Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox and Cobalt Co-catalyzed C(sp^2)-H Functionalization/C-O Bond Formation for Synthesis of Lactones Under Oxidant- and Acceptor-Free Conditions

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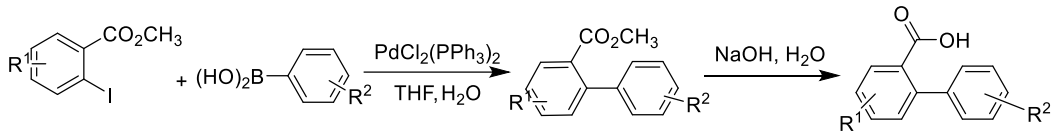
1. General Information

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 36 W compact fluorescent lamps were directly got from the supermarket.

2. Starting Materials

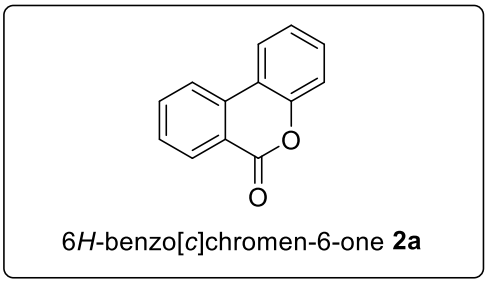


To a 100mL oven-dried Schlenk tube flask equipped with a magnetic stir bar were charged with methyl 2-iodobenzoate (1.9 g, 7.2 mmol), arylboronic acid (9.1 mmol), $PdCl_2(PPh_3)_2$ (246 mg, 5 mol %) and the flask was evacuated and backfilled with Ar for 3 times, consequently THF (25 mL) and 1 M aqueous Na_2CO_3 (25 mL, 2.65g) were added. The reaction mixture was heated at 60 ℃ for12-20 h. The reaction mixture was cooled to room temperature. The reaction mixture was cooled to room temperature and water (60 mL) was added and the products were extracted with DCM (3×15 mL). The organic layers were dried over anhydrous Na_2SO_4, evaporated, and purified by column chromatography (hexane/EtOAc = 50/1). To the purified product of m-methylphenyl benzoate , 3.0 g NaOH (75 mmol,) and H_2O/THF (30 mL, 1:1) solution were added and heated at 80℃ for 2-12 h (TLC monitored). The reaction mixture was cooled to room temperature; The reaction mixture was then acidified and extracted with EtOAc (2 x 60 mL). Combined organic extract was dried (Na_2SO_4) and

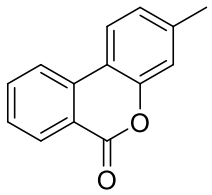
evaporated in vacuo, and the crude reaction mixture was purified by column chromatography on SiO_2 (hexane/EtOAc = 5/1).

3. General procedure for Photocatalyzed C-H Activation/C-O Cyclization

To a Schlenk tube containing a stirring bar was added Arc^+-Mes BF_4^- (0.002 mmol, 2 mol%), $Co(dmgH)_2PyCl$ (0.004 mmol, 4 mol%) and compounds **1** (0.10 mmol), PhCOONa (0.05 mmol, 0.5 equiv.), then the tube was degassed in vacuo and refilled with Ar for 3 times. Anhydrous CH_3CN (2.0 mL) was added via syringe under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 36 W CFL light source and the mixture was stirred for 48 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: 1/20 to 1/10) to give the corresponding products **2**.

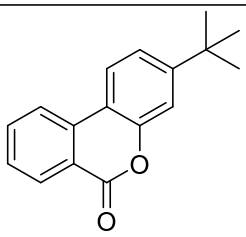


The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2a** (18.8 mg, 96%) as a white solid. M.p. = 88-89 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.77 (m, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.53 – 7.43 (m, 1H), 7.40 – 7.30 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.2, 151.3, 134.9, 134.8, 130.6, 130.4, 128.9, 124.6, 122.8, 121.7, 121.2, 118.0, 117.8. The spectroscopic data correspond to those previously reported in the literature.[2]



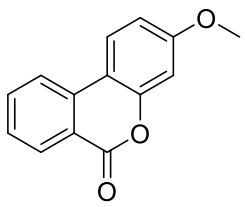
3-methyl-6*H*-benzo[*c*]chromen-6-one **2b**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2b** (17.2 mg, 82%) as a white solid. M.p. = 153-154 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 151.2, 141.3, 135.0, 134.8, 130.5, 128.3, 125.7, 122.5, 121.4, 120.8, 117.8, 115.4, 21.4. The spectroscopic data correspond to those previously reported in the literature.[2]



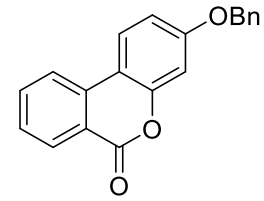
3-(*tert*-butyl)-6*H*-benzo[*c*]chromen-6-one **2c**

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 (20:1 petroleum ether: ethyl acetate) to afford **2c** (21.9 mg, 87%) as a white solid. M.p. = 159-160 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 7.9 Hz, 1H), 8.08 (s, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.35 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.5, 154.7, 151.2, 134.9, 134.8, 130.5, 128.4, 122.4, 122.0, 121.5, 121.0, 115.4, 114.6, 35.0, 31.1. The spectroscopic data correspond to those previously reported in the literature.[4]



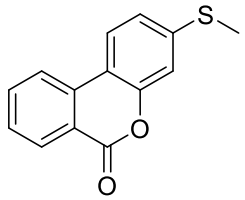
3-methoxy-6*H*-benzo[*c*]chromen-6-one **2d**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2d** (17.9 mg, 79%) as a white solid. M.p. = 142-144 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 8.9 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.78 (t, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 6.95 – 6.81 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.5, 152.6, 135.2, 134.9, 130.5, 127.7, 123.8, 121.1, 120.0, 112.4, 111.1, 101.6, 55.7. The spectroscopic data correspond to those previously reported in the literature.[2]



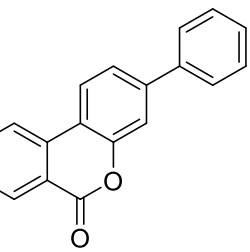
3-(benzyloxy)-6*H*-benzo[*c*]chromen-6-one **2e**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2e** (19.3 mg, 64%) as a white solid. M.p. = 125-126 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.82 – 7.65 (m, 1H), 7.54 – 7.31 (m, 5H), 7.00 – 6.95 (m, 1H), 6.92 (d, *J* = 2.5 Hz, 1H), 5.13 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.5, 160.5, 152.5, 136.1, 135.1, 134.9, 130.5, 128.7, 128.3, 127.8, 127.5, 123.8, 121.1, 120.0, 113.1, 111.4, 102.7, 70.4. The spectroscopic data correspond to those previously reported in the literature.[5]



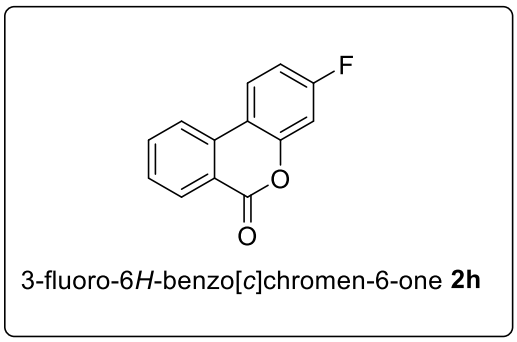
3-(methylthio)-6*H*-benzo[*c*]chromen-6-one **2f**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (15:1 petroleum ether: ethyl acetate) to afford **2f** (19.4 mg, 80%) as a white solid. M.p. = 147-148 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.76 (m, 1H), 7.55 (t, *J* = 8.1 Hz, 1H), 7.23 – 7.14 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 161.1, 151.7, 143.2, 134.9, 134.8, 130.6, 128.4, 122.9, 122.4, 121.4, 120.7, 114.7, 113.7, 15.2. The spectroscopic data correspond to those previously reported in the literature.[4]



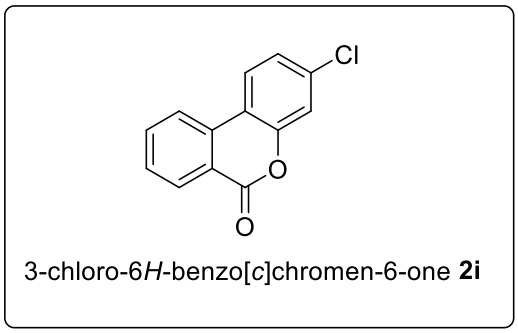
3-phenyl-6*H*-benzo[*c*]chromen-6-one **2g**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2g** (21.8 mg, 80%) as a white solid. M.p. = 113-114 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 7.9 Hz, 1H), 8.01 (dd, *J* = 11.1, 8.5 Hz, 2H), 7.73 (t, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.51-7.46 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.2, 150.6, 142.4, 138.2, 133.8, 133.6, 129.6, 128.1, 127.7, 127.2, 126.0, 122.3, 122.1, 120.6, 120.1, 115.9, 114.8. The spectroscopic data correspond to those previously reported in the literature.[4]



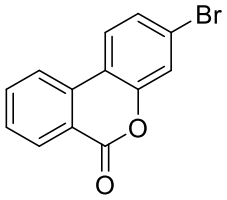
3-fluoro-6*H*-benzo[*c*]chromen-6-one **2h**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2h** (16.9 mg, 79%) as a white solid. M.p. = 153-154 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.0 Hz, 1H), 8.07-8.01 (m, 3H), 7.83 (t, *J* = 7.0 Hz, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.13 – 6.96 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.5 (d, *J* = 251.2 Hz), 160.8, 152.2 (d, *J* = 12.3 Hz), 135.1, 134.3, 130.7, 128.8, 124.4 (d, *J* = 9.9 Hz), 121.5, 120.5, 114.6 (d, *J* = 3.2 Hz), 112.4 (d, *J* = 22.4 Hz), 105.1 (d, *J* = 25.3 Hz). The spectroscopic data correspond to those previously reported in the literature.[2]



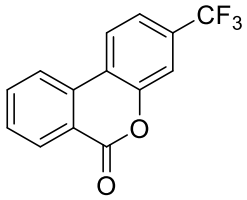
3-chloro-6*H*-benzo[*c*]chromen-6-one **2i**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2i** (11.9 mg, 52%) as a white solid. M.p. = 145-146 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.36 (s, 1H), 7.33 – 7.29 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.6, 151.5, 135.9, 135.1, 134.0, 130.7, 129.2, 125.0, 123.8, 121.7, 120.9, 118.0, 116.7. The spectroscopic data correspond to those previously reported in the literature.[2]



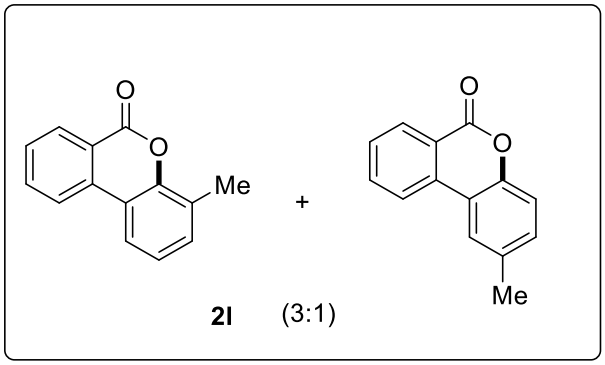
3-bromo-6*H*-benzo[*c*]chromen-6-one **2j**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2j** (15.1 mg, 55%) as a white solid. M.p. = 151-152 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.9 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.84 (t, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.5, 151.5, 135.1, 134.1, 130.8, 129.3, 127.9, 124.0, 123.7, 121.7, 121.1, 120.9, 117.2. The spectroscopic data correspond to those previously reported in the literature.[2]



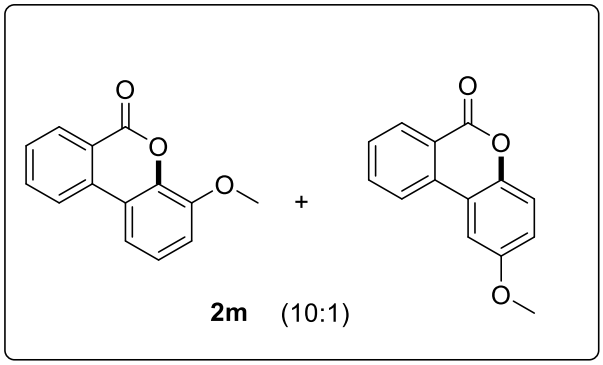
3-(trifluoromethyl)-6*H*-benzo[*c*]chromen-6-one **2k**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (15:1 petroleum ether: ethyl acetate) to afford **2k** (13.7 mg, 52%). as a white solid. M.p. = 123-124 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 7.9 Hz, 1H), 8.18 (t, *J* = 8.1 Hz, 3H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.3, 151.0, 135.2, 133.4, 132.3 (q, *J* = 33.5 Hz), 130.9, 130.2, 124.6, 123.2 (q, *J* = 272.6 Hz), 122.2, 121.7, 121.1 (q, *J* = 3.6 Hz), 115.3 (q, *J* = 4.0 Hz). The spectroscopic data correspond to those previously reported in the literature.[2]



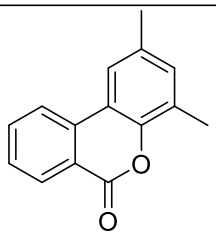
2l (3:1)

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2l** (18.3 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 7.6 Hz, major + minor isomer), 8.22 – 8.06 (m, major + minor isomer), 7.90 (s, 0H), 7.85 – 7.76 (m, major + minor isomer), 7.57 (t, *J* = 7.6 Hz, major + minor isomer), 7.27 (d, *J* = 2.4 Hz, major + minor isomer), 2.50 (s, minor), 2.47 (s, major). The spectroscopic data correspond to those previously reported in the literature.[3]



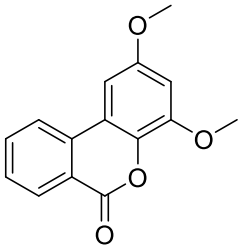
2m (10:1)

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (15:1 petroleum ether: ethyl acetate) to afford **2m** (17.4 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.2, major + minor isomer), 8.06 (d, *J* = 8.1 Hz, major + minor isomer), 7.82 (t, *J* = 7.7 Hz, major + minor isomer), 7.59 (t, *J* = 7.6 Hz, major + minor isomer), 7.48 (d, *J* = 2.9 Hz, major + minor isomer), 7.34 – 7.20 (m, major + minor isomer H), 7.05 (dd, *J* = 9.0, 2.9 Hz, major + minor isomer), 3.98 (s, 0.31H, minor isomer), 3.91 (s, 3H, major isomer). The spectroscopic data correspond to those previously reported in the literature.[3]



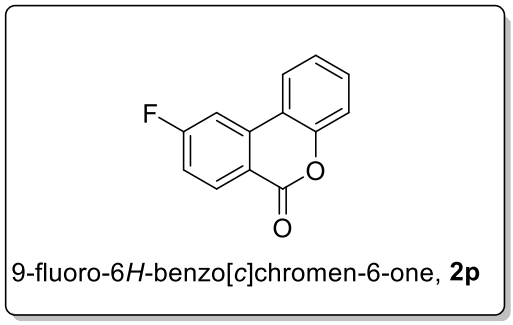
2,4-dimethyl-6*H*-benzo[*c*]chromen-6-one **2n**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2n** (18.8 mg, 84%) as a white solid. M.p. = 171-173 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.56 (t, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 2.46 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 147.8, 135.2, 134.6, 133.4, 132.8, 130.5, 128.5, 126.7, 121.8, 121.1, 120.3, 117.3, 21.1, 15.9. The spectroscopic data correspond to those previously reported in the literature.[3]



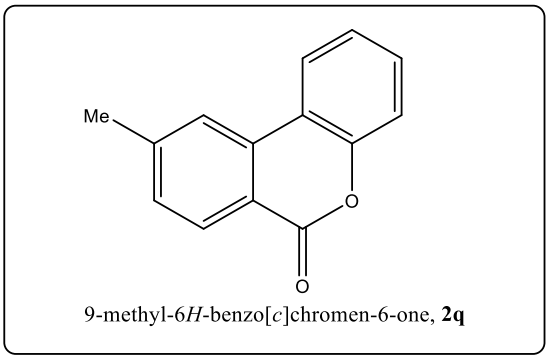
2,4-dimethoxy-6*H*-benzo[*c*]chromen-6-one **2o**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (15:1 petroleum ether: ethyl acetate) to afford **2o** (21.0 mg, 82%) as a white solid. M.p. = 207-208 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.80 (t, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.62 (s, 1H), 3.95 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.6, 156.4, 148.8, 134.8, 134.6, 130.6, 128.9, 122.0, 121.4, 118.5, 101.3, 96.0, 56.2, 55.7. The spectroscopic data correspond to those previously reported in the literature.[3]



