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Supporting Information for

Transition-metal Free Synthesis of 1,1-benzyldiboronate Esters with a Fully Substituted Benzylic Center via Diborylation of Lithiated Carbamates

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1. General

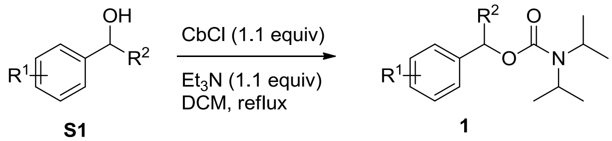
All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using standard Schlenk techniques .

THF, Et_2O, CH_2Cl_2 were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were purchased and used as received. *N,N*-Diisopropyl carbamic acid ester **1a**[1] and (*S*)-**1a**[2] were synthesized according to the literature procedures and the characterization data are consistent with those reported in the literature.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Zhongke-Niujin 400 spectrometer at ambient temperature. IR spectra were recorded on a Thermo Fisher Nicolet 6700 FT-IR Analyzer. HPLC data were collected on a Shimadzu LC-20AT sepectrometer. Optical Rotation was recorded on a Perkin Elmer 341 polarimerter. High-resolution mass spectroscopy data were obtained on a Agilent 6530 spectrometer at Suzhou Research Institute of LICP and a Thermo Fisher Scientific LTQ FT Ultra at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

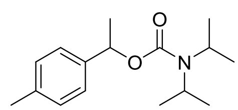
[1] Alonso, E.; Guijarro, D.; Martínez, P.; Ramón, D. J.; Yus M. *Tetrahedron* **1999**, *55*, 11027.
[2] Watson, C. G.; Aggarwal, V. K. *Org. Lett.* **2013**, *15*, 1346.

2. General procedure for the synthesis of N,N-Diisopropyl carbamic acid ester



Carbamates **1** was synthesized according to literature procedure.[2] To a 25-mL flask charged with **S1** (5 mmol), , *N*,*N*-diisopropylchloroformamide (900.1 mg, 5.5 mmol) and CH_2Cl_2 (5 mL) was added Et_3N (568.0 μL, 5.5 mmol) in one portion. The mixture was stirred at 50 ˚C for 12 h. After cooling to room temperature, the reaction mixture was quenched with water. The mixture was then extracted with ethyl acetate (10 mL x 3). The combined organic phase was then washed with brine (20 mL×1), and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel to give corresponding carbamate **1**.

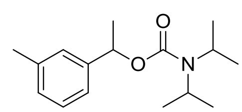
1b: 1.19 g, 90% yield.



1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.81 (d, *J* = 6.2 Hz, 1H), 4.10 (br, 1H), 3.73 (br, 1H), 2.34 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.20 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.4, 136.5, 128.6, 125.6, 72.1, 45.7 (br), 44.8 (br.), 22.3, 21.0 (br), 20.6, 20.3 (br); IR (KBr film) 2971, 2930, 2873, 1690, 1436, 1368, 1285, 1157, 1132, 1066, 1047, 815 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{26}NO_2$ ($[M+H]^+$) 264.1885, found 264.1886.

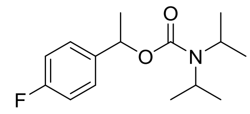
1c: 1.11 g, 85% yield.



1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 1H), 7.16 (s, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 5.80 (d, *J* = 6.3 Hz, 1H), 4.11 (br, 1H), 3.77 (br, 1H), 2.35 (s, 3H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.21 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 142.8, 137.1, 127.8, 127.6, 126.2, 122.4, 72.2, 45.4 (br), 44.8 (br), 22.3, 20.9, 20.8 (br), 20.1 (br); IR (KBr film) 3026, 2971, 2930, 2872, 1690, 1436, 1368, 1285, 1157, 1132, 1066, 1047, 783, 769 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{26}NO_2$ ($[M+H]^+$) 264.1885, found 264.1885.

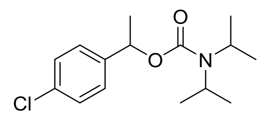
1d: 1.22 g, 91% yield.



1d

[1]H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.4 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.81 (q, *J* = 6.8 Hz, 1H), 4.10 (br. s, 1H), 3.75 (br. s, 1H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.20 (s, 12H); [13]C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244 Hz), 154.6, 138.3 (d, *J* = 3 Hz), 127.5 (d, *J* = 8 Hz), 114.9 (d, *J* = 21 Hz), 71.8, 46.1 (br), 45.0 (br), 22.4, 21.3 (br), 20.5 (br); IR (KBr film) 2972, 2934, 2875, 1691, 1513, 1436, 1369, 1286, 1223, 1157, 1133, 1067, 1047, 835 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}FNO_2Na$ ($[M+Na]^+$) 290.1635, found 290.1635.

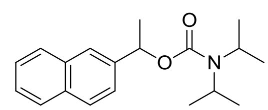
1e: 1.23 g, 87% yield.



1e

[1]H NMR (400 MHz, $CDCl_3$) δ 7.28-7.34 (m, 4H), 5.81 (d, *J* = 5.5 Hz, 1H), 4.10 (br, 1H), 3.76 (br, 1H), 1.53 (d, *J* = 6.6 Hz, 3H), 1.21-1.19 (br, 12H); [13]C NMR (100 MHz, $CDCl_3$) δ 154.7, 141.2, 133.0, 128.4, 127.3, 71.8, 46.3 (br), 45.1 (br), 22.5, 21.4 (br), 20.5 (br); IR (KBr film) 3028, 2972, 2933, 2876, 1691, 1494, 1438, 1370, 1288, 1219, 1157, 1133, 1069, 1047, 827 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{22}ClNO_2Na$ ($[M+Na]^+$) 306.1339, found 306.1338.

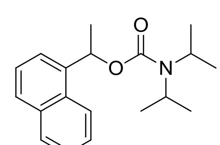
1f: 1.35g, 90% yield.



1f

[1]H NMR (400 MHz, $CDCl_3$) δ 7.82-7.85 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.48-7.44 (m, 2H), 6.03 (q, *J* = 6.1 Hz, 1H), 4.11 (br, 1H), 3.81 (br, 1H), 1.65 (d, *J* = 6.4 Hz, 3H), 1.23 (s, 12H); [13]C NMR (101 MHz, $CDCl_3$) δ 155.0, 140.1, 133.2, 132.8, 128.1, 128.0, 127.6, 126.0, 126.0, 124.8, 124.2, 72.7, 46.3 (br), 45.2 (br), 22.6, 21.3 (br), 20.6 (br); IR (KBr film) 2999, 2969, 2927, 1691, 1437, 1369, 1289, 1157, 1129, 1048, 818, 766 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{25}NO_2Na$ ($[M+Na]^+$) 322.1885, found 322.1899.

1g: 1.42 g, 95% yield.

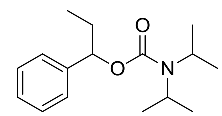


1g

[1]H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.45-7.52 (m, 3H), 6.64 (d, *J* = 6.4 Hz, 1H), 4.01 (br, 1H), 3.92 (br, 1H),1.71 (d, *J* = 6.3 Hz, 3H), 1.21-1.22 (m, 12H); [13]C NMR (101 MHz, $CDCl_3$) δ 154.6, 138.3, 133.5, 130.1, 128.5, 127.7, 125.8, 125.2, 125.0, 123.1,

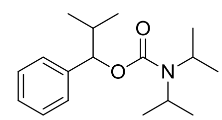
122.6, 69.3, 45.9 (br), 45.2 (br), 21.9, 21.1 (br), 20.5 (br.); IR (KBr film) 3050, 2970, 2933, 2874, 1689, 1433, 1369, 1292, 1157, 1133, 1046, 798, 777 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{26}NO_2$ ($[M+H]^+$) 322.1885, found 322.1898.

1h: 1.19 g, 90% yield.


1h

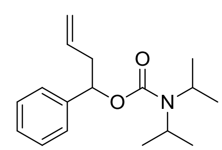
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.32 (m, 4H), 7.28-7.24 (m, 1H), 5.63 (t, *J* = 6.7 Hz, 1H), 4.05 (s, 1H), 3.83 (s, 1H), 2.02-1.89 (m, 1H), 1.89-1.76 (m, 1H), 1.22 (s, 12H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.4, 128.1, 127.2, 126.4, 77.7, 46.1 (br), 45.2 (br), 29.7, 21.4 (br), 20.5 (br), 9.9; IR (KBr film) 2970, 2935, 2877, 1692, 1437, 1368, 1316, 1303, 1286, 1216, 1158, 1133, 1050, 768, 699 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{26}NO_2$ ($[M+H]^+$) 264.1885, found 264.1881.

1i: 1.19 g, 86% yield.


1i

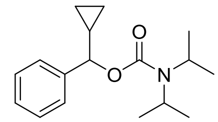
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.31 (m, 5H), 5.50 (d, *J* = 6.6 Hz, 1H), 3.95 (br, 2H), 2.07-2.16 (m, 1H), 1.22 (s, 12H), 0.97-0.99 (m, 3H), 0.83-0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 140.3, 127.8, 127.0, 126.7, 81.1, 45.8 (br), 45.3 (br), 33.7, 21.3 (br.), 20.4 (br.), 18.7, 18.3; IR (KBr film) 3032, 2967, 2931, 2874, 1692, 1432, 1367, 1313, 1299, 1287, 1157, 1132, 1049, 768, 700 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}NO_2Na$ ($[M+H]^+$) 278.2042, found 278.2043.

1j: 1.10g, 80% yield.


1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.33 (m, 4H), 7.28-7.26 (d, *J* = 4.3 Hz, 1H), 5.77 (dd, *J* = 18.5, 11.4 Hz, 2H), 5.00-5.10 (m, 2H), 3.94-4.18 (m, 1H), 3.64-3.93 (m, 1H), 2.72-2.65 (1H), 2.62-2.55 (1H), 1.21 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.9, 133.6, 128.1, 127.4, 126.3, 117.6, 75.6, 46.2 (br), 45.1 (br), 41.2, 21.3 (br), 20.4 (br); IR (KBr film) 2999, 2969, 2927, 1691, 1436, 1368, 1289, 1153, 1129, 1048, 767, 702 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}NO_2Na$ ($[M+Na]^+$) 298.1885, found 298.1881.

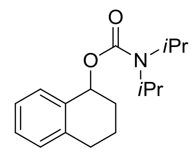
1k: 1.10 g, 80% yield.



1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.40 (m, 4H), 7.25-7.29 (m, 1H), 5.19 (d, *J* = 8.6 Hz, 1H), 4.09 (br, 1H), 3.81 (br, 1H), 1.23 (s, 12H), 0.52-0.62 (m, 3H), 0.38-0.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.9, 127.7, 126.9, 126.0, 79.5, 45.5 (br), 44.8 (br), 20.9 (br), 20.1 (br), 16.5, 3.3, 2.6; IR (KBr film) 3032, 2967, 2932, 2874, 1692, 1432, 1367, 1314, 1299, 1287, 1157, 1132, 1049, 768, 700 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{26}NO_2$ ($[M+H]^+$) 276.1885, found 276.1884.

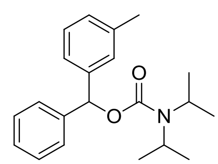
1l: 1.13 g, 82% yield.



1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.4 Hz, 1.3 Hz, 1H), 7.10-7.22 (m, 3H), 5.95 (t, *J* = 4.8 Hz, 1H), 4.14 (br, 1H), 3.68 (br, 1H), 2.83-2.88 (m, 1H), 2.71-2.78 (m, 1H), 1.81-2.06 (m, 4H), 1.19-1.21 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 137.3, 135.3, 129.1, 128.6, 127.3, 125.6, 69.8, 46.2 (br), 44.8 (br), 29.3, 28.9, 21.2 (br), 20.5 (br), 19.0; IR (KBr film) 3028, 2969, 2928, 2870, 2855, 1681, 1670, 1440, 1368, 1286, 1148, 1133, 1064, 1047, 766, 735 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}NO_2Na$ ($[M+Na]^+$) 298.1885, found 298.1885.

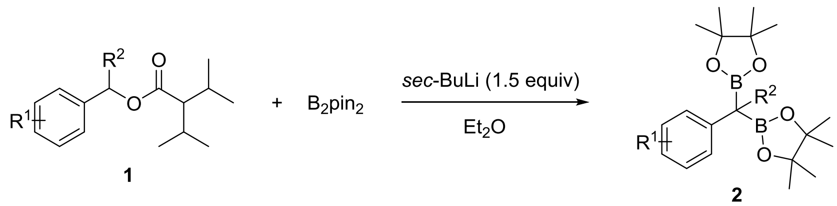
1m: 1.43. g, 88% yield.



1m

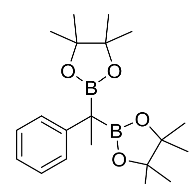
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.44 (m, 4H), 7.24-7.34 (m, 4H), 7.24, 7.14 (d, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 4.07 (br, 2H), 2.39 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 141.4, 141.1, 137.9, 128.3, 128.2(2), 128.2(1), 127.7, 127.4, 127.0, 124.0, 77.7, 46.4 (br), 45.6 (br), 21.5 (br), 21.4, 20.6 (br.); IR (KBr film) 3063, 3030, 2997, 2969, 2932, 2873, 1697, 1432, 1368, 1288, 1152, 1132, 1047, 783, 766, 768 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}NO_2Na$ ($[M+Na]^+$) 348.2042, found 348.2037.

3. General procedures for the synthesis of Bis(boronates)



To a 25-mL fire-dried flask charged with **1** (0.5 mmol) and anhydrous Et_2O (2 mL) was added *sec*-BuLi (577 µL, 1.3 M in cyclohexane/hexane, 0.75 mmol,) in a dropwise fashion within 5 minutes at –78 °C. The reaction mixture was stirred for 0.5 h at –78 °C. A solution of B_2pin_2 (0.75 mL, 1 M in anhydrous diethyl ether, 0.75 mmol) was added and the resulting mixture was stirred for 0.5 h at –78 °C. Then the reaction mixture was allowed to stired at room temperature for additional 0.5 h. Aquesous HCl (1%, 10 mL) was added to quench the reaction. The reaction mixture mixture was then extracted with ethyl acetate (10 mL x 3). The combined organic phases were washed with saturated brine (20 mL×1) and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE/EtOAc (petroleum ether : EtOAc = 80:1) as the eluent to give corresponding 1,1-diboron **2**.

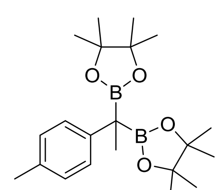
2a, [CAS: 428819-24-3]: 164.7 mg, 92% yield.



2a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.20-7.27 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 1.45 (s, 3H), 1.22 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 128.2, 127.8, 124.3, 83.3, 24.6, 18.6 (B-benzylic carbon signal not observed); The characterization data are consistent with those reported in the literature.[3]

2b, [CAS: 1609628-47-8]161.9 mg, 87% yield.

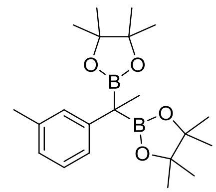


2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 2.28 (s, 3H), 1.59 (s, 2H), 1.43 (s, 3H), 1.22 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 133.4, 128.5, 127.9, 83.1, 24.5, 20.8, 18.6 (B-benzylic carbon signal not observed); The characterization data are consistent with those reported in the literature.[3]

[3] Wommack, A. J.; Kingsbury, J. S. *Tetrahedron Lett.* **2014**, *55*, 3163.

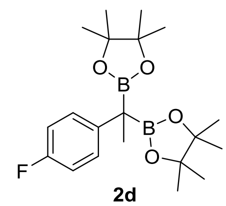
2c: 161.9 mg, 87% yield.



2c

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.08-7.16 (m, 3H), 6.90 (d, *J* = 5.0 Hz, 1H), 2.30 (s, 3H), 1.59 (s, 3H), 1.43 (s, 3H), 1.23 (s, 24H); ^{13}C NMR (100 MHz, CD_2Cl_3) δ 145.0, 137.0, 128.7, 127.6, 125.6, 125.1, 83.2, 25.6, 24.5, 21.6, 18.8 (B-benzylic carbon signal not observed); IR (ATR) 3042, 2980, 2932, 2870, 1489, 1463, 1371, 1331, 1309, 1267, 1140, 1081, 967, 860, 848 cm^{-1}; HRMS (DART) calcd. for $C_{21}H_{35}{}^{10}B_2O_4$ ($[M+H]^+$) 371.2789, found 371.2792.

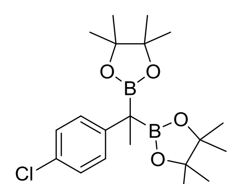
2d: 118.6 mg, 63% yield.



2d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.9 Hz, 2H), 6.92 (t, *J* = 8.8 Hz, 2H), 1.43 (s, 3H), 1.22 (d, *J* = 2.0 Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 242 Hz), 140.4, 129.3 (d, *J* = 8 Hz), 114.4 (d, *J* = 21 Hz), 83.3, 29.6, 24.5, 18.4 (B-benzylic carbon signal not observed); IR (ATR) 3048, 2982, 2933, 2875, 1508, 1460, 1373, 1310, 1271, 1223, 1143, 1087, 968, 853 cm^{-1}; HRMS (DART) calcd. for $C_{20}H_{32}{}^{10}B_2FO_4$ ($[M+H]^+$) 375.2538, found 375.2539.

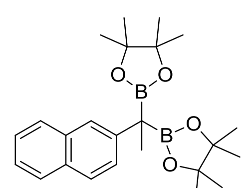
2e, [CAS 1609628-49-0]: 113.6 mg, 58% yield.



2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.29 (m, 2H), 7.19-7.21 (m, 2H), 1.43 (s, 3H), 1.21 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 129.9, 129.3, 127.7, 83.3, 24.5, 17.8 (B-benzylic carbon signal not observed); The characterization data are consistent with those reported in the literature.[3]

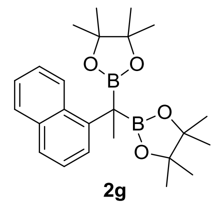
2f: 136.8 mg, 67% yield.



2f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.78 (m, 4H), 7.57 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.32-7.43 (m, 2H), 1.56 (s, 3H), 1.23 (s, 12H), 1.23 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) 142.7, 133.7, 131.3, 128.7, 127.6, 127.2, 126.6, 125.2, 124.5, 124.4, 83.3, 24.6, 17.8 (B-benzylic carbon signal not observed); IR (KBr film) 3066, 2979, 2926, 2870, 1468, 1448, 1381, 1372, 1340, 1317, 1268, 1214, 1141, 1081, 967, 860, 821, 757 cm^{-1}; HRMS (DART) calcd for $C_{24}H_{35}{}^{10}B_2O_4$ ($[M+H]^+$) 407.2789, found 407.2790.

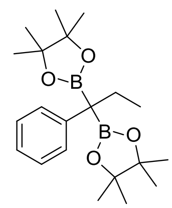
2g: 153.0 mg, 75% yield.



2g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-8.03 (m, 1H), 7.79 (dd, *J* = 5.8, 3.5 Hz, 1H), 7.62-7.64 (m, 1H), 7.32-7.43 (m, 4H), 1.61 (s, 3H), 1.28 (2, 12H), 1.25 (2, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 134.4, 132.5, 128.7, 126.1, 126.0, 125.8, 125.7, 124.7, 124.2, 83.4, 24.8, 24.6, 20.3 (B-benzylic carbon signal not observed); IR (ATR) 3041, 2985, 2931, 2872, 1464, 1448, 1380, 1372, 1340, 1319, 1272, 1217, 1143, 1080, 965, 851, 802, 781 cm^{-1}; HRMS (DART) calcd. for $C_{24}H_{35}{}^{10}B_2O_4$ ($[M+H]^+$) 407.2789, found 407.2788.

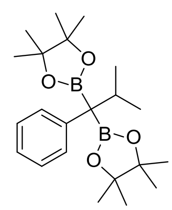
2h [CAS: 1609628-50-3]: 145.0 mg, 78% yield.



2h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.36 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 1.97 (q, *J* = 7.3 Hz, 2H), 1.26-1.23 (m, 24H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 130.0, 127.8, 124.6, 83.2, 27.1, 24.8, 24.6, 12.1 (B-benzylic carbon signal not observed); The characterization data are consistent with those reported in the literature.[3]

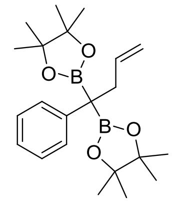
2i: 123.6 mg, 64% yield.



2i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.26 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.12 (t, *J* = 6.8 Hz, 1H), 2.44-2.51 (m, 1H), 1.27 (s, 24H), 0.84 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 132.5, 127.1, 124.9, 83.2, 31.5, 24.8, 24.7, 21.3 (B-benzylic carbon signal not observed); IR (KBr film) 3053, 2978, 2929, 2872, 1495, 1469, 1379, 1371, 1347, 1317, 1255, 1137, 1095, 976, 854, 700 cm^{-1}; HRMS (DART) calcd for $C_{22}H_{36}{}^{10}B_2O_4$ ($[M+H]^+$) 385.2945, found 385.2947.

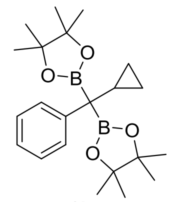
2j: 128.7 mg, 67% yield.



2j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.38 (m, 2H), 7.18-7.25 (m, 2H), 7.04-7.12 (m, 1H), 5.65-5.76 (m, 1H), 4.80-4.92 (m, 2H), 2.72 (d, *J* = 6.9 Hz, 2H), 1.24 (s, 12H), 1.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.8, 129.8, 127.7, 124.6, 115.4, 83.3, 37.9, 24.6, 24.5 (B-benzylic carbon signal not observed); IR (KBr film) 3048, 2982, 2933, 2875, 1508, 1460, 1373, 1310, 1271, 1223, 1143, 1087, 968, 853 cm^{-1}; HRMS (DART) calcd for $C_{22}H_{35}{}^{10}B_2O_4$ ($[M+H]^+$) 383.2789, found 383.2790.

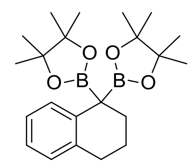
2k: 96.0 mg, 50% yield.



2k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.41 (m, 2H), 7.20-7.24 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 1.23 (s, 24H), 0.44-0.50 (m, 2H), 0.30-0.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.8, 129.8, 127.7, 124.6, 115.4, 83.3, 37.9, 24.6, 24.5 (B-benzylic carbon signal not observed); IR (KBr film) 3057, 2977, 2927, 2856, 1494, 1461, 1371, 1315, 1266, 1136, 967, 852, 700 cm^{-1}; HRMS (DART) calcd for $C_{22}H_{35}{}^{10}B_2O_4$ ($[M+H]^+$) 383.2789, found 383.2792.

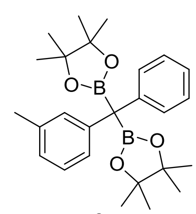
2l [CAS: 428819-23-2]: 101.7 mg, 53% yield.



2l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.9 Hz, 1H), 7.02-7.09 (m, 1H), 6.98-6.99 (m, 2H), 2.74 (t, *J* = 6.2 Hz, 2H), 1.97-2.08 (m, 2H), 1.68-1.78 (m, 2H), 1.20 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.5, 135.7, 130.5, 129.0, 124.7, 123.8, 83.2, 30.3, 27.8, 24.7, 24.5, 23.1 (B-benzylic carbon signal not observed); The characterization data are consistent with those reported in the literature.[3]

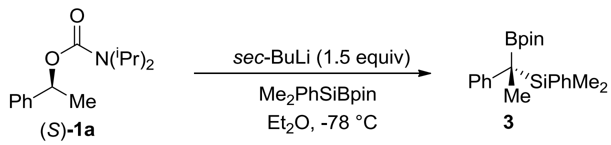
2m: 80.4 mg, 37% yield.



2m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.26 (m, 4H), 7.06-7.13 (m, 4H), 6.93 (t, *J* = 4.1 Hz, 1H), 2.26 (s, 3H), 1.23 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.2, 137.2, 131.4, 130.3, 127.9, 127.8, 127.7, 125.8, 124.7, 83.6, 24.6, 24.5, 21.6 (B-benzylic carbon signal not observed); IR (KBr film) 3059, 2978, 2928, 2868, 1495, 1371, 1344, 1312, 1266, 1215, 1165, 1138, 975, 854, 699 cm^{-1}; HRMS (DART) calcd for $C_{26}H_{37}{}^{10}B_2O_4$ ($[M+H]^+$) 433.2945, found 433.2950.

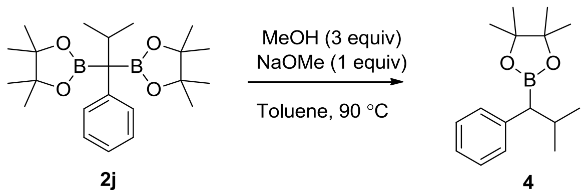
5. Silaboration of Carbamte (S)-1a



To a 25-mL fire-dried flask charged with (*S*)-**1a** (125 mg, 0.5 mmol, 96% ee) and anhydrous Et_2O (2 mL) was added *sec*-BuLi (577 μL, 1.3 M in cyclohexane/hexane, 0.75 mmol,) in a dropwise fashion within 5 minutes at –78 °C. The reaction mixture was stirred for 0.5 h at –78 °C. A solution of $Me_2PhSiBpin$ (0.75 mL, 1 M in anhydrous diethyl ether, 0.75 mmol) was added and the resulting mixture was stirred for 0.5 h at –78 ℃. Then the reaction mixture was allowed to stired at room temperature for additional 0.5 h. Aquesous HCl (1%, 10 mL) was added to quench the reaction. The reaction mixture mixture was then extracted with ethyl acetate (10 mL x 3). The combined organic phases were washed with saturated brine (20 mL ×1) and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using PE as the eluent to give corresponding 1,1-siylboronate **3** (173 mg, 95%). $[\alpha]_D^{20}$ = -45 (c = 0.06, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.32 (m, 9H), 7.06 (t, *J* = 6.0 Hz, 1H), 1.41 (s, 3H), 1.21 (s, 6H), 1.18 (s, 6H), 0.32 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 137.1, 134.9, 128.7, 127.4, 127.3, 126.9, 123.6, 83.0, 25.0, 24.7, 16.5, 4.3, 4.2 (B-benzylic carbon signal not observed); IR (KBr film) 3068, 2967, 2872, 1598, 1396, 1467, 1354, 1302, 1268, 1144, 965 cm^{-1}; HRMS (DART) calcd for $C_{22}H_{35}N^{10}BO_2Si$ ($[M+NH_4]^+$) 383.2561, found 383.2559. The enantiopurity of **3** was determined by HPLC analysis using a chiral stationary phase of the alcohol obtained by oxidation with $NaBO_3$•$4H_2O$ in THF/H_2O (1: 1).[4] Daicel Chiralpak IC column (25 cm), 5% *i*PrOH in hexane, 1.0 mL/min., 254 nm, t_R = 4.05 (major), 4.33 (minor), 92% ee.

