Electronic Supplementary Information for

Pd/C-Catalyzed Dehydrogenation of 2-Cinamoylbenzoic Acids to 3-Benzylidene-3H-isochroman-1,4-diones

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General information:

All reagents were obtained from commercial suppliers unless otherwise stated. DMA were distilled from magnesium sulfate under vacuum. The Pd/C was first washed with acetone and then was dried under reduced pressure at 80 ^{o}C before used. All corresponding glassware was oven dried (120 ^{o}C) and cooled under a stream of Argon gas.

Flash chromatography was performed using silica gel (300-400 mesh) with solvents distilled prior to use. Visualization was achieved under a UV lamp (254 nm and 365 nm).

^{1}H NMR (400MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$. Chemical shifts are reported in parts per million and coupling constants are in hertz. The chemical structures of products were confirmed by GC-MS (Agilent Technologies, GC7683B, MS5973) and ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz).

The following abbreviations are used: EtOAc: ethyl acetate; DMA: *N, N*-dimethylacetamide; PE: petroleum ether; CH_3CN: acetonitrile; EtOH: ethyl alcohol; MeOH: methanol; TLC: Thin-Layer Chromatography.

General procedure for synthesis of substrates:

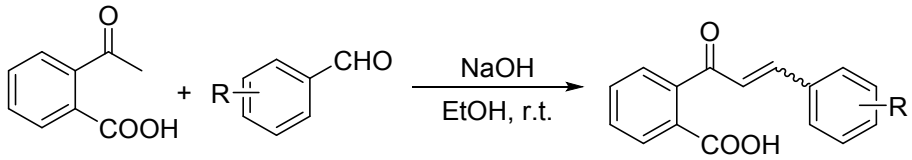
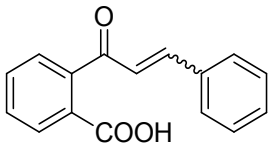


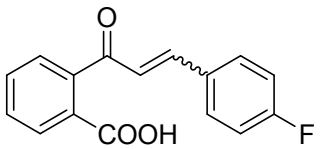
Fig S1. General procedure for synthesis of substrates

To a mixture of 2-acetylbenzoic acid (20 mmol) benzaldehyde (20 mmol), sodium hydroxide (2.4 g, 60 mmol) was added alcohol (30 mL) Then the mixture was stirred for 12 hours at room temperature. After the reaction was completed, hydrochloric acid (10 % in water) was added to the mixture before solid was no longer precipitated. The precipitate part was washed by water (20 ml) three times, dried and purified by recrystallization to give the product.

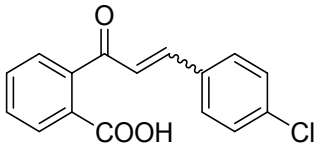
Substrates:



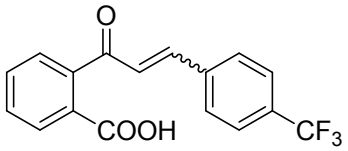
2-(3-Phenyl-1-oxo-2-propen-1-yl)-benzoic acid (1a). Yellow solid, yield: 90%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.38 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 7.3, 2.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.17 (d, *J* = 16.3 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H).



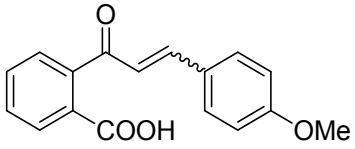
2-[3-(4-Fluorophenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1b). White solid, yield: 90%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 16.3 Hz, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 16.3 Hz, 1H).



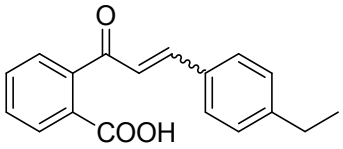
2-[3-(4-Chlorophenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1c). White solid, yield: 88%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.55 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.48 - 7.36 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 16.3 Hz, 1H), 6.98 (d, *J* = 16.3 Hz, 1H).



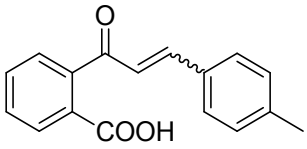
2-[3-[4-(Trifluoromethyl)phenyl]-1-oxo-2-propen-1-yl]-benzoic acid (1d). White solid, yield: 86%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 6.9 Hz, 1H), 7.59 (m, 4H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 16.3 Hz, 1H), 7.07 (d, *J* = 16.1 Hz, 1H).



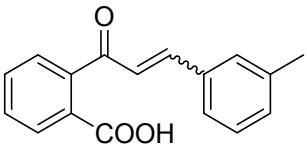
2-[3-(4-Methoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1e). Yellow solid, yield: 91%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (m, 3H), 7.15 (d, *J* = 16.2 Hz, 1H), 6.97 - 6.83 (m, 3H), 3.82 (s, 3H).



2-[3-(4-Ethylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1f). Yellow solid, yield: 92%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 6.9 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 3H), 7.23 - 7.11 (m, 3H), 7.00 (d, *J* = 16.2 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).

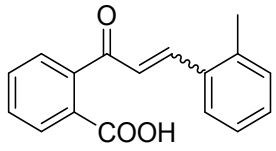


2-[3-(4-Methylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1g). Yellow solid, yield: 90%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 - 7.35 (m, 3H), 7.20 - 7.11 (m, 3H), 6.99 (d, *J* = 16.3 Hz, 1H), 2.35 (s, 3H).

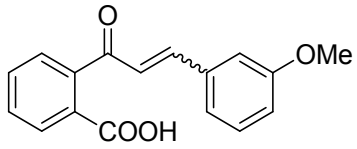


2-[3-(3-Methylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1h). Yellow solid, yield: 89%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.82 (s, 1H), 7.94 (d, *J* = 7.7 Hz,

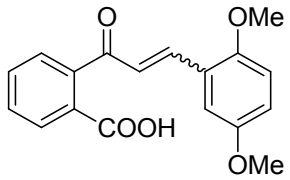
1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.21 - 7.08 (m, 3H), 7.08 - 6.99 (m, 2H), 6.91 (d, *J* = 16.2 Hz, 1H), 2.20 (s, 3H).



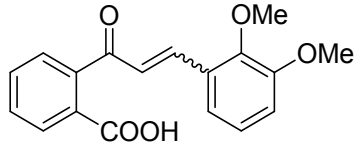
2-[3-(2-Methylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1i**). White solid, yield: 88%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.51 (s, 1H), 8.07 (d, *J* = 7.7 Hz,1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.60 - 7.47 (m, 3H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.21 - 7.12 (m, 2H), 6.94 (d, *J* = 16.1 Hz, 1H), 2.25 (s, 3H).



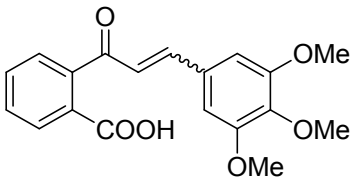
2-[3-(3-Methoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1j**). Yellow solid, yield: 87%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 16.3 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.05 - 6.98 (m, 2H), 6.93 (m, 1H), 3.81 (s, 3H).



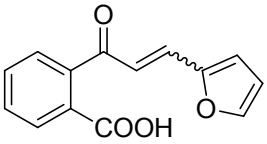
2-[3-(2,5-Dimethoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1k**). Yellow solid, yield: 87%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.51 - 7.39 (m, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.09 - 6.94 (m, 2H), 6.82 (m, 1H), 6.71 (d, *J* = 9.0 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H).



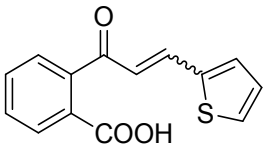
2-[3-(2, 3-Dimethoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1l**). Yellow solid, yield: 85%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 6.9 Hz, 1H), 7.51 (d, *J* = 16.3 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.10 - 6.99 (m, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H).



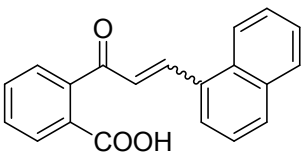
2-[3-(3,4,5-Trimethoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1m**). Yellow solid, yield: 85%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H), 6.72 (s, 2H), 3.87 (s, 3H), 3.86 (s, 6H).



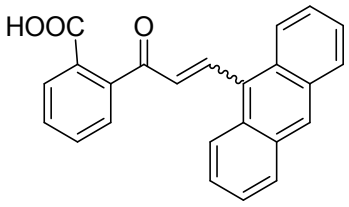
2-[3-(2-furyl)-1-oxo-2-propen-1-yl]-benzoic acid (1n). Yellow solid, yield: 95%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 15.9 Hz, 1H), 6.92 (d, *J* = 15.9 Hz, 1H), 6.63 (d, *J* = 3.3 Hz, 1H), 6.47 (dd, *J* = 3.3, 1.7 Hz, 1H), 2.93 (d, *J* = 30.2 Hz, 1H).



2-[3-(2-Thienyl)-1-oxo-2-propen-1-yl]-benzoic acid (1o). Yellow solid, yield: 90%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.59 (s, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 6.3 Hz, 2H), 7.32 (d, *J* = 15.9 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.07 - 6.98 (m, 1H), 6.83 (d, *J* = 15.9 Hz, 1H).



2-[3-(1-Naphthalenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1p**). Yellow solid, yield: 84%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 - 8.03 (m, 2H), 7.96 - 7.88 (m, 1H), 7.88 - 7.81 (m, 2H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.70 (m, 1H), 7.58 (m, 1H), 7.54 - 7.40 (m, 4H), 7.11 (d, *J* = 15.9 Hz, 1H).



2-[3-(9-Anthracenyl)-1-oxo-2-propen-1-yl]-benzoic acid (**1q**). Yellow solid, yield: 86%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.62 (s, 1H), 8.61 (s, 1H), 8.08 (m, 5H), 7.95 (d, J = 16.5 Hz, 1H), 7.82 (t, J = 7.5 Hz, 1H), 7.70 (m, 2H), 7.55 (m, 4H), 6.88 (d, J = 16.5 Hz, 1H).

General procedure for synthesis of 3-(Phenylmethylene)-1H-2-Benzopyran-1,4-(3H)-dione compounds

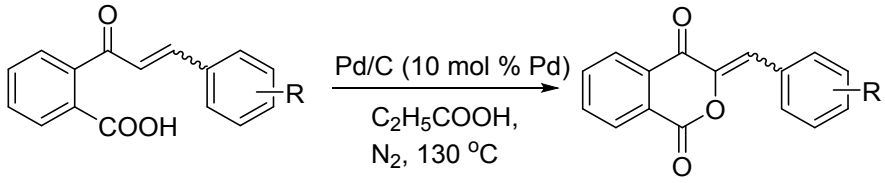
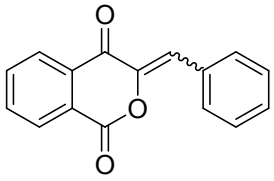
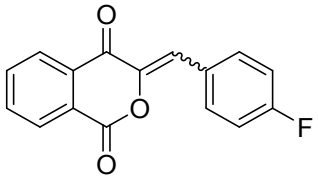


Fig S2. Synthesis of 3-(Phenylmethylene)-1H-2- Benzopyran-1,4-(3H)-dione in propionic acid.

α-Phenylpropionyl bezonic acid (0.25 mmol), propionic acid (1 mL), Pd/C (26.5 mg, 0.025 mmol Pd) were added In a clean oven-dried schlenk reaction tube with magnetic stir-bar under protection of N_2. Then the tube was heated to 130 °C in a preheated oil bath. The reaction mixture was stirred for 24 h. TLC showed complete consumption of starting material. After the reaction was completed, the solvent was evaporated under reduced pressure. The residue was purified via column chromatography through silica gel and PE/ EtOAc as eluate to give product.

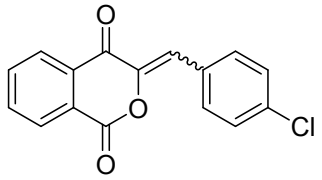


3-(Phenylmethylene)-1*H*-2-Benzopyran-1,4(3*H*)-dione (2a). Yellow solid, yield: 83%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 - 8.24 (m, 1H), 8.24 - 8.14 (m, 1H), 7.91 (d, *J* = 6.9 Hz, 2H), 7.84 - 7.75 (m, 2H), 7.43 - 7.31 (m, 3H), 7.13 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.77, 157.00, 143.97, 134.06, 134.04, 132.36, 131.12, 130.95, 129.57, 129.51, 127.91, 125.82, 119.46. HRMS: m/z calcd for $C_{16}H_{10}O_3$: 250.0630; found: 250.0631.

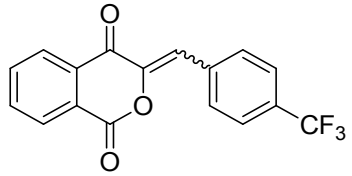


3-[(4-Fluorophenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2b). Yellow solid, yield: 87%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 - 8.31 (m, 1H), 8.31 - 8.24 (m, 1H), 8.02-7.99 (m, 2H), 7.95 - 7.82 (m, 2H), 7.21 - 7.06 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.67, 157.86, 145.17, 136.61, 135.21, 133.31, 133.23, 130.69,

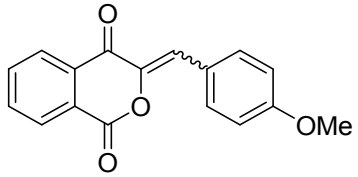
130.47, 129.26, 126.92, 126.79, 118.93. HRMS: m/z calcd for $C_{16}H_9FO_3$: 268.0536; found: 268.0534.



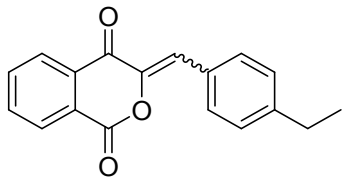
3-[(4-Chlorophenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2c). Yellow solid, yield: 82%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 - 8.33 (m, 1H), 8.28-8.26 (m, 1H), 7.93-7.88 (m, 4H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.74, 157.99, 144.67, 135.17, 135.14, 134.32, 134.24, 133.38, 130.65, 128.32, 126.89, 126.80, 119.20, 116.31, 116.10. HRMS: m/z calcd for $C_{16}H_9ClO_3$: 284.0240; found: 284.0241.



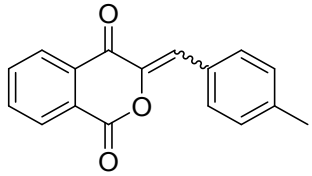
3-[(4-trifluoromethylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2d). Yellow solid, yield: 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35-8.34 (m, 1H), 8.29-8.26 (m, 1H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.92-7.90 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.18 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.70, 157.61, 145.94, 135.40, 135.31, 135.22, 133.08, 131.98, 131.52 (d, *J* = 33.1 Hz), 130.75, 126.97, 126.73, 125.75, 125.71, 123.79 (d, *J* = 271.9 Hz), 117.98. HRMS: m/z calcd for $C_{17}H_9F_3O_3$: 318.0504; found: 318.0503.



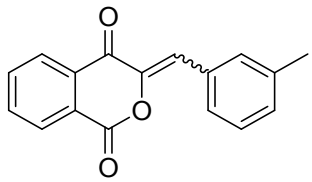
3-[(4-Methoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2e). Yellow solid, yield: 67%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 - 8.31 (m, 1H), 8.31 - 8.22 (m, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.92 - 7.82 (m, 2H), 7.20 (s, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.58, 161.58, 158.31, 143.97, 135.01, 134.82, 134.28, 133.72, 130.52, 126.86, 126.79, 124.94, 120.87, 114.53, 55.43. HRMS: m/z calcd for $C_{17}H_{12}O_4$: 280.0736; found: 280.0735.



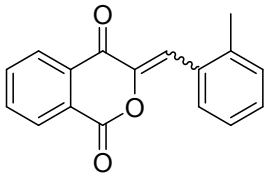
3-[(4-Ethylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2f). Yellow solid, yield: 63%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 - 8.29 (m, 1H), 8.28 - 8.20 (m, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.88 - 7.81 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.18 (s, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.70, 158.12, 147.51, 144.65, 135.01, 134.93, 133.53, 132.36, 130.54, 129.54, 128.55, 126.89, 126.80, 120.80, 28.96, 15.23. HRMS: m/z calcd for $C_{18}H_{14}O_3$: 278.0943; found: 278.0941.



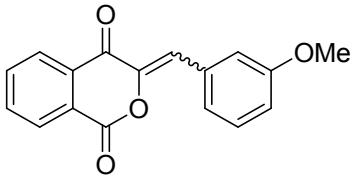
3-[(4-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2g). Yellow solid, yield: 58%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34-8.32 (m, 1H), 8.27 - 8.25 (m, 1H), 7.92 - 7.81 (m, 4H), 7.31 - 7.14 (m, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.61, 158.09, 144.60, 141.28, 134.99, 134.91, 133.46, 132.25, 130.51, 129.74, 129.28, 126.83, 126.77, 120.71, 21.70. HRMS: m/z calcd for $C_{17}H_{12}O_3$: 264.0786; found: 264.0786.



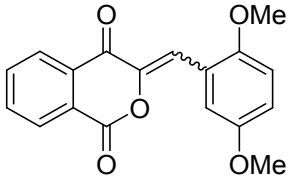
3-[(3-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2h). Yellow solid, yield: 60%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (m, 1H), 8.21 (m, 1H), 7.89 - 7.77 (m, 3H), 7.68 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.66, 157.97, 144.90, 138.47, 134.98, 134.95, 133.38, 132.82, 131.92, 131.43, 130.52, 129.28, 128.84, 126.85, 126.77, 120.62, 21.44. HRMS: m/z calcd for $C_{17}H_{12}O_3$: 264.0786; found: 264.0785.



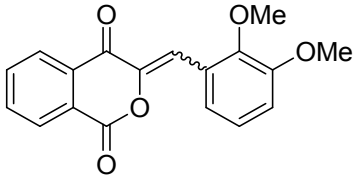
3-[(2-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2i). Yellow solid, yield: 83%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 - 8.32 (m, 1H), 8.31 - 8.21 (m, 2H), 7.89 (m, 2H), 7.49 (s, 1H), 7.36 - 7.28 (m, 2H), 7.25 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.03, 158.16, 144.96, 139.41, 135.11, 135.09, 133.44, 131.37, 130.62, 130.60, 130.54, 130.33, 126.9**1**, 126.88, 126.54, 117.68, 20.40. HRMS: m/z calcd for $C_{17}H_{12}O_3$: 264.0786; found: 264.0786.



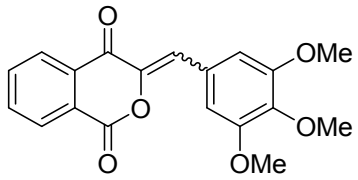
3-[(3-Methoxyphenyl)methylene]-1*H*-2-benzopyran-1,4(3*H*)-dione (2j). Yellow solid, yield: 63%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 - 8.27 (m, 1H), 8.27 - 8.19 (m, 1H), 7.91 - 7.81 (m, 2H), 7.57 - 7.48 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 6.94 (m, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.71, 159.64, 157.84, 145.07, 135.05, 133.33, 133.13, 130.56, 129.82, 126.83, 124.86, 120.26, 116.90, 116.48, 55.30. HRMS: m/z calcd for $C_{17}H_{12}O_4$: 280.0736; found: 280.0735.



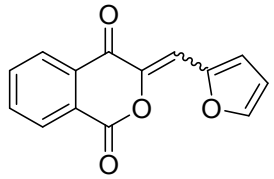
3-[(2,5-Dimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2k). Yellow solid, yield: 64%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 - 8.23 (m, 2H), 7.99 (d, *J* = 3.1 Hz, 1H), 7.87 (m, 2H), 7.74 (s, 1H), 6.95 (m, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.65, 158.00, 153.70, 153.41, 145.06, 134.98, 134.85, 133.62, 130.47, 126.84, 121.44, 118.60, 116.08, 114.32, 111.79, 56.21, 55.79. HRMS: m/z calcd for $C_{18}H_{14}O_5$: 310.0841; found: 310.0841.



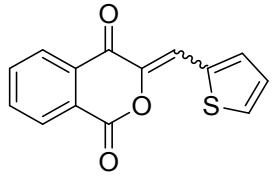
3-[(2,3-Dimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2l). Yellow solid, yield: 54%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 - 8.30 (m, 1H), 8.29 - 8.23 (m, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.87 (m, 2H), 7.69 (s, 1H), 7.16 (t, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.76, 158.11, 152.62, 149.45, 145.54, 135.09, 135.00, 133.49, 130.53, 126.86, 126.81, 126.19, 124.37, 123.65, 114.66, 114.32, 61.77, 55.88. HRMS: m/z calcd for $C_{18}H_{14}O_5$: 310.0841; found: 310.0840.



3-[(3,4,5-Trimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2m). Red solid, yield: 73%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 - 8.22 (m, 1H), 8.22 - 8.14 (m, 1H), 7.89 - 7.77 (m, 2H), 7.20 (s, 2H), 7.01 (s, 1H), 3.91 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.31, 157.65, 152.99, 144.53, 134.93, 134.83, 133.32, 130.34, 127.29, 126.65, 126.60, 120.15, 109.34, 60.91, 56.05. HRMS: m/z calcd for $C_{19}H_{16}O_6$: 340.0947; found: 340.0947.

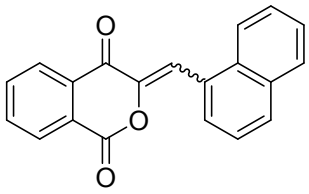


3-(2-Furanylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2n). Yellow solid, yield: 60%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 - 8.31 (m, 1H), 8.31 - 8.21 (m, 1H), 7.96 - 7.80 (m, 2H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.43 (d, *J* = 3.6 Hz, 1H), 7.25 (s, 1H), 6.64 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.83, 157.98, 148.77, 145.86, 142.94, 135.12, 134.93, 133.51, 130.68, 126.87, 126.72, 119.00, 113.59, 109.12. HRMS: m/z calcd for $C_{14}H_8O_4$: 240.0423; found: 240.0422.

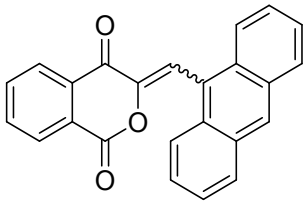


3-(2-Thienylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2o). Yellow solid, yield: 93%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 - 8.32 (m, 1H), 8.32 - 8.21 (m, 1H), 7.91-7.86 (m, 2H), 7.69 (d, *J* = 5.0 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.51 (s, 1H), 7.22 - 7.11 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.98, 157.82, 143.03,

135.12, 135.10, 134.95, 134.40, 133.62, 133.53, 130.71, 127.89, 126.93, 126.73, 114.83. HRMS: m/z calcd for $C_{14}H_8O_3S$: 256.0194; found: 256.0196.