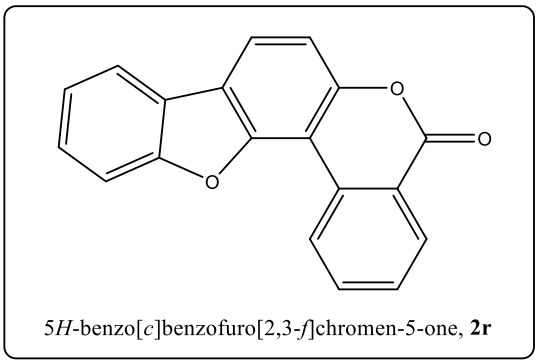
9-fluoro-6*H*-benzo[*c*]chromen-6-one, **2p**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2p** (15.4 mg, 72%) as a white solid. M.p. = 144-145 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.98 – 7.84 (m, 2H), 7.53 – 7.35 (m, 2H), 7.28-7.22 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 250.8 Hz), 160.2, 150.8, 131.2, 130.4, 124.8, 124.3 (d, *J* = 7.9 Hz), 123.1, (d, *J* = 23.1 Hz), 123.0 (d, *J* = 8.1 Hz), 122.6, 117.8, 117.4, 116.1 (d, *J* = 23.2 Hz). The spectroscopic data correspond to those previously reported in the literature.[6]



9-methyl-6*H*-benzo[*c*]chromen-6-one, **2q**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (20:1 petroleum ether: ethyl acetate) to afford **2q** (17.2 mg, 82%) as a white solid. M.p. = 145-146 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 8.07 – 7.98 (m, 2H), 7.64 (d, *J* = 10.1 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.38-7.30 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 160.4, 150.0, 138.2, 135.0, 131.2, 129.4, 128.9, 123.4, 121.5, 120.7, 120.1, 117.2, 116.7, 20.3. The spectroscopic data correspond to those previously reported in the literature.[6]



5*H*-benzo[*c*]benzofuro[2,3-*f*]chromen-5-one, **2r**

The reaction was carried out according to the general procedure on 0.1 mmol scale (48 h). The residue was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **2r** (22.0 mg, 77%) as a yellowish solid. M.p. = 189-191 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.04 (d, *J* = 8.1 Hz, 1H), 8.44 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 3H), 7.71 – 7.57 (m, 2H), 7.54 – 7.45 (m, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.0, 155.5, 151.2, 149.7, 134.2, 131.9, 129.3, 127.9, 125.9, 125.6, 122.5, 122.1, 120.3, 120.0 (2C), 119.3, 111.9, 110.8, 104.6. The spectroscopic data correspond to those previously reported in the literature.[3]

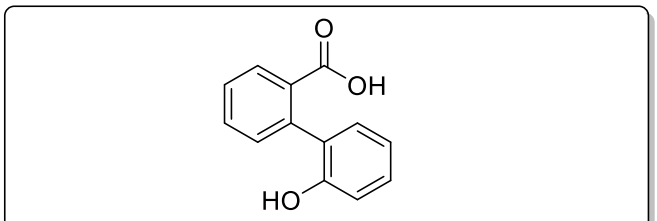
4. **Synthetic Utility of Methodology**

Gram experiment procedure

A 250 ml Schlenk tube containing a stirring bar was added Arc^{+}-Mes BF_4^{-} (0.2 mmol, 82.8 mg, 2 mol%), $Co(dmgH)_2PyCl$ (0.4 mmol, 161.2 mg, 4 mol%) and compounds **1a** (10 mmol, 1.98 g), PhCOONa (5.0 mmol, 0.72g, 0.5 equiv.), then the tube was degassed in vacuo and refilled with Ar for 3 times. Anhydrous CH_3CN (80 mL) was added via syringe under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 36 W CFL light source and the mixture was stirred for 60 h at room temperature. The resulting mixture was diluted with EtOAc (100 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 1/10) to give the corresponding products **2a**, white solid (90%, 1.76 g).

General procedure for the synthesis 2'-hydroxy-[1,1'-biphenyl]-2-carboxylic acid[7]

Following a modified procedure in the literature, the lactone **2a** (0.25 mmol, 49mg) and LiOH monohydrate (252 mg, 6 mmol, 24 equiv.) was charged to a 25 mL flask. To this mixture was then added MeOH (4 mL), THF (2 mL), and H_2O (1 mL). The reaction was then stirred for 24 h at room temperature and followed the course of the reaction by TLC until completion. The MeOH and THF was then removed in vacuo, and the resulting residue was diluted with H_2O (15mL), ice and EtOAc (20 mL). After acidification with 2M HCl (pH 4-5), the solution was extracted with EtOAc for three times. The combined organic extract was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The crude product was washed with AcOEt furnishing the final hydroxyacids without further purification **3** 50 mg (91 % yield) as a white solid. M.p. = 176-178 ℃.



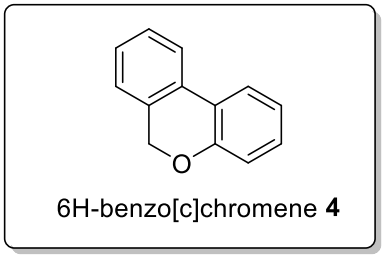
2'-hydroxy-[1,1'-biphenyl]-2-carboxylic acid **3**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (dd, J = 7.9, 0.9 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.72 (m, 1H), 7.60 – 7.48 (m, 1H), 7.47 – 7.40 (m, 1H), 7.33-7.27 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.2, 151.2, 134.8, 134.7, 130.5, 130.4, 128.8, 124.5, 122.7, 121.6, 121.1, 118.0, 117.7. The spectroscopic data correspond to those previously reported in the literature.[2]

General procedure for the synthesis 6H-benzo[c]chromene[8]

A cooled solution of lactone **2a** (392.4 mg, 2 mmol) in a mixture of BF_3·Et_2O (5 mL) and THF (10 mL) was added over 15 min to a suspension of $NaBH_4$ (250 mg, 6.6 mmol) in THF (5 mL) under nitrogen while maintaining the reaction temperature below 10 ℃. The reaction mixture was then raised within 30 min to the reflux temperature, kept under reflux for 1 h, and then cooled to −3 ℃. Cold HCl aq. (2 N, 8 mL) was then cautiously added, and the temperature was allowed to increase to 25 ℃. Water (40 mL) was added, and the reaction mixture was extracted with $CHCl_3$ (3 × 50

mL). The combined extracts were evaporated, and the oily residue was heated at 80 ℃ with 2 N NaOH aq. (80 mL) for 20 min. The resulting mixture was cooled and extracted with ether (4 × 30 mL). The ether extracts were combined, dried over Na_2SO_4, and concentrated in vacuo. The product was isolated by flash chromatography (PE/EA = 20:1) as a colorless liquid **4** (284 mg, 78% yield) as a colorless liquid.

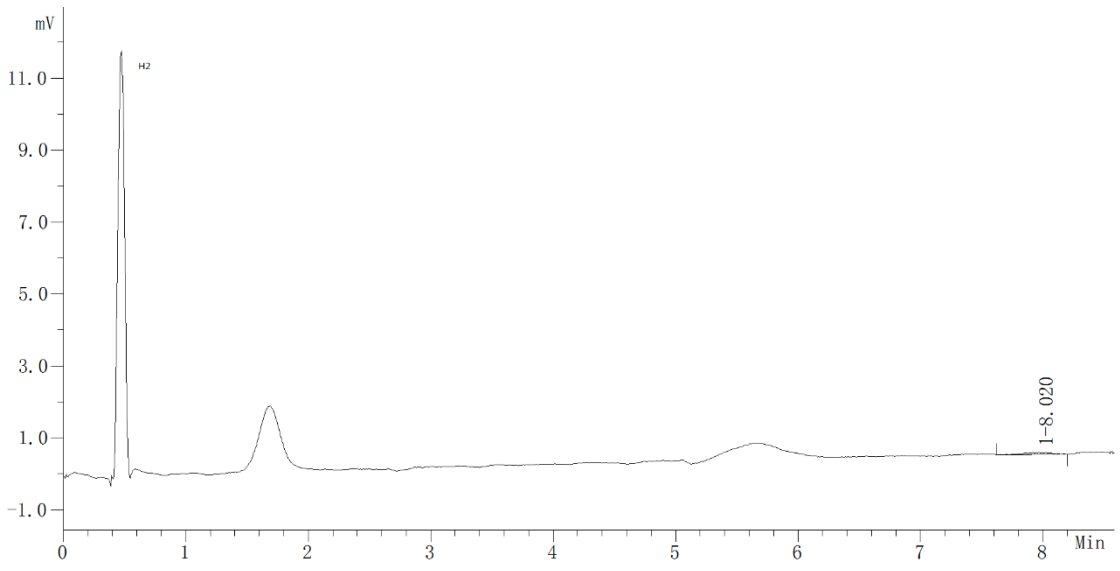


6H-benzo[c]chromene **4**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.50 (m, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.16 (dt, *J* = 16.6, 7.7 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 5.03 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.7, 130.4, 129.1, 128.4, 127.4, 126.6, 123.6, 122.2, 121.9, 121.1, 121.0, 116.3, 67.4. The spectroscopic data correspond to those previously reported in the literature.

5. Mechanism experiment

To a Schlenk tube containing a stirring bar was added compounds **1a** (0.10 mmol, 19.8 mg), Arc^+-Mes BF_4^- (0.002 mmol,1.2 mg, 2 mol%), $Co(dmgH)_2PyCl$ (0.004 mmol, 3.3 mg 4 mol%) and PhCOONa (0.05 mmol, 7.2 mg 0.5 equiv.), then the tube was degassed in vacuo and refilled with Ar for 3 times. Anhydrous CH_3CN (2.0 mL) was added via syringe under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 36 W CFL light source and the mixture was stirred for 48 h at room temperature. After completion of the reaction, H_2 was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, heliumas a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector, oven temp. 90 ^{o}C, TCD temp. 100 ^{o}C, injection temp. 100 ^{o}C, CURR: 70). Under this condition, H_2 was shown as a positive peak.


mV
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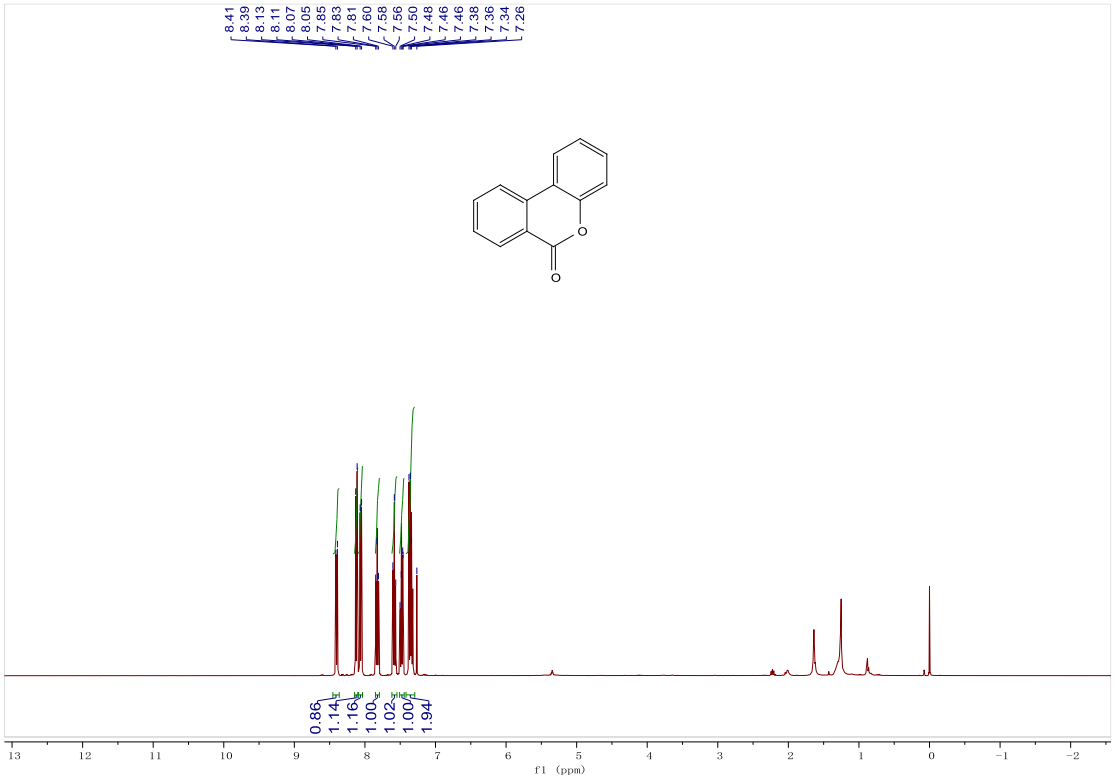
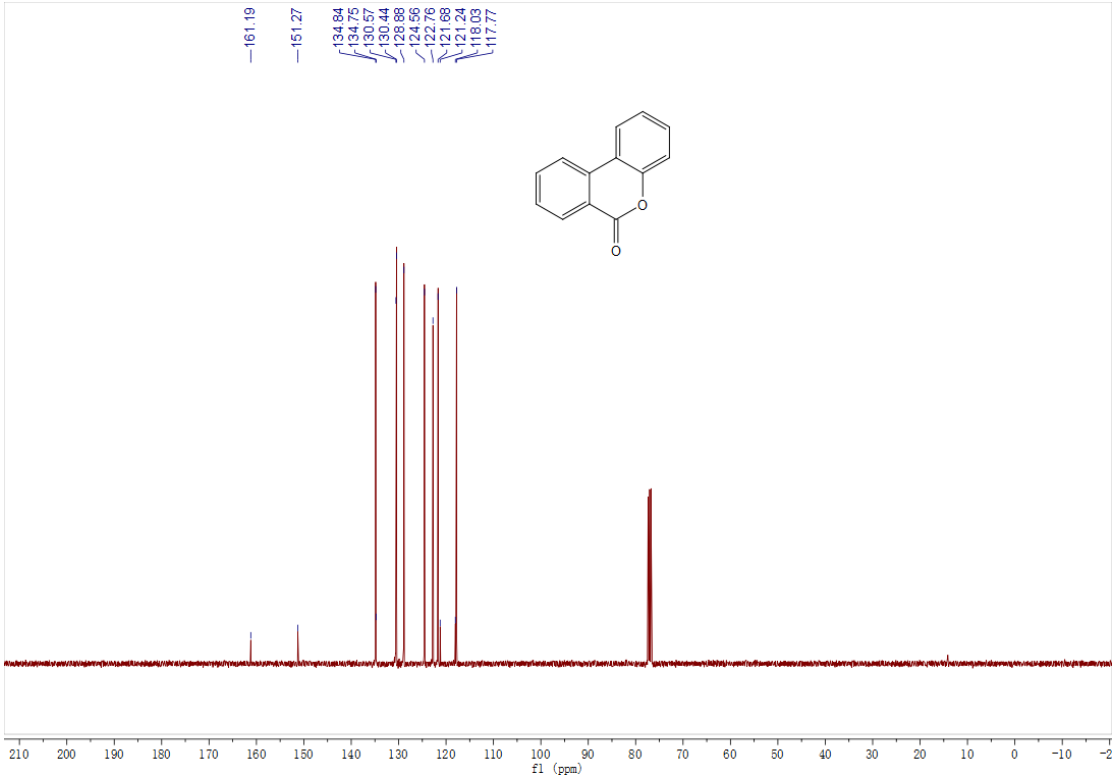
9.0
7.0
5.0
3.0
1.0
-1.0
H2
1-8.020
0
1
2
3
4
5
6
7
8
Min

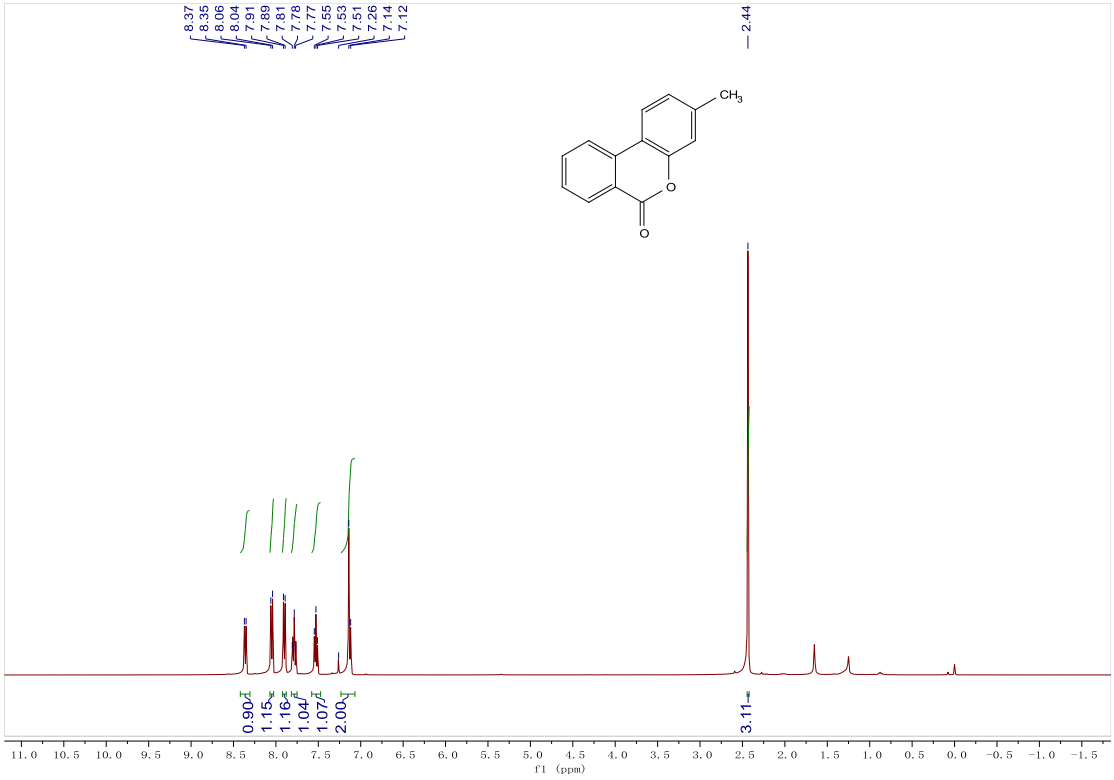
6. Copies of ^{1}H NMR, ^{13}C NMR Spectra