[4] Meng, F.; Jang, H.; Hoveyda, A. H. *Chem. - Eur. J.* **2013**, *19*, 3204.

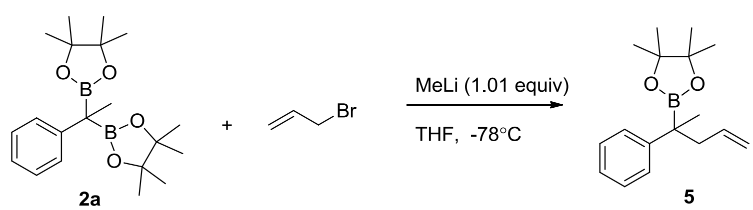
5. Protodeboronation of 2i



Compound **4** [CAS: 1257661-32-7] was synthesized according to a known procedure.[5] To a dried 10 mL reaction tube was added **2i** (101.0 mg, 0.26 mmol), NaOMe (14.2 mg, 0.26 mmol), MeOH (32.0 μL, 0.79 mmol) and toluene (2.0 mL). The mixture was stirred at 90 °C for 12 h. The reaction was quenched by HCl aquerous (1%, 5 mL) and extracted with EtOAc (3 × 10 ml). The combined organic phase was washed with saturated brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel using PE/EtOAc (40:1) as the eluent to give **4** as a colorless oil (50.4 mg, yield: 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.26 (m, 4H), 7.10-7.14 (m, 1H), 2.06-2.17 (m, 1H), 1.96 (d, *J* = 10.4 Hz, 1H), 1.20 (s, 6H), 1.17 (s, 6H),1.03 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 129.0, 128.1, 125.1, 83.1, 31.0, 29.7, 24.6, 24.5, 23.1, 22.0 (B-benzylic carbon signal not observed).

6. Deborylation/alkylation to access tertiary boronic esters 4

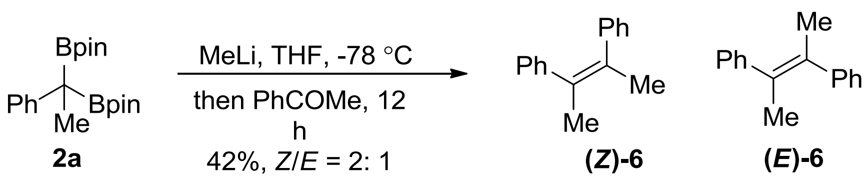


Compound 4 [CAS: 1257661-33-8] was synthesized according to a known procedure.[3] To a 25 mL flask charged with **2a** (358 mg, 1 mmol) and THF (10 ml) was added MeLi (0.64 mL of a 1.6 M Et_2O solution, 1.01 mmol) at –78 °C. After stirring at –78 °C for 10 min., allyl bromide was added dropwise and the resulting mixture was then allowed to stir at –78 °C for addtioonal 1 h, then r. t. for 12 h. Aqueous HCl (10%, 10 mL) was added to quench the reaction and the mixture was extracted with EtOAc (25 mL X 3). The combined organic phase was washed with brine anddried over Na_2SO_4. After

[5] Li, H.; Wang, L.; Zhang, Y.; Wang, J. B. *Angew. Chem. Int. Ed*. **2012**, *51*, 2943.

removal of the solvent, the residue was purified by flash chromatography on silica gel using PE/EtOAc (100: 1) as the eluent to give **5** as a colorless oil (240.6 mg, yield: 89%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.25 (m, 4H), 7.04-7.08 (m, 1H), 5.56-5.71 (m, 1H), 4.89-4.97 (m, 2H), 2.55 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.34 (dd, *J* = 13.6, 7.1 Hz, 1H), 1.13 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 136.3, 128.0, 126.7, 125.1, 116.8, 83.4, 43.8, 24.6, 21.3 (B-benzylic carbon signal not observed).

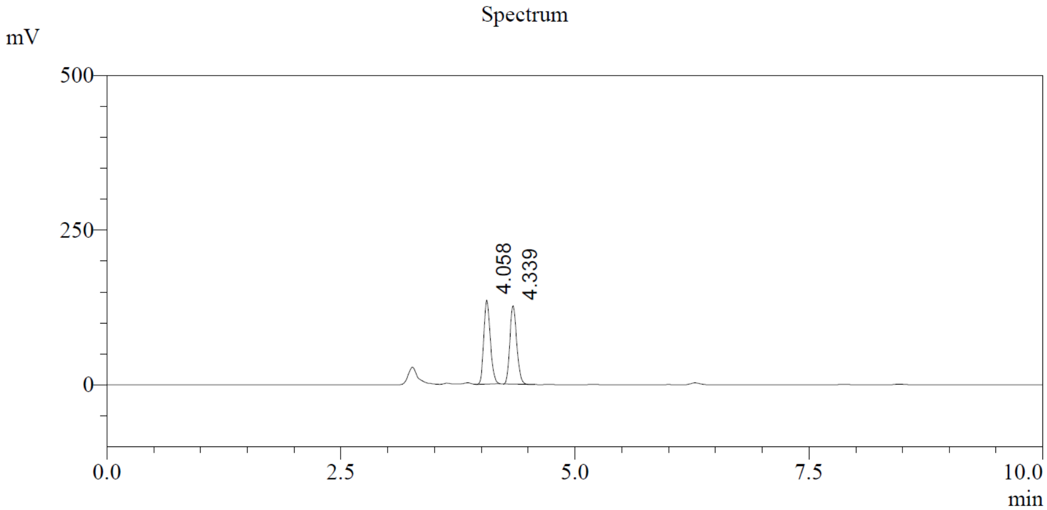
7. Boron-Wittig Reaction of 2a with Acetophenone



To a 25-mL flask charged with **2a** (358 mg, 1 mmol) and anhydrous THF (10 ml), was added MeLi (0.64 mL of a 1.6 M Et_2O solution, 1.01 mmol) at –78 ℃. After stirring at –78 ℃ for 10 min., acetophenone (121 mg, 1.01 mmol) was added dropwise. The resulting mixture was then allowed to stir at –78 ℃ for addtional 1 h, then r. t. for 12 h. Aqueous HCl (10%, 10 mL) was added to quench the reaction and the mixture was extracted with DCM (10 mL × 3). The combined organic phases were washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by flash chromatography on silica gel using PE as the eluent to give the corresponding stilbene **6 as** a mixture of *Z* and *E* isomers (*Z*/*E* = 2:1, 43.1 mg, 42% yield). the characterization data are consistent with literature reported.[6]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.5 Hz, 1H), 7.22-7.30 (m, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.1 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 2.16 (–Z) (s, 3H), 1.88 (–E) (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.6 (–Z), 144.4 (–E), 133.0 (–E), 132.9 (–Z), 129.1 (–Z), 128.2 (–E), 128.1 (–E), 127.5(–Z), 126.2 (–E), 125.5 (–Z), 22.5 (–E), 21.5(–Z).

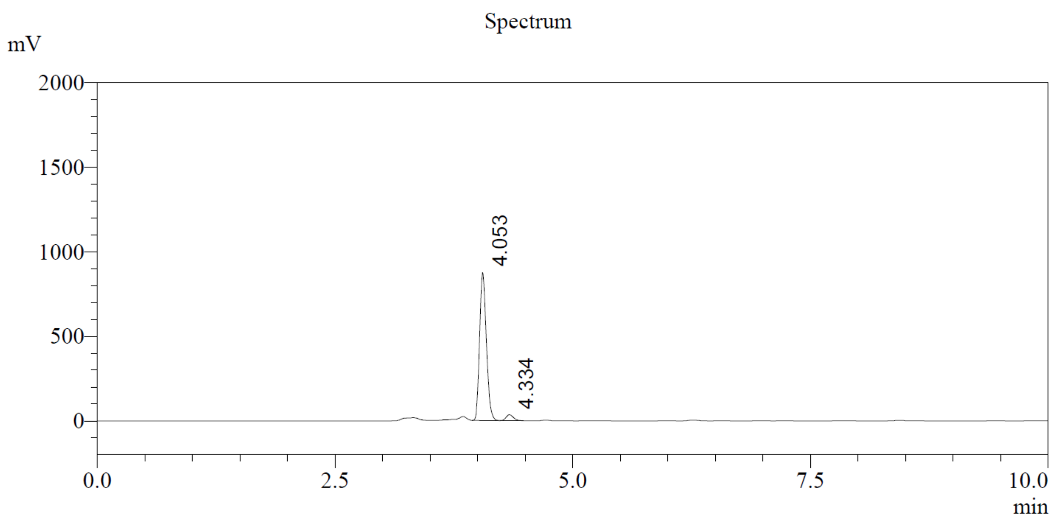
[6] Rele, S. M.; Nayak, S. K.; Chattopadhyay, S. *Tetrahedron* **2008**, *64*, 7225.

8. HPLC data of 1,1-silaboronate ester 3



???A 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	4.058	136258	661136	50.674
2	4.339	126225	643550	49.326
Total				100.000

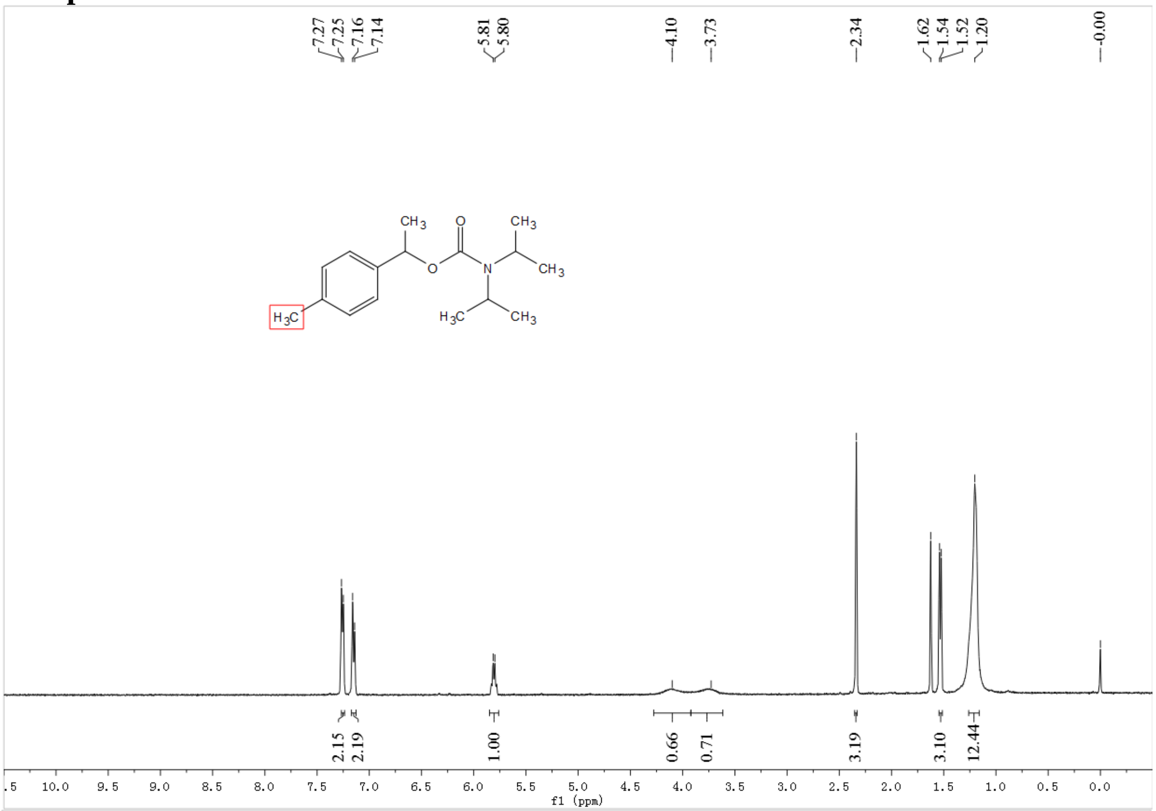


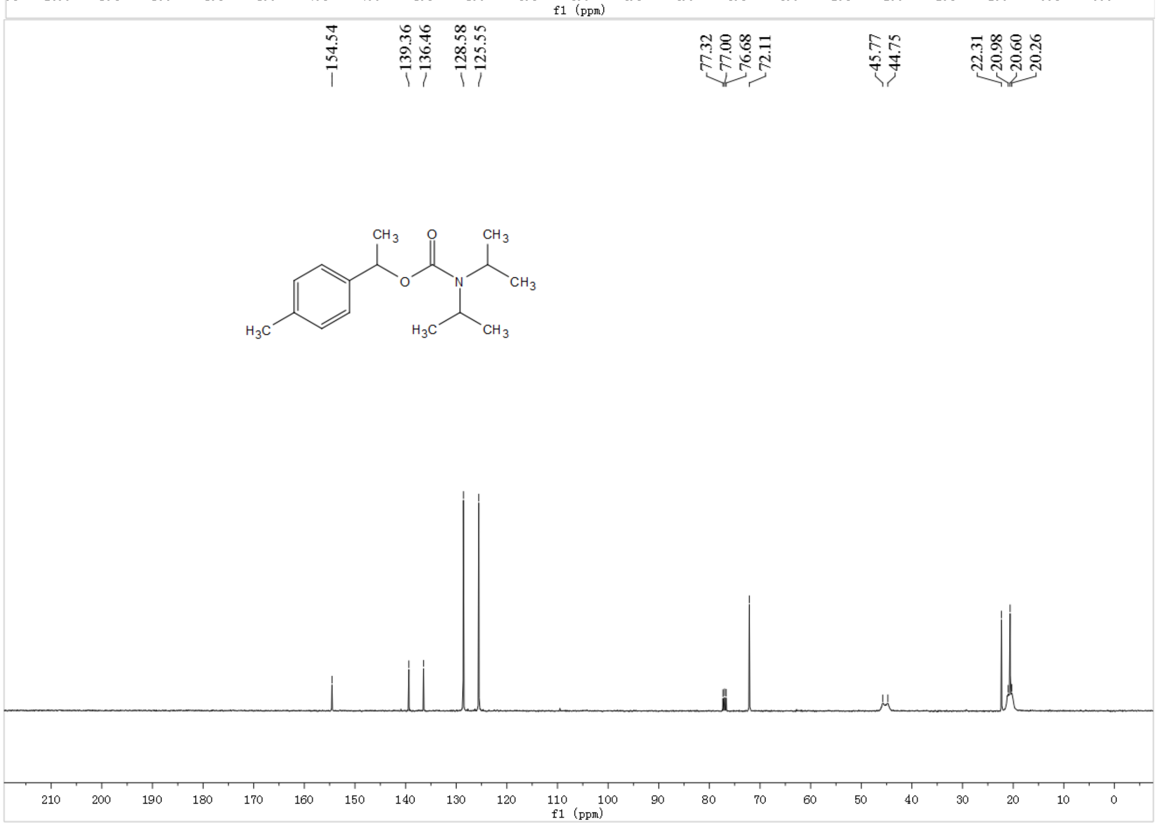
???A 254nm

Peak ID	Ret. Time	Height	Area	Area%
1	4.053	877271	4350012	95.926
2	4.334	35407	184745	4.074
Total				100.000

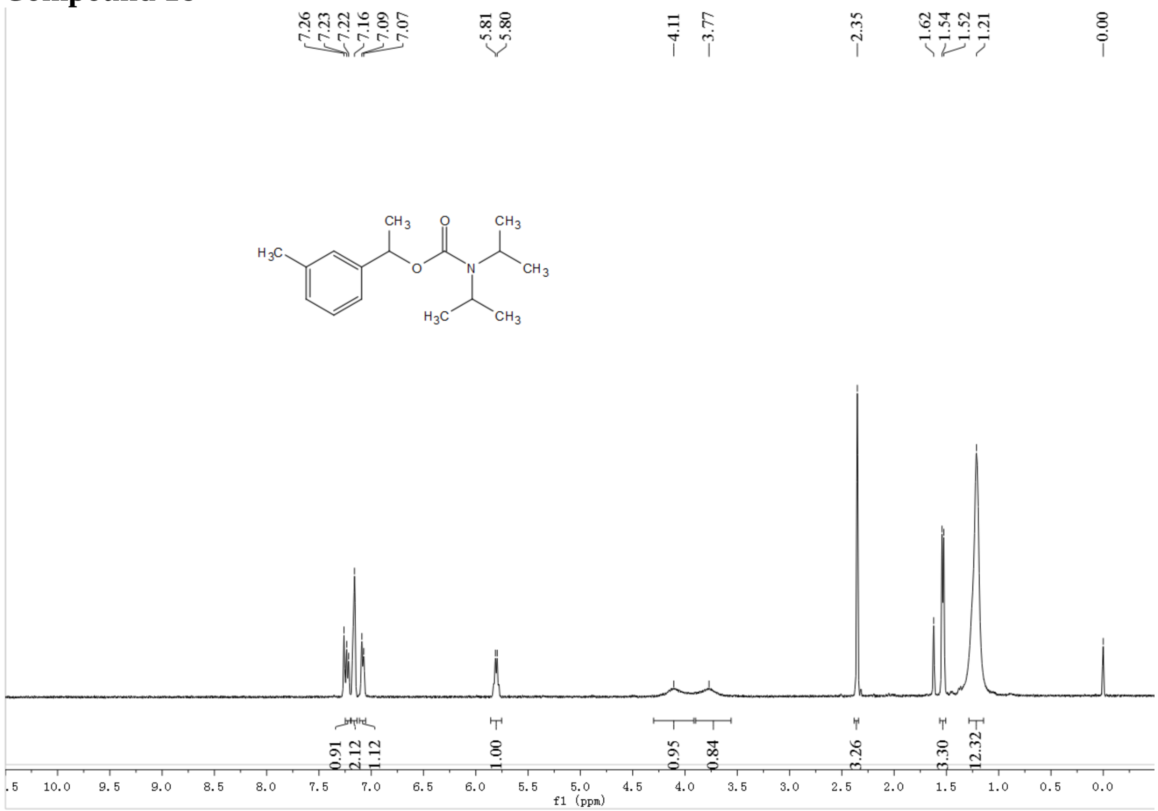
9. ^{1}H NMR and ^{13}C NMR data of Compounds 1-6

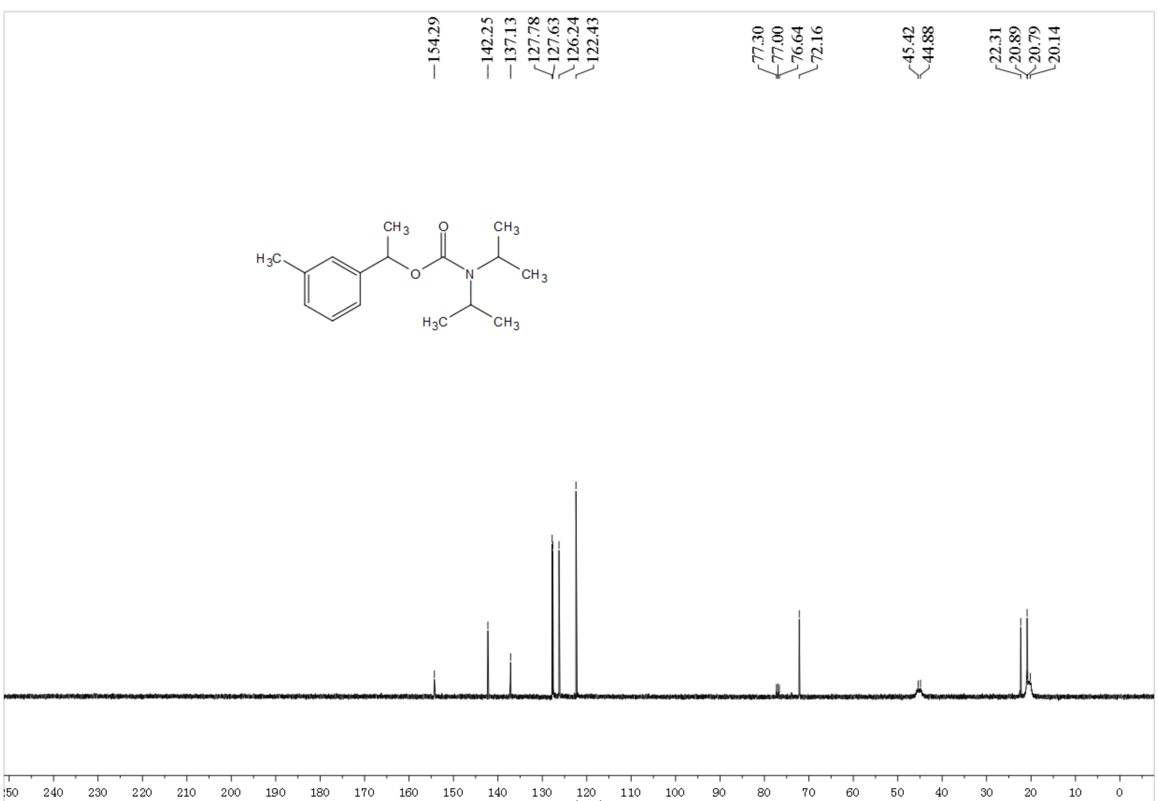
Compound 1b



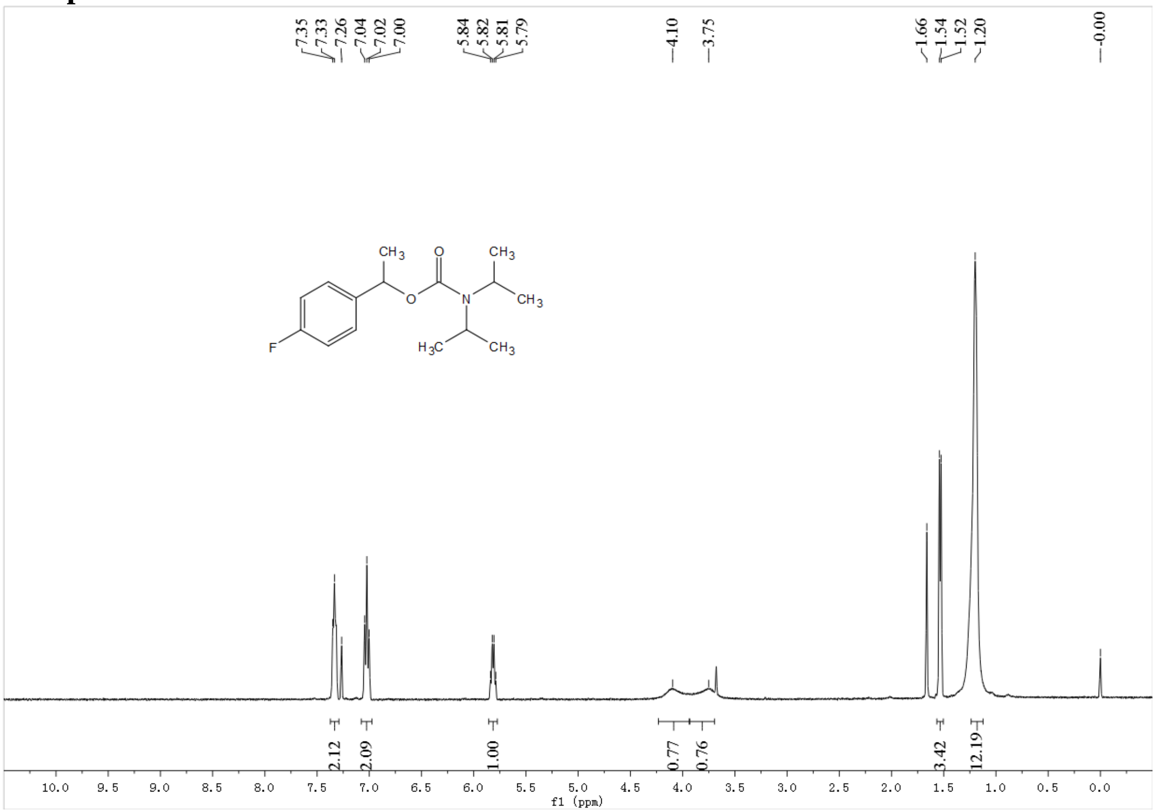


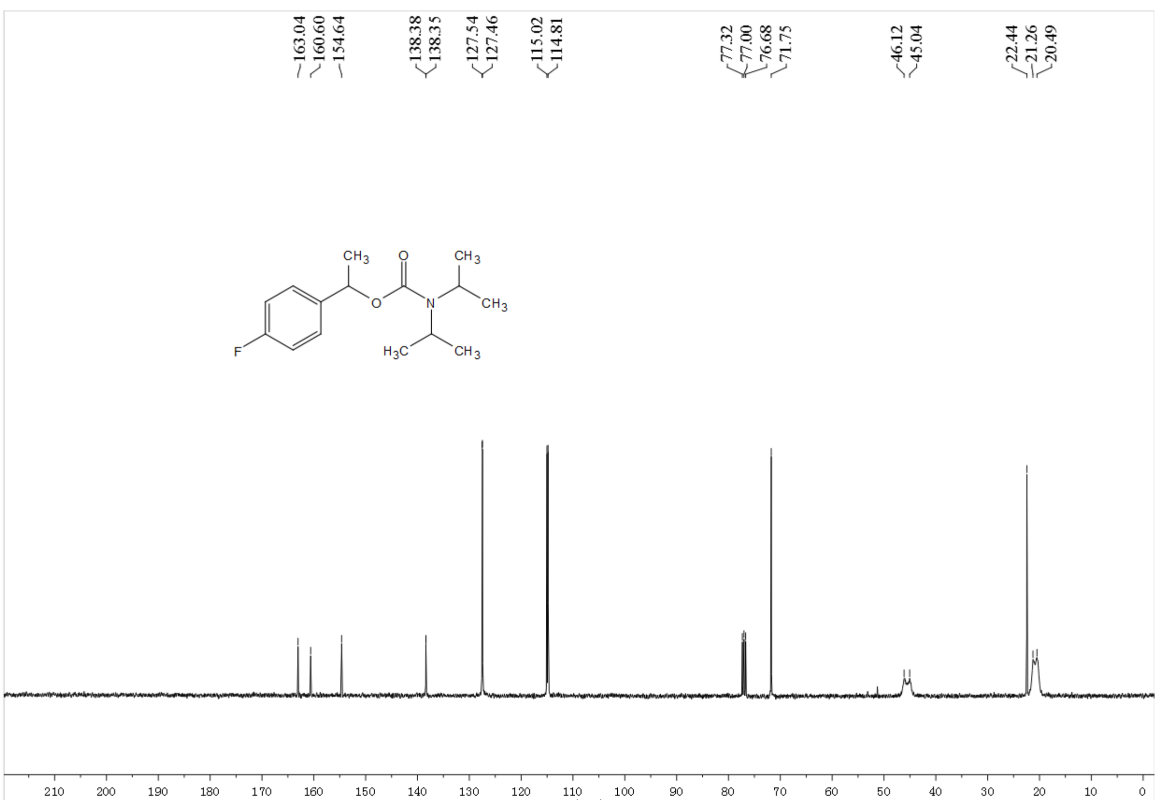
Compound 1c


7.26
7.23
7.22
7.16
7.09
7.07
5.81
5.80
4.11
3.77
2.35
1.62
1.54
1.52
1.21
0.00
0.91
2.12
1.12
1.00
0.95
0.84
3.26
3.30
12.32
f1 (ppm)

