

Supporting Information

Green and efficient: oxidation of aldehydes to carboxylic acids and acid anhydrides with air

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1. General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^1H NMR: CDCl_3 7.26 ppm, ^{13}C NMR: CDCl_3 77.0 ppm, ^1H NMR: DMSO 2.50 ppm, ^{13}C NMR: 40.0 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Chromatographic purifications were carried out on a Biotage Isolera Four instrument. Mass spectra were performed on a spectrometer operating on ESI-TOF. GC-MS were obtained by EI on a Shimadzu GC-MS 2010.

2. Experimental procedure

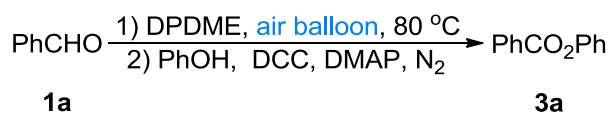
(a) General procedure for the synthesis of acid **2** and **4**

A mixture of aldehyde **1** (0.6 mmol) and DPDME (0.43 mL, 2.4 mmol) was added to a 5 mL round flask with an air balloon at room temperature. The reaction typically took 10 hours. The progress of the reaction was monitored by TLC or GC-MS. Upon completion, the reaction was cooled down to room temperature and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the desired **2** and **4**.

(b). Oxidation of **1a** on **1** mol with air

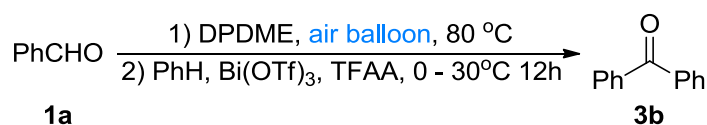
A mixture of benzaldehyde **1a** (106 g, 1 mol) and DPDME (550 ml) was added to a 1000 mL round-bottomed flask with an air bag at room temperature, then the contents were stirred at 80 °C for 40 hours. Upon completion, the reaction was cooled down to room temperature and concentrated under reduced pressure. The crude product was purified via recrystallization with petroleum ether/ethyl acetate (1 : 1) to give 113.1 g of **2a** in 93 % yield.

(c). One-pot synthesis of phenyl benzoate



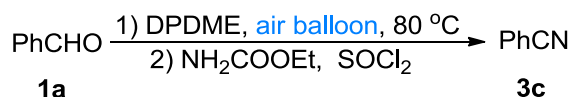
A mixture of benzaldehyde **1a** (0.6 mmol) and DPDME (0.43 mL, 2.4 mmol) was added to a 5 mL round flask with an air balloon at room temperature, then the contents were stirred at 80 °C for 10 hours. The contents were cooled to room temperature, phenol (0.6 mmol) was added under N₂ atmosphere, DCC (0.9 mmol), DMAP (0.3 mmol) was slowly added and stirred for 8 hours at room temperature. The reaction was quenched by adding water and extracted with EtOAc. The organic layer was washed with water and brine, dried over MgSO₄, filtered and evaporated under reduced pressure to afford the crude product which was further purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent. The overall yield was 88.3 %.

(d). One-pot synthesis of benzophenone



A mixture of benzaldehyde **1a** (0.6 mmol) and DPDME (0.43 mL, 2.4 mmol) was added to a 5 mL round flask with an air balloon at room temperature, then the contents were stirred at 80 °C for 10 hours. The contents were cooled to room temperature, then benzene (94 mg, 1.2 mmol), and Bi(OTf)₃ (40.0 mg, 0.06 mmol), TFAA (0.13 mL, 0.9 mmol) was added at 0 °C. The mixture was magnetically stirred at 30 °C for 12 hours. After the reaction mixture has been evaporated in vacuo, 5 mL of hexane was added to the gummy residue. The resulted solution was treated with ultrasonic cleaner bath (200 W) for 5 min. pale yellowish solid of Bi(OTf)₃ precipitated. The precipitate was filtered with suction. The filtrate was evaporated under the reduced pressure to give the crude product, which was further purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent. The overall yield was 86 %.

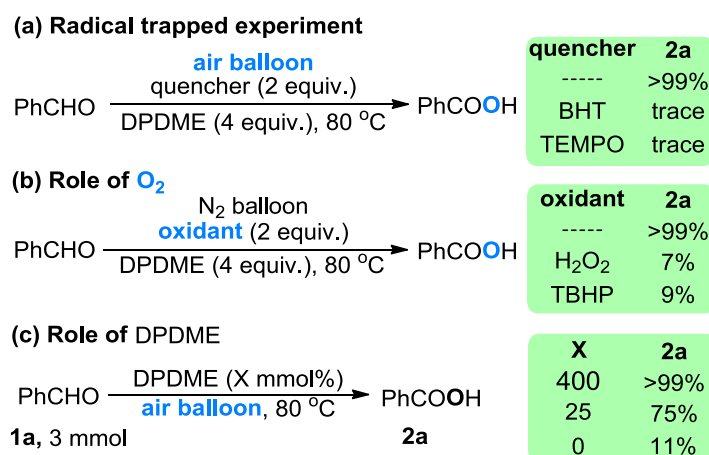
(e). One-pot synthesis of benzonitrile



A mixture of benzaldehyde **1a** (0.6 mmol) and DPDME (0.43 mL, 2.4 mmol) was added to a 5 mL round flask with an air balloon at room temperature, then the contents were stirred at 80 °C for 10 hours. The contents were cooled to room temperature, ethyl carbamate (0.66 mmol) was added. The mixture was stirred at 75 °C with the dropwise addition of SOCl₂ (44 µL, 0.6 mmol) in DPDME (1 mL) solution over a period of about 5 min. The mixture was subsequently stirred at 75 - 80 °C for another 4

h. The progress of the reaction was monitored by TLC. The reaction mixture was diluted with water and extracted with EtOAc (3x10 ml). The organic layer was washed with saturated solution of Na_2CO_3 and followed by water and brine. The organic layer was dried over anhydrous Na_2SO_4 . The mixture was filtered and evaporated under reduced pressure to afford the crude product, which was further purified by silica gel column chromatography with petroleum ether/ethyl acetate as eluent. The overall yield was 85 %.

3. Mechanism Research



(a) Radical trapped experiment:

A mixture of benzaldehyde **1a** (61 μ L, 0.6 mmol), DPDME (0.43 mL, 2.4 mmol) and 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO, 186 mg, 1.2 mmol) or butylret hydroxytoluen (BHT, 264 mg, 1.2 mmol) was added to a 10 mL round-bottomed flask with an air balloon at room temperature, then the contents were stirred at 80 $^{\circ}$ C for 10 hours. The reaction was cooled down to room temperature and analyzed by GC-MS showed trace product formation.

(b) Role of O_2 :

A mixture of benzaldehyde **1a** (61 μ L, 0.6 mmol), DPDME (0.43 mL, 2.4 mmol) and hydrogen peroxide (103 μ L, 1.2 mmol) or 2-hydroperoxy-2-methylpropane (TBHP, 115 μ L, 1.2 mmol) was added to a 10 mL round-bottomed flask with an air balloon at room temperature, then the contents were stirred at 80 $^{\circ}$ C for 10 hours. The reaction was cooled down to room temperature and analyzed by GC-MS showed that **2a** was obtained in 7% and 9% yields respectively.

(c) Role of DPDME

A mixture of benzaldehyde **1a** (305 μ L, 3 mmol) and DPDME (135 μ L, 0.75 mmol) was added to a 5 mL round-bottomed flask with an air balloon at room temperature, then the contents were stirred at

80 °C for 12 hours. The reaction was cooled down to room temperature and analyzed by GC-MS showed 75% product formation.

A mixture of benzaldehyde **1a** (305 μ L, 3 mmol) was added to a 5 mL round-bottomed flask with an air balloon at room temperature, then the contents were stirred at 80 °C for 15 hours. The reaction was cooled down to room temperature and analyzed by GC-MS showed 11% product formation.

4. Characterization data of products

benzoic acid (2a)^[1]: ¹H NMR (400 MHz, DMSO) δ 12.97 (s, 1 H), 7.96 - 7.93 (m, 2 H), 7.65 - 7.60 (m, 1 H), 7.52 - 7.48 (m, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.8, 133.4, 131.2, 129.8, 129.1.

4-methylbenzoic acid (2b)^[1]: ¹H NMR (400 MHz, DMSO) δ 12.80 (s, 1 H), 7.83 (d, J = 8.0 Hz, 2 H), 7.30 (d, J = 8.0 Hz, 2 H), 2.36 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 167.8, 143.6, 129.8, 129.6, 128.5, 21.6.

4-isopropylbenzoic acid (2c)^[1]: ¹H NMR (400 MHz, DMSO) δ 12.81 (s, 1 H), 7.86 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.0 Hz, 2 H), 3.01 - 2.90 (m, 1 H), 1.21 (d, J = 6.8 Hz, 6 H); ¹³C NMR (100 MHz, DMSO) δ 167.8, 154.1, 130.0, 128.9, 127.0, 34.0, 24.1.

[1,1'-biphenyl]-4-carboxylic acid (2d)^[2]: ¹H NMR (400 MHz, DMSO) δ 13.01 (s, 1 H), 8.02 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 2 H), 7.74 (d, J = 7.2 Hz, 2 H), 7.50 (t, J = 7.2 Hz, 2 H), 7.42 (t, J = 7.2 Hz, 1 H); ¹³C NMR (100 MHz, DMSO) δ 167.7, 144.8, 139.5, 130.5, 130.1, 129.6, 128.8, 127.5, 127.3.

4-hydroxybenzoic acid (2e)^[1]: ¹H NMR (400 MHz, DMSO) δ 12.42 (s, 1 H), 10.21 (s, 1 H), 7.78 (d, J = 8.8 Hz, 2 H), 6.82 (d, J = 8.4 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.7, 162.1, 132.0, 121.8, 115.6.

4-methoxybenzoic acid (2f)^[1]: ¹H NMR (400 MHz, DMSO) δ 12.63 (s, 1 H), 7.89 (d, J = 8.8 Hz, 2 H), 7.02 (d, J = 8.8 Hz, 2 H), 3.82 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 167.5, 163.3, 131.8, 123.5, 114.3, 55.9.

4-(trifluoromethoxy)benzoic acid (2g)^[3]: ¹H NMR (400 MHz, DMSO) δ 13.26 (s, 1 H), 8.06 (d, J = 8.8 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 166.7, 152.0, 132.2, 130.4, 121.2, 120.0 (q, J = 255.9 Hz); ¹⁹F NMR (376 MHz, DMSO) δ -56.7.

4-((tert-butyl)dimethylsilyloxy)benzoic acid (2h)^[4]: ¹H NMR (400 MHz, DMSO) δ 12.65 (s, 1 H), 7.85 (d, J = 8.4 Hz, 2 H), 6.93 (d, J = 8.8 Hz, 2 H), 0.95 (s, 9 H), 0.22 (s, 6 H); ¹³C NMR (100 MHz, DMSO) δ 167.4, 159.7, 131.9, 124.4, 120.2, 26.0, 18.5, -4.1.

4-mercaptobenzoic acid (2i)^[51]: ¹H NMR (400 MHz, DMSO) δ 13.07 (s, 1 H), 7.93 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.2, 141.3, 130.9, 130.2, 126.6.

4-(methylthio)benzoic acid (2j)^[61]: ¹H NMR (400 MHz, DMSO) δ 12.86 (s, 1 H), 7.85 (d, J = 8.8 Hz, 2 H), 7.34 (d, J = 8.8 Hz, 2 H), 2.52 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 167.6, 145.3, 130.2, 127.2, 125.4, 14.4.

4-((trifluoromethyl)thio)benzoic acid (2k)^[71]: ¹H NMR (400 MHz, DMSO) δ 13.43 (s, 1 H), 8.05 (d, J = 8.4 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 166.9, 136.4, 133.8, 131.0, 130.1 (d, J = 282.3 Hz); ¹⁹F NMR (376 MHz, DMSO) δ -41.4.

4-(trifluoromethyl)benzoic acid (2l)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.49 (s, 1 H), 8.13 (d, J = 8.0 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 166.7, 135.1, 133.3 (q, J = 31.6 Hz), 130.6, 126.1 (q, J = 3.8 Hz), 124.4 (q, J = 270.9 Hz); ¹⁹F NMR (376 MHz, DMSO) δ -61.6.

4-fluorobenzoic acid (2m)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.08 (s, 1 H), 8.03 - 7.98 (m, 2 H), 7.35 - 7.29 (m, 2 H); ¹³C NMR (100 MHz, DMSO) δ 166.9, 165.5 (d, J = 248.9 Hz), 132.7 (d, J = 9.5 Hz), 127.9, 116.2 (d, J = 21.9 Hz); ¹⁹F NMR (376 MHz, DMSO) δ -106.9.

4-chlorobenzoic acid (2n)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.20 (s, 1 H), 7.94 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.0, 138.3, 131.7, 130.1, 129.3.

4-bromobenzoic acid (2o)^[81]: ¹H NMR (400 MHz, DMSO) δ 13.19 (s, 1 H), 7.86 (d, J = 8.4 Hz, 2 H), 7.71 (d, J = 8.8 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.1, 132.2, 131.8, 130.5, 127.4.

4-nitrobenzoic acid (2p)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.69 (s, 1 H), 8.32 (d, J = 8.8 Hz, 2 H), 8.17 (d, J = 8.8 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 166.3, 150.6, 136.9, 131.2, 124.3.

4-(chloromethyl)benzoic acid (2q)^[91]: ¹H NMR (400 MHz, DMSO) δ 13.06 (s, 1 H), 7.94 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 4.83 (s, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.4, 142.9, 131.1, 130.2, 129.5, 45.8.

4-cyanobenzoic acid (2r)^[2]: ¹H NMR (400 MHz, DMSO) δ 13.60 (s, 1 H), 8.06 (s, 2 H), 8.01 (s, 2 H); ¹³C NMR (100 MHz, DMSO) δ 133.6, 118.7, 115.5.

4-(methoxycarbonyl)benzoic acid (2s)^[3]: ¹H NMR (400 MHz, DMSO) δ 13.37 (s, 1 H), 8.06 (s, 4 H), 3.88 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 167.1, 166.1, 135.3, 133.7, 130.1, 129.9, 53.0.

3-methylbenzoic acid (2t)^[3]: ¹H NMR (400 MHz, DMSO) δ 12.89 (s, 1 H), 7.76 (s, 1 H), 7.74 (d, *J* = 7.6 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 2.36 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 167.9, 138.4, 134.0, 131.2, 130.2, 129.0, 127.0, 21.3.

3-chlorobenzoic acid (2u)^[3]: ¹H NMR (400 MHz, DMSO) δ 13.34 (s, 1 H), 7.90 - 7.88 (m, 2 H), 7.71 - 7.68 (m, 1 H), 7.54 (t, *J* = 8.0 Hz, 1 H); ¹³C NMR (100 MHz, DMSO) δ 166.6, 133.8, 133.4, 133.2, 131.2, 129.3, 128.4.

2-methylbenzoic acid (2v)^[3]: ¹H NMR (400 MHz, DMSO) δ 12.82 (s, 1 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.46 - 7.42 (m, 1 H), 7.28 (t, *J* = 8.4 Hz, 2 H), 2.51 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 169.2, 139.5, 132.2, 132.0, 130.9, 130.7, 126.4, 21.8.

2-chlorobenzoic acid (2w)^[10]: ¹H NMR (400 MHz, DMSO) δ 13.41 (s, 1 H), 7.79 - 7.77 (m, 1 H), 7.56 - 7.51 (m, 2 H), 7.45 - 7.41 (m, 1 H); ¹³C NMR (100 MHz, DMSO) δ 167.3, 133.1, 132.1, 132.0, 131.3, 131.1, 127.8.

3,4-dichlorobenzoic acid (2x)^[10]: ¹H NMR (400 MHz, DMSO) δ 13.51 (s, 1 H), 8.05 (d, *J* = 2.0 Hz, 1 H), 7.88 (dd, *J* = 8.0, 1.8 Hz, 1 H), 7.77 (d, *J* = 8.4 Hz, 1 H); ¹³C NMR (100 MHz, DMSO) δ 165.9, 136.3, 132.0, 131.9, 131.6, 131.5, 129.8.

2,6-dimethoxybenzoic acid (2y)^[11]: ¹H NMR (400 MHz, DMSO) δ 12.73 (s, 1 H), 7.31 (t, *J* = 8.4 Hz, 1 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 3.75 (s, 6 H); ¹³C NMR (100 MHz, DMSO) δ 167.2, 156.6, 130.9, 114.8, 104.6, 56.3.

2,4,6-trimethylbenzoic acid (2z)^[1]: ¹H NMR (400 MHz, DMSO) δ 12.96 (s, 1 H), 6.87 (s, 2 H), 2.23 (s, 9 H); ¹³C NMR (100 MHz, DMSO) δ 171.3, 138.5, 134.1, 133.0, 128.5, 21.1, 19.8.

2,3,4,5,6-pentafluorobenzoic acid (2aa)^[12]: ¹H NMR (400 MHz, DMSO) δ 14.75 (s, 1 H); ¹³C NMR (100 MHz, DMSO) δ 160.4, 146.4 - 146.1 (m), 144.1 - 143.6 (m), 141.6 - 141.3 (m), 139.3 - 138.9 (m), 136.8 - 136.4 (m), 110.0 - 109.6 (m); ¹⁹F NMR (376 MHz, DMSO) δ -140.55 - -140.62 (m, 2F), -151.15 (t, *J* = 22.6 Hz, 1F), -161.58 - -161.69 (m, 2F).

terephthalic acid (2ab)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.31 (s, 2 H), 8.04 (s, 4 H); ¹³C NMR (100 MHz, DMSO) δ 167.2, 134.9, 130.0.

furan-2-carboxylic acid (2ac)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.07 (s, 1 H), 7.91 (s, 1 H), 7.21 (d, *J* = 3.2 Hz, 1 H), 6.66 - 6.64 (m, 1 H); ¹³C NMR (100 MHz, DMSO) δ 159.8, 147.6, 145.4, 118.2, 112.6.

thiophene-2-carboxylic acid (2ad)^[11]: ¹H NMR (400 MHz, DMSO) δ 13.07 (s, 1 H), 7.88 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.73 (dd, *J* = 4.0, 1.2 Hz, 1 H), 7.18 (dd, *J* = 5.0, 4.0 Hz, 1 H); ¹³C NMR (100 MHz, DMSO) δ 163.4, 135.1, 133.8, 133.7, 128.7.

isonicotinic acid (2ae)^[10]: ¹H NMR (400 MHz, DMSO) δ 13.71 (s, 1 H), 8.78 (d, *J* = 6.0 Hz, 2 H), 7.81 (d, *J* = 6.0 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 166.7, 151.2, 138.6, 123.3.

benzo[d][1,3]dioxole-5-carboxylic acid (2af)^[6]: ¹H NMR (400 MHz, DMSO) δ 12.78 (s, 1 H), 7.54 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.36 (d, *J* = 1.6 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 1 H), 6.12 (s, 2 H); ¹³C NMR (100 MHz, DMSO) δ 167.1, 151.7, 148.0, 125.5, 125.1, 109.3, 108.6, 102.5.

2-naphthoic acid (2ag)^[13]: ¹H NMR (400 MHz, DMSO) δ 13.08 (s, 1 H), 8.61 (s, 1 H), 8.12 (d, *J* = 5.6 Hz, 1 H), 8.03 - 7.96 (m, 3 H), 7.68 - 7.59 (m, 2 H); ¹³C NMR (100 MHz, DMSO) δ 168.0, 135.4, 132.7, 131.0, 129.8, 128.9, 128.7, 128.6, 128.2, 127.3, 125.7.

Ferrrocene Monocarboxylic Acid (2ah)^[14]: ¹H NMR (400 MHz, DMSO) δ 12.15 (s, 1 H), 4.70 (t, *J* = 2.0 Hz, 2 H), 4.44 (t, *J* = 2.0 Hz, 2 H), 4.21 (s, 5 H); ¹³C NMR (100 MHz, DMSO) δ 172.7, 72.4, 71.6, 70.4, 70.0.

hexanoic acid (2ai)^[15]: ¹H NMR (400 MHz, DMSO) δ 11.96 (s, 1 H), 2.18 (t, *J* = 7.4 Hz, 2 H), 1.52 - 1.45 (m, 2 H), 1.30 - 1.22 (m, 4 H), 0.86 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, DMSO) δ 175.0, 34.1, 31.3, 24.7, 22.4, 14.3.

octanoic acid (2aj)^[12]: ¹H NMR (400 MHz, DMSO) δ 11.95 (s, 1 H), 2.18 (t, *J* = 7.2 Hz, 2 H), 1.52 - 1.45 (m, 2 H), 1.25 (s, 8 H), 0.85 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, DMSO) δ 175.0, 34.2, 31.7, 29.0, 28.9, 25.0, 22.6, 14.4.

dodecanoic acid (2ak)^[2]: ¹H NMR (400 MHz, DMSO) δ 11.96 (s, 1 H), 2.17 (t, *J* = 7.4 Hz, 2 H), 1.47 (t, *J* = 7.0 Hz, 2 H), 1.24 (s, 16H), 0.85 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, DMSO) δ 175.0, 34.2, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 25.0, 22.6, 14.4.

6-methoxy-6-oxohexanoic acid (2al)^[16]: ¹H NMR (400 MHz, DMSO) δ 12.02 (s, 1 H), 3.58 (s, 3 H), 2.30 (t, *J* = 7.0 Hz, 2 H), 2.20 (t, *J* = 7.0 Hz, 2 H), 1.51 (m, 4 H); ¹³C NMR (100 MHz, DMSO) δ 174.8, 173.7, 51.7, 33.8, 33.5, 24.5, 24.5.

6-oxoheptanoic acid (2am)^[17]: ¹H NMR (400 MHz, DMSO) δ 11.99 (s, 1 H), 2.42 (t, *J* = 6.8 Hz, 2 H), 2.20 - 2.17 (m, 2 H), 2.06 (s, 3 H), 1.46 - 1.43 (m, 4 H); ¹³C NMR (100 MHz, DMSO) δ 208.8, 174.9, 42.9, 34.0, 30.2, 24.5, 23.3.

5-chloropentanoic acid (2an)^[18]: ¹H NMR (400 MHz, DMSO) δ 11.99 (s, 1 H), 3.63 (t, *J* = 6.4 Hz, 2 H), 2.24 (t, *J* = 7.2 Hz, 2 H), 1.76 - 1.69 (m, 2 H), 1.64 - 1.58 (m, 2 H); ¹³C NMR (100 MHz, DMSO) δ 174.8, 45.6, 33.3, 32.0, 22.4.

5-bromopentanoic acid (2ao)^[18]: ¹H NMR (400 MHz, DMSO) δ 12.10 (s, 1 H), 3.53 (t, *J* = 6.4 Hz, 2 H), 2.25 (t, *J* = 7.2 Hz, 2 H), 1.84 - 1.77 (m, 2 H), 1.64 - 1.56 (m, 2 H); ¹³C NMR (100 MHz, DMSO) δ 174.8, 35.3, 33.2, 32.1, 23.7.

cyclopentanecarboxylic acid (2ap)^[15]: ¹H NMR (400 MHz, DMSO) δ 11.96 (s, 1 H), 2.66 - 2.58 (m, 1 H), 1.79 - 1.74 (m, 2 H), 1.70 - 1.48 (m, 6 H); ¹³C NMR (100 MHz, DMSO) δ 178.0, 43.8, 30.1, 26.0.

cyclohexanecarboxylic acid (2aq)^[11]: ¹H NMR (400 MHz, DMSO) δ 11.98 (s, 1 H), 2.21 - 2.14 (m, 1 H), 1.81 - 1.78 (m, 2 H), 1.67 - 1.63 (m, 2 H), 1.58 - 1.54 (m, 1 H), 1.36 - 1.13 (m, 5 H); ¹³C NMR (100 MHz, DMSO) δ 177.3, 42.7, 29.2, 26.0, 25.5.

adamantane-1-carboxylic acid (2ar)^[12]: ¹H NMR (400 MHz, DMSO) δ 11.99 (s, 1 H), 1.95 (s, 3 H), 1.78 (d, *J* = 2.4 Hz, 6 H), 1.69 - 1.62 (m, 6 H); ¹³C NMR (100 MHz, DMSO) δ 179.0, 39.0, 36.5, 27.9.

1-(*tert*-butoxycarbonyl)pyrrolidine-2-carboxylic acid (2as)^[19]: ¹H NMR (400 MHz, DMSO) δ 12.50 (s, 1 H), 4.08 - 4.03 (m, 1 H), 3.30 - 3.24 (m, 2 H), 2.23 - 2.08 (m, 1 H), 1.88 - 1.74 (m, 3 H), 1.39 (s, 3 H), 1.34 (s, 6 H); ¹³C NMR (100 MHz, DMSO) δ 174.8, 153.6, 79.1, 59.1, 46.6, 30.8, 29.9, 28.6, 28.4, 24.4, 23.6.

4-hydroxy-3,5-dimethoxybenzoic acid (2at)^[20]: ¹H NMR (400 MHz, DMSO) δ 12.61 (s, 1 H), 9.23 (s, 1 H), 7.20 (s, 2 H), 3.80 (s, 6 H); ¹³C NMR (100 MHz, DMSO) δ 167.8, 147.9, 140.7, 120.8, 107.3, 56.4.

2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid (2au)^[21]: ¹H NMR (400 MHz, DMSO) δ 12.42 (s, 1 H), 7.98 (d, *J* = 2.4 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.68 - 7.64 (m, 1 H), 7.58 - 7.51 (m, 2 H), 7.48 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 5.29 (s, 2 H), 3.63 (s, 2 H); ¹³C NMR (100 MHz, DMSO) δ 190.7, 173.2, 160.3, 140.5, 137.5, 136.4, 133.6, 132.3, 129.7, 129.4, 129.3, 128.8, 125.0, 121.1, 73.2.

2-(4-isobutylphenyl)propanoic acid (2av)^[22]: ¹H NMR (400 MHz, DMSO) δ 12.24 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 3.62 (q, *J* = 7.2 Hz, 1 H), 2.41 (d, *J* = 7.2 Hz, 2 H), 1.85 - 1.75 (m, 1 H), 1.34 (d, *J* = 6.8 Hz, 3 H), 0.85 (d, *J* = 6.8 Hz, 6 H); ¹³C NMR (100 MHz, DMSO) δ 176.0, 140.0, 139.0, 129.5, 127.6, 44.8, 44.7, 30.1, 22.7, 19.0.

2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoic acid (2aw)^[23]: ¹H NMR (400 MHz, DMSO) δ 12.27 (s, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 3.62 (q, *J* = 7.2 Hz, 1 H), 2.95 (dd, *J* = 13.2, 3.6 Hz, 1 H), 2.46 - 2.33 (m, 2 H), 2.27 - 2.20 (m, 1 H), 2.11 - 2.02 (m, 1 H), 1.96 - 1.82 (m, 2 H), 1.74 - 1.62 (m, 1 H), 1.52 - 1.42 (m, 1 H), 1.33 (d, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, DMSO) δ 175.9, 139.3, 139.0, 129.3, 127.8, 50.5, 44.8, 38.0, 35.0, 29.2, 20.5, 19.0.

(1S,4aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid

(2ax)^[24]: ¹H NMR (400 MHz, DMSO) δ 12.12 (s, 1 H), 7.15 (d, J = 8.0 Hz, 1 H), 6.96 (d, J = 8.0 Hz, 1 H), 6.84 (s, 1 H), 2.86 - 2.69 (m, 3 H), 2.29 (d, J = 12.8 Hz, 1 H), 2.02 (d, J = 11.2 Hz, 1 H), 1.89 - 1.75 (m, 2 H), 1.71 - 1.61 (m, 2 H), 1.58 - 1.38 (m, 3 H), 1.16 (s, 3 H), 1.15 (d, J = 5.2 Hz, 6 H), 1.12 (s, 3 H); ¹³C NMR (100 MHz, DMSO) δ 179.9, 147.2, 145.5, 134.6, 127.0, 124.5, 124.2, 46.8, 45.2, 38.3, 36.9, 36.7, 33.4, 30.0, 25.3, 24.4, 21.6, 18.6, 16.9.

5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (2ay)^[25]: ¹H NMR (400 MHz, DMSO) δ 12.13

(s, 1 H), 6.97 (d, J = 7.2 Hz, 1 H), 6.70 (s, 1 H), 6.62 (d, J = 7.2 Hz, 1 H), 3.90 (t, J = 5.6 Hz, 2 H), 2.24 (s, 3 H), 2.08 (s, 3 H), 1.70 - 1.58 (m, 4 H), 1.12 (s, 6 H); ¹³C NMR (100 MHz, DMSO) δ 179.3, 157.0, 136.6, 130.5, 123.0, 121.0, 112.5, 68.1, 41.5, 37.0, 25.5, 25.3, 21.6, 16.0.

phenyl benzoate (3a)^[26]: ¹H NMR (400 MHz, DMSO) δ 8.14 (d, J = 7.2 Hz, 2 H), 7.76 (t, J = 8.0 Hz,

1 H), 7.62 (t, J = 8.0 Hz, 2 H), 7.48 (t, J = 8.0 Hz, 2 H), 7.34 - 7.28 (m, 3 H); ¹³C NMR (100 MHz, DMSO) δ 165.1, 151.1, 134.6, 130.3, 130.1, 129.5, 126.5, 122.4.

benzophenone (3b)^[8]: ¹H NMR (400 MHz, DMSO) δ 7.73 (d, J = 7.2 Hz, 4 H), 7.68 (t, J = 7.6 Hz, 2

H), 7.56 (t, J = 7.6 Hz, 4 H); ¹³C NMR (100 MHz, DMSO) δ 196.3, 137.5, 133.2, 130.1, 129.1.

benzonitrile (3c)^[27]: ¹H NMR (400 MHz, DMSO) δ 7.84 (d, J = 6.8 Hz, 2 H), 7.72 (t, J = 7.6 Hz, 1 H),

7.58 (t, J = 7.6 Hz, 2 H); ¹³C NMR (100 MHz, DMSO) δ 133.9, 132.7, 130.0, 119.3, 111.8.

isobenzofuran-1,3-dione (4a)^[28]: ¹H NMR (400 MHz, DMSO) δ 8.05 - 8.01 (m, 2 H), 7.95 - 7.91 (m,

2 H); ¹³C NMR (100 MHz, DMSO) δ 162.7, 136.1, 131.2, 125.7.

5-fluoroisobenzofuran-1,3-dione (4b)^[29]: ¹H NMR (400 MHz, CDCl₃) δ 8.06 (q, J = 4.0 Hz, 1 H),

7.69 (dd, J = 6.8, 2.4 Hz, 1 H), 7.62 - 7.57 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 167.3 (d, J = 259.9 Hz), 161.5, 134.2 (d, J = 10.2 Hz), 128.3 (d, J = 10 Hz), 127.1 (d, J = 2.6 Hz), 123.9 (d, J = 24.0 Hz), 113.0 (d, J = 24.7 Hz); ¹⁹F NMR (376 MHz, DMSO) δ -97.3 - -97.4 (m, 1F).

5-bromoisobenzofuran-1,3-dione (4c)^[29]: ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 1.2 Hz, 1 H), 8.05 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 161.3, 139.3, 132.8, 131.4, 129.7, 128.8, 126.8.

5-(*tert*-butyl)isobenzofuran-1,3-dione (4d)^[30]: ¹H NMR (400 MHz, CDCl₃) δ 8.02 - 7.93 (m, 2 H), 7.86 - 7.62 (m, 1 H), 1.40 (s, 6 H), 1.37 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 174.6, 173.4, 163.3, 162.8, 161.2, 156.1, 133.5, 131.8, 131.6, 129.6, 128.6, 128.5, 127.7, 126.1, 125.4, 122.5, 36.0, 35.2, 31.0, 31.0.

5,5'-oxybis(isobenzofuran-1,3-dione) (4e)^[31]: ¹H NMR (400 MHz, DMSO) δ 8.19 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 2.0 Hz, 2 H), 7.75 (d, *J* = 2.4 Hz, 1 H), 7.73 (d, *J* = 2.4 Hz, 1 H); ¹³C NMR (100 MHz, DMSO) δ 162.9, 162.0, 134.9, 128.6, 127.5, 127.4, 115.9.

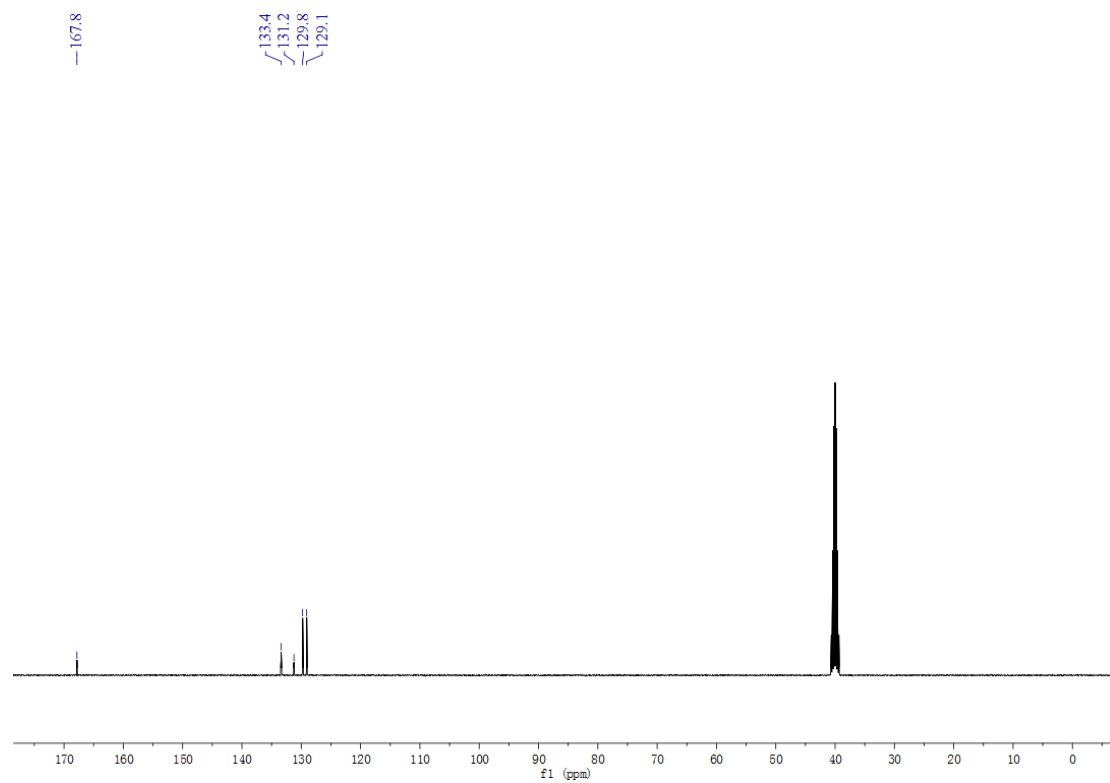
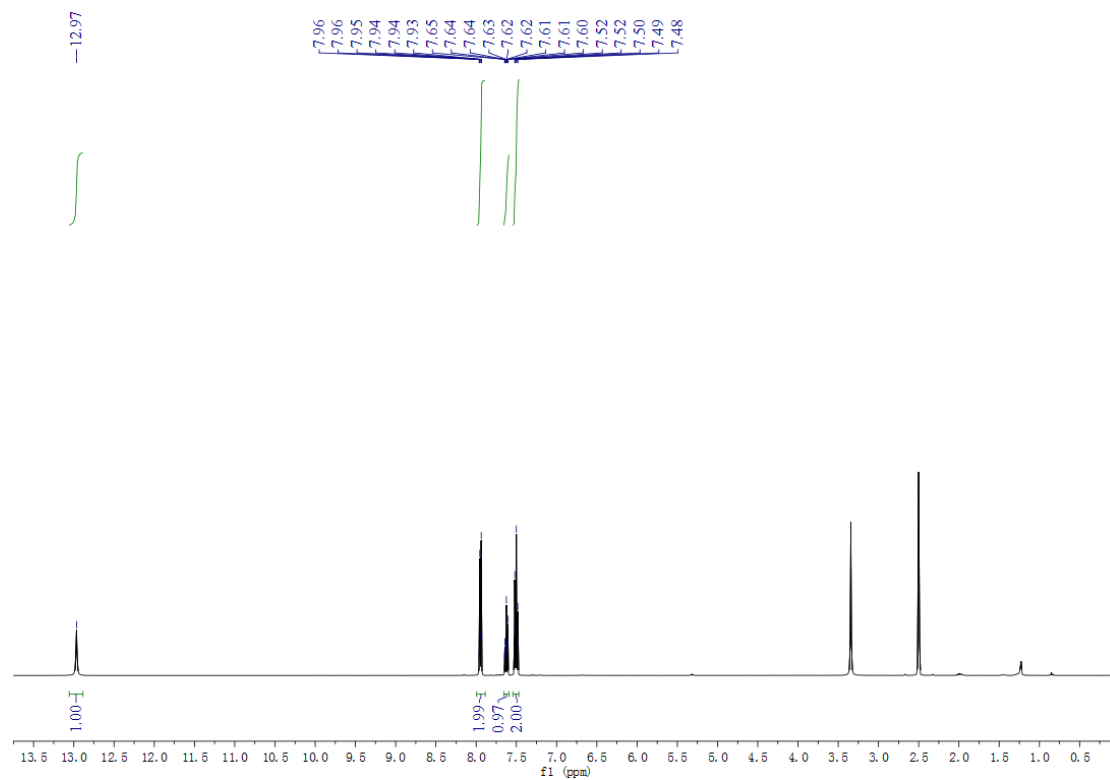
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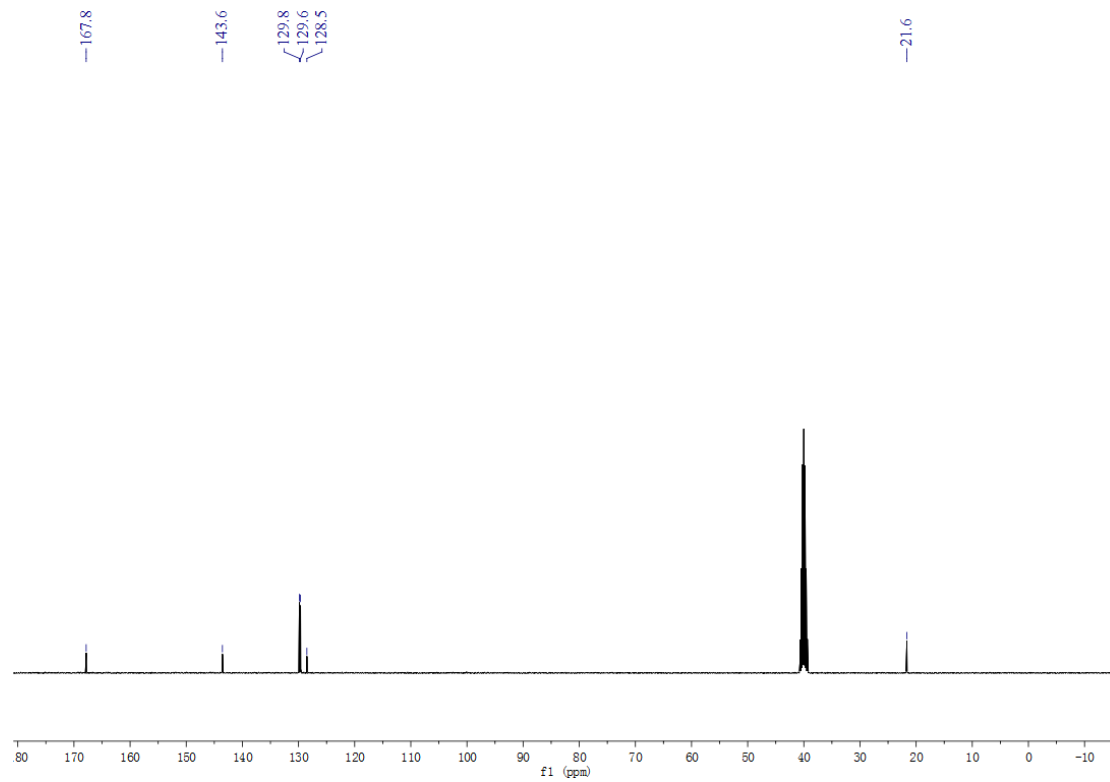
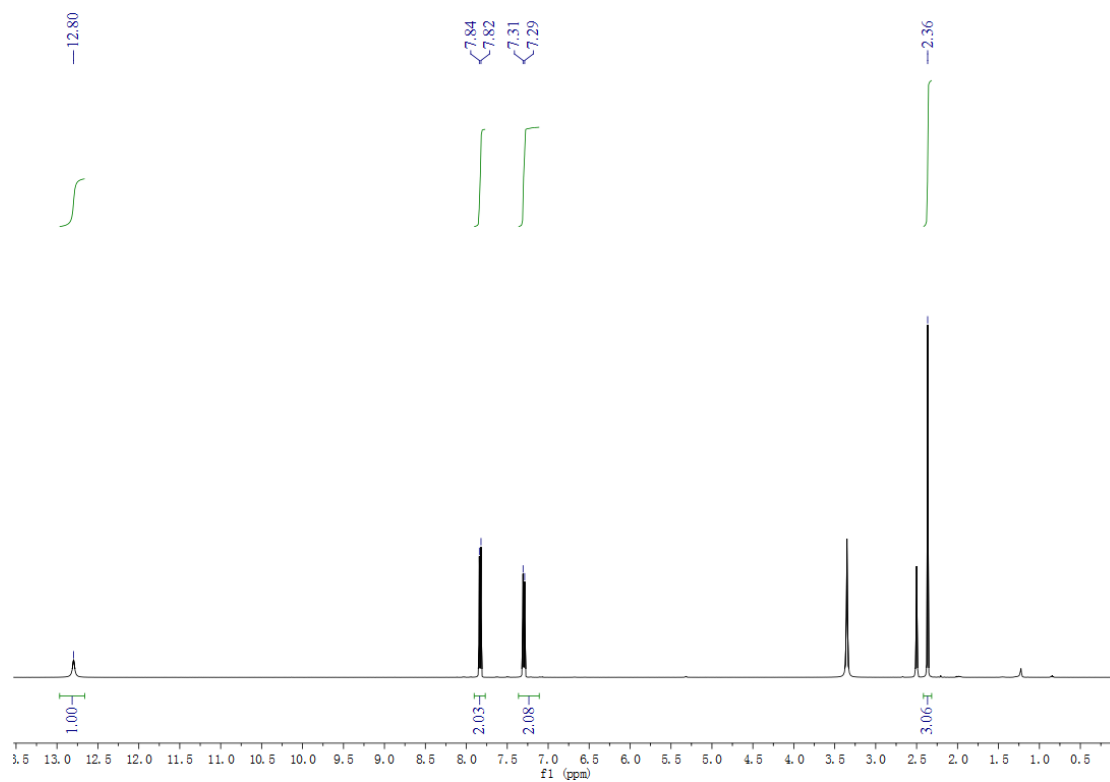
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6. ^1H and ^{13}C NMR spectra

