Supporting information

Direct oxidation of C(sp2)-C(sp3) bond from benzyltrimethylsilanes to phenols

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1. General information

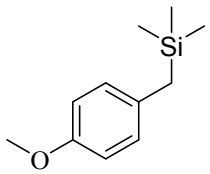
All reagents were purchased from commercial sources unless otherwise noted. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by treatment with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. Flash column chromatography was performed using 300-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^{1}H NMR spectra were reported in δ ppm referenced to an internal $SiMe_4$ standard. Chemical shifts for ^{13}C NMR spectra were reported in parts per million relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The abbreviations s, d, dd, t, q and m stand for the resonance multiplicity singlet, doublet, doublet of doublets, triplet, quartet and multiplet, respectively. GC-MS analysis was performed on 6890N-5973N/Agilent.

2. Preparation and characterization of benzyltrimethylsilanes

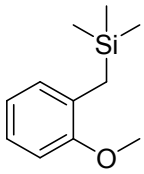
2.1 Preparation of benzyltrimethylsilanes

Benzyltrimethylsilanes **1 - 13, 15 - 20** were prepared according to the literature procedure.[1] An oven-dried two neck round-bottom flask containing magnesium powder (0.18 g, 7.5 mmol, 1.5 equiv), a grain of iodine and dry THF (20 mL) was cooled to 0℃ under nitrogen. Then trimethylsilyl chloride (0.6 mL, 1.2 equiv.) was added, followed by the dropwise addition of a solution of the bromide (5.0 mol, 1.0 equiv.) in THF (5 mL) over a period of 15 min. After the addition was completed, the reaction mixture was stirred overnight and poured 10 mL statured NH_4Cl, The resulting mixture was extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with brine (20 mL), dried $MgSO_4$ and concentrated to obtain the residue. The residue was purified by flash column chromatography to give the benzyltrimethylsilanes.

2.2 Characterization of benzyltrimethylsilanes

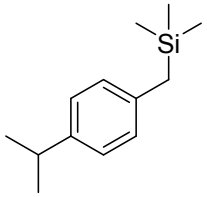


(4-methoxybenzyl)trimethylsilane (1)
Colorless liquid, 79% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.02 (s, 2H), 0.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.46, 132.30, 128.77, 113.61, 55.18, 25.66, -1.96. **GC−MS** (EI, QMS, m/z) 194 (30%), 179 (100%), 121, 73.



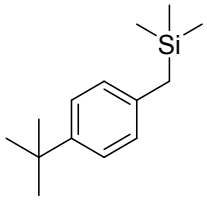
(2-methoxybenzyl)trimethylsilane (2)

Colorless liquid, 82% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 – 6.95 (m, 2H), 6.88 – 6.75 (m, 2H), 3.79 (s, 3H), 2.10 (s, 2H), -0.02 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.42, 129.41, 129.24, 124.93, 120.16, 109.81, 54.83, 20.47, -1.59. **GC−MS** (EI, QMS, m/z) 194 (50%), 179(100%), 164, 149, 73.



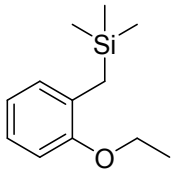
(4-isopropylbenzyl)trimethylsilane (3)

Colorless liquid, 90% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 5.0, 2.6 Hz, 2H), 6.98 (dd, *J* = 7.7, 2.2 Hz, 2H), 3.12 – 2.77 (m, 1H), 2.09 (s, 2H), 1.31 (s, 6H), 0.04 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.23, 137.52, 127.94, 126.12, 33.54, 26.43, 24.12, -1.86. **GC−MS** (EI, QMS, m/z) 206 (31%), 191, 113, 73 (100%).



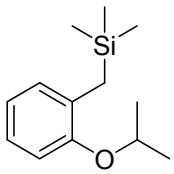
(4-(tert-butyl)benzyl)trimethylsilane (4)

Colorless crystal, 85% yield; m.p 33.1-33.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 2.08 (s, 2H), 1.34 (s, 9H), 0.04 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 146.48, 137.14, 127.68, 124.94, 34.17, 31.45, 26.28, -1.85. **GC−MS** (EI, QMS, m/z) 220 (28%), 205, 117, 73 (100%).

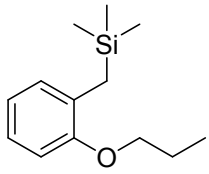


(2-ethoxybenzyl)trimethylsilane (5).

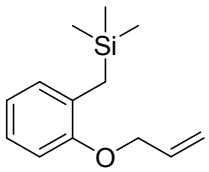
Colorless liquid, 79% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 6.97 (m, 1H), 6.90 – 6.76 (m, 1H), 4.02 (q, J = 7.0 Hz, 1H), 2.14 (s, 1H), 1.45 (t, J = 7.0 Hz, 1H), 0.01 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 155.74, 129.41, 129.20, 124.85, 119.92, 110.46, 62.86, 20.44, 14.95, -1.51. **GC−MS** (EI, QMS, m/z) 208 (34%), 179 (100%), 163, 149, 73.



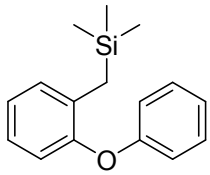
(2-isopropoxybenzyl)trimethylsilane (6).
Colorless liquid, 72% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 – 6.74 (m, 4H), 4.65 – 4.49 (m, 1H), 2.14 (s, 2H), 1.38 (d, J = 6.0 Hz, 6H), 0.03 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 154.49, 129.96, 129.67, 124.71, 119.62, 111.76, 68.88, 22.16, 20.49, -1.34. **GC−MS** (EI, QMS, m/z) 222 (41%), 179 (100%), 165, 149, 173.



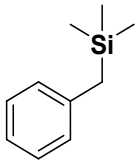
trimethyl(2-propoxybenzyl)silane (7).
Colorless liquid, 80% yield; **^{1}H NMR** (400 MHz, CDCl3) δ 7.12 – 6.75 (m, 4H), 3.89 (t, J = 6.5 Hz, 2H), 2.13 (s, 2H), 1.91 – 1.75 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H), -0.01 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 155.83, 129.35, 129.25, 124.84, 119.88, 110.52, 68.97, 22.79, 20.27, 10.78, -1.52. **GC−MS** (EI, QMS, m/z) 222 (30%), 179 (100%), 163, 149, 73.



(2-(allyloxy)benzyl)trimethylsilane (8).
Colorless liquid, 66% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 6.95 (m, 2H), 6.93 – 6.71 (m, 2H), 6.23 – 5.99 (m, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 10.6 Hz, 1H), 4.59 – 4.45 (m, 2H), 2.16 (s, 2H), 0.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.40, 133.79, 129.51, 129.46, 124.85, 120.33, 116.70, 111.01, 68.40, 20.46, -1.54. **GC−MS** (EI, QMS, m/z) 220 (16%), 193, 179, 163, 149, 135, 73 (100%).

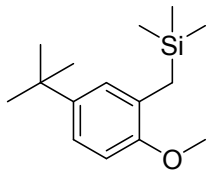


trimethyl(2-phenoxybenzyl)silane (9).
Colorless liquid, 75% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 6.84 (m, 9H), 2.12 (s, 2H), 0.05 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.51, 153.37, 132.30, 130.35, 129.61, 125.20, 123.47, 122.42, 118.93, 117.83, 20.75, -1.42. **GC−MS** (EI, QMS, m/z) 256 (34%), 241, 225, 151, 73 (100%).



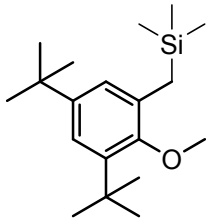
Benzyltrimethylsilane (10)

Colorless liquid, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 6.92 (m, 5H), 2.11 (s, 2H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.48, 128.10, 128.02, 123.83, 27.05, -1.93. GC−MS (EI, QMS, m/z) 164 (30%), 149, 121, 73 (100%).



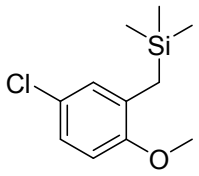
(5-tert-butyl-2-methoxybenzyl)trimethylsilane (11).

Colorless liquid, 71% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 6.96 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 2.12 (s, 2H), 1.32 (s, 9H), 0.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.25, 142.61, 128.34, 126.98, 121.19, 109.18, 54.91, 33.86, 31.54, 20.61, -1.62. **GC−MS** (EI, QMS, m/z) 250 (26%), 235 (100%), 219, 205, 73.



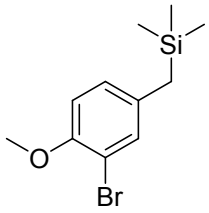
(3,5-di-tert-butyl-2-methoxybenzyl)trimethylsilane (12).

Colorless liquid, 60% yield; **^{1}H NMR** (400 MHz, CDCl3) δ 7.07 (d, J = 2.5 Hz, 1H), 6.89 (d, J = 2.5 Hz, 1H), 3.74 (s, 3H), 2.12 (s, 2H), 1.40 (s, 9H), 1.31 (s, 9H), -0.02 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.88, 144.96, 141.56, 132.86, 125.56, 120.00, 60.67, 35.10, 34.28, 31.57, 31.18, 21.44, -1.35. **GC−MS** (EI, QMS, m/z) 306 (23%), 291 (100%), 276, 261, 73, 57.



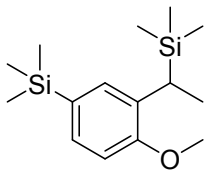
(5-chloro-2-methoxybenzyl)trimethylsilane (13)

Colorless liquid, 52% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.94 (d, *J* = 2.6 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 3.76 (s, 3H), 2.06 (s, 2H), -0.02 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.04, 131.44, 128.86, 124.91, 124.48, 110.79, 55.13, 20.62, -1.65. **GC−MS** (EI, QMS, m/z) 228(34%), 213, 198, 183, 120, 73.



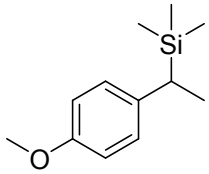
(3-bromo-4-methoxybenzyl)trimethylsilane (14)

To 50 ml flask was added (4-methoxybenzyl)trimethylsilane (**1**) (0.97 g, 5 mmol), LiBr (0.47 g, 5.5 mmol, 1.1 equiv.), $Na_2S_2O_8$ (1.78 g, 7.5 mmol,) and CH_3CN (20 mL) , the mixture was stirred at 55 ℃ for 6 h, After the reaction was completed, the solvent was concentrated in vacuo. The residue was purified by flash column chromatography to give **14**. Yellow liquid: 63% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.1 Hz, 1H), 6.88 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 1.98 (s, 2H), -0.01 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ: 152.68, 134.20, 132.47, 127.70, 111.92, 111.24, 56.25, 25.47, -2.00. **GC−MS** (EI, QMS, m/z) 272 (16%), 257, 90, 73 (100%).



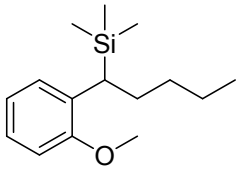
(4-methoxy-3-(1-(trimethylsilyl)ethyl)phenyl)trimethylsilane (15).

Colorless liquid, 60% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.14 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 2.69 (q, *J* = 7.6 Hz, 1H), 1.32 (d, *J* = 7.6 Hz, 3H), 0.24 (s, 9H), -0.09 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.91, 133.93, 132.04, 130.53, 130.14, 109.16, 54.80, 20.73, 14.52, -0.91, -3.18. **GC−MS** (EI, QMS, m/z) 280 (45%), 265(100%), 235, 177, 73.

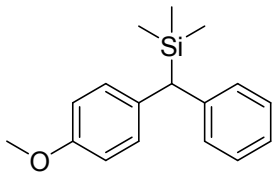


(1-(4-methoxyphenyl)ethyl)trimethylsilane (16).

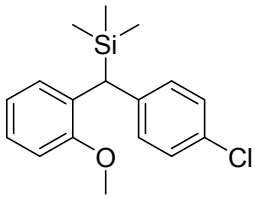
Colorless liquid, 90% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 16.9 Hz, 2H), 3.80 (s, 3H), 2.13 (q, *J* = 7.6 Hz, 1H), 1.36 (d, *J* = 7.6 Hz, 3H), -0.03 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.67, 137.89, 127.35, 113.45, 55.15, 28.56, 15.04, -3.33. **GC−MS (EI, QMS, m/z)** 208 (10%), 193(100%), 177, 165, 135, 73.



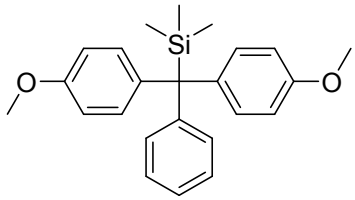
(1-(2-methoxyphenyl)pentyl)trimethylsilane (17).
Colorless liquid, 63% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 6.81 (m, 4H), 3.79 (s, 3H), 2.63 (dd, *J* = 11.3, 4.4 Hz, 1H), 1.95 – 1.65 (m, 2H), 1.42 – 1.16 (m, 4H), 0.86 (t, *J* = 6.6 Hz, 3H), -0.07 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.97, 132.64, 127.14, 124.63, 120.26, 109.92, 55.03, 31.57, 28.55, 27.50, 22.62, 13.98, -2.85. **GC−MS** (EI, QMS, m/z) 250 (23%), 235, 179(100%), 163, 73.



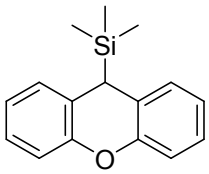
((4-methoxyphenyl)(phenyl)methyl)trimethylsilane (18)
White solid, 70% yield; m.p 51.6-52.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.11 (m, 7H), 6.94 – 6.82 (m, 2H), 3.82 (s, 3H), 3.51 (s, 1H), 0.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.22, 143.36, 135.00, 129.75, 128.48, 128.21, 124.88, 113.70, 55.16, 44.88, -1.70. **GC−MS** (EI, QMS, m/z) 270 (18%), 179, 163, 91 (100%), 73.



((4-chlorophenyl)(2-methoxyphenyl)methyl)trimethylsilane (19).
White solid, 71% yield; m.p 53.6-54.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.1 Hz, 1H), 7.19 – 7.06 (m, 5H), 6.93 – 6.79 (m, 2H), 3.96 (s, 1H), 3.74 (s, 3H), 0.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.87, 141.95, 131.09, 130.29, 130.08, 129.92, 128.07, 126.57, 120.35, 110.69, 55.17, 37.01, -1.48. **GC−MS** (EI, QMS, m/z) 304 (7%), 289, 195, 165, 125, 73 (100%).



(bis(4-methoxyphenyl)(phenyl)methyl)trimethylsilane (20).
Light yellow solid, 71% yield; m.p 66.5-67.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.13 (m, 3H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 6H), 0.13 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 157.13, 147.34, 139.10, 130.93, 129.80, 127.81, 125.18, 113.15, 55.14, 51.72, 1.62. **GC−MS** (EI, QMS, m/z) 376(< 1%), 361 (100%), 303, 73.



trimethyl(9H-xanthen-9-yl)silane (21)[2]

To 50 ml flask was added 9H-xanthene (0.91 g, 5 mmol) and dry THF (10 ml) under N_2 , then the mixture was cooled to -78 ℃, followed by the dropwise addition of a solution of the n-BuLi (5 ml, 1.2 N in THF), the mixture went on stirring for 2 h. trimethylsilyl chloride (0.6 mL, 6 mmol 1.2 equiv.) was added, the reaction mixture was stirred for 3 h and poured 10 mL statured NH_4Cl, The resulting mixture was extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with brine (20 mL), dried $MgSO_4$ and concentrated to obtain the residue. The residue was purified by flash column chromatography to give the benzyltrimethylsilanes **21**. Yellow solid, 70% yield; m.p 119.0-120.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 2H), 7.03 – 6.91 (m, 6H), 3.38 (s, 1H), -0.04 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.92, 127.49, 126.12, 125.40, 122.99, 116.13, 34.71, -3.36. **GC−MS** (EI, QMS, m/z) 254 (27%), 239, 181 (100%), 152, 73.

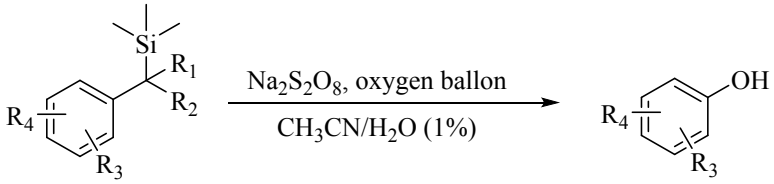
References:

[1] A. R. Beard, S. J. Hazell, J. Mann, et al. *Chem. Soc., Perkin Trans. 1*, 1993, **11**, 1235.

[2] V. Georgakilas, G. P. Perdikomatis, A. S. Triantafyllou, et al. *Tetrahedron*, 2002, **58**, 2441.

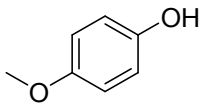
3. General procedure for oxidation of benzylsilanes and spectral data of products

3.1 General Procedure for oxidation of benzylsilanes



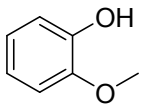
Benzyltrimethylsilane (0.2 mmol) and $Na_2S_2O_8$ (70.2 mg, 0.3 mmol) were placed in a 5 mL tube. The tube was evacuated and backfilled with O_2. Then CH_3CN (2.0 mL) was added, the reaction mixture was stirred at 55 ℃ and monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography to afford phenol product.

3.2 Spectral data of products



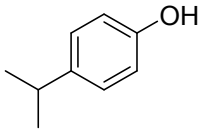
2-methoxyphenol (1a)

White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, J = 9.6 Hz, 2H), 6.77 (d, J = 9.6 Hz, 2H), 4.53 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.60, 149.44, 116.04, 114.85, 55.81. MS: $[M]^+$ found 124.



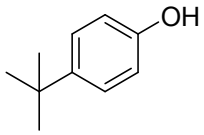
2-methoxyphenol (2a)

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.78 (m, 4H), 5.64 (s, 1H), 3.87 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 146.54, 145.64, 121.42, 120.10, 114.50, 110.69, 77.32, 77.00, 76.68, 55.82. MS: $[M]^+$ found 124.



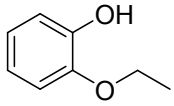
4-isopropylphenol(3a)

White solid, m.p 61.8-63.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.68 (s, 1H), 3.00 – 2.73 (m, 1H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.43, 141.22, 127.44, 115.04, 77.32, 77.00, 76.68, 33.26, 24.19. MS: $[M]^+$ found 136.



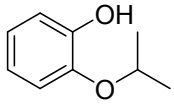
4-(tert-butyl)phenol (4a)

White solid, m.p 97.1-97.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.66 (s, 1H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.11, 143.47, 126.41, 114.70, 34.05, 31.51. MS: $[M]^+$ found 150.



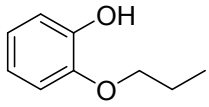
2-ethoxyphenol (5a).

Light yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.75 (m, 4H), 5.70 (s, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.77, 145.73, 121.27, 120.03, 114.42, 111.55, 64.34, 14.84. MS: $[M]^+$ found 138.



2-isopropoxyphenol (6a).

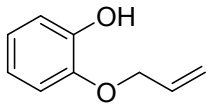
Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.81 (m, 4H), 5.80 (s, 1H), 4.59 (hept, *J* = 6.1 Hz, 1H), 1.38 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.58, 144.54, 121.34, 119.94, 114.56, 113.32, 77.21, 77.00, 76.79, 71.51, 22.10. . MS: $[M]^+$ found 152.



2-propoxyphenol (7a).

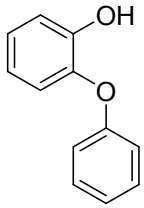
Light yellow liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.66 (m, 4H), 5.73 (s, 1H),

3.96 (t, J = 6.6 Hz, 2H), 1.87 – 1.74 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 145.77, 121.21, 119.98, 114.41, 111.61, 77.32, 77.00, 76.68, 70.27, 22.46, 10.36. MS: $[M]^+$ found 152.



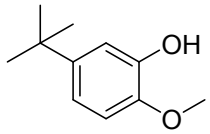
2-(allyloxy)phenol (8a).

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.76 (m, 4H), 6.04 (ddd, J = 21.5, 10.7, 5.5 Hz, 1H), 5.71 (s, 1H), 5.39 (dd, J = 18.0, 2.2 Hz, 1H), 5.30 (dd, J = 10.5, 1.3 Hz, 1H), 4.58 (dt, J = 5.5, 1.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.83, 145.47, 132.81, 121.68, 120.01, 118.25, 114.68, 112.15, 69.73. MS: $[M]^+$ found 150.



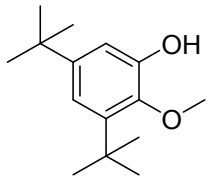
2-phenoxyphenol (9a).

Light yellow solid, m.p 102.1-102.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 8.0 Hz, 2H), 7.19 – 7.00 (m, 5H), 6.95 – 6.80 (m, 2H), 5.63 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.75, 147.49, 143.46, 129.85, 124.75, 123.58, 120.60, 118.87, 117.97, 116.17. MS: $[M]^+$ found 186



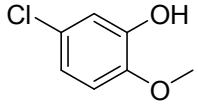
5-tert-butyl-2-methoxyphenol (10a).

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 2.3 Hz, 1H), 6.90 – 6.75 (m, 2H), 3.87 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.02, 144.79, 144.26, 116.45, 112.14, 110.15, 55.94, 34.20, 31.44. MS: $[M]^+$ found 186



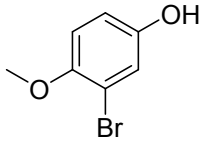
3, 5-di-tert-butyl-2-methoxyphenol (11a)

White solid. m.p 123.0-124.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 2.3 Hz, 1H), 6.87 (d, J = 2.3 Hz, 1H), 5.18 (s, 1H), 3.82 (s, 3H), 1.40 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.81, 146.91, 144.26, 142.10, 115.79, 111.63, 60.89, 35.27, 34.58, 31.42, 31.04. MS: $[M]^+$ found 236



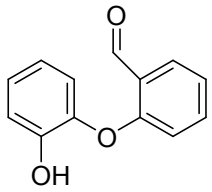
5-chloro-2-methoxyphenol (12a).

Light yellow solid, m.p 213.5-215.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 2.4 Hz, 1H), 674 - 6.83 (m, 2H), 5.65 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.29, 145.36, 126.18, 119.77, 115.05, 111.30, 77.32, 77.00, 76.68, 56.14. MS: $[M]^+$ found 158.



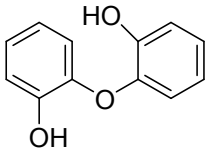
3-bromo-4-methoxyphenol (13a)

Light yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 2.7 Hz, 1H), 6.84 – 6.74 (m, 2H), 4.72 (s, 1H), 3.87 (d, J = 11.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.37, 149.75, 120.49, 114.91, 113.00, 111.88, 56.85. MS: $[M]^+$ found 202.



2-(2-hydroxyphenoxy)benzaldehyde (21a)

White solid. m.p 117.6-118.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.92 (dd, J = 7.7, 1.7 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.16 – 7.04 (m, 2H), 6.98 – 6.82 (m, 3H), 5.94 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.44, 159.10, 147.76, 142.92, 135.94, 129.58, 126.63, 125.92, 123.75, 120.91, 119.80, 117.68, 116.96. MS: $[M]^+$ found 214.



2,2'-oxydiphenol (21b)

White solid. m.p 120.3-121.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 - 7.04 (m, 4H), 6.85 - 6.83 (m, 4H), 5.68 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.01, 143.31, 125.06, 120.89, 118.07, 116.46. MS: $[M]^+$ found 202.

4. Isotope labeling trials

Both H_2O^{18} and O_2^{18} labeling trials of substrate **19** were carried under standard conditions. GCMS perform conditions: oven start with 100 ℃(1 min), then 30 ℃/min elevate to 240 ℃. GCMS analysis showed that peaks holding at 3.26 min and 3.56 min indicated 2-methoxyphenol and 4-Chlorobenzaldehyde respectively.

