Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

^{n}BuLi-Promoted *anti*-Markovnikov Selective Hydroboration of Unactivated Alkenes and Internal Alkynes

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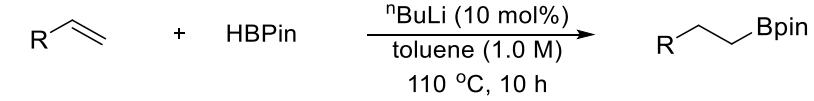
General Information

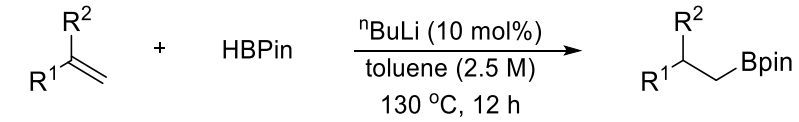
All the reactions were conducted under an N_2 atmosphere with standard vacuum-line techniques, and the glassware was dried in an oven (140 °C). Pinacolborane (HBpin) was purchased from Energy Chemical Co. Ltd and was stored in the refrigerator, n-Butyllithium (^{n}BuLi, 2.5 M in hexane) was purchased 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 analyses were performed on a Shimadzu QP2010 SE using a DB-5MS column (30 m, 0.25 mm I.D.).

^{n}BuLi-Promoted *anti*-Markovnikov Selective Hydroboration



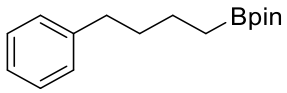
0.5 mmol 1.2 equiv

General procedure A (GPA): 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, 20 µL, 0.05 mmol, 10 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature (rt). The α-alkene substrate (0.5 mmol) was then added dropwise and the reaction mixture was stirred at 110 °C for 10 h. After completion of the reaction, the reaction mixture was allowed to cool to r.t. 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 GC-MS analysis. The product was purified by chromatography on silica gel.



0.5 mmol 1.2 equiv

General procedure B (GPB): In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.2 mL, 2.5 M), HBpin (87 µL, 0.6 mmol, 1.2 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 alkene or alkyne substrate (0.5 mmol) was then added dropwise and the reaction mixture was stirred at 130 °C for 12 h. After completion of the reaction, the reaction mixture was allowed to cool to r.t. 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 GC-MS analysis. The product was purified by chromatography on silica gel.

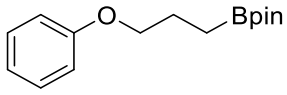


4,4,5,5-tetramethyl-2-(4-phenylbutyl)-1,3,2-dioxaborolane (3a)

Following **GPA** using but-3-en-1-ylbenzene (66.1 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[1] (119.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, 2H), 7.1 (m, 3H), 2.5 (t, *J* = 8.0 Hz, 2H), 1.5 (m, 2H), 1.4 (m, 2H), 1.2 (s, 12H), 0.7 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 128.4, 128.2, 125.5, 82.9, 35.8, 34.3, 24.9, 23.8.

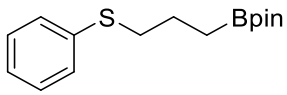


4,4,5,5-tetramethyl-2-(3-phenoxypropyl)-1,3,2-dioxaborolane (3b)

Following **GPA** using (allyloxy)benzene (77.1 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[2] (118.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 2H), 6.9 (m, 3H), 3.9 (t, *J* = 6.7 Hz, 2H), 1.9 (m, 2H), 1.2 (s, 12H), 0.9 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 129.5, 120.5, 114.7, 83.2, 69.6, 24.9, 23.9.



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

Following **GPA** using allyl(phenyl)sulfane (75.1 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 94% yield (130.5 mg).

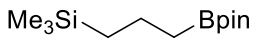
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (d, *J* = 7.5 Hz, 2H), 7.3 (m, 2H), 7.1 (m, 1H), 2.9 (t, *J* = 8.0 Hz, 2H), 1.8 (m, 2H), 1.2 (s, 12H), 0.9 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 128.9, 128.6, 125.5, 83.2, 35.6, 24.9, 24.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.09 (s).

IR (neat, cm^{-1}) 1733, 1372, 1237, 1044, 913, 847, 729.

HRMS (EI) calculated for $C_{15}H_{23}BO_2S$ $[M]^+$ m/z 277.1543, found 277.1538.



trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (3d)

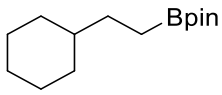
Following **GPA** using allyltrimethylsilane (57.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 79 % yield[6] (95.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.4 (m, 2H), 1.2 (s, 12H), 0.8 (t, *J* = 7.7 Hz, 2H), 0.5 (m, 2H), -0.1 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 25.0, 20.2, 18.7, -1.5.

IR (neat, cm^{-1}) 2978, 1370, 1311, 1144, 865, 831, 757.

HRMS (EI) calculated for $C_{11}H_{24}BO_2Si$ $[M\text{-}CH_3]^+$ m/z 226.1669, found 226.1673.

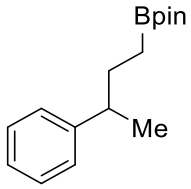


2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

Following **GPA** using vinylcyclohexane (55.1 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[3] (107.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.7 (m, 5H), 1.2 (m, 18H), 0.8 (m, 2H), 0.7 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 40.1, 33.1, 31.5, 26.9, 26.6, 24.9.



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

Following **GPA** using but-3-en-2-ylbenzene (61.1 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 (119.5 mg).

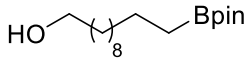
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 2H), 7.2 (m, 3H), 2.7 (m, 1H), 1.7 (m, 2H), 1.3 (m, 15H), 0.7 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 128.2, 127.2, 125.7, 82.9, 42.2, 32.7, 24.8, 21.6.

^{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.



11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecan-1-ol (3g)

Following **GPA** using undec-10-en-1-ol (85.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a colorless liquid in 85% yield (126.6 mg).

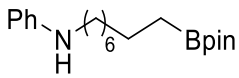
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.6 (t, *J* = 6.7 Hz, 2H), 1.9 (s, 1H), 1.5 (m, 2H), 1.2 (m, 16H), 1.2 (s, 12H), 0.7 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 63.0, 32.8, 32.5, 29.7, 29.6, 29.6, 29.5, 29.5, 25.8, 24.9, 24.0.

^{11}B NMR (128 MHz, CDCl3) δ 33.93.

IR (neat, cm^{-1}) 3380, 2923, 1372, 1316, 1143, 967, 732.

HRMS (ESI) calculated for $C_{17}H_{36}BO_3$ $[M+H]^+$ m/z 298.2788, found 298.2786.



N-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)aniline (3h)

Following **GPA** using N-(oct-7-en-1-yl)aniline (102.7 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a colorless liquid in 77% yield (127.4 mg).

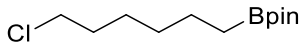
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, 2H), 6.7 (t, *J* = 7.3 Hz, 1H), 6.6 (d, *J* = 7.9 Hz, 2H), 3.6 (s, 1H), 3.1 (t, *J* = 7.1 Hz, 2H), 1.6 (m, 2H), 1.4 (m, 10H), 1.3 (s, 12H), 0.8 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 129.2, 117.0, 112.7, 82.9, 44.0, 32.4, 29.6, 29.4, 29.4, 27.2, 24.9, 24.0.

^{11}B NMR (128 MHz, CDCl3) δ 34.02.

IR (neat, cm^{-1}) 2925, 1735, 1602, 1506, 1372, 1237, 1143, 731.

HRMS (ESI) calculated for $C_{20}H_{35}BNO_2$ $[M+H]^+$ m/z 331.2792, found 331.2791.

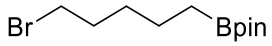


2-(6-chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

Following **GPA** using 6-chlorohex-1-ene (59.3 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 81% yield[4] (169.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.5 (t, *J* = 6.8 Hz, 2H), 1.7 (m, 2H), 1.4 (m, 4H), 1.3 (m, 2H), 1.2 (s, 12H), 0.7 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 45.2, 32.6, 31.6, 26.7, 24.9, 23.9.

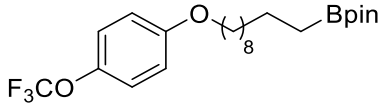


2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

Following **GPA** using 5-bromopent-1-ene (78.5 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 88% yield[5] (121.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.4 (t, *J* = 6.9 Hz, 2H), 1.8 (m, 2H), 1.4 (m, 4H), 1.2 (s, 12H), 0.8 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 34.1, 32.7, 30.9, 24.9, 23.3.



4,4,5,5-tetramethyl-2-(10-(4-(trifluoromethoxy)phenoxy)decyl)-1,3,2-dioxaborolane (3k)

Following **GPA** using 1-(dec-9-en-1-yloxy)-4-(trifluoromethoxy)benzene (158.2 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 87% yield (193.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1 (d, *J* = 8.8 Hz, 2H), 6.9 (d, *J* = 9.1 Hz, 2H), 3.9 (t, *J* = 6.5 Hz, 2H), 1.8 (m, 2H), 1.3 (m, 14H), 1.2 (s, 12H), 0.8 (t, *J* = 7.7 Hz, 2H).

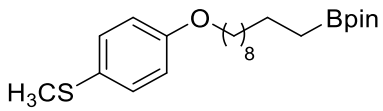
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 142.4, 122.3, 120.6 (q, *J* = 256.5 Hz), 115.1, 82.8, 68.4, 32.4, 29.5, 29.5, 29.3, 29.3, 29.2, 26.0, 24.7, 24.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -58.4.

^{11}B NMR (128 MHz, CDCl3) δ 34.0.

IR (neat, cm^{-1}) 1736, 1507, 1373, 1239, 1045, 913, 730.

HRMS (ESI) calculated for $C_{23}H_{40}BF_3NO_4$ $[M+NH_4]^+$ m/z 461.3033, found 461.3020.



4,4,5,5-tetramethyl-2-(10-(4-(trifluoromethoxy)phenoxy)decyl)-1,3,2-dioxaborolane (3l)

Following **GPA** using (4-(dec-9-en-1-yloxy)phenyl)(methyl)sulfane (189.2 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 94% yield (190.8 mg).

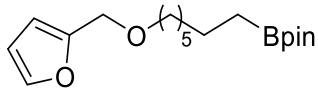
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 8.7 Hz, 2H), 6.8 (d, *J* = 8.7 Hz, 2H), 3.9 (t, *J* = 6.6 Hz, 2H), 2.4 (s, 3H), 1.8 (m, 2H), 1.3 (m, 14H), 1.2 (s, 12H), 0.8 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 130.2, 128.4, 115.2, 82.9, 68.1, 32.5, 29.6, 29.6, 29.4, 29.3, 26.1, 24.9, 24.1, 18.2.

^{11}B NMR (128 MHz, CDCl3) δ 33.95.

IR (neat, cm^{-1}) 1732, 1493, 1238, 1044, 910, 847, 728.

HRMS (ESI) calculated for $C_{23}H_{43}BNO_3S$ $[M+NH_4]^+$ m/z 423.3088, found 423.3068.



2-(7-(furan-2-ylmethoxy)heptyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)

Following **GPA** using 2-((hept-6-en-1-yloxy)methyl)furan (97.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (5-10% EtOAc in hexanes) to provide the title compound as a yellow liquid in 70% yield (112.7 mg).

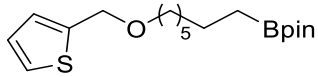
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (dd, *J* = 1.7, 0.8 Hz, 1H), 6.3 (m, 2H), 4.4 (s, 2H), 3.4 (t, *J* = 6.8 Hz, 2H), 1.6 (m, 2H), 1.3 (m, 8H), 1.2 (s, 12H), 0.7 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 142.6, 110.1, 108.9, 82.8, 70.4, 64.7, 32.3, 29.6, 29.2, 26.0, 24.8, 23.9.

^{11}B NMR (128 MHz, CDCl3) δ 35.27.

IR (neat, cm^{-1}) 2928, 1736, 1464, 1372, 1239, 1145, 731.

HRMS (ESI) calculated for $C_{18}H_{35}BNO_4$ $[M+NH_4]^+$ m/z 339.2690, found 339.2690.



4,4,5,5-tetramethyl-2-(7-(thiophen-2-ylmethoxy)heptyl)-1,3,2-dioxaborolane (3n)

Following **GPA** using 2-((hept-6-en-1-yloxy)methyl)thiophene (105.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (5-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 75% yield (126.5 mg).

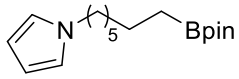
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.0 (m, 2H), 4.6 (s, 2H), 3.4 (t, *J* = 6.7 Hz, 2H), 1.6 (p, *J* = 6.7 Hz, 2H), 1.3 (m, 8H), 1.2 (s, 12H), 0.7 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 126.5, 126.1, 125.6, 82.8, 70.2, 67.3, 32.3, 29.6, 29.2, 26.0, 24.8, 23.9.

^{11}B NMR (128 MHz, CDCl3) δ 34.56.

IR (neat, cm^{-1}) 1732, 1446, 1238, 1044, 911, 728.

HRMS (ESI) calculated for $C_{18}H_{35}BNO_3S$ $[M+NH_4]^+$ m/z 355.2462, found 355.2463.



1-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-1H-pyrrole (3o)

Following **GPA** using 1-(hept-6-en-1-yl)-1H-pyrrole (82.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a yellow liquid in 80% yield (116.4 mg).

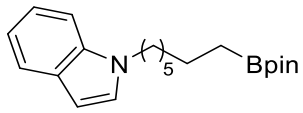
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.6 (t, *J* = 2.1 Hz, 2H), 6.1 (t, *J* = 2.1 Hz, 2H), 3.9 (t, *J* = 7.2 Hz, 2H), 1.8 (m, 2H), 1.4 (t, *J* = 6.8 Hz, 2H), 1.3 (m, 18H), 0.8 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 120.4, 107.7, 82.9, 49.6, 32.2, 31.6, 28.9, 26.7, 24.8, 23.9.

^{11}B NMR (128 MHz, CDCl3) δ 34.54.

IR (neat, cm^{-1}) 2929, 1736, 1372, 1237, 1044, 914, 727.

HRMS (ESI) calculated for $C_{17}H_{31}BNO_2$ $[M+H]^+$ m/z 291.2479, found 291.2480.



1-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-1H-indole (3p)

Following **GPA** using 1-(hept-6-en-1-yl)-1H-indole (106.6 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a yellow liquid in 80% yield (136.4 mg).

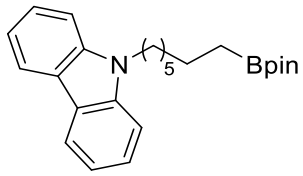
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7 (d, *J* = 7.9 Hz, 1H), 7.4 (d, *J* = 8.2 Hz, 1H), 7.3 (m, 1H), 7.1 (m, 2H), 6.5 (m, 1H), 4.1 (t, *J* = 7.2 Hz, 2H), 1.9 (m, 2H), 1.4 (m, 2H), 1.3 (s, 18H), 0.8 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 128.6, 127.8, 121.3, 120.9, 119.1, 109.4, 100.8, 82.9, 46.4, 32.3, 30.3, 29.1, 27.0, 24.9, 24.0.

^{11}B NMR (128 MHz, CDCl3) δ 34.61.

IR (neat, cm^{-1}) 2982, 1734, 1372, 1238, 1044, 910, 729.

HRMS (ESI) calculated for $C_{21}H_{33}BNO_2$ $[M+H]^+$ m/z 341.2635, found 341.2633.



9-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-9H-carbazole (3q)

Following **GPA** using 9-(hept-6-en-1-yl)-9H-carbazole (132.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a purple liquid in 72% yield (140.5 mg).

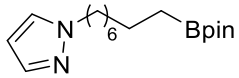
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2 (d, *J* = 7.7 Hz, 2H), 7.5 (m, 2H), 7.4 (d, *J* = 8.2 Hz, 2H), 7.3 (m, 2H), 4.3 (t, *J* = 7.3 Hz, 2H), 1.9 (m, 2H), 1.4 (m, 8H), 1.3 (s, 12H), 0.8 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 125.6, 122.8, 120.4, 118.7, 108.7, 82.9, 43.1, 32.4, 29.2, 29.0, 27.3, 24.9, 24.0.

^{11}B NMR (128 MHz, CDCl3) δ 34.48.

IR (neat, cm^{-1}) 2976, 1737, 1484, 1372, 1348, 1144, 749.

HRMS (ESI) calculated for $C_{25}H_{35}BNO_2$ $[M+H]^+$ m/z 391.2792, found 391.2793.



1-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)-1H-pyrazole (3r)

Following **GPA** using 1-(oct-7-en-1-yl)-1H-pyrazole (89.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a colorless liquid in 83% yield (127.0 mg).

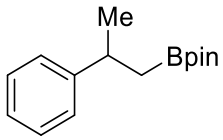
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (d, *J* = 1.7 Hz, 1H), 7.3 (d, *J* = 2.1 Hz, 1H), 6.2 (d, *J* = 2.0 Hz, 1H), 4.1 (t, *J* = 7.2 Hz, 2H), 1.8 (m, 2H), 1.3 (m, 10H), 1.2 (s, 12H), 0.7 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 128.8, 105.1, 82.9, 52.2, 32.3, 30.5, 29.2, 29.1, 26.6, 24.8, 23.9.

^{11}B NMR (128 MHz, CDCl3) δ 33.94.

IR (neat, cm^{-1}) 2925, 1513, 1373, 1317, 1144, 967, 747.

HRMS (ESI) calculated for $C_{17}H_{32}BN_2O_2$ $[M+H]^+$ m/z 306.2588, found 306.2588.

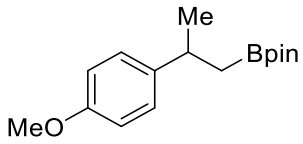


4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (5a)

Following **GPB** using prop-1-en-2-ylbenzene (59.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 93% yield[7] (114.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, 4H), 7.1 (m, 1H), 3.0 (m, 1H), 1.3 (d, *J* = 6.9 Hz, 3H), 1.2 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 128.2, 126.6, 125.7, 83.0, 35.8, 24.9, 24.8, 24.7.

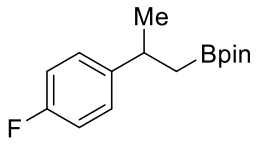


2-(2-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

Following **GPB** using 1-methoxy-4-(prop-1-en-2-yl)benzene (74.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 64% yield[8] (88.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 8.6 Hz, 2H), 6.8 (d, *J* = 8.5 Hz, 2H), 3.8 (s, 3H), 3.0 (m, 1H), 1.3 (d, *J* = 6.9 Hz, 3H), 1.2 (s, 12H), 1.1 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 141.5, 127.5, 113.6, 83.0, 55.3, 35.1, 25.3, 24.9, 24.8.



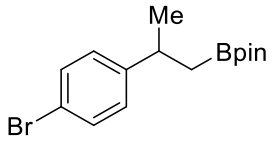
2-(2-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)

Following **GPB** using 1-fluoro-4-(prop-1-en-2-yl)benzene (68.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 88% yield[9] (116.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, 2H), 6.9 (t, *J* = 8.7 Hz, 2H), 3.0 (m, 1H), 1.2 (d, *J* = 6.9 Hz, 3H), 1.1 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 244.4 Hz), 144.9 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 8.1 Hz), 114.9 (d, *J* = 21.2 Hz), 83.2, 35.3, 25.3, 24.9, 24.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.2.

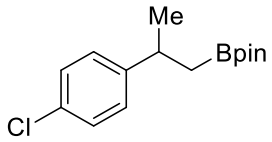


2-(2-(4-bromophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)

Following **GPB** using 1-bromo-4-(prop-1-en-2-yl)benzene (98.5 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 79% yield[10] (128.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (d, *J* = 8.2 Hz, 2H), 7.1 (d, *J* = 8.1 Hz, 2H), 3.0 (m, 1H), 1.2 (d, *J* = 6.9 Hz, 3H), 1.2 (s, 12H), 1.1 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 131.2, 128.5, 119.2, 83.1, 35.3, 24.8, 24.7, 24.7.

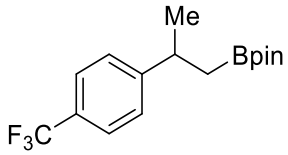


2-(2-(4-chlorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)

Following **GPB** using 1-chloro-4-(prop-1-en-2-yl)benzene (76.3 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 88% yield[10] (123.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 8.5 Hz, 2H), 7.2 (d, *J* = 8.4 Hz, 2H), 3.0 (m, 1H), 1.2 (d, *J* = 6.9 Hz, 3H), 1.2 (s, 12H), 1.1 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 131.3, 128.3, 128.1, 83.2, 35.4, 25.0, 24.9, 24.8.

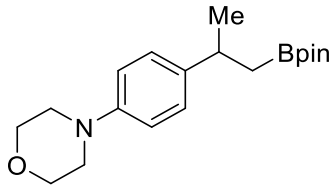


4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)propyl)-1,3,2-dioxaborolane (5f)

Following **GPB** using 1-(prop-1-en-2-yl)-4-(trifluoromethyl)benzene (93.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 80% yield[8] (125.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (m, 2H), 7.3 (m, 2H), 3.1 (m, 1H), 1.3 (d, *J* = 6.9 Hz, 3H), 1.2 (m, 14H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 128.2 (q, *J* = 32.3 Hz), 127.1, 125.3 (q, *J* = 4.0 Hz), 124.6 (q, *J* = 272.7 Hz), 83.3, 35.9, 24.9, 24.8, 24.7.



4-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)phenyl)morpholine (5g)

Following **GPB** using 4-(4-(prop-1-en-2-yl)phenyl)morpholine (101.6 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (10-20% EtOAc in hexanes) to provide the title compound as a yellow liquid in 70% yield (115.8 mg).

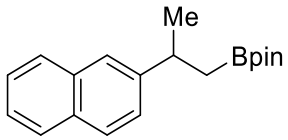
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 8.5 Hz, 2H), 6.8 (d, *J* = 8.6 Hz, 2H), 3.8 (m, 4H), 3.1 (m, 4H), 3.0 (m, 1H), 1.2 (d, *J* = 6.9 Hz, 3H), 1.2 (s, 12H), 1.1 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 141.1, 127.2, 115.8, 82.9, 67.0, 49.8, 34.9, 24.9, 24.8, 24.7.

^{11}B NMR (128 MHz, CDCl3) δ 34.50.

IR (neat, cm^{-1}) 1611, 1514, 1365, 1143, 1119, 968, 729.

HRMS (ESI) calculated for $C_{19}H_{31}BNO_3$ $[M+H]^+$ m/z 331.2428, found 331.2428.

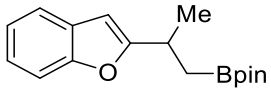


4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (5h)

Following **GPB** using 2-(prop-1-en-2-yl)naphthalene (84.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a white solid in 91% yield[11] (134.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 (m, 3H), 7.7 (s, 1H), 7.4 (m, 3H), 3.3 (m, 1H), 1.4 (d, *J* = 6.9 Hz, 3H), 1.3 (m, 2H), 1.2 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 133.7, 132.2, 127.8, 127.7, 127.6, 125.9, 125.8, 125.0, 124.5, 83.1, 36.0, 24.9, 24.8.

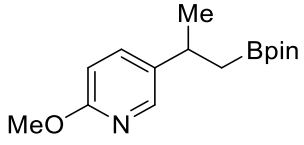


2-(2-(benzofuran-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5i)

Following **GPB** using 2-(prop-1-en-2-yl)benzofuran (79.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 60% yield[15] (86.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (m, 1H), 7.4 (d, *J* = 7.6 Hz, 1H), 7.2 (m, 2H), 6.4 (s, 1H), 3.2 (m, 1H), 1.4 (d, *J* = 6.9 Hz, 3H), 1.3 (m, 1H), 1.2 (s, 12H), 1.1 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 154.6, 129.1, 123.1, 122.3, 120.4, 110.8, 99.9, 83.3, 29.7, 25.0, 24.9, 21.5.



2-methoxy-5-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)pyridine (5j)

Following **GPB** using 2-methoxy-5-(prop-1-en-2-yl)pyridine (74.6 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (5-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 82% yield (113.5 mg).

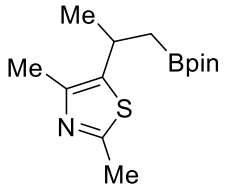
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (s, 1H), 7.4 (d, *J* = 8.5, 1H), 6.6 (d, *J* = 8.5 Hz, 1H), 3.9 (s, 3H), 3.0 (m, 1H), 1.2 (d, *J* = 6.9 Hz, 3H), 1.1 (s, 12H), 1.1 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 144.9, 137.2, 137.0, 110.4, 83.2, 53.4, 32.6, 24.9, 24.9, 24.8.

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

IR (neat, cm^{-1}) 2976, 1606, 1492, 1366, 1281, 1144, 1030.

HRMS (ESI) calculated for $C_{15}H_{25}BNO_3$ $[M+H]^+$ m/z 277.1958, found 277.1960.



2,4-dimethyl-5-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)thiazole (5k)

Following **GPB** using 2,4-dimethyl-5-(prop-1-en-2-yl)thiazole (76.6 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (5-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 59% yield (82.0 mg).

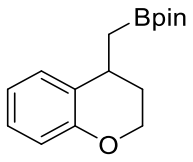
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.3 (m, 1H), 2.6 (s, 3H), 2.3 (s, 3H), 1.2 (d, *J* = 6.9 Hz, 3H), 1.2 (s, 12H), 1.1 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 145.1, 140.2, 28.8, 26.0, 24.9, 24.7, 19.2, 15.1.

^{11}B NMR (128 MHz, CDCl3) δ 33.61.

IR (neat, cm^{-1}) 1734, 1372, 1097, 1044, 913, 847, 729.

HRMS (ESI) calculated for $C_{14}H_{25}BNO_2S$ $[M+H]^+$ m/z 281.1730, found 281.1732.

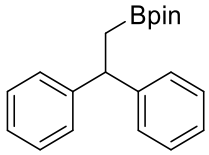


2-(chroman-4-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5l)

Following **GPB** using 4-methylenechromane (73.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 72% yield[14] (99.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 7.6, 1H), 7.1 (t, *J* = 7.7, 1H), 6.8 (t, *J* = 7.4, 1H), 6.8 (d, *J* = 8.2, 1H), 4.2 (m, 1H), 4.2 (m, 1H), 3.1 (m, 1H), 2.1 (m, 1H), 1.8 (m, 1H), 1.4 (m, 1H), 1.3 (d, *J* = 9.8 Hz, 12H), 1.1 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 128.9, 128.4, 127.2, 120.2, 116.7, 83.4, 64.1, 30.1, 29.9, 25.1, 24.8.

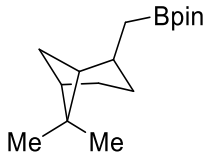


2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5m)

Following **GPB** using ethene-1,1-diyldibenzene (90.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 98% yield[12] (150.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 8H), 7.1 (m, 2H), 4.3 (t, *J* = 8.5 Hz, 1H), 1.6 (d, *J* = 8.5 Hz, 2H), 1.0 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 128.3, 127.7, 125.9, 83.1, 46.6, 24.6.



2-((6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5n)

Following **GPB** using 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (68.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 84% yield (110.5 mg).

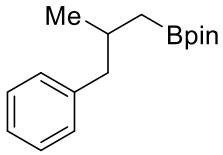
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.2 (m, 1H), 2.0 (m, 1H), 1.8 (m, 1H), 1.7 (m, 3H), 1.6 (m, 1H), 1.3 (d, *J* = 9.9 Hz, 1H), 1.2 (s, 14H), 1.2 (s, 3H), 0.8 (s, 3H), 0.7 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 48.6, 40.7, 39.6, 31.2, 26.9, 24.8, 24.7, 24.3, 23.1, 20.2.

^{11}B NMR (128 MHz, CDCl3) δ 34.11.

IR (neat, cm^{-1}) 2981, 1735, 1464, 1372, 1234, 913, 730.

HRMS (EI) calculated for $C_{16}H_{29}BO_2$ $[M]^+$ m/z 263.2291, found 263.2286.

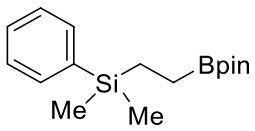


4,4,5,5-tetramethyl-2-(2-methyl-3-phenylpropyl)-1,3,2-dioxaborolane (5o)

Following **GPB** using (2-methylallyl)benzene (61.1 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 78% yield[13] (101.0mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 2H), 7.2 (m, 3H), 2.6 (m, 1H), 2.4 (m, 1H), 2.0 (m, 1H), 1.2 (s, 12H), 0.9 (m, 4H), 0.7 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 129.4, 128.1, 125.7, 83.0, 46.2, 31.9, 25.0, 24.9, 22.1.

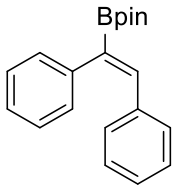


dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane (5p)

Following **GPB** using dimethyl(phenyl)(vinyl)silane (81.2 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-10% EtOAc in hexanes) to provide the title compound as a colorless liquid in 85% yield[16] (123.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (m, 2H), 7.3 (m, 3H), 1.2 (s, 12H), 0.8 (m, 4H), 0.2 (s, 6H).

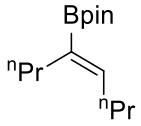
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 133.7, 128.7, 127.6, 83.0, 24.8, 8.5, -3.5.



(Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a)

Following **GPB** using 1,2-diphenylethyne (89.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-5% EtOAc in hexanes) to provide the title compound as a yellow solid in 85% yield[17] (130 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (s, 1H), 7.2 (m, 2H), 7.2 (m, 3H), 7.1 (m, 5H), 1.3 (s, 12H).

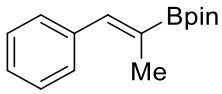


(Z)-4,4,5,5-tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (7b)

(4.8: 1 mixture of E/Z isomer)

Following **GPB** using oct-4-yne (55.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 92% yield[18] (108 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.3 (t, *J* = 7.1 Hz, 1H), 2.1 (m, 4H), 1.4 (m, 4H), 1.2 (s, 12H), 0.9 (m, 6H).

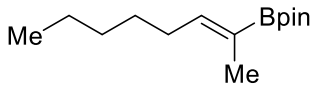


(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (7c)

(2: 1 mixture of regioisomer)

Following **GPB** using prop-1-yn-1-ylbenzene (58.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 81% yield[19] (99 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (m, 4H), 7.2 (m, 2H), 2.0 (d, *J* = 1.8 Hz, 3H), 1.3 (s, 12H).

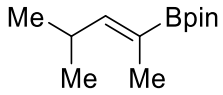


(Z)-4,4,5,5-tetramethyl-2-(oct-2-en-3-yl)-1,3,2-dioxaborolane (7d)

(3.7: 1 mixture of regioisomer)

Following **GPB** using oct-2-yne (55.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 90% yield[20] (107 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.3 (m, 1H), 2.1 (m, 2H), 1.7 (s, 3H), 1.3 (m, 6H), 1.3 (s, 12H), 0.9 (m, 3H).

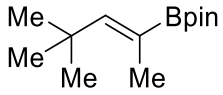


(Z)-4,4,5,5-tetramethyl-2-(4-methylpent-2-en-3-yl)-1,3,2-dioxaborolane (7e)

(16.6: 1 mixture of regioisomer)

Following **GPB** using 4-methylpent-2-yne (41.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 60% yield[21] (63 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.1 (dd, *J* = 9.1, 1.8 Hz, 1H), 2.7 (m, 1H), 1.7 (d, *J* = 1.7 Hz, 3H), 1.3 (s, 12H), 1.0 (d, *J* = 6.7 Hz, 6H).



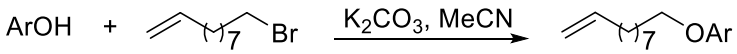
(Z)-2-(4,4-dimethylpent-2-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7f)

(50: 1 mixture of regioisomer)

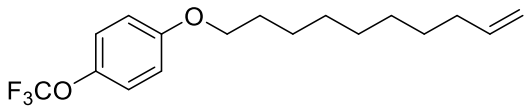
Following **GPB** using 4,4-dimethylpent-2-yne (48.0 mg, 0.5 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 77% yield[22] (86 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.3 (s, 1H), 1.8 (s, 3H), 1.2 (s, 12H), 1.1 (s, 9H).

Substrate Synthesis



General procedure C (GPC): A 100 mL round-bottom flask was charged with substituted phenol (5.0 mmol, 1.0 equiv), 10-bromo-1-decene (1.3 g, 6.0 mmol, 1.2 equiv), K_2CO_3 (818.0 mg, 6.0 mmol, 1.2 equiv) and acetonitrile (20.0 mL). The reaction was stirred under reflux for 12 h. After cooling to r.t., saturated NH_4Cl (aq.) was added to quench the reaction. The mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was concentrated in vacuo, and the residue was purified by column chromatography to afford the pure product.



1-(dec-9-en-1-yloxy)-4-(trifluoromethoxy)benzene

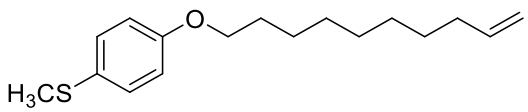
Following **GPC** using 4-(trifluoromethoxy)phenol (890.0 mg, 5.0 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 80% yield (1.26 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1 (d, *J* = 8.7 Hz, 2H), 6.9 (m, 2H), 5.8 (m, 1H), 5.0 (m, 2H), 3.9 (t, *J* = 6.5 Hz, 2H), 2.0 (m, 2H), 1.8 (m, 2H), 1.3 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 142.6, 139.3, 122.5, 120.7 (q, *J* =256.5 Hz), 115.2, 114.3, 68.5, 34.0, 29.6, 29.5, 29.3, 29.2, 29.0, 26.1.

IR (neat, cm^{-1}) 2927, 1506, 1241, 1195, 1159, 910, 838.

HRMS (EI) calculated for $C_{17}H_{23}F_3O_2$ $[M]^+$ m/z 316.1645, found 316.1642.



(4-(dec-9-en-1-yloxy)phenyl)(methyl)sulfane

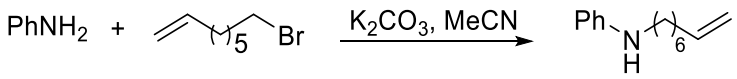
Following **GPC** using 4-(methylthio)phenol (700.0 mg, 5.0 mmol, 1.0 equiv), the crude product was purified by column chromatography (0-1% EtOAc in hexanes) to provide the title compound as a colorless liquid in 85% yield (1.17 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (d, *J* = 8.7 Hz, 2H), 6.8 (d, *J* = 8.7 Hz, 2H), 5.8 (m, 1H), 5.0 (m, 2H), 3.9 (t, *J* = 6.6 Hz, 2H), 2.4 (s, 3H), 2.1 (m, 2H), 1.8 (m, 2H), 1.4 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 139.3, 130.3, 128.5, 115.3, 114.3, 68.2, 33.9, 29.5, 29.5, 29.3, 29.2, 29.0, 26.1, 18.2.

IR (neat, cm^{-1}) 2923, 1595, 1493, 1297, 1241, 909, 821.

HRMS (EI) calculated for $C_{17}H_{26}OS$ $[M]^+$ m/z 278.1699, found 278.1701.



N-(oct-7-en-1-yl)aniline

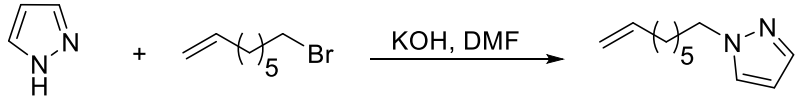
A 100 mL round-bottom flask was charged with aniline (465.0 mg, 5.0 mmol, 1.0 equiv), 8-bromo-1-octene (1.14 g, 6.0 mmol, 1.2 equiv), K_2CO_3 (818.0 mg, 6.0 mmol, 1.2 equiv) and acetonitrile (20.0 mL). The reaction was stirred under reflux for 12 h. After cooling to r.t., saturated NH_4Cl (aq.) was added to quench the reaction. The mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was concentrated in vacuo and the residue was purified by column chromatography to afford the pure product as a colorless liquid in 70% yield (710.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (m, 2H), 6.7 (m, 1H), 6.6 (m, 2H), 5.8 (m, 1H), 5.0 (m, 2H), 3.6 (s, 1H), 3.1 (t, *J* = 7.1 Hz, 2H), 2.0 (m, 2H), 1.6 (m, 2H), 1.4 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 139.1, 129.3, 117.1, 114.4, 112.7, 44.0, 33.8, 29.6, 29.0, 28.9, 27.1.

IR (neat, cm^{-1}) 2925, 1601, 1504, 1318, 1259, 908, 746.

HRMS (ESI) calculated for $C_{14}H_{22}N$ $[M+H]^+$ m/z 204.1747, found 204.1744.



1-(oct-7-en-1-yl)-1H-pyrazole

To a solution of 1H-pyrazole (340.0 mg, 5.0 mmol, 1.0 equiv) in DMF (8.0 mL), was added 8-bromo-1-octene (1.2 g, 6.0 mmol, 1.2 equiv) and KOH (336.0 mg, 6.0 mmol,

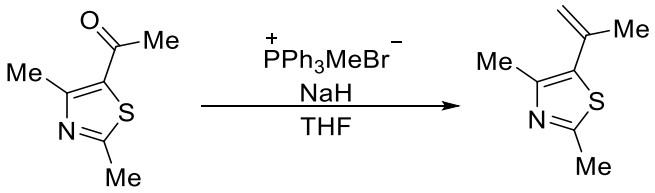
1.2 equiv). The mixture was heated to 70 °C and stirred for 3 h. The solution was allowed to cool to r.t. and water (20.0 mL) was added to the solution. Then the solution was extracted with ethyl acetate. The organic phase was washed with water and dried over Na_2SO_4. The solvent was concentrated in vacuo, and the residue was purified by column chromatography to afford the pure product as a yellow liquid in 90% yield (802 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (d, *J* = 1.8 Hz, 1H), 7.3 (d, *J* = 2.2 Hz, 1H), 6.2 (t, *J* = 2.0 Hz, 1H), 5.7 (m, 1H), 4.9 (m, 2H), 4.1 (t, *J* = 7.2 Hz, 2H), 2.0 (m, 2H), 1.8 (m, 2H), 1.3 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.8, 128.7, 114.3, 105.1, 52.0, 33.6, 30.4, 28.6, 28.5, 26.4.

IR (neat, cm^{-1}) 2729, 1604, 1512, 1395, 1090, 910, 746.

HRMS (ESI) calculated for $C_{11}H_{19}N_2$ $[M+H]^+$ m/z 179.1543, found 179.1542.



2,4-dimethyl-5-(prop-1-en-2-yl)thiazole

A solution of methyl triphenylphosphoniumbromide (2.2 g, 6.0 mmol, 1.2 equiv) in anhydrous THF (10.0 mL) was cooled to 0 °C under argon, followed by addition of ^{n}BuLi (2.5 M in hexane, 2.4 mL, 6.0 mmol, 1.2 equiv). The reaction mixture was stirred at 0 °C for 1 h, and then a solution of 1-(2,4-dimethylthiazol-5-yl)ethan-1-one (776.0 mg, 5.0 mmol, 1.0 equiv) in anhydrous THF (4.0 mL) was added dropwise. The resulting mixture was warmed to r.t. and kept stirring for 12 h. reaction mixture was concentrated under reduced pressure to yield a residue which was further purified over silica gel flash column chromatography to afford the product as a yellow liquid in 80% yield (613 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.1 (s, 1H), 5.0 (s, 1H), 2.6 (s, 3H), 2.4 (s, 3H), 2.0 (t, *J* = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 147.2, 135.8, 133.1, 115.9, 25.1, 19.0, 16.8.