3-(1-Naphthalenylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2p). Yellow solid, yield: 66%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 7.4 Hz, 1H), 8.33 - 8.21 (m, 2H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.90 - 7.77 (m, 4H), 7.56 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.75, 158.12, 145.61, 135.06, 133.59, 133.33, 132.38, 131.05, 130.63, 130.56, 129.02, 127.76, 127.18, 126.84, 126.76, 126.17, 125.76, 123.34, 116.18. HRMS: m/z calcd for $C_{20}H_{12}O_3$: 300.0786; found: 300.0785.



3-(9-Anthracenylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2q). Red solid, yield: 76%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (s, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 8.19-8.15 (m, 5H), 8.07-7.99 (m, 2H), 7.97 (s, 1H), 7.61-7.54 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.28, 157.94, 147.23, 135.26, 135.11, 133.26, 130.77, 129.82, 129.10, 128.65, 128.21, 127.48, 126.37, 126.17, 126.11, 125.75, 125.61, 115.61. HRMS: m/z calcd for $C_{24}H_{14}O_3$: 350.0943; found: 350.0945.

Procedure of the rearrangement reaction:

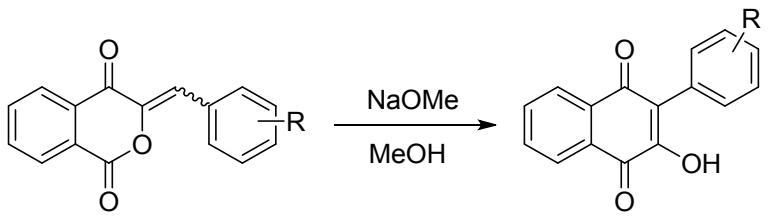
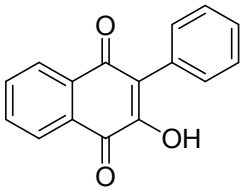


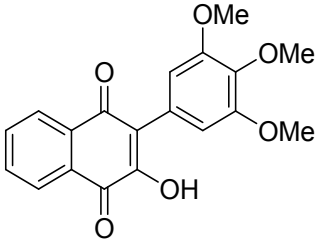
Fig S3. Procedure of the rearrangement reaction.

In a 25 mL round flask was added **2a** (0.5 mmol, 125 mg); Methanol (5 mL); Sodium methoxide (0.6 mmol, 32.4 mg). Then the mixture was stirred at room temperature for 24 h. Acetic acid was added dropwise to no more solid separated out. The mixture was filtered and the residue was washed by water (2 mL) for three times, dried and recrystallized to give the product.

Products of rearrangement:

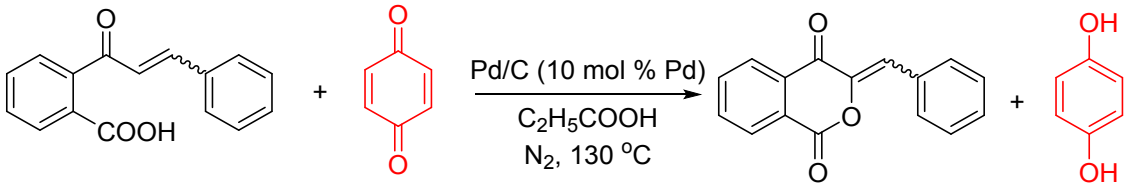


2-Hydroxy-3-phenyl-1,4-naphthalenedione (3a). Yellow solid, yield: 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20-8.24 (m, 1H), 8.16-8.18(m, 1H), 7.81-7.85 (m, 1H), 7.74-7.78 (m, 1H), 7.60 (s, 1H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.40-7.44 (m, 1H); HRMS: m/z calcd for $C_{16}H_{10}O_3$: 250.0630; found: 250.0632.



2-Hydroxy-3-(3,4,5-trimethoxyphenyl)-1,4-naphthalenedione (3m). Yellow solid, yield: 70%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 6.77 (s, 2H), 3.92 (s, 3H), 3.89 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.73, 152.81, 152.14, 138.48, 135.36, 133.24, 132.83, 129.25, 127.34, 126.19, 125.16, 122.11, 108.19, 60.89, 56.19. HRMS: m/z calcd for $C_{19}H_{16}O_6$: 340.3267; found: 340.3266.

Verification of HPdH species



α-Phenylpropionyl bezonic acid (0.25 mmol), propionic acid (1 mL), Pd/C (26.5 mg, 0.025 mmol Pd) and **p-benzoquinone** (0.25 mmol) were added in a clean oven-dried schlenk reaction tube with magnetic stir-bar under protection of N_2. Then the tube was heated to 130 °C in a preheated oil bath. The reaction mixture was stirred for 24 h. After the reaction was completed, the solvent was evaporated under reduced pressure. The residue was purified via column chromatography through silica gel and PE/ EtOAc as eluate. The **p-benzenediol** generated in reaction was detected by EI-MS.

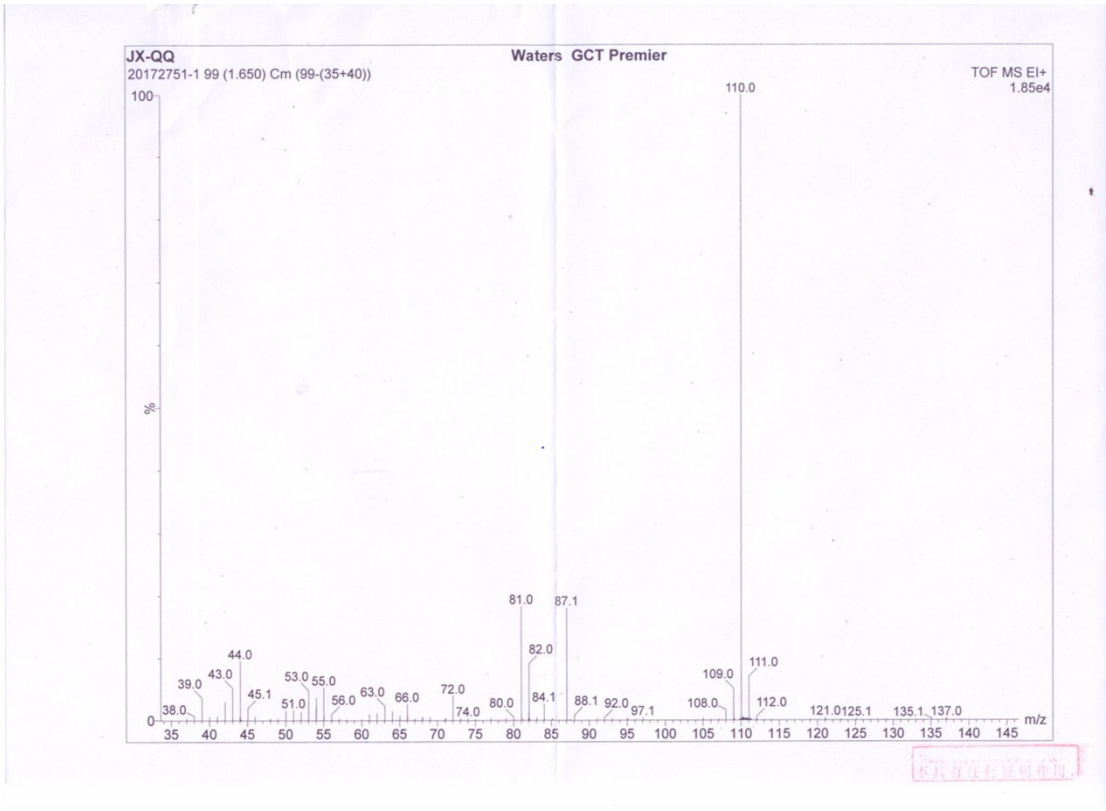
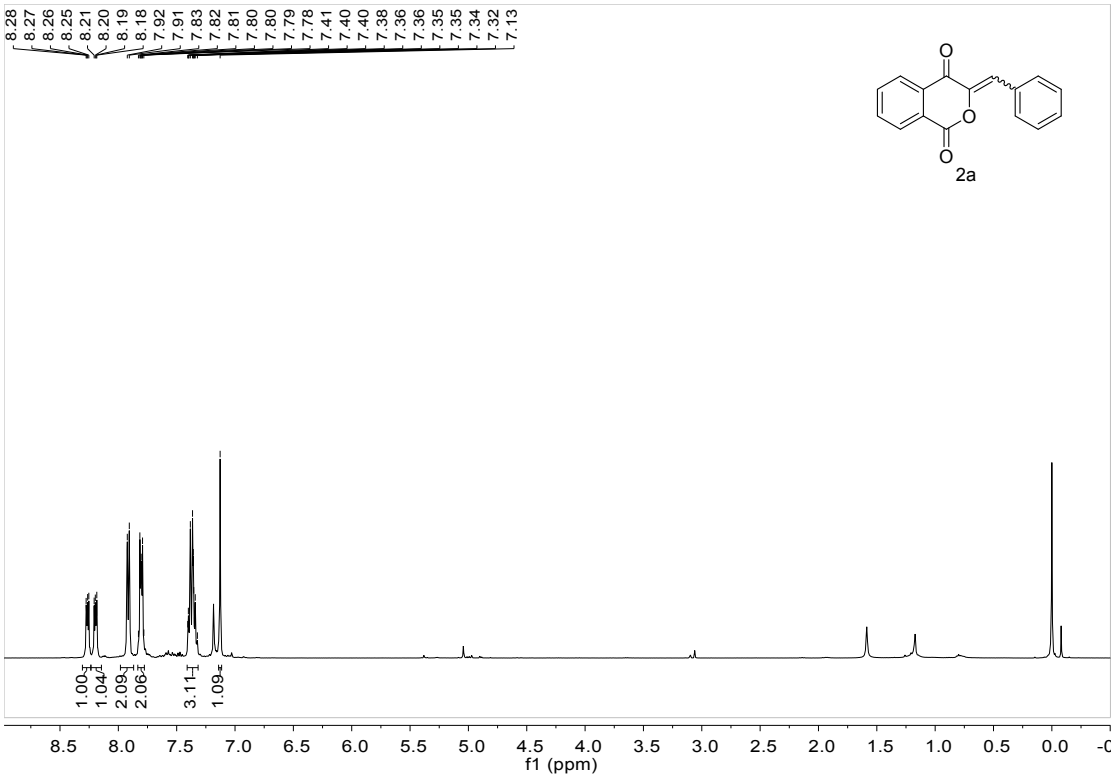


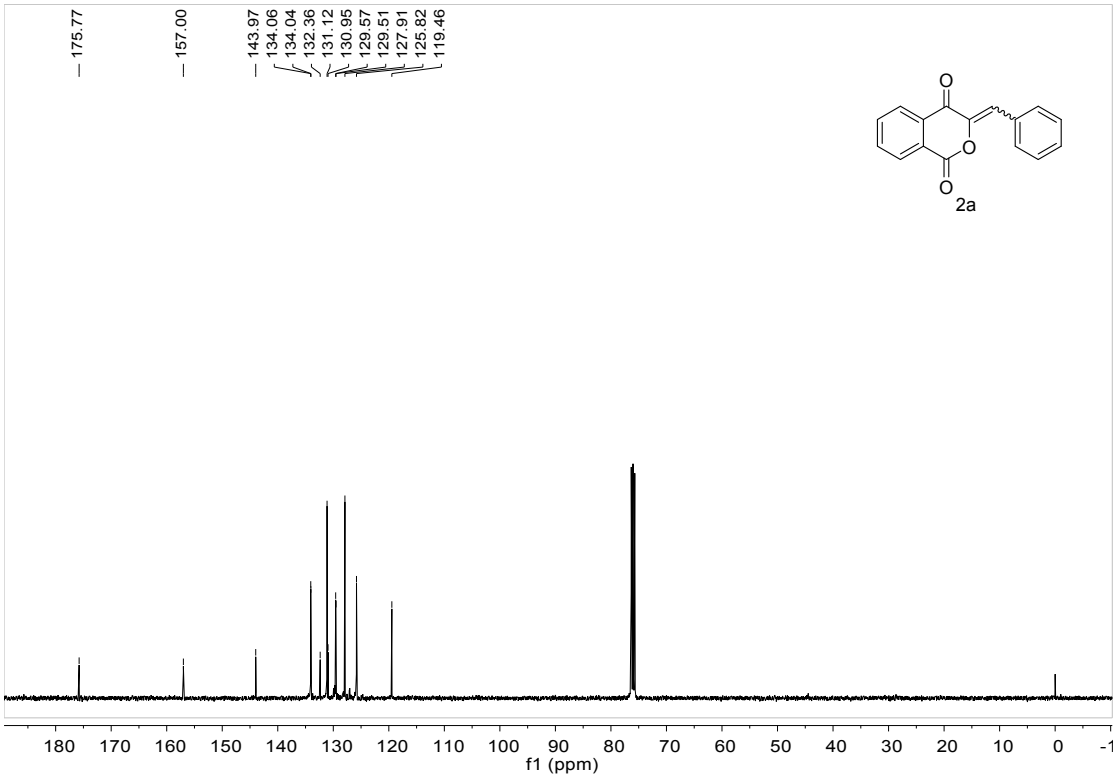
Fig S4. EI-MS spectra of p-benzenediol.

NMR spectra

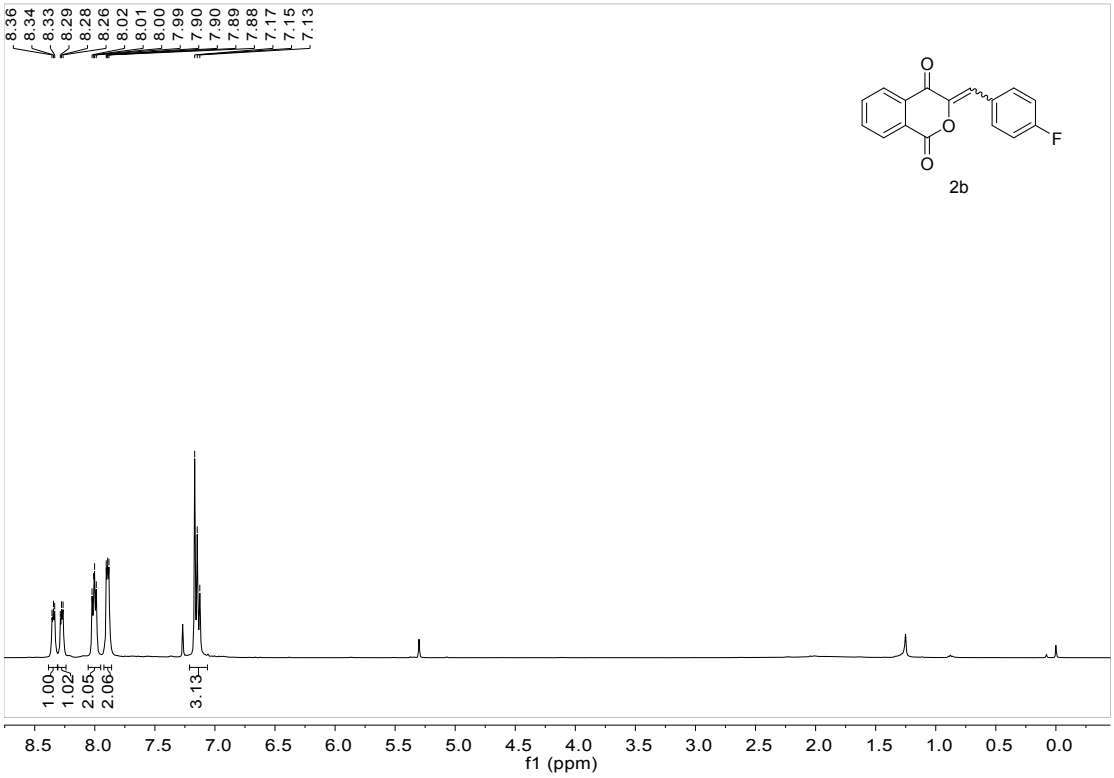
^{1}H NMR of 3-(Phenylmethylene)-1H-2-Benzopyran-1,4(3H)-dione (2a) in $CDCl_3$



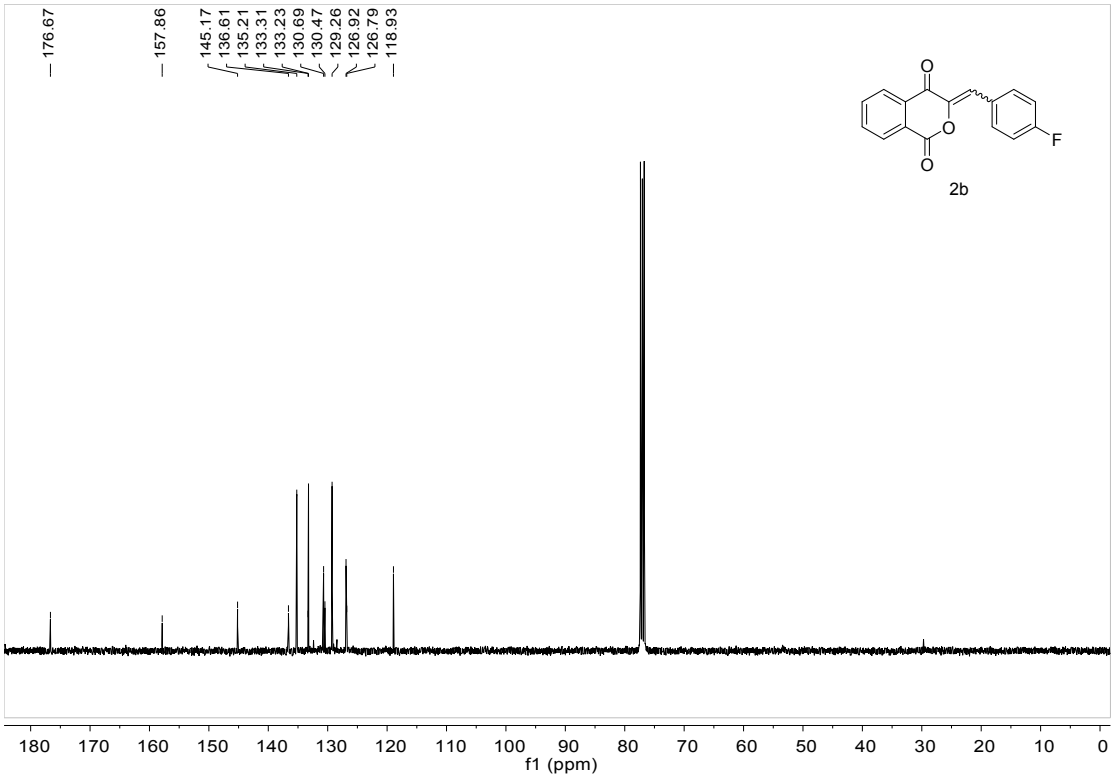
^{13}C NMR of 3-(Phenylmethylene)-1H-2-Benzopyran-1,4(3H)-dione (2a) in $CDCl_3$



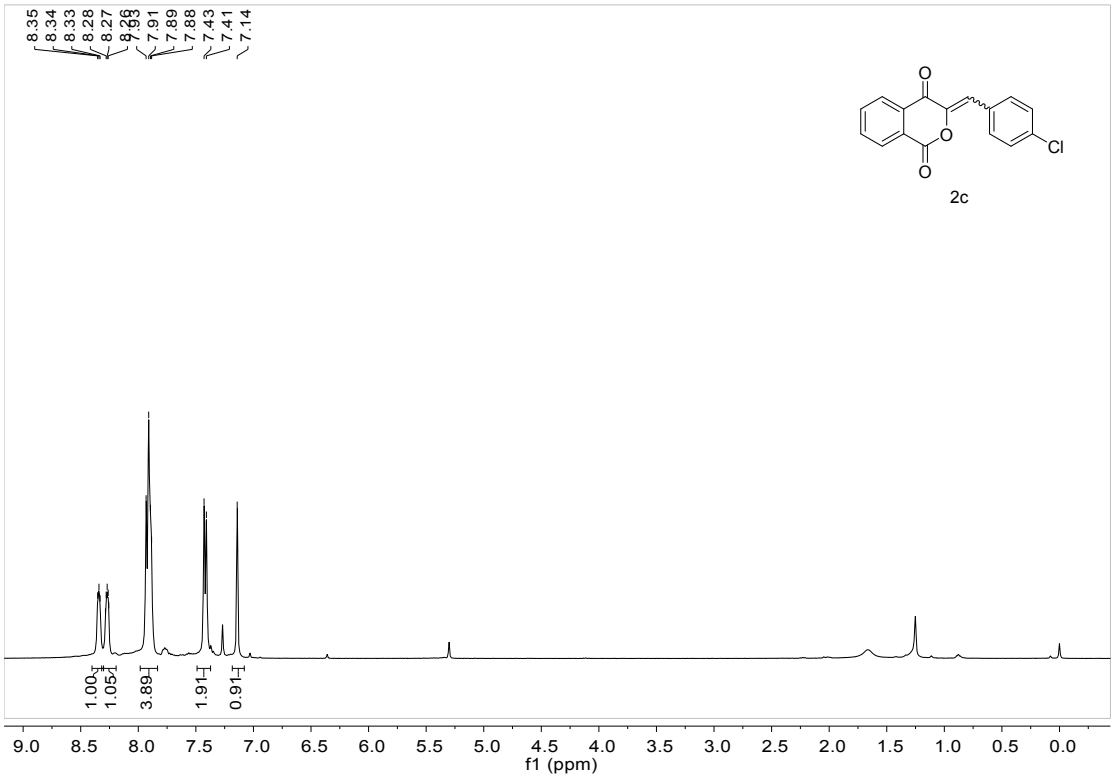
^{1}H NMR of 3-[(4-Fluorophenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2b) in $CDCl_3$