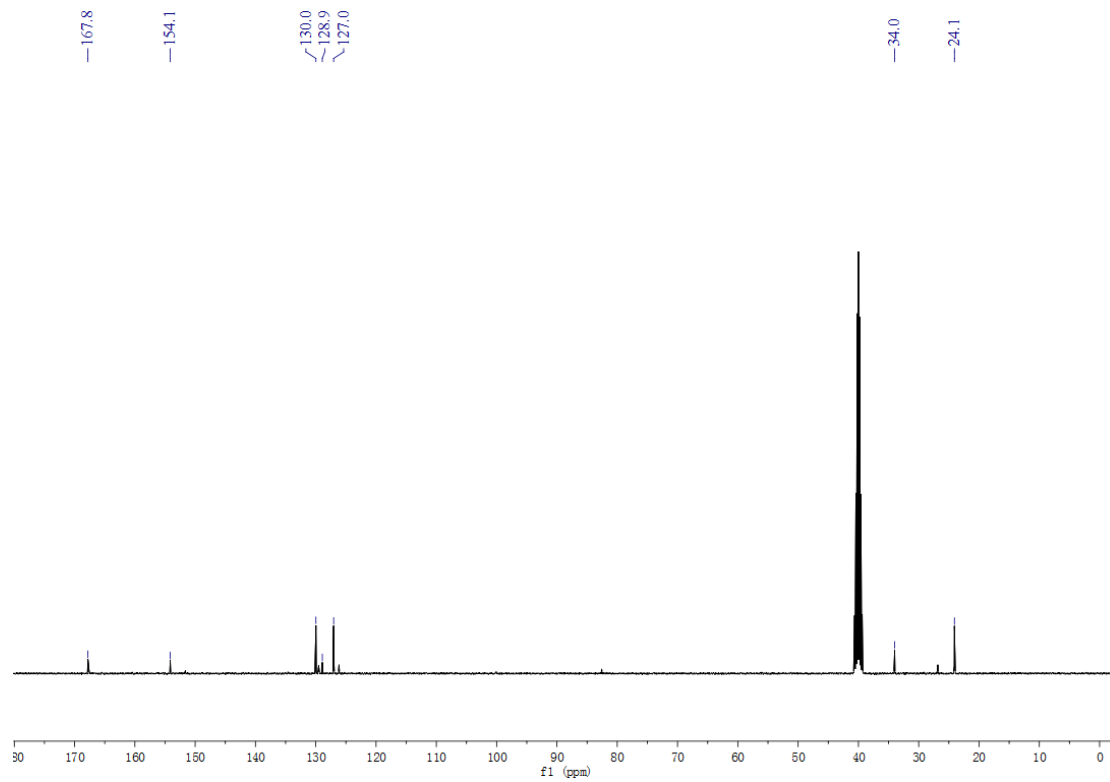
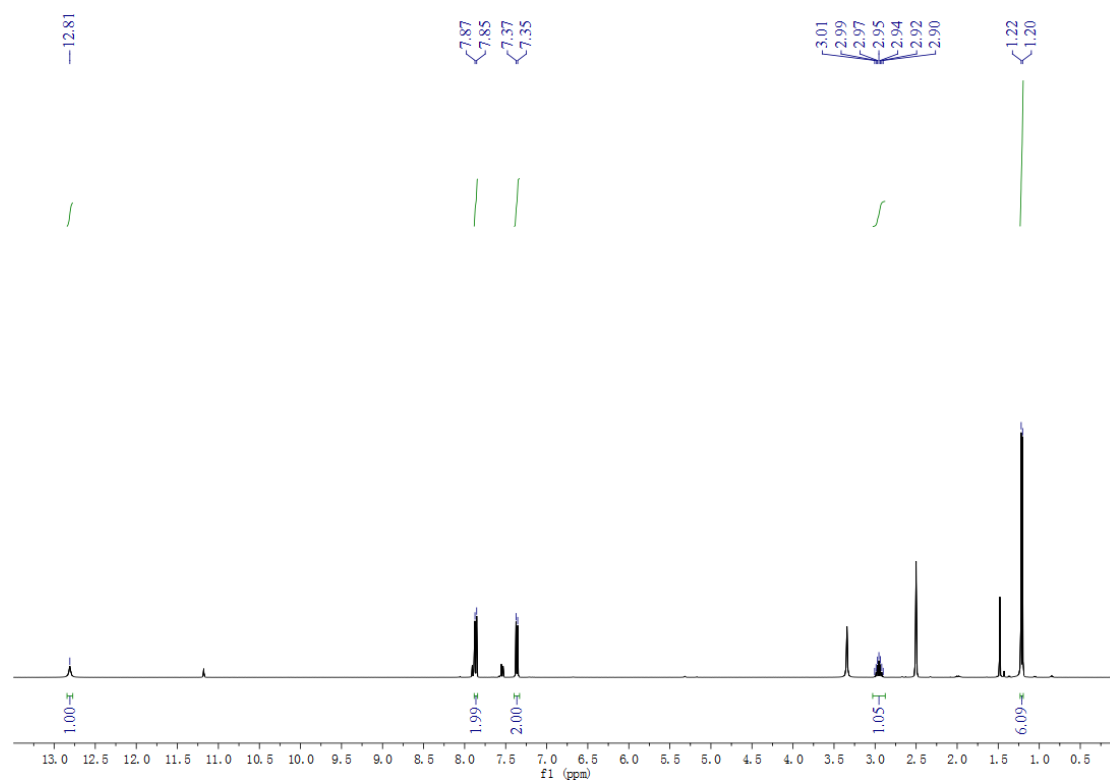
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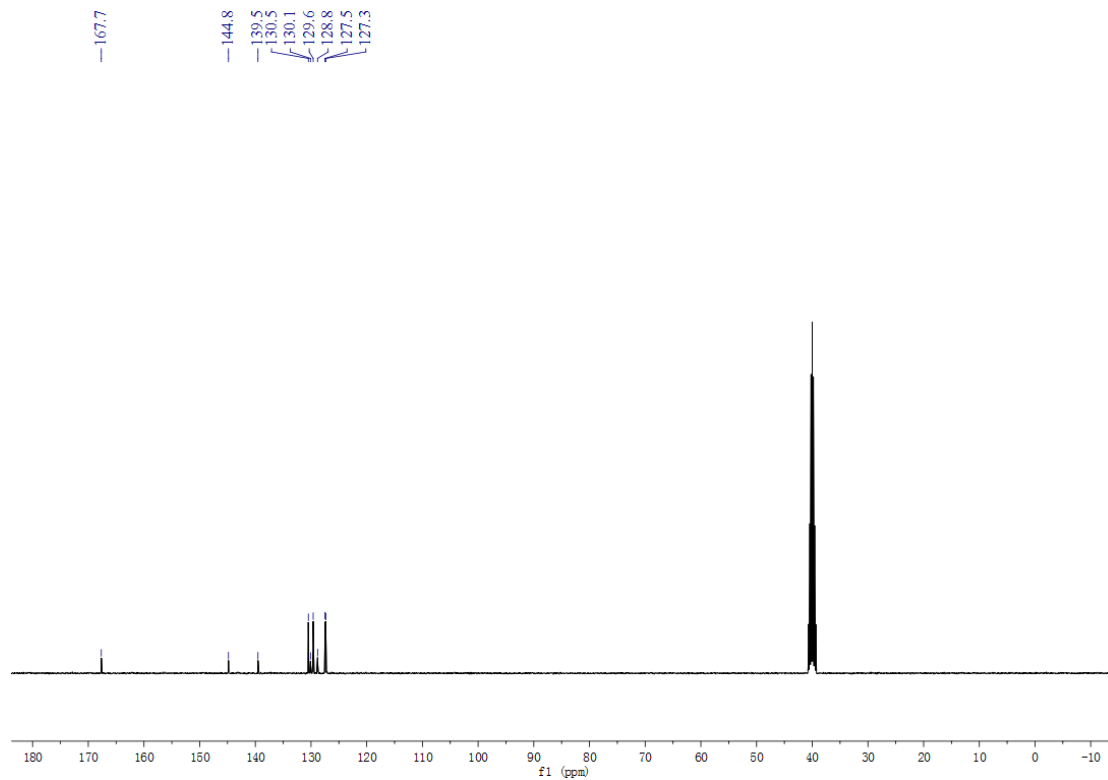
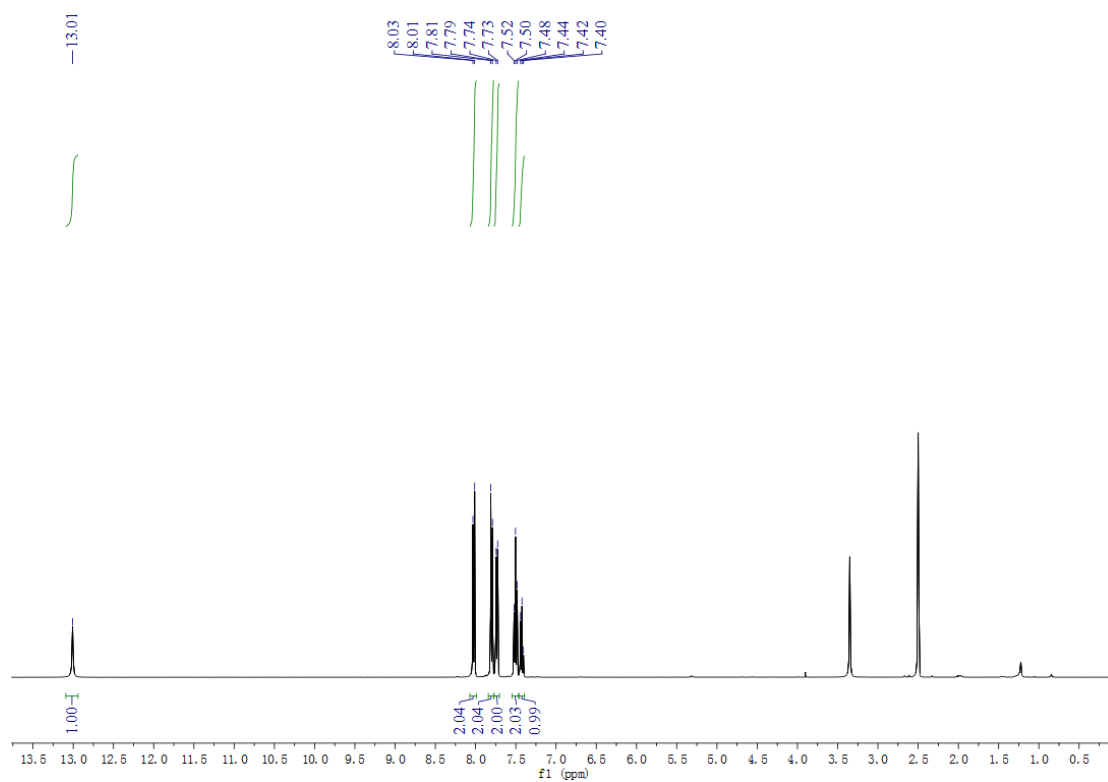
4-methylbenzoic acid (2b)



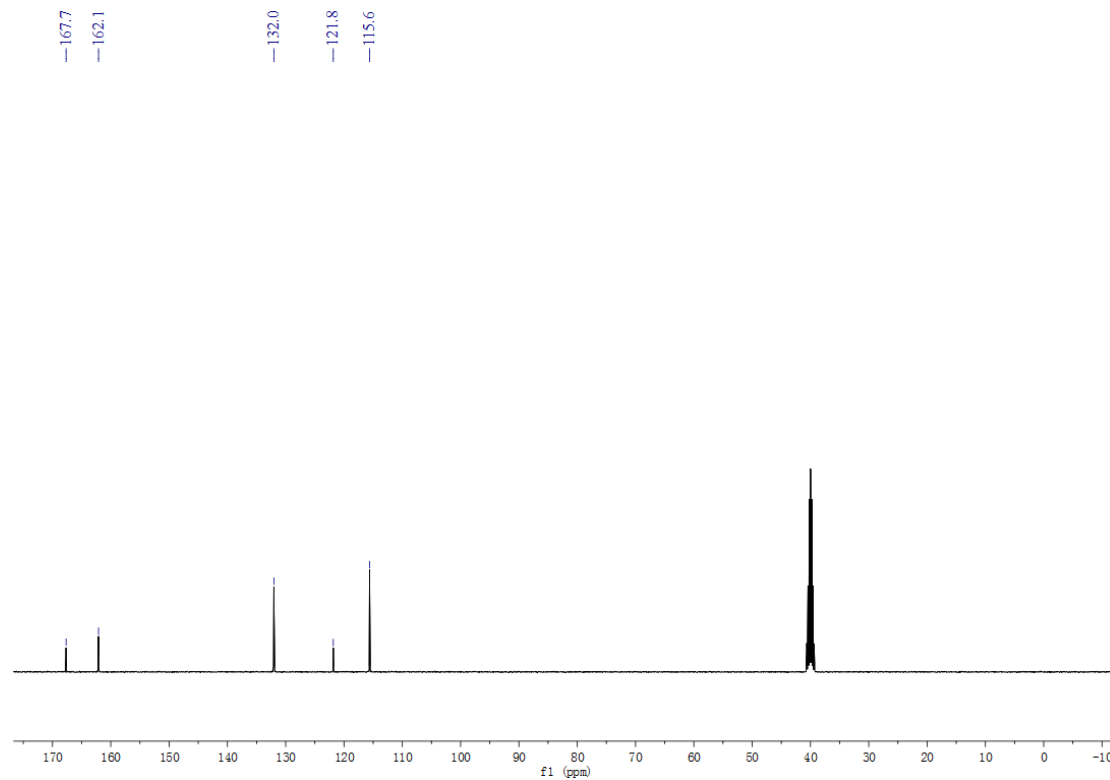
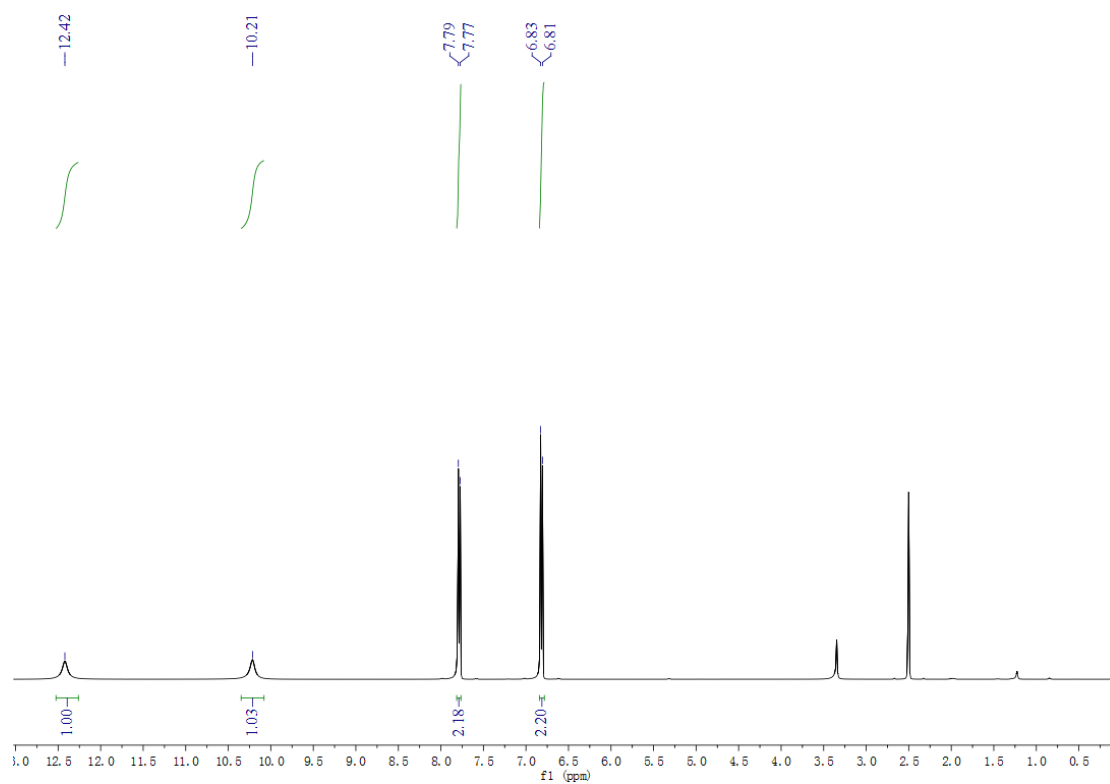
4-isopropylbenzoic acid (2c)



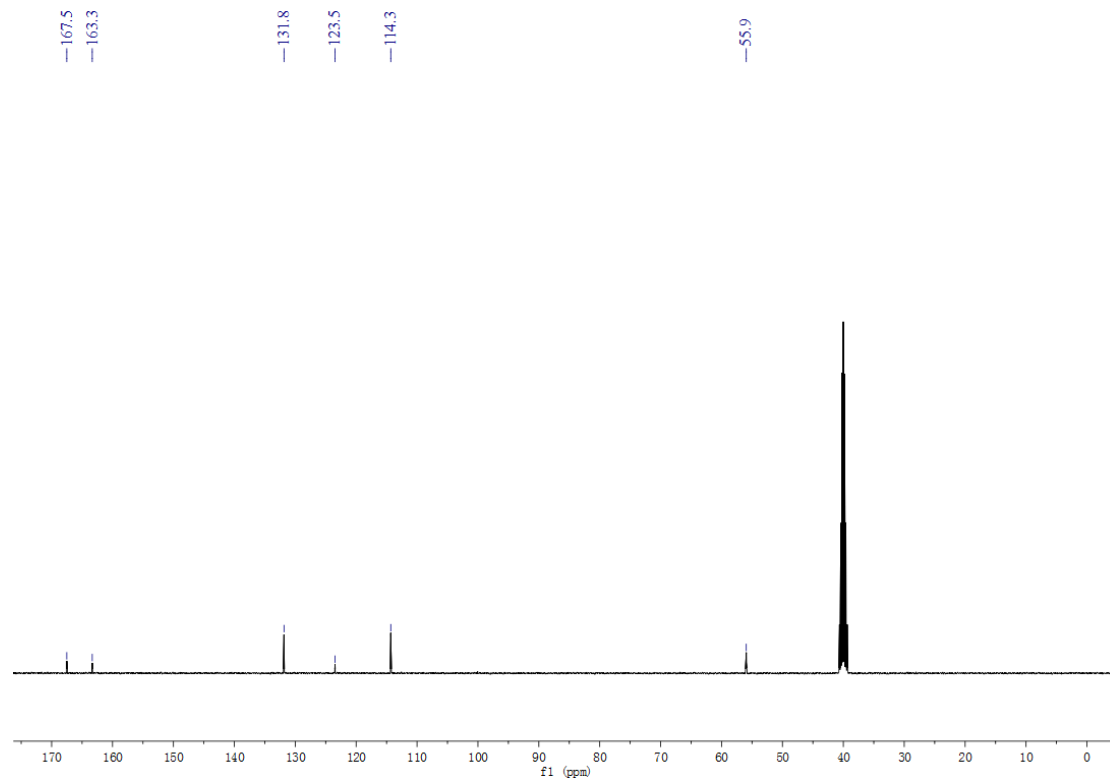
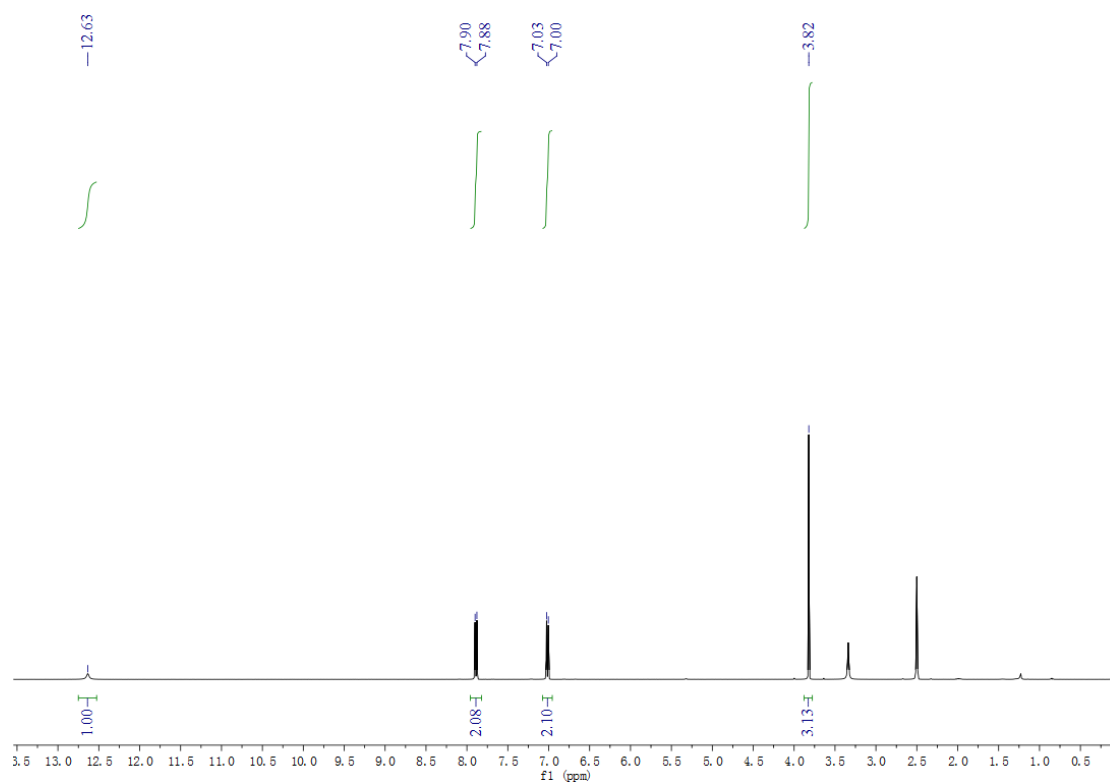
[1,1'-biphenyl]-4-carboxylic acid (2d)



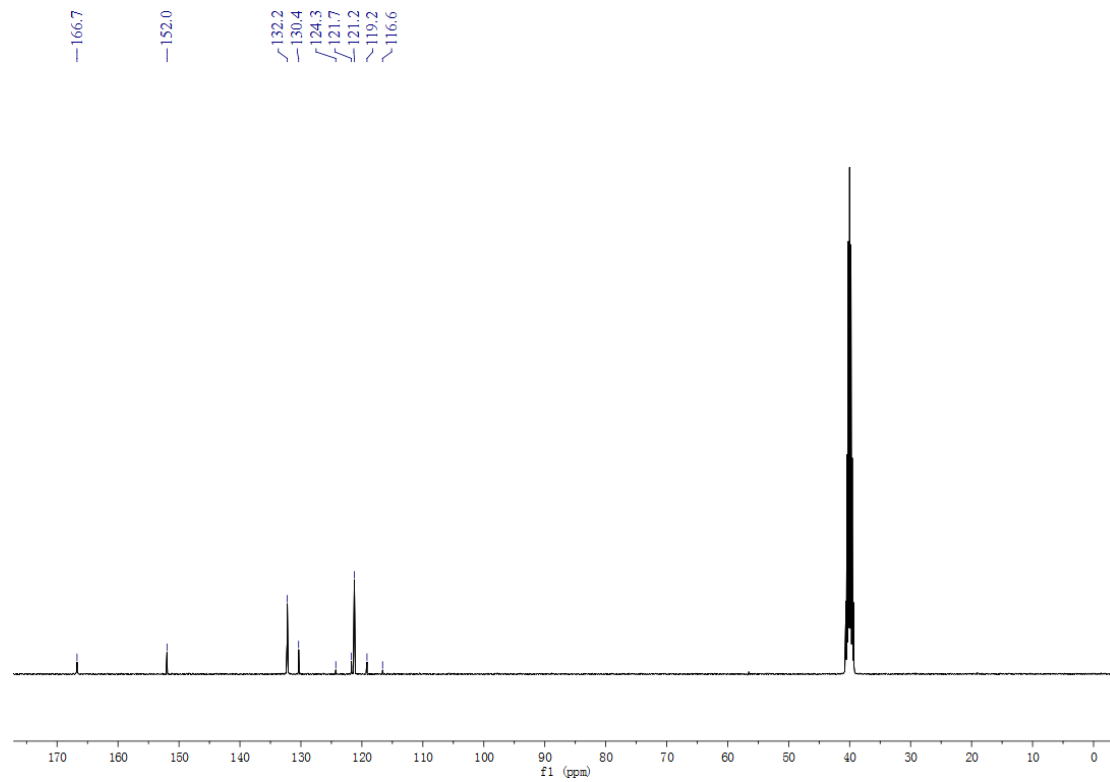
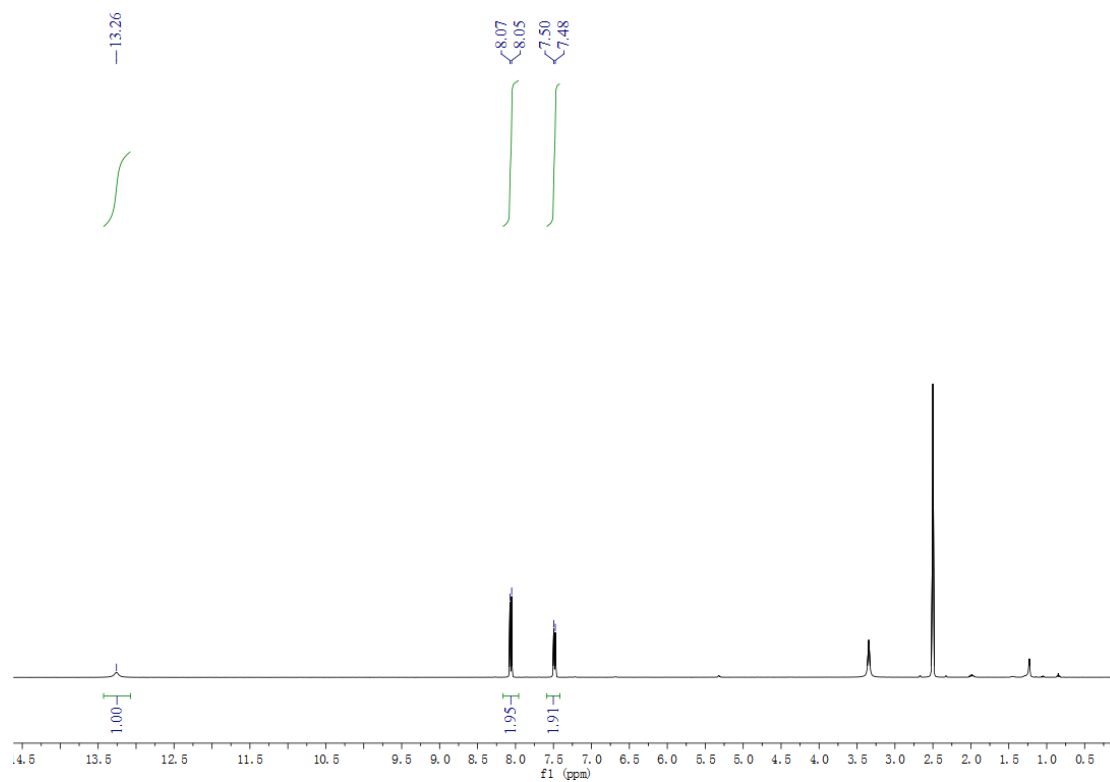
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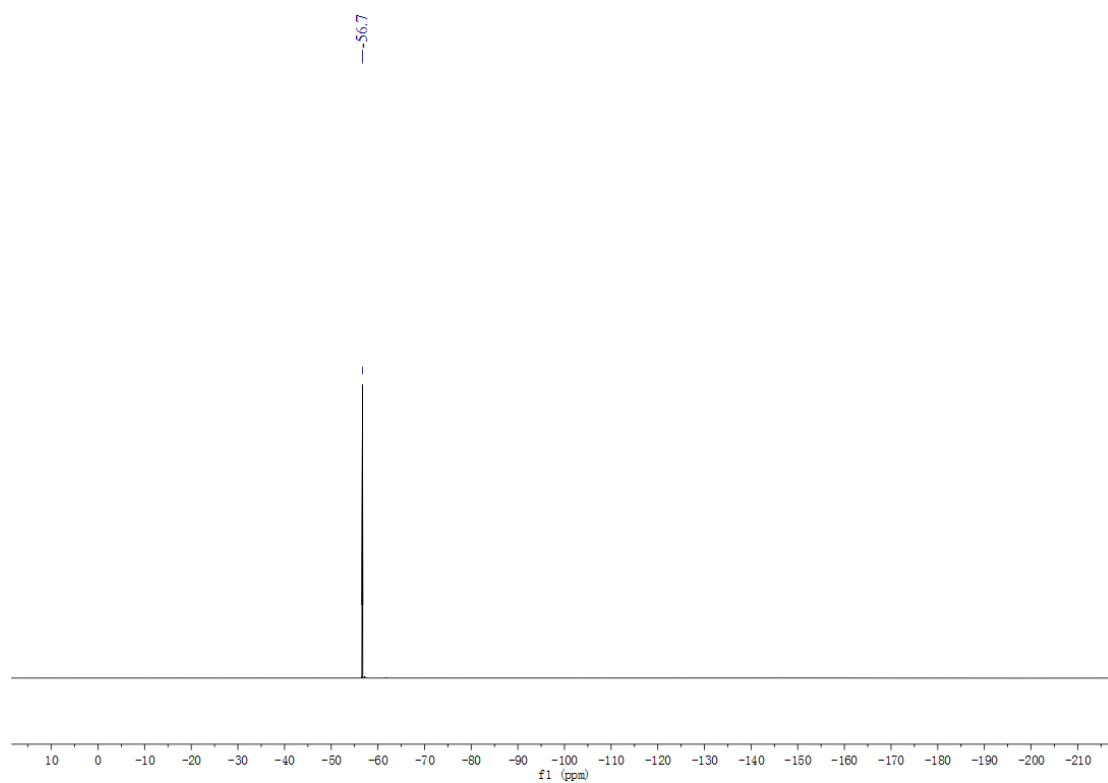


4-methoxybenzoic acid (2f)

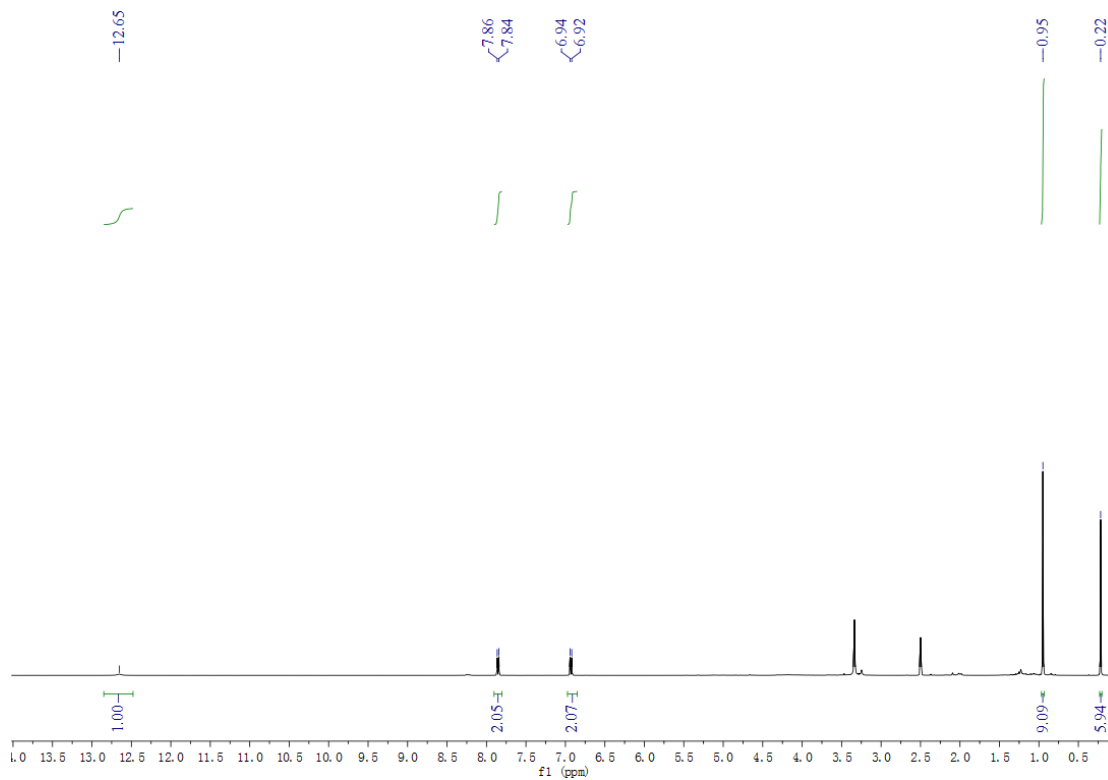


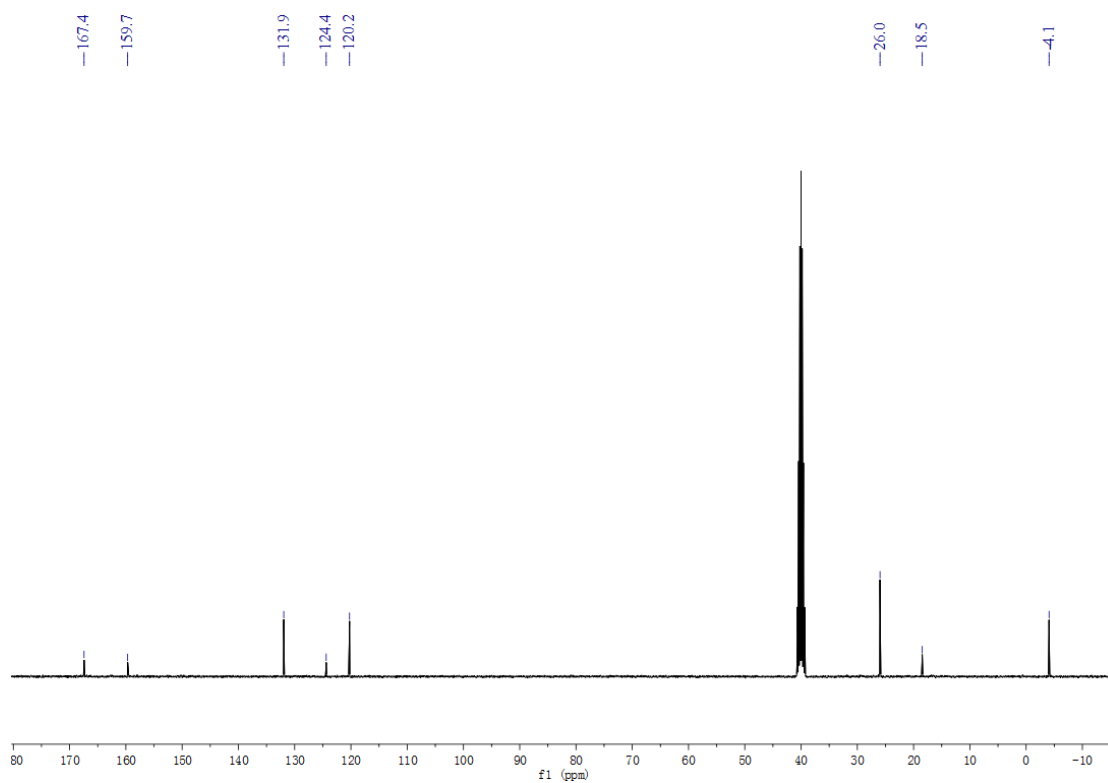
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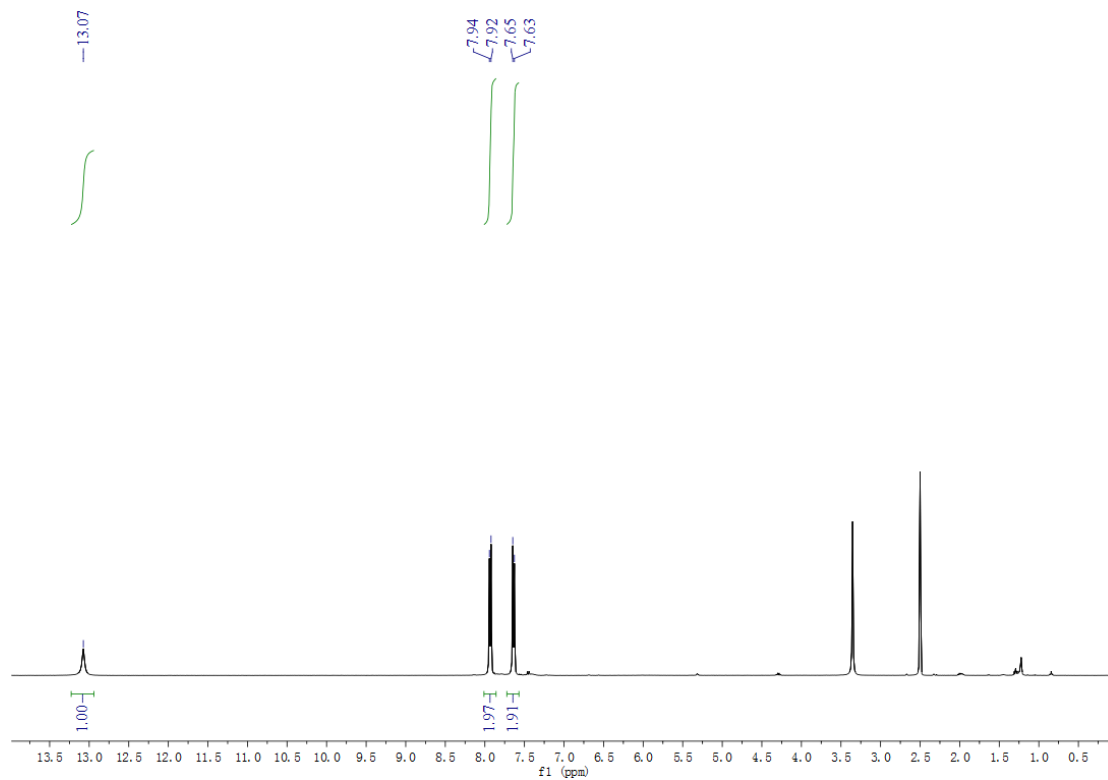


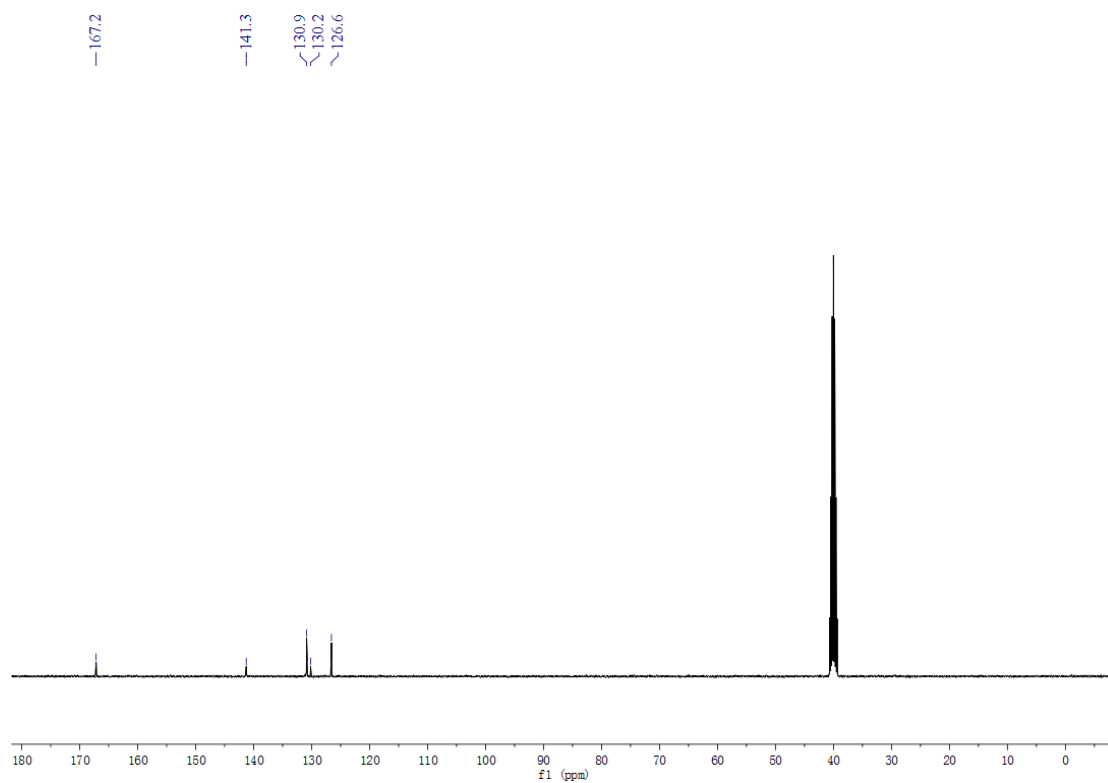
4-((*tert*-butyldimethylsilyl)oxy)benzoic acid (2h)



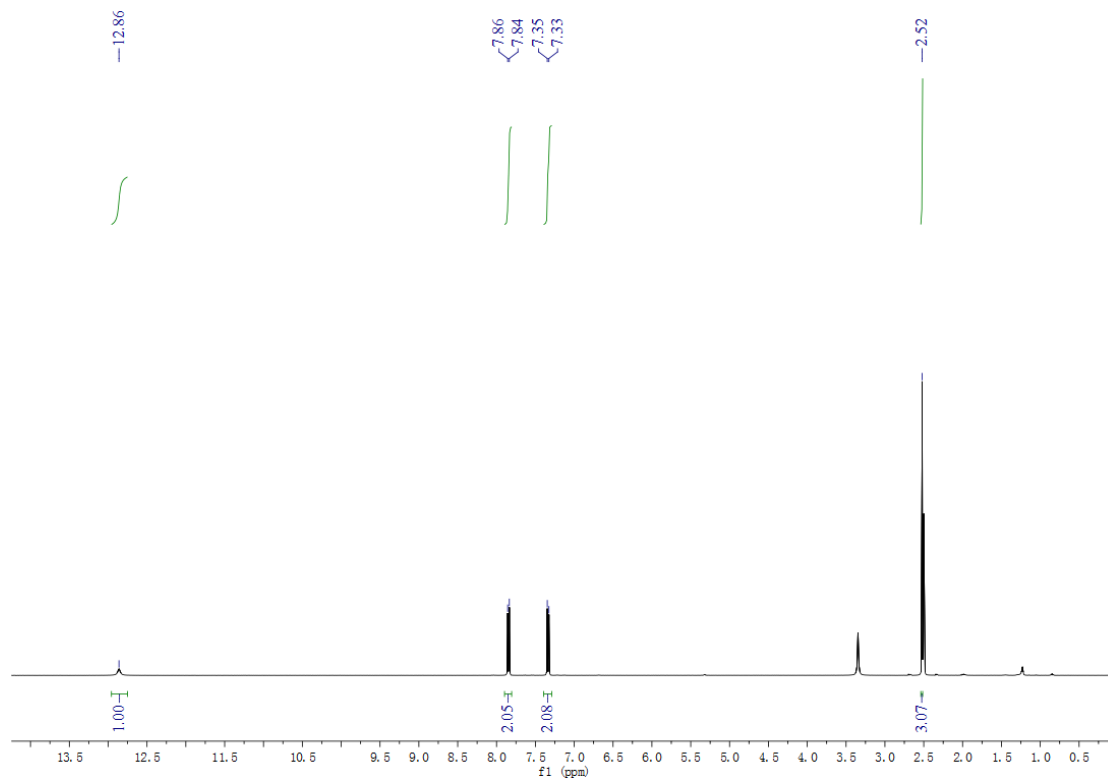


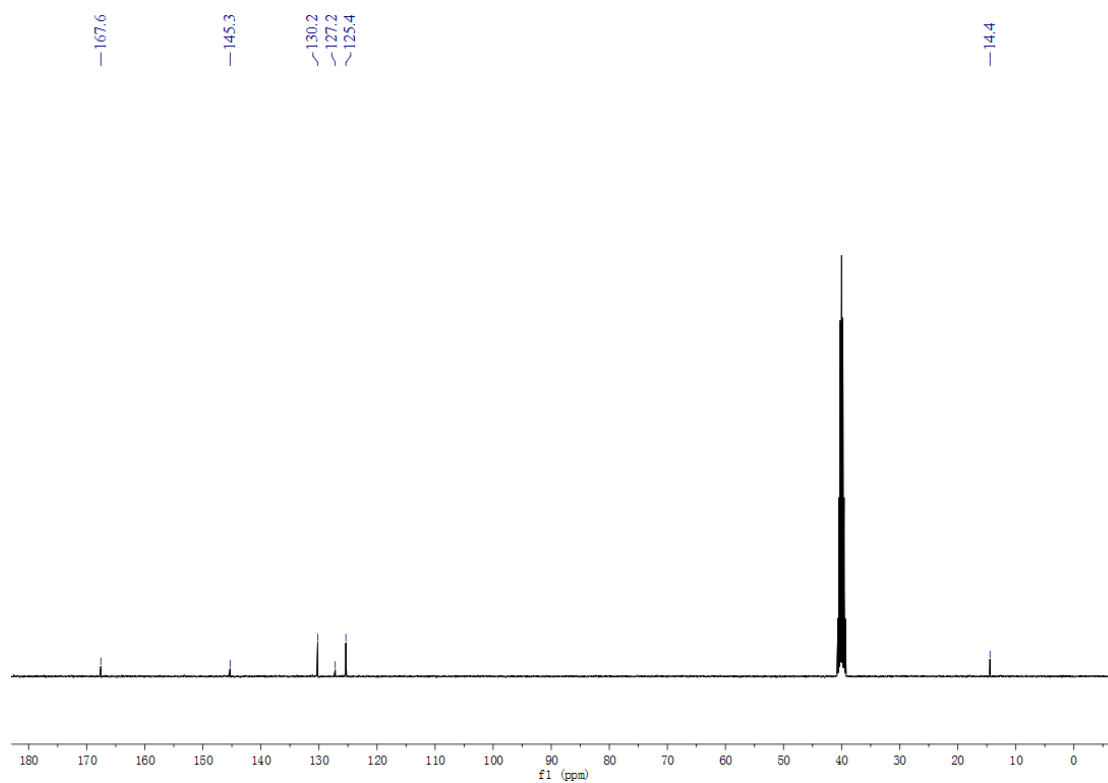
4-mercaptobenzoic acid (2i)