IR (neat, cm^{-1}) 1608, 1531, 1438, 1375, 1182, 889.

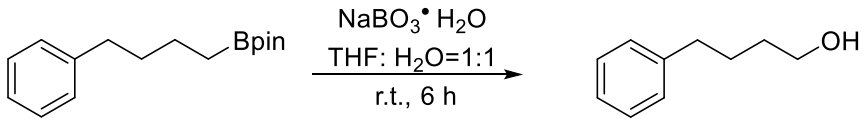
HRMS (ESI) calculated for $C_8H_{12}NS$ $[M+H]^+$ m/z 154.0685, found 154.0684.

Gram-Scale Reaction and Transformation of Product

Procedure for gram-scale reaction

In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (5.0 mL, 1.0 M), HBpin (870 µL, 6.0 mmol, 1.2 equiv) and ^{n}BuLi (2.5 M in hexane, 100 µL, 0.025 mmol, 5 mol %) were added sequentially. Then the mixture was stirred for 5 min at room temperature. The 4-phenyl-1-butene (751.1 µL, 5.0 mmol) was then added dropwise, and the reaction mixture was stirred at 110 ^{o}C for 18 h. After completion of the reaction, the reaction mixture was allowed to cool to r.t. 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 GC-MS analysis. The product was purified by chromatography on silica gel as a colorless liquid in 89% yield (1.15 g).

Transformation of 3a

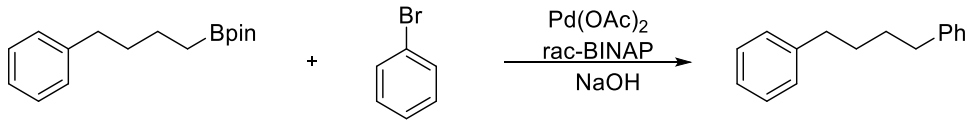


3a **8**

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 95% yield[23] (28 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 2H), 7.2 (m, 3H), 3.6 (t, *J* = 6.4 Hz, 2H), 2.6 (t, *J* = 7.5 Hz, 2H), 1.7 (m, 2H), 1.6 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.9, 62.9, 35.7, 32.4, 27.7.

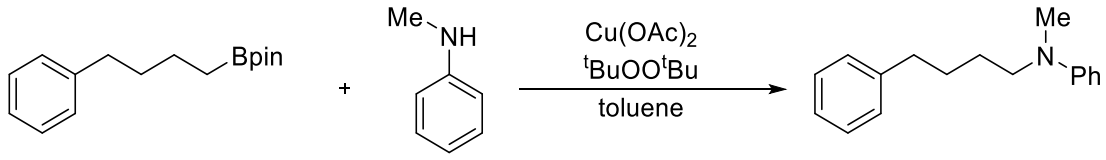


3a **9**

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. The reaction mixture was stirred at r.t. 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 the product in 55% yield[24] (23 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 4H), 7.2 (m, 6H), 2.6 (m, 4H), 1.7 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 128.5, 128.4, 125.8, 35.9, 31.2.



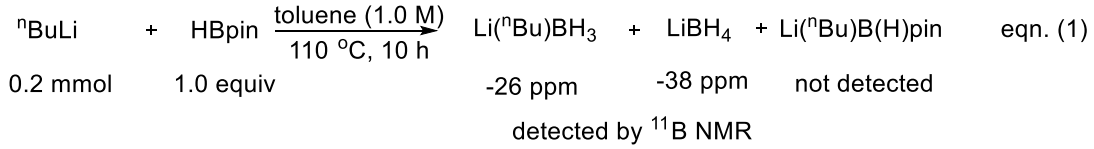
3a **10**

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 tBuOOtBu (58.5 mg, 0.4 mmol, 2.0 equiv) were added. The reaction mixture was allowed to stir at 80 ^{o}C for 48 h, after cooling to r.t., 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 60% yield[25] (28.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 3H), 7.2 (m, 4H), 6.7 (m, 3H), 3.3 (t, J = 6.8 Hz, 2H), 2.9 (s, 3H), 2.6 (t, J = 7.0 Hz, 2H), 1.6 (m, 4H).

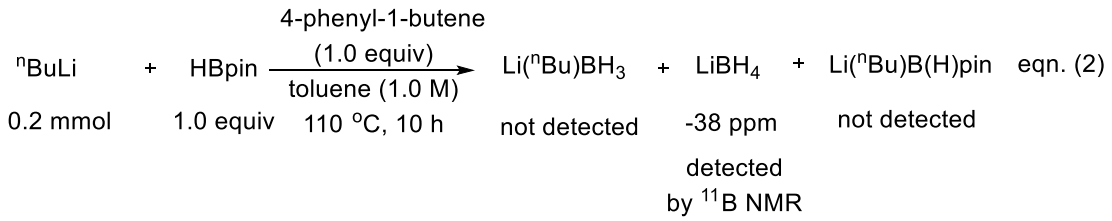
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 142.5, 129.3, 128.5, 128.5, 125.9, 116.0, 112.2, 52.8, 38.5, 36.0, 29.2, 26.6.

Mechanistic Studies



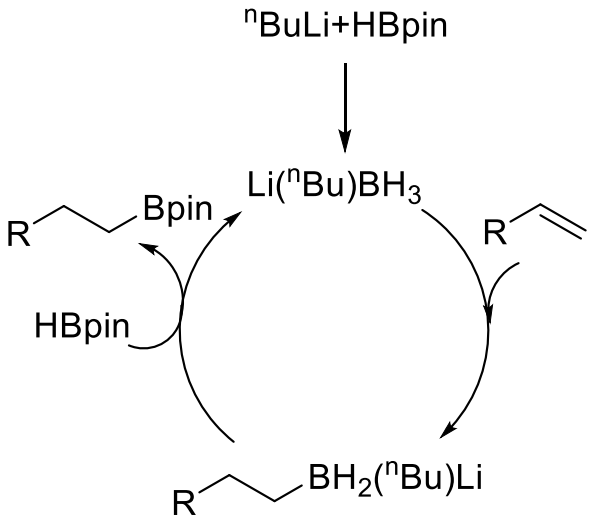
In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.2 mL, 1.0 M), HBpin (29.0 µL, 0.2 mmol, 1.0 equiv) and ^{n}BuLi (2.5 M in hexane, 80.0 µL, 0.2 mmol, 1.0 equiv) were added sequentially. Then the reaction mixture was stirred at 110 ^{o}C for 10 h. After cooling to room temperature, the crude reaction mixture was used for ^{11}B NMR analysis.

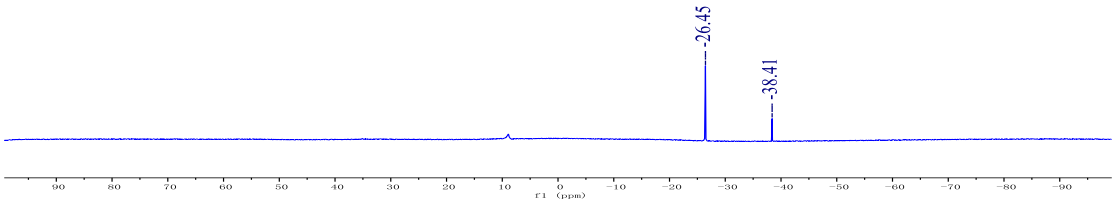
Li(^{n}Bu)BH$_3$ (-26 ppm) and LiBH$_4$ (-38 ppm) were detected by ^{11}B NMR analysis.

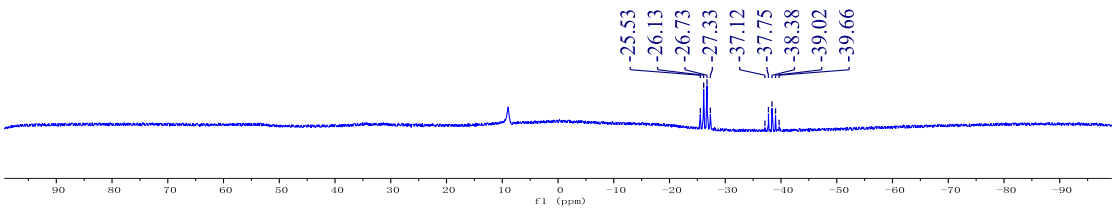


In a nitrogen-purged Schlenk tube containing a magnetic stirring bar, toluene (0.2 mL, 1.0 M), HBpin (29.0 µL, 0.2 mmol, 1.0 equiv), ^{n}BuLi (2.5 M in hexane, 80.0 µL, 0.2 mmol, 1.0 equiv) and 4-phenyl-1-butene (30.0 µL, 0.2 mmol, 1.0 equiv) were added sequentially. Then the reaction mixture was stirred at 110 ^{o}C for 10 h. After cooling to room temperature, the crude reaction mixture was used for ^{11}B NMR analysis.

We observed that the peak for LiBH$_4$ by ^{11}B NMR analysis, but the peak for Li(^{n}Bu)BH$_3$ was not detected. Since LiBH$_4$ is less reactive towards 1-alkene as reported in the literature (Tetrahedron Lett. 2003, 44, 8077), we prefer that Li(^{n}Bu)BH$_3$ to be the active species but not exclude the possibility of other boron-hydride species. The role of ^{n}BuLi supposed to activate HBpin to form a mixture of boron-hydride species as real catalysts. Based on these findings, we proposed a possible mechanism, as shown below.


nBuLi+HBpin
Li(nBu)BH3
Bpin
R
R
HBpin
R
BH2(nBu)Li


-26.45
-38.41
f1 (ppm)


-25.53
-26.13
-26.73
-27.33
-37.12
-37.75
-38.38
-39.02
-39.66
f1 (ppm)

References

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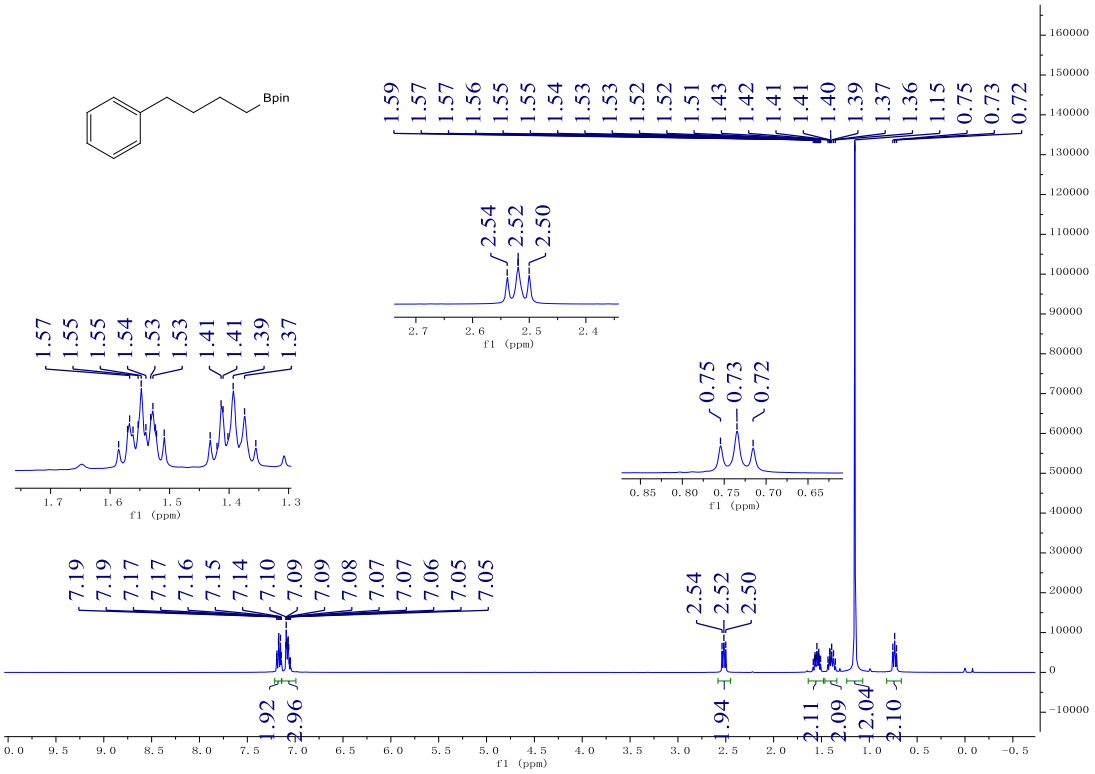
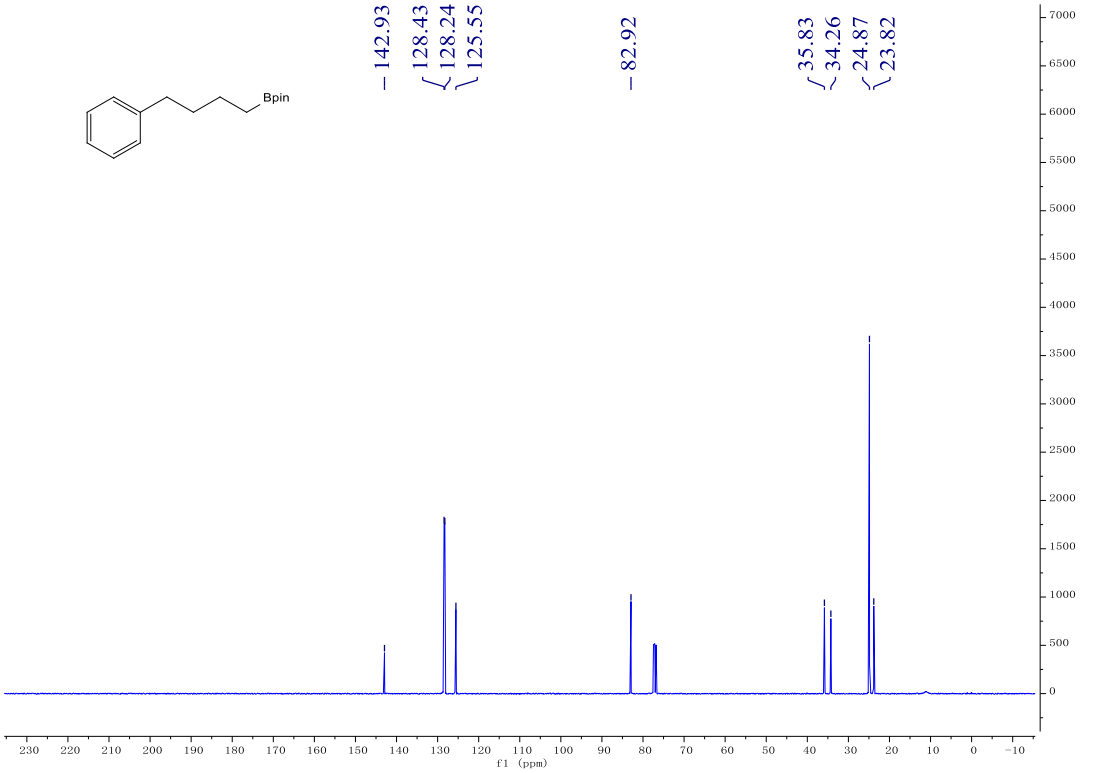
NMR Spectra

3a





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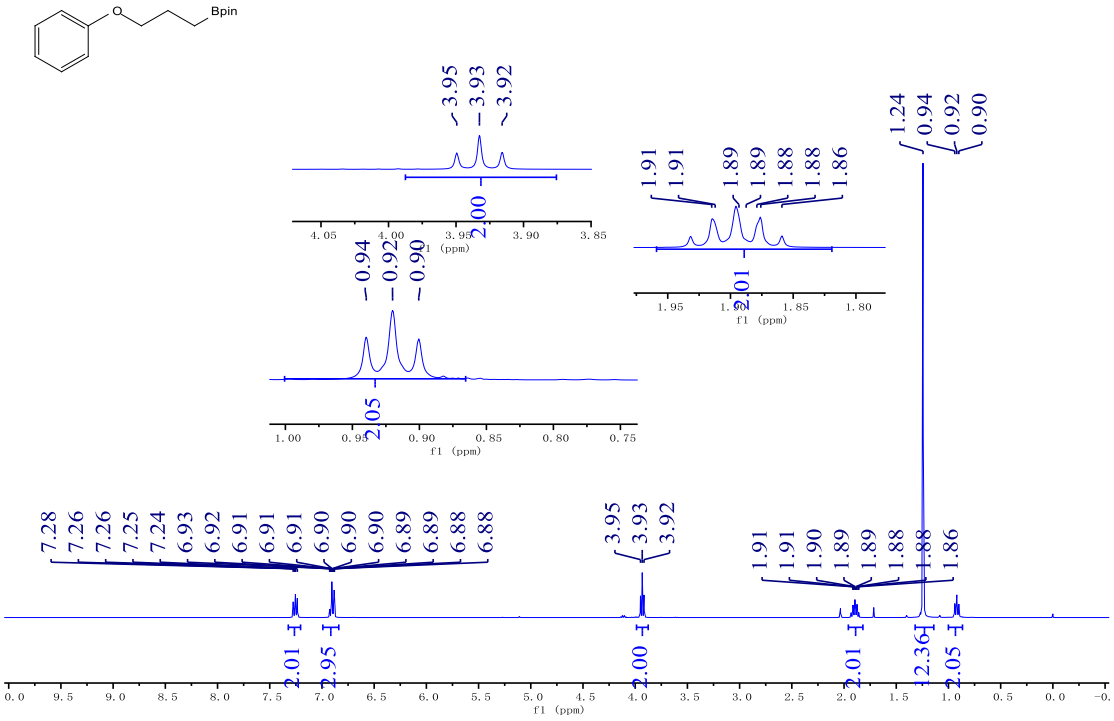
Bpin
O
3.95
3.93
3.92
2.00
1.91
1.91
1.89
1.89
1.88
1.88
1.86
2.01
1.24
0.94
0.92
0.90
0.94
0.92
0.90
2.05
7.28
7.26
7.26
7.25
7.24
6.93
6.92
6.91
6.91
6.91
6.90
6.90
6.90
6.89
6.89
6.88
6.88
3.95
3.93
3.92
1.91
1.91
1.90
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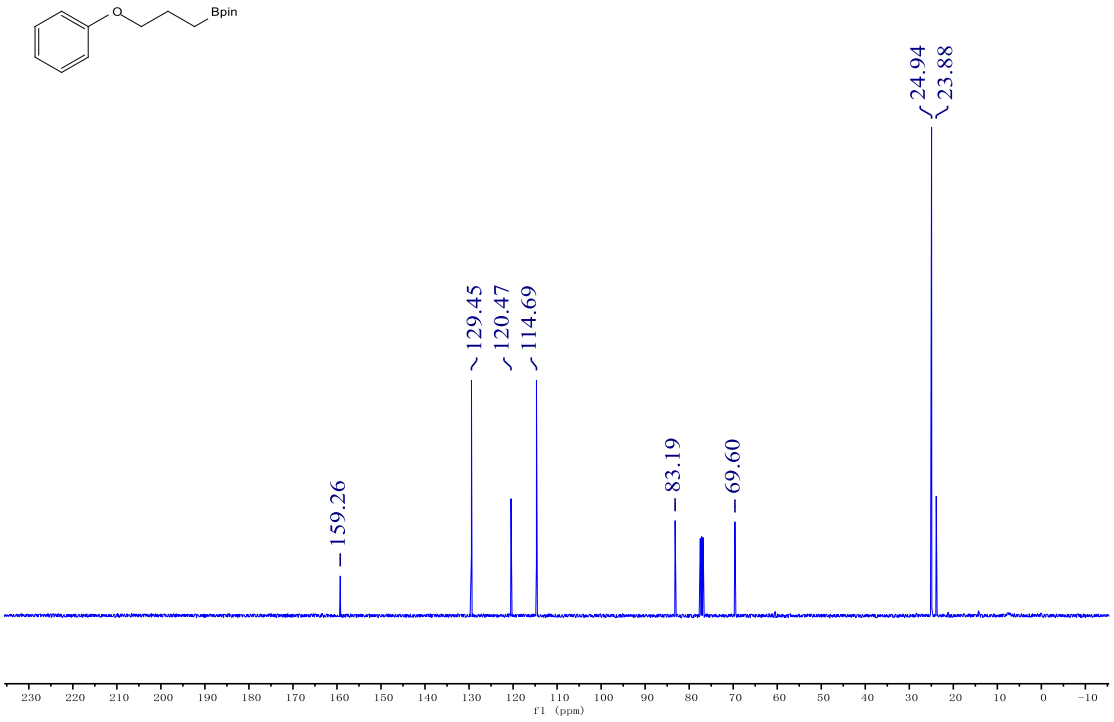
2.00
2.01
12.36
2.05
f1 (ppm)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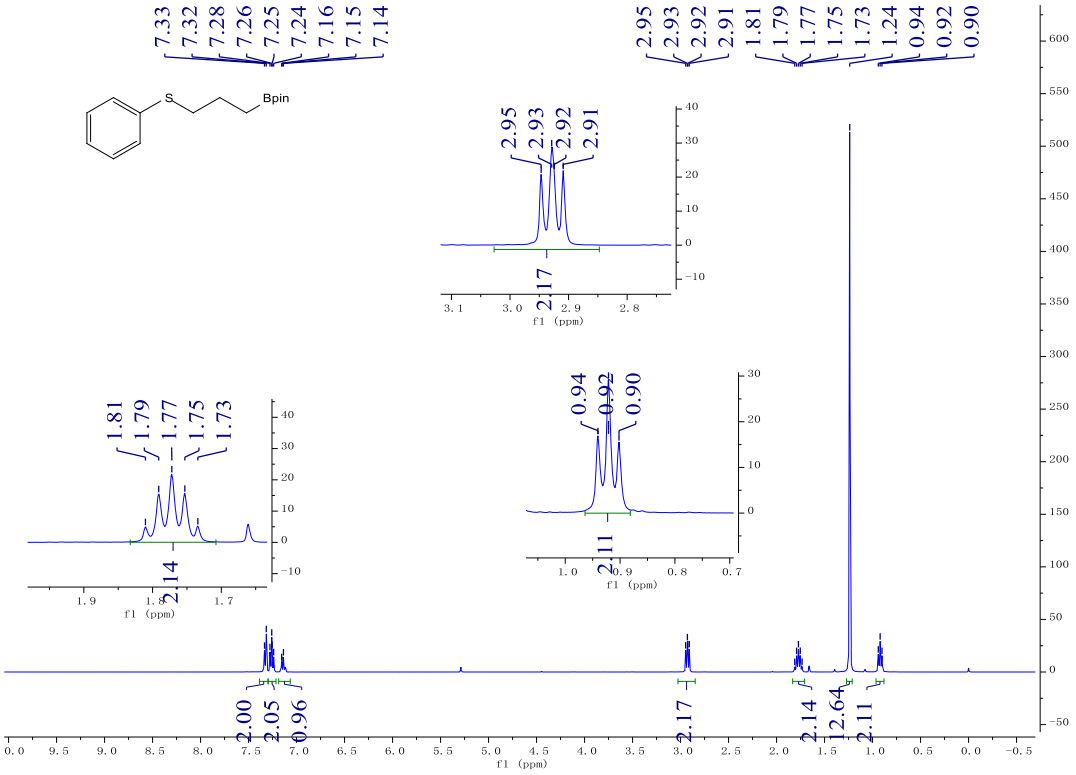
159.26
83.19
69.60
f1 (ppm)

3c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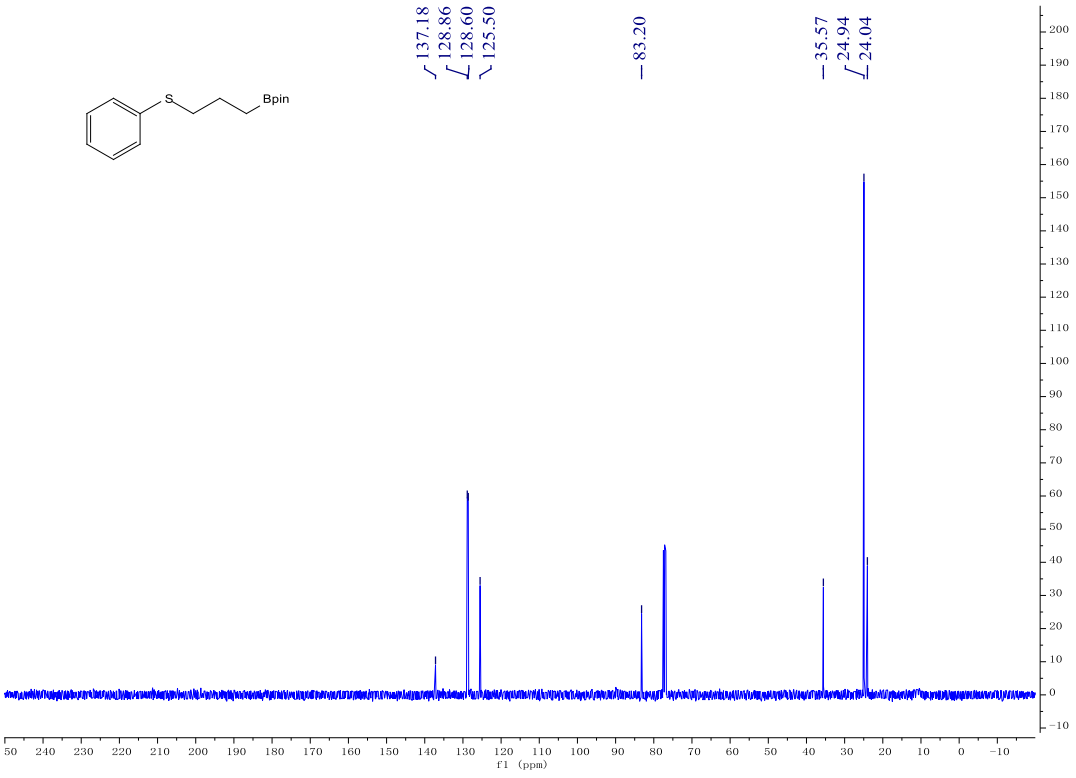
7.32
7.28
7.26
7.25
7.24
7.16
7.15
7.14
2.95
2.93
2.92
2.91
1.81
1.79
1.77
1.75
1.73
1.24
0.94
0.92
0.90
Bpin
S
2.00
2.05
0.96
2.17
2.14
12.64
2.11
f1 (ppm)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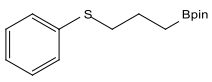
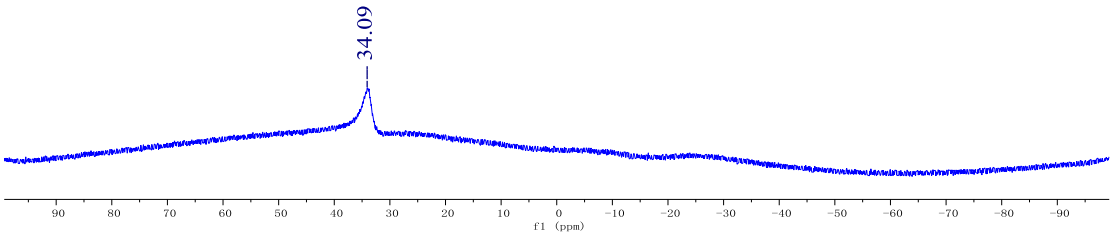
128.60
125.50
83.20
35.57
24.94
24.04
Bpin
S
f1 (ppm)


S
Bpin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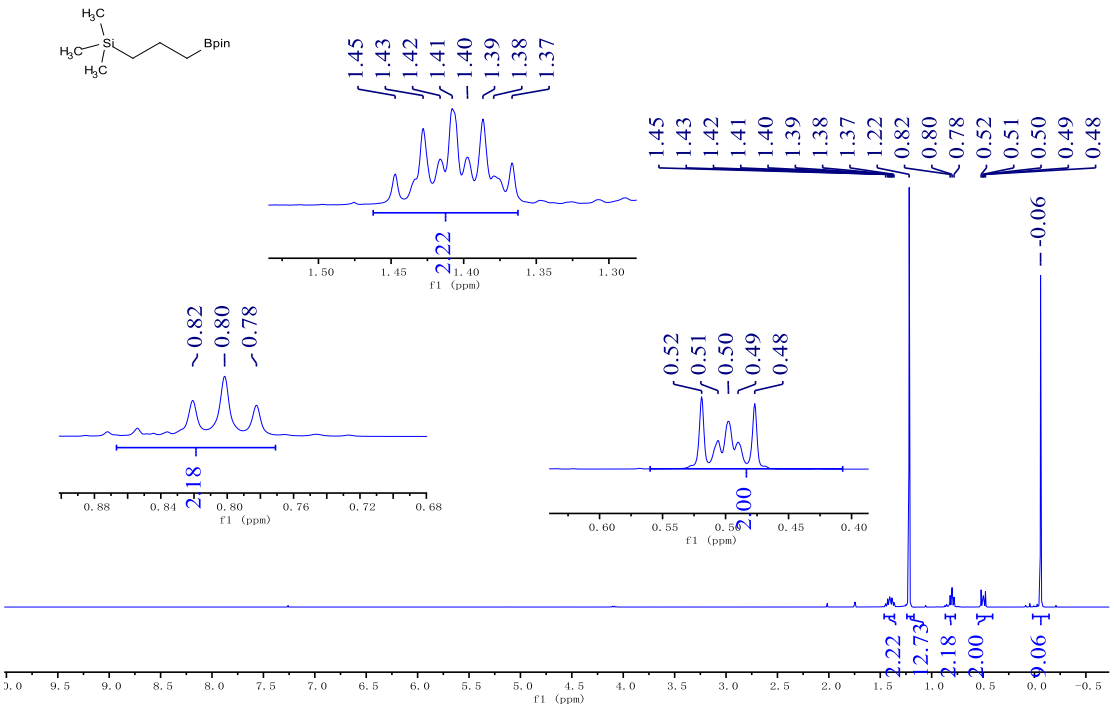
3d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Si
H3C
H3C
Bpin
1.45
1.43
1.42
1.41
1.40
1.39
1.38
1.37
2.22
f1 (ppm)
0.82
0.80
0.78
2.18
f1 (ppm)
0.52
0.51
0.50
0.49
0.48
2.00
f1 (ppm)
1.45
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.22
0.82
0.80
0.78
0.52
0.51
0.50
0.49
0.48
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2.22
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2.18
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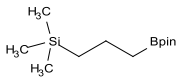
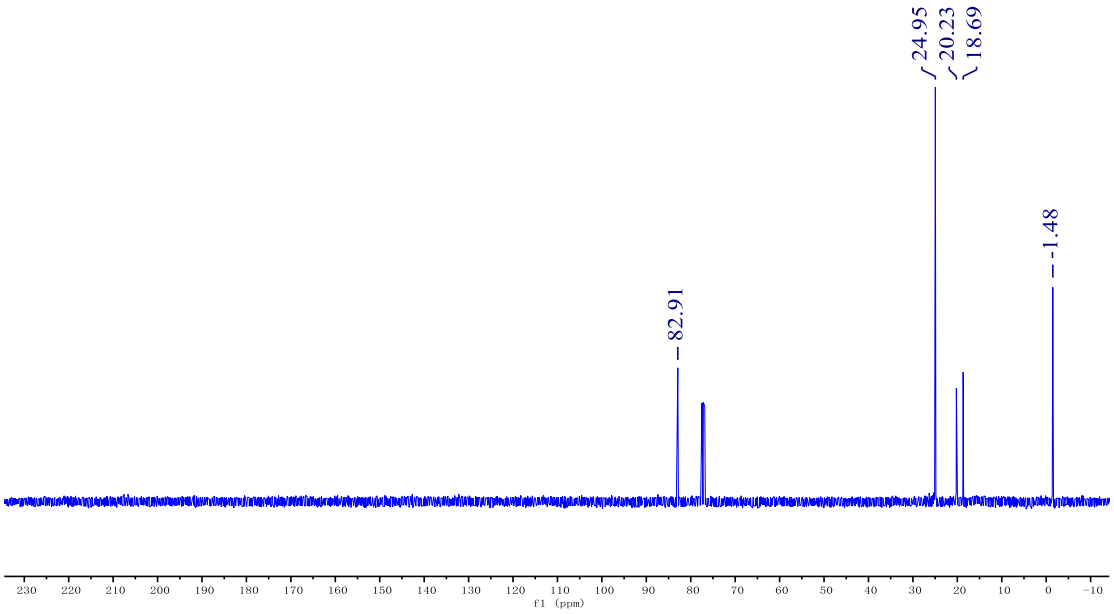
9.06
f1 (ppm)


H3C
Si
H3C
H3C
Bpin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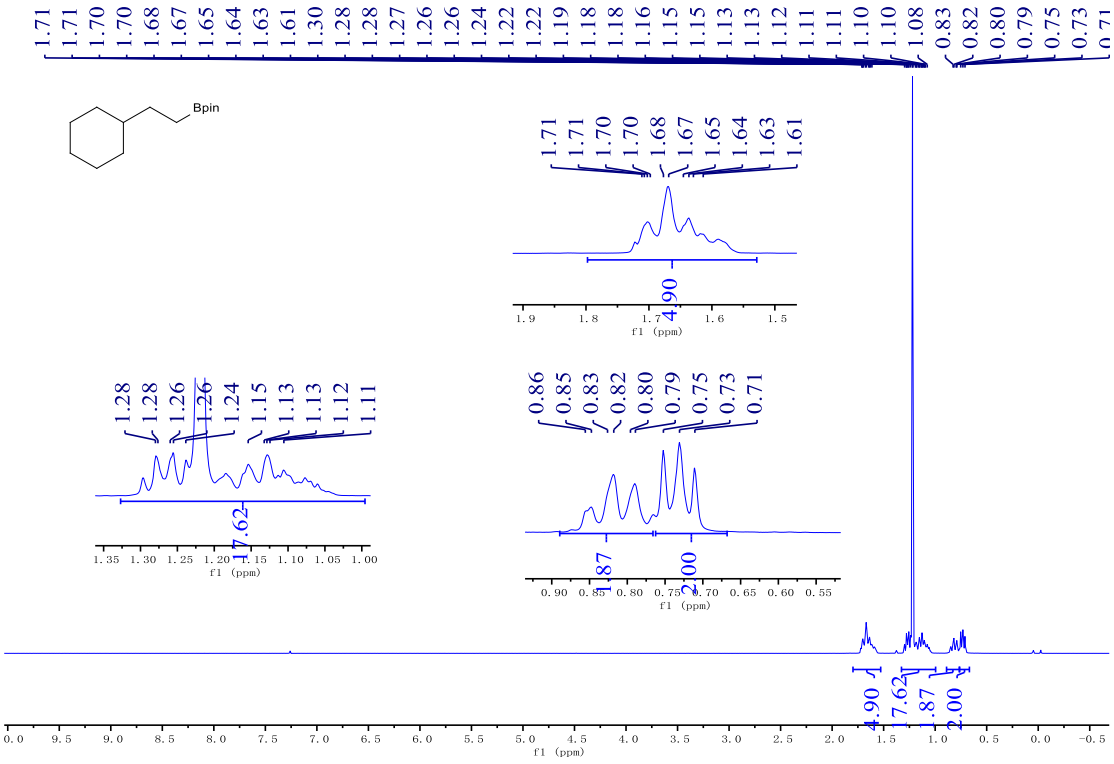
-1.48
82.91
f1 (ppm)

3e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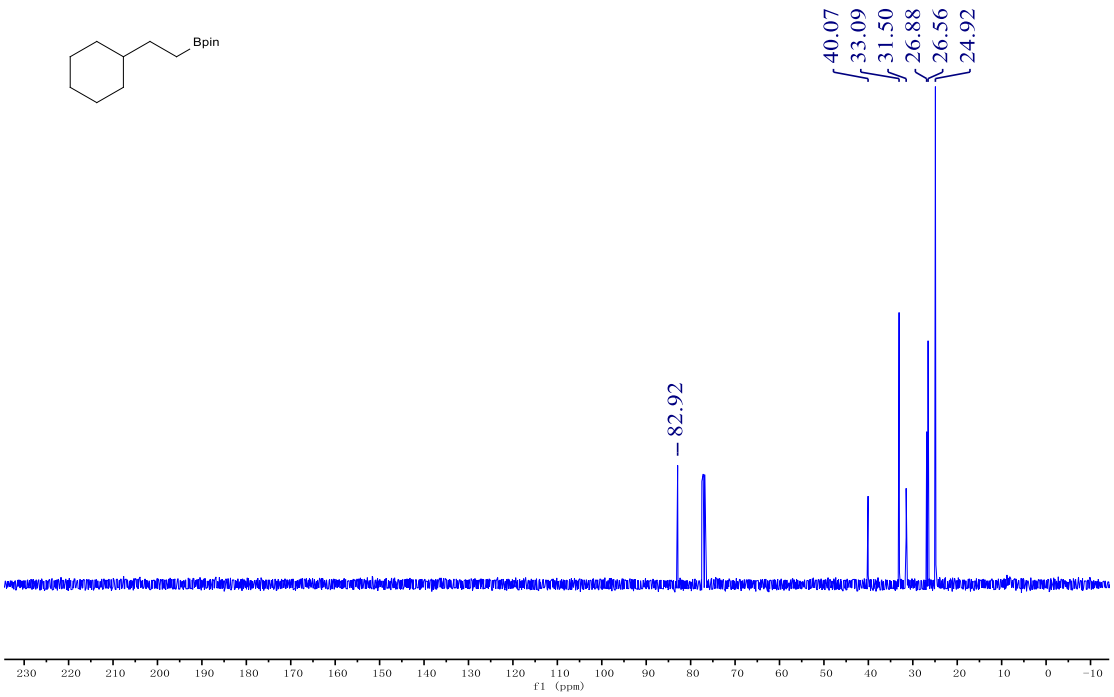
f1 (ppm)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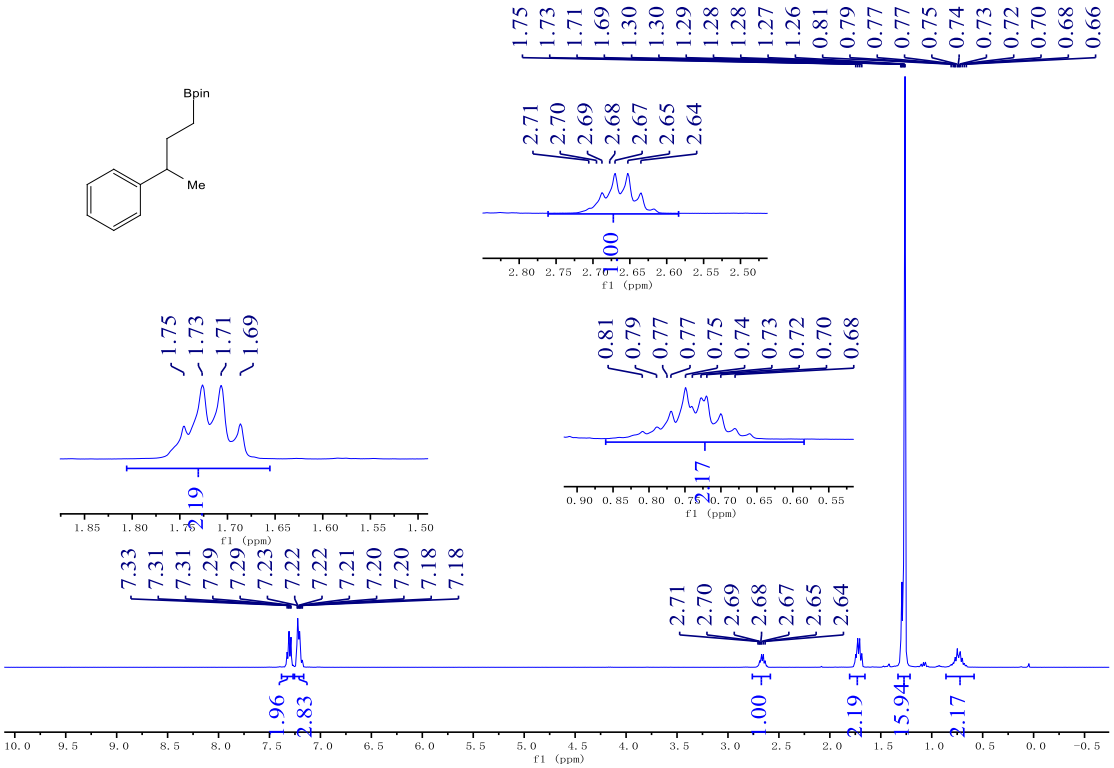
31.50
26.88
26.56
24.92
82.92
f1 (ppm)

