Supporting Information

Base-Catalysed Reductive Relay Hydroboration of Allylic Alcohols with Pinacolborane to Form Alkylboronic Esters

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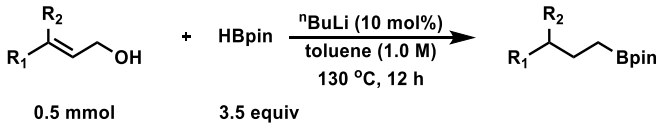
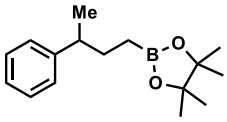
General Information

All the reactions were conducted under a N_2 atmosphere with standard vacuum-line techniques, and the glassware was dried in oven (140 °C) or flame-dried. Pinacolborane (HBpin) was purchased from Energy Chemical Co. Ltd and was stored in the refrigerator, n-Butyllithium (^{n}BuLi, 2.5 M in hexane) was purchased from Energy Chemical Co. Ltd and was stored in the refrigerator. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy. NMR spectra were recorded on an Agilent 400 MHz or 600MHz, Varian 400 MHz or Bruker 400 MHz spectrometers and were calibrated using residual solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). The carbons directly attached to the boron atoms were not detected in some cases due to quadrupolar relaxation. All IR spectra were taken on a BRUKER TENSOR 27 FT-IR spectrometer. EI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier, and ESI-HRMS spectra were obtained on a Thermo Fisher Scientific LTQ FT Ultra or an Agilent Technologies 6224 TOF LC/MS. GC-MS analysis were performed on a Shimadzu QP2010 SE using a DB-5MS column (30 m, 0.25 mm I.D.).

Base-Catalysed Reductive Relay Hydroboration of Allylic Alcohols



General procedure A (GPA): In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.5 mL, 1.0 M), HBpin (254 µL, 1.75 mmol, 3.5 equiv) and ^{n}BuLi (2.5 M in hexane, 20µL, 0.05 mmol, 10 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature (rt). The allylic alcohol substrate (0.5 mmol) was then added dropwise and the reaction mixture was stirred at 130 ^{o}C for 12h. After completion of the reaction, the reaction mixture was allowed to cool to rt and quenched by HCl (1.0 M in EtOAc). Then the reaction mixture was directly filtered through a short pad of silica gel, eluting with EtOAc. The solvent was removed in vacuo. The linear/branched ratios of crude product mixtures were determined at this stage by ^{1}H NMR and GC-MS analysis. The product was purified by chromatography on silica gel.



4,4,5,5-tetramethyl-2-(3-phenylbutyl)-1,3,2-dioxaborolane (3a)

Following **GPA** using 3-phenylbut-2-en-1-ol (74 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 92% yield (119 mg).

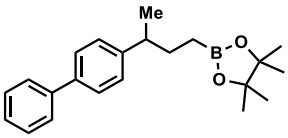
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 2H), 7.17 (m, 3H), 2.63 (m, 1H), 1.69 (m, 2H), 1.25 (m, 15H), 0.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 128.3, 127.3, 125.8, 82.9, 42.3, 32.8, 24.9, 21.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.34 (s).

IR (neat, cm^{-1}) 1737, 1371, 1235, 1145, 1044, 846, 701.

HRMS (ESI) calculated for $C_{16}H_{29}BNO_2$ $[M+NH_4]^+$ *m/z* 277.2321, found 277.2322.



2-(3-([1,1'-biphenyl]-4-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

Following **GPA** using 3-([1,1'-biphenyl]-4-yl)but-2-en-1-ol (112 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 97% yield (163 mg).

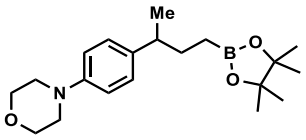
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.67 (m, 1H), 1.71 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.21 (s, 12H), 0.75 (m, 2H).

^{13}C NMR (101 MHz, cdcl$_3$) δ 146.7, 141.3, 138.8, 128.8, 127.7, 127.07, 127.06, 127.0, 82.9, 41.9, 32.8, 24.9, 21.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.93 (s).

IR (neat, cm^{-1}) 1732, 1372, 1239, 1044, 909, 728, 648.

HRMS (ESI) calculated for $C_{22}H_{33}BNO_2$ $[M+NH_4]^+$ *m/z* 353.2635, found 353.2629.



4-(4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl)morpholine (3c)

Following **GPA** using 3-(4-morpholinophenyl)but-2-en-1-ol (117 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (1-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 88% yield (150 mg).

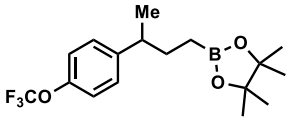
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 3.84 (m, 4H), 3.11 (m, 4H), 2.55 (m, 1H), 1.63 (m, 2H), 1.23 (m, 15H), 0.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 139.3, 127.8, 115.8, 82.8, 67.1, 49.8, 41.3, 32.9, 24.90, 24.89, 21.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.13 (s).

IR (neat, cm^{-1}) 2959, 1612, 1514, 1368, 1314, 1143, 928.

HRMS (ESI) calculated for $C_{20}H_{33}BNO_3$ $[M+H]^+$ *m/z* 345.2584, found 345.2583.



4,4,5,5-tetramethyl-2-(3-(4-(trifluoromethoxy)phenyl)butyl)-1,3,2-dioxaborolane (3d)

Following **GPA** using 3-(4-(trifluoromethoxy)phenyl)but-2-en-1-ol (116 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 88% yield (151 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.63 (m, 1H), 1.66 (m, 2H), 1.22 (d, *J* = 4.5 Hz, 15H), 0.68 (m, 2H).

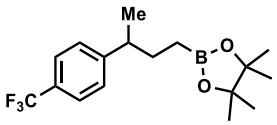
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 146.3, 128.5, 120.9, 120.7 (q, *J* = 257.6 Hz), 83.1, 41.8, 32.8, 24.9, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.95 (s).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.91 (s).

IR (neat, cm^{-1}) 1509, 1370, 1254, 1219, 1143, 967, 847.

HRMS (EI) calculated for $C_{17}H_{24}BF_3O_3$ $[M]^+$ *m/z* 343.1807, found 343.1799.



4,4,5,5-tetramethyl-2-(3-(4-(trifluoromethyl)phenyl)butyl)-1,3,2-dioxaborolane (3e)

Following **GPA** using 3-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (108 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 96% yield (157 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.69 (m, 1H), 1.69 (m, 2H), 1.23 (m, 15H), 0.67 (m, 2H).

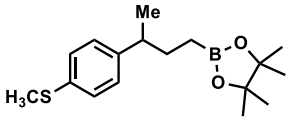
^{13}C N(MR (101 MHz, $CDCl_3$) δ 151.6, 128.0 (q, *J* = 32.3 Hz), 127.5, 125.12 (q, *J* = 3.7 Hz), 127.4 (q, *J* = 272.7 Hz), 82.9, 42.1, 32.5, 24.75, 24.74 , 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28 (s).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.96 (s).

IR (neat, cm^{-1}) 1618, 1370, 1322, 1162, 1119, 1067, 840.

HRMS (EI) calculated for $C_{17}H_{24}O_2F_3B$ $[M]^+$ *m/z* 327.1858, found 327.1865.



4,4,5,5-tetramethyl-2-(3-(4-(methylthio)phenyl)butyl)-1,3,2-dioxaborolane (3f)

Following **GPA** using 3-(4-(methylthio)phenyl)but-2-en-1-ol (97 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 93% yield (142 mg).

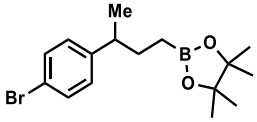
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.59 (m, 1H), 2.45 (s, 3H), 1.64 (m, 2H), 1.21 (m, 15H), 0.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 135.1, 127.8, 127.2, 82.9, 41.7, 32.7, 24.89, 24.88, 21.7, 16.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.81 (s).

IR (neat, cm^{-1}) 1494, 1368, 1315, 1142, 966, 817, 730.

HRMS (ESI) calculated for $C_{17}H_{28}BO_2S$ $[M+H]^+$ *m/z* 306.1934, found 306.1930.

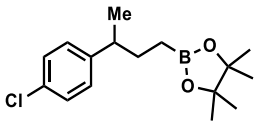


2-(3-(4-bromophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)[3]

Following **GPA** using 3-(4-bromophenyl)but-2-en-1-ol (114 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 85% yield (143 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 2.58 (m, 1H), 1.63 (m, 2H), 1.20 (m, 15H), 0.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 131.3, 129.1, 119.4, 83.0, 41.8, 32.6, 24.9, 24.9, 21.7.



2-(3-(4-chlorophenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

Following **GPA** using 3-(4-chlorophenyl)but-2-en-1-ol (91 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 91% yield (134 mg).

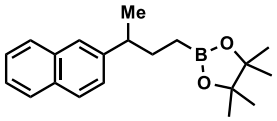
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 2.60 (m, 1H), 1.64 (m, 2H), 1.21 (m, 15H), 0.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 131.4, 128.6, 128.4, 83.0, 41.7, 32.7, 24.91, 24.89, 21.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.99 (s).

IR (neat, cm^{-1}) 1736, 1372, 1236, 1044, 914, 730, 634.

HRMS (EI) calculated for $C_{16}H_{24}BClO_2$ $[M]^+$ *m/z* 293.1594, found 293.1604.

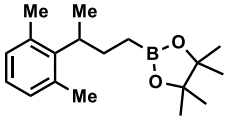


4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)butyl)-1,3,2-dioxaborolane (3i)[3]

Following **GPA** using 3-(naphthalen-2-yl)but-2-en-1-ol (99 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 90% yield (138 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 8.1 Hz, 3H), 7.59 (s, 1H), 7.38 (m, 3H), 2.79 (m, 1H), 1.76 (m, 2H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.20 (s, 12H), 0.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 133.7, 132.3, 127.9, 127.7, 126.2, 125.8, 125.5, 125.1, 83.0, 42.4, 32.7, 24.9, 24.9, 21.8.



2-(3-(2,6-dimethylphenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

Following **GPA** using 3-(2,6-dimethylphenyl)but-2-en-1-ol (88 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 99% yield (145 mg).

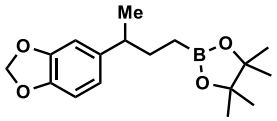
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 3H), 3.19 (m, 1H), 2.35 (m, 6H), 1.82 (m, 2H), 1.29 (d, *J* = 7.3 Hz, 3H), 1.22 (s, 12H), 0.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 136.5, 130.4, 125.5, 83.0, 37.5, 29.3, 24.97, 24.95, 21.9, 18.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.35 (s).

IR (neat, cm^{-1}) 1465, 1370, 1317, 1143, 966, 846, 732.

HRMS (ESI) calculated for $C_{18}H_{33}BNO_2$ $[M+NH_4]^+$ *m/z* 305.2635, found 305.2632.



2-(3-(benzo[d][1,3]dioxol-5-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)

Following **GPA** using 3-(benzo[d][1,3]dioxol-5-yl)but-2-en-1-ol (96 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 91% yield (138 mg).

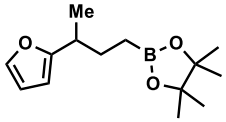
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (m, 2H), 6.61 (m, 1H), 5.90 (s, 2H), 2.55 (m, 1H), 1.61 (m, 2H), 1.20 (m, 15H), 0.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.6, 141.7, 120.2, 108.1, 107.5, 100.8, 83.0, 42.1, 32.9, 24.9, 22.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.48 (s).

IR (neat, cm^{-1}) 1485, 1439, 1368, 1234, 1143, 1038, 808.

HRMS (ESI) calculated for $C_{17}H_{29}BNO_4$ $[M+NH_4]^+$ *m/z* 321.2220, found 321.2224.



2-(3-(furan-2-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)

Following **GPA** using 3-(furan-2-yl)but-2-en-1-ol (69 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 83% yield (104 mg).

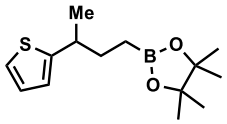
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 1H), 6.25 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.95 (d, *J* = 3.1 Hz, 1H), 2.76 (m, 1H), 1.77 (m, 1H), 1.62 (m, 1H), 1.22 (m, 15H), 0.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 140.6, 109.9, 103.7, 83.0, 35.3, 30.2, 24.9, 18.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.40 (s).

IR (neat, cm^{-1}) 2976, 1456, 1369, 1316, 1143, 846, 728.

HRMS (ESI) calculated for $C_{14}H_{24}BO_3$ $[M+H]^+$ *m/z* 250.1849, found 250.1847.



4,4,5,5-tetramethyl-2-(3-(thiophen-2-yl)butyl)-1,3,2-dioxaborolane (3m)

Following **GPA** using 3-(thiophen-2-yl)but-2-en-1-ol (77 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 86% yield (114 mg).

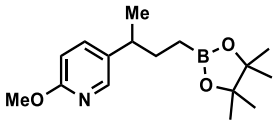
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (m, 1H), 6.89 (m, 1H), 6.77 (m, 1H), 2.96 (m, 1H), 1.71 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.22 (s, 12H), 0.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 126.4, 122.7, 122.4, 83.0, 37.5, 33.8, 24.9, 22.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.91 (s).

IR (neat, cm^{-1}) 2976, 1456, 1368, 1314, 1143, 908, 690.

HRMS (ESI) calculated for $C_{13}H_{21}BNO_2S$ $[M+H-CH3]^+$ *m/z* 266.1621, found 266.1622.



2-methoxy-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)pyridine (3n)

Following **GPA** using 3-(6-methoxypyridin-3-yl)but-2-en-1-ol (90 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (2-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 92% yield (133 mg).

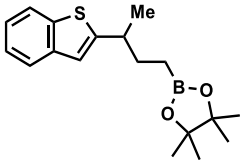
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.59 (m, 1H), 1.64 (m, 2H), 1.22 (m, 15H), 0.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 145.4, 137.4, 135.1, 110.6, 83.0, 53.3, 38.8, 32.6, 24.9, 24.87, 21.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.34 (s).

IR (neat, cm^{-1}) 2976, 1606, 1493, 1372, 1320, 1145, 831.

HRMS (ESI) calculated for $C_{16}H_{27}BNO_3$ $[M+H]^+$ *m/z* 291.2115, found 291.2118.



2-(3-(benzo[b]thiophen-2-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)

Following **GPA** using 3-(benzo[b]thiophen-2-yl)but-2-en-1-ol (102 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 73% yield (115 mg).

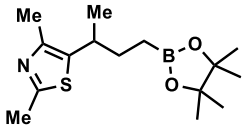
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.26 (m, 2H), 7.01 (s, 1H), 3.02 (m, 1H), 1.79 (m, 2H), 1.37 (d, *J* = 6.9 Hz, 3H), 1.23 (s, 12H), 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 140.0, 138.9, 123.9, 123.2, 122.7, 122.2, 119.3, 82.9, 38.3, 33.1, 24.8, 22.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.39 (s).

IR (neat, cm^{-1}) 2974, 1456, 1370, 1317, 1144, 968, 744.

HRMS (EI) calculated for $C_{18}H_{25}BO_2S$ $[M]^+$ m/z 315.1705, found 315.1704.



2,4-dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)thiazole (3p)

Following **GPA** using 3-(2,4-dimethylthiazol-5-yl)but-2-en-1-ol (92 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 83% yield (122 mg).

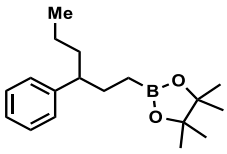
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (m, 1H), 2.60 (s, 3H), 2.29 (s, 3H), 1.69 (m, 1H), 1.56 (m, 1H), 1.22 (m, 15H), 0.73 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 145.9, 138.0, 82.9, 34.6, 33.9, 24.78, 24.76, 23.2, 19.1, 14.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.71 (s).

IR (neat, cm^{-1}) 2976, 1371, 1318, 1182, 1144, 967, 846.

HRMS (EI) calculated for $C_{15}H_{26}BNO_2S$ $[M]^+$ m/z 294.1814, found 294.1817.



4,4,5,5-tetramethyl-2-(3-phenylhexyl)-1,3,2-dioxaborolane (3q)

Following **GPA** using 3-phenylhex-2-en-1-ol (88 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (2-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 97% yield (139 mg).

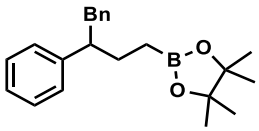
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 3H), 2.44 (m, 1H), 1.77 (m, 1H), 1.59 (m, 3H), 1.24 (m, 14H), 0.84 (t, *J* = 7.3 Hz, 3H), 0.64 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 128.2, 127.9, 125.8, 82.9, 48.2, 38.7, 31.3, 24.93, 24.89, 20.9, 14.3.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.62 (s).

IR (neat, cm^{-1}) 1452, 1371, 1315, 1143, 967, 846, 699.

HRMS (ESI) calculated for $C_{18}H_{33}BNO_2$ $[M+NH_4]^+$ *m/z* 305.2635, found 305.2631.



2-(3,4-diphenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)

Following **GPA** using 3,4-diphenylbut-2-en-1-ol (112 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 87% yield (146 mg).

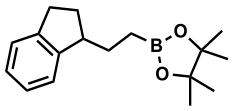
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (m, 8H), 7.01 (m, 2H), 2.93 (m, 1H), 2.84 (m, 1H), 2.76 (m, 1H), 1.84 (m, 1H), 1.70 (m, 1H), 1.19 (s, 12H), 0.64 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.9, 129.1, 128.1, 128.0, 127.96, 125.9, 125.6, 82.9, 50.3, 43.3, 30.1, 24.86, 24.81.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.33 (s).

IR (neat, cm^{-1}) 1735, 1372, 1235, 1044, 915, 847, 731.

HRMS (ESI) calculated for $C_{22}H_{33}BNO_2$ $[M+NH_4]^+$ *m/z* 353.2635, found 353.2638.

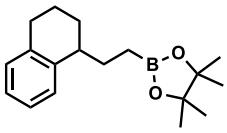


2-(2-(2,3-dihydro-1H-inden-1-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)[3]

Following **GPA** using 2-(2,3-dihydro-1H-inden-1-ylidene)ethan-1-ol (80 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 82% yield (111 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H), 7.13 (m, 2H), 3.05 (m, 1H), 2.91 (m, 1H), 2.80 (m, 1H), 2.26 (m, 1H), 1.94 (m, 1H), 1.69 (m, 1H), 1.51 (m, 1H), 1.24 (s, 12H), 0.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 144.2, 126.3, 126.0, 124.5, 124.0, 83.1, 47.1, 31.8, 31.4, 29.3, 25.0, 24.9.

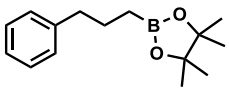


4,4,5,5-tetramethyl-2-(2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethyl)-1,3,2-dioxaborolane (3t)[3]

Following **GPA** using 2-(3,4-dihydronaphthalen-1(2H)-ylidene)ethan-1-ol (87 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 70% yield (100 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.3 Hz, 1H), 7.07 (m, 3H), 2.70 (m, 3H), 1.74 (m, 6H), 1.24 (s, 12H), 0.87 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.1, 129.1, 129.0, 125.5, 125.5, 83.1, 39.7, 31.2, 29.9, 26.7, 25.0, 24.9, 19.7.

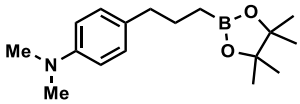


4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (3u)[1]

Following **GPA** using (E)-3-phenylprop-2-en-1-ol (67 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 57% yield (70 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.16 (m, 3H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.73 (m, 2H), 1.24 (s, 12H), 0.82 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 128.7, 128.3, 125.7, 83.1, 38.7, 26.3, 25.0.



N,N-dimethyl-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline (3v)

Following **GPA** using (E)-3-(4-(dimethylamino)phenyl)prop-2-en-1-ol (89 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (2-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 67% yield (97 mg).

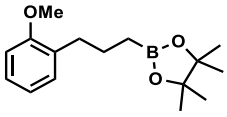
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 2.89 (s, 6H), 2.51 (m, 2H), 1.68 (m, 2H), 1.23 (s, 12H), 0.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 131.2, 129.2, 113.1, 82.9, 41.1, 37.7, 26.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.42 (s).

IR (neat, cm^{-1}) 1615, 1519, 1445, 1369, 1315, 1142, 730.

HRMS (ESI) calculated for $C_{17}H_{29}BNO_2$ $[M+H]^+$ *m/z* 289.2322, found 289.2321.

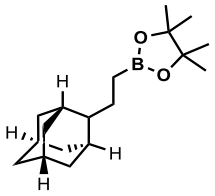


2-(3-(2-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3w)[2]

Following **GPA** using (E)-3-(2-methoxyphenyl)prop-2-en-1-ol (82 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (2-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 72% yield (99 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (m, 2H), 6.84 (m, 2H), 3.79 (s, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.69 (m, 2H), 1.24 (s, 12H), 0.83 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 131.2, 130.1, 126.9, 120.3, 110.2, 83.0, 55.3, 32.8, 25.0, 24.6.



2-(2-((1r,3r,5r,7r)-adamantan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3x)

Following **GPA** using 2-((1r,3r,5R,7S)-adamantan-2-ylidene)ethan-1-ol (89 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 93% yield (134 mg).

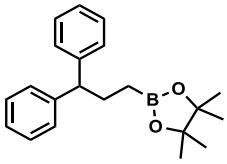
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (m, 12H), 1.54 (t, *J* = 6.4 Hz, 3H), 1.45 (d, *J* = 12.2 Hz, 2H), 1.25 (s, 12H), 0.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 46.9, 39.5, 38.6, 31.7, 31.6, 28.5, 28.2, 26.7, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.04 (s).

IR (neat, cm^{-1}) 2981, 1737, 1372, 1235, 1044, 917, 732.

HRMS (EI) calculated for $C_{18}H_{31}BO_2$ $[M]^+$ *m/z* 289.2453, found 289.2458.

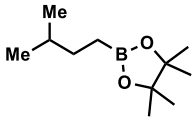


2-(3,3-diphenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3y)[3]

Following **GPA** using 3,3-diphenylprop-2-en-1-ol (105 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 93% yield (150 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 8H), 7.20 (m, 2H), 3.89 (t, *J* = 7.6 Hz, 1H), 2.20 (m, 2H), 1.27 (s, 12H), 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 128.4, 128.1, 126.0, 83.0, 53.8, 30.1, 24.9.

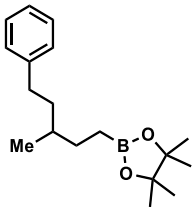


2-isopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3z)[4]

Following GP using 3-methylbut-2-en-1-ol (43 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 78% yield (77 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (m, 1H), 1.29 (m, 14H), 0.86 (d, *J* = 6.6 Hz, 6H), 0.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 33.0, 30.3, 24.9, 22.3.

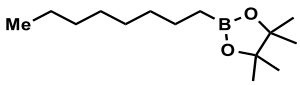


4,4,5,5-tetramethyl-2-(3-methyl-5-phenylpentyl)-1,3,2-dioxaborolane (4a)[3]

Following **GPA** using 3-methyl-5-phenylpent-2-en-1-ol (88 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 99% yield (142 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.14 (m, 3H), 2.60 (m, 2H), 1.65 (m, 1H), 1.45 (m, 3H), 1.29 (m, 1H), 1.22 (s, 12H), 0.92 (d, *J* = 6.2 Hz, 3H), 0.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 128.4, 128.2, 125.5, 82.9, 38.6, 34.6, 33.5, 30.9, 24.9, 19.2.

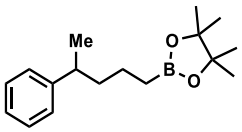


4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (4b)[5]

Following **GPA** using (E)-oct-2-en-1-ol (64 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 86% yield (103 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (m, 2H), 1.25 (d, *J* = 7.2 Hz, 22H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 32.4, 31.9, 29.4, 29.2, 24.8, 24.0, 22.7, 14.1.



4,4,5,5-tetramethyl-2-(4-phenylpentyl)-1,3,2-dioxaborolane (4c)

Following **GPA** using (E)-4-phenylpent-2-en-1-ol (81 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 93% yield (107 mg).

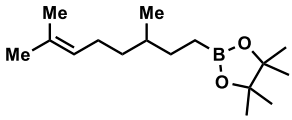
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.16 (m, 3H), 2.68 (m, 1H), 1.58 (m, 2H), 1.34 (m, 2H), 1.21 (d, *J* = 5.0 Hz, 15H), 0.75 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 128.3, 127.1, 125.8, 82.9, 41.3, 39.8, 24.93, 24.91, 22.5, 22.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.89 (s).

IR (neat, cm^{-1}) 2979, 1736, 1373, 1317, 1235, 1044, 731.

HRMS (EI) calculated for $C_{17}H_{27}BO_2$ $[M]^+$ *m/z* 273.2140, found 273.2136.



2-(3,7-dimethyloct-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4d)

Following **GPA** using geraniol (0.5 mmol, 1.0 equiv.), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide the title compound as a colorless liquid in 79% yield (105 mg).

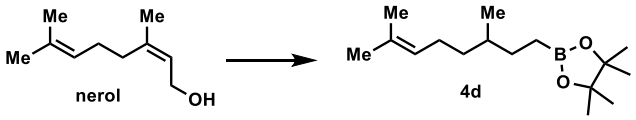
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.1 (m, 1H), 2.0 (m, 2H), 1.7 (s, 3H), 1.6 (s, 3H), 1.4 (m, 4H), 1.2 (s, 12H), 1.1 (m, 1H), 0.9 (d, *J* = 6.4 Hz, 3H), 0.7 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.9, 125.1, 82.8, 36.7, 34.6, 30.9, 25.7, 25.6, 24.8, 24.8, 19.1, 17.6.

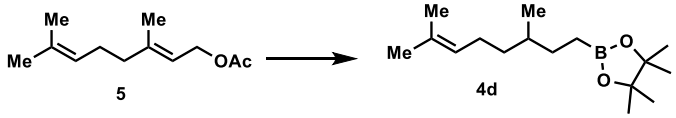
^{11}B NMR (128 MHz, $CDCl_3$) δ 34.73 (s).

IR (neat, cm^{-1}) 1458, 1371, 1316, 1144, 967, 847.

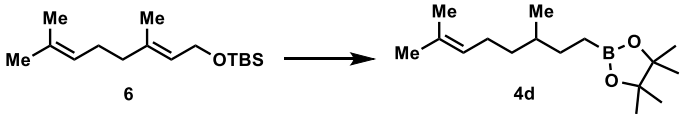
HRMS (ESI) calculated for $C_{16}H_{32}BO_2$ $[M+H]^+$ *m/z* 266.2526, found 266.251.



Following **GPA** using nerol (0.5 mmol, 1.0 equiv.), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide **4d** in 64% yield (85 mg).



Following **GPA** using **5** (0.5 mmol, 1.0 equiv.), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide **4d** in 55% yield (73 mg).

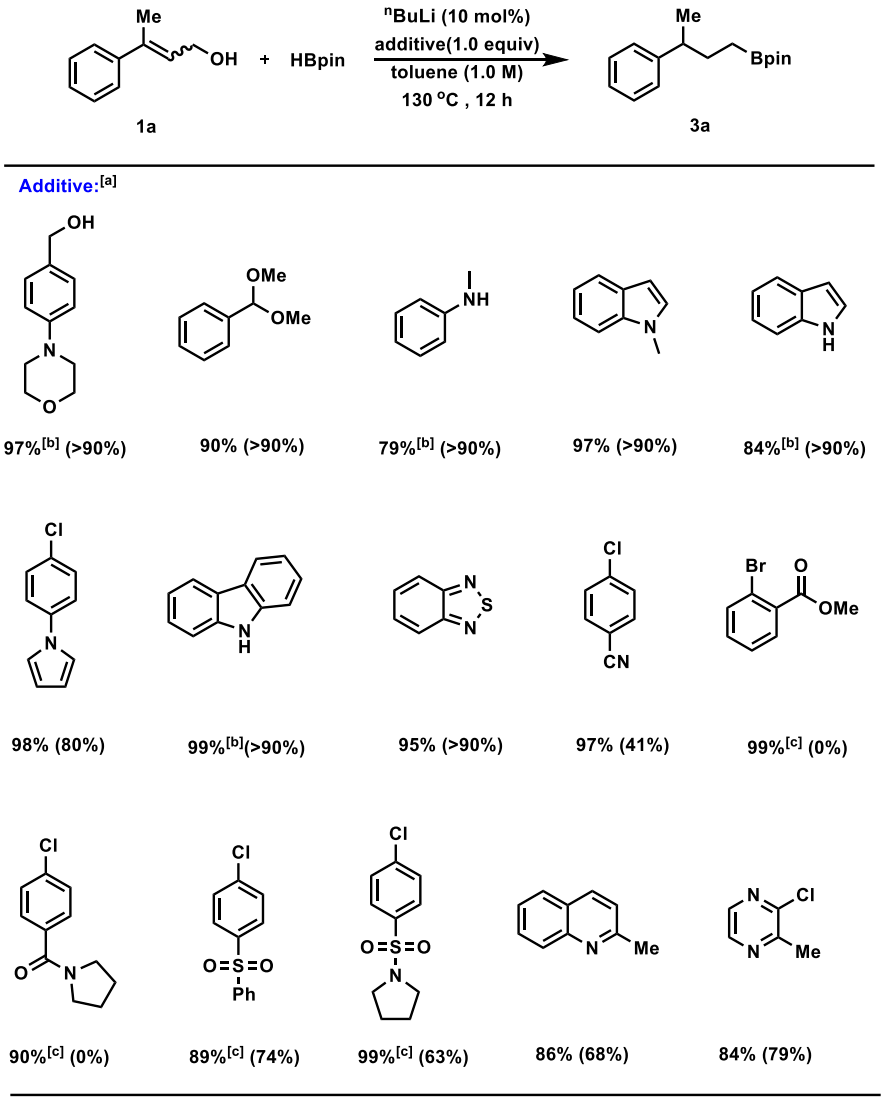


Following **GPA** using **6** (0.5 mmol, 1.0 equiv.), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide **4d** in 64% yield (85 mg).

Following **GPA** using **7** (0.5 mmol, 1.0 equiv.), the crude product was purified by column chromatography (0-2% EtOAc in hexanes) to provide **4d** in 84% yield (112 mg).

Additive-Based Robustness Screen

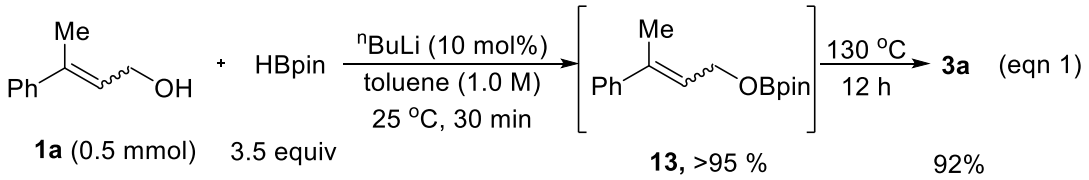
In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.5 mL, 1.0 M), HBpin (3.5 equiv or 4.5 equiv or 5.5 equiv) and ^{n}BuLi (2.5 M in hexane, 20μL, 0.05 mmol, 10 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature. The allylic alcohol substrate (0.5 mmol) and the additive (0.5 mmol, 1.0 equiv) were then added and the reaction mixture was stirred at 130 ^{o}C for 12 h. After completion of the reaction, the reaction mixture was allowed to cool to rt and quenched by HCl (1.0 M in ethyl acetate). Then the reaction mixture was directly filtered through a short pad of silica gel (eluting with ethyl acetate) to give the crude product. The solvent was removed in vacuo and the yield of crude product was determined by ^{1}H NMR and GC-MS analysis.



Functional-group compatibility. Each additive was examined individually. Recovery of additive was shown in parenthesis. The yield and recovery of additive were determined by ^{1}H NMR analysis using 1,3,5-trimethyl-benzen as an internal standard.

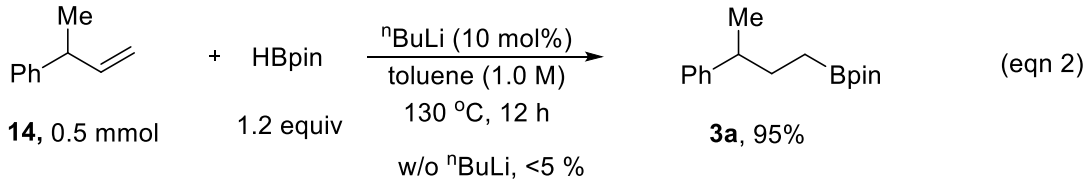
[a]: reaction condition: **1a** (0.2 mmol), HBpin (3.5 equiv.); [b]: 4.5 equiv. HBpin; [c]: 5.5 equiv. HBpin.

Mechanistic Study



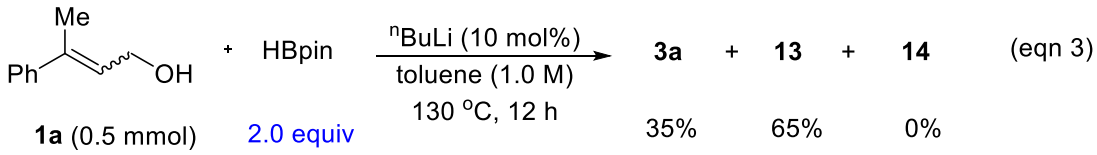
In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.5 mL, 1.0 M), HBpin (254 µL, 1.75 mmol, 3.5 equiv) and ^{n}BuLi (2.5 M in hexane, 20 µL, 0.05 mmol, 10 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature. The allylic alcohol **1a** (74 mg, 0.5 mmol) was then added dropwise and the reaction mixture was stirred at 25 °C for 30 min. The solvent was removed in vacuo. The crude reaction mixture was used for NMR analysis. Compound **13** was determined by ^{1}H NMR and ^{11}B NMR (22.33 ppm) analysis in near quantitative yield.

For comparison, in another nitrogen-purged Schlenk tube, the reaction was performed following above procedure stirred at 25 °C for 30 min and then 130 °C for 12 h. After work-up and isolation, product **3a** was obtained in 92% yield (119 mg).



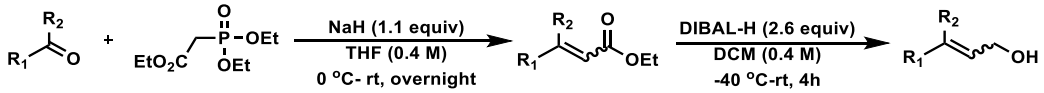
In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.5 mL, 1.0 M), HBpin (87 µL, 0.6 mmol, 1.2 equiv) and ^{n}BuLi (2.5 M in hexane, 20µL, 0.05 mmol, 10 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature. The alkene substrate **14** (66mg, 0.5 mmol) was then added dropwise and the reaction mixture was stirred at 130 ^{o}C for 12 h. After completion of the reaction, the reaction mixture was allowed to cool to rt and quenched by HCl (1.0 M in EtOAc). Then the reaction mixture was directly filtered through a short pad of silica gel (eluting with EtOAc) to give the crude product. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel to give the product (**3a**) in 95% yield (123 mg).

Following above procedure but without addition of ^{n}BuLi, almost no product **3a** (<5 % yield) was detected by NMR analysis.



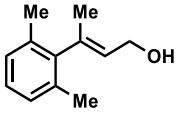
In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.5 mL, 1.0 M), HBpin (145 µL, 1.0 mmol, 2.0 equiv) and ^{n}BuLi (2.5 M in hexane, 20 µL, 0.05 mmol, 10 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature. The allylic alcohol **1a** (74 mg, 0.5 mmol) was then added dropwise and the reaction mixture was stirred at 130 ^{o}C for 12 min. After cooling to room temperature, the solvent was removed in vacuo. The crude reaction mixture was used for NMR analysis. Compound **3a** and **13** were obtained in 35% and 65% of NMR yield, respectively.

Substrate Synthesis



General procedure B (GPB): To a suspension of NaH (11 mmol, 1.1 equiv) in THF (20.0 mL) was added triethylphosphonoacetate (12 mmol, 1.2 equiv) dropwise at 0 °C under nitrogen atmosphere. After stirring for 1 h at room temperature, a solution of ketone (10 mmol, 1.0 equiv) in THF (5.0mL) was added dropwise. The reaction mixture was stirred overnight at room temperature and quenched by addition of water. DCM was added and the organic layer was separated, the aqueous layer was extracted with DCM twice and the combined organic layer was dried over Na_2SO_4. The solvent was removed in vacuo to get the corresponding α, β-unsaturated ester, which was used in the next step without further purification.

DIBAL-H (1.5 M in toluene, 17.3 mL, 2.6 equiv) was added dropwise to a solution of the α, β-unsaturated ester in DCM (25.0 mL) at -40 °C. The reaction mixture was stirred at room temperature for 4 h and quenched with saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated. The crude material was purified by flash chromatography to afford the corresponding allylic alcohol.