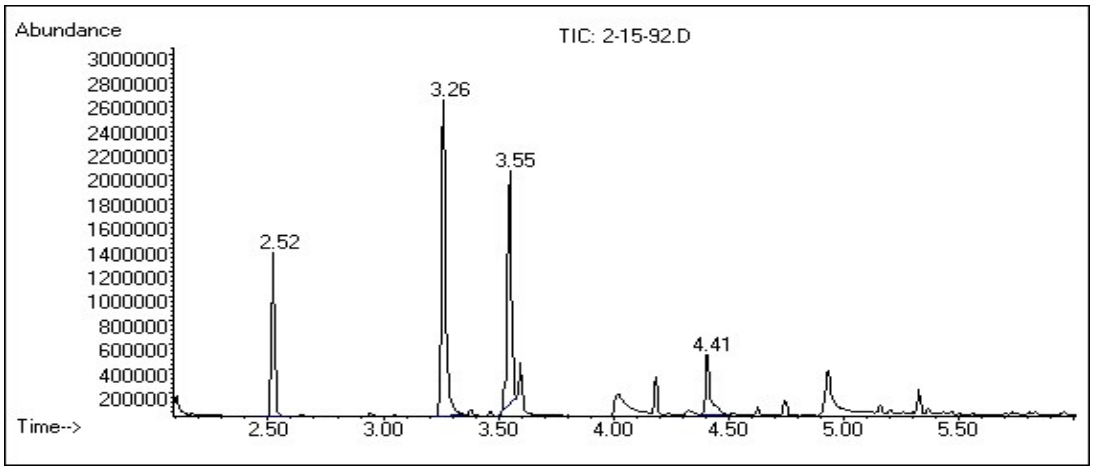


Figure 4-1. Total ion chromatography of substrate 19 subjected to H_2O^{18}

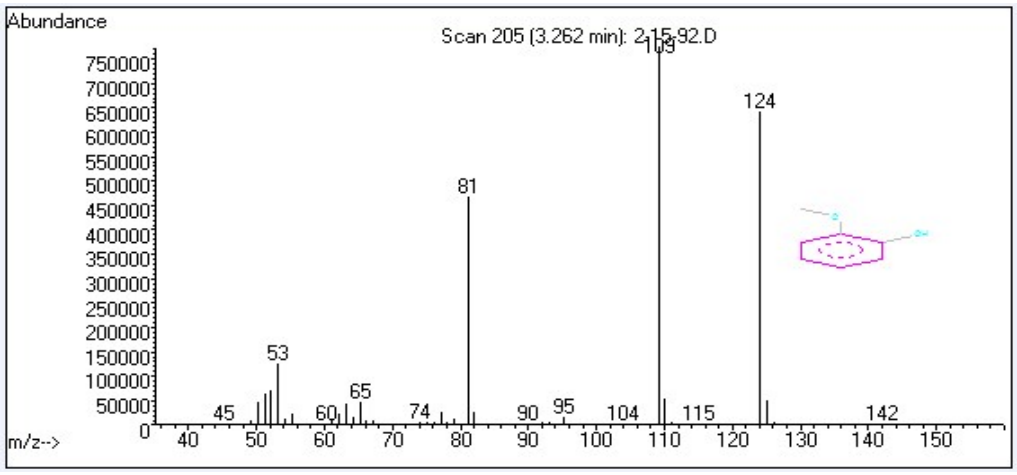


Figure 4-2. Total ion chromatography of H_2O^{18} labeling experiment

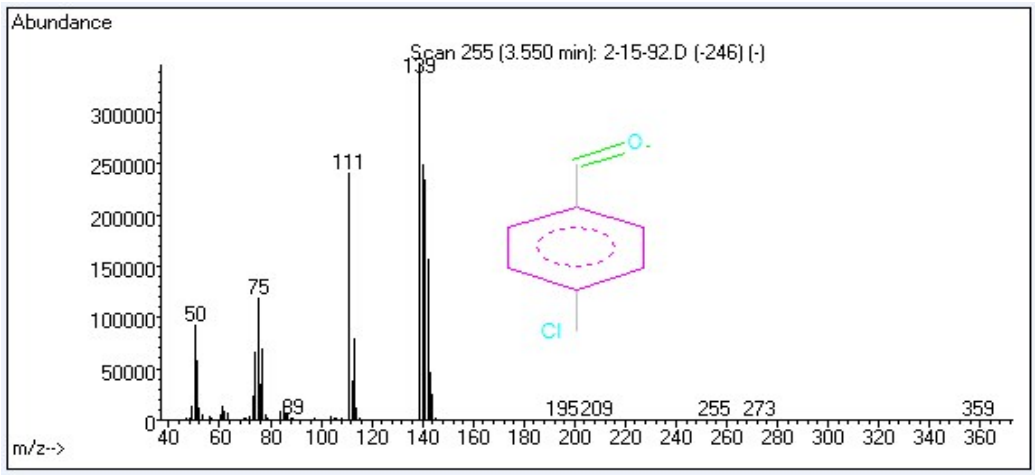


Figure 4-3 Mass spectrum of 4-Chlorobenzaldehyde from H_2O^{18} labeling trial

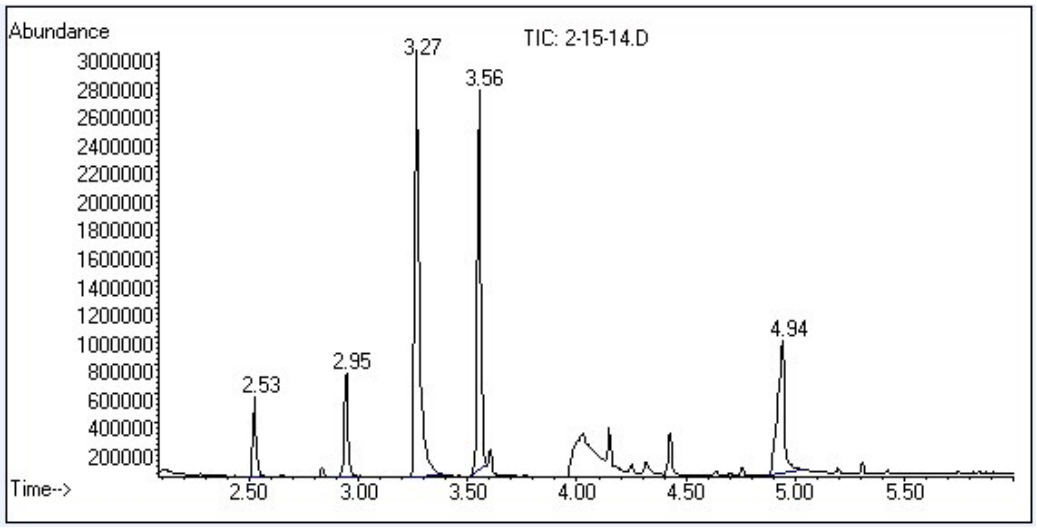


Figure 4-4 Total ion chromatography of substrate 19 subjected to $^{18}O_2$

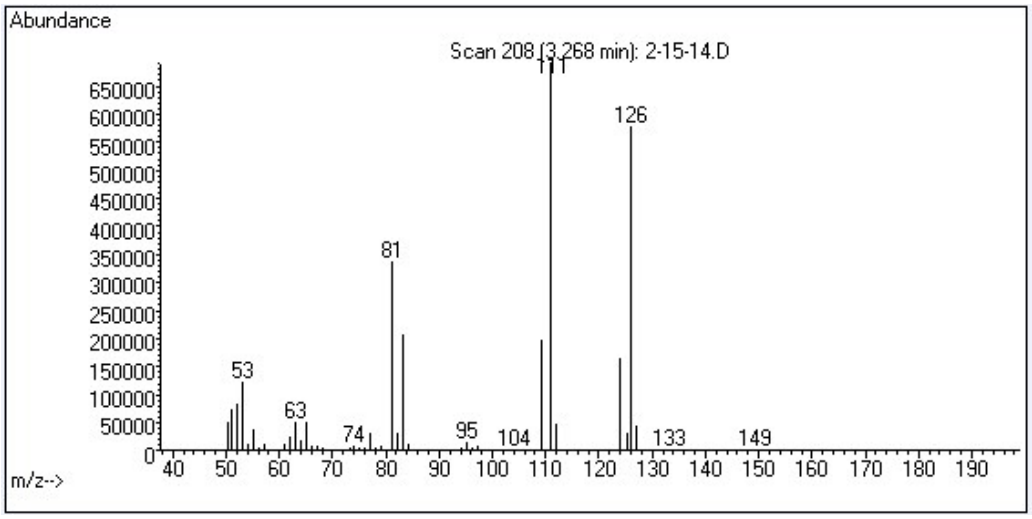


Figure 4-5 Mass spectrum of 2-methoxyphenol (2b) from $^{18}O_2$ labeling trial

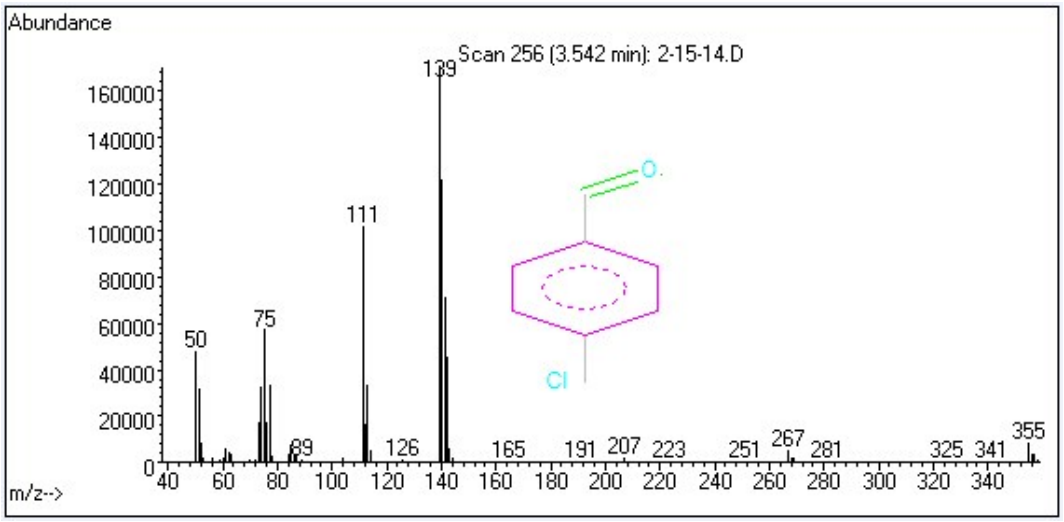
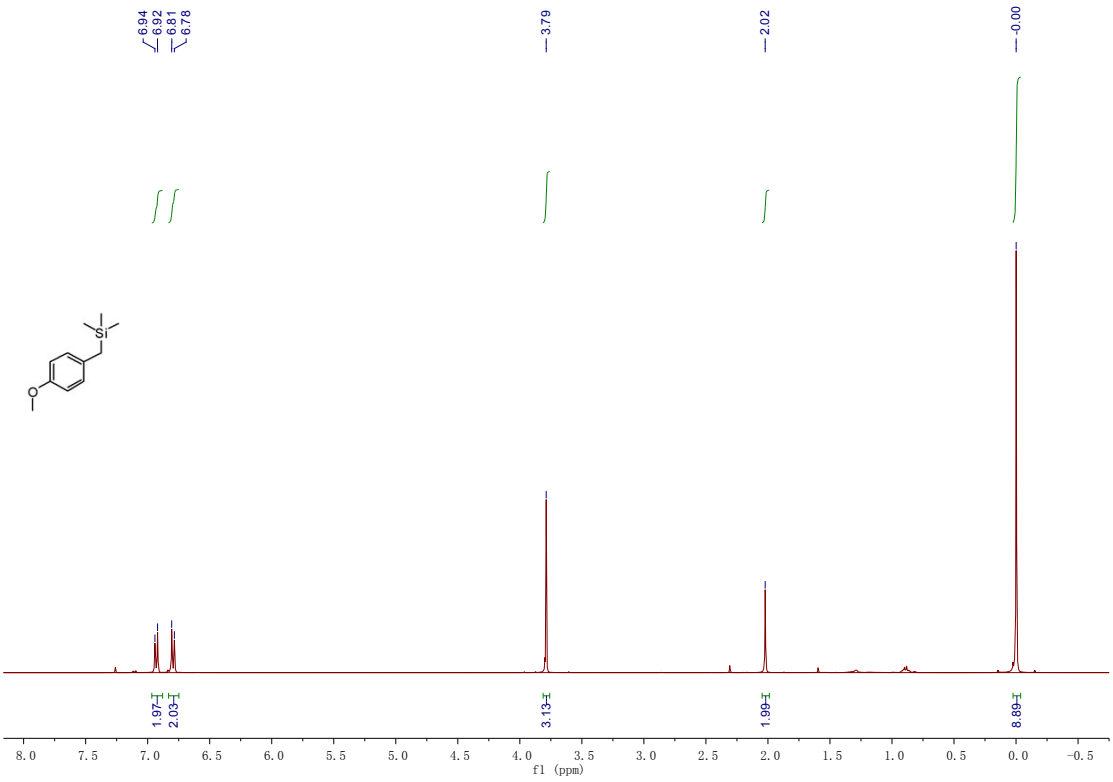
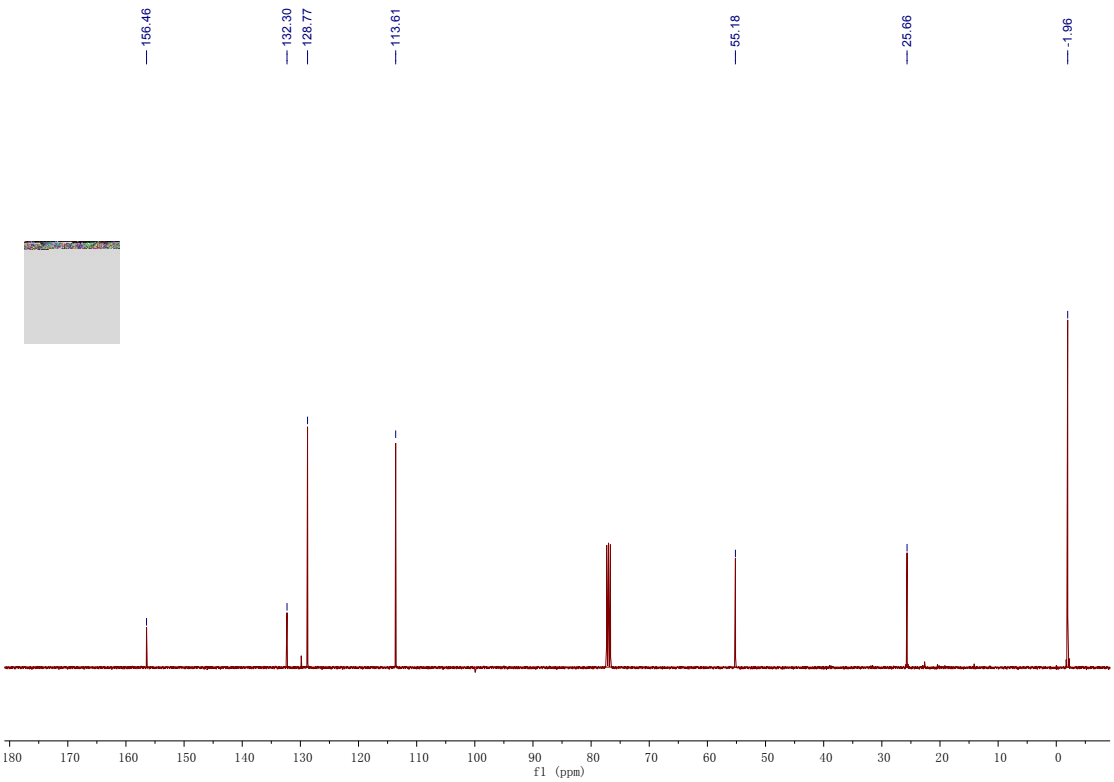


Figure 4-6 Mass spectrum of 4-Chlorobenzaldehyde from $^{18}O_2$ labeling trial

5. NMR spectrum of benzyltrimethylsilanes

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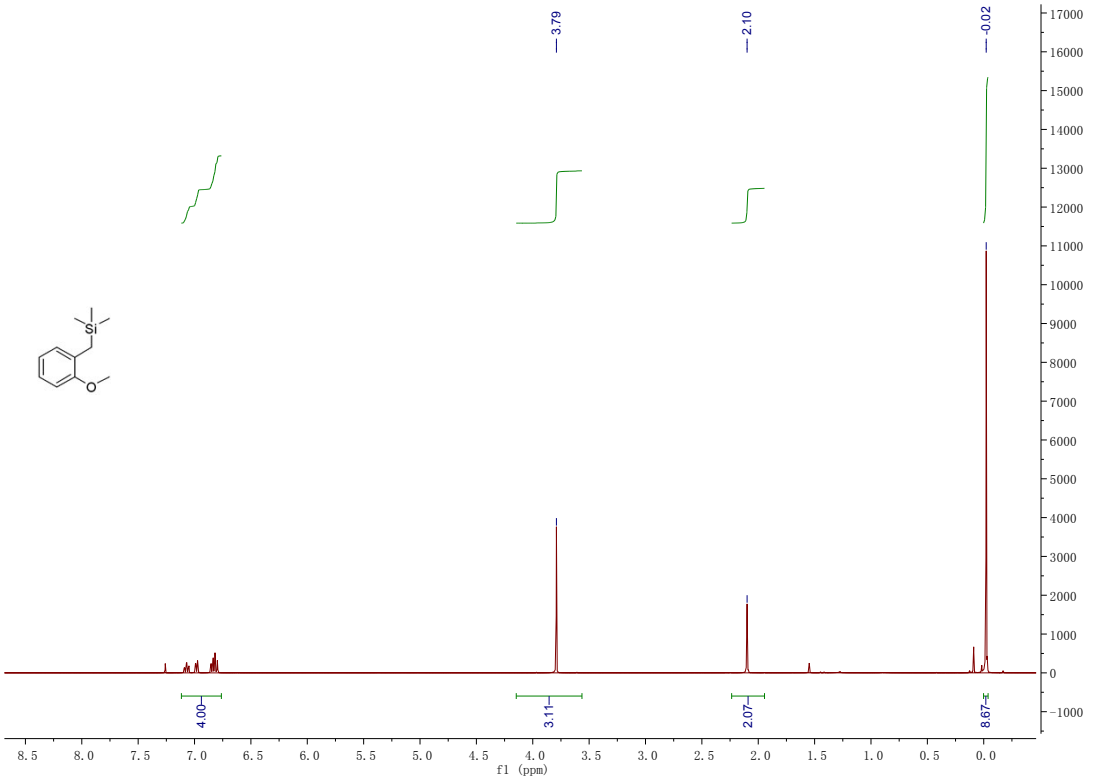
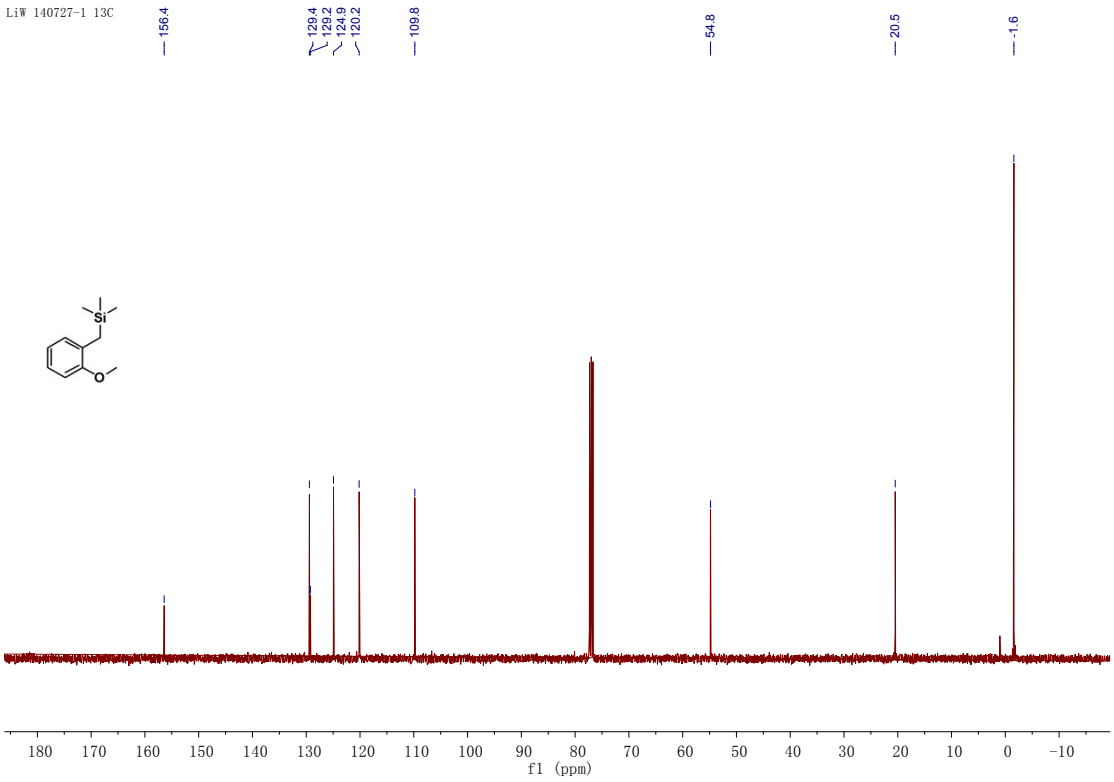
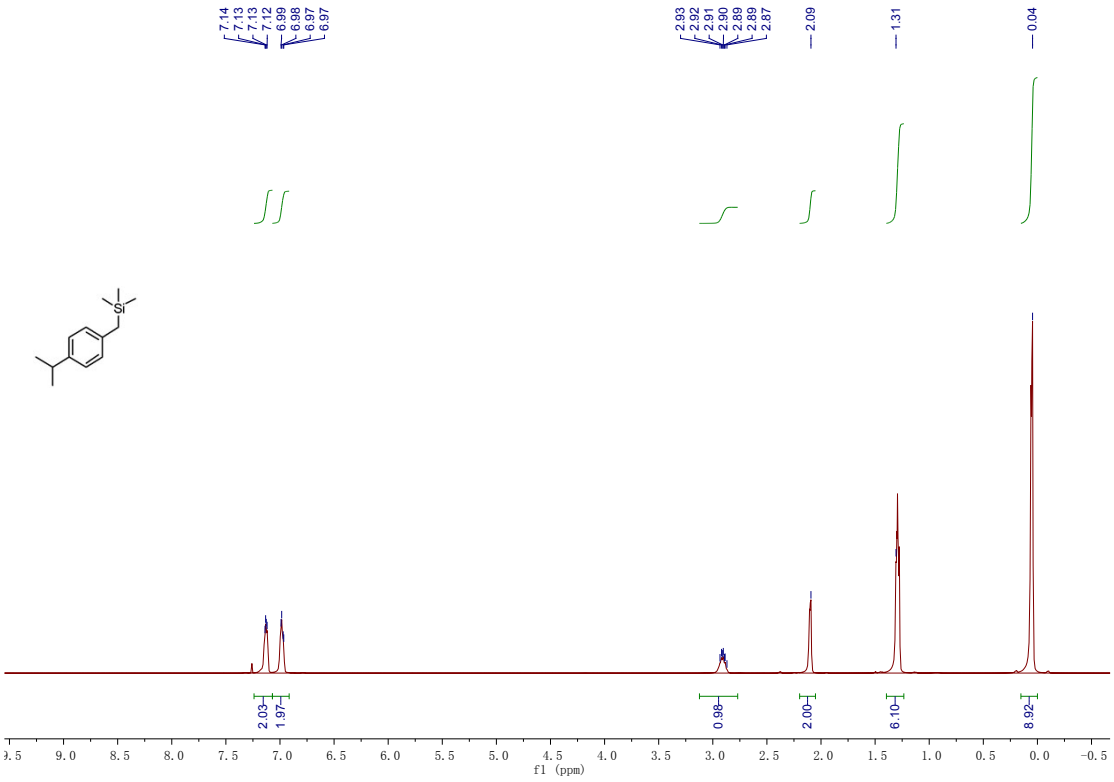
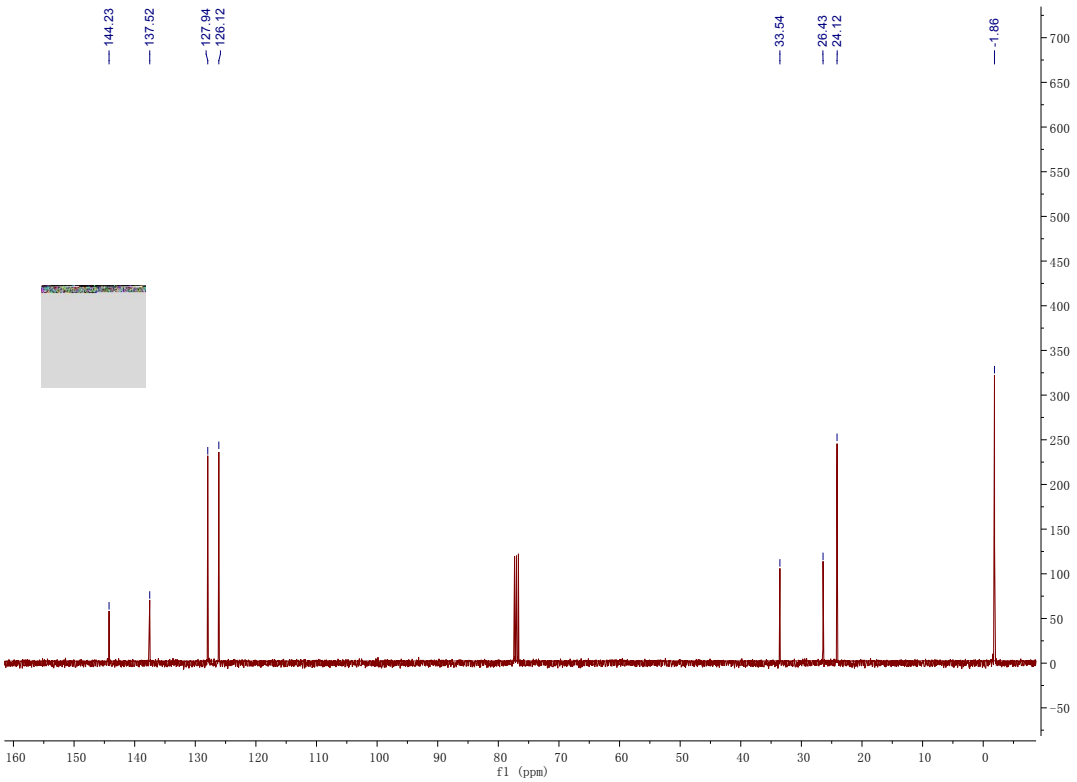
132.30
128.77
113.61
55.18
25.66
-1.96
f1 (ppm)


3.79
2.10
-0.02
Si
O
4.00
3.11
2.07
8.67
f1 (ppm)

LiW 140727-1 13C



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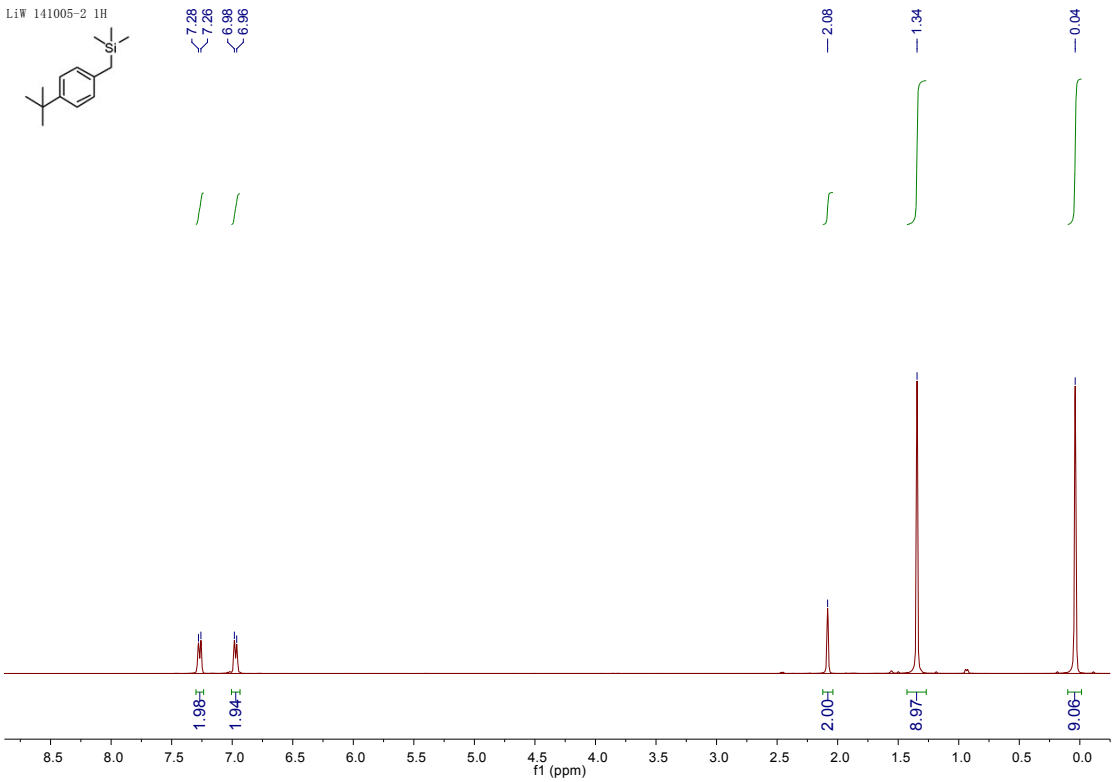
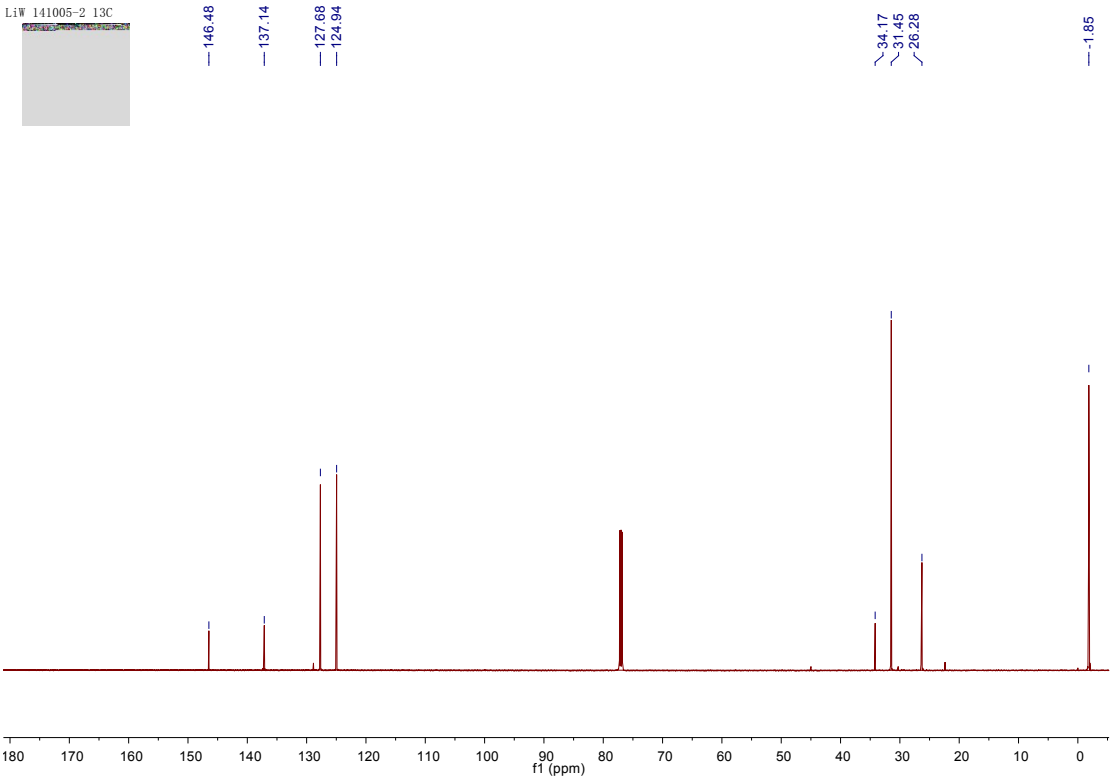
137.52
127.94
126.12
33.54
26.43
24.12
1.86
f1 (ppm)