3f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Me
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1.73
1.71
1.69
1.30
1.30
1.29
1.28
1.28
1.27
1.26
0.81
0.79
0.77
0.77
0.75
0.74
0.73
0.72
0.70
0.68
0.66
2.71
2.70
2.69
2.68
2.67
2.65
2.64
7.33
7.31
7.31
7.29
7.29
7.23
7.22
7.22
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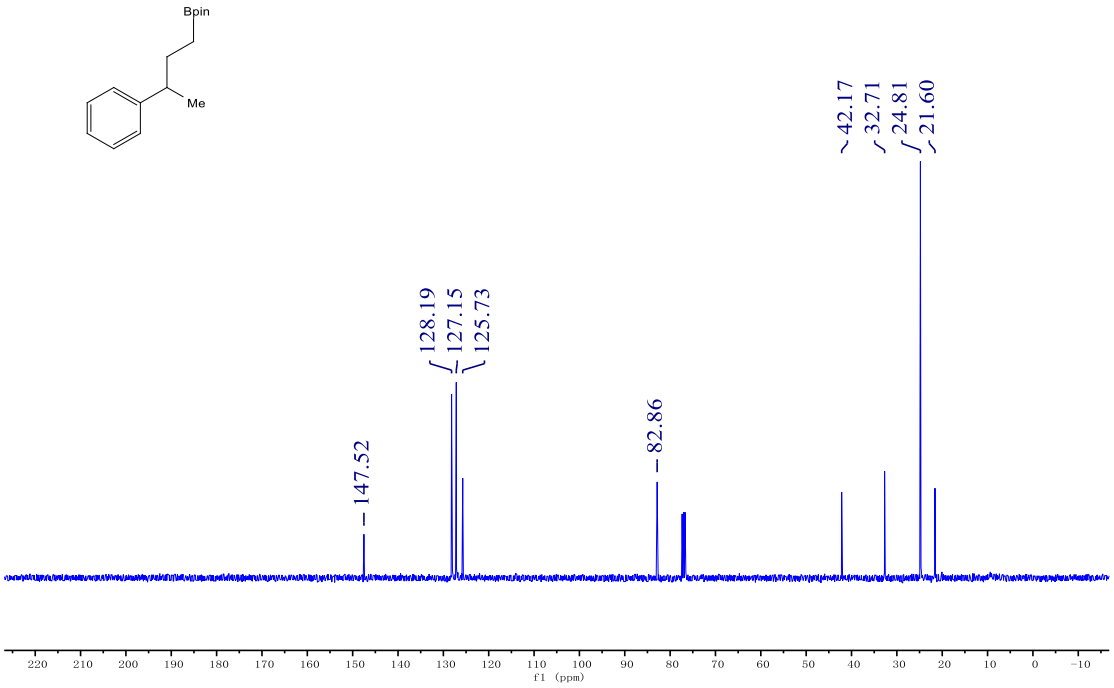
2.17
f1 (ppm)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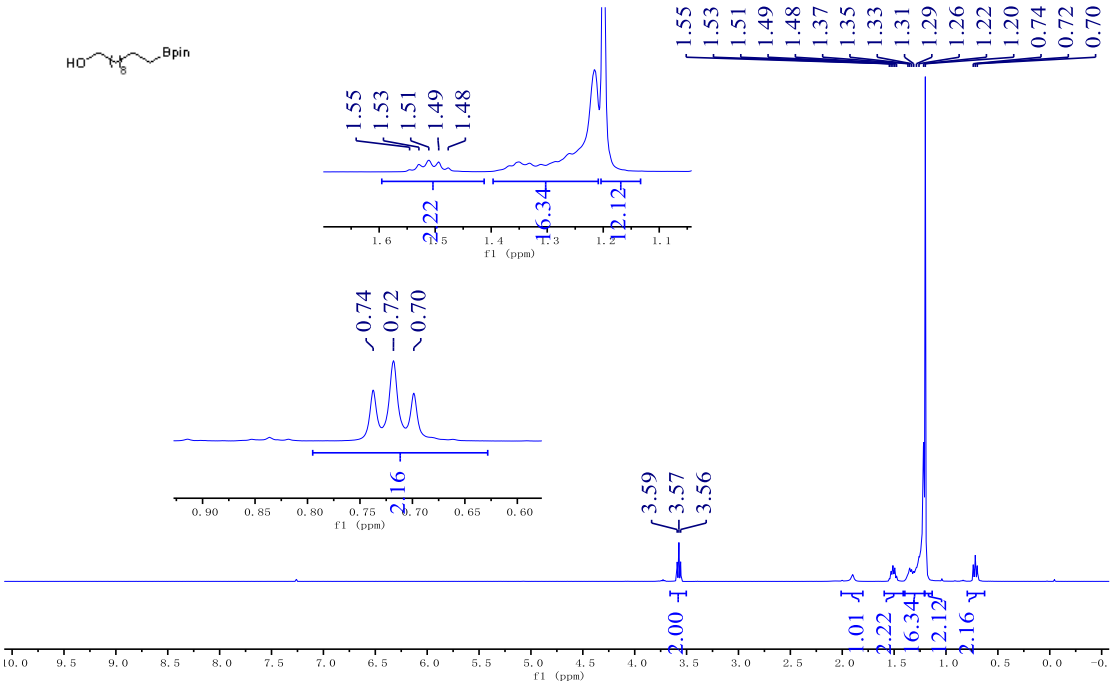
21.60
f1 (ppm)

3g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Bpin
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1.53
1.51
1.49
1.48
1.37
1.35
1.33
1.31
1.29
1.26
1.22
1.20
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0.70
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3.56
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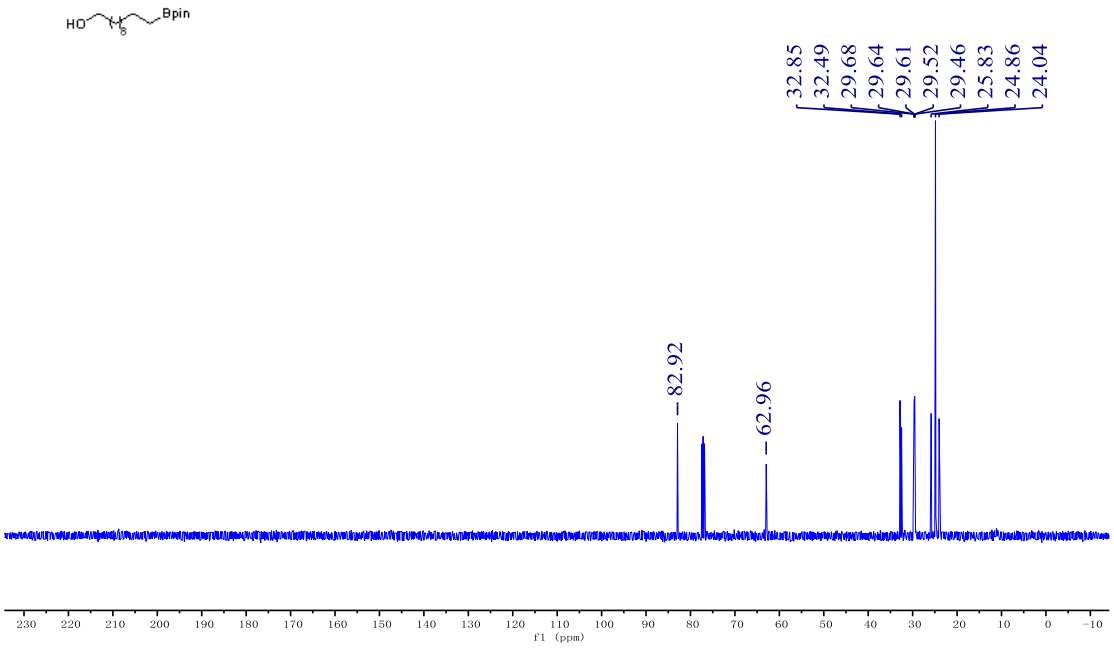
16.34
2.12
2.16
f1 (ppm)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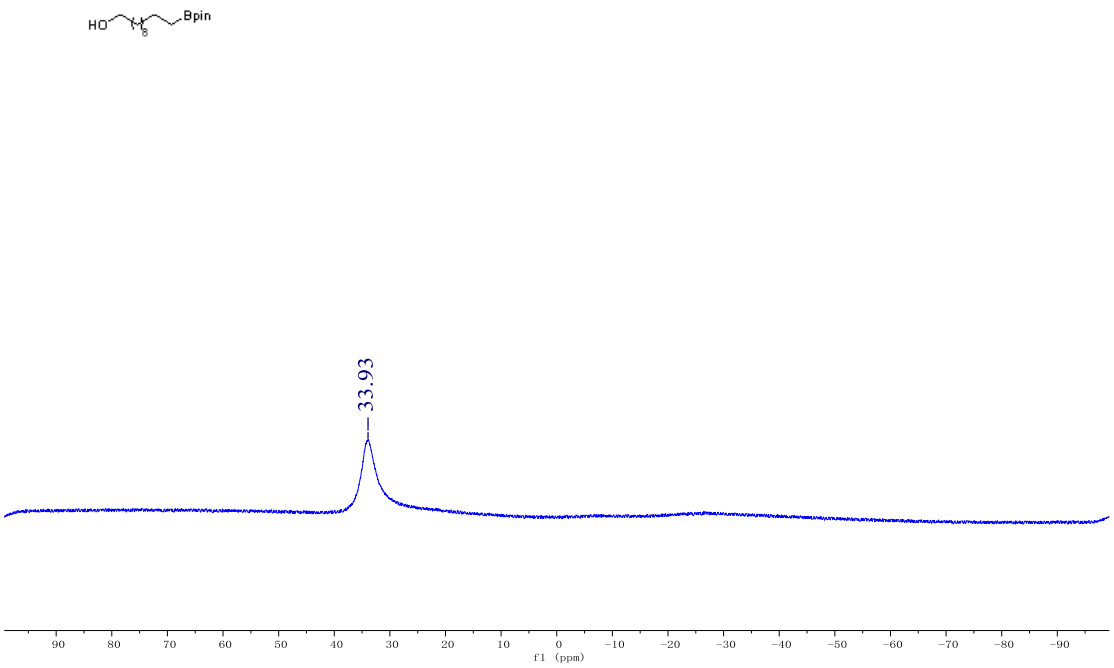
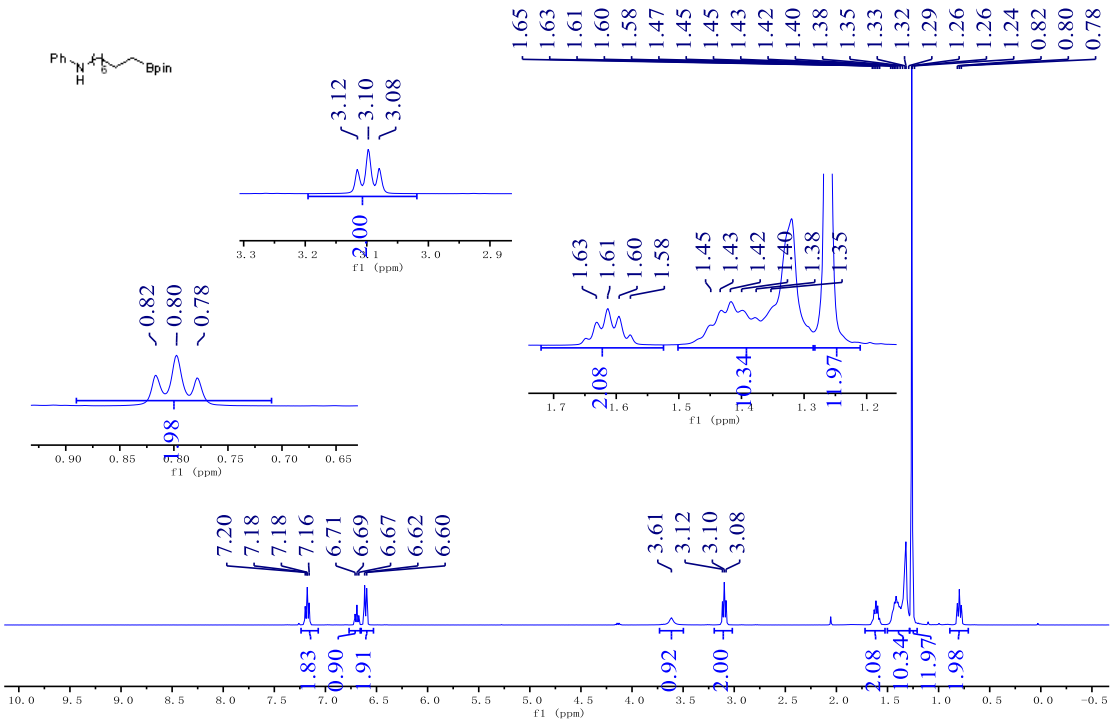
f1 (ppm)


HO
Bpin
8
33.93
f1 (ppm)

3h


Ph
N
H
6
Bpin
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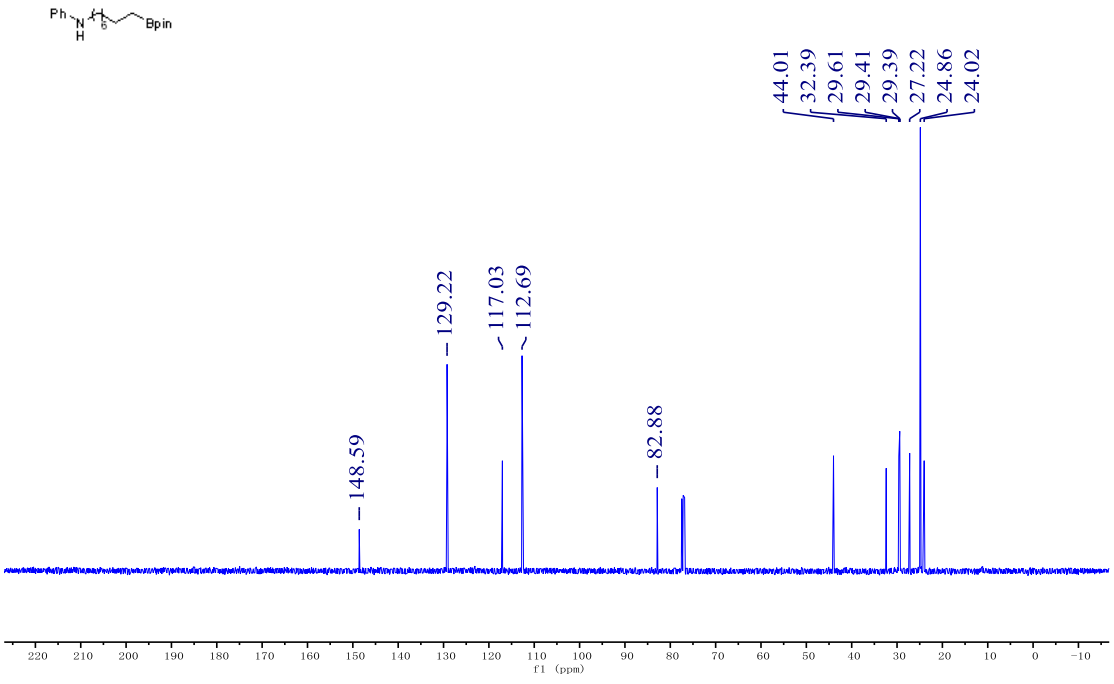
3.12 3.10 3.08
2.00
0.82 0.80 0.78
1.98
1.63 1.61 1.60 1.58 1.45 1.43 1.42 1.40 1.38 1.35
2.08 10.34 11.97
7.20 7.18 7.18 7.16 6.71 6.69 6.67 6.62 6.60
3.61 3.12 3.10 3.08
1.83 0.90 1.91 0.92 2.00 2.08 10.34 11.97 1.98
f1 (ppm)


Ph
N
H
6
Bpin
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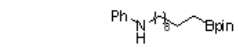
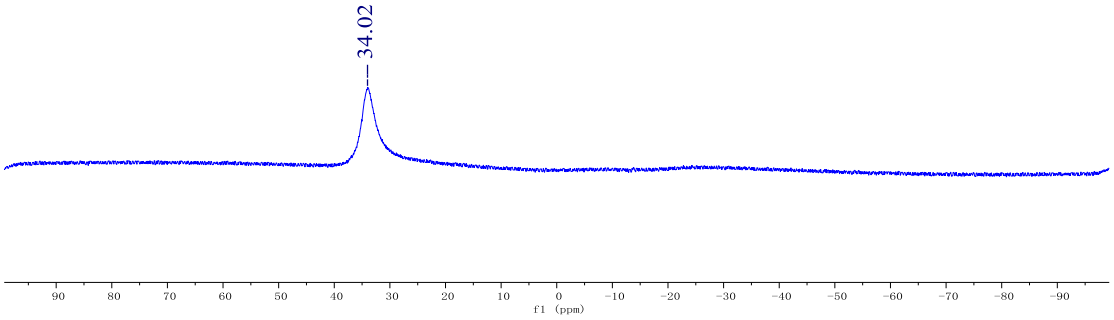
148.59
129.22
117.03
112.69
82.88
f1 (ppm)


Ph
N
H
Bpin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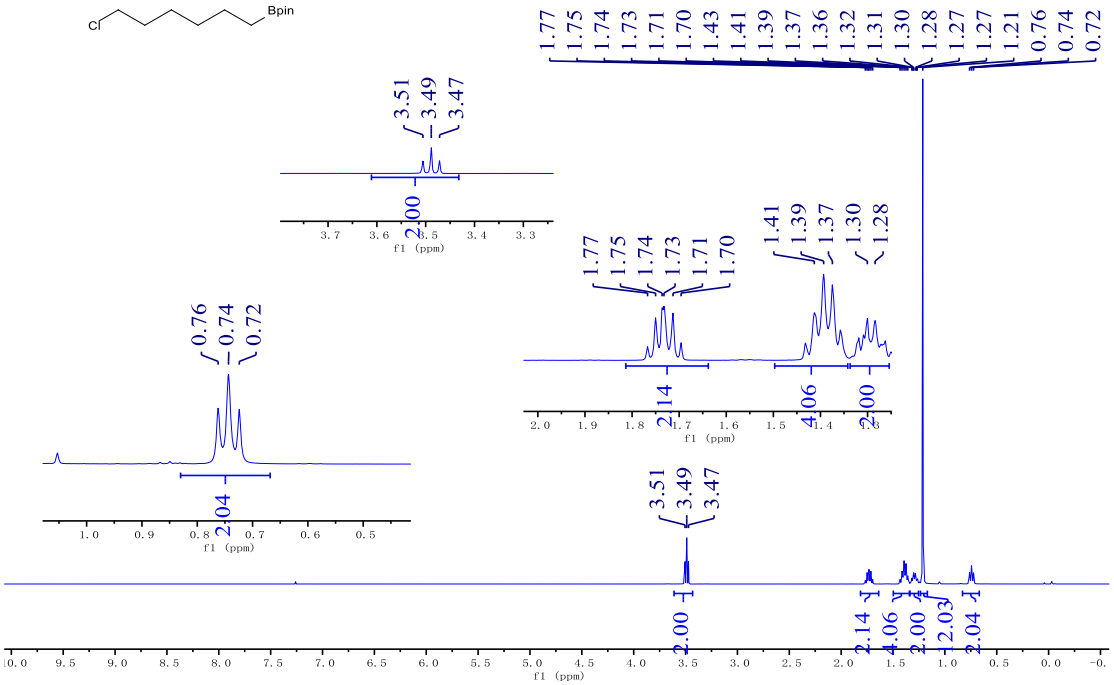
f1 (ppm)

3i


Cl
Bpin
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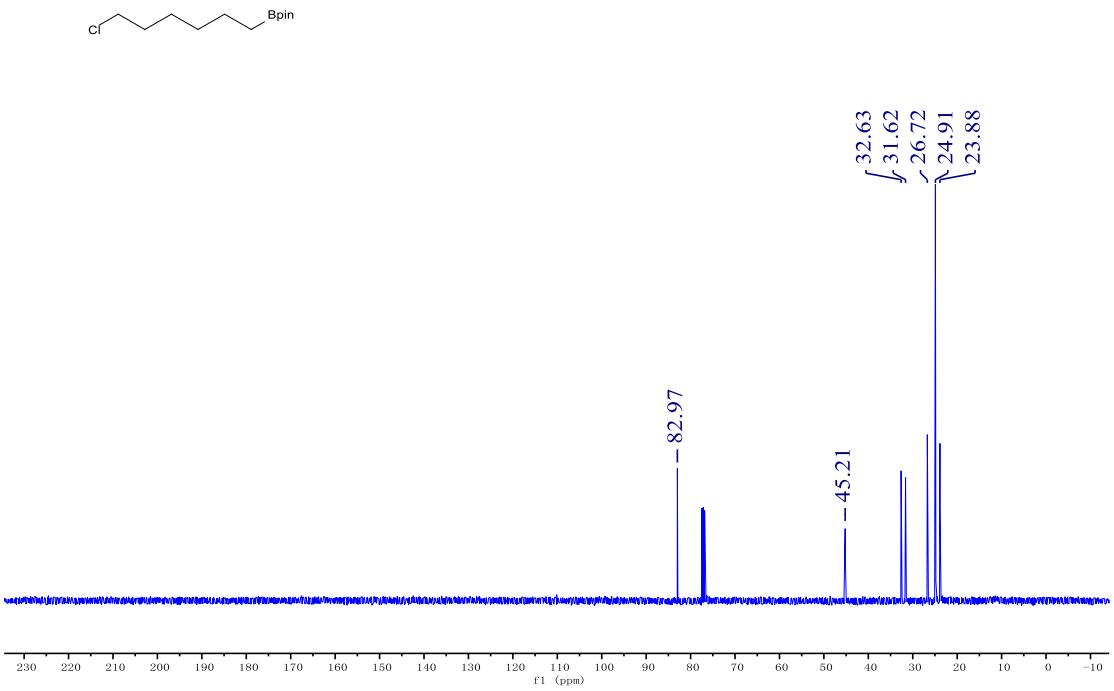
3.49
3.47
2.00
0.76
0.74
0.72
2.04
1.77
1.75
1.74
1.73
1.71
1.70
1.41
1.39
1.37
1.30
1.28
2.14
4.06
2.00
2.03
2.04
f1 (ppm)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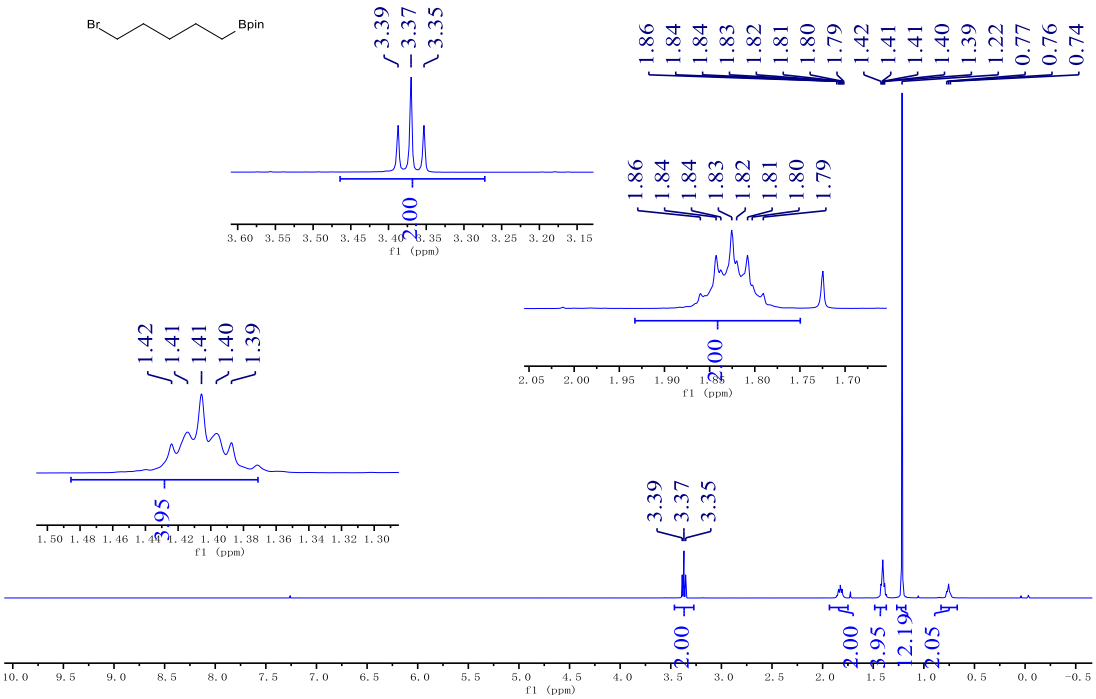
45.21
f1 (ppm)

3j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1.84
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1.81
1.80
1.79
1.42
1.41
1.41
1.40
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1.22
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0.76
0.74
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3.95
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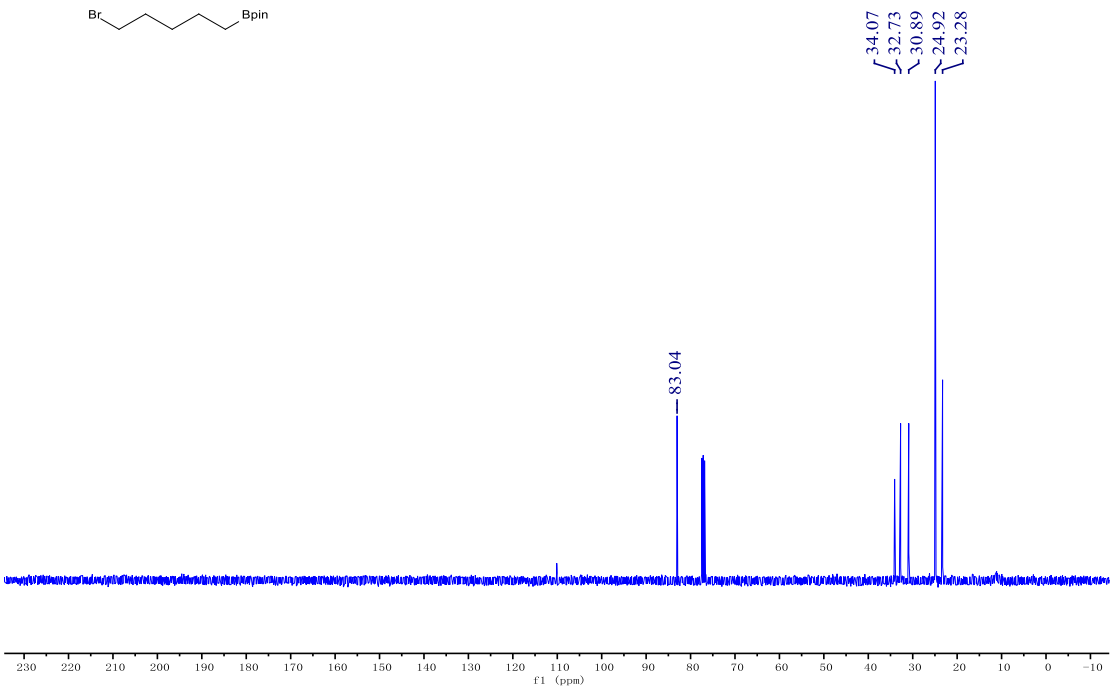
2.05
f1 (ppm)


Br
Bpin
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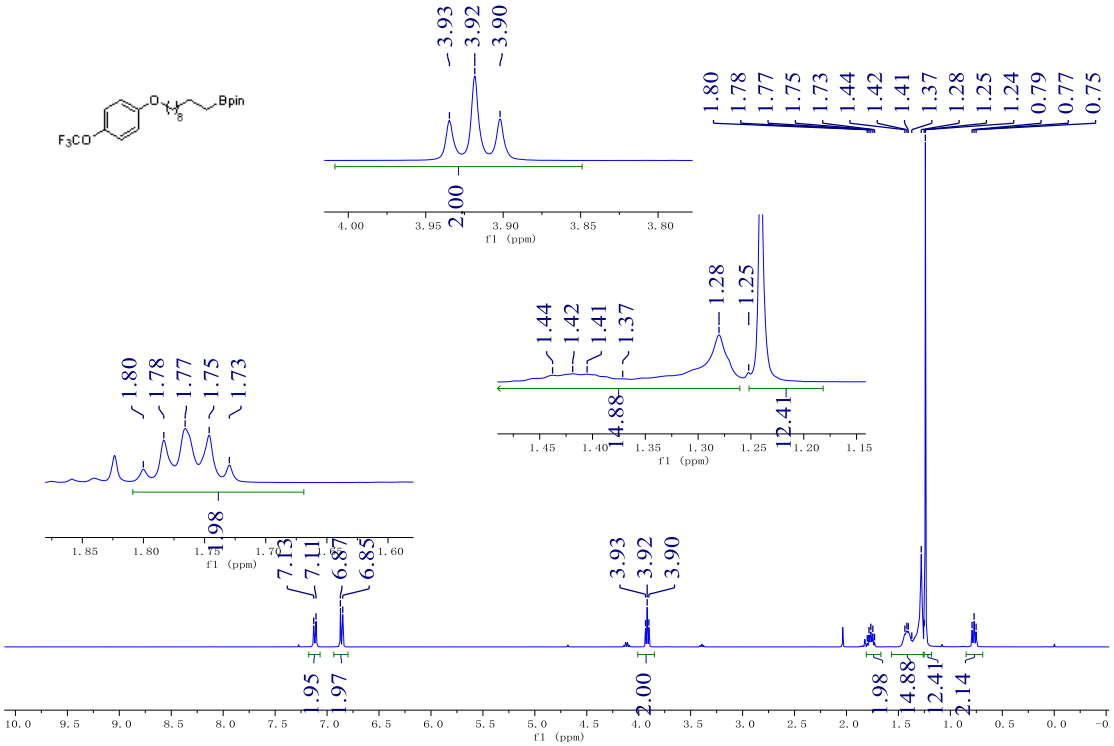
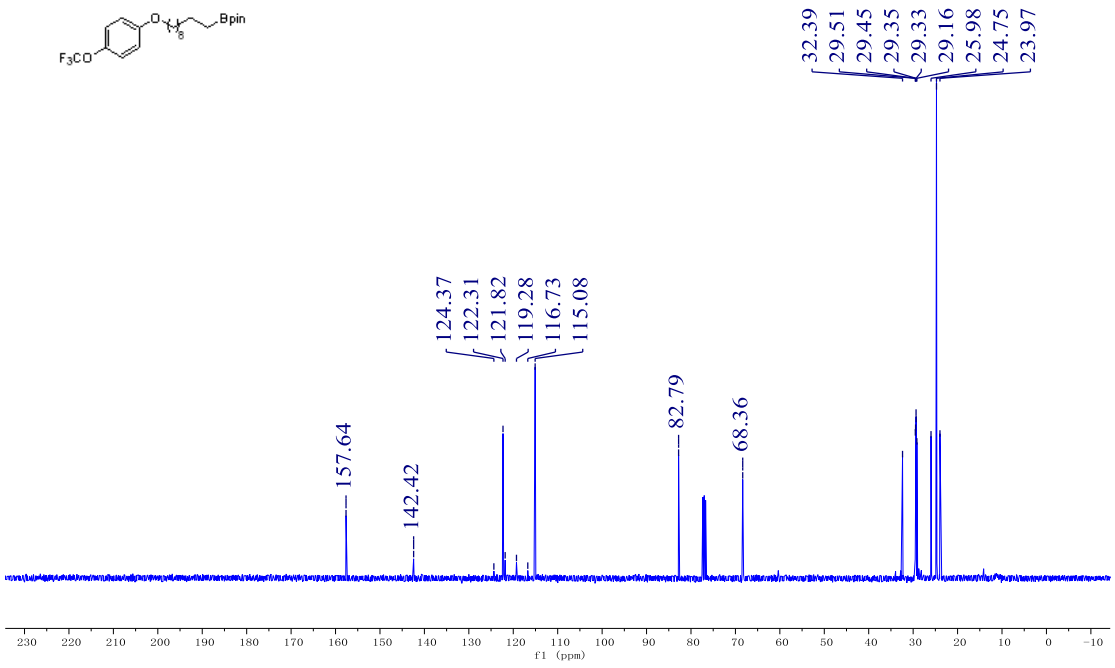
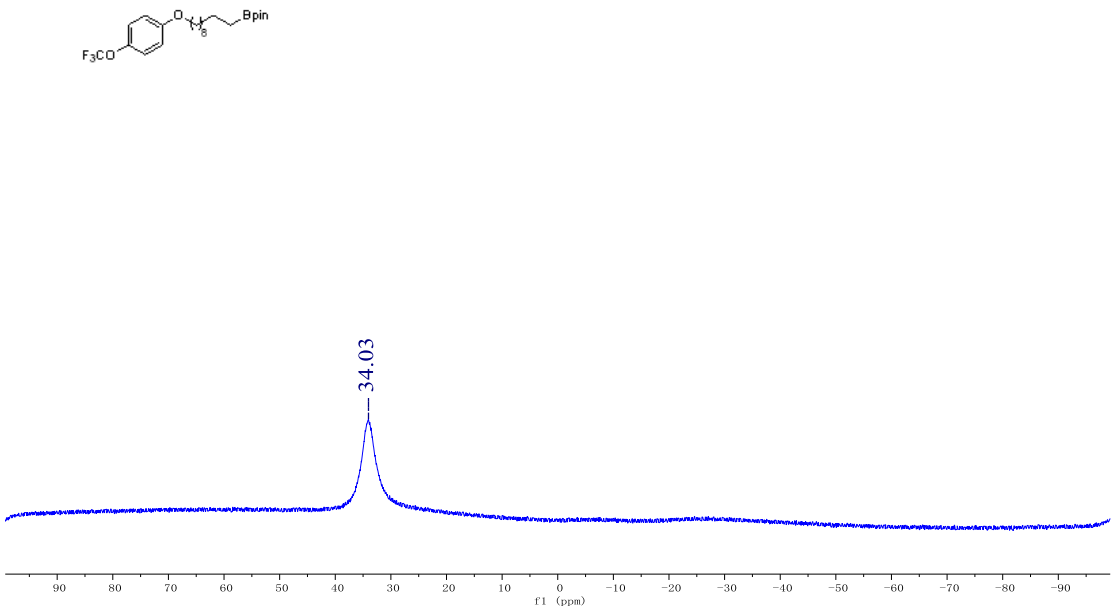
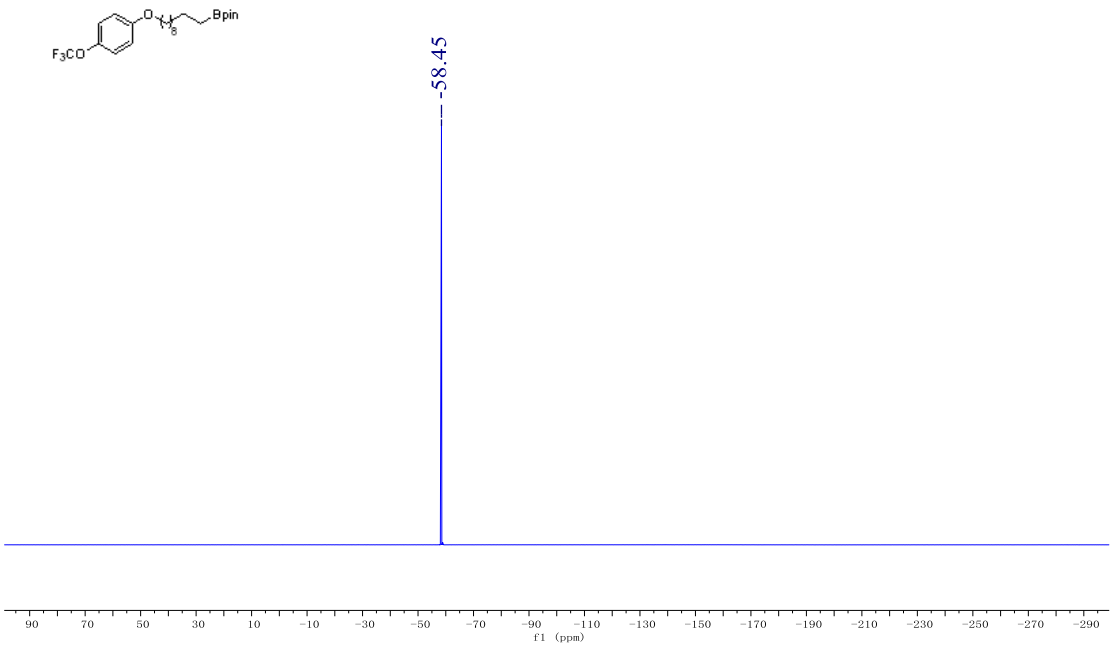
30.89
24.92
23.28
83.04
f1 (ppm)

3k

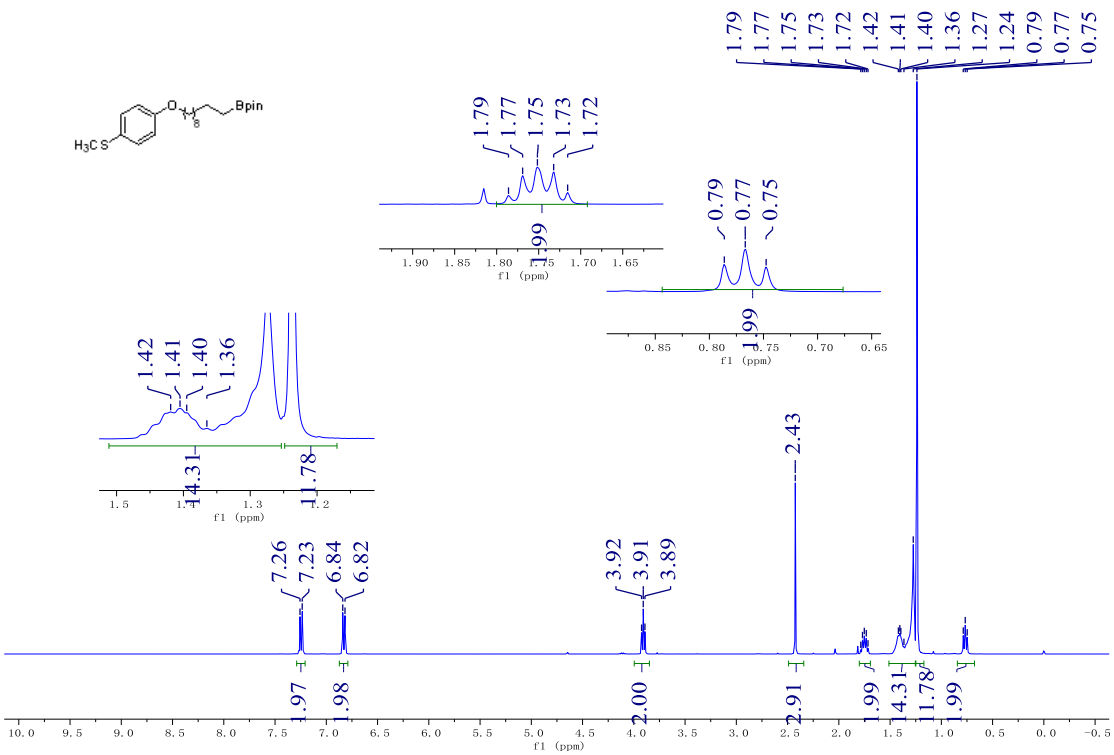

Bpin
F3CO
3.93
3.92
3.90
2.00
1.80
1.78
1.77
1.75
1.73
1.44
1.42
1.41
1.37
1.28
1.25
1.24
0.79
0.77
0.75
14.88
12.41
1.98
7.13
7.11
6.87
6.85
1.95
1.97
2.14
f1 (ppm)