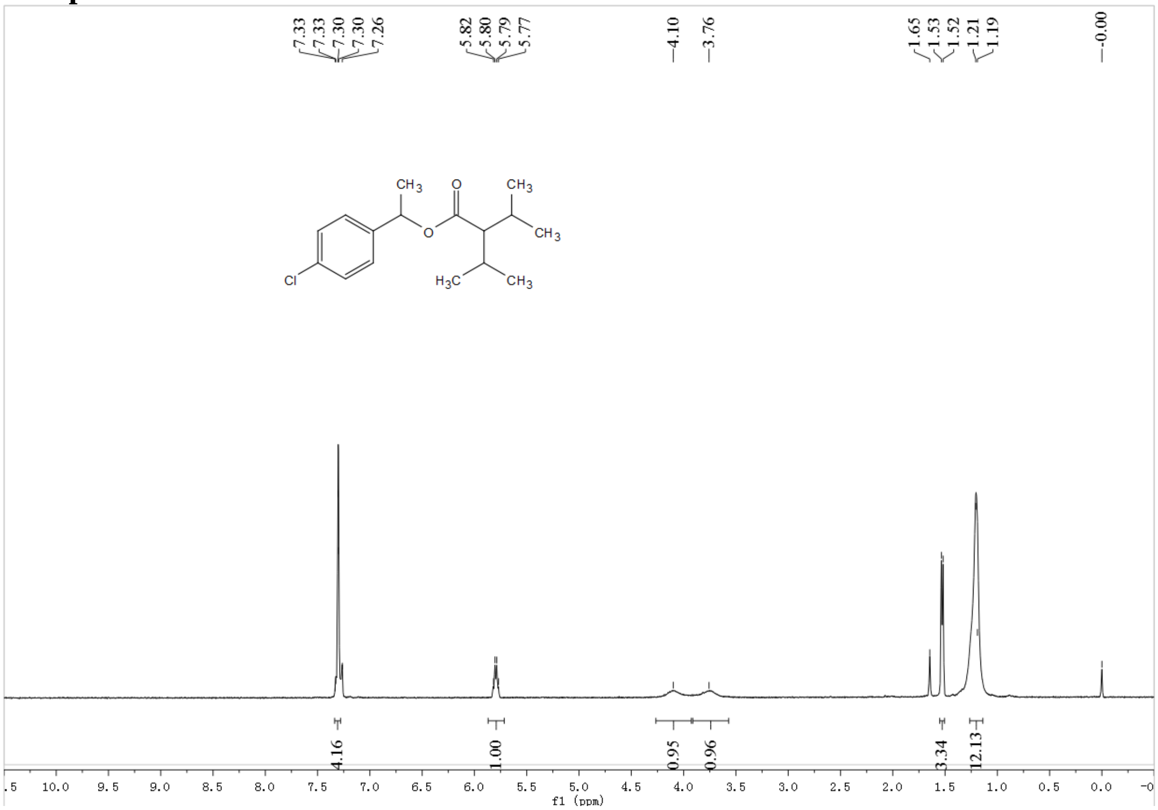

154.29
142.25
137.13
127.78
127.63
126.24
122.43
77.30
77.00
76.64
72.16
45.42
44.88
22.31
20.89
20.79
20.14
f1 (ppm)

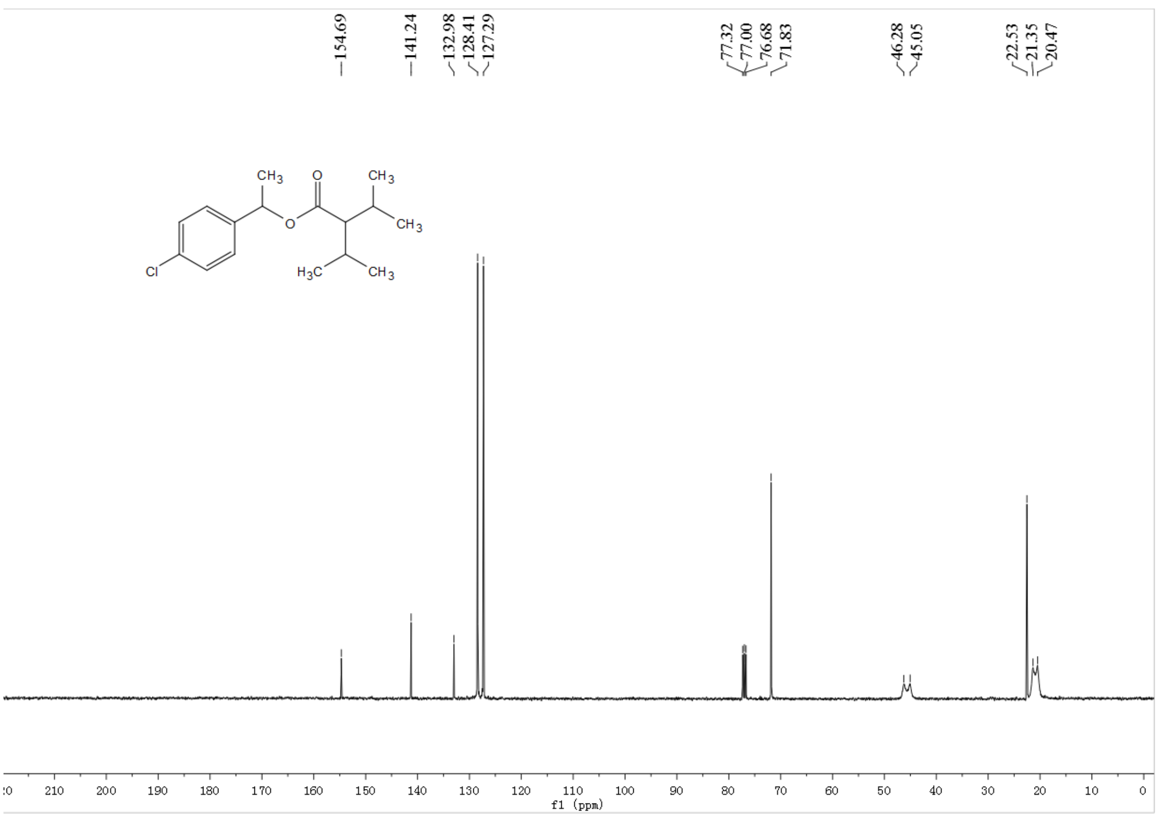
Compound 1d


7.35
7.33
7.26
7.04
7.02
7.00
5.84
5.82
5.81
5.79
4.10
3.75
1.66
1.54
1.52
1.20
-0.00
2.12
2.09
1.00
0.77
0.76
3.42
12.19
f1 (ppm)

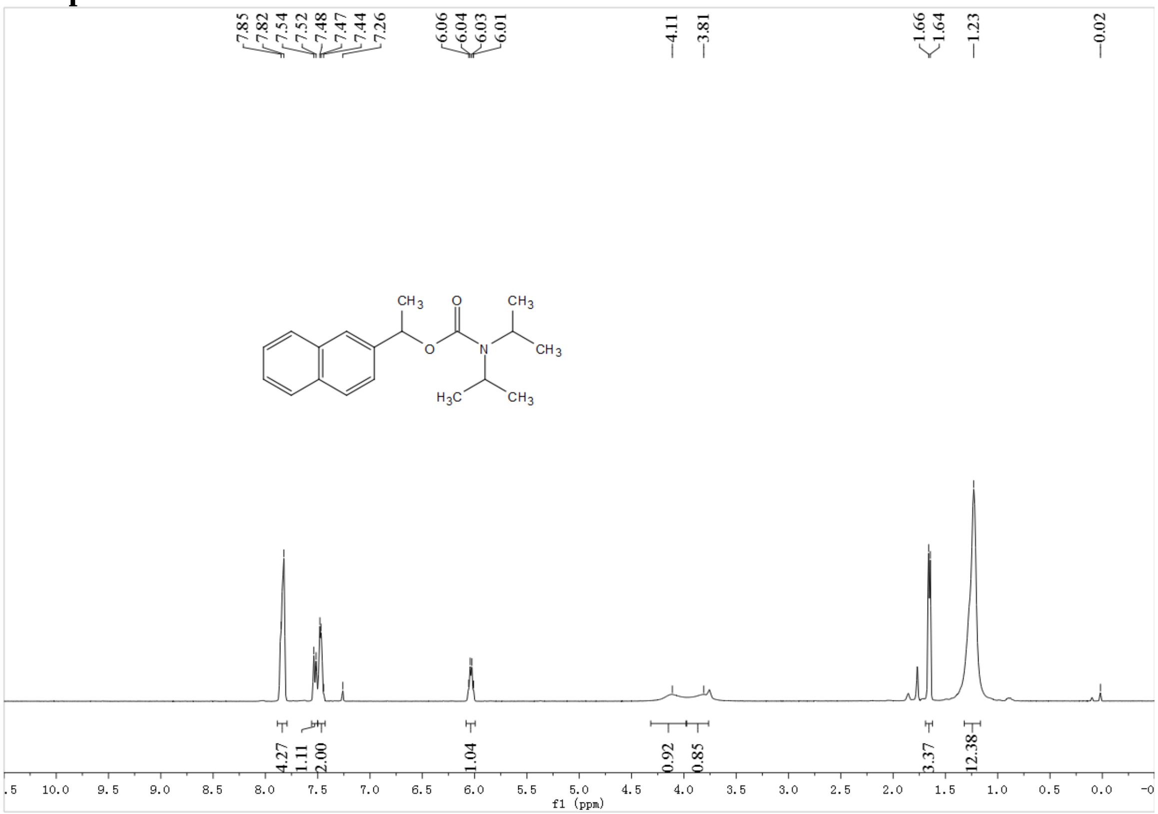

163.04
160.60
154.64
138.38
138.35
127.54
127.46
115.02
114.81
77.32
77.00
76.68
71.75
46.12
45.04
22.44
21.26
20.49
f1 (ppm)

Compoud 1e

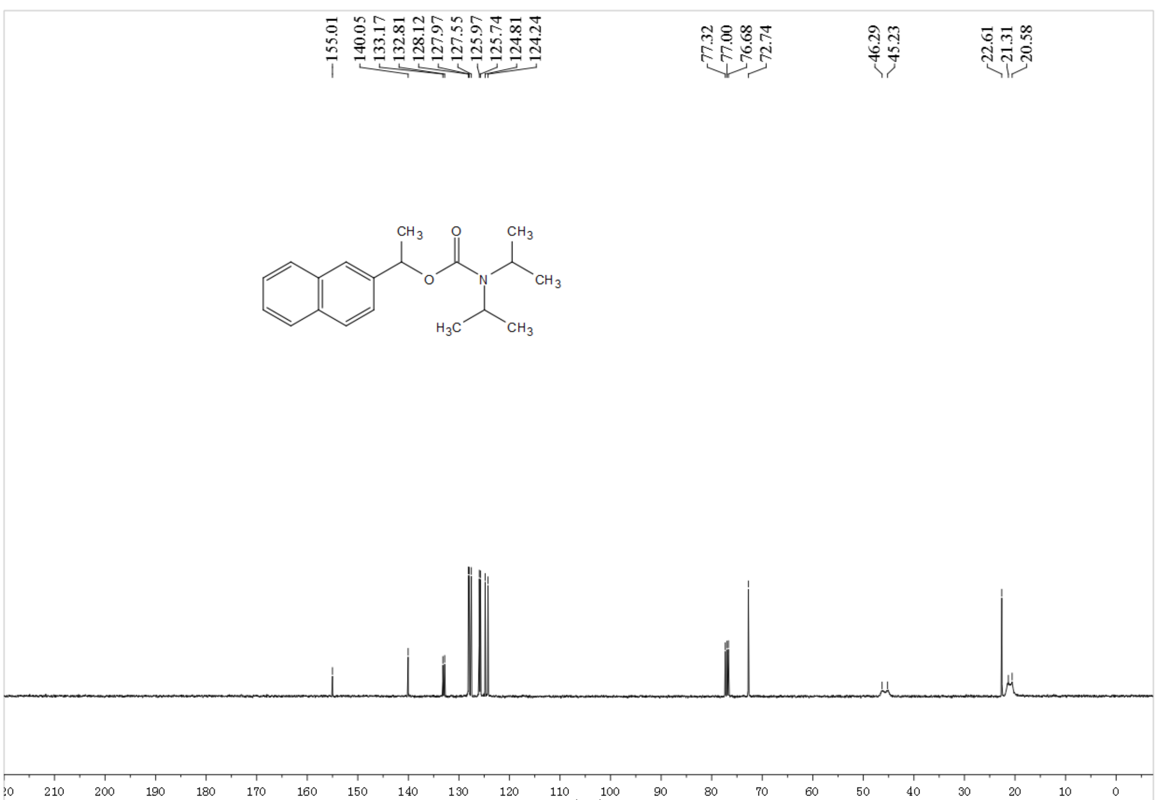

7.33
7.33
7.30
7.30
7.26
5.82
5.80
5.79
5.77
4.10
3.76
1.65
1.53
1.52
1.21
1.19
-0.00
4.16
1.00
0.95
0.96
3.34
12.13
f1 (ppm)


154.69
141.24
132.98
128.41
127.29
77.32
77.00
76.68
71.83
46.28
45.05
22.53
21.35
20.47
f1 (ppm)

Compound 1f

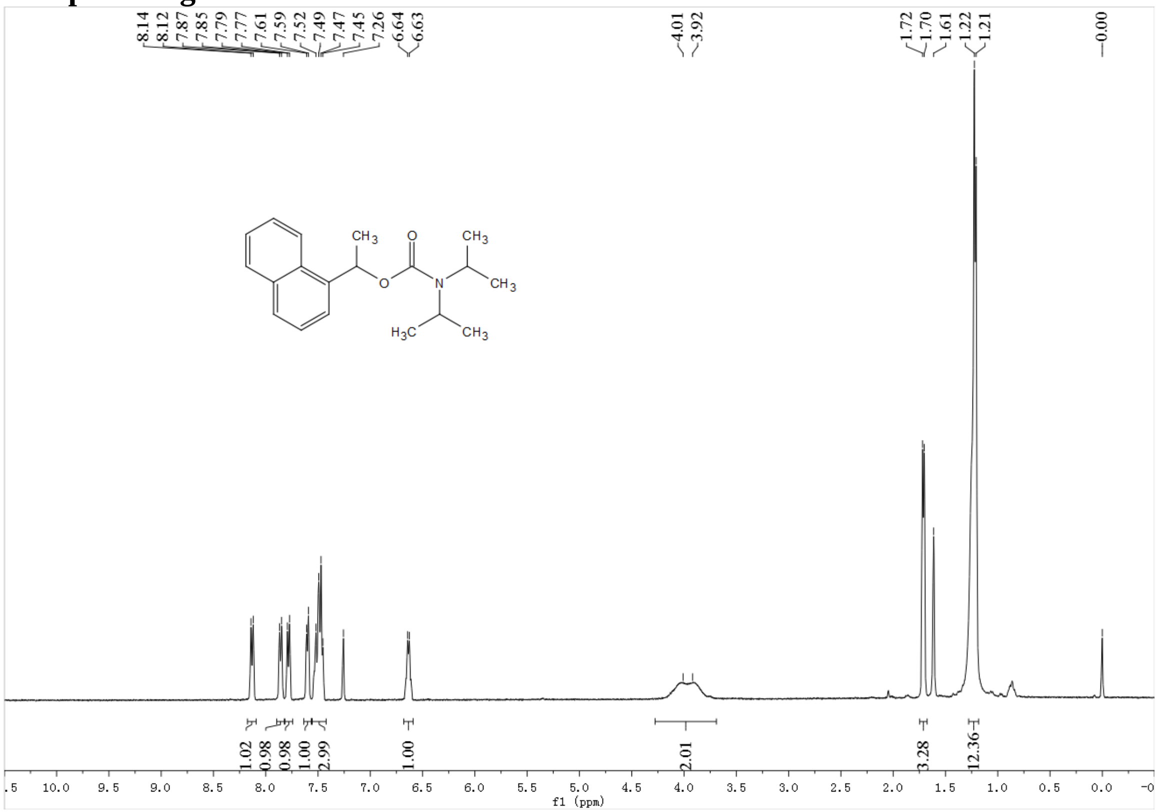


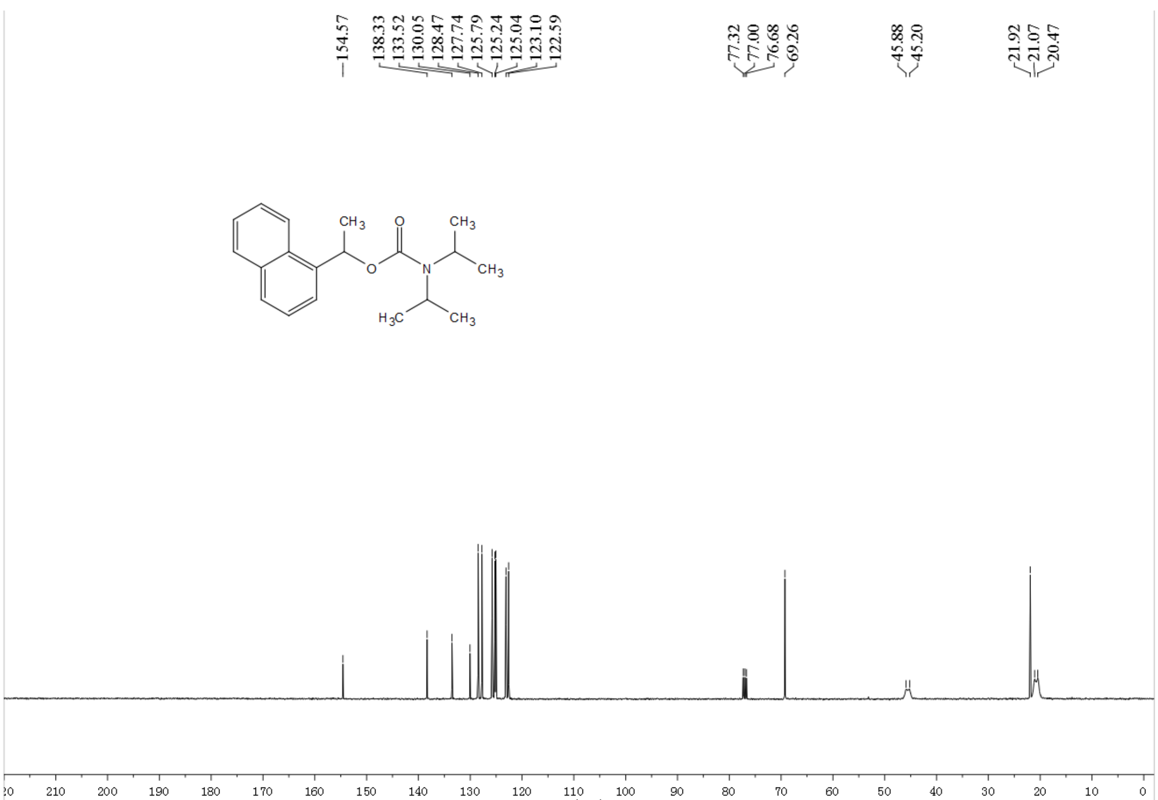
7.85
7.82
7.54
7.52
7.48
7.47
7.44
7.26
6.06
6.04
6.03
6.01
4.11
3.81
1.66
1.64
1.23
0.02
4.27
1.11
2.00
1.04
0.92
0.85
3.37
12.38
f1 (ppm)



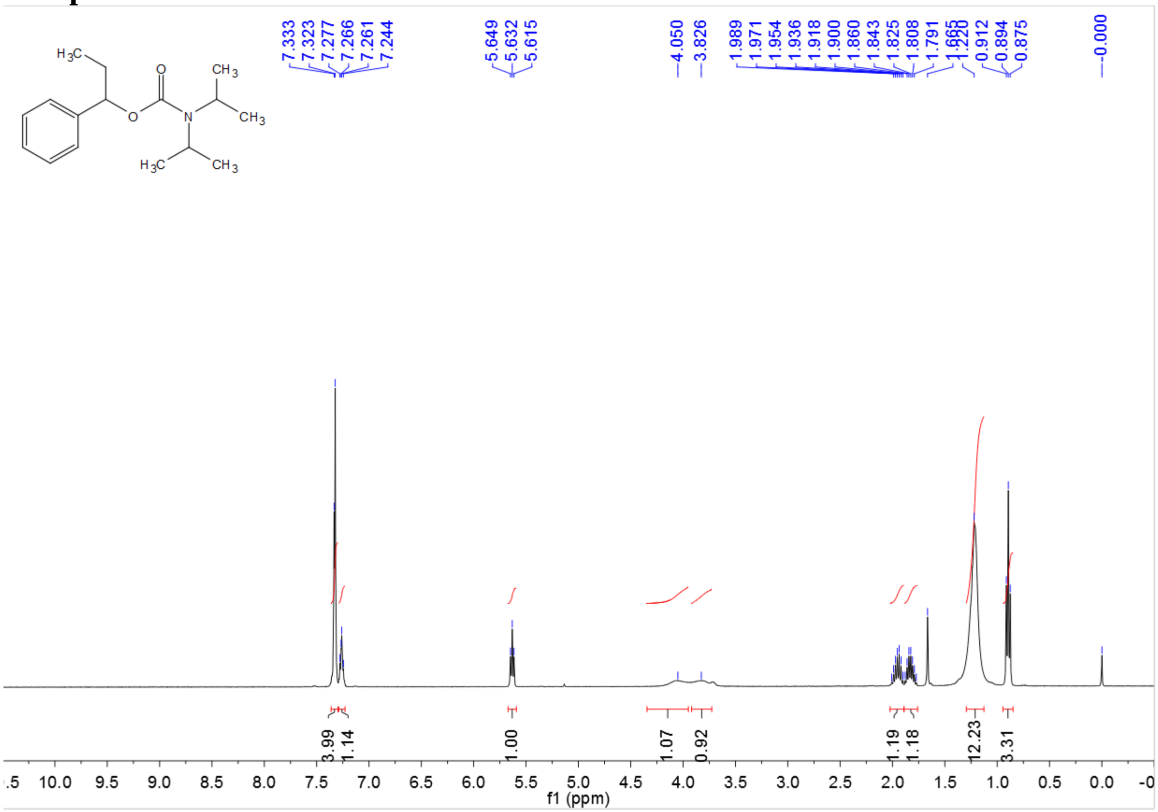
155.01
140.05
133.17
132.81
128.12
127.97
127.55
125.97
125.74
124.81
124.24
77.32
77.00
76.68
72.74
46.29
45.23
22.61
21.31
20.58
f1 (ppm)