3-(2,6-dimethylphenyl)but-2-en-1-ol

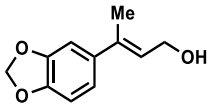
Following **GPB** using 1-(2, 6-dimethylphenyl) ethan-1-one (10.0 mmol), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound in 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (m, 3H), 5.40 (m, 1H), 4.31 (d, *J* = 6.6 Hz, 2H), 2.20 (s, 6H), 1.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.0, 134.8, 127.9, 127.4, 126.5, 59.3, 19.7, 17.4.

IR (neat, cm^{-1}) 3318, 2918, 1463, 1375, 995, 766, 571.

HRMS (EI) calculated for $C_{12}H_{16}O$ $[M]^+$ *m/z* 176.1196, found 176.1195.



3-(benzo[d][1,3]dioxol-5-yl)but-2-en-1-ol

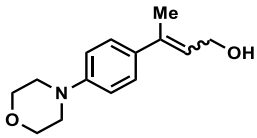
Following **GPB** using 1-(benzo[d][1,3]dioxol-5-yl)ethan-1-one (10.0 mmol), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound in 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 5.89 (t, *J* = 6.8 Hz, 1H), 4.33 (d, *J* = 6.7 Hz, 2H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.9, 137.4, 137.1, 125.4, 119.3, 107.9, 106.3, 101.0, 59.9, 16.2.

IR (neat, cm^{-1}) 3326, 2883, 1503, 1484, 1435, 1227, 800.

HRMS (EI) calculated for $C_{11}H_{12}O_3$ $[M]^+$ *m/z* 192.0781, found 192.0778.



3-(4-morpholinophenyl)but-2-en-1-ol

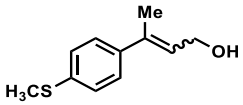
Following **GPB** using 1-(4-morpholinophenyl)ethan-1-one (10.0 mmol), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound in 40% yield (4:1 mixture of E/Z isomer).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.91 (m, 1H), 4.31 (d, *J* = 6.7 Hz, 2H), 3.84 (m, 4H), 3.13 (m, 4H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 134.3, 128.7, 126.5, 124.7, 115.2, 66.8, 59.8, 49.2, 15.8.

IR (neat, cm^{-1}) 3383, 2853, 1606, 1514, 1229, 1116, 924.

HRMS (ESI) calculated for $C_{14}H_{20}NO_2$ $[M+H]^+$ *m/z* 234.1489, found 234.1493.



3-(4-(methylthio)phenyl)but-2-en-1-ol

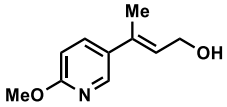
Following **GPB** using 1-(4-(methylthio)phenyl)ethan-1-one (10.0 mmol), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound in 60% yield (4:1 mixture of E/Z isomer).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 5.96 (m, 1H), 4.34 (d, *J* = 6.7 Hz, 2H), 2.48 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.3, 128.3, 126.4, 126.2, 126.1, 59.9, 15.9, 15.9.

IR (neat, cm^{-1}) 3324, 2917, 1591, 1488, 1434, 1106, 992.

HRMS (EI) calculated for $C_{11}H_{14}OS$ $[M]^+$ *m/z* 194.0760, found 194.0757.



3-(6-methoxypyridin-3-yl)but-2-en-1-ol

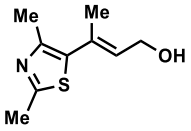
Following **GPB** using 1-(6-methoxypyridin-3-yl)ethan-1-one (10.0 mmol), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound in 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.5 Hz, 1H), 7.46 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 5.78 (m, 1H), 4.20 (d, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 143.5, 136.1, 133.3, 131.5, 126.6, 110.1, 59.1, 53.5, 15.5.

IR (neat, cm^{-1}) 3317, 2945, 1599, 1491, 1365, 1283, 1019.

HRMS (ESI) calculated for $C_{10}H_{14}NO_2$ $[M+H]^+$ *m/z* 180.1019, found 180.1019.



3-(2,4-dimethylthiazol-5-yl)but-2-en-1-ol

Following **GPB** using 1-(2,4-dimethylthiazol-5-yl)ethan-1-one (10.0 mmol), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound in 40% yield.

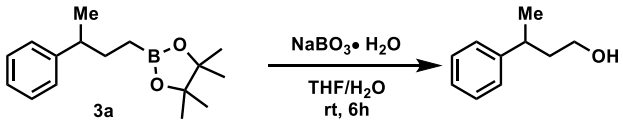
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (m, 1H), 4.87 (s, 1H), 4.33 (d, *J* = 6.5 Hz, 2H), 2.60 (s, 3H), 2.37 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 146.1, 134.4, 131.5, 127.9, 58.6, 18.7, 18.6, 16.2.

IR (neat, cm^{-1}) 3286, 2920, 1536, 1437, 1184, 1010, 728.

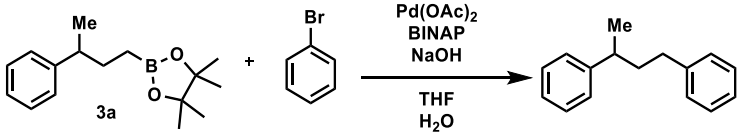
HRMS (ESI) calculated for $C_9H_{14}NOS$ $[M+H]^+$ *m/z* 184.0791, found 184.0794.

Transformation of Alkylboronic Ester 3a



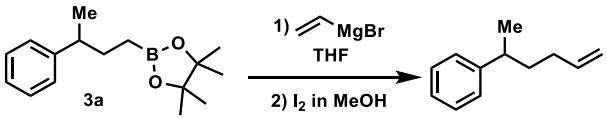
To a solution of **3a** (52.0 mg, 0.2 mmol, 1.0 equiv) in THF: H_2O (2.0 mL, 1:1(v/v)) was added sodium perborate (59.9 mg, 0.6 mmol, 3.0 equiv). The reaction mixture was stirred for 6 h at room temperature. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel chromatography to get the product in 92% yield (27.3 mg) [6].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 9.9, 5.2 Hz, 2H), 7.16 (m, 3H), 3.52 (m, 2H), 2.85 (m, 1H), 1.82 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 3H).



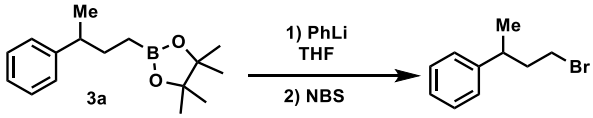
To a nitrogen-purged Schlenk tube containing a magnetic stirring bar, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), *rac*-BINAP (14.9 mg, 0.024 mmol, 0.12 equiv) and NaOH (120.0 mg, 3.0 mmol, 15.0 equiv) and THF (1.0 mL) were added sequentially. The reaction mixture was stirred at rt for 30 min. **3a** (52.0 mg, 0.2 mmol, 1.0 equiv), bromobenzene (47.1 mg, 0.3 mmol, 1.5 equiv) and H_2O (0.2 mL) were then added. The reaction mixture was stirred for 16 h at 100 °C. Then the mixture was quenched with water and extracted with ethyl acetate. The solvent was concentrated in vacuo. The residue was purified by silica gel chromatography to give product in 70% yield (29.4 mg) [7].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 10H), 2.72 (m, 1H), 2.51 (m, 2H), 1.91 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 3H).



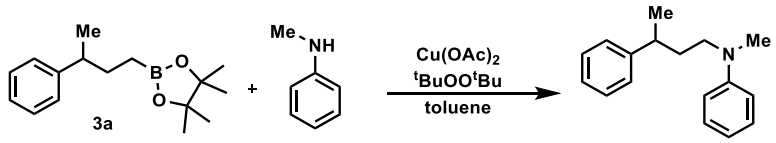
Vinylmagnesium bromide solution (1.0 M in THF, 0.8 ml, 0.8 mmol, 4.0 equiv) was added to a solution of **3a** (52.0 mg, 0.2 mmol, 1.0 equiv) in THF (3.0 mL) at –78 °C and the reaction mixture was stirred at rt for 30 min. Then a solution of iodine (203 mg, 0.8 mmol, 4.0 equiv) in MeOH (3.0 mL) was added and stirred for another 30 min at r.t. Upon completion of the reaction, the reaction mixture was quenched with sat. $Na_2S_2O_3$ (aq.) and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography to get the product in 63% yield (20.2 mg) [8].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.18 (m, 3H), 5.79 (m, 1H), 4.96 (m, 2H), 2.71 (m, 1H), 1.96 (m, 2H), 1.67 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 3H).



In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, **3a** (52.0 mg, 0.2 mmol, 1.0 equiv) and THF (1.0 mL) was added. A solution of phenyllithium (1.0 M in Et_2O, 0.4 ml, 0.4 mmol, 2.0 equiv) was then added dropwise at rt. The reaction mixture was allowed to stir at r.t. for 30 min. The resulting solution was added a solution of NBS (71.2 mg, 0.4 mmol, 2.0 equiv) in THF (1.0 mL) dropwise. After stirring at r.t. for 1 h, saturated $Na_2S_2O_3$ solution was added. The mixture was extracted with ethyl acetate twice, dried over Na_2SO_4 and concentrate. The residue material was purified by flash column chromatography and the product was obtained in 77% yield (32.8 mg) [9].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.22 (m, 3H), 3.33 (m, 1H), 3.20 (m, 1H), 2.97 (m, 1H), 2.12 (m, 2H), 1.30 (d, *J* = 7.0 Hz, 3H).



In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, **3a** (52.0 mg, 0.2 mmol, 1.0 equiv), N-methylaniline (32.1 mg, 0.3 mmol, 1.5 equiv), $Cu(OAc)_2$ (1.8 mg, 0.01 mmol, 5.0 mol%), toluene (1.0 ml) and di-*tert*-butyl peroxide (58.5 mg, 0.4 mmol, 2.0 equiv) were added sequentially. The reaction mixture was allowed to stir at 80 ^oC for 24 h, After cooling to rt, saturated $Na_2S_2O_3$ solution was added. The mixture was extracted with ethyl acetate twice, dried over Na_2SO_4 and concentrate. the residue was purified by column chromatography on silica gel to afford the product in 52% yield (24.9 mg) [10].

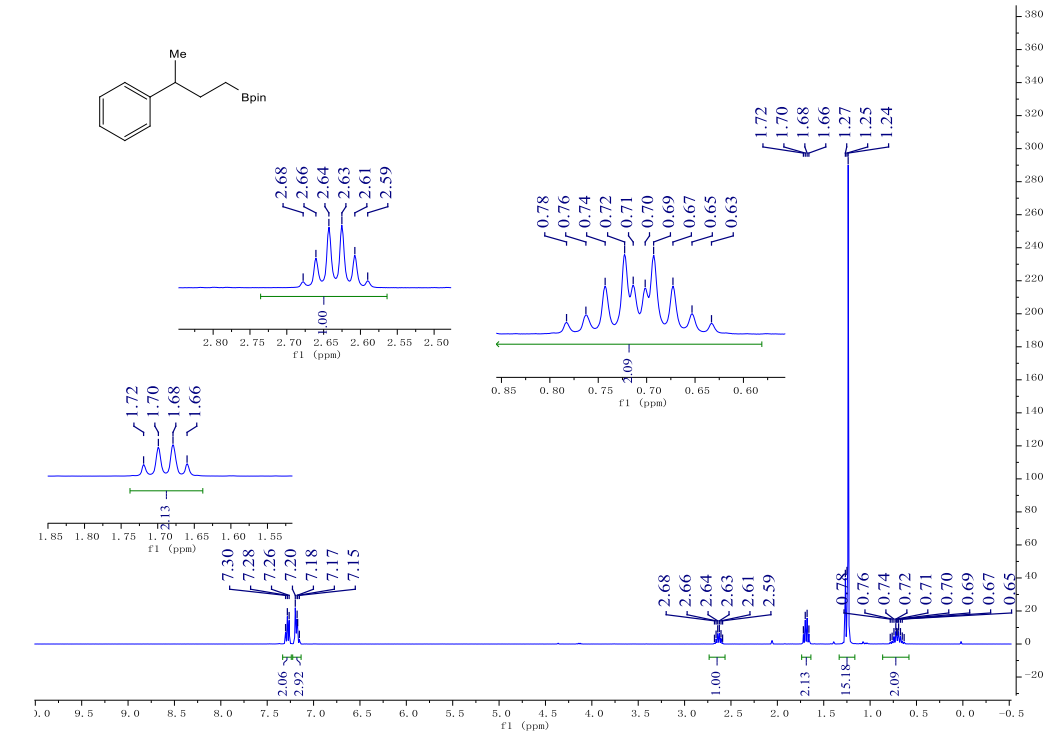
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.21 (m, 5H), 6.65 (m, 1H), 6.58 (d, *J* = 8.3 Hz, 2H), 3.19 (m, 2H), 2.85 (s, 3H), 2.69 (m, 1H), 1.86 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H)

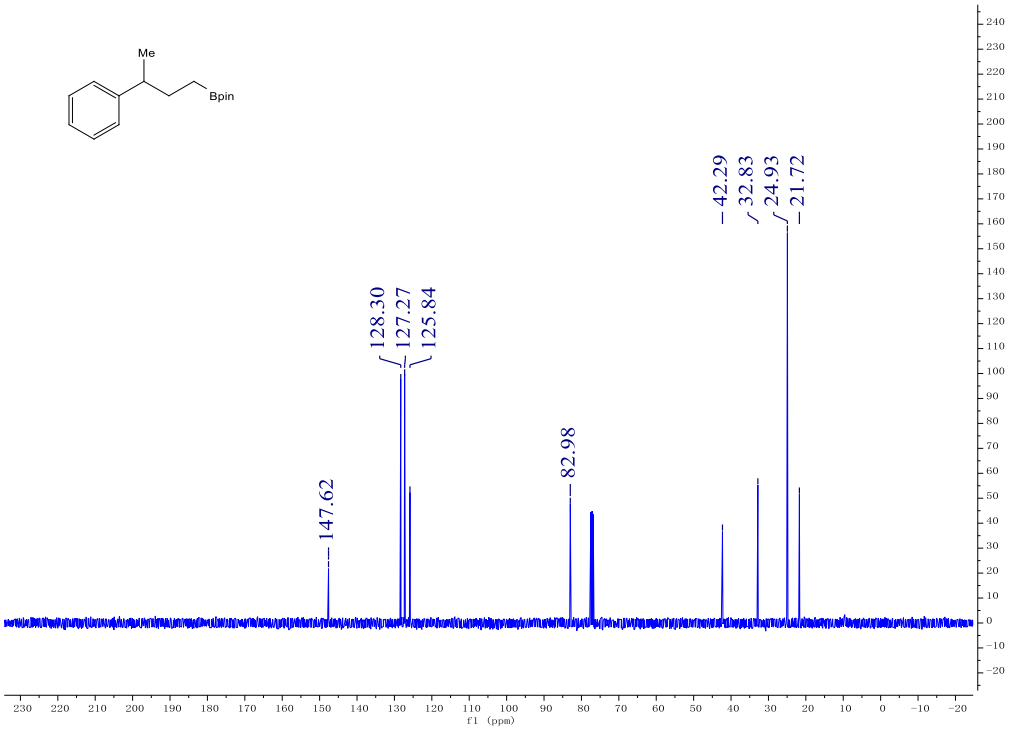
References

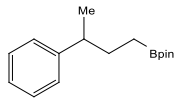
1. A. Joshi-Pangu, X. Ma, M. Diane, S. Iqbal, R. J. Kribs, R. Huang, C. Y. Wang and M. R. Biscoe, *J. Org. Chem.*, 2012, **77**, 6629-6633.
2. J. Zheng, J.-B. Sortais and C. Darcel, *ChemCatChem*, 2014, **6**, 763-766.
3. D. Wang, X. S. Xue, K. N. Houk and Z. Shi, *Angew. Chem., Int. Ed.*, 2018, **57**, 16861-16865.
4. I. G. Smilovic, E. Casas-Arce, S. J. Roseblade, U. Nettekoven, A. Zanotti-Gerosa, M. Kovacevic and Z. Casar, *Angew. Chem., Int. Ed.*, 2012, **51**, 1014-1018.
5. A. J. Ruddy, O. L. Sydora, B. L. Small, M. Stradiotto and L. Turculet, *Chem. Eur. J.*, 2014, **20**, 13918-139
6. D. A. Gandamana, B. Wang C. T. Bolte, Benoit, G. Fabien and C. Shunsuke, *Angew. Chem. Int. Ed.*, 2018, **57**, 6181.
7. H. Wang, L. Li, X. F. Bai, J. Y. Yang, K. F. Shang and L. W. Xu, *Adv. Synth. Catal.*, 2013, **355**, 341.
8. M. Murai, K. Nishimura and K. Takai, *Chem. Commun*. 2019, **55**, 2769.
9. M. Stratakis, C. Raptis, N. Sofikiti, C. Tsangarakis, G. Kosmas and I. P Zaravinos,*Tetrahedron*, 2006, **62**, 10623-10632.
10. J. Su, Y. Zhou and X. Xu, *Org. Biomol. Chem.*, 2019, **17**, 2013

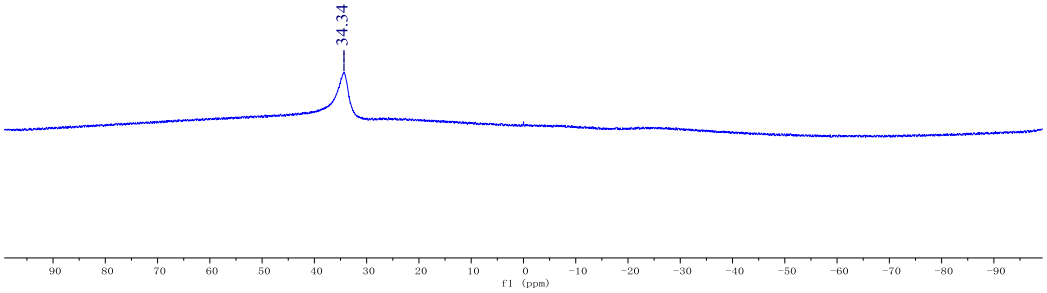
NMR Spectra

3a

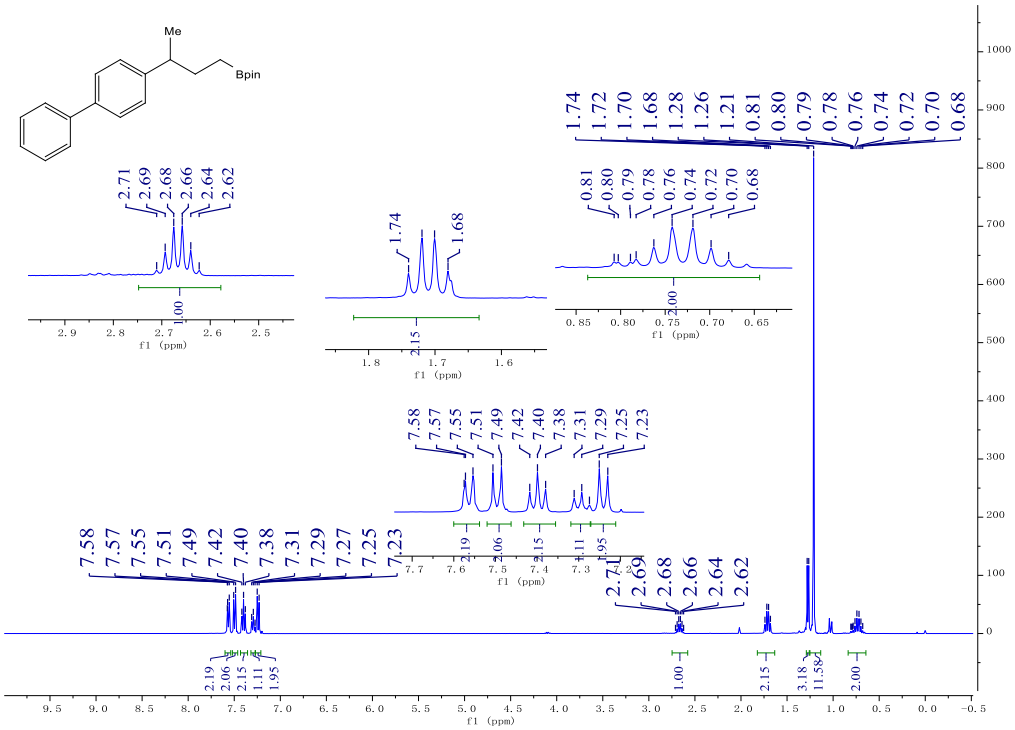


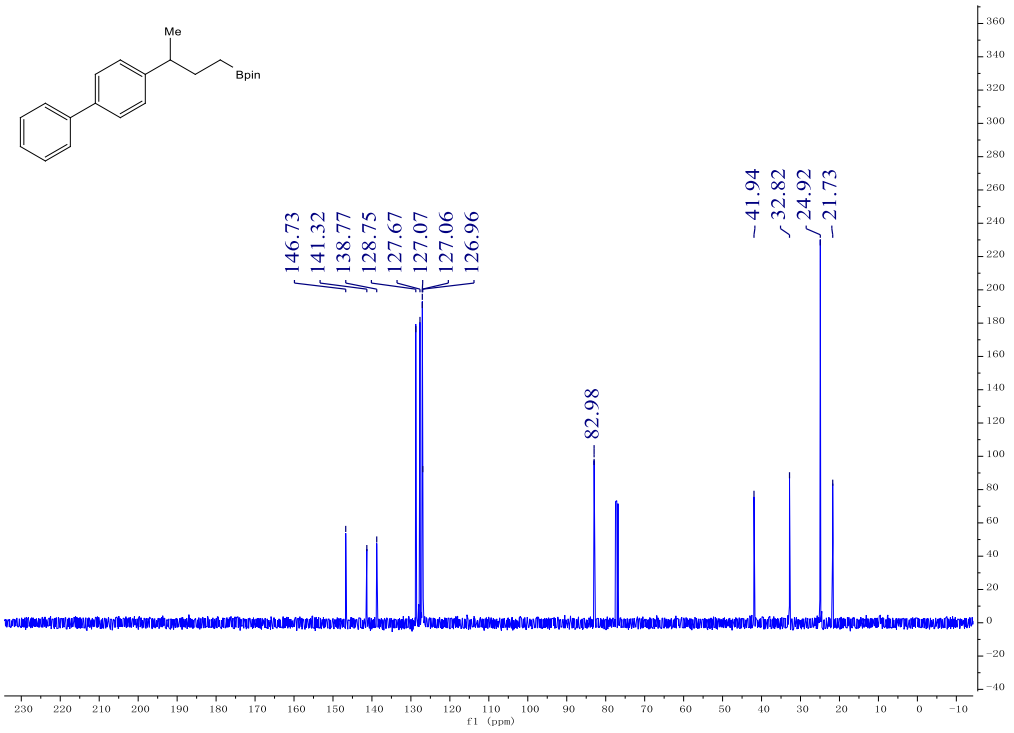


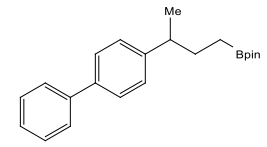


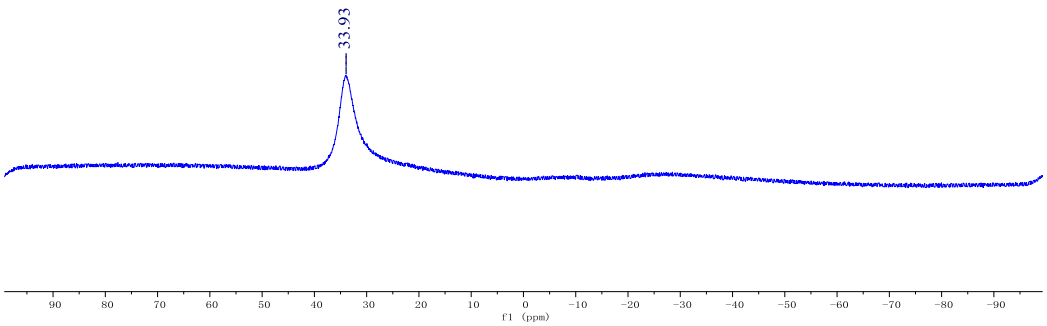


3b

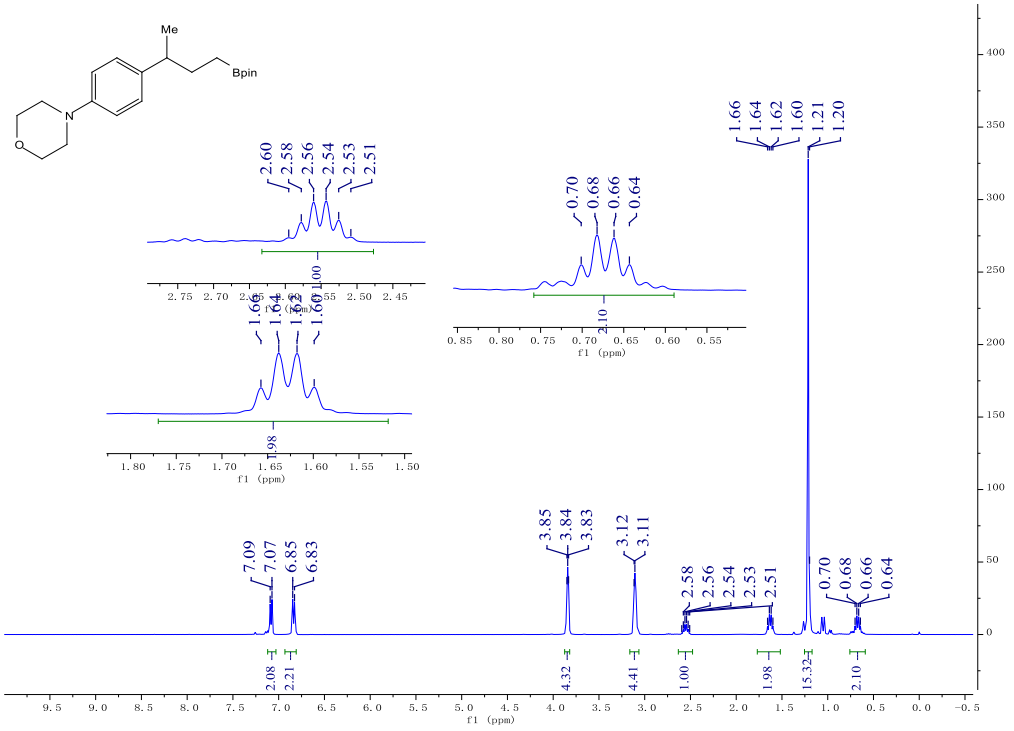


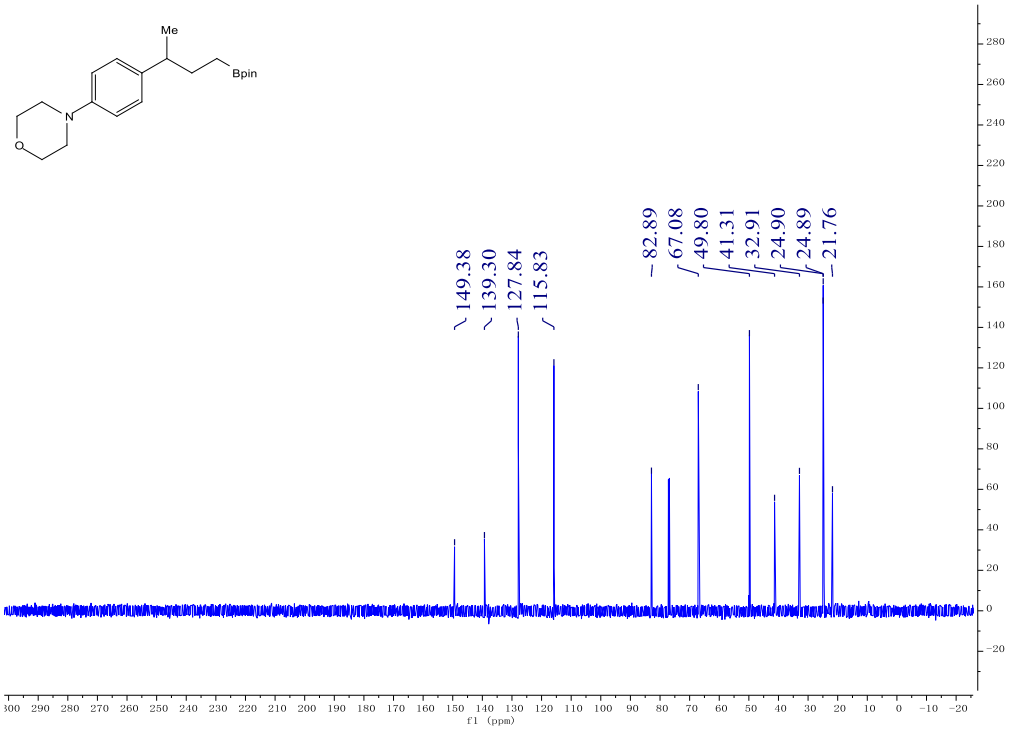

Me
Bpin
146.73
141.32
138.77
128.75
127.67
127.07
127.06
126.96
82.98
41.94
32.82
24.92
21.73
f1 (ppm)

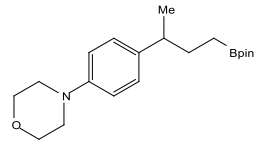

Me
Bpin

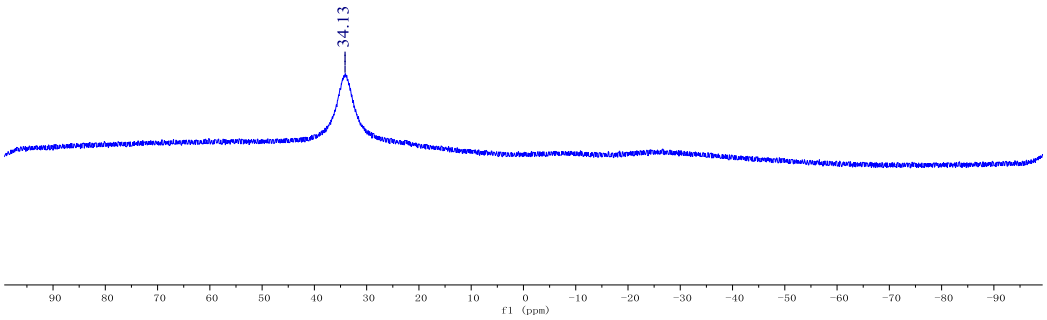

33.93
f1 (ppm)

3c

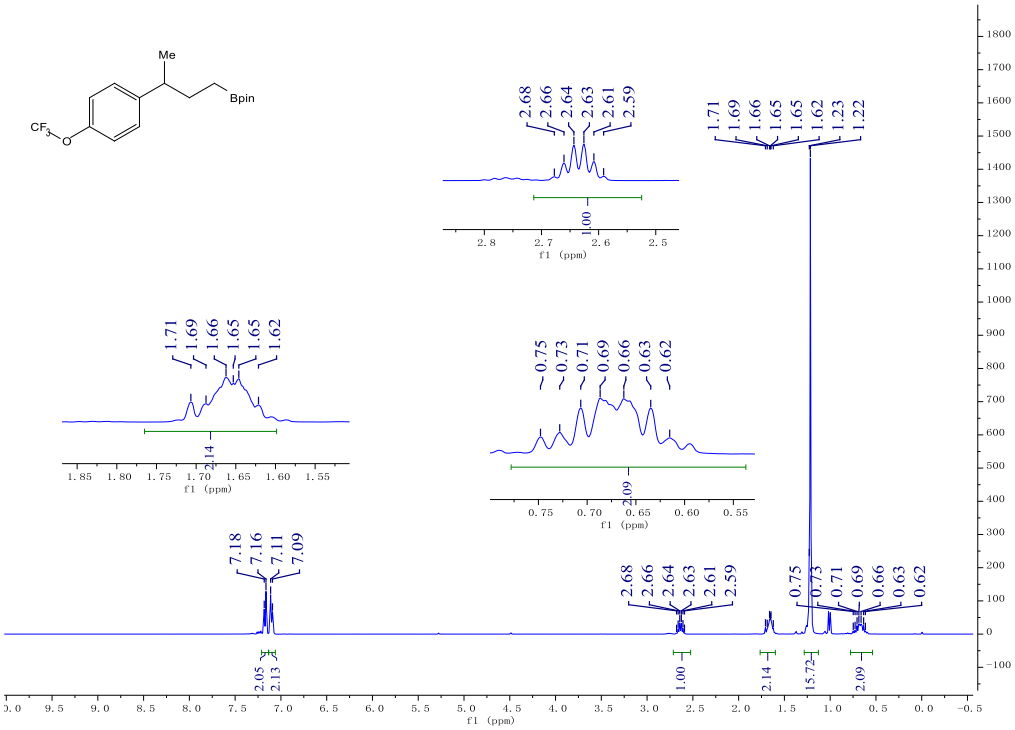

Me
Bpin
N
O
7.09
7.07
6.85
6.83
3.85
3.84
3.83
3.12
3.11
2.58
2.56
2.54
2.53
2.51
1.66
1.64
1.62
1.60
1.21
1.20
0.70
0.68
0.66
0.64
f1 (ppm)

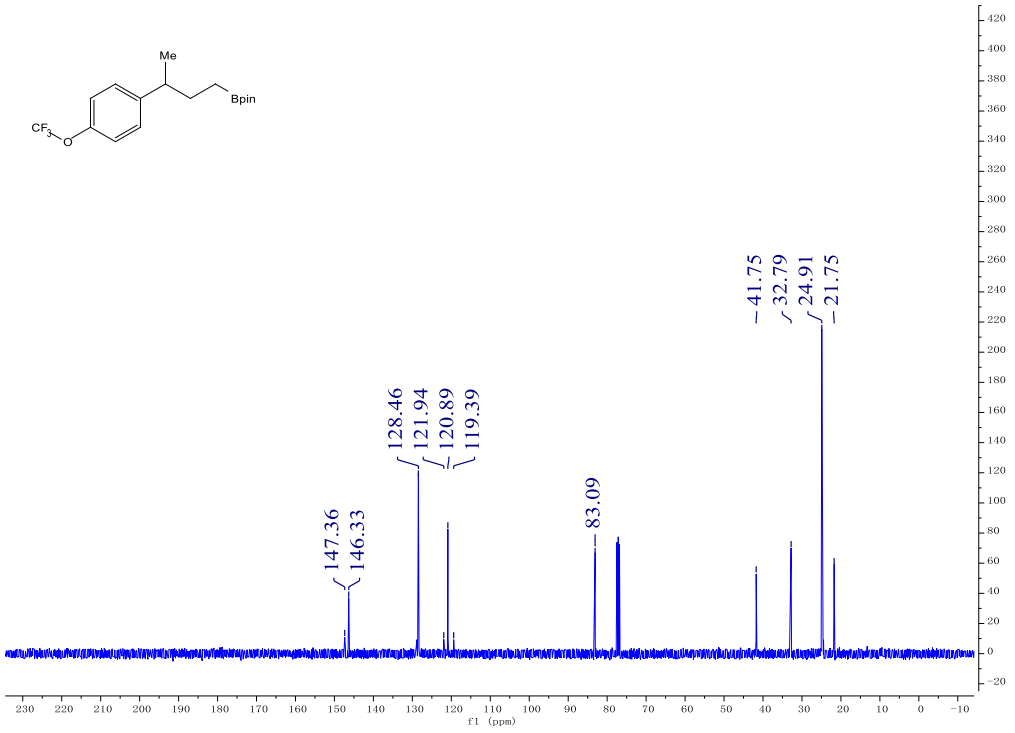

Me
Bpin
N
O
149.38
139.30
127.84
115.83
82.89
67.08
49.80
41.31
32.91
24.90
24.89
21.76
f1 (ppm)