LiW 141005-2 1H
Si
7.28
7.26
6.98
6.96
2.08
1.34
0.04
1.98
1.94
2.00
8.97
9.06
f1 (ppm)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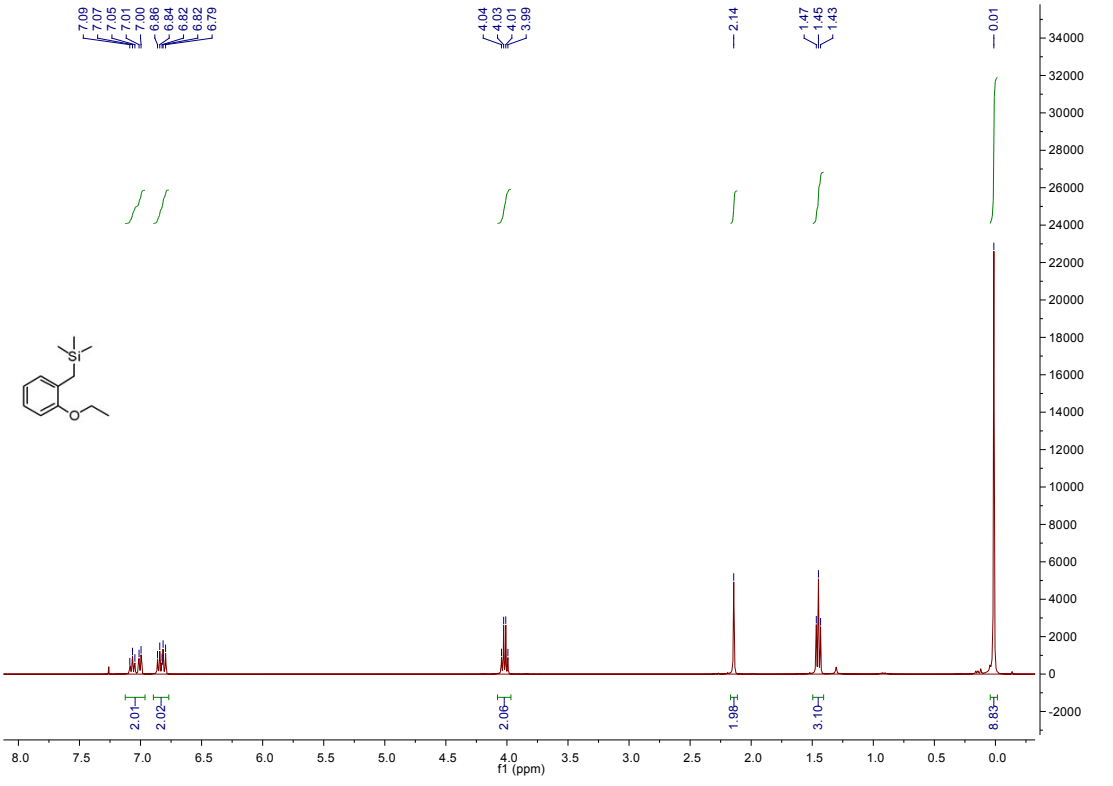
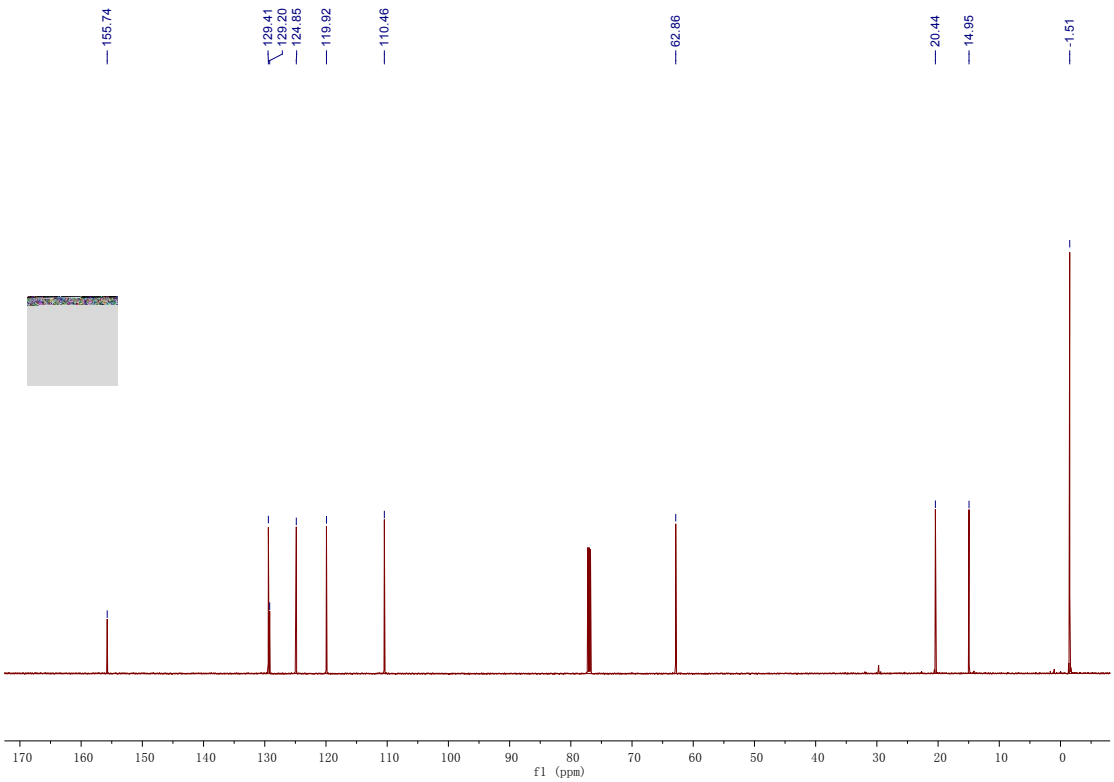
31.45
26.28
-1.85
f1 (ppm)


7.09
7.07
7.05
7.01
7.00
6.86
6.84
6.82
6.82
6.79
4.04
4.03
4.01
3.99
2.14
1.47
1.45
1.43
0.01
Si
O
2.01
2.02
2.06
1.98
3.10
8.83
f1 (ppm)


155.74
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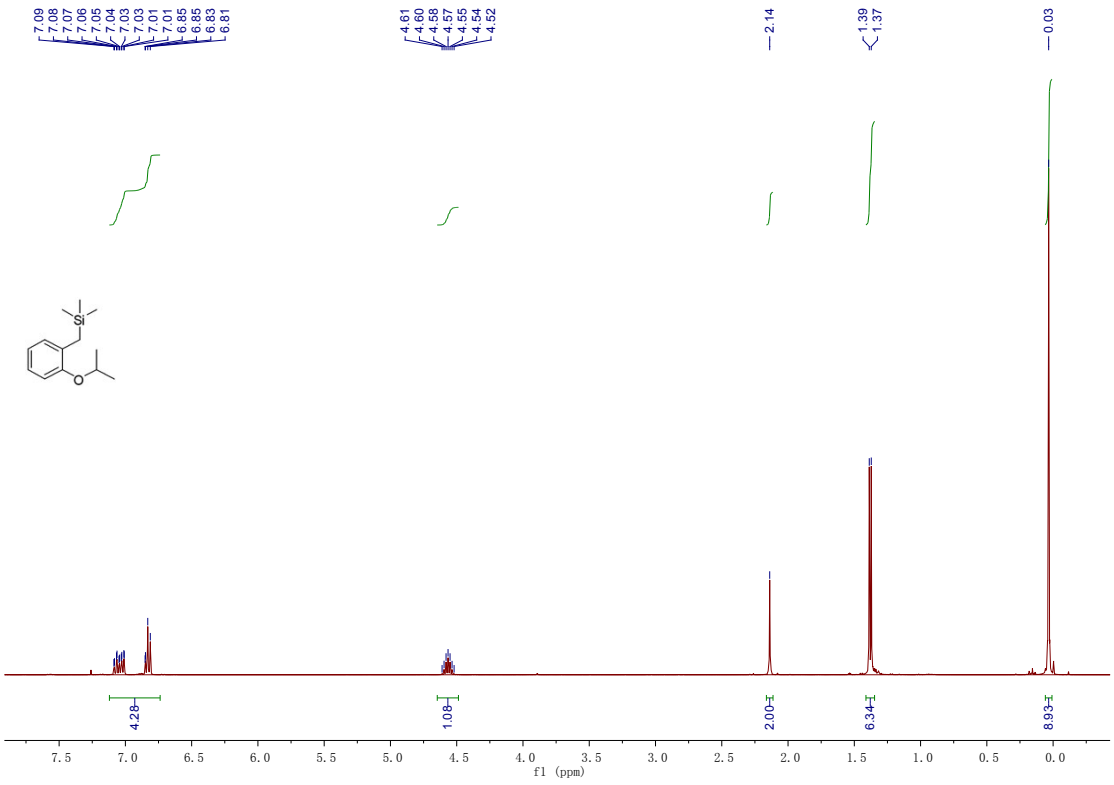
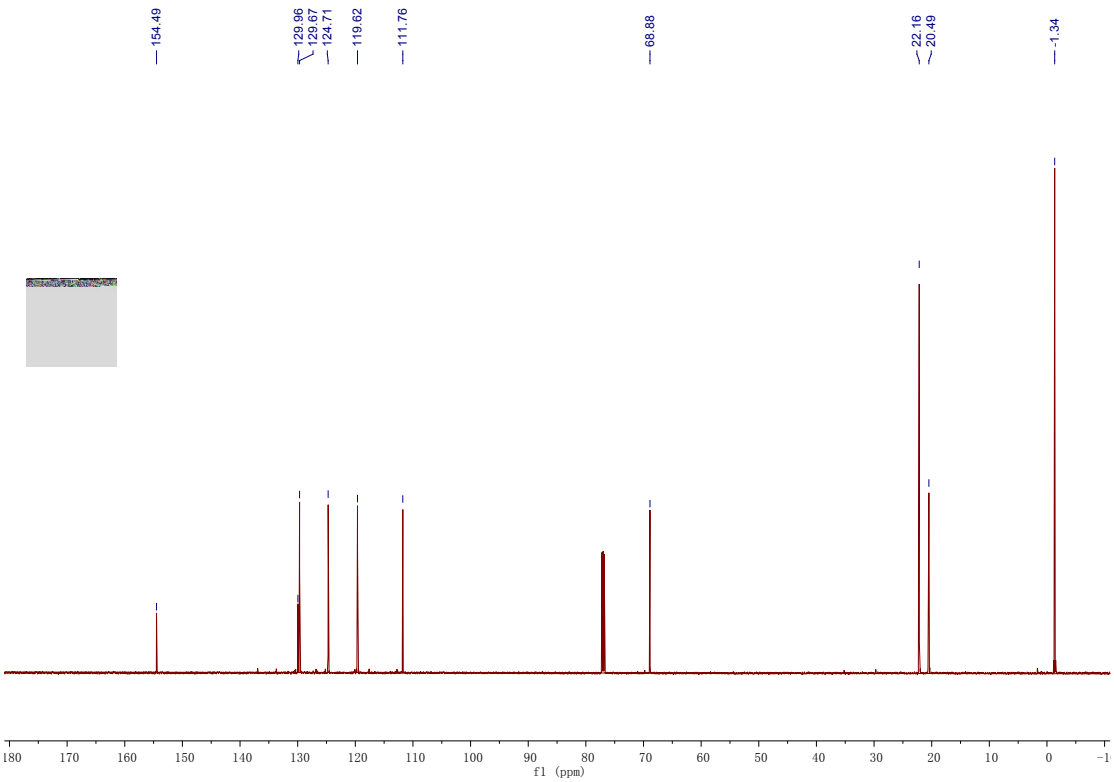
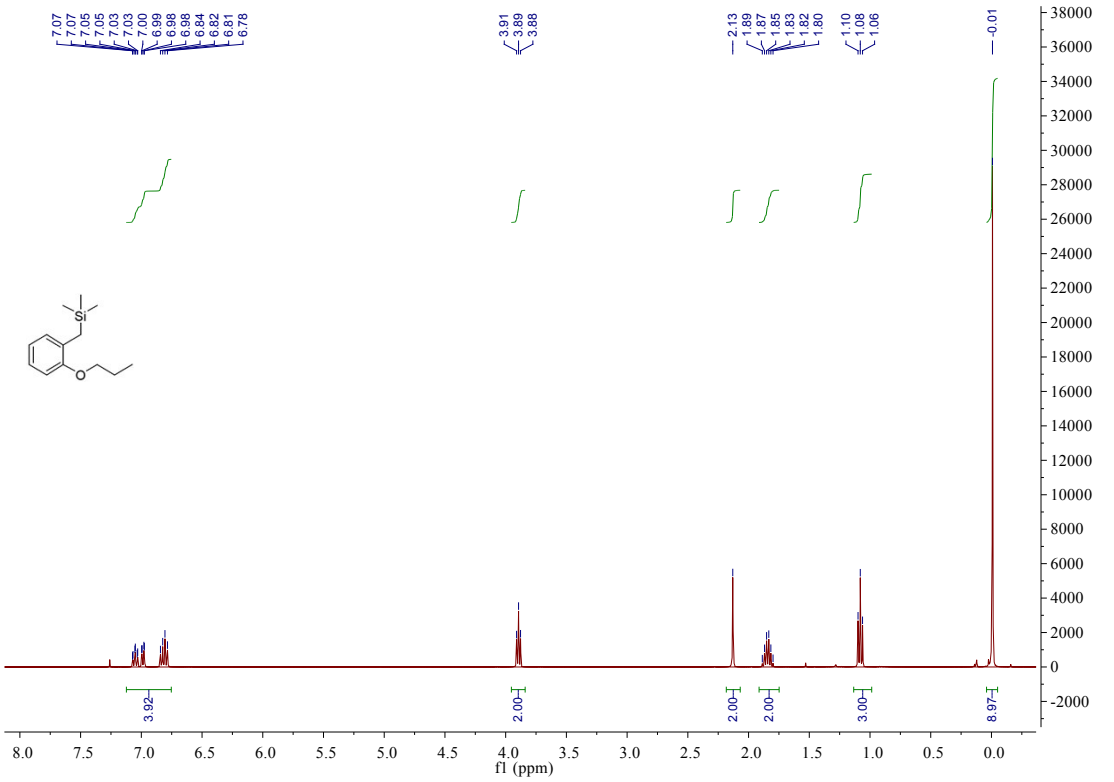
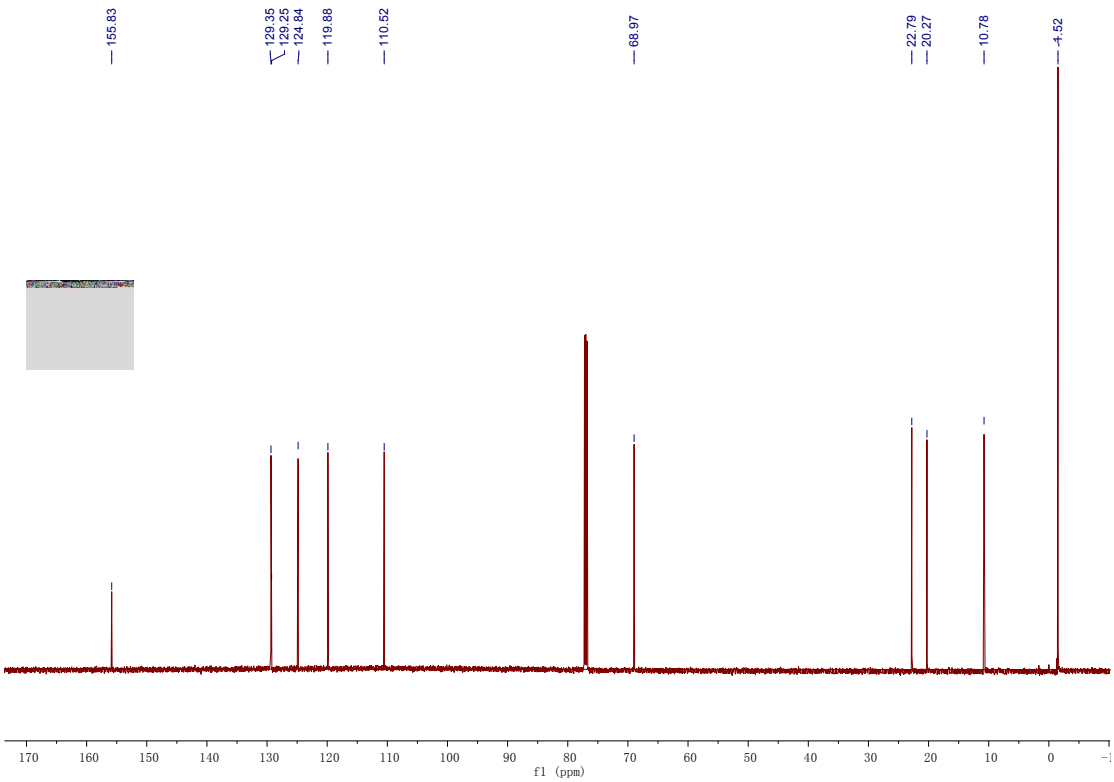
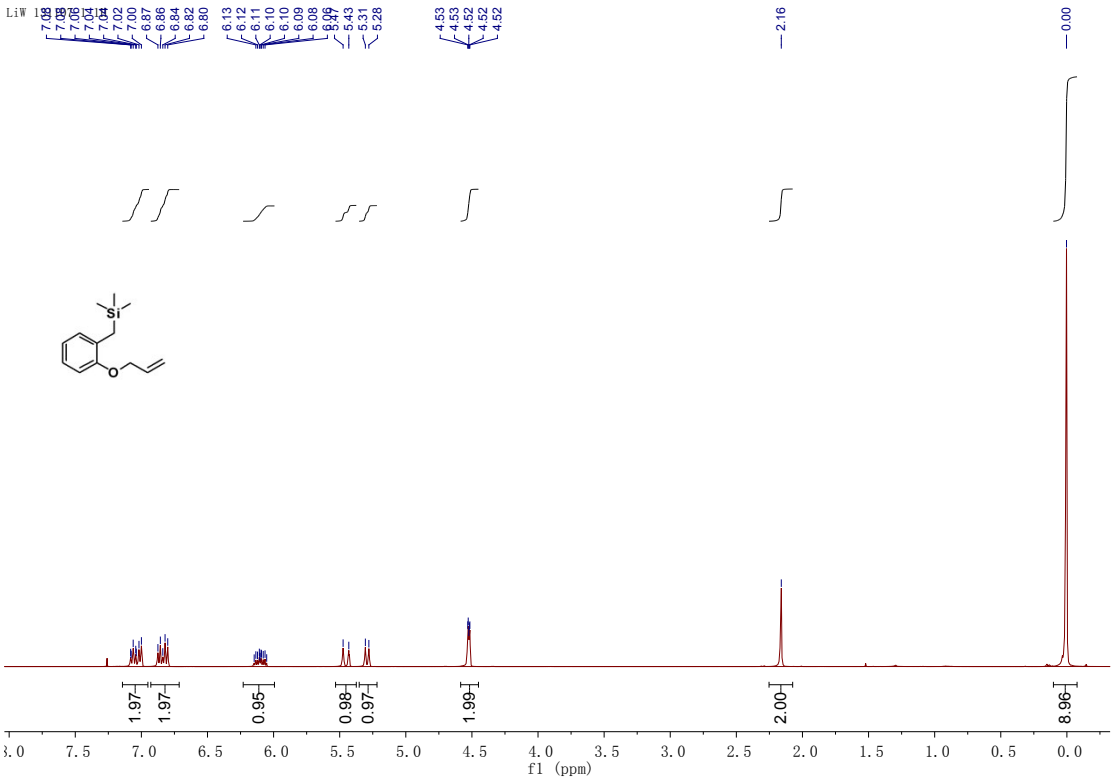
129.20
124.85
119.92
110.46
62.86
20.44
14.95
-1.51
f1 (ppm)

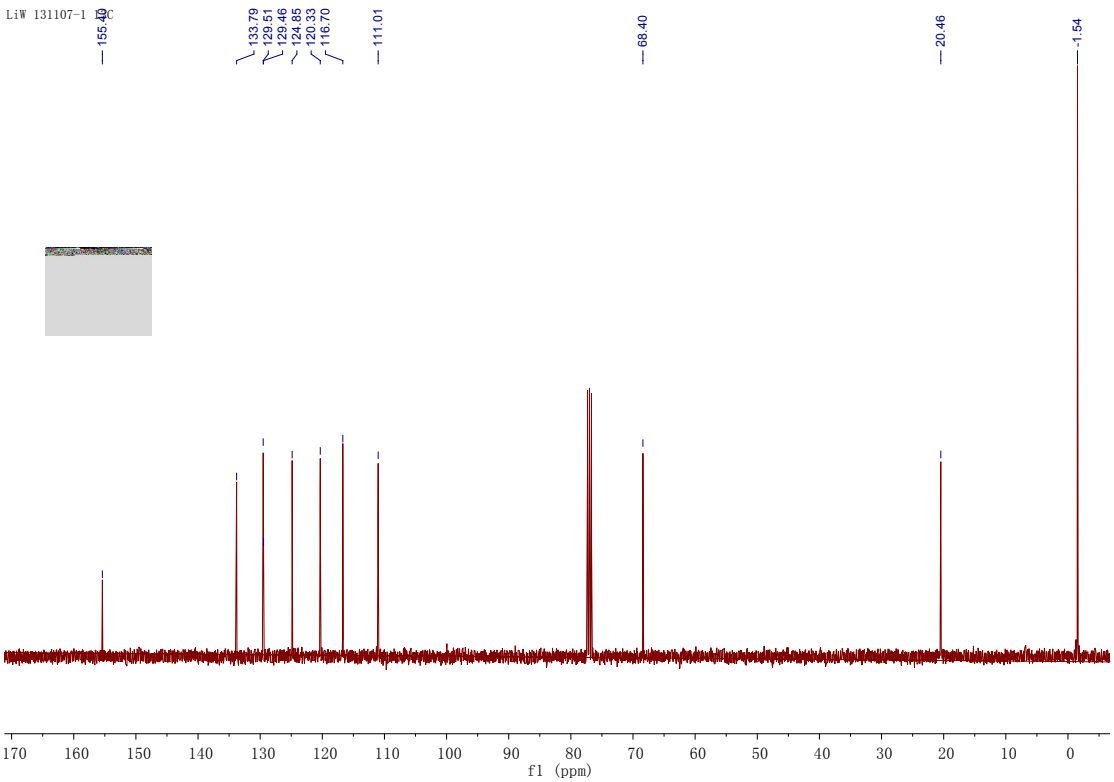

7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.03
7.01
7.01
6.85
6.85
6.83
6.81
4.61
4.60
4.58
4.57
4.55
4.54
4.52
2.14
1.39
1.37
0.03
Si
O
4.28
1.08
2.00
6.34
8.93
f1 (ppm)

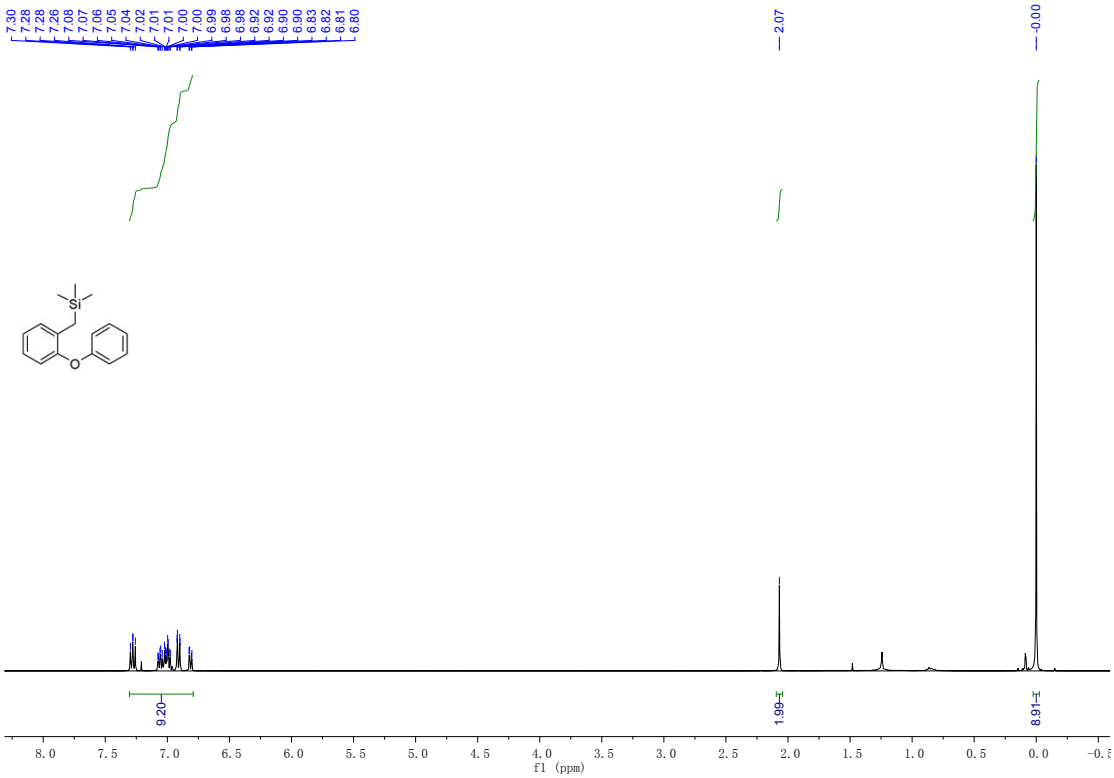

154.49
129.96
129.67
124.71
119.62
111.76
68.88
22.16
20.49
-1.34
f1 (ppm)

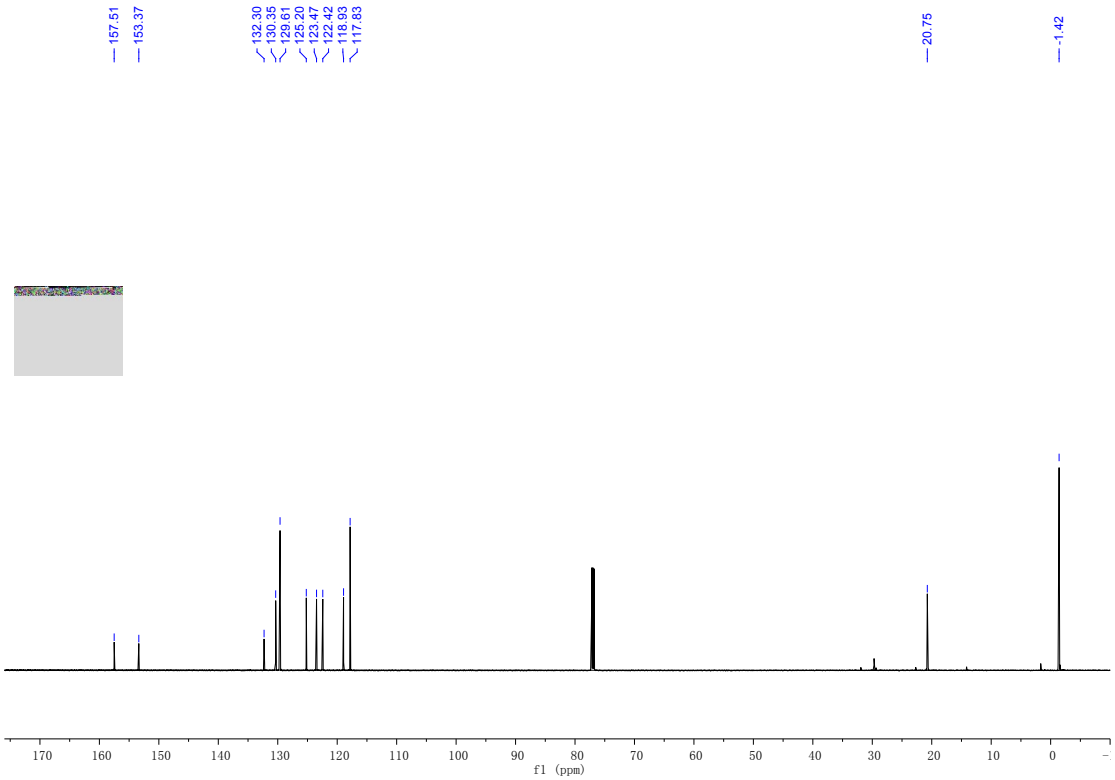

7.07
7.07
7.05
7.05
7.03
7.03
7.00
6.99
6.98
6.98
6.84
6.82
6.81
6.78
3.91
3.89
3.88
2.13
1.89
1.87
1.85
1.83
1.82
1.80
1.10
1.08
1.06
-0.01
Si
O
3.92
2.00
2.00
2.00
3.00
8.97
f1 (ppm)