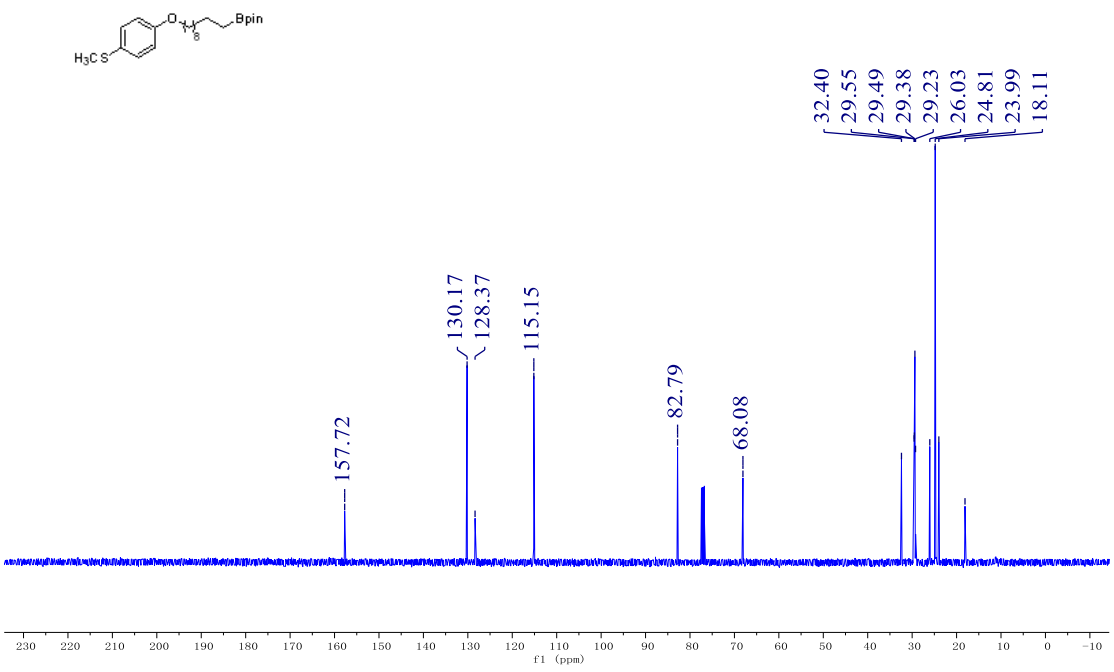

Bpin
F3CO
32.39
29.51
29.45
29.35
29.33
29.16
25.98
24.75
23.97
124.37
122.31
121.82
119.28
116.73
115.08
157.64
142.42
82.79
68.36
f1 (ppm)

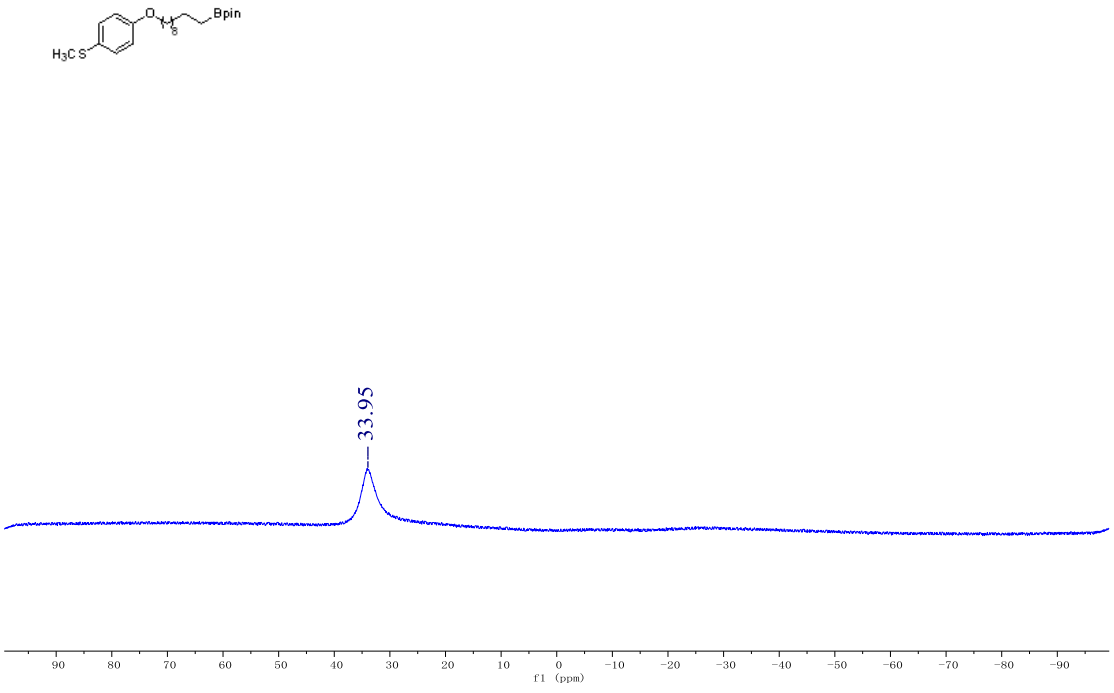

Bpin
F3CO
34.03
f1 (ppm)


Bpin
F3CO
-58.45
f1 (ppm)

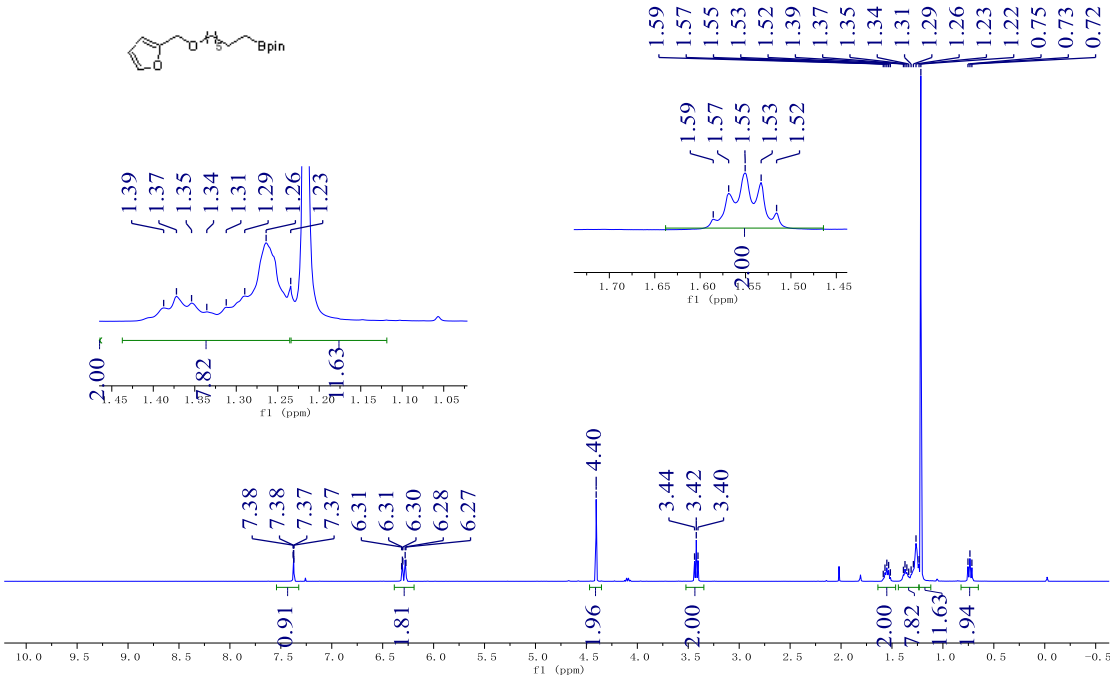
3l

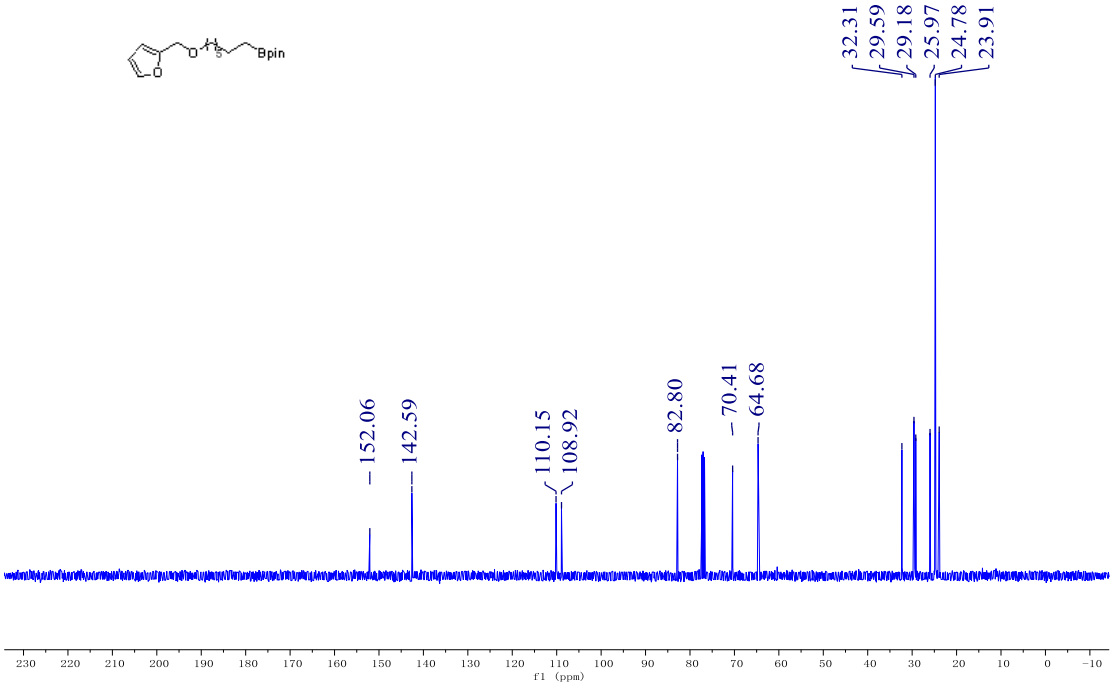

Bpin
H3CS
1.79
1.77
1.75
1.73
1.72
1.42
1.41
1.40
1.36
1.27
1.24
0.79
0.77
0.75
2.43
3.92
3.91
3.89
7.26
7.23
6.84
6.82
1.97
1.98
2.00
2.91
1.99
14.31
11.78
1.99
f1 (ppm)

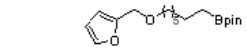

Bpin
H3CS
8
32.40
29.55
29.49
29.38
29.23
26.03
24.81
23.99
18.11
130.17
128.37
115.15
82.79
68.08
157.72
f1 (ppm)

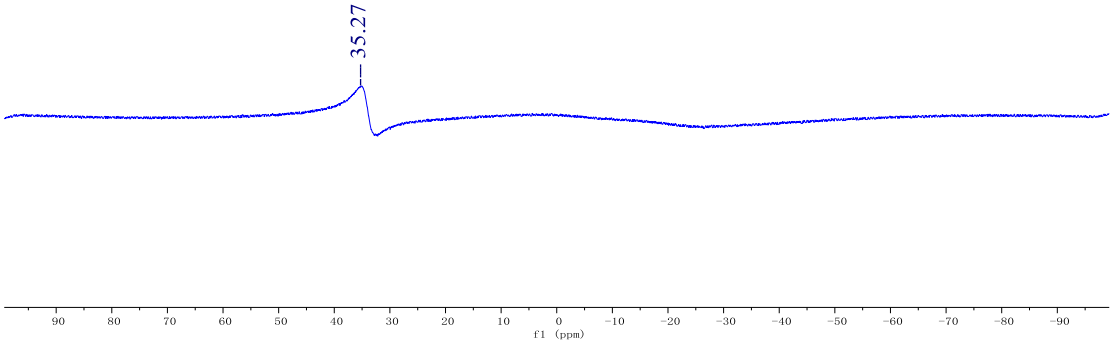

Bpin
H3CS
8
33.95
f1 (ppm)

3m

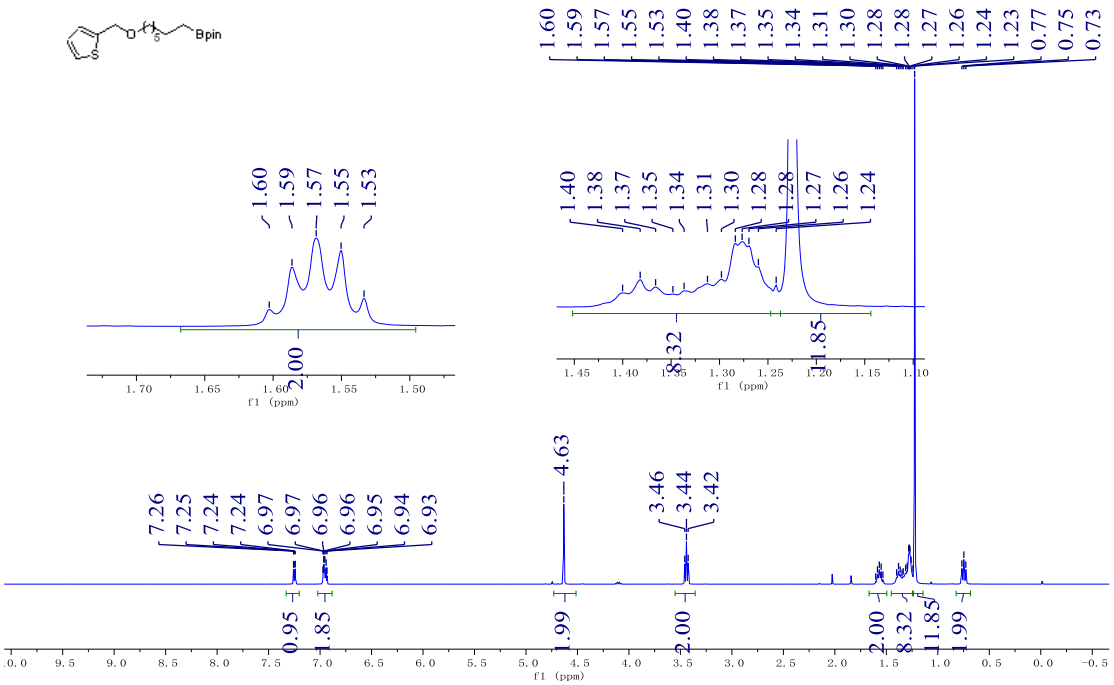

Bpin
1.59
1.57
1.55
1.53
1.52
1.39
1.37
1.35
1.34
1.31
1.29
1.26
1.23
1.22
0.75
0.73
0.72
2.00
7.82
11.63
7.38
7.38
7.37
7.37
6.31
6.31
6.30
6.28
6.27
4.40
3.44
3.42
3.40
0.91
1.81
1.96
2.00
2.00
7.82
11.63
1.94
f1 (ppm)

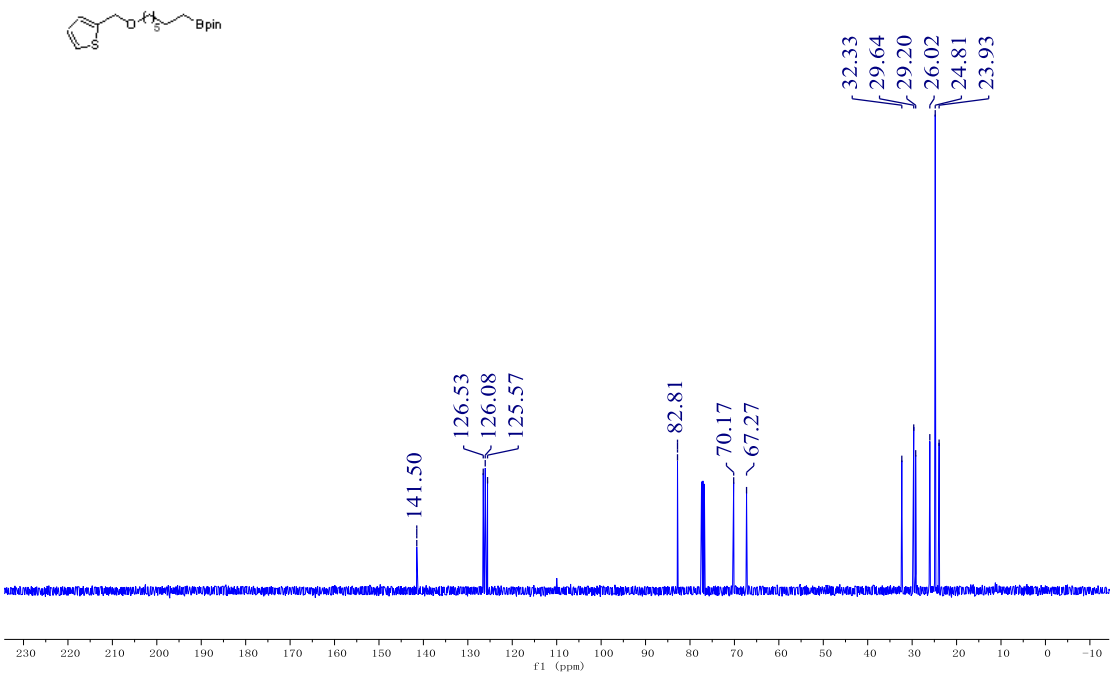

Bpin
32.31
29.59
29.18
25.97
24.78
23.91
152.06
142.59
110.15
108.92
82.80
70.41
64.68
f1 (ppm)

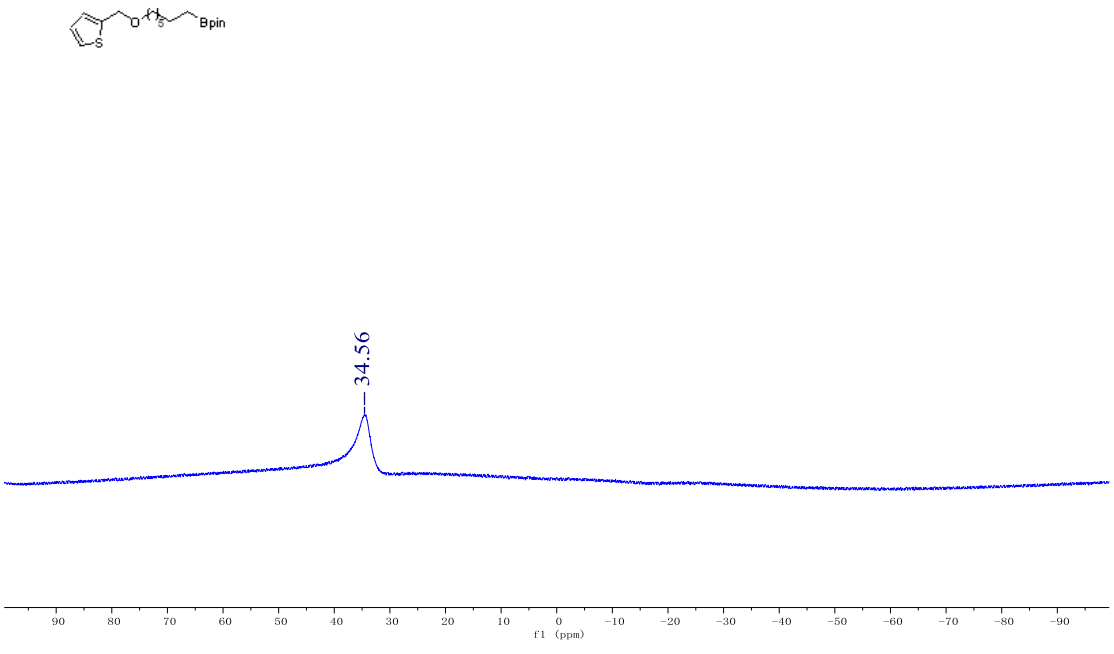

Bpin


35.27
f1 (ppm)

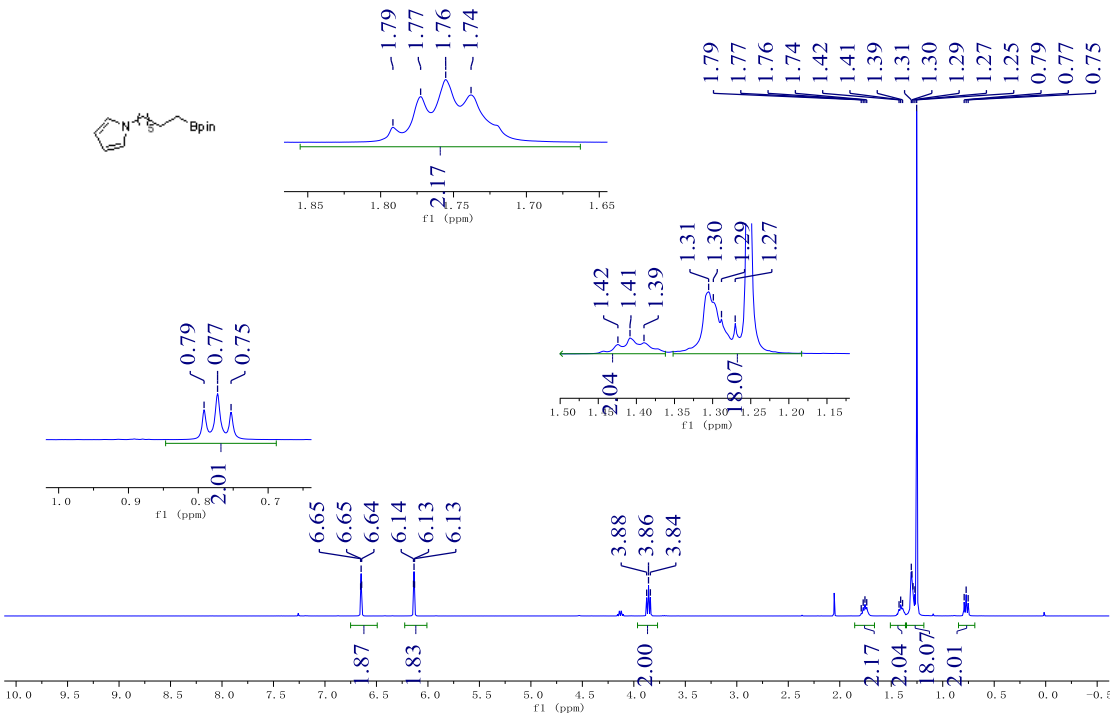
3n

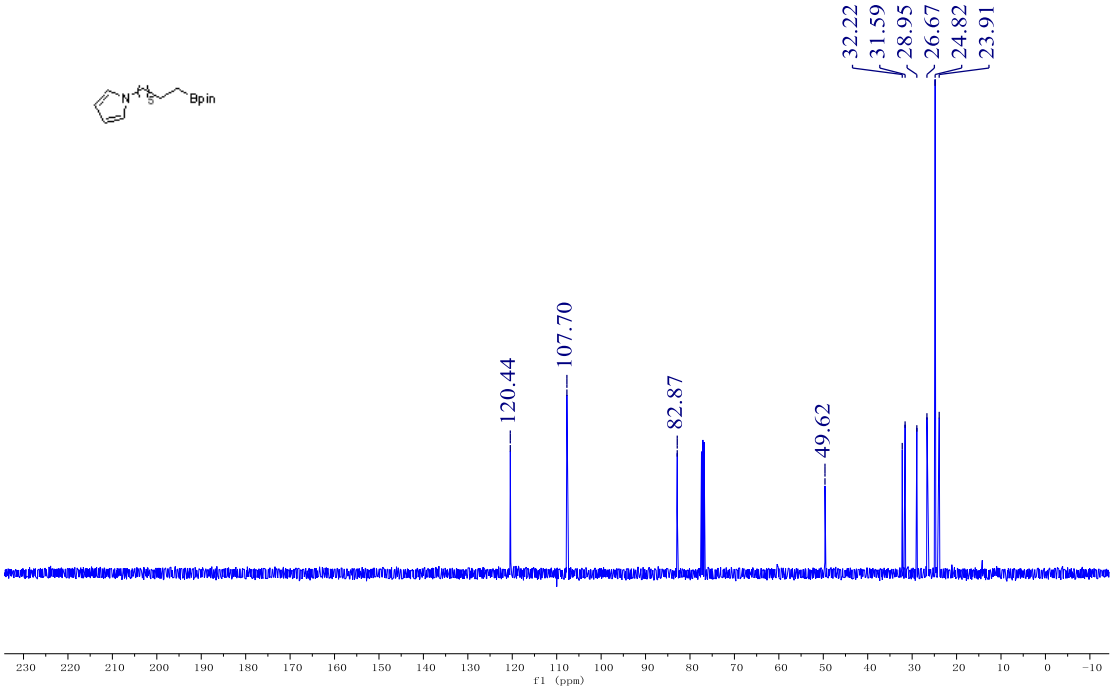

Bpin
1.60
1.59
1.57
1.55
1.53
1.40
1.38
1.37
1.35
1.34
1.31
1.30
1.28
1.28
1.27
1.26
1.24
1.23
0.77
0.75
0.73
2.00
8.32
11.85
f1 (ppm)
7.26
7.25
7.24
7.24
6.97
6.97
6.96
6.96
6.95
6.94
6.93
4.63
3.46
3.44
3.42
0.95
1.85
1.99
2.00
2.00
8.32
11.85
1.99
f1 (ppm)

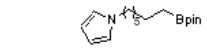

Bpin
32.33
29.64
29.20
26.02
24.81
23.93
141.50
126.53
126.08
125.57
82.81
70.17
67.27
f1 (ppm)

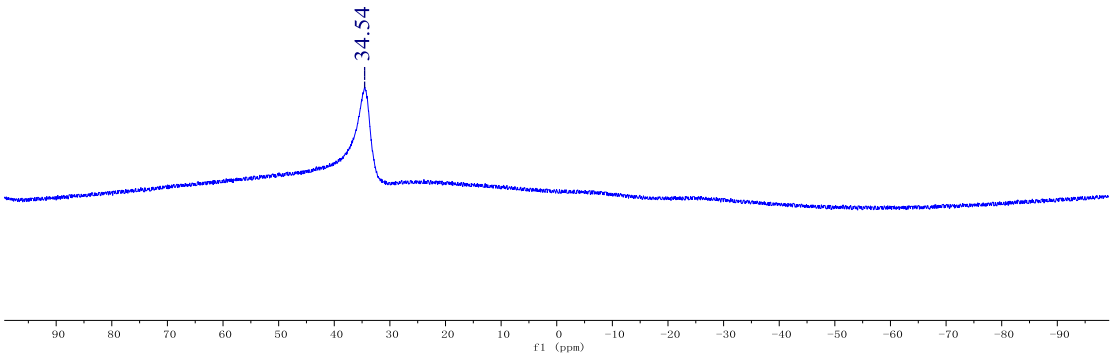

Bpin
34.56
f1 (ppm)

3o

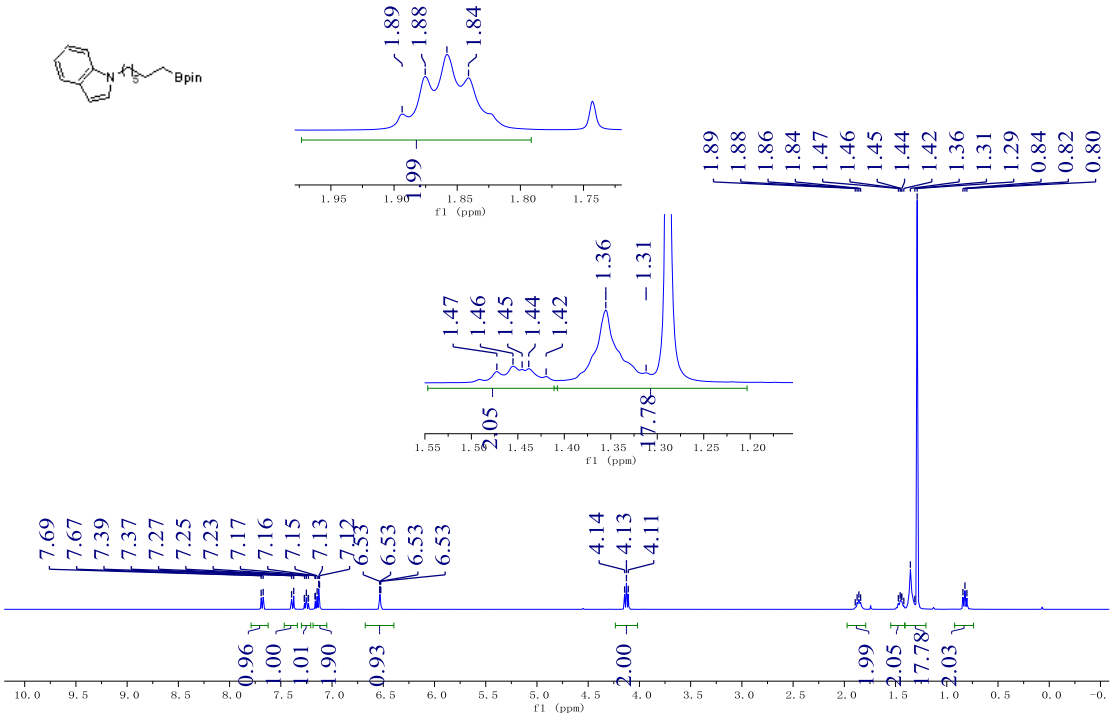

Bpin
1.79
1.77
1.76
1.74
1.42
1.41
1.39
1.31
1.30
1.29
1.27
1.25
0.79
0.77
0.75
6.65
6.65
6.64
6.14
6.13
6.13
3.88
3.86
3.84
1.87
1.83
2.00
2.17
2.04
18.07
2.01
f1 (ppm)

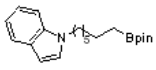

Bpin
32.22
31.59
28.95
26.67
24.82
23.91
120.44
107.70
82.87
49.62
f1 (ppm)

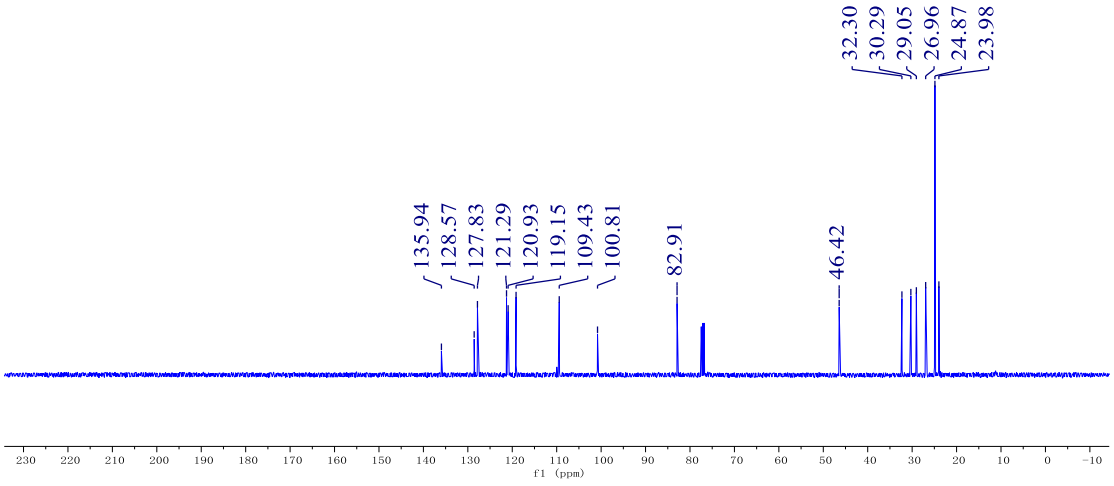

Bpin

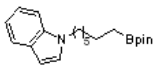

34.54
f1 (ppm)

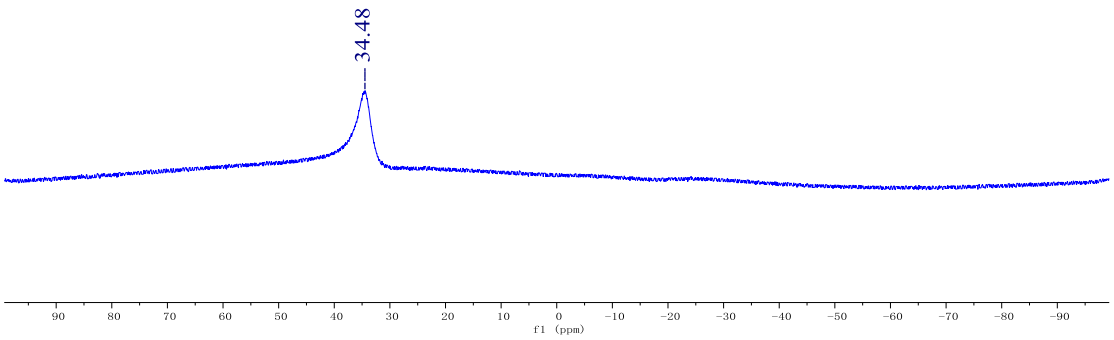
3p


Bpin
1.89
1.88
1.84
1.99
1.47
1.46
1.45
1.44
1.42
1.36
1.31
2.05
17.78
1.89
1.88
1.86
1.84
1.47
1.46
1.45
1.44
1.42
1.36
1.31
1.29
0.84
0.82
0.80
7.69
7.67
7.39
7.37
7.27
7.25
7.23
7.17
7.16
7.15
7.13
7.12
6.53
6.53
6.53
6.53
4.14
4.13
4.11
0.96
1.00
1.01
1.90
0.93
2.00
1.99
2.05
17.78
2.03
f1 (ppm)

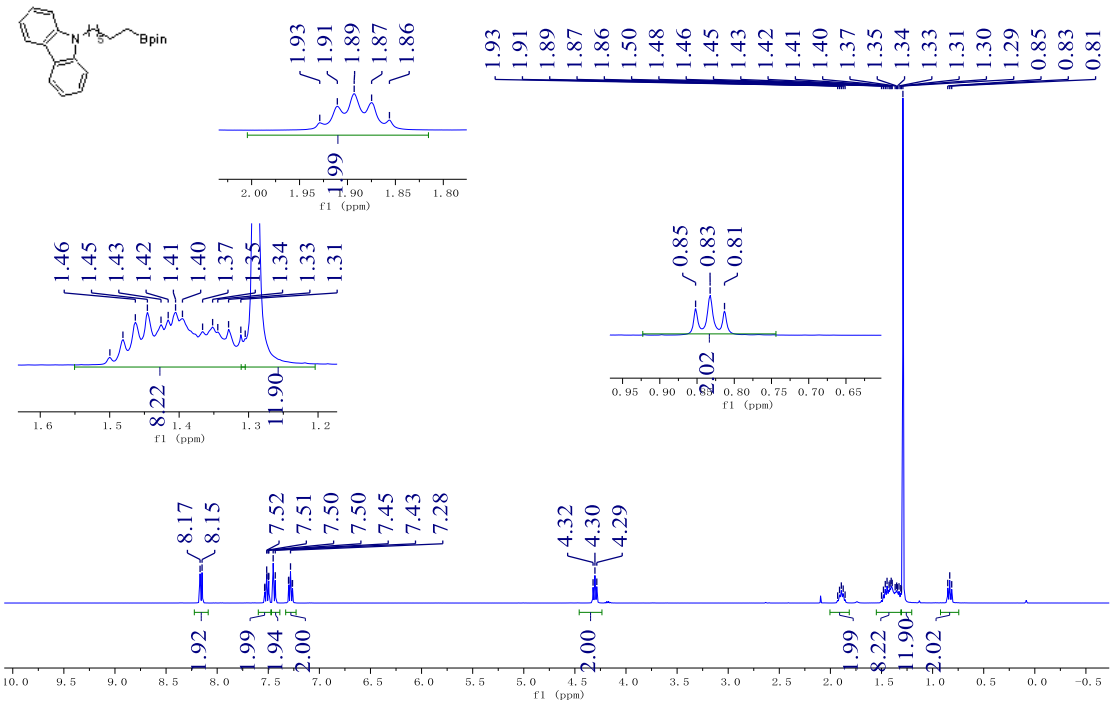

Bpin

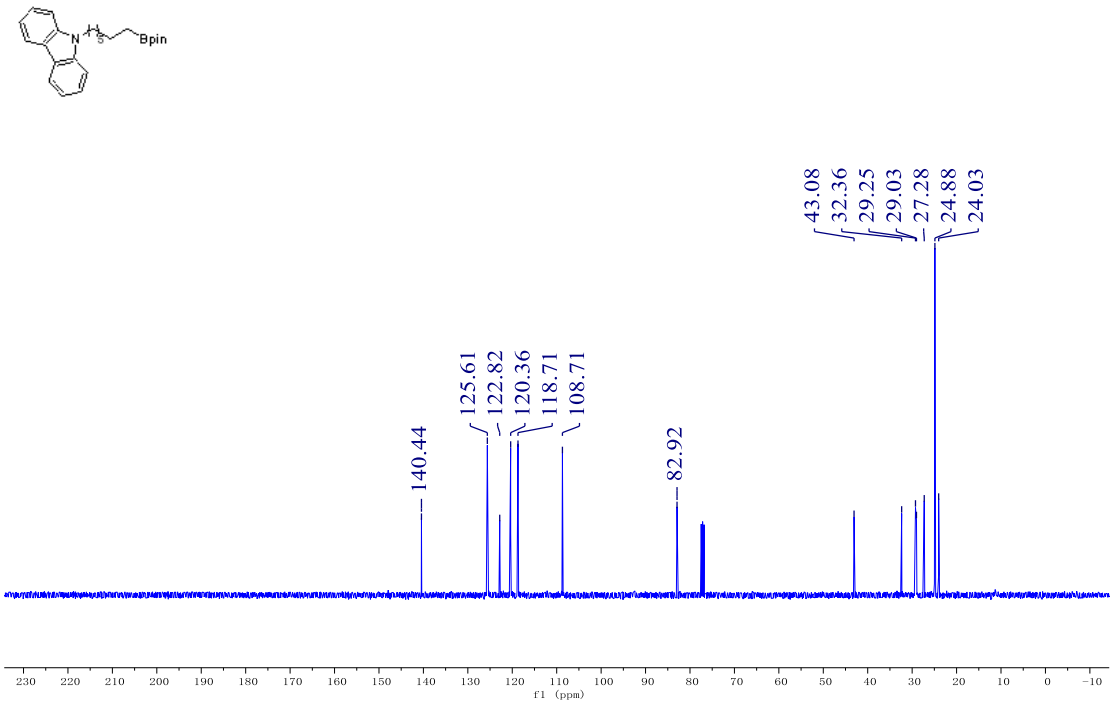

135.94
128.57
127.83
121.29
120.93
119.15
109.43
100.81
82.91
46.42
32.30
30.29
29.05
26.96
24.87
23.98
f1 (ppm)

