Selective Reduction of Carboxylic Acids to Aldehydes with Hydrosilane *via* Photoredox Catalysis

Muliang Zhang,[†] Nan Li,[†] Xingyu Tao,[†] Rehanguli Ruzi,[†] Shouyun Yu,*[†] Chengjian Zhu*[†‡]

[†]State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, (P. R. China)

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032 (P. R. China)
E-mail: cjzhu@nju.edu.cn

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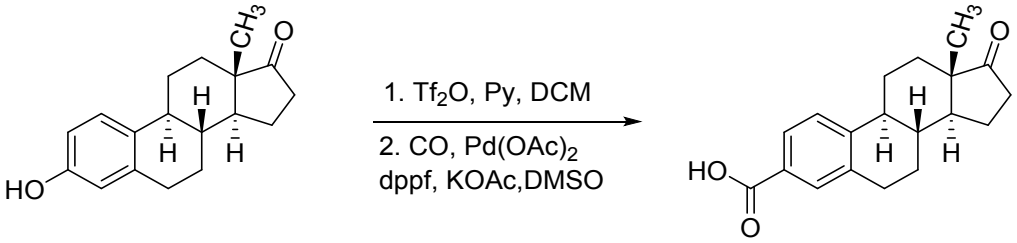
1. General Information

All reactions were carried out under Ar atmosphere unless otherwise noted. All reagents and solvents were obtained from commercial suppliers and used without further purification. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin- layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE Ⅲ-400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectra were obtained using an Agilent 6210 Series TOF LC-MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. The Blue Leds lamp were directly got from the supermarket.

2. Starting Materials

Estrone acid was synthesized by a previously reported method.[1]

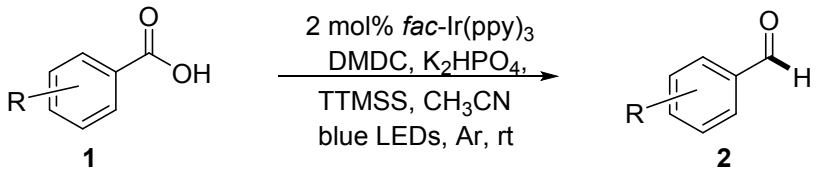


Step 1. Pyridine (10.0 mmol, 2.0 equiv) was added to a stirring solution of estrone (5.0 mmol, 1.0 equiv) in DCM (25 mL) under Ar. Then, triflic anhydride (6.0 mmol, 1.2 equiv) was added dropwise to

the mixture in an ice bath. The mixture was warmed to room temperature and stirred for 5 h. Then, the reaction was quenched by the addition of water. The layers were separated, and the aqueous phase was extracted with DCM (30 mL × 3). The combined organic phase was washed with brine, dried over sodium sulfate, filtered, and evaporated under reduced pressure to afford the corresponding crude trifluoromethane-sulfonate substituted compound. The crude compound was used without further purification.

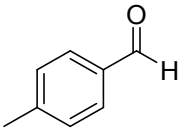
Step 2: $Pd(OAc)_2$ (0.25 mmol, 5 mol %), 1,1′-bis(diphenylphosphino) ferrocene (1 mmol, 20 mol %), and potassium acetate (20 mmol, 4 equiv) were added to the crude compound in DMSO (50 mL). The reaction mixture was stirred at 60 °C under a balloon of CO overnight. The mixture was then cooled to room temperature, quenched with 1 M HCl (pH < 3), and extracted with EtOAc (50 mL× 3). The combined organic phase was washed with brine, dried over sodium sulfate, filtered, and evaporated under reduced pressure to afford the corresponding crude carboxylic acid. The crude carboxylic acid was purified by column chromatography on silica gel to obtain the corresponding acid.

3. General Procedure for Photoredox Catalyzed Direct Formation of Aldehydes from Carboxylic Acids



A 10 mL oven-dried Schlenk-tube was charged with photocatalyst *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.02 equiv, 1.3 mg), the corresponding acid (**1**, 0.1 mmol), K_2HPO_4 (0.2 mmol, 2.0 equiv, 34.8 mg). The tube was evacuated and backfilled with Ar (three times), dimethyl dicarbonate (0.3 mmol, 3.0 equiv, 40.2 mg), tris(trimethylsilyl)silane (0.2 mmol, 2.0 equiv, 49.7 mg), in CH_3CN (2 mL) were added by syringe under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 5W blue LEDs lamb and the mixture was stirred for 6 - 24 h at room temperature. The resulting mixture was diluted with EtOAc (15 mL). The organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/50 to 1/20) to give the corresponding aldehyde products **2**.

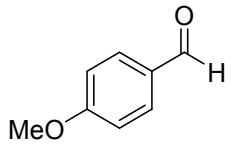
4-methylbenzaldehyde **2a**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2a**

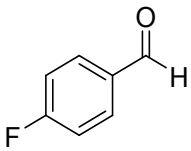
(11.1mg, 92%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.95 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 191.98, 145.54, 134.20, 129.84, 129.71, 21.87. Characterization data matched those previously reported.[2]

4-methoxybenzaldehyde **2b**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (40:1 petroleum ether: ethyl acetate) to afford **2b** (12.3mg, 90%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.88 (s, 1H), 7.83 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.83, 164.61, 131.97, 129.92, 114.31, 55.57. Characterization data matched those previously reported.[2]

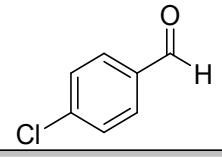
4-fluorobenzaldehyde **2c**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2c**

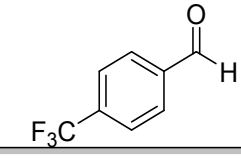
(11.1mg, 89%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.97 (s, 1H), 8.02 – 7.84 (m, 2H), 7.25 – 7.17 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.49, 166.52 (d, J = 256.7 Hz), 132.97 (d, J = 2.7 Hz), 132.22 (d, J = 9.7 Hz), 116.35 (d, J = 22.3 Hz). Characterization data matched those previously reported.[2]

4-chlorobenzaldehyde **2d**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (3 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2d** (12.4mg, 88%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.98 (s, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.82, 140.91, 134.71, 130.89, 129.43. Characterization data matched those previously reported.[2]

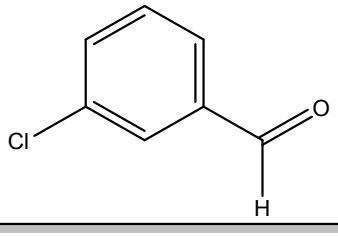
4-(trifluoromethyl)benzaldehyde **2e**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2e** (12.3mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H),

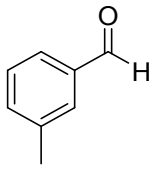
8.02 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 191.06, 138.65, 135.60 (q, J = 32.7 Hz), 129.90, 126.11 (q, J = 3.7 Hz), 123.42 (9, J = 272.9 Hz). Characterization data matched those previously reported.[6]

3-chlorobenzaldehyde **2f**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (30 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2f** (11.9mg, 85%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.89 – 7.84 (m, 2H), 7.77 (d, *J* = 4.2 Hz 1H), 7.66 – 7.55 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-d) δ 190.83, 137.82, 135.48, 134.40, 130.38, 129.33, 127.97. Characterization data matched those previously reported.[10]

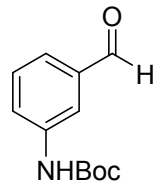
3-methylbenzaldehyde **2g**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2g**

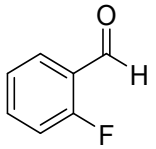
(10.9mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.69-7.67 (m, 2H), 7.45-7.39 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.53, 138.88, 136.47, 135.26, 129.98, 128.86, 127.18, 21.14. Characterization data matched those previously reported.[10]

tert-butyl (3-formylphenyl)carbamate **2h**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2h** (18.9mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.93 (s, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.16, 152.63, 139.40, 137.15, 129.65, 124.10, 119.30, 80.82, 28.30. Characterization data matched those previously reported.[7]

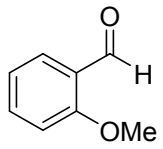
2-fluorobenzaldehyde **2i**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column

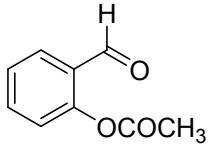
chromatography (50:1 petroleum ether: ethyl acetate) to afford **2i** (11.0mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.37 (s, 1H), 7.87 (td, *J* = 7.5, 1.8 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 10.3, 8.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.17 (d, *J* = 6.7 Hz), 164.67 (d, *J* = 258.7 Hz), 136.35 (d, *J* = 9.1 Hz), 133.98 (d, *J* = 258.1 Hz), 128.68 (d, *J* = 1.8 Hz), 124.63 (d, *J* = 3.7 Hz), 116.50 (d, *J* = 20.5 Hz). Characterization data matched those previously reported.[11]

2-methoxybenzaldehyde **2j**



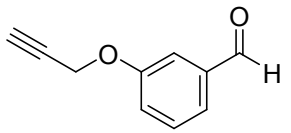
The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (40:1 petroleum ether: ethyl acetate) to afford **2j** (10.9mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.47 (s, 1H), 7.82 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.66 – 7.40 (m, 1H), 7.09 – 6.81 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.80, 161.83, 135.97, 128.49, 124.81, 120.64, 111.64, 55.62. Characterization data matched those previously reported.[3]

2-formylphenyl acetate **2k**



The reaction was carried out according to the general procedure on 0.1 mmol scale (24 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2k** (0.69g, 84%). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.11 (s, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.68 – 7.53 (m, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100MHz, Chloroform-d) δ 188.78, 169.26, 151.48, 135.32, 131.32, 128.04, 126.45, 123.50, 20.87. Characterization data matched those previously reported.[12]

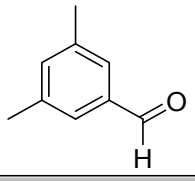
3-(prop-2-yn-1-yloxy)benzaldehyde **2l**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (30:1 petroleum ether: ethyl acetate) to afford **2l** (13.4mg, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.55 – 7.42 (m, 3H), 7.31 – 7.20 (m, 1H), 4.76 (d, *J* = 2.4 Hz, 2H), 2.56 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.85,

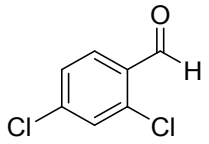
157.01, 136.73, 129.12, 123.06, 121.06, 112.51, 76.85, 75.12, 54.92. Characterization data matched those previously reported.[4]

3,5-dimethylbenzaldehyde **2m**



The reaction was carried out according to the general procedure A on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2m** (12.5mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.48 (s, 2H), 7.26 (s, 1H), 2.39 (s, 6H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.81, 138.76, 136.58, 136.21, 127.57, 21.07. Characterization data matched those previously reported.[6]

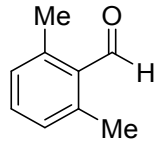
2,4-dichlorobenzaldehyde **2n**



The reaction was carried out according to the general procedure on 0.1 mmol scale (3 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2n** (14.6mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.41 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.48 (s, 1H), 7.38 (d, J = 10.3 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.44, 141.08, 138.51, 130.92, 130.44, 130.30, 127.95. Characterization data matched those

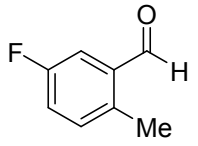
previously reported.[5]

2,6-dimethylbenzaldehyde **2o**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2o** (11.2mg, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.62 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 2.60 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.58, 141.15, 132.99, 132.44, 129.71, 20.50. Characterization data matched those previously reported.[8]

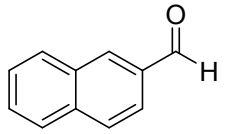
5-fluoro-2-methylbenzaldehyde **2p**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6h). The residue was purified by flash column chromatography (50:1 petroleum ether: ethyl acetate) to afford **2p** (11.8mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 7.49 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.29 – 7.13 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.07, 161.26 (d, *J* = 246.4 Hz),

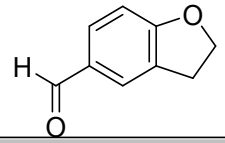
136.27 (d, J = 3.3 Hz), 135.25 (d, J = 5.6 Hz), 133.34 (d, J = 6.9 Hz), 120.76 (d, J = 21.3 Hz), 116.84 (d, J = 21.8 Hz), 18.43. Characterization data matched those previously reported.[11]

2-naphthaldehyde **2q**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6h). The residue was purified by flash column chromatography (30:1 petroleum ether: ethyl acetate) to afford **2q** (13.8mg, 88%).. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.37 (s, 1H), 9.24 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.62 – 7.54 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.57, 136.69, 135.31, 133.74, 131.41, 130.54, 129.09, 128.50, 126.98, 124.89. Characterization data matched those previously reported.[11]

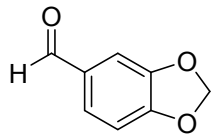
2,3,3a,7a-tetrahydrobenzofuran-5-carbaldehyde **2r**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (30:1 petroleum ether: ethyl acetate) to afford **2r** (11.9mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.81 (s, 1H),

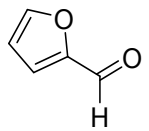
7.72 (s, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.67 (t, *J* = 8.8 Hz, 2H), 3.24 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.57, 165.62, 132.88, 130.37, 128.46, 125.90, 109.55, 72.41, 28.71. Characterization data matched those previously reported.[9]

benzo[*d*][1,3]dioxole-5-carbaldehyde **2s**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2s** (12.0 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.74 (s, 1H), 7.49 – 7.18 (m, 2H), 6.86 (d, J = 7.9 Hz, 1H), 6.00 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.31, 153.12, 148.72, 131.89, 128.68, 108.36, 106.94, 102.10. Characterization data matched those previously reported.[2]

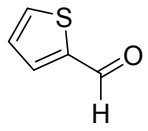
furan-2-carbaldehyde **2t**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2t**

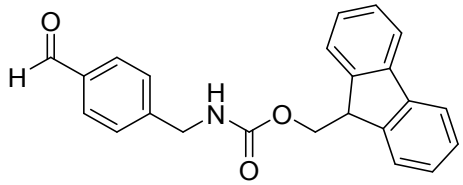
(7.2mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 7.63 (s, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 6.54 (dd, *J* = 3.6, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.49, 150.54, 145.71, 118.72, 110.20. Characterization data matched those previously reported.[11]

thiophene-2-carbaldehyde **2u**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2u** (7.4mg, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 7.78 (dd, *J* = 9.1, 3.6 Hz, 2H), 7.25 – 7.20 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.06, 143.96, 136.49, 135.17, 128.39. Characterization data matched those previously reported.[11]

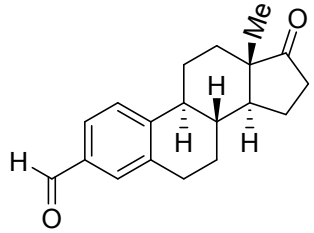
(9*H*-fluoren-9-yl)methyl (4-formylbenzyl)carbamate **2v**



The reaction was carried out according to the general procedure on 0.1 mmol scale (6 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2v** (29.4mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H),

7.80 (dd, *J* = 25.2, 7.7 Hz, 4H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.40 (q, *J* = 7.3 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 2H), 5.21 (s, 1H), 4.50 (d, *J* = 6.6 Hz, 2H), 4.44 (d, *J* = 6.3 Hz, 2H), 4.22 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.84, 156.50, 145.47, 143.78, 141.37, 135.97, 135.65, 130.14, 127.74, 127.07, 124.95, 120.03, 66.71, 47.32, 44.72. HRMS (ESI) Calcd for $C_{23}H_{21}NO_3$ $[M+H]^+$: 358.1438, found: 358.1438.

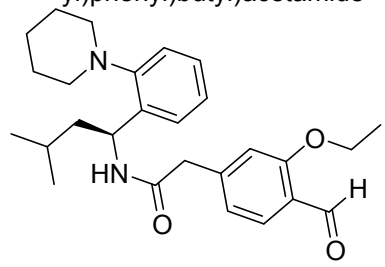
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3-carbaldehyde **2w**



The reaction was carried out according to the general procedure on 0.1 mmol scale (24 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2w** (20.0mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 3.09 – 2.93 (m, 2H), 2.58 – 2.41 (m, 2H), 2.38 - 2.32 (m, 1H), 2.22 – 2.12 (m, 1H), 2.11 – 2.02 (m, 2H), 1.99-1.96 (m, 1H), 1.67 – 1.43 (m, 6H), 0.91 (s, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 220.41, 192.26, 147.10, 137.52, 134.29, 130.23, 127.25, 126.07, 50.55, 47.87, 44.89, 37.76, 35.81, 31.55, 29.19, 26.19, 25.59, 21.61, 13.82. HRMS (ESI)

Calcd for $C_{19}H_{23}O_2$ $[M+H]^+$: 283.1693, found: 283.1694.

(*S*)-2-(3-ethoxy-4-formylphenyl)-*N*-(3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)acetamide **2x**



The reaction was carried out according to the general procedure on 0.1 mmol scale (24 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2x** (36.6mg, 84%).^{1}H NMR (400 MHz, Chloroform-d) δ 10.44 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.13 – 7.00 (m, 2H), 6.95 – 6.80 (m, 2H), 5.36 (q, J = 8.5 Hz, 1H), 4.13 – 3.93 (m, 2H), 3.54 (s, 2H), 2.93 (s, 2H), 2.62 (s, 2H), 1.80 – 1.47 (m, 9H), 1.42 (t, J = 7.0 Hz, 3H), 0.92 (d, J = 6.5 Hz, 6H).^{13}C NMR (100 MHz, Chloroform-d) δ 189.56, 168.49, 161.54, 152.52, 144.01, 138.58, 128.64, 127.98, 127.83, 125.14, 123.71, 122.93, 121.34, 113.11, 64.17, 50.07, 46.69, 44.51, 26.79, 25.36, 24.13, 22.77, 22.56, 14.59. HRMS (ESI) Calcd for $C_{27}H_{37}N_2O_3$ $[M+H]^+$: 437.2799, found: 437.2710.

Gram-scale reaction procedures

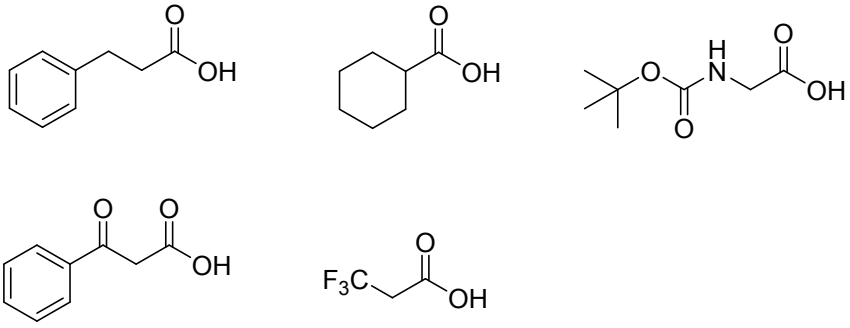
A 250 mL oven-dried Schlenk-tube was charged with photocatalyst *fac*-Ir(ppy)$_3$ (0.1 mmol, 0.01 equiv, 65 mg), the corresponding acid

(**1k**, 10 mmol, 1.80 g), K_2HPO_4 (20 mmol, 2.0 equiv, 3.48 g). The tube was evacuated and backfilled with Ar (three times), dimethyl dicarbonate (30 mmol, 3.0 equiv, 4.02 g), tris(trimethylsilyl)silane (20 mmol, 2.0 equiv, 4.97 g), in CH_3CN (100 mL) were added under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 24 W blue LEDs lamb and the mixture was stirred for 48 h at room temperature. The resulting mixture was diluted with EtOAc (50 mL). The organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/50 to 1/20) to give the corresponding aldehyde product **2k** (1.28 g, 78%).