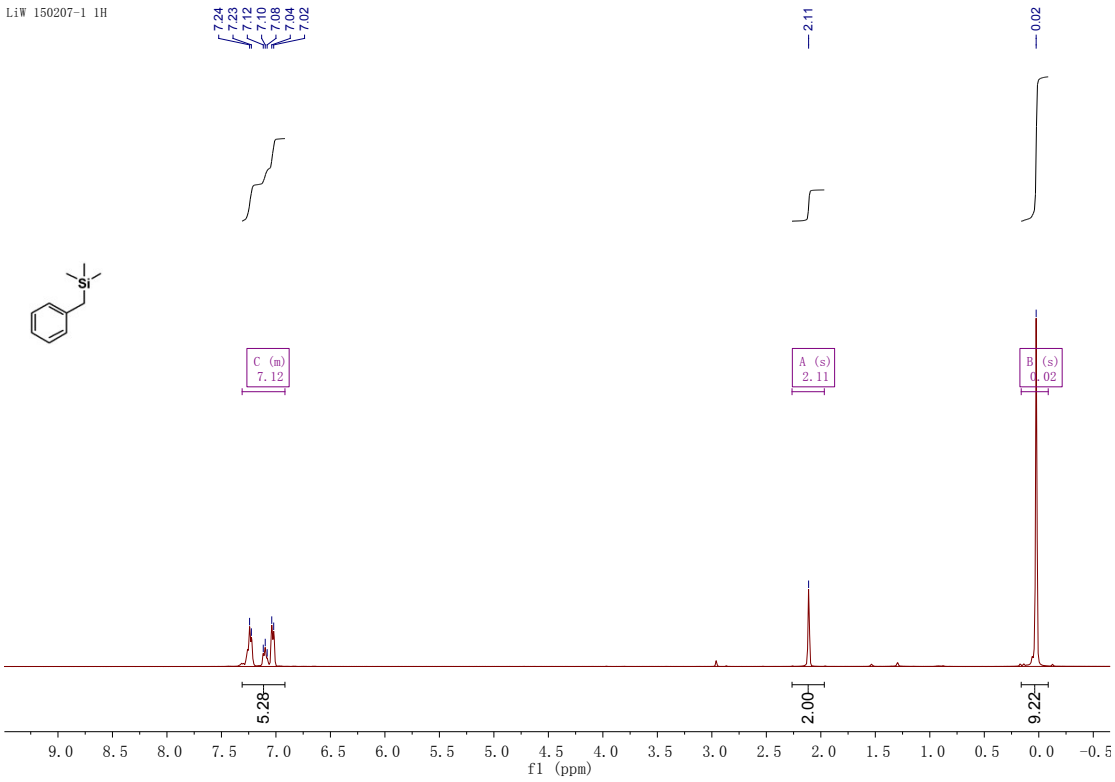

155.83
129.35
129.25
124.84
119.88
110.52
68.97
22.79
20.27
10.78
4.52
f1 (ppm)


LiW 1
6.13
6.12
6.11
6.10
6.10
6.09
6.08
5.43
5.31
5.28
4.53
4.53
4.52
4.52
4.52
2.16
0.00
Si
O
1.97
1.97
0.95
0.98
0.97
1.99
2.00
8.96
f1 (ppm)

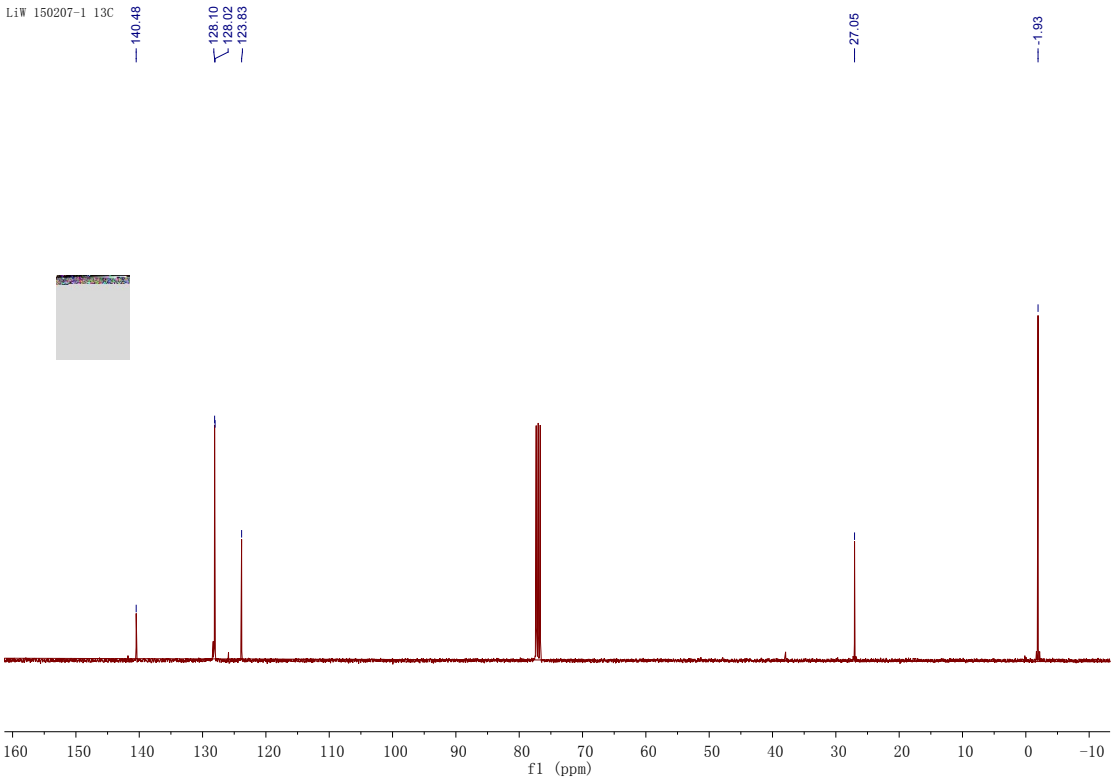

LiW 131107-1 13C
155.40
133.79
129.51
129.46
124.85
120.33
116.70
111.01
68.40
20.46
-1.54
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

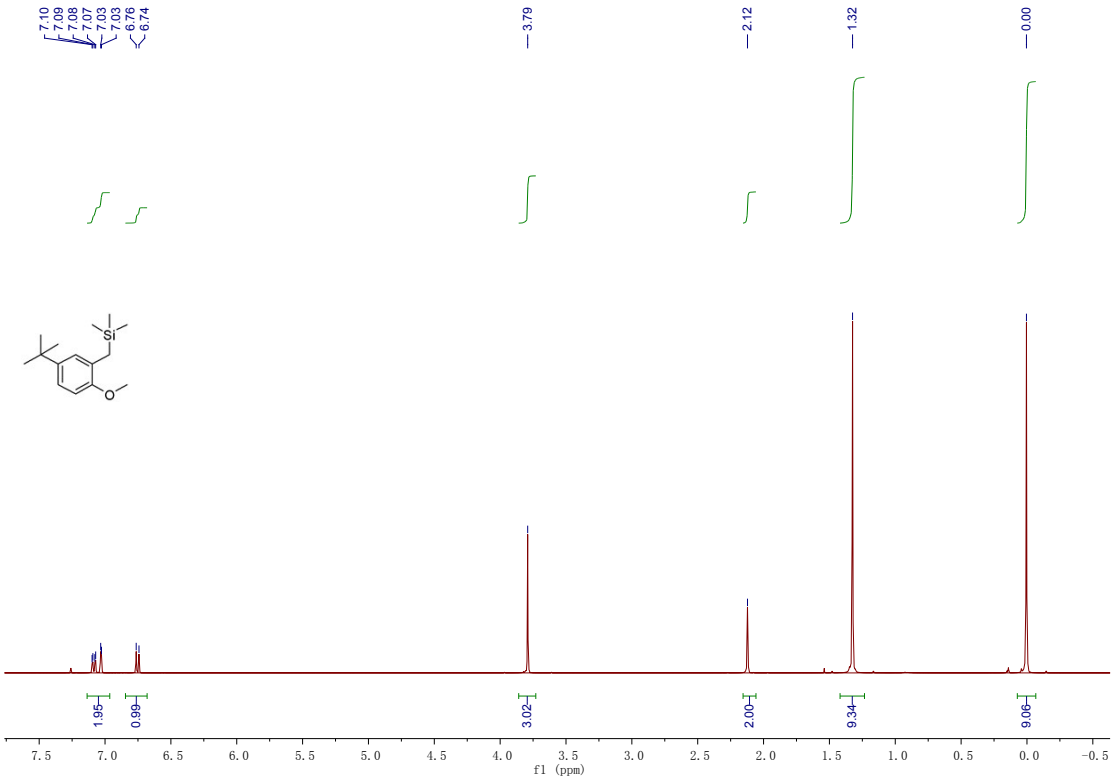

7.30
7.28
7.28
7.26
7.08
7.07
7.06
7.05
7.04
7.02
7.01
7.01
7.00
7.00
6.99
6.98
6.92
6.90
6.90
6.83
6.82
6.81
6.80
2.07
0.00
9.20
1.99
8.91
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

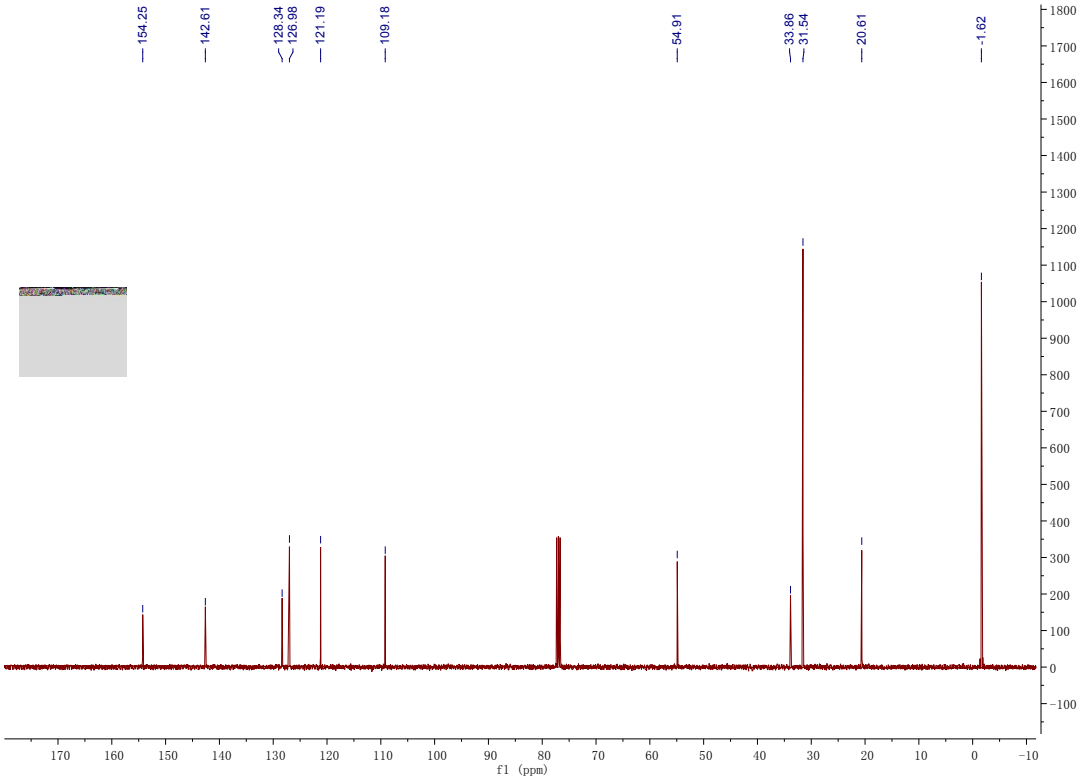

157.51
153.37
132.30
130.35
129.61
125.20
123.47
122.42
118.93
117.83
20.75
-1.42
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

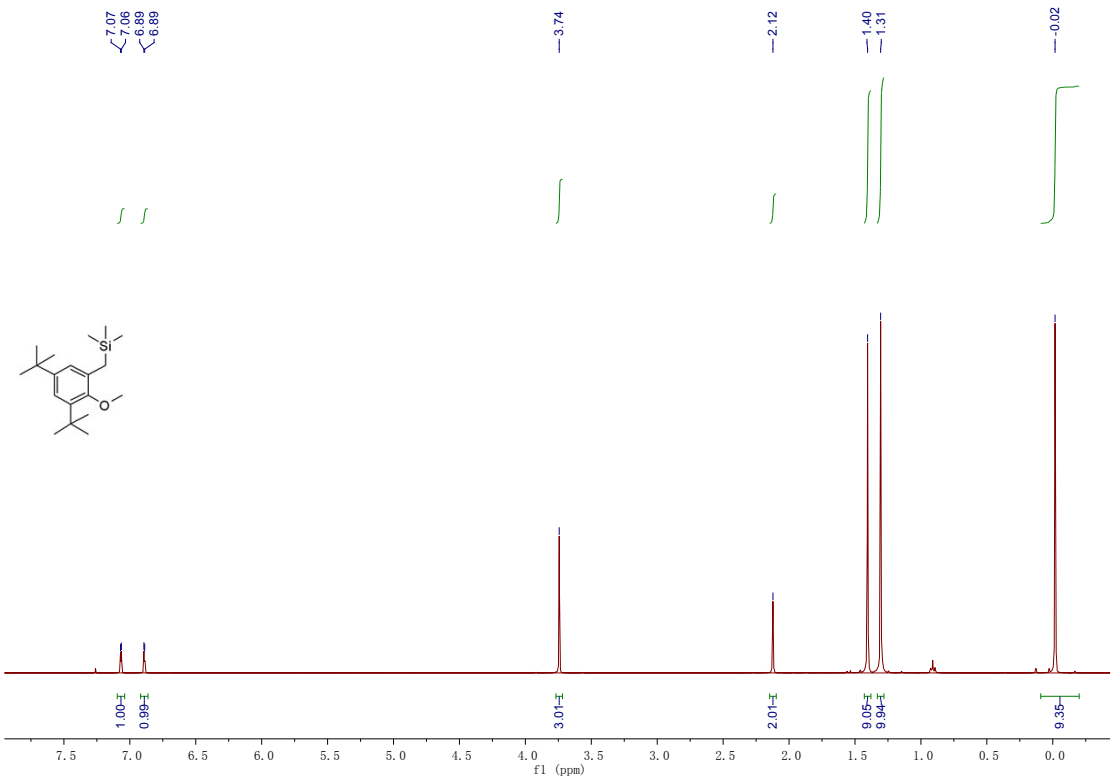

LiW 150207-1 1H
7.24
7.23
7.12
7.10
7.08
7.04
7.02
2.11
0.02
Si
C (m)
7.12
A (s)
2.11
B (s)
0.02
5.28
2.00
9.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

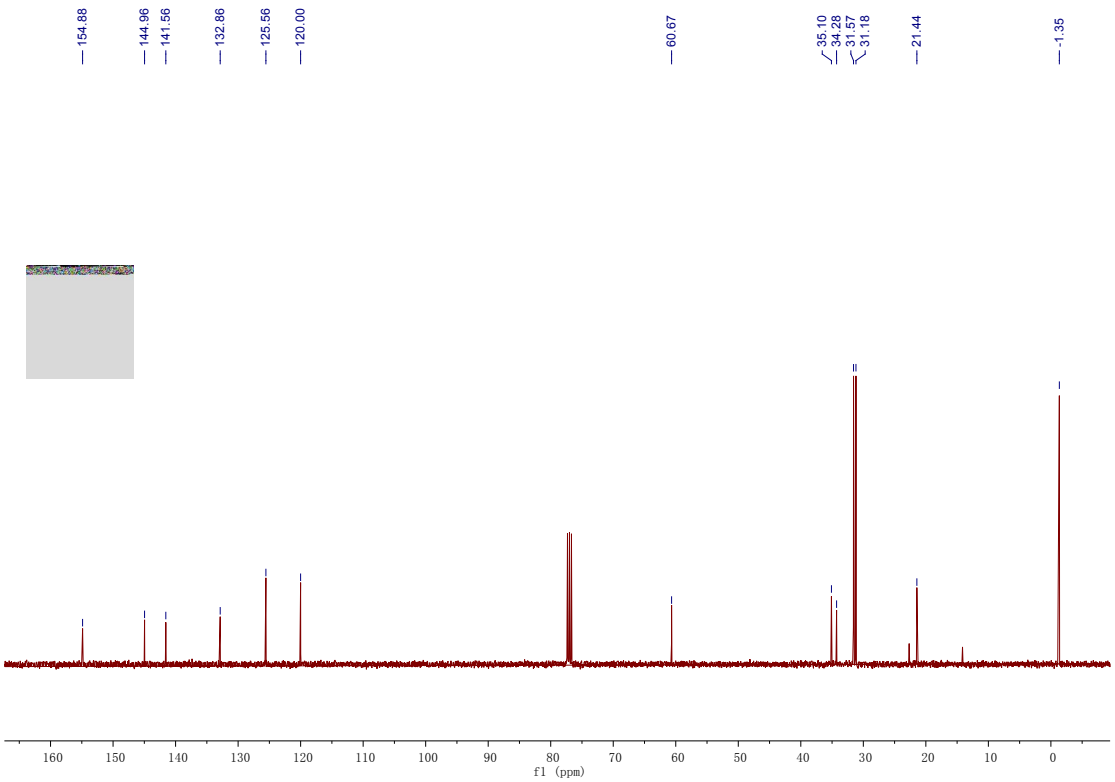
LiW 150207-1 13C

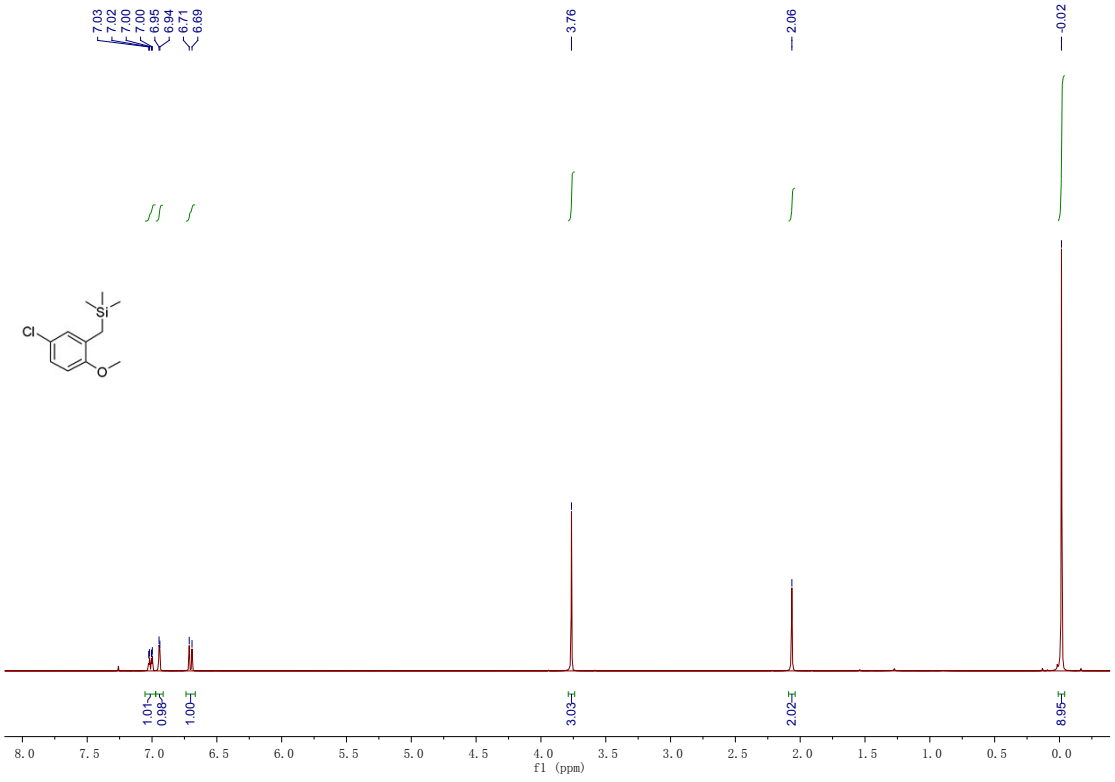


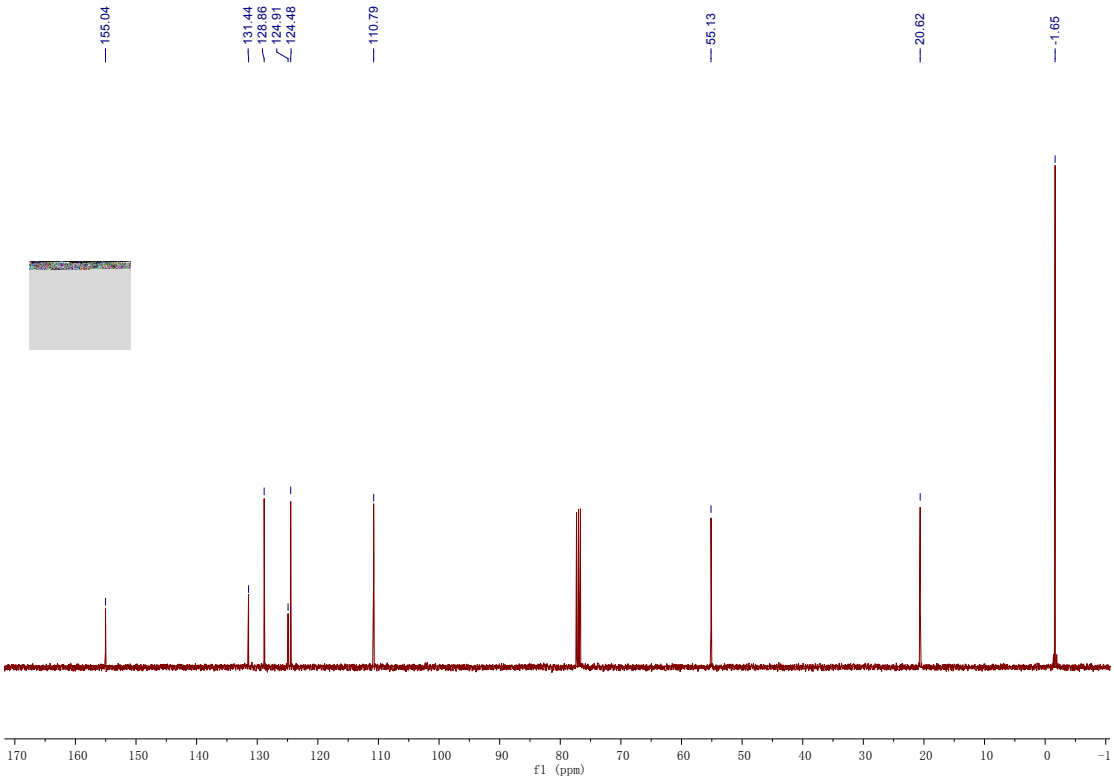


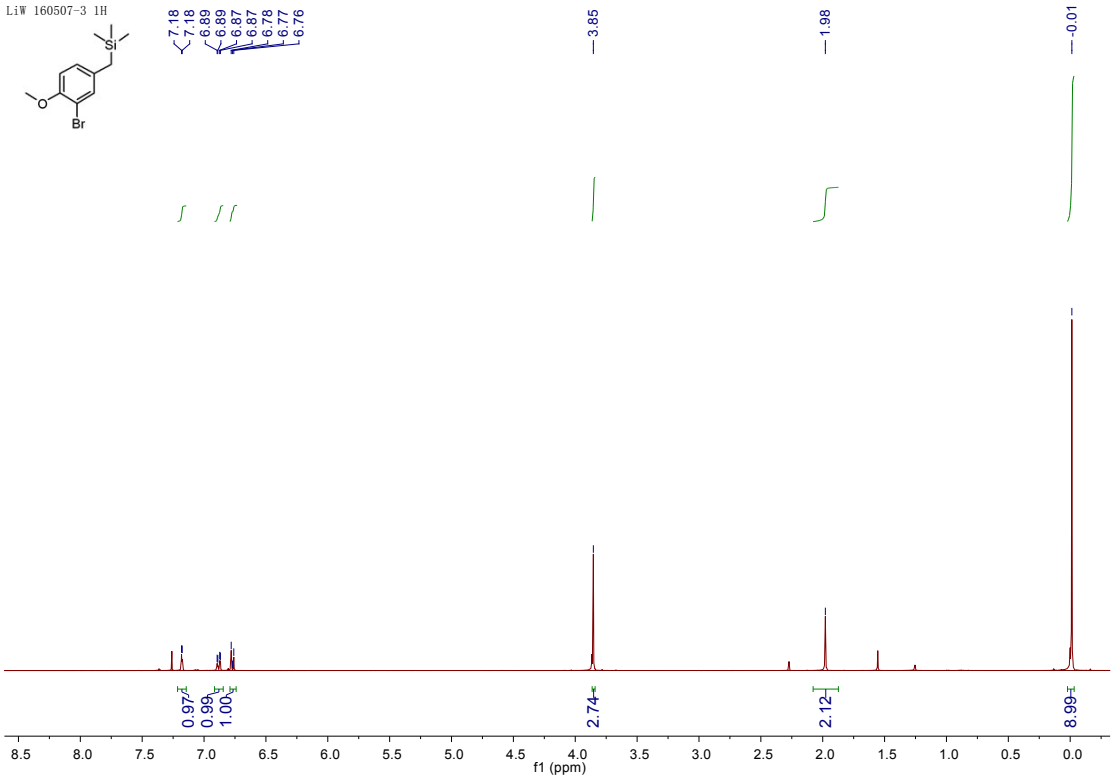

154.25
142.61
128.34
126.98
121.19
109.18
54.91
33.86
31.54
20.61
1.62
f1 (ppm)