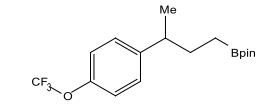


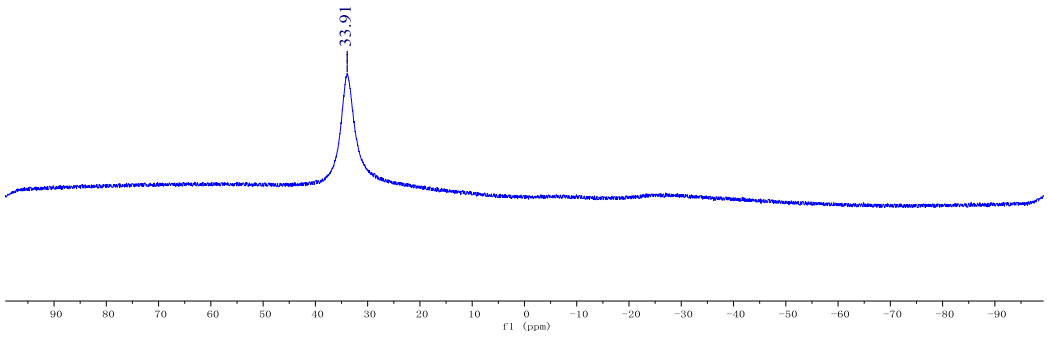


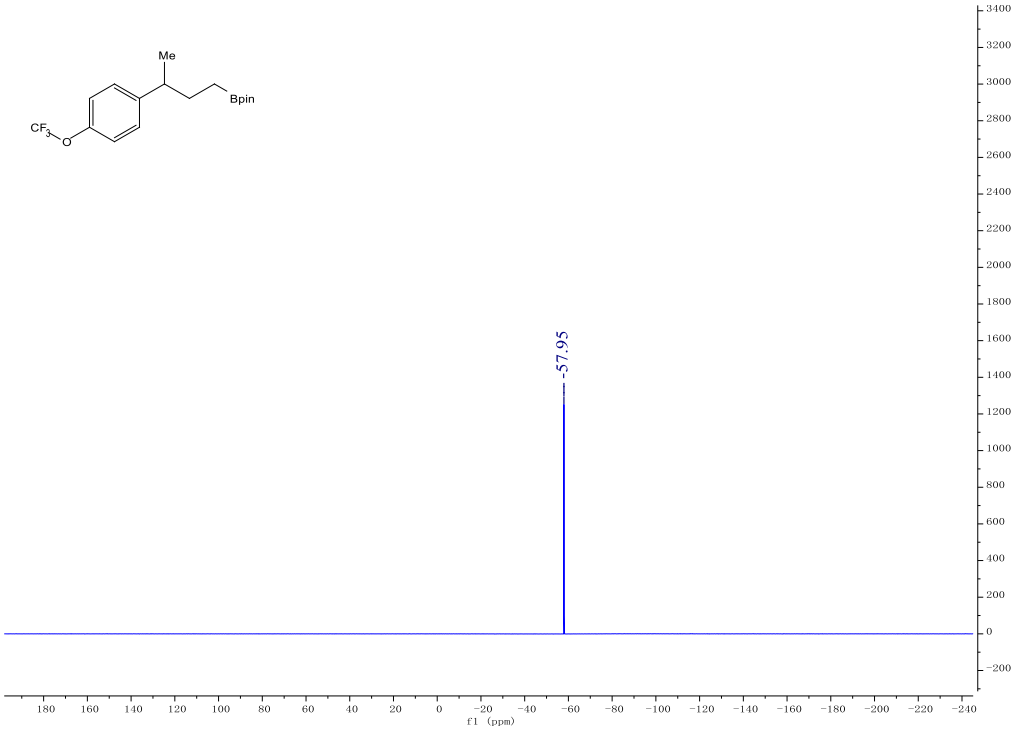
3d



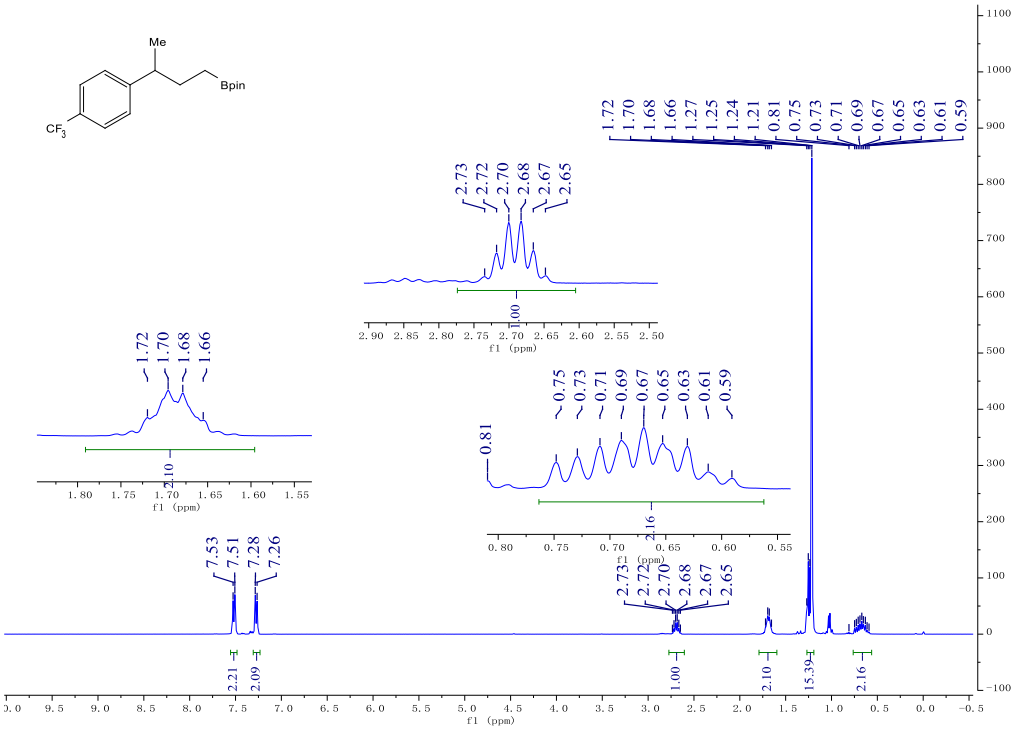

Me
Bpin
CF3
O
147.36
146.33
128.46
121.94
120.89
119.39
83.09
41.75
32.79
24.91
21.75
f1 (ppm)

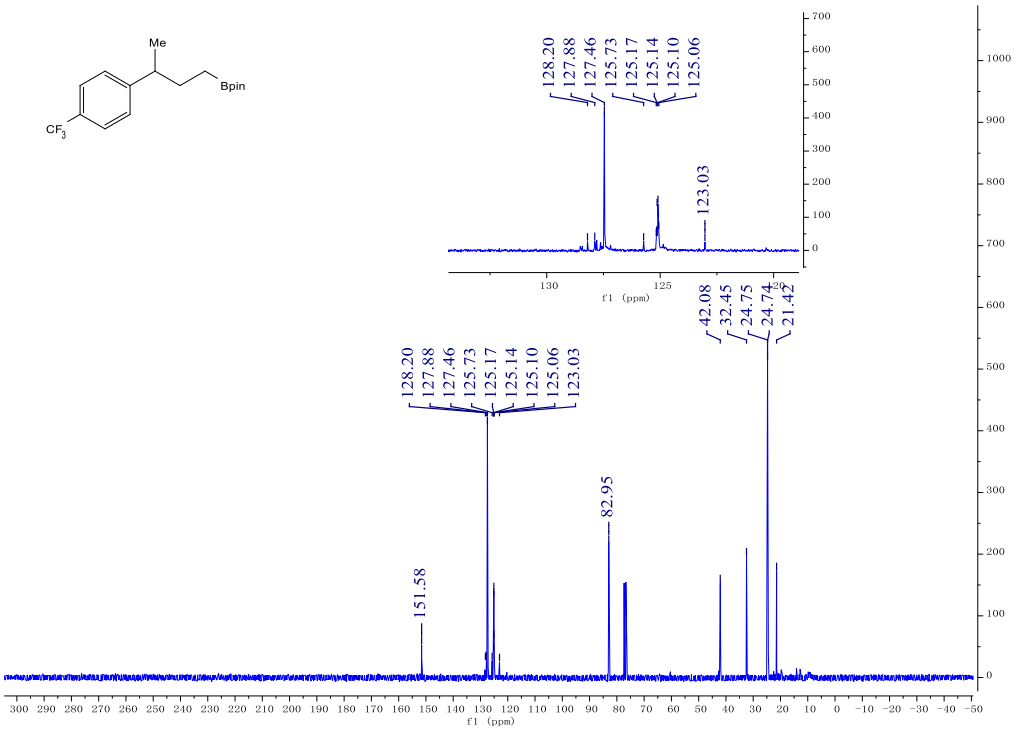

Me
Bpin
CF3
O

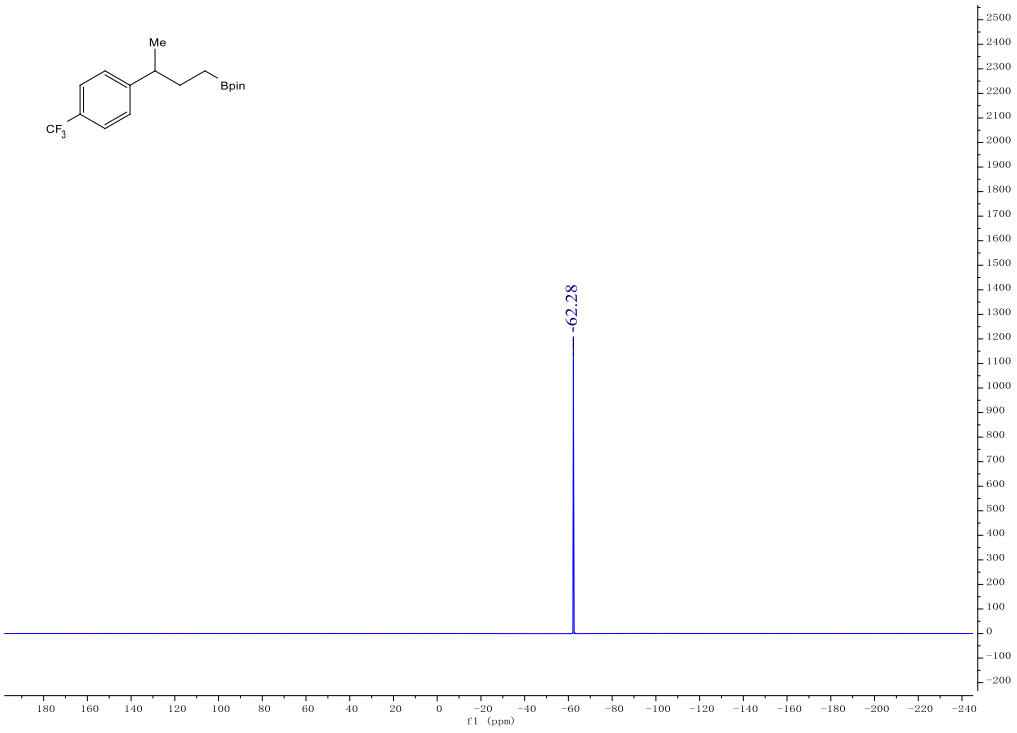

33.91
f1 (ppm)

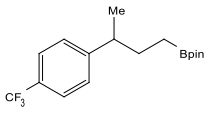

Me
Bpin
CF3
O
-57.95
f1 (ppm)

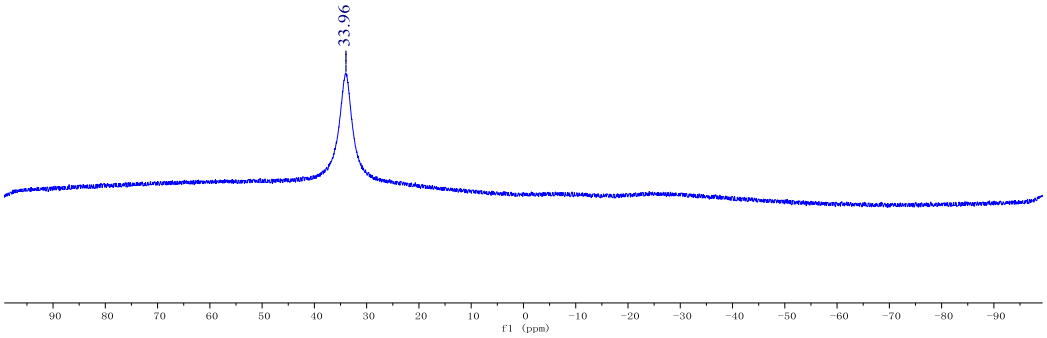
3e


Me
Bpin
CF3
7.53
7.51
7.28
7.26
2.73
2.72
2.70
2.68
2.67
2.65
1.72
1.70
1.68
1.66
1.27
1.25
1.24
1.21
0.81
0.75
0.73
0.71
0.69
0.67
0.65
0.63
0.61
0.59
2.21
2.09
1.00
2.10
15.39
2.16
f1 (ppm)

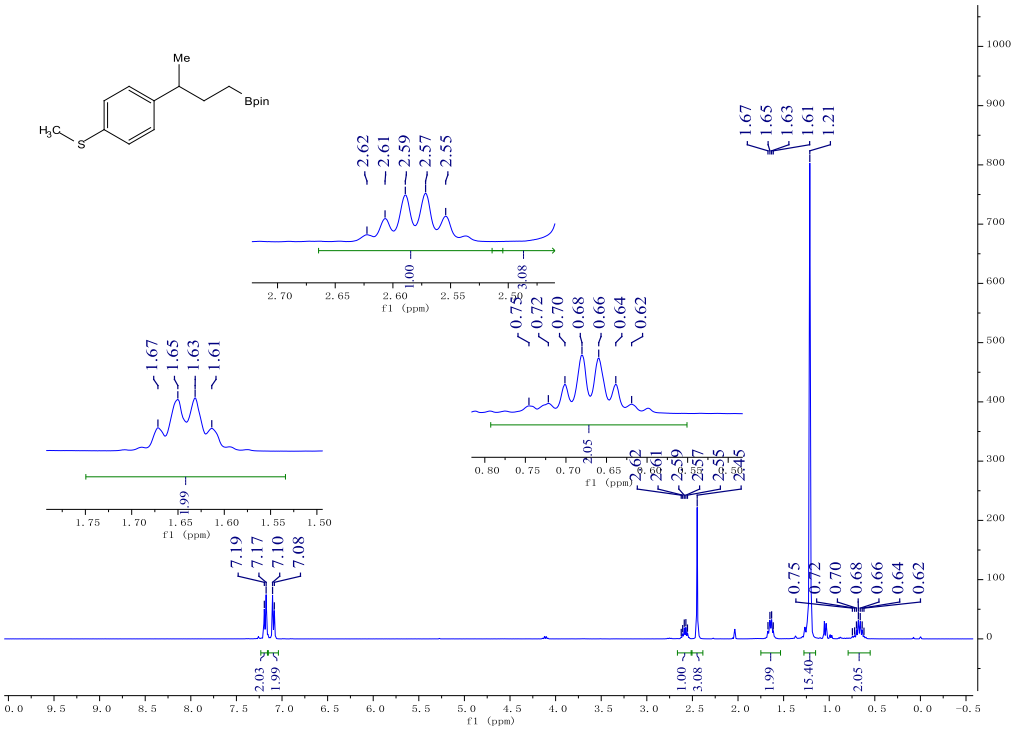

Me
Bpin
CF3
128.20
127.88
127.46
125.73
125.17
125.14
125.10
125.06
123.03
42.08
32.45
24.75
24.74
21.42
82.95
151.58
f1 (ppm)

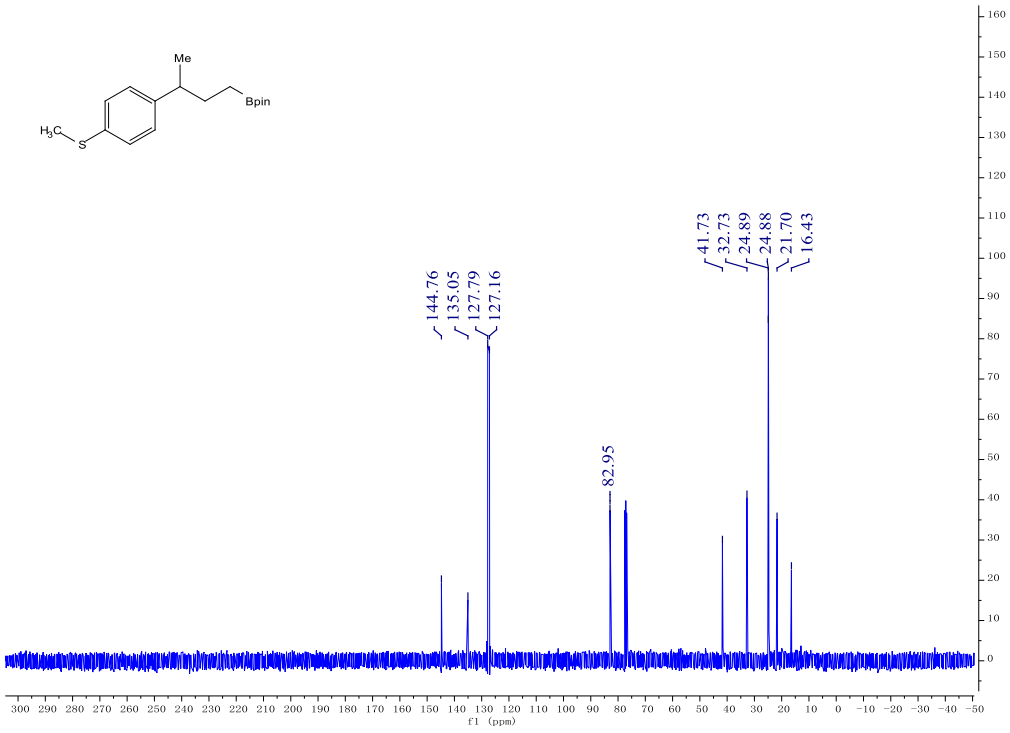

Me
Bpin
CF3
-62.28
f1 (ppm)

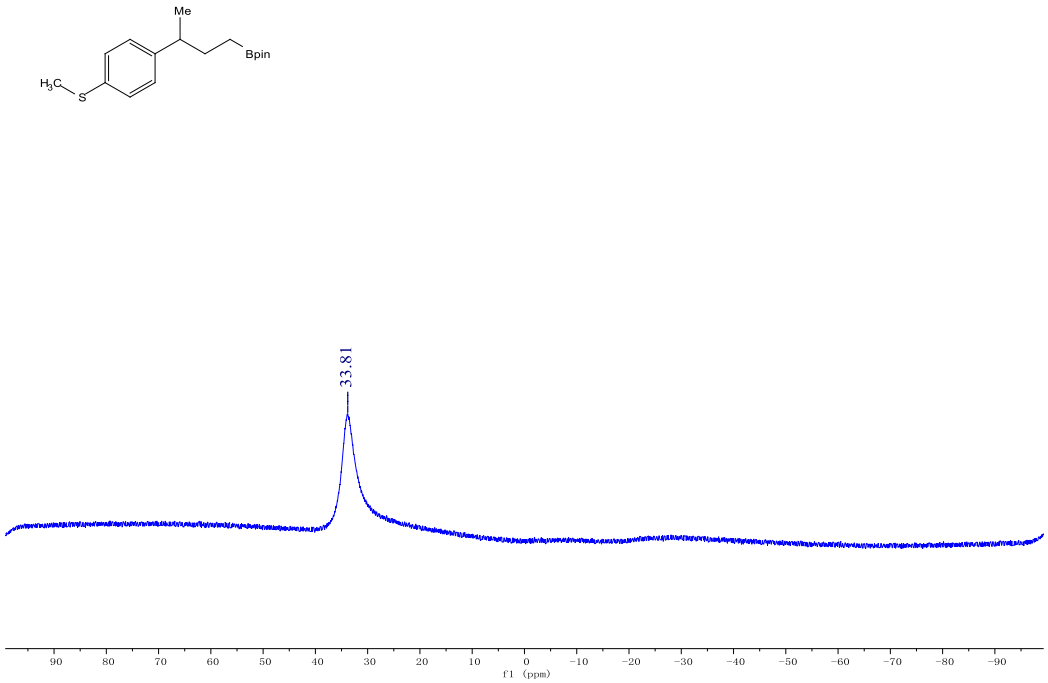

Me
Bpin
CF3


33.96
f1 (ppm)

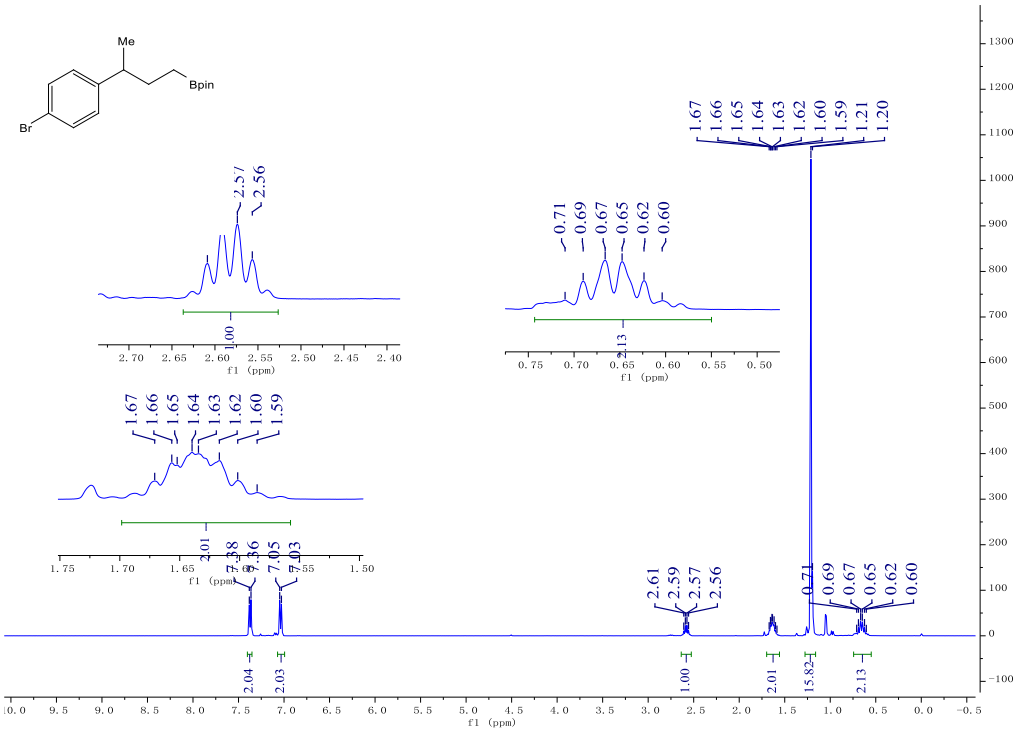
3f

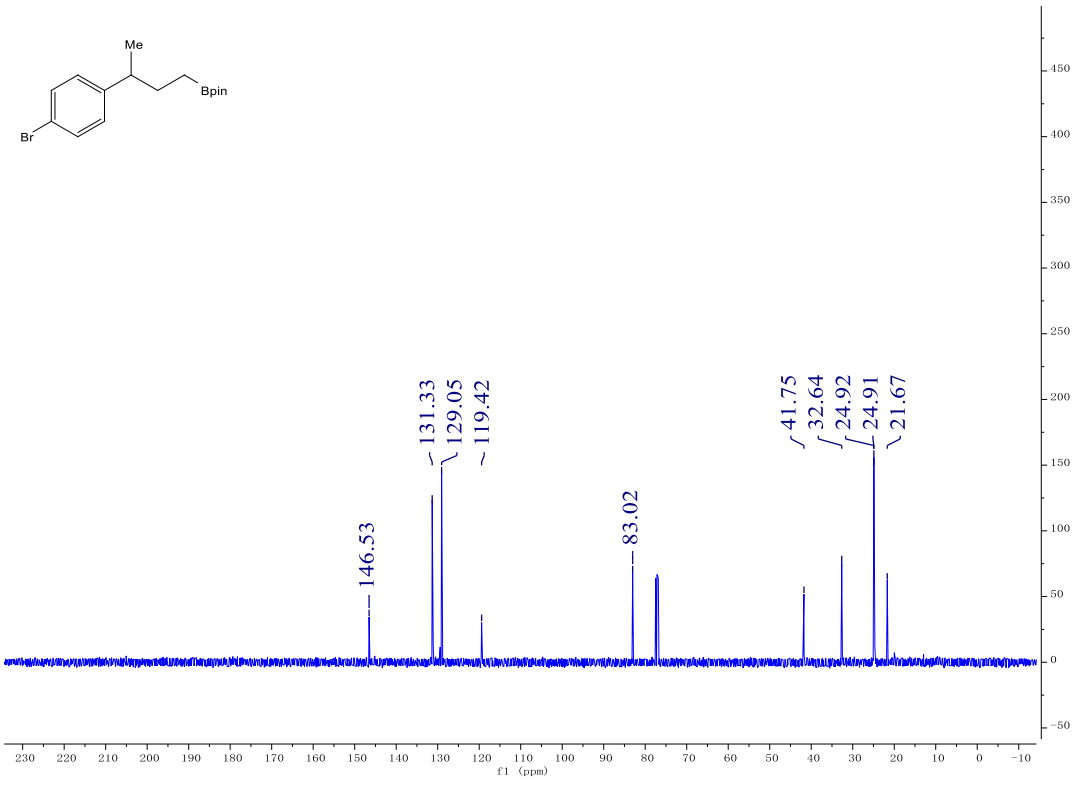

Me
Bpin
H3C
S
2.62
2.61
2.59
2.57
2.55
1.67
1.65
1.63
1.61
1.21
0.75
0.72
0.70
0.68
0.66
0.64
0.62
7.19
7.17
7.10
7.08
f1 (ppm)


Me
Bpin
H3C
S
144.76
135.05
127.79
127.16
82.95
41.73
32.73
24.89
24.88
21.70
16.43
f1 (ppm)

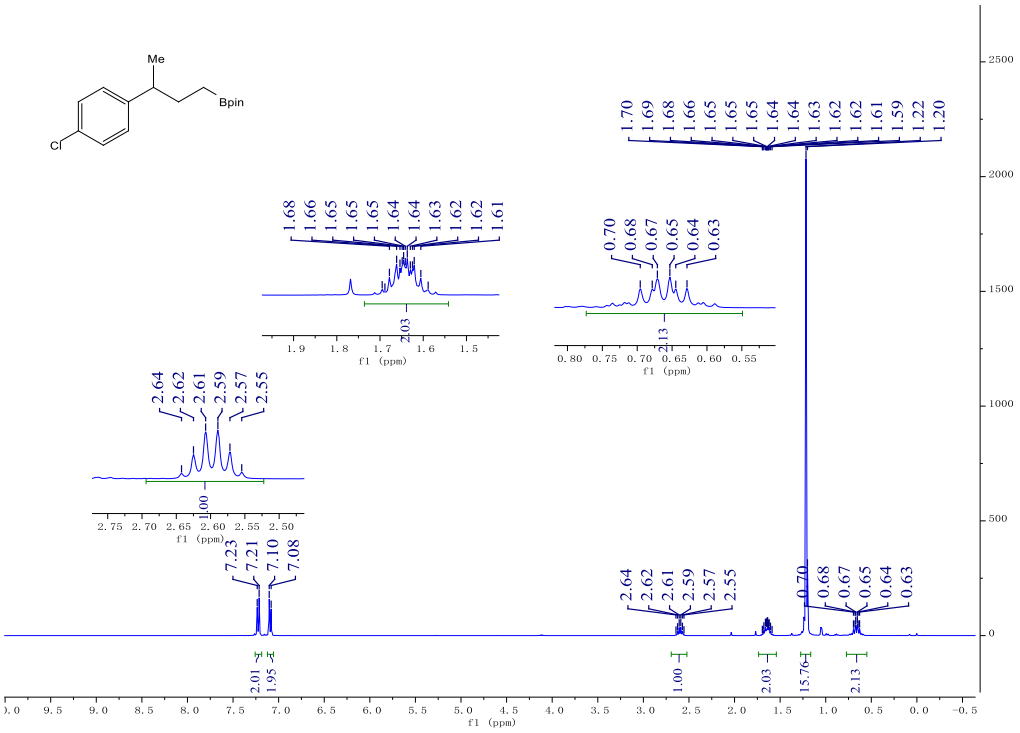

Me
Bpin
H3C
S
33.81
f1 (ppm)

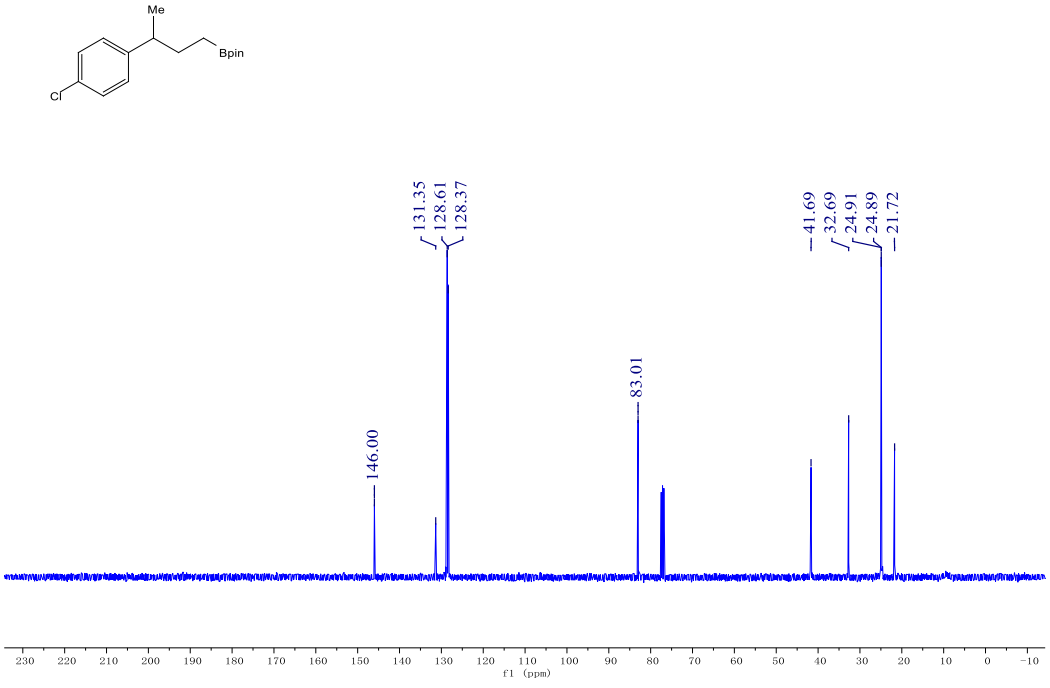
3g

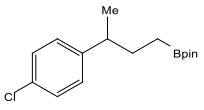

Me
Bpin
Br
1.67
1.66
1.65
1.64
1.63
1.62
1.60
1.59
1.21
1.20
2.57
2.56
0.71
0.69
0.67
0.65
0.62
0.60
2.61
2.59
2.57
2.56
7.38
7.36
7.05
7.03
f1 (ppm)

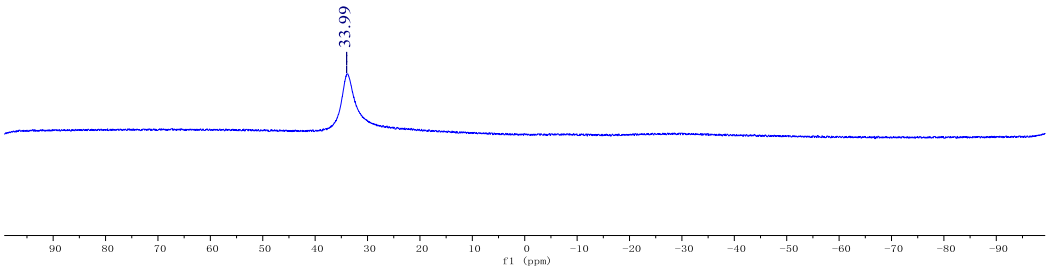

Me
Bpin
Br
146.53
131.33
129.05
119.42
83.02
41.75
32.64
24.92
24.91
21.67
f1 (ppm)

3h

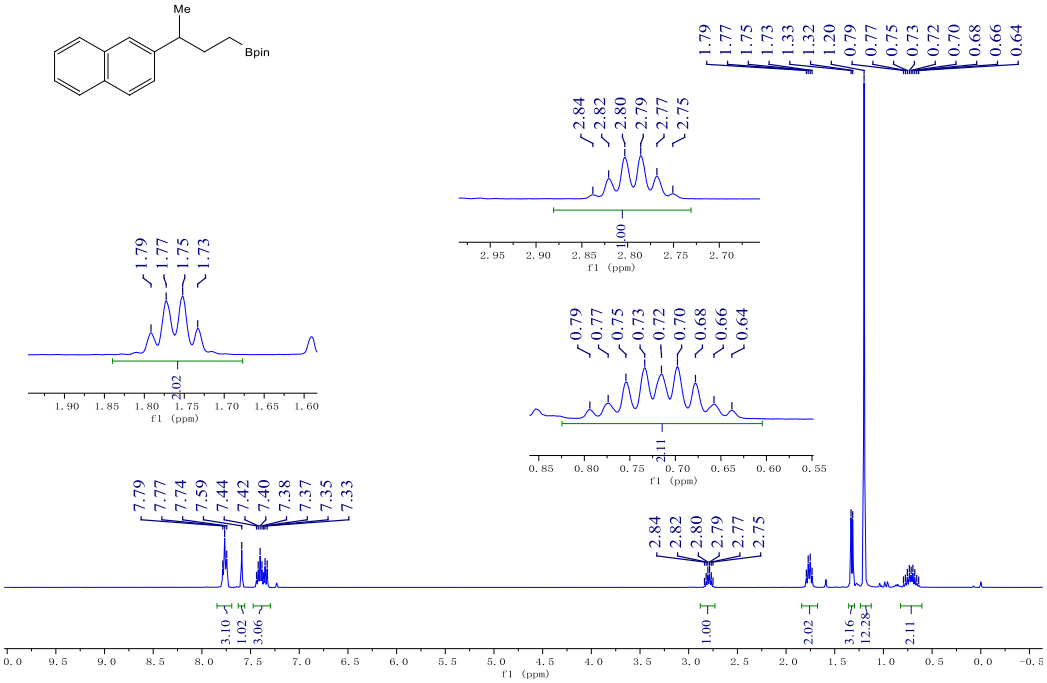

Me
Bpin
Cl
f1 (ppm)

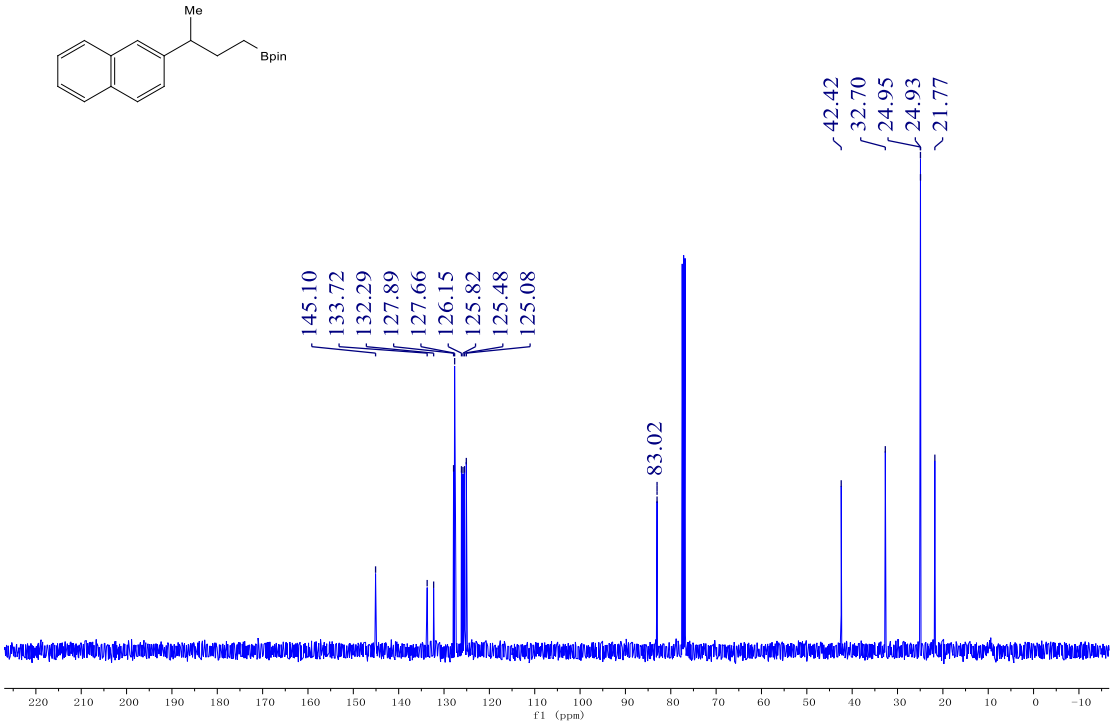

Me
Bpin
Cl
146.00
131.35
128.61
128.37
83.01
41.69
32.69
24.91
24.89
21.72
f1 (ppm)