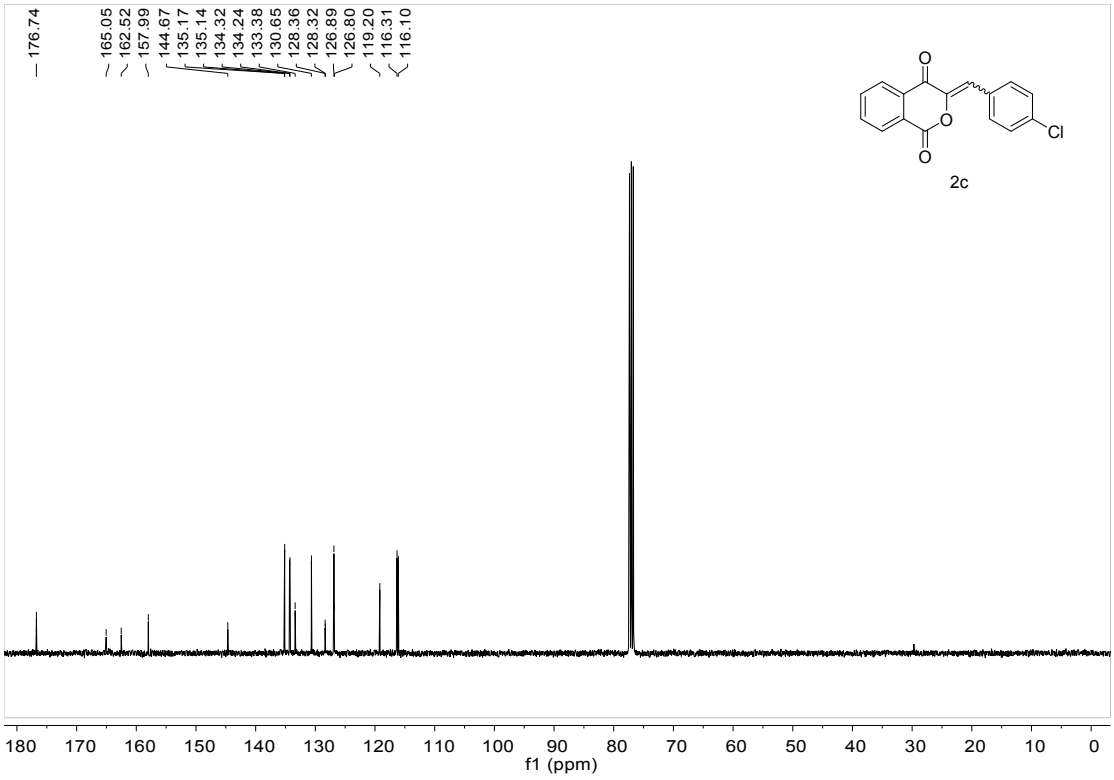
^{13}C NMR of 3-[(4-Fluorophenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2b) in $CDCl_3$



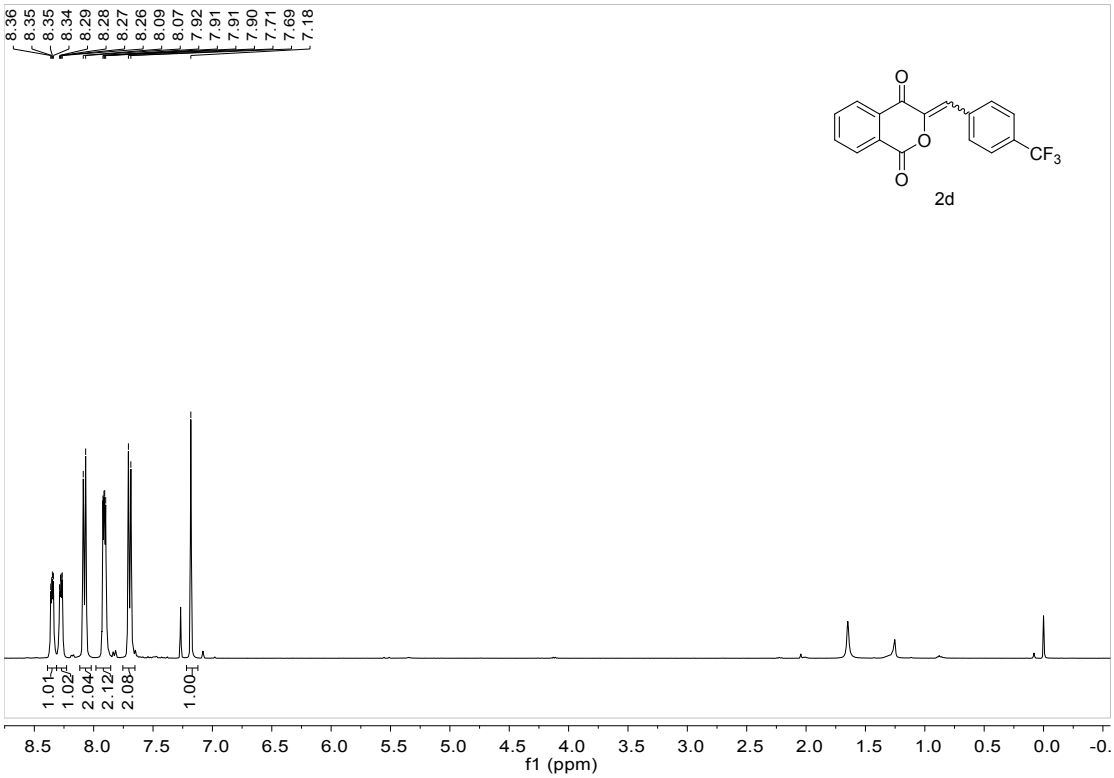
^{1}H NMR of 3-[(4-Chlorophenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2c) in $CDCl_3$



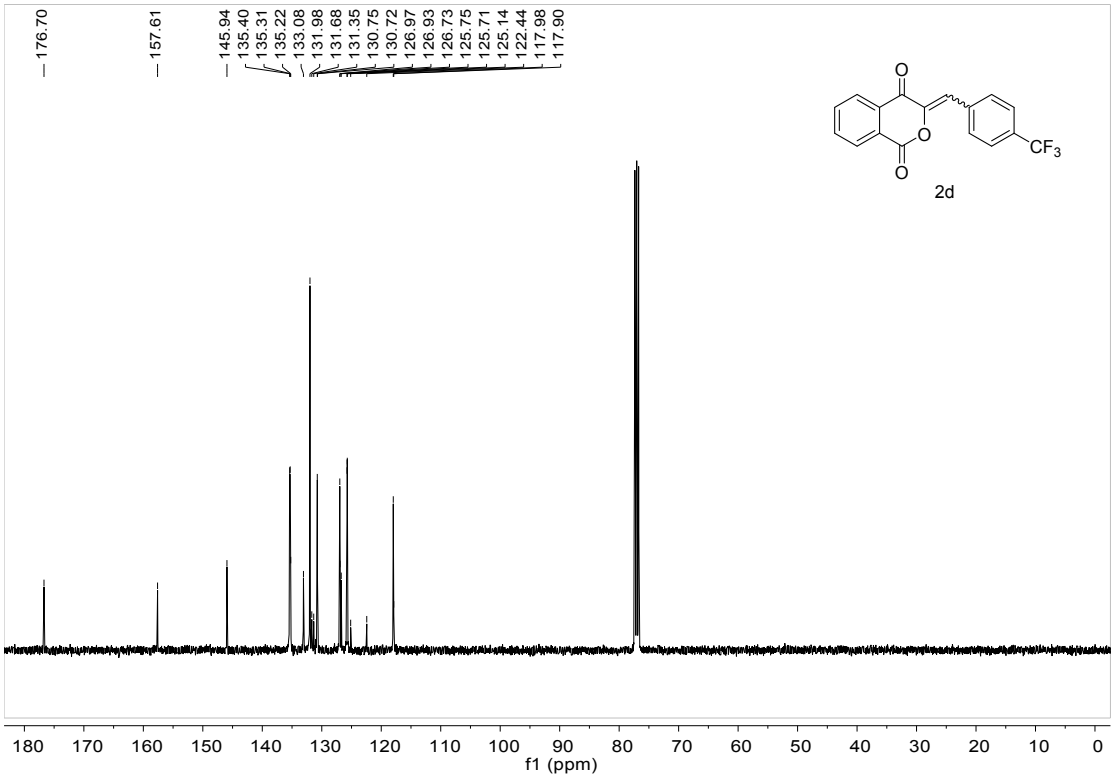
^{13}C NMR of 3-[(4-Chlorophenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2c) in $CDCl_3$



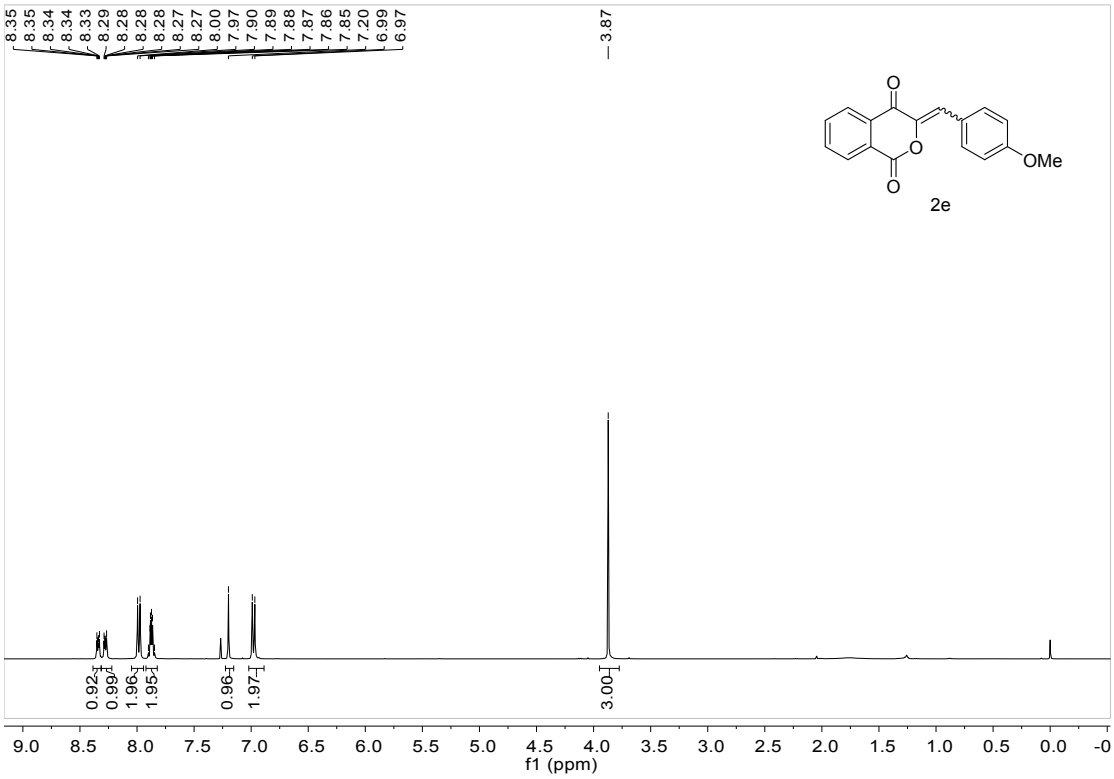
^{1}H NMR of 3-[(4-trifluoromethylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2d) in $CDCl_3$



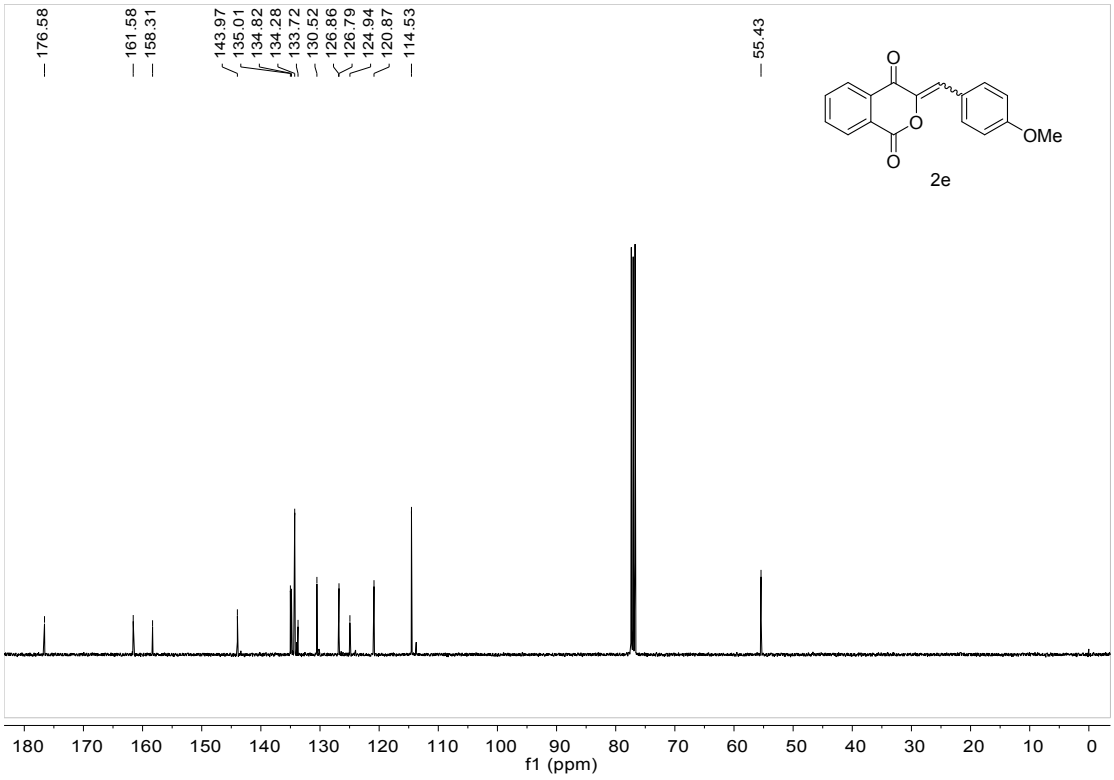
^{13}C NMR of 3-[(4-trifluoromethylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2d) in $CDCl_3$



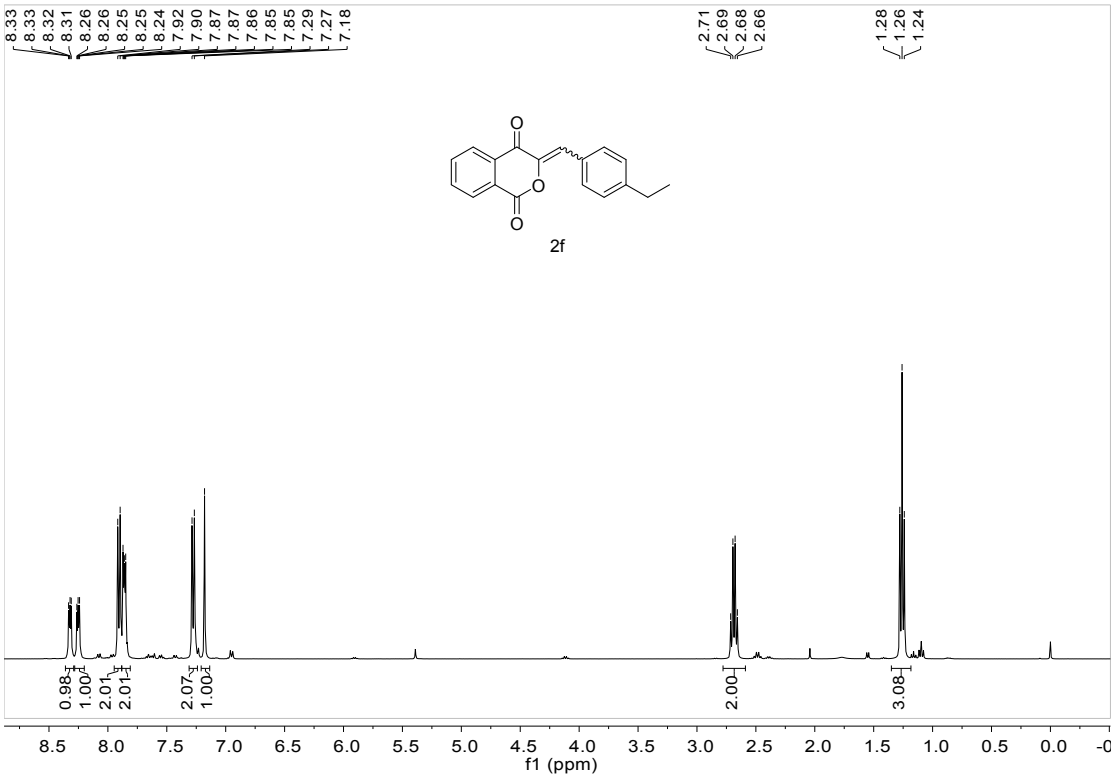
^{1}H NMR of 3-[(4-Methoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2e) in $CDCl_3$



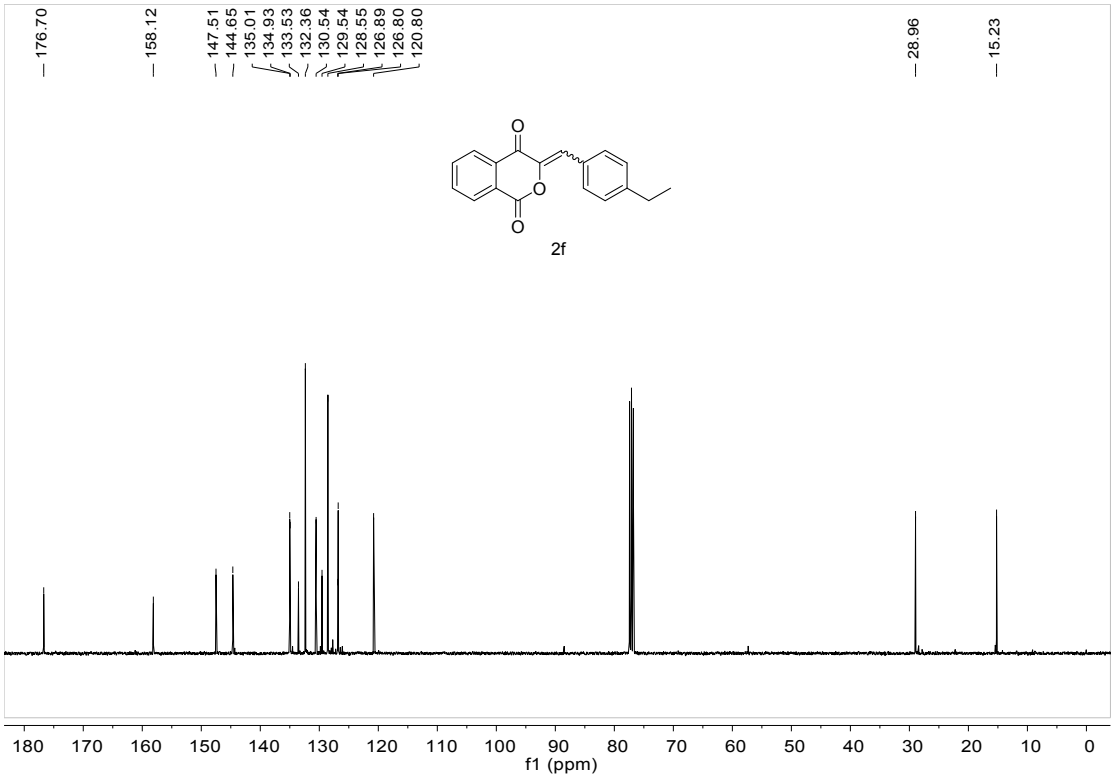
^{13}C NMR of 3-[(4-Methoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2e) in $CDCl_3$



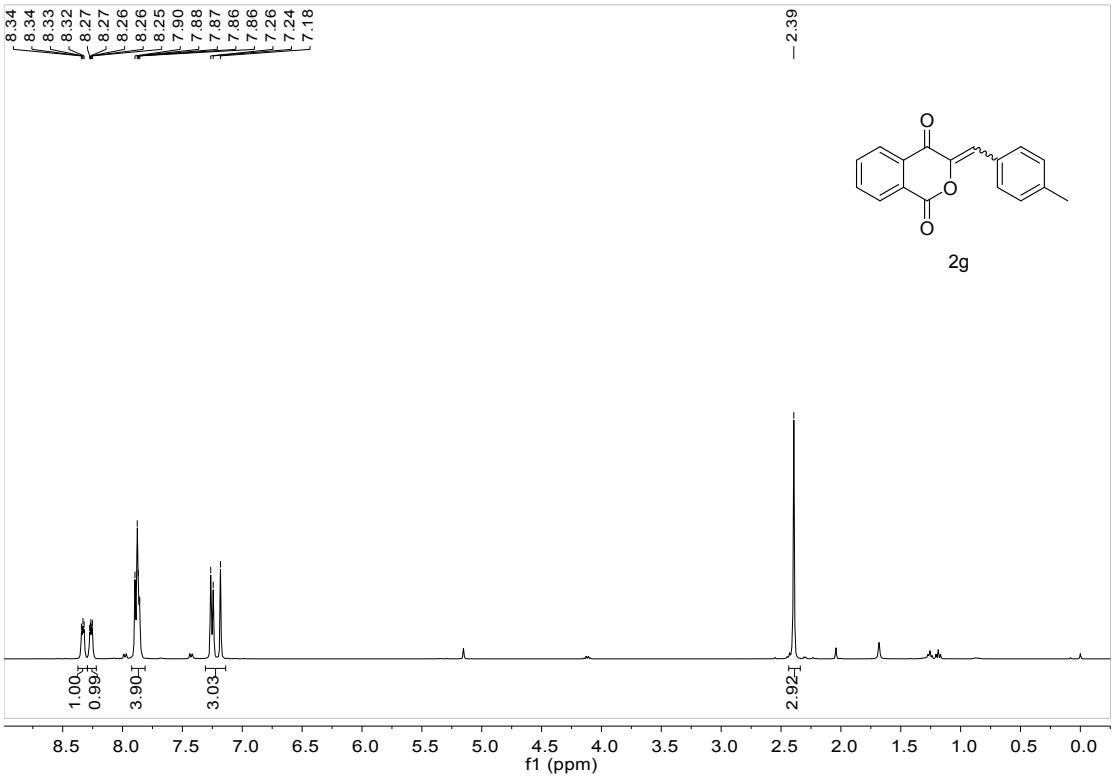
^{1}H NMR of 3-[(4-Ethylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2f) in $CDCl_3$