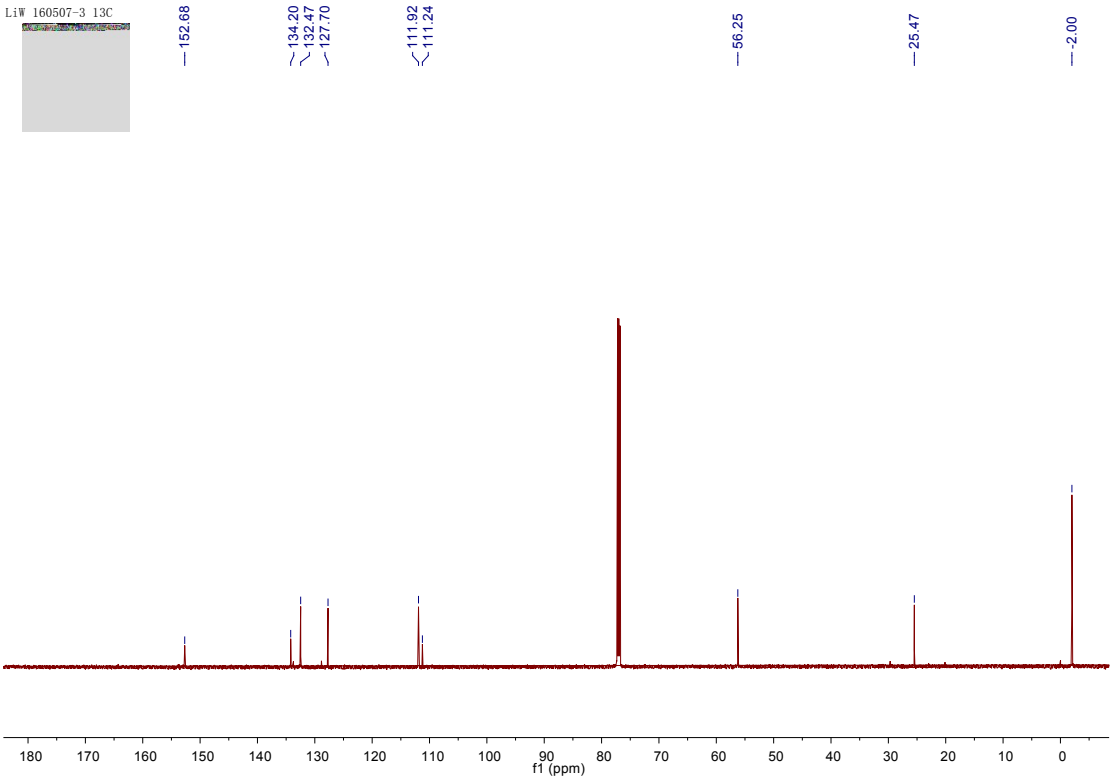

7.07
7.06
6.89
6.89
3.74
2.12
1.40
1.31
0.02
Si
O
1.00
0.99
3.01
2.01
9.05
9.94
9.35
f1 (ppm)

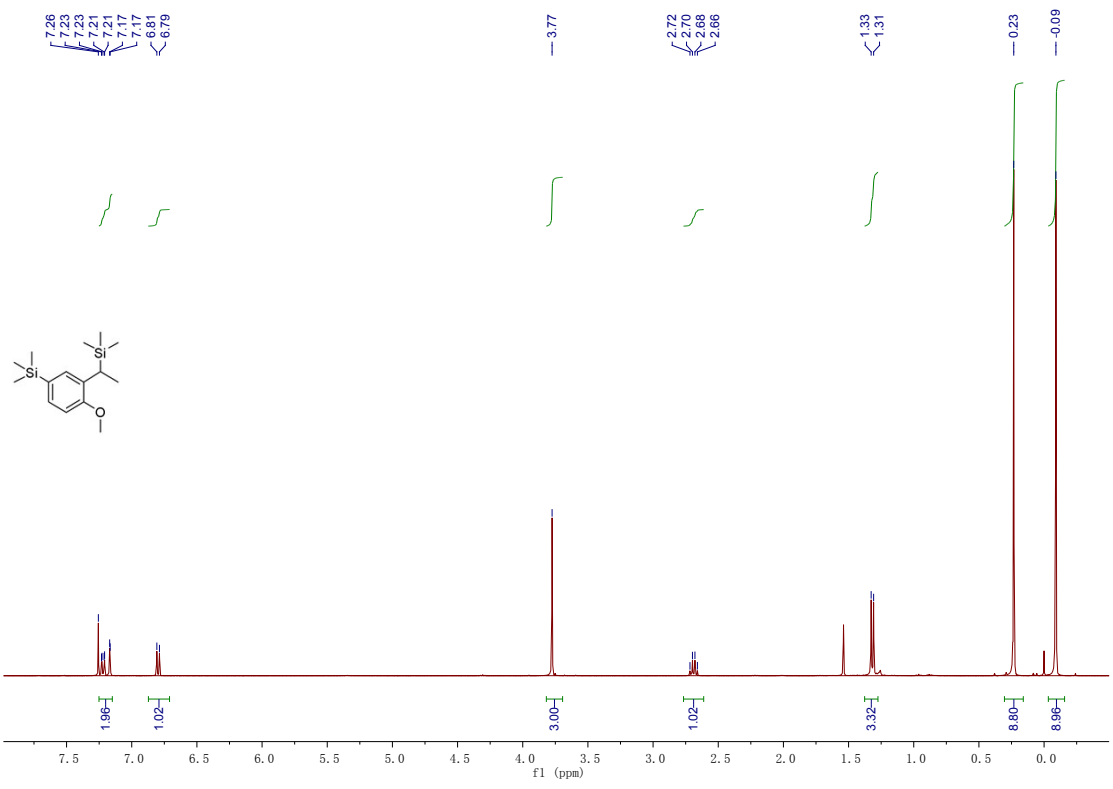

154.88
144.96
141.56
132.86
125.56
120.00
60.67
35.10
34.28
31.57
31.18
21.44
-1.35
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

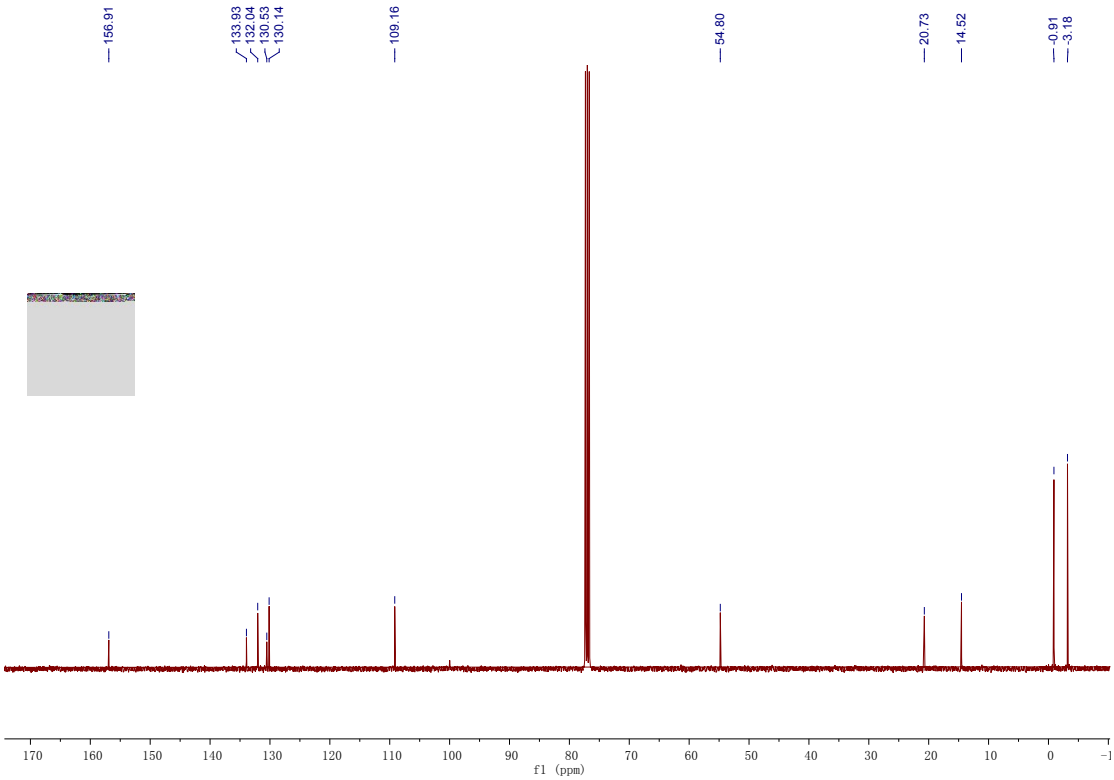

7.03
7.02
7.00
7.00
6.95
6.94
6.71
6.69
3.76
2.06
-0.02
Si
Cl
O
1.01
0.98
1.00
3.03
2.02
8.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

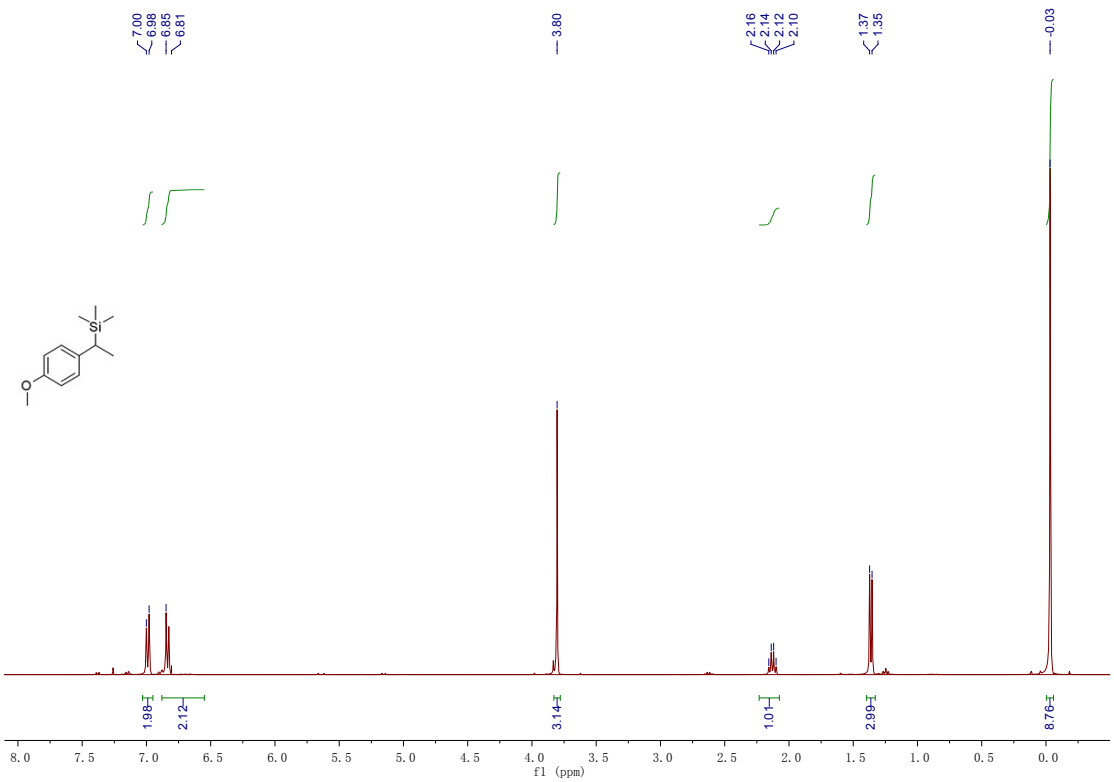

155.04
131.44
128.86
124.91
124.48
110.79
55.13
20.62
-1.65
f1 (ppm)

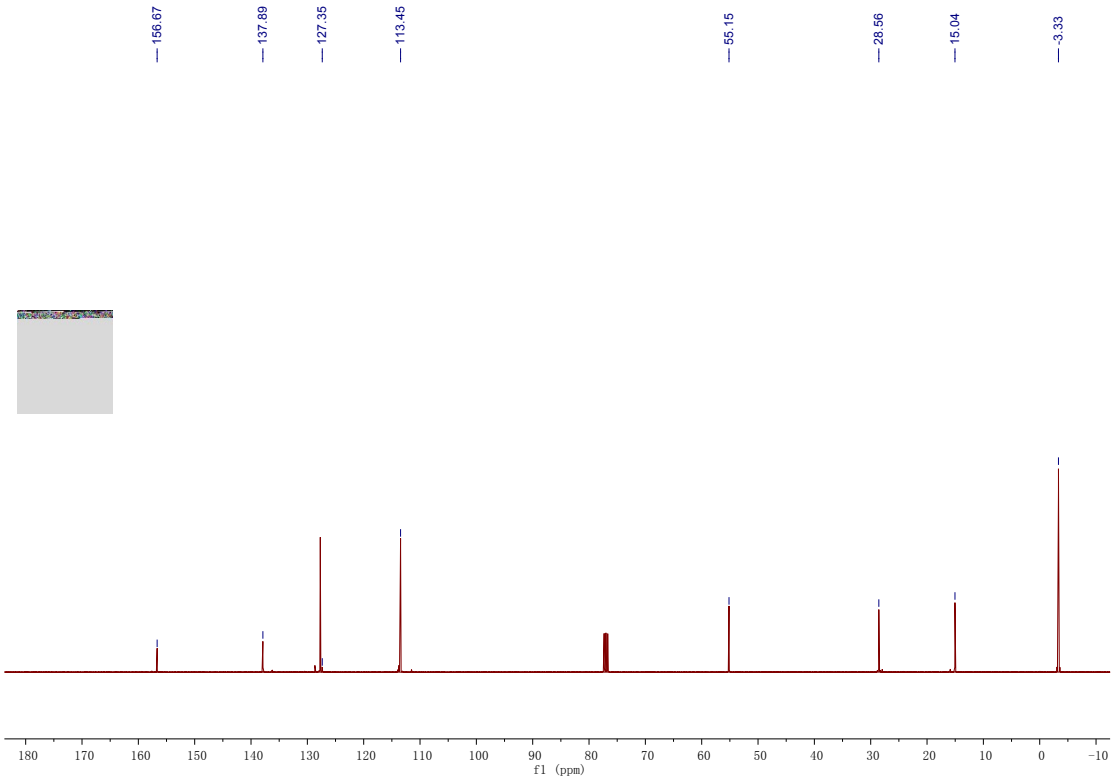

LiW 160507-3 1H
Si
O
Br
7.18
7.18
6.89
6.89
6.87
6.87
6.78
6.77
6.76
3.85
1.98
-0.01
0.97
0.99
1.00
2.74
2.12
8.99
f1 (ppm)

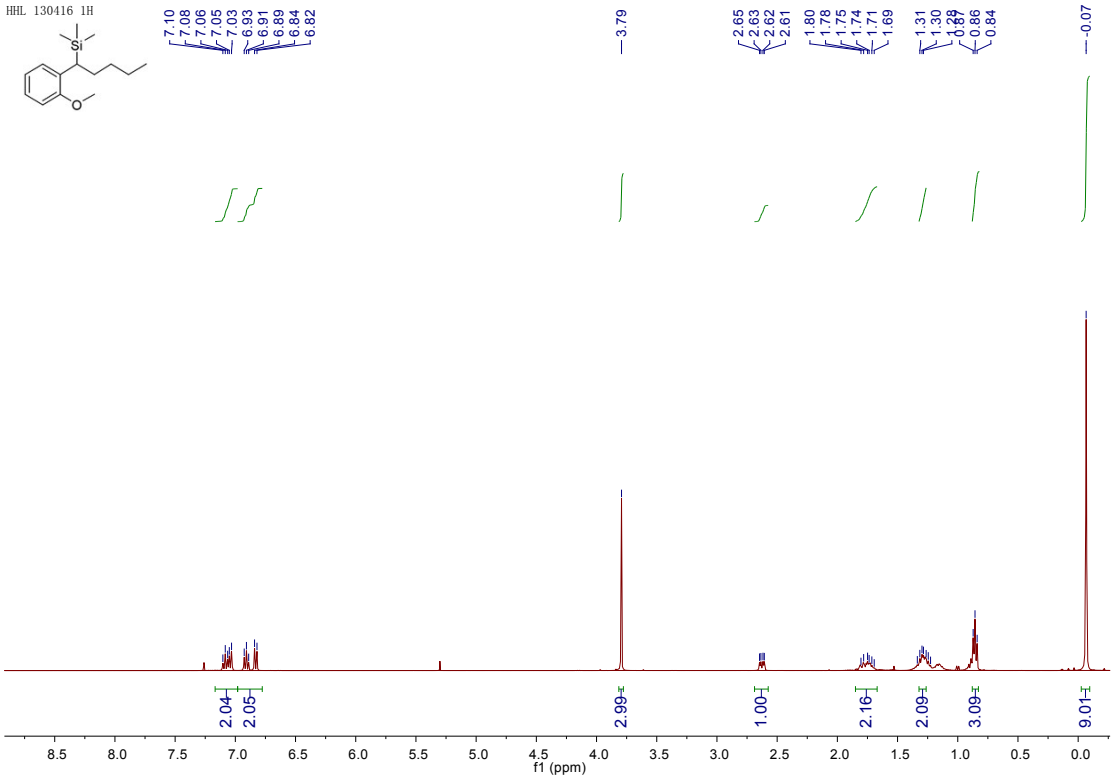

LiW 160507-3 13C
152.68
134.20
132.47
127.70
111.92
111.24
56.25
25.47
-2.00
f1 (ppm)

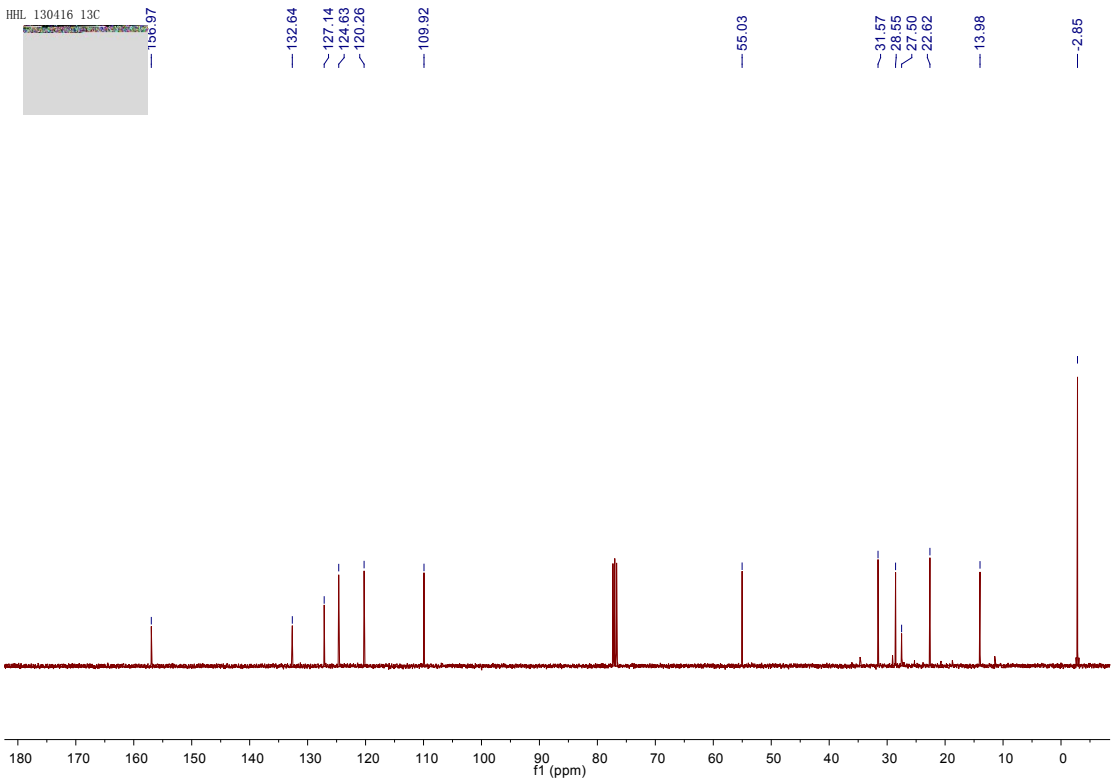

7.26
7.23
7.23
7.21
7.21
7.17
7.17
6.81
6.79
3.77
2.72
2.70
2.68
2.66
1.33
1.31
0.23
-0.09
Si
Si
O
1.96
1.02
3.00
1.02
3.32
8.80
8.96
f1 (ppm)

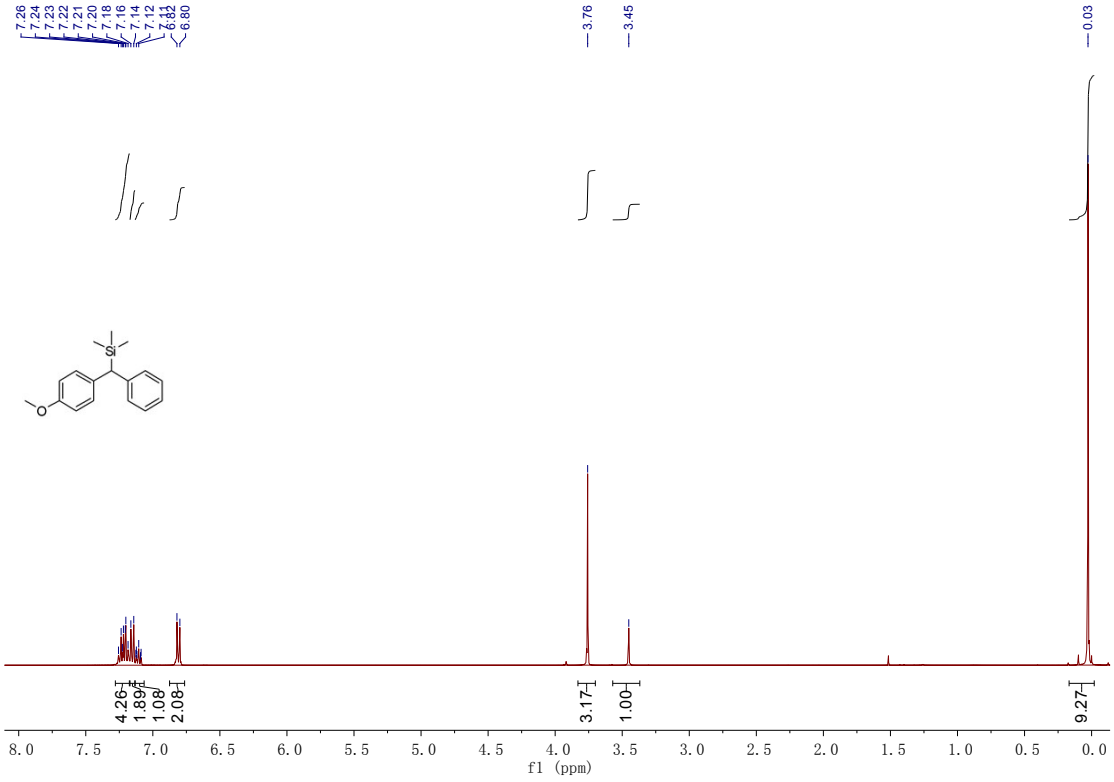

156.91
133.93
132.04
130.53
130.14
109.16
54.80
20.73
14.52
-0.91
-3.18
f1 (ppm)

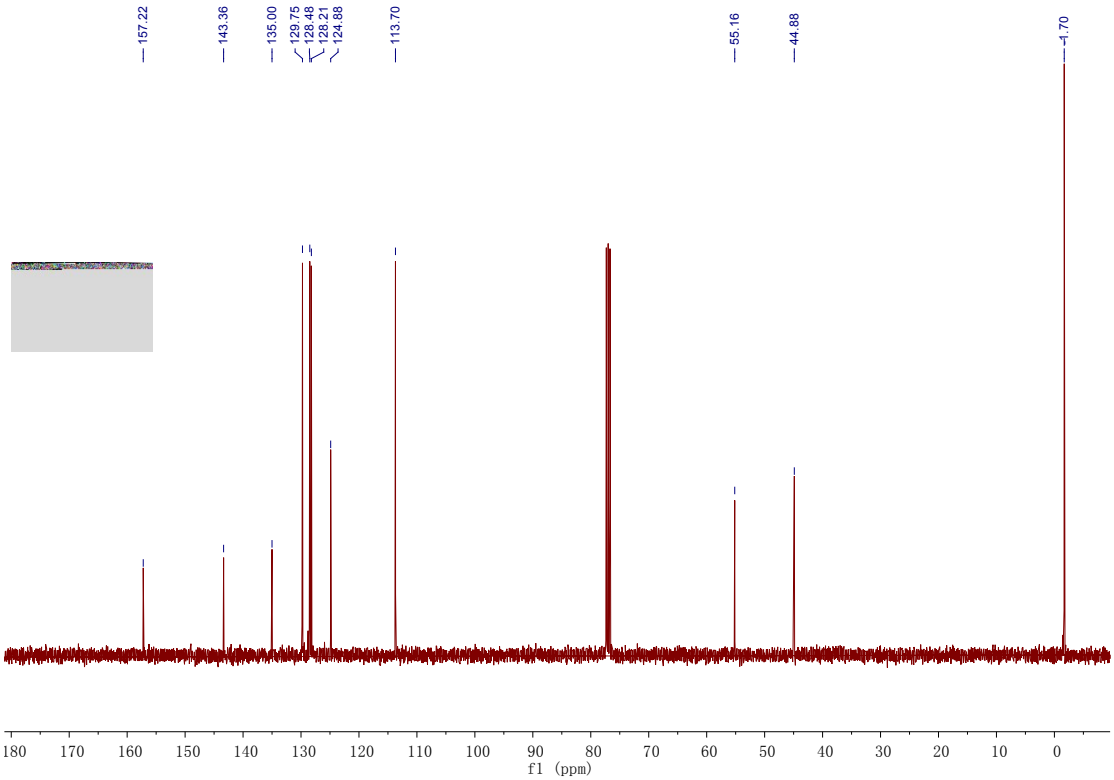

7.00
6.98
6.85
6.81
3.80
2.16
2.14
2.12
2.10
1.37
1.35
-0.03
Si
O
1.98
2.12
3.14
1.01
2.99
8.76
f1 (ppm)

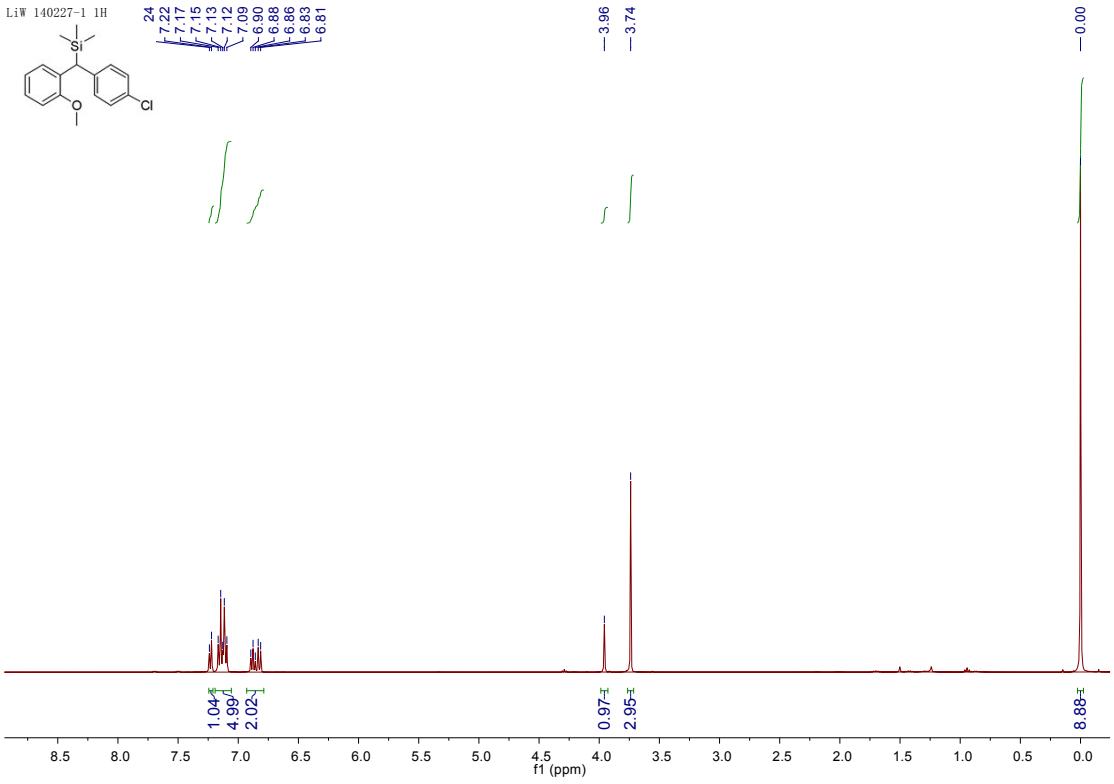

156.67
137.89
127.35
113.45
55.15
28.56
15.04
-3.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