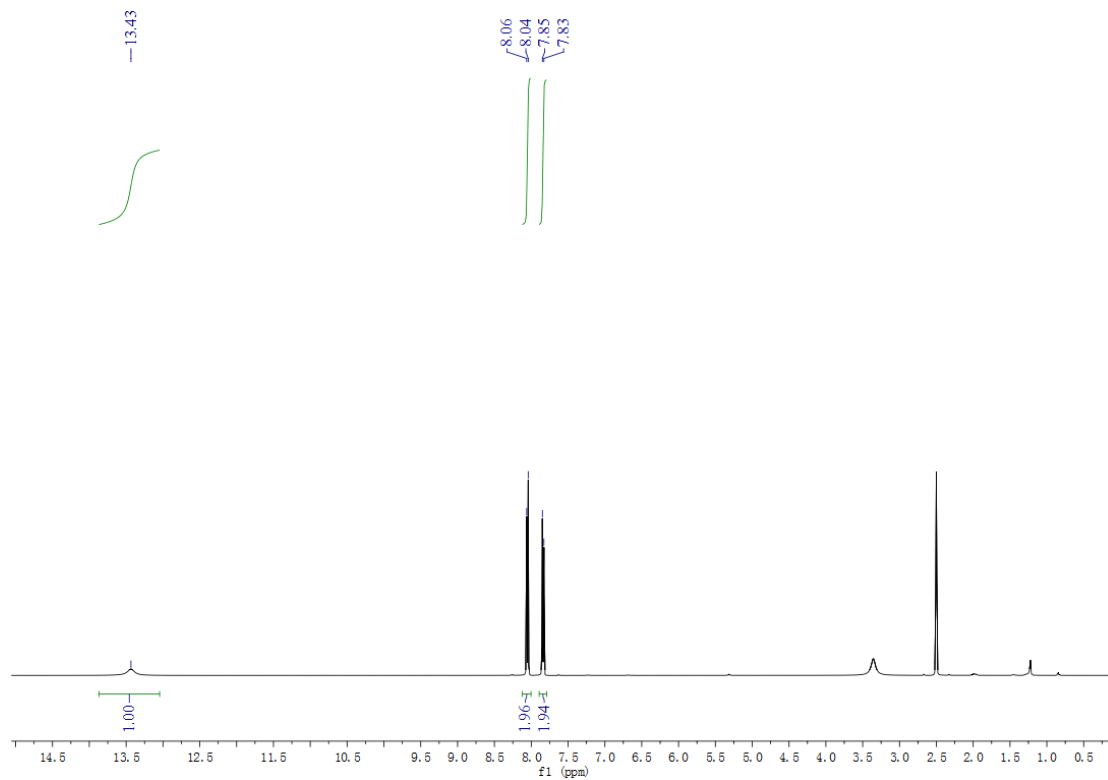


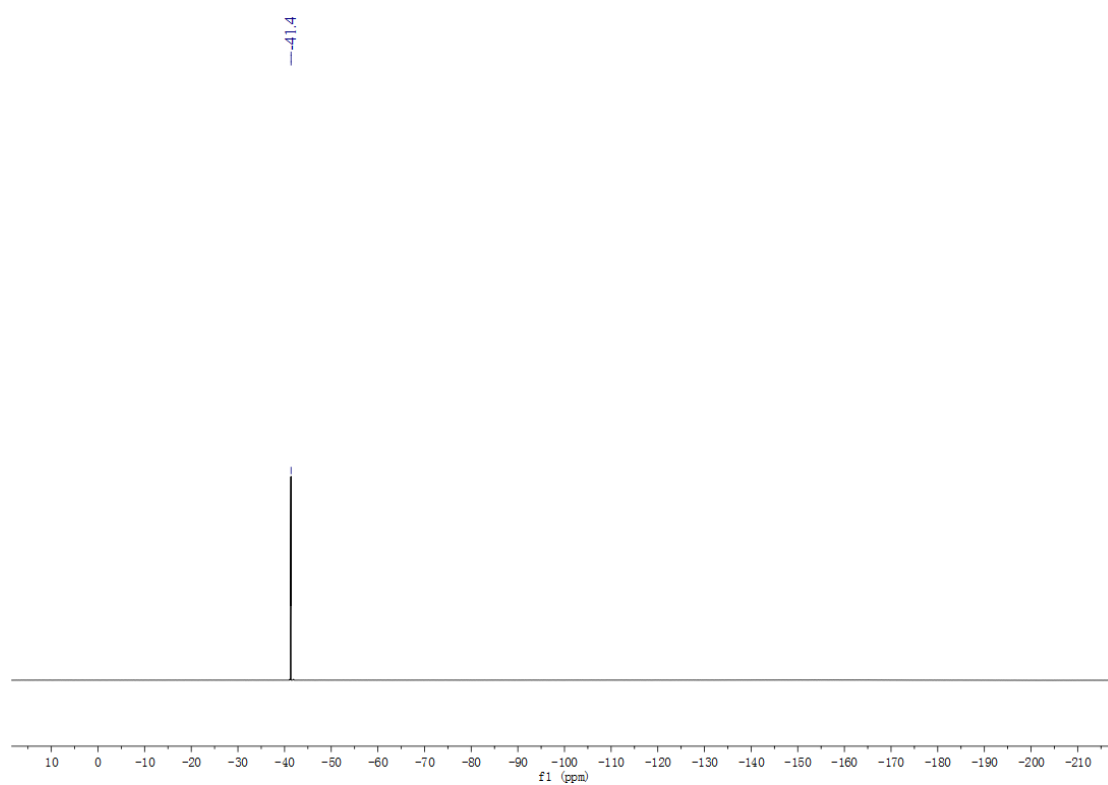
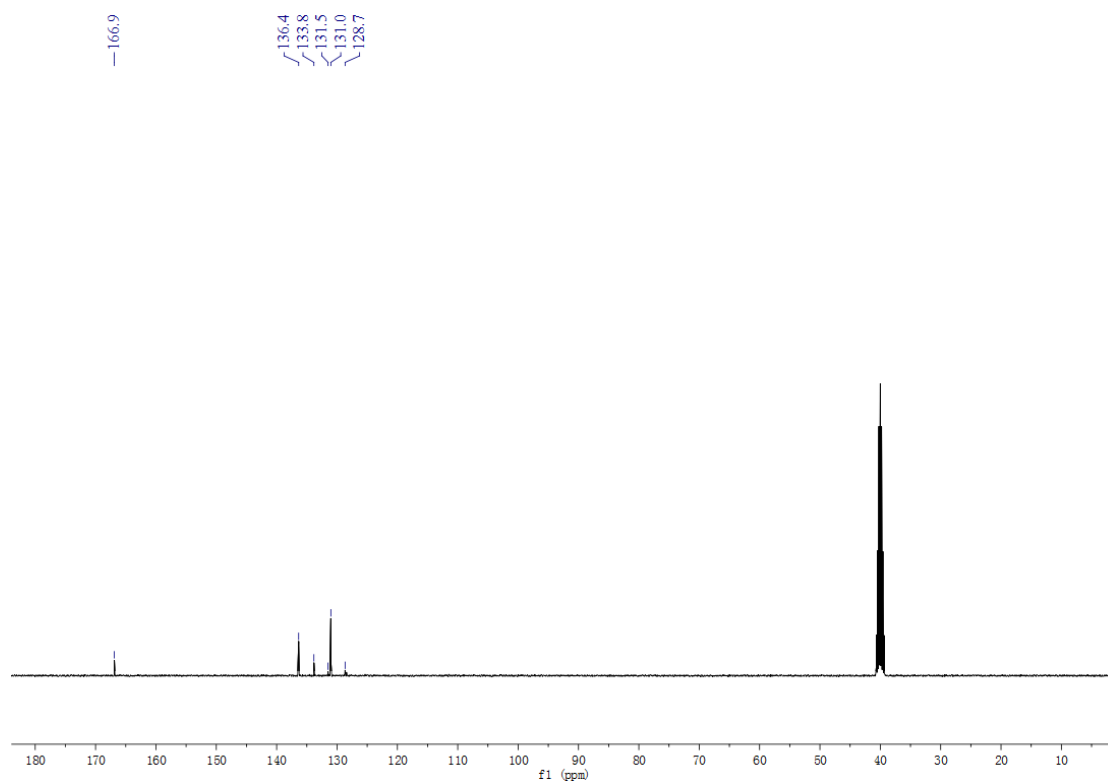
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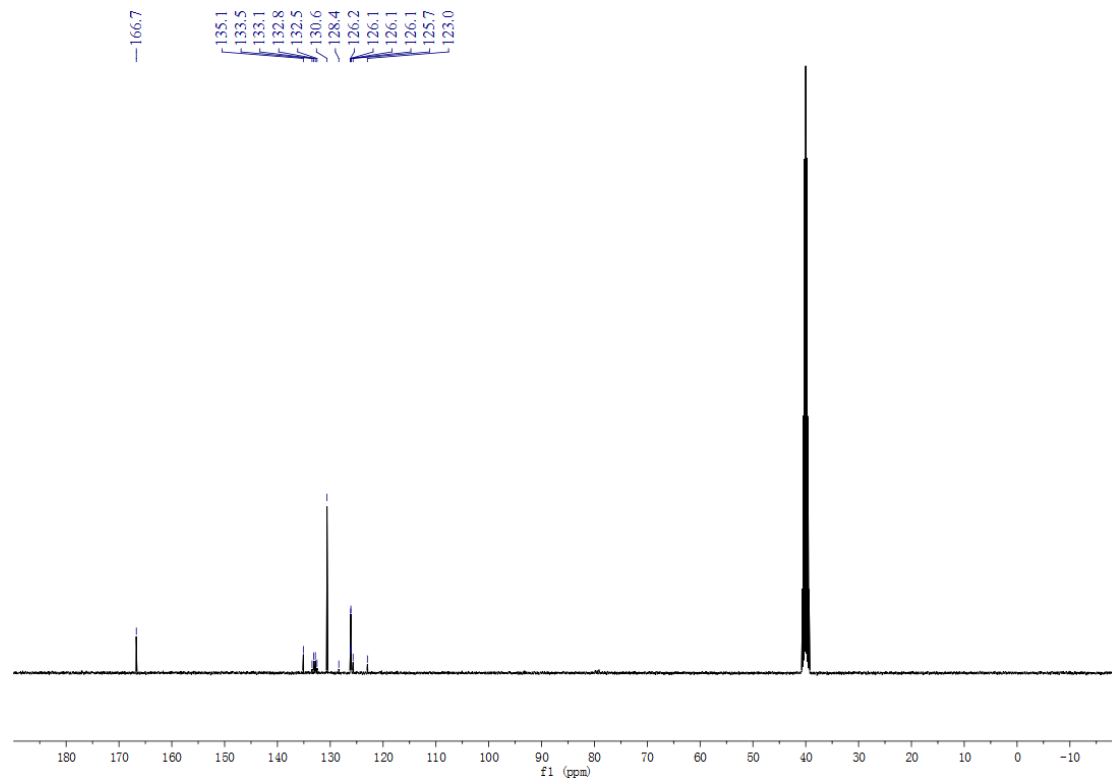
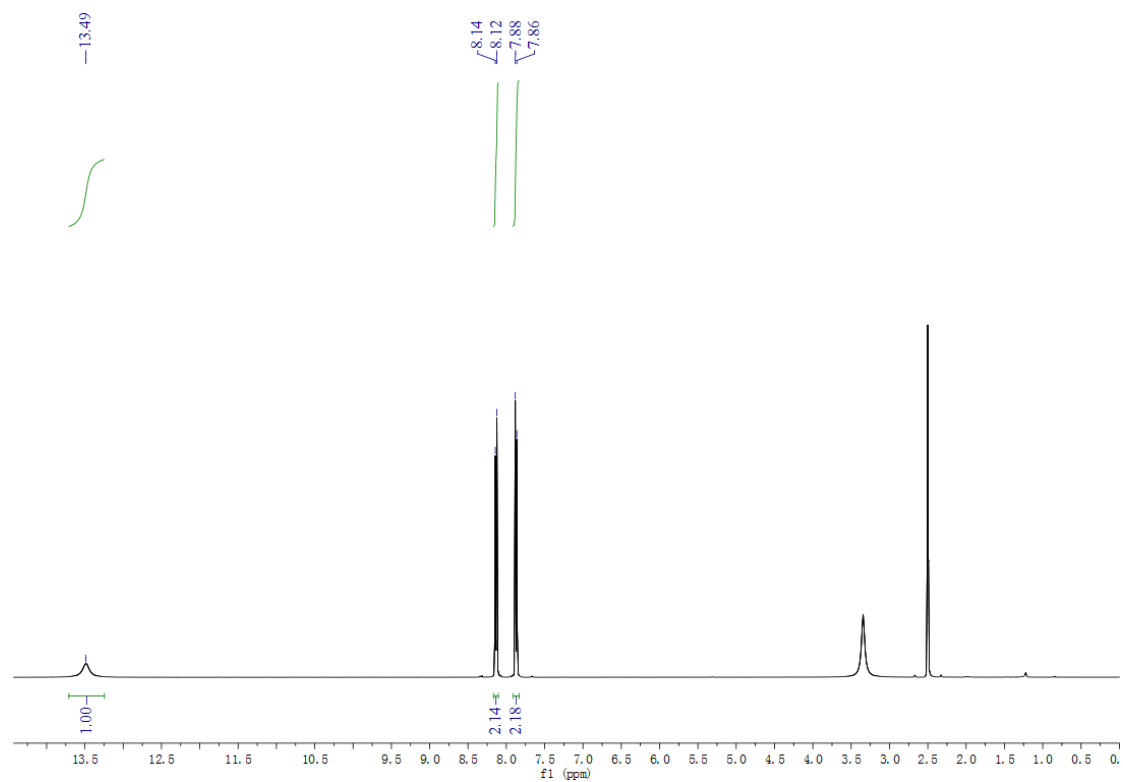


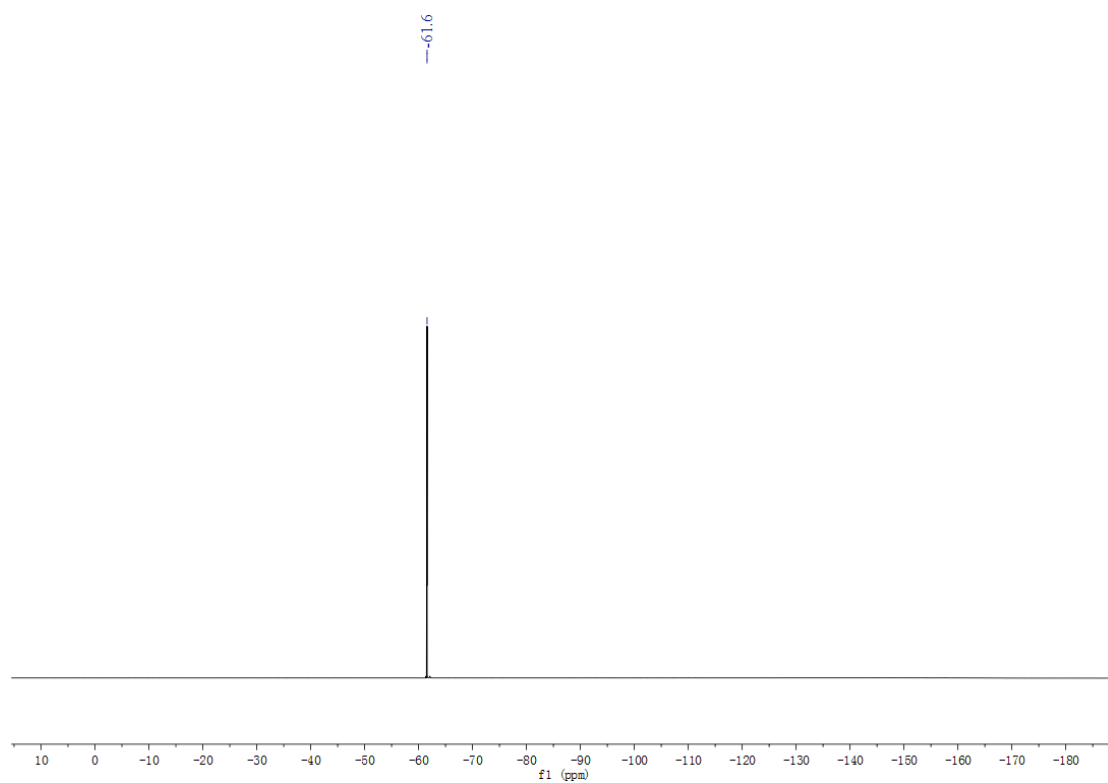
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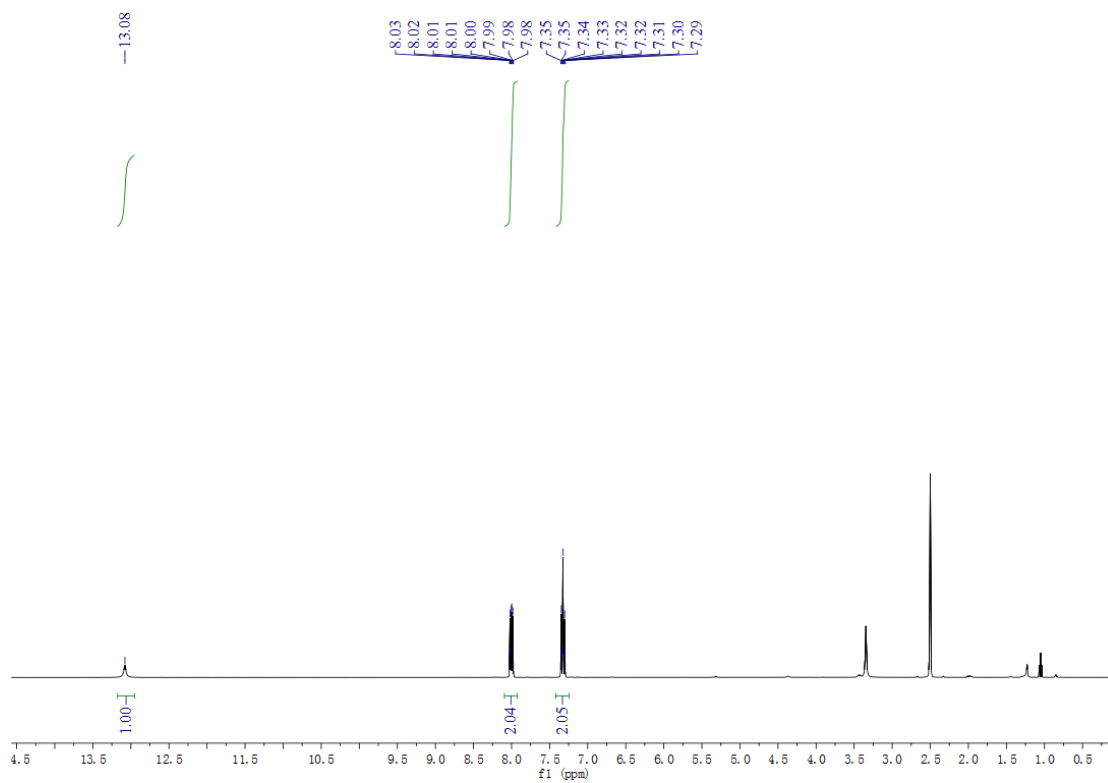


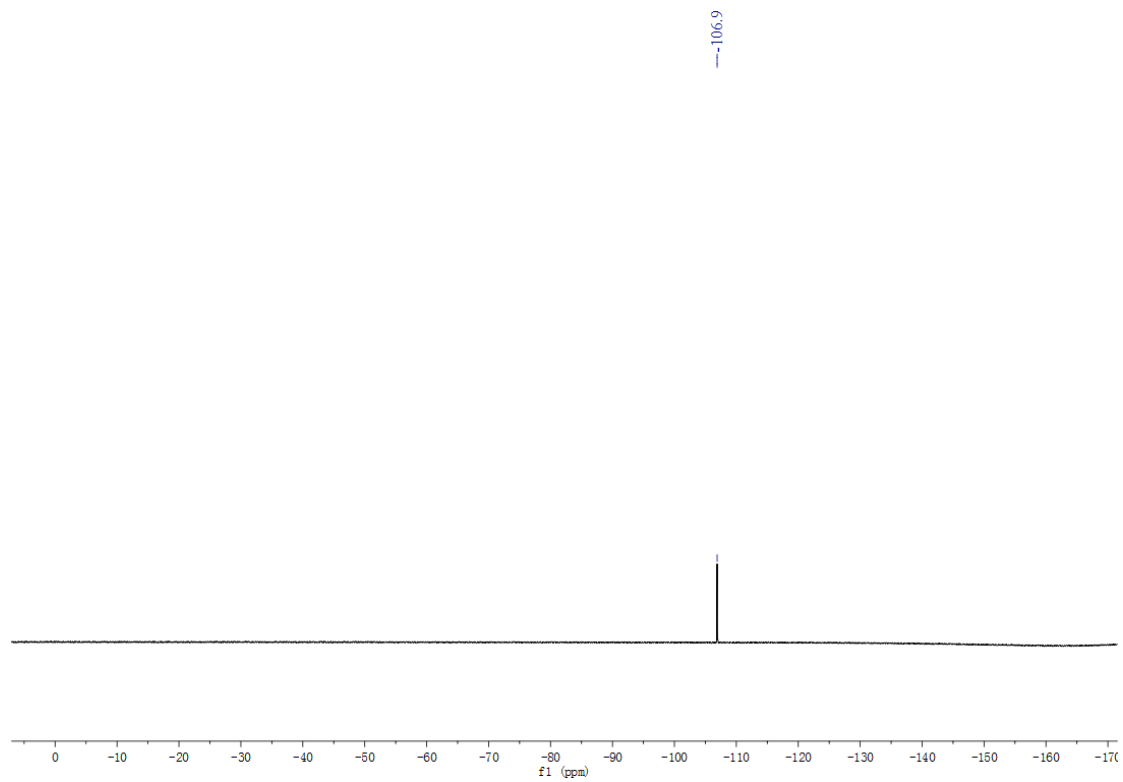
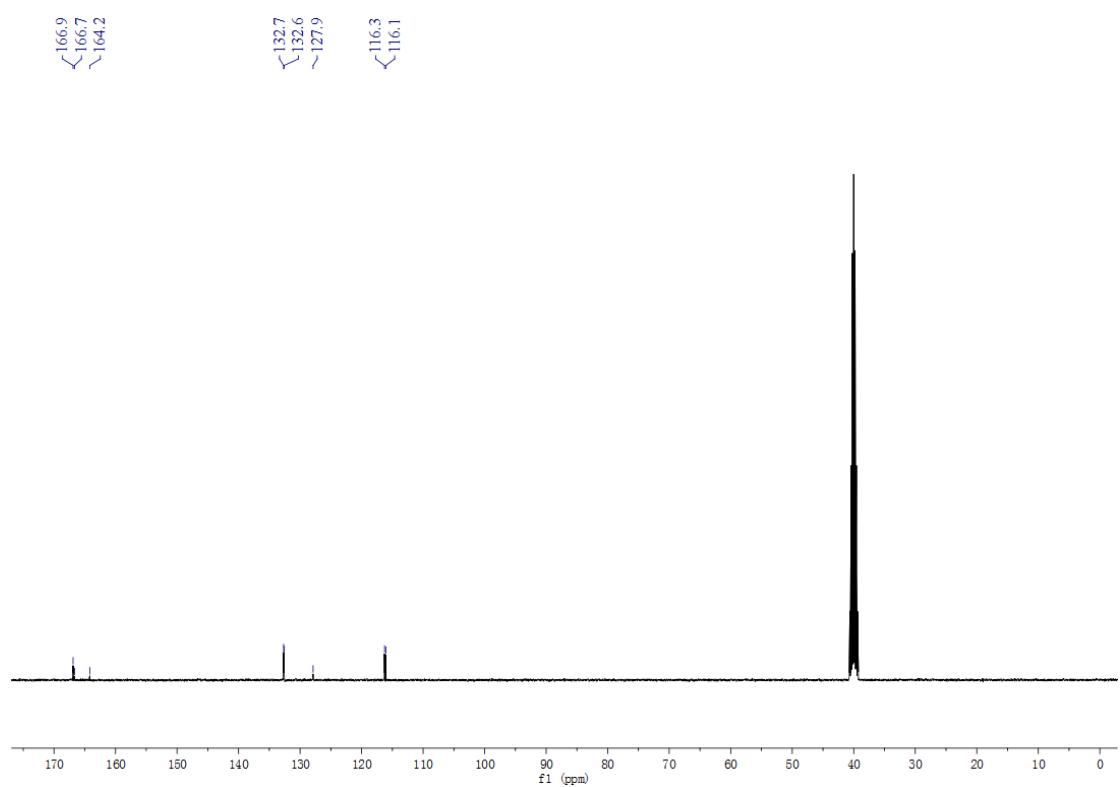
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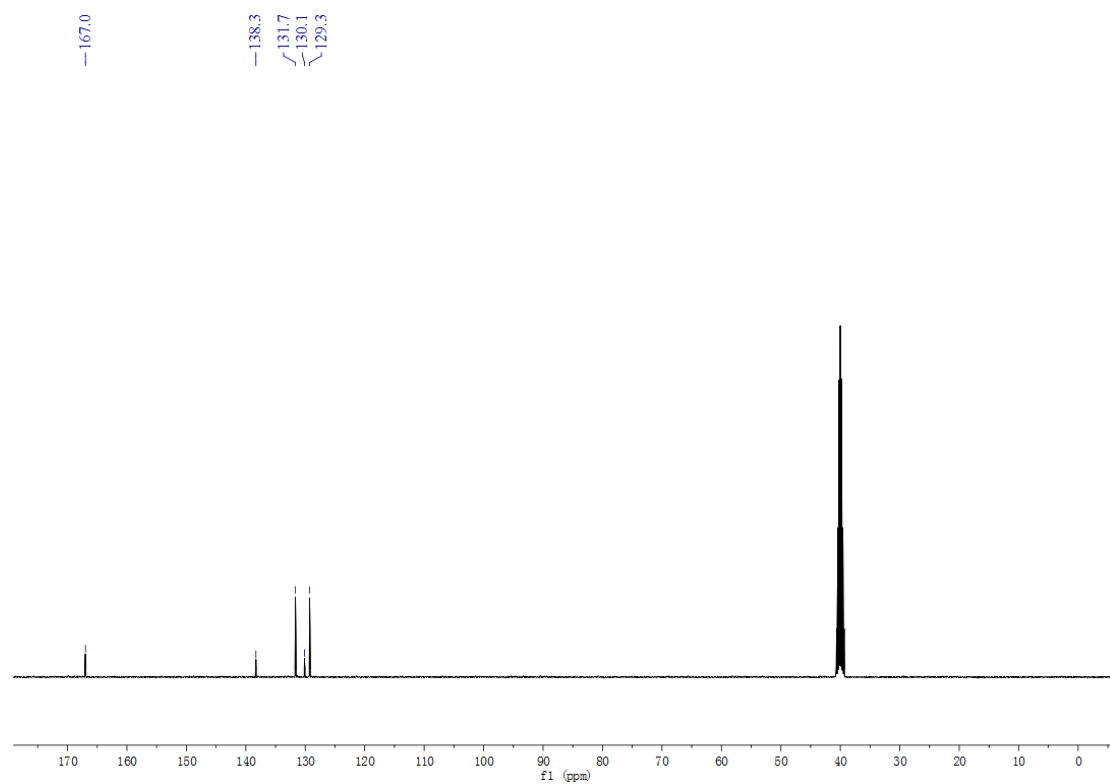
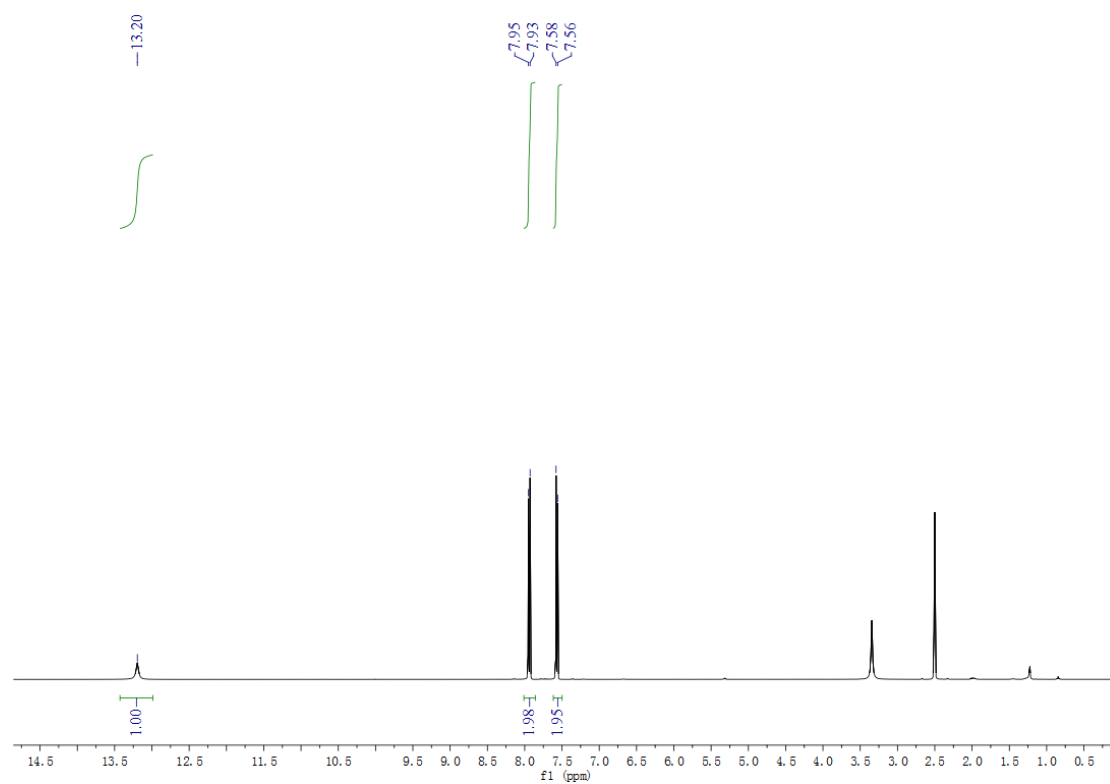


4-fluorobenzoic acid (2m)

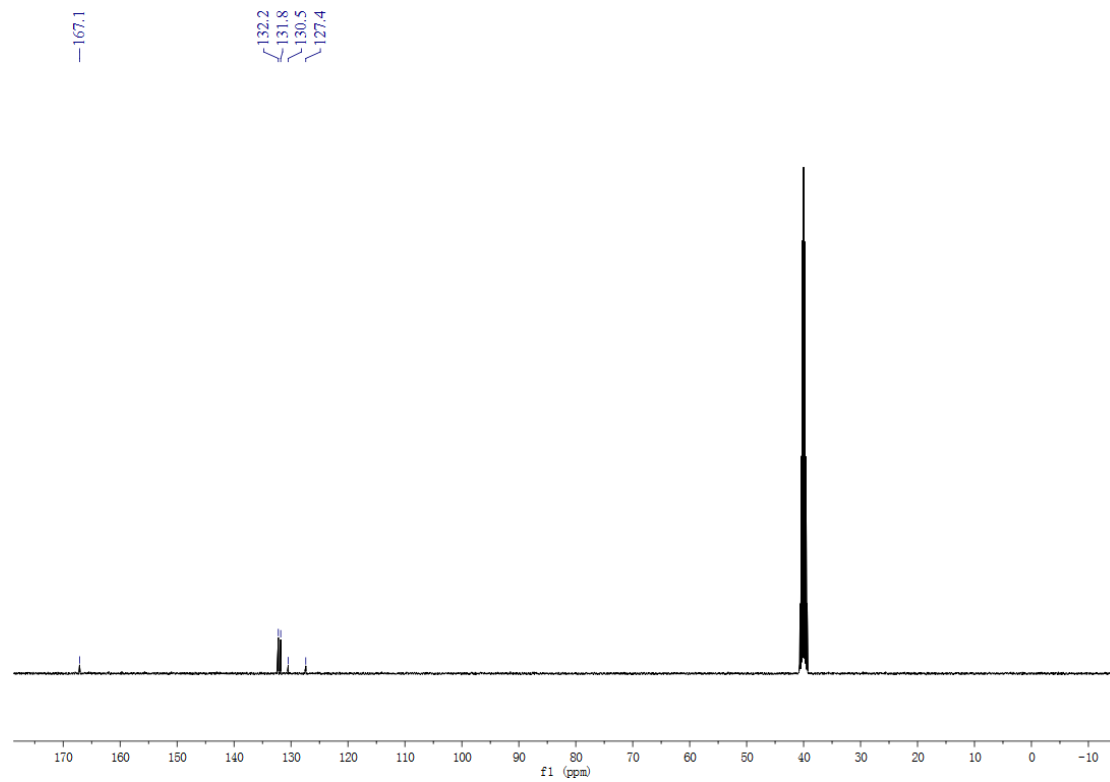
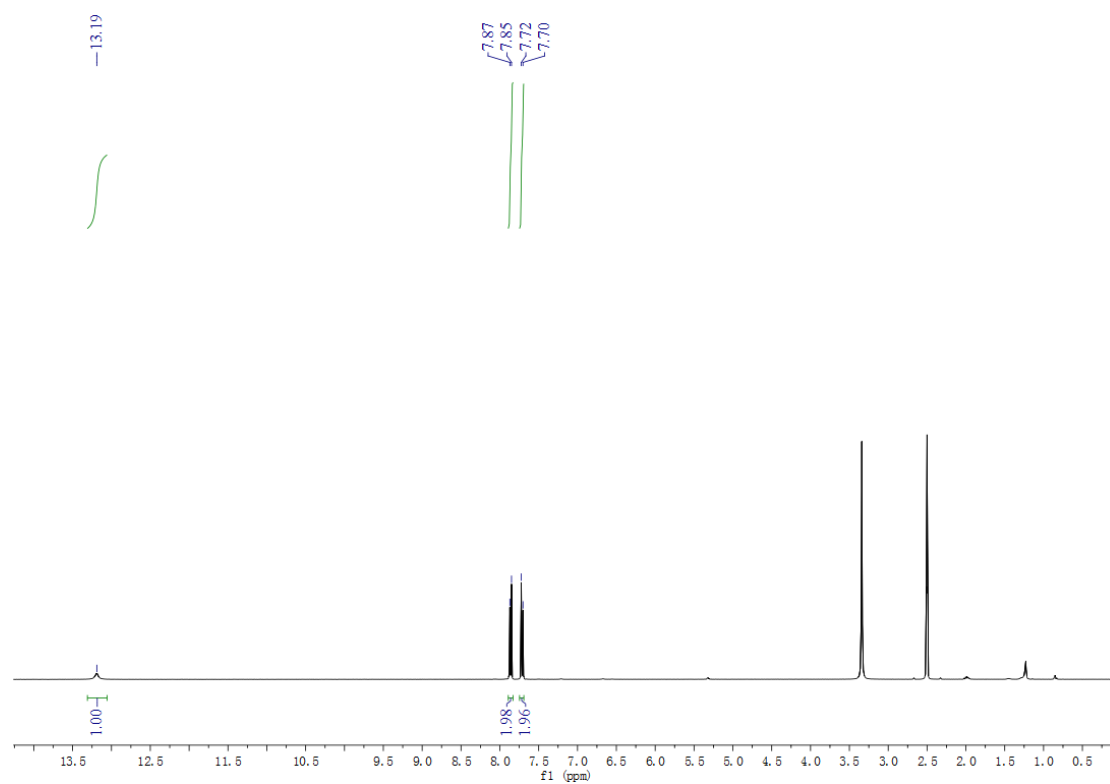




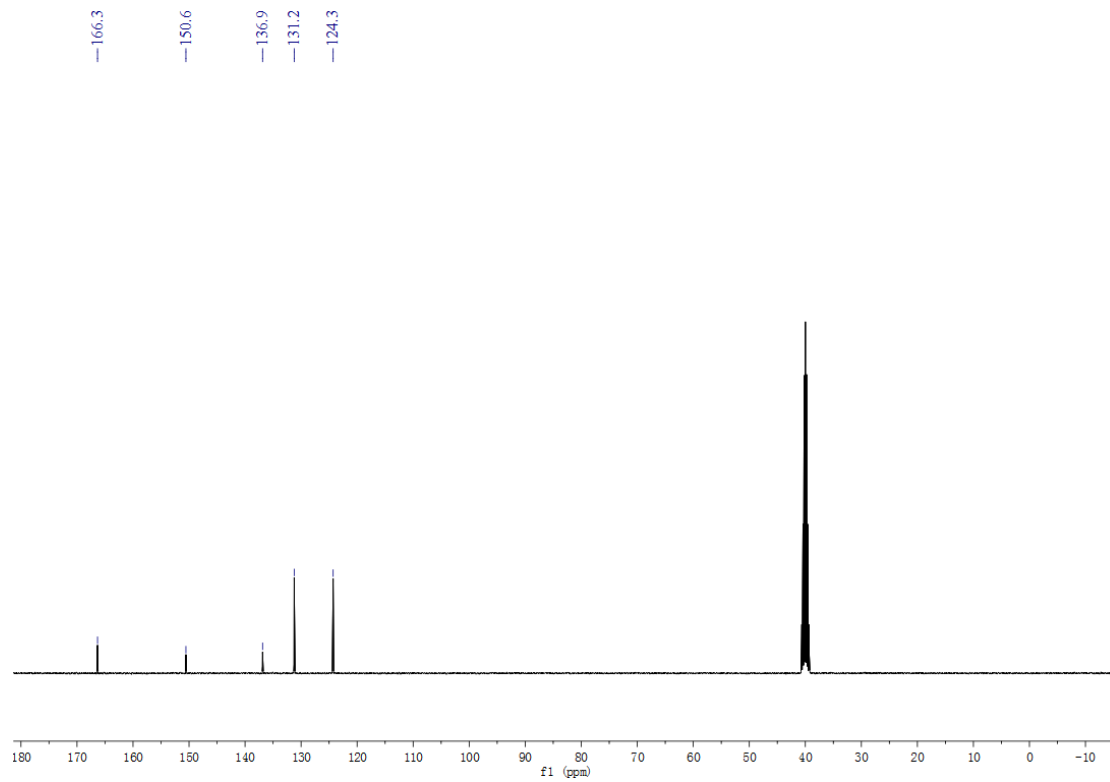
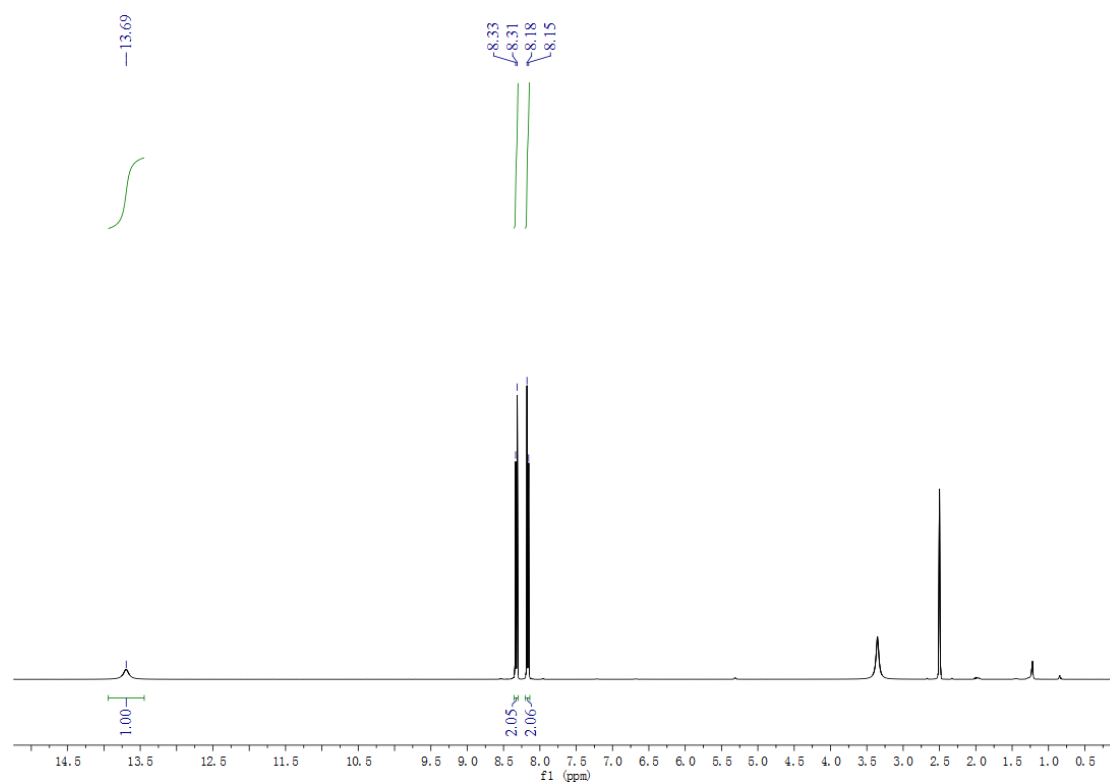
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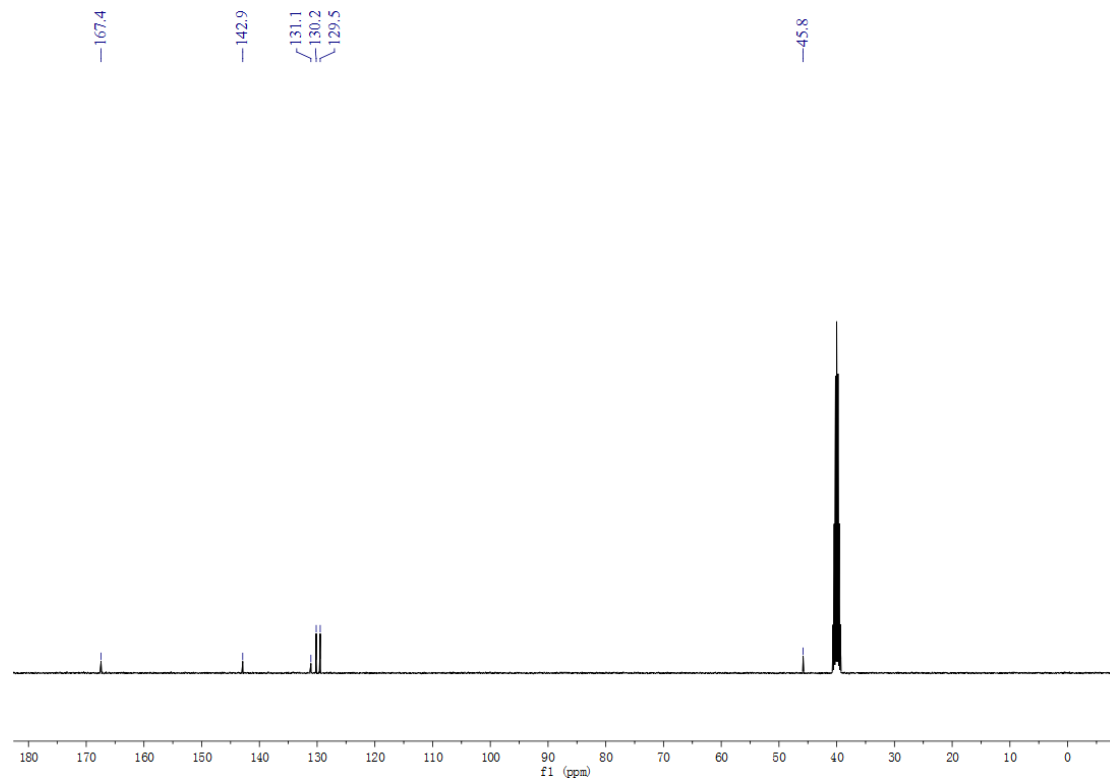
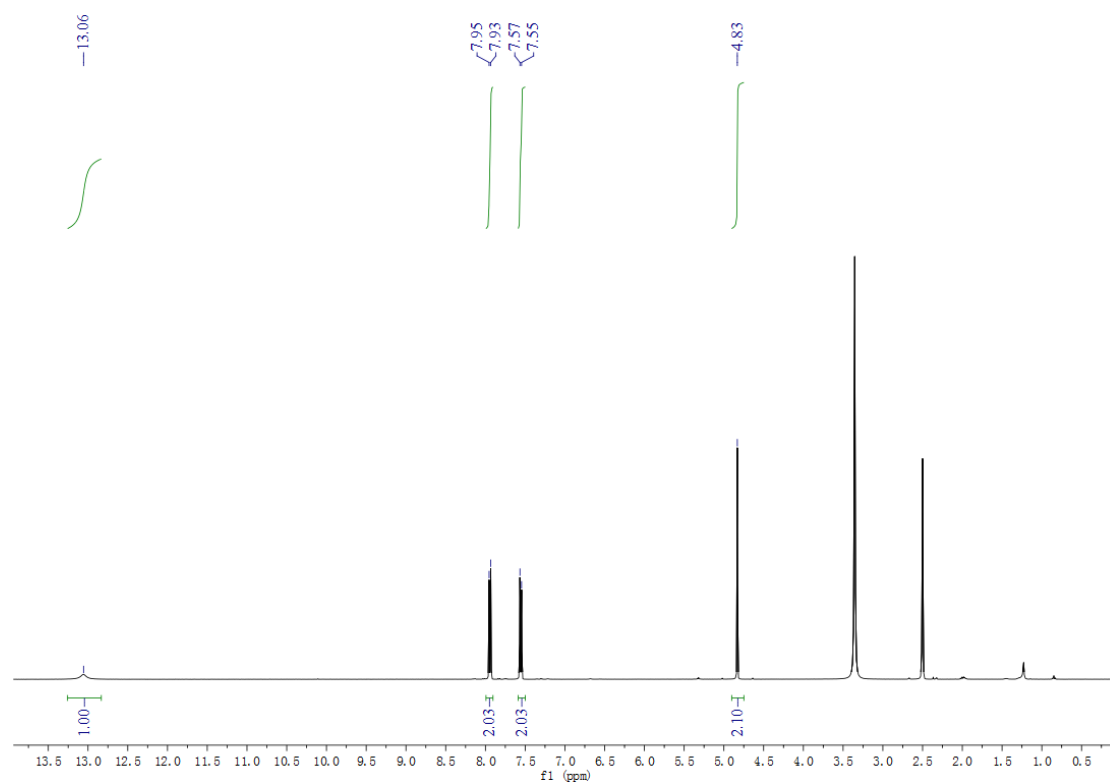
4-bromobenzoic acid (2o)