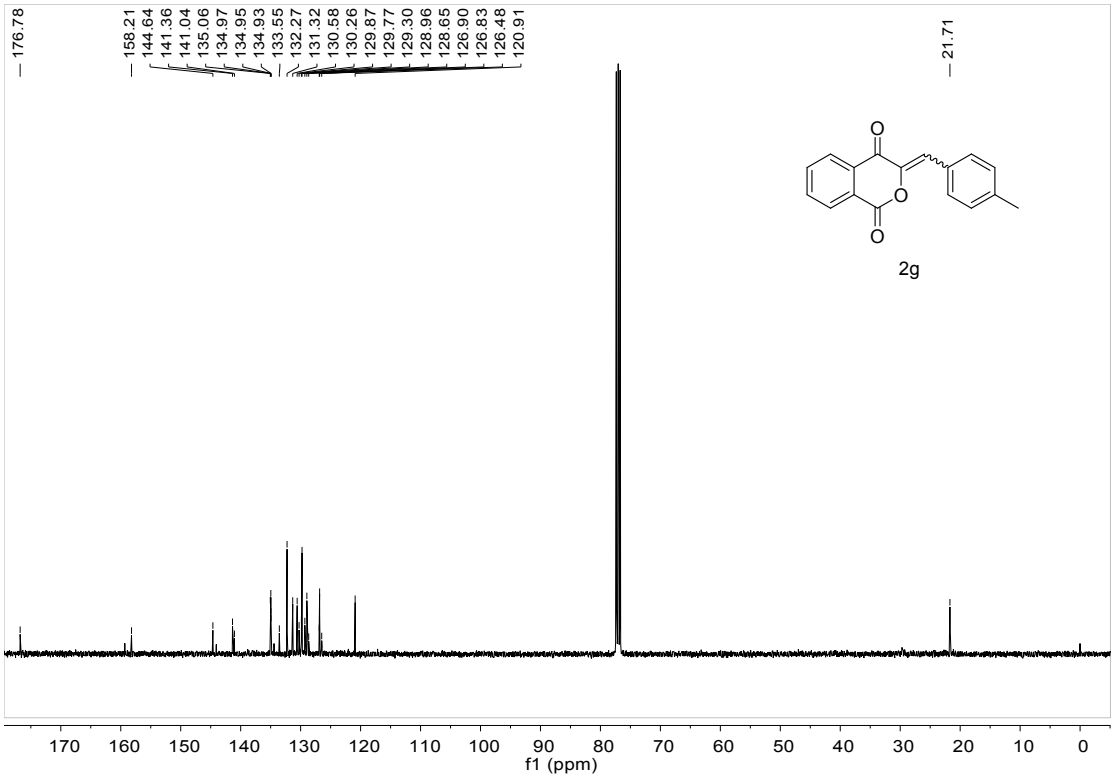
^{13}C NMR of 3-[(4-Ethylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2f) in $CDCl_3$



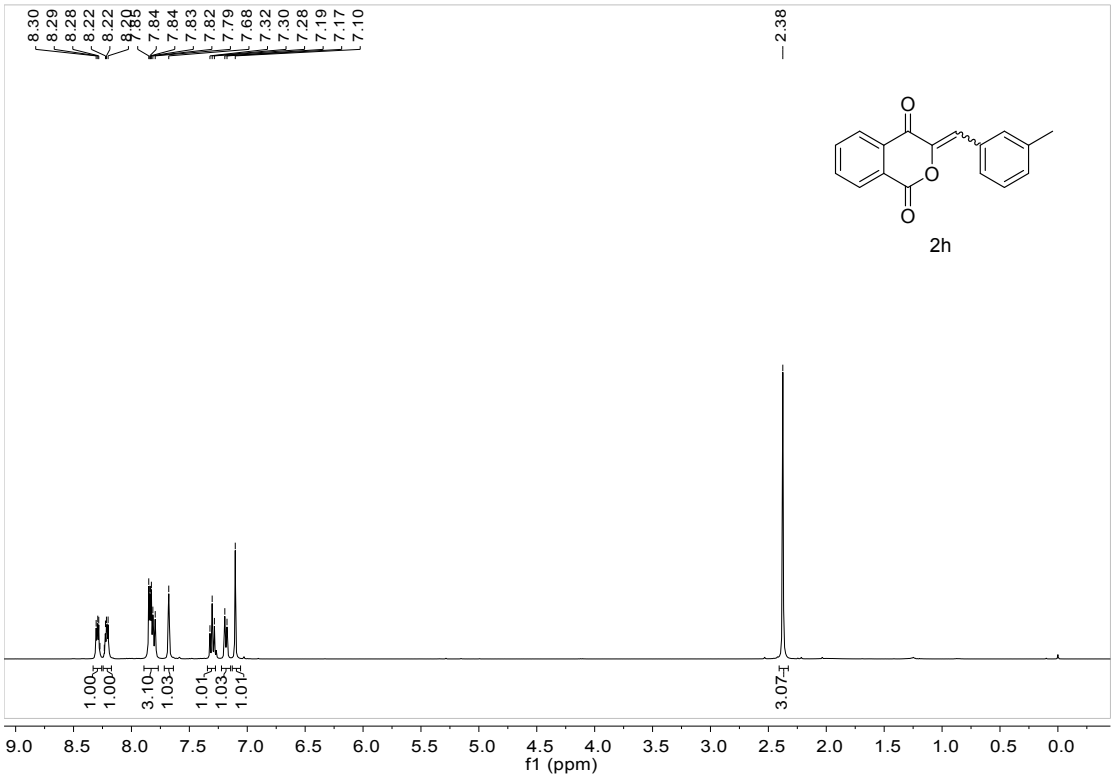
^{1}H NMR of 3-[(4-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2g) in $CDCl_3$



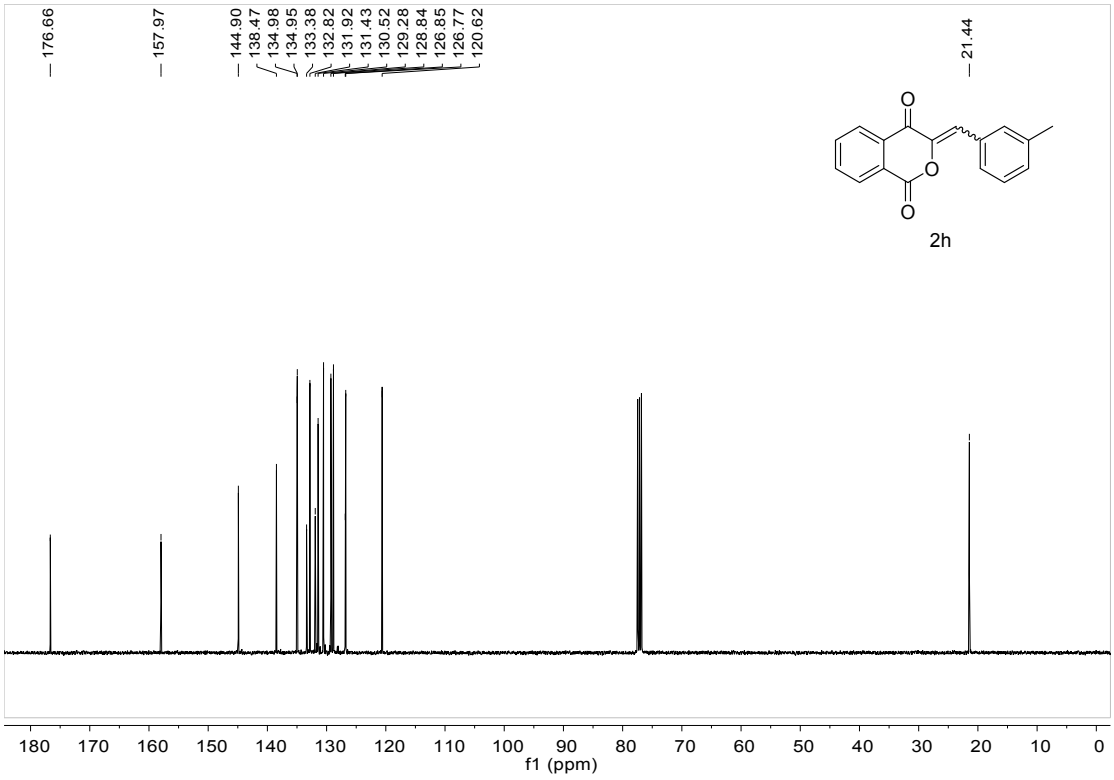
^{13}C NMR of 3-[(4-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2g) in $CDCl_3$



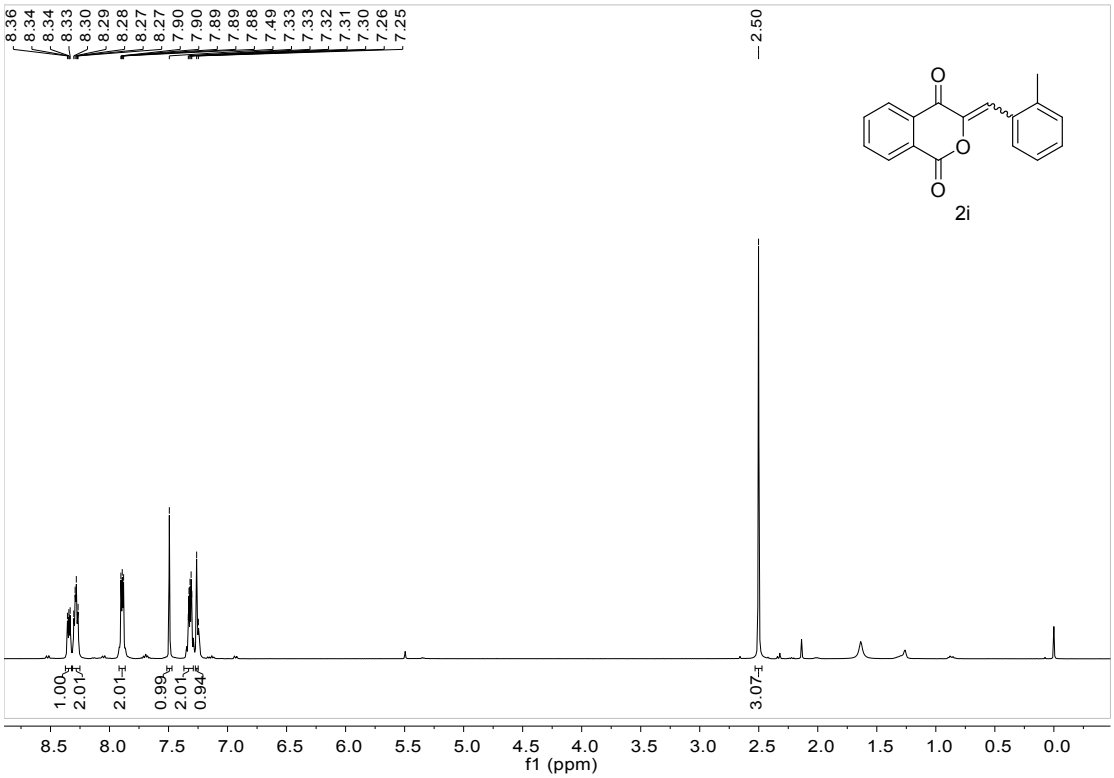
^{1}H NMR of 3-[(3-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2h) in $CDCl_3$



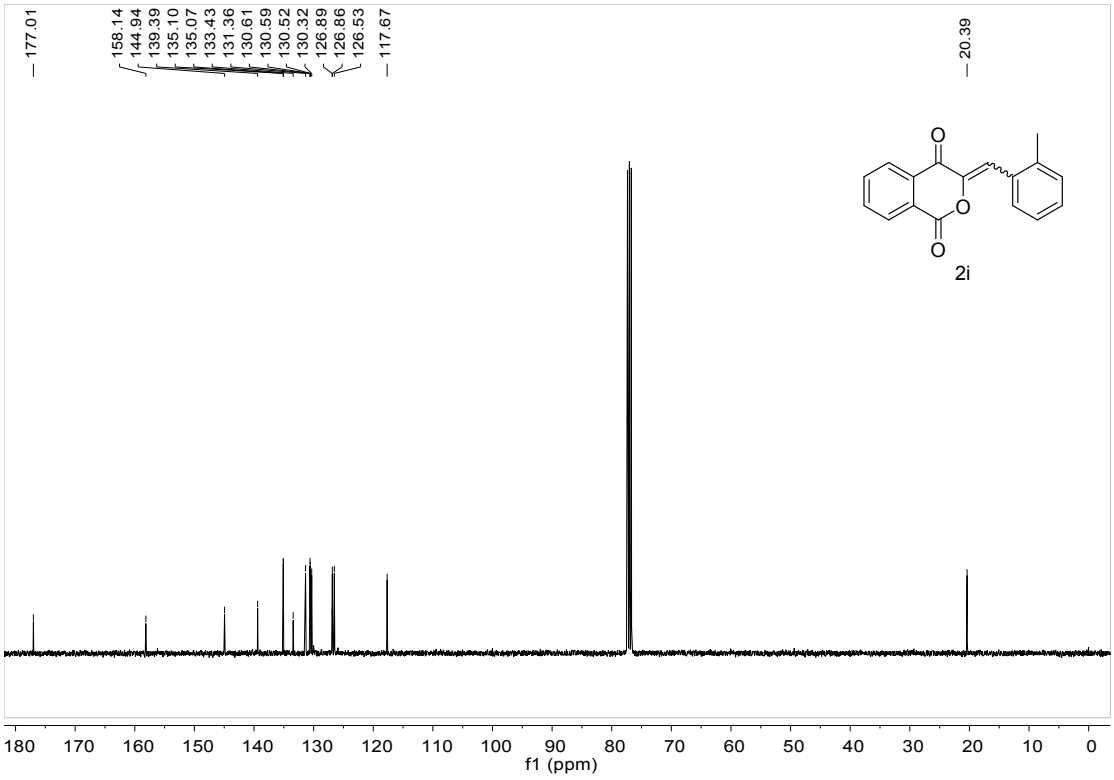
^{13}C NMR of 3-[(3-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2h) in $CDCl_3$



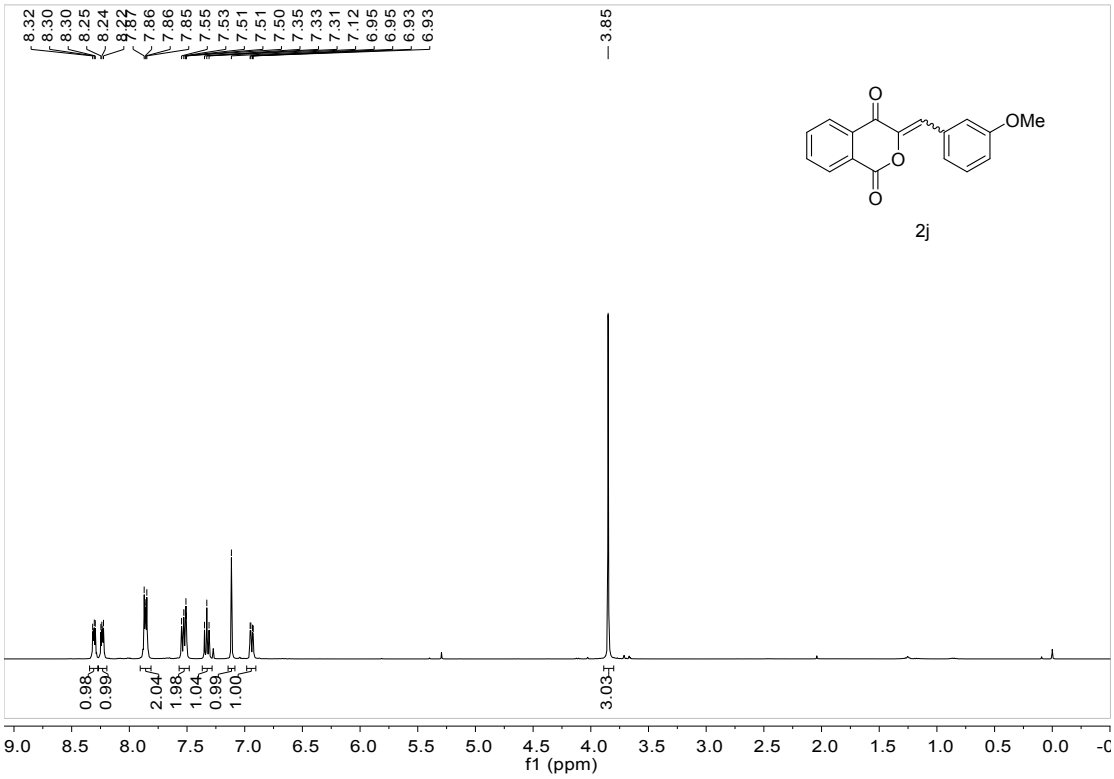
^{1}H NMR of 3-[(2-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2i) in $CDCl_3$



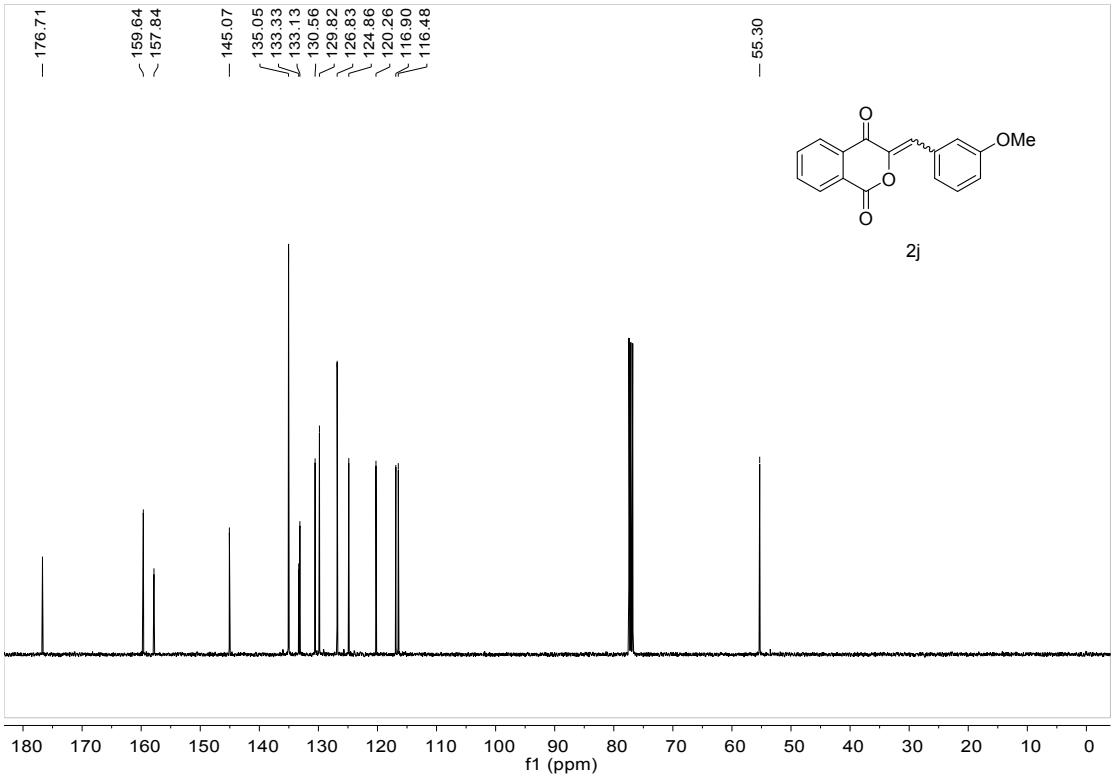
^{13}C NMR of 3-[(2-Methylphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2i) in $CDCl_3$



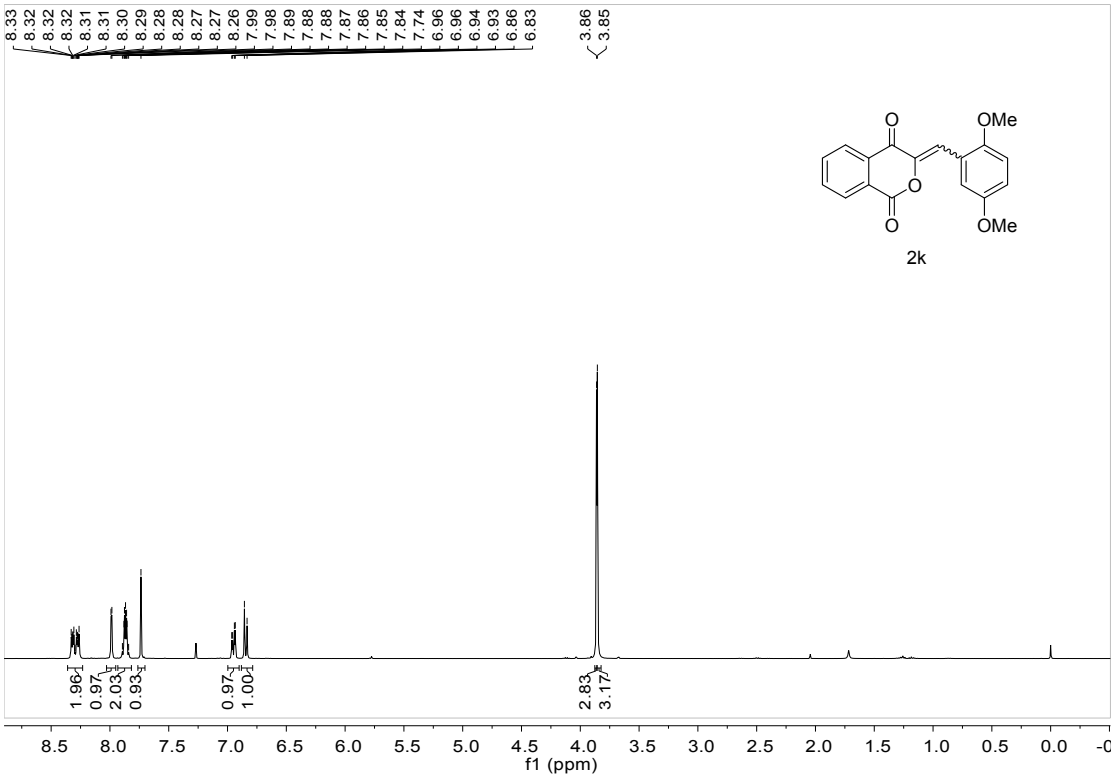
^{1}H NMR of 3-[(3-Methoxyphenyl)methylene]-1*H*-2-benzopyran-1,4(3*H*)-dione (2j) in $CDCl_3$