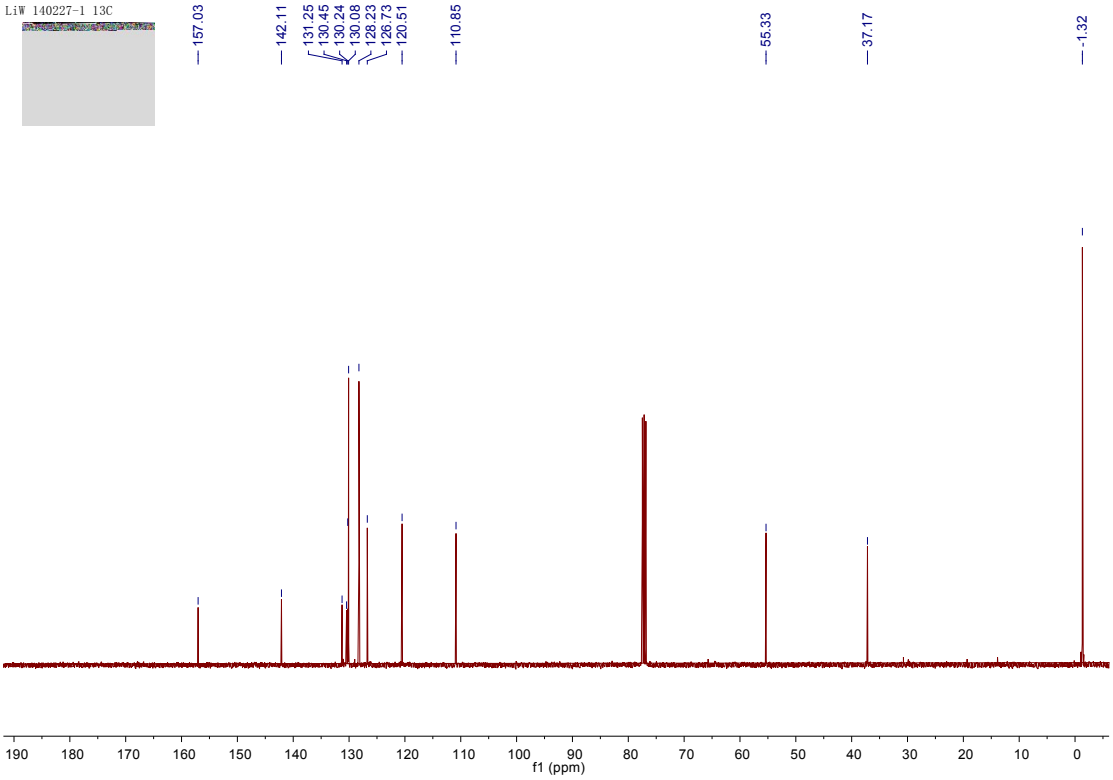

HHL 130416 1H
Si
O
7.10
7.08
7.06
7.05
7.03
6.93
6.91
6.89
6.84
6.82
3.79
2.65
2.63
2.62
2.61
1.80
1.78
1.75
1.74
1.71
1.69
1.31
1.30
1.28
0.87
0.86
0.84
-0.07
2.04
2.05
2.99
1.00
2.16
2.09
3.09
9.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

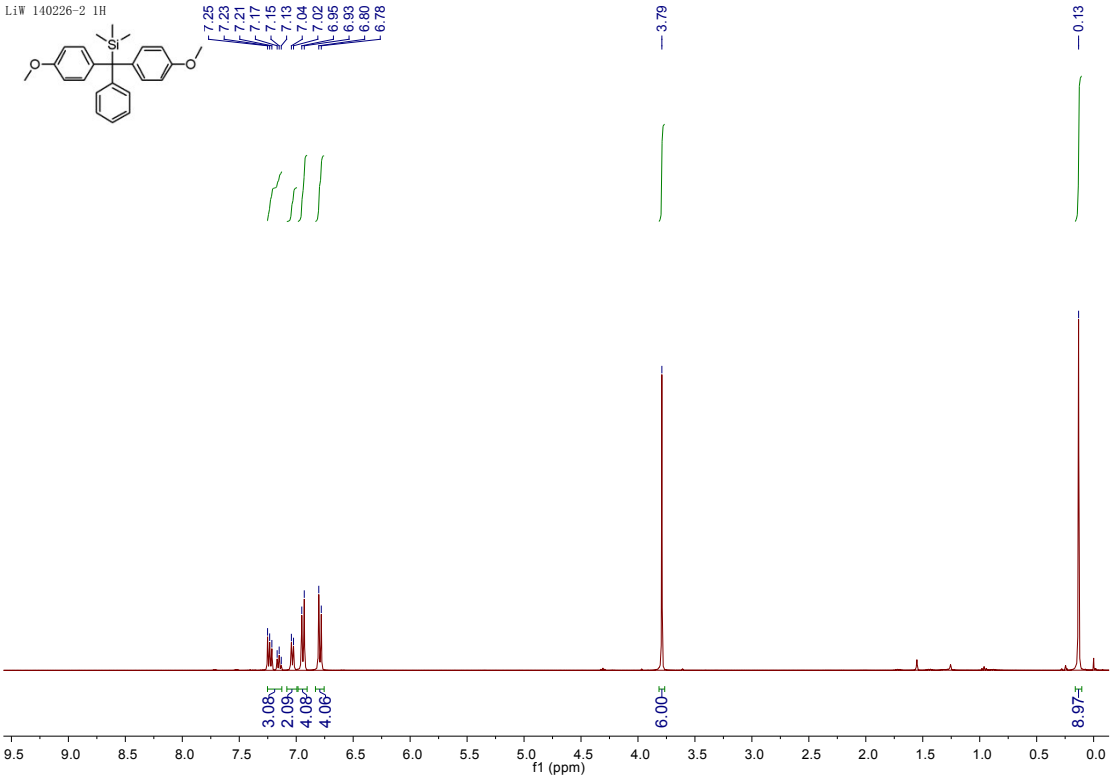

HHL 130416 13C
158.97
132.64
127.14
124.63
120.26
109.92
55.03
31.57
28.55
27.50
22.62
13.98
-2.85
f1 (ppm)

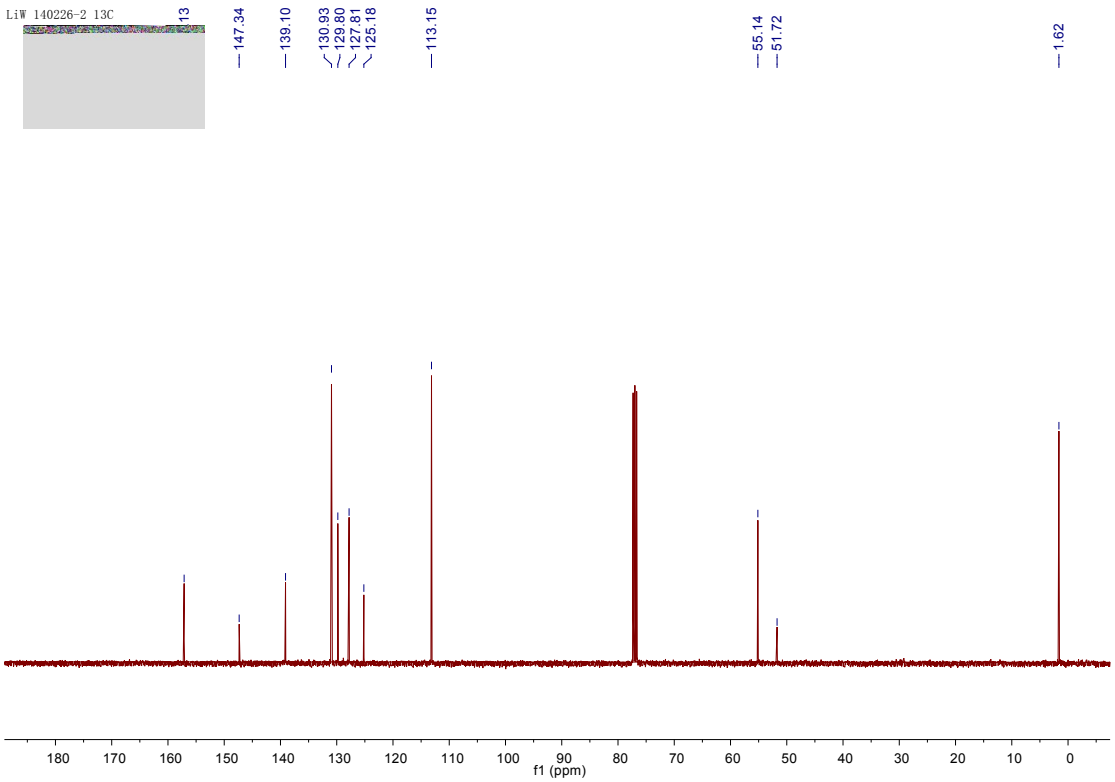

7.26
7.24
7.23
7.22
7.21
7.20
7.18
7.16
7.14
7.12
6.82
6.80
3.76
3.45
0.03
Si
O
4.26
1.89
1.08
2.08
3.17
1.00
9.27
f1 (ppm)

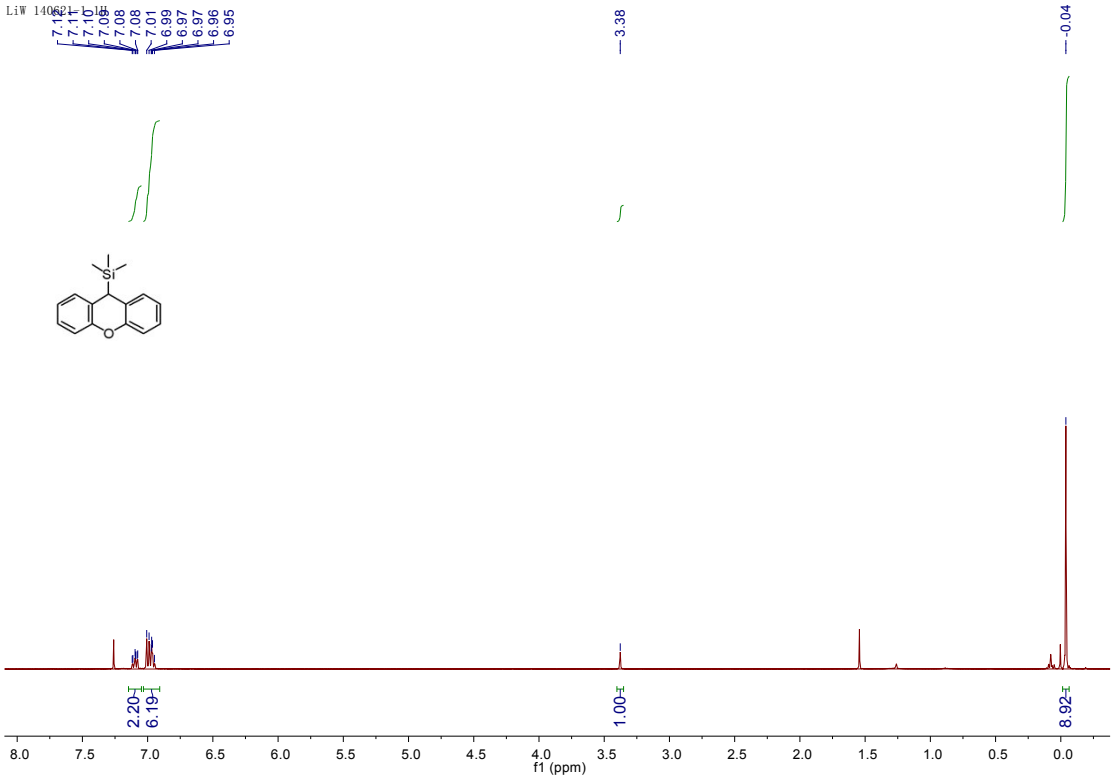

157.22
143.36
135.00
129.75
128.48
128.21
124.88
113.70
55.16
44.88
-1.70
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

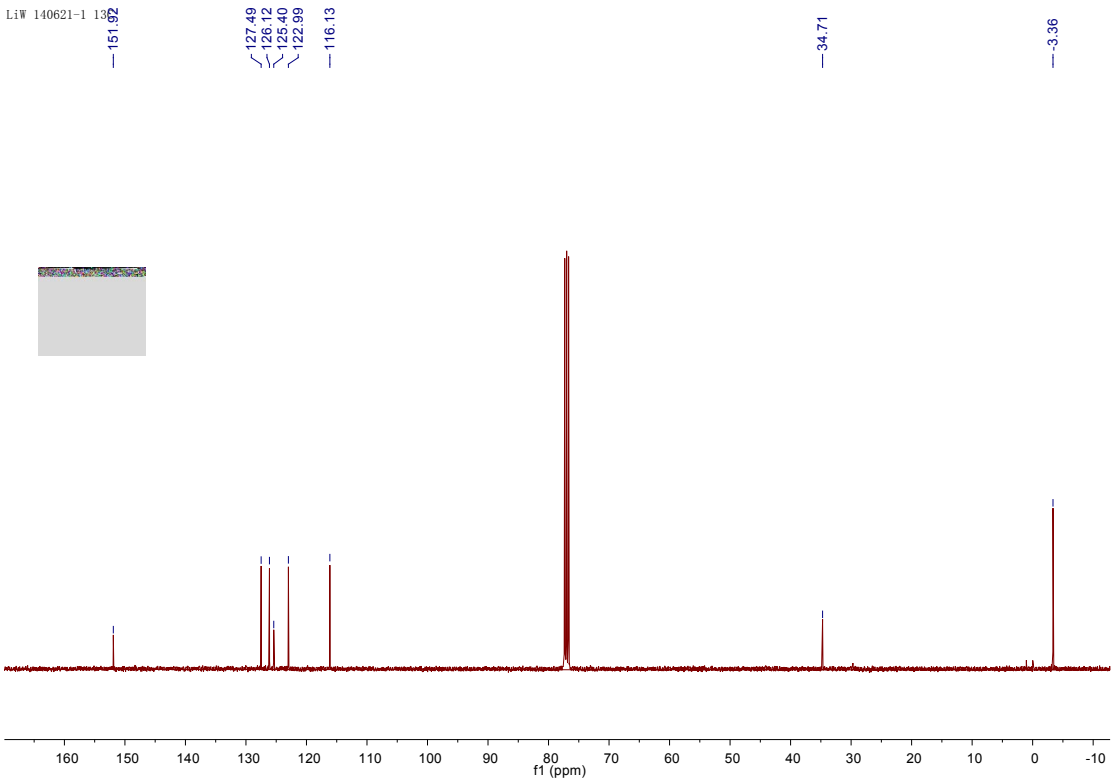

LiW 140227-1 1H
Si
O
Cl
7.24
7.22
7.17
7.15
7.13
7.12
7.09
6.90
6.88
6.86
6.83
6.81
3.96
3.74
0.00
1.04
4.99
2.02
0.97
2.95
8.88
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LiW 140227-1 13C
157.03
142.11
131.25
130.45
130.24
130.08
128.23
126.73
120.51
110.85
55.33
37.17
-1.32
f1 (ppm)

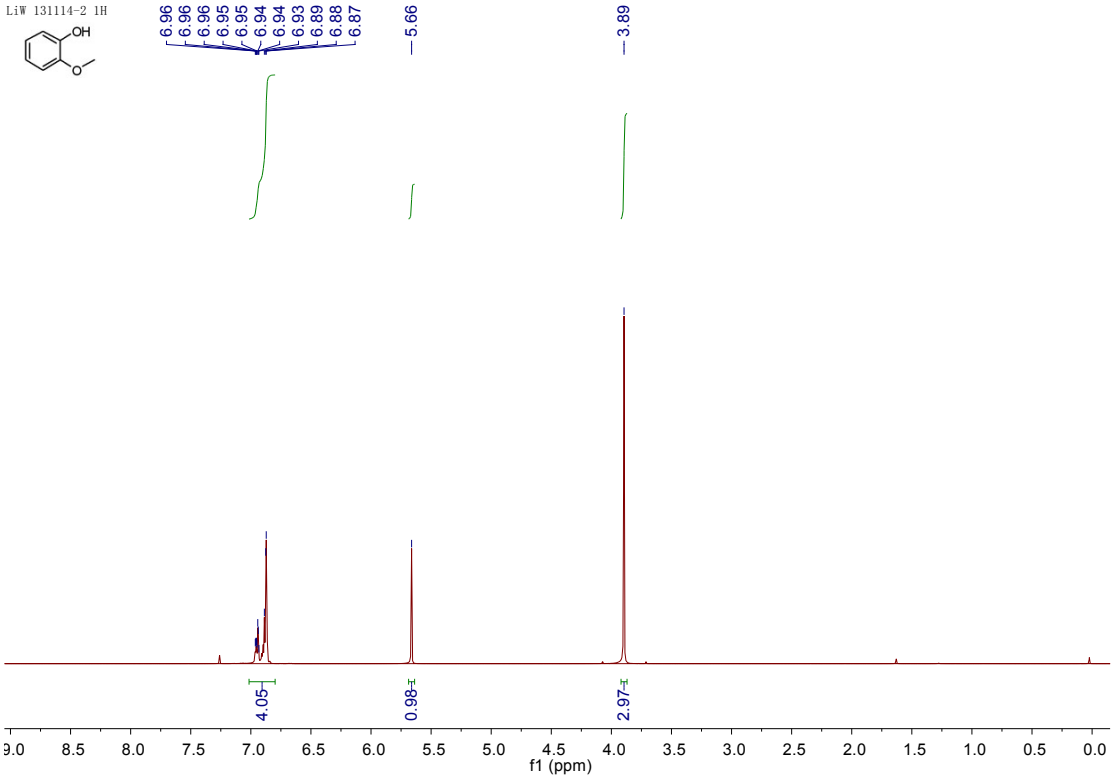

LiW 140226-2 1H
7.25
7.23
7.21
7.17
7.15
7.13
7.04
7.02
6.95
6.93
6.80
6.78
3.79
0.13
3.08
2.09
4.08
4.06
6.00
8.97
f1 (ppm)

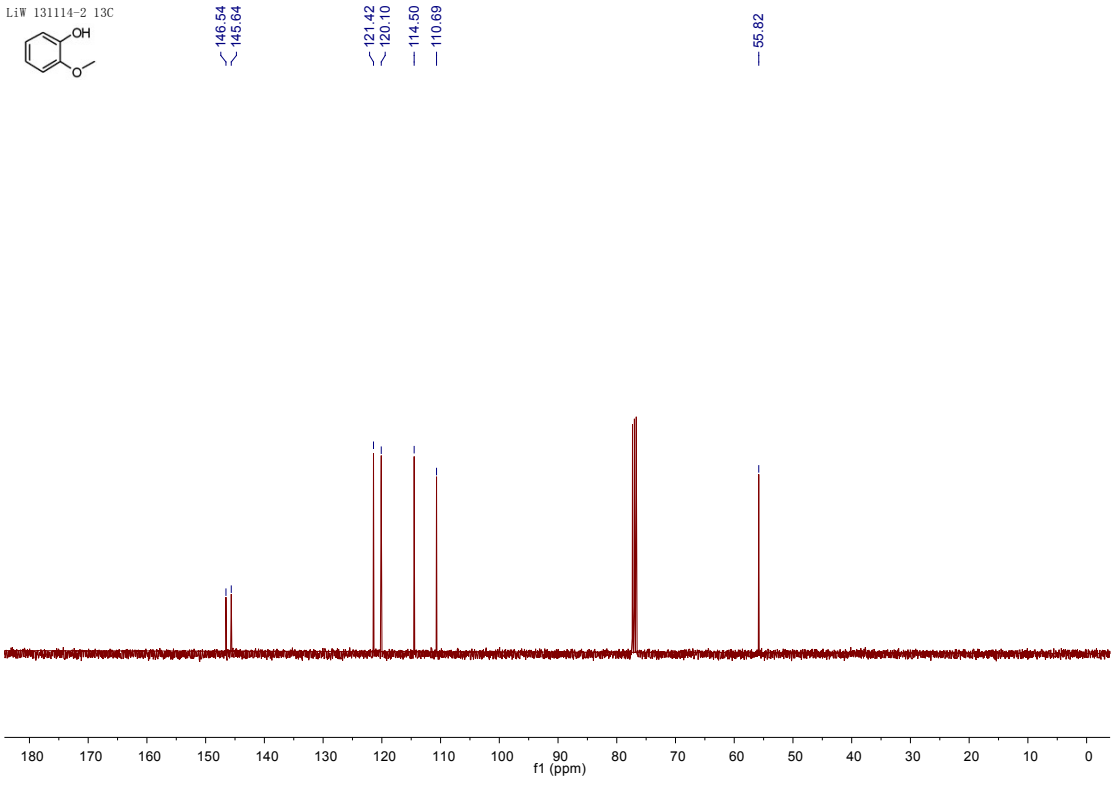

LiW 140226-2 13C
147.34
139.10
130.93
129.80
127.81
125.18
113.15
55.14
51.72
1.62
f1 (ppm)


7.11
7.10
7.08
7.08
7.01
6.99
6.97
6.96
6.95
3.38
-0.04
Si
O
2.20
6.19
1.00
8.92
f1 (ppm)

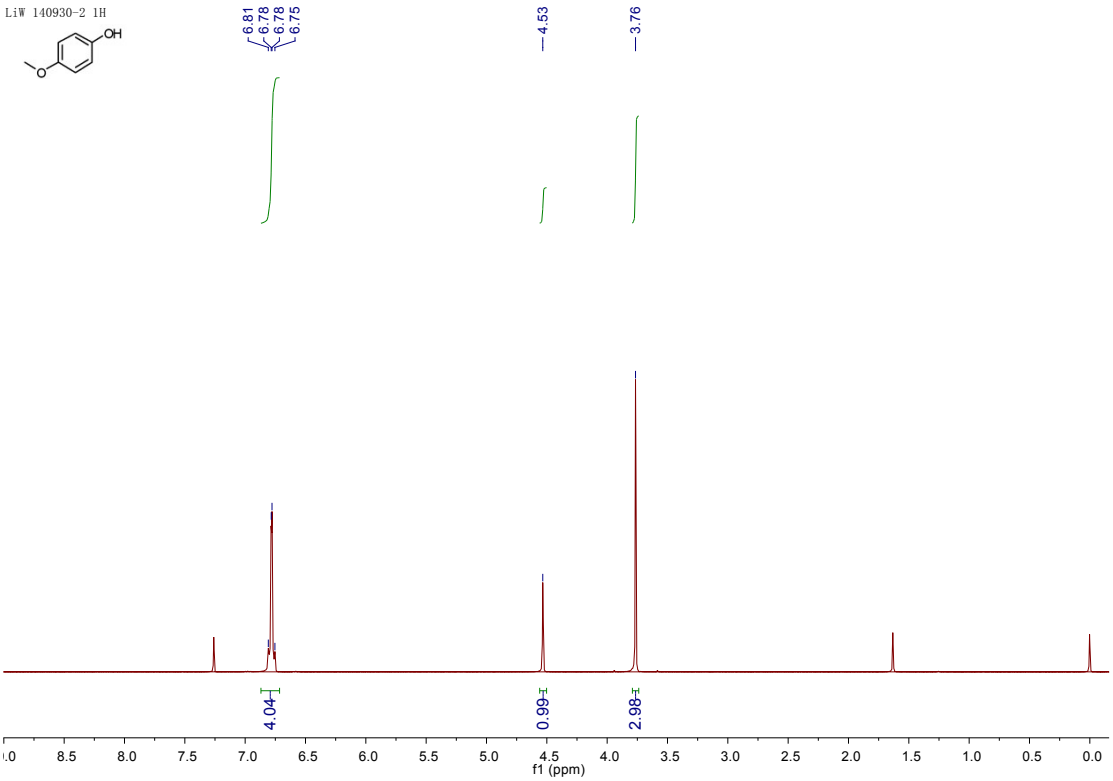

LiW 140621-1 13
151.92
127.49
126.12
125.40
122.99
116.13
34.71
-3.36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

