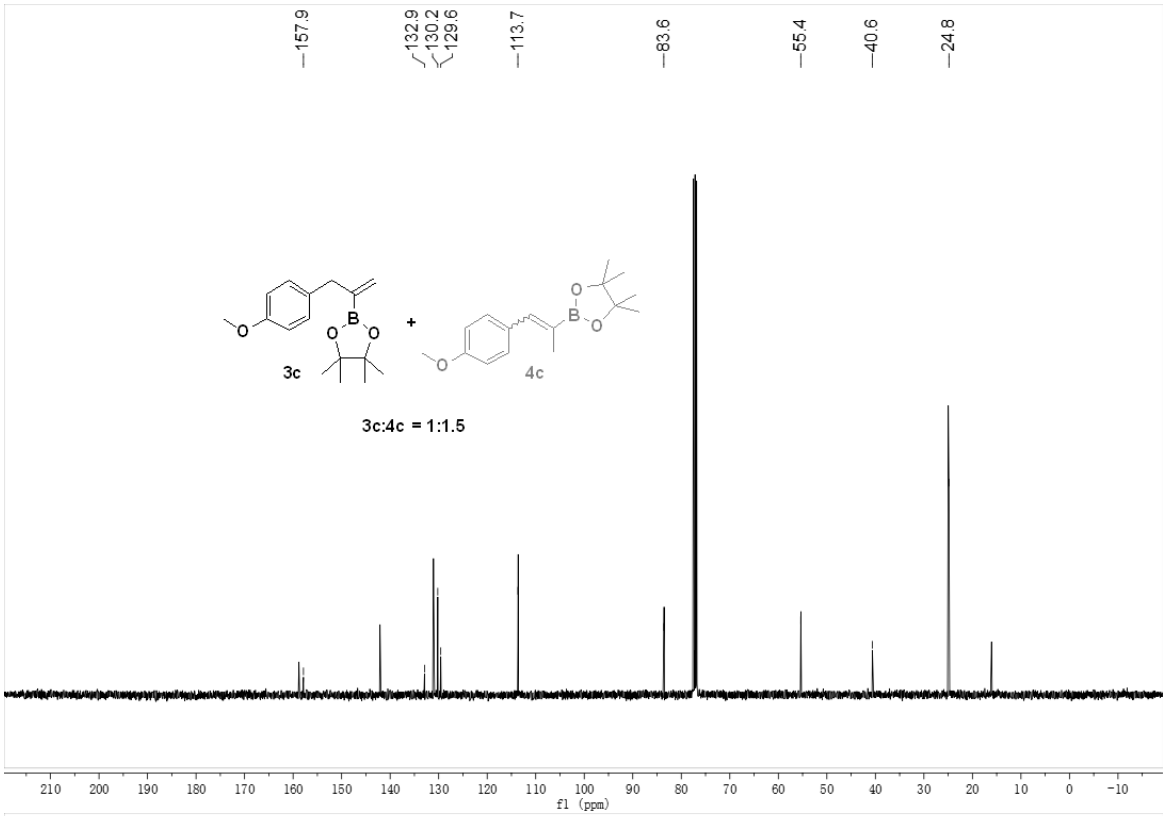

140.8
129.9
129.3
128.2
125.8
83.6
41.5
24.8
3a
4a
3a:4a = 3:1
f1 (ppm)

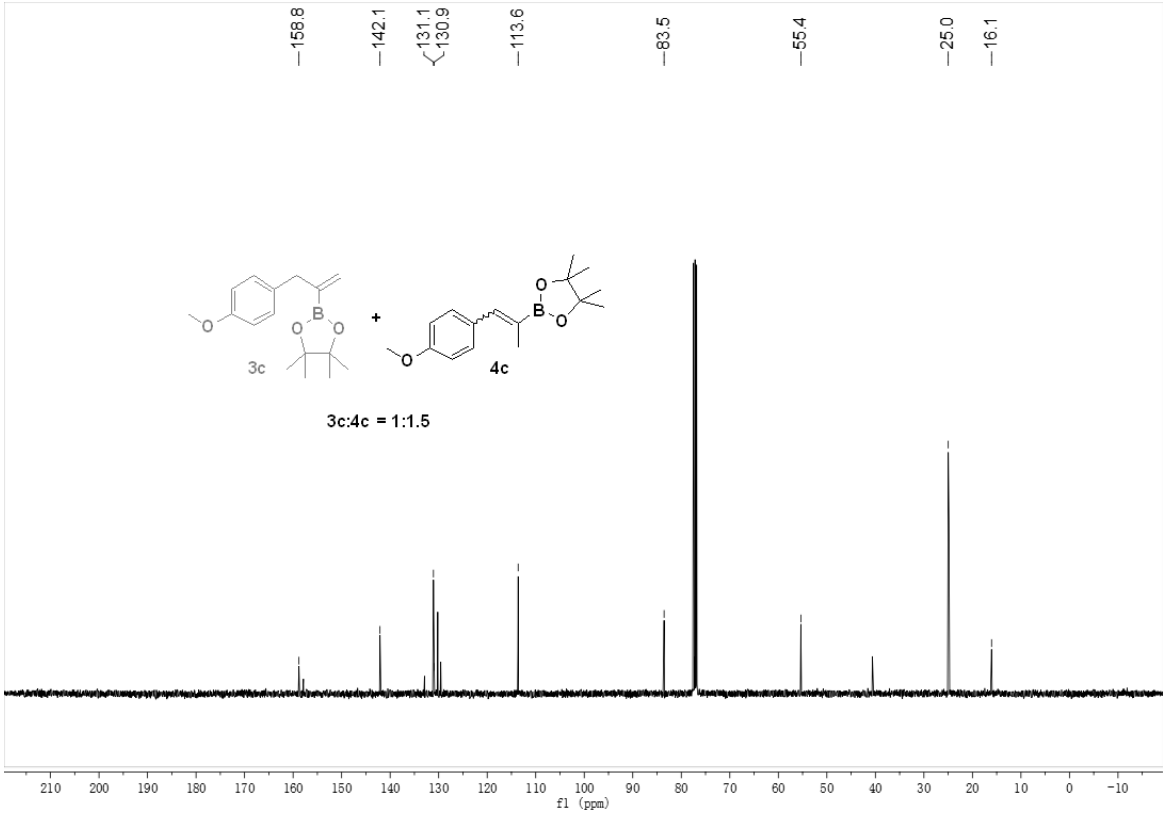

7.23
7.20
7.19
7.17
7.15
7.13
6.92
6.91
6.77
6.75
6.74
6.71
6.70
6.69
6.69
5.83
5.54
5.54
4.55
4.54
4.53
4.52
4.52
4.51
4.49
3.44
1.32
1.31
1.22
3b
4b
3b:4b = 1.7:1
1.86
1.32
2.53
1.00
0.99
1.61
2.08
3.04
3.15
12.13
f1 (ppm)