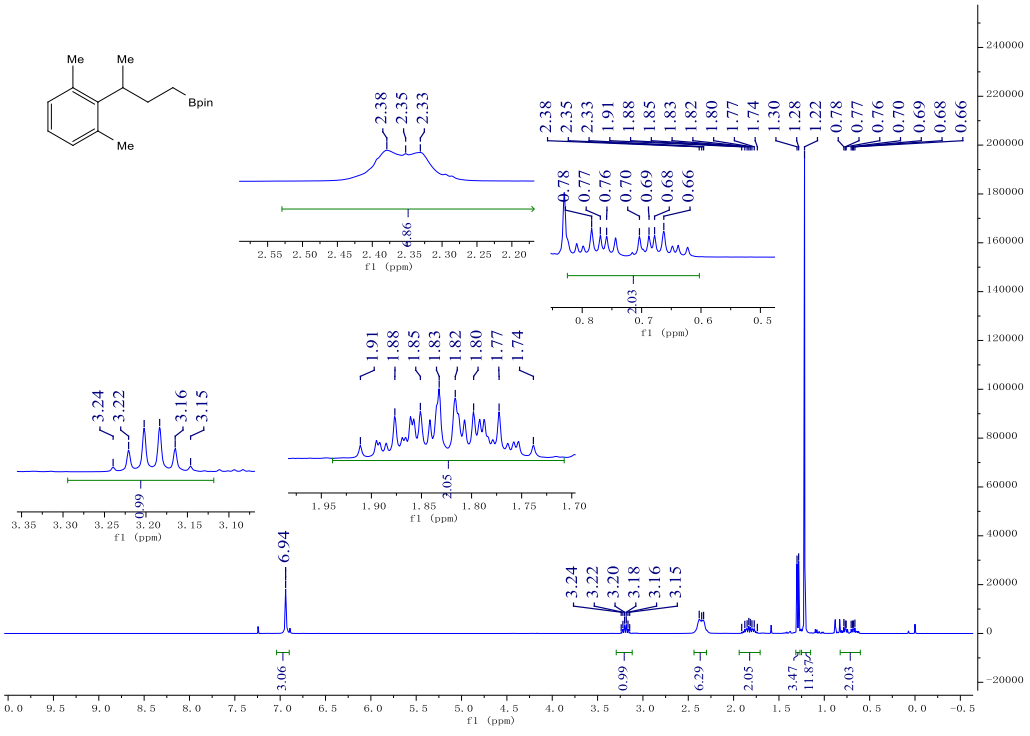


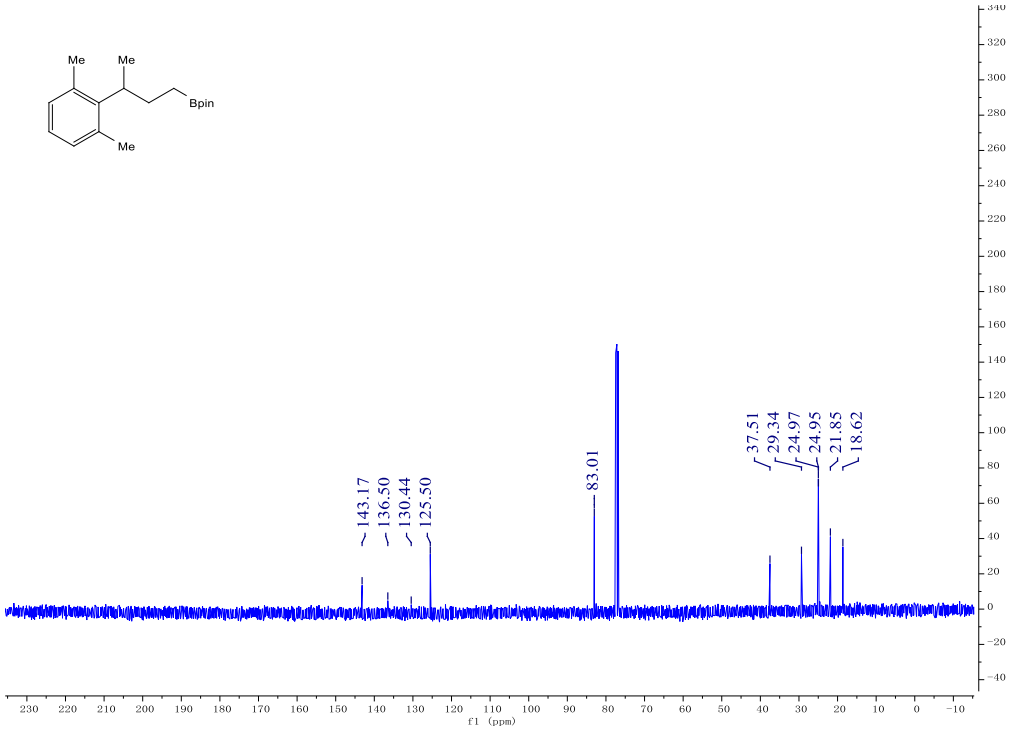
3i

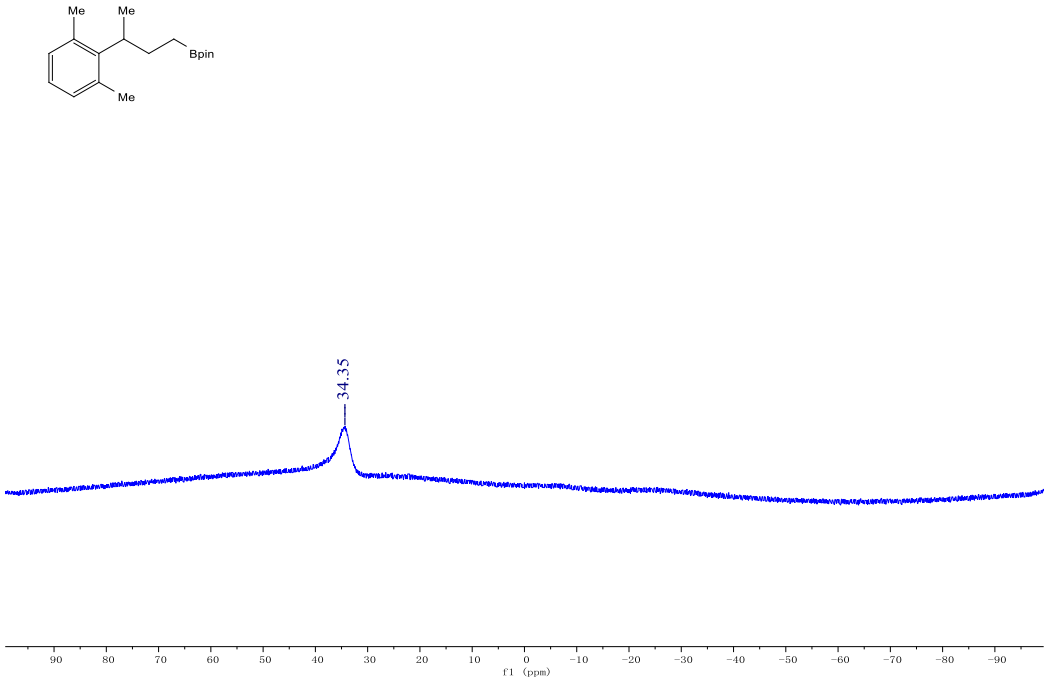



Me
Bpin
42.42
32.70
24.95
24.93
21.77
145.10
133.72
132.29
127.89
127.66
126.15
125.82
125.48
125.08
83.02
f1 (ppm)

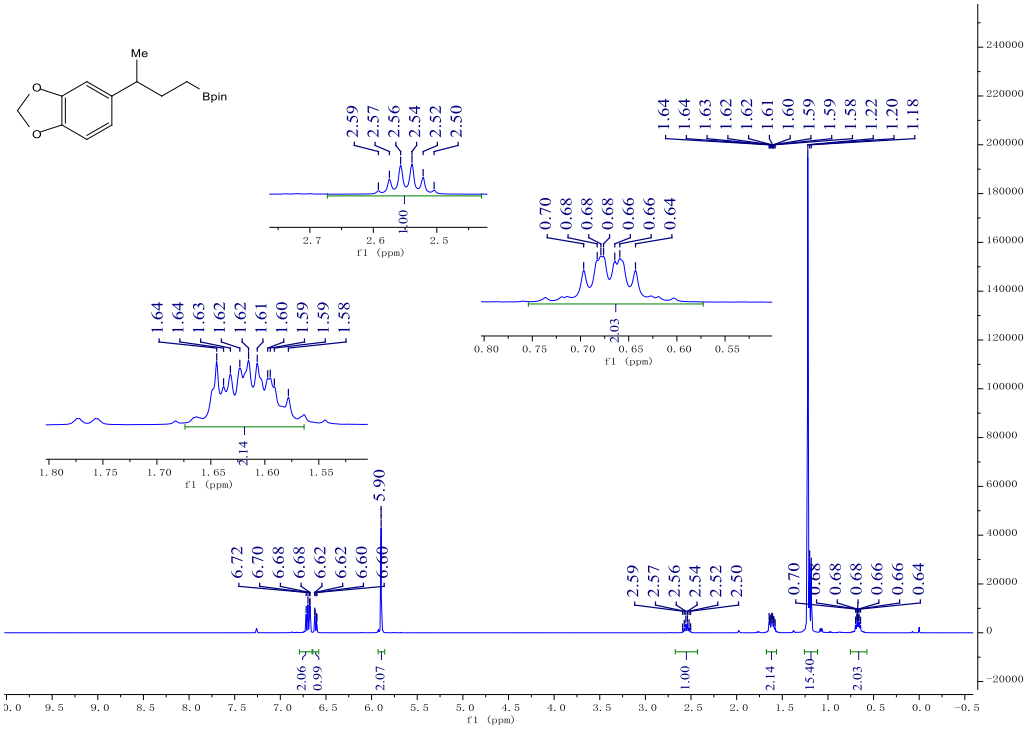
3j

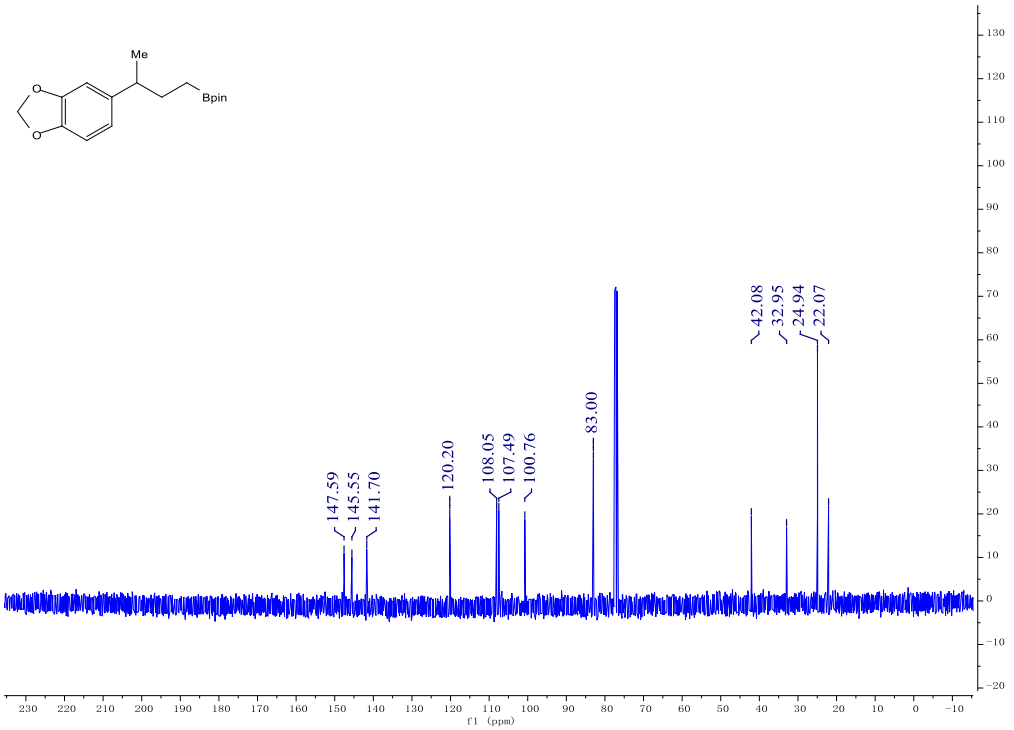

Me
Me
Bpin
Me
2.38
2.35
2.33
1.91
1.88
1.85
1.83
1.82
1.80
1.77
1.74
1.30
1.28
1.22
0.78
0.77
0.76
0.70
0.69
0.68
0.66
3.24
3.22
3.20
3.18
3.16
3.15
6.94
f1 (ppm)

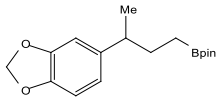

Me
Me
Bpin
Me
143.17
136.50
130.44
125.50
83.01
37.51
29.34
24.97
24.95
21.85
18.62
f1 (ppm)

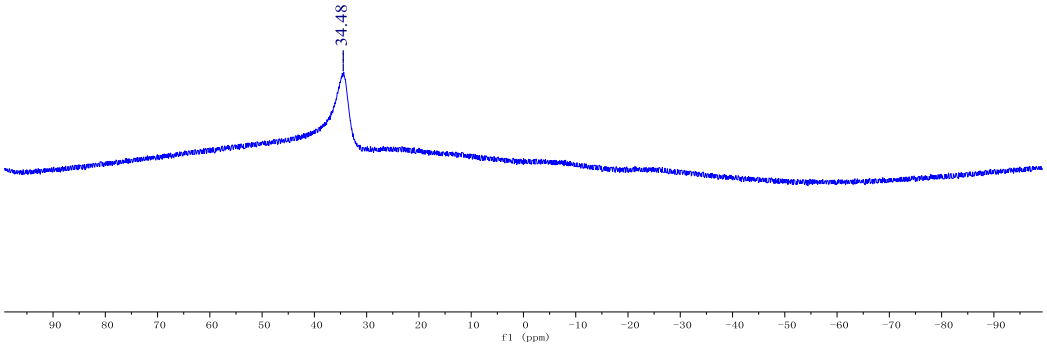

Me
Me
Bpin
Me
34.35
f1 (ppm)

3k

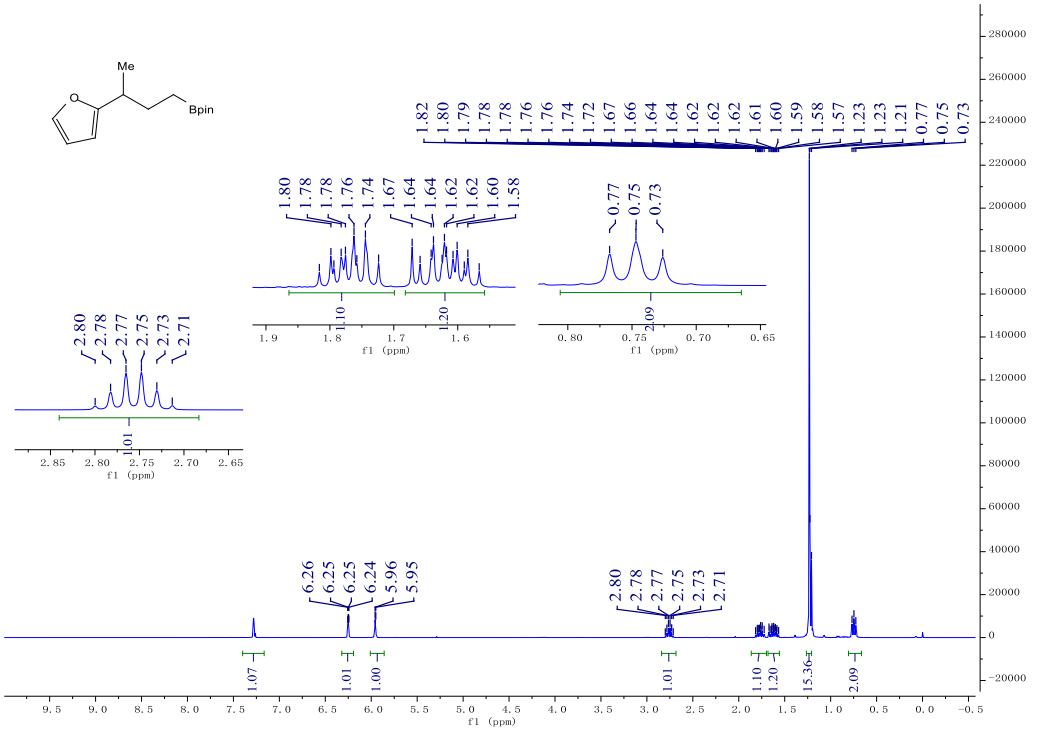


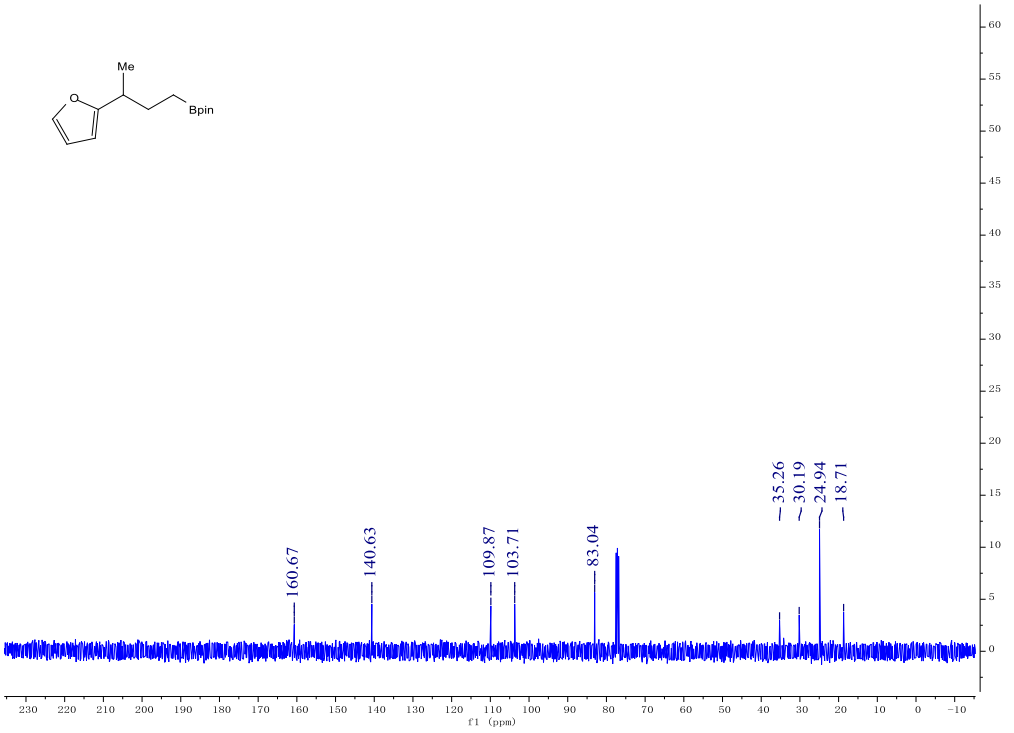


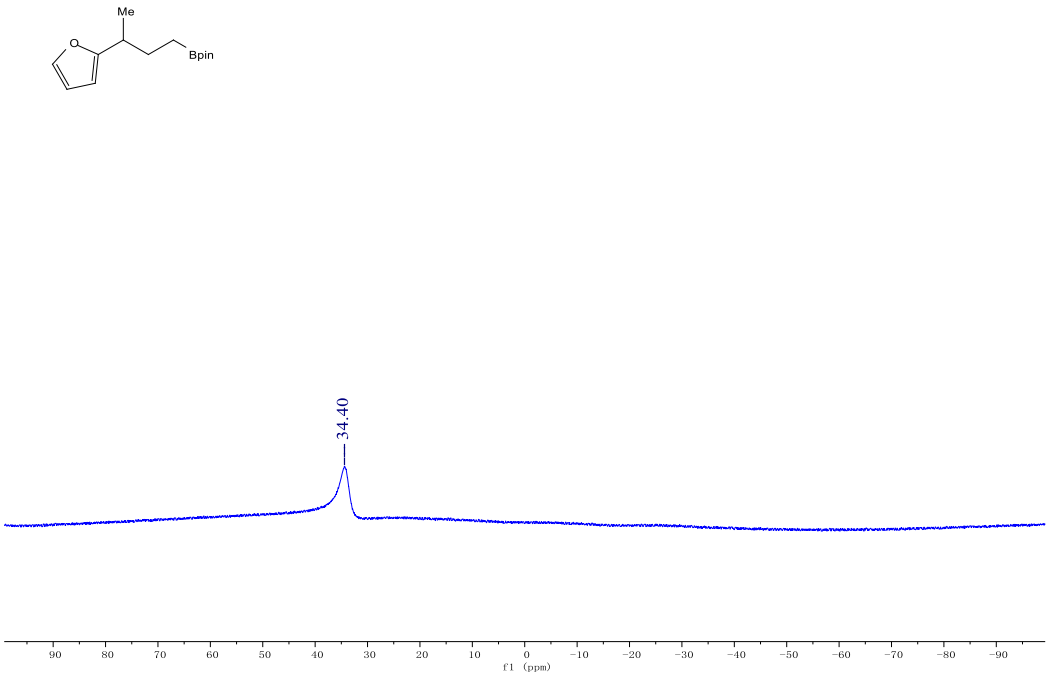




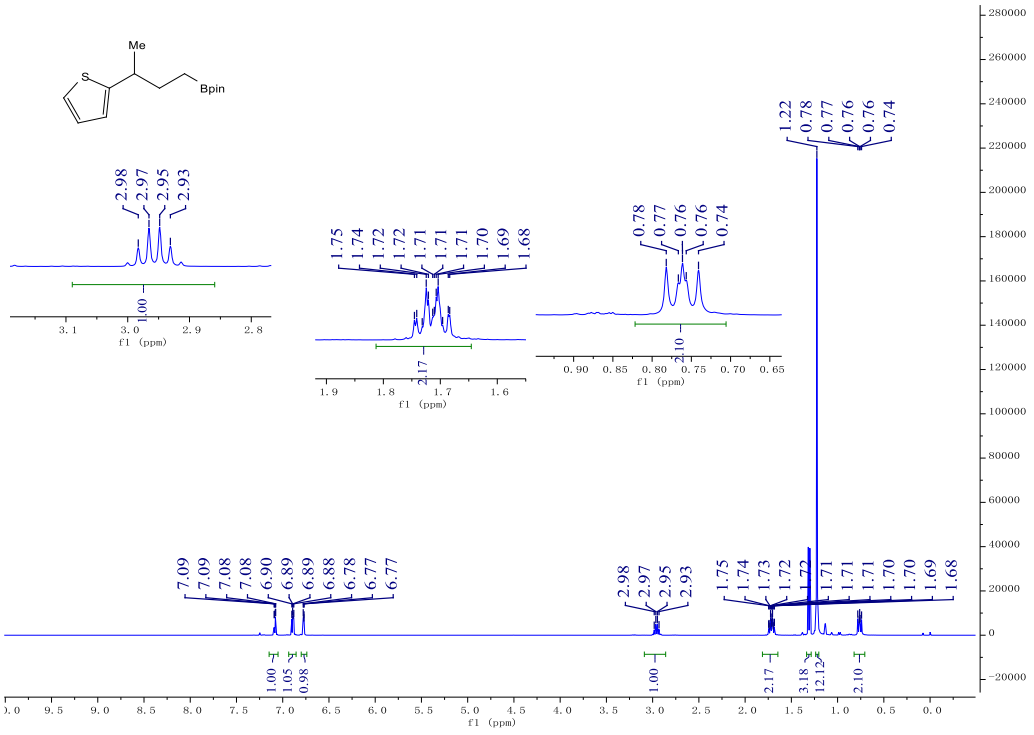
3l




Me
O
Bpin
160.67
140.63
109.87
103.71
83.04
35.26
30.19
24.94
18.71
f1 (ppm)


Me
O
Bpin
34.40
f1 (ppm)

3m


Me
S
Bpin
2.98
2.97
2.95
2.93
1.75
1.74
1.72
1.72
1.71
1.71
1.71
1.70
1.69
1.68
0.78
0.77
0.76
0.76
0.74
1.22
0.78
0.77
0.76
0.76
0.74
7.09
7.09
7.08
7.08
6.90
6.89
6.89
6.88
6.78
6.77
6.77
2.98
2.97
2.95
2.93
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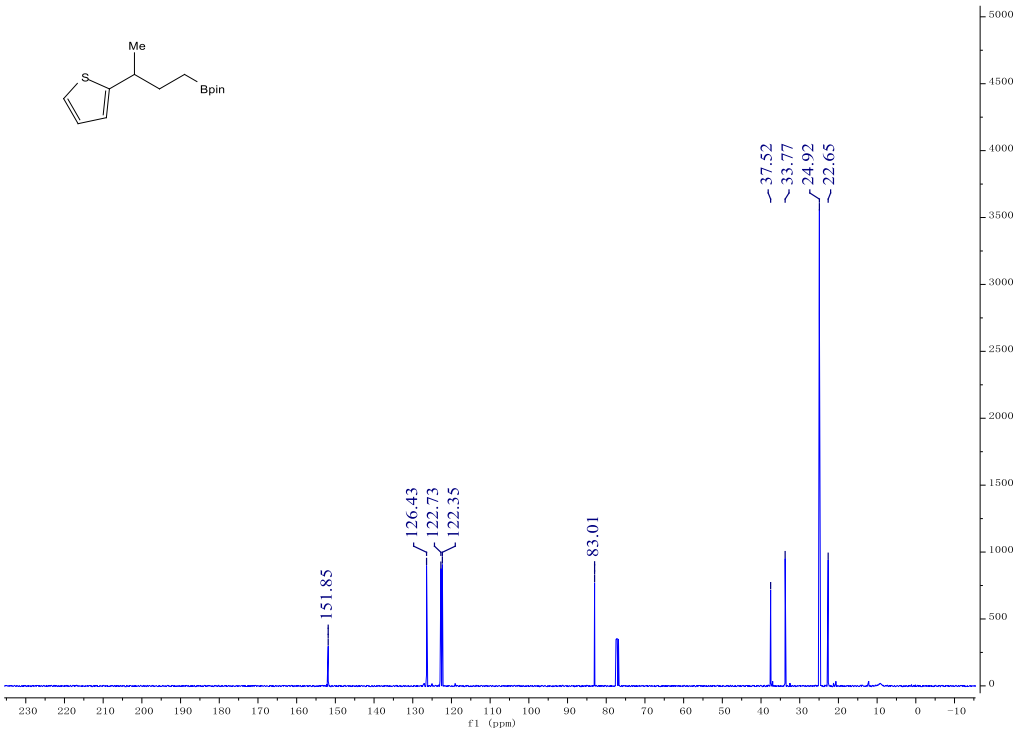
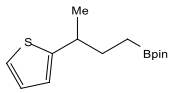
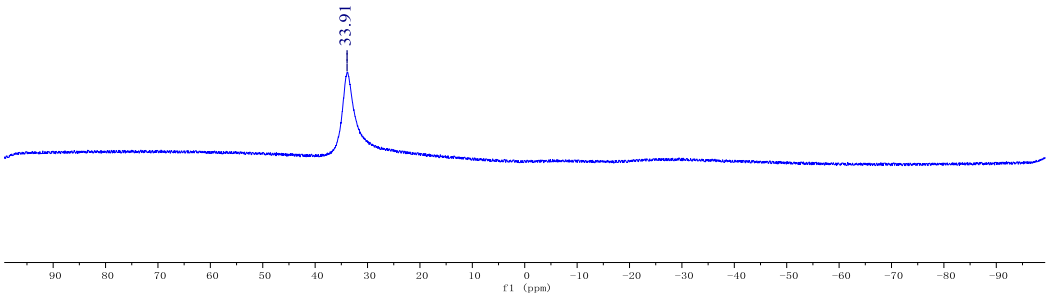
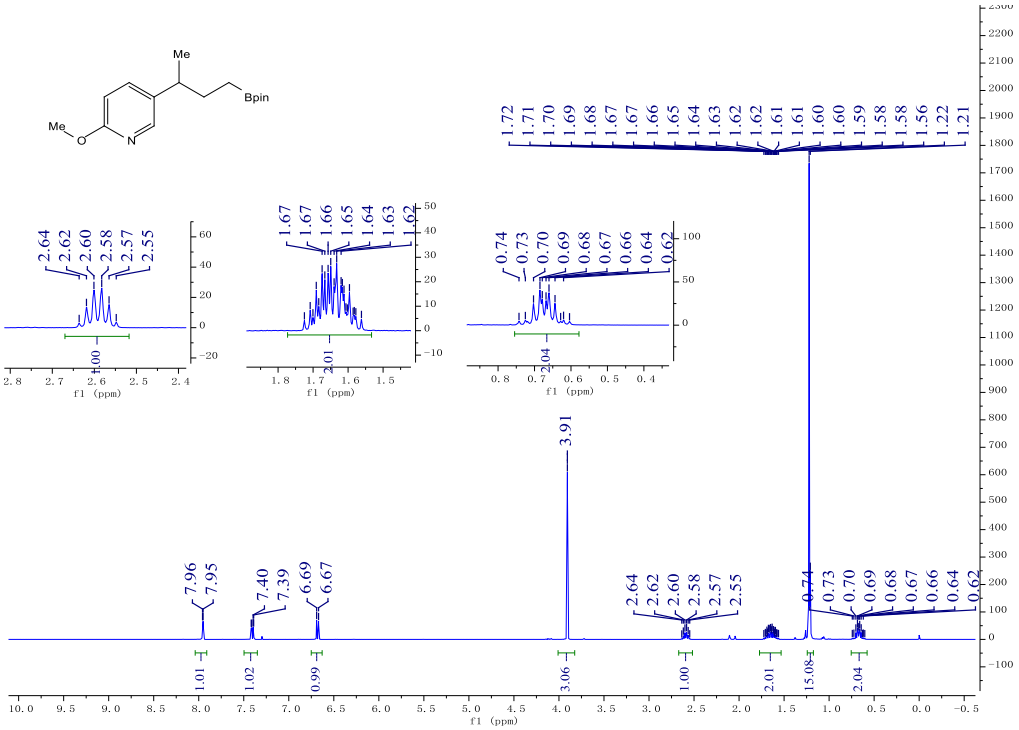
1.71
1.70
1.70
1.69
1.68
f1 (ppm)

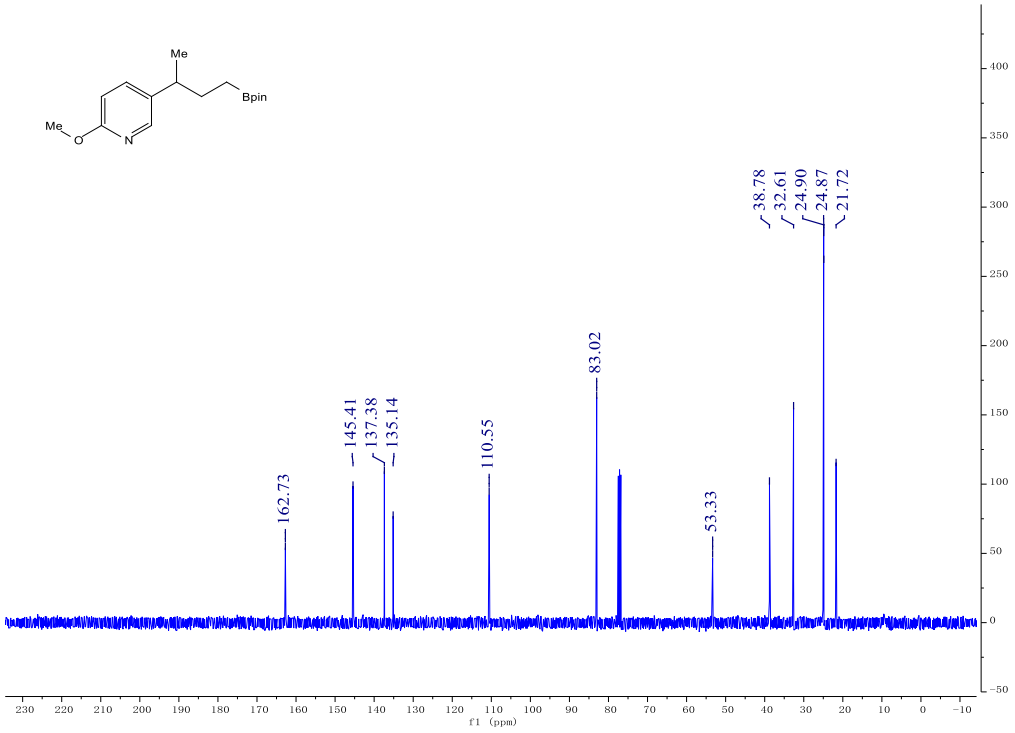

Me
S
Bpin
151.85
126.43
122.73
122.35
83.01
37.52
33.77
24.92
22.65
f1 (ppm)