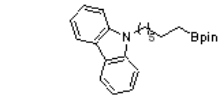

Bpin

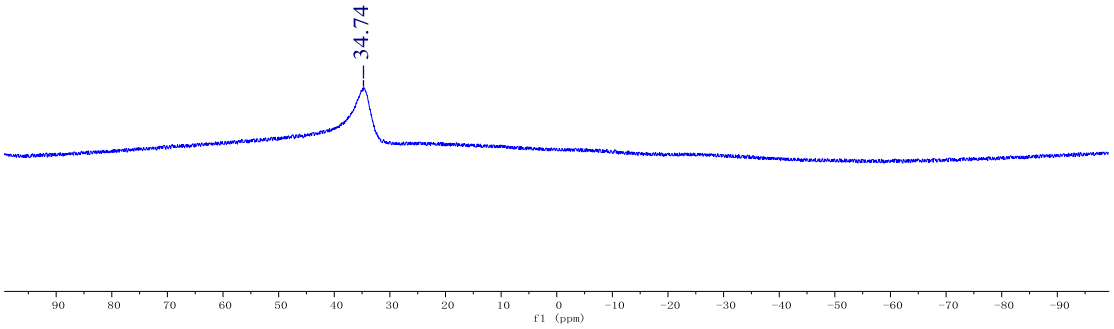

34.48
f1 (ppm)

3q

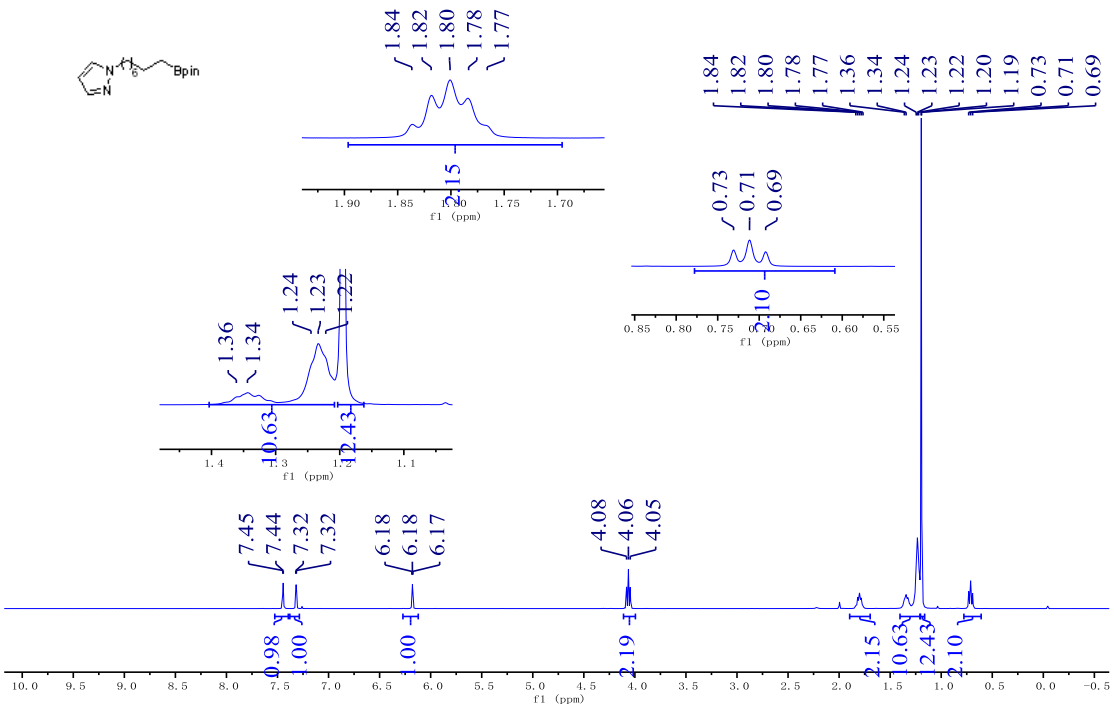

Bpin
1.93
1.91
1.89
1.87
1.86
1.99
1.46
1.45
1.43
1.42
1.41
1.40
1.37
1.35
1.34
1.33
1.31
8.22
11.90
0.85
0.83
0.81
2.02
8.17
8.15
7.52
7.51
7.50
7.50
7.45
7.43
7.28
4.32
4.30
4.29
1.92
1.99
1.94
2.00
2.00
1.99
8.22
11.90
2.02
f1 (ppm)

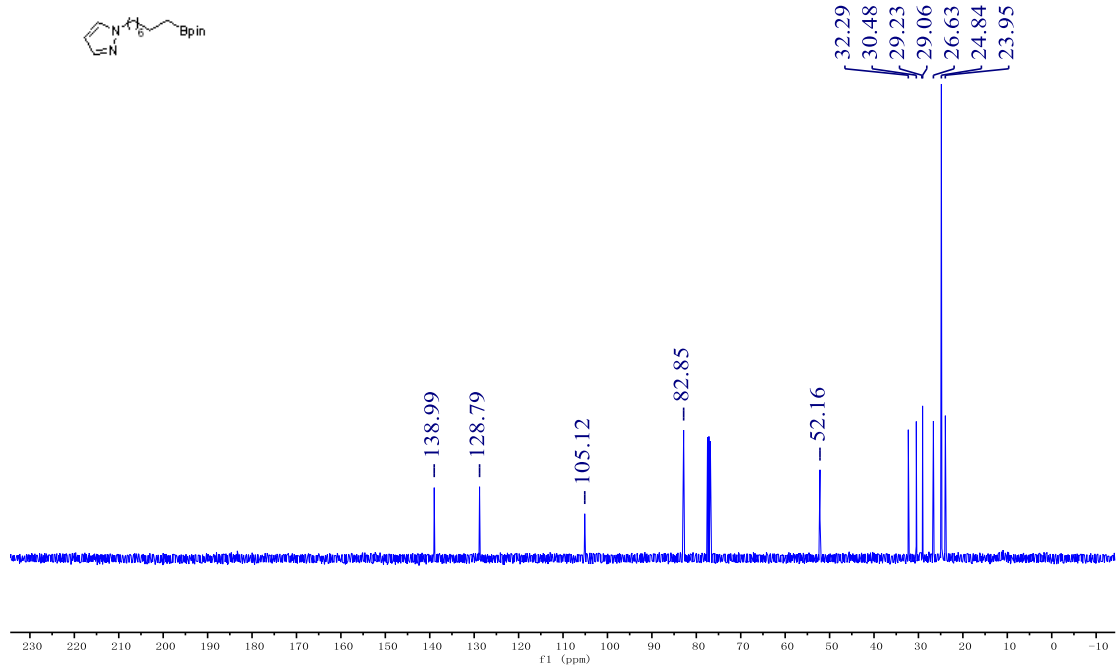

Bpin
43.08
32.36
29.25
29.03
27.28
24.88
24.03
140.44
125.61
122.82
120.36
118.71
108.71
82.92
f1 (ppm)

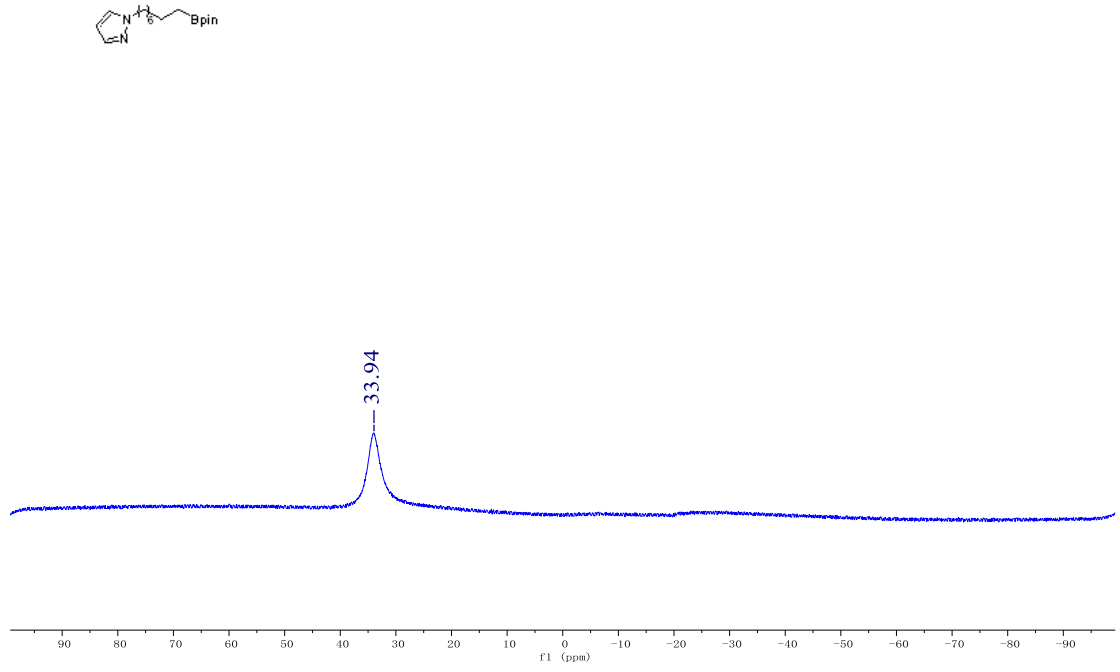

N
Bpin


34.74
f1 (ppm)

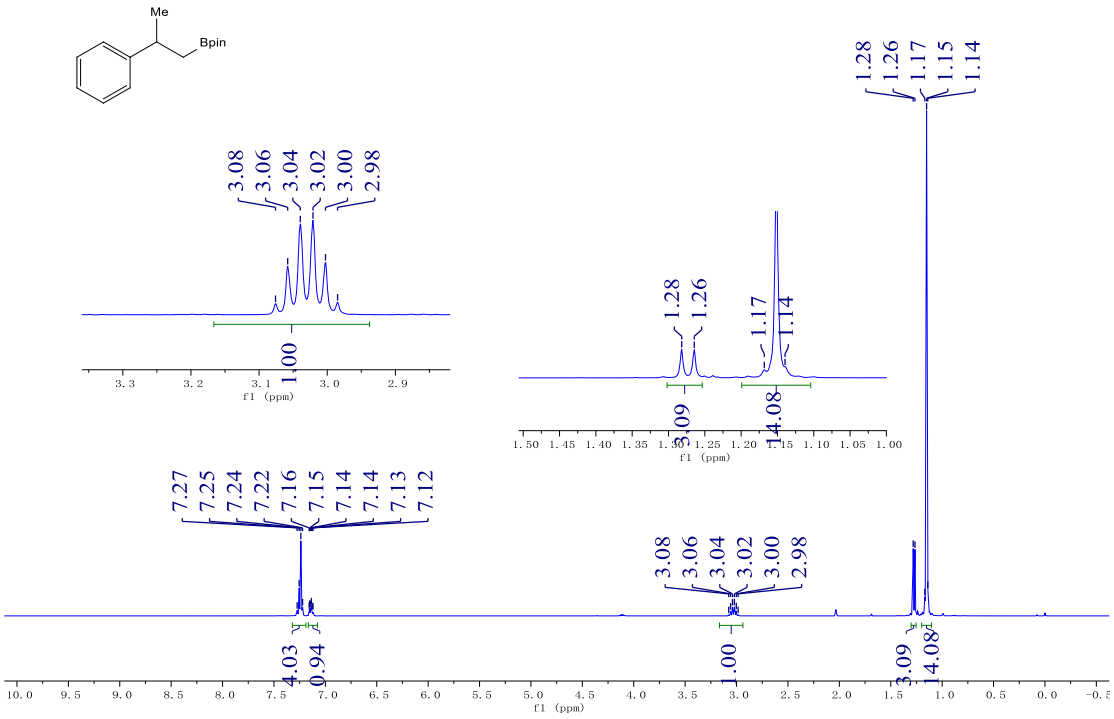
3r

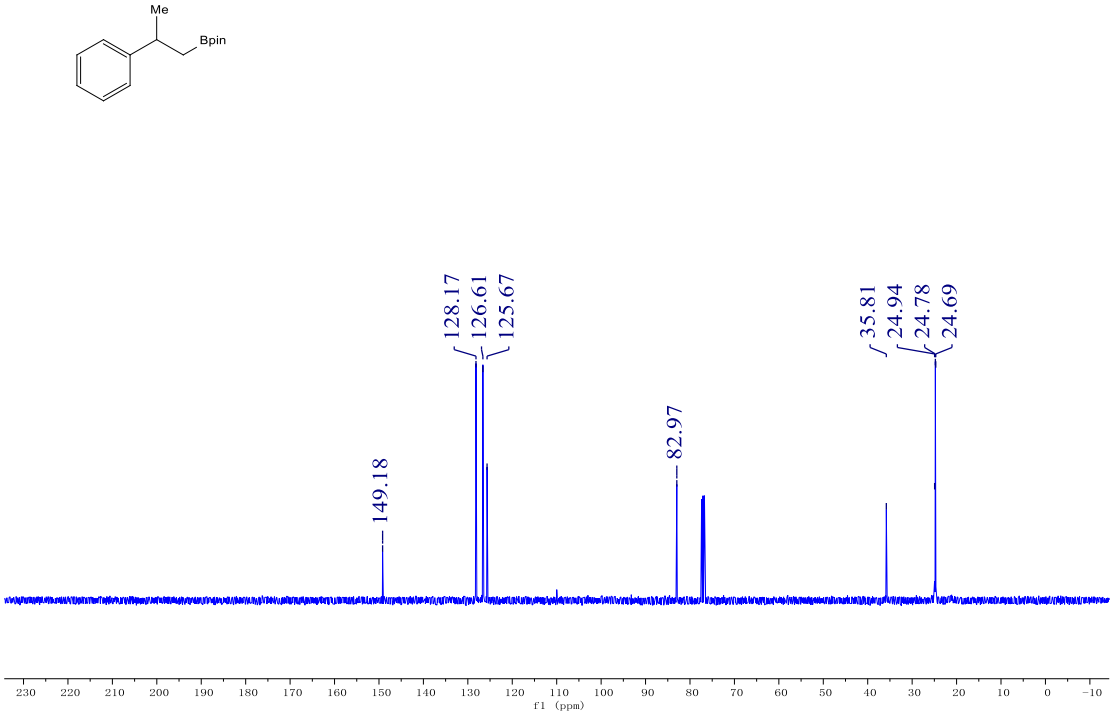

N
N
Bpin
1.84
1.82
1.80
1.78
1.77
2.15
1.36
1.34
1.24
1.23
1.22
10.63
12.43
0.73
0.71
0.69
2.10
7.45
7.44
7.32
7.32
6.18
6.18
6.17
4.08
4.06
4.05
0.98
1.00
1.00
2.19
2.15
10.63
12.43
2.10
f1 (ppm)


Bpin
32.29
30.48
29.23
29.06
26.63
24.84
23.95
138.99
128.79
105.12
82.85
52.16
f1 (ppm)

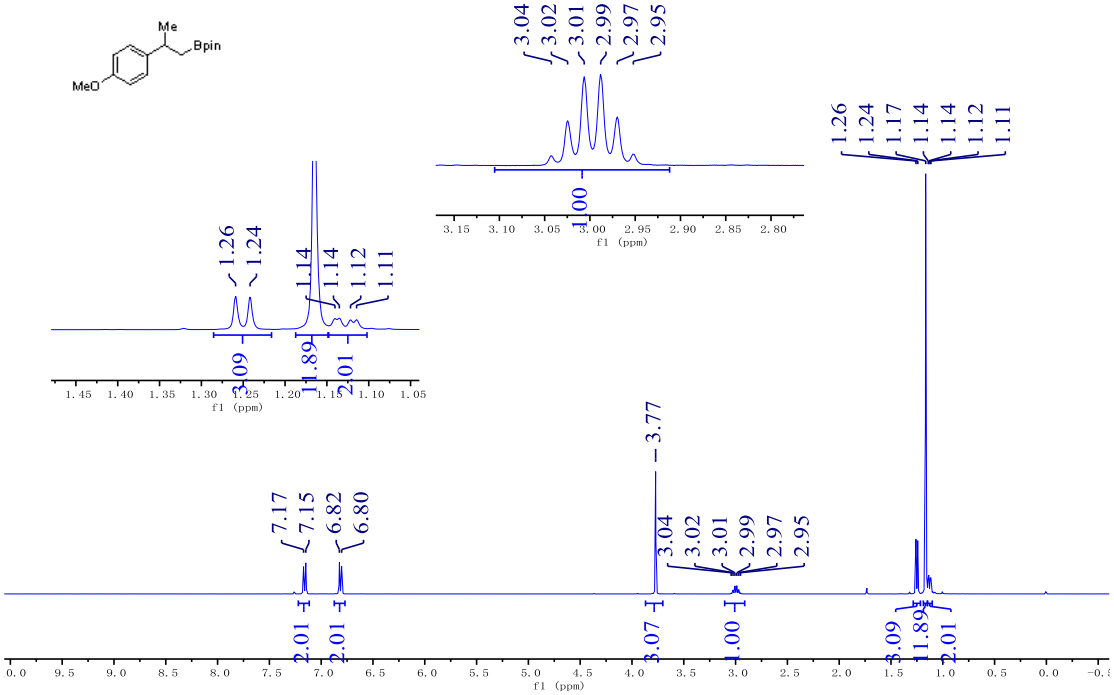

Bpin
33.94
f1 (ppm)

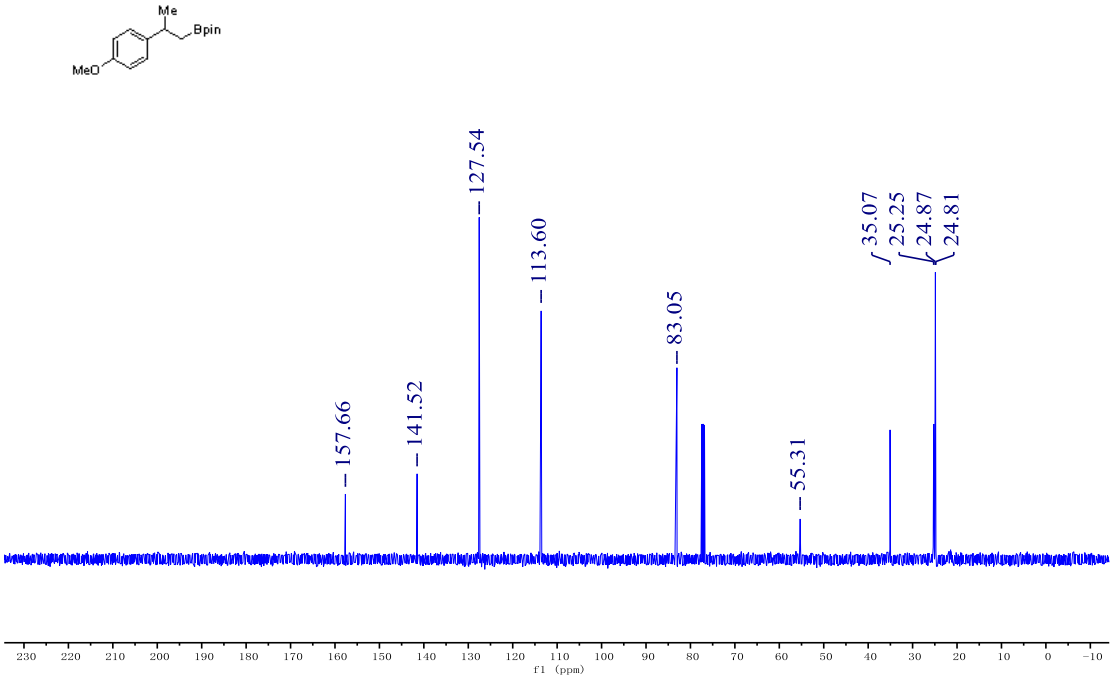
5a


Me
Bpin
3.08
3.06
3.04
3.02
3.00
2.98
1.00
1.28
1.26
1.17
1.14
3.09
4.08
7.27
7.25
7.24
7.22
7.16
7.15
7.14
7.14
7.13
7.12
4.03
0.94
f1 (ppm)

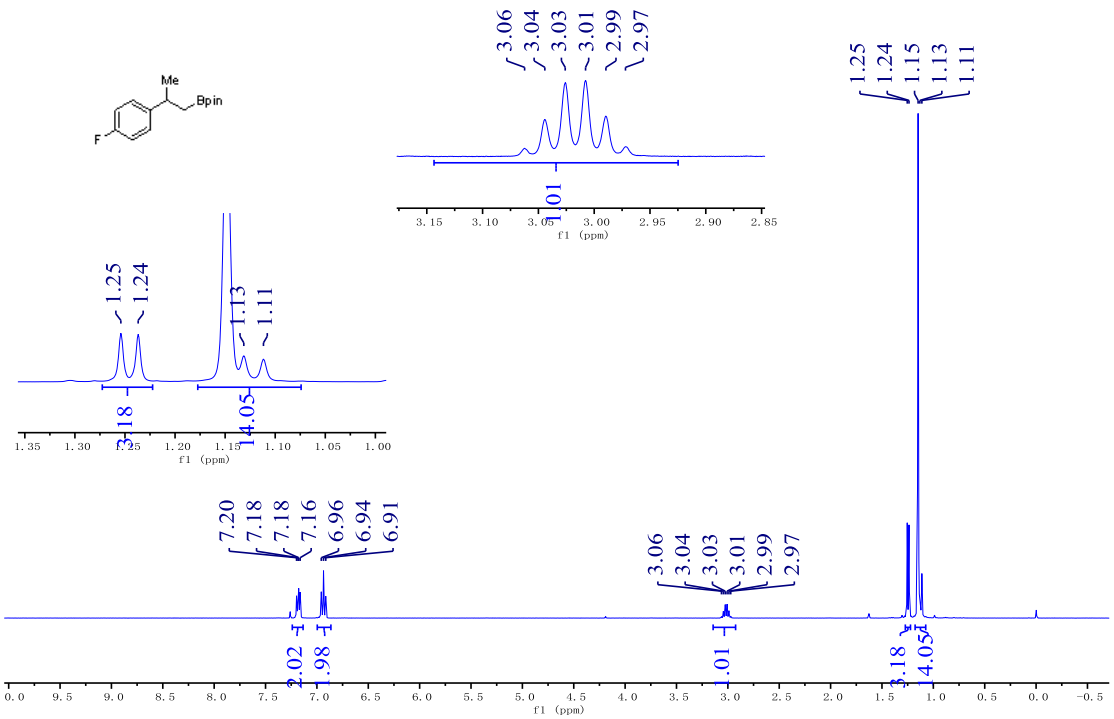

Me
Bpin
128.17
126.61
125.67
149.18
82.97
35.81
24.94
24.78
24.69
f1 (ppm)

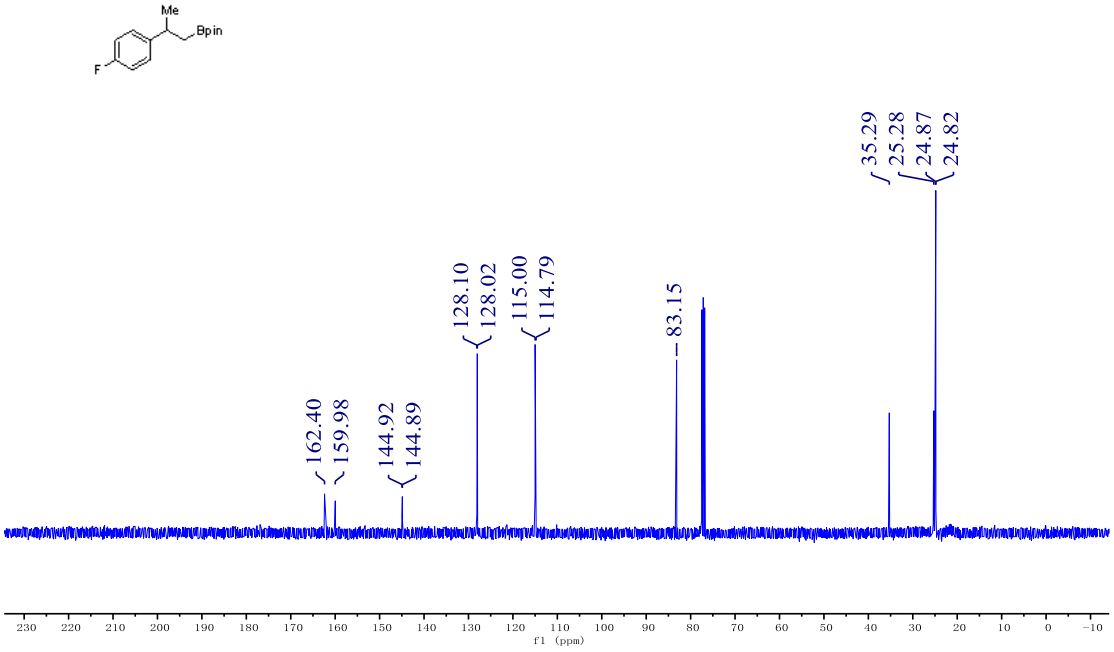
5b

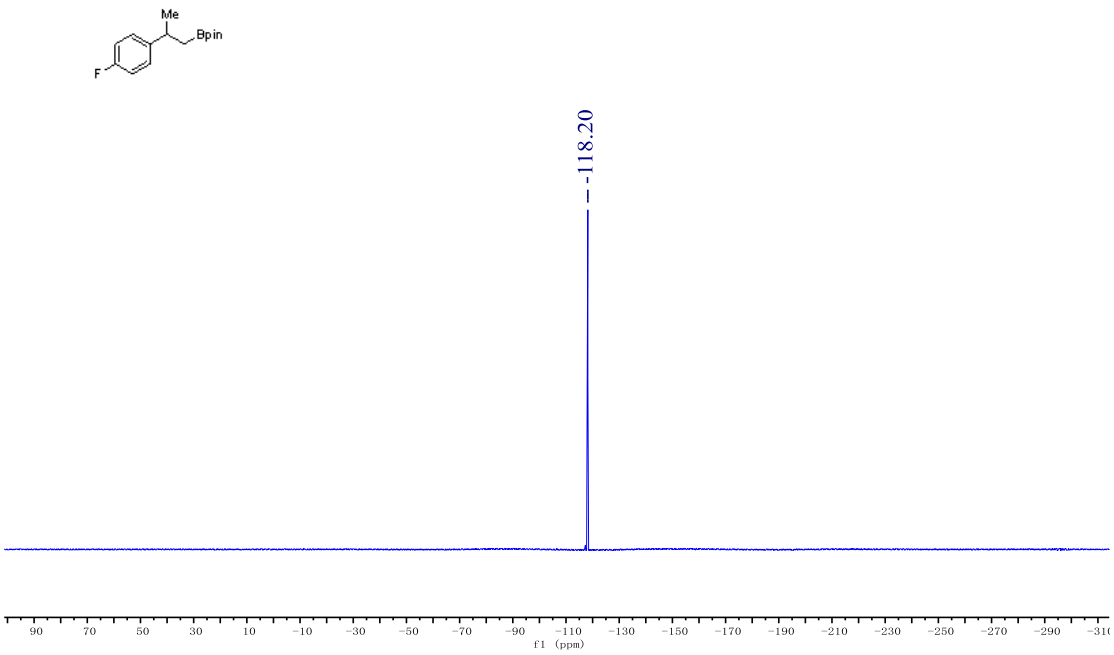

Me
Bpin
MeO
7.17
7.15
6.82
6.80
3.77
3.04
3.02
3.01
2.99
2.97
2.95
1.26
1.24
1.17
1.14
1.14
1.12
1.11
2.01
2.01
3.07
1.00
3.09
11.89
2.01
f1 (ppm)


Me
Bpin
MeO
157.66
141.52
127.54
113.60
83.05
55.31
35.07
25.25
24.87
24.81
f1 (ppm)

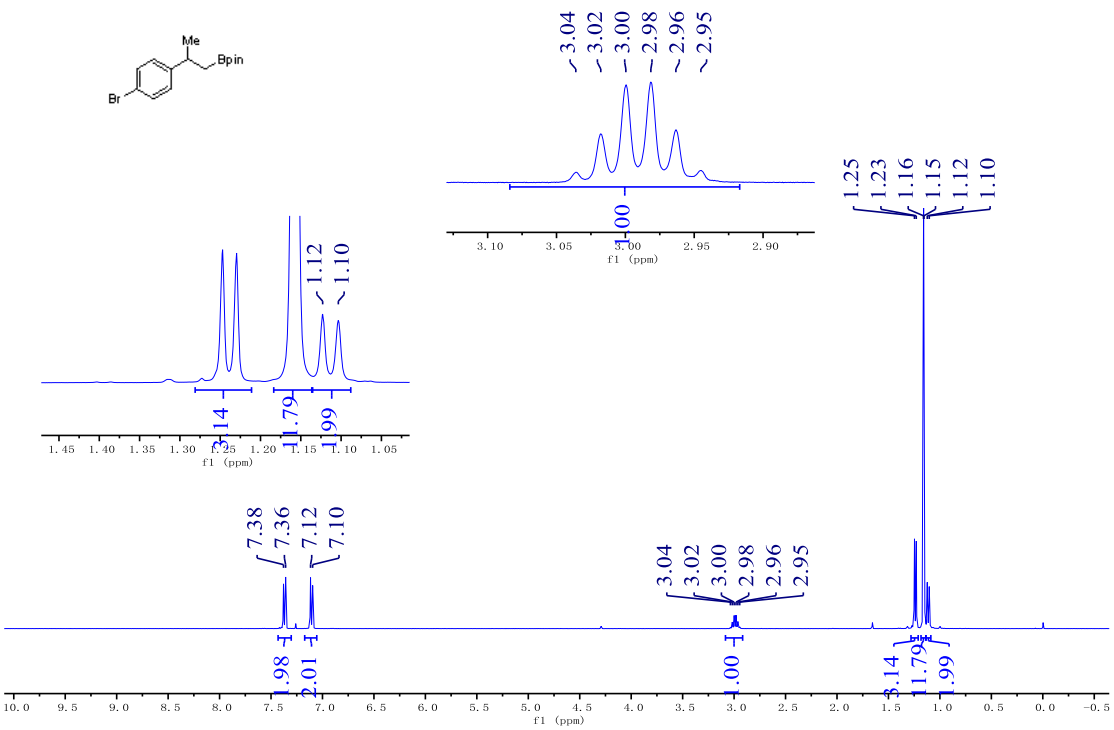
5c

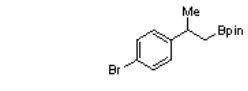

Me
Bpin
F
3.06
3.04
3.03
3.01
2.99
2.97
1.01
f1 (ppm)
1.25
1.24
1.13
1.11
3.18
14.05
f1 (ppm)
1.25
1.24
1.15
1.13
1.11
7.20
7.18
7.18
7.16
6.96
6.94
6.91
3.06
3.04
3.03
3.01
2.99
2.97
2.02
1.98
1.01
3.18
14.05
f1 (ppm)

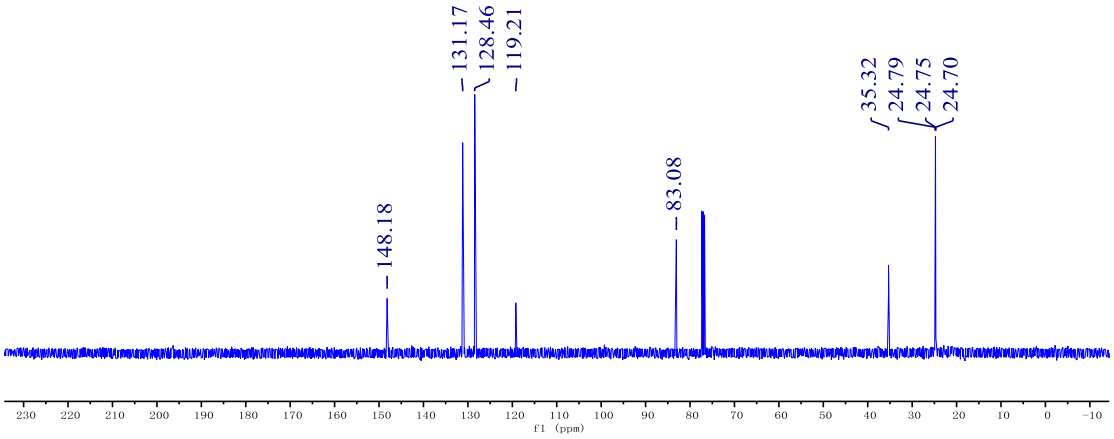

Me
Bpin
F
35.29
25.28
24.87
24.82
128.10
128.02
115.00
114.79
83.15
162.40
159.98
144.92
144.89
f1 (ppm)


Me
Bpin
F
-118.20
f1 (ppm)

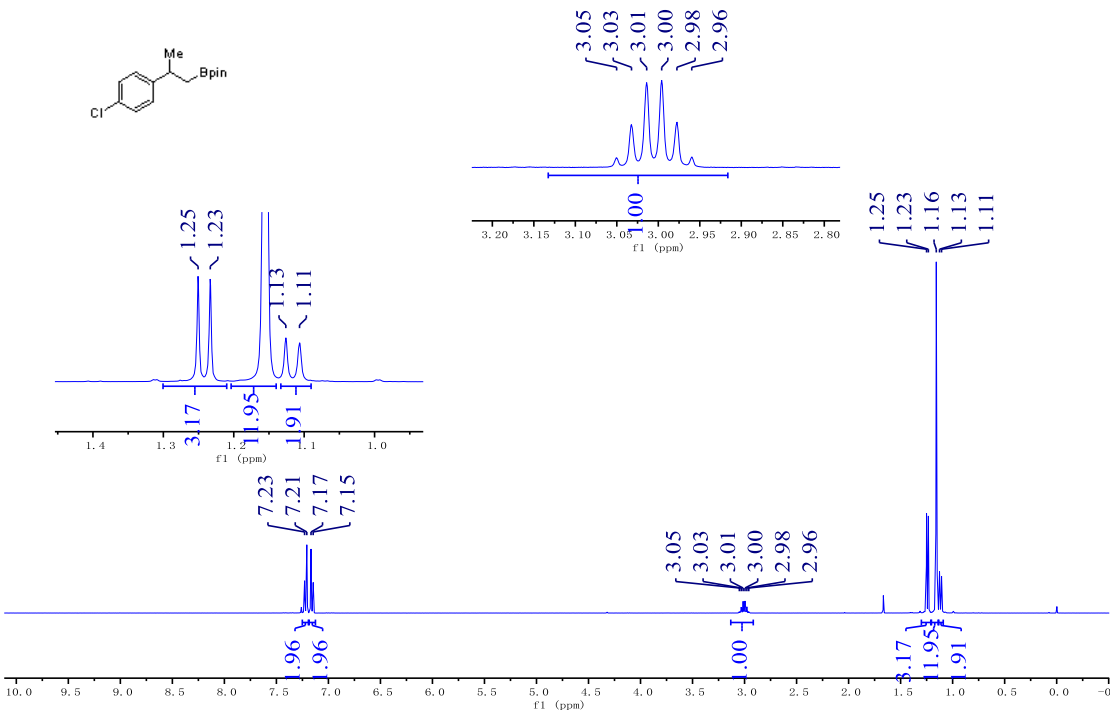
5d

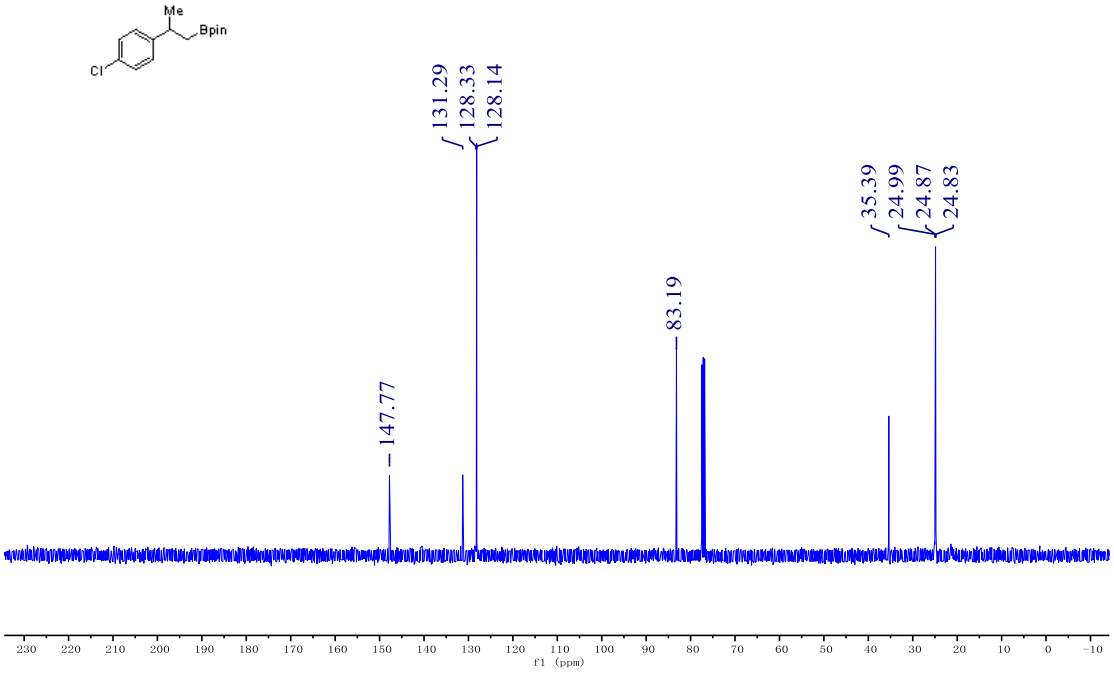

Me
Bpin
Br
3.04
3.02
3.00
2.98
2.96
2.95
1.25
1.23
1.16
1.15
1.12
1.10
7.38
7.36
7.12
7.10
f1 (ppm)


Me
Bpin
Br

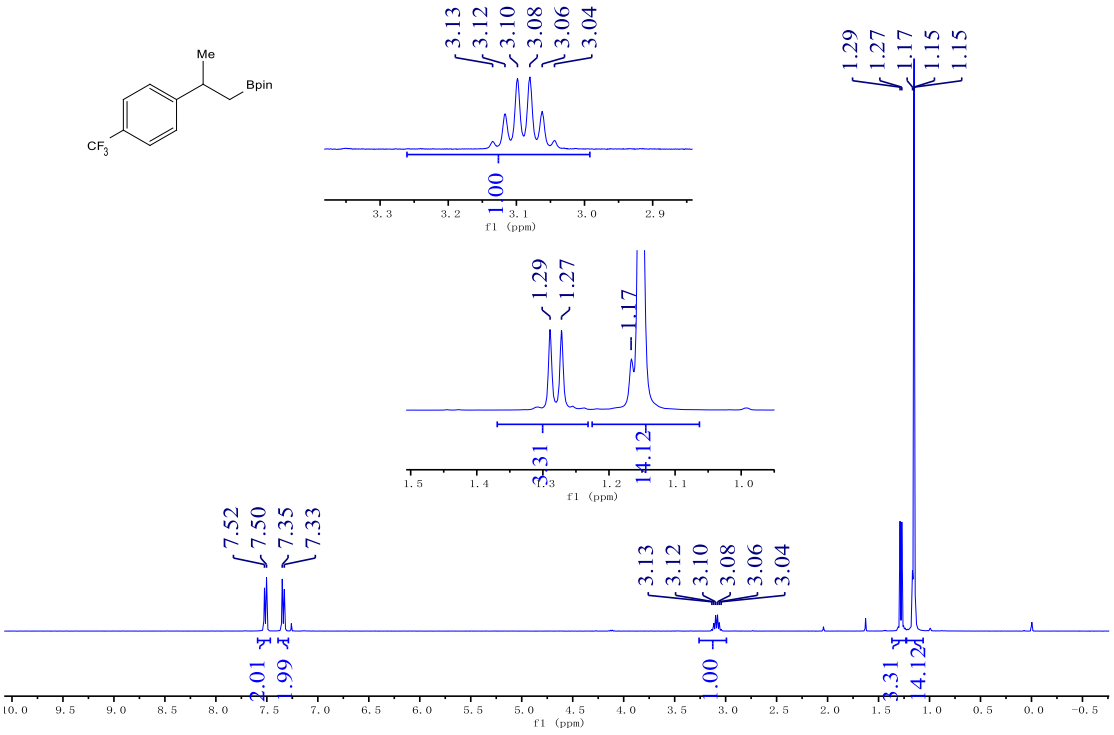

131.17
128.46
119.21
148.18
83.08
35.32
24.79
24.75
24.70
f1 (ppm)