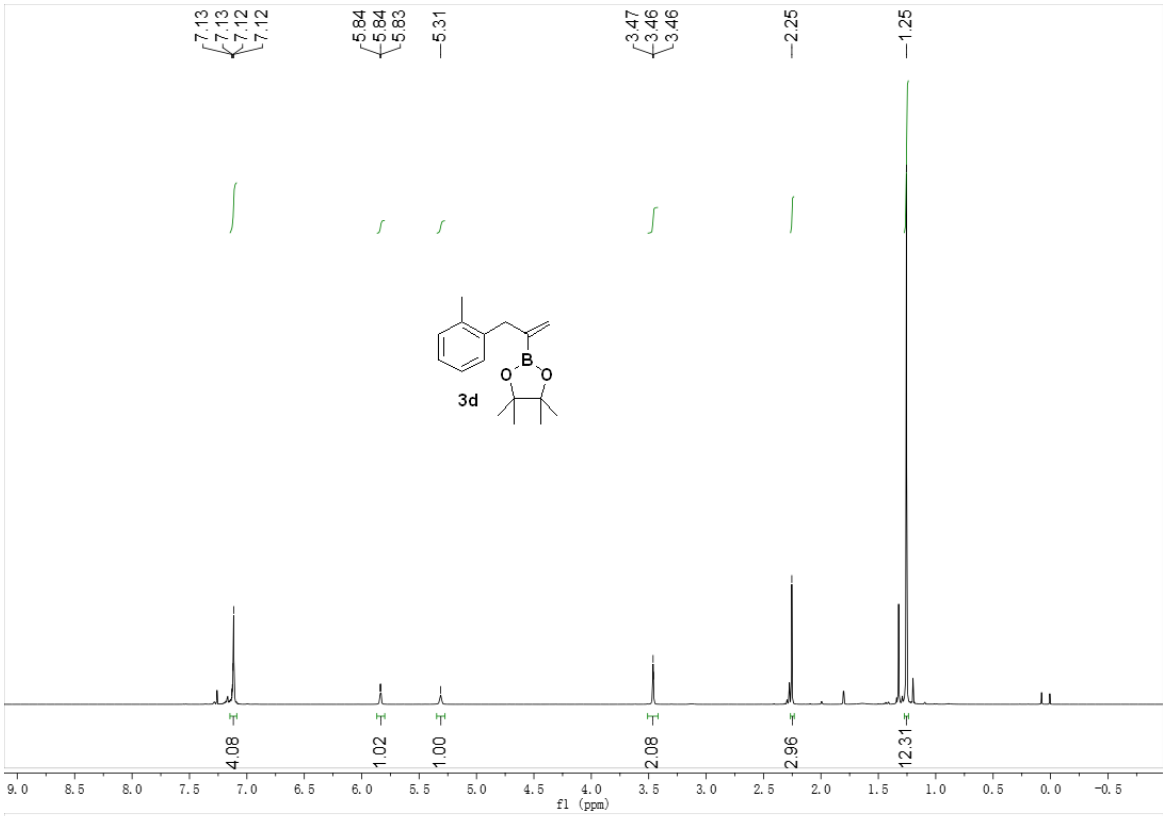

158.0
142.5
142.4
130.0
129.1
122.0
121.6
117.0
116.8
115.3
113.5
83.7
83.6
70.1
69.8
41.5
29.9
25.0
24.8
22.3
16.1
3b
4b
3b:4b = 1.7:1
f1 (ppm)

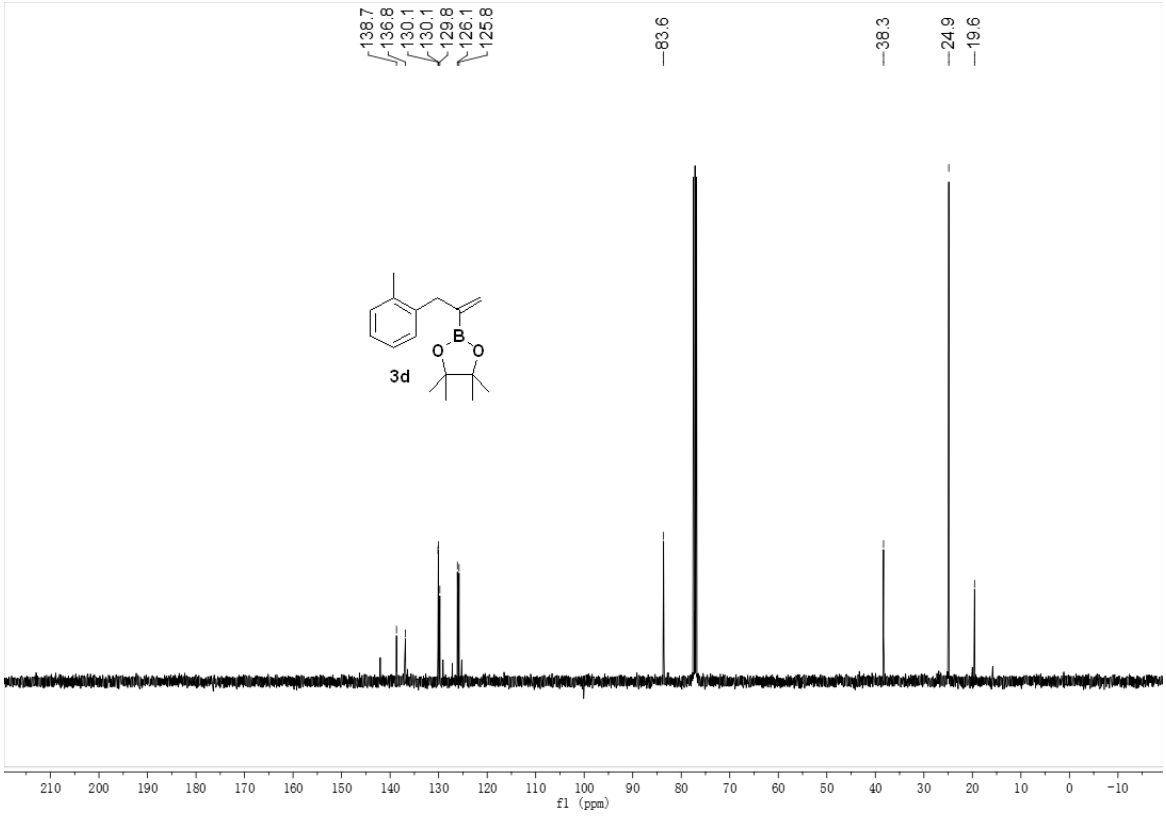

7.12
7.09
6.82
6.79
5.81
5.80
5.50
3.78
3.42
1.21
3c
4c
3c:4c = 1:1.5
2.09
2.03
1.00
0.97
2.99
1.96
12.07
f1 (ppm)