A 100 mL oven-dried Schlenk-tube was charged with photocatalyst *fac*-$Ir(ppy)_3$ (0.05 mmol, 0.01 equiv, 33 mg), the corresponding acid (**1x**, 5 mmol, 2.26 g), K_2HPO_4 (10 mmol, 2.0 equiv, 1.74 g). The tube was evacuated and backfilled with Ar (three times), dimethyl dicarbonate (15 mmol, 3.0 equiv, 2.01 g), tris(trimethylsilyl)silane (10 mmol, 2.0 equiv, 2.49 g), in CH_3CN (50 mL) were added under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 24 W blue LEDs lamb and the mixture was stirred for 48 h at room temperature. The resulting mixture was diluted with EtOAc (25 mL). The organic layers were washed with H_2O and brine, dried over

anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/20 to 1/5) to give the corresponding aldehyde product **2x** (1.74 g, 80%).

Unsuccessful substrates:



4. Mechanism experiment

Luminescence quenching experiment (Stern–Volmer Studies)

The luminescence quenching experiment was taken using a Cary Eclipse fluorescence spectrophotometer (Varian, USA). The experiments were carried out in 1.0 x 10^{-6} mol/L *fac*-Ir(ppy)$_3$ of in anhydrous CH_3CN at 25 ^oC. Different concentration (0, 0.05, 0.1, 0.15, 0.20, 0.25, 0.30 M) of quencher in anhydrous CH_3CN were degassed by sparging with nitrogen for 15 minutes in 10 mm path length quartz cuvette, irradiated at 375 nm and emission intensity collected at 520 nm.

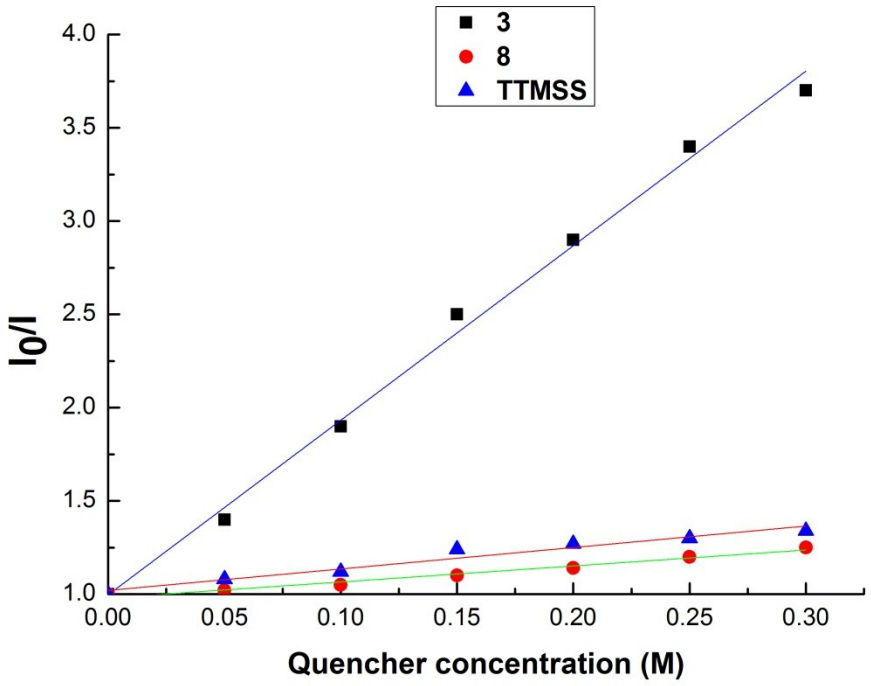
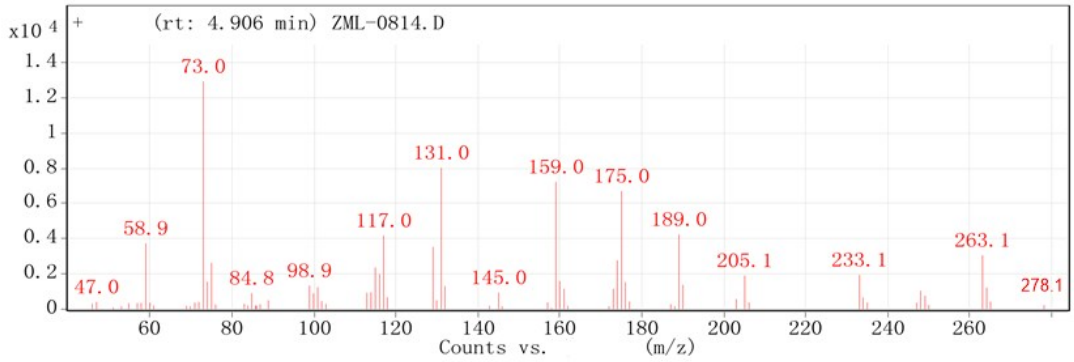


Figure S1. *fac*-Ir(ppy)$_3$ emission quenching with **3**, **8**, TTMSS.

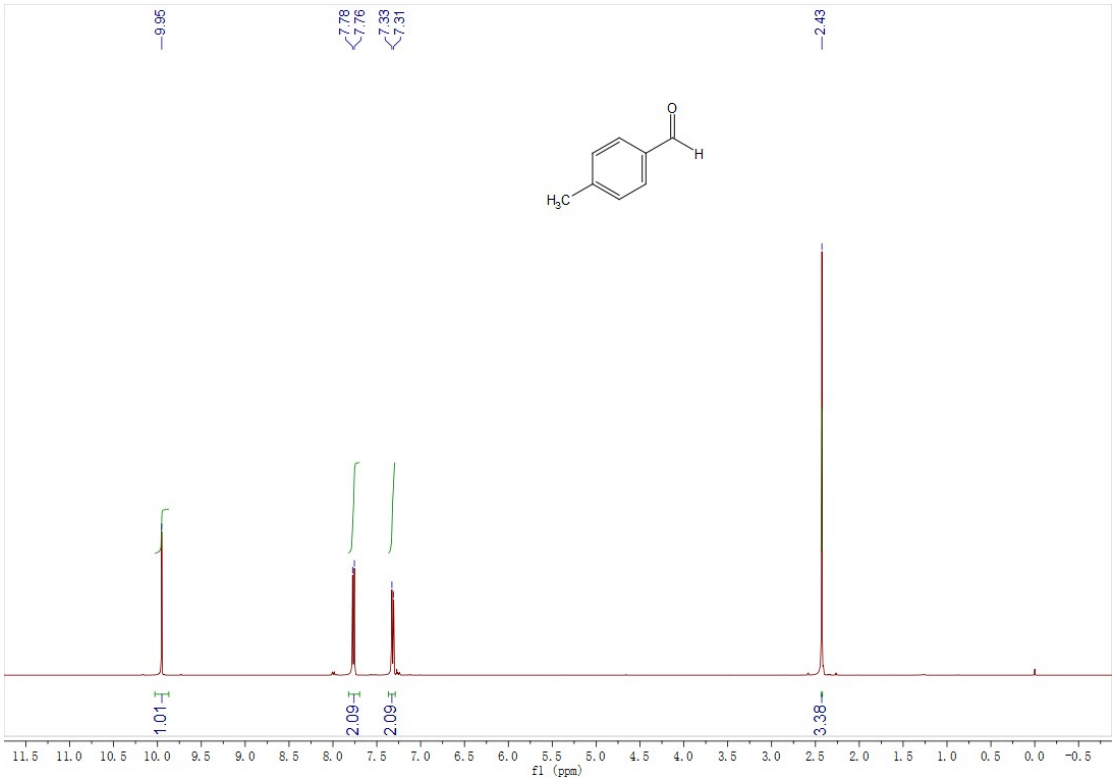
As shown in Figure S1 the emission intensity of the excited state of photocatalyst *fac*-Ir(ppy)$_3$ is decreased only in the presence of (methyl carbonic) 4-methylbenzoic anhydride **3**. In contrast, when solutions of (methyl carbonic) 3-oxo-3-phenylpropanoic anhydride **8**, TTMSS have been employed, no obvious fluorescence quenching has been observed. These results strongly support the role of mixed aromatic anhydride **3** as oxidative quencher of the excited state of *fac*-Ir(ppy)$_3$ proposed in Scheme 5 of the manuscript.

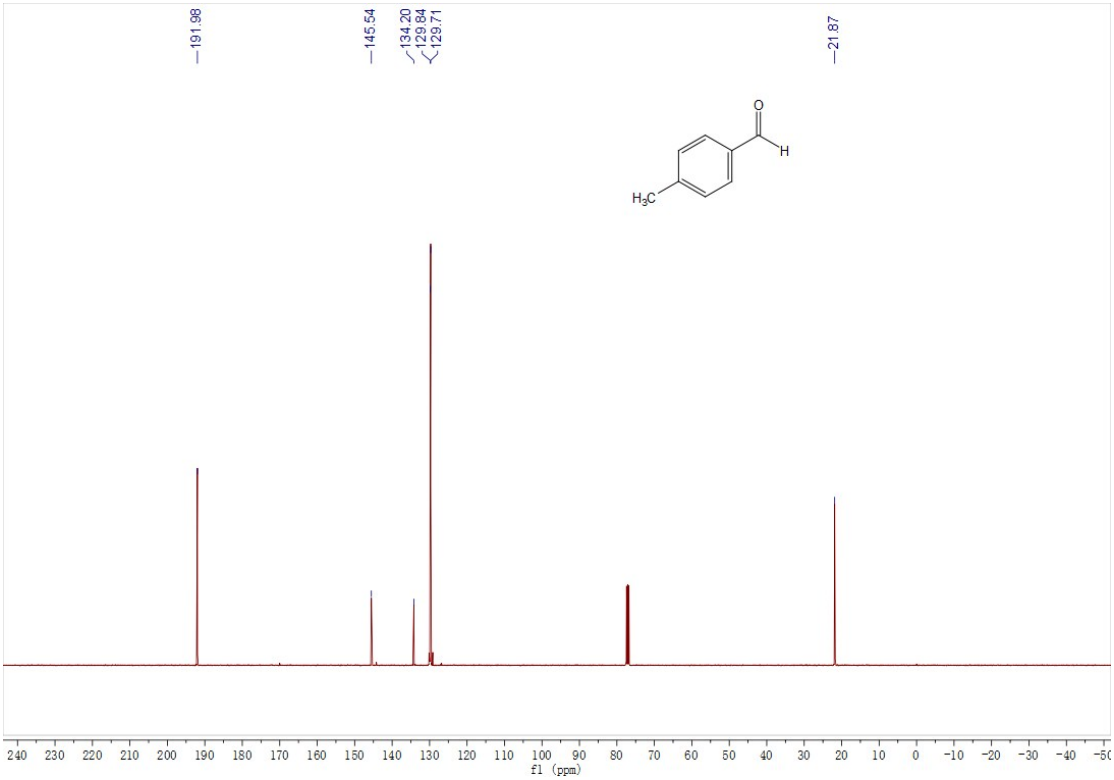
Copy of GC−MS Spectra



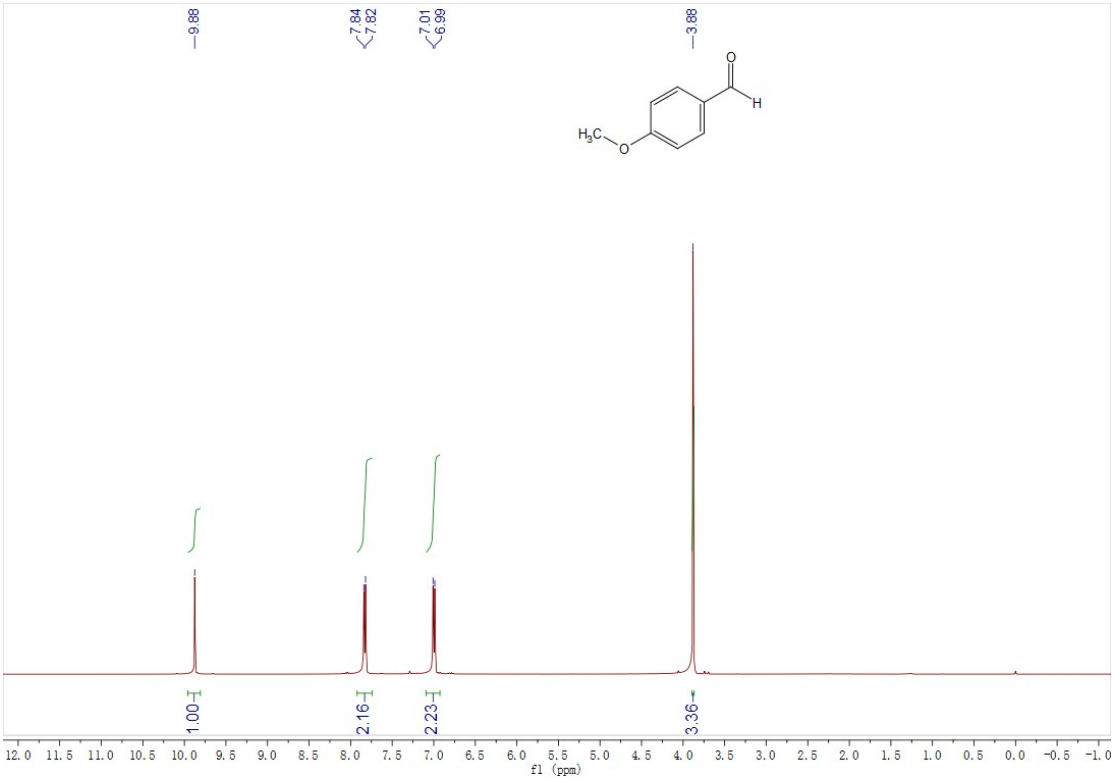
5. Copies of ^{1}H NMR, ^{13}C NMR Spectra