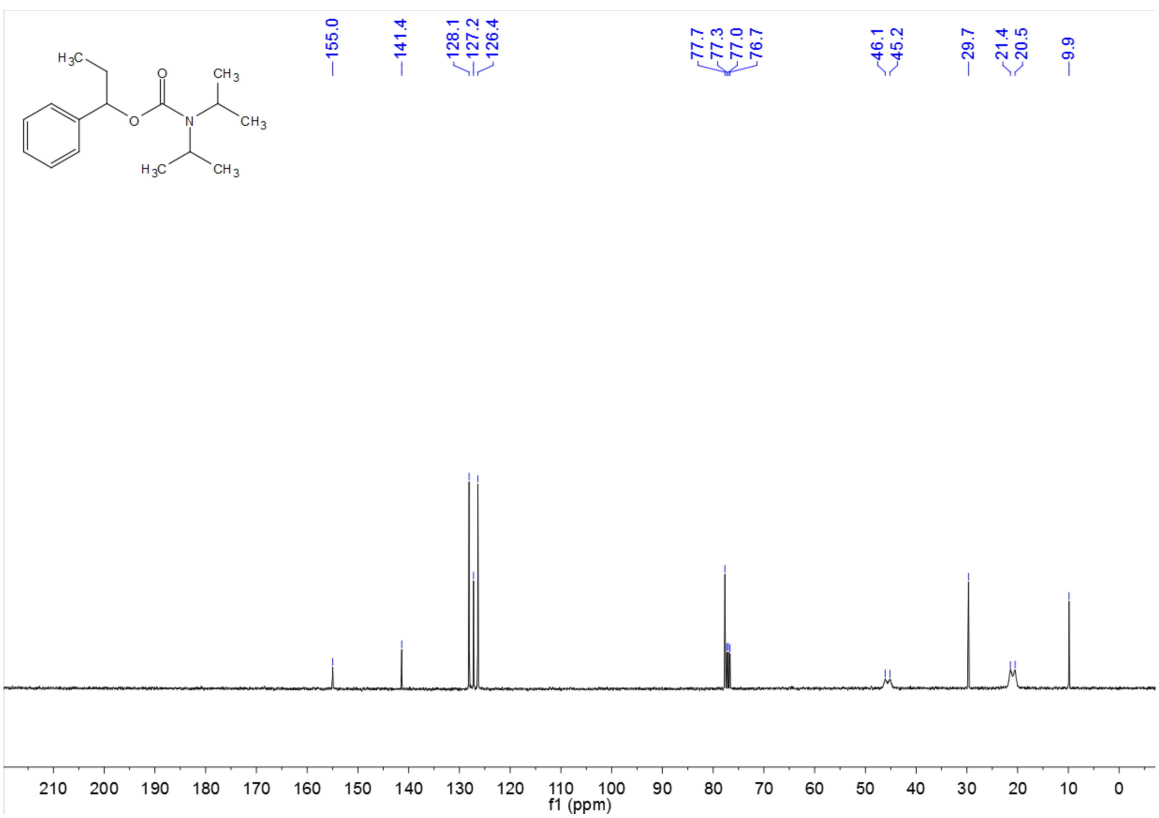
Compound 1g



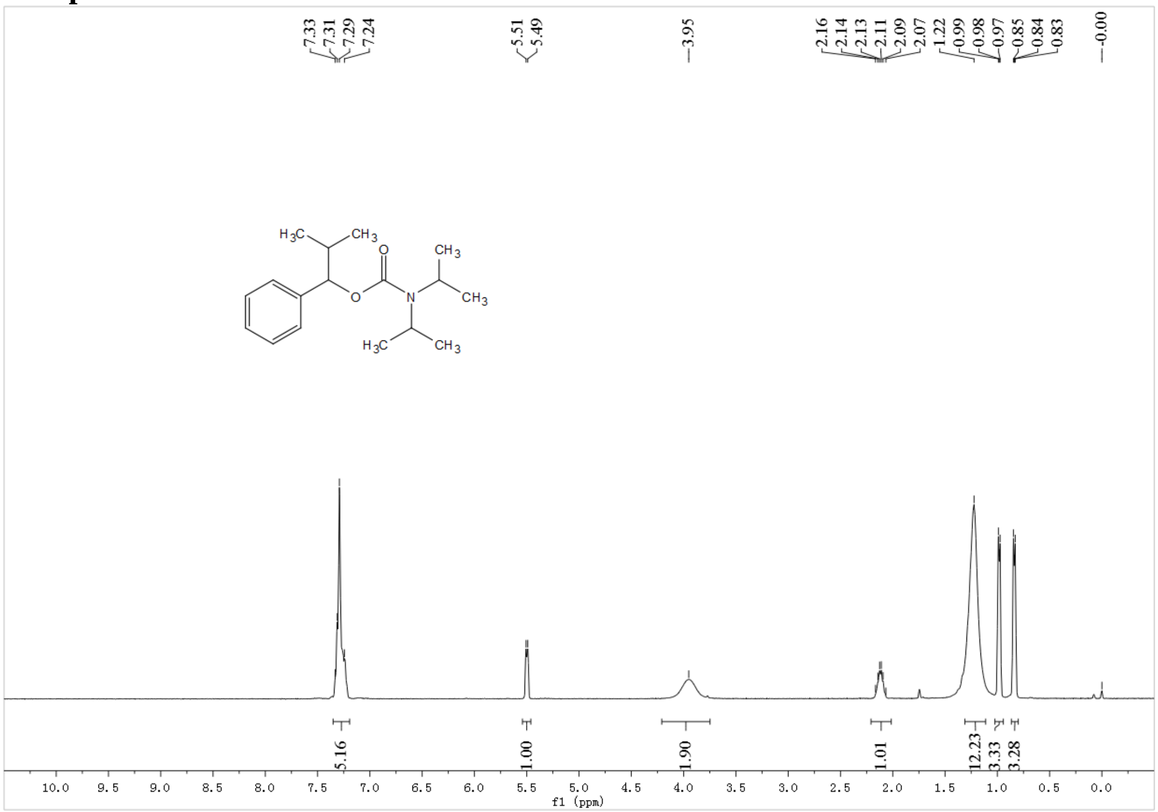


Compound 1h

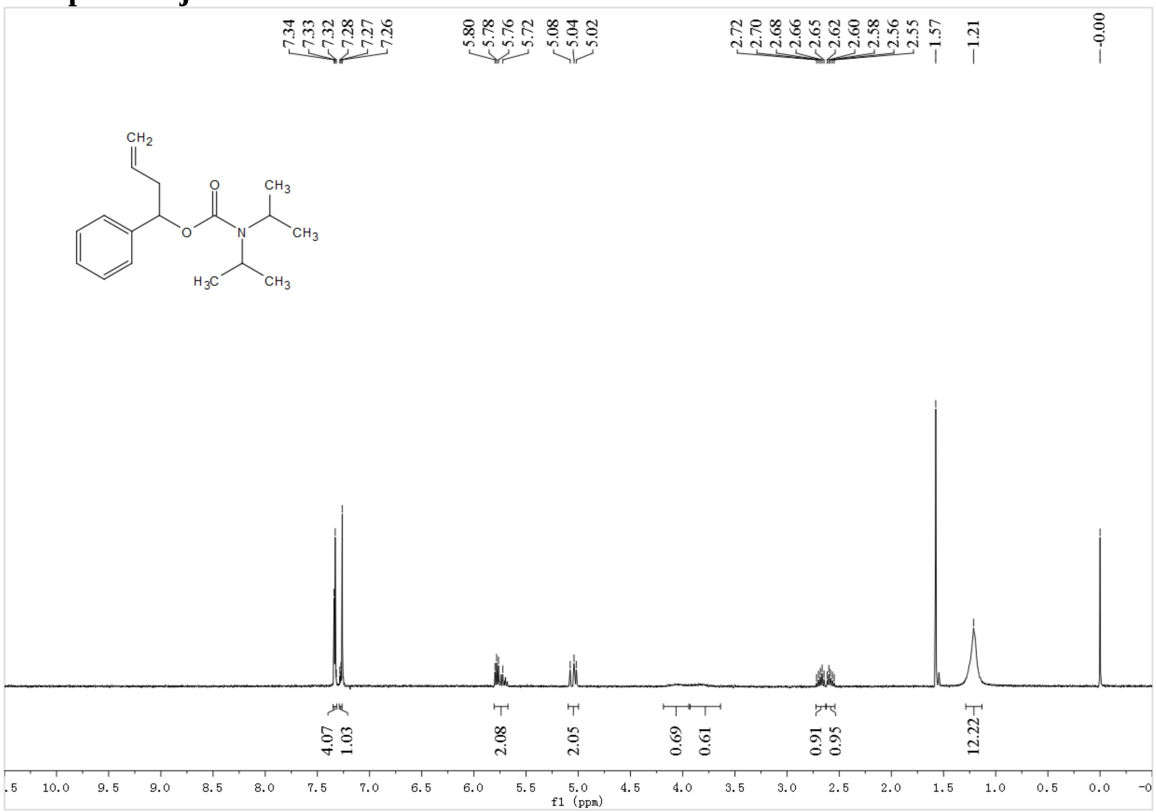

7.333
7.323
7.277
7.266
7.261
7.244
5.649
5.632
5.615
4.050
3.826
1.989
1.971
1.954
1.936
1.918
1.900
1.860
1.843
1.825
1.808
1.791
1.665
1.220
0.912
0.894
0.875
0.000
3.99
1.14
1.00
1.07
0.92
1.19
1.18
12.23
3.31
f1 (ppm)

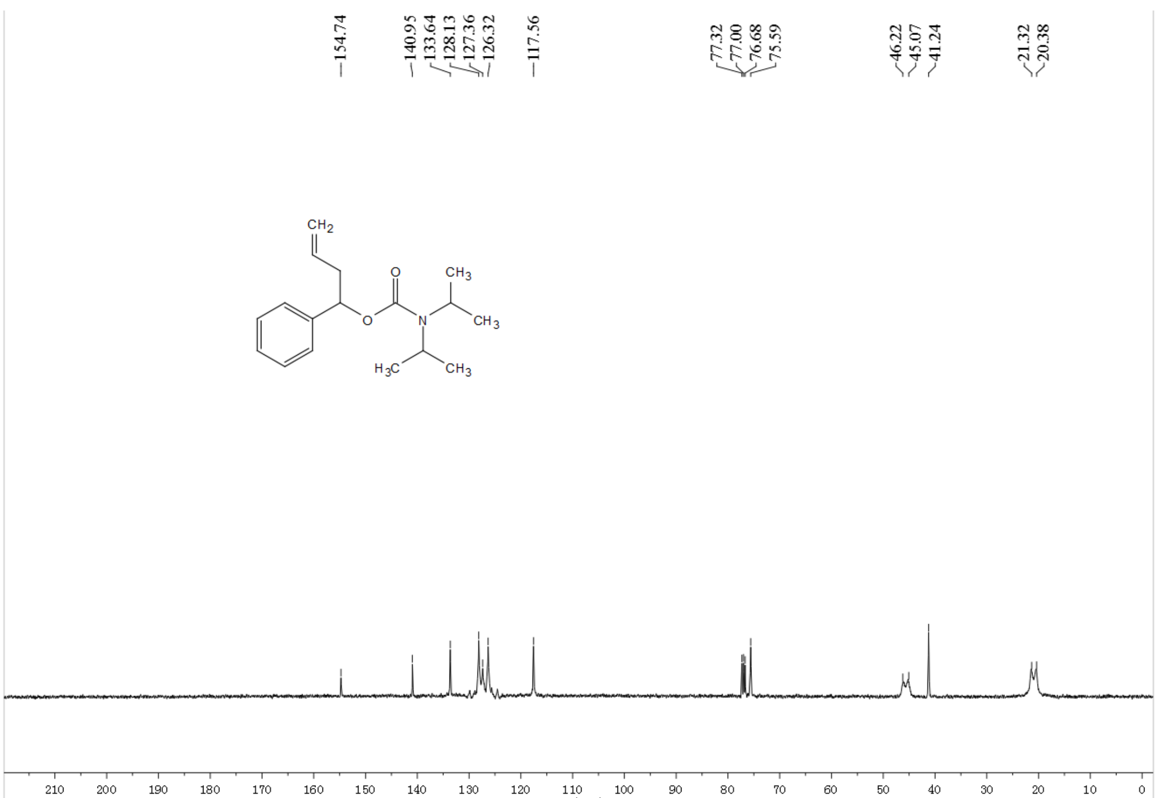

155.0
141.4
128.1
127.2
126.4
77.7
77.3
77.0
76.7
46.1
45.2
29.7
21.4
20.5
9.9
f1 (ppm)

Compound 1i

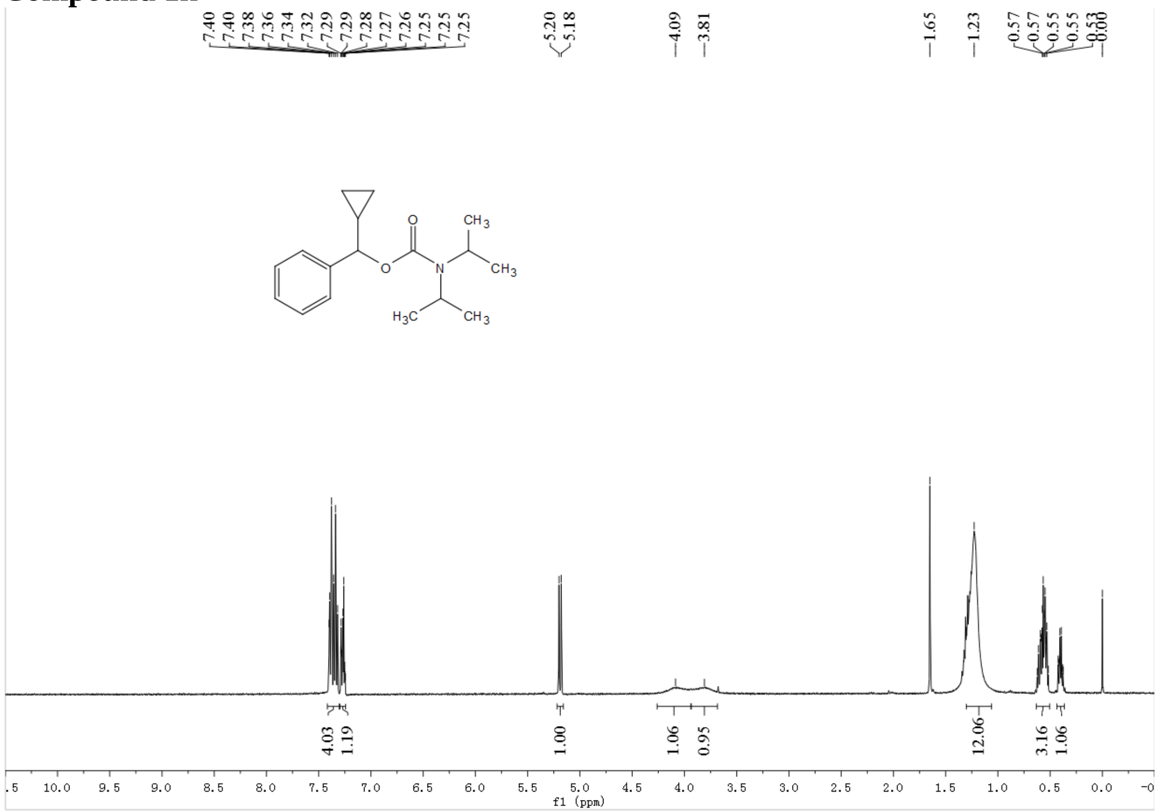


Compound 1j

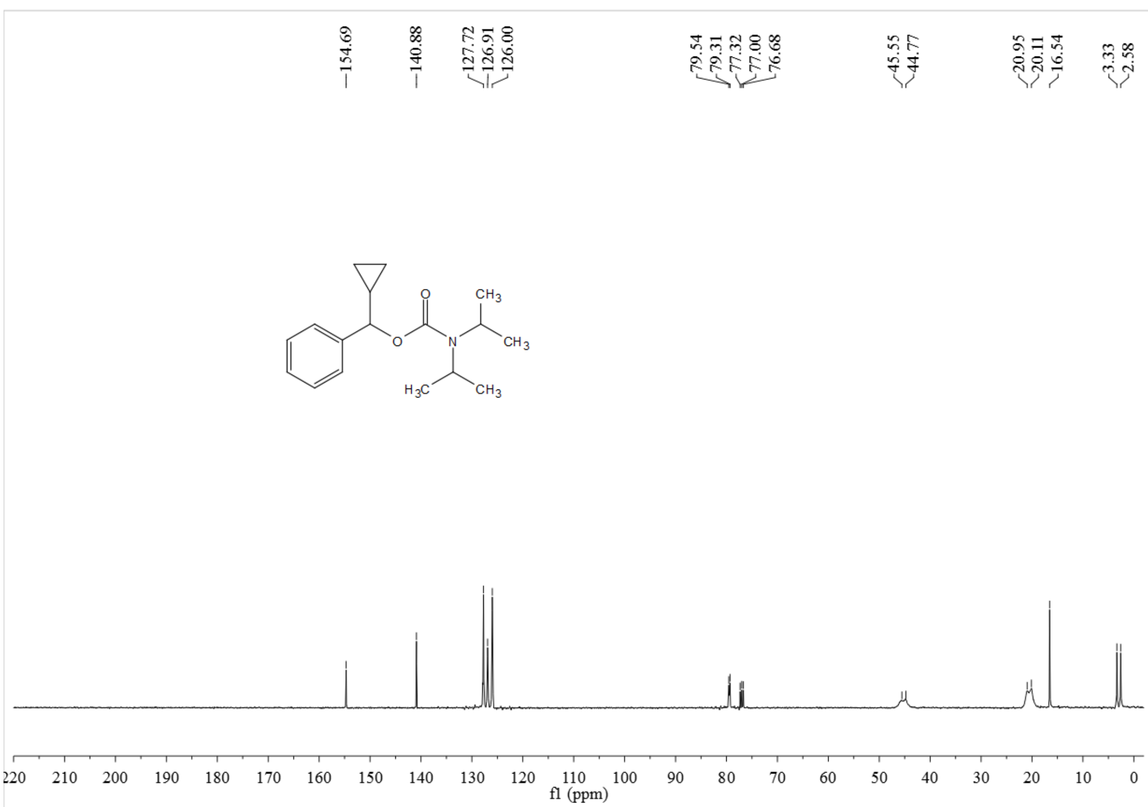




Compound 1k

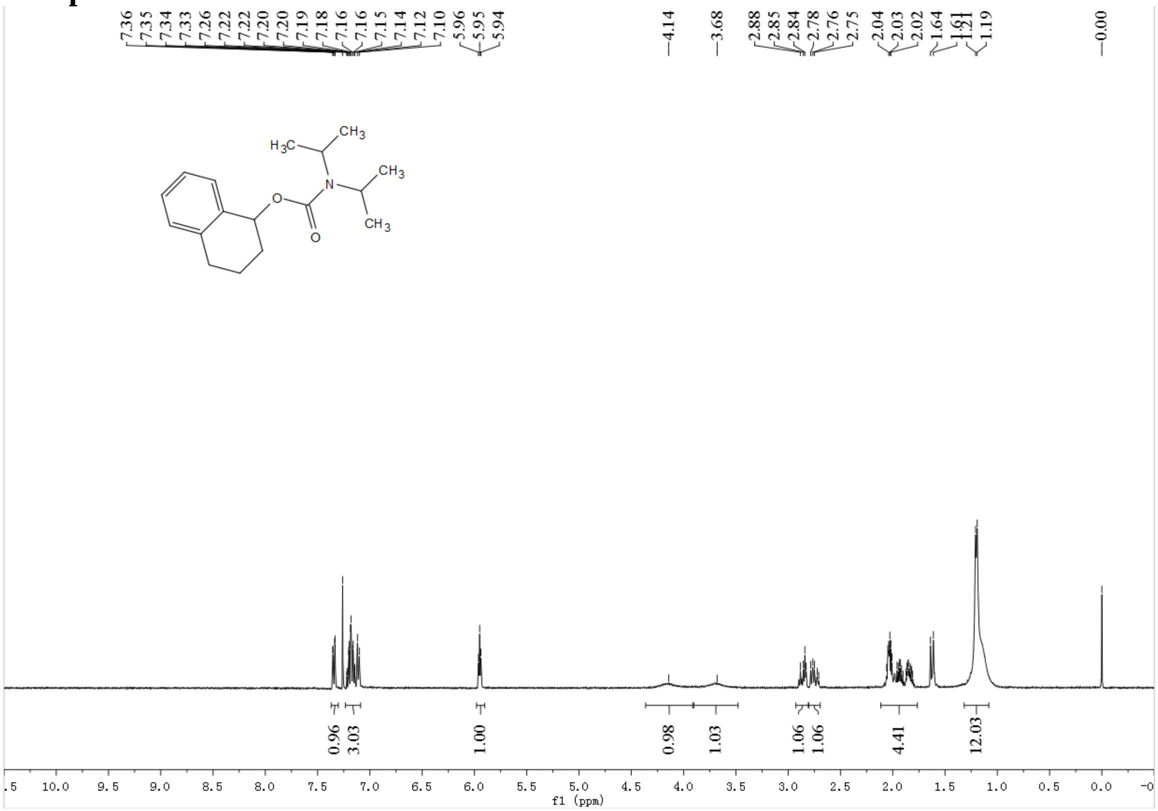


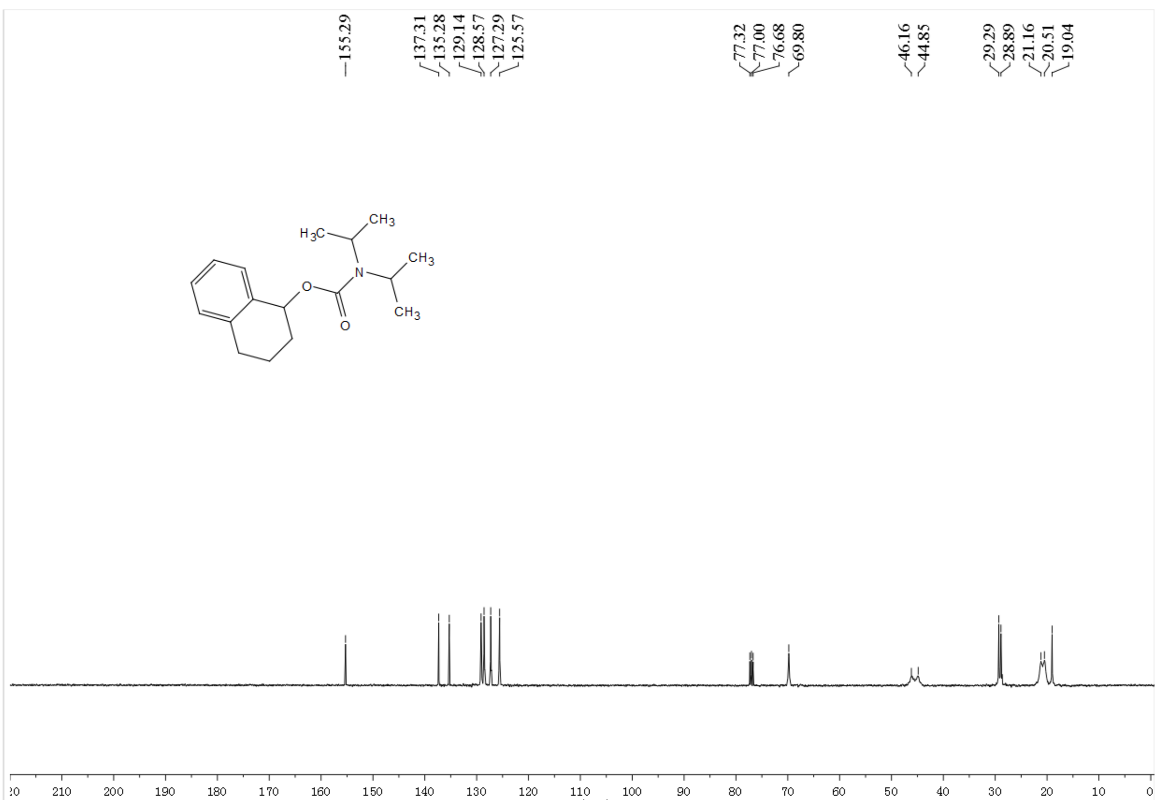
7.40
7.40
7.38
7.36
7.34
7.32
7.29
7.29
7.28
7.27
7.26
7.25
7.25
7.25
5.20
5.18
4.09
3.81
1.65
1.23
0.57
0.57
0.55
0.55
0.53
0.00
CH3
O
O
N
CH3
H3C
CH3
4.03
1.19
1.00
1.06
0.95
12.06
3.16
1.06
f1 (ppm)



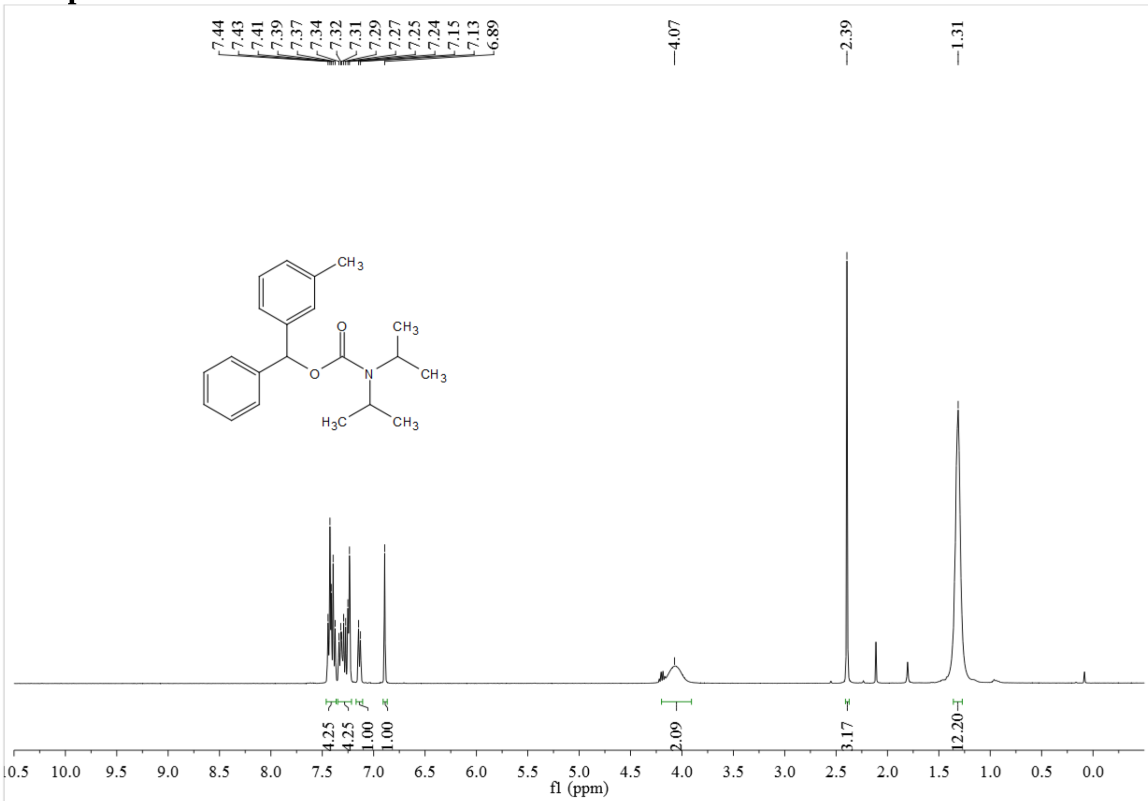
154.69
140.88
127.72
126.91
126.00
79.54
79.31
77.32
77.00
76.68
45.55
44.77
20.95
20.11
16.54
3.33
2.58
CH3
O
O
N
CH3
H3C
CH3
f1 (ppm)

