Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Highly efficient oxidative cleavage of olefins with O_2 under catalyst-, initiator- and additive-free conditions

Jinhua Ou,[a,c] Saiyu He,[a] Wei Wang,[a] Hong Tan,[a] Kai-Jian Liu[b*]

[a]*Department of Material and Chemical Engineering, Hunan Institute of Technology, 421002, Hengyang, China*

[b]*Hunan Provincial Engineering Research Center for Ginkgo biloba, Hunan University of Science and Engineering, Yongzhou 425100, China*

[c]*Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China*

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1. General information

Unless otherwise specified, all reagents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. All solvents were obtained from commercial suppliers (http://www.tansoole.com, For 1,4-dioxane: Product ID: 01182303, http://www.tansoole.com/upload/detail/01/H8N9_QFPY_01182303.html) and used with freshly distilled. ^{1}H 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 (^{1}H NMR: $CDCl_3$ 7.26 ppm, ^{13}C NMR: $CDCl_3$ 77.0 ppm, ^{1}H 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.

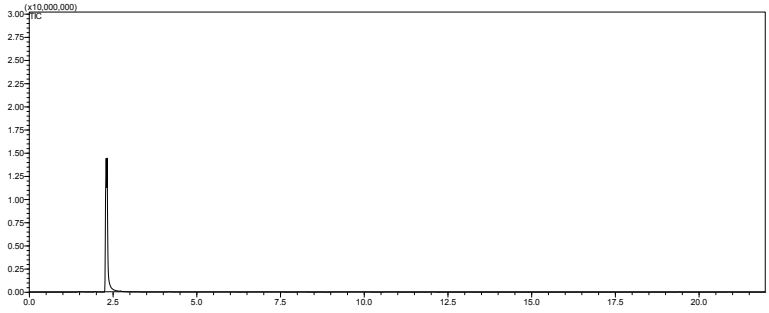


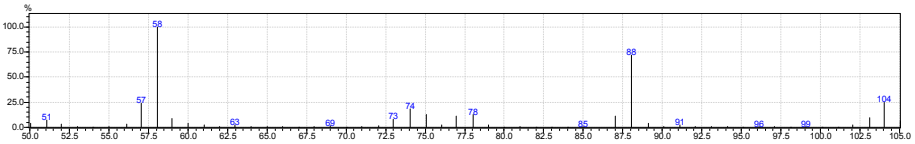
Figure 1. freshly distilled 1,4-dioxane by GC-MS

2. Experimental procedure

(a). General procedure for the synthesis of carbonyl compound 2

A mixture of alkene **1** (0.45 mmol) and freshly distilled 1,4-dioxane (1.5 mL) was added to a 5 mL round flask with an O_2 balloon at room temperature, then the contents were stirred at 80℃. The reaction typically took 16 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**.

MS of 1,4-dioxan-2-ol



(b). Oxidation of 1a on 100 mmol with O_2

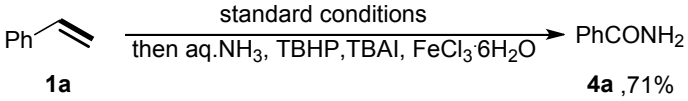
Special caution should be exercised when performing the scale-up oxidation reaction considering the potential explosion risk of the peroxides in 1,4-dioxane

A mixture of styrene **1a** (10.42g, 100 mmol) and freshly distilled 1,4-dioxane (300 ml) was added to a 1000 mL round-bottomed flask with an 25 L O_2 bag at room temperature, then the contents were stirred at 80℃for 35 hours. Upon completion, the reaction was cooled down to room temperature and concentrated under reduced pressure. The reaction was cooled down to room temperature and analyzed by GC-MS showed 85% product formation.

(c). Oxidation of 1a on 550 mmol with air

A mixture of styrene **1a** (57.31g, 550 mmol) and freshly distilled 1,4-dioxane (1200 ml) was added to a 3 L round-bottomed flask with 1W air pressure pump at room temperature, then the contents were stirred at 80℃ for 90 hours. Upon completion, the reaction was cooled down to room temperature and analyzed by GC-MS showed 79 % product formation.

(d). One-pot synthesis of Benzamide

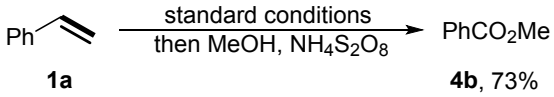


1a **4a** ,71%

A mixture of styrene (0.6 mmol) and freshly distilled 1,4-dioxane (2 mL) was added to a 10 mL round flask with an O_2 balloon at room temperature, then the contents were stirred at 80℃ for 16 hours. The contents were cooled to room temperature, *tetra*-butyl ammonium iodide (44.25 mg, 0.12 mmol, 20 mol %), $FeCl_3 \cdot 6H_2O$ (24.3mg, 0.09 mmol, 15 mol %), aq. ammonia (0.6 mmol) and TBHP (70 wt % in water, 0.53 mL, 3.6 mmol, 6 equiv) were added. The reaction mixture was stirred at 80 ℃ for 18 h. After the reaction over (TLC), the contents were cooled to room temperature and then extracted with ethyl acetate (3 x 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, 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 71%.

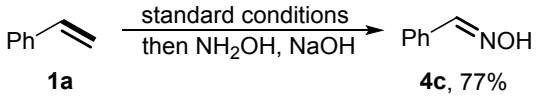
(e). One-pot synthesis of Methyl benzoate



1a **4b**, 73%

A mixture of styrene (0.6 mmol) and freshly distilled 1,4-dioxane (2 mL) was added to a 10 mL round flask with an O_2 balloon at room temperature, then the contents were stirred at 80℃ for 16 hours. The contents were cooled to room temperature, Methanol (0.39 mL, 9.6 mmol, 16 equiv) and $(NH_4)_2S_2O_8$ (0.21 g, 0.9 mmol, 1.5 equiv) were added. The mixture was then stirred at 60 °C for 4 hours. After cooling to room temperature, distilled water (10 mL) was used to dissolve the solid and the product was extracted by ethyl acetate (3 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, 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 73 %.

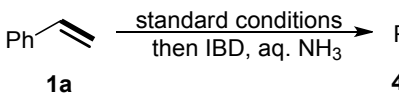
(f). One-pot synthesis of benzaldehyde oxime



1a **4c**, 77%

A mixture of styrene (0.6 mmol) and freshly distilled 1,4-dioxane (2 mL) was added to a 10 mL round flask with an O_2 balloon at room temperature, then the contents were stirred at 80℃ for 16 hours. The contents were cooled to room temperature, Hydroxylamine hydrochloride (0.05 g, 0.72 mmol) was dissolved in water (0.5 mL) and neutralized with aqueous sodium hydroxide solution (10 %). The contents were added slowly to this mixture with stirring in a water bath at 20 °C. The mixture was stirred at room temperature for 1 hour (with monitoring by TLC). The residue was diluted with water and extracted three times with ethyl acetate. The combined organic phase was washed with brine and dried with anhydrous sodium sulfate. 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 77 %.

(g). One-pot synthesis of benzonitrile

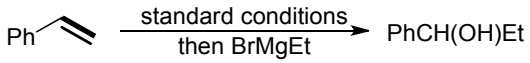


1a **4d**,75%

A mixture of styrene (0.6 mmol) and freshly distilled 1,4-dioxane (2 mL) was added to a 10 mL

round flask with an O_2 balloon at room temperature, then the contents were stirred at 80℃ for 16 hours. The contents were cooled to room temperature. Iodosobenzene diacetate (0.66 mmol) and aq. ammonia (5 ml of a 28–30% solution) were added. After completion of reaction (monitored by TLC), the reaction mixture was diluted with water and extracted with ethyl acetate (3x20 ml). The organic layer was washed with saturated solution of Na_2SO_3 and followed by saturated solution of Na_2CO_3, 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 75 %.

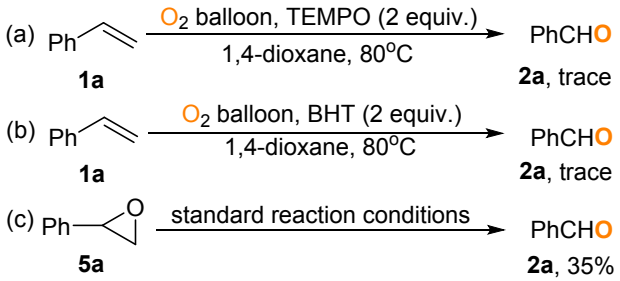
(h). One-pot synthesis of 1-phenyl-1-propanol



1a **4e**,75%

A mixture of styrene (0.6 mmol) and freshly distilled 1,4-dioxane (2 mL) was added to a 10 mL round flask with an O_2 balloon at room temperature, then the contents were stirred at 80℃ for 16 hours. The contents were cooled to 30℃, the addition of a 1,4-dioxane solution of EtMgBr (1.0 M, 0.9 mL, 0.9 mmol) started under N_2. After completion of the EtMgBr addition, the mixture was further stirred at 30℃ for 24 h, and water (10 mL) was added. After usual aqueous workup, The mixture was 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 75 %.

3. Control experiments



(1) Radical trapped experiment (a or b)

A mixture of styrene **1a** (0.6 mmol), freshly distilled 1,4-dioxane (2 mL) and 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO, 186 mg, 1.2 mmol) or butyleret hydroxytoluen (BHT, 264 mg, 1.2 mmol) was added to a 10 mL round-bottomed flask with an O_2 balloon at room temperature, then the contents were stirred at 80 ℃ for 12 hours. The reaction was cooled down to room temperature and analyzed by GC-MS showed trace product formation.

(2) EPR experiment

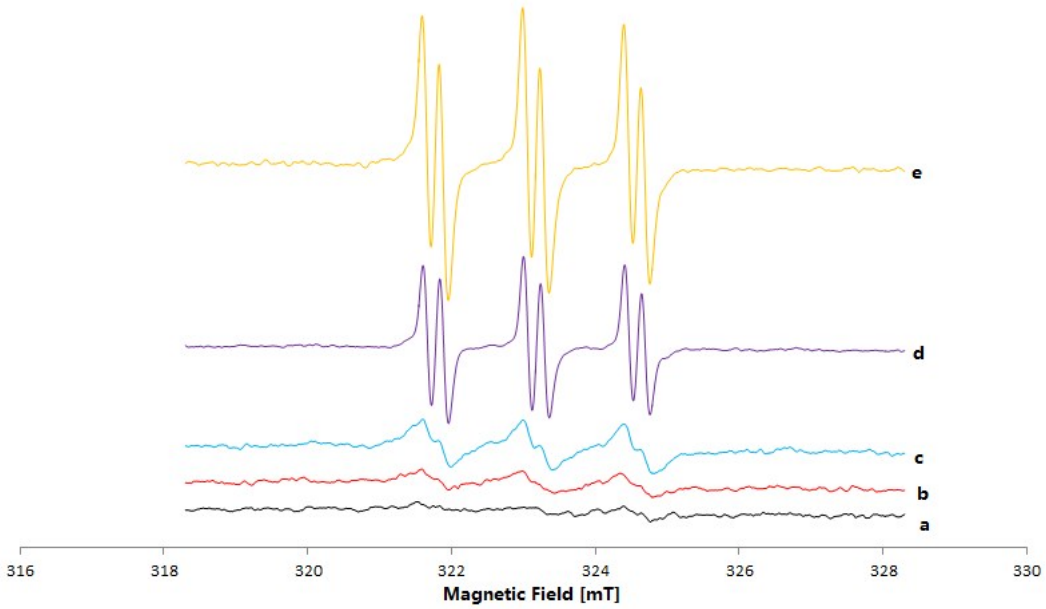
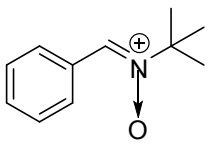


Figure 3. EPR spectrum of the radical trapping experiment: a) R.T.; b) 35℃; c) 50℃; d) 65℃; e) 80℃.

Measurement conditions: Power 1 mW, Frequency 9.439 GHz, Center field 336.638 mT, Sweep width 10mT, Modulation width 0.1 mT, Sweep time 1.0 min, Time constant 0.1s, Amplitude 400.

The EPR experiment was monitored under following conditions: PBN (*N-tert-Butyl*-α-phenylnitrone)  (17.7 mg) was dissolved in dimethoxy dipropyleneglycol (1mL) to

form a 100 mM solution. The mixture was stirred under oxygen atmosphere at different for 5 min at different temperatures, after that 40 uL of the mixture was transferred to a flat cell and was measured, a strong signal with a g = 2.002, A_N = 1.41 mT, A_H = 0.226 mT, which was coincident with a peroxyl radical was observed Figure 3.

(3) Oxidation of styrene oxide 5a

A mixture of styrene oxide (0.6 mmol) and freshly distilled 1,4-dioxane (2 mL) was added to a 10 mL round-bottomed flask with an O_2 balloon at room temperature, then the contents were stirred at 80 ℃ for 16 hours. The reaction was cooled down to room temperature and analyzed by GC-MS showed 35% product formation.

(4) Effect of reaction temperature

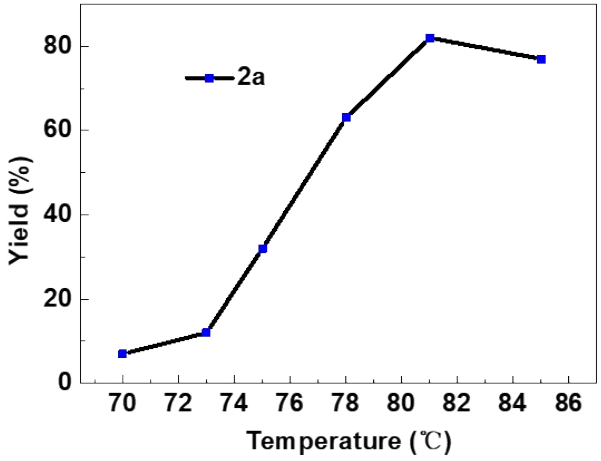


Figure 1 Influence of reaction temperature on the yield

We investigated the influence of reaction temperature on the yield of acid **2a** as shown in Figure 1 and found the reaction system is sensitive to temperature. The results indicated a low yield (7%) of **2a** was obtained when the reaction was conducted at 70 °C, whereas the yield of **2a** has a sharp rise with the increasing of temperature from 75°C to 81°C. Based on the above observations, we speculated that the 1,4-dioxane/O_2 system can not be initiated to produce 1,4-dioxanyl peroxyl radical at or below 70 °C, therefore it almost has no effect on the oxidation to perform the reaction under this condition. In addition, further increasing the temperature would reduce the yield, which can possibly be attributed to the generation of benzoic acid **3a**.

4. Characterization data of products

benzaldehyde (2a)[1]: colorless liquid (39 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1 H), 7.90 - 7.87 (m, 2 H), 7.66 - 7.61 (m, 1 H), 7.55 - 7.52 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 136.3, 134.5, 129.7, 129.0.

4-methylbenzaldehyde (2b)[2]: colorless liquid (43 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 145.5, 134.0, 129.7, 129.6, 21.8.

4-*iso*-propylbenzaldehyde (2c)[1]: colorless liquid (52 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 3.02-2.95 (m, 1 H), 1.27 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 156.2, 134.4, 130.0, 127.1, 34.4, 23.6.

4-(*tert*-butyl)benzaldehyde (2d)[3]: colorless liquid (59 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 158.3, 133.9, 129.6, 125.9, 35.2, 31.0.

[1,1'-biphenyl]-4-carbaldehyde (2e)[3]: white solid (65 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 7.2 Hz, 2 H), 7.51 - 7.47 (m, 2 H), 7.44 - 7.40 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 147.1, 139.6, 135.1, 130.2, 129.0, 128.4, 127.6, 127.3.

4-methoxybenzaldehyde (2f)[1]: colorless liquid (49 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 164.5, 131.9, 129.7, 114.2, 55.5.

4-(methylthio)benzaldehyde (2g)[4]: colorless liquid (52 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 2.52 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 147.9, 132.9, 129.9, 125.1, 14.6.

4-(benzyloxy)benzaldehyde (2h)[4]: light yellow solid (74 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1 H), 7.85 (d, *J* = 8.8 Hz, 2 H),7.45 - 7.36 (m, 5 H), 7.08 (d, *J* = 8.8 Hz, 2 H), 5.15 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 163.7, 135.9, 132.0, 130.0, 128.7, 128.3, 127.5, 115.1, 70.2.

4-(trifluoromethoxy)benzaldehyde (2i)[5]: colorless liquid (65 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 153.4, 134.4, 131.5, 120.7, 120.2 (q, *J* = 257.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6.

4-(dimethylamino)benzaldehyde (2j)[6]: white solid (51 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 3.09 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 154.2, 131.9, 125.1, 111.0, 40.1.

4-fluorobenzaldehyde (2k)[1]: colorless liquid (46 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1 H), 7.94 - 7.89 (m, 2 H), 7.24 - 7.19 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 166.5 (d, *J* = 255.0 Hz), 132.9 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 9.7 Hz), 116.4 (d, *J* = 22.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.3.

4-chlorobenzaldehyde (2l)[1]: colorless liquid (54 mg, 85 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 140.9, 134.6, 130.9, 129.4.

4-bromobenzaldehyde (2m)[2]: white solid (51 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 135.0, 132.4, 130.9, 129.7.

4-(chloromethyl)benzaldehyde (2n)[7]: white solid (57 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 4.63 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 143.8, 136.1, 130.1, 129.1, 45.2.

4-(trifluoromethyl)benzaldehyde (2o)[3]: colorless liquid (58 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 138.6 (d, *J* = 1.0 Hz), 135.5 (q, *J* = 32.3 Hz), 129.9, 126.1 (d, *J* = 3.6 Hz), 123.4 (q, *J* = 271.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.

4-nitrobenzaldehyde (2p)[2]: light yellow solid (48 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1 H), 8.40 (d, *J* = 8.8 Hz, 2 H), 8.08 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 151.1, 140.0, 130.5, 124.3.

4-formylbenzonitrile (2q)[3]: white solid (43 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 138.7, 132.9, 129.9, 117.7, 117.5.

methyl 4-formylbenzoate (2r)[8]: white solid (60 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 166.0, 139.1, 135.0, 130.1, 129.5, 52.6.

3-methylbenzaldehyde (2s)[2]: colorless liquid (44 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 7.68-7.64 (m, 2 H), 7.45-7.39 (m, 2 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 138.9, 136.4, 135.3, 130.0, 128.8, 127.2, 21.1.

2-methylbenzaldehyde (2t)[2]: colorless liquid (40 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1 H), 7.80 (d, *J* = 7.6 Hz, 1 H), 7.48 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 2.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 140.6, 134.1, 133.6, 132.0, 131.7, 126.3, 19.6.

3,4-dichlorobenzaldehyde (2u)[9]: white solid (64 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1 H), 7.96 (d, *J* = 2.0 Hz, 1 H), 7.72 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 139.1, 135.7, 133.9, 131.3, 131.2, 128.4.

3,4,5-trimethoxybenzaldehyde (2v)[5]: white solid (64 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1 H), 7.13 (s, 2 H), 3.94 (s, 3 H), 3.93 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 153.5, 143.4, 131.6, 106.6, 60.9, 56.2.

terephthalaldehyde (2w)[2]: white solid (45 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 2 H), 8.06 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 139.9, 130.1.

benzo[*d*][1,3]dioxole-5-carbaldehyde (2x)[5]: white solid (48 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1 H), 7.40 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.31 (d, *J* = 1.2 Hz, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 6.06 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 153.0, 148.6, 131.8, 128.7, 108.3, 106.8, 102.1.

2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde (2y)[10]: yellowish brown solid (54 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1 H), 7.41 - 7.39 (m, 2 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 4.35 - 4.28 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 149.2, 143.9, 130.6, 124.2, 118.3, 117.7, 64.7, 64.0.

1-naphthaldehyde (2z)[3]: yellow oil (56 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1 H), 9.26 (d, *J* = 8.8 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 8.00 (dd, *J* = 7.2, 1.2 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.72 - 7.68 (m, 1 H), 7.65 - 7.58 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 136.6, 135.1, 133.5, 131.1, 130.3, 128.9, 128.3, 126.8, 124.7.

2-naphthaldehyde (2aa)[3]: white solid (57 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1 H), 8.35 (s, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 7.98 - 7.95 (m, 2 H), 7.92 (d, *J* = 8.8 Hz, 1 H), 7.65 (td, *J* = 6.8, 1.4 Hz, 1 H), 7.60 (td, *J* = 6.8, 1.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 136.4, 134.6, 134.0, 132.6, 129.5, 129.1, 128.0, 127.1, 122.7.

acetophenone (2ab)[11]: colorless liquid (47 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.95 (m, 2 H), 7.59-7.54 (m, 1 H), 7.48 - 7.45 (m, 2 H), 2.61 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 136.8, 132.9, 128.4, 128.1, 26.4.

3,7-dimethyloct-6-en-1-yl 4-formylbenzoate (2al): colorless oil (105 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.19 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 5.11 - 5.07 (m, 1H), 4.43 - 4.36 (m, 2 H), 2.07 - 1.95 (m, 2 H), 1.87 - 1.79 (m, 1 H), 1.67 (s, 3 H), 1.64 (t, *J* = 5.6 Hz, 1 H), 1.60 (s, 3 H), 1.42 - 1.38 (m, 1 H), 1.30 - 1.21 (m, 2 H), 0.98 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 165.6, 139.0, 135.4, 131.5, 130.1, 129.5, 124.4, 64.1, 36.9, 35.4, 29.5, 25.7, 25.3, 19.5, 17.7. HRMS (ESI) calcd for $C_{18}H_{24}O_3Na$ $[M+Na]^+$: 311.1618, found 311.1621.

(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-formylbenzoate (2am): white solid (100 mg, 78%) M.P.: 66.7-68.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.21 (d, *J* = 8.0 Hz, 2 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 5.14 (dd, *J* = 10.0, 1.2 Hz, 1 H), 2.53 - 2.46 (m, 1 H), 2.14 - 2.08 (m, 1 H), 1.82 - 1.74 (m, 2

H), 1.43 (t, *J* = 13.2 Hz, 1 H), 1.35-1.28 (m, 1 H), 1.15 - 1.11 (m, 1 H), 0.97 (s, 3 H), 0.92 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 165.7, 139.0, 135.8, 130.1, 130.0, 129.5, 81.3, 49.1, 47.9, 44.9, 36.8, 28.0, 27.4, 19.7, 18.9, 13.6. HRMS (ESI) calcd for $C_{18}H_{22}O_3Na$ $[M+Na]^+$: 309.1461, found 309.1468.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-formylbenzoate (2an): white solid (142 mg, 75%) M.P.: 198.7-199.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 5.47 (d, *J* = 4.8 Hz, 1 H), 4.94 - 4.86 (m, 1 H), 2.52 - 2.44 (m, 2 H), 2.15 - 2.06 (m, 2 H), 1.98 - 1.94 (m, 2 H), 1.89 - 1.84 (m, 2H), 1.75 - 1.67 (m, 4 H), 1.56 - 1.47 (m, 2 H), 1.32 - 1.25 (m, 4 H), 1.11 (s, 3 H), 0.96 (t, *J* = 7.2 Hz, 1 H), 0.90 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 164.9, 139.6, 139.0, 135.7, 130.1, 129.5, 122.3, 75.1, 51.7, 50.1, 47.5, 38.1, 36.9, 36.8, 35.8, 31.5, 31.4, 30.8, 27.7, 21.9, 20.3, 19.4, 13.5. HRMS (ESI) calcd for $C_{27}H_{32}O_4Na$ $[M+Na]^+$: 443.2193, found 443.2191.

(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 4-acetylbenzoate (2ao): colorless oil (97 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2 H), 8.00 (d, *J* = 8.8 Hz, 2 H), 5.86 (s, 1 H), 4.73 (d, *J* = 5.6 Hz, 4 H), 2.64 (s, 3 H), 2.21 - 2.17 (m, 4 H), 2.04 - 1.96 (m, 1 H), 1.91 - 1.85 (m, 1 H), 1.74 (s, 3 H), 1.58 - 1.47 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 165.6, 149.5, 140.1, 134.1, 132.3, 129.8, 128.2, 126.2, 108.8, 69.3, 40.7, 30.4, 27.2, 26.9, 26.4, 20.7. HRMS (ESI) calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1461, found 321.1465.

Benzamide (4a)[12]: white solid (51 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 6.30 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 133.3, 132.0, 128.6, 127.3.

Methyl benzoate (4b)[13]: colorless liquid (60 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 132.8, 130.1, 129.5, 128.3, 52.0.

benzaldehyde oxime (4c)[14]: colorless liquid (56 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1 H), 8.21 (s, 1 H), 7.62 - 7.59 (m, 2 H), 7.43 - 7.40 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 130.1, 128.8, 127.0.

benzonitrile (4d)[15]: colorless liquid (46 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.58 (m, 3 H), 7.46 (t, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7, 132.0, 129.0, 118.8, 112.3.

1-phenylpropan-1-ol (4e)[16]: colorless liquid (61 mg, 75%); ^{1}H NMR (400 MHz, DMSO) δ 7.32 - 7.28 (m, 4 H), 7.24 - 7.18 (m, 1 H), 5.12 (d, *J* = 4.0 Hz, 1 H), 4.45 - 4.41 (m, 1 H), 1.64 - 1.53 (m, 2 H), 0.81 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO) δ 146.7, 128.4, 127.0, 126.3, 74.1, 32.6, 10.6.