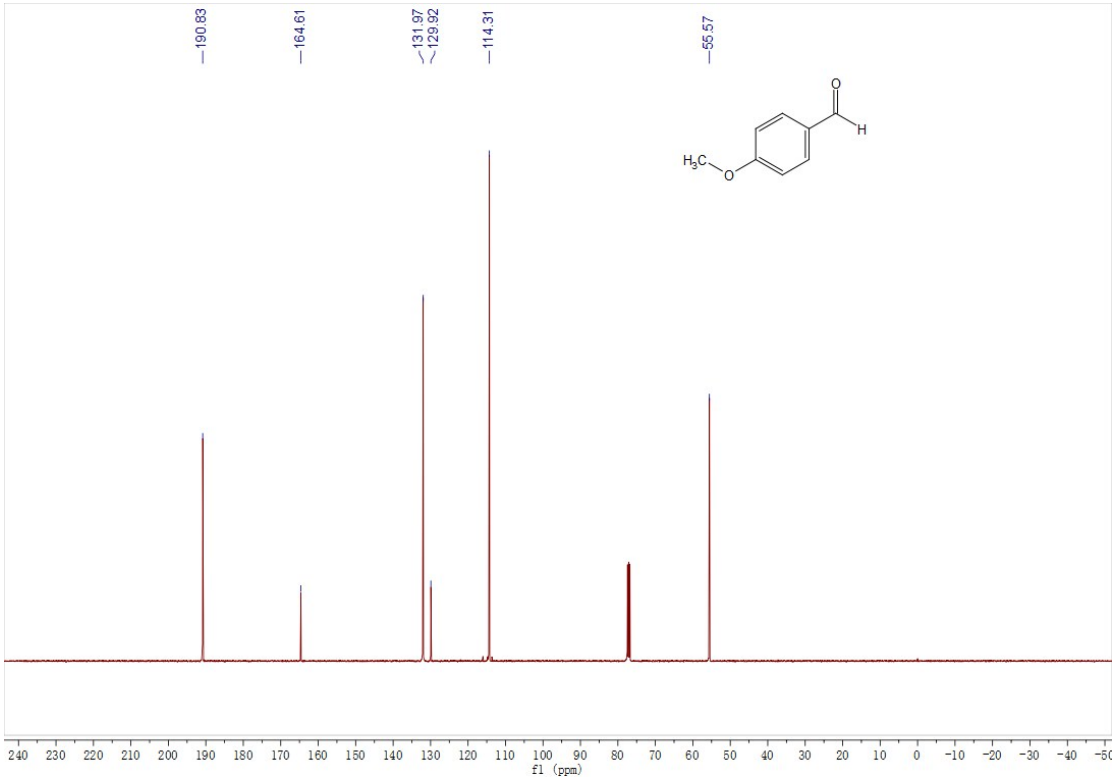
4-methylbenzaldehyde 2a



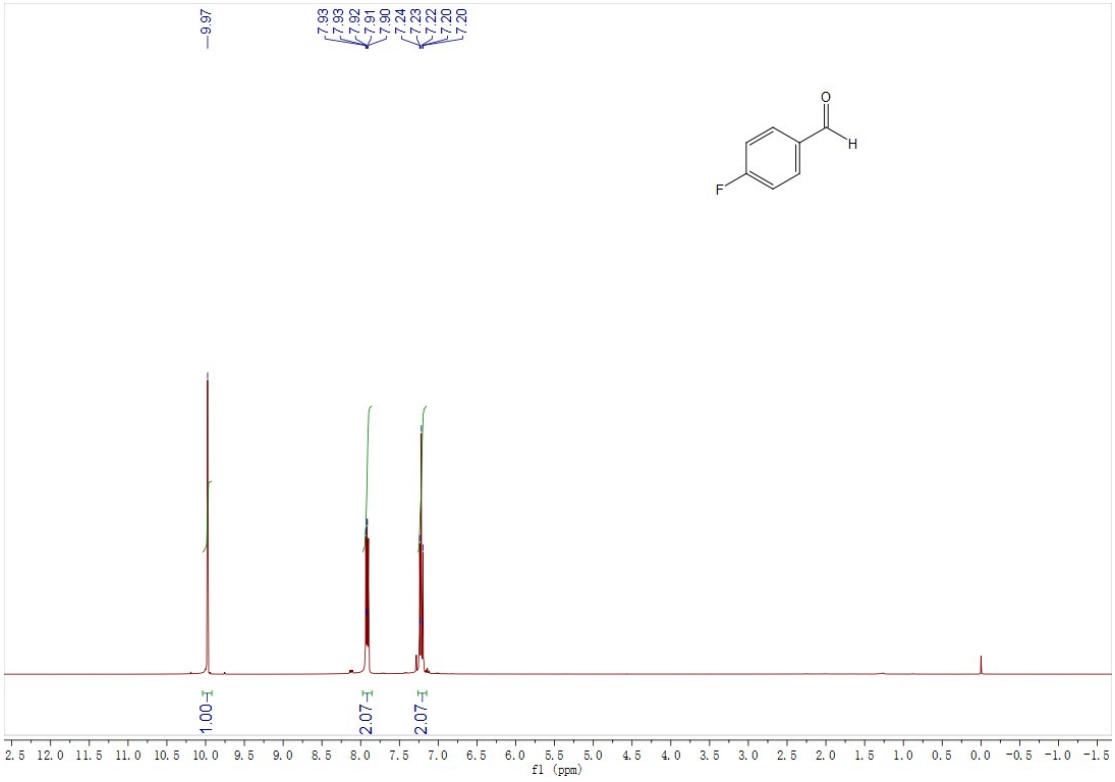


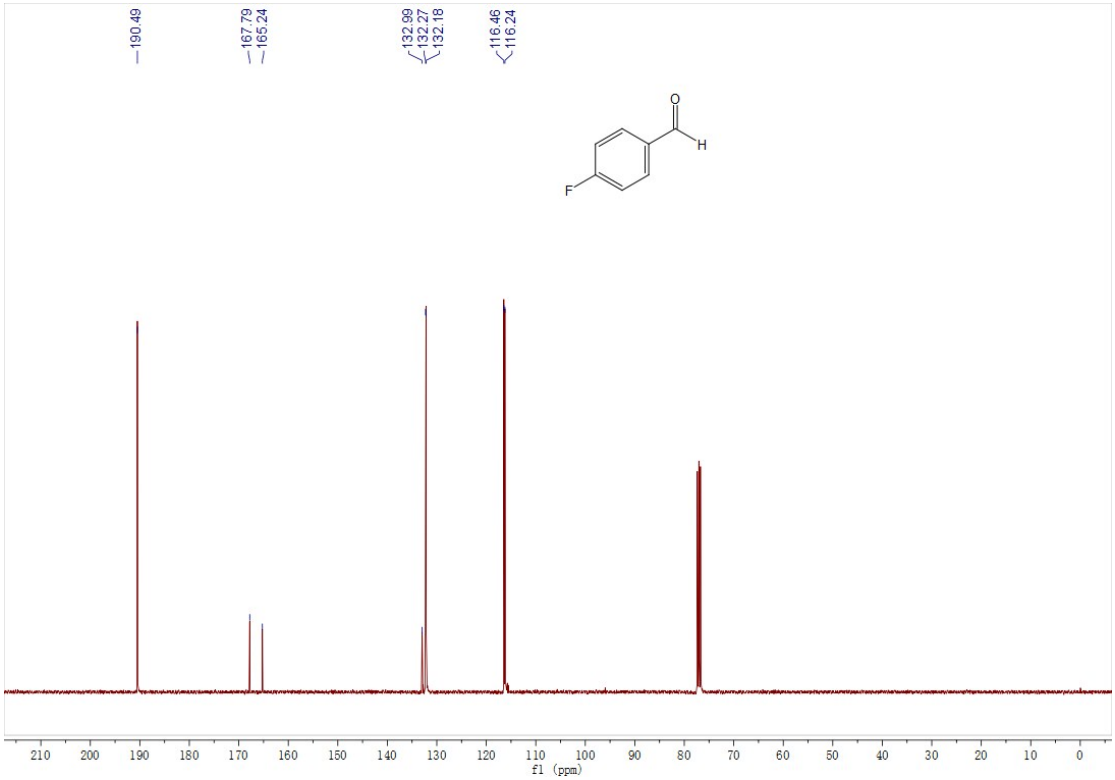
4-methoxybenzaldehyde 2b



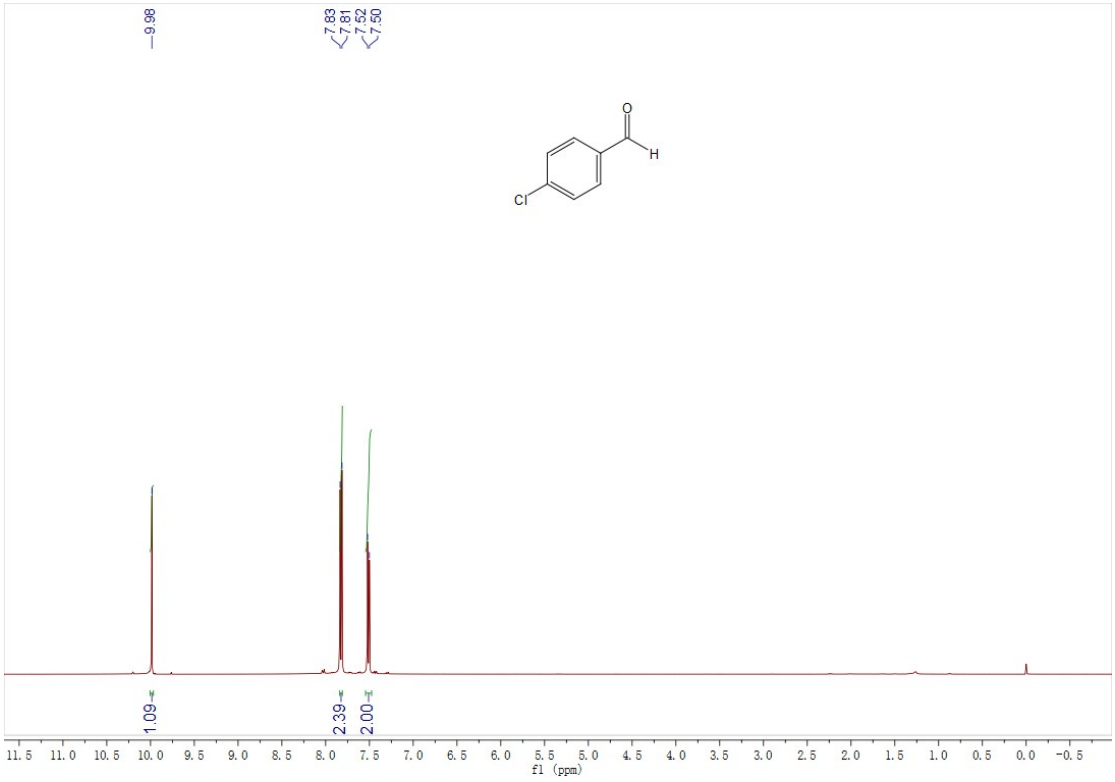


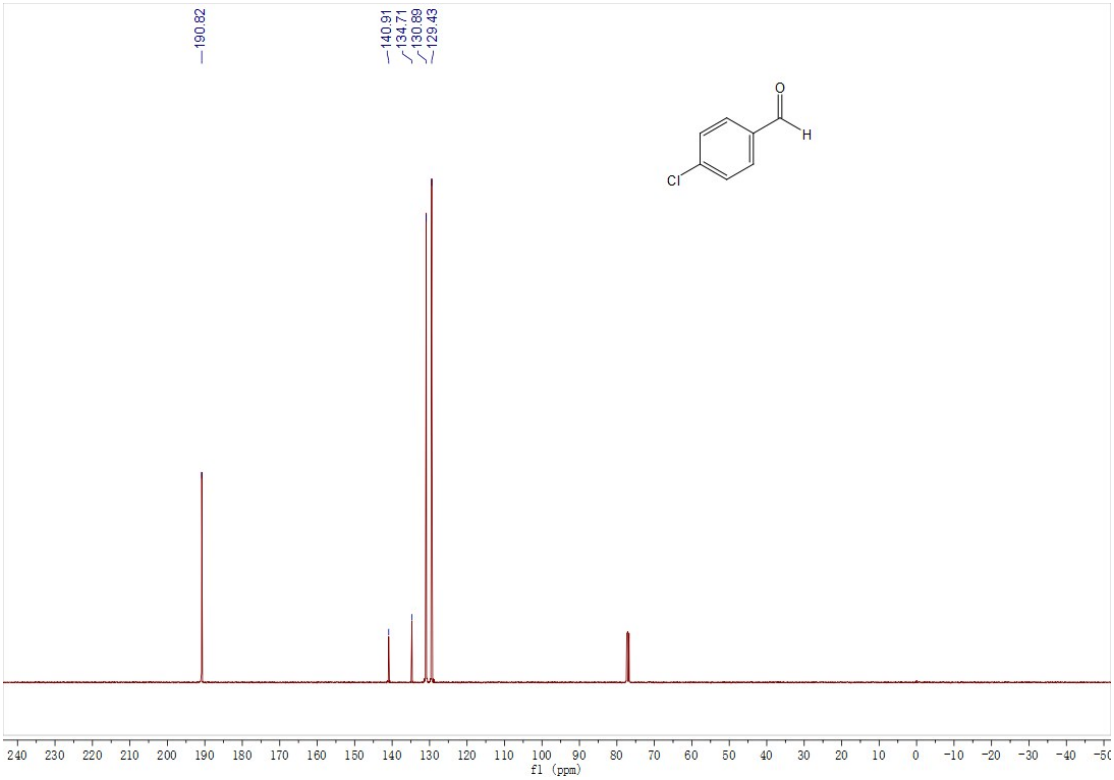
4-fluorobenzaldehyde 2c



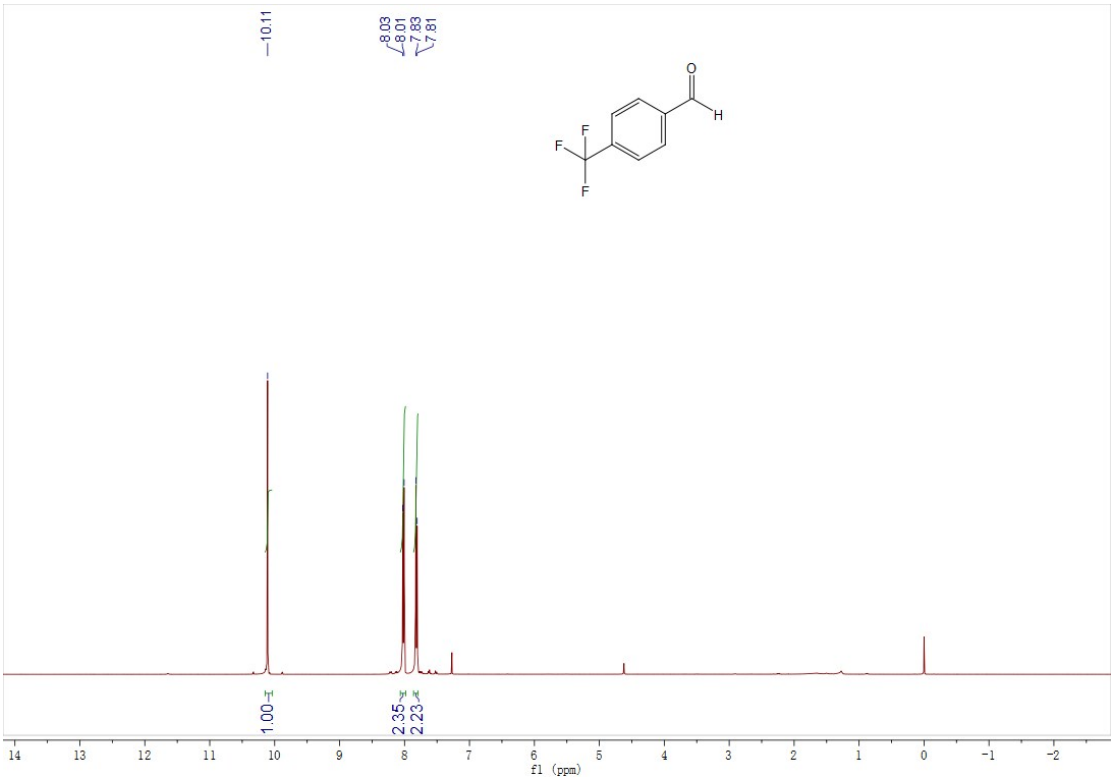


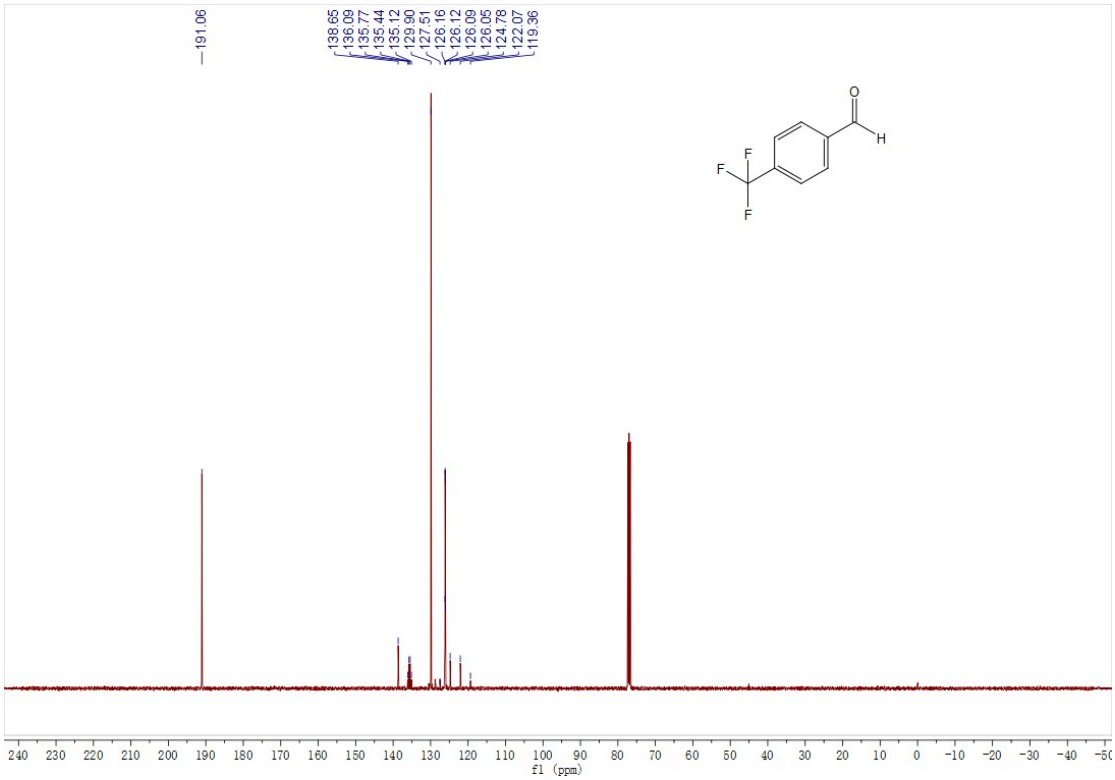
4-chlorobenzaldehyde 2d