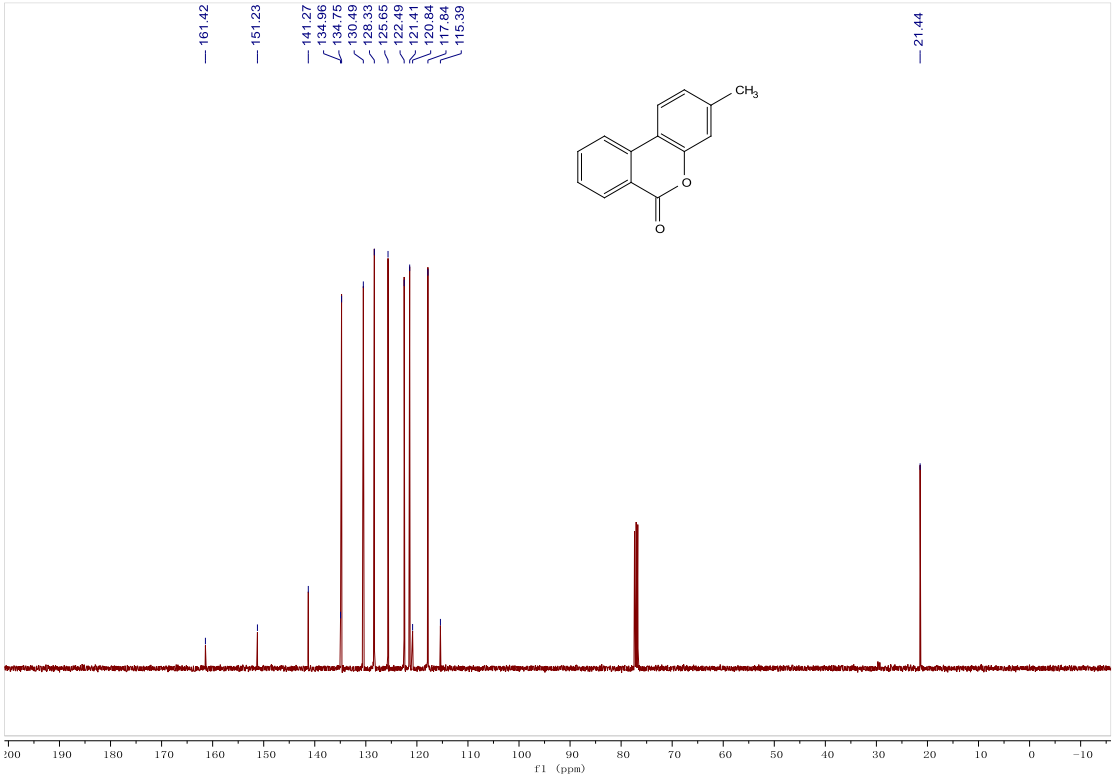
6H-benzo[c]chromen-6-one 2a



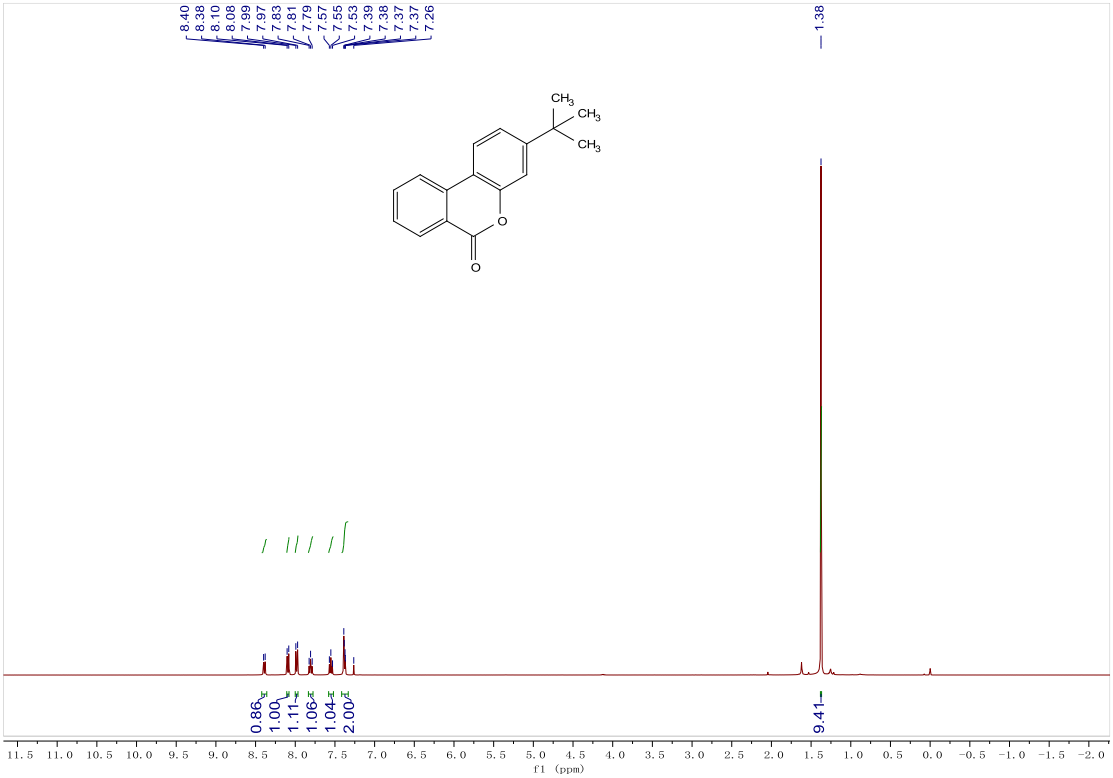


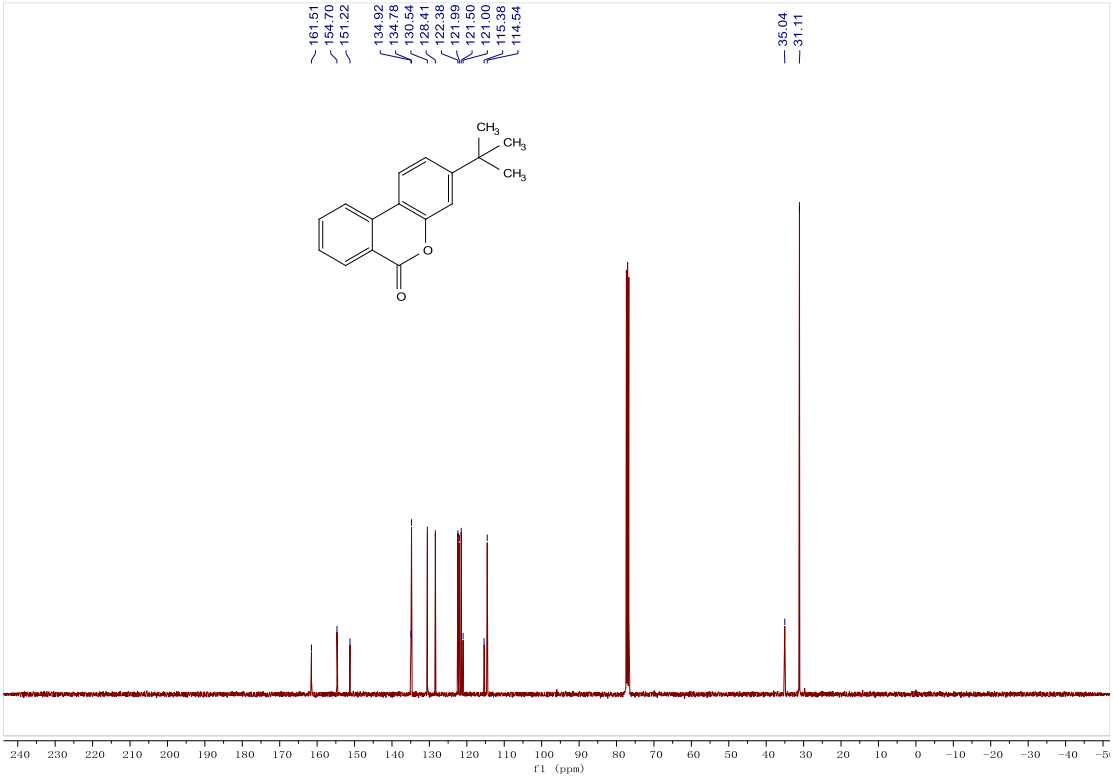
3-methyl-6H-benzo[c]chromen-6-one 2b



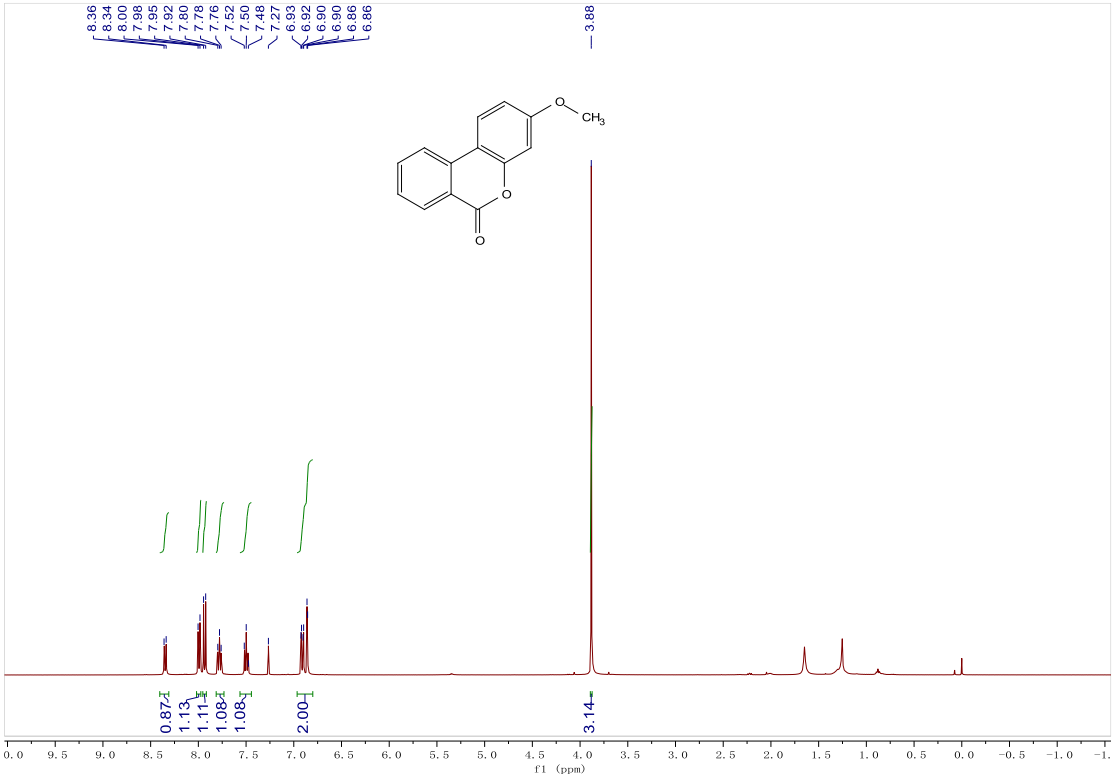


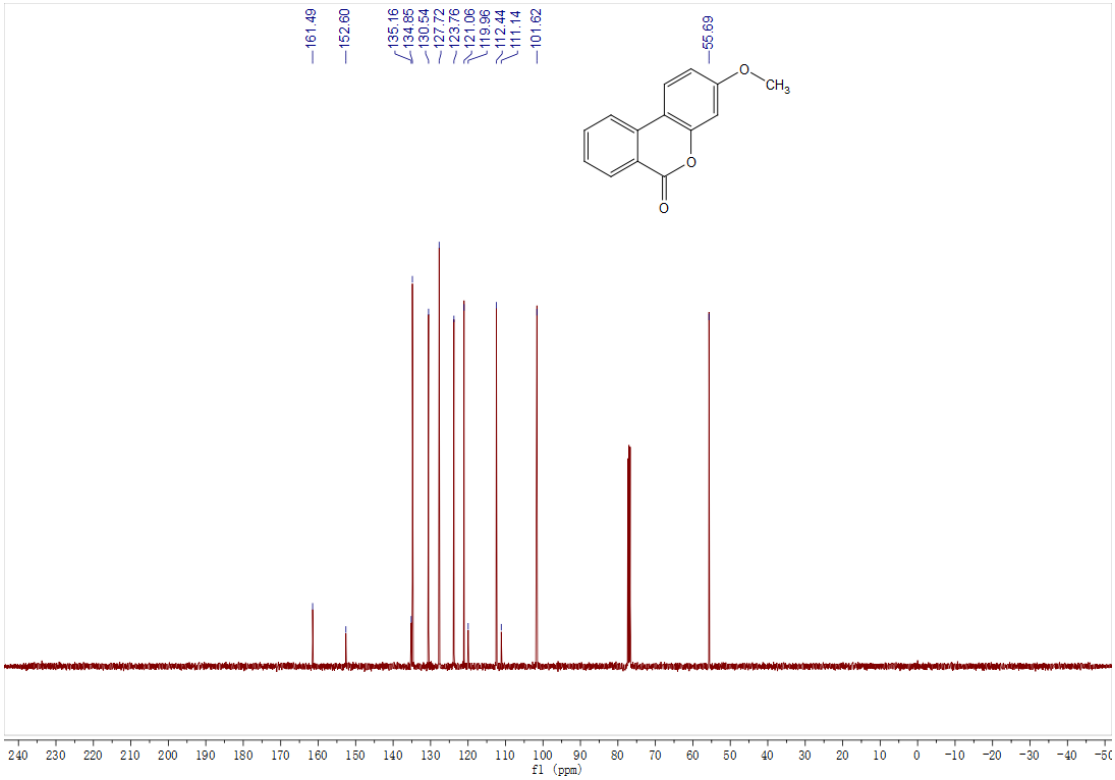
3-(tert-butyl)-6H-benzo[c]chromen-6-one 2c