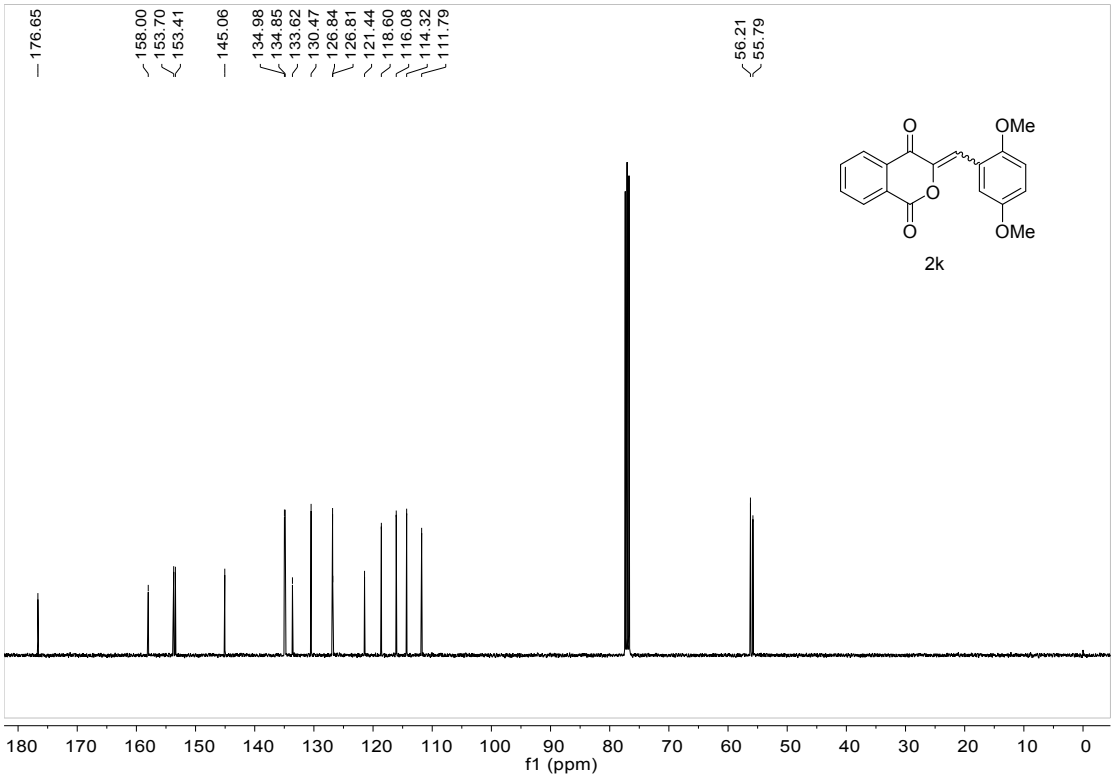
^{13}C NMR of 3-[(3-Methoxyphenyl)methylene]-1*H*-2-benzopyran-1,4(3*H*)-dione (2j) in $CDCl_3$



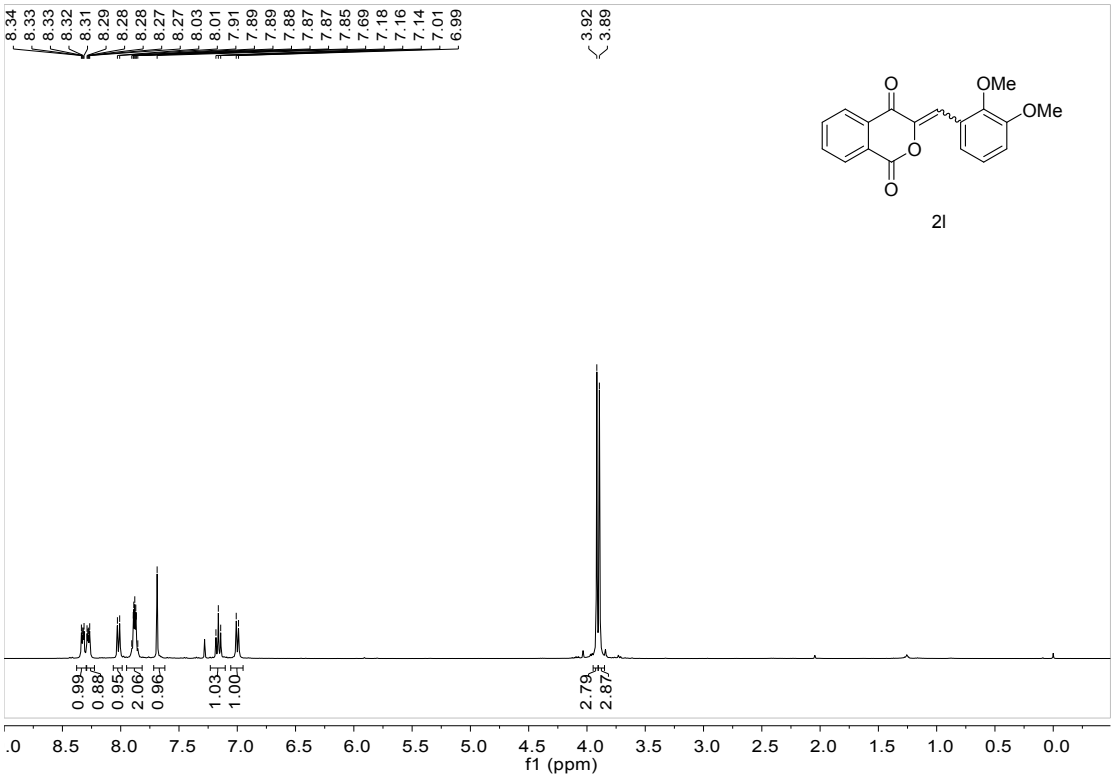
^{1}H NMR of 3-[(2,5-Dimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2k) in $CDCl_3$



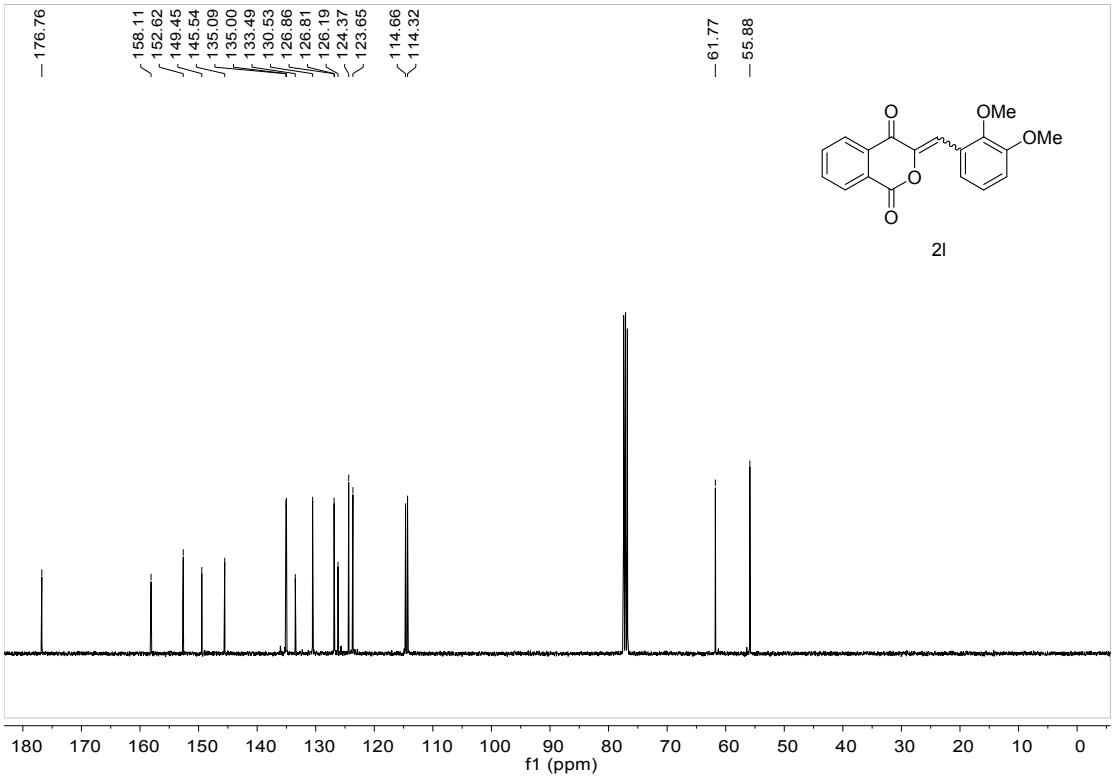
^{13}C NMR of 3-[(2,5-Dimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2k) in $CDCl_3$



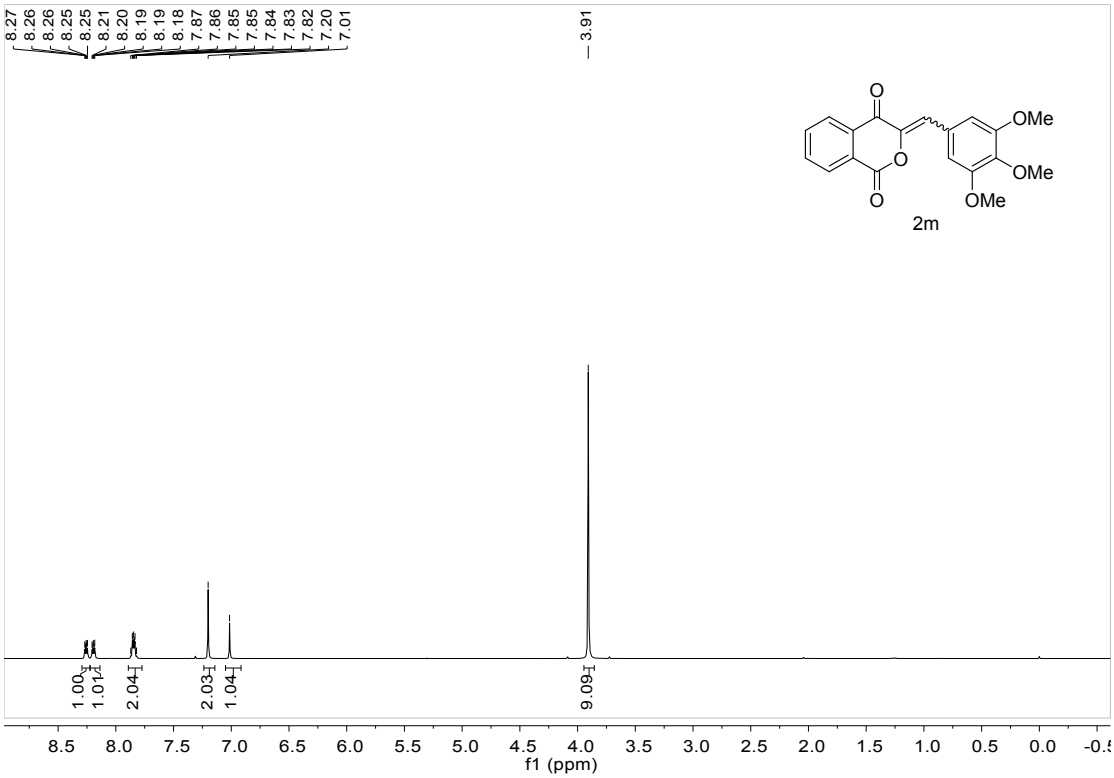
^{1}H NMR of 3-[(2,3-Dimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2l) in $CDCl_3$



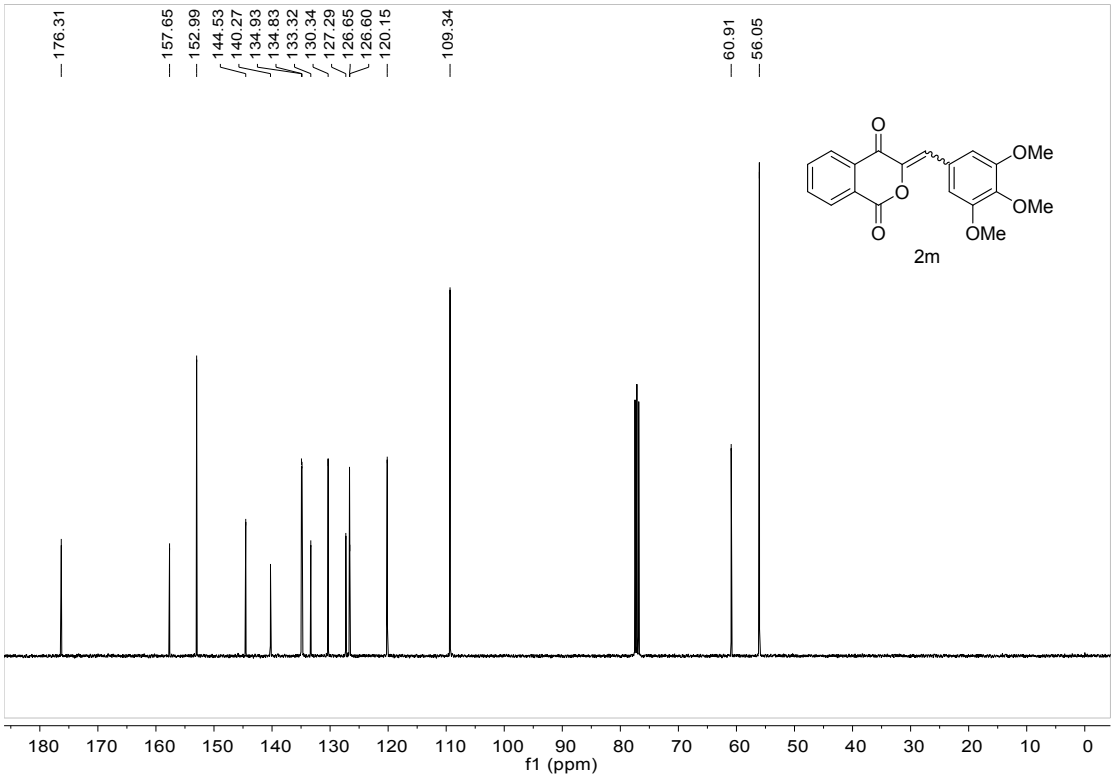
^{13}C NMR of 3-[(2,3-Dimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2l) in $CDCl_3$



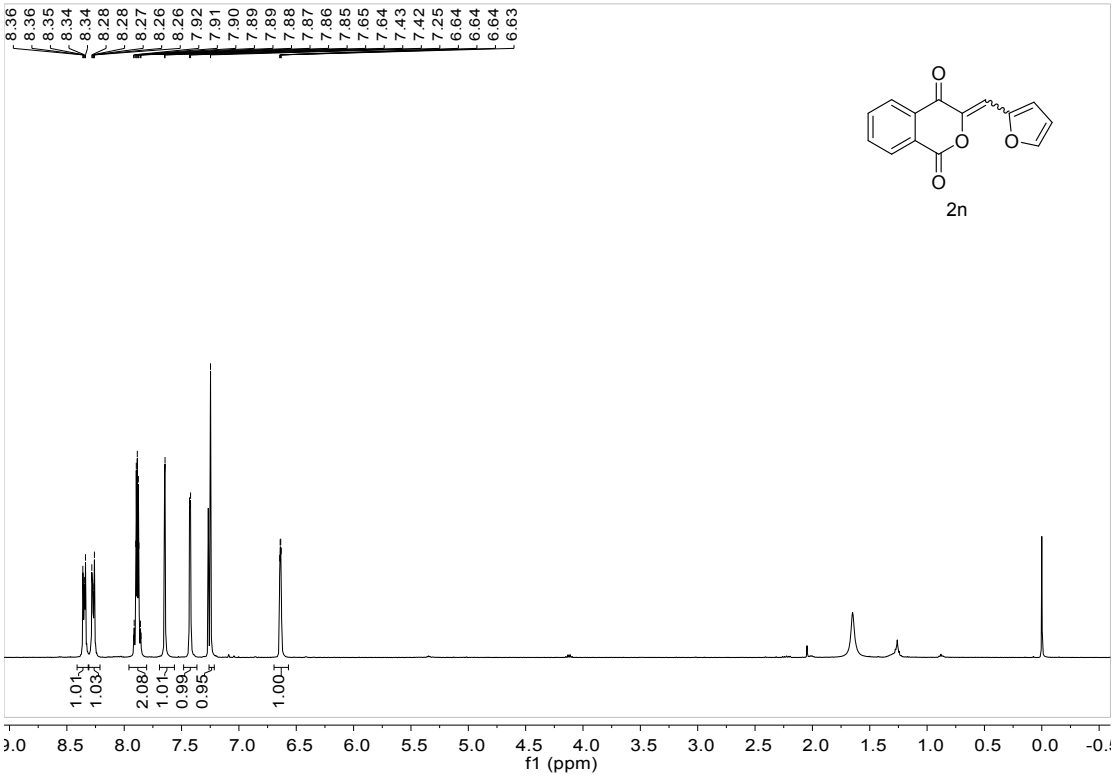
^{1}H NMR of 3-[(3,4,5-Trimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2m) in $CDCl_3$



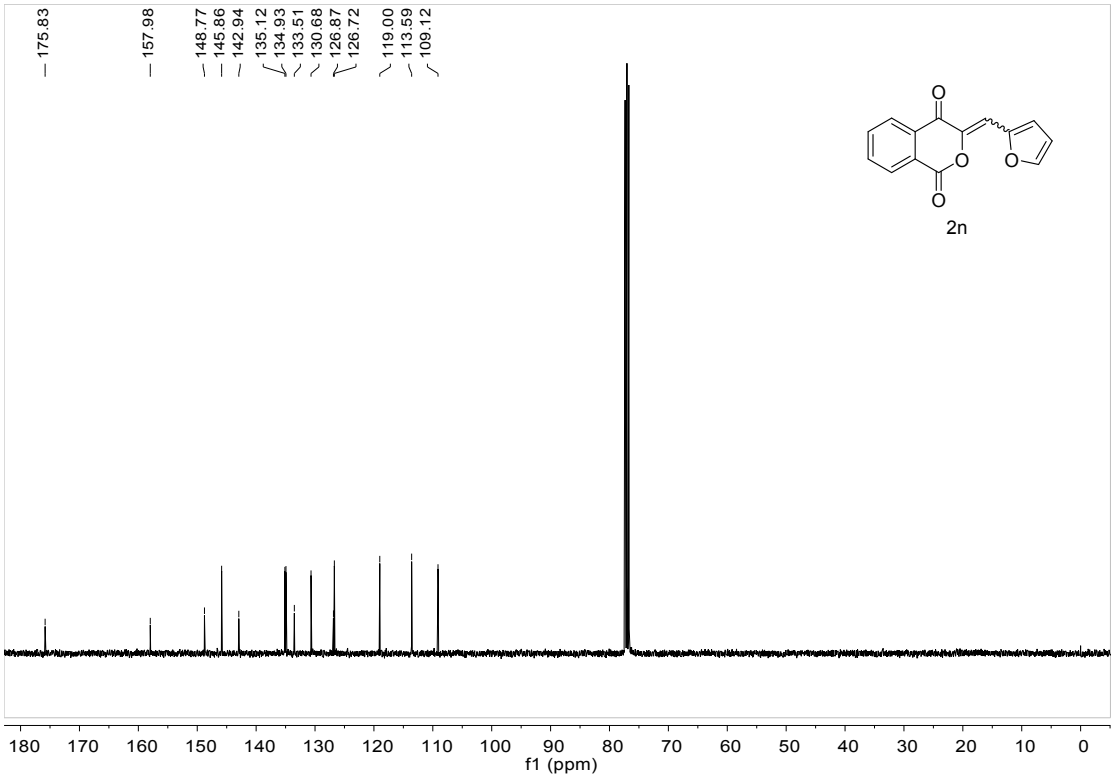
^{13}C NMR of 3-[(3,4,5-Trimethoxyphenyl)methylene]-1H-2-benzopyran-1,4(3H)-dione (2m) in $CDCl_3$



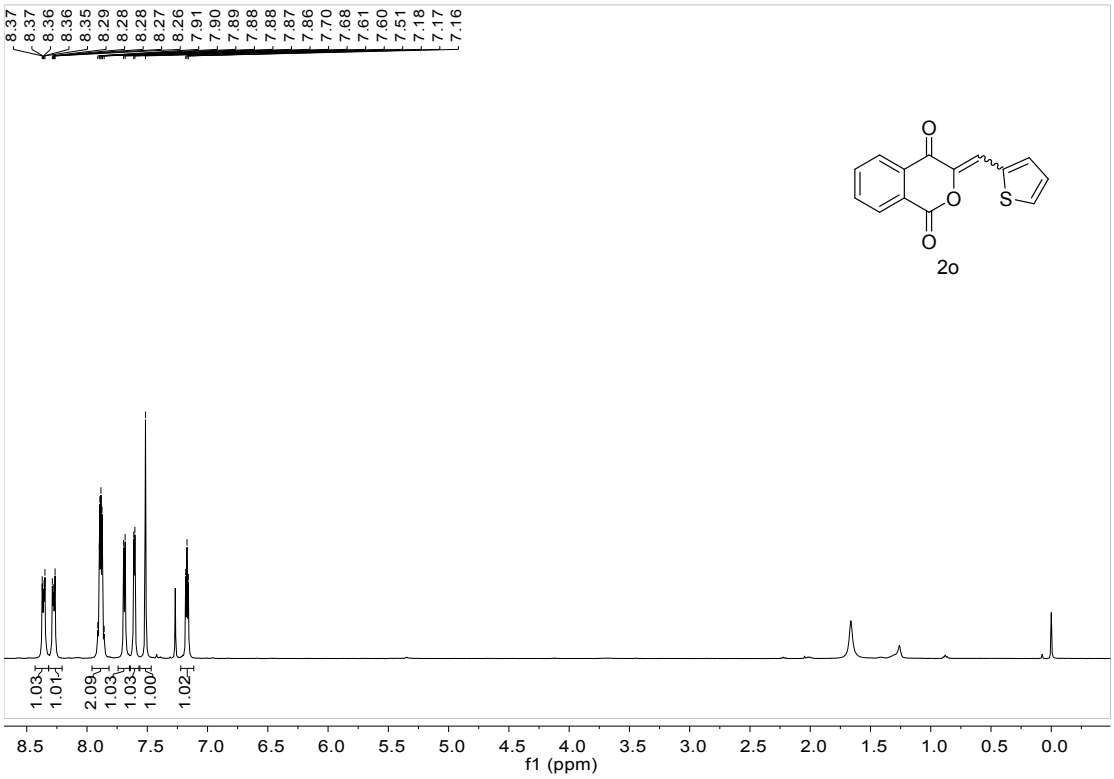
^{1}H NMR of 3-(2-Furanylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2n) in $CDCl_3$