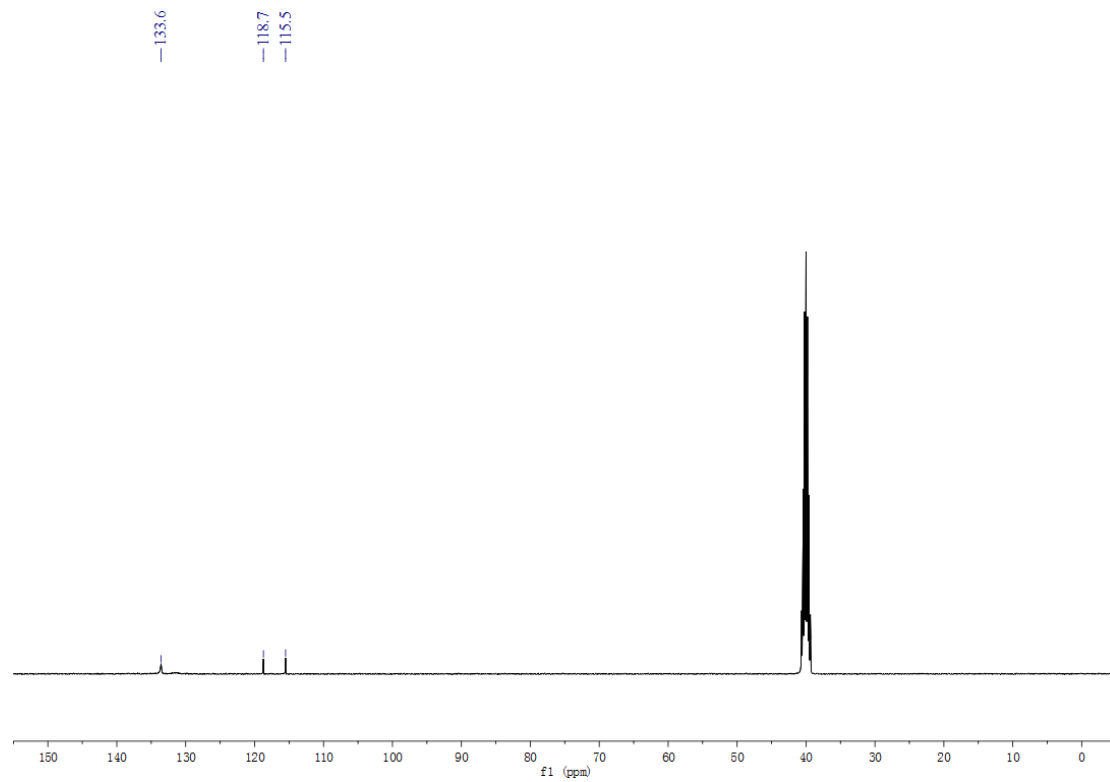
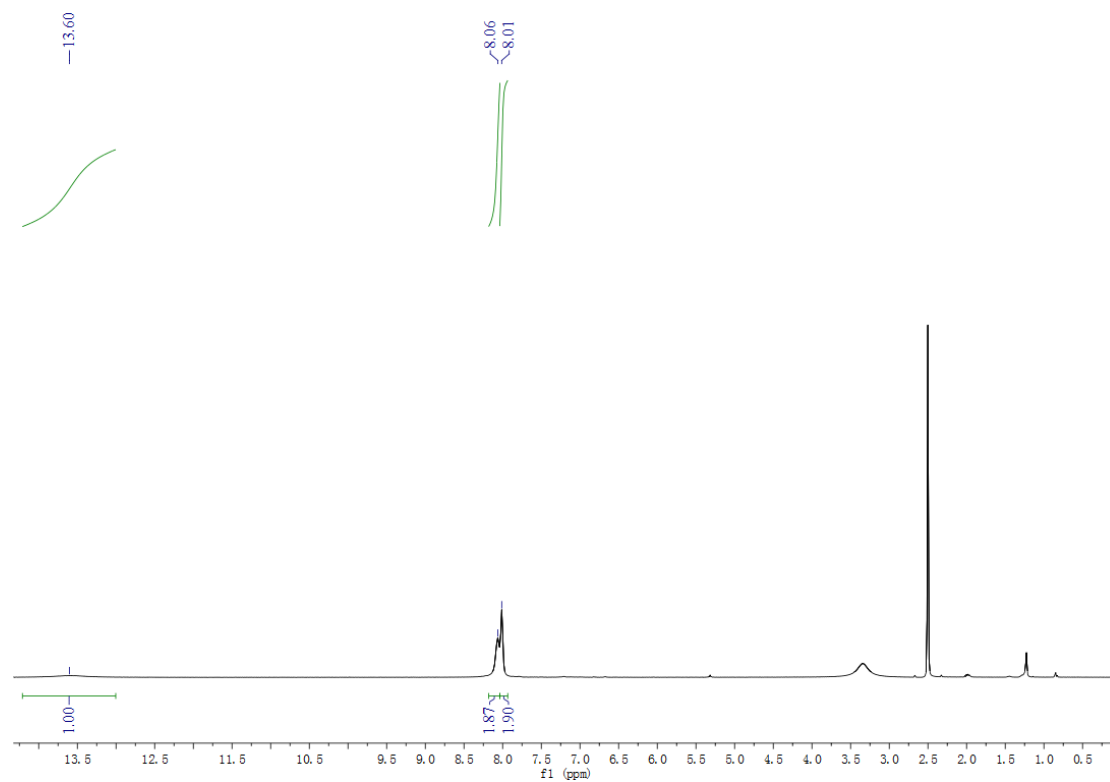
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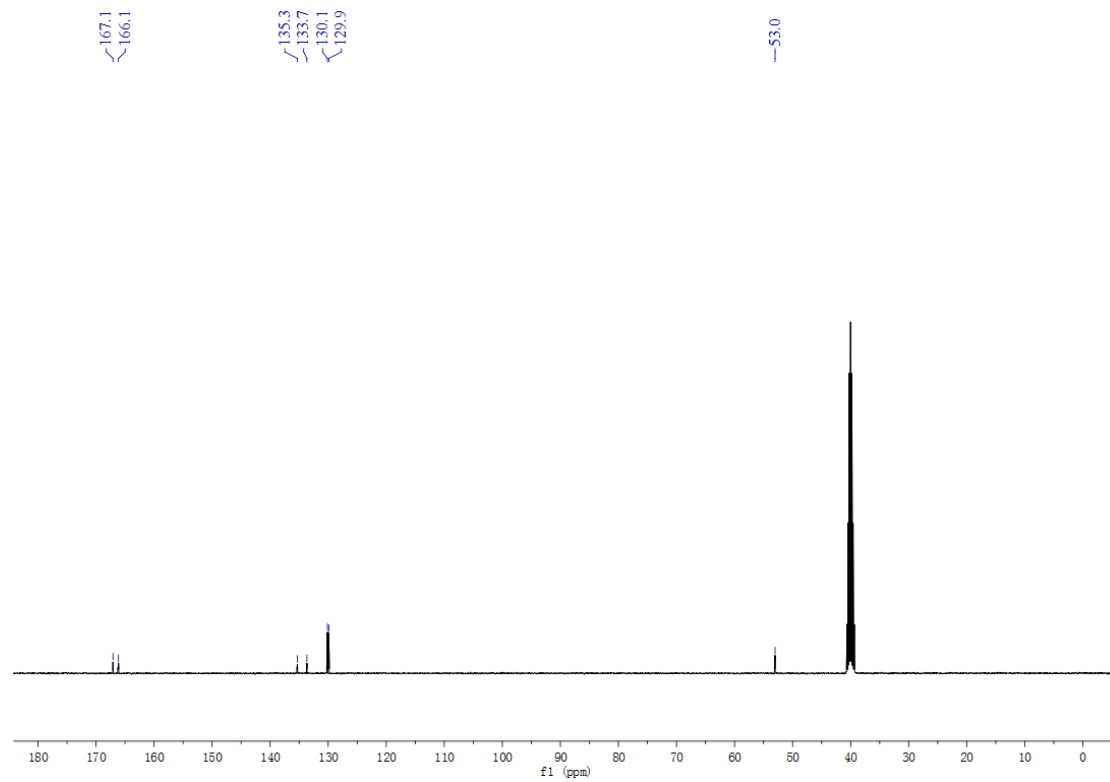
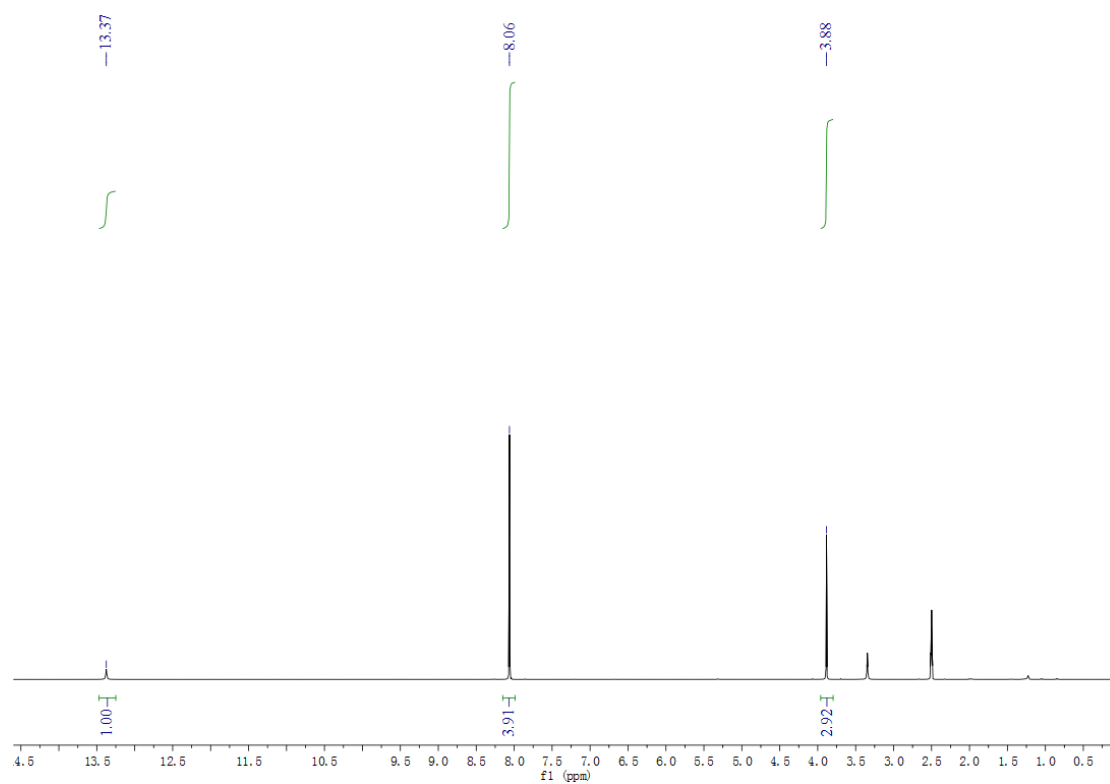
4-(chloromethyl)benzoic acid (2q)



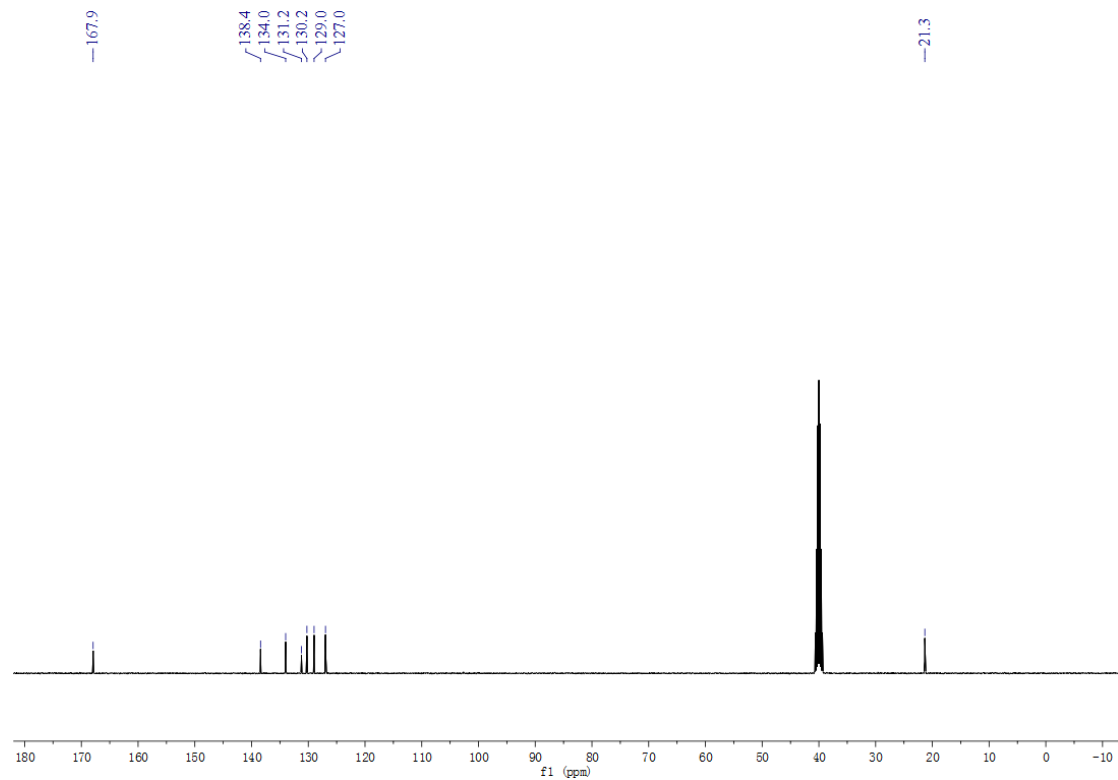
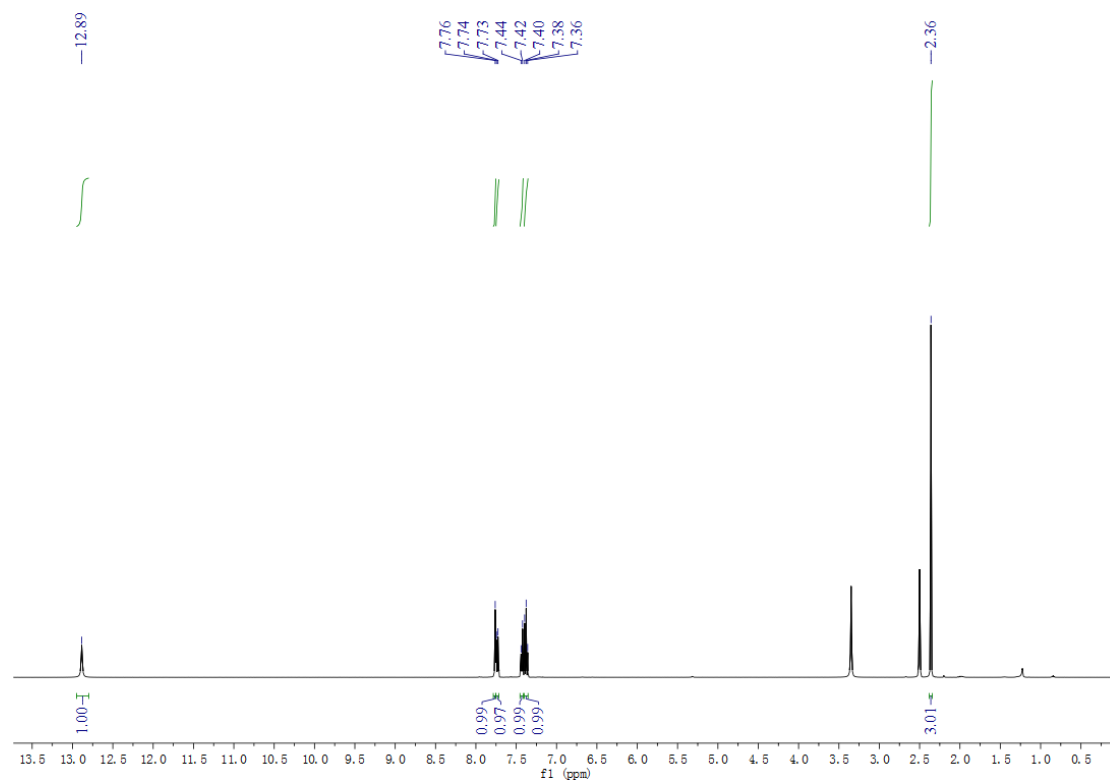
4-cyanobenzoic acid (2r)



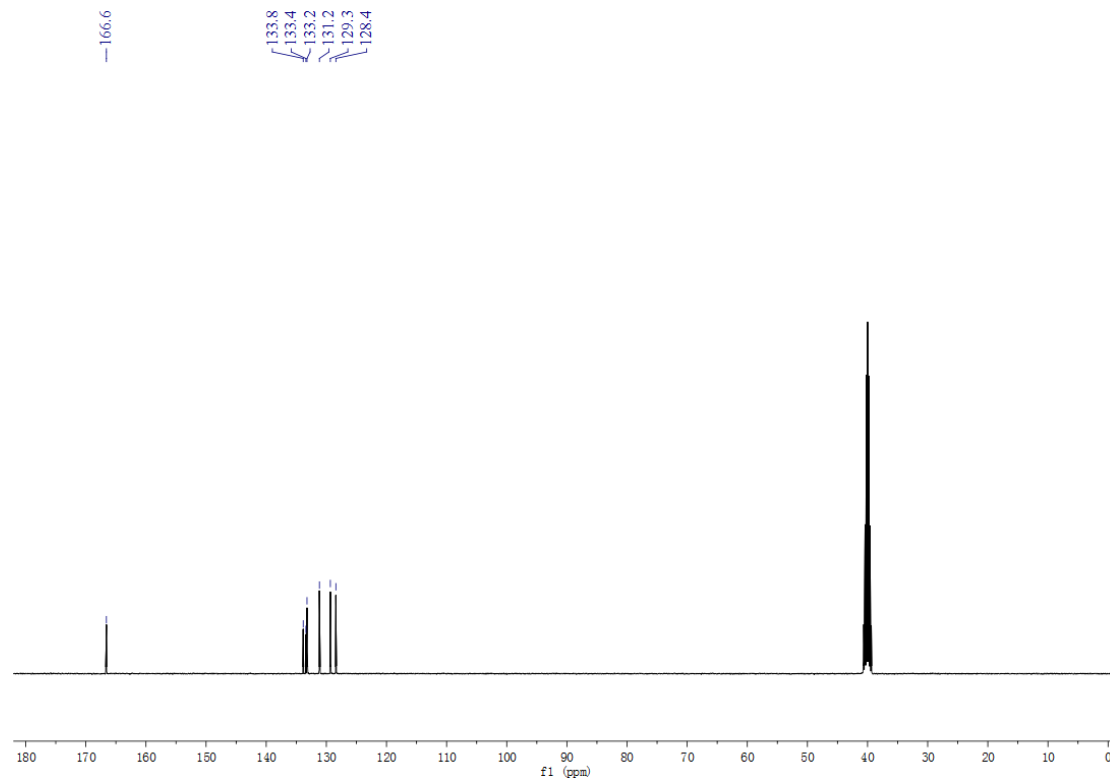
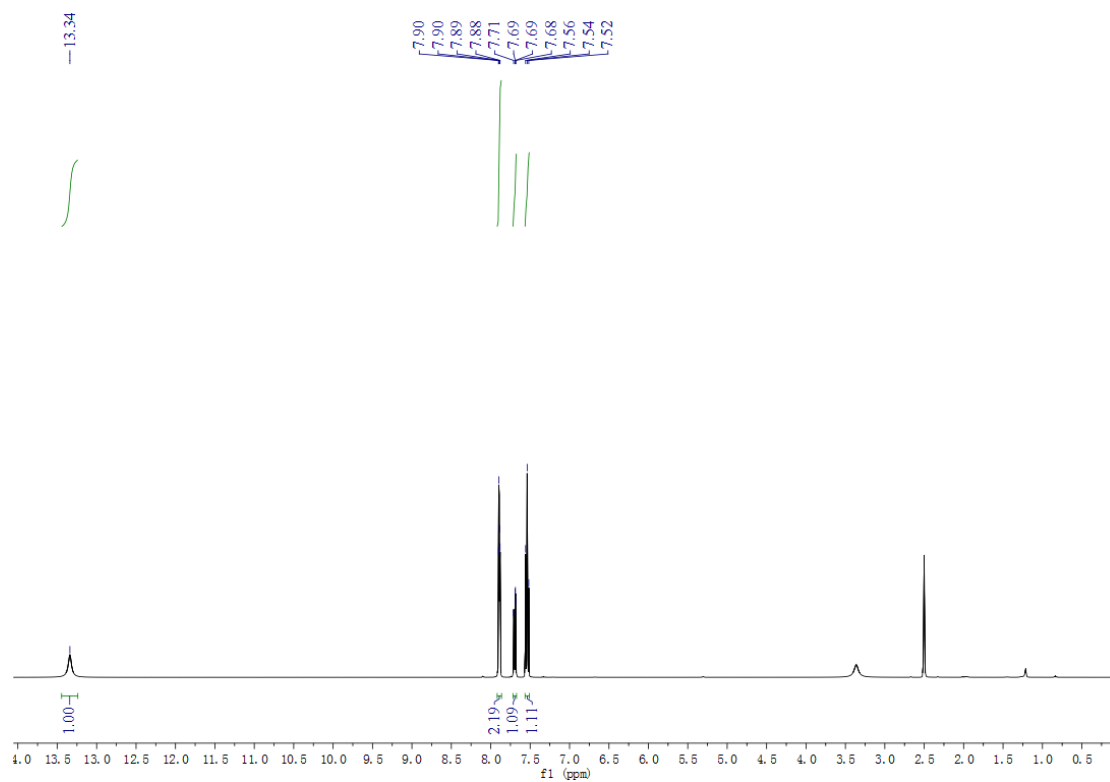
4-(methoxycarbonyl)benzoic acid (2s)



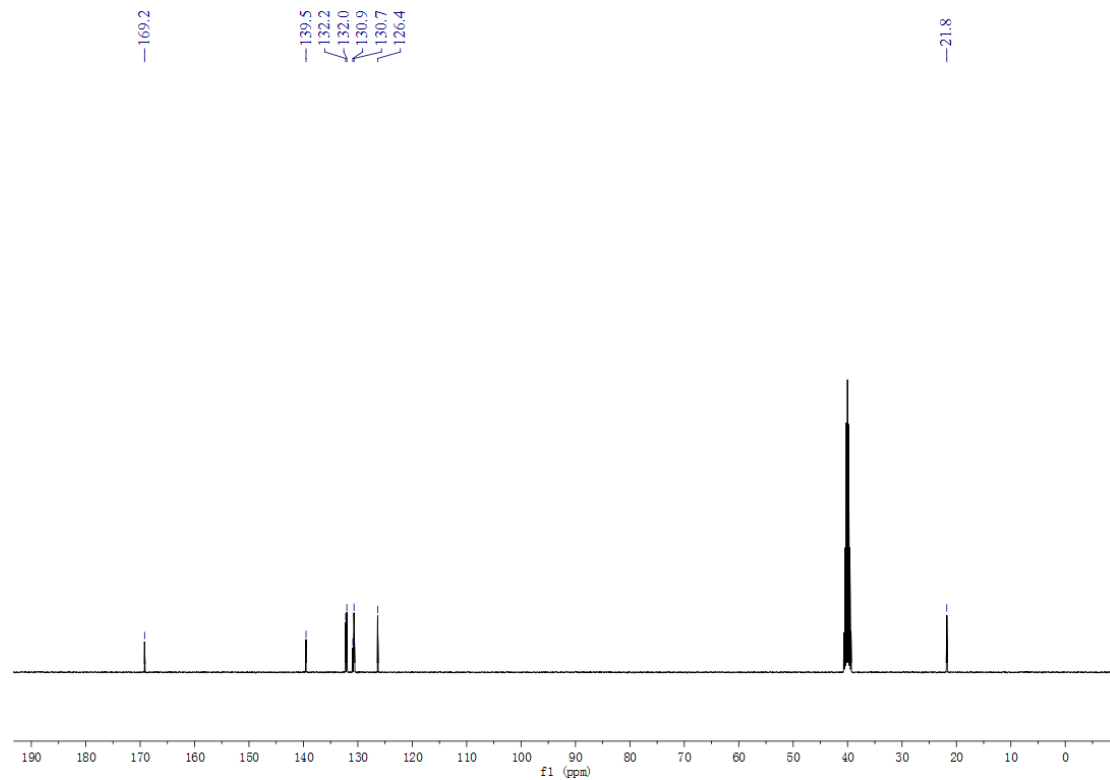
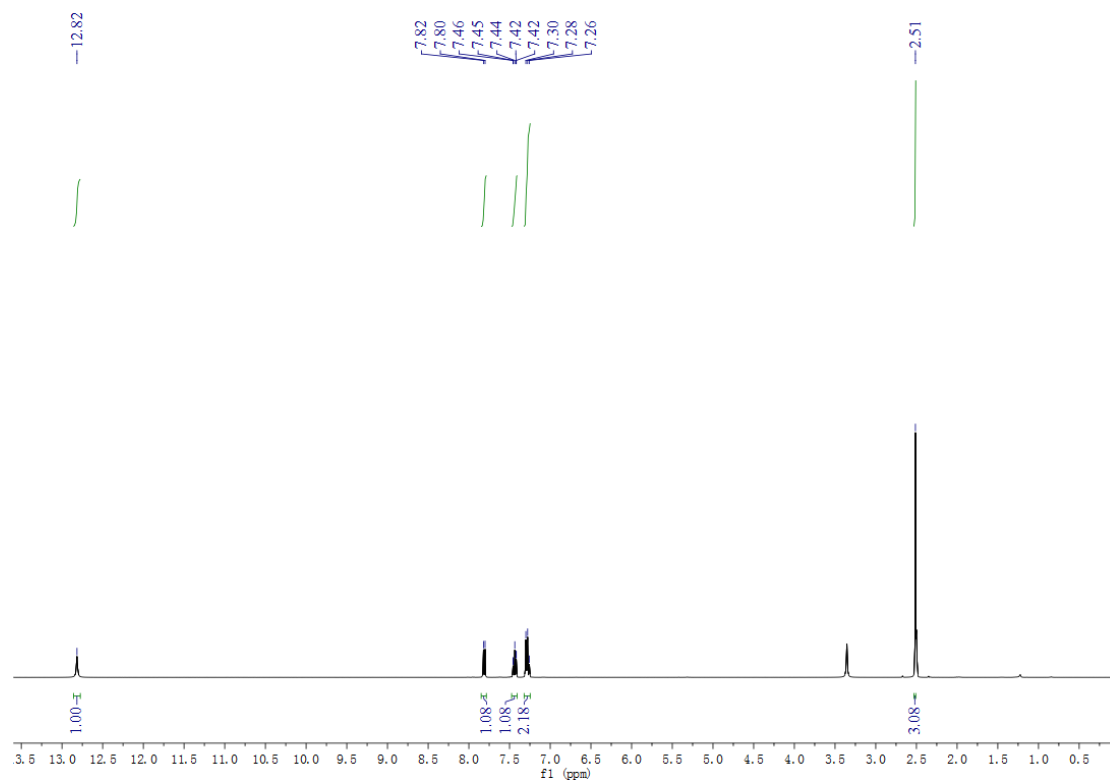
3-methylbenzoic acid (2t)



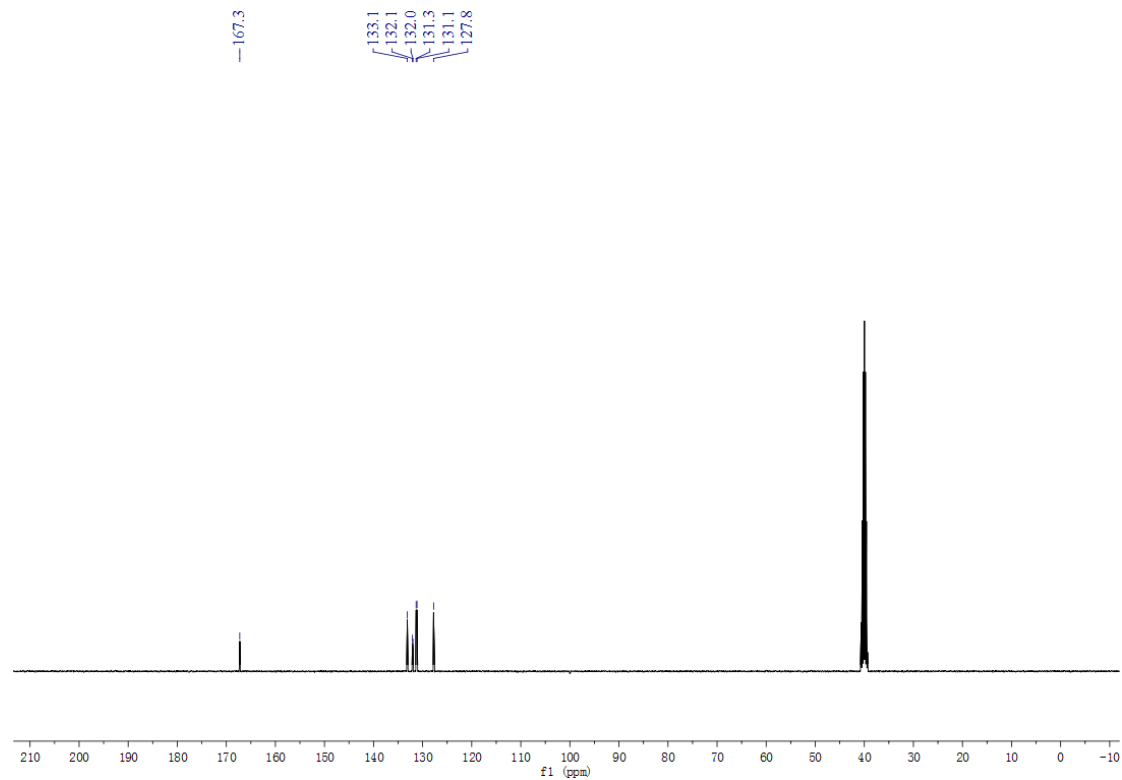
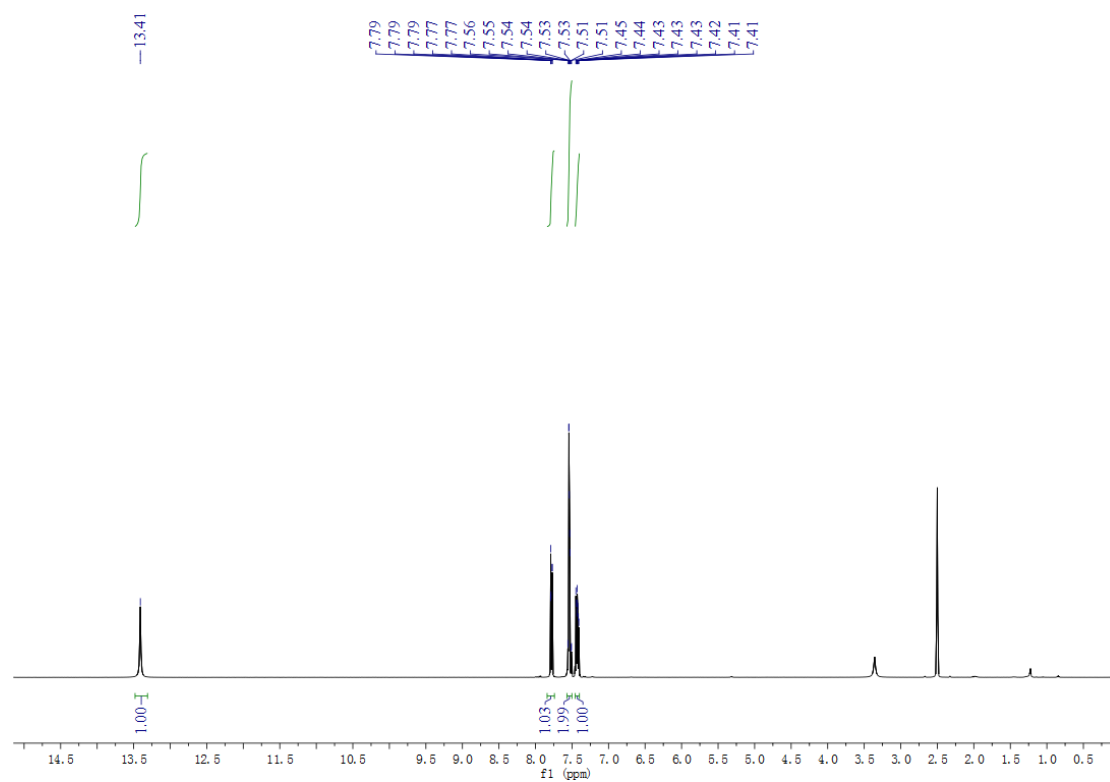
3-chlorobenzoic acid (2u)



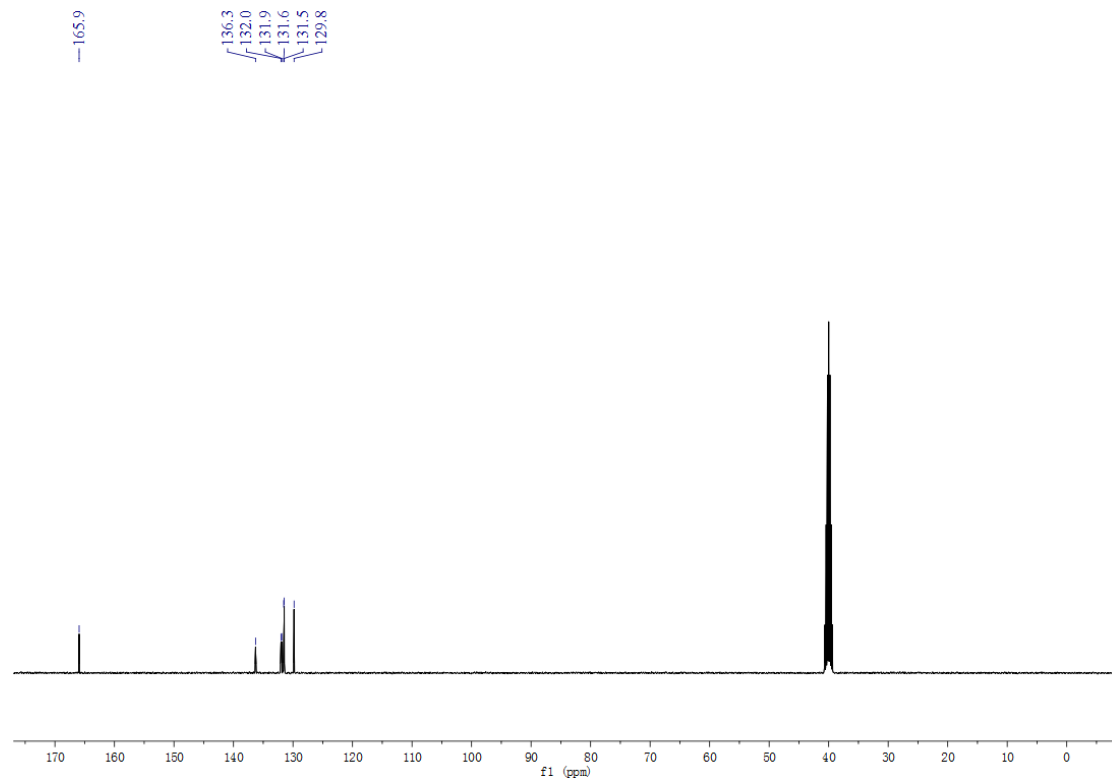
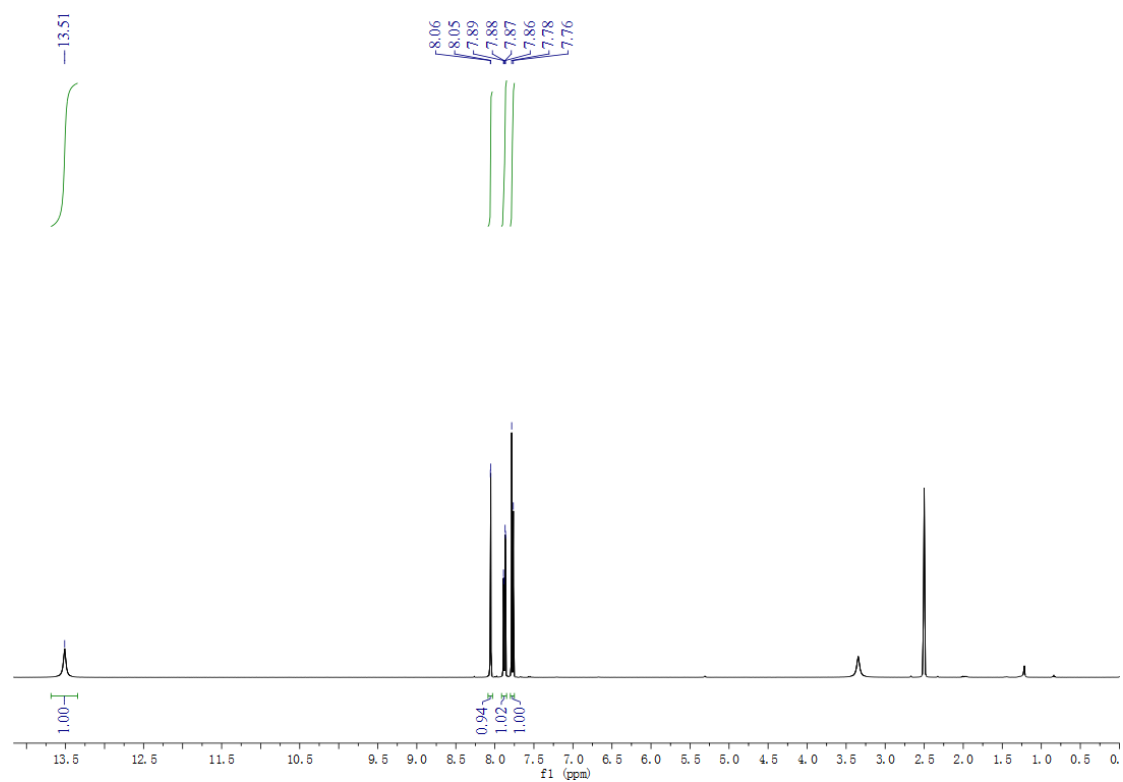
2-methylbenzoic acid (2v)



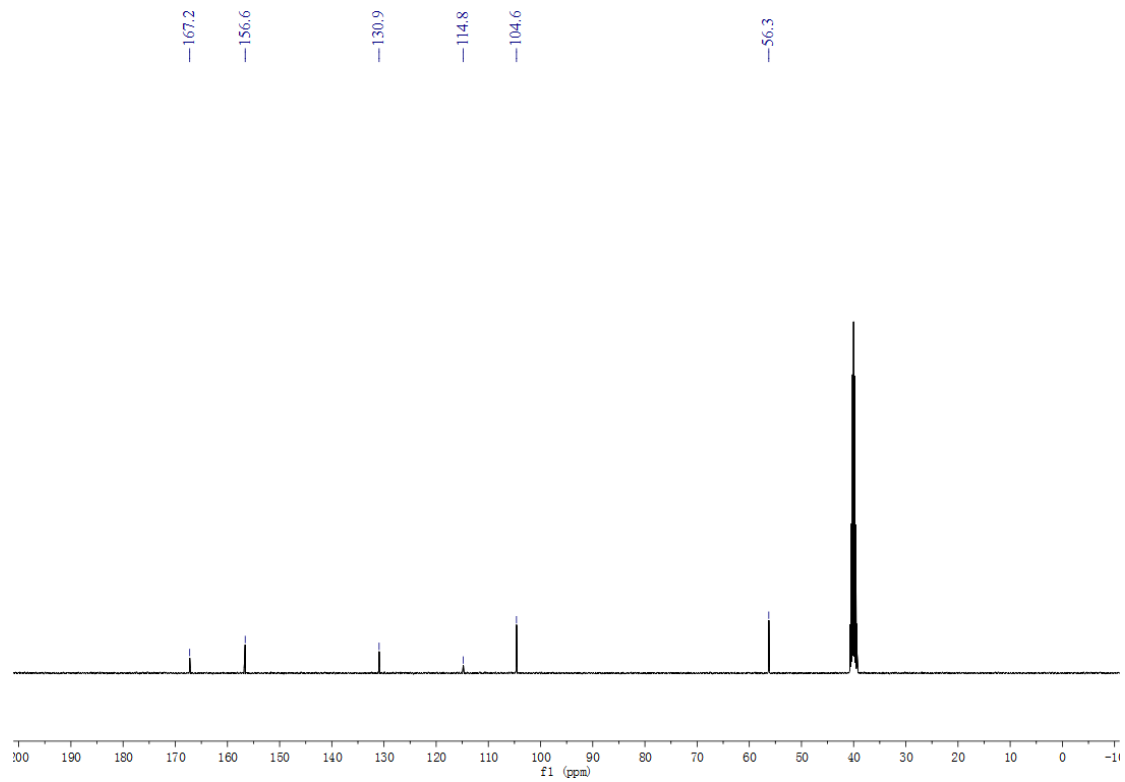
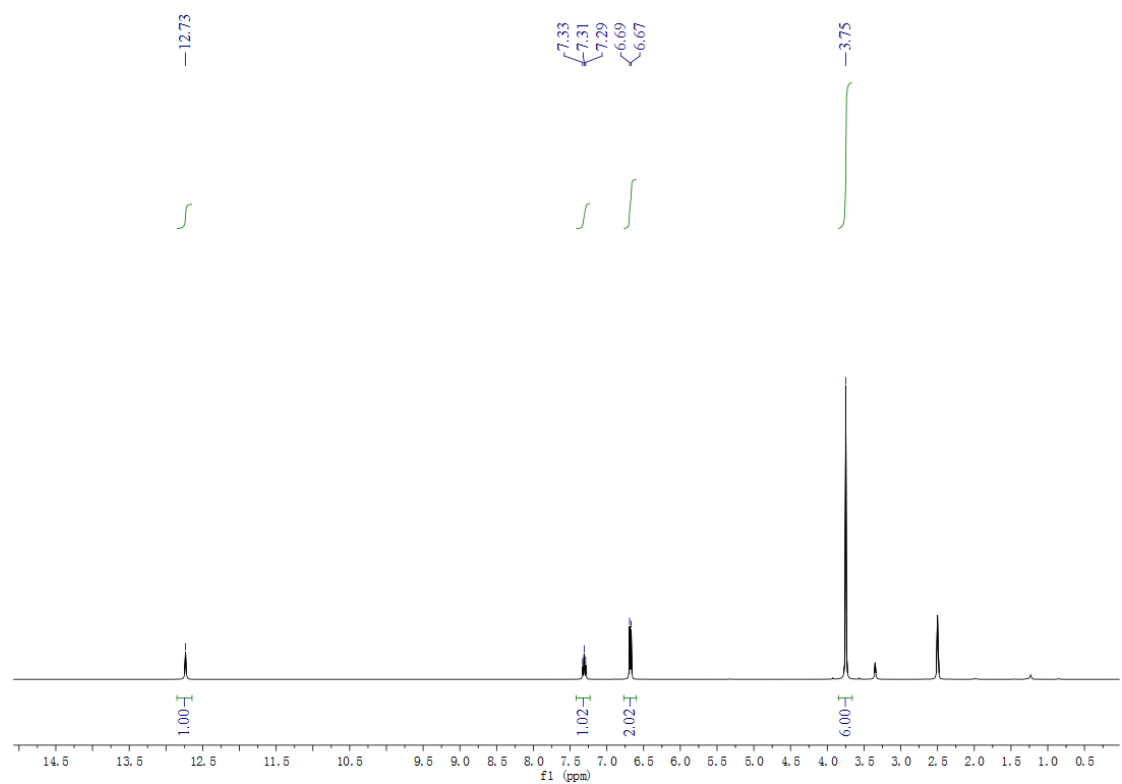
2-chlorobenzoic acid (2w)



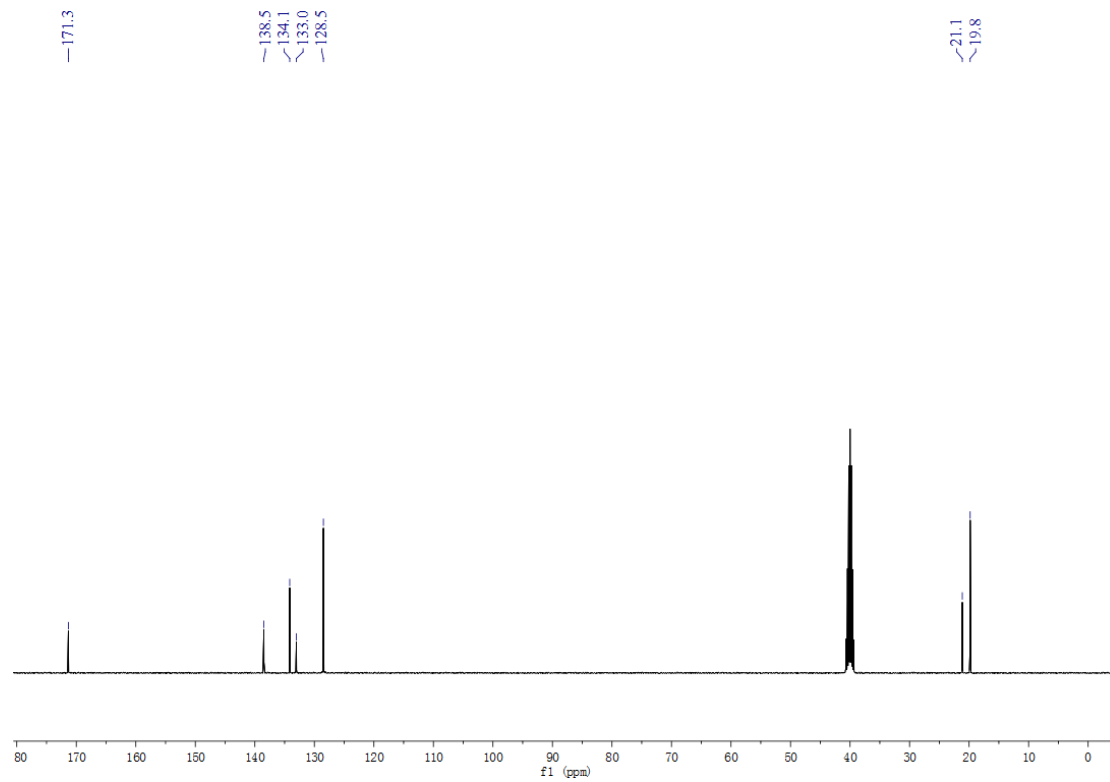
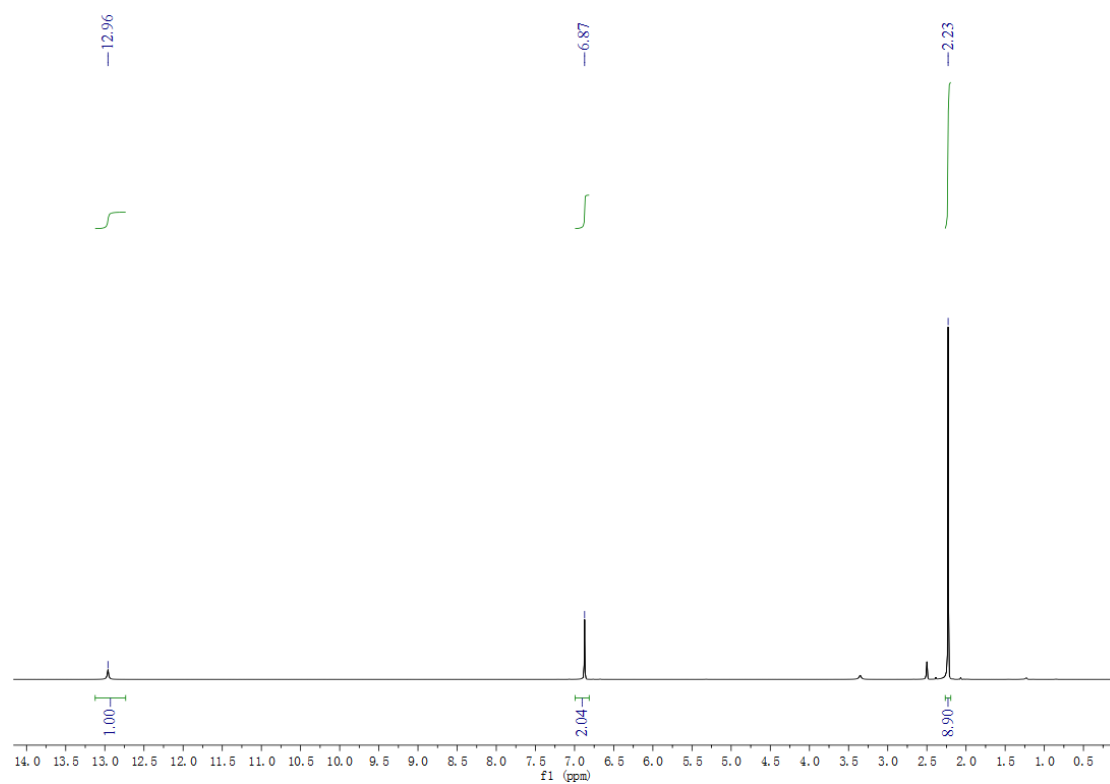
3,4-dichlorobenzoic acid (2x)