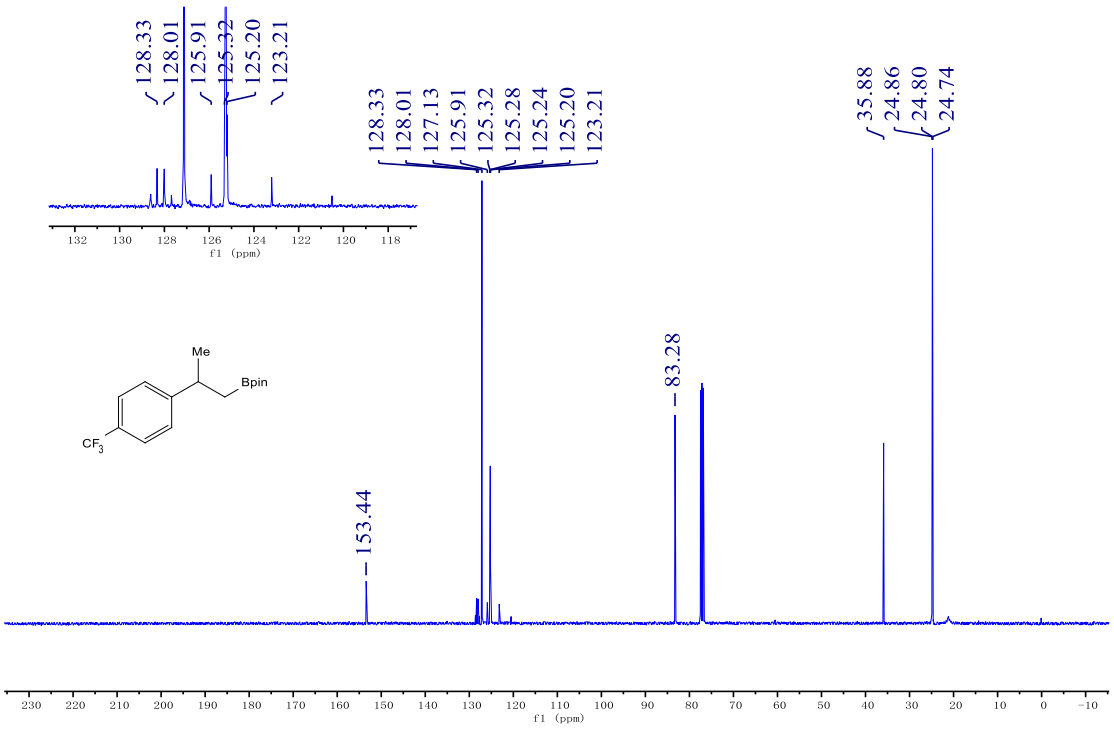
5e


Me
Bpin
Cl
3.05
3.03
3.01
3.00
2.98
2.96
1.00
1.25
1.23
1.13
1.11
3.17
1.95
1.91
7.23
7.21
7.17
7.15
1.96
1.96
1.25
1.23
1.16
1.13
1.11
f1 (ppm)

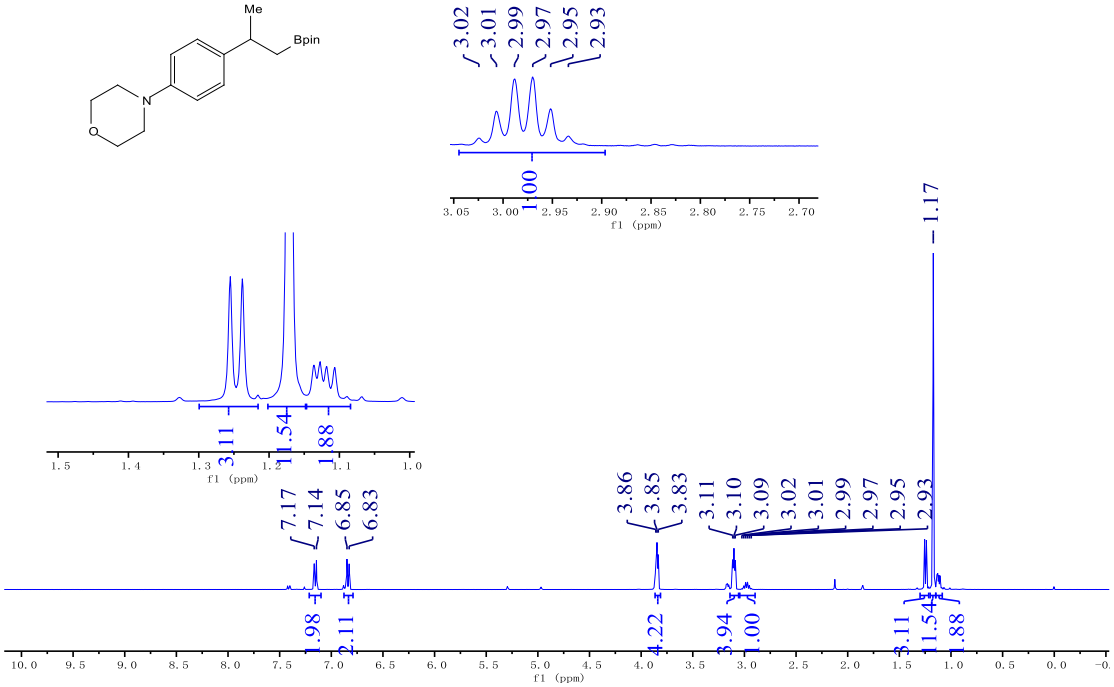

Me
Bpin
Cl
131.29
128.33
128.14
147.77
83.19
35.39
24.99
24.87
24.83
f1 (ppm)

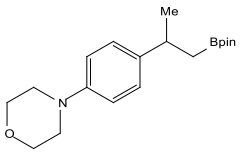
5f

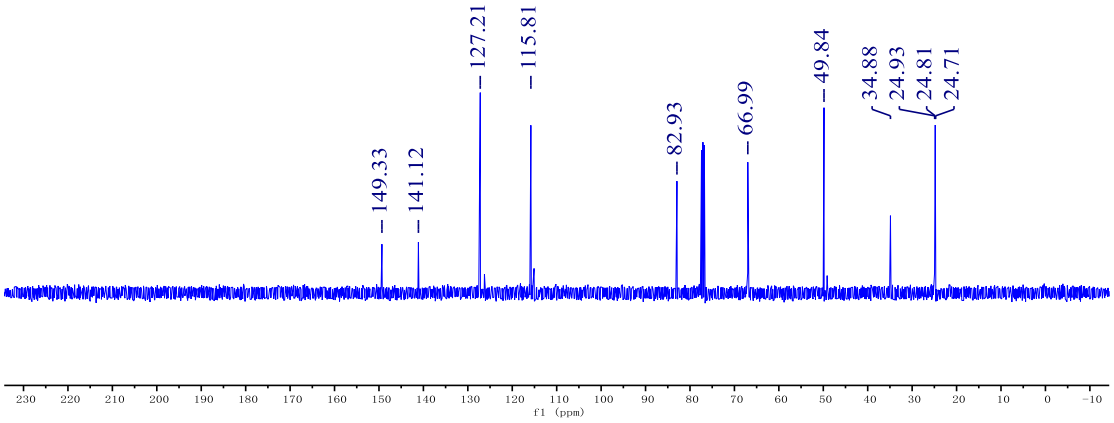

Me
Bpin
CF3
3.13
3.12
3.10
3.08
3.06
3.04
1.00
1.29
1.27
1.17
1.15
1.15
2.31
14.12
7.52
7.50
7.35
7.33
2.01
1.99
1.00
3.31
4.12
f1 (ppm)

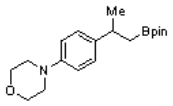

128.33
128.01
125.91
125.32
125.20
123.21
128.33
128.01
127.13
125.91
125.32
125.28
125.24
125.20
123.21
35.88
24.86
24.80
24.74
83.28
153.44
Me
Bpin
CF3
f1 (ppm)

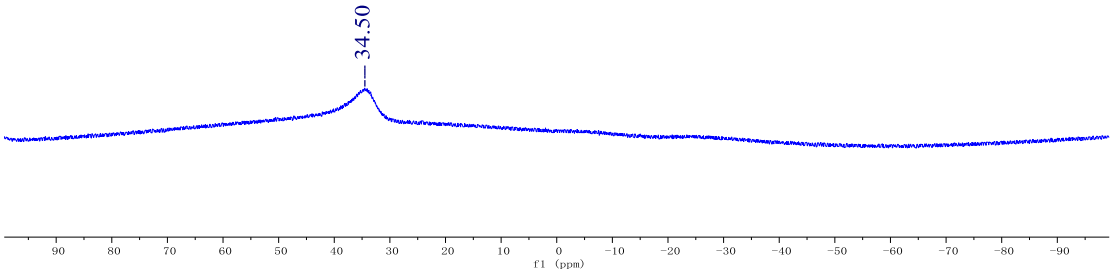
5g


Me
Bpin
N
O
3.02
3.01
2.99
2.97
2.95
2.93
1.00
3.11
1.54
1.88
1.17
7.17
7.14
6.85
6.83
3.86
3.85
3.83
3.11
3.10
3.09
3.02
3.01
2.99
2.97
2.95
2.93
1.98
2.11
4.22
3.94
1.00
3.11
11.54
1.88
f1 (ppm)

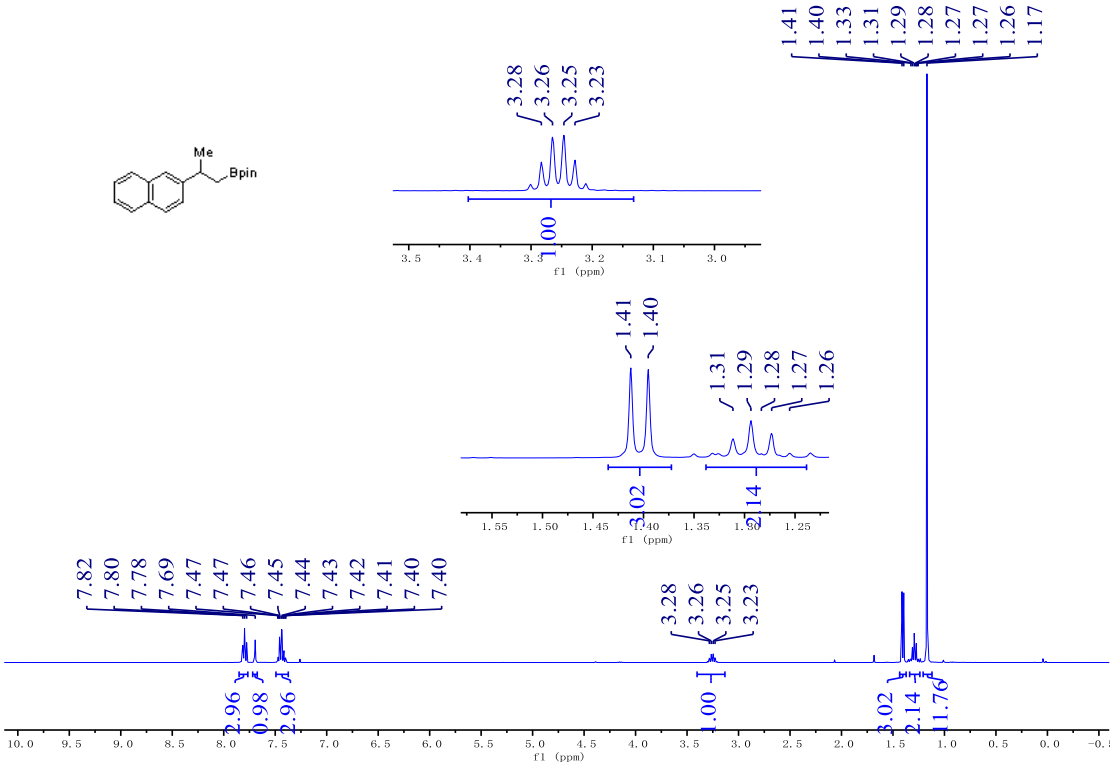

Me
Bpin
N
O

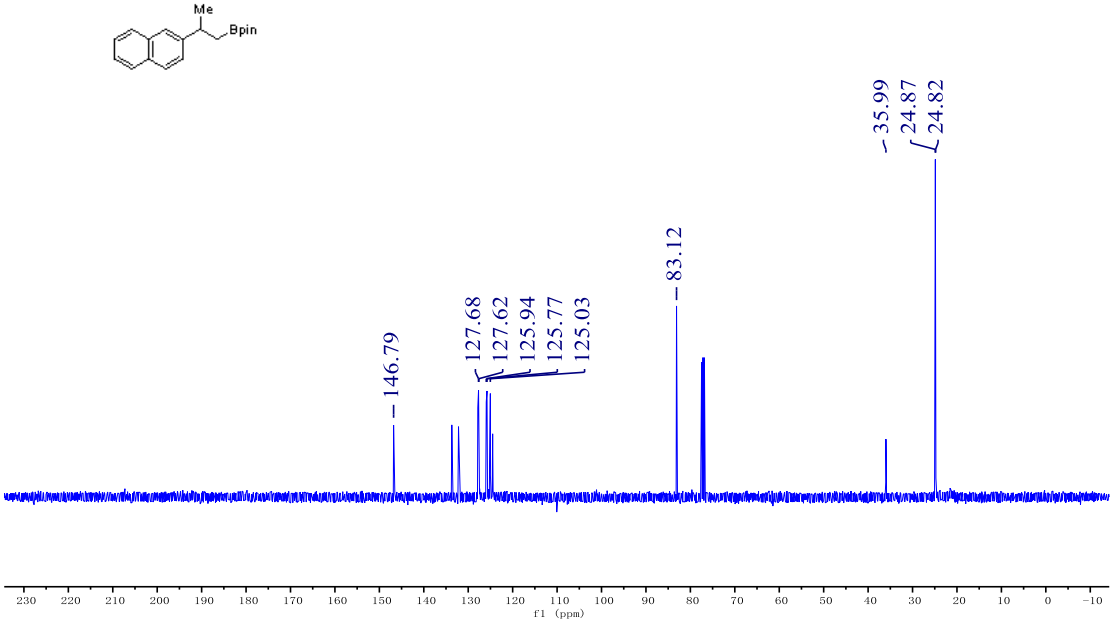

149.33
141.12
127.21
115.81
82.93
66.99
49.84
34.88
24.93
24.81
24.71
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Me
Bpin
N
O

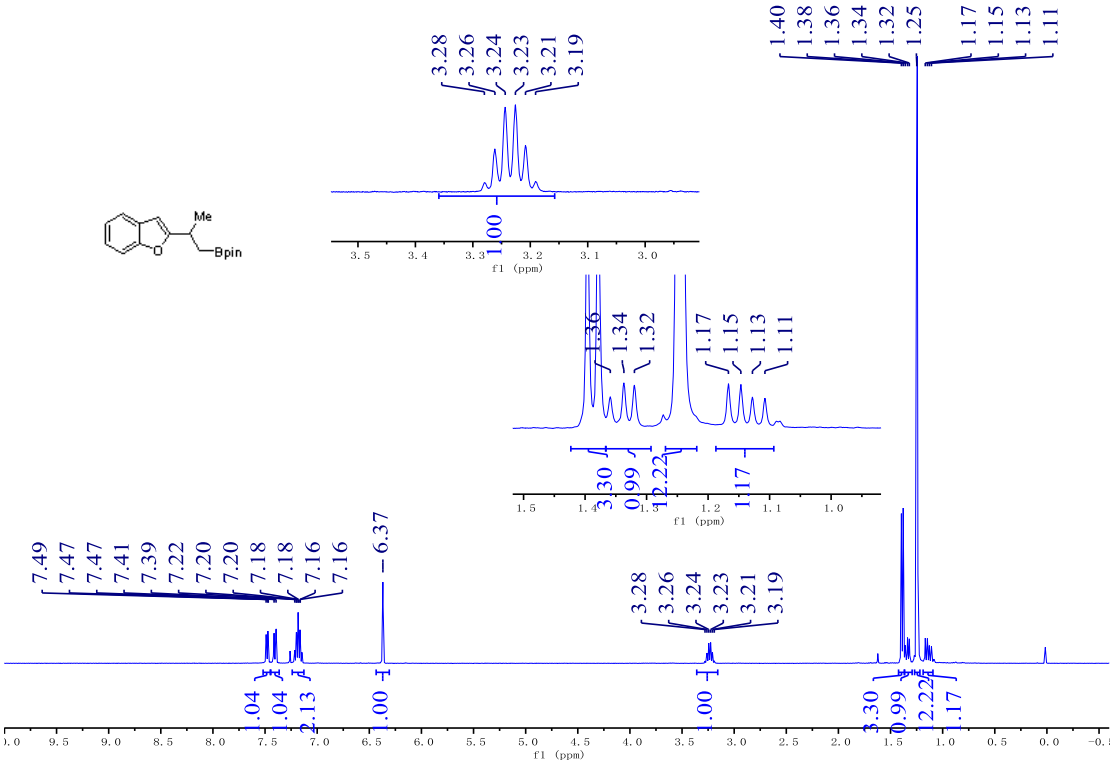

34.50
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

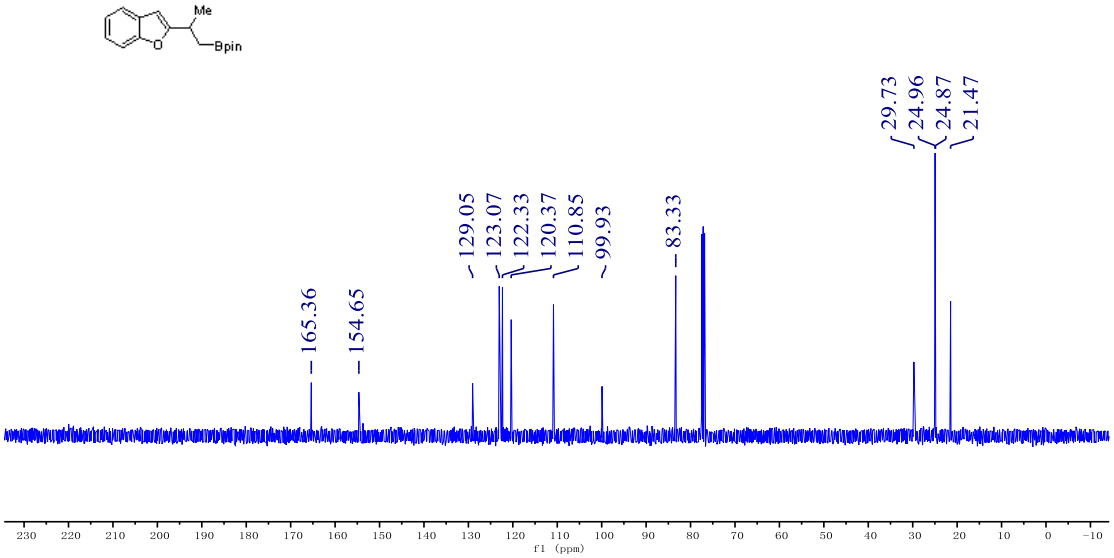
5h


Me
Bpin
1.41
1.40
1.33
1.31
1.29
1.28
1.27
1.27
1.26
1.17
3.28
3.26
3.25
3.23
1.00
f1 (ppm)
1.41
1.40
1.31
1.29
1.28
1.27
1.26
3.02
2.14
f1 (ppm)
7.82
7.80
7.78
7.69
7.47
7.47
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.40
3.28
3.26
3.25
3.23
2.96
0.98
2.96
1.00
3.02
2.14
1.76
f1 (ppm)

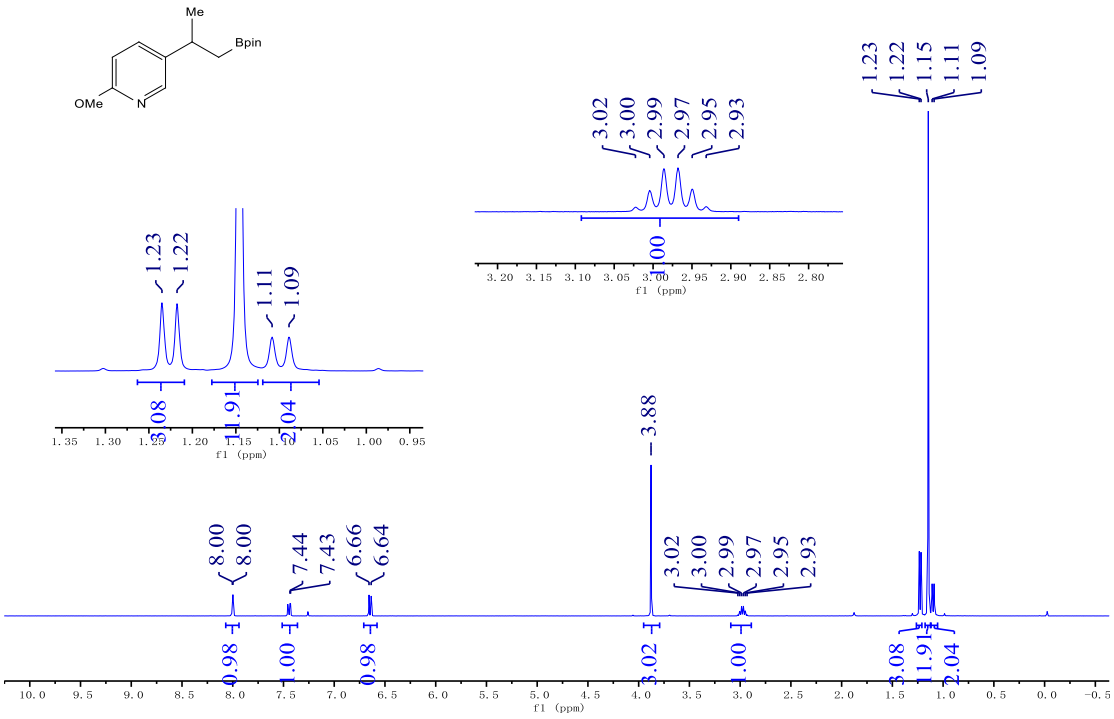

Me
Bpin
35.99
24.87
24.82
83.12
146.79
127.68
127.62
125.94
125.77
125.03
f1 (ppm)

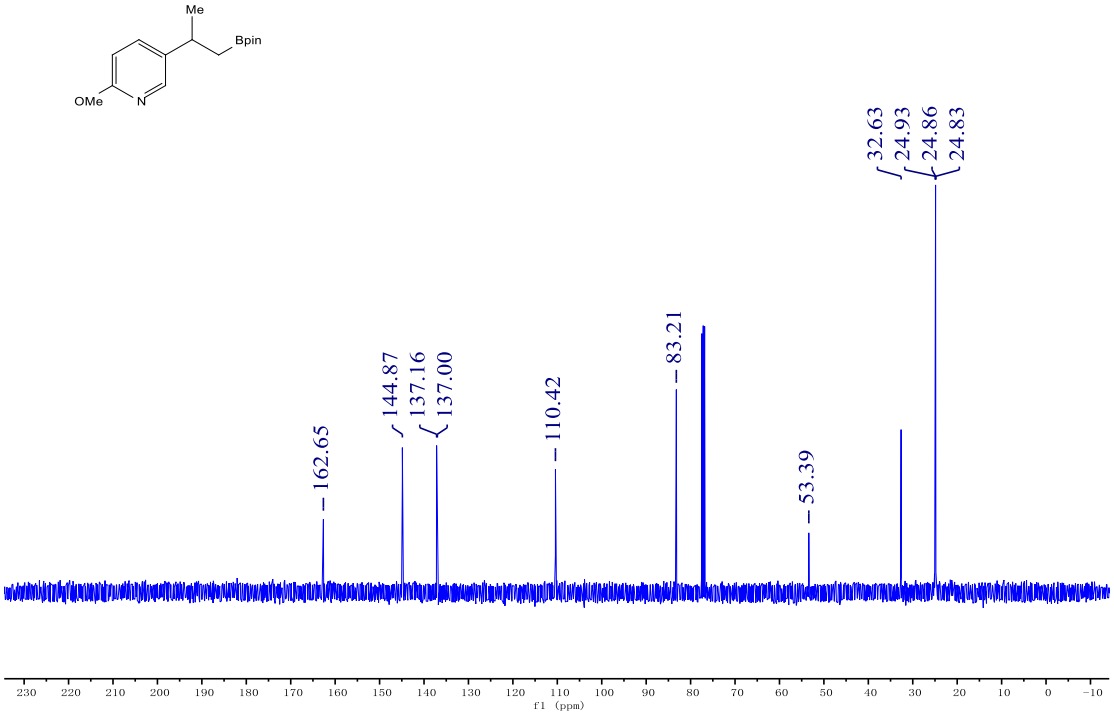
5i

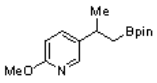

Me
Bpin
7.49
7.47
7.47
7.41
7.39
7.22
7.20
7.20
7.18
7.18
7.16
7.16
6.37
3.28
3.26
3.24
3.23
3.21
3.19
1.40
1.38
1.36
1.34
1.32
1.25
1.17
1.15
1.13
1.11
f1 (ppm)

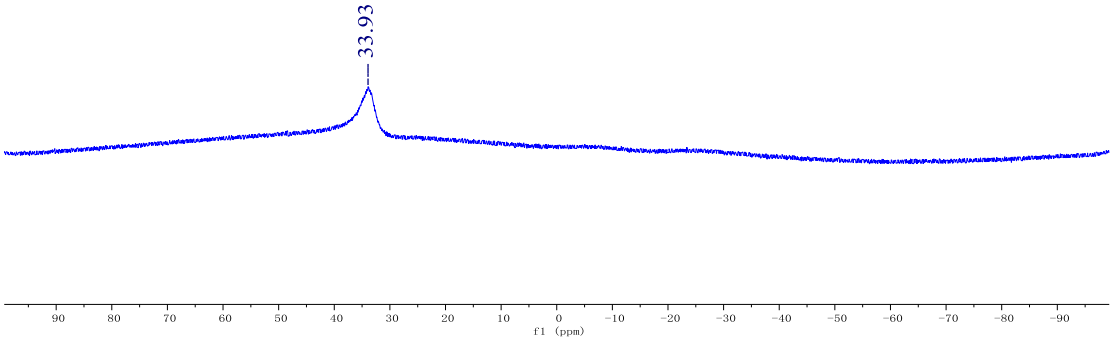

Me
Bpin
165.36
154.65
129.05
123.07
122.33
120.37
110.85
99.93
83.33
29.73
24.96
24.87
21.47
f1 (ppm)

5j

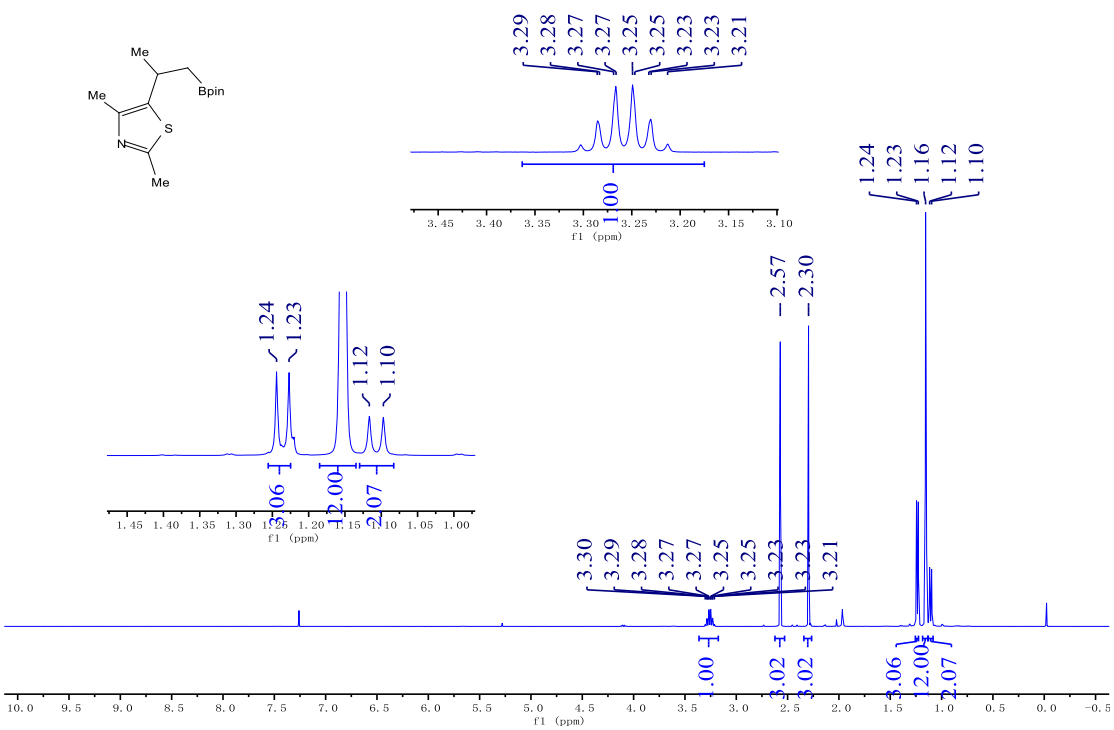

Me
Bpin
OMe
N
1.23
1.22
1.11
1.09
3.02
3.00
2.99
2.97
2.95
2.93
8.00
8.00
7.44
7.43
6.66
6.64
3.88
f1 (ppm)

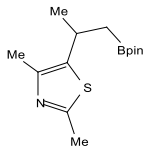

Me
Bpin
OMe
N
162.65
144.87
137.16
137.00
110.42
83.21
53.39
32.63
24.93
24.86
24.83
f1 (ppm)

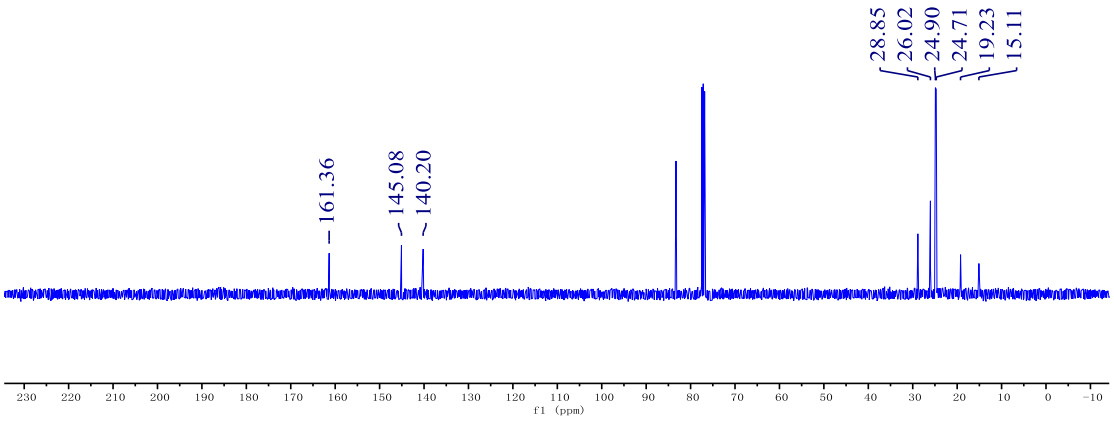

Me
Bpin
MeO
N

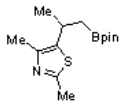

33.93
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

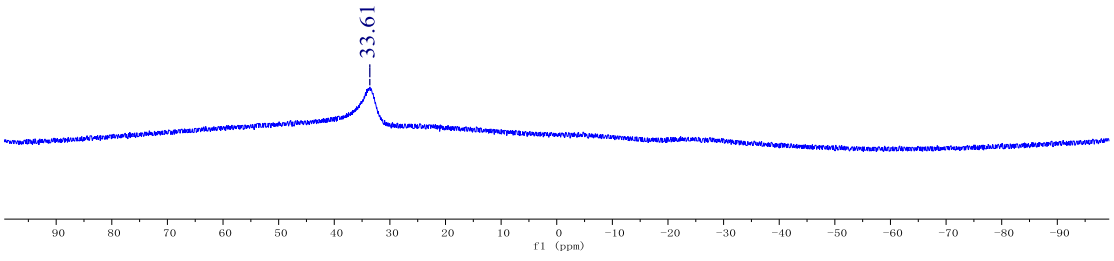
5k


Me
Bpin
Me
S
N
Me
3.29 3.28 3.27 3.27 3.25 3.25 3.23 3.23 3.21
1.00
3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10
f1 (ppm)
1.24 1.23 1.16 1.12 1.10
2.57 2.30
1.24 1.23 1.12 1.10
3.06 2.00 2.07
1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00
f1 (ppm)
3.30 3.29 3.28 3.27 3.27 3.25 3.25 3.23 3.23 3.21
1.00 3.02 3.02 3.06 2.00 2.07
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)

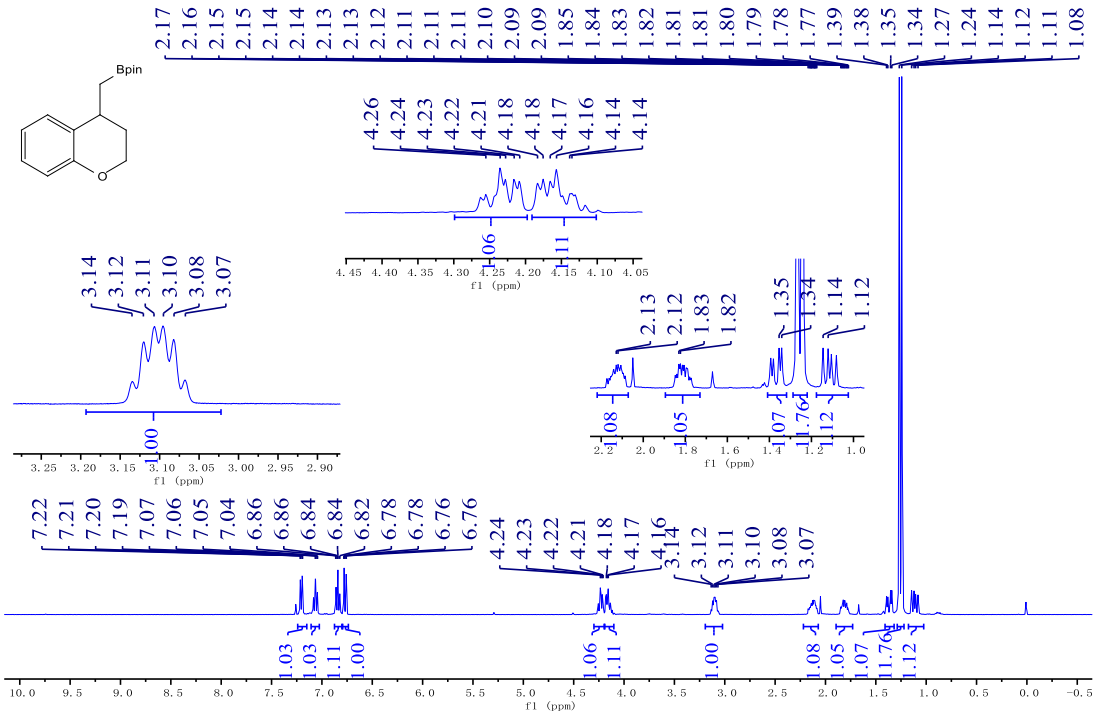

Me
Bpin
Me
S
N
Me

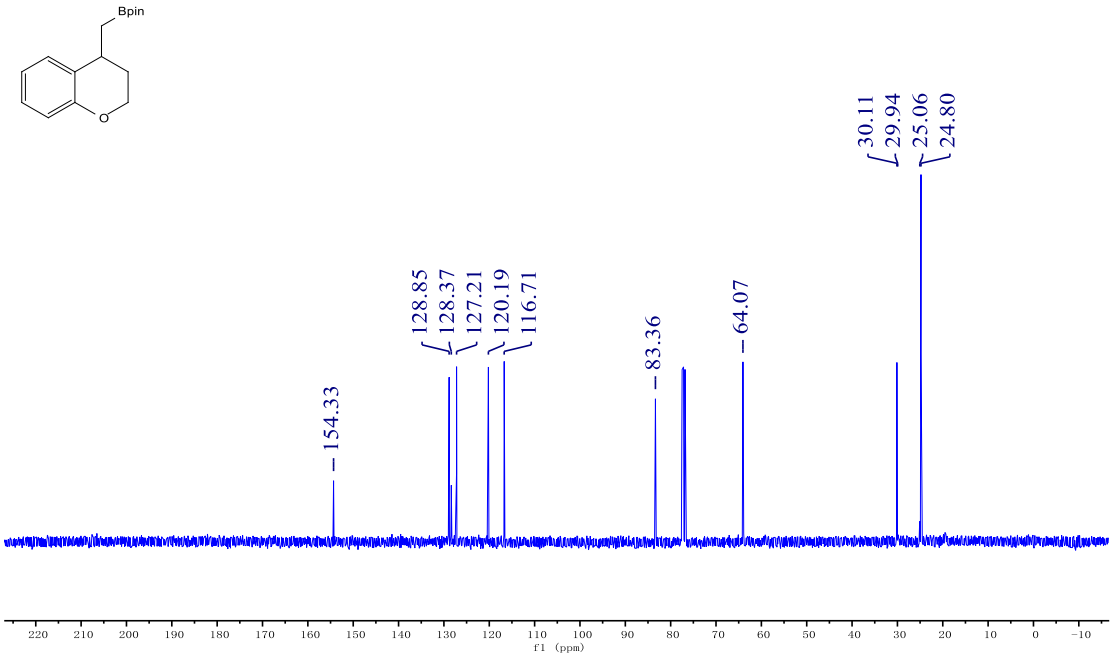

28.85
26.02
24.90
24.71
19.23
15.11
161.36
145.08
140.20
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Bpin
Me
N
S
Me