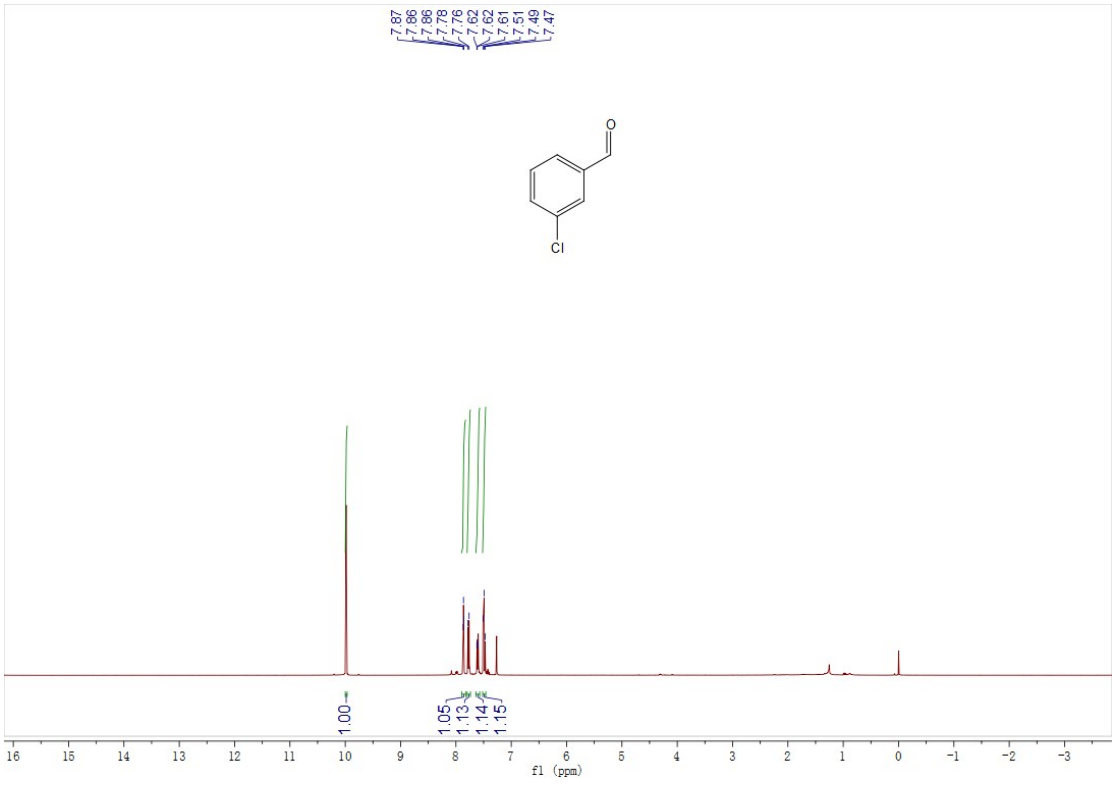


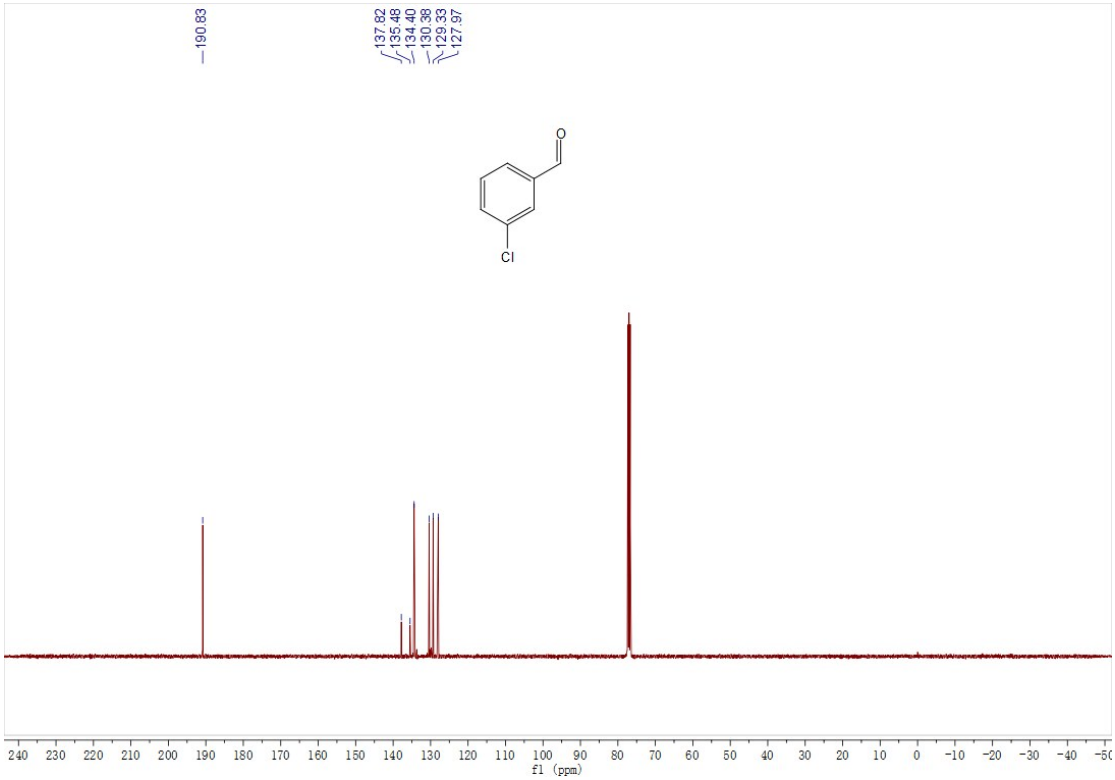
4-(trifluoromethyl)benzaldehyde 2e



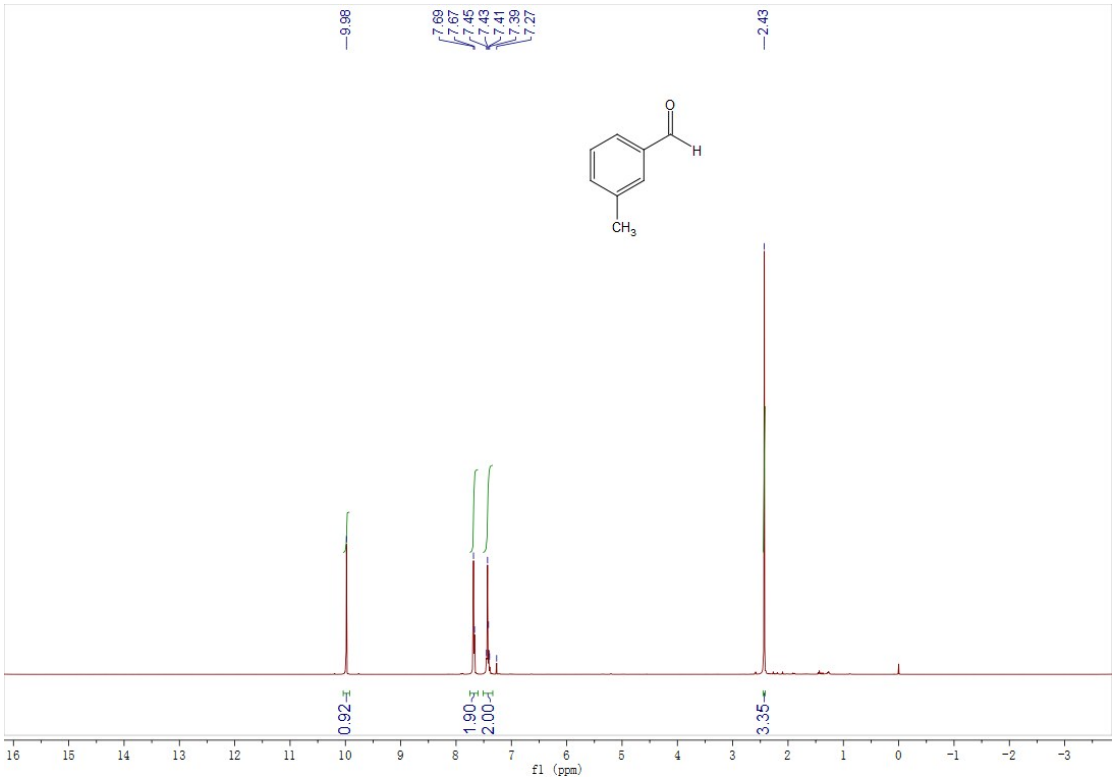


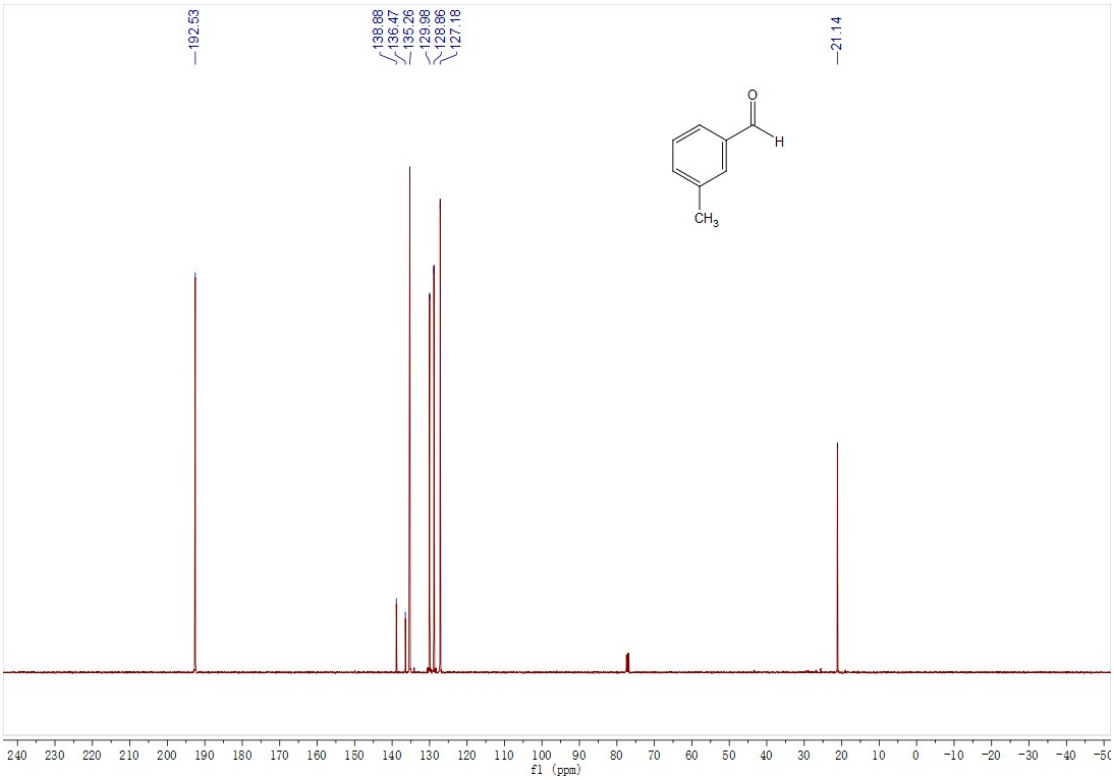
3-chlorobenzaldehyde 2f



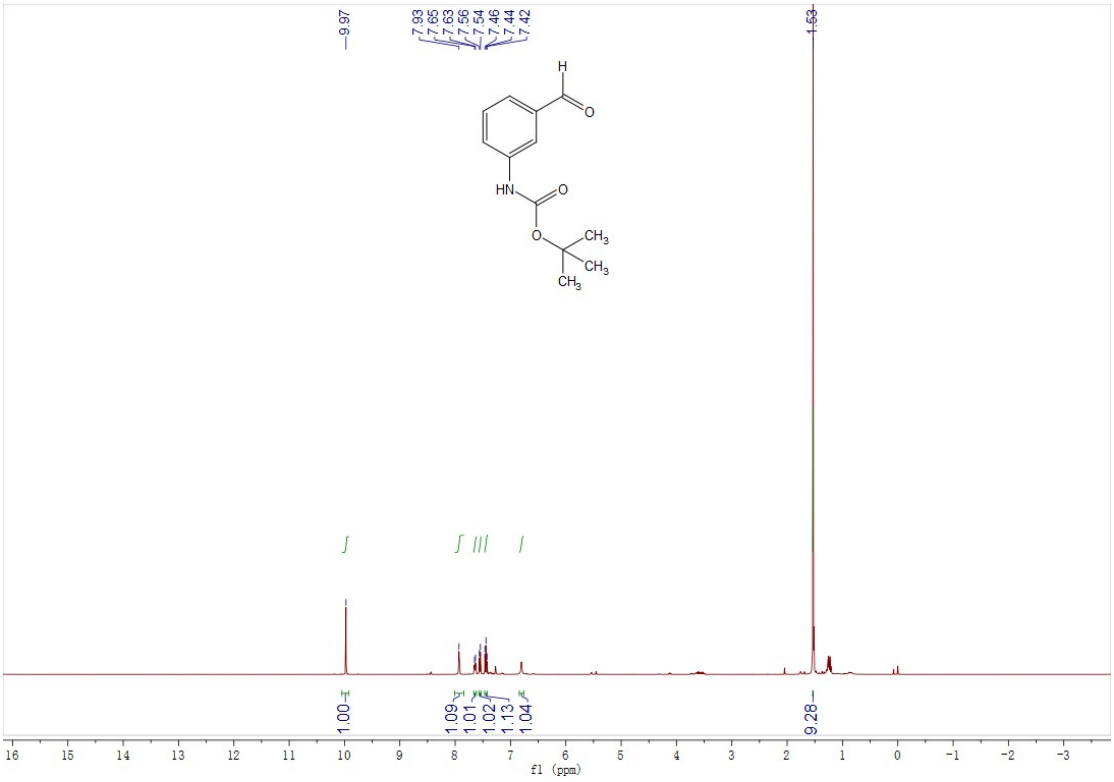


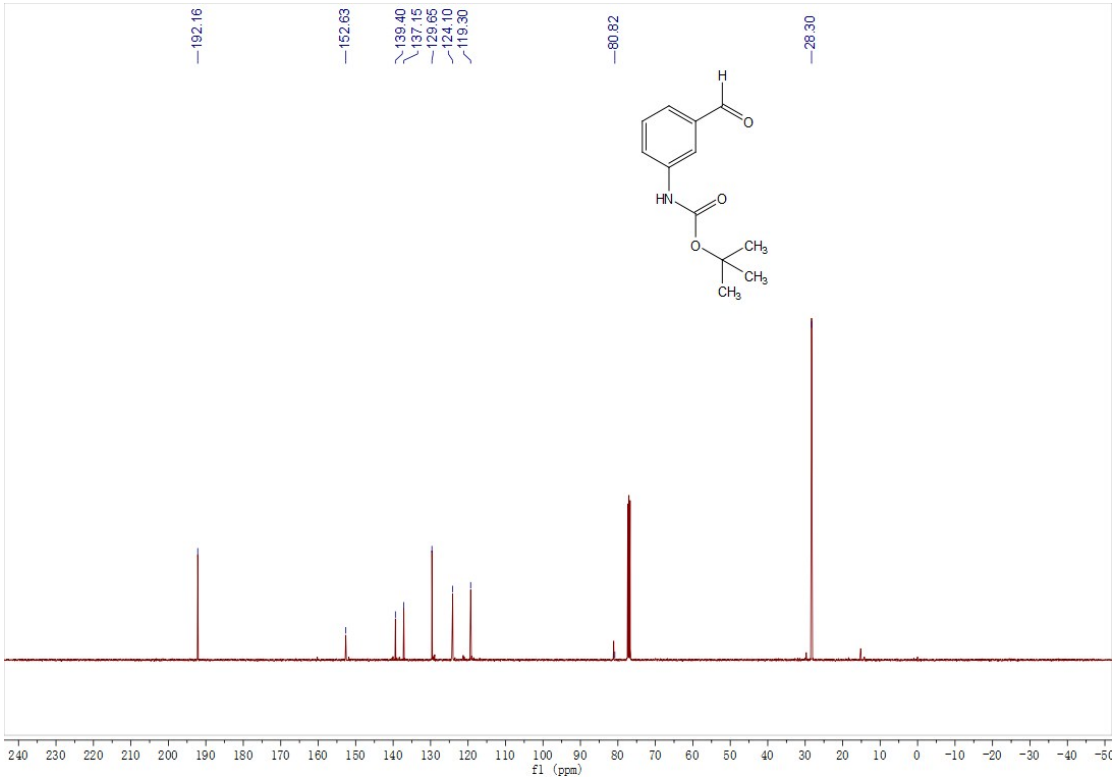
3-methylbenzaldehyde 2g



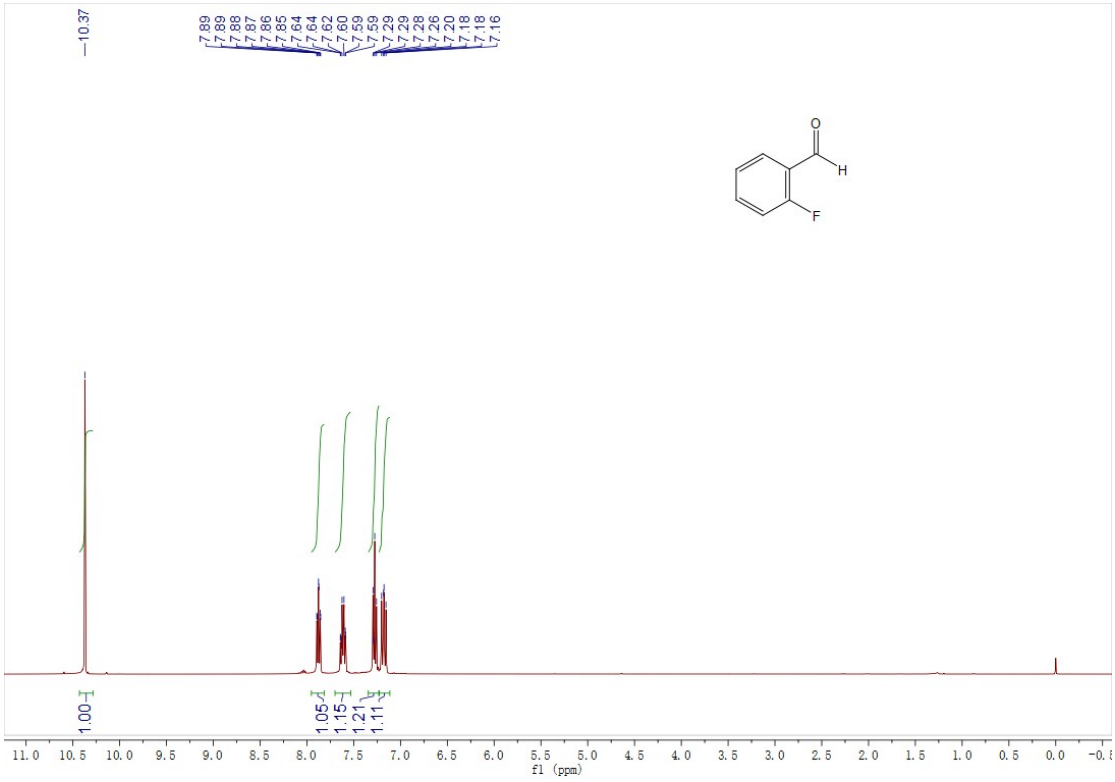


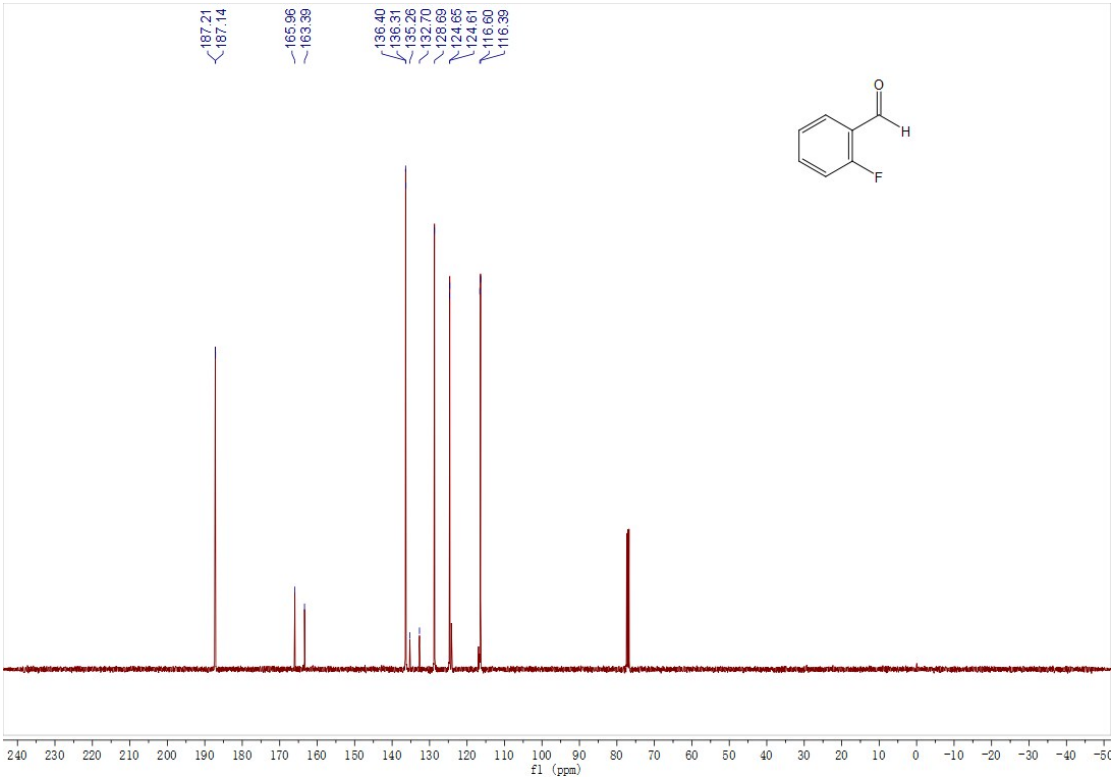