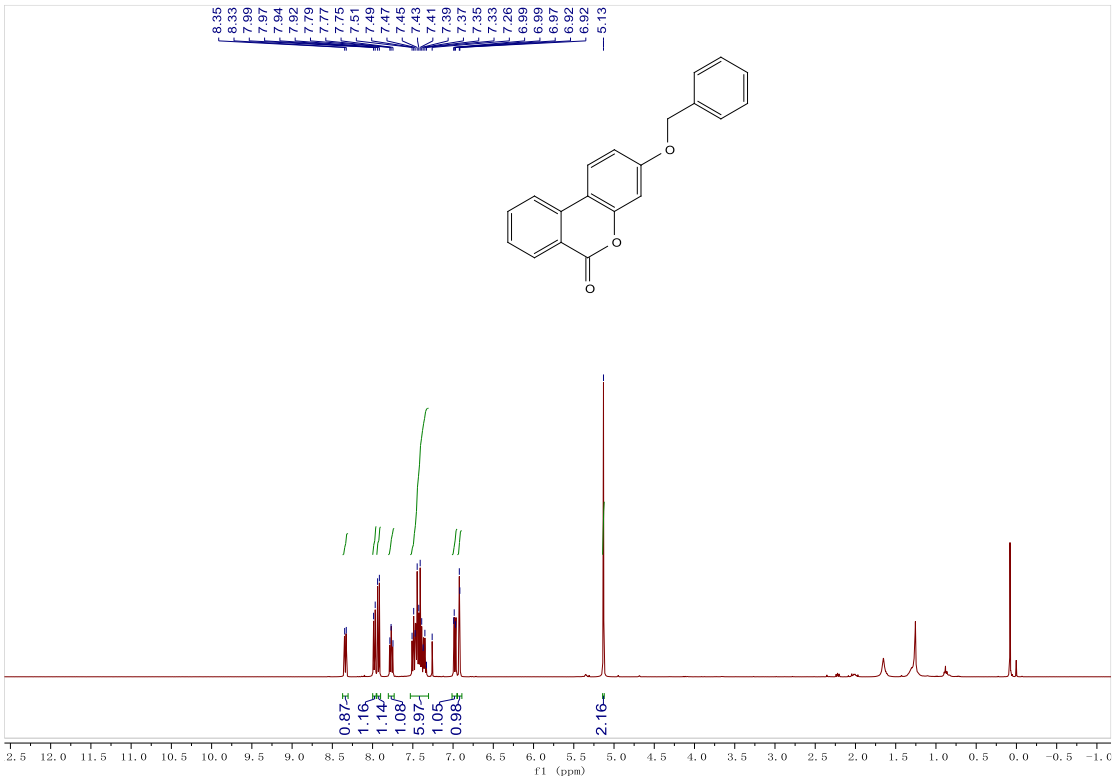


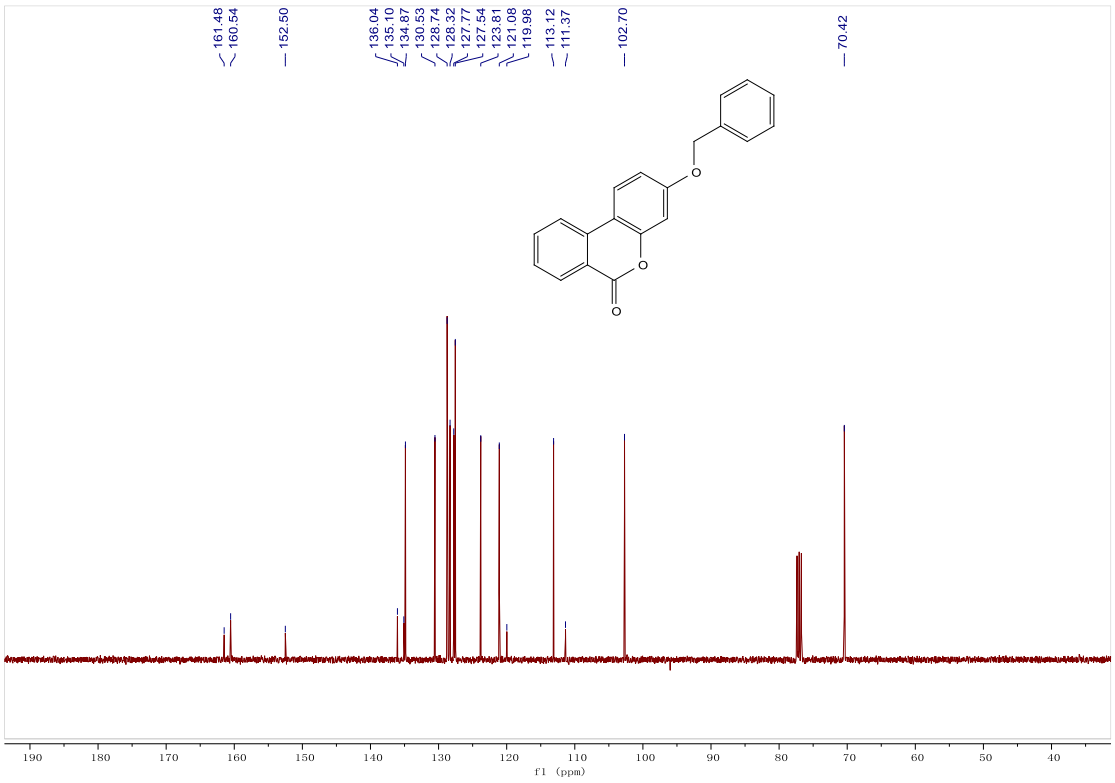
3-methoxy-6H-benzo[c]chromen-6-one 2d



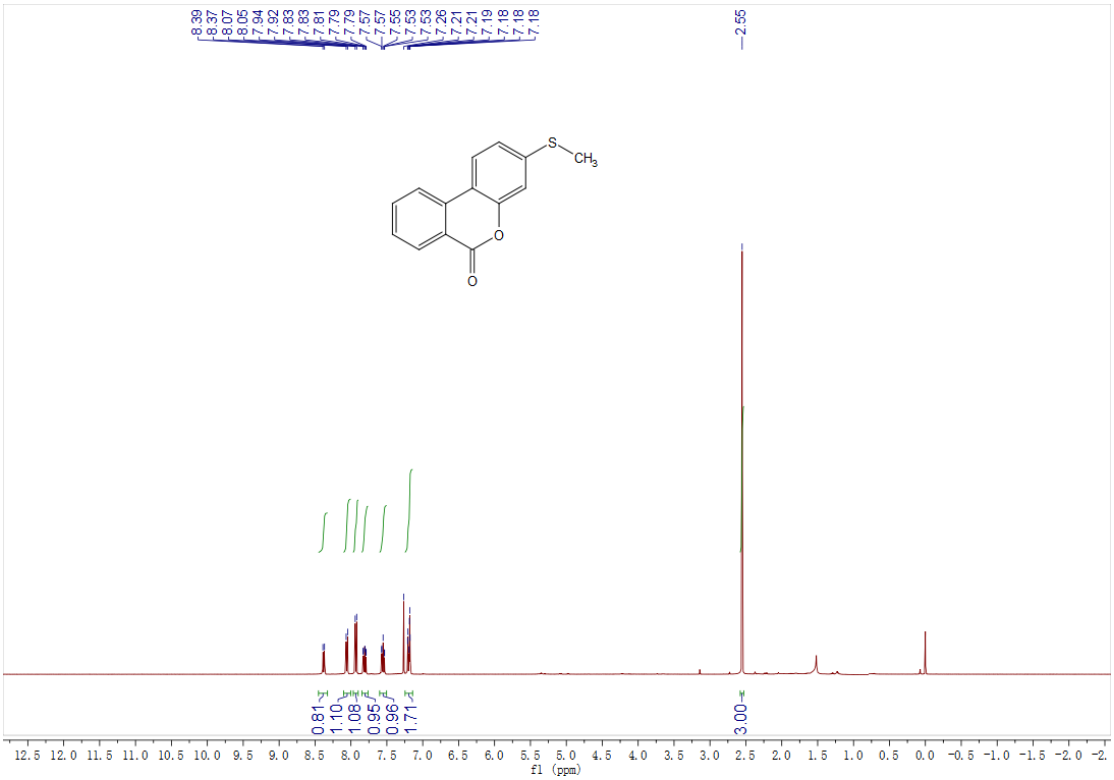


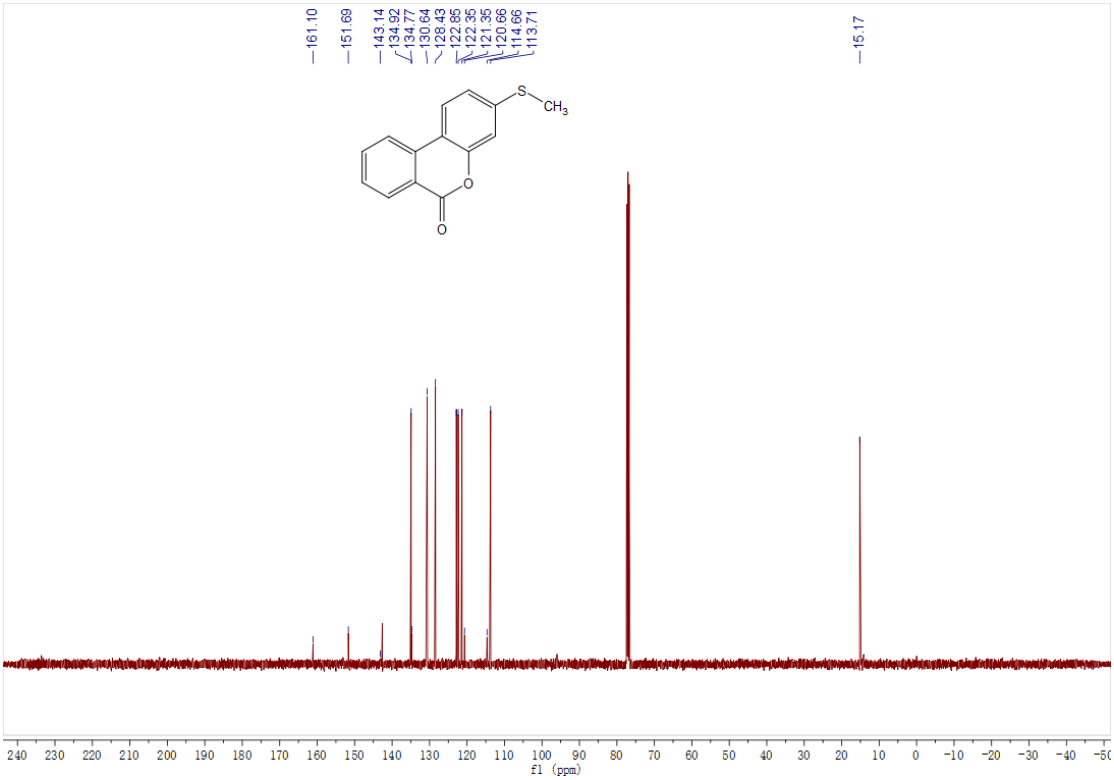
3-(benzyloxy)-6H-benzo[c]chromen-6-one 2e



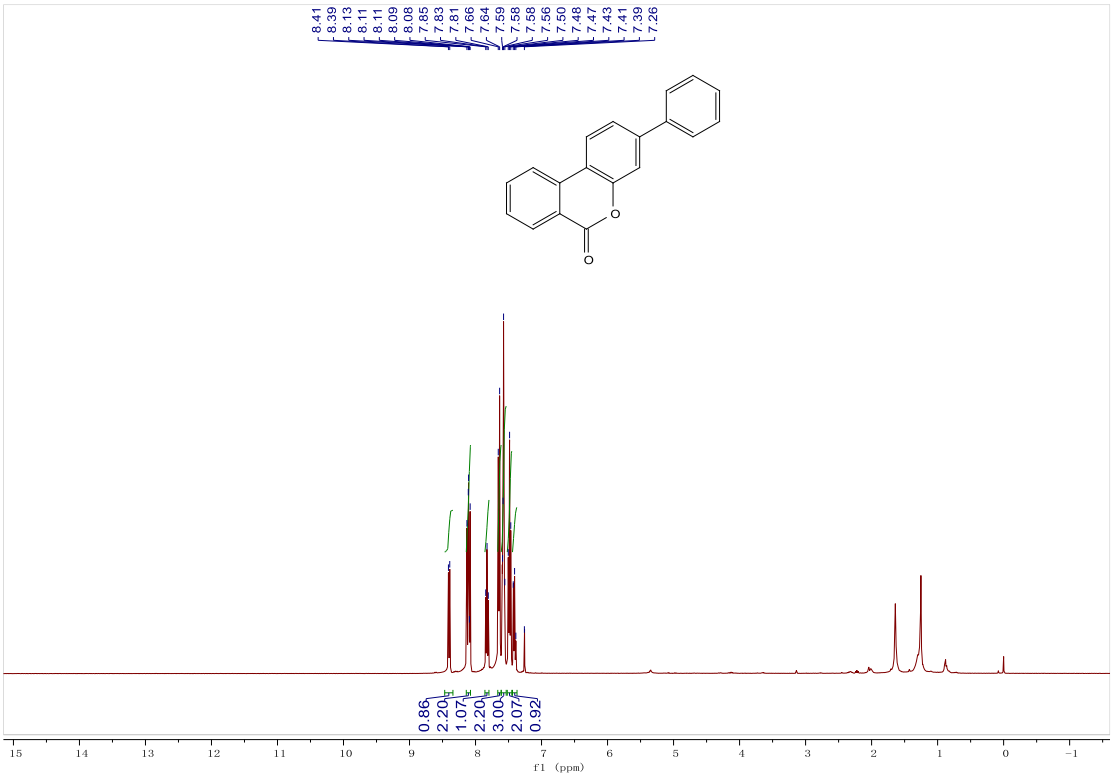


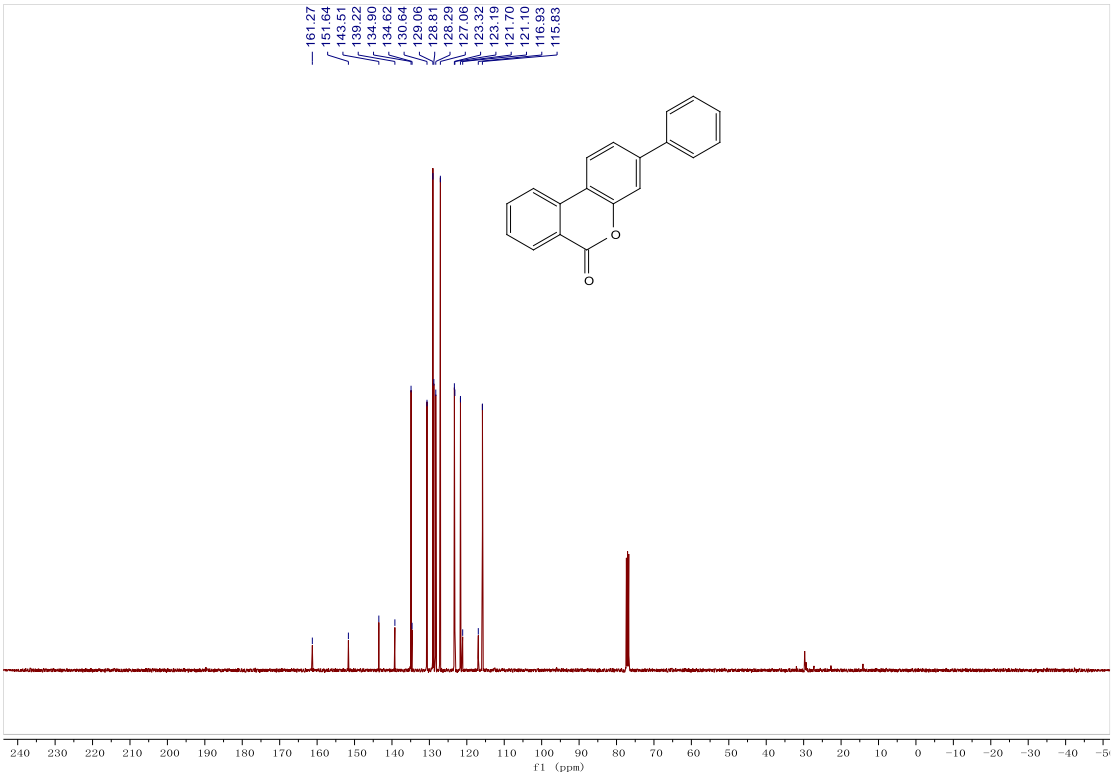
3-(methylthio)-6H-benzo[c]chromen-6-one 2f