5. References

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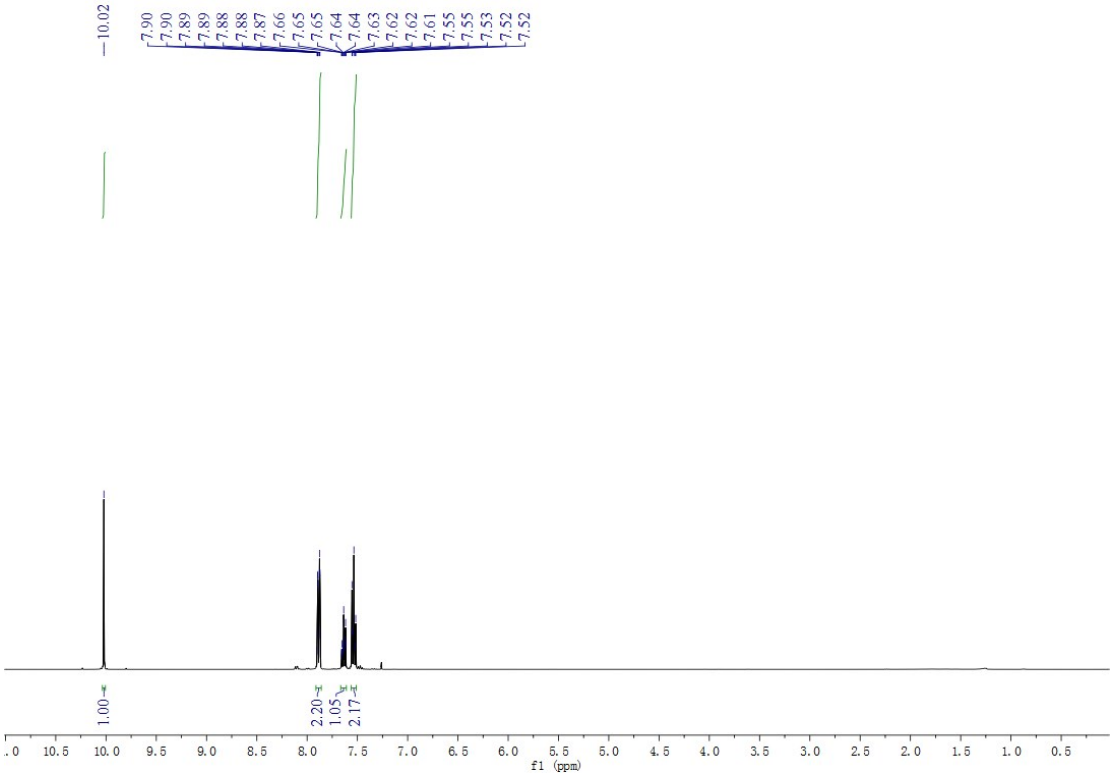
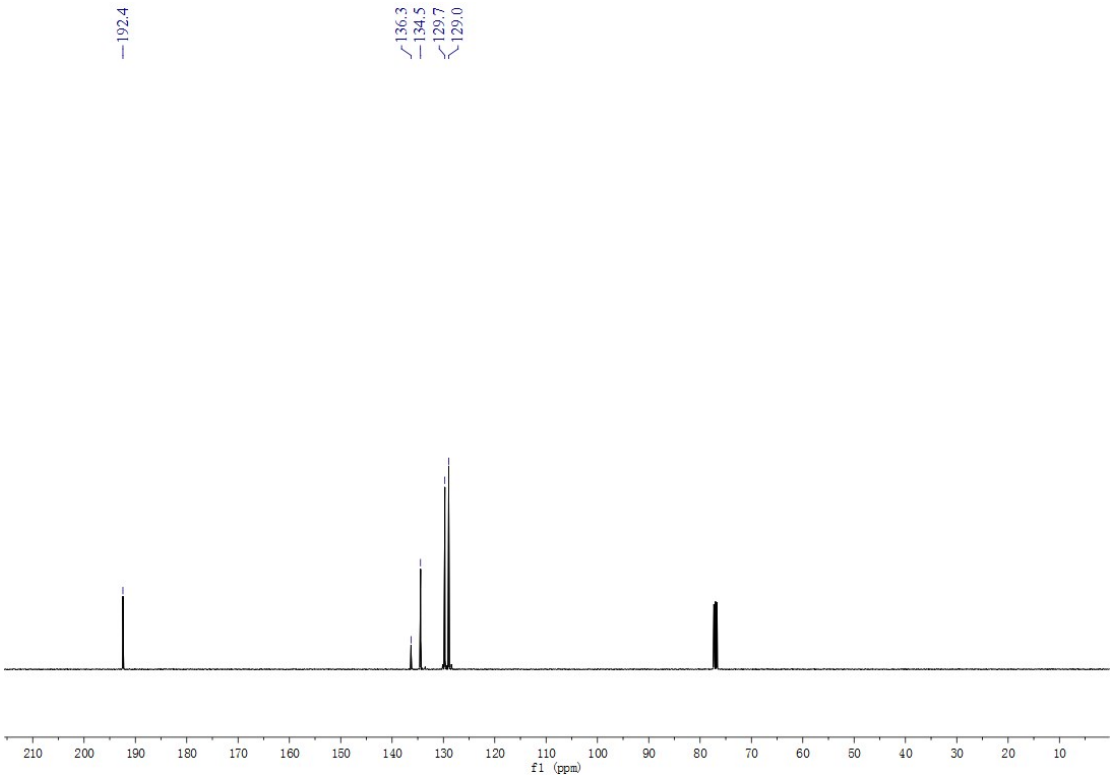
6. ^{1}H and ^{13}C NMR spectra

benzaldehyde (2a)





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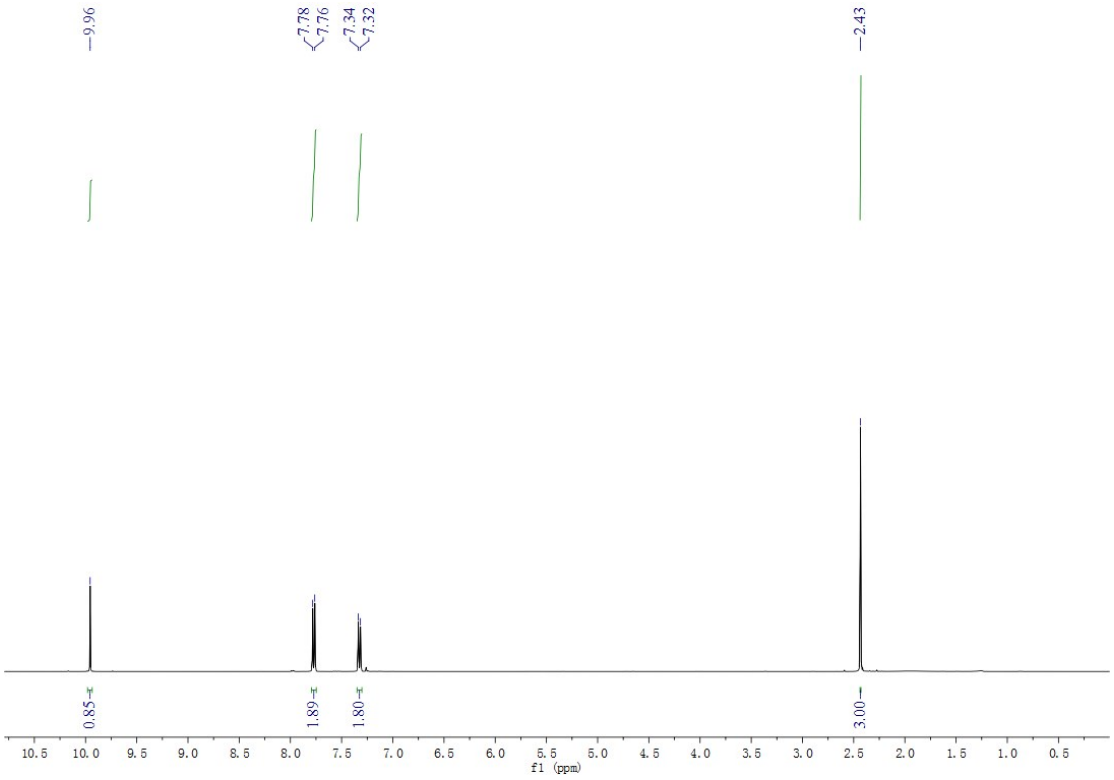
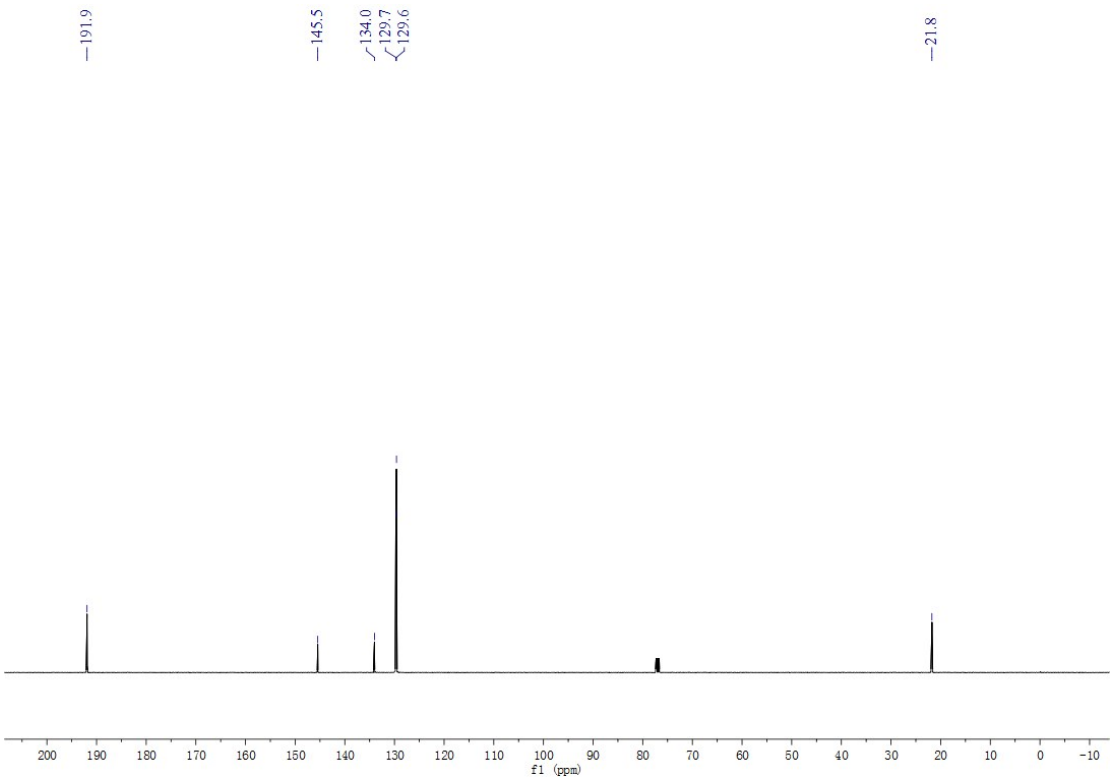
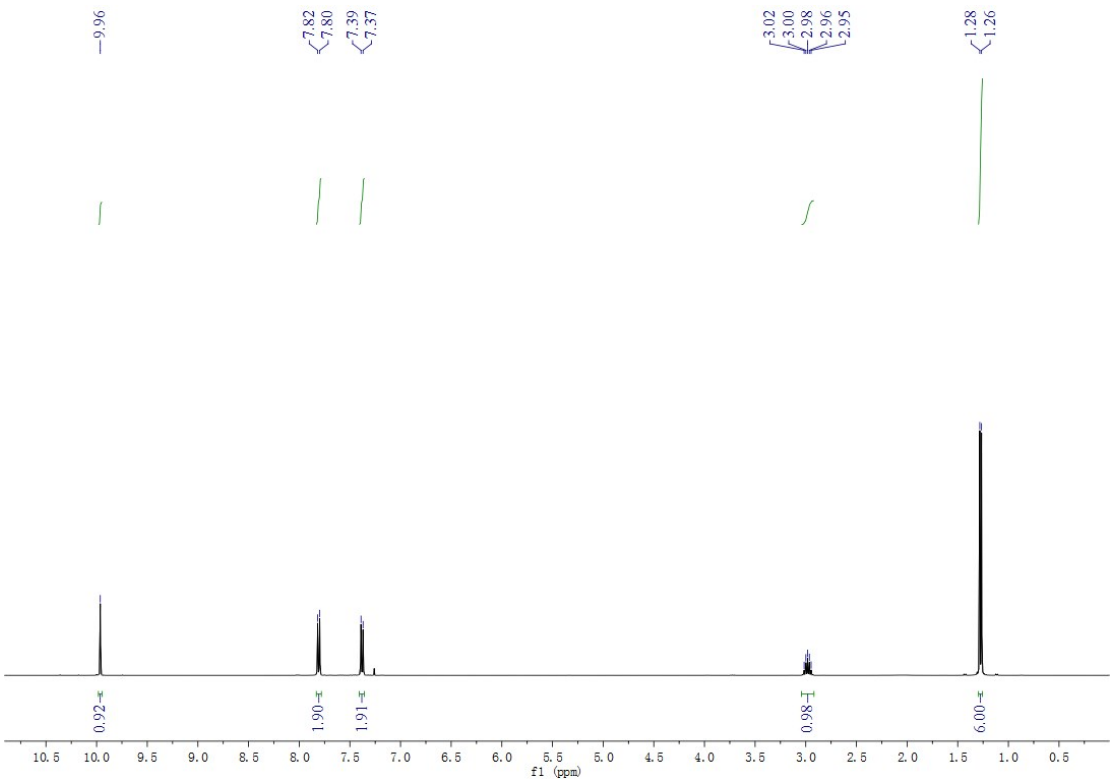
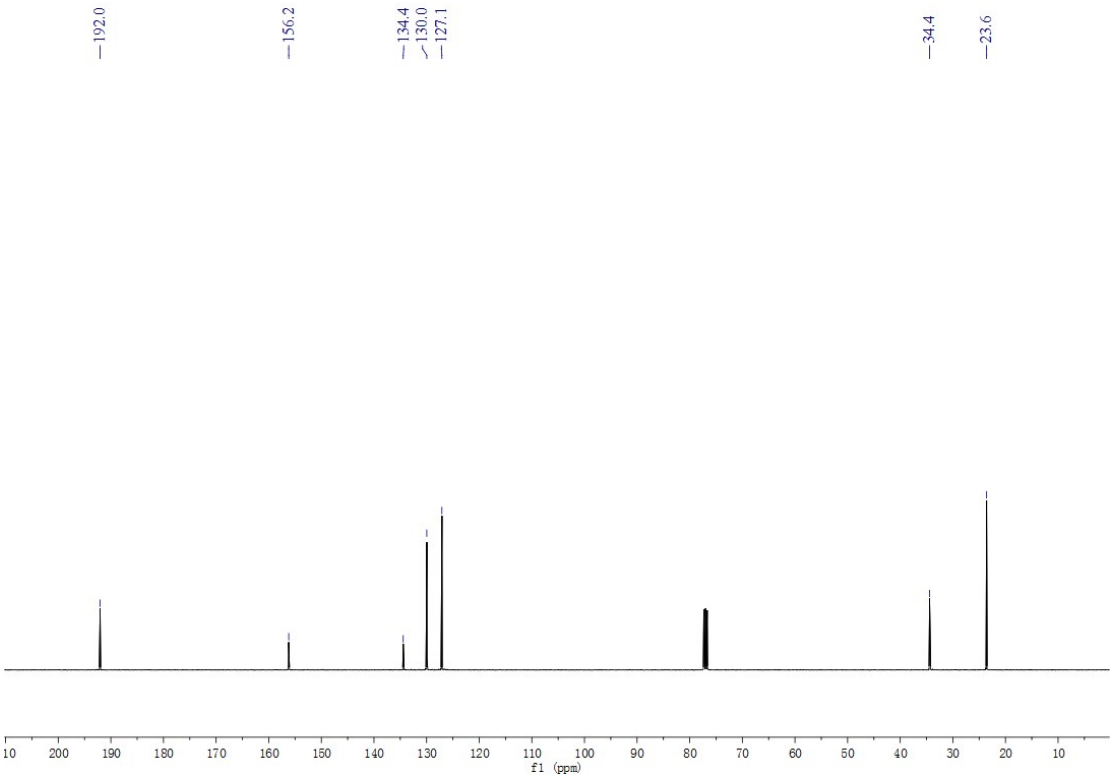


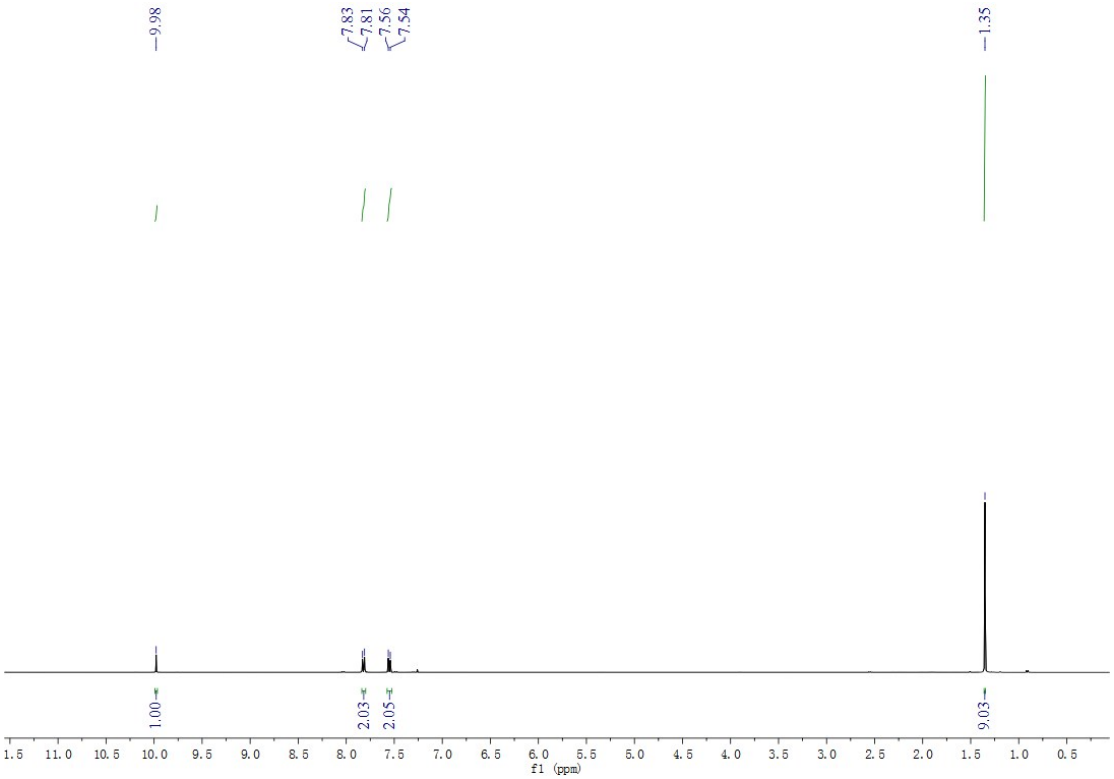


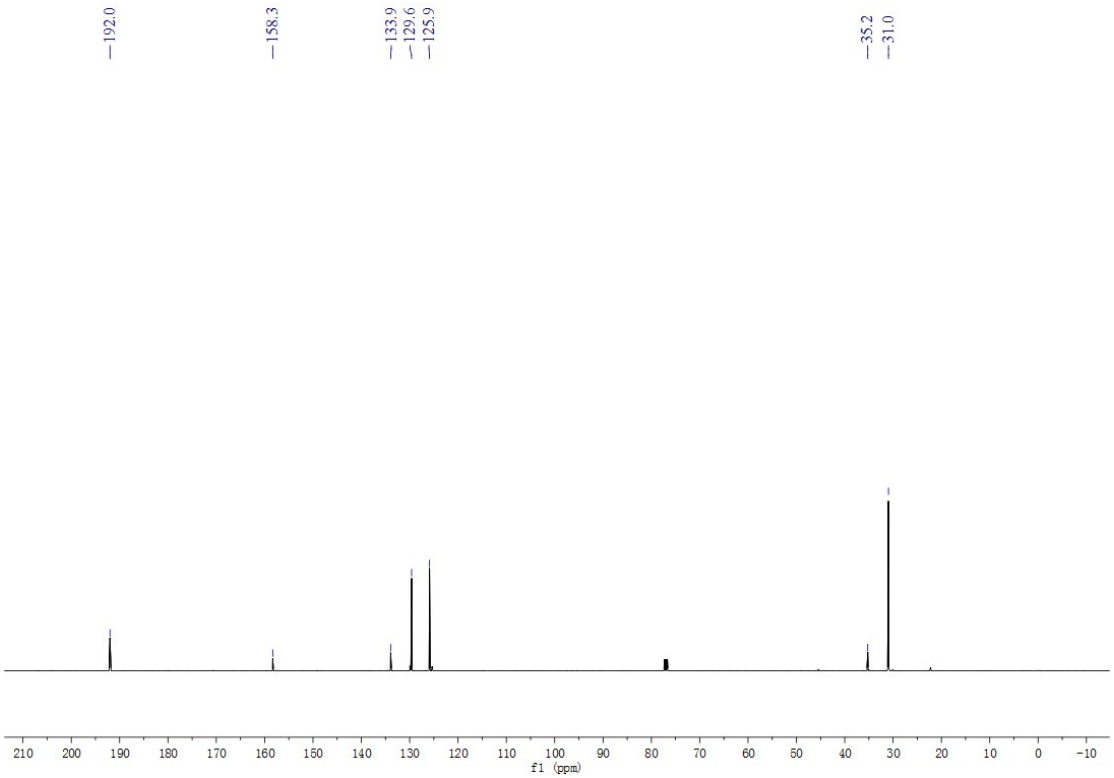
4-*iso*-propylbenzaldehyde (2c)



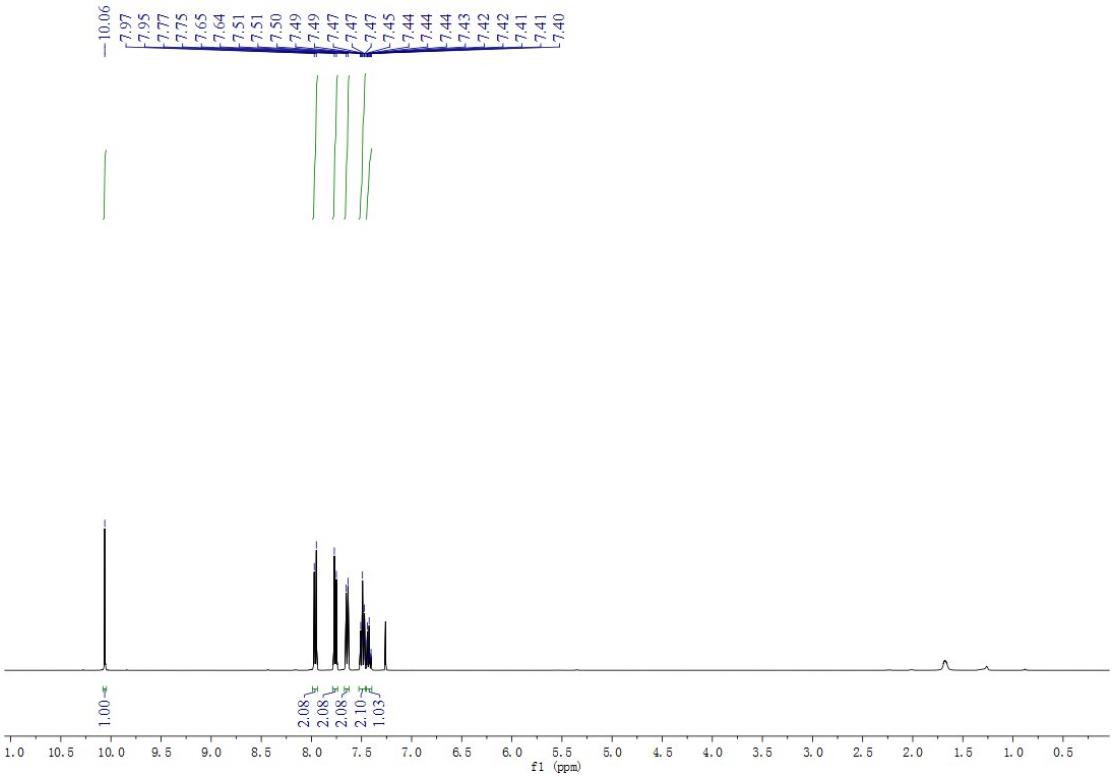


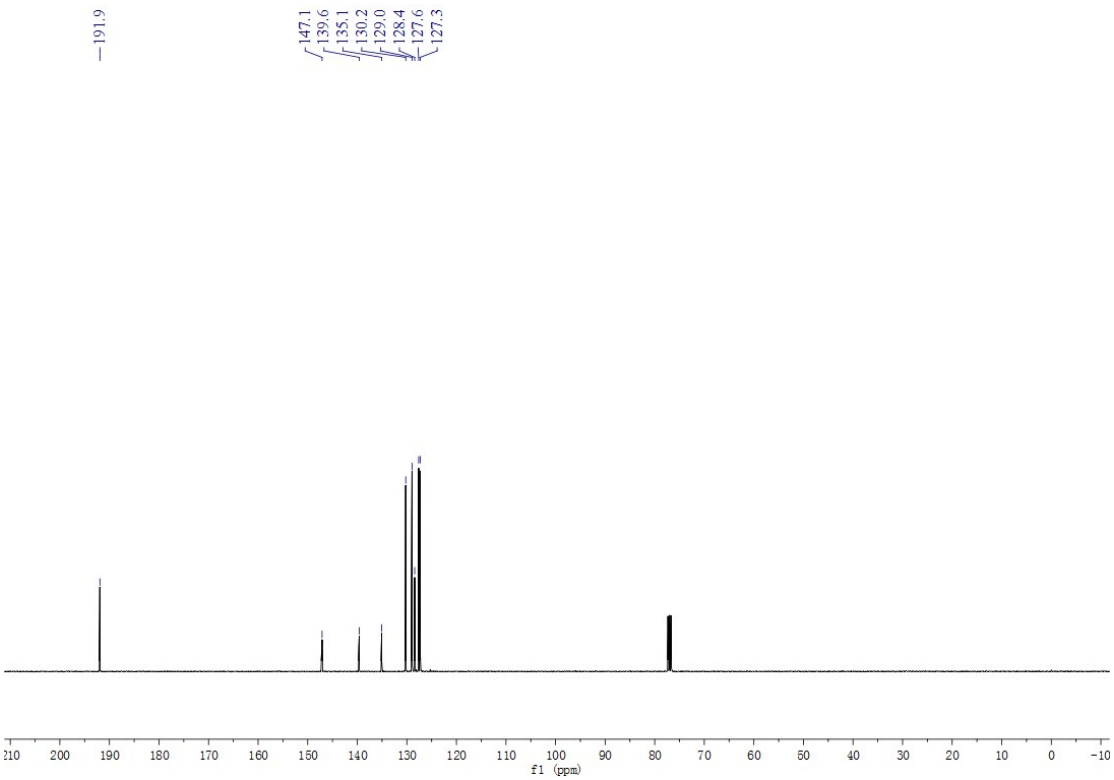
4-(*tert*-butyl)benzaldehyde (2d)





[1,1'-biphenyl]-4-carbaldehyde (2e)





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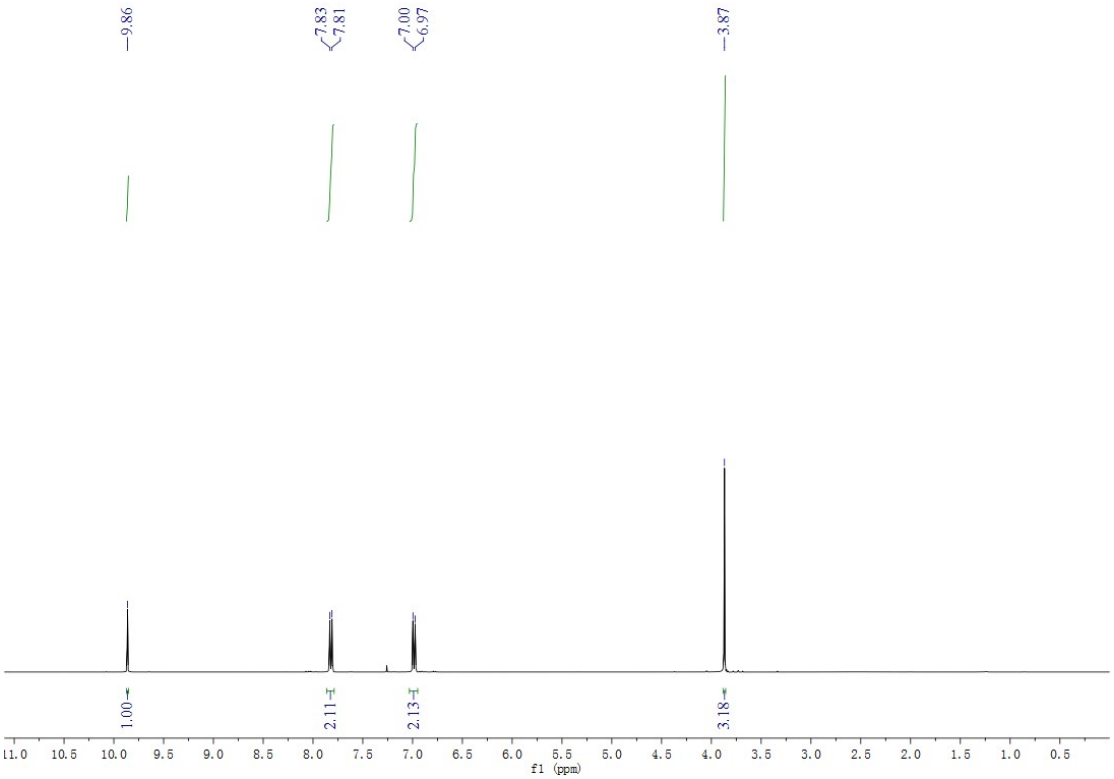
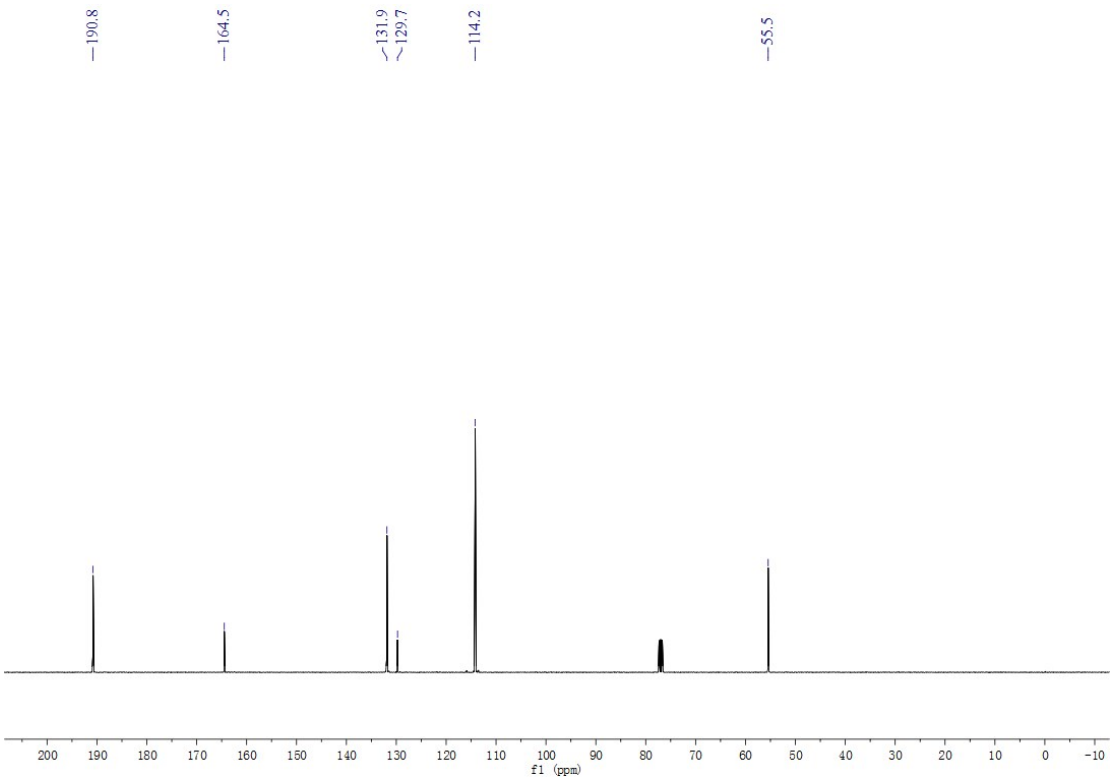
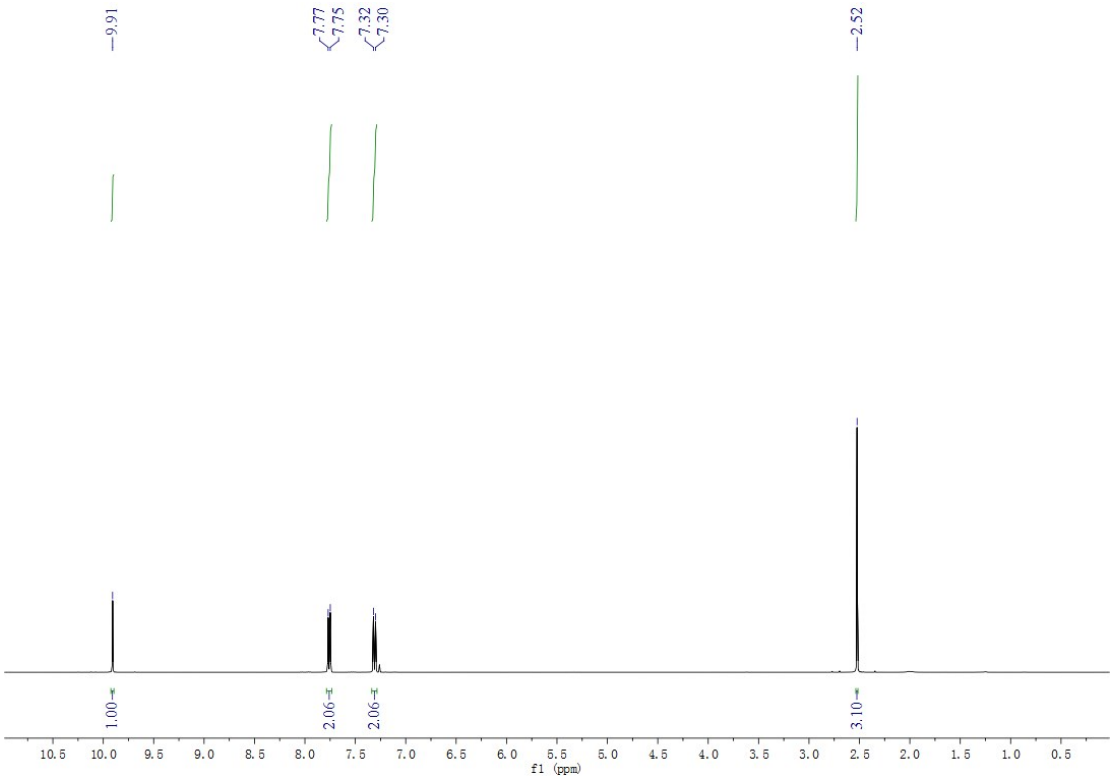
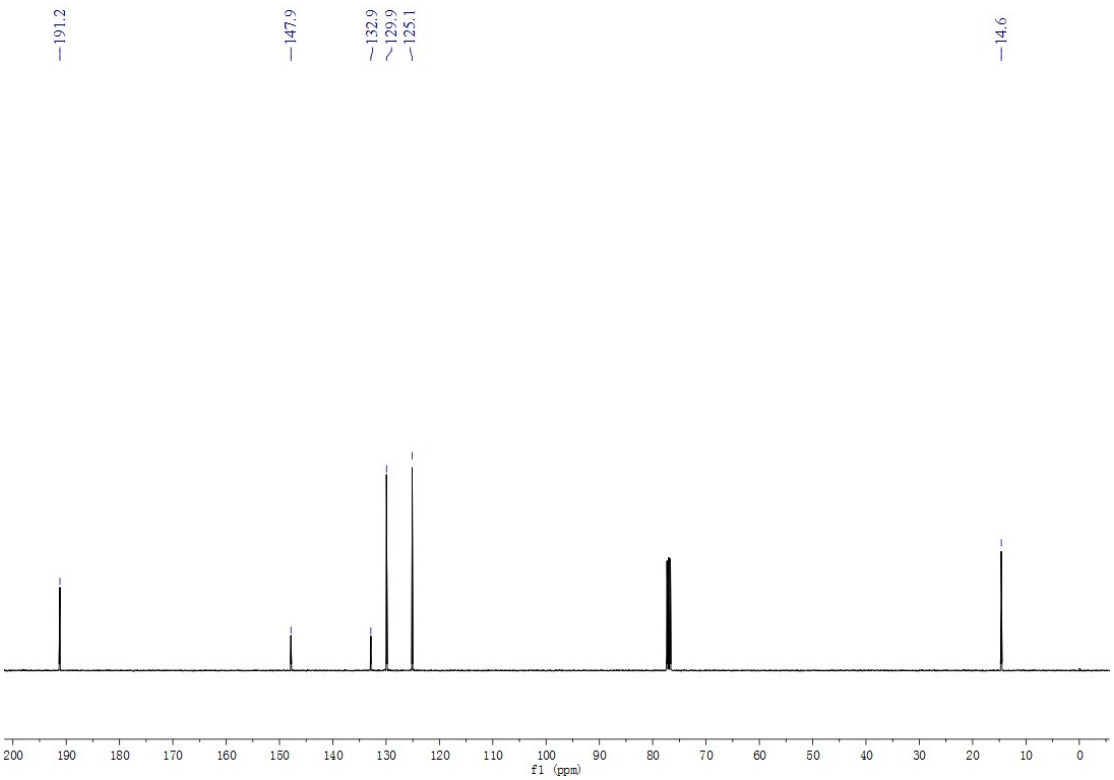