tert-butyl (3-formylphenyl)carbamate 2h



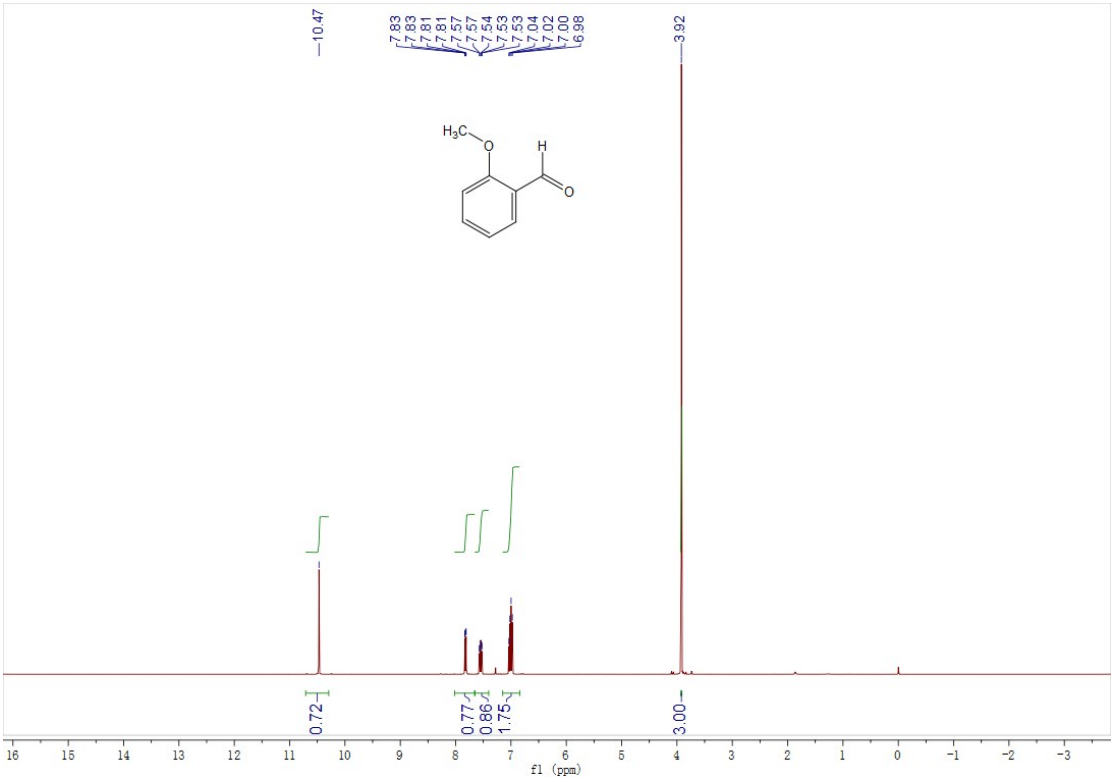


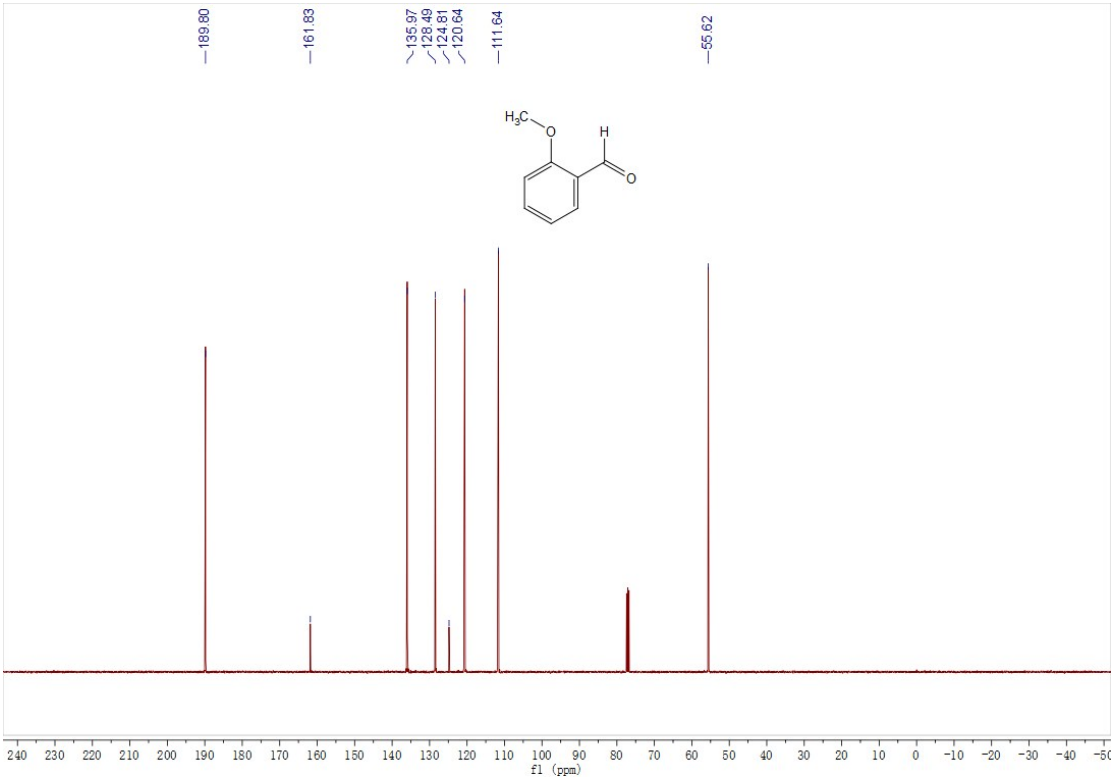
2-fluorobenzaldehyde 2i



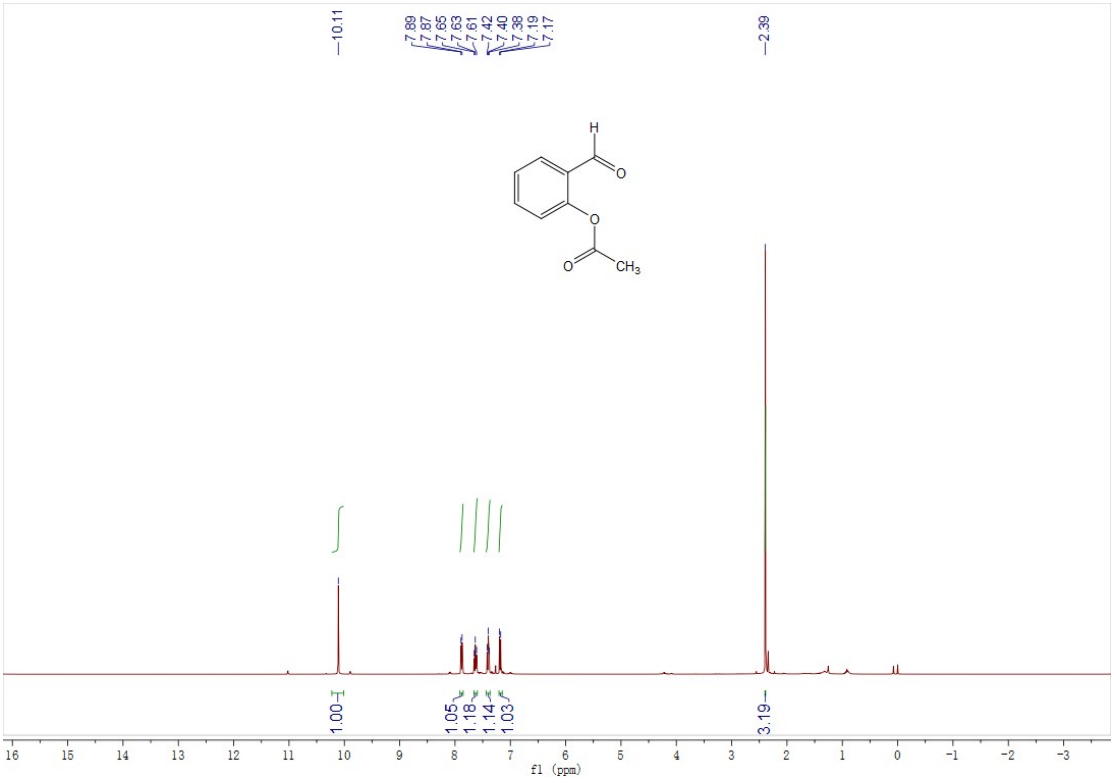


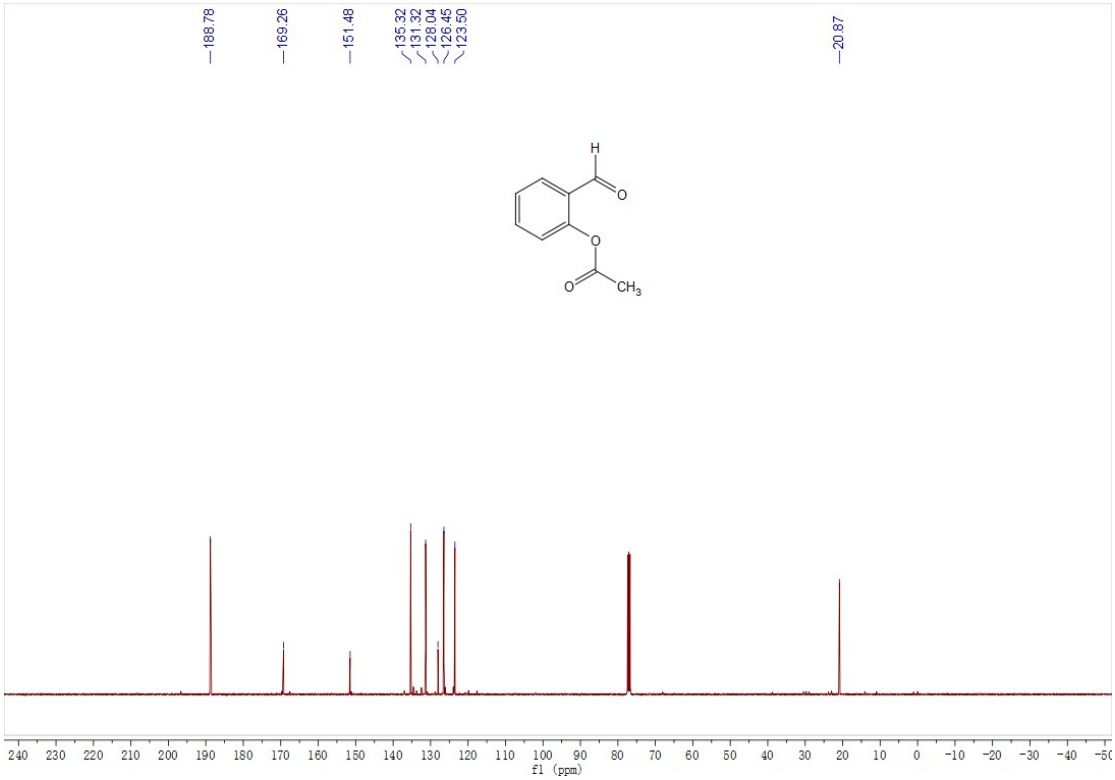
2-methoxybenzaldehyde 2j



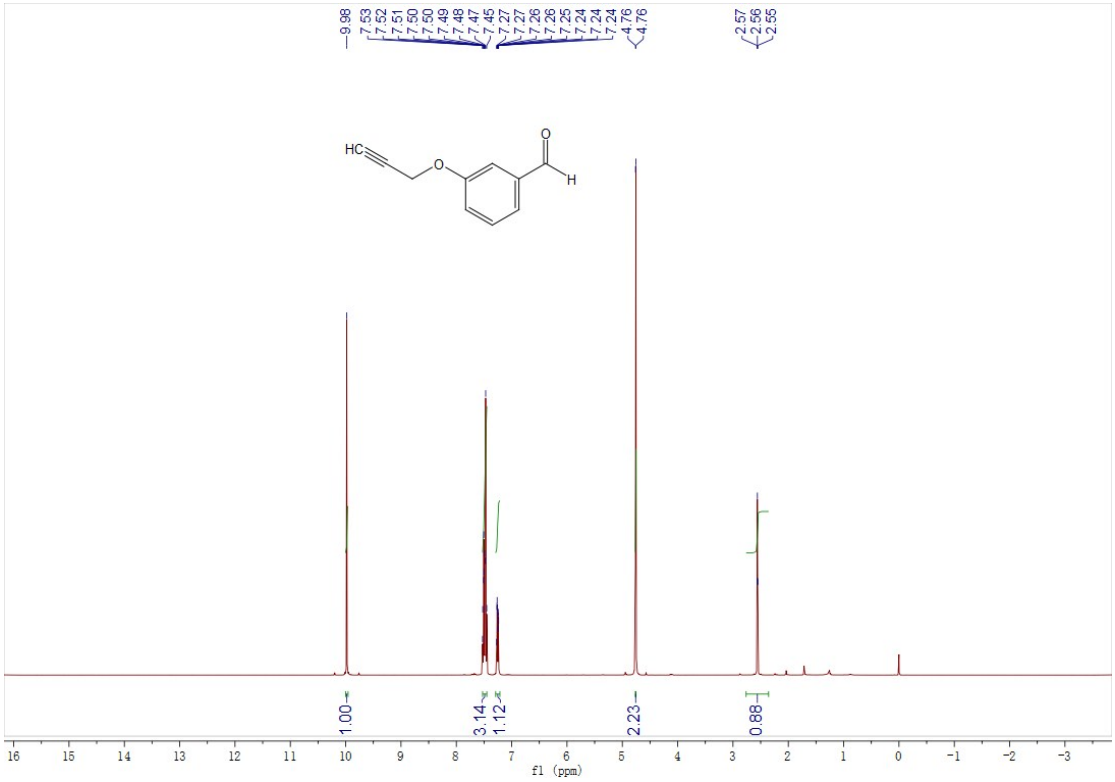


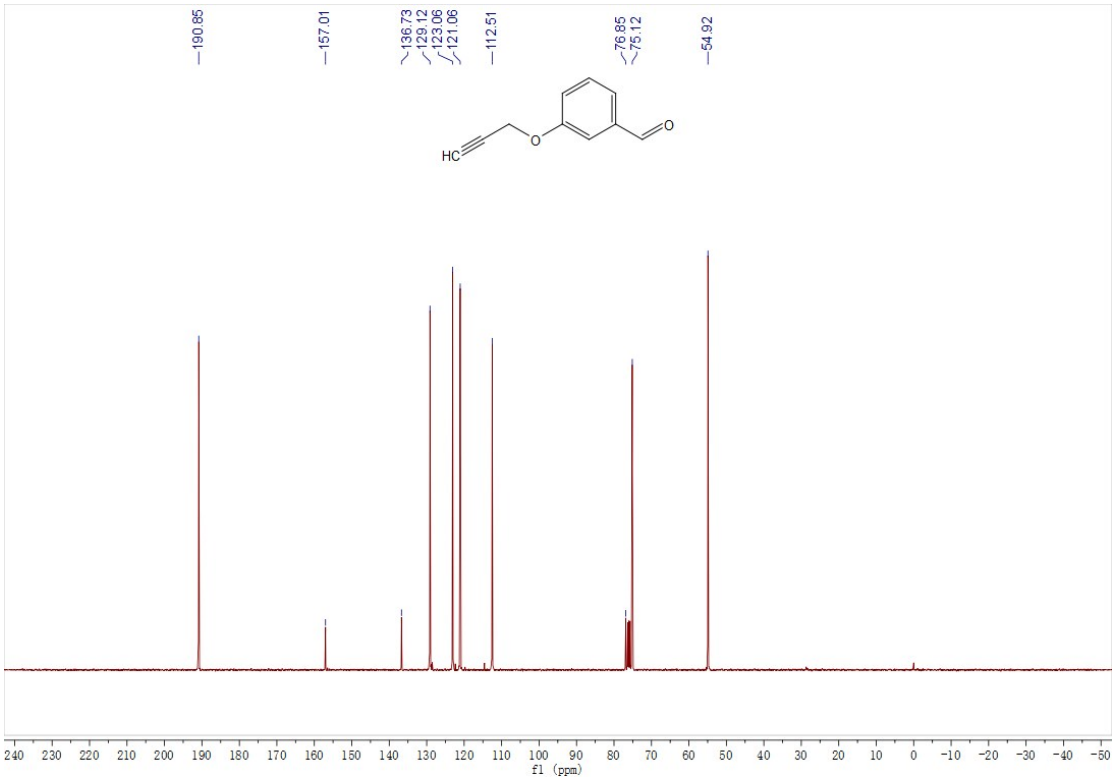
2-formylphenyl acetate 2k