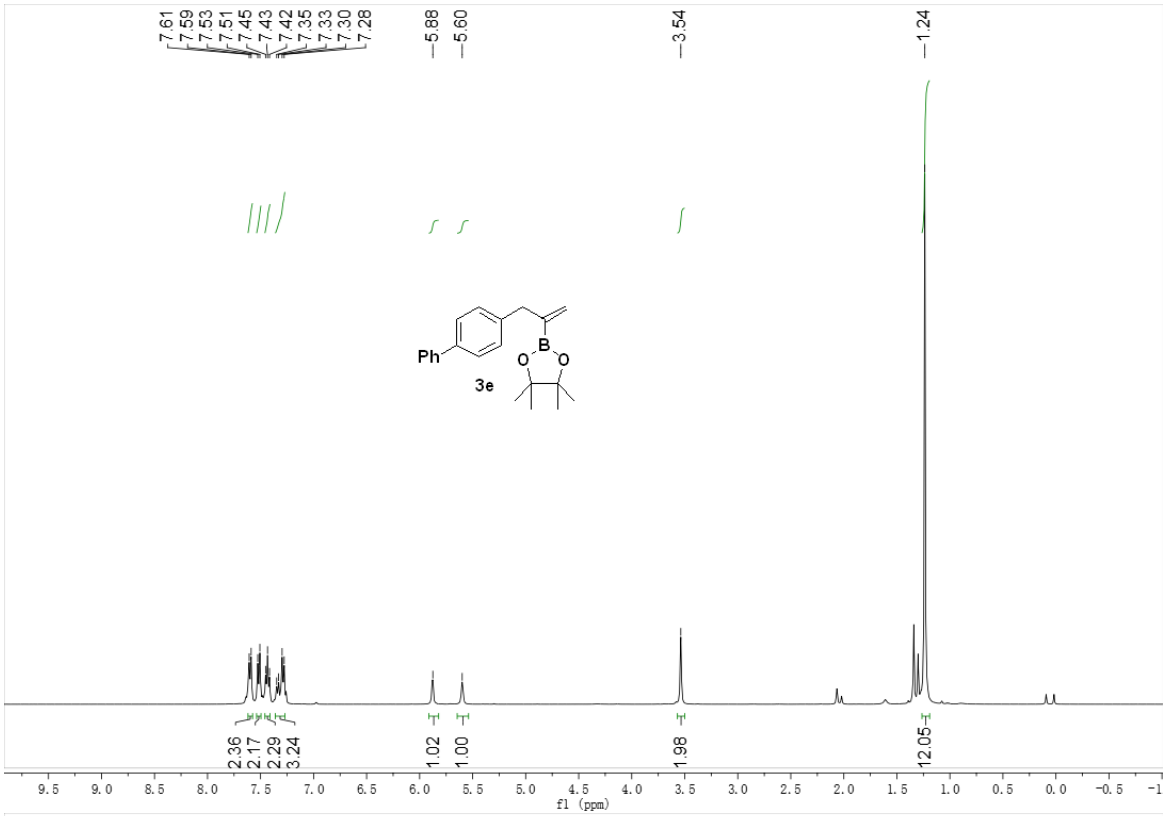

7.38
7.35
7.18
7.18
6.89
6.89
6.88
6.87
3.82
2.00
1.99
1.31
3c
4c
3c:4c = 1:1.5
2.01
0.95
2.12
3.00
3.04
12.06
f1 (ppm)

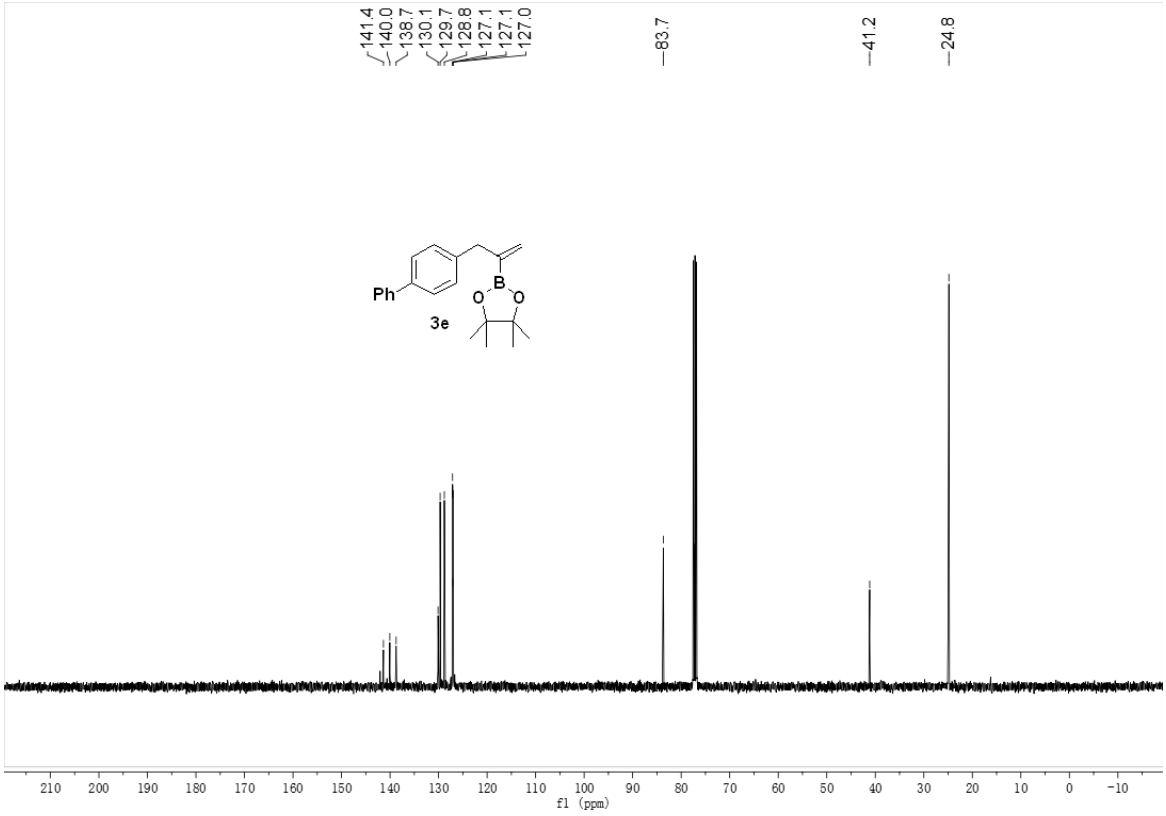

157.9
132.9
130.2
129.6
113.7
83.6
55.4
40.6
24.8
3c
4c
3c:4c = 1:1.5
f1 (ppm)


158.8
142.1
131.1
130.9
113.6
83.5
55.4
25.0
16.1
3c
4c
3c:4c = 1:1.5
f1 (ppm)


7.13
7.13
7.12
7.12
5.84
5.84
5.83
5.31
3.47
3.46
3.46
2.25
1.25
3d
4.08
1.02
1.00
2.08
2.96
12.31
f1 (ppm)