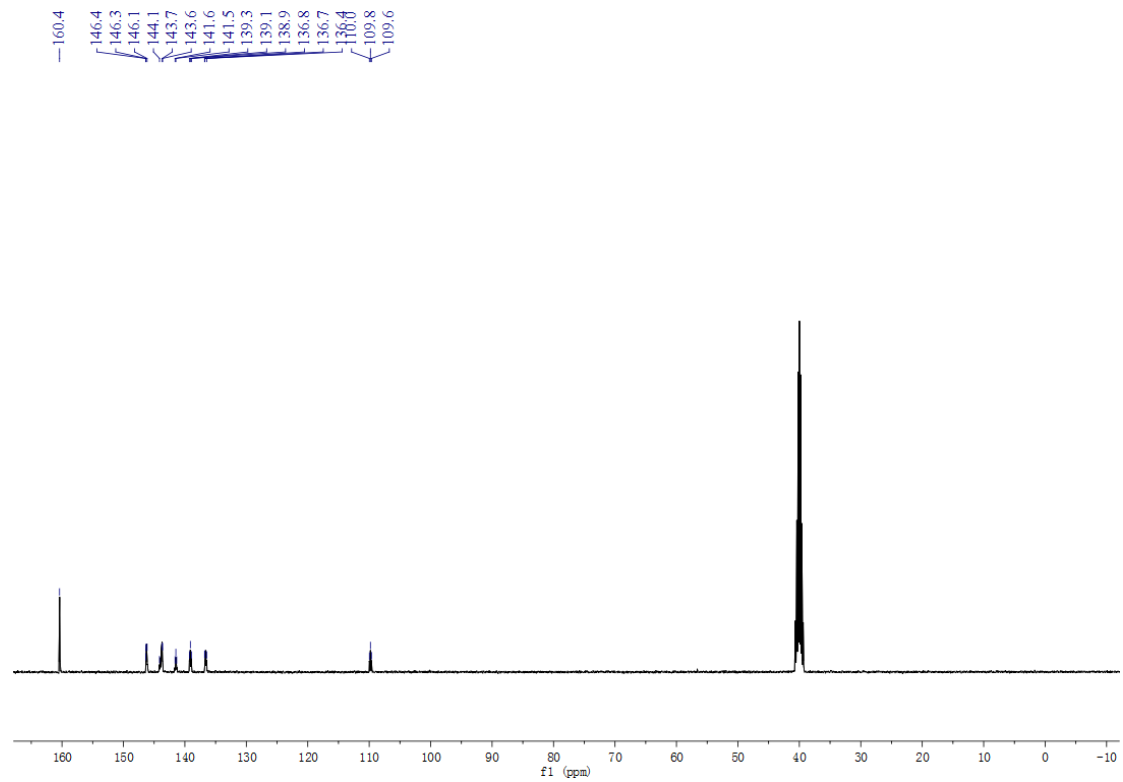
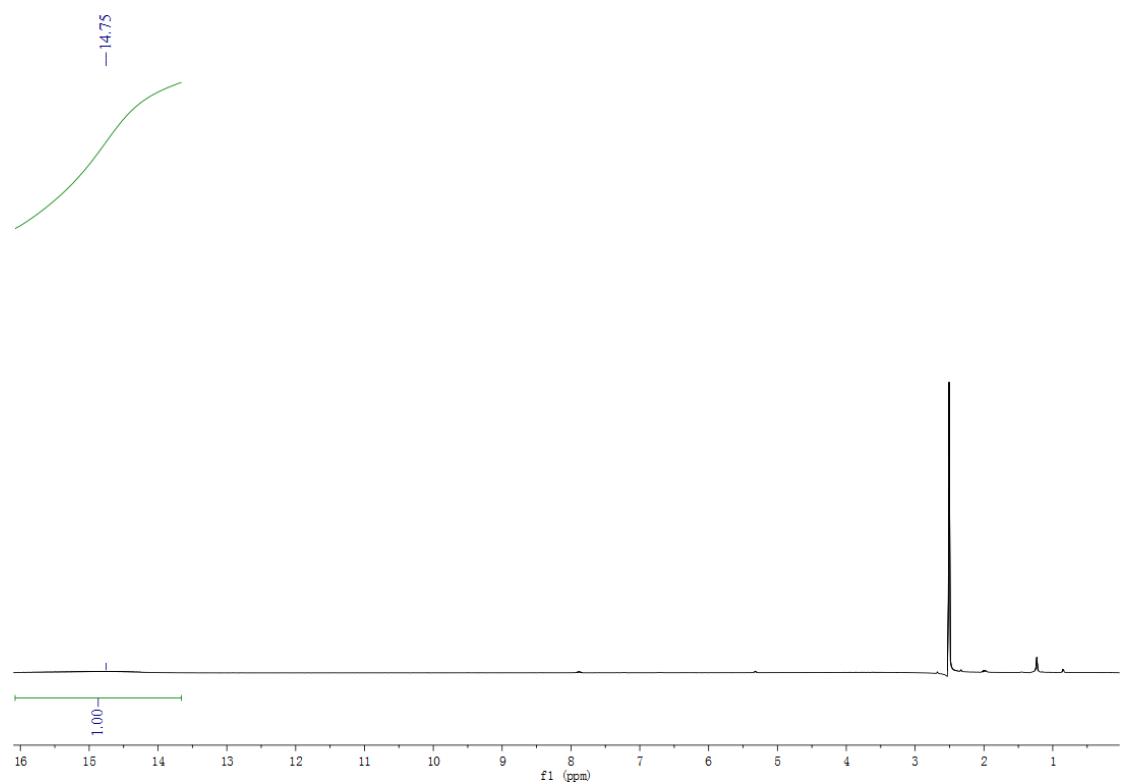
2,6-dimethoxybenzoic acid (2y)

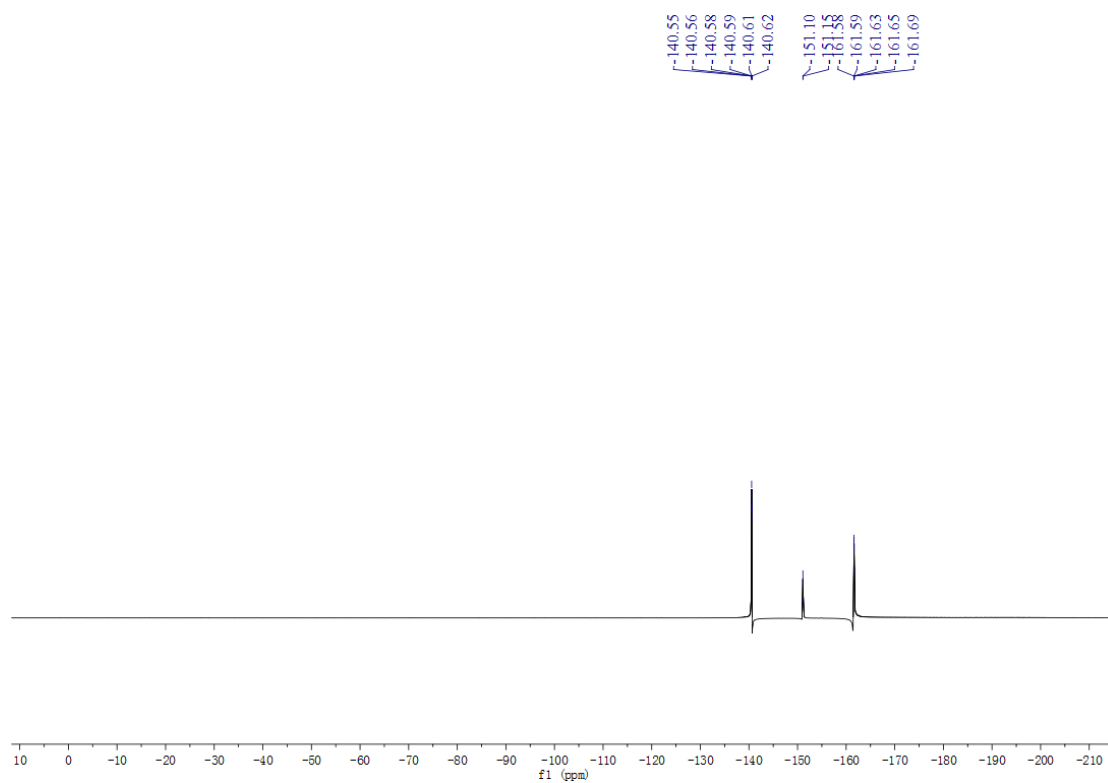


2,4,6-trimethylbenzoic acid (2z)

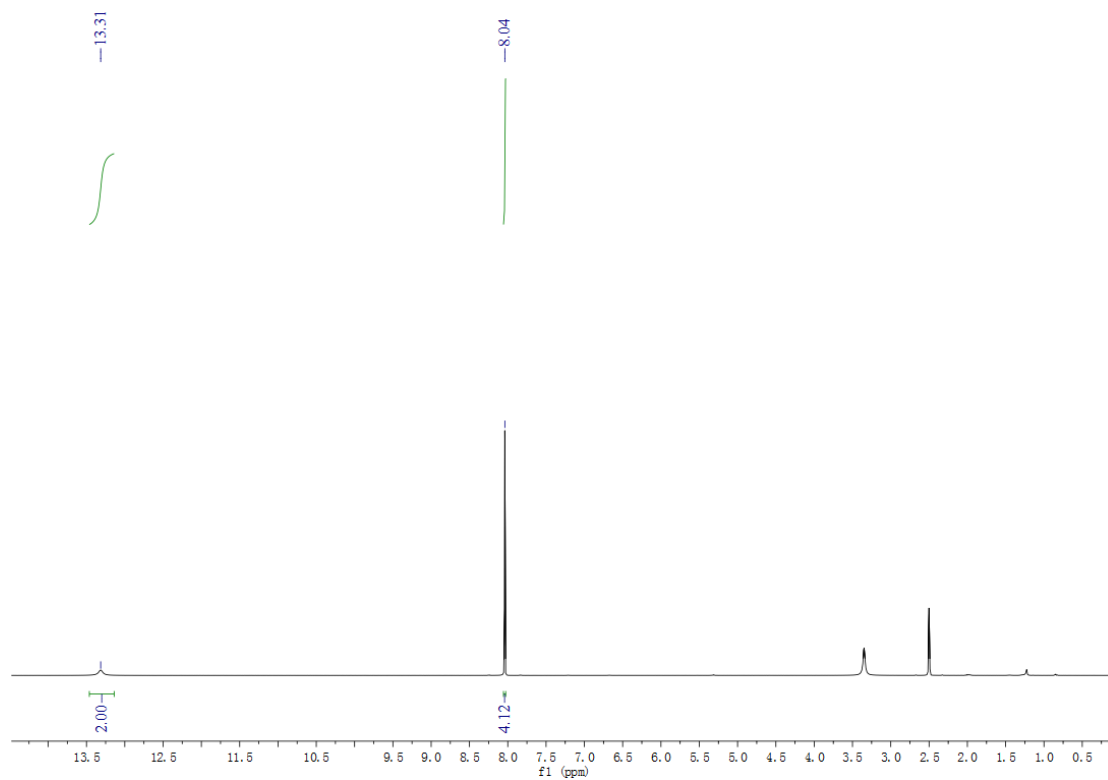


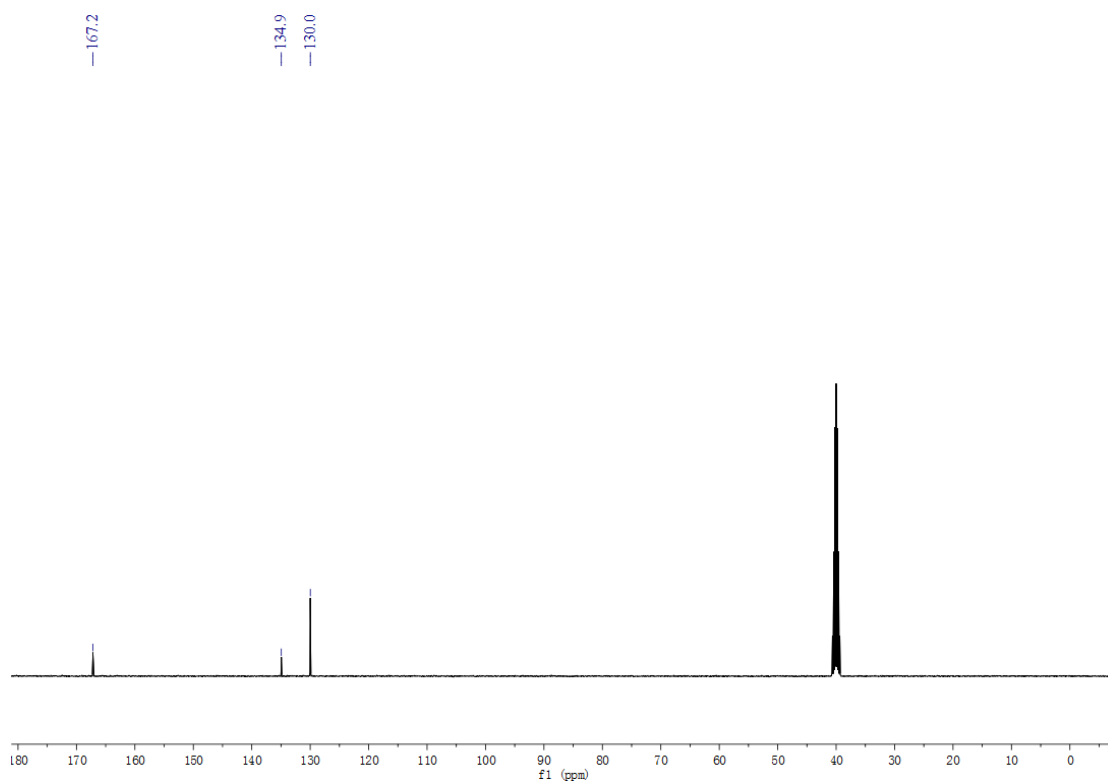
2,3,4,5,6-pentafluorobenzoic acid (2aa)



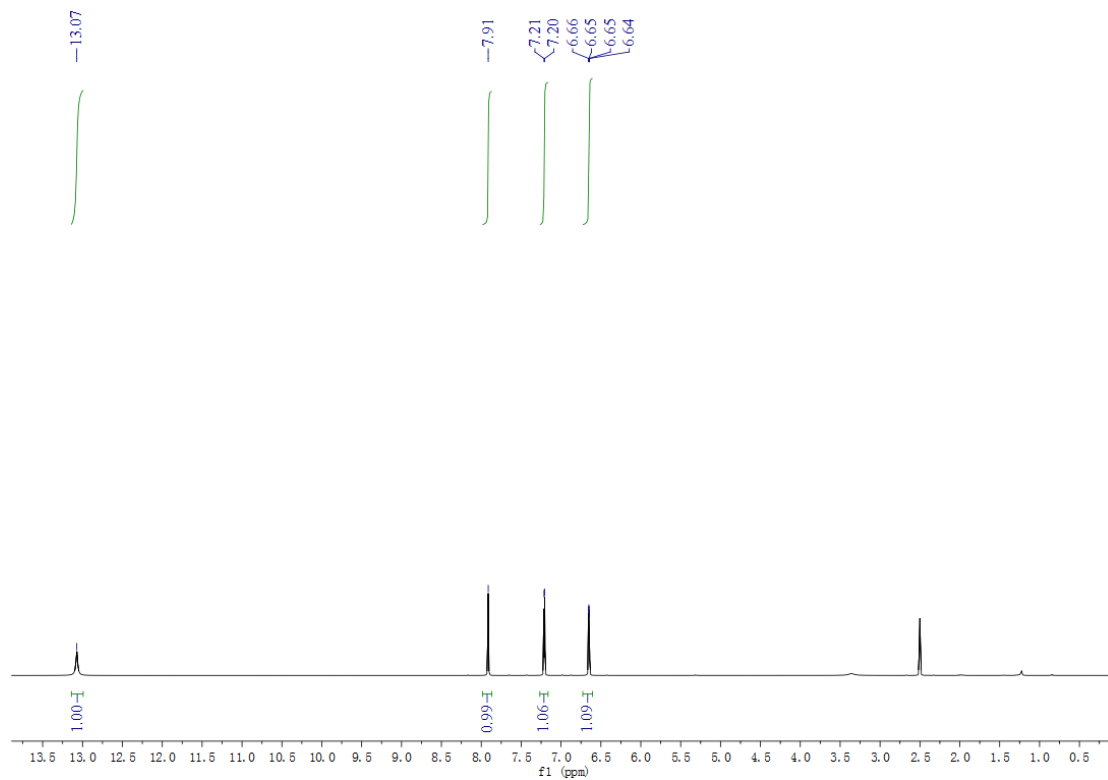


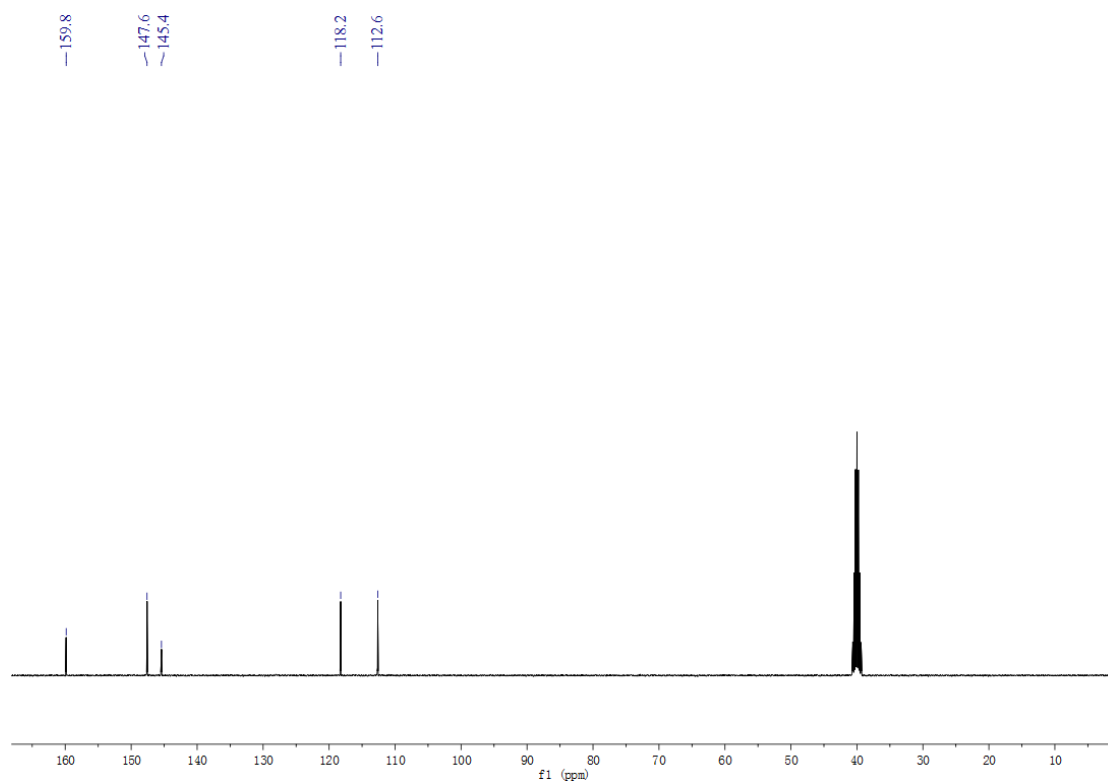
terephthalic acid (2ab)



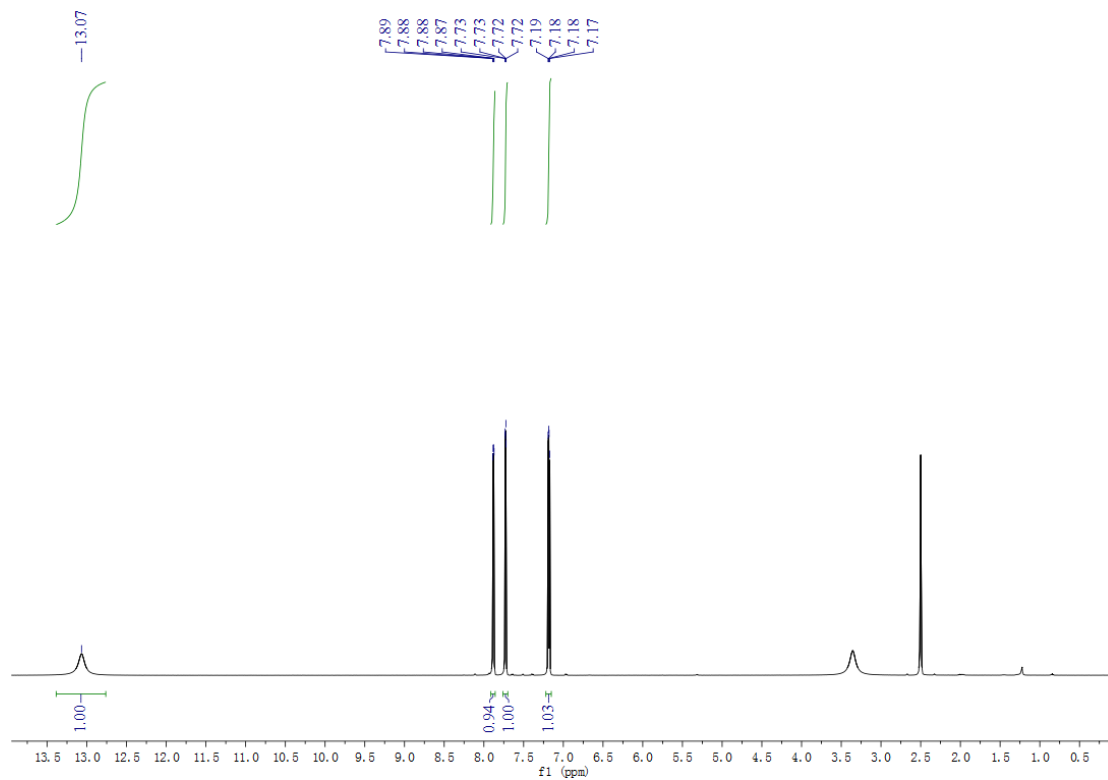


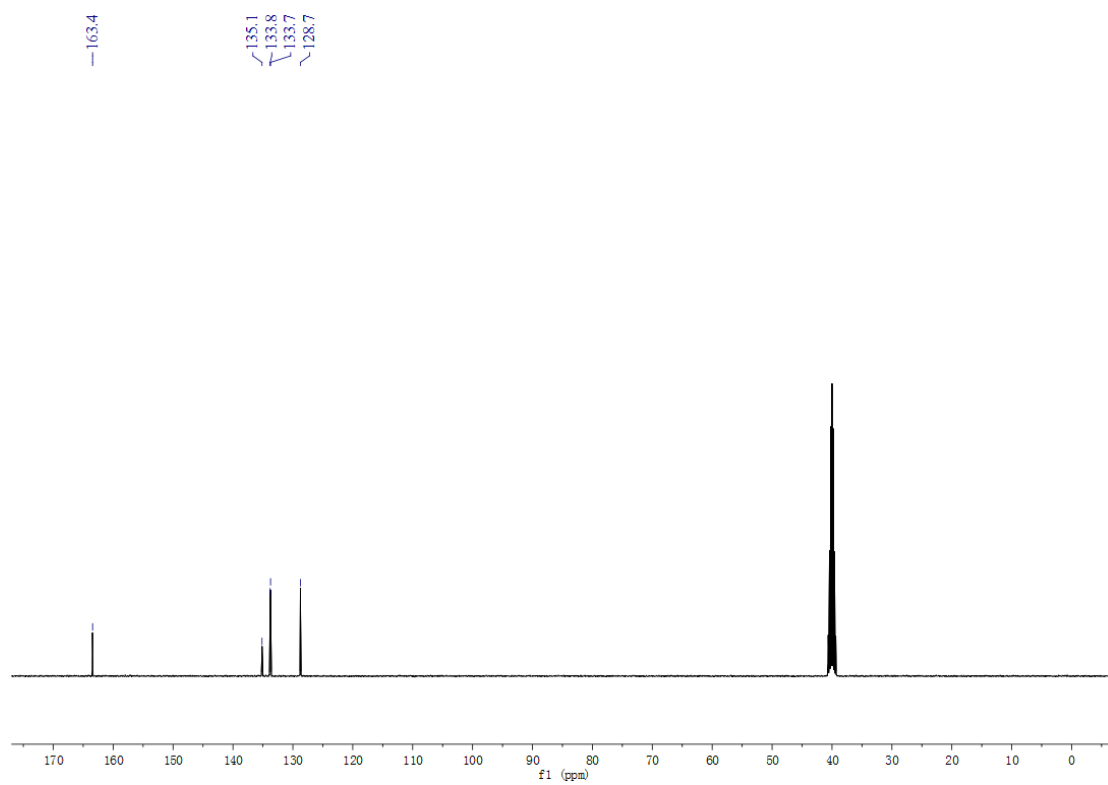
furan-2-carboxylic acid (2ac)



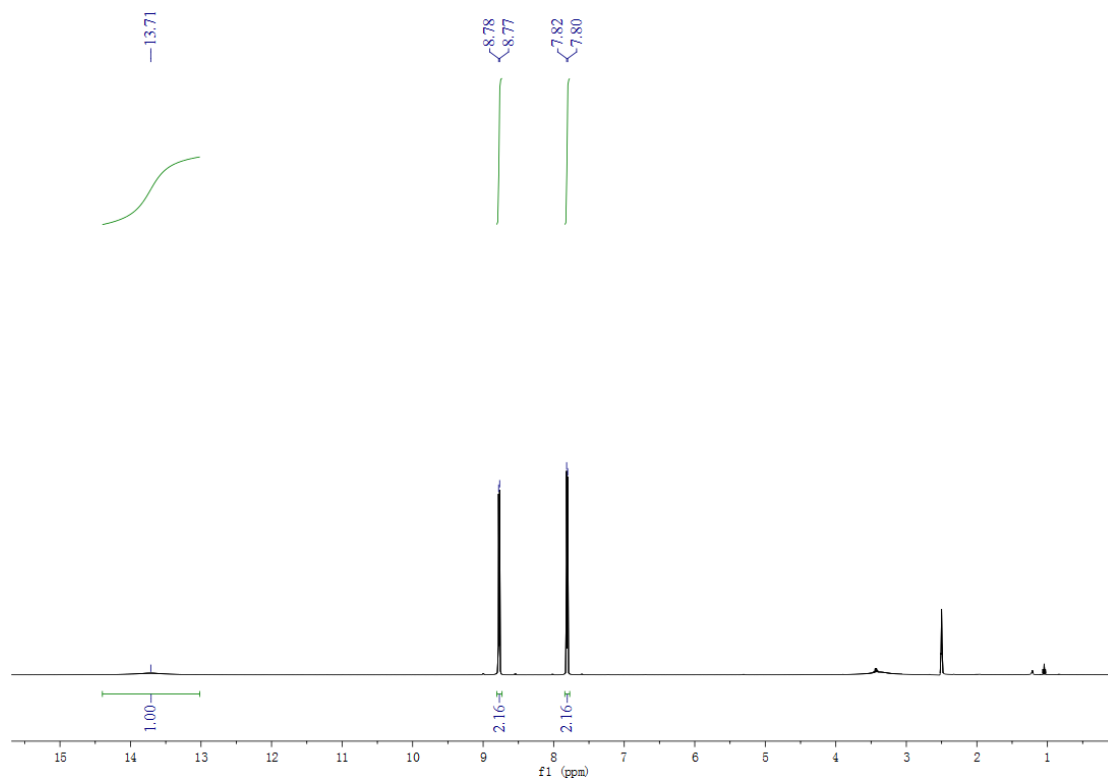


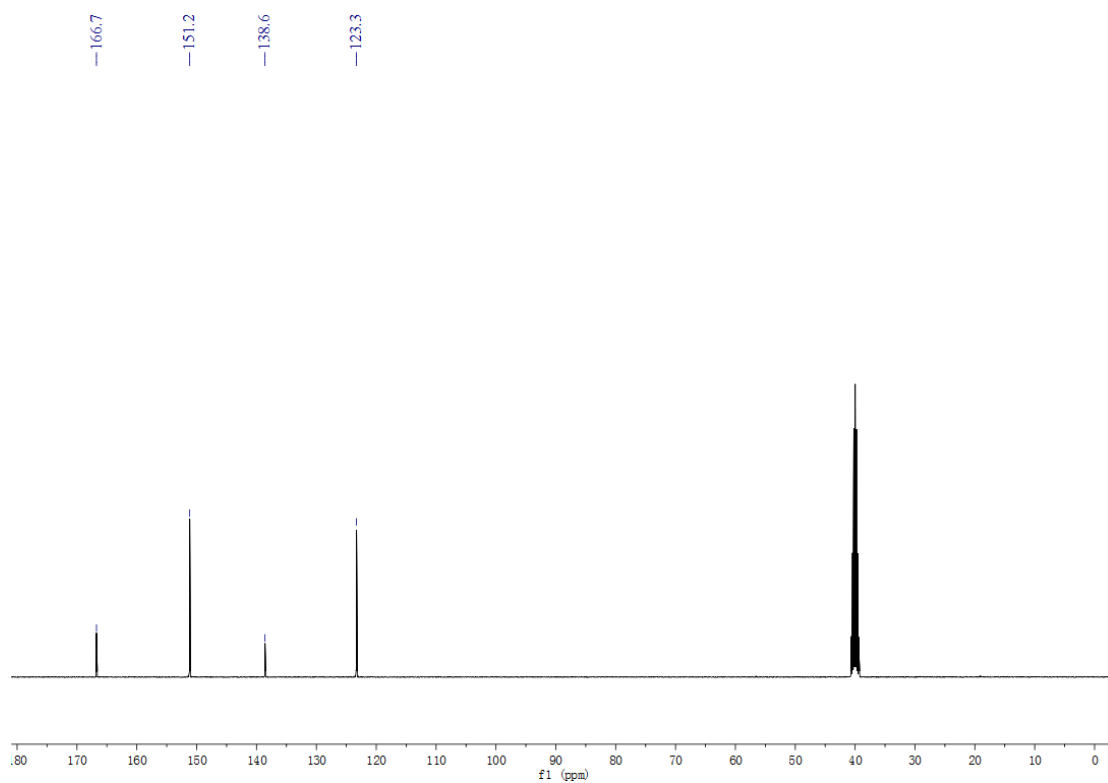
thiophene-2-carboxylic acid (2ad)



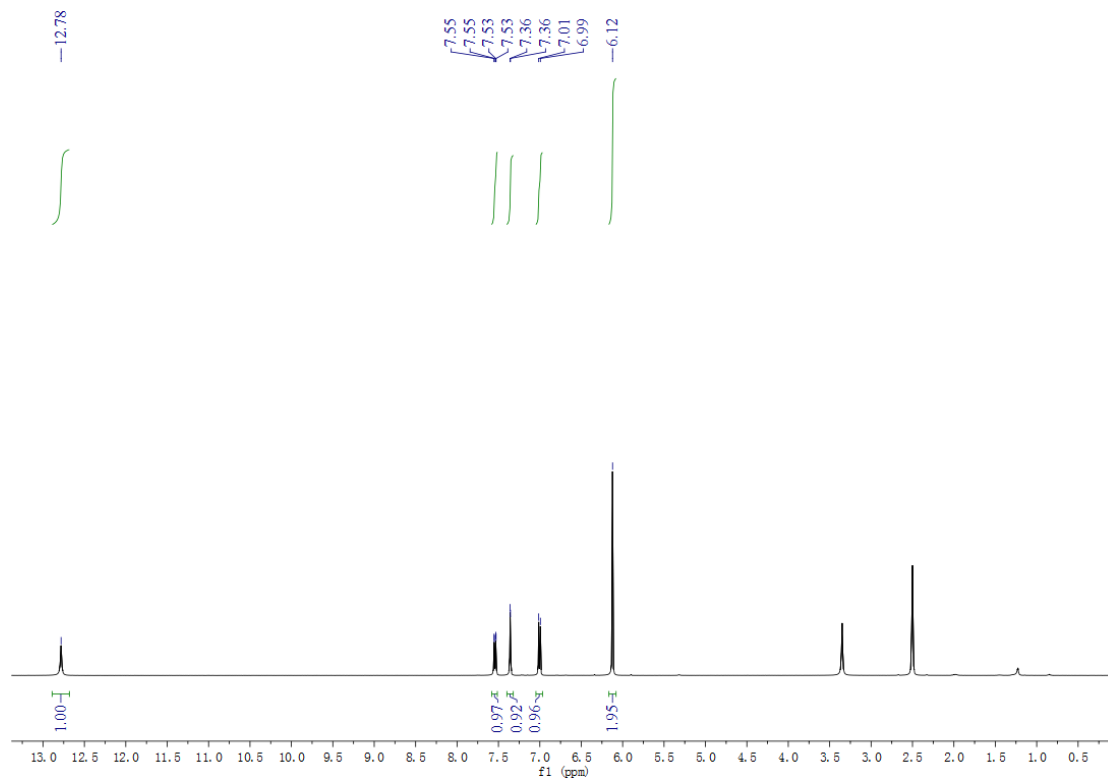


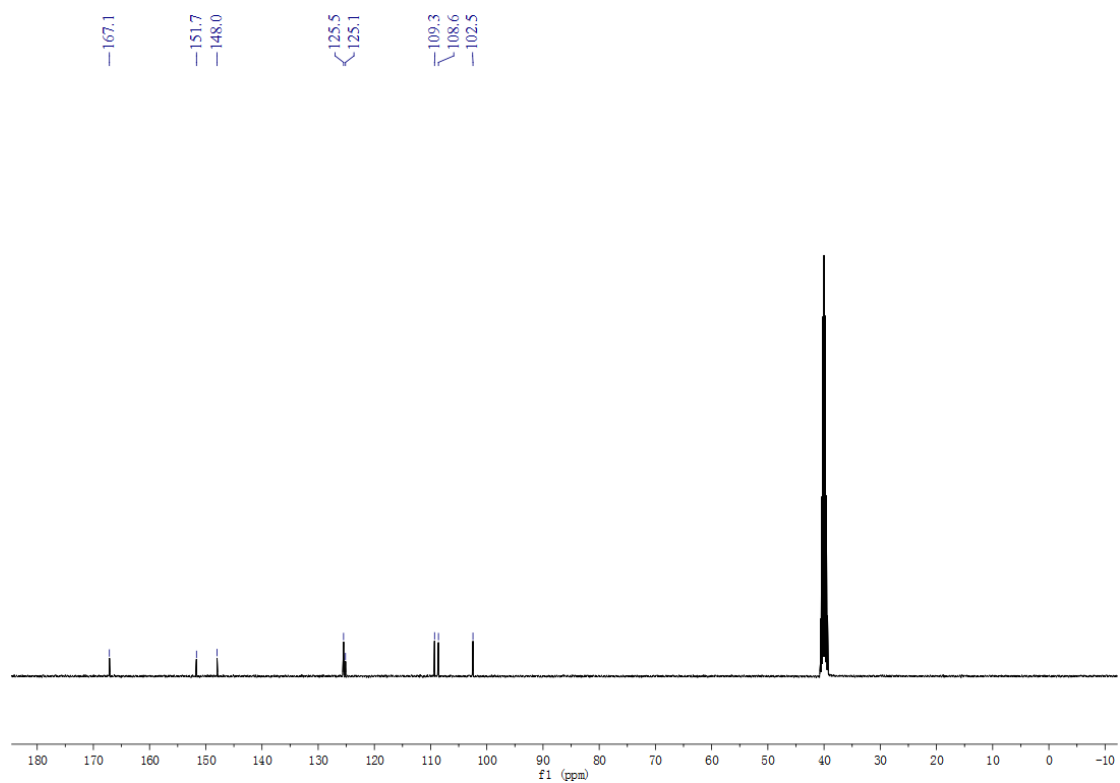
isonicotinic acid (2ae)



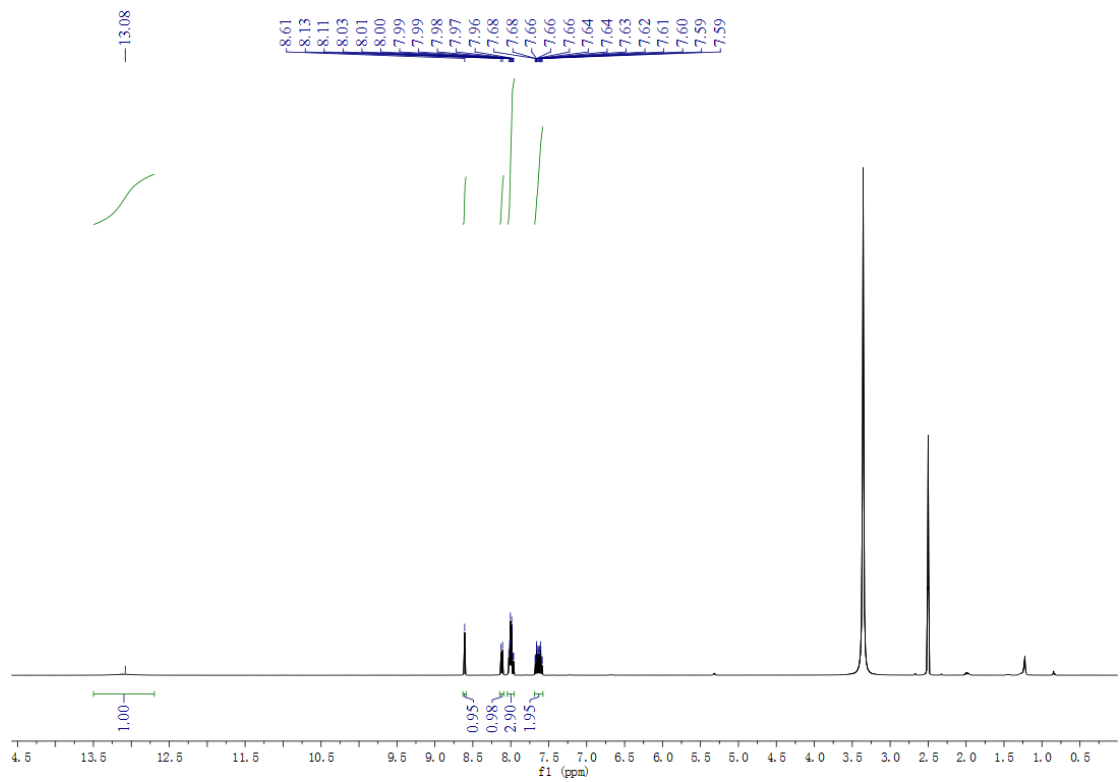


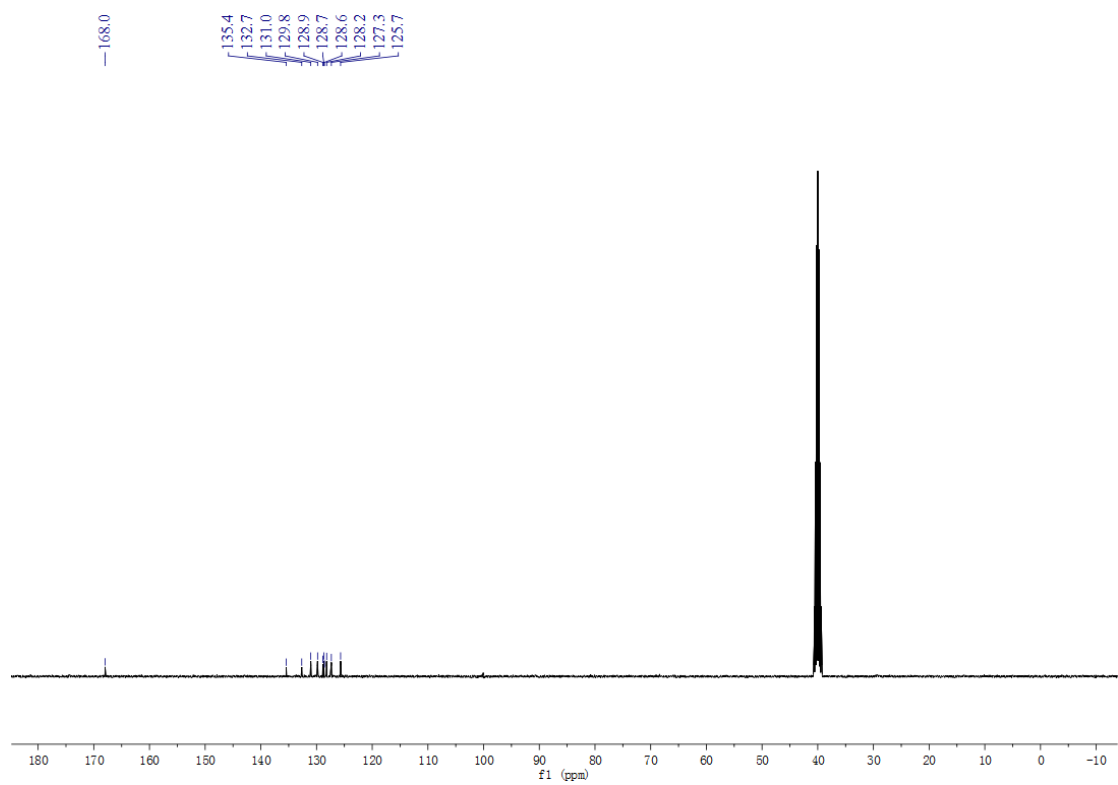
benzo[d][1,3]dioxole-5-carboxylic acid (2af)



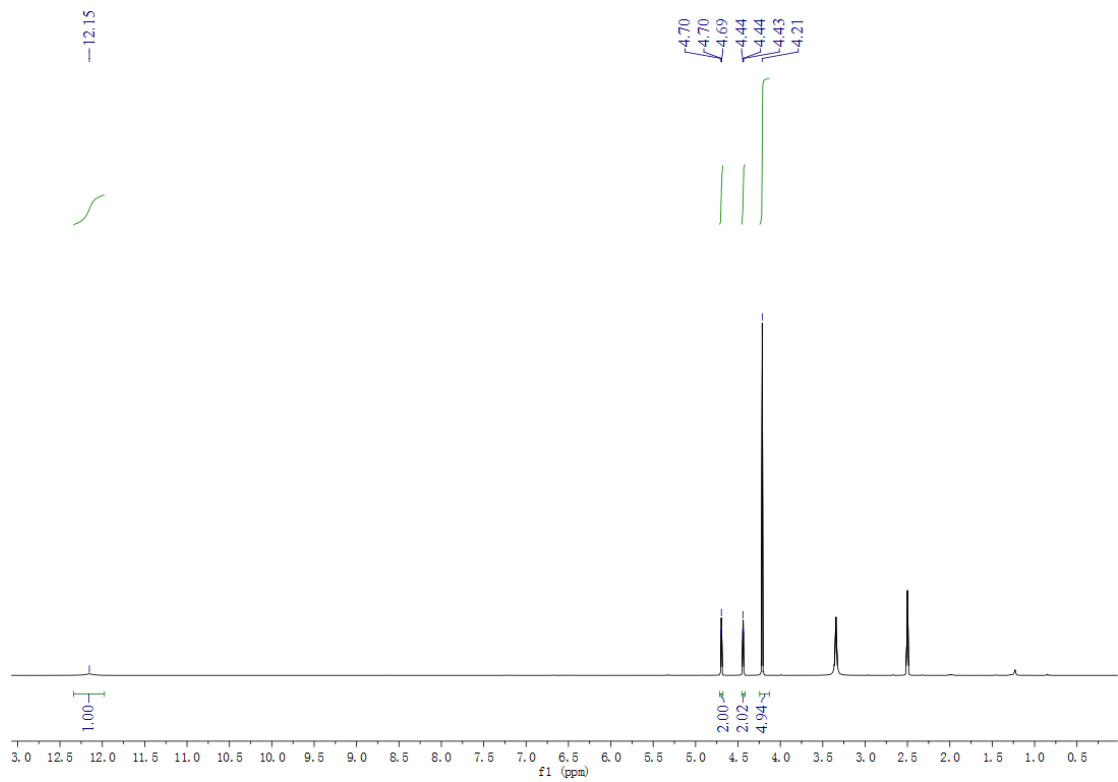


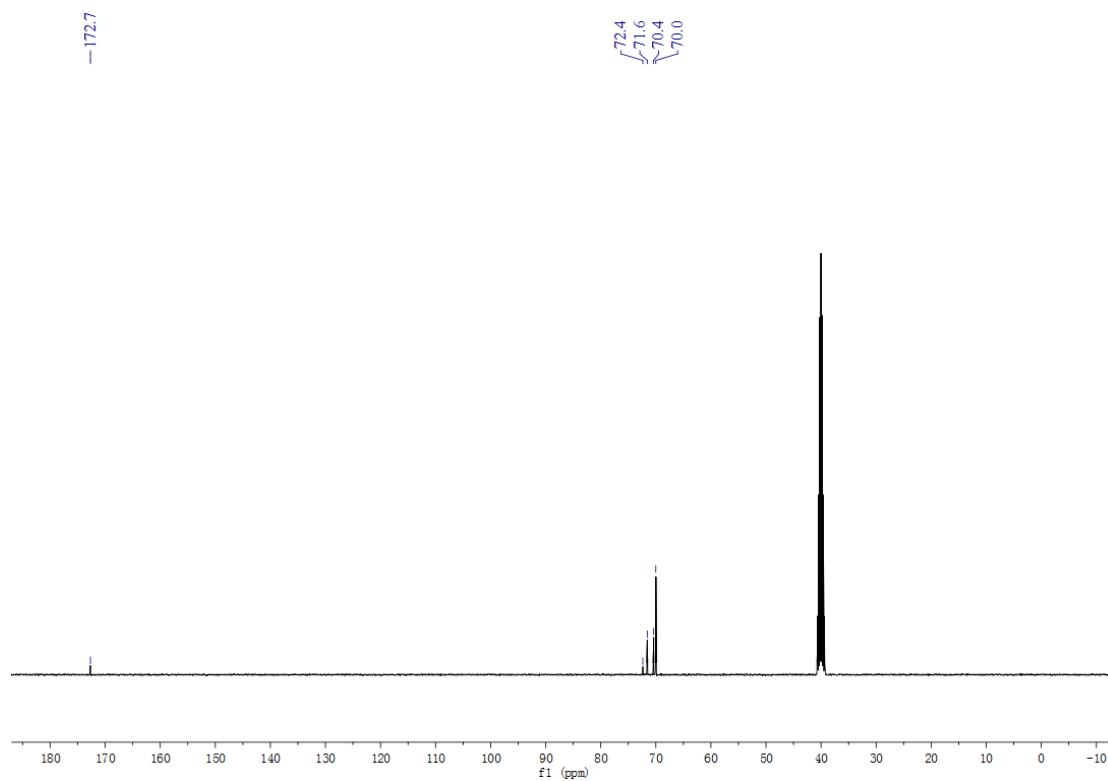
2-naphthoic acid (2ag)