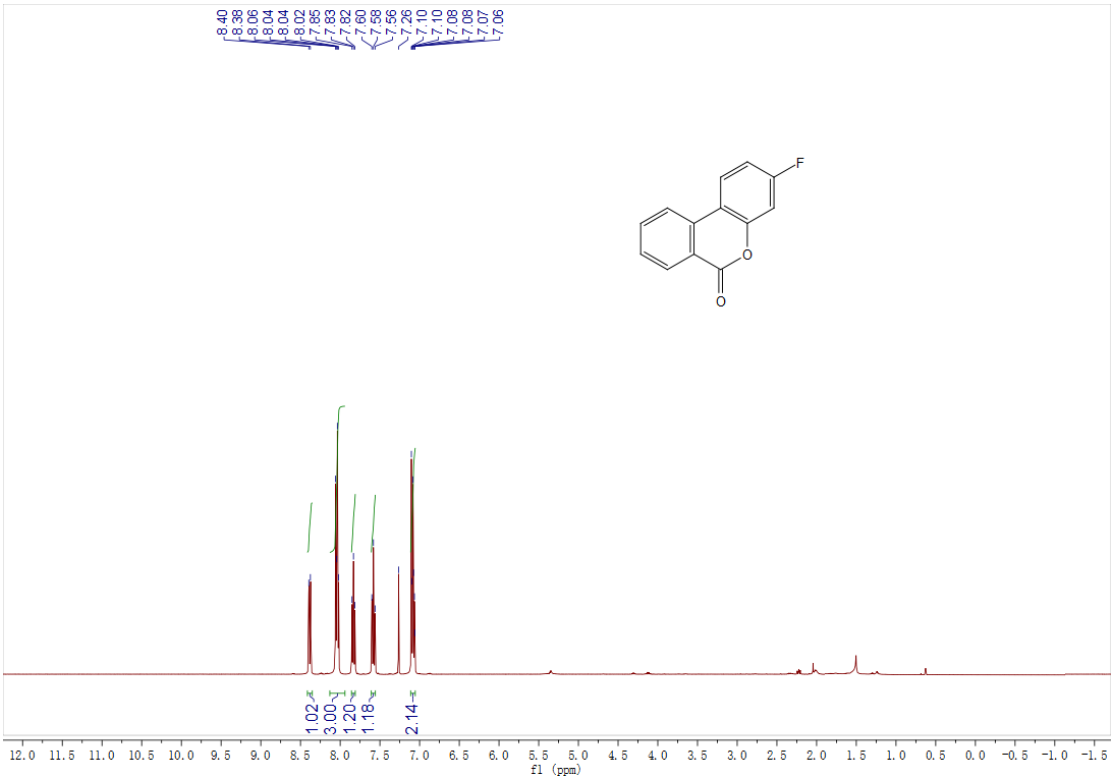


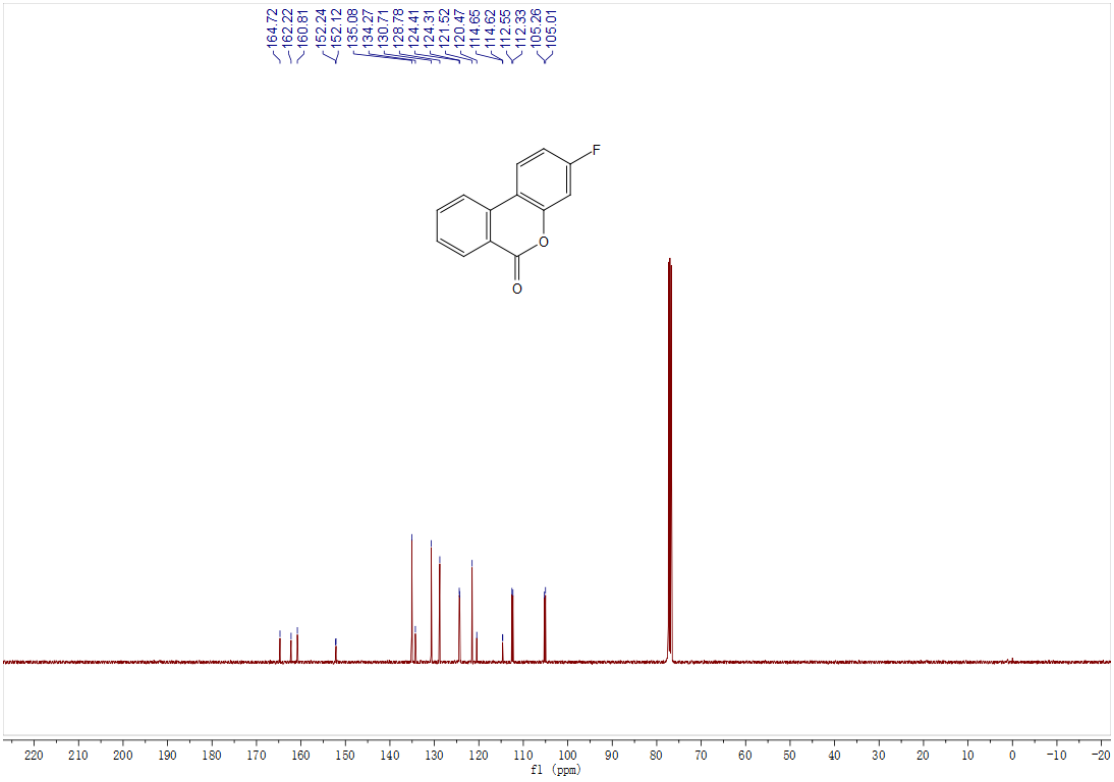
3-phenyl-6H-benzo[c]chromen-6-one 2g



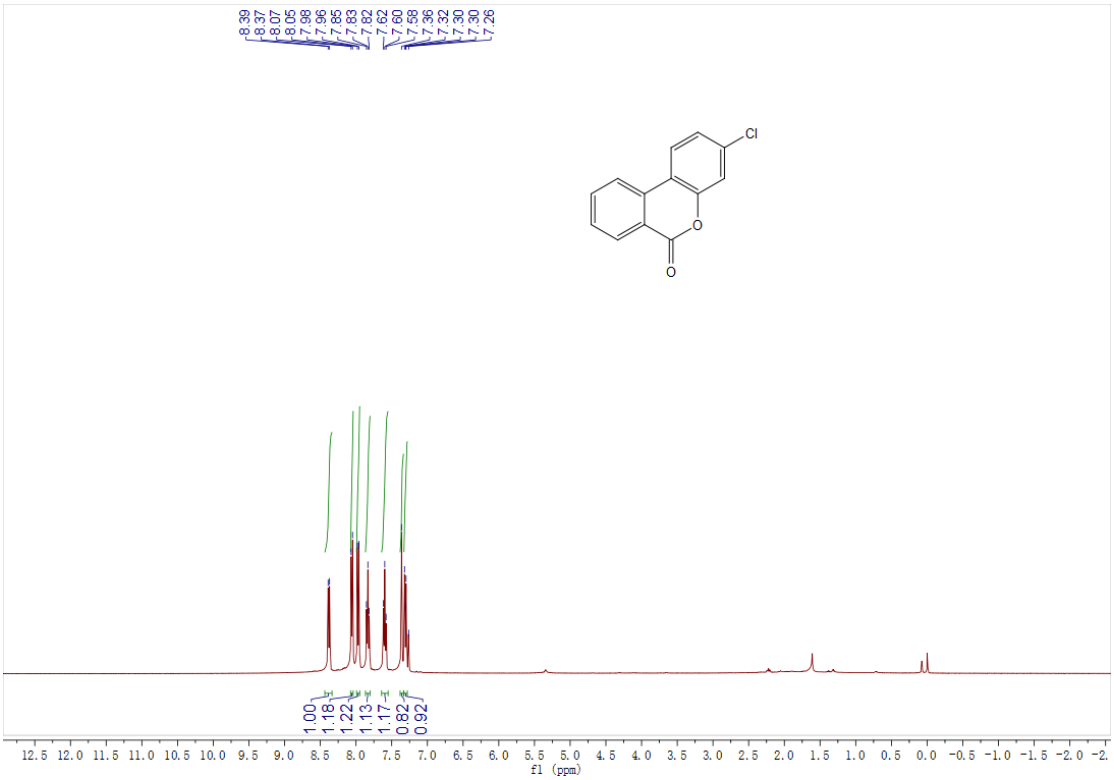


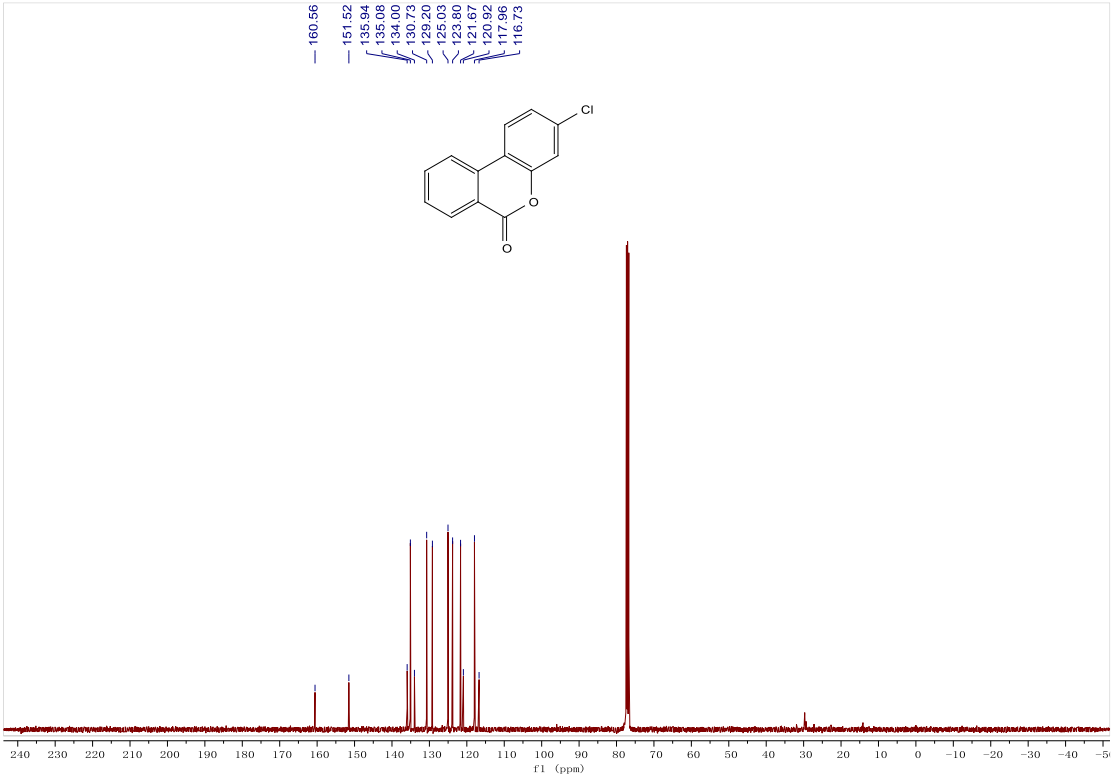
3-fluoro-6H-benzo[c]chromen-6-one 2h



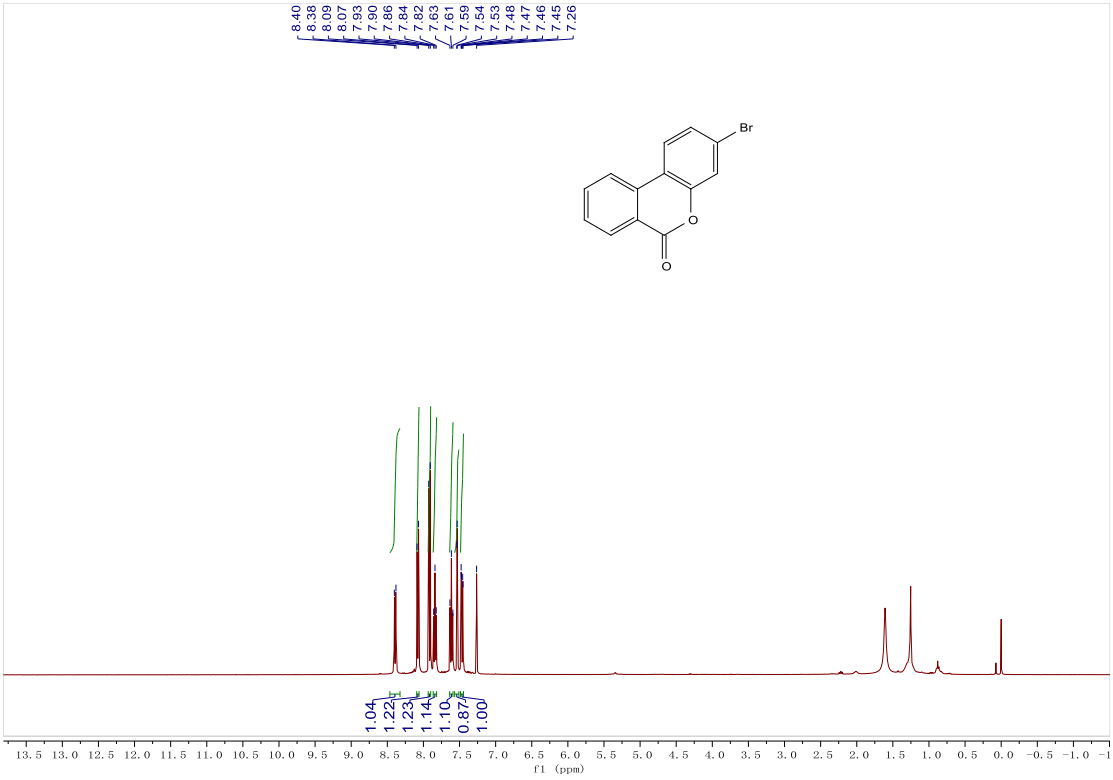


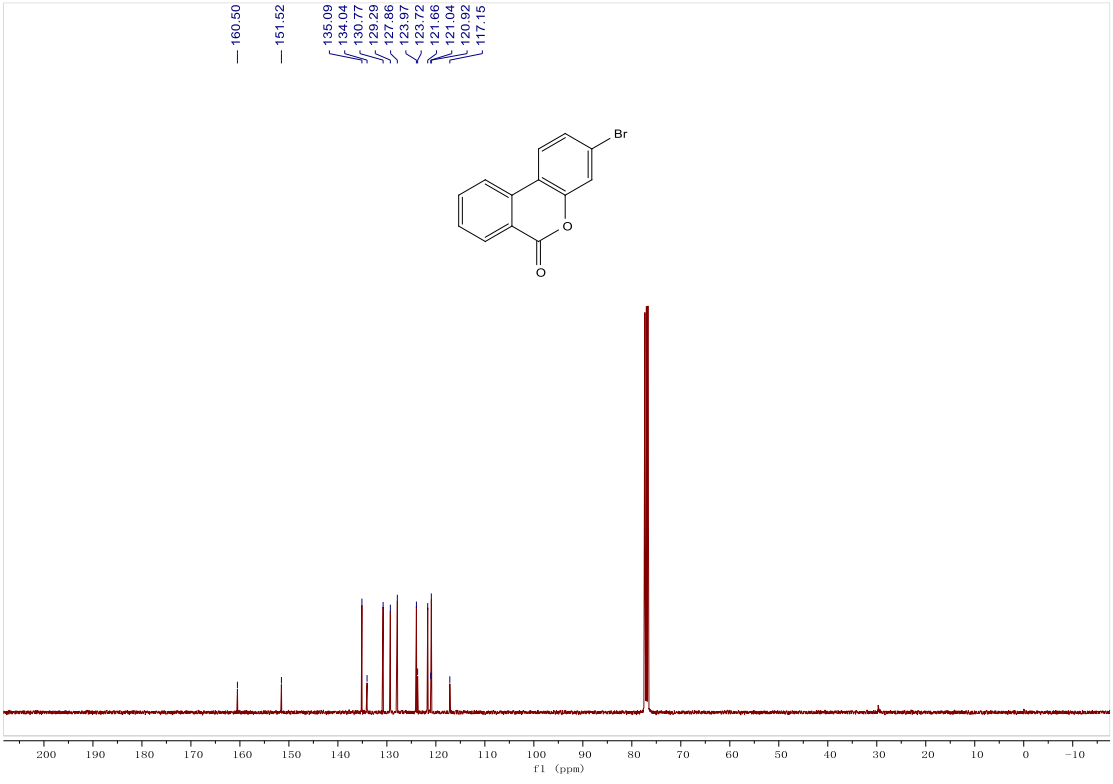
3-chloro-6H-benzo[c]chromen-6-one 2i



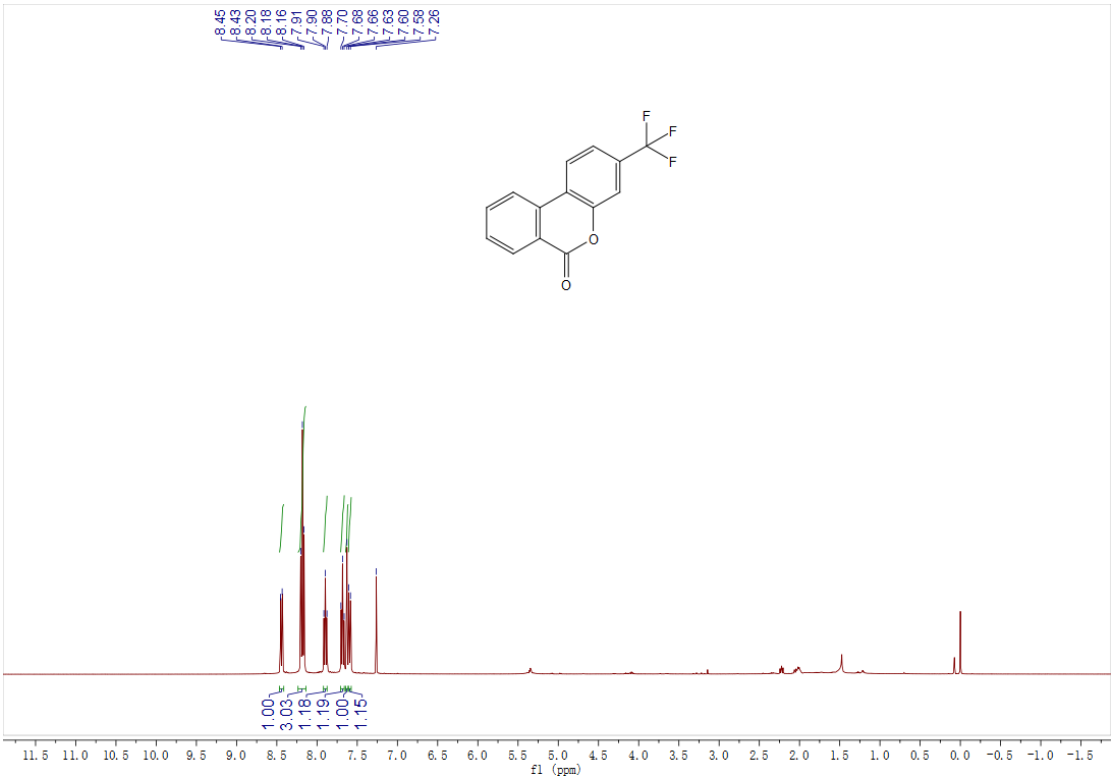


3-bromo-6H-benzo[c]chromen-6-one 2j





3-(trifluoromethyl)-6H-benzo[c]chromen-6-one 2k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8.43
8.20
8.18
8.16
7.91
7.90
7.88
7.70
7.68
7.66
7.63
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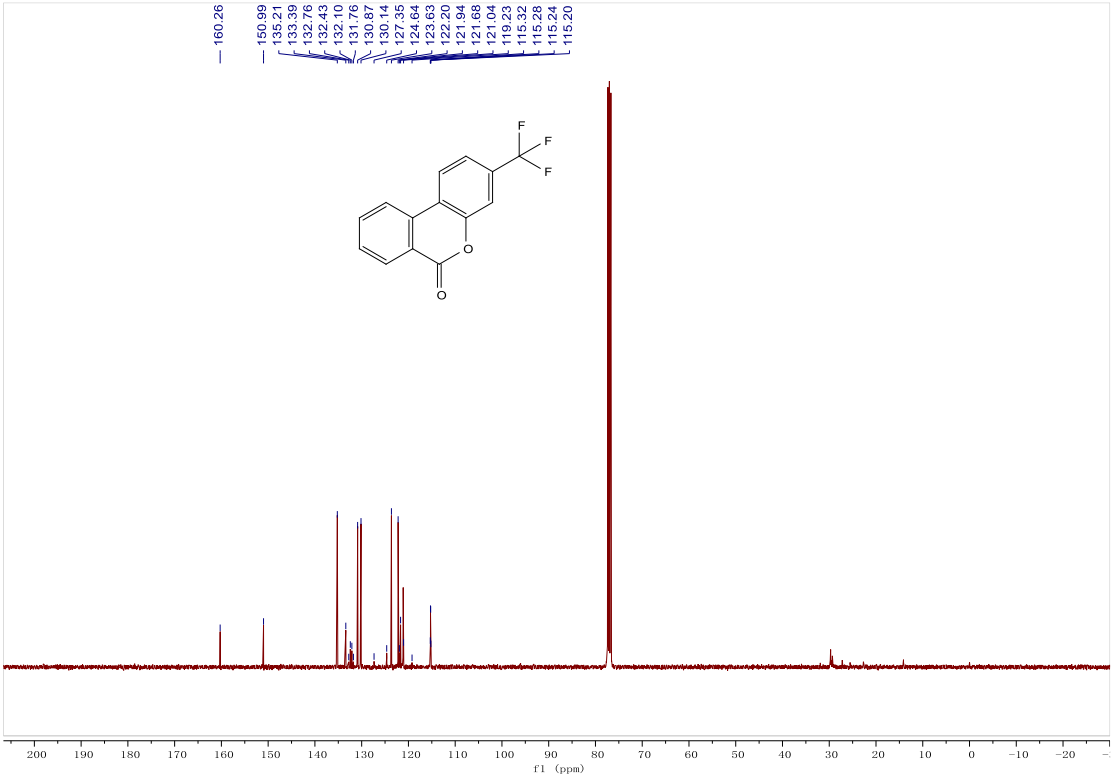
1.18
1.19
1.00
1.15
f1 (ppm)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121.68