138.7
136.8
130.1
130.1
129.8
126.1
125.8
83.6
38.3
24.9
19.6
3d
f1 (ppm)


7.61
7.59
7.53
7.51
7.45
7.43
7.42
7.35
7.33
7.30
7.28
5.88
5.60
3.54
1.24
Ph
B
O
O
3e
2.36
2.17
2.29
3.24
1.02
1.00
1.98
12.05
f1 (ppm)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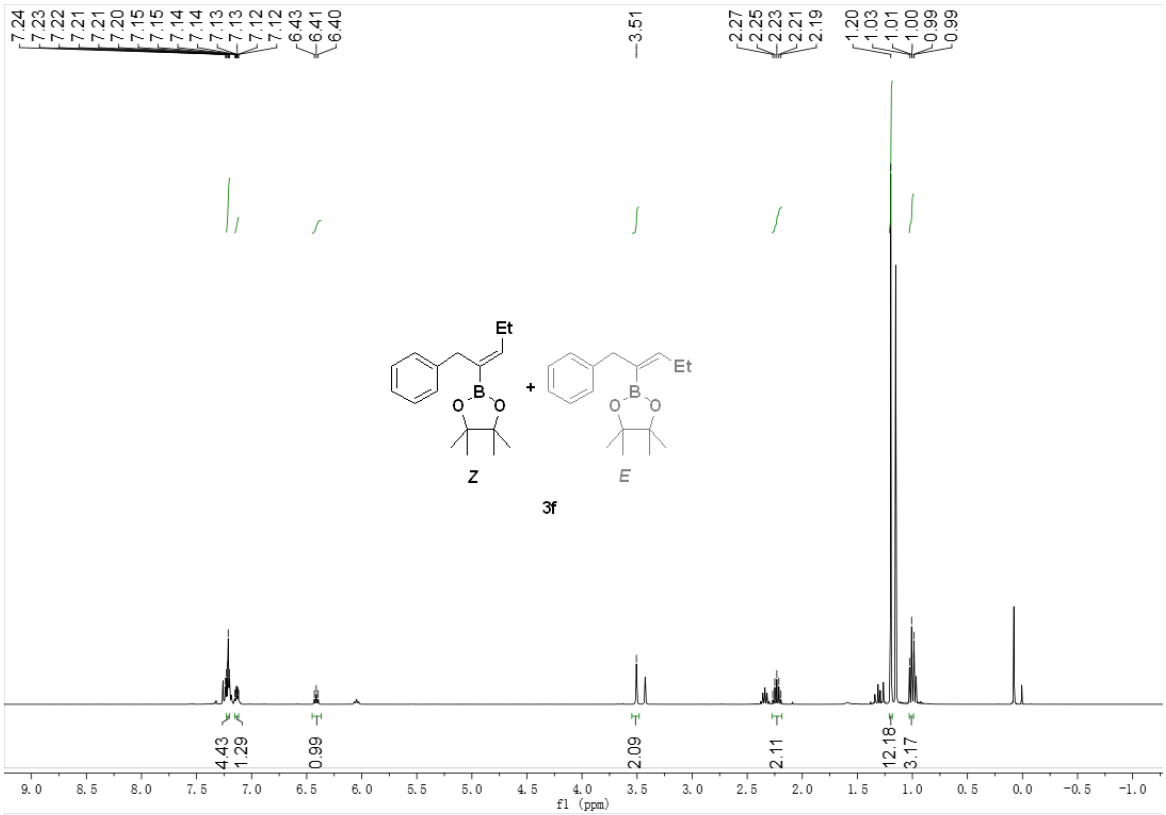
140.0
138.7
130.1
129.7
128.8
127.1
127.1
127.0
83.7
41.2
24.8
Ph
B
O
O
3e
f1 (ppm)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7.23
7.22
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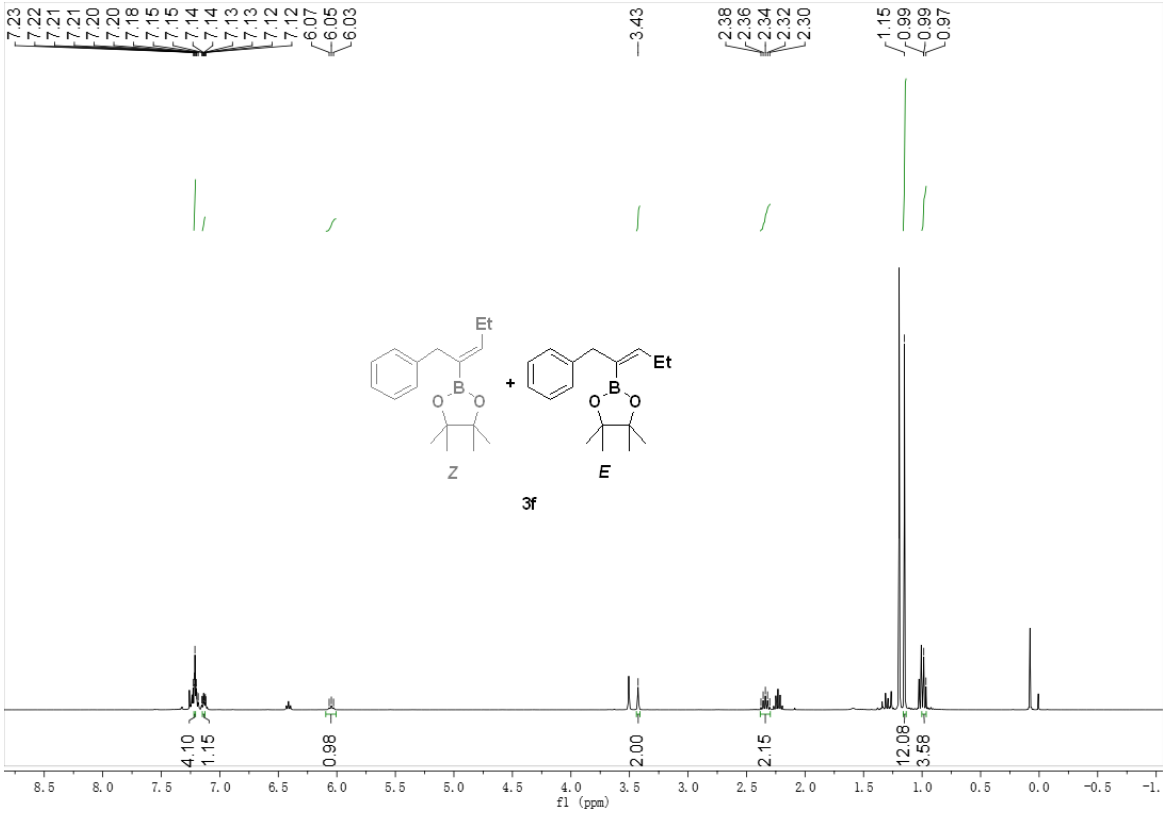
7.14
7.14
7.13
7.13
7.12
7.12
6.43
6.41
6.40
3.51
2.27