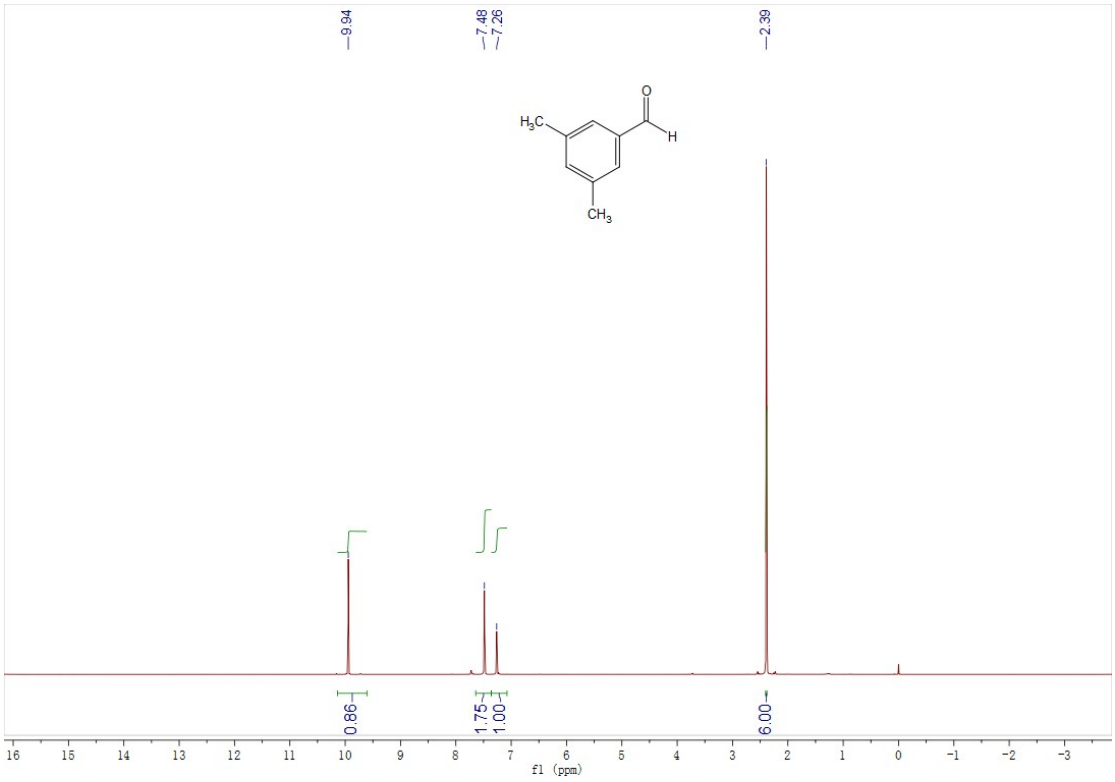


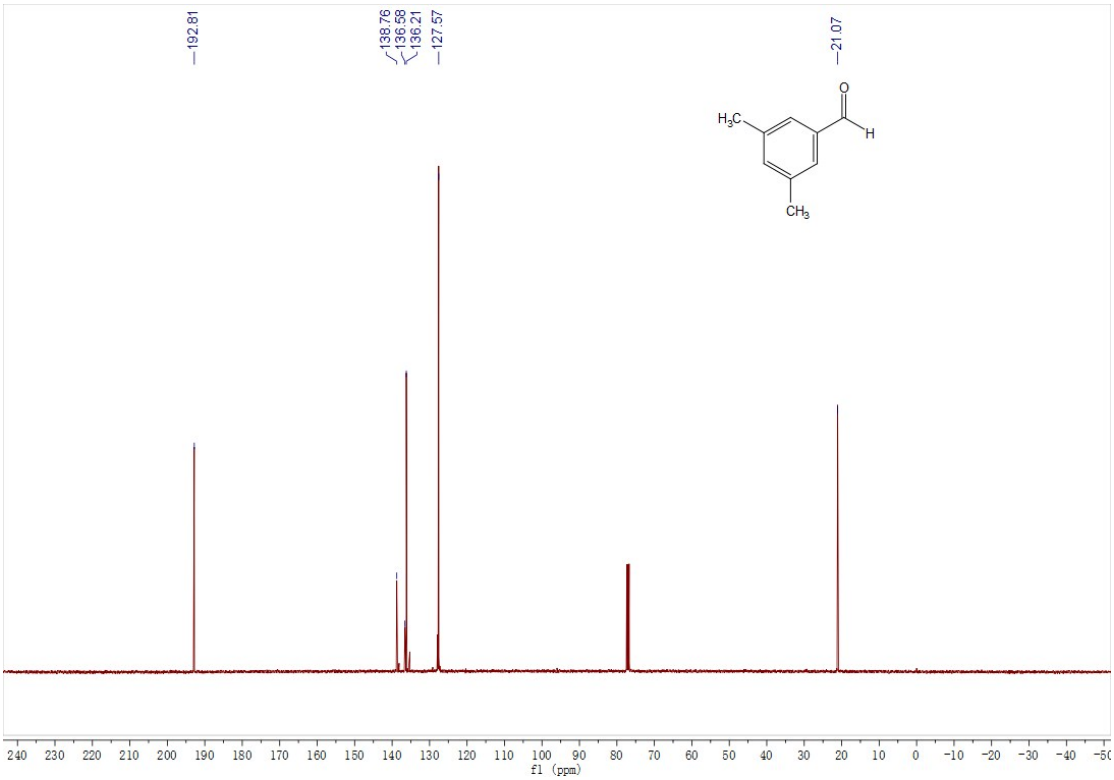
3-(prop-2-yn-1-yloxy)benzaldehyde 2l



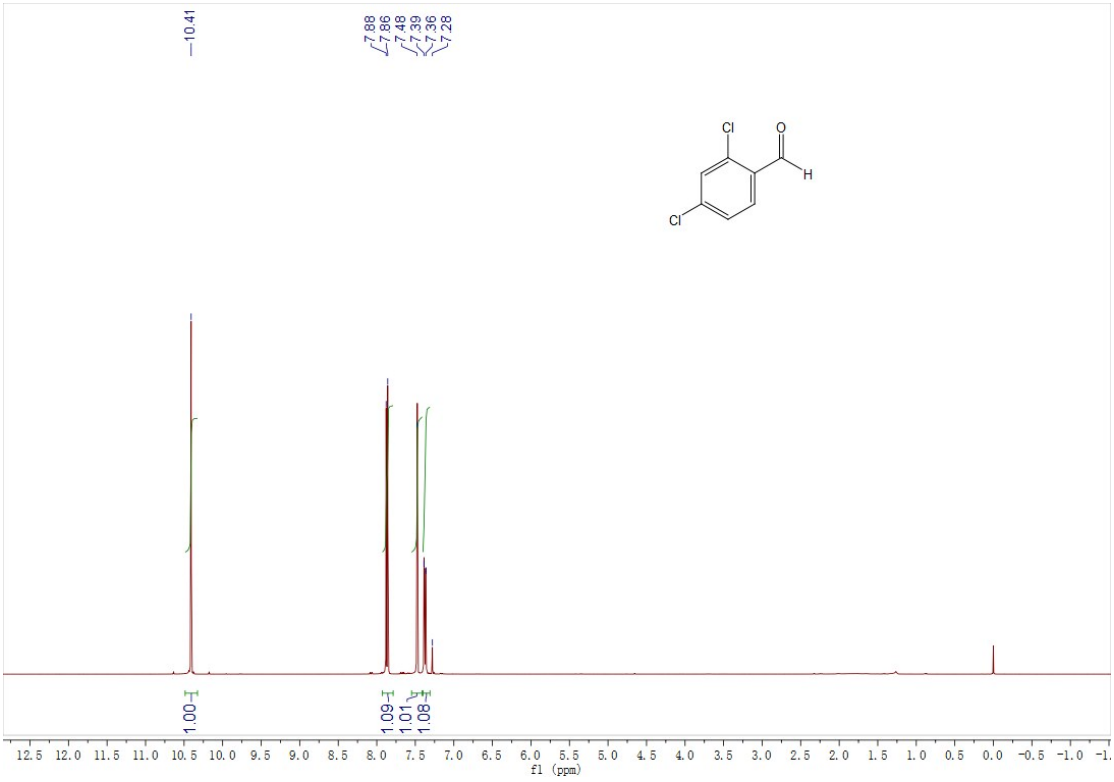


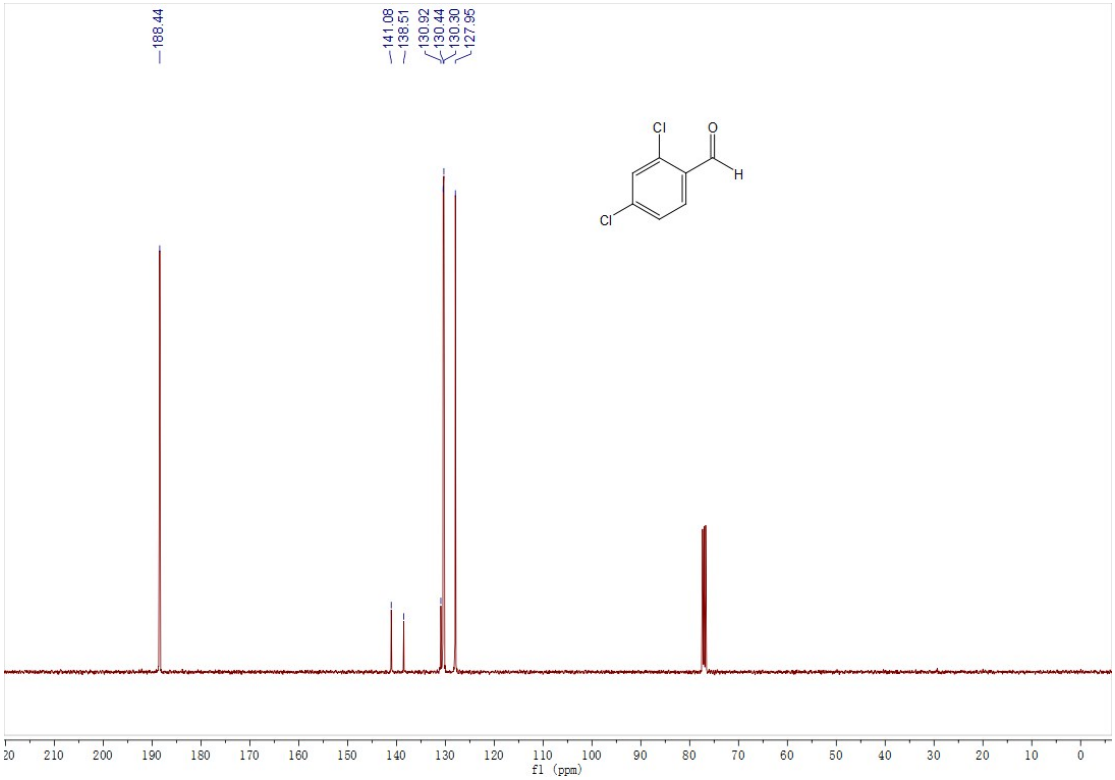
3,5-dimethylbenzaldehyde 2m



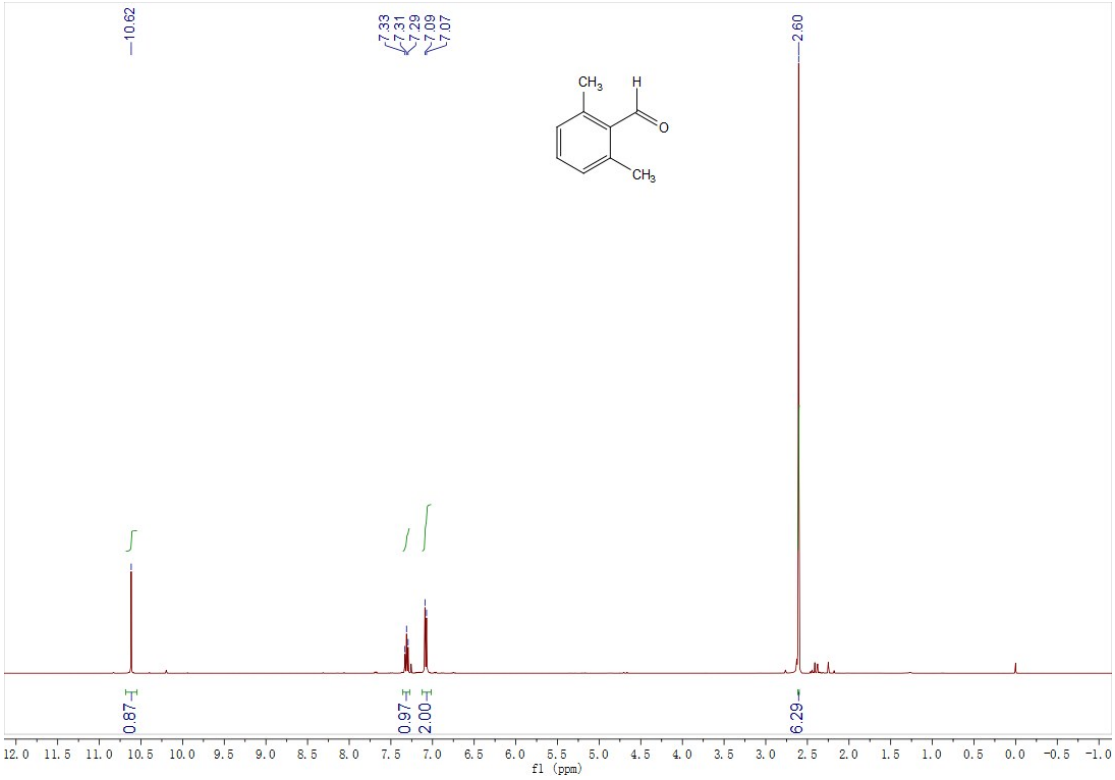


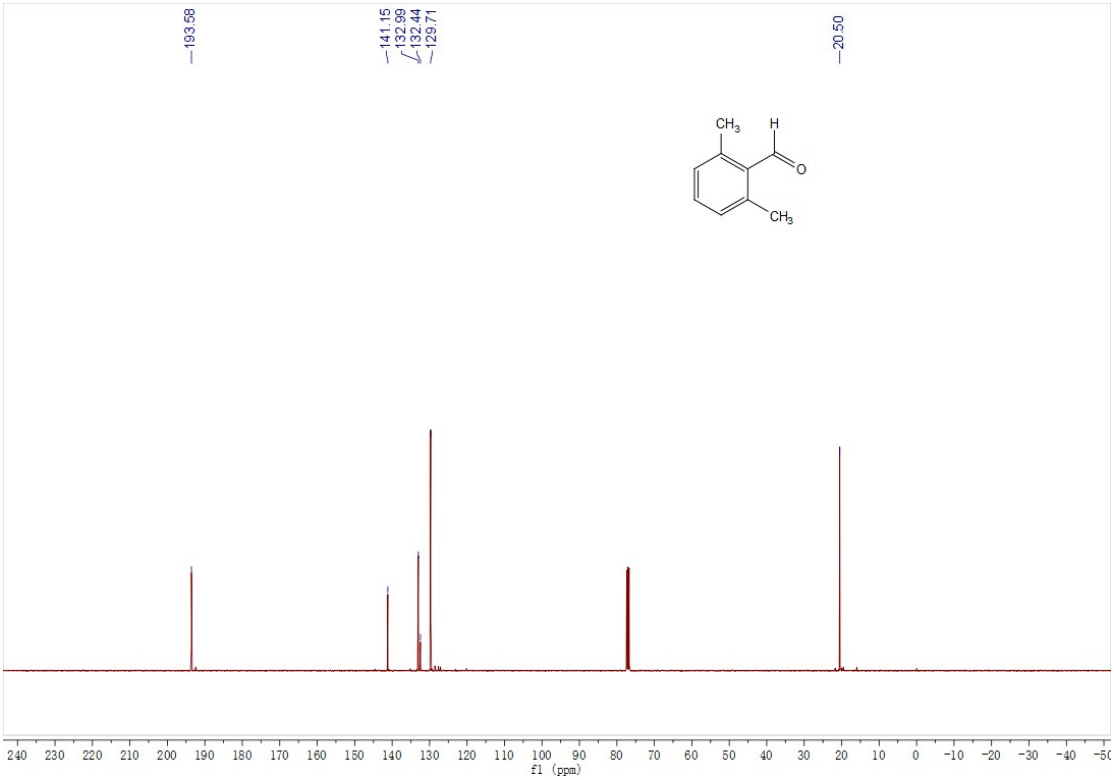
2,4-dichlorobenzaldehyde 2n



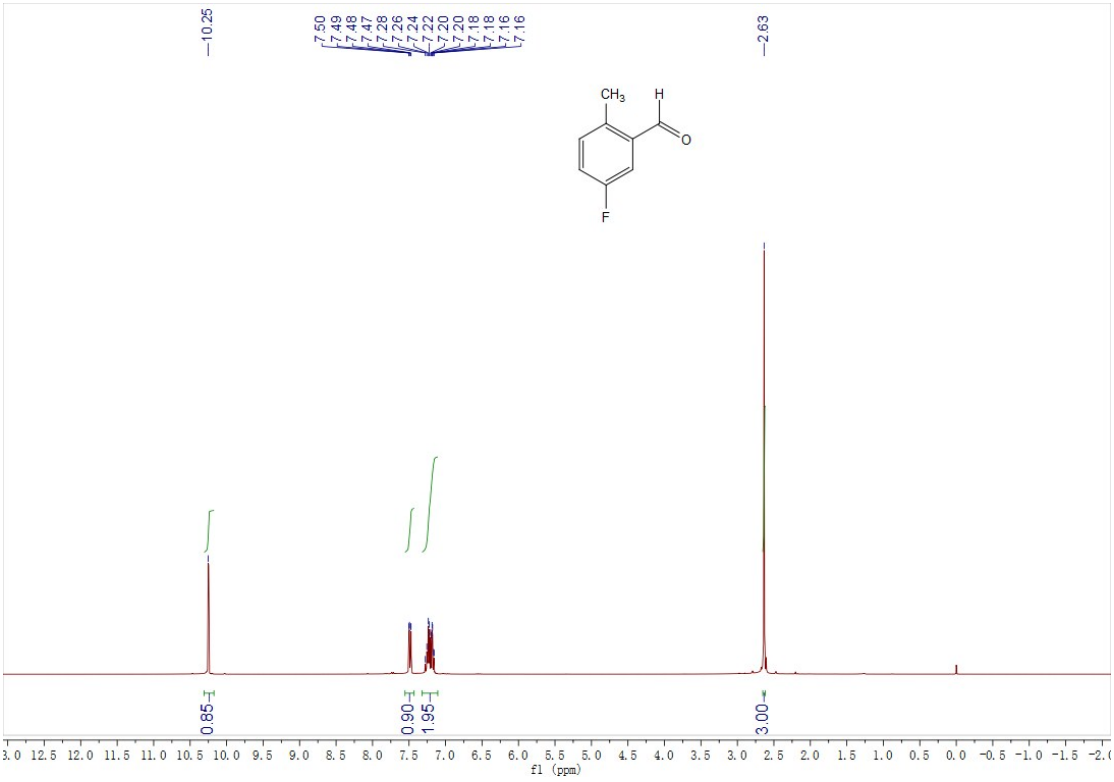


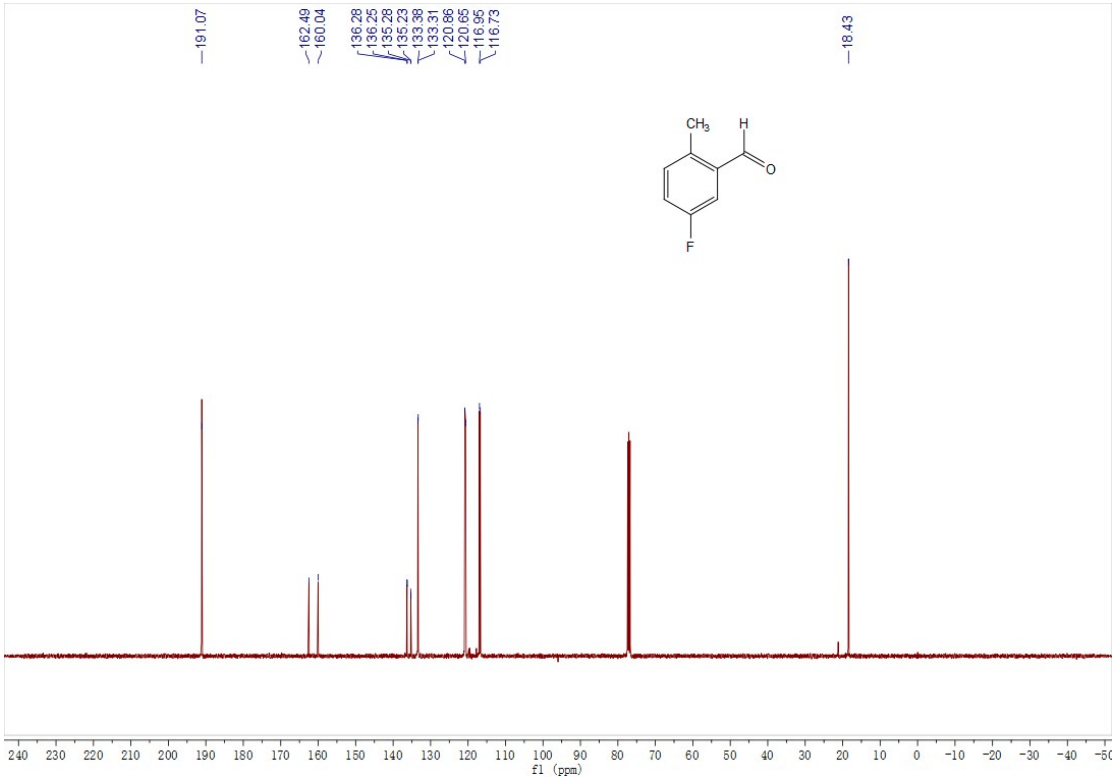