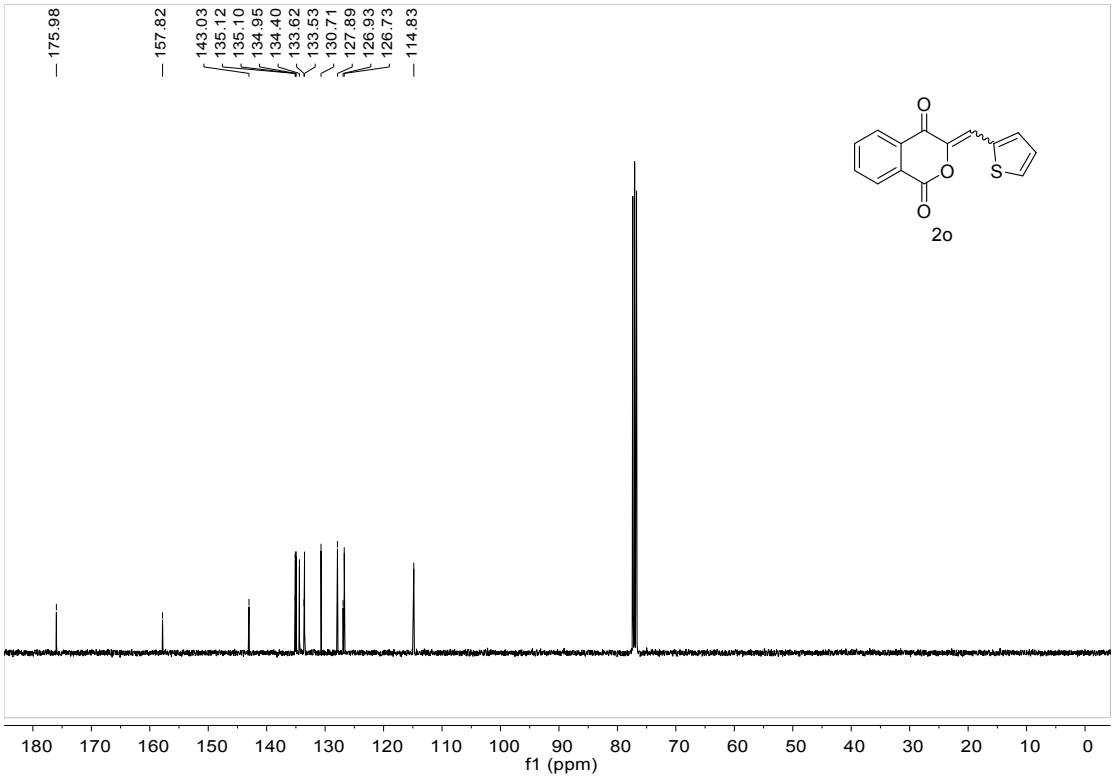
^{13}C NMR of 3-(2-Furanylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2n) in $CDCl_3$



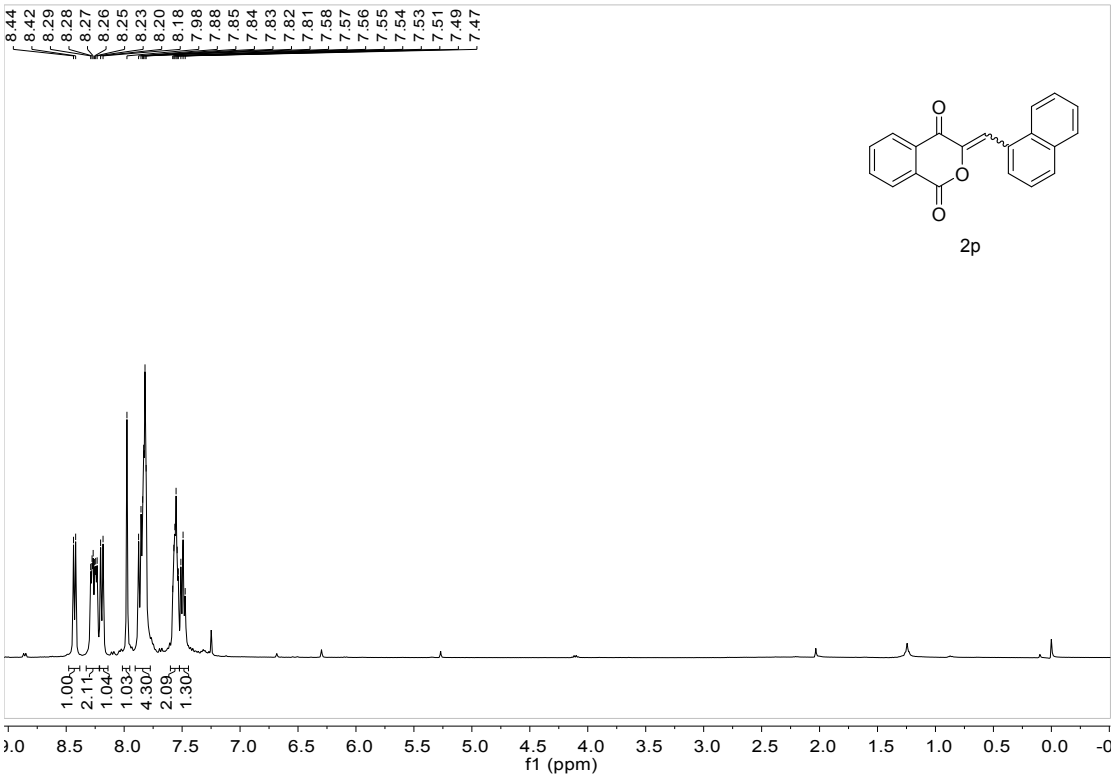
^{1}H NMR of 3-(2-Thienylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2o) in $CDCl_3$



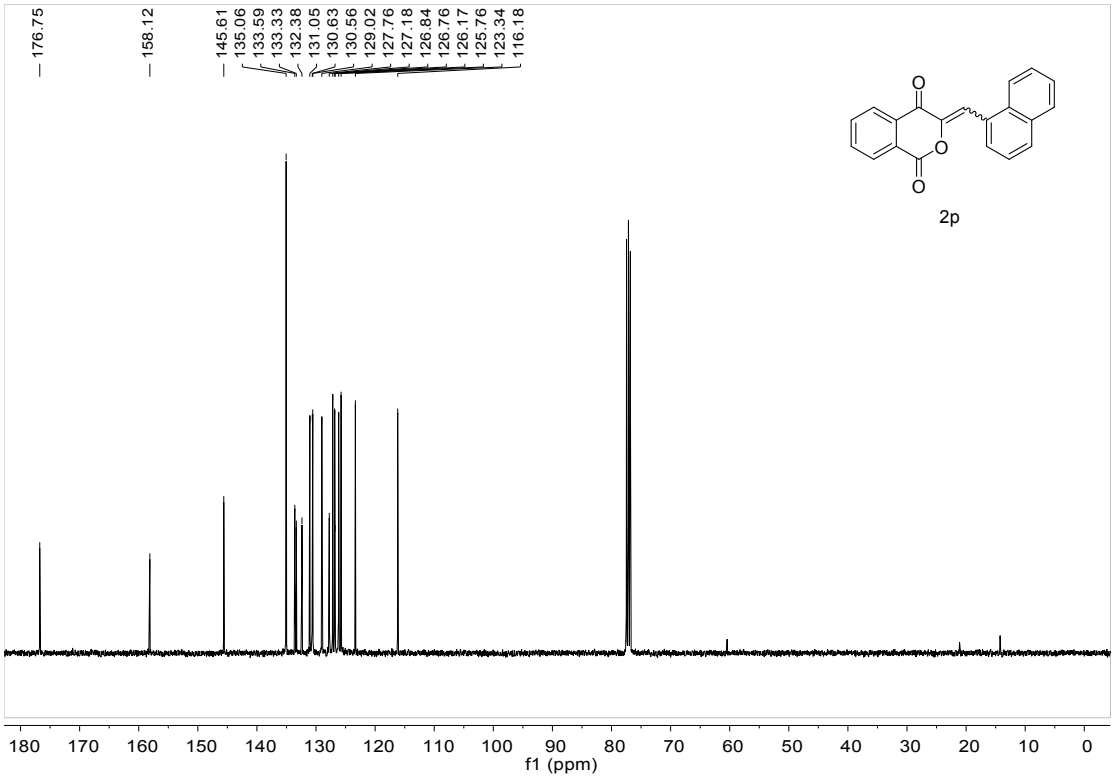
^{13}C NMR of 3-(2-Thienylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2o) in $CDCl_3$



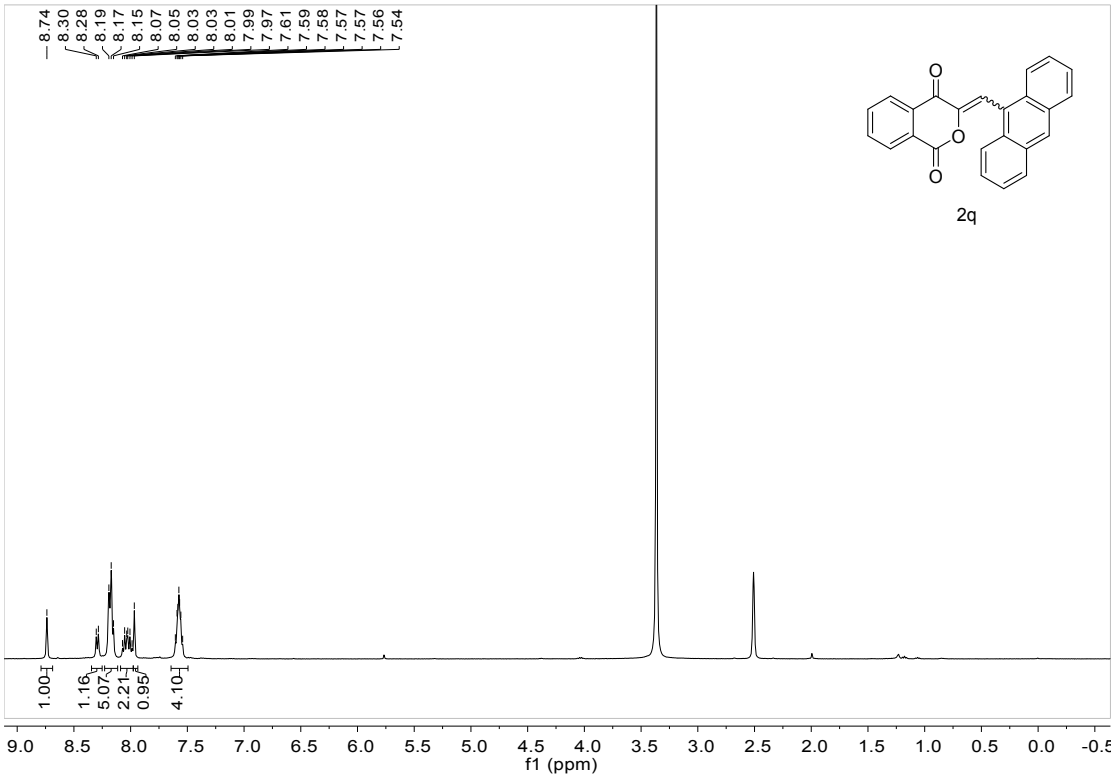
^{1}H NMR of 3-(1-Naphthalenylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2p) in $CDCl_3$



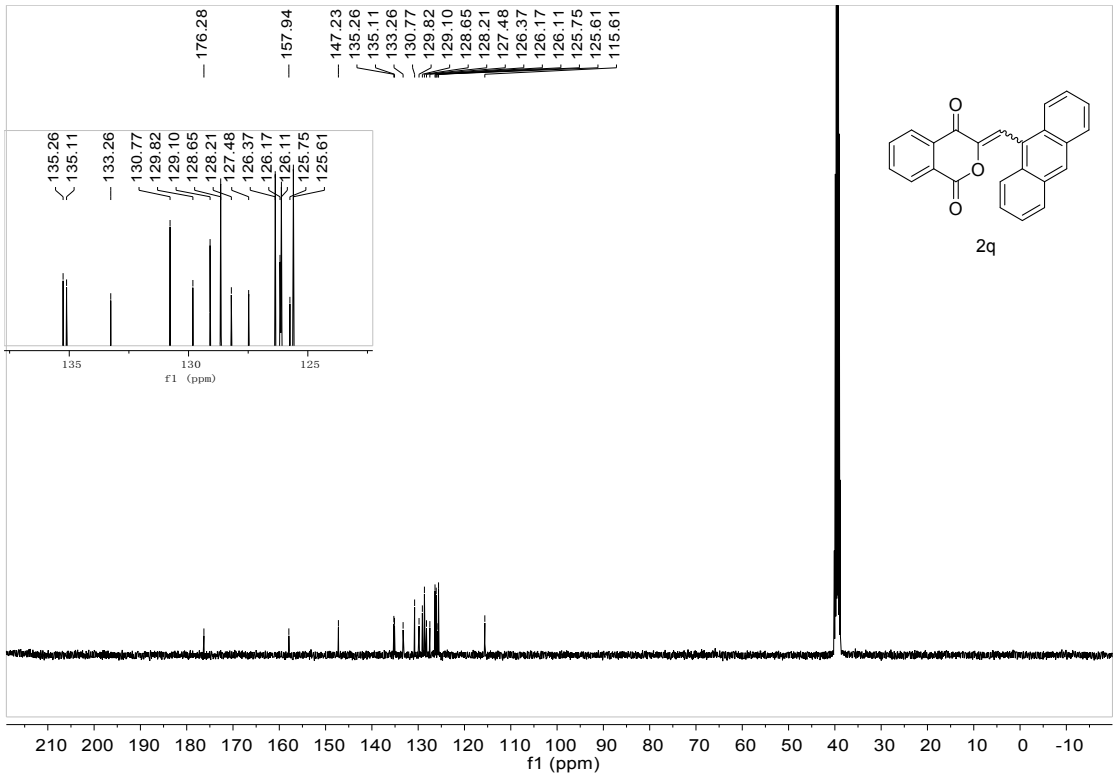
^{13}C NMR of 3-(1-Naphthalenylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2p) in $CDCl_3$



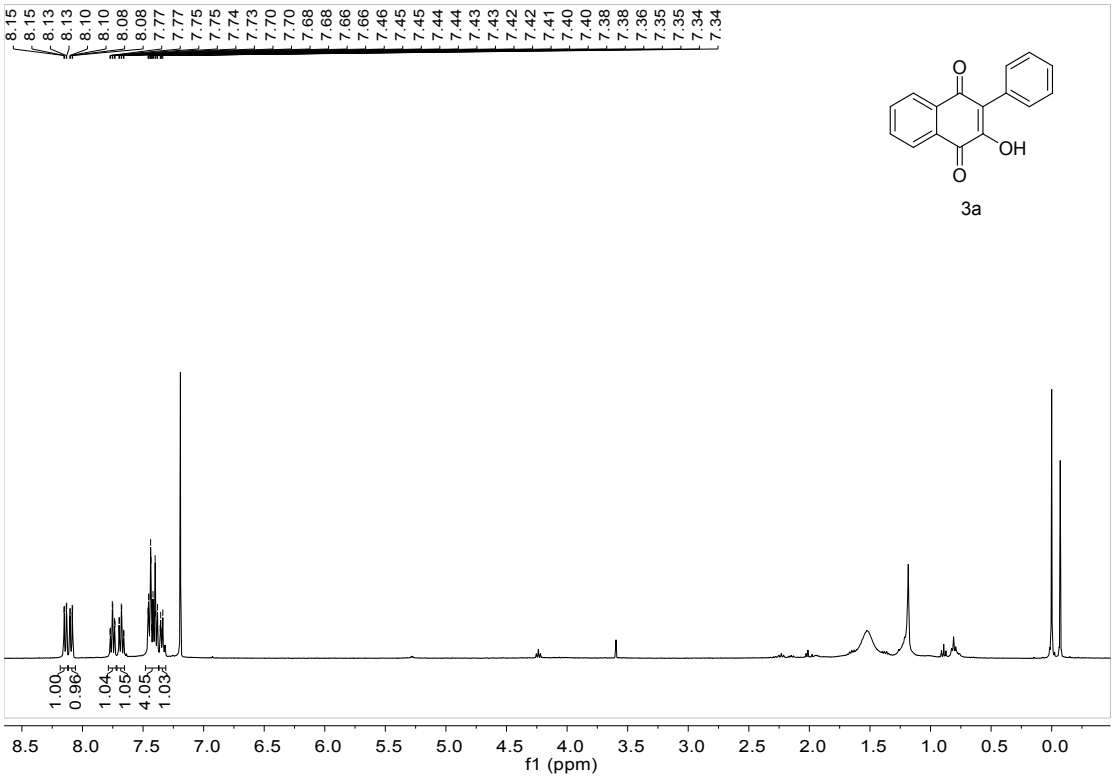
^{1}H NMR of 3-(9-Anthracenylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2q) in $CDCl_3$



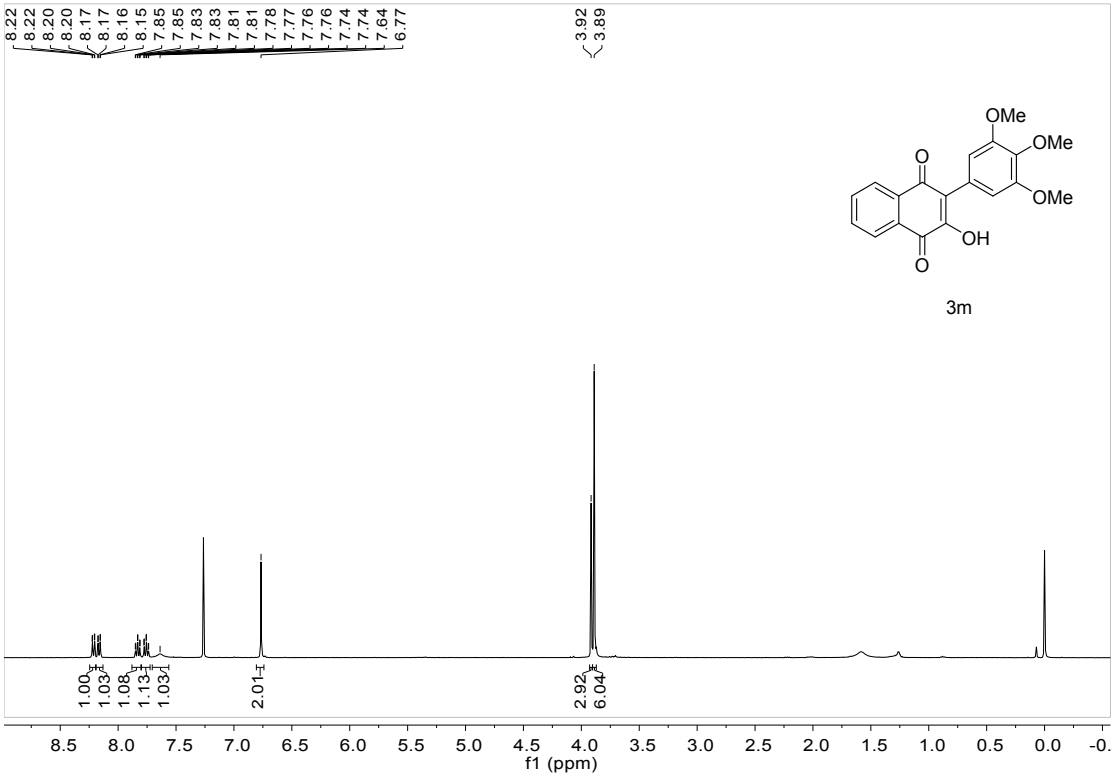
^{13}C NMR of 3-(9-Anthracenylmethylene)-1H-2-benzopyran-1,4(3H)-dione (2q) in $CDCl_3$



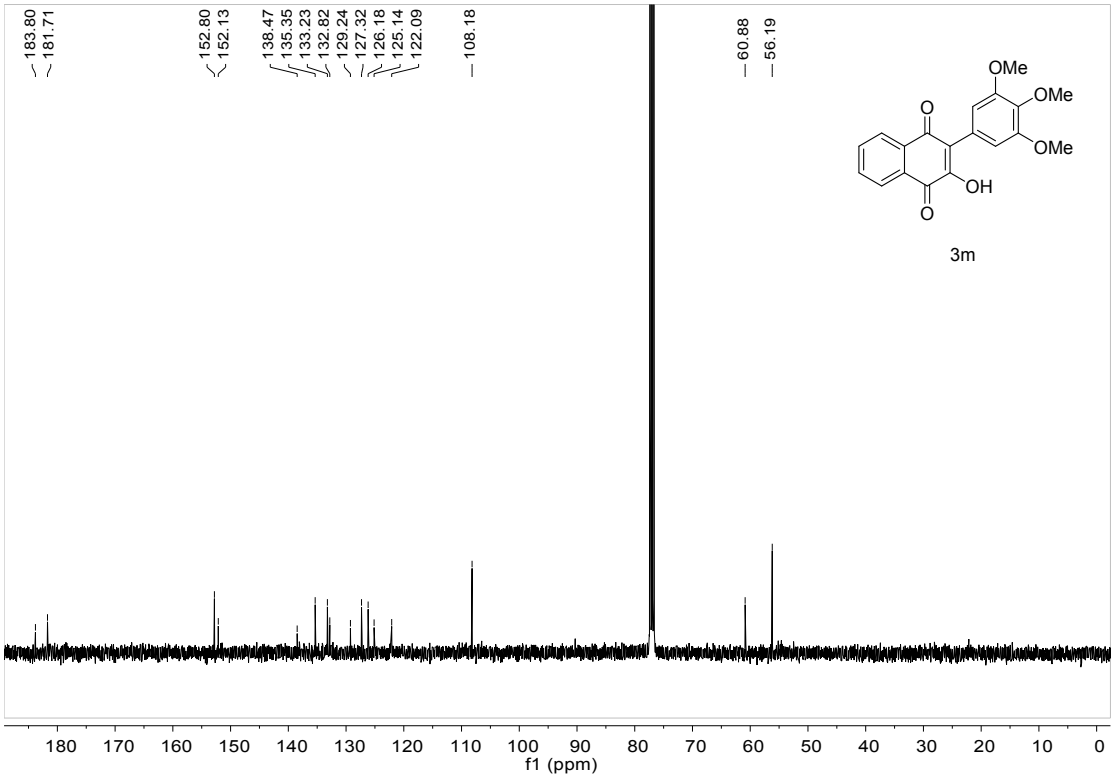
^{1}H NMR of 2-Hydroxy-3-phenyl-1,4-naphthalenedione (3a) in $CDCl_3$