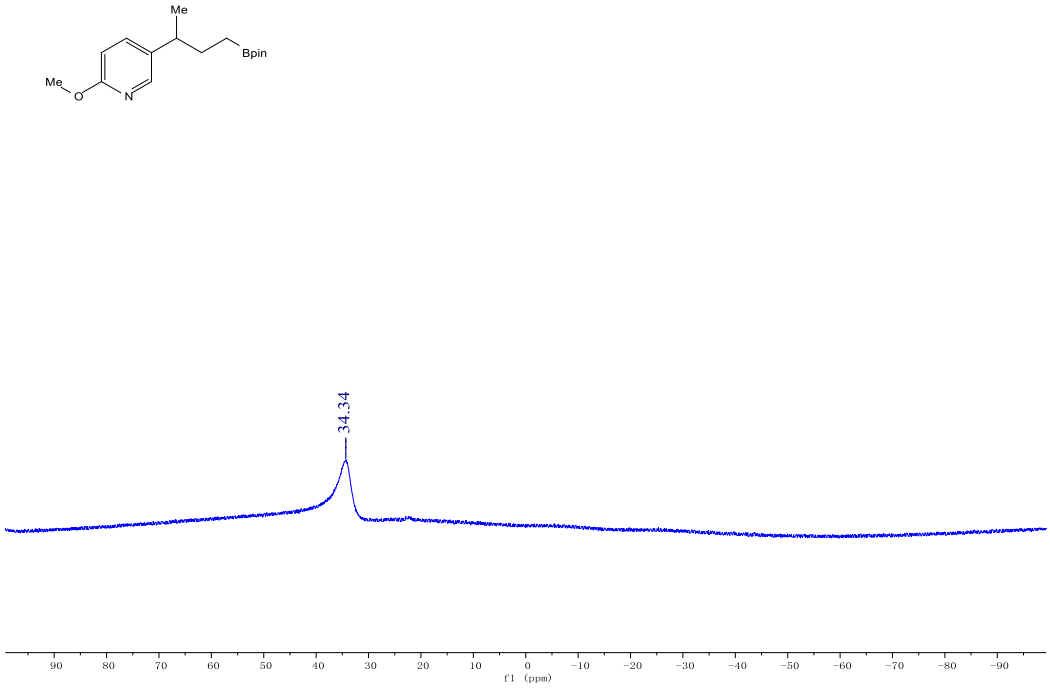




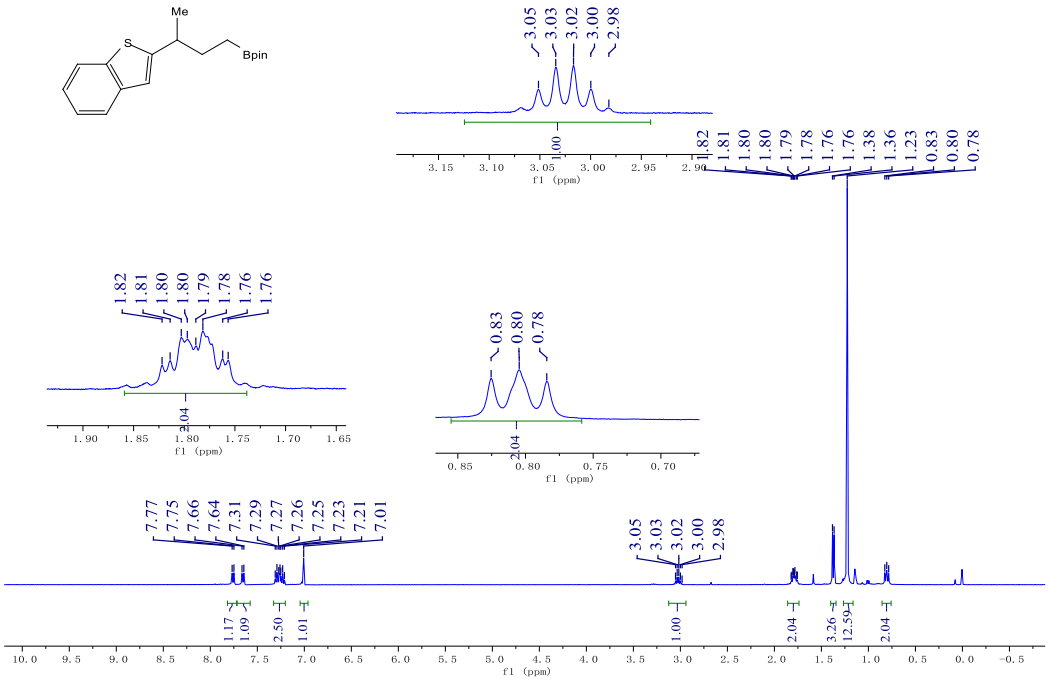
3n

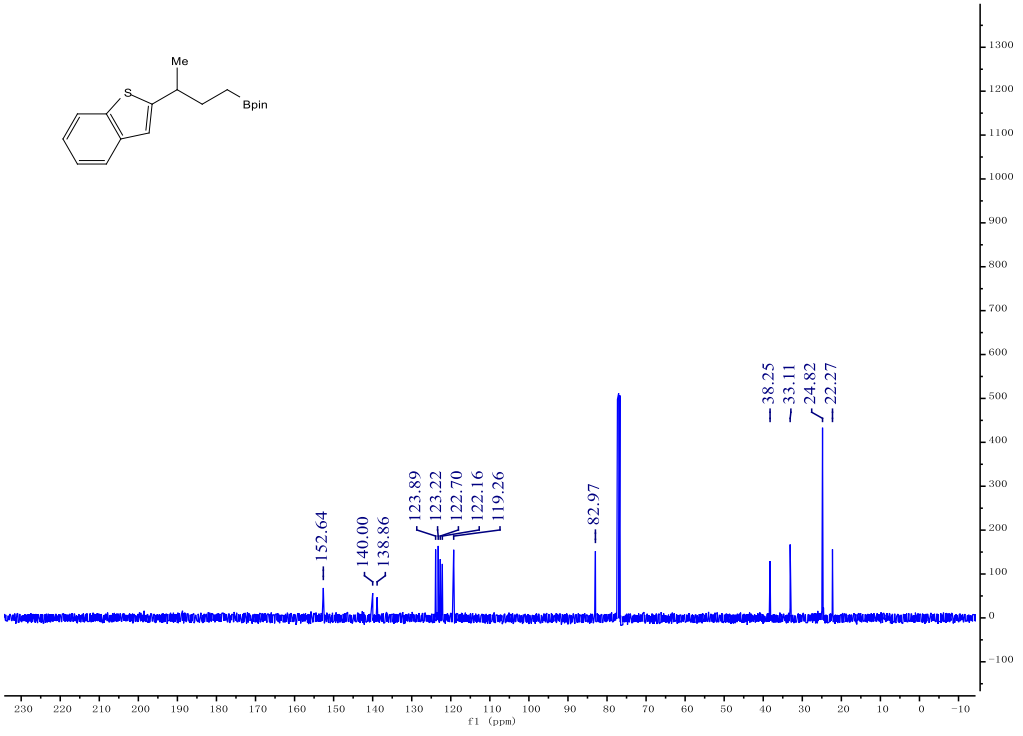


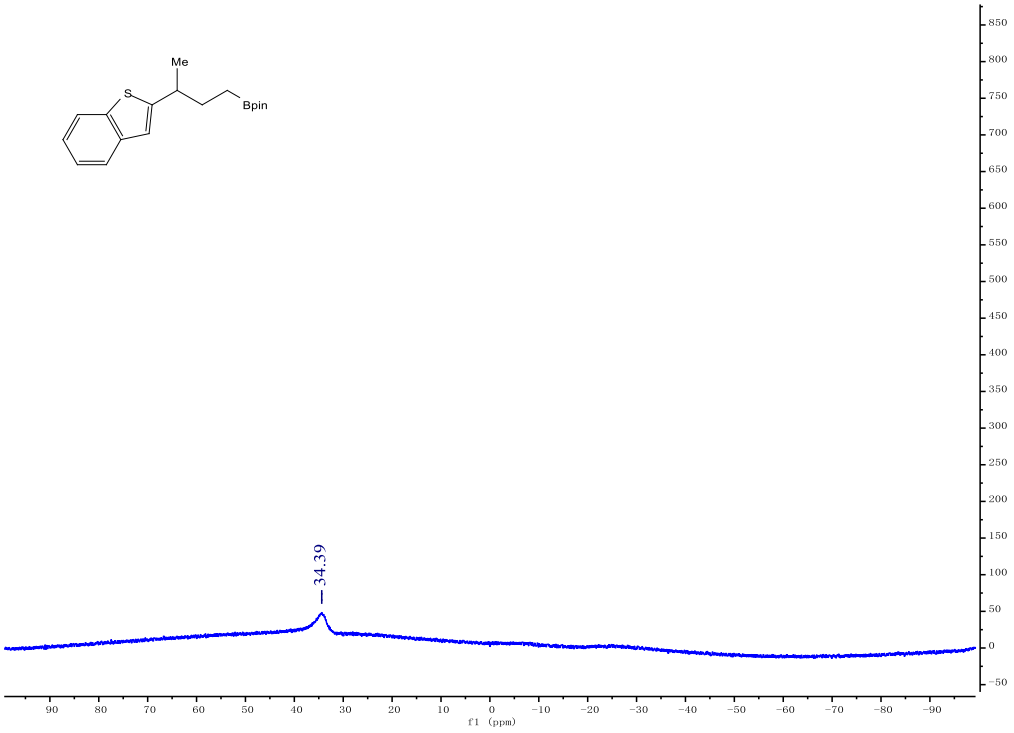

Me
Bpin
Me
O
N
38.78
32.61
24.90
24.87
21.72
83.02
53.33
145.41
137.38
135.14
110.55
162.73
f1 (ppm)


Me
Bpin
Me
O
N
34.34
f1 (ppm)

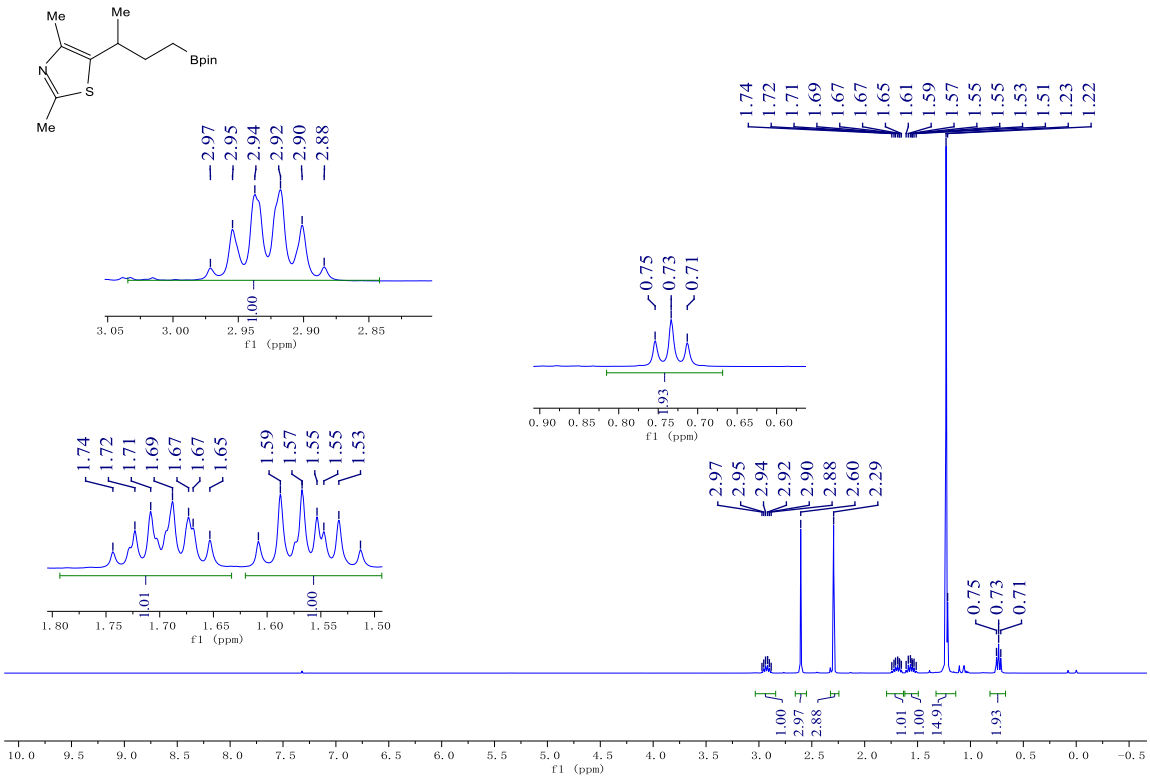
3o

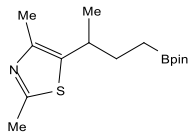

Me
S
Bpin
3.05
3.03
3.02
3.00
2.98
1.82
1.81
1.80
1.80
1.79
1.78
1.76
1.76
1.38
1.36
1.23
0.83
0.80
0.78
7.77
7.75
7.66
7.64
7.31
7.29
7.27
7.26
7.25
7.23
7.21
7.01
f1 (ppm)

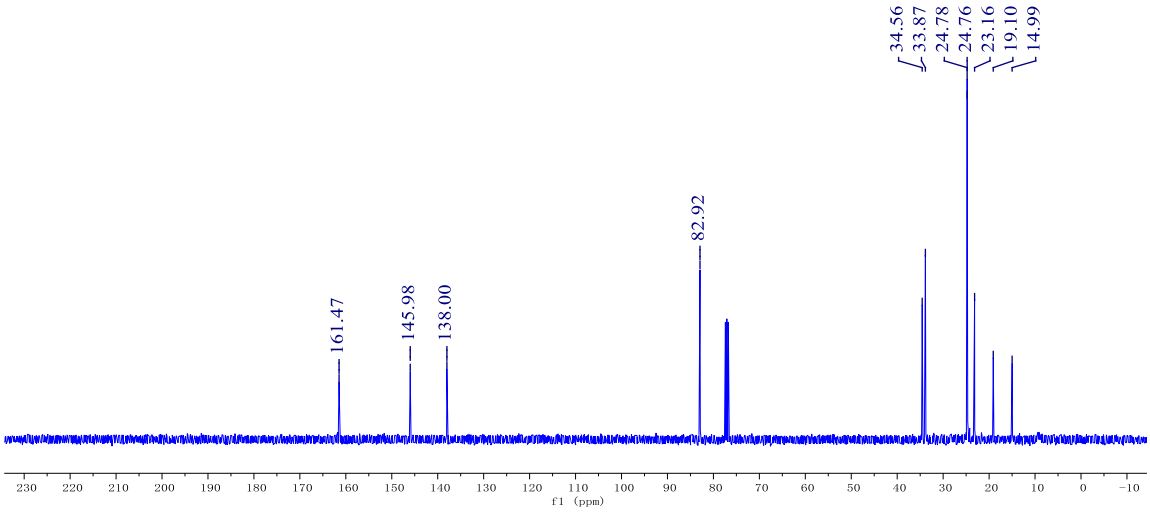

Me
S
Bpin
152.64
140.00
138.86
123.89
123.22
122.70
122.16
119.26
82.97
38.25
33.11
24.82
22.27
f1 (ppm)

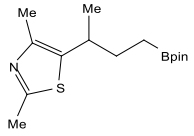

Me
S
Bpin
34.39
f1 (ppm)

3p


Me
Me
N
S
Me
Bpin
2.97
2.95
2.94
2.92
2.90
2.88
1.00
f1 (ppm)
0.75
0.73
0.71
1.93
1.74
1.72
1.71
1.69
1.67
1.67
1.65
1.59
1.57
1.55
1.55
1.53
1.01
1.00
2.60
2.29
1.51
1.23
1.22
14.91
f1 (ppm)

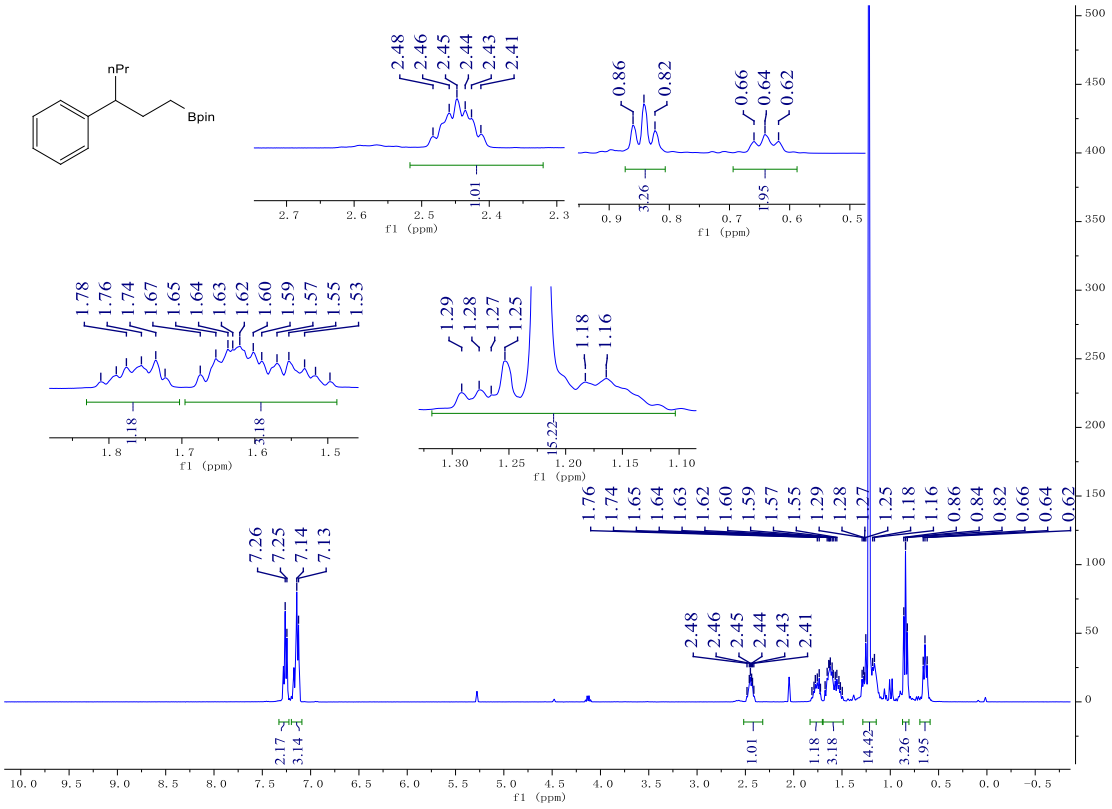

Me
Me
N
S
Me
Bpin

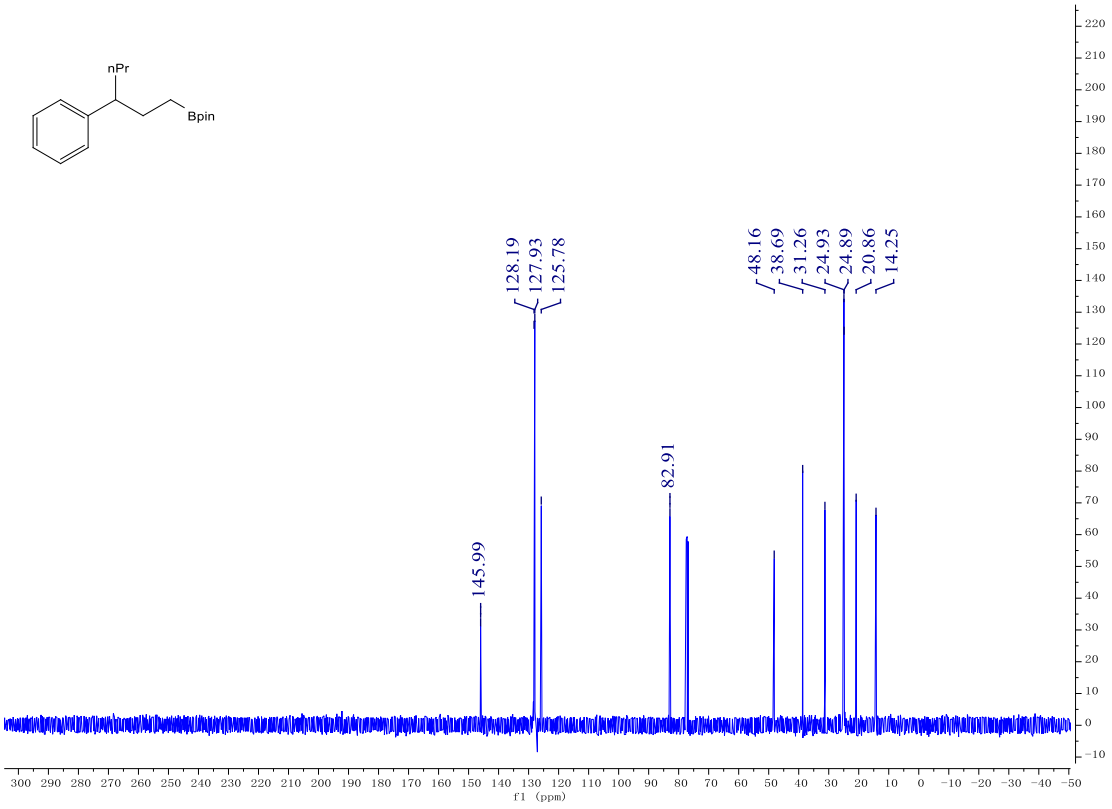

34.56
33.87
24.78
24.76
23.16
19.10
14.99
82.92
161.47
145.98
138.00
f1 (ppm)

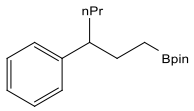

Me
Me
N
S
Me
Bpin

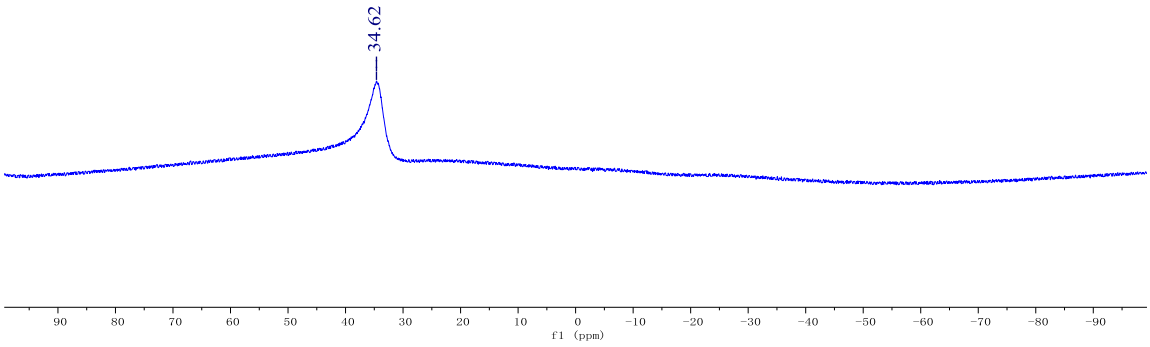
33.71
f1 (ppm)

3q

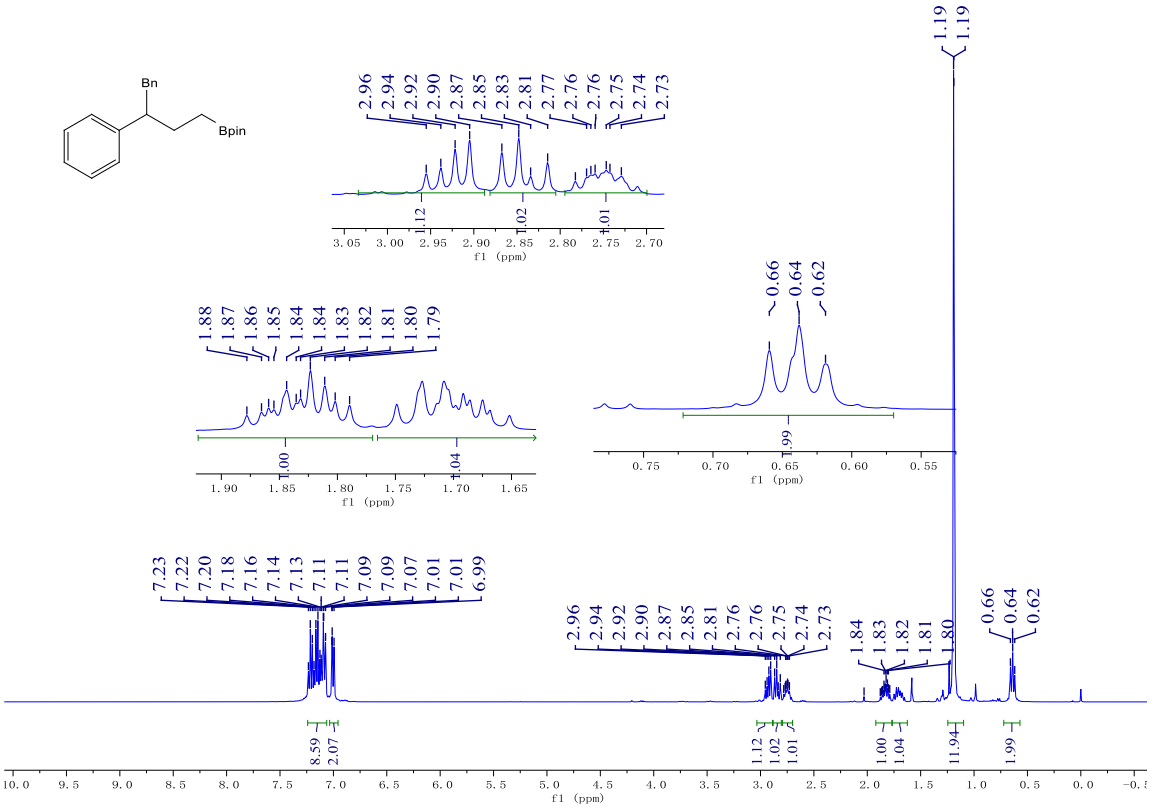

nPr
Bpin
2.48
2.46
2.45
2.44
2.43
2.41
0.86
0.82
0.66
0.64
0.62
1.78
1.76
1.74
1.67
1.65
1.64
1.63
1.62
1.60
1.59
1.57
1.55
1.53
1.29
1.28
1.27
1.25
1.18
1.16
7.26
7.25
7.14
7.13
f1 (ppm)

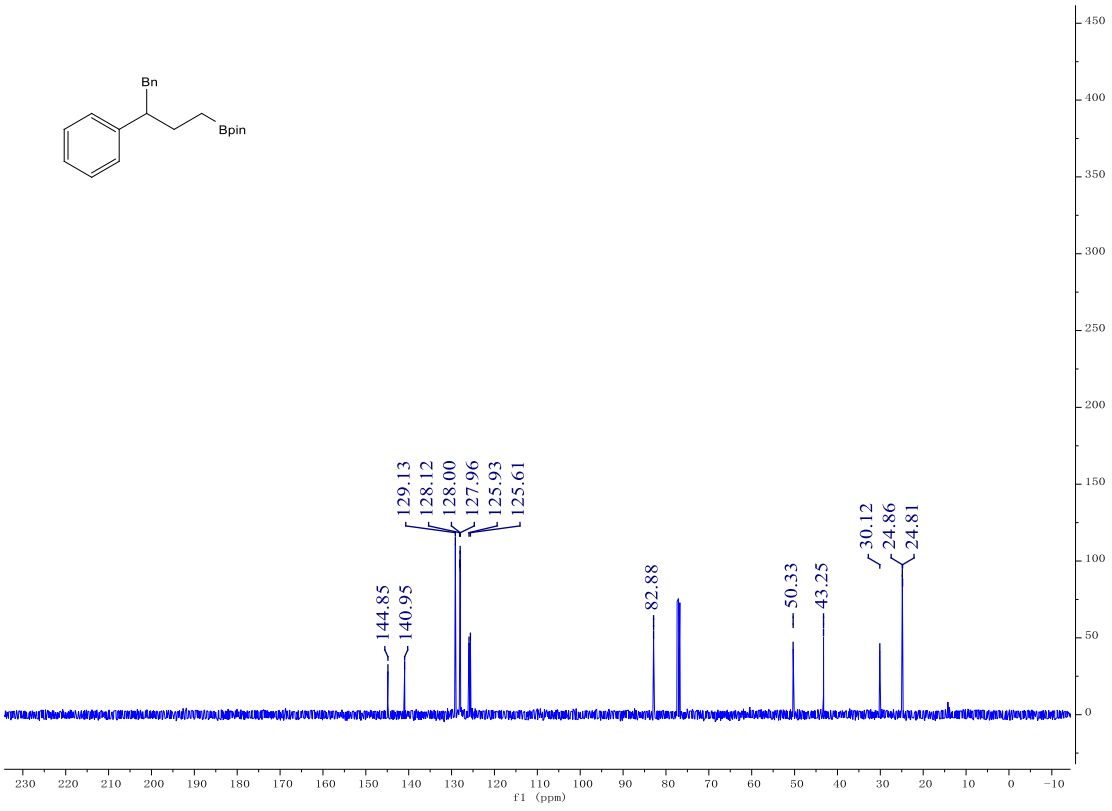

nPr
Bpin
128.19
127.93
125.78
48.16
38.69
31.26
24.93
24.89
20.86
14.25
145.99
82.91
f1 (ppm)

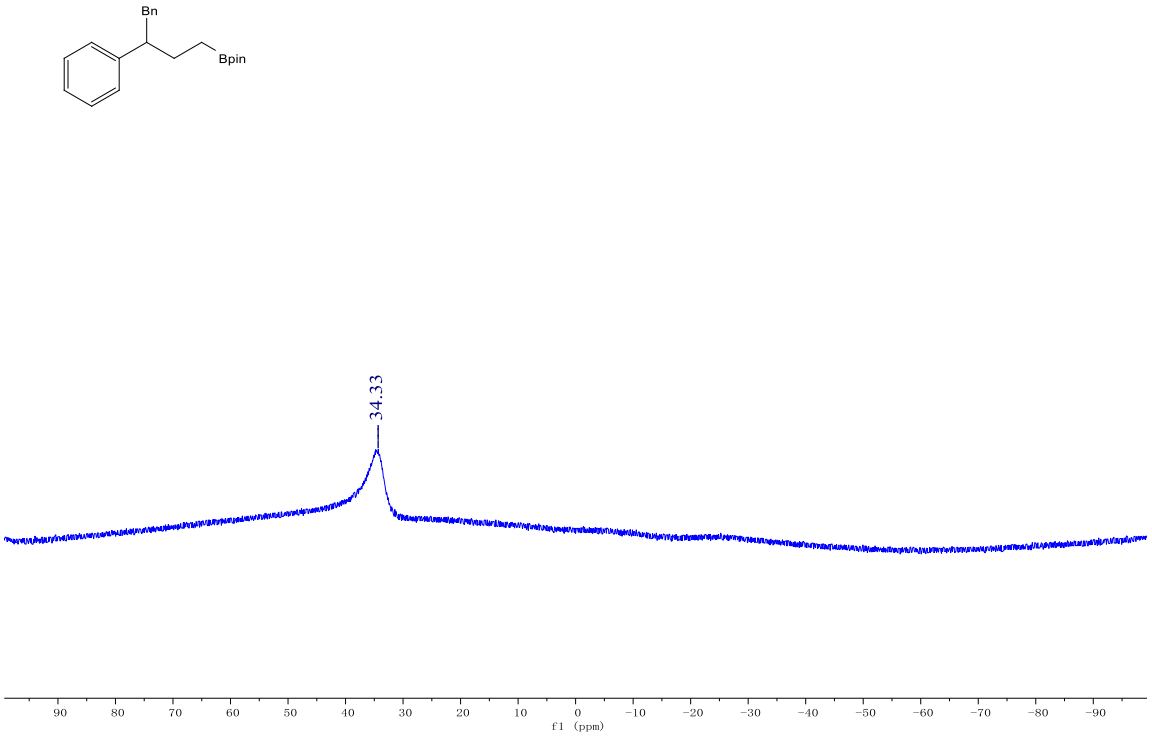




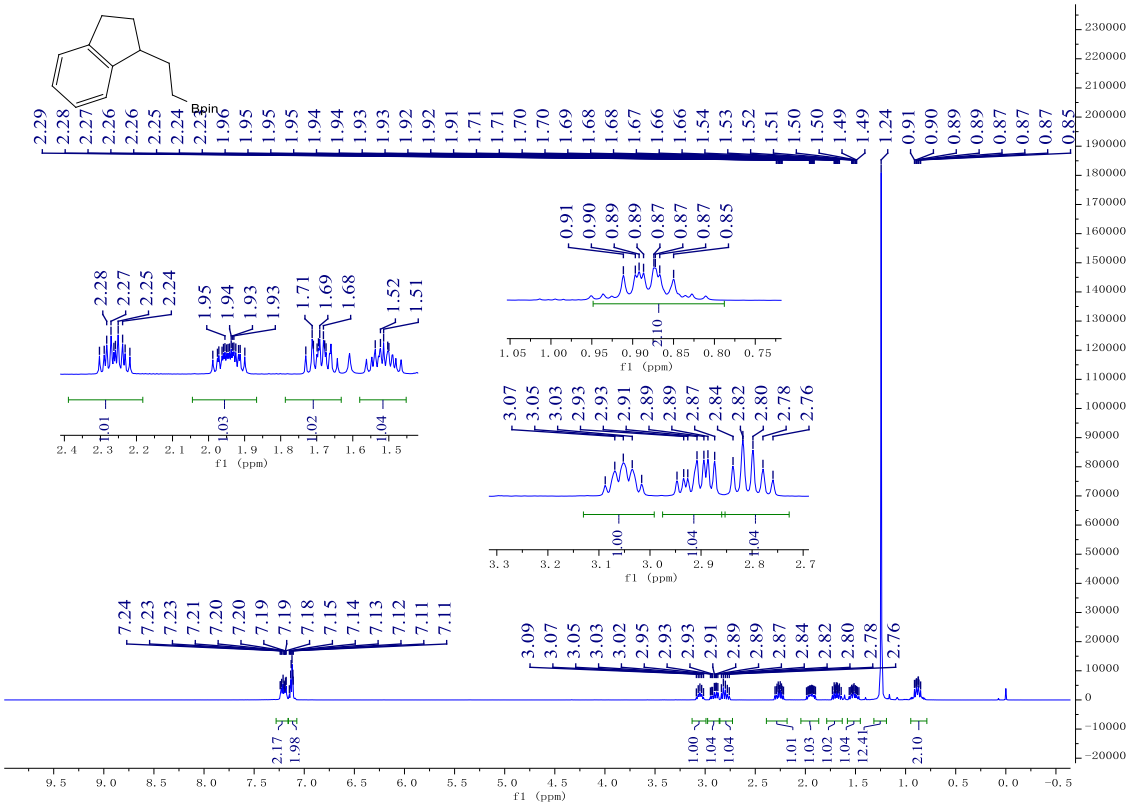
3r

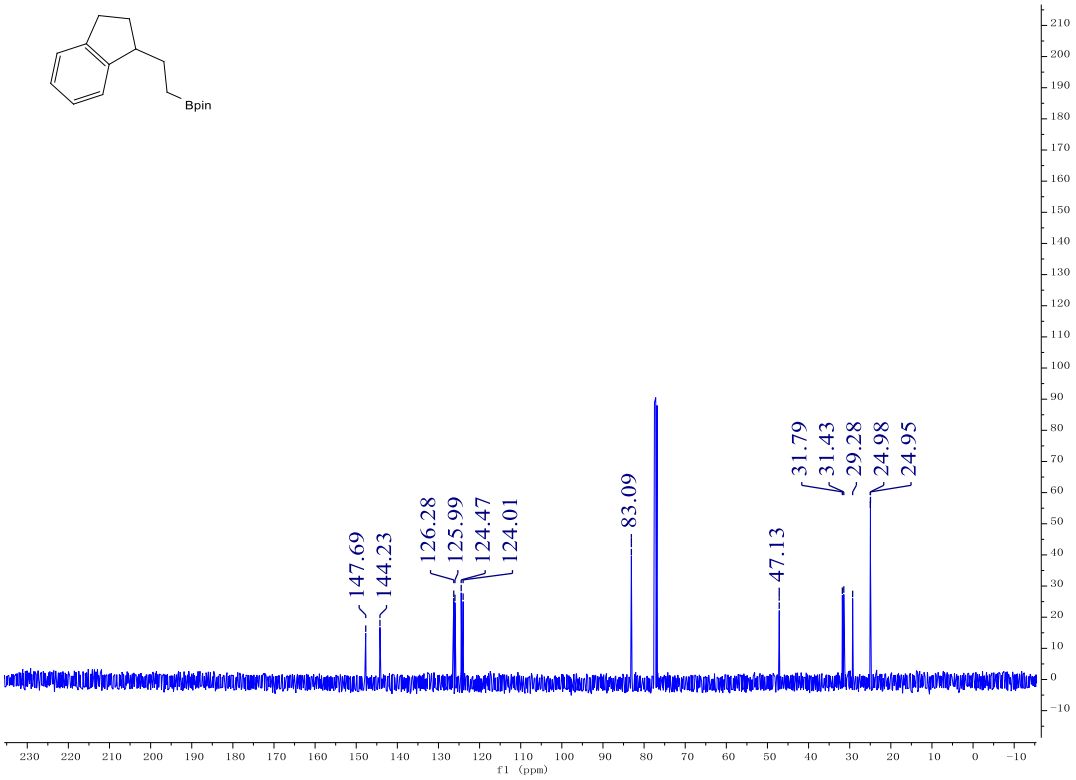



Bn
Bpin
144.85
140.95
129.13
128.12
128.00
127.96
125.93
125.61
82.88
50.33
43.25
30.12
24.86
24.81
f1 (ppm)

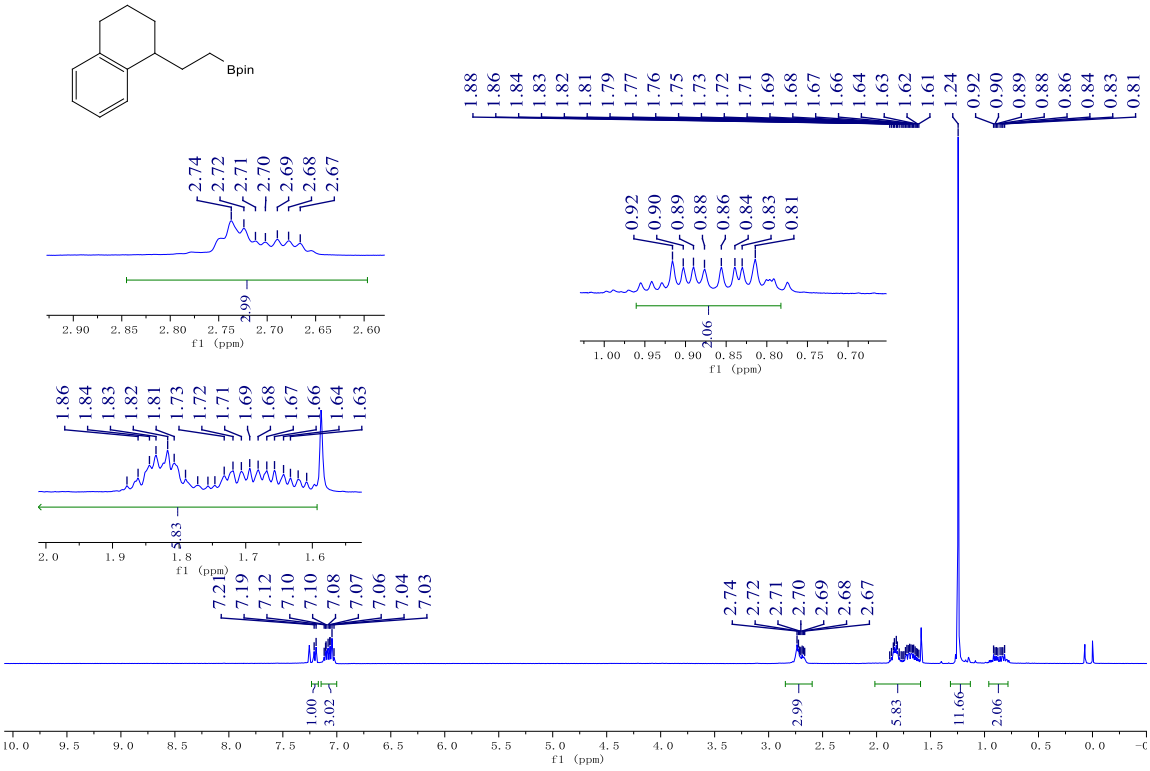

Bn
Bpin
34.33
f1 (ppm)