2,6-dimethylbenzaldehyde 2o



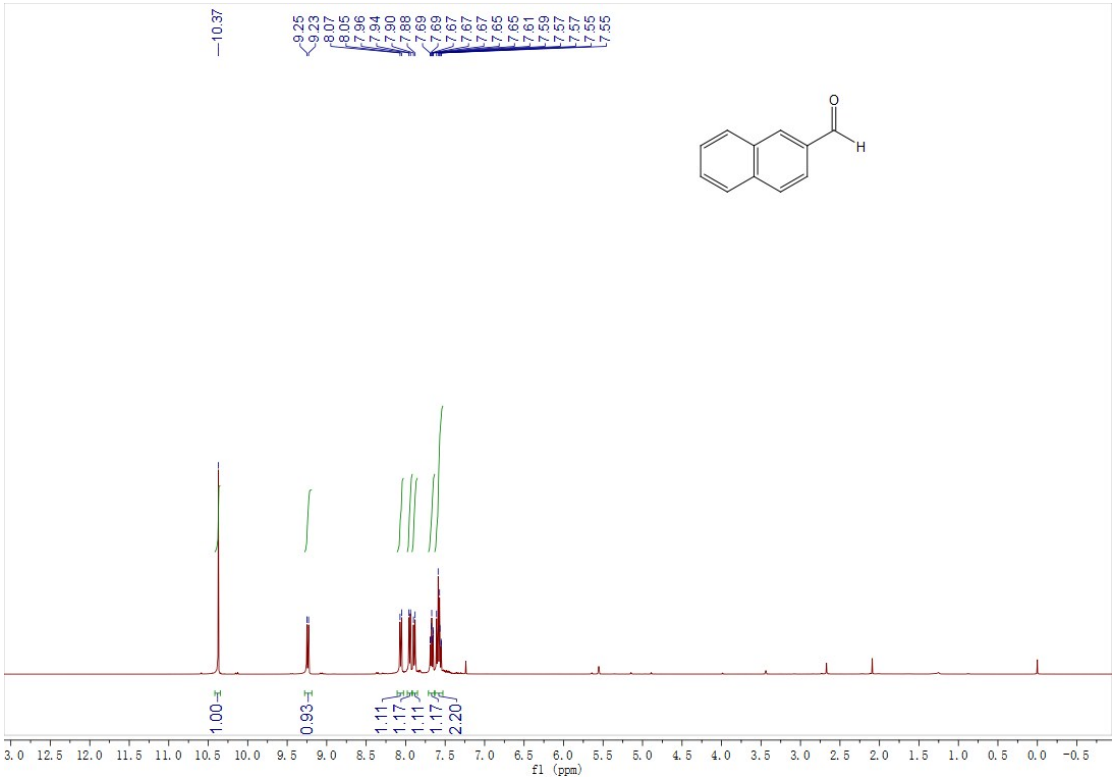


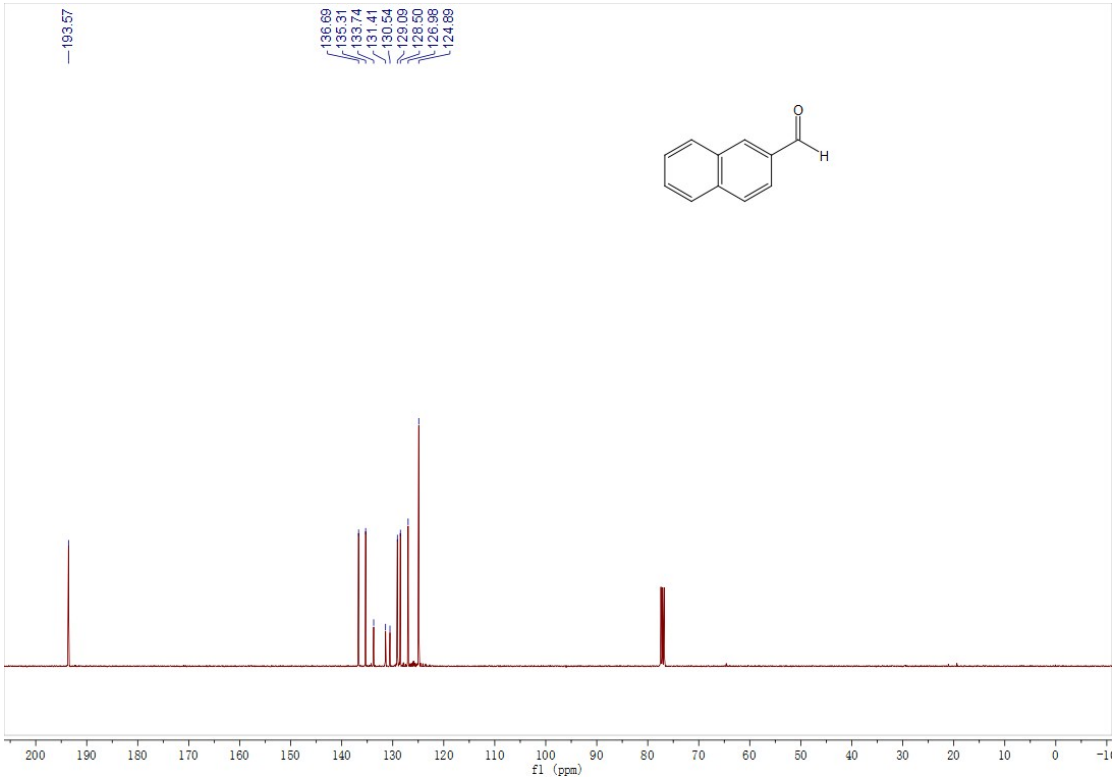
5-fluoro-2-methylbenzaldehyde 2p



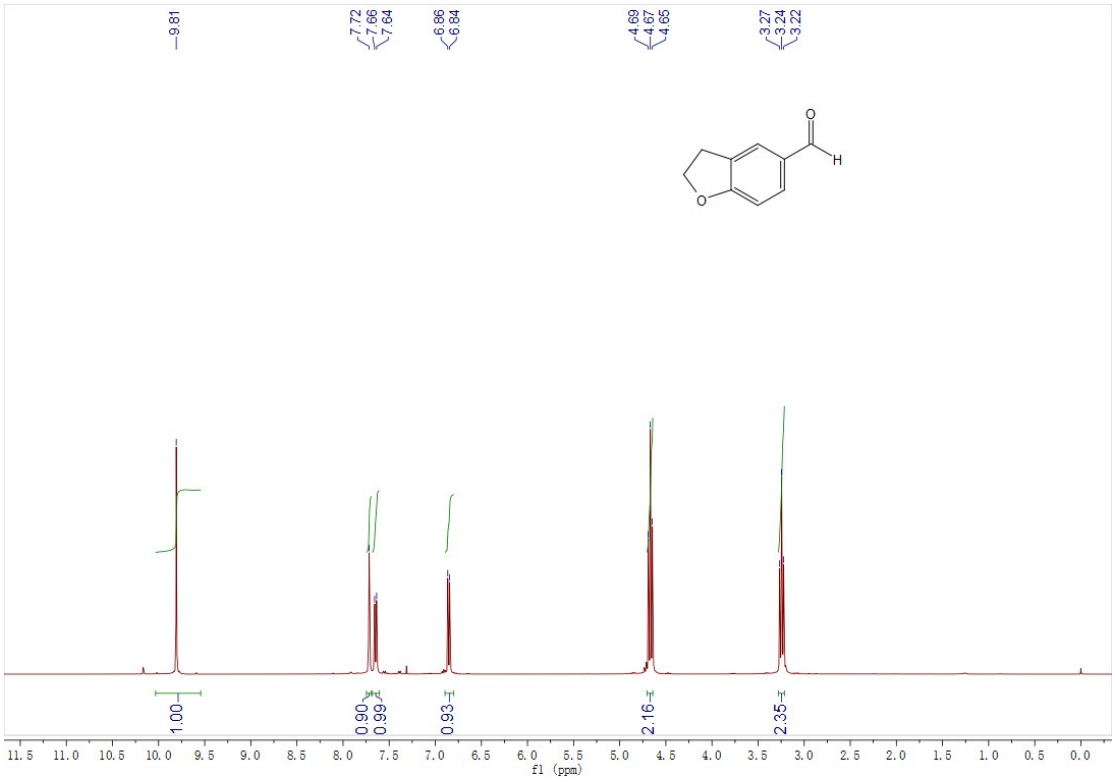


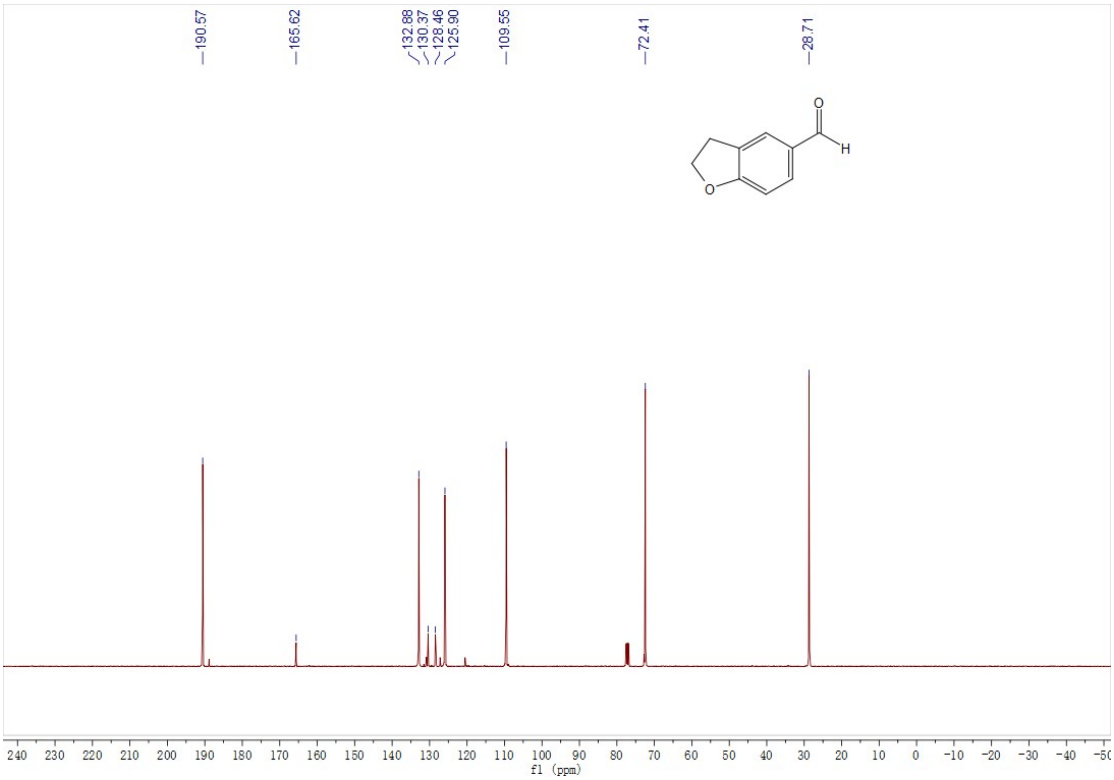
2-naphthaldehyde 2q



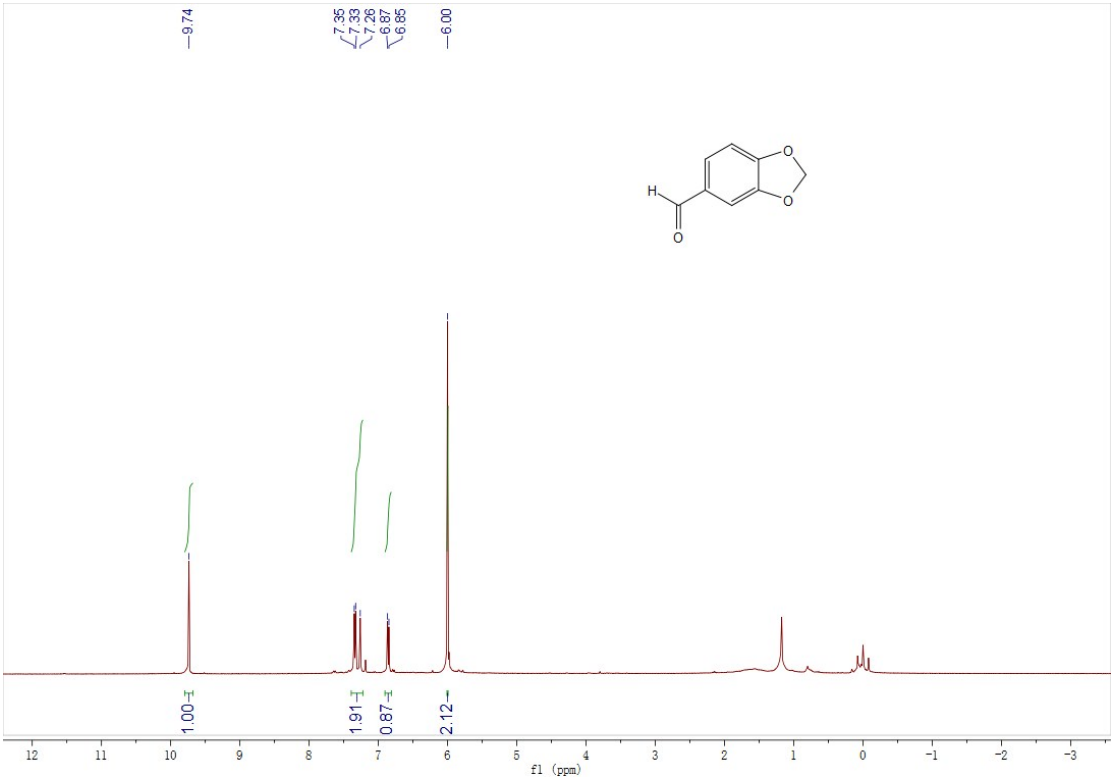


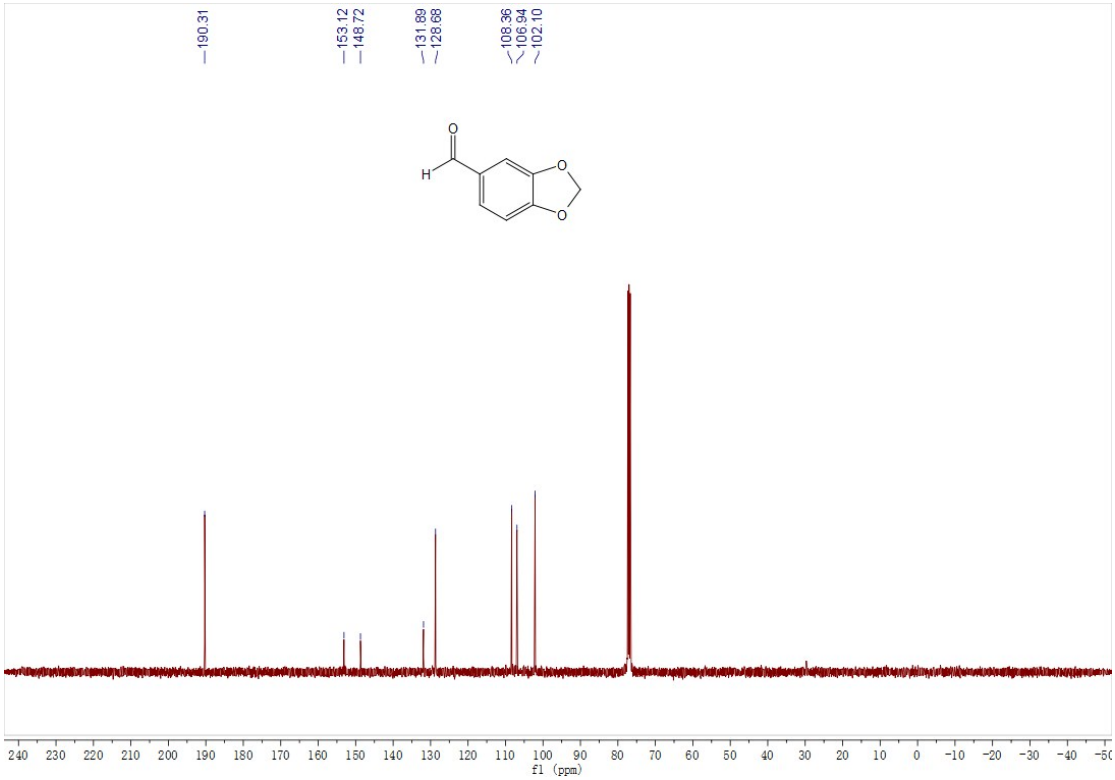
2,3,3a,7a-tetrahydrobenzofuran-5-carbaldehyde 2r