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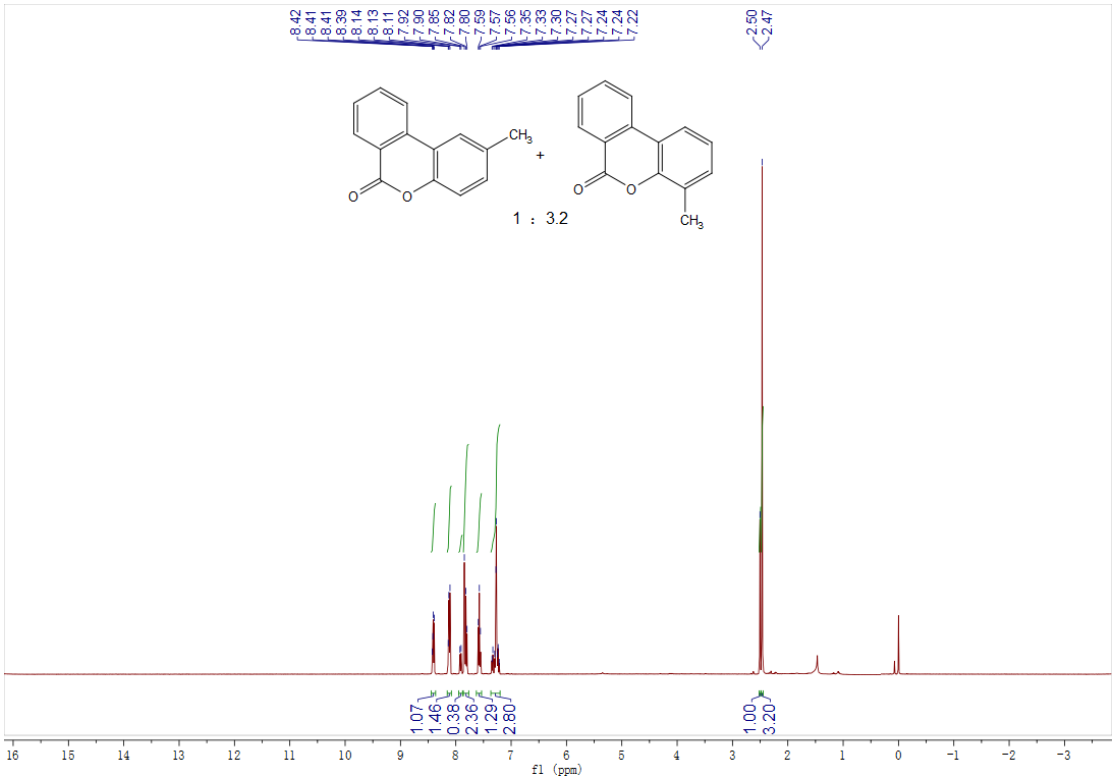
F
F
F
O
O
f1 (ppm)

2l + 2l'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8.14
8.13
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7.85
7.82
7.80
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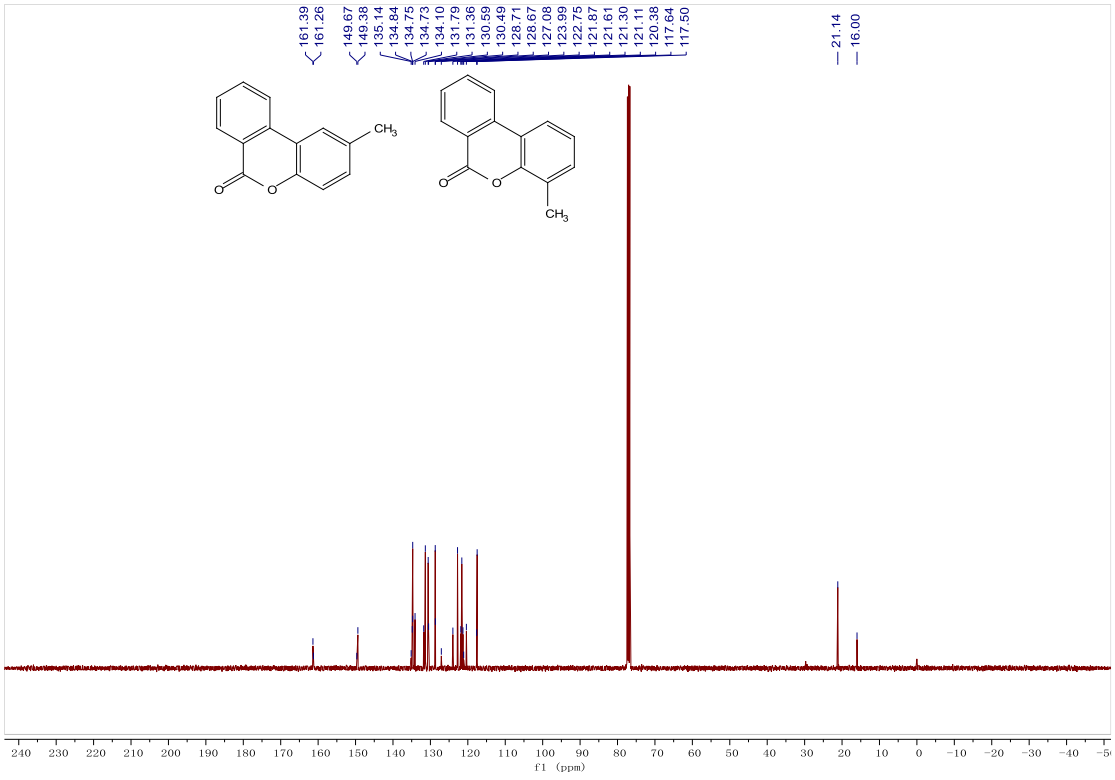
7.56
7.35
7.33
7.30
7.27
7.27
7.24
7.24
7.22
2.50
2.47
CH3
+
O
O
1 : 3.2
CH3
1.07
1.46
0.38
2.36
1.29
2.80
1.00
3.20
f1 (ppm)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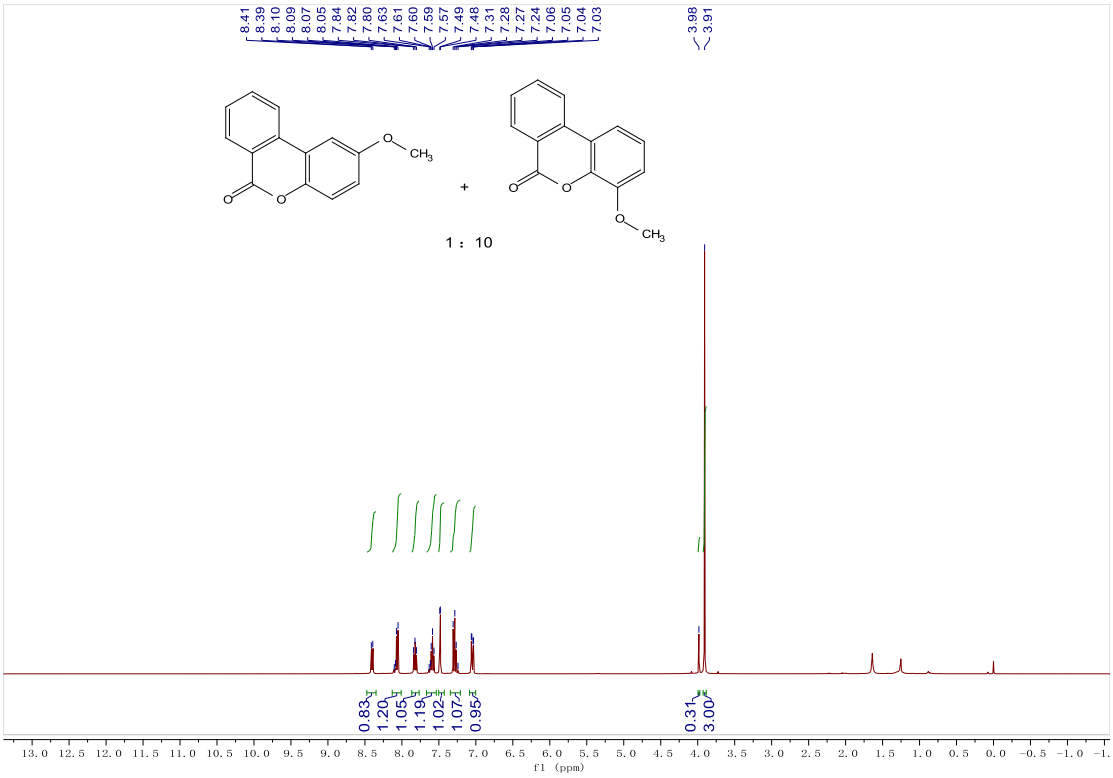
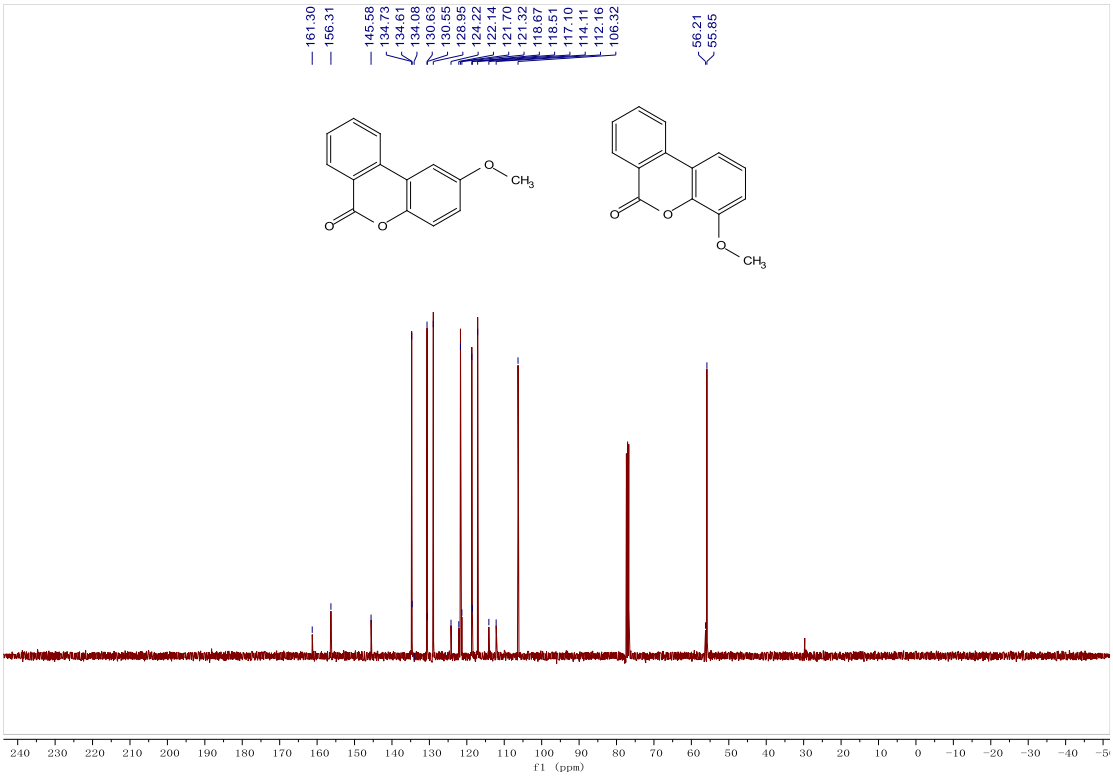
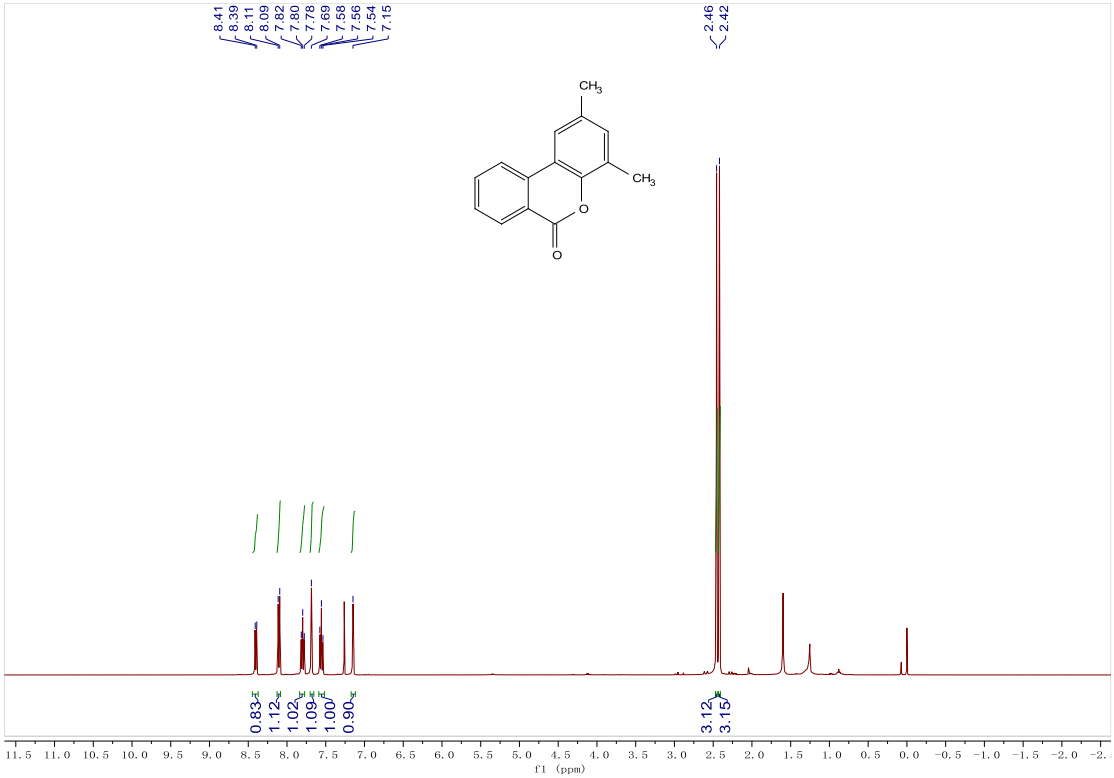
123.99
122.75
121.87
121.61
121.30
121.11
120.38
117.64
117.50
21.14
16.00
CH3
O
O
CH3
f1 (ppm)

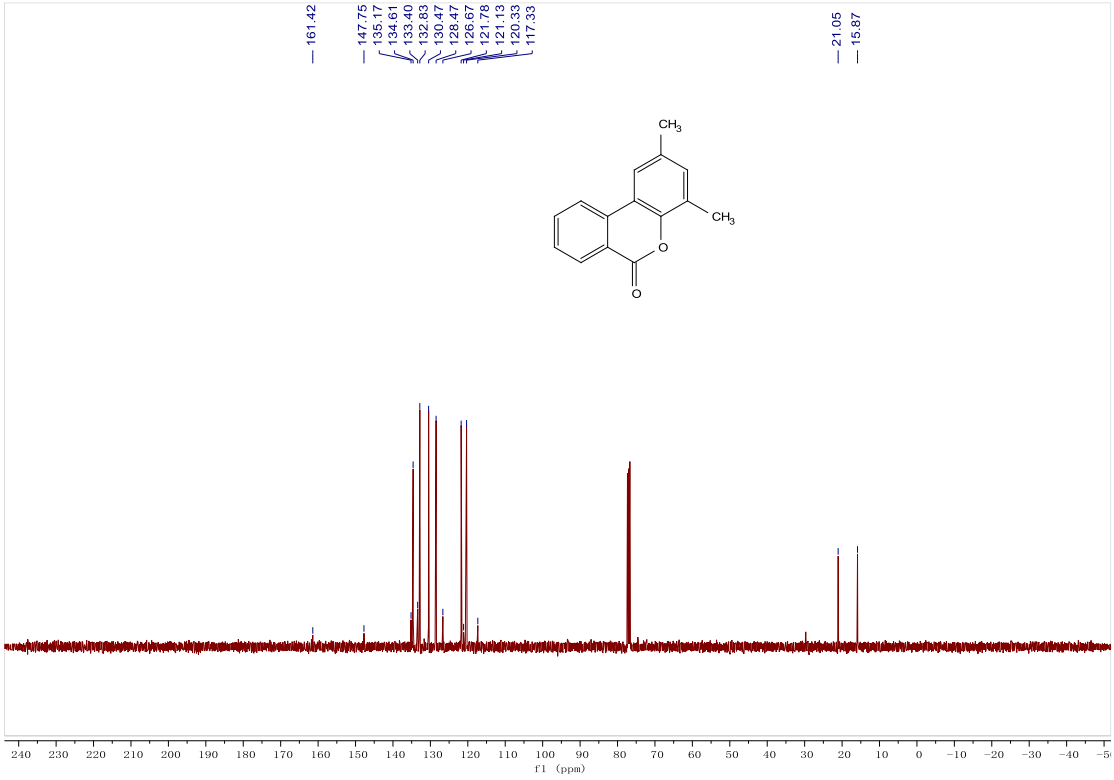
2m + 2m'