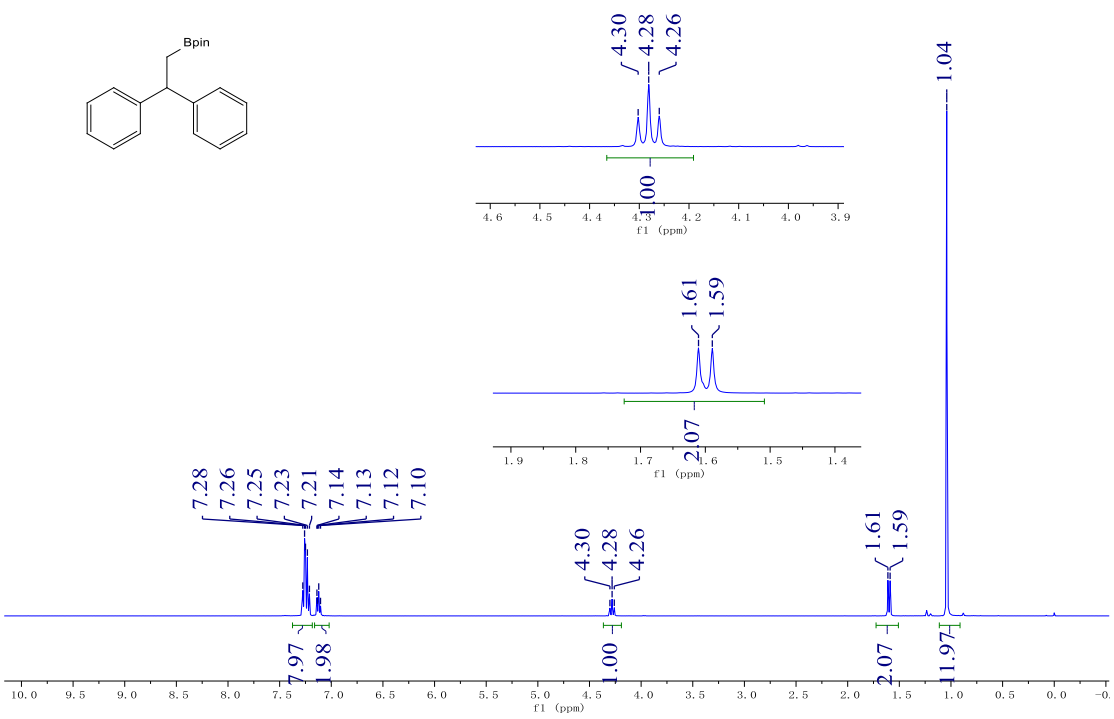

33.61
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

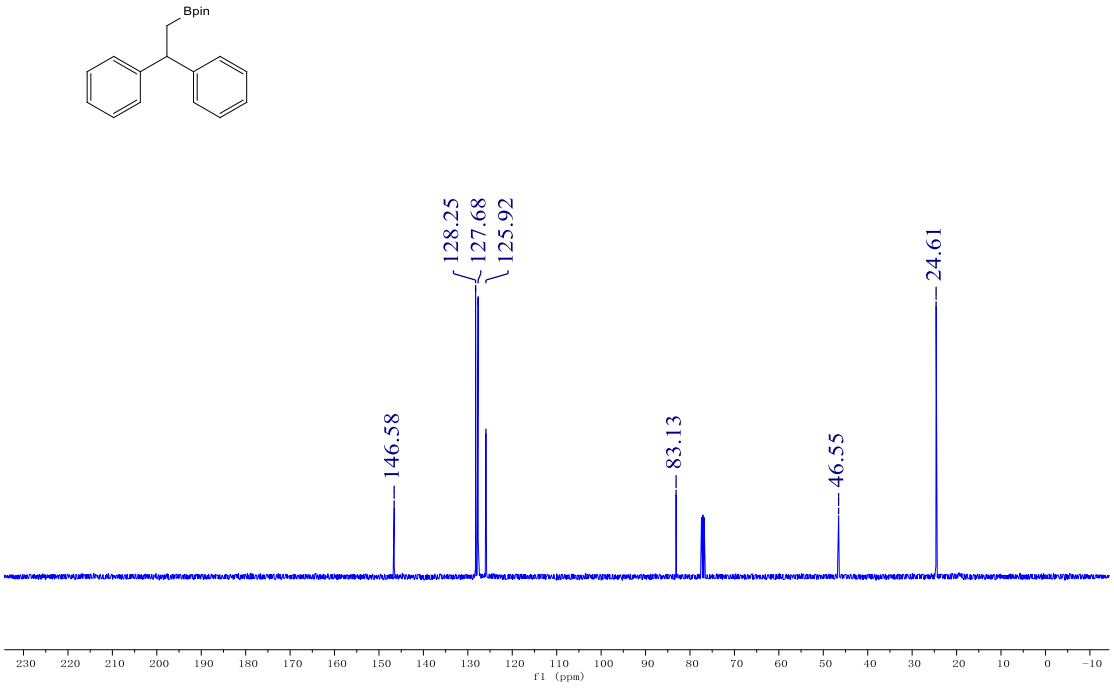
5l


Bpin
O
2.17 2.16 2.15 2.15 2.14 2.14 2.13 2.13 2.12 2.11 2.11 2.11 2.10 2.09 2.09 1.85 1.84 1.83 1.82 1.81 1.81 1.80 1.79 1.78 1.77 1.39 1.38 1.35 1.34 1.27 1.24 1.14 1.12 1.11 1.08
4.26 4.24 4.23 4.22 4.21 4.18 4.18 4.17 4.16 4.14 4.14
3.14 3.12 3.11 3.10 3.08 3.07
2.13 2.12 1.83 1.82 1.35 1.34 1.14 1.12
7.22 7.21 7.20 7.19 7.07 7.06 7.05 7.04 6.86 6.86 6.84 6.84 6.82 6.78 6.78 6.76 6.76
4.24 4.23 4.22 4.21 4.18 4.17 4.16 3.14 3.12 3.11 3.10 3.08 3.07
f1 (ppm)

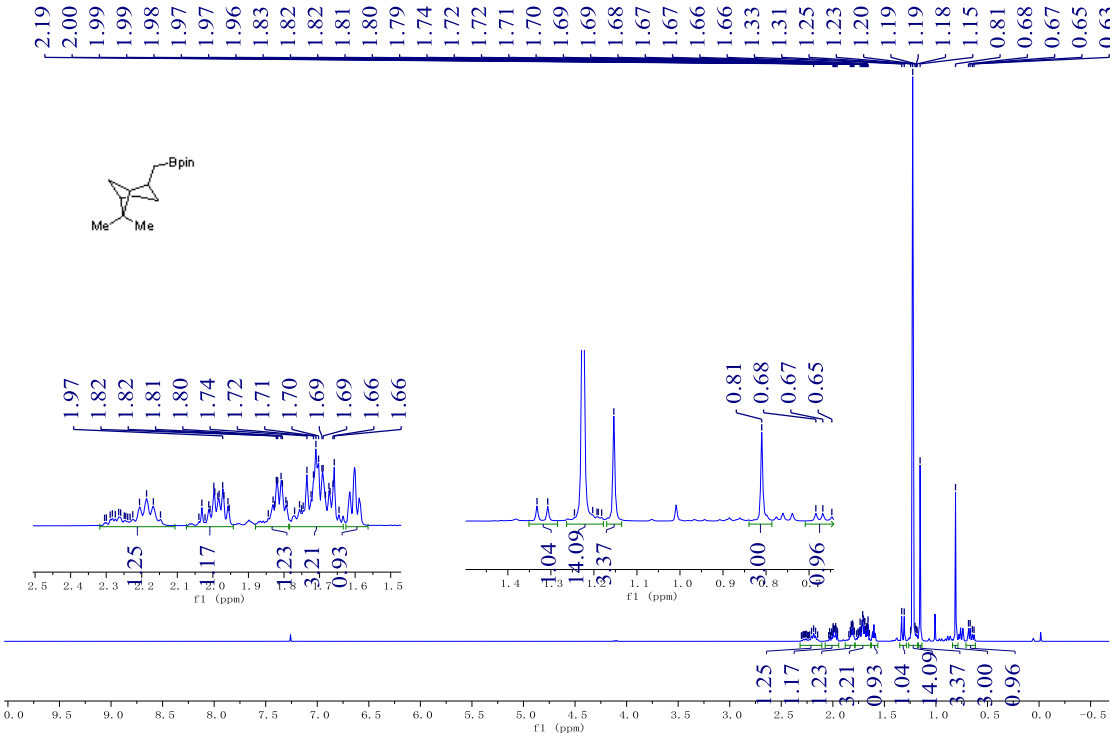

Bpin
O
30.11
29.94
25.06
24.80
128.85
128.37
127.21
120.19
116.71
154.33
83.36
64.07
f1 (ppm)

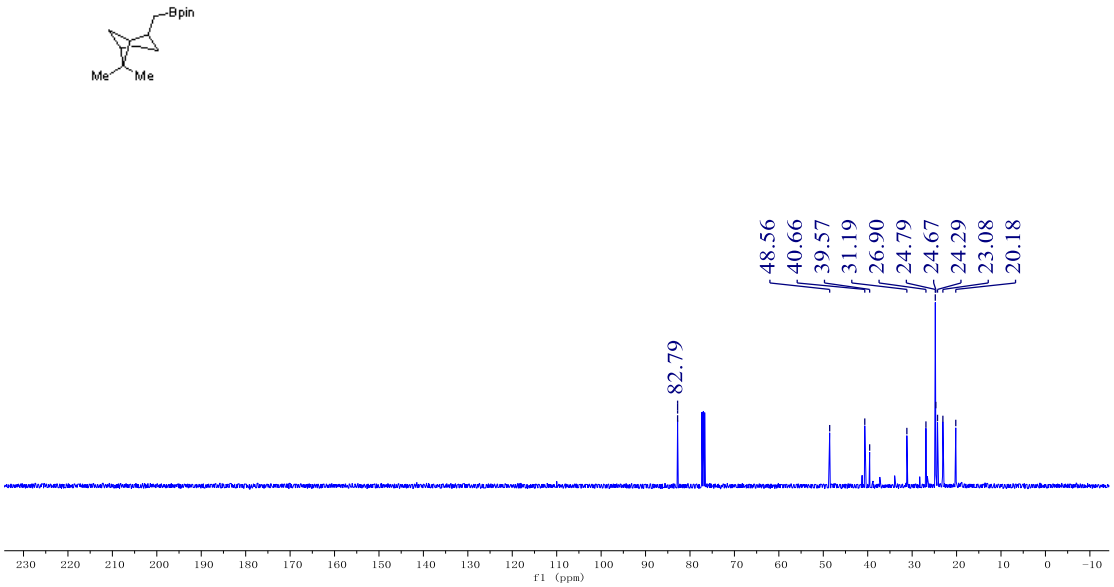
5m

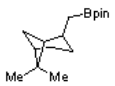

Bpin
4.30
4.28
4.26
1.00
1.61
1.59
2.07
7.28
7.26
7.25
7.23
7.21
7.14
7.13
7.12
7.10
1.04
7.97
1.98
1.00
2.07
11.97
f1 (ppm)

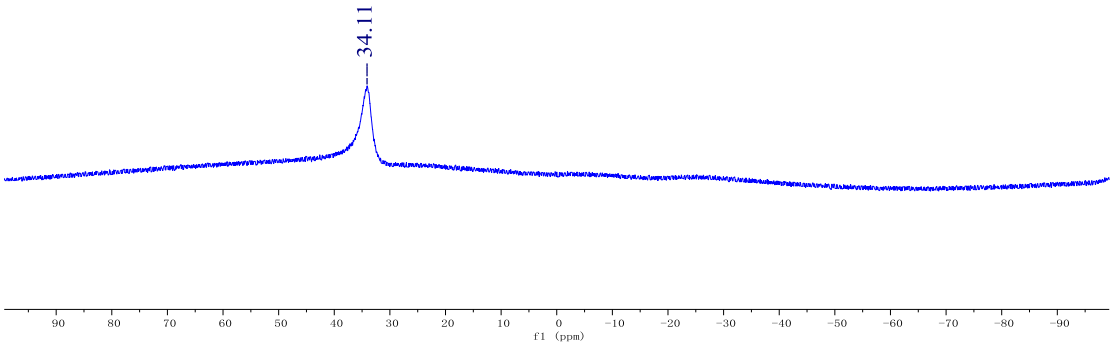

Bpin
128.25
127.68
125.92
24.61
146.58
83.13
46.55
f1 (ppm)

5n

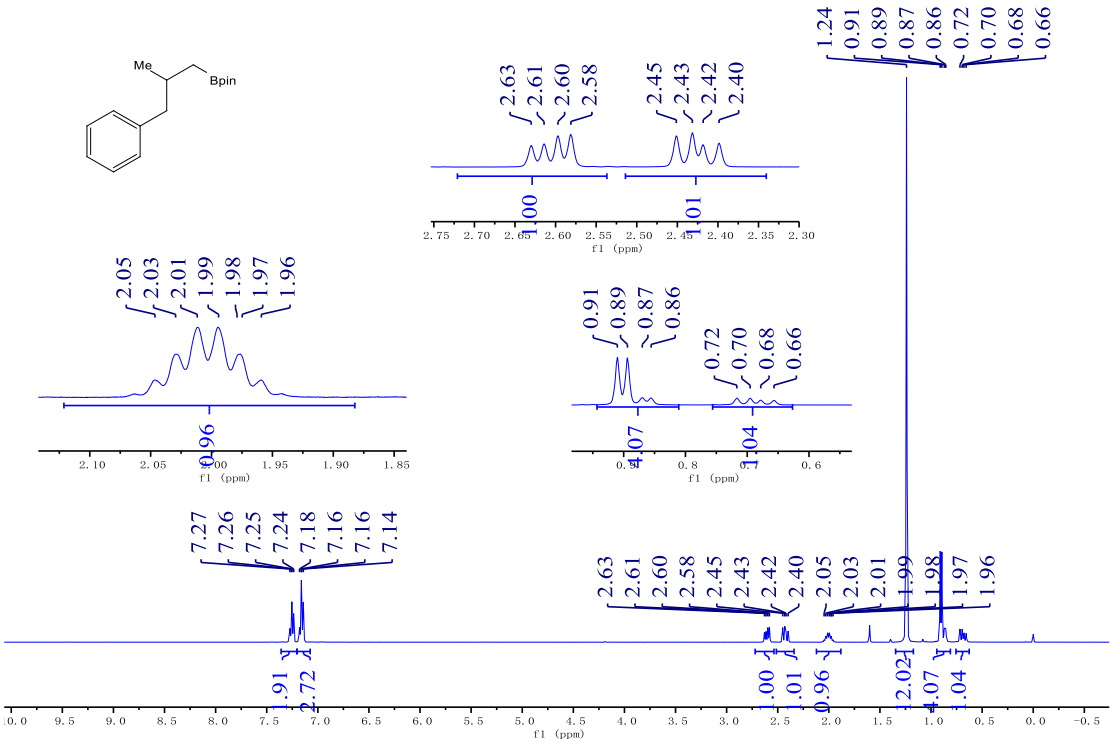


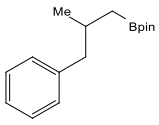


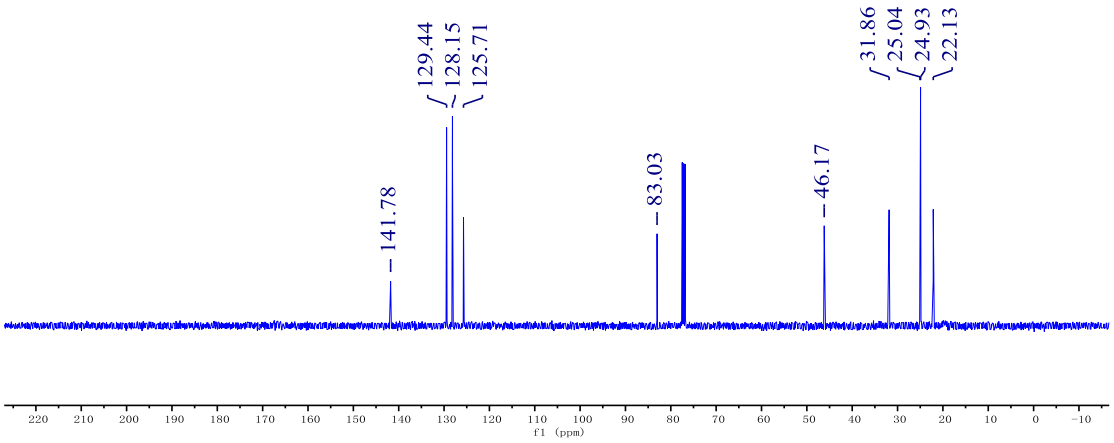

Bpin
Me
Me


34.11
f1 (ppm)

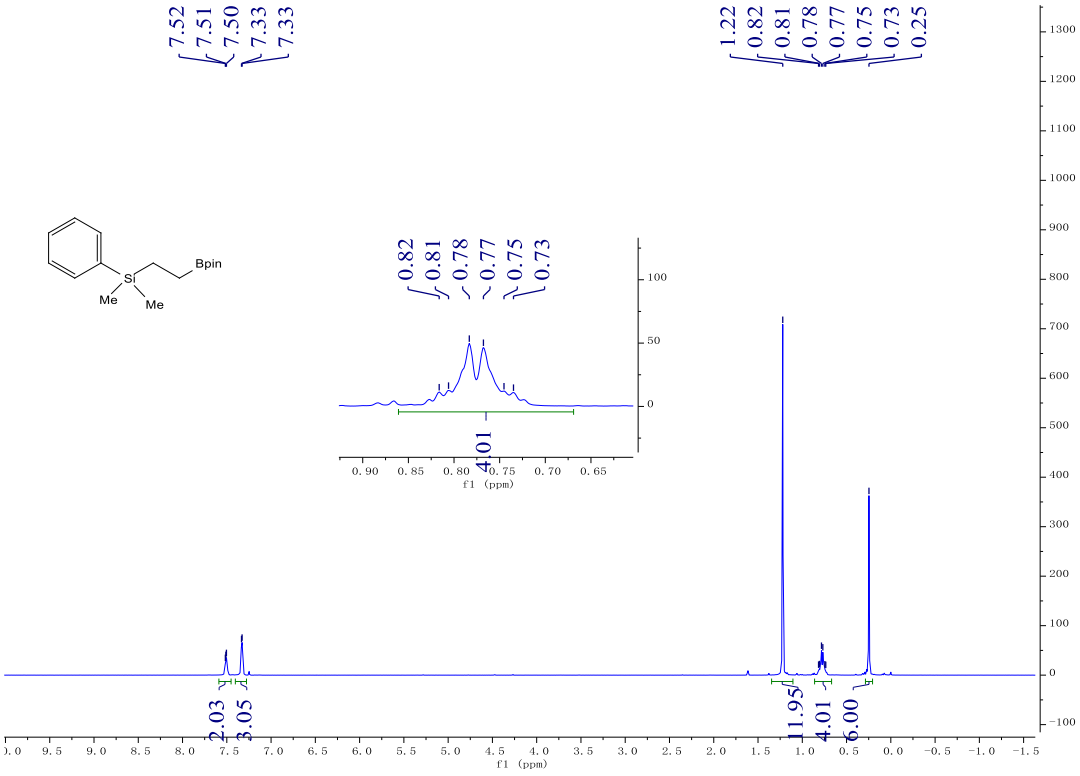
5o

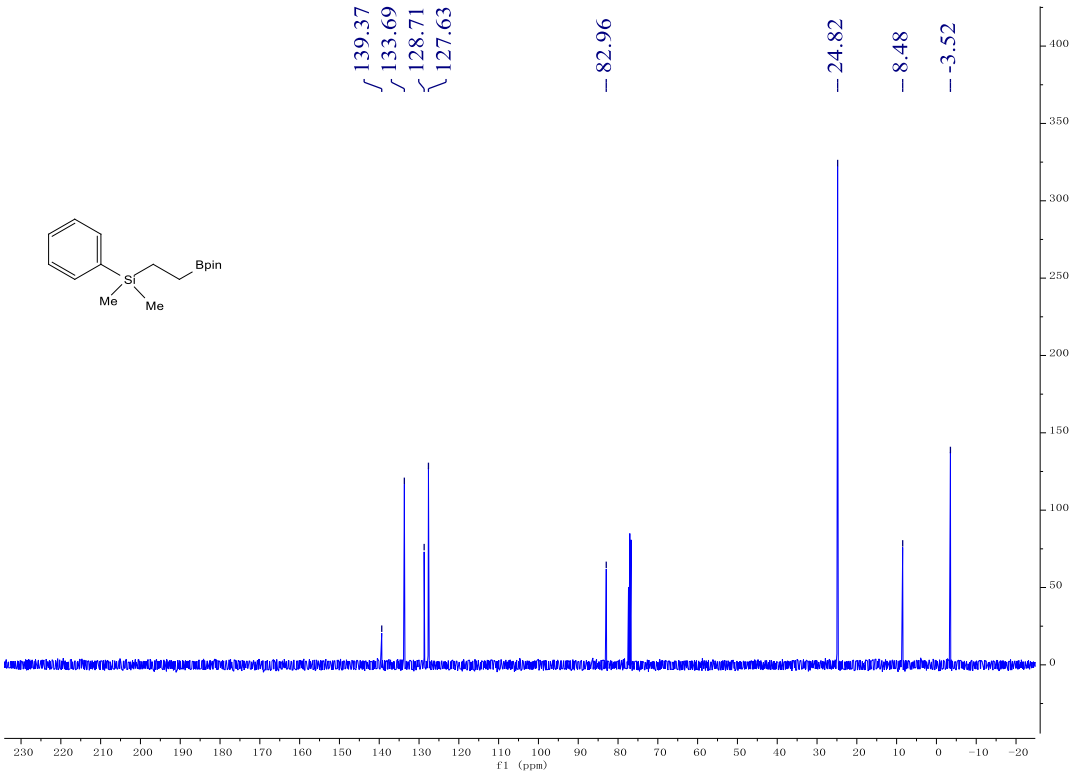

Me
Bpin
1.24
0.91
0.89
0.87
0.86
0.72
0.70
0.68
0.66
2.63
2.61
2.60
2.58
2.45
2.43
2.42
2.40
1.00
1.01
2.05
2.03
2.01
1.99
1.98
1.97
1.96
0.96
4.07
1.04
7.27
7.26
7.25
7.24
7.18
7.16
7.16
7.14
1.91
2.72
2.02
f1 (ppm)


Me
Bpin

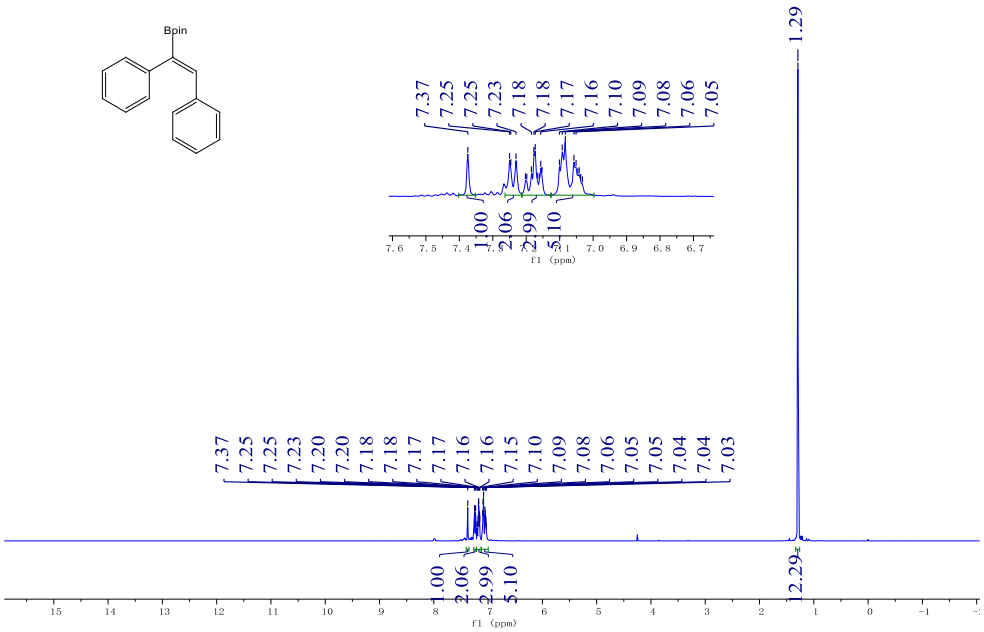

141.78
129.44
128.15
125.71
83.03
46.17
31.86
25.04
24.93
22.13
f1 (ppm)

5p

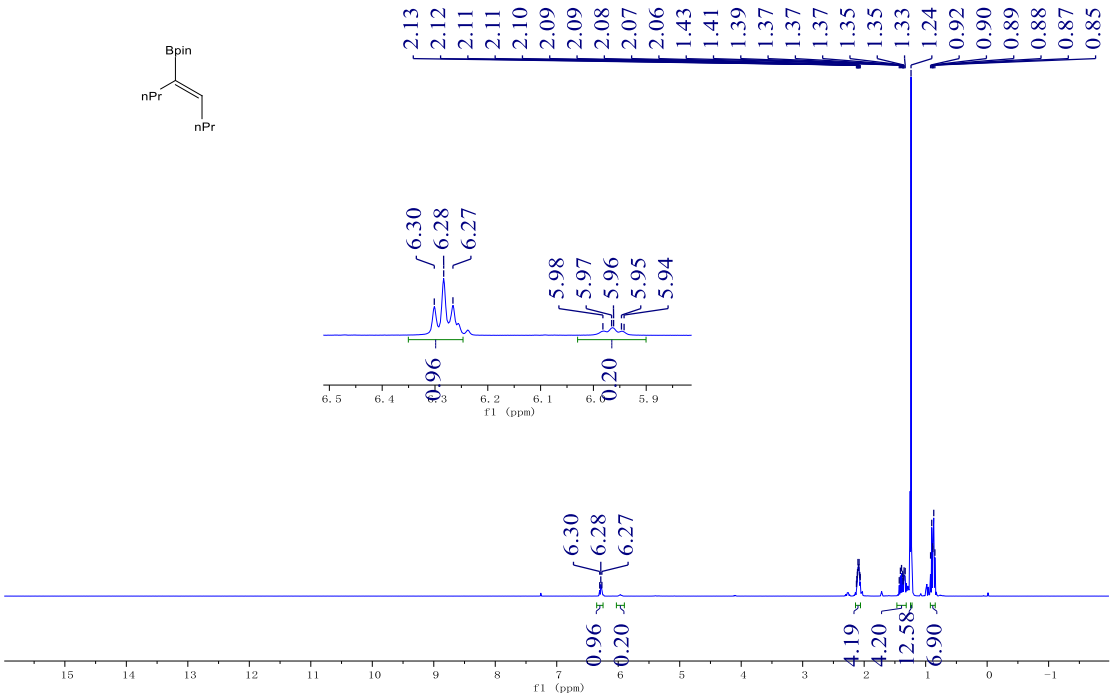

7.52
7.51
7.50
7.33
7.33
1.22
0.82
0.81
0.78
0.77
0.75
0.73
0.25
Bpin
Si
Me
Me
4.01
2.03
3.05
11.95
4.01
6.00
f1 (ppm)


139.37
133.69
128.71
127.63
82.96
24.82
8.48
-3.52
Bpin
Si
Me
Me
f1 (ppm)

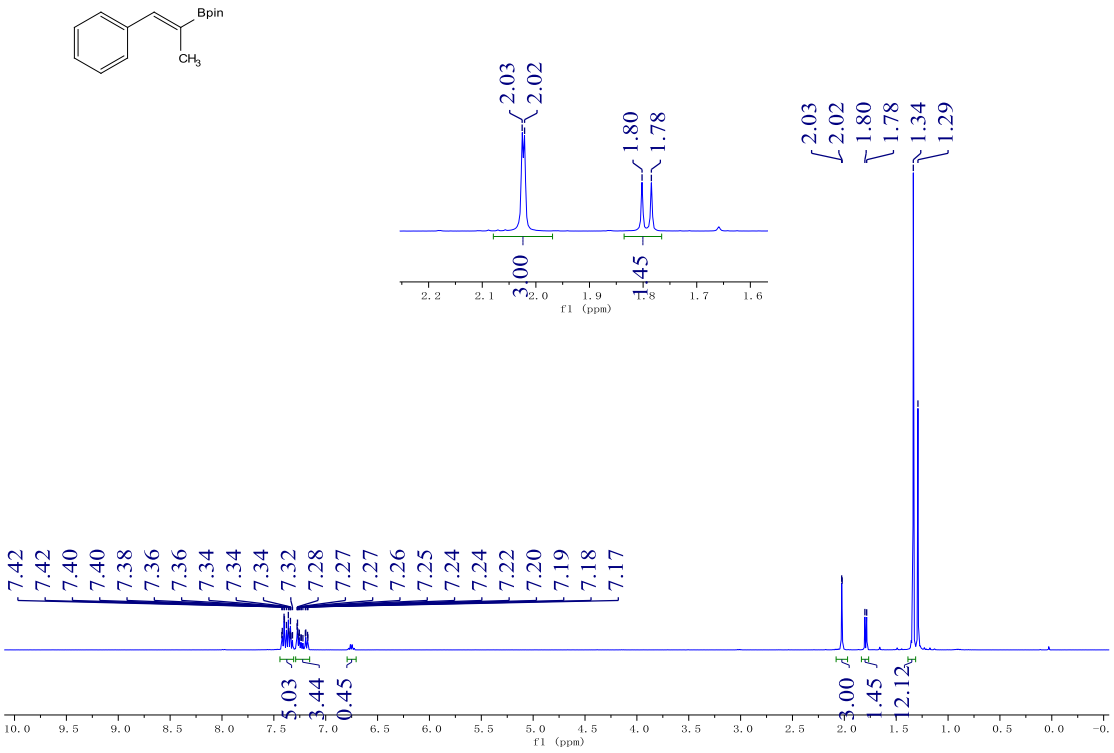
7a


Bpin
1.29
7.37
7.25
7.25
7.23
7.20
7.20
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.10
7.09
7.08
7.06
7.05
7.05
7.04
7.04
7.03
1.00
2.06
2.99
5.10
12.29
f1 (ppm)

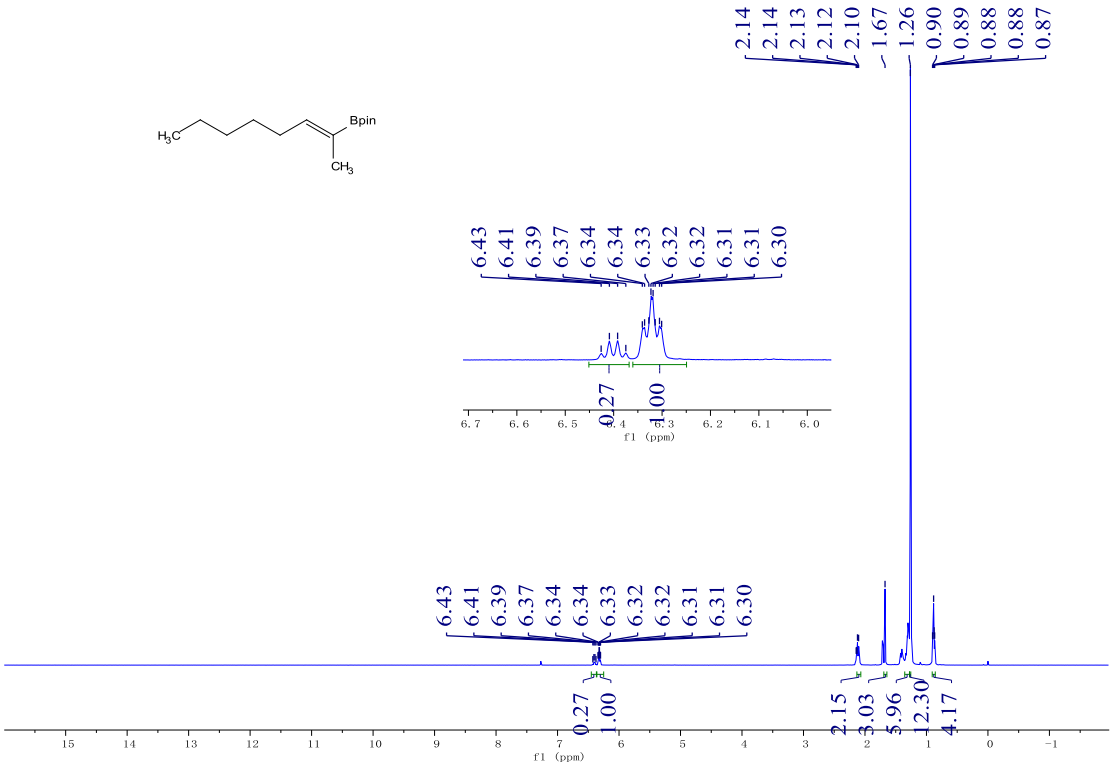
7b


Bpin
nPr
nPr
2.13
2.12
2.11
2.11
2.10
2.09
2.09
2.08
2.07
2.06
1.43
1.41
1.39
1.37
1.37
1.37
1.35
1.35
1.33
1.24
0.92
0.90
0.89
0.88
0.87
0.85
6.30
6.28
6.27
5.98
5.97
5.96
5.95
5.94
0.96
0.20
f1 (ppm)
6.30
6.28
6.27
0.96
0.20
4.19
4.20
12.58
6.90
f1 (ppm)

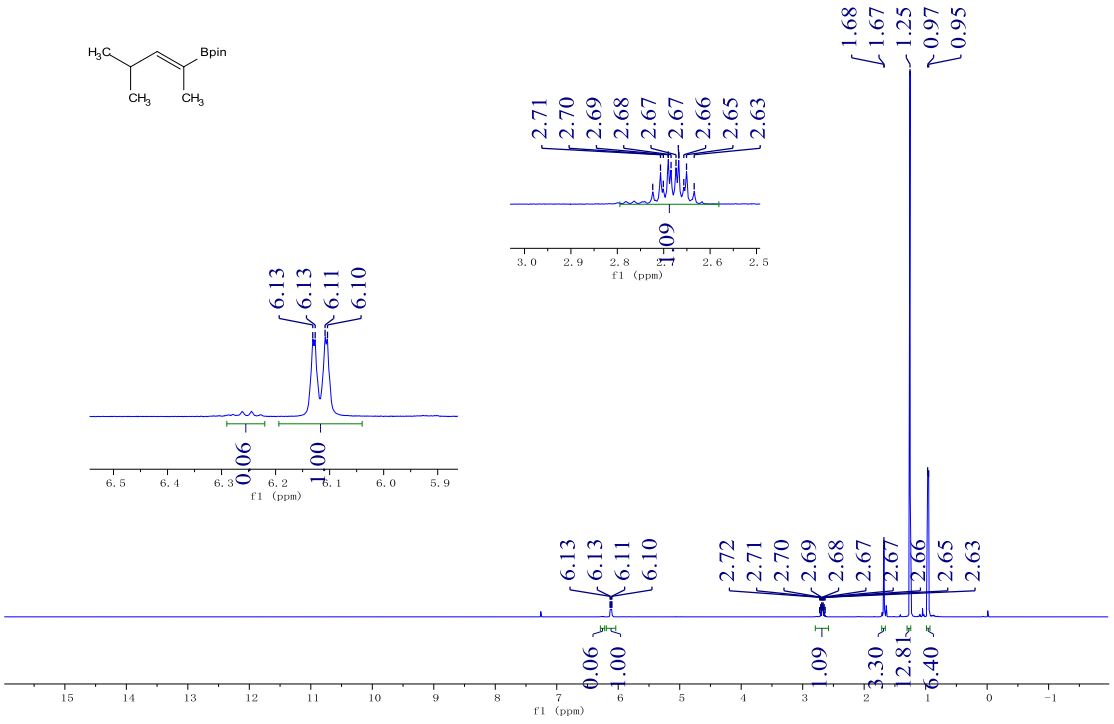
7c


Bpin
CH3
2.03
2.02
1.80
1.78
3.00
1.45
f1 (ppm)
2.03
2.02
1.80
1.78
1.34
1.29
7.42
7.42
7.40
7.40
7.38
7.36
7.36
7.34
7.34
7.34
7.32
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.22
7.20
7.19
7.18
7.17
5.03
3.44
0.45
3.00
1.45
12.12
f1 (ppm)

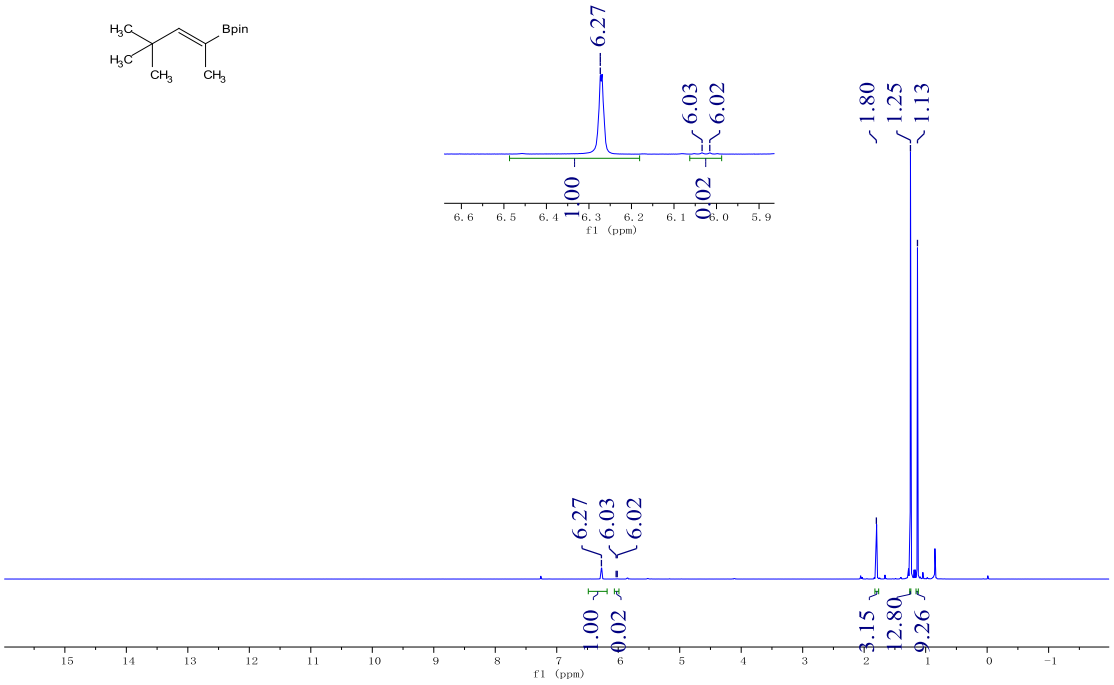
7d

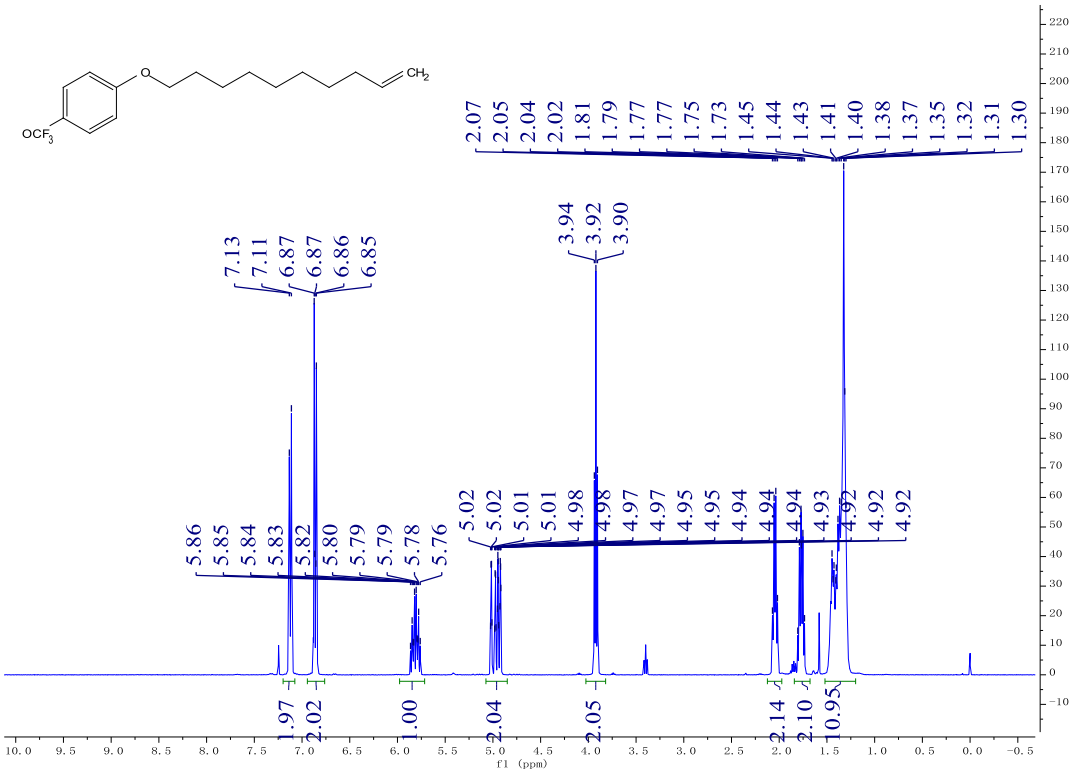

Bpin
H3C
CH3
2.14
2.14
2.13
2.12
2.10
1.67
1.26
0.90
0.89
0.88
0.88
0.87
6.43
6.41
6.39
6.37
6.34
6.34
6.33
6.32
6.32
6.31
6.31
6.30
0.27
1.00
2.15
3.03
5.96
12.30
4.17
f1 (ppm)