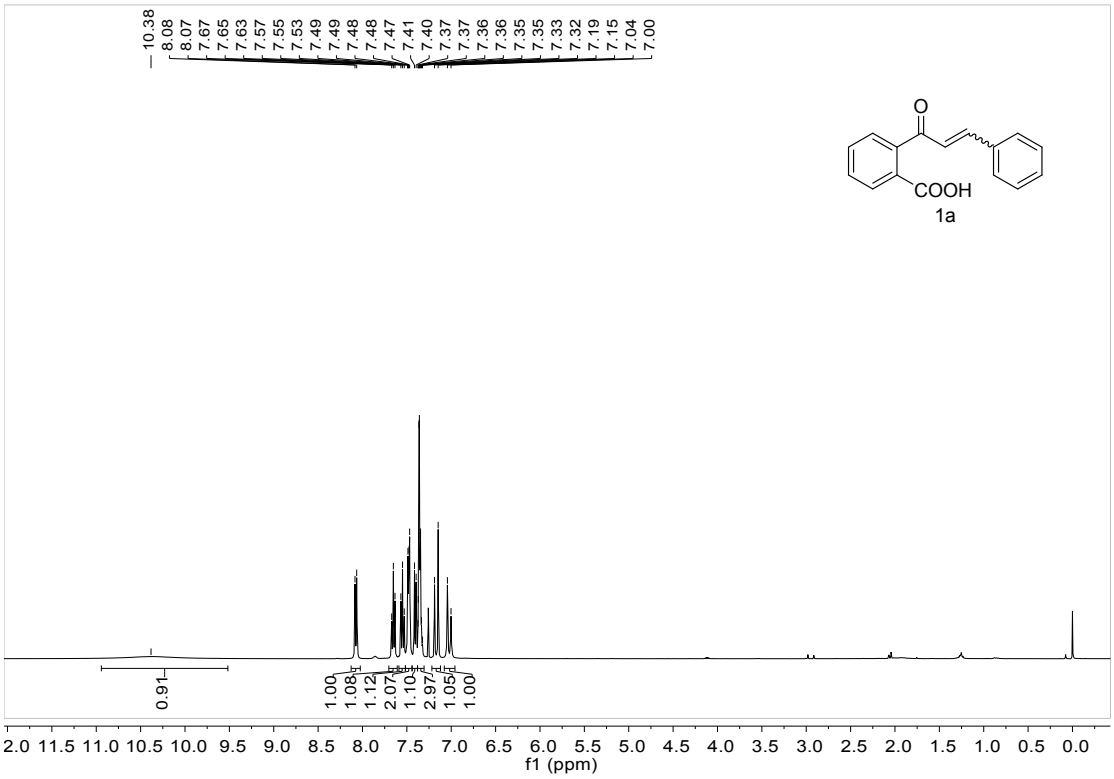
^{1}H NMR of 2-Hydroxy-3-(3,4,5-trimethoxyphenyl)-1,4-naphthalenedione (3m) in $CDCl_3$



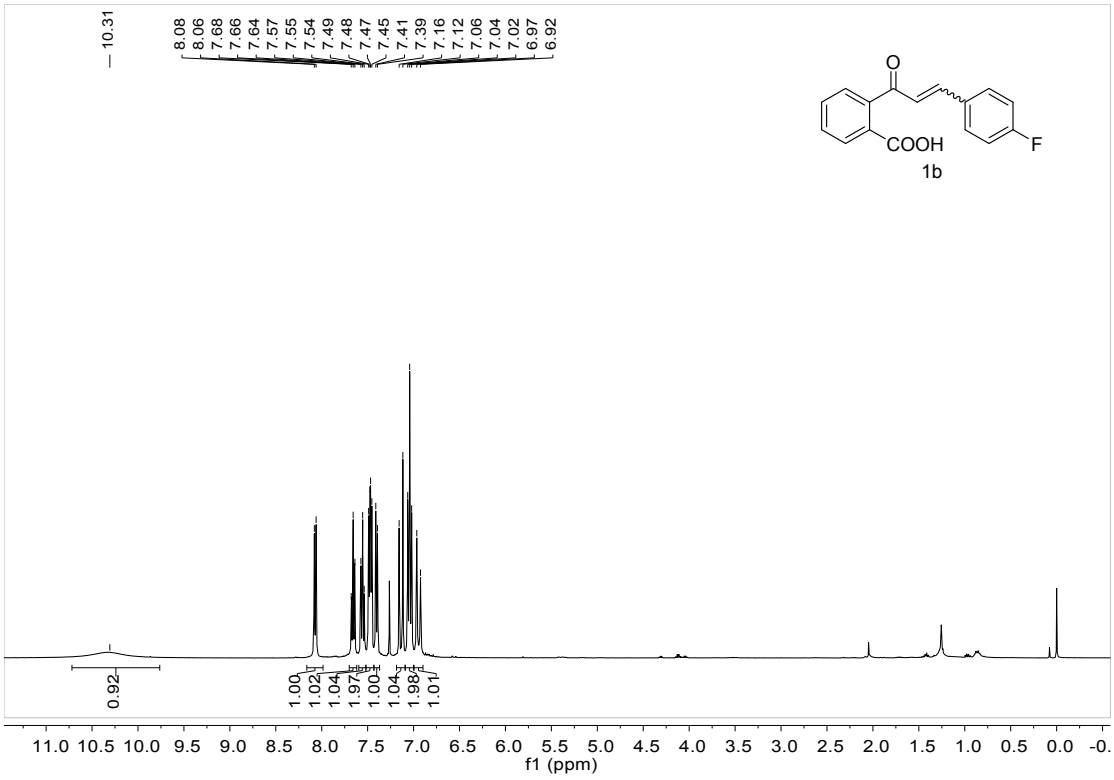
^{13}C NMR of 2-Hydroxy-3-(3,4,5-trimethoxyphenyl)-1,4-naphthalenedione (3m) in $CDCl_3$



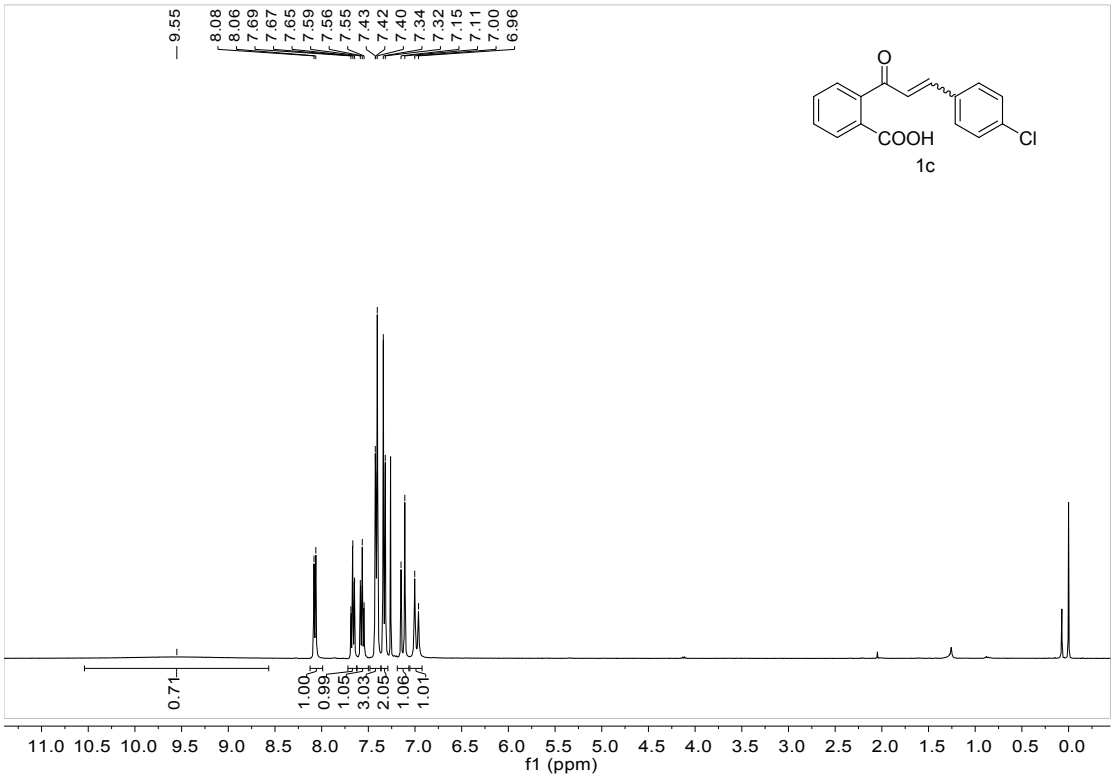
^{1}H NMR of 2-(3-Phenyl-1-oxo-2-propen-1-yl)-benzoic acid (1a) in $CDCl_3$



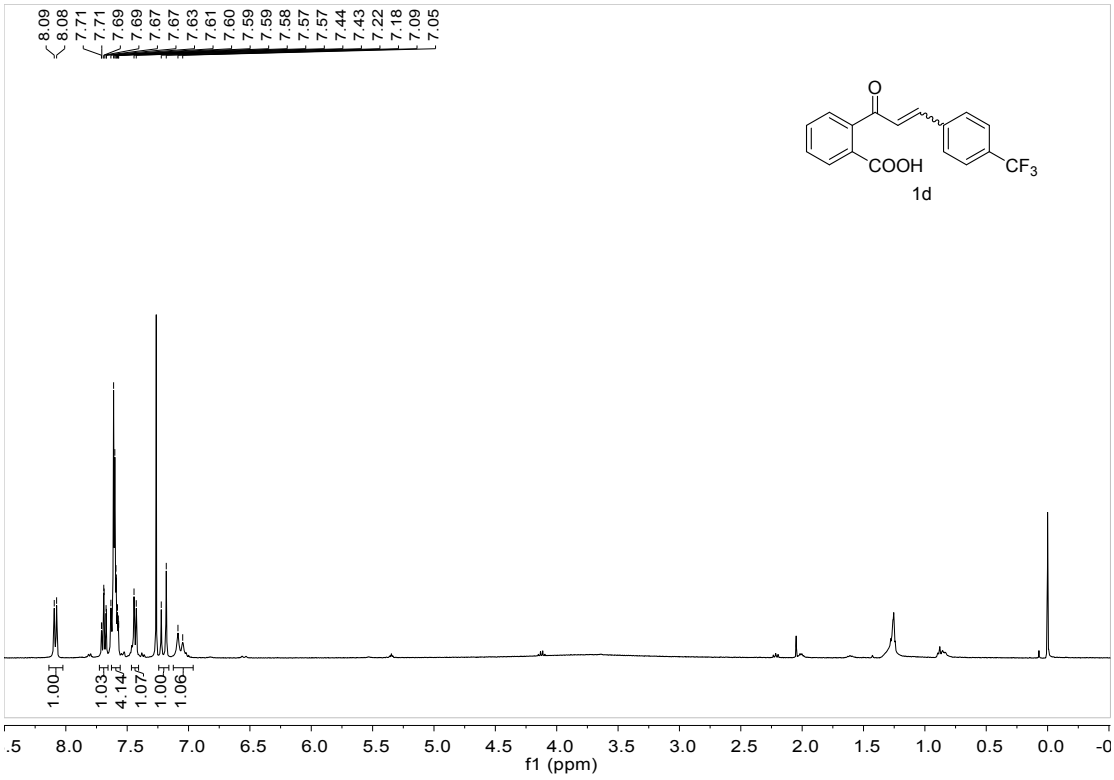
^{1}H NMR of 2-[3-(4-Fluorophenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1b) in $CDCl_3$



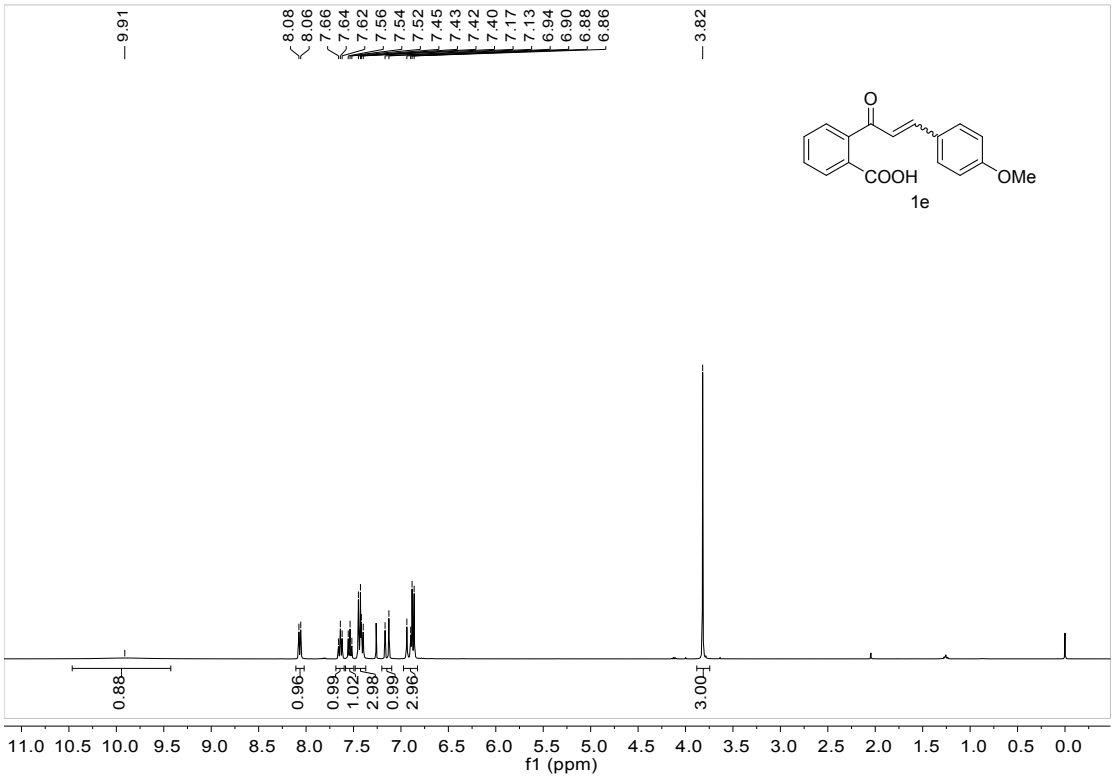
^{1}H NMR of 2-[3-(4-Chlorophenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1c) in $CDCl_3$



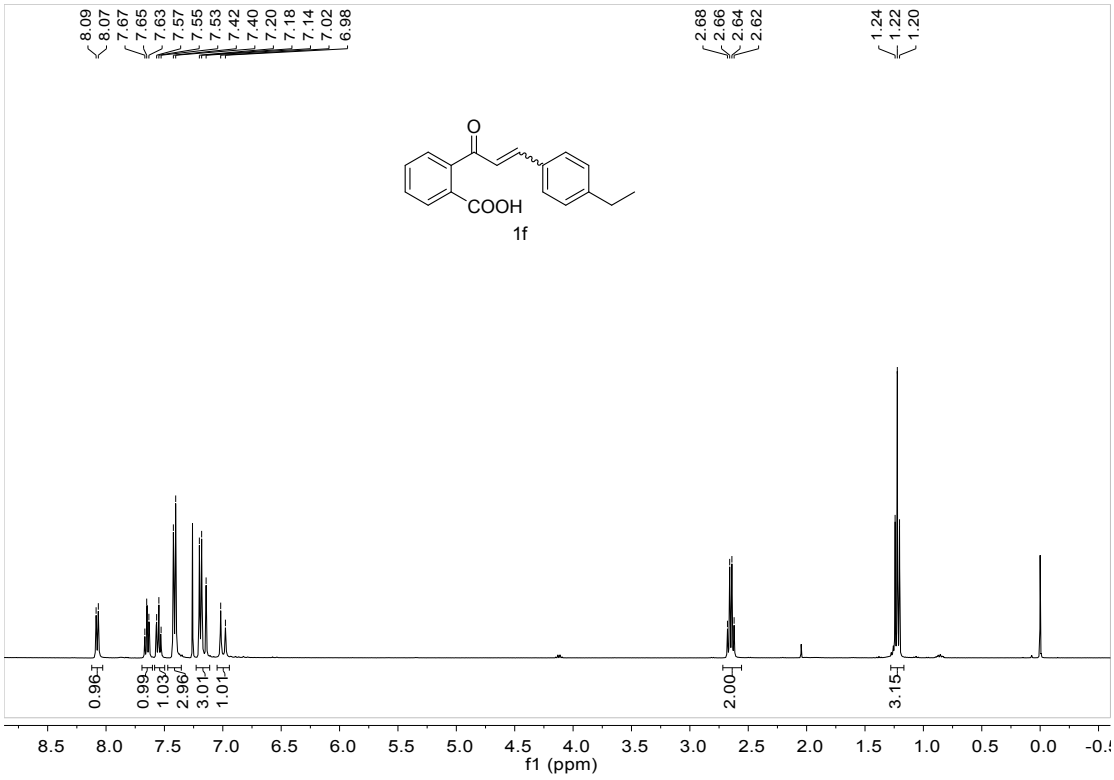
^{1}H NMR of 2-[3-[4-(Trifluoromethyl)phenyl]-1-oxo-2-propen-1-yl]-benzoic acid (1d) in $CDCl_3$



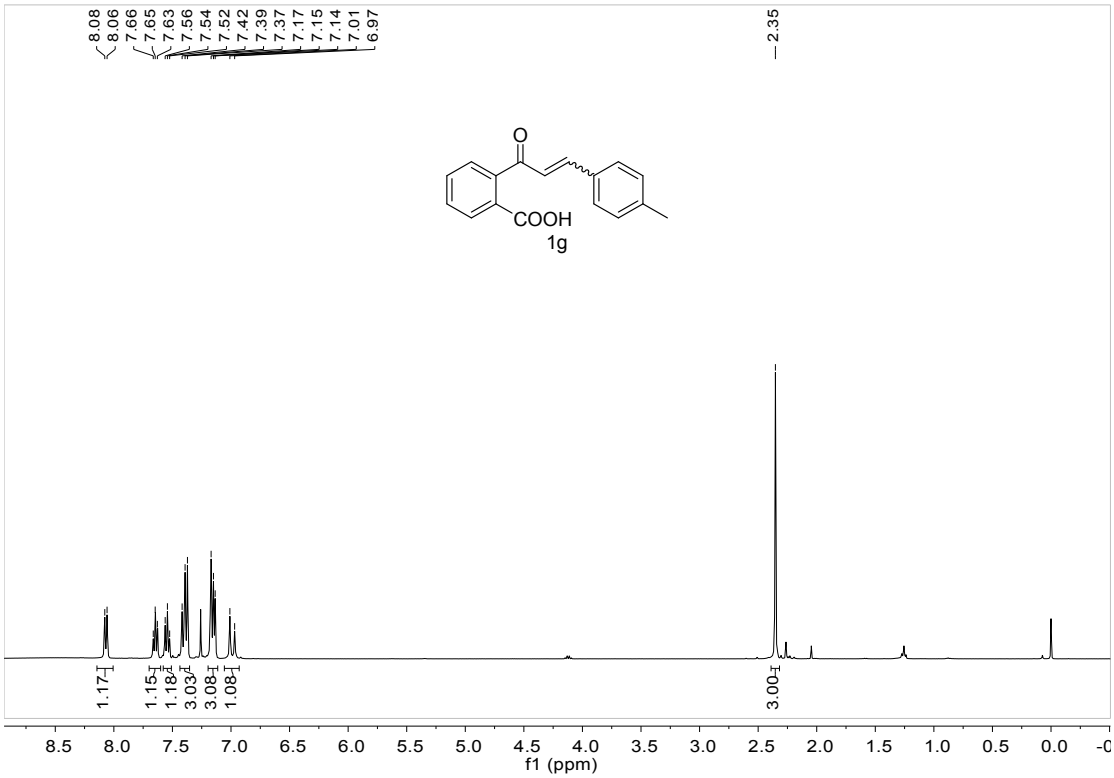
^{1}H NMR of 2-[3-(4-Methoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1e) in $CDCl_3$



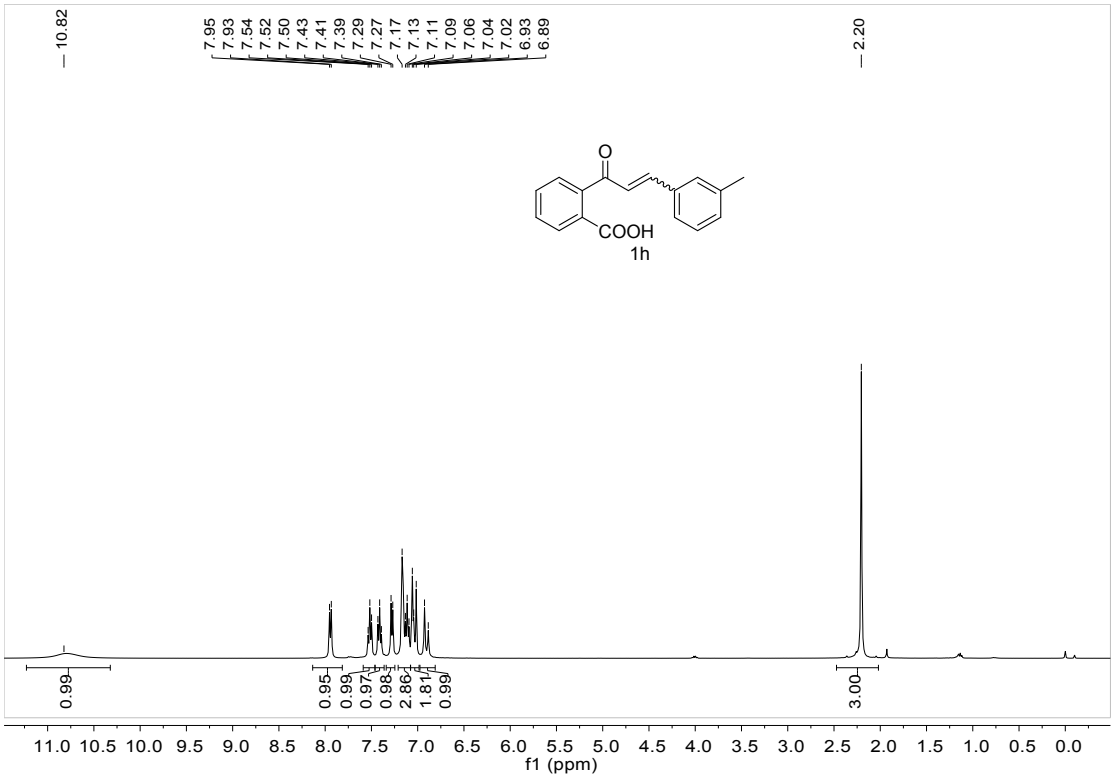
^{1}H NMR of 2-[3-(4-Ethylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1f) in $CDCl_3$