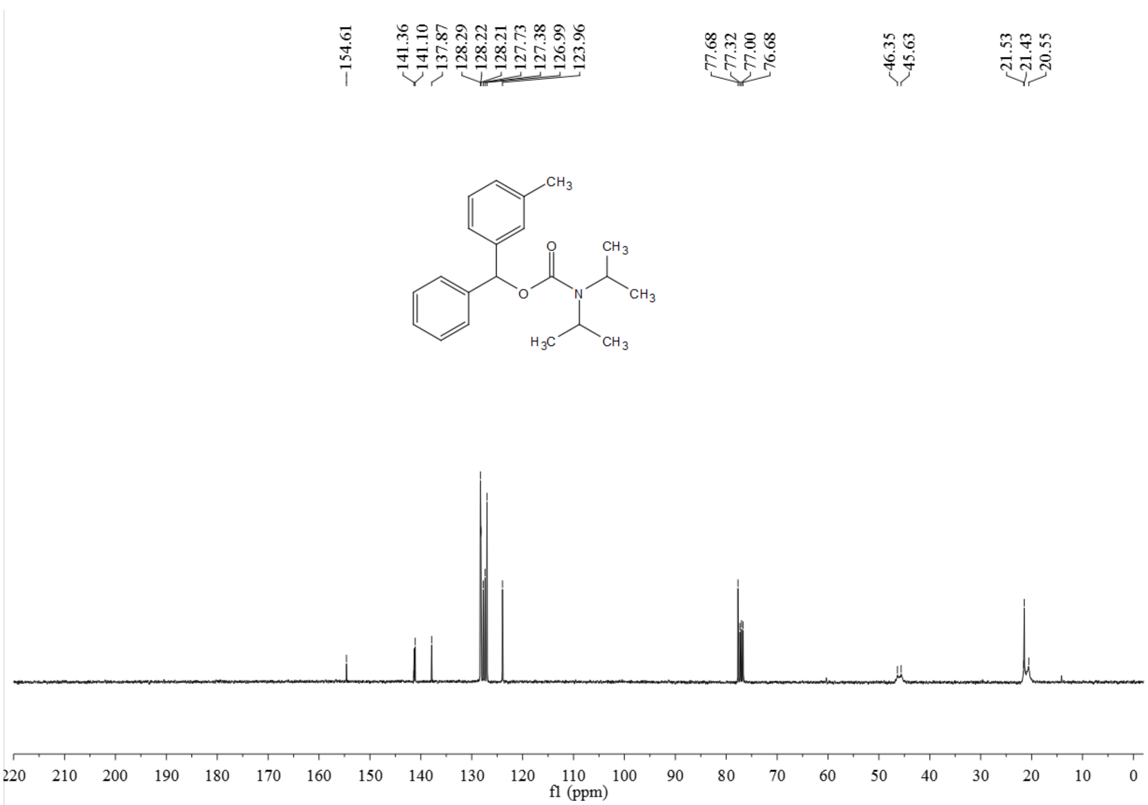
Compound 1l



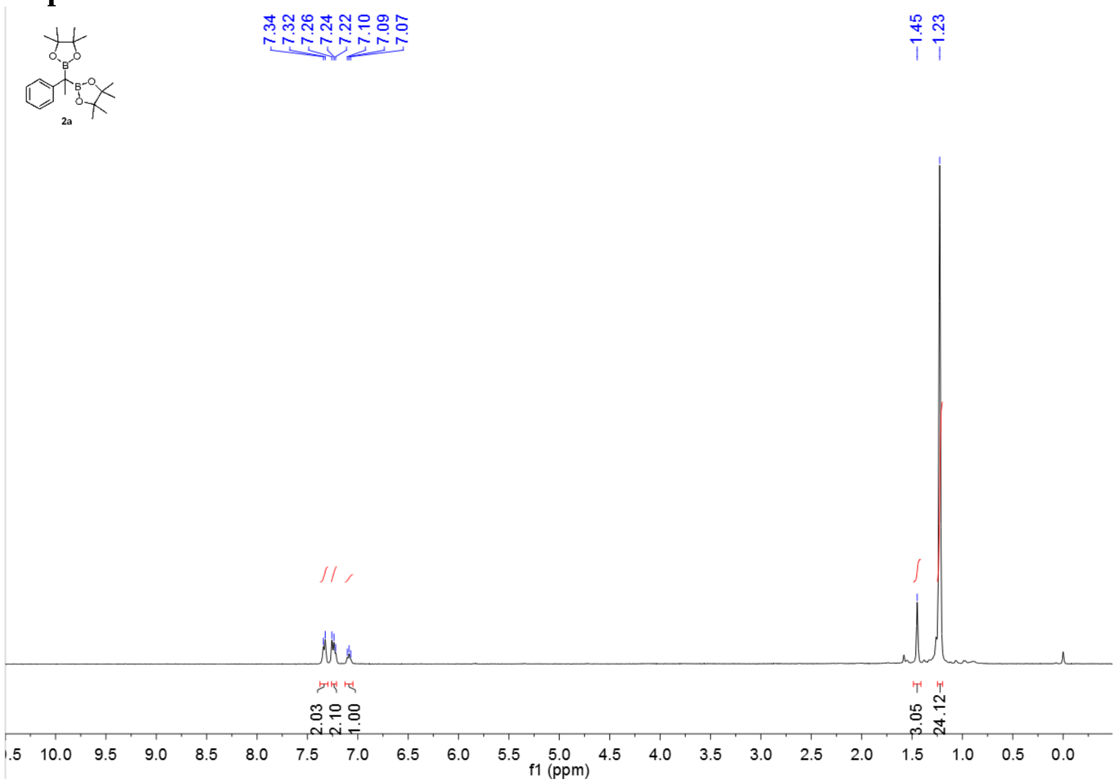


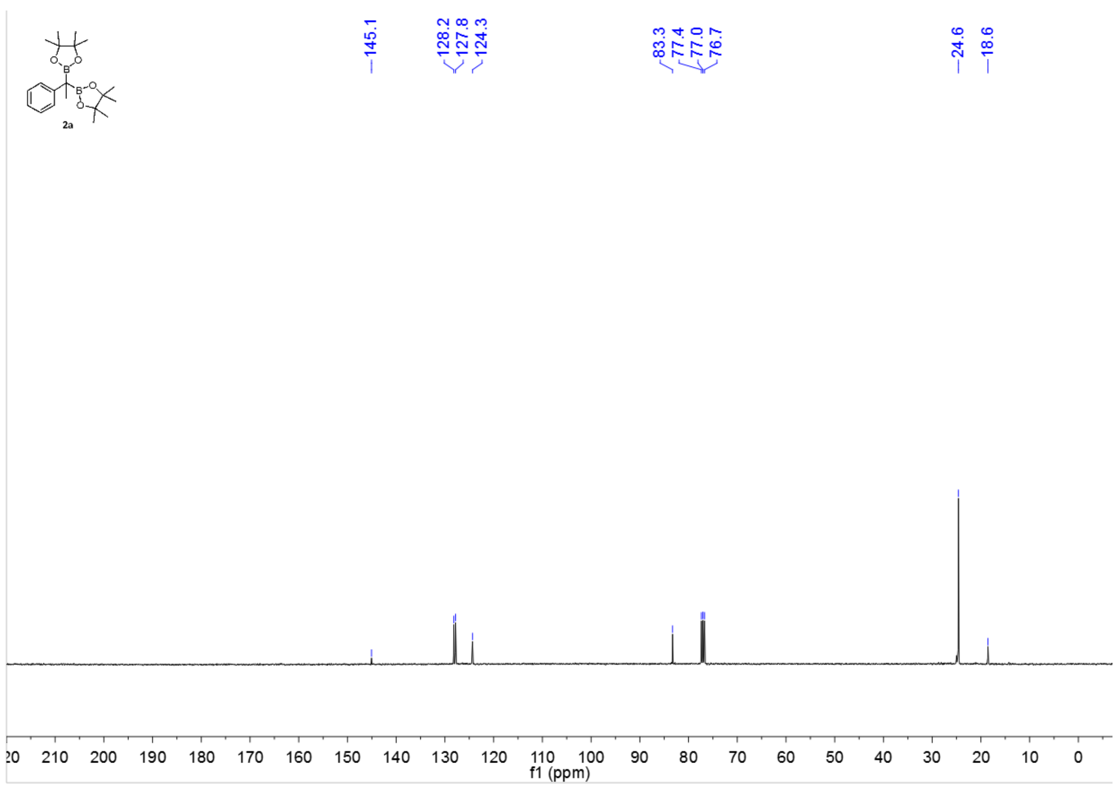
Compound 1m


7.44
7.43
7.41
7.39
7.37
7.34
7.32
7.31
7.29
7.27
7.25
7.24
7.15
7.13
6.89
4.07
2.39
1.31
4.25
4.25
1.00
1.00
2.09
3.17
12.20
fl (ppm)

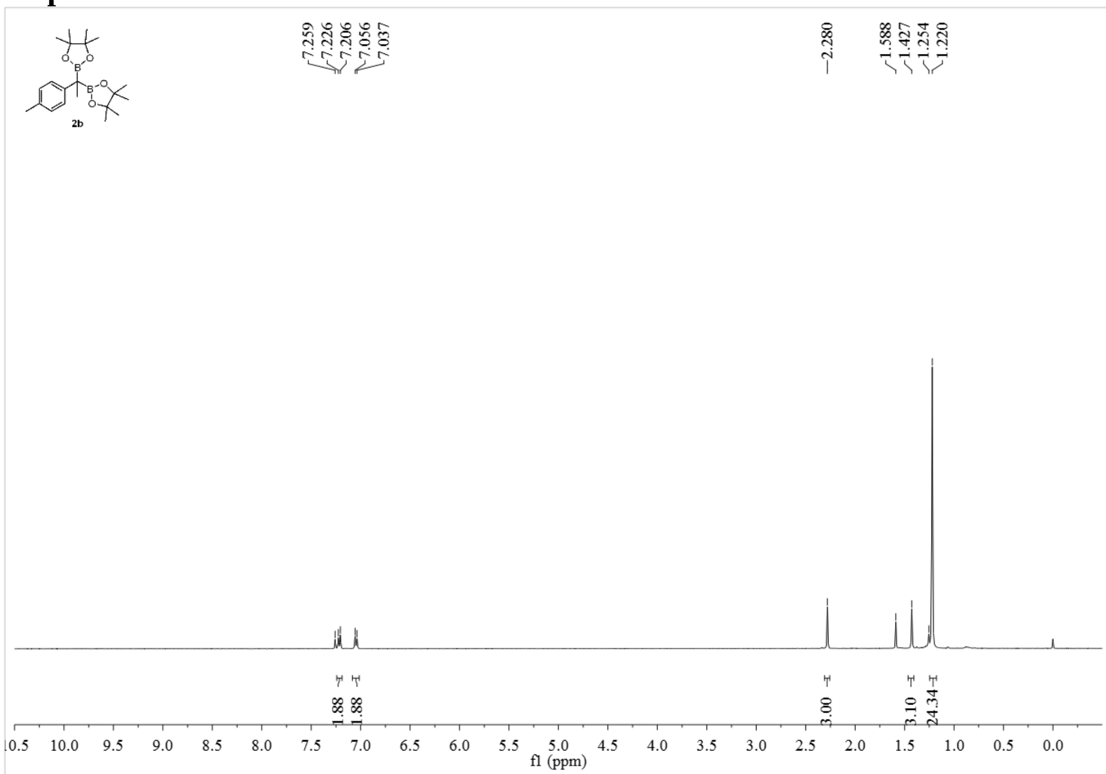

154.61
141.36
141.10
137.87
128.29
128.22
128.21
127.73
127.38
126.99
123.96
77.68
77.32
77.00
76.68
46.35
45.63
21.53
21.43
20.55
fl (ppm)

Compound 2a

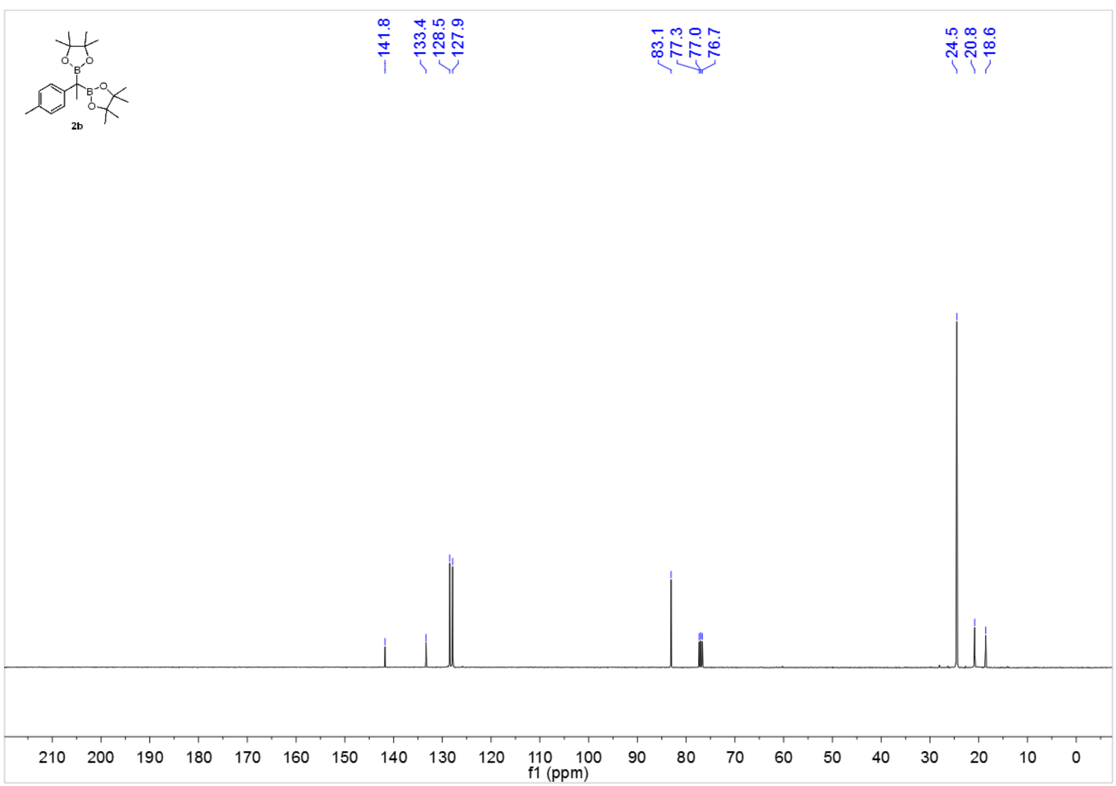

2a
7.34
7.32
7.26
7.24
7.22
7.10
7.09
7.07
1.45
1.23
2.03
2.10
1.00
3.05
24.12
f1 (ppm)


2a
145.1
128.2
127.8
124.3
83.3
77.4
77.0
76.7
24.6
18.6
f1 (ppm)

Compound 2b

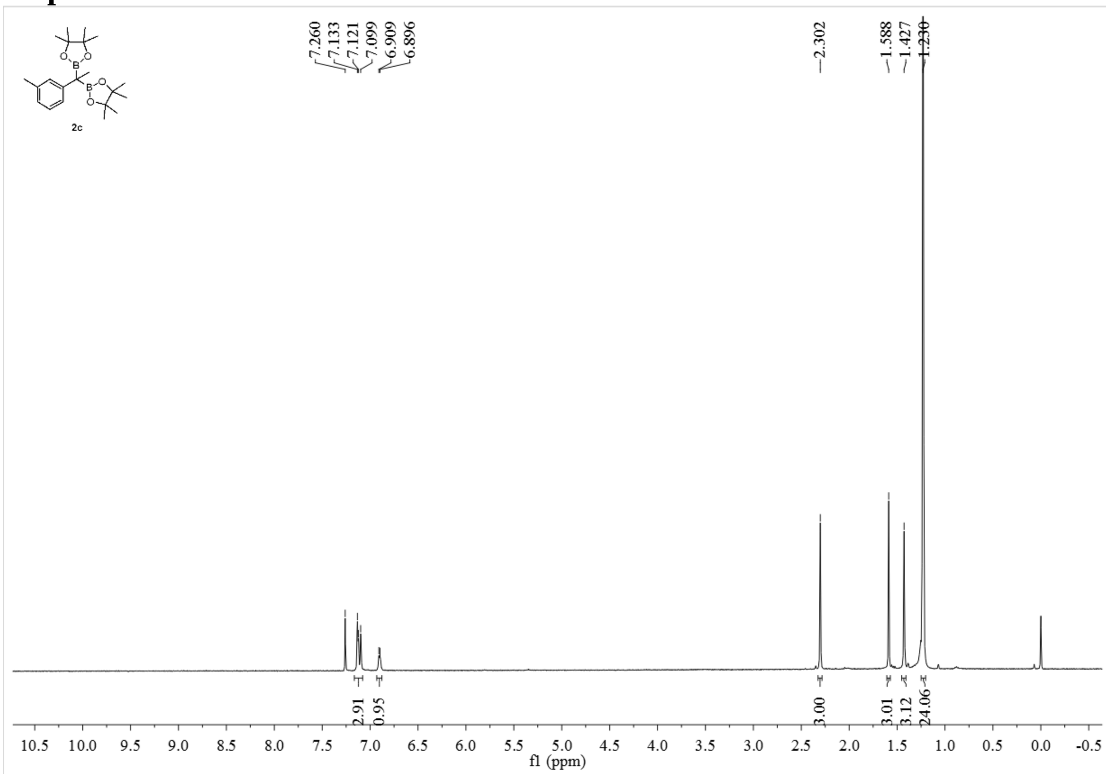


7.259
7.226
7.206
7.056
7.037
2.280
1.588
1.427
1.254
1.220
2b
1.88
1.88
3.00
3.10
24.34
f1 (ppm)

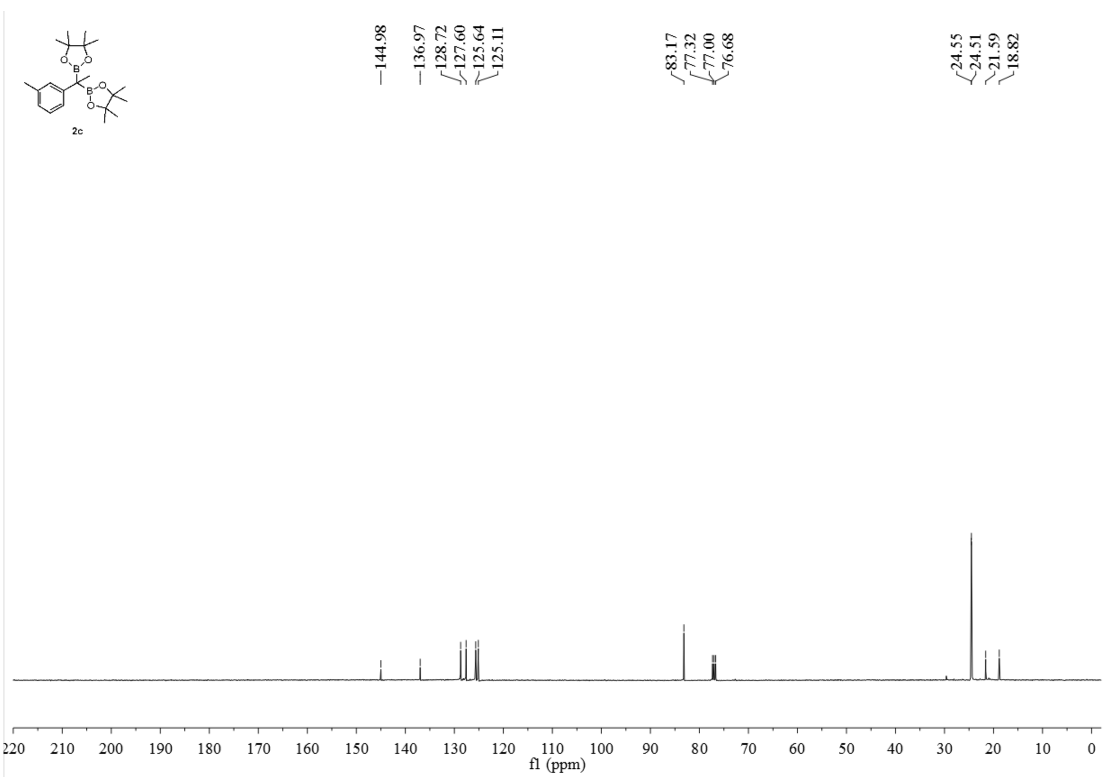


141.8
133.4
128.5
127.9
83.1
77.3
77.0
76.7
24.5
20.8
18.6
2b
f1 (ppm)

Compound 2c

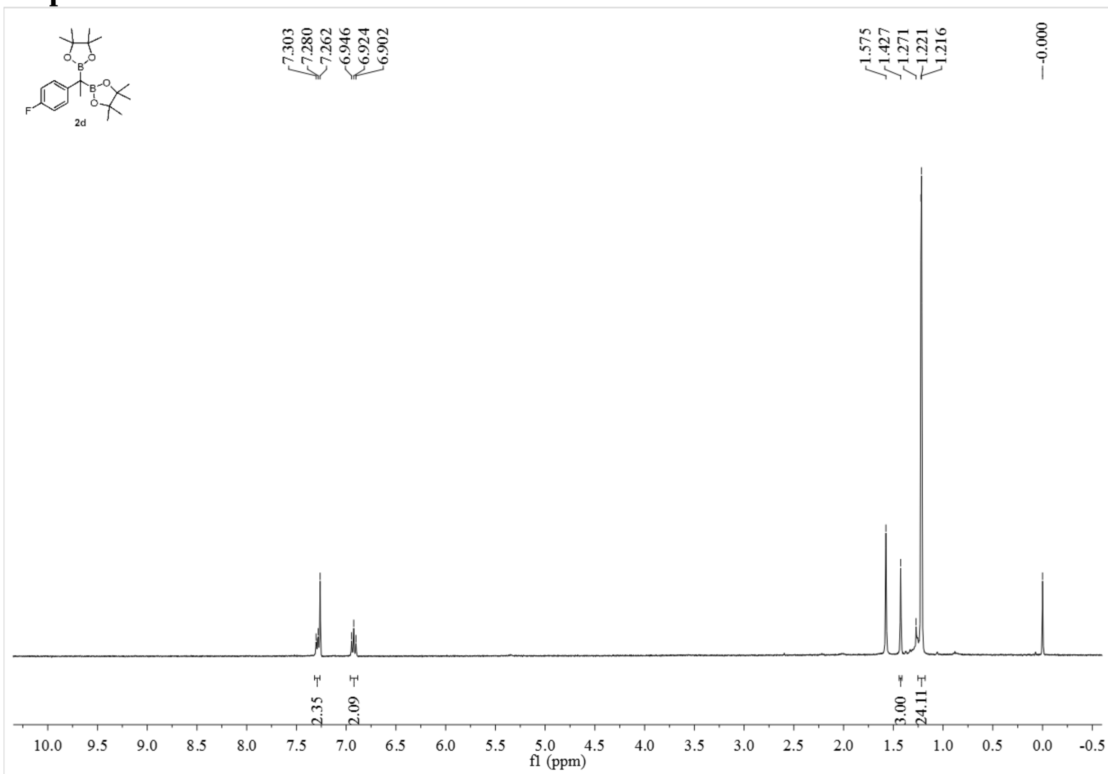


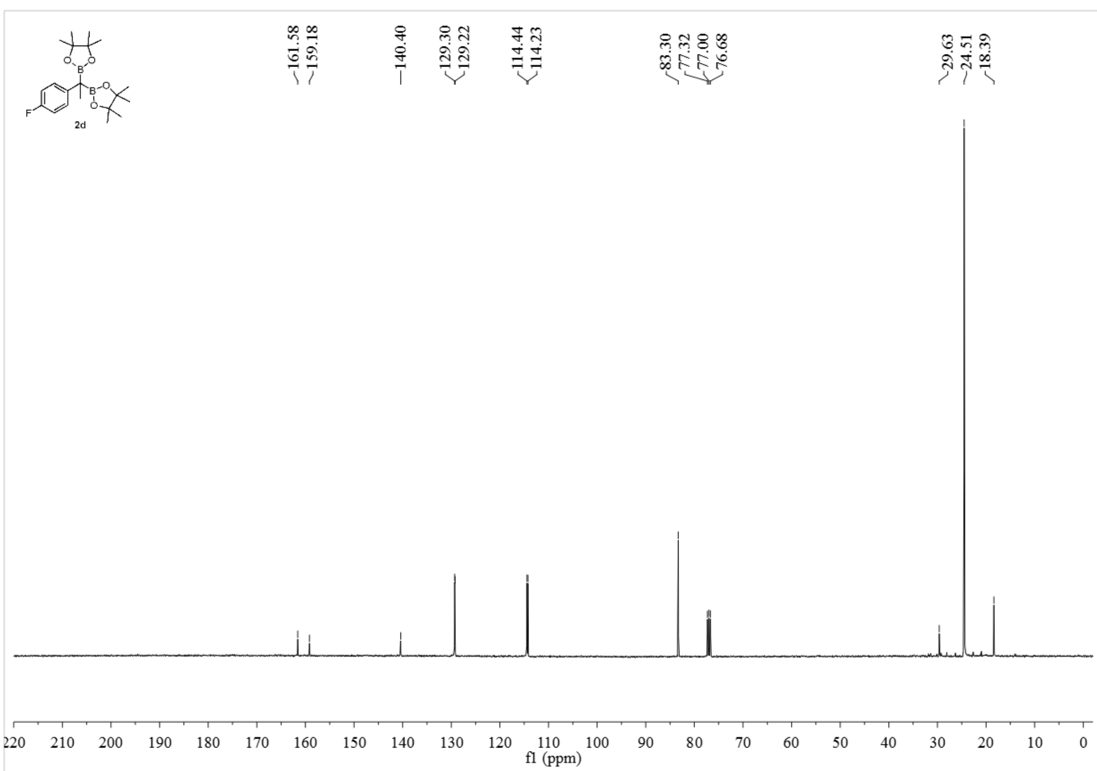
2c
7.260
7.133
7.121
7.099
6.909
6.896
2.302
1.588
1.427
1.230
2.91
0.95
3.00
3.01
3.12
24.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