2.25
2.23
2.21
2.19
1.20
1.03
1.01
1.00
0.99
0.99
Et
B
O
O
+
Et
B
O
O
Z
E
3f
4.43
1.29
0.99
2.09
2.11
12.18
3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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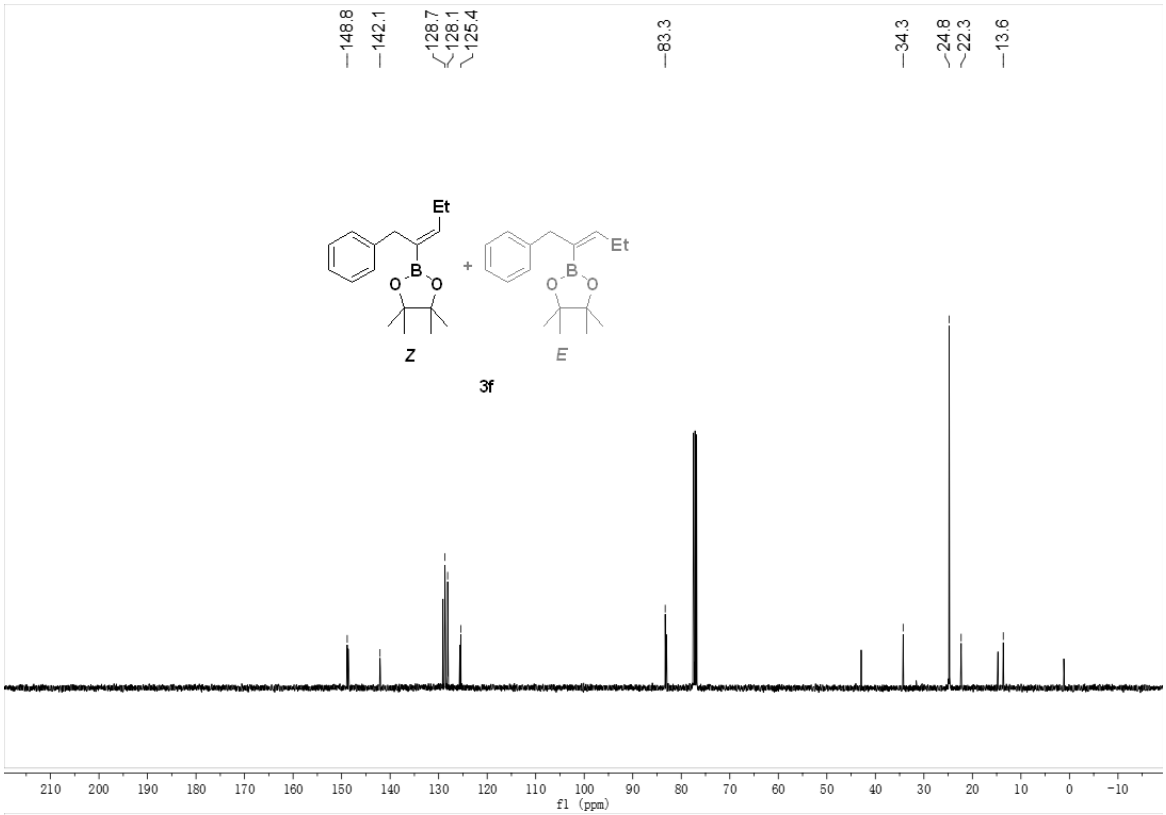
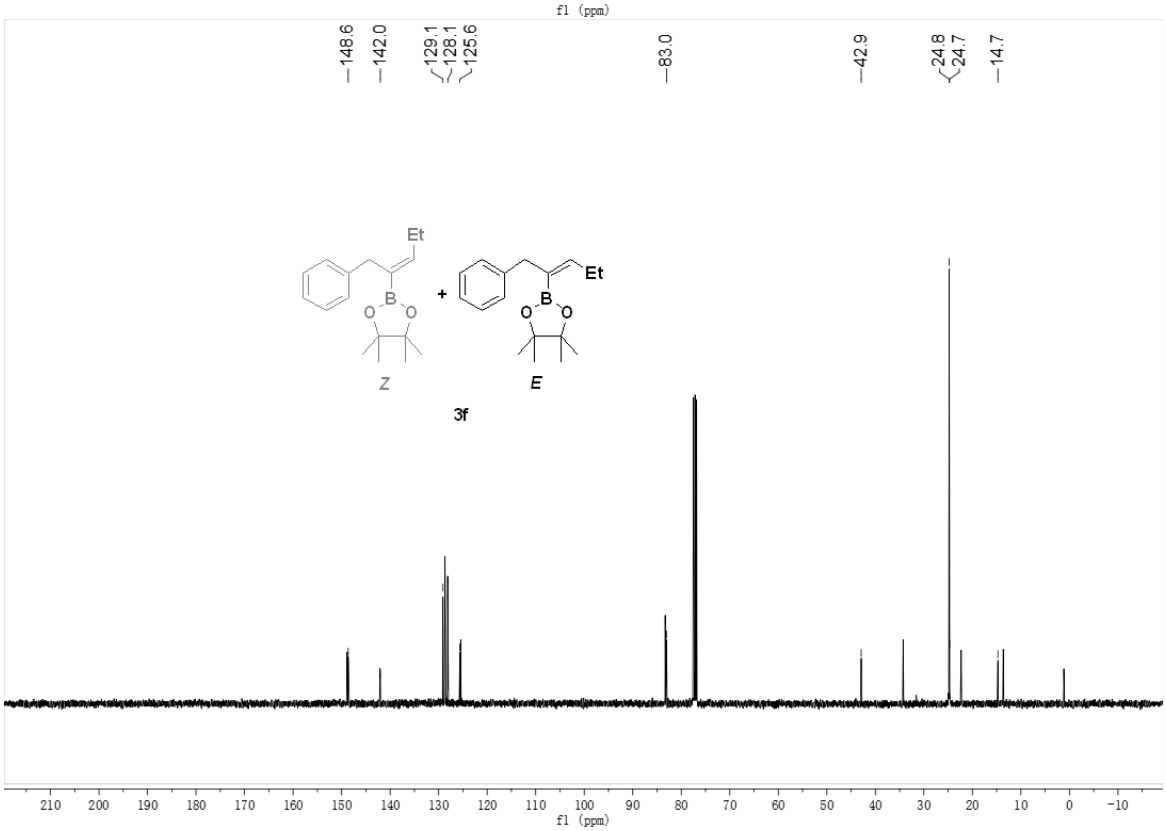
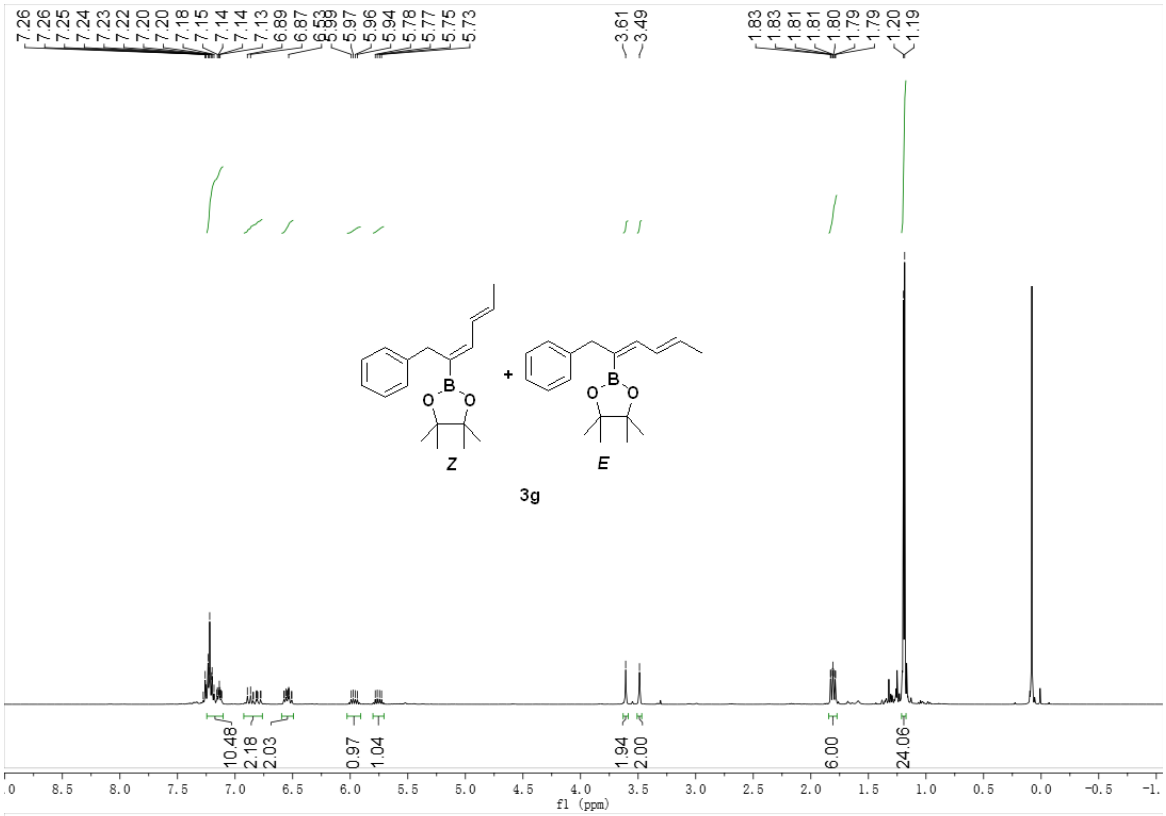
7.22
7.21
7.21
7.20
7.20
7.18
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
6.07
6.05
6.03
3.43
2.38
2.36
2.34
2.32
2.30
1.15
0.99
0.99
0.97
Et
B
O
O
+
Et
B
O
O
Z
E
3f
4.10
1.15
0.98
2.00
2.15
12.08
3.58
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