4-(methylthio)benzaldehyde (2g)





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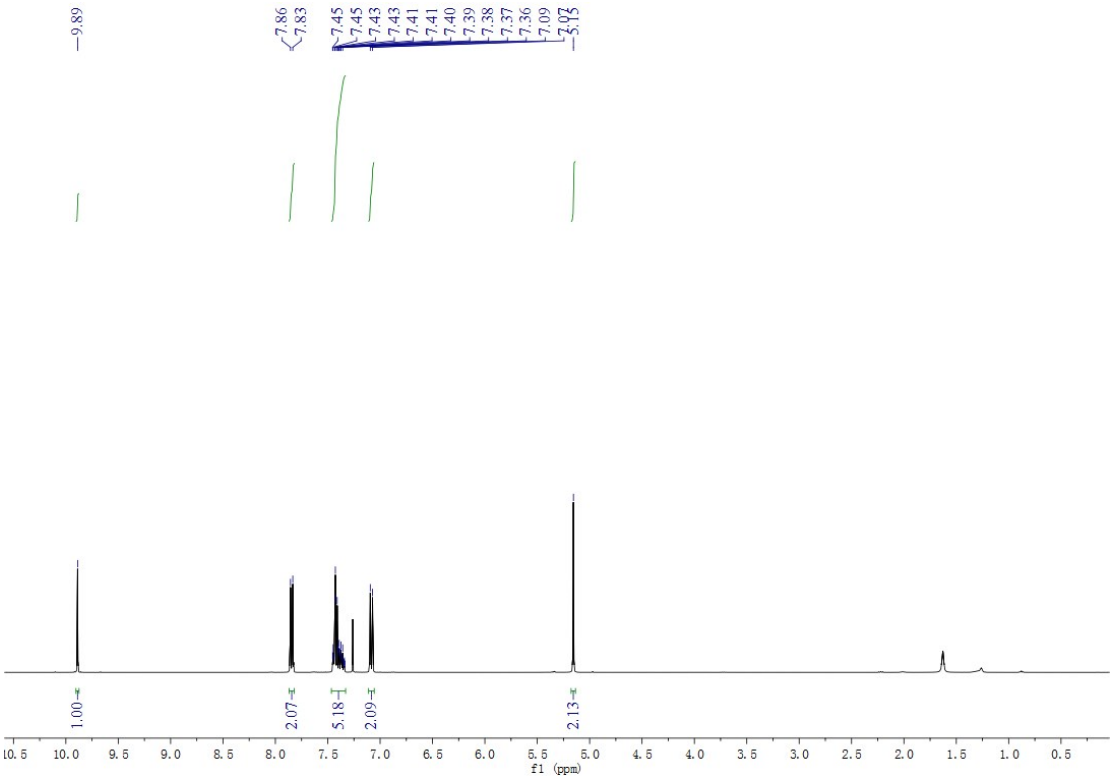

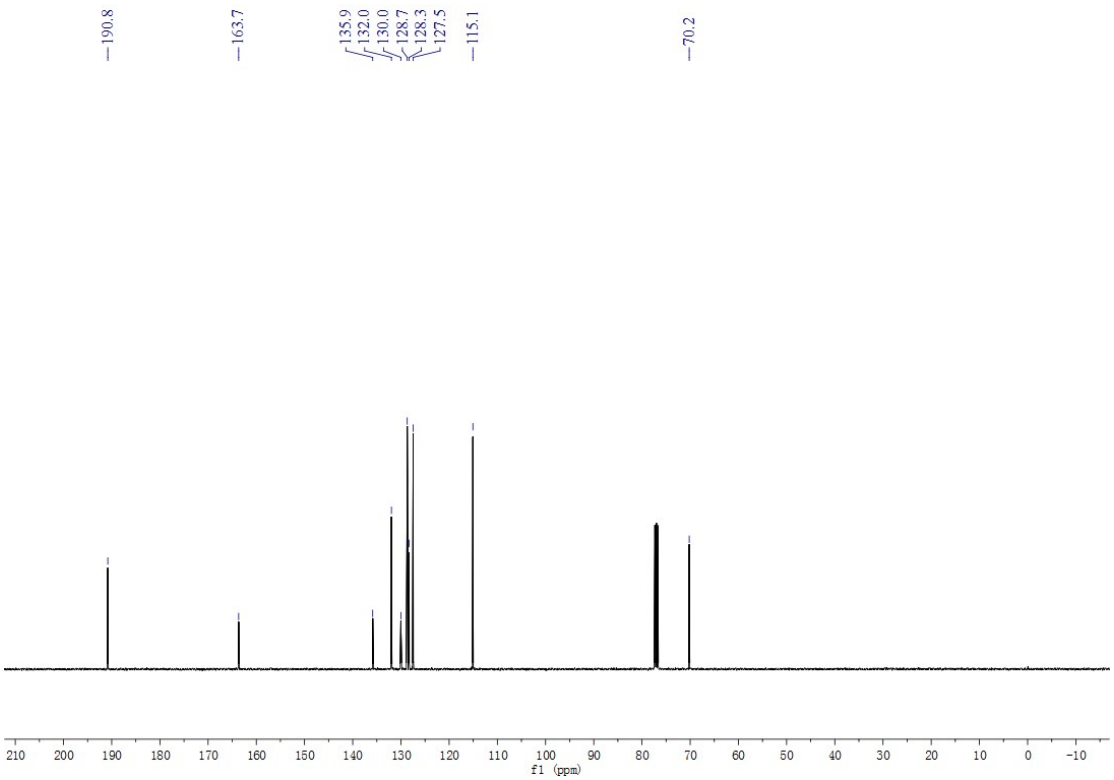

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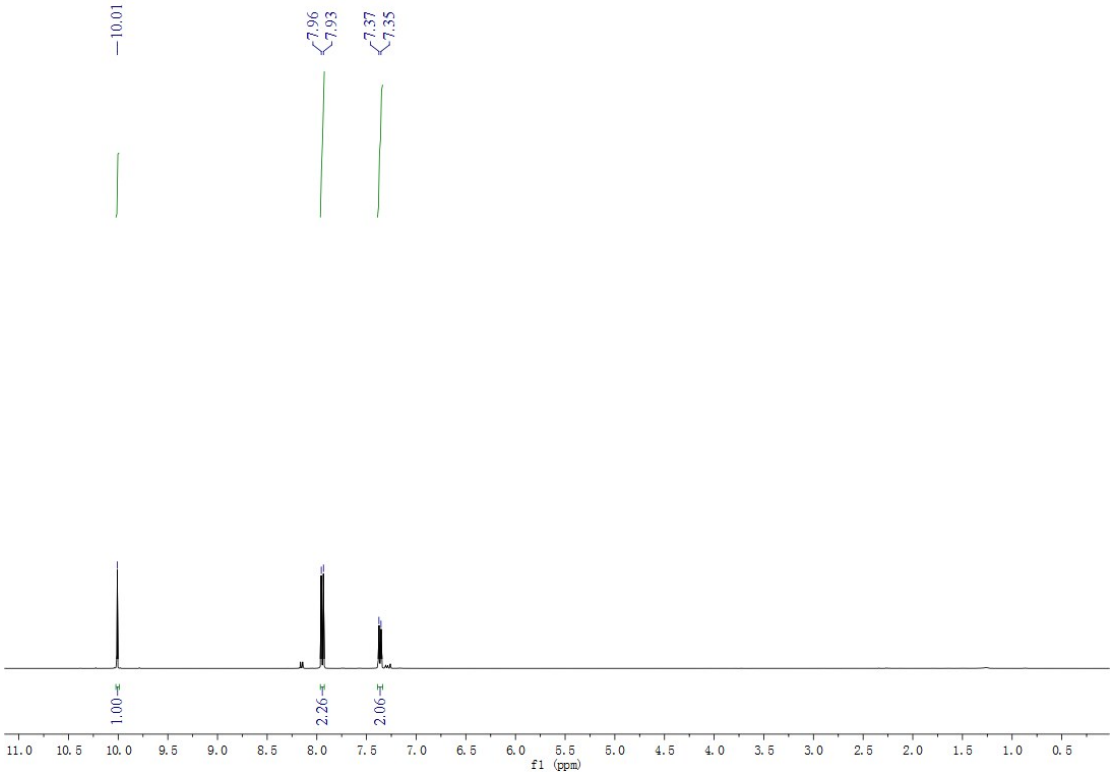

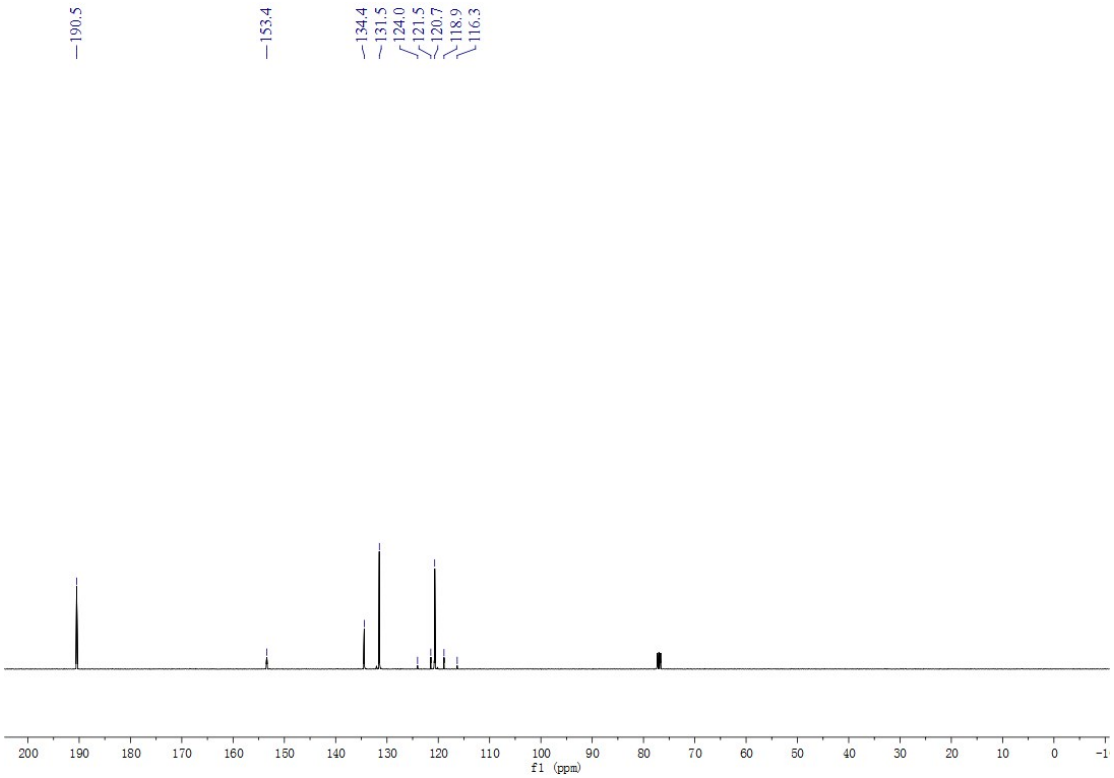
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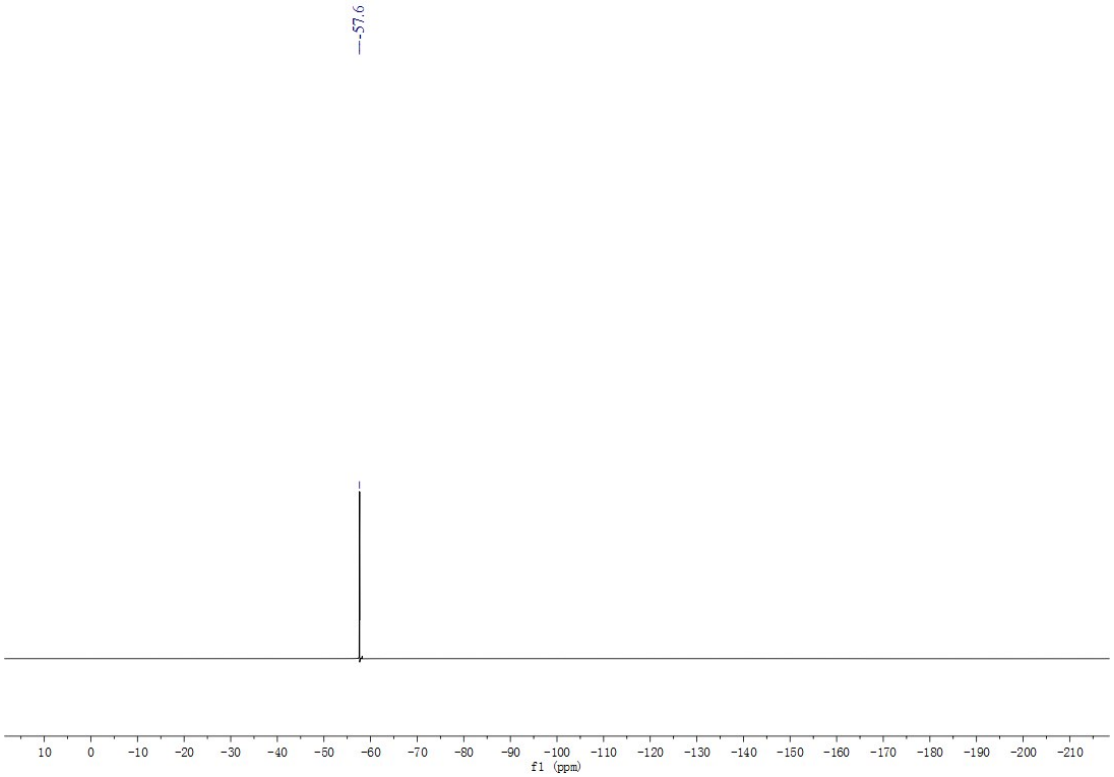
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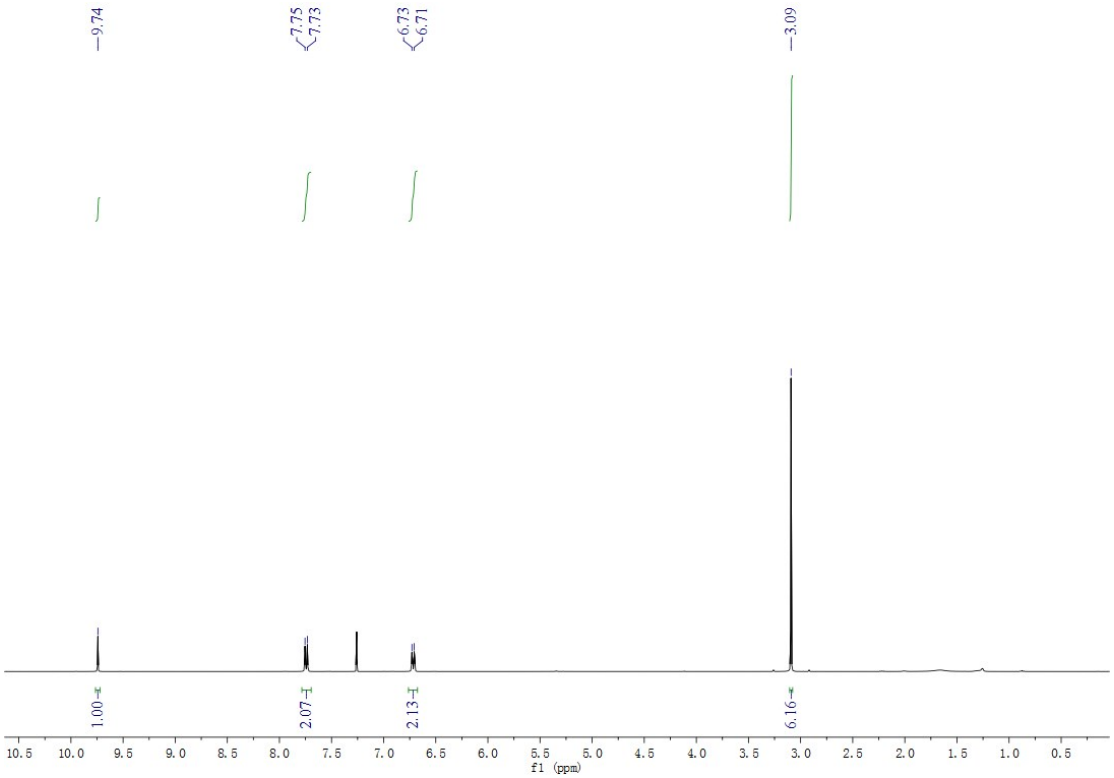
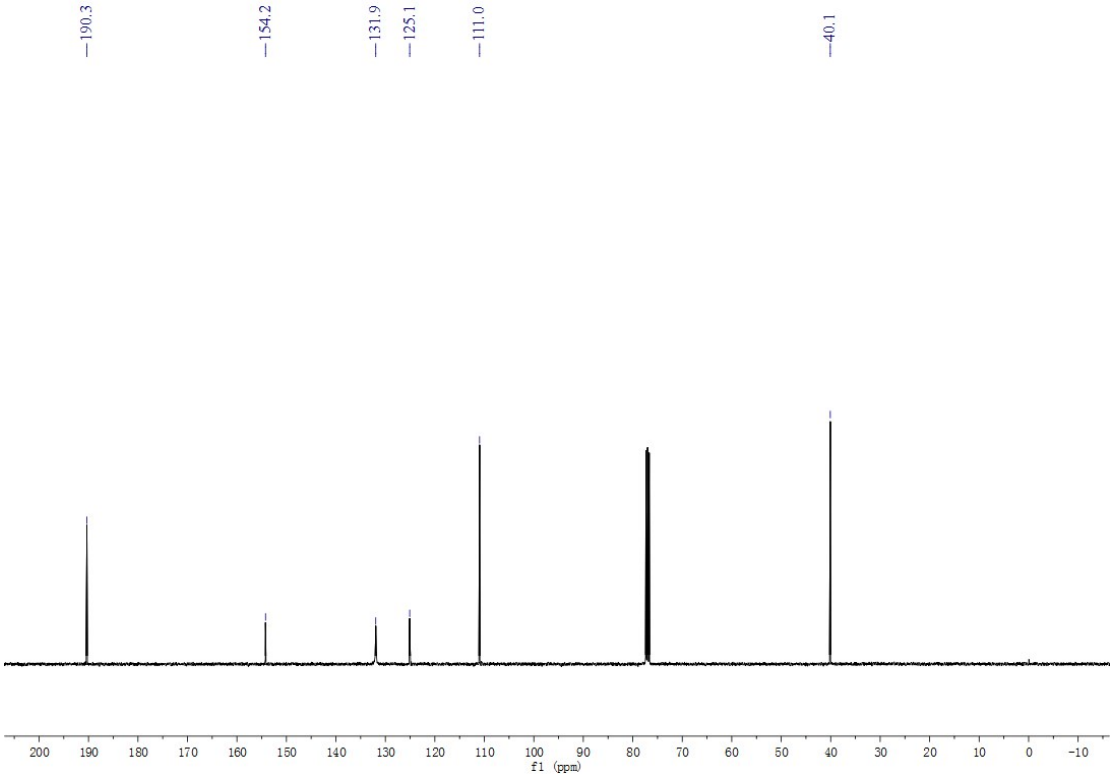
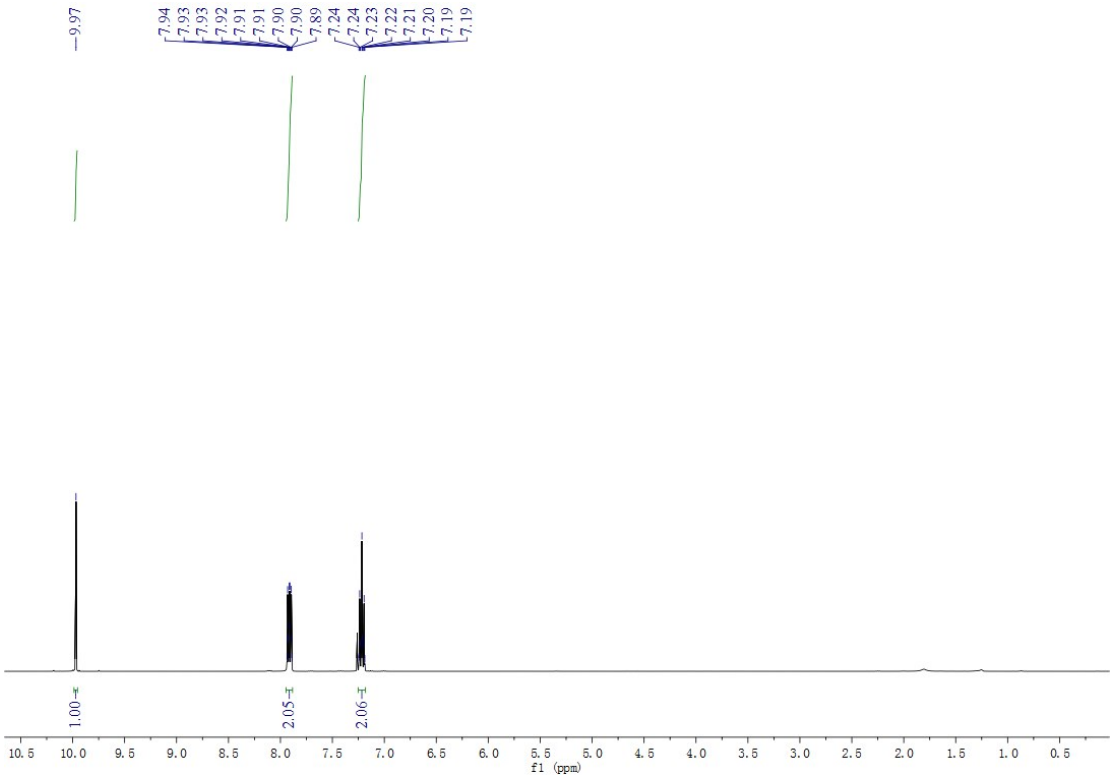