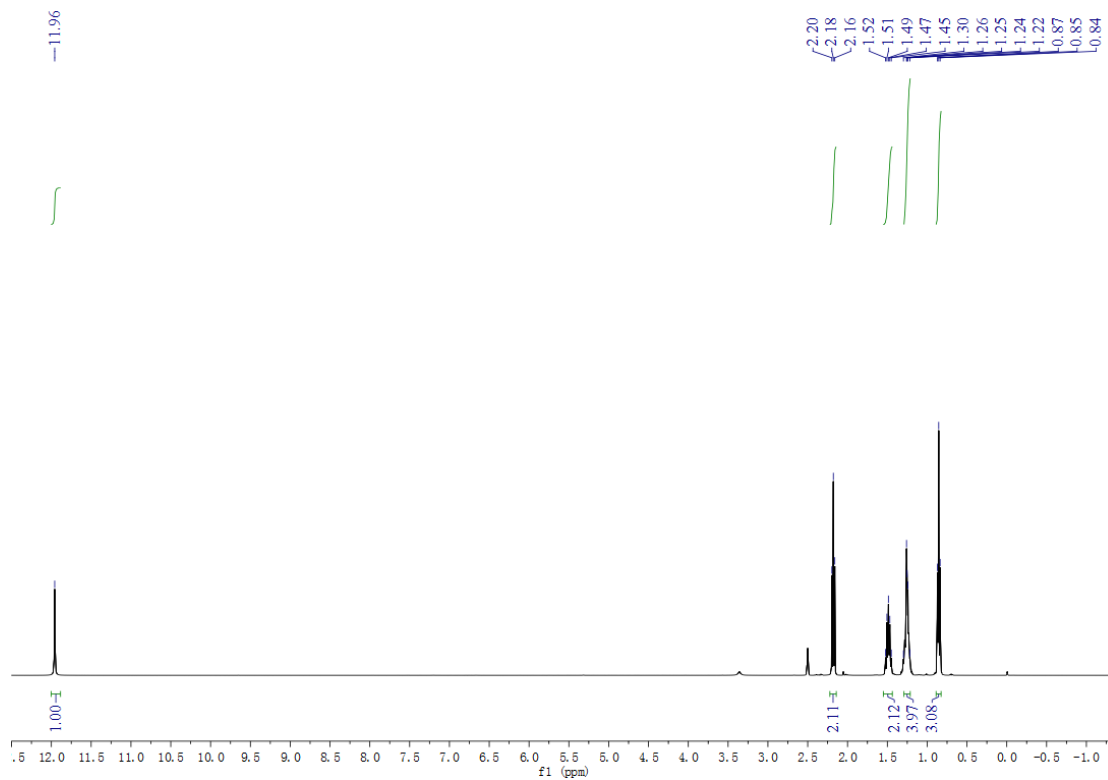


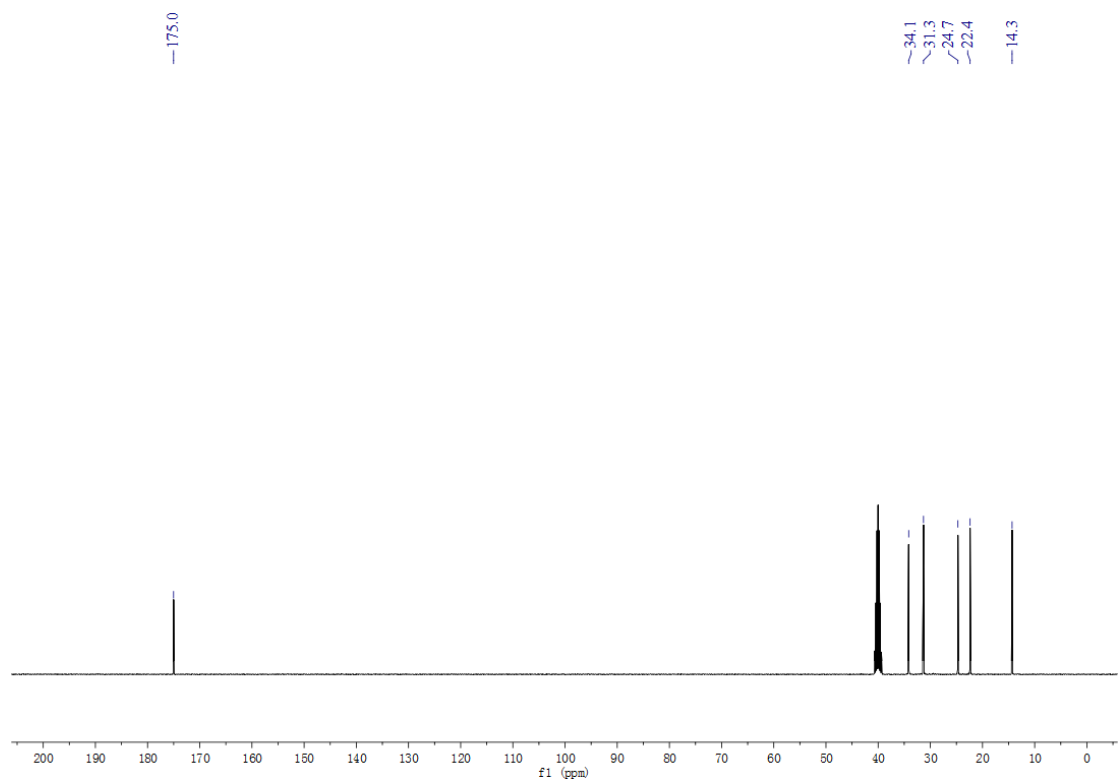
Ferrrocene Monocarboxylic Acid (2ah)



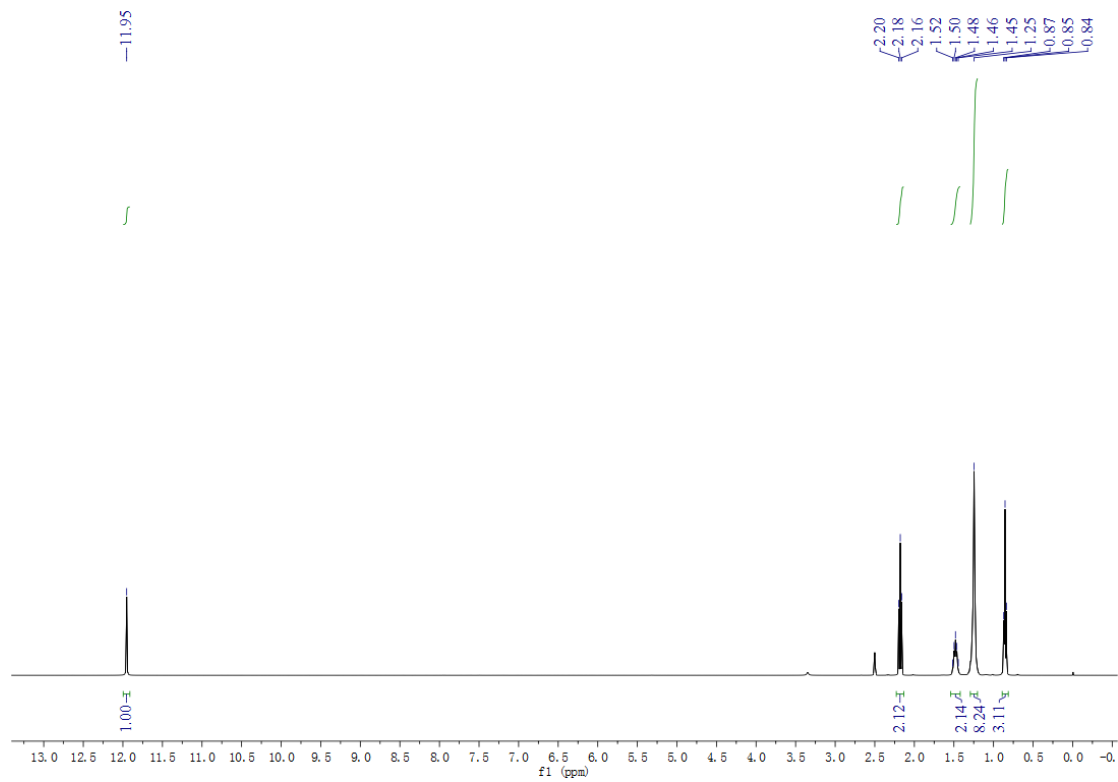


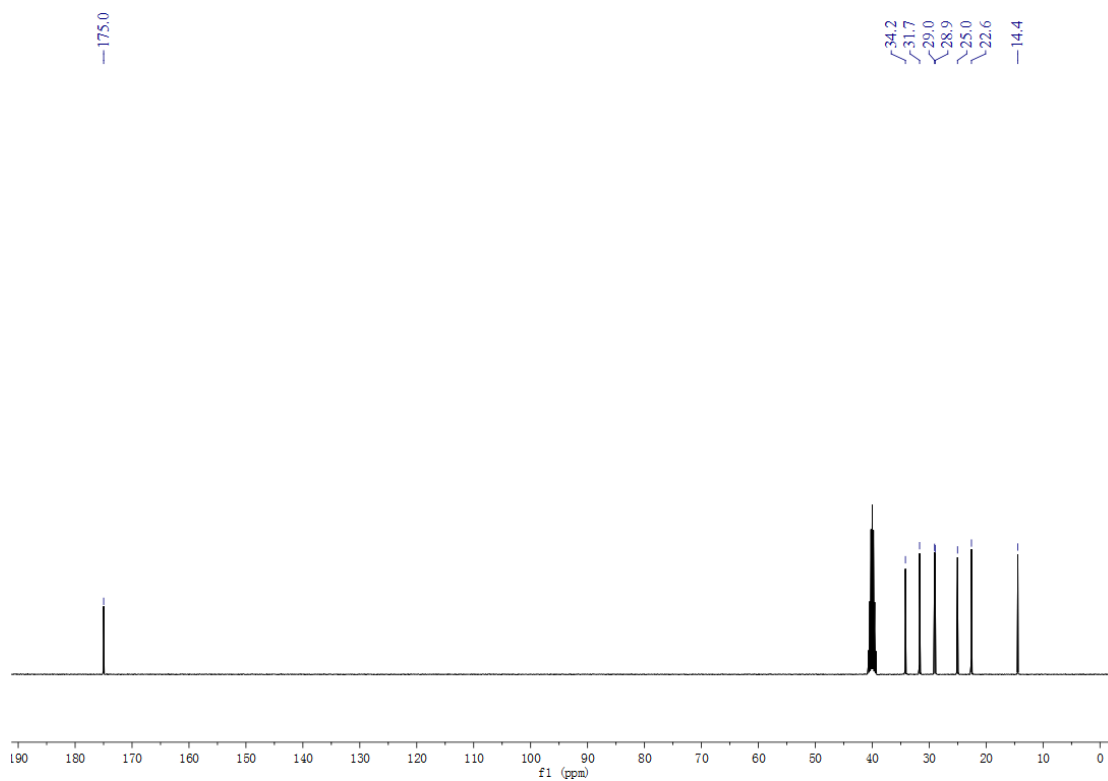
hexanoic acid (2ai)



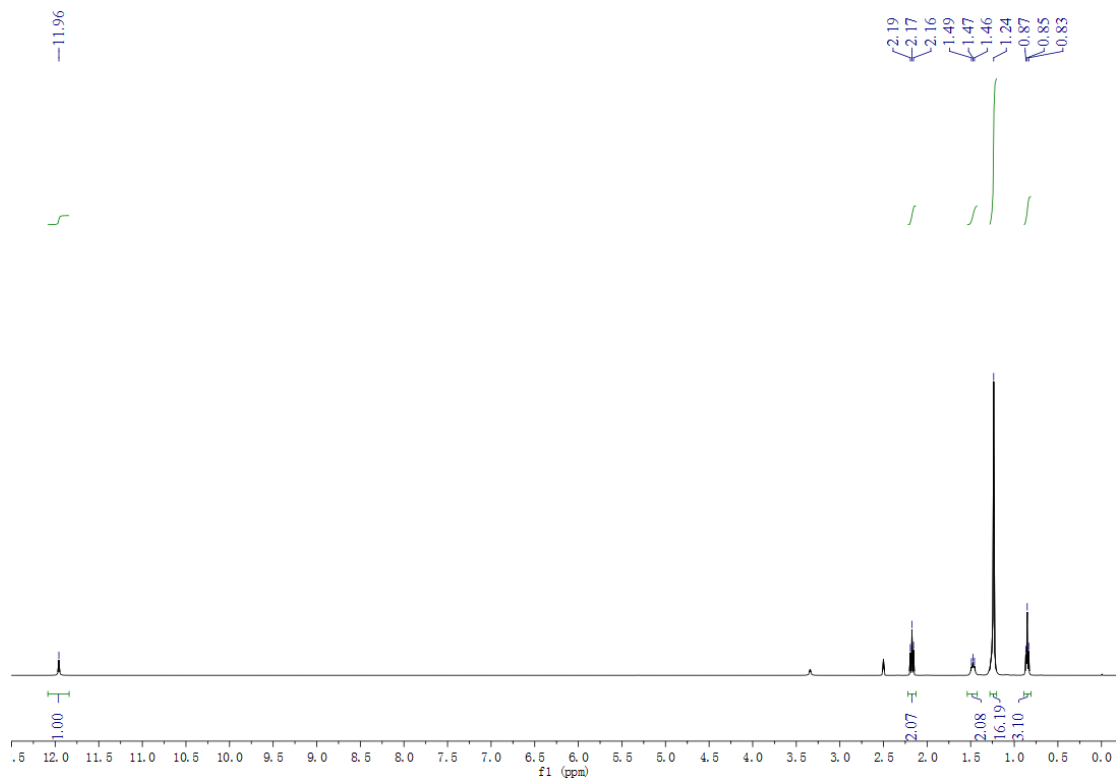


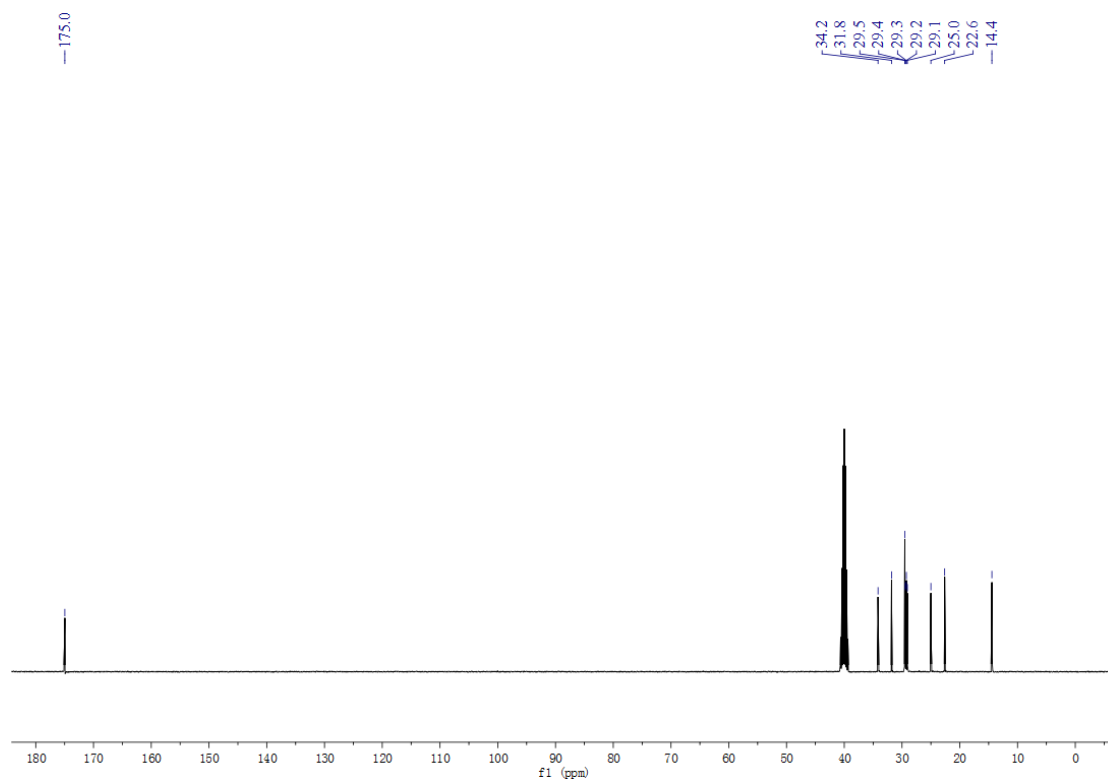
octanoic acid (2aj)



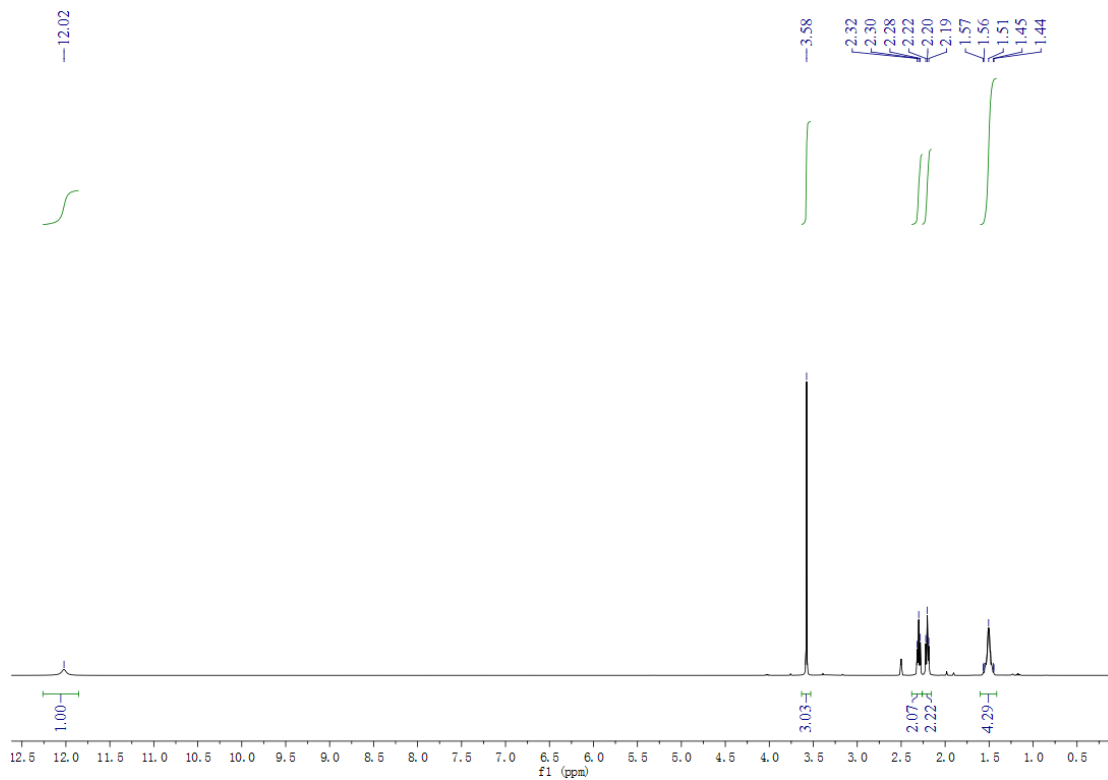


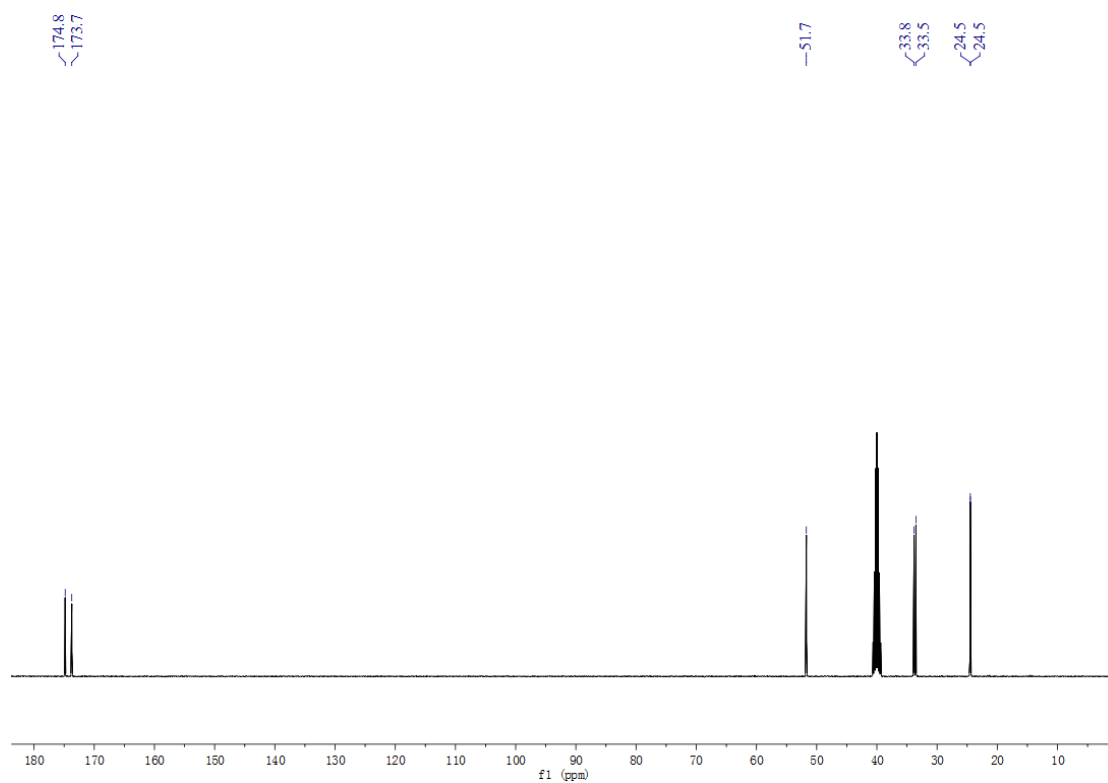
dodecanoic acid (2ak)



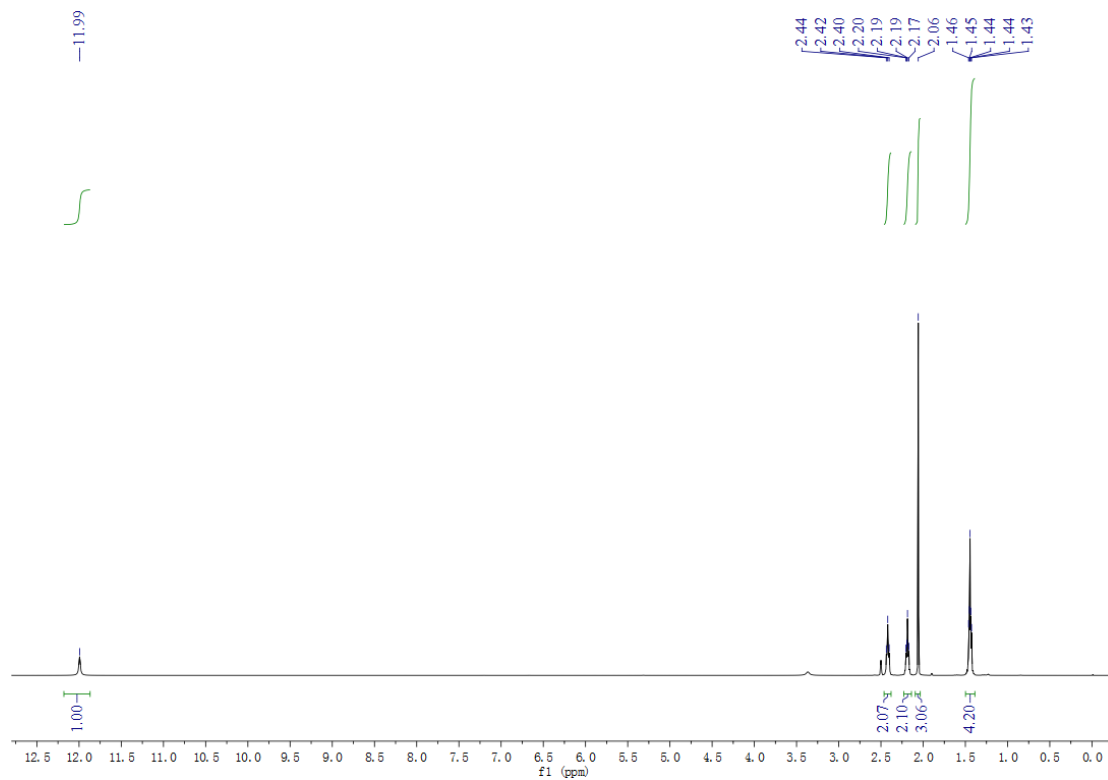


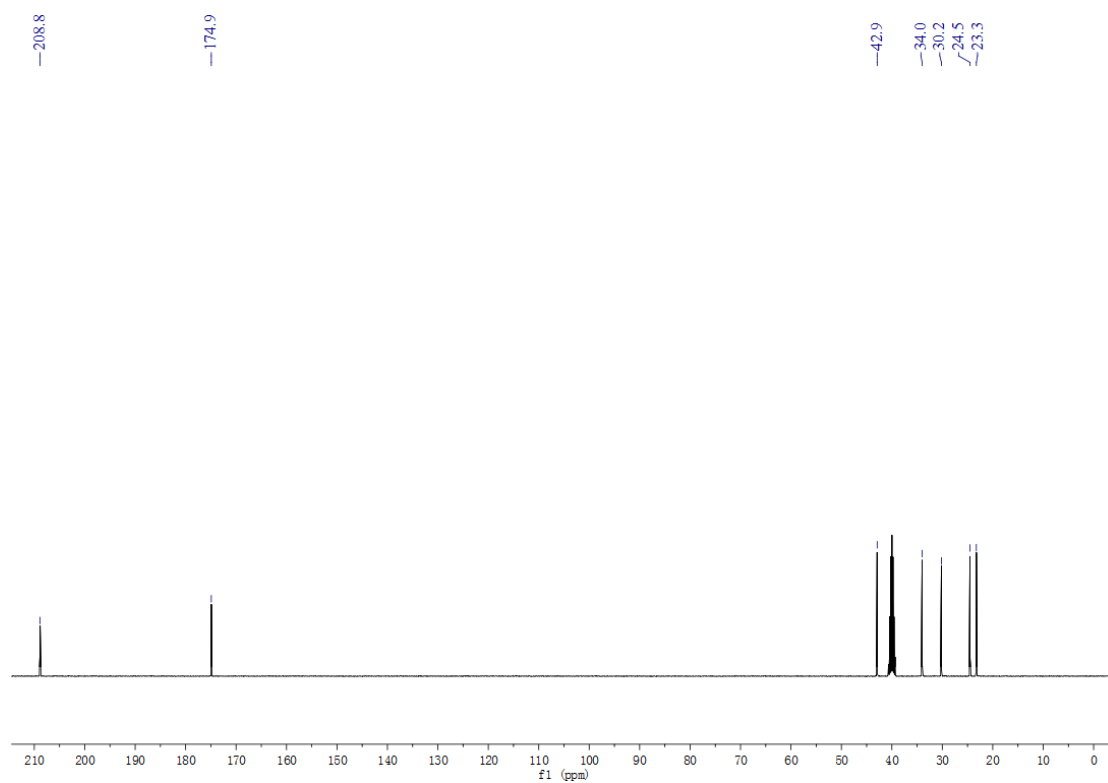
6-methoxy-6-oxohexanoic acid (2a)



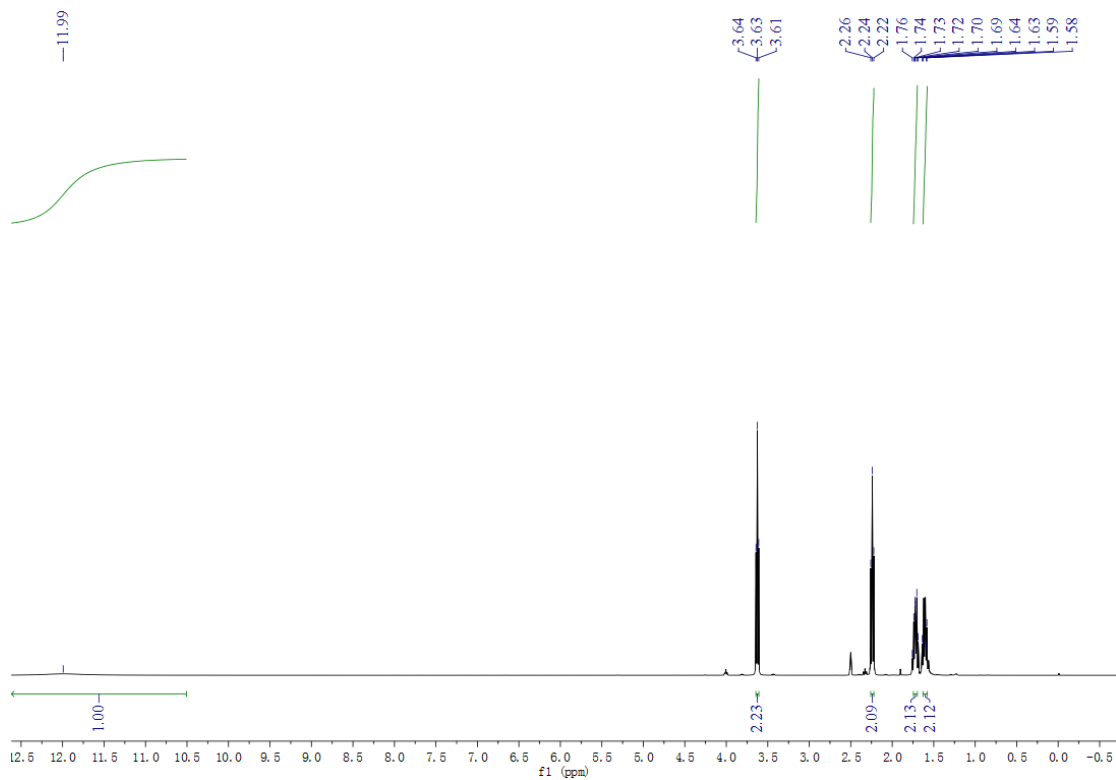


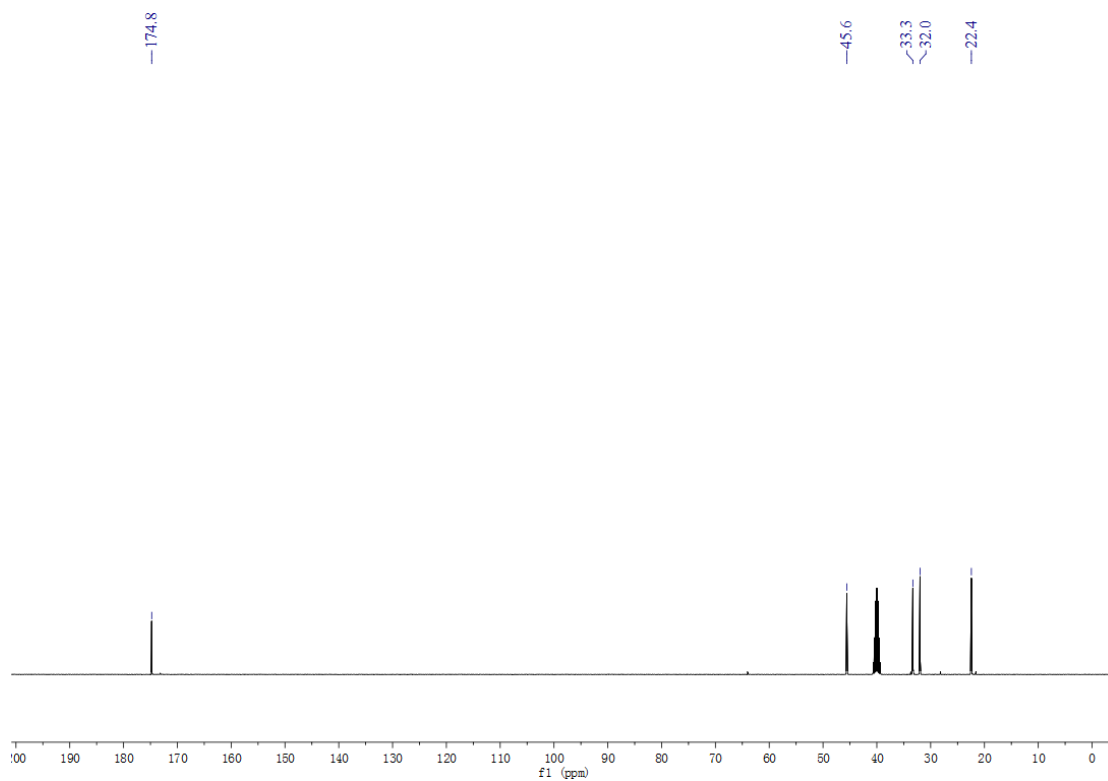
6-oxoheptanoic acid (2am)



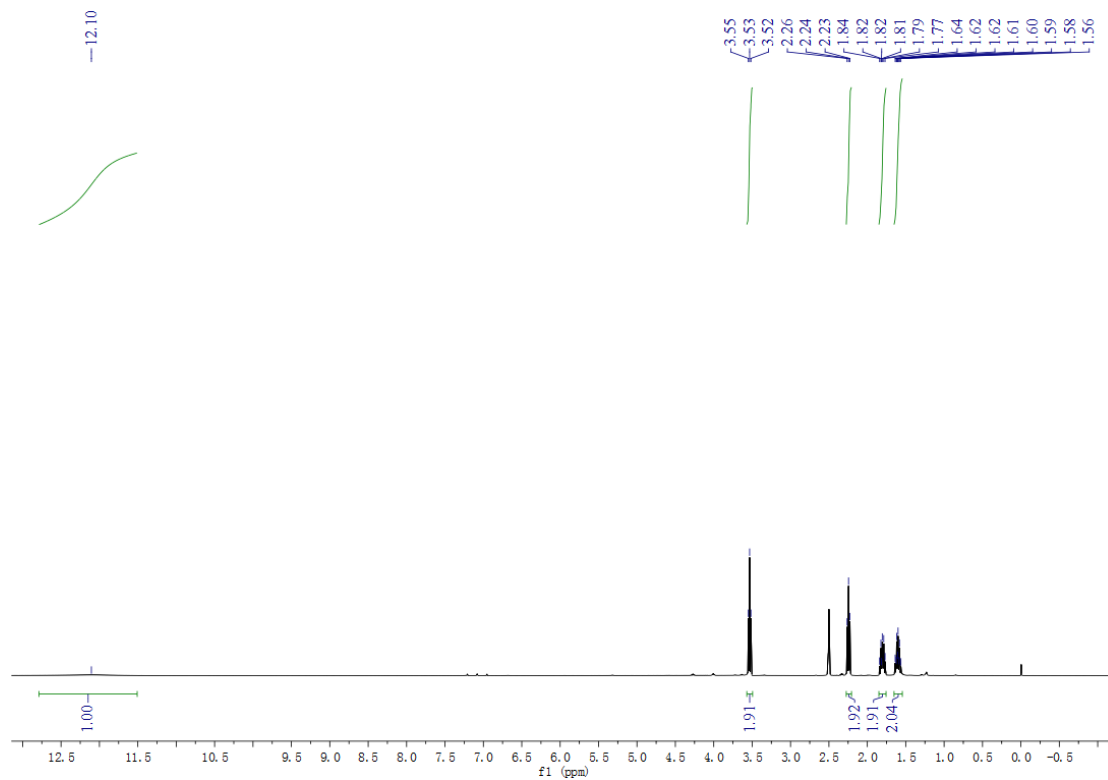


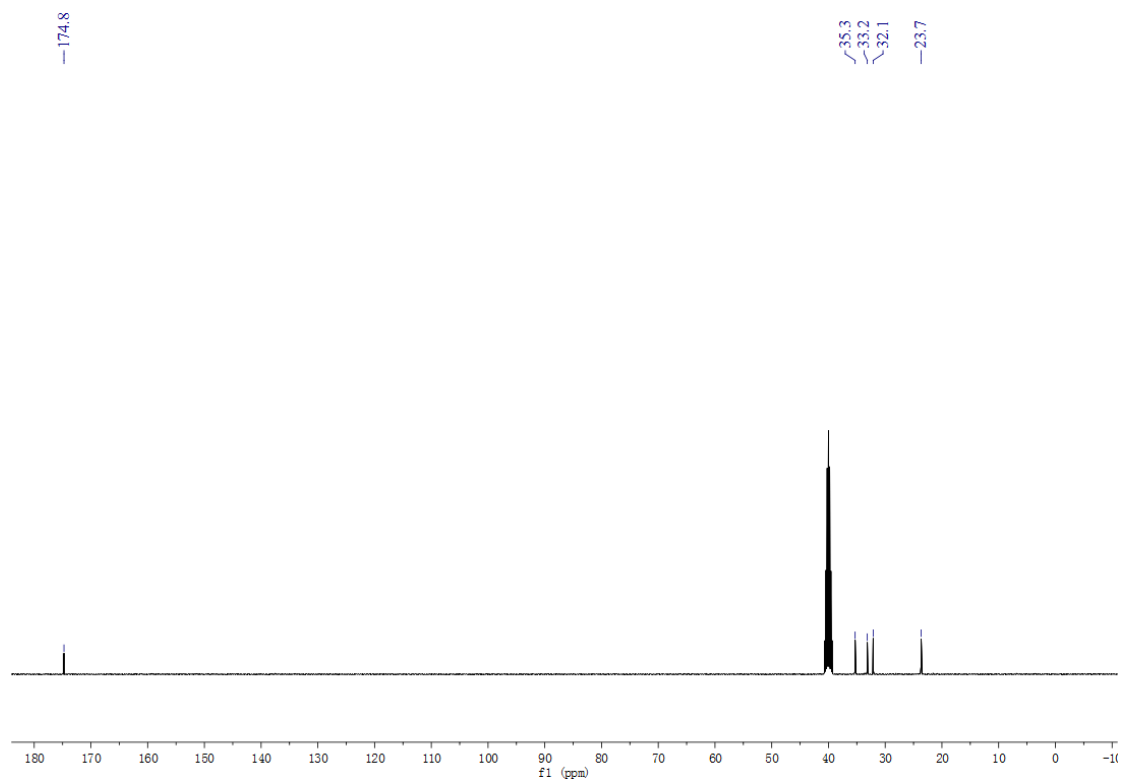
5-chloropentanoic acid (2an)



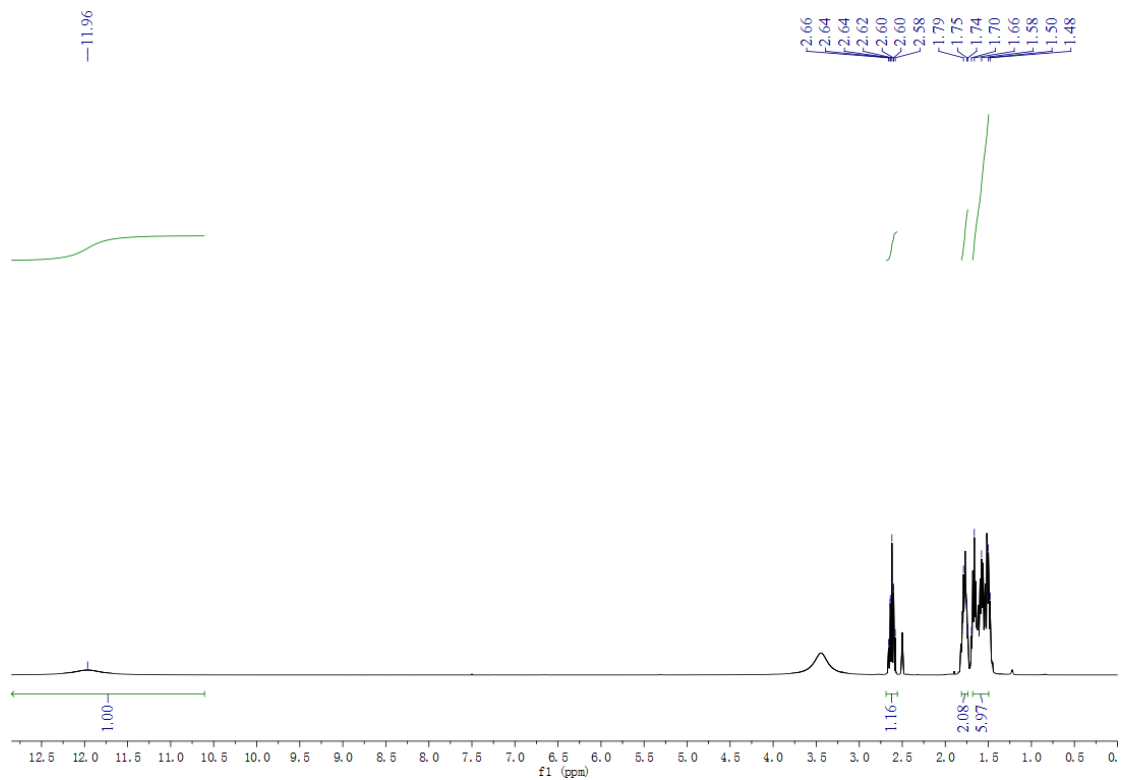


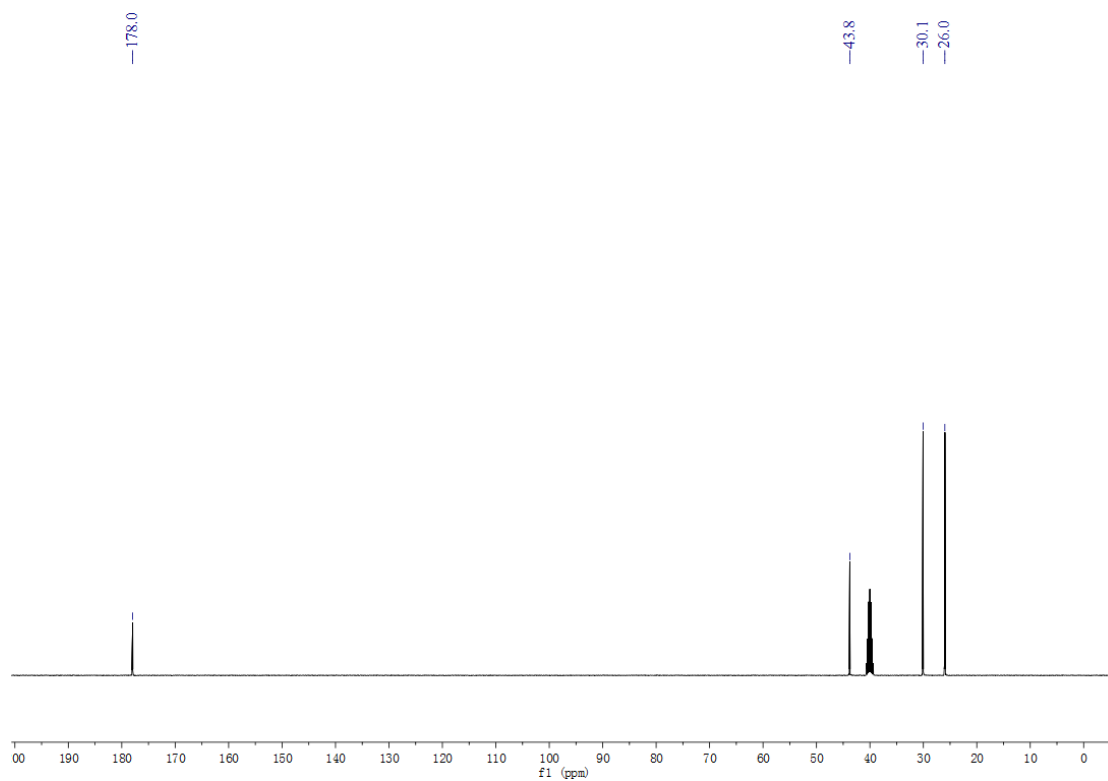
5-bromopentanoic acid (2ao)