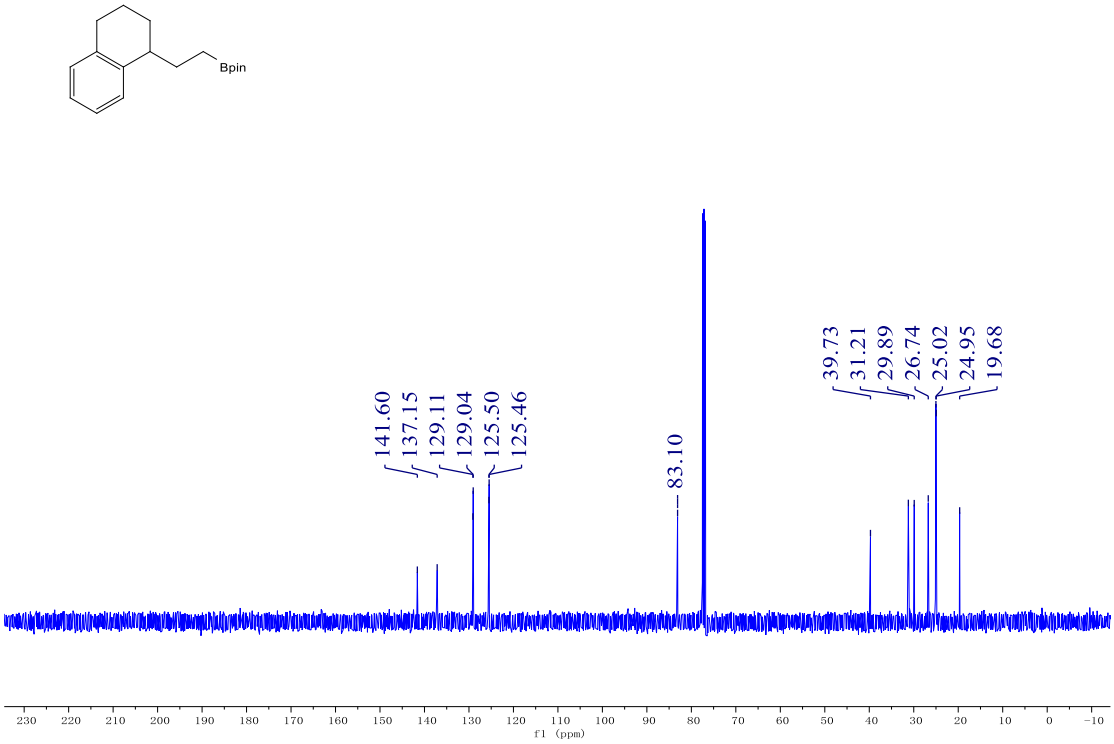
3s



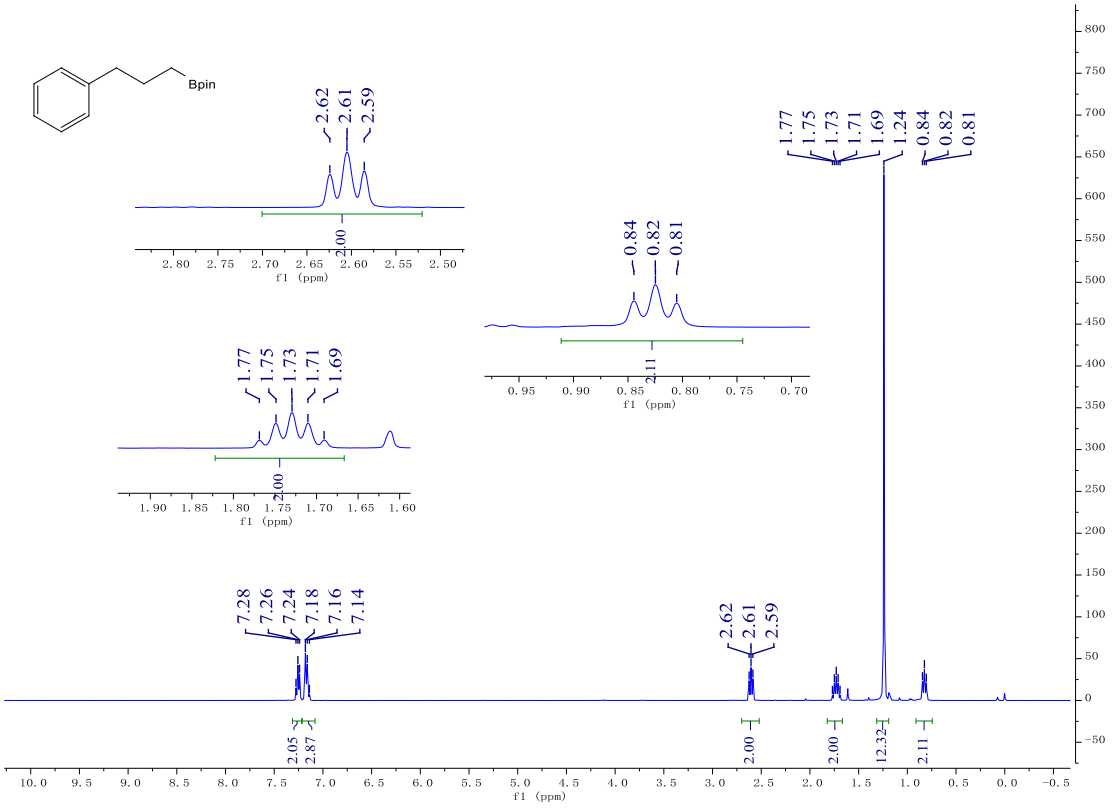


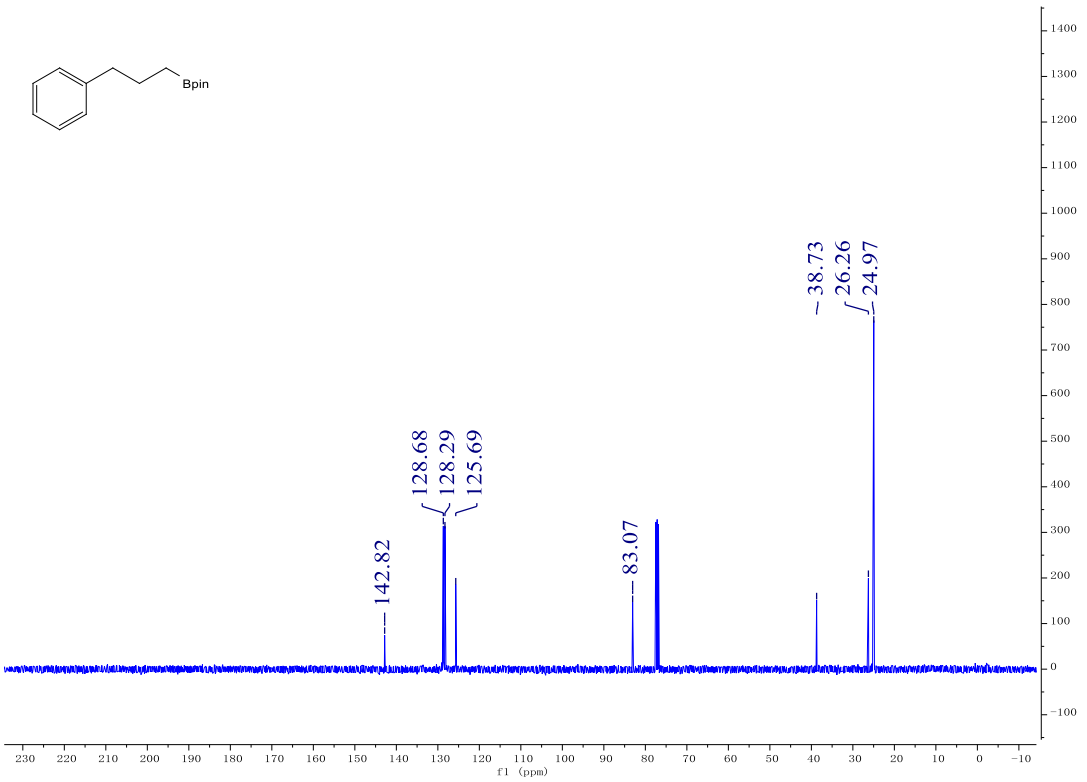
3t


Bpin
1.88
1.86
1.84
1.83
1.82
1.81
1.79
1.77
1.76
1.75
1.73
1.72
1.71
1.69
1.68
1.67
1.66
1.64
1.63
1.62
1.61
1.24
0.92
0.90
0.89
0.88
0.86
0.84
0.83
0.81
2.74
2.72
2.71
2.70
2.69
2.68
2.67
7.21
7.19
7.12
7.10
7.10
7.08
7.07
7.06
7.04
7.03
1.00
3.02
2.99
5.83
11.66
2.06
f1 (ppm)

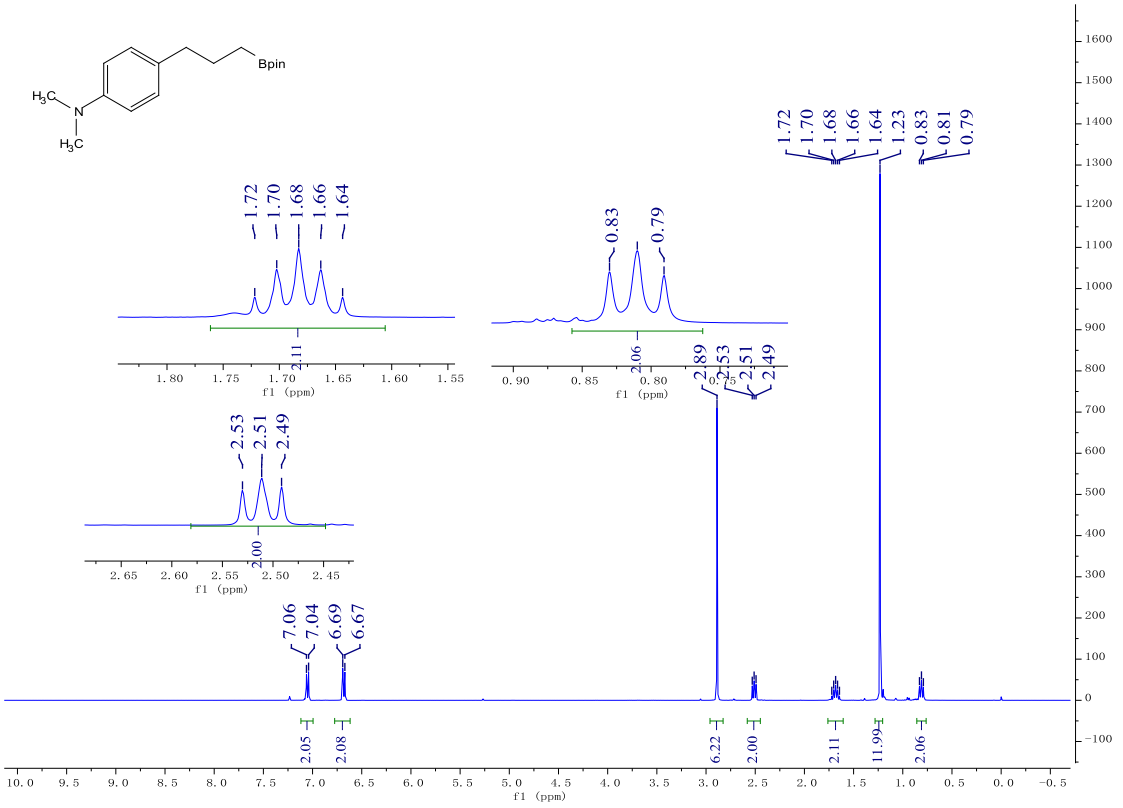

Bpin
141.60
137.15
129.11
129.04
125.50
125.46
83.10
39.73
31.21
29.89
26.74
25.02
24.95
19.68
f1 (ppm)

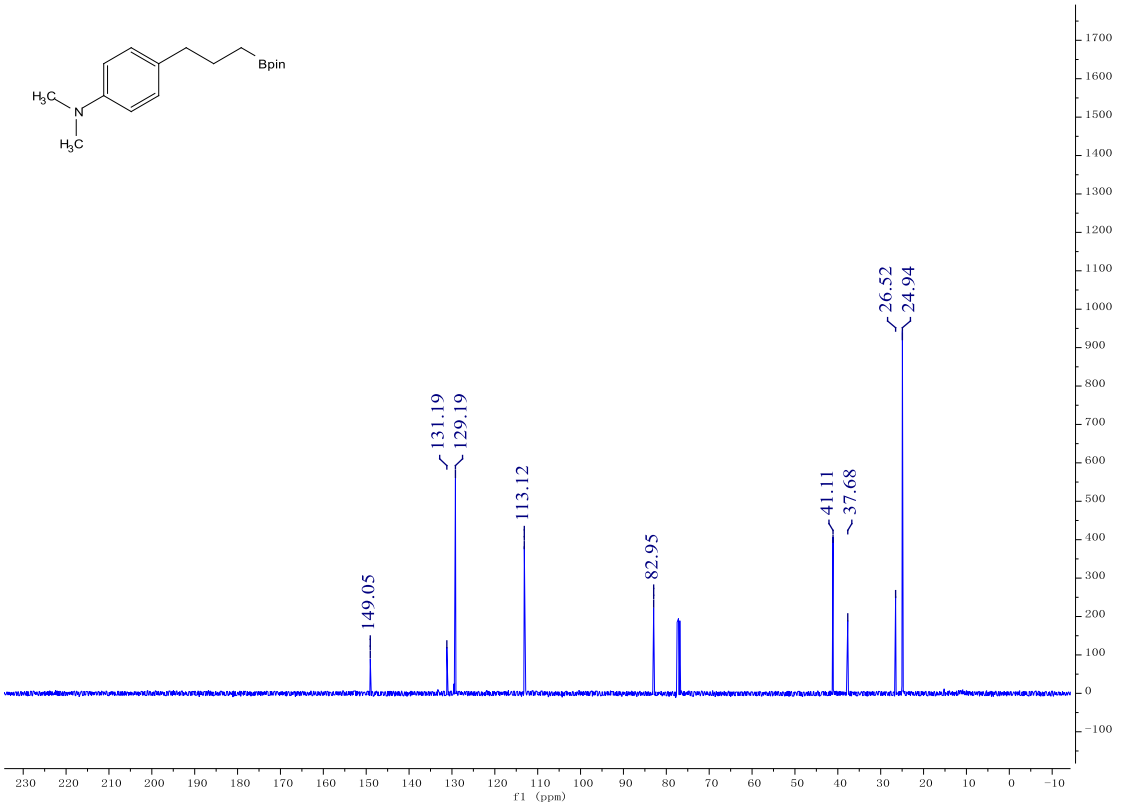
3u

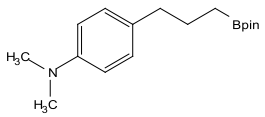

Bpin
2.62
2.61
2.59
2.00
0.84
0.82
0.81
2.11
1.77
1.75
1.73
1.71
1.69
2.00
1.77
1.75
1.73
1.71
1.69
1.24
0.84
0.82
0.81
7.28
7.26
7.24
7.18
7.16
7.14
2.62
2.61
2.59
2.05
2.87
2.00
2.00
12.32
2.11
f1 (ppm)

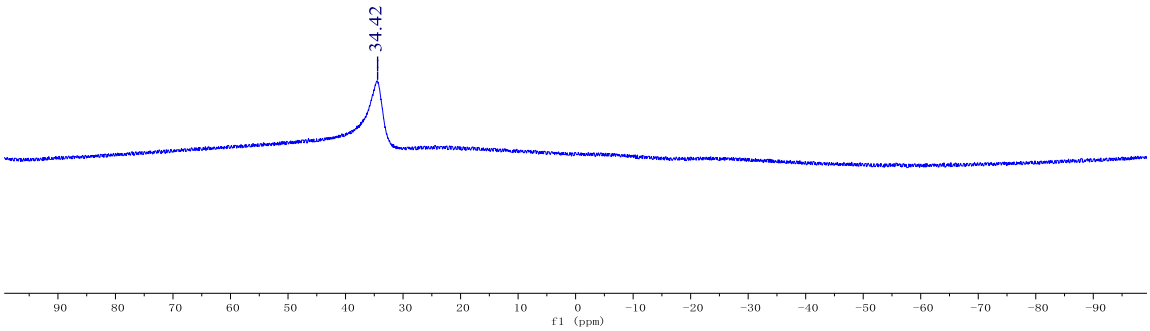

Bpin
38.73
26.26
24.97
128.68
128.29
125.69
142.82
83.07
f1 (ppm)

3v

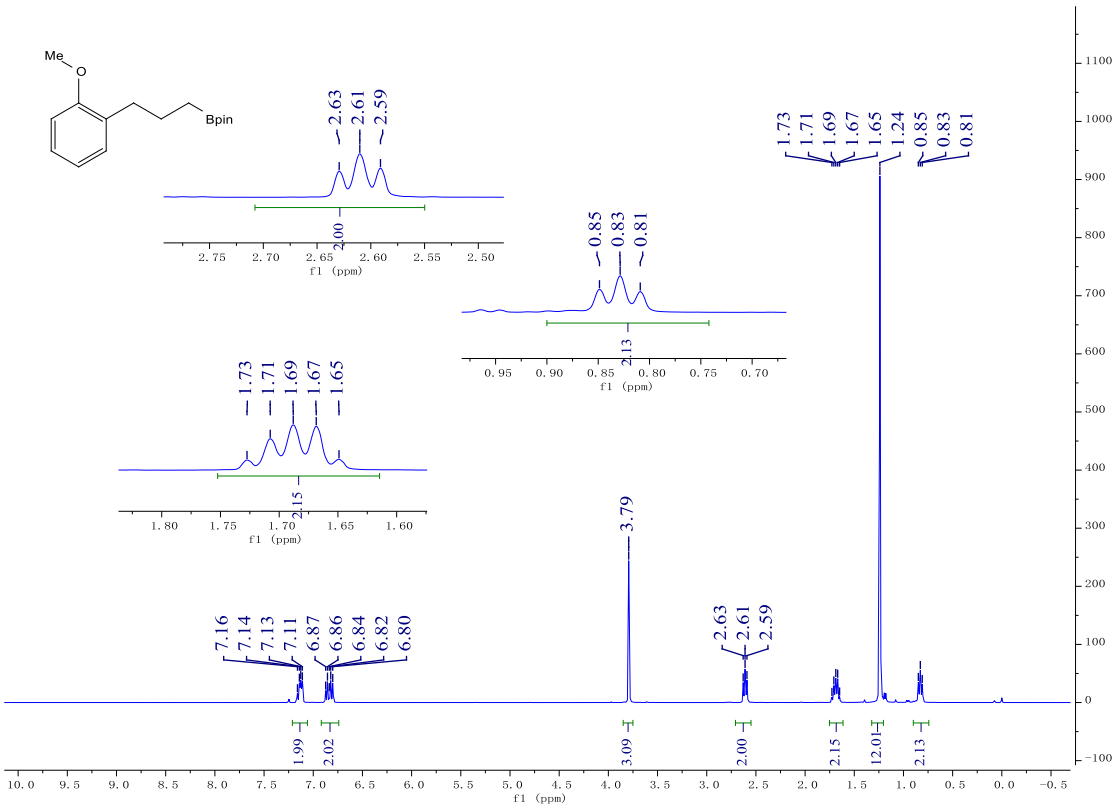

Bpin
H3C
N
H3C
1.72
1.70
1.68
1.66
1.64
1.23
0.83
0.81
0.79
2.89
2.53
2.51
2.49
7.06
7.04
6.69
6.67
2.05
2.08
6.22
2.00
2.11
11.99
2.06
f1 (ppm)

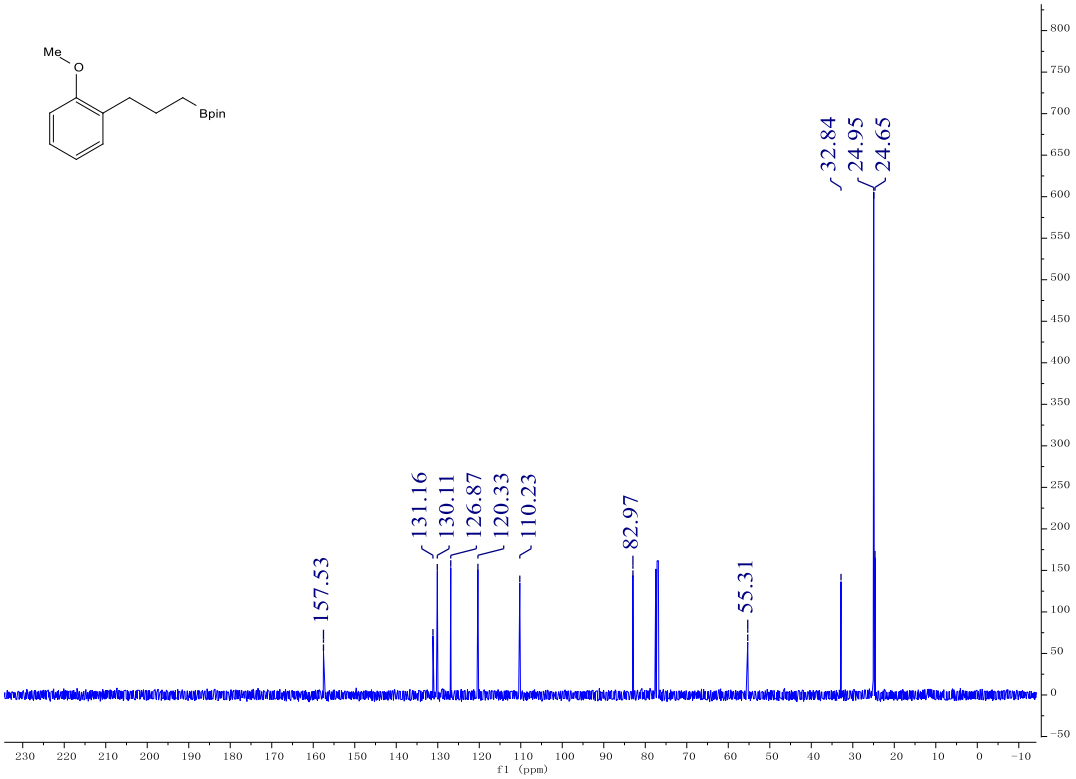

Bpin
H3C
N
H3C
149.05
131.19
129.19
113.12
82.95
41.11
37.68
26.52
24.94
f1 (ppm)


Bpin
H3C
N
H3C

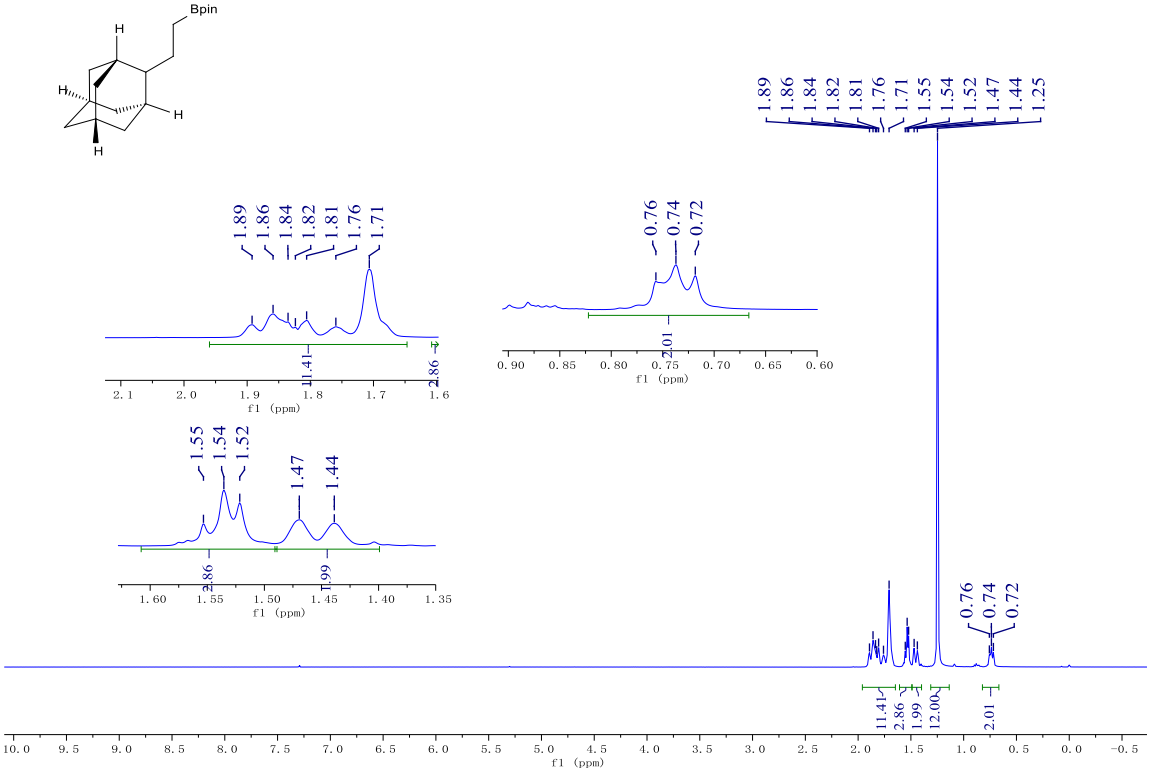

34.42
f1 (ppm)

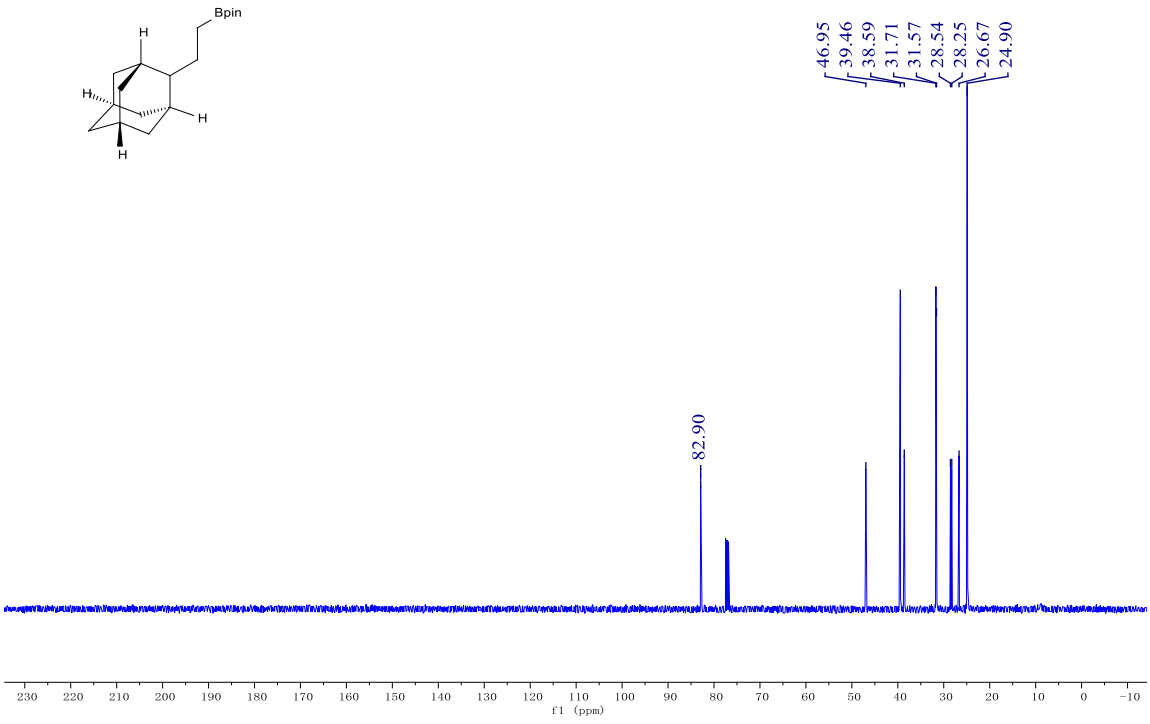
3w

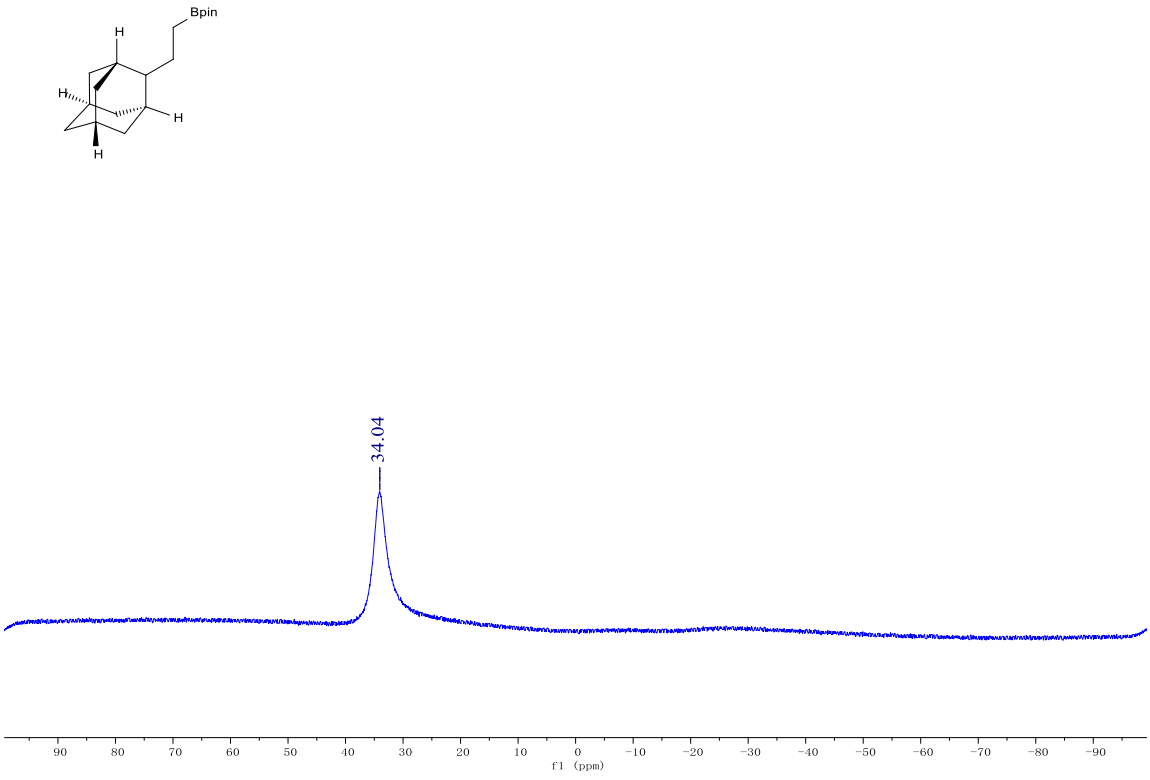

Me
O
Bpin
2.63
2.61
2.59
2.00
0.85
0.83
0.81
2.13
1.73
1.71
1.69
1.67
1.65
2.15
1.24
3.79
7.16
7.14
7.13
7.11
6.87
6.86
6.84
6.82
6.80
1.99
2.02
3.09
2.00
2.15
12.01
2.13
f1 (ppm)


Me
O
Bpin
157.53
131.16
130.11
126.87
120.33
110.23
82.97
55.31
32.84
24.95
24.65
f1 (ppm)

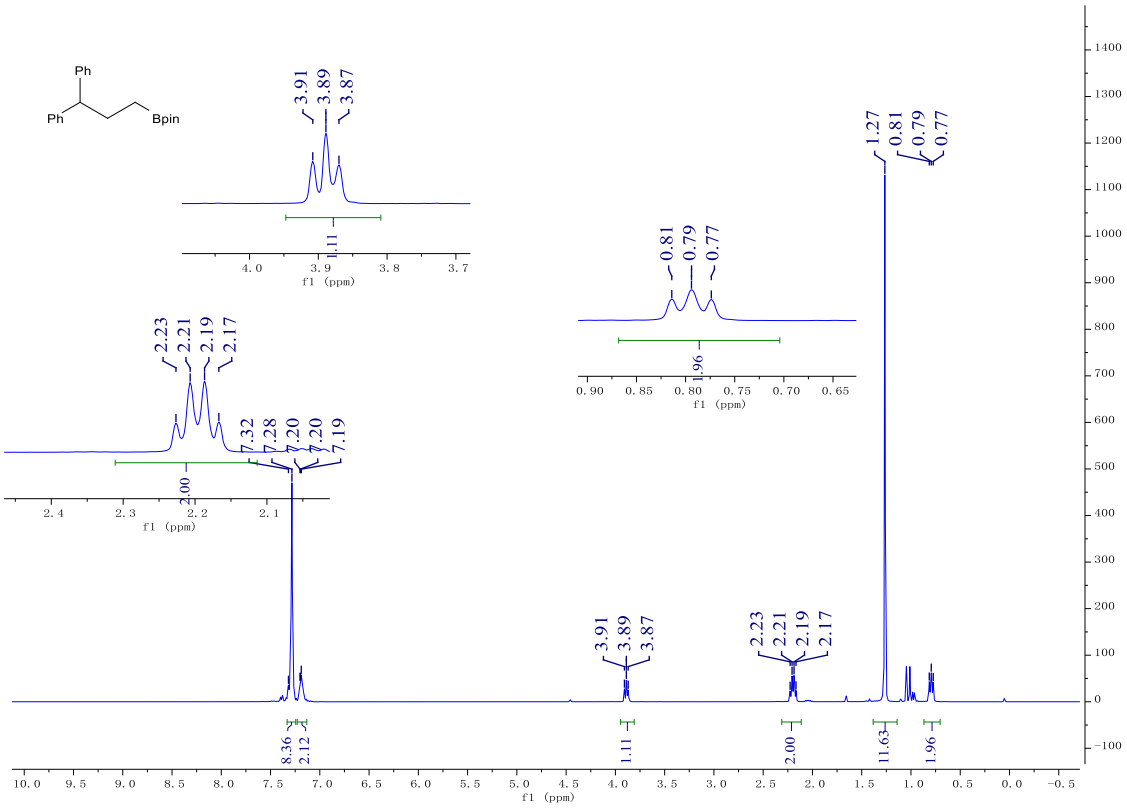
3x

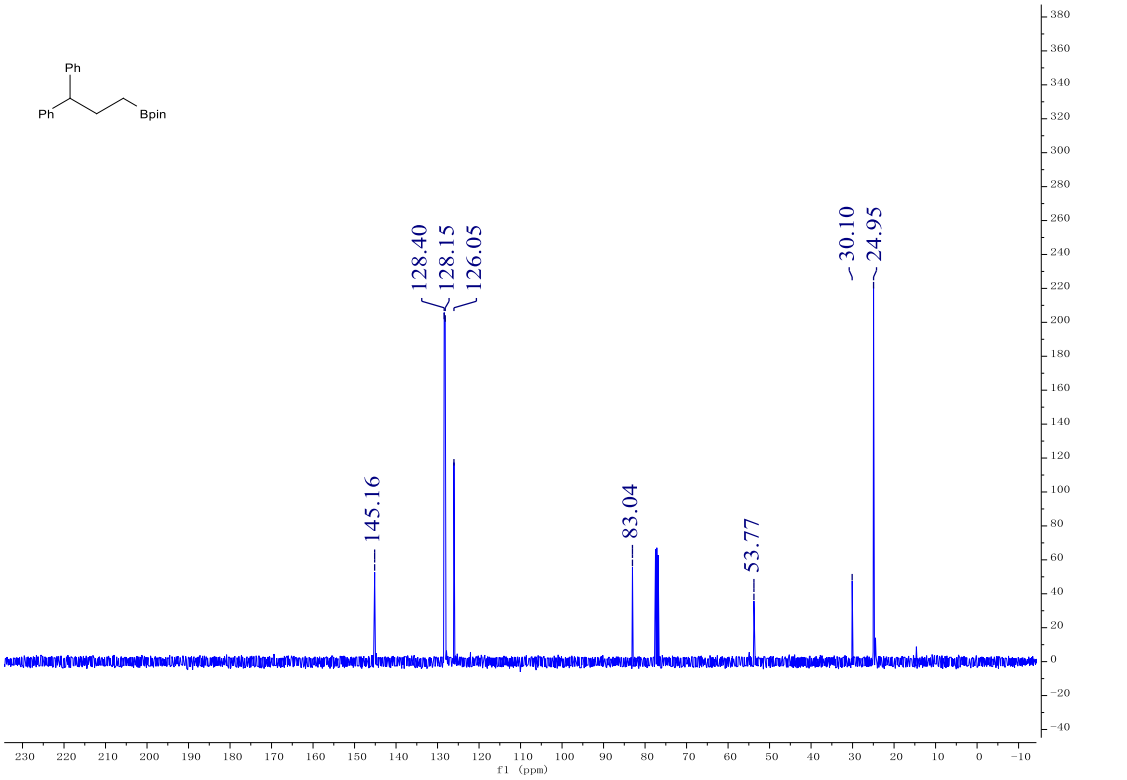

Bpin
H
H
H
H
1.89
1.86
1.84
1.82
1.81
1.76
1.71
1.55
1.54
1.52
1.47
1.44
1.25
0.76
0.74
0.72
11.41
2.86
1.99
12.00
2.01
f1 (ppm)


Bpin
H
H
H
H
46.95
39.46
38.59
31.71
31.57
28.54
28.25
26.67
24.90
82.90
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