4-fluorobenzaldehyde (2k)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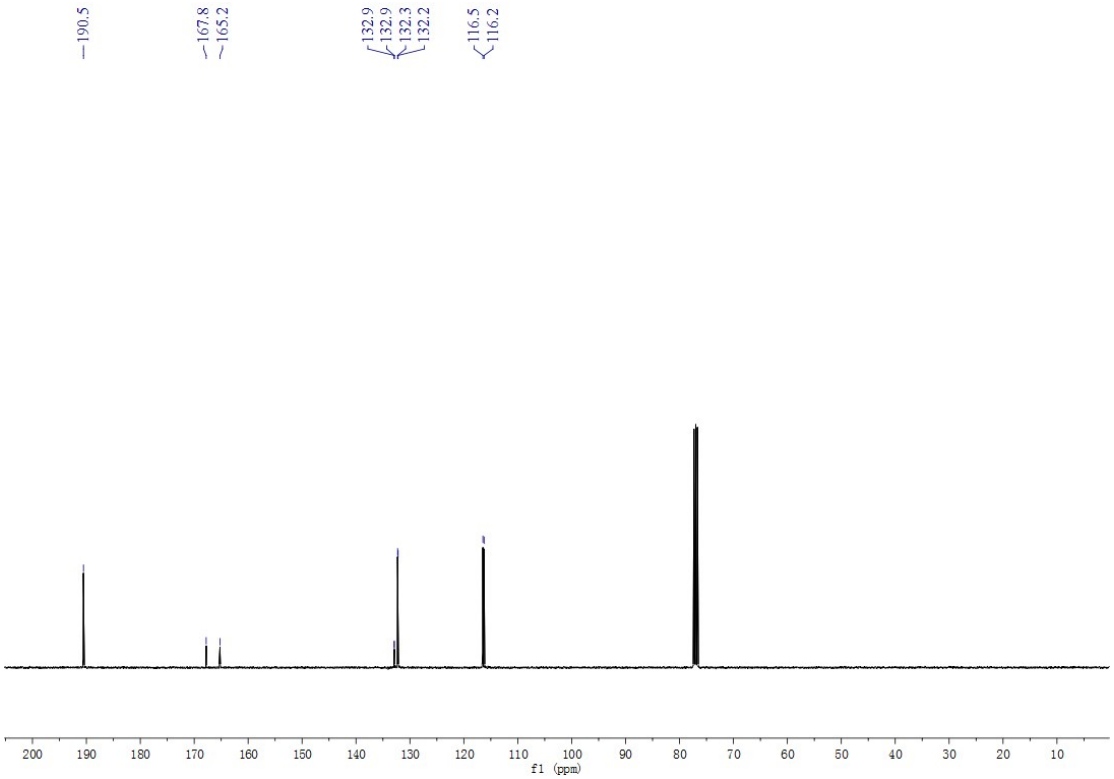
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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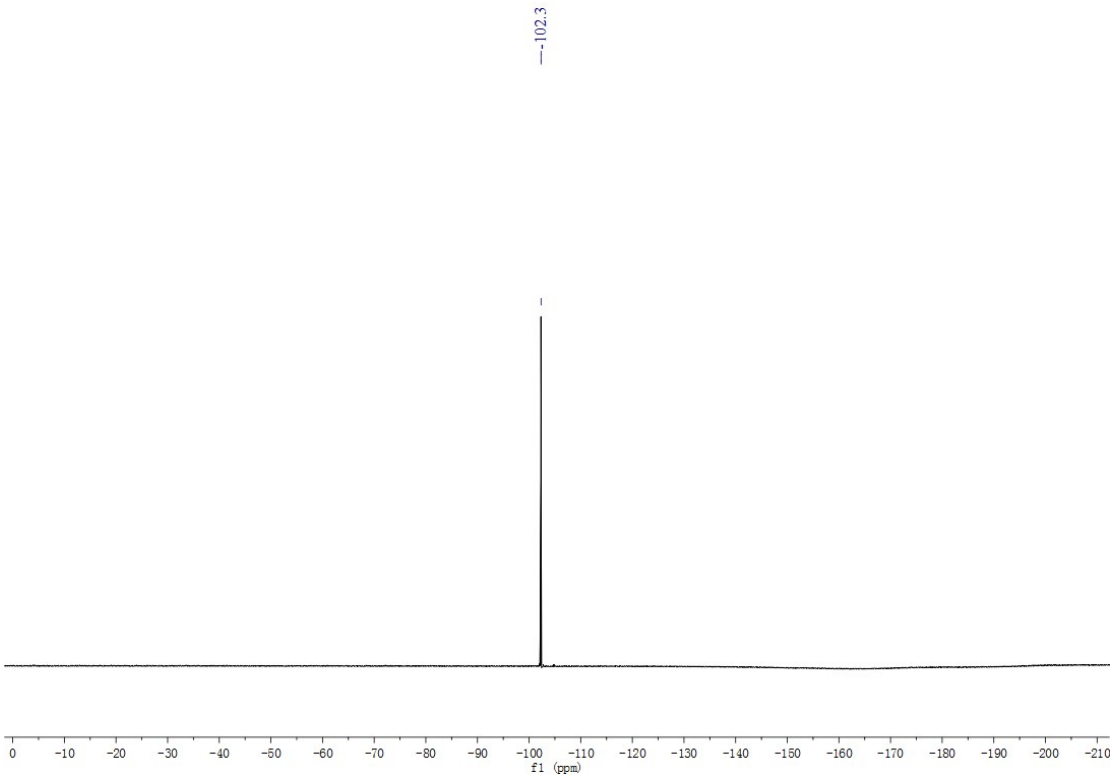
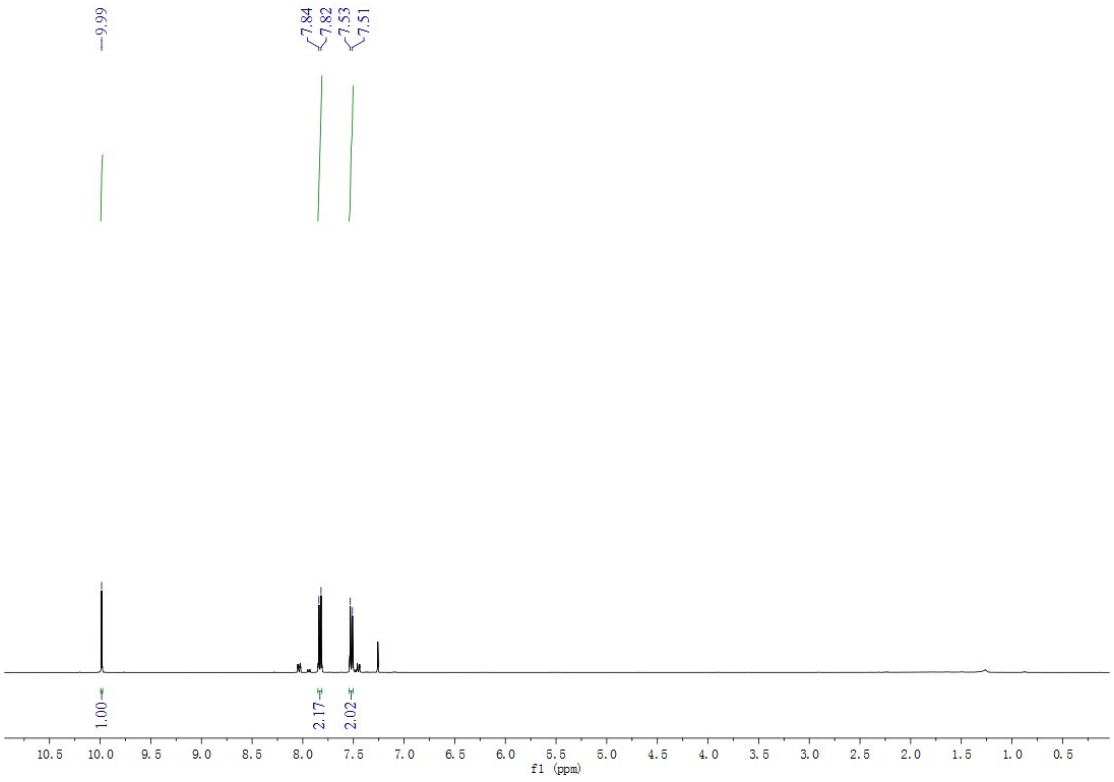
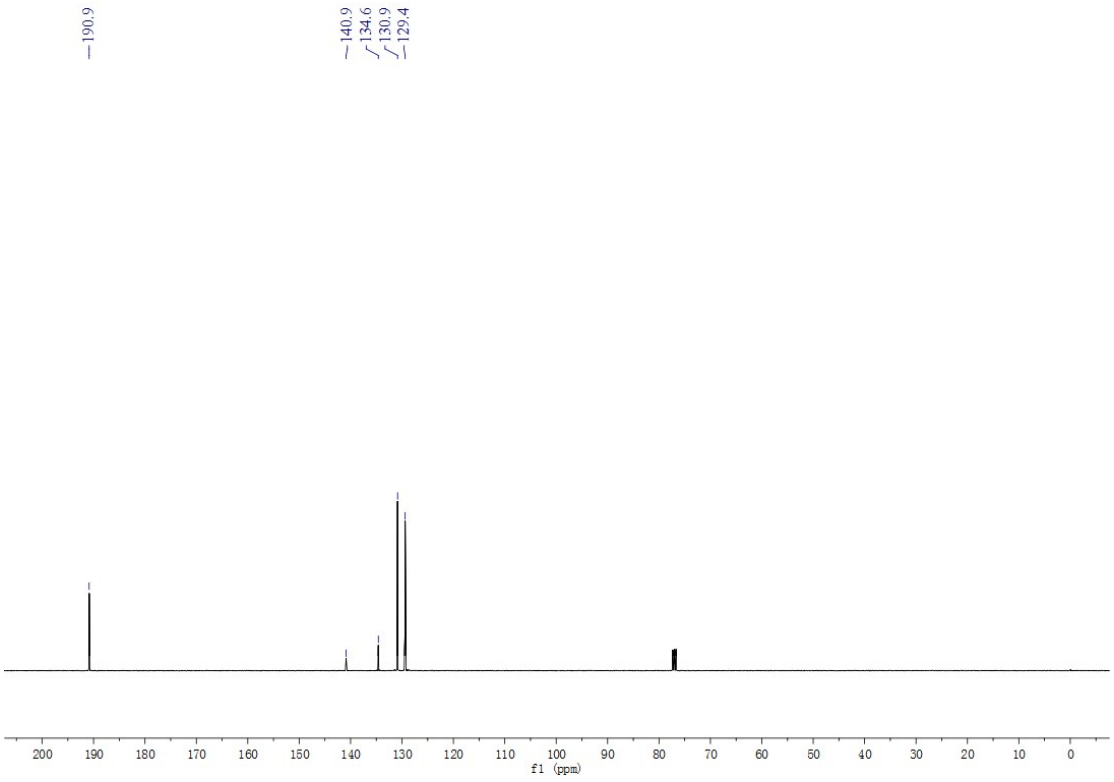
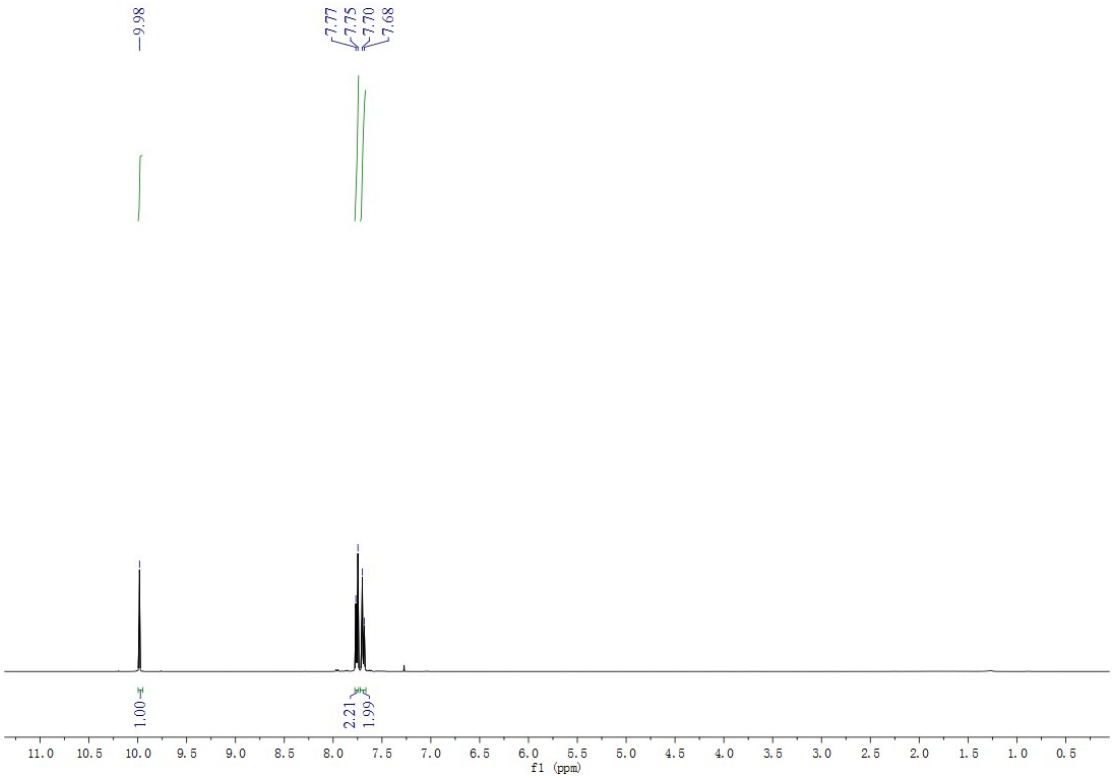


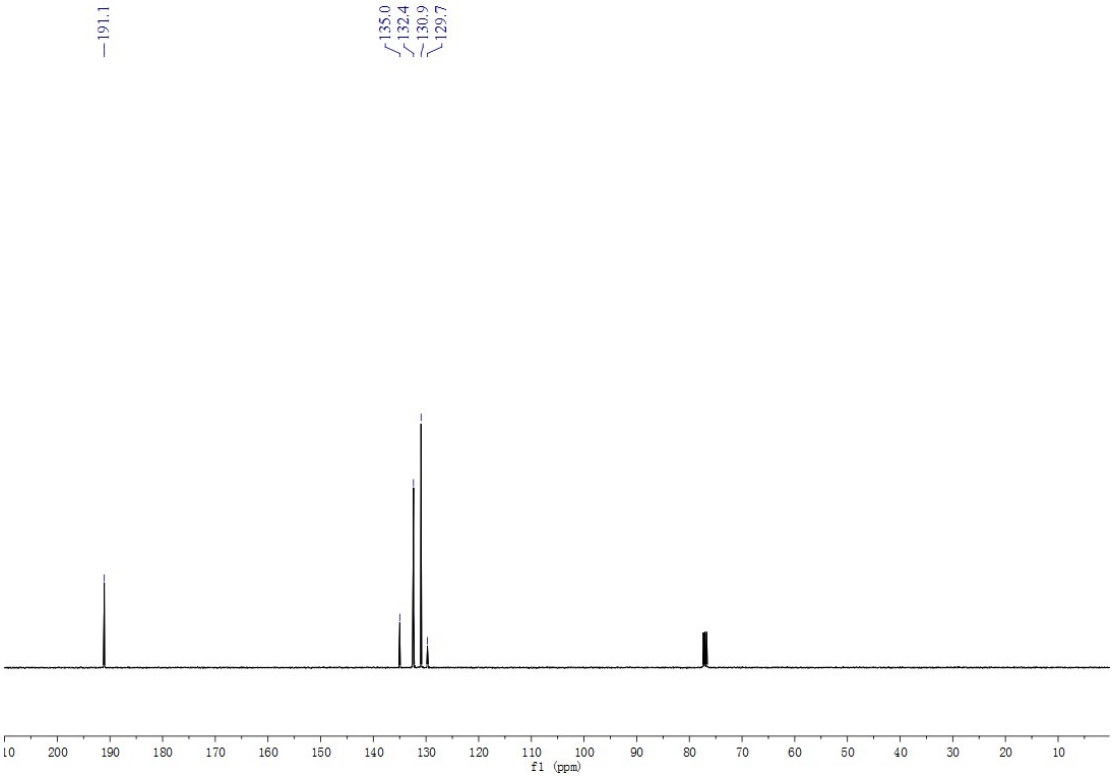
4-chlorobenzaldehyde (2l)



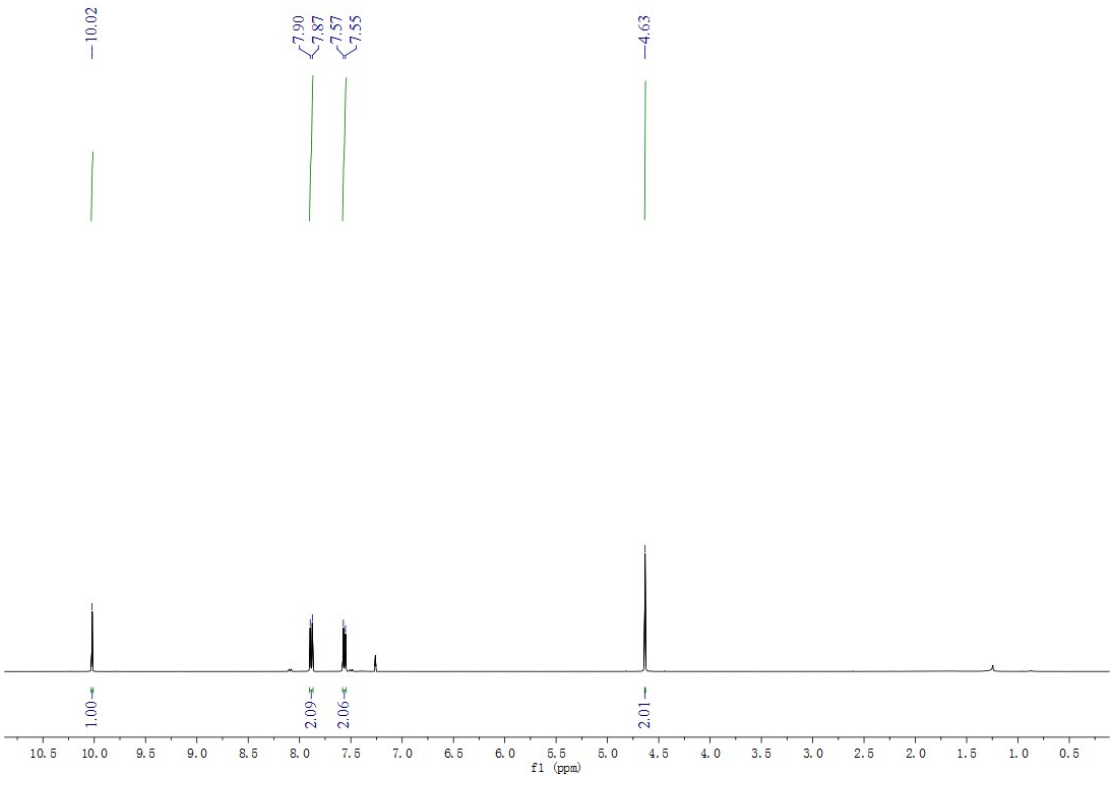


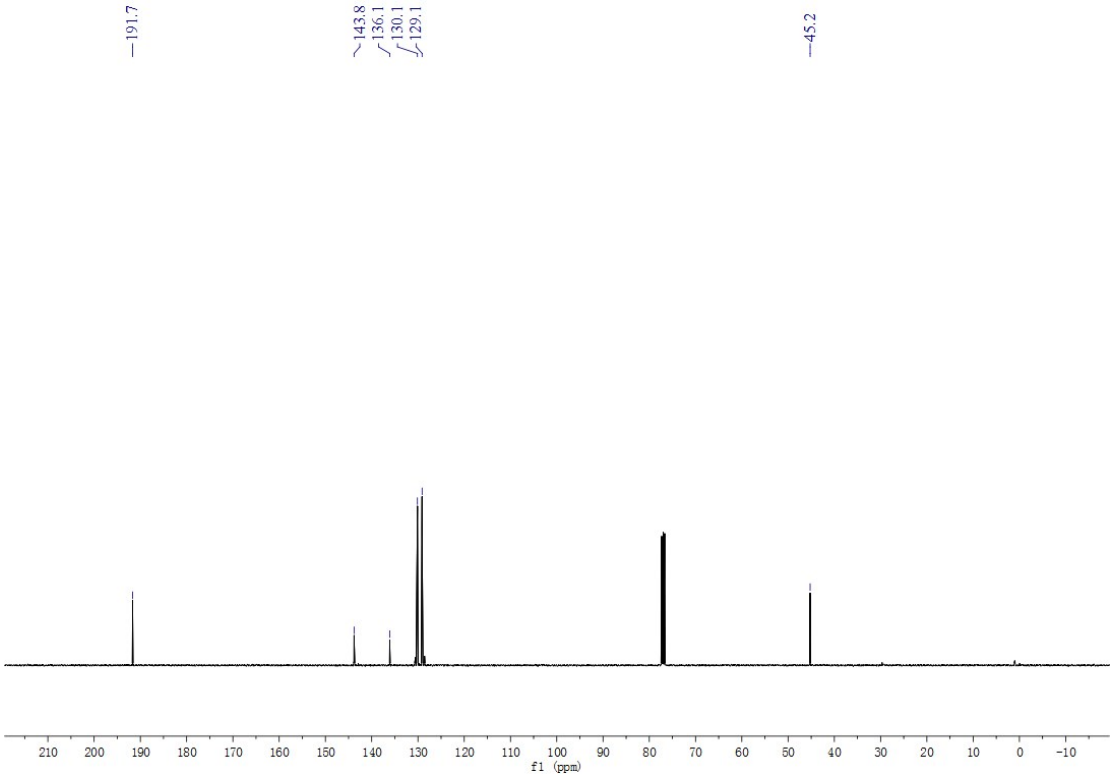
4-bromobenzaldehyde (2m)



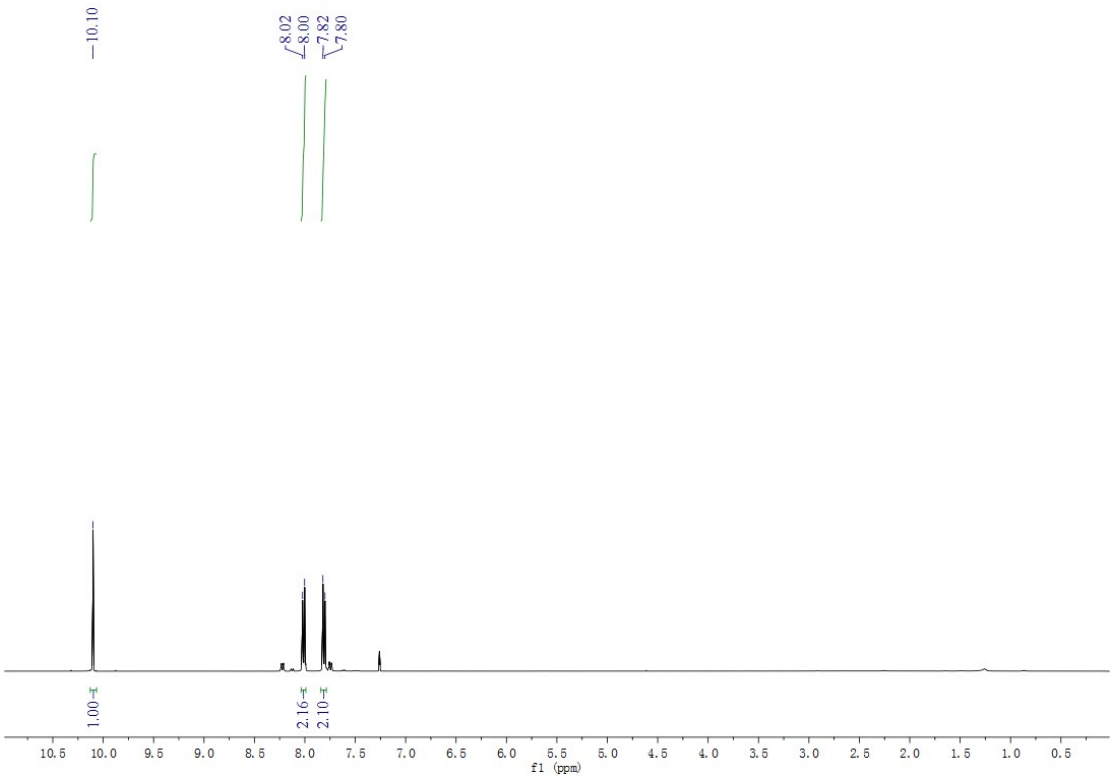


4-(chloromethyl)benzaldehyde (2n)





4-(trifluoromethyl)benzaldehyde (2o)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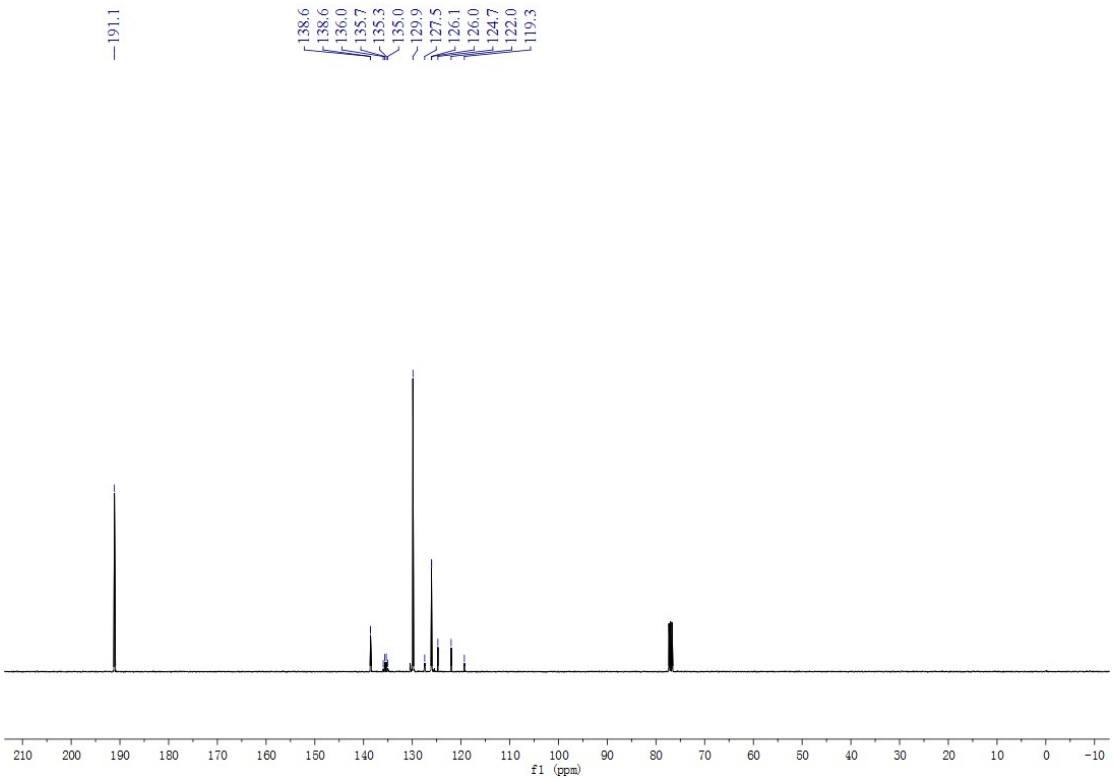
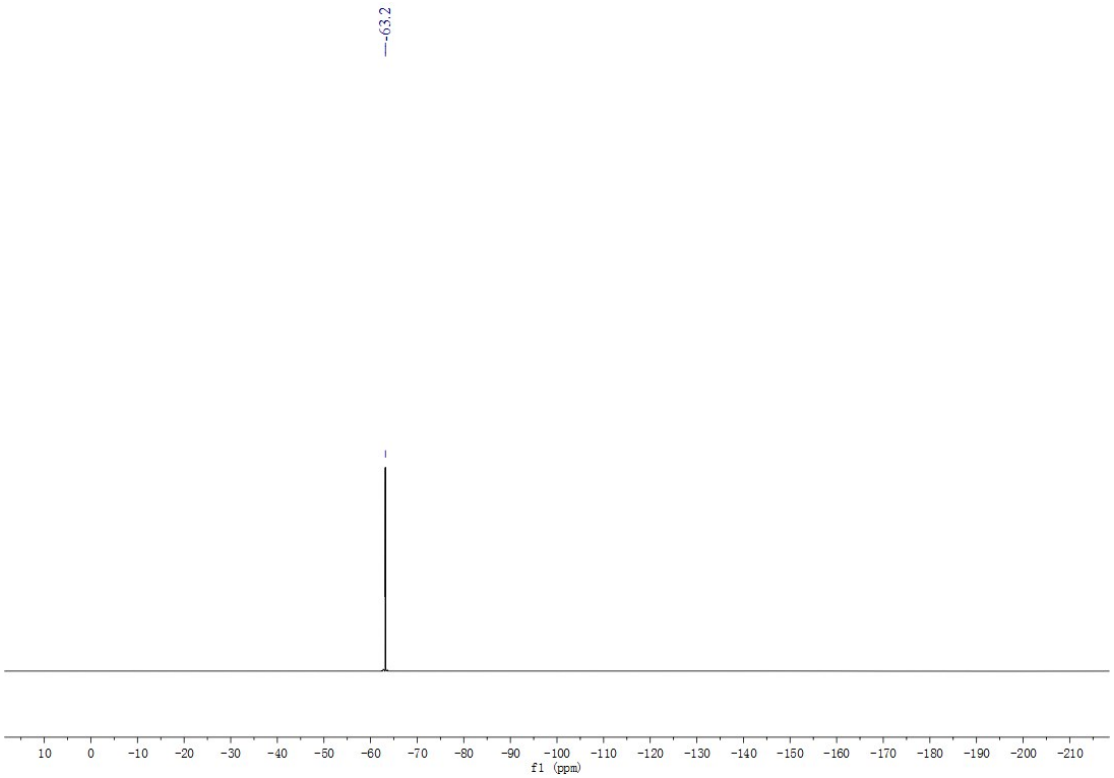
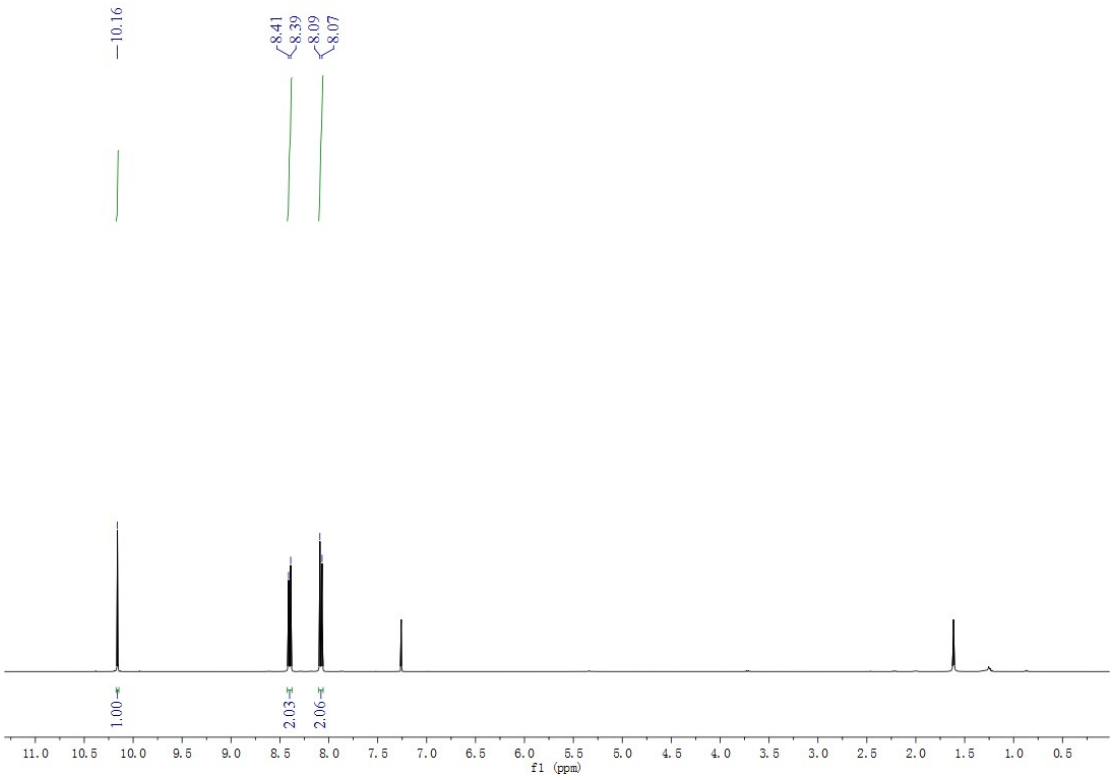
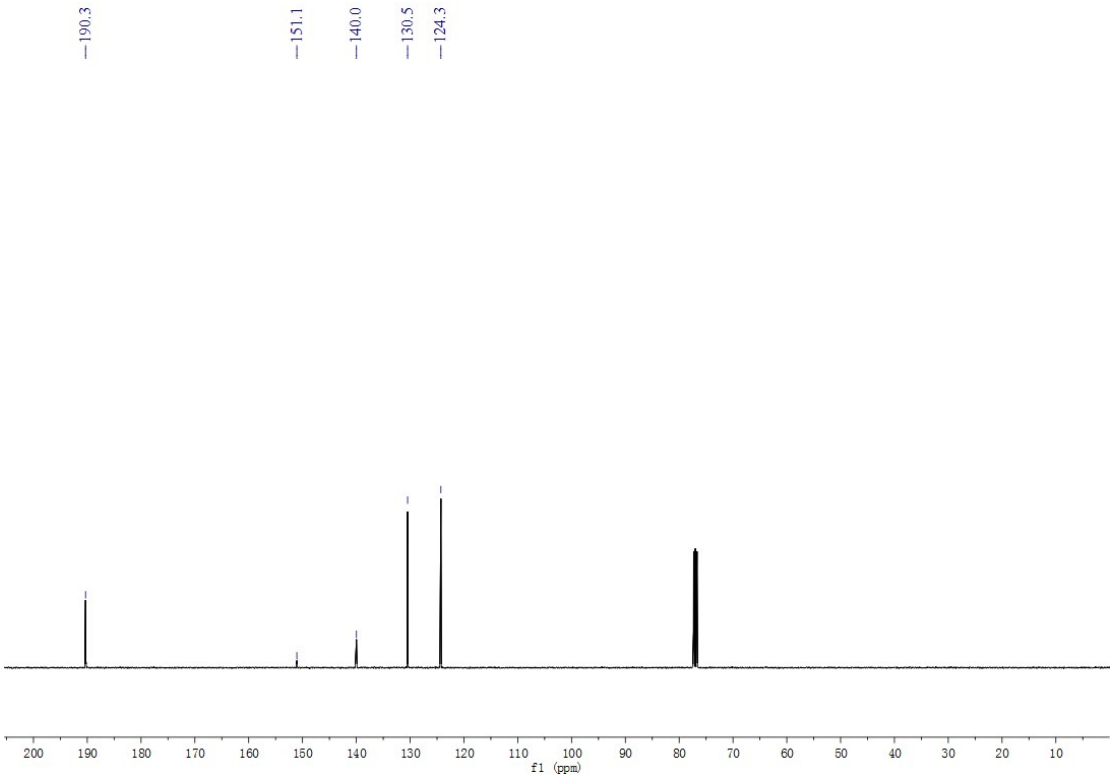
8.02
8.00
7.82
7.80
1.00
2.16
2.10
f1 (ppm)