148.8
142.1
128.7
128.1
125.4
83.3
34.3
24.8
22.3
13.6
Et
Et
Z
E
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


148.6
142.0
129.1
128.1
125.6
83.0
42.9
24.8
24.7
14.7
Et
Et
Z
E
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.26
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7.24
7.23
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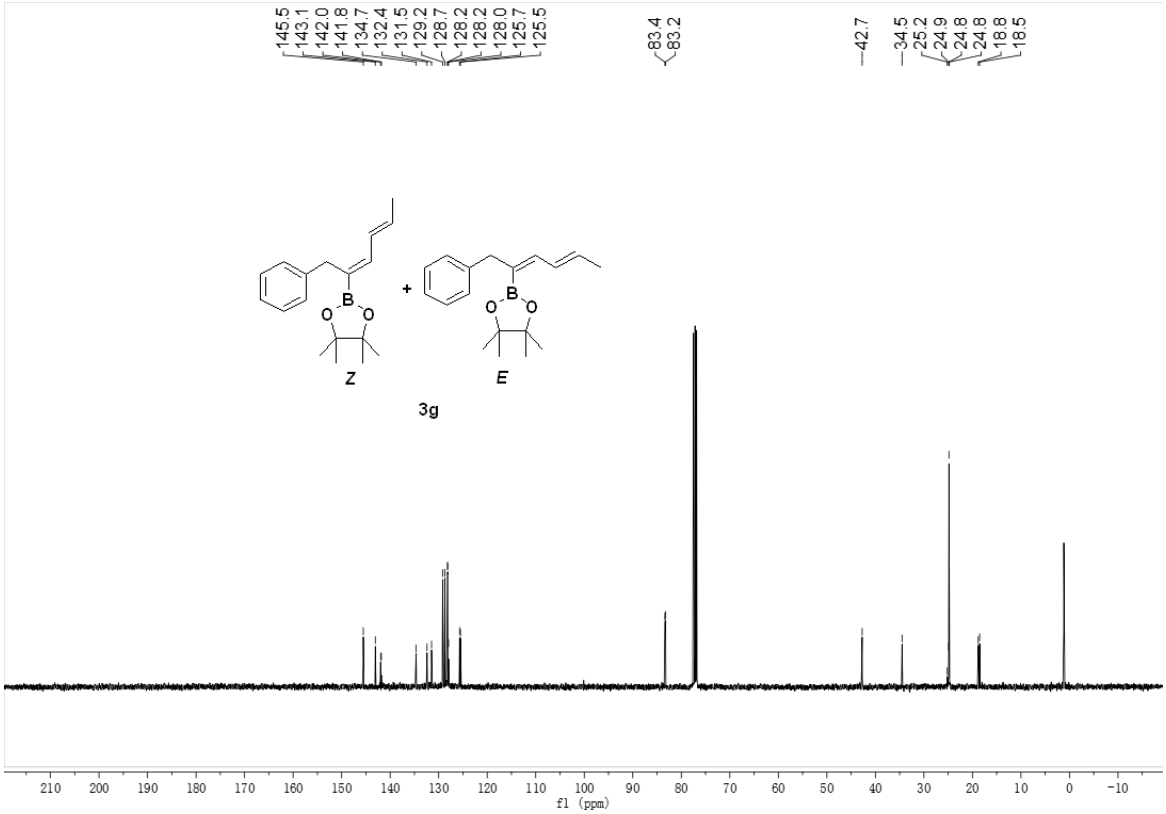
7.20
7.18
7.15
7.14
7.14
7.13