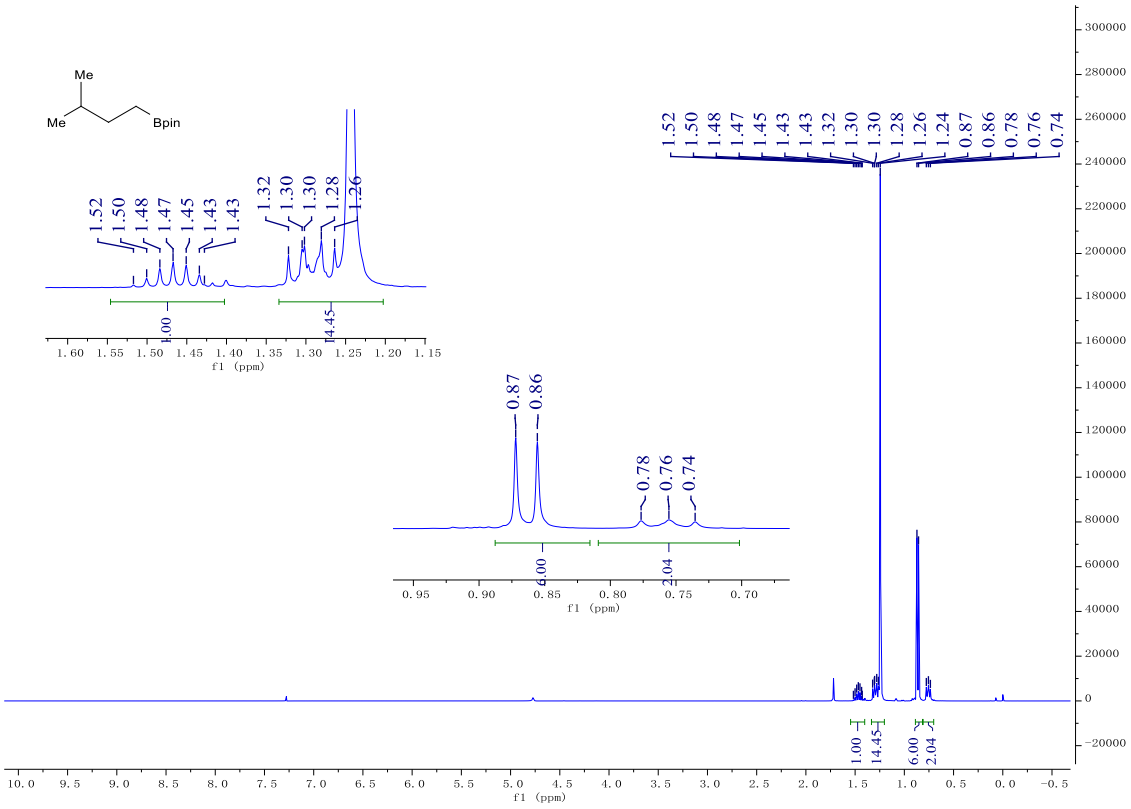

Bpin
H
H
H
H
34.04
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

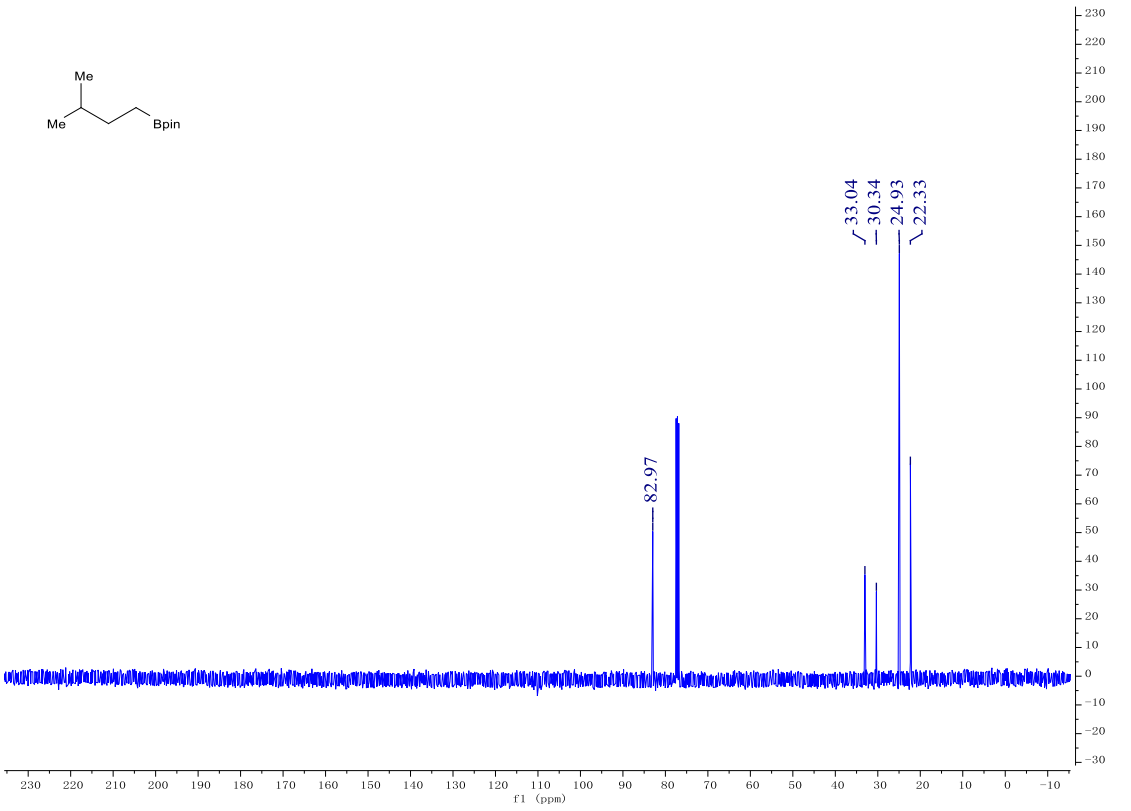
3y


Ph
Ph
Bpin
3.91
3.89
3.87
1.11
4.0
3.9
3.8
3.7
f1 (ppm)
2.23
2.21
2.19
2.17
7.32
7.28
7.20
7.20
7.19
2.00
2.4
2.3
2.2
2.1
f1 (ppm)
0.81
0.79
0.77
1.96
0.90
0.85
0.80
0.75
0.70
0.65
f1 (ppm)
1.27
0.81
0.79
0.77
8.36
2.12
1.11
2.00
11.63
1.96
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)

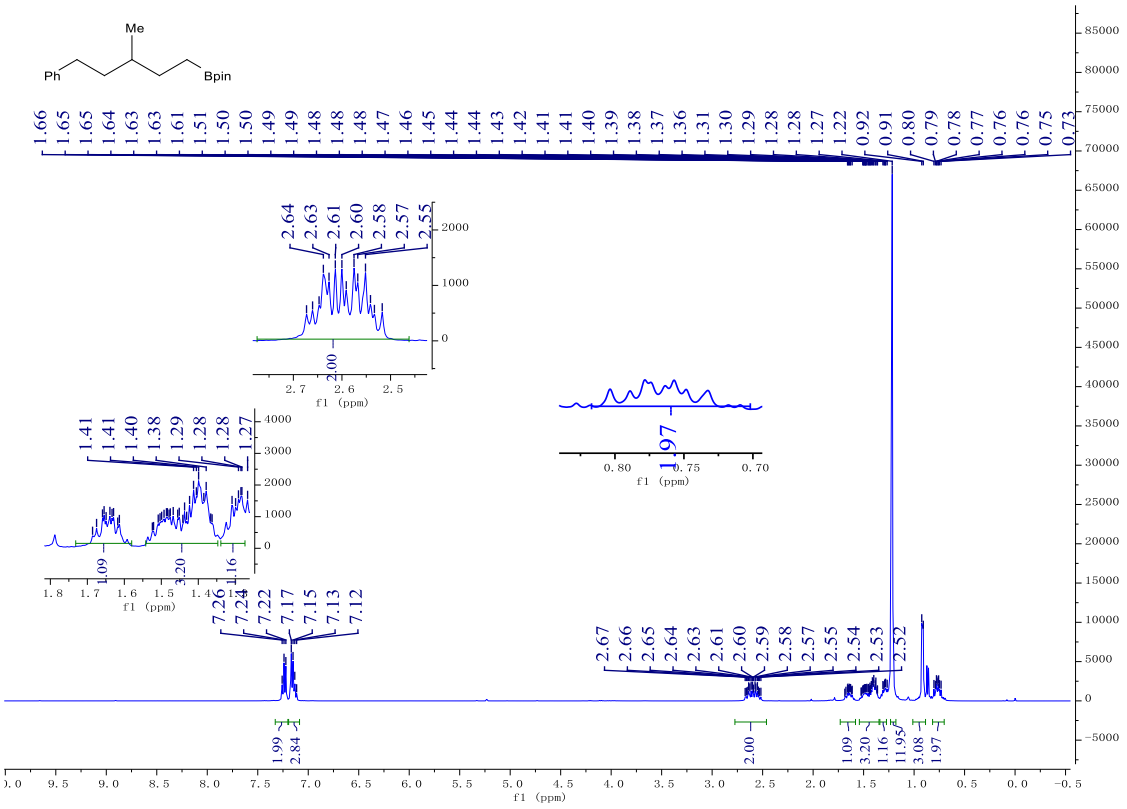

Ph
Ph
Bpin
145.16
128.40
128.15
126.05
83.04
53.77
30.10
24.95
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

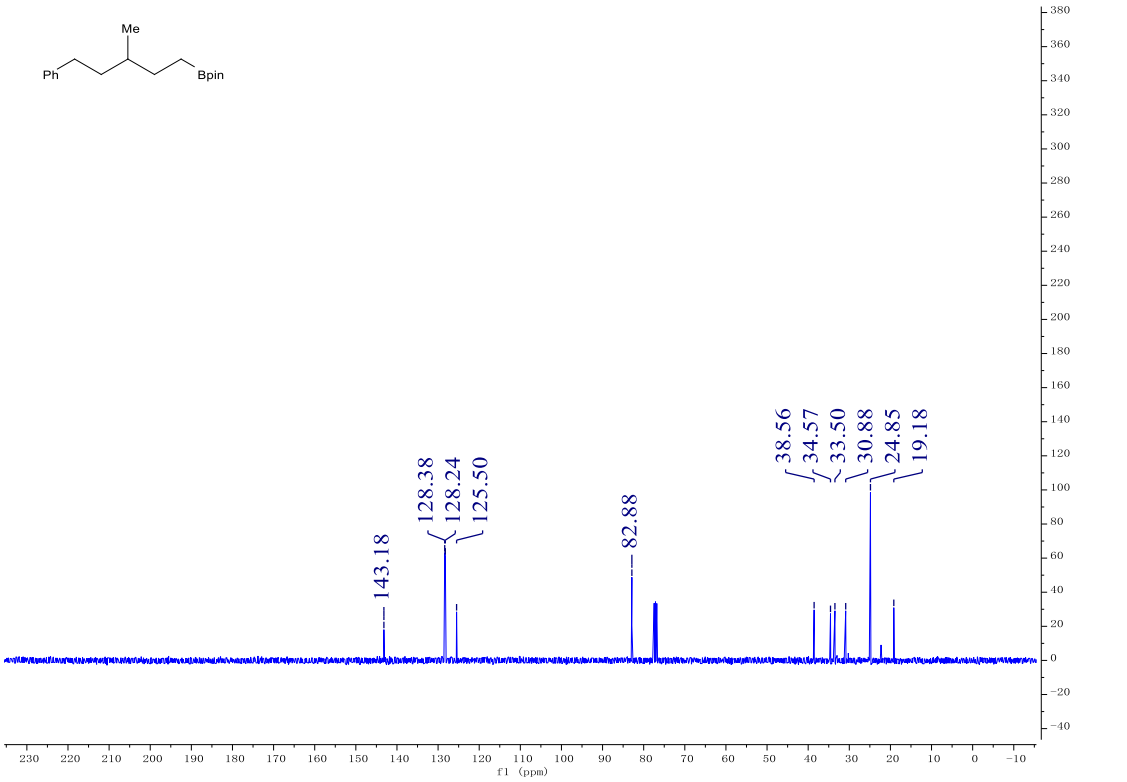
3z


Me
Me
Bpin
1.52
1.50
1.48
1.47
1.45
1.43
1.43
1.32
1.30
1.30
1.28
1.26
1.00
14.45
f1 (ppm)
0.87
0.86
0.78
0.76
0.74
4.00
2.04
f1 (ppm)
1.52
1.50
1.48
1.47
1.45
1.43
1.43
1.32
1.30
1.30
1.28
1.26
1.24
0.87
0.86
0.78
0.76
0.74
1.00
14.45
6.00
2.04
f1 (ppm)

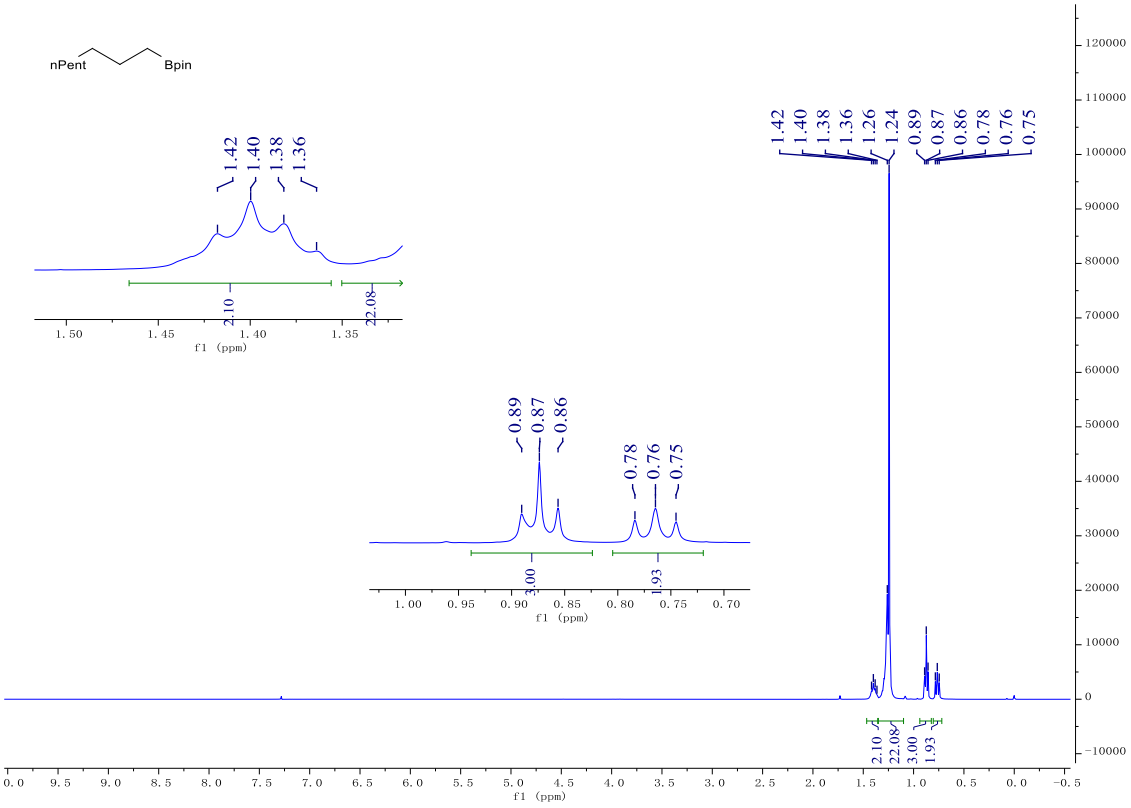

Me
Me
Bpin
33.04
30.34
24.93
22.33
82.97
f1 (ppm)

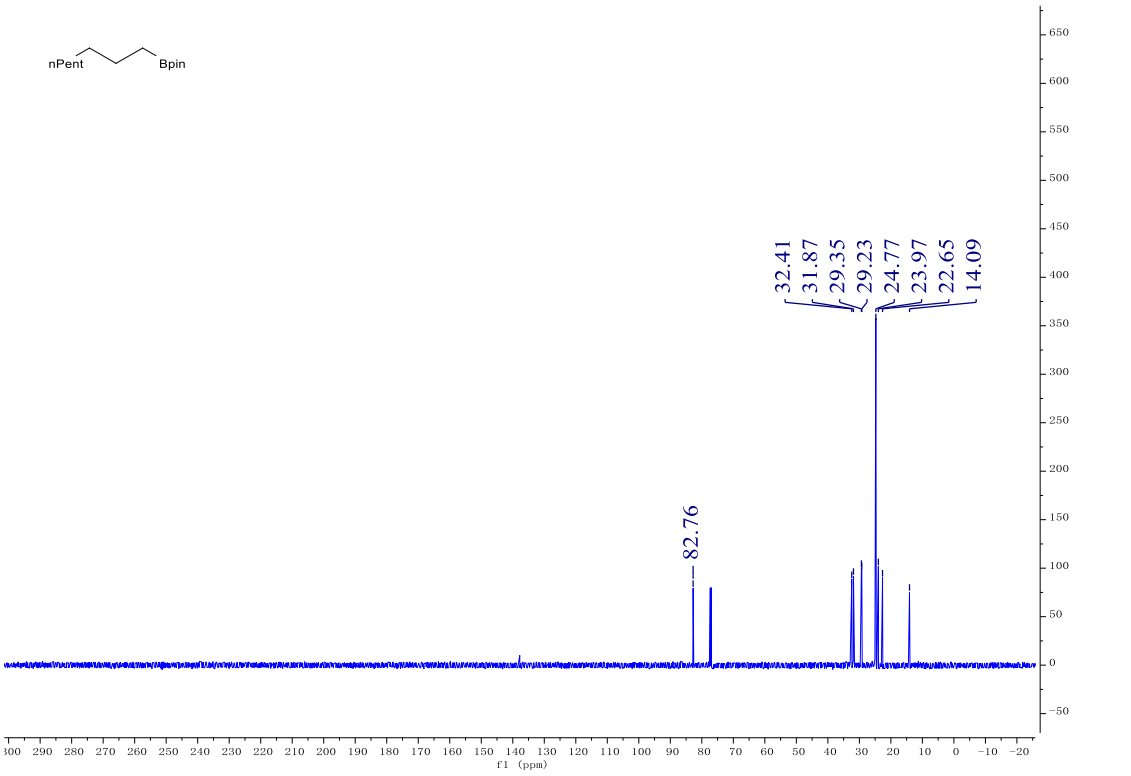
4a


Me
Ph
Bpin
f1 (ppm)

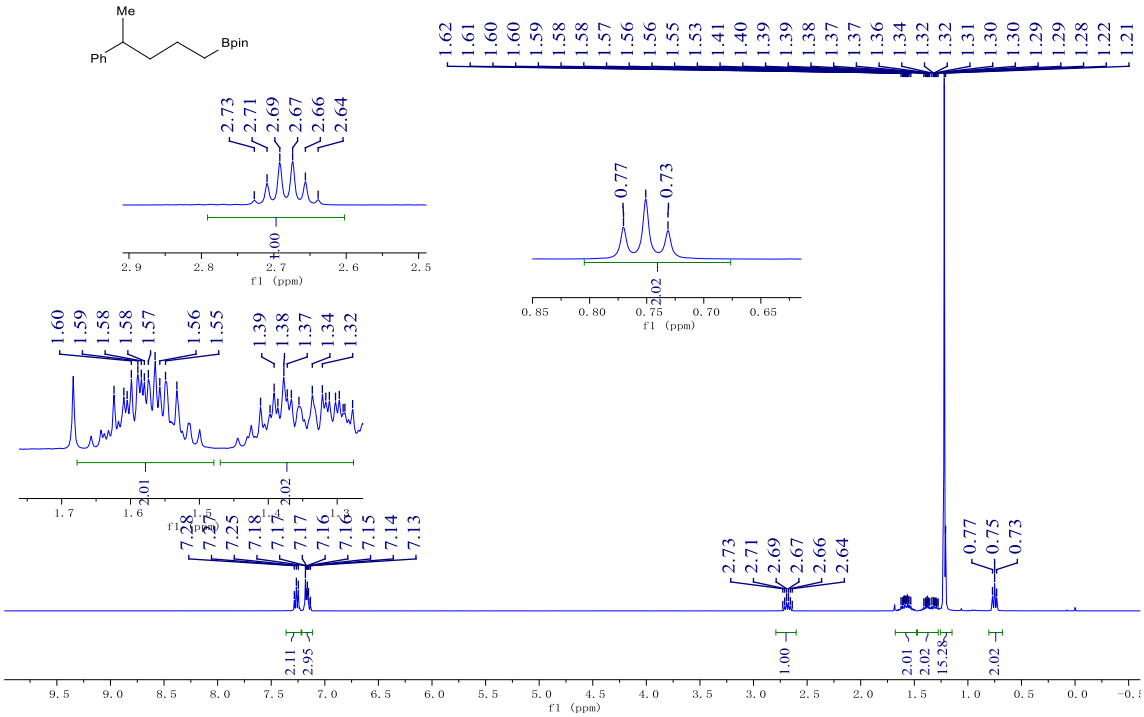

Me
Ph
Bpin
143.18
128.38
128.24
125.50
82.88
38.56
34.57
33.50
30.88
24.85
19.18
f1 (ppm)

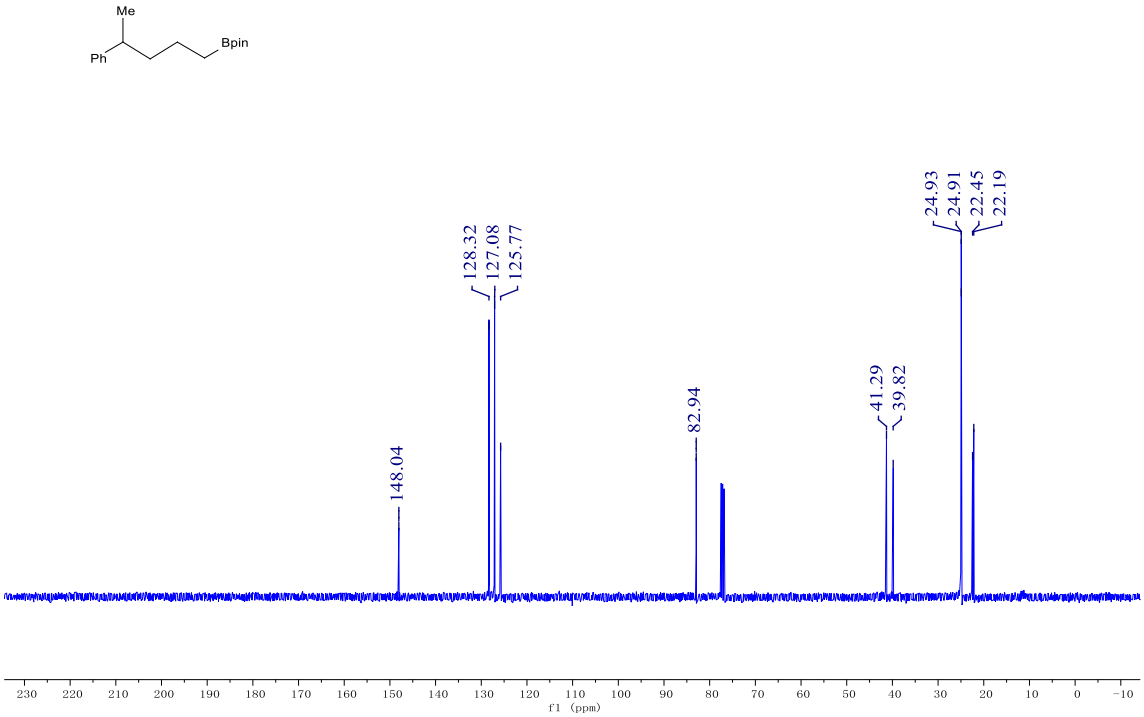
4b

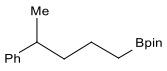

nPent
Bpin
1.42
1.40
1.38
1.36
1.26
1.24
0.89
0.87
0.86
0.78
0.76
0.75
2.10
22.08
3.00
1.93
f1 (ppm)

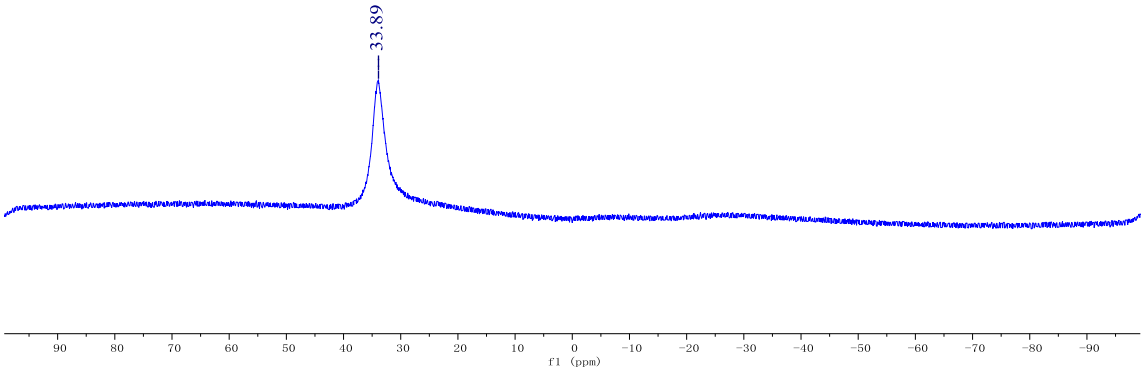

nPent
Bpin
32.41
31.87
29.35
29.23
24.77
23.97
22.65
14.09
82.76
f1 (ppm)

4c

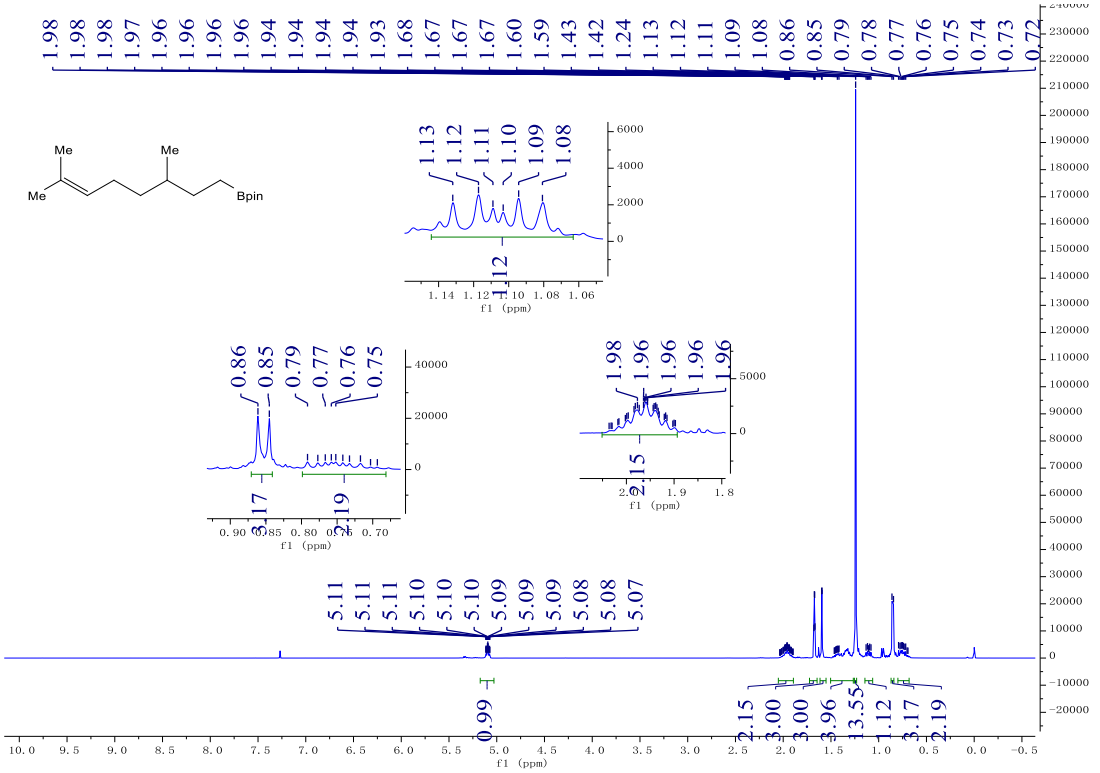

Me
Ph
Bpin
f1 (ppm)

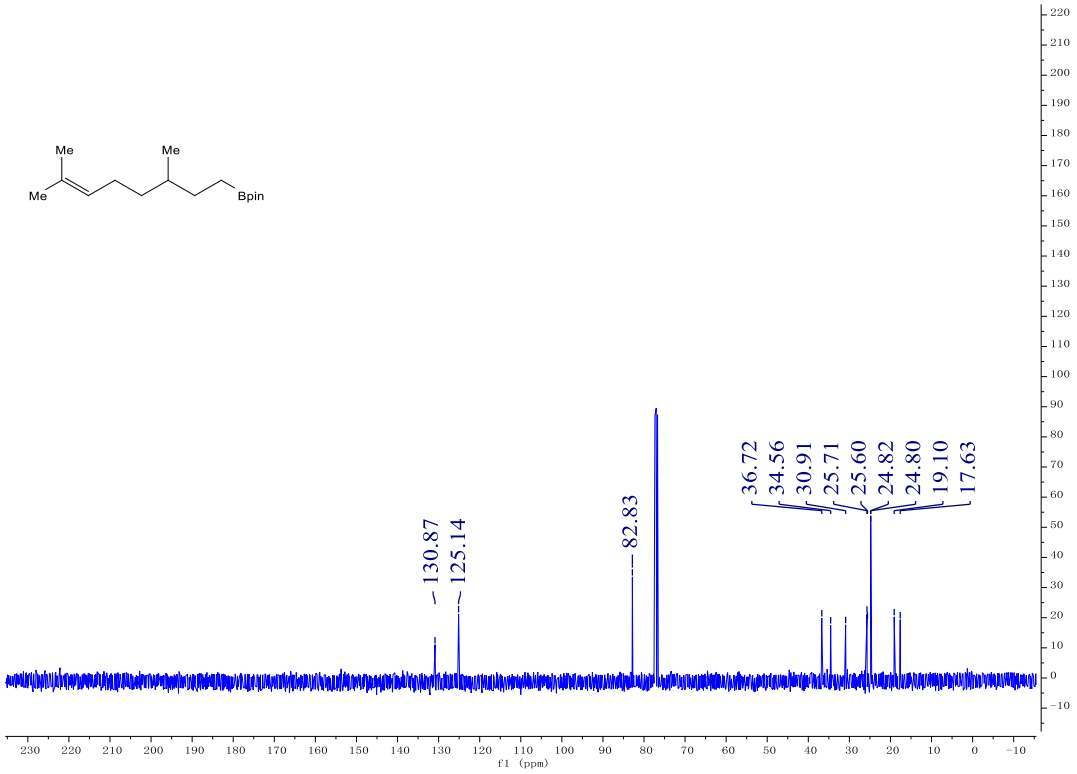

Me
Ph
Bpin
f1 (ppm)

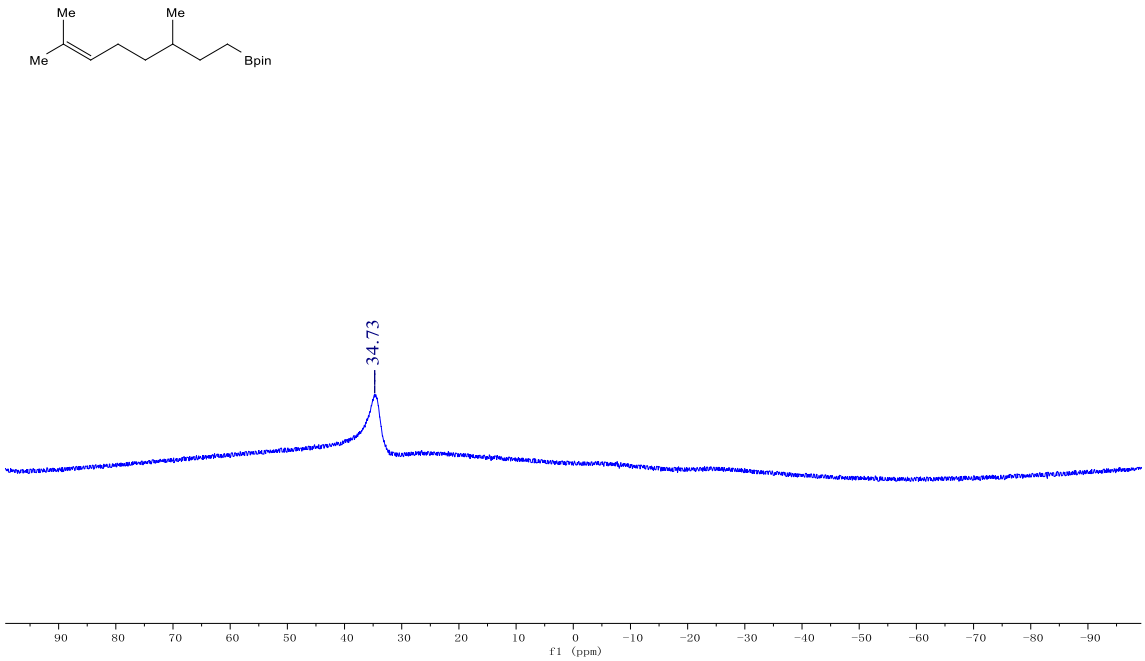


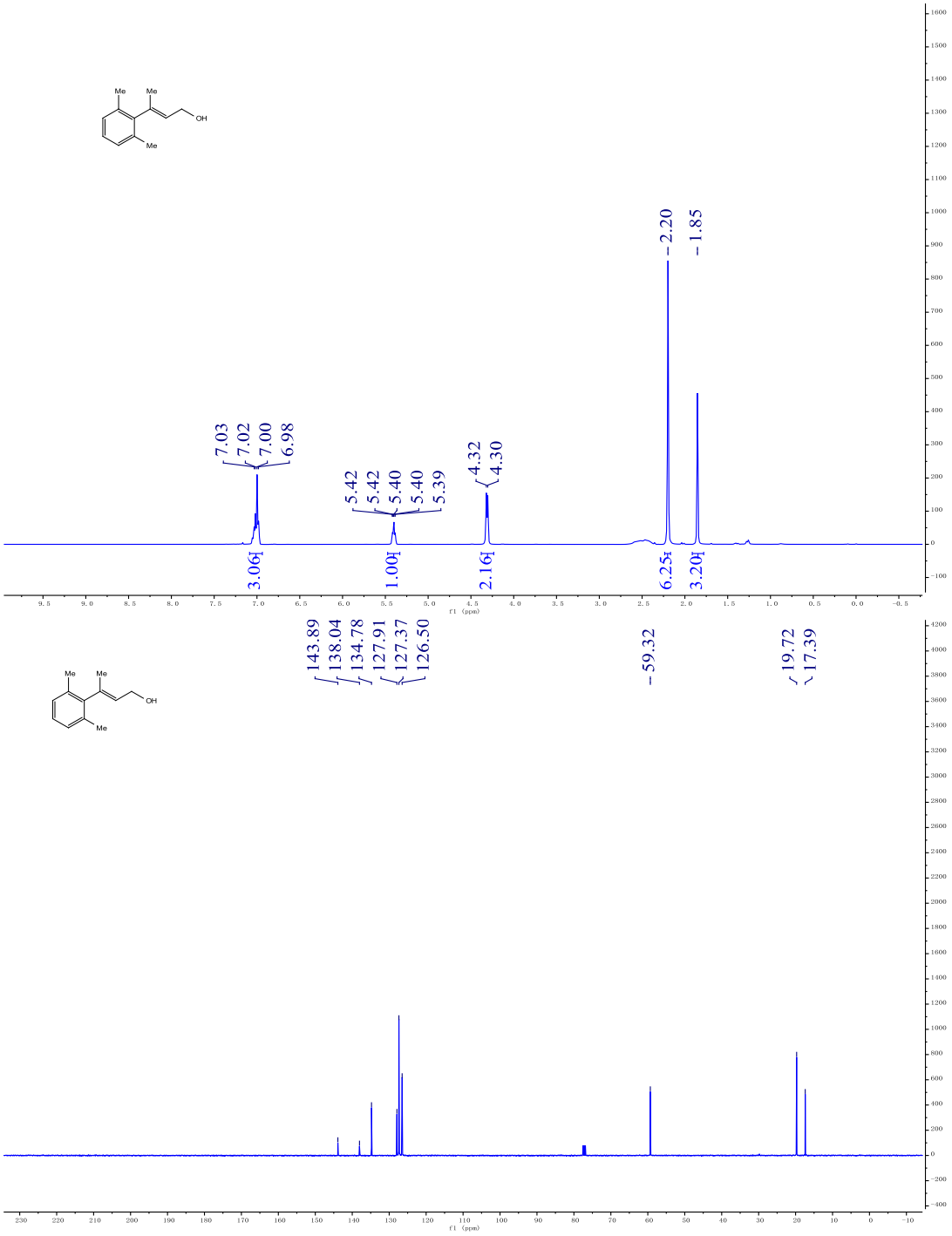


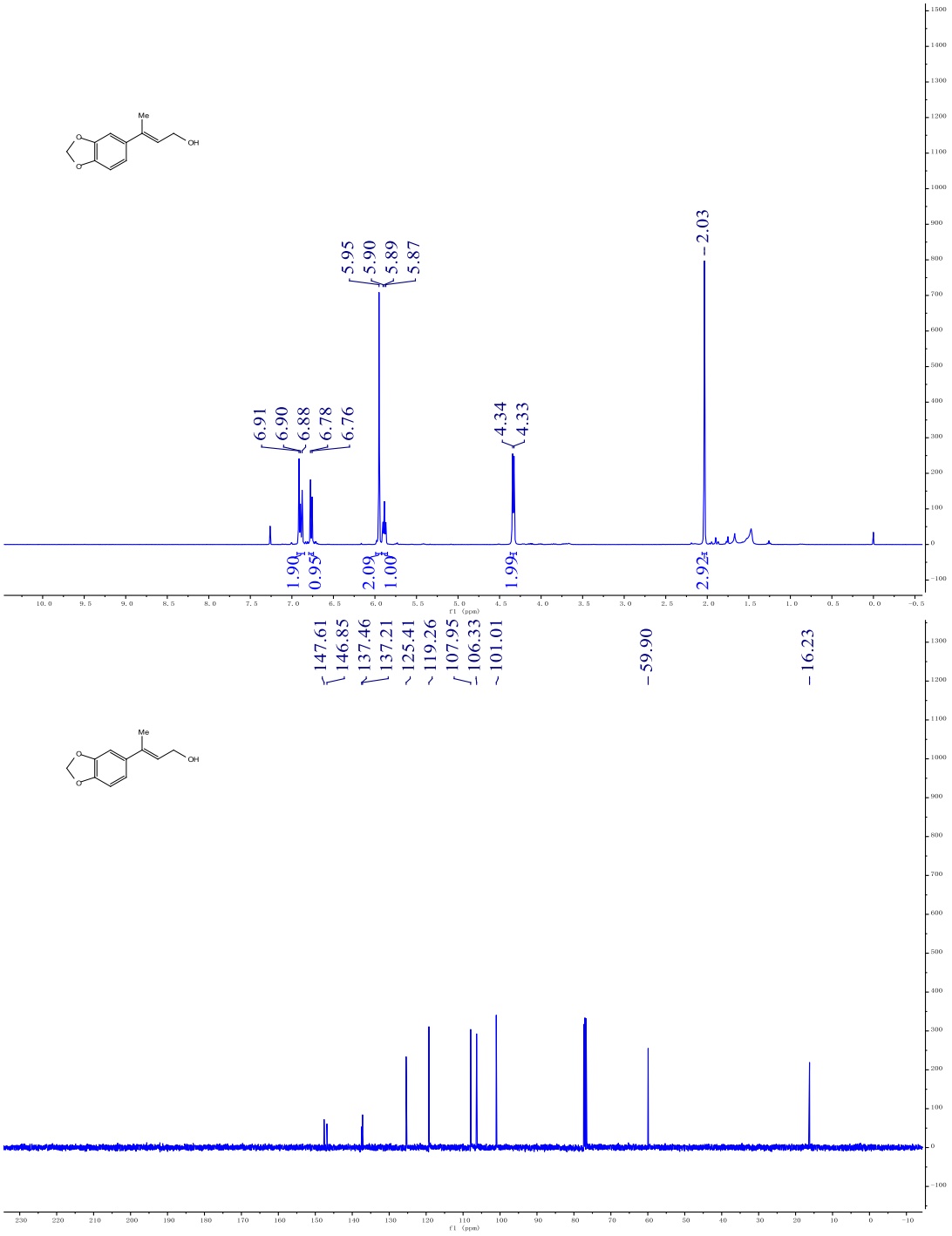
4d

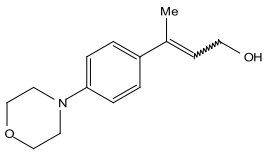


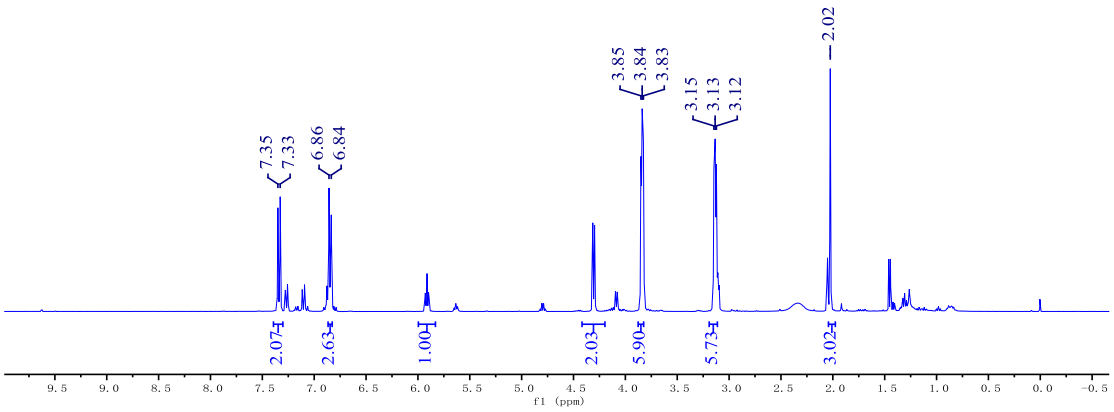

Me
Me
Me
Bpin
130.87
125.14
82.83
36.72
34.56
30.91
25.71
25.60
24.82
24.80
19.10
17.63
f1 (ppm)