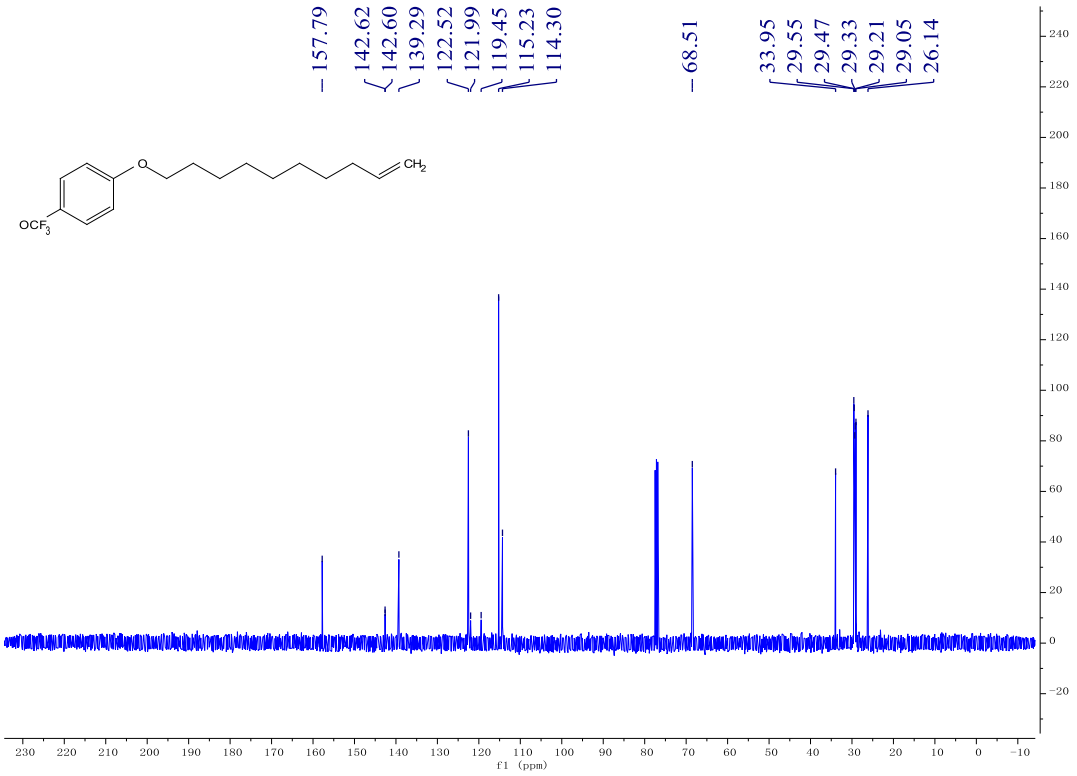
7e

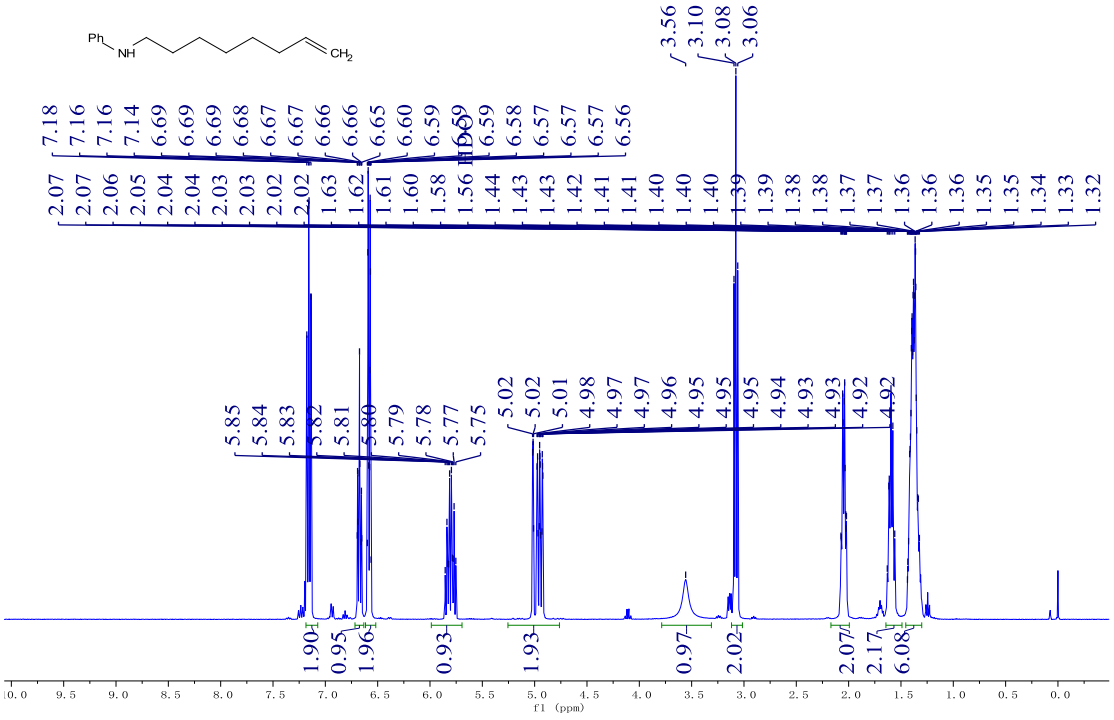

H3C
Bpin
CH3
CH3
1.68
1.67
1.25
0.97
0.95
2.71
2.70
2.69
2.68
2.67
2.67
2.66
2.65
2.63
1.09
6.13
6.13
6.11
6.10
0.06
1.00
2.72
2.71
2.70
2.69
2.68
2.67
2.67
2.66
2.65
2.63
1.09
3.30
12.81
6.40
f1 (ppm)

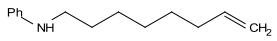
7f

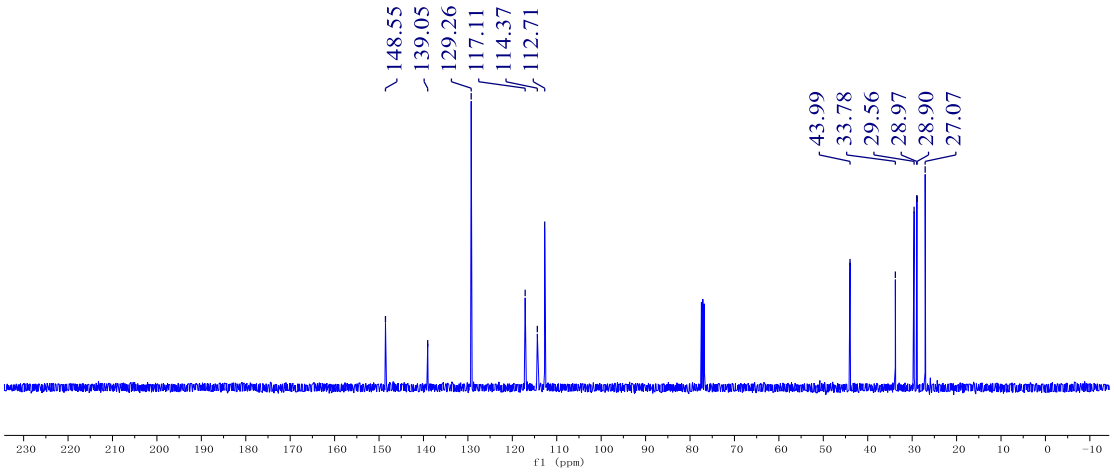

Bpin
6.27
6.03
6.02
1.80
1.25
1.13
1.00
0.02
3.15
12.80
9.26
f1 (ppm)

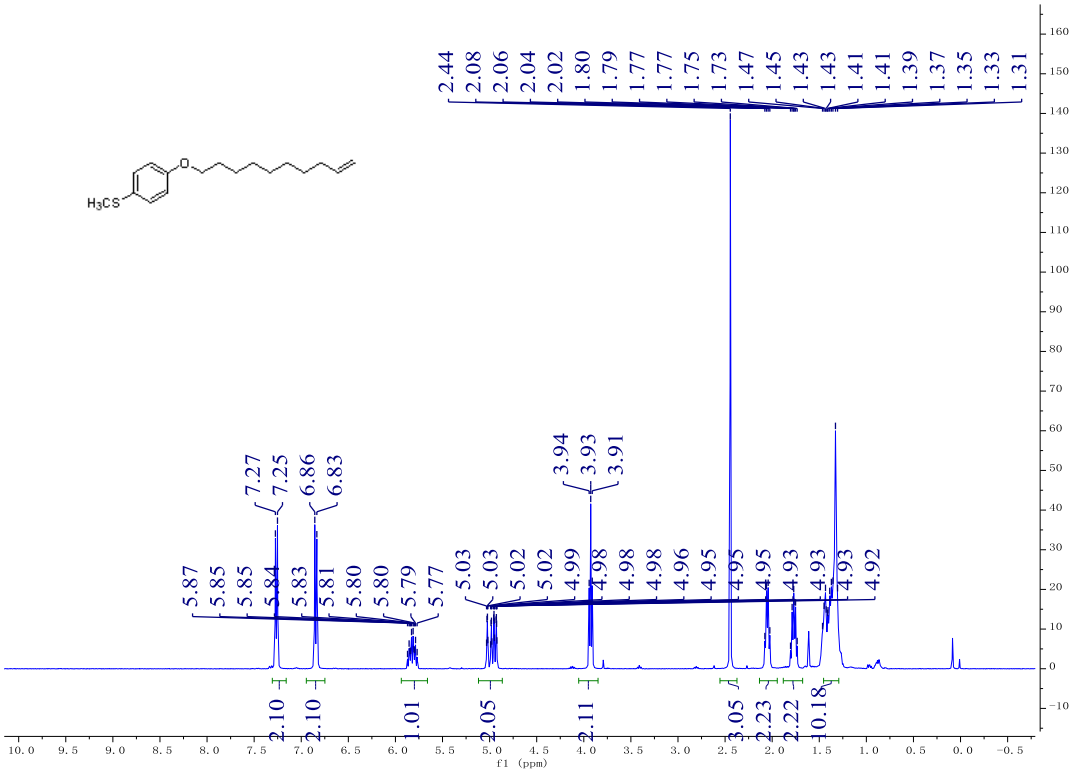

CH2
OCF3
2.07
2.05
2.04
2.02
1.81
1.79
1.77
1.77
1.75
1.73
1.45
1.44
1.43
1.41
1.40
1.38
1.37
1.35
1.32
1.31
1.30
3.94
3.92
3.90
7.13
7.11
6.87
6.87
6.86
6.85
5.86
5.85
5.84
5.83
5.82
5.80
5.79
5.79
5.78
5.76
5.02
5.02
5.01
5.01
4.98
4.98
4.97
4.97
4.95
4.95
4.94
4.94
4.94
4.93
4.92
4.92
4.92
1.97
2.02
1.00
2.04
2.05
2.14
2.10
10.95
f1 (ppm)


157.79
142.62
142.60
139.29
122.52
121.99
119.45
115.23
114.30
68.51
33.95
29.55
29.47
29.33
29.21
29.05
26.14
O
CH2
OCF3
f1 (ppm)


Ph
NH
CH2
3.56
3.10
3.08
3.06
7.18
7.16
7.16
7.14
6.69
6.69
6.69
6.68
6.67
6.67
6.66
6.66
6.65
6.60
6.59
6.59
6.59
6.58
6.57
6.57
6.57
6.56
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.78
5.77
5.75
5.02
5.02
5.01
4.98
4.97
4.97
4.96
4.95
4.95
4.95
4.94
4.93
4.93
4.92
4.92
1.90
0.95
1.96
0.93
1.93
0.97
2.02
2.07
2.17
6.08
f1 (ppm)


Ph
NH
CH2


148.55
139.05
129.26
117.11
114.37
112.71
43.99
33.78
29.56
28.97
28.90
27.07
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)


2.44
2.08
2.06
2.04
2.02
1.80
1.79
1.77
1.77
1.75
1.73
1.47
1.45
1.43
1.43
1.41
1.41
1.39
1.37
1.35
1.33
1.31
7.27
7.25
6.86
6.83
3.94
3.93
3.91
5.87
5.85
5.85
5.84
5.83
5.81
5.80
5.80
5.79
5.77
5.03
5.03
5.02
5.02
4.99
4.98
4.98
4.98
4.96
4.95
4.95
4.95
4.93
4.93
4.93
4.92
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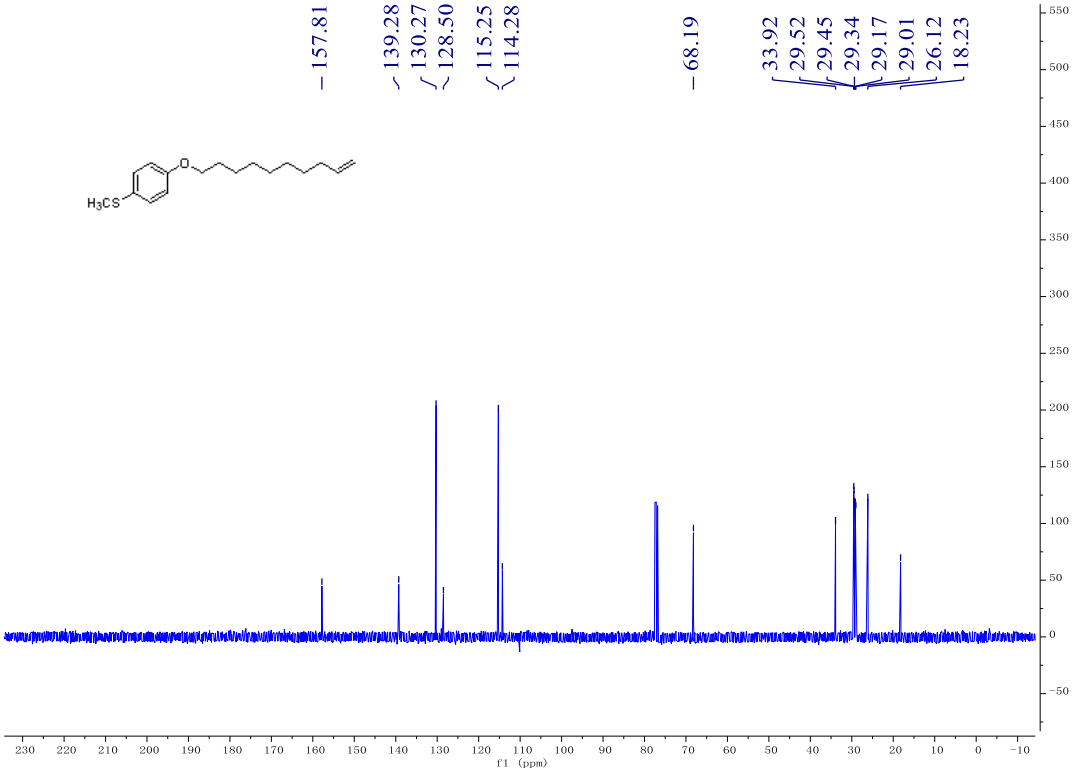
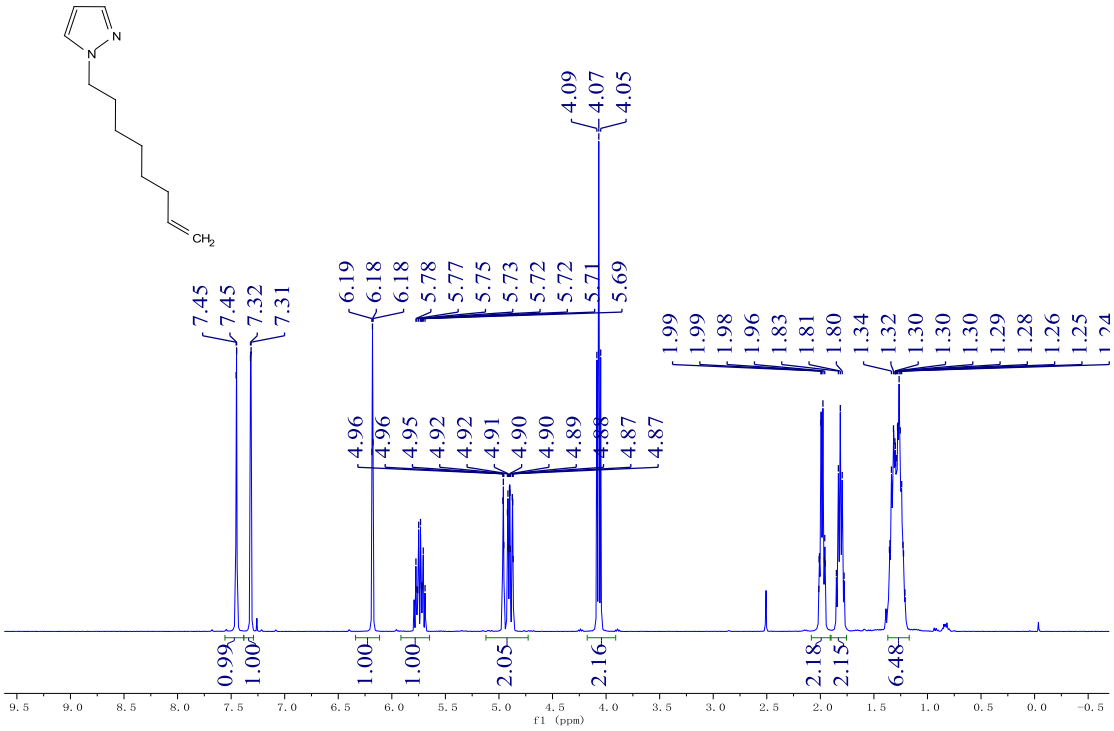
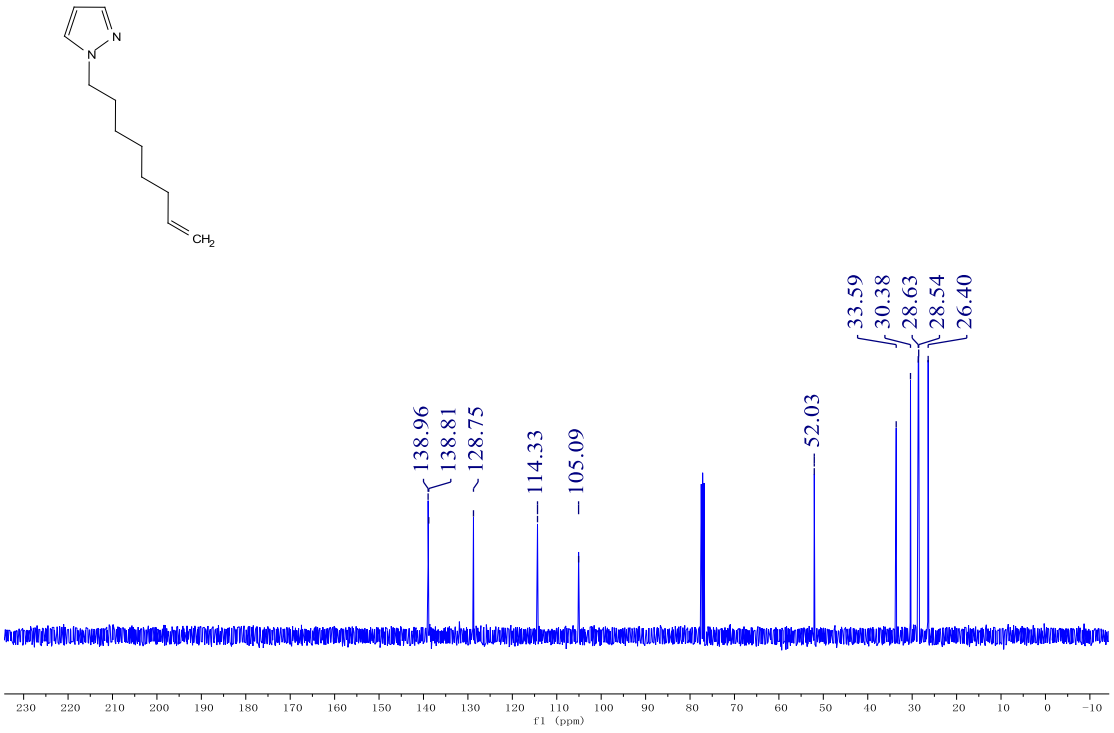
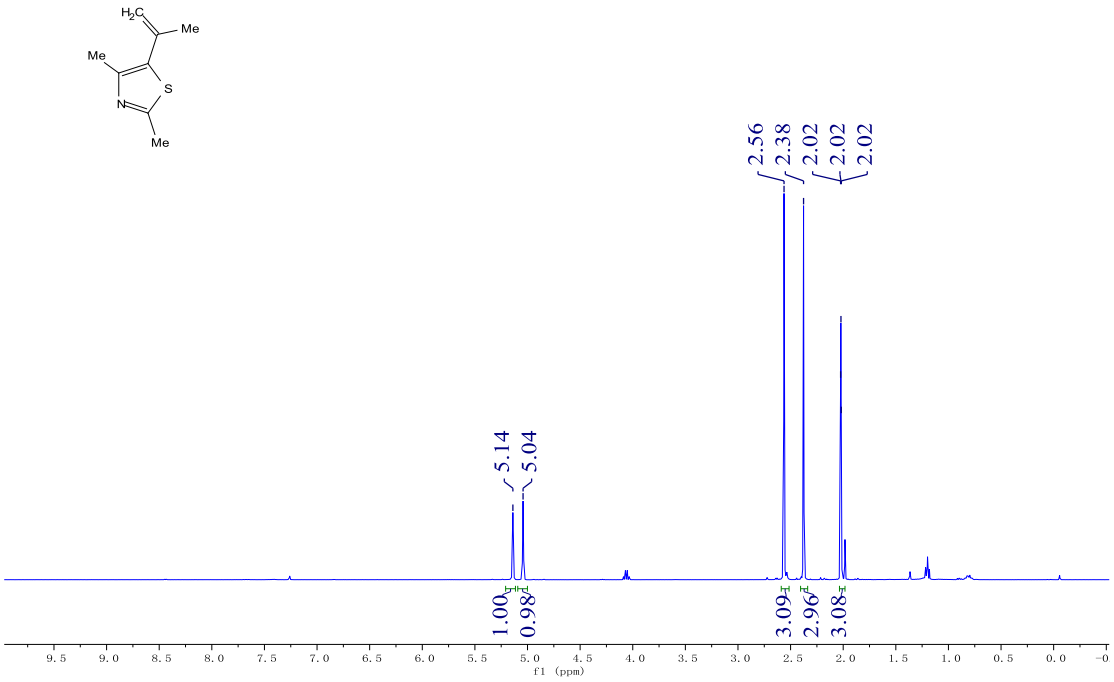
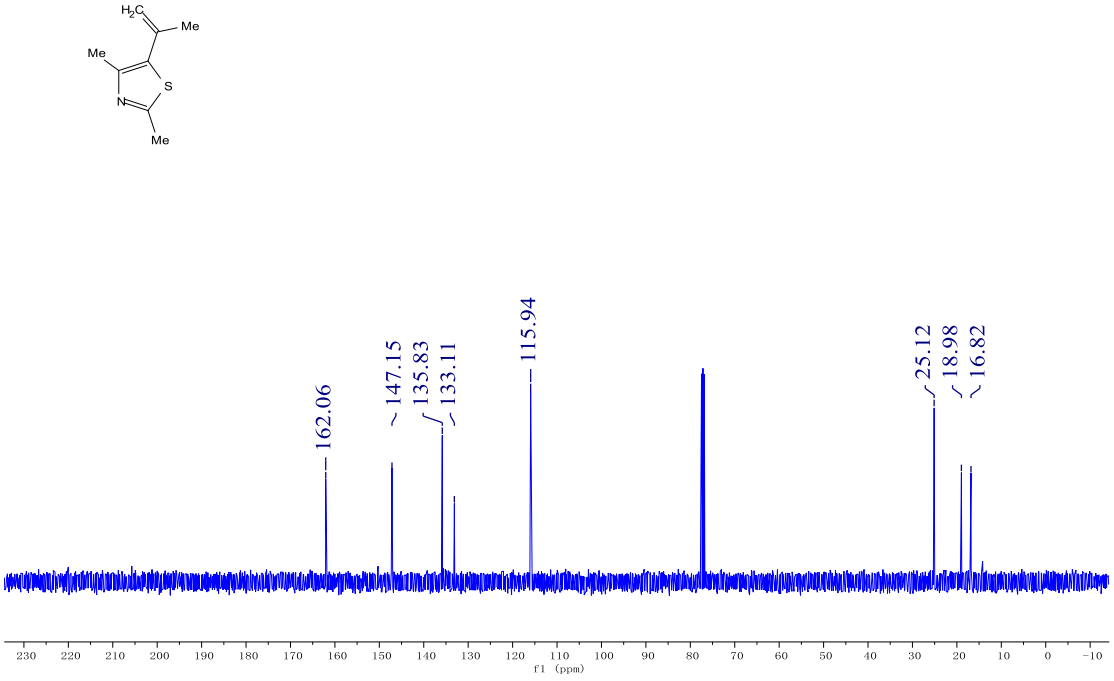
2.10
1.01
2.05
2.11
3.05
2.23
2.22
10.18
H3CS
f1 (ppm)

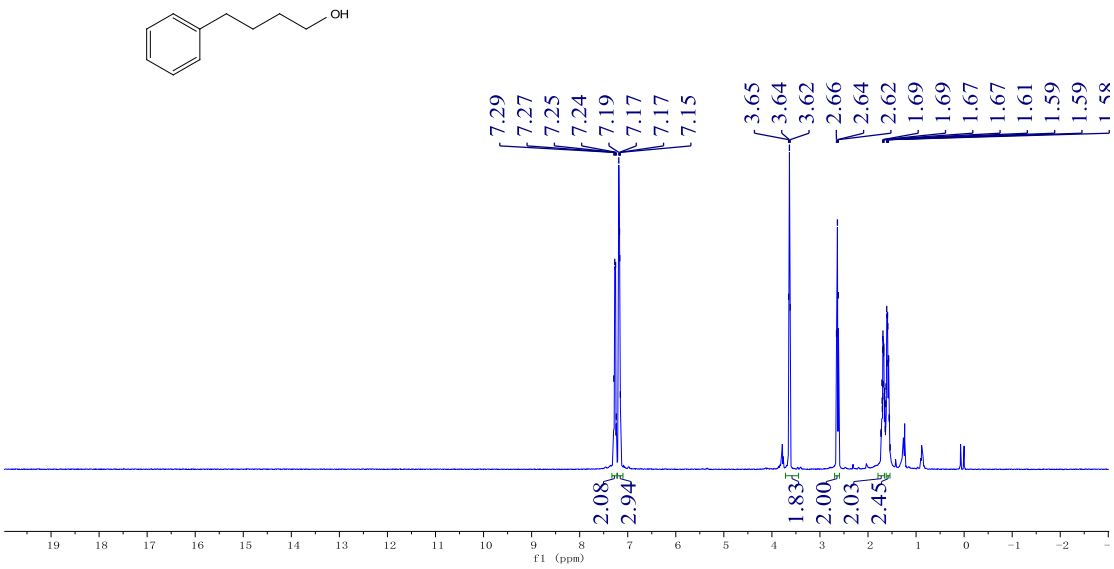

157.81
139.28
130.27
128.50
115.25
114.28
68.19
33.92
29.52
29.45
29.34
29.17
29.01
26.12
18.23
H3CS
f1 (ppm)

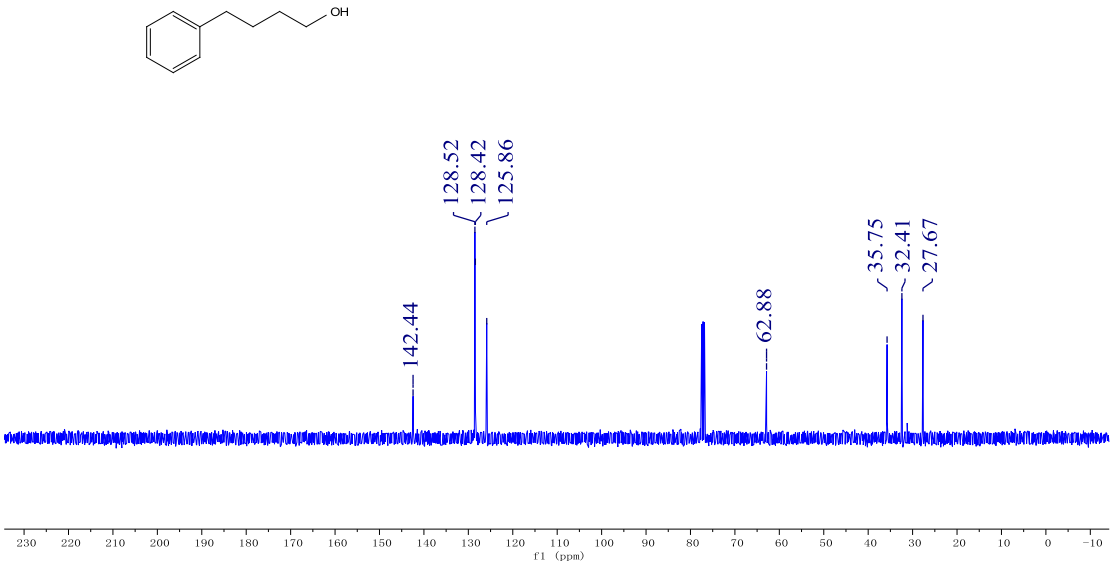

N
N
CH2
7.45
7.45
7.32
7.31
6.19
6.18
6.18
5.78
5.77
5.75
5.73
5.72
5.72
5.71
5.69
4.09
4.07
4.05
1.99
1.99
1.98
1.96
1.83
1.81
1.80
1.34
1.32
1.30
1.30
1.30
1.29
1.28
1.26
1.25
4.96
4.96
4.95
4.92
4.92
4.91
4.90
4.90
4.89
4.88
4.87
4.87
0.99
1.00
1.00
1.00
2.05
2.16
2.18
2.15
6.48
f1 (ppm)

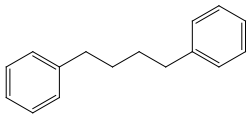

N
N
CH2
138.96
138.81
128.75
114.33
105.09
52.03
33.59
30.38
28.63
28.54
26.40
f1 (ppm)

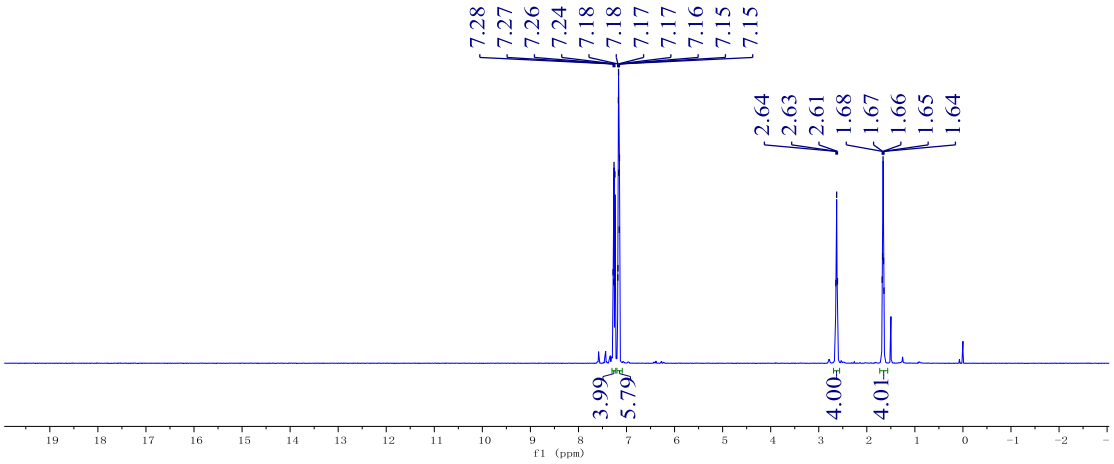

H2C
Me
Me
S
N
Me
2.56
2.38
2.02
2.02
2.02
5.14
5.04
1.00
0.98
3.09
2.96
3.08
f1 (ppm)

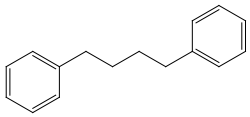

H2C
Me
Me
S
N
Me
162.06
147.15
135.83
133.11
115.94
25.12
18.98
16.82
f1 (ppm)

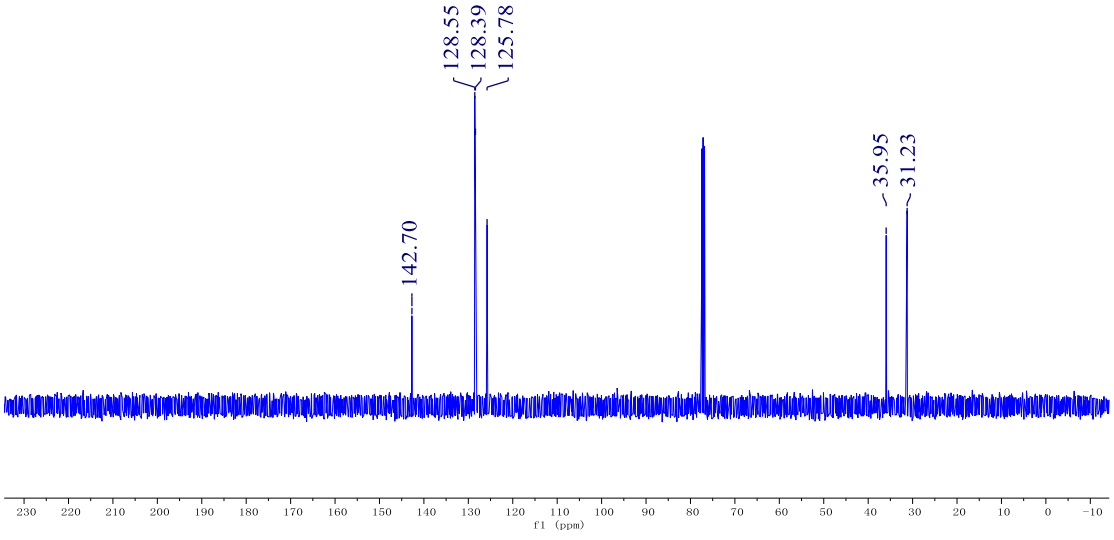

OH
7.29
7.27
7.25
7.24
7.19
7.17
7.17
7.15
3.65
3.64
3.62
2.66
2.64
2.62
1.69
1.69
1.67
1.67
1.61
1.59
1.59
2.08
2.94
1.83
2.00
2.03
2.45
f1 (ppm)

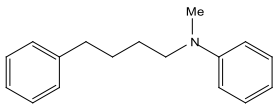

OH
128.52
128.42
125.86
142.44
62.88
35.75
32.41
27.67
f1 (ppm)

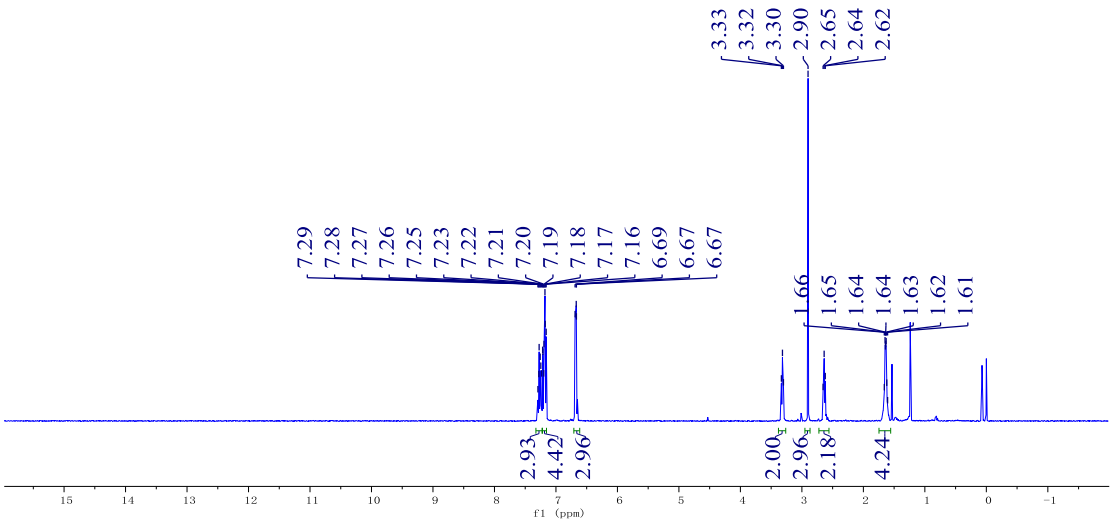


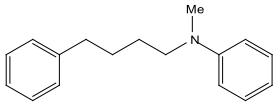

7.28
7.27
7.26
7.24
7.18
7.18
7.17
7.17
7.16
7.15
7.15
2.64
2.63
2.61
1.68
1.67
1.66
1.65
1.64
3.99
5.79
4.00
4.01
f1 (ppm)

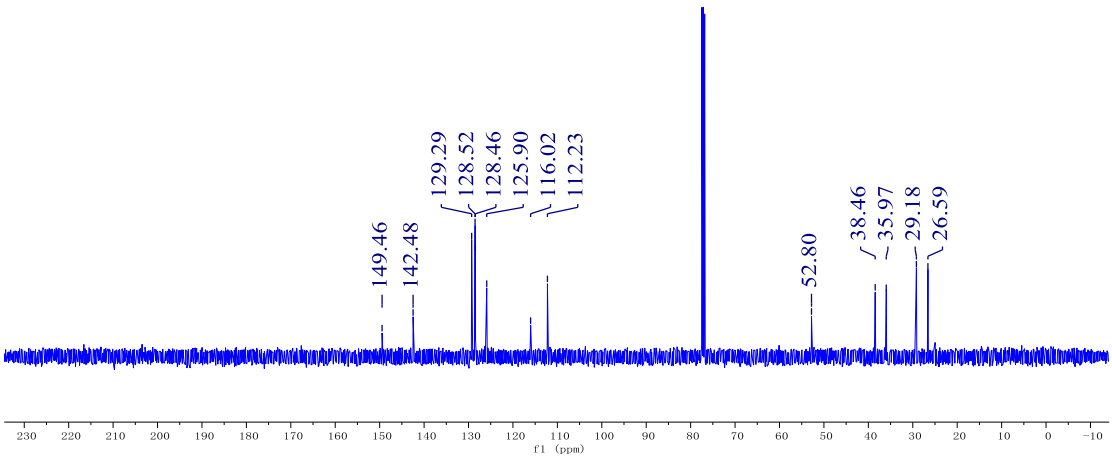



128.55
128.39
125.78
142.70
35.95
31.23
f1 (ppm)


Me
N


3.33
3.32
3.30
2.90
2.65
2.64
2.62
7.29
7.28
7.27
7.26
7.25
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
6.69
6.67
6.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
2.93
4.42
2.96
2.00
2.96
2.18
4.24
f1 (ppm)


Me
N


149.46
142.48
129.29
128.52
128.46
125.90
116.02
112.23
52.80
38.46
35.97
29.18
26.59
f1 (ppm)