6.89
6.87
6.53
5.98
5.97
5.96
5.94
5.78
5.77
5.75
5.73
3.61
3.49
1.83
1.83
1.81
1.81
1.80
1.79
1.79
1.20
1.19
Z
E
3g
10.48
2.18
2.03
0.97
1.04
1.94
2.00
6.00
24.06
f1 (ppm)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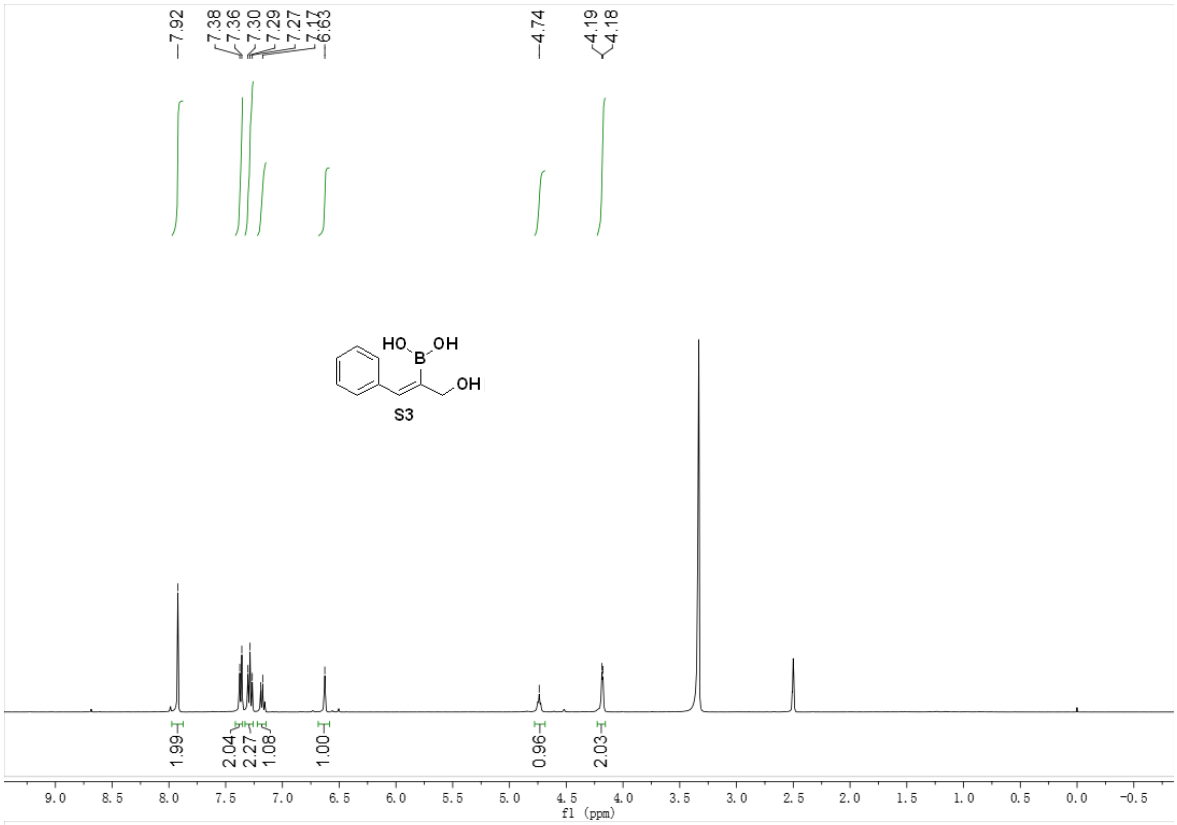
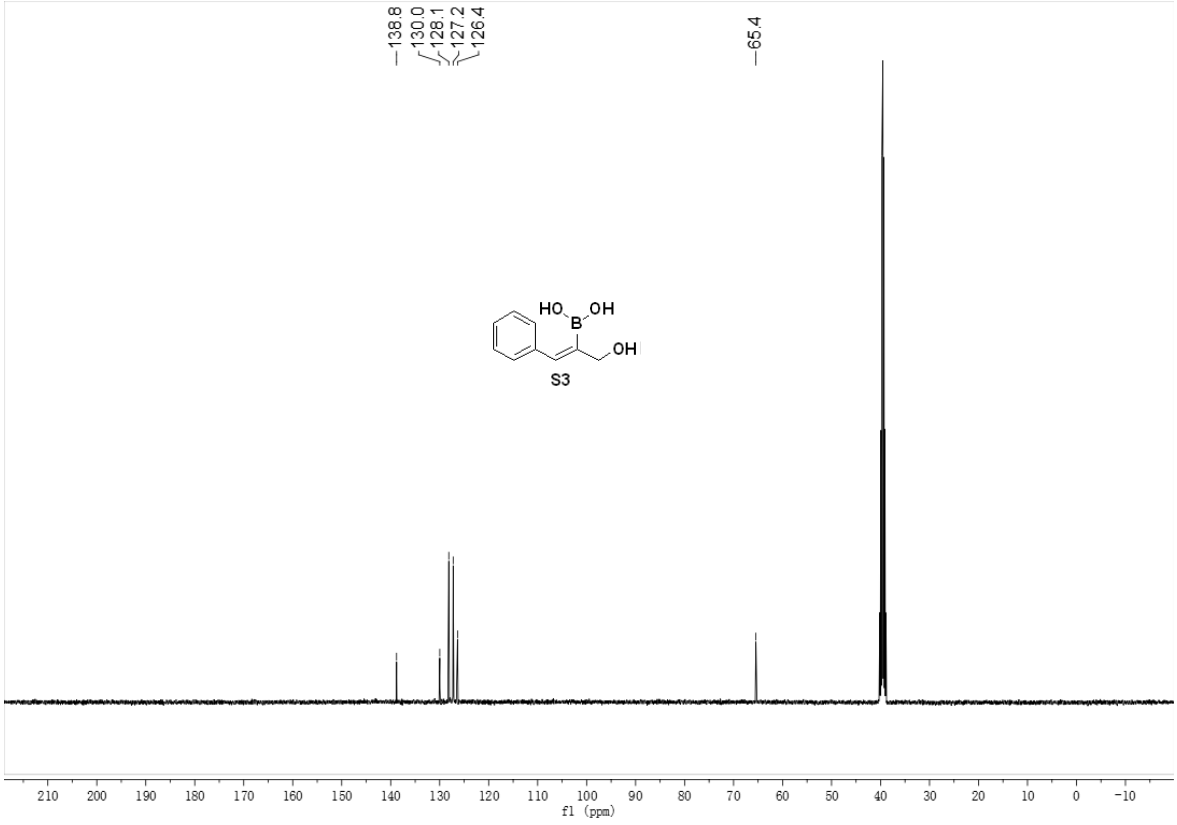
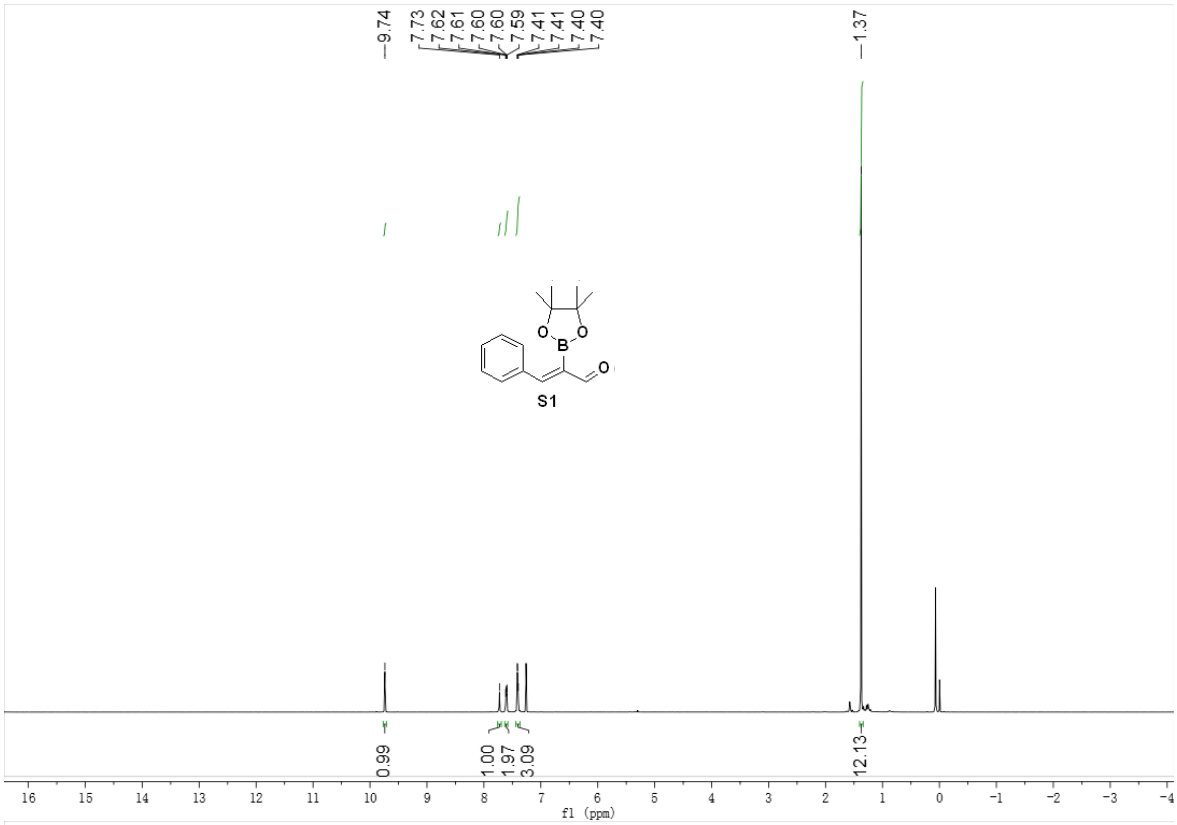
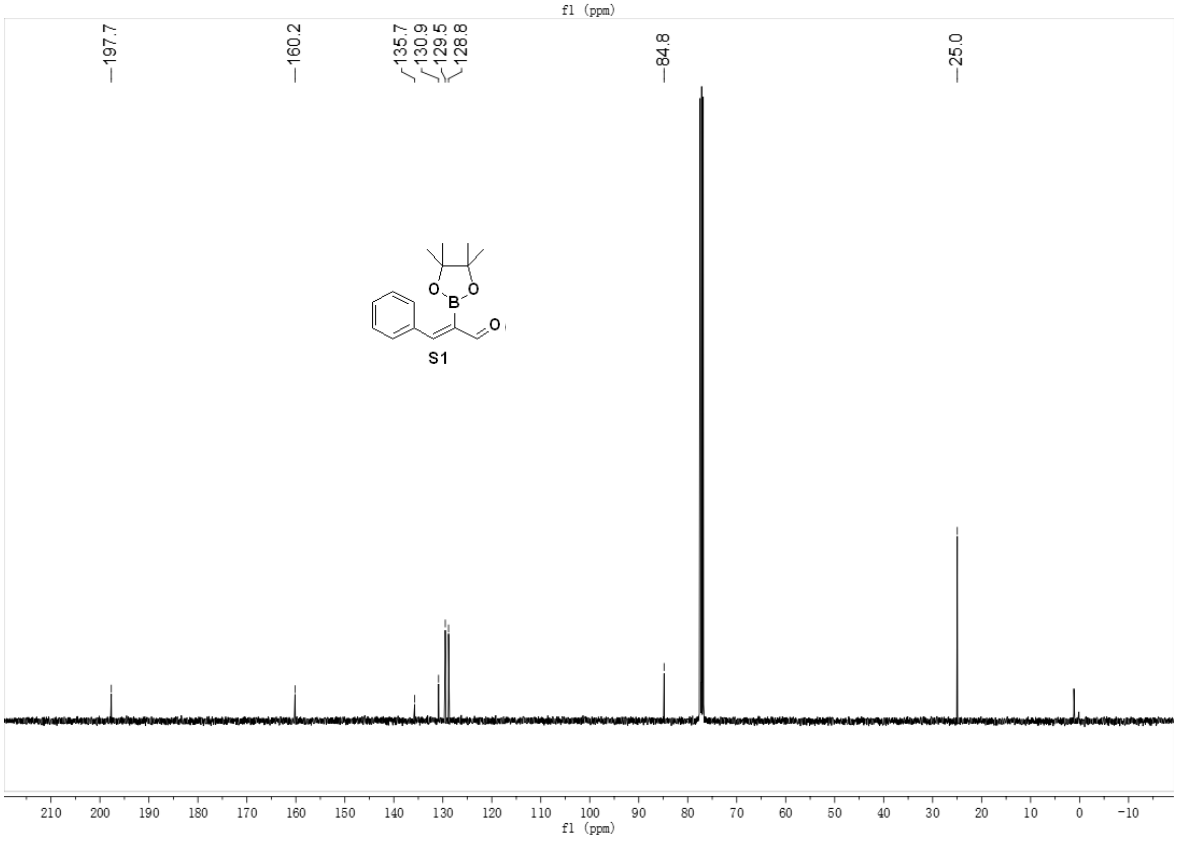
143.1
142.0
141.8
134.7
132.4
131.5
129.2
128.7
128.2
128.2
128.0
125.7
125.5
83.4
83.2
42.7
34.5
25.2
24.9
24.8
24.8
18.8
18.5
Z
E
3g
f1 (ppm)


7.92
7.38
7.36
7.30
7.29
7.27
7.17
6.63
4.74
4.19
4.18
HO
B
OH
OH
S3
1.99
2.04
2.27
1.08
1.00
0.96
2.03
f1 (ppm)


138.8
130.0
128.1
127.2
126.4
65.4
HO
B
OH
OH
S3
f1 (ppm)


9.74
7.73
7.62
7.61
7.60
7.60
7.59
7.41
7.41
7.40
7.40
1.37
S1
0.99
1.00
1.97
3.09
12.13
f1 (ppm)


197.7
160.2
135.7
130.9
129.5
128.8
84.8
25.0
S1
f1 (ppm)