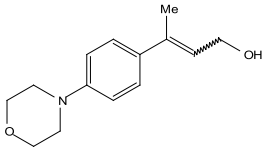

Me
Me
Me
Bpin
34.73
f1 (ppm)

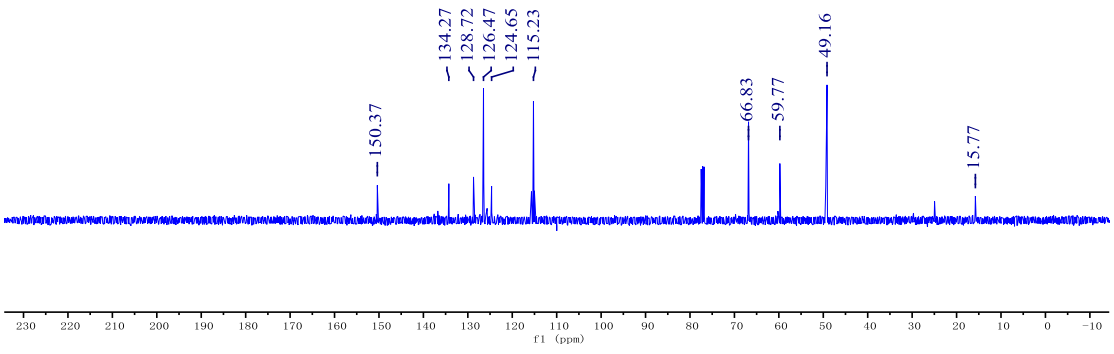

Me
Me
OH
Me
7.03
7.02
7.00
6.98
5.42
5.42
5.40
5.40
5.39
4.32
4.30
2.20
1.85
3.06
1.00
2.16
6.25
3.20
f1 (ppm)
143.89
138.04
134.78
127.91
127.37
126.50
59.32
19.72
17.39
f1 (ppm)

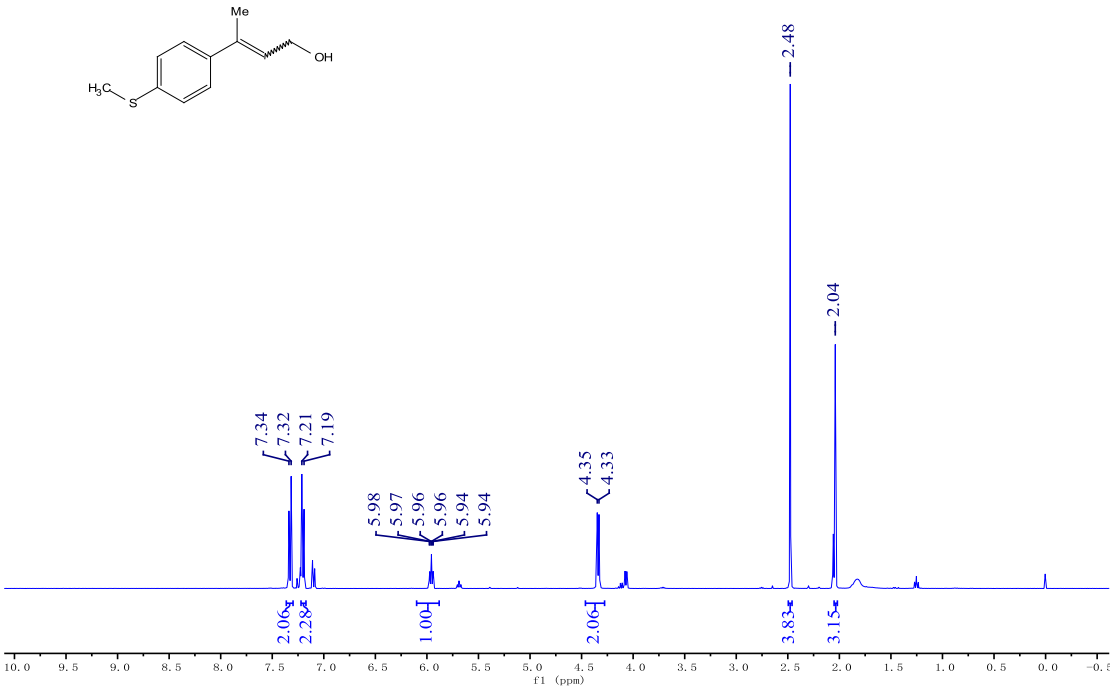

Me
OH
6.91
6.90
6.88
6.78
6.76
5.95
5.90
5.89
5.87
4.34
4.33
2.03
1.90
0.95
2.09
1.00
1.99
2.92
f1 (ppm)
147.61
146.85
137.46
137.21
125.41
119.26
107.95
106.33
101.01
59.90
16.23
Me
OH
f1 (ppm)

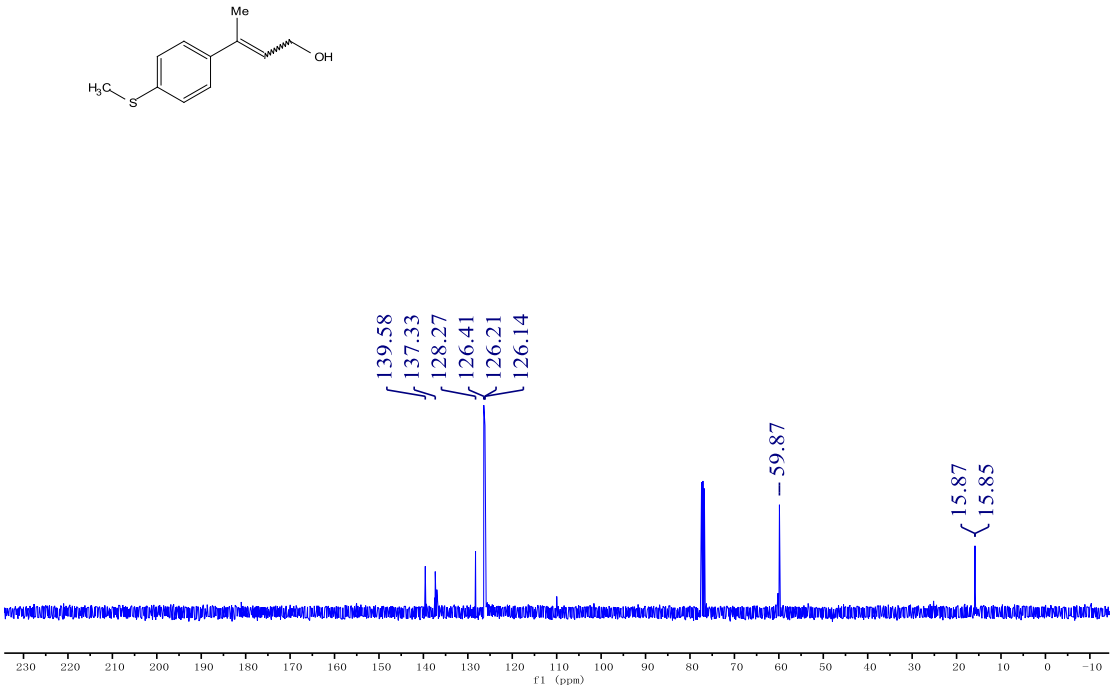

Me
OH
N
O

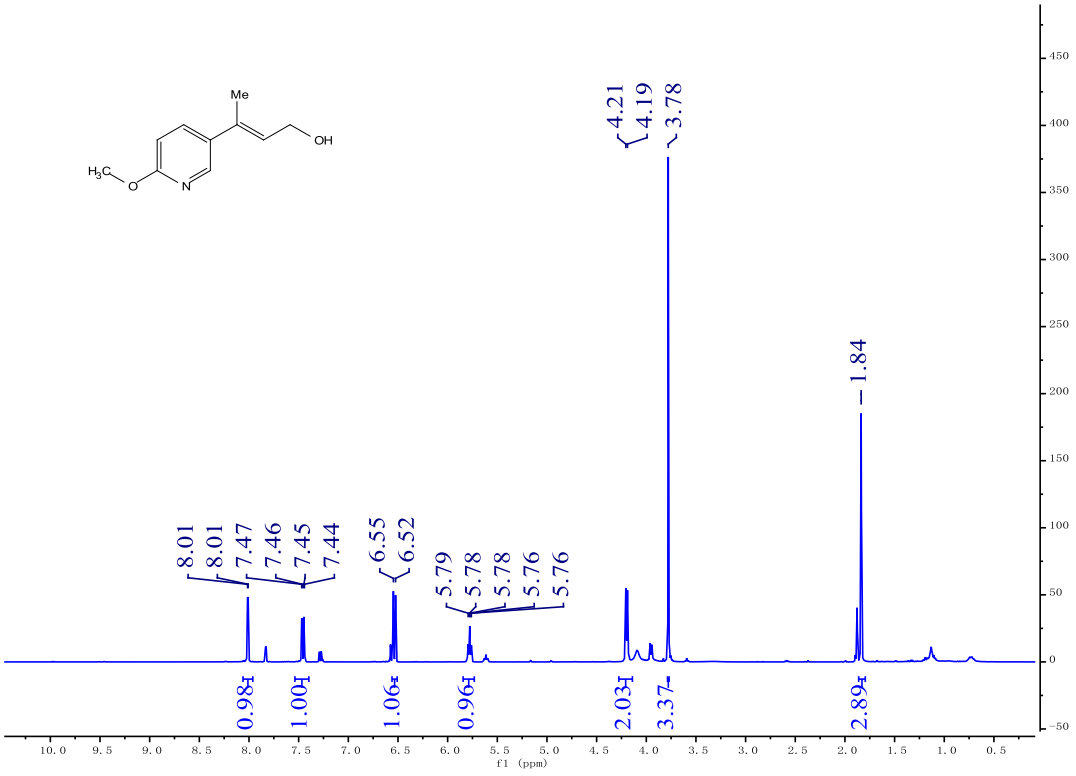

7.35
7.33
6.86
6.84
3.85
3.84
3.83
3.15
3.13
3.12
2.02
2.07
2.63
1.00
2.03
5.90
5.73
3.02
f1 (ppm)

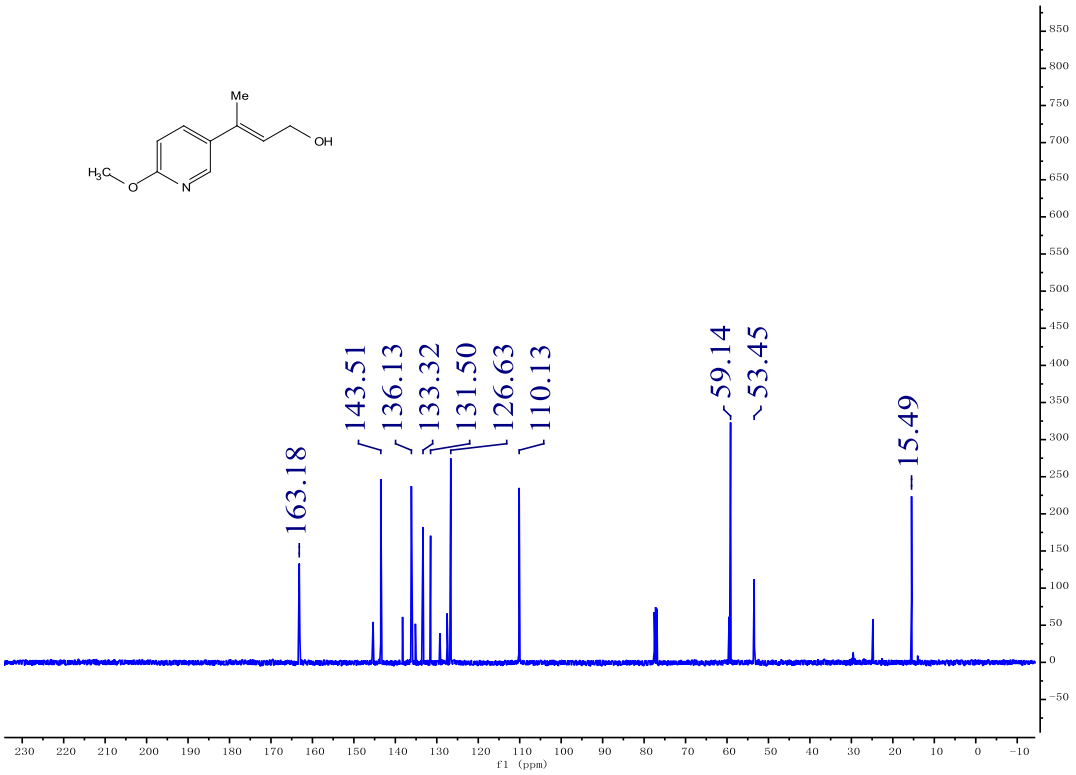

Me
OH
N
O

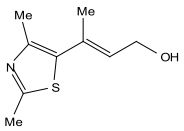

150.37
134.27
128.72
126.47
124.65
115.23
66.83
59.77
49.16
15.77
f1 (ppm)

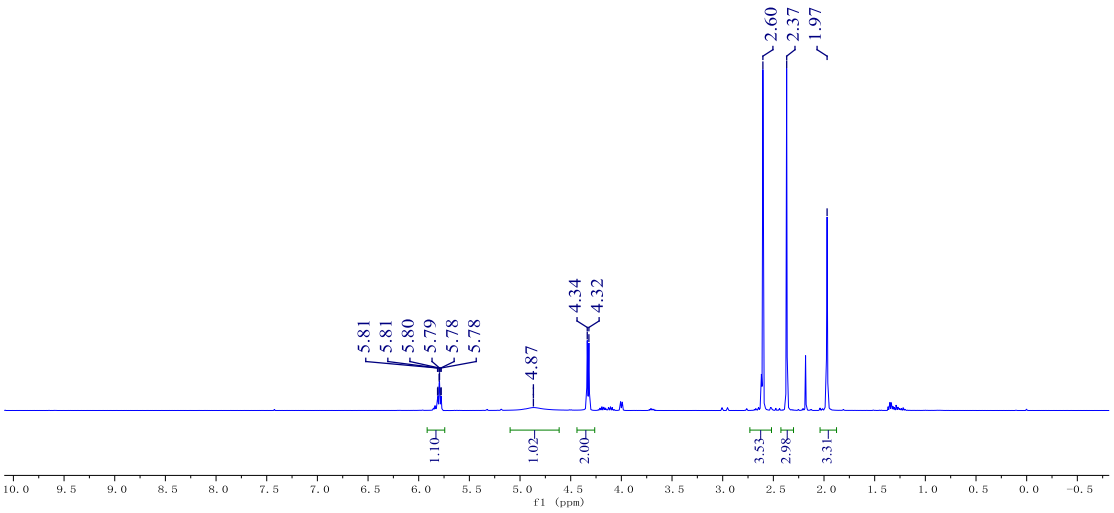

Me
OH
H3C
S
2.48
2.04
7.34
7.32
7.21
7.19
5.98
5.97
5.96
5.96
5.94
5.94
4.35
4.33
2.06
2.28
1.00
2.06
3.83
3.15
f1 (ppm)

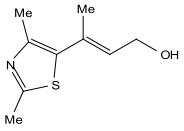

Me
OH
H3C
S
139.58
137.33
128.27
126.41
126.21
126.14
59.87
15.87
15.85
f1 (ppm)

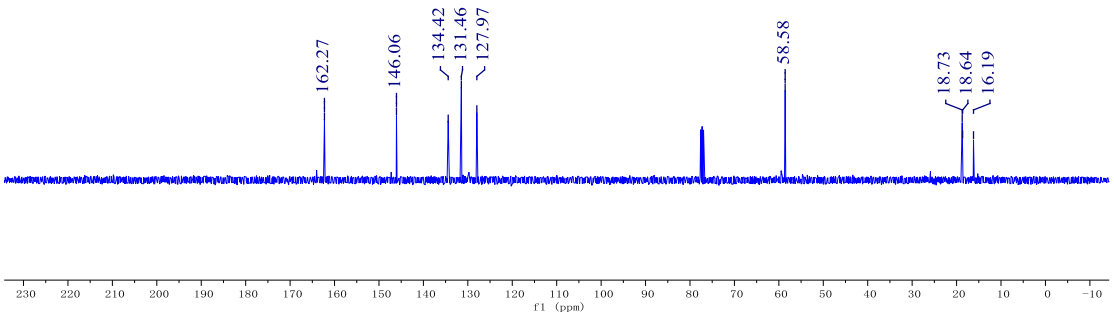

Me
OH
H3C
O
N
8.01
8.01
7.47
7.46
7.45
7.44
6.55
6.52
5.79
5.78
5.78
5.76
5.76
4.21
4.19
3.78
1.84
0.98
1.00
1.06
0.96
2.03
3.37
2.89
f1 (ppm)

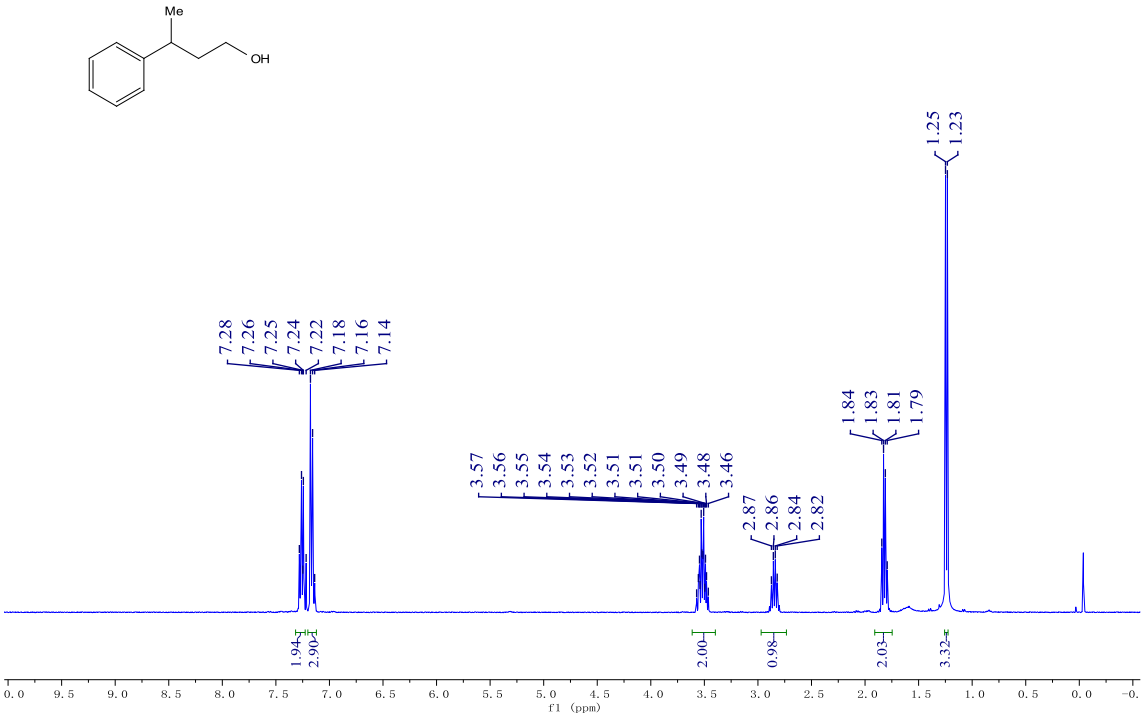

Me
OH
H3C
O
N
163.18
143.51
136.13
133.32
131.50
126.63
110.13
59.14
53.45
15.49
f1 (ppm)

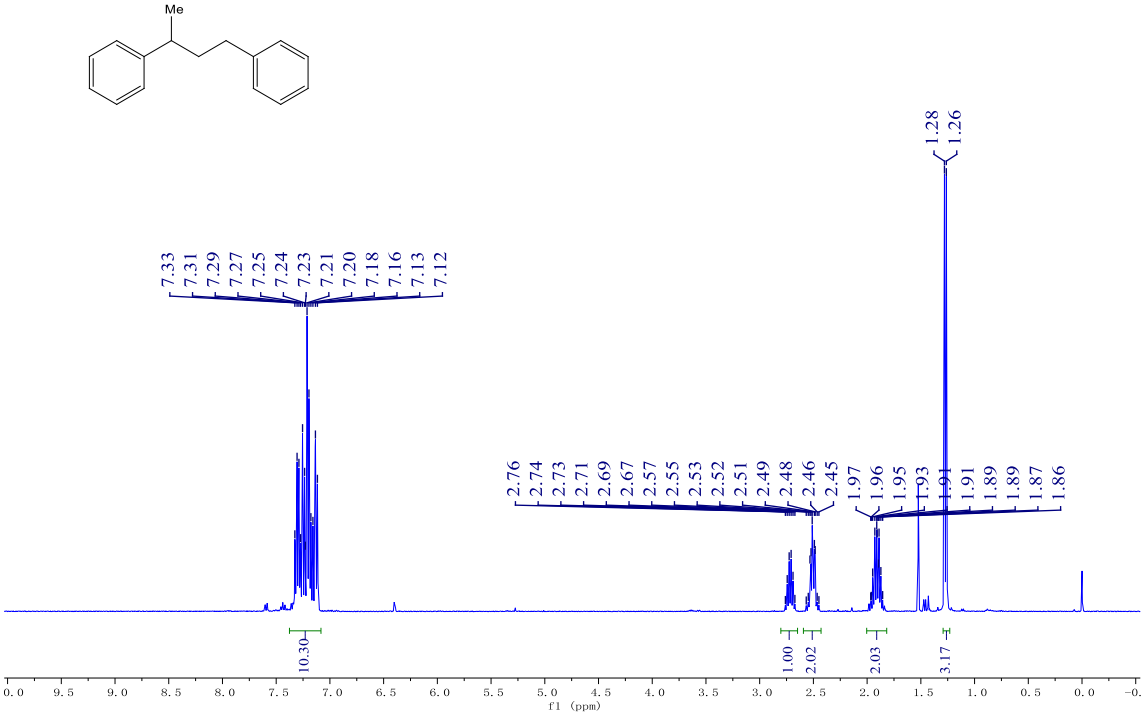

Me
Me
N
S
OH
Me

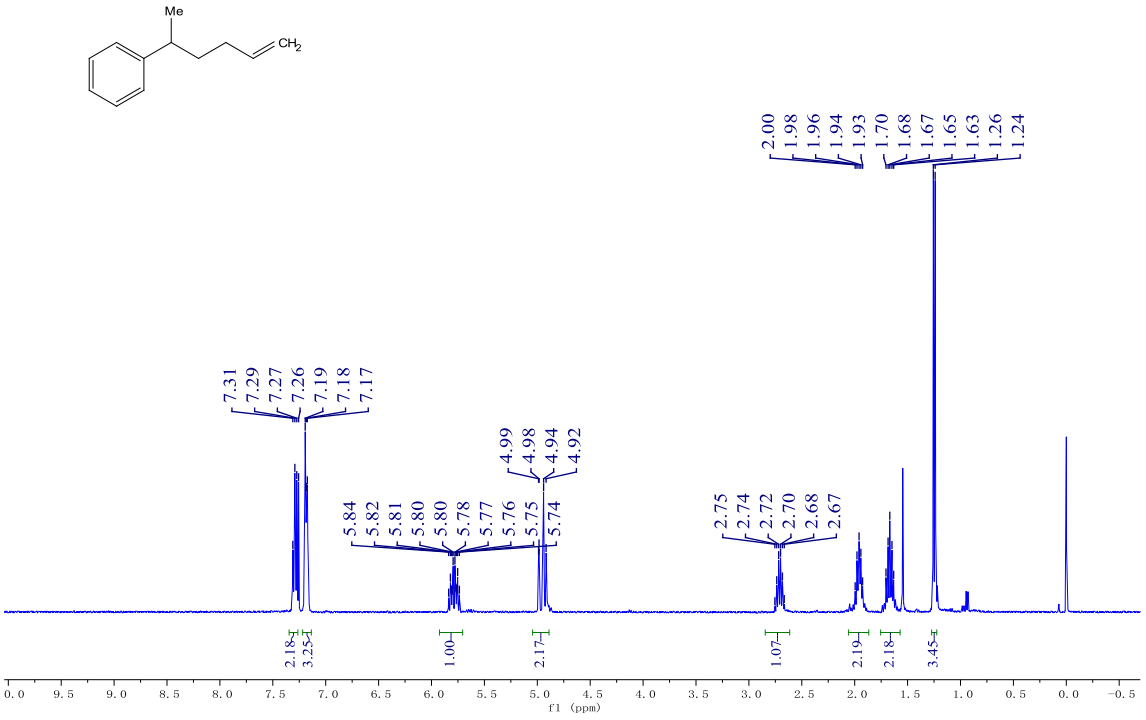

2.60
2.37
1.97
5.81
5.81
5.80
5.79
5.78
5.78
4.87
4.34
4.32
1.10
1.02
2.00
3.53
2.98
3.31
f1 (ppm)

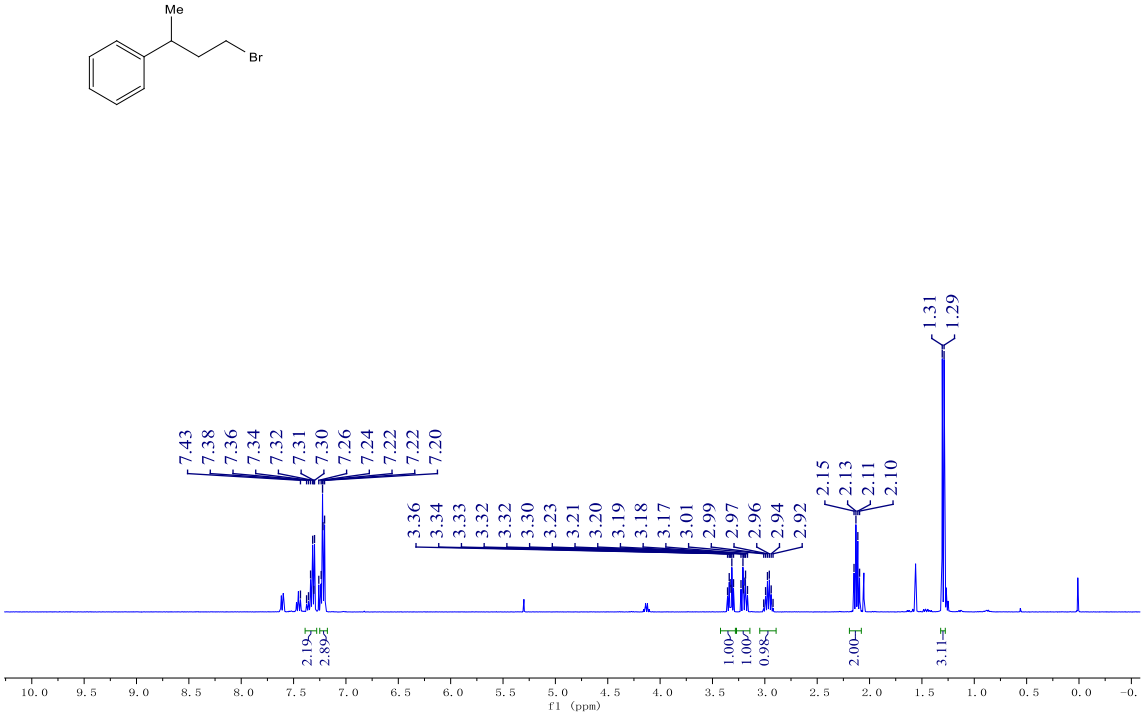

Me
Me
N
S
OH
Me

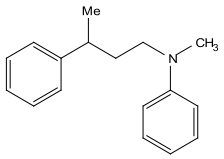

162.27
146.06
134.42
131.46
127.97
58.58
18.73
18.64
16.19
f1 (ppm)

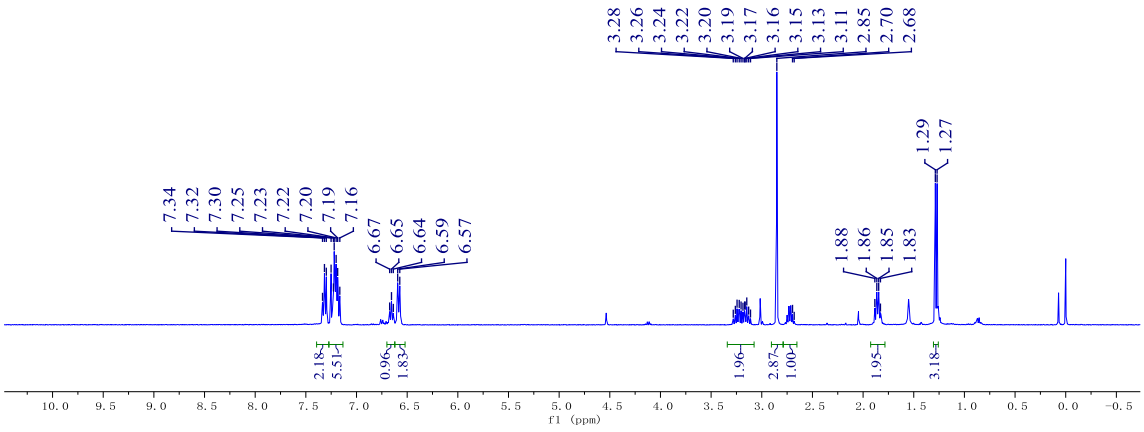

Me
OH
7.28
7.26
7.25
7.24
7.22
7.18
7.16
7.14
3.57
3.56
3.55
3.54
3.53
3.52
3.51
3.51
3.50
3.49
3.48
3.46
2.87
2.86
2.84
2.82
1.84
1.83
1.81
1.79
1.25
1.23
1.94
2.90
2.00
0.98
2.03
3.32
f1 (ppm)


Me
7.33
7.31
7.29
7.27
7.25
7.24
7.23
7.21
7.20
7.18
7.16
7.13
7.12
2.76
2.74
2.73
2.71
2.69
2.67
2.57
2.55
2.53
2.52
2.51
2.49
2.48
2.46
2.45
1.97
1.96
1.95
1.93
1.91
1.91
1.89
1.89
1.87
1.86
1.28
1.26
10.30
1.00
2.02
2.03
3.17
f1 (ppm)


Me
CH2
2.00
1.98
1.96
1.94
1.93
1.70
1.68
1.67
1.65
1.63
1.26
1.24
7.31
7.29
7.27
7.26
7.19
7.18
7.17
4.99
4.98
4.94
4.92
5.84
5.82
5.81
5.80
5.80
5.78
5.77
5.76
5.75
5.74
2.75
2.74
2.72
2.70
2.68
2.67
2.18
3.25
1.00
2.17
1.07
2.19
2.18
3.45
f1 (ppm)


Me
Br
1.31
1.29
7.43
7.38
7.36
7.34
7.32
7.31
7.30
7.26
7.24
7.22
7.22
7.20
2.15
2.13
2.11
2.10
3.36
3.34
3.33
3.32
3.32
3.30
3.23
3.21
3.20
3.19
3.18
3.17
3.01
2.99
2.97
2.96
2.94
2.92
2.19
2.89
1.00
1.00
0.98
2.00
3.11
f1 (ppm)


Me
N
CH3


7.34
7.32
7.30
7.25
7.23
7.22
7.20
7.19
7.16
6.67
6.65
6.64
6.59
6.57
3.28
3.26
3.24
3.22
3.20
3.19
3.17
3.16
3.15
3.13
3.11
2.85
2.70
2.68
1.88
1.86
1.85
1.83
1.29
1.27
2.18
5.51
0.96
1.83
1.96
2.87
1.00
1.95
3.18
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)