191.1
138.6
138.6
136.0
135.7
135.3
135.0
129.9
127.5
126.1
126.0
124.7
122.0
119.3
f1 (ppm)

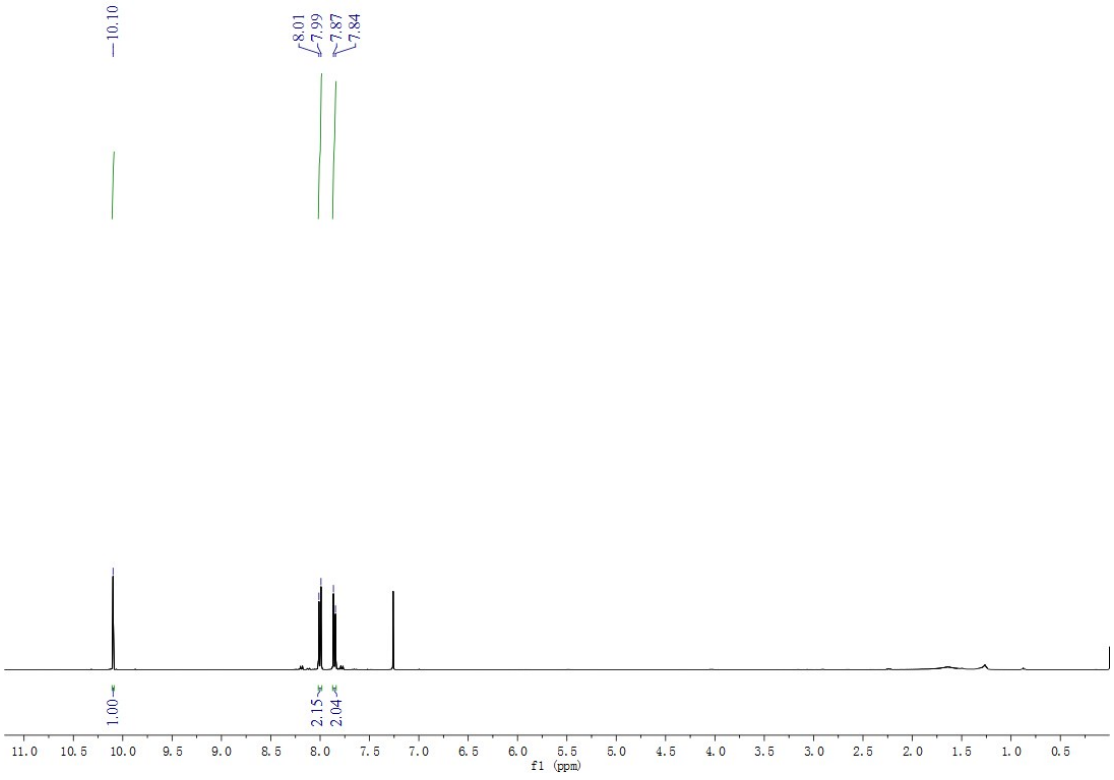


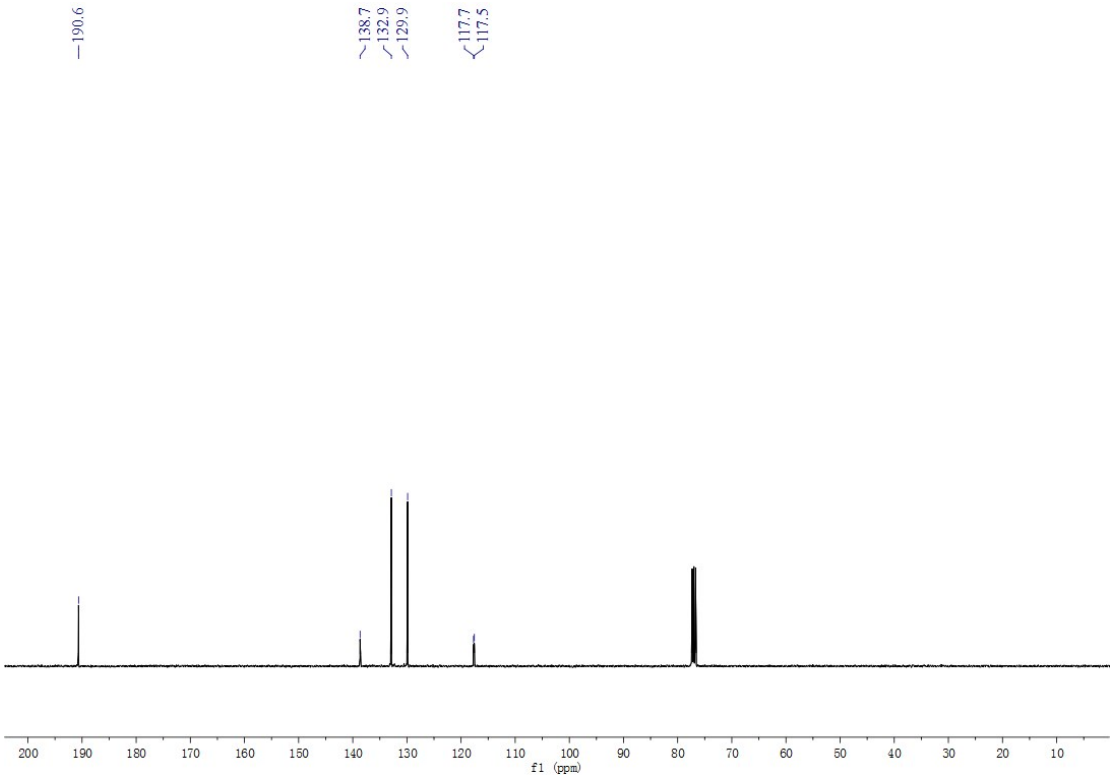
4-nitrobenzaldehyde (2p)



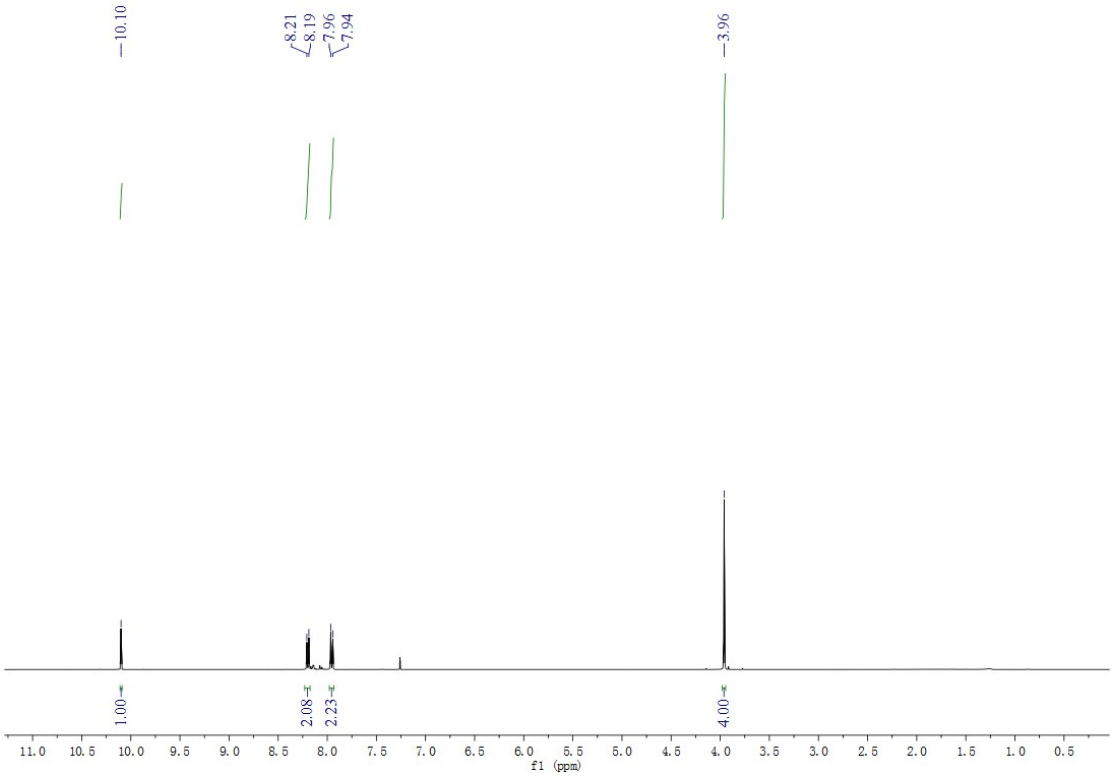


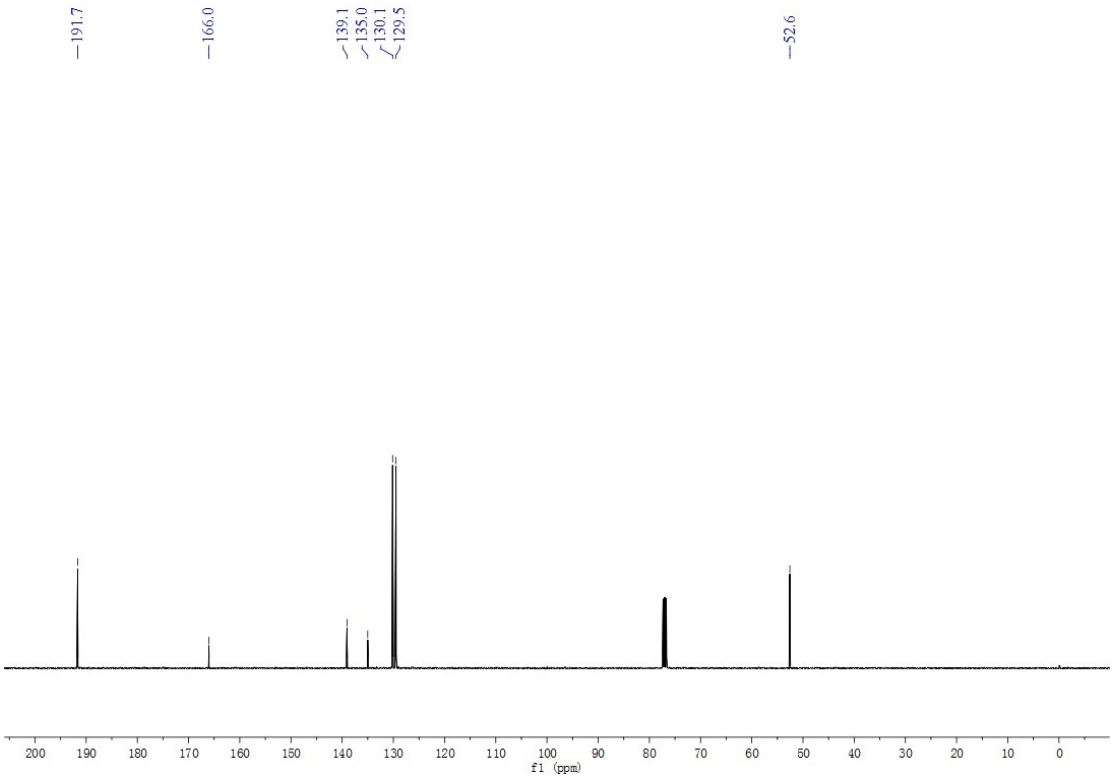
4-formylbenzonitrile (2q)



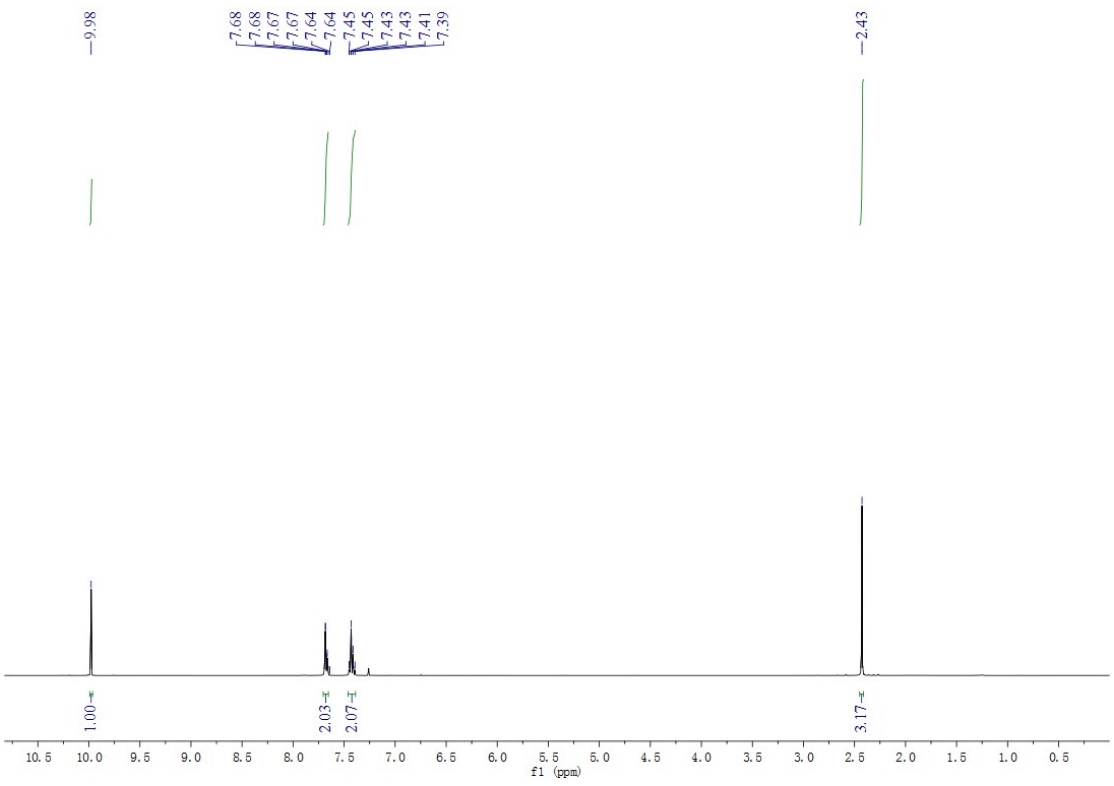


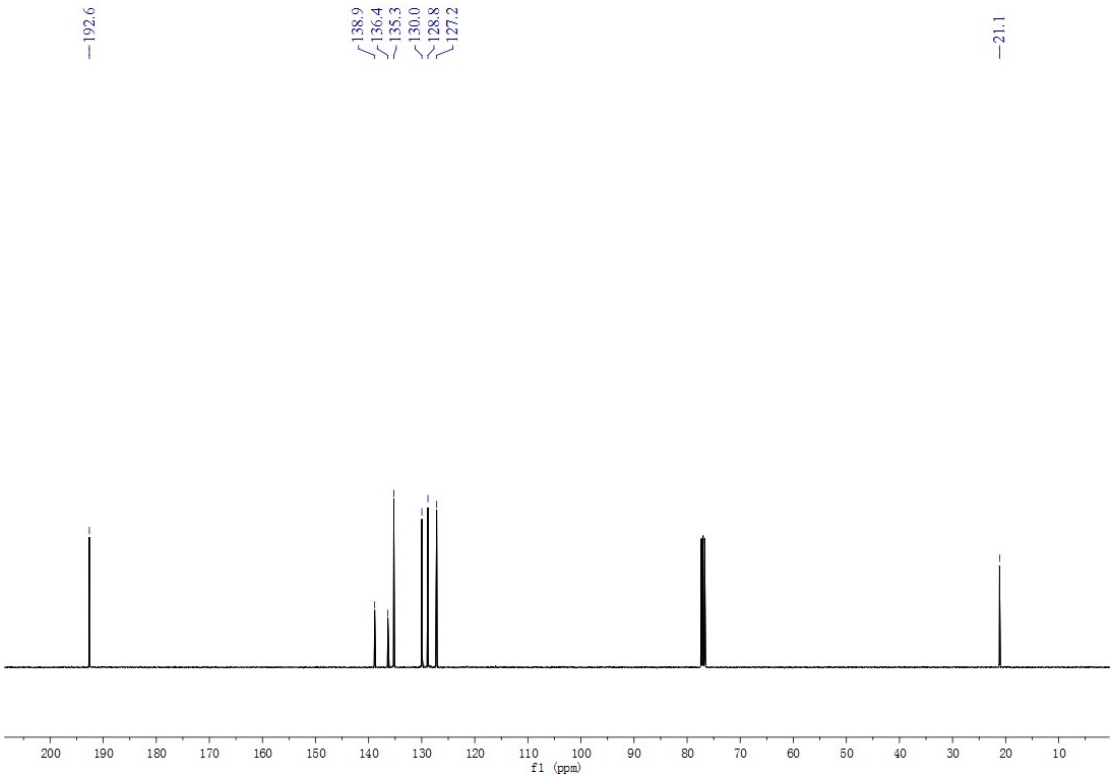
methyl 4-formylbenzoate (2r)



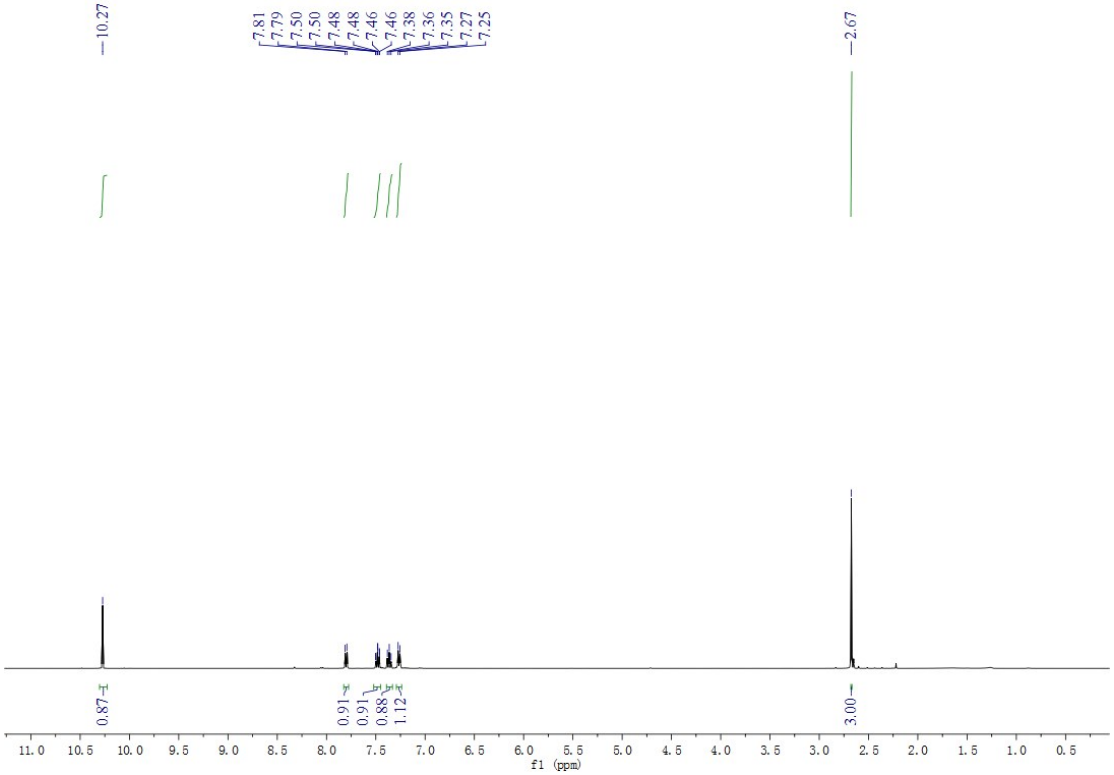


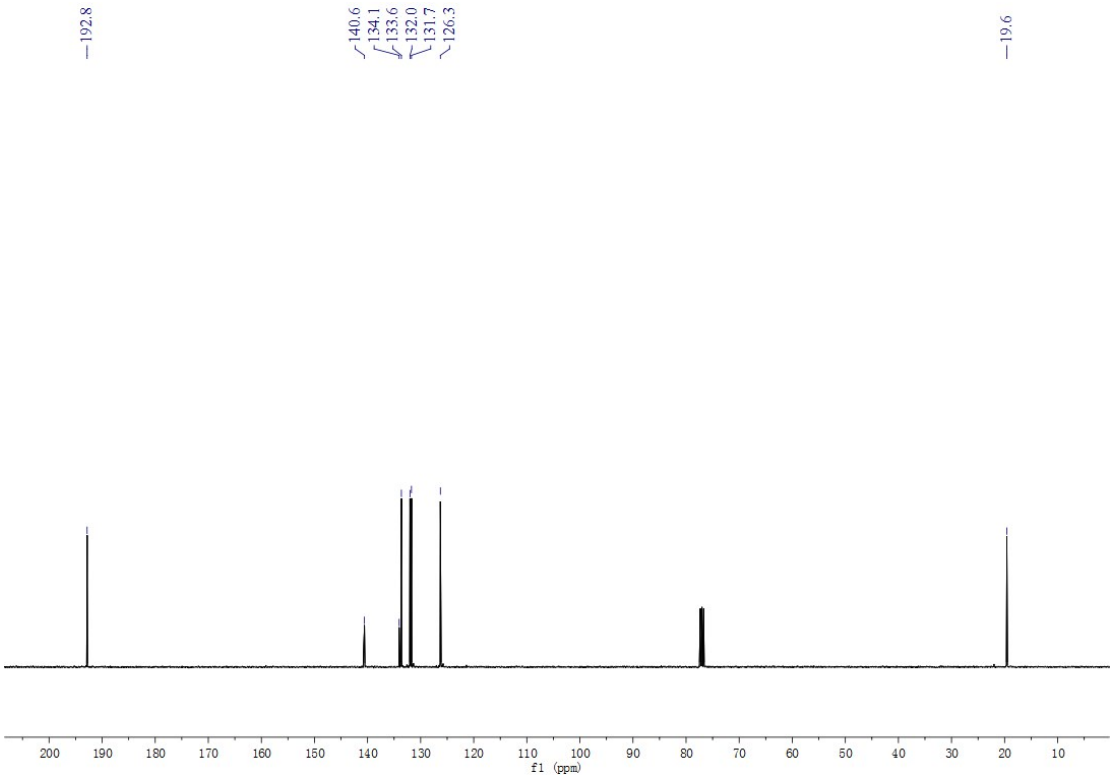
3-methylbenzaldehyde (2s)



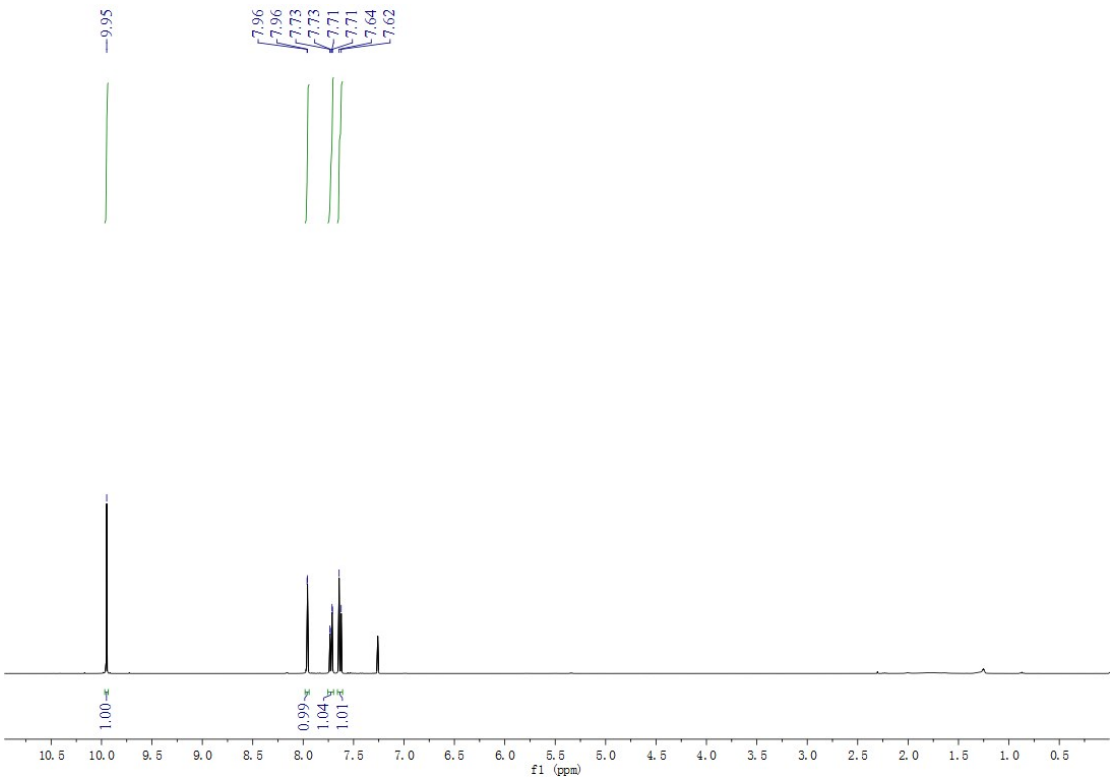


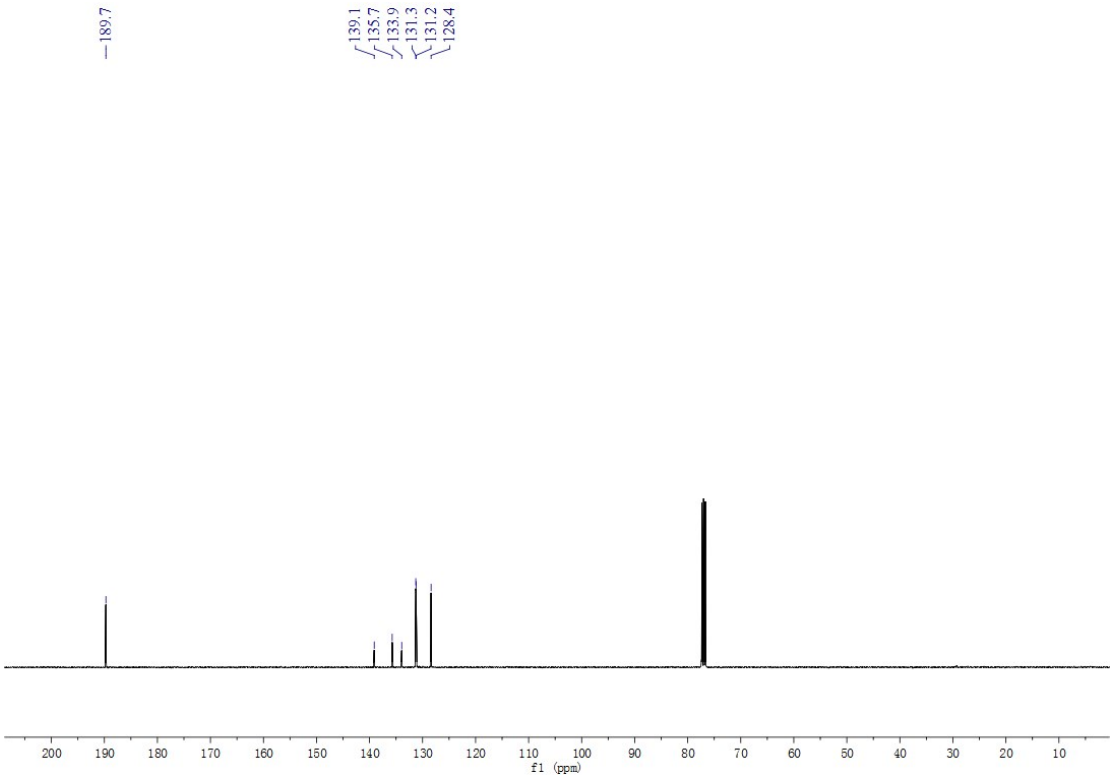
2-methylbenzaldehyde (2t)