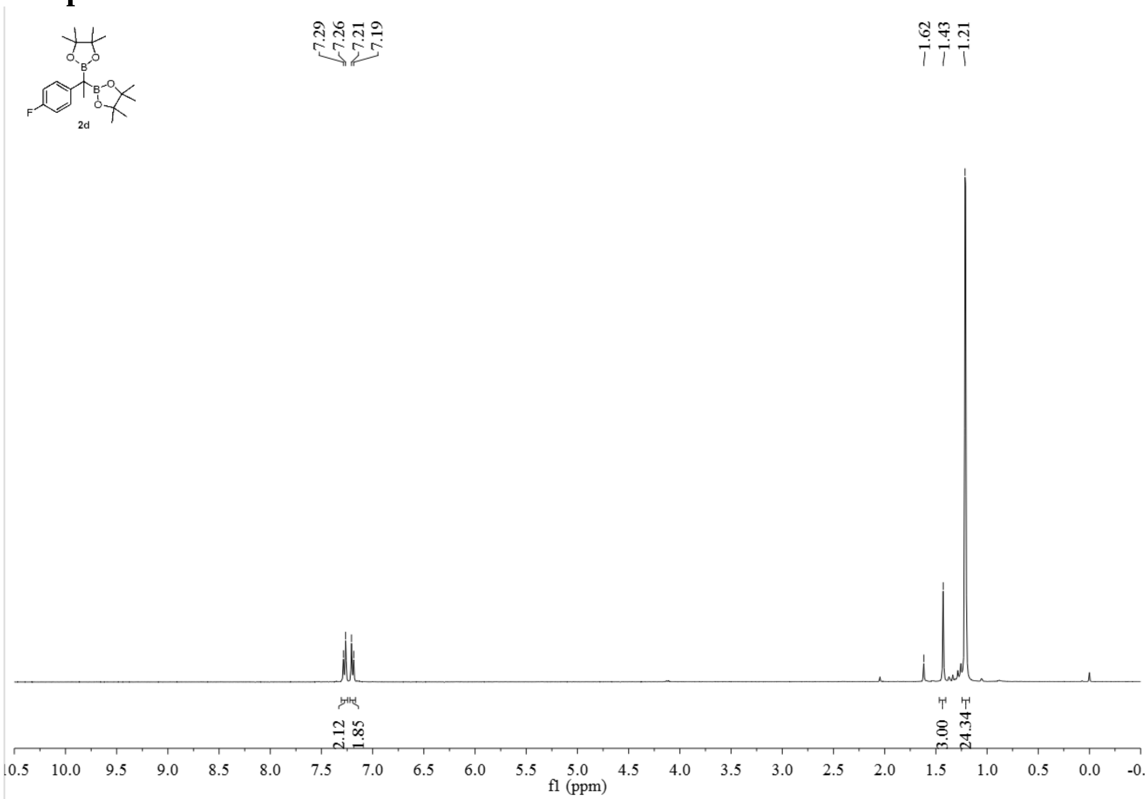
2c
144.98
136.97
128.72
127.60
125.64
125.11
83.17
77.32
77.00
76.68
24.55
24.51
21.59
18.82
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Compound 2d

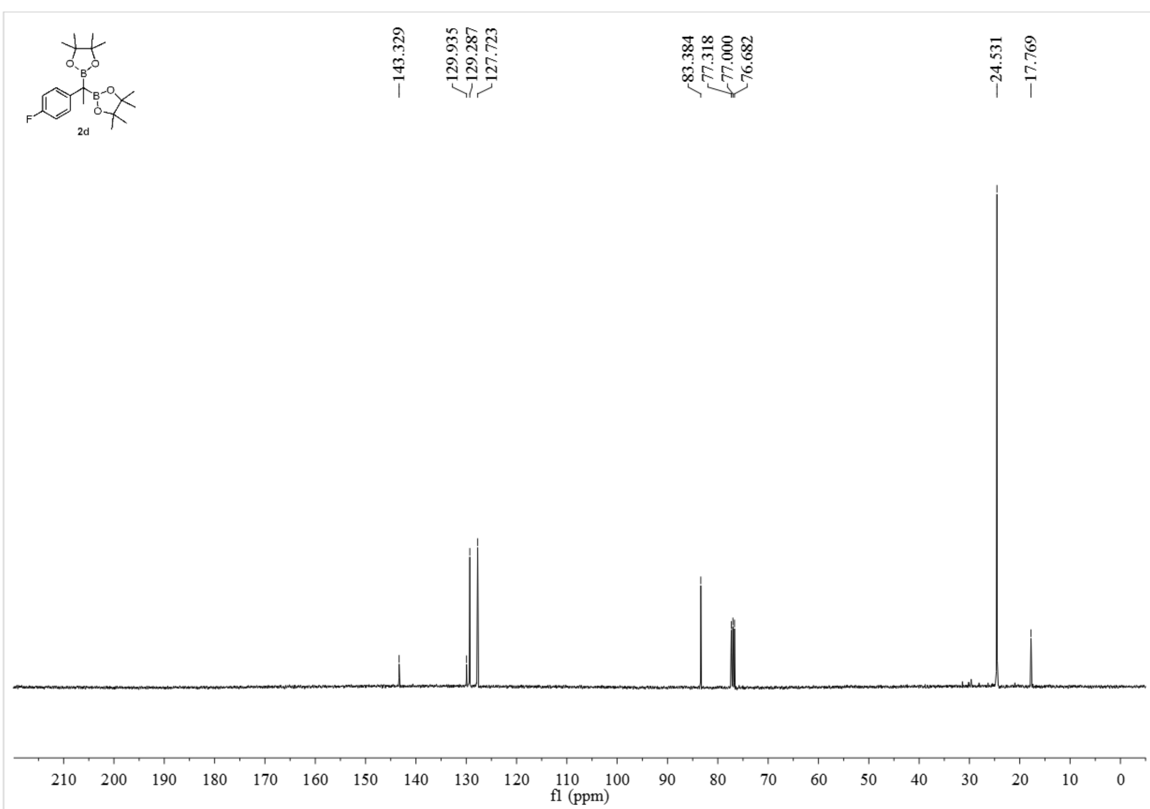

F
2d
7.303
7.280
7.262
6.946
6.924
6.902
1.575
1.427
1.271
1.221
1.216
-0.000
2.35
2.09
3.00
24.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


F
2d
161.58
159.18
140.40
129.30
129.22
114.44
114.23
83.30
77.32
77.00
76.68
29.63
24.51
18.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Compound 2e

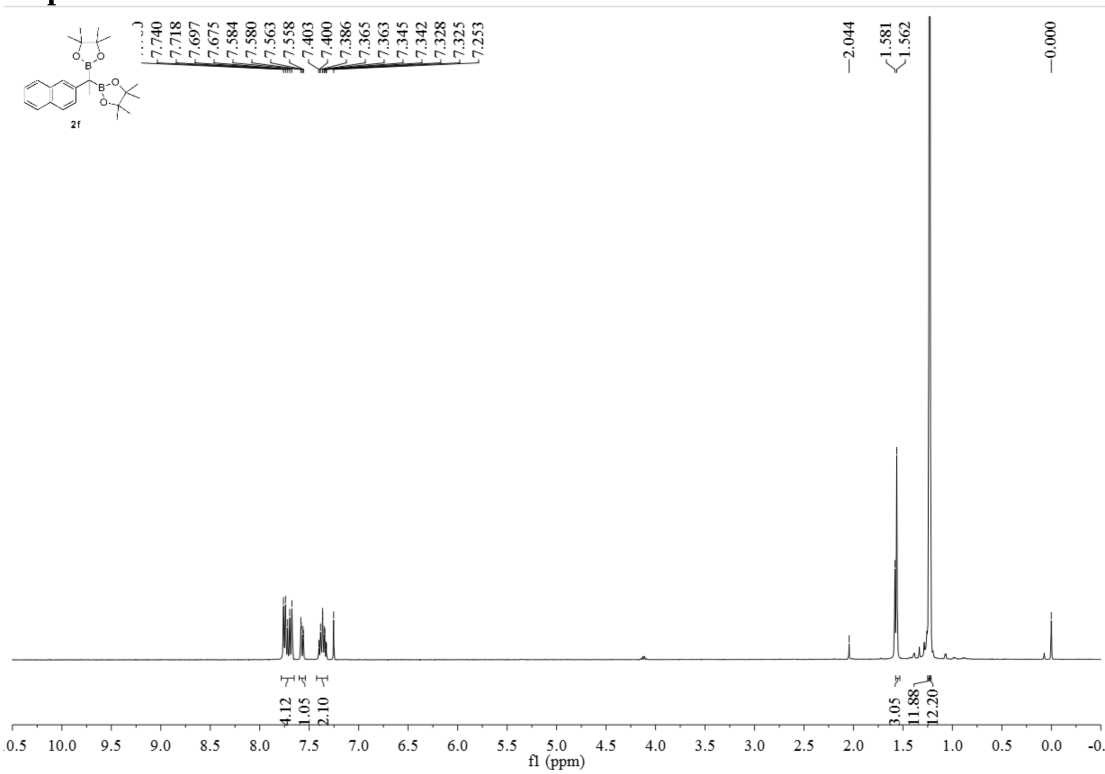


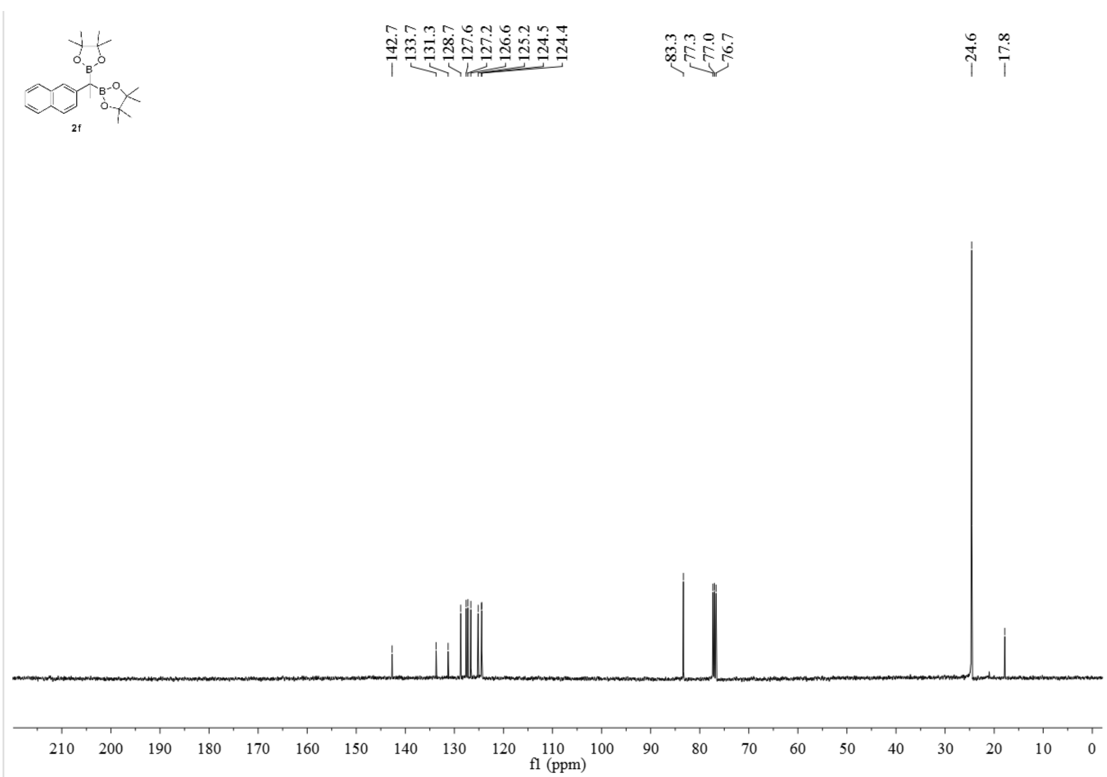
2d
7.29
7.26
7.21
7.19
1.62
1.43
1.21
2.12
1.85
3.00
24.34
f1 (ppm)



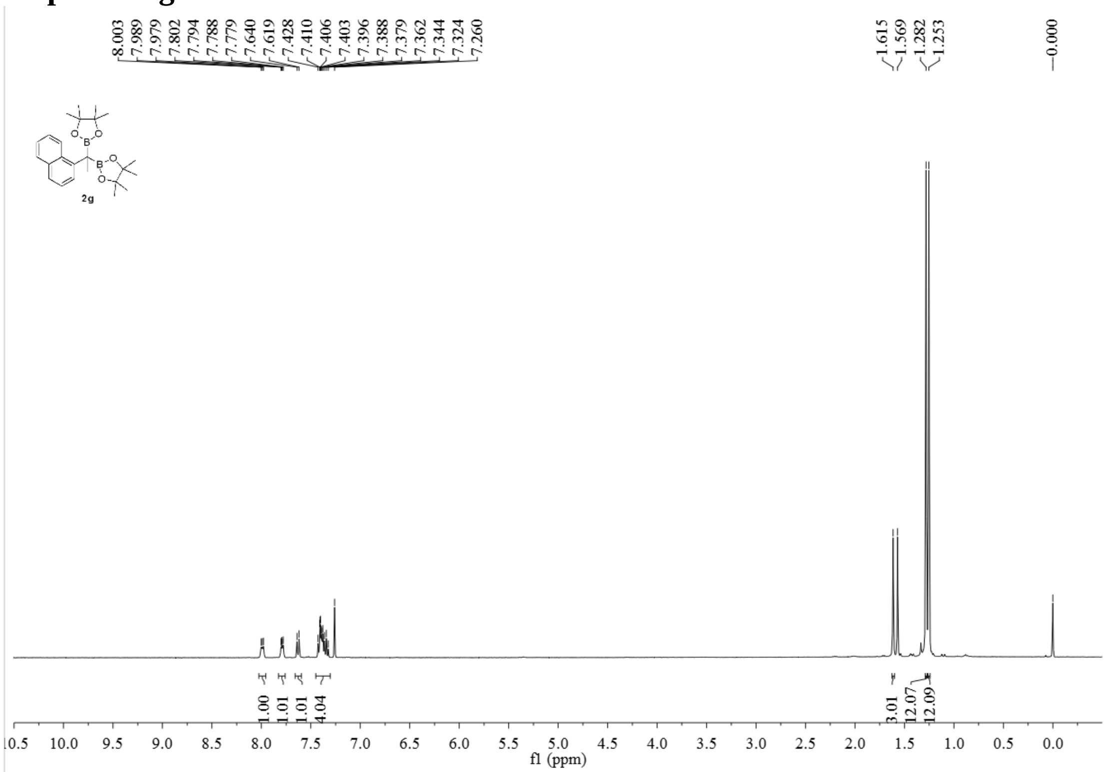
2d
143.329
129.935
129.287
127.723
83.384
77.318
77.000
76.682
24.531
17.769
f1 (ppm)

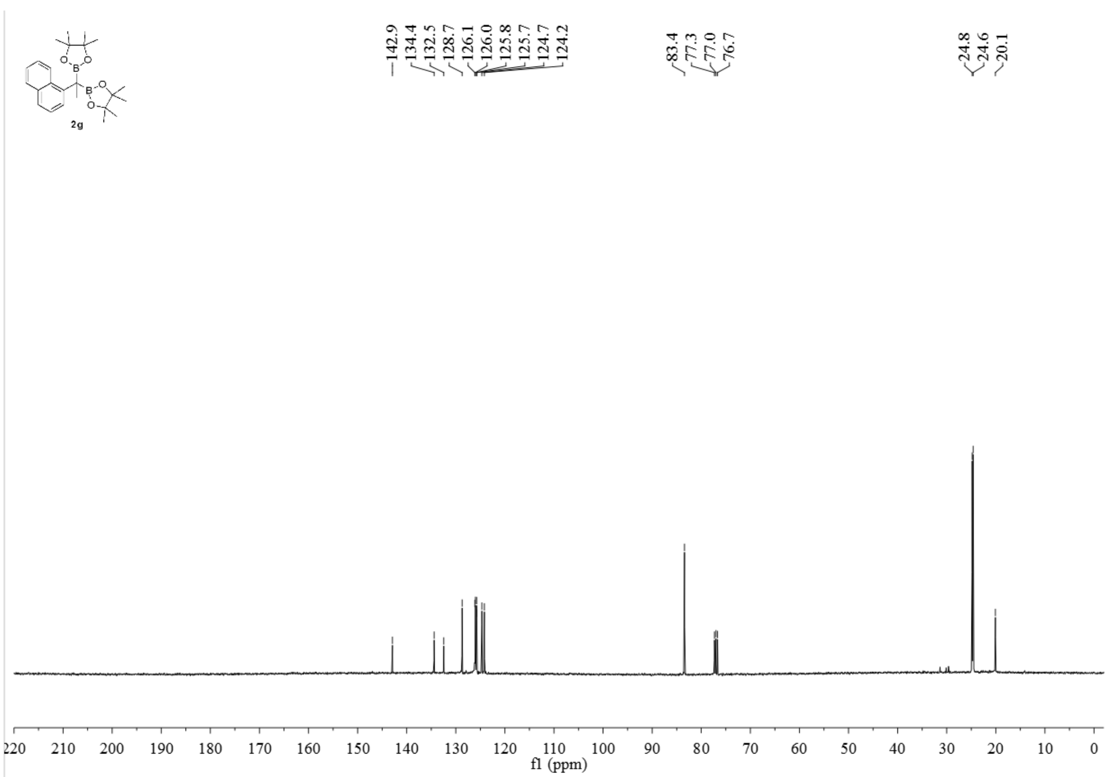
Compound 2f



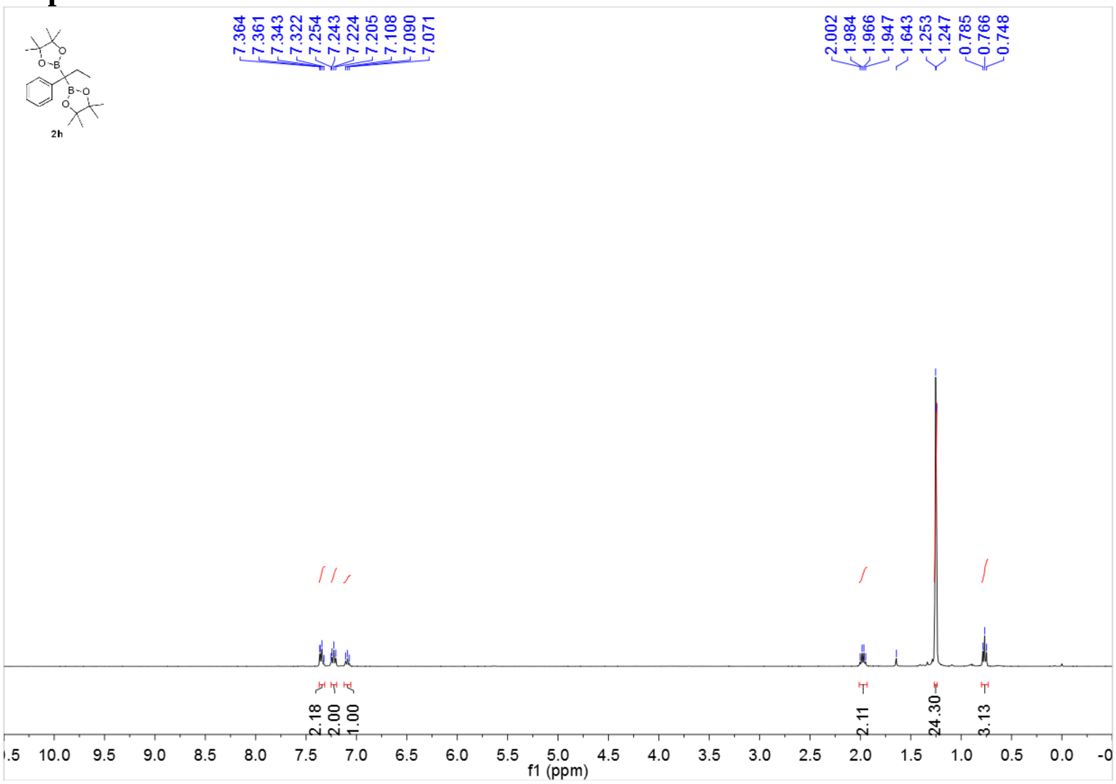


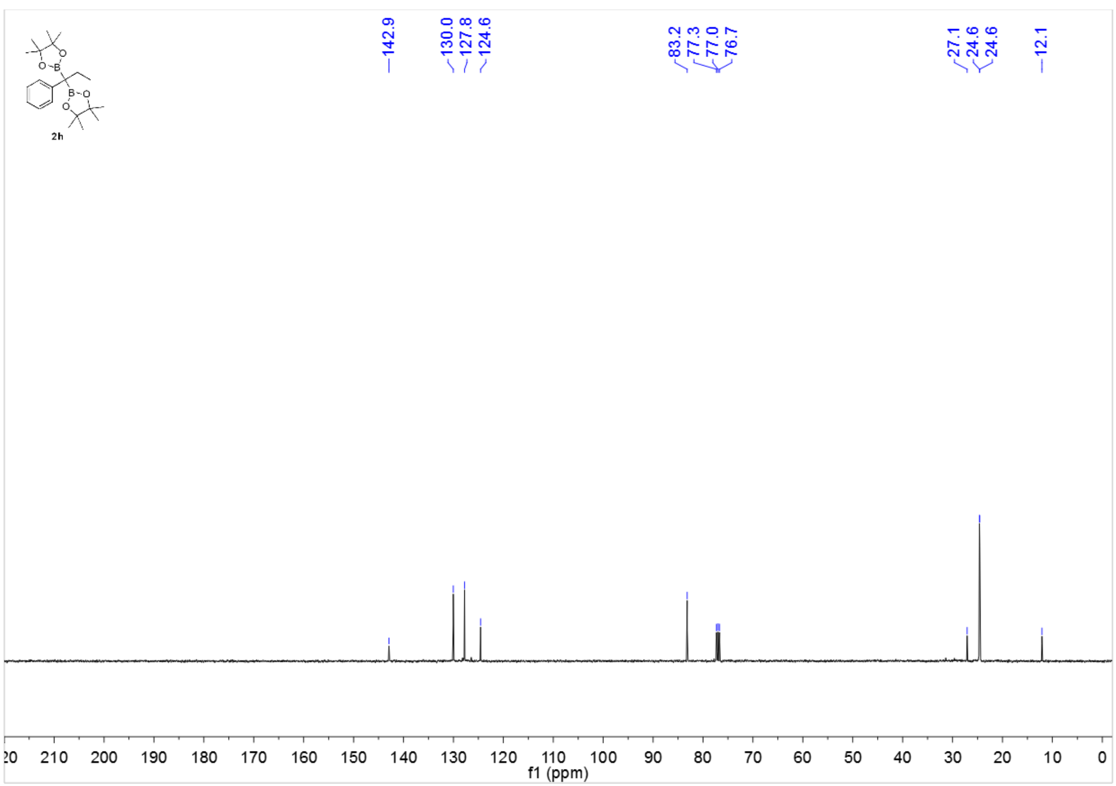
Compound 2g


8.003
7.989
7.979
7.802
7.794
7.788
7.779
7.640
7.619
7.428
7.410
7.406
7.403
7.396
7.388
7.379
7.362
7.344
7.324
7.260
1.615
1.569
1.282
1.253
0.000
2g
1.00
1.01
1.01
4.04
3.01
12.07
12.09
f1 (ppm)

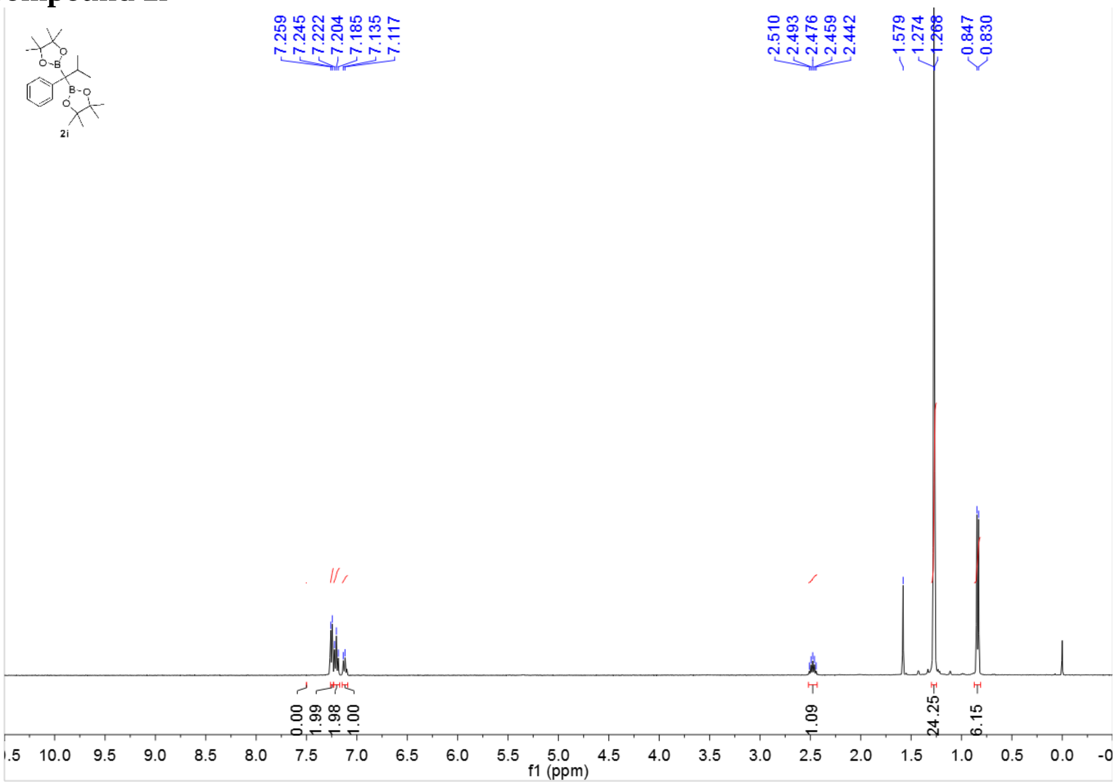

142.9
134.4
132.5
128.7
126.1
126.0
125.8
125.7
124.7
124.2
83.4
77.3
77.0
76.7
24.8
24.6
20.1
2g
f1 (ppm)