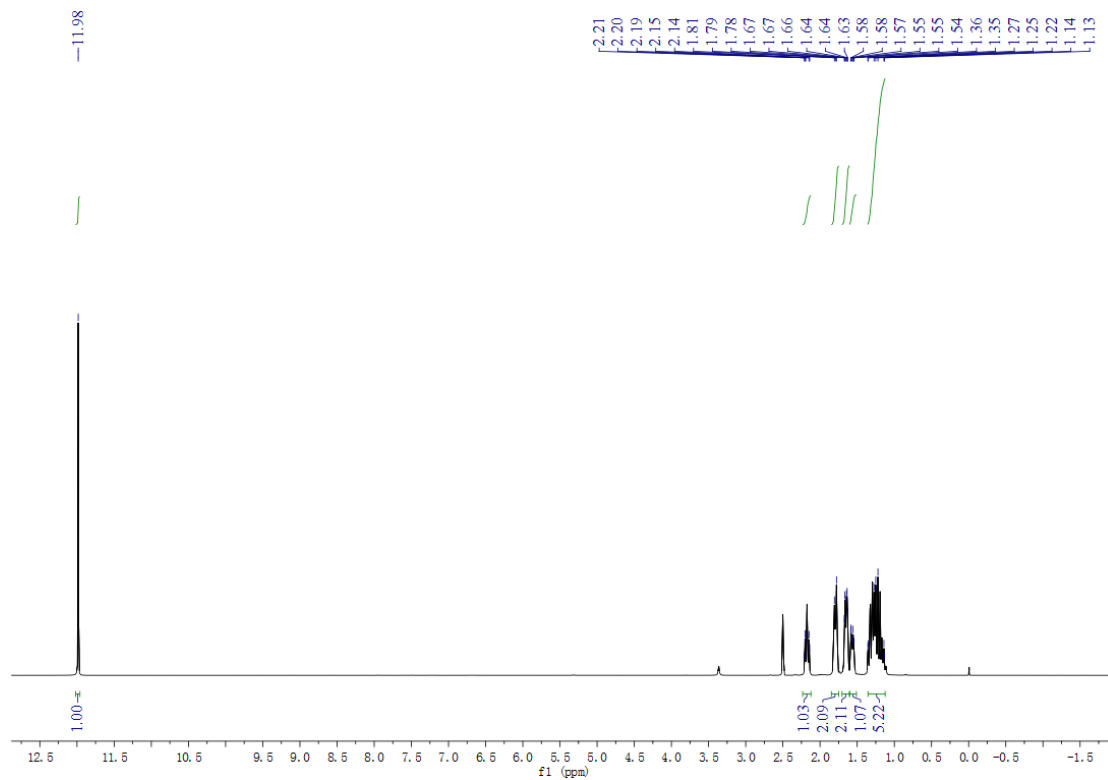


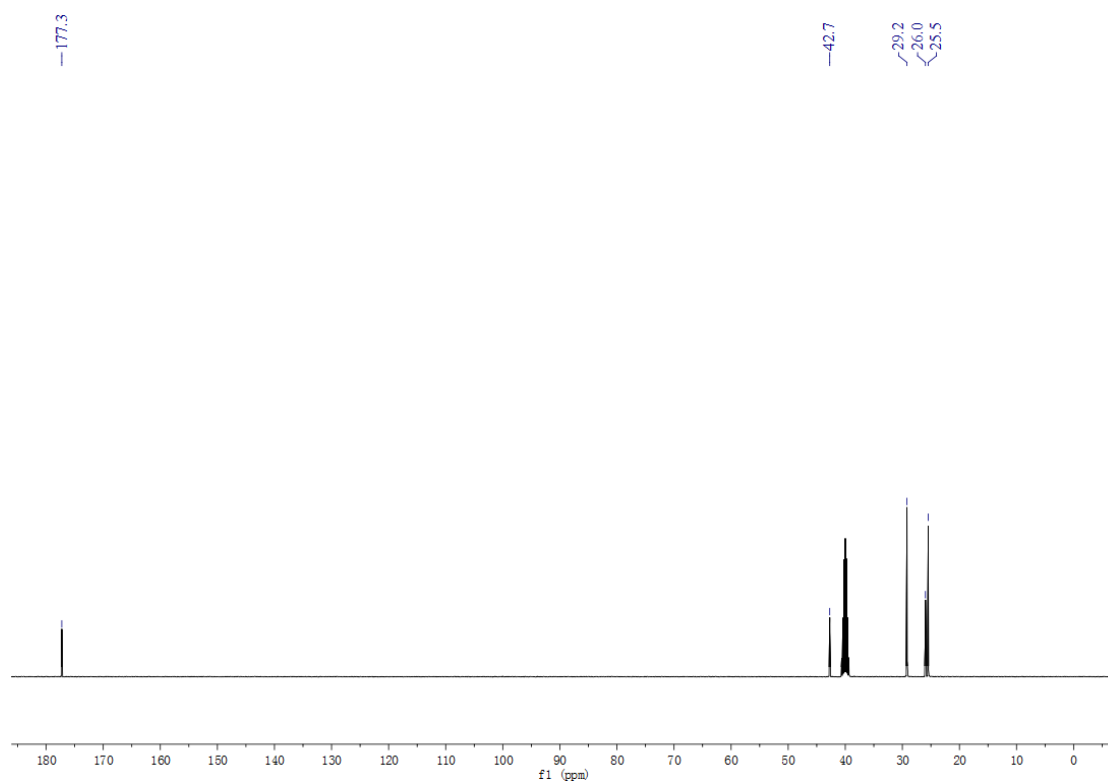
cyclopentanecarboxylic acid (2ap)



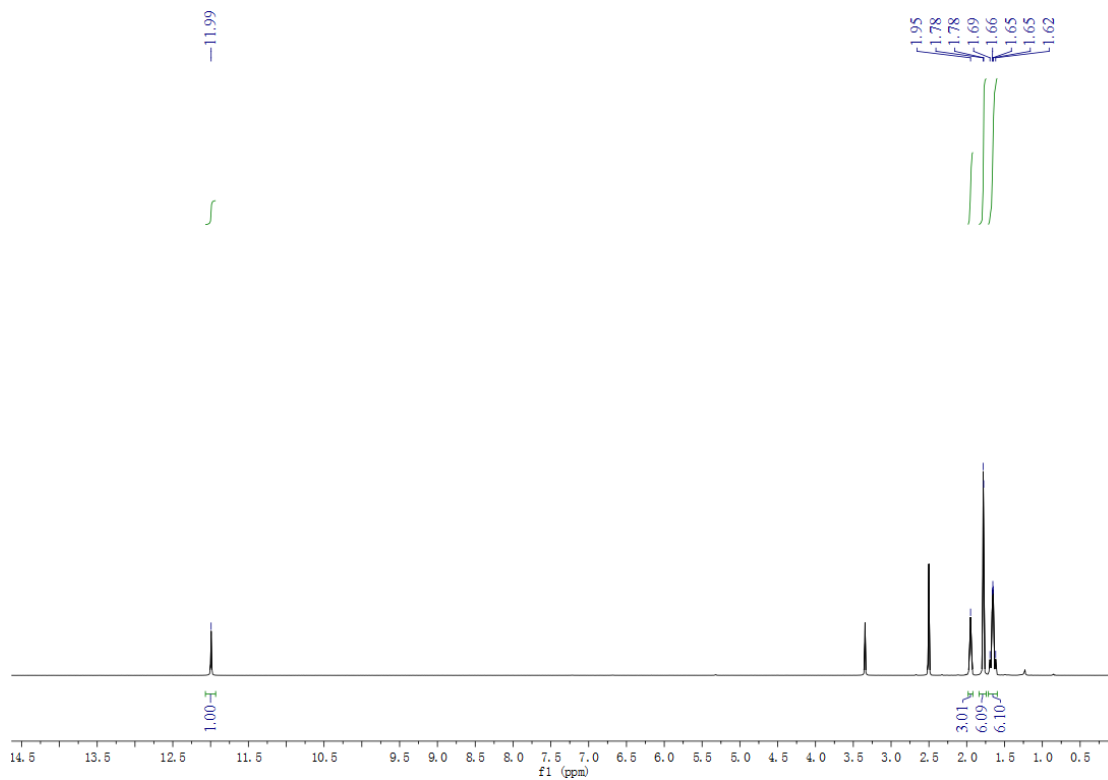


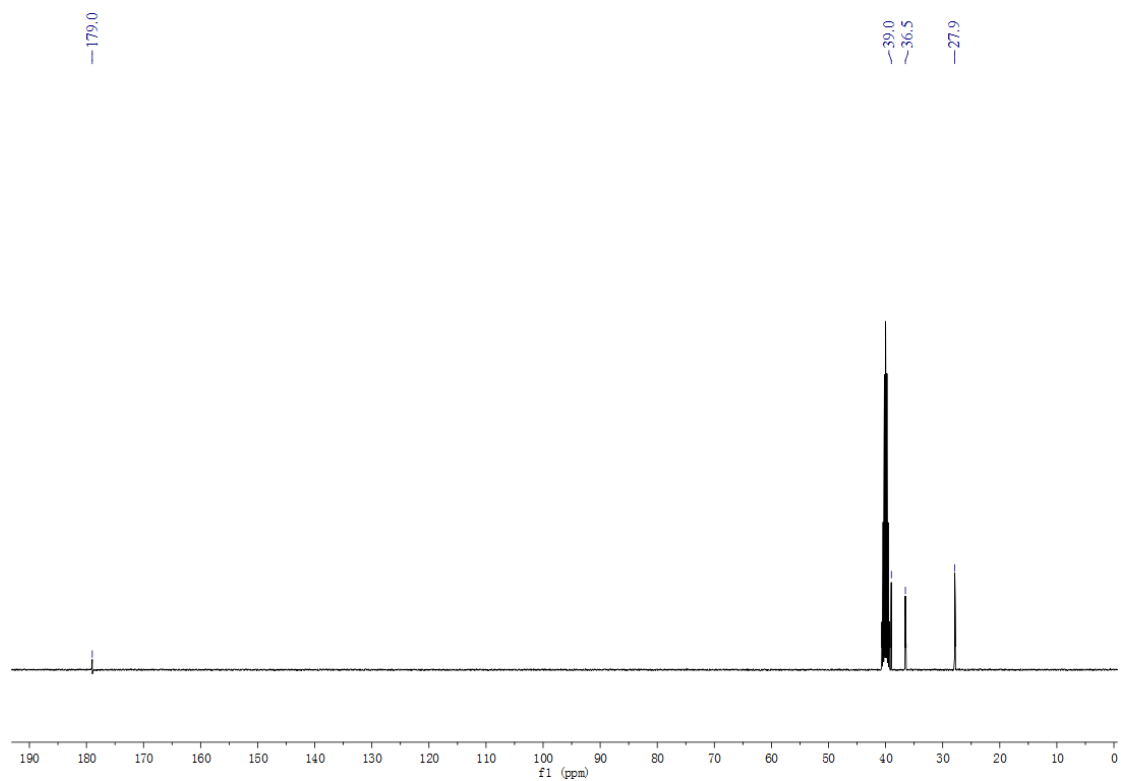
cyclohexanecarboxylic acid (2aq)



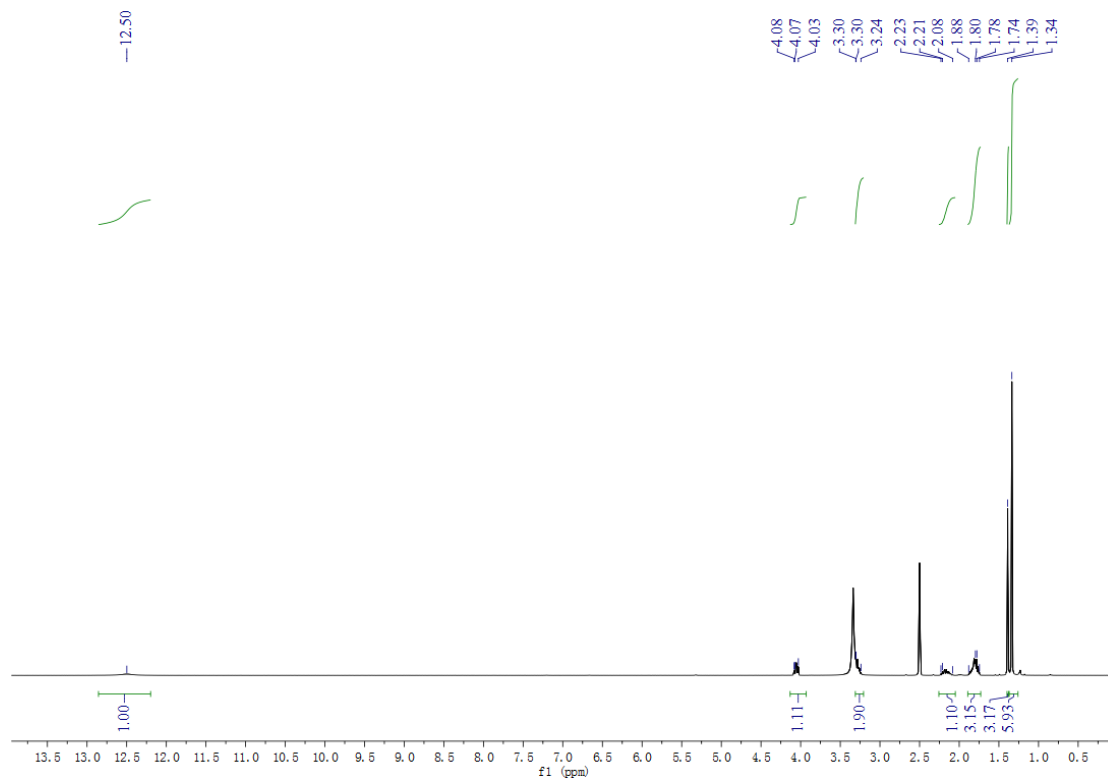


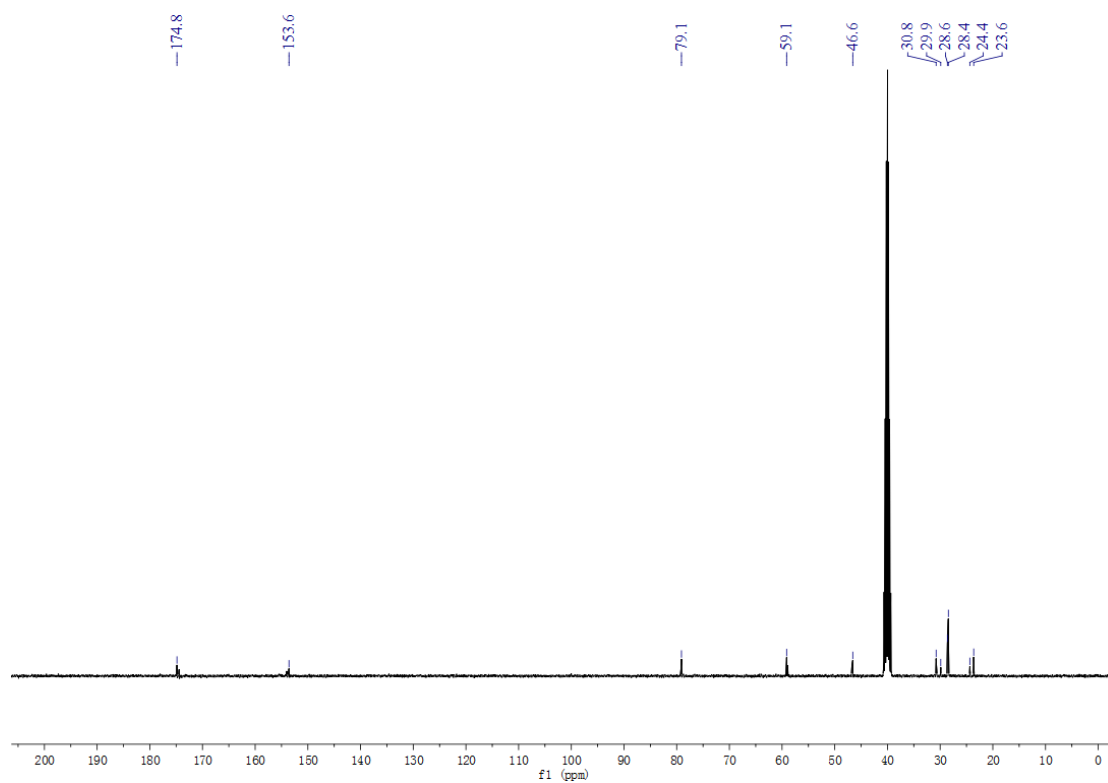
adamantane-1-carboxylic acid (2ar)



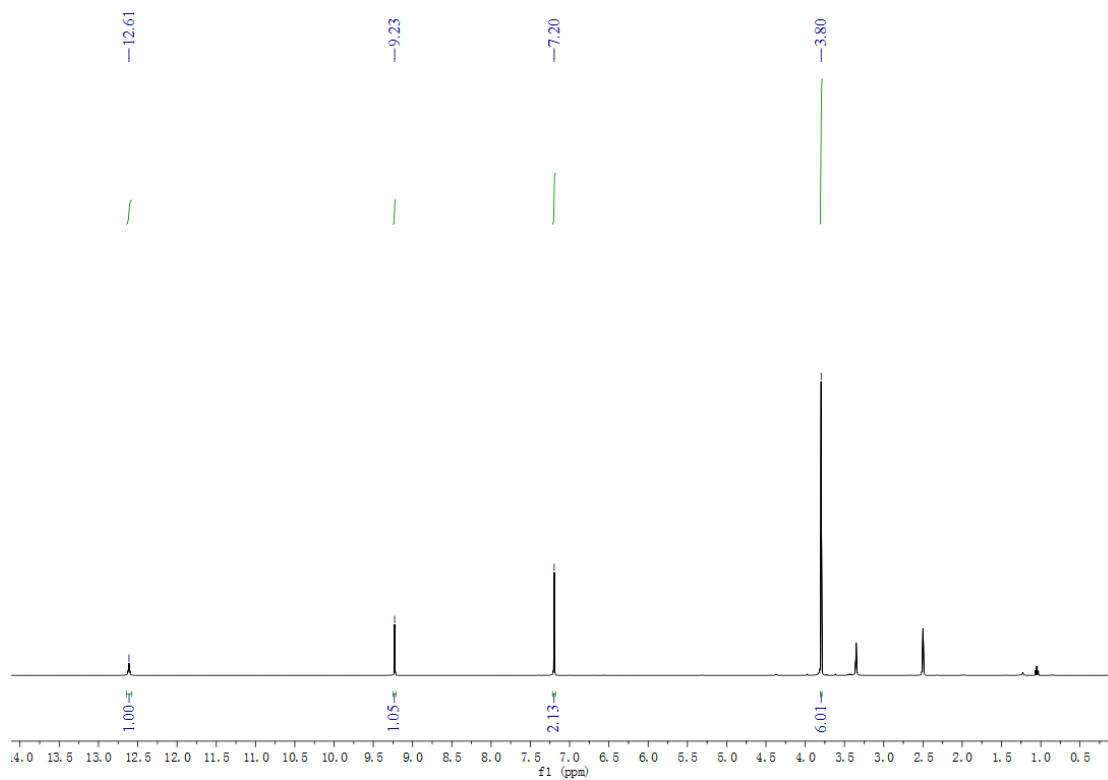


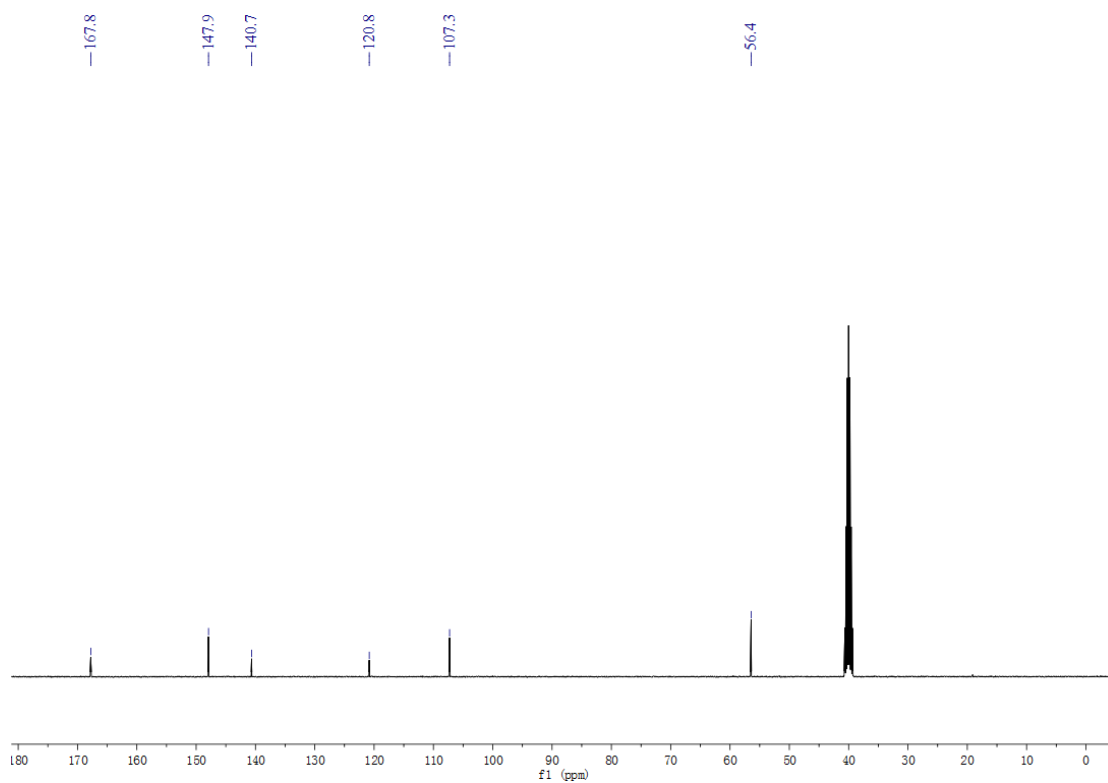
1-(*tert*-butoxycarbonyl)pyrrolidine-2-carboxylic acid (2as)



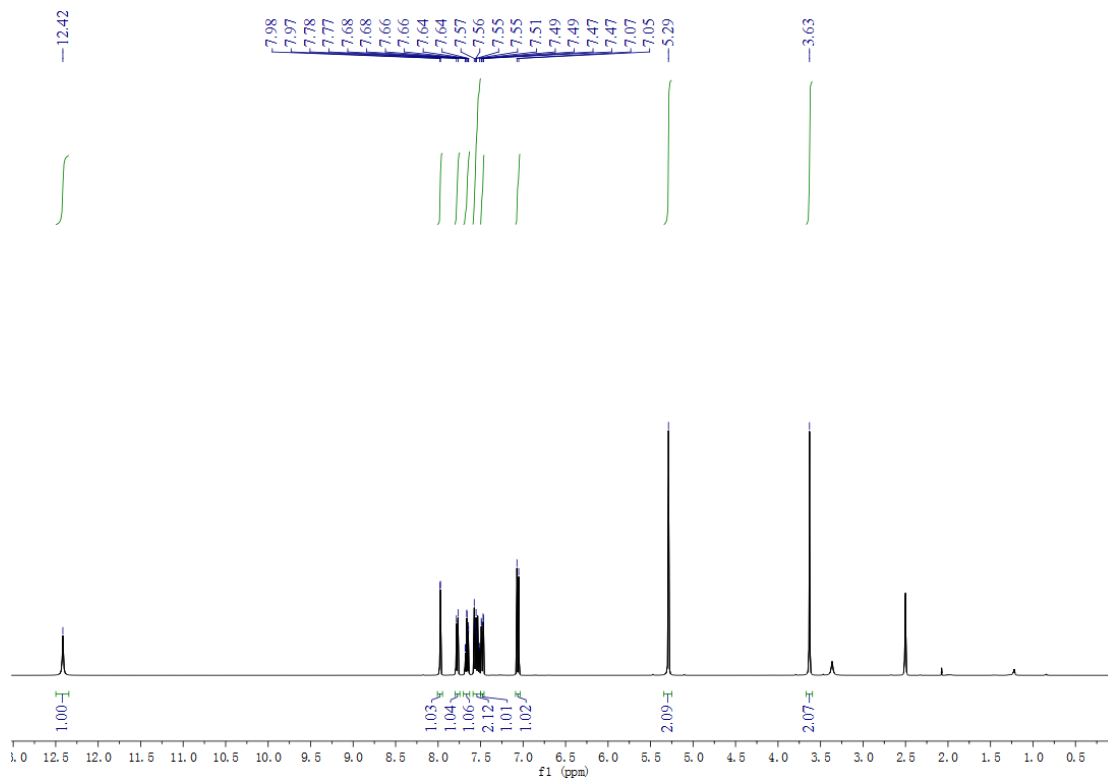


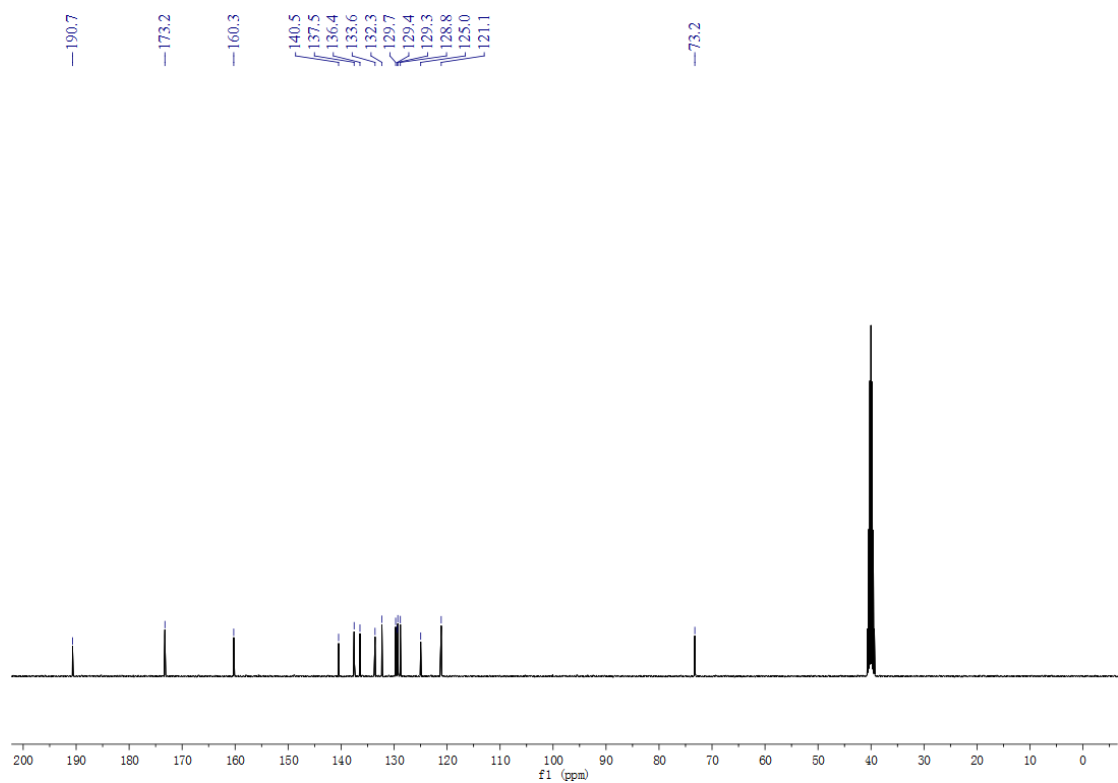
4-hydroxy-3,5-dimethoxybenzoic acid (2at)



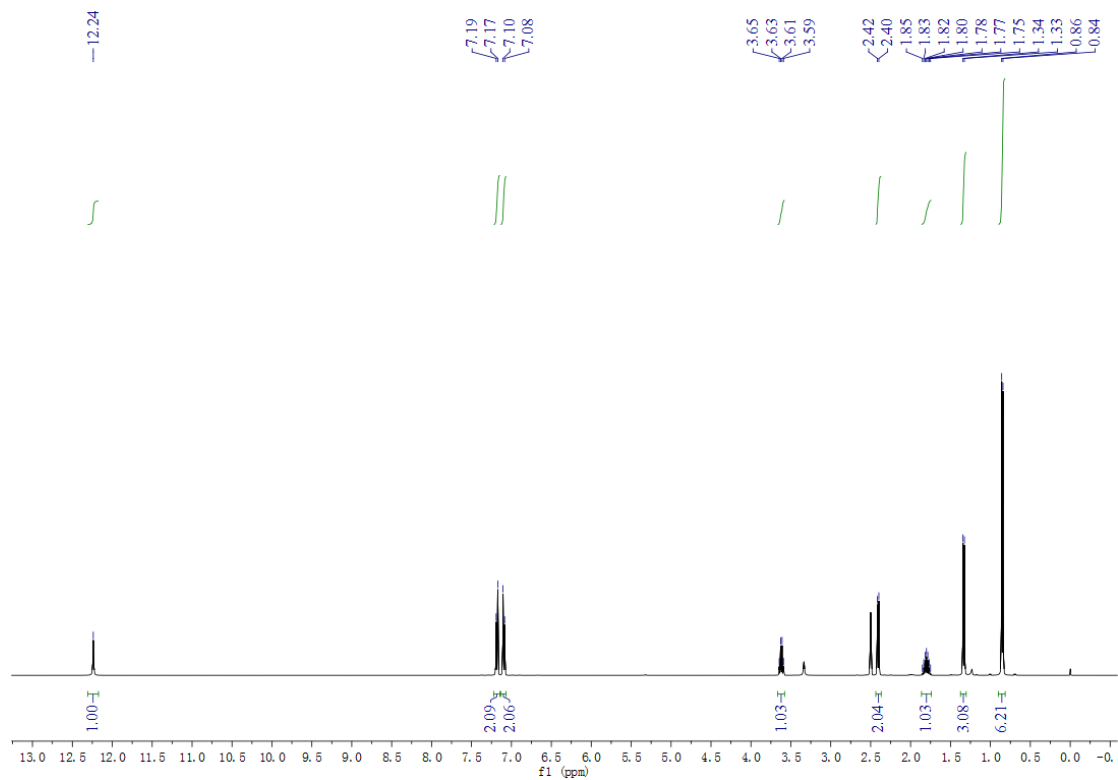


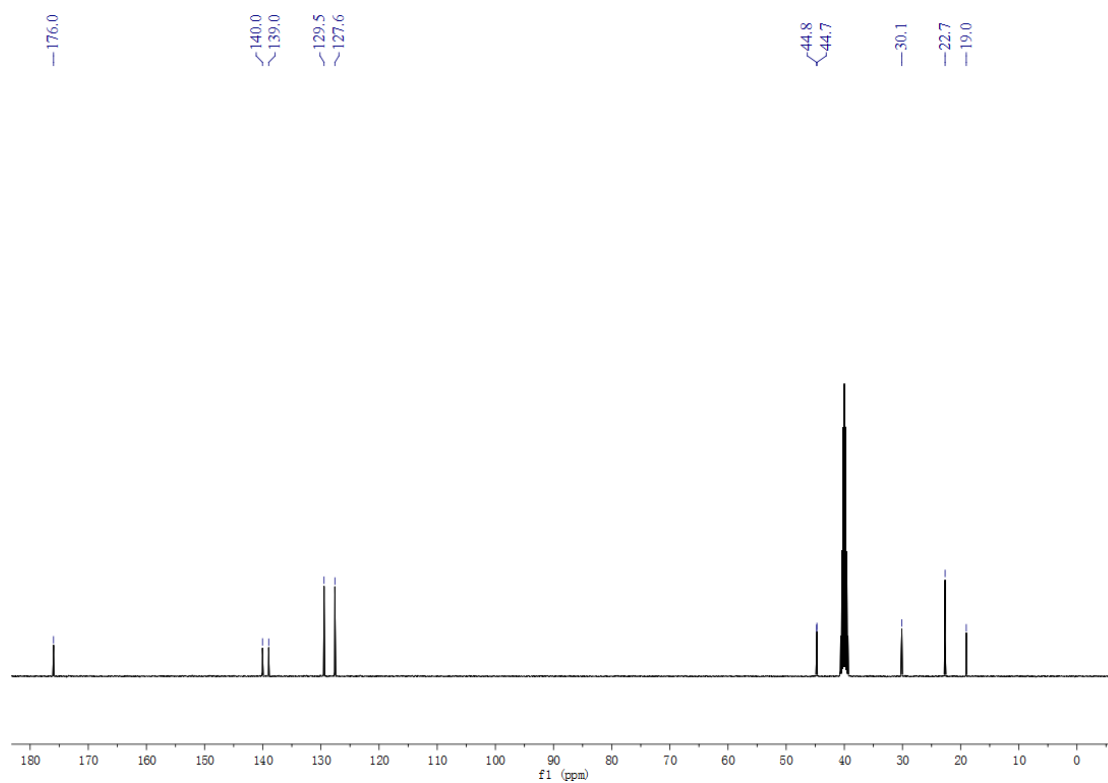
2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid (2au)



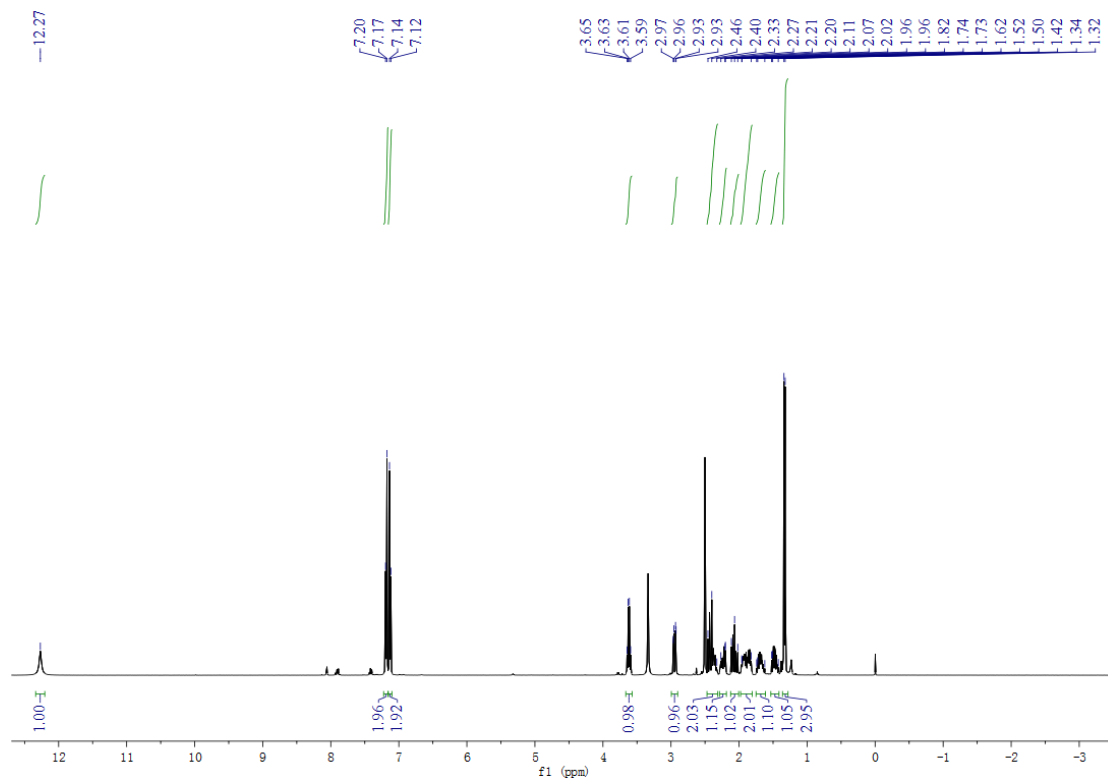


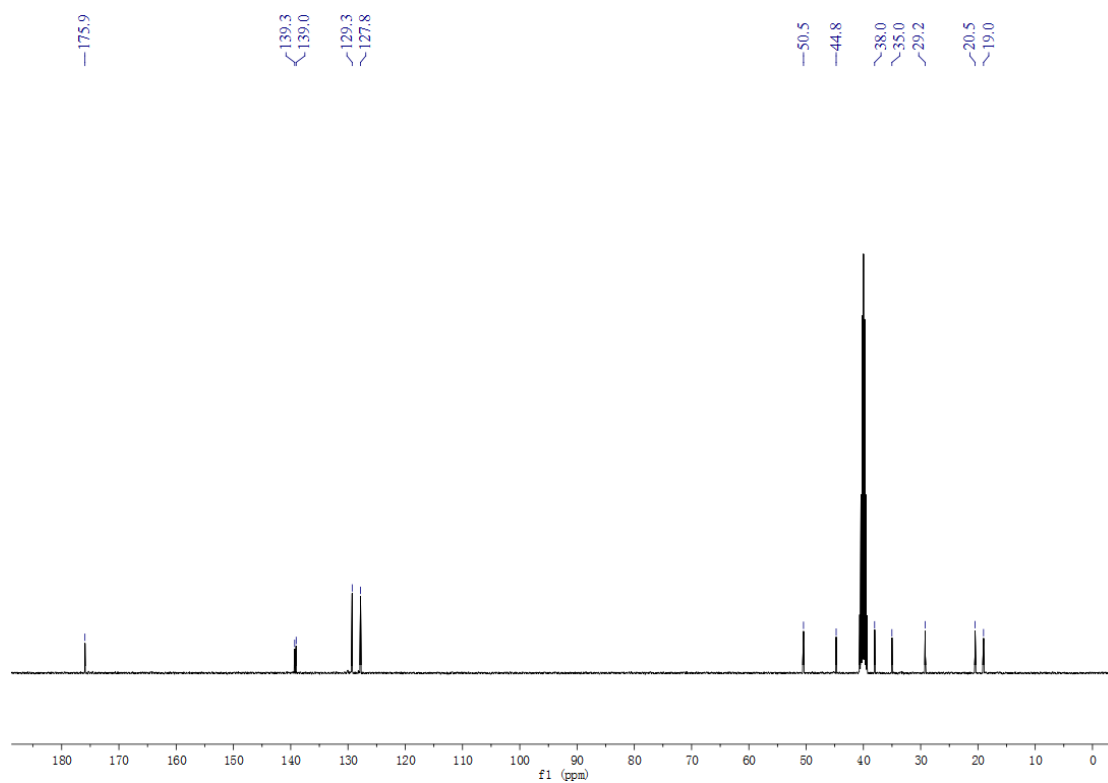
2-(4-isobutylphenyl)propanoic acid (2av)





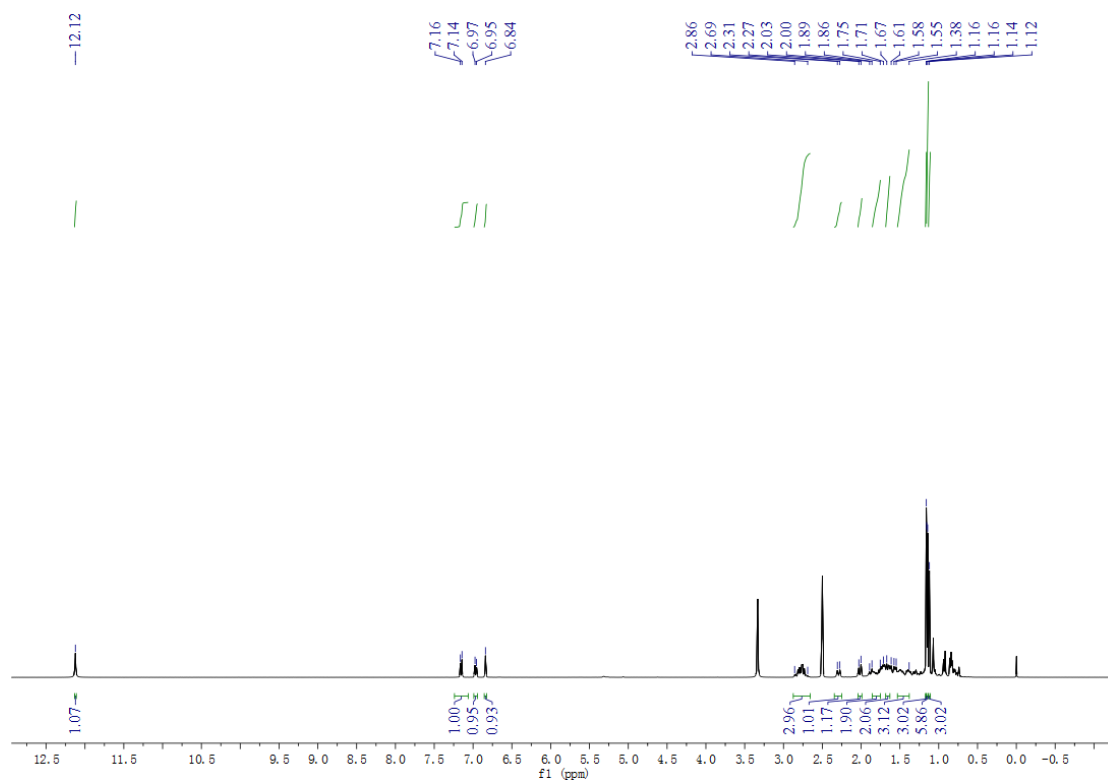
2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoic acid (2aw)

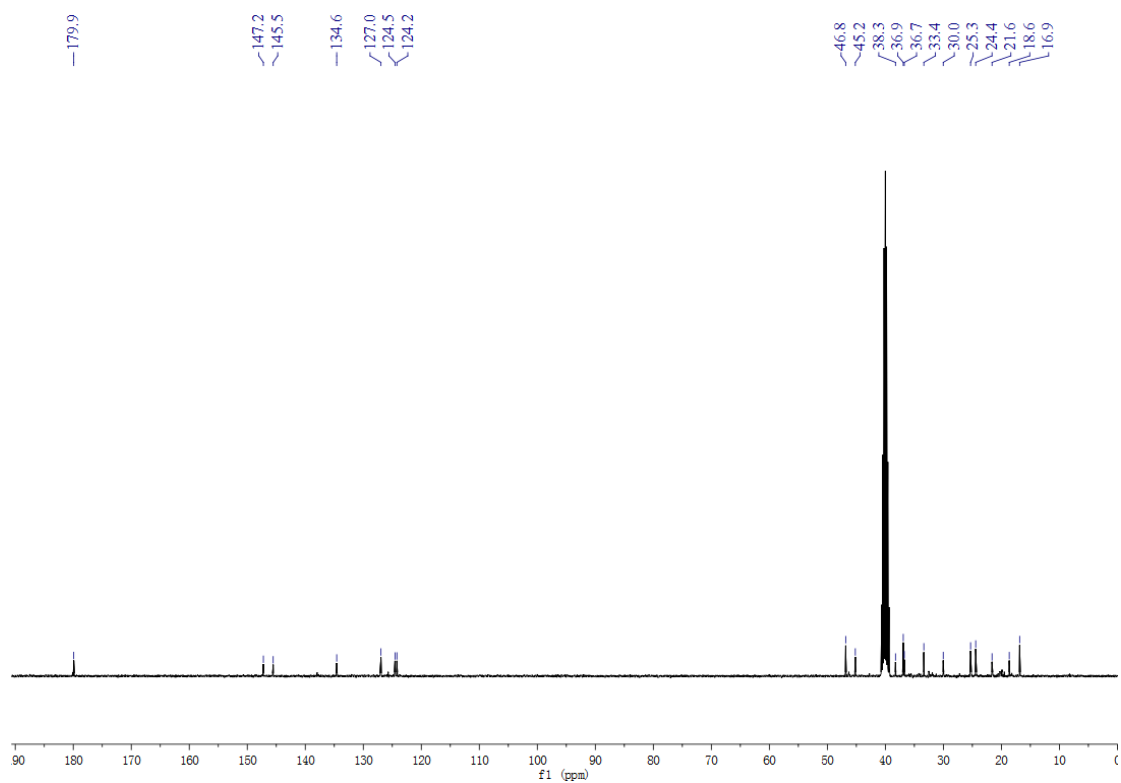




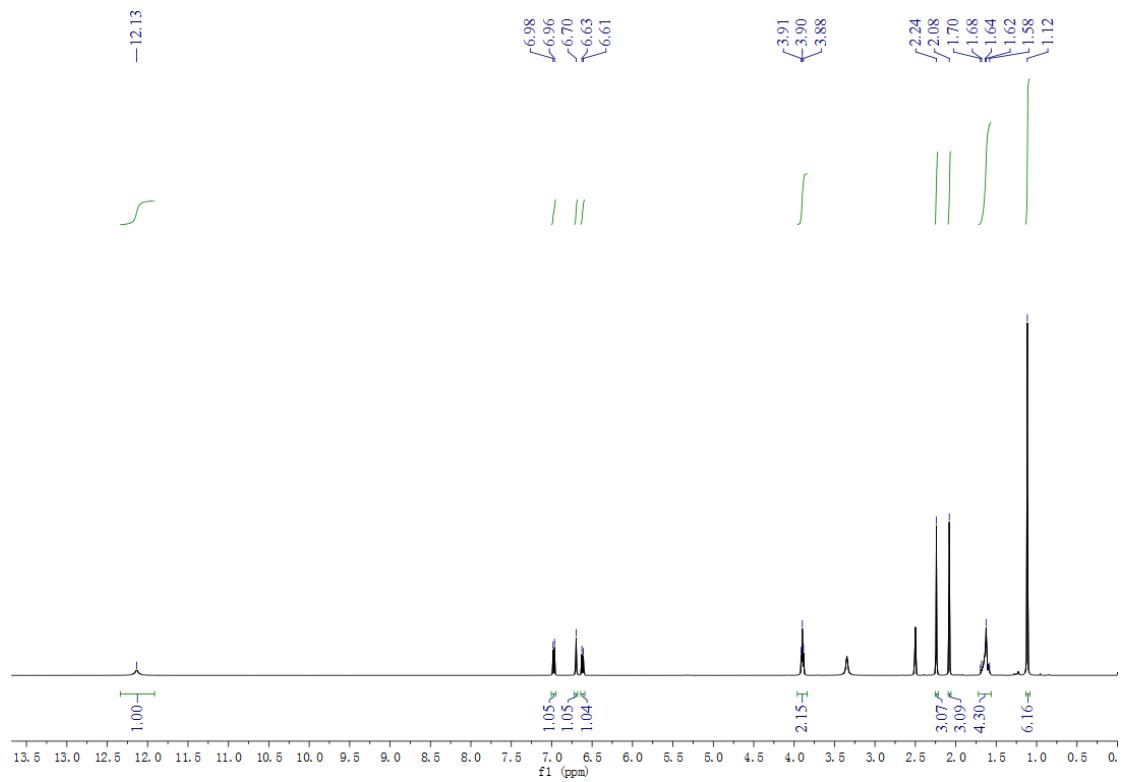
(1S,4aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid