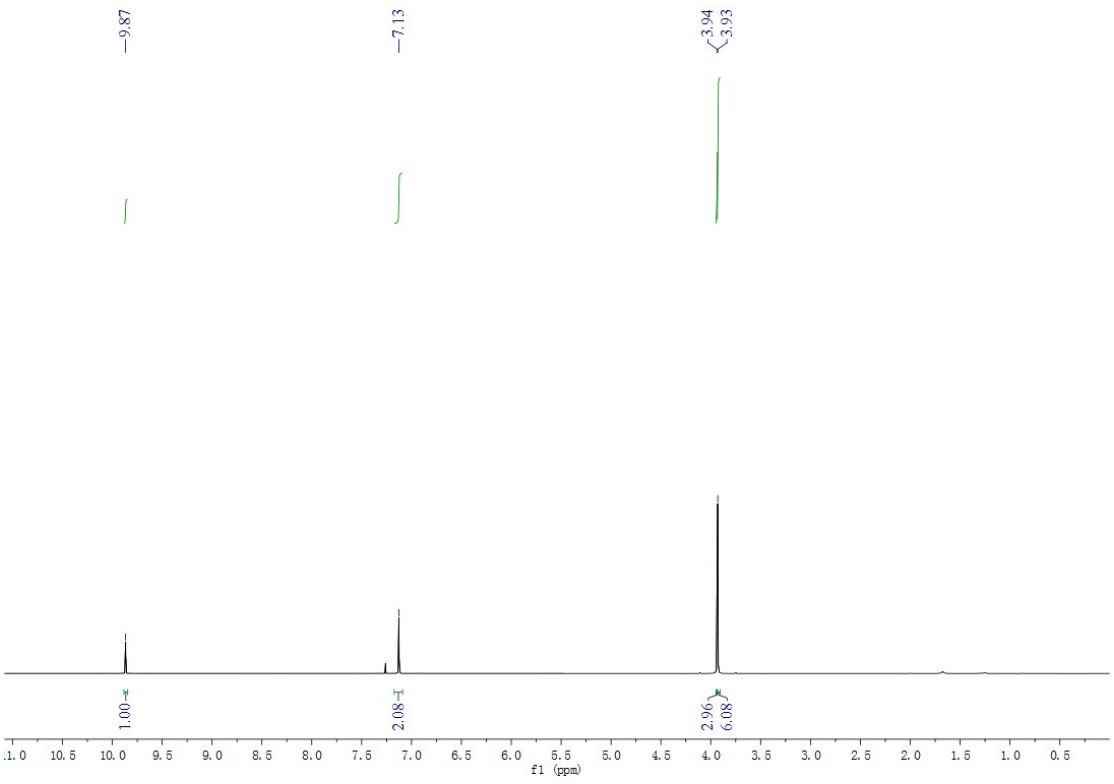


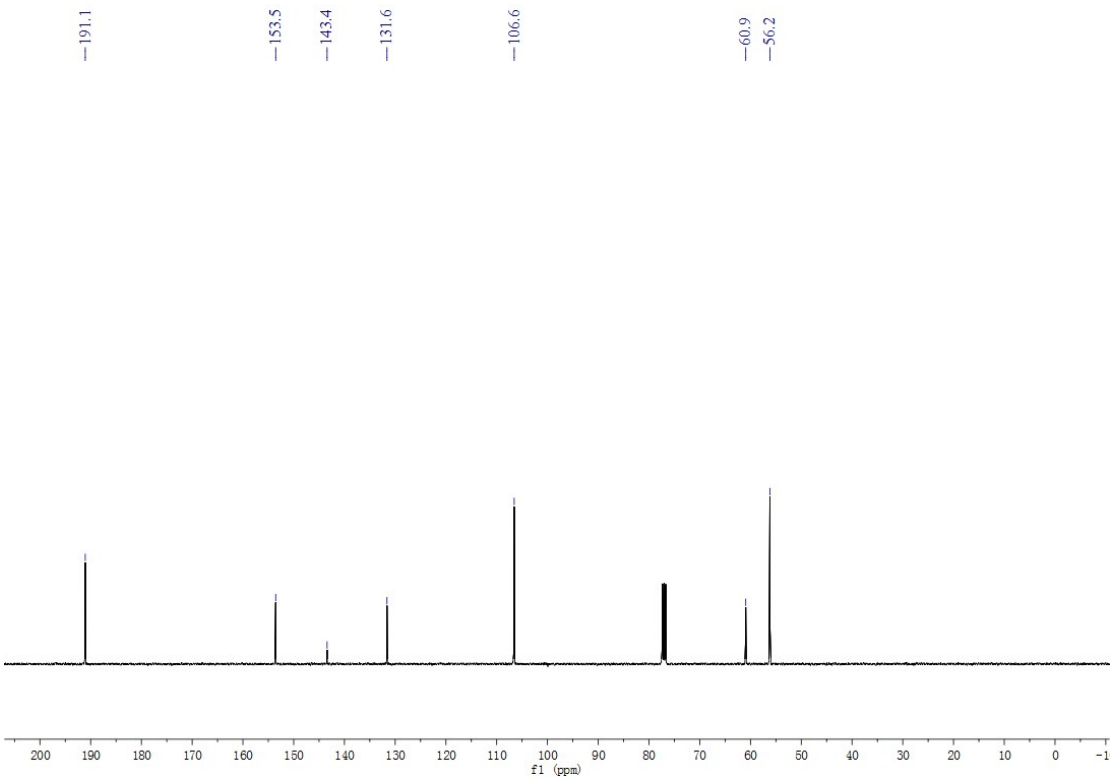
3,4-dichlorobenzaldehyde (2u)



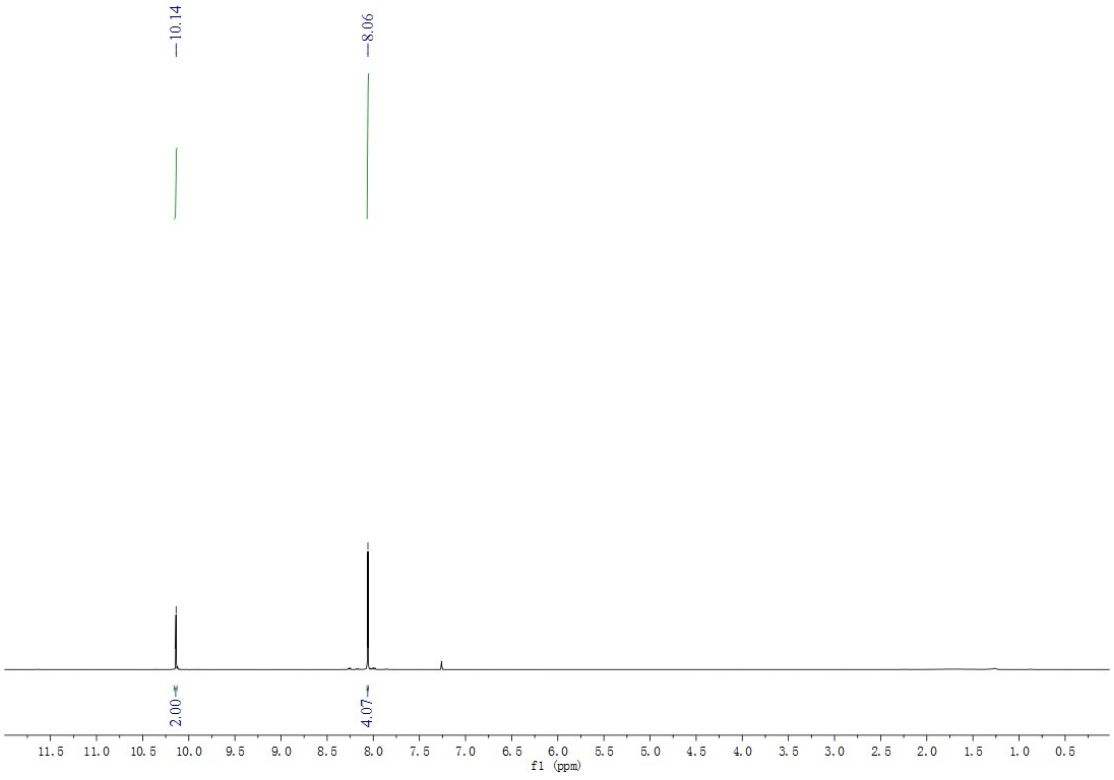


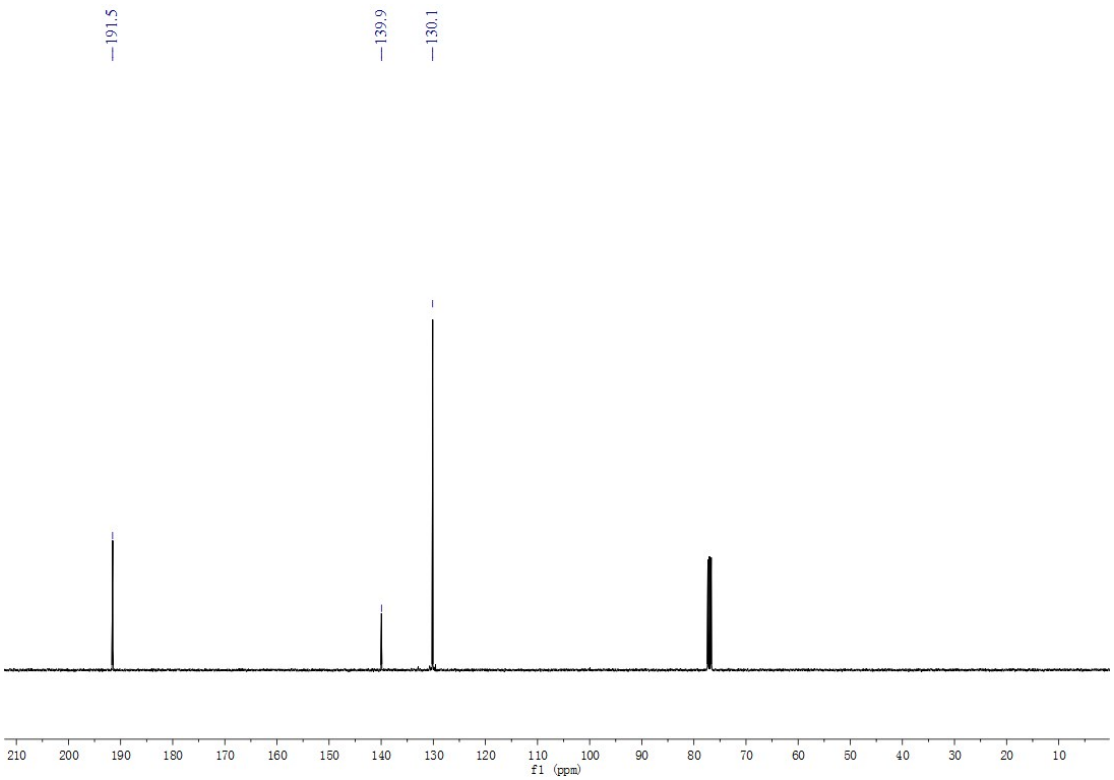
3,4,5-trimethoxybenzaldehyde (2v)



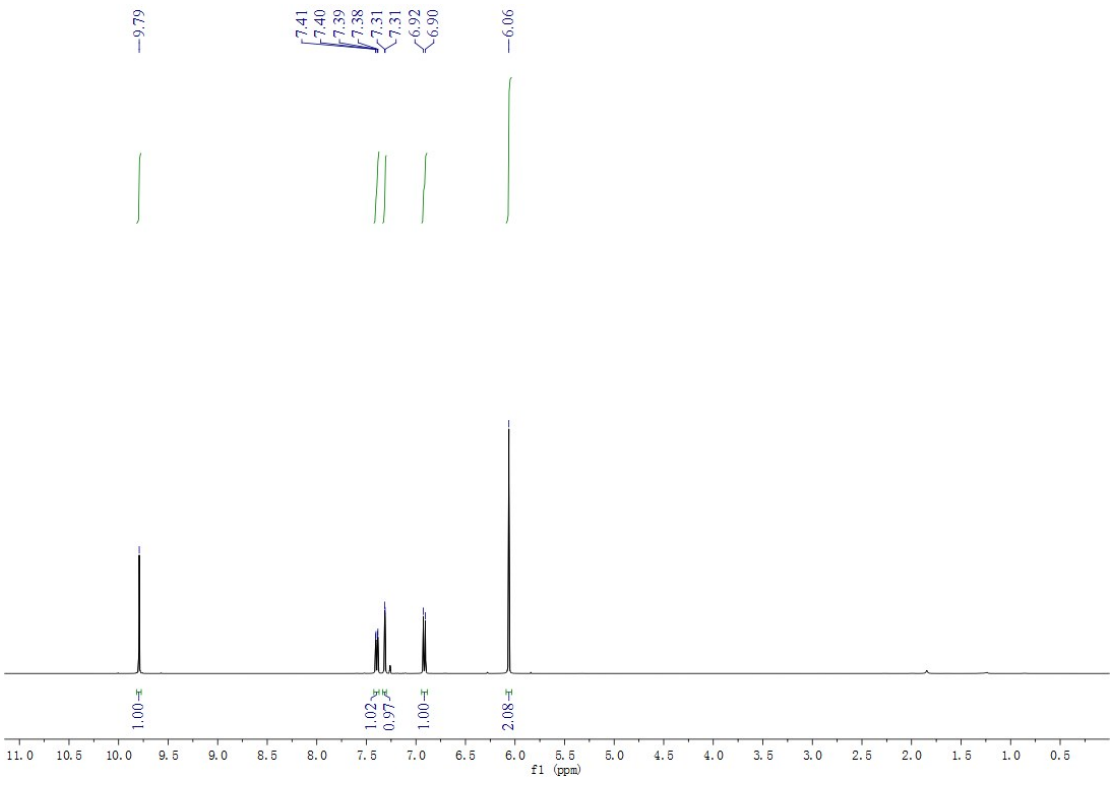


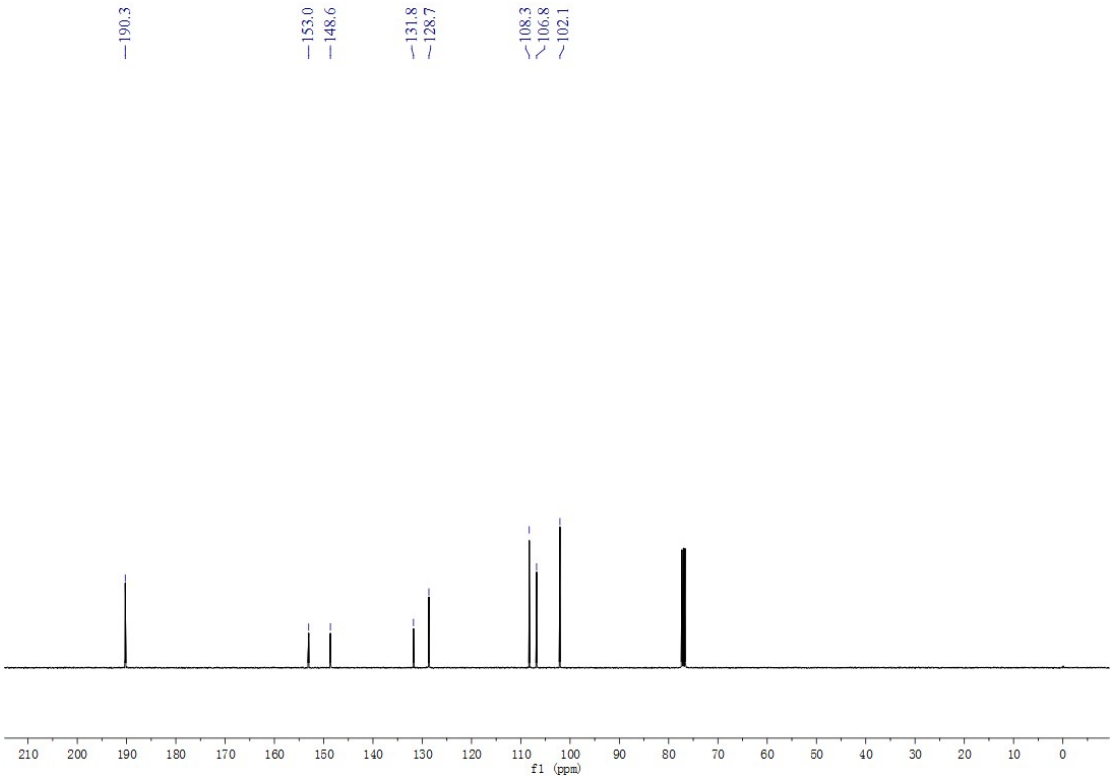
terephthalaldehyde (2w)



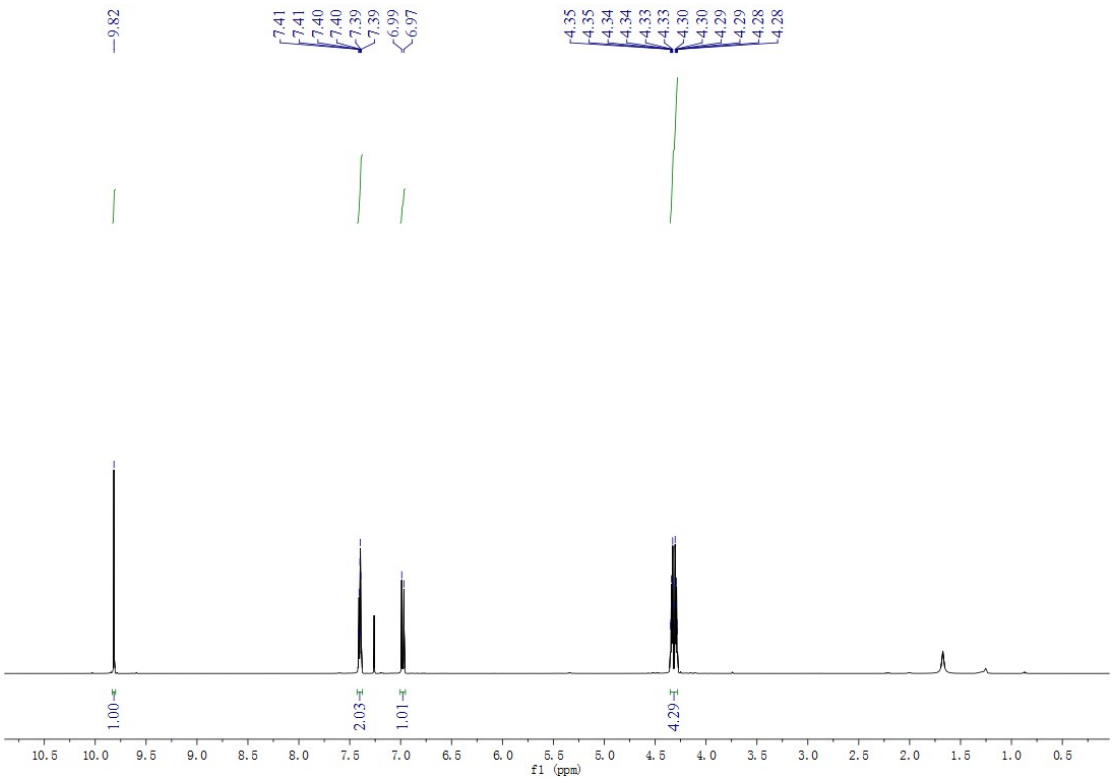


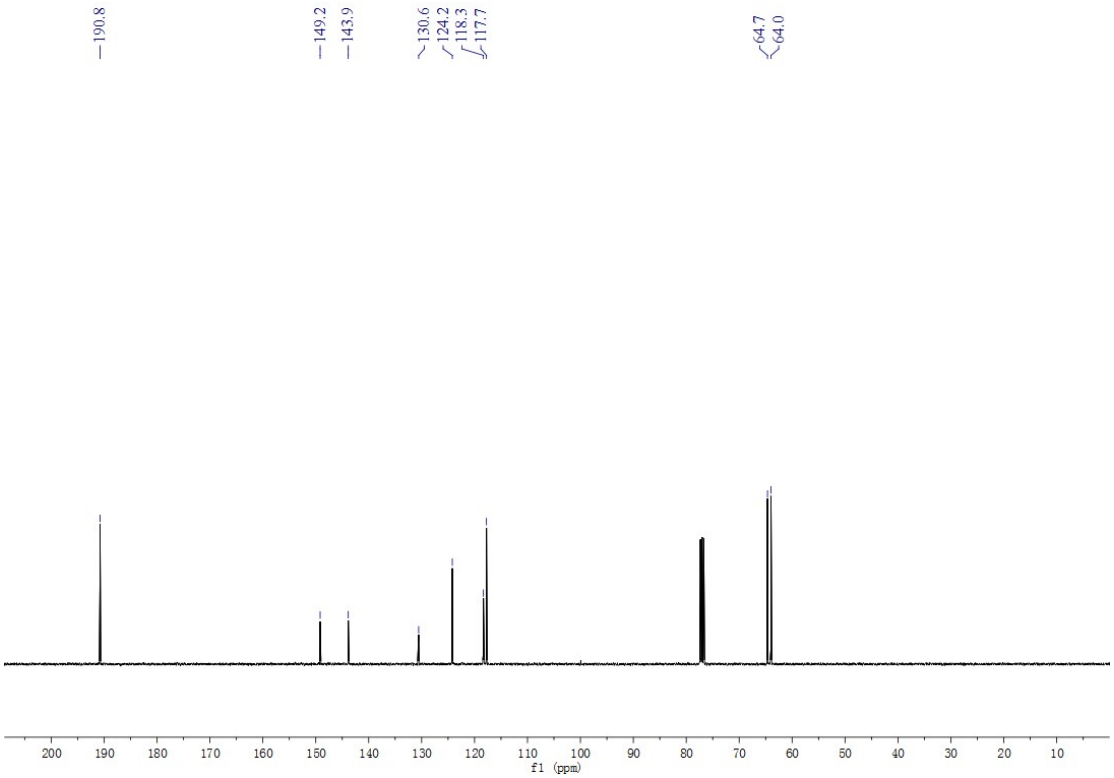
benzo[*d*][1,3]dioxole-5-carbaldehyde (2x)



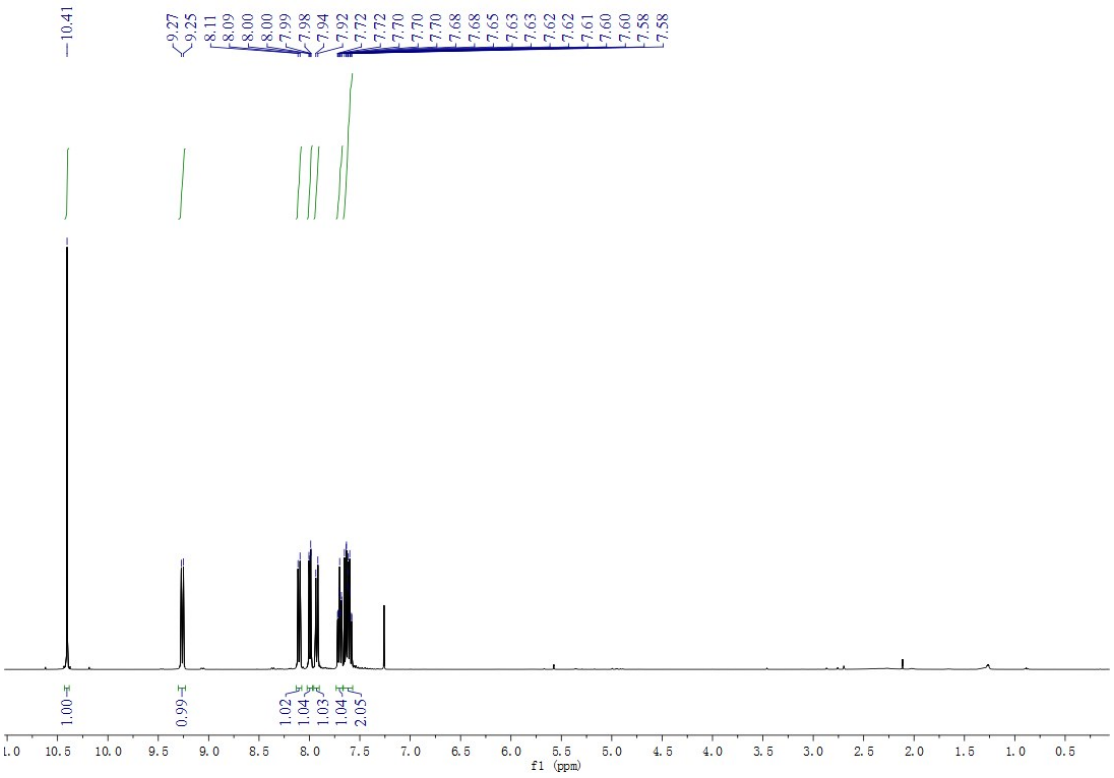


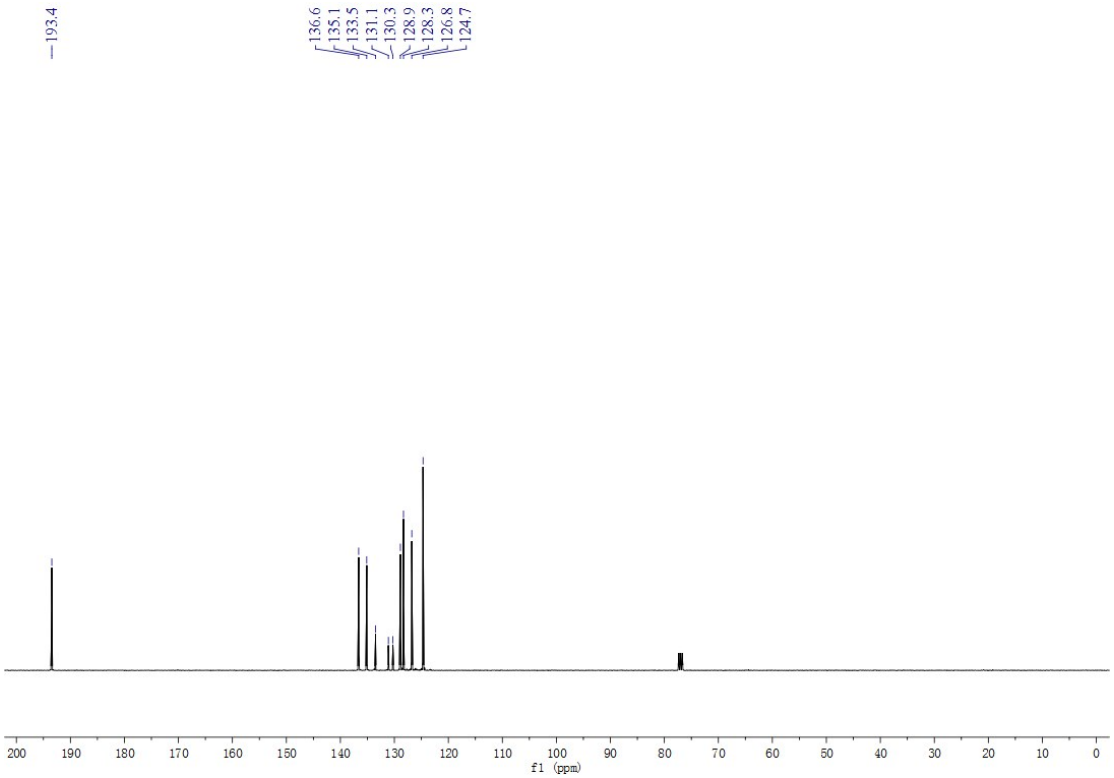
2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde (2y)