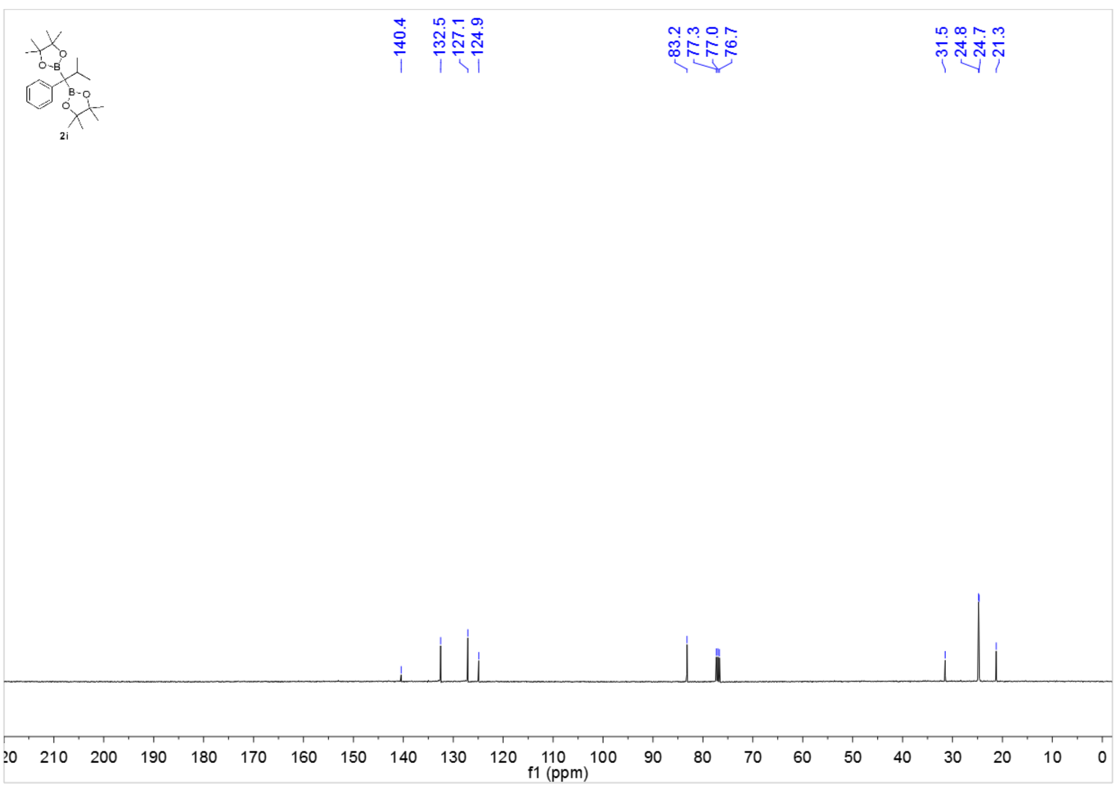
Compound 2h


7.364
7.361
7.343
7.322
7.254
7.243
7.224
7.205
7.108
7.090
7.071
2.002
1.984
1.966
1.947
1.643
1.253
1.247
0.785
0.766
0.748
2.18
2.00
1.00
2.11
24.30
3.13
f1 (ppm)
2h

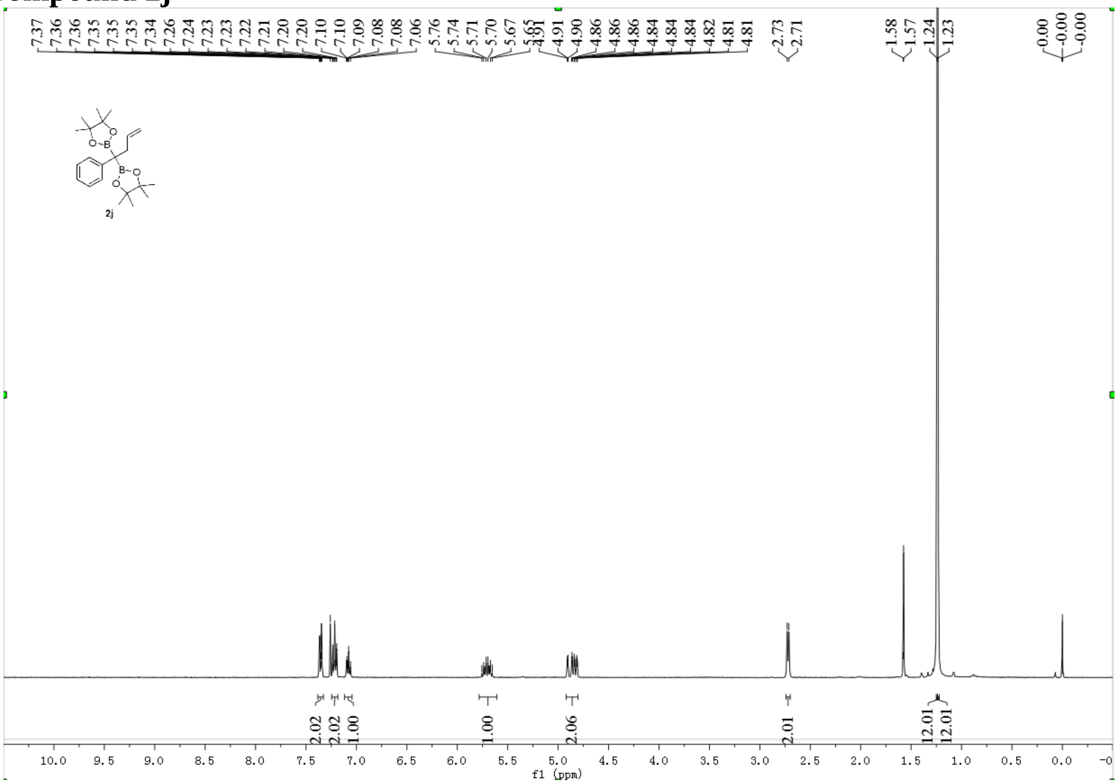

142.9
130.0
127.8
124.6
83.2
77.3
77.0
76.7
27.1
24.6
24.6
12.1
f1 (ppm)
2h

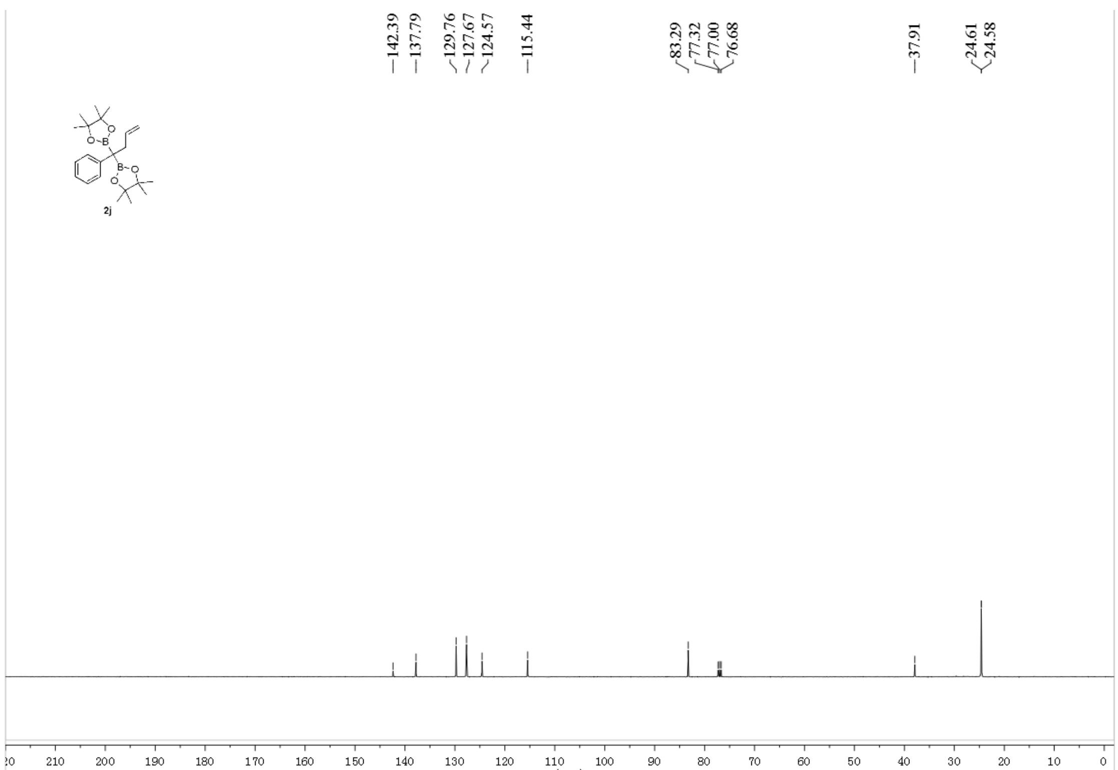
Compound 2i


2i
7.259
7.245
7.222
7.204
7.185
7.135
7.117
2.510
2.493
2.476
2.459
2.442
1.579
1.274
1.268
0.847
0.830
0.00
1.99
1.98
1.00
1.09
24.25
6.15
f1 (ppm)

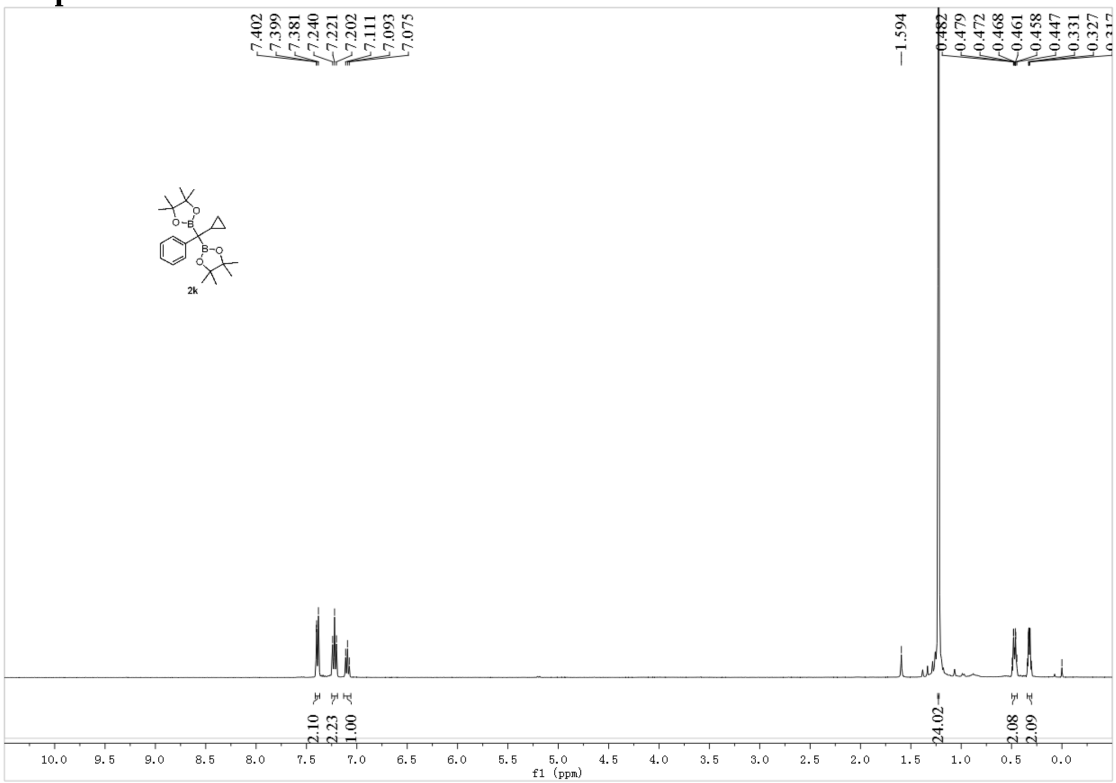

2i
140.4
132.5
127.1
124.9
83.2
77.3
77.0
76.7
31.5
24.8
24.7
21.3
f1 (ppm)

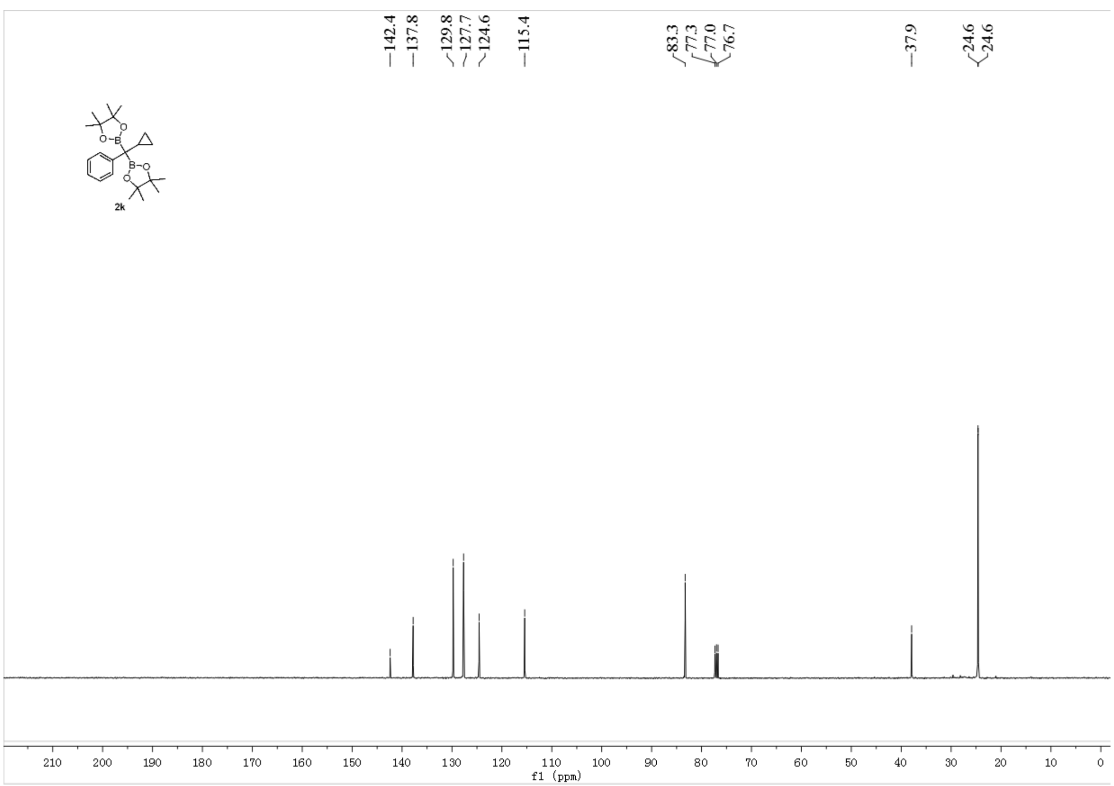
Compound 2j


7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.26
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.10
7.10
7.09
7.08
7.08
7.06
5.76
5.74
5.71
5.70
5.67
5.65
4.91
4.91
4.90
4.86
4.86
4.84
4.84
4.84
4.82
4.81
4.81
2.73
2.71
1.58
1.57
1.24
1.23
0.00
-0.00
-0.00
2j
2.02
2.02
1.00
1.00
2.06
2.01
12.01
12.01
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
f1 (ppm)

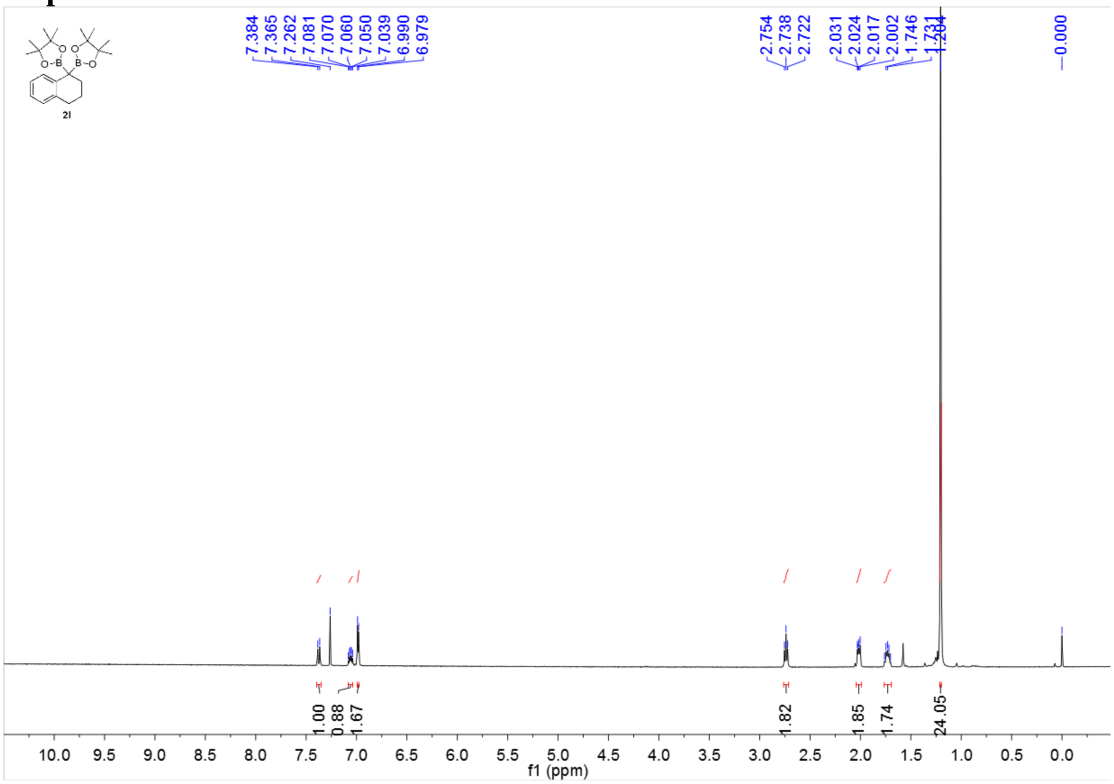

142.39
137.79
129.76
127.67
124.57
115.44
83.29
77.32
77.00
76.68
37.91
24.61
24.58
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound 2k

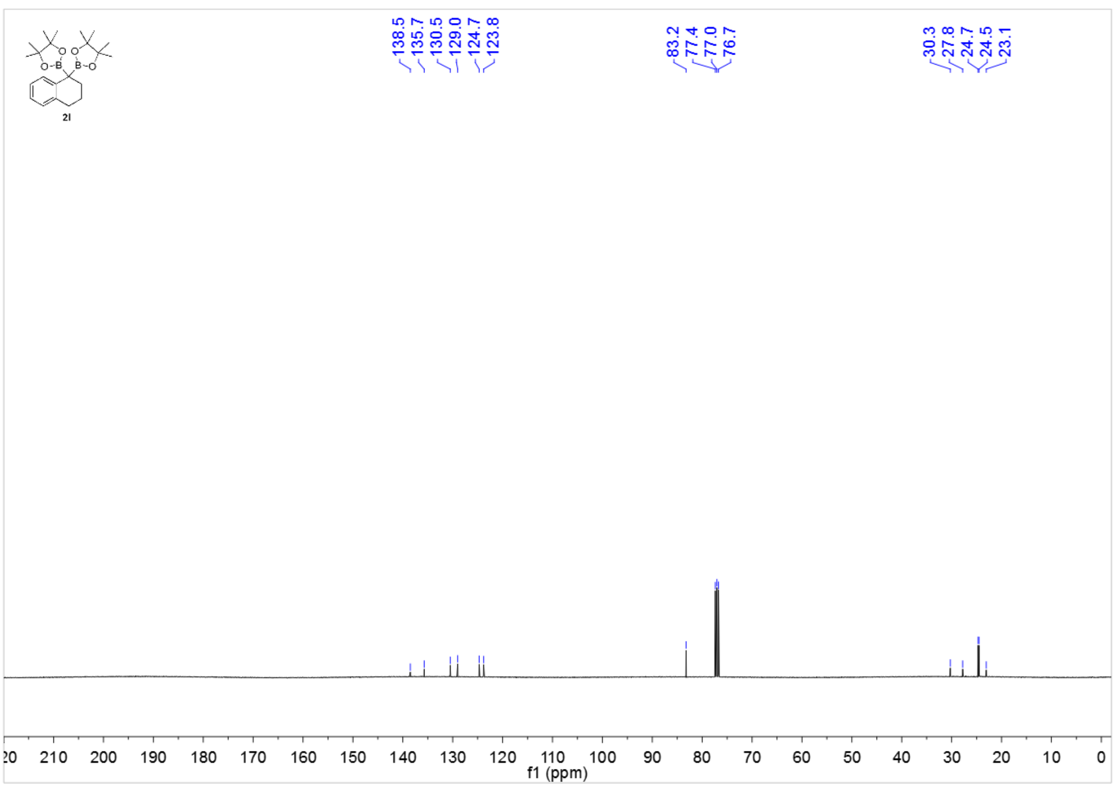




Compound 2l

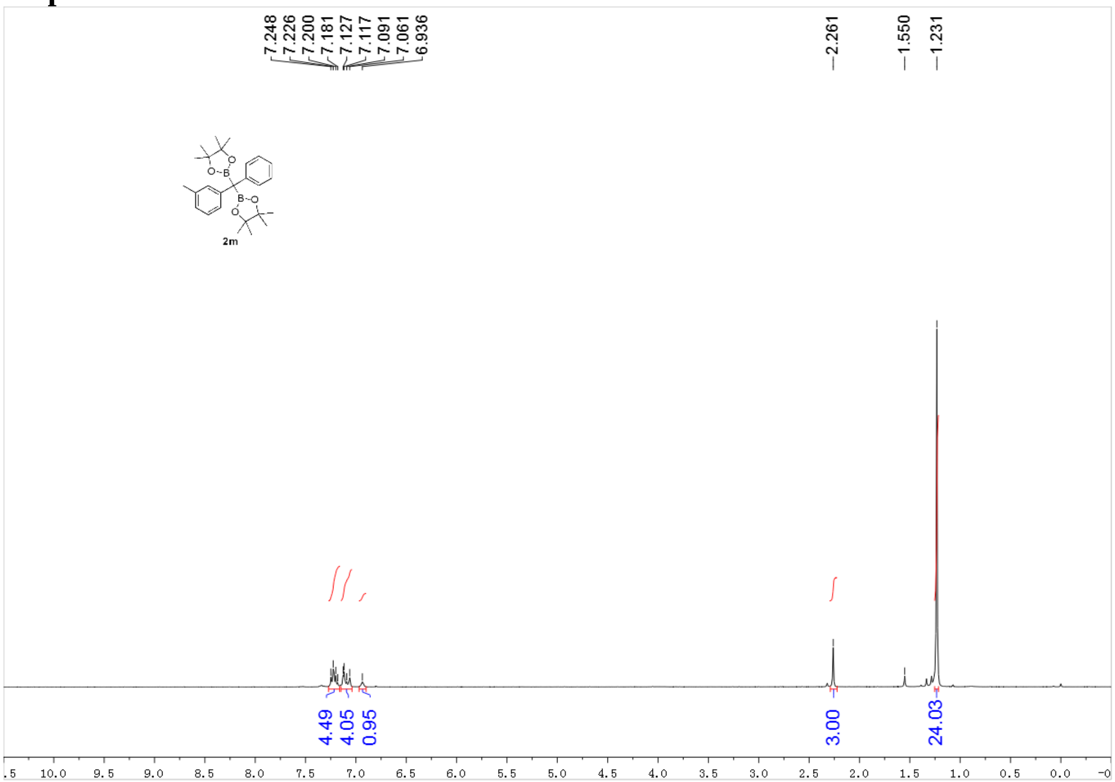


7.384
7.365
7.262
7.081
7.070
7.060
7.050
7.039
6.990
6.979
2.754
2.738
2.722
2.031
2.024
2.017
2.002
1.746
1.731
1.204
0.000
1.00
0.88
1.67
1.82
1.85
1.74
24.05
f1 (ppm)

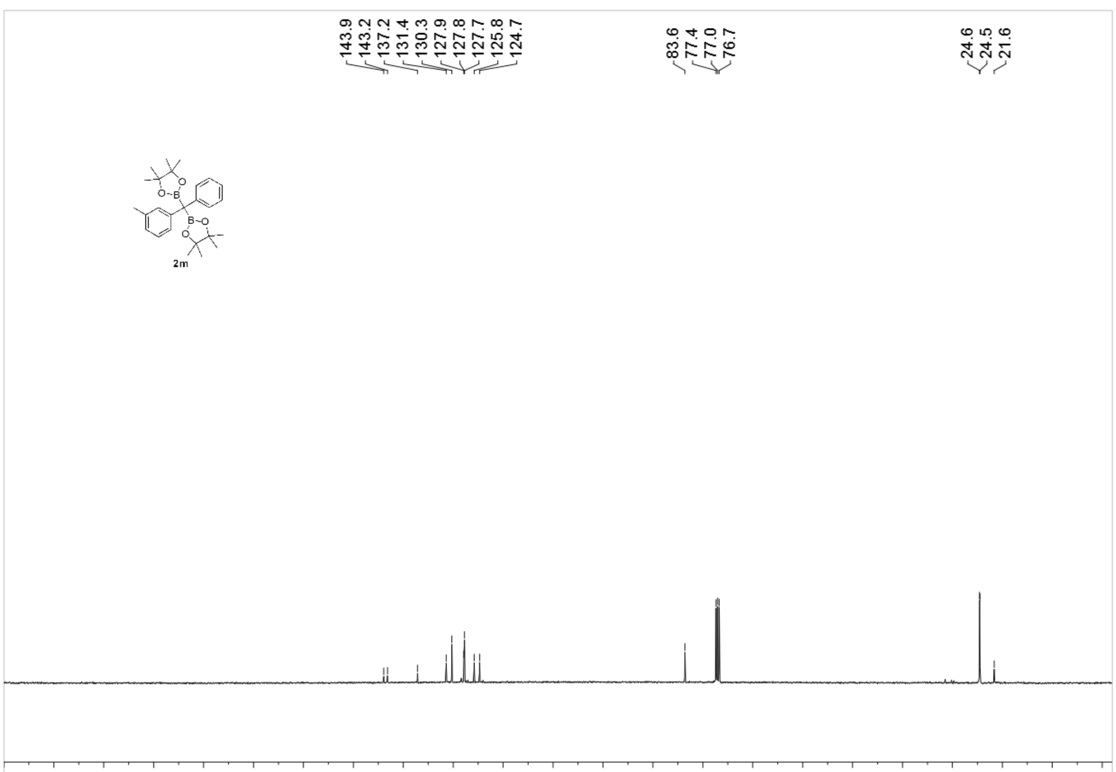


138.5
135.7
130.5
129.0
124.7
123.8
83.2
77.4
77.0
76.7
30.3
27.8
24.7
24.5
23.1
f1 (ppm)