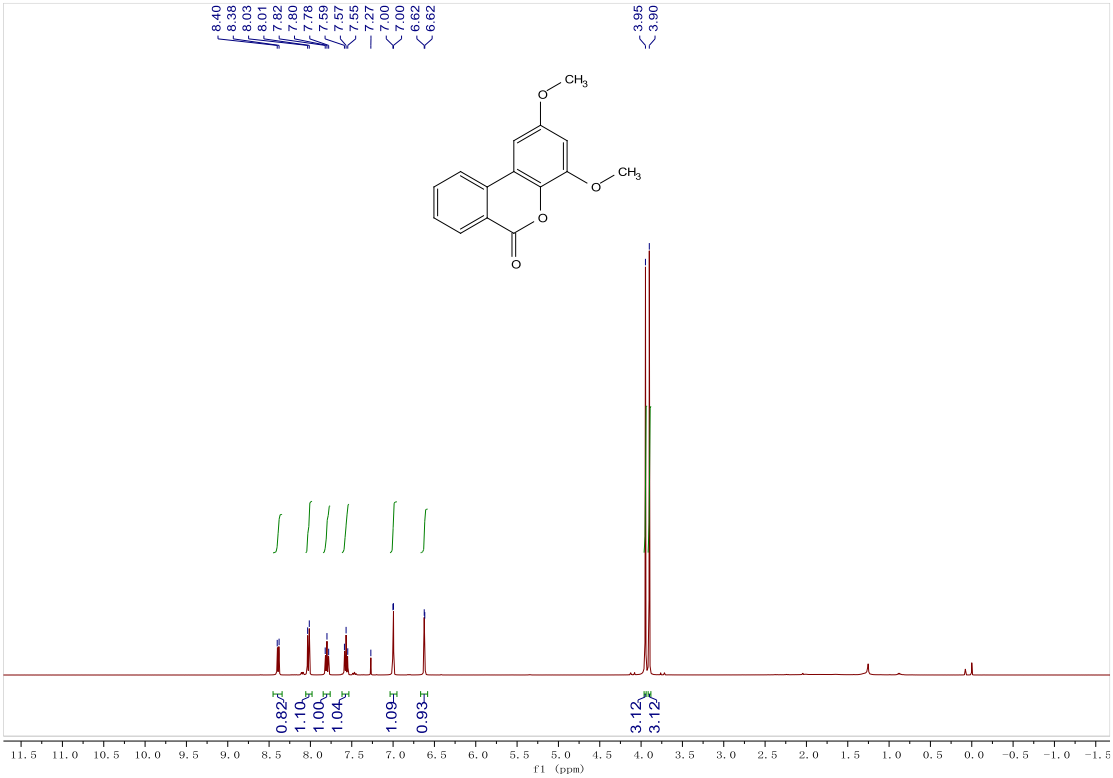


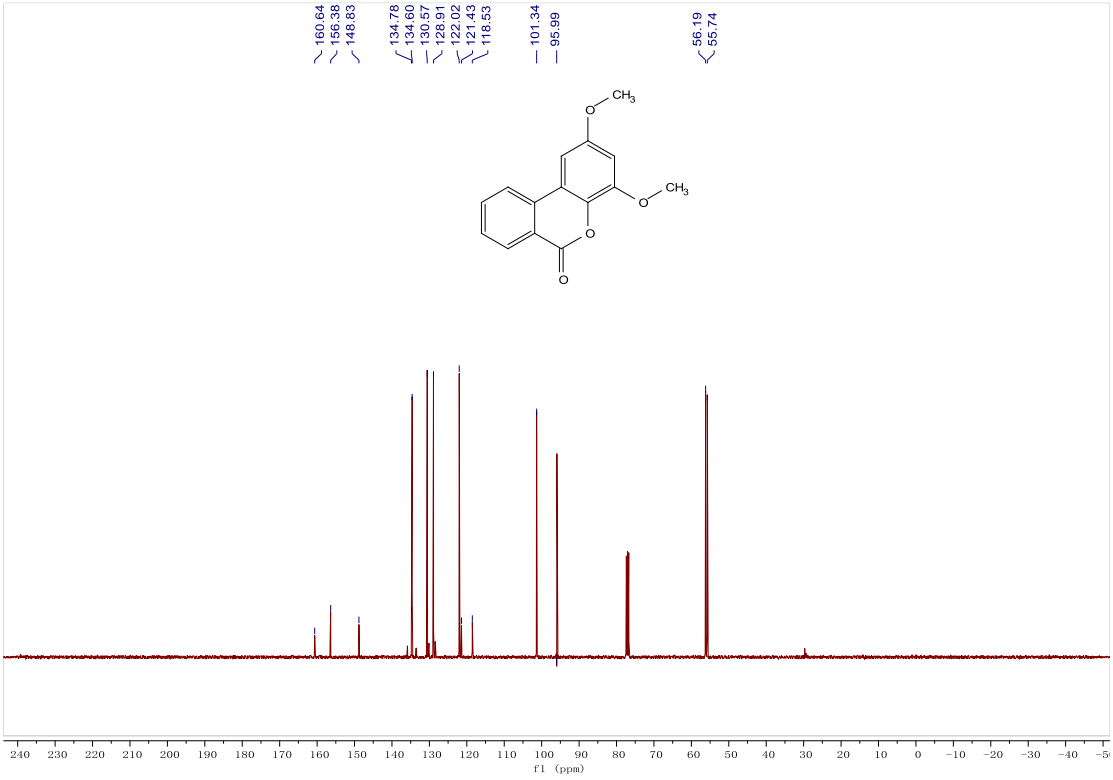
2,4-dimethyl-6H-benzo[c]chromen-6-one 2n



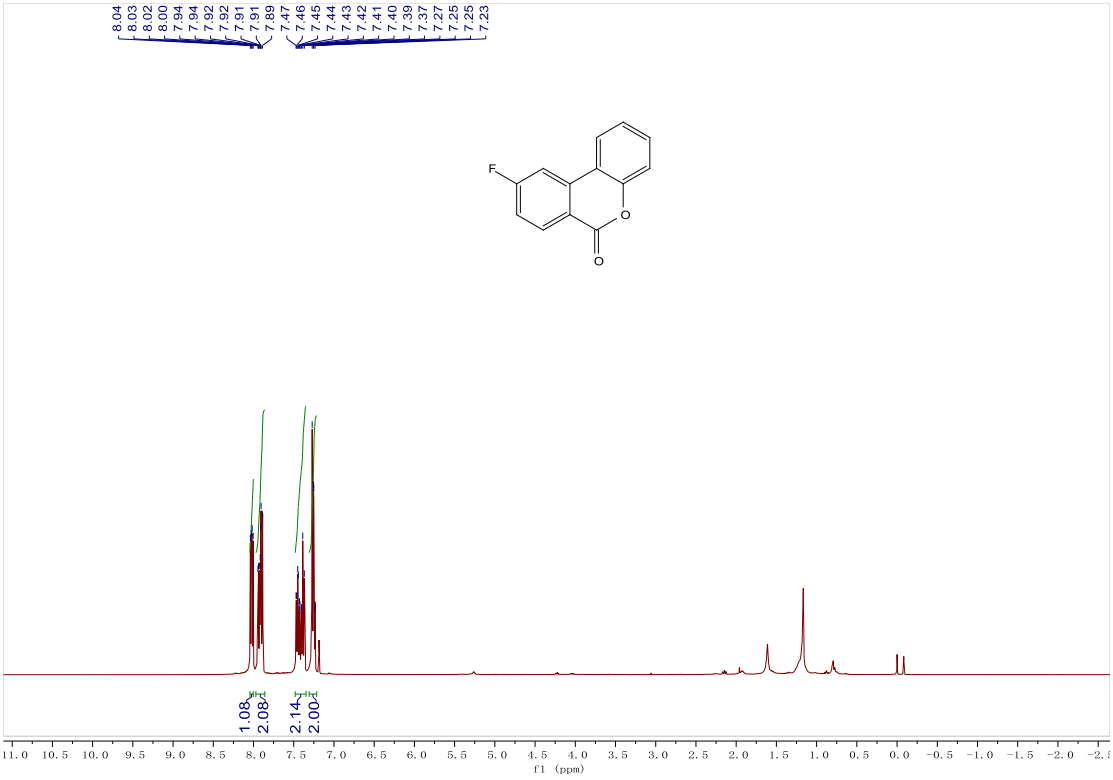


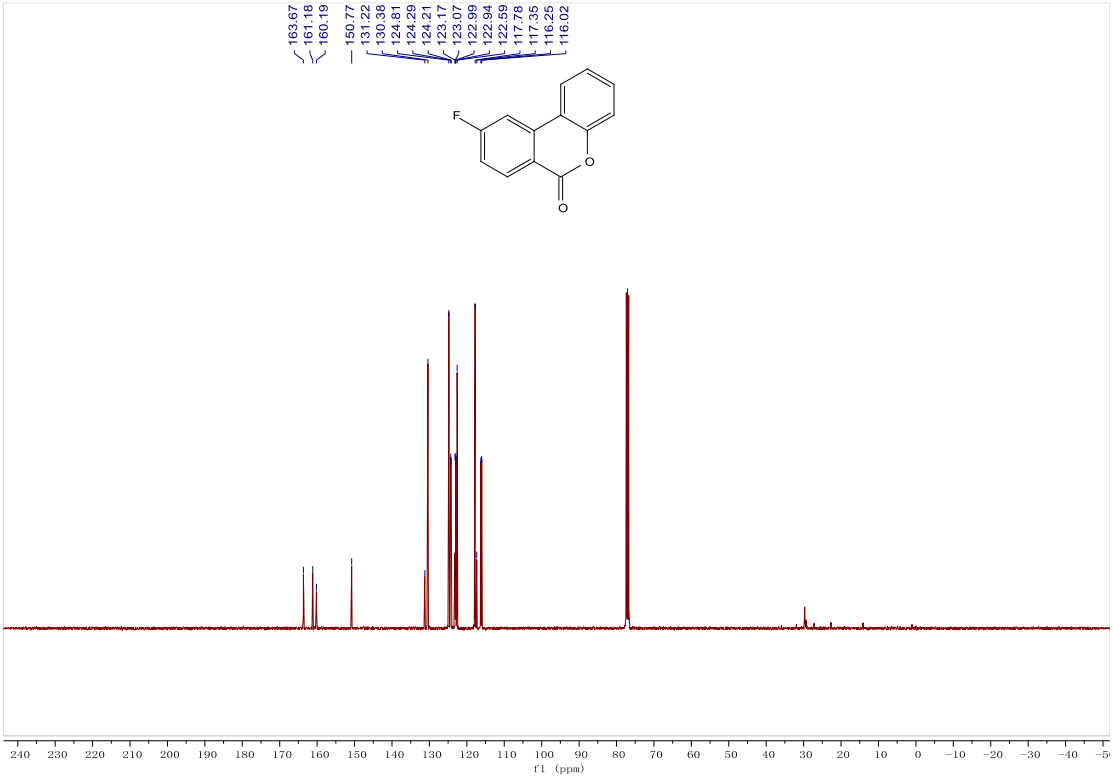
2,4-dimethoxy-6H-benzo[c]chromen-6-one 2o