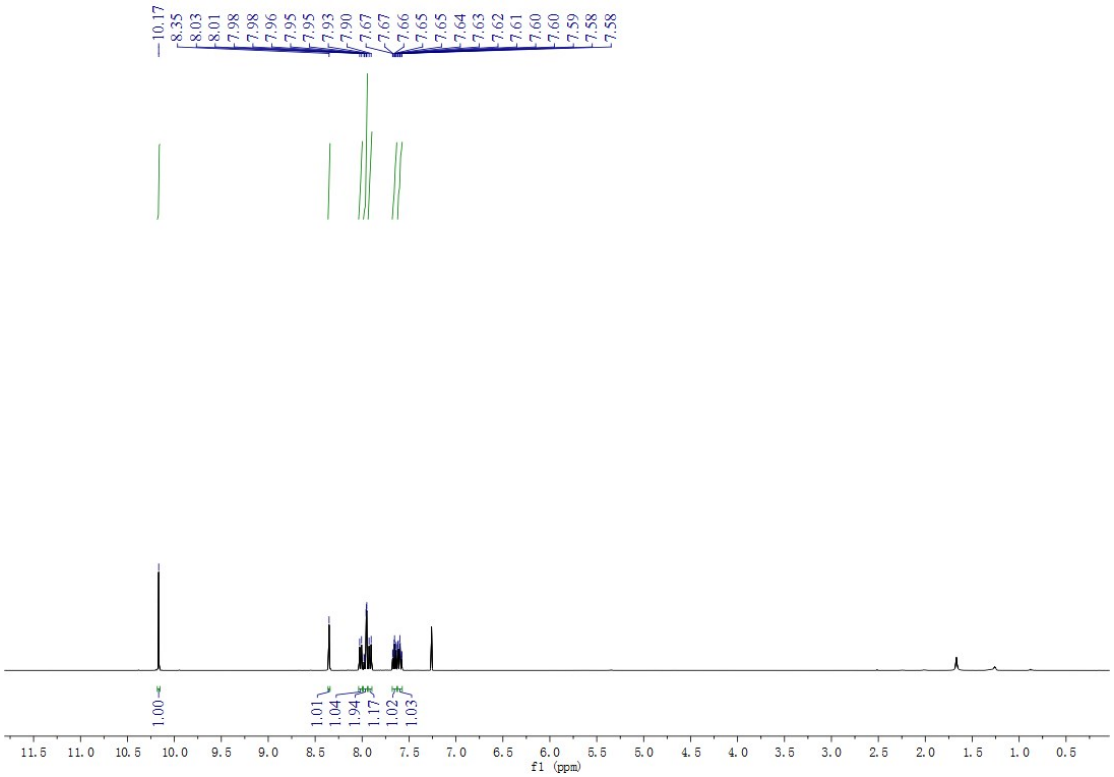


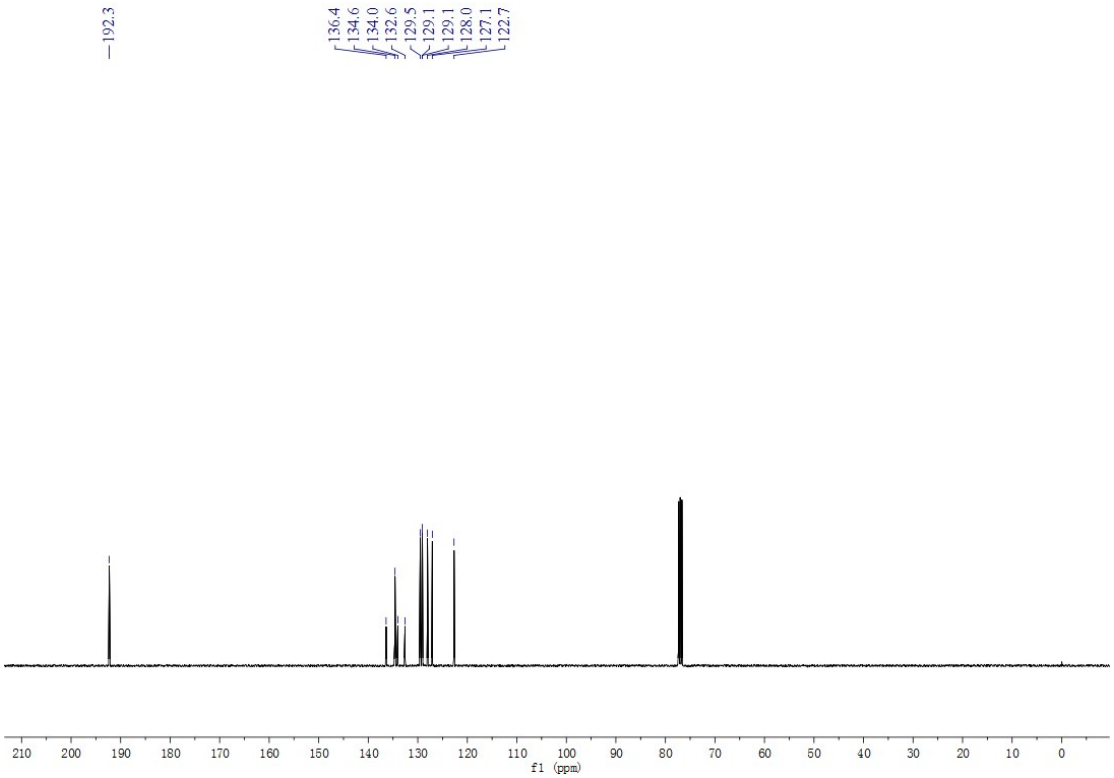
1-naphthaldehyde (2z)



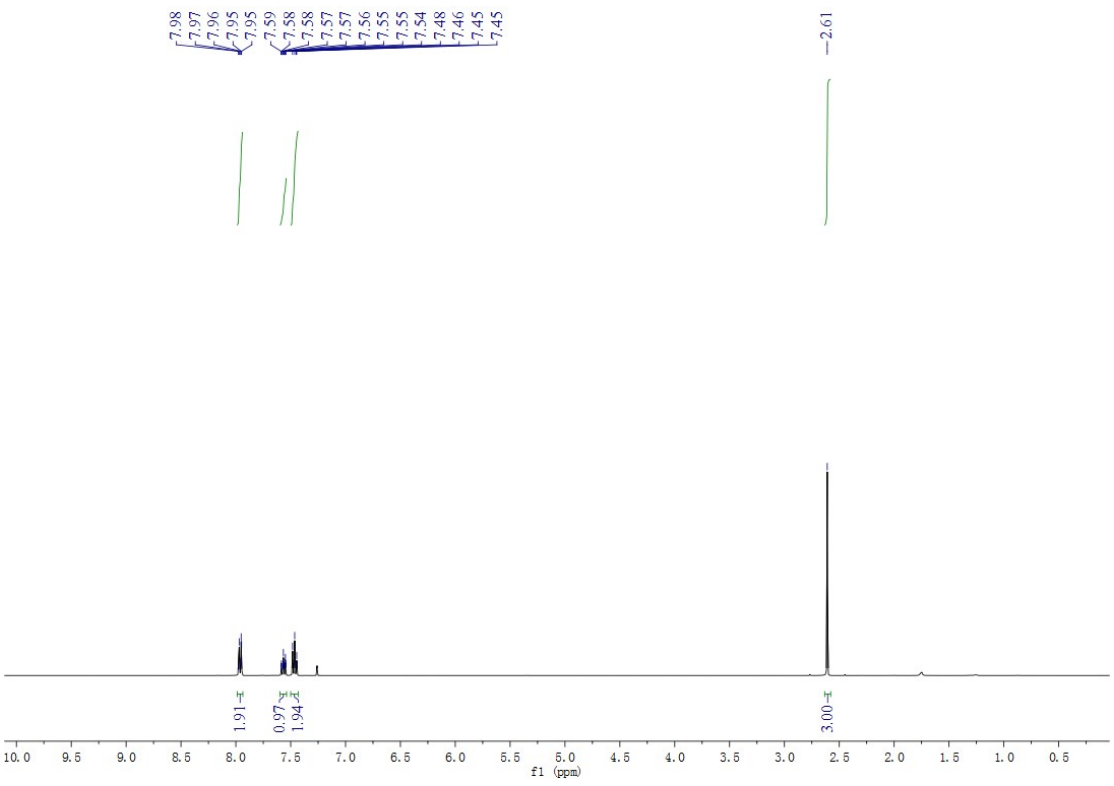


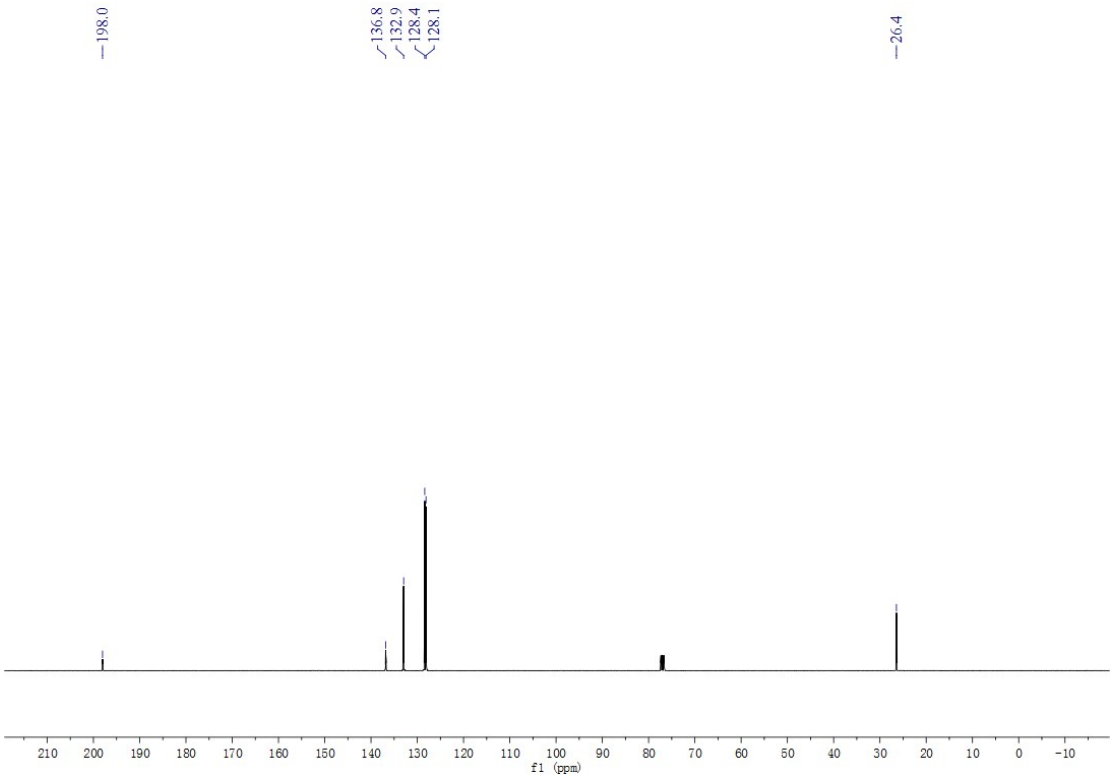
2-naphthaldehyde (2aa)



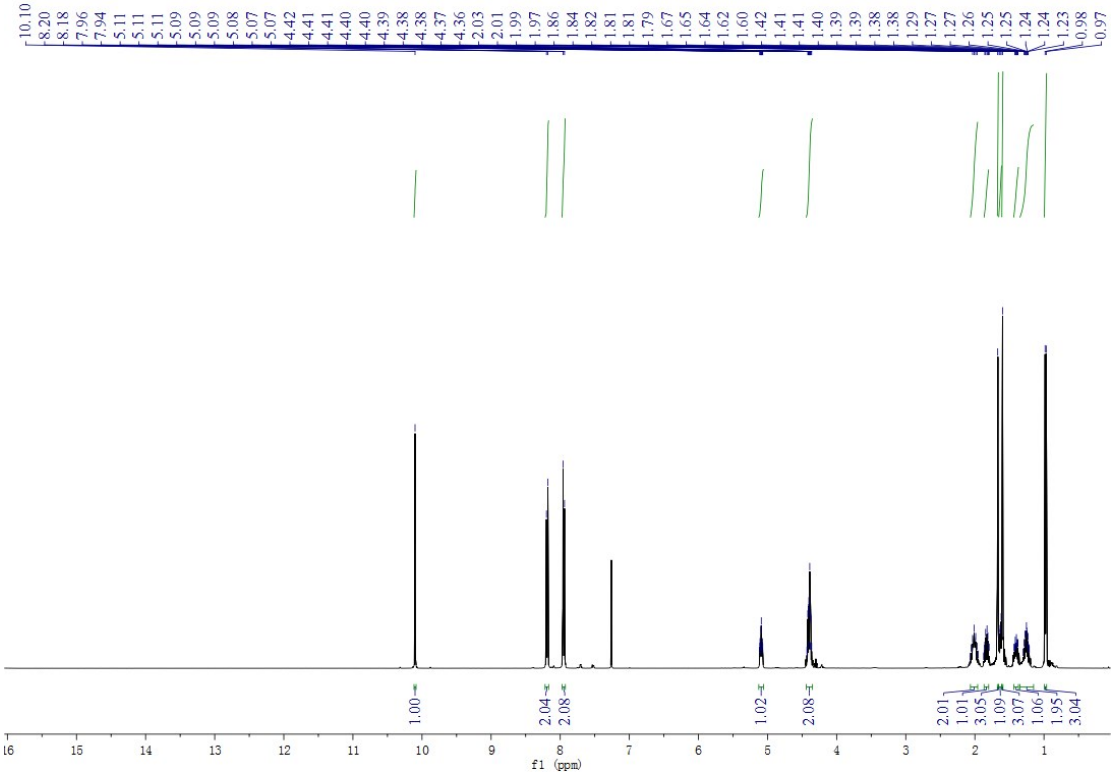


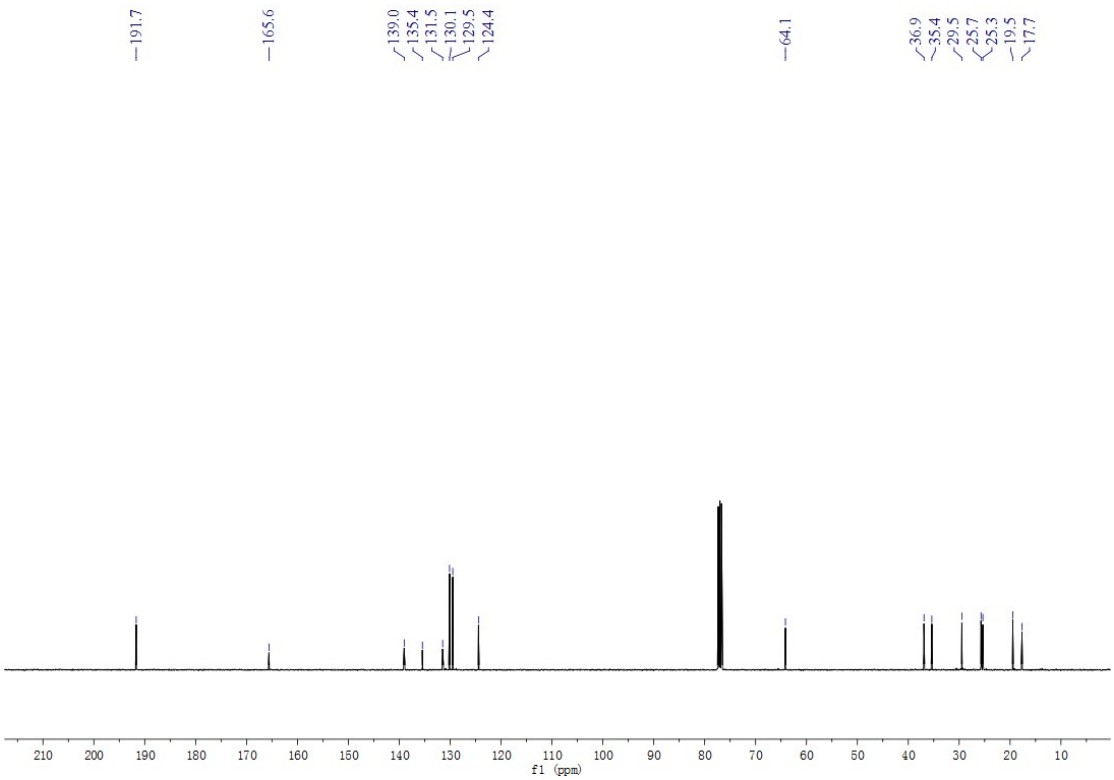
acetophenone (2ab)



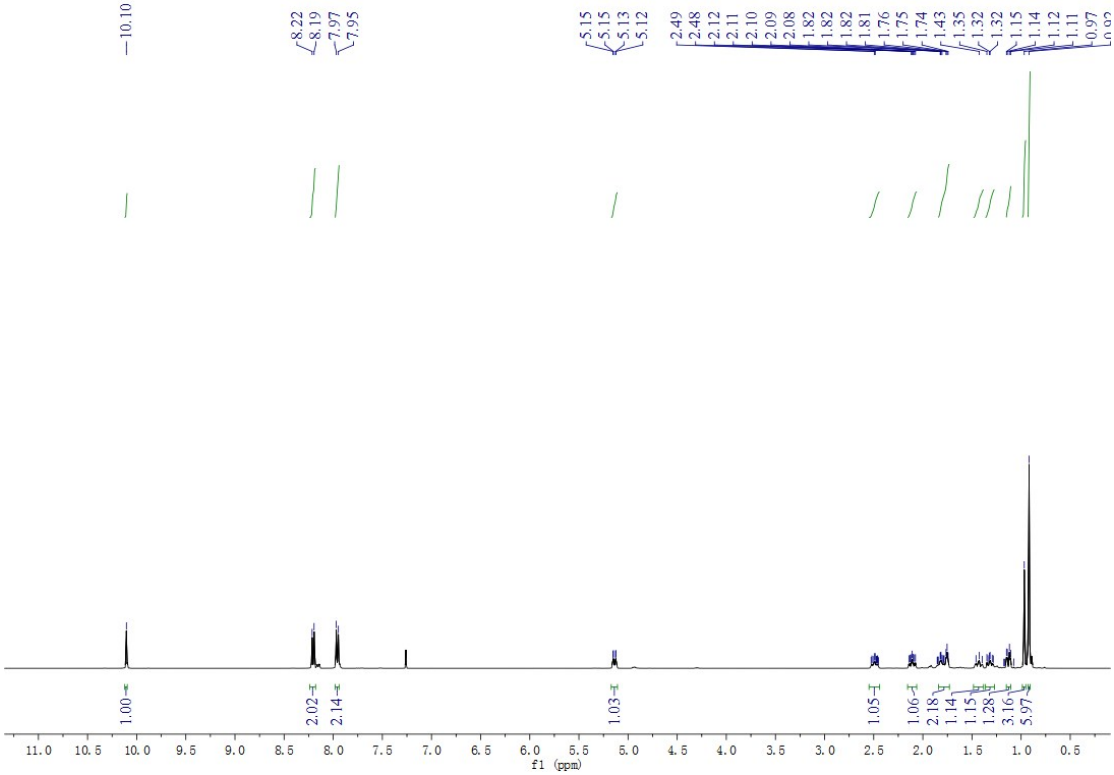


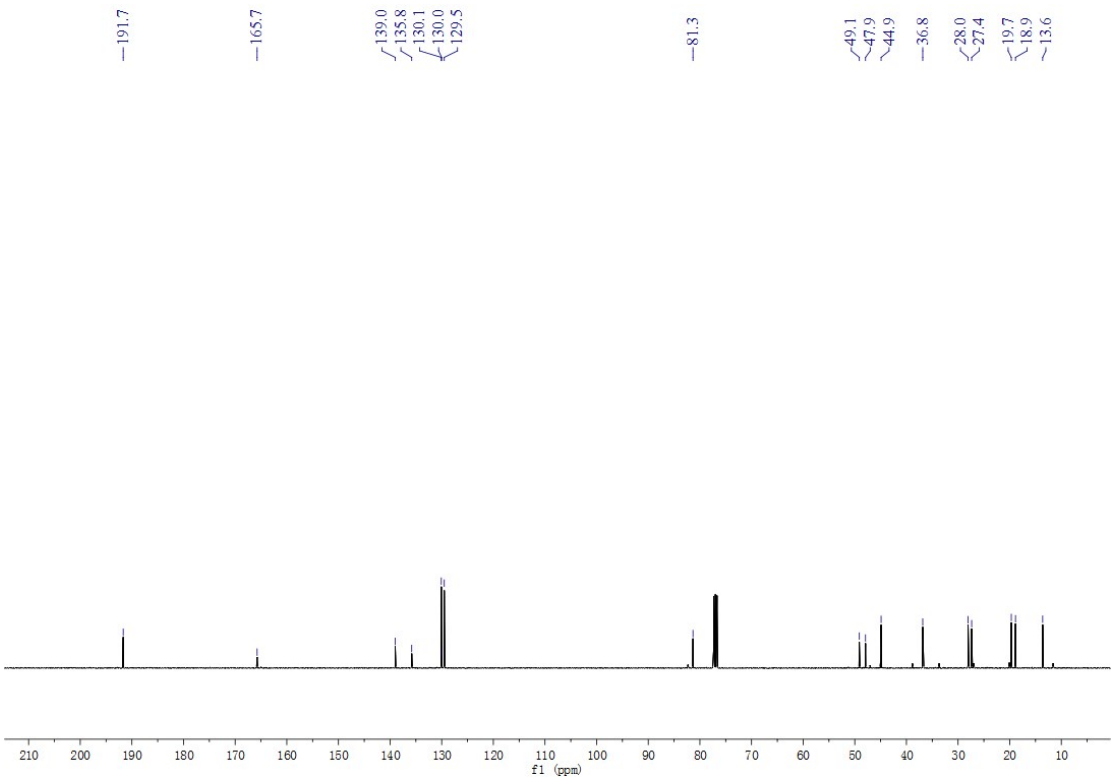
3,7-dimethyloct-6-en-1-yl 4-formylbenzoate (2al)



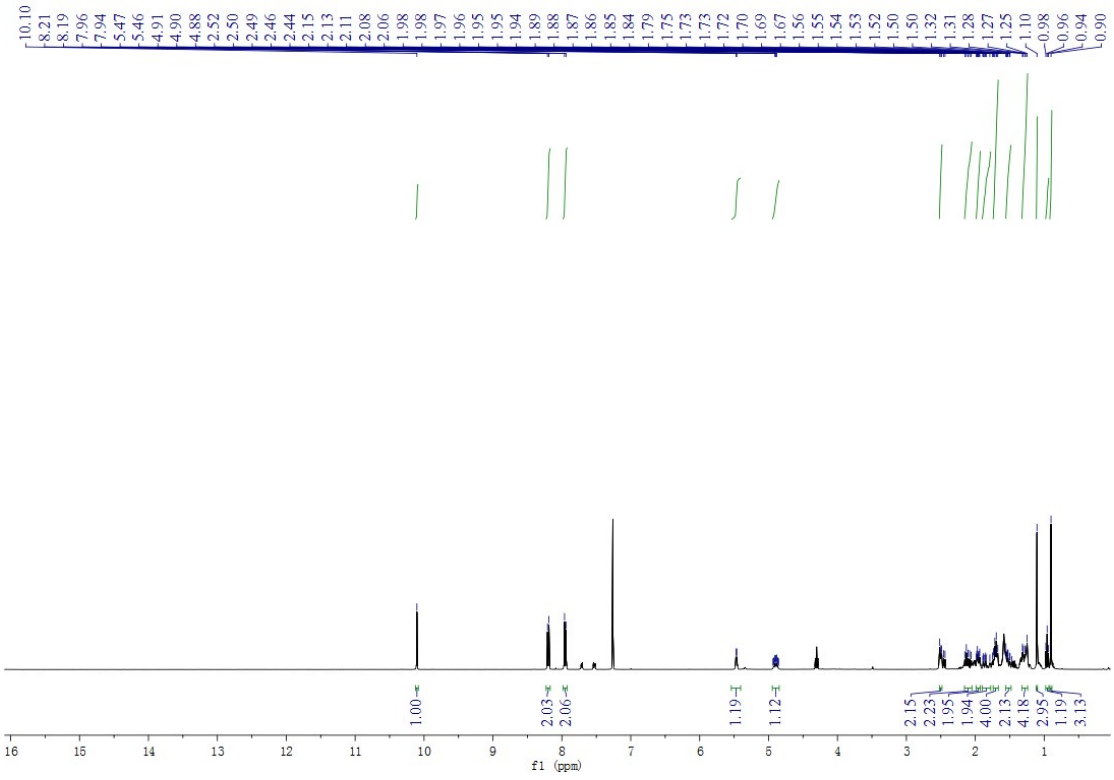


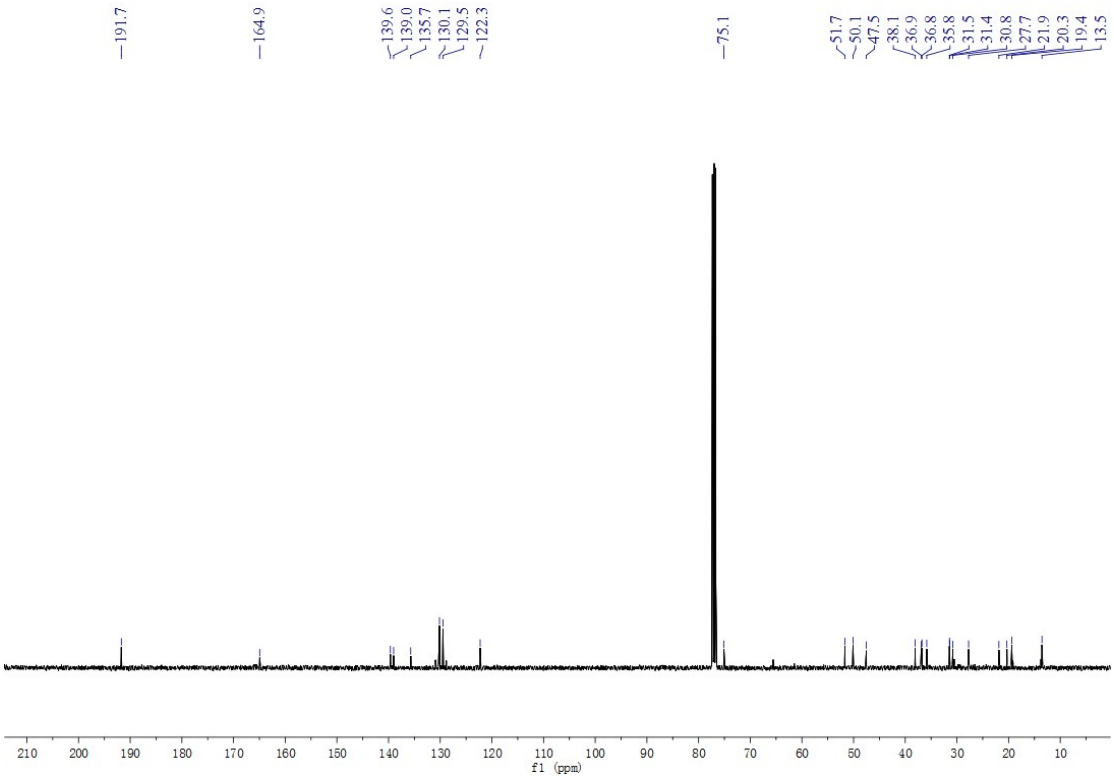
(1R,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-formylbenzoate (2am)



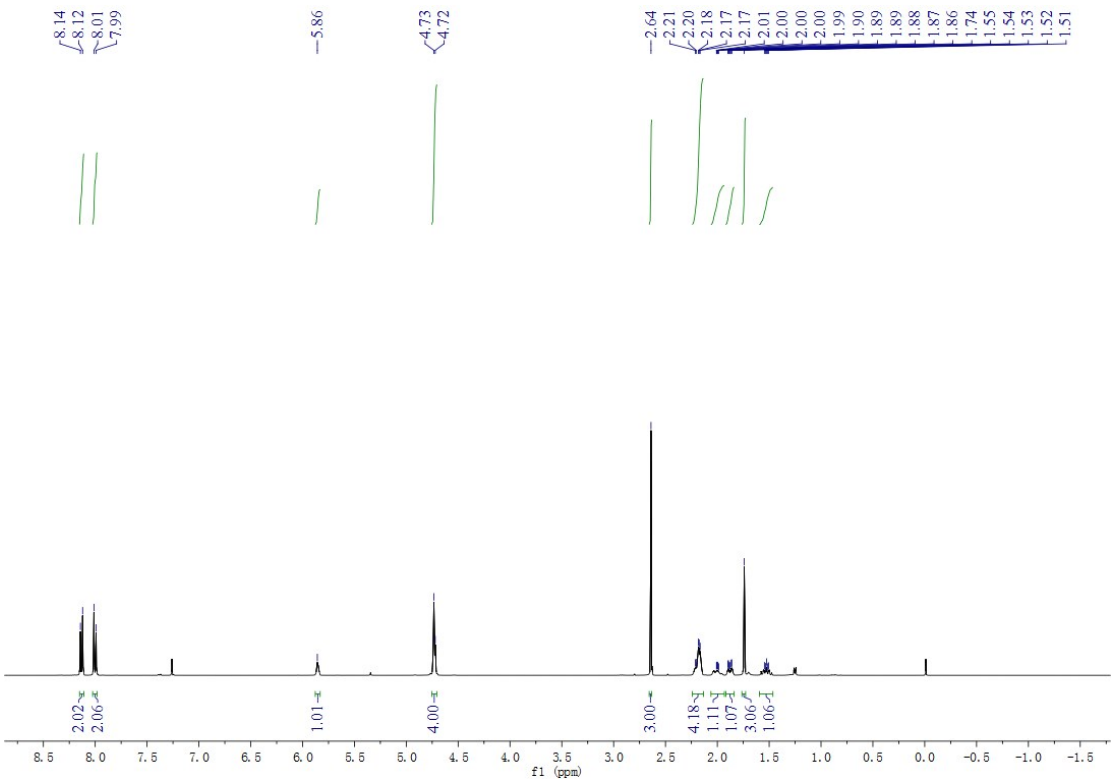


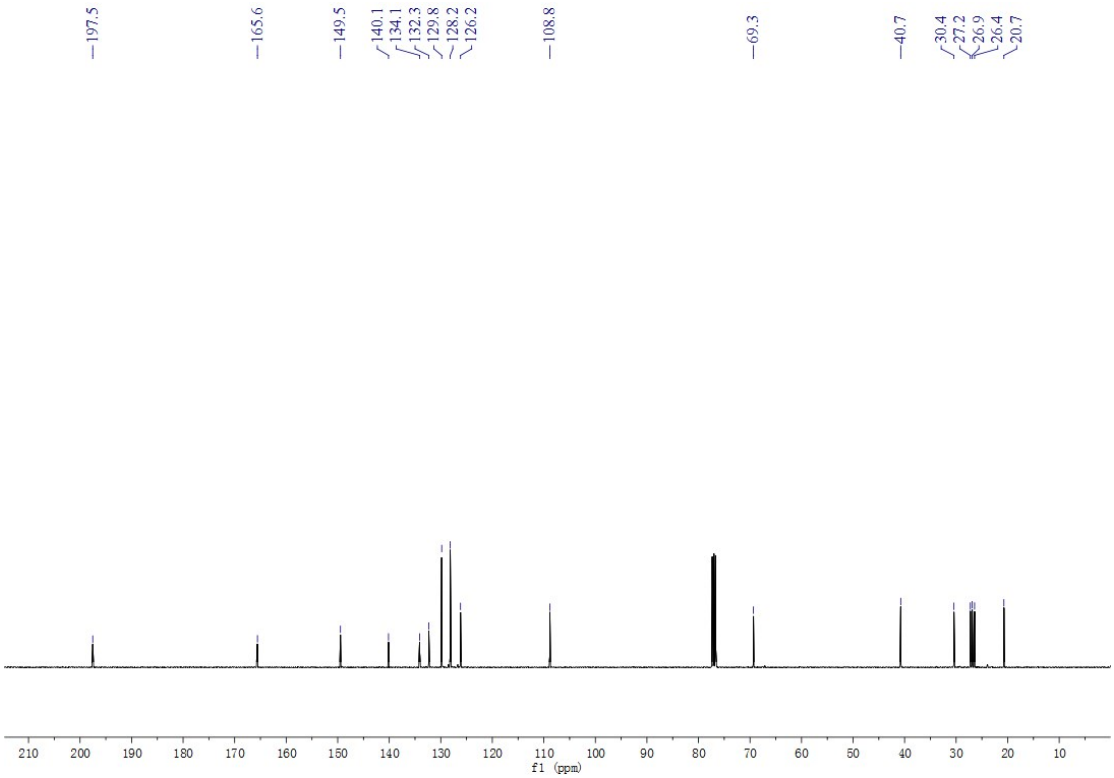
(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-formylbenzoate (2an)