Compound 2m

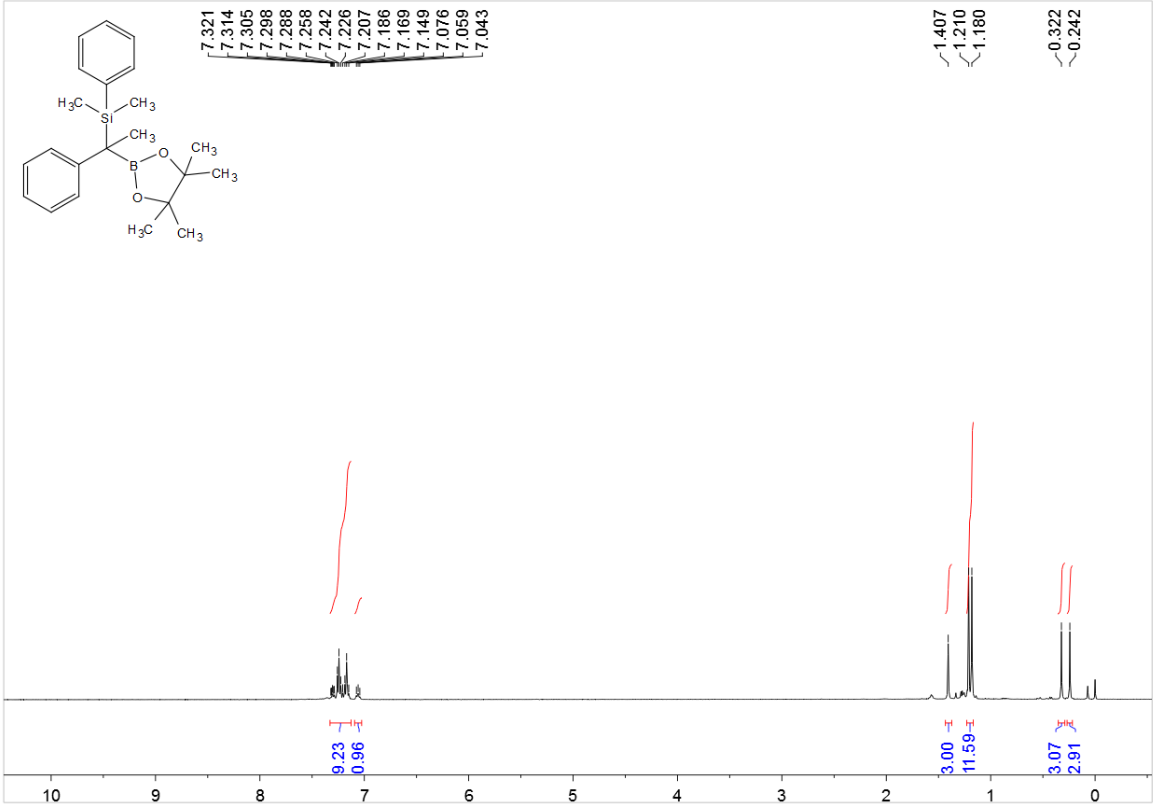


7.248
7.226
7.200
7.181
7.127
7.117
7.091
7.061
6.936
2.261
1.550
1.231
2m
4.49
4.05
0.95
3.00
24.03

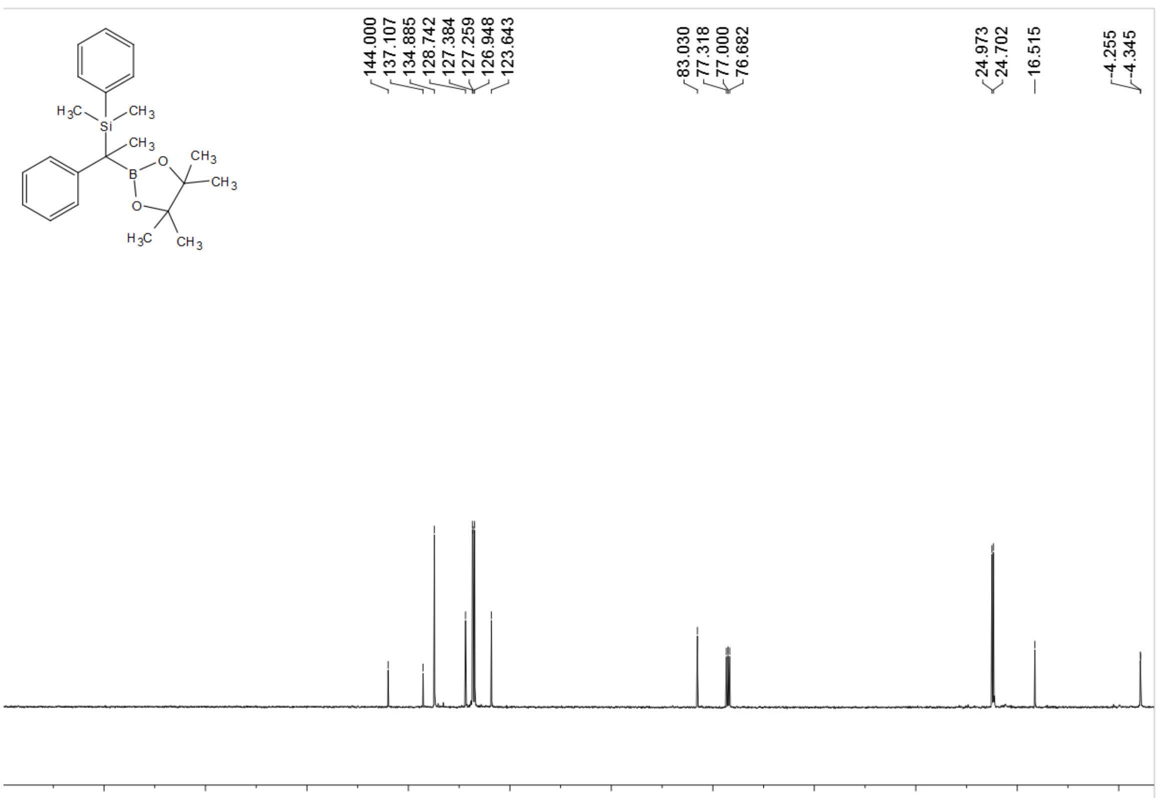


143.9
143.2
137.2
131.4
130.3
127.9
127.8
127.7
125.8
124.7
83.6
77.4
77.0
76.7
24.6
24.5
21.6
2m

Compound 3

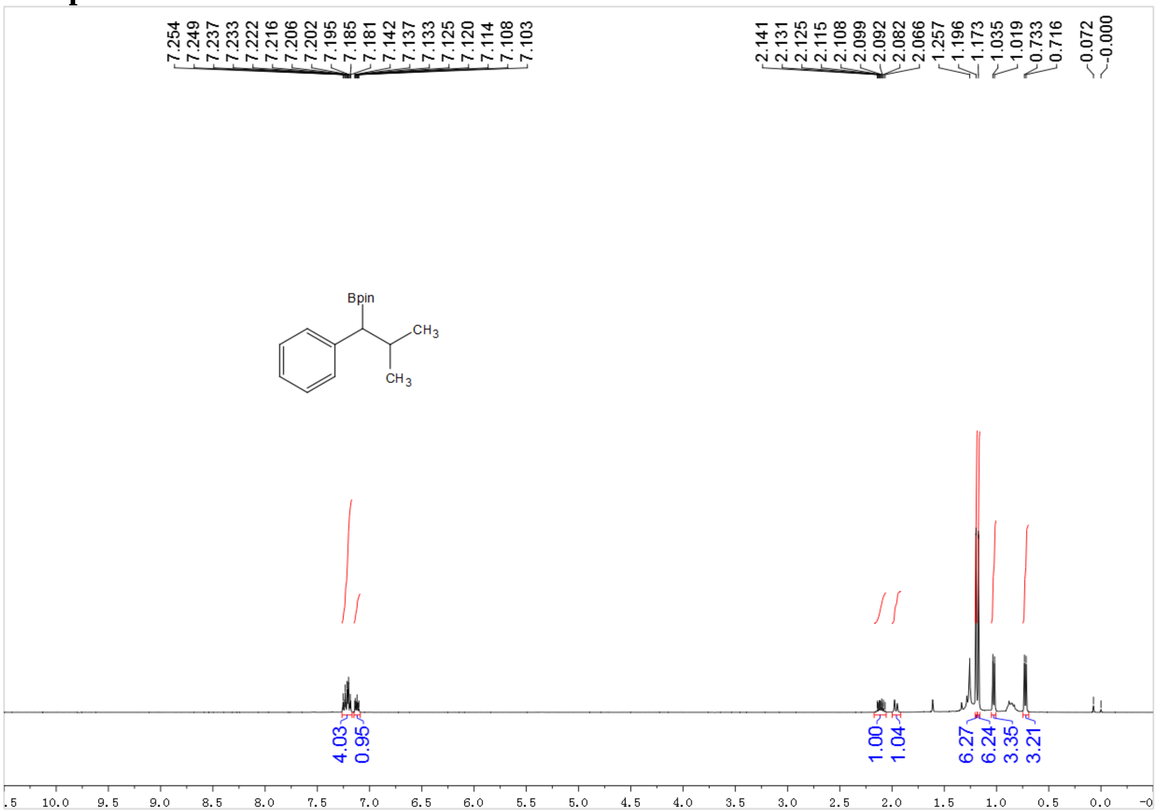


7.321
7.314
7.305
7.298
7.288
7.258
7.242
7.226
7.207
7.186
7.169
7.149
7.076
7.059
7.043
1.407
1.210
1.180
0.322
0.242
9.23
0.96
3.00
11.59
3.07
2.91
10
9
8
7
6
5
4
3
2
1
0

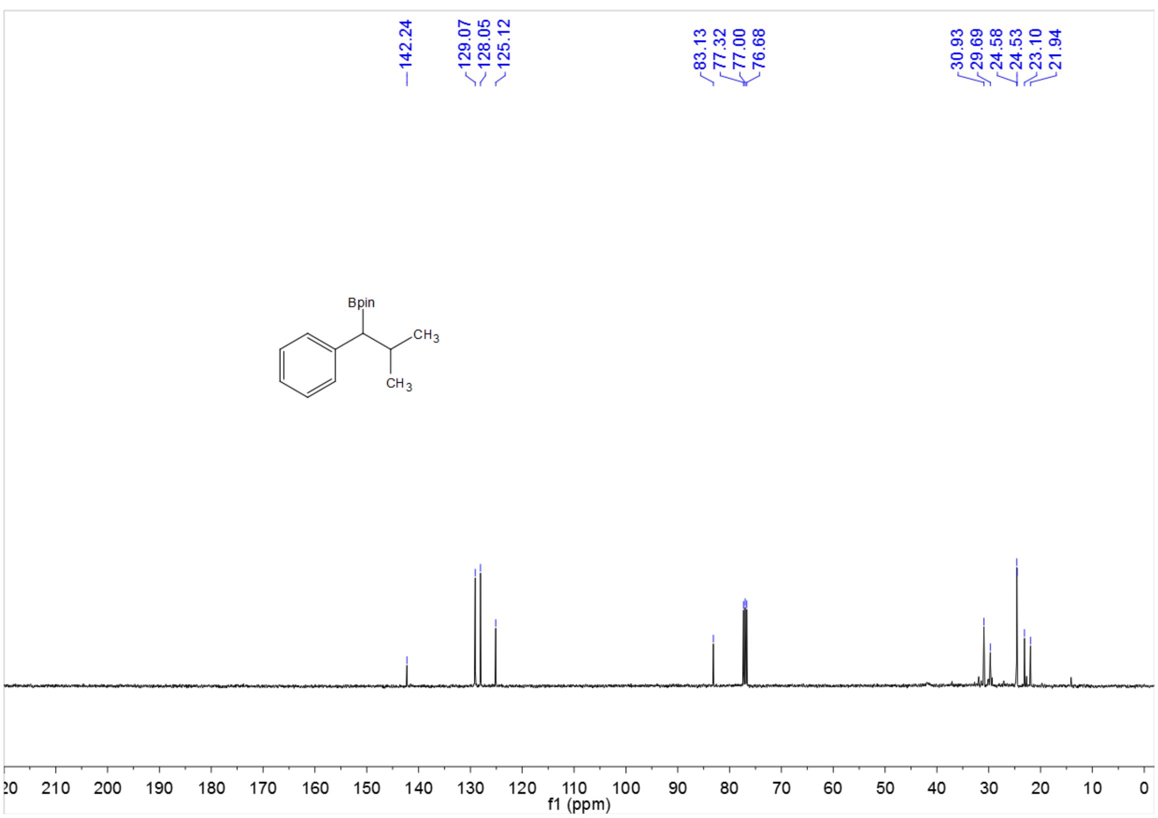


144.000
137.107
134.885
128.742
127.384
127.259
126.948
123.643
83.030
77.318
77.000
76.682
24.973
24.702
16.515
-4.255
-4.345
200
180
160
140
120
100
80
60
40
20
0

Compound 4

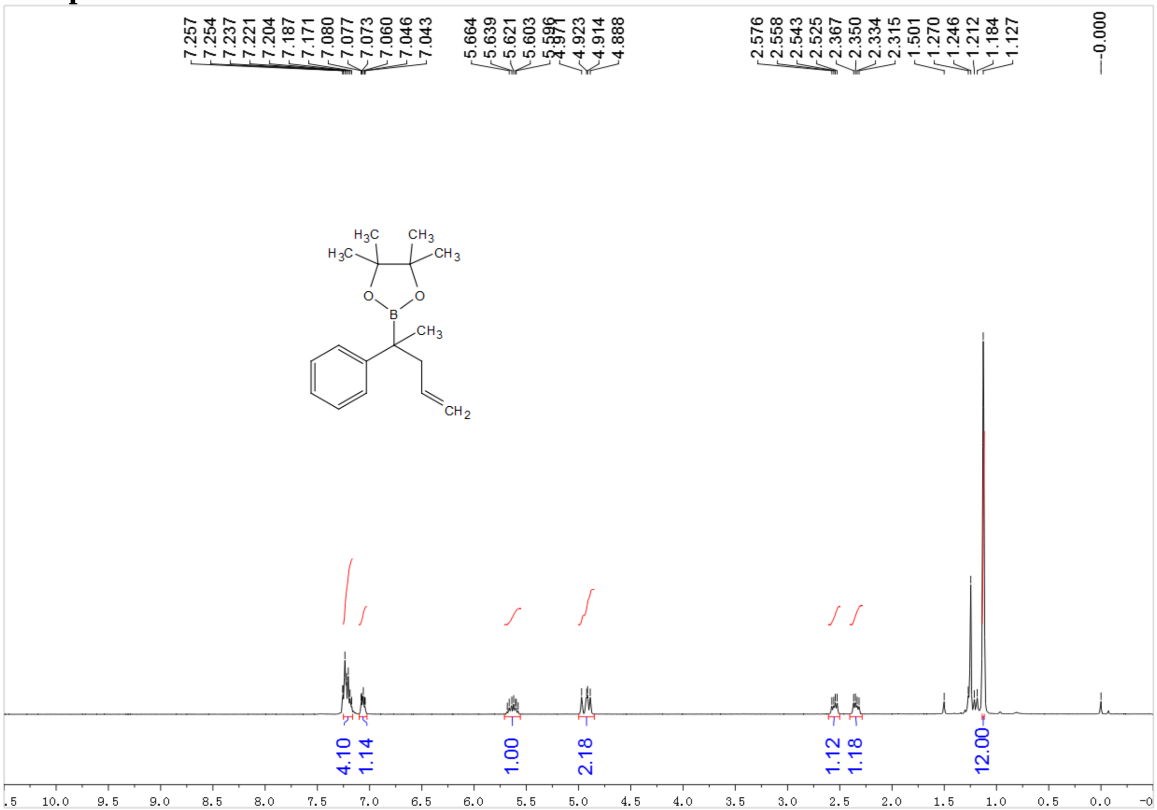


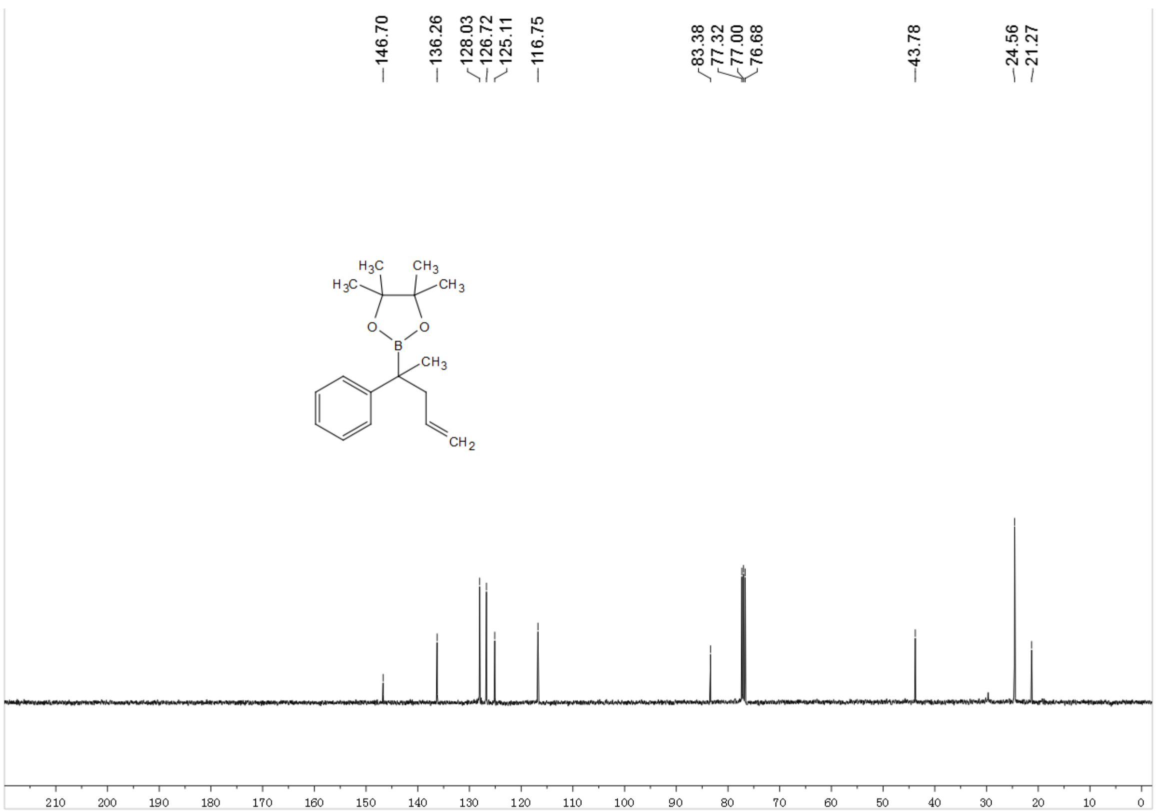
7.254
7.249
7.237
7.233
7.222
7.216
7.206
7.202
7.195
7.185
7.181
7.142
7.137
7.133
7.125
7.120
7.114
7.108
7.103
2.141
2.131
2.125
2.115
2.108
2.099
2.092
2.082
2.066
1.257
1.196
1.173
1.035
1.019
0.733
0.716
0.072
-0.000
Bpin
CH3
CH3
4.03
0.95
1.00
1.04
6.27
6.24
3.35
3.21



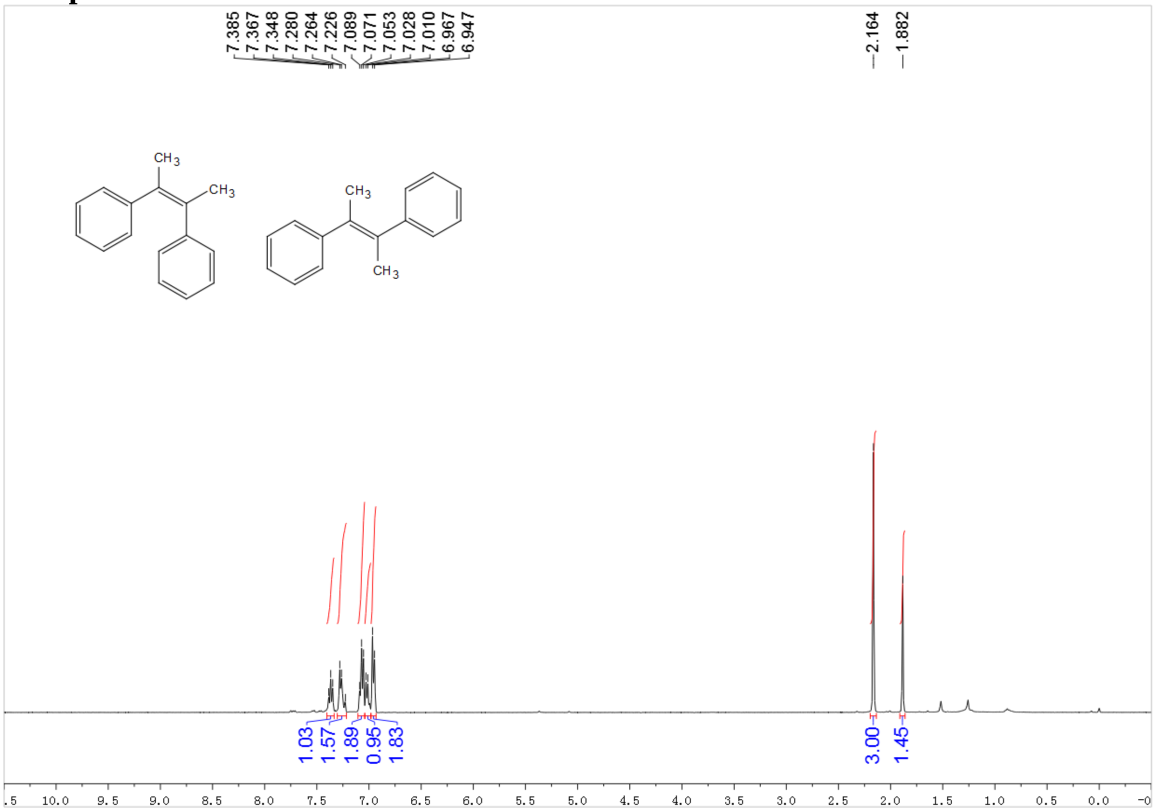
142.24
129.07
128.05
125.12
83.13
77.32
77.00
76.68
30.93
29.69
24.58
24.53
23.10
21.94
Bpin
CH3
CH3
f1 (ppm)

Compound 5

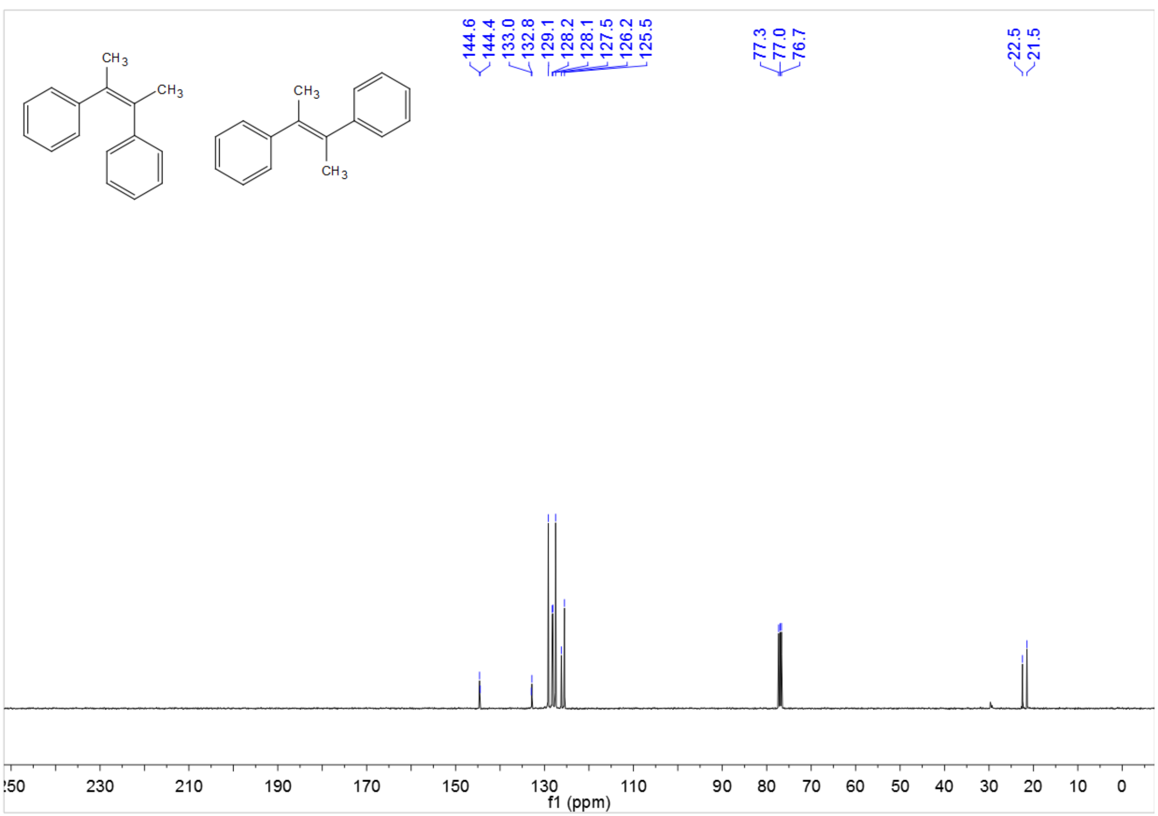




Compound 6



7.385
7.367
7.348
7.280
7.264
7.226
7.089
7.071
7.053
7.028
7.010
6.967
6.947
2.164
1.882
1.03
1.57
1.89
0.95
1.83
3.00
1.45



144.6
144.4
133.0
132.8
129.1
128.2
128.1
127.5
126.2
125.5
77.3
77.0
76.7
22.5
21.5
f1 (ppm)