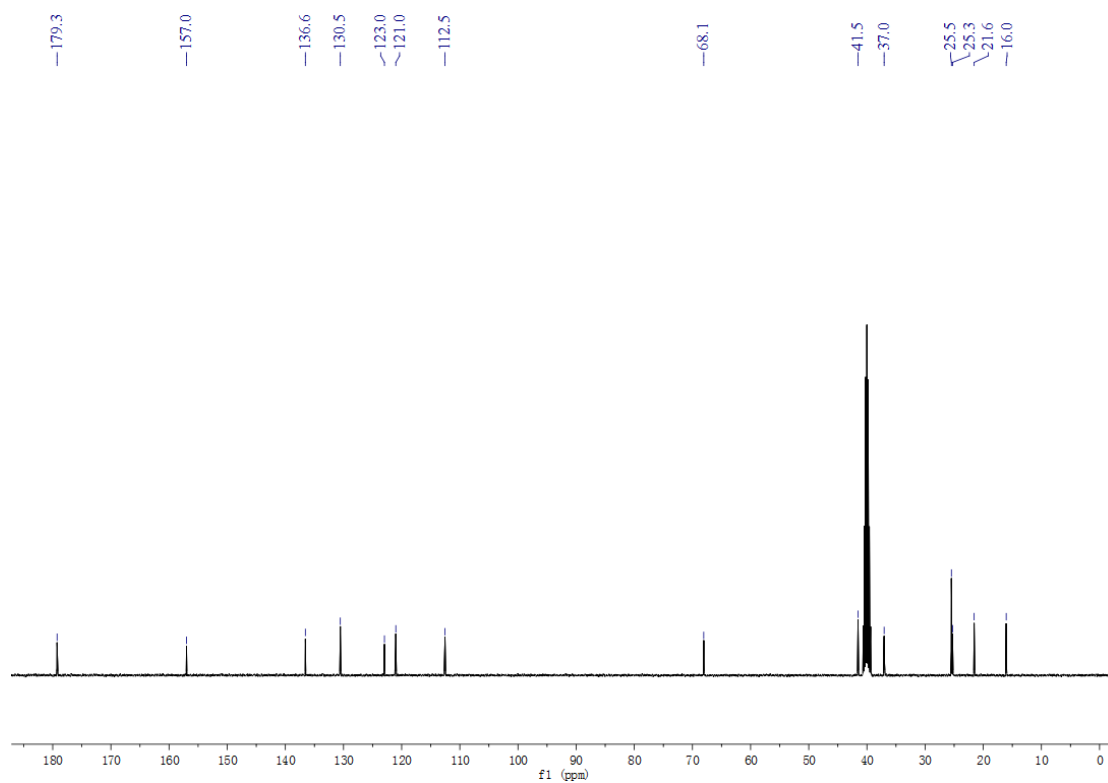
(2ax)



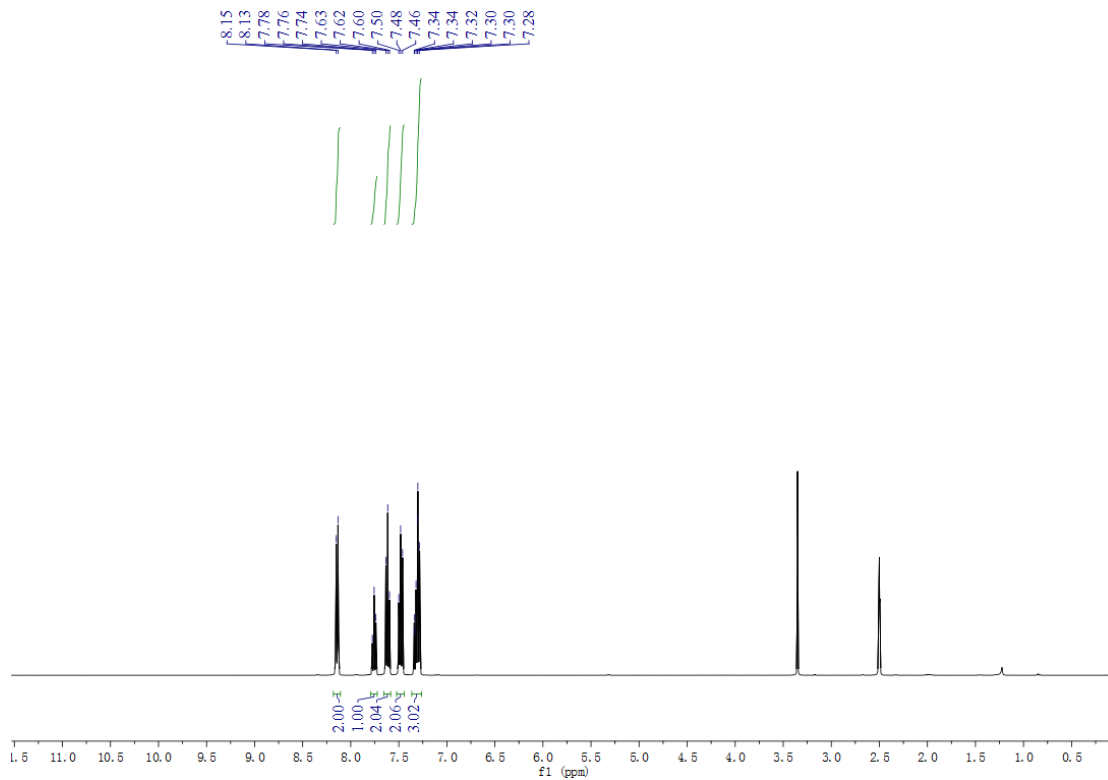


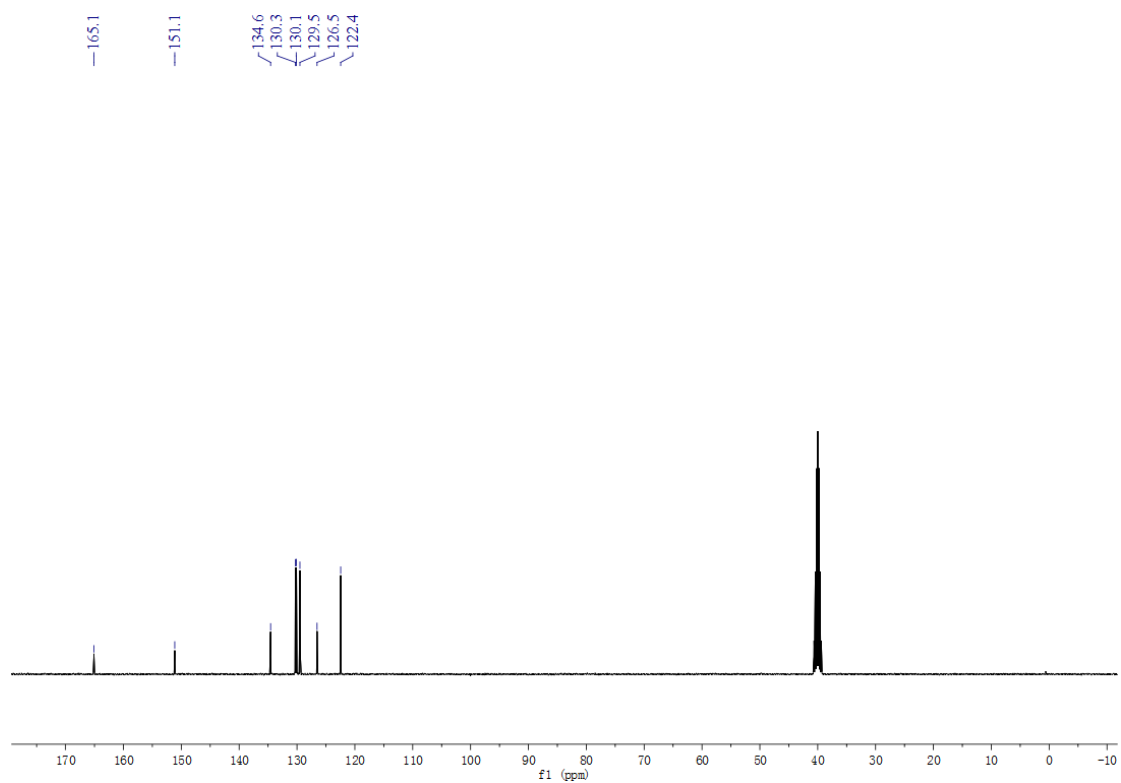
5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (2ay)



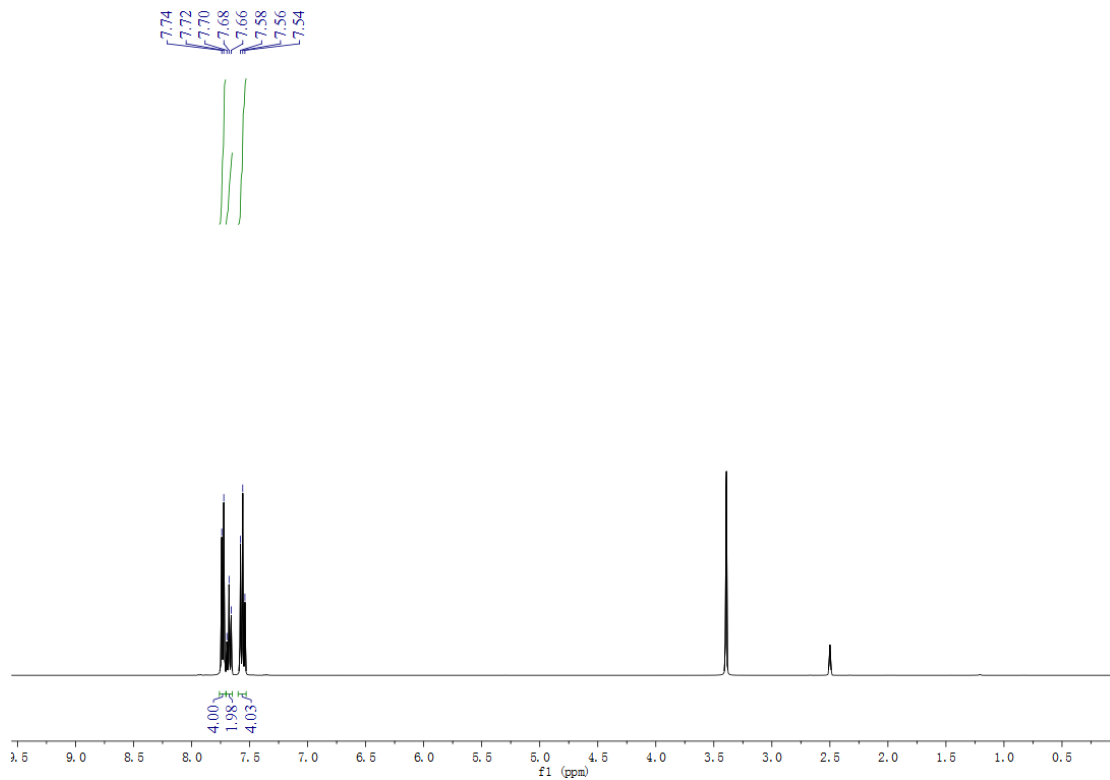


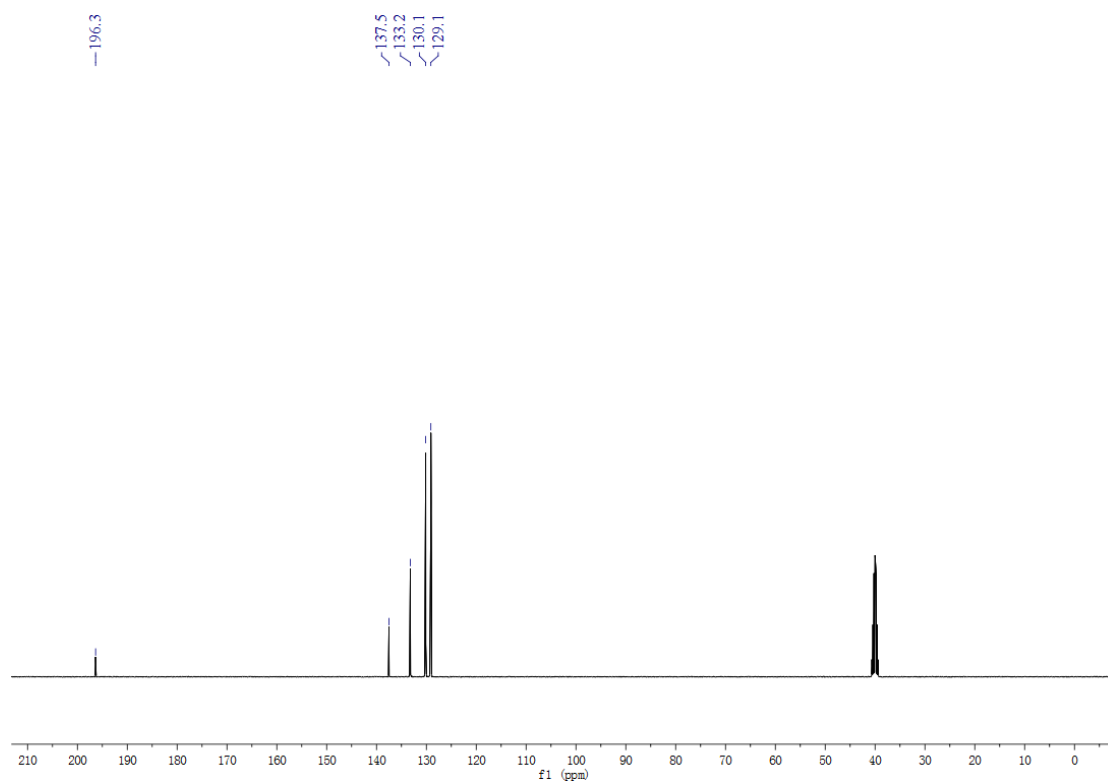
phenyl benzoate (3a)



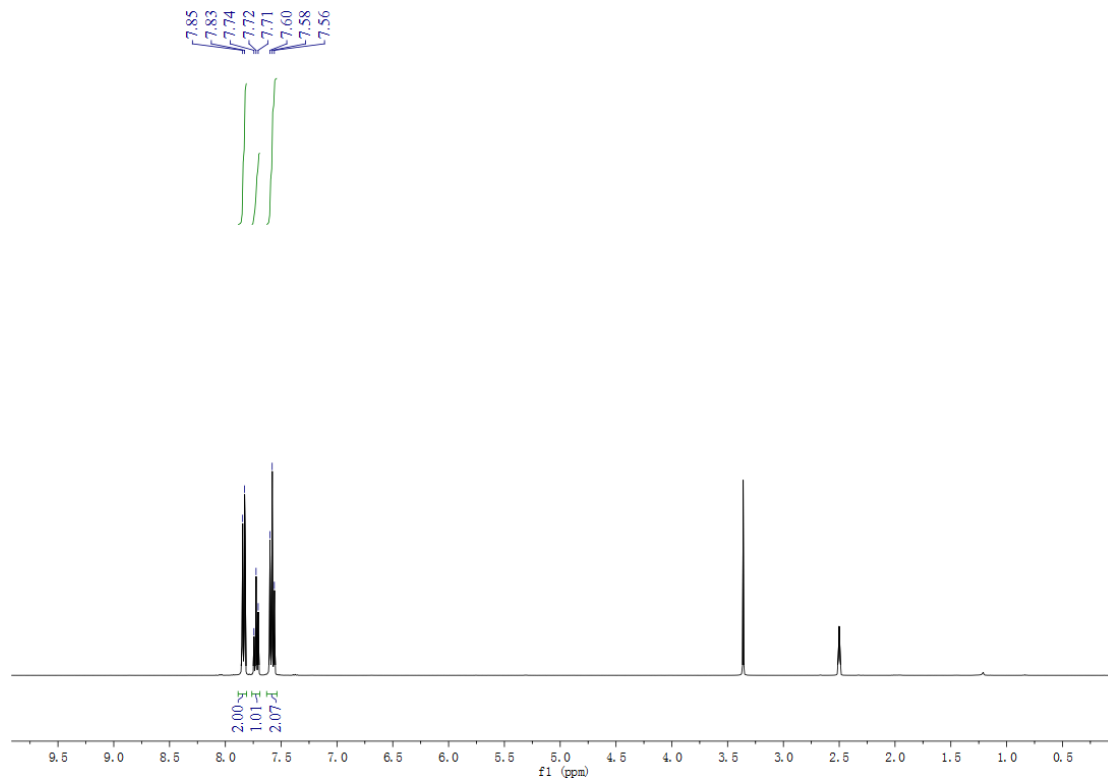


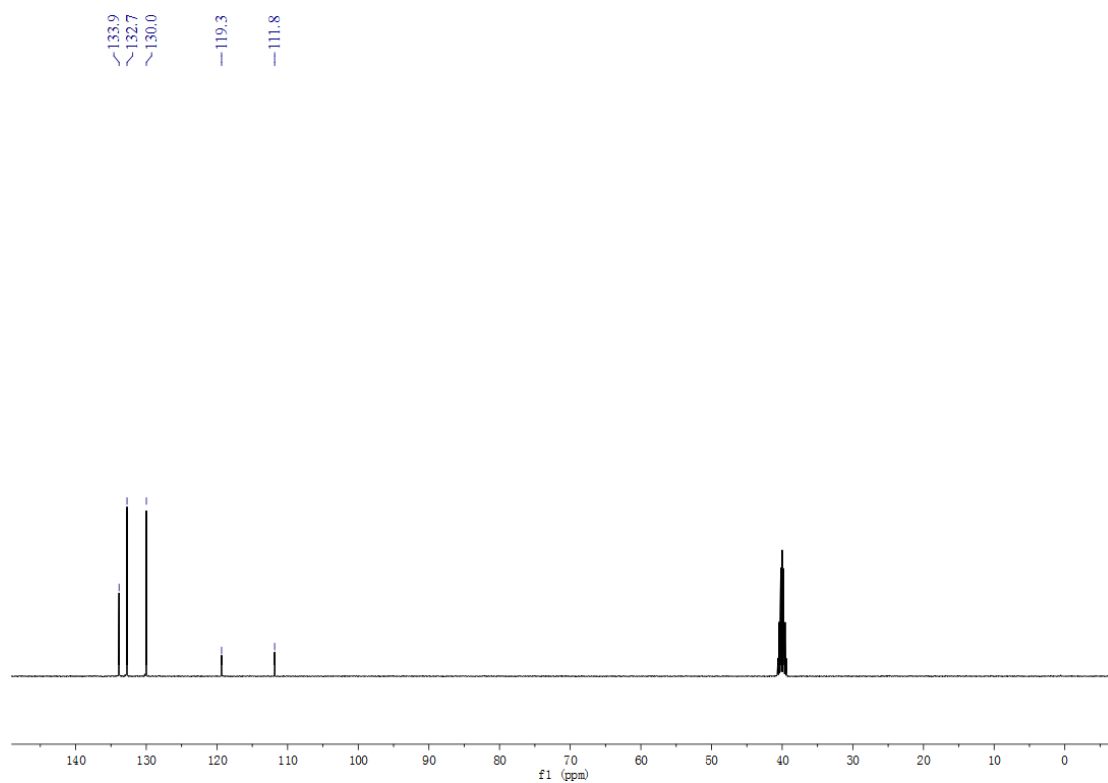
benzophenone (3b)



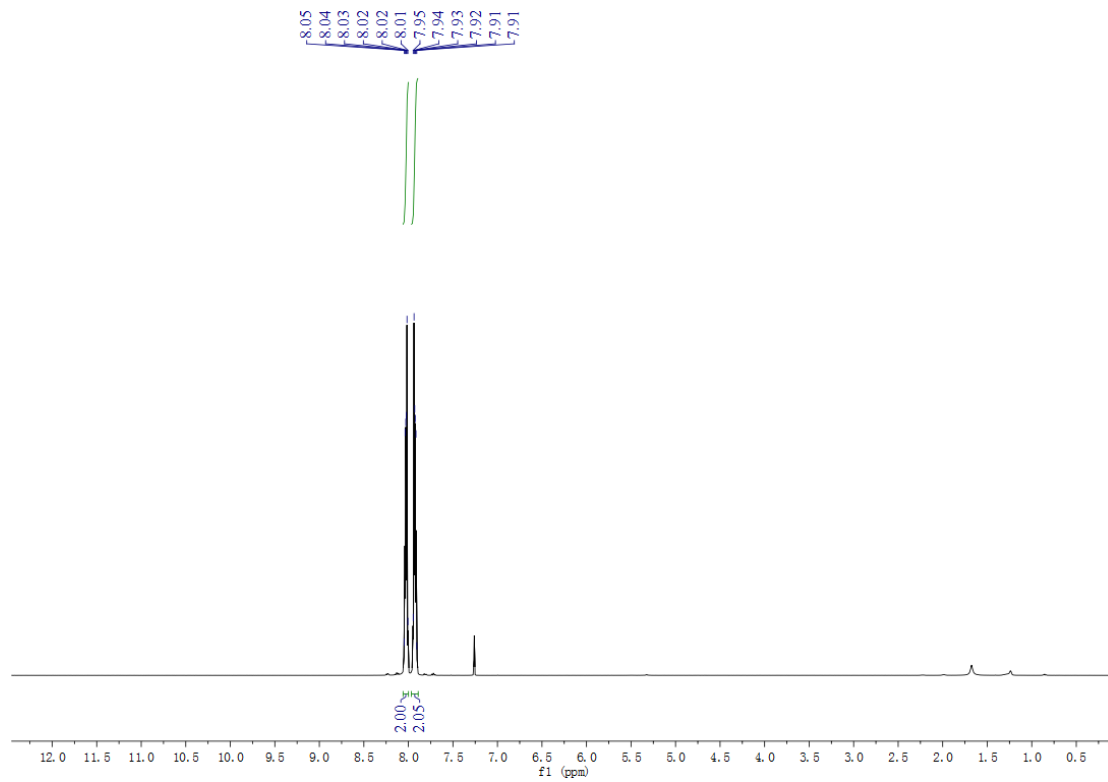


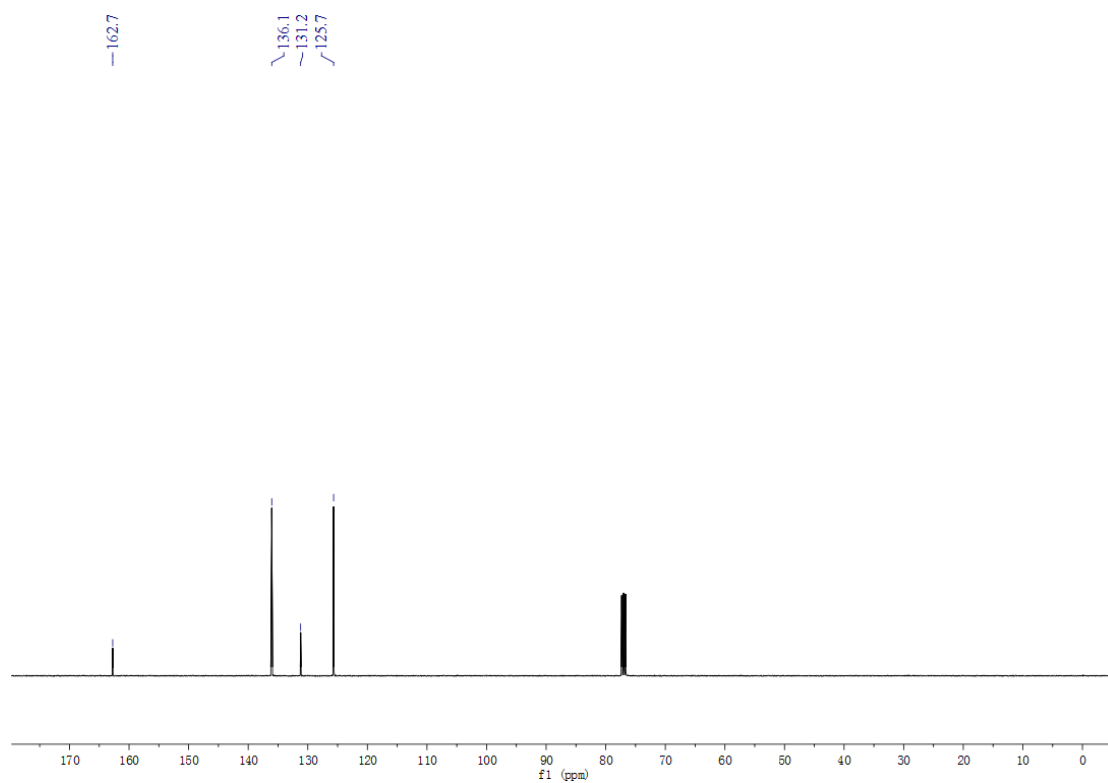
benzonitrile (3c)



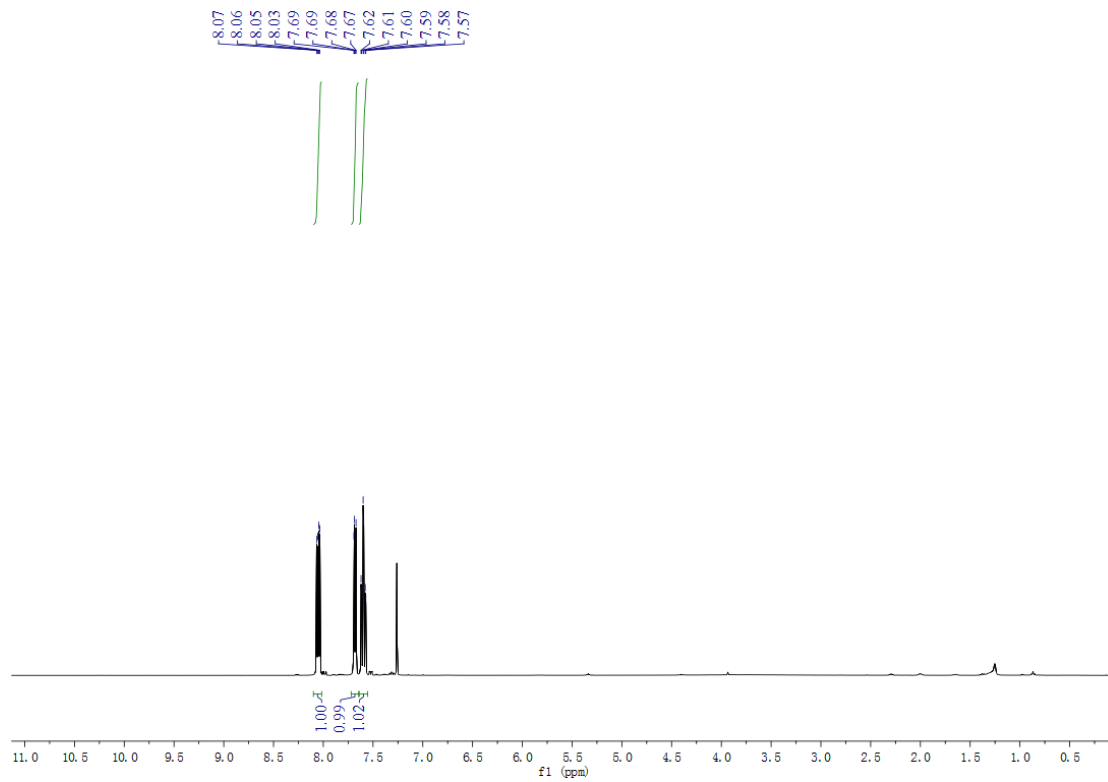


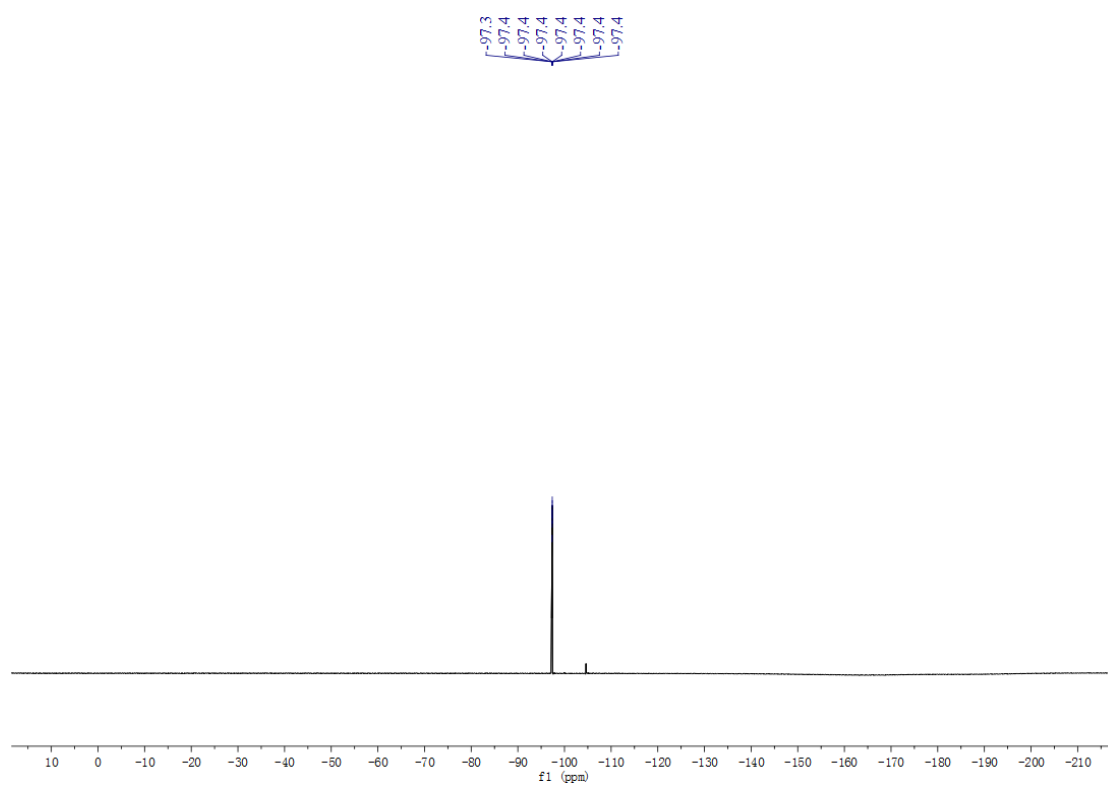
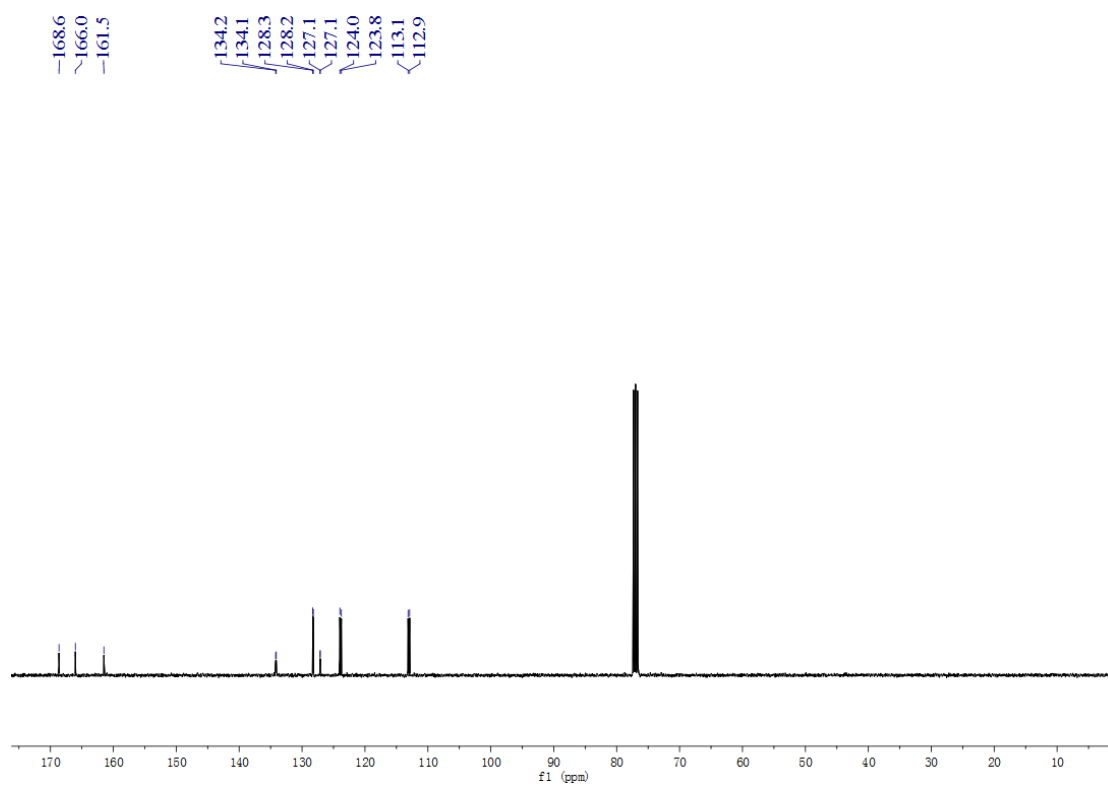
isobenzofuran-1,3-dione (4a)



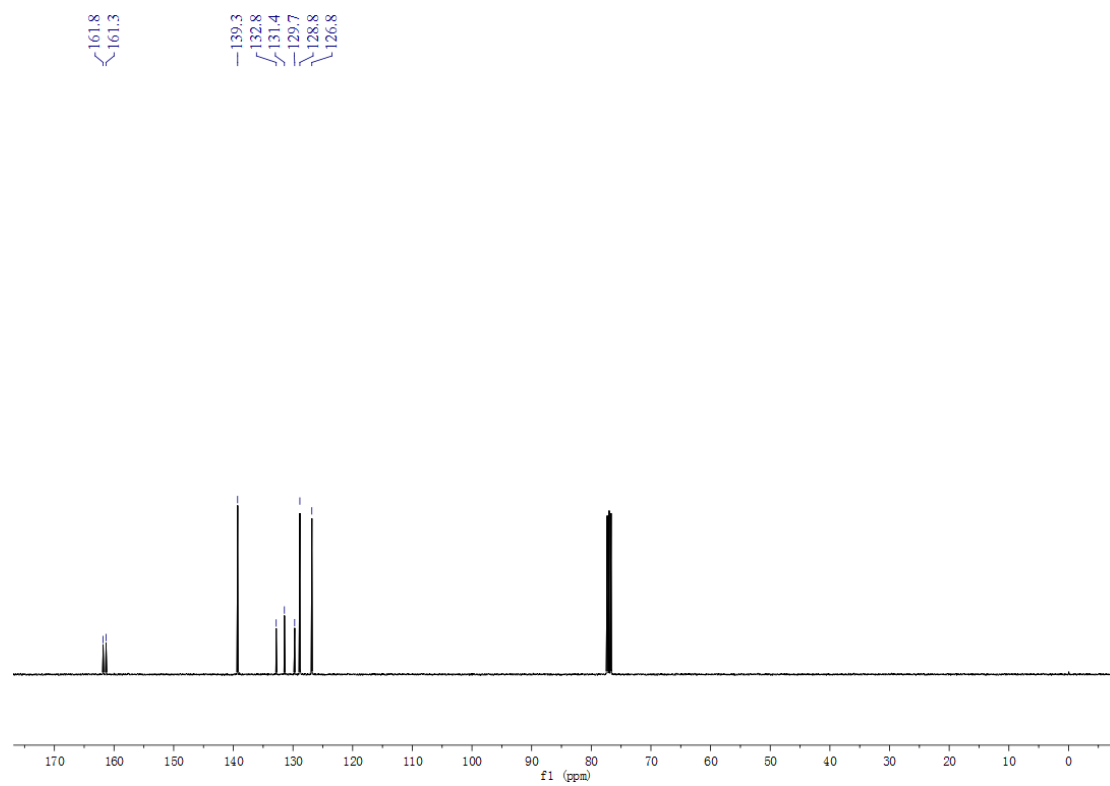
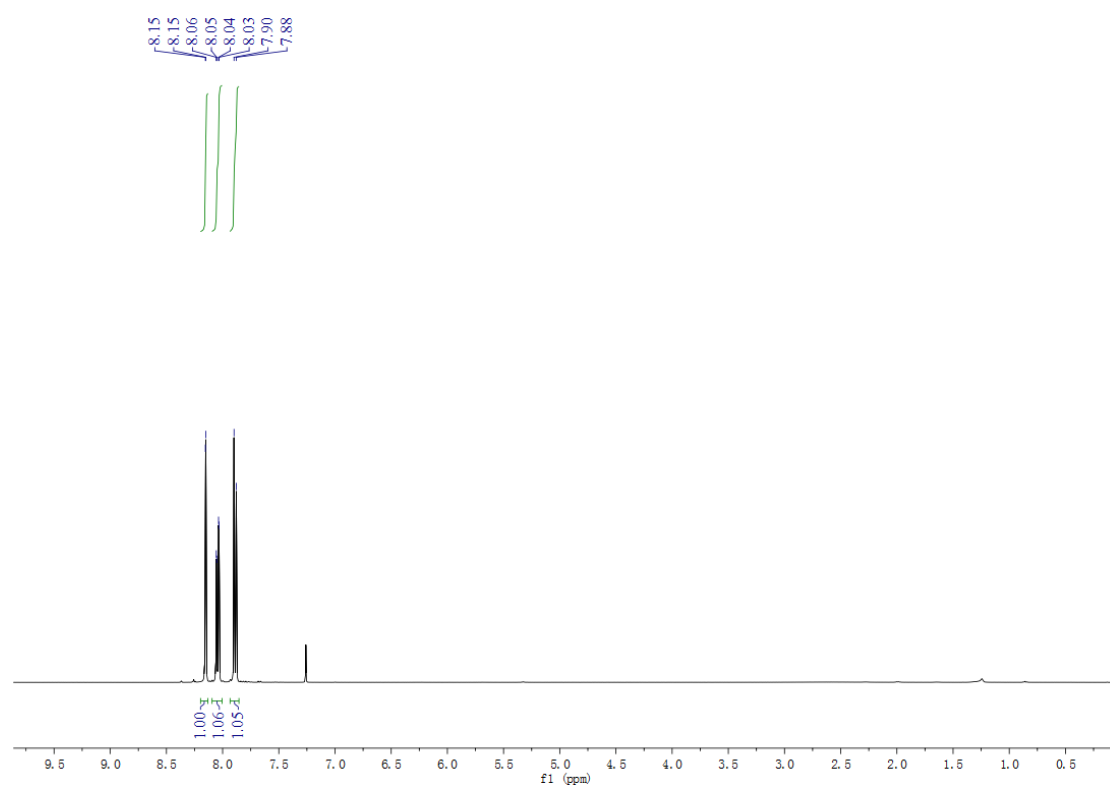


5-fluoroisobenzofuran-1,3-dione (4b)

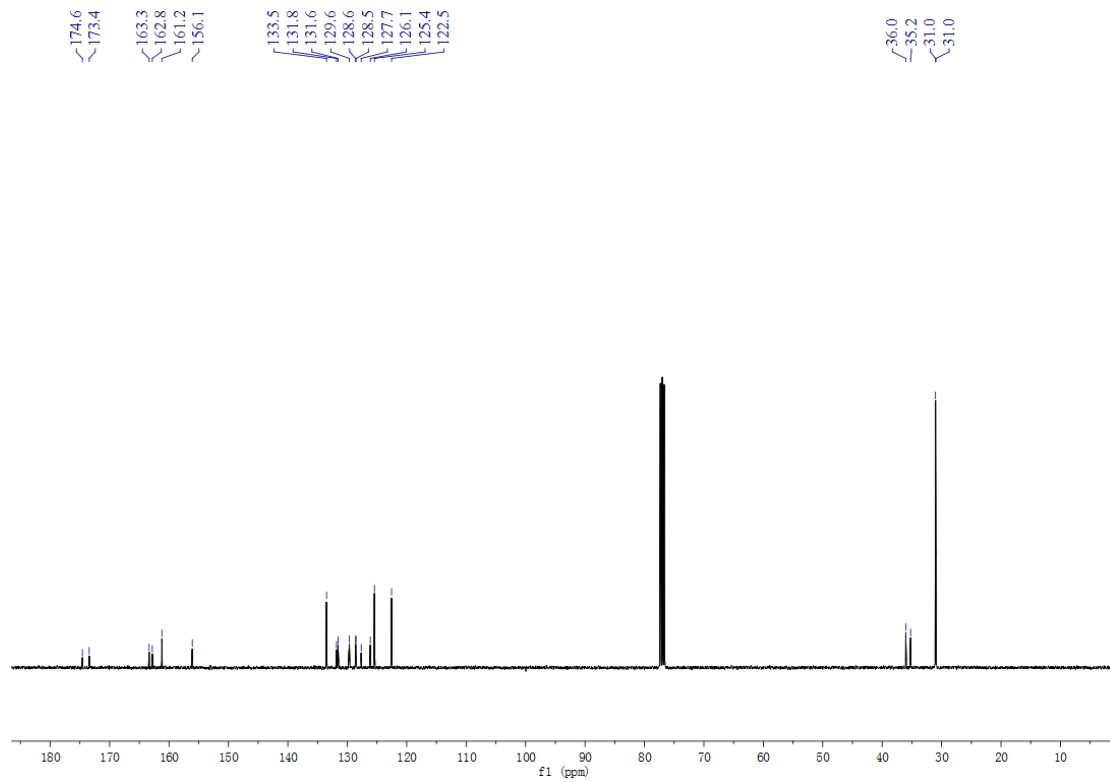
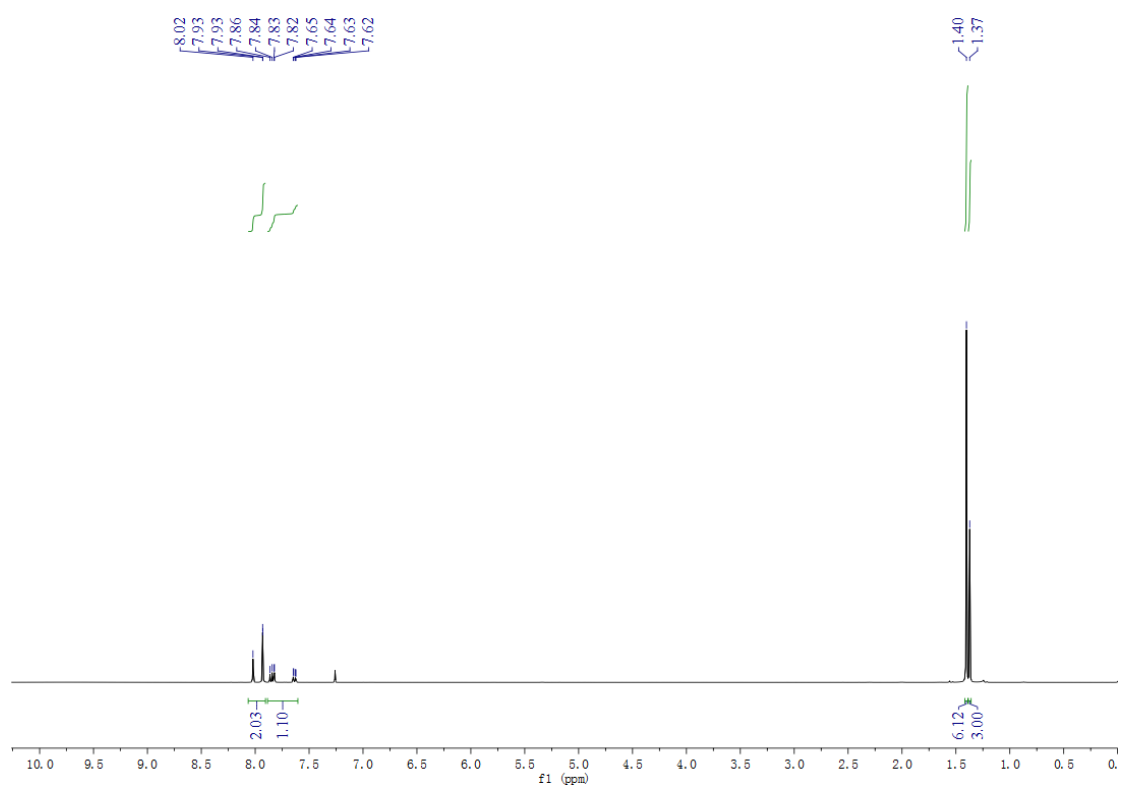




5-bromoisobenzofuran-1,3-dione (4c)



5-(*tert*-butyl)isobenzofuran-1,3-dione (4d)



5,5'-oxybis(isobenzofuran-1,3-dione) (4e)