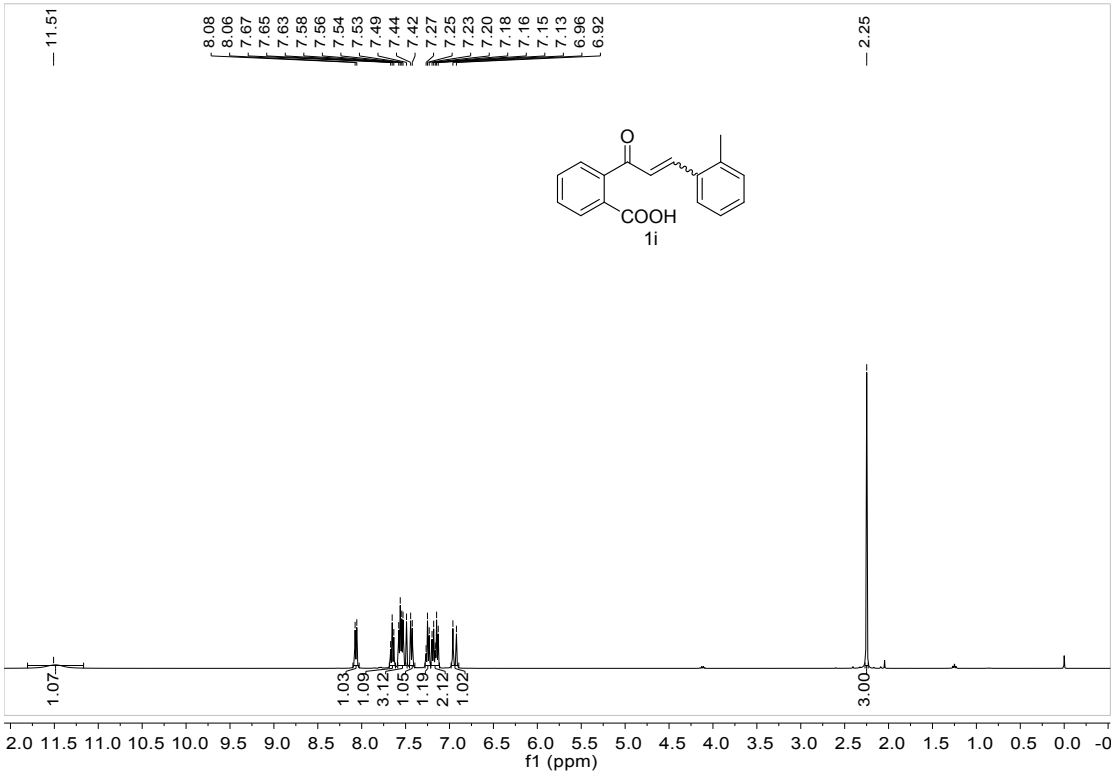
^{1}H NMR of 2-[3-(4-Methylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1g) in $CDCl_3$



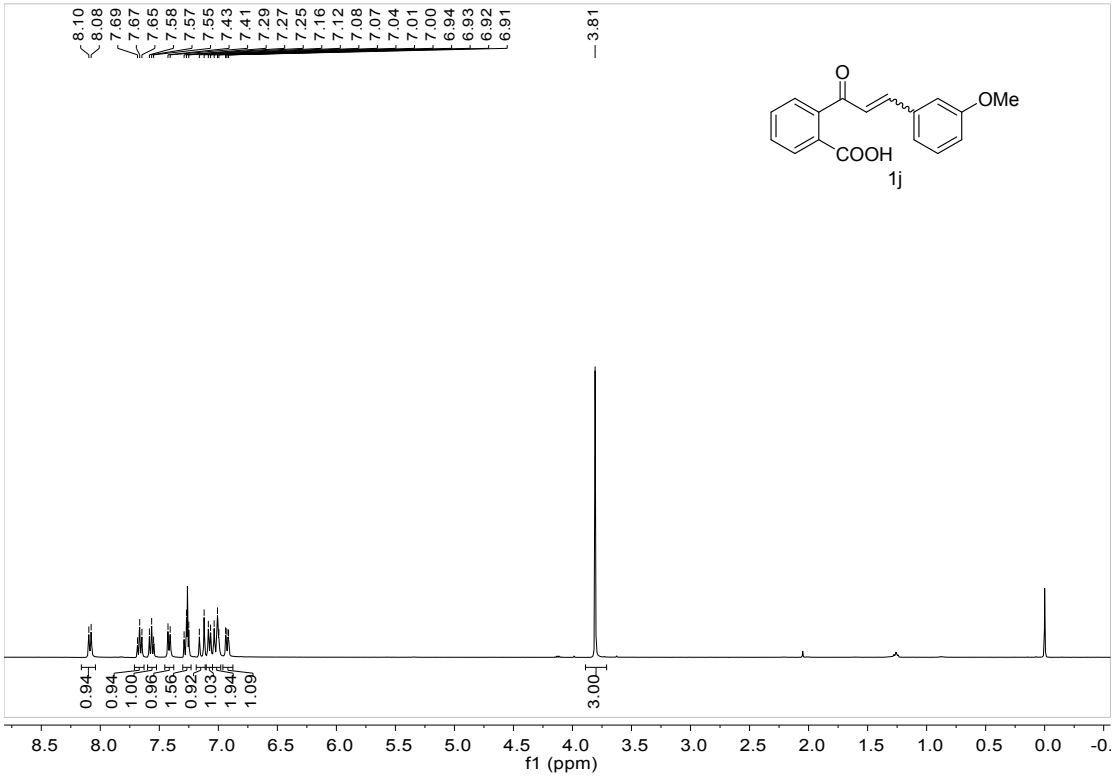
^{1}H NMR of 2-[3-(3-Methylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1h) in $CDCl_3$



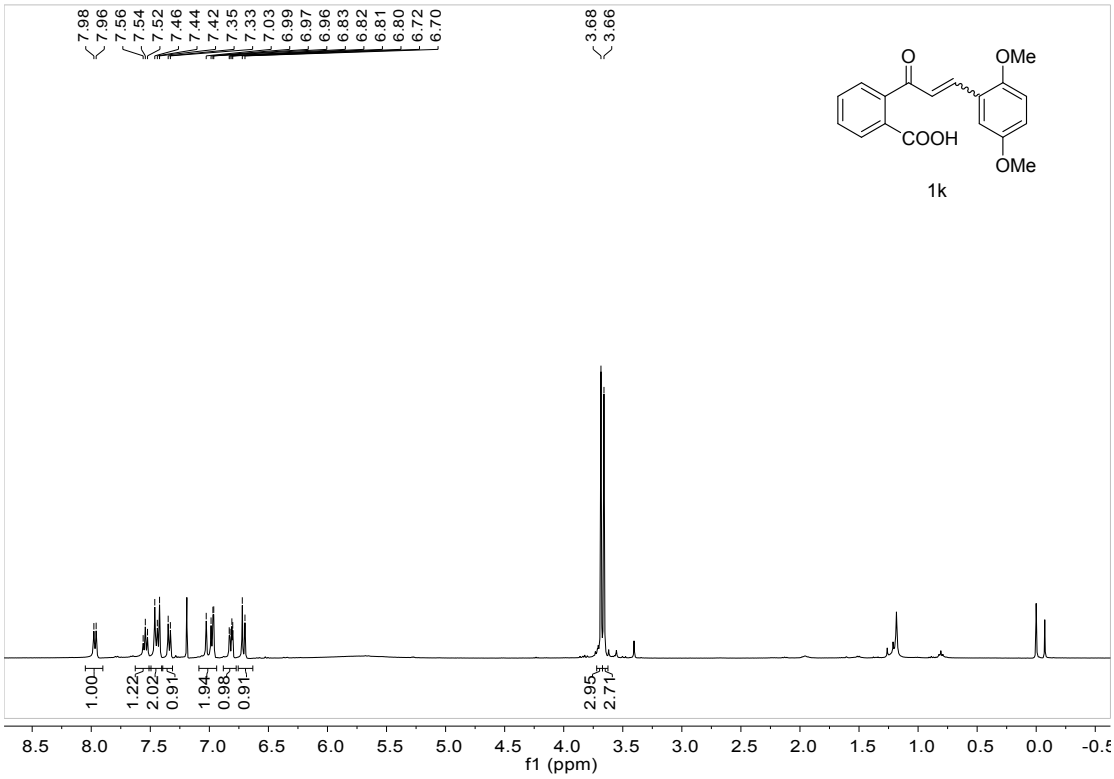
^{1}H NMR of 2-[3-(2-Methylphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1i) in $CDCl_3$



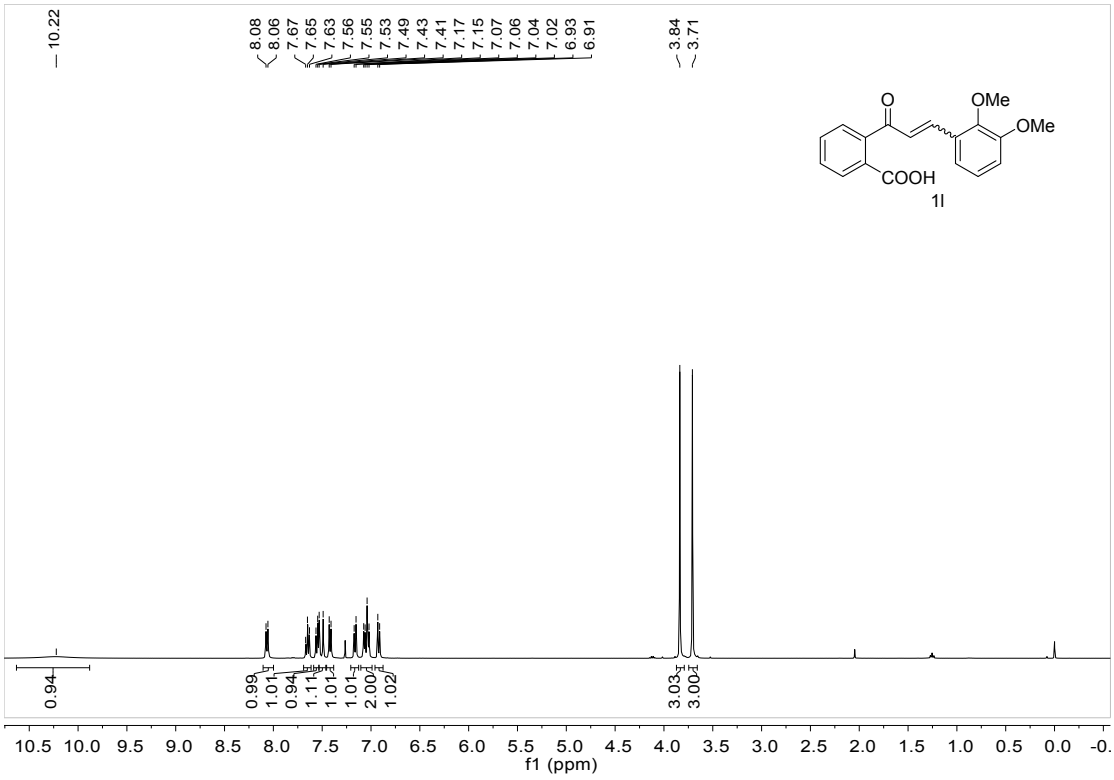
^{1}H NMR of 2-[3-(3-Methoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1j) in $CDCl_3$



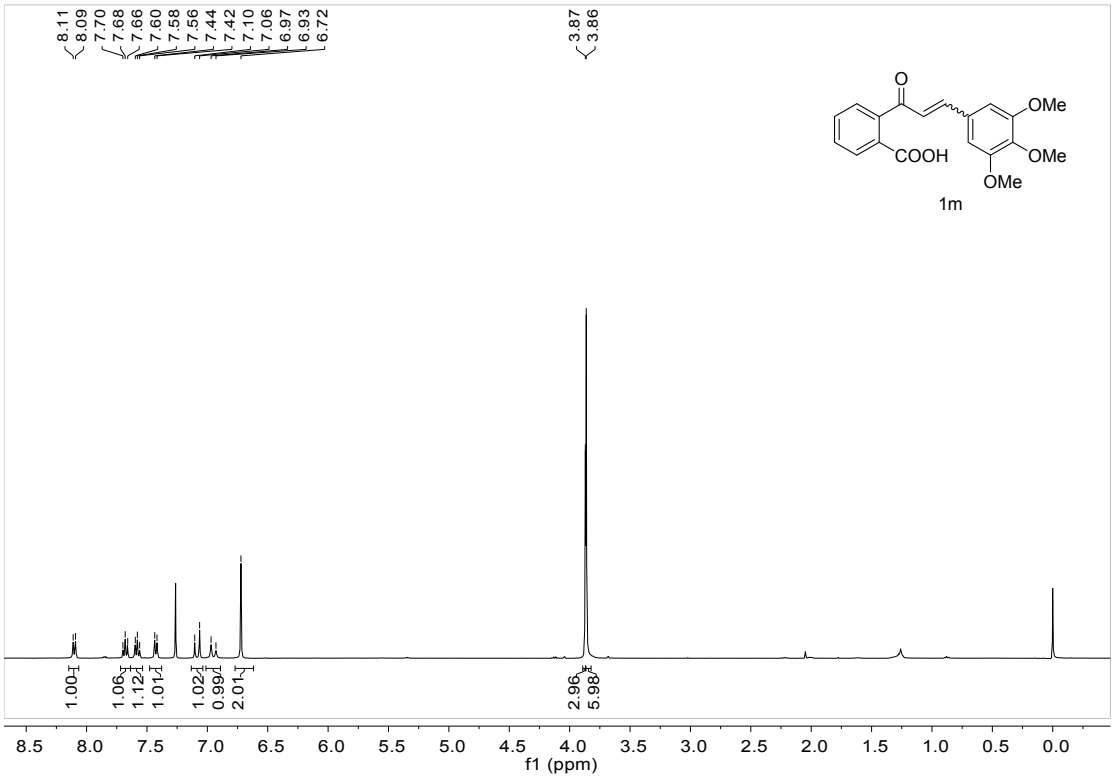
^{1}H NMR of 2-[3-(2,5-Dimethoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1k) in $CDCl_3$



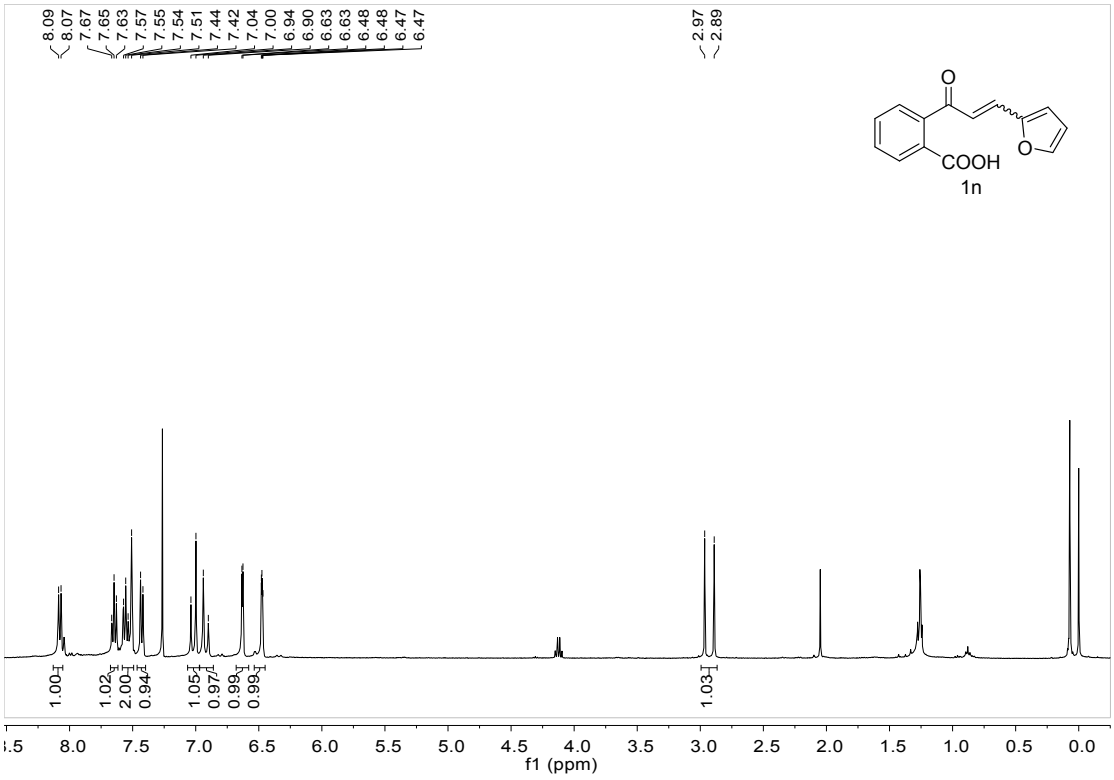
^{1}H NMR of 2-[3-(2, 3-Dimethoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1l) in $CDCl_3$



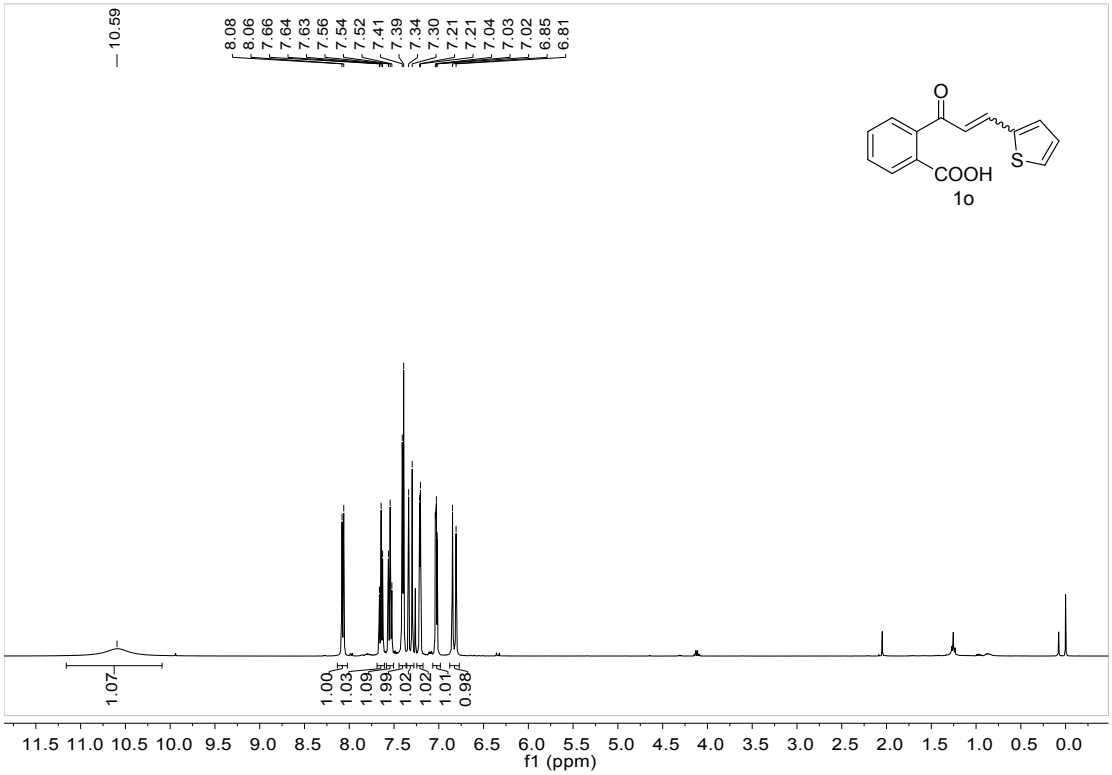
^{1}H NMR of 2-[3-(3,4,5-Trimethoxyphenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1m) in $CDCl_3$



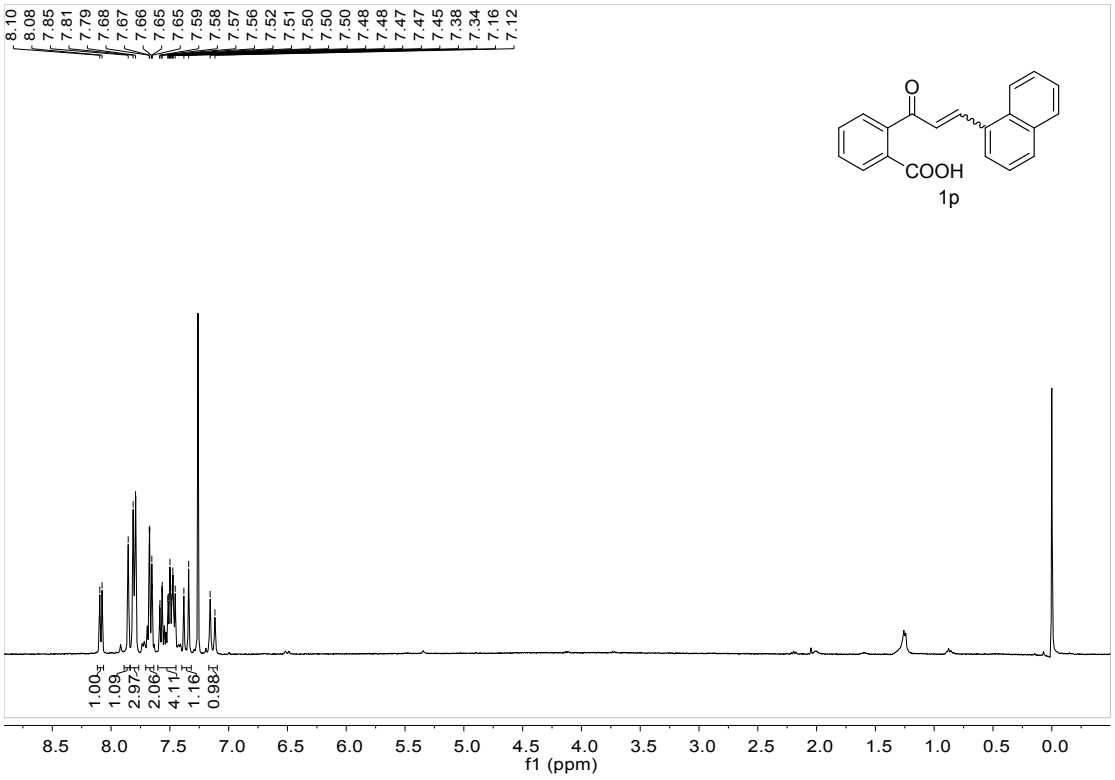
^{1}H NMR of 2-[3-(2-furyl)-1-oxo-2-propen-1-yl]-benzoic acid (1n) in $CDCl_3$



^{1}H NMR of 2-[3-(2-Thienyl)-1-oxo-2-propen-1-yl]-benzoic acid (1o) in $CDCl_3$



^{1}H NMR of 2-[3-(1-Naphthalenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1p) in $CDCl_3$



^{1}H NMR of 2-[3-(9-Anthracenyl)-1-oxo-2-propen-1-yl]-benzoic acid (1q) in $CDCl_3$