6. NMR spectrum of phenols

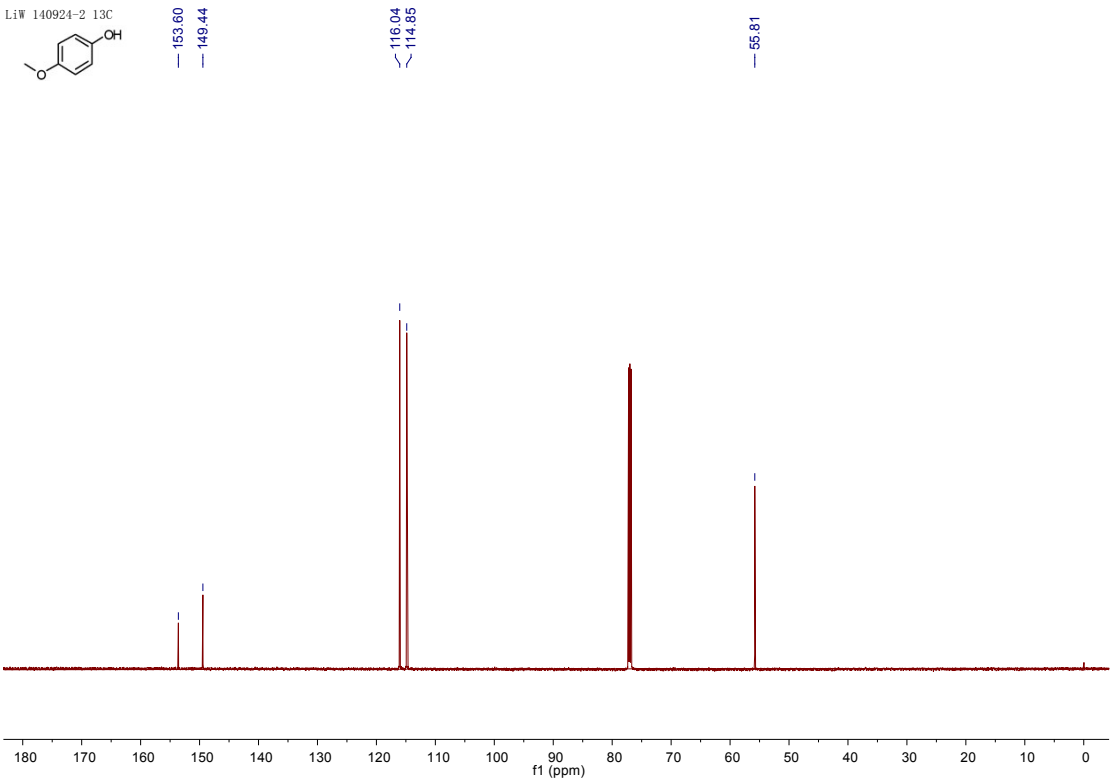




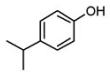
LiW 140930-2 1H



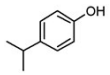
LiW 140924-2 13C

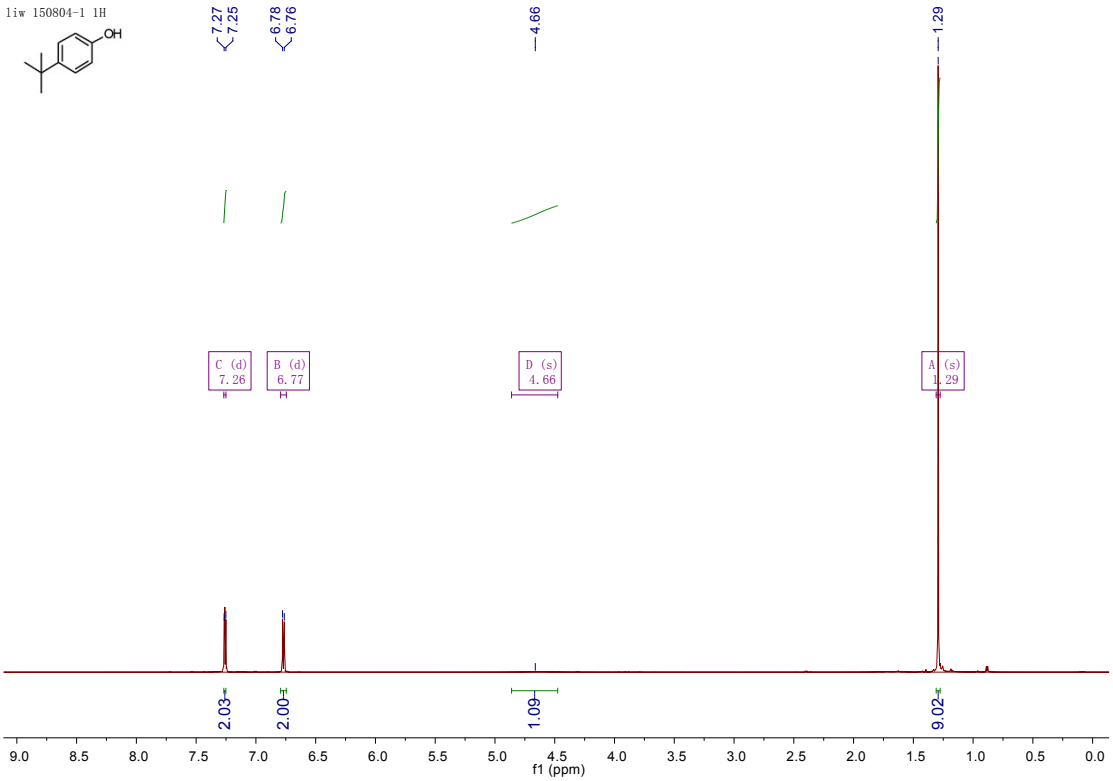


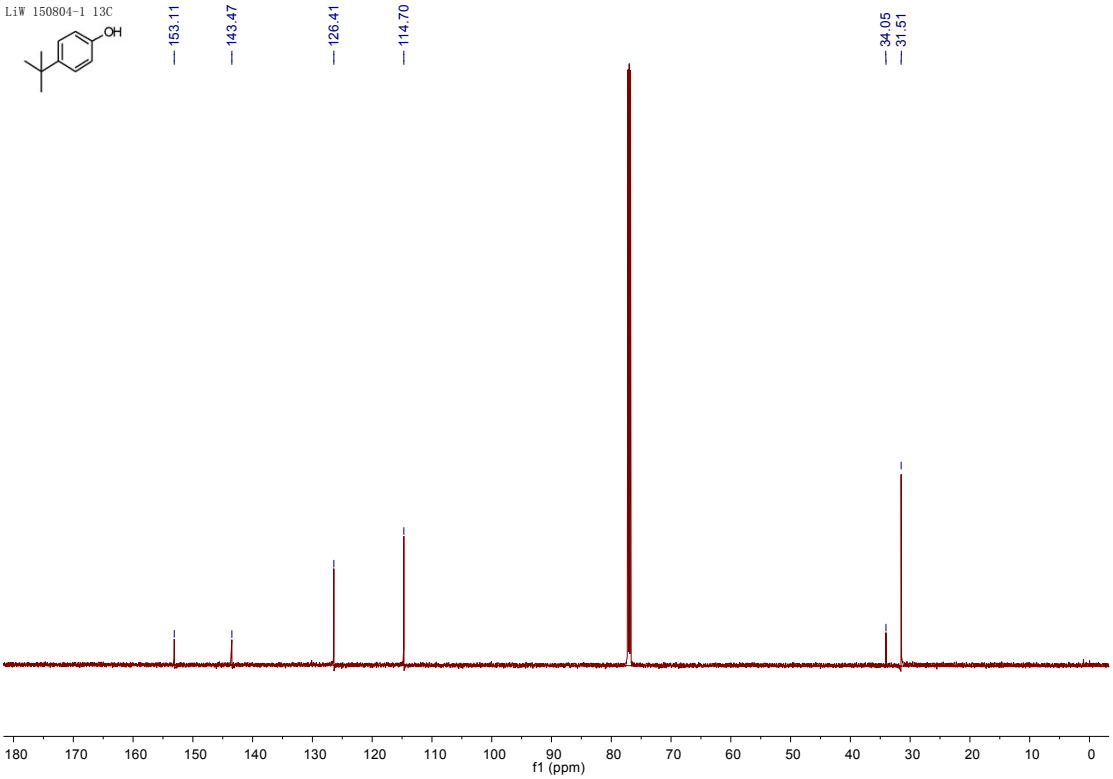
LiW 131114-1 1H

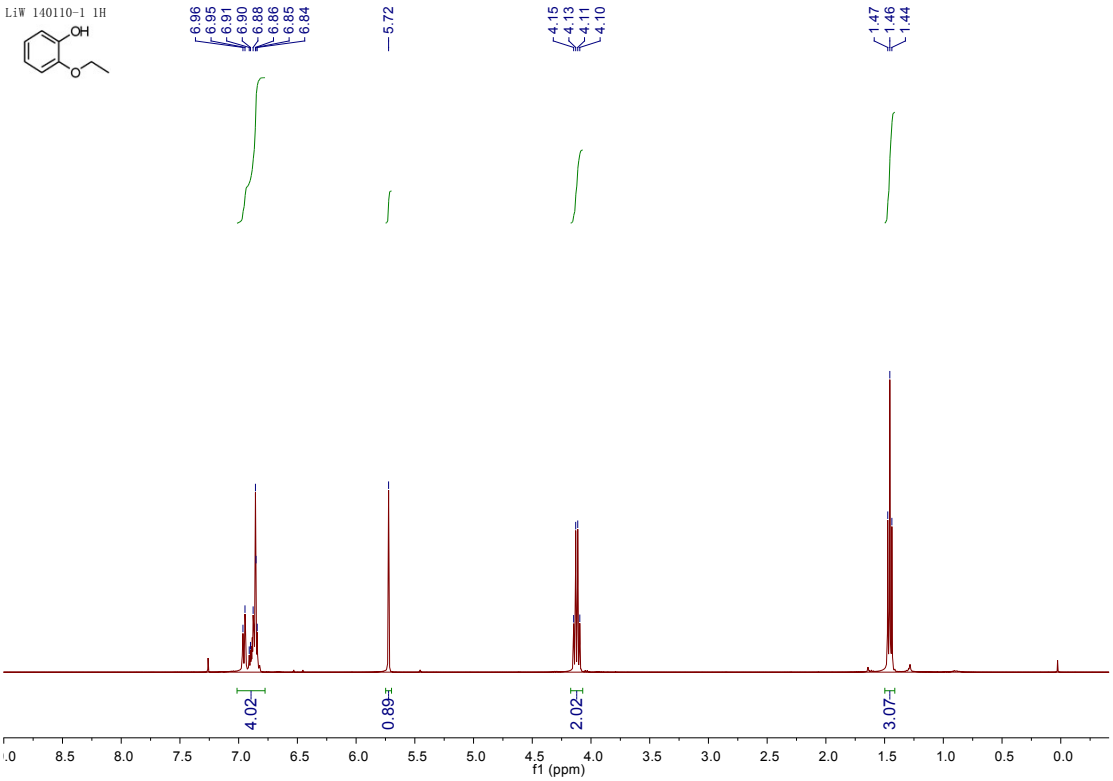


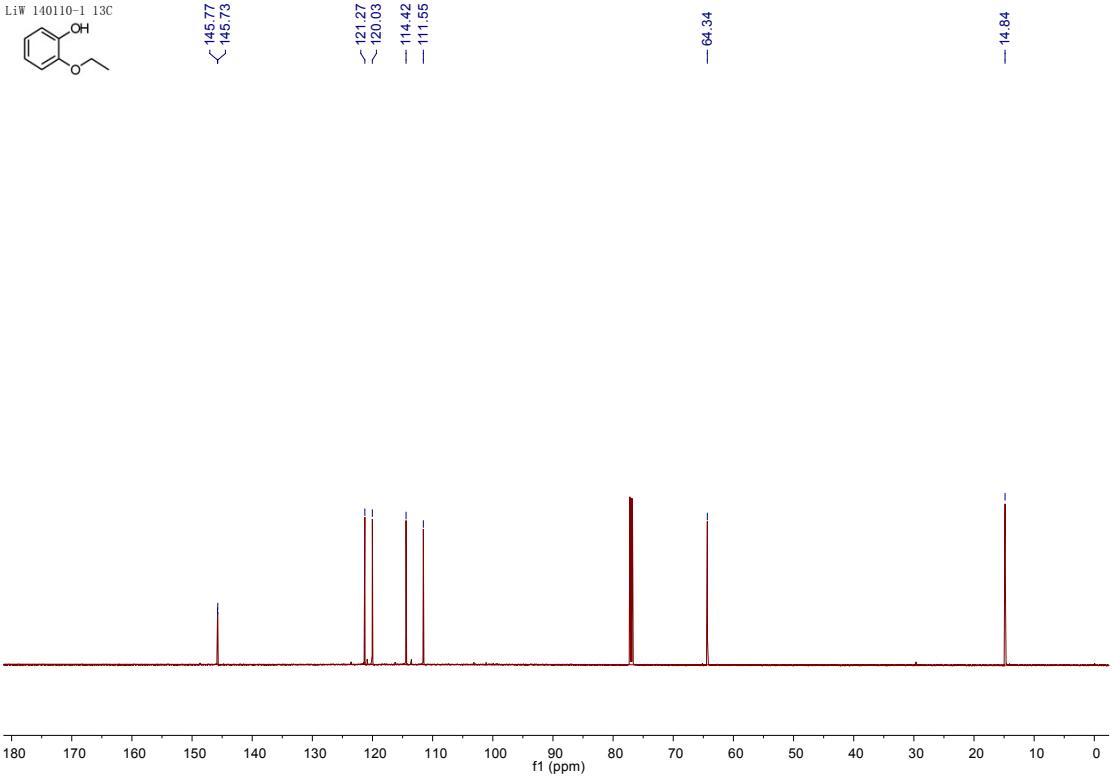
LiW 131114-1 13C

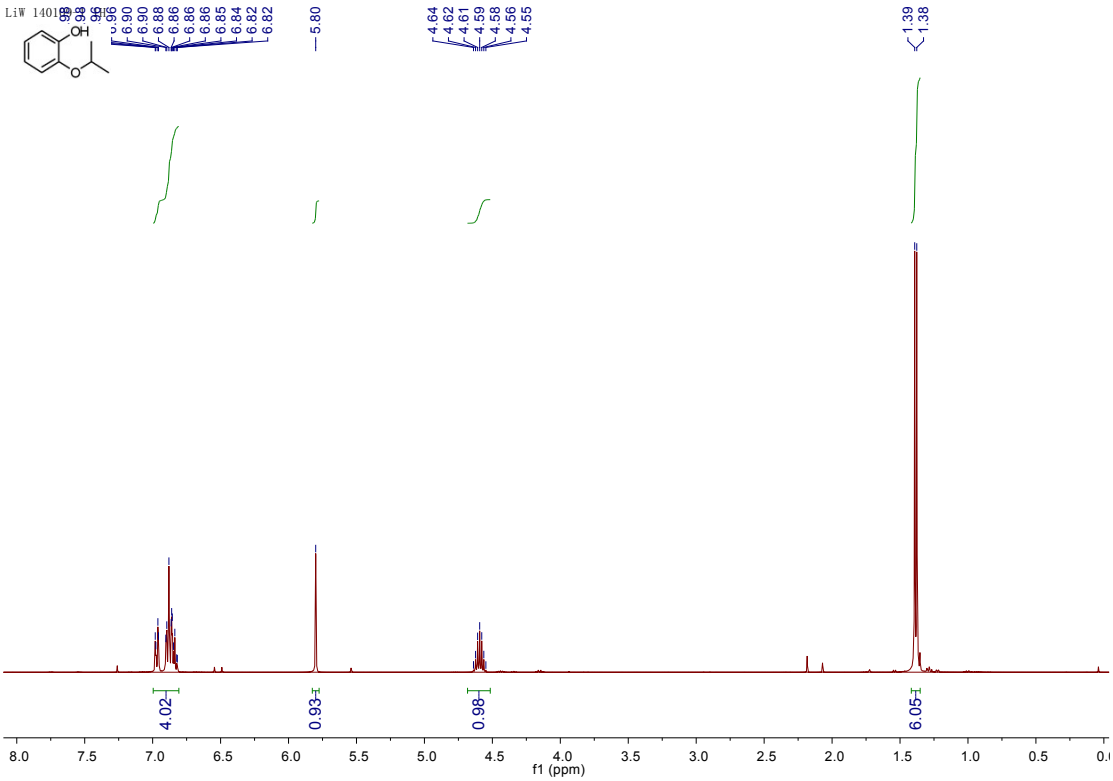


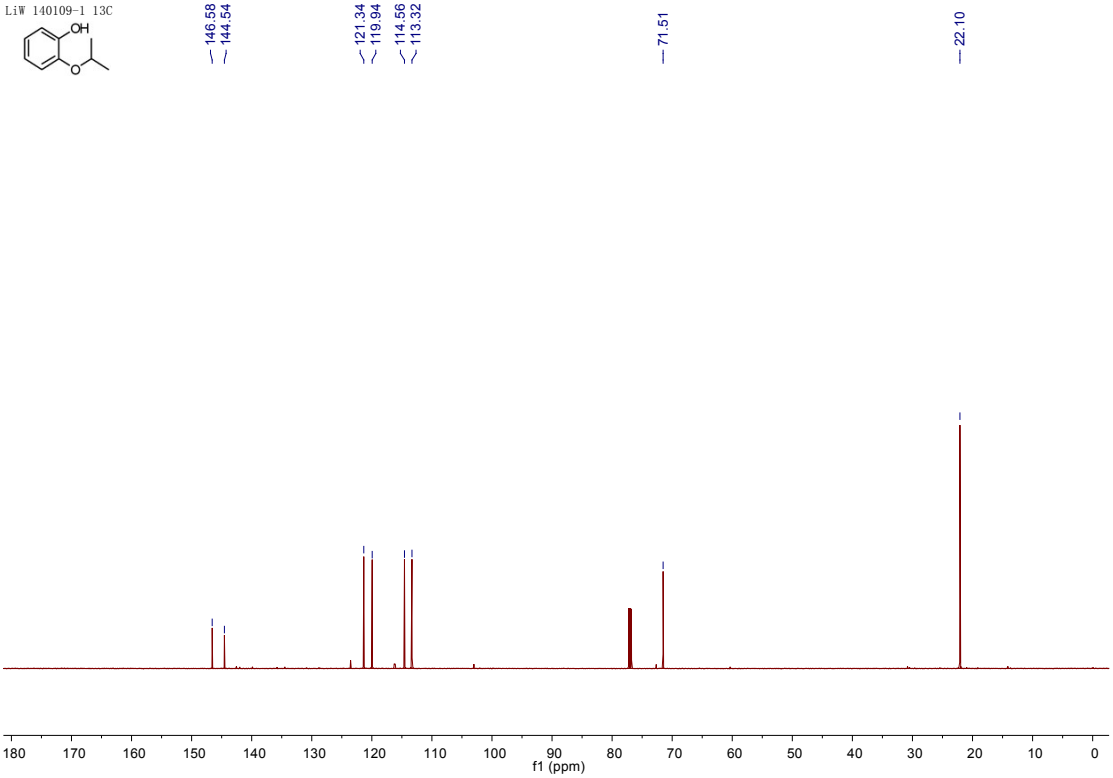

liw 150804-1 1H
OH
7.27
7.25
6.78
6.76
4.66
1.29
C (d)
7.26
B (d)
6.77
D (s)
4.66
A (s)
1.29
2.03
2.00
1.09
9.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

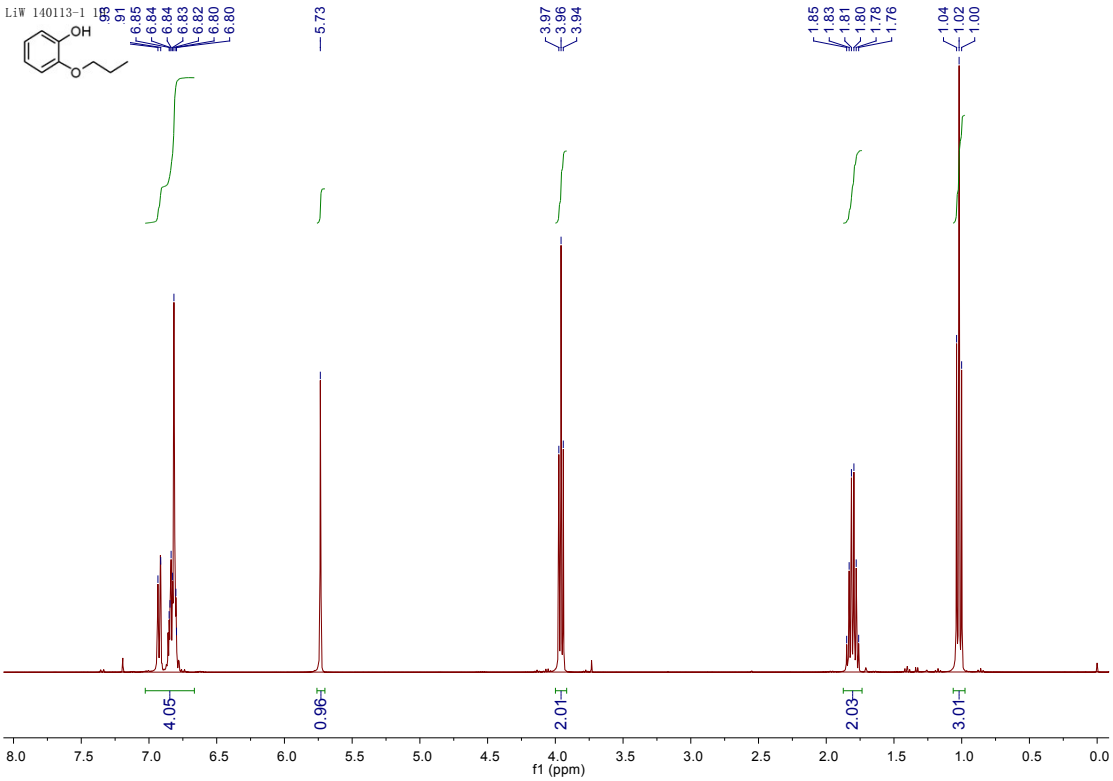

LiW 150804-1 13C
OH
153.11
143.47
126.41
114.70
34.05
31.51
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

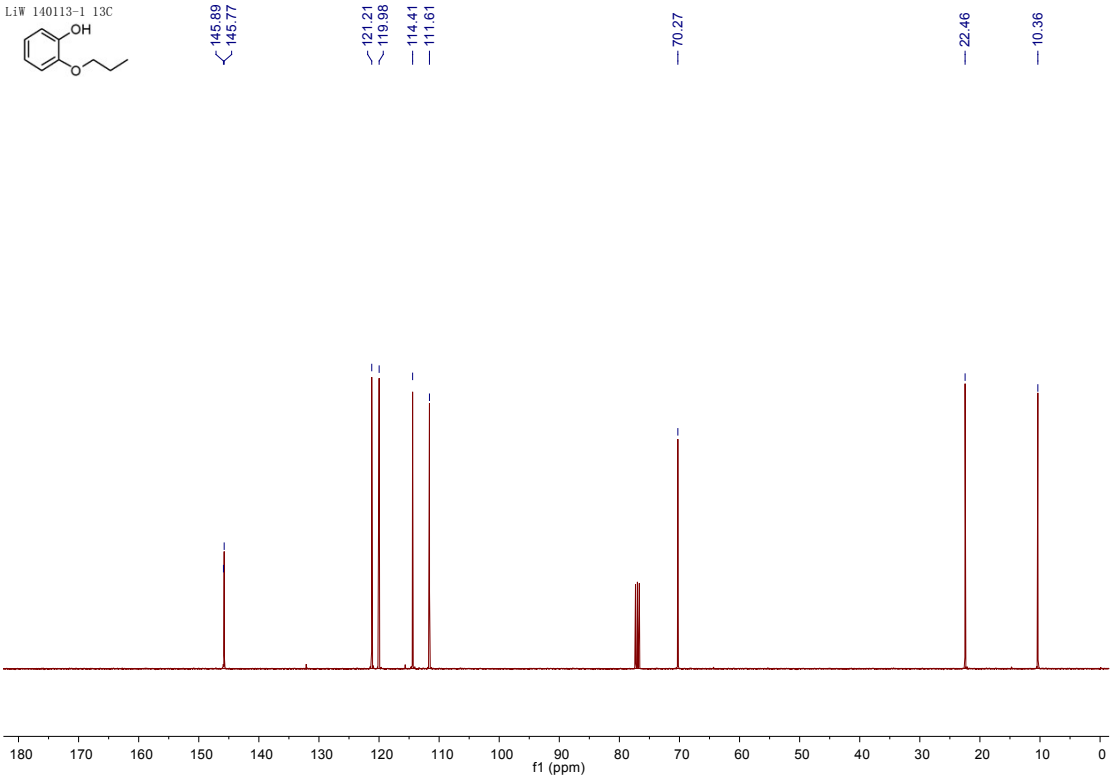

LiW 140110-1 1H
6.96
6.95
6.91
6.90
6.88
6.86
6.85
6.84
5.72
4.15
4.13
4.11
4.10
1.47
1.46
1.44
4.02
0.89
2.02
3.07
f1 (ppm)

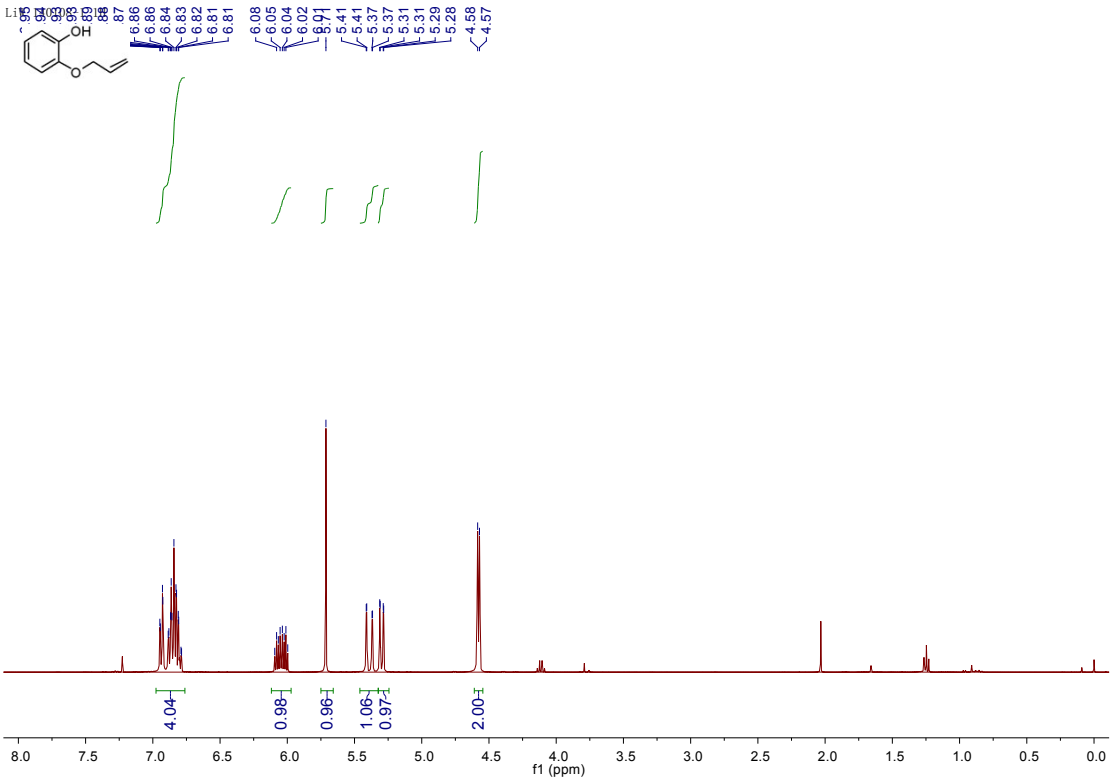

LiW 140110-1 13C
145.77
145.73
121.27
120.03
114.42
111.55
64.34
14.84
f1 (ppm)

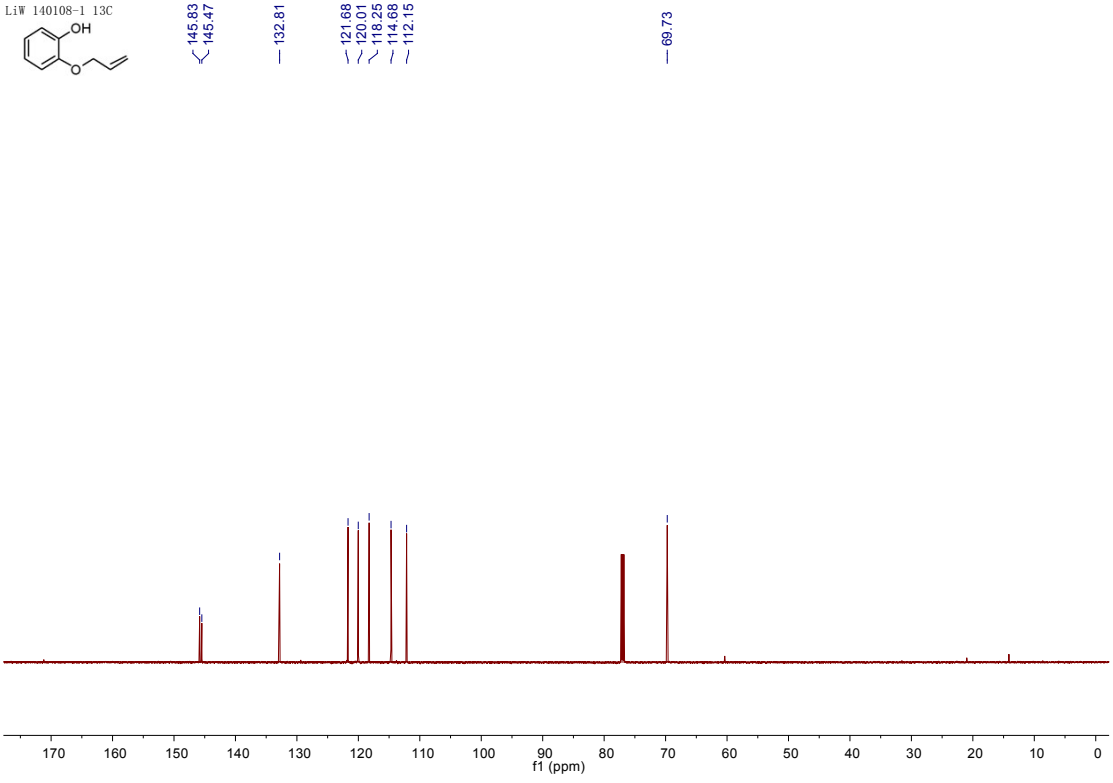

6.90
6.88
6.86
6.86
6.85
6.84
6.82
6.82
5.80
4.64
4.62
4.61
4.59
4.58
4.56
4.55
1.39
1.38
4.02
0.93
0.98
6.05
f1 (ppm)