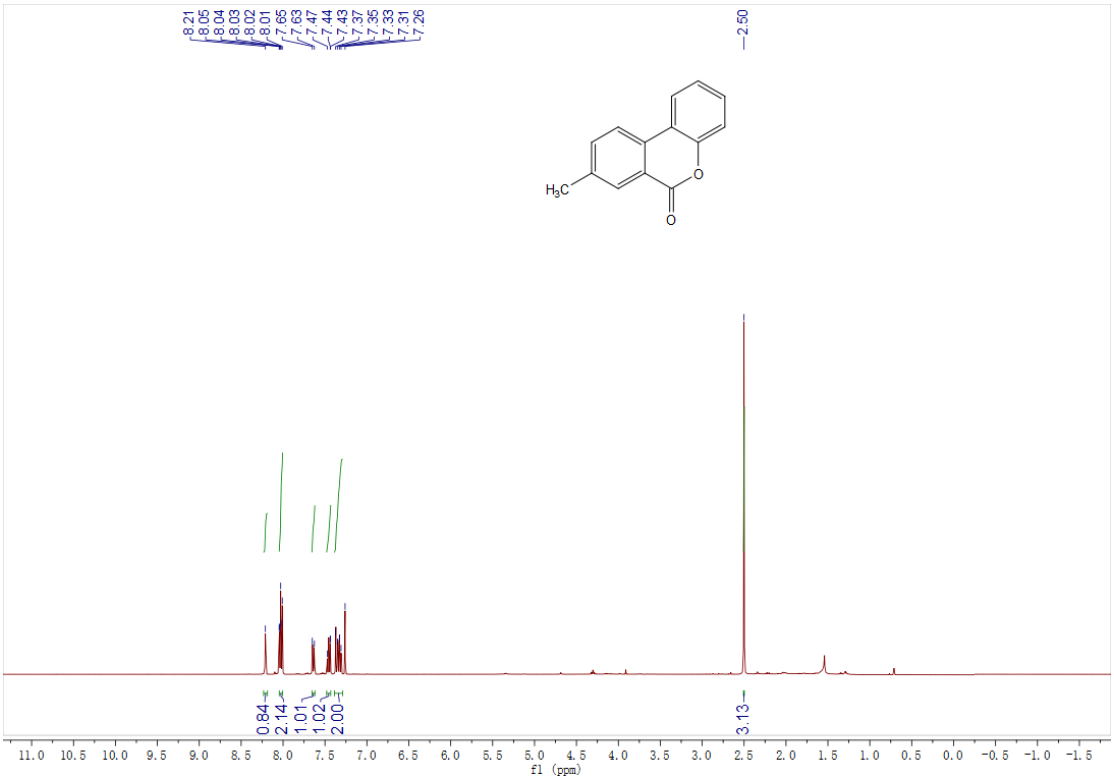


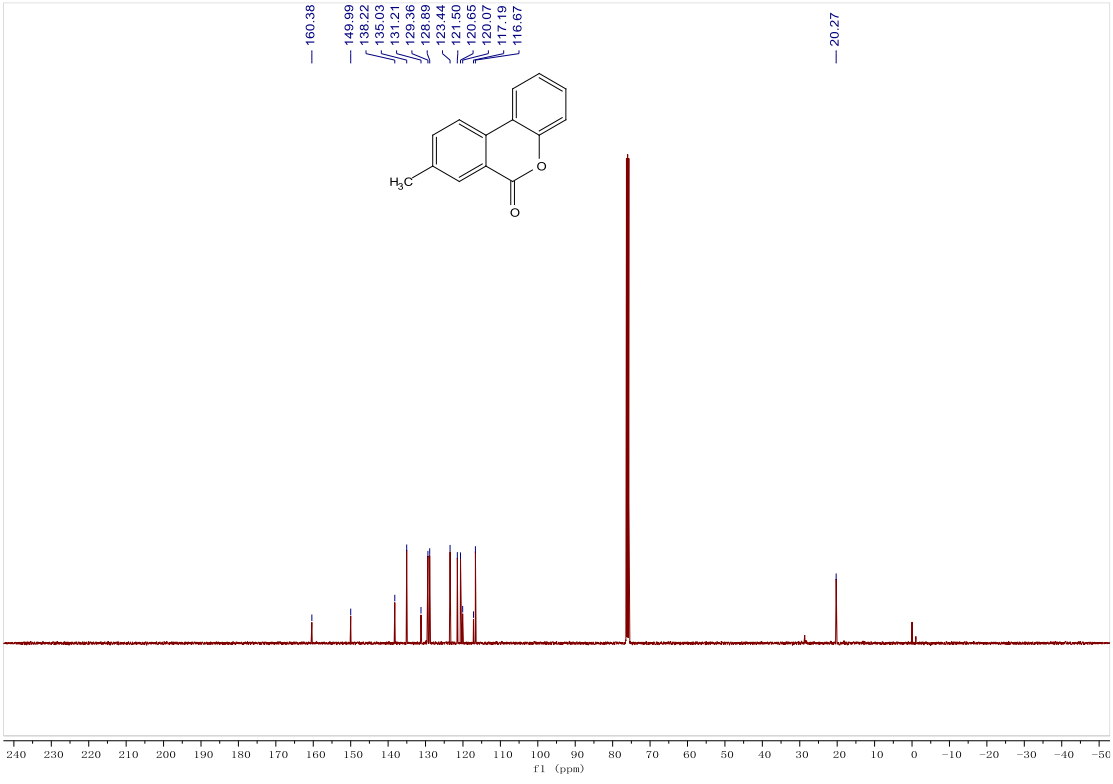
9-fluoro-6H-benzo[c]chromen-6-one, 2p



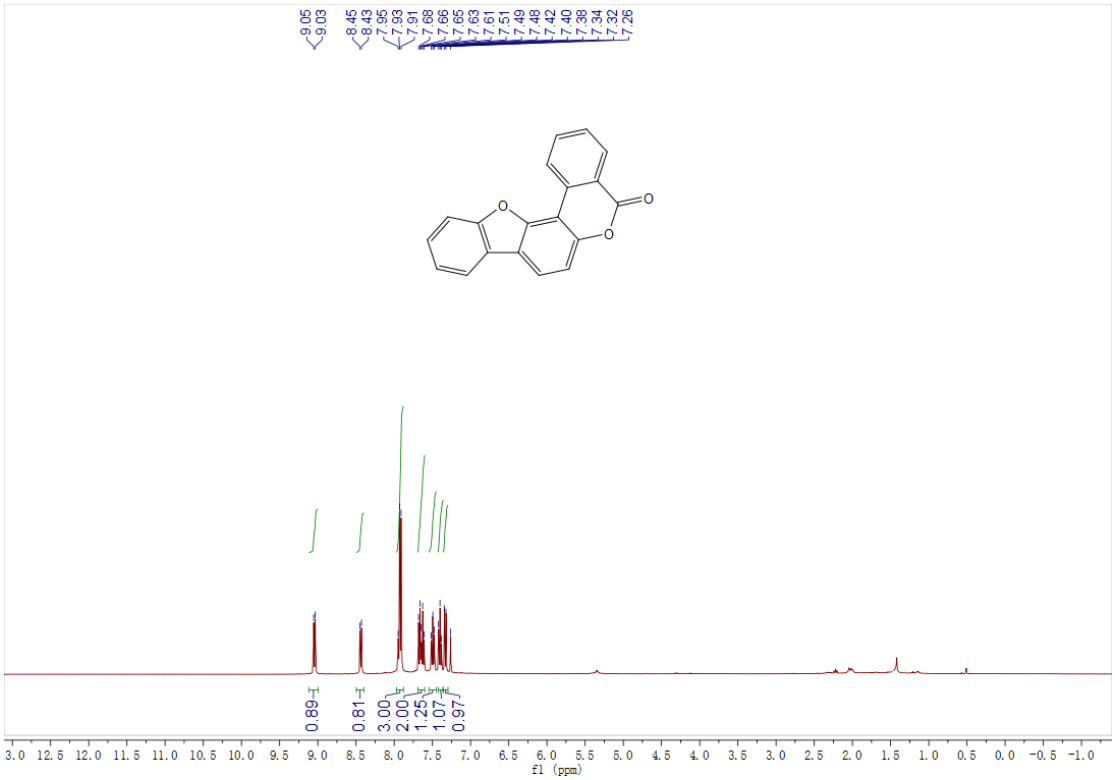


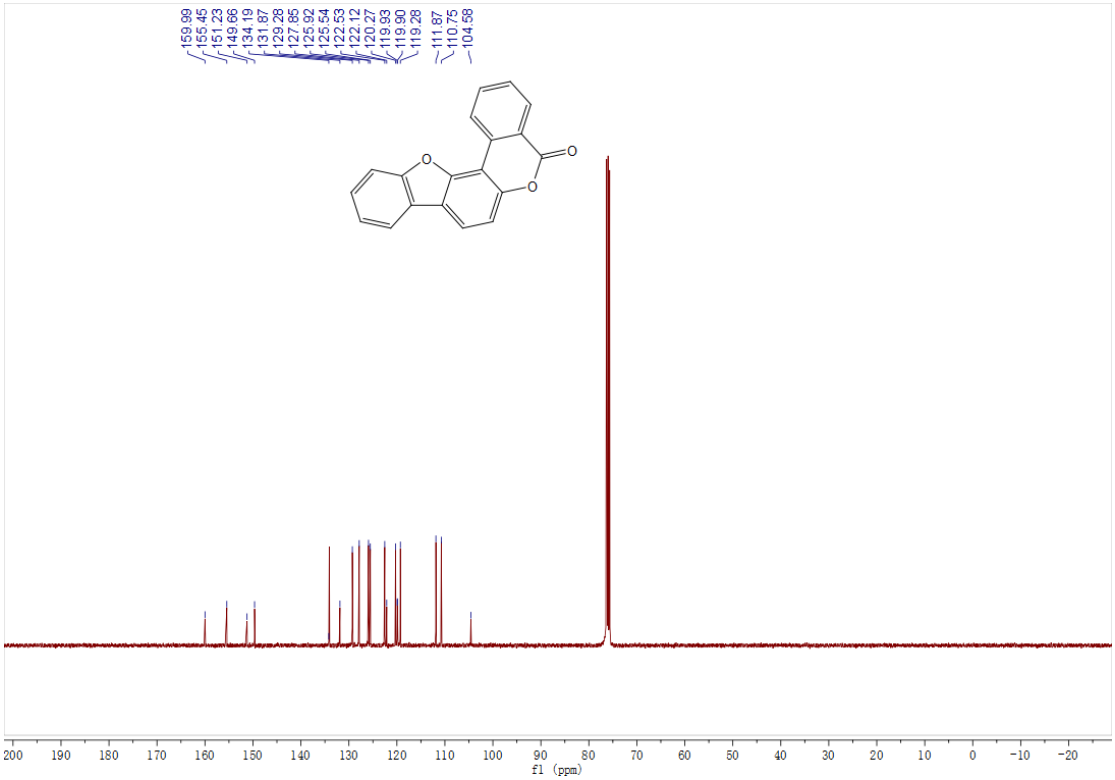
9-methyl-6H-benzo[c]chromen-6-one, 2q



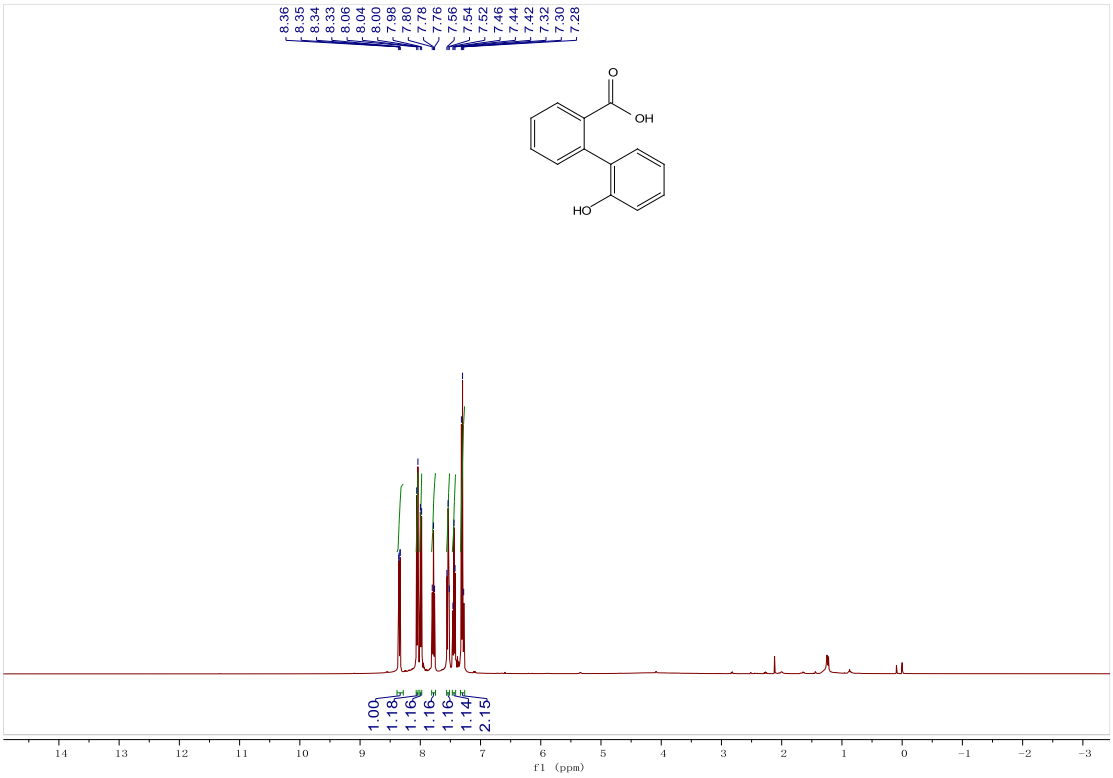


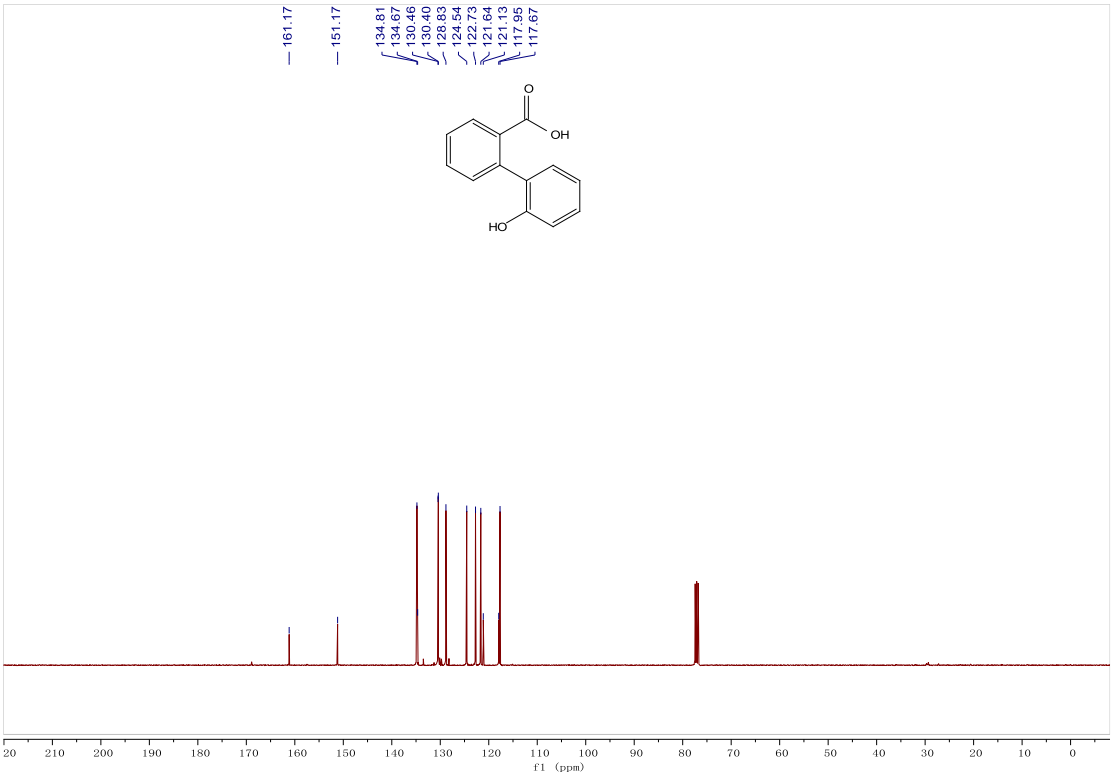
5H-benzo[c]benzofuro[2,3-f]chromen-5-one, 2r



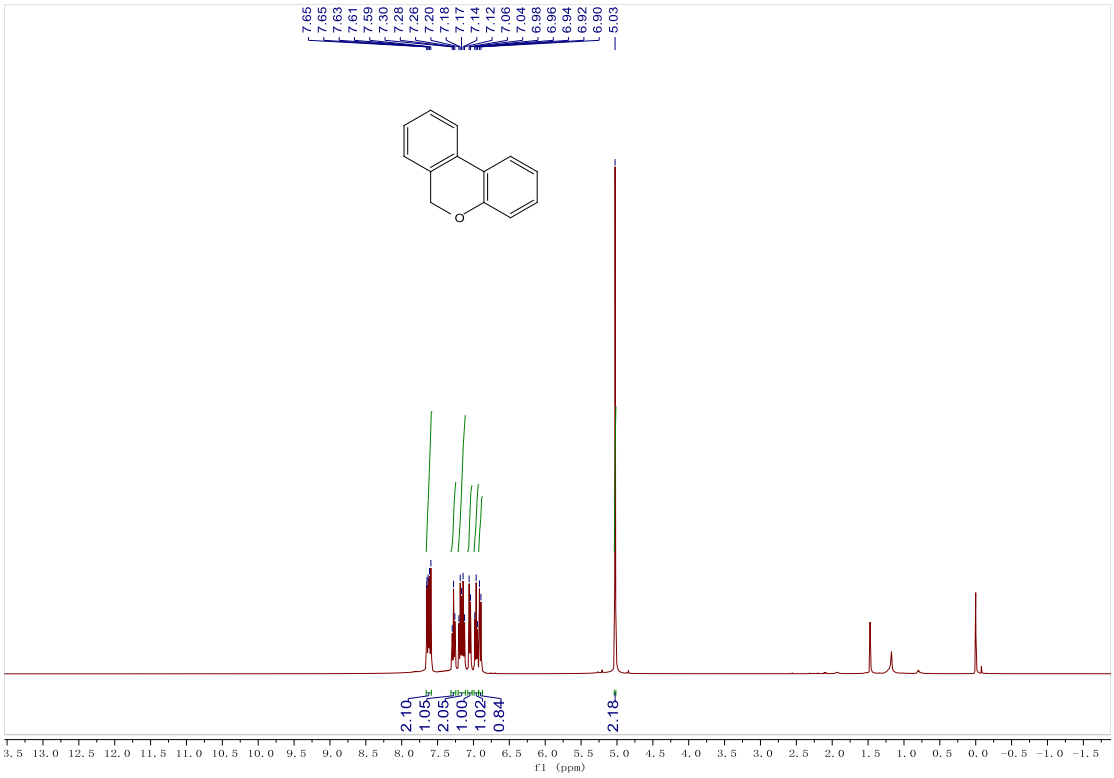


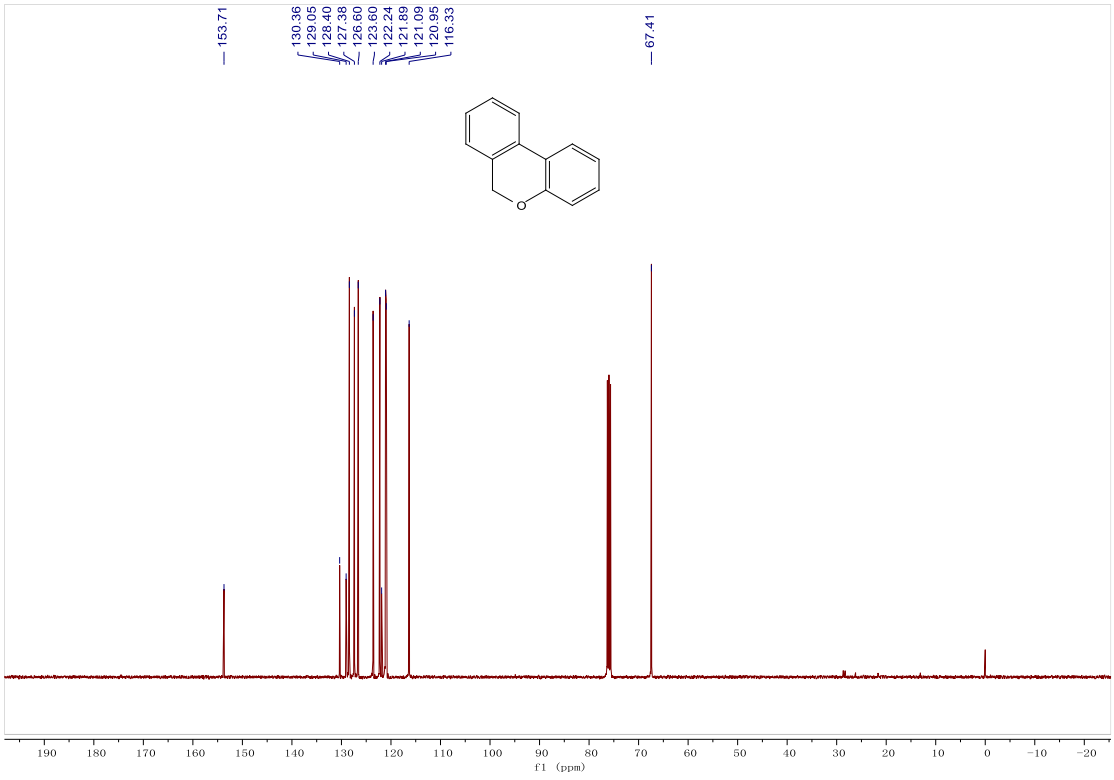
2'-hydroxy-[1,1'-biphenyl]-2-carboxylic acid 3





6H-benzo[c]chromene 4





7.References

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