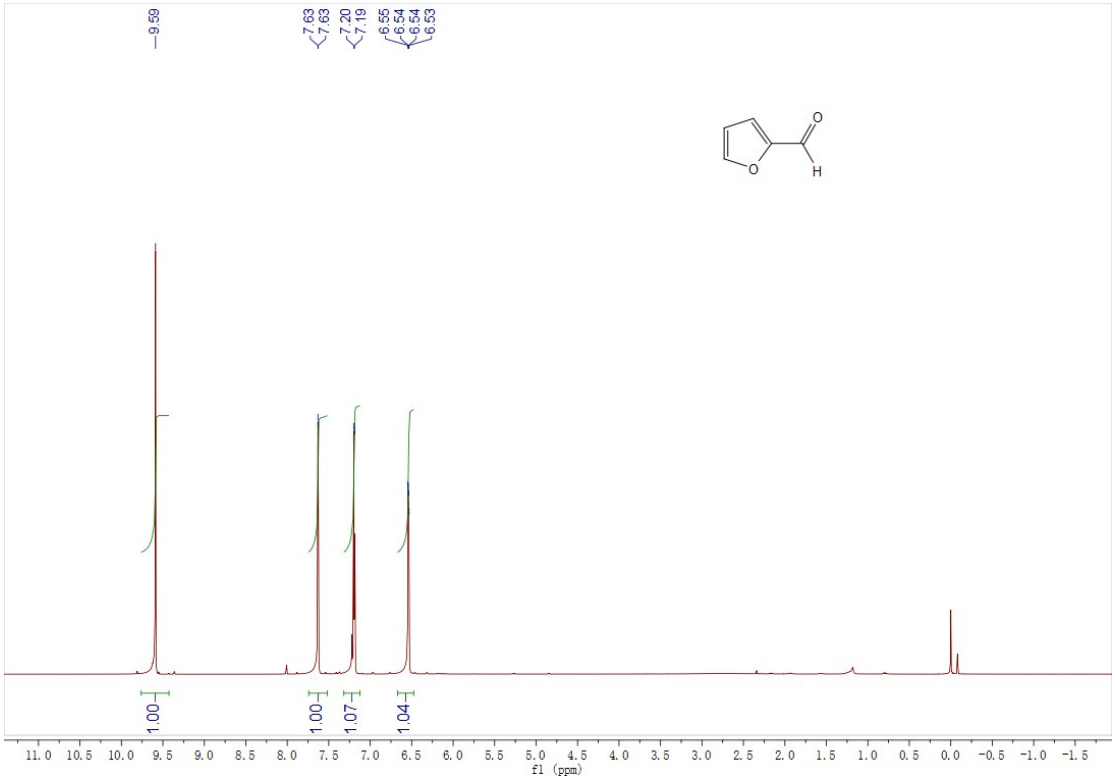


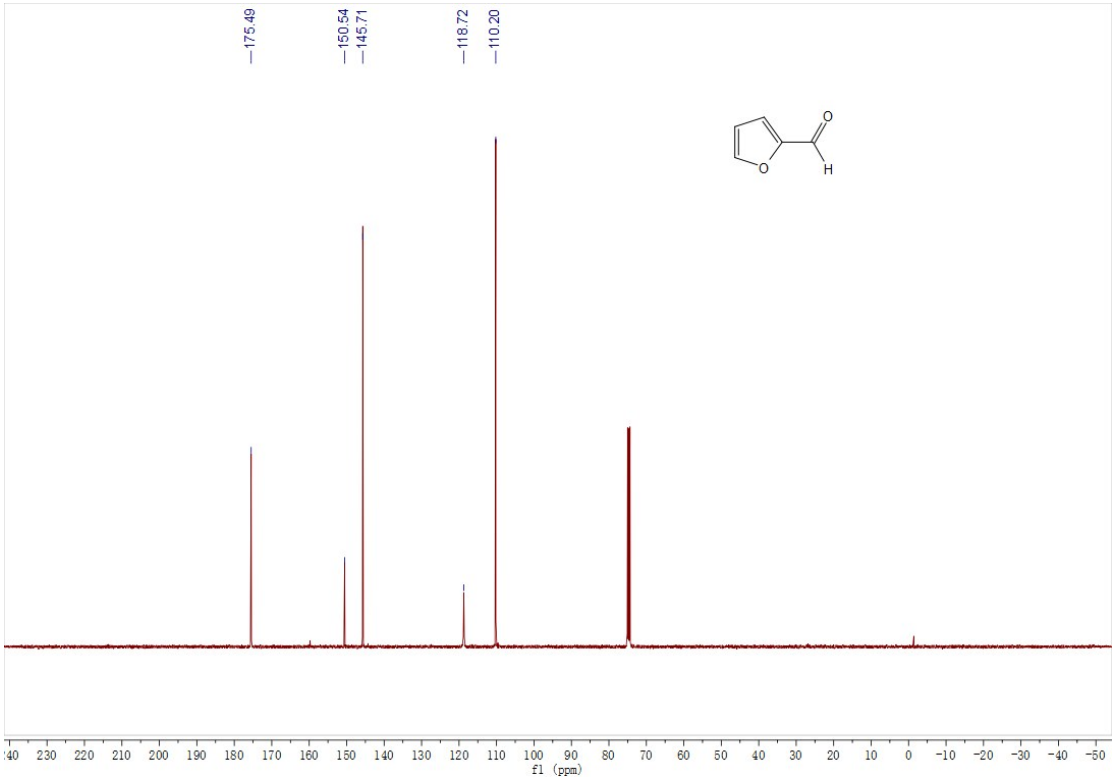
benzo[d][1,3]dioxole-5-carbaldehyde 2s



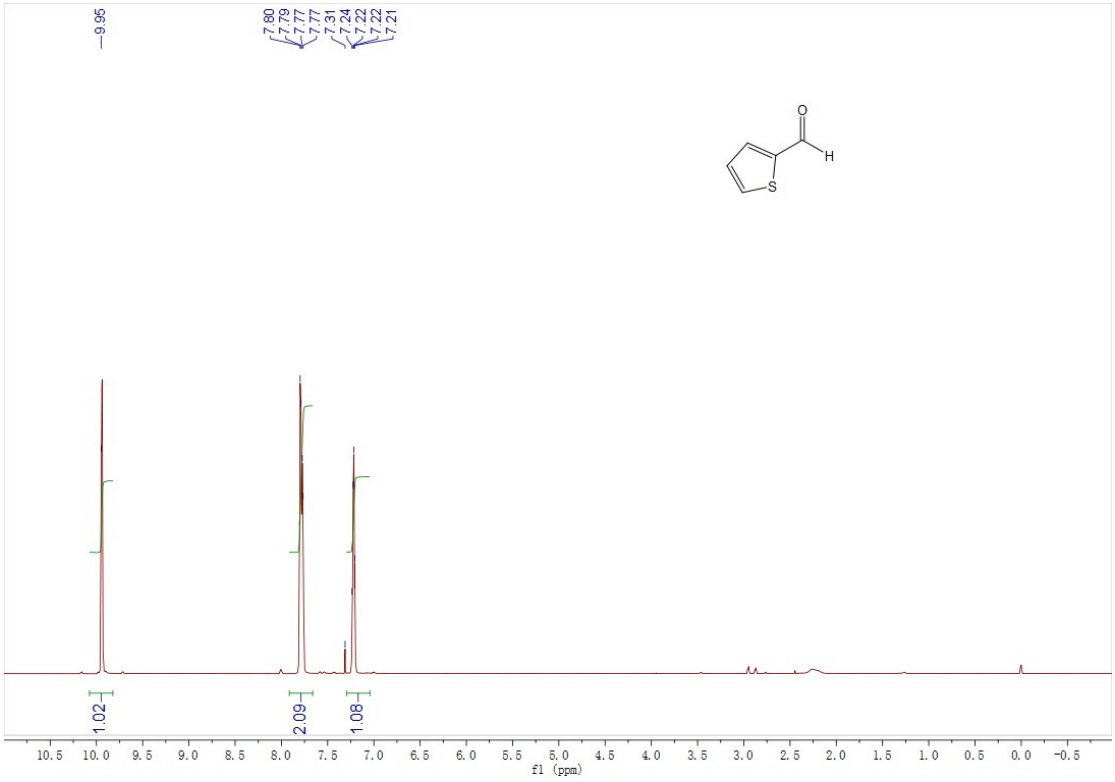


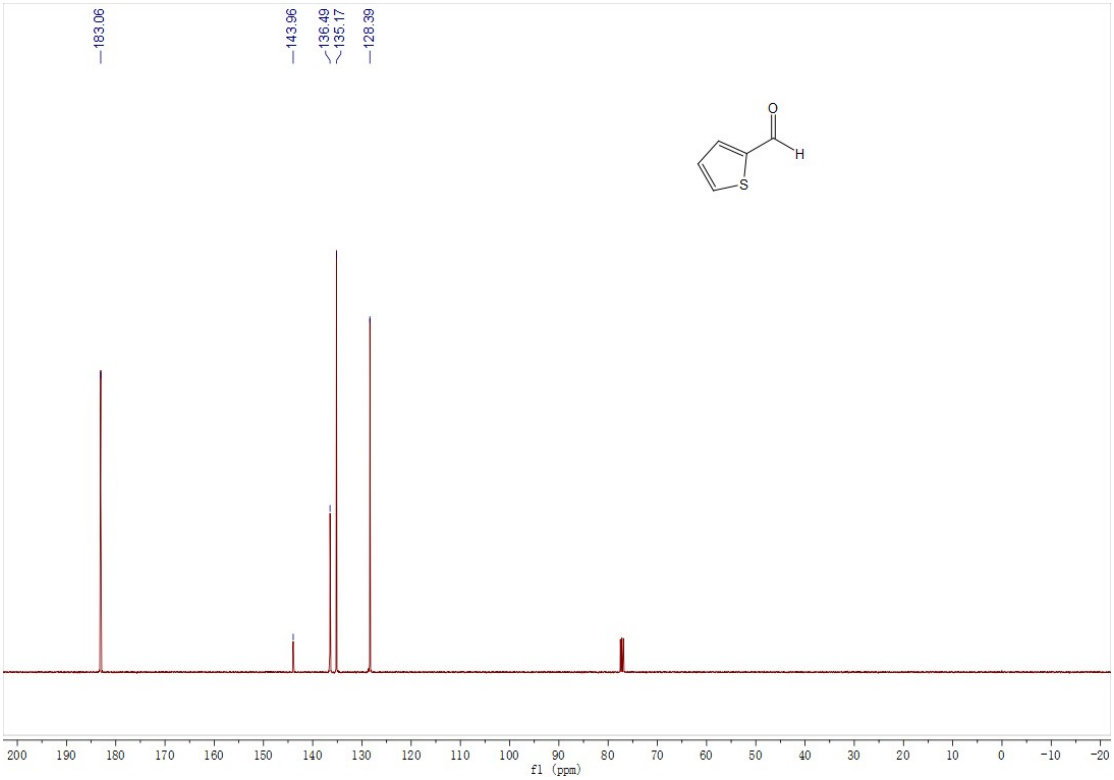
furan-2-carbaldehyde 2t



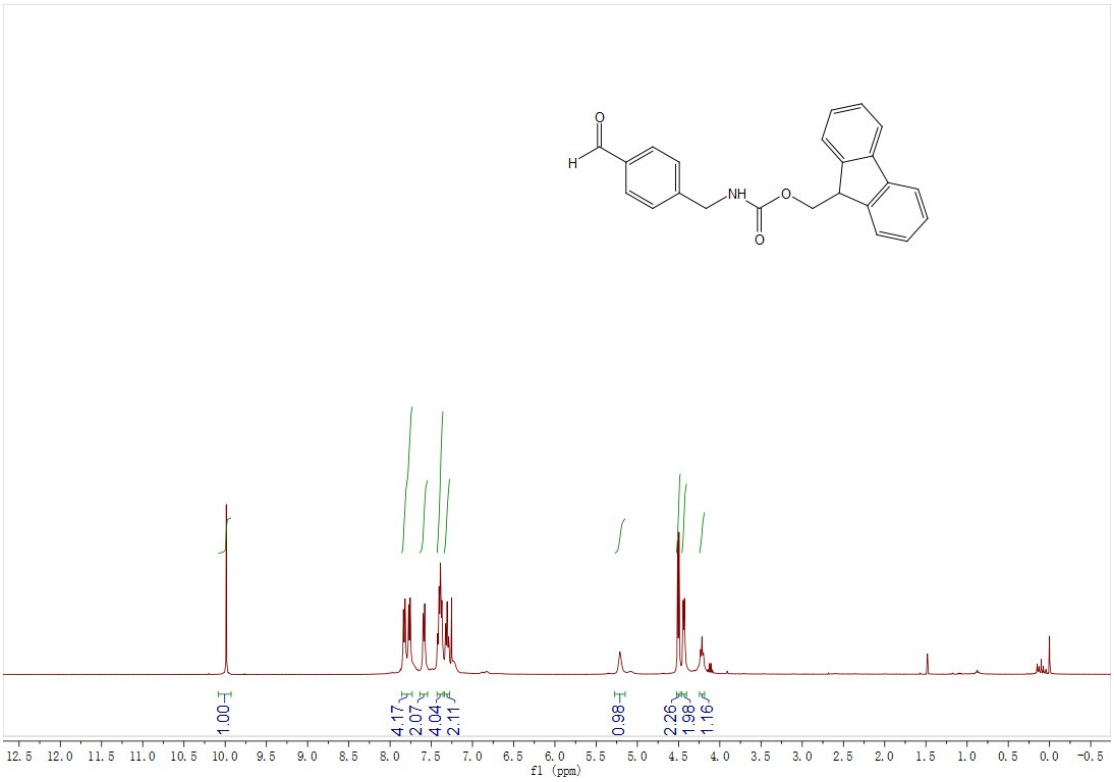


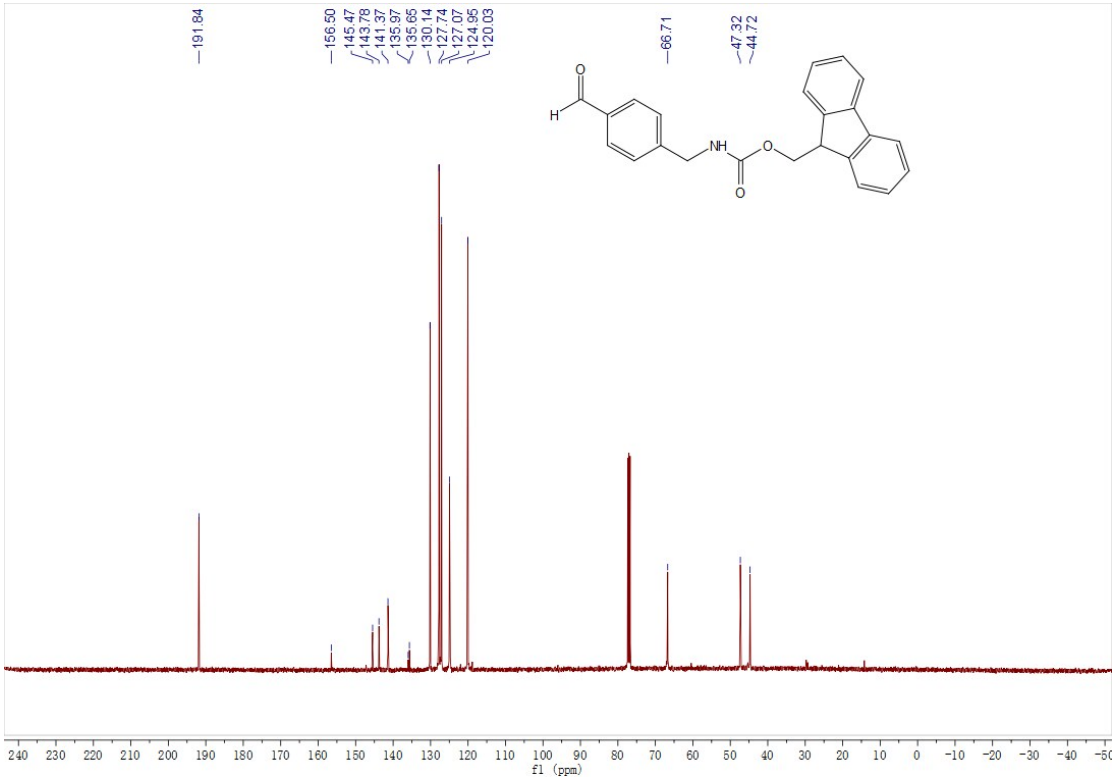
thiophene-2-carbaldehyde 2u



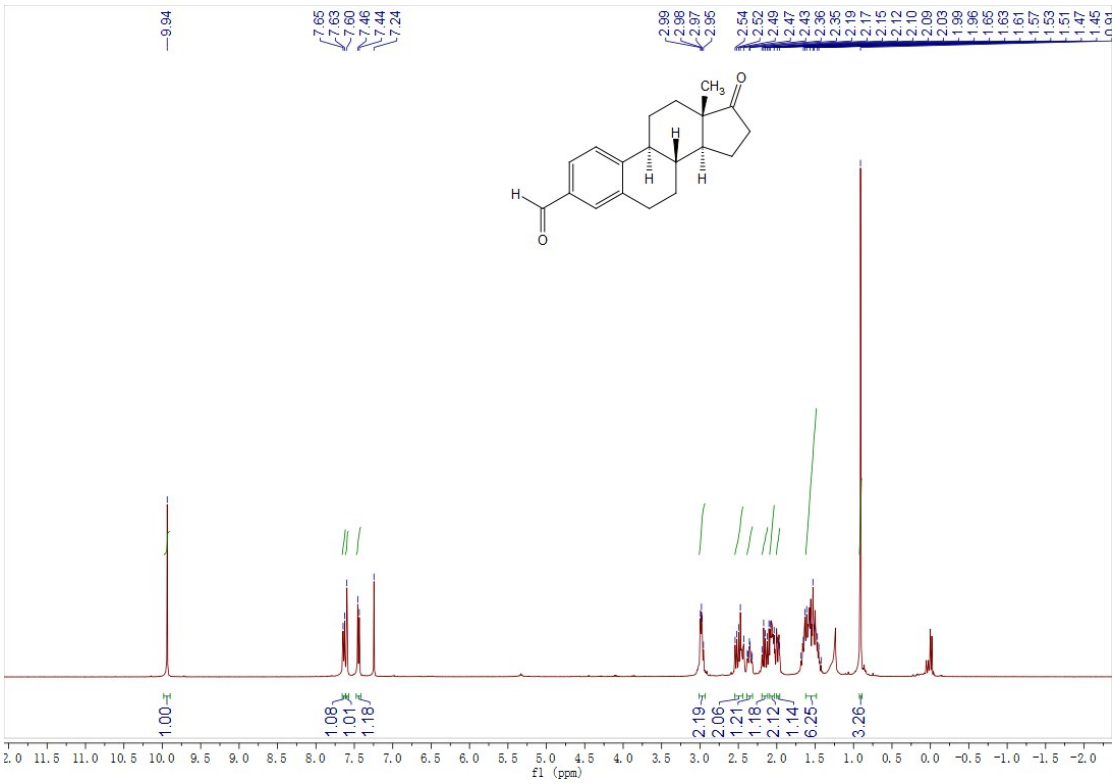


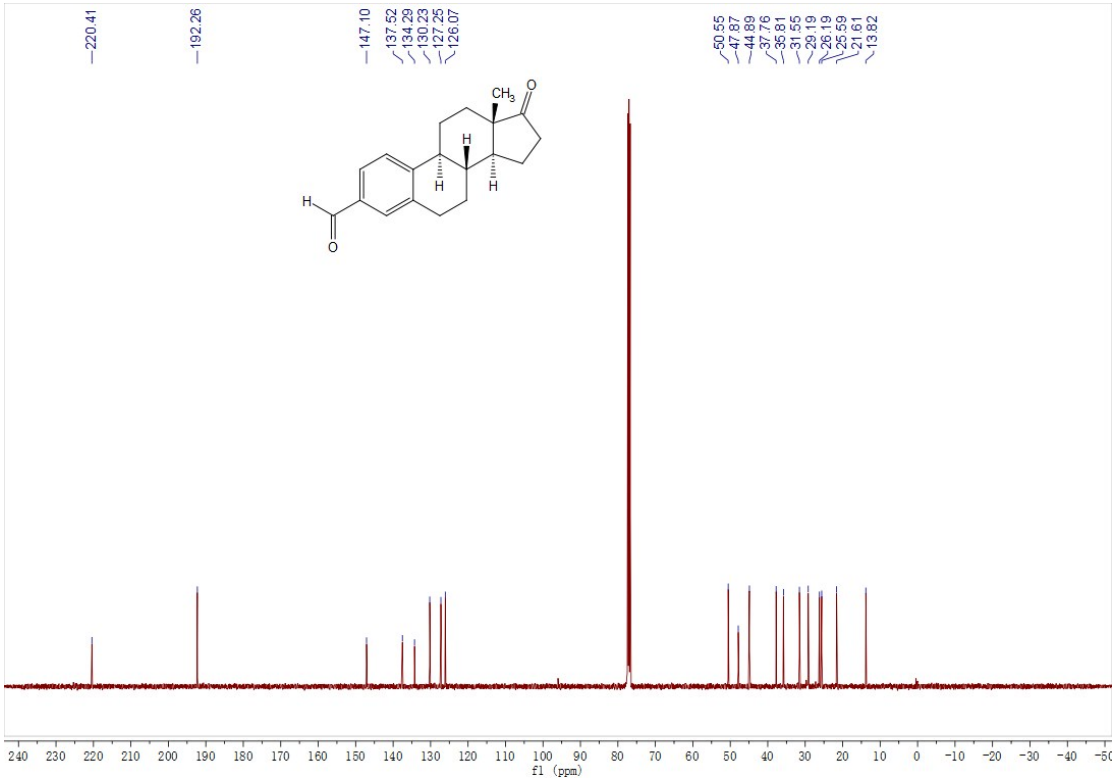
(9H-fluoren-9-yl)methyl (4-formylbenzyl)carbamate 2v



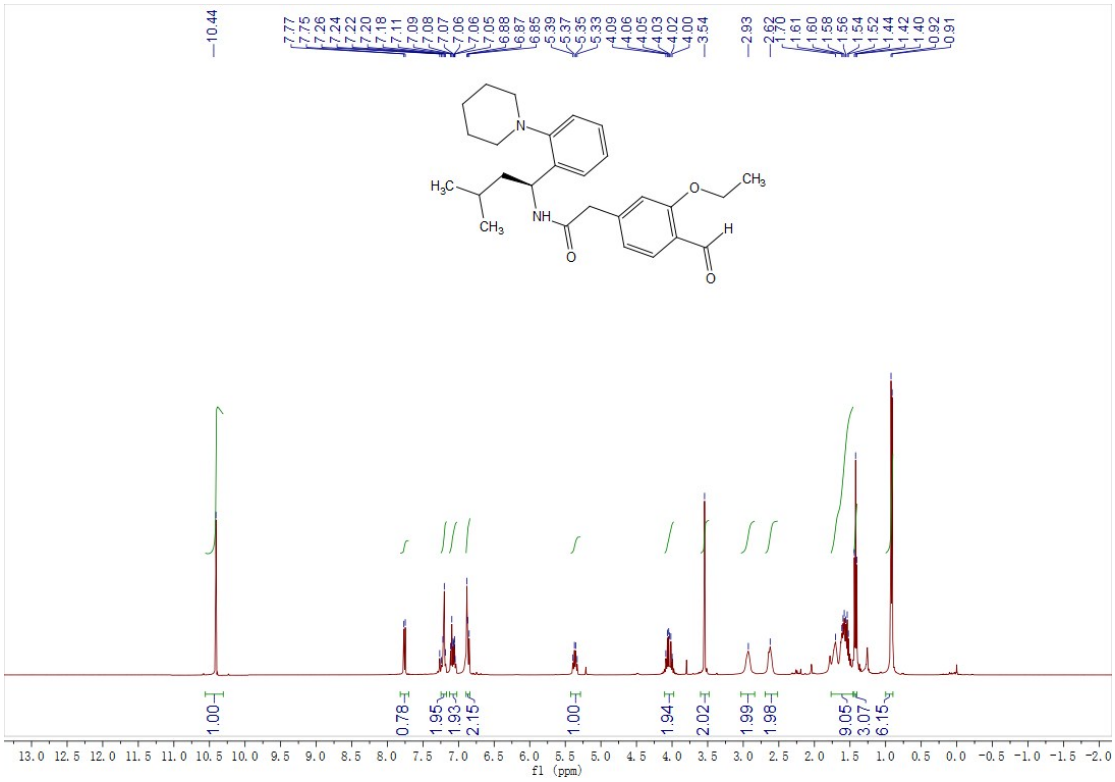


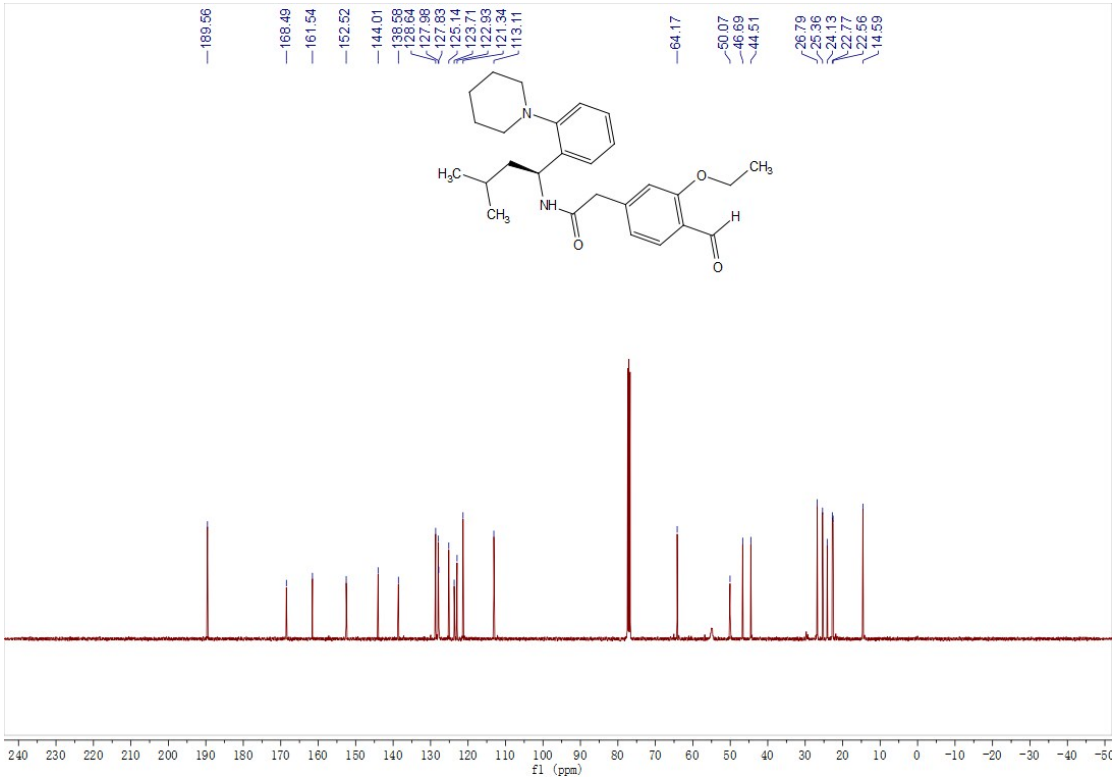
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carbaldehyde 2w





(S)-2-(3-ethoxy-4-formylphenyl)-N-(3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)acetamide 2x





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