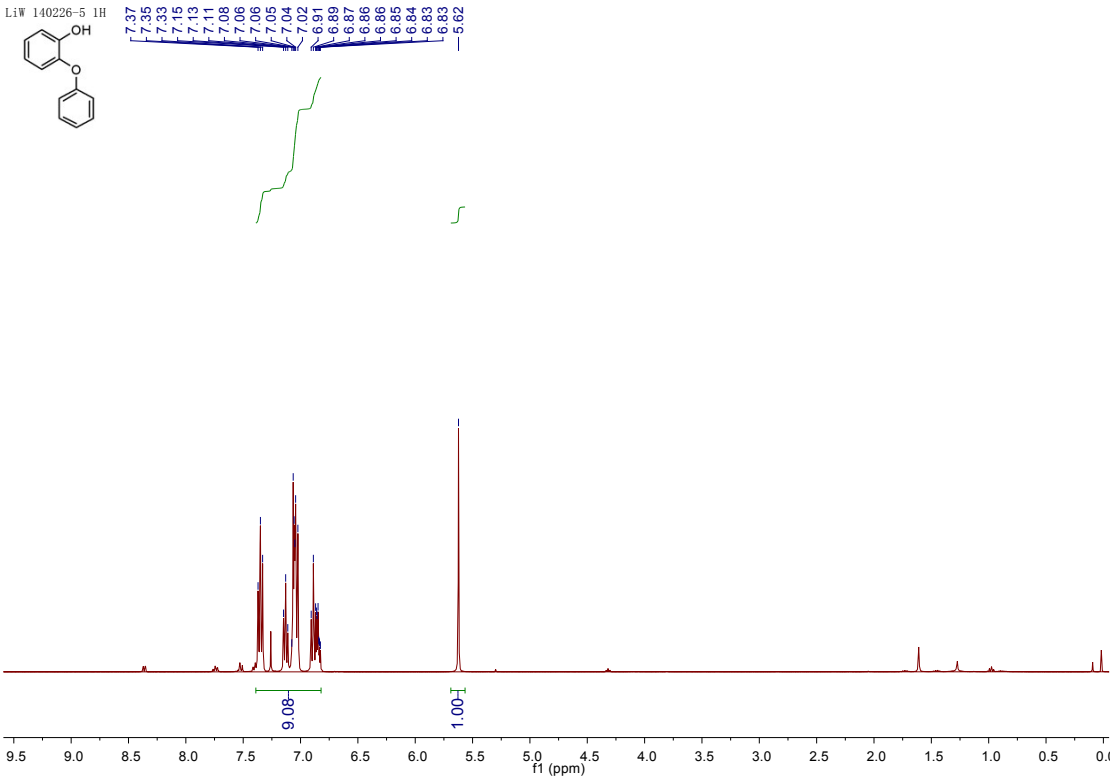

LiW 140109-1 13C
146.58
144.54
121.34
119.94
114.56
113.32
71.51
22.10
f1 (ppm)

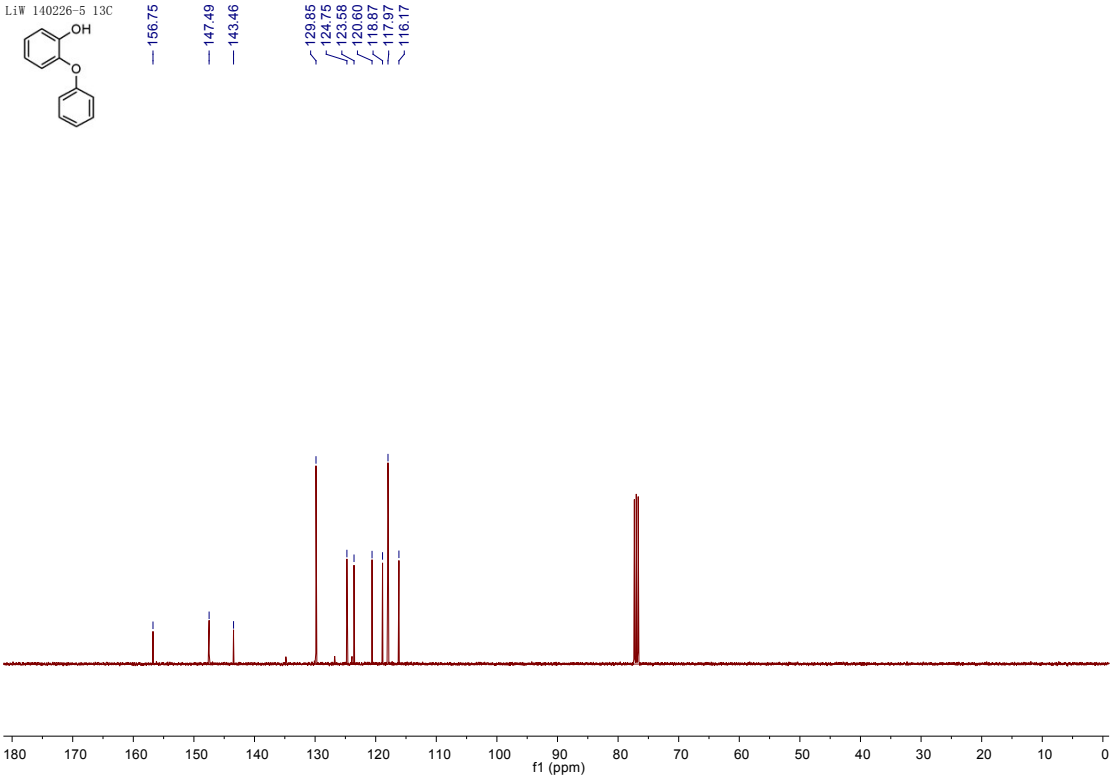

LiW 140113-1 1H
6.85
6.84
6.84
6.83
6.82
6.80
6.80
5.73
3.97
3.96
3.94
1.85
1.83
1.81
1.80
1.78
1.76
1.04
1.02
1.00
4.05
0.96
2.01
2.03
3.01
f1 (ppm)

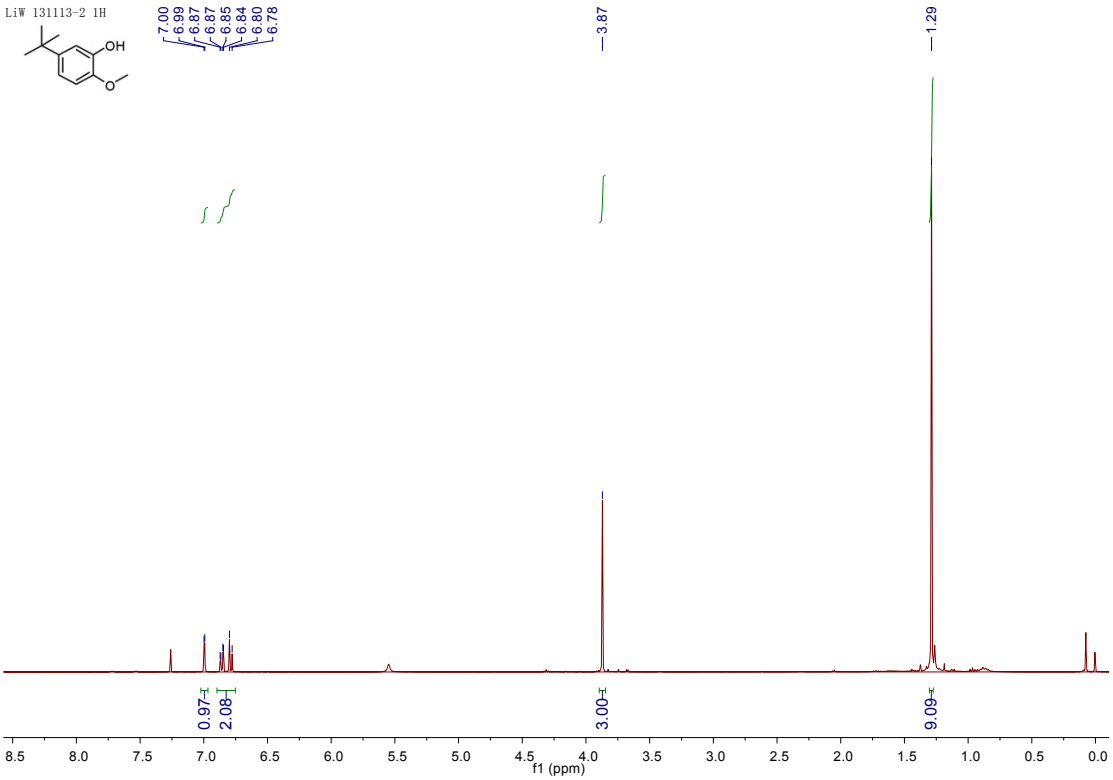

LiW 140113-1 13C
145.89
145.77
121.21
119.98
114.41
111.61
70.27
22.46
10.36
f1 (ppm)

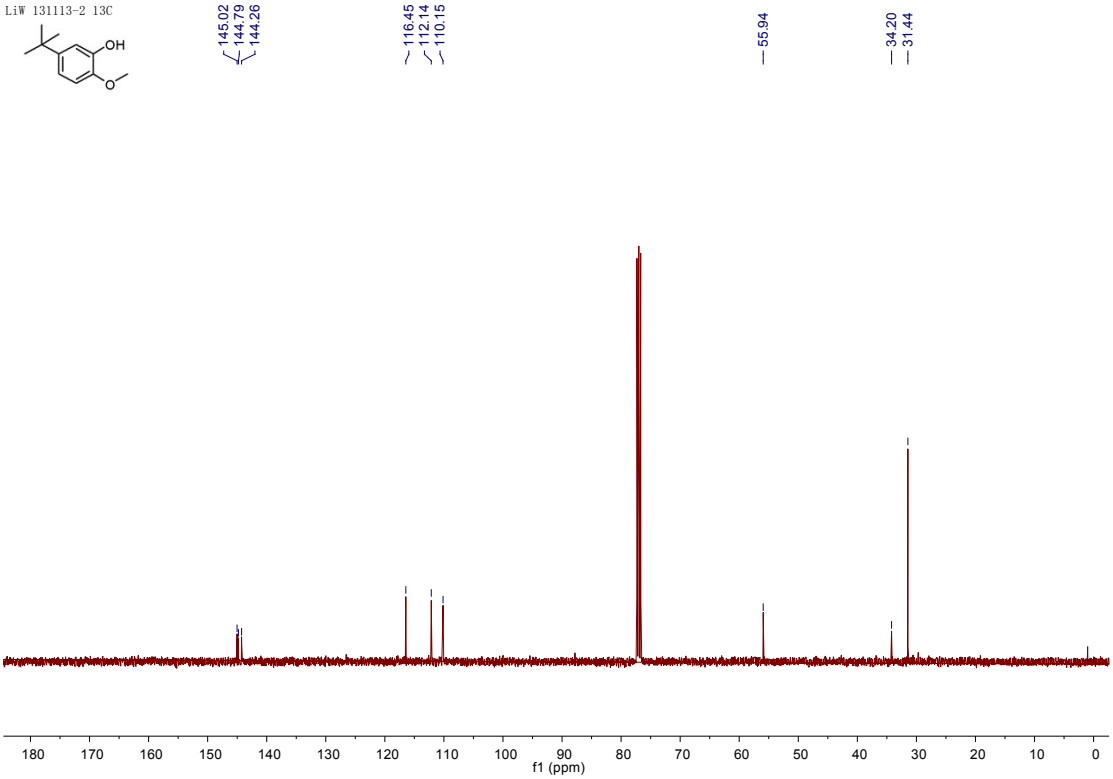

6.86
6.86
6.84
6.83
6.82
6.81
6.81
6.08
6.05
6.04
6.02
5.91
5.71
5.41
5.41
5.37
5.37
5.31
5.31
5.29
5.28
4.58
4.57
4.04
0.98
0.96
1.06
0.97
2.00
f1 (ppm)

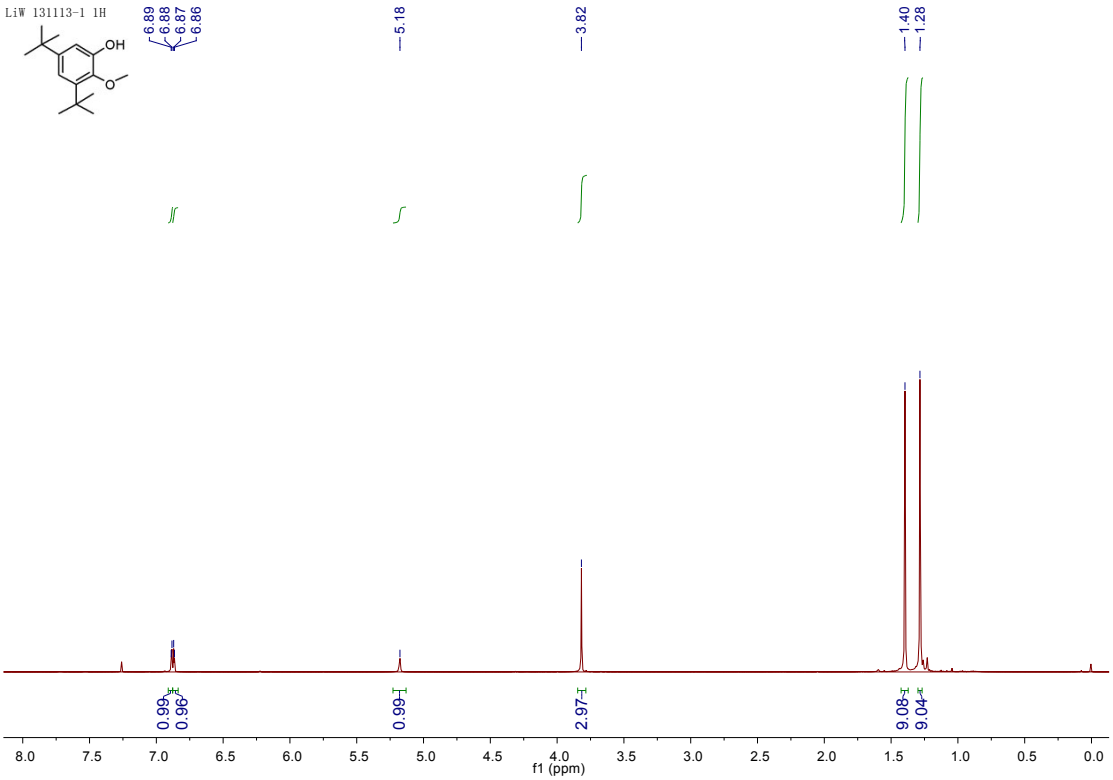

LiW 140108-1 13C
145.83
145.47
132.81
121.68
120.01
118.25
114.68
112.15
69.73
f1 (ppm)

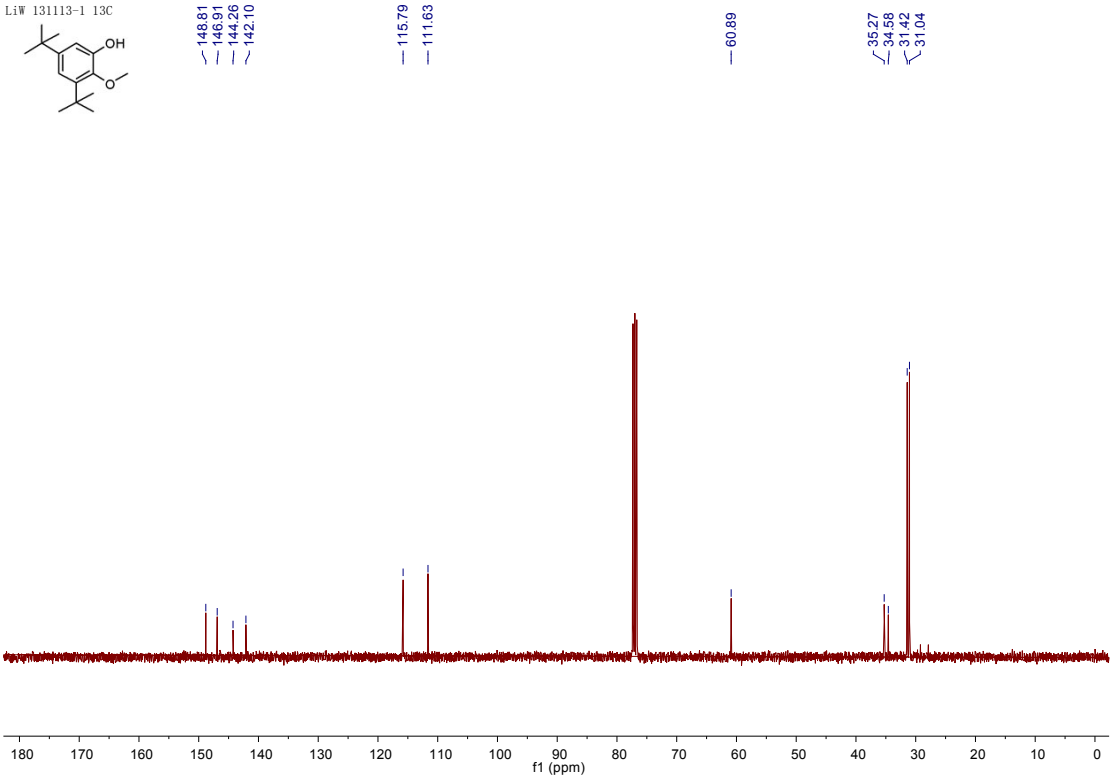

LiW 140226-5 1H
7.37
7.35
7.33
7.15
7.13
7.11
7.08
7.06
7.06
7.05
7.04
7.02
6.91
6.89
6.87
6.86
6.86
6.85
6.84
6.83
6.83
5.62
9.08
1.00
f1 (ppm)

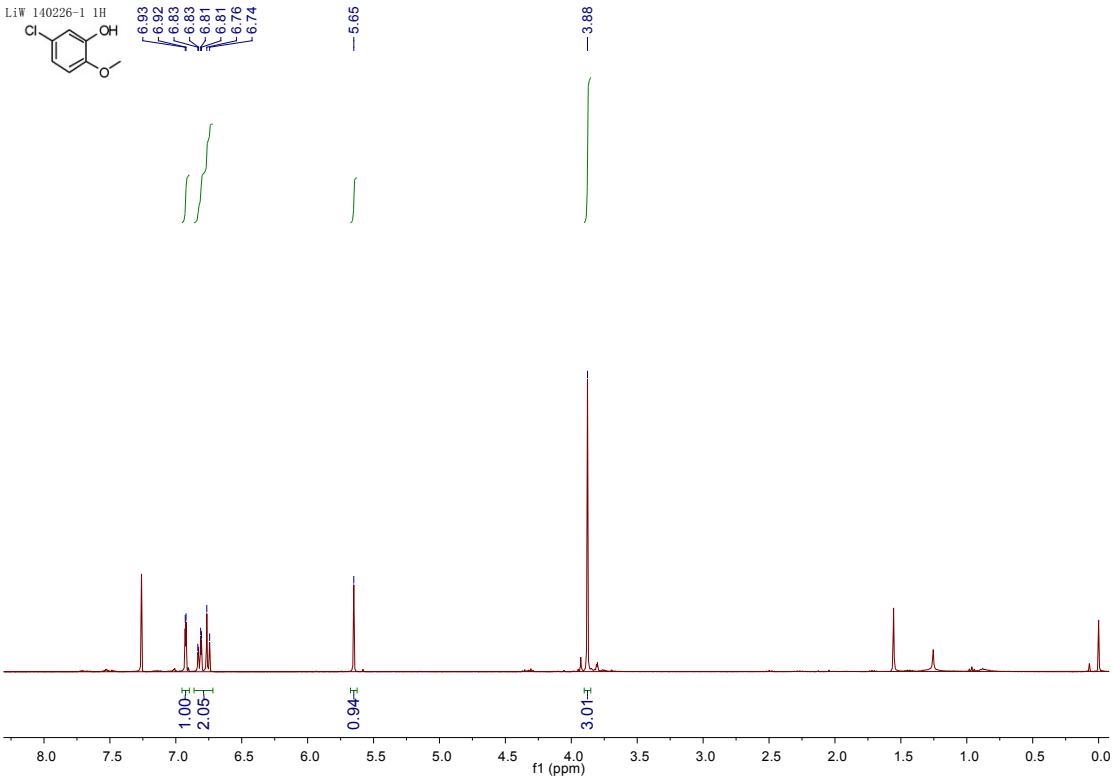

LiW 140226-5 13C
156.75
147.49
143.46
129.85
124.75
123.58
120.60
118.87
117.97
116.17
f1 (ppm)

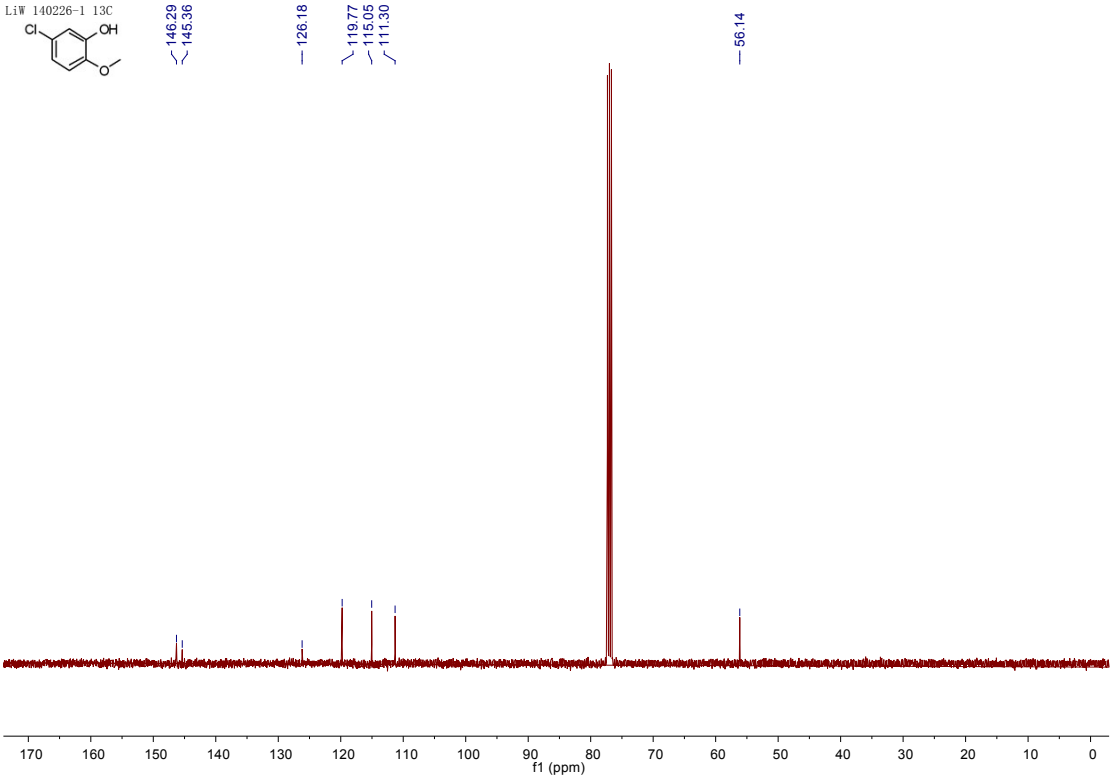

LiW 131113-2 1H
OH
O
7.00
6.99
6.87
6.87
6.85
6.84
6.80
6.78
3.87
1.29
0.97
2.08
3.00
9.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


LiW 131113-2 13C
OH
O
145.02
144.79
144.26
116.45
112.14
110.15
55.94
34.20
31.44
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

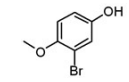

LiW 131113-1 1H
OH
O
6.89
6.88
6.87
6.86
5.18
3.82
1.40
1.28
0.99
0.96
0.99
2.97
9.08
9.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

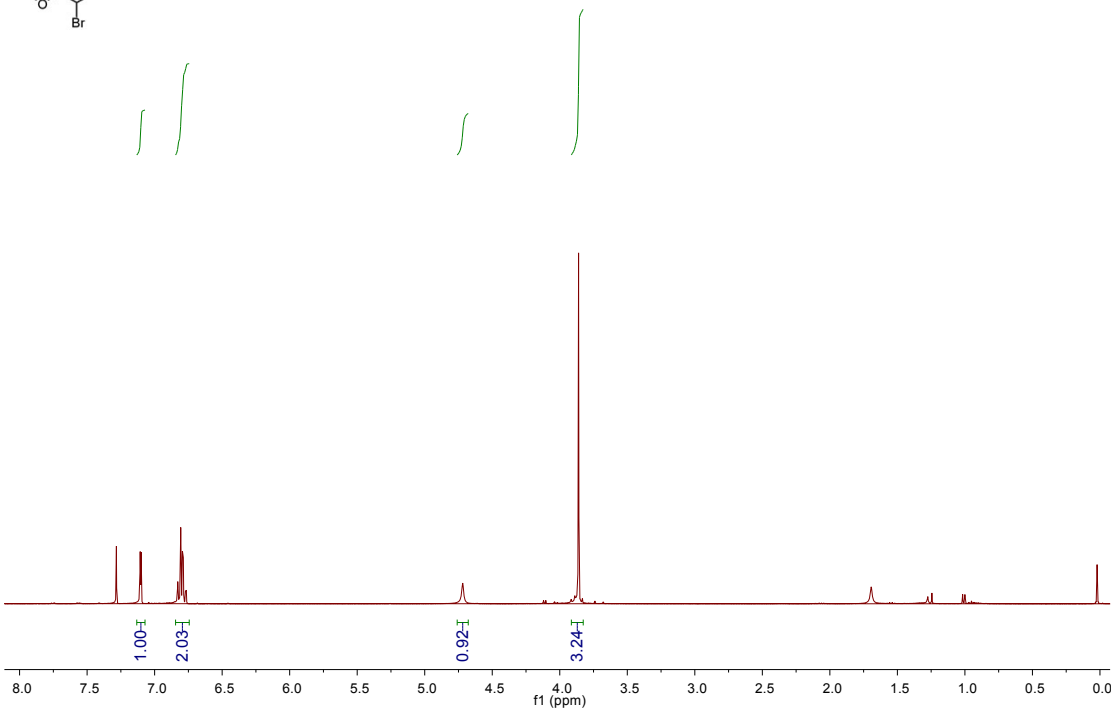

LiW 131113-1 13C
OH
O
148.81
146.91
144.26
142.10
115.79
111.63
60.89
35.27
34.58
31.42
31.04
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


LiW 140226-1 1H
Cl
OH
O
6.93
6.92
6.83
6.83
6.81
6.81
6.76
6.74
5.65
3.88
1.00
2.05
0.94
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

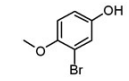

LiW 140226-1 13C
Cl
OH
O
146.29
145.36
126.18
119.77
115.05
111.30
56.14
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

LiW 160507-4 1H

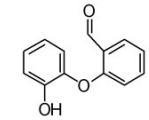


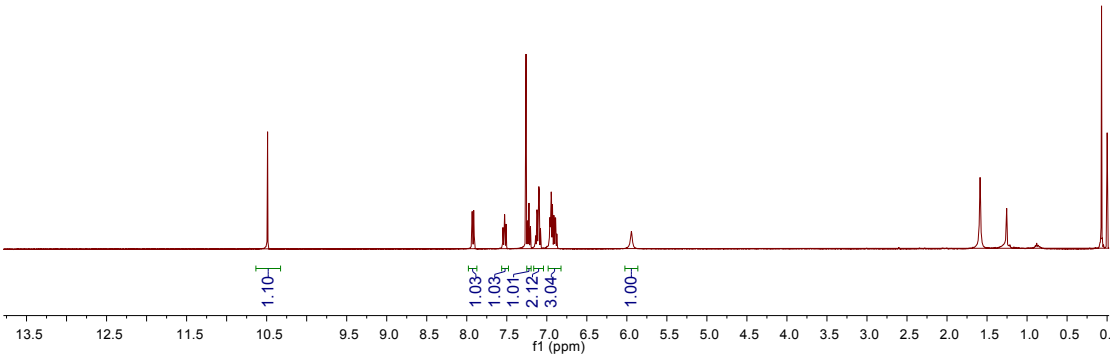


LiW 160507-4 13C

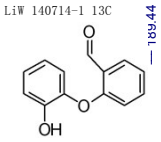


LiW 140714-1 1H

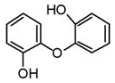




LiW 140714-1 13C



LiW 161221-1 1H



LiW 161221-1 13C