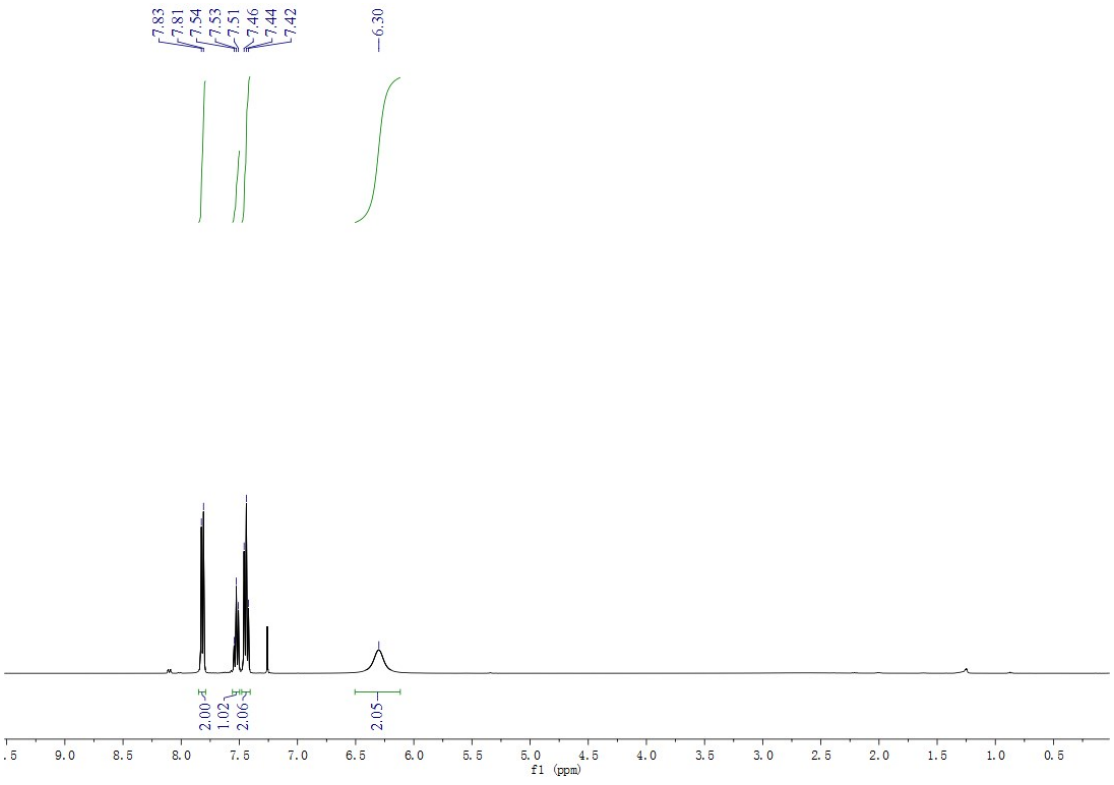


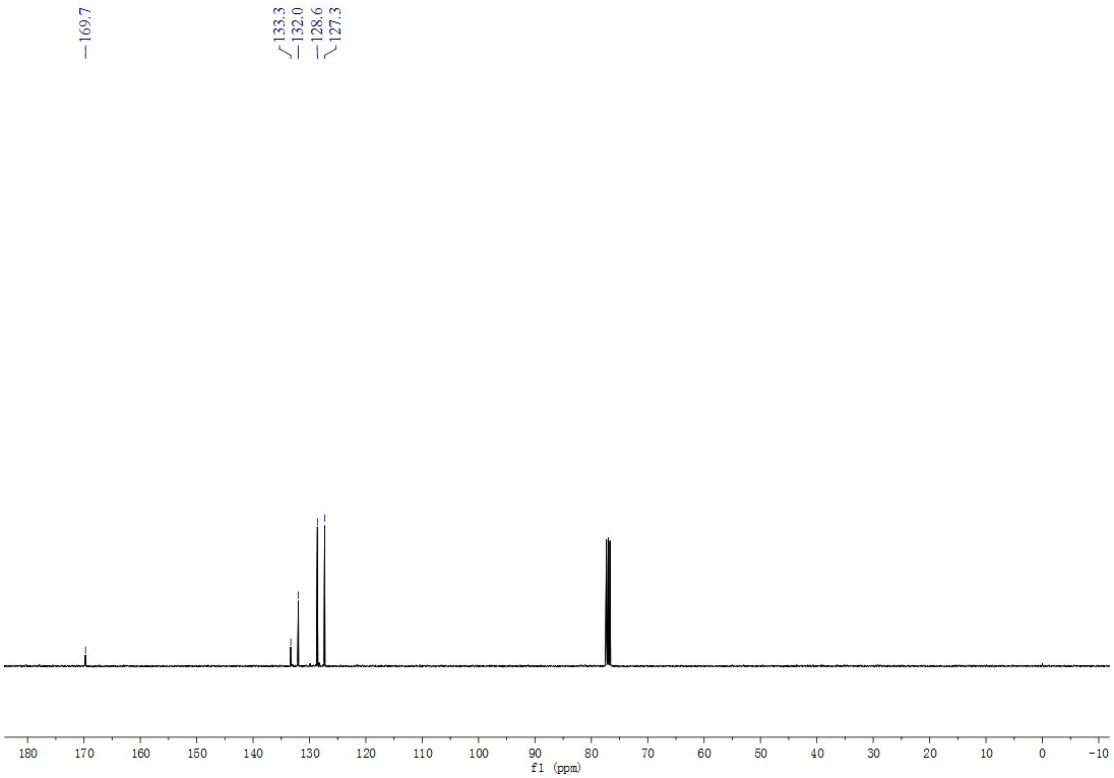
(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 4-acetylbenzoate (2ao)



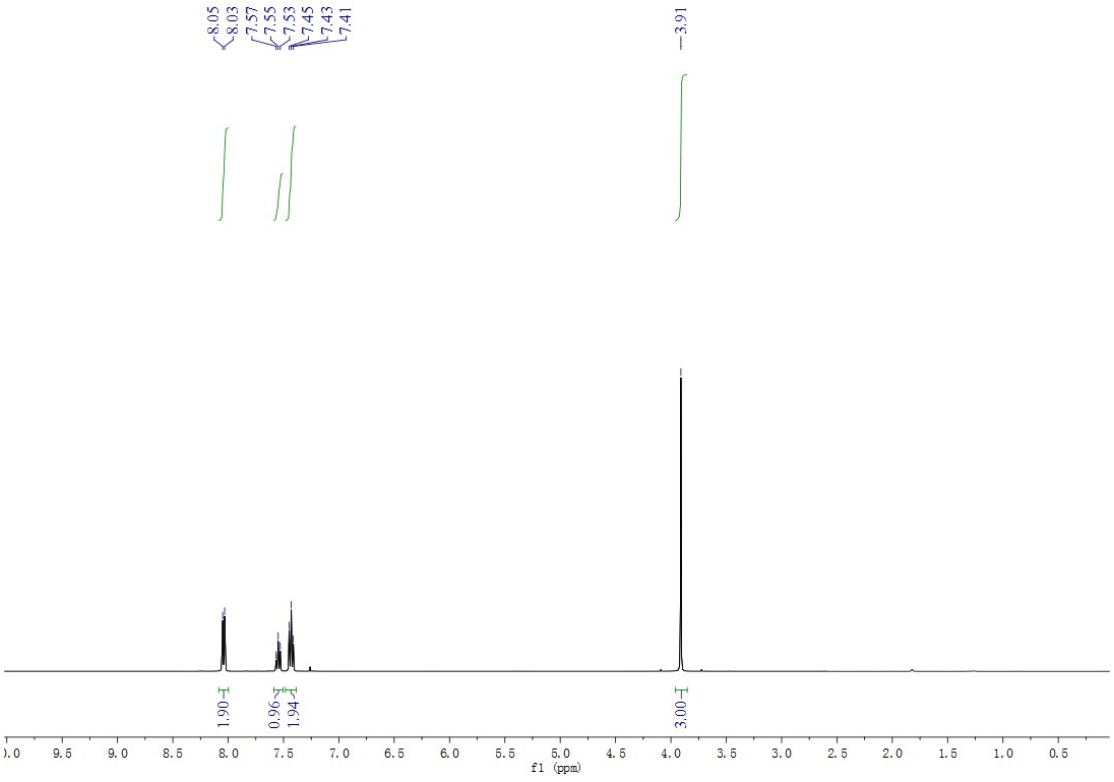


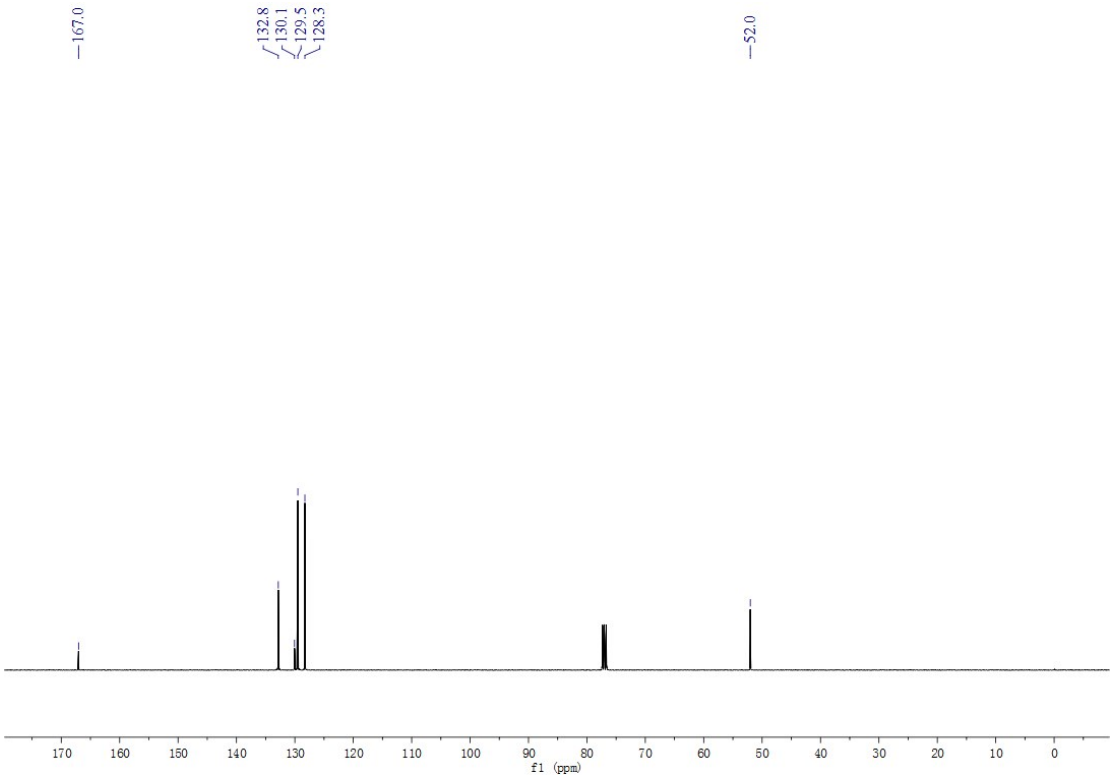
Benzamide (4a)



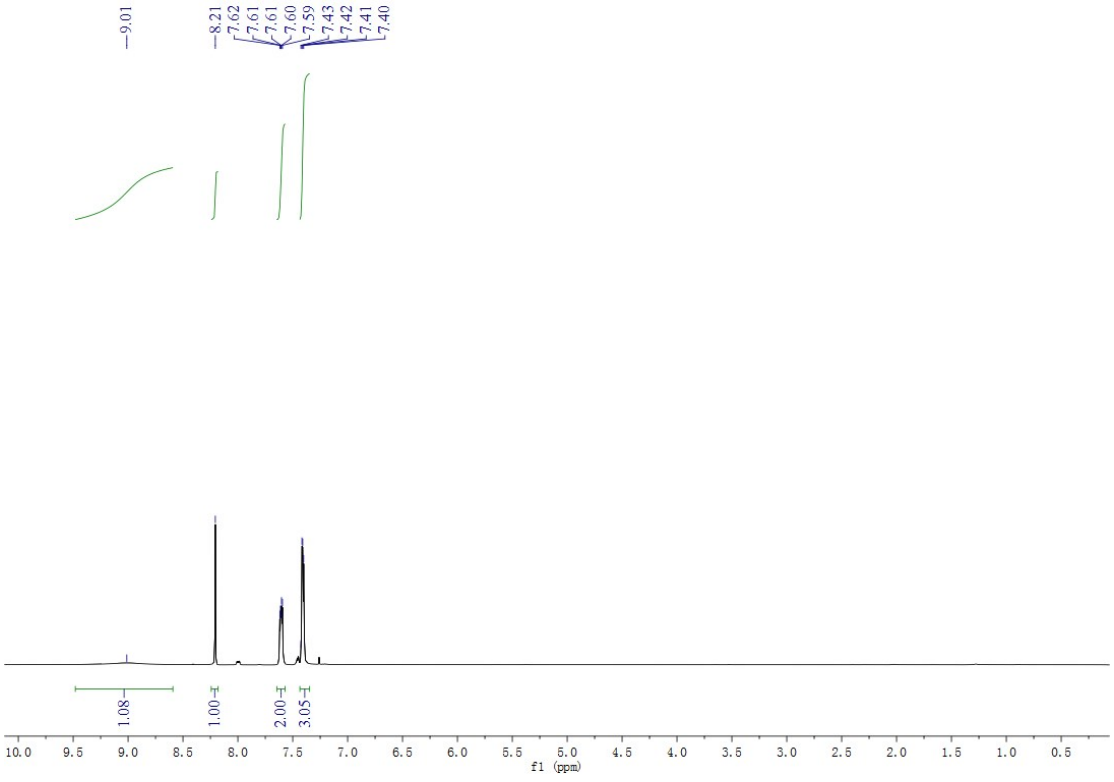


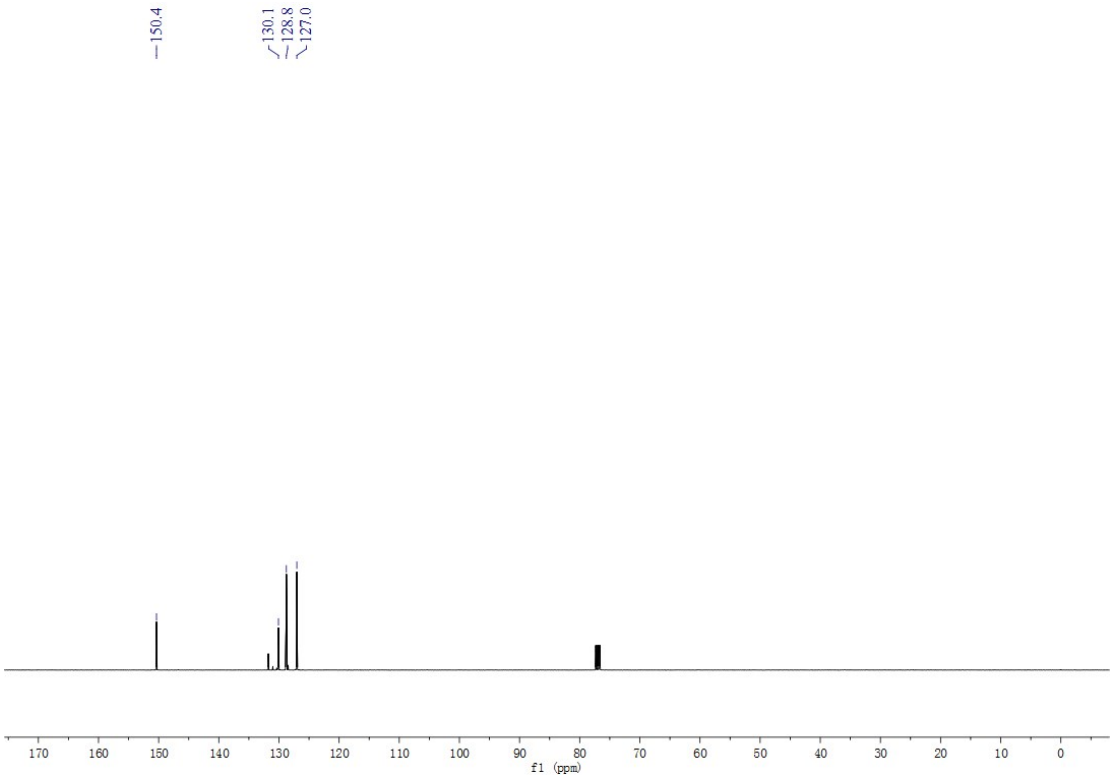
Methyl benzoate (4b)





benzaldehyde oxime (4c)





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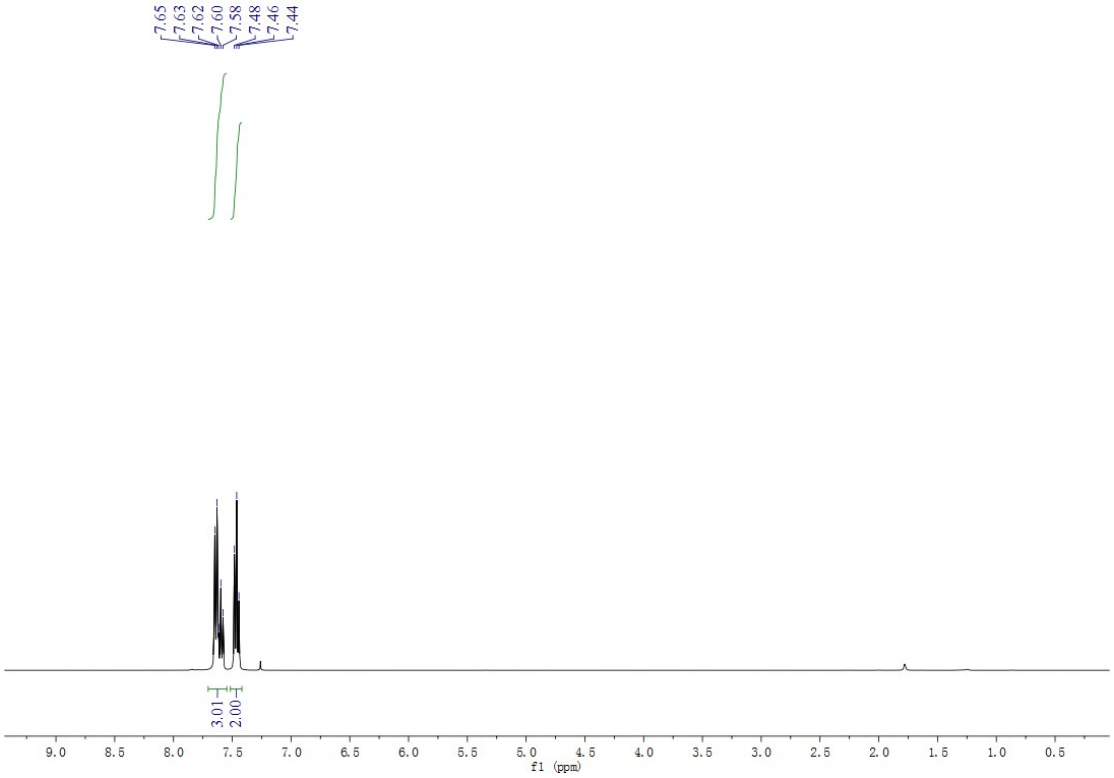
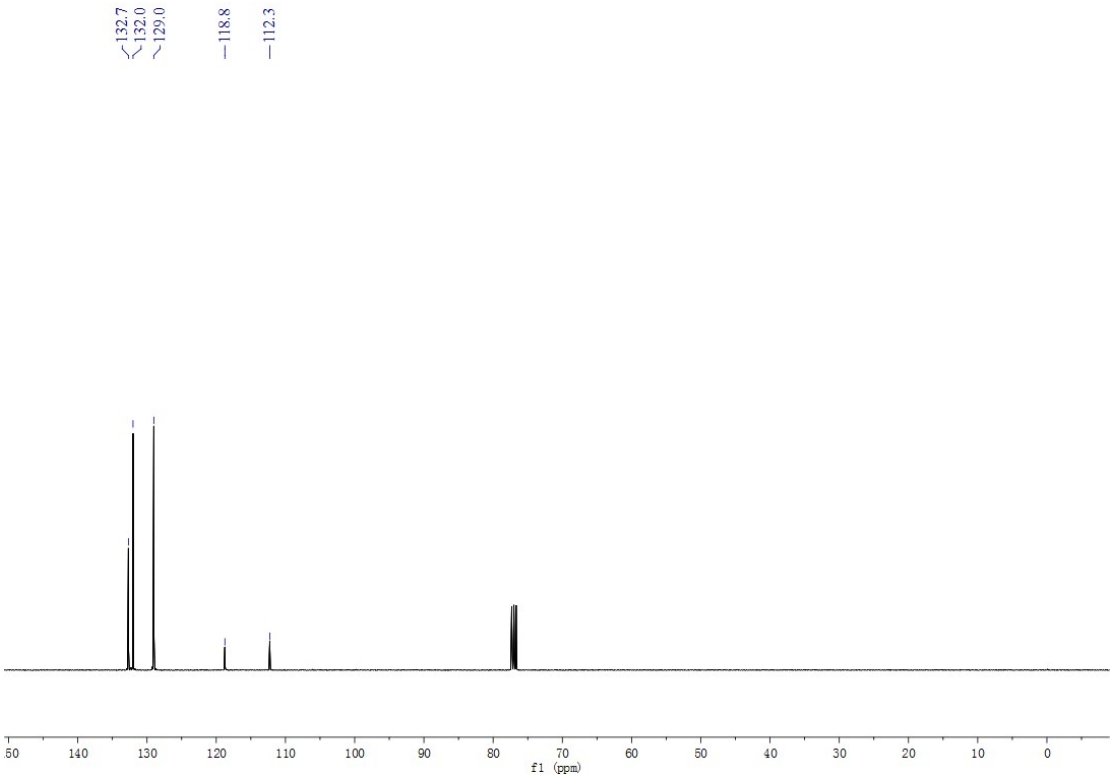
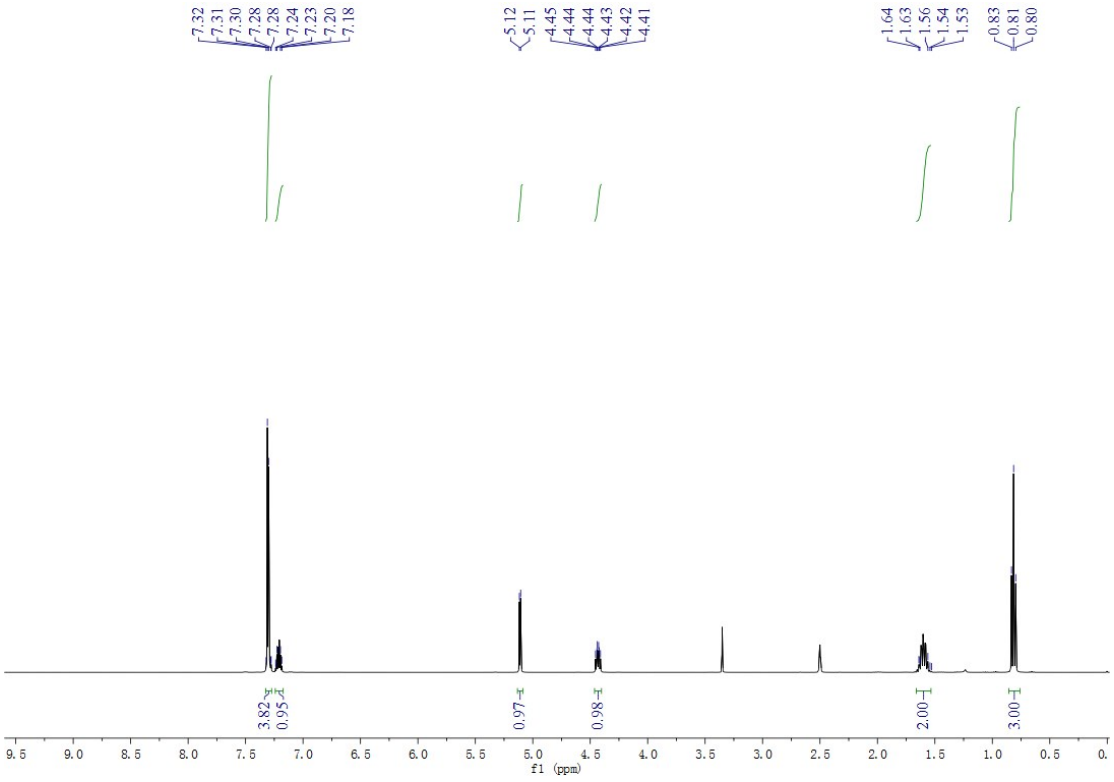
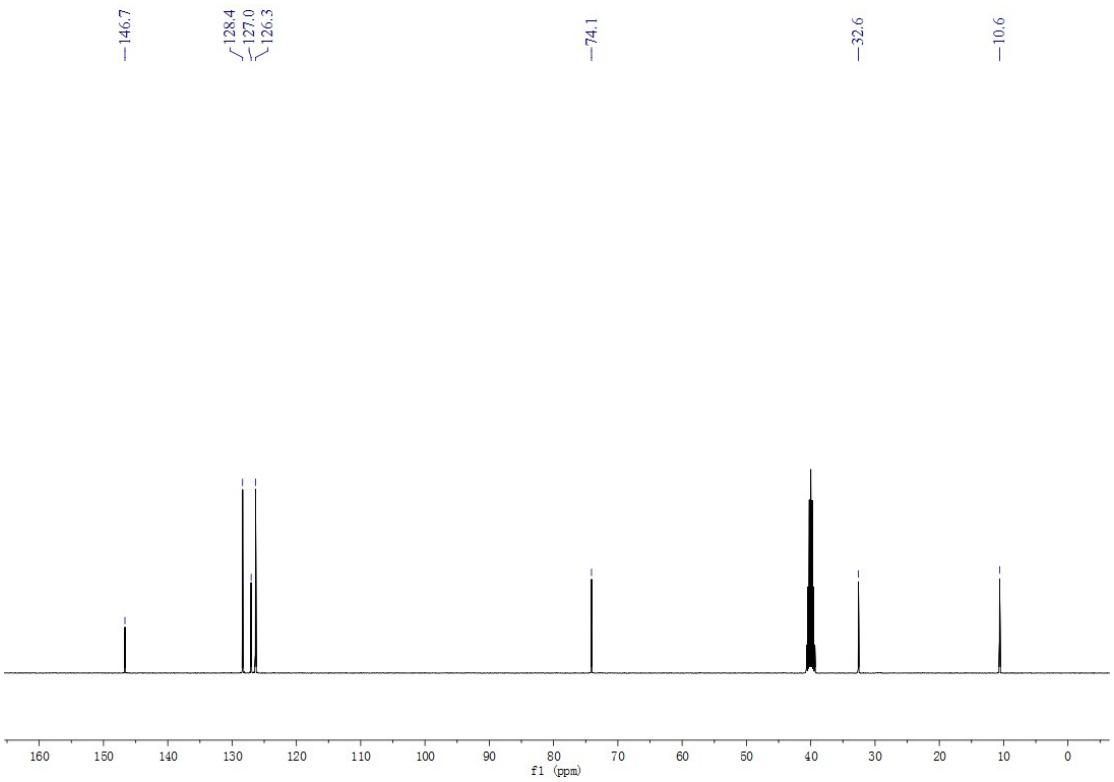
benzonitrile (4d)





1-phenylpropan-1-ol (4e)

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10
0
f1 (ppm)